Electronic Supplementary Information (ESI)

Conjugation versus rotation: good conjugation weakens aggregation-induced emission effect of siloles

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Experimental

General

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. Compounds **1a** and **1b** were prepared according to the methods in the literature.[1] Other chemicals and reagents were purchased from Aldrich and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer in deuterated chloroform using tetramethylsilane (TMS; $\delta = 0$) as internal reference. High resolution mass spectra were recorded on a GCT premier CAB048 mass spectrometer operating in a MALDT-TOF mode. UV-vis absorption spectra

were recorded on a Shimadzu UV-2450 spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer.

Synthesis

1,1-Dimethyl-2,5-di(naphthalen-2-yl)-3,4-diphenylsilole (NpDMS): A solution of lithium naphthalenide (LiNaph) was prepared by stirring a mixture of naphthalene (1.28 g, 10 mmol) and lithium granular (0.07 g, 10 mmol) in dry THF (30 mL) for 4 h at room temperature under nitrogen. A solution of bis(phenylethynyl)dimethylsilane (**1a**) (0.65 g, 2.5 mmol) in THF (20 mL) was then added dropwise into the solution of LiNaph, and the resultant mixture was stirred for 1 h at room temperature. After the solution was cooled to –10 °C, $ZnCl_2$-TMEDA (3.2 g, 12.5 mmol) and 20 mL of THF were added. The fine suspension was stirred for 1 h at room temperature, and $Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol) and 2-bromonaphthalene (1.24 g, 6 mmol) were then added. After refluxed for 12 h, the reaction mixture was cooled to room temperature and terminated by addition of 1 M hydrochloric acid. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed successively with aqueous sodium chloride solution and water, and dried over magnesium sulfate. After filtration, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography using *n*-hexane/dichloromethane as eluent. Yellow solid, yield 77%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.76 (d, 2H, J = 7.6 Hz), 7.72 (d, 2H, J = 8.0 Hz), 7.59 (br, 4H), 7.47–7.74 (m, 4H), 7.09–7.02 (m, 8H), 6.94 (d, 4H, J = 6.0 Hz), 0.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 154.5, 142.0, 138.8, 137.7, 133.6, 131.7, 130.2, 127.8, 127.7, 127.6, 127.5, 127.3, 126.5, 125.9, 125.4, –3.5. HRMS: m/z 514.2098 (M^+, calcd 514.2117).

1-Methyl-2,5-di(naphthalen-2-yl)-1,3,4-triphenylsilole (NpMPS): The procedure was analogous to that described for NpDMS. Yellow solid, yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 7.80 (d, 2H, J = 5.2 Hz), 7.70 (d, 2H, J = 7.2 Hz), 7.59–7.57 (m, 2H), 7.52–7.50 (m, 4H), 7.43–7.37 (m, 7H), 7.10–7.09 (m, 6H), 7.05–6.99 (m, 6H), 0.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 156.0, 140.7,

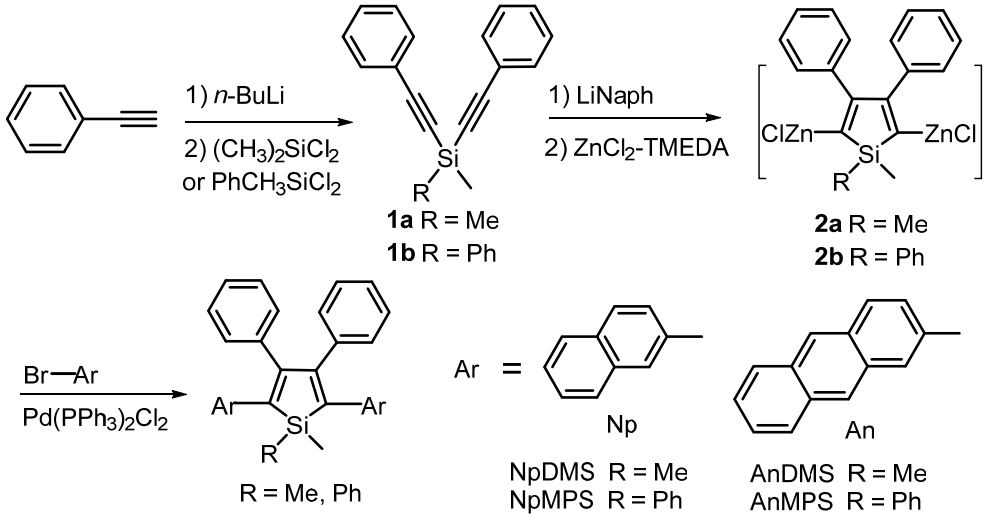
138.9, 137.2, 134.8, 133.5, 133.4, 131.7, 130.2, 130.5, 128.4, 127.9, 127.7, 127.5, 127.2, 126.6, 125.7, 125.4, –6.1. HRMS: *m*/*z* 576.2286 (M^+, calcd 576.2273).

2,5-Di(anthracen-2-yl)-1,1-dimethyl-3,4-diphenylsilole (AnDMS): The procedure was analogous to that described for NpDMS. Yellow solid, yield 47%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.28 (s, 2H), 8.25 (s, 2H), 7.96–7.94 (m, 4H), 7.72 (s, 2H), 7.67 (d, 2H, J = 9.2 Hz), 7.43–7.41 (m, 4H), 7.07–7.01 (m, 6H), 6.93–6.91 (m, 6H), 0.65 (s, 6H). The ^{13}C NMR spectrum is not available due to the poor solubility. HRMS: *m*/*z* 614.2437 (M^+, calcd 614.2430).

2,5-Di(anthracen-2-yl)-1-methyl-1,3,4-triphenylsilole (AnMPS): The procedure was analogous to that described for NpDMS. Yellow solid, yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.23 (s, 2H), 8.13 (s, 2H), 7.93–7.90 (m, 4H), 7.83 (d, 2H, J = 5.2 Hz), 7.66 (s, 2H), 7.62 (d, 2H, J = 9.2 Hz), 7.43–7.40 (m, 7H), 7.11–7.07 (m, 6H), 7.02–7.00 (m, 4H), 7.63 (d, 2H, J = 8.4 Hz), 1.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (TMS, ppm): 156.1, 140.8, 138.9, 136.7, 134.8, 133.7, 131.8, 131.7, 131.5, 130.2, 130.1, 128.4, 128.1, 128.0, 127.9, 127.7, 127.3, 126.7, 125.9, 125.7, 125.3, 125.1, –5.8. HRMS: *m*/*z* 676.2591 (M^+, calcd 676.2586).

Reference

1. S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem. Eur. J.*, 2000, **6**, 1683.



Scheme S1. Synthetic routes to new siloles substituted with polycyclic aromatic hydrocarbons. TMEDA = *N*, *N*, *N*', *N*'-tetramethylethylenediamine.

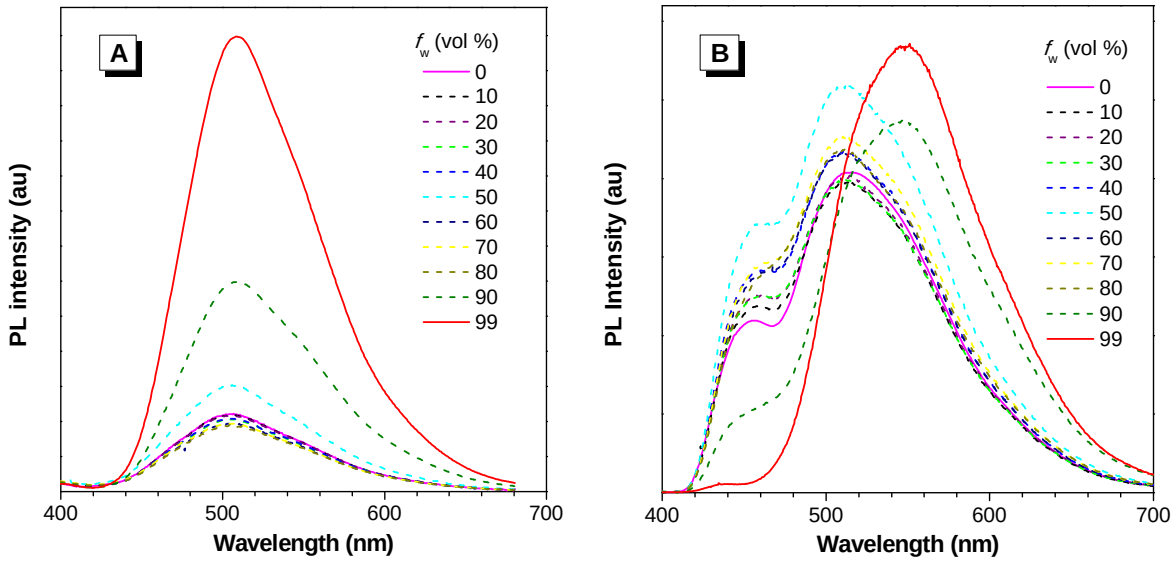


Fig. S1 PL spectra of (A) NpDMS and (B) AnDMS in THF/water mixtures with different water fractions (f_w).

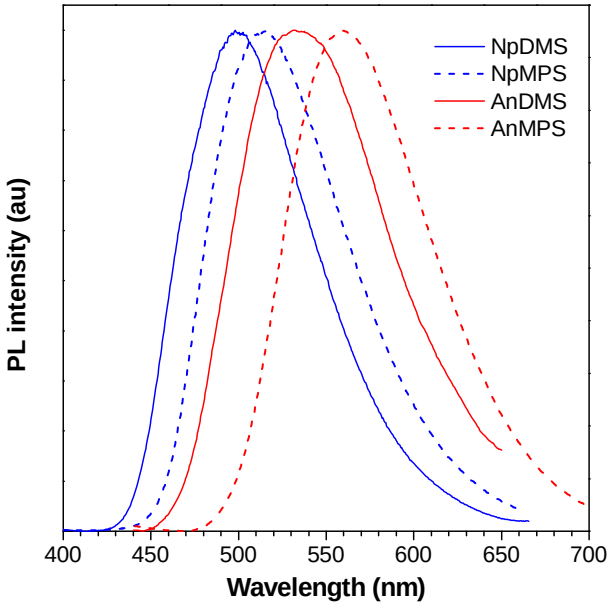
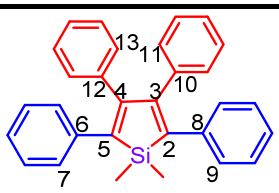


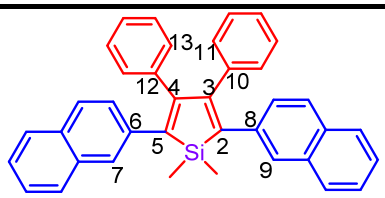
Fig. S2 PL spectra of solid films of new siloles.

Table S1. Selected bond lengths (in Å) of the S_0 and S_1 for isolated DMTPS, NpDMS and AnDMS.

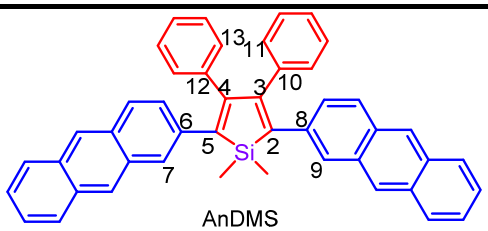
	DMTPS			NpDMS			AnDMS		
	S_0	S_1	$\Delta(S_1–S_0)$	S_0	S_1	$\Delta(S_1–S_0)$	S_0	S_1	$\Delta(S_1–S_0)$
Si-C2	1.530	1.541	0.011	1.887	1.877	–0.010	1.887	1.880	–0.007
C2-C3	1.361	1.427	0.066	1.368	1.436	0.068	1.369	1.423	0.054
C3-C4	1.487	1.426	–0.061	1.511	1.439	–0.072	1.510	1.447	–0.063
C3-C10	1.483	1.471	–0.012	1.492	1.481	–0.011	1.492	1.486	–0.006
C4-C12	1.483	1.471	–0.012	1.492	1.481	–0.011	1.492	1.486	–0.006
C2-C8	1.483	1.447	–0.036	1.477	1.445	–0.032	1.476	1.444	–0.032
C5-C6	1.483	1.447	–0.036	1.477	1.445	–0.032	1.476	1.444	–0.032



DMTPS



NpDMS



AnDMS

Table S2. Calculated emission data for DMTPS, NpDMS and AnDMS.

	E (cm^{-1})	λ (nm)	f	k_r (s^{-1})
DMTPS	21620	462	0.30	0.94×10^8
NpDMS	18088	552	0.50	1.09×10^8
AnDMS	17298	578	0.72	1.44×10^8