Liquid-Crystalline Heterocyclic Phthalocyanine Analogues Based on Thiophene

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The syntheses and mesomorphism of novel octaalkoxymethyl-substituted tetra-2,3-thiophenophorphyrazines, heterocyclic phthalocyanine analogues in which the benzene rings are replaced by thiophene rings, are reported. NMR analysis indicates that these materials exist as isomeric mixtures due to the asymmetry induced by the thiophene ring. Among the attractive features of liquid-crystalline 2,3-thiophenophorphyrazines over phthalocyanines are their lower mesomorphic and isotropic temperatures. These features have resulted in liquid crystallinity at room temperature. Similar to liquid-crystalline phthalocyanine derivatives, metalation with copper raises the transition temperatures.

Introduction

Phthalocyanine (Pc) based solids and liquid crystals[1a] have been extensively studied due to their semiconductive, photoconductive, and NLO properties. The conducting properties of metal-free Pcs, metalated Pcs, liquid-crystalline Pcs, and polymeric Pcs have been the subject of many investigations and have been recently reviewed.[2] Although examples of metal-centered charge-transport mechanisms have been reported,[3] the principle conduction mechanism is electron transport through π energy bands formed by cofacial π interactions between macrocycles.[4] It is generally found in π-stacked conductors that the addition of larger chalcogenide atoms (e.g., S, Se) improves conductivity. This effect is due to an increase in the radial extension of the orbitals which increases both the delocalization (bandwidth) and carrier mobility.[5] We have been investigating thiophene analogues of Pcs in an effort to increase their conductivity and to determine their liquid-crystalline (LC) properties. The substitution of thiophenes for phenyls has been previously shown to provide improved liquid-crystalline properties and lower transition temperatures.[6,7] This latter aspect is important since the high isotropic transition temperatures of many LC Pc complexes have been responsible for problematic degradation.

Tetra-2,3-thiophenophorphrazine (TTP) was briefly studied as an impure copper complex in 1937.[8] The green compound was reportedly obtained in 60% yield by the cyclization of 2,3-thiophenedinitrile; however, the usual purification methods were ineffective and the material was not characterized further. We report herein novel octaalkoxymethyl-substituted TTPs which exhibit superior LC properties (i.e., lower temperature ranges) than analogous Pcs.

Results and Discussion

The synthesis of TTPs is shown in Scheme 1. Thiophenedimethanol (**1**) is prepared by the reduction of 2,3-thiophene dicarboxylic acid according to the procedure of Chadwick.[9] After transformation to the ether, the thiophene ring is iodinated using mercury trifluoroacetate and iodine to give the diiodide **3**. The diiodide is subsequently converted to the dinitrile using copper cyanide in pyridine. Attempts to cyclize **4** under traditional Pc-forming conditions[10] gave **6** in yields of less than 1%, and cyclizations utilizing strong organic bases (i.e., DBU)[11] gave no apparent yield of **6**. However, sodium pentanolate and ammonia-assisted cyclization proceeded to give a 20% yield of **6a**. Under these reaction conditions it is likely that a thiophene equivalent of a diiminoindoline is initially generated in situ at low temperature and is then subsequently cyclized at a high temperature. The substituted TTPs are soluble in organic solvents and are purified by column chromatography. Cu^{II} is readily inserted using sodium pentanolate and anhydrous copper(II) acetate. (Octaalkoxymethyl)phthalocyanines have been previously reported,[1,12,10] and we have prepared new homologues, **8** and **9**, for a direct comparison with **6b** and **7**.

Although we show only one regioisomer for **6a**, **6b**, and **7** in Scheme 1, ^{1}H NMR analysis of the resulting TTPs shows a mixture of the four regioisomers, namely, with the sulfurs in the 1,7,13,19 (shown in Scheme 1); the 1,7,13,21; the 1,7,15,21; and the 1,9,13,21 positions. The diagnostic signals are two sets of overlapping singlets at 5.67 and 5.26 ppm, which indicate the presence of two groupings of inequivalent α-methylene

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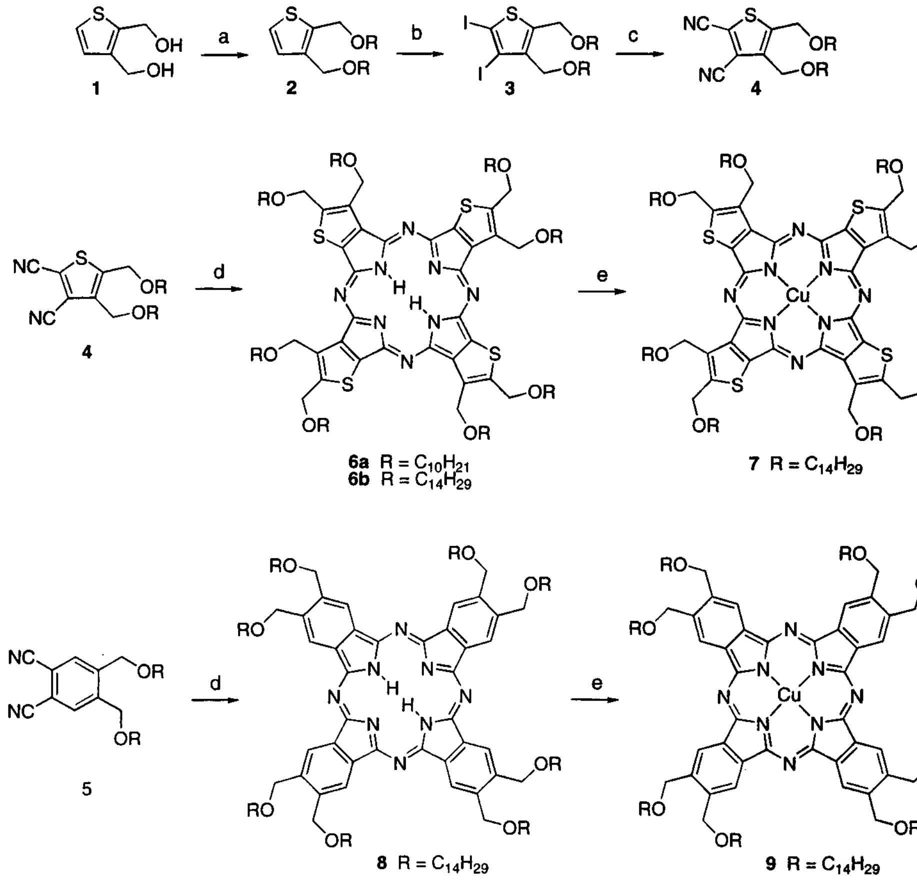
Scheme 1



[a] 2.2 equiv each of NaH and RBr, DME, reflux, 12 h, 60%. [b] 2.0 equiv each of $Hg(COOCF_3)_2$ and I_2, CH_2Cl_2, 98%. [c] 4.0 equivalents of CuCN, pyridine, 110° C, 12 h, 60%. [d] 2.0 equiv of $NaOC_5H_{11}$, $C_5H_{11}OH$, NH_3, room temperature, 1 h, reflux 4 h, 20%. [e] 2.2 equiv of $NaOC_5H_{11}$, $C_5H_{11}OH$, copper acetate.

groups. It is also noteworthy that the protons of the α-methylene groups of **6a** and **6b** are shifted downfield relative to the protons of the inequivalent α-methylene singlets at 4.71 and 4.48 ppm of the dinitrile **4**, by 0.96 and 0.76 ppm, respectively. Similarly, Pc **8** has equivalent α-methylene protons at 5.11 ppm which are shifted downfield 0.38 ppm relative to the equivalent α-methylene protons on the dinitrile **5**. The greater deshielding effect in the TTPs is suggestive of an enhanced ring current in the TTP π system as compared to the Pc π system.

The metal-free and copper TTPs display Soret and Q-band absorbances characteristic of Pcs, as shown in Figure 1. The Q-bands for the TTP derivatives **6a** and **6b** are blue-shifted by 10 nm, to 643 and 690 nm relative to the Pc derivative **8**. The Soret band also shows a broad shoulder centered at ≈400 nm which is red-shifted when compared to the narrow shoulder of **8** at 363 nm. The Q-bands for the copper TTP (**7**) are shifted relative to **9** by 12 and 17 nm, to 599 and 662 nm respectively.

The TTP derivatives **6a**, **6b**, and **7** exhibit stable liquid-crystalline phases and optical microscopy reveals leaf textures with linear birefringent defects which are characteristic of discotic hexagonal phases (D_h). This assignment was also confirmed by X-ray diffraction studies. As shown for **6b** in Figure 3, X-ray diffraction peaks indexing to the (100), (110), and (200) planes of the hexagonal superstructure are observed. The intercolumnar spacings of **6a**, **6b,** and **7** are 29.0, 32.9, and 32.9 Å, respectively. The single halo at wide angle (4.7 Å) is indicative of only short-range (liquidlike) order within the column, and we characterize these phases as discotic hexagonal disordered (D_{hd}).

Compounds **8** and **9** also display D_{hd} mesophases with an intercolumnar spacings of 33.2 and 32.9 Å, respectively. This indicates that the TTP and Pc derivatives have the same relative core size and that the insertion of copper does not affect the intercolumnar distance. In contrast to the previously reported octadodecyloxymethyl Pc derivative, **6a** does not display the peaks indicative of a modulated columnar phase.[13] These peaks are similarly absent for **6b** and **7**.

Figure 3 contrasts the phase behavior of previously studied octa(alkoxymethyl) Pcs[10] with compounds **6a**, **6b**, and **8**. As can be seen, replacement of the benzene groups of the Pcs with thiophenes lowers the crystal-to-D_{hd} transitions and the D_{hd}-to-isotropic transitions by ≈30 and 10 °C, respectively. These decreases are likely due to the regioisomeric mixtures of the TTP derivatives which induce packing disorder within the columns.

Compound **6a** is a room-temperature liquid-crystalline TTP. First heating of a sample precipitated from

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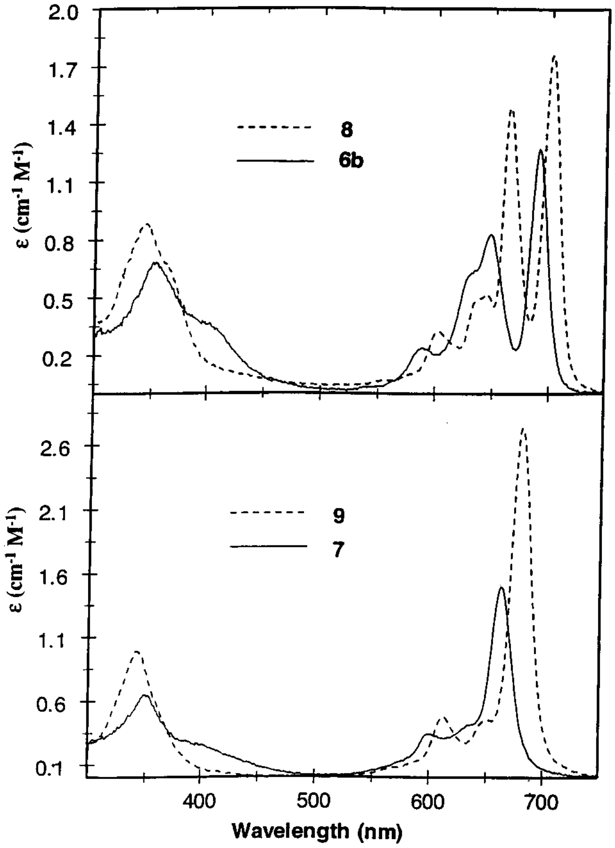

Figure 1. UV–vis spectra for metal-free octakis(tetradecylalkoxymethyl)phthalocyanine (**8**), octakis(tetradecylalkoxymethyl)tetra-2,3-thiophenophorphyrazine (**6b**), octakis(tetradecylalkoxymethyl)phthalocyanine copper(II) (**9**), and octakis(tetradecylalkoxymethyl)tetra-2,3-thiophenophorphyrazine copper(II) (**7**).

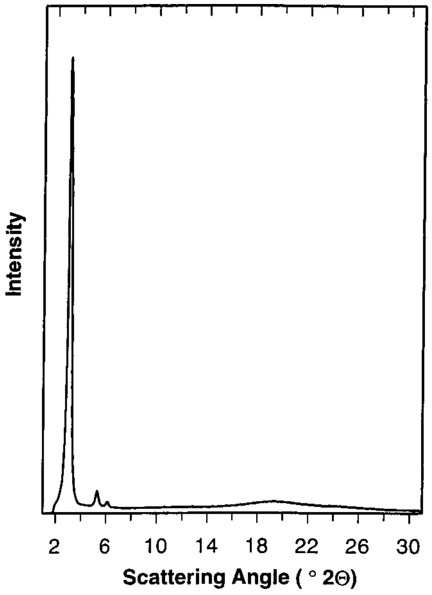

Figure 2. X-ray diffraction pattern of **6b** at 76 °C.

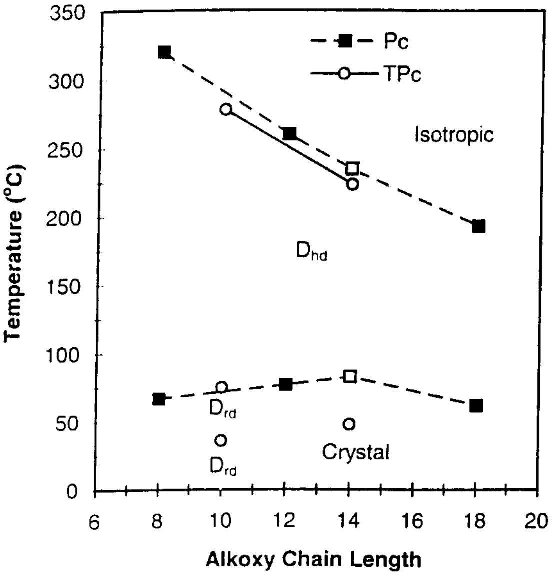

Figure 3. Phase behavior of octaalkoxymethyl Pcs (■ and □) and octaalkoxymethyl TTPs (○). As discussed in text, the D_{hd} phase of **6a** is stable to room temperature after initial heating. Compounds with open symbols were prepared for this publication, and data for compounds with filled symbols (■) was taken from ref 10.

Table 1. Summary of Phase Behavior[a]

compound	phase behavior (Δ*H*)	lattice constant (Å)
6a[c]	D_{rd} 36 (1.3) D_{rd} 75 (1.3) D_{hd} 278[b] I	29.0 (D_{hd})
6b	K 48 (11) D_{hd} 223[b] I	32.9
7	K 49 (11) D_{hd} 258[b] I	32.9
8	K 83 (39) D_{hd} 234 (2) I	33.2
9	K 80 (28) D_{hd} 280 (2) I	33.5

[a] Phase transition temperatures (°C) were taken as the maxima of the DSC peaks on heating. Transition enthalpies (kcal/mol) are given in parentheses. [b] Transition observed only by optical microscopy. [c] D_{rd} phases observed only upon first heating (see text).

ethyl acetate reveals two phase transitions. X-ray diffraction peaks in the low-angle region suggest that initially at room temperature there is a discotic rectangular phase (D_{rd}), with peaks at 34.3 and 25.6 Å, which transforms to another D_{rd} phase at 36 °C (ΔH = 1.3 kcal/mol, XRD peaks at 33.1 and 25.8 Å). With further heating to 75 °C, it transforms to the D_{hd} phase (ΔH = 1.3 kcal/mol) as shown in Table 1. The compound remains in the D_{hd} mesophase on cooling to room temperature, and it is likely that the high viscosity prevents reformation of the initially observed D_{rd} phases. The transitions of **6a**, **6b**, and **7**, to isotropic phases could not be observed by DSC (due to the low isotropic transition enthalpy) and were observed by polarized light microscopy. X-ray diffraction shows that the intercolumnar distance of the D_{hd} mesophase of **6b** is higher than **6a** by about 1 Å per added $-(CH_2)-$ group.

The effect of inserting copper into the octatetradecyloxymethyl TTP and Pc is shown in Table 1. The K to D_{hd} transitions are insensitive to the copper ion, whereas the isotropic temperatures increase 35 °C for **7** and 46 °C for **9**. This behavior is also typically observed in other liquid-crystalline Pcs.

Summary

In summary, substitution of benzene by thiophene creates heterocyclic phthalocyanine analogues which yield phases with lower transition temperatures. Thiophene also introduces changes in the π system relative to Pcs causing blue-shifts in the UV–vis spectra and added deshielding in the NMR spectra. Future investigations will focus on the electronic applications and porperties of these materials.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-250. Chemical shifts are reported in ppm relative to residual $CHCl_3$ ($\delta = 7.24$, ^{1}H; 77.0, ^{13}C). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). UV−vis spectra were recorded using a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded using a Perkin-Elmer 1760-X FTIR, and polystyrene was used as a standard. Laser desorption ionization mass spectrometry was performed from material deposited on a stainless steel target with a Fisons Instruments (Beverly, MA) VG TofSpec time-of-flight mass spectrometer (0.6 m flight tube) outfitted with a N_2 (337 nm, 4 ns pulse) laser. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. Optical characterization was performed using covered microscope slides on a Leitz polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 HT central processor. Transition temperatures and heats of fusion were determined at scan rates of 10 °C min^{-1} using a Perkin-Elmer 7 system differential scanning calorimeter calibrated with indium. Variable-temperature X-ray diffraction was measured using Cu Kα radiation on an Inel CPS 120 position-sensitive detector with a XRG 2000 generator, a fine-focus X-ray tube, and a home-built heating stage. The temperature was regulated with a Minco CT 137 controller with ±1 °C stability. The detector was calibrated using mica and silicon standards obtained from the National Bureau of Standards.

Unless otherwise indicated, all chemicals and solvents were reagent grade and were used as obtained without further purification. Dimethoxyethane (DME) and tetrahydrofuran (THF) were obtained as anhydrous solvents from Aldrich Chemical Co. Inc. Pyridine was distilled onto 4 Å molecular sieves. Mercury trifluoroacetate was prepared according to a previous method. [14] 2,3-Thiophenedimethanol (**1**) was synthesized according to a previous method.[9]

2,3-Bis(tetradecyloxymethyl)thiophene (2): To 3.0 g of **1** in DME was added 12.13 g (1.1 equiv) of 1-bromotetradecane. This solution was added to 2.0 g of NaH in DME and refluxed for 16 h. Upon cooling, the reaction was quenched with 1% HCl, extracted with ether, and dried with $MgSO_4$. The solvent was evaporated, and the product was purified by column chromatography (silica, $CHCl_3$) and recrystallized from acetone/methanol yielding a light yellow solid in 60% yield. mp 56−58 °C. Anal. Calcd for $C_{34}H_{64}O_2S$: C, 76.06; H, 12.01; O, 5.96; S, 5.97. Found: C, 75.89; H, 11.87. ^{1}H NMR ($CDCl_3$; δ) 7.17 (1H, d), 6.98 (1H, d), 4.64 (2H, s), 4.46 (2H, s), 3.45 (2H, t), 3.41(2H, t), 1.54 (4H, m), 1.25 (48H, m), 0.84 (6H, t). ^{13}C ($CDCl_3$; δ): 137.79, 136.50, 128.53, 123.86, 70.26, 65.94, 65.13, 31.86, 29.58, 29.41, 29.30, 26.10, 22.61, 14.01.

2,3-Diiodo-3,4-bis(tetradecyloxymethyl)thiophene (3): To 5.0 g of **2** in methylene chloride was added 2 equiv of $Hg(O_2CCF_3)_2$, this mixture was heated to reflux and let stir for 30 min while cooling to room temperature. Iodine (2 equiv) dissolved in methylene chloride was then slowly added to the solution. The solution was then washed with an aqueous 10% solution of KI and saturated sodium bicarbonate and then with water. The solvent was evaporated and the residue was recrystallized from acetone yielding a white solid in 95% yield, mp 34−36 °C. Anal. Calcd for $C_{34}H_{62}I_2O_2S$: C, 51.78; H, 7.92; I, 32.18; O, 4.06; S, 4.06. Found: C, 51.81; H, 7.88. ^{1}H NMR ($CDCl_3$; δ) 4.68 (2H, s), 4.46 (2H, s), 3.46 (2H, t), 3.42 (2H, t), 1.54 (4H, m), 1.24 (48H, m), 0.86 (6H, t). ^{13}C NMR ($CDCl_3$; δ) 146.87, 137.75, 99.35, 83.29, 70.83, 70.49, 68.63, 65.94, 31.86, 29.61, 29.38, 29.30, 26.13, 22.63, 14.07.

2,3-Dicyano-3,4-bis(tetradecyloxymethyl)thiophene (4): To 5.0 g of **3** in pyridine was added 4 equiv of CuCN and stirred for 12 h at 100 °C. The pyridine was then evaporated, 100 mL of 30% ethylenediamine in water was added, and the mixture was extracted with ether. The ether was evaporated and the crude product purified by column chromatography (silica/$CHCl_3$) to obtain **4** as a white solid in 65% yield, mp 36 °C. Anal. Calcd for $C_{36}H_{62}N_2O_2S$: C, 73.67; H, 10.65; O, 5.45; N, 4.77; S, 5.46. Found: C, 74.06; H, 10.71; N, 4.61. IR (cm^{-1}, KBr) 2223.6 (ν(CN)). ^{1}H NMR ($CDCl_3$; δ) 4.71 (2H, s), 4.48 (2H, s), 3.55 (2H, t), 3.46 (2H, t), 1.57 (4H, m), 1.23 (48H, m), 0.84 (6H, t). ^{13}C NMR ($CDCl_3$; δ) 150.69, 135.59, 120.1, 115.49, 111.70, 111.20, 72.06, 71.47, 66.26, 64.56, 31.89, 29.50, 26.06, 22.68, 14.08.

2,3,8,9,14,15,20,21-Octakis(tetradecyloxymethyl)-25*H*,27*H*-tetra-2,3-thiophenophorphyrazine (6b): 2.5 mL of a 0.052 g/mL solution of $NaOC_5H_{11}$ in HOC_5H_{11} was added to 2.00 g of **4** and purged with ammonia for 1 h at room temperature. Upon heating to reflux (150 °C) the reaction turns from a pale yellow to a green-blue, and this mixture is stirred for 5 h. The reaction is then cooled, diluted with 5 mL of methanol, acidified with 10% HCl and extracted with $CHCl_3$. The product was purified by silica column chromatography using 30/50 $CHCl_3$/hexane (purified yield is 15%). MS *m*/*e* (M^+) 2350. Anal. Calcd for $C_{144}H_{250}N_8O_8S_4$: C, 73.60; H, 10.72; N, 4.77; O, 5.45; S, 5.46. Found: C, 73.35; H, 10.60; N, 4.51. ^{1}H NMR ($CDCl_3$; δ) 5.60 (8H, m), 5.26 (8H, m), 3.85 (16H, m), 1.57 (4H, m), 1.23 (96H, m), 0.82 (24H, m).

2,3,8,9,14,15,20,21-Octakis(tetradecyloxymethyl)tetra-2,3-thiophenophorphyrazine copper(II) (7): To **6b** in THF, was added 2.5 mol equiv of $NaOC_5H_{11}$, and this mixture was refluxed for 2 h. 2.5 mol equiv of anhydrous copper(II) acetate was then added, and this was let reflux for another 2 h. The mixture is filtered and then evaporated. The product was purified by silica column chromatography using $CHCl_3$ (purified yield 95%). MS *m*/*e* (M^+) 2411. Anal. Calcd for $C_{144}H_{248}CuN_8O_8S_4$: C, 71.73; H, 10.37; Cu, 2.64; N, 4.65; O, 5.31; S, 5.32. Found: C, 71.15; H, 10.34; N, 4.58.

1,2-Dicyano-4,5-bis(tetradecyloxymethyl)benzene (5): This compound was prepared according to ref 8. Anal. Calcd for $C_{38}H_{64}N_2O_2$: C, 78.57; H, 11.10; N, 4.82; O, 5.51. Found: C, 78.31; H, 10.85; N, 4.59. ^{1}H NMR ($CDCl_3$; δ) 7.87 (2H, s), 4.73 (4H, s), 3.50 (4H, t), 1.61(4H, m), 1.23(44H, m), 0.85 (6H, t).

2,3,9,10,16,17,23,24-Octakis(tetradecyloxymethyl)-29*H*,31*H*-Phthalocyanine (8): **8** was prepared using the same procedure used for **6b**. The product was purified by silica column chromatography (5/95, THF/$CHCl_3$) and then recrystallized from ethyl acetate. (15% yield). MS *m*/*e* (M^+) 2325. Anal. Calcd for $C_{148}H_{256}N_8O_8$: C, 78.50; H, 11.18; N, 4.82; O, 5.50. Found: C, 78.74; H, 11.23; O; N, 5.19. ^{1}H NMR ($CDCl_3$; δ) 9.11 (8H, s), 5.11 (32H, s), 3.79 (16H, t), 1.85 (16H, m), 1.17 (176H, m), 0.86 (24H, t), −1.89 (2H, s).

2,3,9,10,16,17,23,24-Octakis(tetradecyloxymethyl)-phthalocyanine copper(II) (9): **9** was prepared and purified using the same procedure used for **7** except starting with compound **8** (purified yield 95%). MS *m*/*e* (M^+) 2387. Anal. Calcd for $C_{148}H_{254}CuN_8O_8$: C, 76.47; H, 10.81; Cu, 2.66; N, 4.69; O, 5.36. Found: C, 76.36; H, 10.50; N, 4.70.

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