Synthesis and electron-donating properties of novel norphthalocyanines containing thiacycrown ether-linked tetrathiafulvalene moieties

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Abstract

A novel magnesium-base and metal-free norphthalocyanine (**6** and **7**) containing a peripheral thiacycrown ether-linked tetrathiafulvalene moieties has been synthesized and fully characterized. Electrochemical investigations showed two quasi-reversible one-electron oxidation waves, one irreversible one-electron oxidation wave and two irreversible one-electron reduction waves, indicating that these triads are good π -electron donors. Triad **6** reacted with 2,3,5,6-tetrafluoro-7,7,8,8-tetra-cyanoquinodimethane (F₄TCNQ) to form a charge transfer complex that exhibited absorption bands in the vicinity of 750 and 960 nm. Compound **6** showed evident intramolecular charge transfer interactions in ground states and these may be explained on the basis of density functional theory.

Keywords: norphthalocyanine; tetrathiafulvalene; crown ether; density functional theory

subtitles : Synthesis and properties of the conjugates of norphthalocyanines and tetrathiafulvalene

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The construction of ensembles composed of covalently linked electron donor and acceptor moieties is currently a significant challenge in the field of material science and supramolecular chemistry.¹⁻⁷ Typical examples of this type of ensemble are the polyads derived from tetrathiafulvalene (TTF) derivatives and macrocyclic tetrapyrroles (porphyrin, phthalocyanine and porphyrazine).⁸⁻¹⁰ To date, a wide variety of symmetrical macrocyclic tetrapyrroles have been extensively studied.¹¹⁻¹³ However, there have been only a limited number of reports on concerning unsymmetrical porphyrinic macrocycles,¹⁴⁻¹⁷ mainly because they are much more difficult to be synthesized and purified. In recent years, there has been a growing interest in the properties of the unsymmetrical phthalocyanines (Pcs) because these compounds display high thermal stability, mesogenic behavior, and second- or third-order nonlinear optical properties in solution, and are also capable of forming Langmuir–Blodgett films exhibiting semiconducting properties. Recently, we reported a series of symmetrical porphyrazines (Pzs) bearing tetrathiafulvalene (TTF) units, including the Pzs linked with TTF units containing either crown ether or ethylenedithio spacers.¹⁸ Pzs bearing multi-TTF units show good electron-donating properties and are found to contain four different octa- radical cationic TTF moieties.

In the present work, we describe the synthesis and photophysical and electrochemical properties of two new norphthalocyanine (NPc) derivatives **6** and **7**, composed of one TTF units acting as an electron donor and a single norphthalocyanine ring acting as an acceptor and covalently linked with one thiacyclopentane ether spacers.

The reaction pathways for the preparation of the complexes were shown in Scheme 1. Compound **1** was obtained according to a published procedure¹⁹ and then deprotected by treatment with cesium hydroxide in a mixture of DMF and MeOH after which the resulting thiolate ion was

reacted with excess 2-bromoethanol to give **2** in 59% yield. Tosylation of **2** formed **3**, and the latter was converted to the bis-iodo intermediate **4** by a Finkelstein reaction using sodium iodide in acetone. Subsequently, compound **4** was reacted with an equivalent amount of cis-1,2-dicyano-1,2-ethylenedithiolate disodium salt in DMF and under nitrogen to give the TTF-dicyano-tetrathiacrown ether **5** in good yield (40.5%). The relatively high yields of the cyclization reaction can be attributed to the effect of being high dilution.¹² The IR spectrum of **5** showed a typical C≡N stretching vibration at 2215 cm⁻¹ that disappeared upon tetramerization to the norphthalocyanine **6**. The mixed condensation of 1 equiv. of dithiomaleonitrile **5** (A) and 20 equiv. of phthalonitrile (B) under classic Linstead macrocyclization conditions (magnesium n-Butoxide/n-Butanol) produced two porphyrinic products; the desired norphthalocyanine **6** (AB₃) and the phthalocyanine (B₄). Fortunately, the significant difference in polarity between the products allowed us to readily separate product **6**. Demetallation of **6** with acetic acid gave the free base norphthalocyanine **7** in 66% yield as a deep blue powder. Compound **6** and **7** were soluble in the usual organic solvents with the exception of alcohols. The ¹H -NMR spectra of **6** and **7** were recorded in CDCl₃ at 25°C showed slightly broadened signals except for those originating from the terminal methyl groups. This could be explained as the result of aggregation in concentrated solutions.²⁰ In the ¹H NMR spectrum of **7**, the typical shielding of the inner core NH protons was observed as broad signals at δ=-1.79. The matrix assisted laser desorption/ionization – time of flight (MALDI-TOF) mass spectra of **6** and **7** featured peaks at m/z values of 1103.11 [M]⁺ and 1081.47 [M]⁺, respectively, corresponding to the M⁺ of **6** and **7** (1103.11 and 1081.62). Elemental analyses of these compounds were in accord with the proposed molecular formula.

Scheme 1. Synthetic route to norphthalocyanines (**6** and **7**)

The optical spectra of all norphthalocyanine **exhibited** two main bands, a Soret or B band ($\pi \rightarrow \pi^*$, corresponding to a deep $\pi \rightarrow \text{LUMO}$ transition) between 339-359 nm and another at approximately 650 nm, denoted as the Q band ($\pi \rightarrow \pi^*$) (Figure 1). In general, the four fold symmetric porphyrinic macrocycles all generate similar optical spectra, with single transitions for both the Q and B bands. In contrast, the optical spectra of the unsymmetrical norphthalocyanines **6** and **7**, with three fused benzo rings and one TTF units substituted with a thiacrown ether moiety, clearly **showed** a splitting of the Q band. These optical spectra resemble those reported in the literatures for norphthalocyanines substituted with 2,3-dialkylthio groups in the literatures.²⁰ These differences can be explained using Gouterman's highly simplified four orbital model for the optical

spectra of porphyrinic macrocycles.

Figure 1. Absorption spectra of **6** in CH₂Cl₂ (1×10^{-5} M) after addition of 1 equiv F₄TCNQ.

To further assess the electron-donating properties of the target compounds **6** was doped with an excess of 7,7,8,8-Tetracyanoquinodimethane (TCNQ) in CH₂Cl₂. However, no charge transfer band was observed in the 740 to 1000 nm region, which might be attributed to the presence of the electron-withdrawing NPc ring. In contrast, the addition of one equiv. of 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) to a CH₂Cl₂ solution of **6** (1×10^{-5} M) resulted in the appearance of two new charge transfer absorption bands, centered at λ_{max} of 760 nm and λ_{max} 863 nm in the UV-Vis spectrum (Figure 1). These new bands corresponded to the SOMO–LUMO transition of the cation radical species of the TTF moieties.¹⁷ The formation of the F₄TCNQ^{•−} / TTF^{•+} charge transfer complex in CH₂Cl₂ was also confirmed from FT-IR and electron paramagnetic resonance (EPR) spectra. The FT-IR spectrum of **6** showed the nitrile stretch of the F₄TCNQ radical anion at 2191 cm^{−1} compared with the band at 2222 cm^{−1} generated in the neutral state. In addition, the EPR spectrum of **6** was centered in the vicinities of $g = 2.008$ and 2.002 regions that were characteristic of both a TTF radical cation and a F₄TCNQ radical anion.¹⁷ These

results demonstrated that some charge transfer took place between the TTF unit(s) and F₄TCNQ in solution(Figure 2).

Figure 2. EPR spectrum of the complex of **6** with F₄TCNQ in CH₂Cl₂ at 25 °C.

The electrochemical characterization of compounds **6** and **7** was carried out using cyclic voltammetry in a mixture of CH₂Cl₂ and CH₃CN (7:3, v/v). Figure 3 presented the cyclic and differential pulse voltammograms of **6** within a -2V to +2V potential window. Compound **6** generated two reduction couples ($E_{1/2}$ = -1.42 and -0.95 V) and three oxidation couples ($E_{1/2}$ = 0.47, 0.93 and 1.59 V) within the potential window of the DMC-ACN/Bu₄NPF₆ electrolyte system. These five couples were assigned to NPc⁻³/NPc⁻⁴ (I), NPc⁻²/NPc⁻³(II), TTF⁺/TTF (III), TTF⁺²/ TTF⁺(IV) and NPc⁻¹/NPc⁻²(V) on the basis of results previously published in the literature.¹⁹ Processes I, II and V were irreversible in terms of the ratio of anodic to cathodic peak currents. In contrast, processes III and IV, which can be assigned to the simultaneous first and second oxidations of the TTF unit, were quasi-reversible. These latter two processes have anodic to cathodic peak separation (ΔE) values of 0.183 V and 0.21 V, respectively, and the unity of the I_{pa} / I_{pc} ratios of unity at all scan rates and linear variation of the peak currents. Compound **7** showed similar voltammetric behaviors to **6**, accompanied by significant anodic shifts of the two reduction waves, corresponding

to the demetallation of the magnesium complex **6** (Figure S8).

Figure 3. Cyclic voltammogram of **6** (1×10^{-3} M) in 0.1M tetrabutylammonium hexafluorophosphate in a mixture of $\text{CH}_2\text{Cl}_2/\text{MeCN}(9:1, \text{v/v})$ at 0.1 V s^{-1} (inset: DPV of **6** under the same conditions).

To investigate the nature of the electronic transitions, we performed molecular orbital calculations for **6** at the Perdew-Burke-Erzenrhof (PBE) functional level²² and the basis set effect has been tested using different combination of basis sets for metal and main group atoms. LANL2DZ²³ and 6-31G²⁴ basis sets were used for Mg and the other atoms in all calculations, respectively. All calculations were performed with the B.01 revision of the Gaussian 09 program package.²⁵ Figure 3 showed the HOMO and LUMO levels of **6**. It is evident that the HOMO and LUMO of **6** are significantly different. The electron density distributions of the HOMO are primarily situated on sulfur atoms in dihexyl and TTF moieties, while the LUMO density is mainly concentrated on the Mg norporphyrazines. Generally, dye molecule with this type of electron distribution exhibit the intermolecular charge transfer (ICT) characteristic (Figure 4).²⁶

Figure 4. A diagram showing the HOMO and LUMO levels of compound 6.

In summary, we first synthesized two A₃B-type norphthalocyanines (**6** and **7**) each bearing a single TTF unit linked by a thiacrownetherspacer. These syntheses were confirmed using NMR spectroscopy, MALDI-TOF mass spectrometry and elemental analysis. The ability of compound **6** to function as a donor for F₄TCNQ was established, and evidence for the formation of a charge transfer complex was obtained by UV-vis, EPR and IR spectroscopy. Theoretical calculations were found to be useful as a means of improving our understanding of the electronic structures of the interacting molecules. The complexation of the target compounds with soft metal cations and the synthesis of long alkyl chain analogs are currently being investigated in our laboratory.

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