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A STUDY OF DEVELOPING METAL PHTHALOCYANINES FOR SELF-CLEANING COTTON

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Developing Metal Phthalocyanines

for Self-cleaning Cotton

LUK Ming Yin Anson

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CERTIFICATE OF ORIGINALITY

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Luk Ming Yin Anson

Abstract

Busy lifestyles drive growth in convenience products. This trend dramatically expands the functionality of easy-care textiles by developing diverse functional and smart fibrous materials. Self-cleaning is an advanced treatment that renders the treated material an ability to clean itself with automatic manner or minimal manual cleaning effort; such popular technology in textile material chemistry has been making considerable contributions to functional, hygienic and sustainable textiles.

Organic photocatalysts for self-cleaning possess a number of advantages over the widely-studied nano-scale titanium dioxide (TiO₂), such as light harvesting over the UV-visible spectrum and ease of property modifications via chemical tailoring. Porphyrin is one of the most important and efficient singlet oxygen generators among a family of organic photocatalysts. While metal phthalocyanine(s) (MPc(s)) has very similar properties to those of porphyrin, it has more intense light absorption in visible spectrum, superior stability against chemical, thermal and light and much material costs.

Equal quantities of a number of copper phthalocyanine (CuPc) in various sulphonated forms were loaded to cotton fabric via exhaustion dyeing manners; whereas, the extents of photocatalytic stain decolourisation by such functionalised cotton fabrics were not consistent. Electronic absorption spectroscopies and liquid chromatography-electrospray ionisation-mass spectrometry (LC-ESI-MS) were the major means to determine varied molecular aggregationdissociation behaviours resulted from different molecular configurations of the CuPc dyes.

Other sulphonated phthalocyanines were also applied to cotton fabric for further analysis of phthalocyanine as organic photocatalyst for self-cleaning cotton. The performances of stain decolourisation of the MPc candidates are listed in descending order as: mixture of tetra- and tri- sulphonated zinc phthalocyanines ($ZnPcS_{3-4}$) > di-sulphonated zinc phthalocyanine ($ZnPcS_2$) > di-sulphonated metal-free phthalocyanine (H_2PcS_2) >> poly-sulphonated copper phthalocyanines (DB86) >> tetra-sulphonated nickel phthalocyanine (NiPcS₄). However, the worse stability of ZnPcS₃₋₄ drove the development of cotton fabric co-applied with slightly-aggregated ZnPcS₂ and DB86 in different ratios to relieve the shortcoming of ZnPc stability. This co-system probably enhanced the ZnPc stability estimated by K/S measurement. On the other hand, it is discovered that NiPcS₄ even accommodated in cotton fibre in improved monomeric state could not promote its photocatalytic power due to deficient electron configuration of Ni ion in NiPc; thus, its excellent stability and photocatalytic suppression is a potential for developing it as photocatalytic inhibitor. The visible-light-triggered stain degradation abilities of cotton fabric treated with anatase-TiO₂-coated was found to be weaker than that dyed with CuPc under the identical photocatalytic condition; hence, sulphonated metal phthalocyanines with considerable photo-excited activities undeniably can compete and exceed TiO₂ under the environment with visible light.

Criticism of dye stain decolourisation as photocatalytic activity assessment and separation of the poly-sulphonated MPcs of derivatives by reversed-phase column for LC-ESI-MS analysis were two challenges met in the study. A series of experimental evidences revealed that decolourisation of dye stain is actually more suitable for evaluating the visible-light-driven self-cleaning effect contributed by MPc than that by inorganic photocatalysts on cotton textiles. Through an intensive investigation of the reversed-phase liquid chromatography for sulphonated molecules, unique, simple and efficient separation methods, termed as "gradient elution based on double- and triple- isocratic runs", were established to separate the poly-sulphonated MPcs using neutral mobile phase and conventional C18 columns only. The outcomes acquired from these addressed challenges could certainly raise the overall significance of this research project.

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Academic Journal Papers

Luk, A. M. Y., K. Cheuk, X. Wang and J.H. Xin, *Study of organic photocatalysts based on copper phthalocyanines for self-cleaning effect on cotton.* MRS Bulletin. (Submitted)

Luk, A. M. Y., C.W. Kan, K. Cheuk, J.H. Xin. *Exploring organic photocatalysts based on sulphonated metal phthalocyanines for self-cleaning effect on cotton*. (To be submitted)

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Conference Article

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Lists of Abbreviations

Abbreviated terms

Abs	absorbance
ACN	acetonitrile
AO3	C.I. Acid Orange 3
AO7	C.I. Acid Orange 7
AR1	C.I. Acid Red 1
AY17	C.I. Acid Yellow 17
AY49	C.I. Acid Yellow 49
CuPc	copper(II) phthalocyanine
CuPcs	copper(II) phthalocyanines
CuPcS ₄	copper phthalocyanine-3,4',4'',4'''-tetrasulfonic acid tetrasodium salt
DB189	C.I. Direct Blue 199
DB199	C.I. Direct Blue 199
DB86	C.I. Direct Blue 86
DI	deionized
Eqm.	equilibrium / equilibria
ESI	electrospray ionisation
НОМО	highest occupied molecular orbital
HPLC	high-performance liquid chromatography
ICP-OES	inductively coupled plasma atomic emission spectroscopy
IEX-LC	ion-exchange liquid chromatography
K/S	Kubelka-Munk function
K/S _{total}	average K/S value of the dyed cotton piece,
	measured from 400 to 700 nm at a 5 nm interval, throughout the project
K-M	Kubelka-Munk
LC-MS	liquid chromatography-mass spectrometry
LUMO	lowest unoccupied molecular orbital
МО	C.I. Acid Orange 52
MPc	metal phthalocyanine
MPcs	metal phthalocyanines
MPcSn	poly-sulphonated metal phthalocyanine(s)

MS	mass spectrometry / mass spectrometer
NiPc	nickel(II) phthalocyanine
NiPcS ₄	nickel(II) phthalocyanine-tetrasulfonic acid tetrasodium salt
Pc	phthalocyanine
Pcs	phthalocyanines
RB14	C.I. Reactive Blue 14
RB15	C.I. Reactive Blue 15
RB21	C.I. Reactive Blue 21
RB71	C.I. Reactive Blue 71
RB72	C.I. Reactive Blue 72
RhB	C.I. Acid Red 52
RPLC / RP-HPLC	reversed-phase high-performance liquid chromatography
TX-100	Triton X-100
UV	ultraviolet
UV-Vis	ultraviolet-visible light
v/v	volume to volume
w/v	weight to volume
ZnPc	zinc phthalocyanine
ZnPcs	zinc phthalocyanines

<u>Symbols</u>

с	speed of light
g	gram
h	Planck's constant
kg	kilogram
L	litre
mL	millilitre
m/z	mass-to-charge (ratio)
λ	Lambda; wavelength

1. Introduction

1.1. BACKGROUND OF RESEARCH

Self-cleaning is an advanced technological treatment that contributes to the developments on functional, hygienic and sustainable textiles[1, 2], which are popular R&D issues and innovations in textile industry nowadays. This novel technology renders the treated material an ability to clean itself with automatic manner or minimal manual cleaning effort.

To realise self-cleaning effects on textiles, one of the approaches is to functionalise the substrates with photocatalysts to exert photocatalytic self-cleaning that mainly involves stain degradation and bactericidal activities[3-5]. It is generally believed that this technique demonstrates more active manner of self-cleaning functions when there are appropriate light sources to provide sufficient energy for overcoming the intrinsic band gaps of the photocatalysts and then triggering a series of photo-redox reactions[6, 7]. Considerable attention has been granted to inorganic semiconductors, particularly titanium dioxide (TiO₂), to impart photo-triggered self-cleaning functions to textile materials. They are effective, but limited by lacking visible light activity because of their wide band gap energies. In most cases, they can only utilize UV light energy to activate the reactions, while ~95% of the visible light and infrared spectra of sunlight reached on the surface of earth, in terms of energy[8], cannot be harvested by them. The fastness of TiO₂-finishes on cotton materials, owing to the high

heterogeneity between cotton fibre and such inorganic substance, as well as the hand-feel of treated piece goods are still the typical issues to be tackled. As a result, the fundamental idea of this research study is to develop new self-cleaning systems to address the problem via organic approaches.

Academic researchers had attempted the applications of organic photocatalysts to selfcleaning textiles recently. Porphyrin-based systems are able to demonstrate photocatalytic degradation effect towards organic stains[9, 10] as well as antibacterial performances[11, 12] on cotton fabric in exposure to visible light; however, their relatively poor stabilities, expensive production costs and weak behaviour without incorporating with TiO₂ are the major obstacles for them to become mature in applying to self-cleaning textiles[13].

In this study, metal phthalocyanines (MPcs) are the core substances to be studied and developed to endue cotton pieces with photo-stimulated self-cleaning performances. Metel phthalocyanine (also known as metallophthalocyanine and metallised phthalocyanine) (MPc) is a *p*-type semiconductor that carries the narrower band gap energy (~2.0 eV) than titanium dioxide and porphyrins[14]. The range of radiation absorption of phthalocyanine(s) (Pc(s)) can reach longer wavelengths in the region of visible light and near-infrared when compared with that of porphyrins because of denser delocalised electrons in their more conjugated chemical structure[15]. Therefore, the photo reactions by MPcs can be driven using lower energy as well.

Although Pc is considered as a tetraaaza-derivative of tetrabenzoporphyrin, actually they are not unfamiliar to textile industries, especially for the coloration field. Pc in classified as one of the most essential dye classes according to the Colour Index (constitution numbers in Volume 4 (1971) of Pc: 74000-74999) published he Society of Dyers and Colourists (SDC) and American Association of Textile Chemists and Colourists (AATCC). Owing to unique turquoise blue to green colour, strong colour and tinctorial strengths, promising chemical stability and satisfactory light fastness[16], over forty Pc colorants, including pigments as well as the dye classes of reactive, direct, vat, basic and acid, are available in the markets.

To our knowledge, there are a variety of researches on the photocatalytic and photosensitising properties of Pcs[17-21]; nevertheless, MPcs playing as a role of photocatalyst on textile materials comparatively draw rare scholarly attention. In addition, there is a considerable quantity of on-going researches about photo-treatment of wastewaters and antimicrobial treatments by using Pcs as photocatalysts. This interdisciplinary network probably provides fundamental information, referable ideas and brings benefits to this study topic[22-27].

1.2. OBJECTIVES OF RESEARCH

- (1) To investigate the relationship of factors affecting the self-cleaning effectiveness of MPcs on cotton fabric.
- (2) To evaluate the photocatalytic effectiveness of each system for self-cleaning cotton.
- (3) To characterise the MPc products and the MPc-functionalised cottons.
- (4) To explore and understanding the photo-driven self-cleaning mechanisms of metal phthalocyanines involved.
- (5) To study and tailor more appropriate and effective methods for self-cleaning assessment and characterisation of sulphonated metal phthalocyanines.

1.3. SCOPE AND METHODOLOGY OF RESEARCH

This research focused on imparting self-cleaning performances on cotton material in woven fabric form. The self-cleaning systems are contributed by organic photocatalysts which are derived from MPcs.

The photocatalytic activities of sulphonated MPcs were affected by various factors; different kinds of substitution to the MPc rings and the central atoms/ions of MPcs are the typical factors to be considered and studied in details in this project. Commercial copper phthalocyanine(s) (CuPc(s)) dye products are different sulphonated CuPc derivatives that bear photocatalytic behaviours. Selected CuPc dyes were applied to cotton fabric via exhaustion dyeing techniques and the photocatalytic performances these CuPc-dyed cotton fabrics to degrade various acid dye stains under visible light were compared. Other sulphonated MPcs which were prepared by direct sulphonation of the MPc compounds or ordered from particular chemical suppliers were also used to functionalise the cotton fabric. Various and modified MPc systems developing for self-cleaning cottons were researched to explore their photocatalytic mechanisms in cellulosic substrate. In addition, molecular aggregation is one of the major factors that not only improve the stability of MPcs but also suppress the photo-activity in the self-cleaning systems. Studying these mechanisms was able to seek a unique approach to improve the self-cleaning system contributed by organic photocatalysts. Since this study was still at the development stage to produce self-cleaning cotton with MPcs, decolourisation of acid dyes as stains was the primary assessment to compare the photo-driven activities of the MPc systems applied.

Optical absorption spectrophotometry, inductively coupled plasma - optical emission spectrometry (ICP-OES) and liquid chromatography-mass spectrometry (LC-MS) were the main characterisation techniques to identify the Pc compounds. LC-MS was dominantly relied on throughout the study because it is effective to identify the sulphonated Pcs sourced from dye manufacturers and modified in the laboratory using the newly-designed separation techniques of high-performance liquid chromatography (HPLC). For the cotton substrate functionalised with Pc chemicals, optical absorption spectrometry in terms of K/S value was the typical method to identify aggregation-dissociation behaviours of the MPc candidates existed on the treated cotton fabrics. Decolourisation of dye stains on treated cotton and their stability (or durability) on pristine cotton fabric were examined to determine the overall selfcleaning behaviours offered by the MPc photocatalysts.

Application of MPc to cellulosic fabric is a novel study to develop self-cleaning textiles; there were a few problems encountered during the characterisation work and the photocatalytic activity assessments for MPcs on cotton fabric. A more detailed study was conducted in order to establish proper and reliable methods of characterisations and examinations; therefore, more accurate and factual findings and outcome could be acquired for further analysis.

1.4. SIGNIFICANCE OF RESEARCH

With the increasing demand towards functional and intelligent fibrous materials due to the busy lifestyle and greater desire for convenience, textiles with easy-care functions have become increasingly popular in recent time. Apparels and interior textiles with the capabilities to clean themselves automatically and maintain hygiene of wearer or user with minimal washing are ones of the favourite innovations to support the sustainable development in this century.

The use of TiO_2 as photocatalyst to degrade the organic compounds in the presence of UV is an effective method and has been widely studied in different areas including textile industry. However, its heavy reliance on UV, which is only a small part of sunlight reaching earth surface to trigger the process, for photo-activation is the major shortcoming limiting its applications. Therefore, studies on development of new systems where their photocatalytic activity can be induced by visible light would be a positive value in this field for many current and future applications.

In this study, the introduction of Pc as light-harvesting and photoactive catalysts is particularly attractive given their key role in the photosynthetic apparatus and the relative ease with which a variety of Pc agents can be synthesised. The rich photochemistry's studies and broad photocatalytic applications of phthalocyanines propel us to prepare the self-cleaning cotton fabric with them. To our knowledge, there are absence of academic publications reporting the performances and investigating the mechanisms of photocatalytic self-cleaning demonstrated by different MPcs on cotton fabric.

Separation of poly-sulphonated MPcs by common HPLC methods, including anion exchange chromatography, ion-exchange liquid chromatography and addition of buffering

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system, are basically effective but tend to deteriorate the subsequent detection of electrospray ionisation-mass spectrometry (ESI-MS). Development of novel gradient elution methods based on a set of isocratic runs is favourable to provide efficient, clean and cost-effective separation and purification of poly-sulphonated MPcs or even other poly-sulphonated mixtures for dye and chemical manufacturers.

Pioneering work can provide a valuable template for the possibility of bringing photocatalytic self-cleaning properties to other types of textile fibres to mediate photocatalytic oxidation of organic compounds, leading to an alternative to the conventional methods for the removal of resistant organic pollutants from environment. In addition, significant breakthroughs and outcomes from this project are not only beneficial to self-cleaning technology, but also to the other researches on functional dyeing, multifunctional finishing, phthalocyanine chemistry, separation science and chromatographic technologies.

1.5. CHPATER OUTLINE

The thesis consists of seven chapters which are outlined as follows.

Chapter 1 introduces the background, objectives, scope, general methodology and significance of the research.

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Chapter 2 provides a comprehensive review of literatures including the introduction of self-cleaning technologies, the important techniques for engineering self-cleaning textiles and phthalocyanines in terms of their history, structural and optical characteristics, industrial applications and chemical theories relevant to this study.

Chapter 3 presents a critical study to explore and discuss whether degradation/decolourisation of dye stains is suitable and feasible for evaluating the photocatalytic self-cleaning effectiveness of MPc systems introduced to cotton fabric.

Chapter 4 analyses the relationship between the molecular structures of CuPc derivatives and their photocatalytic behaviours towards dye stain decolourisations; and compares the outstanding CuPc candidates with TiO₂ on cotton fabric and deliver the first stage of work about the newly-designed separation technique cooperated with reversed-phase liquid chromatography (RPLC) for poly-sulphonated MPc mixtures in LC-MS analysis.

Chapter 5 further investigates the MPcs with different metal cores to improve the stability of sulphonated ZnPc on cotton fabric in photo-excited stain removal process and discovers the photocatalytic inhibition property of sulphonated NiPc.

Chapter 6 follows up the HPLC work mentioned in Chapter 4 and assesses the effects of different chromatographic variables to further develop a simple but efficient and valuable elution profiles for separating poly-sulphonated CuPc mixtures by RPLC and LC-MS analysis.

Chapter 7 concludes the outcomes of the PhD research project, indicates the limitations

of this study and proposes the further research tasks, directions and development based on the significant findings and results of this study.

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2.1. INTRODUCTION

This chapter is composed of a comprehensive review of literatures focusing on two major aspects of this study. One aspect concerns about the development of the self-cleaning technologies and the self-cleaning finishes for textiles. Nature of the textile materials, background, current development and limitations of the self-cleaning systems are discussed. Another aspect is related to the main character in this study, phthalocyanines. Their historical development, industrial applications, as well as the phthalocyanine chemistry involved in this study are explored in this section.

2.2. SELF-CLEANING TECHNOLOGIES

This section includes the background, mechanisms and applications of self-cleaning technologies. The background part introduces the origins, brief history and general introduction of self-cleaning technologies. The mechanism part mainly focuses on the theories and working principles of the superhydrophobic and photocatalytic self-cleaning systems. The last part of this section discusses the potential developments and applications of self-cleaning technologies in different fields.

2.2.1. Background

The behaviours that can realise the goal of self-cleaning include bactericidal activity, colorant stain decomposition, deodorisation such as the smell of cigarettes, air cleaning, antigrease, antimould and degradation of organic matters in polluted water[2, 4, 28-32].

Self-cleaning is commonly considered as a biomimetic technology that imitate the nonwetting and natural cleaning functions of Lotus leaves. Lotus leaf represents "the sign of purity" for thousands of years, dirt and pathogens can be washed off the surfaces of Lotus (and some other plants) with rain or dew. Upon the development of the high-resolution scanning electron microscope, two German botanists, Barthlott and Neinhuis, had studied and discovered that the specially structural features on the plant leaves, together with their waxy surface chemistry, result in the non-wettability of plant leaves[33, 34]. In other words, Lotus-effect is viewed as the water-repellency of leaves surface based on surface roughness established via different microstructures (trichomes, cuticular folds and wax crystals), together with the hydrophobic properties of the epicuticular wax. Thus, the contaminating particles can be collected and removed by the rolling water droplets to maintain the clean surface[35, 36].

Apart from lotus leaf (*Nelumbo nucifera gaertn*), Guo et al.[37, 38] had examined rice leaf (*Oryza sativa L.*), taro leaf (*Colocasia*), India canna (*Canna generalis bailey*), purple setcreasea (*Setcreasea purpurea boom*), Chinese watermelon (*Bennincasa hispida cogn*), ramee leaf (*Boehmeria iongispica steud*) and perfoliate knotweed (*Polygonum perroliatum L.*)

and concluded that the hierarchical micro-and nanostructure is not the only parameter for establishing a superhydrophobic surface, but also the unitary nanoscale or sub-nanoscale which was discovered on the surface structure of the ramee leaf and the Chinese watermelon. Such similar unitary structure on copper alloy also demonstrated the excellent superhydrophobicity to support their findings. Insects such as water strider's legs, fishing spider's legs and butterfly's rings are the typical examples that the superhydrophobic surfaces appear at the bodies of animals[39-42].

Lotus-effect coating is mainly applied to self-cleaning windows, optical lens, windshields, exterior paints for constructions and awnings, tarpaulins, tents, marquees, utensils, roof tiles, textiles, solar panels, and applications requiring a reduction of drag in fluid flow such as traffic guidance and signs[43-45]. Samaha et al.[46-48] suggest that the superhydrophobic surface is potentially used in marine environments for drag-reduction purposes; for instance, such technology can help submarines overcome the skin-friction drag produced on their bodies in order to save a great deal of energy.

In contrast to the hydrophobically self-cleaning effect, there is another self-cleaning approach belonging to hydrophilic nature, which is widely reckoned by the material chemists and engineers. Photocatalysts are applied to the substrate surface to decompose the organic dirt via a series of chemical processes when exposed to light. Such photocatalysis also associate with the biomimicry concept because it mimics the photosynthesis of the natural green plants and some microorganisms (termed as photoautotrophs) that use the energy from sunlight to produce glucose from carbon dioxide and water[49, 50]. Photocatalytic selfcleaning is an approach of utilising the light (e.g. UV and visible light) for triggering the redox reactions to chemically degrade the organic dirt and other impurities in/on the exerted medium. Therefore, light source such as UV and visible light, oxygen and air humidity are involved in these photocatalytic self-cleaning reactions.

The researches of photocatalysis were originated from different catalysis laboratories in Europe. In UK, Stone investigated the photoadsorption/desorption of oxygen on zinc oxide (ZnO)[51] first, followed by the photocatalytic oxidation of CO on the same ZnO[52]. He subsequently changed to use titanium dioxide (TiO₂), also known as titania, in rutile phase for oxygen photo-adsorption and selective isopropanol oxidation in acetone[53, 54]. This is one of the significant literatures to mention OH• radicals as oxidants formed by neutralising the surface OH⁻ by photo-holes (h⁺). In the same period of time, Hauffe was also conducting a study on the photocatalytic oxidation of CO on ZnO[55, 56] in Germany; these publications were the first ones to include the term "photocatalysis" in the title. It can be concluded that, the photoactive properties of ZnO and titania started to be studied in the late 1960s, but it mainly focused on the study of photo electrochemical solar energy conversion. In 1972, Fujishima and Honda presented their discovery on photocatalytic water splitting by TiO₂ electrode in the presence of UV light ($\lambda < 415$ nm)[57, 58]. This outcome accelerated a

globalisation of photocatalysis and a preferential development in Japan.

2.2.2. Mechanisms

2.2.2.1. SUPERHYDROPHOBICITY

A surface that can exhibit superhydrophobicity usually possesses high static contact angle (CA), low CA hysteresis and low sliding angle when a water droplet contacting the surface. CA (θ) is an angle between the surface and the water meniscus near the line of contact (see Figure 2-1) and it is able to indicate the wettability of a surface. Surfaces are identified as hydrophobic when CA > 90° and hydrophilic when CA < 30°. Superhydrophilic surfaces can show CA < 5° while the CA of superhydrophobic surfaces for Lotus-effect selfcleaning need to reach 150-180°[59-61]. Although the water CA is a criterion for evaluating the hydrophobicity of a surface, it is not sufficient to justify the self-cleaning property because on such superhydrophobic surfaces, water needs to bead up and roll off the surface to remove the dirt. Thus, sliding property of the surface that can be determined by CA hysteresis and sliding angle, is also the necessary parameters to establish a lotus-effect.



Figure 2-1. Static contact angle measurement for hydrophobic (surface A) and hydrophilic (surface B) surfaces.

A water droplet is deposited on the surface and the water CA is measured by a goniometer. CA hysteresis is calculated by the difference between advancing CA (θ_a) and receding CA (θ_r), which are the contact angles measured in dynamic mode. The advancing CA is measured during the growth while the receding CA is measured at the receding stage of a water drop. Figure 2-2 clearly illustrates the measurements of advancing and receding contact angles. CA hysteresis is influenced by the roughness and heterogeneity of a surface; it is therefore a vital feature of a solid-liquid interface to represent the "stickiness" of the surface or the amount of energy dissipated when a drop flows along a solid surface[62-64].


Figure 2-2. Schematic diagram of measurement of (a) advancing and (b) receding contact angles by needle method. The advancing or receding contact angle is obtained only after the contact line starts moving[63].

Besides CA and CA hysteresis, sliding angle (SA) angle, also known as the tilt angle, is also used for evaluating surface hydrophobicity. It is defined as the critical angle at which a water droplet with a certain weight begins to slide down or roll off smoothly on the inclined (tilted) surface, as shown in Figure 2-3. Compared with CA hysteresis, the sliding angle can be measured more easily and accurately to evaluate the surface hydrophobicity. SA mostly reflects (but not equal) the difference between the advancing and receding contact angles, so surfaces with low CA hysteresis normally give a very low sliding angle (see Figure 2-3). Desirable self-cleaning surfaces usually have a low water roll-off angle of $\sim 3^{\circ}$ [65, 66].



Figure 2-3. Schematic diagram of measurement of sliding angle and its relationship with advancing and receding contact angles (θ_a and θ_r)[67].

There are two states of superhydrophobicity in terms of the modes of surface wetting. Based on the experimental data obtained in various studies, two empirical models have been proposed to explain the different surface wetting properties. In other words, these two models demonstrate the relation between surface roughness and hydrophobicity via explaining the two possible states to result in superhydrophobicity. Referring to Figure 2-4, liquid enters the texture and follows the solid surface in Wenzel's model but the liquid droplet suspends above the rough surface, leaving air inside the texture, in Cassie-Baxter's model.



Figure 2-4. Schematic diagram of (a) Wenzel's model and (b) Cassie-Baxter's model.

The Wenzel's model illustrates that the hydrophobicity can be enhanced by an increase in surface area due to textured effect. In this case, increase in roughness of the surface tends to raise not only the CA but also the CA hysteresis of the liquid droplet owing to the growth of the contact area. Once the roughness is over certain level, the Wenzel state shifts to the Cassie–Baxter state to lower down the CA hysteresis since the increased fraction of air trapped in the surface leads to the suspension of water droplets on top of the surface. This effect is able to further improve the superhydrophobicity of the surface[68-75]. This is one of the reasons to explain the importance of developing a hierarchical structure with convex shaped nanostructures on superhydrophobic self-cleaning surface, in addition to the introduction of repellent chemistry.

2.2.2.2. PHOTOCATALYSIS

Mills and Le Hunte[76] reckon that photocatalysis can be considered as an acceleration of a photoreaction, also known as a "photo-induced" or "photo-activated" reaction, by the presence of a catalyst, but not a chemical reaction catalysed by light. Therefore, "photocatalysis" includes the process of "photosensitisation", i.e. a process by which a photochemical or photophysical alteration occurs in one chemical species through the initial absorption of radiation by another chemical species called the photosensitiser.

On the other hand, Ohtani[77] suggests that photocatalysis (or photocatalytic reaction) is

a chemical reaction induced by photo-absorption of a solid material called "photocatalyst", which remains unchanged throughout the reaction. Thus, such solid i.e., photocatalyst acts catalytically without change in the presence of light and he believes this explanation to be more consistent with most definitions. Based on this definition, photocatalysts absorb light to be excited to a higher energy state; it is similar to a sensitising molecule working in homogeneous photoreaction systems. While sensitisers are not solids, they can be considered as photocatalysts if they are reproduced after the photo-induced reaction processes; a sensitiser should not be considered as a "catalyst" instead.



Figure 2-5. Energy band diagram of a titania particle excited for pollutant degradation in exposure to ultraviolet radiation (E: activation energy to overcome the bandgap, e⁻: electron, h⁺: hole)

Photocatalytic self-cleaning is a technology that can perform chemical breakdown of organic dirt through photo-redox reactions in the presence of light[58, 78]. Such self-cleaning effect can be introduced to a surface by coating it with a photocatalyst. Although many metal oxides have comparable photocatalytic activities, titania is a leading photocatalyst among them owing to relatively low production cost, chemical stability, non-toxicity, biocompatibility as well as exceptionally high photocatalytic activity under UV[58]. Figure 2-5 presents the basic principle how TiO₂ exhibits self-cleaning to decompose the organic dirt. When a semiconductor-typed catalyst is illuminated with photons (hv) whose energy is equal to or greater than their bandgap energy (E_g), i.e. $hv \ge E_g$, there is absorption of these photons and generation of electron-hole pairs, which dissociate into free photo-electrons in the conduction band and photo-holes in the valence band, within the bulk particle. To have an efficient photocatalysis by the semiconductor, the different interfacial electron processes involving eand h⁺ must compete effectively with the major deactivation processes, typically for exciton recombination.

Generally speaking, all metal oxides have the same oxidation ability, i.e., the same potential of the top of the valence band, since the valence bands of metal oxides are mainly composed of the same O 2p atomic orbitals; the potential of the conduction band varies depending on the kind of metals[79]. The power of TiO₂ photocatalysts driving the photocatalytic reaction under UV irradiation in the presence of air or oxygen is sufficiently high; Ohtani[77, 80] elucidates that TiO₂ has high reduction ability to inject photo-excited electrons into molecular oxygen adsorbed on the TiO₂ surface. It is necessary that photocatalytic reactions are completed with consuming the same numbers of electrons and positive holes. Even if the potential of positive holes is high enough, it cannot effectively be utilised when the photo-excited electrons are not consumed. Since TiO₂ has a relatively higher reduction ability of oxygen under photo-irradiation among the various metal oxides as potential semiconductor photocatalysts, it is able to gain stronger electron utilisation to drive photo-oxidation by positive holes (or intermediate species produced by them) that bear high oxidation ability. In contrast, other metal oxides have high oxidation but low reduction abilities, their photocatalytic activities will not be high expectedly.



Figure 2-6. Change in the electronic structure of a semiconductor compound as the growth of number N of monomeric units from unity to clusters of more than 2000 (CB: conduction band, VB: valence band).

For many compounds, the energy necessary for photo-exciting the particle is reduced with the increase of number of monomeric units (N) in a particle. When N is much greater than 2000, it is possible to end up with a particle which exhibits the band electronic structure of a semiconductor as shown in Figure 2-6[76, 81]. The highest occupied energy band i.e. valence band and the lowest unoccupied energy band i.e. conduction band are separated by a band gap (E_g), which is a region lacking of energy levels in a perfect crystal.

2.2.3. Self-cleaning applications

Lotus-effect coatings have been becoming mature in the industry since a patent on technical micro- and nanostructured self-cleaning surfaces was assigned[82]. This patent and the introduction of the trademark "Lotus-Effect" motivate the uses of superhydrophobic coatings on various fields as follows[83, 84],

- Building and engineering materials, including glass, roofing, siding, flooring, windows, texturing compounds, concrete, facade paints, lacquer additives, tiles, steels and alloys[85-94].
- Marine equipment and supplies including docks, piers, buoys, drilling platforms[95-98].
- Sanitary including toilets, sinks, bathtubs, shower curtains, swimming pools, kitchen surfaces, equipment[99, 100].

- Transportation including automobiles and boats[99].
- Versatile industrial and daily products made of plastics and textiles[36, 101-106].

Reversible switching surface between superhydrophobicity and superhydrophilicity has been developed and can be applied in functional textiles, intelligent microfluidic switching, controllable drug delivery, and thermally responsive filters[107-110]. Stiction is a typical problem to limit the widespread use and reliability of the micro-electromechanical systems; Lotus-effect coating is one of the approaches to tackle the problem due to its good combination of rough surface and hydrophobic materials[111, 112]. Furthermore, contaminants accumulated on the surface of the exterior insulators will create a conductive layer which can cause larger risks of leakage currents, dry band arcing, and ultimately flashover. Li and coworkers[113] claim the superhydrophobic coating is capable of resisting the atmospheric and chemical degradations by salt-containing air, airborne pollutants, rain and humidity. Lotuseffect-coated surface also exhibits high tracking resistance that is desirable for glass, porcelain, and composite insulators with improved surface dielectric properties, line and station insulators, bushings, instrument transformers and related devices, as well as other applications requiring tracking resistance[83]. Even though the application potential of lotuseffect materials is enormous, preparation costs, mechanical stability and durability of such coatings have to be improved.

For photocatalytic self-cleaning, material chemists and engineers propose the term "self-

cleaning" may give a misleading meaning about "a surface need not be cleaned at all". In fact, the functions of photocatalytic self-cleaning materials can be reckoned as extending the intervals between cleaning cycles significantly, as well as easily removing the dirt and stains adhering on the self-clean surface. Hence, fewer detergents are required and polluted water is discharged to diminish the environmental pollution, wear and tear of materials and personnel costs. In other words, photocatalytic self-cleaning is a low-maintenance and trouble-free solution. Photo-excited self-cleaning is usually a multifunctional technology comprising solar-protection and anti-fogging (for glass), air-purification, water purification as well as antimicrobial properties; the following has summarised the commercial uses of photocatalytic self-cleaning[114], which is mainly developed by TiO₂ coating,

- On glass: mirrors for vehicles and indoor uses, windows, tunnel, street lights, and vehicles[50, 115-120]
- On tile: kitchen, bathroom, building roof, and walls[121-126]
- On textile and fibre: hospital garments, medical devices, house hold appliances, interior furnishing and protective clothing[127-131]
- On plastic/polycarbonate: automotive industry and buildings[115, 132-135]
- For wastewater treatment[136-139]
- For air purification[140-143]
- For antimicrobial[144-149]



Figure 2-7. Schematic explanation of the working mechanism of self-cleaning glasses and tiles (from left to right)

Tiles and glass windows modified with thin films of transparent TiO₂ photocatalysts has been employed in constructing building materials to bear photocatalytic self-cleaning performances[126, 150-153]. Figure 2-7 illustrates the basic working principle of the cleaning process of the self-cleaning windows and roof tiles, on which the apparent dirt were first degraded by the photocatalysts absorbing sunlight and then washed away with rain or water. To exert this effect, UV light, oxygen and air humidity are required; and the level of UV light present in normal daylight is sufficient to trigger the photocatalytic reaction. Due to the satisfactory mechanical endurance and consistent photocatalytic activity, commercial brands including Activ[™], RadianceTi[™], Sunclean[™], Bioclean[™] and Hydrotech[™], have become popular in the industrial uses[114]. Hydrotech[™] is a technique of spraying a liquid suspension of TiO₂ onto the substrate's surface; it has been successfully applied in building materials, coatings and paints made by TOTO Ltd. Photocatalytic cements, commercially available in form of TX Aria[™], TX Active[™], TX Arca[™] and TioCem[™][154], are claimed to be capable of reducing the air pollution in the urban area if a city is covered with these cement products to a considerable extent[155]. On the other hand, once the TiO₂ coating is exposed to sunlight or UV radiation, such coated surface will become (supre-)hydrophilic to confer an anti-fogging property[156]. This technology has been developed for clean and glare-free windows, automotive mirrors, headlights, and bathroom's mirrors and tiles. On the superhydrophilic surface of photocatalytic glass/mirror/tile, water droplets tend to spread and form a continuous film to run off and remove the loosely-deposited dirt with it; meanwhile, watermarks will not leave on the coated surface. In addition, for the coated mirrors and glasses, light scattering resulting from the presence of condensed water droplets can be eliminated to maintain clear and unhindered view (see Figure 2-8).



Figure 2-8. Anti-fogging effect of the tile and mirror[157] coated with a thin film of TiO₂.

2.3. SELF-CLEANING TEXTILES

Since the behaviours that can realise the goal of self-cleaning include bactericidal activity, colorant stain decomposition, deodorisation such as the smell of cigarettes, air cleaning, antigrease, antimould and degradation of organic matters in polluted water[2, 4, 28-32], there is a board definition of self-cleaning; nevertheless, textile with self-cleaning property can generally be defined as cleaning itself automatically or with the minimal human cleaning effort.

Self-cleaning textiles are originally designed for tablecloths and men's suits to get rid of coffee, tea, wine and other stains; or where large awnings, tents and other architectural structures to remove dirt and maintain spotlessly clean without the necessity of conventional washing or cleaning. These finishes are certainly contributed by the Lotus-effect technologies. Grateful to the development of photocatalysts on self-cleaning field[32, 158-161], introducing the photo-chemically active agents, typically TiO₂, confers treated fibrous materials to decompose the organic matters so as to improve the ease, effectiveness and efficiency of cleaning. The applications of self-cleaning finishes in the industries of apparel and home textiles become mature upon the significant researches' achievements in the last 10-15 years. Such technology, for example, can be applied for removals of body odour on clothes and tobacco odours on curtains to stay 'ever fresh', as well as antimicrobial functions on hospital sheets to reduce incidence of cross-infections.

2.3.1. Lotus effect approaches

Water-repellent textiles bearing (super-)hydrophobic property have been developed for over 50 years; therefore, the development of self-cleaning textiles based on the hydrophobic or even superhydrophobic approach is not a totally new topic for textile chemistry and finishing[162, 163]. The first patent for making textile surfaces with a hydrophobic layer, which is formed by hydrolysing the ether solution of monomeric methyl-dihalogenosilanes i.e., methyl silicone dihalide (e.g., methyl dichlorosilane) with mixture of ice and water, was released in 1945. However, the terms "water-proofing" and "water-repellent" appear in the patent instead of "superhydrophobic" [164]. Different from other solid substrates such as metal sheets, glass and ceramics, surfaces of textile materials have their own intrinsic advantages about high flexibility and inherent micrometre-scale roughness coming from fibre and fabric structure[165]. Superhydrophobic coatings can easily be applied to textile surface by adding secondary nanoscale roughness, followed by surface hydrophobisation. There are two primary techniques that are generally followed to fabricate superhydrophobic surfaces, (1) making a rough surface from a low surface energy material and (2) modifying a rough surface using a material of low surface energy[166].

The poor water repellency of cellulose tends to limit its uses and encourage numerous material scientists to develop various treatments to enhance the hydrophobicity of cellulosic materials. Despite the fact that superhydrophobic cotton have been significantly studied and

applied for ~20 years, many earlier methods are considered complicated and time consuming as well. Competitive outcomes delivered by "facile" and "simple" applications probably increase the research values on the topic of superhydrophobic cotton.

Liu et al.[167] reported a one-step, cost-effective and environmentally-friendly technique to prepare superhydrophobic surface on cotton fabric with organosilica sol-gel-based coating, which was obtained via cohydrolysis and polycondensation of a tetraethyl orthosilicate (TEOS), 3-azido-propyltriethoxysilane and long-chain siloxane (HDTMS, C16) in ethanol solution at the low temperature. The sol was then applied to cotton fabric by "dip-pad-dry-UV cure" technique to establish an effective coating with a static contact angle up to 151.6°. Even after being washed for 30 times, the specimen still exhibited a water CA of 130°. Multifunctional finishes on cotton materials are usually attractive in textile science. Vasiljevic et al.[168] tailored a sol-gel coating with optimised structure to demonstrate not only Lotus-effect, but also oil-repellent, antibacterial and flame retardant properties on cotton fabric.

Leathers are the second soft substrates that researchers are recently interested in to impart superhydrophobic self-cleaning effects. Due to their desirable traits, including high tensile strength, flexibility, resistance to tearing, puncturing, and abrasion, and permeability to air and water, leathers have applications in footwear, furnishings, automotive industry, clothing, bookbinders, gloves, sports gears, bags, and cases. Synthetic leathers based on polyurethane (PU) and poly(vinyl chloride) (PVC) have been a growing demand in the market because of cost reduction and tailor flexibility; however, unsatisfactory liquid-repellency and unwanted

stickiness at elevated temperatures are the main deficiencies of synthetic leathers.



Figure 2-9. Schematic diagram and procedures for fabrication of superhydrophobic and superoleophobic synthetic leather[169].

Gurera and Bhushan[169] claimed that they were the first time to fabricate superhydrophobic surface on synthetic leather using multi-layered nanocomposite coating structure (see Figure 2-9). The coated surface exhibited high mechanical durability and maintained these properties up to 70 °C. Casas et al.[170] had developed novel multifunctional nanotechnology systems to grow nanostructured coatings onto textile and leather for manufacturing the upholstery used on seating for public spaces and vehicles. Apart from the comparisons of different formulations, particle size, contact angles and surface roughness of 25 finished products were diversely analysed to give a comprehensive study. There are other

researches that attempt to promote the Lotus-effect on silicone rubber[171] and polycarbonate[172] with relatively facile processes.

2.3.2. Photocatalysis approaches

Various photocatalysts of inorganic and organic categories and their applications in selfcleaning textiles are introduced in the following.

2.3.2.1. INORGANIC PHOTOCATALYSTS

TiO₂ is one of the promising inorganic photocatalysts to be utilised in different fields including self-cleaning textiles. This concept was first introduced by Daoud and Xin[173] who successfully developed self-cleaning cotton by applying anatase TiO₂ colloid to cotton fibres using the conventional dip-pad-dry-cure process. The TiO₂ nanoparticles were produced on cellulose fibres at low temperature from an aqueous titania sol that was obtained through hydrolysis and condensation reactions of titanium isopropoxide in water.

Cotton and cellulosic textiles coated with this TiO₂ nanocrystalline film could deliver satisfactory photocatalytic self-cleaning properties including antibacterial functions, decolourisation of dye stains and degradation of coffee and red wine stains[30, 158, 174, 175]. Further modifications of this self-cleaning system to enhance the photocatalytic activities,

strengthen the utilisation of visible light for activation, simplify the preparation process of anatase-TiO₂ sol and explore other properties or applications of the TiO₂ film were studied and developed[131, 159, 176-182]. Wool and polyester fibres coated with the anatase-TiO₂ with particular fabrication techniques were also investigated [4, 183-188]. TiO₂ in rutile crystalline form is also widely studied and reported for self-cleaning textiles[189-193] because commercial TiO₂ product, Degussa P-25, is composed of 70% anatase and 30% rutile. It is considered as a benchmark photocatalyst with its outstanding photocatalytic capability.

Other metal oxides, typically zinc oxide (ZnO), have comparable UV-photocatalytic selfcleaning effects on textiles. It is discovered that ZnO nanoparticle with smaller particle size (up to 9 nm) could achieve more outstanding photocatalytic stain decomposition and washfastness on the cotton fabric or other textile fibres but weaker UV protection factor (UPF) than the nano-TiO₂ with 35 nm of particle size[3, 194, 195]. In addition, sufficiently nano-sized ZnO-coated cotton fibre was also imparted with significant flame-retardant and antibacterial characteristics[196-198]. Since the intrinsic bandgap of ZnO is wider than TiO₂, researchers had attempted to modify the ZnO system to have more potent and diverse photocatalytic activities[196, 199, 200].

2.3.2.2. ORGANIC PHOTOCATALYSTS

Relative to the inorganic photocatalysts, organic photocatalysts applied to the selfcleaning textile materials tend to gain rare scholar attentions; thus, the development is still not as mature as the TiO₂ and ZnO-based self-cleaning systems. A thin film of metal porphyrins meso-tetra(4-carboxyphenyl)porphyrin such as (TCPP) and meso-tetra(4sulfonatophenyl)porphyrin (TPPS) with Fe(II), Co(II), Ni(II), Cu(II) or Zn(II)[9, 10, 201-203] and metal-fee porphyrins such as meso-tetra(4-carboxyphenyl) porphyrin (TCPP), meso-tetra(4sulfonatophenyl)porphyrin (TPPS), 4,4',4"'-(5,10,15,20-porphyrintetrayl)tetrabenzonitrile (TCNPP) and 5,10,15,20-tetra(pyridin-3-yl)porphyrin (TPyP)[13, 201, 202, 204] in conjunction with TiO₂ was established on cotton or polyester fibre' surfaces. Owing to the strong visible light absorption, such porphyrin substances acting as dye sensitiser to aid the TiO₂ nanocrystals to functionalise the substrate materials with visible-light-induced photocatalytic selfcleaning properties.

Furthermore, light-activated antimicrobial textiles can be fabricated with porphyrin-based systems, including grafting of protoporphyrin IX and zinc protoporphyrin IX to nylon fibres with polyacrylic acid scaffold[205], various types of charges of amino porphyrins and *meso-*arylporphyrin covalently grafted on cotton fabric using a triazine derivative as spacer[12, 206], polyurethane nanofabric produced by the "Nanospider" electrospinning technique and doped with 5,10,15,20-tetraphenylporphyrin (TPP), zinc 5,10,15,20-tetraphenylporphyrin (ZnTPP)

or/and zinc phthalocyanine (ZnPc)[207, 208] as well as electrospinning polymeric nanofibers of polyurethane, polystyrene, polycaprolactone and polyamide 6 doped with TPP[209]. The photo-activated antibacterial textile materials have been suggested to be used for privacy curtains in hospital rooms, laboratory coats for medical personnel, or other fibres or plastic surfaces within the hospital environment with normal rooms' illumination. Nevertheless, the material costs of porphyrin-type compounds are relatively more expensive than metal oxides or other organic photocatalysts (such as the porphyrin's derivatives, metal phthalocyanines). The lightfastness and serviceability concerns of porphyrin-treated materials make people doubtful whether they are stable enough for long-term services.

The main character in this project, metal phthalocyanine(s) (MPc(s)), had been reported in several publications concerning playing as a role of dye sensitisers to TiO₂ for exhibiting self-cleaning function of cotton fabric activated by visible light[210-212]. A number of patent documents recommend that various MPcs can act as photoactive agents for photo-bleaching the dirt and stains and photo-decompose the microorganisms adhering on textile fabric under visible light[213-221], but there are extremely limited academic results to support and evidence these ideas as well.

2.3.2.3. APPLICATION OF PHOTOCATALYTIC SELF-CLEANING TEXTILES

Development of photocatalytic self-cleaning technology to textile materials has been making a significant contribution to functional, hygienic and protective textiles. By the strong photo-redox reactions, unpleasant odours, such as perspiration, shoe, vehicle and cigarette smoke, as well as organic stains, such as coffee, red wine and oil, which cannot effectively be removed by laundry or dry-cleaning, can be removed by the photocatalyst(s) on the treated fibre surfaces to perform anti-fouling and anti-odour effects. As many photocatalysts are considered as good UV absorbers, photocatalytic self-cleaning textiles with proper physical features often provide excellent UV blocking[222]. Tung and Daoud[6] recommend that TiO₂ coating on medical garments, such as, operating gowns, hospital patient gowns, surgical gloves, masks, surgical caps, can inhibit the growth of bacteria on their surface to maintain cleanliness and germ-free to a marked extent.

Self-cleaning household products, such as kitchen cloths, bath towels, furniture fabrics are becoming popular nowadays. Domestic cleaning and disinfection products usually contain chemicals, such as bleaching agents and alcohols. However, contact with those chemicals could cause harm to health. Moreover, these agents can only provide a short-term cleaning effect. Self-cleaning fibrous materials coated with TiO₂ nanoparticles could be an alternative solution as they are proven to have durable dust-proof and antibacterial performances. In addition, organic contaminants can be oxidised by TiO₂ nanoparticles under low intensity light

irradiation. Therefore, these materials can offer effective protection against dust, infectious bacteria and microorganisms[29].

On the other hand, commercial antimicrobial products contain leaching antimicrobial agents which may possibly penetrate the skin and cause skin allergy[223]. These household products can firmly be coated with TiO₂ nanoparticles that would not leach. Moreover, titania on the surface can generate active radicals which will only decompose the microorganisms when they come into contact; because the outermost layer (stratum corneum) of human skin tends to protect the dermis layer from absorbing the active oxidising substances produced by TiO₂[224]. Furthermore, most of the limitations of leaching-type antimicrobial agents can be overcome as the self-cleaning surface is immobilised[223]. A hygienic environment is beneficial to a healthier and more sustainable life, particularly for children and the elderly.

Air filters loaded with photocatalysts can be placed in ventilation systems (smokestack, air conditioner, and stovepipe) and engines (motors). Incorporation of TiO₂ into air filters is able to clean the air from airborne organic contaminants[225, 226]. Installation of self-cleaning air filters in the opening of smokestacks and engines probably eliminate or reduce the emission of harmful gases[227, 228]. Self-cleaning air filters are suggested to be installed in air purifiers and air conditioners to maintain the indoor air quality[229, 230]. Thus, the occurrence of air-induced allergies, such as sick building syndrome (SBS) or nasal allergy, can also be reduced.

2.3.3. Comparisons between two self-cleaning approaches

Self-cleaning effect by the photocatalytic agents is more advantageous to the application on textiles, than that by superhydrophobic coating[28]. Photocatalytic coating possesses decomposition capability towards organic substances under the irradiation of lights or radiations (UV), instead of blockage of such organic matters to be adsorbed by textile fibres only. Superhydrophobic surfaces are found prone to absorbing oily stain[71] and these surfaces realised by the complex hierarchical textures are relatively delicate to be destroyed by mechanical impact or wear that occurs in daily uses and laundry. Once a tiny amount of highly penetrable stain is stickily retained and trapped on textile surface or the well-patterned surface collapses, such "self-cleaning" surface will malfunction due to the lack of any degradation ability towards the stained surface. Those are the reasons why modification to superhydrophobic surface tends to be a "passive" self-cleaning technique while the materials functionalised with photocatalytic agents (such as titania and metal oxides) for self-cleaning purpose are considered as an "active" self-cleaning style.

Furthermore, the preparation of TiO₂-based self-cleaning surface is less complicated, compared to fabrication of the superhydrophobic layer. This photo-induced self-cleaning system is able to exhibit robust, durable and multifunctional properties not only of self-cleaning, but also of antimicrobial, deodorant and UV-blocking particularly when TiO₂ is employed, while the superhydrophobicity rendered by hierarchical structure are fragile with limited durability. Hence, photocatalyst-based self-cleaning coatings become more suitable for textiles which are usually subject to washing, rubbing and various environmental conditions, in contrast, the aging and durability problems of the biomimic repellent surface limit the long-term uses on textile materials.

2.4. PHTHALOCYANINES

2.4.1. History

Phthalocyanine (Pc) was first found as a highly coloured by-product in the chemical conversion of some ortho-(1,2)-disubstituted benzene derivatives. In 1907, von Braun and Tscherniak discovered a dark-blue insoluble substance during the preparation of orthocyanobenzamide from phthalimide and acetic acid (see Scheme 2-1) at the South Metropolitan Gas Company in London. In 1927, de Diesbach and von der Weid, of Fribourg University, acquired a 23%-yield of bluish side product with exceptional stability during the synthesis of phthalonitrile from ortho-dibromobenzene with copper(I) cyanide in pyridine under reflux at 200 °C (see Scheme 2-2)[15, 231, 232]. These by-products were believed as metal-free phthalocyanine (H₂Pc) and copper phthalocyanine (CuPc) respectively.



Scheme 2-1. Trial production of ortho-cyanobenzamide from phthalimide and acetic acid.



Scheme 2-2. Trial synthesis of phthalonitrile from ortho-dibromobenzene with copper(I) cyanide.

The more detailed investigation of Pc, which was widely viewed as the first discovery event of Pc, started from 1928 and this Pc material was also obtained accidentally. During the course of the industrial production of phthalimide from phthalic anhydride in the Grangemouth plant of Scottish Dyes, ammonia was passed into molten phthalic anhydride contained in iron vessels and it was observed that traces of a dark blue substance were formed in the molten imide in certain preparations. Examined by the two employees from Scottish Dyes, Dandridge and Dunsworth, it was surprising that this iron-containing material had exceptional stability, poor solubility in various solvent and easy crystal formation. Furthermore, the contained iron was not able to be eliminated by treating with concentrated sulphuric acid. Their preliminary studies revealed that the properties of this iron-containing by-product had potential as a commercial pigment; a patent describing the preparation and properties of the substance was

granted in 1929[233].

Since Imperial Chemical Industries (ICI) acquired Scottish Dyes of Grangemouth in 1928; and the special properties of the Pc substance aroused academic interest, ICI initially invited Professor Jocelyn F. Thorpe, of Imperial College (London), to study the structure of this novel coloured substance. He finally passed the project to Reginald P. Linstead, a newly appointed lecturer of Imperial College at that time, to work the research committee of the Dyestuffs Group of Imperial Chemical Industries and report a series of findings about the structure of Pc and the synthesis of some of its metal derivatives in the Journal of the Chemical Society in 1934[234-239].

2.4.2. Chemical structure

Pc is a synthetic organic chemical compound having a structure of being a flat, symmetrical, and planar aromatic macrocycle that contains four iminoisoindoline units[240]. The phthalocyanines are structurally similar to the natural pigments chlorophyll and haemin, which are the derivatives of porphyrin (Figure 2-10); hence, Pc can be considered as the tetraaaza-derivative of tetra-benzoporphyrin consisting of four isoindole units connected by four nitrogen atoms that form together a planar and an internal 16-membered ring of alternate carbon and nitrogen atom[15]. For example, metal-free phthalocyanine (H₂Pc) can exactly be

named 29*H*,31*H*-tetrabenzo[*b*,*g*,*l*,*q*]-5,10,15,20- tetraazaporphyrin.

Over seventy metals or semimetals as cations in different oxidation states can be chelated by the macrocycle of Pc in its central cavity, where the two hydrogen atoms can be substituted by the cations, to form different MPcs (Figure 2-10). MPc in general shows brilliant and intense colours. Besides, the peripheral hydrogen atoms in the benzene rings can also be substituted by halogen atoms or other functional groups such as amino, nitro, alkoxy, carboxyl and sulphonyl etc.[241]. The internal and external positions of the fused benzene ring are also commonly known as α - and β -positions respectively[242, 243].



Figure 2-10. Chemical structures of (a) H₂Pc, (b) metal-free porphyrin and (c) MPc.

Pcs have their own special electronic and physicochemical characteristics, and could be organised into different condensed systems[244, 245]. Pcs are planar aromatic macrocycles constituted by four isoindole units linked together through nitrogen atoms. The dianionic ligand with 42 π -electrons distributing over 32 carbon and 8 nitrogen atoms exhibits a pronounced

aromatic character according to the Hückel rule (4n+2) with n = 10. Nevertheless, the more dominant electronic delocalisation generally occurs in the inner ring, which is constituted by 16 atoms (i.e., carbon and nitrogen atoms) and 18 π -electrons, the outer benzene rings tend to maintain their electronic structures[246]. Such combination of aromaticity in an extended π system including four fused benzenoid aromatics is essential not only for strong absorption in visible spectrum, λ = 650-750 nm, to result in intense turquoise colour; but also an excellent thermal and chemical stability of the most planar Pcs when in solid state.

2.4.3. Physicochemical properties

2.4.3.1. OPTICAL ABSORPTION [247]

Pcs have intense turquoise blue or green colours because of their remarkably strong absorption of light. Light is an electromagnetic wave and thus its propagation is accompanied by a change in electric and magnetic fields. As there are many electrons, which are negatively-charged, in a molecule, they are directly affected, in particular, by the electric field caused by light propagation. It should be noted that dye molecules (at most ~1 nm in diameter) are generally much smaller than the wavelength of visible light (380-780 nm); hence, it can be assumed that the light demonstrates an equal effect on the whole Pc molecule. When a molecule is subjected to an electromagnetic wave (e.g., visible light for dye) and then excited

to higher energy states, it absorbs the light and its electrons vibrate according to the wavelength i.e., frequency. At a specific frequency particular to the molecule, the electrons vigorously shake in this excited molecule and their electron distribution is significantly rearranged to such an extent that an electric dipole is generated (known as resonance).

Each compound has a resonant wavelength (also frequency) for each electronic excitation, but normally it has more than one electronically excited state. Visible light can only excite the electrons in the outermost shell of a molecule, such as those in π -orbitals in aromatic compounds or d-orbitals in transition metal compounds, to the lowest excited states. Because of a molecule absorbing light according to the transitions from the ground state to excited states, optical absorption spectrum sometimes is also referred to as "electronic absorption spectrum".

Figure 2-11 presents the characteristic absorption spectrum of MPc dissolved in a liquid medium. It is characterised by (1) the appearance of an intense absorption band at ~670 nm termed the Q band (logarithm of coefficient extinction (ϵ) ~5), associated with certain less intense (logarithm of coefficient extinction (ϵ) ~4) satellites at its blue flank (600-650 nm), (2) the appearance of a less intense but broad band at ~350 nm, named the Soret or B band, and (3) transparency in the other spectral regions (spectral windows). It should be noted that, the Q-band absorption is assigned to a π - π * transition from the highest occupied molecular orbital (HOMO), of a_{1u} symmetry, to the lowest unoccupied molecular orbital (LUMO) of e_g symmetry.



Figure 2-11. Absorption spectrum of copper phthalocyanine-3,4',4",4"'-tetrasulphonic acid tetrasodium salt dissolved in 50/50 DI water/ethanol (concentration: 20 mg/L).

As Pcs mainly absorb red light intensely and are transparent in the other spectral regions (400–600 nm and >750 nm), this is the reason why Pcs show an intense blue colour under visible light in general.

2.4.3.2. PHOTOCATALYSIS

Singlet oxygen (O₂ ($^{1}\Delta_{g}$)) is one of the reactive oxygen species (ROS) to bear very strong oxidising power[248, 249]. O₂ ($^{1}\Delta_{g}$) belongs to the lowest excited state and its electronic state is presented in Figure 2-12. Since the direct excitation from triplet molecular oxygen O₂ ($^{3}\Sigma_{g}$)

to O_2 ($^1\Delta_g$) is forbidden, O_2 ($^1\Delta_g$) is generally produced by the energy transfer from a photosensitizer to O_2 ($^3\Sigma_g$). Following Figure 2-13, the photosensitiser is excited to the lowest excited singlet (S_1) state by the absorption of light ($h\nu$) and then converted into the lowest excited triplet (T_1) state. When the electrons of the photosensitiser return from T_1 to the ground state (S_0), such energy can be transferred to the O_2 ($^3\Sigma_g$) to generate O_2 ($^1\Delta_g$), which shows luminescence at around 1270 nm.



Figure 2-12. Electronic configurations of O_2 (${}^{1}\Sigma_g$), O_2 (${}^{1}\Delta_g$), and O_2 (${}^{3}\Sigma_g$)[17].



Figure 2-13. Mechanism of generating singlet oxygen via photosensitisation process.

As a satisfactory photosensitiser to generate O₂ ($^{1}\Delta_{g}$) [17, 250], many Pcs possess high absorption coefficient (extinction coefficient, ε) in visible light region (Q-band), sufficient energy transfer for exciting oxygen at T₀ (O₂ ($^{3}\Sigma_{g}$)) to S₁ (O₂ ($^{1}\Delta_{g}$)) ($E_{T} \ge 95$ kJ/mol), high quantum yield of the triplet state ($\Phi_{T} > 0.4$), long triplet state lifetimes ($T_{T} \ge 1 \mu s$) and convincing photostability.

2.4.3.3. MOLECULAR AGGREGATION

In solution chemistry of Pcs, when two or more Pc molecules come close to one another, dimers or even aggregates will be formed regardless of whether they are chemically bonded[251-253]. When the distance between the Pc compounds is longer or shorter than the van der Waals distance of 3.4 Å, the interaction of their transition dipole moments or overlapping of their π -conjugation systems tends to occur respectively. These effects result in significant difference of the observed optical absorption spectra, particularly in the Q-band region, compared with the superposition of the spectra of the monomeric Pcs[254-258].

The effect of molecular dimerisation and aggregation to the Q-band, which represents a π - π * transition from the HOMO of a_{1u} symmetry to the LUMO of e_g symmetry, in optical absorption spectra of Pcs in solution can be interpreted based on exciton coupling theory[252, 259, 260] (assuming the distance between the adjacent Pc molecules >3.4 Å to neglect the effects of the π -clouds overlapping). Figure 2-14 illustrates splitting of the ¹E_u excited state into two energy levels (Q₊ and Q₋) by exciton coupling for two adjacent MPc molecules.



Figure 2-14. Simplified schematic diagram of exciton coupling model of the Q-band of dimeric MPc complexes (vertical single-headed arrows: electronic transition; horizontal single-headed arrows: dipole moment transition (phase transition)).

The relative orientation of the transition dipole moments (horizontal single-headed arrows in Figure 2-14) determines which of these energy levels contribute to light absorption. For the cofacial dimers, transitions to the higher energy levels are allowed and the hypsochromic shift (blue shift) of Q-band occurs relative to its position in the monomeric molecular spectrum; there is no light absorption as the lower energy exciton interaction has no net dipole change. In contrast, for two MPcs encountering in "edge to edge" manner, such Q-band is bathochromic-shifted (red-shifted) from its position in the isolated molecular spectrum.



Figure 2-15. Absorption spectrum of 20 mg/L of Direct Blue 86 dissolved in 0.1% Triton X-100 (aq.).

Nevertheless, cofacial dimer and aggregates dominantly exist due to the planar structure of Pc molecules and significantly strong benzene-benzene attraction among the macrocyclic rings; unless the metal ion of the macrocyclic ligand has axial ligands to sterically hinder cofacial aggregation or the peripheral substituents are capable of coordination to the central metal ion in the cavity of another macrocycle[261]. Hence, the two peaks appearing in Q-band absorption were useful to determine the contents of monomeric Pc and dimeric Pc in a medium respectively by the ones at longer and shorter wavelengths[23, 240, 262] (see Figure 2-15).

Besides the influence of the optical absorption spectra, molecular aggregation is also one of the factors to determine the photocatalytic activities of Pcs. In photo-initiated processes, the formation of Pc dimers drives triplet-triplet annihilation (TTA) (also known as bimolecular triplet annihilation) to cause quenching of the excited triplet electron state of the complexes; therefore, the quantum yield of ${}^{1}O_{2}({}^{1}\Delta_{g})$ tends to be suppressed[23, 263-266]. TTA is an energy transfer mechanism between two molecules in their triplet state as shown in Figure 2-16. When TTA happens between two photosensitiser molecules in their excited



Figure 2-16. Jablonski diagram describing inhibition of photosensitised O_2 ($^1\Delta_g$) generation by photon upconversion via biomolecular triplet annihilation.

state, one O_2 (${}^{1}\Delta_{g}$) (produced from Photosensitiser B in Figure 2-16), can transfer its excited state energy to the adjacent O_2 (${}^{1}\Delta_{g}$) molecule (produced from Photosensitiser A in Figure 2-16); so that one O_2 (${}^{1}\Delta_{g}$) molecule will return to its ground state while another O_2 (${}^{1}\Delta_{g}$) molecule will further be excited to its higher energy states, typically to become $O_2({}^{1}\Sigma_{g})$ at S_2 level. This process is known as photon upconverison[267, 268]. Although one of the singlet oxygen can be promoted to much higher energy level, generally $O_2({}^{1}\Sigma_{g})$, its very short lifetime makes itself relaxing to the triplet ground state instantaneously[269]. As a result, it can be imagined that every TTA process waste two potential singlet oxygen molecules; molecular aggregation of Pcs dependent on the accommodation media exert a considerable impact about restraining photocatalytic performances of Pcs.

2.4.4. Applications

2.4.4.1. As colorants

Pcs, exclusively CuPcs including the chloro- and bromo- substituted derivatives, are widely used as blue and green colorants for decades owing to their extraordinary colour strength and fastness properties to light, weathering and numerous solvents[243, 270]. About 25% of synthetic organic pigments are Pcs and their derivatives. In about 80,000-tonne worldwide production, valued over one billion U.S. dollars, there are over 95% are applied in

colorants while only small portions are supplied to produce the new tailor-made thin films materials. The usage of colorants contains ~40% for printing inks, ~30% varnish or paints, ~20% for colouring plastics and ~10% for other finishes. Pcs colorants can be converted as dyestuffs when the auxochromes such as $-NH_2$, -COOH and $-SO_3H$, etc. are attached to this dye molecule[271]. Commercial dyes extensively developed in various application classes have been summarised in Table 2-1.

Application	Colour Index Generic Name												Total
Class Colour													
Direct Blue	86	87	189	199	262								5
Direct Green	75												1
Reactive Blue	3	7	11	14	15	18	21	23	25	30	35	38	24
	41	57	58	63	71	72	80	85	88	91	92	95	
Reactive Green	2	4	5	9	12	13	14	18	58	77			10
Mordant Green	54												1
Solvent Blue	24	25	42	44	46	52	55	64	67	70	75		11
Solvent Green	22												1
Vat Blue	29	57											2
Acid Blue	185	197	228	242	243	249	254	255	275	279			10
Acid Green	97												1
Basic Blue	33	63	82										3
											0	verall	69

Table 2-1. Phthalocyanine dyes categorised in different application classes in Colour Index (C.I.)[272].
2.4.4.2. FOR OPTICAL, ELECTRONIC AND PHOTOELECTRONIC DEVICES

The strong infrared absorption of palladium phthalocyanine (PdPc) compounds (see Figure 2-17) is a dominant property to be developed as the leading Pc infrared absorbers for Compact Disk-Rewritable (CD-R); as the "writing" and "reading" processes of a CD-R involve infrared laser for data input (irradiating the rotating disk with a high intensity laser beam along the pregoove) and data reading (observing the reflection by a low intensity on the disk)[243]. The bulky substituting groups can reduce undesirable molecular aggregation, which tends to weaken the extinction coefficient and hence the absorptivity and reflectivity. Partial bromination allows fine tuning of the film absorbance and improves reflectivity. The palladium atom mainly controls the position of the absorption band, together with improving the photostability and the efficiency of the radiationless transition from the excited state[273, 274].



Figure 2-17. Typical PdPc derivatives for producing CD-R.

Pc colorants are also the key component to establish the translucent colour filters of liquid crystal displays (LCDs). It is a two-dimensional periodic arrays of colour absorptive surfaces in the three primary colours, red, green and blue, of the additive colour mixture and a crucial part for generating colour by filtering white light from a back layer in the display (see Figure 2-18)[275].



Figure 2-18. Configuration of an LCD display[243].

The colorants for constructing the colour filters require satisfactory colourfastness, colour uniformity, colour intensity and colour stability. Adequate fineness, uniformity and globular particle (20-30 nm) shapes with minimal agglomeration are necessary to avoid light scattering in the display. Figure 2-19 demonstrates that Pcs cover two of the three primary colours; ε-form of CuPc generally serve for the primary colour blue and the chloro-/bromo-CuPc is usually responsible for the primary colour green.



Figure 2-19. Transmission spectra of the three pigments for building up fundamental colours red, green and blue of an LCD display[243].

MPcs can act as light-sensitive photoconductors in (electrophotographic or xerographic) photocopiers and laser printers. During the xerographic process, the photoconductor is essential to develop electrostatic image under illumination, and then a template is produced to deliver a positive image of the original on a printout. Nowadays, more than 90% organic photoconductors based on the Y-modification of titanyl phthalocyanine (TiOPc i.e. (Ti=O)²⁺Pc²⁻) is employed. Low material cost, high photoconductivity, excellent photostability and high absorbance of visible light with long wavelength are the advantages of TiOPc as photoconductor in electrophotographic photocopiers and laser printers[276, 277].

On the other hand, MPcs have been applied on photovoltaic devices, typically for organic

p-n junction solar cells and dye-sensitised solar cells[278-280]. MPcs are able to provide high crystalline order in solid state, *p*-conductivity and photoconductivity, intense absorption in the visible spectrum, right electronic energy levels and good photostability to establish a solar cell system. An intrinsic absorber layer, composed of ZnPc or CuPc, for visible light as *p*-type conductor couples with C_{60} (fullerene) as *n*-type conductor to form p-n junction system[281-285]. 1,8,15,22-tetrafluorophthalocyanine can play as roles of absorber and *p*-conductor[286] and hexadecafluorophthalocyanine is employed as absorber and *n*-conductor[287].

2.4.4.3. FOR PHOTODYNAMIC THERAPY (PDT)

Photodynamic therapy (PDT) is a non-invasive therapeutic treatment for various tumours and non-malignant diseases. This technique involves the (1) photosensitiser (PS) that located in the target tissue to be treated, typically an organic dye, and (2) a low intensity laser radiation of a certain wavelength which can excite the PS to generate reactive oxygen species (ROS) functioning as cytotoxic agents, such as superoxide (O_2^-), hydrogen peroxide (H_2O_2), and hydroxyl radical (HO^-)[288], to kill the target cells in form of structural damage[289, 290]. Generally, PDT is considered as a two-step approach; PS molecules are introduced into the organism, followed by the tissue-localised PS exposed to laser radiation of specific wavelength to produce ROS through a series of photophysical and photochemical pathways. This method has been employed as therapy against different tumour types, such as skin, bladder, oral cavity, and others[291].

Porphyrins and phthalocyanines are the macrocyclic-type PS widely studied for PDT[288, 292]. Starting from 1980s, Lier and his team members had extensively studied and reported the photodynamic performances, biological activities, physicochemical properties, synthesis, analytical methods various sulphonated or substituted Pc compounds metallised with Zn, GaCl, AlCl, Cu, Mg, Mn, Ni, Co, VO, Fe, and CrF[263, 293-306]. One of the important findings which is relevant and correlated to this project of MPc for self-cleaning cotton is the photosensitisation efficiency of MPc molecules dependent on the extent of molecular aggregation in a medium[289, 307]. Triplet excited states are not inhibited to lead to self-quenching and so triplet energy can be transferred to oxygen to trigger the following PDT mechanism.

2.4.4.4. FOR CATALYSIS AND PHOTOCATALYSIS

Metal phthalocyanines can be efficient catalysts and photocatalysts in oxidation reactions using molecular oxygen as oxidant. The detailed catalytic and photocatalytic reactions are summarised and reported by Kaliya et al.[308] and Wöhrle et al.[309]. Wastewater treatment is one of the popular applications based on the photocatalytic property of MPcs[32, 310, 311].

3.1. INTRODUCTION

There are a number of methods to evaluate the activities of photocatalyst exerting selfcleaning effect; whereas, decolourisation of dyes (acting as stains) is the one of the common ways to be followed in many researches. This is because, the degradation of dye stains can be monitored by a facile spectrophotometric or colorimetric technique. Dyes which are easily accessible in the markets are also considered as industrial pollutants in effluents; hence, degrading such dye stains can simulate the practical applications of the self-cleaning systems to a certain extent. However, some scholars criticize the limitations and realities of using dyes as model compounds (as stains) for assessing various activities of photocatalytic systems[77, 312-315].

As colouring agents, dyes themselves possess relatively large photo-absorption or extinction coefficients. Many researches have listed a number of problems arisen from dye decolourisation as an activity evaluation method especially for visible-light-induced photocatalysts. Firstly, dye itself absorbs visible light and its degradation can be initiated from the excited dye in terms of direct photolysis or photo-fading[316-318] and dye sensitisation[319, 320] but not the excited photocatalyst; therefore such decolourisation results obtained may not indicate the intrinsic photocatalytic effects of the self-cleaning systems. Secondly, the visible-light-absorbing dyes are able to attenuate the incident light flux applicable for the photocatalyst, or, shield the photocatalyst samples to the irradiation to cause possible underestimation of the intrinsic activity of the catalyst materials under visible light. Thirdly, the decolourisation of dye tends to represent the specific conversion of chromophoric groups instead of a complete degradation (or mineralization) of the dye stains. It implies that dye decolourisation belongs to the selective degradation of a specific functional group in a molecule of dye stains, but an overall degradation can be inefficient. Fourthly, monitor of the decolourisation by absorbance measurement at a single wavelength of the dye stains can be inaccurate because there is usually a spectral change when the intermediate products are generated during the decolourisation process. The Beer's law that relates the absorbance to the dye concentration is not highly compatible to the assessment system. Fifthly, most commercially available dyes have typically 70–90% purity. The unknown components in a dye product may interfere with the photocatalytic decomposition of such parent dye.

Although the above problems reveal the deficiencies of dye decolourisation for evaluating the photocatalytic activity of the self-cleaning substrates, this chapter attempts to demonstrate that using dyes as stain indicators are still feasible, suitable and acceptable throughout this self-cleaning study. Different from the inorganic photocatalysts (semiconductors) discussed by the previous scholars[77, 312-315], MPcs which are organic photocatalysts derive a distinct case to them as well.

3.2. METHODOLOGY

The experimental details of a series of work about investigation of the acid dyes as model compounds for the MPc activity assessments are provided in this section.

3.2.1. Materials

Acid dyes acted as coloured stains to indicate the photocatalytic activities demonstrated by the MPcs under visible light irradiation. Both C.I. Acid Orange 3 (AO3) and C.I. Acid Yellow 49 (AY49) was supplied by Hangzhou Chungyo Chemicals. C.I. Acid Red 1 (AR1), C.I. Acid Orange 7 (AO7), Rhodamine B (RhB; i.e., C.I. Acid Red 52) and C.I. Acid Yellow 17 (AY17) were ordered from Aldrich. Methyl orange (MO; i.e., C.I. Acid Orange 52) was purchased from Acros Organics. Red wine and coffee powder was manufactured by Barefoot Merlot and Waitrose (essential Waitrose rich roast coffee) respectively. All the products were used as received. The chemical information of the acid dyes utilised in this chapter are listed in Table 3-1 for reference. All of the acid dyes and stains were directly used without purification.

C.I. Generic Name	Chemical Structure	Empirical	Molecular
		Formula	Weight
Acid Orange 3	$ \begin{array}{c} & \overset{SO_3 \cdot Na^+}{\qquad \qquad \qquad$	C ₁₈ H ₁₃ N4NaO7S	452.37
Acid Orange 7		$C_{16}H_{11}N_2NaO_4S$	350.32
Acid Orange 52 (Methyl orange)	H ₃ C _N CH ₃	$C_{14}H_{14}N_3NaO_3S$	327.33
Acid Red 1	HN HO HN CH ₃ SO ₃ ['] Na ⁺	C ₁₈ H ₁₃ N ₃ Na ₂ O ₈ S ₂	509.42
Acid Red 52 (Rhodamine B)	H ₃ C N O O N ⁺ CH ₃	C27H29N2NaO7S2	580.65
Acid Yellow 17	H ₃ C ¹ CH ₃	C16H10Cl2N4Na2O7S2	551.29
Acid Yellow 49	$H_{3}C$ $H_{3}C$ N $H_{3}C$ N $H_{3}C$ H_{3	C ₁₆ H ₁₂ Cl ₂ N ₅ NaO ₃ S	448.26

Table 3-1. Chemical information of the selected acid dye stains

Regarding the MPcs as photocatalysts, copper phthalocyanine-3,4',4",4"'-tetrasulphonic acid tetrasodium salt (CuPcS₄) and nickel (II) phthalocyanine-tetrasulphonic acid tetrasodium salt (NiPcS₄) were purchased from Aldrich. C.I. Direct Blue 86 (DB86) and zinc phthalocyanine (ZnPc) were the Tokyo Chemical Industry's products. C.I. Direct Blue 199 (DB199), C.I. Reactive Blue 15 (RB15) and C.I. Reactive Blue 21 (RB21) were sourced from Everlight Chemical. C.I. Reactive Blue 14 (RB14) was offered by Jiangsu World Chemical. Chlorosulphonic acid was bought from Acros Organics. NaCl and Na₂CO₃ were offered by International Laboratory USA. Triton X-100 (TX-100) and Ethanol were produced by VWR. Diadavin EWN-M 200% was manufactured by Tanatex Chemicals. All of the dyes and chemical reagents were directly used without purification.

3.2.2. Experimental details

3.2.2.1. Assessment of light stability of the dye stains

Cotton fabrics (5×5 cm) were spotted with 60 µL of dye stain solutions by micropipette. The concentrations of AO3, MO, AR1, RhB, AY17 and AY49 solutions were 0.2 % w/v while that of AO7 solution was 1.8% w/v. All stained samples were first dried in a dark room which was air-conditioned at ~20 °C for at least 1 hour and exposed to visible light source, Philips TL-D 18W/827 1SL/25, for 86 hr. Measured by light meter (Tenmars TM-208), the average light intensities of the source were 35.9 and 0.254 W/m² for visible light and UV respectively.

The changes in concentrations of the dye stains on fabric specimens were monitored by determining the reflectance spectra (400-700 nm) of the stained areas via a reflectance spectrophotometer (Macbeth ColorEye 7000A) and capturing the image of the stained specimens by photo scanner (Epson Perfection V370) without photo adjustments, at different time intervals during the course of irradiation. For the reflectance spectrophotometry, the fabric specimens were measured according to the measurement conditions shown in Table 3-2, the face side of a fabric specimen was measured 4 times at every 90° of fabric geometry. Through Kubelka-Munk expression, the spectral K/S values were converted from the measured reflectance following Equation 3-1, to represent the spectral absorption behaviours of the colorant stains on cotton. The K/S values of the colorant stains themselves, i.e., excluding the substrate absorption, were subsequently acquired following Equation 3-2. The sum of K/S values (∑K/S* values) of the dye stains within 400-700nm collected at 10 nm intervals were calculated following Equation 3-3.

Equation 3-1.

$$K/S_{D+F} = \frac{(1-R_N)^2}{2R_N}$$

Equation 3-2.

$$K/S_D = K/S_{D+F} - K/S_F$$

Equation 3-3.

$$\Sigma K/S_{D}^{*} = \sum_{\lambda} K/S_{D}$$

where K is the absorption coefficient of the stained fabric
S is the scattering coefficient of the stained fabric
D is the dye stain
F is the fabric substrate
R_N is the reflectance value of the spotted part of the sample
λ is absorption wavelengths from 400-700 nm with a 10 nm-interval

Table 3-2. Measurement conditions set for Macbeth ColorEye 7000A.

Set-up location	Parameter		
On touch pad	Calibrated reflectance (CAL REFL)		
	Aperture small area view (APERT SAV)		
	Lens large area view (LENS SAV)		
	UVD65		
	Specular o	ompo	nent exclude (SCE)
On SCOPE [®] programme	Aperture	:	Small
	UV	:	Included
	Specular	:	Excluded
	Mode	:	Reflectance

3.2.2.2. VERIFICATION OF DYE SENSITISATION ABSENT IN CUPC-SELF-CLEANING SYSTEM

To determine the excitation energy between LUMO and HOMO ($\Delta E_{LUMO-HOMO}$) of the dye

stains and MPc dyes on cotton fabric, stained and MPc-dyed cotton fabrics were prepared in

the following.

For the stained samples, cotton fabrics (5×5 cm) were spotted with 60 μ L of dye stain solutions by micropipette. The concentrations of AO3, AO7, MO, AR1, RhB, AY17 and AY49 solutions were 0.32, 0.1, 0.62, 0.125, 0.0825, 0.29 and 0.1% w/v respectively. All stained samples were first dried in a dark room which was air-conditioned at ~20 °C for at least 1 hour.

All the MPc-dyed samples were dyed at the specified % depths to achieve K/S ~1 at the peak of the Q-band absorption representing the MPc monomers. CuPcS₄, NiPcS₄ and the sulphonated ZnPc were introduced to cotton fabric (10×10 cm; 2.000 - 2.020 g) via direct dyeing method, of which the dyeing recipes and dyeing profile are presented in Table 3-3 and Figure 3-1 respectively. The sulphonated ZnPc was obtained by sulphonation of ZnPc (0.3 g) with chlorosulphonic acid (3.6 g) at 120 °C for 1 hour. The cooled-down reaction product was then dissolved in DI water and neutralised with soda ash to make up 1% w/v sulphonated ZnPc solution. Liquid chromatography-mass spectrometry (LC-MS) analysed this solution to be composed of tetra- and tri- sulphonated ZnPcs mainly (the detailed experimental are mentioned in Chapter 5). RB14 and RB21 were applied to cotton pieces (10×10 cm; 2.000 -2.020 g) via reactive dyeing technique following the recipes and dyeing profile in Table 3-4 and Figure 3-2 respectively. Each piece of dyed cotton was rinsed with running tap water at room temperature for 1 min; and subsequently washed by: (1) TX-100 (0.1% w/v) / ethanol (2% v/v) aqueous solution at 80 °C water bath for 10 min under uniform agitation (150 rpm);

and then (2) nonionic detergent, Diadavin EWN-M 200%, solution (0.1% w/v) at 90 °C for 30 min under uniform agitation (150 rpm). All the washed samples were finally oven-dried at 60 – 70 °C for 1.5 hours.

Table 3-3. Recipes for preparation of $CuPcS_4$, NiPcS₄ and sulphonated ZnPc-dyed cotton fabric with the peaks of Q-bands indicating the monomeric MPcs at K/S ~1.

		CuPcS₄	NiPcS₄	Sulphonated ZnPc
Dye	(% o.w.f.)	0.33	1	0.2
NaCl	(% o.w.f.)	60	60	60
Na ₂ CO ₃	(% o.w.f.)	0.5	0.5	0.5
D.I. water		#	#	#
Fabric weight	(g)	2	2	2
Liquor ratio	(L:kg)	50:1	50:1	50:1

Used for making up to total bath volume



Figure 3-1. Exhaustion dyeing profile for application of DB86, NiPcS₄ and sulphonated ZnPc dyes to cotton fabric individually.

		RB14	RB21
Dye	(% o.w.f.)	2	0.1
NaCl	(g/L)	60	60
Na ₂ CO ₃	(g/L)	10	10
D.I. water		#	#
Fabric weight	(g)	2	2
Liquor ratio	(L:kg)	40:1	40:1

Table 3-4. Recipes for preparation of RB14 and RB21-dyed cotton fabric with the peaks of Q-bands indicating the monomeric MPcs at K/S ~1.

Used for making up to total bath volume



Figure 3-2. Exhaustion dyeing profile for application of RB14 and RB21 dyes to cotton fabric individually.

The reflectance spectra of the stained and dyed cotton pieces within the visible light spectrum at 5 nm intervals were obtained by reflectance spectrophotometer, Datacolor 650. The face side of a fabric specimen was measured 4 times at every 90° of fabric geometry. Following Equation 3-4, the K/S spectra of the stained and dyed fabrics were converted from their corresponding measured reflectance spectra. The K/S spectrum of each MPc dye or stain

itself, i.e., excluding the substrate absorption, was determined with Equation 3-5; and the wavelengths of absorption peaks (λ_{max}) of each sample were recorded. The energy gap between HOMO and LUMO were calculated with Equation 3-6.

Equation 3-4.

$$K/S_{D+F} = \frac{(1-R_N)^2}{2R_N}$$

Equation 3-5.

$$K/S_{D} = K/S_{D+F} - K/S_{F}$$

where K is the absorption coefficient of the dyed or stained fabric

S is the scattering coefficient of the dyed or stained fabric

D is the MPc dye or stain

F is the fabric substrate

 R_N is the reflectance value of the dyed sample or spotted part of sample

Equation 3-6.

$$\Delta E_{\rm LUMO-HOMO} = \frac{ch}{\lambda_{max}}$$

where $\Delta E_{LUMO-HOMO}$ is excitation energy between HOMO and LUMO c is light speed (3.00×10⁸ m/s) h is Planck's constant (6.626×10⁻³⁴ J s) λ_{max} is the wavelength with the maximum K/S value

i.e., peak wavelength

3.2.2.3. SPECTROPHOTOMETRIC ANALYSIS OF THE MPC DYES AND ACID DYE STAINS

All the MPc-dyed samples were dyed at the specified % depths to achieve K/S = 1-1.5 at the peak of the Q-band absorption representing the MPc monomers. DB86, DB199, CuPcS₄, NiPcS₄ and the sulphonated ZnPc were introduced to cotton fabric (10×10 cm; 2.000 – 2.020 g) via direct dyeing method, of which the dyeing recipes and dyeing profile are presented in Table 3-5 and Figure 3-1 respectively. The sulphonated ZnPc was prepared as same as the one in Section 3.2.2.2 and LC-MS analysed it to be tetra- and tri- sulphonated mainly. RB14, RB15 and RB21 were applied to cotton pieces (10×10 cm; 2.000 – 2.020 g) via reactive dyeing technique following the recipes and dyeing profile in Table 3-6 and Figure 3-2 respectively. Each piece of dyed cotton was rinsed with running tap water at room temperature for 1 min; and subsequently washed by: (1) TX-100 (0.1% w/v) / ethanol (2% v/v) aqueous solution at

80 °C water bath for 10 min under uniform agitation (150 rpm); and then (2) nonionic detergent, Diadavin EWN-M 200%, solution (0.1% w/v) at 90 °C for 30 min under uniform agitation (150 rpm). All the washed samples were finally oven-dried at 60 – 70 °C for 1.5 hours.

To prepare the stained samples with the maximum K/S value within 1 and 2, cotton fabrics $(5 \times 5 \text{ cm})$ were spotted with 60 µL of dye stain solutions by micropipette. The concentrations of AO3, AO7, MO, AR1, RhB, AY17 and AY49 solutions were 0.32, 0.06, 0.62, 0.125, 0.0825, 0.29 and 0.1% w/v respectively. All stain samples were first dried in a dark room which was air-conditioned at ~20 °C for at least 1 hour.

		DB86	DB199	CuPcS₄	NiPcS₄	Sulphonated
						ZnPc
Dye	(% o.w.f.)	0.08	0.085	0.34	1	0.2
NaCl	(% o.w.f.)	60	60	60	60	60
Na ₂ CO ₃	(% o.w.f.)	0.5	0.5	0.5	0.5	0.5
D.I. water		#	#	#	#	#
Fabric weight	(g)	2	2	2	2	2
Liquor ratio	(L:kg)	50:1	50:1	50:1	50:1	50:1

Table 3-5. Recipes for preparation of DB86, DB199, CuPcS₄, NiPcS₄ and sulphonated ZnPc-dyed cotton fabric with the peaks of Q-bands indicating the monomeric MPcs at K/S = 1-1.5.

Used for making up to total bath volume

		RB14	RB15	RB21
Dye	(% o.w.f.)	1.7	0.6	0.1
NaCl	(g/L)	60	60	60
Na ₂ CO ₃	(g/L)	10	10	10
D.I. water		#	#	#
Fabric weight	(g)	2	2	2
Liquor ratio	(L:kg)	40:1	40:1	40:1

Table 3-6. Recipes for preparation of RB14, RB15 and RB21-dyed cotton fabric with the peaks of Qbands indicating the monomeric MPcs at K/S = 1-1.5.

Used for making up to total bath volume

The reflectance spectra, from 400 to 700 nm, of the MPc-dyed and stained cotton pieces with a 5-nm interval were obtained by reflectance spectrophotometer, Datacolor 650. The face side of a fabric specimen was measured 4 times at every 90° of fabric geometry. As same as the method mentioned in Section 3.2.2.2., the K/S spectrum of each MPc dye or stain itself, i.e., excluding the substrate absorption, was acquired following Equation 3-4 and 3-5. Each K/S spectrum of the MPc-dyed and stained cottons were normalised to have the maximum absorption at K/S = 1 to report.

3.2.2.4. LIGHT STABILITY TEST OF RED WINE- AND COFFEE- STAINED COTTON

Cotton fabrics (5×5 cm) were spotted with 60 μ L of red wind and coffee solutions by micropipette. The red wine was directly extracted as purchased and 0.5 g of the coffee powder

was dissolved in 50 mL of DI water for spotting onto the cotton pieces. All the stained samples were first dried in a dark room which was air-conditioned at ~20 °C for at least 1 hour and exposed to simulated daylight source, Verivide D65 "Artificial Daylight" 18W/ T8, for 70 hours. Measured by light meter (Tenmars TM-208), the average light intensities of the source were 11.76 and 0.11 W/m² for visible light and UV respectively. The images of the stained specimens were captured by photo scanner (Epson Perfection V370) without photo adjustments, at different time intervals during the course of irradiation.

3.3. RESULTS AND DISCUSSION

As mentioned in Section 3.1 based on Choi and his colleagues' viewpoint[312], dye decolourisation tests are suffered from five problems that make the photocatalytic activity assessment insufficiently reliable as a standard method. The five problems include (1) degradation of dye stains via direct photolysis or dye sensitisation rather than the photocatalytic reactions directly driven by the photocatalysts, (2) the performance of visible-light-induced photocatalysts, shielded by the dye stain, tended to be underestimated, (3) transformation of chromophores of the dye stains not equivalent to full degradation or mineralisation, (4) dye decolourisation monitored by absorbance measurement at a single wavelength not accurate enough and (5) market-available dyes generally with inadequate

purity delivering non-dependable photocatalytic activity results. Despite such severe conclusion against the dye decolourisation test by Choi and his colleagues, as well as the other researches[313-315], photocatalytic self-cleaning involving the MPcs can be considered as a different case with the following discussion.

3.3.1. Assessment of light stability of the dye stains

Dye can be decomposed by direct photolysis (i.e., photo-fading) or dye sensitisation in photocatalytic reactions when exposed to a light source. Among numerous commercially available acid dyes, the seven dye stains were selected based on their colourfastness to light first. Table 3-7 has summarized their fastness ratings which were recorded in a dyestuff handbook[321].

	AO3	A07	МО	AR1	RhB	AY17	AY49
AATCC ^a	5-6	5	-	4	2-3	7	-
ISO ^b	5-6	4	-	5	2-3	7	5-6

Table 3-7. Blue wool lightfastness standard ratings of the selected dye stains referring to[321].

Standards: ^aAATCC TM 16; ^bISO 105/B

Although there is no lightfastness information of MO, it is also selected since MO is one of the most common model compounds for photocatalytic degradation analysis[322-324]. Up the same reason, while RhB has significantly weak lightfastness property among the selected stain candidates, it is still on the candidate list because there is a great deal of publications concerning decomposition of RhB by a series of novel photocatalytic systems[325-330]. The dye stains were spotted on cotton fabrics and then irradiated with visible light (Philips TL-D 18W/827 1SL/25) for 86 hours, their degrees of photolysis are demonstrated in Figure 3-3 in terms of K/S value (details in Table 3-8). The visual appearance of the irradiated samples is presented in Figure 3-4.

	Irradiation hour				
Stain	0	19	45	86	
AO3	100.0	100.7	100.6	98.6	
AO7	100.0	82.1	70.0	54.6	
МО	100.0	93.7	91.5	90.2	
AR1	100.0	95.0	89.9	87.2	
RhB	100.0	69.2	47.8	37.5	
AY17	100.0	96.3	92.5	90.0	
AY49	100.0	100.7	98.4	96.4	

Table 3-8. Changes of K/S values (%) of dye stains on cotton fabrics at different irradiation time.



Figure 3-3. Degradation of the selected acid dyes as stains on cotton fabric by photolysis under exposure to visible light source (Philips[®] TL-D 18W/827 1SL/2).



Figure 3-4. Photos of the irradiated samples corresponding to Figure 3-3.

The purpose of developing self-cleaning cotton is to functionalise the cotton fabric with photo-driven degradation property towards daily stains. It is almost impossible to ensure the daily stains such as red wine and coffee we encountered are highly homogeneous; in contrast, the less pure acid dyes with sufficient light stability are more desirable for the use to examine the photo-activated stain decolourisation effects. Through this experiment, a more comprehensive understanding of the light stability of these seven dye stains are obtained.

The lightfastness information and degradation result indicate that RhB is the weakest one among the candidates. Such visual changes are also obvious in Figure 3-4. The light stability of both AO7 and AR1 was considered similar according to the lightfastness property; however, Figure 3-3 clearly illustrates the light stability of AR1 over that of AO7 and being comparable to that of AY17 and MO. The differences between the lightfastness information and the experimental results of photolytic resistance are possibly attributed to distinct light sources and substrates applied in the set-ups. After 86-hour exposure to the visible light, four candidates, AO3, AY49, MO and AY17, could retain at least 90% in terms of K/S function; thus, it is believed that these four acid dyes are persistent enough for the dye decolourisation tests conducted under the visible light source selected for the study. In other words, they are suffered from nearly negligible photolysis problem in the research condition.

3.3.2. Verification of dye sensitisation absent in CuPc-self-cleaning system

In addition to photolysis, dye sensitisation that also interferes the intrinsic performance of a photocatalyst is another problem concerning dye decolourisation as the visible-light-induced activity evaluation. To our knowledge, these systems mostly involve inorganic photocatalysts[77, 312-315], whereas MPcs in this study belong to organic photocatalysts. To further justify whether the dye sensitisation is viable in CuPc systems, the excitation energy between HOMO and LUMO ($\Delta E_{LUMO-HOMO}$) and the corresponding electronic energy levels of HOMO and LUMO are required. Table 3-9 summarises the calculated $\Delta E_{LUMO-HOMO}$ based on the maximum absorption wavelengths of the acid dyes and MPcs in terms of K/S function on cotton fabric. Such gap energy of the CuPc dyes, sulphonated ZnPcs and NiPcS₄ are significantly lower than that of acid dyes which were selected as model compounds for activity assessments. This implies that the MPcs involved in this research can intrinsically be excited by a proper visible-light source for the photocatalytic self-cleaning reactions, without the need of dye sensitisation by the dye stains.

Zheng et al.[331] attempted to determine the energy levels of HOMO and LUMO of the CuPcS₄ and the dye stains (see Table 3-10) and deduced that there is absence of dye sensitisation mechanisms in the photocatalytic reactions driven by CuPc under visible light. Hence, it can properly be referred to justify dye sensitisation not valid to promote photo-induced decolourisation of those stains by the MPcs on cotton fabric.

	λ _{max} (nm)	Estimated Δ <i>E</i> _{LUMO-HOMO} (eV)
AO3	≦400	≦3.11
AO7	490	2.54
МО	460	2.70
AR1	510, 545	2.44, 2.28
RhB	565	2.20
AY17	≦400	≦3.11
AY49	410	3.03
CuPcS ₄	625, 675	1.84-1.99
RB14	620, 675	1.84-2.00
RB21	675	1.84
Sulphonated ZnPcs	670	1.85
NiPcS ₄	615, 665	1.87-2.02

Table 3-9. Maximum absorption wavelengths (in terms of K/S function) and the estimated excitation energy (HOMO–LUMO gap) of different dye stains and MPcs accommodated to cotton fabric.

Table 3-10. The measured energy levels of CuPcS₄ and the ionic dyes by cyclic voltammetry, according

to Zheng et al.'s study[331].

	HOMO ^a (eV)	LUMO ^b (eV)
CuPcS ₄	-5.20	-3.97
MO	-4.86	-3.79
Acid Orange	-4.72	-3.74
Acid Yellow	-4.83	-3.76
Methylene Blue	-4.85	-3.77
Methylene Violet	-5.00	-3.70
RhB	-4.75	-3.75

^a HOMO (ev) = $-(4.8 - 0 + eE_{ox}^{onset})$. ^b LUMO (ev) = $-(4.8 - 0 + eE_{red}^{onset})$.

The E_{ox}^{onset} and E_{red}^{onset} were VS. Ag/Ag⁺ reference electrode. The Ag/Ag⁺ reference electrode was calibrated using a ferrocene/ferrocenium redox couple as an internal standard, whose oxidation potential was set as -4.8 eV with respect to vacuum level.

3.3.3. Spectrophotometric analysis of the MPc dyes and acid dye stains

Besides the concerns of photolysis and dye sensitisation, Choi and his colleagues[312] also mentioned the dye stains may shield the visible-light absorption of photocatalysts to lead to underestimation of the activity, and, it is not accurate to monitor dye decolourisation by absorbance measurement at a single wavelength. However, it is found that these concerns are less dominant in the MPc's self-cleaning systems.



Figure 3-5. Spectral K/S profiles of various MPcs and acid dyes as stains on cotton fabric in the study.

Figure 3-5 plots the absorption curves of the MPc dyes and different dye stains on cotton fabric (K/S function against wavelength). The major absorption peaks of MPc dyes in the visible light region, i.e., Q-bands, distribute from 600 to 700 nm. Referring to Section 2.4.3, the Q-band of MPc usually consists of two peaks and the one with longer wavelength (~at 670 nm for the sulphonated MPcs) represents the monomeric MPc molecules, which are the active species for photocatalytic reaction. In contrast, the absorption regions of the selected acid dyes occupy the visible light spectrum of 400-600 nm.

To minimise the shielding problem, RhB, AR1 and AO7 should be eliminated among the candidates because their absorption curves have relatively serious overlap towards those of the MPc dyes. In spite of the fact that RhB and AO7 are the common model compounds for the photocatalytic activity assessments appearing in a considerable amount of research paper, their poorer stability to visible light and risk of attenuating the incident light flux available to the MPc photocatalysts are obviously not favoured in this research.

While AO3, AY17, AY49 and MO have minimal overlap towards the MPc photocatalysts, Choi and his colleagues doubted the accuracy of monitoring the dye decolourisation by absorbance measurement at a single wavelength. Throughout this project including the light stability tests for the acid dyes in this chapter, a full spectrum (at least within visible light region) of each sample was measured and collected. The concentration changes of the acid dyes (in terms of K/S function) were then acquired by the integrated method i.e., summation of the spectral K/S values (or absorbance values for UV-Visible spectroscopy) over a wavelength range with a specific nanometre interval. The accuracy of the monitoring method can be enhanced to express more actual degradations of the dye stains. Nevertheless, with a close observation of Figure 3-5, the complete absorption peaks of two dye stains, AO3 and AY17, are probably beyond the visible light region when they were in cellulosic medium. Figure 3-6 shows the absorption behaviours of these two dyes in DI water within 300-700 nm; their absorption peaks also locate beyond the visible light region. This effect became more serious when these two dyes were accommodated in cellulosic fibre, probably due to the broadening and hypsochromic shifts of the absorption peaks. As a result, AO3 and AY17 are not the primary choices for the photocatalytic activity evaluations since their degradations cannot fully be monitored by reflectance spectrophotometer.



Figure 3-6. UV-Vis absorption curves of AO3 and AY17 (concentration: 40 mg/L) dissolved in DI water.

3.3.4. Further discussion on dye decolourisation tests

Concerning the problems of dye products generally with inadequate purity and specific transformation of the chromophoric groups instead of complete degradation, it is admitted an unavoidable limitation of the dye decolourisation tests for the activity assessment. Nevertheless, considering from another perspective, these limitations are still acceptable in this project.

The purpose of developing self-cleaning cotton is to functionalise the cotton fabric with photo-driven degradation property towards daily stains. It is difficult to guarantee the daily stains such as red wine and coffee we encountered are highly homogeneous; moreover, Figure 3-7 illustrates that the light stability of red wine and coffee stains, which were examined under the light source with weak intensities in shorter exposure duration, are also not strong enough as the model compounds for this research. In contrast, the less pure acid dyes with sufficient light stability are more desirable for the use to stimulate the conditions for self-cleaning examinations.

Even though decolourisation of dye stain possibly reflects conversion of the chromophore of the acid dye but not the full mineralisation or decomposition, the photocatalytic capabilities of the MPcs can be impartially compared via the decolourisation rates of the same dye stain. Furthermore, surface with "photocatalytic self-cleaning" function is not equal to "a surface need not be cleaned at all". If the outcomes of pollutant degradations are able to promote a convenient cleaning, complete mineralisation of the organic stains is not imperative for a selfcleaning system actually.



Figure 3-7. Photos of the cotton samples stained with red wine and coffee captured at specified irradiation hour.

3.4. CONCLUSION

The problems raised by Choi et al. and other researchers[77, 312, 313, 315] are discussed and addressed in this chapter. Seven acid dyes, AO3, AO7, MO, AR1, RhB, AY17 and AY49, were selected as the candidates to be studied whether they are appropriate for the MPc-self-cleaning project. Their lightfastness information was investigated and stability to a specific visible light source were assessed. AO3, AY49, MO and AY17, which were able to retain at least 90% (in terms of K/S function) after exposure to the visible light in 86 hours,

were found to be sufficiently steady to overcome the **photolysis** problem in the research condition. Determined via K/S spectra representing the absorptions of MPcs and acid dyes in cotton fabric, the $\Delta E_{LUMO-HOMO}$ of various MPc photocatalysts involved in the project are significantly lower than those of the selected dye stains. Together with the Zheng et al.'s result concerning the measured energy levels of the HOMO and LUMO of CuPcS₄ and the dye stains via cyclic voltammetry[331], it can be confirmed that the self-cleaning system of MPcs are basically contributed by their intrinsic photocatalytic properties instead of the aid of dye sensitisation by the dye stains. The spectral K/S profiles of various MPc dyes and acid dyes provide a clear picture to choose the proper dye stains with minimal spectral overlap. This can avoid the risk of **shielding** the visible light absorbed by the MPc photocatalysts to result in possible underestimation of the photocatalytic performances. In addition, more accurate monitoring of the stain decolourisations via K/S measurement (by reflection mode) over the major absorption ranges can be conducted.

Though not a perfect and ideal evaluation by dye decolourisation, it is reckoned that using acid dyes as model compounds are acceptable to stimulate the daily and more actual conditions for self-cleaning, as well as to compare the photocatalytic effects of various MPcs in terms of rate of converting the chromophoric group of the same stain by photo-redox reactions. Based on the above findings, Figure 3-8 concludes the applicability of the seven selected acid dyes for this project.



Figure 3-8. Priority of the seven candidates of acid dyes as stains for subsequent evaluation of photocatalytic activities in the project.

4.1. INTRODUCTION

As popular turquoise blue and green colorants, CuPc compounds applied on textiles draw rarely scholar attention to investigate their photocatalytic self-cleaning performances. In this chapter, several CuPc dyes were selected and applied to cotton fabric via exhaustion dyeing techniques, which are considered as facile and uniform uptake of CuPcs to the cotton fabrics. Decolourisations of dye stains by different CuPc candidates grafted on cotton fabric were conducted in exposure to household fluorescent tubes (visible light). Although the cotton substrate was grafted with the same amount of the CuPc and irradiated under the same conditions, the extents of the stain removals, which were compared by reflectance spectrometry and the images captured by digital scanner, were discovered to be distinct among the CuPcs. Analysing the CuPc derivatives using spectroscopic methods, liquid chromatography - mass spectrometry (LC-MS) and inductively coupled plasma - optical emission spectrometry (ICP-OES), it is believed that their different molecular structures varied their aggregation behaviours in cotton fibre because of the steric hindrance and molecular symmetry; therefore, they exert such various rates of photocatalysis for stain decolourisations. In addition, anatase-TiO₂ was coated on the same cotton fabric to degrade the stains under the irradiation of fluorescent tube with UV-filtered in comparison to the self-cleaning effects of CuPc-dyed cotton triggered by the same visible light source.

4.2. METHODOLOGY

Experimental of preparation of self-cleaning cotton fabric with various CuPc dyes and TiO₂, as well as the unique characterisation studies are described as follows.

4.2.1. Materials

Four CuPc dyes, CuPcS₄, DB86, RB14 and RB21, were ordered from Aldrich, Tokyo Chemical Industry, Jiangsu World Chemical and Everlight Chemical respectively. NaCl was supplied by Unichem and Na₂CO₃ was obtained from Tianjin Fuchen. Triton X-100 (TX-100) and absolute ethanol (EtOH) were purchased from VWR. Nonionic detergent, Diadavin EWN-M 200%, is a surfactant product of Tanatex Chemicals. The anatase TiO₂ sol was prepared by Dr. Xiaowen Wang following the sol-gel process reported in his previous publication[158]. All of these chemicals were directly used without further purification. Plain weave cotton fabric which was scoured and bleached when ordered was utilised as the self-cleaning substrate.

Acid dyes acted as coloured stains to indicate the photocatalytic activities demonstrated by the MPcs under visible light irradiation. Acid Yellow 49 (AY49) and Acid Orange 7 (AO7) were ordered from Aldrich. Methyl Orange (MO) was obtained from Acros Organics. All the products were used as received without purification.

4.2.2. Sample preparations

4.2.2.1. CUPC-DYED COTTON FABRIC

For CuPcS₄ and DB86, specified weights of CuPc dye and Na₂CO₃ powders were dissolved into 100 mL of deionised water at room temperature, followed by placing each piece of cotton fabric (10×10 cm; 2.000 - 2.020 g) into the dye-bath. The dyeing set-ups were heated up to 95 °C under uniform agitation (130 rpm) via a water bath. Known volume of NaCl(aq.) was gradually pipetted to the dyeing solution during this 90-minute direct dyeing process. Each piece of dyed cotton was separately rinsed with running tap water at room temperature for 1 min and then oven-dried at 60 – 70 °C for 1 hr. The detailed dyeing profile follows Figure 3-1.

For RB14 and RB21, specified weights of CuPc dye and NaCl powders were dissolved into 80 ml of deionised water at room temperature, followed by fully immersing each piece of cotton fabric (10×10 cm; 2.000 - 2.020 g) into the dye-bath. The dyeing set-ups were heated up to 85 °C under uniform agitation (150 rpm) via a water bath. Controlled volume of Na₂CO₃(aq.) was gradually pipetted to the dyeing solution during this 100-minute dyeing task. Each piece of dyed cotton was rinsed with running tap water at room temperature for 1 min;
and subsequently washed by: (1) TX-100 (0.1% w/v) / EtOH (2% v/v) aqueous solution at 80 °C water bath for 10 min under uniform agitation (150 rpm); and then (2) nonionic detergent, Diadavin EWN-M 200%, solution (0.1% w/v) at 90 °C for 30 min under uniform agitation (150 rpm). All the washed samples were finally oven-dried at 60 – 70 °C for 1 hr. The detailed dyeing profile follows Figure 3-2.

4.2.2.2. TIO2-COATED COTTON FABRIC

The anatase TiO₂ sol was prepared following the sol-gel process reported in a previous publication[158]. To coat nanocrystalline TiO₂ film on the cotton fabric with the as-prepared TiO₂ sol, the cotton pieces were respectively padded with 1.25, 2.5 and 5% w/v of TiO₂ padding liquor at 5 rpm with a nip pressure of 1-1.2 kg/m² using padded pneumatic-type horizontal padding machine (Rapid Labortex Co Ltd, Taipei, Taiwan). The padded pieces were then cured in curing oven (Mathis Labdryer Labor-Trockner Type LTE, Werner Mathis AG Co, Switzerland) at 150 °C air temperature with the fan speed of 1500 rpm for 2 min.

4.2.3. Assessment of photocatalytic activities of the treated fabrics

The photocatalytic self-cleaning activities of functionalised cotton fabrics were assessed by monitoring the decrease in concentrations of the colorant stains on the fabrics in exposure to visible light. AO7, AY49 and MO were selected as the dye stains in this study because the absorption ranges of these three stains do not overlap with the ones of the CuPc dyes in visible light spectrum (all measured when accommodated to cotton medium). Each colorant stain was completely dissolved into deionised water in a known concentration. Pristine cotton, CuPcdyed cotton and TiO₂-coated cotton pieces (5×5 cm) were spotted with 60 µL of the selected stain solution via a micropipette. These stained samples were dried in a dark room with air conditioning at ~20 °C for at least 1 hr.

To have more detailed analysis on the photocatalytic activities of the treated cotton, the dried samples were exposed to light irradiation for 85-90 hr. The irradiation of all samples was conducted in a light box equipped with household energy-saving fluorescent tubes, Philips TL-D 18W/827 1SL/25, and a sheet of UV-shield film, 3M Sun Control Window Film (NV-35), above the sample stage. The average light intensity on the surface of the sample stage was 22.8 W/cm^2 containing the UV content of 0.6 μ W/cm² irradiance.

The changes in concentrations of the colorant stains on fabrics were determined by measuring the reflectance spectra (400-700 nm) of the stained samples via a reflectance spectrophotometer (Datacolor 650) at different time intervals, during the course of irradiation.

Through Kubelka–Munk expression, the spectral K/S values were converted from the measured reflectance following Equation 3-1, to represent the spectral absorption behaviours of the colorant stains on cotton. The K/S values of the colorant stains themselves, i.e., excluding the substrate absorption, were subsequently acquired following Equation 3-2. The sum of K/S values of the dye stain in their own absorption wavelength regions (AO7: 485-495 nm, AY49: 400-500 nm and MO: 400-540 nm; collected at 5 nm intervals) in visible light spectrum, which represent their concentrations on the spotted samples, were calculated following Equation 4-1.

Equation 4-1.

$$\Sigma \text{ K/S}_{\text{D}} = \sum_{\lambda} \text{ K/S}_{\text{D}}$$

where	K is the absorption coefficient of the dyed fabric
	S is the scattering coefficient of the dyed fabric
	D is the colorant stain
	F is the dyed fabric substrate
	R_{N} is the reflectance value of the spotted part of the sample
	λ is absorption wavelengths of the colorant stain within 485-495 nm
	(AO7), 400-500 nm (AY49) or 400-540 nm (MO) with a 5 nm-interval

The sum of K/S value of each colorant stain spotted on pristine cotton fabric (60 μ L) had been calibrated to be correlated to the actual concentration of the dye stain solution in 60 μ L on the cotton fabric. Therefore, initial concentration of the stain (C₀) and the concentration of the stain remained at specific irradiation time (C_t) were determined to plot the decolourisation curves of the stains. The image of each specimen was directly captured by Perfection V370 Photo Scanner (Epson, Nagano Prefecture, Japan) without any photo adjustments.

4.2.4. Analysis of aggregation behaviours of the CuPc derivatives

UV-visible absorption spectra of the CuPc dyes dissolved in aqueous media and grafted on cotton fibre (i.e., to be dyed in piece form) were obtained by Double Beam Spectrophotometer UH5300 (Hitachi, Tokyo, Japan) and Cary 300 UV-Vis Spectrophotometer (Agilent Technologies, California, US) respectively. For the absorption curves of CuPc-dyed fabrics derived from the Kuelka-Munk analysis (K/S values as a function of visible light region's wavelength), their reflectance spectra were gained by the Datacolor 650[™], (Datacolor, Lucerne, Switzerland); and the spectral K/S curves of the CuPc dyes on cotton were converted from their corresponding measured reflectance spectra following Equations 4-2, 4-3 and 4-4. Equation 4-2.

$$K/S_{CuPc+P} = \frac{(1-R_D)^2}{2R_D}$$

Equation 4-3.

$$K/S_{CuPc} = K/S_{CuPc+P} - K/S_P$$

Equation 4-4.

$$\Sigma K/S_{CuPc}^* = \sum_{\lambda} K/S_{CuPc}$$

where	K is the absorption coefficient of the dyed fabric
	S is the scattering coefficient of the dyed fabric
	CuPc is the copper phthalocyanine dye
	P is the pristine fabric substrate
	$R_{\mbox{\scriptsize D}}$ is the reflectance value of the dyed fabric
	λ is wavelengths of the CuPc dye within 400 to 700 nm
	with a 5 nm interval

4.2.5. Characterisation of the CuPc dyes

Absorption spectra of the CuPc dyes dissolved in aqueous media were firstly determined to identify whether they belong to the MPc following Section 4.2.4. To confirm the Pcs metallised with which metal ion, the optical emission spectra of each CuPc sample and the Cu standards dissolved in deionised water in specified concentrations were acquired via Agilent 5100 inductively coupled plasma - optical emission spectrometry (ICP-OES) coupled with Agilent SPS 4 Autosampler. Liquid chromatography-mass spectrometry (LC-MS) were employed to verify and distinguish the derivative structures and components of the four CuPc dye products, which were also dissolved in deionised water in specified concentrations for analysis. Before the LC-MS analysis, RB14 in deionised water (0.22% w/v) was firstly refluxed in 0.11% (w/v) NaOH solution at 85 °C for 1 hr to be stabilised via hydrolysis; and then the hydrolysed product was neutralised by 1 N H₂SO₄(aq.) to pH 7. The LC-MS instrument is composed of Waters e2695 Separation Module, XSelect CSH C18 Column (130Å, 5 μ m, 3 × 250 mm), 2998 Photodiode Array (PDA) Detector and ACQUITY QDa Mass Detector.

4.3. RESULTS AND DISCUSSION

4.3.1. Photocatalytic studies of CuPc-dyed cotton

In order to simulate the actual self-cleaning situation more closely, the dye stains in known volumes were directly spotted onto the CuPc-dyed cotton fabrics and the photocatalytic activities of the CuPc derivatives on cotton fibre were measured via reflectance spectrophotometry. Figure 4-1 reveals that the dye stain, AO7 and AY49, were decomposed by the cotton fabrics functionalised with photo-active CuPcs and Table 4-1 compares the absorption behaviours of that CuPc samples via K/S analysis. It is generally known that the CuPc ring serves as the chromophore of each derivative to present turquoise blue colour; calculating the sum of K/S values in visible light spectrum (Σ K/S* values) of the samples effectively represents the quantities of CuPc molecules (Table 4-1) applied to the cotton pieces.

CuPc derivatives	∑ K/S *ª	K/S at 675 nm ^b
DB86	48.8	2.5
CuPcS ₄	53.7	1.8
RB14	54.3	2.3
RB21	52.3	3.9

Table 4-1. Summary of K/S values of each CuPc's graph shown in Figure 4-2.

^a average value of the whole dyed cotton piece, measured from 400 to 700 nm at a 5 nm interval

^b peak exhibited by the monomeric CuPc molecules

Despite the fact that the cotton samples were loaded with the closely equivalent amounts

of CuPc molecules, distinct photocatalytic activities on the stain degradation were



Figure 4-1. Photocatalytic degradation of (a) AO7 (0.1% w/v; 60 μL) and (b) AY49 (0.35% w/v; 60 μL) by different CuPc-dyed cotton fabrics under irradiation of Philips TL-D 18W/827 1SL/25; (c) photos of the stained samples (i) before exposure to visible light and (ii) after exposing to visible light for 85 hr.

clearly observed in Figure 4-1. DB86 and RB21 tended to exhibit stronger decolourisation powers towards the stains, especially for the less persistent stain, AO7 (Figure 4-1a); the weakness of CuPcS₄ was more obvious when discolouring AY49, a relatively more persistent colorant (Figure 4-1b). Photos of the stained samples were given in Figure 4-1c to present the extents of stain removals by the CuPc-dyed cotton. In spite the fact that AO7 is categorised as "not recommended" model compound for photocatalytic assessment in Chapter 3, the purpose of selecting AO7 in the first evaluation was to compare the stain decolourisation abilities of particular CuPcs, CuPcS₄, RB14 and RB21, thoroughly by getting a fuller picture instead.



Figure 4-2. Photocatalytic degradation of AY49 (0.35% w/v; 60 μ L) by different uptakes of DB86, RB21, CuPcS₄ and RB14 on cotton fabrics; figures next to dye labels indicating the Σ K/S* values representing the amount of CuPc dyes loaded to the cotton substrate.

To have a thorough analysis on the photo-induced stain-removal performances of the CuPc candidates, cotton pieces were loaded with three different quantities of each CuPc to degrade the AY49 spots on them with activation by the same visible light source; and the results are summarised on Figure 4-2. It is found that RB21 and DB86 had better photocatalytic performance towards AY49 decolourisation at the three various uptakes on the cotton fabric than CuPcS₄ and RB14. The performance improvement of RB21 upon the increase in the quantity on the cotton substrate was more pronounced than that of DB86. On the other hand, loading more CuPcS₄ or RB14 to cotton substrate could not effectively advance the AY49 decolourisation under visible light. These differences indicate that various molecular structures of the CuPc derivatives are the key factors to influence the photocatalytic efficiency.

4.3.2. Aggregation analysis of CuPc-dyed cotton

According to the previous researches[23, 263, 332-334] and Section 2.4.3, molecular aggregation of MPc in dimeric form is a typical factor to suppress its photocatalytic activities; and the Q-band absorption, which is assigned to a π - π * transition from the highest occupied molecular orbital (HOMO) of a_{1u} symmetry, to the lowest unoccupied molecular orbital (LUMO) of e_g symmetry, of a MPc is able to indicate its dissociation and aggregation properties in a

particular medium. The absorption behaviours of the CuPcs grafted on cotton fibre are presented by K/S spectra in Figure 4-3 to show their Q-band absorptions (550-700 nm). The dissociations of DB86 and RB21 in cotton fibre were better than those of CuPcS₄ and RB14; thus, it is the major reason why both DB86 and RB21 offer stronger and more effective (i.e., less quenching) stain decolourisation power than both CuPcS₄ and RB14 under visible light.



Figure 4-3. Spectral K/S graphs of the CuPcs on cotton fabric in visible light spectrum (sum of K/S values listed on Table 4-1).

The dissociation characteristics of these four CuPc dyes in TX-100 solution via the UV-Vis absorption spectrometry (see Figure 4-4) were also investigated. By dissolving the CuPc dyes (20 mg/L) in 0.1% w/v TX-100 solution, only DB86 and RB21 could be well disaggregated in this aqueous condition; whereas CuPcS₄ and RB14 had not improved to a



Figure 4-4. UV/Vis absorption spectra of DB86 (a), RB21 (b), CuPcS₄ (c) and RB14 (d) in different % w/v concentrations of Triton X-100 solution (dye concentration: 20 mg/L) (∇: CuPc derivatives in monomeric form; ▼: CuPc derivatives in dimeric form).

considerable extent. Among these four candidates, it is believed that RB14 is the most serious aggregated one as RB14 molecules were still unable to be dissociated by 1% w/v TX-100 solution. Nevertheless, RB14 in Figure 4-5 demonstrates it could be disaggregated by cotton fibre to some extent owing to like dissolves like principle and its certain molecular advantage (to be further explained in the following parts), therefore RB14-loaded cotton was not the worst

case in the stain decolourisation tests. In Figure 4-5, the absorption behaviours of cotton fabrics dyed with RB14 in various depths was further determined; such different concentrations of RB14 loaded to cotton fibre were still able to exhibit noticeable dissociation effect.



Figure 4-5. UV/Vis absorption spectra of RB14-dyed cotton in various % depths (on weights of fabric to be dyed) (∇: CuPc derivatives in monomeric form; ▼: CuPc derivatives in dimeric form).

4.3.3. Identification of the molecular structures of CuPc dyes

The existence of Q-band and Soret band presented in the UV-Vis absorption spectra of the four CuPc solutions (Figure 4-4) is the typical characteristic of MPcs[247, 335]. Following the optical absorption determination, ICP-OES analysis of the four candidates was conducted to further confirm which MPc they belong to. Results in Figure 4-6 clearly reveal that the four

MPc dyes are metallised with Cu²⁺ ion i.e., CuPcs.



Figure 4-6. ICP-OES spectra of DB86, CuPcS₄, RB14, RB21 and Cu²⁺ ICP standards with maximum emission wavelengths at ~327.398 nm (theoretically 327.395 nm).

As mentioned above, it is believed that the various molecular structures of CuPc compounds are the critical factor which results in distinct photocatalytic activities towards stain decolourisations on cotton fabrics. A series of LC-MS tests were conducted to investigate the molecular structures of the four CuPc dyes. CuPcS₄ was analysed under isocratic condition (50/50 water/acetonitrile), while the other three dyes were evaluated using gradient elution (starting from water to 50/50 water/acetonitrile) to provide better sample



Figure 4-7. LC-MS analysis of CuPcS₄ (150 ppm) in 50/50 water/acetonitrile: (a) UV-Vis spectrum collected by PDA spectrophotometer and captured at 2.726 min of the inset PDA chromatogram; (b) ESI mass spectrum extracted at 2.752 min of the inset total ion chromatogram (negative mode).

separation for subsequent identifications by mass spectrometry. Figure 4-7 summarises the results of CuPcS4 which was first studied by PDA spectrophotometer and then by ESI mass spectrometry. Typical CuPc's electronic absorption spectrum plotted in Figure 4-7(a) evidently reveals that CuPcS₄ is monomerically present in 50/50 water/acetonitrile condition to be analysed by the ESI mass spectrometer, to generate Figure 4-7(b) spectrum. Table 4-2 lists the corresponding ionised CuPcS₄ molecules matching the major peaks and it confirms the molecular structure of CuPcS₄.

Table 4-2. Interpretation of Figure 4-6(b)'s mass spectrum and the molecular structure of CuPcS₄



Everzol Turquoise Blue G, which is widely recognised as Reactive Blue 21 (RB21) in the colorant industry[321], was dissolved in deionised water in 50, 100 and 200 ppm, and then studied by gradient elution method starting from 100% water to 50/50 water/acetonitrile in 16 min. As shown by chromatogram detected by PDA spectrophotometer in Figure 4-8(a), different CuPc derivatives were preliminarily partitioned out after passing through the C18 reversed-phase column and nearly the same partition results were gained from the three



Figure 4-8. LC-MS analysis of RB21 sample (200 ppm) under gradient elution; (a) PDA chromatogram; (b) UV-Vis absorption spectra of Reactive Blue 21 molecule dissolved in 50/50 water/acetonitrile; (c) total negative-ion chromatogram and (d) mass spectrum of the Reactive Blue 21 molecule eluted out and injected into ESI mass spectrometer at 10.756 min.



Figure 4-8 (cont'd). LC-MS analysis of RB21 sample (200 ppm) under gradient elution; (a) PDA chromatogram; (b) UV-Vis absorption spectra of Reactive Blue 21 molecule dissolved in 50/50 water/acetonitrile; (c) total negative-ion chromatogram and (d) mass spectrum of the Reactive Blue 21 molecule eluted out and injected into ESI mass spectrometer at 10.756 min.

samples with different concentrations. The major component, i.e., the one with the largest absorbance, in the sample is identified as the Reactive Blue 21 molecule with the supports of the corresponding UV-Vis absorption spectrum (referring to Figure 4-8(b)) and the ESI-mass spectrometry at 10.756 min (see Figures 4-8(c-d)). All the components in RB21 sample analysed with mass spectrometry are summarised in Table 4-3 for reference.

m/z	Assignment	m/z	Assignment	
223.18	CuPc–(SO ₃ -)4	377.97	7.97 CuPc–(SO ₃ ⁻)(R) CuPc–(SO ₃ ⁻) ₄ ;	
269.68*	[CuPc-(SO ₃ ⁻) ₂ (R ⁻)] ⁻		CuPc–(SO ₃)(R ⁻) CuPc–(SO ₃ ⁻) ₄ ;	
271.28	CuPc–(SO ₃ ⁻) ₃		CuPc-(SO ₃ -)(R-) CuPc-	
			(SO ₃ H)(SO ₃ -) ₃	
288.98	CuPc–(SO ₃ -) ₃ (R-)	386.47	CuPc-(SO ₃ H)(SO ₃ ⁻) ₂ (R ⁻);	
297.87	CuPc–(SO ₃ H)(SO ₃ -) ₃		CuPc–(SO ₃ -) ₃ (R)	
304.68	CuPc–(SO ₃ Na)(SO ₃ -) ₃	407.16	.16 CuPc–(SO ₃ H)(SO ₃ -) ₂	
352.57	CuPc-(SO ₃ -) ₃ (R ₁)	418.96	6 CuPc–(SO ₃ Na)(SO ₃ -) ₂	
358.57*	CuPc-(SO ₃ -) ₂ (R-)	446.16	CuPc–(SO ₃ H) ₂ (SO ₃ ⁻) ₂	
		498.85	CuPc–(SO₃⁻)(R⁻)	

Table 4-3. Interpretation of mass spectra of the RB21 samples and the deduced molecular structures



DB86 was initially investigated by the LC-MS using the isocratic elution (50/50 water/acetonitrile). However, the components of the sample were found not as simple as the commonly known constitution, i.e., copper (II) phthalocyanine-disulphonic acid disodium salt $(CuPc-(SO_3 Na^+)_2)$. It is generally considered that simple reversed-phase chromatography without ion-pairing or/and buffering systems performs weak separation of the organic dye matrices[336-339], especially for the planar CuPc rings with different degrees of sulphonation only. However, Figure 4-9(a) illustrates the liquid chromatographic partitioning result of the DB86 sample by a specially designed gradient elution based on doubly isocratic runs (abbreviated as "double-isocratic method"), where the mobile phase started from water to 80/20 water/acetonitrile (5 min), returned to 100% water (5 min) and finally switched to 50/50 water/acetonitrile to elute all the components away from the C18 column, in this study. Figures 4-9(b-d) are the electronic absorption spectra captured from the three partitions; typical fingerprint of the CuPc distinctly appears in the absorption spectra.

Supported by the corresponding mass spectra in Figure 4-10 with the interpretation by Table 4-4, it is clearly confirmed that the 1st, 2nd and 3rd partitions are CuPc–(SO₃⁻Na⁺)₄, CuPc– (SO₃⁻Na⁺)₃ and CuPc–(SO₃⁻Na⁺)₂ respectively. With the use of the double-isocratic method, CuPc–(SO₃⁻Na⁺)₄ and CuPc–(SO₃⁻Na⁺)₃ could be moderately separated while CuPc–(SO₃⁻Na⁺)₂ was successfully isolated from the DB86 sample. This finding also indicates there is a considerable polarity difference between the disulphonated CuPc and



Figure 4-9. Separation of DB86 sample (250 ppm) by double-isocratic method; (a) PDA chromatogram; (b-d) UV-Vis absorption spectra of 1st to 3rd CuPc portions separated from the DB86 sample at 7.096, 8.142 and 18.070 min respectively.



Figure 4-9 (cont'd). Separation of DB86 sample (250 ppm) by double-isocratic method; (a) PDA chromatograms; (b-d) UV-Vis absorption spectra of 1st to 3rd CuPc portions separated from the DB86 sample at 7.096, 8.142 and 18.070 min respectively.



Figure 4-10. ESI-MS analysis of DB86 (250 ppm) corresponding to Figure 4-8. (a) Total negative-ion chromatogram; (b-d) mass spectra of 1st to 3rd CuPc portions separated from the DB86 sample.



Figure 4-10 (cont'd). ESI-MS analysis of DB86 (250 ppm) corresponding to Figure 4-9. (a) Total negative-ion chromatogram; (b-d) mass spectra of 1st to 3rd CuPc portions separated from the DB86 sample.

m/z	Assignment
223.02	CuPc–(SO ₃ -) ₄
270.92	CuPc–(SO ₃ -) ₃
283.22	CuPc–(SO ₃ H)(SO ₃ ⁻) ₃ CuPc–(SO ₃ ⁻) ₃ ;
	CuPc– (SO3 ⁻)4 CuPc–(SO3 ⁻)2
297.82	CuPc–(SO ₃ H)(SO ₃ -) ₃
304.92	CuPc–(SO₃Na)(SO₃⁻)₃
366.73	CuPc–(SO ₃ ⁻) ₂
417.73	CuPc–(SO ₃ Na)(SO ₃ -) ₂
735.36	CuPc–(SO ₃ H)(SO ₃ -)

Table 4-4. Interpretation of Figure 4-8's mass spectra and the molecular structures of the CuPcs in DB86.

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trisulphonated CuPc in sodium salt forms. It is believed that further adjustment to the gradient elution plan will be able to isolate these three sulphonated CuPc completely. Referring to the signal intensities of the three sodium salts of sulphonated CuPcs recorded in mass spectra, it is estimated that there are 25.7% CuPc–(SO₃·Na⁺)₄, 37.1-39.2% CuPc–(SO₃·Na⁺)₃ and 35-37.2% CuPc–(SO₃·Na⁺)₂ in the DB86 sample. Since the main components in DB86, i.e., the trisulphonated and certain disulphonated CuPcs, belong to asymmetrical molecules, the CuPc can thus be adequately dissociated in cotton fibre to achieve superior photocatalytic behaviours.

The stabilised RB14 sample was also separated by the double-isocratic method. Figure 4-11 presents the chromatograms firstly detected by PDA spectrophotometer, followed by the mass spectrometer in negative mode. The two separated portions from RB14 sample were



Figure 4-11. Chromatographic diagrams obtained from ESI-MS analysis of RB14 (400 ppm). (a) PDA chromatogram; (b) total negative-ion chromatogram.



Figure 4-12. UV-Vis absorption spectra of two CuPc portions separated from the RB14 sample determined by PDA detector at (a) 7.875 and (b) 17.954 min.

prone to be dimeric no matter whether they existed in aqueous (at 7.875 min) or water/acetonitrile (at 17.954 min) eluting media, referring to their absorption behaviours shown in Figure 4-12. This evidence further explains why RB14 possesses limited photocatalytic selfcleaning function than other asymmetrical CuPc, such as RB21. The information gained from the mass spectra is directly summarised in Table 4-5 which indicates the molecular structure of the RB14 sample. Via the double-isocratic method, CuPc substituted with two to three sulphonates together with one reactive anchor group (R) were eluted out in the 1st portion while the CuPc substituted with one sulphonate and one reactive anchlor group were the mainly 2nd eluted portion, after identifying by the mass spectrometer. Nevertheless, unlike the contrast between CuPcS₄ and DB86, the absorption spectra of these two portions reveal that degrees of sulphonation of the RB14's CuPc ring result in negligible effect on molecular dissociation. It implies that the linearly long reactive anchor group of RB14, shown in Table 4-5, probably leads to the aggregation of the RB14's molecules to a considerable extent.

In summary, a solely tetrasulphonated CuPc, CuPcS₄, possesses a more symmetrical molecular structure than DB86 where the majority is composed of relatively asymmetrical triand di-sulphonated CuPcs. As a result, CuPcS₄ tends to aggregate in cotton fibre significantly which suppresses its photocatalytic efficiency to decolourise the coloured stain during irradiating to visible light. While both RB14 and RB21 substituted with reactive anchor groups Table 4-5. Major peaks of the RB14 molecules, ionised via $-SO_3H \rightarrow -SO_3^-$ process, collected from the

corresponding total negative-ion chromatogram shown in Figure. 4-10(b).

1 st Portion		2 nd Port	ion
<u>m/z</u>	Assignment	<u>m/z</u>	Assignment
255.82	[CuPc–(SO ₃ H) ₂ (R ₂) CuPc–(SO ₃ H) ₂ (R ₂)] ⁻¹⁰ ; [CuPc–(SO ₃ H) ₂ (R ₂)] ⁻⁵	453.53	[CuPc–(SO ₃ H)(R ₁) CuPc–(SO ₃ H)(R ₂)] ⁻⁵
258.12	[CuPc–(SO ₃ H) ₃ (R ₁) CuPc–(SO ₃ H) ₃ (R ₂)] ⁻¹⁰	456.21	[CuPc-(SO ₃ H)(R ₁) CuPc-(SO ₃ H)(R ₁)] ⁻⁵
259.63	[CuPc–(SO ₃ H) ₃ (R ₁) CuPc–(SO ₃ H) ₃ (R ₁)] ⁻¹⁰ ;	560.94	[CuPc-(SO ₃ H)(R ₂) CuPc-(SO ₃ H)(R ₂)] ⁴⁻ ;
	[CuPc-(SO ₃ H) ₃ (R ₁)] ⁻⁵		[CuPc-(SO ₃ H)(R ₂)] ²⁻
284.36	[CuPc-(SO ₃ H) ₃ (R ₂) CuPc-(SO ₃ H) ₃ (R ₂)] ⁻⁹	572.94	[CuPc-(SO ₃ ⁻ Na ⁺)(R ₂) CuPc-(SO ₃ ⁻ Na ⁺)(R ₂)] ⁴⁻ ;
			[CuPc-(SO ₃ ⁻ Na ⁺)(R ₂)] ²⁻
300.16	[CuPc-(SO ₃ H) ₂ (R ₂) CuPc-(SO ₃ H) ₂ (R ₂)] ⁻⁸ ;	621.95	[CuPc-(SO ₃ Na)(SO ₃ H)(R ₁) CuPc-(SO ₃ Na)(SO ₃ H)(R ₁)] ⁻⁴ ;
	[CuPc-(SO ₃ H) ₂ (R ₂)] ⁻⁴		[CuPc-(SO ₃ Na)(SO ₃ H)(R ₁)] ⁻²
304.82	[CuPc-(SO ₃ H) ₂ (R ₂) CuPc-(SO ₃ H) ₂ (R ₂)] ⁻⁸ ;		
	[CuPc-(SO ₃ H) ₂ (R ₂)] ⁻⁴	<u>Ke</u>	<u>ey</u>
320.18	[CuPc-(SO ₃ H) ₃ (R ₂) CuPc-(SO ₃ H) ₃ (R ₂)] ⁻⁸ ;	RE	314 molecules in LC-MS system:
	[CuPc-(SO ₃ H) ₃ (R ₂)] ⁴⁻	Г	
322.41	[CuPc-(SO ₃ H) ₃ (R ₁) CuPc-(SO ₃ H) ₃ (R ₂)] ⁻⁸		(SO ₃ H)
325.82	[CuPc-(SO ₃ Na)(SO ₃ H) ₂ (R ₂)] ⁻⁴		N N N N N N N N N N N N N N N N N N N
365.89	[CuPc-(SO ₃ H) ₃ (R ₂) CuPc-(SO ₃ H) ₃ (R ₂)] ⁻⁷		
400.55	[CuPc-(SO ₃ H) ₂ (R ₂) CuPc-(SO ₃ H) ₂ (R ₂)] ⁻⁶		
	[CuPc-(SO ₃ H) ₂ (R ₂)] ⁻³		L L L
406.69	[CuPc-(SO ₃ H) ₂ (R ₁) CuPc-(SO ₃ H) ₂ (R ₁)] ⁻⁶ ;		
	[CuPc-(SO ₃ H) ₂ (R ₁)] ⁻³	L	
427.13	[CuPc-(SO ₃ H) ₃ (R ₂) CuPc-(SO ₃ H) ₃ (R ₂)] ⁻⁶ ;	D	Different R groups:
	[CuPc–(SO ₃ H) ₃ (R ₂)] ⁻³		CI / non-stablised form
432.83	[CuPc-(SO ₃ H) ₃ (R ₁) CuPc-(SO ₃ H) ₃ (R ₁)] ⁻⁶ ;	F	$R_1: -S_1 - NH - C_2H_4 - NH - N SO_3H$
	[CuPc–(SO ₃ H) ₃ (R ₁)] ⁻³		

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NH

stablised via hydrolysis

ŞO₃H

\$O₃H

were confirmed as non-symmetrical molecular structure via the LC-MS analysis, it is discovered that the linearly long anchor group of RB14 molecule is not effective to disaggregate the CuPc macrocycles in many media. Hence, the photocatalytic power of RB14 tends to be not as superior as that of RB21, which chemically graft onto the cellulosic polymer chain with suitable length of anchor group to deliver convincing molecular dissociation.

4.3.4. Comparison of visible-light photocatalytic performance between CuPc

and TiO₂

The photocatalytic self-cleaning functions exhibited by TiO₂ generally require UV activation owing to its high intrinsic band gap energy. However, TiO₂ induced by visible light source is still able to decolourise the coloured stain based on dye sensitisation mechanisms[315, 340, 341]. To compare the photocatalysis of CuPc and TiO₂ on cotton fibre triggered by visible light, cotton fabric functionalised with CuPc or TiO₂ were spotted with visible-light-fast stains, AY49 and MO; and the results are summarised on Figure 4-13. AY49, which is considered as a relatively weaker stain compared to MO, could be faded by TiO₂, while the decolourisation performances of DB86 and RB21 were still more potent. For the MO stain, both of these CuPc dyes exhibited their extraordinary photocatalytic power under visible light; whereas TiO₂-samples were almost inert to degrade the MO on them (see Figure 4-14).



Figure 4-13. Photocatalytic degradation of (a) AY49 (0.35% w/v; 60 µL) and (b) MO (0.155% w/v; 60 µL) by the cotton fabric padded with different concentrations of TiO₂ sol or dyed with DB86 (total K/S value measured from 400 to 700 nm at5 nm interval = 48.3) and RB21 (total K/S value measured from 400 to 700 nm at 5 nm interval = 54.9).



Figure 4-14. Photos of the stained samples of Figure 4-13's results, (i) before exposure to visible light and (ii) after exposing to visible light for 85 hr (for AY49) or 90 hr (for MO).

Substrate	e weight: 2 grams				
	Dyeing	<u>Uptake</u>	<u>Uptake</u>	<u>Est. molar</u>	No. of mole
	<u>depth (%)</u>	<u>(%)</u>	amount (g)	<u>mass (mol/g)</u>	on substrate (mol)
DB86 ^a	0.25	41.0	0.00205	734.20 -	2.79×10 ⁻⁶ –
				816.25 °	2.51×10 ⁻⁶
RB21 ^a	0.35	49.4 ^b	0.00346	1079.55 –	2.98×10 ⁻⁶ –
				1159.61 °	3.2×10 ⁻⁶
	<u>Pad liquor</u>	Wet	<u>Uptake</u>	<u>Est. molar</u>	No. of mole
	concentration (w/v %)	pick-up (%)	amount (g)	<u>mass (mol/g)</u>	on substrate (mol)
TiO ₂	1.25	67.4	0.0169	186.91 ^d	9.02×10 ⁻⁵
	5	60.9	0.0609	186.91 ^d	3.26×10 ⁻⁴

Table 4-6. Summary of amounts of CuPcs and TiO₂ for treating cotton fabric

^a assuming 100% pure for calculations

^b represented by fixation percent on cotton fabric excluding unfixed RB21

^c estimated by the LC-MS results in this study

^d referred to the mechanism proposed by Kong et al.[177]

Both DB86 and RB21 could achieve superior visible-light-induced photocatalysis to TiO_2 , even at lower dosages than TiO_2 . Table 4-6 summarises the dosages of various samples for this decolourisation experiment. The weights of TiO_2 applied to cotton substrate were at least 8.2 to 29.7 and 4.9 to 17.6 times more than those of DB86 and RB21 respectively. If molar ratios are considered, cotton fabric treated with 5% w/v TiO_2 padding solution could be over 100 times more than the two CuPc-dyed samples. Since CuPc members are generally classified as mild organic photoactive agents among the phthalocyanine family in photochemistry[342], such significant contrasts provide further evidence that certain MPcs are potentially capable of acting as effective photocatalysts to functionalise cotton textiles to achieve self-clearing performances.

4.4. CONCLUSION

This study revealed that functionalising cotton fabric with CuPc is able to promote the photocatalytic self-cleaning performance to degrade the coloured stains under visible light. Although there are various CuPc compounds available in the market, the study discovered that loading the equal amounts of these compounds to the cotton substrate would not offer the comparable photocatalytic activities towards stain decolourisations. Based on the studies of CuPc's aggregations in aqueous and cellulosic environments, the relatively inferior CuPc derivatives tended to behave poorer dissociation in many media. Therefore, it is believed that molecular structure of CuPc is the significant factor to determine its photocatalytic power.

Optical absorption spectrophotometry, ICP-OES and LC-MS were the characterisation techniques utilised in this study in order to identify the molecular structures of the four CuPc candidates in this study and determine the favourable disaggregating structures of CuPc dyes

in cotton. These techniques can be used in future to estimate the photocatalytic powers of other MPc compounds for self-cleaning cotton. When analysing CuPcs using LC-MS, a gradient elution system based on doubly isocratic runs to separate the complex CuPc compounds such as the DB86 and RB14 was developed without the use of buffering or ionpairing reagents which tend to complicate the investigation at mass-spectrometry-phase.

Comparing photocatalytic performances of TiO_2 under visible light, CuPcs in terms of DB86 and RB21 showed more superior performances of stain decolourisation than that of TiO_2 under visible light. The application quantities of DB86 and RB21 were substantially smaller than that of the TiO_2 in terms of weight as well as the number of moles. The outcomes achieved in this study enables further identification of other MPcs applied to cotton and likely to other cellulosic materials with the self-cleaning function activated by visible light sources.

5.1. INTRODUCTION

Chapter 4 had studied how different sulphonated-substituted MPcs in form of CuPcs influence the photocatalytic self-cleaning activity; in addition, the photocatalytic performance of a MPc is also determined by the central atom / ion[342-345]. Metal-free phthalocyanine (H₂Pc), nickel phthalocyanine (NiPc), CuPc and zinc phthalocyanine(s) (ZnPc(s)) in sulphonated forms were studied in this chapter, these sulphonated MPc dyes applied to the cotton fabric as base substrate were researched for developing photocatalytic self-cleaning cotton textiles. Particular sulphonated MPcs were introduced to cotton fabric in different ratios of the co-sulphonated MPc dyes and via modified exhaustion technique, in order to investigate their further improvements on the photo-induced stain fading and resistance to self-degradation.

5.2. METHODOLOGY

Experimental of preparation of self-cleaning cotton fabric with various MPc dyes and evaluation of the photocatalytic activities of the self-cleaning cotton samples are described as follows.

5.2.1. Materials

DB86, H₂Pc and ZnPc were manufactured by Tokyo Chemical Industry. Nickel (II) phthalocyanine-tetrasulfonic acid tetrasodium salt (NiPcS₄) were purchased from Aldrich. Chlorosulphonic acid for sulphonating the H₂Pc and ZnPc was bought from Acros Organics. NaCl and Na₂CO₃ used for exhaustion dyeing were offered by International Laboratory USA. TX-100 and Dimethyl sulfoxide (DMSO) purchased from VWR and Duksan Pure Chemicals respectively. MO and AY49 acted as dye stains were supplied by Acros Organics and Hangzhou Chungyo Chemicals respectively. Plain weave cotton fabric which was scoured and bleached when ordered was utilised as the self-cleaning substrate. All the chemicals were directly used without prior purifications.

5.2.2. Sample preparation

5.2.2.1. PHOTOCATALYTIC STUDIES OF SULPHONATED MPCS ON COTTON FABRIC

The sulphonated ZnPcs and H₂Pc were obtained by sulphonation of ZnPc or H₂Pc (0.3 g) with chlorosulphonic acid (3.6 g). The reaction underwent at 120 °C for 1 hour to obtain triand tetra-sulphonated ZnPc mixture (ZnPcS₃₋₄) while the reaction could be controlled at 100 °C for 2 hours to acquire the di-sulphonated ZnPc (ZnPcS₂) or di-sulphonated H₂Pc (H₂PcS₂). The cooled-down reaction product was then dissolved in DI water and neutralised
with soda ash to make up 1% w/v sulphonated ZnPc or H_2Pc solution. Their degrees of sulphonation had already been confirmed with LC-MS according to the double-isocratic method as same as the one reported in Section 4.3.3.

Specified weights of DB86, NiPcS₄, H₂PcS₂, ZnPcS₂ or ZnPcS₃₋₄ were dissolved into 100 ml of deionised water at room temperature, followed by placing each piece of cotton fabric (10×10 cm; 2.000 – 2.020 g) into the dye bath. The dyeing set-ups were heated up to 95 °C under uniform agitation (190 rpm) via a water bath. Known volume of NaCl (aq.) was gradually pipetted to the dyeing solution during this 90-minute direct dyeing process. Each piece of dyed cotton was separately rinsed with running tap water at room temperature for 1 min and then oven-dried at 50 °C for at least 1 hour. The detailed dyeing profile and recipes follow Figure 3-1 and Table 5-1 respectively.

		DB86	NiPcS₄	H ₂ PcS ₂	ZnPcS₂	ZnPcS ₃₋₄
Dye	(% o.w.f.)	0.57	0.42	2	0.2	2
NaCl	(% o.w.f.)	60	60	60	60	60
Na ₂ CO ₃	(% o.w.f.)	0.5	0.5	0.5	0.5	0.5
D.I. water		#	#	#	#	#
Fabric weight	(g)	2	2	2	2	2
Liquor ratio	(L:kg)	50:1	30:1	50:1	50:1	50:1

Table 5-1. Recipes for preparation of different sulphonated MPc-dyed cotton fabrics.

Used for making up to total bath volume

5.2.2.2. INVESTIGATION OF CO-MPC SYSTEMS APPLIED FOR SELF-CLEANING COTTONS

The sulphonated ZnPcs and H_2Pc employed, as well as the whole dyeing and rinsing experimental were as same as the ones mentioned in Section 5.2.2.1. The detailed dyeing profile and recipes follow Figure 3-1 and Table 5-2 respectively.

		ZnP	CS₂ : DB86		S₂ : NiPcS₄	
	1:1	1:2	2:1	1:1	1:2	2:1
ZnPcS ₂ (% o.w.f.)	0.025	0.017	0.033	0.025	0.017	0.033
DB86 (% o.w.f.)	0.125	0.083	0.17	-	-	-
NiPcS ₄ (% o.w.f.)	-	-	-	1.25	0.83	1.67
NaCl (% o.w.f.)	60	60	60	60	60	60
Na ₂ CO ₃ (% o.w.f.)	0.5	0.5	0.5	0.5	0.5	0.5
D.I. water	#	#	#	#	#	#
Fabric weight (g)	2	2	2	2	2	2
Liquor ratio (L:kg)	50:1	50:1	50:1	50:1	50:1	50:1

Table 5-2. Recipes for preparation of ZnPcS₂/DB86 and ZnPcS₂/NiPcS₄ co-dyed cotton fabric.

Used for making up to total bath volume

5.2.2.3. EXPLORATION OF THE FEASIBILITY OF NICKEL PHTHALOCYANINE

The dyeing procedures of $NiPcS_4$ on cotton fabric followed the one mentioned in Section

5.2.2.1. with specific dyeing recipes on Table 5-3.

		Water medium	DMSO/TX-100 aq. medium
NiPcS ₄	(% o.w.f.)	2	0.5
NaCl	(% o.w.f.)	60	60
Na ₂ CO ₃	(% o.w.f.)	0.5	0.5
DMSO	(mL/L)	-	100
TX-100	(g/L)	-	10
D.I. water		#	#
Fabric weight	(g)	2	2
Liquor ratio	(L:kg)	50:1	30:1
Dyeing tempe	rature (°C)	95	65

Table 5-3. Recipes for preparing NiPcS₄-dyed cotton in two different dyeing media.

Used for making up to total bath volume

5.2.3. Evaluation of photocatalytic activities of the treated fabrics

The photocatalytic stain fading activities of the functionalised cotton fabrics were assessed by monitoring the decrease in concentration of the colorant stains, AY49 and MO selected in this Chapter, on the fabric in exposure to visible light irradiation from household energy-saving fluorescent tubes. The detailed experimental is referred to Section 4.2.3.

5.2.4. Quantification of the residual MPc contents on cotton fabrics after photocatalytic activity tests

After the specified irradiation hour, the samples collected from Section 5.2.3 were further

analysed for their residual MPc contents on the cotton fabrics. All irradiated (time=t) and unirradiated (time=0) samples were cooled down in the dark with air conditioning at ~20 °C for at least 1 hour. The changes of MPc contents of the stained part were determined by measuring the reflectance spectra (400-700 nm) of the stained fabric samples, via a reflectance spectrophotometer (Datacolor 650) before and after the stained samples to be irradiated.

Through Kubelka–Munk expression, the spectral K/S values were converted from the measured reflectance following Equation 5-4, to represent the spectral absorption behaviours of the colorant stain on cotton. The K/S values of the sulphonated MPc itself, i.e., excluding the substrate absorption, were subsequently acquired following Equation 5-5. The Σ K/S* values of the MPc in 520-700 nm collected at a 5 nm interval in visible light spectrum, which represent their quantities in the stained areas, were calculated following Equation 5-6. The Σ K/S* of each MPc-dyed sample on pristine cotton fabric had been calibrated to be correlated to the actual dyeing % depths of the calibration samples. Therefore, initial content (C₀) and the content remained after being irradiated for 45 hr (C₄₅) of MPc were determined.

Equation 5-1.

$$K/S_{MPc+F} = \frac{(1-R_N)^2}{2R_N}$$

Equation 5-2.

$$K/S_{MPc} = K/S_{MPc+F} - K/S_{F}$$

Equation 5-3.

$$\Sigma K/S_{MPc}^{\star} = \sum_{\lambda} K/S_{MPc}$$

where K is the absorption coefficient of the dyed fabric
S is the scattering coefficient of the dyed fabric
MPc is the sulphonated MPc dye
F is the dyed fabric substrate
R_N is the reflectance value of the spotted part of the sample *λ* is absorption wavelengths of the colorant stain within 520-700 nm

5.3. RESULTS AND DISCUSSION

5.3.1. Photocatalytic studies of sulphonated MPcs on cotton fabric

Cotton fabrics functionalised with DB86 (i.e., sulphonated CuPcs), H₂PcS₂, NiPcS₄, ZnPcS₂ and ZnPcS₃₋₄ at consistent loading quantity (see Figure 5-1) were spotted with the primary dye stains mentioned in Chapter 3 for assessing their photocatalytic self-cleaning effects under visible light. The decolourisations of AY49 and MO by the MPc-dyed cotton in

exposure to 45-hour visible light are reported in Figure 5-2 and the corresponding visual results are attached in Table 5-4 for comparison.



Figure 5-1. K/S spectra of the sulphonated MPcs on cotton fabrics in visible light region; the $\Sigma K/S^*$ (average value of the dyed cotton piece, measured from 400 to 700 nm at a 5 nm interval) of DB86, ZnPcS₂, ZnPcS₃₋₄, H₂PcS₂ and NiPcS₄ are 86.2, 79.7, 85.5, 86.0 and 86.2 respectively.



Figure 5-2. Photo-driven decolourisation of (a) AY49 (0.35% w/v; 60 μ L) and (b) MO (0.155% w/v; 60 μ L) by different MPc-dyed cotton fabrics under irradiation of Philips TL-D 18W/827 1SL/25.

Table 5-4. Photos of the stained samples, corresponding to the results in Figure 5-2, before exposure to visible light and after exposing to visible light for 45 hr.



CuPc is commonly reckoned as a mild photoactive agent among the Pc family[342, 343, 345], Figure 5-2 also reflects the same case when DB86 was accommodated to cotton textiles to conduct photocatalytic decolourisations of AY49 and MO under visible light and compare with other sulphonated MPcs. It is surprising that cotton fabric applied with NiPcS₄, which is generally considered to have similar photocatalytic power to the CuPc, exhibited adverse photocatalytic ability towards the stain degradations under visible light; it seemed to retain the dye stain against photolysis instead of undergoing photocatalytic degradation. The two sulphonated ZnPcs and H_2PcS_2 demonstrated more remarkable degradation performances than the DB86 and NiPcS₄. Many researchers usually recognised ZnPc as one of the potent MPc photocatalysts but H_2Pc as a less active photocatalyst[342, 343, 345].

One of the reasons relates to the property of the electron configurations of the central atoms of the MPcs (see Figure 5-3). Zn^{2+} with a fully-filled 3d orbital demonstrate diamagnetic spin paring configuration, where all electrons are paired and the individual magnetic effects are cancelled out each other. Both the spin paring configurations of Cu^{2+} and Ni^{2+} ions belong to paramagnetic that having unpaired electrons and the individual magnetic effects cannot be cancelled out each other. The unpaired electrons bear a magnetic moment and more unpaired electrons can develop stronger magnetic moment to cause the atoms or ions to be interfered by external magnetic field. Diamagnetic Zn^{2+} ion in ZnPc possesses increased fluorescence

quantum yield without significant quenching of fluorescence, so its photocatalytic power is the strongest among the MPcs in this study. Cu²⁺ ion in CuPc is less paramagnetic than Ni ion in NiPc; in addition, the Cu²⁺ ion in CuPc bearing a fully-filled 3d orbital tended to improve the sulphonated CuPcs' photocatalytic behaviour over NiPcS₄.



Figure 5-3. Electron configurations of Ni²⁺, Cu²⁺ and Zn²⁺ ions in their MPcs (blue electron pins ($\uparrow\downarrow$) representing the electron transferred to by the bond formation with H₂Pc).

ZnPcS₃₋₄ demonstrated stronger photocatalytic activity than ZnPcS₂ to decolourise the AY49 and MO stains. As studied in Chapter 4, degree of sulphonation would not directly and chemically vary the photocatalytic activities of the sulphonated MPcs; it is believed that the ZnPcS₃₋₄ mixture exhibited more favourable dissociation effect than ZnPcS₂ to generate more photo-active monomeric species existed in cotton fabric, according to Figure 5-1. The sulphonated forms of H₂Pc, NiPc, CuPc and ZnPc accommodated to cotton fibre, one of the most versatile cellulosic fibres in the industries, provide new findings of their photocatalytic properties to contribute the researches of photocatalysis and photosensitisation by MPcs.

Despite the extraordinary photocatalytic degradation of the acid dye stains, there was a stability problem occurred in H₂PcS₂ and both sulphonated ZnPcs. Table 5-5 summarises the MPc contents left on the dyed cotton fabric after the 45-hour irradiation to visible light. It was discovered that all the samples had much smaller quantities of MPc contents retained on cotton fabrics when they were applied to decolourise AY49 than applied to fade MO under visible light. It was probably attributed to the self-degradation effect by which the sulphonated MPc decompose the dye stains together with itself via a series of photo-redox reactions in exposure to an activation light source. Hence, the more vigorous the photocatalytic activity, the higher the risk of self-degradation side effect it tended to contribute to.

Table 5-5. Percentage of MPc remained (C_{45}/C_0) on cotton fabric after 45-hour photocatalytic activity assessment under visible light.

Sulphonated MPc	Content	(%)
	<u>AY49 as stain</u>	<u>MO as stain</u>
DB86	97.8	98.2
NiPcS ₄	98.9	99.1
H ₂ PcS ₂	36.3	46.2
ZnPcS ₂	52.8	57.2
ZnPcS ₃₋₄	12.3	12.8

Based on the explanation of self-degradation side effect, it is only limited to compare an individual MPc to degrade different dye stains (with different persistency), but it is thorough

enough for comparing different sulphonated MPc candidates, the photocatalytic activities and stability of which are dominantly controlled by their intrinsic properties. For example, although ZnPcS₂ demonstrated better visible-light-activated stain removals than H₂PcS₂ on cotton, it could still retain over 50% content. On the other hand, the ZnPcS₂ was more resistant to self-degradation than ZnPcS_{3.4} and H₂PcS₂, one of the factors should be ascribed to such gentle molecular aggregation that could lighten the influence of self-degradation to a certain extent.

5.3.2. Investigation of co-MPc systems applied for self-cleaning cottons

Since the stabilities of different sulphonated MPcs dyed on cotton fabric were distinct in the photo-excited decolourisation process of the dye stains, the sulphonated MPcs were coapplied to the cotton fabric for further investigation of their photocatalytic performances. Figure 5-4 plots the spectral K/S graphs of the co-MPcs-dyed samples which were prepared in different ratios of ZnPcS₂/DB86 and ZnPcS₂/NiPcS₄, as well as the sole DB86 and ZnPcS₂dyed samples. Figure 5-5(a) compares their photocatalytic decolourisation powers towards AY49. The performances of the ZnPcS₂/DB86 systems to photocatalytically fade AY49 were between those of the sole ZnPcS₂ and DB86 at the equivalent MPc quantity levels. In addition, the higher ZnPcS₂:DB86 ratio tended to exhibit more effective decolourisation of AY49 and it was more significant when the ZnPcS₂:DB86 ratio reached 2:1. While the photo-excited activities of $ZnPcS_2/DB86$ systems were not as attractive as the sole $ZnPcS_2$, the stabilities of

the ZnPcS₂/DB86 co-dyed cotton fabrics were worth to be focused on in Figure 5-6.



Figure 5-4. K/S spectra of the co-MPc dyes in different ratios, sole DB86 and sole $ZnPcS_2$ on cotton fabrics, the blanket next to each sample label representing the $\Sigma K/S^*$ values.



Figure 5-5. Photocatalytic decolourisation of (a) AY49 (0.35% w/v; 60 μ L) by cotton fabric functionalised with different co-MPc dyes, DB86 and ZnPcS₂; (b) AY49 (0.35% w/v; 60 μ L) and MO (0.62% w/v; 60 μ L) by lightly ZnPcS-dyed cotton fabric (Σ K/S* = 9.03), under irradiation of Philips TL-D 18W/827 1SL/25.



Figure 5-6. Changes of K/S spectra of the ZnPcS₂/DB86, DB86 and ZnPcS₂ after 45-hour photocatalytic degradation assessment on cotton fabric in exposure to Philips TL-D 18W/827 1SL/25.

The stabilities of ZnPcS₂/DB86 co-dyed systems can be considered to be improved to a considerable extent. Even though the ZnPcS₂/DB86 was actually less stable than sole DB86

on cotton fabric and the increased ZnPcS₂/DB86 ratio tended to slightly weaken the system stabilities during the photocatalytic self-cleaning process, their stabilities were substantially enhanced when compared to the sole ZnPcS₂ applied to cotton fabric. To further estimate the effectiveness of the ZnPcS₂/DB86 co-dyed systems on cotton fabric, the weighted average contents of sole DB86 (weighing factor = 1) and sole ZnPcS₂ (weighing factor = 2) left after 45-hour photocatalytic activity test was estimated ~50.5% of the MPc content left; it may imply that there was over 22% stability enhancement by the ZnPcS₂/DB86 systems. It can be deduced that if the amounts of sole DB86 and sole ZnPcS₂ applied to cotton fabric were reduced to achieve the identical loading contents of the DB86 and ZnPcS₂ respectively in 2 ZnPcS₂ : 1 DB86 system, their stabilities would be much worse as well due to poorer lightfastness properties.

5.3.3. Exploration of the feasibility of NiPc

As shown in Figure 5-5(a), the ZnPcS₂/NiPcS₄ co-dyed systems on cotton demonstrated certain improvement on the photocatalytic activity of NiPcS₄ to decolourise the AY49 under the visible light as well. Nevertheless, if the results are compared with Figure 5-5(b), where much smaller quantity of ZnPcS₂ loaded to the cotton fabric ($\Sigma K/S^* = 9.03$), the decolourisation of AY49 were still better than the ZnPcS₂/NiPcS₄ co-dyed systems with the $\Sigma K/S^*$ values within

68 to 74. Even though such $ZnPcS_2$ encountered the more persistent dye stain, MO, in higher concentration (more concentrated than the one in Figure 5-2 four times), its photocatalytic performance was still over the $ZnPcS_2/NiPcS_4$ systems. It can be concluded that NiPc possibly inhibits the photo-active capability of $ZnPcS_2$ and other MPcs including itself in the co-application systems.

Referring to Figures 5-1 and 5-4, the spectral K/S curves of NiPcS₄ in visible light region commonly presented serious dimerisation or aggregation in cotton fibre medium. To explore whether the restrained photocatalysis of NiPcS₄ related to their significant aggregation in cotton fibre, two NiPcS₄-dyed cotton fabrics were respectively prepared in an aqueous medium in the presence of DMSO and TX-100 and in water medium for exhaustion dyeing processes. Figure 5-7 indicates the improved monomerisation effect of NiPcS₄ on cotton by introducing the DMSO and TX-100 to the dyeing medium. The monomeric NiPcS4 delivered slight advance on the photo-induced decolourisation of AY49 and MO; thus, it is believed that the detrimental effects of paramagnetic spin pairing and unfilled 3d orbital in the electron configuration of Ni²⁺ ion in NiPcS₄ on the photocatalytic self-cleaning cotton were significantly dominant.



Figure 5-7. K/S spectra of NiPcS₄ dyed to cotton fabric via different application media (the sume of K/S value (average value of the dyed cotton piece, measured from 400 to 700 nm at a 10 nm interval) of (a) and (b) were 23.2 and 24.1 respectively.)



Figure 5-8. Photocatalytic decolourisation of (a) AY49 (0.35% w/v; 60 μ L) and (b) MO (0.155% w/v; 60 μ L) by cotton fabric applied with NiPcS₄ by different dyeing media, under irradiation of Philips TL-D 18W/827 1SL/25.

5.4. CONCLUSION

This chapter discovers that sulphonated ZnPcs and H₂Pc have more pronounced photocatalytic stain decolourisation than sulphonated CuPc and NiPc in exposure to visible light source; however, their potent photocatalytic powers led to self-degradation impact to deteriorate the stability during the photocatalytic process instead. Both disulphonated ZnPc and DB86 were co-dyed to cotton fabric to gain a satisfactory balance between the photocatalytic power and the stability. It was estimated that the stability could be further enhanced in the ZnPcS₂/DB86 system on cotton. On the other hand, as the ZnPcS₂/NiPcS₄ co-dyed systems on cotton fabric only had slight upgrade of the photocatalytic property.

NiPcS₄ was specially exhausted to cotton fabric to maintain relatively larger amount of photo-active monomeric species; however, the improvement on the stain decolourisation was quite limited, probably owing to the unfavourable intrinsic characteristics of Ni²⁺ ion in NiPc. Although NiPc is not a desirable photocatalyst developed for self-cleaning cotton, its excellent stability and photocatalytic inhibition (indicated by the worse performances of ZnPcS₂/NiPcS₄ systems than that of sole ZnPcS₂) are possible for serving other purposes and expanding to various uses.

6. Further Liquid Chromatography-Mass Spectrometry Analysis of the Sulphonated CuPcs

6.1. INTRODUCTION

Liquid chromatography-mass spectrometry (LC-MS) is a major analytical technique to physically separate the mixutures of MPc dyes with high-performance liquid chromatography (HPLC) and identify the separated MPc compounds, fragmented ions and impurities via mass spectrometric analysis throughout this project. In the LC-MS system, reversed-phase high-performance liquid chromatography (RPLC), which is commonly classified as involving distribution of lowly to moderately polar solutes between a polar mobile phase and a relatively nonpolar stationary phase, was employed for physical separation. Single stage mass spectrometer equipped with an electrospray ionisation (ESI) source, a considerably soft ionisation produces little to no fragmentation, and a linear quadrupole mass analyser with unit-mass resolution was applied to analyse the RPLC-separated analytes based on their mass-to-charge (m/z) ratios.

As mentioned in the previous chapters, the structural information of the MPc compounds as photocatalysts in this research is essential to be determined since it is one of the dominant factors to influence their dissociation and aggregation behaviours in cotton fibre. Seriously aggregated and extensively dissociated MPc molecules tend to exhibit inferior photocatalytic activity towards stain decolourisation and have poor stability under prolonged exposure to light respectively. Degree of sulphonation is one of the main sources of structural derivations of the commercial MPc dye products. It is because direct sulphnoation of MPc rings with oleum or chlorosulphonic acid is the common and facile method to synthesise such sulphonated MPcs as direct dyes or intermediates for further modifications to reactive dyes[306, 346, 347]. Hence, identification and even quantification of the poly-sulphonated species in the MPc dyes are crucial for determining the relationship between the molecular structures and photoexcited self-cleaning performances of MPcs in this study.

There are several techniques to separate the poly-sulphonated metal phthalocyanines (MPcS_n) by HPLC; choosing an anion-exchange column which retains the sample's molecules based on the dynamic interactions between the sulphonated MPc anions and the cationic stationary phases (i.e., ionic nature of the packings in the column) is a theoretically desired method to separate the MPcS_n samples. However, the scope of application of this ion-exchange liquid chromatography (IEX-LC) is mainly for analysing amino acids mixtures in clinical diagnosis, the products of hydrolysis of nucleic acids and inorganic ions of the lanthanoids and rare earth elements[348]. It is not as versatile as RPLC. The elution of IEX-LC is commonly constituted of buffer solutions for separating the sulphonates and carboxylates[349-352], which is not favourable for the further analysis by an ESI-MS in my experience. Capillary electrophoresis is another technique to separate sulphonated Pc mixtures according to the degree of sulphonation, but the separation outcome from Schofield

et al.[353] are not satisfactory actually.

Many HPLC researchers[354, 355] agree that RPLC is the most popular separation executed in the HPLC systems (65-90%) due to its simplicity, versatility, flexibility and scope of application. The hydrocarbon-like stationary phases, for which the column packings are usually established with a ligand such as octadecyl (C18), octyl (C8), phenyl, or cyano-propyl chemically bonded to microporous silica particles, are desirable for use with gradient elution as it can be equilibrated swiftly upon the modifications of mobile phase compositions[356]. Nevertheless, it is generally agreed that there is a great challenge of separating the MPcS_n mixtures by RPLC. The different degrees of sulphonation on MPcs bear relatively small polarity differences to the reversed phase environment, especially for the commonly-used C18 columns. While MPcs (before sulphonation) are naturally hydrophobic and the central Pc rings of their sulphonated derivatives can still reserve a large extent of hydrophobicity, their cyclic molecular structures have less advantageous interactions to the packing materials in reversed-phase columns than the relatively linear molecules such as azo dyes.

lon-pair chromatography is a modified RPLC technique to separate the ionic or partially ionic compounds that are initially coupled with ion-pairing reagents by reversed-phase columns. Such ion-pairing reagents are typically long-chain alkyl ions for coupling with the oppositely-charged analyte compounds in order to improve the separation efficiency by extending the retention of analyte components in reversed-phase columns[357-360]. Although there are a number of effective methods reported to separate the MPcS_n samples using ionpair chromatography with reversed phase C18 columns[337, 338, 361, 362], as well as volatile ion-pairing reagents discovered and claimed to be proper for the IEX-LC-ESI-MS system[363-368], experienced chromatography researchers usually recommend that "as a general rule, we try to avoid using any / all ion pairing reagents with LC-MS or LC-MS/MS systems."[369]. It is widely believed that those ion-pairing reagents tend to contaminate the entire LC-MS system for months to years. They also raise the background levels to lead to additional noise for the detections. If the ESI-MS is employed, such ion-pairing reagents with poor volatility will result in signal suppression to considerable extents. Moreover, to our knowledge, those publications about the developments of "new and potent" ion-pairing reagents for LC-MS have seldom mentioned how to maintain the LC-MS instruments via a guaranteed cleaning process. On the other hand, addition of acidic buffer solutions into the eluent composition is also a feasible separation method for the MPcS_n in RPLC[336, 361, 370-372]; but if the analysis is followed by the MS detector, the choice of acidic buffers and the ease of analyte ionisation will be diminished. In my experience, it can be concluded that, ion-pairing reagents and buffer solutions involved in the RPLC-MS unavoidably reduce the signal-to-noise ratio of a mass spectrometer to a certain extent; this will be more serious in the ESI-MS which is well-known for its multiple-charged ionisation technique.

As encountering the above technical challenges in the RPLC-ESI-MS study, a novel

separation method is reported in this chapter. By establishing various gradient elution profiles for the RPLC, the poly-sulphonated CuPcs (CuPcS_n), ZnPcs and H₂Pc (i.e., ZnPcS₂, ZnPcS₃₋₄ and H₂PcS₂ in Chapter 5) could be separated successfully and then identified by the ESI-MS within 20 min clearly. The MPcS_n were separated with the commercially available analytical C18 columns without the additions of buffers or ion-pairing reagents; and the elution is composed of the common HPLC and ideal LC-MS solvents i.e., Milli-Q water, acetonitrile (ACN) and methanol (MeOH). Therefore, it is believed that these special separation techniques can be considered to be simple, efficient, cost-saving, easy-cleaning, convenientmaintenance and suitable for direct analyte extraction and purification.

6.2. METHODOLOGY

Experimental of analysing various MPc dyes by RPLC-MS in this study are introduced in the following.

6.2.1. Materials

ACN and MeOH with HPLC grade was supplied by Anaqua Chemicals and Duksan Pure Chemicals respectively. Water involved in HPLC running is purified by Thermo Scientific GenPure ultrapure water system. Nylon-membrane syringe filters (25 mm diameter and 0.22 µm pore) were manufactured by Membrane Solutions. The reversed-phase columns utilised in this study included Waters XSelect CSH C18 Column (XSelect), Alltech Platinum C18 Column (Platinum), Alltech AlphaBond C18 Column (Alphabond) and Grace VisionHT C18 HL Column (Vision). Owing to its poly-sulphonated characteristics found in Chapter 4, DB86 supplied by Tokyo Chemical Industry was dissolved in Milli-Q water as analyte for evaluating the elution trials throughout this Chapter.

6.2.2. Experimental details

Analytical HPLC assays were carried out under room temperature with one of the C18 columns mentioned in the Section 6.2.1 on a Waters Alliance HPLC System, which consisted of an e2695 Separation Module, 2998 Photodiode Array (PDA) Detector and an Acquity QDa Mass Detector. All the analyte samples were dissolved into water in specified concentrations and then filtered with nylon-membrane syringe filters, before injection into the column. 10 μ L of analyte was injected into the column via the auto-sampler for every run. Different elution plans are provided and discussed in the Section 6.3. Generally, the mobile phase started with 100% water and ended with 50%/50% water/ACN in 20 to 25 min. The flow rate was 0.3 to 0.9 mL/min dependent on the C18 selected for the analysis; the separation by reversed-phase

column was conducted at 25 °C. The PDA Detector was set up to collect the Max Plot chromatogram from 250 to 800 nm and the QDa Mass Detector was adjusted to have 15V cone voltage and obtain scan masses from 30 to 1250 m/z in both positive and negative ion modes during a run cycle.

6.3. RESULTS AND DISCUSSION

6.3.1. Gradient elution based on doubly-isocratic runs in different C18

columns

As presented in Chapter 4, Direct Blue 86 (DB86) supplied by Tokyo Chemical Industry and RB14 produced by Jiangsu World Chemical were successfully separated by a newlydeveloped gradient elution based on doubly-isocratic runs (abbreviated as "double-isocratic method") with XSelect column and identified by the ESI-MS.

The DB86 solution of 250 ppm was used for further investigation of the double-isocratic method cooperated with different reversed-phase C18 columns. The gradient profile of the double-isocratic method is presented in Table 6-1 and the PDA chromatograms of the DB86 separated by the selected C18 columns are shown in Figure 6-1. Compared with the PDA chromatogram of using XSelect column, those of using Platinum and Vision columns could separate the poly-sulphonated CuPcs in the DB86 but the resolution on the PDA



Figure 6-1. PDA chromatograms of separating the DB86 sample (250 ppm) by double-isocratic method with (a) XSelect, (b) Platinum, (c) Vision and (d) Alphabond C18 columns.

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)
1	Eqm. wash	а	100	0
2	5	а	80	20
3	5	а	100	0
4	10	а	50	50

Table 6-1. Gradient elution based on double-isocratic run.

^a Flow rate (mL/min): 0.3 (XSelect), 0.9 (Platinum and Vision), 0.55 (Alphabond)

chromatogram by Vision column was much better than that by Platinum column; thus the performance of Vision column can be inferred to be closely comparable to XSelect column. Alphabond column, which is the longest column among the four candidates, did not separate the CuPcS_n in the DB86 effectively through this elution plan. All the separation, especially by XSelect and Vision column, with this double-isocratic method were completed within 20 minutes, it is markedly more efficient than the normal gradient methods which usually finish in 40-60 minutes.

	Mass (<i>m</i>)						
Charge (z)	CuPc-(SO ₃ H) ₄	CuPc-(SO ₃ H) ₃	CuPc-(SO ₃ H) ₂	CuPc-(SO₃H)₁			
0	896.32	816.26	736.20	656.13			
-1	895.32	815.26	735.20	655.13			
-2	447.16	407.13	367.10	-			
-3	297.77	271.09	-	-			
-4	223.08	-	-	-			

Table 6-2. Mass-to-charge ratio (m/z) of CuPcS_n species ionised by ESI-MS.

Figures 6-2 to 6-5 demonstrate the total negative-ion chromatograms and mass spectra in details to verify and further compare the efficiencies of separating the CuPcS_n in the DB86 by these four C18 columns. The possible m/z ratios of the mono- to tetra-sulphonated CuPcs was listed in Table 6-2 for reference. As discussed in Chapter 4, XSelect column could isolate the di-sulphonated CuPc (CuPcS₂) from the poly-sulphonated mixtures and partially separate the tri- and tetra-sulphonated CuPc (CuPcS₃ and CuPcS₄) as shown in Figure 6-2.

Although Platinum column seemed to separate several components from the DB86 sample in the PDA chromatogram, the mass spectra in Figure 6-3 show that the sulphonated CuPcs eluted out were not separated well; the retention time of the major CuPcS_n was at ~4.4 min. Figures 6-4(a) to (d) are total negative-ion chromatogram and the corresponding mass spectra of the DB86 separated by Vision column to explain the effectiveness of the doubleisocratic method cooperated with Vision column. According to the chromatogram in Figure 6-4(a), the mixture of CuPcS₄ and CuPcS₃ eluted out in first 5 min were partially separated as the CuPcS₄ had slightly shorter retention time than the CuPcS₃; CuPcS₂ could successfully be isolated from the poly-sulphoanated mixtures. Regardless of the retention time of each component due to the column specifications different, such achieved separation was consistent to the outcome by XSelect column. These results imply that the strength of the double-isocratic method is sufficient for isolating the CuPcS₂ but limited to further obtain the independent CuPcS₃ and CuPcS₄ compounds.



Figure 6-2. ESI-MS analysis of the DB86 (250 ppm) separated by XSelect column, corresponding to Figure 6-1(a). (a) Total negative-ion chromatogram; (b-d) mass spectra of 1st to 3rd CuPc components separated from the DB86 sample.



Figure 6-3. ESI-MS analysis of the DB86 (250 ppm) separated by Platinum column, corresponding to Figure 6-1(c). (a) Total negative-ion chromatogram; (b-d) significant mass spectra of the poly-CuPc components separated from the DB86 sample at the specified time.



Figure 6-4. ESI-MS analysis of the DB86 (250 ppm) separated by Vision column, corresponding to Figure 6-1(d). (a) Total negative-ion chromatogram; (b-d) mass spectra of 1st to 3rd species of the poly-CuPc components separated from the DB86 sample at the specified time.



Figure 6-5. ESI-MS analysis of the DB86 (250 ppm) separated by Alphabond column, corresponding to Figure 6-1(b). (a) Total negative-ion chromatogram; (b-e) significant mass spectra of the poly-CuPc components separated from the DB86 sample at the specified time.



Figure 6-5 (cont'd). ESI-MS analysis of the DB86 (250 ppm) separated by Alphabond column, corresponding to Figure 6-1(b). (a) Total negative-ion chromatogram; (b-e) significant mass spectra of the poly-CuPc components separated from the DB86 sample at the specified time.

Comparing the separation results with Alphabond column, the mass spectra in Figure 6-5 illustrates the retention time of $CuPcS_n$ within 7-7.5 min. Even though the whole $CuPcS_n$ could not be separated, the mass spectra in Figures 6-5(c) and (d) indicate that the more hydrophilic species $CuPcS_4$ and $CuPcS_3$ were eluted out earlier than $CuPcS_2$. Monosulphonated CuPc ($CuPcS_1$) was not found throughout the analysis by the four C18 columns; it may be filtered out during the manufacturing process because of its poor water solubility to deteriorate the dyeing efficiency.

Although the above four columns belong to the reversed-phase columns packed with octadecyl carbon chain (C18)-bonded silica (USP classification L1, i.e., packings to be octadecyl silane chemically bonded to porous or non-porous silica or ceramic micro-particles, 1.5 to 10 µm in diameter, or a monolithic rod[373]), their separation performances towards the

DB86 were not all consistent. Moldoveanu and David[354, 374] indicate that the performance of a bonded phase silica column can be determined by four factors, (1) the base silica material and its pretreatment, (2) the type of stationary phase bonded onto the silica, (3) carbon load i.e. the amount of stationary phase material bonded onto the silica and (4) presence of secondary bonding (i.e. end-capping) reactions.

Column's	Pore	Surface	Particle	Particle	Column's internal	Carbon	End-
brand and model	diameter /	area /	size/	sharp	diameter $ imes$ length /	load /	capped
	Å	m ² g ⁻¹	μm		mm	%	
Waters XSelect CSH	130	185	5	Spherical	3.0 × 250	15	Yes
C18 Column							
Alltech Platinum	100	200	5	Spherical	4.6 imes250	6	Yes
C18 Column							
Alltech AlphaBond	125	300	10	Irregular	3.9 imes 300	10	Yes
C18 Column							
Grace VisionHT	120	220	5	Spherical	4.6 × 250	11	Yes
C18 HL Column							

Table 6-3. Comparisons of specifications of the four RPLC C18 columns in this study[375-378]

Table 6-3 summarises the specifications of the four C18 columns to explore the causes of their performance disparity. All the four columns have the same type of stationary phase bonded onto the silica, i.e., columns packed with octadecyl carbon chain-bonded silica (C18), and the residual silanols had been completely reacted with bonding reagent to have endcapping; so it is believed that factors (2) and (4) are not the key factors leading to such variations of the separation results. The characteristics of base silica material, including the pore size and distribution, particle size and shape, surface area and degree of activity tend to affect the final performance of a bonded phase column. On the other hand, increase of carbon load of the stationary phase generally enhances the hydrophobicity of the column to strengthen the reversed-phase retention. Comparing XSelect and Vision columns, both of which were similarly potent to isolate the CuPcS₂ and partially separate the CuPcS₃ and CuPcS₄ from the CuPcS_n. While Vision possessed the lower carbon load than XSelect, its smaller pore diameter and greater surface area in the silica-packed column were probably able to compensate the weaker carbon load % to achieve comparable reversed-phase retention and separation performance towards the DB86 sample. Platinum carries much finer pore diameter than XSelect and Vision and similar surface area to them, but its significantly poorer carbon load can explain its inferior separation behaviour to the CuPcS_n.

Alphabond is a relatively special column to the other three choices. Its larger particle size and irregular shape of silica were not beneficial to establishing a suitable stationary phase with adequate retention power towards the sulphonated CuPcs. Nevertheless, it is reckoned that its longer column length, superior surface area of the packings and desirable carbon load provide a noteworthy potential of Alphabond column to separate the CuPcS_n with the doubleisocratic method. Table 6-4 demonstrates a modified double-isocratic method designed for Alphabond column that successfully resembled the separation outcome by the XSelect and

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)
1	Eqm. wash	0.7	100	0
2	5	0.7	88	12
3	5	0.7	100	0
4	10	0.7	50	50

Table 6-4. Modified double-isocratic method for Alphabond.

Vision columns; the detailed separation results are presented in Figure 6-6. In contrast, various modified double-isocratic methods were attempted for Platinum column but it was quite challenging to reach acceptable separation effects. It can be concluded that the carbon load is a substantially determining factor of a C18 column for separating the MPcS_n with the newly-designed double-isocratic method.



Figure 6-6. Separation of the DB86 (250 ppm) by Alphabond column via a modified double-isocratic method. (a) PDA chromatogram; (b) total negative-ion chromatogram; (c-e) mass spectra of tetra-, triand di-sulphonated CuPcs separated from the DB86 sample at the specified time.


Figure 6-6 (cont'd). Separation of the DB86 (250 ppm) by Alphabond column via a modified doubleisocratic method. (a) PDA chromatogram; (b) total negative-ion chromatogram; (c-e) mass spectra of tetra-, tri- and di- sulphonated CuPcs separated from the DB86 sample at the specified time.

6.3.2. Development of gradient elution based on triply-isocratic runs

In order to have more effective separation of $CuPcS_n$ in the DB86 sample, gradient elution based on triply-isocratic runs (abbreviated as "triple-isocratic method") was further studied and developed. In the basis of the double-isocratic method, the first isocratic run, which was conducted at 80/20 water/ACN for 5 min, was divided into two runs to establish the tripleisocratic method performed with Vision C18 column.

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)
1	Eqm. wash	0.9	100	0
2	1	0.9	80	20
3	1.5	0.9	100	0
4	2	0.9	80	20
5	5	0.9	100	0
6	10	0.9	50	50

Table 6-5. First trial of a gradient elution based on triple-isocratic run (ISC³-T1).

Table 6-5 and Figure 6-7(a) shows the first attempt of the triple-isocratic method (ISC³-T1) and the corresponding separation result in terms of the PDA chromatogram respectively. There were two tall peaks locating at ~4.7 min and ~14.8 min as well as one small peak at ~7.3 min; these peaks were further identified by the ESI-MS and the results of mass spectra are summarised in Figure 6-8. The CuPcS₃ and CuPcS₄ were mainly eluted out from the



Figure 6-7. PDA chromatograms of separating DB86 (250 ppm) with various trial triple-isocratic methods (a) ISC³-T1, (b) ISC³-T2, (c) ISC³-T3 by Vision C18 column and double-isocratic method (d) ISC²-MeOH by XSelect column.



Figure 6-8. Separation results of Figure 6-7(a) confirmed by ESI-MS; (a) total negative-ion chromatogram and (b-d) mass spectra of the corresponding three peaks.

column at ~4.7 min and little CuPcS₃ was found eluted out at ~7.3 min, i.e., the small peak between the two tall peaks. CuPcS₂ was still successfully isolated and eluted out from the column at ~14.8 min to complete the whole separation procedures. The division of 80/20 water/ACN isocratic elution into two runs by 1-min 100% water wash implies that certain CuPcS₃ could be partitioned and eluted out from the column at different retention time.

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)
1	Eqm. wash	0.9	100	0
2	1	0.9	85	15
3	1.5	0.9	100	0
4	2	0.9	80	20
5	5	0.9	100	0
6	10	0.9	50	50

Table 6-6. Second trial of a gradient elution based on triple-isocratic run (ISC³-T2).

The second attempt of the triple-isocratic method (ISC³-T2) was to increase the hydrophilicity of the mobile phase in the first isocratic water/ACN elution, in order to have better separation of CuPcS₄ and CuPcS₃. Table 6-6 lists the elution profile and Figure 6-7(b) reveals the corresponding PDA chromatogram. The peak at ~7.3 min became more significant and the peak at ~4.7 min was shortened and broadened to approach the peak at ~7.3 more. It can be considered a clear evidence to indicate certain portion of CuPcS₃ shifted to be eluted out later, by increasing the hydrophilicity of the mobile phase in first isocratic wash. However,

when the first two water/ACN isocratic runs shifted to be more hydrophilic in the third attempt of triple-isocratic method (ISC³-T3 (see Table 6-7)), the resolutions of both peaks at ~4.7 and ~7.3 min became poor as shown in Figure 6-7(c). It is noted that the partitioning between $CuPcS_n$ and the stationary phase (with high carbon load) was quite sensitive to such tuning of water to ACN ratio in mobile phase.

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)
1	Eqm. wash	0.9	100	0
2	1	0.9	85	15
3	1.5	0.9	100	0
4	2	0.9	85	15
5	5	0.9	100	0
6	10	0.9	50	50

Table 6-7. Third trial of a gradient elution based on triple-isocratic run (ISC³-T3).

Table 6-9 compares the polarities of water, ACN and MeOH; the Hildebrand solubility parameter and solvent strength for silica adsorbent of MeOH are higher than those of ACN but their polarity indices are vice versa instead. This information is not clear enough to reflect the interaction of ACN and MeOH to CuPcS_n, therefore double-isocratic method where the ACN in mobile phase was replaced by MeOH as presented in Table 6-9. After over 20 minutes, there were only CuPcS₄ and CuPcS₃ eluted out. The mobile phase was switched to 50/50 water/ACN manually and the remaining CuPcS₂ could be washed out from the column at ~32

Solvent	δ	P'	3
ACN	12.1	5.8	0.52
MeOH	14.5	5.1	0.70
Water	23.4	10.2	-

Table 6-8. Polarity of water, ACN and MeOH[356]

 δ = Hildebrand solubility parameter; P' = Polarity index;

 ε = Solvent strength for silica adsorbent

Table 6-9. Trial of a gradient elution based on double-isocratic run by replacing ACN with MeOH (ISC²-

MeOH).

Flow	Duration (min)	Flow rate	Water (%)	MeOH (%)
1	Eqm. wash	0.9	100	0
2	5	0.9	80	20
3	5	0.9	100	0
4	10	0.9	50	50

min (see Figure 6-9). Although the resolution and separation efficiency by ISC^2 -MeOH was much poorer than the original double-isocratic method, the findings from Figures 6-7(d) and 6-9 had offered some hints to verify interaction of MeOH to $CuPcS_n$ deposited on the stationary phase, which is formed by the silica packing of C18 column, is in-between those of water and ACN.

Triple-isocratic method in which the mobile phase composition in the first isocratic wash was composed of 85/10/5 water/ACN/MeOH was set up following Table 6-10. The duration of the first isocratic wash (85/10/5 water/ACN/MeOH) from 0.5 to 2 min were tested to analyse



Figure 6-9. Separation results of Figure 6-7(c) confirmed by ESI-MS at different retention time.

the DB86 sample and the separation results were presented in the PDA chromatograms in Figure 6-10. When t = 1 min, the resolution of the separation was the most defined among the five sample runs, and there were no significant peaks appeared within 8 to 9 min as well. Mass spectra in Figure 6-11 indicates that the peaks at 4.905, 7.411 and 14.852 min were CuPcS₄, CuPcS₃ and CuPcS₂ respectively; separation task of the CuPcS_n in DB86 had successfully been completed.

Flow	Duration (min)	Flow rate	Water (%)	ACN (%)	MeOH (%)
1	Eqm. wash	0.9	100	0	0
2	t	0.9	85	10	5
3	1.5	0.9	100	0	0
4	2	0.9	85	20	0
5	5	0.9	100	0	0
6	10	0.9	50	50	0

Table 6-10. Gradient elution based on triple-isocratic run (with MeOH in mobile phase)

t = 0.5, 0.75, 1, 1.5 and 2 min



Figure 6-10. PDA chromatograms of separating DB86 (250 ppm) by Vision C18 column with various duration time (t) of the first isocratic wash composed of 85/10/5 water/ACN/MeOH corresponding to the elution plan in Table 6-10.



Figure 6-10 (cont'd). PDA chromatograms of separating DB86 (250 ppm) by Vision C18 column with various duration time (t) of the first isocratic wash composed of 85/10/5 water/ACN/MeOH corresponding to the elution plan in Table 6-10.



Figure 6-11. Separation results of Figure 6-10 at t = 1 min confirmed by ESI-MS; (a) total negative-ion chromatogram and (b-d) mass spectra of the corresponding three peaks.



Figure 6-12 (cont'd). Separation results of Figure 6-10 at t = 1 min confirmed by ESI-MS; (a) total negative-ion chromatogram and (b-d) mass spectra of the corresponding three peaks.

6.4. CONCLUSION

By studying the factors of (1) specifications of reversed-phase columns, (2) interactions between different (polarities of) solvents and the sulphonated CuPcs deposited on the mobile phase constructed by C18 silica, as well as (3) duration of the particular isocratic run, a series of experimental results were acquired to develop simple, unique and efficient gradient elutions based on doubly- and triply- isocratic runs successfully. It is suggested that, if di-sulphonated MPcs is required to be isolated from the MPcS_n, the simpler double-isocratic method will be useful enough to achieve the purpose. Provided that tetra- or tri- sulphonated MPc is extracted,

more precise triple-isocratic method will be the most appropriate technique to fulfil the purpose.

7.1. OVERALL CONCLUSION

Metal phthalocyanines in sulphonated forms were introduced to functionalise cotton fabric with photocatalytic property by facile and steady textile exhaustion dyeing approaches. To evaluate and compare the visible-light-triggered self-cleaning activities of the treated fabrics, stain decolourisation was employed to express the photocatalytic activities of the selfcleaning systems composed of MPcs.

A number of sulphonated copper phthalocyanine compounds with different substituents, which were used as direct dyes and reactive dyes in textile industry, were loaded to the cotton substrate in equal quantities but the functionalised fabrics had not demonstrated the comparable photocatalytic activities towards stain decolourisations. A series of analysis by optical absorption spectroscopies discovered that, distinct aggregation and dissociation behaviours of the CuPc candidates existed in the cellulosic medium owing to their different molecular structures, which were further confirmed by liquid chromatography-electrospray ionisation-mass spectrometry.

While cotton fabric dyed with well-dissociated CuPcs, i.e., C.I. Direct Blue 86 (a polysulphonated CuPcs sourced from Tokyo Chemical Industry) and C.I. Reactive Blue 21, were evaluated to have more superior stain decolourisations than that coated with nanocrystalline TiO₂ (anatase) under visible light, CuPc was actually a mild photocatalyst among other MPcs on cotton. Sulphonated zinc phthalocyanines and metal-free phthalocyanine prepared in the laboratory tended to deliver much stronger and more efficient photocatalytic performances under the identical photo-driven stain fading condition. Nevertheless, the unsatisfactory stability of sulphonated ZnPcs limited its development as all-rounded organic photocatalysts for self-cleaning cotton. The di-sulphonated ZnPc, which was gently-aggregated in cotton fibre to have better balance between the stability and photocatalytic activity than tetra- and trisulphonated ZnPcs, was co-applied with the DB86 to cotton fabric. This approach tended to alleviate the stability problem estimated by K/S measurement as well. Even though the tetrasulphonated nickel phthalocyanine was attempted to be dyed on cotton fabric with more monomeric species or cooperated with ZnPcS₂, it is believed that the intrinsic deficiency of NiPc relating to the undesirable electron configuration of nickel ion (i.e., partially-filled 3d orbital and paramagnetic spin paring configurations) is the determining factor to hinder its photocatalytic power.

During studying the photocatalytic self-cleaning effects of the cotton fabrics functionalised with different MPcs, this project encountered two technical and analytical challenges which finally tackled via a series of experiments. The first concern is that many scholars criticise the feasibility of dye decolourisation assessments for indicating the photocatalytic activities of the self-cleaning systems. Through a number of analysis, it can be concluded that careful selection of colorant stains with adequate light stability against photolysis effect (photo-fading), wider energy gap between HOMO and LUMO, lower LUMO level, as well as defined absorption region with minimal spectral overlapping to MPc photocatalysts in visible light region will provide a reliable and acceptable method for examining visible-light-driven selfcleaning effects on cotton fabric conferred by MPcs.

The second challenge relates to separating the mixtures of poly-sulphonated MPc derivatives by reversed-phase column for liquid chromatography-mass spectrometry. By investigating the different specifications of C18 reversed phase columns and liquid chromatographic variables including the mobile phase compositions and elution duration, unique gradient elution based on doubly- and triply- isocratic runs were founded. This novel separation technique is valuable for its simplicity without involving any pH buffers and ion-pairing reagents, efficiency for separation, direct purification and extraction of the MPcS_n samples within a 30-min run, as well as cost-saving due to easy cleaning and handy maintenance of LC-MS system where only neutral and common solvents used for the mobile phase components.

7.2. RECOMMENDATION FOR FUTURE WORK

Further research work based on the outcomes of this thesis is recommended and listed in the following.

7.2.1. Self-cleaning substrates

MPc-self-cleaning systems are possibly studied and developed on other textile substrates, comprising other cellulosic fibres, polyamides, polyesters and polyurethanes.

7.2.2. MPc photocatalysts

- (1) Other commercial CuPc dyes in direct and reactive forms can be further studied to enrich the investigation about how the molecular structures of CuPc compounds influence the photocatalytic performances in cotton substrate.
- (2) Other potential MPc candidates with different central atoms or ions[263, 342, 379, 380], such as AlCl²⁻, SiCl₂²⁻ and Ga²⁻, can be prepared in sulphonated or other water-soluble forms and applied to the textile materials for studying and developing photo-activated self-cleaning textiles.

- (3) MPc compounds with other substituents, such as cationic functional groups and longer alkyl-chains, are worth to be researched in terms of their photocatalytic behaviours.
- (4) NiPc or NiPcS₄ can be further studied and applied as photocatalytic inhibitor in other fields of uses instead of developing as an effective photosensitising agent.

7.2.3. Dye stains as model compounds

- (1) The intrinsic energy gap between the organic substances i.e., the acid dye stains and MPc compounds can be further investigated and compared with other advanced techniques, such as ultra-violet photoelectron spectroscopy.
- (2) More thorough mechanisms of the stain decompositions are suggested to be explored to support the mechanisms of the photocatalytic self-cleaning reactions exhibited by the MPcs and then contribute to the advanced theory of photocatalysis, phthalocyanine chemistry and photolysis issue of organic dyes.

7.2.4. High-performance liquid chromatography and mass-spectrometry

(1) A variety of CuPc dye products, MPc derivatives and even other sulphonated organic

dyes can be further analysed with the newly-designed gradient elution based on doubly- and triply- isocratic runs to verify the diversity and available of this elution systems.

- (2) Quantification of the MPcS_n samples to determine the degrees of sulphonation can be further investigated to develop a reliable system with the plenty of data from photodiode array detector and mass spectrometer.
- (3) Other reversed-phased columns such as C8 or modified C18 columns as well as normal phase columns can be utilised to compare the separation results or/and cooperate with gradient elution based on doubly- and triply- isocratic runs.

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