



Polymer composites with photo-responsive phthalocyanine for patterning in color and fluorescence



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ABSTRACT

Polymer composites containing stimuli responsive small molecules have been explored for various applications, including patterning and data storage. Phthalocyanines (Pc) have been widely synthesized and used as dyes, catalysts, and optical limiting materials, as well as active components in modern organic electronic devices. The solubility of Pcs and miscibility with a polymer matrix require the use of covalently attached alkyl side chains that rarely serve any other purpose than solubility. Herein we report a polymer composite with a novel cobalt (II) Pc dye with alkyl chains connected through a photolabile linker. The materials are synthesized using standard reactions and characterized by FTIR, MALDI, and absorption and emission spectroscopies. Upon UV irradiation in solution or in the polymer films, the alkyl groups are cleaved rendering the Pc core insoluble and turning on fluorescence of the small molecule byproduct. This observation is in direct contrast to treatment of similar Pc molecules that lack the photoresponsive group. PMMA and PDMS films are patterned with resolution down to 250 μm using only 0.1 wt% of our tailored Pc molecule. This work presents a fundamental method for patterning in polymer films by tuning the solubility, color, and fluorescence of a Pc based system and could ultimately be used for sensing, data storage, or pigmentation.

1. Introduction

The chemistry of stimuli responsive small molecules has garnered much recent attention, though their use in polymer films has been explored to a lesser degree [1]. However, incorporation of such responsive small molecules into a polymer matrix has the potential to lead to unique patterning and data storage capabilities [2]. Conjugated organic small molecules have been widely synthesized and used as dyes [3], catalysts [4], optical limiting materials [5], and in optoelectronics [6,7]. An oft-cited advantage of these organic materials include solution processability (e.g., use of roll-to-roll processing), in contrast to more energy intensive methods required for inorganic materials [8]. Phthalocyanines (Pcs), heterocyclic aromatic small molecules, are thermally and chemically stable [9], and have been used in organic transistors [10,11], sensors [12], diodes [13], solar cells [14–16], and optical storage devices [17,18], and as pigments [19] and dyes [20,21]. Although much research efforts have focused on tuning the chemical composition of conjugated organic small molecules to control absorption, emission, charge mobility, self-assembly, and stability, their use as responsive moieties in polymer composites has been less widely studied.

Metallated Pcs can be synthesized from phthalic anhydride or phthalonitrile, and are typically processed by thermal vapor deposition [12,22,23]. To render Pcs solutions processable and miscible with polymers, linear or branched alkyl groups are typically

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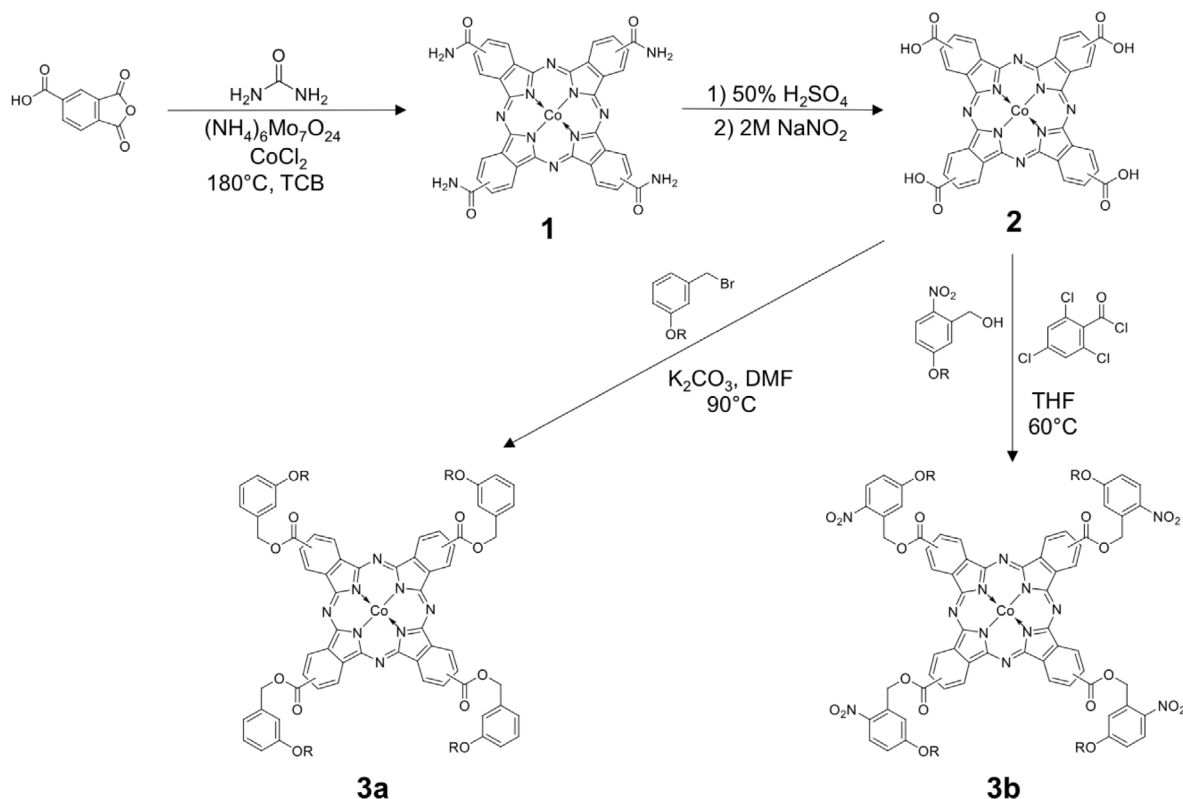


Fig. 1. Synthetic route to prepare phthalocyanine cobalt (II) tetra carboxylic acid (2), non-photolabile tetra ester (3a) and photolabile tetra ester (3b). R = hexyl.

covalently attached to the Pc core through alkylation processes [24]. These “greasy” substituents are necessary to ensure solubility, but unfortunately are rarely exploited for any other purpose [25]. As such, tailoring the solubility of Pcs can be beneficial to a number of different systems. Previous approaches to tailoring the solubility of conjugated organic molecules include removal of solubilizing alkyl groups after processing [26–29]. For example, Thomas and coworkers incorporated a photolabile linker between an alkyl chain and the conjugated backbone of polythiophene, such that the alkyl group could be removed following irradiation to give an insoluble polymer, either in the thin film or in solution [26,27]. Likewise, Fréchet and coworkers introduced a thermally cleavable linker between an alkyl group and polythiophene chain [28]. While similar methods have also been reported for conjugated polymers based on benzothiadiazole and pyrrole [29], such systems have not been widely exploited.

Herein, we report the synthesis of a phthalocyanine molecule bearing photocleavable alkyl chains and demonstrate its photoresponsive behavior upon UV irradiation in polymer composites for patterning applications. Changes in solubility and emission for this tailored Pc are in distinct contrast to the analogue without the photolabile linker. The Pc core bearing cobalt was synthesized from phthalic anhydride and then functionalized using a Yamaguchi esterification [30,31]. The tailored Pc is incorporated as an additive into films of PMMA and PDMS, and show similar response, an important observation given that solid state or thin film photochromic properties are essential for many practical applications [32]. In fact, fluorescent or colored patterns with resolution down to $250\ \mu\text{m}$ can be realized in the polymer films using a photomask. This work presents a fundamental method for patterning in polymer films by tuning the solubility, color, and fluorescence of a Pc-based system that can ultimately be used to control pigmentation, and optoelectronic properties.

2. Results and discussion

The Pcs used in these studies were prepared using a standard synthetic route as shown in Fig. 1. Pc tetra amide cobalt (II) (compound 1) was synthesized as previously reported from commercially available benzene tricarboxylic anhydride, urea, cobalt (II) chloride, and ammonium molybdate [30]. A mixture of isomers of the tetra amide 1 was obtained, and the amides were converted to carboxylic acids in an aqueous sulfuric acid and sodium nitrite solution. The tetra acid 2 is sparingly soluble in methanol, acetone, diethyl ether, and ethyl acetate. To improve solubility of the Pc core in common organic solvents and render it processable with common polymers, the carboxylic acids of 2 were converted to benzyl esters bearing n-hexyl chains. This transformation was realized using benzyl alcohols or bromides prepared by tandem alkylation and reduction of 5-hydroxy-2-nitrobenzaldehyde and 3-hydroxybenzaldehyde (see Fig. S1). Conversion of 2 to 3a was realized using a simple $\text{S}_\text{N}2$ reaction, while the conversion of 2 to 3b was completed by a Yamaguchi esterification [31,33]. Pc 3a bears standard benzyl esters while Pc 3b bears benzyl esters with an ortho-nitro group, thereby imparting photolability under UV irradiation [34]. Such molecular design allows for the influence of

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