

Electronic Supplementary Information

Mechanochromic cyclodextrins

*Yuki Sugita^a, Daisuke Aoki^{*a,b}, Masatoshi Tokita^a and Hideyuki Otsuka^{*a}*

^a. Department of Chemical Science and Engineering, Tokyo Institute of Technology,
2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

^b. JST-PRESTO, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

Corresponding Authors

*E-mail: daoki@polymer.titech.ac.jp

*E-mail: otsuka@mac.titech.ac.jp

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1. General Information

Materials

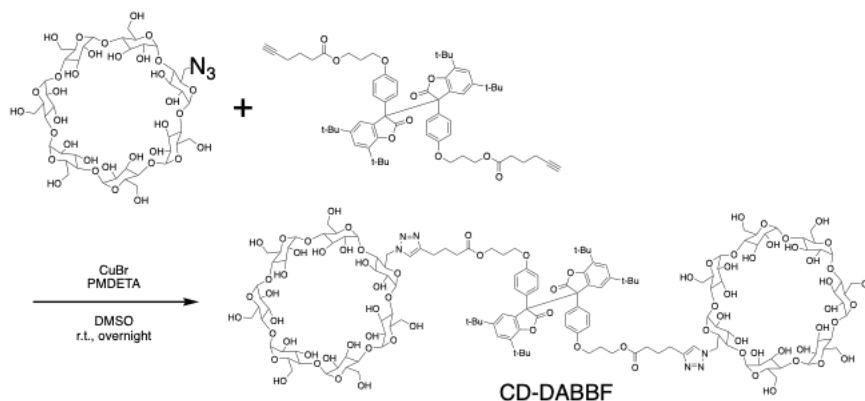
All solvents and reagents from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, and Kanto Chemical were used as received, unless otherwise noted. Copper (I) bromide (CuBr) was washed with acetic acid and then washed with methanol and dried in vacuo. DABBF-dialkyne¹ and CD-N₃² were synthesized according to the previously published methods.

Instruments

¹H NMR spectroscopic measurements were carried out using 500 MHz and 400 MHz Bruker spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* (CDCl₃) or dimethyl sulfoxide-*d*₆ (DMSO-*d*₆). ¹H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane. The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet; br, broad. FT-IR spectroscopic measurement was recorded on a JASCO FT/IR-4100 with a KBr plate. UV-vis absorption measurements were carried out on a JASCO V-650 spectrophotometer. Size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000 and 2500) and a differential refractive index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards ($M_n = 4430\text{--}3242000$; $M_w/M_n = 1.03\text{--}1.08$) were used to calibrate the SEC system. Electrospray ionization mass spectrometry (ESI-TOFMS) measurements were carried out on Bruker micrOTOF II. Wide-angle X-ray diffraction (WAXD) measurements were performed using a D8 DISCOVER (Bruker) equipped with a rotating-anode Cu-K α radiation source ($\lambda = 0.1542$ nm) operated at 50 kV and 100 mA and a VANTEC-500 detector. All measurements were carried out at room temperature under atmospheric pressure. WAXD patterns were recorded in two-dimension. The diffraction intensities were circular averaged and plotted against 2θ , where θ is the Bragg angle.

2. Synthesis Procedure

2.1. CD-DABBF



A solution of CD-N₃ (7.8 g, 6.7 mmol), DABBF-dialkyne (2.2 g, 2.2 mmol) and CuBr (0.96 g, 6.7 mmol) in dry DMSO (50 mL) was degassed by three freeze-pump-thaw cycles and filled with N₂. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (4.68 mL, 3.9 g, 22 mmol) was then added, and the mixture was stirred overnight at r.t. The resulting solution was precipitated into acetone and filtrated. The crude product was dissolved in 1 N hydrochloric acid and reprecipitated into acetone twice. Following washed with water, the residue was reprecipitated into acetone once again to gain CD-DABBF as a white solid (6.8 mg, 92%). ¹H NMR and FT-IR spectra of CD-DABBF are shown in Figs. S1 and S2.

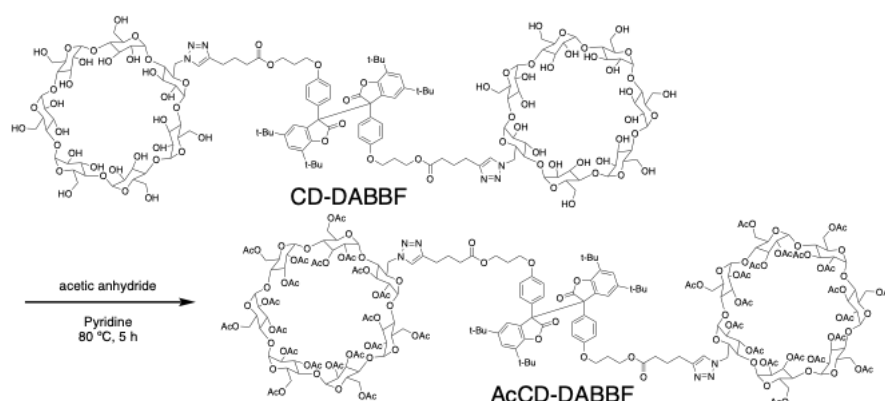
¹H NMR (400 MHz, DMSO-*d*₆): δ /ppm = 7.78 (s, 1H), 7.30 (br, 4H), 6.90 (s, 2H), 4.79 (br, 28H), 4.13 (t, 2H), 4.02 (t, 2H), 3.59 (br, 28H), 3.28 (br, 14H), 2.57 (t, 2H), 2.34 (t, 2H), 2.00 (br, 2H), 1.81 (br, 2H), 1.20 (br, 9H), 1.02 (br, 9H).

¹³C NMR (100 MHz, DMSO-*d*₆): δ /ppm = 24.63, 29.77, 31.68, 33.30, 34.47, 49.17, 51.81, 57.69, 60.48, 72.53, 73.56, 81.94, 102.36, 114.12, 123.67, 132.19, 133.37, 146.30, 148.80, 159.38, 173.63.

FT-IR (KBr, cm⁻¹): 3376, 2956, 1795, 1726, 1607, 1510, 1460, 1413, 1365, 1300, 1273, 1250, 1155, 1082, 1032, 936, 885, 821, 759, 706, 582, 449, 437, 410.

ESI-TOF-MS (m/z): [M+Na]⁺ calcd. for C₇₃H₁₀₆N₃O₃₉Na, 1671.6296; Found, 1671.6323.

2.2. AcCD-DABBF



Under a nitrogen atmosphere, a dispersion of CD-DABBF (1.0 g, 0.30 mmol) in pyridine (6 mL) was added acetic anhydride (2.3 mL, 2.5 g, 24 mmol) and stirred for 24 h at 60 °C. The resulting solution was precipitated into water and filtrated. The crude product was dissolved in acetone and reprecipitated into water once again to gain AcCD-DABBF as a white solid (1.0 g, 66%). ^1H NMR and FT-IR spectra of AcCD-DABBF are shown in Fig. S3 and S4.

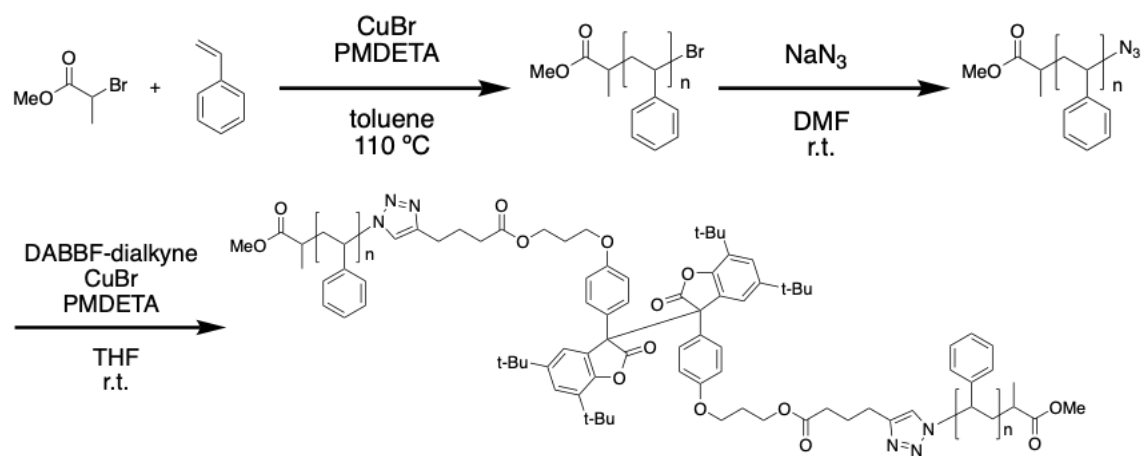
^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ/ppm = 7.67 (s, 1H), 7.29 (br, 2H), 7.17 (br, 2H), 6.91 (br, 2H), 5.16 (br, 7H), 5.03 (br, 7H), 4.69 (br, 7H), 4.35 (br, 7H), 4.20 (br, 7H), 4.05 (br, 7H), 3.81 (br, 9H), 3.54 (t, 2H), 2.59 (t, 2H), 2.31 (t, 2H), 2.14 (dd, 2H), 1.96 (br, 2H), 1.81 (dd, 2H), 1.34 (br, 9H), 1.20 (br, 9H).

^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ/ppm = 20.95, 24.78, 29.85, 31.54, 33.15, 34.33, 51.67, 55.34, 61.22, 62.83, 70.03, 70.48, 76.94, 97.07, 114.12, 124.26, 132.19, 133.22, 146.59, 148.80, 159.09, 170.55, 173.63.

FT-IR (KBr, cm^{-1}): 2962, 2107, 1748, 1608, 1510, 1435, 1371, 1237, 1173, 1140, 1046, 956, 902, 822, 764, 651, 603, 460, 405.

ESI-TOF-MS (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{113}\text{H}_{146}\text{N}_3\text{O}_{59}\text{Na}$, 2511.8409; Found, 2511.8471.

2.3. PS-DABBF



PS-DABBF¹ were synthesized according to the previously published methods shown in the above scheme. A GPC profile of PS-DABBF is shown in Fig. S5.

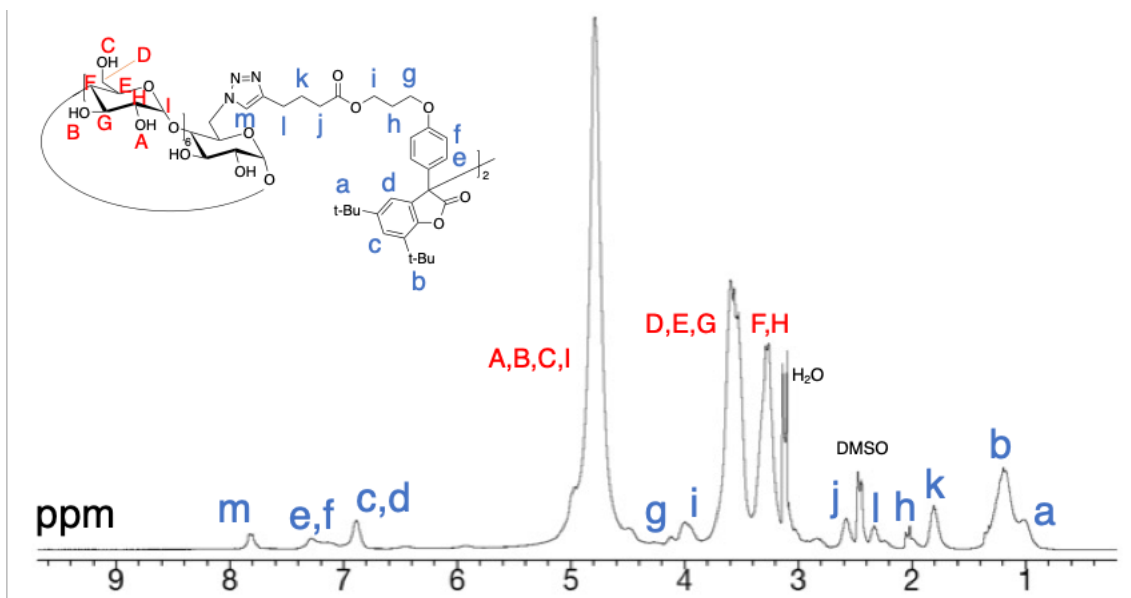


Fig. S1 ¹H NMR spectrum of CD-DABBF (400 MHz, DMSO-*d*₆).

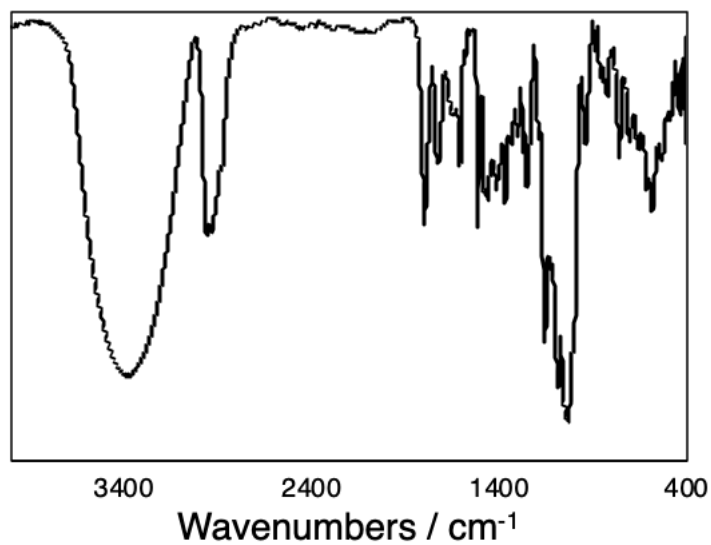


Fig. S2 FT-IR spectrum of CD-DABBF.

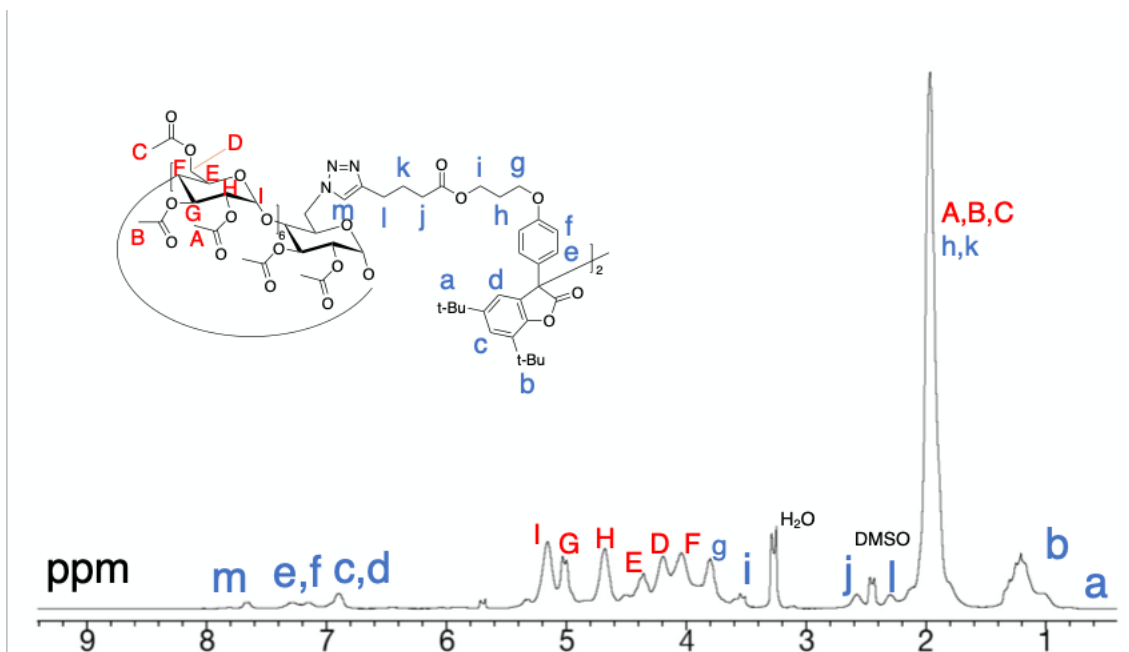


Fig. S3 ^1H NMR spectrum of AcCD-DABBF (400 MHz, $\text{DMSO-}d_6$).

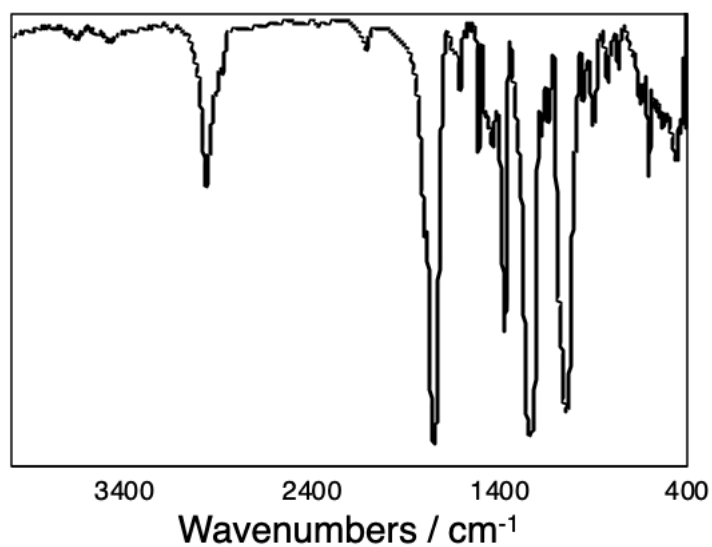


Fig. S4 FT-IR spectrum of AcCD-DABBF.

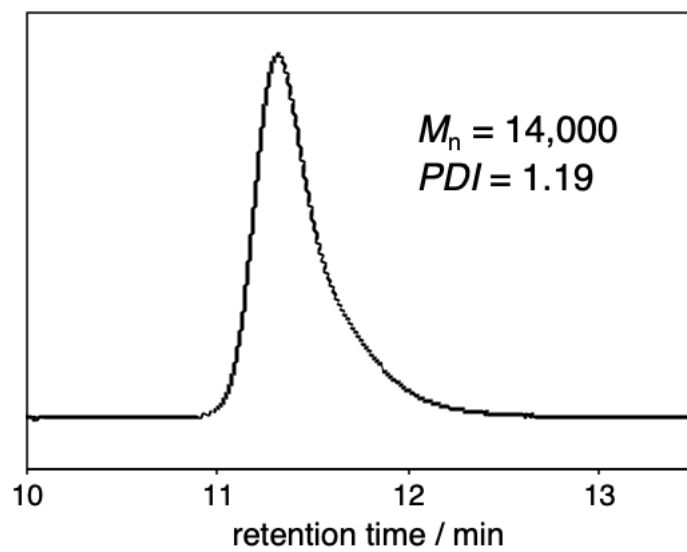


Fig. S5 A GPC profile of PS-DABBF.

3. Grinding Tests and EPR Study in Solid State

Grinding tests of **CD-DABBF**, **AcCD-DABBF**, **DABBF-diol** and **PS-DABBF** were performed on a Retsch Mixer Mill MM 400. The mechanical energy was controlled by vibrational frequency and grinding time. A powdered sample (50 mg) and a stainless ball (d = 5 mm) were placed in the grinding jar and ball-milled for 10 min at 30 Hz. The ground samples were transferred into an EPR 5 mm glass capillary, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The spectra of the ground samples were measured using a microwave power of 0.1 mW and field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.125 mT/s at r.t. The concentration of the radicals formed from the cleavage of DABBF was determined by comparing the area of the observed integral spectrum with a 0.02 mM solution of TEMPOL in benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The g value was calculated according to the following equation: $g = h\nu/\beta H$ where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field.

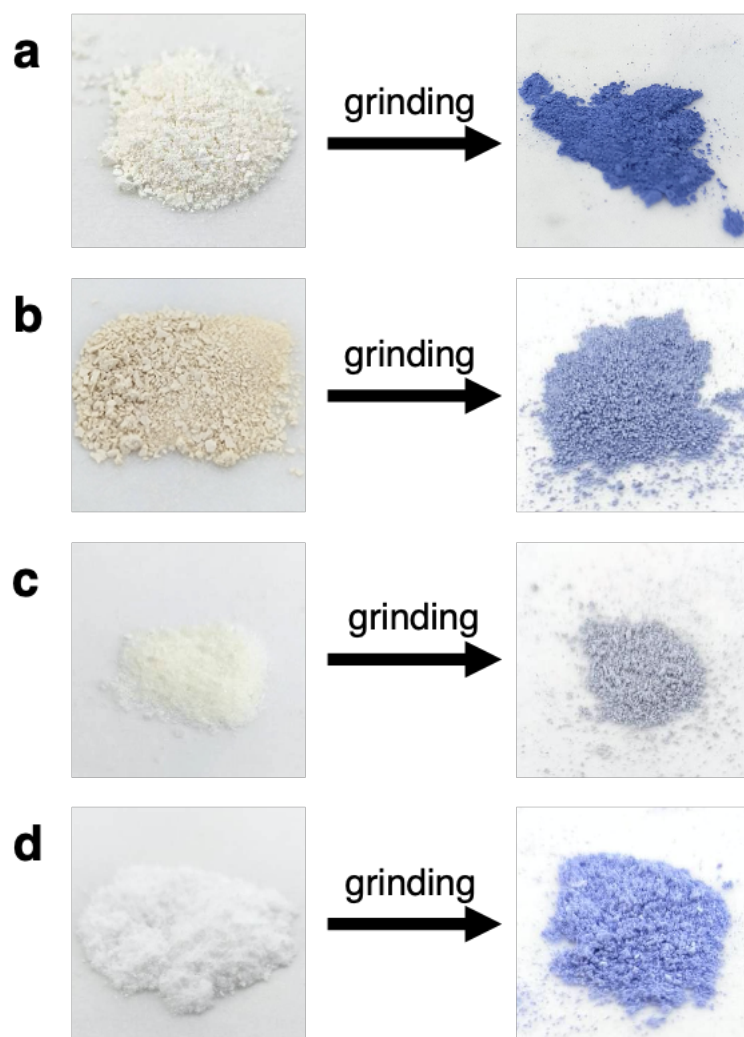


Fig. S6 Photographs of (a) CD-DABBF, (b) AcCD-DABBF, (c) DABBF-diol and (d) PS-DABBF before and after grinding using a ball mill (30 Hz, 10 min) at room temperature.

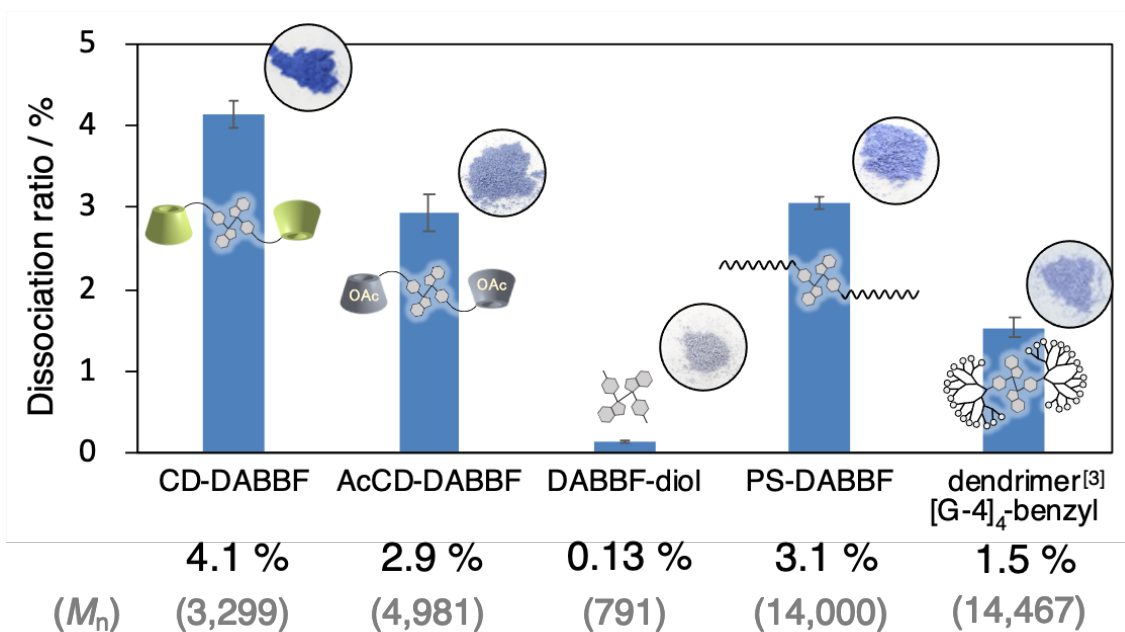


Fig. S7 Dissociation ratio (%) of DABBF skeletons of CD-DABBF, AcCD-DABBF, DABBF-diol, PS-DABBF and [G-4]₄-benzyl dendrimer³ after grinding using a ball mill (30 Hz, 10 min) at room temperature.

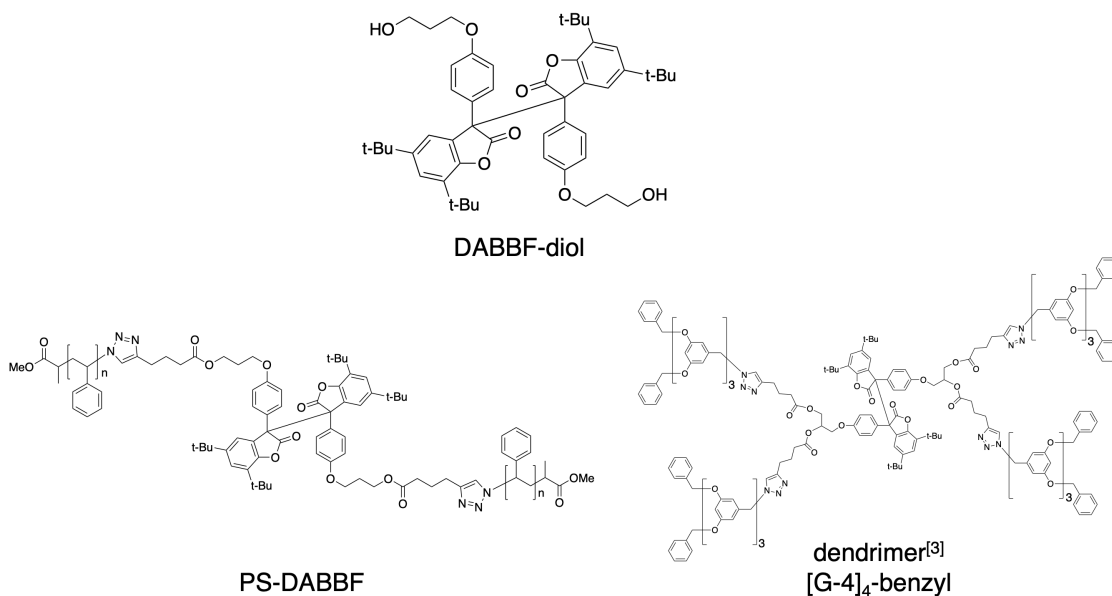


Fig. S8 Chemical structures of DABBF-diol, PS-DABBF, and [G-4]₄-benzyl dendrimer³.

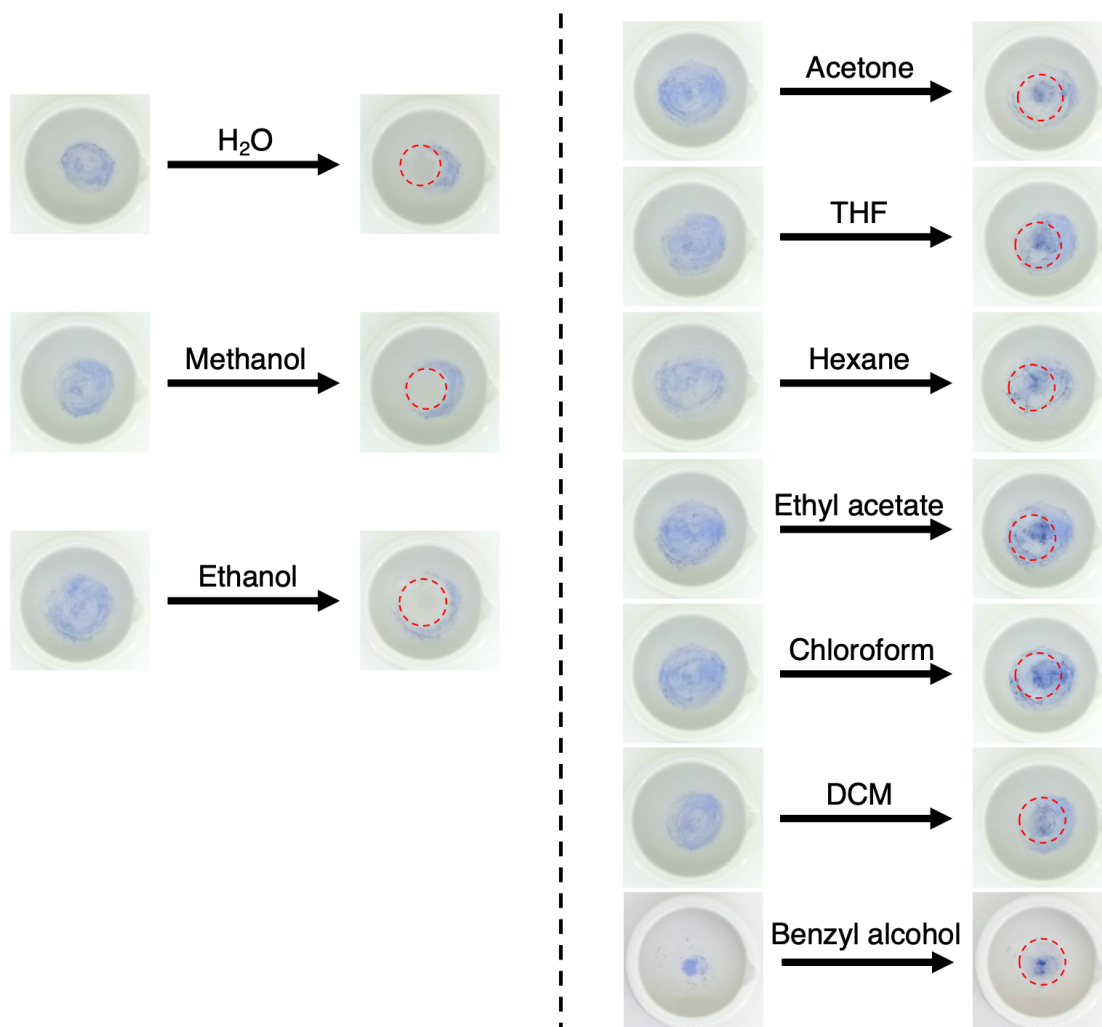


Fig. S9 Photographs of ground CD-DABBF before and after adding each solvent.

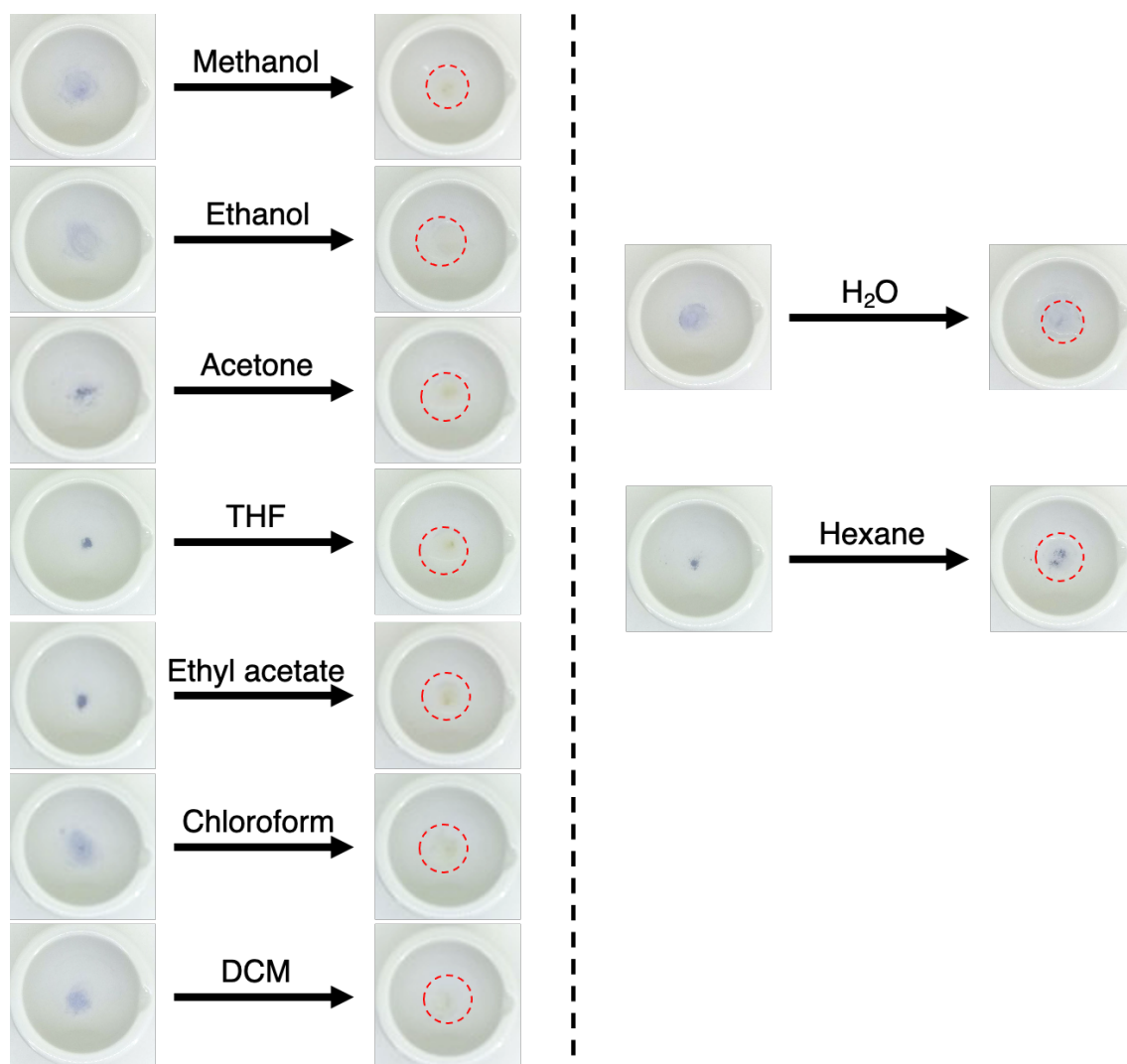


Fig. S10 Photographs of ground AcCD-DABBF before and after adding each solvent.

References

1. H. Oka, K. Imato, T. Sato, T. Ohishi, R. Goseki, H. Otsuka, *ACS Macro. Lett.*, **2016**, *5*, 1124–1127.
2. B. A. Ondrusek, H. Chung, *ACS Omega.*, **2017**, *2*, 3951–3957.
3. T. Watabe, K. Ishizuki, D. Aoki, H. Otsuka, *Chem. Commun.* **2019**, *55*, 6831–6834.