Synthesis and Photoresponsive Properties of Cu-Phthalocyanine with Azobenzene Groups

Ki-Jong Han and Kwang-Yol Kay

Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea. *E-mail: kykay@ajou.ac.kr

Received April 30, 2005

Key Words: Cu-phthalocyanine, Azobenzene, UV irradiation, Isomerization

There has been extensive interest in the physical and chemical properties of phthalocyanines (Pc) owing to their intriguing electrical, optical, photochemical and catalytic properties. 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. 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. Recently, many new phthalocyanines with long alkyl, alkoxy, alkylthio and alkoxyphenoxy groups have been prepared to study on their diverse functionality such as liquid crystalline properties as well as highly ordered thin film properties.

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) Ac_2O, THF. (b) RBr, K_2CO_3, MeCN. (c) 6N HCl, EtOH. (d) phenol, NaNO_2, 35% HCl, H_2O/THF. (e) 4,5-dichlorophthalonitrile, K_2CO_3, THF. (f) CuCl_2, DBU, n-pentanol.
The latter was employed in order to disrupt the molecular aggregation associated with the large π-system. The \(^1\)H NMR spectra of I 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\(_2\)-) resonated in the region δ 3.95 as a broad band.

The UV/Vis spectra of the phthalocyanine (I) in chloroform showed the typical pattern, mainly the \(\pi-\pi^*\) 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 alkoxyazo benzene 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, \(\pi-\pi^*\) transition, trans form)\(^{11}\) were overlapped with the Soret band of I. Irradiation of 365 nm light proved this overlapping and exhibited the expected photoresponsive behavior of I. For example, dark incubation of a chloroform solution (10\(^{-5}\) M) of I served to maximize the absorption at 360 nm (\(\varepsilon_{\text{max}}\) – 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 \(\varepsilon = 7880\) to \(\varepsilon = 8600\) in absorbance at around 450 nm (n-\(\pi^*\) transition, cis form)\(^{12}\) (Figure 2). A photostationary state was reached within approximately 420 seconds.

These isomerization behaviors together with thermal and other optical properties of I are very similar to the results of Zn-phthalocyanine\(^{14}\) with the same azobenzene substituents synthesized recently by us. Interestingly, the isomerization ratio of I(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 precoated Merck silica gel 60 F254 TLC plate. Purification was performed by flash column chromatography by using Merck 230-400 mesh silica gel. 1H-NMR (CDCl3, δ 7.2 Hz, 6H); Anal. Calcd for C47H92O2N2: C 77.16, H 8.80, N 7.99. Found C 77.23, H 8.77, N 7.90.

Synthetic procedure for 7 and 1. A mixture of 4-(4-octadecyloxy)phenylazo)phenol (6, 932 mg, 2.0 mmol), K2CO3 (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), CuCl2 (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; Rf = 0.5 (in 100% chloroform); mp 133-134 °C (recrystallized from ethanol); FT-IR (KBr): ν = 2921, 2850, 1598, 1492, 1247, 1145 cm⁻¹; 1H-NMR (CDCl3, 400 MHz): δ = 8.20-7.45 (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 (CHCl3, 10⁻³ M): λmax (nm) [ε] = 360[84900], 687[69800]; MALDI-TOF MS : m/z 3862, 3433, 3003, 699, 659. Anal. Calcd for C27H66N2O2Cu: C 76.20, H 8.57, N 7.90. Found C 76.20, H 8.57, N 7.90.

**Compound (1):** 89.2% yield; Rf = 0.7 (THF : chloroform = 1 : 10); mp > 379 °C (decomp. recrystallized from ethanol); FT-IR (KBr): ν = 2921, 2850, 1598, 1492, 1247, 1145 cm⁻¹; 1H-NMR (CDCl3, 400 MHz): δ = 8.20-7.45 (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 (CHCl3, 10⁻³ M): λmax (nm) [ε] = 360[84900], 687[69800]; MALDI-TOF MS : m/z 3862, 3433, 3003, 699, 659. Anal. Calcd for C27H66N2O2Cu: C 76.20, H 8.57, N 7.90.

Acknowledgements. The authors thank the Ministry of Education of Korea for financial support (BK 21 program).

References

14. Han, K.-J.; Kay, K.-Y. Heterocycles 2004, 63, 2869.