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TTF–porphyrin dyads as novel photoinduced electron transfer systems

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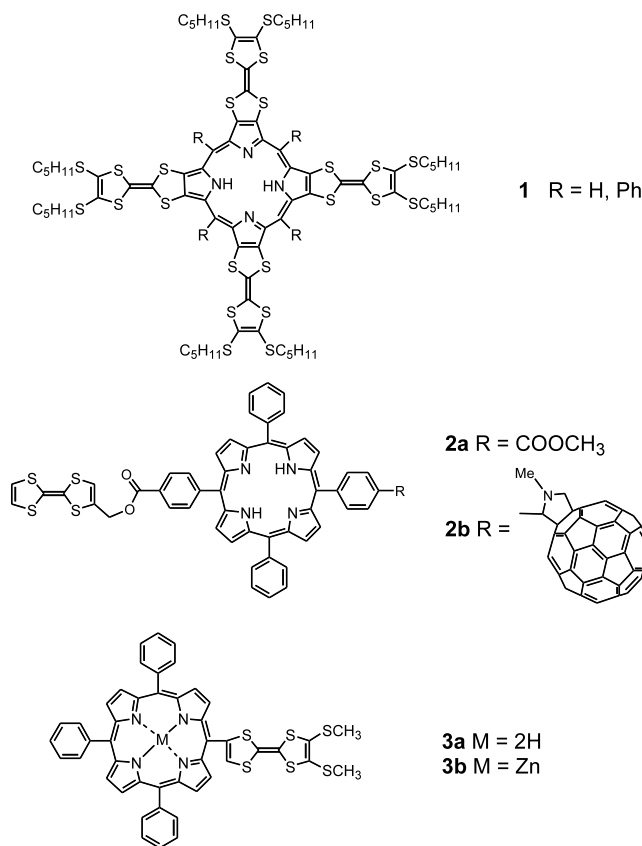
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This paper is dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday

Abstract—A TTF-linked porphyrin dyad and its zinc complex have been synthesized as novel photosystems with a redox-active pendant. The two chromophores of these dyads are not interactive in the absorption spectra, but the fluorescence of the porphyrin chromophore is dramatically quenched by intramolecular electron transfer from the TTF pendant. © 2002 Elsevier Science Ltd. All rights reserved.

Synthetic porphyrins with a redox-active pendant are very useful in understanding porphyrin-based energy transfer and electron transfer processes in photosynthesis.¹ In particular, various electron acceptor-linked porphyrins, such as porphyrin–quinones^{1c,d} and porphyrin–fullerenes,^{1e,f} have been extensively studied as artificial photosynthetic models that can demonstrate efficient photoinduced electron-transfer from the porphyrin chromophore to the acceptor. There are also many donor-linked porphyrin compounds, such as porphyrin–cyanines,² porphyrin–carotenes,³ and porphyrin–arenes,⁴ but they have been developed mostly in terms of the architecture of light-harvesting porphyrin systems with efficient energy transfer from the donor pendants. By combining porphyrins with the well-known strong electron donor, tetrathiafulvalene (TTF), one might design intriguing donor-porphyrin dyad systems that are expected to show efficient electron transfer rather than energy transfer from the donor to the porphyrin core. Only two papers on molecular systems including both TTF and porphyrin units have been reported so far. Becher and co-workers recently prepared compounds **1**, in which the porphyrin core is directly annelated with four TTF units at the periphery.⁵ These compounds behave like fully π -conjugated single component molecules, which are of no use for the study of intramolecular electron transfer. On the other hand, the Arizona group developed the nonconjugated

TTF–porphyrin dyad **2a** and TTF–porphyrin–fullerene triad **2b** as mimics for photosynthetic reaction centers.⁶ Although the triad **2b** demonstrates photoinduced elec-



Keywords: porphyrin; tetrathiafulvalene; electron transfer; photo-physics.

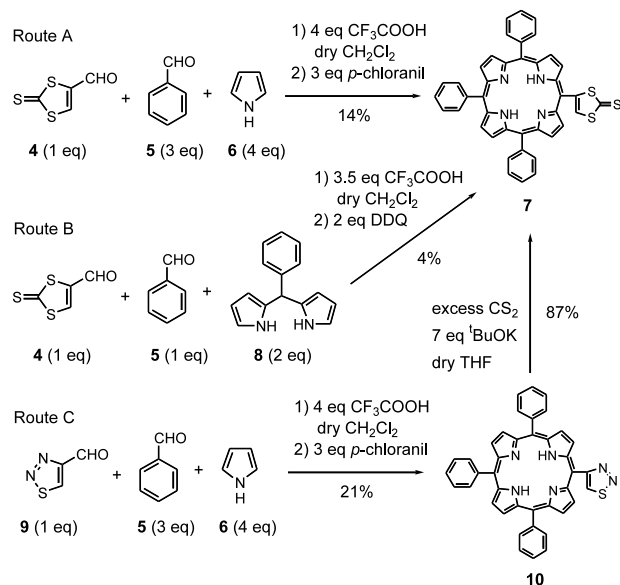
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tron transfer, the direct electron transfer between the TTF and porphyrin units in the dyad **2a** is not remarkable because of the weak electronic coupling via many nonconjugated bonds between these two chromophores. In this context, we decided to prepare the TTF–porphyrin dyad system **3**, in which the TTF unit is set at the *meso*-position of the porphyrin core. Both components are directly bonded but not virtually conjugated owing to the orthogonal orientation of the two π -conjugated planes, so this system provides an ideal model to evaluate the feasibility of efficient photoinduced electron transfer between TTF and porphyrin. Here we would like to report the synthesis and properties of the TTF-linked porphyrin **3a** and its zinc complex **3b**.

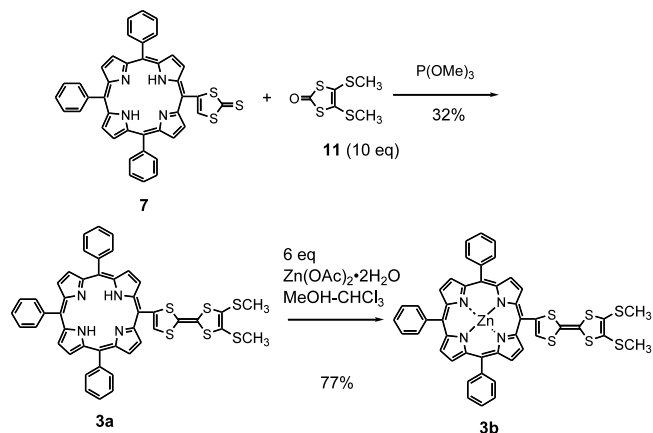
In the synthesis of **3**, a key intermediate is the porphyrin **7** with one 2-thioxo-1,3-dithiol-4-yl group and three phenyl groups at the *meso*-positions.⁷ Such unsymmetrical porphyrins are not so easy to synthesize as symmetrically substituted porphyrins. After considerable synthetic exploration, we found that compound **7** was obtained by three different routes, as shown in Scheme 1. Route A is based on the Lindsey-type hybrid condensation⁸ of 1 equiv. of 4-formyl-1,3-dithiole-2-thione (**4**),⁹ 3 equiv. of benzaldehyde (**5**), and 4 equiv. of pyrrole (**6**) in dry dichloromethane in the presence of 4 equiv. of trifluoroacetic acid for 3 h at room temperature, followed by dehydrogenation with 3 equiv. of *p*-chloranil in boiling dichloromethane for 2 h. This reaction produced a mixture of many porphyrin derivatives differing in *meso*-substitution, which were separated by column chromatography on silica gel with 1:1 dichloromethane–hexane to give **7** in 14% yield.¹⁰ Route B uses the MacDonald-type condensation¹¹ of 1 equiv. of **4**, 1 equiv. of **5**, and 2 equiv. of 5-phenyldipyrromethane (**8**),¹² but **7** was obtained in only 4% yield. Improved yield was attained in a two-step route (Route C) starting with 5-formyl-1,2,3-thiadiazole (**9**).¹³ The first step is the Lindsey-type hybrid condensation leading to the formation of the porphyrin **10** linked with a 1,2,3-thiadiazol-4-yl group (21%), and the second is the conversion of **10** to **7** (87%) on treatment with excess carbon disulfide and 7 equiv. of potassium *t*-butoxide in dry tetrahydrofuran for 1 h at room temperature.¹⁴ The two-step yield of Route C is 18%.

Compound **7** thus obtained was coupled with 10 equiv. of 4,5-bis(methylthio)-1,3-dithiol-2-one (**11**)¹⁵ in trimethyl phosphite under reflux for 1 h to give the desired cross-coupling compound **3a** in 32% yield (Scheme 2). Furthermore, treatment of **3a** with 6 equiv. of zinc acetate dihydrate in methanol–chloroform under reflux for 3 h afforded the zinc complex **3b** in 77% yield.

The cyclic voltammograms of **3a** and **3b** in dichloromethane show four reversible redox waves, and the half-wave oxidation potentials are summarized together with those of the related compounds in Table 1. It is reasonable to assign that the first and second waves of **3a** ($E_{1/2}$ 0.52 and 0.93 V) are due to the TTF unit, because these oxidation potentials are very close to those of 2,3,5,6-tetrakis(methylthio)tetrathiafulvalene (**12**) ($E_{1/2}$ 0.52 and 0.88 V). The third and fourth waves



Scheme 1. Three synthetic routes to the key porphyrin intermediate **7**.



Scheme 2. Synthesis of TTF-linked porphyrins **3a** and **3b**.

($E_{1/2}$ 1.29 and 1.51 V) are due to the porphyrin unit, and appear at much higher potentials than the redox waves of the porphyrin derivatives **7**, **10**, and **13a**. This suggests the Coulombic influence of the initially oxidized TTF unit, which retards the following oxidation of the porphyrin unit. Similar multi-redox waves are also observed in the voltammogram of **3b**, where the redox waves due to the zinc porphyrin unit are shifted to lower potentials by ca. 0.2 V than those of the free-base porphyrin.

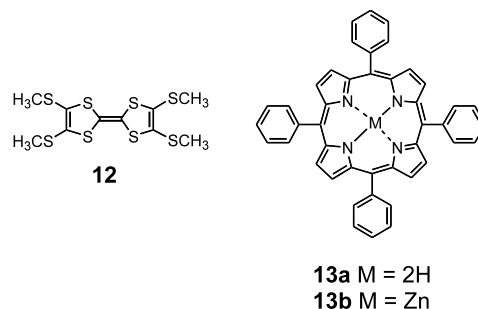


Table 1. Oxidation potentials and spectral data of TTF-linked porphyrins and related compounds

Compound	$E_{1/2}$ (V) ^a	Absorption maximum (nm) ^b	Emission maximum (nm) ^c	$\Phi_f^{c,d}$	$\Phi_f^{d,e}$
3a	0.52, 0.93, 1.29, 1.51	421.5 (5.56), 518 (4.29), 553 (3.92), 594 (3.84), 650.5 (3.53)	651, 717	0.035	0.012
3b	0.47, 0.91, 1.07, 1.27	426 (5.53), 553.5 (4.32), 594.5 (3.73)	602, 650	0.015	0.011
7	1.22, 1.35	424.5 (5.63), 518 (4.33), 553 (3.98), 593 (3.81), 649 (3.55)	654, 718	0.043	0.038
10	1.09, 1.37 ^f	420 (5.65), 515 (4.31), 550 (3.88), 591.5 (3.77), 648 (3.48)	651, 715	0.12	0.10
12	0.52, 0.88	310 (4.19), 333 (4.15)	Nil ^g		
13a	1.03, 1.37	418.5 (5.64), 514.5 (4.31), 548.5 (3.93), 592 (3.76), 648 (3.62)	651, 715	0.19	0.14
13b	0.84, 1.15	422 (5.71), 550 (4.39), 588 (3.54)	598, 646	0.058	0.058

^a Versus Ag/AgCl in dichloromethane with 0.1 M Bu₄NPF₆ as supporting electrolyte.^b Measured in toluene.^c Measured in toluene on irradiation of the Soret band.^d Determined using quinine sulfate as a standard.^e Measured in THF on irradiation of the Soret band.^f Irreversible wave and oxidation peak potential.^g No fluorescence.

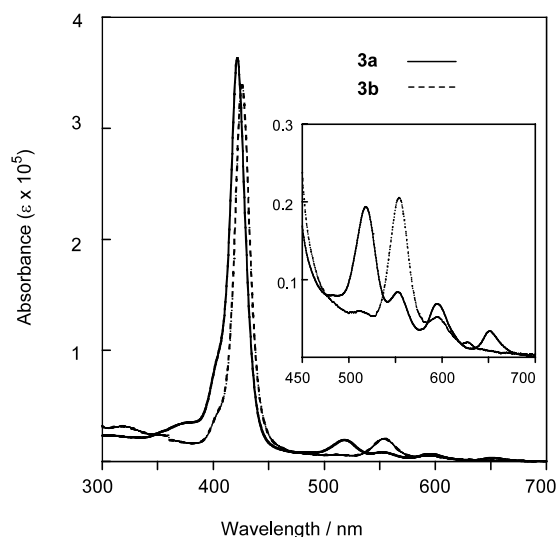
The electronic absorption spectra of **3a** and **3b** in toluene is interpreted in terms of simple superimposition of the electronic transitions of the two constituent chromophores, as shown in Figure 1 (see also Table 1 for the absorption data). For example, in the spectrum of **3a**, the porphyrin unit is attributable to a very strong absorption at 421.5 nm (Soret band) and four weak absorptions at 518, 553, 594, and 650.5 nm (Q band), whereas the TTF unit to weak broad absorptions in the region of 300–350 nm. A comparison of these absorption data with those of the porphyrin derivatives **7**, **10**, and **13** indicates that there is apparently no electronic interaction between the two chromophores in the ground state, supporting nonconjugation due to the orthogonal *meso*-linkage. On the other hand, this is not the case for the emission spectrum of **3a**. As demon-

strated in Figure 2, the porphyrin fluorescence of **3a** in toluene is quenched by 82% as compared to tetraphenylporphyrin **13a**. The quenching is more pronounced in polar tetrahydrofuran (91%). These results evidently indicate that a substantial amount of electron transfer occurs from the TTF pendant to the porphyrin chromophore in the excited state.¹⁶ Similar large quenching is also observed for the zinc porphyrin **3b** as compared to the zinc tetraphenylporphyrin (**13b**), 74% in toluene and 81% in tetrahydrofuran. The smaller quenching ratios of **3b** than those of **3a** suggest that the electron transfer of **3b** is retarded by elevation of the HOMO level of the zinc porphyrin. Another interesting result is the molecular sensing function such that the fluorescence of **3a** is sensitive to the oxidation of the TTF unit. When **3a** was oxidized with 0.25 equiv. of FeCl₃ in toluene, the fluorescence intensity was enhanced by 12%. Presumably electron release from the TTF unit to the porphyrin is depressed by the oxidation of the former. However, further chemical oxidation using a large amount of FeCl₃ resulted in the decrease of the fluorescence intensity, because the porphyrin unit itself is also oxidized.

In conclusion, we have succeeded in the synthesis of novel porphyrin compounds bearing a TTF unit at the *meso*-position. These dyads can function not only as multi-redox systems with Coulombic interactions between the two different chromophores but also as photosystems with efficient intramolecular electron transfer from the TTF pendant to the photoexcited porphyrin core. Thus, they are potentially capable of molecular sensing or switching applications.

Acknowledgements

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**Figure 1.** Electronic absorption spectra of **3a** and **3b** in toluene.

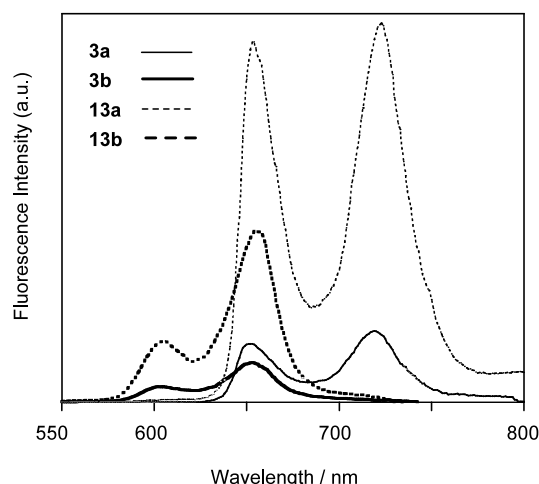


Figure 2. Fluorescence spectra of **3a**, **3b**, **13a**, and **13b** in toluene, excited at the Soret band and normalized to the absorbance.

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- All new porphyrin compounds **3**, **7**, and **10** were characterized by spectroscopic and elemental analyses. Selected data of **3a**: purple powder; mp >300°C; FAB-MS m/z 832 (M^+); 1H NMR ($CDCl_3$) δ –2.74 (bs, 2H, NH), 2.44 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 6.94 (s, 1H, TTF-H), 7.76 (m, 9H, Ph-H), 8.19 (m, 6H, PhH), 8.80 (AB m, 4H, pyrrole-H), 8.90 (d, $J=4.6$ Hz, 2H, pyrrole-H), 9.43 (d, $J=4.6$ Hz, 2H, pyrrole-H); ^{13}C NMR ($CDCl_3$) δ 19.25, 21.29, 117.25, 120.73, 122.33, 126.72, 126.79, 127.90, 128.07, 134.46, 134.51, 141.75. Anal. calcd for $C_{46}H_{32}N_4S_6$: C, 66.32; H, 3.87; N, 6.72%. Found: C, 66.17; H, 3.85; N, 6.52%. **3b**: reddish purple powder; mp >300°C; High-resolution FAB-MS m/z 894.0087 (M^+). Calcd m/z 894.0086; 1H NMR ($CDCl_3$) δ 2.27 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 6.92 (s, 1H, TTF-H), 7.76 (m, 9H, Ph-H), 8.20 (m, 6H, Ph-H), 8.91 (AB m, 4H, pyrrole-H), 9.00 (d, $J=4.6$ Hz, 2H, pyrrole-H), 9.53 (d, $J=4.6$ Hz, 2H, pyrrole-H). **7**: purple fine crystals from 1:1 acetone–methanol; mp >300°C; FAB-MS m/z 671 (M^+); 1H NMR ($CDCl_3$) δ –2.77 (bs, 2H, NH), 7.69 (s, 1H, olefinic), 7.77 (m, 9H, Ph-H), 8.19 (m, 6H, Ph-H), 8.83 (AB m, $J=4.8$ Hz, 4H, pyrrole-H), 8.95 (d, $J=4.9$ Hz, 2H, pyrrole-H), 9.25 (d, $J=4.9$ Hz, 2H, pyrrole-H); ^{13}C NMR ($CDCl_3$) δ 104.20, 121.30, 122.48, 126.85, 128.01, 130.68, 134.47, 134.57, 141.53, 141.69, 145.78, 212.44. Anal. calcd for $C_{41}H_{26}N_4S_3$: C, 73.40; H, 3.91; N, 8.35%. Found: C, 73.35; H, 3.85; N, 8.37%. **10**: purple fine crystals from 1:1 acetone–methanol; mp >300°C; FAB-MS m/z 623 (M^++1), 594 (M^+-28); 1H NMR ($CDCl_3$) δ –2.72 (bs, 2H, NH), 7.77 (m, 9H, Ph-H), 8.22 (m, 6H, Ph-H), 8.76 (d, $J=4.9$ Hz, 2H, pyrrole-H), 8.86 (AB, $J=4.8$ Hz, 4H, pyrrole-H), 8.91 (d, $J=4.9$ Hz, 2H, pyrrole-H), 9.20 (s, 1H, olefinic); ^{13}C NMR ($CDCl_3$) δ 105.93, 120.87, 121.76, 126.78, 127.89, 134.53, 134.60, 138.76, 141.85, 163.29. Anal. calcd for $C_{40}H_{24}N_6S$: C, 77.15; H, 4.21; N, 13.50%. Found: C, 77.22; H, 4.16; N, 13.54%.
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