Electronic Supplementary Information (ESI)

Water Content and Guest Size Dictate the Mechanical Properties of Cyclodextrin Mediated Hydrogels

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Contents

1. Materials and Methods

Materials.

Acrylamido-methyl ether-modified αCD (αCDAAmMe) was prepared as previously reported.[1]

All materials as follows were purchased from commercial suppliers and used without further purification unless otherwise stated:

11-bromo-1-undecanol (97%, ACROS Organics), p-toluenesulfonic acid monohydrate (≥98.5%, Aldrich), 4,4'-Bipyridine (BiPy, 98%, Alfa Aesar) 2,4-dinitrochlorobenzene (99%, ACROS Organics), 4-methoxyphenol (MEHQ, 98+%, Alfa Aesar), Acrylic acid (99%, 200 ppm MEHQ as inhibitor, Sigma-Aldrich), Methyl iodide (≥99.0%, Sigma-Aldrich), aniline (≥99.5%, Aldrich), 3-(tert-butyl)aniline (97%, Alfa Aesar), 3,5-di-tert-butylaniline (97%, Alfa Aesar), benzoyl peroxide (BPO, 97% dry weight wet with 25% water, Alfa Aesar), N,N,N′,N′-tetramethyl ethylenediamine (TEMED, 99% Sigma Aldrich), dimethylacrylamide (DMAam, 99%, 500 ppm MEHQ inhibitor, ACROS Organics) DMAam was run through an alumina column prior to use to remove the MEHQ inhibitor.

All solvents and common reagents were purchased from commercial sources (Sigma Aldrich or Fisher Scientific) and used without purification Milli-Q water (18.2 MΩ·cm) was used in the preparation of all none-deuterated aqueous solutions.

Nuclear Magnetic Resonance (NMR) Spectroscopy: For small molecules ^{1}H NMR were acquired in DMSO-D6, MeOD-D_4 or D_2O at 298K and recorded on a Bruker AVANCE 500 with TCI Cryoprobe system (500 MHz) a 400 MHz Avance III HD Smart Probe Spectrometer being controlled by TopSpin2. 2D Rotating frame Overhauser Effect Spectroscopy NMR (2D ROESY NMR) experiments were carried out on a Bruker AVANCE 500 with TCI Cryoprobe system using a standard pulse sequence 'easy-roesy' with 2 s relaxation delay and 0.2 s mixing time. For the hydrogels, ^{1}H NMR and 2D Nuclear Overhauser Effect Spectroscopy NMR (2D NOESY NMR) measurements were performed with an Agilent VNS600 mainly at 30 °C. The hydrogels were dried and subsequently swollen again with D_2O in NMR tubes prior to the measurement. For 2D NOESY NMR, the mixing time was set to 200 ms. To suppress the water peak, presaturation and a diffusion filter process were performed on all measurements.

Fourier-transform infrared spectroscopy (FTIR). FTIR spectra were recorded with a Perkin Elmer Spectrum 100 instrument (Waltham, MA, USA).

High Resolution Mass Spectrometry (HRMS). HRMS spectra were collected on either a Waters Vion IMS Qtof (PV), a Waters' Xevo G2-S bench top QTOF equipped with an ASAP (Atmospheric Solids Analysis Probe) source (MV, BV, DBV) or a Waters LCT Premier (BiPyDNB, MeBiPy, PhBiPy, ^{t}BuPhBiPy, $^{t}Bu_2$PhBiPy)

Oscillatory rheological analysis: Rheological characterisation was carried out using a TA instruments discovery HR2 Hybrid Rheometer fitted with an 8 mm sandblasted geometry in order to reduce potential sample slippage from the stiff samples. Temperature was measured and maintained using the built-in platinum resistance thermocouple. Gap zeroing, rotational, and geometrical, inertia and friction calibrations were performed prior to using the rheometer. Dynamic oscillatory strain amplitude sweeps were conducted at ω = 10 rad/s. Dynamic oscillatory frequency sweep measurements were conducted at γ = 1% oscillation strain. For each hydrogel type three samples were taken from different areas of the gel and averages were calculated with error bars plotted as 95% confidence intervals. For step-strain measurements a 20 mm geometry was used and the sample was enclosed in a humid environment to negate the effect of evaporation. Low strain time sweeps were performed at γ = 1%, ω = 1 rad/s, t = 600 s while high strain sweeps were performed at γ = 500%, ω = 1 rad/s, t = 600 s.

Moisture analyzation: The water contents of the hydrogels were tuned using a moisture analyzer (heating type moisture analyzer MS-70, AND Co., Ltd.). The fully swollen hydrogels were dried at 100 °C in the moisture analyzer until they reached a specific target weight and then left overnight to equilibrate prior to mechanical testing.

After all measurements were performed, the hydrogels were then completely dried *in vacuo* at 100 °C for 5 days. The water contents of the hydrogels (W_{water}) was calculated by the following equation: (W_{water} refer as actual water contents of the hydrogels.)

$$W_{water}\ \text{wt}\ \% = \frac{W - W_{dry}}{W} \times 100$$

(W: weight of the hydrogel prior to drying,

W_{dry}: weight of the hydrogel after drying *in vacuo* at 100 ℃ for 5 days)

Uniaxial Tensile Testing: The mechanical properties of the hydrogels were determined using universal tensile testing apparatus (AG-X plus autograph, Shimadzu). The obtained hydrogels were fully swollen by immersion in excess water for 48 hours. Then, the hydrogels were cut into approximately 20 pieces and dried using a moisture analyzer as described in the above procedure. After standing overnight at room temperature in a sealed container, the hydrogels were tested at a stretching rate of 1 mm/s. For the tensile tests, at least 3 specimens were used.

Small Angle X-ray Scattering (SAXS) measurement: Internal structures of hydrogels and dried gels were determined by SAXS at the BL40B2 beam line in SPring-8, Nishi-harima, Japan. The lengths of the scattering vector, q, were 0.1~1.0 nm^{-1}, where $q = 4\pi\sin\theta/\lambda$ (2θ and λ are the scattering angle and the wavelength, respectively). For the hydrogels, λ and the camera length were 0.1 nm and 2282 mm, respectively. Water contents of hydrogels were roughly tuned prior to measurement as described in the moisture analyzation section. The water contents were finely tuned again just before the SAXS measurements. After each SAXS measurement, the mass of the test hydrogel was recorded in order to calculate accurate water content. For the dried gels, the values for λ and camera length were 0.07 nm and 2281 mm, respectively. The dried gels were obtained by *in situ* drying at 175~185 °C on a heating stage for at least for 5 minutes. *In situ* SAXS measurements for the dried gels were performed when the temperature of the heating stage was stable at a specific set temperature.

Differential Scanning Calorimetry (DSC): Thermal properties of the dried gels were evaluated by DSC equipment (NEXTA DSC200, Hitachi High-Tech Science) with a measuring program (0-200 °C with a heat rate of 10 °C/min under N_2 atmosphere). The obtained hydrogels were dried as described in the above procedure prior to DSC measurements. The dried gels underwent heating from 0 to 200 °C followed by cooling to 0 °C with a rate of 10 °C/min under an N_2 atmosphere prior to the main measurement to erase any thermal history of the materials.

2. Synthesis of viologen monomers

As exemplified by PhBiPyC11OAc in **Fig. S1** a general synthesis for all viologen compounds was used.

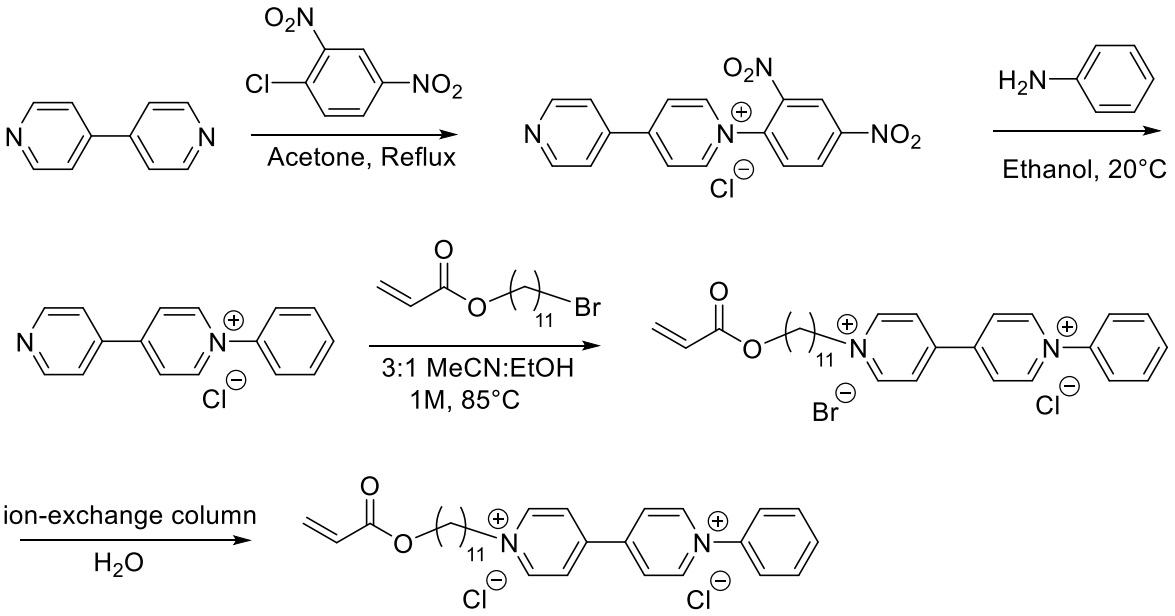

Fig. S1: Synthetic route of 1-(11-(acryloyloxy)undecyl)-1'-phenyl-[4,4'-bipyridine]-1,1'-diium bromide chloride (PhBiPyC11OAc).

11-bromoundecyl acrylate (BrC11OAc)

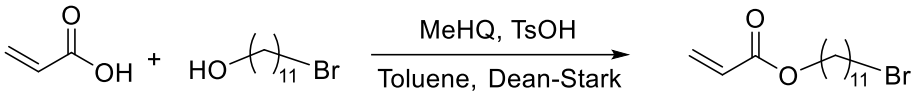

Fig. S2: Synthetic route of 11-bromoundecyl acrylate (BrC11OAc).

11-bromo-1-undecanol (10 g, 39.8 mmol), p-toluenesulfonic acid monohydrate (TsOH, 11.36 g, 59.73 mmol, 1.5 eq.) and 4-methoxyphenol (MEHQ, added as inhibitor, 0.49 g, 3.98 mmol, 0.1 eq.) were dissolved in toluene (150 mL) in a round bottom flask with a stirrer bar. Dean-Stark apparatus was added and the mixture was refluxed for 2 hours until sufficiently dry. Acrylic acid (4.30 g, 59.73 mmol, 1.5 eq.) was added and the mixture was heated under reflux for 48 h. After cooling to room temperature, the solution was washed with 10% NaOH solution (3 × 100 mL), dried with magnesium sulfate and the solvent was removed under vacuum. Purification by column chromatography (hexane:ethyl acetate 0% → 10%) afforded the product as a transparent, light yellow oil (5.45 g, 45%). (R_f 10% Ehtyl acetate:Hexane = 0.47)

^{1}H NMR (600 MHz, DMSO-d_6) δ 6.31 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.16 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.93 (dd, *J* = 10.4, 1.5 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.51 (t, *J* = 6.7 Hz, 2H), 1.78 (dt, *J* = 14.5, 6.8 Hz, 2H), 1.59 (dt, *J* = 8.1, 6.5 Hz, 2H), 1.36 (dt, *J* = 10.2, 6.5 Hz, 2H), 1.32 – 1.23 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 165.85, 131.51, 128.86, 64.47, 35.35, 32.76, 29.39, 29.37, 29.15, 28.64, 28.59, 28.02, 25.86.

FT-IR (neat): 2926 (C-H alkenyl), 2856 (C-H alkyl), 1725 (C=O), 1637 (C=C), 1466, 1407, 1296, 1272, 1189, 1060, 984, 967, 810.

These results were in good agreement with literature data.[2]

1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium chloride (BiPyDNB)

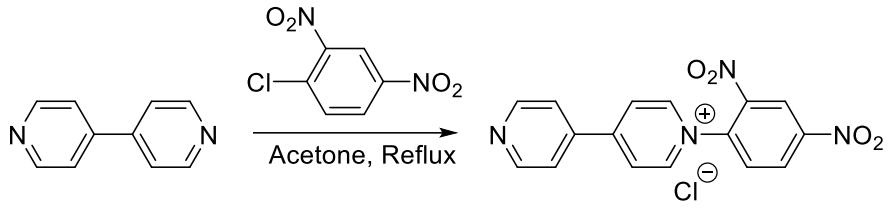

Fig. S3: Synthetic route for 1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium chloride (BiPyDNB).

1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium was prepared via. A modified literature protocol, briefly;4,4'-Bipyridine (3.51 g, 22.5 mmol) and 2,4-dinitrochlorobenzene (3.05 g, 15 mmol, 0.67 eq.) were dissolved in acetone (25 mL) and heated under reflux for 14 hours. The precipitate was collected by vacuum filtration and washed with several portions of dichloromethane, drying under reduced pressure at 40°C yielded the pure product as a yellow powder (2.97 g, 41%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 – 9.55 (m, 2H), 9.16 (d, *J* = 2.5 Hz, 1H), 9.02 (dd, *J* = 8.7, 2.5 Hz, 1H), 9.00 – 8.93 (m, 4H), 8.47 (d, *J* = 8.7 Hz, 1H), 8.24 – 8.18 (m, 2H).

^{13}C NMR (101 MHz, DMSO) δ 155.45, 151.66, 150.93, 149.59, 147.15, 143.60, 140.81, 138.96, 132.62, 130.72, 125.65, 122.67.

FT-IR (neat): 2988 (C-H aryl),1637 (C=C aryl), 1609, 1533 (N-O), 1344, 1223, 1075, 919.

HRMS: Calculated for $[M\text{-}Cl]^{1+}$, $C_{16}H_{11}N_4O_4^+$: 323.0775, found: 323.0791.

These results were in good agreement with literature data.[3]

1-methyl-[4,4'-bipyridin]-1-ium iodide (MeBiPy)

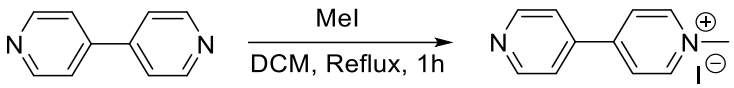

Fig. S4: Synthetic route for 1-methyl-[4,4'-bipyridin]-1-ium iodide (MeBiPy)

1-methyl-[4,4'-bipyridin]-1-ium iodide was prepared according to a literature procedure. Briefly; 4,4'-bipyridine (10.0 g, 64 mmol) was dissolved in 150 mL dichloromethane (DCM). Methyl iodide (5.0 mL, 81 mmol) in DCM (50 mL) was added drop-wise to the stirred flask. The mixture was then heated under reflux for 1 hour and left to cool to room temperature with stirring. The product was separated via vacuum filtration and then recrystalized from methanol and washed with ether yielding the product as yellow crystals (15.44 g, 81%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (d, J = 6.6 Hz, 2H), 8.89 – 8.83 (m, 2H), 8.66 – 8.60 (m, 2H), 8.08 – 8.02 (m, 2H), 4.41 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 152.30, 151.47, 146.60, 141.30, 125.43, 122.34, 48.11.

FT-IR: 3025 (C-H aryl), 2982 (C-H alkyl), 1957, 1640 (C=C aryl), 1600, 1547, 1415, 1333, 1221, 1194, 994, 862, 814, 714, 656.

HRMS: Calculated for $[M\text{-}Cl]^{1+}$, $C_{11}H_{11}N_2^+$: 171.0917, found: 171.0924.

These results were in good agreement with literature data.[4]

1-phenyl-[4,4'-bipyridin]-1-ium chloride (PhBiPy)

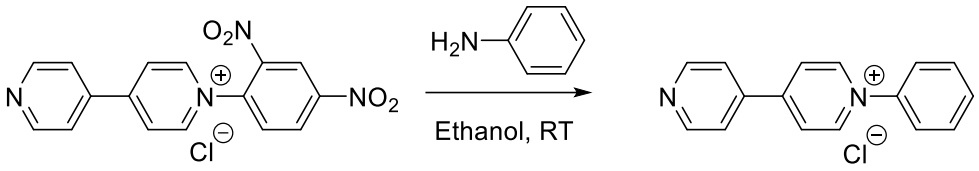

Fig. S5: Synthetic route for 1-phenyl-[4,4'-bipyridin]-1-ium chloride (PhBiPy).

BiPyDNB (1.08 g, 3.00 mmol) and aniline (293.35 g, 3.15 mmol, 1.05 eq.) were dissolved in ethanol (10 mL) and stirred for 24 h at room temperature. The solution was then concentrated to ~1 mL and precipitated into ethyl acetate ~250 mL. Vacuum filtration followed by drying under reduced pressure at 40 °C yielded the product as a yellow/orange powder (597 mg, 85% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 – 9.47 (m, 2H), 8.98 – 8.87 (m, 2H), 8.85 – 8.75 (m, 2H), 8.21 – 8.14 (m, 2H), 7.99 – 7.89 (m, 2H), 7.84 – 7.70 (m, 3H).

^{13}C NMR (101 MHz, DMSO) δ 151.57, 145.93, 131.78, 130.67, 129.74, 125.78, 125.25, 123.88, 122.56, 120.30.

FT-IR (neat): 3017 (C-H Aryl), 1635 (C=C aryl), 1597, 1489, 1442, 1412, 1333, 1257.

HRMS: Calculated for $[M+H]^{1+}$, $C_{16}H_{13}N_2^+$+H: 234.1151, found: 234.1120.

These results were in good agreement with literature data.[5]

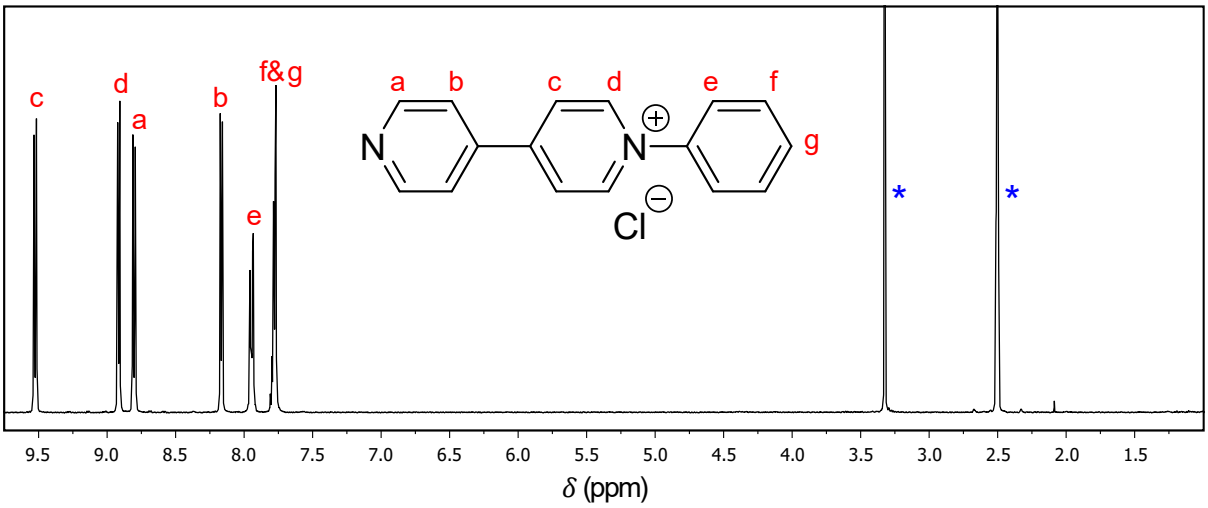

Fig. S6: ^{1}H NMR spectrum of PhBiPy. Recorded in DMSO-$D_{6.}$ (* = DMSO, water).

1-(11-(acryloyloxy)undecyl)-1'-phenyl-[4,4'-bipyridine]-1,1'-diium bromide chloride (PV)

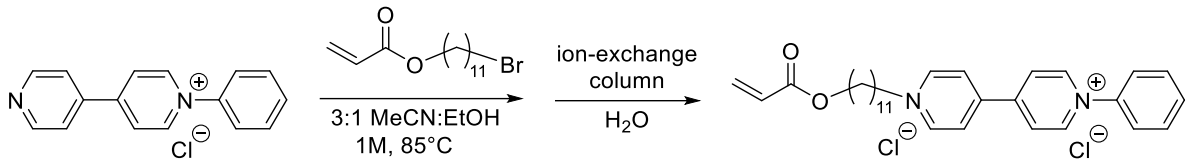

Fig. S7: Synthetic route for 1-(11-(acryloyloxy)undecyl)-1'-phenyl-[4,4'-bipyridine]-1,1'-diium bromide chloride (PhBiPyC11OAc).

PhBiPy (537 mg, 2 mmol) and BrC11OAc (3.05 g, 10 mmol, 5 eq.) were dissolved in a 3:1 acetonitrile:ethanol mixture (2 mL, 2 M concentration of PhBiPy) in a 10 mL round bottom flask. The flask was then fitted with a septum and the mixture was heated to 85 °C with stirring. After 48 hours, conversion (by NMR) was typically >80%. The solution was then precipitated into ether and recrystallized in a minimum amount of hot acetonitrile to give the mixed salt product as needle-like crystals. Finally the compound was dissolved in the minimum amount of deionized water, passed through an ion exchange column and dried by rotary evaporation and desiccation in a vacuum oven to yield 1-(11-(acryloyloxy)undecyl)-1'-phenyl-[4,4'-bipyridine]-1,1'-diium chloride, **PV** as a pale yellow, powder (360 mg, 31% isolated yield)

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.73 – 9.67 (m, 2H), 9.46 (d, J = 6.5 Hz, 2H), 9.00 – 8.91 (m, 4H), 8.02 – 7.94 (m, 2H), 7.87 – 7.77 (m, 3H), 6.32 (dd, J = 17.2, 1.7 Hz, 1H), 6.17 (dd, J = 17.3, 10.3 Hz, 1H), 5.94 (dd, J = 10.2, 1.7 Hz, 1H), 4.73 (t, J = 7.5 Hz, 2H), 4.10 (t, J = 6.6 Hz, 2H), 2.00 (p, J = 6.8 Hz, 2H), 1.61 (p, J = 6.5 Hz, 2H), 1.36 – 1.26 (m, 12H).

^{13}C NMR (101 MHz, DMSO) δ 165.98, 149.73, 148.55, 146.32, 142.68, 132.01, 131.85, 130.69, 128.85, 127.28, 127.04, 125.32, 64.52, 61.22, 40.63, 40.42, 40.21, 40.00, 39.79, 39.58, 39.37, 31.32, 29.33, 29.31, 29.24, 29.06, 28.89, 28.53, 25.91, 25.80.

FT-IR: 3000 (C-H Aryl), 2920 (C-H alkenyl), 2851 (C-H alkyl), 1717 (C=O), 1633 (C=C), 1436, 1407, 1189.

HRMS: Calculated for $[M\text{-}2Cl]^{2+}$, $C_{30}H_{38}N_2O_2^{2+}$: 458.2928, found: 458.2920.

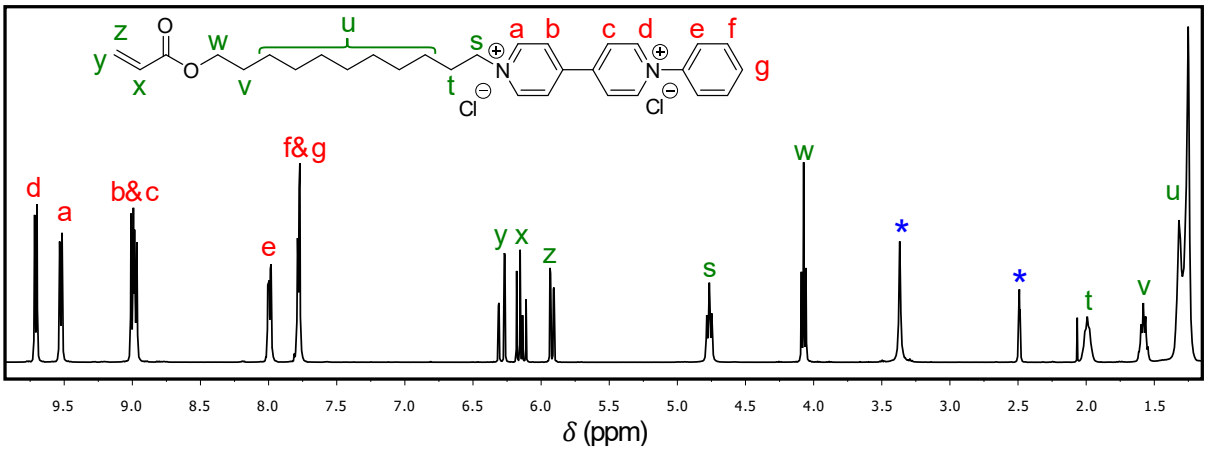

Fig. S8: ^{1}H NMR spectrum of PV. Recorded in DMSO-D_6.
(* = DMSO, water)

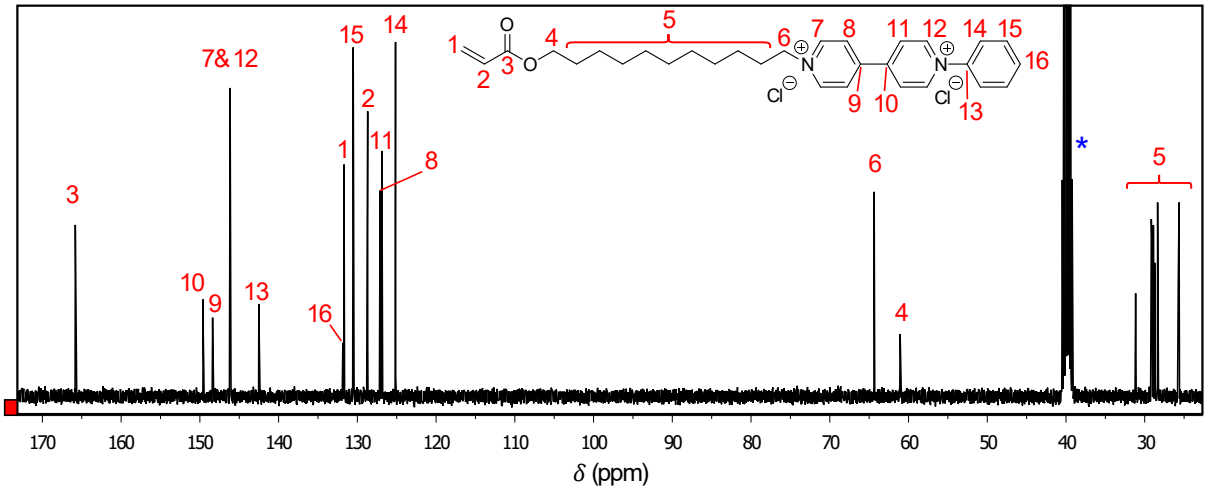

Fig. S9: ^{13}C NMR spectrum of PV. Recorded in DMSO-D_6.
(* = DMSO)

Products with different aryl groups were synthesized via the same synthetic procedures as PhBiPy and PhBiPyC11OAc with the exception of MeBiPyC11OAc which used MeBiPy synthesized as described above.

1-(3-(tert-butyl)phenyl)-[4,4'-bipyridin]-1-ium chloride (^{t}Bu$_1$PhBiPy)

Synthesized using PhBiPy procedure with 3-(tert-butyl)aniline, 1.80 g, 84%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.57 – 9.50 (m, 2H), 8.95 – 8.89 (m, 2H), 8.82 – 8.75 (m, 2H), 8.20 – 8.14 (m, 2H), 7.94 (t, *J* = 2.0 Hz, 1H), 7.84 – 7.72 (m, 2H), 7.70 (t, *J* = 7.8 Hz, 1H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, DMSO-d_6)) δ 153.86, 153.43, 151.57, 146.04, 142.80, 141.11, 130.37, 128.68, 125.76, 122.59, 122.38, 122.35, 35.54, 31.38.

FT-IR: 3011 (C-H aryl) , 2966 (C-H alkyl), 2948, 2862, 1632 (C=C aryl), 1610, 1490, 1428, 1409, 1220, 1064, 992, 875, 822, 805, 702, 650.

HRMS: Calculated for $[M\text{-}Cl]^{1+}$, $C_{20}H_{21}N_2^+$: 234.1699, found: 289.1725.

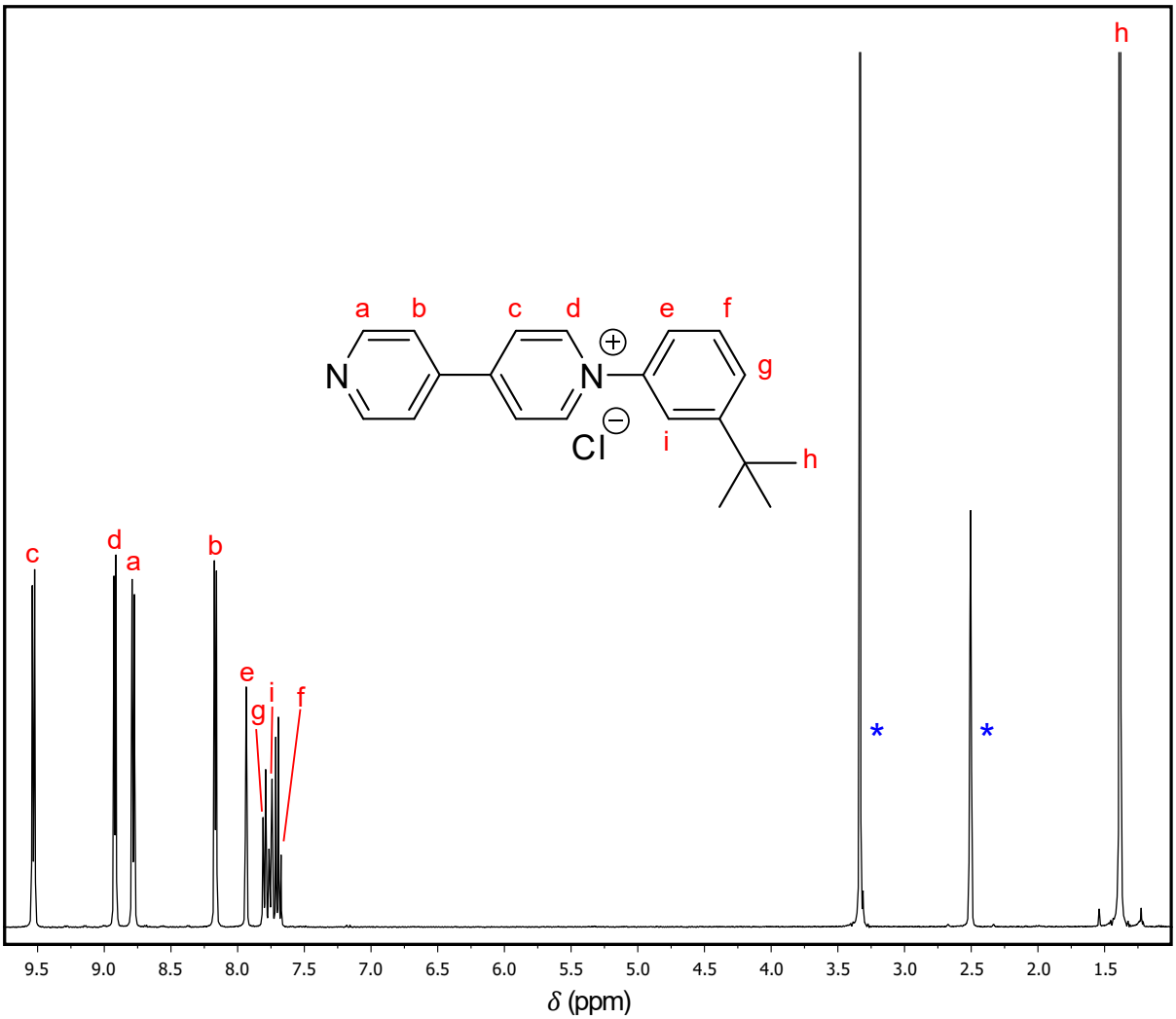

Fig. S10: ^{1}H NMR spectrum of ^{t}Bu$_{1}$PhBiPy. Recorded in DMSO-D$_{6}$.

(* = DMSO, water)

1-(3,5-di-tert-butylphenyl)-[4,4'-bipyridin]-1-ium chloride (^{t}Bu$_2$PhBiPy)

Synthesized using PhBiPy procedure with 3,5-di-tert-butylaniline, 890 g, 78%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 – 9.51 (m, 2H), 8.99 – 8.90 (m, 2H), 8.84 – 8.73 (m, 2H), 8.21 – 8.15 (m, 2H), 7.79 – 7.73 (m, 3H), 1.39 (s, 18H).

^{13}C NMR (151 MHz, DMSO-d_6) 13C NMR (101 MHz, DMSO) δ 153.87, 153.44, 151.58, 146.06, 142.81, 141.12, 130.38, 128.69, 125.76, 122.60, 122.40, 122.37, 35.55, 31.39.

FT-IR: 3110, 3027 (C-H aryl) , 2962 (C-H aklyl), 2870, 1635 (C=C aryl), 1590, 1479, 1435, 1408, 1365, 1219, 1083, 873, 816, 707.

HRMS: Calculated for $[M+H]^{1+}$,$C_{24}H_{29}N_2^+$+H: 346.2404, found: 346.2370.

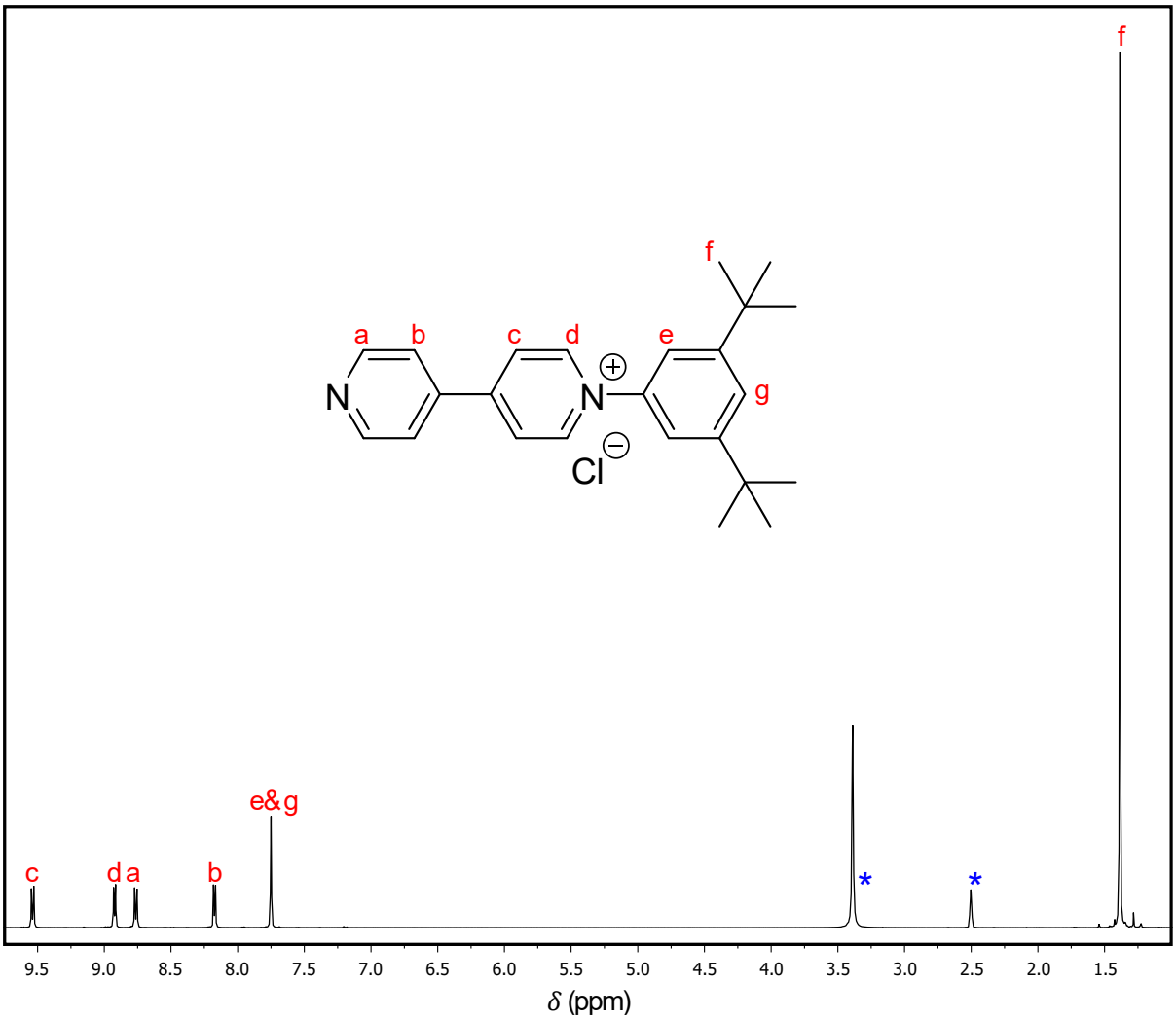

Fig. S11: ^{1}H NMR spectrum of $^{t}Bu_2PhBiPy$. Recorded in DMSO-D_6.

(* = DMSO, water)

1-(11-(acryloyloxy)undecyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium bromide iodide (MV)

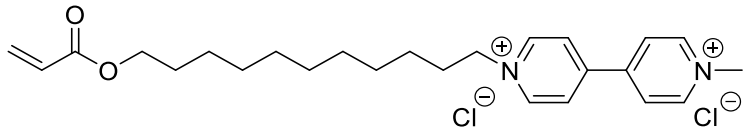

Fig. S12: 1-(11-(acryloyloxy)undecyl)-1'-methyl-[4,4'-bipyridine]-1,1'-diium bromide iodide (MV).

Synthesized using the PV procedure with MeBiPy, 500 mg,
82% conversion, 41% isolated yield.

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.41 – 9.37 (m, 2H), 9.30 (d, J = 6.4 Hz, 2H), 8.81 – 8.74 (m, 4H), 6.31 (dd, J = 17.3, 1.6 Hz, 1H), 6.16 (dd, J = 17.3, 10.3 Hz, 1H), 5.94 (dd, J = 10.4, 1.6 Hz, 1H), 4.68 (t, J = 7.5 Hz, 2H), 4.44 (s, 3H), 4.09 (t, J = 6.7 Hz, 2H), 2.04 – 1.91 (m, 2H), 1.59 (p, J = 6.7 Hz, 2H), 1.33 – 1.24 (m, 14H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.98, 148.94, 148.57, 147.09, 146.23, 131.82, 128.86, 127.02, 126.57, 64.51, 61.24, 48.47, 31.24, 29.31, 29.29, 29.22, 29.04, 28.86, 28.52, 25.88, 25.79.

FT-IR: 2991 (C-H Aryl), 2920, (C-H alkenyl) 2853 (C-H alkyl), 1719 (C=O), 1638 (C=C), 1198, 824.

HRMS: Calculated for $[M\text{-}2Cl]^{2+}$, $C_{25}H_{36}N_2O_2^{2+}$: 396.2777, found: 396.2775

These results were in good agreement with literature data.[6]

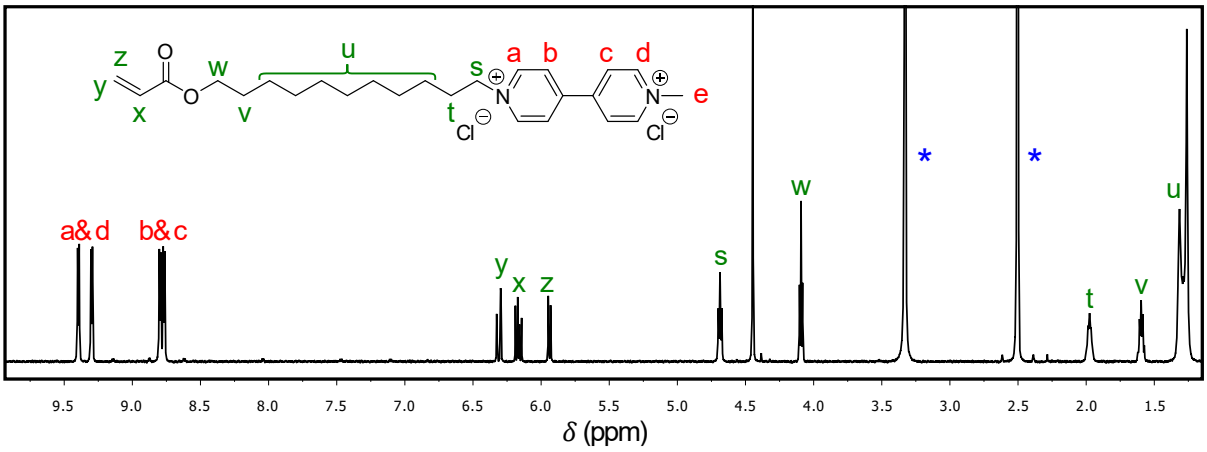

Fig. S13: ^{1}H NMR spectrum of MV. Recorded in DMSO-D$_6$.

(* = DMSO, water)

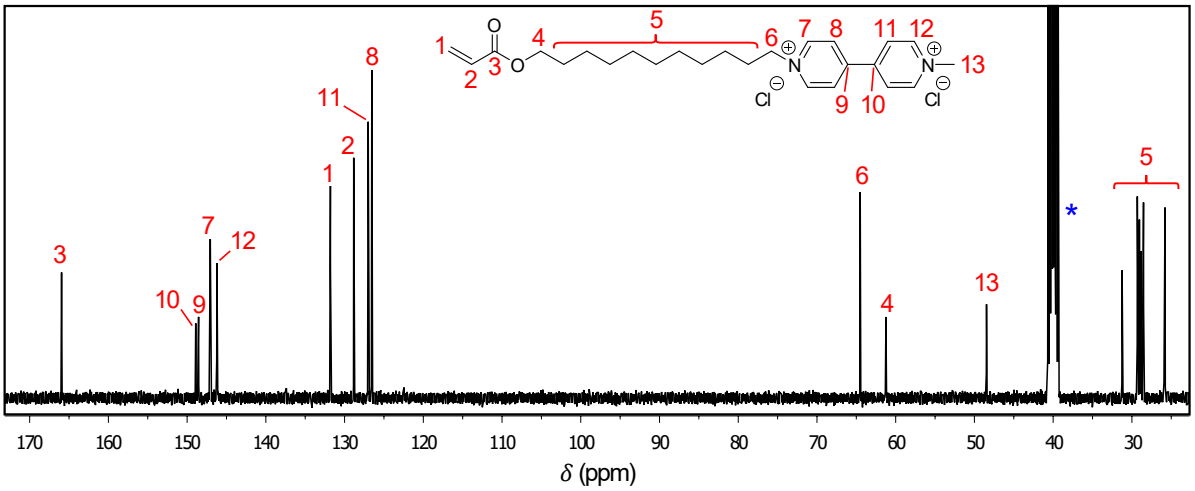

Fig. S14: ^{13}C NMR spectrum of MV. Recorded in DMSO-D$_6$.

(* = DMSO)

1-(11-(acryloyloxy)undecyl)-1'-(3-(tert-butyl)phenyl)-[4,4'-bipyridine]-1,1'-diium bromide chloride (BV)

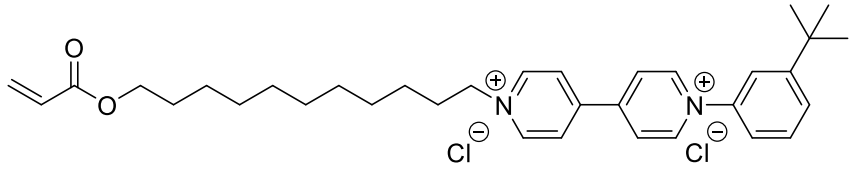

Fig. S15: 1-(11-(acryloyloxy)undecyl)-1'-(3-(tert-butyl)phenyl)-[4,4'-bipyridine]-1,1'-diium bromide chloride (BV).

Synthesized using the PV procedure with $^{t}Bu_1PhBiPy$, 371 mg, 80% conversion, 29% isolated yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.74 – 9.67 (m, 2H), 9.57 – 9.48 (m, 2H), 9.00 – 8.92 (m, 4H), 7.96 (t, *J* = 2.1 Hz, 1H), 7.79 (dddd, *J* = 8.1, 3.4, 2.1, 1.1 Hz, 2H), 7.69 (t, *J* = 7.9 Hz, 1H), 6.29 (dd, *J* = 17.3, 1.7 Hz, 1H), 6.14 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.92 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.76 (t, *J* = 7.5 Hz, 2H), 4.07 (t, *J* = 6.6 Hz, 2H), 1.99 (p, *J* = 7.0 Hz, 2H), 1.56 (dt, *J* = 13.8, 7.0 Hz, 2H), 1.37 (s, 9H), 1.35 – 1.23 (m, 14H).

^{13}C NMR (101 MHz, DMSO) δ 165.98, 153.86, 149.62, 148.61, 146.43, 146.33, 142.71, 131.85, 130.38, 128.95, 128.85, 127.29, 126.94, 122.48, 122.40, 64.52, 61.23, 35.54, 31.35, 29.33, 29.31, 29.25, 29.06, 28.90, 28.53, 25.92, 25.81, 25.79.

FT-IR: 3037 (C-H Aryl), 2954 (C-H alkenyl), 2927 (C-H alkyl),, 2855, 1726 (C=O), 1636 (C=C), 1431, 1408, 1185, 984, 811, 708.

HRMS: Calculated for $[M+H]^{2+}$, $C_{34}H_{46}N_2O_2^{2+}$+H: 515.3638, found: 515.3641.

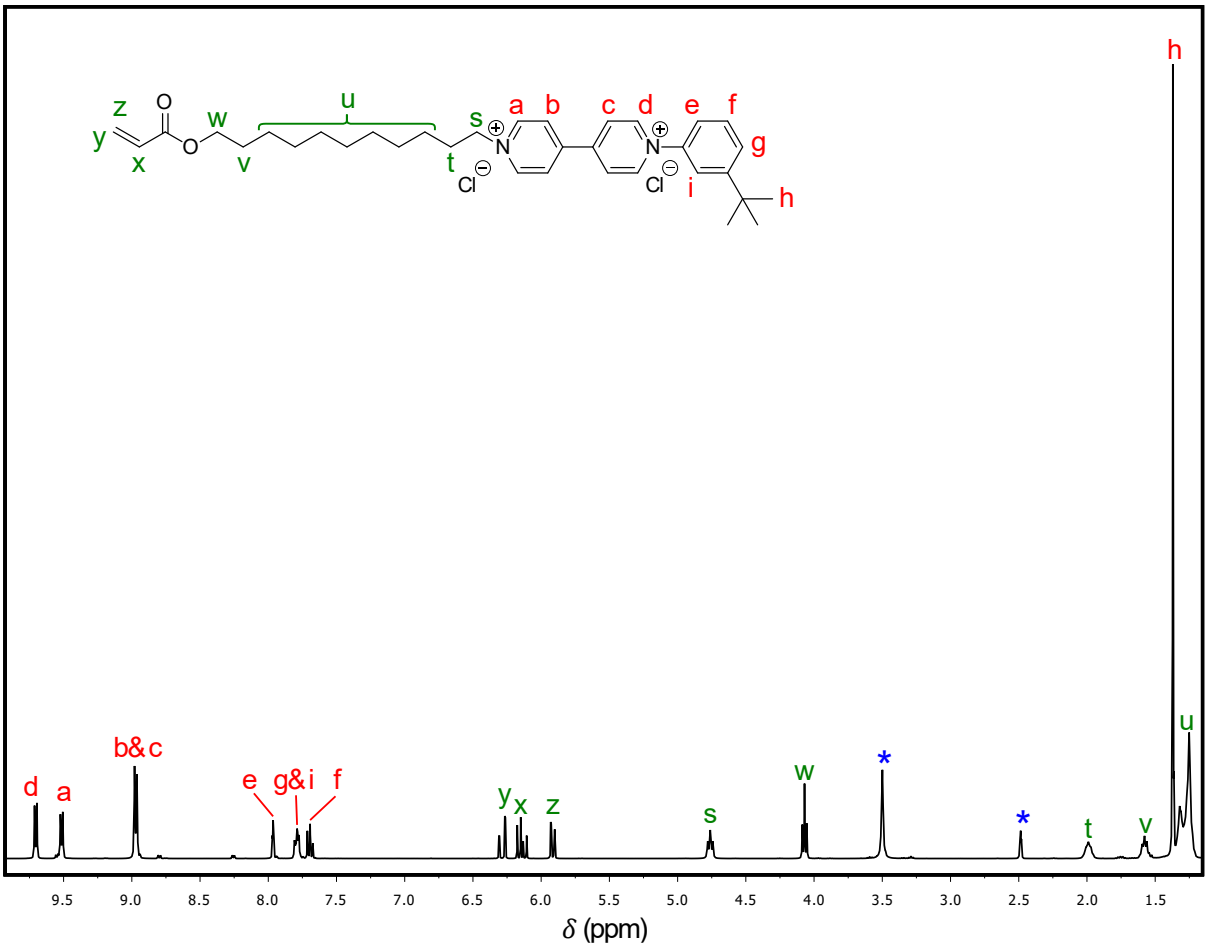

Fig. S16: ^{1}H NMR spectrum of BV. Recorded in DMSO-D_6.

(* = DMSO, water)

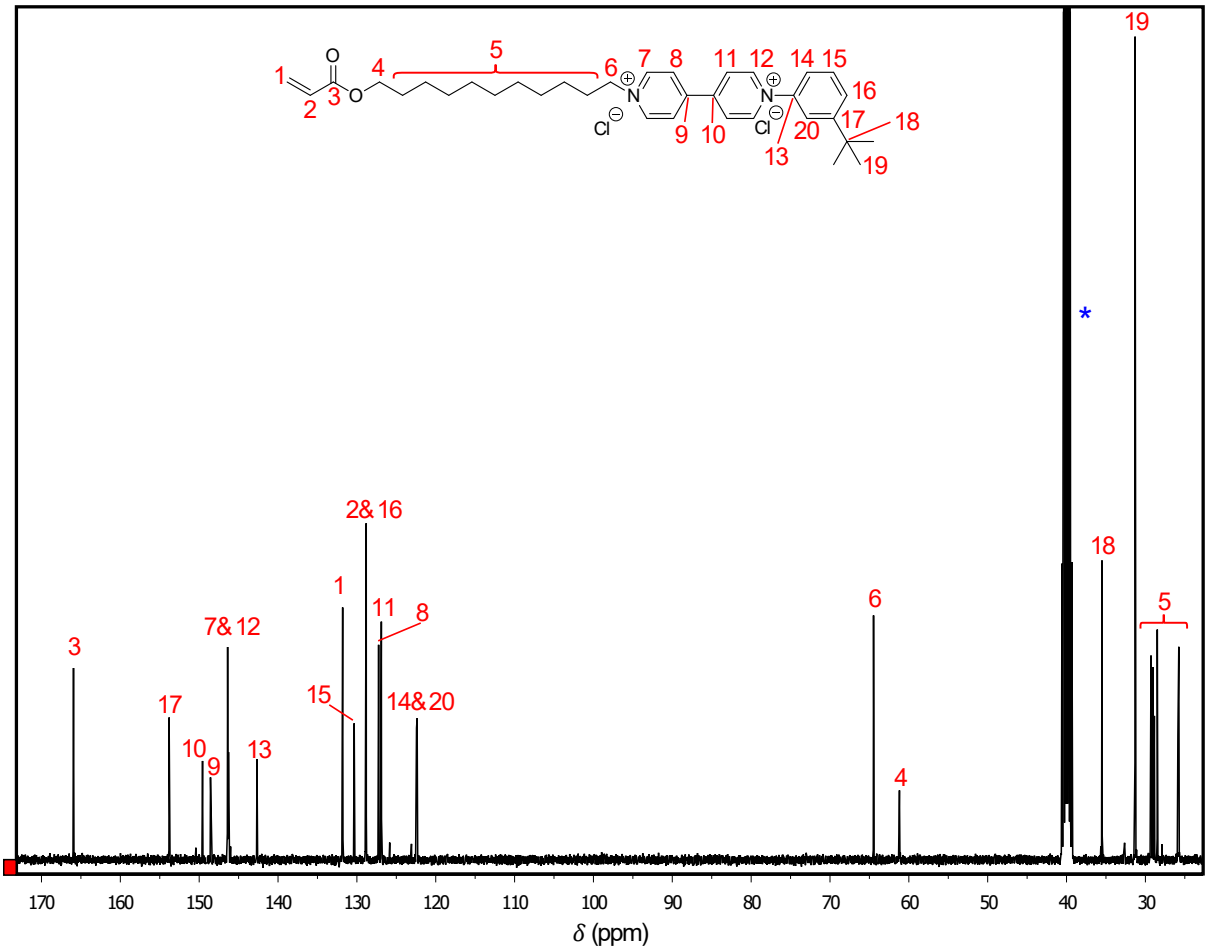

Fig. S17: ^{13}C NMR spectrum of BV. Recorded in DMSO-D_6.

(* = DMSO)

1-(11-(acryloyloxy)undecyl)-1'-(3,5-di-tert-butylphenyl)-[4,4'-bipyridine]-1,1'-diium bromide chloride (DBV)

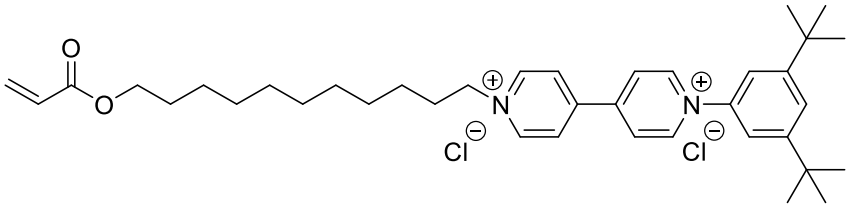

Fig. S18: 1-(11-(acryloyloxy)undecyl)-1'-(3,5-di-tert-butylphenyl)-[4,4'-bipyridine]-1,1'-diium bromide chloride (DBV).

Synthesized using the PV procedure with $^{t}Bu_2PhBiPy$, 270 mg,
86% conversion, 29% isolated yield.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.71 – 9.65 (m, 2H), 9.44 (d, *J* = 6.5 Hz, 2H), 8.91 (dd, *J* = 6.9, 5.0 Hz, 4H), 7.80 (t, *J* = 1.6 Hz, 1H), 7.76 (d, *J* = 1.7 Hz, 2H), 6.32 (dd, *J* = 17.2, 1.7 Hz, 1H), 6.17 (dd, *J* = 17.3, 10.3 Hz, 1H), 5.94 (dd, *J* = 10.3, 1.7 Hz, 1H), 4.73 (t, *J* = 7.5 Hz, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 2.01 (p, *J* = 7.4 Hz, 2H), 1.61 (p, *J* = 6.8 Hz, 2H), 1.40 (s, 18H), 1.37 – 1.25 (m, 14H).

^{13}C NMR (101 MHz, DMSO) δ 165.99, 153.43, 149.52, 148.68, 146.53, 146.32, 142.68, 131.85, 128.85, 127.29, 126.83, 119.72, 64.52, 61.25, 35.66, 31.45, 31.35, 29.33, 29.31, 29.25, 29.06, 28.90, 28.53, 25.93, 25.81.

FT-IR: 3000 (C-H Aryl), 2959, 2925 2920 (C-H alkenyl), 2852 (C-H alkyl), 1720, (C-H alkyl), 1630 (C=C), 1423, 1198, 841, 812 704.

HRMS: Calculated for $[M+H]^{2+}$, $C_{38}H_{54}N_2O_2^{2+}$+H : 571.4264, found: 571.4246.

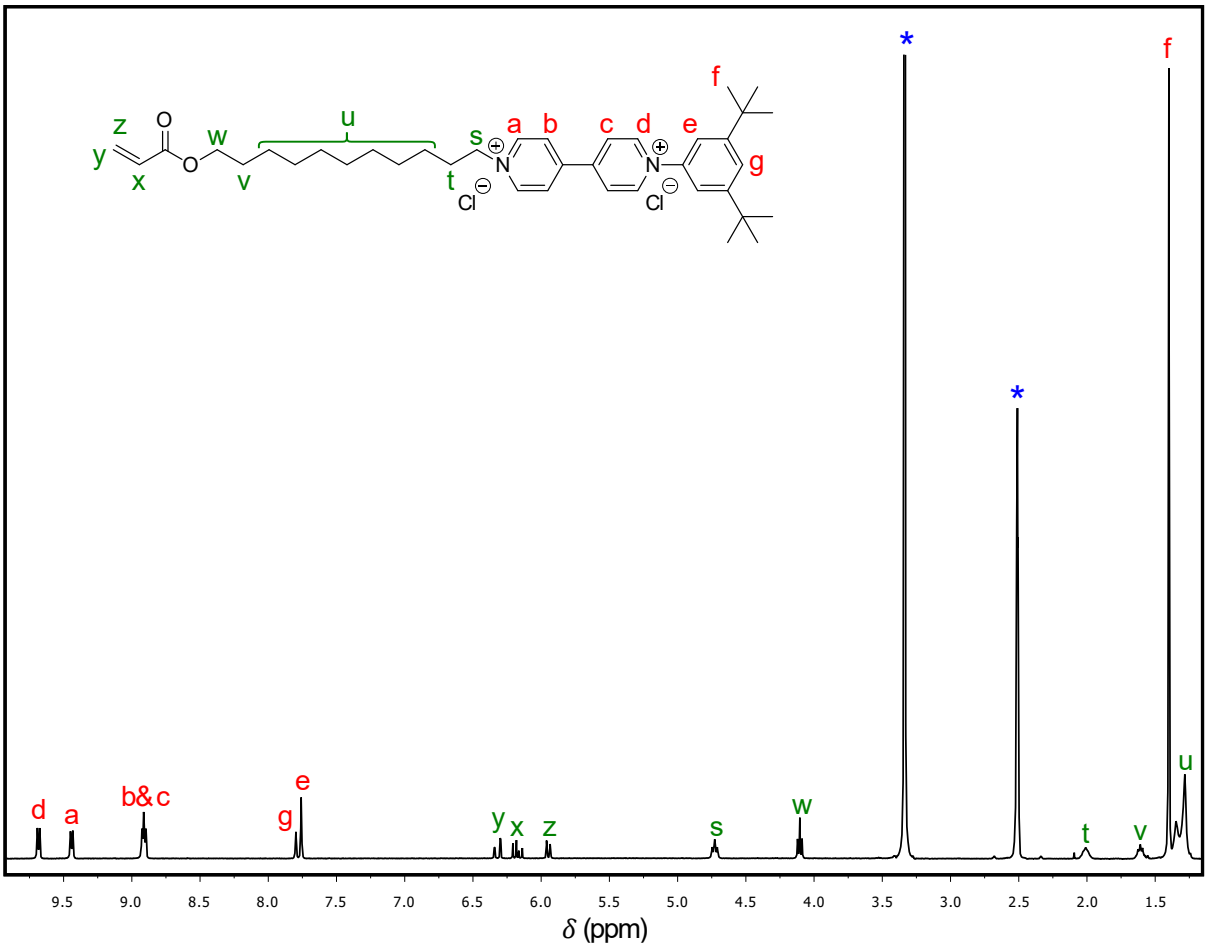

Fig. S19: ^{1}H NMR spectrum of DBV. Recorded in DMSO-D_6.

(* = DMSO, water)

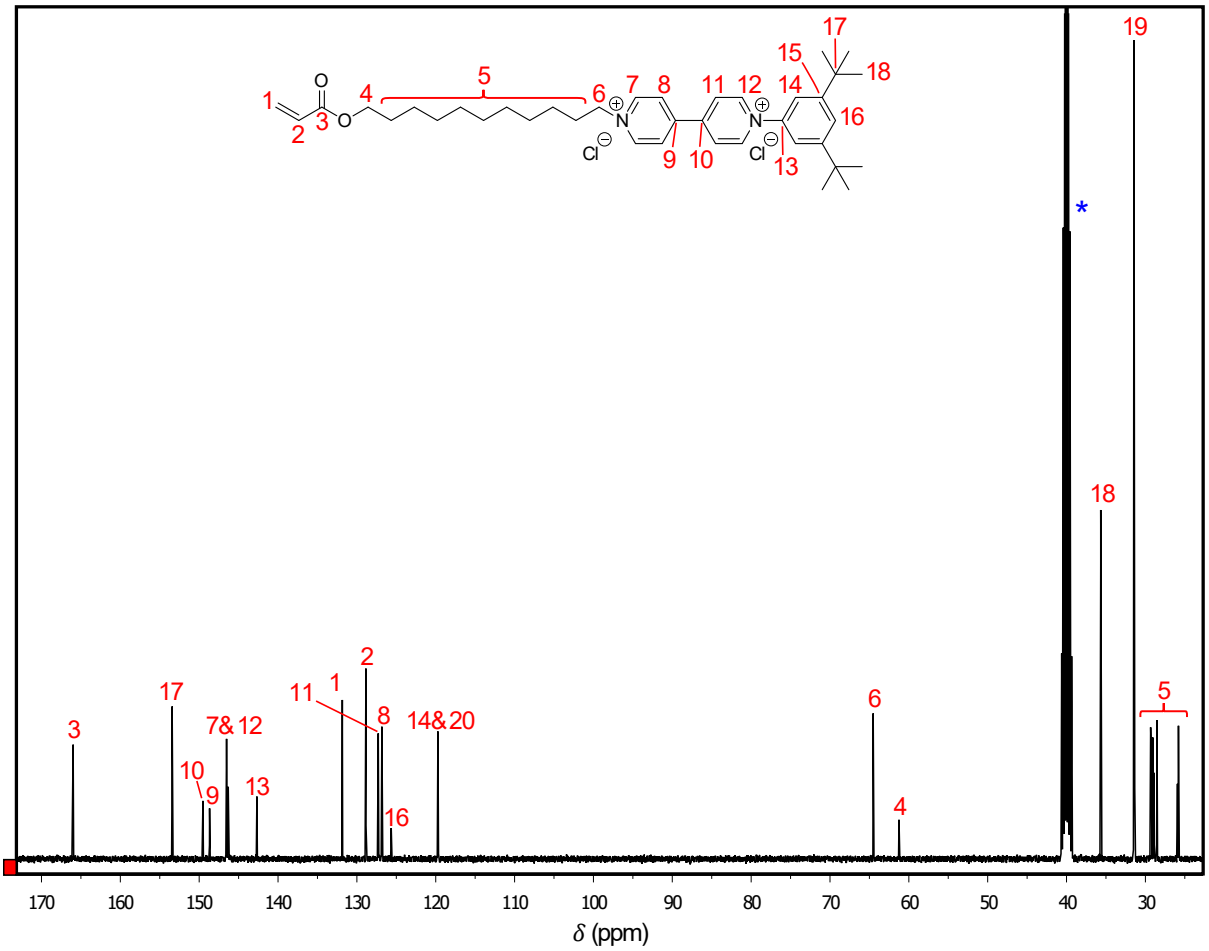

Fig. S20: ^{13}C NMR spectrum of DBV. Recorded in DMSO-D_6. (* = DMSO)

3. 2D ROESY NMR measurements of monomer solutions

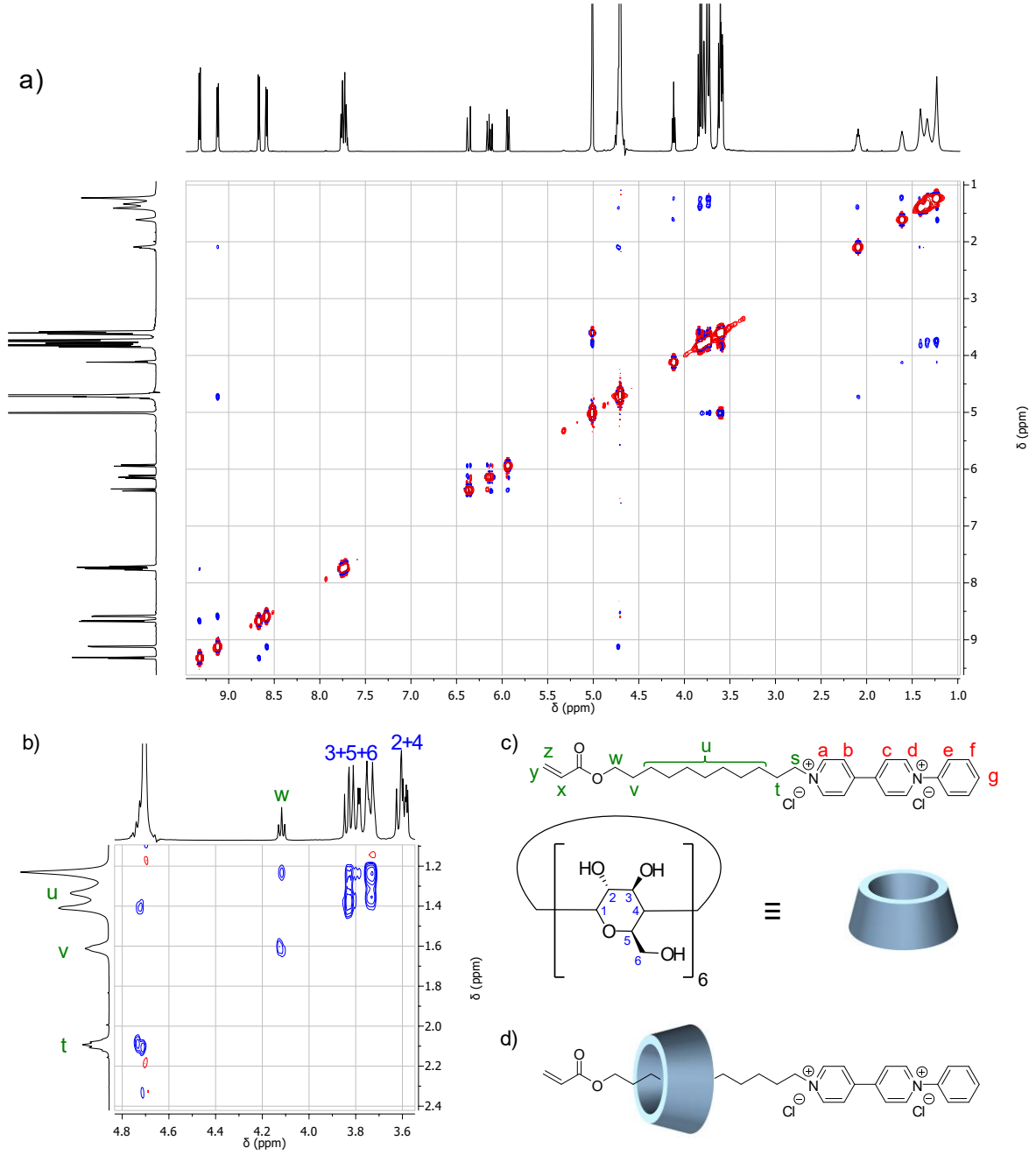

Fig. S21: 2D ROESY NMR spectrum of a mixture of αCD with PV (D_2O, 500 MHz, 25 °C). a) Full spectrum b) Zoomed spectrum to highlight interaction of αCD with the alkyl chain. c) Labelled structure of PV and αCD d) Proposed structure of the inclusion complex.

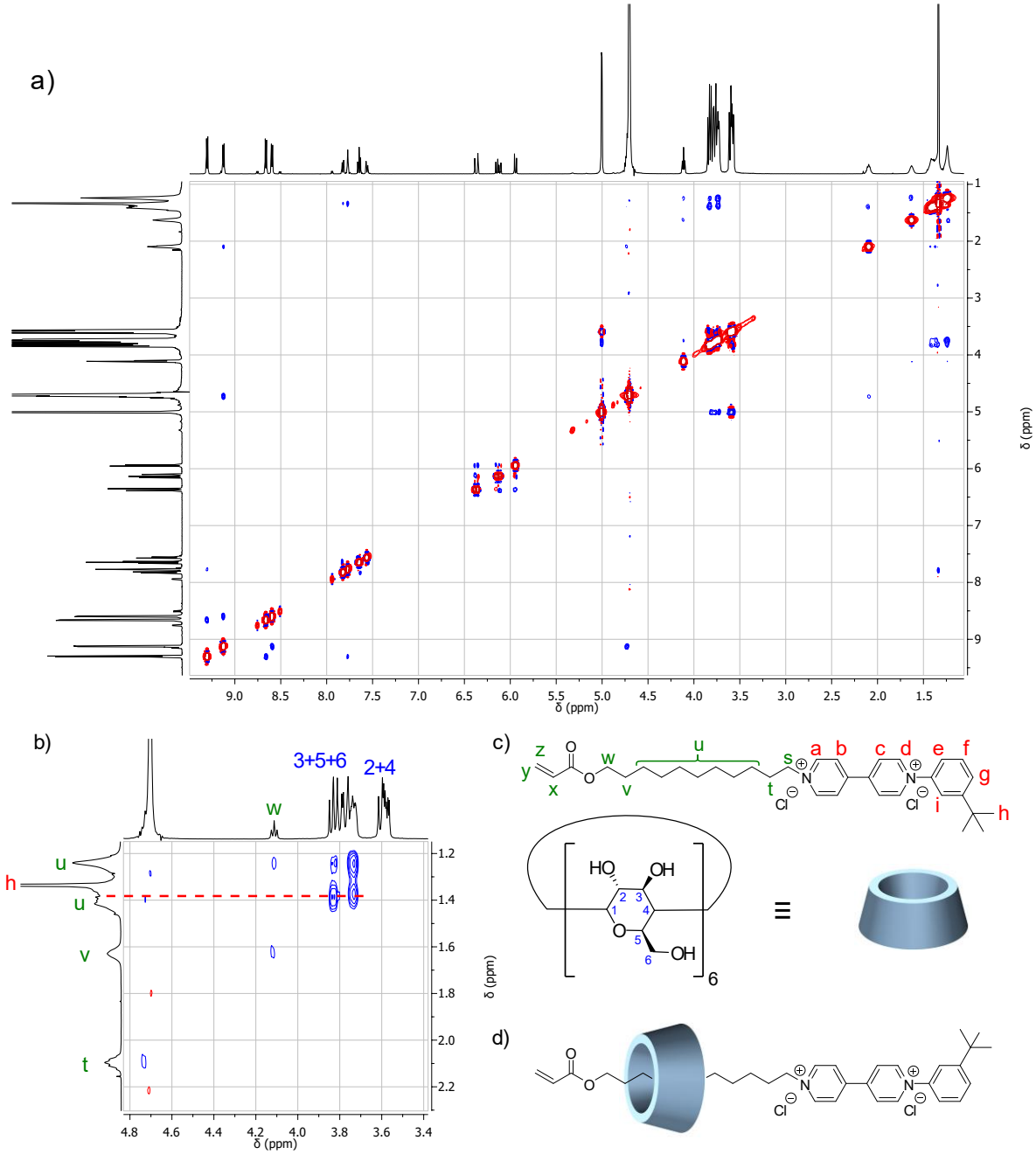

Fig. S22: 2D ROESY NMR spectrum of a mixture of αCD. with BV (D_2O, 500 MHz, 25 °C). a) Full spectrum b) Zoomed spectrum to highlight interaction of αCD with the alkyl chain but not the t-butyl group c) Labelled structure of BV and αCD d) Proposed structure of the inclusion complex.

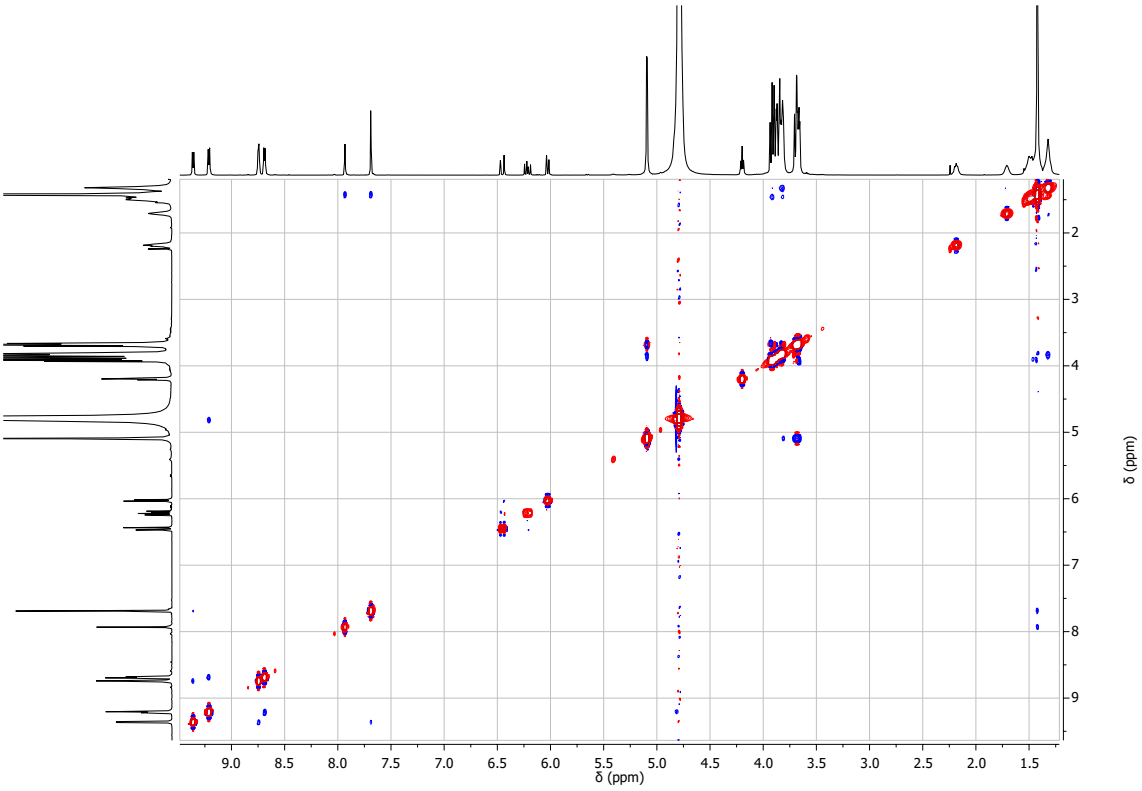

Fig. S23: Full 2D ROESY NMR spectrum of a mixture of αCD with DBV (D_2O, 500 MHz, 25 °C).

4. Preparation of the hydrogels

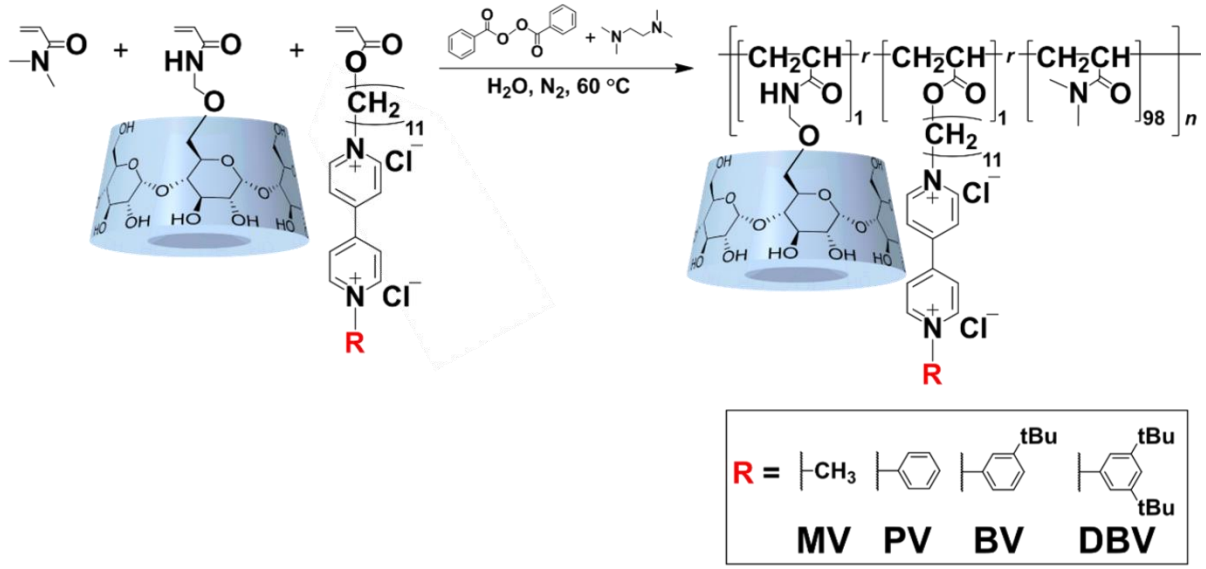

Fig. S24: Polymerization scheme for the the preparation of hydrogels.

All hydrogels were prepared via a generic procedure as exemplified with αCD-MV below:

αCDAAmMe (63.4 mg, 0.06 mmol, 1 mol%) was initially dissolved in water (1.5 mL) in a 6 dram (22 mL) vial with heating from a heat-gun and sonication. Once αCDAAmMe had fully dissolved, MV (28.0 mg, 0.06 mmol, 1 mol%) was added and dissolved with further sonication for one hour. In another vial, benzoyl peroxide (BPO) (8.7 mg, 0.036 mmol) was dissolved in N,N-Dimethylacrylamide (DMAam, inhibitor removed as stated above) (582.9 mg, 605.9 µL, 5.88 mmol, 98 mol%). The DMAam/BPO solution was then carefully pipetted into the aqueous solution of αCDAAmMe and MV leading to a stable dispersion of BPO in a DMAam/water mixed solvent. The vial was then fitted with a septum, placed into an ice-bath and degassed by purging with nitrogen for 20 minutes. After this time, the septum was removed, and *N,N,N′,N′*-Tetramethyl ethylenediamine (TEMED) (4.2 mg, 5.4 µL, 0.036 mmol) was added. The solution was then sonicated in an ice bath for 30 seconds before being transferred via pipette into a laboratory-made open-topped mould consisting of a u-shaped piece of butyl rubber (2 cm width × 3 cm height × 2 mm thickness) clamped upright between two pieces of polypropylene sheet. The mould was then placed into an oven at 60°C for 2 hours, after which the resulting hydrogel could be removed from the mould and swollen in water as previously described.

Table S1: Amounts of reagents used for the polymerisation of each type of hydrogel.

Hydrogel	αCDAAmMe (mg)	Guest (mg)	BPO (mg)	TEMED (μL)	DMAam (μL)	H_2O (μL)
αCD-MV	63.4	28.0	8.7	5.4	605.9	1500
αCD-PV	63.4	34.4	8.7	5.4	605.9	1500
αCD-BV	63.4	37.8	8.7	5.4	605.9	1500
αCD-DBV	63.4	41.2	8.7	5.4	605.9	1500

5. NMR measurements of the hydrogels

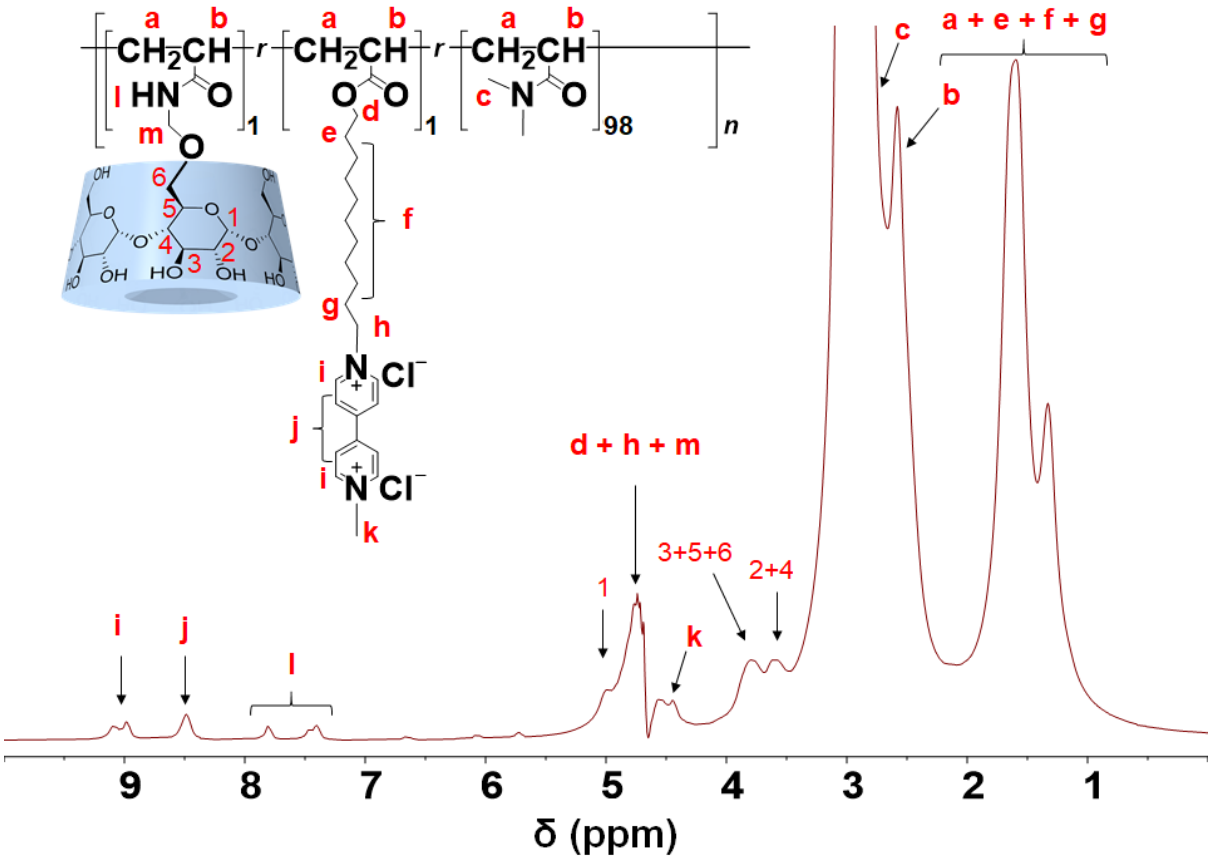

Fig. S25: ^{1}H NMR spectrum of αCD-MV in D_2O at 30 ºC.

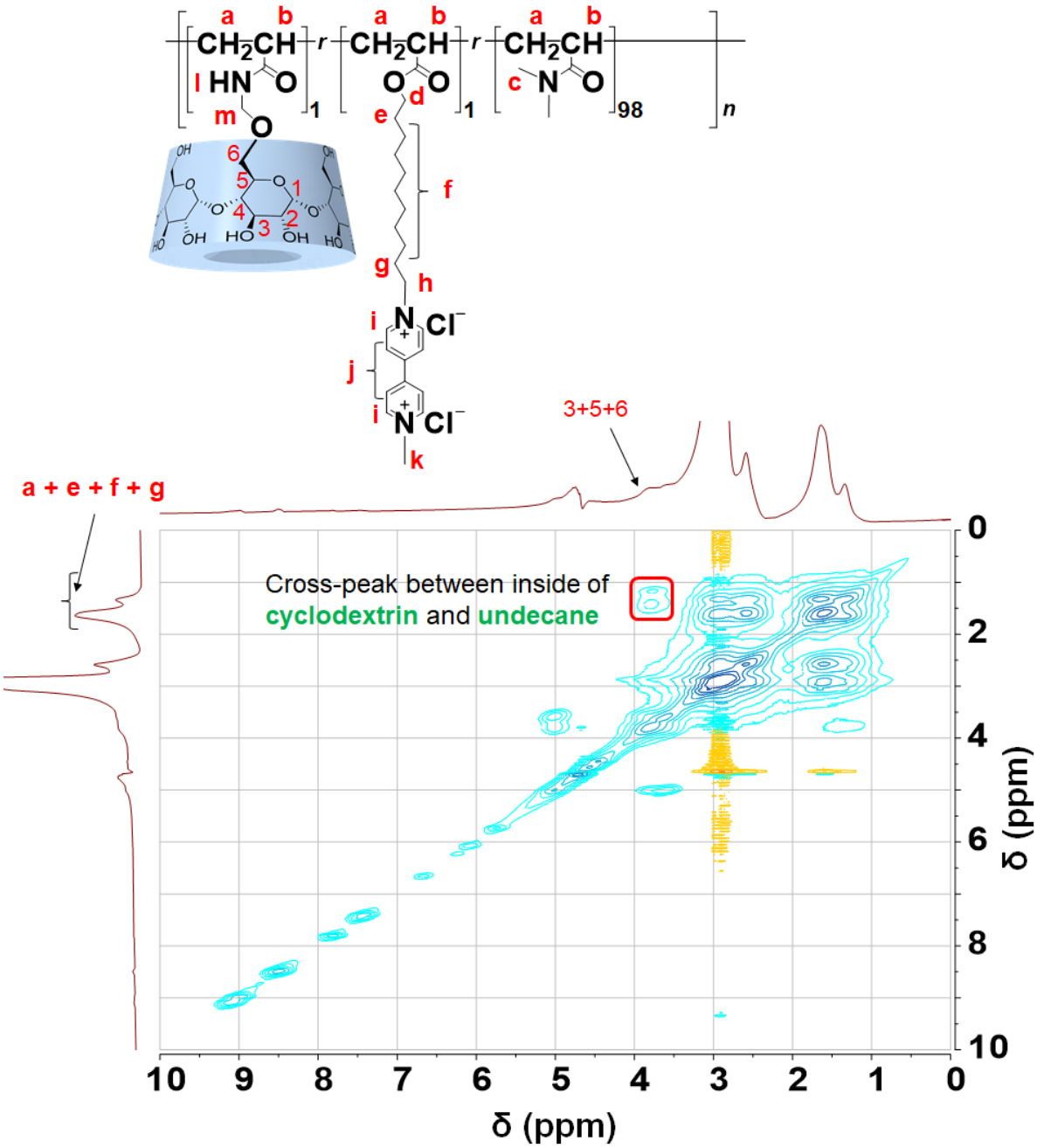

Fig. S26: 2D NOESY NMR spectrum of αCD-MV in D_2O at 30 ºC.

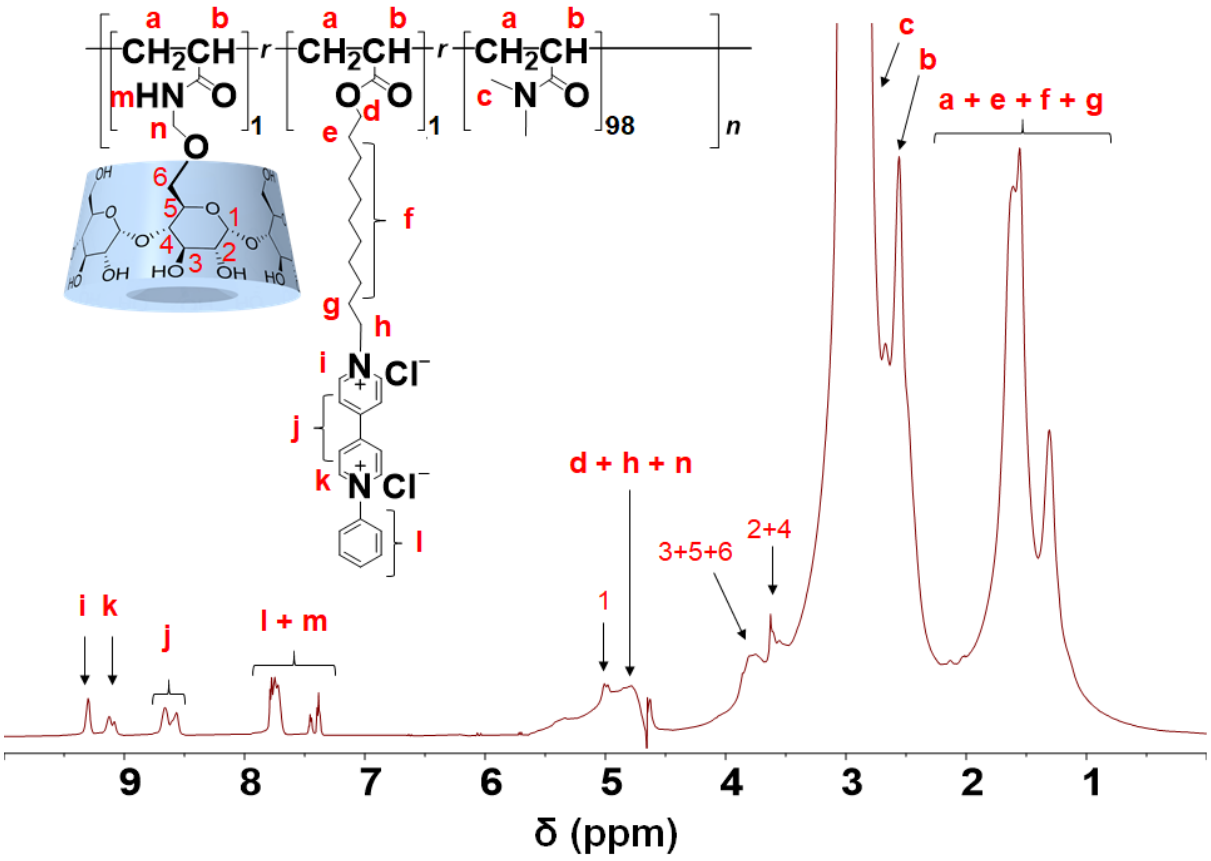

Fig. S27: ^{1}H NMR spectrum of αCD-PV in D_2O at 30 ºC.

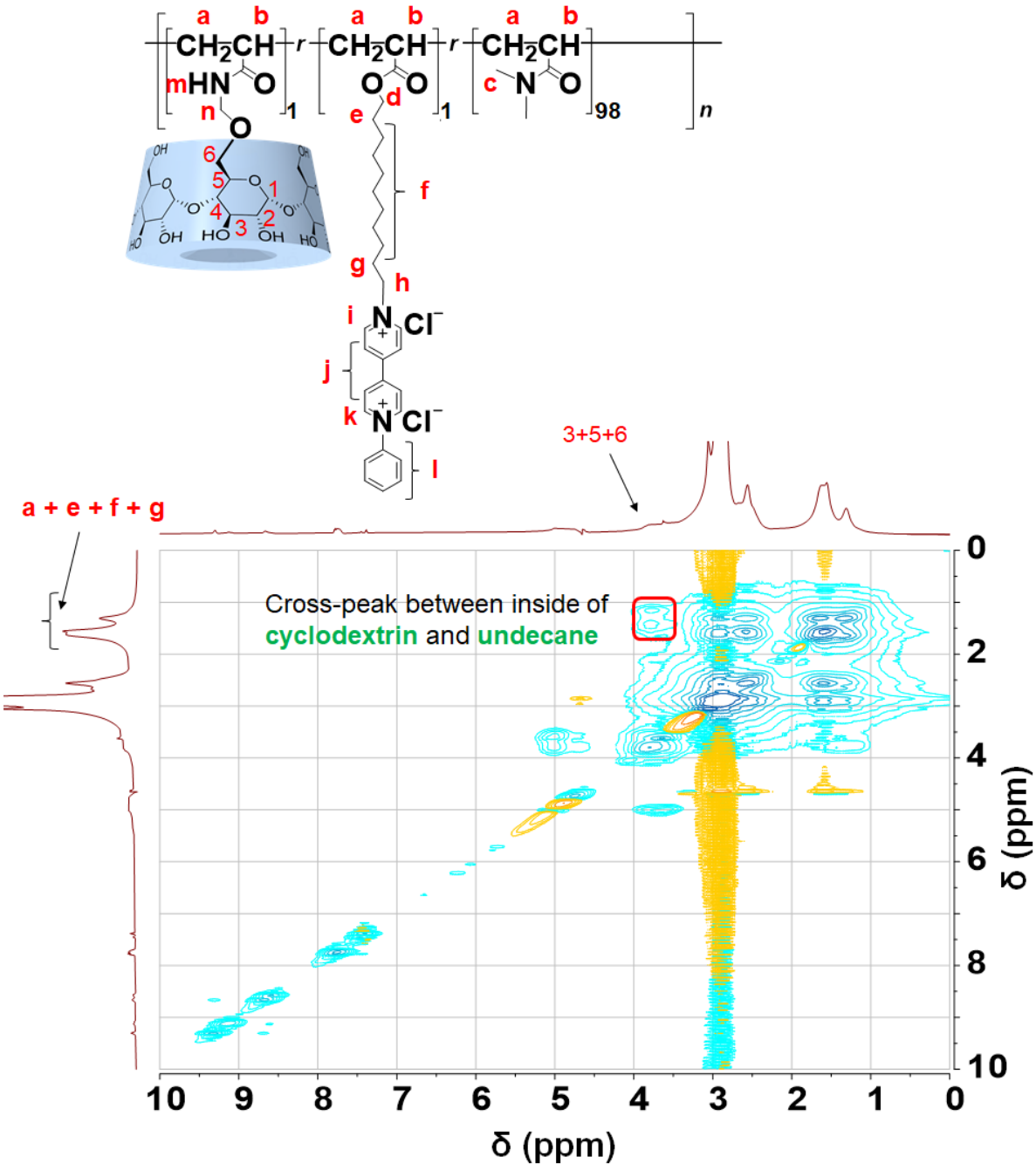

Fig. S28: 2D NOESY NMR spectrum of αCD-PV in D_2O at 30 ºC.

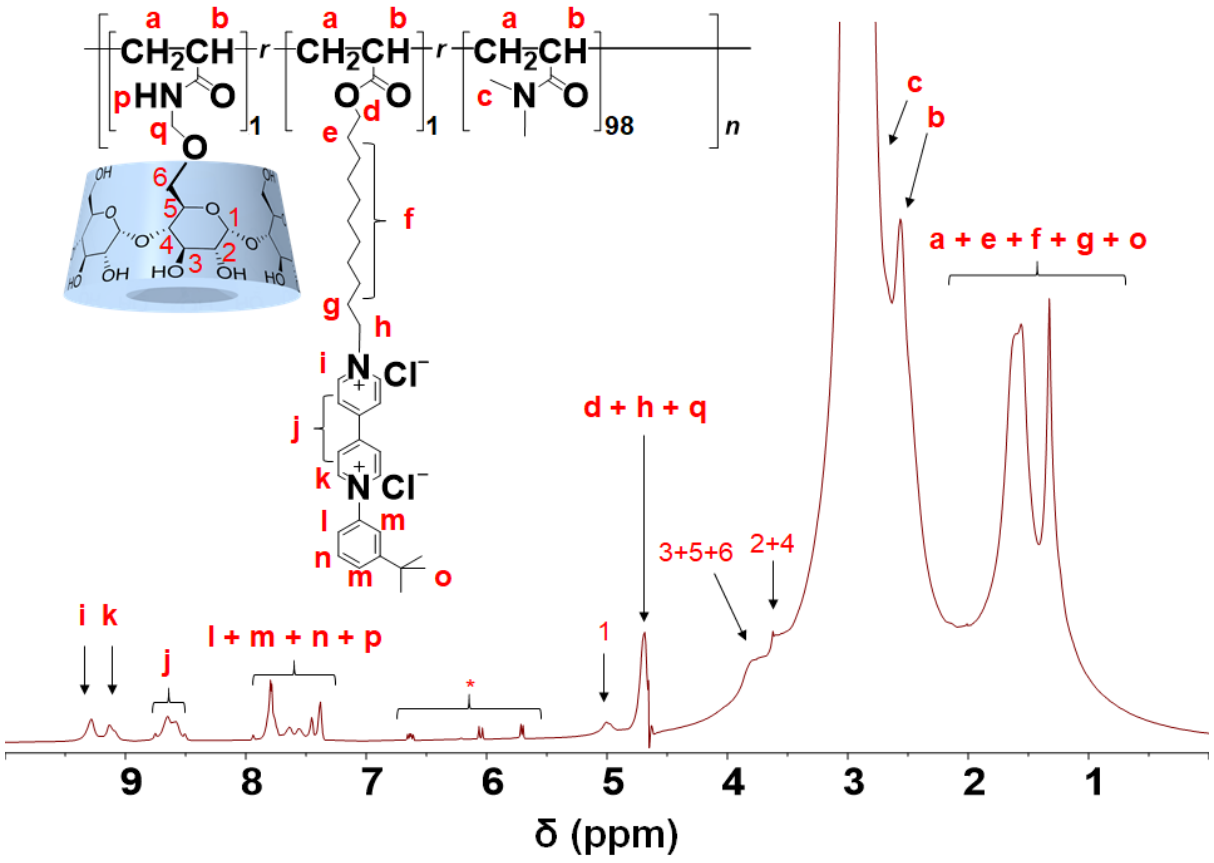

Fig. S29: ^{1}H NMR spectrum of αCD-BV in D_2O at 30 ºC. (* = residual monomers)

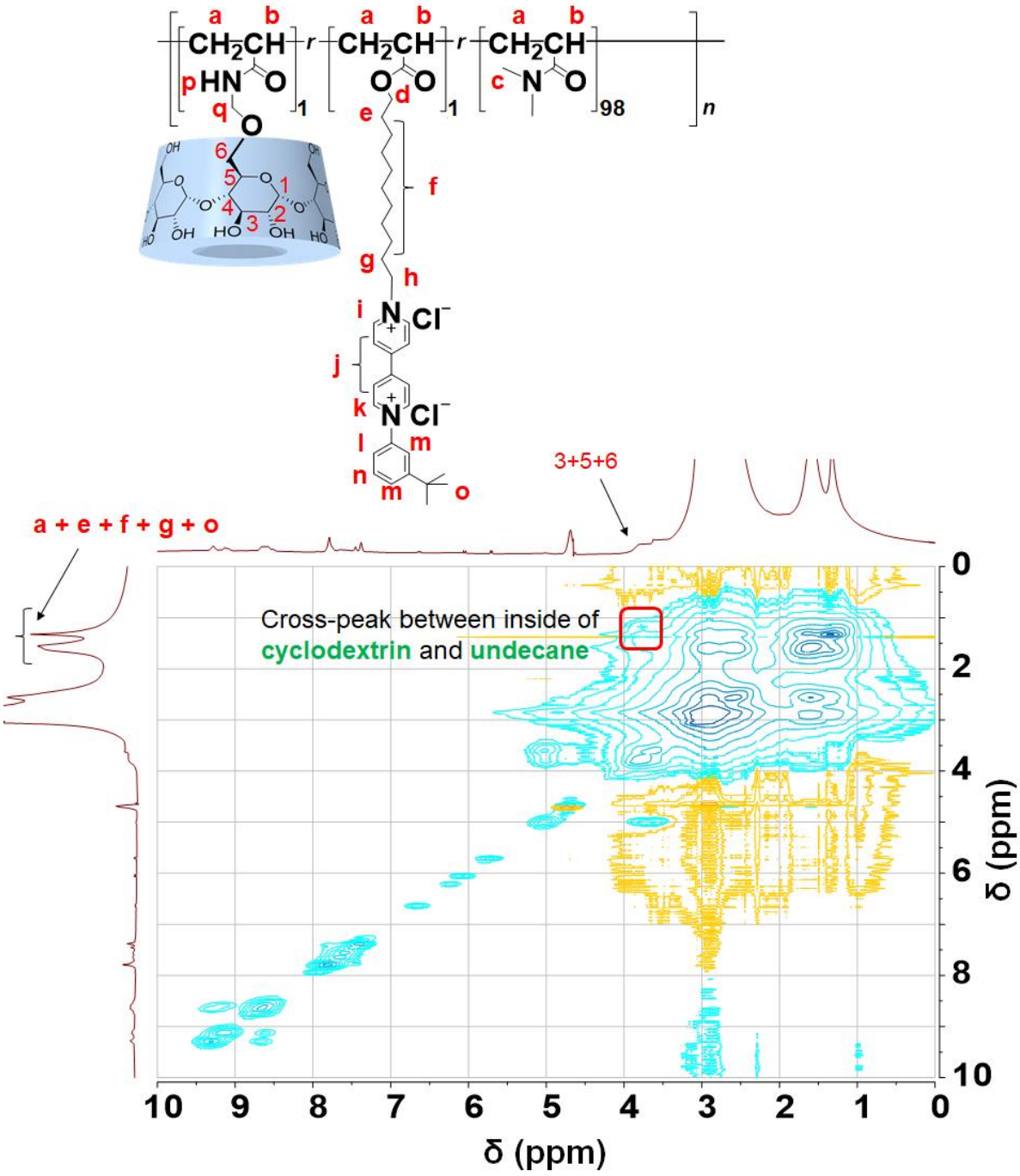

Fig. S30: 2D NOESY NMR spectrum of αCD-BV in D_2O at 30 ºC.

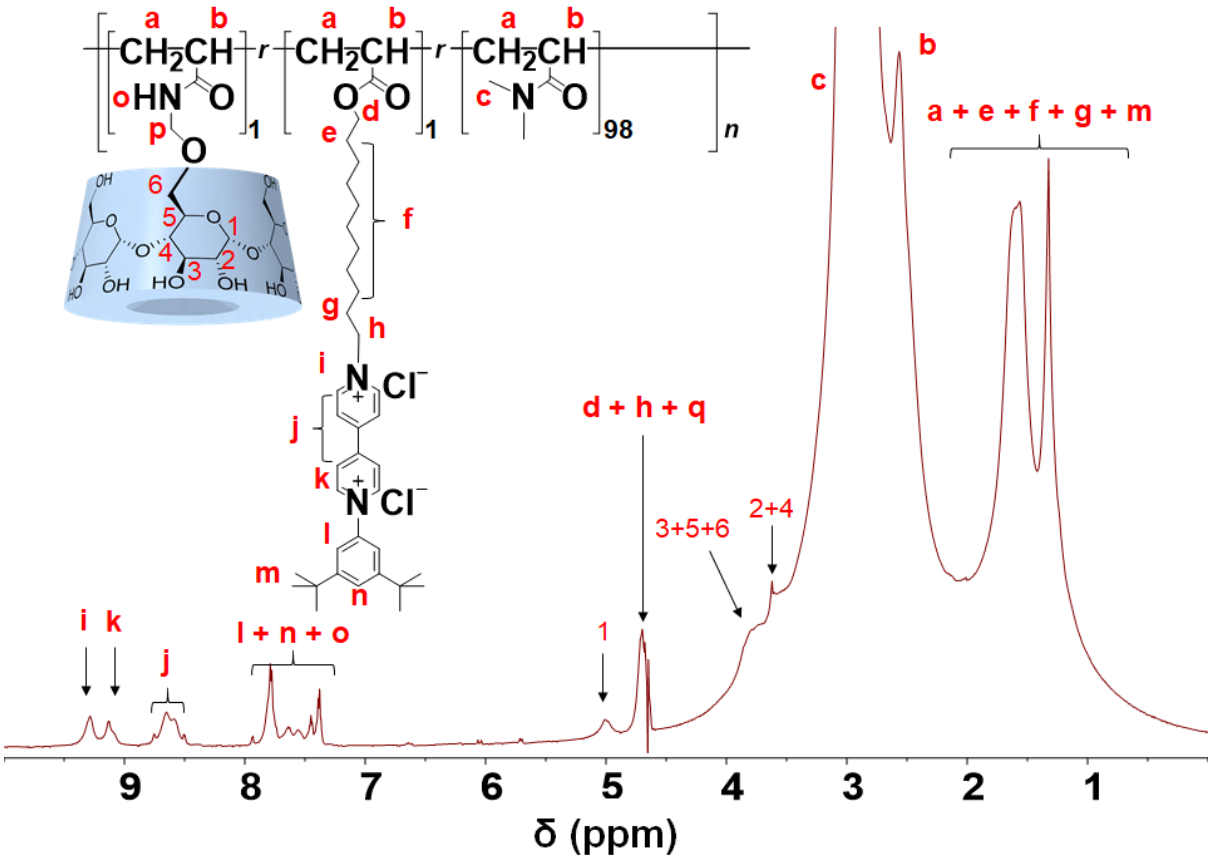

Fig. S31: ^{1}H NMR spectrum of αCD-DBV in D_2O at 30 ºC.

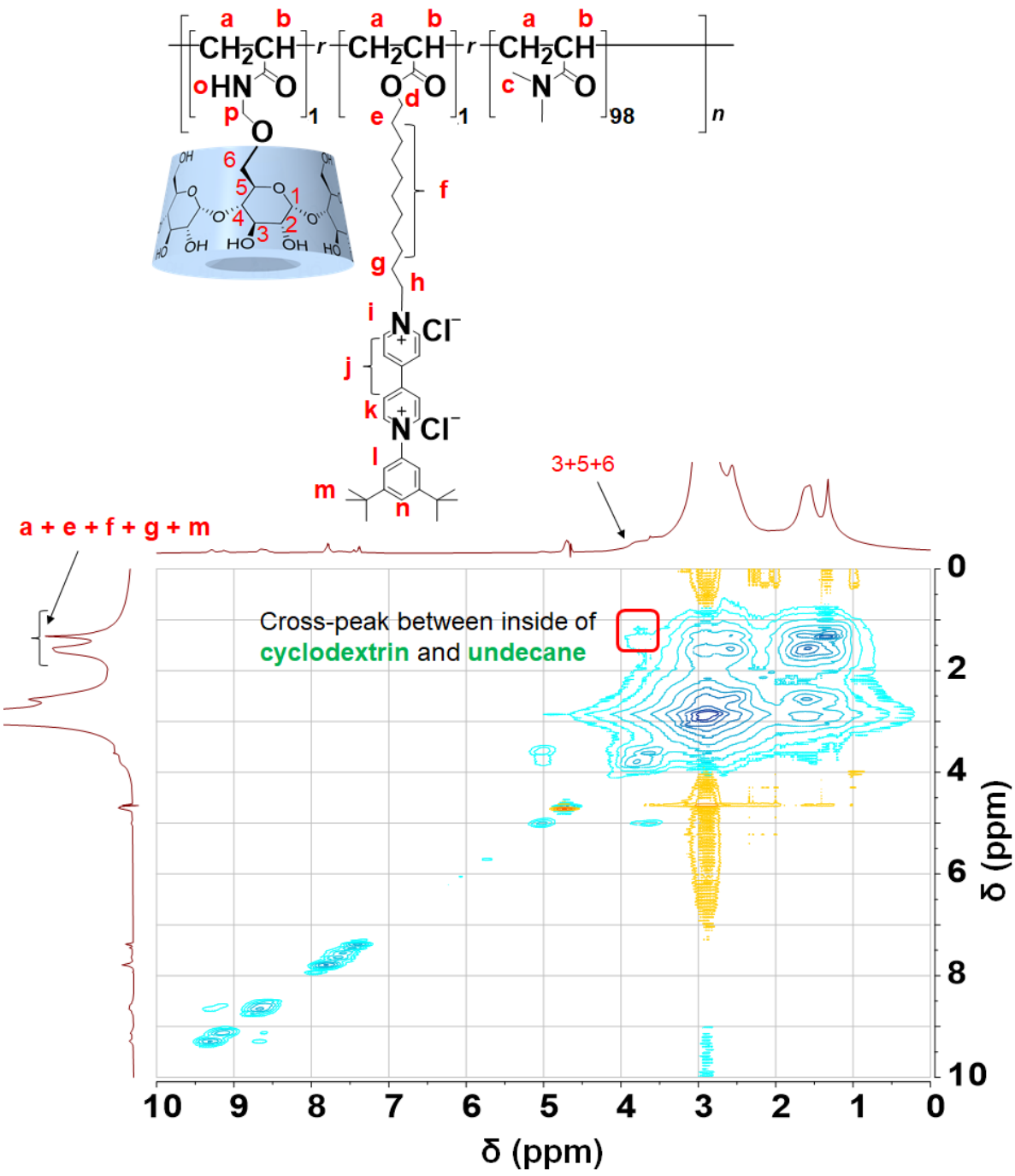

Fig. S32: 2D NOESY NMR spectrum of αCD-DBV in D_2O at 30 ºC.

6. Rheological studies on reversibility of the hydrogels

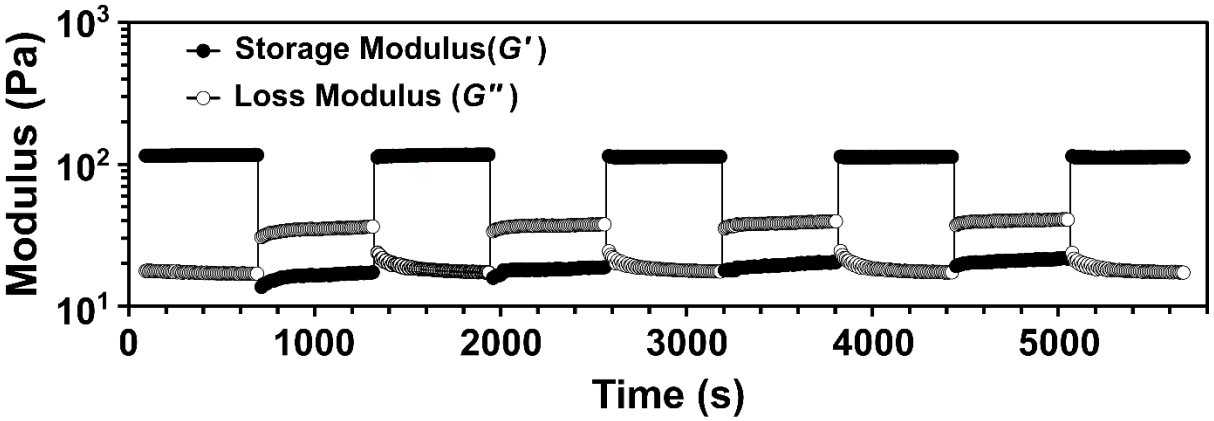

Fig. S33: Continuous step-strain rheological measurements on a fully swollen sample of αCD-MV at 25 °C. High-amplitude oscillatory parameters: strain γ = 500%, angular frequency ω = 1 rad s^{-1}, low-amplitude oscillatory parameters: strain γ = 1%, angular frequency ω = 1 rad s^{-1}.

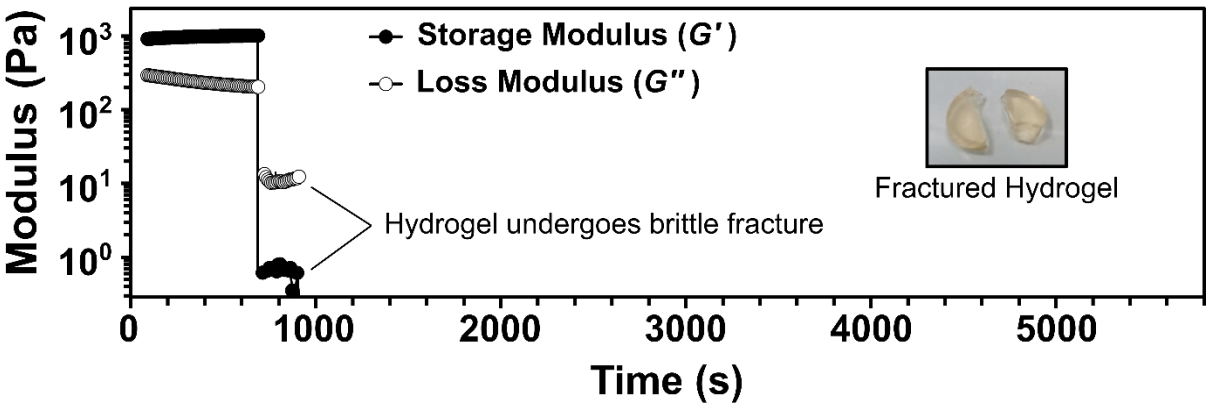

Fig. S34: Continuous step-strain rheological measurements on a fully swollen sample of αCD-DBV at 25 °C. High-amplitude oscillatory parameters: strain γ = 500%, angular frequency ω = 1 rad s^{-1}, low-amplitude oscillatory parameters: strain γ = 1%, angular frequency ω = 1 rad s^{-1}. Inset: The fractured hydrogel sample after a high strain is applied – this was observed at all high strains tested.

7. Water tuning for the tensile tests

Table S2: Weights of water content tuned αCD-MV for tensile tests.

W_{water} (wt %)	17	23	41	55	64
Weight of hydrogels (mg)	88.5	101	120	145	193
Weight of dried gels (mg)	73.3	77.7	70.6	65.9	69.3

Table S3: Weights of water content tuned αCD-PV for tensile tests.

W_{water} (wt %)	12	26	32	47	56	76
Weight of hydrogels (mg)	76.6	97.0	113	154	175	301
Weight of dried gels (mg)	67.3	72.1	76.8	82.1	77.6	73.0

Table S4: Weights of water content tuned αCD-BV for tensile tests.

W_{water} (wt %)	15	26	36	55	71
Weight of hydrogels (mg)	88.7	105	221	166	265
Weight of dried gels (mg)	75.8	77.9	141	75.2	77.9

Table S5: Weights of water content tuned αCD-DBV for tensile tests.

W_{water} (wt %)	12	28	39	45	55	67
Weight of hydrogels (mg)	94.9	111	128	137	160	216
Weight of dried gels (mg)	83.9	80.1	78.1	74.8	71.5	71.8

8. Tensile test results of the hydrogels

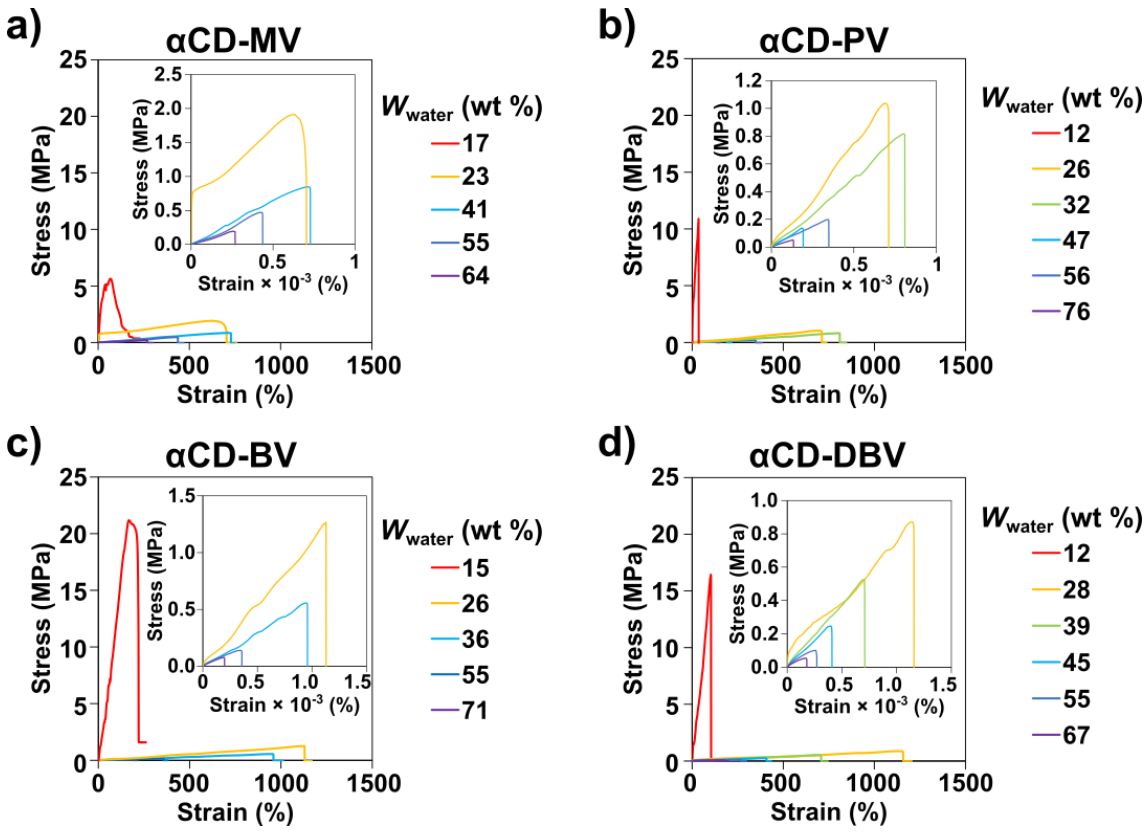

Fig. S35: Stress-strain curves of the hydrogels at different water contents.

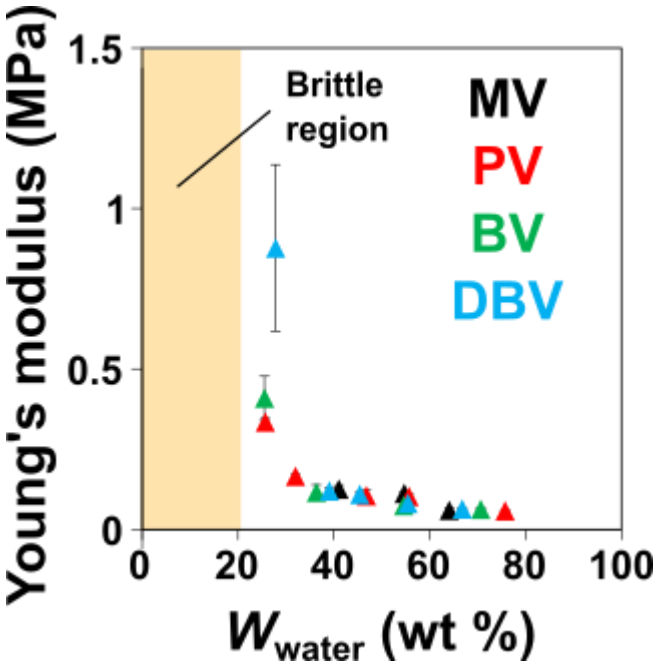

Fig. S36: Magnified plot of Young's modulus versus W_{water}

9. Water tuning for the SAXS measurements

Table S6: Weights of water content tuned αCD-MV for SAXS measurements.

W_{water} (wt %)	11	22	36
Weight of hydrogels (mg)	31.4	28.0	34.1
Weight of dried gels (mg)	28.1	21.8	21.9

Table S7: Weights of water content tuned αCD-PV for SAXS measurements.

W_{water} (wt %)	17	23	44
Weight of hydrogels (mg)	27.7	29.6	49.8
Weight of dried gels (mg)	23.1	22.9	27.8

Table S8: Weights of water content tuned αCD-BV for SAXS measurements.

W_{water} (wt %)	18	26	53
Weight of hydrogels (mg)	24.8	31.4	54.2
Weight of dried gels (mg)	20.4	23.3	25.3

Table S9: Weights of water content tuned αCD-DBV for SAXS measurements.

W_{water} (wt %)	18	40	56
Weight of hydrogels (mg)	33.4	41.3	58.7
Weight of dried gels (mg)	27.4	24.8	25.9

10. SAXS measurement of the dried gels at high temperature

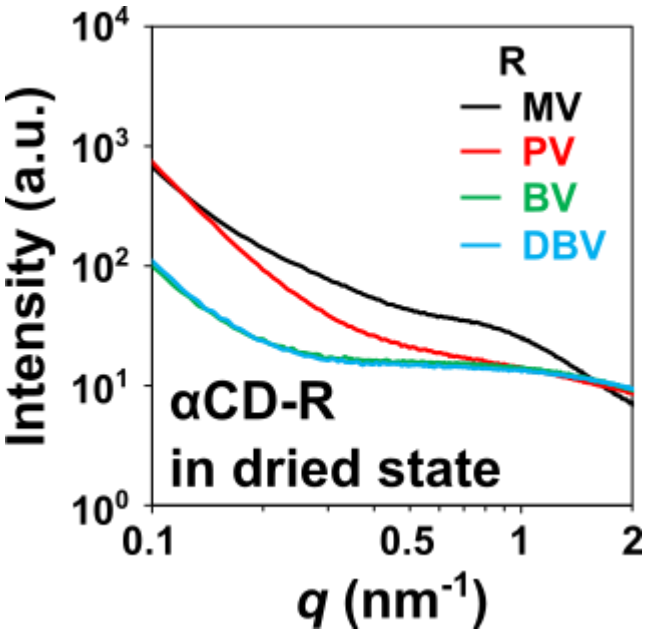

Fig. S37: SAXS profiles of the dried gels with four different guests at T_g + 50 °C. SAXS profiles of αCD-BV and αCD-DBV were completely overlapped in the range.

Reference

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