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Unusual Aggregation of Nanosized Six-Arm Star Oligofluorenes

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1c. A mixture of **1b** (336 mg, 0.6 mmol), CuI (2 mg, 0.012 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.006 mmol) and trimethylamine (10 mL) in a Schlenk tube was carefully degassed and charged with nitrogen. Trimethylsilylacetylene (100 μL, 0.7 mmol) was injected and the tube was sealed at once. The reaction mixture was stirred at room temperature for 24 h. After the removal of the solvent, the residue was purified by chromatography on silica gel eluting with petrol ether to afford **1c** as a colorless oil (262 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, d), 7.67-7.63 (3H, m), 7.57 (1H, d), 7.53 (1H, s), 7.47-7.44 (4H, m), 7.36 (1H, t), 1.99-1.97 (4H, m), 1.20-1.04 (20H, m), 0.81 (6H, t), 0.62-0.61 (4H, m), 0.29 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 151.5, 142.2, 142.0, 141.2, 140.3, 131.9, 129.4, 127.9, 126.9, 126.8, 122.2, 121.9, 120.9, 120.2, 107.0, 94.6, 55.9, 41.0, 32.4, 30.6, 29.9, 24.3, 23.2, 14.7, 0.74. Anal. Calcd for $C_{40}H_{54}Si$: C, 85.34; H, 9.67. Found: C, 84.20; H, 9.56.

1d. 1c (202 mg, 0.36 mmol) was dissolved in dry dichloromethane. Then tetrabutylammonium fluoride (1 M in THF, 540 μL, 0.54 mmol) was added. The mixture was stirred at room temperature for 10 min. The reaction mixture was poured onto a short pad of silica gel. Chromatography eluting with dichloromethane afforded **1d** as a colorless oil in a yield of 98%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (1H, d), 7.66 (3H, d), 7.58 (1H, d), 7.54 (1H, s), 7.50-7.45 (4H, m), 7.37 (1H, t), 3.15 (1H, s), 2.00-1.96 (4H, m), 1.20-1.05 (20H, m), 0.81 (6H, t), 0.64 (4H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 151.6, 142.2, 141.4, 140.2, 131.9, 129.5, 127.9, 127.2, 126.8, 122.2, 121.0, 120.8, 120.3, 85.4, 55.9, 41.0, 32.4, 30.6, 29.9, 24.4, 23.3, 14.7. Anal. Calcd for $C_{37}H_{46}$: C, 90.55; H, 9.45. Found: C, 90.40; H, 9.56.

A1. A mixture of **1b** (290 mg, 0.49 mmol), **1d** (200 mg, 0.4 mmol), CuI (2 mg, 0.008 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.004 mmol), THF (6 mL) and diisopropylamine (4 mL) in a Schlenk tube was carefully degassed and charged with nitrogen. The tube was sealed and the reaction mixture was stirred at

60 ^{o}C for 24 h. After the removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (v/v, 6:1) to afford **1e** as a white solid (260 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (2H, d), 7.73-7.67 (6H, m), 7.61-7.57 (8H, m), 7.49 (4H, t), 7.38 (2H, t), 2.05-2.01 (8H, m), 1.21-1.18 (40H, m), 0.81 (12H, t), 0.68 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.4, 151.7, 142.2, 141.7, 141.2, 140.4, 131.4, 129.5, 126.8, 126.6, 122.2, 120.9, 120.4, 91.3, 56.0, 41.1, 32.5, 30.7, 29.9, 24.4, 23.3, 14.7. Anal. Calcd for $C_{72}H_{90}$: C, 90.51; H, 9.49. Found: C, 90.62; H, 9.62.

2c. The general procedure for synthesis of **1c** was followed. **2b** (480 mg, 0.49 mmol), CuI (2 mg, 0.01 mmol), $Pd(PPh_3)_2Cl_2$ (3 mg, 0.005 mmol) and trimethylsilylacetylene (90 μL, 0.64 mmol) were used. The reaction mixture was stirred at room temperature for 24 h. After the removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (v/v, 8:1) to afford **2c** as a white solid (400 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (2H, d), 7.76 (1H, d), 7.70 (1H, s), 7.68-7.65 (4H, m), 7.62-7.59 (4H, m), 7.50-7.47 (4H, m), 7.37 (1H, t), 2.09-1.98 (8H, m), 1.22-1.10 (40H, m), 0.84-0.78 (16H, m), 0.68 (4H, m), 0.31 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 140.9, 140.8, 140.7, 131.9, 129.4, 127.9, 126.9, 126.8, 126.7, 122.3, 122.1, 120.0, 121.8, 120.9, 120.6, 120.2, 107.0, 94.6, 56.0, 41.0, 32.4, 30.7, 29.5, 24.4, 23.2, 14.7, 0.74. Anal. Calcd for $C_{69}H_{94}Si$: C, 87.09; H, 9.96. Found: C, 86.92; H, 10.30.

2d. The general procedure for synthesis of **1d** was followed. **2c** (378 mg, 0.4 mmol) and tetrabutylammonium fluoride (1 M in THF, 600 μL, 0.6 mmol) were used. The mixture was stirred at room temperature for 10 min. The reaction mixture was poured onto a short pad of silica gel. Chromatography eluting with dichloromethane afforded **2d** as a white solid in a 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (3H, t), 7.69-7.64 (5H, m), 7.61-7.58 (4H, m), 7.51-7.46 (4H, m), 7.37 (1H, t), 3.15 (1H, s), 2.08-2.01 (8H, m), 1.21-1.08 (40H, m), 0.83-0.77 (12H, m), 0.69 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.4, 151.7, 142.4, 141.8, 141.0, 140.8, 140.7, 131.9, 129.4, 127.9, 127.8, 126.8, 127.2, 126.9, 126.7, 122.3, 122.1, 121.0, 120.8, 120.7, 120.3, 85.5, 56.0, 41.1, 32.4, 30.7, 29.9, 24.5, 23.2, 14.7. Anal. Calcd for $C_{66}H_{86}$: C, 90.14; H, 9.86. Found: C, 90.25; H, 9.61.

A2. The general procedure for synthesis of **A1** was followed. **2b** (391 mg, 0.4 mmol), **2d** (292 mg, 0.33 mmol), CuI (1 mg, 0.006 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg, 0.003 mmol), THF (6 mL) and diisopropylamine (4 mL) were used. The reaction mixture was stirred at 60 ^{o}C for 24h. After the removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (v/v, 5:1) to afford **A2** as a white solid (382 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (6H, t), 7.74 (2H, d), 7.70-7.66 (8H, m), 7.63-7.59 (12H, m), 7.49 (4H, t), 7.37 (2H, t), 2.08-2.06 (16H, m), 1.22-1.10 (80H, m), 0.83-0.78 (24H, m), 0.75 (16H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.4, 151.8, 142.4, 141.7, 141.6, 141.0, 140.8, 140.3, 131.4, 129.4,

127.9, 126.9, 126.8, 126.7, 126.6, 122.3, 122.1, 120.9, 120.6, 120.4, 91.4, 56.0, 41.1, 32.4, 30.7, 29.9, 24.5, 23.3, 14.7. Anal. Calcd for $C_{130}H_{170}$: C, 90.11; H, 9.89. Found: C, 89.76; H, 9.65.

3a. A mixture of **2b** (1.07 g, 1.1 mmol), 4**,**4,5,5-tetramethyl-2-(2-(trimethylsilyl)-9,9-dioctylfluoren-7-yl)-1,3,2-dioxaborolane (0.77 g, 1.3 mmol), THF (20 mL), water (5 mL) and $NaHCO_3$ (1.37 g, 20 mmol) was carefully degassed before and after $Pd(PPh_3)_4$ (25 mg, 0.02 eq) was added. The mixture was stirred and refluxed for 36 h. Dichloromethane was added, the organic layer was separated, the aqueous layer was extracted with dichloromethane three times, and the combined organic layer was dried over $MgSO_4$ and evaporated to dryness. Chromatography on silica gel eluting with hexane afforded **3a** as a white solid (1.01 g, 70%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.79 (5H, m), 7.75-7.60 (13H, m), 7.54-7.48 (4H, m), 7.38 (1H, t), 2.11-2.03 (12H, m), 1.27-1.13 (60H, m), 0.84-0.79 (30H, m), 0.33 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 152.5, 151.0, 141.4, 141.3, 141.0, 140.9, 140.8, 129.6, 128.0, 127.0, 126.9, 122.4, 122.3, 120.8, 120.0, 91.4, 56.1, 55.9, 41.2, 41.0, 32.6, 30.9, 30.8, 30.0, 24.7, 23.4, 14.9, 0.00. Anal. Calcd for $C_{96}H_{134}Si$: C, 87.60; H, 10.26. Found: C, 87.65; H, 10.18.

3b. A solution of ICl (1 mL, 1 mmol) in dichloromethane was added dropwise to a solution of **3a** (0.87 g, 0.66 mmol) in dichloromethane (10 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. Then a larger excess of aqueous $NaHSO_3$ solution was added to destroy the remained ICl. The organic layer was separated and the aqueous layer was extracted with dichloromethane three times. The combined organic layer was dried over $MgSO_4$ and evaporated to dryness. The residue was purified by chromatography on silica gel eluting with dichloromethane to afford **3b** as a white solid (0.89 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.81 (4H, m), 7.76 (1H, d), 7.69-7.61 (14H, m), 7.51-7.48 (3H, m), 7.38 (1H, t), 2.13-1.96 (12H, m), 1.27-1.12 (60H, m), 0.85-0.72 (30H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.4, 151.6, 141.2, 140.9, 140.8, 140.7, 136.5, 132.8, 129.4, 127.9, 127.8, 126.9, 126.8, 126.7, 122.3, 122.1, 122.0, 120.7, 120.6, 56.1, 56.0, 41.1, 41.0, 40.9, 32.4, 30.7, 30.6, 29.9, 24.6, 24.5, 24.4, 23.2, 14.7. Anal. Calcd for $C_{93}H_{125}I$: C, 81.54; H, 9.20. Found: C, 80.88; H, 8.98.

3c. The general procedure for synthesis of **1c** was followed. **3b** (289 mg, 0.21 mmol), CuI (1 mg, 0.004 mmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 0.002 mmol) and trimethylsilylacetylene (40 μL, 0.27 mmol) were used. The reaction mixture was stirred at room temperature for 24 h. After the removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (v/v, 5:1) to afford **3c** as a white solid (263 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.80 (4H, m), 7.76 (1H, d), 7.70-7.59 (13H, m), 7.49-7.47 (4H, m), 7.37 (1H, t), 2.08-2.01 (12H, m), 1.20-1.11 (60H, m), 0.83-0.68 (30H, m), 0.30 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.8, 151.7, 150.9, 141.8, 141.1, 140.5, 140.2, 140.1, 140.0, 128.8, 127.2, 126.3, 126.2, 121.6, 121.5, 121.4, 120.0, 106.4, 93.9, 55.4, 55.3, 40.5, 40.4, 31.8, 30.1, 29.3, 23.9, 23.8, 22.6,

14.1, 0.1. Anal. Calcd for $C_{98}H_{134}Si$: C, 87.83; H, 10.08. Found: C, 87.78; H, 10.04.

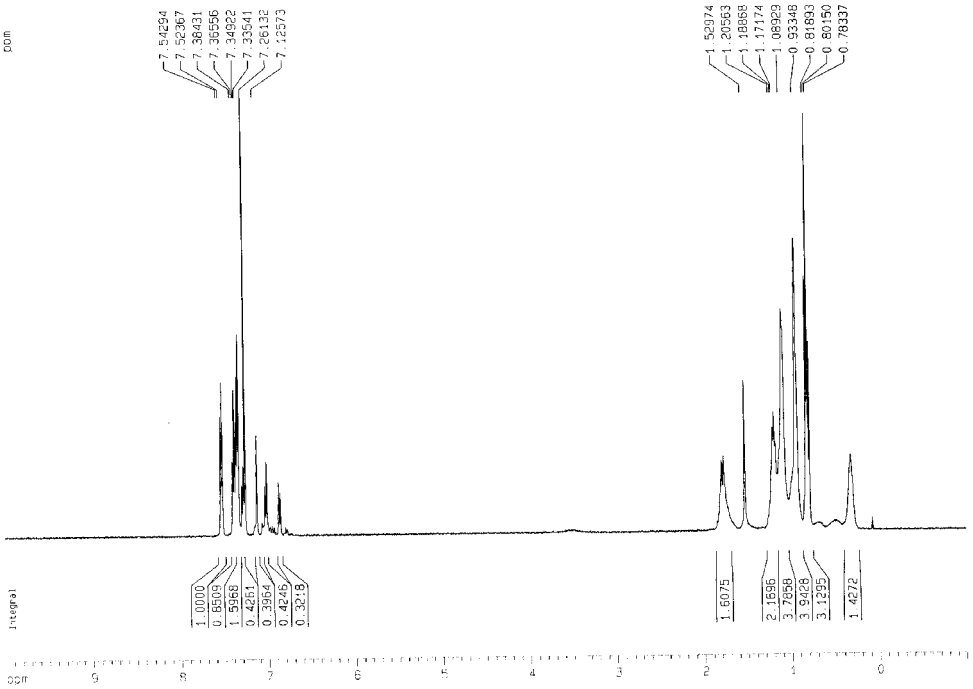
3d. The general procedure for synthesis of **1d** was followed. **3c** (244 mg, 0.18 mmol) and tetrabutylammonium fluoride (1 M in THF, 270 μL, 0.27 mmol) were used. The mixture was stirred at room temperature for 10 min. The reaction mixture was poured onto a short pad of silica gel. Chromatography eluting with dichloromethane afforded **3d** as a white solid in a yield of 99%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.77 (5H, m), 7.70-7.59 (13H, m), 7.52-7.47 (4H, m), 7.37 (1H, t), 3.15 (1H, s), 2.08-2.02 (12H, m), 1.20-1.11 (60H, m), 0.83-0.70 (30H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 151.8, 151.7, 151.0, 141.8, 140.3, 140.1, 139.5, 128.8, 127.2, 126.6, 126.3, 126.2, 126.1, 121.6, 121.5, 120.0, 119.6, 84.8, 55.4, 55.3, 40.4, 40.3, 31.8, 30.1, 30.0, 29.7, 29.2, 23.9, 23.8, 22.6, 14.1. Anal. Calcd for $C_{95}H_{126}$: C, 89.98; H, 10.02. Found: C, 89.53; H, 10.18.

A3. The general procedure for synthesis of **A1** was followed. **3b** (298 mg, 0.22 mmol), **3d** (230 mg, 0.18 mmol), CuI (1 mg, 0.004 mmol), $Pd(PPh_3)_2Cl_2$ (1 mg, 0.002 mmol), THF (6 mL) and diisopropylamine (4 mL) were used. The reaction mixture was stirred at 60 ^{o}C for 24 h. After removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/dichloromethane (v/v, 4:1) to afford **A3** as a white solid (432 mg, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.79 (10H, m), 7.75 (2H, d), 7.69-7.59 (28H, m), 7.49 (4H, t), 7.37 (2H, t), 2.09 (12H, m), 1.23-1.11 (60H, m), 0.84-0.79 (30H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 152.4, 142.4, 141.2, 140.8, 140.7, 140.6, 129.4, 127.9, 126.9, 126.8, 126.7, 126.6, 122.3, 122.2, 122.1, 120.9, 120.6, 91.4, 56.0, 41.1, 32.5, 32.3, 30.7, 29.9, 24.6, 24.5, 23.3, 14.7. Anal. Calcd for $C_{188}H_{250}$: C, 89.96; H, 10.04. Found: C, 89.88; H, 10.13.

(a)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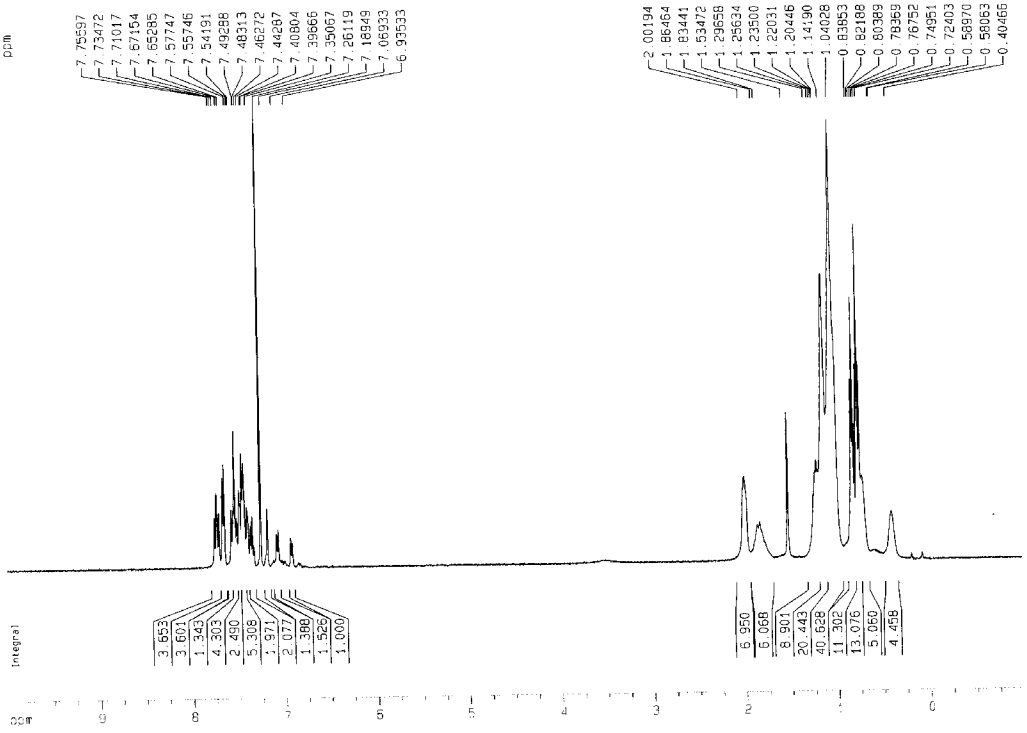
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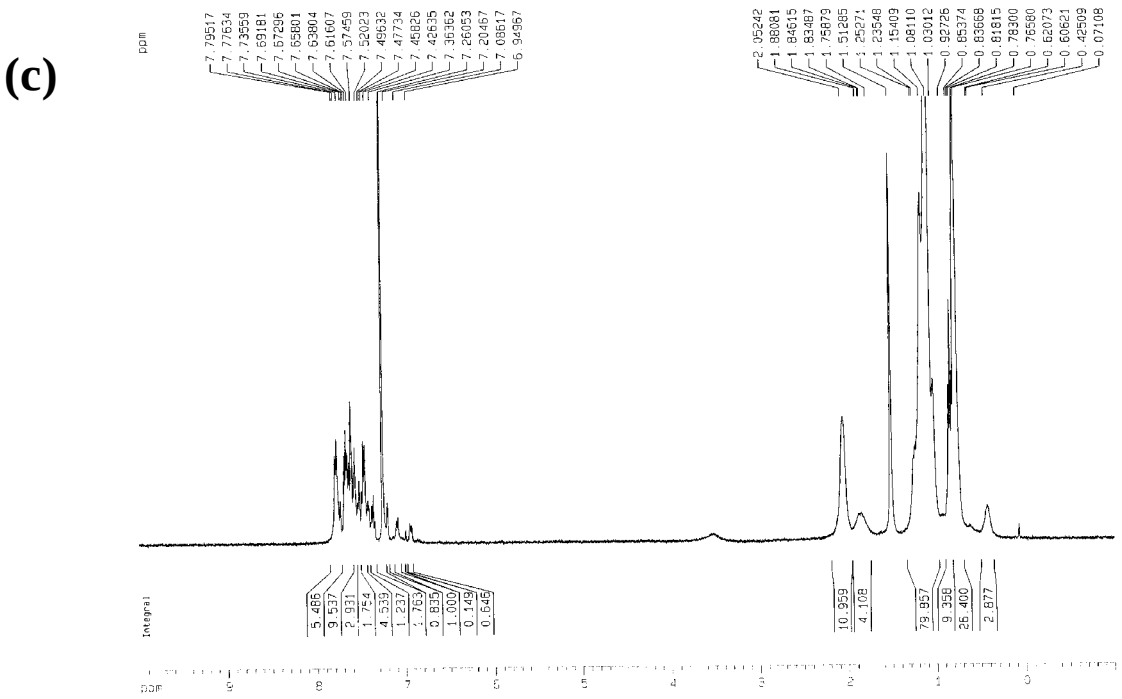
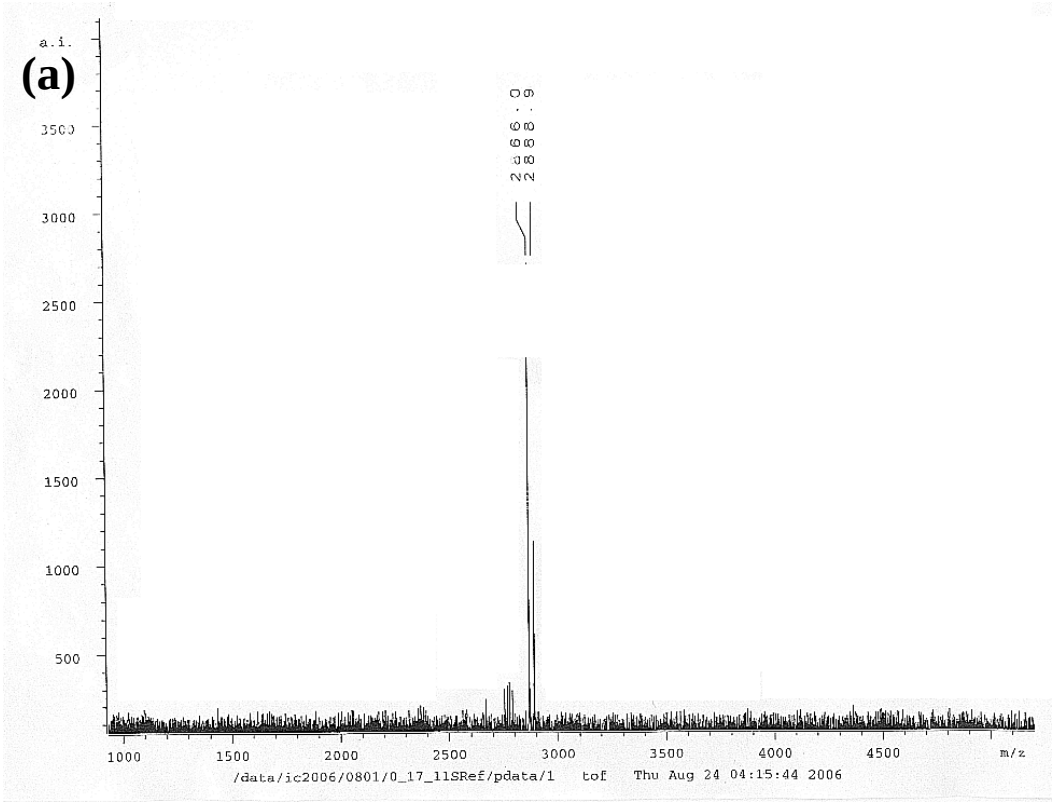
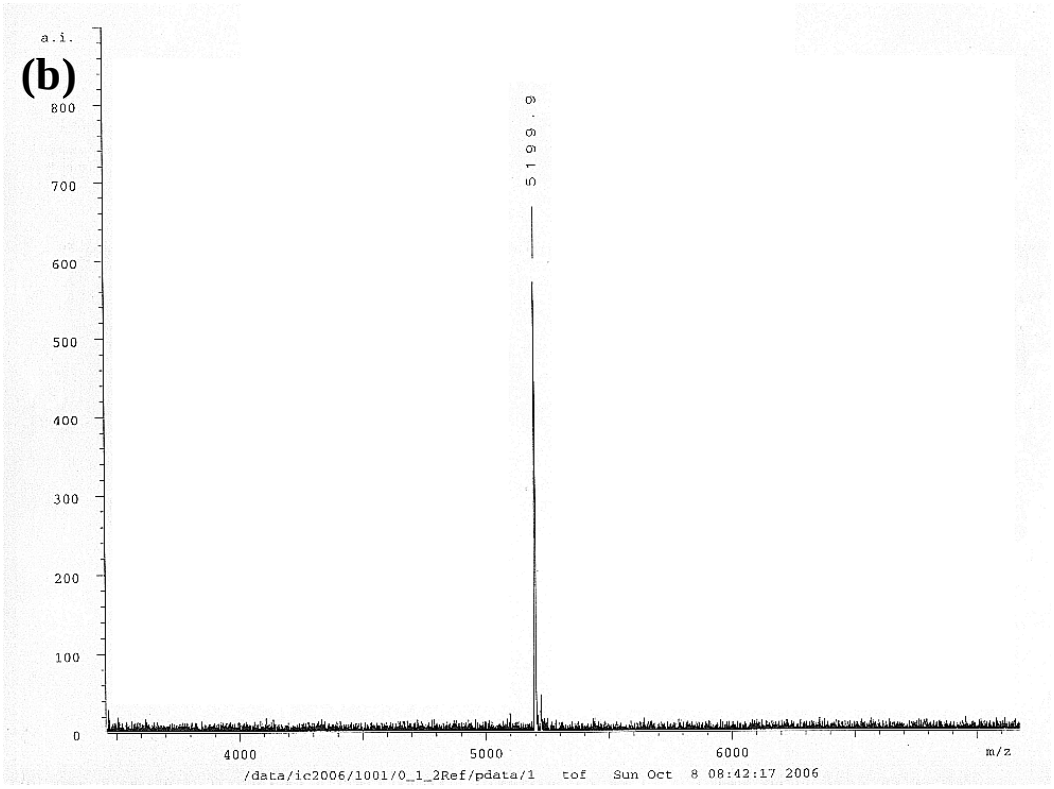


Figure S1. ^{1}H NMR spectra of **SF1** (a), **SF2** (b) and **SF3** (c).





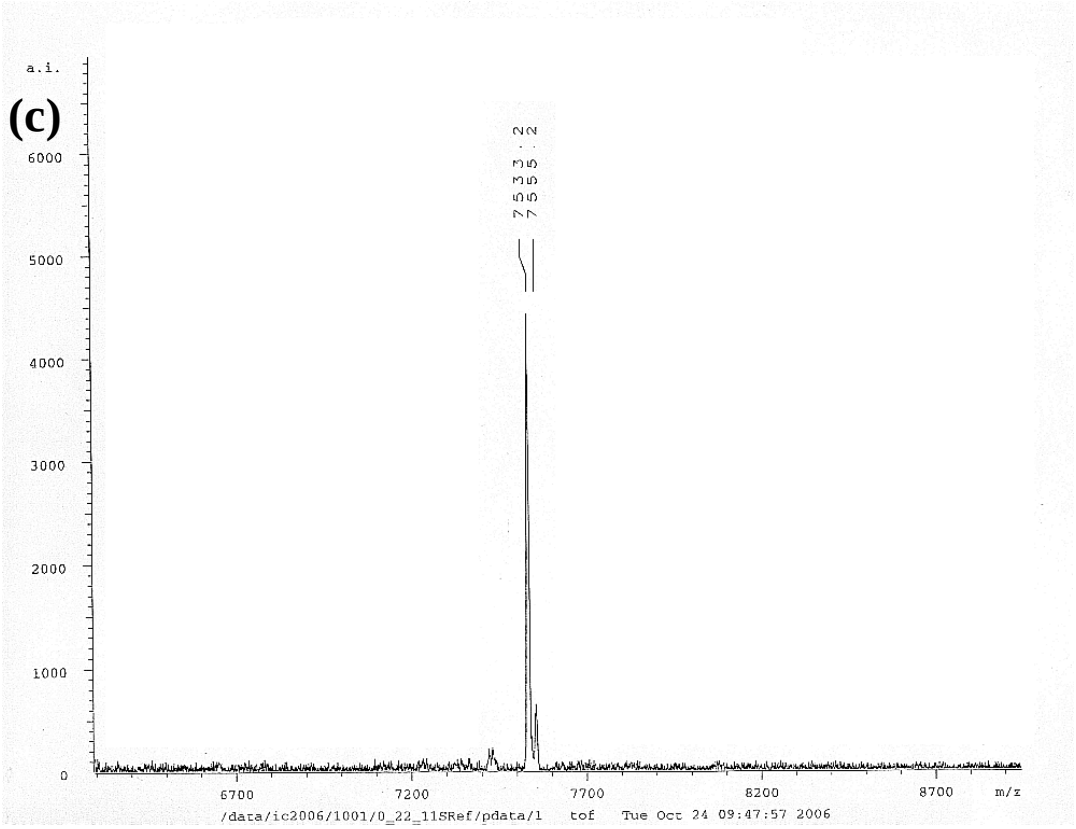


Figure S2. MALDI-TOF mass spectra of **SF1** (a), **SF2** (b) and **SF3** (c).

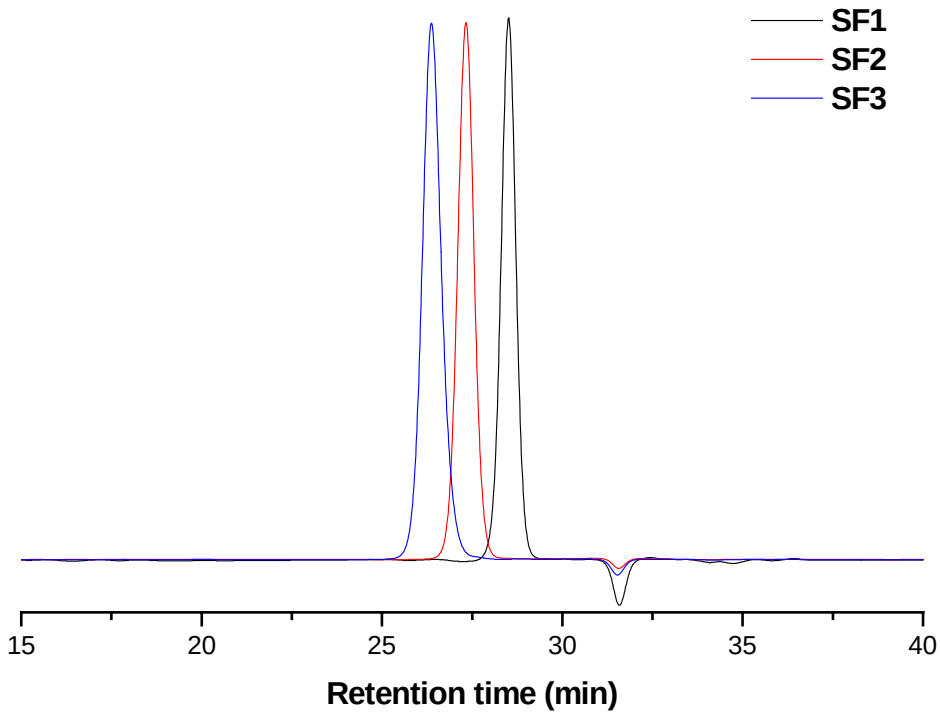


Figure S3. GPC traces of **SF1**, **SF2** and **SF3**.

Table S1. Optical properties of **SF1-SF3.**

Compd.	λ_{abs}(nm) (THF)	λ_{abs}(nm) (film)	λ_{PL}(nm) (THF)	λ_{PL}(nm) (film)	Φ_{PL}[a] (THF)
SF1	327	330	372	380	0.95
SF2	350	347	392	410	0.95
SF3	363	359	407	435	0.96

[a] 9, 10-Diphenylanthrancene as the reference standard.

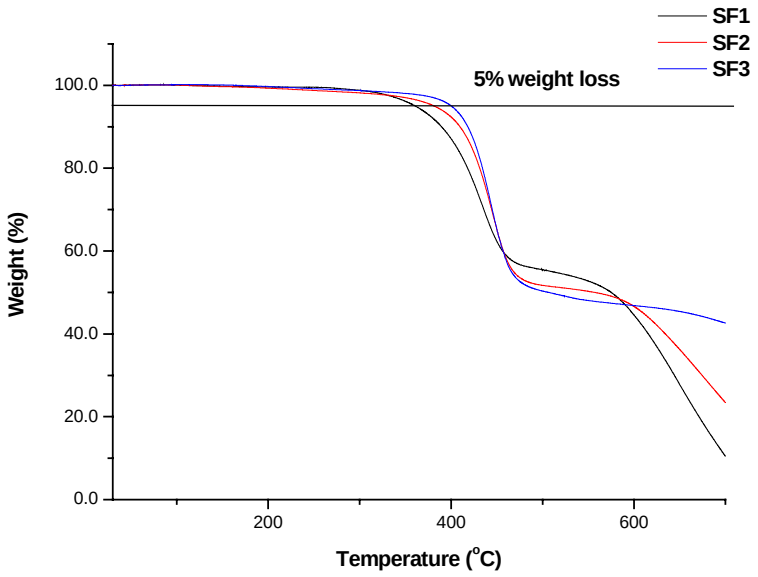


Figure S4. TGA traces of **SF1**, **SF2** and **SF3**.

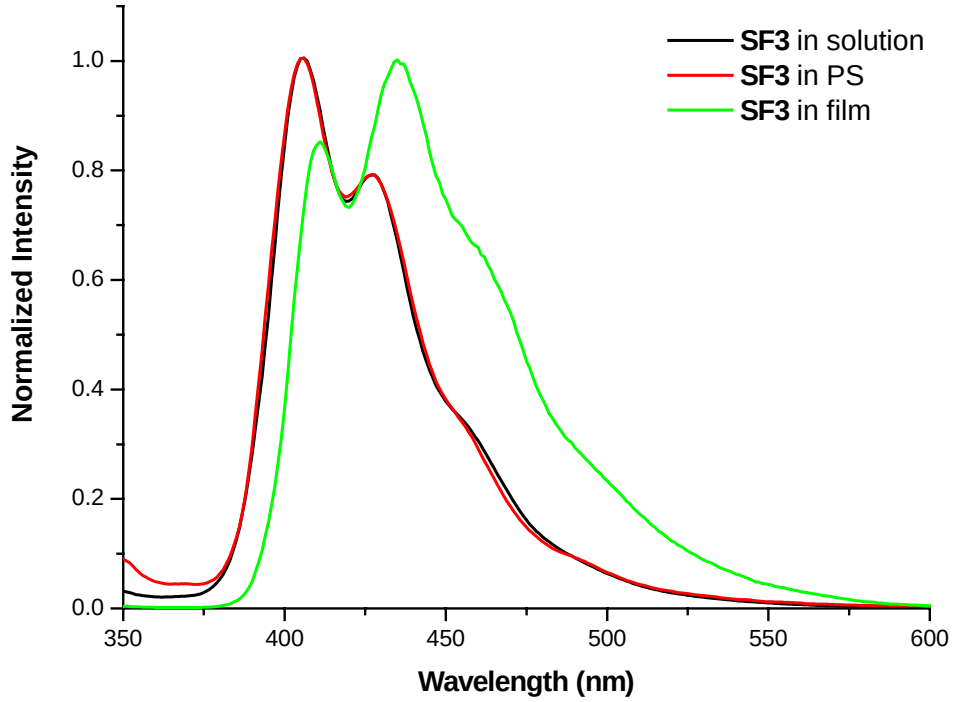


Figure S5. Emission spectra of **SF3** in THF solution, dispersed in PS film, and in neat solid film.

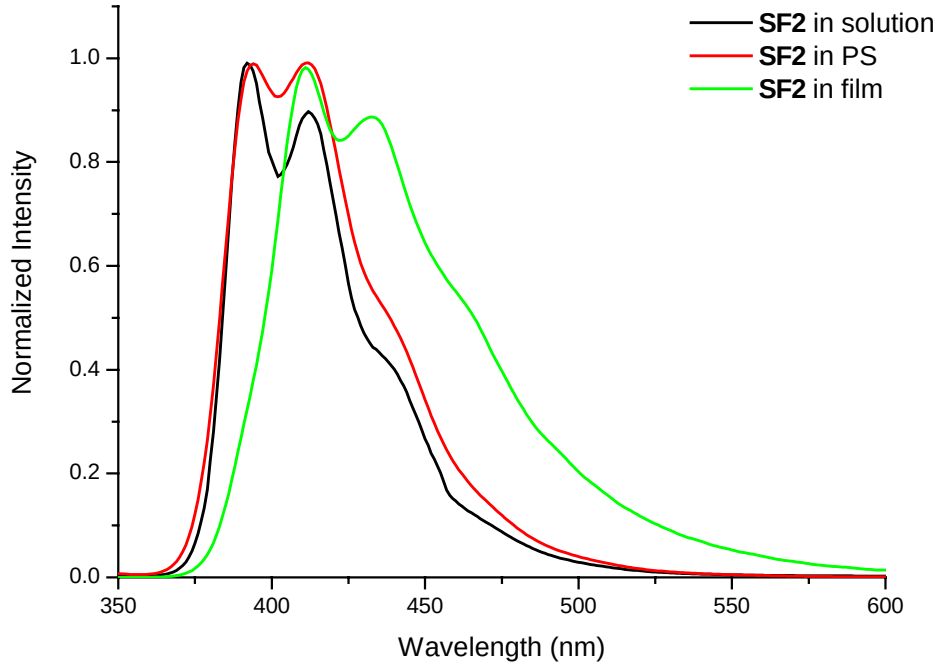


Figure S6. Emission spectra of **SF2** in THF solution, dispersed in PS film, and in neat solid film.

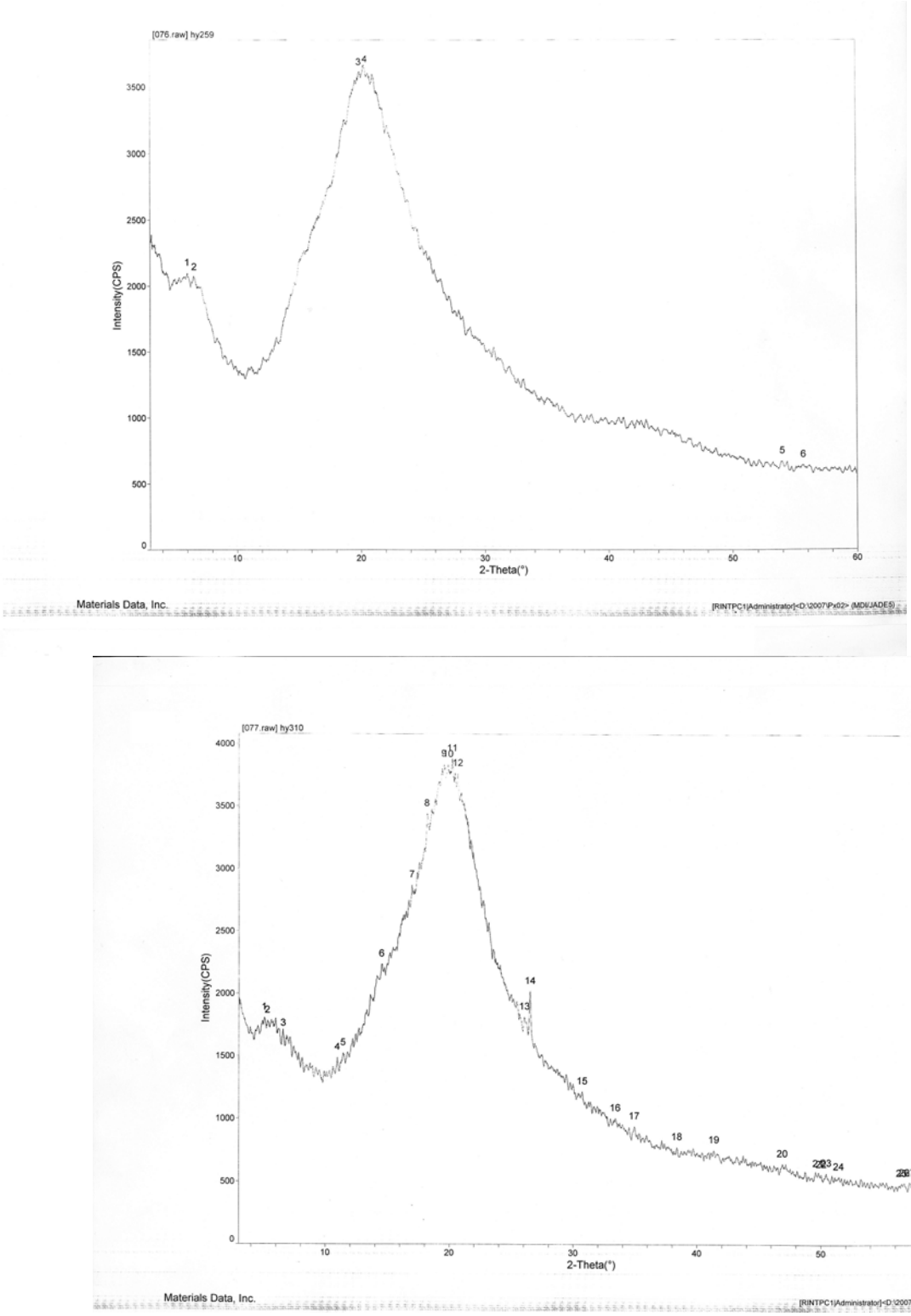


Figure S7. XRD spectra of **SF2** (top) and **SF3** (bottom).