SUPPLEMENTARY INFORMATION

Selective and very Efficient Dye Scavenging by a pH-Responsive Molecular Hydrogelator

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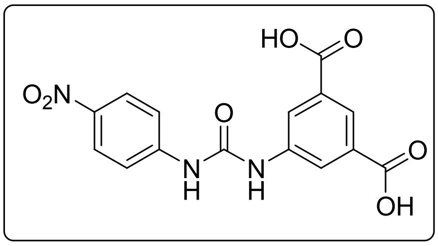
CONTENTS:

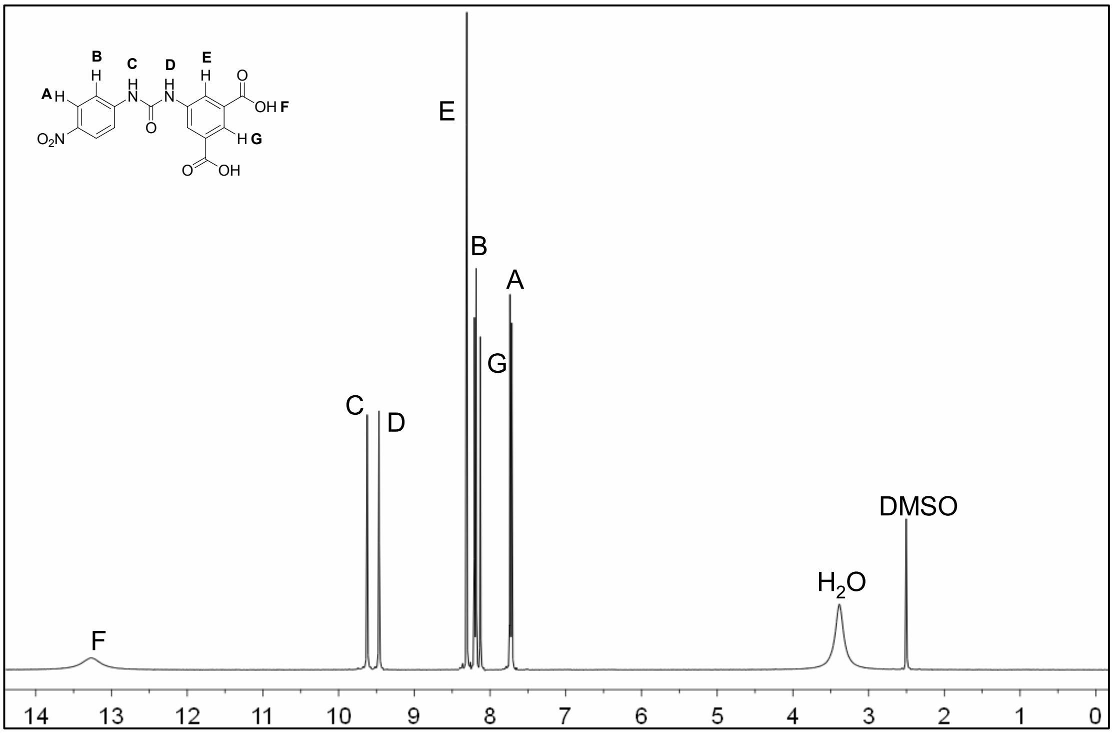
(A) Synthesis and characterization of 5-(3-(4-nitrophenyl)ureido)isophthalic acid (compound 1)



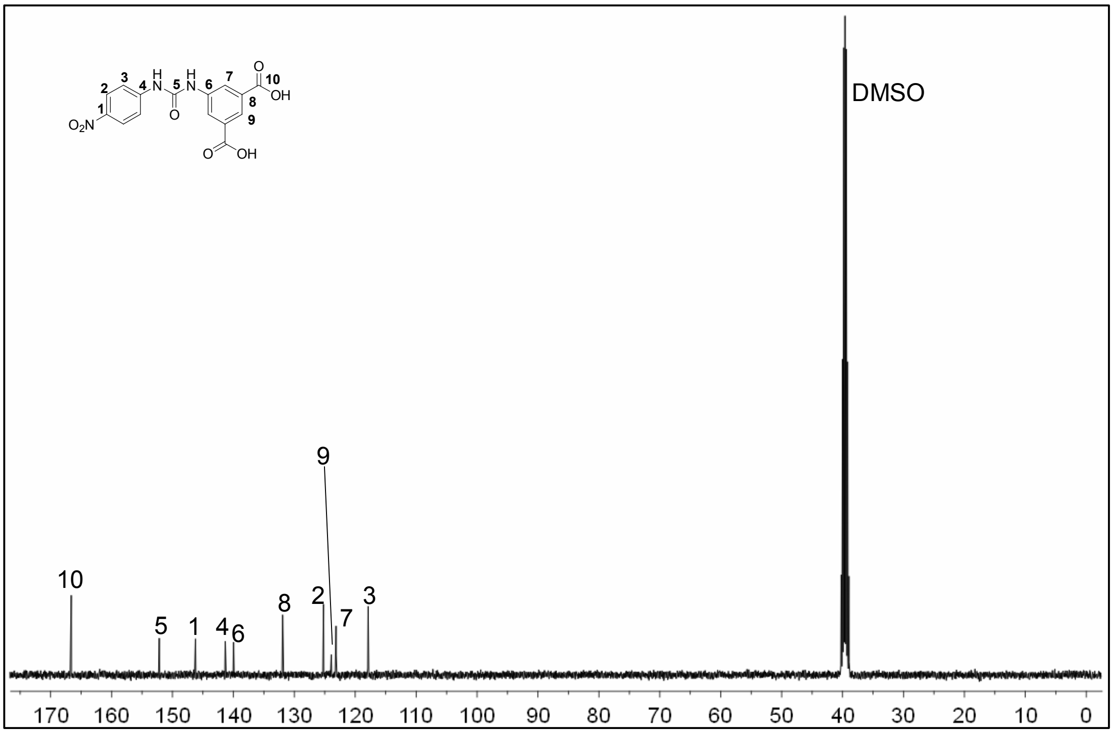
A solution of 4-nitrophenyl isocyanate (0.64 g, 3.9 mmol) in 50 mL of dry THF was added dropwise over a solution of 5-aminoisophthalic acid (0.78 g, 4.3 mmol) in 50 mL of dry THF in presence of 8.62 mmol of triethylamine. The mixture was stirred at room temperature for 24 h and the solvent was evaporated under vacuum. The resulting yellow solid was treated with 50 mL of 1 M aqueous NaOH and the insoluble material removed by filtration. The red solution was treated with aqueous HCl to obtain a yellow gel (pH=3). The gel phase was filtered, washed with distilled water and finally the solvent was evaporated under vacuum to yield compound **1** as a yellow solid.

Yield = 1.25 g, 92 %; m.p. = 296-297 ºC; IR (KBr) ν = 3493, 3377, 1714, 1616, 1601, 1569, 1506 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d6): δ = 7.72 (2 H, d, J = 9.2 Hz), 8.12 (1 H, s), 8.19 (2 H, d, J = 9.2 Hz), 8.30 (2 H, s), 9.46 (1 H, s), 9.62 (1 H, s), 13.26 (2 H, br,s) ppm; ^{13}C-NMR (400 MHz, DMSO-d6): δ = 117.810, 123.075, 123.845, 125.138, 131.849, 139.903, 141.266, 146.149, 152.095, 166.543 ppm; ESI-MS *(m/z)* = 346.0677 $[M + H]^+$; $C_{15}H_{11}N_3O_7$,

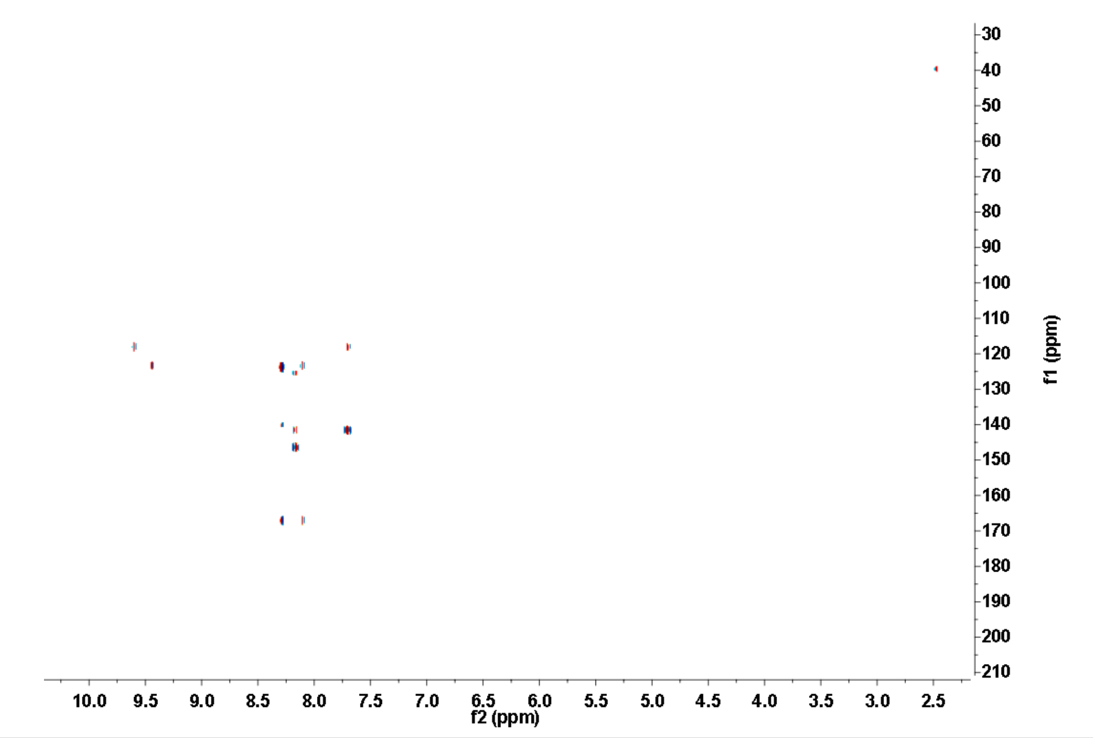
^{1}H-NMR spectra of **1** (400 MHz, DMSO-d6, 0.2 M)



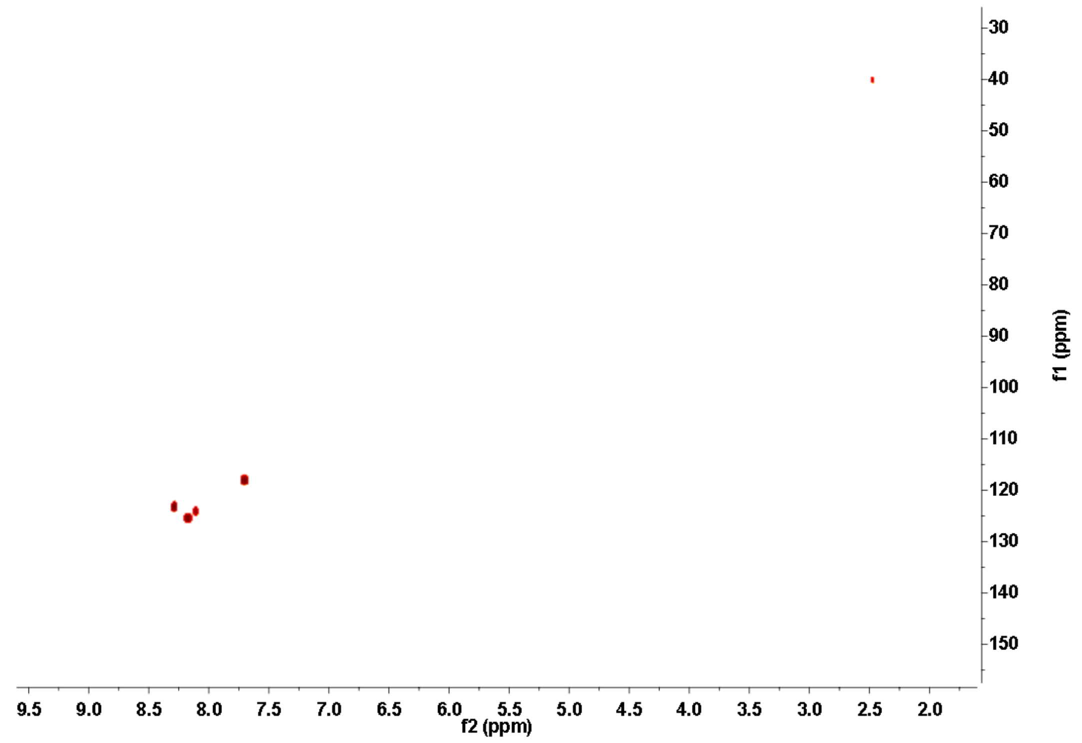
^{13}C-NMR spectra of **1** (400 MHz, DMSO-d6, 0.2 M)



HMBC-NMR spectra of **1** (400 MHz, DMSO-d6, 0.2 M)



HSQC-NMR spectra of **1** (400 MHz, DMSO-d6, 0.2 M)



(B) Hydrogel formation procedures

1. In water-methanol mixtures

In a typical procedure 5 mg of compound **1** (14.5 10-2 mmol) were heated in a screw-capped vial containing 1 mL of a 9:1 water:methanol mixture until complete dissolution. Upon to cooling to room temperature a gel was formed after *ca*. 5 minutes.

2. pH tuning with HCl

In a typical procedure 5 mg of compound **1** (14.5 10-2 mmol) were dissolved in 0.5 mL of 0.1 M aqueous NaOH. pH was carefully adjusted to *ca*. 3 with a 0.1 M aqueous solution of HCl to yield instantaneously a hydrogel. In order to improve gel homogeneity the system can be heated in a screw capped vial at 90 ºC for several minutes and then sonicated at room temperature for 5 minutes.

3. pH tuning with glucono-δ-lactone

In a typical procedure 5 mg of compound **1** (14.5×10^{-2} mmol) were dissolved in 0.5 mL of 0.1 M aqueous NaOH. The solution was acidified by slow hydrolysis of glucono-δ-lactone (0.5 mL of 0.2 M aqueous solution).[1]

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[1] Adams, D. J.; Butler, M. F.; Frith, W. J.; Kirkland, M.; Mullen, L.; Sanderson, *Soft Matter* **2009**, *5*, 1856-1862

(C) Thermal stability studies

The vials containing the gels were immersed in an oil bath with controlled temperature and the gel stability upon vial inversion was tested.

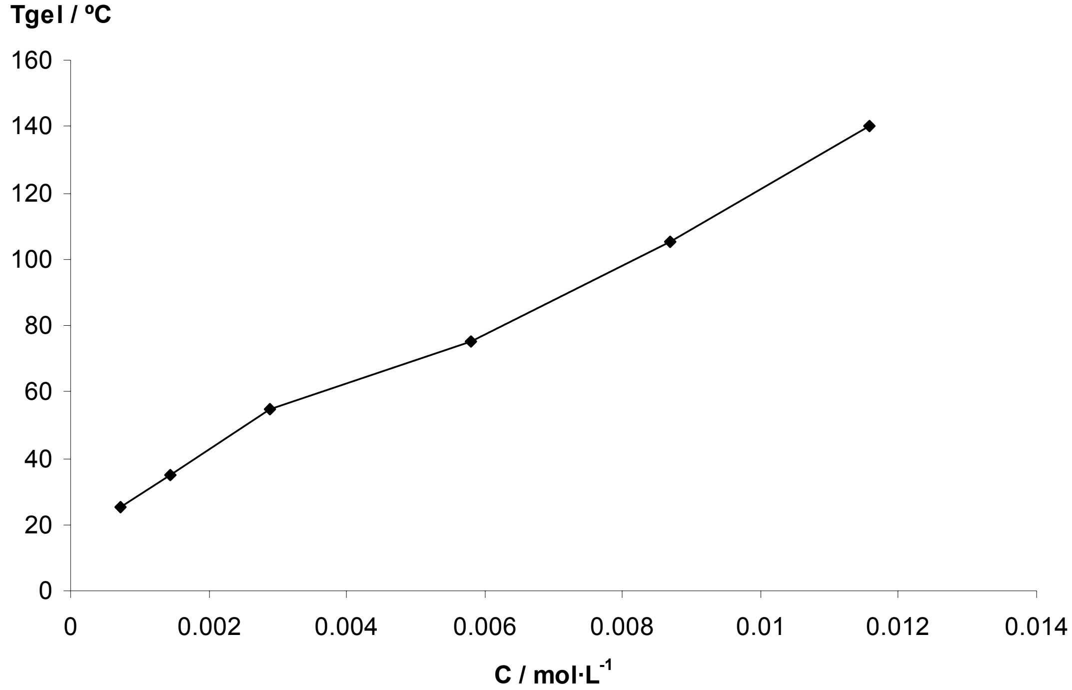


Figure S1. Dependence of thermostability of hydrogels formed by compound **1** on the concentration of gelator. The gels were obtained by acidification with aqueous HCl of a solution of **1** in basic water and sonication.

(D) ^{1}H-NMR spectra of deprotonated gelator and hydrogel.

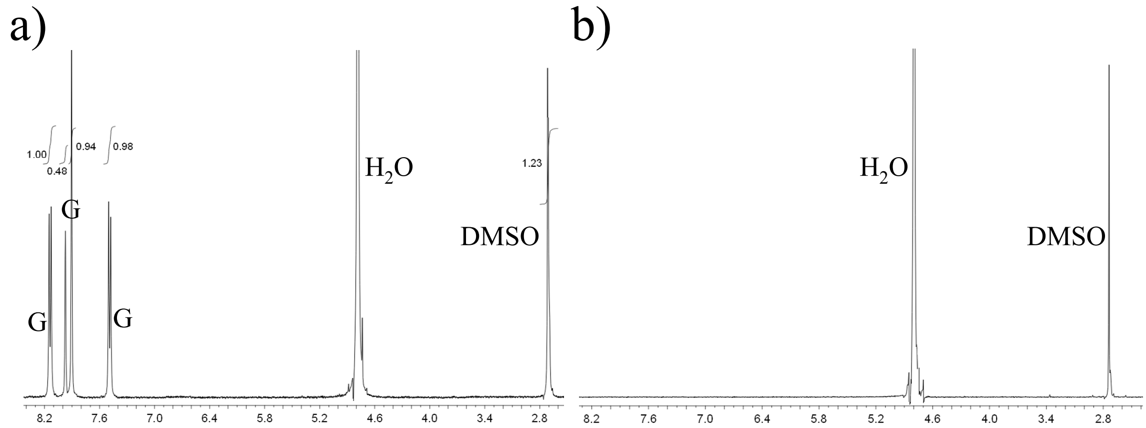


Figure S2. a) ^{1}H-NMR spectrum of compound **1** in D_2O (pH=12, DMSO is used as internal standard). b) ^{1}H-NMR spectrum after hydrogel formation at pH= 3. (G = signals corresponding to gelator **1**)

(E) Thermochromatic and solvatochromatic properties of the hydrogels.

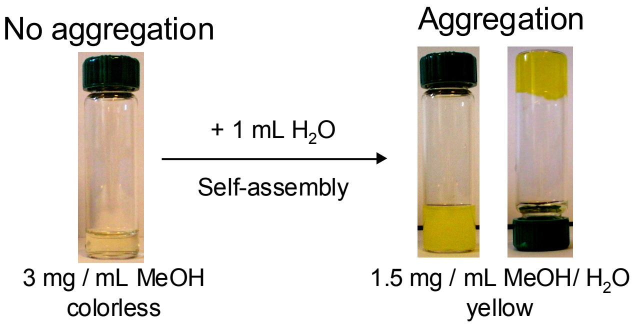


Figure S3. Colour changes observed upon addition of water to a solution in methanol dissolution**.**

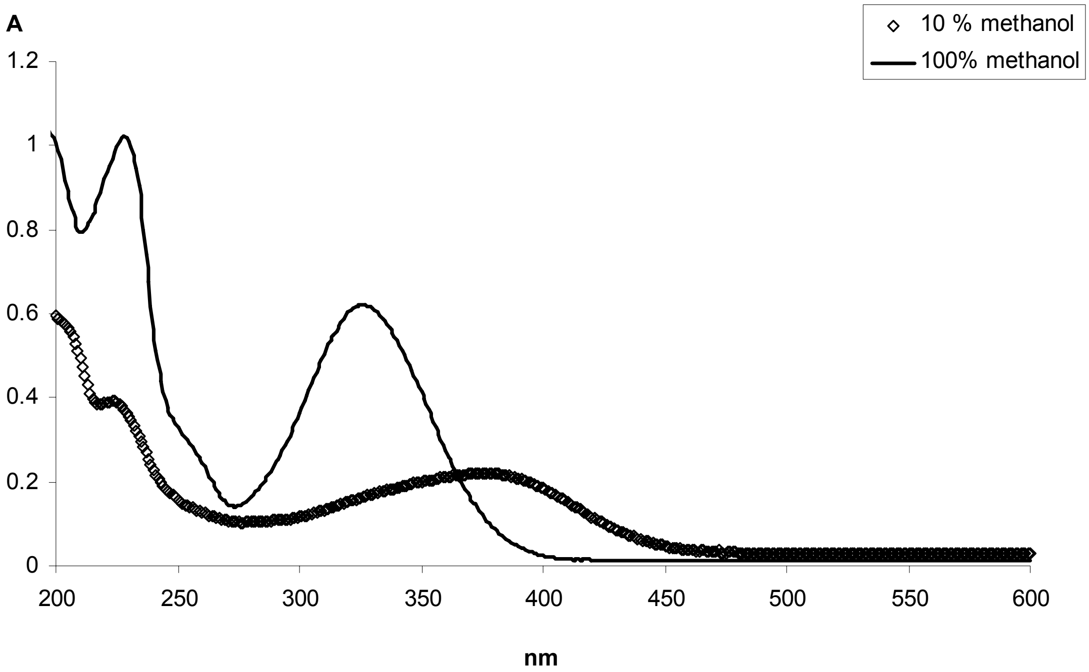


Figure S4. UV-vis spectra of compound **1** (1.5 mM) in methanol and in methanol:water 10:90.

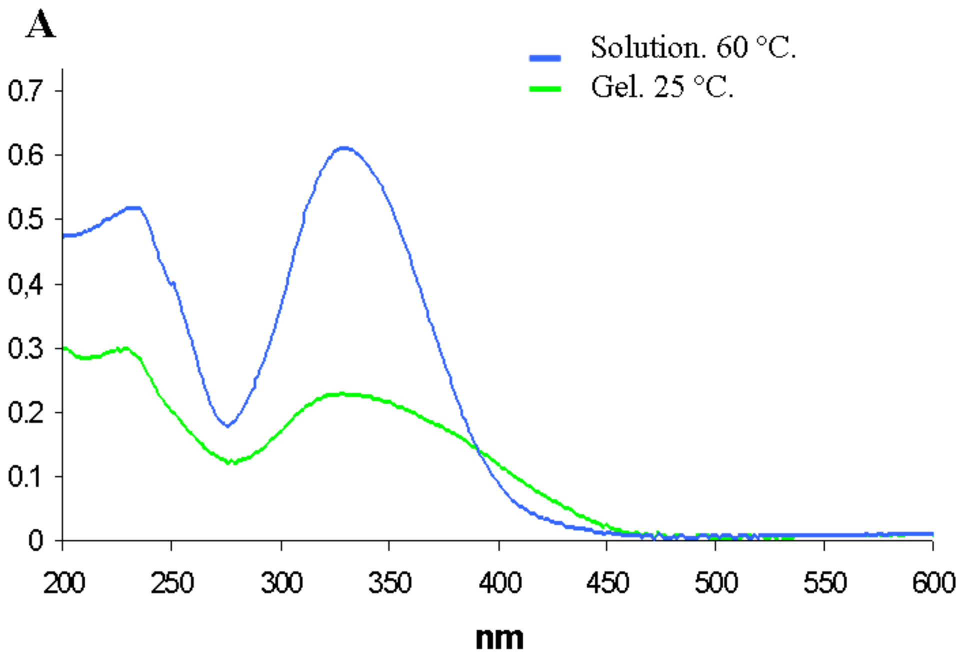


Figure S5. UV-vis spectra of compound **1** (1.5 mM in 80:20 H_2O:MeOH) at different temperatures.

(F) X-Ray Powder diffraction

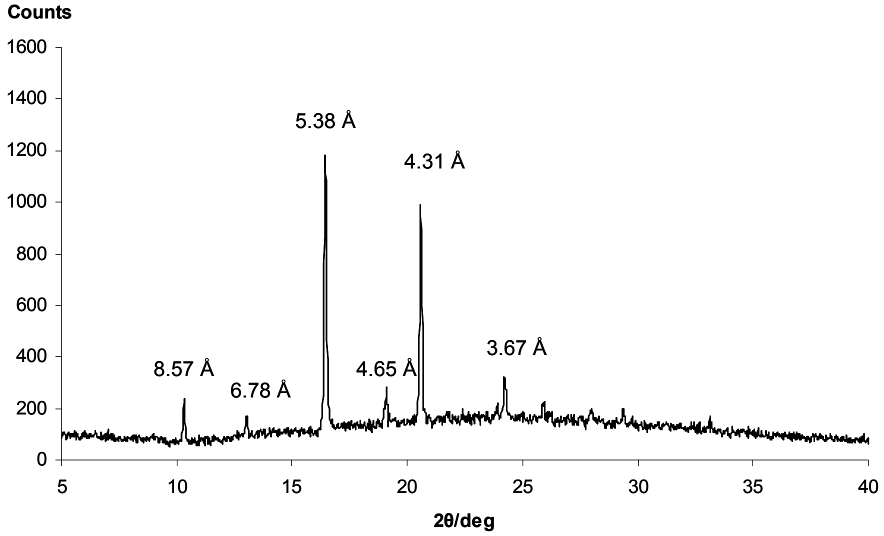
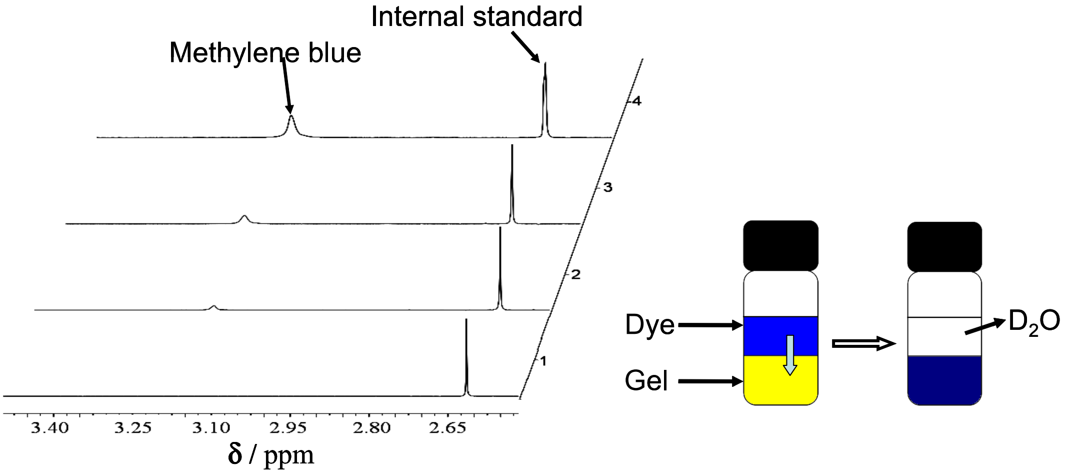
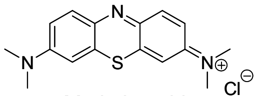


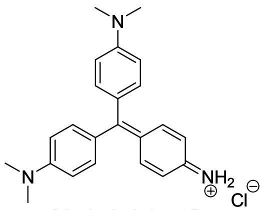
Figure S6. Powder XRD profile of the xerogel of compound **1**. (Obtained from a gel formed in a 9:1 water:methanol mixture).

(G) Dye adsorption studies

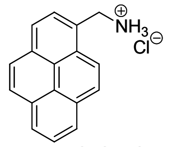




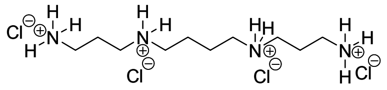
Methylene blue



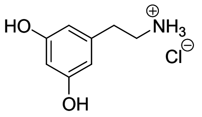
Methyl violet 2B



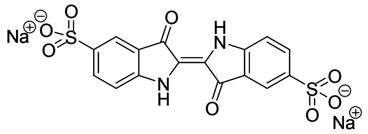
1-Pyrenemethylamine hydrochloride



Spermine tetrahydrochloride

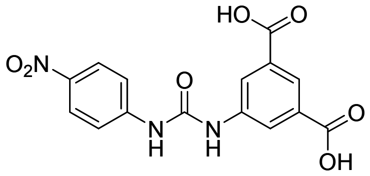


Dopamine hydrochloride

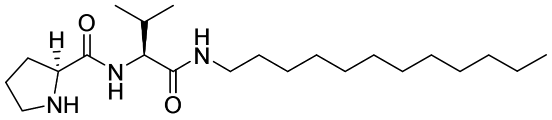


Indigo carmine

Figure S7. Structure of the dyes used in the experiments reported in Table 1. ^{1}H-NMR spectra of a solution of methylene blue (7.3 mM, 1 mL) deposited on a hydrogel formed by **1** (1 mL, 14.5 mM) recorded at different times (4 = 1h, 3 = 6 h, 2 = 24 h, 1 = 48 h).



1



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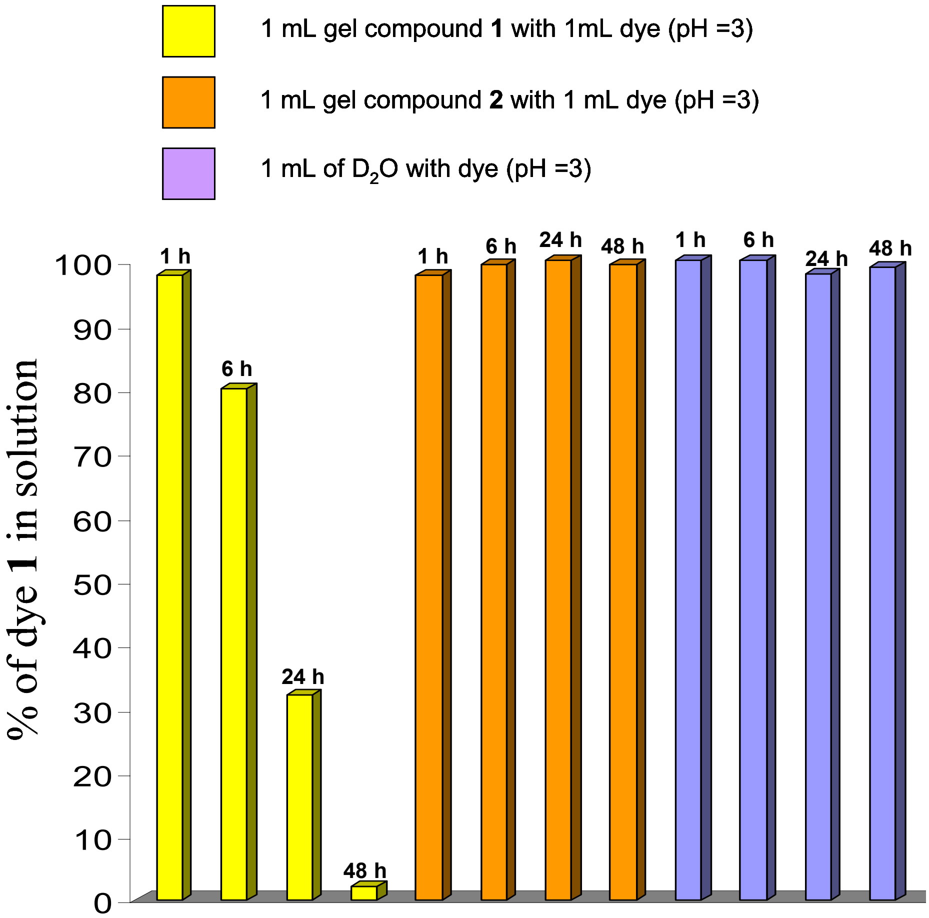

Figure S8. Time dependence of the variation of dye concentration for methylene blue solutions (7.3 mM, 1 mL) deposited on 1 mL of the hydrogels formed by **1** and **2**[2] (14.5 mM).

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[2] Rodríguez-Llansola, F.; Miravet, J.F.; Escuder, B.; *Chem Commun*, **2009**, 7303-7305.

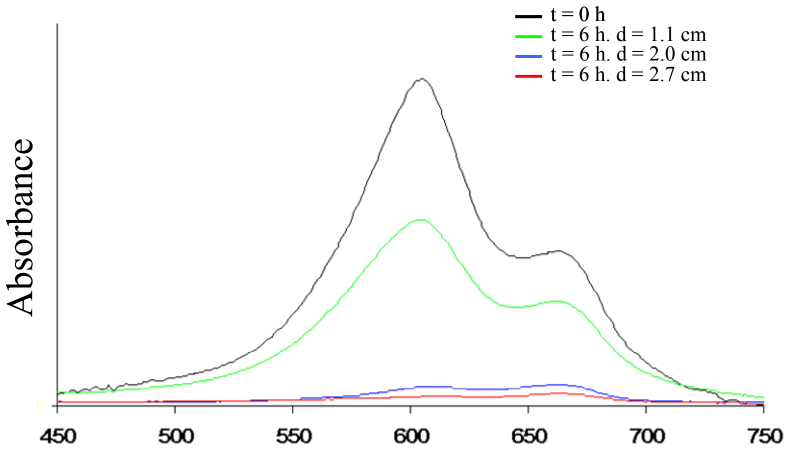

Figure S9. Effect of vial shape on the kinetics of the absorption of methylene blue in the hydrogels formed by **1**. A solution of methylene blue (3.5 mM, 1.5 mL) was deposited on 1 mL of the hydrogel (14.5 mM) formed in vials of different diameter of compound **1**. After 6 hours the solution of dye was analysed by UV-vis spectroscopy.

Table S1. Efficiency of dye removal by the pH-tuning gel formation approach. ([Dye] = 2 mM, [gelator] = 3 mM$^{a)}$

	(absorbed dye/gelator) molar ratio	**(absorbed dye/gelator) mass ratio**
Methylene blue 604 nm	0.73	0.79
Methyl violet 2B 539 nm	0.58	0.79
Indigo carmine 611 nm	0.09	0.1

a) A solution of dye (4 mL, 1mg/mL) was added to a solution of gelator at basic pH. Addition of 0.5 mL of 0.1 M aqueous HCl provoked the desired gelation. After filtration, the solutions were analysed by UV-vis spectroscopy.

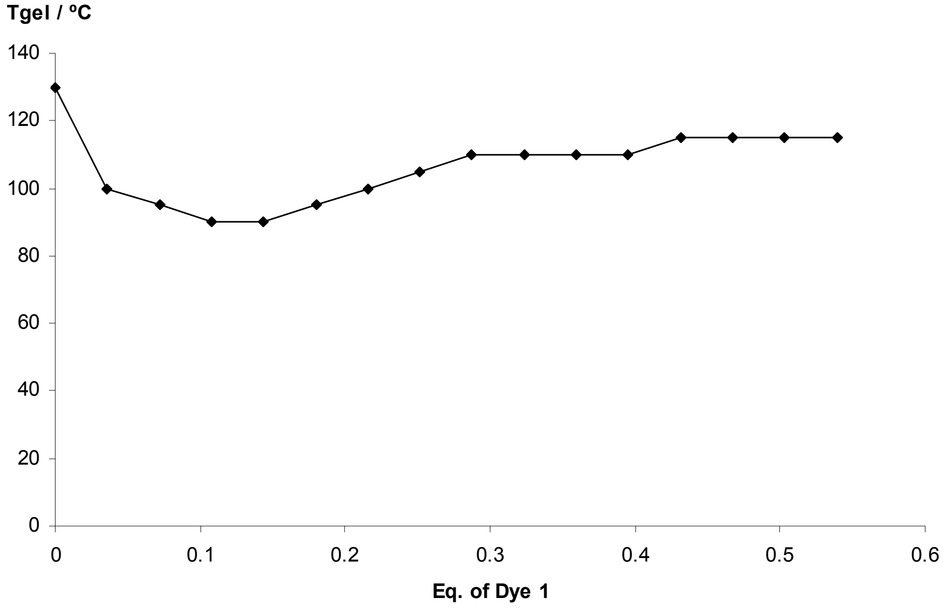

Figure S10. Variation of thermal stability of hydrogel formed by **1** (8.7 mM) with the addition of methylene blue (gels were formed by pH-tuning in the presence of the dye by addition of glucono-δ-lactone).

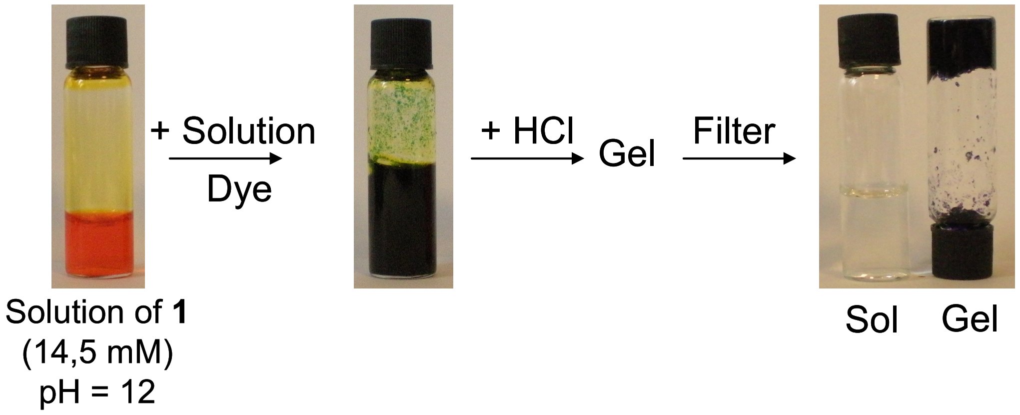

Figure S11. Methylene blue removal process by pH-triggered hydrogel formation. The final pictures on the right side show the result of filtering through a sintered glass half of the gel sample, remaining the other half as a gel in the vial.

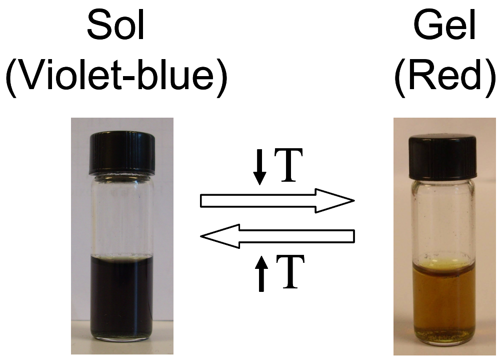

Figure S12. Reversible hydrogel formation by **1** in the presence of methyl violet 2B

(H) Crystal structure data

Crystal data for 5-(3-(4-nitrophenyl)ureido)isophthalic acid (compound **1**): $C_{15}H_{11}N_3O_7$ M = 345.27, monoclinic, $P2_1/c$, a = 15.9755(5), b = 18.8482(4), c = 26.1414(11) Å, β = 106.689(4)°; V = 7539.9(5) Å^3, Z = 4, D = 1.217 g cm^{-3}, $F(000)$ = 2848.0. T= 150 °K; μ (Mo-K_α) = 0.099 mm $^{-1}$. 16647 Independent reflections were collected on an Oxford Diffraction Gemini-S-Ultra diffractometer . The structure was solved by direct methods and refined on F^2 using SHELXL97. Final conventional R factor 0.0654, wR2 0.1875. All the solvent molecules were removed from the final cif file using SQUEEZE.

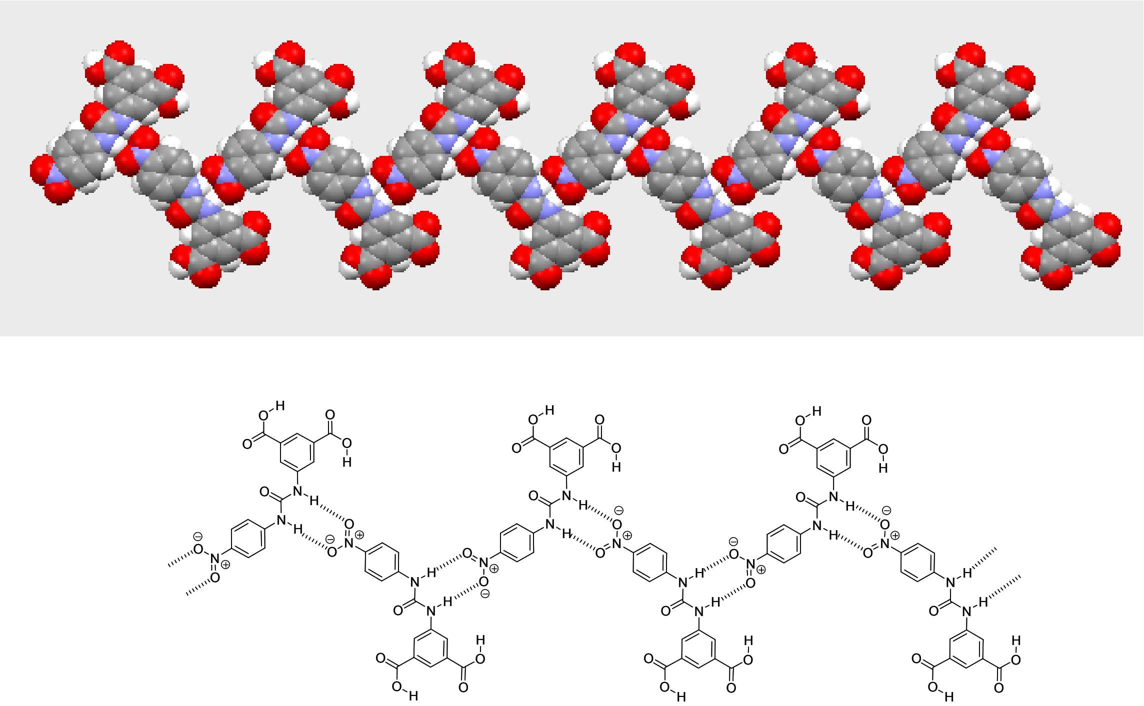

Figure S13. Space-filling and schematic representation of the ribbons formed by hydrogen bonding between urea and nitro groups in the crystal structure of compound **1**.

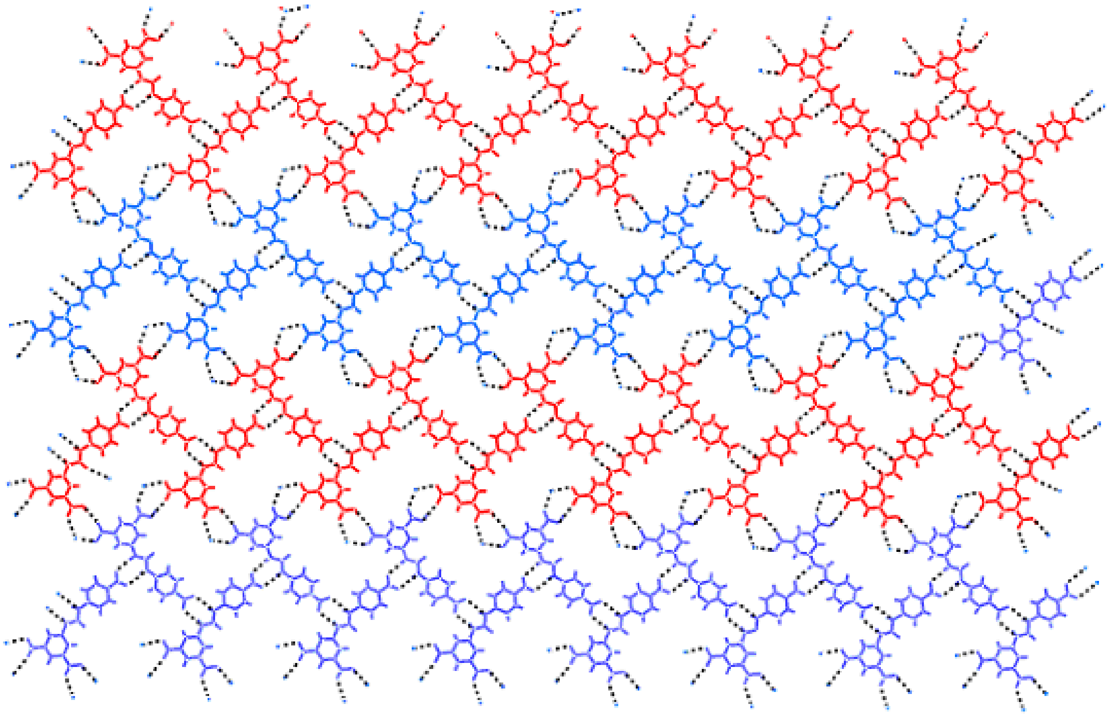

Figure S14. Wireframe representation of a layer found in the crystal structure of **1**. Successive ribbons formed by urea-nitro hydrogen bonding are colored in red and blue.