Supporting Information

High compression strength single network hydrogels with pillar[5]arene junction points

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S1: Experimental section

Materials and Methods

Materials

Unless otherwise stated, all solvents and chemicals used in this work were analytical grade and used without further purification. Dichloromethane (DCM, 99.8%), hexane (99.0%), diethyl ether (DEE, 99.8%), extra dry *N,N*-dimethylformamide (DMF, 99.8%), *N,N*-dimethylacetamide (DMA, 99%), hydroquinone (>99%), ethyl bromoacetate (>97%), ethyl acetate (99.9%), methanol (99.9%), 4,4'-Bipyridine (98.0%), acetonitrile (99.9%), iodomethane (99.0%), tetrahydrofuran (99.0%), 1,4-dimethoxybenzene (99.0%), paraformaldehyde (95.0%), boron trifluoride diethyl etherate (> 46% BF_3 basis), succinic acid (99.0%), azelaic acid (98.0%), bisphenol A (> 99.0%), 2-naphthol (98%), fluorescein sodium (> 95.0%) and Sigmacoat were purchased from Sigma-Aldrich (Overijse, Belgium). 2-Isopropenyl-2-oxazoline (Sigma-Aldrich, 98.0%) was distilled over CaH_2 under reduced pressure before use. Tetrahydrofuran (Sigma-Aldrich, THF) was freshly distilled over Na/benzophenone under Ar flow before use. *n*-Butyllithium solution 2.5 M in hexanes (Sigma-Aldrich, n-BuLi) was used as received. Potassium hydroxide (KOH, >99.9%), potassium carbonate (>99.0%), methyl orange (>98.0%), methylene blue (>98%) and methyl red hydrochloride (>98.0%) were obtained from Tokyo Chemical Industries. De-ionised water (DW) was prepared with a resistivity less than 18.2 MΩ x cm using an Arium 611 from Sartorius with the Sartopore 2 150 (0.45 + 0.2 μm poresize) cartridge filter.

Instrumentation

Size exclusion chromatography (SEC) was typically performed with an Agilent 1260 system equipped with a diode array detector and a refractive index detector to which was added multi-

angle light scattering detector miniDawn Treos II. The column set was 2x PLGEL MIXED-D (300 x 75 mm) columns and a guard column (50 x 7.5mm MIXED-D), and the eluent *N*,*N*-dimethylacetamide with 50 mM LiCl. Samples were filtered (0.2 μm PTFE filter) before injection. Wyatt ASTRA 7 was used to process the data.

^{1}H NMR spectra were recorded at 25 °C on a Bruker instrument operating at 400 MHz. Chemical shifts (δ) are referenced to $CDCl_3$ (δ 7.24 ppm) or DMSO-d6 (δ 2.50 ppm).

Infrared spectra were measured on a PERKIN-ELMER 1600 series FTIR spectrometer and were reported in wavenumber (cm^{-1}).

ESI-MS spectra were acquired on a quadrupole ion trap LC mass spectrometer (Thermo Finnigan MAT LCQ mass spectrometer) equipped with electrospray ionization.

The residual concentration of the pollutant in each sample was determined by UV–Vis analyses carried out on a Varian Cary 100 Bio UV-VIS spectrophotometer equipped with a Cary temperature and stir control, by measuring the absorbance of the solutions at the characteristic absorption peak of each pollutant. The amount of pollutant was calculated from the corresponding calibration curve prepared using standard solutions of known concentrations.

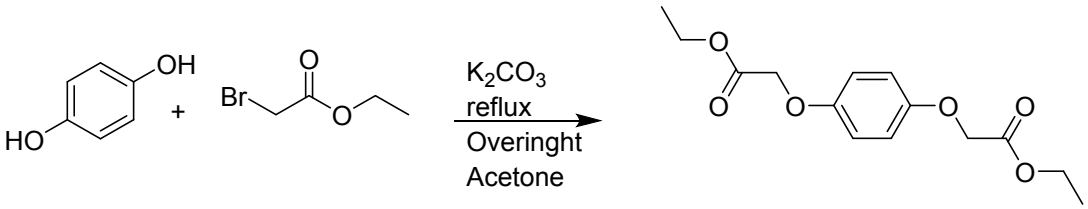
Rheology was measured on an Anton Paar MCR 302 rheometer equipped with a CTD 180 oven. Measurements were carried out with a gap of 0.5 mm, strain of γ = 0.1 % and an angular frequency ranging from ω = 0.01-100 rad/s.

Stress-strain measurements were performed on a Tinius-Olsen H10KT tensile tester equipped with a 25 N load cell using ASTM standard type IV dog bones (ISO 527-2-2B). The dog bone shaped samples had an effective gauge length of 12 mm, a width of 2 mm, and a thickness of ±1 mm, and they were cut using a Ray-Ran hand operated cutting press. The tensile measurements were performed using a preload of 0.01 and a pulling speed of 10 mm/min until sample failure. The stress σ was recorded as a function of strain ε. Five samples were used to obtain the average data. The elastic modulus was determined as the slope in the linear region of the stress-strain curves corresponding to 0%–10% strain.[1]

Compression tests of the hydrogels were performed using a Tinius-Olsen H10KT compression tester equipped with a 100 N load cell. The hydrogels were cut into tablet shape with a diameter of 4-10 mm and the height of ~4 mm. The compression rate of samples is 10 mm/min for all of the compression experiments. Five samples were used to obtain the average data. The compression modulus was calculated as the slope in the linear region of the stress-strain curve corresponding to 5%–10% strain.[1] For the successive loading-unloading tests, the compression rate was set at 0.86 mm/min and the toughness was estimated by the area below the stress–strain curve of the loading cycle for each sample. The dissipated energy was calculated as the area of compressive loading-unloading cycle. The compressive cycles were applied with the strain from 0 to 25 %.

The X-ray intensity data were collected at 100 K, on a Rigaku Oxford Diffraction Supernova Dual Source (Cu at zero) diffractometer equipped with an Atlas CCD detector using ω scans and CuKα (λ = 1.54184 Å) radiation. Using Olex2[2], the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the ShelXL[4] refinement package using Least Squares minimization.

Synthesis of diethyl 2,2'-(1,4-phenylenebis(oxy))diacetate



Scheme S1. Synthesis of diethyl 2,2'-(1,4-phenylenebis(oxy))diacetate.

The synthesis was performed using the classic Williamson etherification method as previously reported by Newton et al.[5] Briefly, a mixture of corresponding hydroquinone (90.8 mmol, 10 g), ethyl bromoacetate (199.8 mmol, 33.3 g), and potassium carbonate (199.8 mmol, 27.6 g) in acetone (200 mL) was heated under reflux for overnight. After completion of the reaction, the

reaction mixture was filtered, the filtrate was evaporated, and the residue was purified by a silica column with an eluent of hexane: ethyl acetate 10:1 to afford the product (15 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (s, 4H), 4.56 (s, 4H), 4.25 (t, J = 7.1 Hz, 4H), 1.29 (t, J = 7.1 Hz, 6H).

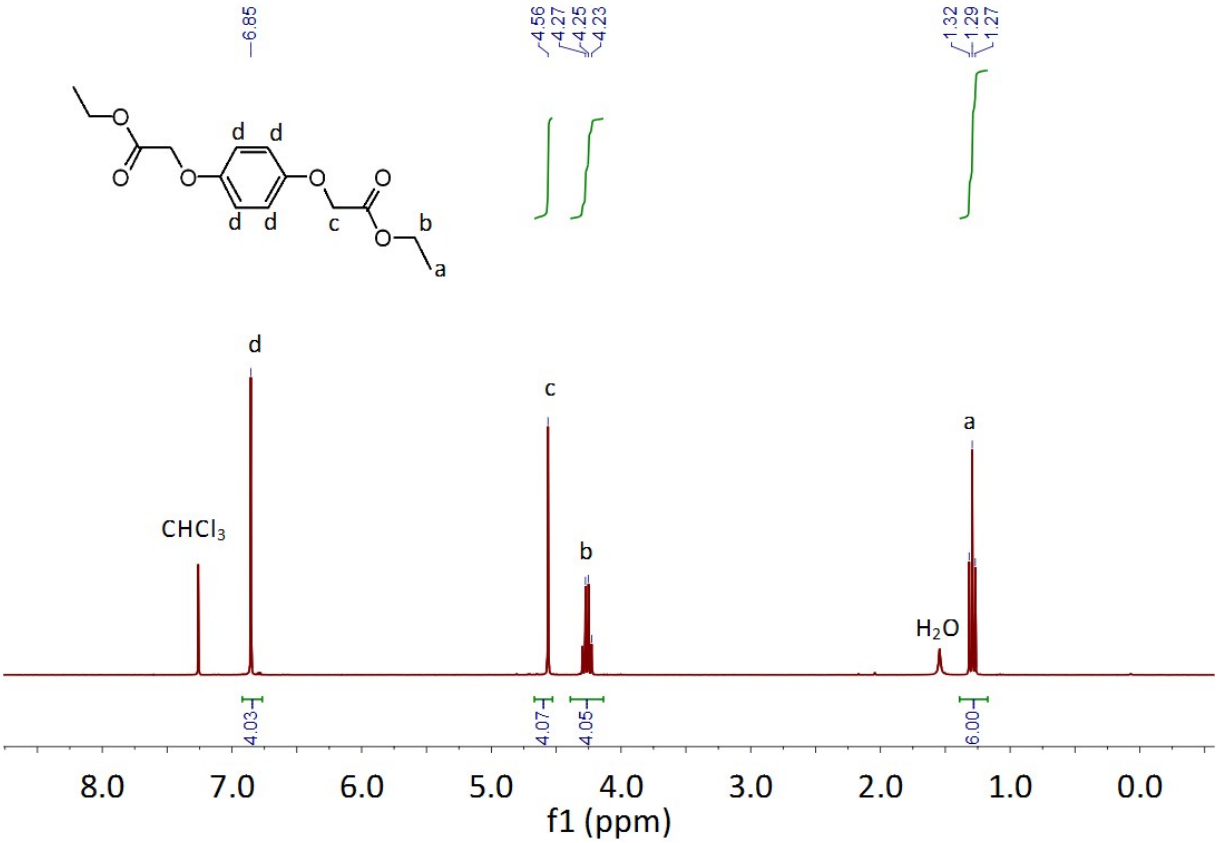


Figure S1. ^{1}H-NMR spectrum of diethyl 2,2'-(1,4-phenylenebis(oxy))diacetate in $CDCl_3$.

Synthesis of diethyl 2,2'-(1,4-phenylenebis(oxy))diacetic acid (PhDA)

A solution of diethyl 2,2'-(1,4-phenylenebis(oxy))diacetate (1g, 3.54 mmol) and KOH (992 mg, 17.72 mmol) in 80 mL of a mixture of MeOH/H_2O (3:1) was stirred at 50 ^{o}C overnight. After cooling, the precipitate was filtered and redissolved in 10 mL water. The solution was neutralized with 10 mL of 4 M HCl and filtered. The product was obtained after drying in the vacuum oven as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.92 (s, 2H), 6.83 (s, 4H), 4.59 (s, 4H).

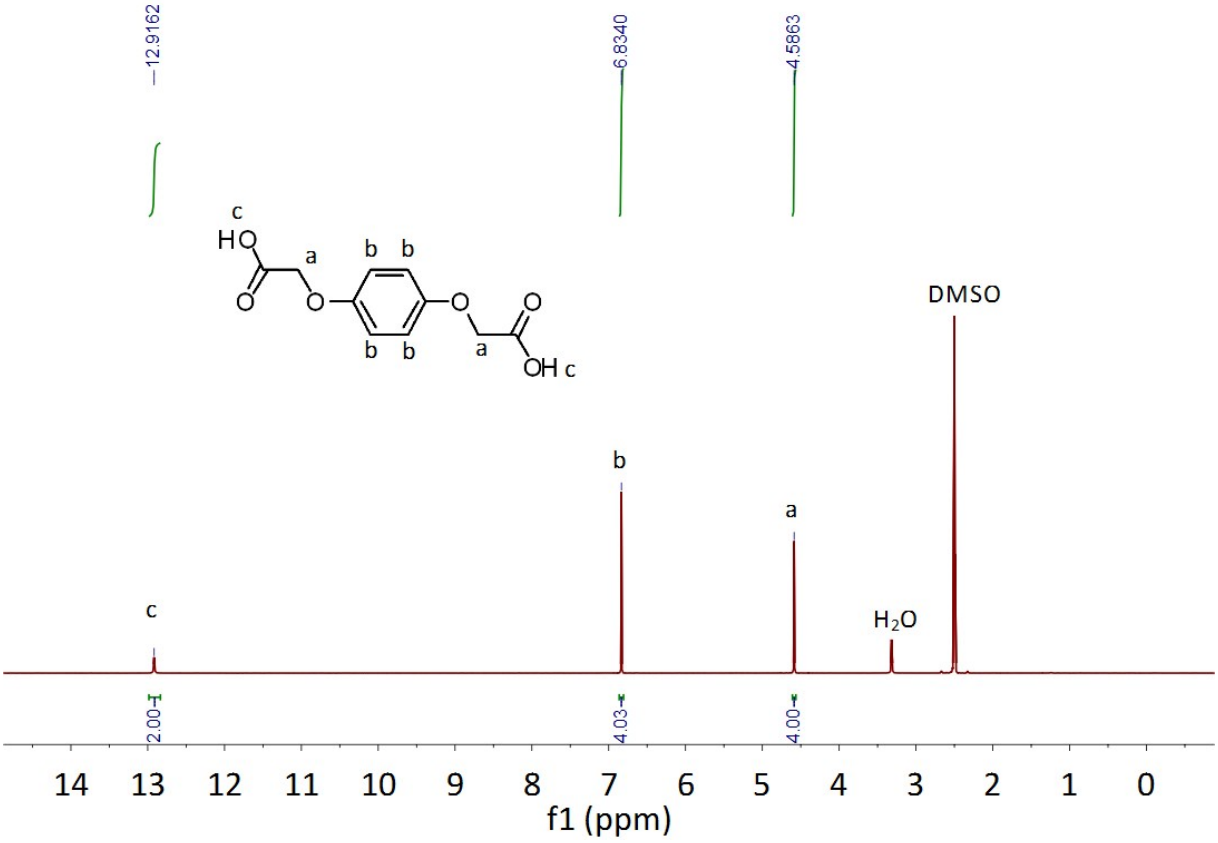


Figure S2. [1]H-NMR spectrum of 2,2'-(1,4-phenylenebis(oxy))diacetic acid in DMSO-d6.

Synthesis of 1,1'-Dimethyl-4,4'-bipyridinium diiodide (methyl viologen diiodide)

The synthesis was performed by following the protocol of Ugozzoli et al.[6] Briefly, 4,4'-bipyridine (2.499 g, 0.016 moles) and iodomethane (5.678 g, 0.040 moles) were dissolved in acetonitrile (150 ml) and refluxed overnight. Then, the reaction mixture was cooled down to room temperature and filtered. The product was washed with ethyl acetate 3 times and dried in vacuum oven overnight. [1]H NMR (400 MHz, DMSO-d_6) δ 9.29 (d, J =8.0 Hz, 4H), 8.77 (d, J = 8.0 Hz, 4H), 4.44 (s, 6H).

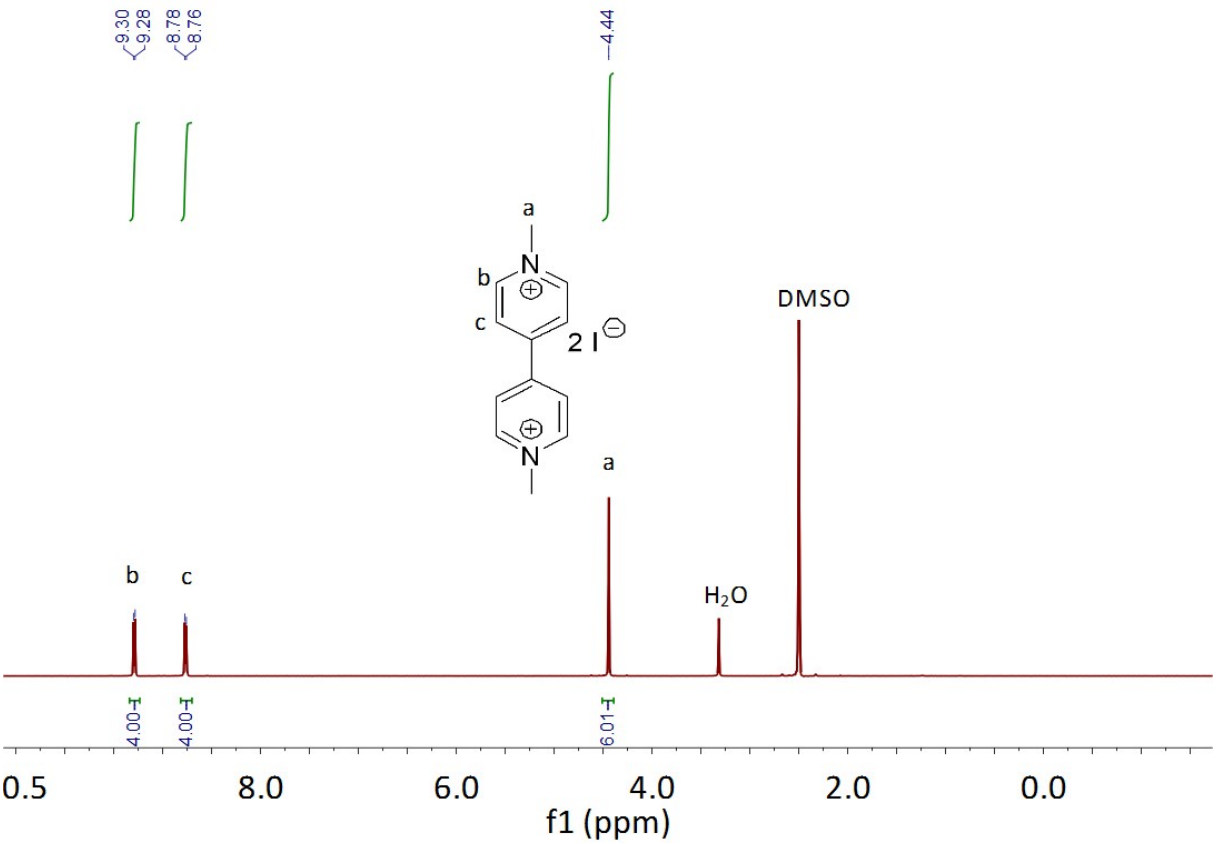
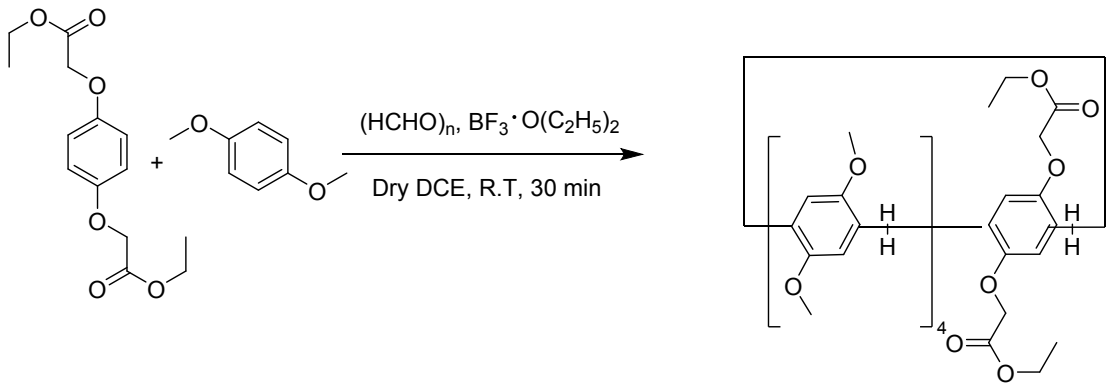


Figure S3. ^{1}H-NMR spectrum of methyl viologen diiodide in DMSO-d6.

Synthesis of pillar[5]arene di-(ethyl 2-phenoxyacetate)



Scheme S2. Synthesis of pillar[5]arene di-(ethyl 2-phenoxyacetate).

The synthesis was performed by adapting a previously reported procedure as follows.[7] 1,4-dimethoxybenzene (2.76 g, 20 mmol) was dissolved in 80 mL of dry 1,2-dichloroethane. After bubbling for 20 min with argon, diethyl 2,2'-(1,4-phenylenebis(oxy))diacetate (1.41 g, 5 mmol) and paraformaldehyde (0.75 g, 25 mmol) were added under argon and the mixture was stirred at room temperature for 50 min. Subsequently, boron trifluoride diethyl etherate (2.7 mL, 25

mmol) was added, and the mixture was stirred under the protection of argon at room temperature for 10 min and followed by TLC. The solution was diluted by 200 mL DCM and washed with water twice, the organic layer was collected and separated by column using hexane/DCM/ethyl acetate (200:1:5) to yield the product as a white solid (600 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.70 (m, 10H), 4.55 (s, 4H), 3.72 (dt, J = 14.7, 5.9 Hz, 34H), 3.13 (q, J = 7.0 Hz, 4H), -0.25 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.21, 150.54, 150.52, 150.29, 150.22, 149.29, 128.64, 128.49, 128.39, 127.89, 114.39, 114.29, 113.56, 113.46, 113.21, 65.89, 60.82, 55.81, 55.69, 55.68, 55.57, 29.55, 29.48, 28.93, 12.29. MS (m/z): HRMS (ESI) calcd. for $C_{51}H_{62}NO_{14}$ ($[M+NH_4]^+$):912.4170, found:912.4148.

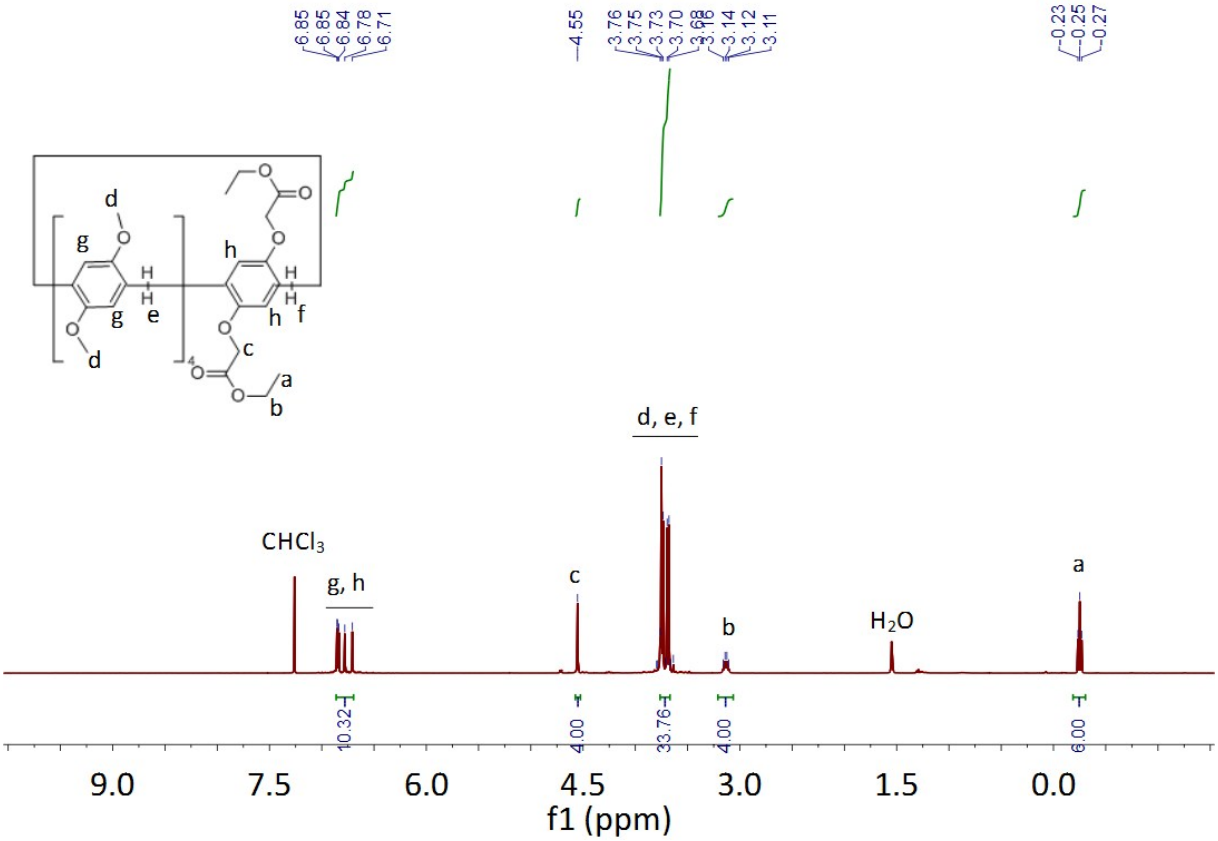


Figure S4. ^{1}H-NMR spectrum of pillar[5]arene di-(ethyl 2-phenoxyacetate) in $CDCl_3$.

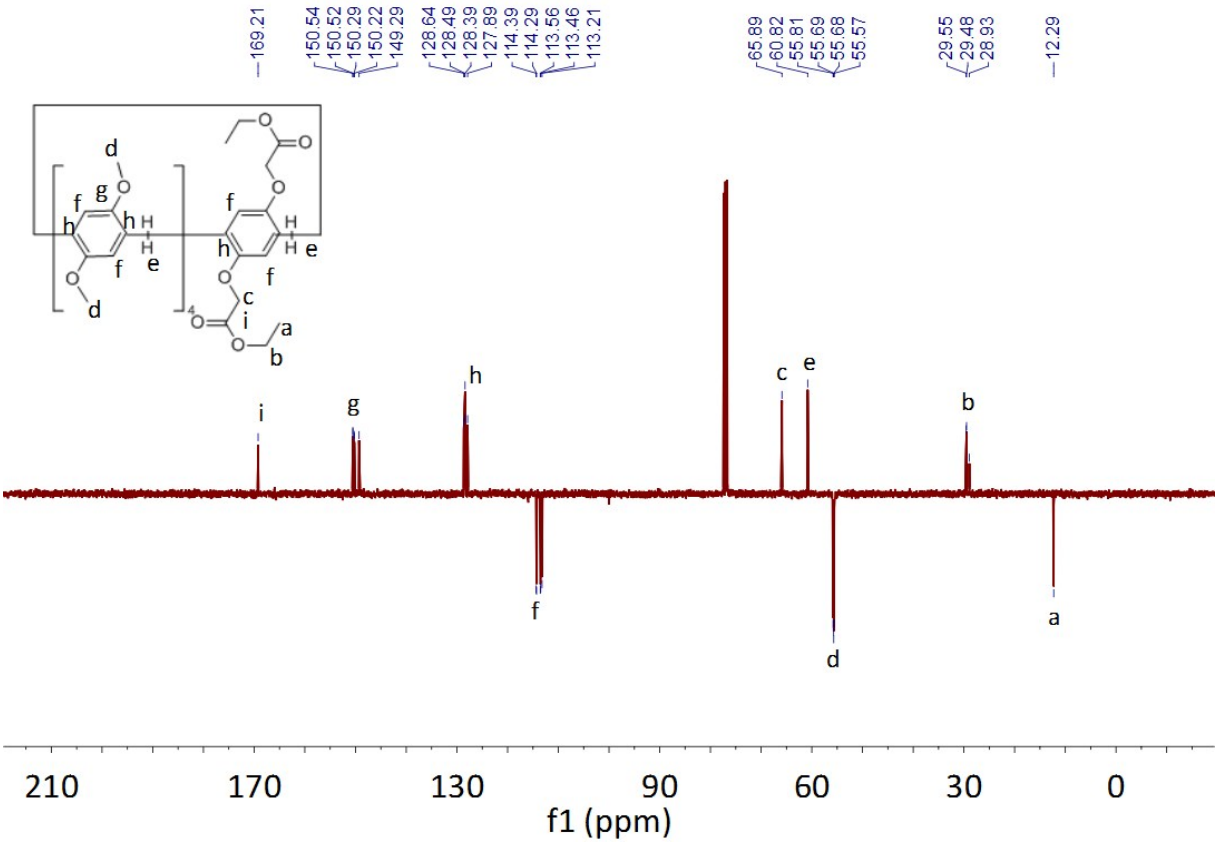


Figure S5. ^{13}C-NMR spectrum of pillar[5]arene di-(ethyl 2-phenoxyacetate) in $CDCl_3$.

Crystals for crystal structure determination were obtained by slow evaporation of a methanol solution containing the ester. Crystal Data: $C_{51}H_{58}O_{14}$ (M = 894.97 g/mol): triclinic, space group P-1 (no. 2), a = 9.6444(3) Å, b = 12.2441(3) Å, c = 19.4216(4) Å, α = 93.6475(17)°, β = 99.9526(19)°, γ = 92.348(2)°, V = 2251.20(10) Å3, Z = 2, T = 100.0(1) K, μ(CuKα) = 0.789 mm^{-1}, *Dcalc* = 1.320 g/cm3, 42196 reflections measured (7.244° ≤ 2Θ ≤ 150.888°), 9132 unique (R_{int} = 0.0398, R_{sigma} = 0.0291) which were used in all calculations. The final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1197 (all data).

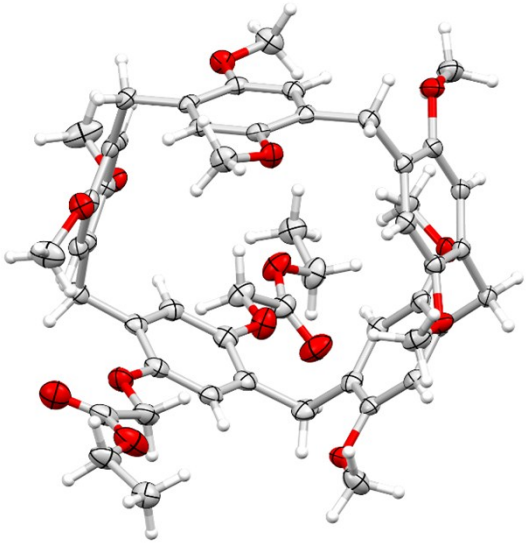
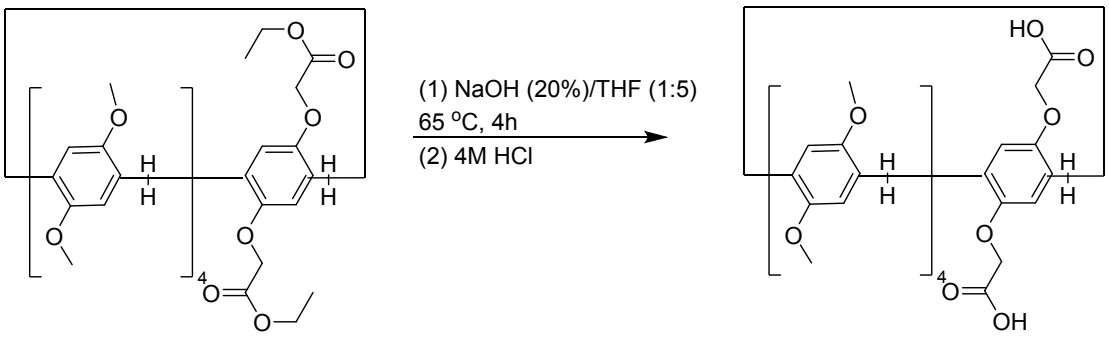


Figure S6. Asymmetric unit of the crystal structure of pillar[5]arene di-(ethyl 2-phenoxyacetate) showing thermal displacement ellipsoids at the 50% probability level.

Synthesis of pillar[5]arene di-(phenoxyacetic acid) (PA5)



Scheme S3. Synthesis of pillar[5]arene di-(phenoxyacetic acid).

A solution of the pillar[5]arene di-(ethyl 2-phenoxyacetate) and 20% aqueous NaOH (30.0 mL) in THF was stirred at 65 °C overnight. After cooling, the solution was neutralized with 10 mL of 4 M HCl. Two layers were separated, and the organic layer was collected. Another 100 mL (2x) of DCM was added to the residual aqueous solution and extracted. The organic layers were collected, and the solvent was evaporated under low pressure. The crude product was further purified by column chromatography (SiO_2; hexane/DCM/ethyl acetate 100:1:5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 – 6.55 (m, 10H), 4.52 (s, 4H), 3.84 – 3.60 (m, 34H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.73, 151.89, 150.95, 150.68, 150.09, 148.80, 129.23, 128.87, 128.34, 127.83, 127.40, 116.39, 114.63, 114.56, 114.04, 113.52, 65.80, 57.56, 56.07, 55.97, 55.95, 30.10, 29.75,

29.37. MS (m/z): MS (m/z): HRMS (ESI) calcd. for $C_{47}H_{54}NO_{14}$ ($[M+NH_4]^+$):856.3544, found:856.3292.

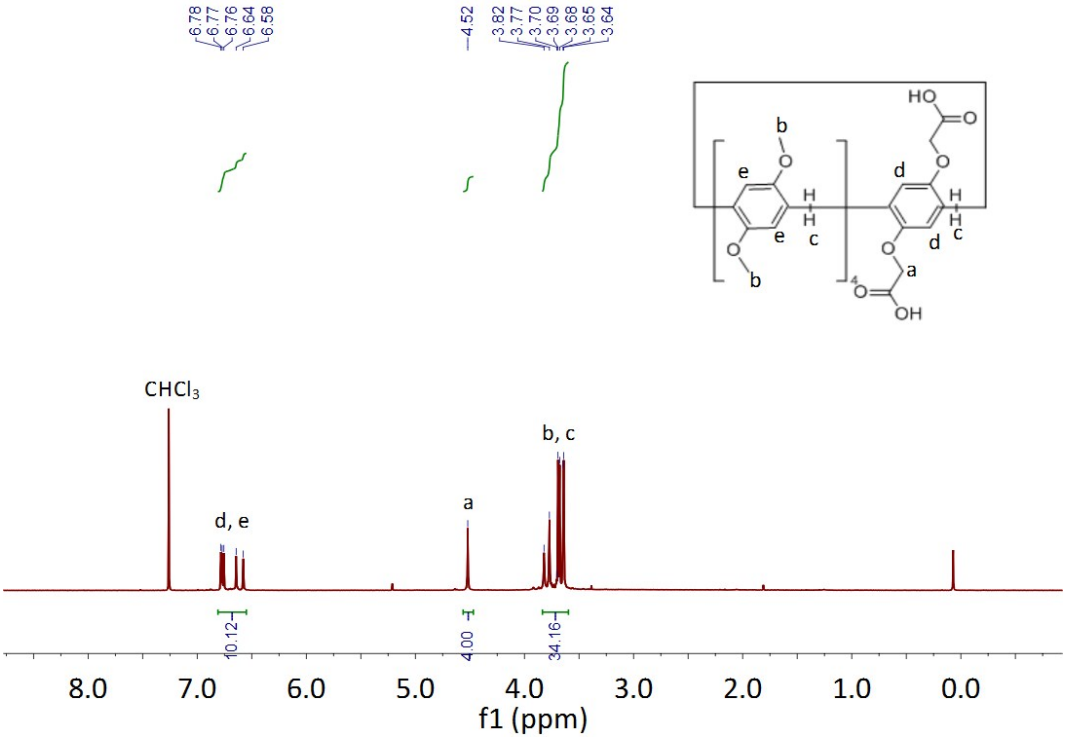


Figure S7. ^{1}H-NMR spectrum of pillar[5]arene di-(phenoxyacetic acid) in $CDCl_3$.

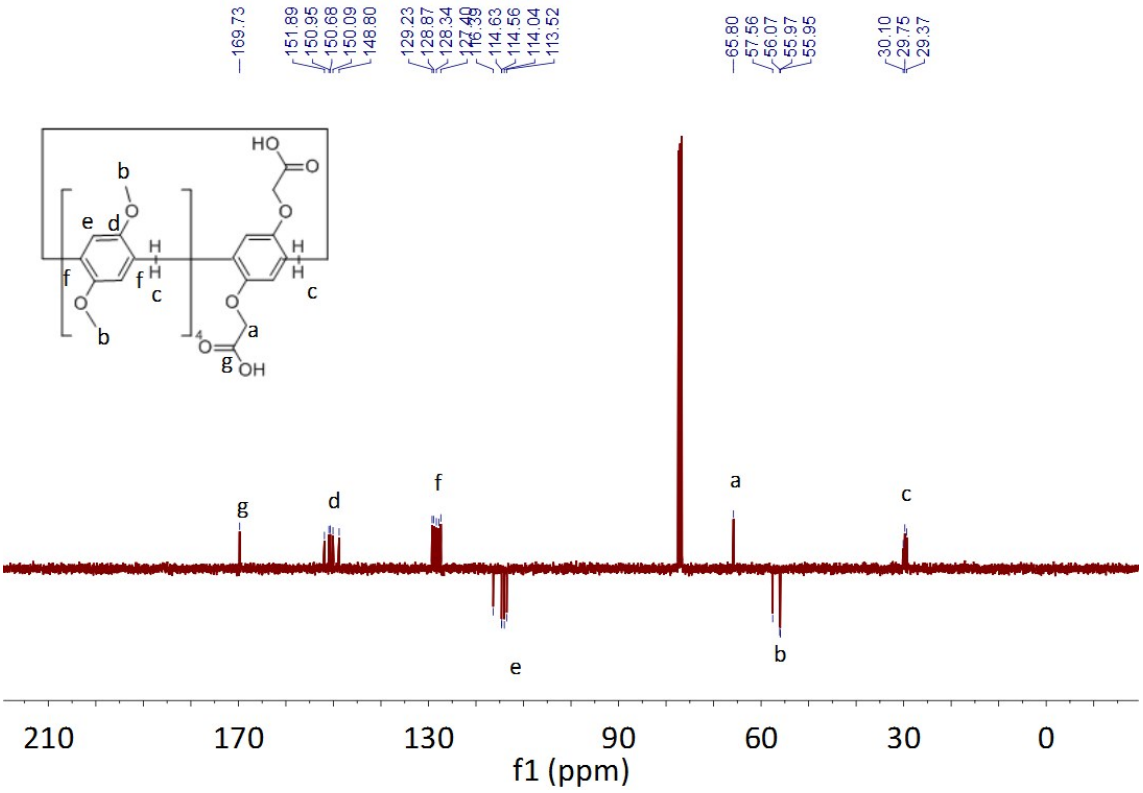


Figure S8. ^{13}C-NMR spectrum of pillar[5]arene di-(phenoxyacetic acid) in $CDCl_3$.

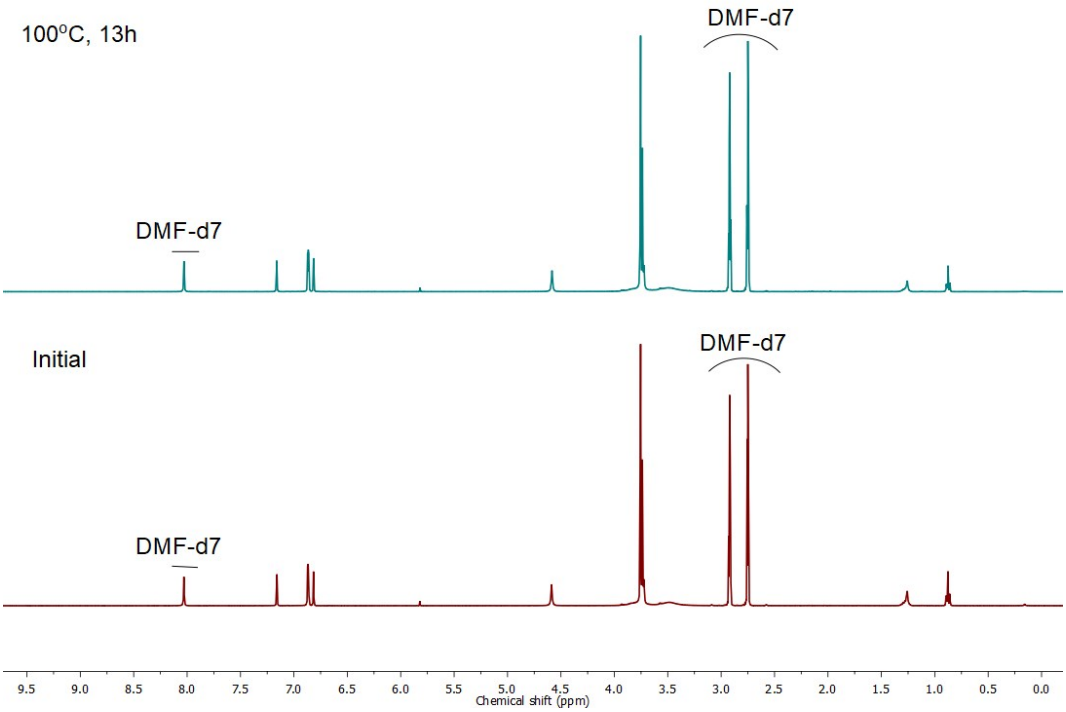


Figure S9. ^{1}H-NMR spectra of PA5 in DMF-d7 before (bottom) and after heating for 13h at 100 °C (top) demonstrating its stability.

Synthesis of Poly(2-isopropenyl-2-oxazoline) (PiPOx) hydrogels.

Swelling degree and compression experiments.

PiPOx and the corresponding amount of cross-linker were weighted in a glass tube, then N,N'-dimethylformamide (DMF) was added, and the solution was vortexed for 10 minutes. The reaction mixture was purged with Ar and placed in an oil bath preheated at 100 °C for 13h. The polymer concentration was kept constant at 20 wt%, and the COOH/iPOx molar ratio was varied between 0.01 and 0.2 for PA5. When PhDA, and azelaic acid were used as cross-linkers two ratios were tested 0.03 and 0.05, respectively. At the end of the reaction time, the vials were removed from the bath, broken and the resulting hydrogel rods were cut with a sharp blade into even disk-shaped samples with a diameter of 5 mm and a thickness of 3 mm. The disks were placed first in ethanol for 2 days at room temperature, and next in de-ionized water for another 2 days to complete extraction and solvent exchange. The water and isopropanol were changed

daily to remove the unreacted acid and polymer. The swollen disks were dried until a constant weight was reached at room temperature.

Tensile testing

A 20 wt.% PiPOx solution was prepared by dissolving 1.0 g of polymer and the corresponding amount of cross-linker into the appropriate amount of DMF. The reaction mixture was very well stirred and transferred using a syringe and needle into the space between two parallel glass plates, which were previously hydrophobized, separated by a 1 mm rubber gasket, in order to obtain plate-shaped hydrogels of uniform thickness. The reactor was then introduced into a constant temperature oven and kept at 100°C for 13 hours. At the end of the reaction time, the reactor was opened, the hydrogel plate was taken out and purified as described above. The hydrogel was then cut into the desired shapes which were kept into de-ionized water for 24 h to reach the equilibrium swollen state and were then mechanically tested.

Hydrophobization procedure. The clean glass plates were immersed in Sigmacote solution for 5 min. Then the excess of solution was removed, and the treated glass plates were dried at room temperature in the fume hood. Finally, the glass plates were washed 3 times with de-ionized water, dried at room temperature and stored for further use.

Gel fraction determination

For gel fraction determination, part of the hydrogel disks were first dried to constant weight (W_0), followed by the purification procedure as described before. The final weight of the disks (W_{ext}) was recorded as well. The gel fraction (GF) was calculated according to the following equation:

$$GF = \frac{W_{ext}}{W_0} \qquad \text{(S1)}$$

Swelling experiments and mesh size calculations

The swelling behavior of the synthesized hydrogels was determined by placing a weighed dry polymer network disk (W_x) into de-ionized water (pH = 5.6) at room temperature (25 °C). The

swollen disks were removed from the water bath at specific time intervals, wiped superficially with filter paper, weighed (*Wy*) and sunk back into the water. The measurements were carried out until the weight of the swollen gel reached a constant value, corresponding to the equilibrium swelling degree (ESD). The experiments were done in duplicate, and the average value measurements were reported. The swelling degree at various time intervals, expressed as amount of water absorbed by 1 g of dry polymer network, was calculated with equation (S2):

$$SD(\%) = \frac{W_y - W_x}{W_x} \times 100 \qquad \text{(S2)}$$

The ESD was determined as the value corresponding to the curve plateau of the swelling degree (SD) – time plots

Calculation of average molecular weight between cross-links ($\bar{M}_c$), cross-linking density (ρ_c), and mesh size (ξ) was based on the equilibrium swelling theory, assuming Gaussian distribution of cross-linked polymer chains. Flory-Rehner equation was used to determine $\bar{M}_c$.[8]

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\frac{\bar{\nu}}{V_1} \cdot \left(\ln\left(1 - \upsilon_2\right) + \upsilon_2 + \chi_{12}\upsilon_2^2\right)}{\nu_2^{1/3} - \frac{\nu_2}{2}} \qquad \text{(S3)}$$

Where $\bar{M}_n$ represents the number average molecular weight of the uncross-linked polymer, $\bar{\nu}$ is the specific volume of the polymer (0.943 cm^3/g for PiPOx), V_1 is the molar volume of the solvent (18 cm^3/mol), ν_2 is the polymer volume fraction in the equilibrium swollen hydrogel, and χ_{12} is the polymer-solvent interaction parameter and was estimated according to van Krevelen method[9] (0.3478 for water-PiPOx interaction).

The polymer volume fraction (υ_2) was determined using the following equation:

$$\upsilon_2 = \left(1 + \frac{\rho_p}{\rho_s} \cdot \left(\frac{W_e}{W_i} - 1\right)\right)^{-1} \qquad \text{(S4)}$$

Where ρ_p is the polymer density (1.061 g/cm^3), ρ_s is the solvent density (1.000 g/cm^3 for water), W_e is the mass of the hydrogel disk at equilibrium and W_i is the initial mass of the dry polymer network.

The cross-linking density ρ_c was calculated as the reciprocal of $\bar{\nu} \cdot \bar{M}_c$; the product of specific volume and the number-average molecular weight between cross-links, according to equation (S5).[10]

$$\rho_c = \frac{1}{\bar{\nu} \cdot \bar{M}_c} \tag{S5}$$

The mesh size ξ (in nm) of the polymer network was calculated using equation (S5):[10]

$$\xi = (v_2)^{-1/3} \cdot \left(\frac{2 \cdot C_n \cdot \bar{M}_c}{M_r}\right)^{1/2} \cdot l \tag{S6}$$

Where C_n is the polymer characteristic ratio, M_r is the molecular weight of the repeating units of the polymer (111.14 g/mol for PiPOx), and l is the length of an individual C–C bond (0.154 nm). The value of 9.76 for poly(*N*-vinylpyrrolidone)[11] was used as C_n due to the structural resemblance of the two polymers.

S2: Synthesis and network characterization PiPOx hydrogels

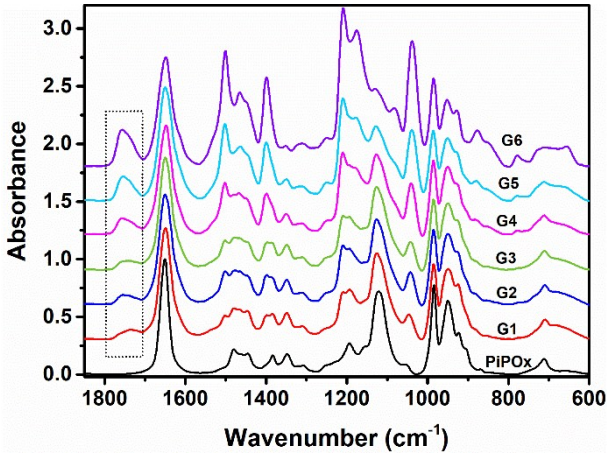


Figure S10. FT-IR spectra of G1-G6 dry polymer networks.

Table S1. Network parameters for PiPOx hydrogels.

Code	n_{COOH}/n_{iPOx}	PA5 (mol %)	GF[a)]	$\bar{M}_c\,(Da)_{b)}$	ρ_c x 10^{-4} (mol/cm^3)[c)]	ξ (nm)[d)]
G1	0.03	1.5	0.96	2015	5.27	38.63
G2	0.05	2.5	0.96	897	11.82	15.11
G3	0.07	3.5	0.98	354	29.98	5.57
G4	0.1	5	0.99	201	52.70	3.15
G5	0.15	7.5	0.99	70	152.23	1.16
G6	0.2	10	0.99	43	245.02	0.76
PhDA	0.05	-	0.93	421	25.19	6.67
AAz	0.05	-	0.95	706	15.03	11.6

[a)] gel fraction calculated according to equation S1

[b)] average molecular weight between cross-links, calculated with equation S3

[c)] cross-linking density calculated with equation S5

[d)] mesh size calculated with equation S6

S3: Rheological characterization of PiPOx hydrogels.

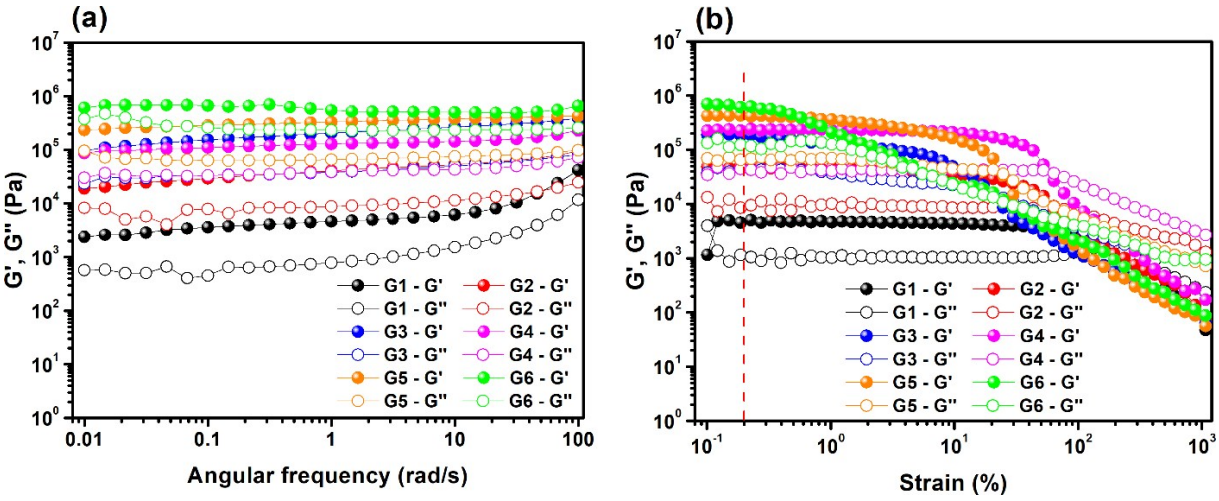


Figure S11. Rheological characterization of G1-G6 hydrogels swollen in de-ionized water at equilibrium: (a) strain sweep measurements were performed using a fixed 3 rad/s frequency, and (b) frequency sweep measurements were performed using a fixed 1% strain.

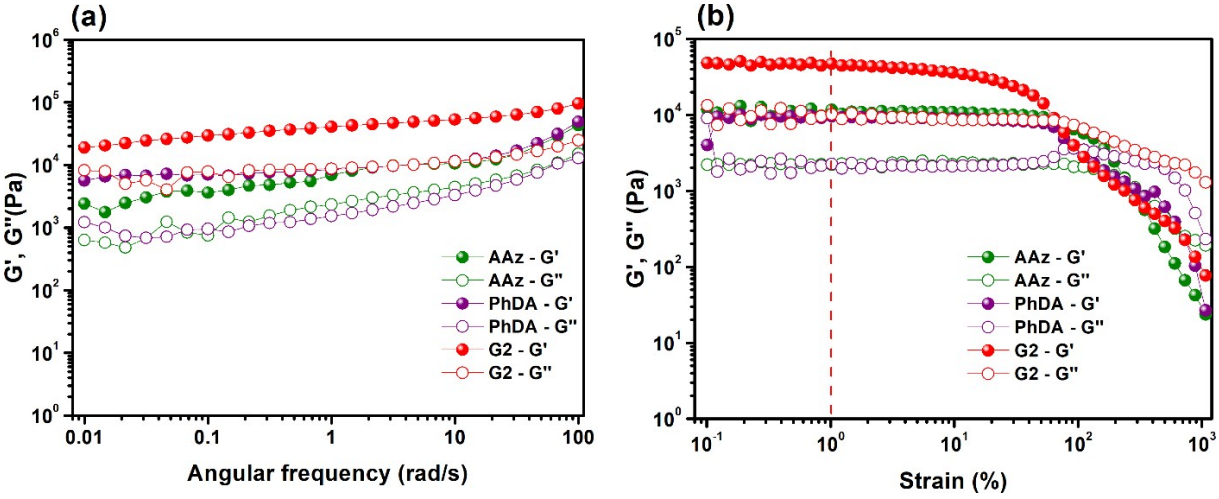


Figure S12. Rheological characterization of G2, AAz and PhDA hydrogels swollen in de-ionized water at equilibrium: (a) strain sweep measurements were performed using a fixed 3 rad/s frequency, and (b) frequency sweep measurements were performed using a fixed 1% strain.

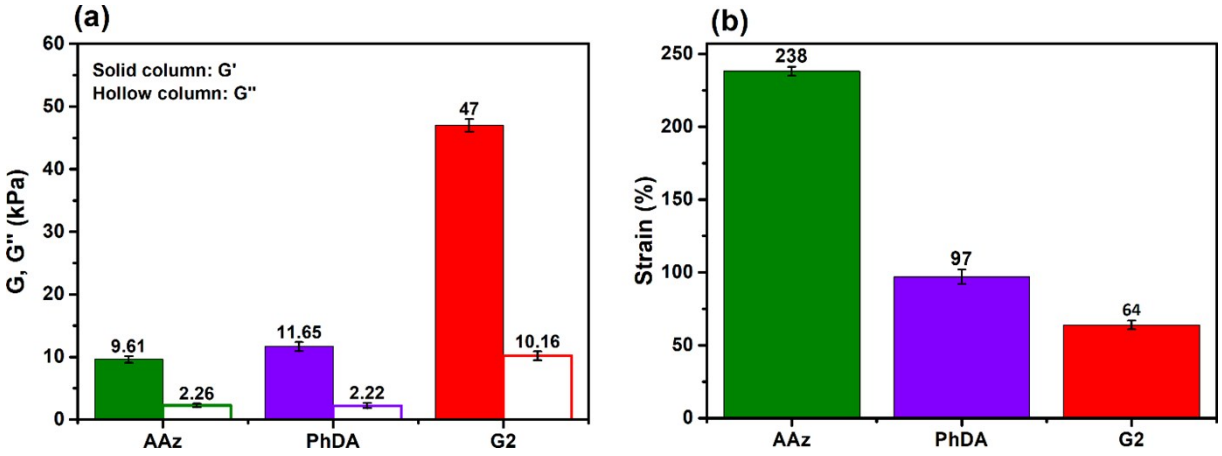


Figure S13. Rheological characterization of G2, AAz and PhDA hydrogels swollen in de-ionized water at equilibrium: (a) the G' and G'' values obtained from strain sweep experiments at 1 % strain, and (b) the breaking strain obtained from strain sweep experiments.

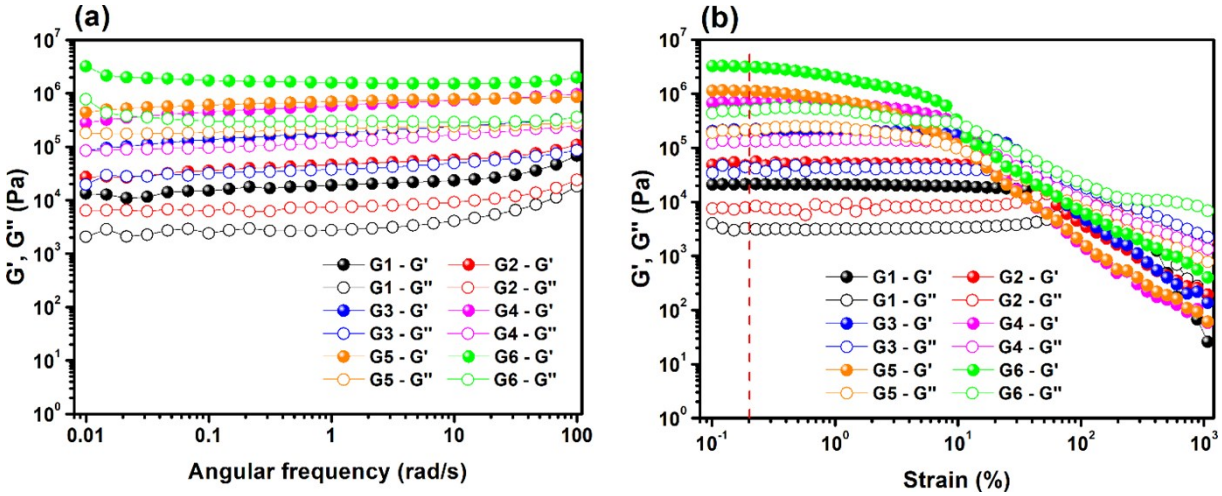


Figure S14. Rheological characterization of G1-G6 hydrogels swollen in MV solution at equilibrium: (a) strain sweep measurements were performed using a fixed 3 rad/s frequency, and (b) frequency sweep measurements were performed using a fixed 1% strain.

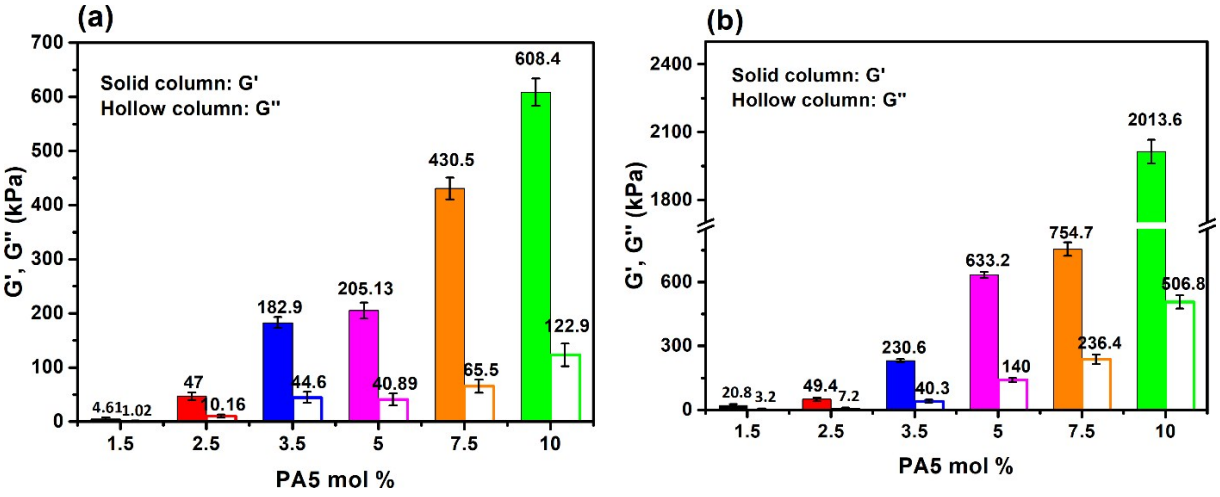


Figure S15. The G' and G'' values obtained from strain sweep experiments at 0.2 % strain for G1-G6 hydrogels swollen at equilibrium in: (a) de-ionized water and (b) MV solution, respectively.

S4: Compression and tensile characterization of PiPOx hydrogels.

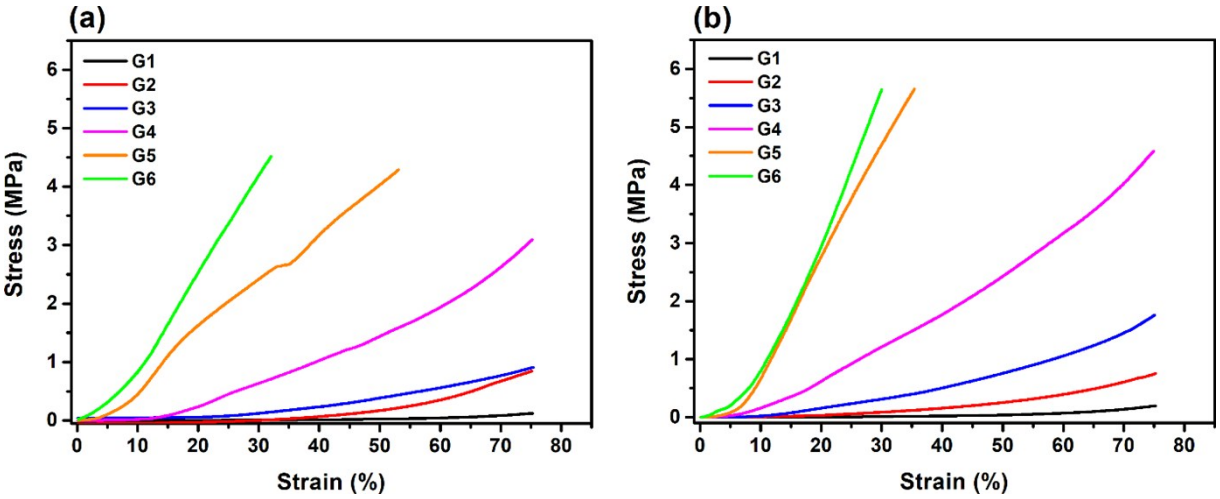


Figure S16. Stress-strain curves of G1-G6 hydrogels under compressive mode after swelling at equilibrium in: (a) de-ionized water and (b) 5mM MV solution, respectively.

Table S2. Summary of the mechanical properties of PiPOx hydrogels swollen in de-ionized water (DW) and in methyl viologen solution (MV), respectively.

Code	n_{COOH}/n_{iPOx}	**Compressive modulus (kPa)**		**Tensile modulus (kPa)**		**Breaking stress (kPa)**[a)]	
		DW	**MV**	**DW**	**MV**	**DW**	**MV**
G1	0.03	0.13	0.21	0.25	0.39	20	26
G2	0.05	0.23	0.42	1.25	3.54	30	70
G3	0.07	0.41	0.65	9.01	12.93	163	250
G4	0.1	1.04	3.14	-	-	-	-
G5	0.15	57.85	77.7	-	-	-	-
G6	0.2	102.8	124.5	-	-	-	-
PhDA	0.05	0.11	-	0.18	-	8	-
AAz	0.05	0.06	-	0.25	-	12	-

[a)]calculated from tensile stress-strain curves.

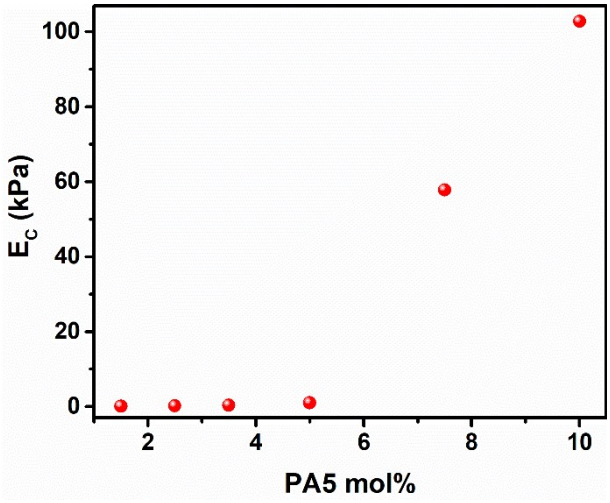


Figure S17. Variation of compression modulus with the PA5 mol%

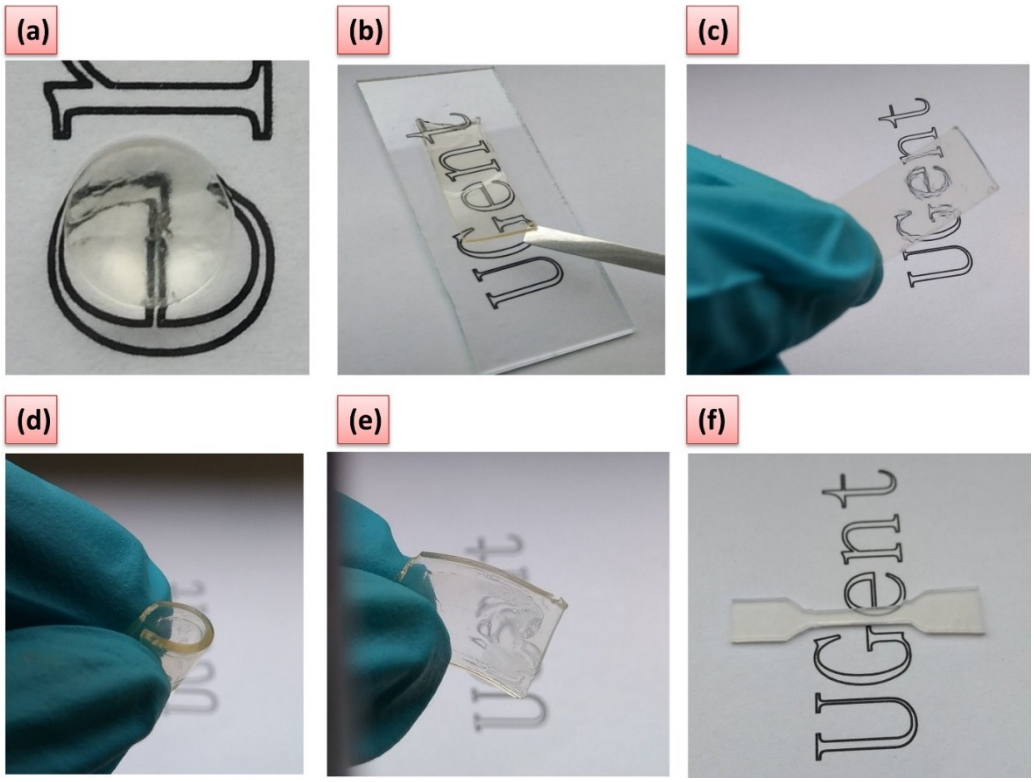


Figure S18. Photographs of the G2 hydrogel showing: (a) the disk-shaped hydrogel, (b) successful construction of the transparent film (1 mm thick), (c) the mechanical stability of the film, (d) bending of the film without any breakage, (e) recovery to its original states, and (f) the typical samples for the tensile test experiment.

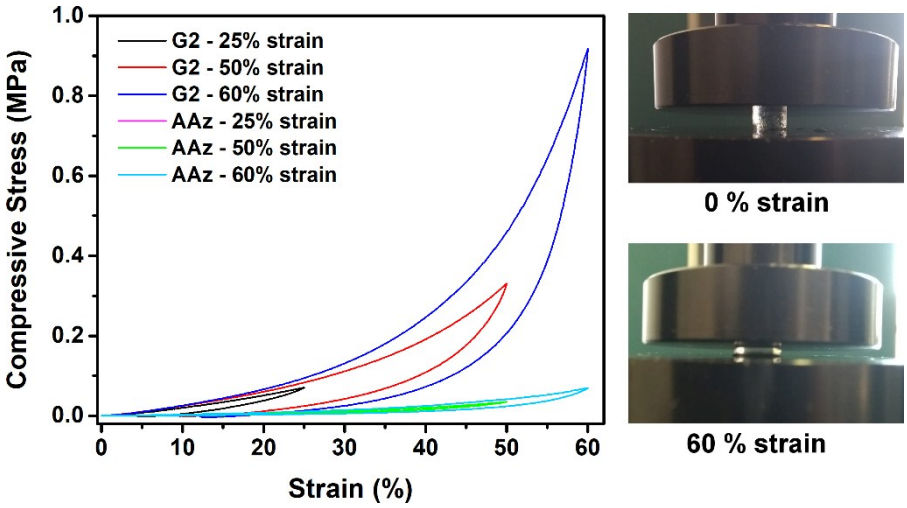


Figure S19. Sequential loading-unloading compression tests without resting time between the consecutive loading cycle at increasing levels of maximum strain for G2 and AAz hydrogels. The digital photos show the G2 hydrogel at 0 % (top) and 60 % strain (bottom), respectively.

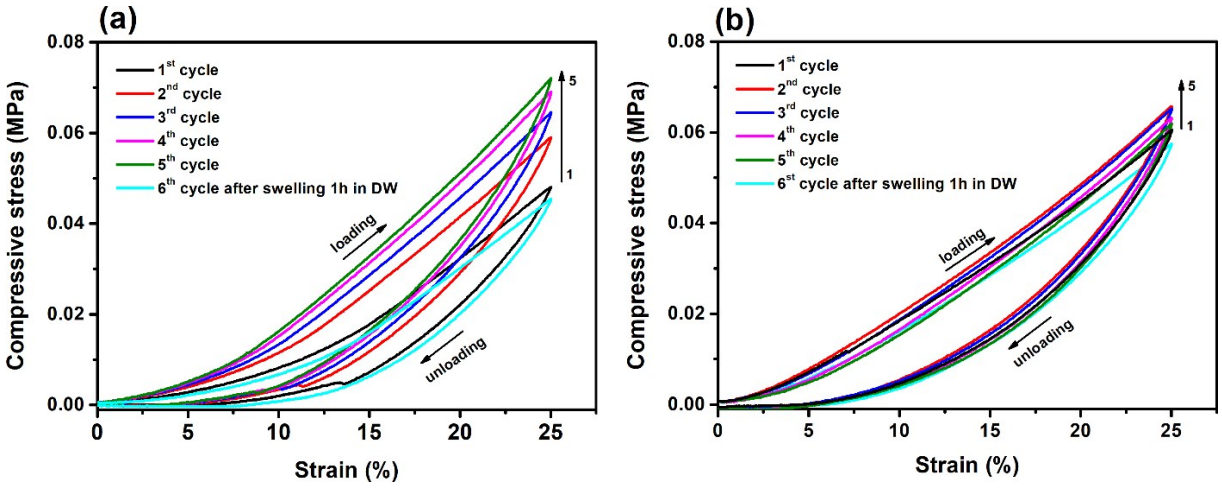


Figure S20. Sequential loading-unloading compression tests without resting time between the consecutive loading cycle at 25% strain for: (a) G2 swollen in DW and (b) G2 swollen in MV solution.

Table S3. Summary of hydrogels mechanical property parameters determined from loading-unloading cycles up to strain of 25% using a compression rate of 0.86 mm/min

Code	Cycle[a)]	AAz	PhDA	G2	G2-MV
Toughness (kJ/m^3)[b)]	1	89.57	106.1	417.6	652.7
	2	100.2	125.1	553.5	695.2
	3	100.5	119.1	616.8	684.7
	4	101.8	122.4	667.1	641.5
	5	104.4	121.6	696.3	614.7
	6	78	90.2	384.11	600.8
Dissipated energy (kJ/m^3)[c)]	1	18.5	28.6	159.2	270.5
	2	20.4	30.4	203.4	284.6
	3	19.5	30.1	224.7	273.7
	4	20.9	32.7	242.8	256.6
	5	20.7	35.6	254.3	246.1
	6	14.7	23.4	152.8	248.5
Recovery efficiency(%)[d)]	6	79.4	81.8	96.0	91.8

[a)] During loading–unloading tests, no resting time was given between the first 5 consecutive loading cycles, while before the 6th cycle the hydrogels were re-swollen for 60 min in de-ionized water.

[b)] toughness was estimated by the area below the stress–strain curve of the loading cycle for each sample.

[c)] dissipated energy was calculated as the area of compressive loading-unloading cycle.

[d)] the recovery was determined as the ratio between the area of the 6th hysteresis loop to the first hysteresis loop.

S5: Applications of PiPOx-PA5 hydrogels

Water purification

The efficiency of pollutant removal (in %) was determined using the following equation[12]:

$$E_{pollutant} = \frac{[C]_0 - [C]_t}{[C]_0} \cdot 100 \quad \text{(S6)}$$

where $[C]_0$ and $[C]_t$ represents the initial concentration of the solution containing the pollutant and the concentration at time t after hydrogel immersion in mmol/L.

The amount of pollutant bound to the adsorbent was determined using the following equation[12]:

$$q_t = \frac{([C]_0 - [C]_t) \cdot M_w \cdot V}{m} \quad \text{(S7)}$$

where q_t (mg/g) is the amount of micropollutant adsorbed per gram of adsorbent G6 at time t, $[C]_0$ and $[C]_t$ represents the initial concentration of the solution containing the pollutant and the concentration at time t after hydrogel immersion in mmol/L; m (mg) is the mass of hydrogel G6 used in the experiment, M_w (g/mol) is the molar mass of the micropollutant and V denotes the volume of the pollutant solution used.

The experiments involving water purification were performed at 25 °C in water.

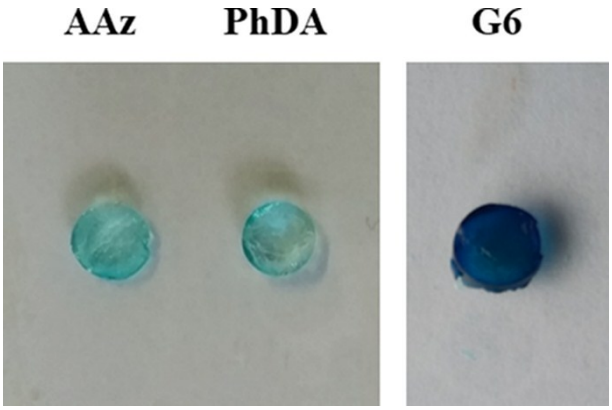


Figure S21. Digital photos showing the color changes of the PiPOx-AAz, PiPOx-PhDA, and G6 hydrogels after swelling in 0.05 mM solution of methylene blue for 24 h.

Table S4. The equilibrium uptake percentage and amount of micropollutant adsorbed per gram of G6

Pollutant	**Uptake (%)**		**Uptake q_e (mg/mL)**	
	PiPOx-AAz	**PiPOx-PhDA**	**PiPOx-AAz**	**PiPOx-PhDA**
Bisphenol A	7	4	2.4	1.4
2-Naphthol	5	3	0.7	0.4
Fluorescein sodium	0	0	0	0
Methyl orange	0	0	0	0
Methylene blue	10	7	5	3.2
Methyl red	9	6	4.1	2.6

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