Synthesis, Self-Assembly, and Nonlinear Optical Properties of Conjugated Helical Metal Phthalocyanine Derivatives

Joseph M. Fox,* Thomas J. Katz,*# Sven Van Elshocht, Thierry Verbiest, Martti Kauranen, André Persoons, Tienthong Thongpunchang, Todd Krauss, and Louis Brus#

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027, and the Laboratory of Chemical and Biological Dynamics, K.U. Leuven, Celestijnenlaan 200D, B-3001 Heverlee, Belgium

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Abstract: Molecules in which the cores of copper and nickel octaazaphthalocyanines are fused to four nonracemic [7]helicenes are constructed. CD and UV-vis absorption spectroscopy show that these compounds aggregate when dissolved in 75% EtOH–25% CHCl₃, but not in 60% EtOH–40% CHCl₃. The UV-vis absorption spectra of films of the nickel phthalocyanine are similar to those of solutions of the aggregated molecules, suggesting that the structures of the aggregates in the neat samples and in solution are similar. A calculation based on molecular mechanics shows that the energy is minimized when the molecules stack in a chiral superstructure with a core-to-core distance of ca. 3.4 Å. Atomic Force Microscopic images are in accord with this structure if on the surface of mica the stacks are isolated and perpendicular to the surface. In Langmuir films, the molecules stack in the opposite way, with the stacking axis parallel to the water. Although the molecules are remarkably symmetrical, their Langmuir–Blodgett films give very large second-order nonlinear optical responses, dominated by the ca. 21 pm/V components of the susceptibility tensors that are allowed only because the materials are chiral.

Introduction

In the 1930s, Robertson determined the crystal structures of the nickel, copper, platinum, and metal-free phthalocyanines and discovered that these compounds assemble into stacks. Subsequently, phthalocyanine derivatives were found that stack in solution and in the liquid phase, and stacking was found to give rise to a number of interesting properties, such as semiconductivity and conductivity.

We consider in this paper a way to use this propensity to incorporate stacking properties into nonracemic helical conjugated molecules. Although nonracemic helicenes that stack display unique optical properties, stacking in helicenes has until now been limited to those that have one set of functional groups, quinones at the termini, phenol ethers elsewhere. The thought was that if appropriate structures that fuse helicene and phthalocyanine cores, such as 1a and 1b, could be prepared and stacked, they might give rise to the uncommon properties of chiral columns of helical conjugated molecules. The phthalocyanine core, or more precisely the octaazaphthalocyanine core, might even enhance those properties. Thus, a stacked nonracemic helicene, unlike the racemic, exhibits a large second-order nonlinear optical response, which might be augmented by the phthalocyanine. Since in 1, helicene and phthalocyanine

Columbia University.
K.U. Leuven.


(8) It is unclear how 1a and 1b are to be named in Linstead’s nomenclature as derivatives of porphyrinate, but it is easy to refer to them as Hanack et al. do, as aza-analogues of phthalocyanine.
moieties are fused and conjugated, the π electrons might delocalize over both. The fusion and conjugation of the two moieties also distinguishes structure 1 from the nonracemic phthalocyanine ligands prepared previously. There were seven, and their chirality derives from side chains that possess stereogenic centers or from binaphthol units to which the phthalocyanines are linked by ether bonds. Also notable among the features of structures 1a and 1b are the side chains on structure 1, which should increase solubility and make it possible to prepare thin films to facilitate studying and applying the optical and morphological properties of the pure materials.

We report here the synthesis of the nickel and copper derivatives 1a and 1b. We present evidence from spectroscopy and from atomic force microscopy that these macrocycles aggregate both in solution and neat. We calculate how the molecules should stack. And we show that the second-order nonlinear optical response of the neat materials is remarkably large.

Results and Discussion

Synthesis of 1a and 1b. Although structure 1 is complex, we devised a simple synthesis (Scheme 1) from [7]helicenecbisquinone (M)-2, a compound that can be prepared in eight easy steps from 9,10-phenanthroquinone. Zinc in the presence of Ac_{2}O reduces and acetylates (M)-2, giving tetraacete 3 in quantitative yield. The acetate functions can then be converted into ethers by combining 3 with Cs_{2}CO_{3} and dodecyl iodide in a mixture of DMF and MeOH. The yield of 4 was 96%. Known methods for converting diphenylmethylenedioxyarenes into dihydroxyarenes (H_{2}, Pd/C, reductive deactivation in 1,2-diethoxyethane, followed by oxidation with chloranil, failed to give 5 in good yield. Treating 4 with any of the following failed as well: 1 M HCl in dioxane, B_{2}C_{1}, in CH_{2}Cl_{2}, chlorocatacholborane in CH_{2}-


12 Fusing benzenes rings to the peripheries of phthalocyanines and quinoxalinonaphthyrazines has little effect on the longest wavelength absorption band (the Q-band) when the fusion is to a bond that is not tangent to a ligand-centered circle. However, the first hyperpolarizabilities of phthalocyanines do not correlate with this absorption wavelength. For the effects of extended conjugation on the nonlinear optical properties of phthalocyanines, see ref 11c.


Scheme 1*" (a) Zn, Ac_2O, Et,N, 105 °C, 30 min (100%). (b) Cs_2CO_3, C_2H_5I, 8:1 DMF-MeOH, 105 °C, 2 h (96%). (c) DDQ, CH_2Cl_2, H_2O, 16 h (66%). (d) diaminomaleonitrile, AcOH, reflux, 2.5 h (81%). (e) Cu(OAc)_2, N,N'-dimethylamin ethanol, 150 °C for 1.5 h, then 140 °C for 3.5 h (30%). (f) Ni(OAc)_2, N,N'-dimethylamin ethanol, 140 °C, 3 h (20%).

Cl_2 and AlCl_3 in CH_2Cl_2. In the best case (hydrogenolysis), a mixture was formed from which 5 could be isolated in only low yield (<25%). However, treatment with 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in wet CH_2Cl_2, a combination previously known to cleave electron-rich benzyl ethers, converts 4 into 5 in 66% yield. Diaminomaleonitrile in refluxing AcOH then gives the phthalocyanine precursor, 6, in 81% yield. When heated at 140–150 °C with Cu(OAc)_2 or Ni(OAc)_2 in N,N'-dimethylanethanol, it gives phthalocyanine derivates 1a and 1b in 20 and 30% yields, respectively. Both are green solids, soluble in hexane, benzene, CH_2Cl_2, CHCl_3, and CCl_4. They are insoluble in MeOH, EtOH, and CH_2CN. Copper derivative 1a melts at 149 °C, and nickel derivative 1b at 135 °C.

CD and UV–Vis Absorption Spectra of Solutions. The CD- and UV–vis absorption spectra of the copper derivative (1a) are displayed in Figure 1. Table 1 lists the peaks. An intense long wavelength π–π* transition, the Q-band, is characteristic of the UV–vis absorption spectra of phthalocyanines, and a peak at 726 nm (ε = 3.3 × 10^4) in the UV–vis absorption spectrum of a 5 × 10^{-6} M solution of 1a in 60% EtOH–40% CHCl_3 was assigned to this transition. The sharpness of the peak indicates that in this solution 1a is monomeric. In the CD


(26) Stillman, M. J.; Nyokong, T. in ref 2a, Vol. 1, Chapter 3.

(27) See: ref 26, p 183.
aggregate or aggregate further when the polarity of the solvent is increased. The increased aggregation when the solvent is changed has been attributed to solvent–solvent interactions excluding the phthalocyanines. The implication is that in 75% EtOH–25% CHCl₃ the molecules are aggregated. The CD spectrum of 1a also changes significantly. Most strikingly, the CD peak at long wavelength splits, which can occur only if the chromophores on neighboring molecules couple. Previous examples of such splitting can be found among the spectra of associated chiral phthalocyanines and other aggregated molecules with disk-shaped cores, such as porphyrins. The aggregation in 75% EtOH–25% CHCl₃ must be extensive even when the concentration is 1 × 10⁻⁶ M, for the CD spectrum (displayed in the Supporting Information) is the same as that of the more concentrated solution in Figure 1a. Other spectroscopic changes that occur on aggregation are a broadening and increase in intensity of the negatively dichroic peaks between 320 and 430 nm and a decrease in the intensity of the positive CD peak at 286 nm.

The CD and UV–vis absorption spectra of nickel phthalocyanine 1b are shown in Figure 2, and the peaks are specified in Table 2. The UV–vis absorption spectrum of a 5 × 10⁻⁶ M solution in 60% EtOH–40% CHCl₃ includes a sharp Q-band absorption at 723 nm (ε = 2.4 × 10⁵), characteristic of a monomeric phthalocyanine. The corresponding peak in the CD spectrum (at 723 nm, Δε = 91) is positive. As in the case of 1a, increasing the amount of EtOH in the CHCl₃ solvent from 60% to 75% changes the absorption and CD spectra in ways characteristic of molecular aggregation. In the UV–vis absorption spectrum, the Q-band (720 nm, ε = 1.3 × 10⁵) broadens, becomes less intense, and shifts slightly to the blue. In the CD spectrum, as in the spectrum of 1a, it splits.

CD and UV–Vis Absorption Spectra of Films of 1b. A film suitable for absorption spectroscopy was prepared by casting a CH₂Cl₂ solution of 1b onto a quartz disk, placing a second quartz disk on top, heating the sample on a hot stage at 155 °C, and cooling it to room temperature. Unfortunately, the same procedure applied to 1a did not give high-quality films. The CD and UV–vis absorption spectra of the film of 1b are provided in Table 2.

Figure 1. CD (top, scale at left) and UV–vis absorption spectra (bottom, scale at right) of 5 × 10⁻⁶ M solutions of 1a in 75% EtOH–25% CHCl₃ (---), 70% EtOH–30% CHCl₃ (-----), and 60% EtOH–40% CHCl₃ (—).
Table 2. Peaks in the UV–Vis Absorption and CD Spectra of 1b in Two Solvents and Neat

<table>
<thead>
<tr>
<th>UV–Vis Absorption $\lambda_{\text{max}}$ ($\epsilon \times 10^3$)</th>
<th>in 60% EtOH–40% CHCl$_3$</th>
<th>in 75% EtOH–25% CHCl$_3$</th>
<th>film$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>723 (2.4)</td>
<td>720 (1.3)</td>
<td>722 (1.3)</td>
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<tr>
<td>650 (0.71)</td>
<td>653 (0.50)</td>
<td>649 (0.57)</td>
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<tr>
<td>426 (1.2)</td>
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<tr>
<td>360 (2.2)</td>
<td>367 (1.9)</td>
<td>363 (1.8)</td>
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<td>288 (1.9)</td>
<td>285 (1.9)</td>
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</tr>
<tr>
<td>266 (2.2)</td>
<td>260 (2.1)</td>
<td>265 (2.9)</td>
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<thead>
<tr>
<th>CD $\lambda$ ($\Delta\epsilon$)</th>
<th>in 60% EtOH–40% CHCl$_3$</th>
<th>in 75% EtOH–25% CHCl$_3$</th>
<th>film$^a$</th>
</tr>
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<tbody>
<tr>
<td>723 (91)</td>
<td>720 (80)</td>
<td>730 (111)</td>
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</tr>
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<td>650 (20)</td>
<td>655 (–14)</td>
<td>650 (–7.6)</td>
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<td>487 (22)</td>
<td>555 (30)</td>
<td>589 (–1)</td>
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<td>424 (–127)</td>
<td>416 (–381)</td>
<td>420 (–176)</td>
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<td>373 (–222)</td>
<td>387 (–477)</td>
<td>393 (–181)</td>
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<tr>
<td>322 (–388)</td>
<td>322 (–392)</td>
<td>323 (–249)</td>
<td></td>
</tr>
<tr>
<td>283 (348)</td>
<td>283 (134)</td>
<td>291 (181)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Wavelengths are in nm. *For the thickness and density of the film, see footnote 33.

Figure 2. CD (top, scale at left) and UV–vis absorption spectra (bottom, scale at right) of 1b as a 5 × 10$^{-6}$ M solution in 75% EtOH–25% CHCl$_3$ (---), as a 5 × 10$^{-6}$ M solution in 60% EtOH–40% CHCl$_3$ (-----), and as a thin film (—).

displayed in Figure 2, and the peaks are specified in Table 2.$^{33}$ Both imply that in the film, as in 75% EtOH–25% CHCl$_3$ solution, the molecules are aggregated. Thus the UV–vis absorption spectrum is much more similar to that of 1b in this solvent than in 60% EtOH–40% CHCl$_3$, and the CD spectrum$^{34}$ displays a split peak at long wavelengths.

Calculations. To see whether molecules of 1a and 1b plausibly fit together in a stack, a calculation was performed with the MacroModel program and MM3 force field.$^{35}$ Because the molecules are so large, to perform the calculation with an available computer the dodecyloxys were replaced by methoxys. It also was assumed that the cores of adjacent phthalocyanines would be separated by less than 7 Å apart and methoxys replaced dodecyloxys.

For the thickness and density of the film, see footnote 33.

(33) The thickness of the film of 1b was calculated to be 4.3 × 10$^{-4}$ nm by assuming that its density is 0.85 and that the extinction coefficient of the peak at 722 nm is the same for the film as for the solution in 75% EtOH–25% CHCl$_3$.


Figure 3. The lowest energy conformation of two phthalocyanine ligands of structure 1, as calculated with the MacroModel program and MM3 force field. The darker phthalocyanine is on top. The phthalocyanine cores were constrained to be no more than 7 Å apart and methoxys replaced dodecyloxys.
substrates, which were subsequently studied by Atomic Force Microscopy (AFM) in the tapping mode (Figures 4 and 5). The AFM images show many small round particles of uniform diameter, which agrees with the model in Figure 3 if the molecules are stacked with their helix axes perpendicular to the surface. The diameters measured for the particles (8–10 nm) are artificially enlarged by the diameter of the AFM tip,36 but their heights could be measured with an accuracy of ±0.1 nm. The heights of 20 particles in a sample of 1a were found to be between 2.0 and 4.5 nm. The average was 3.2 ± 0.7 nm. For 1b, the heights of 64 particles were found to be between 1.2 and 3.0 nm, with an average of 2.3 ± 0.4 nm. If the phthalocyanines assemble as depicted in Figure 3 and the distance between the surface and the phthalocyanine closest to it is 3.4 Å, the measured heights imply that the stacks of 1a contain an average of ca. 8 molecules and those of 1b an average of ca. 6. In several cases the stacks formed on top of larger areas, presumed to be single layers of phthalocyanines, that were 7 Å high, and then the heights of the stacks were measured from the tops of these areas. Figure 5 illustrates such a case in which the dimensions of the larger area are ca. 100 × 45 nm.

Table 3. Magnitudes of the Components of the Second-Order Susceptibility Tensors in pm/V of Five-Layer LB Films of 1a and 1b

<table>
<thead>
<tr>
<th>sample</th>
<th>$\chi_{xx}$</th>
<th>$\chi_{yy}$</th>
<th>$\chi_{zz}$</th>
<th>$\chi_{yz}$</th>
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<tbody>
<tr>
<td>1a</td>
<td>24</td>
<td>3</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>1b</td>
<td>19</td>
<td>4</td>
<td>3</td>
<td>15</td>
</tr>
</tbody>
</table>

*The thicknesses of both films were taken to be 30 nm and their refractive indices to be unity.

Particles of larger diameter were also observed although less frequently. (These are not displayed in Figures 4 or 5.) They may be small crystals, for after standing for 2 days, a $5 \times 10^{-5}$ M solution of 1b in 75% EtOH–25% CHCl$_3$ formed a precipitate.

**Nonlinear Optical Properties.** The beam of a Nd:YAG laser ($\lambda = 1064$ nm, 50 Hz, 8 ns pulses), initially polarized in the plane of incidence, was passed through a rotating quarter waveplate and focused at an incident angle of 45° onto five-layer Langmuir Blodgett (LB) films of 1a and 1b deposited on alkylsilanized glass. Transmitted second-harmonic light was resolved into components polarized parallel and perpendicular to the plane of incidence. The intensity of the second-harmonic light as a function of the rotation angle about the surface normal showed that in its surface plane each film was isotropic.37 Consequently, if $z$ in a Cartesian coordinate system is the direction of the normal to the surface, and the components of the second-order nonlinear polarization at frequency $2\omega$ are $P_{2\omega} = \sum_{ijkl} g_{ijkl} E_{i}(\omega)E_{j}(\omega)$ (where $E(\omega)$ is a component of the fundamental beam’s electric field),38 there are only four independent components of the second-order susceptibility tensor: $\chi_{xzx}$, $\chi_{xxz}$, $\chi_{zyz}$, and $\chi_{zzx}$.39 All four can be evaluated if the intensities and polarizations of the fundamental and second-harmonic beams are analyzed.40 The values found are summarized in Table 3.

The thickness of the films was taken to be 30 nm. The reason that the Langmuir isotherms showed the areas of compressed films of 1a to be 1.6 nm$^2$/molecule and those of 1b to be 1.7 nm$^2$/molecule. These figures imply that the molecules are oriented in the same way that columnar helicenes and columnar discotic molecules are oriented in Langmuir and Langmuir–Blodgett films41 and the way a copper phthalocyanine is in evaporatively deposited films,42 that is, with the perpendiculars to the phthalocyanine rings nearly parallel to the water surface. Thus, the measured areas agree with those calculated for the molecules oriented in this way with side chains extended,43 and they do not agree with those calculated for the same molecules oriented with the phthalocyanine rings parallel to the surface.44 Accordingly, each layer should be ca. 6 nm thick, that is, approximately the diameter of the molecule as viewed from the perpendicular to the phthalocyanine ring system.43

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(39) $\chi_{xx} = \chi_{yy} = -\chi_{yy} = -\chi_{zz} = \chi_{zz} = \chi_{yz} = \chi_{zz} = \chi_{yz} = \chi_{zz}$.
(43) The diameter of the aromatic core of the ring system is 2.7 nm and that of two extended dodecyl side chains is ca. 3.5 nm (see footnote 19 in ref 7b). If the molecules are separated by 0.34 nm (see text above), the surface area of the molecules in this “edge-on” orientation would be 0.35 × 6 = 2 nm$^2$.
(44) The face area should be $\pi \times 3^2 = 28$ nm$^2$. 

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**Figure 4.** Atomic force microscopic height image of six stacks of phthalocyanines 1b on mica. As the coordinate out of the plane of the page increases to its maximum, 3 nm, the shade becomes lighter.

**Figure 5.** Atomic force microscopic height image of two stacks of phthalocyanines 1a. As the coordinate out of the plane of the page increases to its maximum, 7 nm, the shade becomes lighter.
For molecules such as 1a and 1b, whose structures have D₄ᵥ symmetry, the only components of the molecular hyperpolarizability tensor that can differ from zero are those associated with chirality. These components can contribute only to chiral macroscopic susceptibility components. For the films considered here this means only to χ(2)zzz. It is therefore reasonable that this component has the largest magnitude. Moreover, its large value for both molecules—notable in particular because of their high symmetry—agrees with the discovery reported previously, that the second-order nonlinear optical response is greatly enhanced when chiral molecules organize into supramolecular arrays.

Unclear, however, is why χzzz for 1b is so large. The observation is reminiscent of and the value similar in magnitude to the achiral component of the second-order susceptibility tensor exhibiting by films of a planar achiral copper phthalocyanine. These components can contribute only to chiral superstructures. Isolated stacks of the phthalocyanines in which the axes of stacking are perpendicular to the surface of the mica substrate could be observed by Atomic Force Microscopy. Although the molecules are highly symmetrical, the second-order nonlinear optical response of their Langmuir–Blodgett films on glass, in which they are stacked with their edges on the surface, is notably large.

Conclusions

An efficient synthesis provides novel helical phthalocyanines in nonracemic form. Their CD and UV–vis absorption spectra show that they aggregate when dissolved in 75% EtOH—25% CHCl₃ and as pure materials. A calculation with the MacroModel program and MM3 force field implies that the molecules stack with their cores separated by ca. 3.4 Å and that the stacks have chiral superstructures. Isolated stacks of the phthalocyanines in which one of the edges on the surface is perpendicular to the surface of the mica substrate could be observed by Atomic Force Microscopy. Although the molecules are highly symmetrical, the second-order nonlinear optical response of their Langmuir–Blodgett films on glass, in which they are stacked with their edges on the surface, is notably large.

Experimental Section

CH₂Cl₂ and Et₂N were distilled from CaH₂, DMF (Aldrich, anhydrous, 99.8%) and MeOH were boiled and cooled under N₂ to free them of oxygen. Zn dust (Aldrich, <10 μm, 98.4%) was activated prior to use. Glassware was flame-dried under vacuum and cooled under N₂. Reactions were run under N₂. Additions by syringe were made through rubber septa. “Chromatography” refers to “flash chromatography.” The matrix for FAB mass spectra was 2-nitrophenyl trifluoroacetate (2-NP-TFA) and for MALDI-TOF mass spectra was 2,5-dihydroxybenzoic acid. The MALDI-TOF spectra were obtained using a Reflex II reflectron linear TOF mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser. Mass spectra were recorded in reflectron mode at a repeller voltage of 2.5 kV.

MeOH was added to the product, and after this had been filtered through Celite, which was rinsed with CH₂Cl₂. The yield was 0.123 g (60%) of a yellow oil, [Mr]D₂ = −1600 (c 0.050, CH₂Cl₂). IR (CCl₄) 2927, 2856, 1744, 1676 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 8.33 (d, 2H, J = 8.5 Hz), 8.11 (d, 2H, J = 8.5 Hz), 7.85 (m, 4H), 7.40 (m, 4H), 7.04 (s, 2H), 6.27 (d, 2H, J = 8.6 Hz), 5.70 (d, 2H, J = 8.6 Hz), 4.36 (m, 2H), 4.16 (m, 2H), 3.98 (m, 2H), 3.90 (m, 2H), 2.76 (m, 2H), 2.57 (m, 2H), 2.01 (m, 4H), 1.90 (m, 4H), 1.61 (m, 8H), 1.51–1.13 (m, 8H), 1.06 (m, 8H), 0.91 (m, 22H), 0.60 (m, 8H) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 138.4, 138.2, 138.4, 129.8, 128.8, 128.1, 126.8, 126.7, 125.4, 124.8, 124.6, 119.7, 119.0, 118.2, 117.6, 105.6, 103.3, 97.5, 68.8, 68.4, 67.2, 32.0, 29.8 (m) ppm; HRMS (FAB) calcd for C₁₀₂H₁₆₀O₈K₄9 1552.1750, found 1552.1733.

Experimental

CH₃Cl and Et₃N were distilled from CaH₂, DMF (Aldrich, anhydrous, 99.8%) and MeOH were boiled and cooled under N₂ to free them of oxygen. Zn dust (Aldrich, <10 μm, 98.4%) was activated prior to use. Glassware was flame-dried under vacuum and cooled under N₂. Reactions were run under N₂. Additions by syringe were made through rubber septa. “Chromatography” refers to “flash chromatography.” The matrix for FAB mass spectra was 2-nitrophenyl octyl ether (Aldrich) and for MALDI-TOF mass spectra was trans-3-indoleacrylic acid (Aldrich). Bovine insulin (Sigma) was the calibrant for the MALDI-TOF spectra. The Atomic Force Microscope, a NanoScope IIIa from Digital Instruments, was outfitted with a transducer of 10 nN force that was activated in situ with CO₂ plasma. The tip was mounted on a silicon cantilever with a spring constant of 0.17 N m⁻¹. The tip was used to locate features to a precision of ±0.1 μm. The images were recorded in tapping mode with a scan rate of 1 Hz and an amplitude set point of 2.0 nm. The images were analyzed with the software from Digital Instruments.

1D-NMR (CDCl₃, 500 MHz) δ 8.69 (d, 2H, J = 8.6 Hz), 8.58 (d, 2H, J = 8.6 Hz), 7.76 (s, 2H), 6.34 (d, 2H, J = 8.6 Hz), 5.76 (d, 2H, J = 8.6 Hz), 4.37 (m, 2H), 4.19 (m, 2H), 3.99 (m, 2H), 3.89 (m, 2H), 2.73 (m, 4H), 2.02 (m, 4H), 1.88 (m, 4H), 1.7–1.2 (m, 8H), 1.13 (m, 4H), 0.96 (m, 4H), 0.89 (m, 18H), 0.77 (m, 12H), 0.55 (m, 2H), 0.43 (m, 2H) ppm; ¹³C NMR (CDCl₃, 125 MHz) δ 151.7, 147.3, 147.0, 142.5, 134.9, 129.7.

KOAc was added to the matrix.
128.9, 125.0, 124.2 (2 peaks), 121.7, 121.4, 118.9, 114.5, 106.6, 104.7, 100.5, 68.9, 68.7, 67.9, 32.0, 29.8 (m), 29.7, 29.4 (m), 29.1, 28.1, 26.6, 24.5, 22.7, 14.1 ppm; HRMS (FAB) calcd for C_{106}H_{160}O_{6}N_{4} 1586.2371, found 1586.2358.

**Copper Phthalocyanine 1a.** A solution of Cu(OAc)_{2} (0.25 mL of a 0.013 M solution in N,N-dimethylthanolamine) was added to 6 (0.020 g, 0.013 mmol) in a 0.5 mL tube. After it had been at 150 °C for ca. 2 min, the tube was sealed, and heating was continued at 150 °C for 1.5 h, and then at 140 °C for 3.5 h. To mix the contents, the tube was occasionally inverted. The reaction mixture was cooled and partitioned between CH_{2}Cl_{2} and H_{2}O, and the organic layer, after it had been dried (Na_{2}SO_{4}) and freed of solvent, was loaded onto a chromatography column, which was sequentially eluted with hexane, 25% CH_{2}Cl_{2}, 75% hexane, and 1:1 CH_{2}Cl_{2}-hexane. The yield of 1a, a green solid, mp 149 °C, [α]_{D} − 2050 (c 0.007, CH_{2}Cl_{2}), was 6 mg (30%). IR (CCl_{4}) 2927, 2855, 1739, 1709 cm\(^{-1}\); \(^{1}H\) NMR (CDCl_{3}, 400 MHz) \(δ\) 12.0−10.7 (m, 8H), 9.1−8.7 (m, 8H), 7.9 (m, 8H), 6.6 (m, 8H), 6.2 (m, 8H), 4.5 (m, 8H), 4.3 (m, 16H), 4.0 (m, 8H), 3.3−2.9 (m, 16H), 2.3−0.5 (m, 552H) ppm; MALDI-TOF calcd for C_{64}H_{108}O_{24}N_{4}Cu (M + 1) 6410.4, found 6410.8.\(^{50}\)

**Nickel Phthalocyanine 1b.** A solution of Ni(OAc)_{2}·4H_{2}O (0.25 mL of a 0.013 M solution in N,N-dimethylthanolamine) was added to 6 (0.020 g, 0.013 mmol) in a 0.5 mL tube. After the mixture had been at 140 °C for ca. 2 min, the tube was sealed and heated at this temperature for 3 h. To mix the contents, the tube was occasionally inverted. The reaction mixture was cooled and partitioned between CH_{2}Cl_{2} and H_{2}O. The organic layer was dried (Na_{2}SO_{4}) and, after the solvents had been removed under reduced pressure, chromatography (eluting first with 30% CH_{2}Cl_{2} and then with 40% CH_{2}Cl_{2}) gave 4 mg (20%) of 1a, a green solid, mp 135 °C, [α]_{D} −1650 (c 0.012, CH_{2}Cl_{2}). IR (CCl_{4}) 2927, 2855, 1741, 1605 cm\(^{-1}\); \(^{1}H\) NMR (CDCl_{3}, 400 MHz) \(δ\) 10.57 (d, 8H, J = 8.5 Hz), 9.01 (d, 8H, J = 8.5 Hz), 7.27 (8H), 6.44 (d, 8H, J = 8.5 Hz), 5.90 (d, 8H, J = 8.5 Hz), 4.52 (m, 8H), 4.35 (m, 8H), 4.09 (m, 8H), 3.98 (m, 8H), 3.0−2.9 (m, 16H), 2.22 (m, 16H), 1.97 (m, 16H), 1.80 (m, 16H), 1.6−1.2 (m, 320 H), 1.05 (m, 16H), 0.93 (t, 24H, J = 7.0 Hz), 0.86 (t, 24H, J = 6.8 Hz), 0.8−0.5 (m, 96H), 0.42 (t, 24H, J = 7.1 Hz) ppm. \(^{13}C\) NMR (CDCl_{3}, 75 MHz) \(δ\) 152.2, 147.5, 147.4, 146.7, 144.8, 144.4, 134.1, 129.0, 127.6, 125.5, 124.2, 123.9, 120.7, 119.7, 106.5, 104.4, 99.4, 69.1, 68.6, 67.9, 32.0, 31.5, 29.9 (m), 29.5, 29.4, 29.2, 28.9, 28.1, 26.7, 26.5, 25.5, 22.7, 22.2, 14.1, 13.7 ppm; MALDI-TOF calcd for C_{64}H_{108}Ni_{16}O_{24} (M + 1) 6405.6, found 6405.6.\(^{50}\)

**Preparation of the LB Films.** Helical phthalocyanines 1a and 1b as \(2 \times 10^{-4}\) M solutions in hexane were spread onto Millipore ultrapure water at 20 °C in a KSV minitrough. After the hexane had evaporated, the surface was compressed slowly to a pressure of 5 mN/m. After 30 min had been allowed to pass for the surface to stabilize, five layers were transferred by the horizontal lifting procedure to optical quality glass slides that had been silanized with octadecyltrichlorosilane to make them hydrophobic.

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**Supporting Information Available:** Graphs showing the \(^{1}H\) and \(^{13}C\) NMR and IR spectra of 1b, 2−6, the \(^{1}H\) NMR and IR spectrum of 1a, the MALDI-TOF mass spectra of 1a and 1b, and the CD spectrum of a 1 × 10^{-6} M solution of 1a in CH_{2}Cl_{2} (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.