

Selective and highly efficient dye scavenging by a pH-responsive molecular hydrogelator

Article

Accepted Version

Rodriguez-Llansola, F., Escuder, B., Miravet, J. F., Hermida-Merino, D., Hamley, I. W. ORCID: <https://orcid.org/0000-0002-4549-0926>, Cardin, C. J. ORCID: <https://orcid.org/0000-0002-2556-9995> and Hayes, W. ORCID: <https://orcid.org/0000-0003-0047-2991> (2010) Selective and highly efficient dye scavenging by a pH-responsive molecular hydrogelator. Chemical Communications, 46 (42). pp. 7960-7962. ISSN 1359-7345 doi: 10.1039/c0cc02338h Available at <https://centaur.reading.ac.uk/8225/>

It is advisable to refer to the publisher's version if you intend to cite from the work. See [Guidance on citing](#).

To link to this article DOI: <http://dx.doi.org/10.1039/c0cc02338h>

Publisher: The Royal Society of Chemistry

All outputs in CentAUR are protected by Intellectual Property Rights law, including copyright law. Copyright and IPR is retained by the creators or other copyright holders. Terms and conditions for use of this material are defined in the [End User Agreement](#).

www.reading.ac.uk/centaur

CentAUR

Central Archive at the University of Reading

Reading's research outputs online

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

Francisco Rodríguez-Llansola,^a Beatriu Escuder,^{a*} Juan F. Miravet,^{a*} Daniel Hermida-Merino,^b Ian. W. Hamley,^b Christine J. Cardin^b and Wayne Hayes^{a*}

⁵ Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

A structurally simple low molecular weight hydrogelator derived from isophthalic acid forms robust pH-responsive hydrogels capable of highly efficient and selective dye adsorption.

Molecular gels represent an intriguing type of organic nanostructured soft material. Molecular gelators form elongated supramolecular aggregates that further evolve to nanofibrillar networks which entrap the solvent to yield a gel.¹ This type of soft matter is of interest in areas such as responsive materials, catalysis or electronic and photonic materials.² Practical applications of molecular hydrogelators are especially appealing due to the biological relevance of water as a solvent. In recent years several structurally diverse molecular hydrogelators have been described.^{1f,g} A topical aspect within this field is the stimuli responsiveness associated with molecular gels. In addition to their characteristic temperature and concentration dependence, the formation of molecular gels can be controlled by different stimuli. In particular, the presence of pH sensitive groups in the structure of the gelator can be exploited advantageously for the controlled formation of molecular gels.^{1g} Herein we report a structurally very simple, pH-responsive bisaromatic hydrogelator (**1**) that is derived from isophthalic acid and contains a urea functional group. The molecule reported is a remarkable example of a molecular hydrogelator capable of selective and extremely efficient incorporation of dyes into the formed hydrogel network. In this paper we additionally report on the fascinating layered solid state structure of the gelator **1** which provides a framework to account for the dramatic dye uptake capabilities of this urea in its hydrogel form.

The interaction of molecular gel fibers with different guest species has been reported.³ The incorporation of dyes in hydrogels formed by a tripeptide derivative which forms gels at basic pH values has been described revealing that molecular hydrogels can potentially be used to remove industrial dyes from waste water.^{4a} The use of gels of ionic liquids for dye removal has also been reported recently.^{4b} The bisaromatic hydrogelator **1** was prepared in high yield by direct addition of 5-aminoisophthalic acid to 4-nitrophenyl isocyanate and exhaustively characterized (see SI). Hydrogels were formed above a concentration of 0.9 mM (0.3 mg mL⁻¹) by acidification with aqueous HCl of a solution of **1** in basic water and sonication. Alternatively, for a slow and homogeneous acidification of the system, the hydrolysis of water soluble glucono- δ -lactone can be used.⁵ Furthermore,

the gelation in neutral water was also possible in the presence of small amounts (ca. 10 % v/v) of polar organic solvents such as methanol or DMSO when accompanied by gentle heating until complete dissolution was attained and the solution was then allowed to cool to 25 °C. The gels were found to be significantly more stable upon increasing the concentration of gelator (see SI). Remarkably, the hydrogels were stable at temperatures above the boiling point of water when the gelator concentration was higher than 9 mM.

The gelation process by pH tuning provoked a colour change from red-orange to yellow associated with the protonation of the carboxylate groups (see Fig. 1). The observed yellow colour in the gel samples was attributed to intermolecular interactions. Solutions of compound **1** in MeOH are colourless but upon increasing the proportion of water in the system, aggregation takes place giving rise to the observed yellow colour which correlates with the observed absorption above 400 nm (see SI, Fig. S3 and S4).

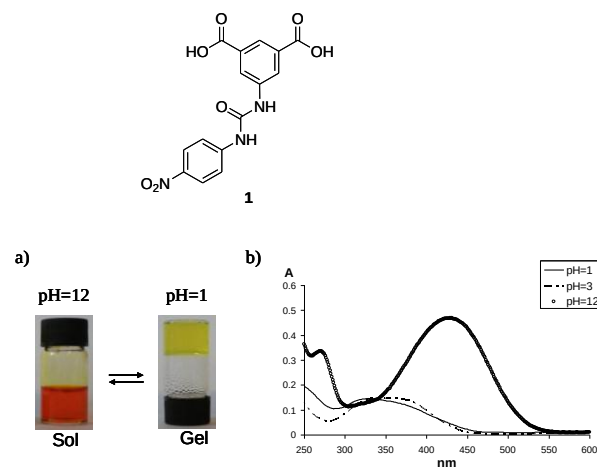


Fig. 1. a) Pictures of vials containing a 3 mM aqueous solution of compound **1** (left) and the hydrogel formed upon acidification (right) b) UV-vis spectra of compound **1** (1.5 mM) at different pH values.

The morphology of the gel obtained by pH-tuning was observed by Atomic Force Microscopy (AFM) to reveal the presence of a network of nanofibers that were several microns in length and less than 50 nm in width (Fig.2). The X-ray powder diffraction pattern of a xerogel from a hydrogel of **1** revealed the crystalline nature of the fibrillar network (SI, Figure S6).

Needle-like crystals of **1** suitable for single crystal X-ray

analysis were obtained from slow evaporation of a solution of compound **1** in a 7:3 water:methanol mixture. The bisaromatic hydrogelator **1** crystallized in the monoclinic system with a dramatic layered structure. These layers are formed by ribbons of molecules formed by intermolecular hydrogen bonding between the urea NH units and nitro moieties.⁶ The layer is constructed by connection of the ribbons by intermolecular hydrogen bonding among the carboxylic acid functional groups at the ribbon edges (see SI, Figs. S13-S15).

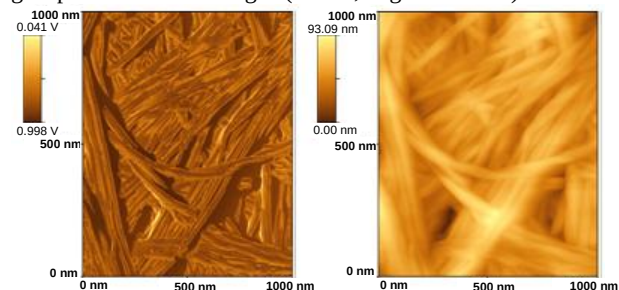


Fig. 2. Atomic Force Microscopy images of xerogels obtained from the hydrogel formed by **1** (0.9 mM).

The X-ray powder diffraction pattern of a xerogel from a hydrogel of **1** revealed the crystalline nature of the fibrillar network (SI, Fig. S6) and showed that the arrangement found in the fibers is a polymorph of that described in the crystal structure mentioned above, which presents different diffraction peaks.

FT-IR studies unveiled that the xerogels formed by **1** presented a 2D arrangement of intermolecular hydrogen bonds related to that found in the crystal structure. The FT-IR and ATR grazing angle spectra showed that the carbonyl stretching band intensity was reduced significantly when the sample was irradiated in grazing angle mode (see Fig. 4a). According to previous studies,⁷ these results indicate a preferred orientation of the studied hydrogen bonding groups in a plane, suggesting that the hydrogen bonding array is oriented along the axis of a nanofiber.

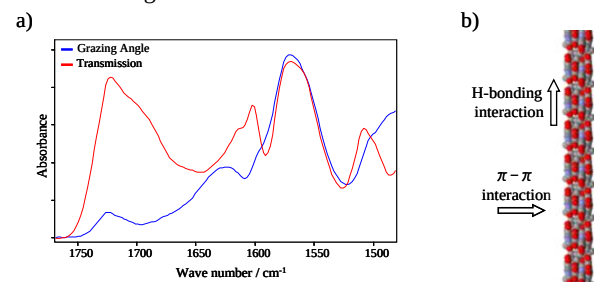


Fig. 4. a) Transmission vs. grazing angle ATR FT-IR spectra for xerogels of compound **1**. b) Proposed orientation of the hydrogen bonding interactions within the fibers

Therefore, a model is proposed for **1** in which the π - π -stacking and hydrogen bonding interactions are orthogonally related with weaker aromatic interactions that lie perpendicular to the fiber axis (Fig. 4b). In the model gel fibers can be seen as a the result of a frustrated crystallization caused by the partial ionization of carboxylic acid units that would preclude the formation of extended 2D hydrogen arrays as those observed in the crystal structure and favour the

formation of elongated assemblies

Interestingly, the crystalline layered structures have in common an inherent ability to mimic clays by intercalation of guest molecules.⁸ With this concept in mind, the potential for incorporation of guest molecules into the hydrogel fibres was tested. A preliminar study revealed that these hydrogels were very efficient in the adsorption of methylene blue. As shown in Fig. 5, a very small quantity of hydrogel (2 mL, 20 mM) is able to complete decolour a 500 mL solution of methylene blue with a dye concentration of 8 mg L⁻¹. It has to be noted that the adsorption of methylene blue into molecular hydrogels is not a general property. For example, adsorption of the dye was not observed when a hydrogelator that did not feature aromatic units that was available in our laboratories was studied (see SI, Figure S8).

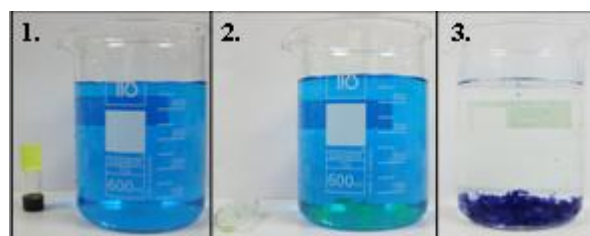


Fig.5. Pictures of the methylene blue removal process. (1) Solution of methylene blue in water (500 mL, 8 mg mL⁻¹) and vial containing a hydrogel of **1** (2 mL, 20 mM); (2) Solution of methylene blue with the hydrogel fragments deposited at the bottom of the beaker. (3) Picture of the system after 72 hours.

In a more detailed study, the adsorption of six different compounds into the gel was studied (see Table 1) including two planar, positively charged aromatic compounds that are used commonly as dyes, methylene blue and violet blue 2B. Additionally, two cationic aromatic compounds 1-pyrene methylammonium hydrochloride and dopamine, and an anionic dye, indigo carmine were used as possible guests. The last substrate studied was spermine, an aliphatic tetracationic substrate that is known to interact with negatively charged DNA strands. For the adsorption studies, solutions containing the different guests were deposited over a hydrogel obtained by pH-tuning. Since spermine does not exhibit a strong UV-vis chromophore, the adsorption was monitored by ¹H NMR spectroscopy for all of the above dyes.

Noticeably the hydrogel formed by compound **1** was extremely selective in the adsorption of the positively charged dyes methylene blue and methyl violet 2B. When a solution of these dyes (7.25 mM, 1 mL) was deposited on 1 mL of the hydrogel (14.5 mM), the dyes could not be detected by NMR spectroscopy in the original solution after 48 hours. The fact that the aliphatic tetracation spermine was not adsorbed at all under the same conditions supports the hypothesis that intercalation constitutes the main driving force for the aggregation rather than purely electrostatic interactions. Negligible adsorption into the gel was measured for positively charged dopamine or anionic indigo carmine. In contrast, 62 % of the initial concentration 1-pyrene methyl ammonium hydrochloride was adsorbed on the hydrogel fibers. The selectivity observed in the interaction with methylene blue

and methyl violet 2B in comparison to the other aromatic substrates reveals that the adsorption is also selective to the nature of the aromatic moiety.

Table 1. Adsorption of different species on the hydrogel formed by **1**.^a

Adsorbate	% Adsorbed
Methylene blue	98
Methyl Violet 2B	97
1-Pyrenemethylamine	62
Spermine	<1
Dopamine	<1
Indigo carmine	<1

^a Determined by NMR. A solution in D₂O of these species (7.25 mM, 1 mL) with DMSO as internal standard was deposited for 48 h on 1 mL of the hydrogel formed with D₂O (14.5 mM). The structure of the adsorbates is depicted in the SI

For a solution of the dye deposited over a hydrogel formed in a vial the maximum amount of dye adsorption and the kinetics of the process are very dependent on the vial dimensions, namely, in the contact area between gel and solution (see SI, fig. S9). These results indicate, that for this experimental setup, a diffusion controlled adsorption is taking place. For example, for vials with a diameter of 2.7 cm quantitative dye removal was observed in less than 6 hours. Importantly, the removal of dyes from solutions was tested taking advantage of the pH-responsive nature of hydrogel formed by **1**. For example, when aqueous HCl is added to a solution of methylene blue and the gelator a gel is formed. Filtration of the system afforded a colourless solution and, according to UV-vis spectroscopy, the dye was removed very effectively (>99%) (see SI, Fig. S12). Similar results were obtained for methyl violet 2B but for indigo carmine this procedure was significantly less efficient. Noticeably, the dye removal efficiency using this procedure is unprecedented – the dye-hydrogelator ratio was almost equimolar in the formed gels (see SI, Table S1). The measured removal efficiency parameter determined by UV-vis spectroscopy for methylene blue and methyl violet 2B was ca. 800 mg of dye per gram of gelator, a significant enhancement when compared to the values described for related systems. For example, the tripeptide based hydrogel aforementioned exhibited values of 7.36 mg g⁻¹ for Rhodamine B and 10.56 mg g⁻¹ for the dye direct red 80.^{4a} The dye removal efficiency is also notable when compared to the adsorption of methylene blue to a common adsorbent such as active charcoal which exhibits an efficiency of up to ca. 400 mg g⁻¹.⁹

Regarding the interaction on the gelator and the dyes, a direct proof on the intimate interaction taking place in this system is the fact that the thermal stability of the gels was significantly affected by the presence of the dyes (see SI, Fig. S10).

Finally, gel regeneration can be achieved easily. For example, after repetitive extractions with chloroform to remove the dye, the gel can be regenerated by dissolution in basic water followed by acidification.

In summary, a new simple urea-based compound capable of forming robust, pH-responsive hydrogels with outstanding dye scavenging properties has been described. It is to be noted that the hydrogels are comprised of a self-assembled nanofibrillar network as revealed by microscopy studies.

Interestingly, in this case a crystal structure of the gelator can be obtained which serves as a reference for a possible structural arrangement in the gel nanofibers which, as shown by X-ray diffraction studies possess a microcrystalline structure. A related 2D hydrogen bonding array was inferred for the xerogel by grazing angle IR spectroscopy. A remarkable fact is that the nanofibers interact selectively with positively charged dyes such as methylene blue and methyl violet 2B. The nanofibrillar structure provides with a stimuli responsive functional material which presents a very high aspect ratio. The pH responsiveness of the system gives an outstanding added value for potential practical applications. Dye solutions at basic pH containing the ionized, soluble, hydrogelator can be transformed easily into hydrogels upon acidification. Filtration of these systems affords colorless dye-free solution. With this procedure the hydrogels present an unprecedented capacity of dye removal with ca. 0.8 g of dye being captured by 1 g of the gelating component of the hydrogel. The extraordinary dye removal capabilities were found to be specific for this particular gelator and were attributed to its acidic character and its aromatic units. In addition to employment in industrial scale tasks such as waste water treatment, applications for hydrogels of this type in controlled drug release (especially gene therapy agents such as DNA intercalating drugs) are also envisaged.

Notes and references

^a Departament de Química Inorgànica i Orgànica, Universitat Jaume I, Avda. Sos Baynat s/n, 12071 Castelló, Spain; E-mail: escuder@uji.es, miravet@uji.es

^b Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD; E-mail: w.c.hayes@reading.ac.uk

† Electronic Supplementary Information (ESI) available: Experimental details and crystal structure description. See DOI: 10.1039/b000000x/

- (a) *Molecular Gels: Materials with Self-Assembled Fibrillar Networks*; R. Weiss, G.; P. Terech, Eds.; Springer, 2005; (b) P. Terech, R. G. Weiss, *Chem. Rev.*, 1997, **97**, 3133; (c) D. J. Abdallah, R. G. Weiss, *Adv. Mater.*, 2000, **12**, 1237; (d) J. van Esch, B. L. Feringa, *Angew. Chem. Int. Ed.*, 2000, **39**, 2263; (e) O. Gronwald, S. Shinkai, *Chem. Eur. J.*, 2001, **7**, 4328; (f) L. A. Estroff, A. D. Hamilton, *Chem. Rev.*, 2004, **104**, 1201; (g) M. De Loos, B. L. Feringa, J. H. van Esch, *Eur. J. Org. Chem.*, 2005, 3615; (h) A. R. Hirst, D. K. Smith *Chem. Eur. J.*, 2005, **11**, 5496; (i) M. George, R. G. Weiss, *Acc. Chem. Res.*, 2006, **39**, 489.
- (a) A. R. Hirst, B. Escuder, J. F. Miravet, D. K. Smith, *Angew. Chem. Int. Ed.*, 2008, **47**, 8002; (b) S. Banerjee, R. K. Das, U. Maitra, *J. Mater. Chem.*, 2009, **19**, 6649.
- (a) M.-O.M. Piepenbrock, G.O. Lloyd, N. Clarke, J.W. Steed, *Chem. Rev.*, 2010, **110**, 1960; (b) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S.-I. Kawano, N. Fujita, S. Shinkai, *Angew. Chem. Int. Ed.*, 2006, **45**, 1592; (c) B. Escuder, J. F. Miravet, J. A. Sáez, *Org. Biomol. Chem.*, 2008, **6**, 4378; (d) U. Maitra, S. Mukhopadhyay, A. Sarkar, P. Rao, S. S. Indi, *Angew. Chem. Int. Ed.*, 2001, **40**, 2281.
- (a) B. Adhikari, G. Palui, A. Banerjee, *Soft Matter*, 2009, **5**, 3452; (b) S. Dutta, D. Das, A. Dasgupta, P. K. Das, *Chem. Eur. J.*, 2010, **16**, 1493.
- D. J. Adams, M. F. Butler, W. J. Frith, M. Kirkland, L. Mullen, P. Sanderson, *Soft Matter*, 2009, **5**, 1856.
- S. George, A. Nangia, C.-K.Lam, T. C. W. Mak, J.-F. Nicoud, *Chem. Commun.*, 2004, 1202.
- S. E. Paramonov, H. Jun, J. D. Hartgerink, *J. Am. Chem. Soc.*, 2006, **128**, 7291.
- M. J. Zaworotko, *Chem. Commun.*, 2001, 1.
- S. Mukherjee, S. Bhattacharya, *J. Am. Chem. Soc.* 1949, **71**, 1725.