Star-Shaped Stilbenoid Phthalocyanines

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Star-shaped stilbenoid zinc phthalocyanines with π-conjugated oligo(*p*-phenylenevinylene)s (OPVs) have been prepared for fine-tuning of absorption and fluorescence bands. The direct introduction of OPV segments at β-positions of Zn phthalocyanines induced shifts in the Q-band and emission band compared to the complex lacking OPV side chains. Furthermore, these shifts strongly depended on the number and the length of OPV side chains. The stilbenoid phthalocyanine modified with flexible alkyl chains forms a discotic mesophase in the bulk. The structure of the mesophase was analyzed by X-ray and UV−vis measurements. This compound organized spontaneously into one-dimensional columnar assemblies by intermolecular $\pi-\pi$ and van der Waals interactions.

Introduction

Design and synthesis of multicomponent giant molecules with precise sizes and shapes have attracted much attention because of their potential for use in the fabrication of nanoscopic electronic and photonic molecular devices.[1] The hybridization of molecular components enables the creation of interesting physical properties such as a highly efficient electron/energy transfer within a designed molecule.[2] Owing to their rigid geometry as well as their unique electronic and photonic properties, phthalocyanines and their metal complexes are attractive building components. Phthalocyanine-based multicomponent systems have been explored, including porphyrins, ferrocenes, tetrathiafulvalenes, oligopyridyl−metal complexes, dendrimers, and C_{60}.[3−9] Recently, phthalocyanines with π-conjugated oligomers and polymers have become the subject of intense research.[10] Lindsey and co-workers synthesized Pc-cored pentads in which four porphyrin molecules were covalently linked with one Pc through phenylethyne linkers.[11] They found that the electronic communication between each component through conjugate linkages enabled rapid intermolecular energy transfer. Several research groups also synthesized phthalocyanine dimers and cyclic oligomers linked through ethynyl, butadiynyl, diethynyl, and phenylenevinylene linkers. Hanack and co-workers reported the first synthesis of an OPV-bridged phthalocyanine dimer.[12] Torres and co-workers reported the syntheses of butadiynyl- and ethynyl-bridged metallophthalocyanine dimers and designed push−pull heterodimetallic phthalocyanine dimers for the investigation of the second-order nonlinear optical properties.[13] Cook and Heeney succeeded in isolating diphthalocyaninatodehydro[12]annulene by the coupling reaction of diethynylated phthalocyanine and investi-

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gated its thermotropic liquid crystallinity.[14]

Lengthy π-conjugated oligomers have been utilized as building blocks for the formation of well-defined supramolecular structures.[15] Organization of π-conjugated oligomers was achieved by using thermotropic and lyotropic liquid crystallinity, self-assembly of block copolymers, and complexation through noncovalent bonds such as hydrogen bonds.[16−18] Organizational control over the orientation of π-conjugated oligomers is important for developing nanoscopic molecular systems. For example, efficient charge transport was observed in the organization of mono- and bithiophenes in which the thiophene rings were arranged by the formation of intermolecular hydrogen bonds between urea groups.[19]

In this paper, we describe syntheses of novel star-shaped phthalocyanine derivatives with four or eight lengthy OPV side chains and their self-organization properties. Direct attachments of π-conjugated oligomers with the phthalocyanine ring may offer the possibility of tuning the position of the absorption and fluorescence spectra of phthalocyanines. Self-organization of star-shaped phthalocyanines may enable the creation of unique columnar structures as a result of the stacking of central phthalocyanine rings.[20] The electron conducting properties of the phthalocyanine assemblies have been extensively investigated.[21] The organization of star-shaped phthalocyanines provides two paths for an electron or charge transfer: the stacking of phthalocyanine rings and the arrangement of OPV side chains. We will show that star-shaped phthalocyanine with flexible alkyl chains forms a thermotropic discotic mesophase.

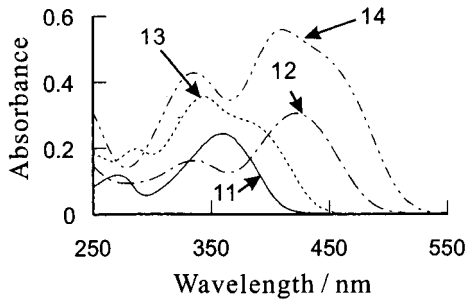

Figure 1. UV−vis spectra of dicyanides **11**−**14** in CH_2Cl_2. [**11**−**14**] = 10.0 μM.

Table 1. Spectroscopic Data for 6−9, 11−14, and 16−19

	absorption,[a] λ_{max}, nm (log ϵ, M^{-1} cm^{-1})	emission,[b] λ_{max}, nm
6	328 (4.47)	420
7	400 (4.68), 328 (4.39)	480
8	360 (4.50), 318 (4.62)	475
9	430 (4.79), 392 (4.87), 330 (4.66)	507
11	358 (4.38)	506
12	422 (4.47), 334 (4.20)	550
13	390 (4.45), 344 (4.58)	538
14	446 (4.68), 410 (4.75), 334 (4.63)	574
16	712 (5.14), 338 (5.15)	724
17	726 (5.22), 390 (5.21)	738
18	738 (5.25), 346 (5.16)	747
19	762 (5.29), 394 (5.39)	773

[a] In CH_2Cl_2 solution. [b] In degassed CH_2Cl_2 solution.

Results and Discussion

Syntheses of Phthalocyanine Precursors. Phthalocyanine precursors **11**−**15** were synthesized from 4,5-dibromoxylene as a starting material through seven synthetic-step procedures as shown in Scheme 1. One or two CH_3 groups in the starting material were converted into CH_2Cl groups. Phosphonate compounds **4** and **5** were obtained from 4,5-dibromo-2-methylbenzyl chloride and 1,2-dichloromethyl-4,5-dibromobenzene by a Michaelis−Arbuzov reaction. Wittig−Horner coupling reactions between phosphonates and aldehydes **1**−**3** gave compounds **6**−**10** in yields of 60−70%.[22] In the final step, the bromides in **6**−**10** were transformed into dinitriles **11**−**15** by treatment with CuCN in 1-methyl-2-pyrrolidone (NMP). Five pure phthalocyanine precursors were isolated as colored crystals and fully characterized using ^1H and ^{13}C NMR spectroscopy, mass spectrometry, FT-IR, and elemental analysis. The products exhibit an IR absorption band around 950 nm arising from the wagging vibration of the trans-configured double bonds. UV−vis spectra of synthesized phthalocyanine precursors **11**−**14** are shown in Figure 1, and the absorption maxima (λ_{max}) and molar absorption coefficients (ϵ) of **6**−**14** are collected in Table 1. The smallest compound **6** exhibits the λ_{max} at 328 nm corresponding to the $\pi-\pi^*$ transition of stilbene. The λ_{max} and the emission maximum of dinitrile **11** were red-shifted compared to that of the parent compound **6**, implying that the conversion of the dibromide into the dinitrile affected the length of the π-conjugated system. Furthermore, the λ_{max} and the emission maxima also shift to lower energies with the extent for the π-system as the OPV length increases.

Syntheses of Star-Shaped Stilbenoid Phthalocyanines. Star-shaped stilbenoid phthalocyanines **16**−

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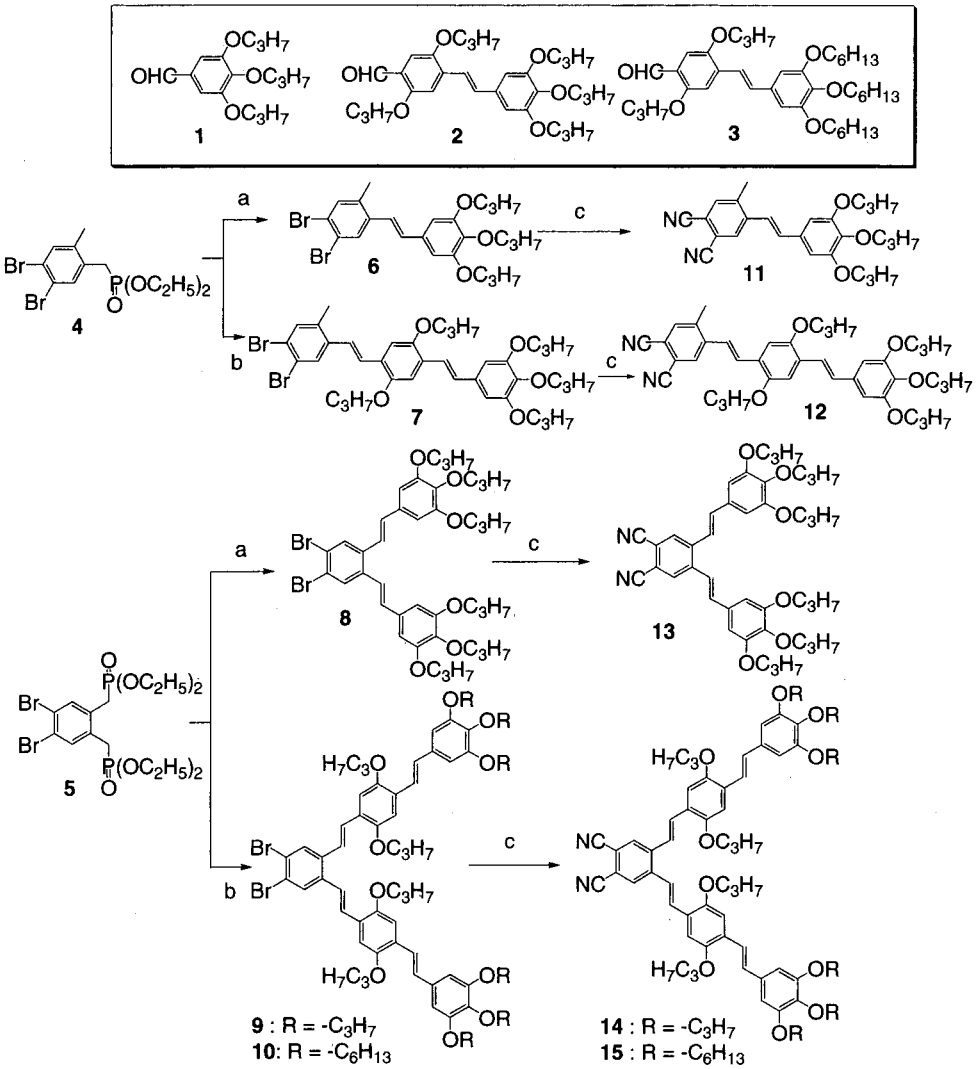
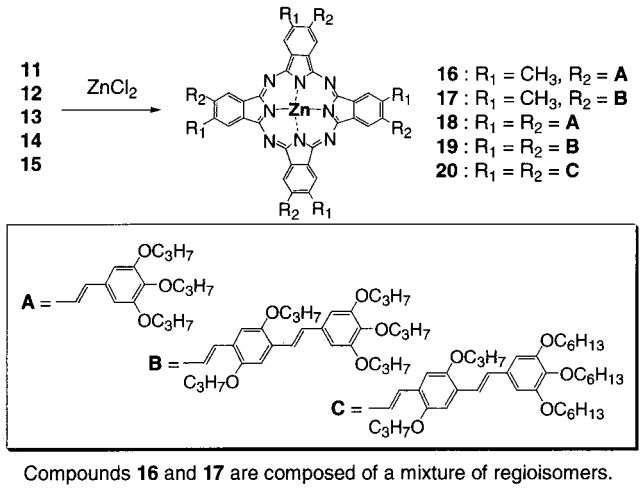
Scheme 1



a: **1**, *t*BuOK, THF; b: **2** or **3**, *t*BuOK, THF; c: CuCN, NMP

Scheme 2



Compounds **16** and **17** are composed of a mixture of regioisomers.

20 with four or eight OPV side chains were prepared by two methods (Scheme 2). Linear dinitriles **11** and **12** were converted into corresponding tetra-substituted zinc phthalocyanines **16** and **17** by heating at 140 °C in *n*-hexanol in the presence of $ZnCl_2$ and diazabicyclo-[5.4.0]undec-7-ene (DBU) in yields of 60 and 61%, respectively. However, tetracyclization of **13** gave corresponding octa-substituted phthalocyanine **18** in only 13% yield by using the DBU method. Compounds **19** and **20**, possessing eight OPV side chains, could not be obtained by the DBU method. Dinitriles **14** and **15** were converted into **19** and **20** by refluxing in 2-(dimethylamino)ethanol in the presence of $ZnCl_2$. After purification with column chromatography, ≈20% of pure **19** and **20** were isolated. All stilbenoid phthalocyanines were fully characterized by ^{1}H NMR and matrix-assisted laser-desorption ionization time-of-flight (MALDI-TOF)-mass spectrometry, and they were highly soluble in $CHCl_3$, toluene, THF, and pyridine. The introduction of alkyl groups within the OPV side chains improved solubility of stilbenoid phthalocyanines in organic solvents.

Figures 2 and 3 show UV−vis and fluorescence spectra of compounds **16**−**19**. Zinc phthalocyanines **16**−**19** decorated with different OPV side chains exhibited a sharp Q peak at 712, 726, 738, and 762 nm, respectively.[23] The position of the Q-band peaks shifts to a longer wavelength with an increase in the OPV's length

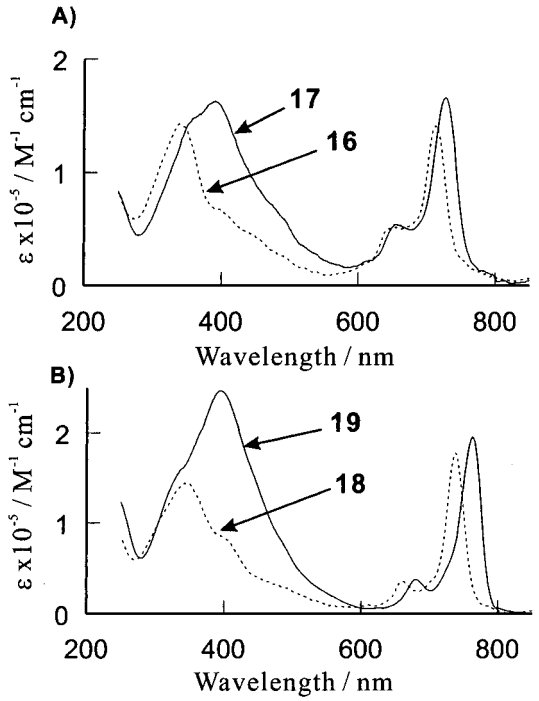


Figure 2. UV−vis spectra of **16**−**19** in CH_2Cl_2: (a) **16** and **17**; (b) **18** and **19**.

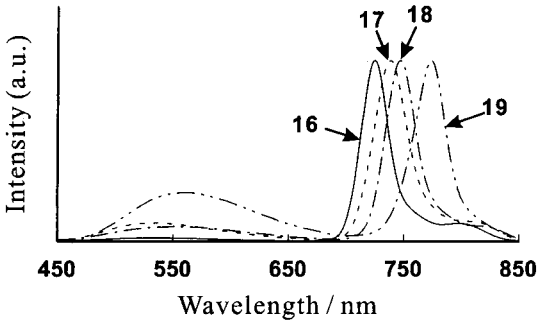


Figure 3. Steady-state fluorescence spectra of **16**−**19** upon excitation at the absorption maximum of the stilbenoid components. The measurements were carried out in degassed CH_2Cl_2 solution at room temperature. All spectra are normalized to a constant absorbance at the excitation wavelength.

and number. The absorption maximum of the Q-band for the largest compound **19** shifts to 84 nm compared to that of zinc(II) tetra(*tert*-butyl)phthalocyanine (Zn-(*t*-Bu)$_4$Pc) lacking the OPV side chains (λ_{max} = 678 nm), and the λ_{max} of **19** was almost equal to that of zinc(II) tetra(*tert*-butyl)naphthalocyanine (Zn(*t*-Bu)$_4$Nc) (λ_{max} = 778 nm). Broad absorptions are observed in the range of 300−600 nm for **16**−**19,** ascribed to the sum of the $\pi-\pi^*$ transitions of OPV side chains and the Soret bands of the Zn phthalocyanine core. Thus, direct introduction of OPV side chains into the Zn phthalocyanine core resulted in fine-tuning of the position of the Q-band, and the synthesized star-shaped stilbenoid phthalocyanines could absorb a large part of the visible light region from 350 to 800 nm. The emission also shifted with an increase in the OPV length, as shown in Figure 3. With the excitation at the absorption band of OPV side chains in **19**, the emission was mostly from the Zn phthalocyanine core, and the residual fluorescence from the OPV units was weak. A mixture of Zn-(*t*-Bu)$_4$Pc and **14** showed no emission peaks from the Zn(*t*-Bu)$_4$Pc with excitation at the absorption band of **14**. This result suggested an efficient intramolecular energy transfer from the OPV side chains to the Zn phthalocyanine core.

Aggregation Behavior of Stilbenoid Phthalocyanine. Phthalocyanine macrocycles substituted with flexible alkyl chains form a discotic liquid-crystalline phase in which the columnar aggregates are ordered in a two-dimensional hexagonal lattice.[24] Stilbenoid compounds were also investigated as a liquid-crystalline material. Meier and co-workers reported liquid-crystalline behaviors of stilbenoid dendrimers containing peripheral trihexyloxy-substituted benzene rings.[15b,c] The interaction of the rigid skeletons and the microscopic phase segregation between rigid skeletons and surrounding alkoxy chains induces the formation of mesophases. The combination of a disklike phthalocyanine core with stilbenoid side chains may exhibit unique aggregation behavior because of their intermolecular $\pi-\pi$ interactions. In this context, we synthesized trihexyloxy-substituted stilbenoid phthalocyanine **20**. This compound contains two rigid skeletons: a central phthalocyanine core and eight OPV chains. Phthalocyanine **20** and its parent compound **15** displayed reversible thermotropic liquid-crystalline behavior. Differential scanning calorimetry (DSC), temperature-controlled polarizing optical microscopy, and X-ray diffraction (XRD) were performed to study the phase behaviors of **15** and **20**. DSC experiments showed that dinitrile **15** exhibits two endothermic peaks at 28 °C (ΔH = 11.5 kJ/mol) and 148 °C (ΔH = 69.7 kJ/mol), corresponding to the phase transition from the crystalline into the liquid crystalline and the melting transition, respectively. Polarization microscopy revealed a birefringent pattern (Figure 4a). On the other hand, the zinc phthalocyanine **20** exhibited a DSC peak at 16 °C (ΔH = 43.4 kJ/mol). Upon further heating, a second small transition was found at 220 °C, and the viscosity was critically reduced above this temperature. When **20** was slowly cooled from the isotropic phase, homeotropically aligned patterns shaped as six-pointed stars appeared under the optical microscope, which is characteristic for the hexagonal columnar mesophase D_h (Figure 4b).[25]

The structure of the mesophase of **20** was determined by XRD at 156 °C. The X-ray diagram of **20** displays a high-intensity reflection at the low Bragg angle, a set of weak reflections in the small-angle region, and an amorphous halo and a broad reflection at the higher angle (Figure 4c). The observed reflections of the mesophase can be indexed to a hexagonal unit cell with *a*

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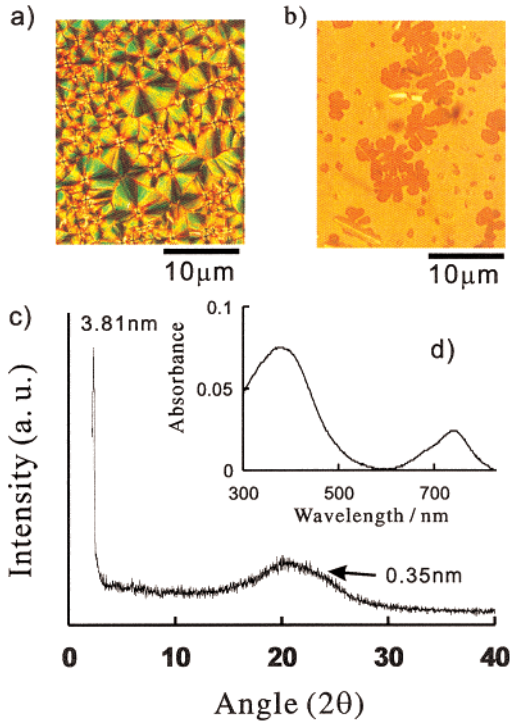

Figure 4. (a) Polarized optical micrograph of **15** at 72 °C after cooling from the isotropic phase. (b) Digitate stars under an uncrossed polarized microscope when the isotropic liquid of **20** is cooled slowly. Some linear birefringent defects are present. (c) Temperature-controlled XRD pattern of **20** at 156 °C. (d) Temperature-controlled UV−vis spectra of a thin film of **20** at 130 °C.

= 3.93 nm. The intense reflection at 3.81 nm can be attributed to the (100) reflection of a D_h mesophase. Small peaks observed around 2.2 and 1.9 nm results from (110) and (200) reflections, respectively. The center-to-center distance of **20** along the *a* axis is very close to the diameter of the rigid segment within **20** as calculated from the molecular model. The diffuse halo at around 0.43 nm is characteristic for a liquidlike order of alkyl chains. In addition, **20** exhibited a broad reflection around *d*-spacing of 0.35 nm because of the intracolumnar stacking distance between the phthalocyanine cores. Figure 4d shows the UV−vis spectra of the thin film of **20** on a quartz plate at 130 °C. The spectra of **20** in chloroform solution exhibited a sharp Q-band at 773 nm that is characteristic for nonaggregated phthalocyanine species. In contrast, the spectrum of the thin film is broadened, and the Q-band is blue-shifted to 735 nm. This spectral change can be ascribed to the formation of phthalocyanine stacks. Furthermore, the $\pi-\pi^*$ transition of the OPV segment is blue-shifted to $\lambda_{max} = 377$ nm. Meijer and co-workers reported UV−vis spectral changes of hydrogen-bonded OPV derivatives by the formation of supramolecular stacks in solvents.[26] The observed blue shift suggests the aggregation of OPV segments within the columnar structure. On the basis of the XRD pattern and UV−vis spectral data, we assume that stilbenoid phthalocyanine **20** assembles into noncovalent one-dimensional columnar aggregates containing the ordered stacking of phthalocyanine stacks and surrounding OPV aggregates, as shown in Figure 5. One-dimensional columnar aggregates of stilbenoid phthalocyanines can be regarded as molecular electron-conducting wires through the ordered stacking of phthalocyanines and the arrangement of OPV side chains. The electron conductivity within the columnar aggregates may be tunable by the alteration of OPV side chains.

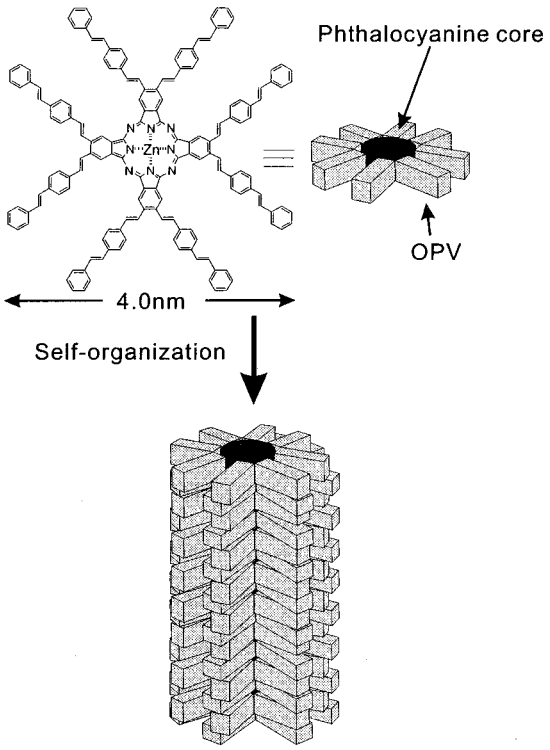

Figure 5. Schematic representation of the columnar aggregate of **20** in the liquid-crystalline state.

Conclusion

Novel star-shaped stilbenoid phthalocyanines functionalized with lengthy OPV chains have been successfully synthesized. The direct introduction of OPV chains at β-positions of Zn phthalocyanines induces shifts in the Q-band and the emission band compared to the complex lacking OPV side chains. Fluorescence spectroscopy of the stilbenoid phthalocyanines provides evidence of an efficient photoinduced intramolecular energy transfer between the OPV side chains and the phthalocyanine core. That stilbenoid phthalocyanine with flexible alkyl chains organized into one-dimensional columnar aggregates, as could be concluded from DSC, temperature-controlled polarizing optical microscopy, XRD, and UV−vis measurements. OPV side chains are arranged along with the ordered stacks of phthalocyanine cores. Work is underway in our laboratory to measure the electronic conductivity of the self-organized film made of stilbenoid phthalocyanines.

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 FT-NMR spectrometer operating in $CDCl_3$ solution at 400.13 MHz for ^{1}H. Chemical shifts were relative to internal TMS. Elemental analyses were performed with Perkin-Elmer series II CHNS/O analyzer 2400. IR spectra were obtained on a JASCO FS-420 spectrometer as KBr pellets. MALDI-TOF mass spectra were obtained on a Per-

(26) Schenning, A. P. H. J.; Jonkheijm, P.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 409.

Septive Biosystems Voyager DE-Pro spectrometer with dithranol as a matrix. UV−vis and fluorescence spectra were recorded on a JASCO V-570 and a JASCO FP-750. XRD patterns were measured with Cu Kα radiation using a Rigaku Geigerflex. Melting points were recorded using a Shibata MEL-270 melting point apparatus and are corrected.

Materials. All chemicals were purchased from commercial suppliers and used without purification. The precursor 4,5-dibromo-2-methylbenzyl alcohol, 3,4,5-tri(propoxy)benzaldehyde (**1**), (*E*)-4-(3,4,5-tri(propoxy)styryl)-2,5-bis(propoxy)benzaldehyde (**2**), and (*E*)-4-(3,4,5-tri(hexyloxy)styryl)-2,5-bis-(propoxy)benzaldehyde (**3**) were synthesized by the literature methods.[2,7b,22] All solvents were distilled before each procedure. Adsorption column chromatography was performed using alumina (Wako, 200 mesh) or silica gel (Wakogel C-200, 200 mesh). Analytical thin-layer chromatography was performed on commercial Merck plates coated with silica gel 60 F_{254} or aluminum oxide 60 F_{254}.

1,2-Acetoxymethyl-4,5-dibromobenzene. *N*-Bromosuccinimide (NBS) (10.4 g, 58.3 mmol), 1,2-dibromo-4,5-dimethylbenzene (7.5 g, 28.4 mmol), and benzoyl peroxide (BPO) (0.18 g, 0.76 mmol) in 200 mL of CCl_4 were refluxed with stirring for 3 h. After filtration to remove the reacted succinimide, the solvent was removed to give the brominated compound (11.8 g, 98%) as a pale yellow solid, which was used without further purification. The bromination was checked by ^{1}H NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (s, Ar, 2H), 4.62 (s, $-CH_2$-Br, 4H). The brominated compounds (11.0 g, 26.2 mmol) and CH_3COOK (58.0 g, 59.1 mmol) were dissolved in 120 mL of acetone. After refluxing overnight, the mixture was filtrated and the solvent was removed. Water was added and the mixture was extracted with $CHCl_3$ three times. The organic layers were combined and washed with water and brine, subsequently dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by recrystallization three times from methanol to give 1,2-acetoxymethyl-4,5-dibromobenzene (14.0 g, 47%) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, Ar, 2H), 5.08 (s, OCH_2, 4H), and 2.01 (s, $-COCH_3$, 6H). FT-IR (KBr): ν 1752 cm^{-1} (C═O). Anal. Calcd for $C_{12}H_{12}O_4Br_2$: C, 37.93; H, 3.18. Found: C, 37.86; H, 3.26.

1,2-Dibromo-4,5-dihydroxymethylbenzene. 1,2-Acetoxymethyl-4,5-dibromobenzene (9.9 g, 26.0 mmol) was dissolved 10 wt % methanolic sodium hydroxide solution and refluxed for 2 h. The reaction mixture was poured into water and the white precipitate was collected. After the solution was dried in vacuo, recrystalizations from petroleum ether gave 1,2-dibromo-4,5-dihydroxymethylbenzene (7.7 g, 98%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, Ar, 2H), 4.57 (s, $-CH_2OH$, 4H). FT-IR (KBr): ν 3425 cm^{-1} (OH). Anal. Calcd for $C_8H_8O_2Br_2$: C, 32.47; H, 2.72. Found: C, 32.50; H, 2.78.

1,2-Dichloromethyl-4,5-dibromobenzene. 1,2-Dibromo-4,5-dihydroxymethylbenzene (7.0 g, 25.0 mmol) was dissolved in 100 mL of CH_2Cl_2 and 0.9 mL of dry DMF. $SOCl_2$ (4.34 mL) was added to the solution of **2** and the reaction mixture was stirred for 30 min. The solvent and excess $SOCl_2$ were removed under vacuum. The resulting solid was dissolved in Et_2O and then washed with water, dried over $MgSO_4$, and evaporated to dryness. The product was purified by column chromatography (silica gel, CH_2Cl_2). Recrystallization from methanol gave a white crystal (4.75 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, Ar, 2H), 4.63 (s, $-CH_2Cl$, 4H). Anal. Calcd for $C_8H_6Cl_2Br_2$: C, 28.87; H, 1.82. Found: C, 28.90; H, 1.85.

4,5-Dibromo-2-methylbenzyl chloride was synthesized following the same procedure of 1,2-dichloromethyl- 4,5-dibromobenzene from 4,5-dibromo-2-methylbenzyl alcohol. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, Ar, 1H), 7.47 (s, Ar, 1H), 4.49 (s, 2H, CH_2Cl), 2.53 (s, $-CH_3$, 3H). Anal. Calcd for $C_8H_7ClBr_2$: C, 32.20; H, 2.36. Found: C, 32.30. H, 2.35.

Diethyl(3,4-dibromo-2-methylbenzyl)phosphonate (4). Triethylphosphite (5.0 mL, 31.1 mmol) and 4,5-dibromo-2-methylbenzyl chloride (4.3 g, 14.4 mmol) were stirred at 160 °C for 6 h. The excess triethylphosphite was removed by distillation in vacuo. The residue was purified by column chromatography (silica gel, ethyl acetate) to give **4** (3.7 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, Ar, 1H), 7.42 (s, Ar, 1H), 4.02 (m, 4H, OCH_2), 3.07 (d, 2H, CH_2P), 2.32 (s, 3H, CH_3), 1.27 (t, $-OCH_2CH_3$, 6H).

Bisphosphonate **5** was synthesized following the same procedure of **4** from 1,2-dichloromethyl-4,5-dibromobenzene. Yield: 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, Ar, 2H), 4.01 (m, 8H, OCH_2), 3.30 (d, 4H, CH_2P), 1.26 (t, $-OCH_2CH_3$, 12H).

(*E*)-4-(3,4,5-Tripropoxystylryl)-1,2-dibromo-5-methylbenzene (6). A solution of 3,4,5-tri(propoxy)benzaldehyde (2.0 g, 5.0 mmol) and **4** (1.4 g, 6.0 mmol) in dry THF was added dropwise to a solution of *t*-BuOK (2.2 g, 19.0 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature and poured into cooled water. After addition of 17 mL of 6 M HCl aqueous solution, the aqueous phase was extracted with CH_2Cl_2. The combined organic layer was washed with water, dried over $MgSO_4$, and evaporated to dryness. Recrystallization from methanol gave a pale yellow crystal (1.60 g, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, Ar, 1H), 7.42 (s, Ar, 1H), 6.98 (d, olef*H*,1H), 6.87 (d, olef*H*,-1H), 6.70 (s, Ar, 2H), 3.97 (m, $OCH_2CH_2CH_3$, 6H), 2.34 (s, CH_3, 3H), 1.81 (m, $OCH_2CH_2CH_3$, 6H), 1.05 (m, $OCH_2CH_2CH_3$, 9H). Anal. Calcd for $C_{24}H_{30}Br_2O_2$: C, 57.77; H, 5.75. Found: C, 57.80; H, 5.80. MALDI-TOF-Ms (dithranol) *m*/*z*: 525 (M + H).

Compounds **7**−**10** were synthesized by the same procedure of **6**.

7. This was prepared from **4** and **2**. Recrystallization from methanol gave a yellow crystal. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, Ar, 1H), 7.43 (s, Ar, 1H), 7.34 (d, olef*H*, 1H), 7.25 (d, Ar, 2H), 7.03 (m, olef*H*, 3H), 6.74 (s, Ar, 2H), 3.97 (m, $OCH_2CH_2CH_3$, 10H), 2.34 (s, CH_3, 3H), 1.81 (m, OCH_2CH_2-CH_3, 10H), 1.05 (m, $OCH_2CH_2CH_3$, 15H). Anal. Calcd for $C_{38}H_{48}Br_2O_5$: C, 61.30; H, 6.50. Found: C, 61.40. H, 6.50. MALDI-TOF-Ms (dithranol) *m*/*z*: 743 (M + H).

8. This was prepared from **5** and **1**. Recrystallization from methanol gave a yellow crystal. Yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, Ar, 2H), 7.11 (d, olef*H*, 2H), 6.89 (d, olef*H*, 2H), 6.71 (s, Ar, 4H), 3.96 (m, $OCH_2CH_2CH_3$, 12H), 1.82 (m, $OCH_2CH_2CH_3$, 12H), 1.07 (m, $OCH_2CH_2CH_3$, 18H). Anal. Calcd for $C_{40}H_{52}Br_2O_6$: C, 60.92; H, 6.65. Found: C, 60.88; H, 6.70. MALDI-TOF-Ms (dithranol) *m*/*z*: 787 (M + H).

9. This was prepared from **5** and **2**. Recrystallization from 2-methoxyethanol gave an orange crystal. Yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, Ar, 2H), 7.30−7.38 (m, Ar and olef*H*, 6H), 7.08 (m, olef*H*, 6H), 6.74 (s, Ar, 4H), 3.97 (m, OCH_2-CH_2CH_3, 20H), 1.82 (m, $OCH_2CH_2CH_3$, 20H), 1.05 (m, OCH_2-CH_2CH_3, 30H). Anal. Calcd for $C_{66}H_{88}Br_2O_{10}$: C, 66.66, H, 7.24. Found: C, 66.70; H, 7.30. MALDI-TOF-Ms (dithranol) *m*/*z*: 1223 (M + H).

10. This was prepared from **5** and **3**. Recrystallization from 2-methoxyethanol gave an orange crystal. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, Ar, 2H), 7.43 (s, Ar, 4H), 7.34 (d, olef*H*, 2H), 7.08 (m, olef*H*, 6H), 6.74 (s, Ar, 4H), 3.97 (m, OCH_2-CH_2CH_3, 20H), 1.82 (m, $OCH_2CH_2CH_3$, 20H), 1.49 (m, CH_2, 12H), 1.35 (m, CH_2, 24H), 1.09 (t, CH_3, 6H), 1.03 (t, CH_3, 6H), 0.90 (m, CH_3, 18H). Anal. Calcd for $C_{86}H_{124}Br_2O_{10}$: C, 69.90; H, 8.46. Found: C, 69.95; H, 8.50. MALDI-TOF-Ms (dithranol) *m*/*z*: 1475 (M + H).

(*E*)-4-(3,4,5-Tripropoxystylryl)-1,2-dicyano-5-methylbenzene (11). The mixture of **6** (0.6 g, 1.10 mmol) and CuCN (0.6 g, 6.84 mmol) in 10 mL of NMP was refluxed for 4 h under N_2. After it was cooled, the reaction mixture was poured into 100 mL of 10 wt % aqueous ethylenediamine solution and air was allowed to flow through the solution for 8 h. The remaining solid was filtrated and washed with 10 wt % aqueous ethylenediamine solution several times. The product was purified by column chromatography (silica gel, CH_2Cl_2). Recrystallization from methanol gave a yellow crystal (0.3 g, 34%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, Ar, 1H), 7.58 (s, Ar, 1H), 7.04 (s, olef*H*, 2H), 6.74 (s, Ar, 2H), 4.00 (m, $OCH_2CH_2CH_3$, 6H), 2.51 (s, CH_3, 3H), 1.81 (m, $OCH_2CH_2CH_3$, 6H), 1.05 (m, OCH_2-CH_2CH_3, 9H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 135.83, 133.96, 133.80, 131.24, 130.73, 125.33, 122.62, 122.01, 116.50, 108.24, 106.26, 75.43, 71.30, 23.83, 23.14, 22.94,20.53, 19.63, 10.82. FT-IR (KBr): ν 2232 cm^{-1} (CN). Anal. Calcd for $C_{26}H_{30}N_2O_2$:

C, 74.61; H, 7.22; N, 6.69. Found: C, 74.44; H, 7.37; N, 6.51. EI-Ms *m*/*z*: 418.

Dinitriles **12**−**15** were synthesized from dibromides **7**−**10** following the same procedure of **11**.

12. Yield: 34%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, Ar, 1H), 7.57 (s, Ar, 1H), 7.32−7.43 (m, Ar and olef*H*, 3H), 7.04−7.12 (m, olef*H*, 3H), 6.75 (s, Ar, 2H), 4.00 (m, $OCH_2CH_2CH_3$, 10H), 2.51 (s, CH_3, 3H), 1.83 (m, $OCH_2CH_2CH_3$, 10H), 1.10 (m, $OCH_2CH_2CH_3$, 15H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 153.69, 152.42, 151.14, 143.21, 141.57, 135.57, 133.24, 131.57, 130.51, 130.24, 129.52, 125.00, 123.23, 122.52, 116.22, 113.95, 113.25, 112.93, 110.30, 105.96, 75.54, 71.81, 71.20, 71.08, 23.90, 23.25, 23.22, 23.15,20.63, 11.19, 11.13, 10.97. FT-IR (KBr): ν 2233 cm^{-1} (CN). Anal. Calcd for $C_{40}H_{48}N_2O_5$: C, 75.44; H, 7.60; N, 4.40. Found: C, 75.22; H, 7.53; N, 4.26. MALDI-TOF-Ms (dithranol) *m*/*z*: 636 (M + H).

13. Yield: 77%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, Ar, 2H), 7.18 (d, olef*H*, 2H), 7.04 (d, olef*H*, 2H), 6.74 (s, Ar, 4H), 3.97 (m, $OCH_2CH_2CH_3$, 12H), 1.81 (m, $OCH_2CH_2CH_3$, 12H), 1.03 (m, $OCH_2CH_2CH_3$, 18H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 153.66, 151.89, 151.25, 138.83, 137.83, 133.45, 131.76, 129.70, 128.38, 128.20, 126.50, 125.40, 123.60, 122.80, 116.26, 112.52, 110.50, 105.85, 75.53, 71.72, 71.29, 71.18, 23.90, 23.25, 23.15, 11.13, 11.08, 10.97. FT-IR (KBr): ν 2232 cm^{-1} (CN). Anal. Calcd for $C_{42}H_{52}N_2O_6$: C, 74.09; H, 7.70; N, 4.11. Found: C, 74.20; H, 7.60; N, 4.16. MALDI-TOF-Ms (dithranol)-*m*/*z*: 680 (M + H).

14. Yield: 50%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, Ar, 2H), 7.43 (s, Ar, 4H), 7.35 (d, olef*H*, 2H), 7.09 (m, olef*H*, 6H), 6.75 (s, Ar, 4H), 3.97 (m, $OCH_2CH_2CH_3$, 20H), 1.85 (m, $OCH_2CH_2CH_3$, 20H), 1.10 (m, $OCH_2CH_2CH_3$, 30H). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 153.69, 152.33, 151.17, 141.75, 139.04, 133.24, 131.99, 131.85, 130.44, 129.47, 125.28, 123.78, 122.53, 116.32, 113.39, 112.87, 110.28, 105.95, 75.54, 71.77, 71.20, 71.14, 23.90, 23.24, 23.15, 11.13, 11.08, 10.97. FT-IR (KBr): ν 2231 cm^{-1} (CN). MALDI-TOF-Ms (dithranol) *m*/*z*: 1116 (M + H).

15. Yield: 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, Ar, 2H), 7.43 (s, Ar, 4H), 7.34 (d, olef*H*, 2H), 7.09 (m, olef*H*, 6H), 6.74 (s, Ar, 4H), 4.00 (m, OCH_2, 20H), 1.81 (m, CH_2, 20H), 1.51 (m, CH_2, 12H), 1.34 (m, CH_2, 24H), 1.09 (m, CH_3, 6H), 1.01 (m, CH_3, 6H), 0.90 (m, CH_3, 18H). FT-IR (KBr): ν 2231 cm^{-1} (CN). MALDI-TOF-Ms (dithranol): *m*/*z* 1369 (M + H).

Tetracyclization of Dicyanides (16−18). A mixture of $ZnCl_2$ (32.6 mg, 0.25 mmol), **11** (0.1 g, 0.24 mmol), and DBU (0.1 mL) in 2.0 mL of 1-hexanol was heated at 140 °C with stirring for 24 h. After the mixture was cooled, the solvent was removed and the residue was washed with methanol several times to remove excess Zn ion. The residue was purified by column chromatography (activated alumina) using CH_2Cl_2 as an eluent to give zinc phthalocyanine **16**. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (br, Ar, 8H), 6.55−7.12 (m, Ar and olef*H*, 16H), 4.00 (br, $OCH_2CH_2CH_3$, 24H), 2.08−2.43 (m, CH_3, 12H), 1.85 (br, $OCH_2CH_2CH_3$, 24H), 1.08 (br, $OCH_2CH_2CH_3$, 36H). MALDI-TOF-Ms (dithranol): *m*/*z* 1737 (M + H).

Zinc phthalocyanines **17** and **18** were synthesized from **12** and **13** by the same procedure of **16**.

17. Yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (br, Ar, 8H), 6.55−7.65 (m, Ar and olef*H*, 40H), 4.01 (br, $OCH_2CH_2CH_3$, 40H), 2.08−2.46 (m, CH_3, 12H), 1.86 (br, $OCH_2CH_2CH_3$, 40H), 1.10 (br, $OCH_2CH_2CH_3$, 60H). MALDI-TOF-Ms (dithranol): *m*/*z* 2609 (M + H).

18. Yield: 13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (br, Ar, 8H), 7.30−7.80 (m, olef*H*, 16H), 6.73−7.10 (m, Ar, 16H), 3.99 (br, $OCH_2CH_2CH_3$, 48H), 1.84 (br, $OCH_2CH_2CH_3$, 48H), 1.06 (br, $OCH_2CH_2CH_3$, 72H). MALDI-TOF-Ms (dithranol): *m*/*z* 2788 (M + H).

Tetracyclization of Dicyanides (19 and 20). A mixture of $ZnCl_2$ (30.0 mg, 0.22 mmol) and **14** (0.1 g, 89.5 μmol) in 3.0 mL of 2-(dimethylamino)ethanol was heated under reflux with stirring for 36 h. After the mixture was cooled, the solvent was removed and the residue was washed with methanol several times to remove excess Zn ion. The residue was purified by column chromatography (activated alumina) using CH_2Cl_2 as an eluent to give **19**. Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (br, Ar, 8H), 6.72−8.04 (m, Ar and olef*H*, 64H), 4.01 (br, $OCH_2CH_2CH_3$, 80H), 1.84 (br, $OCH_2CH_2CH_3$, 80H), 1.07 (br, $OCH_2CH_2CH_3$, 120H). MALDI-TOF-Ms (dithranol): *m*/*z* 4535 (M + H).

20. Yield: 20%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (br, Ar, 8H), 6.71−8.06 (m, Ar and olef*H*, 64H), 4.00 (br, $OCH_2CH_2CH_3$, 80H), 1.83 (br, CH_2, 80H), 1.53 (br, CH_2, 48H), 1.35 (br, CH_2, 96H), 0.99−1.08 (br, CH_3, 120H). MALDI-TOF-Ms (dithranol): *m*/*z* 5577 (M + K).

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