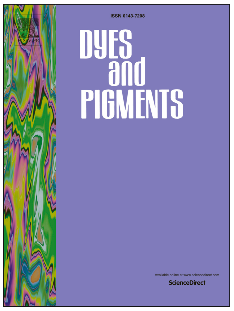

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PII: S0143-7208(18)30794-0
DOI: 10.1016/j.dyepig.2018.06.042
Reference: DYPI 6849

To appear in: *Dyes and Pigments*

Received Date: 10 April 2018
Revised Date: 3 June 2018
Accepted Date: 24 June 2018

Please cite this article as: Khayat Z, Zali-Boeini H, Novel sugar-based azo dyes as multistimuli responsive supramolecular gelators and chemosensors, *Dyes and Pigments* (2018), doi: 10.1016/j.dyepig.2018.06.042.

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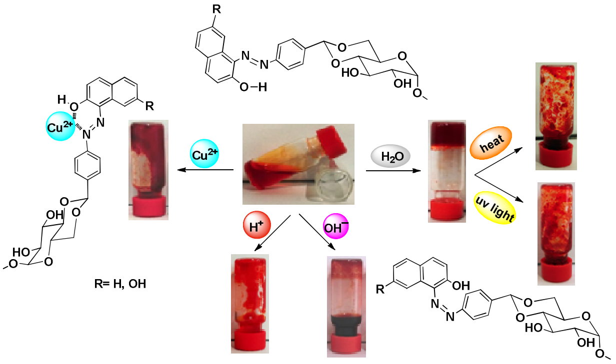

Novel sugar-based supergelators comprising azo dyes were synthesized and their thermo-, pH-, and photo-responsive behavior were investigated. Gelator **2b** was successfully utilized as chemosensor for selective detection of Cu^{2+} ion *via* supramolecular sol-gel conversion.

Novel Sugar-based Azo Dyes as Multistimuli Responsive Supramolecular Gelators and Chemosensors

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Key words: Azo dye; Supramolecular; Gelator; Multistimuli responsive; Chemosensor

Abstract: Some novel sugar-based and multistimuli responsive supramolecular gelators, containing azobenzene moieties were synthesized and characterized through their microscopic, rheological, and spectroscopic measurements. The sol-gel behavior of these low molecular weight gelators in response to temperature, UV-Vis light irradiation, pH changes, and in the presence of various metal cations was investigated. Compounds **2b** and **2d** were found to be as supergelators (gelator concentration≤ 1%) in a mixture of DMF/H_2O (1:1) and exhibited very good response toward temperature, light, pH, and metal ions. Moreover, compound **2b** showed selective gel-sol response toward Cu^{2+} among a wide variety of two and three-valent metal ions.

1. Introduction

Supramolecular gels involve low molecular weight gelators (LMWGs) which self-assemble via non-covalent interactions including hydrogen bonding, π-π stacking, ion-dipole, van der Waals forces, solvophobic and electrostatic interactions to form a three dimensional micro and/or nano-scale network structure which entraps the solvent and prevent its fluidity [1].

A fascinating category of LMWGs, are multi-stimuli responsive supramolecular gelators (MRSGs). The assembling processes of these smart materials are affected by various external stimuli such as heat, light, ultrasound, redox, and pH changes [2]. In recent years, MSRGs have attracted substantial attention, because of their potential applications as sensors [3], drug delivery systems [4], optoelectronic devices [5], phase selective gels [6], shape memory [7] and display devices [8], molecular motors [9], and other applications [10].

Introduction of suitable responsive units into gelator molecules, leads to development of novel stimuli-responsive gels. As examples, the introduction of azobenzene [11] or stilbene [12] moieties leads to photo-stimuli molecular gelators, capable of forming photoresponsive supramolecular gels. There are some reports on the azobenzene-derived organogelators containing cholesterol [13] or aryl ether [14] segments. In order to achieve a right balance between hydrophilicity and hydrophobicity in a molecular gelator and to produce hydrogelators, hydrophilic blocks like peptide [15], saccharide [16], or PEG parts [11b] have been introduced into the structure of gelators.

In this paper, we report novel sugar based, light, pH, and metal ion responsive organogelators (aqueous/organogelators), incorporating aryl azo moieties as photoresponsive and hydroxyl and azo substituted aromatic groups as pH and metal ion responsive binding sites. The study encompasses thermal, spectroscopic, microscopic, and rheometeric characterization of the resultant gels. The effect of pH changes, UV/VIS light exposure, and addition of various metal ions has also been investigated.

2. Experimental section

2.1 Materials and Instruments

All chemicals were purchased from commercial suppliers and used without further purification. The solvents were dried and purified using standard methods, prior to use. All yields refer to isolated products. Thin layer chromatography (TLC) was applied to monitor progress of the reactions over Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer, referenced to residual solvent protons and signals are reported in ppm (δ). Infrared spectra were obtained using a Jasco FTIR-6300 spectrometer as KBr pellets. Rheological studies were done by an Anton Paar, MCR 301 reometer. FE-SEM analysis was performed using a Tescan Mira3 scanning electron microscope.

2.2 General Procedure for the Synthesis of Diazenyl benzaldehydes 1a-d

A) Preparation of diazonium salt: 4-Aminobenzaldehyde (0.61 g, 5.0 mmol) was added to a mixture of H_2O (10 mL), acetone (5 mL) and HCl (32%, 2 mL) in a small beaker placed in an ice-salt bath and stirred for 5 min. Then, the temperature was kept below 0°C (-5 to 0°C) and a solution of $NaNO_2$ (0.50 g, 7.25 mmol) in water (6.5 mL) was added dropwise. After completion of the reaction and KI-starch test (To avoid an excess of nitrous acid), the diazonium salt solution was stirred at same temperature for further 30 min.

B) Coupling reaction with hydroxyaromatics: In a 50 mL round bottomed flask containing a solution of NaOH (0.60 g, 15 mmol) in water (6.5 mL), the corresponding hydroxyaromatic (6.25 mmol) was dissolved. The flask was placed in an ice bath to maintain the temperature below 5°C, and the cold diazonium solution was added dropwise with vigorous stirring. After completion of the addition, the reaction mixture was stirred for 60 min in an ice bath and a further 30 min at room temperature. Then, the pH was adjusted to four by addition of a solution of HCl (10%). The mixture was stirred 5 min more and the precipitate was filtered and washed with water until the filtrate became neutral. In the case of **1c**, the dried crude product was triturated in a mixture of n-hexane: ethyl acetate (1:1, 15 mL) at 50°C for 15 min to remove the minor impurities and filtered to obtain the desired dyes as reddish orange powders.

2.3 Spectroscopic data for the compounds 1a-d

(E)-4-((4-hydroxyphenyl)diazenyl)benzaldehyde (1a). Orange solid (95%); ^{1}H NMR (400 MHz, DMSO- d_6) δ 10.09 (s, 1H), 8.09 (d, *J*= 8.4 Hz, 2H), 7.97 (d, *J*=8.4 Hz, 2H), 7.87 (d, *J*=8.4 Hz, 2H), 6.97 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 192.6, 162.4, 155.4, 145.2, 136.7, 130.7, 125.5, 122.6, 116.2

(E)-4-((2-hydroxynaphthalen-1-yl)diazenyl)benzaldehyde (1b). Bright red solid (86%); ^{1}H NMR (400 MHz, DMSO- d_6) δ 16.23 (s, 1H), 10.00 (s, 1H), 8.46 (d, *J*=8.0 Hz, 1H), 7.98 (d, *J*=8.6 Hz, 2H), 7.76 (d, *J*=8.6 Hz, 2H), 7.71 (d, *J*=9.6 Hz, 1H), 7.56 (m, 2H), 7.44 (dt, J= 7.5 Hz, 1.2 Hz, 1H), 6.74 (d, *J*=9.6 Hz, 1H) ^{13}C NMR (100 MHz, DMSO- d_6) δ 190.9, 179.5, 147.7, 143.0, 133.5, 133.3, 131.6, 129.6, 129.1, 128.8, 128.5, 127.2, 126.4, 122.4, 117.1.

(E)-4-((4-hydroxynaphthalen-1-yl)diazenyl)benzaldehyde (1c). Redish brown solid (65%); ^{1}H NMR (400 MHz, DMSO- d_6) δ 9.91 (s, 1H), 8.63 (d, *J*=8.0 Hz, 1H), 8.28 (d, *J*=9.6 Hz, 1H), 8.10 (d, *J*=7.6 Hz, 1H), 7.92 (d, *J*=8.4 Hz, 2H), 7.79 (d, *J*=8.4 Hz, 2H), 7.66 (t, *J*=7.2 Hz, 1H), 7.47 (t, *J*=7.2 Hz, 1H), 6.63 (d, *J*=9.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.3, 178.6, 153.7, 135.3, 134.1, 131.7,131.2,130.3, 128.6, 125.9, 124.7, 123.5, 122.5, 121.2, 117.6.

(E)-4-((2,7-dihydroxynaphthalen-1-yl)diazenyl)benzaldehyde (1d). Bright red solid (92%); ^{1}H NMR (400 MHz, DMSO- d_6) δ 9.93 (s, 1H), 7.95 (d, *J*=8.0 Hz, 2H), 7.84-7.75 (m, 3H), 7.73 (d, *J*=9.6 Hz, 1H), 7.48 (d, *J*=8.4 Hz, 1H), 6.86 (dd, *J*=8.4 Hz, 2.0 Hz, 1H), 6.40 (d, *J*=9.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 191.5, 178.1, 160.9, 148.2, 143.2, 135.1, 133.0, 131.3, 131.2, 130.9, 121.2, 120.5, 117.1, 116.4, 107.7.

2.4 General procedure for the synthesis of benzylidene glucopyranosides 2a-d

Under an argon atmosphere, methyl-α-D-glucopyranoside (1.13 g, 5.8 mmol) was added to a solution of an azo dye **1** (5 mmol) in DMF (17-30 mL). After dissolution, *p*-TsOH (0.09 g, 0.5 mmol) was added and the resulting solution was stirred at room temperature for 15 min. Then, trimethyl orthoformate (1.6 mL, 15 mmol) was added dropwise and the mixture was stirred at room temperature for further 20 min, followed by 4 h stirring under reduced pressure. Progress of the reaction was monitored by TLC. Afterwards, the reaction mixture was quenched by adding saturated aqueous sodium bicarbonate solution. Then water (20 mL) and a few ice cubes were added and the precipitate (in the case of **2b** and **2d**, gel-like precipitate) was suction filtered and washed with water (10 mL). To remove the residual azo dye, the crude product was extracted several times with a mixture of n-hexane: ethyl acetate (5:1) to achieve the pure compounds as deep red to reddish orange solids. In the case of compound **2b**, the pure product was obtained *via* recrystallization from DMF followed by washing with ethyl acetate.

2.5 Spectroscopic data for the compounds 2a-2d

(2R,4aR,6S,7R,8R,8aS)-2-(4-((E)-(4-hydroxyphenyl)diazenyl)phenyl)-6-methoxyhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol (2a). Orange solid (35%); mp>250°C; ^{1}H NMR (400 MHz, DMSO- d_6) δ 7.92-7.84(m, 4H), 7.69 (d, *J*=8.6 Hz, 2H), 7.01 (d, *J*=8.6 Hz, 2H), 5.73 (s, 1H), 5.30 (d, *J*=3.4 Hz, 1H), 5.10 (d, *J*=5.6 Hz, 1H), 4.71 (d, *J*=3.2 Hz, 1H), 4.26 (dd, *J*=9.6 Hz, 4.4 Hz, 1H), 3.79 (t, *J*=10.0 Hz, 1H), 3.71-3.62 (m, 2H), 3.51.3.32 (m, 5H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 161.1, 152.2, 145.2, 139.6, 127.4, 124.9, 121.8, 115.9, 100.5, 100.3, 81.4, 72.4, 69.8, 68.2, 62.3, 54.7; Anal. Calcd. for $C_{20}H_{22}N_2O_7$: C, 59.70; H, 5.51; N, 6.96 Found: C, 59.85; H, 5.47; N, 6.88.

(2R,4aR,6S,7R,8R,8aS)-2-(4-((E)-(2-hydroxynaphthalen-1-yl)diazenyl)phenyl)-6-methoxyhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol (2b). Bright red solid (44%); mp>250°C; ^{1}H NMR (400 MHz, DMSO- d_6) δ 15.84 (s, 1H), 8.53 (d, *J*=8.2 Hz, 1H), 7.96 (d, *J*=9.4 Hz, 1H), 7.86 (d, *J*=8.4 Hz, 2H), 7.78 (d, *J*=7.8 Hz, 1H), 7.67-7.56 (m, 3H), 7.47 (t, *J*=7.3 Hz, 1H), 6.90

(d, *J*=9.4 Hz, 1H), 5.65 (s, 1H), 5.29 (d, *J*=3.5 Hz, 1H), 5.09 (d, *J*=5.3 Hz, 1H), 4.65 (d, *J*=3.5 Hz, 1H), 4.21 (dd, *J*=9.7 Hz, 4.6 Hz, 1H), 3.73 (t, *J*=10.2 Hz, 1H), 3.66-3.57 (m, 3H), 3.42 (t, *J*=9.2 Hz, 1H), 3.33 (s,1H), 3.30-3.23 (m, 2H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 174.3, 145.0, 140.4, 137.0, 132.7, 129.33, 129.2, 128.9, 127.9, 127.8, 126.0, 124.3, 121.4, 118.3, 100.5, 100.3, 81.4, 72.4, 69.8, 68.2, 62.3, 54.7; Anal. Calcd. for $C_{24}H_{24}N_2O_7$: C, 63.71; H, 5.35; N, 6.19 Found: C, 63.89; H, 5.31; N, 6.12.

***(2R,4aR,6S,7R,8R,8aS)-2-(4-((E)-(4-hydroxynaphthalen-1-yl)diazenyl)phenyl)-6-methoxyhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol* (2c).** Red solid (30%); mp: 207°C (decomposes); ^{1}H NMR (400 MHz, DMSO- d_6) δ 9.07-8.80 (b, 1H), 8.27 (s, 1H), 8.10-7.91 (b, 3H), 7.78 (t, *J*=7.2 Hz, 1H), 7.74-7.63 (m, 3H), 7.13-6.96 (b, 1H), 5.68 (s, 1H), 5.30 (d, *J*=4.8 Hz, 1H), 5.10 (d, *J*=6.4 Hz, 1H), 4.67 (d, *J*=3.7 Hz, 1H), 4.23 (dd, *J*=9.8 Hz, 4.7 Hz, 1H), 3.75 (t, *J*=10.1 Hz, 1H), 3.70-3.59 (m, 3H), 3.55-3.25 (m, 4H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 167.0, 131.6, 128.6, 127.5, 122.6, 111.5, 107.4, 100.5, 100.4, 81.4, 72.4, 69.9, 68.2, 62.4, 54.7; Anal. Calcd. for $C_{24}H_{24}N_2O_7$: C, 63.71; H, 5.35; N, 6.19 Found: C, 63.85; H, 5.29; N, 6.14.

***(2R,4aR,6S,7R,8R,8aS)-2-(4-((E)-(2,7-dihydroxynaphthalen-1-yl)diazenyl)phenyl)-6-methoxyhexahydropyrano[3,2-d][1,3]dioxine-7,8-diol* (2d).** Red solid (41%); mp: 245°C (decomposes); ^{1}H NMR (400 MHz, DMSO- d_6) δ 7.83(d, *J*=2.2 Hz, 1H), 7.82-7.75 (m, 3H), 7.62-7.55 (m, 3H), 6.91 (dd, *J*=8.4 Hz, 2.4 Hz, 1H), 6.60 (d, *J*=9.2 Hz, 1H), 5.63 (s, 1H), 5.45-5.01 (b, 2H), 4.64 (d, *J*=3.6 Hz, 1H), 4.19 (dd, *J*=9.8 Hz, 4.6 Hz, 1H), 3.72 (t, *J*=10.2 Hz, 1H), 3.65-3.57 (m, 3H), 3.50-3.25 (m, 4H); ^{13}C NMR (100 MHz, DMSO- d_6) δ 171.1, 159.2, 145.1, 140.8, 136.7, 135.1, 130.9, 129.4, 127.9, 121,2, 120.0, 117.9, 116.0, 105.8, 100.5, 100.3, 81.4, 72.4, 69.8, 68.2, 62.3, 54.7; Anal. Calcd. for $C_{24}H_{24}N_2O_8$: C, 61.53; H, 5.16; N, 5.98 Found: C, 61.70; H, 5.11; N, 5.91.

2.6 Typical procedure for the gelation tests

In a small vial, 5-10 mg of the gelator was dissolved in 0.5 mL of the organic solvent upon heating. After cooling down to 40°C, 0.5 mL water was added, slightly shaken, and set aside at room temperature. After 30 min, the vial inversion test was performed.

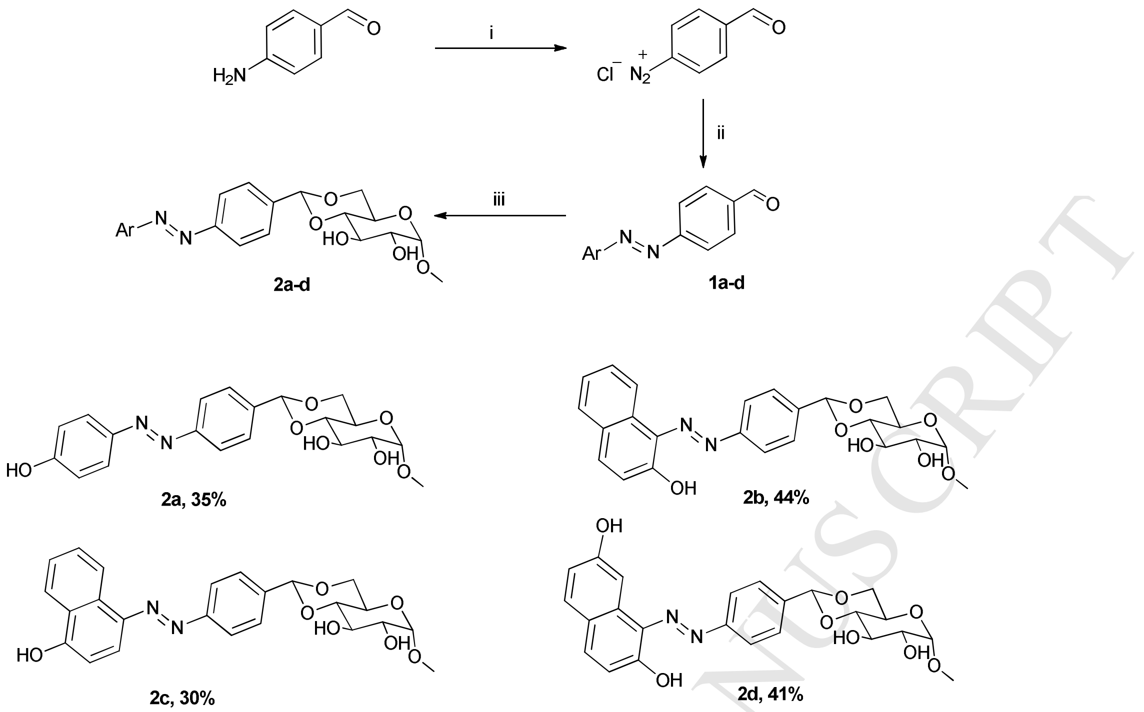
2.7 Typical procedure for gel to sol transition temperature (T_{gel}) measurement

Gel samples in critical gelation concentrations of each gelator in various solvents were prepared and placed in a water bath at 25°C for 5 min. The vial was then taken out of the bath and vial inversion test was carried out to observe weather the sample had kept its gel state or not. When the sample maintained its gel state, the bath was adjusted to 30°C, the vial was placed in it for another 5 min, and the same operation was done. The procedure was regularly repeated while the temperature of the water bath was raised by 5°C, until the gel dropped upon vial inversion.

3. Results and discussion

3.1 Syntheses

A series of 4,6-benzylidene glucopyranosides containing phenyl or naphthylazo moieties linked to methyl-α-D-glucopyranoside (**2a**-**d**), were synthesized through the following steps: the phenyl or naphthylazo dyes (**1a**-**d**) were synthesized through diazotization reaction of 4-aminobenzaldehyde followed by azo coupling with the corresponding phenol or naphthol derivatives. The as-synthesized azo dyes were used as the precursors for the synthesis of compounds **2a**-**d** *via* their acetalization reaction with methyl-*α*-D-glucopyranoside. The structure of final products and the synthetic pathway has been outlined in scheme 1.



Scheme 1. Molecular structure and synthetic pathway for preparation of compounds **2a-d**; Reagents and conditions: (i) $NaNO_2$, HCl (aq), -5 to 0 ºC; (ii) ArH, NaOH (aq), 0 ºC; (iii) Me-*α*-D-glucopyranoside, trimethyl orthoformate, *p*-TsOH, DMF, r.t.

3.2 Investigation of gelation abilities

The gelation ability of the products **2a-d** was investigated in various solvents. A weighed amount of each sample was mixed with the corresponding solvent and heated to dissolve. After cooling down to ambient temperature, equal volume of water was added, slightly shaken, and set aside. In the case of compounds **2b** and **2d**, instant gelation occurred in DMF and DMSO. These gelators made stable gels that did not flow down upon the vial inversion test even at low concentrations. The critical gelation concentration (CGC) of the gelator **2b** in 1:1 DMF/H2O was 1% (w/v, 17.8 mM). While, compound **2c** formed partial gels in the aforementioned solvents and conditions, **2a** was not a gelator.

Table 1. Gelation test results for the compounds **2a-2d**^{a}

Solvent	2a	2b	2c	2d
DMF:H2O (1:1)	S	G	PG	G

DMSO:H2O(1:1)	S	G	PG	G
MeOH:H2O(1:1)	S	PG	PG	PG

[a] S, G and PG stand for solution, gel, and partial gel respectively.

The gelation test results are summarized in Tables 1 and 2. Due to minimum gel concentration (gelator concentration≤ 1%), the compounds **2b** and **2d** can be referred to as supergelators.

Table 2. Critical gelation concentration and sol-gel transition temperature for compounds **2b** and **2d** [a]

Compound	Solvent	CGC[a] (%)	Tgel[b] (°C)
2b	DMF:H2O	0.5	70
	DMSO:H2O	1	65
2d	DMF:H2O	0.8	60
	DMSO:H2O	1	55

[a] Critical Gelation Concentration; [b] Gel to Sol Transition Temperature.

The Fig. 1 shows FE-SEM images of xerogel **2b** obtained from lyophilizing a gel comprising 1.5% compound **2b** in DMF/H_2O (1:1). As seen in the figure 1, a dense aggregation of uneven thin sheets are responsible for the formation of gel state.

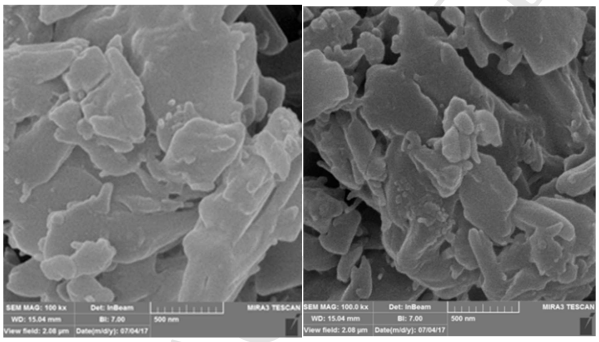
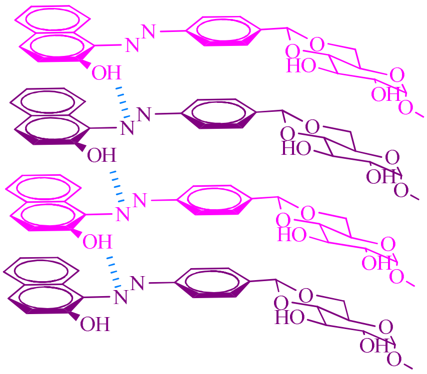
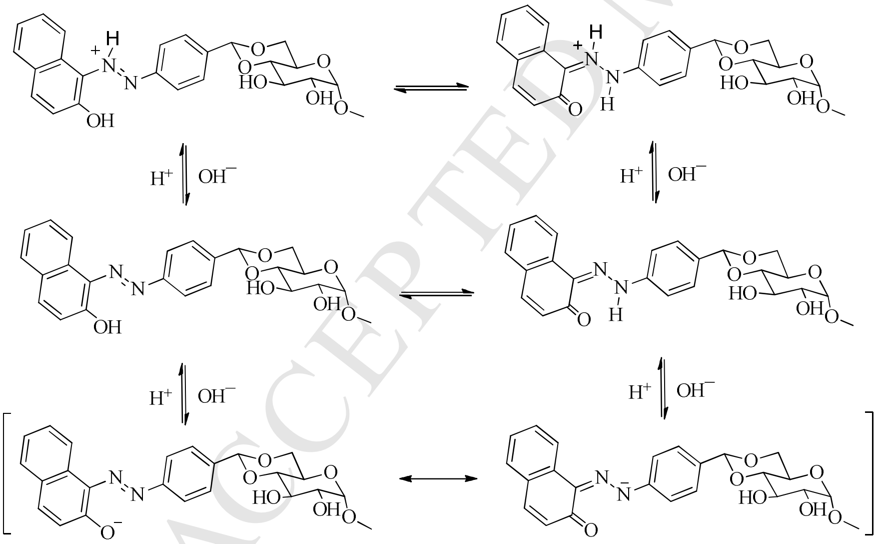


Figure 1. FE-SEM images of xerogel **2b** obtained from a 1.5% compound 2b in DMF/H2O (1:1).

Scheme 2 graphically illustrates the probable self-assembly mechanism for the compound **2b**. As shown in the scheme 2, the main interactions that lead to aggregates are hydrogen bonding and face-to-face π-π stacking of aromatic rings. UV light exposure can lead to trans to cis isomerization, disturbing the hydrogen bonding and stacking of the rings, and to collapse the gel state. Moreover, addition of Cu^{2+} ions can prevent gel formation due to coordination of Cu^{2+} ions with O and N atoms (from OH and azo moieties) and disrupting the inter- and intramolecular hydrogen bondings. As displayed in scheme 3, the pH changes can also affect the self-assembly process *via* deprotonation of OH groups in basic medium or protonation of nitrogen atoms of the azo moieties under acidic conditions.



Scheme 2. Graphical illustration of supramolecular interactions responsible for the gelation of **2b**



Scheme 3. Possible equilibrium of azo and hydrazone tautomers of **2b** and its anion at different pH conditions

Representative photographs in Fig. 2a and 2b show thermoresponsiveness of the gelators **2b** and **2d** in a 1:1 mixtures of DMF/H_2O. As it is clear from Fig. 2a, when a solution of **2b** in a 1:1

mixtures of DMF/H_2O is prepared by heating to a suitable temperature (Table 2), after cooling to room temperature the mixture is solidified to a red color firm gel (Fig. 2b).

3.3 Investigation of pH responsiveness

The pH responsiveness of the gelators **2b** and **2d** has been studied. As shown in Fig. 2c, when 2% solutions of gelator **2b** in DMF was prepared and equal volumes of H_2O, 0.05 M solutions of NaOH, or HCl were added (total concentration of gelator was 1%), quite different results were obtained. However, in the case of a 1:1 DMF/H_2O solution of compound **2b** a firm opaque gel was produced. After addition of NaOH solution (0.05 M→0.025 M, pH= 12.4) an immediate color change from red to dark-red (or dark-purple for high concentrations of $OH^{‾}$) was occurred and formation of gel was mostly inhibited. Surprisingly, once a solution of HCl (0.05 M→0.025, pH= 1.6) was added to a solution of compound **2b** in DMF, the gel formation process was not prevented but a distinct color change from deep red to rather bright red was detected. It was revealed that, higher concentrations of NaOH (>0.05 M) and/or HCl (up to 0.2 M, pH= 0.7) completely inhibit the gel formation of compound **2b** accompanied with a drastic color change to a bright red for addition of HCl. At higher concentrations of HCl (>0.2 M), gelation did not occur but, rather a precipitate was formed. As TLC test confirmed, it was simply because the acetal moiety is decomposed to the original dye in strong acidic media. As shown in Fig. 2d, gelator **2b** can be successfully utilize as a pH responsive gel. The same behavior for compound **2d** was observed, but it is explicitly unveiled that in this case even lower concentrations of $OH^{‾}$ and/or H^+ (less than 0.05%) can inhibit the formation of gel. In one hand, sensitivity of the compound **2d** towards pH changes was higher than compound **2b** and on the other hand, gelator **2b** made stronger gels in a mixture of 1:1 DMF/H_2O (at 0.5 % concentration) compared with gelator **2d** (table 2). Therefore, both gelators **2b** and **2d** could be effectively used as a pH responsive sol-gel colorimetric sensor at pH range of 0.7<pH<1.6 for acidic medium and pH>12.4 for basic solutions. A reasonable conclusion supported by these observations is that, the main driving force for aggregation of gelator molecules may be the hydrogen bonding interaction of phenolic OH (although π-π stacking interactions are also notable) which is disrupted in basic media.

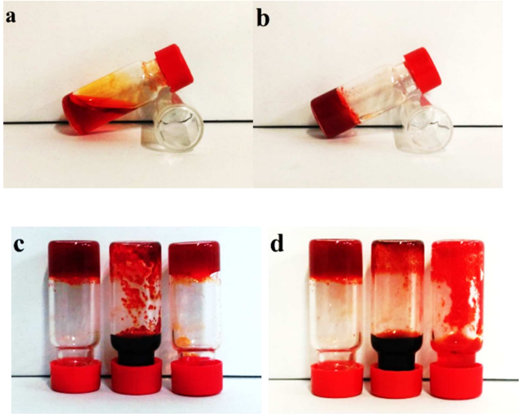


Figure 2. (a) Sol of 1% gelator **2b** in 1:1 DMF/H_2O; (b) gel of 1% gelator **2b** in 1: 1 DMF/H_2O; (c) from left to right: **2b** in DMF/H_2O, DMF/NaOH 0.05 M and DMF/ HCl 0.05 M; (d) **2b** in DMF/H_2O, DMF/NaOH 0.1 M and DMF/ HCl 0.1 M.

It is more likely, protonation of one of azo nitrogens in acidic medium and afterwards disturbing the hydrogen bonding interactions (due NH…OH repulsion), is responsible for inhibiting gel formation, reducing the resonance efficiency, and therefore a clear color change to a vivid red.

*3.4 Investigation of the effect of metal ions on gelation of compounds **2b** and **2d***

In order to investigate the response of the gelators toward metal ions, a 2% solution of gelator **2b** in DMF was prepared and to the vial, equal volumes of 0.1 M aqueous solutions of different M^{2+} and/or M^{3+} cations were added and shaken slightly (total concentration for **2b** and metal ions were 2.21×10^{-2} and 5×10^{-2} M respectively). The vials were set aside for an hour and after that, the vial inversion test was done. As shown in figure 3a, among nine cations were examined, aqueous solution of Cu^{2+} was the only metal ion that prevented gelation of the DMF solution of **2b** alongside with a color change from red to reddish-brown. To confirm the inhibiting effect of adding Cu^{2+} ions on the gelation of compound **2b**, the FE-SEM image of gelator **2b** in the presence of Cu^{2+} ion was prepared (Scheme 3b). As it is unveiled in scheme 3b, all thin sheets that were responsible for the gel formation are deformed and/or collapsed. The IR spectra of gelator **2b** before and after addition of Cu^{2+} ion showed distinct changes (Scheme 3c), implying that, there is a strong interaction between gelator **2b** and Cu^{2+} ions leading to total destruction of gel state. Therefore, gelator **2b** can be successfully use for selective detection of Cu^{2+} ion among different two and three-valent metal ions in the solution. The test was also carried out for **2d** in a similar manner and almost the same results were obtained. The only difference in this case was that, the gel-sol conversion was happened faster than in the case **2b** in the presence of Cu^{2+} ion (5×10^{-2} M).

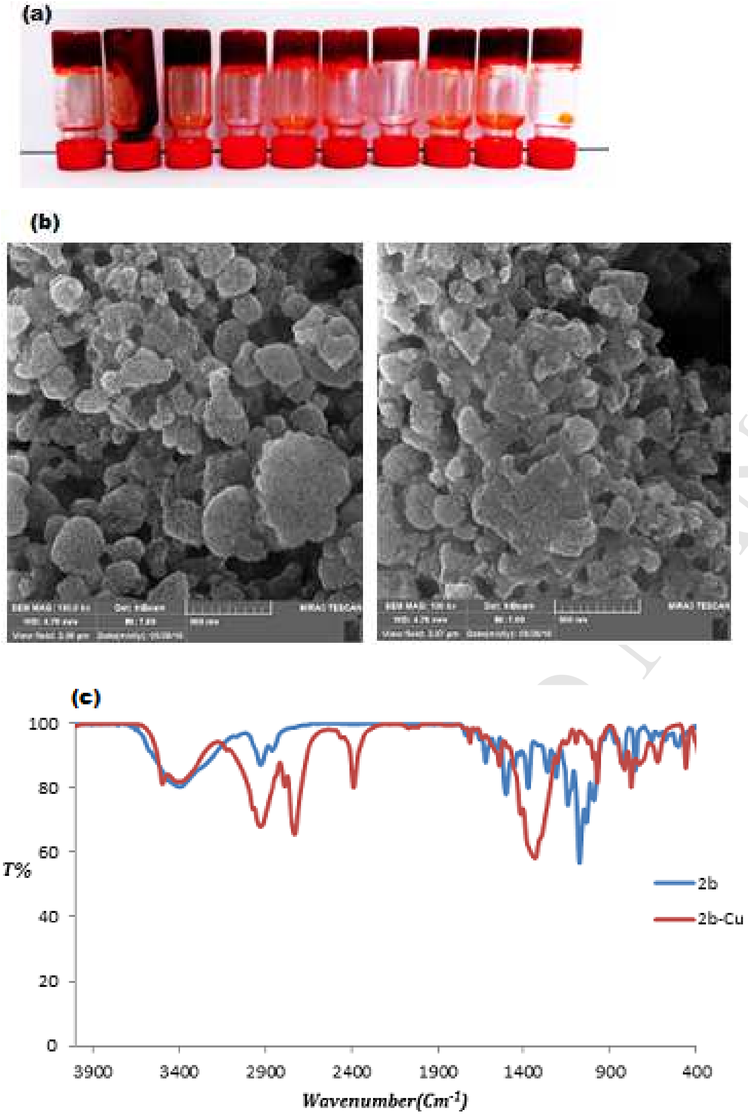


Figure 3. (a) Photograph of selective gel-sol response of a solution of Cu^{2+} ion among various metal ions (0.1 M) to gelator **2b** (4.42×10^{-2} M, 2%); The sequence of added metal ions from left to right is as follows: Pb^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, Fe^{3+}, Hg^{2+}, H_2O; (b) FE-SEM image of gelator **2b** in the presence of Cu^{2+} ion; (c) The IR spectra of gelator **2b** before and after addition of Cu^{2+} ion .

*3.5 Investigation of photoresponse of compounds **2b** and **2d***

Gel to sol phase transition could be triggered by UV light irradiation in a dye/gelator *via* trans-cis photoisomerization of a double bond such as azo functional group under certain wavelengths. Intrigued by the fact that, the synthesized gelators **2b** and **2d** have an azo functional group, we decided to investigate their photoresponsiveness under different frequencies of UV light. To study the effect of UV light, a sample gel containing 1% of gelator **2b** in 1:1 DMF/H_2O mixture was prepared and exposed to UV light (254 or 360 nm, Fig. 4). Interestingly, after 30 min of exposure, the gel collapsed. It was also found that, a sample gel comprising of compounds **2b** or **2d** could be transform to sol state after prolong (typically 2-4 days) expose to day light. This fact demonstrate that, trans-cis photoisomerization is even occurred very slowly under daylight conditions, while gel state could be persist for a long time (over 2 months) if stored in the dark.

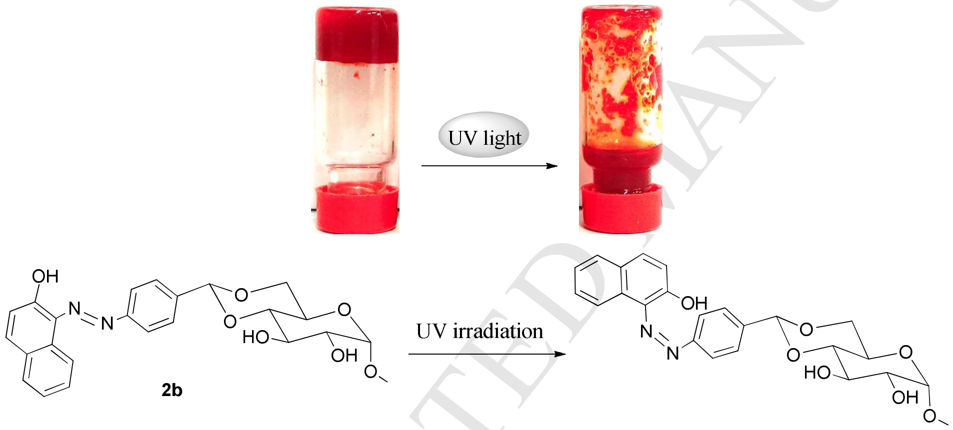


Figure 4. Photo-response of gelator **2b** when irradiated with UV light (254 nm, 400 W, 30 min).

*3.6 Visco-elastic behavior of compound **2d***

In order to investigate the visco-elastic behavior of the gels, storage and loss moduli (G' and G") measurements on a gel composed 1% compound **2d** in DMF/H_2O (1:1) were done in strain and frequency sweep modes. As shown in Fig. 5a, G' and G" remained approximately constant below a strain value of 1%. Above this critical strain value, a gradual decline of G' and G" values was observed, demonstrating a partial disruption of the gel.

Figure 5b shows the independence of G' and G" from frequency under 0.5% constant strain. In addition, higher G' values compared to G", imply the dominance of elastic character of the sample.

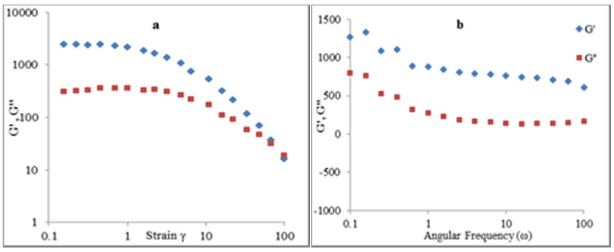


Figure 5. Rheological Data of compound **2d** 1% gel in 1:1 DMF/H_2O (a) Strain sweep under constant frequency of 1 rad/s; (b) Frequency sweep under constant 0.5% strain.

4. Conclusions

In conclusion, we have synthesized four sugar-based azo dye as multistimuli responsive supramolecular gelators. Compounds **2b** and **2d** were supergelators (gelator concentration$\leq$ 1%) in a mixture of DMF/H_2O while compounds **2a** and **2c** were unsuccessful to form a firm and uniform gel. Gelators **2b** and **2d** showed good thermoresponsive and photoresponsive behavior. Photoresponse of these gelators were rather fast (30-60 min) at UV (254 and 360 nm) and very slow in daylight (2-5 days). The investigation of pH responsiveness of Gelators **2b** and **2d** revealed that, they made a gel at pH range of 1.6<pH<12.4 and at pH higher than 12.4 and/or lower than 1.6 they transform to sol state. In addition, gelator **2b** was effectively applied for selective detection of Cu^{2+} ion among a wide variety of two and three-valent metal ions.

Acknowledgements

We are grateful to the University of Isfahan research council for financial support of this work.

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