

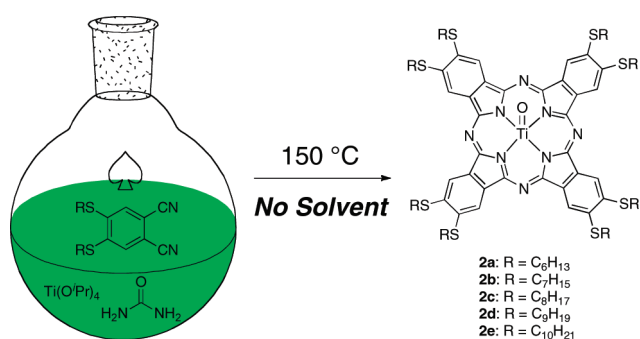
Solvent-Free Synthesis of Soluble, Near-IR Absorbing Titanyl Phthalocyanine Derivatives

Mayank Mayukh, Clarissa M. Sema, Jessica M. Roberts, and Dominic V. McGrath*

Department of Chemistry, University of Arizona, Tucson, Arizona 85721, United States

mcgrath@u.arizona.edu

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Solvent-free synthesis of a series of alkylthio-substituted titanyl phthalocyanine (TiOPc) derivatives starting from the corresponding phthalonitriles (Pn) is reported. This methodology eliminates the formation of the unmetallated phthalocyanine (H_2Pc), a side product that makes purification difficult. The alkylthio groups on the reported derivatives enhance solubility in common organic solvents and shift the absorption to the near-IR region.

We report herein solvent-free conditions for the synthesis of soluble, near-IR absorbing titanyl phthalocyanine (TiOPc)¹ derivatives. Solvent-free conditions are environmentally friendly and industrially economical² and in this context effectively eliminate the formation of nonmetallated phthalocyanine (H_2Pc), a side product that interferes with purification of TiOPcs. The usual route to the synthesis of TiOPcs, which involves heating a solution of a phthalonitrile (Pn) derivative and urea in a polar protic organic solvent such as 1-pentanol, commonly leads to a mixture of H_2Pc and TiOPc. Urea is necessary as a source of ammonia during

the formation of TiOPc and derivatives.^{3–5} Yao et al. elucidated that the key steps in the macrocyclization leading to TiOPc were (1) generation of ammonia in situ by reaction between 1-octanol, the solvent, and urea at elevated temperature by carbamate formation⁵ and (2) adduct formation between ammonia and $Ti(OR)_4$ followed by TiOPc formation. Interestingly, when aprotic solvents were used, poor yields of TiOPc resulted along with H_2Pc contamination.⁵ However, subsequent use of these or similar conditions (e.g., urea and 1-pentanol) to prepare TiOPc derivatives led to significant amounts of H_2Pc contamination.^{3,4} Yet we have found here that when the reaction to form TiOPc derivatives was performed in a urea melt, the formation of H_2Pc was completely eliminated. It is well-known that urea undergoes decomposition in the melt to produce ammonia and biuret via isocyanic acid formation.^{6,7}

Interest in TiOPc stems from its high electrical polarizability and condensed-phase organization^{8,9} that result in photophysical and optical properties such as photoconductivity,¹⁰ third-order nonlinear susceptibility,¹¹ and near-IR absorptivity.^{9,12} TiOPc and its derivatives therefore find application as xerographic photoreceptors,¹⁰ gas sensors,¹³ optical limiting agents,¹⁰ photodynamic therapy (PDT) sensitizers, and donor materials in organic solar cells.^{12,14} Interest in soluble derivatives of TiOPc stems from the insolubility of TiOPc in common organic solvents¹ inhibiting purification by all but nonideal methods such as entrainer sublimation¹⁰ and acid pasting¹⁵ and necessitating expensive vapor deposition for processing.¹² Soluble derivatives can be processed into thin films by reel-to-reel wet coating,¹⁶ inkjet printing,¹⁷ or spin-coating.^{3–5,18–20}

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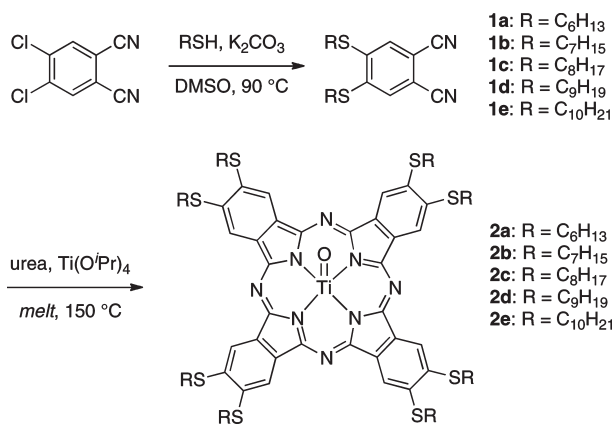
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SCHEME 1. Synthesis of Pn 1a–e and TiOPc 2a–e



The particular TiOPc derivatives we report are octakis(alkylthio) derivatives,^{20,21} substituent moieties that serve to render the TiOPc soluble in a wide range of organic solvents while bathochromically shifting the Q-band relative to the parent chromophore. They are also responsible for secondary sulfur–sulfur noncovalent interactions that can strongly influence condensed-phase organization.²²

We chose to prepare alkylthio-substituted TiOPc derivatives because of the possibility of optimized condensed-phase organization and near-IR absorbance for use in organic solar cells. Pn derivatives **1a–e** were synthesized via nucleophilic aromatic substitution of dichlorophthalonitrile with alkyl thiols under basic conditions (Scheme 1). Intensely colored impurities were removed upon treatment with activated charcoal, and Pns **1a–e** were obtained as colorless solids in good yields after purification by flash chromatography.

We were prompted to attempt the solvent-free conditions described herein upon observing a trend toward lower amounts of H₂Pc formed during the cyclization reaction with lower concentrations of 1-pentanol used in the reaction. The intense green color of H₂Pc masks the dark, nearly black color of the TiOPc (a near-IR absorber) when they form as a mixture, and the presence of H₂Pc is discerned by TLC or mass spectrometry (see the Supporting Information). Attempts to separate the mixtures of H₂Pc and TiOPc failed due to coelution.

Macrocyclization of **1a–e** to the corresponding Pc compounds was accomplished by heating the Pn to its melting point and subsequently adding urea and Ti(OiPr)₄ to the molten Pn. The reaction mixture was then maintained at 150 °C for 24 h. We found no evidence of H₂Pc by TLC or mass spectrometry when the reaction was performed in a urea melt (see the Supporting Information). Presumably, the higher concentration of reactants under solvent-free conditions favorably affects the reaction kinetics leading only to the metalated product. TiOPc compounds **2a–e** were obtained as intensely colored, nearly black solids in moderate yields of 34–42%, except for **2a**, which consistently was obtained in a much lower yield of 16%. In the case of **2b–e**, these yields

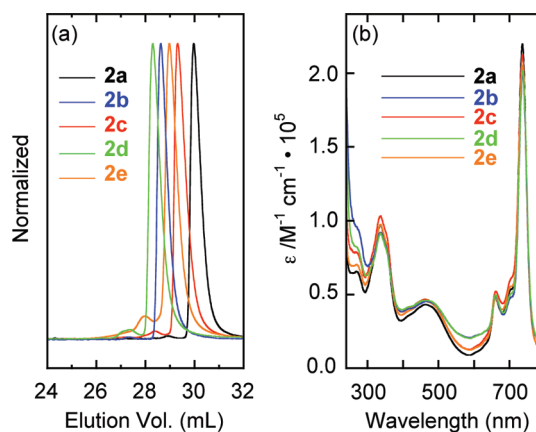


FIGURE 1. (a) GPC in THF and (b) UV–vis in DCM (ca. 10^{−6} M) for TiOPc **2a–e**.

were higher than reported for a similar TiOPc prepared using the method reported by Yao.^{4a,5} Purification of **2a–e** was accomplished by a combination of precipitation and flash chromatography. The deviation from the purple color of parent unmodified TiOPc chromophore is believed to be due the bathochromic effect of the alkylthio substituents at the peripheral positions.^{20b}

All compounds were characterized by gel permeation chromatography (GPC), mass spectrometry, UV–vis spectroscopy, NMR, and thermal and elemental analysis (see the Supporting Information). Elemental analysis results are all in close agreement with the expected values. The GPC traces of octakis(alkylthio) Pc compounds **2a–e** were indicative of monodisperse materials, and a hydrodynamic size increase was observed commensurate with the increase in molecular weight on proceeding from **2a** → **2e** (Figure 1a). Because of solution aggregation only ¹H NMR could be obtained for **2a–e**.

The appearance of the UV–vis spectra was similar for **2a–e**, consistent with the identical nature of the central Pc chromophore in all five compounds (Figure 1b). Metalation of the macrocycle was confirmed by the collapsed Q-band at 736 nm for all Pcs, with associated vibronic bands at 661 and 700 nm. The absorptivities at the λ_{max} of the Q-bands of were all ca. 2 × 10⁵ M^{−1} cm^{−1} as determined by Beer's law analysis (see the Supporting Information). The observed bathochromic shift of the Q-band, about 36 nm relative to the unsubstituted TiOPc,⁹ arising from the mixing of 3p orbital on sulfur with π-orbitals of the phthalocyanine core,²³ is typical of a Pc substituted with alkylthio groups at the peripheral positions.²⁴

The octakis(alkylthio) TiOPcs **2a–e** reported here exhibit appreciable solubility in both CHCl₃ and THF, freely soluble at least up to the 10^{−2} M concentration range, in contrast to unmodified TiOPc which is poorly soluble in organic solvents such as CHCl₃ (ca. 8 × 10^{−5} M) and THF (ca. 2 × 10^{−5} M). In addition, **2a–e** showed no signs of aggregation in CHCl₃ in the micromolar range (≤10^{−5} M), as evident from a lack of broadening of the Q-band maxima at 739 nm in the UV–vis spectra as well as a linear response in the corresponding Beer's

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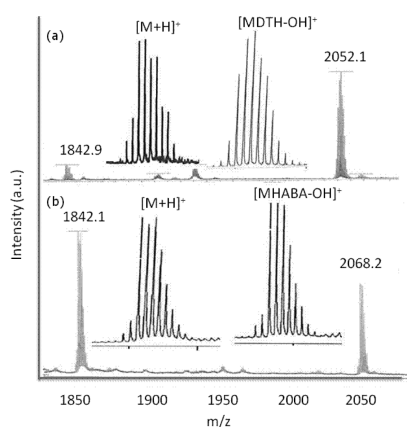


FIGURE 2. MALDI-TOF mass spectrometry data for **2d** in (a) DTH and (b) HABA.

law plots. Aggregation of **2a–e** was evident at even lower concentrations in THF, with an aggregate band, apart from the Q-band maxima at 731 nm, at 815 nm in the UV–vis spectra. Despite the tendency to aggregate in solution, no liquid crystalline behavior was evident from the differential scanning calorimetry (DSC) traces (see the Supporting Information).

The MALDI-TOF mass spectrometry characterization of **2a–e** revealed evidence of adduct formation between the analyte compounds and the matrix material. With two different matrices, dithranol (DTH) and 2-(4-hydroxyphenylazo)benzoic acid (HABA), we observed that the base or otherwise significant peak in the mass spectra of **2a–e** corresponded to an adduct of the matrix material and the respective TiOPc derivative with loss of OH (Figure 2). A likely possibility is in situ chemical reaction between **2a–e** and the MALDI matrices. Indeed, the axial substitution of TiOPcs with catechols and related diols is well established^{4a,25} and has even been used for the recognition of chiral catechols.²⁶ Axial substitution of TiOPc to form 5- and 7-membered chelate rings with diols such as catechol and 2,2'-biphenol, respectively, has been reported.²⁷ However, reaction between DTH and TiOPcs, which leads to the formation of a 6-membered chelate, is unprecedented. We attempted to prepare the DTH-TiOPc adduct (**2a–DTH**) in refluxing CHCl_3 but obtained only insoluble product that resisted characterization. An attempt to produce an isolable HABA–**2a** adduct was similarly unsuccessful. However, a hetrocyclic complex has been reported that supports the proposed structure of the HABA-TiOPc adduct (see Supporting Information).²⁸

In summary, we have reported a solvent-free route to soluble TiOPc derivatives that eliminates the formation of H_2Pc side product. With this method, we have prepared a series of octakis(alkylthio)-substituted TiOPc derivatives

from cyclization of the corresponding phthalonitriles in molten urea. We are currently investigating effect of alkylthio chain length on the behavior of TiOPcs in the condensed phase with the possibility of retaining the near-IR absorption of the unmodified TiOPc.

Experimental Section

4,5-Bis(hexylthio)phthalonitrile (1a). A mixture of hexane-1-thiol (6.0 g, 50.7 mmol), K_2CO_3 (14.0 g, 101.3 mmol), and DMSO (200 mL) was stirred at ambient temperature for 30 min. Dichlorophthalonitrile (4.0 g, 20.3 mmol) was added, and the reaction mixture was maintained at 80 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature, quenched with brine (100 mL), extracted into ether (2 × 100 mL), and washed with water (2 × 100 mL), and the solvent was removed under reduced pressure to obtain a yellow solid. Activated carbon was used to decolorize the compound, when necessary. Further purification using flash chromatography (SiO_2 , 10:90 ethyl acetate/hexanes) afforded **1a** (5.17 g, 70%) as a colorless solid: mp 70–72 °C (lit.²⁹ mp 71 °C); ^1H NMR (500 MHz, CDCl_3) δ 7.38 (s, 2H), 3.00–2.97 (t, $J = 15$ Hz, 4H), 1.75–1.69 (p, $J = 30$ Hz, 4H), 1.50–1.44 (m, 4H), 1.32–1.29 (m, 8H), 0.90–0.87 (m, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.2, 128.1, 115.6, 111.0, 32.7, 31.2, 28.5, 28.0, 22.4, 13.9; MS (EI) m/z 360.1 $[\text{M}]^+$, $\text{C}_{20}\text{H}_{28}\text{N}_2\text{S}_2$ requires 360.1. Anal. Calcd for $\text{C}_{20}\text{H}_{28}\text{N}_2\text{S}_2$: C, 66.62; H, 7.83; N, 7.77. Found: C, 66.74; H, 8.06; N, 8.02.

4,5-Bis(heptylthio)phthalonitrile (1b)²⁹. Following the procedure for **1a**, heptane-1-thiol (4.7 g, 35.5 mmol), K_2CO_3 (7.0 g, 50.7 mmol), and dichlorophthalonitrile (2.0 g, 10.1 mmol), after flash chromatography (SiO_2 , 10:90 ethyl acetate/hexanes), afforded **1b** (3.3 g, 84%) as a colorless solid: mp 72–74 °C (lit.²⁹ mp 61 °C); ^1H NMR (500 MHz, CDCl_3) δ 7.39 (s, 2H), 3.00–2.98 (t, $J = 10$ Hz, 4H), 1.76–1.70 (p, $J = 30$ Hz, 4H), 1.48–1.44 (p, $J = 20$ Hz, 4H), 1.34–1.26 (m, 12H), 0.88 (m, 6H); ^{13}C NMR (500 MHz, CDCl_3) δ 144.2, 128.1, 115.6, 111.0, 32.7, 31.6, 28.8, 28.7, 28.1, 22.5, 14.0; MS (EI) m/z 388.2 $[\text{M}]^+$, $\text{C}_{22}\text{H}_{32}\text{N}_2\text{S}_2$ requires 388.2. Anal. Calcd. for $\text{C}_{22}\text{H}_{32}\text{N}_2\text{S}_2$: C, 67.99; H, 8.30; N, 7.21. Found: C, 67.67; H, 8.10; N, 7.21.

4,5-Bis(octylthio)phthalonitrile (1c)³⁰. Following the procedure for **1a**, octane-1-thiol (2.3 g, 15.6 mmol), K_2CO_3 (8.6 g, 62.4 mmol), and dichlorophthalonitrile (1.2 g, 6.2 mmol), after flash chromatography (SiO_2 , 10:90 ethyl acetate/hexanes), afforded **1c** (2.2 g, 86%) as a colorless solid: mp 56–58 °C (lit.³⁰ mp 62 °C); ^1H NMR (500 MHz, CDCl_3) δ 7.42 (s, 2H), 3.04–3.01 (t, $J = 14.5$ Hz, 4H), 1.79–1.73 (p, $J = 29.5$ Hz, 4H), 1.53–1.47 (m, 4H), 1.33–1.29 (m, 16H), 0.91–0.88 (m, 6H); ^{13}C NMR (500 MHz, CDCl_3) δ 144.6, 128.5, 116.0, 111.4, 33.2, 32.2, 29.55, 29.52, 29.3, 28.5, 23.1, 14.5; MS (EI) m/z 416.2 $[\text{M}]^+$, $\text{C}_{24}\text{H}_{36}\text{N}_2\text{S}_2$ requires 416.2. Anal. Calcd. for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{S}_2$: C, 69.18; H, 8.71; N, 6.72. Found: C, 69.17; H, 8.90; N, 6.57.

4,5-Bis(nonylthio)phthalonitrile (1d). Following the procedure for **1a**, nonane-1-thiol (4.2 g, 26.6 mmol), K_2CO_3 (5.3 g, 38.0 mmol), and dichlorophthalonitrile (1.5 g, 7.0 mmol), after flash chromatography (SiO_2 , 3:97 ethyl acetate/hexanes), afforded **1d** (2.6 g, 78%) as a colorless solid: mp 74–76 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.38 (s, 2H), 3.00–2.98 (t, $J = 10$ Hz, 4H), 1.74–1.71 (p, $J = 15$ Hz, 4H), 1.48–1.45 (p, $J = 15$ Hz, 4H), 1.34–1.27 (m, 20H), 0.88–0.86 (t, $J = 10$ Hz, 6H); ^{13}C NMR (500 MHz, CDCl_3) δ 144.2, 128.1, 115.6, 111.0, 32.8, 31.9, 29.4, 29.2, 29.1, 28.9, 28.1, 22.7, 14.1; MS (EI) m/z 444.2 $[\text{M}]^+$,

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$C_{26}H_{40}N_2S_2$ requires 444.2. Anal. Calcd for $C_{26}H_{40}N_2S_2$: C, 70.22; H, 9.07; N, 6.30. Found: C, 69.92; H, 9.12; N, 6.39.

4,5-Bis(decylthio)phthalonitrile (1e). Following the procedure for **1a**, decane-1-thiol (2.7 g, 15.6 mmol), K_2CO_3 (8.6 g, 62.4 mmol), dichlorophthalonitrile (1.2 g, 6.2 mmol), and DMSO (50 mL), after flash chromatography (SiO_2 , 10:90 ethyl acetate/hexanes), afforded **1e** (2.25 g, 76%) as a colorless solid: mp 54–56 °C; 1H NMR δ (500 MHz, $CDCl_3$) 7.38 (s, 2H), 3.00–2.97 (t, $J = 14.5$ Hz, 4H), 1.75–1.69 (p, $J = 30$ Hz, 4H), 1.47–1.43 (m, 4H), 1.33–1.25 (m, 24H), 0.87–0.84 (m, 6H); mp. 54–56 °C; ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 128.5, 116.0, 111.5, 33.2, 32.3, 29.9, 29.8, 29.7, 29.5, 29.3, 28.5, 23.1, 14.5; MS (EI) m/z 472.2 $[M]^+$, $C_{28}H_{44}N_2S_2$ requires 472.2. Anal. Calcd for $C_{28}H_{44}N_2S_2$: C, 71.13; H, 9.38; N, 5.93. Found: C, 70.81; H, 9.46; N, 6.10.

2,3,9,10,16,17,23,24-Octakis(hexylthio)phthalocyaninatooxotitanium(IV) (2a)²⁰. A mixture of Pn **1a** (4.1 g, 11.4 mmol) and urea (0.3 g, 5.7 mmol) was heated under argon to the melting point of the Pn (70 °C). $Ti(OPr)_4$ (1.62 g, 5.70 mmol) was then added via syringe to the melt, and the temperature was raised and maintained at 150 °C for 24 h. The reaction mixture was allowed to cool to room temperature, precipitated in methanol (100 mL), and centrifuged. The precipitate was dispersed and centrifuged in water (40 mL) and methanol (40 mL), sequentially. Finally, the brown-black precipitate was dispersed in acetone, filtered, and washed copiously with acetone until the filtrate was colorless. The precipitate was air-dried to obtain a black powder, which was then redissolved in a minimum amount of DCM and mixed with silica gel (30 g). Solvent was removed from the silica slurry on the rotovap, and then it was further dried under high vacuum to obtain a free-flowing powder, which was subjected to flash chromatography (SiO_2 , 0:100 to 50:50 ethyl acetate/hexanes). After concentration of the eluted product, it was dispersed in acetone and then centrifuged. The precipitate was dried at 35–40 °C for 24 h under vacuum to obtain **2a** (0.73 g, 16%) as a black solid: UV (λ_{max} , nm) 736; 1H NMR δ (500 MHz, $CDCl_3$) 8.82–8.78 (br s, 8H), 3.56–3.45 (br s, 16H), 2.07 (br s, 16H), 1.75–1.68 (br s, 16H), 1.64–1.47 (br s, 32H), 0.98 (m, 24H); MS (MALDI) m/z 1505.7 $[M + H]^+$, $C_{80}H_{113}N_8OS_8Ti$ requires 1505.6; 1714.9 $[(MDTH) - OH]^+$, $C_{94}H_{121}N_8O_3S_8Ti$ requires 1714.7; 1730.0 $[(MHABA) - OH]^+$, $C_{93}H_{121}N_{10}O_3S_8Ti$ requires 1730.6. Anal. Calcd for $C_{80}H_{112}N_8OS_8Ti$: C, 63.79; H, 7.50; N, 7.44. Found: C, 63.42; H, 7.54; N, 7.50.

2,3,9,10,16,17,23,24-Octakis(heptylthio)phthalocyaninatooxotitanium(IV) (2b). Following the procedure for **2a**, Pn **1b** (1.00 g, 2.57 mmol), urea (0.08 g, 1.3 mmol), and $Ti(OPr)_4$ (0.37 g, 1.3 mmol) after flash chromatography afforded **2b** (0.44 g, 42%) as a black solid: UV (λ_{max} , nm) 736; 1H NMR δ (500 MHz, $CDCl_3$) 8.82–8.81 (br s, 8H), 3.61–3.35 (br s, 16H), 2.15 (br s, 16H), 1.71–1.70 (br s, 16H), 1.49–1.16 (br m, 48H), 0.92 (m, 24H); MS (MALDI) m/z 1618.8 $[M + H]^+$, $C_{88}H_{129}N_8OS_8Ti$ requires 1618.7; 1826.7 $[(MDTH) - OH]^+$, $C_{102}H_{137}N_8O_3S_8Ti$ requires 1826.8; 1841.9

$[(MHABA) - OH]^+$, $C_{101}H_{137}N_{10}O_3S_8Ti$ requires 1841.8. Anal. Calcd for $C_{88}H_{128}N_8OS_8Ti$: C, 65.31; H, 7.97; N, 6.92. Found: C, 64.86; H, 7.95; N, 7.02.

2,3,9,10,16,17,23,24-Octakis(octylthio)phthalocyaninatooxotitanium(IV) (2c). Following the procedure for **2a**, Pn **3** (0.88 g, 2.1 mmol), urea (0.06 g, 1.0 mmol), and $Ti(OPr)_4$ (0.31 g, 1.1 mmol) after flash chromatography afforded **2c** (0.31 g, 34%) as a black solid: UV (λ_{max} , nm) 736; 1H NMR δ (500 MHz, $CDCl_3$) 8.73–8.70 (br s, 8H), 3.47 (br s, 16H), 2.04 (br s, 16H), 1.93–1.90 (br s, 16H), 1.53–1.24 (br m, 64H), 0.90 (m, 24H); MS (MALDI) m/z 1730.8 $[M + H]^+$, $C_{96}H_{145}N_8OS_8Ti$ requires 1730.8; 1938.9 $[(MDTH) - OH]^+$, $C_{110}H_{153}N_8O_3S_8Ti$ requires 1938.9; 1953.1 $[(MHABA) - OH]^+$, $C_{109}H_{153}N_{10}O_3S_8Ti$ requires 1953.9. Anal. Calcd for $C_{96}H_{145}N_8OS_8Ti$: C, 66.63; H, 8.39; N, 6.47. Found: C, 66.23; H, 8.46; N, 6.61.

2,3,9,10,16,17,23,24-Octakis(nonylthio)phthalocyaninatooxotitanium(IV) (2d). Following the procedure for **2a**, Pn **1d** (0.80 g, 1.50 mmol), urea (0.05 g, 0.8 mmol), and $Ti(OPr)_4$ (0.37 g, 1.3 mmol) after flash chromatography afforded **2d** (0.35 g, 42%) as a black solid: UV (λ_{max} , nm) 736; 1H NMR δ (500 MHz, $CDCl_3$) 8.73 (br s, 8H), 3.50 (br s, 16H), 2.06 (br s, 16H), 1.95 (br s, 16H), 1.75–1.24 (br m, 80H), 0.87–0.85 (m, 24H); MS (MALDI) m/z 1842.9 $[M + H]^+$, $C_{104}H_{161}N_8OS_8Ti$ requires 1843.0; 2051.1 $[(MDTH) - OH]^+$, $C_{118}H_{169}N_8O_3S_8Ti$ requires 2051.1; 2066.2 $[(MHABA) - OH]^+$, $C_{117}H_{169}N_{10}O_3S_8Ti$ requires 2066.1. Anal. Calcd. for $C_{104}H_{160}N_8OS_8Ti$: C, 67.78; H, 8.75; N, 6.08. Found: C, 67.39; H, 8.84; N, 6.12.

2,3,9,10,16,17,23,24-Octakis(decylthio)phthalocyaninatooxotitanium(IV) (2e). Following the procedure for **2a**, Pn **1e** (1.23 g, 2.60 mmol), urea (0.08 g, 1.3 mmol), and $Ti(OPr)_4$ (0.37 g, 1.3 mmol) after flash chromatography afforded **2e** (0.45 g, 35%) as a black solid: UV (λ_{max} , nm) 736.5; 1H NMR δ (500 MHz, $CDCl_3$) 8.73 (br s, 8H), 3.50 (br s, 16H), 2.06 (br s, 16H), 1.95 (br s, 16H), 1.75–1.24 (br m, 96H), 0.87–0.85 (m, 24H); MS (MALDI) m/z 1955.3 $[M + H]^+$, $C_{112}H_{177}N_8OS_8Ti$ requires 1954.1; $[(MDTH) - OH]^+$ 2163.3, $C_{126}H_{185}N_8O_3S_8Ti$ requires 2163.2; 2178.4 $[(MHABA) - OH]^+$, $C_{125}H_{185}N_{10}O_3S_8Ti$ requires 2178.1. Anal. Calcd for $C_{112}H_{176}N_8OS_8Ti$: C, 68.81; H, 9.07; N, 5.73. Found: C, 68.44; H, 8.93; N, 5.82.

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Supporting Information Available: Experimental details and characterization data for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.