

Synthesis and Photoresponsive Properties of Cu-Phthalocyanine with Azobenzene Groups

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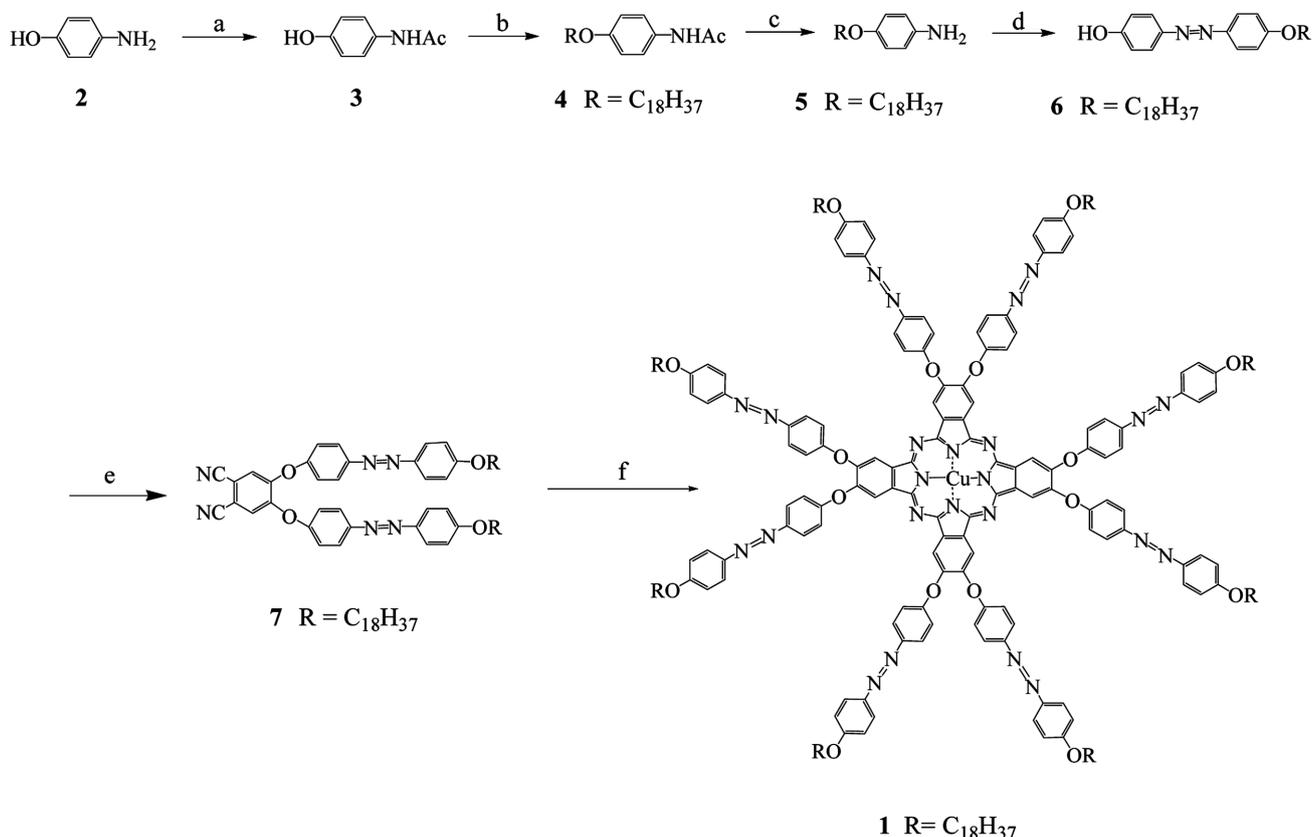
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There has been extensive interest in the physical and chemical properties of phthalocyanines (Pc) owing to their intriguing electrical, optical, photochemical and catalytic properties.¹ A particularly attractive feature of Pc is the dependence of the properties of the molecule on the nature of the peripheral functional groups, as well as the electronic properties of the central metal cations in the phthalocyanine ring.² Unsubstituted phthalocyanines are not very soluble and tend to aggregate in solution; however, the addition of peripheral chains can increase solubility, processibility, and facilitate the formation of discotic mesophase.³ Recently, many new phthalocyanines with long alkyl,⁴ alkoxy,⁵ alkylthio⁶ and alkoxyphenoxy⁷ groups have been prepared to study on their diverse functionality such as liquid crystalline properties^{2,3,9} as well as highly ordered thin film properties.⁸

In line with these aspects, we report herein the first synthesis of copper-phthalocyanine (**1**) with eight photoisomerizable azobenzene groups at the periphery. This macrocycle incorporated with eight long-chain azobenzene substituents exhibit *trans-cis* isomerization properties upon irradiation of UV/VIS light.

The synthetic routes to octasubstituted copper phthalocyanine (**1**) are shown in Scheme 1. From commercially available 4-hydroxyaniline (**2**) azobenzene derivative (**6**) was obtained *via* several steps, and then converted to the dinitrile (**7**). Cyclization of dicyanobenzene derivative (**7**) with copper chloride and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-pentanol led to the formation of **1** in good yield. This macrocycle possesses good solubility in common organic solvents and was purified mainly by column



Scheme 1. Reaction conditions: (a) Ac₂O, THF. (b) RBr, K₂CO₃, MeCN. (c) 6N HCl, EtOH (d) phenol, NaNO₂, 35% HCl, H₂O/THF. (e) 4,5-dichlorophthalonitrile, K₂CO₃, THF. (f) CuCl₂, DBU, *n*-pentanol.

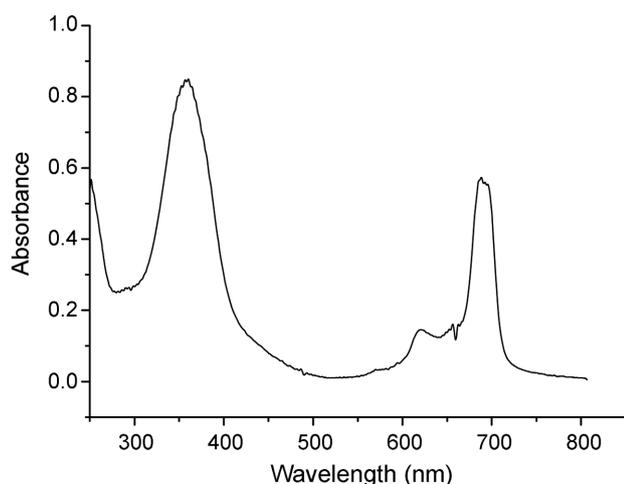


Figure 1. Absorption Spectrum of **1**.

chromatography with chloroform mixed with THF as eluent. The latter was employed in order to disrupt the molecular aggregation associated with the large π -system. The ^1H NMR spectra of **1** in CDCl_3 , showed only broad resonances due to the aliphatic side chains; the aromatic protons appeared as broad signals deshielded in the regions δ 7.45-8.20 and 6.70-7.11 assignable to the ring protons and azobenzene protons. Eight methylene protons (O-CH_2 -) resonanced in the region δ 3.95 as a broad band.

The UV/VIS spectra of the phthalocyanine (**1**) in chloroform showed the typical pattern, mainly the π - π^* transition of the heteroaromatic 18- π electron system (Figure 1): A large intense Q band in the visible region of around 687 nm was accompanied by more or less resolved weak satellite bands. In the ultraviolet region of around 360 nm the characteristic Soret or B band was also observed. Peripheral substitution of phthalocyanine by alkoxyazobenzene chains gave bathochromic shifts of both the Q band (687 nm) and Soret band (360 nm) compared to the unsubstituted Cu-phthalocyanine (Soret band 343 nm, Q band 683 nm in CHCl_3).¹⁰ However, absorption bands of azogroups (around 350 nm, π - π^* transition, *trans* form)¹¹ were overlapped with the Soret band of **1**: Irradiation of 365 nm light proved this overlapping and exhibited the expected photoresponsive behavior of **1**. For example, dark incubation of a chloroform solution (10^{-5} M) of **1** served to maximize the absorption at 360 nm ($\epsilon_{\text{max}} = 84900$) corresponding to the *trans*-azobenzene chromophore. Irradiation of this solution with 365 nm light resulted in partial photoisomerization to *cis*-azobenzene, as evidenced by a decrease in the absorbance at 360 nm and a small increase from $\epsilon = 7880$ to $\epsilon = 8600$ in absorbance at around 450 nm (n - π^* transition, *cis* form)¹¹ (Figure 2). A photostationary state was reached within approximately 420 seconds. At this state we could estimate the yield of the isomerized azobenzene groups to be about 25% on the basis of the contribution ratio of the Soret band and azobenzene groups for the molar absorptivity at 360 nm. In most of Cu-phthalocyanines^{10,12,13} the general ratio of Soret band and Q

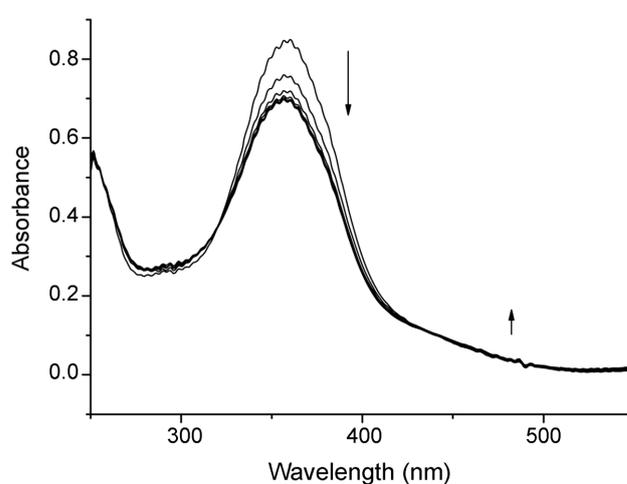


Figure 2. Absorption Spectrum of **1** under irradiation (365 nm: 0, 30, 60, 120, 240, 360 and 420s).

band was found to be about 2 : 5. From this ratio we derived the molar absorptivity contribution of azobenzene groups in **1**. This value thus obtained (around 61,900) is bigger than the molar absorptivity of **7** (around 30,000), but it seems to be reasonable because compound (**1**) has eight azobenzene groups. Finally we could deduce the yield of the isomerized azobenzene groups from the change value (around 15,100) of molar absorptivity after irradiation. Thermal reversion to the original dark-incubated spectrum was observed over the course of approximately 15 h at 293 K in the dark. However, exposure to bright sunlight for a period of only several seconds also effects almost complete reversions to the *trans* isomer. This partial isomerization phenomena of **1** can be ascribed to not enough space for eight azobenzene groups in **1** to undergo *trans-cis* isomerization.

The mesophase behaviors of **1** were not observed by differential scanning calorimetry (DSC) and polarized optical microscopy: The DSC thermograms of **1** showed only a single endothermic peak within the range of 25-400 $^{\circ}\text{C}$, but no well-defined transition was observed, showing gradual decomposition with decreasing volume above 380 $^{\circ}\text{C}$. Polarized optical microscopy showed neither melt nor mesophase for **1** upon heating or cooling between 30 and 320 $^{\circ}\text{C}$.

These isomerization behaviors together with thermal and other optical properties of **1** are very similar to the results of Zn-phthalocyanine¹⁴ with the same azobenzene substituents synthesized recently by us. Interestingly, the isomerization ratio of **1**(25%) was smaller than the Zn-phthalocyanine (30%). This difference was clearly influenced by changing central metals, and also indicated that the electronic properties of central metals could affect the isomerization of azobenzene groups at the periphery far distant from the central core. Therefore, on the basis of these results, a suitable selection of central metal atoms can provide the possibility to increase the *trans-cis* isomerization ratio.

At present, we are exploring to synthesize some phthalocyanines with different transition metals for this purpose.

Experimental Section

Solvents and all commercially available reagents were used without any purification. Analytical thin layer chromatography was performed on pre-coated Merck silica gel 60 F254 TLC plate. Purification was performed by flash column chromatography by using Merck 230-400 mesh silica gel. ^1H NMR and ^{13}C NMR spectral data were obtained on a Jeol JNM-ECP 400 MHz NMR spectrometer. IR spectra were recorded using a Jasco FT/IR-410 spectrophotometer with internal calibration.

Synthetic procedure for 7 and 1. A mixture of 4-(4-octadecyloxyphenylazo)phenol (**6**, 932 mg, 2.0 mmol), K_2CO_3 (552 mg, 4.0 mmol), 4,5-dichlorophthalonitrile (197 mg, 1.0 mmol) and 18-crown-6 (80 mg, 0.3 mmol) in acetone (50 mL) was heated at reflux for 12 h. Upon cooling, the solution was filtered and the filtrate was evaporated. The crude solids were purified by chromatography (silica gel, 100% chloroform) to give **7** (751 mg, 73.2%) as a bright orange solid.

A mixture of **7** (300 mg, 0.293 mmol), CuCl_2 (38 mg, 0.28 mmol) and 1.8-diazabicyclo[5.4.0]-undec-7-ene (0.2 mL) in n-pentanol (5 mL) was heated to reflux for 12 h. After the solution was cooled it was diluted with MeOH and the green precipitates were filtered. The crude solids were purified by chromatography (silica gel, 10% THF/chloroform) to give **1** (280 mg, 89.2%) as a green solid.

The characterizations of 7 and 1.

Compound (7): 73.2% yield; $R_f = 0.5$ (in 100% chloroform); mp 133-134 °C (recrystallized from ethanol); FT-IR (KBr): $\nu = 2917, 2850, 2233, 1581, 1490, 1245, 1145 \text{ cm}^{-1}$; ^1H -NMR (CDCl_3 , 400 MHz): $\delta = 8.10\text{-}7.90$ (m, 10H), 7.21-7.15 (m, 4H), 7.03-6.99 (m, 4H), 4.08-4.03 (t, $J = 6.3$ Hz, 4H), 1.85-1.80 (m, 4H), 1.59-1.13 (m, 60H), 0.90-0.88 (t, $J = 7.2$ Hz, 6H); Anal. Calcd for $\text{C}_{68}\text{H}_{92}\text{N}_6\text{O}_4$: C 77.23, H 8.77, N 7.95. Found C 77.16, H 8.80, N 7.99.

Compound (1): 89.2% yield; $R_f = 0.7$ (THF : chloroform

= 1 : 10); mp > 379 °C (decomp, recrystallized from ethanol); FT-IR (KBr): $\nu = 2921, 2850, 1598, 1492, 1392, 1247, 1145 \text{ cm}^{-1}$; ^1H -NMR (CDCl_3 , 400 MHz): $\delta = 8.20\text{-}7.45$ (s, 40H), 7.10-6.70 (s, 32H), 3.94 (s, 16H), 1.78 (s, 16H), 1.60-0.98 (m, 240H), 0.87 (t, $J = 7.2$ Hz, 24H); UV/VIS (CHCl_3 , 10^{-5}): λ_{max} (nm) [ϵ] = 360[84900], 687[69800]; MALDI-TOF MS : m/z 3862, 3433, 3003, 699, 659. Anal. Calcd for $\text{C}_{272}\text{H}_{368}\text{N}_{24}\text{O}_{16}\text{Cu}$: C 76.09, H 8.64, N 7.83. Found C 76.20, H 8.57, N 7.90.

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