Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information

A Phthalocyanine-Subphthalocyanine Heterodinuclear Dimer: Comparison of Spectroscopic Properties with Those of Homodinuclear Dimer of Constituting Units

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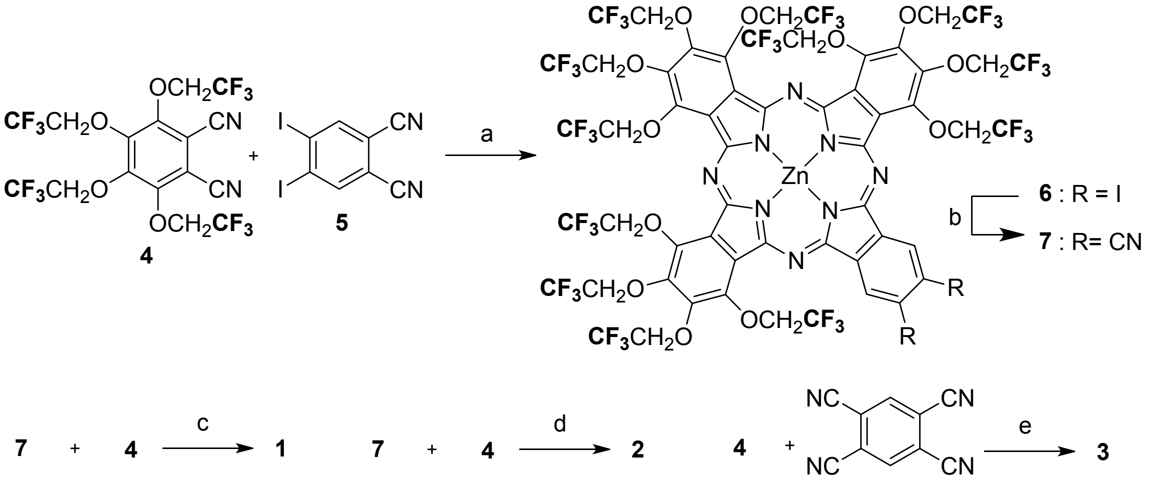
Supplemental methods

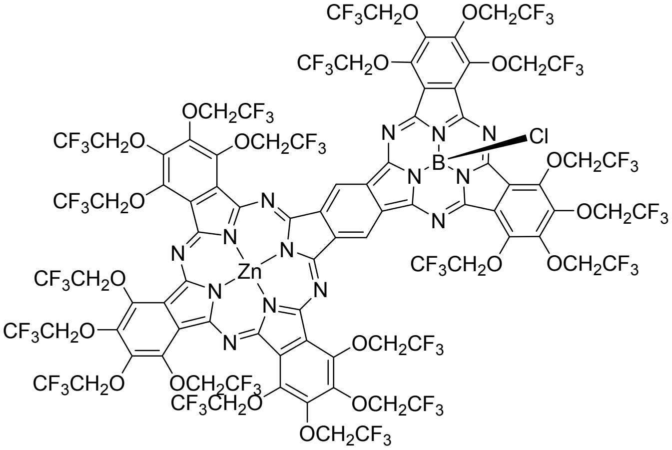
General information.

All reactions were performed in oven-dried under positive of nitrogen. Solvents were transferred *via* syringe and were introduced into the reaction vessels though a rubber septum. All of the reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and 7% phosphomolybdic acid or $KMnO_4$ or *p*-anisaldehyde in ethanol/heat. Column chromatography was carried out on a column packed with silica gel (60N spherical neutral size 63-210 μm). The ^{1}H NMR (600 or 300 MHz), ^{19}F NMR (188 MHz), and spectra for solution in $CDCl_3$ or acetone-d_6 were recorded on a Varian Bruker 600 or Varian Mercury 300, chemical shifts (δ) are expressed in ppm downfield from internal TMS or acetone-d_6. UV-vis spectra were recorded with a JASCO V-530 spectrometer. IR spectra were recorded on a JASCO FT/IR-200 spectrometer. Fluorescence spectroscopy was recorded with JASCO FP-6200 Fluorospectrometer. MALDI-TOF mass spectra were taken on a SHIMADZU Axima CFR Plus.



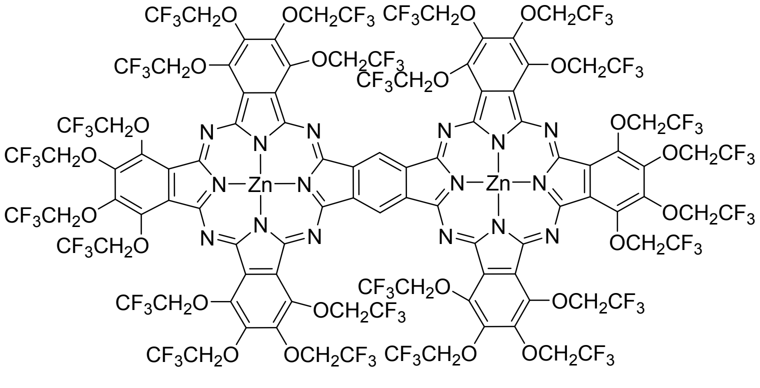
Scheme S1. a) $ZnCl_2$, *N,N*–dimethylaminoethanol, 110 °C, 4 h, 62%; b) $Zn(CN)_2$, $Pd(PPh_3)_4$, pyridine, DMF, 120 °C, 79%; c) BCl_3, *p*-xylene, 130°C, 3 h, 18%; d) $ZnCl_2$, *N,N*–dimethylaminoethanol, 120 °C, 4 h, 6%; e) BCl_3, *p*-xylene, 140 °C, 4 h, 0.72%

ZnPc-SubPc fused hetero-dimer 1



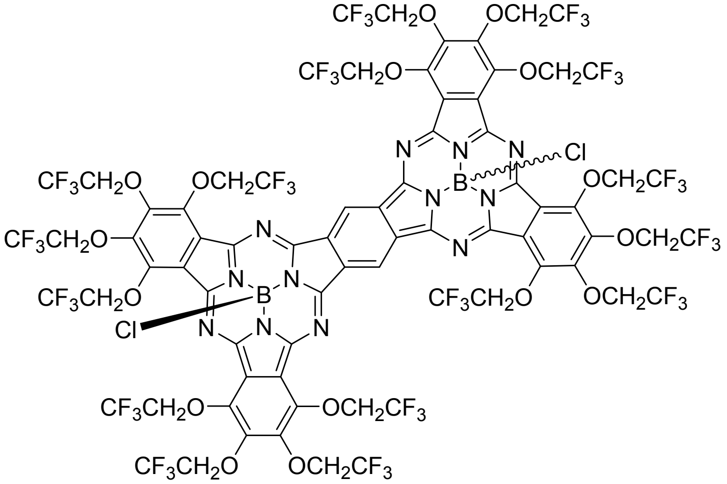
BCl_3 (2.0 mL, 1M solution in *p*-xylene) was added to a mixture of compound 23,24-dicyano-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (15 mg, 0.00831mmol) and 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (43.3 mg, 0.0831 mmol) under an argon atmosphere. The reaction mixture was heated at 130 ºC for 3 h. The reaction solution was then flushed with argon and the solvent was evaporated. The resulting solid was purified by flash silica gel column chromatography (ethyl acetate : hexane = 30 : 70) to give product as a blue solid (4.3 mg, 18 %).; ^1H NMR ($CDCl_3$) δ 4.6-5.0 (brm, 18H), 5.3-5.8 (brm, 18H), 6.0-6.1(brm, 4H), 10.8 (s, 2H); ^{19}F NMR ($CDCl_3$) δ-75.3 (brm, 6F), -74.7 (brm, 24F), -73.9 (brm, 30F); IR (KBr): 3857, 3736, 3446, 2974, 2881, 1696, 1457, 1279, 1164, 1069, 972, 666 cm^{-1}; UV-visible: (dioxane) [λ_{max} nm (log ε)] 360 (4.82), 663 (4.40), 718 (4.89), 738 (4.84), 801 (5.27); Fluorescence (dioxane): λ_{em} = 722, 810 nm Φ_F= 0.095; MALDITOF MS (dithranol) m/z = 2887.2-2893.2 (isotopic pattern)

ZnPc-ZnPc fused homo-dimer 2



A mixture of 23,24-dicyano-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (20 mg, 0.011 mmol), 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (52 mg, 0.10 mmol), Zinc(II) chloride (7.6 mg, 0.055 mmol) in *N*,*N*-dimethylaminoethanol (1 ml) was heated at 120 ºC for 3 h. After cooling to room temperature, the reaction mixture was diluted with water. The precipitate was collected by filtration and washed with water. The resulting solid was purified by flash silica gel column chromatography (ethyl acetate : hexane = 60 : 40) to give product as a green solid (2.3 mg, 6 %);^{1}H NMR (acetone-*d$_6$*) δ 5.1-5.4 (brm, 22H), 5.7-5.9 (brm, 18H), 6.0-6.1 (brm, 8H), 11.4 (s, 2H); ^{19}F NMR (acetone-*d$_6$*) δ -74.1(brm, 12F), -73.7 (brm, 12F), -73.2 (brm, 48F); IR (KBr): 3853, 3736, 2974, 2881, 1717, 1595, 1486, 1455, 1438, 1273, 1144, 1073, 970, 823, 662 cm^{-1}; UV-visible: (dioxane) [λ_{max} nm (log ε)] 368 (5.06), 745 (4.96), 802 (4.67), 853 (5.36); Fluorescence (dioxane): λ_{em} = 722 nm Φ_F = 0.054; MALDITOF MS (dithranol) m/z = 3428.9-3432.9 (isotopic pattern)

SubPc-SubPc fused homo-dimer 3

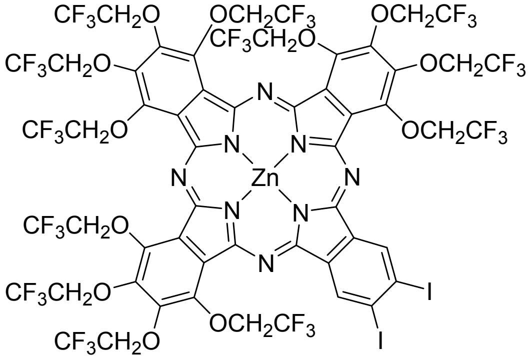


BCl$_3$ (4.08 mL, 1 M solution in *p*-xylene) was added to a mixture of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (2.0 g, 3.8 mmol) and 1,2,4,5-tetracyanobenzene (116 mg, 0.48 mmol) under an argon atmosphere. The reaction mixture was heated at 140 ºC for 4 h. The reaction solution was then flushed with argon and the solvent was evaporated. The resulting solid was purified twice by flash silica-gel column chromatography (ethyl acetate : hexane = 80 : 20, then, ethyl acetate: hexane = 90 : 10 to 88 : 12) to afford two isomers of SubPc-SubPc **3** (first fraction: 3.6 mg, 0.24%; second fraction: 7.3 mg, 0.48%).

3 (First fraction); ^{1}H NMR (acetone-*d$_6$*) δ 4.7-5.0 (brm, 16H), 5.5-5.7 (brm, 12H), 6.1-6.2 (brm, 4H), 10.3 (s, 2H); ^{19}F NMR (acetone-*d$_6$*) δ -73.6 (brm, 18F), -74.2 (brm, 30F); IR (KBr): 3445, 2965, 2929, 1607, 1457, 1433, 1282, 1165, 1132, 1072, 967, 832, 699, 665, 548 cm^{-1}; UV-visible: (dioxane) [λ_{max} nm (log ε)] 333 (4.70), 463 (4.63), 628 (4.69), 673 (4.56), 730 (4.98); Fluorescence (dioxane): λ_{em} = 623, 743 nm Φ_F = 0.31; MALDITOF MS (dithranol) m/z = 2349.7-2350.7 (isotopic pattern)

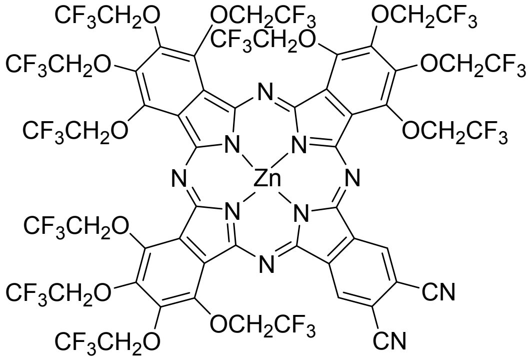
3 (Second fraction); ^{1}H NMR (acetone-*d$_6$*) δ 4.7-5.1 (brm, 16H), 5.5-5.8 (brm, 12H), 6.0-6.2 (brm, 4H), 10.3 (s, 2H); ^{19}F NMR (acetone-*d$_6$*) δ -73.6 (brm, 18F), -74.2 (brm, 30F); IR (KBr): 3435, 2925, 2854, 1717, 1490, 1458, 1435, 1282, 1164, 1071, 966, 793, 696 cm^{-1}; UV-visible: (dioxane) [λ_{max} nm (log ε)] 332 (4.62), 461 (3.93), 628 (4.57), 668 (4.48), 724 (4.91); Fluorescence (dioxane): λ_{em} = 623, 739 nm Φ_F = 0.28; MALDITOF MS (dithranol) m/z = 2349.6-2351.5 (isotopic pattern)

23,24-Diiodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (6)



A mixture of 3,4,5,6-tetrakis(2,2,2-trifluoroethoxy)phthalonitrile (3.0 g, 5.8 mmol), 4,5-diiodophthalonitrile (200 mg, 0.5 mmol) and zinc(II) chloride (359 mg, 2.6 mmol) in *N*,*N*-dimethylaminoethanol(9 ml) was heated at 110 ºC for 3 h. After cooling to room temperature, the reaction mixture was diluted with water. The precipitate was collected by filtration and washed with water. The resulting crude product was purified by flash silica gel column chromatography (ethyl acetate : hexane = 30 : 70) to give product as a green solid (649.3 mg, 62 %);^{1}H NMR (acetone-d_6) δ 5.1-5.3 (brm, 12H), 5.6-5.7 (brm, 4H), 5.8-5.9 (brm, 8H), 9.4 (s, 2H); ^{19}F NMR (acetone-d_6) δ -74.1(brm, 6F), -73.6(brm, 6F), -73.0 (brm, 24F); IR (KBr): 3853, 3735, 3445, 2970, 2881, 1699, 1654, 1558, 1541, 1507, 1489, 1457, 1275, 1163, 1068 cm^{-1}; MALDITOF MS (dithranol) m/z = 2004.8-2009.8 (isotopic pattern)

23,24-Dicyano-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (7)



A mixture of compound 23,24-diiodo-1,2,3,4,8,9,10,11,15,16,17,18-dodecakis(2,2,2-trifluoroethoxy)phthalocyaninate zinc(II) (328 mg, 0.16 mmol), tetrakis(triphenylphosphine)palladium(II) (18.9 mg, 0.016 mmol), Zinc(II) cyanide (46.1 mg, 0.39 mmol) and pyridine (13.2 µl, 0.16 mmol) in *N*,*N*-dimethylformamide (3 ml) was heated at 120 ºC for 48 h. After cooling to room temperature, the reaction mixture was diluted with 10 wt% NH_3 aqueous solution. The precipitate was collected by filtration and washed with water. The resulting crude product was purified by flash silica gel column chromatography (ethyl acetate : hexane = 40 : 60) to give product as a green solid (121.6 mg, 41 %); ^{1}H NMR (acetone-d_6) δ5.1-5.3 (brm, 12H), 5.5-5.7 (m, 4H), 5.8-6.0 (brm, 8H), 8.5 (s, 2H); ^{19}F NMR (acetone-d_6) δ -74.1(brm, 6F), -73.7 (brm, 6F), -73.1 (brm, 24F); IR (KBr): 3853, 3735, 3445, 2970, 2881, 1699, 1654, 1558, 1541, 1507, 1489, 1457, 1275, 1163, 1068 cm^{-1}; MALDITOF MS (dithranol) m/z = 1801.2-1806.2 (isotopic pattern)

Supplemental Figures

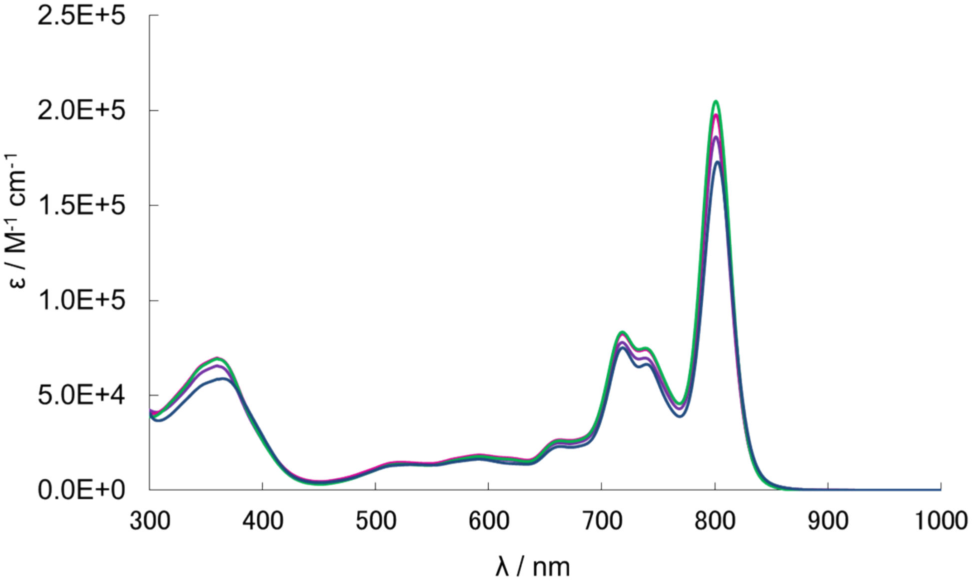


Figure S1. UV-visible spectra of 1 in dioxane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

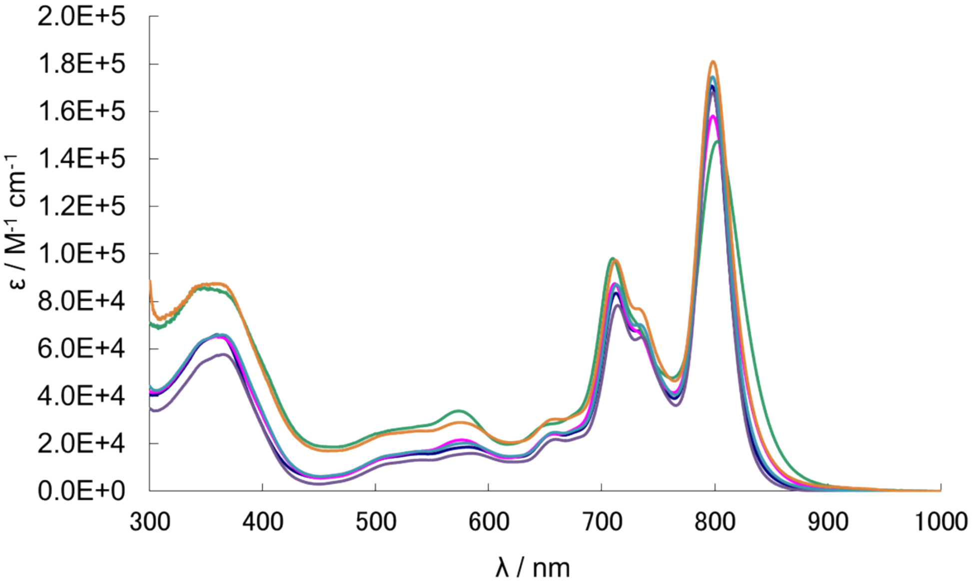


Figure S2. UV-visible spectra of 1 in trifluorotoluene: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple), 1x10^{-5} M with 1 vol% pyridine (sky blue), 1x10^{-6} M with 1 vol% pyridine (orange).

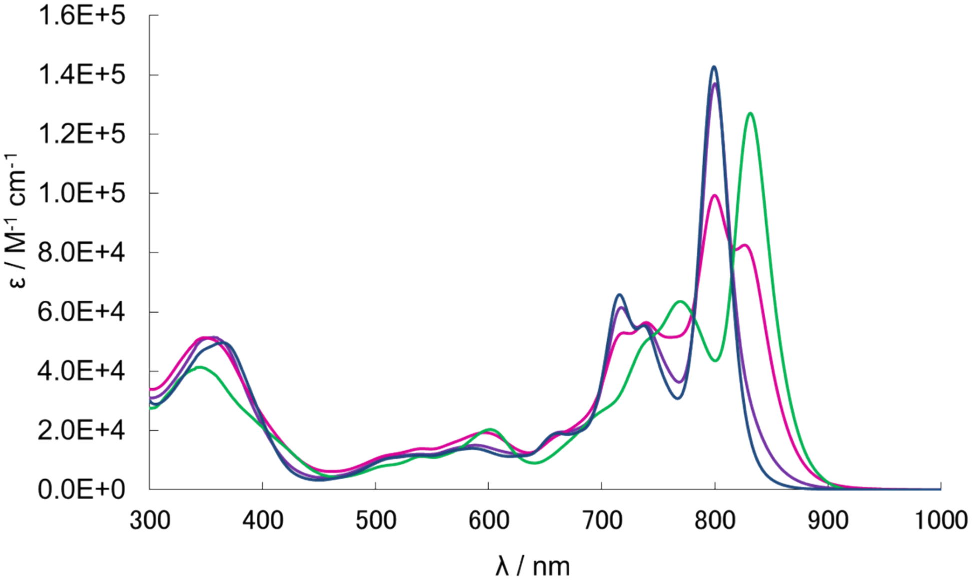


Figure S3. UV-visible spectra of 1 in dichloromethane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

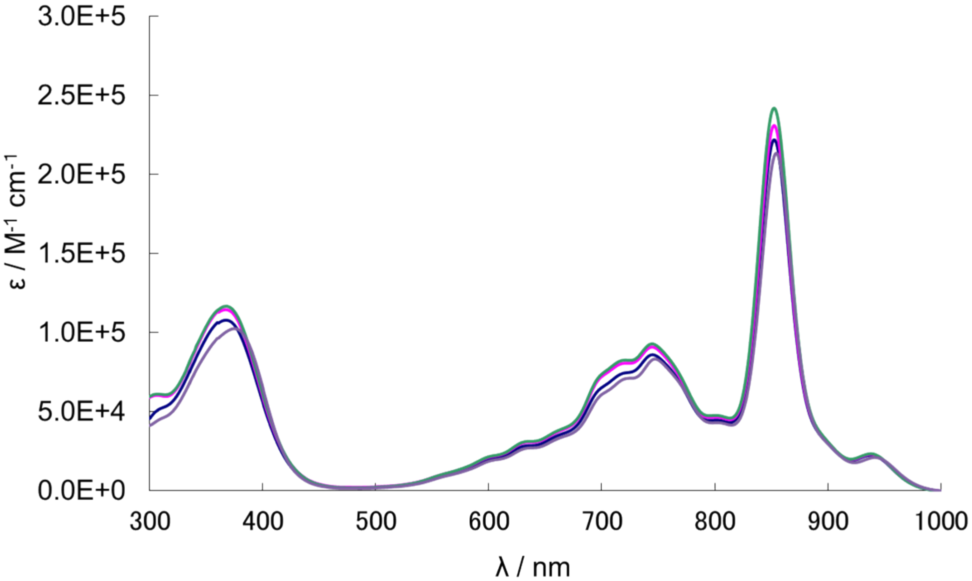


Figure S4. UV-Visible spectra of 2 in dioxane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

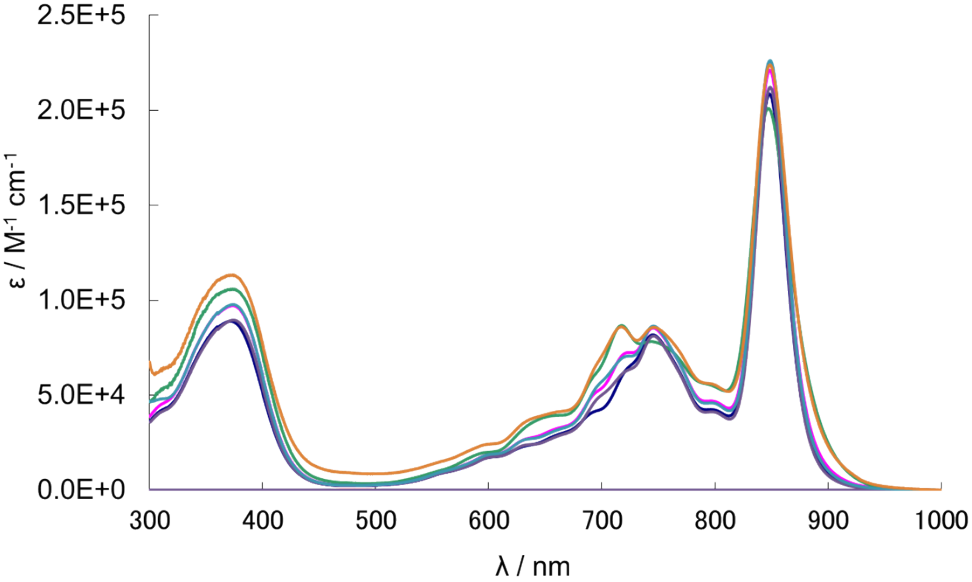


Figure S5. UV-Visible spectra of 2 in trifluorotoluene: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple), 1x10^{-5} M with 1 vol% pyridine (sky blue), 1x10^{-6} M with 1 vol% pyridine (orange).

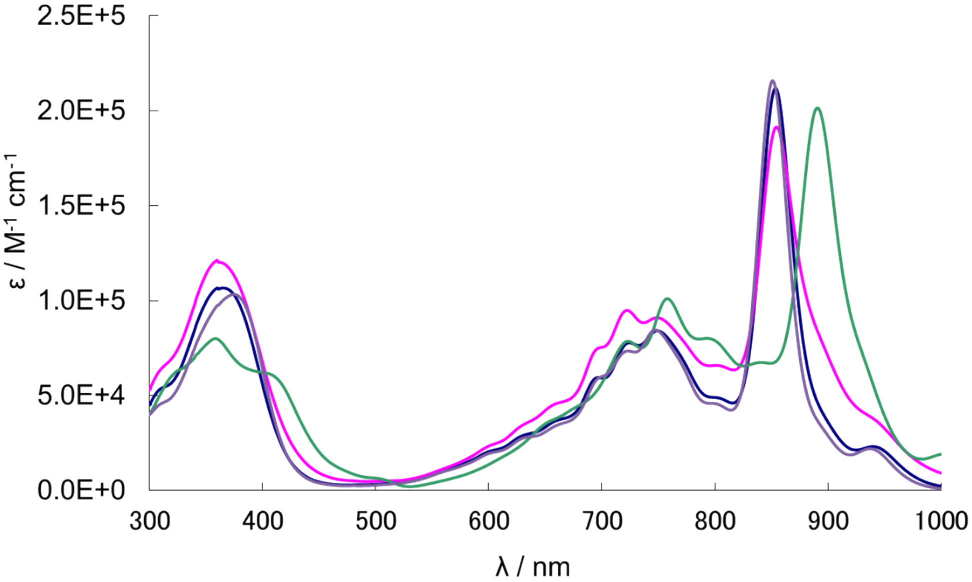


Figure S6. UV-Visible spectra of 2 in dichloromethane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

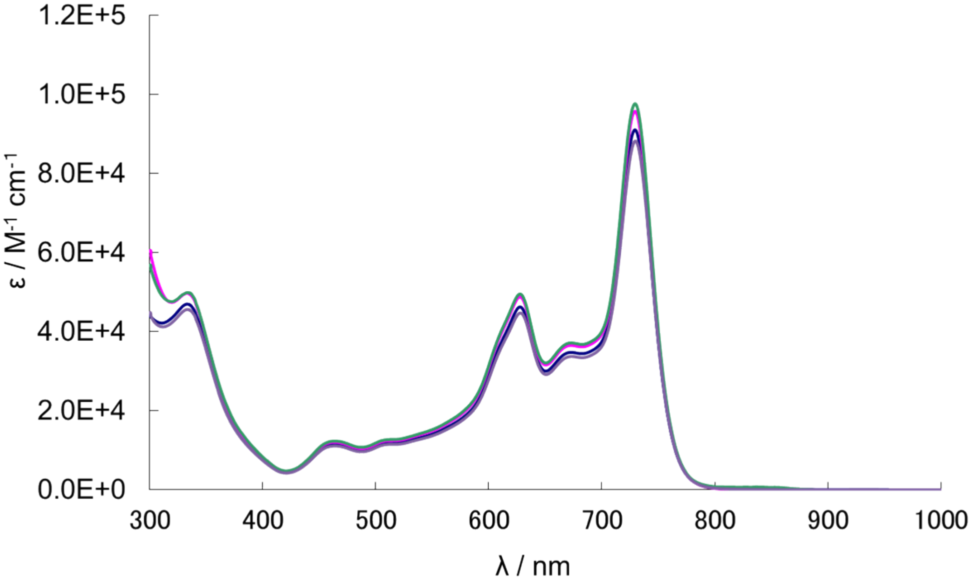


Figure S7. UV-Visible spectra of 3 (first fraction) in dioxane: $1\text{x}10^{-4}$ M (blue), $1\text{x}10^{-5}$ M (pink), $1\text{x}10^{-6}$ M (green), $1\text{x}10^{-4}$ M with 1 vol% pyridine (purple).

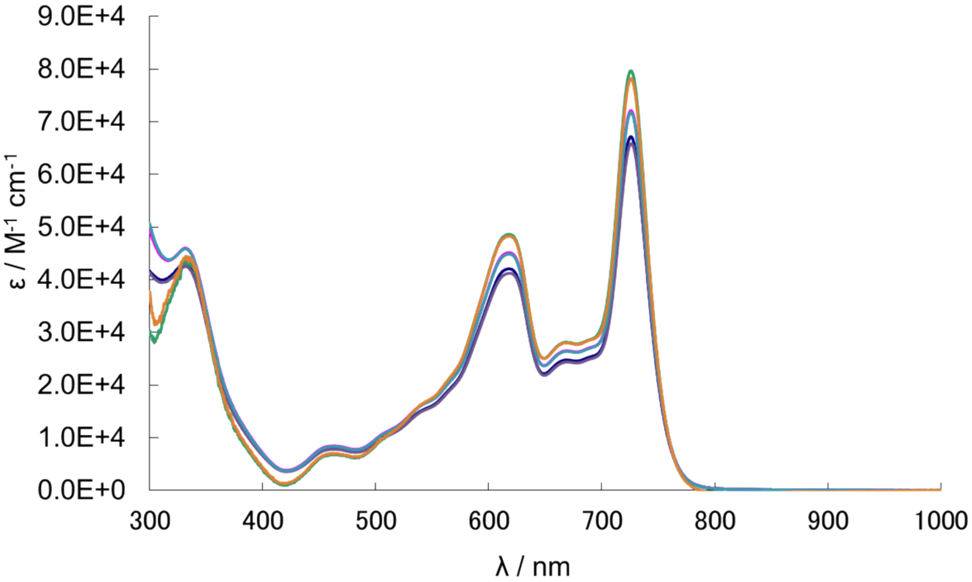


Figure S8. UV-Visible spectra of 3 (first fraction) in trifluorotoluene: $1\text{x}10^{-4}$ M (blue), $1\text{x}10^{-5}$ M (pink), $1\text{x}10^{-6}$ M (green), $1\text{x}10^{-4}$ M with 1 vol% pyridine (purple), $1\text{x}10^{-5}$ M with 1 vol% pyridine (sky blue), $1\text{x}10^{-6}$ M with 1 vol% pyridine (orange).

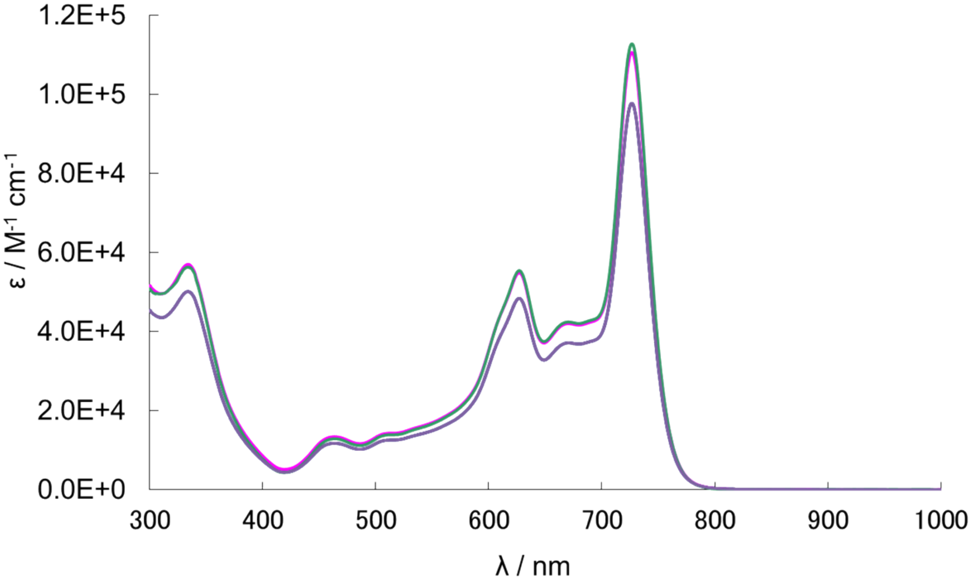


Figure S9. UV-Visible spectra of 3 (first fraction) in dichloromethane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

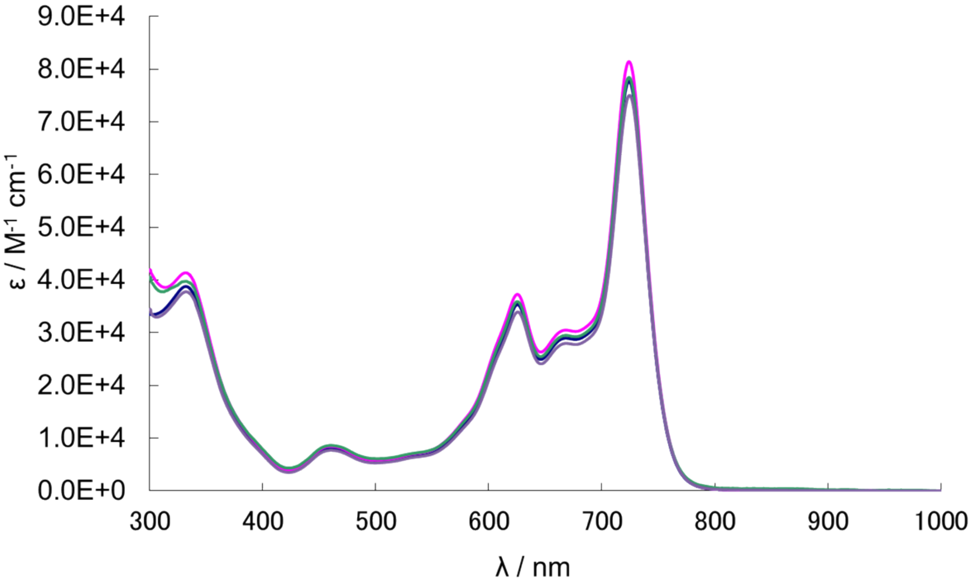


Figure S10. UV-Visible spectra of 3 (second fraction) in dioxane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

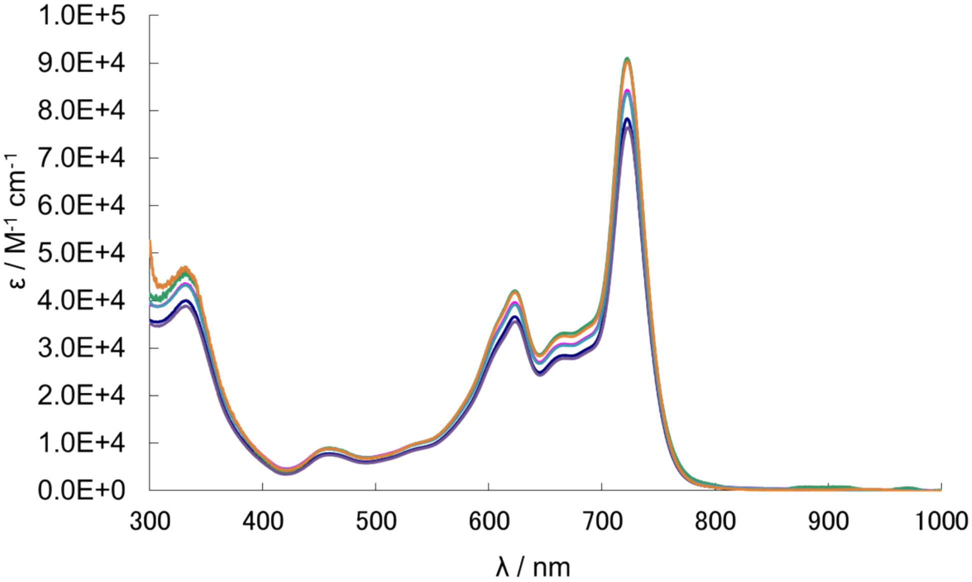


Figure S11. UV-Visible spectra of 3 (second fraction) in trifluorotoluene: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple), 1x10^{-5} M with 1 vol% pyridine (sky blue), 1x10^{-6} M with 1 vol% pyridine (orange).

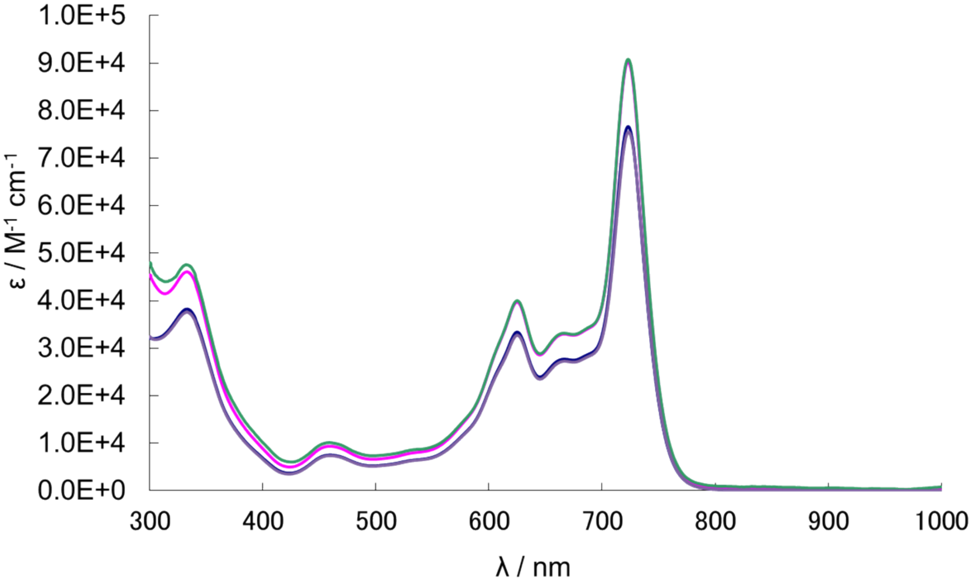


Figure S12. UV-Visible spectra of 3 (second fraction) in dichloromethane: 1x10^{-4} M (blue), 1x10^{-5} M (pink), 1x10^{-6} M (green), 1x10^{-4} M with 1 vol% pyridine (purple).

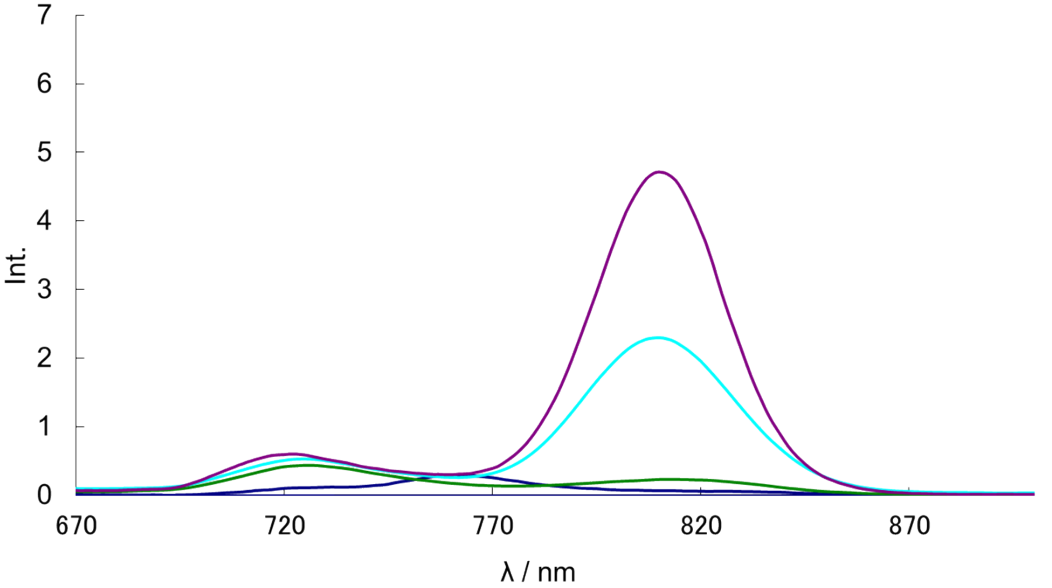


Figure S13. Fluorescence spectra of 1 excitation wavelength at 650 nm: dichloromethane (blue), trifluorotoluene (green), trifluorotoluene with 1 vol% pyridine (sky blue), dioxane (purple).

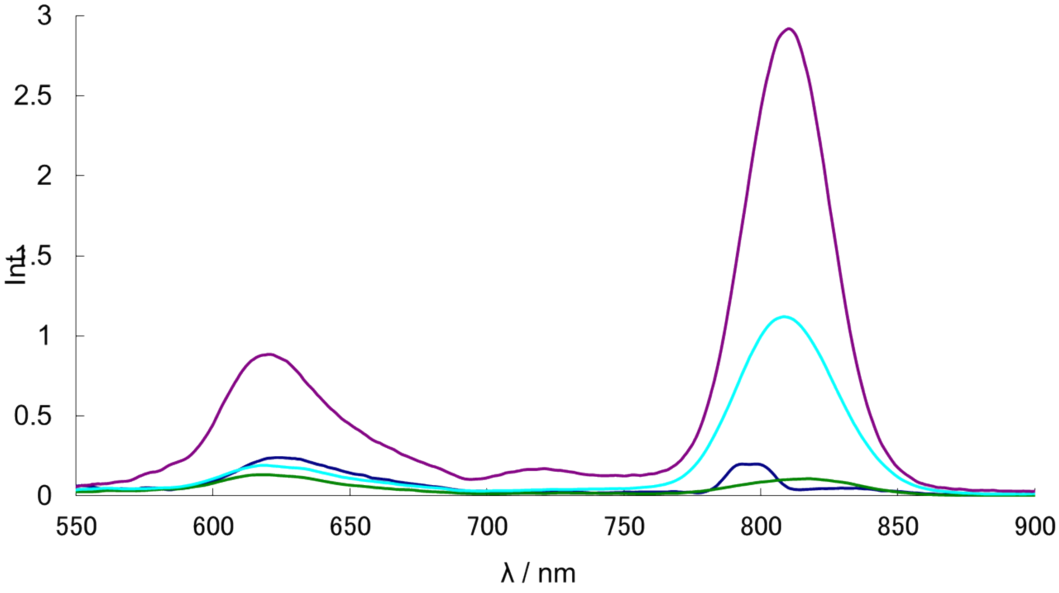


Figure S14. Fluorescence spectra of 1 excitation wavelength at 530 nm: dichloromethane (blue), trifluorotoluene (green), trifluorotoluene with 1 vol% pyridine (sky blue), dioxane (purple).

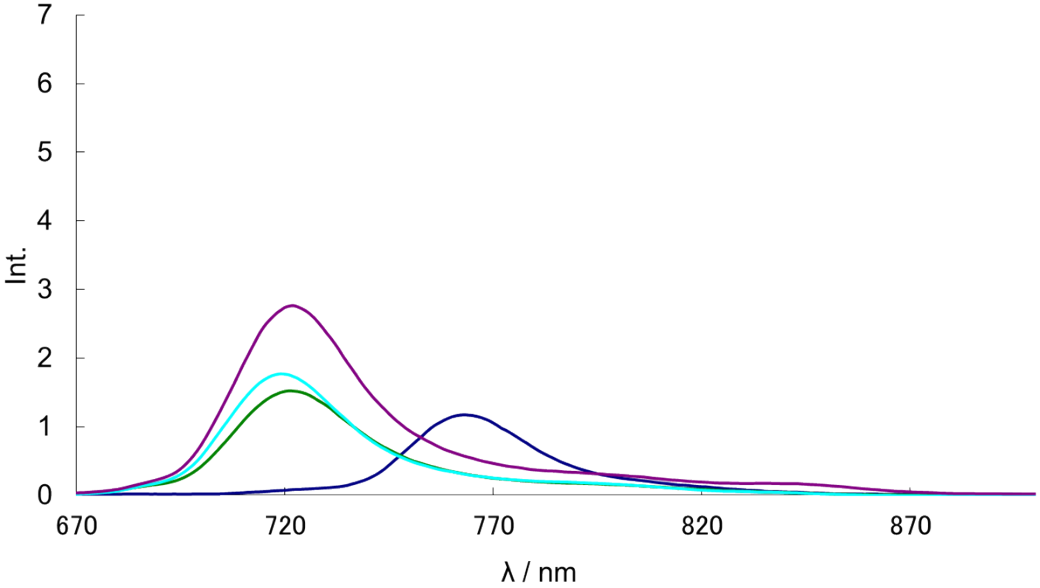


Figure S15. Fluorescence spectra of 2 excitation wavelength at 650 nm: dichloromethane (blue), trifluorotoluene (green), trifluorotoluene with 1 vol% pyridine (sky blue), dioxane (purple).

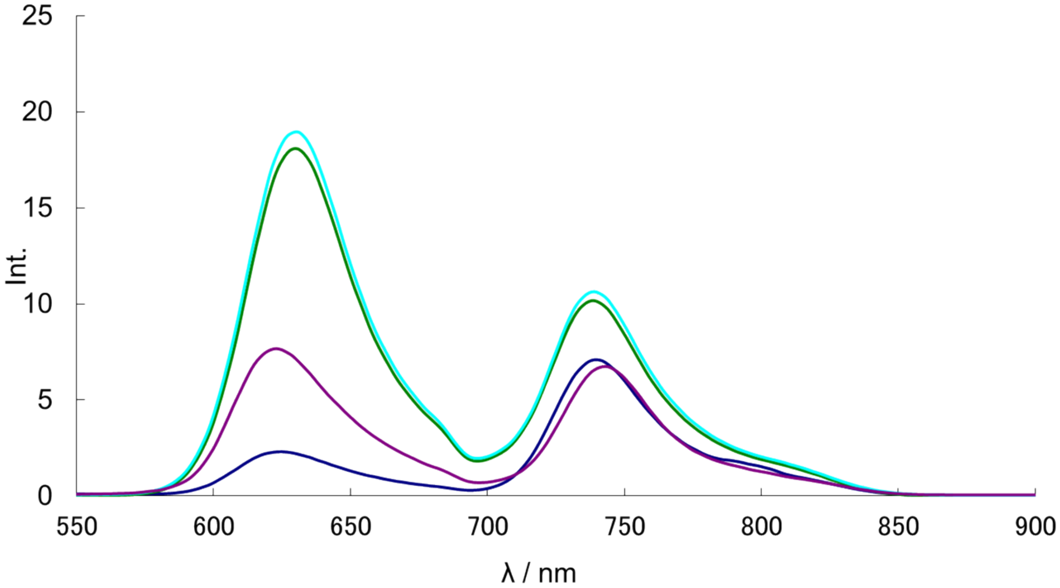


Figure S16. Fluorescence spectra of 3 (first fraction) with excitation wavelength at 530 nm: dichloromethane (blue), trifluorotoluene (green), trifluorotoluene with 1 vol% pyridine (sky blue), dioxane (purple).

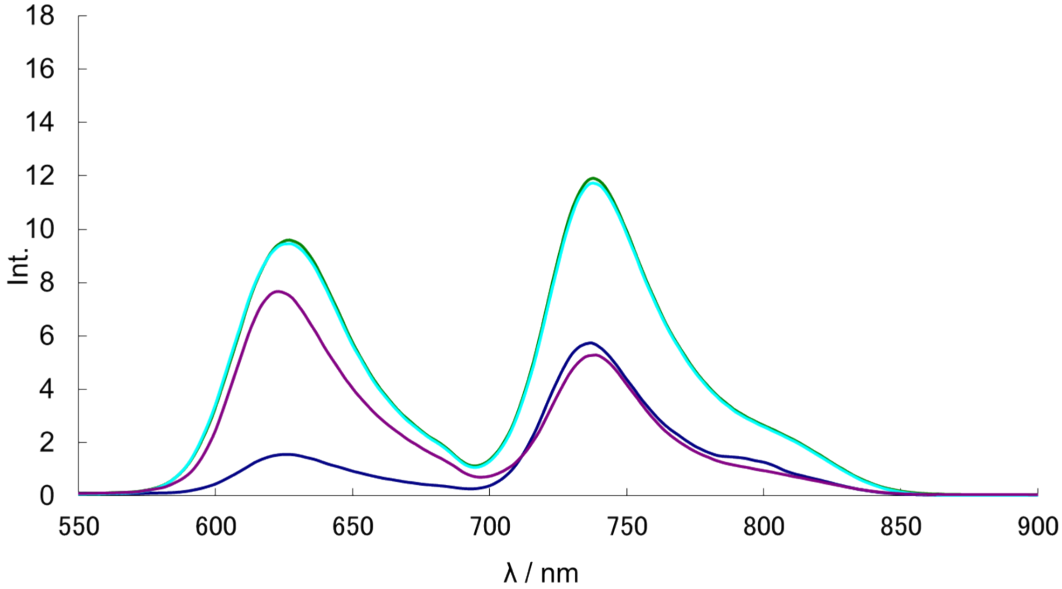
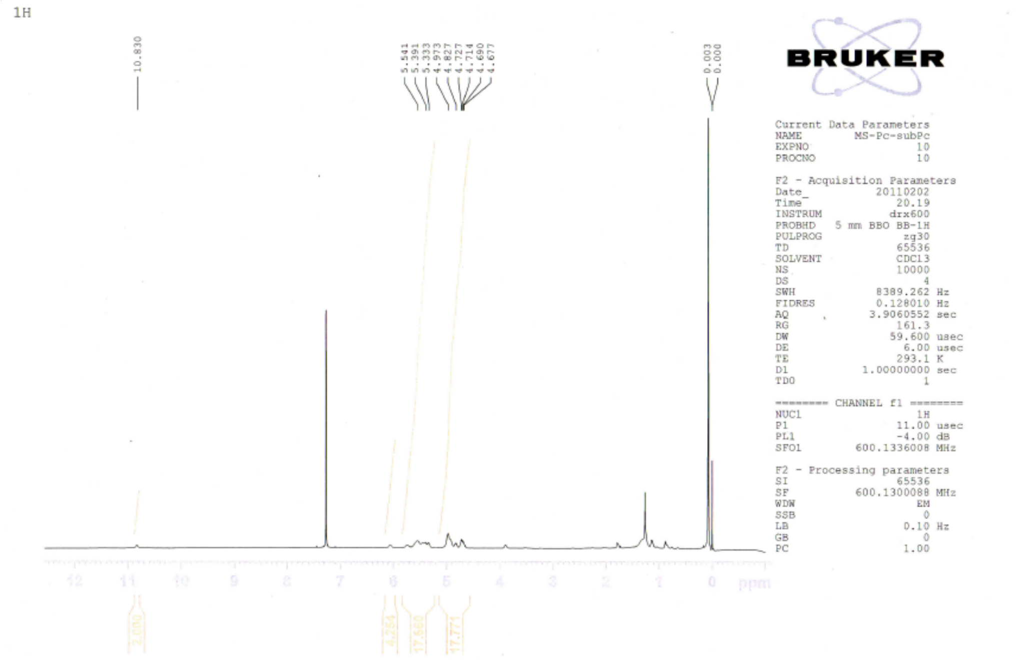


Figure S17. Fluorescence spectra of 3 (second fraction) with excitation wavelength at 530 nm: dichloromethane (blue), trifluorotoluene (green), trifluorotoluene with 1 vol% pyridine (sky blue), dioxane (purple).



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PROCNO                 10

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Figure S18. ^{1}H NMR of heterodimer 1 in $CDCl_3$

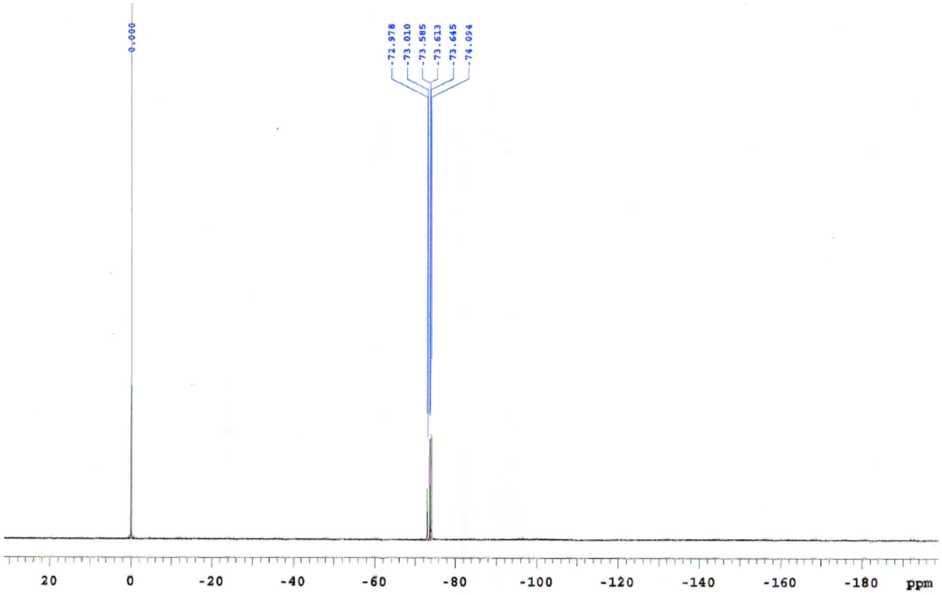

Figure S19. ^{19}F NMR of 1 in CDCl$_3$

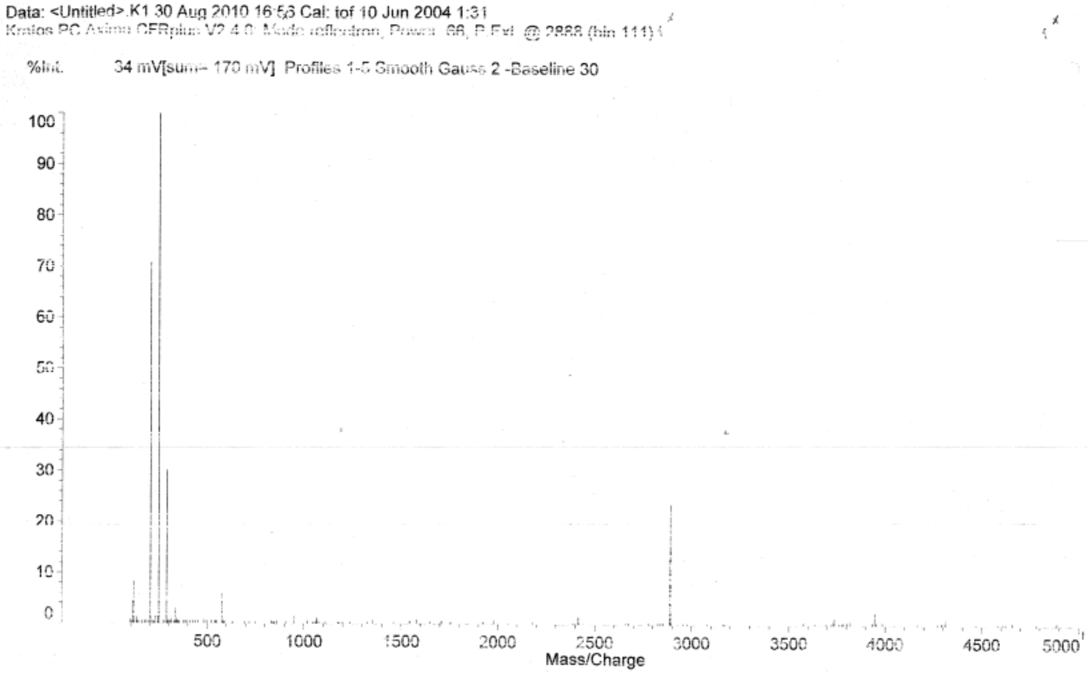

Figure S20. MALDI-TOF MS of 1

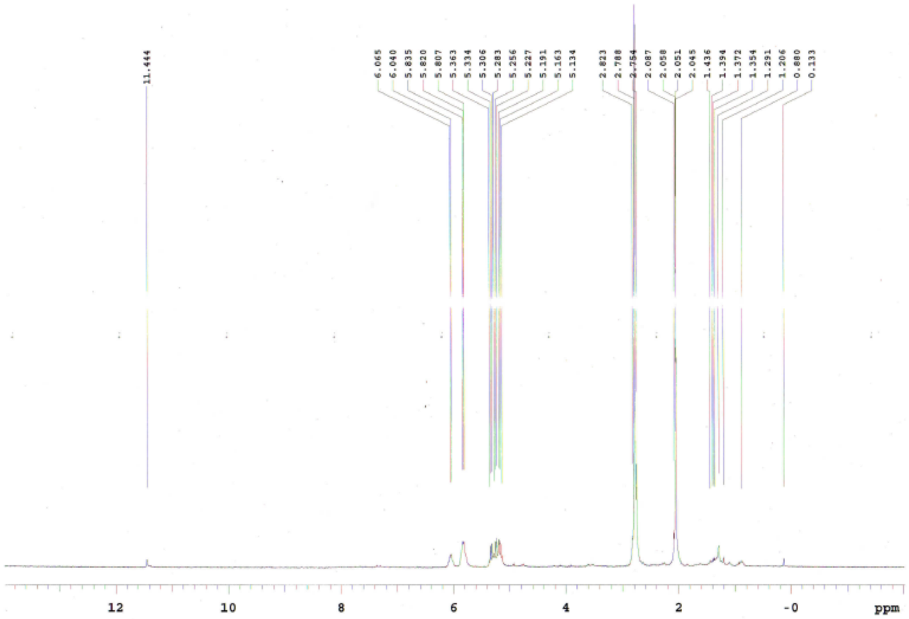

Figure S21. ^{1}H NMR of 2 in Acetone-d_6

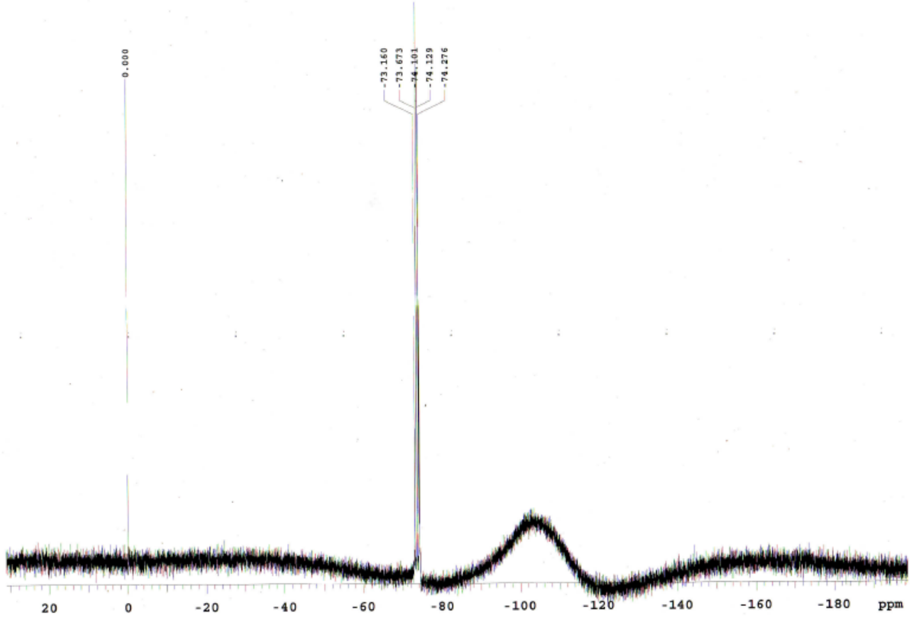

Figure S22. ^{19}F NMR of 2 in Acetone-d_6

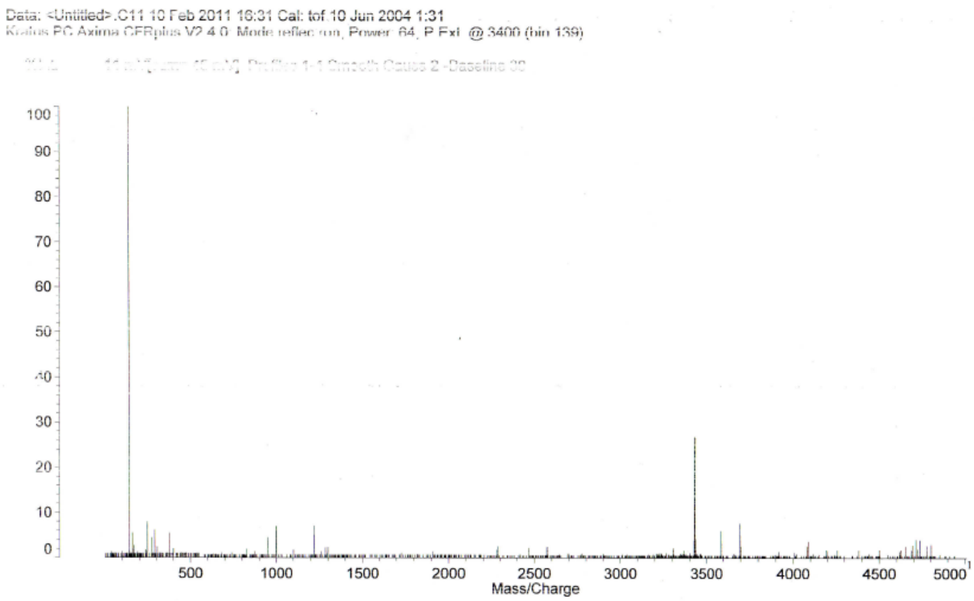

Figure S23. MALDI-TOF MS of 2

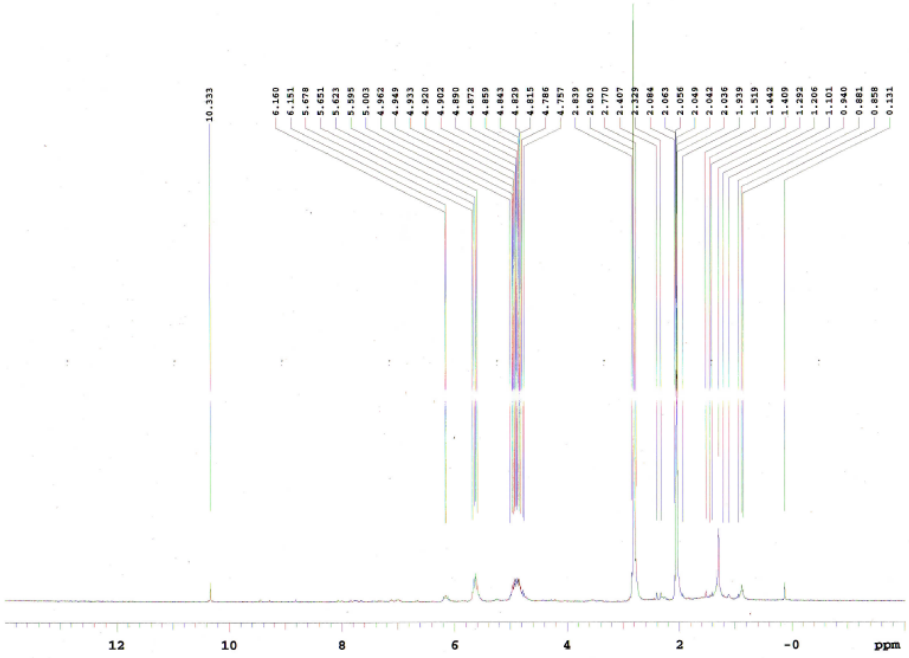

Figure S24. ^{1}H NMR of 3 (first fraction) in Acetone-d_6

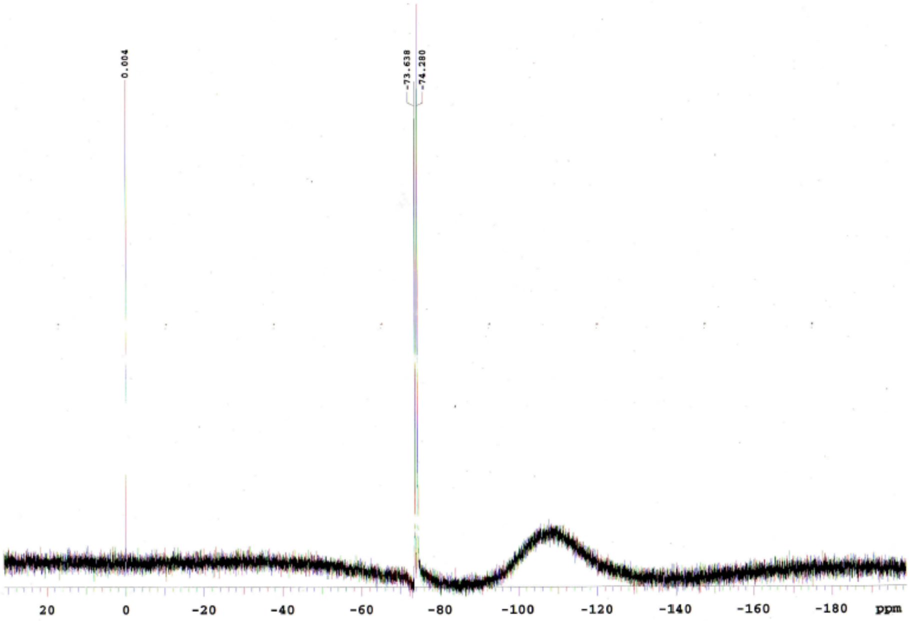

Figure S25. ^{19}F NMR of 3 (first fraction) in Acetone-d_6

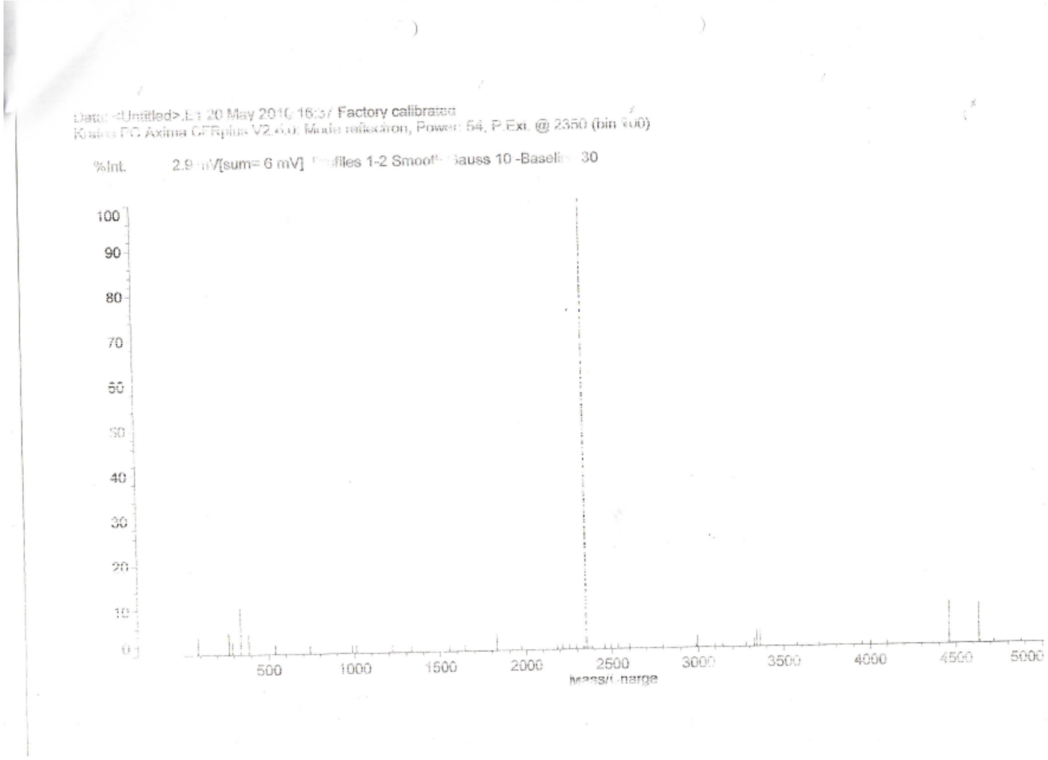

Figure S26. MALDI-TOF MS of 3 (first fraction)

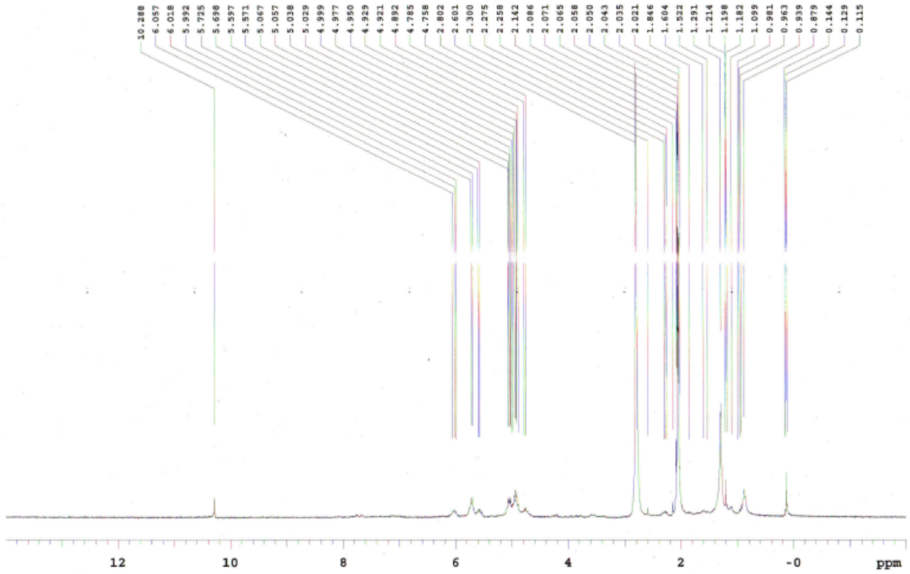

Figure S27. ^{1}H NMR of 3 (second fraction) in Acetone-d_6

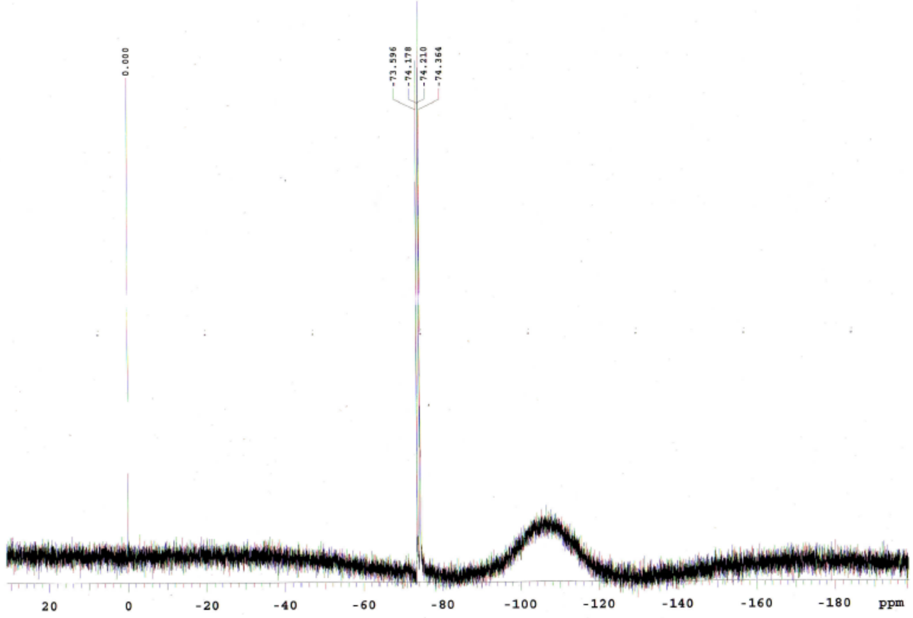

Figure S28. ^{19}F NMR of 3 (second fraction) in Acetone-d_6

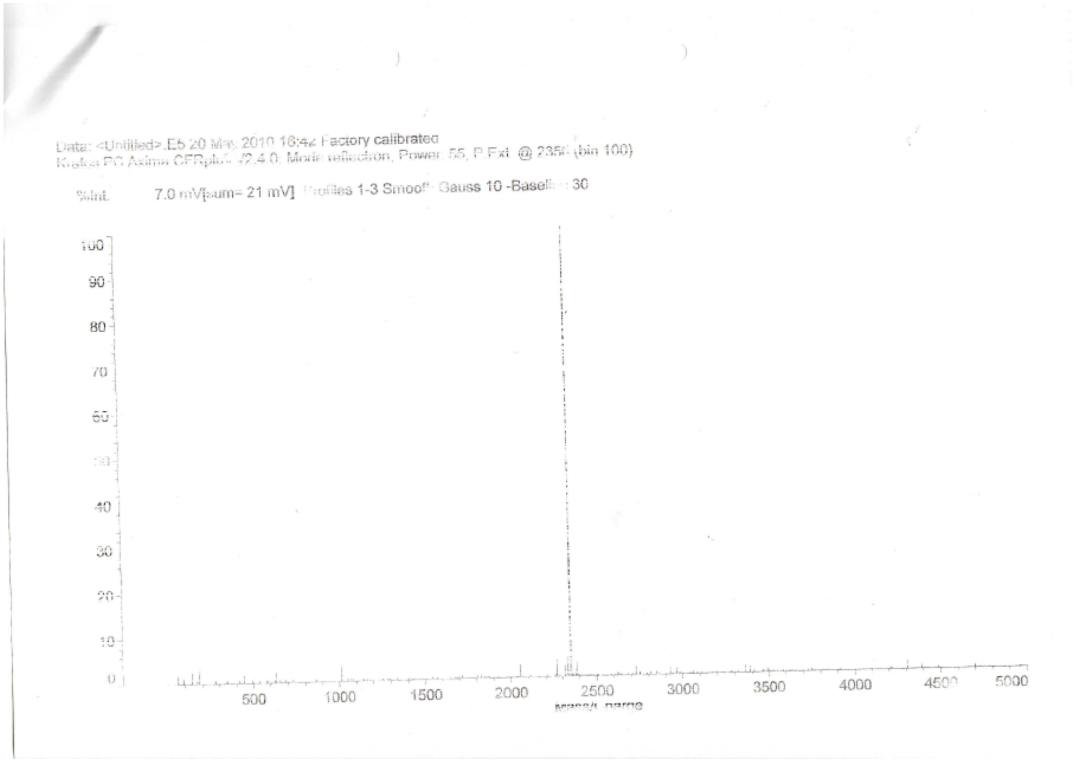

Figure S29. MALDI-TOF MS of 3 (second fraction)

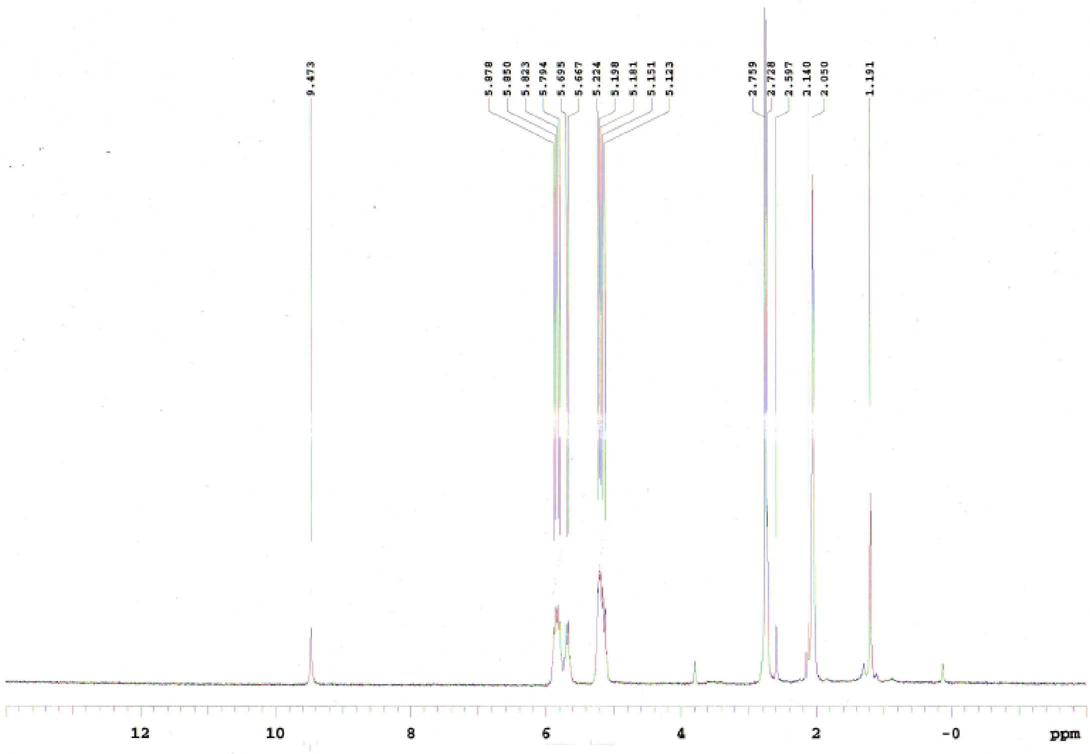

Figure S30. ^{1}H NMR of 6 in Acetone-d6

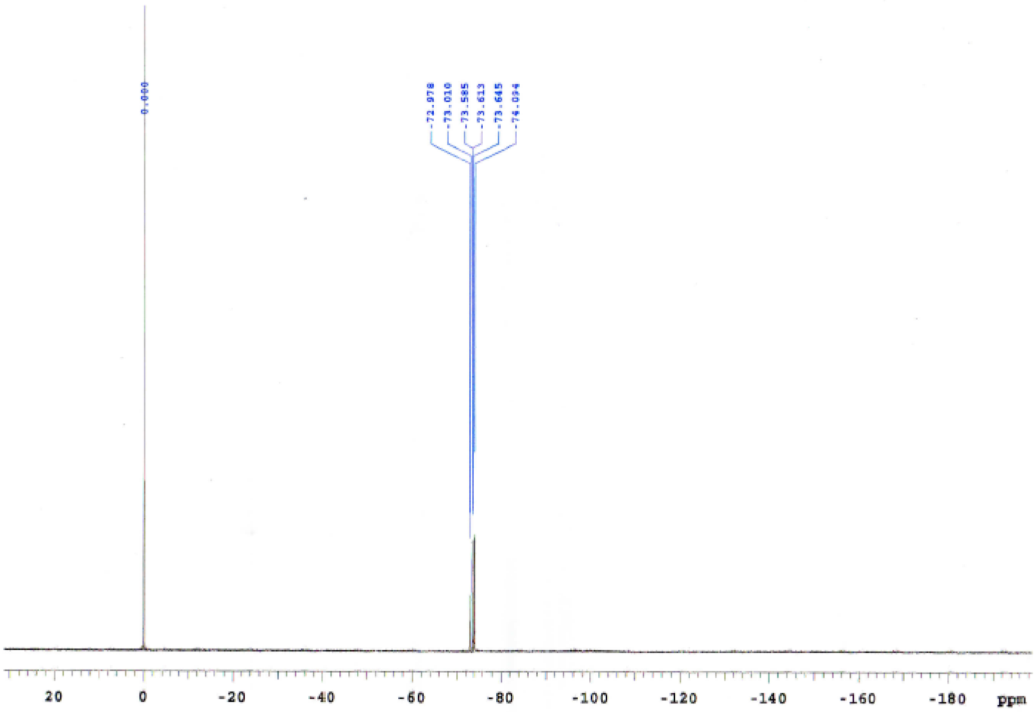

Figure S31. ^{19}F NMR of 6 in Acetone-d_6

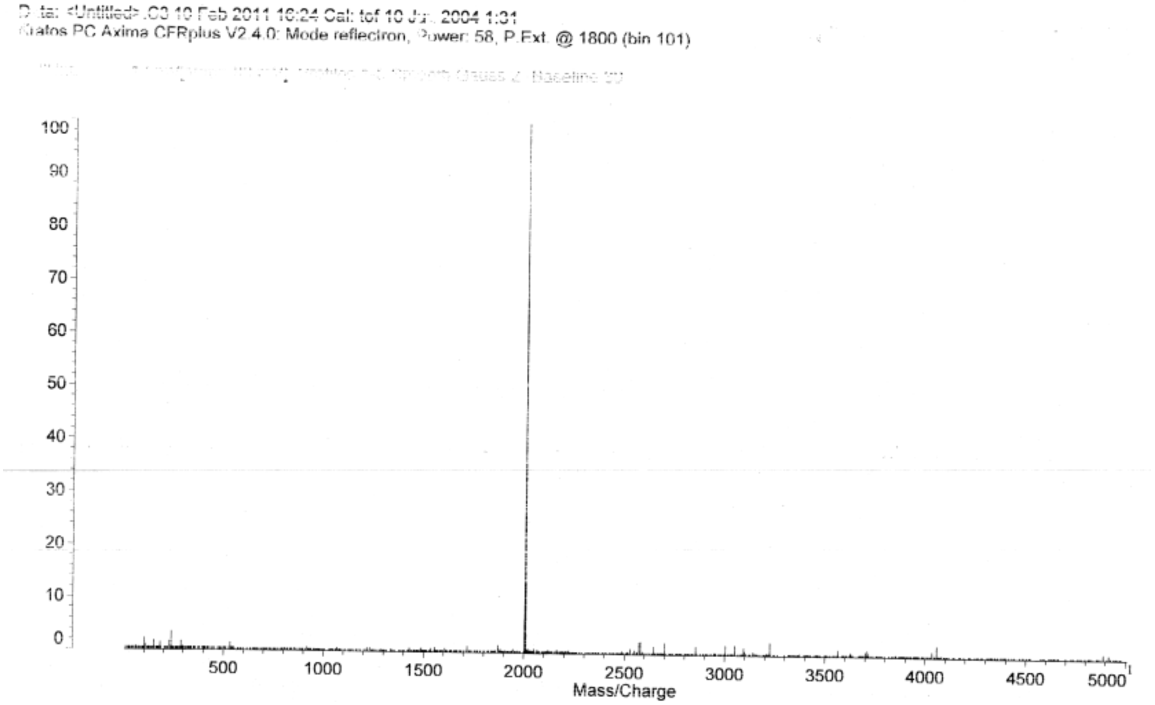
D ta: <Untitled> .C3 10 Feb 2011 16:24 Cal: tof 10 Ju . 2004 1:31
ratos PC Axima CFRplus V2.4.0: Mode reflectron, ower: 58, P.Ext. @ 1800 (bin 101)

Figure S32. MALDI-TOF MS of 6

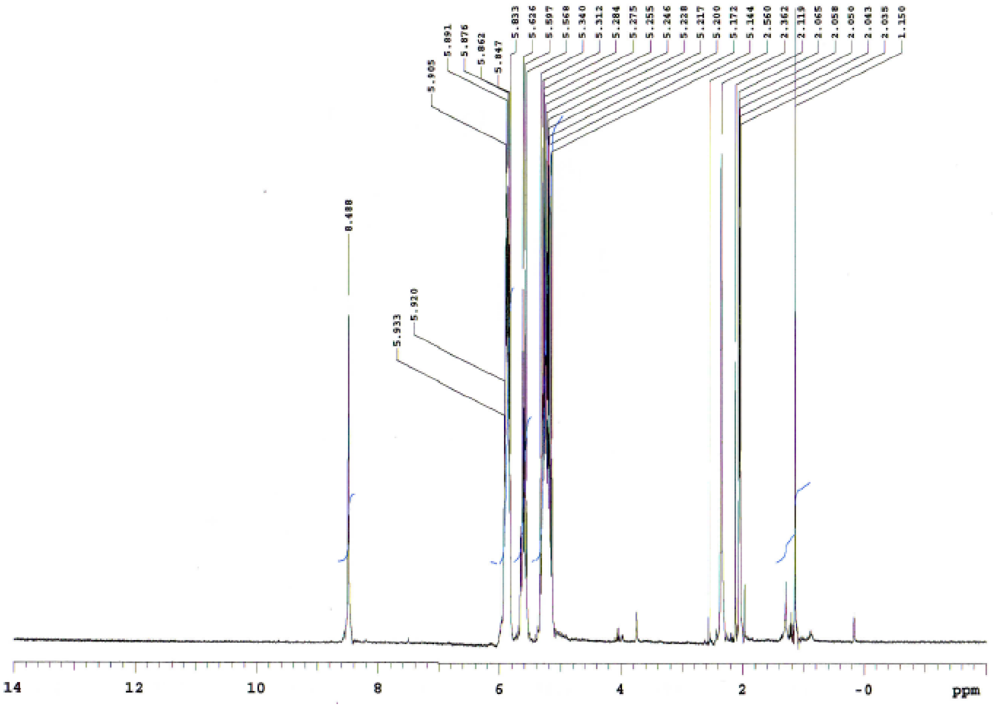

Figure S33. ^{1}H NMR of 7 in Acetone-d_6

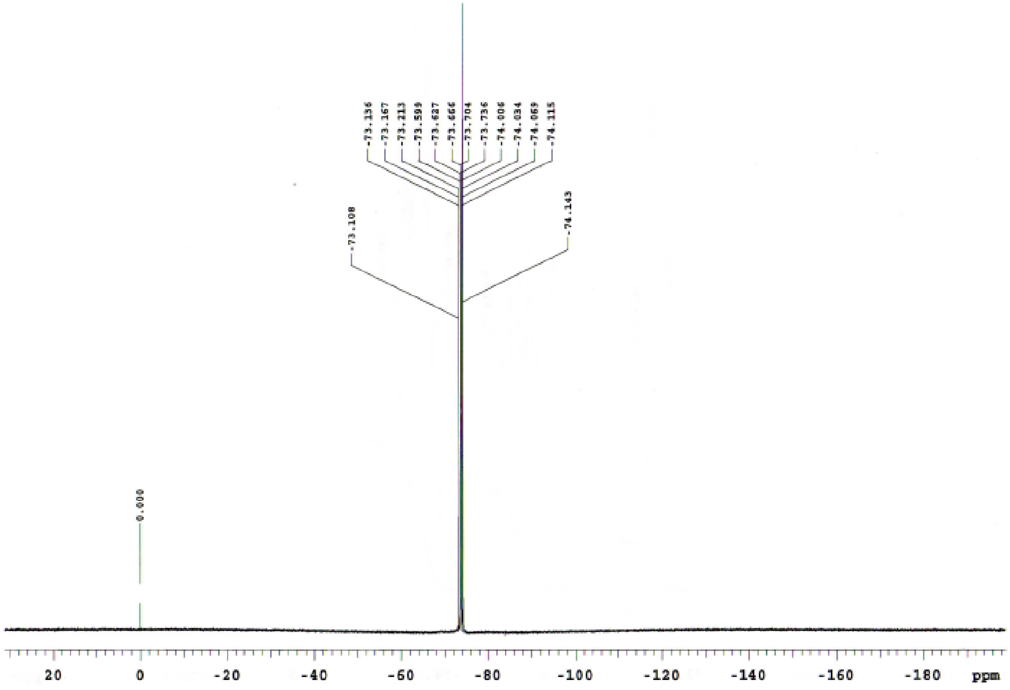

Figure S34. ^{19}F NMR of 7 in Acetone-d_6

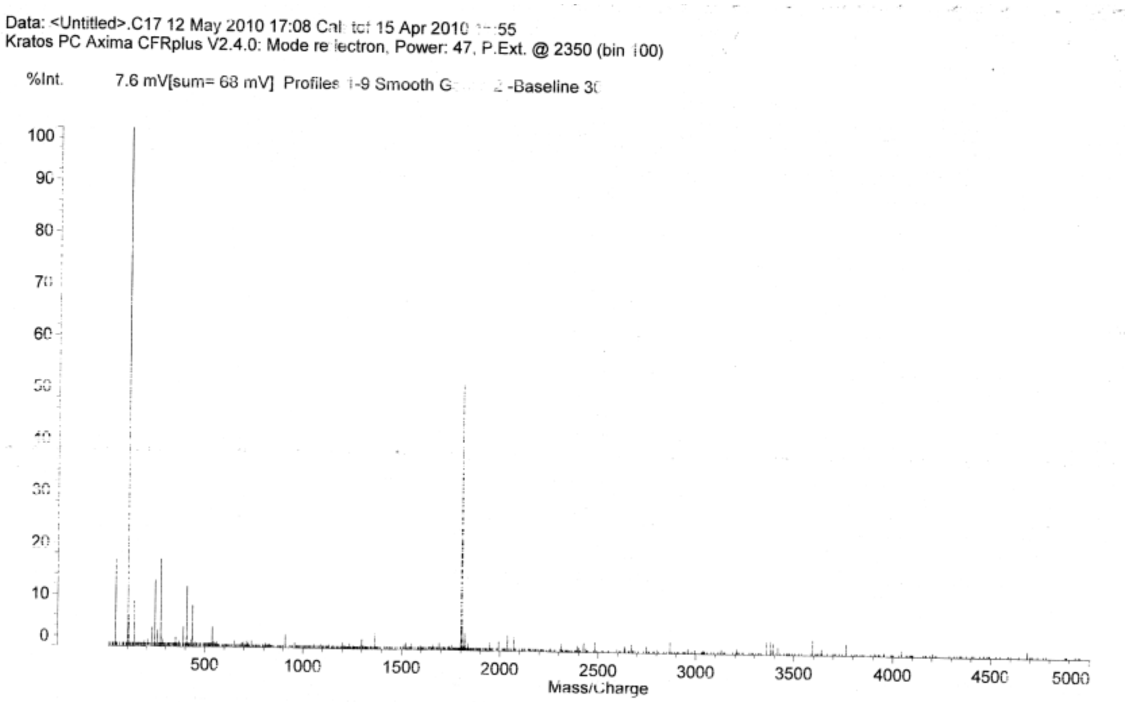

Figure S35. MALDI-TOF MS of 7

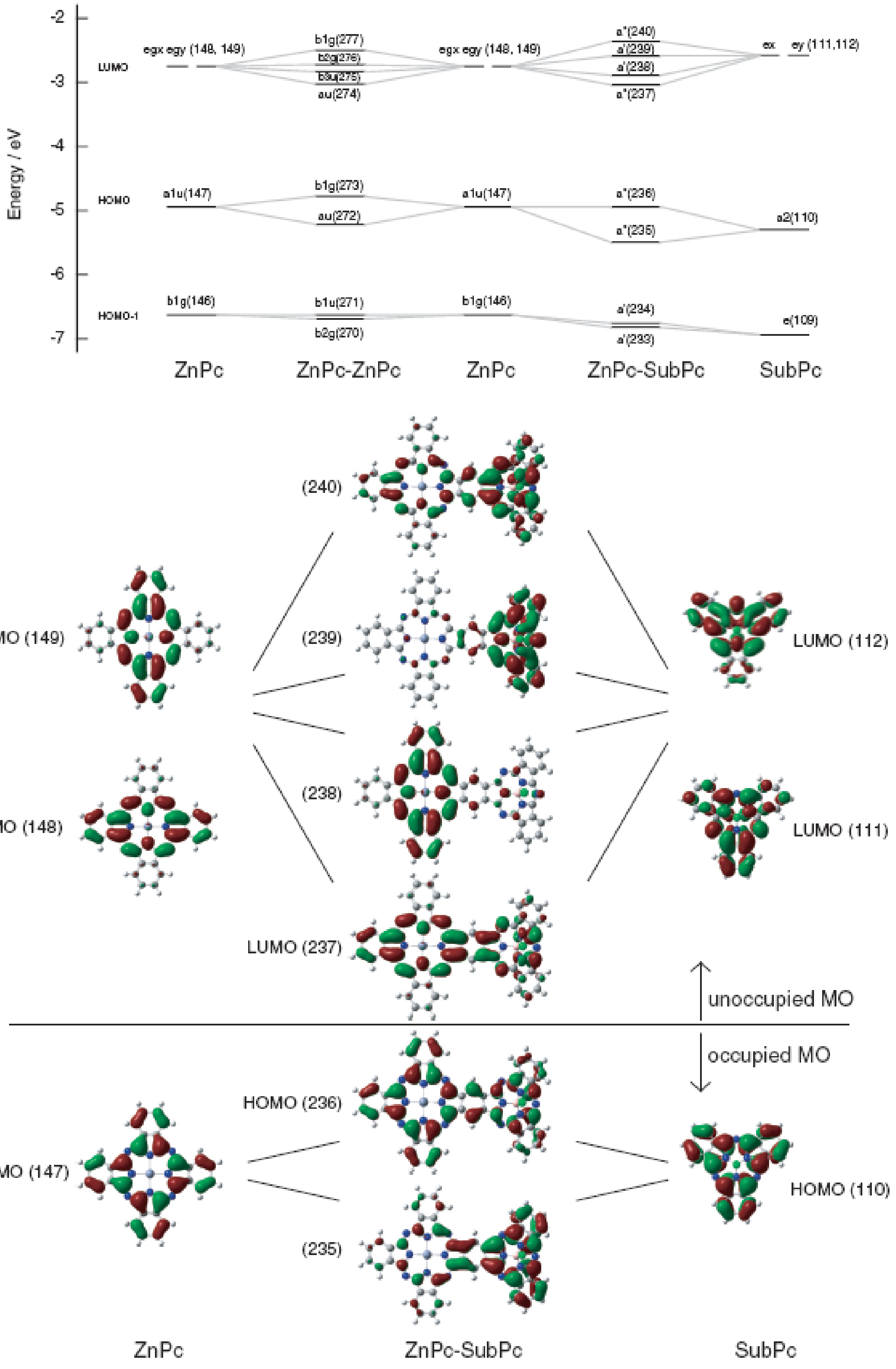

Figure S36. Frontier molecular orbitals of 1, ZnPc, and SubPc

Table S1. Calculated Transition Energies, Oscillator Strengths (f), and Configurations for ZnPc-ZnPc, ZnPc-SubPc, and SubPc-SubPc[a]

	energy/eV	energy/nm	*f*	Configuration
[ZnPc-ZnPc]	1.6316	760	1.6316	0.7054(273,274)
	1.7610	656	0.2198	-0.1355(272,276), 0.6890(273,275)
	2.2759	545	0.5099	0.1195(264,274), 0.6788(272,276)
[ZnPc-SubPc]	1.7693	701	1.1740	0.7007(236,237)
	1.8928	655	0.2596	-0.1116(235,238), 0.6838(236,238)
	2.6411	470	0.2758	0.6863(235,239)
[SubPc-SubPc]	1.9692	630	0.9453	0.7041(199,200)
	2.1131	587	0.2033	0.6969(199,201)
	2.8363	437	0.2945	0.1140(193,200), 0.6886(198,202)

[a] Excited states with less than 3eV and f greater than 0.1 are shown. [b] (a,b) represents a configuration a→b; configurations greater than 0.1 are shown.

Reference [12]

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C. 01,Gaussian, Inc., Wallingford CT, 2009.