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[5]Helicene-Fused Phthalocyanine Derivatives. New Members of the Phthalocyanine Family

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Abstract: An efficient synthetic route to fuse [5]helicene moieties around the phthalocyanine core is reported. The helicene moiety was constructed by the Diels−Alder reaction of 3,4,3′,4′-tetrahydro-1,1′-dinaphthyl and dibromobenzyne. Subsequent cyanation, oxidation, O-alkylation, and cyclic tetramerization resulted in octaalkoxy phthalocyanine derivatives which showed high solubility in common organic solvents and displayed strong absorption in the near-IR region.

Organic materials with linear optical absorptions in the near-IR to far-red (700−1500 nm) region have the potential for numerous applications, such as IR sensing and display devices.[1−4] Phthalocyanine (Pc) derivatives, by virtue of their unique highly delocalized cyclic π-electron system, absorb strongly in the near-IR region and exhibit a number of outstanding physical properties, such as semiconductive,[5,6] nonlinear optical,[4,7] electrochromic,[2] photovoltaic,[8−10] liquid crystalline,[11,12] and catalytic[13,14] properties. These properties offer a wide range of applications, namely, electrooptical devices (e.g., optical limiter),[15] electronic sensors,[16] optical data storage,[17,18] electrochromic displays for laser address storage systems,[2] and heterogeneous catalysis.[19]

Our research group has been engaged in the development of Pc systems that exhibit strong Q-band absorption in the near-IR region by polybenzannulation (fusing aromatic rings)[20] or by polyphenyl substitutions[21] around the Pc core. Because Pc is insoluble in common organic solvents, the synthesis of the polybenzannulated Pc systems should be carefully designed so that the intermediates and the final Pc derivatives are soluble to perform the synthetic scheme and fully characterize the Pc derivatives. Recently, Katz et al.[22] reported new polybenzannulated Pc derivatives in which four [7]helicene moieties are π-conjugated with the Pc core through pyrazine rings. These helicene-fused Pc derivatives are also peripherally substituted with several dodecyloxy groups for the purpose of improving solubility in common organic solvents.

More recently, we reported for the first time the synthesis of a new class of polybenzannulated Pc derivatives which contain fused [5]helicene moieties.[20] These derivatives, called helicenocyanines (Hc), are soluble in common organic solvents (even in the absence of solubilizing groups such as aliphatic chains) and exhibit a significant red shift of Q-band absorptions. We ascribe this high solubility to the out-of-plane geometries of helicene moieties, which leads to more free volume between the molecules, thereby increasing opportunities for the penetration of solvent molecules, such as chloroform and THF. These Hc derivatives differ from those prepared by Katz and co-workers in that there is no pyrazine ring as a part of the polybenzannulated system. The pyrazine ring between the Pc core and the benzannulated residue is believed to terminate, or merely contribute to, the effect of extended π conjugation on the optical properties of Pc, such as the red shift of the Q band.[2,3] In this note, we report an efficient synthetic route to [5]helicene-fused polybenzannulated Pc derivatives (**1a**−**c**), called benzohelicenocyanines (BHc), which contain an additional aromatic ring as part of the benzannulation compared to that of Hc.

The synthesis of BHc, shown in Scheme 1, began with the preparation of the dibromo compound **3** by a Diels−Alder reaction of **2**[23] with 4,5-dibromobenzyne, which was generated in situ by the addition of *t*-BuLi to 1,2,4,5-tetrabromobenzene.[24] Initially, attempts to aromatize **3** using DDQ resulted in a mixture of products.[25] Conse-

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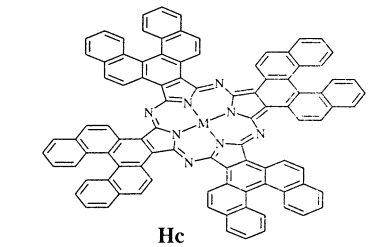
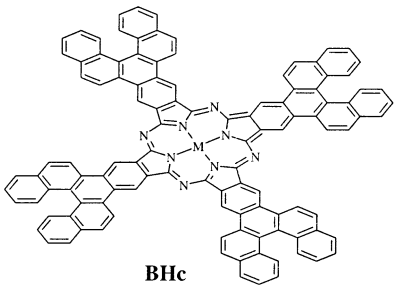


Hc

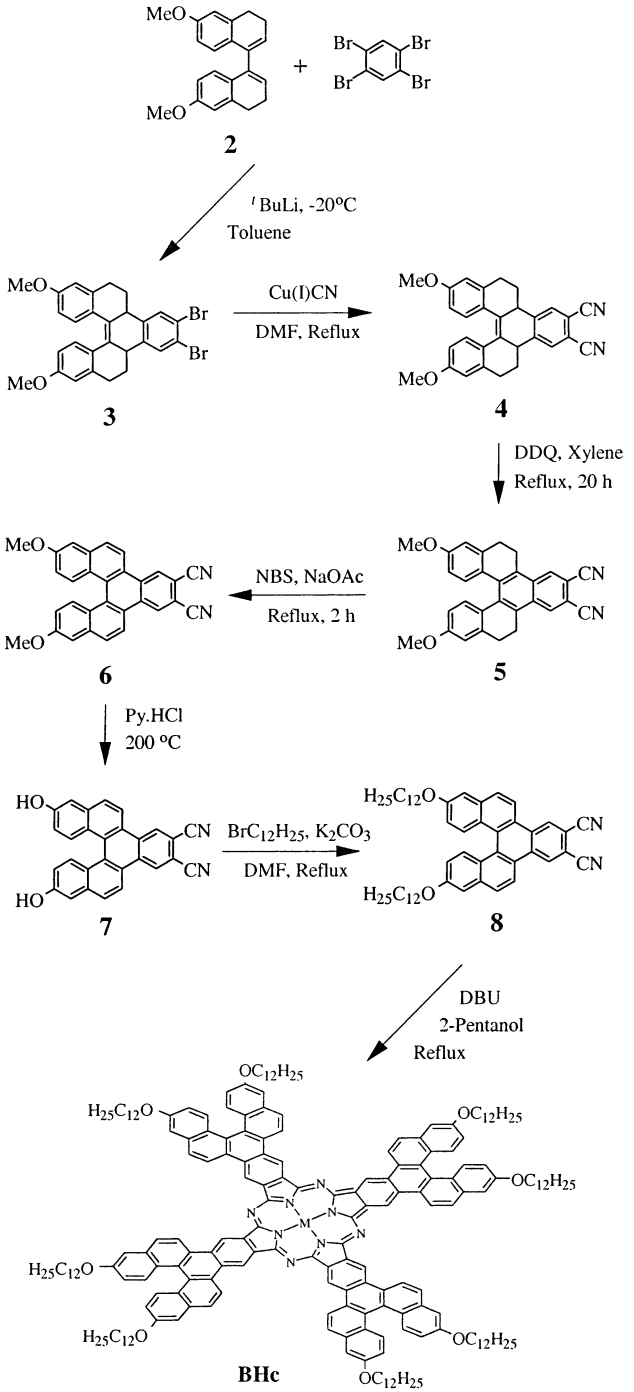


BHc

quently, we first converted **3** to the dinitrile **4**, which underwent smooth oxidation with DDQ to give the naphthalodinitrile derivative **5**. The complete aromatization of **5** did not occur, even under strong conditions such as a longer time and higher equivalents of DDQ. However, the desired aromatization occurred when **5** was treated with NBS and NaOAc to afford **6**.[26] The attachment of the dodecyl groups was performed at this stage by the deprotection of **6** using pyridine hydrochloride to produce **7**,[27] followed by the O-alkylation of **7** with dodecyl bromide, carried out in the presence of K_2CO_3 in DMF, to obtain the target dinitrile **8**. The cyclic tetramerization of **8** to metal-free BHc (**1a**) was performed using the hindered base DBU.[28] The metallohelicenocyanines (**1b** and **1c**) were prepared by adding the appropriate metal salts during the cyclization reactions. Because [5]helicene is chiral, we expect that the final BHc is a statistical mixture of four compounds (two meso and two racemic). It is practically impossible to separate these isomers by common column chromatographic techniques. MALDI-TOF mass spectroscopy confirmed the expected value of *m*/*z* of the protonated molecular ions.

All the BHc was found to be readily soluble in common organic solvents, such as THF, toluene, and chloroform. The electronic absorption spectra of **1a**−**c** are dominated by the two major bands, a phenomenon typical of Pc derivatives (Table 1).[2] The higher-energy B band splits into multiple absorptions, whereas the Q band at the far-red end of the visible spectrum appears as an intense doublet. In comparison with the spectral data of our previously reported unsubstituted Hc derivatives,[20] the Q band of BHc is bathochromically shifted by about 60 nm (Figure 1) because of an increase in benzannulation. Our previous study indicates that a red shift of about 10 nm is common to Pc derivatives when attached with alkoxy substituents.[21]

SCHEME 1



1a (M = 2H), **1b** (M = Zn), **1c** (M = Pb)

The BHc was also characterized by fluorescence spectroscopy. While the radiation at or near λ_{max} of the Q-band absorptions exhibited a weak fluorescence intensity, very strong fluorescence was observed when the samples were irradiated at or near the λ_{max} of the B-band absorptions (Figure 2). Table 1 shows the absorption and emission maxima of BHc in toluene. All derivatives exhibit unique fluorescence characteristics that are composed of two peaks, one at about 500 nm and the other

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TABLE 1. Linear Optical Properties of BHc[a]

compd	B band (nm)	Q band (nm)	excitation wavelength (nm)	emission wavelength (nm)
1a	322, 439	708, 793	321	495, >900
1b	331, 430	709, 781	331	448, 879
1c	337, 428	731, 831	336	452, 880

[a] All experiments were conducted in toluene.

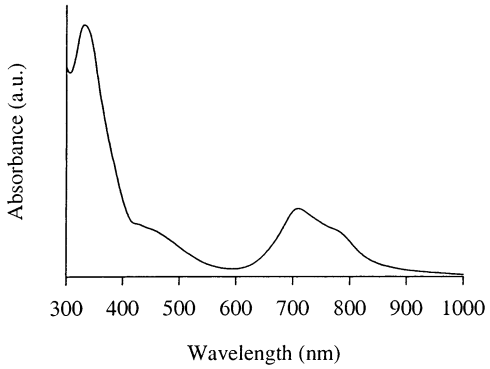

FIGURE 1. UV−visible absorption spectrum in toluene of **1b**.

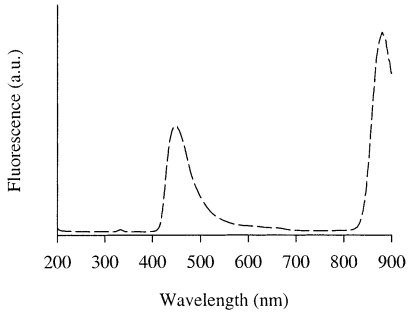

FIGURE 2. Fluorescence spectrum in toluene of **1b**.

near 900 nm. Because of the unavailability of commercial infrared detectors (above 900 nm) for fluorescence measurements, we could not estimate the fluorescence quantum yield of BHc. We plan to investigate this unusual behavior by laser transient-absorption spectroscopy in the future.

In summary, a convenient synthetic route to the benzannulation of Hc has been accomplished. Compared to ordinary Pc derivatives, BHc offers extended π conjugation in the Pc plane that shifts the lowest-energy optical absorption to near-IR, with the possibility of further shifting to diode laser wavelengths for information storage by the oxidative fusion of a helicene moiety, which is under current investigation.

Experimental Section

General Procedures. All melting points are uncorrected. IR spectra were recorded as KBr pellets or neat films. ^{1}H NMR and ^{13}C NMR spectra were recorded on a $CDCl_3$ solution unless specified otherwise. Gravity-flow column chromatography was performed on 70−230-mesh, 60-Å silica gel and 150-mesh, 58-Å activated neutral aluminum oxide. TLC analyses were performed using 250-μm silica gel flexible plates and 250-μm aluminum oxide flexible plates. Preparative TLC was performed over silica gel on 1000-μm, 20 × 20-cm^2 silica gel plates. Unless otherwise noted, common commercial reagents were used as received from the commercial suppliers without further purification. Toluene, xylene, and benzene were distilled from CaH_2 under an argon atmosphere. Dimethylformamide was purchased as anhydrous grade. Diethyl ether and THF were distilled over sodium−benzophenone, under an argon atmosphere, immediately prior to use. All reactions involving moisture- and air-sensitive reagents were carried out under an argon (high-purity grade, passed through a column of anhydrous calcium sulfate) atmosphere.

3,14-Dimethoxy-8,9-dibromo-5,6,6a,10b,11,12-hexahydrobenzo[5]helicene (3). A solution of 9.20 g (28.89 mmol) of 6,6′-dimethoxy-3,4,3′,4′-tetrahydro-1,1′-dinaphthyl (**2**)[23] and 13.43 g (33.09 mmol) of 1,2,4,5-tetrabromobenzene in 400 mL of dried toluene was stirred under an argon atmosphere in a 1-L, three-neck, round-bottomed flask. To the stirred solution was added a solution of 27 mL of 1.7 M *t*-BuLi (45.90 mmol) in 100 mL of dry hexane dropwise slowly over a period of 3 h at −20 °C. The reaction mixture was stirred at this temperature for 2 h, at room temperature for 1 h, and at 50 °C for 3 h. Methanol (10 mL) was added. The solution was washed with 2 × 300 mL of water and dried with Na_2SO_4. The solvent was removed under reduced pressure to yield a dark brown solid. The crude was then purified by column chromatography over neutral alumina using hexane and diethyl ether (100:0 → 25:75) as the eluent. The pure fractions were collected, and the removal of solvent gave an off-white solid that was recrystallized in a hexane−chloroform mixture to obtain 4.06 g (26%) of **3** as white needles. Mp: 191−193 °C. FTIR (KBr): 1241 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53 (s, 2H), 6.92 (dd, 2H, J = 3.12, 8.66 Hz), 6.67 (d, 2H, J = 2.53 Hz), 6.43 (dd, 2H, J = 2.68, 8.67 Hz), 3.78 (s, 6H), 3.36 (q, 2H, J = 4.57 Hz), 3.22 (t, 4H, J = 4.44 Hz), 2.46 (q, 2H, J = 4.32 Hz), 1.99 (t, 2H, J = 4.15 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.91, 139.10, 133.05, 131.55, 130.22, 127.31, 113.08, 111.56, 55.54, 40.20, 29.78. Anal. Calcd for $C_{28}H_{24}Br_2O_2$: C, 60.98; H, 4.38. Found: C, 60.70; H, 4.22.

3,14-Dimethoxy-8,9-dicyano-5,6,6a,10b,11,12-hexahydrobenzo[5]helicene (4). To a 100-mL, three-neck, round-bottomed flask were transferred 3.99 g (7.22 mmol) of **3**, 2.76 g (30.51 mmol) of cuprous cyanide, and 50 mL of anhydrous DMF. The reaction mixture was stirred and heated at reflux for 12 h under an argon atmosphere. The reaction mixture was allowed to cool to room temperature and was poured into 300 mL of concentrated aqueous ammonia. Air was bubbled through the suspension overnight. The precipitate was vacuum filtered and extracted using a Soxhlet extractor with 250 mL of $CHCl_3$ over a period of 10 h. The solvent was evaporated under reduced pressure, and the crude mixture was chromatographed over neutral alumina using a hexane and chloroform mixture (1:1) as the eluent to obtain a pale yellow powder. The product was recrystallized from benzene to yield 1.82 g (57%) of pure **4** as yellow needles. Mp: 250−251 °C. FTIR (KBr): 2230, 1246 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (s, 2H), 6.94 (d, 2H, J = 8.66 Hz), 6.70 (d, 2H, J = 2.33 Hz), 6.47 (dd, 2H, J = 2.53, 8.66 Hz), 3.81 (s, 6H), 3.51 (q, 2H, J = 4.31 Hz), 3.16 (t, 4H, J = 4.41 Hz), 2.50 (q, 2H, J = 4.30 Hz), 2.08 (t, 2H, J = 4.09 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.91, 144.11, 138.50, 133.46, 131.15, 129.01, 128.41, 126.24, 115.76, 113.21, 112.80, 111.54, 55.25, 40.32, 35.07, 29.34. Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30. Found: C, 81.25; H, 5.39; N, 5.19.

3,14-Dimethoxy-8,9-dicyano-5,6,11,12-tetrahydrobenzo-[5]helicene (5). A total of 1.81 g (4.71 mmol) of **4** and 6.58 g (28.30 mmol) of DDQ were placed in an oven-dried, 250-mL flask, followed by 150 mL of dried xylene. The solution was stirred and refluxed for 20 h. The mixture was cooled to room temperature and filtered. The solvent was removed from the dark red filtrate under reduced pressure. The dark brown solid was collected and chromatographed over neutral alumina using chloroform−hexane (3:1) as the eluent. The product was recrystallized from the chloroform−hexane mixture to give pure **5** as yellow needles. Mp: 291−293 °C. Yield: 0.99 g (55%). FTIR (KBr): 2229, 1253 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 2H), 7.07 (dd, 2H, J = 3.30, 8.67 Hz), 6.89 (d, 2H, J = 2.76 Hz), 6.55 (dd, 2H, J = 2.61, 8.67 Hz), 3.86 (s, 6H), 3.57 (t, 4H, J = 12.39 Hz), 3.09 (t, 4H, J = 14.90 Hz). ^{13}C NMR (75 MHz,

$CDCl_3$): δ 159.37, 139.42, 135.57, 134.54, 131.81, 131.66, 130.77, 127.46, 116.68, 112.56, 111.79, 108.92, 55.34, 29.29, 25.04. Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.43; H, 5.01; N, 6.33. Found: C, 81.29; H, 4.86; N, 6.55.

3,14-Dimethoxy-8,9-dicyanobenzo[5]helicene (6). To a 250-mL flask was added 0.94 g (2.11 mmol) of **5**, 0.76 g (4.29 mmol) of NBS, 0.04 g (0.02 mmol) of benzoyl peroxide, and 55 mL of carbon tetrachloride. The mixture was brought to reflux and stirred for 3 h. A solution consisting of 2.19 g (26.70 mmol) of NaOAc and 22 mL of acetic acid was added in one portion, and the stirring was continued for another 2 h. The mixture was cooled to room temperature. The solution was washed with 2 × 100 mL of water, 100 mL of a 10% $NaHCO_3$ solution, and 100 mL of water. The organic phase was dried with anhydrous Na_2SO_4. Removal of the solvent gave a bright yellow solid, which was chromatographed over silica gel using $CHCl_3$ and benzene (1:1) to give compound **6** as a bright yellow powder. Mp: 286 °C (melted and decomposed). Yield: 0.90 g (97%). FTIR (KBr): 2228, 1245 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.54 (s, 2H), 7.38 (s, 2H), 7.27 (s, 2H), 7.07 (d, 2H, J = 8.52 Hz), 6.88 (d, 2H, J = 2.61 Hz), 6.55 (dd, 2H, J = 2.70, 8.70 Hz), 3.84 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.36, 139.42, 135.57, 134.54, 131.82, 131.67, 130.77, 128.42, 127.46, 116.69, 112.56, 111.79, 108.90, 55.35, 29.29, 25.02. Anal. Calcd for $C_{30}H_{18}N_2O_2$: C, 82.18; H, 4.14; N, 6.39. Found: C, 81.97; H, 4.07; N, 6.14.

3,12-Dihydroxy-7,8-dicyano[5]helicene (7). To a 25-mL, long-neck, thick-walled (2 mm) ampule were added 0.90 g (2.00 mmol) of **6** and 1.39 g (12.01 mmol) of pyridine hydrochloride. The mixture was stirred and heated to 200 °C under an argon atmosphere for 4 h to complete the deprotection. The reaction mixture was allowed to cool to 80 °C, then transferred into 50 mL of water, and stirred for 15 min. The dark brown solid was separated by vacuum filtration and washed with water. The crude product was purified by preparative thin-layer chromatography over silica gel, eluting with diethyl ether to yield 0.92 mg (98%) of **7** as a dark yellow powder, which seemed to be unstable over a period of time. FTIR (KBr): 3384, 2229 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 9.35 (s, 2H), 8.77 (d, 2H, J = 9.09 Hz), 8.03 (d, 2H, J = 8.94 Hz), 7.93 (d, 2H, J = 9.21 Hz), 7.40 (d, 2H, J = 2.43 Hz), 6.96 (dd, 2H, J = 2.52, 9.20 Hz), 3.30 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.62, 136.11, 132.23, 131.56, 130.84, 128.91, 128.62, 125.50, 121.26, 117.69, 117.16, 111.41, 110.31, 14.28. Anal. Calcd for $C_{28}H_{14}N_2O_2$: C, 81.94; H, 3.44; N, 6.83. Found: C, 81.70; H, 3.24; N, 6.98.

3,12-Didodecoxy-7,8-dicyanobenzo[5]helicene (8). To a 25-mL, three-neck flask equipped with a condenser were added 0.74 g (1.80 mmol) of **7**, 0.98 g (3.78 mmol) of bromododecane, 1.00 g (7.20 mmol) of K_2CO_3, and 10 mL of dimethylformamide. The mixture was stirred under an argon atmosphere and heated to 110 °C for 12 h. The reaction mixture was allowed to cool to room temperature, then diluted, and stirred for 15 min in 250 mL of water. Vacuum filtration gave 0.77 g (57%) of **8** as a dark yellow solid. FTIR (KBr): 2229, 1244 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.96 (s, 2H), 8.46 (d, 2H, J = 9.10 Hz), 8.03 (d, 2H, J = 8.92 Hz), 7.98 (d, 2H, J = 9.27 Hz), 7.30 (d, 2H, J = 2.41 Hz), 6.96 (dd, 2H, J = 2.53, 9.25 Hz), 4.18 (t, 4H, J = 6.42 Hz), 1.91 (q, 4H, J = 6.68 Hz), 1.54 (q, 4H, J = 6.52 Hz), 1.29 (m, 32H), 0.89 (t, 6H, J = 6.42 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.50, 135.12, 131.82, 128.64, 125.70, 125.20, 120.09, 107.05, 68.35, 32.00, 29.73, 29.53, 29.44, 26.21, 22.78, 14.22. Anal. Calcd for $C_{52}H_{62}N_2O_2$: C, 83.60; H, 8.37; N, 3.75. Found: C, 83.94; H, 8.53; N, 3.77.

General Procedure for the Preparation of BHc. In a 100-mL flask, the requisite amounts of dinitrile and appropriate metal salts (for metallo derivatives) were dissolved in isopentanol (35 mL). To this solution was added 1 equiv of DBU, and the mixture was refluxed for 40 h. After cooling to room temperature, the mixture was diluted with 40 mL of 1:1 aqueous methanol and stirred at about 60 °C for 30 min. The solids were collected by vacuum filtration, washed with hot water (50 mL) and methanol (50 mL), and extracted with methanol overnight in a Soxhlet extractor. The crude product (residue) was purified using the methods described below to obtain pure Hc.

Tetrakis-*β*-5,10,22,27,39,44,56,61-octadodecyloxy-69*H*,-71*H*-benzohelicenocyanine (1a). Starting with 0.27 g (0.36 mmol) of **8**, the crude product was chromatographed over a silica gel preparative TLC plate using chloroform as the eluent to obtain the title compound as a dark purple solid. Yield: 0.09 g (32%). UV−vis (toluene; λ_{max}): 322, 439, 708, 793 nm. ^1H NMR (300 MHz, $CDCl_3$): δ 9.07 (b, 8H), 8.62 (b, 8H), 7.97 (b, 16H), 7.27 (b, 8H), 6.91 (b, 8H), 4.14 (b, 16H), 1.89 (b, 16H), 1.53 (b, 16H), 1.28 (b, 128H), 0.89 (b, 24H). MALDI−TOF−MS: m/z 2991.4 (100) [MH^+]. Anal. Calcd for $C_{208}H_{250}N_8O_8$: C, 83.5; H, 8.42; N, 3.75. Found: C, 83.85; H, 8.70; N, 3.49.

Zinc Tetrakis-*β*-5,10,22,27,39,44,56,61-octadodecyloxybenzohelicenocyanine (1b). Starting with 0.18 g (0.24 mmol) of **8** and 0.001 g (0.08 mmol) of $ZnCl_2$, the crude product was chromatographed over a silica gel preparative TLC plate using chloroform as the eluent to obtain the title compound as a dark purple solid. Yield: 0.07 g (37%). UV−vis (toluene; λ_{max}): 331, 430, 709, 781 nm. ^1H NMR (300 MHz, $CDCl_3$): δ 9.05 (b, 8H), 8.56 (b, 8H), 7.91 (b, 16H), 7.21 (b, 8H), 6.85 (b, 8H), 4.10 (b, 16H), 1.85 (b, 16H), 1.46 (b, 16H), 1.28 (b, 128H), 0.89 (b, 24H). MALDI−TOF−MS: m/z 3054.8 (100) [MH^+]. Anal. Calcd for $C_{208}H_{248}N_8O_8Zn$: C, 81.8; H, 8.18; N, 3.67. Found: C, 81.21; H, 7.78; N, 3.40.

Lead Tetrakis-*β*-5,10,22,27,39,44,56,61-octadodecyloxybenzohelicenocyanine (1c). Starting with 0.09 g (0.11 mmol) of **8** and 0.001 g (0.03 mmol) of $PbCl_2$, the crude product was chromatographed over a silica gel preparative TLC plate using chloroform as the eluent to obtain the title compound as a dark purple solid. Yield: 0.02 g (23%). UV−vis (toluene; λ_{max}): 337, 428, 731, 831 nm. ^1H NMR (300 MHz, $CDCl_3$): δ 9.07 (b, 8H), 8.57 (b, 8H), 7.91 (b, 16H), 7.22 (b, 8H), 6.85 (b, 8H), 4.13 (b, 16H), 1.88 (b, 16H), 1.47 (b, 16H), 1.28 (b, 128H), 0.90 (b, 24H). Anal. Calcd for $C_{208}H_{248}N_8O_8Pb$: C, 78.1; H, 7.82; N, 3.51. Found: C, 77.75; H, 7.56; N, 3.29.

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Supporting Information Available: Fluorescence, UV−vis, and ^1H and ^{13}C NMR spectra of selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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