Light Emission of [10]Cyclophenacene through Energy Transfer from Neighboring Carbazolylphenyl Dendrons

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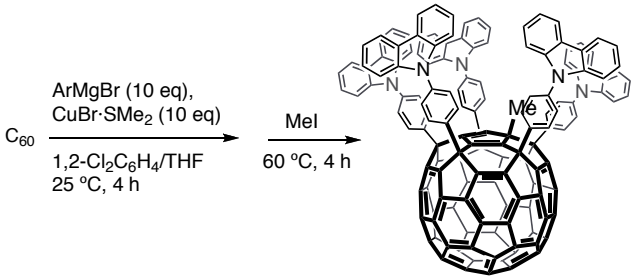
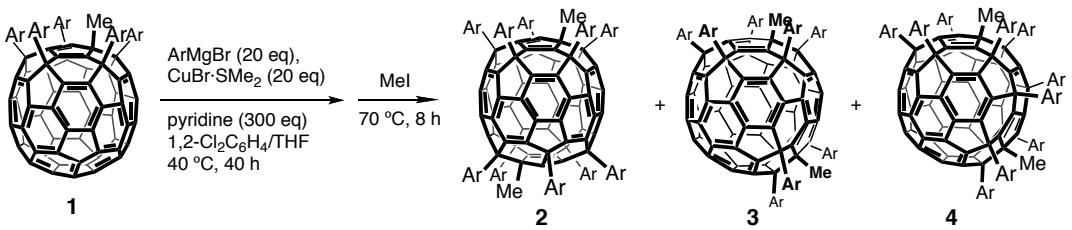
Synthesis of Penta-carbazolylphenyl[60]fullerene (1)



Copper(I) bromide-dimethyl sulfide complex (1.71 g, 8.31 mmol) and THF (10 mL) were placed a 200-mL two neck, round-bottomed flask under an atmosphere of nitrogen. Carbazolylphenyl magnesiumbromide (CzPhMgBr, 27.8 mL, 0.30 M, 8.34 mmol) was then introduced. After that, a solution of C_{60} (500 mg, 0.694 mmol) in 1,2-$Cl_2C_6H_4$ (35 mL) was introduced. The mixture was kept on stirring for 4 h at room temperature. 2.2 ml of MeI was then added and the mixture was stirred for 4 h at 60 ºC. The reaction solution was concentrated and filtered through a pad of silica gel. The solution was concentrated and purified with silica gel chromatography and HPLC. The desired product (1.35 g, 92%) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.0 Hz, 4H), 8.17 (d, J = 8.55 Hz, 4H), 8.07 (d, J = 8.0 Hz, 10H), 7.69–7.61 (m, 10H), 7.44 (d, J = 8.55 Hz, 2H), 7.41–7.05 (m, 30H), 1.91 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.46, 156.86, 154.76, 152.69, 148.89, 148.84, 148.77, 148.58 148.45, 148.36, 148.25, 147.91, 147.47, 147.34, 147.31, 147.12, 145.56, 145.37, 144.79, 144.69, 144.55, 144.53, 144.34, 144.06, 143.80, 143.69, 143.08, 142.89,141.33, 140.51, 140.46, 140.38,138.46, 137.81, 137.73, 137.09, 136.77, 131.32, 130.34, 129.76, 127.45, 127.20, 126.46, 126.25, 126.22, 126.07, 123.54, 120.40, 120.38, 120.33, 120.22, 120.19, 109.46, 109.28, 62.62, 62.42, 60.90, 60.39, 57.99, 34.66. APCI-MS (–): calcd for $C_{151}H_{63}N_5Cl$ ([M + Cl]$^-$) 1980.4772, found 1980.6669. Anal. Calcd for $C_{151}H_{63}N_5$: C, 93.14; H, 3.26, N, 3.60. Found: C, 92.92; H, 3.54; N, 3.36.

Synthesis of decaadduct **2**



A mixture of penta-adduct **1** (500 mg, 0.256 mmol), carbazolylphenylmagnesium bromide (17 mL × 0.30 M in THF, 5.10 mmol) and CuBr·SMe_2 (1.06 g, 5.16 mmol) in 1,2-dichlorobezene (10 mL) and pyridine (6.2 mL, 76.6 mmol) was stirred under nitrogen for 40 hrs at 50 °C. MeI (4.9 mL) was added then, the

temperature of solution was heated to 70 °C and kept on 8 hrs. After evaporating the solvents, the residue was resolved into 50 mL of $CHCl_3$. The solution was filtrated through a pad of silica gel and then. The filter was concentrated and reprecipitation. The obtained solid was further purified with HPLC (first, Cosmosil-Buckyprep column, 20 × 250 mm, eluent: toluene/ isopropanol = 7/3; then Develosil RPFULLERENE column, 20 × 250 mm, eluent: toluene/acetonitrile = 45/55). 150 mg of compound **2** (yield: 18%) and some of crude compound **3** and **4** were obtained. The one-pot deca-addition: A 1,2-$Cl_2C_6H_4$ (2.6 mL) solution of C_{60} (30 mg, 0.042 mmol) was added to a mixture of an organocopper reagent prepared from carbazolylphenylmagnesium bromide (5.3 mL × 0.24 M in THF, 1.3 mmol) and $CuBr{\cdot}SMe_2$ (259 mg, 1.3 mmol) in presence of pyridine (2.5 mL). The mixture was heated to 40 °C and stirred for 95 hrs. After adding of MeI (1 mL), the reaction was warmed to 50 °C and kept on 38 hrs. The mixture was filtered through a pad of silica gel. The yield of **2** (20%) was determined for the crude product by HPLC analysis (area ratio at 350 nm). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50–8.35 (m, 16H, Ar), 8.10–8.05 (m, 20H, Ar), 7.92–7.73 (m, 20H, Ar), 7.57–7.06 (m, 64H, Ar), 2.22 (br, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ 162.38, 161.99, 161.92, 161.85, 161.50, 160.02, 159.51, 159.17, 158.83, 156.44, 156.22, 155.87, 155.75, 155.60, 155.47, 155.40, 155.34, 155.25, 154.98, 152.22, 151.69, 151.20, 151.10,151.06, 148.36, 148.11, 147.74, 147.71, 147.64, 147.54, 147.49, 147.34, 147.30, 147.25, 147.15, 147.03, 146.37, 146.32, 146.06, 146.02, 145.98, 145.87, 145.79, 145.75, 145.66, 145.63, 145.38, 145.29, 144.72, 144.49, 144.32, 40.59, 140.53, 140.29, 140.12, 138.48, 138.42, 137.69, 137.21, 137.12, 137.08, 131.19, 131.11, 130.27, 130.25, 129.69, 127.38, 127.06, 127.03, 126.15, 126.10, 125.99, 123.42, 120.31, 120.28, 120.25,120.23, 109.29, 109.26,109.12, 62.80, 62.74, 62.68, 62.35, 62.28, 62.20, 61.40,61.37, 58.53, 58.51, 34.55, 34.44, 34.33. MALDI-TOF MS: calcd for $C_{242}H_{127}N_{10}$ ($[M + H]^+$) 3172.02, found 3172.01. Anal. Calcd for $C_{244}H_{134}N_{10}O_2$ ($M + 2CH_3OH$): C, 90.51; H, 4.17, N, 4.33. Found: C, 90.53; H, 4.26; N, 3.97.

^{1}H NMR of **1**

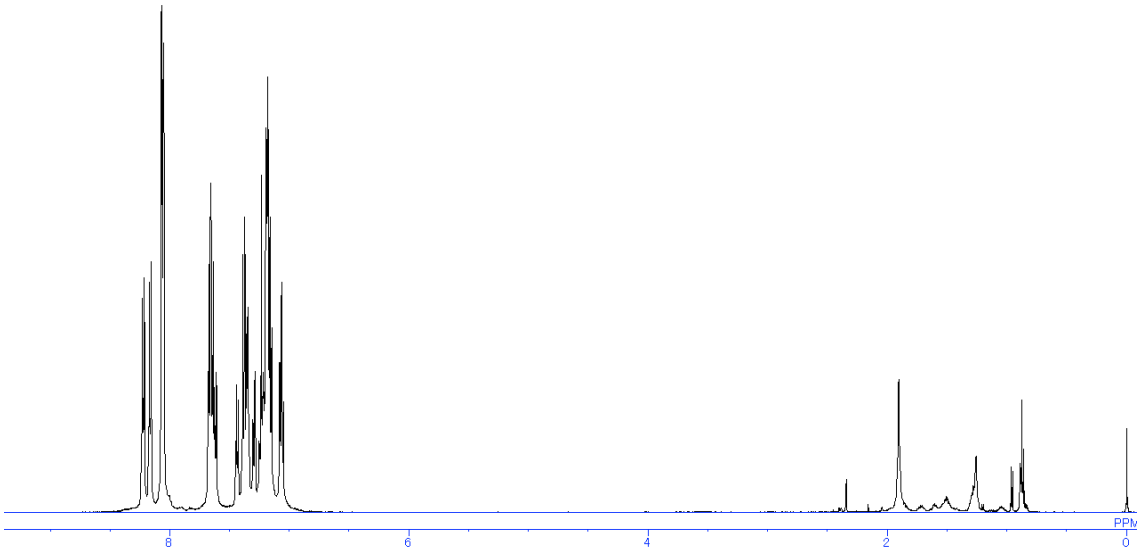


Figure S1. ^{1} H NMR spectrum of **1** in $CDCl_3$.

^{13}C NMR of **1**

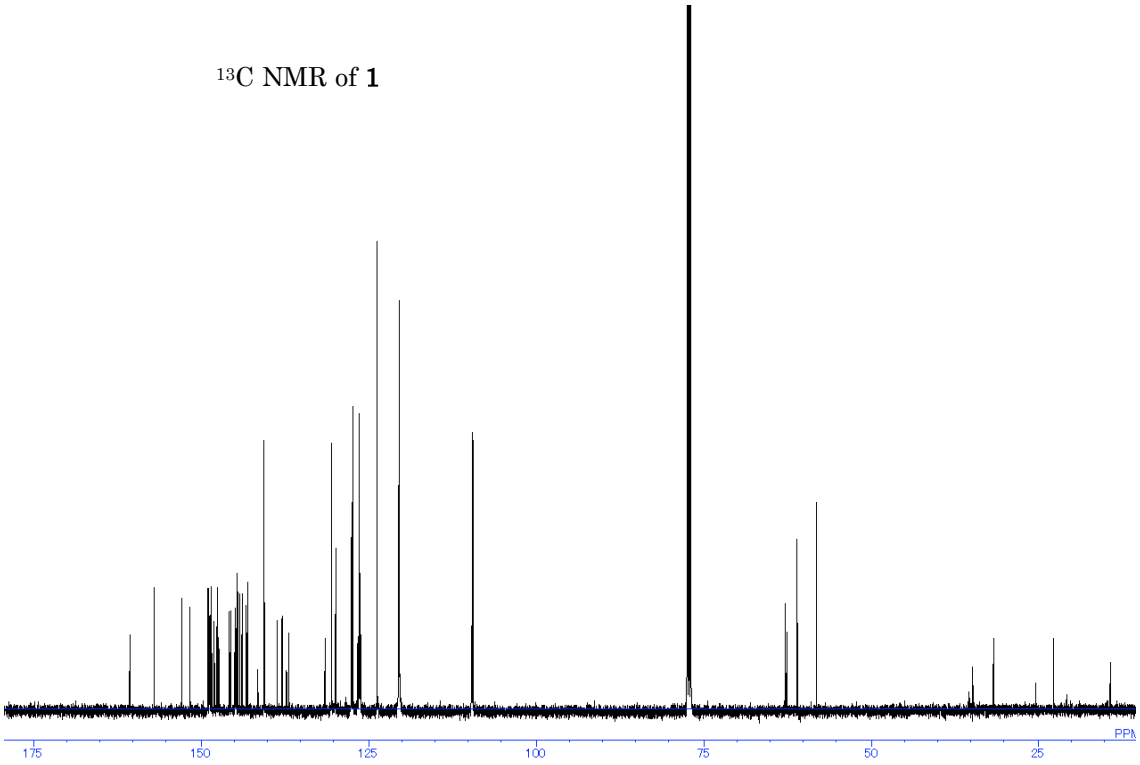


Figure S2. ^{13} C NMR spectrum of **1** in $CDCl_3$.

^{1}H NMR of **2**

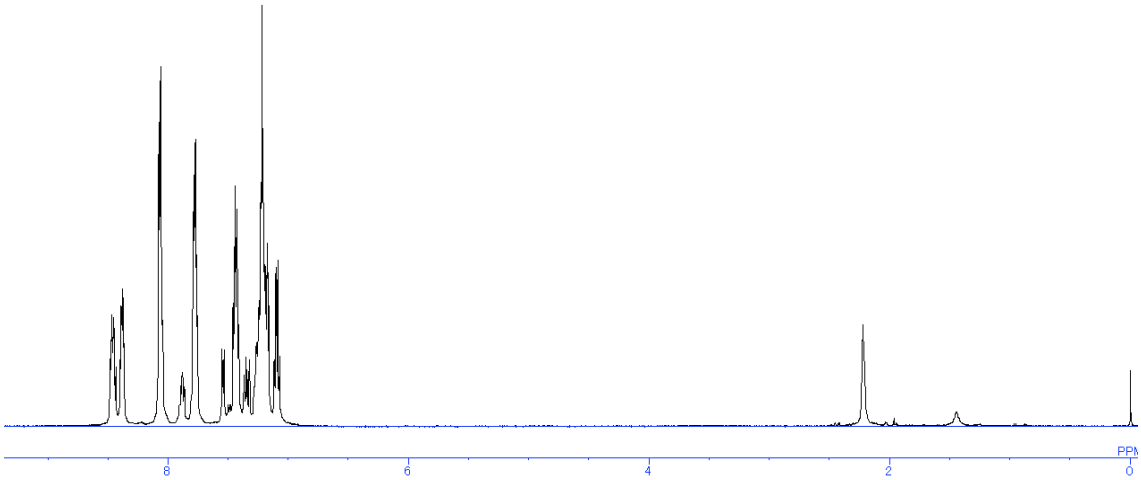


Figure S3. ^{1} H NMR spectrum of **2** in $CDCl_3$.

^{13}C NMR of **2**

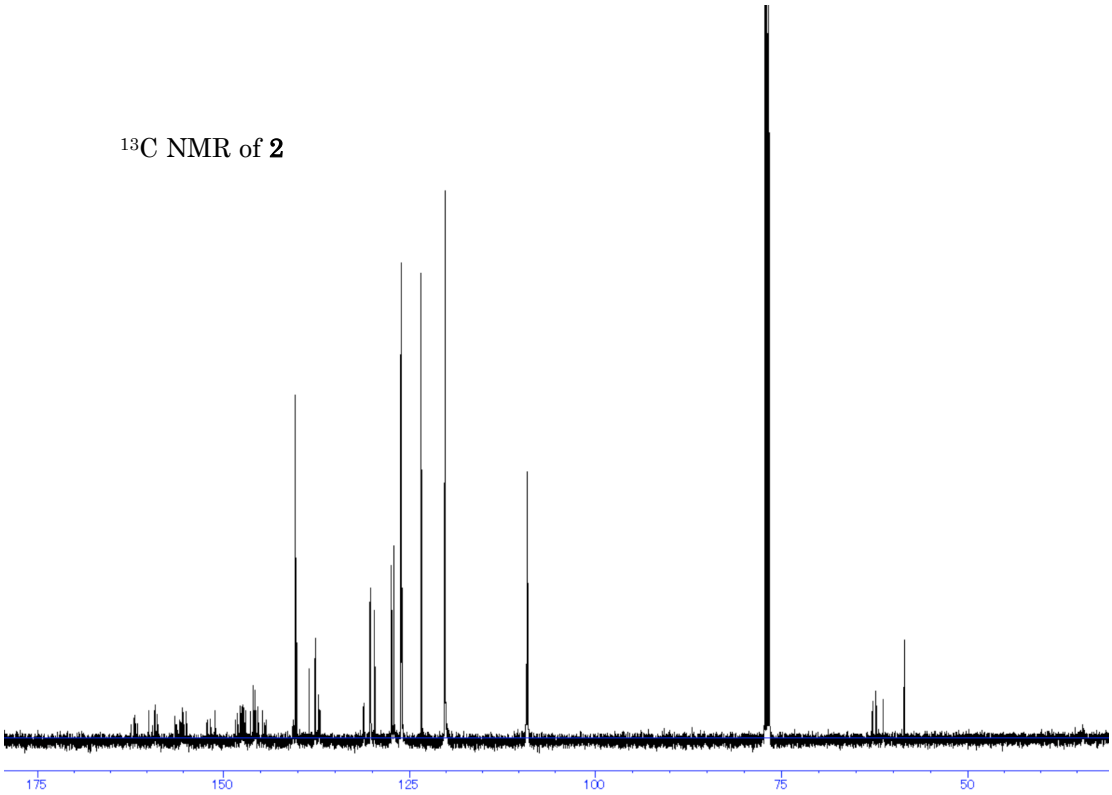


Figure S4. ^{13} C NMR spectrum of **2** in $CDCl_3/CS_2$.

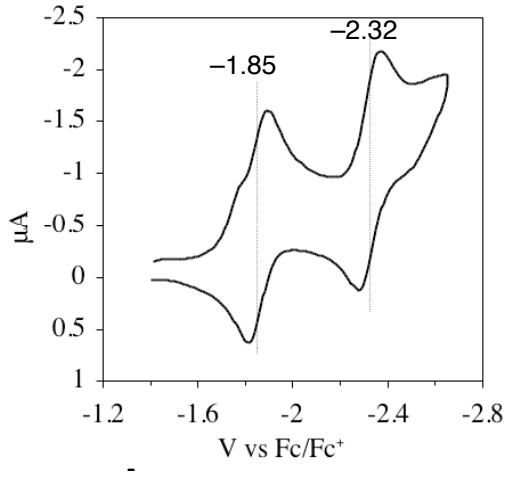


Figure S5. Cyclic voltammogram of **2**. Measurement was performed at the scan rate of 100 mV/s at 25 ºC in THF containing [^{n}Bu$_4$N][ClO$_4$] as supporting electrolyte.

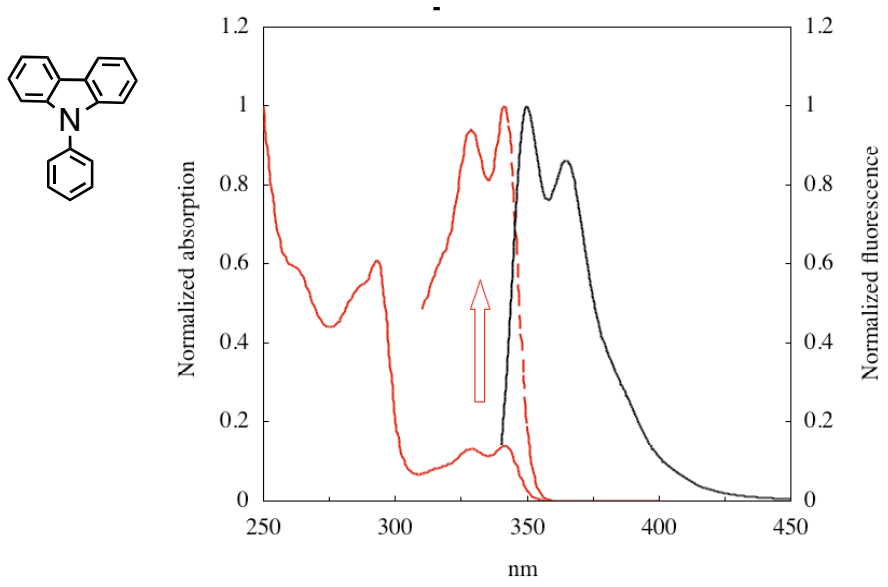


Figure S6. Absorption and fluorescence spectra of 9-phenylcarbazole (2×10^{-5} M) in chloroform at 25 °C, λ_{ex} = 334 nm. The absorption in range of 310–360 nm is enlarged.

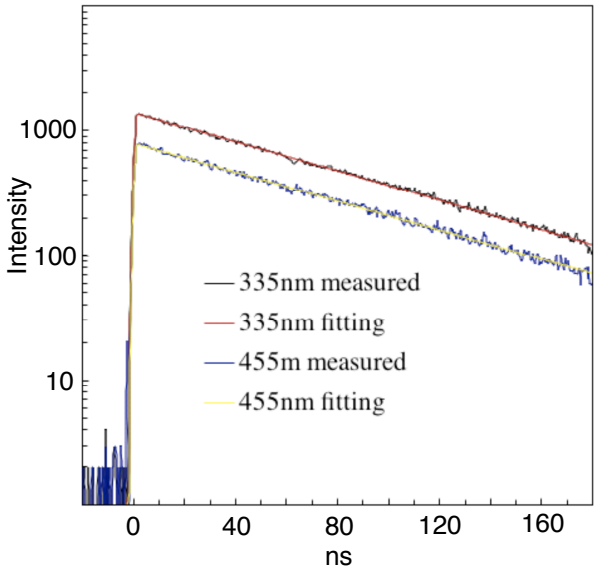


Figure S7. Fluorescence decay of **2** upon excitation of 335 and 455 nm, respectively. The red and yellow curves are fitting lines of their single exponential fluorescence decays of **2** with lifetime of 74 and 75 ns, respectively.

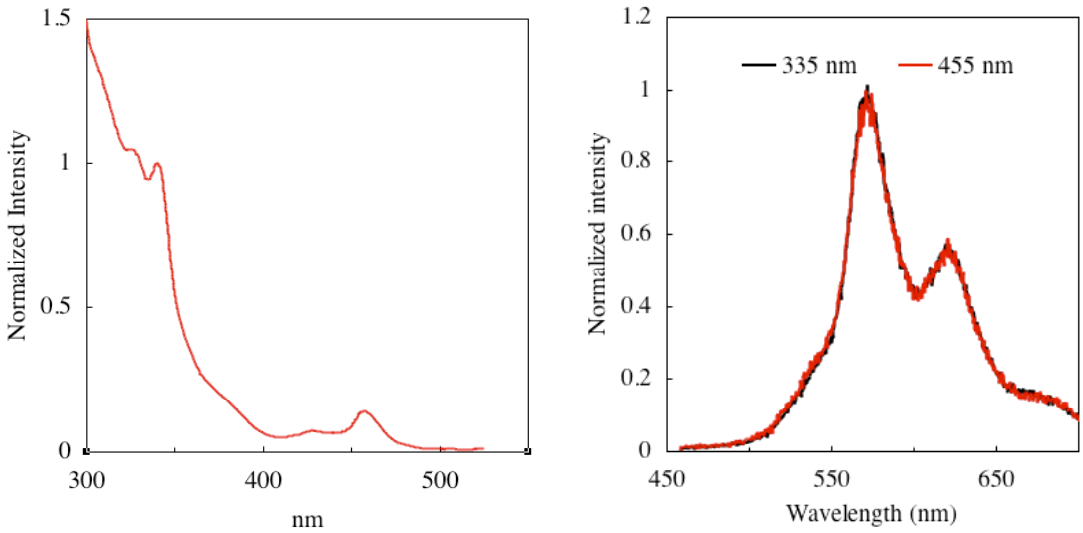


Figure S8. Left: Excitation fluorescence spectrum of **2** in chloroform, monitored at 566 nm. Right: fluorescence spectra of **2**, excited at 335 and 455 nm.

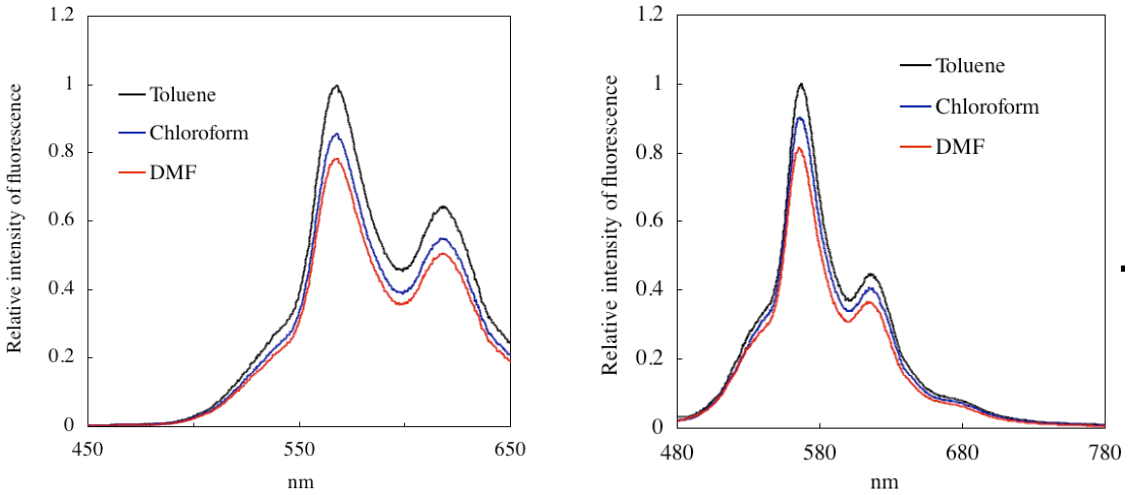


Figure S9. Fluorescence spectra of **2** (2.5~3.2 × 10^{-5} M) in various solvents at 25 °C, left: λ_{ex} = 334 nm, right: λ_{ex} = 456 nm.

Table S1. Fluorescence quantum of deca-adduct **2** in different solvents.

Solvents	Dielectric constant	ϕ_{fl}[a]
Toluene	2.38	0.21
Chloroform	4.81	0.19
DMF	36.7	0.17

a Excitation at 456 nm. The yields were determined by comparison with rhodamine 101 in ethanol (ϕ_{fl} = 1).