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## Versatile supramolecular pH-tolerant hydrogels which demonstrate pH-dependent selective adsorption of dyes from aqueous solution<sup>†</sup>

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We report a novel gelator functionalised with hydrazides (as replacements for carboxylic acids) which, as a result, is able to assemble into hydrogels across a wide pH range – this gelator exhibits pH-switchable dye adsorption-desorption dependent on protonation of the target dyes and their resulting interactions with the self-assembled gel nanofibres.

Supramolecular gels are fascinating colloidal soft materials in which molecular-scale information programmed into a gelator gets translated up to nanoscale fibres via self-assembly and then directs the macroscopic performance of the material.<sup>1</sup> These materials have great potential for applications - there has been significant interest in self-assembling hydrogels, which may find uses in aqueous environments ranging from nanomedicine to environmental science.<sup>2</sup> In recent times, some attention has begun to focus on using low-cost supramolecular gels to adsorb pollutants from water.<sup>3</sup> Self-assembled gels are intriguing materials for this purpose, as they are highly porous, and their internal nanostructuring should ensure they can bring high surface areas into contact with the pollutant, giving rise to effective adsorption. Das and co-workers have done significant work in this area,<sup>4</sup> reporting a dried organogel which adsorbed crystal violet and other dyes, with dye removal being dependent on the gelator structure,<sup>4a</sup> and a more effective system which formed ionogels.4b They also developed pH-responsive hydrogels which could be recycled and re-used.4c Banerjee and co-workers have reported metallo-hydrogels and tri-peptide hydrogels, demonstrating that they can act as re-usable dye extraction agents.<sup>5</sup> Hayes, Escuder and co-workers used a series of urea-derived gels to get extremely effective uptake of dyes from aqueous solution - these gels formed at low pH on protonation of a carboxylic acid and then adsorbed amine-based dyes, such as methylene blue, through acid-amine

interactions.<sup>6</sup> Other groups have also recently begun to explore this area.<sup>7</sup>

It is noteworthy that, in general terms, most low-molecularweight hydrogelators are strongly pH dependent. Most commonly, the protonation of a carboxylic acid group ( $pK_a$  *ca.* 4–5) plays an integral role in hydrogelation, which only then occurs at lower pH values.<sup>6,8</sup> Furthermore, many of the syntheses are multi-step and not easily amenable to scale-up. We therefore became interested in developing hydrogels capable of pollutant uptake, and set the following criteria for their design: (i) simple synthetic procedures, (ii) pH-tolerant gels, (iii) selective pollutant uptake. This communication reports our initial progress.

We decided to employ a gelator based on dibenzylidene sorbitol (DBS). DBS is a 'butterfly-amphiphile' well-known to gelate organic fluids and synthesised by simple one-step condensation between sorbitol and two equivalents of benzaldehyde.9,10 However, DBS does not dissolve well in aqueous solvents. We recently reported that DBS-CO<sub>2</sub>H is an effective, but pH-dependent, hydrogelator.<sup>11</sup> With this in mind, we considered potential replacements for the carboxylic acid which might be more pH tolerant, yet still provide sufficient hydrophilicity to support hydrogelation. As such, we alighted on the hydrazide functional group. Hydrazides have only rarely been noted as potential organogelators.<sup>12</sup> We therefore synthesised DBS-hydrazide (Scheme 1) using a simple, high yielding, two-step synthetic procedure adapted from those known for DBS. Condensation of two equivalents of methyl-ester-functionalised benzaldehyde with sorbitol gave the 1,3,2,4-substituted product (DBS-CO2Me) in 77% yield after simple washing for purification. Subsequent reaction with hydrazine hydrate led to DBS-CONHNH2 product in excellent 91% yield.

Initially, we probed the ability of this compound to form gels in water and discovered that it formed hydrogels. Gelation was



Scheme 1 Synthesis of novel hydrogelator DBS–CONHNH<sub>2</sub>.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental details for synthesis of DBS-CONHNH<sub>2</sub> and characterisation data for all compounds. Spectra from UV-vis adsorption assays, details of dye adsorption from mixtures and pseudo second order kinetics for kinetic studies of dye adsorption. See DOI: 10.1039/c3cc45969a



Fig. 1 Scanning (A) and transmission (B) electron microscopy images of xerogel formed (from  $H_2O$ ) by DBS–CONHNH<sub>2</sub>. Scale bars 100 nm.

achieved by application of a simple heat-cool cycle. To form the most consistent and reproducible gels, a small amount of DMSO was added to enhance solubility (4% v/v). Thermally stable gels were always formed in the absence of DMSO, but a small amount of gelator often remained undissolved - as such, DMSO was added to enhance reproducibility. We monitored the effect of DMSO addition on gel thermal stability and found that up to 5%, it was very limited (see ESI,<sup>†</sup> Fig. S2), but at higher loadings, the  $T_{gel}$  value decreased. Scanning and transmission electron microscopy on dried samples of the xerogel indicated a well-defined nanofibrillar morphology, with fibre diameters of ca. 10 nm (Fig. 1). This is consistent with the formation of solvated, highly porous nanomaterials with high surface areas, potentially capable of coming into contact with pollutant species. Variable temperature circular dichroism (VT-CD) measurements (ESL<sup>+</sup> Fig. S3) indicated the formation of temperature sensitive chiral nanostructures with a peak maximum at ca. 270 nm, indicative of chiral nanoscale organisation of the aromatic 'wings' of the gelator within the self-assembled gel network.

Most interestingly, DBS-CONHNH2 formed gels across a very broad pH range from 2 to 11.5 (Fig. 2). Furthermore, the  $T_{gel}$  value of the 10 mM hydrogel of DBS-CONHNH2 was constant at ca. 70 °C across this range (ESI,<sup>†</sup> Fig. S2). We reason that this pH-independent gelation reflects the choice of hydrazide functional group, which has a  $pK_a$  value < 3.0, meaning it should remain mainly in its neutral form across this range. This pH-independent gelation behaviour is in contrast to many supramolecular hydrogels which contain carboxylic acid functional groups and are, as such, highly pH dependent, only forming effective gels under conditions of controlled acidification, typically with pH < 5.8,11 Unlike previous low molecular weight hydrogelators, this system may therefore be appropriate for dye adsorption across a wide pH range. It should also be noted that this hydrazide-functionalised system forms gels at biologically and environmentally relevant pH values - we suggest that hydrazides may be effective and general replacements for carboxylic acids in other hydrogelators, to make them more pH tolerant.

We probed the ability of this gel to remove different pollutant dyes (Fig. 3) from water, performing an experiment in which a gel was formed in a cuvette from 0.5 ml of water and 4 mg of gelator (*i.e.* 0.8% wt/vol sample of gel). A concentrated solution of dye was



Fig. 2 pH independent gel formation from pH 2 to 11.5.



Fig. 3 Dyes tested for adsorption onto hydrogels.





then pipetted onto the top of this gel, in order to determine the maximum possible dye uptake (Fig. 4). This mixture was left to stand and the maximum amount of removal of the dye from the aqueous supernatant was monitored by UV-vis spectroscopy (ESI, $\dagger$  Fig. S4). We performed this experiment both using pure water, and then at controlled pH values of 2 and 12 with pH adjustment using HCl and NaOH (both 0.1 M).

The maximum possible dye adsorption values (700–1050 mg  $g^{-1}$ Fig. 4) are highly competitive with the best previously reported supramolecular gel nanomaterials - indeed it is very rare to achieve such high loadings as those here, with reported values typically being  $<100 \text{ mg g}^{-1.4-7}$  The best previously reported value for dye adsorption using a supramolecular gelator was *ca.* 1000 mg  $g^{-1}$  for MB uptake6 - our new system is clearly competitive with this. It is difficult to calculate an exact molar stoichiometry of uptake, as dyes are not provided from commercial sources in pure form. However, based on indicated purities, we calculate that the gelator can adsorb near stoichiometric amounts of dye. This is suggestive of the fact that the nanoscale fibres inherent within the gel network provide a highly accessible 'solid-like' system with remarkably high surface area to maximise dye uptake. Indeed, it appears that almost every molecule which is self-assembled into the gel network has activity. We also found that a mixture of AB25 and NBB could be simultaneously adsorbed from acidic solution by the gel (ESI,<sup>+</sup> Fig. S5) - reflective of real-world conditions where mixtures of dyes may be present.

Clearly, as illustrated in Fig. 4, the solution pH controls the selectivity of the gel network towards dye adsorption in a remarkable manner. In basic media, MB was selectively adsorbed, whereas in acidic media, AB25 and NBB were selectively removed. The system is therefore quite different to the acid-functionalised gelators investigated previously, which only show good uptake of MB at

 Table 1
 Data from the kinetics of dye adsorption fitted to a pseudo second order mechanism

	pН	Max uptake in kinetic run (mg $g^{-1}$ )	Rate of uptake, $k_2$ (g mg <sup>-1</sup> h <sup>-1</sup> )
MB	11.5	770	$0.9 imes10^{-4}$
AB25	2.4	876	$1.9 imes10^{-4}$
NBB	2.4	668	$2.5 \times 10^{-4}$

low pH values.<sup>6</sup> We suggest that the protonation states of the dyes play a key role in determining their ability to interact with our nanoscale gel network. This is discussed in more detail below.

To probe the kinetics of dye adsorption onto the gel we followed uptake over time, and fitted the data to both pseudo first order and pseudo second order kinetics. We found a significantly better fit of all data when applying pseudo second order kinetics (Table 1, ESI,<sup>†</sup> Fig. S4,  $R^2 \ge 0.99$ ). This is often the case when studying adsorption, and supports the view that chemically-specific interactions between the gel nanofibres and the pollutant dyes are occurring.<sup>13</sup> We ran all of the experiments so that the gel was becoming almost saturated with dye by the end of the kinetic run. All dyes showed fairly similar rates of uptake, however, at pH 2.4 AB25 and NBB were taken up significantly more quickly than MB.

In order to consider the effect of pH on dye adsorption, it is informative to consider the structures of the dyes. It should be assumed that all sulfonic acids, as strong acids, exist in anionic form across the entire pH range, however, the amine groups (and phenols) will be protonated or deprotonated dependent on the  $pK_a$  values of the dyes. We suggest that dyes may be best adsorbed by this hydrogel when their charge is lowest. For MB, this will be at high pH, where the amines are not protonated and it only has +1 charge. For the other dyes it will be at low pH, where the amines are protonated, and can therefore somewhat counteract the negative charge of the sulfonate(s). AB25 has two amine groups whereas NBB only has one, and this possibly explains why the former dye has a higher degree of uptake as it will have a lower net charge. We suggest that when the dyes are more highly charged, they prefer to be solvated in water rather than interacting with the supramolecular hydrogel fibres through hydrogen bond interactions. As such, the gel fibres can distinguish between different families of dye (amine-based and sulfonate-based) under different pH regimes.



Fig. 5 Desorption of AB25 from DBS–CONHNH<sub>2</sub> hydrogel into 0.1 M NaOH sampling the supernatant at time 0, 20 min, 40 min and 3 h.

To recycle the gel, we reasoned that changing pH may be a way of desorbing dyes from the gel. Gels with adsorbed AB25 (and NBB) were indeed shown to be cleaned when exposed to a supernatant basic solution (NaOH<sub>aq</sub>, 0.1 M) (Fig. 5). Adsorption–desorption is therefore pH switchable – with AB25 (and NBB) being adsorbed in acidic conditions and desorbed in basic conditions – a simple mechanism for gel recycling.

In summary, DBS-CONHNH<sub>2</sub> is a novel pH-tolerant hydrogelator. Indeed, we suggest that the hydrazide group may be a broadly applicable replacement for carboxylic acids which can extend the pH range over which gels form. Gels of DBS-CONHNH<sub>2</sub> can achieve very high levels of dye adsorption, with pH controlling dye protonation and hence selectivity. As such, DBS-CONHNH<sub>2</sub> has ambidextrous ability to extract different types of dye under different conditions of pH. Furthermore, changing pH can be used to control dye adsorption–desorption and give rise to gel recycling. In current and future work, we are developing a range of materials to adsorb different pollutant species under controlled conditions and exploring how they cooperate and/or can have their uptake properties tuned and controlled by nanoscale engineering.

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