## **ChemComm**



## COMMUNICATION

**View Article Online** 

## Modifying a known gelator scaffold for nitrite detection†

Cite this: Chem. Commun., 2014, 50 7813

Received 4th April 2014, Accepted 27th May 2014

DOI: 10.1039/c4cc02504k

www.rsc.org/chemcomm

Danielle M. Zurcher, Yash J. Adhia, Julián Díaz Romero and Anne J. McNeil\*

The process of selecting and modifying a known gelator scaffold to develop a new nitrite-based sensor is described. Five new azo-sulfonate gelators were discovered and characterized. The most promising scaffold exhibits a stable diazonium intermediate, proceeds in a high yield, and gels nitrite-spiked tap, river, and pond water.

Small molecule-based gels are being explored for a variety of different applications.1 Identifying an appropriate gelator for a specific application can be quite simple if the final gel state is all that matters. For example, different growth factors have been added to known peptide-based gelators and used as scaffolds in tissue engineering.<sup>2</sup> On the other hand, identifying an appropriate gelator can be quite challenging if the solution-togel phase transition is important to the application (e.g., sensing). In this case, one needs not only a gelator, but also a non-gelling, structurally related precursor. As a consequence, in our previous work, we found it easier to design a new gelator than to modify a known gelator for sensing applications.3,4 Nevertheless, we were motivated to explore the alternative approach<sup>5</sup> given the inherent challenges in designing new gelators, and the fact that there are over 1000 reported small molecule gelators. Herein we demonstrate that modifying a known gelator for a new application can be successful. Specifically, we will highlight how a known gelator scaffold was first targeted and then modified to develop a gel-based sensor for detecting nitrite in aqueous solutions.

Nitrite (NO<sub>2</sub><sup>-</sup>) contamination of water is a global concern because of its detrimental effects on human health.<sup>8,9</sup> Nitrite sensors based on electrochemical<sup>10</sup> and colorimetric methods,<sup>11</sup> among others, 12 have been developed, however, sample

Department of Chemistry and Macromolecular Science and Engineering Program, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan, 48109-1055, USA. E-mail: ajmcneil@umich.edu

pre-treatment is often required. In contrast, sensors based on molecular gelation are portable and can operate in complex media (e.g., opaque samples).3,5,13 To develop a molecular gel-based sensor for nitrite, the first step involved identifying a chemical transformation that can be mediated by nitrite. Herein, the Griess reaction was chosen because of its high selectivity for nitrite, short reaction time, and high yield. 14 In the original Griess reaction, sulfanilic acid reacts with nitrous acid to form a diazonium ion, which is then reacted with α-naphthylamine to generate a red-violet azo dye (eqn (1)).15

The next step was to identify a gelator that can be formed via the Griess reaction. A search of the small molecule gel literature revealed a surprisingly large number of azo-containing organogelators<sup>16-27</sup> and a few hydrogelators.<sup>28-31</sup> In most cases, an azobenzene moiety was added to a known gelator scaffold to generate a light-responsive transition (via the trans-to-cis azobenzene isomerization). Because the non-azo-functionalized precursor is also a gelator, most of these scaffolds are unsuitable for sensing. We focused our attention solely on hydrogelators with scaffolds wherein the azo-functional group was part of the core structure (rather than an appendage). Only one promising scaffold fit these parameters: azo-sulfonates.<sup>31</sup> These azo-compounds can be accessed via the Griess reaction between an aniline derivative and sodium 6-hydroxynaphthalene-2-sulfonate, which are both non-gelling in aqueous solutions (eqn (2)). Azosulfonates 3c and 3f were reported to gel aqueous buffers, albeit at high concentrations.31 Thus, we began our studies by modifying this scaffold to develop a gelation-based nitrite sensor for environmental samples.

<sup>†</sup> Electronic supplementary information (ESI) available: Synthetic procedures, spectroscopic data, gel screening data, rheological data, microscopy data, thermogravimetric analysis data, UV-vis spectroscopic data, and in situ gelation procedures. See DOI:

$$\begin{array}{c} NH_2 \\ \\ 1a-g \\ \hline a R = CH_3 \\ b R = CI_3 \\ c R = CF_3 \\ d R, R' = CH_3 \\ e R, R' = CH_3 \\ g R, R' = H \\ \end{array}$$

(2)

Communication

We focused our efforts on meta-substituted derivatives because Hamada and co-workers previously reported that most para-substituted derivatives were nongelators under aqueous conditions. 31 In total, seven azosulfonates (3a-3g) were synthesized and screened for gelation (Table 1 and ESI†). 32 All seven compounds formed gels in either borax buffer (65 mM, pH = 13) or EtOH/borax buffer (9/1 v/v).33 Because the ultimate goal is to use aqueous samples from the environment, we focused on lowering the critical gel concentration (cgc) in neat borax buffer. The unsubstituted derivative (3g) was too soluble, so a single methyl- (3a), chloro- (3b) or trifluoromethyl- (3c) substituent was introduced to increase the hydrophobicity.34 The most hydrophobic compound (3c) within this series gave the lowest ege in borax buffer. Introducing a second, identical substituent (3d-f) had a large effect on cgc when R = Cl and a surprisingly small effect on cgc when R = CF<sub>3</sub>. Overall, the dichlorosubstituted derivative (3e) exhibited the lowest cgc, although 3b, 3c and 3f were only slightly higher.

The mechanical strength and morphology of gels of 3a–g were characterized using rheology and scanning electron microscopy, respectively.<sup>35</sup> Rheological testing of all gelators at 1.5 times the cgc revealed the expected 10-fold (or larger) storage modulus (G') relative to the loss modulus (G'') in both the frequency and oscillating stress sweep experiments, confirming its gel-like nature (cf., Fig. 1A and ESI $\dagger$ ).<sup>36</sup> Optical and scanning electron microscopy was performed on each gel near or above its cgc to determine the morphology.<sup>37</sup> Consistent with most molecular gels, anisotropic fibers of varying widths were observed (cf., Fig. 1B and ESI $\dagger$ ).

Table 1 Critical gel concentrations (cgc) in different conditions<sup>a</sup>

Azosulfonate	egc (mM)	
	EtOH/borax buffer $^b$ (9/1, v/v)	Borax buffer <sup>b</sup>
3a	$23.5 \pm 0.4$	Precipitate
3 <b>b</b>	$43\pm3$	$29.4 \pm 0.9^{c}$
3c	Precipitate	$24.2\pm0.8$
3d	$35.5\pm0.2$	Precipitate
3e	$16.7\pm0.6$	$21.3\pm0.5$
3f	Precipitate	$27\pm1$
3g	$30.0 \pm 0.5$	Soluble

<sup>&</sup>lt;sup>a</sup> The error reported as a standard deviation is based on 3 samples. Each compound was screened for gelation at concentrations ≤2 wt%. The term "precipitate" was used when any amount of precipitate was observed. <sup>b</sup> Borax buffer (65 mM, pH = 13). <sup>c</sup> The solvent consisted of borax buffer (65 mM)/ $H_2SO_4$  (4 M)/ $H_2O$  (7.6/2/0.4, v/v/v).

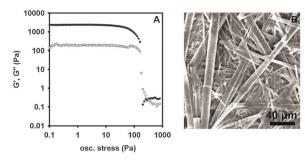


Fig. 1 (A) Oscillating stress sweep for a gel of **3e** (32 mM in borax buffer,  $G'(\bullet)$  and  $G''(\bullet)$ ). (B) Scanning electron microscope image of a gel of **3e** (37 mM in EtOH/borax buffer (9/1, v/v)).

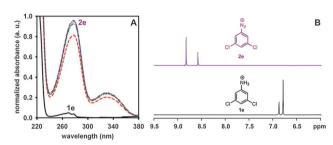


Fig. 2 (A) Plot of the normalized absorbance *versus* wavelength for the reaction of  ${\bf 1e}$  (4.8  $\times$  10<sup>-4</sup> mmol) with NaNO<sub>2</sub> (4.8  $\times$  10<sup>-4</sup> mmol) at room temperature in 4 M aq. H<sub>2</sub>SO<sub>4</sub> (0 min (black solid), 2 min (red dashed) 10 min (green dash dot), 30 min (blue dot), 60 min (purple dash dot)). (B) <sup>1</sup>H NMR spectra (in  $d_6$ -DMSO) acquired before (bottom) and 15 min after (top) adding NaNO<sub>2</sub> (0.03 mmol) to  ${\bf 1e}$  (0.03 mmol) in 4 M aq. H<sub>2</sub>SO<sub>4</sub> at rt.

The Griess reaction is typically carried out at lower temperatures (e.g., 0 °C), presumably due to concerns about diazonium ion stability. 14 Nevertheless, a practical and portable sensor should operate at ambient temperatures. Thus, UV-vis spectroscopy was used to monitor the rate of diazonium ion formation (2a–g) and decomposition at room temperature. Gratifyingly, diazonium ions 2b (Cl), 2c (CF<sub>3</sub>), 2e (Cl/Cl) and 2f (CF<sub>3</sub>/CF<sub>3</sub>) were stable at ambient temperatures for at least an hour (cf., Fig. 2A and ESI†). 14 NMR spectroscopy was used to confirm that a single, stable species was formed during the reaction (Fig. 2B). In contrast, the CH<sub>3</sub>-substituted derivatives (2a, 2d) showed presumed loss of nitrogen after 2 min and the unsubstituted derivative (2g) decomposed after 30 min. Based on these results, our further studies focused solely on those gelators formed through stable diazonium intermediates (i.e., 3b, 3c, 3e and 3f).

One concern that emerged from the syntheses of **3a–g** was the moderate-to-low isolated yields (*e.g.*, 17% yield for **3e**, see ESI†). The sensitivity of a gel-based sensor depends on both the critical gel concentration and the yield of the reaction used to generate the gelator. For example, although **3e** exhibited the lowest overall cgc, its low reaction yield could ultimately make it less suitable in the sensor platform. Because the low synthetic yields were presumably due to the extensive purification required to remove the excess salts, we used <sup>1</sup>H NMR spectroscopy to quantify the *in situ* reaction yield for **3b**, **3c**, **3e**, and **3f** using an internal standard (*cf.*, Fig. 3 and ESI†). Gratifyingly, all four reactions proceeded with yields exceeding 85% (ESI†).



ChemComm

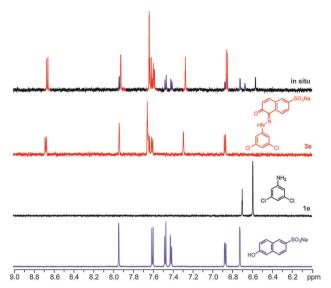


Fig. 3 <sup>1</sup>H NMR spectra of the crude reaction mixture (without workup) for the reaction of 1e (0.0078 mmol) with NaNO<sub>2</sub> (0.0071 mmol) and sodium 6-hydroxynaphthalene-2-sulfonate (0.0078 mmol) in deuterated borax buffer (top), and the corresponding starting materials and products under the same solvent conditions.

Gelator 3e was ultimately selected for the sensor platform on the basis of its low cgc, stable diazonium ion intermediate, and high reaction conversion. We tested the nitrite sensor in different water sources by spiking each sample with NaNO2 because the natural [NO<sub>2</sub><sup>-</sup>] in non-polluted water is low. Vials containing 1e (suspended in 4 M H<sub>2</sub>SO<sub>4</sub>) were treated with the spiked water samples for 10 min, followed by adding sodium 6-hydroxynaphthalene-2-sulfonate (in borax buffer). The resulting samples were heated to dissolve all solids and then allowed to cool to room temperature. The bright red/orange color is indicative of azosulfonate formation (Fig. 4).

As evident in Fig. 4, the gel-based nitrite sensor proved to be quite robust as it gelled tap water, river and pond water, as well as water drawn from a muddy pond. The non-spiked water samples serve as a negative control. Surprisingly, the cgc determined under these reaction conditions was significantly lower (9.3 mM) than that observed with the isolated (and purified) compound (21.3 mM). We suspected that the change in pH from our

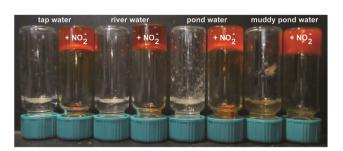


Fig. 4 Gel formation is observed after a heat-cool cycle when tap water, river water, pond water, and muddy pond water containing NaNO2 were reacted with 1e for 10 min, followed by sodium 6-hydroxynaphthalene-2sulfonate (see ESI† for experimental details).

screening conditions (pH = 13) to the reaction conditions (pH = 9) might play a role given the acidic hydrazine proton  $(pK_a \sim 11)^{.38}$  Indeed, a similar cgc was observed for isolated 3e when the pH matched those of the reaction conditions (9.5  $\pm$  0.3 mM, see ESI†). Overall, the detection limit<sup>39</sup> in these studies was 500 ppm, which is above the EPA minimum set for safe drinking water (1 ppm).9 We have previously demonstrated that using a smaller vial leads to a lower cgc, which can be attributed to an increase in the surface area between the container and the gel. Herein, the detection limit dropped to 90 ppm using a 1.5 mL vial (instead of 4 mL, see ESI†).40 Further reducing this detection limit will require either identifying a better gelator or a reaction that is catalytic in nitrite, wherein each nitrite produces more than one gelator molecule.

In conclusion, these studies reveal that known gelators can be successfully modified and then utilized in targeted applications. Herein we demonstrated that by altering the substituents on the precursor aniline ring, we were able to develop a nitrite sensor that is operable under ambient temperatures in aqueous, environmental samples. The impact of these studies is expected to be large considering that over a thousand small molecules have been reported to form gels<sup>7</sup> and each of these compounds represent potential starting points for developing other gelationbased applications.

## Notes and references

- 1 For recent reviews, see: (a) S. S. Babu, V. K. Praveen and A. Ajayaghosh, Chem. Rev., 2014, 114, 1973-2129; (b) S. I. Stupp and L. C. Palmer, Chem. Mater., 2014, 26, 507-518; (c) M. D. Segarra-Maset, V. J. Nebot, J. F. Miravet and B. Escuder, Chem. Soc. Rev., 2013, 42, 7086-7098; (d) S. S. Babu, S. Prasanthkumar and A. Ajayaghosh, Angew. Chem., Int. Ed., 2012, 51, 1766–1776; (e) D. Das, T. Kar and P. K. Das, Soft Matter, 2012, 8, 2348-2365; (f) L. E. Buerkle and S. J. Rowan, Chem. Soc. Rev., 2012, 41, 6089–6102; (g) D. Díaz Díaz, D. Kühbeck and R. J. Koopmans, Chem. Soc. Rev., 2011, 40, 427-448; (h) W. T. Truong, Y. Su, J. T. Meijer, P. Thordarson and F. Braet, Chem. - Asian J., 2011, 6, 30-42; (i) B. Escuder, F. Rodríguez-Llansola and J. F. Miravet, New J. Chem., 2010, 34, 1044–1054; (j) S. Banerjee, R. K. Das and U. Maitra, J. Mater. Chem., 2009, 19, 6649-6687; (k) A. R. Hirst, B. Escuder, J. F. Miravet and D. K. Smith, Angew. Chem., Int. Ed., 2008, 47, 8002-8018.
- 2 For leading references, see: (a) M. J. Webber, E. J. Berns and S. I. Stupp, Isr. J. Chem., 2013, 53, 530-554; (b) J. B. Matson, R. H. Zha and S. I. Stupp, Curr. Opin. Solid State Mater. Sci., 2011, 15, 225-235; (c) H. Cui, M. J. Webber and S. I. Stupp, *Biopolymers:* Peptide Science, 2010, 94, 1-18.
- 3 (a) S. C. Bremmer, A. J. McNeil and M. B. Soellner, Chem. Commun., 2014, **50**, 1691–1693; (b) S. C. Bremmer, J. Chen, A. J. McNeil and M. B. Soellner, Chem. Commun., 2012, 48, 5482-5484; (c) K. N. King and A. J. McNeil, Chem. Commun., 2010, 46, 3511-3513; (d) J. Chen and A. J. McNeil, J. Am. Chem. Soc., 2008, 130, 16496-16497
- 4 See also: (a) K. K. Carter and A. J. McNeil, Langmuir, 2014, 30, 3522–3527; (b) M. L. Muro-Small, J. Chen and A. J. McNeil, *Langmuir*, 2011, 27, 13248-13253; (c) J. Chen, J. W. Kampf and A. J. McNeil, Langmuir, 2010, 26, 13076-13080.
- 5 J. Chen, W. Wu and A. J. McNeil, Chem. Commun., 2012, 48, 7310-7312.
- 6 The rational design of gelators remains a challenge. Some key factors are being uncovered. For recent examples, see: (a) N. Yan, Z. Xu, K. K. Diehn, S. R. Raghavan, Y. Fang and R. G. Weiss, J. Am. Chem. Soc., 2013, 135, 8989-8999; (b) H. Xu, J. Song, T. Tian and R. Feng, Soft Matter, 2012, 8, 3478-3486; (c) J. Gao, S. Wu and M. A. Rogers, J. Mater. Chem., 2012, 22, 12651-12658; (d) M. Raynal and L. Bouteiller, Chem. Commun., 2011, 47, 8271-8273; (e) see also, ref. 4.
- 7 J. H. van Esch, Langmuir, 2009, 25, 8392-8394.
- 8 For leading references, see: (a) N. S. Bryan and H. van Grinsven, Advances in Agronomy, Elsevier, Amsterdam, 2013, ch. 3, vol. 119, pp. 153-182; (b) D. M. Manassaram, L. C. Backer and D. M. Moll,

- Environ. Health Perspect., 2006, 114, 320–327; (c) A. R. Townsend, R. W. Howarth, F. A. Bazzaz, M. S. Booth, C. C. Cleveland, S. K. Collinge, A. P. Dobson, P. R. Epstein, E. A. Holland, D. R. Keeney, M. A. Mallin, C. A. Rogers, P. Wayne and A. H. Wolfe, Front. Ecol. Environ., 2003, 1, 240–246.
- 9 United States Environmental Protection Agency, http://water.epa.gov/drink/contaminants, (accessed March 2014).
- 10 For a recent example, see: X.-H. Pham, C. A. Li, K. N. Han, B.-C. Huynh-Nguyen, T.-H. Le, E. Ko, J. H. Kim and G. H. Seong, Sens. Actuators, B, 2014, 193, 815–822.
- 11 For a recent example, see: H. Zhang, S. Qi, Y. Dong, X. Chen, Y. Xu, Y. Ma and X. Chen, *Food Chem.*, 2014, **151**, 429–434.
- 12 For recent reviews, see: (a) J. Dutt and J. Davis, J. Environ. Monit., 2002, 4, 465–471; (b) M. J. Moorcroft, J. Davis and R. G. Compton, Talanta, 2001, 54, 785–803.
- 13 For recent examples, see: (a) K. Liu, T. Liu, X. Chen, X. Sun and Y. Fang, ACS Appl. Mater. Interfaces, 2013, 5, 9830–9836; (b) Z. Sun, Z. Li, Y. He, R. Shen, L. Deng, M. Yang, Y. Liang and Y. Zhang, J. Am. Chem. Soc., 2013, 135, 13379–13386; (c) K. K. Kartha, S. S. Babu, S. Srinivasan and A. Ajayaghosh, J. Am. Chem. Soc., 2012, 134, 4834–4841.
- 14 J. B. Fox, Jr., Anal. Chem., 1979, 51, 1493-1502.
- 15 (a) J. P. Griess, Philos. Trans. R. Soc., 1864, 679; (b) J. P. Griess, Ber. Dtsch. Chem. Ges., 1879, 12, 426.
- 16 Crown ethers: (a) J. H. Jung, Y. Ono and S. Shinkai, *Tetrahedron Lett.*, 1999, 40, 8395–8399; (b) Y. Ono, Y. Kanekiyo, K. Inoue, J. Hojo and S. Shinkai, *Chem. Lett.*, 1999, 23–24.
- 17 Cholesterol derivatives: (a) Y. Wu, S. Wu, G. Zou and Q. Zhang, Soft Matter, 2011, 7, 9177-9183; (b) C. Wang, Q. Chen, F. Sun, D. Zhang, G. Zhang, Y. Huang, R. Zhao and D. Zhu, J. Am. Chem. Soc., 2010, 132, 3092-3096; (c) N. Koumura, M. Kudo and N. Tamaoki, Langmuir, 2004, 20, 9897-9900; (d) J. H. Jung, S. Shinkai and T. Shimizu, Chem. Mater., 2003, 15, 2141-2145; (e) K. Sakurai, Y. Ono, J. H. Jung, S. Okamoto, S. Sakurai and S. Shinkai, J. Chem. Soc., Perkin Trans. 2, 2001, 108-112; (f) Y. Ono, K. Nakashima, M. Sano, J. Hojo and S. Shinkai, Chem. Lett., 1999, 1119-1120; (g) S. Shinkai and K. Murata, J. Mater. Chem., 1998, 8, 485-495; (h) Y. Ono, K. Nakashima, M. Sano, Y. Kanekiyo, K. Inoue, J. Hojo and S. Shinkai, Chem. Commun., 1998, 1477-1478; (i) H. Kawabata, K. Murata, T. Harada and S. Shinkai, Langmuir, 1995, 11, 623-626; (j) K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda and S. Shinkai, J. Am. Chem. Soc., 1994, **116**, 6664–6676; (k) K. Murata, M. Aoki, T. Nishi, A. Ikeda and S. Shinkai, J. Chem. Soc., Chem. Commun., 1991, 1715-1718.
- 18 Hydrazides: X. Ran, H. Wang, P. Zheng, B. Bai, C. Zhao, Z. Yu and M. Li, *Soft Matter*, 2011, 7, 8561–8566.
- 19 Lipids: (a) P. Duan, Y. Li, L. Li, J. Deng and M. Liu, J. Phys. Chem. B, 2011, 115, 3322-3329; (b) K. Uchida, S. Yamaguchi, H. Yamada, M. Akazawa, T. Katayama, Y. Ishibashi and H. Miyasaka, Chem. Commun., 2009, 4420-4422; (c) J. H. Kim, M. Seo, Y. J. Kim and S. Y. Kim, Langmuir, 2009, 25, 1761-1766; (d) Y. Zhou, M. Xu, T. Yi, S. Xiao, Z. Zhou, F. Li and C. Huang, Langmuir, 2007, 23, 202-208; (e) Y. Zhou, T. Yi, T. Li, Z. Zhou, F. Li, W. Huang and C. Huang, Chem. Mater., 2006, 18, 2974-2981; (f) S. Kume, K. Kuroiwa and N. Kimizuka, Chem. Commun., 2006, 2442-2444; (g) S. J. Lee, S. S. Lee, J. S. Kim, J. Y. Lee and J. H. Jung, Chem. Mater., 2005, 17, 6517-6520; (h) Y. Zhao and X. Tong, Adv. Mater., 2003, 15, 1431-1435; (i) X. Tong and Y. Zhao, J. Mater. Chem., 2003, 13, 1491-1495; (j) J. Mamiya, K. Kanie, T. Hiyama, T. Ikeda and T. Kato, Chem. Commun., 2002, 1870-1871; (k) L. Guan and Y. Zhao, J. Mater. Chem., 2001, 11, 1339-1344; (l) L. Guan and Y. Zhao, Chem. Mater., 2000, 12, 3667-3673.
- 20 Ureas: (a) S. van der Laan, B. L. Feringa, R. M. Kellogg and J. van Esch, *Langmuir*, 2002, 18, 7136–7140; (b) M. de Loos, J. van Esch, R. M. Kellogg and B. L. Feringa, *Angew. Chem., Int. Ed.*, 2001, 40, 613–616.
- 21 Sugars: R. Rajaganesh, A. Gopal, T. M. Das and A. Ajayaghosh, *Org. Lett.*, 2012, 14, 748–751.
- 22 Dicarboxylates: P. Sahoo and P. Dastidar, Cryst. Growth Des., 2012, 12, 5917–5924.

- 23 Dendrons: (a) Z.-X. Liu, Y. Feng, Z.-C. Yan, Y.-M. He, C.-Y. Liu and Q.-H. Fan, *Chem. Mater.*, 2012, 24, 3751–3757; (b) Y. Ji, G.-C. Kuang, X.-R. Jia, E.-Q. Chen, B.-B. Wang, W.-S. Li, Y. Wei and J. Lei, *Chem. Commun.*, 2007, 4233–4235.
- 24 Glycolurils: K. Tiefenbacher, H. Dube, D. Ajami and J. Rebek Jr., Chem. Commun., 2011, 47, 7341–7343.
- Cyclohexyl amides: (a) M. Moriyama, N. Mizoshita and T. Kato, *Polym. J.*, 2004, 36, 661–664; (b) M. Moriyama, N. Mizoshita, T. Yokota, K. Kishimoto and T. Kato, *Adv. Mater.*, 2003, 15, 1335–1338.
- 26 Melamine derivatives: (a) S. Yagai, T. Karatsu and A. Kitamura, Langmuir, 2005, 21, 11048–11052; (b) S. Yagai, T. Nakajima, K. Kishikawa, S. Kohmoto, T. Karatsu and A. Kitamura, J. Am. Chem. Soc., 2005, 127, 11134–11139.
- 27 Semicarbazides: (a) P. Deindörfer, R. Davis and R. Zentel, Soft Matter, 2007, 3, 1308–1311; (b) P. Deindörfer, T. Geiger, D. Schollmeyer, J. H. Ye and R. Zentel, J. Mater. Chem., 2006, 16, 351–358; (c) P. Deindörfer, A. Eremin, R. Stannarius, R. Davis and R. Zentel, Soft Matter, 2006, 2, 693–698.
- 28 Glycolipids: (a) M. J. Clemente, R. M. Tejedor, P. Romero, J. Fitremann and L. Oriol, RSC Adv., 2012, 2, 11419–11431; (b) Y. Lin, A. Wang, Y. Qiao, C. Gao, M. Drechsler, J. Ye, Y. Yan and J. Huang, Soft Matter, 2010, 6, 2031.
- 29 Peptides: (a) Y. Huang, Z. Qiu, Y. Xu, J. Shi, H. Lin and Y. Zhang, Org. Biomol. Chem., 2011, 9, 2149–2155; (b) X. Li, Y. Gao, Y. Kuang and B. Xu, Chem. Commun., 2010, 46, 5364–5366; (c) Y. Matsuzawa and N. Tamaoki, J. Phys. Chem. B, 2010, 114, 1586–1590; (d) Y. Matsuzawa, K. Ueki, M. Yoshida, N. Tamaoki, T. Nakamura, H. Sakai and M. Abe, Adv. Funct. Mater., 2007, 17, 1507–1514; (e) D. Inoue, M. Suzuki, H. Shirai and K. Hanabusa, Bull. Chem. Soc. Jpn., 2005, 78, 721–726.
- 30 Sugars: (a) Y. Ogawa, C. Yoshiyama and T. Kitaoka, Langmuir, 2012, 28, 4404–4412; (b) H. Kobayashi, A. Figgeri, K. Koumoto, M. Amaike, S. Shinkai and D. N. Reinhoudt, Org. Lett., 2002, 4, 1423–1426; (c) H. Kobayashi, K. Koumoto, J. H. Jung and S. Shinkai, J. Chem. Soc., Perkin Trans. 2, 2002, 1930–1936; (d) J. H. Jung, S. Shinkai and T. Shimizu, Nano Lett., 2002, 2, 17–20; (e) M. Amaike, H. Kobayashi and S. Shinkai, Chem. Lett., 2001, 620–621.
- 31 Sulfonates: (a) A. M. Bieser and J. C. Tiller, J. Phys. Chem. B, 2007, 111, 13180–13187; (b) K. Hamada, E. Miyawaki and J.-Y. Jaung, Color. Technol., 2005, 121, 127–131; (c) A. M. Bieser and J. C. Tiller, Chem. Commun., 2005, 3942–3944; (d) K. Hamada, K. Yamada, M. Mitsuishi, M. Ohira and K. Mesuda, J. Chem. Soc., Faraday Trans., 1995, 91, 1601–1605; (e) K. Hamada, K. Yamada, M. Mitsuishi, M. Ohira and K. Miyazaki, J. Chem. Soc., Chem. Commun., 1992, 544–545; (f) V. R. Haller, Kollid Z., 1918, 22, 49–53.
- 32 We screened for gelation in borax buffer because the Griess reaction was previously reported to proceed in high yield in this solvent system. For reference, see: E. Kalatzis, *J. Chem. Soc. B*, 1967, 273–277.
- 33 Although the mechanism of gelation herein is not known, related azosulfonates reveal a prominent 1D coordination polymer involving the metal sulfonate and water in their single-crystal X-ray structures. For reference, see: (a) A. R. Kennedy, H. Stewart, K. Eremin and J. Stenger, Chem. Eur. J., 2012, 18, 3064–3069; (b) A. R. Kennedy, C. McNair, W. E. Smith, G. Chisholm and S. J. Teat, Angew. Chem., Int. Ed., 2000, 39, 638–640.
- 34 The trend in substituent hydrophobicity is CF<sub>3</sub> > Cl > CH<sub>3</sub>. For reference, see: T. Fujita, J. Iwasa and C. Hansch, *J. Am. Chem. Soc.*, 1964, **86**, 5175–5180.
- 35 For a comprehensive review, see: G. Yu, X. Yan, C. Han and F. Huang, *Chem. Soc. Rev.*, 2013, **42**, 6697–6722.
- 36 The strength and stability of these gels were unaffected by adding excess sodium nitrite (ESI†).
- 37 Gels of **3c** were transparent within the limits of our optical microscope. In addition, the scanning electron microscope images only revealed salt crystals from the buffer solution.
- 38 J. Oakes, P. Gratton, R. Clark and I. Wilkes, J. Chem. Soc., Perkin Trans. 2, 1998, 2569–2575.
- 39 The detection limit is based on the total volume of the gel sample and not the volume of nitrite-contaminated water.
- 40 This gel-based sensor was also able to detect sodium nitrite in a certified standard solution from SPEX CertiPrep Group (ESI†).