Permeable Nonaggregating Porphyrin Thin Films That Display Enhanced Photophysical Properties

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Porphyrins bearing bulky alkoxyphenyl substituents at two of the four meso-positions and phenyl phosphonates at the other two have been prepared and used as building blocks for layer-by-layer assembly of conductive-glass-supported thin films via zirconium phosphonate chemistry. Thin-film characterization shows that the addition of sterically demanding 2,6-di(*n*-hexoxy)phenyl substituents to the meso-positions of the porphyrin skeleton can successfully prevent molecular aggregation. Both absorption and emission studies of multilayer thin films provide strong evidence that the new compounds have the ability to form thin films in which very little molecular (chromophore) interaction is present, relative to porphyrins that are not sterically hindered. Furthermore, the films are found to be permeable to selected small redox probes but blocking toward larger ones. Taken together, the sharp absorption spectra, increased emission yields, and permeability are expected to be advantageous for various materials-based applications such as photovoltaics and sensors.

Introduction

The interesting structural, optical, and electrical properties of porphyrins have led them to be of importance in fields ranging from biology to materials chemistry.[1] For example, porphyrins are commonly studied in optical applications involving artificial photosynthetic processes[2−4] and semiconductor sensitization,[5−7] as well as for their ability to function as sensors,[8−10] molecular sieving materials,[11,12] catalysts,[13,14] and biomineralization templates.[15] Furthermore, the well-developed synthetic chemistry in the porphyrin field has rendered the compounds synthetically adaptable to complex supramolecular assemblies and surface functionalization, extending the interest in porphyrins to solid-state and device applications.[16,17] Many of the aforementioned applications require a substantial degree of molecular organization, which can be achieved via thin-film fabrication techniques such as layer-by-layer assembly[3,18,19] and Langmuir−Blodgett techniques.[20−22] Other film fabrication methods such as drop casting,[23] spin-coating, and electropolymerization[24] can also sometimes produce ordered films, especially when the constituent porphyrins have a tendency to self-assemble.

Reflecting both their planarity and high polarizability, porphyrin compounds often show a strong propensity to aggregate, both in the solid state and in solution, and are often observed to form highly complex nanostructures.[25] While the tendency toward aggregation may sometimes be advantageous in the context of device fabrication, it is often detrimental in other respects. In particular, aggregation usually results in shortening of photoexcited-state lifetimes and a loss of luminescence, owing to chromophore self-quenching,[26] thereby limiting the potential uses for porphyrin excited states in photovoltaic and sensing applications.[27] Additionally, it has been found that aggregation can reduce the catalytic efficiency of

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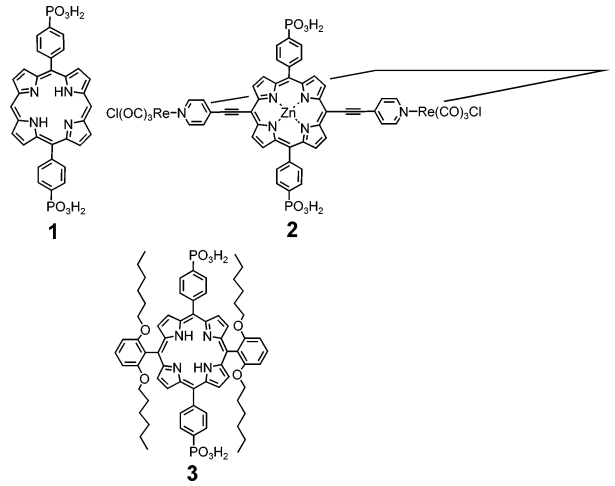
porphyrins.[28] To circumvent these problems, it would be useful to develop versions of these compounds that are amenable to the formation of ordered films and structures yet isolate the chromophoric centers of the compounds both physically and electronically.



We recently reported on the fabrication of ultrathin porphyrin films in micropatterned form based on the diphosphonic acid porphyrin **1**.[29] Related porphyrin chemistry has previously been reported by a number of others.[18,30−33] In each case, the assembly schemes, which utilize well-established zirconium phosphonate chemistry,[34−38] yield oriented films (normal to the surface) of well-defined thickness. Extension of the fabrication chemistry to the analogous porphyrin square compound **2** yields films that are similarly well defined. Additionally, the porosity and molecular permeability of the square films has been established,[39] and their photoelectrochemical properties have been studied.[40] However, both **1** and, to a lesser extent, **2**, display a tendency to aggregate in film environments and are essentially nonemissive, likely limiting their photoelectrochemical utility. Herein, we report on the synthesis and thin-film characterization of diphosphonic acid porphyrin **3**, in which 2,6-di(*n*-hexoxy)-phenyl substituents were added at the meso-positions of the porphyrin skeleton to prevent aggregation. The films exhibit sharp absorption spectra and high emission yields (relative to **1**) and display size-selective permeability toward solution phase molecules. These attributes are expected to make **3** and related compounds well suited to applications where a degree of molecular order is needed yet aggregation of chromophoric components is detrimental.

Experimental Section

Materials. Compounds **1**[29] and **2**[41] were prepared by Dr. Richard Gurney as described previously. 4-(Diethoxyphosphoryl)-benzaldehyde[42] and 2,8-dibutyl-3,7-dimethyldipyrrylmethane[43] were prepared according to literature procedures. All reagents were used as received unless otherwise specified.

Synthesis and Characterization. *1,3-Di(n-hexoxy)benzene (**4**).* Resorcinol (10 g, 0.0908 mol) and *n*-bromohexane (50 mL) were successively added to a stirred suspension of potassium hydroxide (40 g, 0.713 mol) in 160 mL of dimethyl sulfoxide (DMSO). The reaction was allowed to stir overnight at room temperature and was then quenched with 150 mL of water. The product was extracted with dichloromethane (CH_2Cl_2), dried over magnesium sulfate (Mg_2SO_4), and concentrated under reduced pressure. Excess bromohexane was removed via vacuum distillation to yield an orange oil (23.4 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): 7.15 (t, 1H), 6.49 (m, 3H), 3.94 (t, 4H), 1.77 (m, 4H), 1.45 (m, 4H), 1.34 (m, 8H), 0.91 (t, 6H) ppm. HRMS (EI): 278.2240 (M^+, *m/z* calculated), 278.2236 (observed).

*2,6-Di(n-hexoxy)benzaldehyde (**5**).* A three-neck flask was fitted with a pressure-equalizing addition funnel and charged with **4** (9.22 g, 0.0331 mol) and tetramethylethylenediamine (TMEDA) (6 mL) in 120 mL of diethyl ether. The solution was degassed with a stream of N_2 for 15 min and cooled to 0 °C. Under N_2, *n*-butyllithium (1.6 M solution in hexanes, 0.0336 mol) was added dropwise over 20 min and allowed to stir for 3 h. After warming to room temperature, dimethylformamide (DMF) (4 mL) was added dropwise, and the reaction was stirred for an additional 2 h. The reaction was quenched with water, and the product was extracted with ether (3 × 150 mL), dried over $MgSO_4$, and concentrated to leave an oily residue. The product was recrystallized from hexanes to yield a white solid (7.96 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.54 (s, 1H), 7.37 (t, 1H, J = 8.4 Hz), 6.52 (d, 2H, J = 8.4 Hz), 4.02 (t, 4H), 1.82 (m, 4H), 1.47 (m, 4H), 1.32 (m, 8H), 0.89 (t, 6H) ppm. HRMS (EI): 306.2189 (M^+, *m/z* calculated), 306.2194 (observed).

*meso-(2,6-Di(n-hexoxy)phenyl)dipyrromethane (**6**).* **5** (1.8 g, 5.87 mmol) was added to 40 mL of pyrrole and degassed with N_2 for 15 min. Indium trichloride (130 mg, 0.587 mmol) was added, and the reaction was stirred for 1.5 h in the dark. Crushed NaOH (0.9 g, 22.5 mmol) was added, and stirring was continued for an additional hour. After filtration, the pyrrole was removed in vacuo and the residue was purified by column chromatography (silica, 80:20:1 cyclohexane/ethyl acetate/triethylamine) to yield a yellow oil (892 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.49 (s, 2H), 7.06 (t, 1H, J = 8.3 Hz), 6.54 (m, 2H), 6.49 (d, 2H, J = 8.3 Hz), 6.13 (s, 1H), 6.01 (m, 2H), 5.81 (m, 2H), 3.79 (m, 4H), 1.49 (m, 4H), 1.22 (m, 12H), 0.83 (t, 6H, J = 7.1 Hz) ppm. HRMS (EI): 422.2928 (M^+, *m/z* calculated), 422.2931 (observed).

*5,15-Bis[4-(diethoxyphosphoryl)phenyl]-10,20-bis[2,6-di(n-hexoxy)phenyl]porphyrin (**7**).* **6** (500 mg, 1.18 mmol) and 4-(diethoxyphosphoryl)benzaldehyde (286 mg, 1.18 mmol) were added to 200 mL of dry CH_2Cl_2, and the solution was degassed with a stream of N_2. Trifluoroacetic acid (50 μL) was added and the reaction stirred at reflux for 7 h. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (0.4 g, 1.76 mmol) was added, and stirring was continued for an additional hour. The product was isolated via column chromatography (silica, 45:1 CH_2Cl_2/MeOH) and further purified upon recrystallization from CH_2Cl_2/MeOH to yield a purple solid (46 mg, 6%). ^{1}H NMR (400 MHz, $CDCl_3$): 8.84 (d, 4H, J = 4.8 Hz), 8.71 (d, 4H, J = 4.7 Hz), 8.32 (m, 4H), 8.19 (m, 4H), 7.70 (t, 2H, J = 8.5 Hz), 6.99 (d, 4H, J = 8.5 Hz),

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4.40 (q, 8H, $J = 7.2$ Hz), 3.84 (t, 8H, $J = 6.3$ Hz), 1.54 (t, 12H, $J = 7.0$ Hz), 0.95 (m, 8H), 0.54 (m, 16H), 0.41 (m, 8H), 0.26 (t, 12H, $J = 6.3$ Hz) ppm. HRMS (ESI): 1287.6674 (MH^+, *m/z* calculated), 1287.6668 (observed).

*5,15-Bis[4-(dihydroxyphosphoryl)phenyl]-10,20-bis[2,6-di(n-hexoxy)phenyl]porphyrin (**3**).* **7** (30 mg, 0.0233 mmol) was dissolved in 10 mL of dry CH_2Cl_2 under N_2. Bromotrimethylsilane (90 μL) was added, and the reaction was allowed to reflux overnight. The solvent was removed in vacuo, and the remaining solid was stirred in water for 1 h and then filtered and washed with acetone to yield a dark solid (15.6 mg, 57%). ^{1}H NMR (400 MHz, DMSO): 8.82 (4H), 8.76 (4H), 8.27 (4H), 8.17 (4H), 7.81 (2H), 7.19 (4H), 3.93 (8H), 0.91 (8H), 0.40 (8H), 0.32 (8H), 0.21 (8H), 0.06 (12H) ppm. HRMS (FAB): 1175.5422 (MH^+, *m/z* calculated), 1175.5448 (observed).

*4-(Trimethylsilyl)phenylphosphonate (**9**).* Under a flow of Ar, 1-bromo-4-(trimethylsilyl)benzene (3.0 g, 13.3 mmol), triethylamine (1.9 mL), diethyl phosphite (1.8 mL), and $Pd(Ph_3)_4$ (1.059 g, 0.917 mmol) were added to toluene (10 mL). The reaction was stirred overnight at 80 °C under Ar. Upon cooling, diethyl ether was added to the reaction to yield a yellow precipitate, which was discarded. The filtrate was concentrated under reduced pressure, and the product was isolated via column chromatography (silica, 30:1 CH_2Cl_2/MeOH) as dark oil (2.4 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.49 (m, 2H), 7.33 (m, 2H), 3.84 (m, 4H), 1.04 (t, 6H, $J = 7.1$ Hz), 0.019 (s, 9H) ppm. HRMS (EI): 286.1154 (M^+, *m/z* calculated), 286.1149 observed.

*4-Iodophenylphosphonate (**10**).* **9** (1.52 g, 5.31 mmol) was added to dry CH_2Cl_2 and degassed with N_2 for 15 min. Iodochloride (5.2 mL, 1.0 M solution in CH_2Cl_2) was added and the reaction stirred overnight at room temperature. Concentrated aqueous NaOH was added, and the organic layer was separated, dried over $MgSO_4$, and concentrated to yield a dark oil (1.68 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.49 (m, 2H), 7.33 (m, 2H), 3.84 (m, 4H), 1.04 (t, 6H, $J = 7.1$ Hz) ppm. HRMS (EI): 339.9720 (M^+, *m/z* calculated), 339.9715 observed.

*2,8,12,18-Tetrabutyl-3,7,13,17- tetramethyl-5,15-bis(trimethylsilylethynyl)porphyrin (**11**).* 2,8-Dibutyl-3,7-dimethyldipyrrylmethane (1.272 g, 4.44 mmol) and *p*-toluene sulfonic acid (184 mg, 0.97 mmol) were dissolved in methanol (100 mL) under N_2, and the solution was cooled to −20 °C in a dry ice/acetone/propanol bath. 3-Trimethylsilylpropynal (0.602 g, 4.70 mmol) was added, and the solution immediately turned dark blue-green. After 3 h, the reaction was warmed to room temperature and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.887 g, 8.30 mmol) was added, and the reaction was stirred for an additional 30 min. The solvent was removed under reduced pressure and purified via column chromatography (CH_2Cl_2). The product eluted as the first fraction and was recrystallized from CH_2Cl_2/MeOH to yield a blue solid (261 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.01 (s, 2H), 3.97 (t, 8H, $J = 7.7$ Hz), 3.68 (s, 12H), 2.20 (m, 8H), 1.80 (m, 8H), 1.15 (t, 12H, $J = 7.4$ Hz), 0.61 (s, 18H) ppm. HRMS (ESI): 783.5212 (MH^+, *m/z* calculated), 783.5222 (observed).

*[2,8,12,18-Tetrabutyl-3,7,13,17- tetramethyl-5,15-bis(trimethylsilylethynyl)porphinato]zinc(II) (**12**).* **11** (211 mg, 0.270 mmol) and zinc acetate (193 mg, 1.05 mmol, dissolved in MeOH) were added to CH_2Cl_2 (125 mL), and the reaction was allowed to stir overnight. The reaction volume was reduced via rotary evaporation, and the product precipitated upon the addition of MeOH to yield a green solid (205 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.94 (s, 2H), 3.95 (t, 8H, $J = 7.7$ Hz), 3.67 (s, 12H), 2.14 (m, 8H), 1.72 (m, 8H), 1.08 (t, 12H, $J = 7.4$ Hz), 0.53 (s, 18H) ppm. HRMS (ESI): 844.4268 (M^+, *m/z* calculated), 844.4276 (observed).

*[2,8,12,18-Tetrabutyl-3,7,13,17- tetramethyl-5,15-bis(ethynyl)-porphinato]zinc(II) (**13**).* **12** (102.4 mg, 0.121 mmol) was dissolved in dry tetrahydrofuran (THF) (15 mL), and tetrabutylammonium fluoride (1 M in THF, 0.5 mL) was added via syringe. The reaction was stirred under N_2 for 30 min and was then quenched with water. The reaction mixture was filtered to yield a green solid (62 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.05 (s, 2H), 4.56 (s, 2H), 3.99 (t, 8H, $J = 7.6$ Hz), 3.71 (s, 12H), 2.17 (m, 8H), 1.75 (m, 8H), 1.11 (t, 12H, $J = 7.4$ Hz) ppm. HRMS (ESI): 700.3478 (M^+, *m/z* calculated), 700.3480 (observed).

*[2,8,12,18-Tetrabutyl-3,7,13,17- tetramethyl-5,15-bis(4-diethoxyphosphorylphenylethynyl)porphinato]zinc(II) (**14**).* **13** (76.1 mg, 0.109 mmol), 4-iodophenylphosphonate (**10**) (210 mg, 0.617 mmol), and triethylamine (0.370 mL) were added to THF (40 mL), and the solution was degassed via a stream of N_2. $Pd(PPh_3)_4$ (28 mg, 0.0243 mmol) and CuI (20 mg, 0.105 mmol) were added, and the reaction was stirred overnight at 70 °C. Upon removal of the solvent, the residue was chromatographed on silica first with 1:1 THF/hexanes and again with 2.5:1 THF/hexanes. The product was then isolated upon recrystallization with THF/hexanes to yield a green solid (48.2 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.66 (s, 2H), 7.82 (br, 4H), 6.91 (br, 4H), 3.84 (br, 8H), 3.69 (s, 12H), 3.19 (br, 8H), 2.13 (m, 8H), 1.76 (m, 8H), 1.58 (br, 12H), 1.14 (t, 12H, $J = 7.4$ Hz) ppm. LRMS (MALDI-TOF): 1124.5 (M^+, *m/z* calculated), 1124.3 (observed). Anal. Calcd for $C_{64}H_{78}N_4O_6P_2Zn$: C, 68.23; H, 6.98; N, 4.97. Found: C, 68.07; H, 7.01; N, 5.02.

*2,8,12,18-Tetrabutyl-3,7,13,17- tetramethyl-5,15-bis(4-dihydroxyphosphorylphenylethynyl)porphyrin (**8**).* **14** (30 mg, 0.027 mmol) was added to freshly distilled CH_2Cl_2 (10 mL) under N_2. Bromotrimethylsilane (50 μL, 0.38 mmol) was added and the reaction stirred at reflux overnight. Upon removal of the solvent, water was added and the reaction allowed to stir for 2 h. The resulting green solid was filtered to yield 20 mg of product.

Thin-Film Assembly. Thin films were prepared and characterized analogously to the published procedure for **1**[29] and **2**.[39,40] Briefly, phosphorylated glass substrates or indium tin oxide (ITO) electrodes were immersed overnight in 25 mM $ZrOCl_2$ (aq). The platforms were then immersed in a 0.1 mM DMSO solution of porphyrin for 4 h. Following each exposure to Zr^{4+} or porphyrin, the substrates were rinsed in H_2O or DMSO, respectively. Additional layers were assembled through successive treatment with 25 mM $ZrOCl_2$ (15 min.) and 0.1 mM porphyrin, either manually or by using a programmed robotic arm.

Electronic Absorption and Emission Measurements. Electronic absorption spectra were recorded on a Varian Cary 5000 UV−vis−NIR spectrophotometer. Steady-state fluorescence measurements were performed on a Jobin Yvon-SPEX Fluorolog-3 spectrofluorimeter. Thin-film glass substrates were placed at 45° to the incident light, and emission was collected in a right angle configuration.

Electrochemical Measurements. Electrochemical measurements were performed on a CH Instruments potentiostat using a three-electrode configuration with an ITO working electrode, a Pt wire counter electrode, and a pseudo Ag/AgCl reference electrode. With the exception of tris(3,4,7,8-tetramethylphenanthroline)cobalt(II)nitrate ($[Co(tmphen)_3](NO_3)_2$), 2 mM redox probe solutions were prepared in water and contained 0.1 M potassium nitrate as supporting electrolyte. $Co(tmphen)_3^{2+}$ was prepared in a 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution, owing to solubility considerations.

Results and Discussion

Synthesis and Thin-Film Growth of 3. The synthesis of **3** is depicted in Scheme 1 and is based on common porphyrin synthetic strategies. The hexyl-ether functionalities are introduced to the porphyrin skeleton via aldehyde **5**, which is synthesized on the basis of procedures outlined by Therien and co-workers for related compounds.[44] **6** is prepared according to a generalized synthesis of meso-substituted dipyrromethanes described by Laha et al.[45] The MacDonald synthetic strategy[46,47] is then used to prepare porphyrin **7** from **6** and 4-(diethoxyphosphoryl)benzaldehyde, with the exception of a longer reaction time owing to the reduced reactivity of 4-(diethoxyphosphoryl)benzaldehyde. **7** is then hydrolyzed with bromotrimethylsilane (BrTMS) to yield the corresponding

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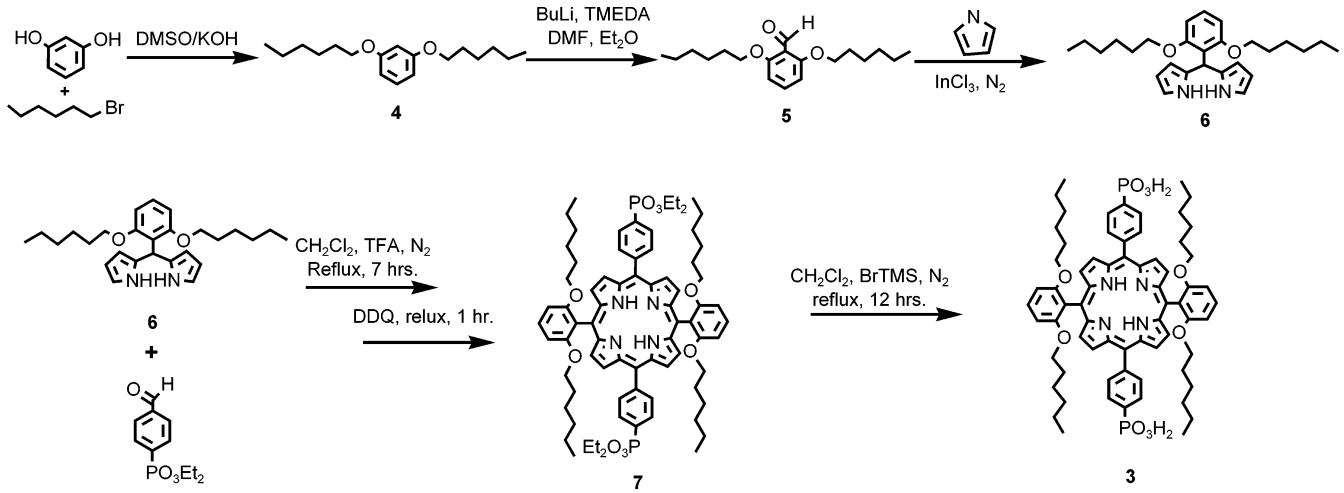
Scheme 1. Synthesis of Diphosphonic Acid Porphyrin 3



diphosphonic acid porphyrin **3**.[48] Thin films of **3** were fabricated on either glass or ITO conducting glass substrates via well-established layer-by-layer deposition techniques with aqueous Zr^{4+}, as reported previously.[29,34,35] A plot of the absorbance at the peak wavelength as a function of deposited layers yields a linear relationship, indicative of a uniform rate of film growth (Figure 1).

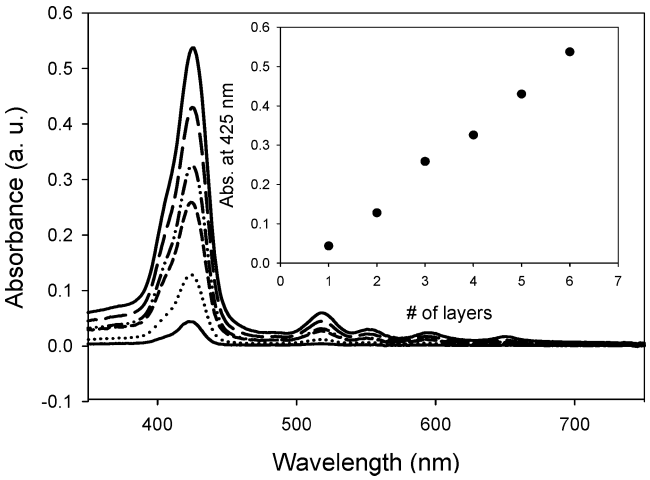


Figure 1. Electronic absorption spectra of **3** multilayer films grown on glass. All spectra have been corrected for the glass substrate scatter. Inset: absorbance at 425 nm as a function of additional layers.

As a point of comparison, we also synthesized compound **8** (Scheme 2), which has a high tendency to aggregate in both solution and thin-film environments. Free-base porphyrin **11** is prepared via the condensation of the β-substituted dipyrromethane with trimethylsilylpropynal according to methods developed by Anderson and co-workers.[49] Especially noteworthy is the low temperature required, owing to the enhanced reactivity of the ethynyl aldehyde. Zinc insertion followed by deprotection yields the bis(ethynyl) porphyrin **13**. A Sonogashira Pd(0)-catalyzed cross-coupling reaction between the ethynylated porphyrin and 4-iodophenylphosphonate (**10**) then yields the diphosphonate porphyrin **14**,[50] which is hydrolyzed with BrTMS to yield **8**. Note that, upon hydrolysis of the phosphonate ester precursor **14**, demetalation to form the free-base derivative is observed, as evidenced by the absorption spectrum. **8** is also found to form films uniformly via layer-by-layer assembly (not shown).

Table 1. Electronic Absorption Data for Porphyrin Solutions and Thin Films

compound	λ_{max} (nm; soln, film)	fwhm (nm; soln, film)
1	407, 387	24, 75
2	450, 456	34, 63
3	420, 425	13, 29
8	432, 410	43, 91

Electronic Absorption Spectra. The zirconium phosphonate fabrication scheme mandates that the porphyrin chromophores are aligned largely perpendicular to the substrate surface and, therefore, renders the porphyrins prone to strong intermolecular interactions and/or aggregation.[18,29] In efforts to reduce aggregation of the diphosphonic acid porphyrin **1** in a thin-film environment, 2,6-di(*n*-hexoxy)phenyl substituents were added at the meso-positions of the porphyrin skeleton. This substitution pattern should force the phenyl groups to be nearly orthogonal to the plane of the porphyrin and prevent significant porphyrin association. (Notably, Therien and co-workers have previously documented its effectiveness in solution environments.[44]) Porphyrin aggregation is characterized by extreme broadening and shifting of the Soret region in the absorption spectrum, as predicted by exciton theory.[51] Therefore, both the orientation of the porphyrins and the degree of aggregation in thin films can be qualitatively assessed via electronic absorption spectroscopy.

The absorption spectra of porphyrin compounds **1**−**3** and **8** in both solution and thin-film environments are presented in Figure 2, and the data are summarized in Table 1. Upon film formation, the spectra of compounds **1**, **2**, and **8** significantly broaden and/or blue-shift relative to those of the solution phase, characteristic of aggregation. In contrast, the absorption spectrum of **3** is only slightly broadened upon thin-film formation, indicative of only a small degree of aggregation in the solid state.

The degree of aggregation within the films is highly dependent on the structure of the porphyrin. Aggregation appears to be most severe with **8**, for which alkyl substitution at the β-positions, rather than at the meso-positions, is known to enhance aggregate formation.[52]

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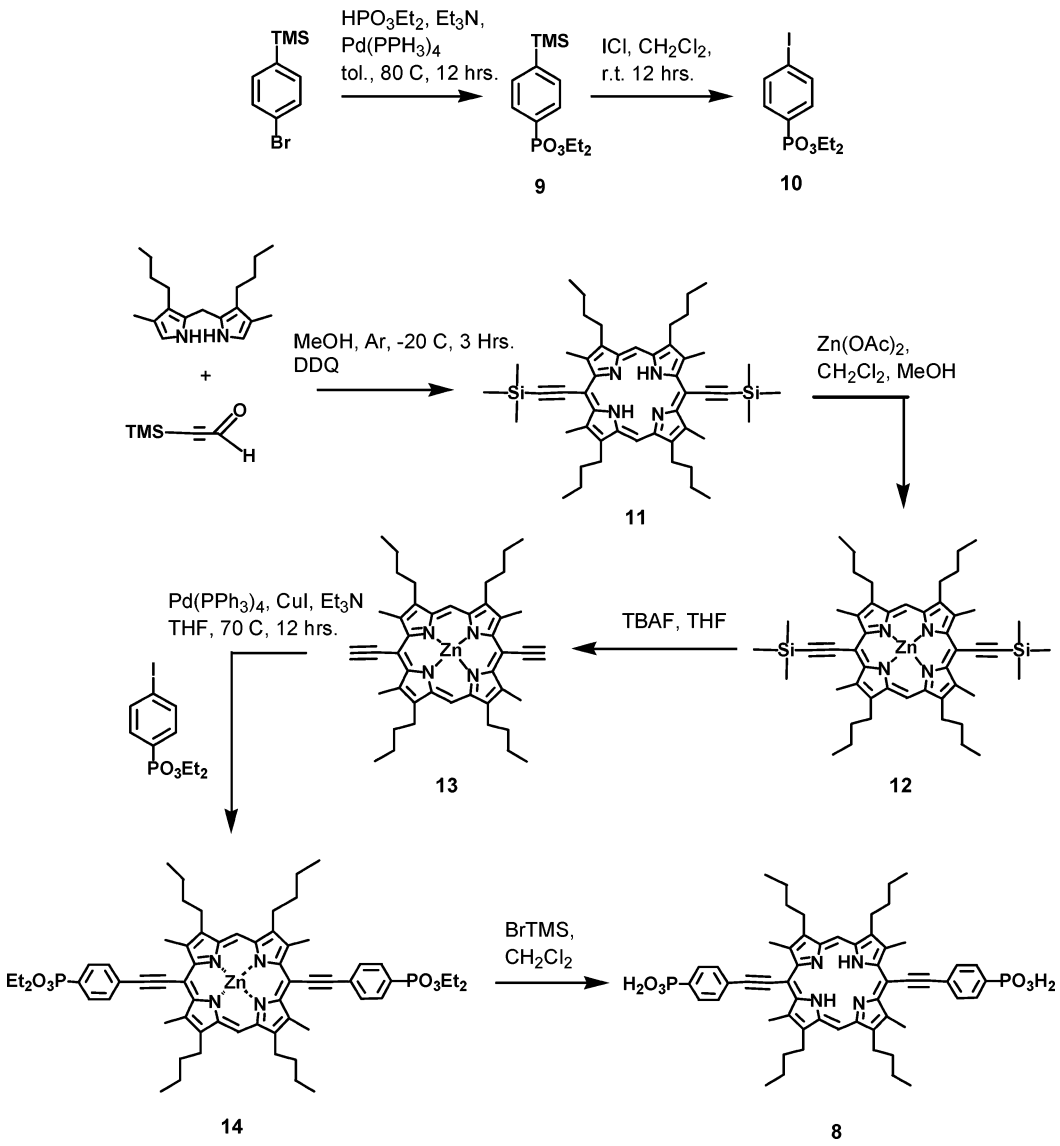
Scheme 2. Synthesis of Porphyrin Compound 8



Furthermore, **8** appears to form aggregates in DMSO solution as well, as evidenced by the relatively large full width at half-maximum (fwhm) value compared to the other porphyrin solutions. Removal of the β-alkyl substituents and addition of *meso*-diphenyl phosphonate groups (compound **1**) produces porphyrins that have a lower tendency to aggregate in solution but still associate significantly in a film environment. Incorporation of the porphyrin chromophore **1** into molecular square **2** via rhenium−pyridine coordination mandates a perpendicular geometry between adjacent porphyrins within the squares, precluding edge-to-face type aggregate formation. However, *inter*molecular association between adjacent square walls is not fully prohibited, and the thin films display an absorption spectrum that is broadened, albeit not to the extent of **1** and **8**.[53] Striking, however, is the sharp Soret band of **3** when compared to compounds **1**−**2** and **8**, indicating that aggregation is all but defeated in a thin-film environment.

(53) Note that, in contrast to **2**, Milic and co-workers have demonstrated that porphyrin tetramers with alkane appendages can form nearly uniform films wherein there is little evidence of intersquare interactions, as evidenced by atomic force microscopy (AFM). Photophysical behavior has yet to be reported. Milic, T.; Garno, J. C.; Batteas, J. D.; Smeureanu, G.; Drain, C. M. *Langmuir* **2004**, *20*, 3974−3983.

Emission Spectra. Increased aggregation is expected to have a deleterious effect on porphyrin excited-state fluorescence yields. Upon excitation of multilayer porphyrin films (where OD = 0.12 for all films, Figure 3, top), only weak emission (Figure 3, bottom) is observed for **1** and emission is barely detectable for **8**, while thin films of **3** give rise to a strong emission signal. The ratio of integrated fluorescence intensity for **3** compared to **1** is 4:1, and qualitatively, the emission intensity is inversely proportional to the degree of aggregation in the films, as evidenced by the absorption spectra. No emission was detected for thin films of **2**, presumably because of both porphyrin intermolecular association and increased intersystem crossing, owing to the presence of rhenium in the compounds. The isolated rhenium squares, however, are known to luminesce in solution environments.

Finally, it is worth noting that aggregation within zirconium phosphonate assembled films of monomeric porphyrins can be reversed and fluorescence partially restored by coassembling the chromophores with site-isolating alkanes.[18] An almost certain structural cost, however, is a loss of molecular permeability.

Electrochemical Assessment of Film Porosity. The ability of thin films to either block or transport redox-active probe molecules can be easily evaluated via

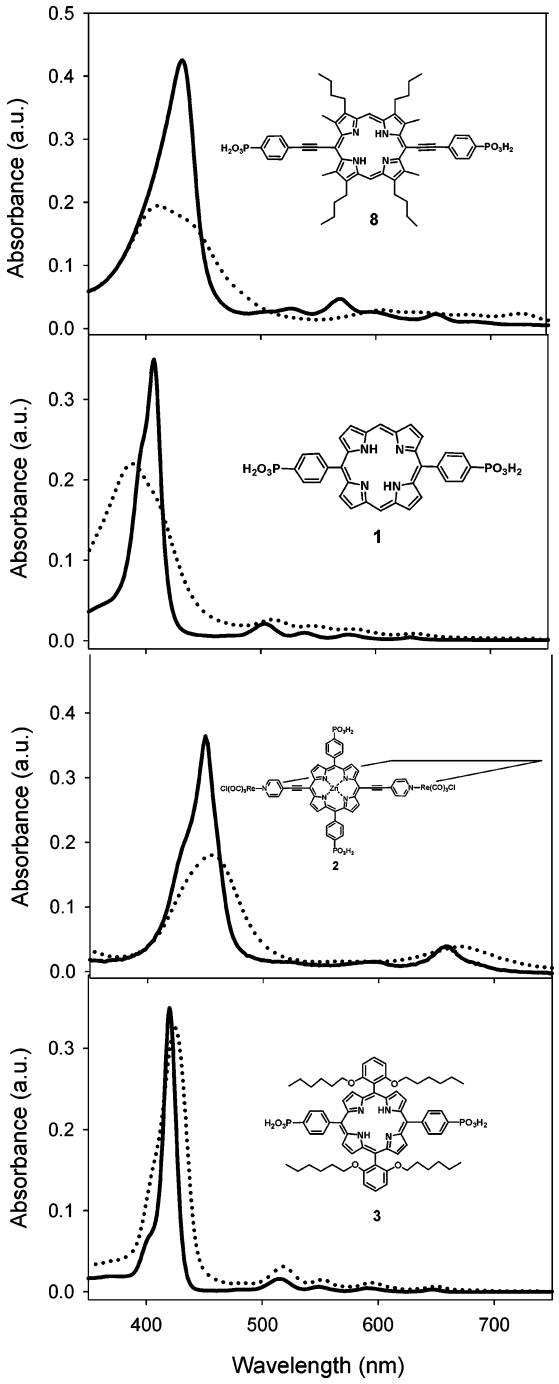


Figure 2. Absorption spectra of porphyrin compounds in DMSO solution (—) and a four-layer film (···).

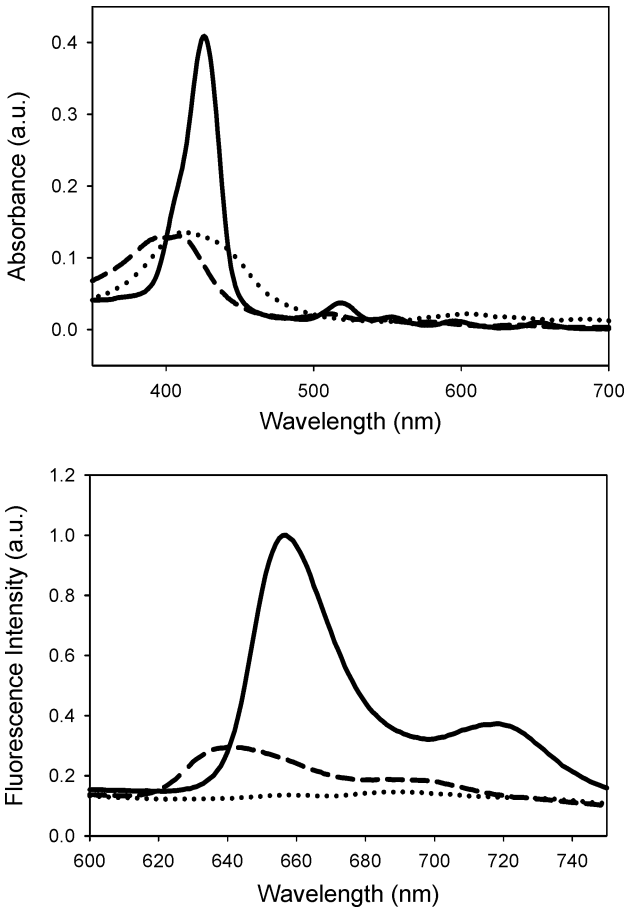


Figure 3. Absorption (top panel) and emission (bottom panel) of multilayer thin films of **1** (- - -), **3** (—), and **8** (···).

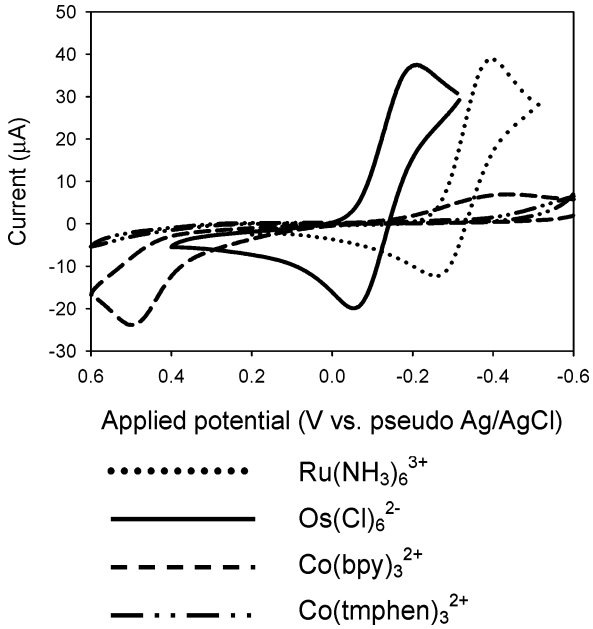


Figure 4. Cyclic voltammograms of selected redox-active probes using two layers of **3** on ITO as the working electrode. Specific conditions are reported in the Experimental Section.

electrochemical measurements if the films are prepared on conductive platforms. Quantitative measurements based on walljet electrochemistry have previously revealed that thin films of **2** are capable of molecular transport and display a size cutoff at just over one-half of the maximum diameter of the cavity of an isolated square.[39] In a similar experiment, a size-exclusion study was performed on a two-layer film of **3** on an ITO electrode based on cyclic voltammetry measurements of $Ru(NH_3)_6^{3+}$ (diameter 5.5 Å), $Os(Cl)_6^{2-}$ (diameter 8.5 Å), $Co(bpy)_3^{2+}$ (diameter 12 Å), and $Co(tmphen)_3^{2+}$ (diameter 15 Å) as redox-active probes. As shown in Figure 4, the two smaller probes are readily transported to the conductive substrate, while transport of the larger $Co(bpy)_3^{2+}$ is severely impeded. Transport of $Co(tmphen)_3^{2+}$ is completely blocked, which indicates that any film defects, such as pinholes or bare spots, are limited to < ~15 Å. The porous nature of the films renders them potentially useful for sensing and sieving applications, while the permeability will allow for collinear film growth with other diphosphonate compounds, provided the size of the compounds remains below the size cutoff of the films.

Conclusion

To summarize, the addition of sterically demanding 2,6-di(*n*-hexoxy)phenyl substituents to the meso-positions of the porphyrin skeleton almost completely eliminates film-based aggregation. Both absorption and emission studies of multilayer thin films provide strong evidence that porphyrin **3** has the ability to form thin films in which very little chromophore/chromophore interaction is present. Furthermore, the films are found to be permeable to small redox probes but blocking toward larger ones. Taken together, the sharp absorption spectra, increased emission yields, and permeability may render thin films of **3** and related phenyl-ether functionalized chromophores useful for various materials-based applications such as sensing, photocatalysis, and photochemical energy conversion.

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