Electronic Supplementary Material (ESI) for ChemComm.


Supporting Information

# Visualization of Slide-ring Effect: A Study on Movable Cross-Linking Point Using Mechanochromism

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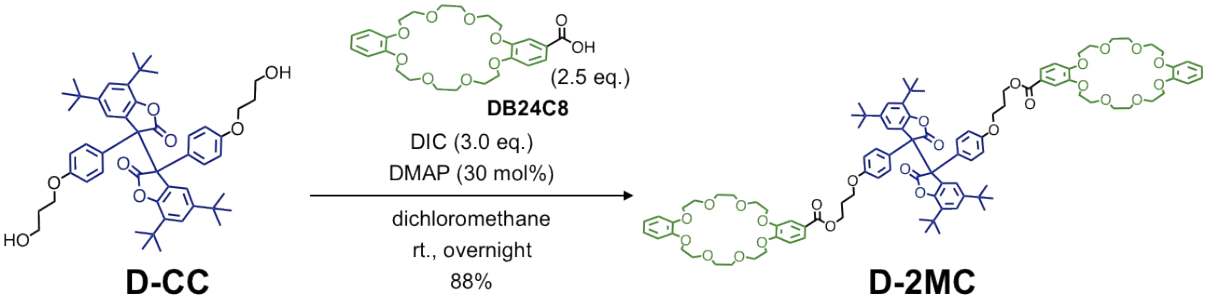
## Materials

All solvents and reagents from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, and Kanto Chemical were used as received, unless otherwise noted. **D-CC**,[1] **DB24C8**,[2] **Axle**[3] were prepared according to previously published methods. Benzoyl peroxide (BPO) was reprecipitated with chloroform / methanol (1 / 3) at room temperature and dried in vacuo. Methyl acrylate (MA) monomer was passed through an ammonia column to remove the inhibitor. Dry dichloromethane was obtained by distillation over $CaH_2$ after being washed with water.

## Instruments

$^1H$ and $^{13}C$ NMR spectroscopic measurements were carried out using a Bruker AVANCE III HD500 spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$), acetone-$d_6$, DMSO-$d_6$, or dichloromethane-$d_2$ ($CD_2Cl_2$). Tensile tests were carried out with dumbbell shaped samples (12 mm × 2 mm × 0.4 mm) at room temperature using a SHIMADZU EZ graph equipped with a 50 N load cell at elongation rate of 10 mm / min. The gel permeation chromatography (GPC) was performed at 30 °C in DMF (with 10 mM LiBr, 0.700 mL / min) using a JASCO PU-1580 system equipped with a set of a TOSOH TSK G2500H and a TOSOH TSK G4000H with a JASCO RI-1530 detector. The number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity index ($M_w$ / $M_n$) of the polymers were calculated on the basis of a polystyrene calibration. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on an RFS-10 (Round Science Inc.) instrument. FAB-MS spectra were obtained at the Center for Advanced Material Analysis, Tokyo Institute of Technology on request. In situ electron paramagnetic resonance (EPR) measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a tensile tester for long strip specimens (ca. 100 mm × 2 mm × 0.4 mm). The effective measuring range was 43.5 mm height. The specimens were stretched to 40, 80, 120, 160, 200, and 230% strains in sequence under a strain rate of 100 mm/min. The spectra were measured at each strain at room temperature using a microwave power of 0.4 mW and field modulation of 0.07 mT with time constant of 0.03 s and a sweep rate of 250 mT/s. The concentration of the radicals formed from the cleavage of DABBF was determined by comparing the area of the observed integral spectrum with a 0.001 mM solution of TEMPOL in benzene, which was placed in a 3 mm glass capillary, degassed, and measured under the same experimental conditions as the samples. The $Mn^{2+}$ signal was used as an auxiliary standard. The g value was determined as 2.003, which is a typical value for carbon centered radicals.

## Synthesis of D-2MC

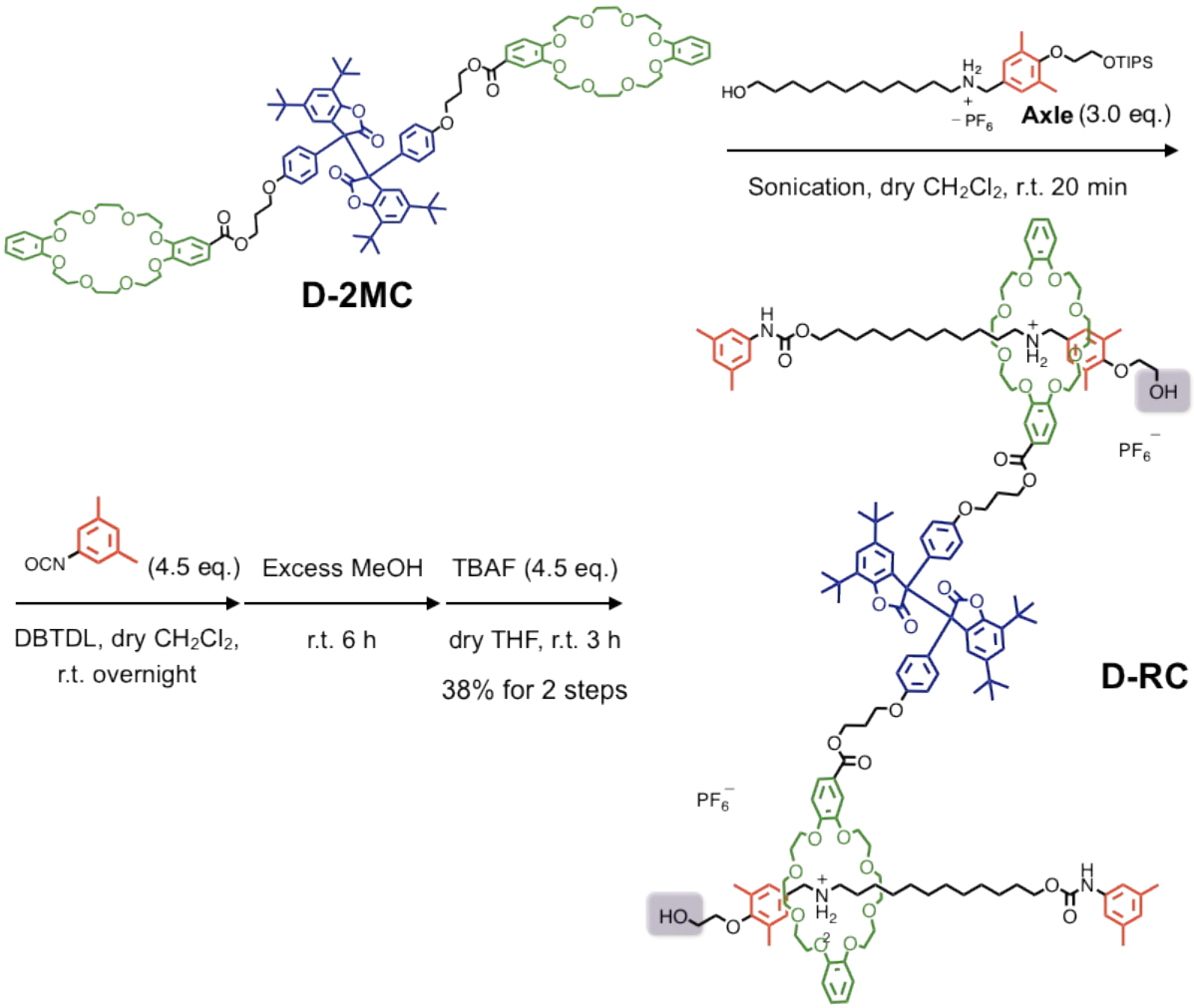



**Scheme S1.** Synthesis of **D-2MC.**

**D-CC** (5.3 g, 6.7 mmol) was mixed in dry dichloromethane (52 mL) with **DB24C8** (8.2 g, 17 mmol, 2.5 eq.) and 4-dimethylaminopyridine (DMAP, 0.38 g, 2.0 mmol, 30 mol%). After degassing followed by charging with argon 3 times, *N,N'*-diisopropylcarbodiimide (DIC, 3.1 mL, 2.5 g, 20 mmol, 3.0 eq.) was added dropwise to the mixture at 0 °C. The mixture was then allowed to warm up to room temperature and react overnight. The residue was washed with 0.1 M HCl aqueous solution once, and water 3 times. The organic layer was concentrated in vacuo. 30 mL dichloromethane was added and the suspension was filtered by a Buchner filter. The filter residue was washed with diethyl ether and the filtrate was concentrated. The residue was purified by column chromatography (silica gel, THF/dichloromethane = 15/85, v/v) to obtain a white solid **D-2MC** (10 g, 5.9 mmol, 88%).

m.p. 81.3–84.9 ºC; FAB-MS (m/z): calcd for $[M + Na]^+$, $C_{100}H_{122}O_{26}Na$, 1761.8122; found, 1761.7970; $^1$H NMR (500 MHz, 298 K, $CD_2Cl_2$)：δ 7.67 (d, $J$ = 10 Hz, 1H), 7.56 (s, 1H), 7.10–7.42 (m, 4H), 6.82–6.98 (m, 7H), 4.48 (t, $J$ = 6 Hz, 2H), 4.08–4.21 (m, 10H), 3.88–3.96 (m, 8H), 3.80–3.86 (m, 8H), 2.25 (m, 2H), 1.04–1.40 (m, 18H); $^{13}$C NMR (125 MHz, 298 K, $CD_2Cl_2$): δ 166.02, 159.07, 153.03, 149.03, 149.00, 148.33, 133.38, 132.22, 124.21, 123.72, 122.93, 121.35, 121.32, 114.47, 114.20, 114.16, 113.13, 112.09, 71.21, 71.12, 71.05, 69.84, 69.67, 69.51, 69.42, 69.19, 69.11, 64.67, 61.57, 34.63, 34.26, 31.25, 29.40, 28.76, 22.01, 20.61; FT-IR (NaCl, cm$^{-1}$): 2956, 2871, 1793, 1712, 1602, 1508, 1456, 1429, 1363, 1272, 1256, 1215, 1130, 1088, 1052, 995, 929, 821, 764.

## Synthesis of D-2MC



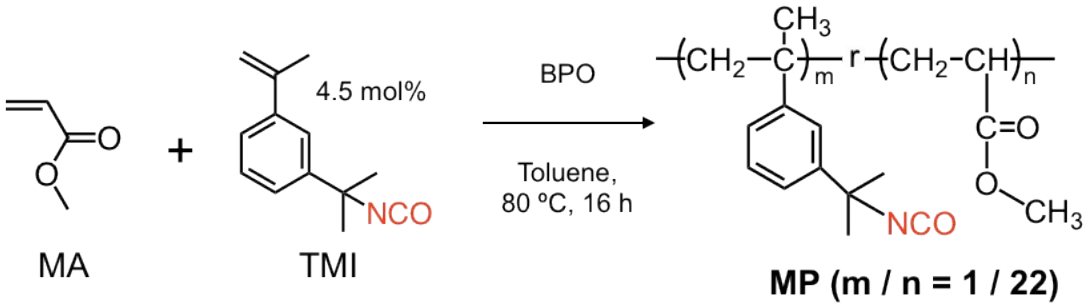

**Scheme S2.** Synthesis of **D-RC.**

In 13 mL dry dichloromethane, **D-2MC** (9.2 g, 5.3 mmol) was mixed with **Axle** (11 g, 16 mmol, 3.0 eq.). The mixture was sonicated for 20 min. To the solution were added 3,5-dimethylphenyl isocyanate (3.5 g, 3.4 mL, 24 mmol, 4.5 eq.) and 3 drops of dibutyltin dilaurate (DBTDL). The mixture was stirred overnight at room temperature under argon atmosphere and quenched by mixing with excess methanol for 6 hours. The solvent was removed in vacuum. To the residue was added 100 mL THF. Tetra-*n*-butylammonium fluoride (TBAF) in THF solution (1 mol/L, 24 mL, 4.5 eq.) was dropwise added to resulting solution at 0 °C. Then the mixture was allowed to warm to room temperature and react for 3 hours. The resultant mixture was poured into ethyl acetate and washed with ammonium chloride aqueous solution. After being dried upon $MgSO_4$, the solution was concentrated in vacuo and then purified by column

chromatography (silica gel, ethyl acetate → $CHCl_3$/MeOH = 100/3, v/v) to afford a white solid **D-RC** (6.2 g, 2.0 mmol, 38% for 2 steps).

m.p. 104.5–106.7 ºC; FAB-MS (m/z): calcd for $[M - H]^+$, $C_{164}H_{223}N_4O_{34}$, 2792.5844; found, 2792.5800; $^1$H NMR (500 MHz, 298 K, $CD_2Cl_2$): δ 7.55 (dd, *J* = 3 Hz, 1H), 7.37 (d, *J* = 2 Hz, 1H), 7.32–6.68 (m, 14H), 6.61 (s, 1H), 6.56 (s, 1H), 4.43–4.34 (m, 4H), 4.16–3.95 (m, 12H), 3.88–3.68 (m, 10H), 3.66–3.60 (m, 8H), 3.58–3.47 (m, 4H), 3.17 (t, *J* = 15 Hz, 2H), 2.21–2.13 (m, 8H), 1.97 (d, *J* = 2 Hz, 6H), 1.56 (quint, *J* = 7 Hz, 2H), 1.35–0.95 (m, 36H); $^{13}$C NMR (125 MHz, 298 K, $CD_2Cl_2$): δ 159.05, 156.04, 153.59, 151.47, 148.97, 147.35, 147.33, 147.20, 138.71, 138.06, 133.42, 131.22, 130.01, 127.51, 124.87, 123.98, 123.41, 121.69, 116.24, 113.16, 113.03, 112.37, 111.50, 73.31, 70.95, 70.39, 70.34, 70.19, 68.38, 68.27, 68.08, 68.05, 65.11, 64.70, 62.05, 61.91, 51.91, 48.90, 34.26, 31.24, 29.48, 29.46, 29.38, 29.28, 29.23, 28.95, 28.69, 26.72, 26.44, 25.81, 21.09, 16.02; FT-IR (NaCl, $cm^{-1}$): 2928, 2871, 1793, 1714, 1604, 1557, 1508, 1457, 1270, 1215, 1127, 1090, 1056, 953, 843, 764.

## Synthesis of MP




**Scheme S3.** Synthesis of **MP.**

Methyl acrylate (MA, 5 mL, 0.06 mol), 3-isopropenyl-α,α-dimethyl-benzene isocyanate (TMI, 0.5 mL, 0.003 mol), benzoyl peroxide (BPO, 0.05 g, 0.2 mmol) were mixed in dry toluene (10 mL). The system was degassed with freeze-pump-thaw cycles and then heated at 80 °C for 16 h. The resulting solution was reprecipitated twice with dry $CHCl_3$ and hexane, and dried in vacuum to afford a white solid (5.0 g, 95%).

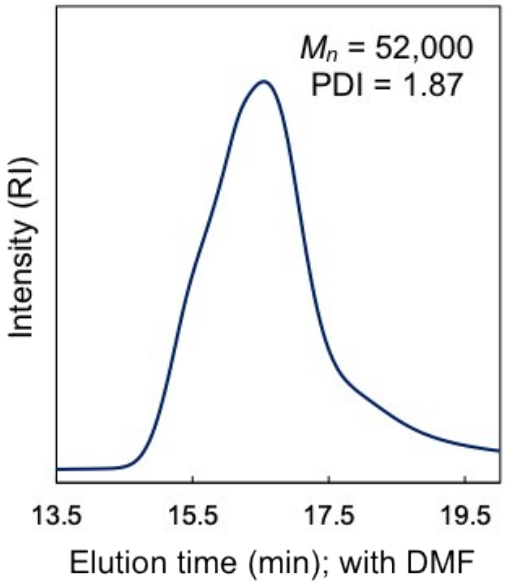



**Figure S1.** GPC profile of **MP.**

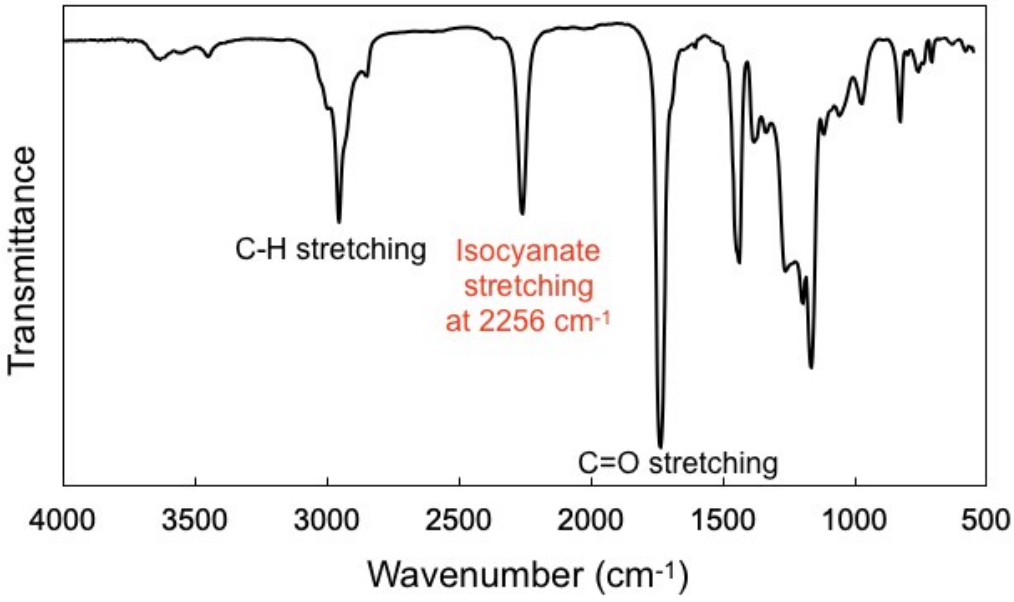



**Figure S2.** IR spectrum of **MP** (NaCl).

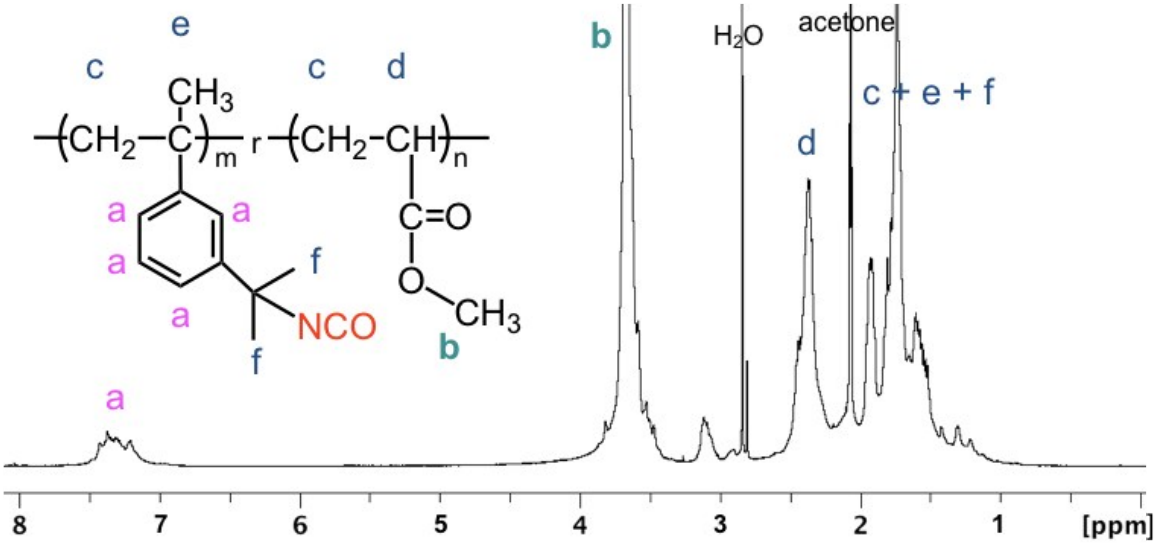


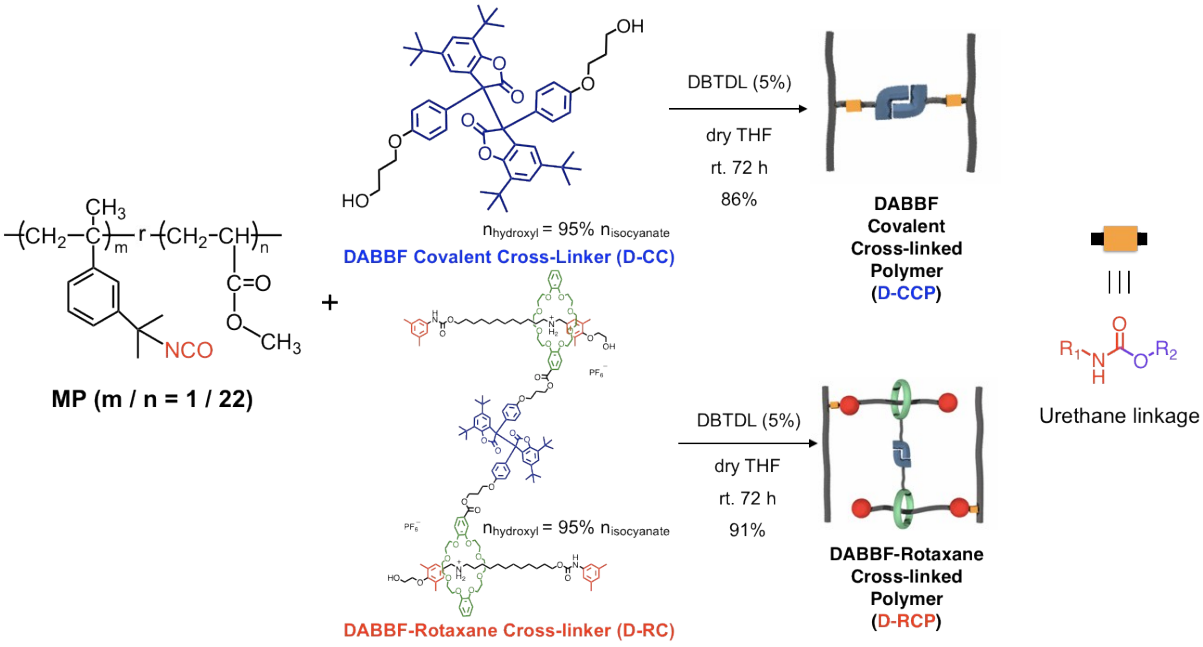

**Figure S3.** $^{1}$H NMR spectrum of **MP** in acetone-$d_6$ (500 MHz, 25 ºC).

**Table S1.** Analysis of $^{1}$H NMR spectrum of **MP**

| Symbol | Origin | Integration value ($^{1}$H NMR) | Integration (a / b) | Proton dosage value (mmol) | Dosage ratio (a / b) |
|---|---|---|---|---|---|
| a | TMI and BPO | set as 1.00 | $0.074 \pm 0.003$ | 12.0 | 0.073 |
| b | MA | $13.6 \pm 0.4$ | | 165 | |

From above **Table S1**, the radical polymerization proceeded quantitatively. Therefore, the composition of **MA** and **TMI** in **MP** was calculated based on dosage amount. That is, TMI, the isocyanate containing unit, accounted for 4.3% and MA, account for 95.7% of the polymer chain. The dosage ratio of cross-linking reaction was based on this result.

## Synthesis of D-RCP and D-CCP




**Scheme S4.** Cross-linking reactions to give **D-CCP** and **D-RCP.**

Synthesis of **D-CCP**

In a Teflon plate, polymer matrix **MP** (2.6 g, containing 1.2 mmol -NCO), **D-CC** (0.46 g, 0.58 mmol), and a catalytic amount of DBTDL were mixed in dry THF to give a homogeneous solution. The solution was allowed to stand for 3 days at room temperature in an argon-charged closed system. Then the solvent was allowed to evaporate naturally at room temperature. The residue after evaporation was taken from the mold and washed with ethyl acetate/methanol (1/1, v/v) solution at 0 °C to afford a white film of **D-CCP** (2.6 g, 86%).

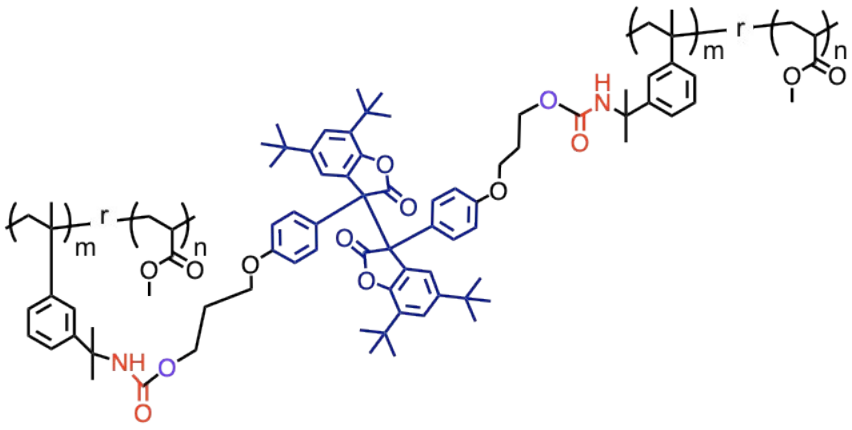



**Figure S4**. Detailed structure of **D-CCP**.

Synthesis of **D-RCP**

In a Teflon plate, polymer matrix **MP** (1.7 g, containing 0.80 mmol -NCO), **D-RC** (1.2 g, 0.38 mmol), and a catalytic amount of DBTDL were mixed in dry THF to give a homogeneous solution. The solution was allowed to stand for 3 days at room temperature in an argon-charged closed system. Then the solvent was allowed to evaporate naturally at room temperature. The residue after evaporation was taken out from the mold and washed with acetate/methanol (1/1, v/v) mixed solution at 0 °C to afford a white film of **D-RCP** (2.6 g, 91%).

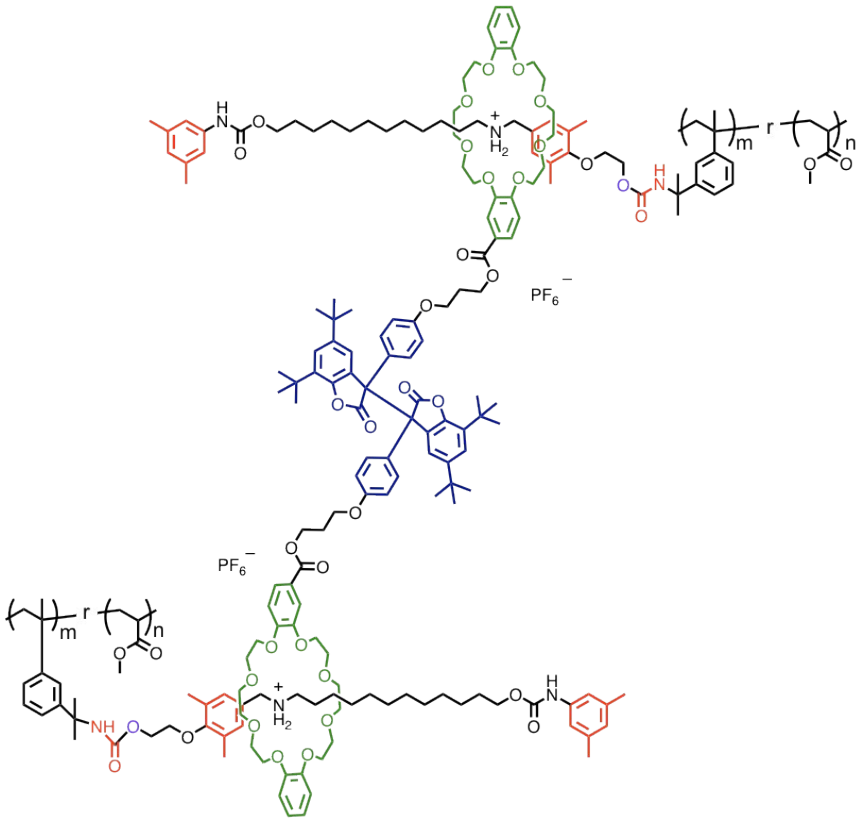



**Figure S5**. Detailed structure of **D-RCP**.

**Thermophysical properties of MP, D-CCP, and D-RCP**

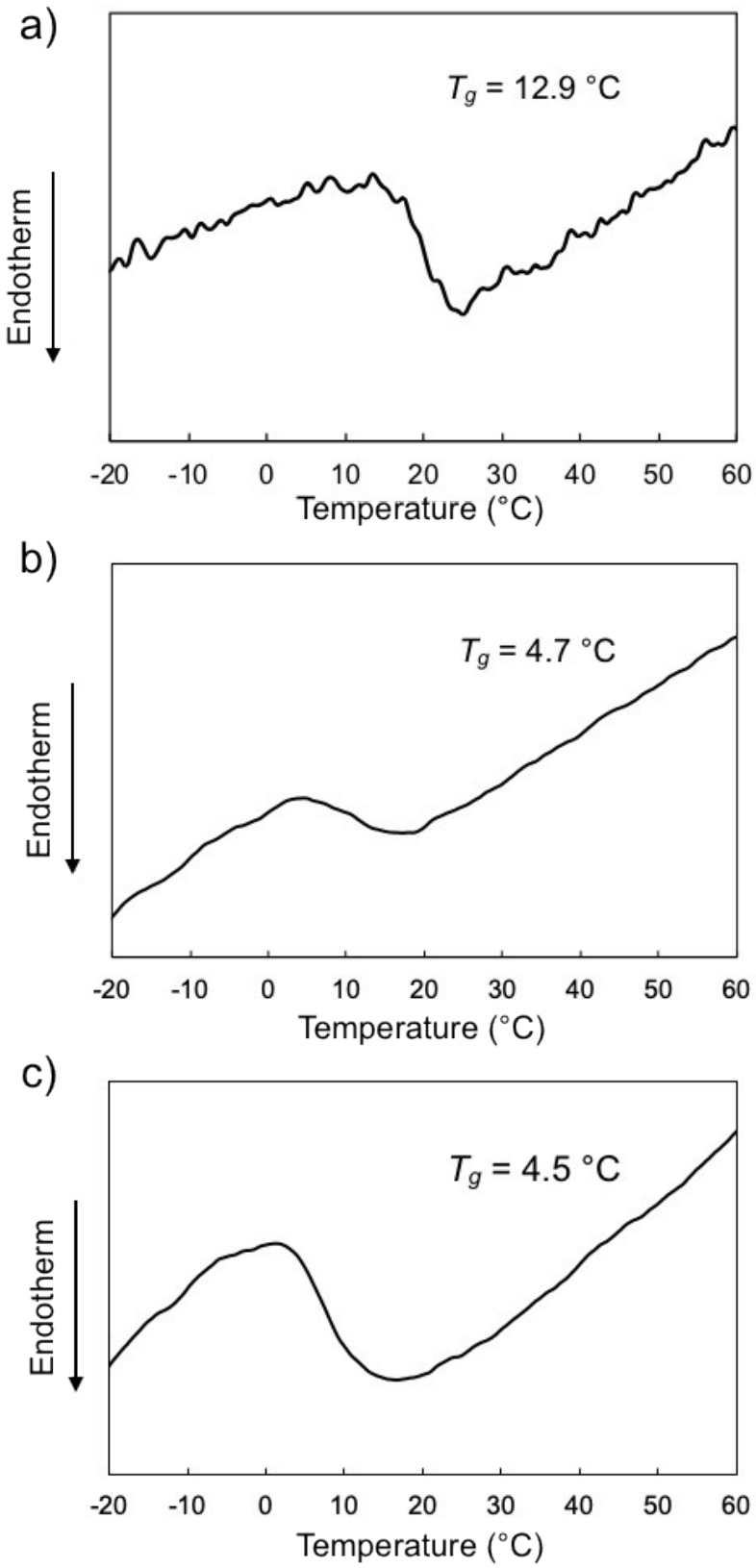


**Figure S6.** DSC charts of (a) **MP**, (b) **D-RCP** and (c) **D-CCP.**

## Results of swelling test and tensile test

Swelling test:

Swelling experiments were performed with 5.0–10 mg of cross-linked polymers in MeOH, THF, and $CHCl_3$ (ca. 5.0 mL) at 0 ºC, to avoid the reorganization of the DABBF skeleton.[1] The swelling ratio was defined as the difference in weight of the swollen gel ($W_{swollen}$) vs, the dried gel ($W_{dry}$), according to equation (1).

$$Swelling\ ratio\ [\%] = \frac{W_{swollen} - W_{dry}}{W_{dry}} \times 100 \qquad (1)$$

**Table S2**. Swelling ratio and tensile test results

| Network polymer | Swelling ratio (%) | | | Tensile test[a] | | |
|---|---|---|---|---|---|---|
| | MeOH | THF | $CHCl_3$ | Max strain (%) | Young's Modulus (MPa)[b] | Fracture energy (MJ / $m^3$) |
| **D-CCP** | 12 ± 3 | 418 ± 31 | 1281 ± 56 | 488 ± 32 | 8.4 ± 0.2 | 6.77 ± 0.45 |
| **D-RCP** | 13 ± 4 | 414 ± 22 | 1314 ± 78 | 568 ± 28 | 3.9 ± 0.3 | 4.41 ± 0.23 |

[a] As an elastomer. [b] Determined by the stress between 0 and 8% strain.

## Selected spectra information

NMR Spectra

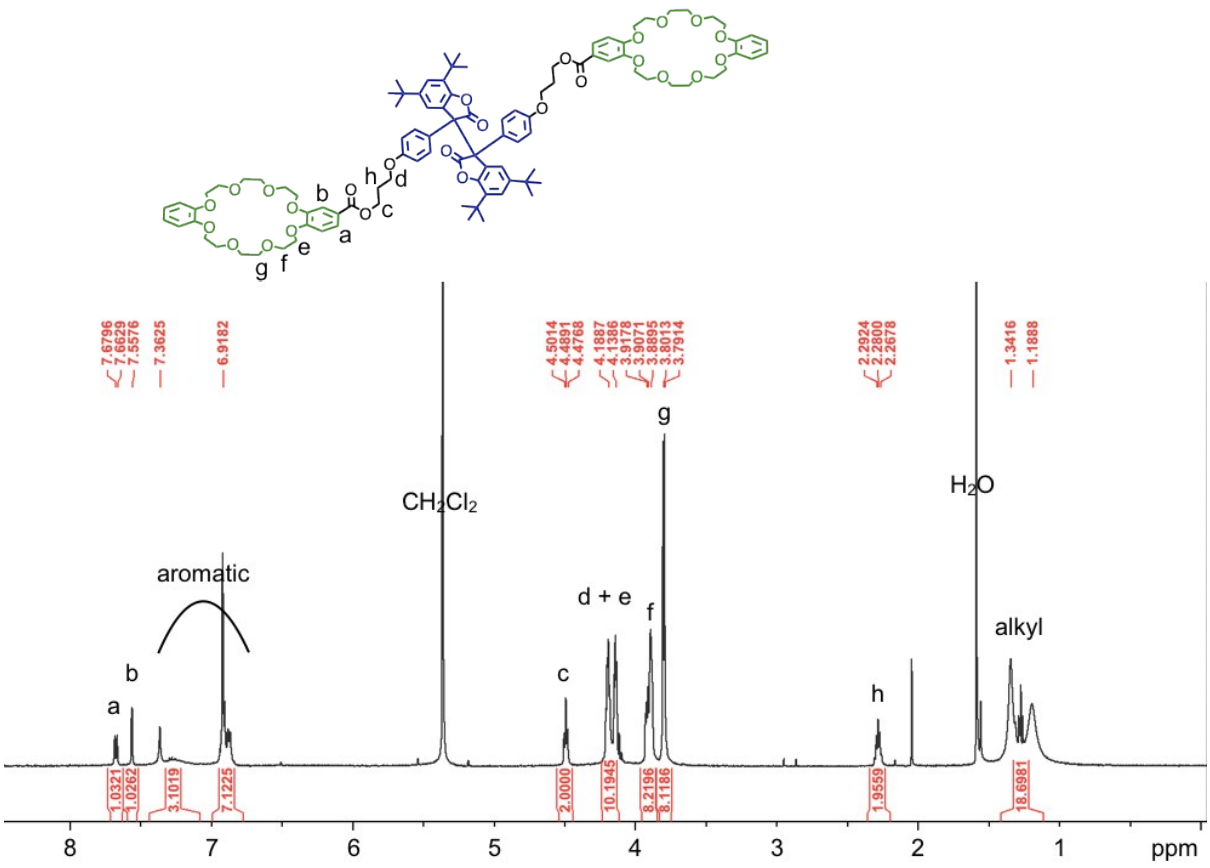



**Figure S7.** $^{1}$H NMR spectrum of **D-2MC** in $CD_2Cl_2$ (500 MHz, 25 ºC).

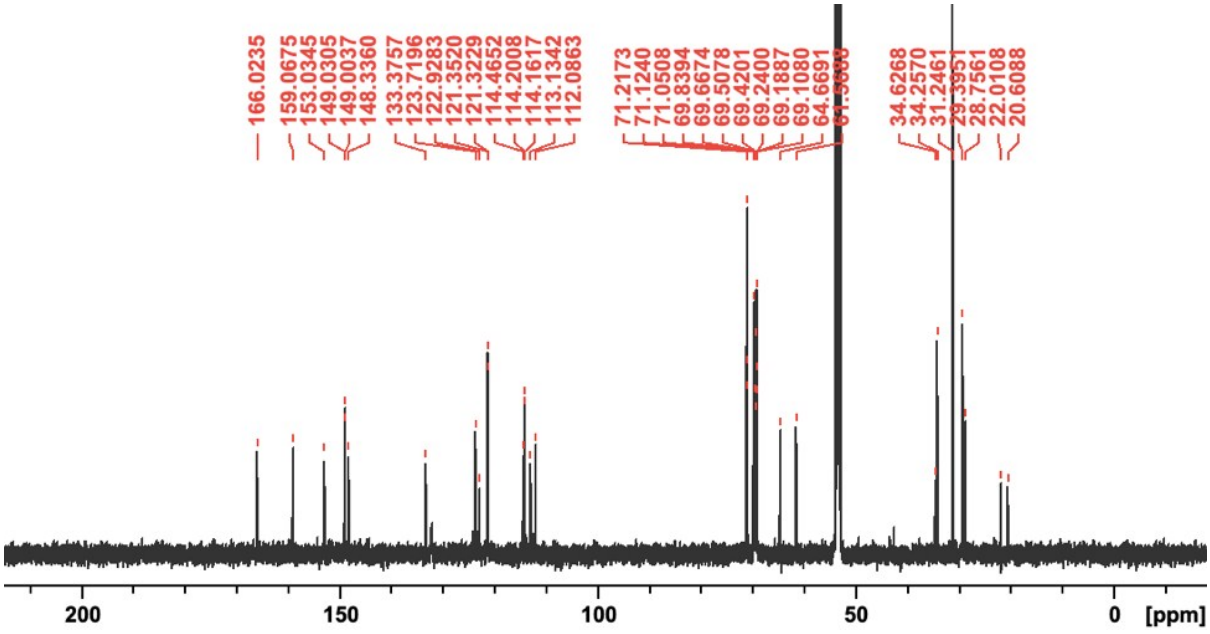



**Figure S8.** $^{13}C$ NMR spectrum of **D-2MC** in $CD_2Cl_2$ (125 MHz, 25 ºC).

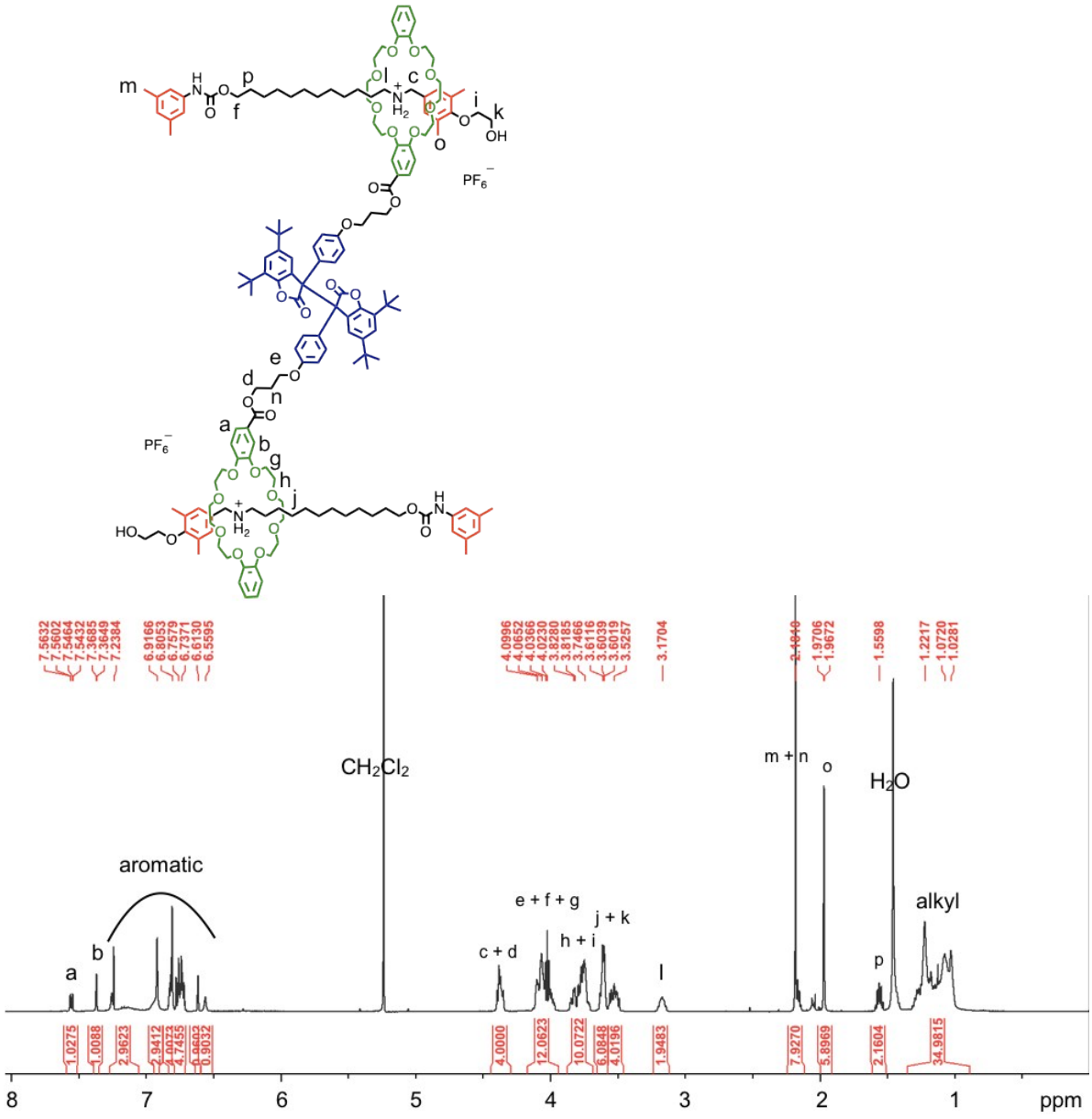



**Figure S9.** $^{1}$H NMR spectrum of **D-RC** in $CD_2Cl_2$ (500 MHz, 25 ºC).

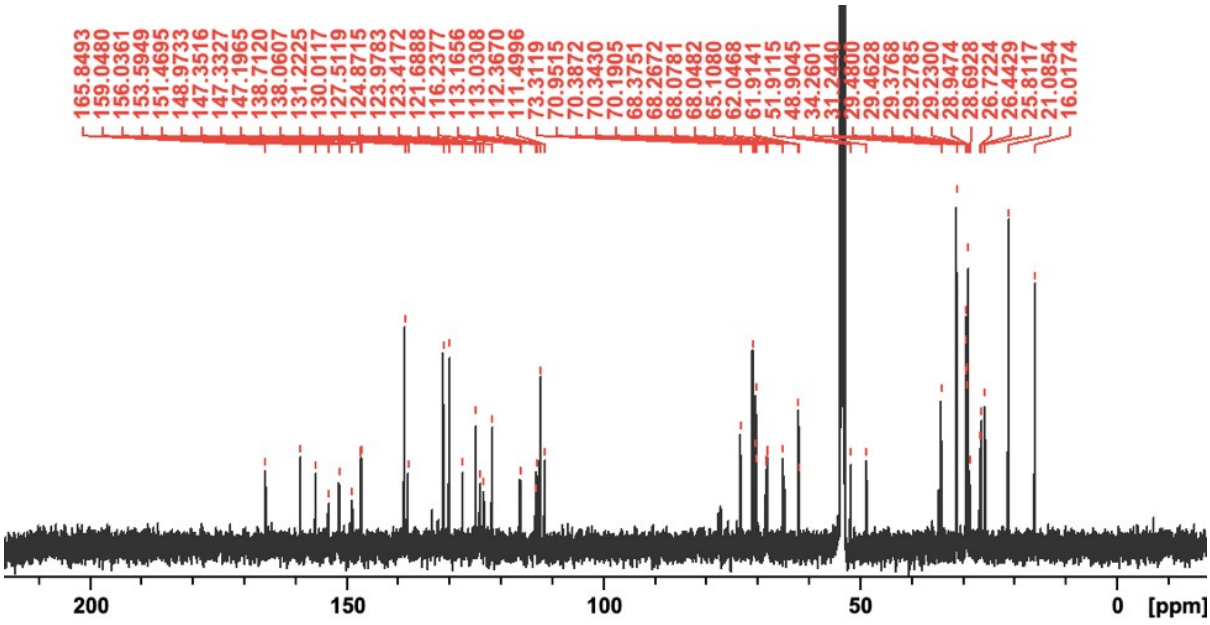



**Figure S10.** $^{13}C$ NMR spectrum of **D-RC** in $CD_2Cl_2$ (125 MHz, 25 ºC).

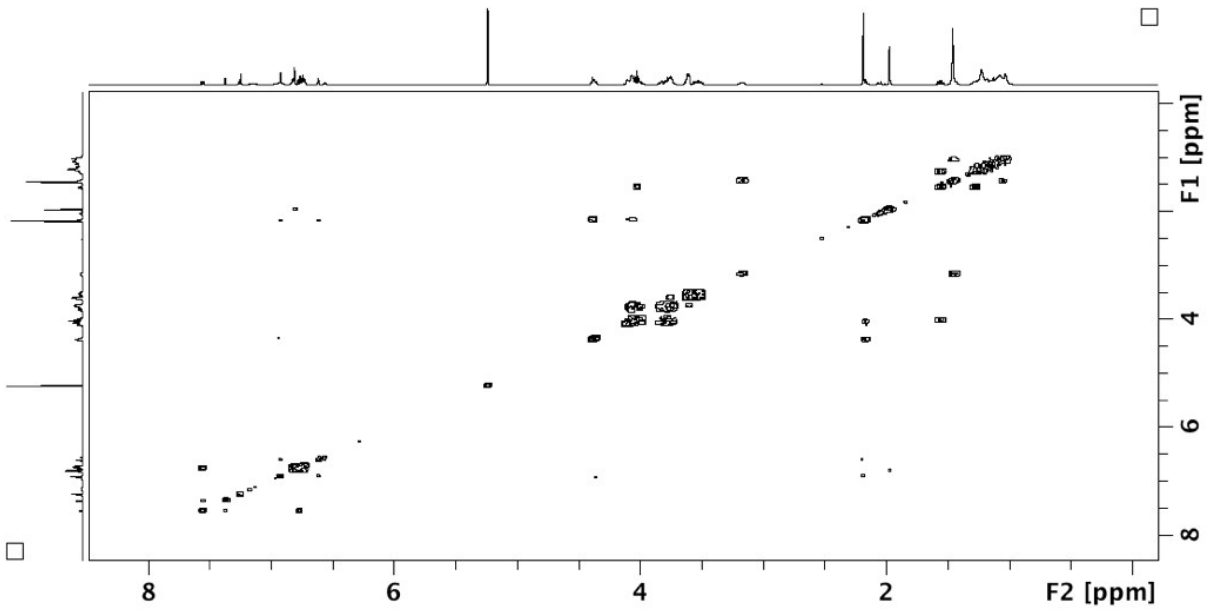



**Figure S11.** 2D H–H COSY NMR spectrum of **D-RC** in $CD_2Cl_2$ (500 MHz, 25 ºC).

IR spectra

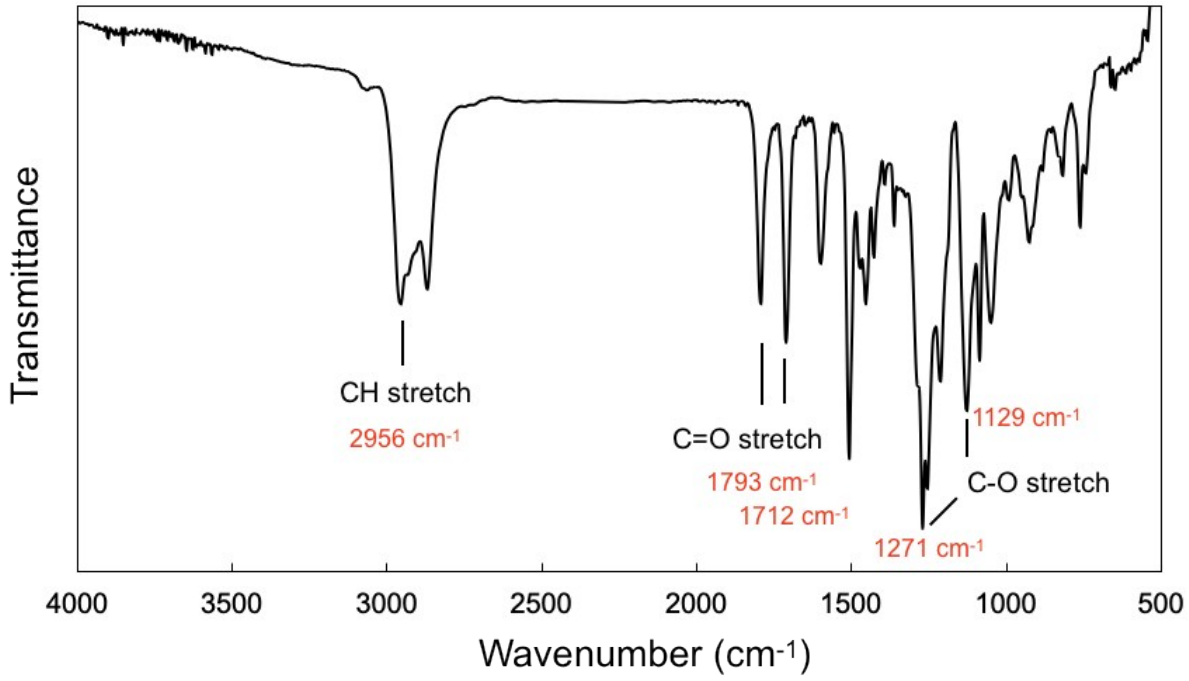



**Figure S12.** IR spectrum of **D-2MC** (NaCl).

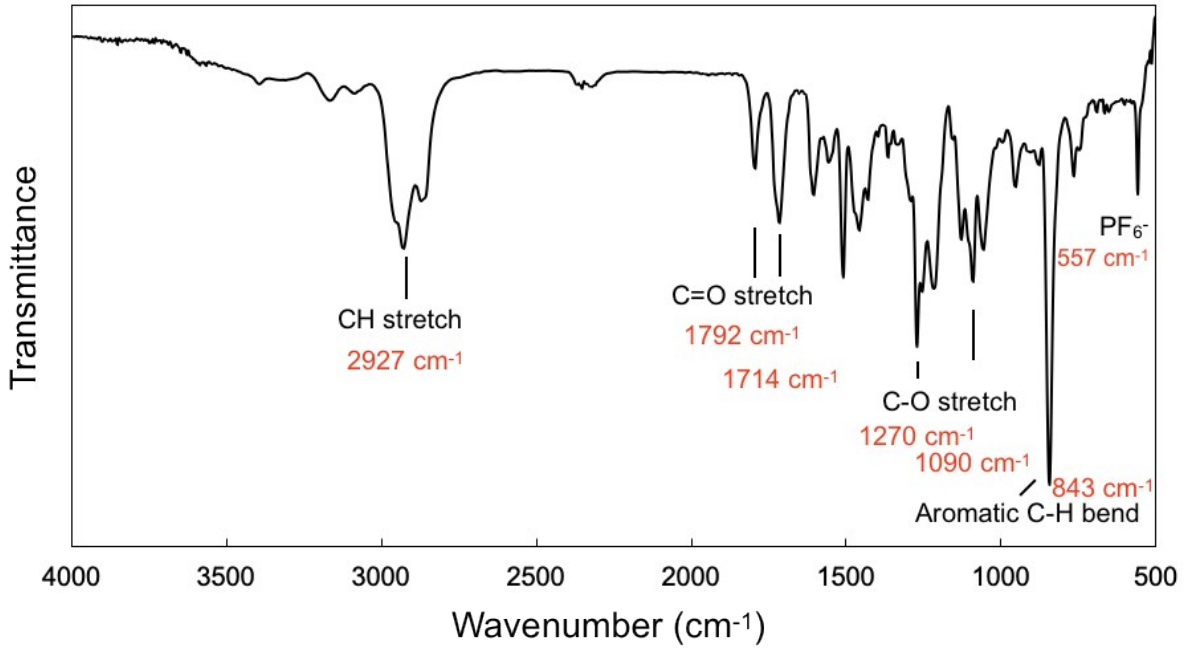



**Figure S13.** IR spectrum of **D-RC** (NaCl).

## References


[1] K. Imato, A. Irie, T. Kosuge, T. Ohishi, M. Nishihara, A. Takahara, H. Otsuka, *Angew. Chem. Int. Ed.,* 2015, **54**, 6168–6172.

[2] D. Feng, X. Li, X. Wang, X. Jiang, Z. Li, *Tetrahedron,* 2004, **60**, 6137–6144.

[3] S. J. Rao, K. Nakazono, X. Liang, K. Nakajima, T. Takata, *Chem. Commun.,* 2019, **55**, 5231–5234.