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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 porphyrin² as well as ruthenium bipyridyl³ and calix[4]arene scaffolds⁴ 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).

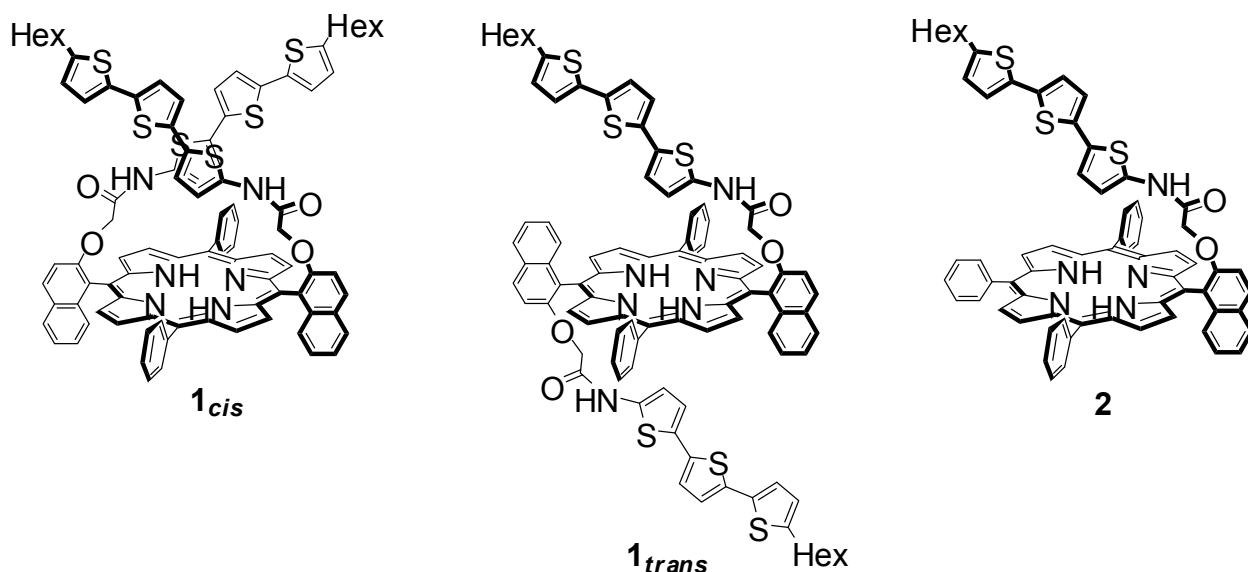
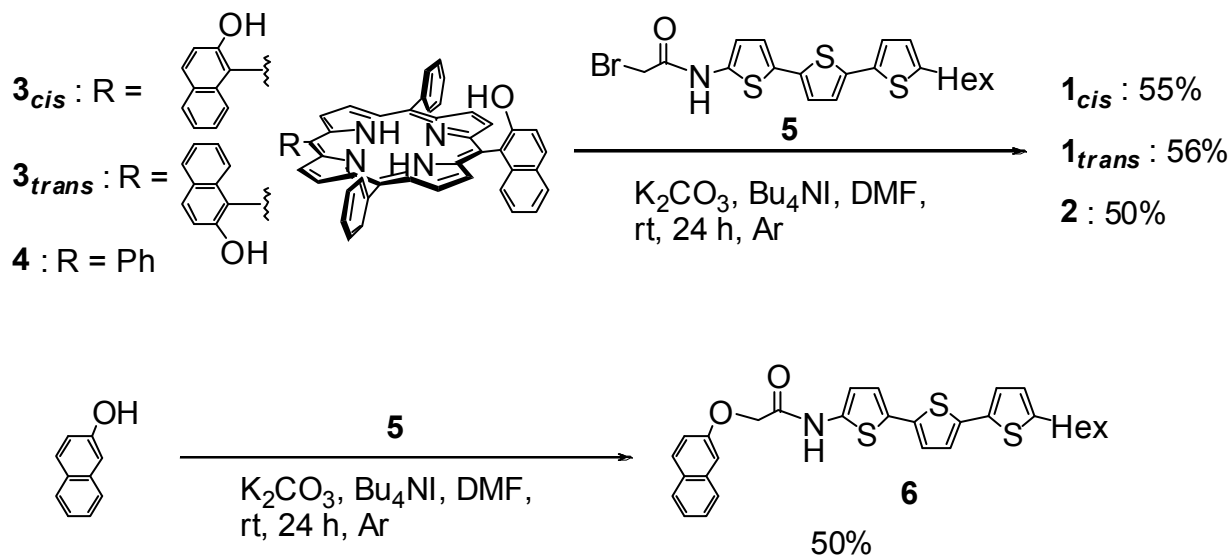


Figure 1. Oligothiophene-porphyrins **1_{cis}**, **1_{trans}**, and **2**

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 ¹H 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 1H NMR of **1_{cis}**, **1_{trans}**, **2**, and **6** (CD_2Cl_2 , 600 MHz)

	-OCH ₂ CO-	-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 $CDCl_3$.

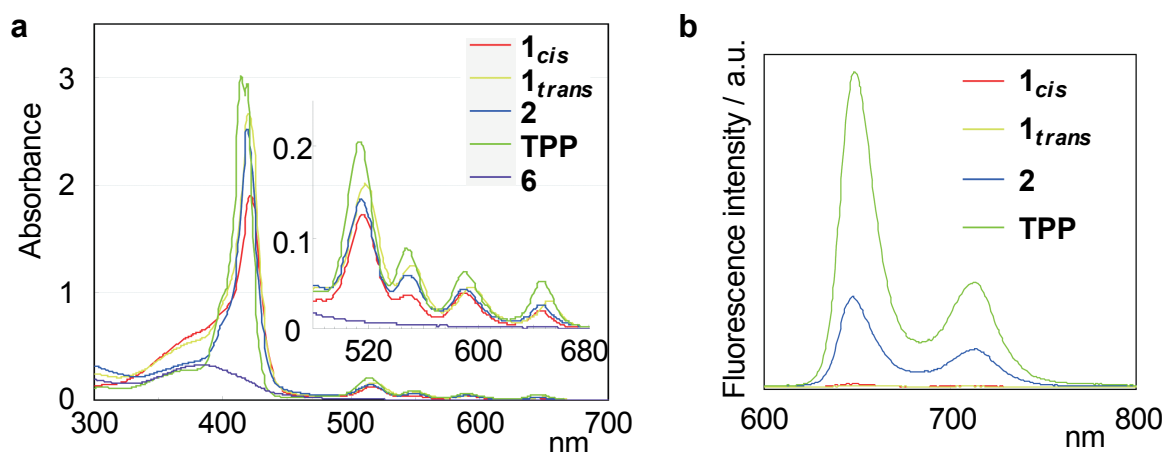


Figure 2. a) Absorption spectra of **1_{cis}**, **1_{trans}**, **2**, **TPP**, and **6** in CH₂Cl₂ (5.0 x 10⁻⁶ M). b) Emission spectra of **1_{cis}**, **1_{trans}**, **2**, and **TPP** in CH₂Cl₂ (5.0 x 10⁻⁶ M) with excitation at Q_y(1,0) band.

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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REFERENCES AND NOTES

- (a) V. S.-Y. Lin, S. G. DiMagno, and M. J. Therien, *Science*, 1994, **264**, 1105; (b) F. Würthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port, and H. C. Wolf, *J. Am. Chem. Soc.*, 1995, **117**, 8090; (c) S. Mikami, K. Sugiura, and Y. Sakata, *Chem. Lett.*, 1997, **26**, 833; (d) N. Ono, H. Miyagawa, T. Ueta, T. Ogawa, and H. Tani, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1595; (e) A. Tsuda and A. Osuka, *Science*, 2001, **293**, 79; (f) G. J. Capitosti, C. D. Guerrero, D. E. Binkley, Jr. C. S. Rajesh, and D. A. Modarelli, *J. Org. Chem.*, 2003, **68**, 247; (g) B. Li, J. Li, Y. Fu, and Z. Bo, *J. Am. Chem. Soc.*, 2004, **126**, 3430; (h) T. Ishi-i, Y. Taguri, S. Kato, M. Shigeiwa, H. Gorohmaru, S. Maeda, and S. Mataka, *J. Mater. Chem.*, 2007, **17**, 3341; (i) H. Yamada, D. Kuzuhara, T. Takahashi, Y. Shimizu, K. Uota, T. Okujima, H. Uno, and N. Ono, *Org. Lett.*, 2008, **10**, 2947; (j) J. Song, S. Y. Jang, S. Yamaguchi, J. Sankar, S. Hiroto, N. Aratani, J.-Y. Shin, S. Easwaramoorthi, K. S. Kim, D. Kim, H. Shinokubo, and A. Osuka, *Angew. Chem. Int. Ed.*, 2008, **47**, 6004.
- (a) T. Hirao and K. Saito, *Tetrahedron Lett.*, 2000, **41**, 1413; (b) K. Saito and T. Hirao, *Tetrahedron*, 2002, **58**, 7491; (c) T. Hirao and K. Saito, *Synlett*, 2002, 415.

3. (a) T. Hirao and K. Iida, *Chem. Commun.*, 2001, 431; (b) X. Shen, T. Moriuchi, and T. Hirao, *Tetrahedron Lett.*, 2003, **44**, 7711.
4. K. Saito and T. Hirao, *Bull. Chem. Soc. Jpn.*, 2002, **75**, 1845.
5. (a) T. Hirao, *Coord. Chem. Rev.*, 2002, **226**, 81; (b) T. Hirao and K. Saito, *Macromol. Symp.*, 2003, **204**, 103; (c) T. Moriuchi and T. Hirao, 'Redox Systems Under Nano-Space Control,' ed. by T. Hirao, Springer, Heidelberg, 2006, pp 3-27.
6. For reviews, see: (a) T. Otsubo, Y. Aso, and K. Takimiya, *J. Mater. Chem.*, 2002, **12**, 2565; (b) G. Barbarella, M. Melucci, G. Sotgiu, *Adv. Mater.*, 2005, **17**, 1581; (c) A. R. Murphy and J. M. J. Frchet, *Chem. Rev.*, 2007, **107**, 1066.
7. T. Hirao, K. Mori, H.-L. Wu, and T. Amaya, The Tenth International Kyoto Conference on New Aspects of Organic Chemistry (IKCOC-10), Kyoto, Japan, Nov. 14, 2006 (abstract: pp 87).
8. K. Sugiyasu and M. Takeuchi, *Chem. Eur. J.*, 2009, **15**, 6350.
9. The ^1H NMR spectrum of **3_{cis}** is identical to the reported one, see: T. Hayashi, T. Miyahara, N. Koide, Y. Kato, H. Matsuda, and H. Ogoshi, *J. Am. Chem. Soc.*, 1997, **119**, 7281.
10. **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 $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -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 **1_{cis}** as a typical one, melting points, ^1H and ^{13}C NMR, and high resolution mass values for **1_{cis}**, **1_{trans}**, **2**: To a DMF solution of **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 **1_{cis}** as a purple solid (28 mg, 0.018 mmol, 53% yield). **1_{cis}**: Mp 155 °C; ^1H 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 = 3.6 Hz, 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)⁺. **1_{trans}** : Mp 148 °C; ¹H NMR (600 MHz, CD₂Cl₂) 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 Hz, 2H), 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); ¹³C NMR (150 MHz, CD₂Cl₂) 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 °C; ¹H NMR (600 MHz, CD₂Cl₂) 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); ¹³C NMR (150 MHz, CD₂Cl₂) 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)⁺.