

Supporting Information

Synthesis and Photophysical Properties of 2-Donor-7-acceptor-9-silafluorenes: Remarkable Fluorescence Solvatochromism and Highly Efficient Fluorescence in Doped Polymer Films

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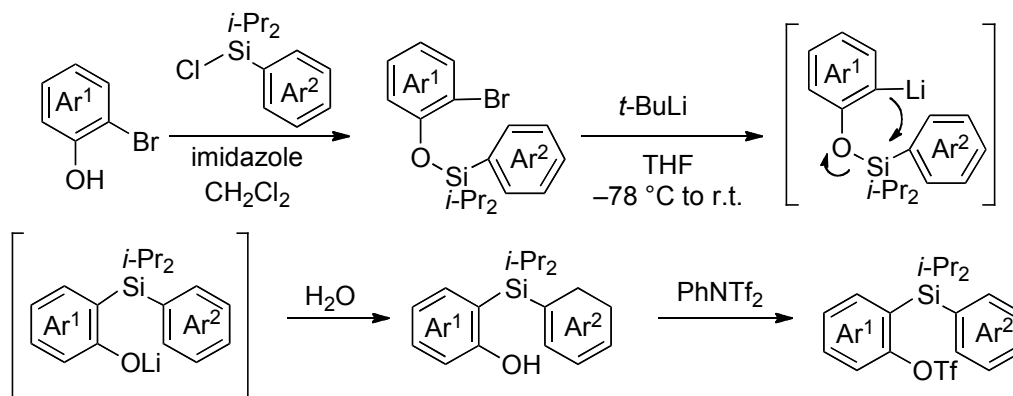
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General Information

Melting points were determined using a Stanford Research Systems MPA100. ^1H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^1H NMR are expressed in parts per million downfield relative to the internal tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 7.26$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; hep, heptet; m, multiplet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with tetramethylsilane as an internal standard ($\delta = 0$ ppm) or chloroform-*d* ($\delta = 77.0$ ppm). ^{19}F NMR spectra were measured on a Varian Mercury 300 (282 MHz) spectrometer with CFCl_3 as an internal standard ($\delta = 0$ ppm). Chemical shift values are given in parts per million downfield relative to the internal standards. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. EI-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL-HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} . Silica gel column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Dichlorodiisopropylsilane was purchased from Tokyo Chemical Industry Co., Ltd. Dimethylacetamide (DMA) was purchased from Wako, Inc. Reagent-grade dichloromethane, diethyl ether, and tetrahydrofuran were passed through two packed columns of neutral alumina and copper oxide under a nitrogen atmosphere before use. All reactions were carried out under an argon atmosphere.

General Procedure for Preparation of 2-(3-Aminophenylsilyl)aryl triflates 6-8

2-(Arylsilyl)aryl triflates **6-8** were prepared according to the following scheme.



Silylation of phenols with chlorosilanes:

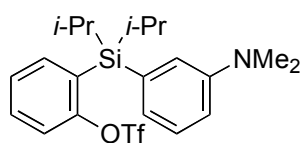
2-(Arylsilyl)phenols were prepared by silylation of the corresponding 2-bromophenols with chloro(diisopropylaryl)silane, followed by retro-Brook rearrangement of the silyl ethers in a manner similar to those reported in the following reference.

Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem. Int. Ed.* **2008**, 47, 9760.

Triflation of 2-silylphenols:

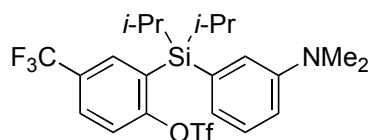
An oven-dried 20-mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with NaH (72 mg, 3 mmol) and DMF (5 mL). A DMF solution (5 mL) of 2-(3-aminophenylsilyl)phenol (3 mmol) was added to the suspension of NaH dropwise at room temperature. The resulting solution was stirred at room temperature for 1 h and then PhNTf₂ (1.07 g, 3 mmol) was added to the solution. The mixture was stirred for 12 h before quenching with saturated aq. NH₄Cl (20 mL). The aqueous layer was extracted with hexane (20 mL × 3). The combined organic layer was washed with saturated aq. NaCl (15 mL), dried over anhydrous MgSO₄, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to 2-(3-aminophenylsilyl)aryl triflates **6-8** as a colorless liquid or solid.

2-[(3-Dimethylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (**6**)



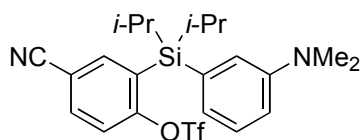
Purification: silica gel column chromatography (hexane/AcOEt 10:1) followed by GPC (CHCl₃). Yield: 21%, colorless oil. TLC: R_f 0.43 (hexane/AcOEt 10:1). ¹H NMR (400 MHz, CDCl₃): δ 0.98 (d, *J* = 7.3 Hz, 6H), 1.07 (d, *J* = 7.5 Hz, 6H), 1.73 (qq, *J* = 7.5, 7.3 Hz, 2H), 2.93 (s, 6H), 6.79–6.90 (m, 3H), 7.25–7.29 (m, 2H), 7.42 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.47–7.52 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 10.7, 17.98, 18.00, 40.8, 113.7, 118.3 (q, *J* = 319.8 Hz), 118.5, 120.1, 124.4, 126.2, 126.3, 128.1, 131.2, 132.4, 139.7, 149.5, 156.2; ¹⁹F NMR (282 MHz, CDCl₃): δ –74.9. IR (neat): ν = 2947, 2866, 1587, 1420, 1213, 1142, 1053, 991, 893, 777, 766, 745, 598, 513 cm^{–1}. MS (FAB) *m/z*: 459 (100, M⁺), 416 (15), 348 (4). Anal. Calcd for C₂₁H₂₈F₃NO₃SSi: C, 54.88; H, 6.14. Found: C, 54.78; H, 6.12.

2-[(3-Dimethylaminophenyl)diisopropylsilyl]-4-trifluoromethylphenyl trifluoromethanesulfonate (7)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 17%, colorless oil. TLC: R_f 0.48 (hexane/AcOEt 10:1). ¹H NMR (400 MHz, CDCl₃): δ 0.98 (d, *J* = 7.3 Hz, 6H), 1.05 (d, *J* = 7.5 Hz, 6H), 1.75 (qq, *J* = 7.5, 7.3 Hz, 2H), 2.93 (s, 6H), 6.79–6.82 (m, 3H), 7.26–7.30 (m, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.80 (d, *J* = 1.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 10.7, 17.7, 17.9, 40.8, 114.3, 118.3 (q, *J* = 319.5 Hz), 118.8, 119.9, 123.4 (q, *J* = 272.0 Hz), 124.3, 128.3, 128.4, 128.5 (q, *J* = 4.6 Hz), 128.7 (q, *J* = 32.7 Hz), 131.3, 136.5 (q, *J* = 3.1 Hz), 149.6, 157.9; ¹⁹F NMR (282 MHz, CDCl₃): δ –62.9, –74.6. IR (neat): ν = 2946, 2868, 1589, 1493, 1425, 1327, 1217, 1136, 1057, 885, 824, 725, 610 cm^{–1}. MS (FAB) *m/z*: 527 (100, M⁺), 484 (8), 350 (13). Anal. Calcd for C₂₂H₂₇F₆NO₃SSi: C, 50.08; H, 5.16. Found: C, 49.92; H, 5.02.

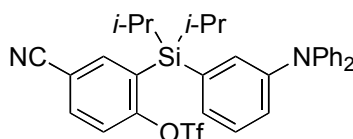
4-Cyano-2-[(3-dimethylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (8a)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 42%, a colorless oil. TLC: R_f 0.25 (hexane/AcOEt 10:1). ¹H NMR (400 MHz, CDCl₃): δ 0.99 (d, *J* = 7.3 Hz, 6H), 1.06 (d, *J* = 7.3 Hz, 6H), 1.73 (qq, *J* = 7.3, 7.3 Hz, 2H), 2.95 (s, 6H), 6.79–6.86 (m, 3H), 7.29 (d, *J* = 8.6

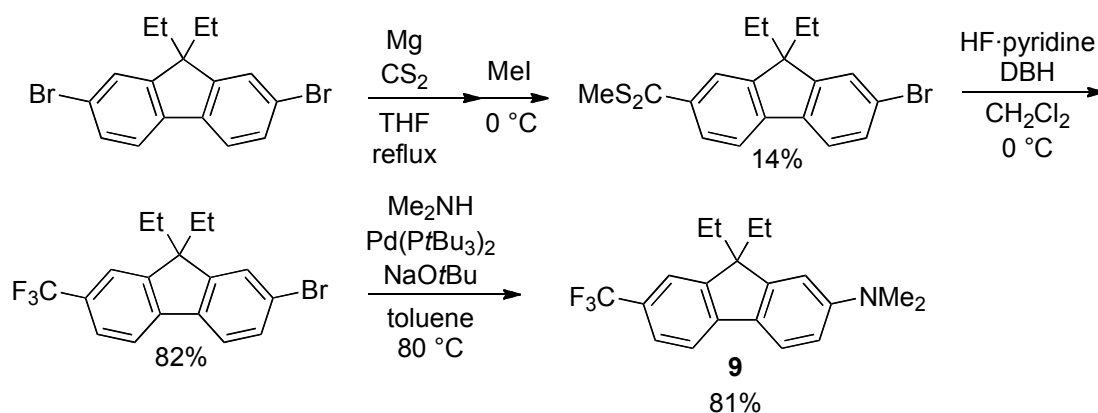
Hz, 1H), 7.56 (d, $J = 8.6$ Hz, 1H), 7.76–7.80 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 10.7, 17.9, 40.6, 111.0, 114.1, 117.5, 118.2 (q, $J = 319.8$ Hz), 119.3, 119.4, 123.8, 128.6, 129.5, 130.7, 134.9, 143.3, 149.7, 158.0; ^{19}F NMR (282 MHz, CDCl_3): δ -74.4. IR (neat): $\nu = 2949, 2868, 2234, 1587, 1566, 1495, 1408, 1348, 1284, 1211, 1138, 1057, 991, 887, 844, 777, 682, 617\text{ cm}^{-1}$. MS (FAB) m/z : 484 (100, M^+), 441 (5), 351 (5). Anal. Calcd for $\text{C}_{22}\text{H}_{27}\text{F}_3\text{N}_2\text{O}_3\text{SSi}$: C, 54.53; H, 5.62. Found: C, 54.53; H, 5.50.

4-Cyano-2-[(3-diphenylaminophenyl)diisopropylsilyl]phenyl trifluoromethanesulfonate (8b)



Purification: silica gel column chromatography (hexane/AcOEt 10:1). Yield: 19%, a colorless solid. Mp: 151.9–152.9 °C. TLC: R_f 0.25 (hexane/AcOEt 10:1). ^1H NMR (400 MHz, CDCl_3): δ 0.92 (d, $J = 7.6$ Hz, 6H), 0.97 (d, $J = 7.6$ Hz, 6H), 1.63 (qq, $J = 7.6, 7.6$ Hz, 2H), 6.98–7.05 (m, 3H), 7.08–7.10 (m, 4H), 7.13–7.16 (m, 2H), 7.22–7.30 (m, 5H), 7.52 (d, $J = 8.6$ Hz, 1H), 7.72 (d, $J = 2.2$ Hz, 1H), 7.76 (dd, $J = 8.6, 2.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 10.4, 17.7, 17.8, 111.1, 117.6, 119.4, 119.8 (q, $J = 317.2$ Hz), 122.7, 124.0, 125.6, 128.9, 129.0, 129.1, 129.5, 130.7, 131.6, 135.0 (2C), 142.9, 147.4, 157.9; ^{19}F NMR (282 MHz, CDCl_3): δ -74.4. IR (KBr): $\nu = 2953, 2926, 1587, 1493, 1422, 1273, 1213, 1140, 891, 844, 754, 696, 619\text{ cm}^{-1}$. MS (FAB) m/z : 608 (37, M^+), 565 (1), 475 (1). Anal. Calcd for $\text{C}_{32}\text{H}_{31}\text{F}_3\text{N}_2\text{O}_3\text{SSi}$: C, 63.14; H, 5.13. Found: C, 62.87; H, 5.13.

Preparation of 2-dimethylamino-7-trifluoromethyl-9,9-diethylfluorene (9)

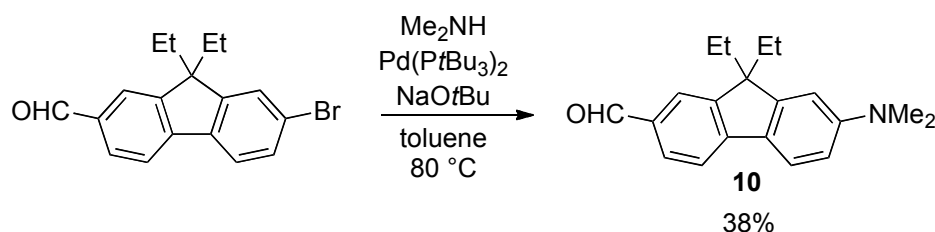


An oven-dried 20 mL Schlenk tube equipped with a magnetic stir bar and a rubber septum was charged with magnesium turnings (0.16 g, 6.5 mmol) and THF (2 mL). To the vigorously

stirred suspension was added 1,2-dibromoethane (43 μ L, 0.5 mmol) dropwise. A small portion of 2,7-dibromo-9,9-diethylfluorene (CAS: 197969-58-7) was added to initiate the reaction. After color of the reaction mixture turned pale orange, the remaining solution of 2,7-dibromo-9,9-diethylfluorene (totally, 1.9 g, 5.0 mmol) in THF (3 mL) was added. The reaction mixture was stirred at room temperature for 6 h before quenching carbon disulfide (0.93 mL, 15.5 mmol). The mixture was further stirred at room temperature for 12 h before methyl iodide (0.47 mL, 7.5 mmol) was added dropwise to the reaction mixture at 0 °C. The resulting mixture was stirred at room temperature for 5 h, then diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (5 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O (15 mL \times 3) and saturated aq. NaCl (15 mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give methyl 7-(dimethylamino)-9,9-dithylfluorene-2-carbodithioate (0.26 g, 0.69 mmol, 14%) as a red oil. A 5 mL polyethylene vial equipped with a magnetic stir bar was charged with 7-(dimethylamino)-9,9-dithylfluorene-2-carbodithioate (0.26 g, 0.69 mmol), 1,3-dibromo-5,5-dimethylhydantoin (0.79 g, 2.8 mmol), and CH_2Cl_2 (2 mL). To the solution was added HF/Py (70/30 wt%, 0.3 mL, F^- : 20 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then poured into an aqueous solution of sodium hydrogencarbonate and sodium hydrogensulfite, and the aqueous layer was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O (15 mL \times 3) and saturated aq. NaCl (15 mL) and dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to give 2-bromo-7-trifluoromethyl-9,9-diethylfluorene (0.21 g, 0.57 mmol, 82%) as a colorless solid. An oven-dried 3 mL vial equipped with a magnetic stir bar was charged with 2-bromo-7-trifluoromethyl-9,9-diethylfluorene (0.21 g, 0.57 mmol), dimethylamine (50 wt% in H_2O , 0.23 mL, 4.6 mmol), $\text{Pd}(\text{P}t\text{Bu}_3)_2$ (31 mg, 0.06 mmol), NaOtBu (0.22 g, 2.3 mmol), and toluene (2 mL). The mixture was heated at 80 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (5 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O (15 mL \times 3) and saturated aq. NaCl (15 mL), and dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/AcOEt 50:1) to give 2-dimethylamino-7-trifluoromethyl-9,9-diethylfluorene (**9**, 0.15 g, 0.46 mmol, 81 %) as a colorless solid. Mp: 80.1–81.0 °C. R_f 0.05 (hexane). ^1H NMR (400 MHz, CDCl_3): δ 0.32–0.35 (m, 6H), 1.93–2.09 (m, 4H), 3.05 (s, 6H), 6.64 (d, J = 2.4 Hz, 1H), 6.73 (dd, J = 8.4, 2.4 Hz, 1H), 7.46–7.47

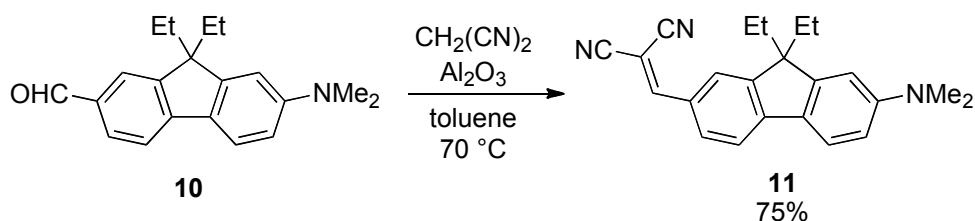
(m, 1H), 7.52 (dm, $J = 7.9$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.60 (d, $J = 7.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 8.6, 33.0, 40.9, 56.3, 106.4, 111.3, 117.8, 119.1 (q, $J = 3.1$ Hz), 120.9, 124.0 (q, $J = 3.8$ Hz), 124.9 (q, $J = 271.9$ Hz), 125.0 (q, $J = 31.2$ Hz), 128.9, 145.6, 149.1, 151.0, 152.1. IR (KBr): $\nu = 2965, 2911, 2359, 1608, 1506, 1361, 1325, 1314, 1161, 1109, 1062, 842, 810, 739$ cm^{-1} . MS (FAB) m/z : 333 (100, M^+), 308 (3), 288 (6). Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{N}$: C, 72.05; H, 6.65. Found: C, 72.04; H, 6.65.

Preparation of 2-dimethylamino-7-formyl-9,9-diethylfluorene (**10**)



An oven-dried 3 mL vial equipped with a magnetic stir bar was charged with 2-bromo-7-formyl-9,9-diethylfluorene (CAS: 225113-39-3, 82 mg, 0.25 mmol), dimethylamine (50 wt% in H_2O , 0.1 mL, 2.0 mmol), $\text{Pd(PtBu}_3)_2$ (13 mg, 0.025 mmol), NaOtBu (96 mg, 1.0 mmol), and toluene (2 mL). The mixture was heated at 80°C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (5 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O (15 mL \times 3) and saturated aq. NaCl (15 mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ AcOEt 10:1) to give 2-dimethylamino-7-formyl-9,9-diethylfluorene (**10**, 28 mg, 0.1 mmol, 38 %) as a yellow solid. Mp: $126.7\text{--}127.4^\circ\text{C}$. R_f 0.10 (hexane/ AcOEt 10:1). ^1H NMR (400 MHz, CDCl_3): δ 0.31–0.34 (m, 6H), 1.93–2.13 (m, 4H), 6.63 (m, 1H), 6.73 (d, $J = 7.7$ Hz, 1H), 7.61–7.66 (m, 2H), 7.77–7.79 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 8.6, 33.0, 40.8, 56.1, 106.1, 111.4, 117.9, 121.7 (2C), 122.5, 131.1, 133.3, 149.0, 149.4, 151.4, 153.2, 192.0. IR (KBr): $\nu = 2959, 2816, 1678, 1589, 1506, 1361, 1296, 1166, 1076, 800, 743, 680$ cm^{-1} . MS (FAB) m/z : 293 (54, M^+), 264 (2), 248 (3). Anal. Calcd for $\text{C}_{20}\text{H}_{23}\text{NO}$: C, 81.87; H, 7.90. Found: C, 81.83; H, 7.98.

Preparation of 2-(2,2-dicyanoethenyl)-9,9-diethyl-7-dimethylaminofluorene (**11**)



An oven-dried 3 mL vial equipped with a magnetic stir bar was charged with **10** (26 mg, 0.09 mmol), malononitrile (12 mg, 0.18 mmol), basic Al_2O_3 (47 mg), and toluene (1 mL). The reaction mixture was stirred at 70 °C for 20 h. The resulting mixture was cooled to room temperature and diluted with CH_2Cl_2 (10 mL). Saturated aq. NH_4Cl (5 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 (20 mL \times 3). The combined organic layer was washed with H_2O (15 mL \times 3) and saturated aq. NaCl (15 mL), dried over anhydrous MgSO_4 , and concentrated under reduced pressure. The residue was purified by recrystallization from hexane/ CH_2Cl_2 to give 2-(2,2-dicyanoethenyl)-9,9-diethyl-7-dimethylaminofluorene (**11**, 23 mg, 75%) as a red solid. Mp: 160.4–161.4 °C. TLC: R_f 0.28 (hexane/AcOEt 2.5:1). ^1H NMR (400 MHz, CDCl_3): δ 0.33–0.37 (m, 6H), 1.93–2.11 (m, 4H), 6.60 (d, J = 2.1 Hz, 1H), 6.73 (dd, J = 8.6, 2.1 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.6 Hz, 1H), 7.72 (s, 1H), 7.78 (dd, J = 8.0, 1.6 Hz, 1H), 7.88 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 8.6, 32.9, 40.7, 56.2, 77.4, 105.7, 111.5, 113.9, 114.9, 118.4, 122.2, 124.1, 127.5, 128.1, 131.9, 149.8, 149.9, 151.8, 153.9, 159.6. IR (KBr): ν = 2959, 2850, 2222, 1566, 1541, 1431, 1357, 1301, 1219, 1182, 1082, 808, 744 cm^{-1} . MS (FAB) m/z : 341 (6, M^+), 242 (1), 176 (4). Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{N}_3$: C, 80.90; H, 6.79. Found: C, 80.60; H, 6.82.

Crystallographic data of 3b.

CCDC–768341 contains the supplementary crystallographic data for **3b**.

Empirical formula	C ₃₁ H ₃₀ N ₂ Si	
Formula weight	458.66	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.4497(7) Å	$\alpha = 90^\circ$.
	b = 13.2197(10) Å	$\beta = 95.9840(10)^\circ$.
	c = 23.800(2) Å	$\gamma = 90^\circ$.
Volume	2644.0(4) Å ³	
Z	4	
Density (calculated)	1.152 Mg/m ³	
Absorption coefficient	0.110 mm ⁻¹	
F(000)	976	
Crystal size	0.50 x 0.50 x 0.50 mm ³	
Theta range for data collection	1.72 to 25.50°.	
Index ranges	-7 ≤ h ≤ 10, -16 ≤ k ≤ 14, -26 ≤ l ≤ 28	
Reflections collected	14091	
Independent reflections	4890 [R(int) = 0.0179]	
Completeness to theta = 25.50°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9472 and 0.9472	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4890 / 24 / 311	
Goodness-of-fit on F ²	1.100	
Final R indices [I > 2σ(I)]	R1 = 0.0724, wR2 = 0.2307	
R indices (all data)	R1 = 0.0845, wR2 = 0.2492	
Largest diff. peak and hole	1.026 and -0.506 e.Å ⁻³	

UV absorption and fluorescence spectra of 1–5 in various solvents (Spectra measured in benzene are omitted for clarity.)

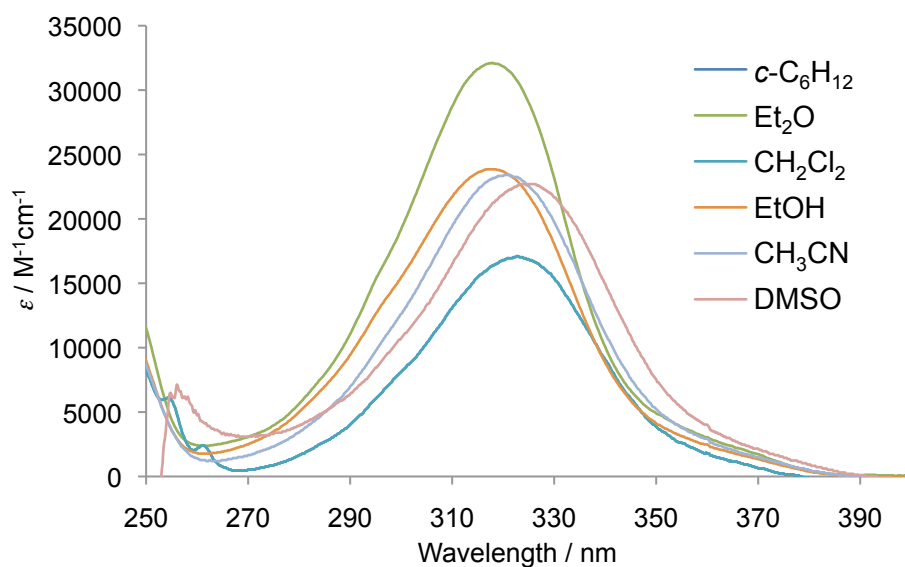


Figure S1. UV absorption spectra of 1 in various solvents.

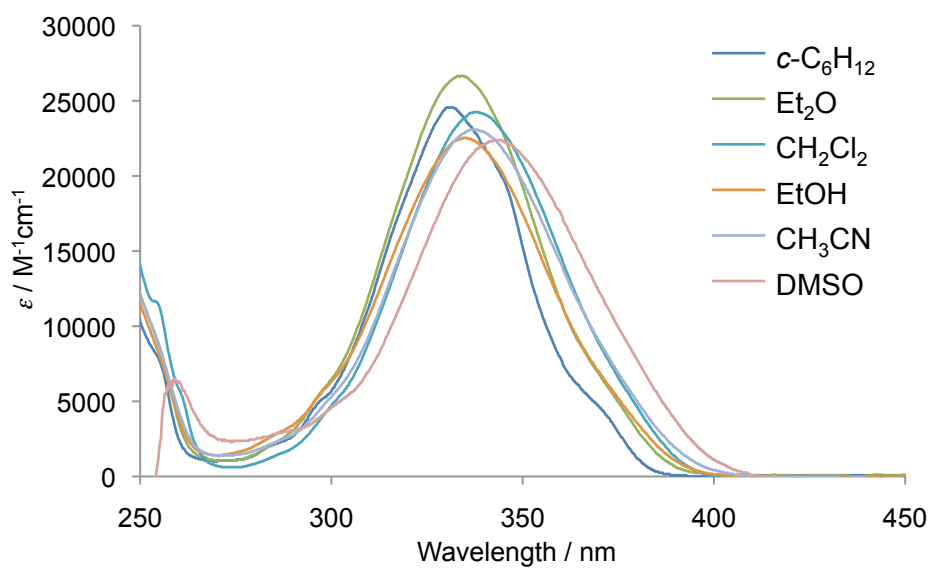


Figure S2. UV absorption spectra of 2 in various solvents.

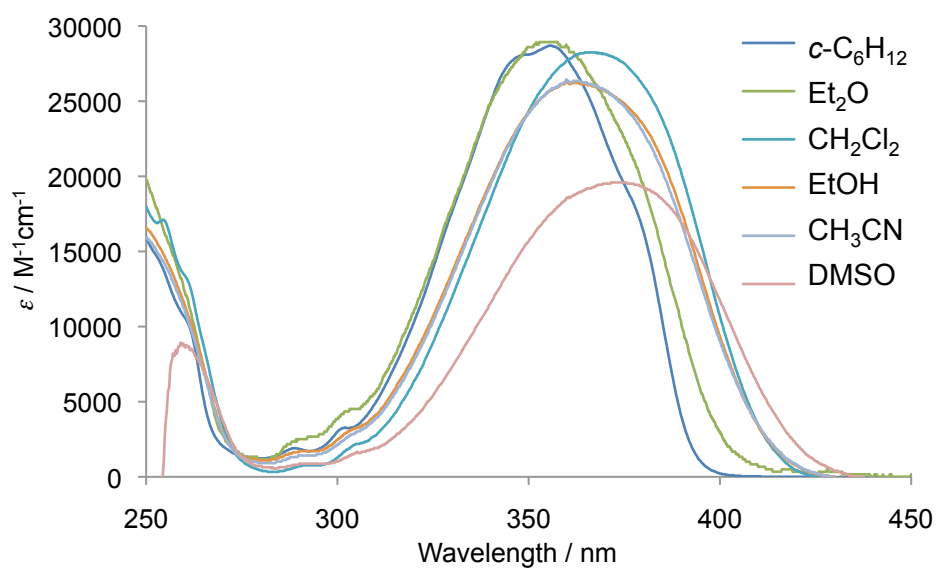


Figure S3. UV absorption spectra of 3a in various solvents.

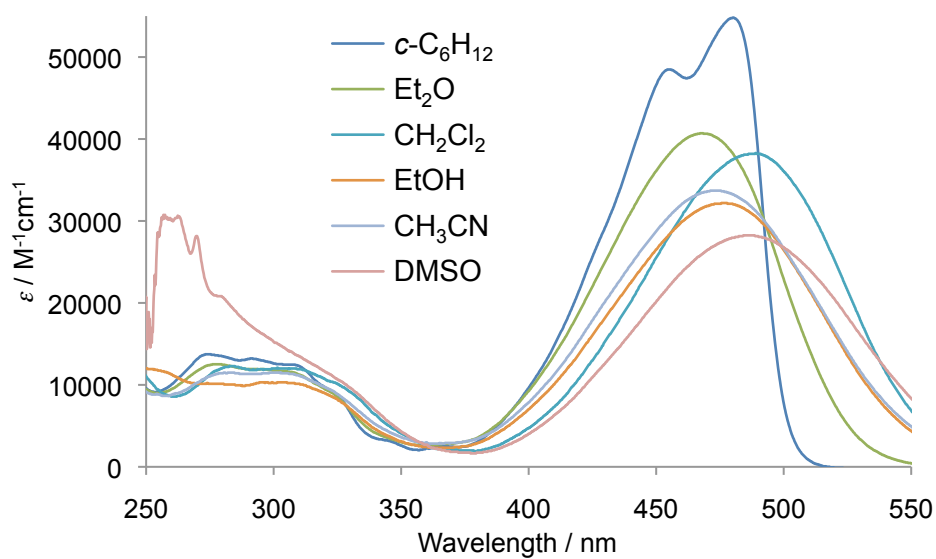


Figure S4. UV absorption spectra of 5a in various solvents.

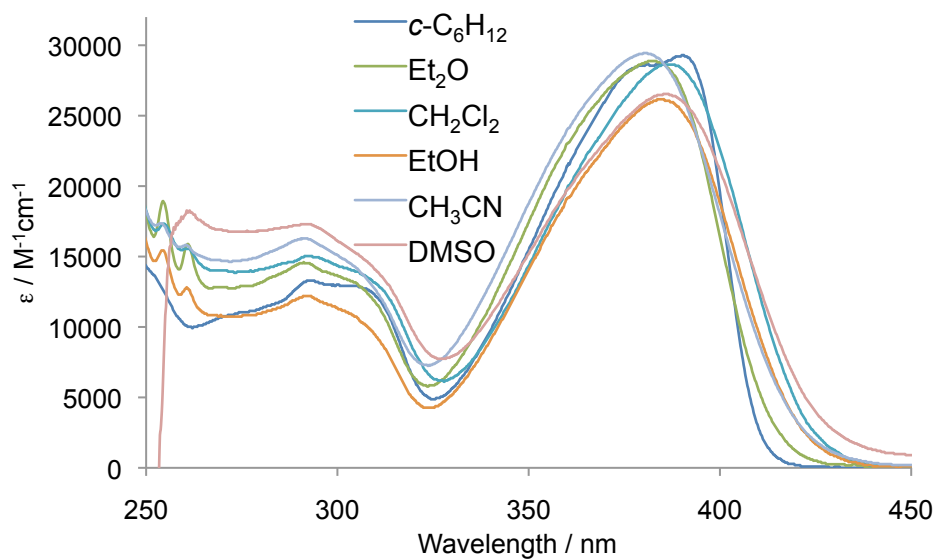


Figure S5. UV absorption spectra of 3b in various solvents.

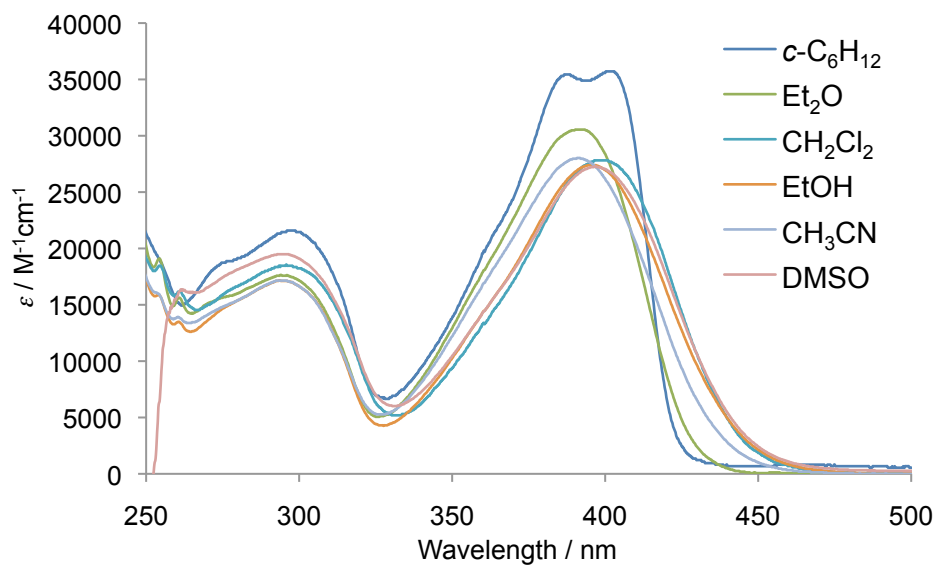


Figure S6. UV absorption spectra of 4b in various solvents.

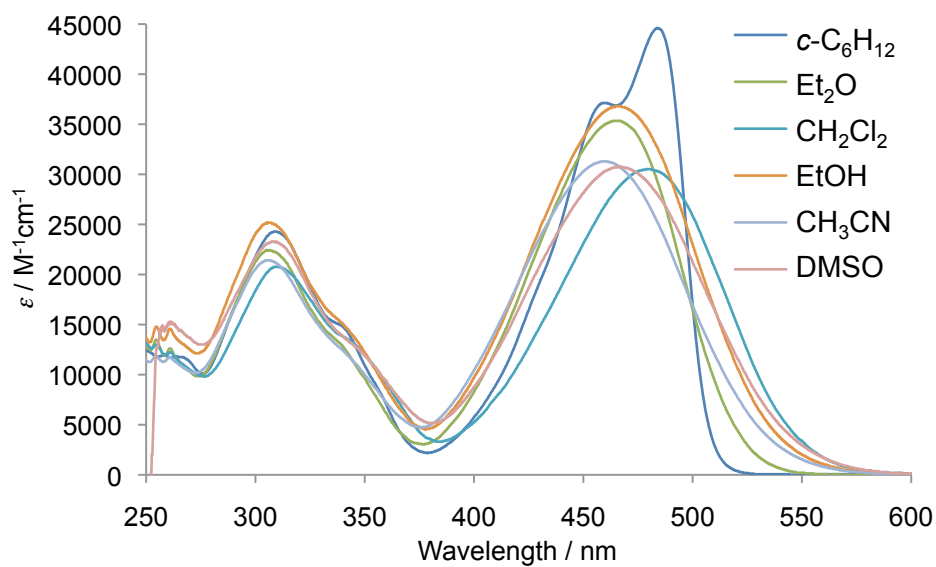


Figure S7. UV absorption spectra of 5b in various solvents.

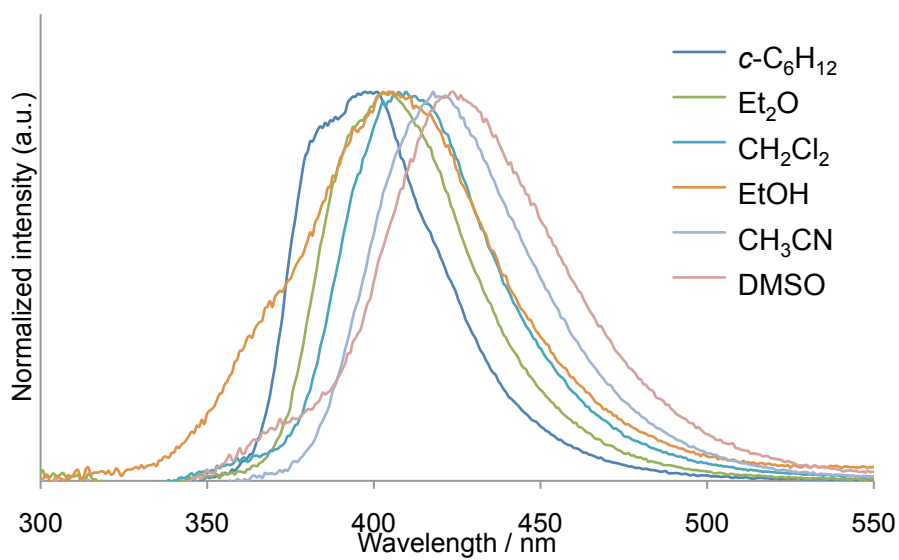


Figure S8. Fluorescence spectra of 1 in various solvents ($\lambda_{\text{ex}} = 290 \text{ nm}$).

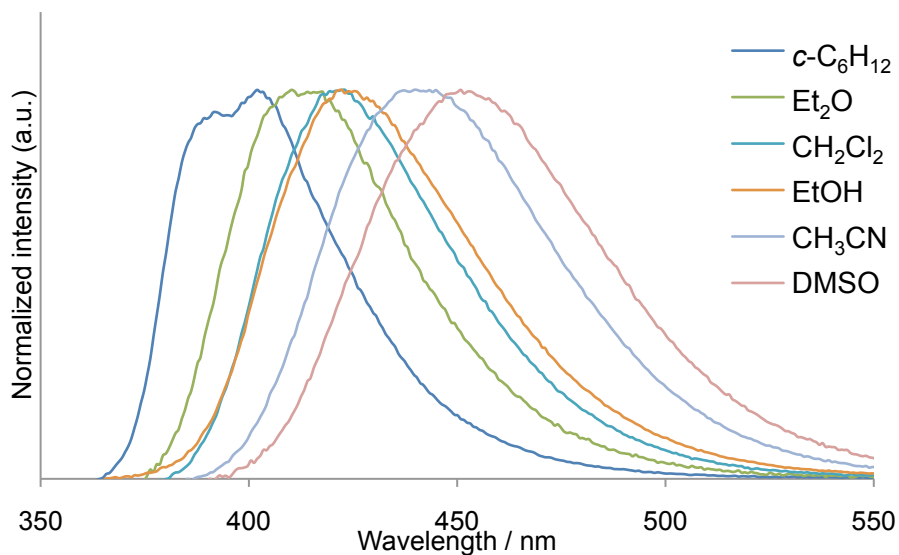


Figure S9. Fluorescence spectra of **2** in various solvents ($\lambda_{\text{ex}} = 290 \text{ nm}$).

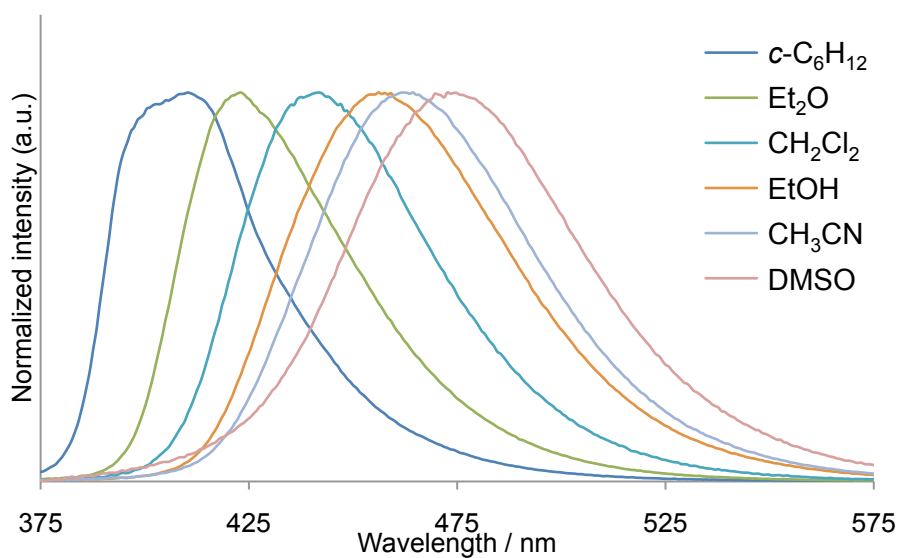


Figure S10. Fluorescence spectra of **3a** in various solvents ($\lambda_{\text{ex}} = 320 \text{ nm}$).

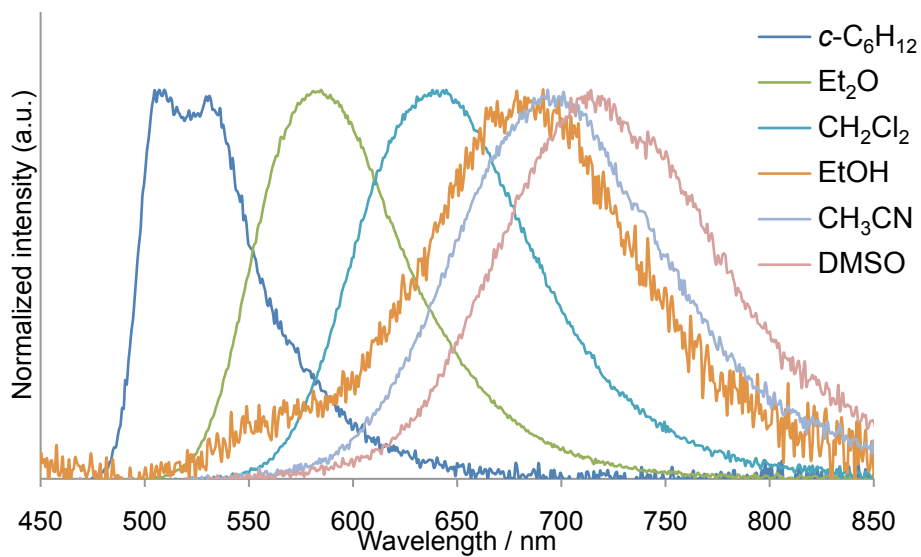


Figure S11. Fluorescence spectra of 5a in various solvents ($\lambda_{\text{ex}} = 390 \text{ nm}$).

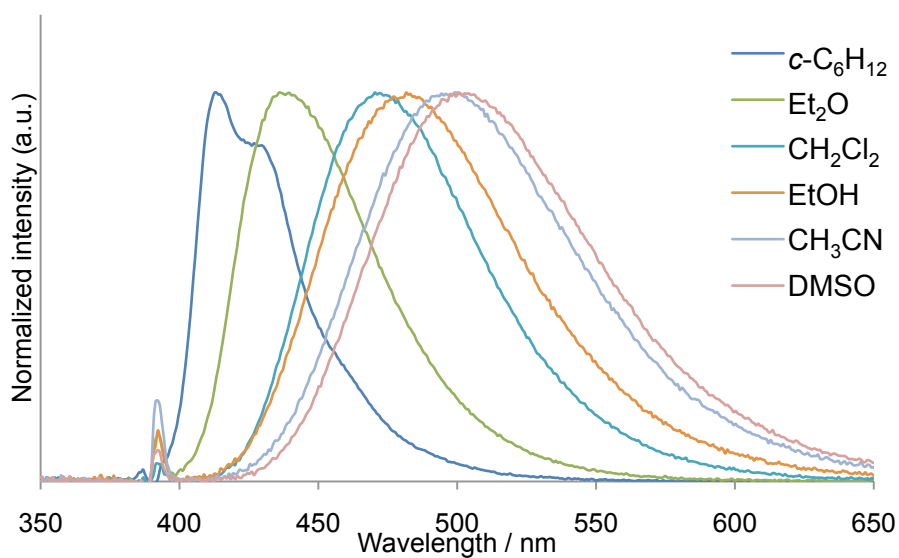


Figure S12. Fluorescence spectra of 3b in various solvents ($\lambda_{\text{ex}} = 390 \text{ nm}$).

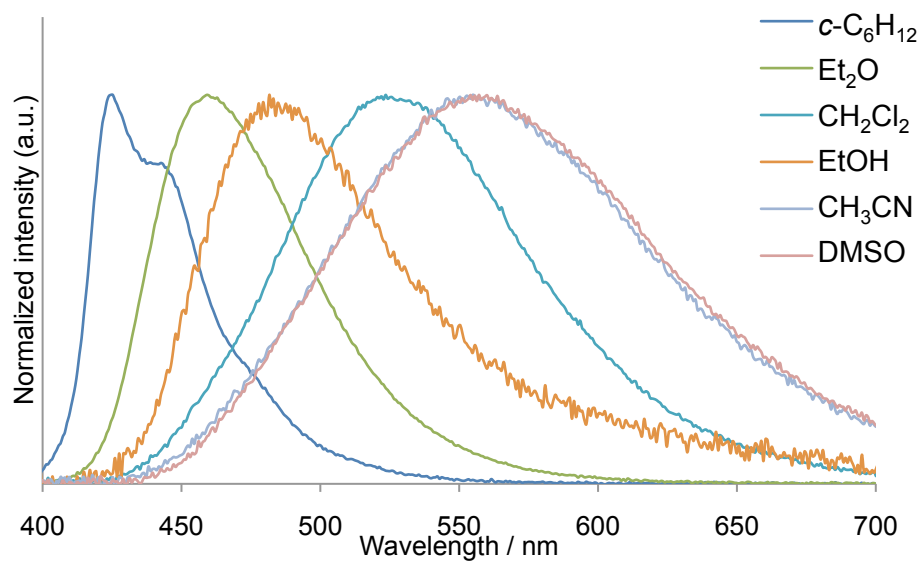


Figure S13. Fluorescence spectra of 4b in various solvents ($\lambda_{\text{ex}} = 390 \text{ nm}$).

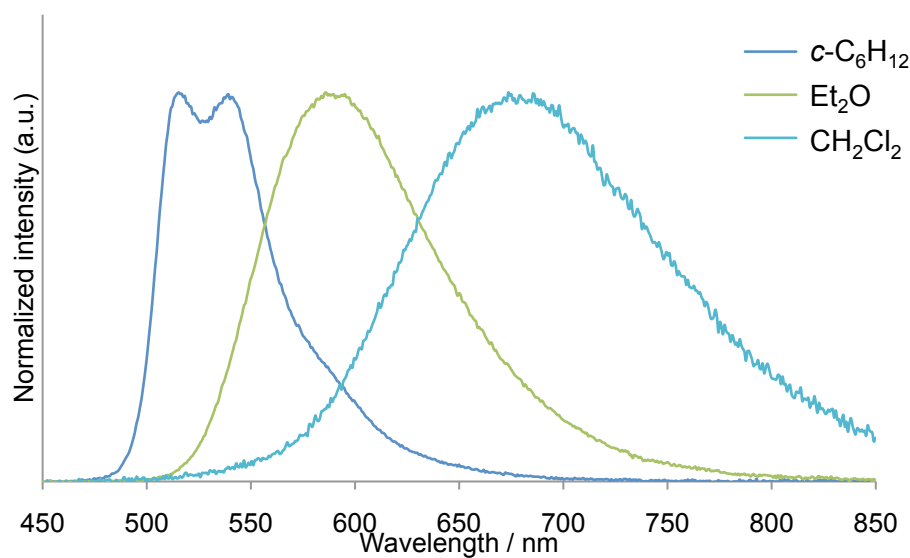


Figure S14. Fluorescence spectra of 5b in various solvents ($\lambda_{\text{ex}} = 430 \text{ nm}$).

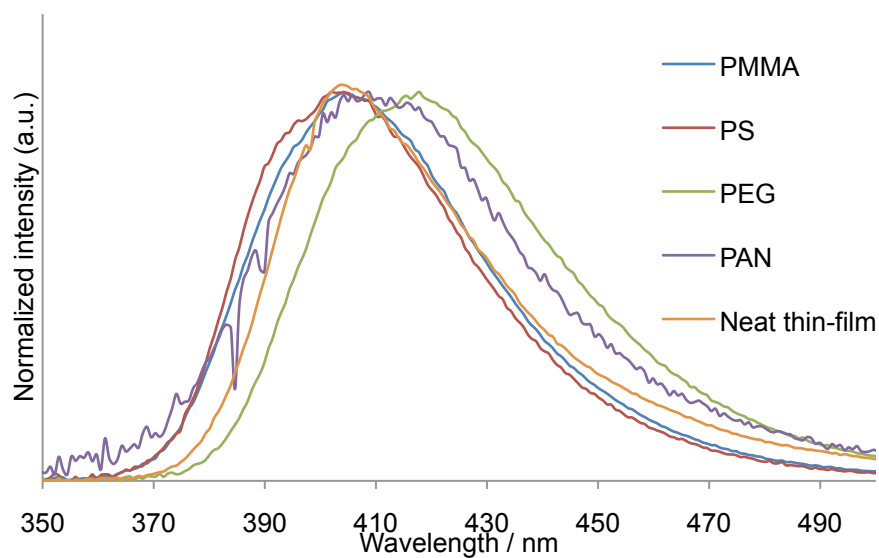
Fluorescence Spectra of 1–5 in the Solid States

Figure S15. Fluorescence spectra of 1 in the solid states ($\lambda_{\text{ex}} = 290$ nm).

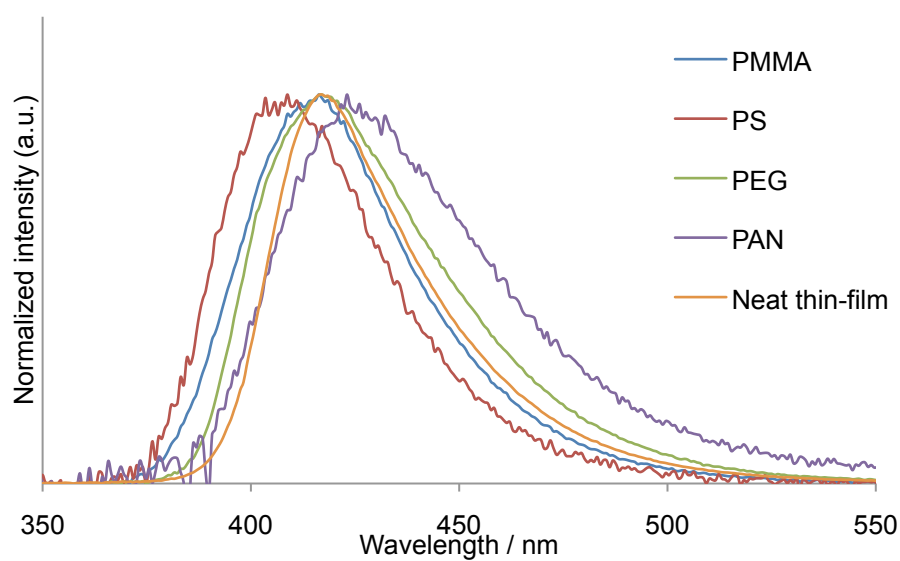


Figure S16. Fluorescence spectra of 2 in the solid states ($\lambda_{\text{ex}} = 290$ nm).

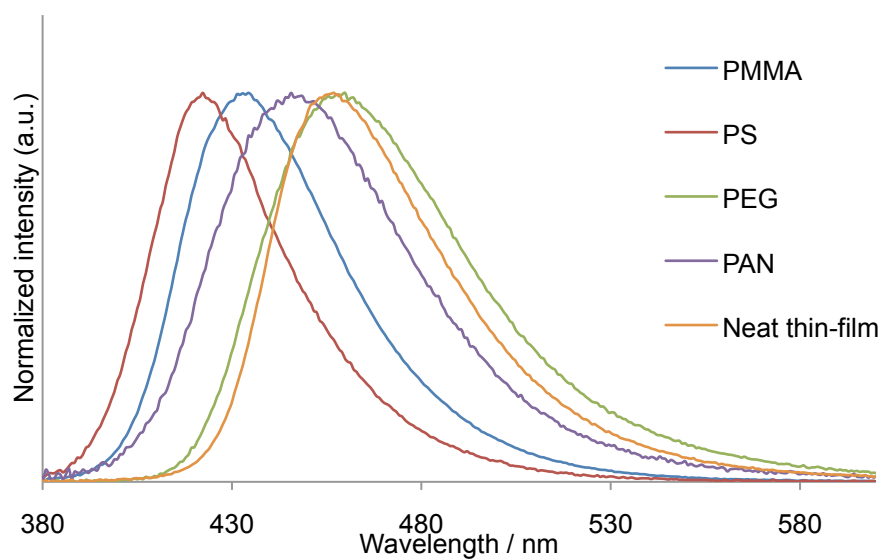


Figure S17. Fluorescence spectra of 3a in the solid states ($\lambda_{\text{ex}} = 320$ nm).

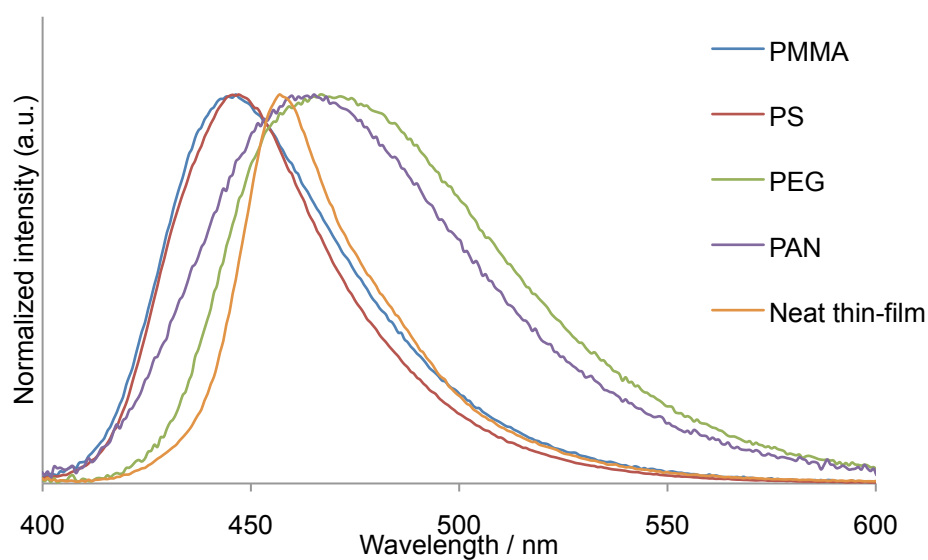


Figure S18. Fluorescence spectra of 3b in the solid states ($\lambda_{\text{ex}} = 390$ nm).

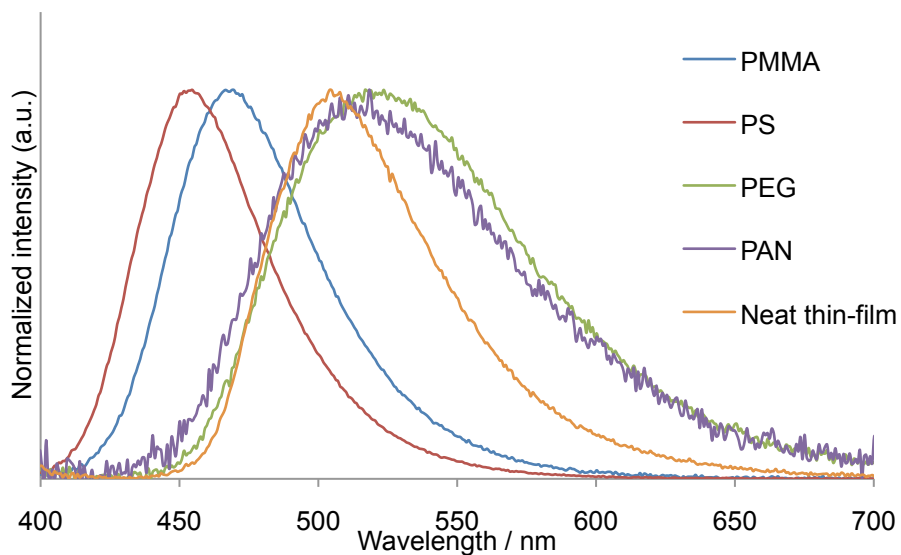


Figure S19. Fluorescence spectra of 4b in the solid states ($\lambda_{\text{ex}} = 390$ nm).

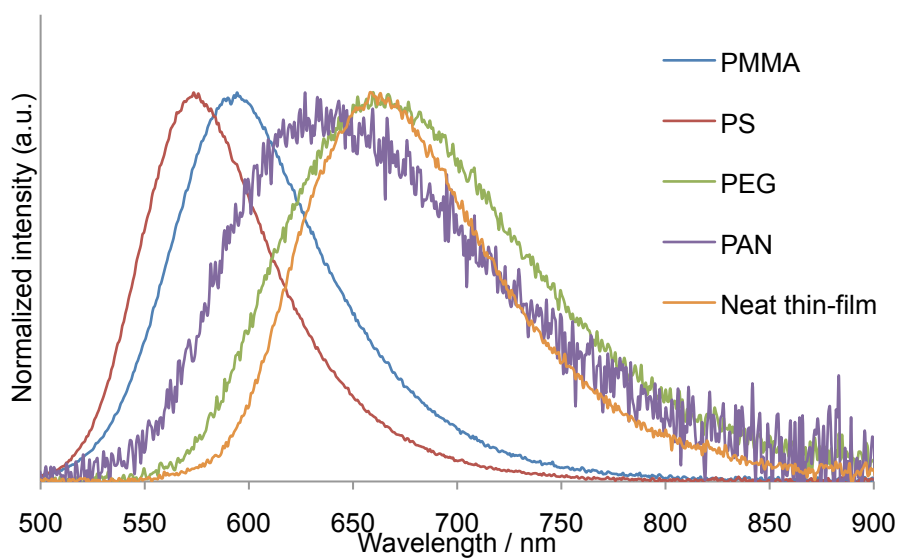


Figure S20. Fluorescence spectra of 5b in the solid states ($\lambda_{\text{ex}} = 430$ nm).

Photophysical Properties of Fluorenes 9–11 in Various Solvents (Spectra measured in benzene are omitted for clarity.)

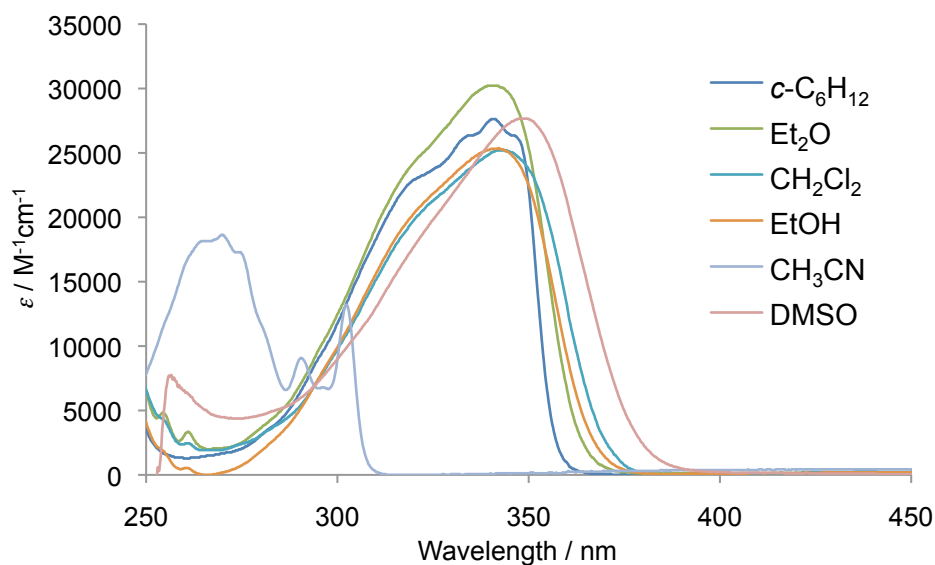


Figure S21. UV absorption spectra of 9 in various solvents.

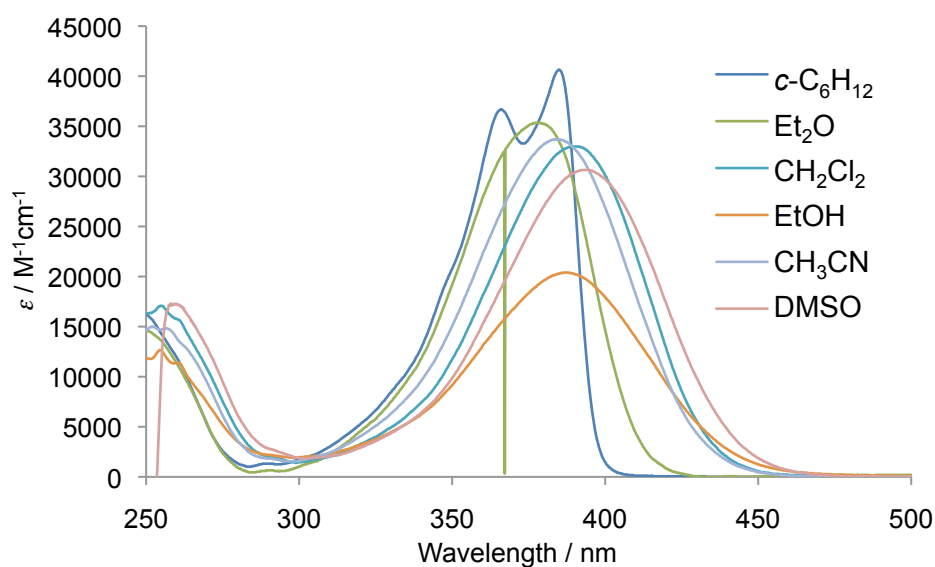


Figure S22. UV absorption spectra of 10 in various solvents.

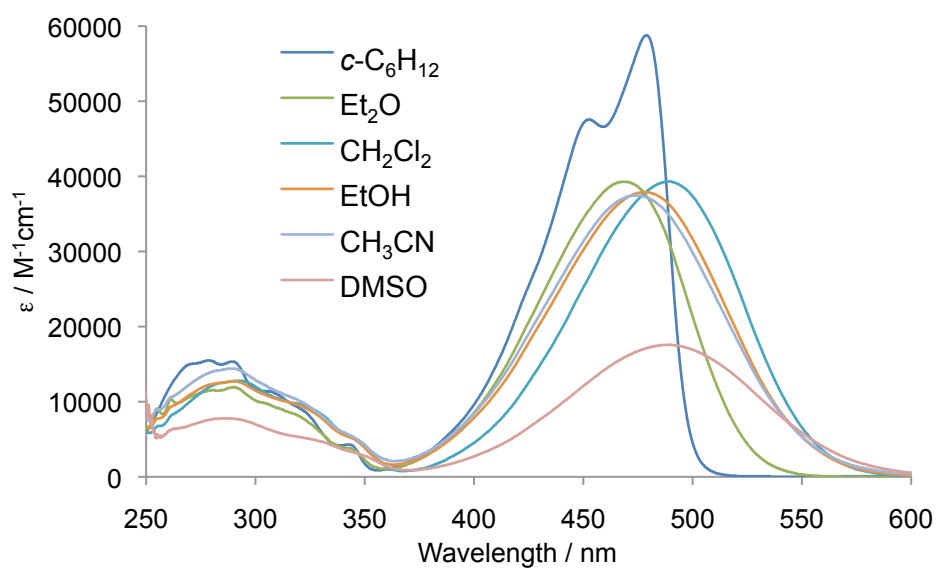


Figure S23. UV absorption spectra of 11 in various solvents.

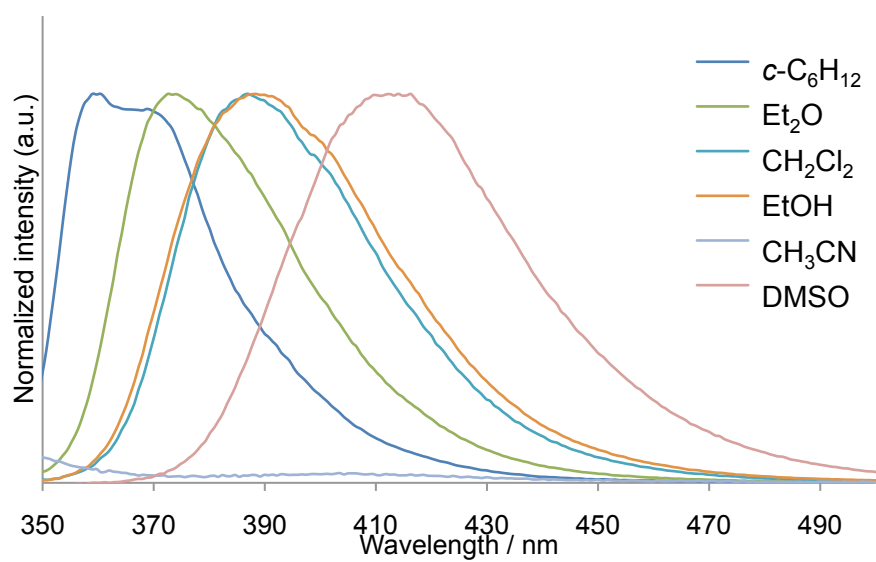


Figure S24. Fluorescence spectra of 9 in various solvents ($\lambda_{\text{ex}} = 300 \text{ nm}$).

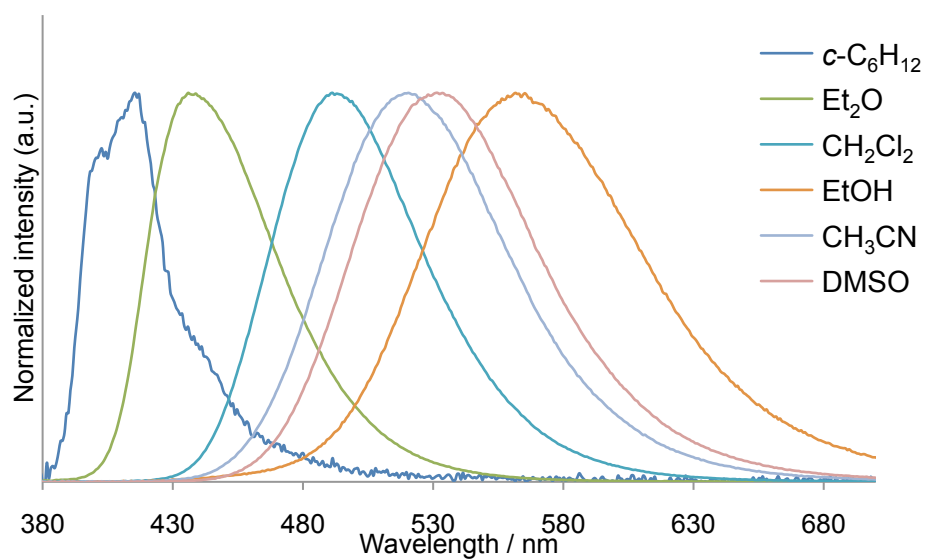


Figure S25. Fluorescence spectra of 10 in various solvents ($\lambda_{\text{ex}} = 360 \text{ nm}$).

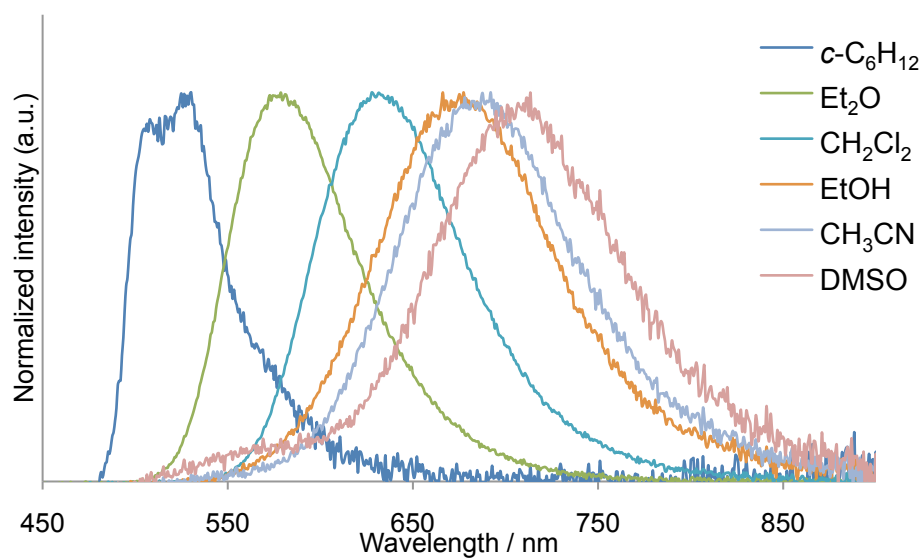


Figure S26. Fluorescence spectra of 11 in various solvents ($\lambda_{\text{ex}} = 430 \text{ nm}$).