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A THREE-DIMENSIONALLY ORIENTED π-CONJUGATED SYSTEM: SYNTHESIS OF THE PORPHYRINS BEARING TERTHIOPHENE PENDANT STRANDS

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Abstract – The porphyrins bearing three-dimensionally oriented terthiophene pendant strands were synthesized to elucidate the conformational behaviour.

Architecturally ordered regulation of π-conjugated molecular chains on a functionalized scaffold is considered to provide efficient and functional nanostructured catalysts and materials. In this context, the introduction of π-conjugated chains into a porphyrin as a scaffold is expected to afford such a π-conjugated system. Covalently connected porphyrins through the π-pyrrole moieties or *meso*-positions have been designed for two-dimensional π-electron systems.[1] Atropisomerism of *meso*-tetrakis(*o*-substituted aryl)porphyrins is considered to have an advantage of aligning pendant strands on the porphyrin plane under dimensional control. We have focused on the redox-active oligoaniline chains, which were demonstrated to be incorporated into a porphyrin[2] as well as ruthenium bipyridyl[3] and calix[4]arene scaffolds[4] to construct the dimensionally oriented π-conjugated systems.[5] In our porphyrin-oligoaniline systems, as represented by the porphyrin bearing the four aniline trimer pendant strands, the photo-induced electron transfer from the phenylenediamine pendant groups to the porphyrin scaffold is indicated under excitation of the porphyrin.[2] In the present study, the oligothiophene-porphyrin compounds with one or two terthiophene pendant strands were designed. As is well known, oligothiophene is one of the most attractive π-conjugated molecules with redox activity, which are applicable for electrical materials such as organic field effect transistors and light emitting diodes.[6] During our investigation,[7] the dimensional controlled porphyrins bearing oligothiophene chains were synthesized.[8] We herein describe the synthesis of the porphyrins **1**$_{cis}$, **1**$_{trans}$, and **2** bearing dimensionally aligned terthiophene chains for the construction of three-dimensionally oriented π-conjugated systems (Figure 1).

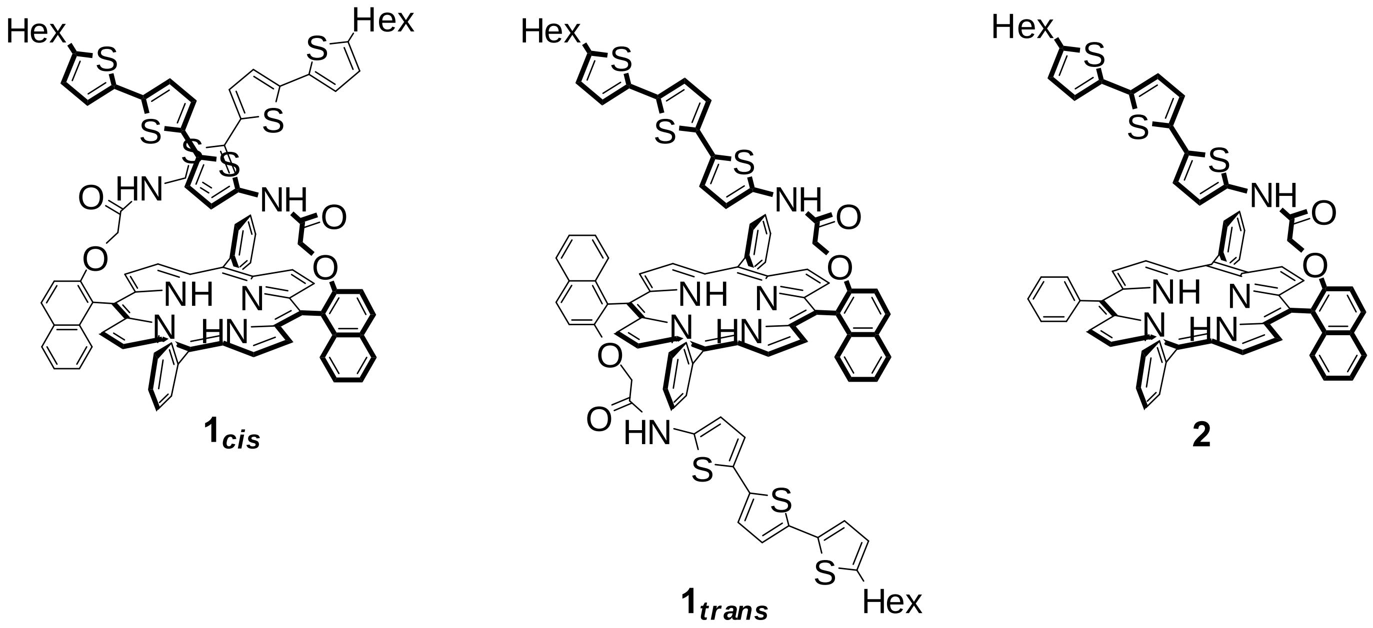
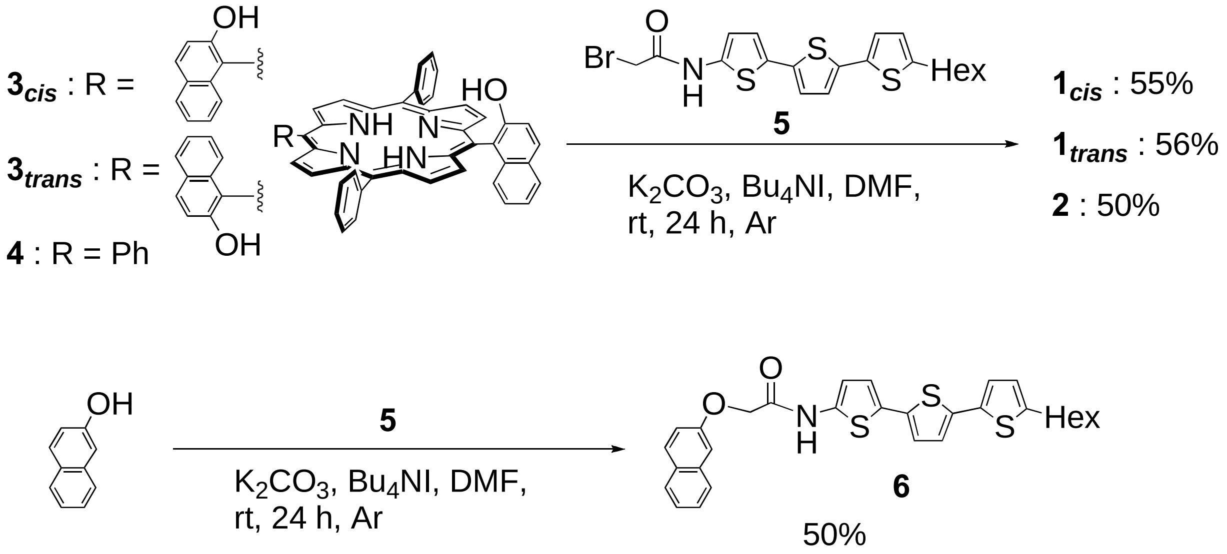


Figure 1. Oligothiophene-porphyrins **1**$_{cis}$, **1**$_{trans}$, and **2**

Scheme 1 shows the synthesis of the above-mentioned oligothiophene-porphyrins **1**$_{cis}$, **1**$_{trans}$, and **2**. These were prepared by the nucleophilic ether formation reaction of the corresponding isolated atropisomeric phenols **3**$_{cis}$,[9] **3**$_{trans}$,[10] and **4**[11] with the bromide **5** bearing the terthiophene moiety under the basic conditions in 55, 56, and 50% yields, respectively.[12] ^{1}H NMR studies suggest the structures of the porphyrins **1**$_{cis}$, **1**$_{trans}$, and **2**. The chemical shifts of the pendant moiety of **1**$_{cis}$, **1**$_{trans}$, and **2**, and the model terthiophene compound **6** are summarized in Table 1. The protons of the terthiophene units, especially the thiophene protons close to the porphyrin ring, were observed in a higher field. The $\Delta\delta(H_a)$ values between the porphyrins **1**$_{cis}$, **1**$_{trans}$, and **2**, and the model terthiophene compound **6** reach more than 5 ppm, and even the $\Delta\delta(H_b)$ values show 2.3-2.4 ppm. The shift is explained by the ring-current effect of the porphyrin π-system. Thus, **1**$_{cis}$, **1**$_{trans}$, and **2** take a leaned conformation of the terthiophene pendant strands toward the porphyrin scaffold in solution. The terthiophene chains are stably positioned on the porphyrin ring.

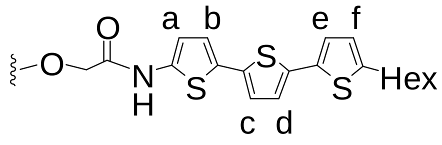
The electronic environment of the π-conjugated systems **1**$_{cis}$, **1**$_{trans}$, and **2** was investigated by UV–vis spectroscopy. The spectra are shown in Figure 2a. Typical Soret and Q bands were observed in these porphyrin derivatives. The molar coefficient of the Soret band of **1**$_{cis}$ was lower than those of the atropisomer **1**$_{trans}$ and the single strand derivative **2**, which might be accounted for by the interaction and/or the small distortion and fluctuation of the porphyrin ring due to the terthiophene moiety, whose absorption was observed around 350 to 450 nm as a broad peak. The fluorescence emission spectroscopy with excitation of the $Q_y(1,0)$ band was studied (Figure 2b). The significant quenching was observed with

1$_{cis}$ and **1**$_{trans}$ bearing the two terthiophene pendant strands. The single strand derivative **2** showed the emission with ca. 30% intensity as compared with that of tetraphenylporphyrin (TPP). However, no quenching occurred with the mixture of TPP and **6**, even in the presence of 10 equivalents of **6**. These findings suggest the dimensionally oriented π-conjugated systems play an important role in the intramolecular photo-induced behaviour.



Scheme 1. Synthesis of 1$_{cis}$, 1$_{trans}$, 2, and 6

Table 1. Chemical shifts in ^{1}H NMR of **1**$_{cis}$, **1**$_{trans}$, **2**, and **6** (CD_2Cl_2, 600 MHz)



	-OCH_2CO-	-CONH-	a	b	c	d	e	f
1$_{cis}$	4.41	5.32	1.49	4.53	5.94	6.67	6.83	6.65
1$_{trans}$	4.68	5.83	1.54	4.64	6.30	6.72	6.77	6.64
2	4.65	5.74	1.36	4.50	6.30	6.77	6.86	6.67
6[a]	4.82	8.90	6.68	6.93 or 6.97	6.99 or 7.02	6.99 or 7.02	6.93 or 6.97	6.68

[a] Measured in $CDCl_3$.

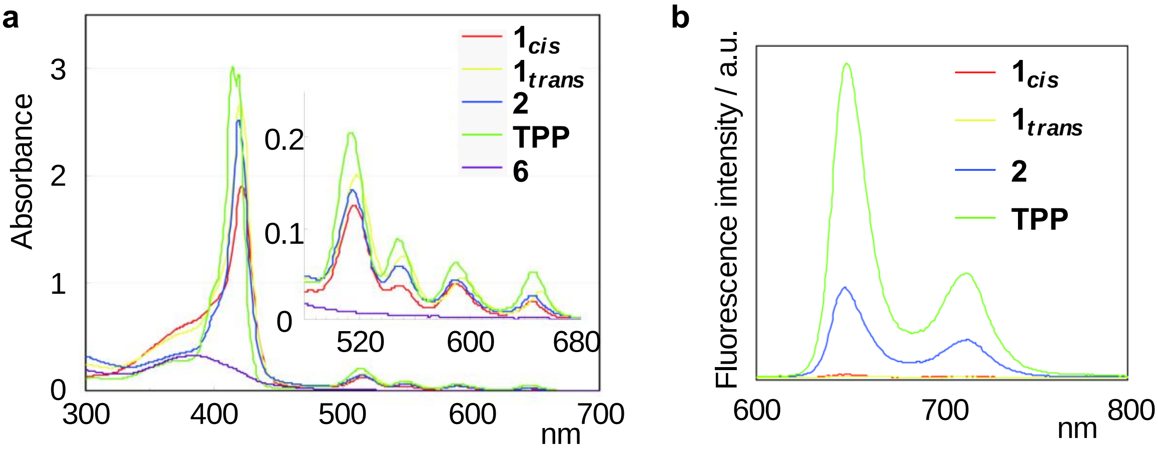


Figure 2. a) Absorption spectra of $\mathbf{1}_{cis}$, $\mathbf{1}_{trans}$, **2**, **TPP**, and **6** in CH_2Cl_2 (5.0 x 10^{-6} M). b) Emission spectra of $\mathbf{1}_{cis}$, $\mathbf{1}_{trans}$, **2**, and **TPP** in CH_2Cl_2 (5.0 x 10^{-6} M) with excitation at $Q_y(1,0)$ band.

In conclusion, the porphyrins bearing the dimensionally oriented terthiophene pendant strands were synthesized. These π-conjugated systems are of potential use in a variety of applications such as redox-active receptors and photo-active catalysts or materials. Further investigation is now in progress.

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10. $\mathbf{3}_{trans}$ was separated from a mixture of *cis* and *trans* isomers according to the reference 9.
11. The porphyrin skeleton for **4** was constructed according to a related procedure described in the reference 9 based on a $BF_3 \cdot Et_2O$-catalyzed condensation of the corresponding benzaldehyde and 2-methoxy-1-naphthaldehyde with pyrrole, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The deprotection of the methyl group with BBr_3 gave **4**.
12. Synthetic procedure for $\mathbf{1}_{cis}$ as a typical one, melting points, ^{1}H and ^{13}C NMR, and high resolution mass values for $\mathbf{1}_{cis}$, $\mathbf{1}_{trans}$, **2**: To a DMF solution of $\mathbf{3}_{cis}$ (26 mg, 0.035 mmol), **5** (65 mg, 0.138 mmol), and K_2CO_3 (48 mg, 0.35 mmol) were added two portions of Bu_4NI under argon at room temperature. After stirring for 24 h at room temperature, the reaction mixture was poured into a solution of Et_2O and water. The aqueous layer was extracted with Et_2O twice. The combined organic layer was washed with water, brine, dried over $MgSO_4$, and evaporated *in vacuo*. The crude residue was purified by silica-gel column chromatography to give $\mathbf{1}_{cis}$ as a purple solid (28 mg, 0.018 mmol, 53% yield). $\mathbf{1}_{cis}$: Mp 155 °C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.81 (d, *J* = 4.2 Hz, 4H), 8.68 (d, *J* = 4.2 Hz, 4H), 8.45 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 2H), 8.19 (m, 2H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.70 (m, 4H), 7.60 (d, *J* = 9.0 Hz, 4H), 7.55 (dd, *J* = 7.8, 7.8 Hz, 4H), 7.33 (dd, *J* = 7.8, 7.8 Hz, 2H), 6.83 (d, *J* = 3.0 Hz, 2H), 6.67 (d, *J* =3.6 Hz, 2H), 6.66 (d, *J* = 3.6 Hz, 2H), 5.94 (d, *J* = 3.6 Hz, 2H), 5.32 (bs, 2H), 4.52 (d, *J* = 3.6Hz, 2H), 4.41 (s, 4H), 2.79 (t, *J* = 7.2 Hz, 4H), 1.67 (tt, *J* = 7.2, 7.2 Hz, 4H), 1.48 (d, *J* = 3.6 Hz, 4H), 1.35-1.32 (m, 12H), 0.93-0.90 (m, 6H), -2.21 (bs, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) 162.98, 155.74, 145.85, 141.68, 137.44, 135.70, 134.89, 134.72, 134.47, 132.81, 131.85, 129.85, 128.23, 127.89, 127.72, 127.22, 125.58, 125.17, 124.93, 123.55, 123.39, 122.89, 121.27,

118.56, 114.44, 113.30, 111.25, 68.03, 31.97, 30.48, 30.07, 29.14, 22.98, 14.27 ppm; HRMS(FAB): Calcd for $C_{92}H_{76}N_6O_4S_6$ 1520.4252; Found 1520.4249 $(M)^+$. $\mathbf{1}_{\textbf{\textit{trans}}}$: Mp 148 ^{o}C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.78 (d, *J* =4.8 Hz, 4H), 8.66 (d, 4.8 Hz, 4H), 8.47 (d, *J* = 9.0 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H,), 8.00 (d, *J* = 6.6 Hz, 4H,), 7.71 (d, *J* = 9.0 Hz, 2H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.63 (dd, 7.2. 7.2 Hz, 4H), 7.52 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 3.0 Hz, 2H), 6.72 (d, *J* = 3.6 Hz, 2H), 6.63 (d, *J* = 3.6 Hz, 2H), 6.29 (d, *J* = 3.6 Hz, 2H), 5.83 (bs, 2H), 4.68 (s, 4H), 4.63 (d, *J* = 4.2 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 4H), 1.67 (tt, *J* = 7.2. 7.2 Hz, 4H), 1.54 (m, 2H), 1.32-1.30 (m, 12H), 0.91-0.87 (m, 6H), -2.29 (bs, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) 162.84, 155.58, 145.26, 140.99, 136.65, 135.39, 134.68, 134.23, 134.04, 133.87, 131.21, 129.32, 127.60, 127.56, 127.17, 127.12, 126.93, 126.52, 126.41, 125.49, 124.49, 124.36, 123.19, 122.99, 122.88, 122.78, 122.36, 120.86, 120.19, 117.88, 114.86, 112.41, 110.11, 103.43, 50.10, 31.27, 31.23, 29.76, 28.41, 22.26, 13.51 ppm; MS(MALDI-TOF): 1522 $(M)^+$. **2** : Mp: 181 ^{o}C; ^{1}H NMR (600 MHz, CD_2Cl_2) δ: 8.91 (d, *J* = 4.8 Hz, 2H), 8.85 (d, *J* = 4.2 Hz, 2H), 8.78 (d, *J* = 4.8 Hz, 2H), 8.59 (d, *J* = 4.2 Hz, 2H), 8.44 (d, *J* = 9.6 Hz, 1H), 8.29 (dd, *J* = 9.0, 9.0 Hz, 2H), 8.21 (d, *J* = 6.6 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 6.6 Hz, 2H), 7.84-7.80 (m, 3H), 7.76-7.72 (m, 4H), 7.70-7.68 (m, 3H), 7.50 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.22 (dd, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 4.2 Hz, 1H), 6.77 (d, *J* = 3.6 Hz, 1H), 6.66 (d, *J* = 3.6 Hz, 1H), 6.30 (d, *J* = 3.6 Hz, 1H), 5.74 (bs, 1H), 4.65 (s, 2H), 4.49 (d, *J* = 3.6 Hz, 1H), 2.78 (t, *J* = 8.4 Hz, 2H), 1.66 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.36 (d, *J* = 3.6 Hz, 1H), 1.33-1.31 (m, 6H), 0.90 (t, *J* = 6.6 Hz, 3H), -2.58 (bs, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ: 162.87, 141.37, 136.78, 134.32, 134.22, 134.04, 131.06, 129.30, 127.53, 127.42, 127.20, 126.85, 126.44, 126.35, 125.73, 124.46, 124.30, 122.84, 122.69, 122.33, 120.82, 120.16, 117.98, 114.73, 110.18, 68.34, 50.11, 45.91, 43.70, 31.25, 29.74, 28.39, 22.25, 19.42, 13.51 ppm; HRMS(FAB): Calcd for $C_{68}H_{53}N_5O_2S_3$ 1067.3361; Found 1067.3357 $(M)^+$.