# Synthesis of Energy Donors Appended Dithiaporphyrin Systems

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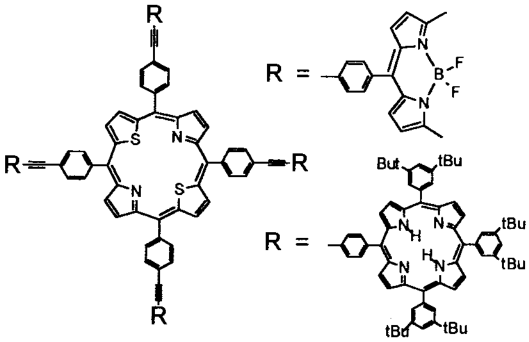
A dithiaporphyrin building block with $N_2S_2$ core is synthesized and used for the construction of $N_2S_2$ porphyrin appended with four *N*,*N*-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl) dipyrrin (BDPY) units and $N_2S_2$ porphyrin appended with four $N_4$ porphyrin units. Steady state fluorescence spectra indicated that there is no energy transfer from an excited BDPY unit to $N_2S_2$ porphyrin unit. However, an efficient energy transfer is observed from $N_4$ porphyrin unit to $N_2S_2$ porphyrin unit.

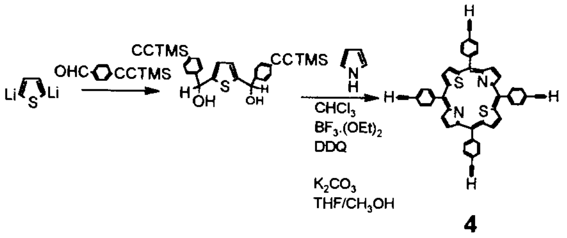
Core modification of porphyrin ring by introducing thiophen, furan, selenophen, tellurophen etc. in place of pyrrole lead to novel heterosubstituted porphyrins which exhibit interesting properties in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states.[1] Recently several unsymmetrical porphyrin dimers such as porphyrin-chlorin, porphyrin-corrole have been synthesized in order to obtain long lived charge transfer state.[2] To construct an unsymmetrical porphyrin array comprised of heterosubstituted porphyrin subunits, one needs an easy access to porphyrin building blocks.[3] Herein we report the first synthesis of heterosubstituted porphyrin building block and its application to the synthesis of two different types of light harvesting systems $(BDPY)_4S_2TPP$ (**1**) and $(H_2TPP)_4S_2TPP$ (**2**). The steady state fluorescence spectra indicated that only **2** acts as light harvesting array and **1** is failed to acts as light harvesting array.



**1**

**2**

The synthetic route for the $N_2S_2$ porphyrin building block is outlined in Scheme 1. 2,5-[4-(2-Trimethylsilylethynyl)phenyl hydroxymethyl] thiophen was prepared in 69% yield by reacting two equivalents of 4[2-(trimethylsilyl)ethynyl]benzaldehyde with one equivalent of dilithium salt of thiophen. The diol was condensed with pyrrole in the presence of $BF_3·(OEt)_2$ in $CHCl_3$ to obtain 5,10,15,20-tetrakis-[4-(2-trimethylsilylethynyl)phenyl]-21,23-dithiaporphyrin, **3** ($S_2TPP$) in 17% yield. The deprotection of **3** with $K_2CO_3$ in THF/methanol gave corresponding ethynyl porphyrin, **4**, in 80% yield. Coupling of **4** with *N*,*N*-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl)dipyrrin (BDPY) in toluene/triethylamine at 35 °C in the presence of $Pd_2(dba)_3$ and $AsPh_3$ gave **1** in 20% yield and coupling with 5,10,15-tri(3,5-di-*t*-butylphenyl)-20-(4-iodophenyl)porphyrin gave the unsymmetrical pentamer, **2** in 37% yield. The Zn(II) derivative, $(ZnTPP)_4S_2TPP$ (Zn**2**) was prepared by following standard methanolic $Zn(OAc)_2$ conditions. All compounds were purified by column chromatography using silica gel as stationary phase and characterized by $^1H$ NMR, MALDI mass, absorption and emission spectroscopies.[4]



**Scheme 1.** Synthetic scheme for the preparation of **4.**

The absorption spectra of $S_2TPP$, BDPY and **1** is shown in Figure 1. The absorption spectra of **1** showed bands corresponding to $S_2TPP$ and BDPY subunits. However, the Soret band of **1** experienced a slight red shift compared to $S_2TPP$ indicating a weak interaction between the subunits. For comparision purpose, we also synthesized four BDPY substituted porphyrin, $(BDPY)_4H_2TPP$. The emission spectra of $(BDPY)_4H_2TPP$ along with **1** recorded at 485 nm is shown as an inset in Figure 1. As evident from the Figure 1, in case of **1** excitation at 485 nm where BDPY absorbs predominately resulted in emission from both the units with a strong emission from the BDPY unit indicating that there is no energy transfer from BDPY to thiaporphyrin unit. The quantum yield of BDPY ($\phi_f = 0.16$) component in **1** is almost similar to free BDPY-I unit ($\phi_f = 0.18$) which is in support with the failure of energy transfer from BDPY unit to thiaporphyrin unit. On the other hand in case of $(BDPY)_4H_2TPP$, excitation at 485 nm resulted in strong quenching of BDPY emission ($\phi_f \approx 0.006$) and increased emission from $N_4$ porphyrin unit suggesting that there is an energy transfer from BDPY to $N_4$ porphyrin unit.[5] The energy transfer occurred in $(BDPY)_4H_2TPP$ is independent of excitation wavelength.

The absorption spectra of Zn**2** and its emission spectrum along with **2** (inset) are shown in Figure 2. The absorption spectrum of pentamer exhibited bands of both $N_4$ and $N_2S_2$ porphyrin monomers and the negligible shifts in the absorption maxima indicate that there is no strong interaction among the porphyrin units. However, the emission spectra shown in Figure 2 clearly indicate that both pentamers **2** and Zn**2** exclusively emit from the central $N_2S_2$ porphyrin core irrespective of excitation wavelength thus suggesting an efficient energy transfer from the peripheral $N_4$ porphyrin unit to $N_2S_2$ porphyrin

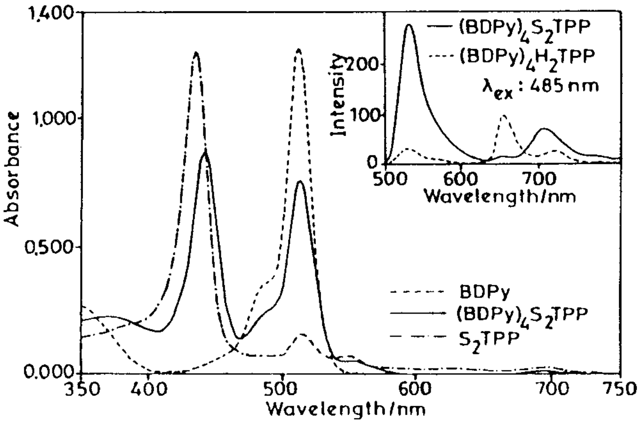


**Figure 1.** Absorption and emission (inset) spectra of **1** recorded in $CH_2Cl_2$.

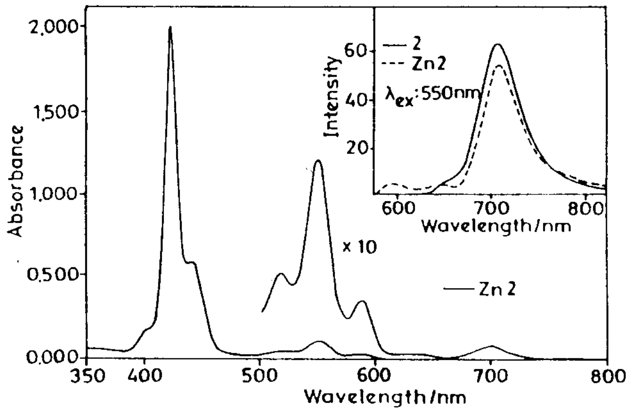


**Figure 2.** Absorption spectrum of **Zn2** and its emission spectrum along with **2** (inset) recorded in $CH_2Cl_2$.

core. The quantum yields of $N_4$ unit in **2** ($\phi_f$ = 0.002) and Zn2 ($\phi_f$ = 0.0016) are greatly diminished compared to $N_4$ monomers[6] and the intensity of the fluorescence bands of $N_2S_2$ unit has enhanced which further supports the energy transfer from $N_4$ unit to $N_2S_2$ unit.

In summary we synthesized the $N_2S_2$ porphyrin building block and coupled to two different types of energy donors. The energy transfer from donor to dithiaporphyrin unit depends mainly on the nature of the donor attached to the dithiaporphyrin unit. The failure of energy transfer from BDPY units to dithiaporphyrin unit may be attributed tentatively to the mismatching of the orientation of the excited state of BDPY conformation with that of ground state dithiaporphyrin unit.[5] However more studies are needed to understand the above observations.

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## References and Notes

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4 Spectral data for selected compounds **3**: $^1$H NMR ($CDCl_3$, δ in ppm) 0.39 (s, 12H, $CH_3$), 7.92 (AA'BB', 8H, Ar), 8.17 (AA'BB', 8H, Ar), 8.65 (s, 4H, β-pyrrole), 9.65 (s, 4H, β-thiophen). LD-MS $C_{64}H_{60}N_2S_2Si_4$ calcd. av. mass 1033.7, obsd. *m/z* 1033.1. UV–vis. ($\lambda_{max}$, nm) 439 (159000), 516 (10200), 551 (5600), 632 (1500), 698 (1900). **4**: $^1$H NMR ($CDCl_3$, δ in ppm) 3.33 (s, 4H, CCH), 7.95 (AA'BB', 8H, Ar), 8.20 (AA'BB', 8H, Ar), 8.67 (s, 4H, β-pyrrole), 9.67 (s, 4H, β-thiophen). LD-MS $C_{52}H_{28}N_2S_2$ calcd. av. mass 744.9, obsd. *m/z* 746.4. UV–vis ($\lambda_{max}$, nm) 439 (168000), 516 (12200), 552 (4600), 633 (1000), 698 (1900). **1**: $^1$H NMR ($CDCl_3$, δ in ppm) 1.54 (s, 24H, $CH_3$), 6.13 (d, *J* = 4.5 Hz, 8H, BDPY pyrrole), 6.79 (d, *J* = 4.5 Hz, 8H, BDPY pyrrole), 7.59 (AA'BB', 8H, Ar), 7.80 (AA'BB', 8H, Ar), 8.05 (AA'BB', 8H, Ar), 8.29 (AA'BB', 8H, Ar), 8.75 (s, 4H, β-pyrrole), 9.75 (s, 4H, β-thiophen). LD-MS $C_{120}H_{80}N_{10}S_2B_4$ calcd. av. mass 1921.4, obsd. *m/z* 1921.3. UV–vis ($\lambda_{max}$, nm) 442 (375000), 514 (154700), 552 (13000), 698 (2900). **2**: $^1$H NMR ($CDCl_3$, δ in ppm) –2.63 (s, 8H, NH), 1.54 (m, 216H, -$CH_3$), 7.83 (m, 12H, Ar), 8.05 (m, 24H, Ar), 8.13 (m, 8H, Ar), 8.22 (d, *J* = 8 Hz, 8H, Ar), 8.34 (d, *J* = 8 Hz, 8H, Ar), 8.41 (d, *J* = 8 Hz, 8H, Ar), 8.88–8.97 (m, 36H, β-pyrrole), 9.89 (s, 4H, β-thiophene). LD-MS $C_{324}H_{332}N_{18}S_2$ calcd. av. mass 4542.5, obsd. *m/z* 4543.9. UV–vis ($\lambda_{max}$, nm) 421 (770000), 441 (240000), 518 (28600), 555 (16900), 592 (6200), 648 (5600), 698 (2300).

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6 The yield of 0.11 for $H_2$TPP was used as reference for **2** and the yield of 0.033 for ZnTPP was used as the reference for Zn**2.**