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PREPARATION AND OPTICAL AND ELECTROCHEMICAL PROPERTIES OF UNSYMMETRICAL PHTHALOCYANINES WITH ONE OR TWO TTF UNITS

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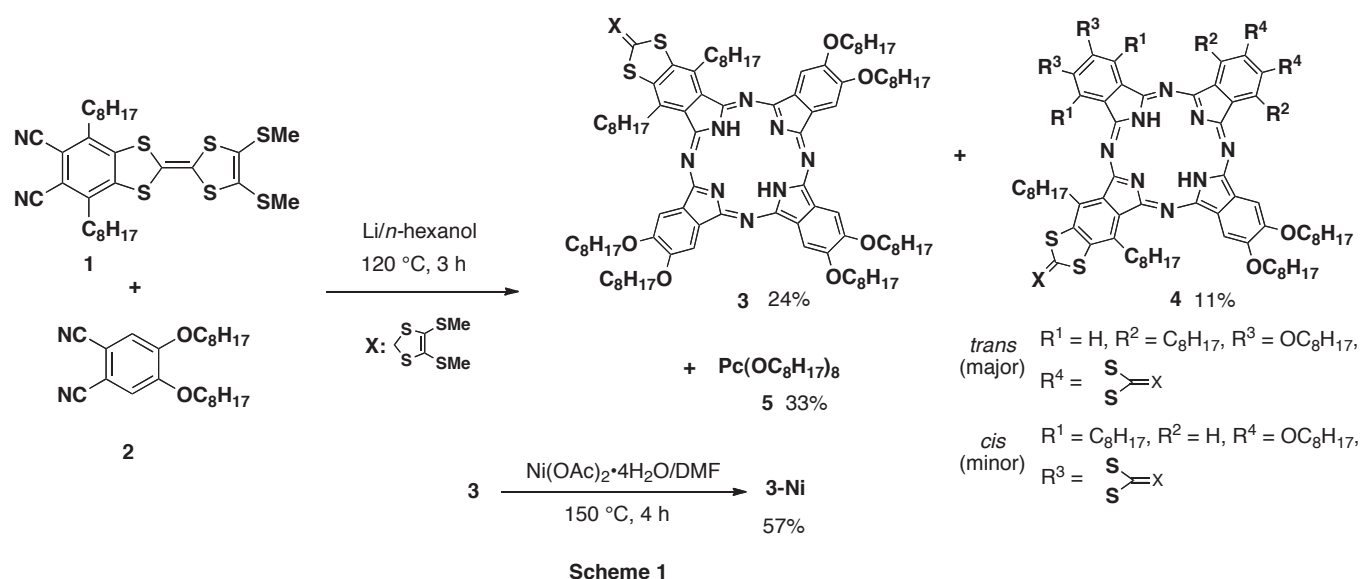
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Dedicated to Prof. Dr. Albert Padwa on the occasion of his 75th birthday.

Abstract – Unsymmetrical phthalocyanines with one or two TTF units were obtained by treating mixed 3,6-dioctyltetrathiafluvalenophthalonitrile and 4,5-dioctoxyphthalonitrile with Li in *n*-hexanol. Their optical and electrochemical properties were examined by UV-vis spectroscopy and cyclic voltammetry.

Phthalocyanines (Pcs) have attracted considerable attention because of their actual and potential applications as catalysis, charge-generating materials, optical devices, sensitizers for photodynamic therapy, and so forth.¹ Unsymmetrical Pcs can show unique properties in nonlinear optics that are different from the symmetrical ones.¹ Three approaches have been used to obtain unsymmetrical derivatives.² On the other hand, there are several reports of hybrid molecules consisting of Pcs and tetrathiafulvalene (TTF), in which the molecules are connected with some linkers.³ In addition, Decurtins prepared Pcs with four TTF scaffolds directly fused to the macrocycles.⁴ In the course of our study, we recently reported Pcs with four TTF units [Pc(TTF)₄] and related compounds.⁵ However, there are a few reports of unsymmetrical Pcs and porphyrins fused with TTF units.⁶ This paper reports the preparation, UV-vis spectroscopy, and electrochemical properties of Pcs with one or two TTF units. In order to generate cationic species, the Pcs were further treated with trifluoroacetic acid (TFA) and

iodine. As a starting compound, 3,6-dioctylphthalonitrile (**1**) with a TTF unit was prepared from 1,4-dichlorobenzene by using a method described previously.^{5a} To synthesize unsymmetrical Pcs, **1** and **2** were mixed in a 1 : 4 ratio and treated with lithium in *n*-hexanol at 120 °C for 3 h (Scheme 1). The blue-green product was purified by column chromatography with silica gel and Bio-beads to give three Pcs: **3** (24%), **4** (11%), and **5** (33%).⁷ Although Pc(TTF)₄ could not be obtained at all, **4** seemed to contain a trace amount of Pc(TTF)₃. Compound **3** was further reacted with nickel (II) acetate at 150 °C for 4 h and the resulting nickel (II) complex was obtained in 57% yield.



Because of aggregative properties, ¹H NMR of the products was measured at 50 °C. Both **3** and **3-Ni** showed one singlet peak for two methylthio groups. In the spectrum of **4**, methylthio groups were observed as three singlet peaks, suggesting that **4** contains the *cis* and *trans* isomers. A matrix assisted laser desorption ionization-time of flight-mass spectrometry (MALDI-TOF-MS) experiment (matrix: dithranol) showed the molecular ion peak for **3** at $m/z = 1775.575 [M^+]$. Compounds **3-Ni** and **4** also revealed corresponding molecular ion peaks at $m/z = 1830.882 [M^+]$ and $m/z = 2011.2 [M^+]$, respectively. In the spectrum of **4**, weak signals of the molecular ion for Pc(TTF)₃ could be found.

The Q-band absorption of **3** was observed as split peaks in the UV-vis spectrum while **3-Ni** showed a sharp signal (Figure 1). The Q band absorption of **4** ($\lambda_{\max} = 725.5 \text{ nm}$) was at a lower energy level than that of **3**. When the CHCl₃ solution of **3** was treated with TFA, the color of the solution changed from green to dark brown.⁸ In contrast, **3-Ni** was blue-green color by the similar treatment. The protonation of metal-free Pcs can occur on the central pyrrole and the *meso* nitrogen atoms while the metal complex was protonated at the *meso* nitrogen atoms. To determine the effect of acid concentration, the UV-vis spectra of **3** and **3-Ni** were measured in the presence of 1 to 100 equiv. of TFA.

However, the spectra did not change under these conditions and a large excess of TFA had to be added to observe spectral changes. When further TFA was added to bring the solution up to 1000 equiv., the Q-band absorptions gradually decreased in intensity. Finally, the absorptions were broadened and observed in the red-shifted regions by the addition of 10 vol% of TFA. When further TFA was added to the solution, no changes of the absorption appeared in the spectra. The protonation of **3** and **3-Ni** is significantly hard and hence may produce monoprotinated species in the solution, respectively.

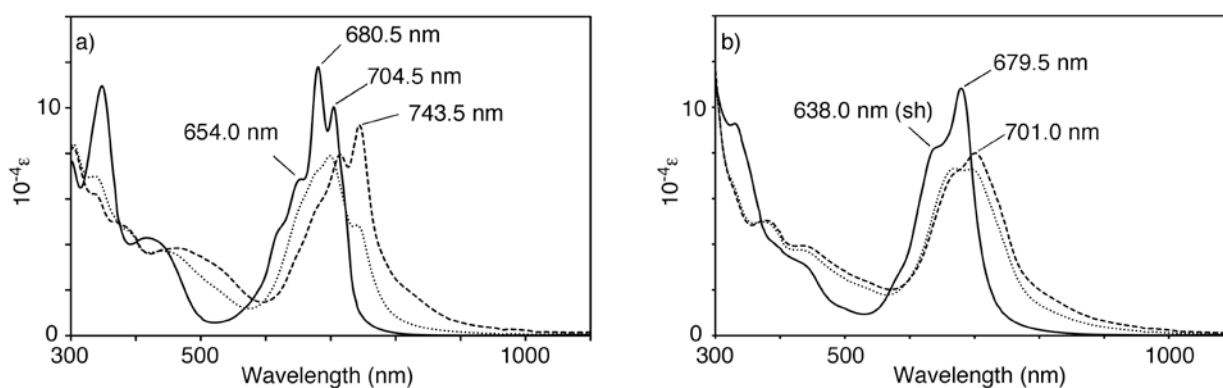


Figure 1. UV-vis spectra of **3** and **3-Ni**: a) **3** was measured in CHCl_3 (solid line), CHCl_3 + 5000 equiv. of TFA (dotted line), CHCl_3 + 10 vol% of TFA (dashed line); b) **3-Ni** was measured in CHCl_3 (solid line), CHCl_3 + 10000 equiv. of TFA (dotted line), CHCl_3 + 10 vol% of TFA (dashed line).

Table 1. Redox potentials (V) vs Ag/AgNO_3

Pc	3rd redn	2nd redn	1st redn	1st oxid	2nd oxid	Pc	2nd redn	1st redn	1st oxid	2nd oxid
3	-1.47 ^a	-1.27 ^a	-0.78 ^a	0.41 ^a	0.72 ^a	3-Ni	-1.36 ^b	-0.98 ^a	0.39 ^a	0.73 ^a
4	-1.44	-1.23	-0.78	0.33	0.75	5	-1.65	-1.13	0.29	

The cyclic voltammetry was measured in CH_2Cl_2 ; scan rate: 200 mV/s; ^aQuasi reversible, ^bIrreversible (E_p/V).

It was reported that when the UV-vis spectrum of Pc bearing eight TTF units, connected by the linker, was measured in the presence of iodine, a new broadened absorption was observed at around 820 nm.^{3b} On measurement of the UV-vis spectrum of **3-Ni** in the presence of 150 equiv. of iodine (CHCl_3), a broadened and slightly blue-shifted Q-band absorption (676.5 nm) was observed in the spectrum. In contrast, **3** showed faint changes in the Q-band absorption under the similar condition, suggesting that the TTF unit of **3** may have lowered reactivity to iodine because of π -conjugation with the Pc unit.

The electrochemical properties of **3**, **4**, and **3-Ni** were determined by cyclic voltammetry (Table 1). The voltammogram of **3** showed two quasi-reversible couples for oxidation, while three quasi-reversible couples were observed for reduction. Compound **4** exhibited two reversible oxidation couples and three reversible reduction couples, which may depend on those of the *trans* isomer. We could observe two quasi-reversible peaks for the oxidation of **3-Ni**, and one quasi-reversible and one irreversible peak for the reduction. It appears that the redox potentials of **3**, **4**, and **3-Ni** are positively shifted in comparison with those of **5**, while the first oxidation potential of **3** is higher than that of **4** and **3-Ni**.

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7. **3**: mp 285 °C (decomp); ¹H NMR (500 MHz, CDCl₃) δ -3.71 (s, 2H, NH), 0.84 (t, J = 6.9 Hz, 6H, CH₃), 0.93-1.07 (m, 18H, CH₃), 1.16-1.60 (m, 56H, CH₂), 1.60-1.70 (m, 12H, CH₂), 1.70-1.78 (m, 4H, CH₂), 1.78-1.94 (m, 12H, CH₂), 2.15-2.32 (m, 12H, CH₂), 2.60 (s, 6H, SCH₃), 3.43-3.99 (m, 4H, CH₂), 4.29 (br, 4H, OCH₂), 4.52-4.71 (m, 8H, OCH₂), 7.94 (br, 2H, ArH), 8.43 (br, 2H, ArH), 8.46 (br, 2H, ArH); MALDI-TOF-MS (m/z) 1775.575 [M⁺]; Anal. Calcd for C₁₀₂H₁₅₀N₈O₆S₈: C, 68.95; H, 8.51; N, 6.31%. Found: C, 68.90; H, 8.54; N, 6.16%; **4**: mp 200 °C (decomp); ¹H NMR (500 MHz, CDCl₃) δ -2.99 (s, 2H, NH), 0.72-1.03 (m, 24H, CH₃), 1.07-1.69 (m, 68H, CH₂), 1.69-1.90 (m, 12H, CH₂), 1.90-2.02 (m, 4H, CH₂), 2.02-2.11 (m, 4H, CH₂), 2.11-2.24 (m, 8H, CH₂), 2.59, 2.600, 2.603 (s, 12H, SCH₃), 3.79-4.61 (m, 16H, CH₂), 7.78-8.33 (m, 4H, ArH); MALDI-TOF-MS (m/z) 1830.882 [M⁺]; **3-Ni**: mp >300 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.88 (br, 6H, CH₃), 0.94-1.07 (m, 18H, CH₃), 1.22-1.60 (m, 56H, CH₂), 1.60-1.70 (m, 12H, CH₂), 1.70-1.77 (m, 4H, CH₂), 1.77-1.93 (m, 12H, CH₂), 2.14-2.29 (m, 12H, CH₂), 2.62 (brs, 6H, SCH₃), 3.26-3.89 (m, 4H, CH₂), 4.29 (br, 4H, OCH₂), 4.54 (br, 4H, OCH₂), 4.59 (br, 4H, OCH₂), 7.63 (br, 2H, ArH), 8.14 (br, 2H, ArH), 8.21 (br, 2H, ArH); MALDI-TOF-MS (m/z) 1830.882 [M⁺].

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