

Poly(γ -glutamic acid) Hydrogels with Water-Sensitive Luminescence Derived from Aggregation-Induced Emission of *o*-Carborane

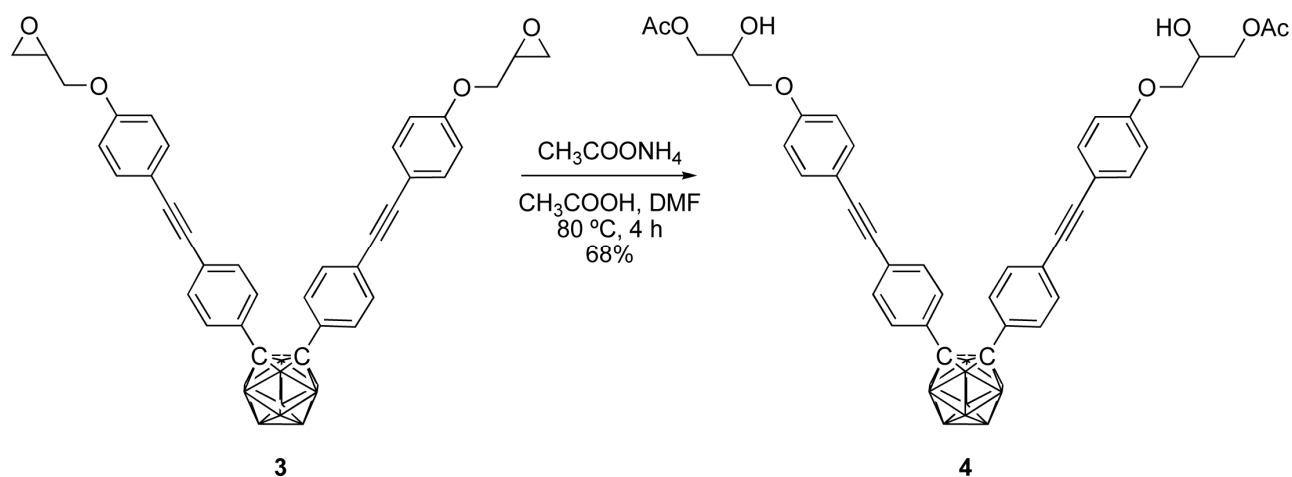
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Experimental section



Scheme S1. Ring-opening reaction of **3**.

Materials. Unless stated otherwise, all other reagents were obtained from commercial sources and used without further purification.

Measurements. ^1H (400 MHz), ^{13}C (100 MHz) and ^{11}B (128 MHz) NMR measurements were recorded on a JEOL JNM-EX400 instrument. ^1H and ^{13}C NMR spectra used 0.05% tetramethylsilane (TMS) as an internal standard and ^{11}B NMR spectra were referenced externally to $\text{BF}_3\cdot\text{Et}_2\text{O}$ at room temperature. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature. Fluorescence emission spectra and absolute quantum yield, measured by integrating sphere method, were recorded on a HORIBA JOBAN YVON Fluoromax-4 spectrofluorometer.

Bis(4-(4-(1-acetoxy-2-hydroxy-propyl-3-oxy)-phenylethynyl)phenyl)-*o*-carborane (4**).** A solution of ammonium acetate in acetic acid (4 M, 0.5 mL) was added to the solution of **3** (32 mg, 0.05 mmol) in DMF (0.5 mL), and the mixture was heated for 4 h. After cooling, the reaction mixture was diluted with CHCl_3 , and washed with 5 wt% K_2CO_3 aq. and brine. The solution was dried over MgSO_4 , and the solvent was removed by rotary evaporator. The crude product was purified by column chromatography to give **4** as a colorless foam (25 mg, 68%). δ (ppm) 7.42 (d, 4H, $J = 8.77$ Hz), 7.39 (d, 8H, $J = 8.53$ Hz), 7.27 (d, 4H, $J = 8.53$ Hz), 6.87 (d, 4H, $J = 8.77$ Hz), 4.33-4.21 (m, 6H), 4.08-3.99 (m, 4H), 3.69-1.77 (br, 10H), 2.56 (br, 2H) ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.2, 158.6, 133.2, 131.2, 130.5, 129.9,

125.8, 115.2, 114.7, 92.0, 87.0, 84.9, 68.7, 68.5, 65.3, 20.8. ^{11}B NMR (128 MHz, CDCl_3): δ (ppm) -2.8, -10.3. HRMS (FAB) Calcd for $\text{C}_{40}\text{H}_{43}\text{B}_{10}\text{O}_8$ $[\text{M}-\text{H}]^+$: m/z 761.3888, Found: m/z 761.3905.

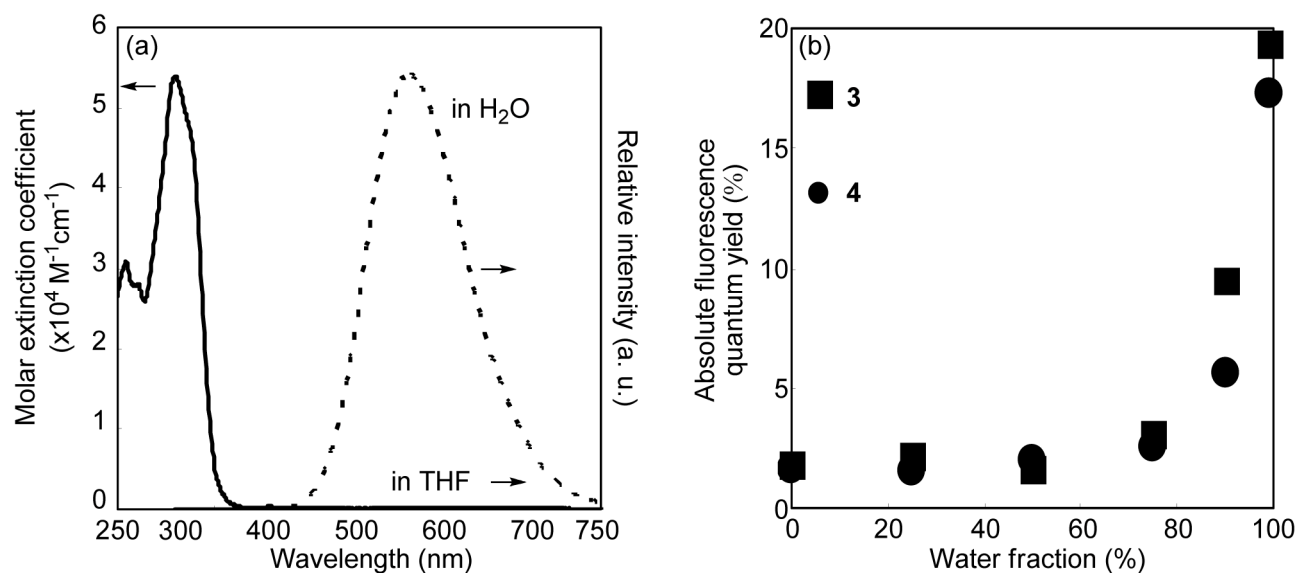


Figure S1. (a) UV-vis and fluorescence spectra of **4** in THF (1.0×10^{-5} mol/L, solid line) and in the mixed solvent of THF/ H_2O = 1/99 (v/v) (1.0×10^{-5} mol/L, dashed line). (b) Dependence of quantum yields of **3** and **4** on solvent compositions of the THF/ H_2O mixture.