Electronic Supplementary Information (ESI)

Synthesis, aggregation-enhanced emission, polymorphism and piezochromism of TPE-cored foldamers with through-space conjugation

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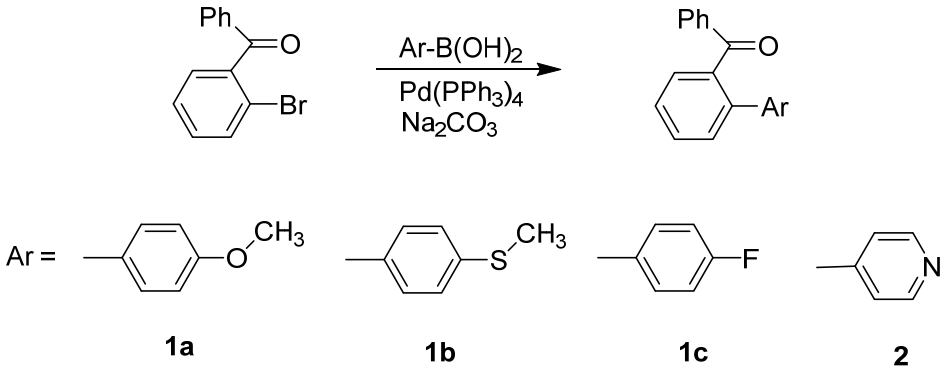
Experimental

General

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Chemicals and reagents were purchased from commercial sources and used as received without further purification. [4'-Methoxy-(1,1'-biphenyl)-2-yl](phenyl)methanone (**1a**) and (*Z*)-1,2-bis[4'-methoxy-(1,1'-biphenyl)-4-yl]-1,2-diphenylethene (*f*-TPE-BPOMe) was prepared according to the known procedures.[1] ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 or 600 spectrometer in deuterated chloroform or acetone at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDT-TOF mode. LC-MS

measurements were carried out on a Waters ACQUITY UPLC H-Class_XEVO TQD. Single crystal X-ray diffraction intensity data were collected on a Bruker–Nonices Smart Apex CCD diffracto-meter with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were measured on a SHIMADZU UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 fluorescence spectrophotometer. Fluorescence quantum yields were measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. The fluorescence life-times were determined by the compact fluorescence lifetime spectrometer C11367 of Hamamatsu. Powder X-ray diffraction patterns were recorded on a Bruker D8 Advance X-ray diffractometer in a degree range of 5 to 45^{o}. Simulated X-ray diffraction patterns were calculated from single crystal structures. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G (d,p). All the calculations were performed using Gaussian 09 package.

Synthesis



Scheme S1. Synthetic routes to 2-phenylmethanone derivatives.

[4'-(Methylthio)-(1,1'-biphenyl)-2-yl](phenyl)methanone (1b): A mixture of 2-bromobenzophenone (2.61 g, 10 mmol), 4-(methylthio)phenylboronic acid (2.52 g, 15 mmol), $Pd(PPh_3)_4$ (350 mg, 0.3 mmol) and Na_2CO_3 (3.18 g, 30 mmol) in 80 ml of toluene/ethanol/water mixture (6/1/1 v/v/v) was heated to reflux for 24 h under nitrogen. The reaction mixture was cooled to room temperature, poured into water. and extracted with dichloromethane for three times. The combined organic layers were dried with magnesium sulfate anhydrous. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of **2** was obtained in 96.4 % yield (2.93 g). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.68–7.64 (m, 2H), 7.59–7.54 (m, 1H), 7.50–7.41 (m, 4H), 7.32–7.27 (m, 2H), 7.20–7.16 (m, 2H), 7.11–7.07 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 198.7, 140.5, 138.8, 137.8, 137.3, 137.0, 133.0, 130.4, 130.0, 129.9, 129.3, 128.8, 128.2, 127.0, 126.3, 15.65. HRMS ($C_{20}H_{16}OS$): *m/z* 304.0951 (M^+, calcd 304.0922).

[4'-Fluoro-(1,1'-biphenyl)-2-yl](phenyl)methanone (1c): The procedure was analogous to that described for **1b**. White solid, yield 73.9 %. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.63 (d, J = 8.1 Hz, 2H), 7.60–7.54 (m, 1H), 7.53–7.49 (m, 1H), 7.48–7.41 (m, 3H), 7.31–7.27 (m, 2H), 7.24–7.18 (m, 2H), 6.91–6.86 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 198.7, 163.0, 161.4, 140.0, 139.0, 137.3, 136.2, 133.0, 130.4, 130.0, 128.8, 128.2, 127.2, 115.3, 115.1. LC-MS ($C_{19}H_{13}FO$): *m/z* 277.2 ($M + H^+$, calcd 277. 1).

Phenyl[2-(pyridin-4-yl)phenyl]methanone (2): The procedure was analogous to that described for **1b**. Yellow solid, yield 85.7 % (2.23 g). ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 8.45 (dd, J = 4.5, 1.6 Hz, 2H), 7.70–7.65 (m, 2H), 7.64–7.61 (m, 1H), 7.57–7.52 (m, 2H), 7.50–7.45 (m, 2H), 7.35–7.30 (m,

2H), 7.19 (dd, J = 4.5, 1.6 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 197.8, 149.6, 148.1, 138.9, 138.5, 137.1, 133.4, 130.7, 129.9, 129.8, 129.1, 128.4, 128.3, 123.8. HRMS ($C_{18}H_{13}NO$): *m/z* 260.1066 (M^+, calcd 259.0997).

(*Z*)-1,2-Bis(4'-(methylthio)-[1,1'-biphenyl]-2-yl)-1,2-diphenylethene (*f*-TPE-BPSMe): To a mixture of **1b** (2.74 g, 9 mmol) and zinc dust (1.75 g, 27 mmol) in 80 mL dry THF was added dropwise $TiCl_4$ (0.1mL, 10.8 mmol) under nitrogen at –78 ^{o}C. After stirring for 15 min at –78 ^{o}C, the reaction mixture was warmed to room temperature for stirring another 15 min and then heated to reflux overnight. The mixture was quenched with saturated Na_2CO_3 solution and extracted with dichloromethane for three times. The combined organic layers were dried with magnesium sulfate anhydrous. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid of *f*-TPE-BPSMe was isolated in 35.7 % yield (1.85 g). ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.15–6.96 (m, 22H), 6.75–6.68 (m, 2H), 5.81 (d, J = 7.3 Hz, 2H), 2.46 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 144.7, 140.9, 140.5, 138.7, 138.6, 136.3, 132.5, 131.3, 129.4, 129.2, 127.6, 127.0, 126.7, 126.4, 126.3, 16.2. HRMS ($C_{40}H_{32}S_2$): *m/z* 576.1936 (M^+, calcd 576.1945).

(*Z*)-1,2-Bis(4'-fluoro-[1,1'-biphenyl]-2-yl)-1,2-diphenylethene (*f*-TPE-BPF): The procedure was analogous to that described for *f*-TPE-BPSMe. White solid, yield 30.5 %. ^{1}H NMR (600 MHz, $CDCl_3$), δ (TMS, ppm): 7.15–7.03 (m, 12H), 6.99 (d, J = 7.0 Hz, 6H), 6.93–6,87 (m, 4H), 6.79–6.73 (m, 2H), 5.82 (d, J = 7.7 Hz, 2H). 13C NMR (150 MHz, $CDCl_3$), δ (TMS, ppm): 162.7, 161.1, 144.5, 141.0, 140.2,

138.8, 137.6, 132.4, 131.2, 130.2, 129.6, 127.7, 127.0, 126.5, 114.6. HRMS ($C_{38}H_{26}F_2$): *m/z* 520.1989 (M^+, calcd 520.2003).

(*Z*)-1,2-Diphenyl-1,2-bis(2-(pyridin-4-yl)phenyl)ethene (*f*-TPE-BPy): The procedure was analogous to that described for *f*-TPE-BPSMe. Yellow solid, yield 32.4 %. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 8.44 (d, J = 5.2 Hz, 4H), 7.20–7.06 (m, 12H), 7.05–6.96 (m, 6H), 6.85–6.78 (m, 2H), 5.83 (d, J = 7.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 149.2, 144.2, 140.9, 138.7, 132.6, 131.2, 129.3, 128.7, 127.9, 127.3, 126.9, 123.7. HRMS ($C_{36}H_{26}N_2$): *m/z* 487.2157 ($M + H^+$, calcd 487.2174).

X-Ray crystallography

Crystal data for *f*-TPE-BPSMe (I) (CCDC 1469211): $C_{40}H_{32}S_2$, MW = 576.78, monoclinic, P 2_1/c, a = 9.6317(6), b = 9.5173(5), c = 33.0419(18) Å, β = 96.269(2)°, V = 3010.8(3) Å^3, Z = 4, Dc = 1.272 g cm^{-3}, μ = 0.205 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1216, T = 173(2) K, $2\theta_{max}$ = 25.25^o (98.0%), 15997 measured reflections, 5362 independent reflections (R_{int} = 0.0465), GOF on F^2 = 1.035, R_1 = 0.0776, wR_2 = 0.1090 (all data), Δe 0.227 and –0.268 eÅ^{-3}.

Crystal data for *f*-TPE-BPSMe (II) (CCDC 1469212): $C_{40}H_{32}S_2$, MW = 576.78, monoclinic, P 2_1/c, a = 16.2653(11), b = 11.5962(6), c = 18.2955(16) Å, β = 115.900(2)°, V = 3104.9(4) Å^3, Z = 4, Dc = 1.234 g cm^{-3}, μ = 0.199 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1216, T = 173(2) K, $2\theta_{max}$ = 25.35^o (98.1%), 16244 measured reflections, 9685 independent reflections (R_{int} = 0.0566), GOF on F^2 = 1.032, R_1 = 0.0907, wR_2 = 0.1053 (all data), Δe 0.250 and –0.371 eÅ^{-3}.

Crystal data for *f*-TPE-BPF (CCDC 1469206): $C_{38}H_{26}F_2$, MW = 520.59, triclinic, P-1, a = 9.3318(6), b = 16.3035(9), c = 18.6019(10) Å, α = 94.673(2)°, β = 90.768(2)°, γ = 100.362(2)°, V = 2773.6(3) Å^3, Z =

4, D_c = 1.247 g cm^{-3}, μ = 0.080 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1088, T = 173(2) K, $2\theta_{max}$ = 25.10^o (98.0%), 21501 measured reflections, 9685 independent reflections (R_{int} = 0.0503), GOF on F^2 = 1.055, R_1 = 0.1145, wR_2 = 0.1049 (all data), Δe 0.164 and –0.193 eÅ^{-3}.

Crystal data for *f*-TPE-BPy (CCDC 1469207): $C_{36}H_{26}N_2$, MW = 486.57, monoclinic, P 2$_1$/n, a = 10.2875(10), b = 9.5469(8), c = 30.516(3) Å, β = 90.739(2)°, V = 2996.9(5) Å^3, Z = 4, D_c = 1.267 g cm^{-3}, μ = 0.245 mm^{-1} (MoKα, λ = 0.71073), F(000) = 1192, T = 173(2) K, $2\theta_{max}$ = 25.40^o (98.3%), 14491 measured reflections, 5432 independent reflections (R_{int} = 0.0485), GOF on F^2 = 1.044, R_1 = 0.1042, wR_2 = 0.1383 (all data), Δe 0.203 and –0.383 eÅ^{-3}.

Additional data

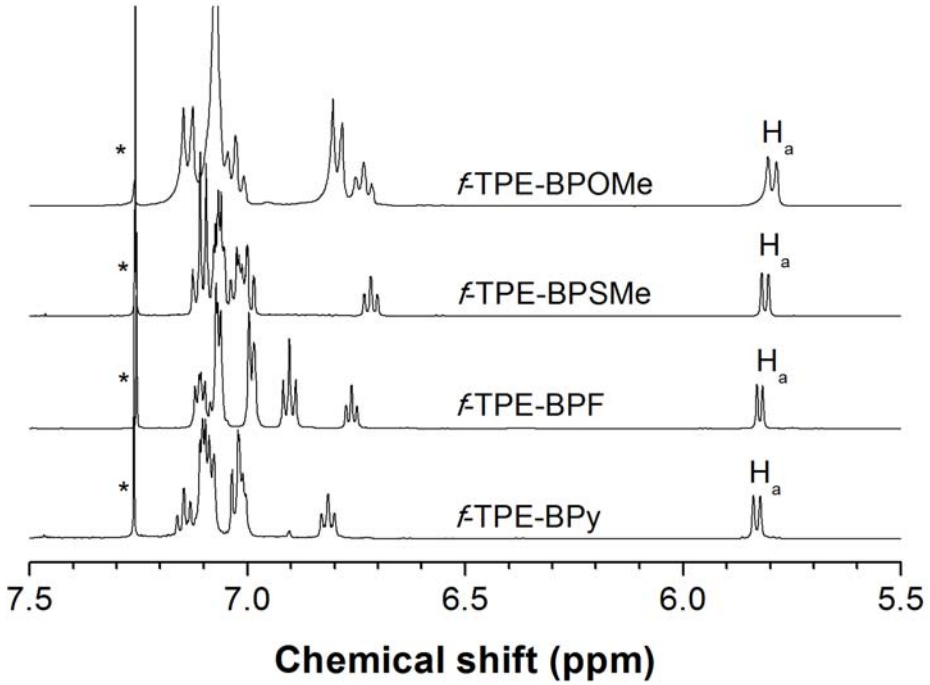


Fig. S1 ^{1}H NMR spectra, with distinctive signals labeled as H_a, of the TPE-cored foldamers in $CDCl_3$, where asterisk denotes solvent peak.

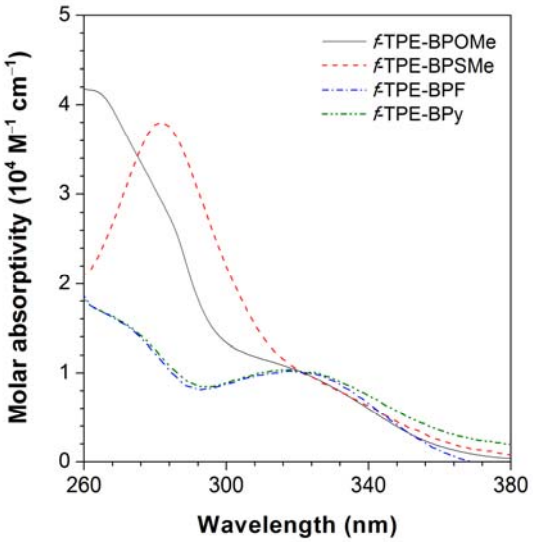


Fig. S2 Absorption spectra of TPE-cored foldamers in THF solution (10^{-5} M).

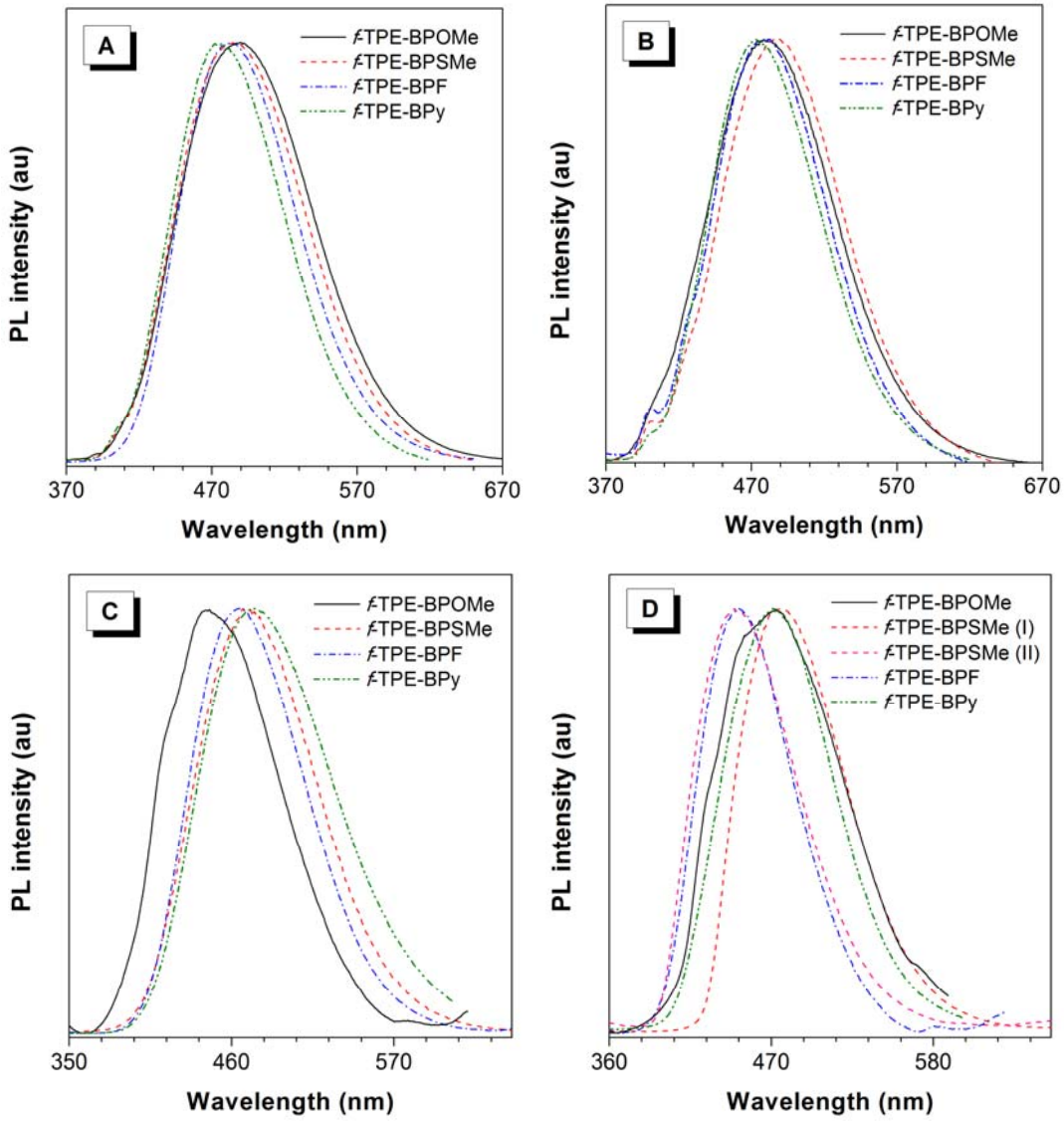


Fig. S3 Photoluminescence (PL) spectra of TPE-cored foldamers in (A) THF solution (10^{-5} M), (B) *n*-hexane solution (10^{-5} M), (C) solid films and (D) crystals.

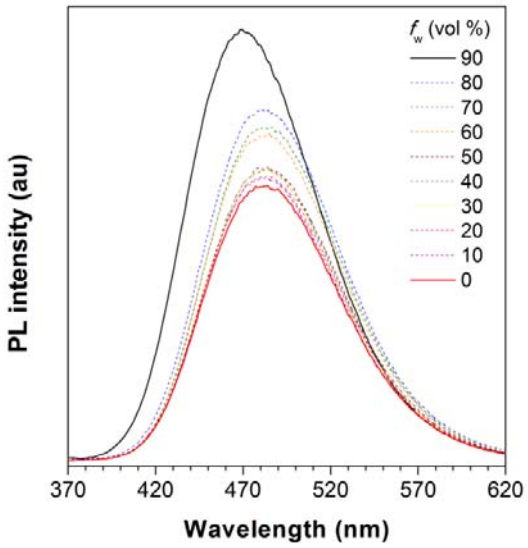


Fig. S4 Photoluminescence (PL) spectra of *f*-TPE-BPF in THF-water mixtures with different water fractions (f_w).

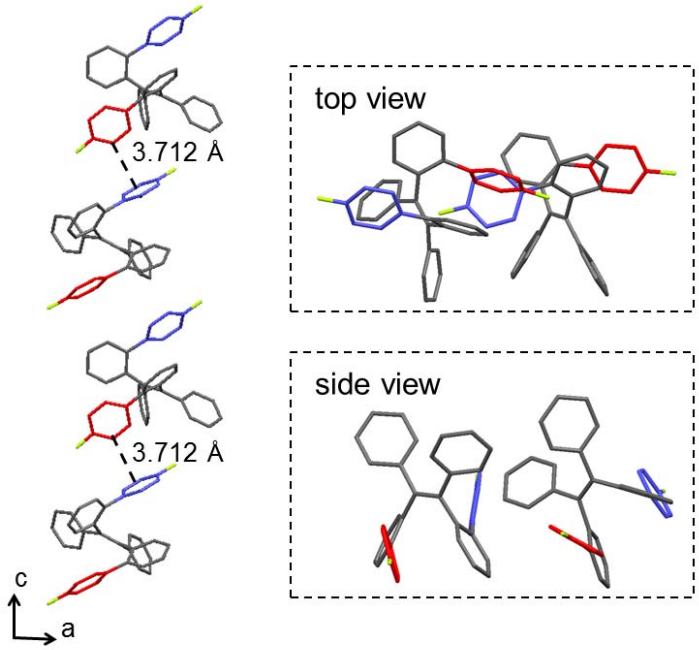


Fig. S5 Crystal packing diagram of *f*-TPE-BPF.

Table S1. Fluorescence lifetimes, radiative relaxation rates and nonradiative relaxation rates of TPE-cored foldamers. [a]

Compound	$\langle\tau\rangle$ (ns)			k_r (ns^{-1})			k_{nr} (ns^{-1})		
	THF	film	crystal	THF	film	crystal	THF	film	crystal
f-TPE-BPOMe	4.0	5.8	6.3	0.048	0.071	0.044	0.203	0.102	0.114
f-TPE-BPSMe	2.4	4.6	4.4,[b] 2.5[c]	0.096	0.113	0.091,[b] 0.112[c]	0.321	0.104	0.136,[b] 0.288[c]
f-TPE-BPF	4.5	6.6	7.3	0.067	0.083	0.064	0.156	0.068	0.073
f-TPE-BPy	4.8	7.5	7.0	0.071	0.067	0.064	0.138	0.067	0.079

[a] THF = THF solution (10^{-5} M); film = drop-casted film on a quartz plate; $\langle\tau\rangle$ = fluorescence lifetimes measured at room temperature in air; k_r = radiative relaxation rate ($k_r = \Phi_F/\langle\tau\rangle$); k_{nr} = nonradiative relaxation rate ($k_r = (1 - \Phi_F)/\langle\tau\rangle$). [b] crystals of *f*-TPE-BPSMe (I). [c] crystals of *f*-TPE-BPSMe (II).

Reference

1. Z. Zhao, B. He, H. Nie, B. Chen, P. Lu, A. Qin and B. Z. Tang, *Chem. Commun.*, 2014, **50**, 1131.