

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

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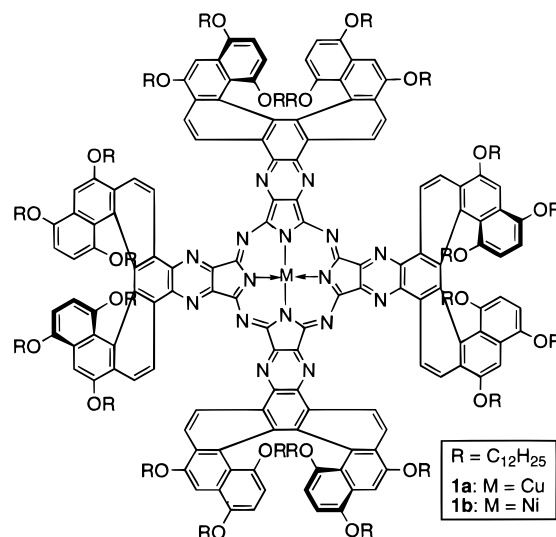
**Abstract:** Molecules in which the cores of copper and nickel octaazaphthalocyanines are fused to four nonracemic [7]helicenes are constructed. CD and UV–vis absorption spectroscopy show that these compounds aggregate when dissolved in 75% EtOH–25% CHCl<sub>3</sub>, but not in 60% EtOH–40% CHCl<sub>3</sub>. 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<sup>1</sup> of the nickel, copper, platinum, and metal-free phthalocyanines<sup>2</sup> and discovered that these compounds assemble into stacks. Subsequently, phthalocyanine derivatives were found that stack in solution<sup>3</sup> and in the liquid phase,<sup>4</sup> and stacking was found to give rise to a number of interesting properties, such as semiconductivity<sup>5</sup> and conductivity.<sup>6</sup>

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.<sup>7</sup> 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.<sup>7</sup> The phtha-



locyanine core, or more precisely the octaazaphthalocyanine core,<sup>8</sup> might even enhance those properties. Thus, a stacked nonracemic helicene, unlike the racemic, exhibits a large second-order nonlinear optical response,<sup>10</sup> which might be augmented by the phthalocyanine.<sup>11</sup> Since in **1**, helicene and phthalocyanine

(8) It is unclear how **1a** and **1b** are to be named in IUPAC's nomenclature as derivatives of porphyrine,<sup>9</sup> but it is easy to refer to them as Hanack et al. do,<sup>2b</sup> as aza-analogues of phthalocyanine.

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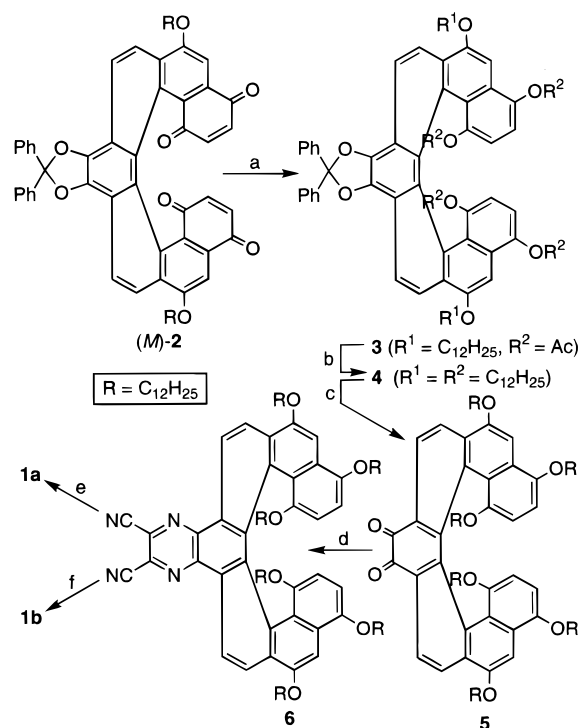
moieties are fused and conjugated, the  $\pi$  electrons might delocalize over both.<sup>12</sup> The fusion and conjugation of the two moieties also distinguishes structure **1** from the nonracemic phthalocyanine ligands prepared previously.<sup>17</sup> There were seven, and their chirality derives from side chains that possess stereogenic centers<sup>17a-c</sup> or from binaphthol units to which the phthalocyanines are linked by ether bonds.<sup>17d,e</sup> 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.<sup>18</sup>

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]helicenebisquinone (*M*)-**2**, a compound that can be prepared in eight easy steps from 9,10-phenanthrenequinone.<sup>19</sup> Zinc in the presence of  $\text{Ac}_2\text{O}$  reduces and acetylates (*M*)-**2**, giving tetraacetate **3** in quantitative yield. The acetate functions can then be converted into ethers by combining **3** with  $\text{Cs}_2\text{CO}_3$  and dodecyl iodide in a mixture of DMF and MeOH. The yield of **4** was 96%. Known methods for converting diphenylmethylenedioxyarenes into dihydroxyarenes ( $\text{H}_2$ , Pd/C;<sup>20</sup> refluxing in dilute  $\text{AcOH}$ <sup>21</sup>), followed by oxidation with chloranil,<sup>22</sup> failed to give **5** in good yield. Treating **4** with any of the following failed as well: 1 M HCl in dioxane,  $\text{BCl}_3$  in  $\text{CH}_2\text{Cl}_2$ , chlorocatacholborane in  $\text{CH}_2\text{-}$

Scheme 1<sup>a</sup>



<sup>a</sup> (a) Zn,  $\text{Ac}_2\text{O}$ ,  $\text{Et}_3\text{N}$ , 105 °C, 30 min (100%). (b)  $\text{Cs}_2\text{CO}_3$ ,  $\text{C}_{12}\text{H}_{25}\text{I}$ , 8:1 DMF–MeOH, 105 °C, 2 h (96%). (c) DDQ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{H}_2\text{O}$ , 16 h (66%). (d) diaminomaleonitrile,  $\text{AcOH}$ , reflux, 2.5 h (81%). (e)  $\text{Cu}(\text{OAc})_2$ , *N,N'*-dimethylaminoethanol, 150 °C for 1.5 h, then 140 °C for 3.5 h (30%). (f)  $\text{Ni}(\text{OAc})_2$ , *N,N'*-dimethylaminoethanol, 140 °C, 3 h (20%).

$\text{Cl}_2$ , and  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$ . 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  $\text{CH}_2\text{Cl}_2$ , a combination previously known to cleave electron-rich benzyl ethers,<sup>23</sup> converts **4** into **5** in 66% yield. Diaminomaleonitrile in refluxing  $\text{AcOH}$  then gives the phthalocyanine precursor, **6**, in 81% yield.<sup>24</sup> When heated at 140–150 °C with  $\text{Cu}(\text{OAc})_2$  or  $\text{Ni}(\text{OAc})_2$  in *N,N'*-dimethylaminoethanol, it gives phthalocyanine derivatives **1a** and **1b** in 20 and 30% yields, respectively.<sup>25</sup> Both are green solids, soluble in hexane, benzene,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ . They are insoluble in MeOH, EtOH, and  $\text{CH}_3\text{CN}$ . 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  $\pi-\pi^*$  transition, the Q-band, is characteristic of the UV–vis absorption spectra of phthalocyanines,<sup>26</sup> and a peak at 726 nm ( $\epsilon = 3.3 \times 10^5$ ) in the UV–vis absorption spectrum of a  $5 \times 10^{-6}$  M solution of **1a** in 60% EtOH–40%  $\text{CHCl}_3$  was assigned to this transition. The sharpness of the peak indicates that in this solution **1a** is monomeric.<sup>27</sup> In the CD

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(12) Fusing benzene rings to the peripheries of phthalocyanines<sup>13</sup> and quinoxalinoporphyrazines<sup>14</sup> 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.<sup>15</sup> However, the first hyperpolarizabilities of phthalocyanines do not correlate with this absorption wavelength.<sup>16</sup> For the effects of extended conjugation on the nonlinear optical properties of phthalocyanines, see ref 11c.

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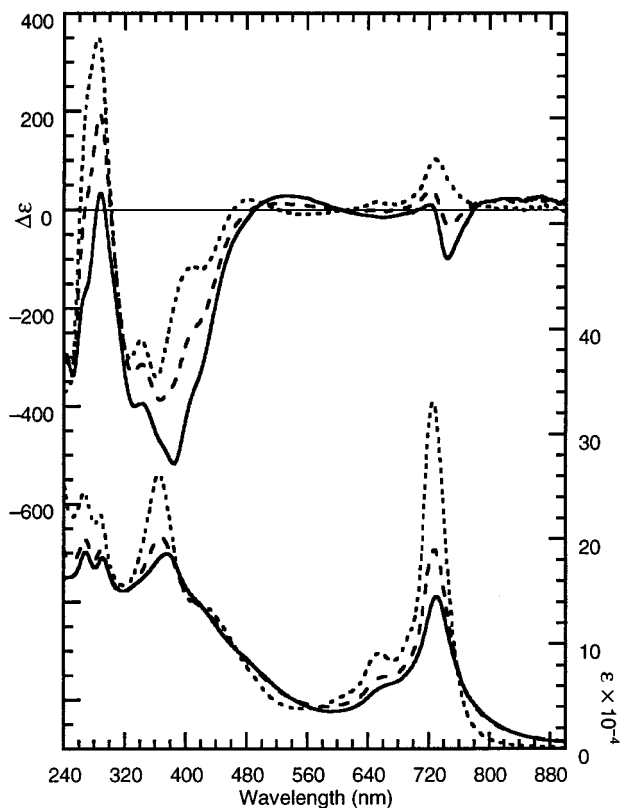
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**Table 1.** Peaks in the UV–Vis Absorption and CD Spectra of **1a** in Two Solvents<sup>a</sup>

UV–vis absorption $\lambda_{\max}$ ( $\epsilon \times 10^{-5}$ )		CD $\lambda$ ( $\Delta\epsilon$ )	
in 60% EtOH–40% CHCl <sub>3</sub>	in 75% EtOH–25% CHCl <sub>3</sub>	in 60% EtOH–40% CHCl <sub>3</sub>	in 75% EtOH–25% CHCl <sub>3</sub>
726 (3.3)	730 (1.5)	727 (108)	730 (110)
654 (0.91)	659 (0.59)	652 (16)	659 (–17)
428 (1.4)		481 (19)	532 (26)
364 (2.6)	375 (1.8)	423 (–120)	420 (–335)
287 (2.2)	290 (1.8)	360 (–340)	384 (–516)
266 (2.4)	268 (1.9)	326 (–303)	334 (–402)
		285 (347)	288 (30)

<sup>a</sup> Wavelengths are in nm.**Figure 1.** CD (top, scale at left) and UV–vis absorption spectra (bottom, scale at right) of  $5 \times 10^{-6}$  M solutions of **1a** in 75% EtOH–25% CHCl<sub>3</sub> (– – –), 70% EtOH–30% CHCl<sub>3</sub> (···), and 60% EtOH–40% CHCl<sub>3</sub> (—).

spectrum the absorption gives rise to an intense positively dichroic peak ( $\Delta\epsilon = 108$ , at 727 nm). We note incidentally that the Q-band is also positively dichroic for a previously known copper phthalocyanine that is substituted with chromophores of (*M*)-helicity, in that case binaphthoxyethoxys.<sup>17d</sup>

Figure 1 also shows that when the ratio of EtOH to CHCl<sub>3</sub> in the solvent is increased, the absorption spectra of **1a** change greatly. The Q-band in 75% EtOH–25% CHCl<sub>3</sub> (at 730 nm) is significantly broader and less intense ( $\epsilon = 1.5 \times 10^5$ ) than when the solvent is 60% EtOH–40% CHCl<sub>3</sub>. Effects of this kind<sup>28</sup> have been observed for a number of phthalocyanines that

(28) For examples of phthalocyanines whose Q-bands broaden and decrease in intensity upon aggregation, see refs 3, 24c, 25b, and 29, footnote 3 in ref 29a, and the following: (a) Vacus, J.; Doppelt, P.; Simon, J.; Memetzidis, G. *J. Mater. Chem.* **1992**, 2, 1065 and footnotes 8–15 therein. (b) Monahan, A. R.; Brado, J. A.; DeLuca, A. F. *J. Phys. Chem.* **1972**, 76, 446. (c) Kalina, D.; Crane, S. W. *Thin Solid Films* **1985**, 134, 109. (d) Fujiki, M.; Tabei, H.; Kurihara, T. *J. Phys. Chem.* **1988**, 92, 1281. (e) Schutte, W. J.; Sluyters-Rehbach, M.; Sluyters, J. H. *J. Phys. Chem.* **1993**, 97, 6069. (f) Duro, J. A.; de la Torre, G.; Torres, T. *Tetrahedron Lett.* **1995**, 36, 8079. (g) van Nostrum, C. F.; Picken, S. J.; Schouten, A.-J.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1995**, 117, 9957.

aggregate or aggregate further when the polarity of the solvent is increased.<sup>25b,29</sup> (The increased aggregation when the solvent is changed has been attributed to solvent–solvent interactions excluding the phthalocyanines.<sup>28b</sup>) The implication is that in 75% EtOH–25% CHCl<sub>3</sub> 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.<sup>30</sup> Previous examples of such splitting can be found among the spectra of associated chiral phthalocyanines<sup>17b–d</sup> and other aggregated molecules with disk-shaped cores, such as porphyrins.<sup>31</sup>

The aggregation in 75% EtOH–25% CHCl<sub>3</sub> must be extensive even when the concentration is  $1 \times 10^{-6}$  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  $5 \times 10^{-6}$  M solution in 60% EtOH–40% CHCl<sub>3</sub> includes a sharp Q-band absorption at 723 nm ( $\epsilon = 2.4 \times 10^5$ ), characteristic of a monomeric phthalocyanine. The corresponding peak in the CD spectrum (at 723 nm,  $\Delta\epsilon = 91$ ) is positive. As in the case of **1a**, increasing the amount of EtOH in the CHCl<sub>3</sub> 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,  $\epsilon = 1.3 \times 10^5$ ) broadens, becomes less intense, and shifts slightly to the blue. In the CD spectrum, as in the spectrum of **1a**, it splits.<sup>32</sup>

**CD and UV–Vis Absorption Spectra of Films of 1b.** A film suitable for absorption spectroscopy was prepared by casting a CH<sub>2</sub>Cl<sub>2</sub> 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

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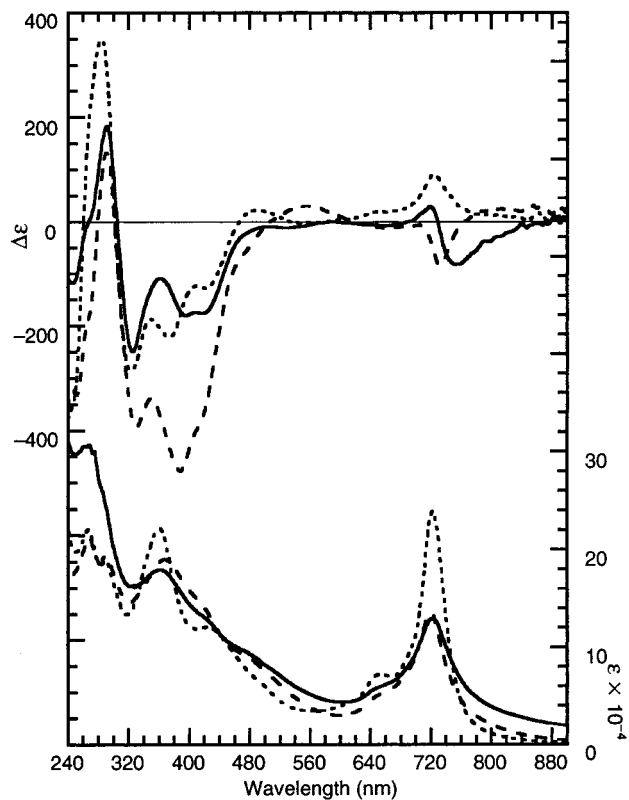
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(32) The peak at 705 nm in the CD spectrum of **1b** in 75% EtOH–25% CHCl<sub>3</sub> is negatively dichroic ( $\Delta\epsilon = -6$ ), probably because a negatively dichroic peak falls just to the blue (662 nm,  $\Delta\epsilon = -13$ ).

**Table 2.** Peaks in the UV–Vis Absorption and CD Spectra of **1b** in Two Solvents and Neat<sup>a</sup>

UV–vis Absorption $\lambda_{\max}$ ( $\epsilon \times 10^{-5}$ )			CD $\lambda$ ( $\Delta\epsilon$ )		
in 60% EtOH–40% CHCl <sub>3</sub>	in 75% EtOH–25% CHCl <sub>3</sub>	film <sup>b</sup>	in 60% EtOH–40% CHCl <sub>3</sub>	in 75% EtOH–25% CHCl <sub>3</sub>	film <sup>b</sup>
723 (2.4)	720 (1.3)	722 (1.3)	723 (91)	720 (80)	730 (111)
650 (0.71)	653 (0.50)	649 (0.57)	650 (20)	655 (–14)	650 (–7.6)
426 (1.2)			487 (22)	555 (30)	589 (–1)
360 (2.2)	367 (1.9)	363 (1.8)	424 (–127)	416 (–381)	420 (–176)
288 (1.9)	285 (1.9)		373 (–222)	387 (–477)	393 (–181)
266 (2.2)	260 (2.1)	265 (2.9)	322 (–288)	322 (–392)	323 (–249)
			283 (348)	283 (134)	291 (181)

<sup>a</sup> Wavelengths are in nm. <sup>b</sup> For the thickness and density of the film, see footnote 33.



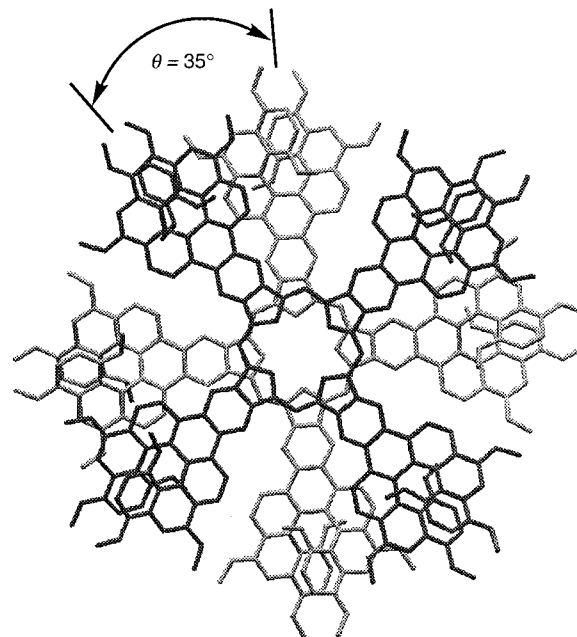
**Figure 2.** CD (top, scale at left) and UV–vis absorption spectra (bottom, scale at right) of **1b** as a  $5 \times 10^{-6}$  M solution in 75% EtOH–25% CHCl<sub>3</sub> (---), as a  $5 \times 10^{-6}$  M solution in 60% EtOH–40% CHCl<sub>3</sub> (···), and as a thin film (—).

displayed in Figure 2, and the peaks are specified in Table 2.<sup>33</sup> Both imply that in the film, as in 75% EtOH–25% CHCl<sub>3</sub> 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<sub>3</sub>, and the CD spectrum<sup>34</sup> 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.<sup>35</sup> Because the molecules are so large, to perform the calculation with an

(33) The thickness of the film of **1b** was calculated to be  $4.3 \times 10^{-4}$  mm 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<sub>3</sub>.

(34) Rotating the film by increments of 15° (between 0° and 360°) did not cause the CD curve to change significantly. This means that it is circular dichroism rather than linear dichroism or birefringence that gives rise to the curves displayed. See: (a) Kuball, H.-G.; Schönhofer, A. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: New York, 1994; Chapter 4. (b) Schönhofer, A.; Kuball, H.-G. *Chem. Phys.* **1987**, *115*, 159. (c) Nordén, B. *Acta Chem. Scand.* **1972**, *26*, 1763. (d) Tunis-Schneider, M. J. B.; Maestre, M. F. *J. Mol. Biol.* **1970**, *52*, 521. (e) Cornell, D. G. *J. Colloid Interface Sci.* **1979**, *70*, 167.

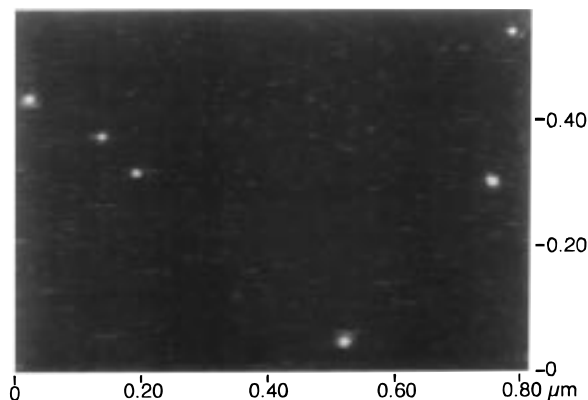


**Figure 3.** The lowest energy conformation of two phthalocyanine ligands of structure **1**, as calculated with the MacroModel program and MM3 force field. The darker phthalocyanine is on top. The phthalocyanine cores were constrained to be no more than 7 Å apart and methoxys replaced dodecyloxys.

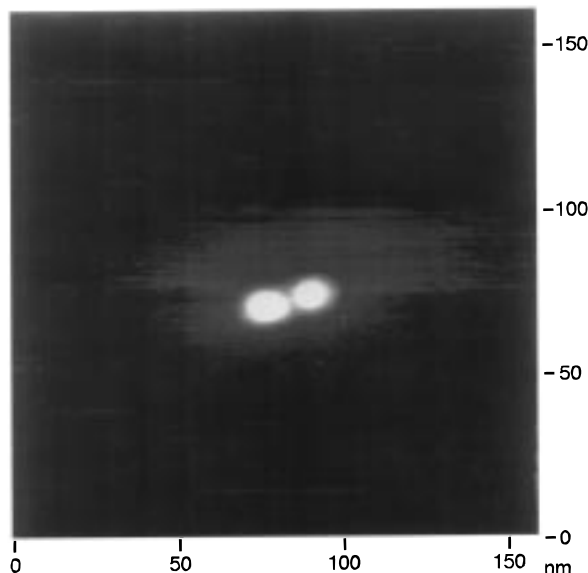
available computer the dodecyloxys were replaced by methoxys. It also was assumed that the cores of adjacent phthalocyanines would be separated by less than 7 Å so they could  $\pi$ -stack. Thus, two phthalocyanine ligands of structure **1**, with R = CH<sub>3</sub>, were confined to lie within this distance, and the conformation of minimum energy for the pair was calculated. Figure 3 displays this conformation. One molecule is rotated with respect to the other by  $\theta = 35^\circ$  to the right (see Figure 3). This conformation is undoubtedly preferred to one in which  $\theta$  is 0°, because in the latter either steric interactions between neighboring helicene moieties would be severe or adjacent cores would have to be separated by an amount (at least 6.9 Å) that would be too large for  $\pi$ -stacking forces to be appreciable. The cores are parallel to one another, with centers separated by 3.4 Å, essentially the  $\pi$ -stacking distance between two aromatic molecules.<sup>1</sup> The methoxy groups were then replaced by butoxys, and the conformation was adjusted to minimize the energy. The core's conformation did not change. Centers remained separated by 3.4 Å, and no steric interferences were detected. Thus no barrier was found to fitting the molecules together at the separation usual for unencumbered phthalocyanines.

**Atomic Force Microscopy.** Micromolar solutions of **1a** and **1b** in 75% EtOH–25% CHCl<sub>3</sub> were spin-coated onto mica

(35) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.



**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.

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,<sup>36</sup> but their heights could be measured with an accuracy of  $\pm 0.1$  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  $3.2 \pm 0.7$  nm. For **1b**, the heights of 64 particles were found to be between 1.2 and 3.0 nm, with an average of  $2.3 \pm 0.4$  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.  $100 \times 45$  nm.

(36) MacroModel<sup>35</sup> calculates a width of ca. 6 nm for phthalocyanines **1** whose dodecyl chains were elongated.

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

sample	$\chi_{xyz}$	$\chi_{xzx}$	$\chi_{zxx}$	$\chi_{zzz}$
<b>1a</b>	24	3	4	6
<b>1b</b>	19	4	3	15

<sup>a</sup> 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%  $\text{CHCl}_3$  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  $45^\circ$  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.<sup>37</sup> 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  $P_i(2\omega) = \sum_{j,k} \chi_{ijk} E_j(\omega) E_k(\omega)$  (where  $E(\omega)$  is a component of the fundamental beam's electric field),<sup>38</sup> there are only four independent components of the second-order susceptibility tensor:  $\chi_{xyz}$ ,  $\chi_{zxx}$ ,  $\chi_{xzx}$ , and  $\chi_{zzz}$ .<sup>39</sup> All four can be evaluated if the intensities and polarizations of the fundamental and second-harmonic beams are analyzed.<sup>40</sup> The values found are summarized in Table 3.

The thickness of the films was taken to be 30 nm. The reason is that the Langmuir isotherms showed the areas of compressed films of **1a** to be  $1.6 \text{ nm}^2/\text{molecule}$  and those of **1b** to be  $1.7 \text{ nm}^2/\text{molecule}$ . 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 films<sup>41</sup> and the way a copper phthalocyanine is in evaporatively deposited films,<sup>42</sup> 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,<sup>43</sup> and they do not agree with those calculated for the same molecules oriented with the phthalocyanine rings parallel to the surface.<sup>43,44</sup> 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.<sup>43</sup>

(37) Zhuang, X.; Wilk, D.; Marrucci, L.; Shen, Y. R. *Phys. Rev. Lett.* **1995**, *75*, 2144.

(38) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

(39)  $\chi_{xyz} = \chi_{xyx} = -\chi_{yxz} = -\chi_{yzx}$ ;  $\chi_{zxx} = \chi_{zzy}$ ;  $\chi_{xzx} = \chi_{xyx} = \chi_{zyx}$ .

(40) Kauranen, M.; Maki, J. J.; Verbiest, T.; Van Elshocht, S.; Persoons, A. *Phys. Rev. B* **1997**, *55*, R1985.

(41) Nuckolls, C.; Katz, T. J.; Verbiest, T.; Van Elshocht, S.; Kuball, H.-G.; Kiesewalter, S.; Lovinger, A. J.; Persoons, A. *J. Am. Chem. Soc.* **1998**, *120*, 8656.

(42) Kumagai, K.; Mizutani, G.; Tsukioka, H.; Yamauchi, T.; Ushioda, S. *Phys. Rev. B* **1993**, *48*, 14488.

(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  $0.35 \times 6 = 2 \text{ nm}^2$ .

(44) The face area should be  $\pi \times 3^2 = 28 \text{ nm}^2$ .

For molecules such as **1a** and **1b**, whose structures have  $D_4$  symmetry, the only components of the *molecular* hyperpolarizability tensor that can differ from zero are those associated with chirality.<sup>45</sup> These components can contribute only to chiral *macroscopic* susceptibility components. For the films considered here this means only to  $\chi_{xyz}$ . 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.<sup>10</sup>

Unclear, however, is why  $\chi_{zzz}$  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 exhibited by films of a planar achiral copper phthalocyanine.<sup>42</sup> In the latter case this has been attributed to electric-quadrupole and magnetic-dipole mechanisms.<sup>46</sup> Perhaps these mechanisms also account for the large values of  $\chi_{zzz}$  in Table 3, but another possibility is that in thin films these phthalocyanines, like others,<sup>5b</sup> combine with oxygen, which would alter the symmetries of the materials. The mass spectra, discussed in the Experimental Section (below) and in footnote 50, provide support for this hypothesis.

## 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% CHCl<sub>3</sub> and as pure materials. A calculation with the Macro-Model 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 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.

## Experimental Section

CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>3</sub>N were distilled from CaH<sub>2</sub>. DMF (Aldrich, anhydrous, 99.8%) and MeOH were boiled and cooled under N<sub>2</sub> to free them of oxygen. Zn dust (Aldrich, <10 μm, 98+%) was activated prior to use.<sup>47</sup> Glassware was flame-dried under vacuum and cooled under N<sub>2</sub>. Reactions were run under N<sub>2</sub>. Additions by syringe were made through rubber septa. “Chromatography” refers to “flash chromatography”.<sup>48</sup> The matrix for FAB mass spectra was 2-nitrophenyl octyl ether (Aldrich) and that 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 commercial 125 μm long silicon cantilever.

**6,13-Bis(dodecyloxy)-9,10-(diphenylmethylenedioxy)-1,4,15,18-tetraacetoxy[7]helicene (3).** A mixture of (*M*)-**2**<sup>19</sup> (0.205 g, 0.205 mmol), Zn (0.199 g, 3.07 mmol), and Et<sub>3</sub>N (2.1 g, 2.9 mL, 20.5 mmol) in 10 mL of Ac<sub>2</sub>O was heated in an oil bath at 105 °C for 30 min. CH<sub>2</sub>Cl<sub>2</sub> was added to the cooled reaction mixture, which was then washed with HCl (1 M) and saturated aqueous NaHCO<sub>3</sub>, dried (Na<sub>2</sub>SO<sub>4</sub>), and freed of solvents at reduced pressure. The residual solid,

when chromatographed (eluting with 25% EtOAc–75% hexane), gave 0.240 g (100%) of **3**, a yellow solid, mp 110–111 °C,  $[\alpha]_D -1615$  (c 0.066, CH<sub>2</sub>Cl<sub>2</sub>). IR (CCl<sub>4</sub>): 2928, 2855, 1765, 1618 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.43 (d, 2H, *J* = 8.5 Hz), 8.18 (d, 2H, *J* = 8.5 Hz), 7.80 (m, 4H), 7.41 (m, 6H), 6.90 (d, 2H, *J* = 8.4 Hz), 6.71 (s, 2H), 6.08 (d, 2H, *J* = 8.4 Hz), 4.32 (m, 2H), 4.08 (m, 2H), 2.41 (s, 6H), 2.00 (m, 4H), 1.60 (m, 4H), 1.50–1.25 (m, 32H), 0.89 (t, 6H, *J* = 6.8 Hz) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 168.9, 168.4, 154.1, 143.6, 142.2, 140.4, 138.4, 129.8, 128.8, 127.1, 126.9, 126.3, 125.0, 124.7, 122.0, 119.7 (2 peaks), 118.9, 117.4, 116.2, 96.9, 69.1, 32.4, 30.1 (m), 30.0, 29.8, 29.7, 26.8, 23.1, 21.9, 19.4, 14.6 ppm; HRMS (FAB) calcd for C<sub>75</sub>H<sub>82</sub>O<sub>12</sub>K (M + K)<sup>49</sup> 1213.5443, found 1213.5476.

**9,10-(Diphenylmethylenedioxy)-1,4,6,13,15,18-hexakis(dodecyloxy)-[7]helicene (4).** A flask containing Cs<sub>2</sub>CO<sub>3</sub> (1.30 g, 4.0 mmol) and **3** (0.24 g, 0.20 mmol) and fitted with a reflux condenser was evacuated and filled with N<sub>2</sub> three times. C<sub>12</sub>H<sub>25</sub>I (1.69 g, 1.71 mL, 5.7 mmol) and DMF (16 mL) were sequentially syringed in. After the mixture had stirred for 30 s, MeOH (2 mL) was syringed in, and the mixture was heated in an oil bath at 105 °C for 2 h. CH<sub>2</sub>Cl<sub>2</sub> was added to the cooled reaction mixture, which was then washed twice with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and freed of solvents at reduced pressure. The residue was loaded onto a chromatography column, which was first washed with hexane to remove C<sub>12</sub>H<sub>25</sub>I and then eluted with 25% benzene–75% hexane. MeOH was added to the product, and after this had been filtered through Celite, **4** was recovered by dissolving it in CH<sub>2</sub>Cl<sub>2</sub>. The yield was 0.324 g (96%) of a yellow oil,  $[\alpha]_D -720$  (c 0.030, CH<sub>2</sub>Cl<sub>2</sub>). IR (CCl<sub>4</sub>) 2927, 2855 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 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, 6H), 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, 84H), 1.06 (m, 8H), 0.91 (m, 22H), 0.60 (m, 8H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 152.5, 147.3, 147.1, 140.9, 137.6, 128.9 (2 peaks), 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), 29.5, 29.4, 29.1, 27.8, 26.6, 26.5, 25.4, 22.7, 14.1 ppm; HRMS (FAB) calcd for C<sub>115</sub>H<sub>170</sub>O<sub>8</sub> 1680.2930, found 1680.2949.

**9,10-Dihydro-9,10-dioxo-1,4,6,13,15,18-hexakis(dodecyloxy)[7]helicene (5).** DDQ (0.318 g, 1.40 mmol) was added to a mixture of **4** (0.206 g, 0.123 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (31 mL) and H<sub>2</sub>O (0.51 mL). After the mixture had stirred at room temperature for 16 h, it was filtered through Celite, which was rinsed with CH<sub>2</sub>Cl<sub>2</sub>. The organic solution was washed with saturated aqueous NaHCO<sub>3</sub> and dried (Na<sub>2</sub>SO<sub>4</sub>), and after the solvents had been removed under reduced pressure, the residue was chromatographed (eluting first with 40% benzene–60% hexane and then with 60% benzene–40% hexane). The yield was 0.123 g (66%) of **5**, a purple wax,  $[\alpha]_D -1680$  (c 0.050, CH<sub>2</sub>Cl<sub>2</sub>). IR (CCl<sub>4</sub>) 2927, 2856, 1744, 1676 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 8.27 (d, 2H, *J* = 8.2 Hz), 8.20 (d, 2H, *J* = 8.2 Hz), 7.05 (s, 2H), 6.31 (d, 2H, *J* = 8.6 Hz), 5.68 (d, 2H, *J* = 8.6 Hz), 4.27 (m, 2H), 4.12 (m, 2H), 3.95 (m, 2H), 3.86 (m, 2H), 2.88 (m, 2H), 2.72 (m, 2H), 1.97 (m, 4H), 1.86 (m, 4H), 1.7–1.0 (m, 108H), 0.87 (m, 22H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 182.5, 151.3, 147.3, 147.2, 143.6, 132.5, 126.7, 126.6, 124.0, 123.8, 120.8, 119.2, 107.3, 105.5, 100.8, 68.9 (2 peaks), 68.6, 32.0, 29.7–29.4 (m), 29.2, 29.1, 28.3, 26.6, 26.4, 25.7, 22.7, 14.1 ppm; HRMS (FAB) calcd for C<sub>102</sub>H<sub>160</sub>O<sub>8</sub>K<sup>49</sup> 1552.1750, found 1552.1733.

**Dicyanopyrazine 6.** A mixture of **5** (0.123 g, 0.081 mmol) and diaminomaleonitrile (0.351 g, 3.25 mmol) was refluxed in AcOH (20 mL) for 2.5 h. CH<sub>2</sub>Cl<sub>2</sub> was added to the cooled reaction mixture, which was washed successively with water, HCl (1 M), and saturated aqueous NaHCO<sub>3</sub>, and dried (Na<sub>2</sub>SO<sub>4</sub>). Chromatography (eluting with 30% benzene–70% hexane) gave 0.105 g (81%) of **6**, an oil,  $[\alpha]_D -820$  (c 0.050, CH<sub>2</sub>Cl<sub>2</sub>). IR (CCl<sub>4</sub>) 2927, 2855, 1612, 1569 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.20 (d, 2H, *J* = 8.6 Hz), 8.55 (d, 2H, *J* = 8.6 Hz), 7.16 (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, 88H), 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; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ 151.7, 147.3, 147.0, 142.5, 134.9, 129.7,

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(49) 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, 26.4, 25.5, 22.7, 14.1 ppm; HRMS (FAB) calcd for  $C_{106}H_{160}O_6N_4$  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'*-dimethylethanolamine) 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  $CH_2Cl_2$  and  $H_2O$ , and the organic layer, after it had been dried ( $Na_2SO_4$ ) and freed of solvent, was loaded onto a chromatography column, which was sequentially eluted with hexane, 25%  $CH_2Cl_2$ –75% hexane, and 1:1  $CH_2Cl_2$ –hexane. The yield of **1a**, a green solid, mp 149 °C,  $[\alpha]_D -2050$  (c 0.007,  $CH_2Cl_2$ ), was 6 mg (30%). IR ( $CCl_4$ ) 2927, 2855, 1739, 1709  $cm^{-1}$ ;  $^1H$  NMR ( $C_6D_6$ , 400 MHz)  $\delta$  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  $C_{424}H_{641}N_{16}O_{24}Cu$  (M + 1) 6410.4, found 6410.8.<sup>50</sup>

**Nickel Phthalocyanine 1b.** A solution of  $Ni(OAc)_2 \cdot 4H_2O$  (0.25 mL of a 0.013 M solution in *N,N'*-dimethylethanolamine) 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  $CH_2Cl_2$  and  $H_2O$ . The organic layer was dried ( $Na_2SO_4$ ) and, after the solvents had been removed under reduced pressure, chromatography (eluting first with 30%  $CH_2Cl_2$ –70% hexane, then with 40%  $CH_2Cl_2$ –60% hexane) gave

(50) For **1a** and **1b**, smaller peaks were also observed with *m/z* 6442.9 and 6438.2, respectively, which correspond to  $M + O_2$ . An  $M + O_2$  peak has previously been observed in the mass spectra of a number of phthalocyanines.<sup>51</sup> It is unlikely that  $O_2$  is absorbed in solution since the NMR spectra of **1b** are those of a diamagnetic compound. Probably  $O_2$  is absorbed by the neat material as by other phthalocyanines.<sup>5b</sup>

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4 mg (20%) of **1a**, a green solid, mp 135 °C,  $[\alpha]_D -1650$  (c 0.012,  $CH_2Cl_2$ ). IR ( $CCl_4$ ) 2927, 2855, 1741, 1605  $cm^{-1}$ ;  $^1H$  NMR ( $CDCl_3$ , 400 MHz)  $\delta$  10.57 (d, 8H,  $J = 8.5$  Hz), 9.01 (d, 8H,  $J = 8.5$  Hz), 7.27 (s, 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)  $\delta$  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  $C_{424}H_{641}N_{16}O_{24}Ni$  (M + 1) 6405.6, found 6405.6.<sup>50</sup>

**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  $^1H$  and  $^{13}C$  NMR and IR spectra of **1b**, **2–6**, the  $^1H$  NMR and IR spectrum of **1a**, the MALDI-TOF mass spectra of **1a** and **1b**, and the CD spectrum of a  $1 \times 10^{-6}$  M solution of **1a** in  $CH_2Cl_2$  (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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