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Supramolecular Stacks of Asymmetric Zinc Phthalocyanines Functionalized with One Tetrathiafulvalene Unit

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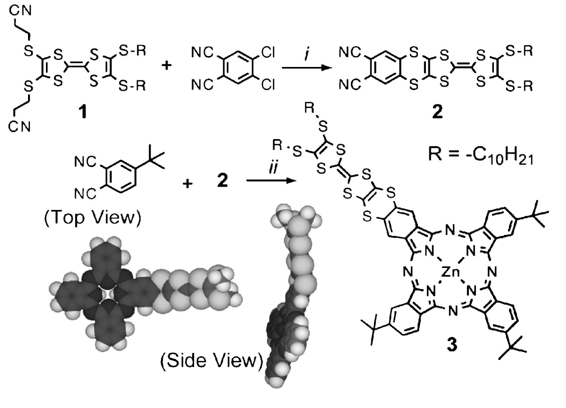
An asymmetric hybrid compound, in which one tetrathiafulvalene (TTF) unit is attached to a zinc phthalocyanine (ZnPc) ring, has been studied by spectroscopy and electrochemistry. Its Langmuir–Blodgett film-forming properties have also been examined.

Since the discovery of semiconductive properties in phthalocyanines and condensed aromatic carbons, an extremely large number of one-dimensional assemblies of organic and metal–organic compounds have been investigated as molecular metals.[1] To obtain highly electrical conducting assemblies, the conjugated molecular components should be arranged in close spatial proximity like in crystals. The use of molecular self-assembly through noncovalent intermolecular interactions provides one possible direction in the exploration of readily accessible soft conducting materials. In this context, there have been many attempts to construct well-defined supramolecular structures involving one-dimensional stacks of conjugated molecular components.[2] Metallophthalocyanines (MPcs) and tetrathiafulvalenes (TTFs) have been used as molecular components for molecular metals.[3] Due to their excellent conductive properties, hybrid compounds composed of MPcs and TTFs have been synthesized in the search for novel optoelectronic materials.[4] Bryce et al. reported the synthesis of Pcs decorated with eight peripheral TTF units.[4a–4d] Cook et al. demonstrated liquid crystalline properties of asymmetric Pc possessing two TTFs.[4e] Nolte et al. reported the formation of self-assembled nanofibers made of tetra(TTF–crown ether)phthalocyanine.[4f] These compounds had spacer groups between the Pc core and TTFs. Here, we present the synthesis of a novel hybrid TTF–Pc compound in which one redox-active TTF is attached directly to the MPc ring to obtain novel molecular systems with unusual electrochemical and structural properties.[4g]

The synthesis of our target molecule **3** is shown in Scheme 1. The TTF derivative **1** was obtained in 70% yield by the standard phosphite-induced cross-coupling of 1,3-dithiole-2-one and -2-thione fragments.[5] Novel phthalocyanine precursor **2** was synthesized in 65% yield by the coupling of 4,5-dichlorophthalonitirile with **1** bearing two cyanoethyl units in the presence of K_2CO_3. The target asymmetric ZnPc **2** was prepared from **1** and 4-*tert*-butylphthalonitrile with a molar ratio of 1:3 with $ZnCl_2$ in dimethylaminoethanol.[6] The required ZnPc **3** was separated by column chromatography as a second fraction. Compounds **2** and **3** were characterized by ^{1}H NMR and MALDI-TOF mass spectra.



Scheme 1.

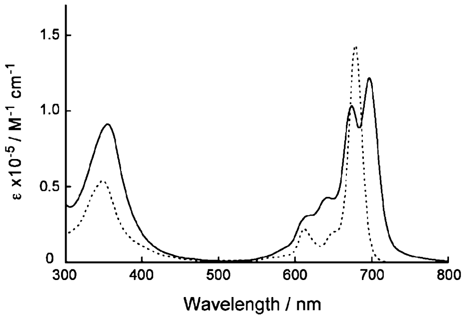


Figure 1. UV–vis spectra of **3** (solid line) and ZnPc(t-Bu)$_4$ (dashed line) in CH_2Cl_2.

Figure 1 shows the absorption spectra of **3** and symmetric tetra(*tert*-butyl)phthalocyaninatozinc complex (ZnPc(t-Bu)$_4$) in CH_2Cl_2. While ZnPc(t-Bu)$_4$ exhibits a single sharp Q-band at $\lambda_{max} = 678$ nm, the TTF-substituted **3** shows a split Q-band absorption at 674 and 697 nm. The splitting of the Q-band appears to be similar to that of low-symmetric Pc derivatives, and the red-shifting is attributed to the enlargement of the π-conjugated system.[7] In the 300–450 nm region, the spectrum of **3** shows superimposed bands of TTF and the Soret band of ZnPc. Compound **3** exhibits a fluorescence peak at 713 nm, which is longer than that of ZnPc(t-Bu)$_4$ (686 nm), which is also indicative of the enlargement of the π-conjugated system. Fluorescence quantum yield of **3** in CH_2Cl_2 is 0.04. This value is very much lower than that obtained for ZnPc(t-Bu)$_4$ lacking the TTF moiety: cf. ZnPc(t-Bu)$_4$, $\Phi = 0.21$. This fluorescence quenching is likely due to an intramolecular electron-transfer reaction between the excited singlet state of the ZnPc and TTF. An electrochemical study of **3** was performed through cyclic voltammetry measurement in CH_2Cl_2 containing 0.1 mol dm^{-3} TBAP as the supporting electrolyte. Compound **2** exhibits two reversible oxidation waves at $E_{1/2} = +0.61$ and $+0.83$ V vs.

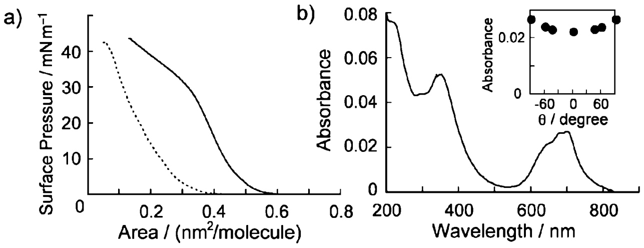


Figure 2. (a) Surface pressure vs. surface area isotherms for **2** (dashed line) and **3** (solid line). (b) UV–vis spectrum of 20-layer LB film of **3** deposited on hydrophobic quartz substrate. The inset shows angular dependence of the Q band intensity for LB film.

SCE. These potentials are almost in accord with the reported potentials for tetrakis(alkylsulfanyl)TTF derivatives.[4b,4c] Since Zn(II) does not undergo redox processes within the potential window in CH_2Cl_2, all oxidation processes of **3** can be ascribed as phthalocyanine ring-centered and TTF oxidations. Compound **3** displays two TTF redox waves at $+0.60$ and $+0.81$ V vs. SCE similar to those of the building block **2**, and the phthalocyanine-ring oxidation [ZnPc(-1)/ZnPc(-2)] is observed at around $+0.4$ V. The oxidation potential shifts to negative by 100 mV compared to ZnPc(*t*-Bu)$_4$,[8] suggesting that the phthalocyanine ring in **3** is easy to oxidize through the electron-donating property of the direct-substituted TTF moiety. These results of UV–vis, fluorescence, and electrochemical analyses suggest the intramolecular electronic interactions between ZnPc and TTF.

The Langmuir–Blodgett (LB) technique is a method for fabricating ordered molecular structures from organic functional molecules. Well-organized thin films have been created from MPcs and TTFs through the LB technique.[9] The pressure–surface area (π–A) isotherms for **2** and **3** on pure water at 18 °C are shown in Figure 2a. Compound **3** shows a steep increase of pressure for the monolayer formation at the air–water interface. The occupied area of **3** is larger than that of **2** (0.28 nm^2/molecule). Assuming the molecular dimension of **3** from the computer-generated molecular model (Scheme 1), the observed occupied area is in agreement with the estimated area for the edge of ZnPc moiety (0.525 nm^2/molecule). This indicates that the phthalocyanine ring planes are oriented perpendicular to the water surface with the side alkyl chains extended into air. Monolayers of **3** were transferred onto a hydrophobic quartz substrate by vertically dipping the substrate through the monolayer at a surface pressure of 20 mN m^{-1}. Y-type depositions occurred with a transfer ratio of about 1.0. Absorption spectrum of 20-layer LB film of **3** is shown in Figure 2b. Compared to the spectrum of **3** in CH_2Cl_2, the Q band of the LB film is broadened compared to that in solution. This spectral change is attributed to the formation of stacks among ZnPcs. The orientation of the molecules in the built-up LB film was analyzed by using the angular dependence of the absorption intensity using polarized light. When the electric vector of the incident light is coupled most strongly with the transition moment of the chromophore, the absorption intensity is maximum.[10] The relative absorption intensity minimizes at $\theta = 0°$ (θ is the angle between the incident light and substrate normal) suggesting the transition moment is tilted by less than 54.7° from the axis perpendicular to the substrate. These results indicate that **3** orient within the built-up LB films through the stacking of aromatic components and the packing of alkyl chains. The electrical conductivity of 20-layer LB films of **3** was measured by using evaporated gold electrodes with a gap distance of 500 µm. The LB films of **3** exhibit a low conductivity in the range 10^{-10}–10^{-9} S cm^{-1} at room temperature.[3a] After exposure of the LB films to I_2 vapor, the conductivity increased to 10^{-5}–10^{-4} S cm^{-1} due to the partial oxidations of TTFs or ZnPcs in the LB film.

In summary, novel asymmetric hybrid ZnPc **3** directly connected with one TTF unit was synthesized and organized through the π–π interaction between aromatic components and the close packing of alkyl chains in the LB film. The integration of molecular components will provide new molecular materials with interesting solution and solid-state properties.

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