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SYNTHESIS AND ABSORPTION PROPERTIES OF ZINC-PHTHALOCYANINES WITH PHOTORESPONSIVE AZOBENZENE GROUPS

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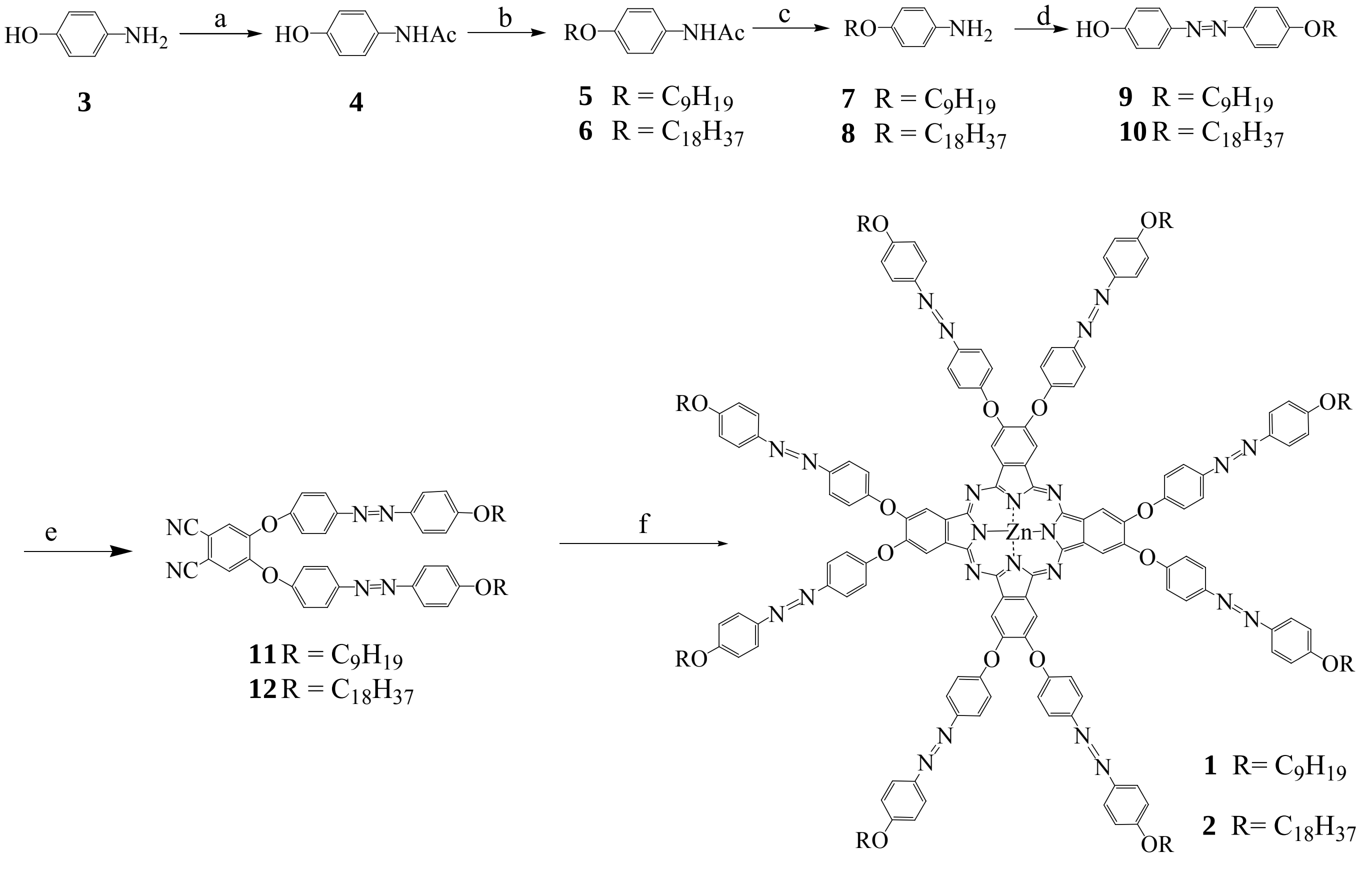
Abstract – The phthalocyanines (**1**) and (**2**) with eight photoisomerizable azobenzene groups have been synthesized and spectroscopically characterized. These macrocycles exhibit partial *trans-cis* isomerzation properties upon irradiation of UV/VIS light.

INTRODUCTION

The physical and chemical properties of phthalocyanines (Pc) have long attracted an interest 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] alkylthio[6] and alkoxyphenoxy[7] 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 zinc-phthalocyanines (**1**) and (**2**) with eight photoisomerizable azobenzene groups at the periphery. These macrocycles incorporated with eight long-chain azobenzene substituents exhibit *trans-cis* isomerization properties upon irradiation of UV/VIS light.

RESULTS AND DISCUSSION

The synthetic routes to octasubstituted zinc phthalocyanines (**1**) and (**2**) are shown in **Scheme 1**. From commercially available 4-hydroxyanilline (**3**) azobenzene derivatives (**9**) and (**10**) were obtained *via* several steps, and then converted to the respective dinitriles (**11**) and (**12**). Cyclization of dicyanobenzene derivatives (**11**) and (**12**) with zinc acetate and 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 1-pentanol led to the formation of **1** and **2**, respectively, in moderate yields. All of these macrocycles possess good solubility in common organic solvents and were purified mainly by column chromatography with hexane mixed with THF as eluent. The latter was employed in order to disrupt the molecular aggregation associated with the large π-system. The ^{1}H NMR spectra of **1** and **2** 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 ($O\text{-}CH_2\text{-}$) resonanced in the region δ 3.95 as a broad band.



Scheme 1

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) $Zn(OAc)_2$, DBU, n-pentanol

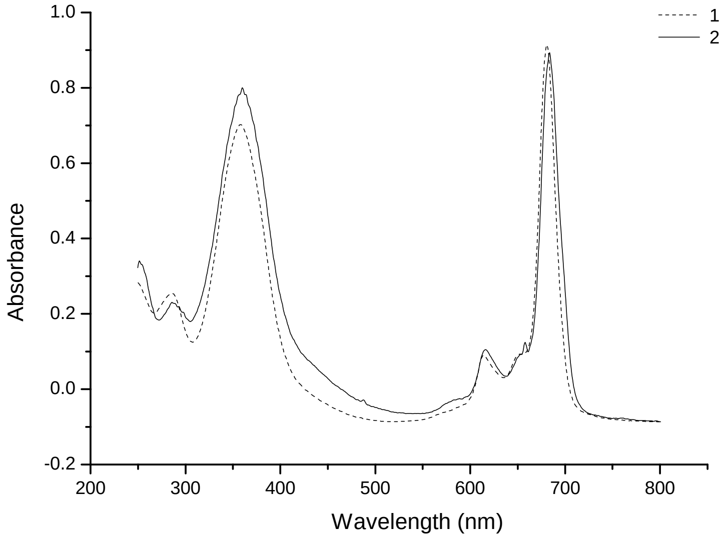


Figure 1. Absorption spectrum of **1** and **2**

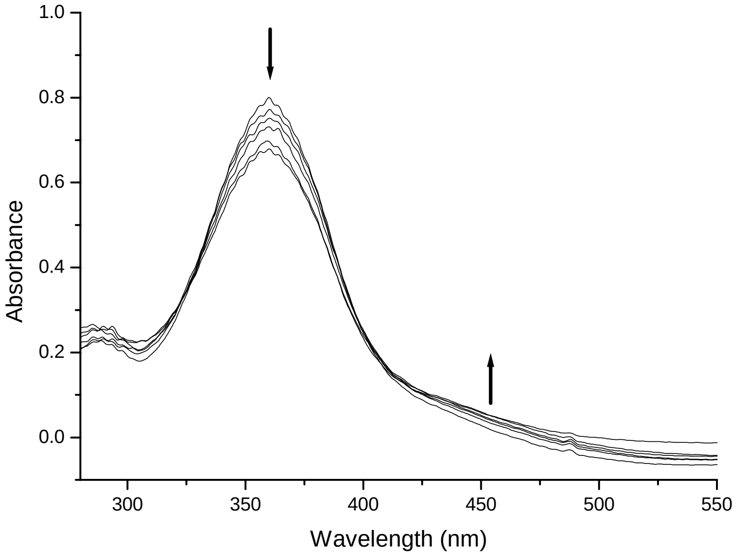


Figure 2. Absorption spectrum of **2** under irradiation conditions(365 nm:0, 30, 60, 120, 360 and 420s)

The UV/VIS spectra of the phthalocyanines (**1**) and (**2**) in chloroform showed the typical pattern, mainly the π- π^*transition of the heteroaromatic 18 - πelectron system (**Figure 1**) : A large intense Q band in the visible region of around 681 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 phthalocyanines by alkoxyazobenzene chains gave bathochromic shifts of both the Q band (681 nm for **1** and 683 nm for **2**) and Soret band (358 nm for **1** and 360 nm for **2**) compared to the unsubstituted Zn-phthalocyanine (Soret band 340 nm, Q band 666 nm in THF).[10] However, absorption bands of azogroups (around 350 nm, π- π^*transition, trans form)[11] were overlapped with the Soret bands of **1** and **2** : Irradiation of 365 nm light proved this overlapping and exhibited the expected photoresponsive behavior of **1** and **2**. For example, dark incubation of a chloroform solution(10^{-5}M) of **2** served to maximize the absorption at 360 nm (ε_{max} = 79730) 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 an increase 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 30% on the basis of the contribution ratio of the Soret band and azobenzene groups for the molar absorptivity at 360 nm. In most of Zn-phthalocyanines[12, 13, 14] the general ratio of Soret band and Q band was found to be about 2:5. From this ratio we derived the molar absorptivity contribution of azobenzene groups in **2**. This value thus obtained (around 42,000) is bigger than the molar absorptivity of **10** (around 30,000), but it seems to be reasonable because compound (**2**) has eight azobenzene groups. Finally we could deduce the yield of the isomerized azobenzene groups from the change value (around 13,000) of molar absorptivity after irradiation . Thermal reversion to the original dark-incubated spectrum was observed over the course of approximately 17 h at 293 K in the dark. However, exposure to bright sunlight for a period of only several seconds also effect almost complete reversions to the *trans* isomer. The compound (**1**) also showed the same trends in *trans-cis* reversible isomerization phenomena. This partial isomerization phenomena of **1** and **2** can be ascribed to not enough space for eight azobenzene groups in **1** and **2** to undergo *trans-cis* isomerization.

The mesophase behaviors of **1** and **2** were not observed by differential scanning calorimetry (DSC) and polarized optical microscopy : The DSC thermograms of **1** and **2** showed only a single endothermic peak within the range of 25 ~ 400℃, but no well-defined transition was observed, showing gradual decomposition with decreasing volume above 380℃. Polarized optical microscopy showed neither melt nor mesophase for **1** and **2** upon heating or cooling between 30 and 320℃.

EXPERIMENTAL

All chemicals and regents were purchased from Aldrich and used as received. 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. ^{1}H 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

General procedure for the synthesis of 1 and 2: A mixture of 4-(4-nonyloxyphenylazo)phenol (**9**, 751 mg, 2.2 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 10 h. Upon cooling, the solution was filtered and the filtrate was evaporated. The crude solids were purified by chromatography (silica gel, 30% THF/hexane) to give **11** (425 mg, 52.7%) as a bright orange solid.

A mixture of **11** (280 mg, 0.35 mmol), $Zn(OAc)_2$ (24 mg, 0.13 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 black precipitates were filtered. The crude solids were purified by chromatography(silica gel, 50% THF/hexane) to give **1** (140 mg, 49%) as a green solid. The octadecyloxy group substituted phthalocyanine (**2**) was synthesized by similar procedure like as **1**.

The characterizations of 11, 12, 1 and 2.

Compound (**11**) : 52.7 % yield; $R_f = 0.4$ (THF : Hexane = 1 : 3); mp 145-146 ℃(recrystallized from ethanol); FT-IR (KBr) : ν = 2921, 2852, 2233, 1581, 1488, 1241, 1145 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ = 8.00 ~ 7.90 (m, 10H), 7.25 ~ 7.14 (m, 4H), 7.06 ~ 6.85 (m, 4H), 4.08 (t, J=6.4 Hz, 4H), 1.80 (m, 4H), 1.40 ~ 1.20 (m, 24H), 0.90 (t, J=7.1 Hz, 6H); Anal. Calcd for $C_{50}H_{56}N_6O_4$: C 74.60, H 7.01, N 10.44. Found C 74.53, H 7.03, N 10.47.

Compound (**12**) : 60.5 % yield; $R_f = 0.5$ (THF : Hexane = 1 : 5); mp 133-134 ℃(recrystallized from ethanol); FT-IR (KBr) : ν = 2917, 2850, 2233, 1581, 1490, 1245, 1145 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ = 8.10 ~ 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 $C_{68}H_{92}N_6O_4$: C 77.23, H 8.77, N 7.95. Found C 77.16, H 8.80, N 7.99.

Compound (**1**) : 49 % yield; $R_f = 0.5$ (THF : Hexane = 1 : 3); mp >368 ℃(decomp, recrystallized from ethanol); FT-IR (KBr) : ν = 2923, 2852, 1598, 1492, 1430, 1392, 1245, 1145 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 400 MHz) : δ = 7.86 ~ 7.46 (s , 40H), 7.11 ~ 6.72 (s, 32H), 3.95 (s, 16H), 1.79(s, 16H) 1.56~1.20 (m, 96H), 0.92 (t, J=7.1 Hz 24H); UV/VIS ($CHCl_3$, 10^{-5}): λ_{max} (nm) [ε] = 249[37910], 286[35030], 358[79850], 614[18620], 681[100990]; MALDI–TOF MS : m/z 2136, 2068, 1820, 1815, 574; Anal. Calcd for $C_{200}H_{224}N_{24}O_{16}Zn$: C 73.11, H 6.87, N 10.23. Found C 73.20, H 6.79, N 10.19.

Compound (**2**) : 56 % yield; $R_f = 0.5$ (THF : Hexane = 1 : 2); mp >379 ℃(decomp, recrystallized from ethanol); FT-IR (KBr) : ν = 2921, 2850, 1598, 1492, 1392, 1247, 1145 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 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 ($CHCl_3$, 10^{-5}): λ_{max} (nm) [ε] = 251[34040], 285[23030], 360[79730], 615[10420], 683[89300]; MALDI–TOF MS : m/z 3914, 3438, 2960, 2583, 2220, 574. Anal. Calcd for $C_{272}H_{368}N_{24}O_{16}Zn$: C 76.06, H 8.64, N 7.83. Found C 76.17, H 8.57, N 7.91.

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