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ARTICLE TYPE

Two-component organogel for visually detecting nitrite anion

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5 Low molecular weight two component gels were obtained from naphthalenediimide undecane acid mixed with several aliphatic and aromatic diamines. The gelation properties, structural character and fluorescence of these two-component gels were studied via methods of scanning electron microscopy, X-ray diffraction and spectral study. Specifically, the gel containing diaminoanthraquinon (DAQ) was sensitive to nitrite anion. The absorbance and emission intensity of the gel in the visible range obviously
10 decreased upon addition of aqueous solution of sodium nitrite. The faded gel collapsed and changed to sediment after detecting and the organic acid could be recycled. The NO₂⁻ detection with the gel provides a convenient method of nitrite analyses that is visible to the “naked-eye”.

Introduction

Nitrite (NO₂⁻) is known to be able to form carcinogenic
15 nitrosamines in the human stomach, from the reaction of nitrite with secondary amines under acidic condition.¹ Besides, nitrate can oxidize Fe(II) in oxyhaemoglobin to Fe(III) and the oxyhaemoglobin turns into methaemoglobin. This process associates with infantile methaemoglobinemia.² However;
20 sodium nitrite is always used as a colour fixative and preservative in meat and fish. If the nitrite was over added, it would be harmful to human's health. Therefore, detecting the nitrite content of food and drinking water is really important and vital. Although numerous techniques have been developed for nitrite
25 determination such as colorimetric procedure,³ spectroscopic determination after enzymatic reduction,⁴ and electrochemical techniques,⁵ most of them involve time-consuming and tedious procedures. In traditional spectroscopic method, aromatic ortho-diamines are commonly used as reactive probes to detect nitrite,
30 which are converted into benzotriazoles in the presence of NO₂⁻.⁶ However, the reaction could be only happened in acidic condition. Recently, Luis's group proved that films including acrylic acid and 1,2- diaminoanthraquinon (DAQ) could detect nitrite.⁷ Herein, for consideration of environmental protection and no
35 more solid wastes, we propose a new way for sensing nitrite using a new kind of two-component low molecular weight (LMW) organogel containing DAQ, a probe for visually sensing nitrite in neutral aqueous solutions.

Over the past decades, LMW organogels have attracted
40 considerable interest because of their diverse applications as smart soft materials.⁸ The solvent immobilized can be either organic or aqueous. The formation of organogels is facilitated by highly directional self-assembly through non-covalent interactions such as π - π stacking, hydrogen bonding, metal-ion
45 coordination, dipole-dipole interactions⁹ into various 3D

aggregates such as rods, long fibers, strands, tubules, or globules.¹⁰ Those gels have been applied as functional soft materials for sensors,¹¹ electrophoretic and electrically conductive matrices,¹² templates for cell growth or the growth of sol-gel
50 structures,¹³ and in many other industrial fields such as cosmetics, oils, and foods.¹⁴ However, most gelators have complicated structures, such as amino-phenol, long hydrophilic substitute chain, glucide, dendritic substitute, cholesteryl and so on.¹⁵ The rationalized design and synthesis of a specifically functionalized
55 gelator is still a challenge. So we hope to find an easier way to make up functional gels without complex molecule structures and intricate synthesizing process.

Hajra Basit et al reported a new kind of hydrogel expediently made from fatty acid and amine.¹⁶ Here, by introducing
60 fluorescent naphthalimide group,¹⁷ we designed and synthesized two novel fatty acids with emission characteristic (compound **1** and **2**, Scheme 1). When the fatty acids mixed with some kinds of amines, complexes could be formed that subsequently self-assembled into supramolecular networks in organic solvents.
65 Interestingly, the red gel formed with **1** and diaminoanthraquinon (DAQ) has colorimetric and fluorescent response to neutral solution of sodium nitrite. The organic acid in the gel is recyclable without producing solid wastes.

Experimental section

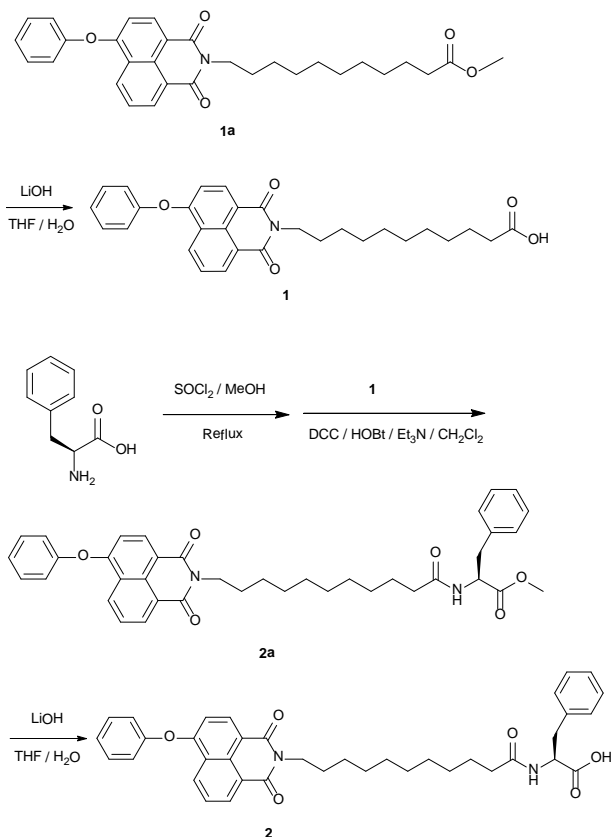
70 Materials and general methods

All reagents were used as received from the supplier without further purification unless explained. Amino-11-undecanoic acid (99.5%), 4-bromo-1,8-naphthalic anhydride ($\geq 95\%$), hexane-1,6-diamine (CP) and ethane-1, 2-diamine anhydrous (99%) were
75 obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai). Other chemicals and solvents were provided from Shanghai No.1 chemical reagent. ¹H NMR and ¹³C NMR spectra were recorded on a Mercuryplus, at 400 and 100 MHz, respectively. Proton

chemical shifts were reported in parts per million downfield from tetramethylsilane. ESI-MS data were recorded on a Waters Quattro Micro API LC-MS-MS spectrometer (Waters, USA). Element analysis was carried out on a VARIOEL3 apparatus (ELEMENTAR). Melting points were recorded on a hot-plate melting point apparatus XT4-100A without further correction.

Synthesis

The synthetic procedure for **1** and **2** was shown in Scheme 1. **1a** was synthesized according to our previous report.¹⁷



Scheme 1 Chemical structure and synthesis route of **1** and **2**

Synthesis of compound 1: LiOH (6.6 g, 276.87 mmol) in 40 mL water was added to a THF solution (40 mL) of **1a** (4.5 g, 9.23 mmol). The mixture was stirred for 3 days and organic solvent was removed by evaporation. The water phase was acidified to pH 2-3 with HCl. The slurry was filtrated and the solid was washed by ether to give **1** as a white powder. Yield 83%, m.p. 110–112 °C. ¹H NMR (400 MHz, DMSO): δ 11.90 (s, 1H), 8.69 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 7.3 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 7.95–7.86 (m, 1H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.39–7.25 (m, 3H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.08–3.95 (m, 2H), 2.16 (t, *J* = 7.3 Hz, 2H), 1.61 (s, 2H), 1.45 (s, 2H), 1.37–1.13 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 177.87, 159.86, 154.91, 132.86, 131.94, 130.42, 129.73, 128.56, 126.53, 125.57, 123.99, 122.72, 120.77, 116.71, 110.70, 77.34, 77.02, 76.70, 40.45, 33.74, 29.36, 29.27, 29.11, 28.98, 28.13, 27.09, 24.68. MS(EI) calculated for C₂₉H₃₂N₂O₅: 474.2 [M + H]⁺, found: 474.4; Anal. Calcd for C₂₉H₃₁N₂O₅: C, 73.49; H, 6.55; N, 2.96. Found: C, 73.63; H, 6.55; N, 2.91.

Synthesis of compound 2a: To a 50 mL anhydrous MeOH

solution of (R)-2-amino-3-phenylpropanoic acid (4.50 g, 27.23 mmol), drops of thionyl chloride (98%) were added slowly during stirring. The mixture was refluxed for 8 h. Then the solvent was removed under reduced pressure. The pale powder was washed by ethyl acetate. This dried powder (2.35 g, 10.9 mmol) was then mixed with **1** (4.3 g, 9.08 mmol), DCC (3.75 g, 18.16 mmol), HOBT (1.23 g, 9.08 mmol) and Et₃N (9.18 g, 9.08 mmol) in dry CH₂Cl₂ (150 mL). The mixture was stirred and refluxed for 12 h at room temperature in nitrogen atmosphere. Then the solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel (chloroform/petroleum ether = 4: 1 (v/v)) to give **2a** as a white powder. Yield 67%, m.p. 81–83 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.65 (dd, *J* = 17.6, 7.6 Hz, 2H), 8.43 (d, *J* = 8.2 Hz, 1H), 7.76 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.34–6.94 (m, 8H), 6.88 (d, *J* = 8.2 Hz, 1H), 5.93 (d, *J* = 7.3 Hz, 1H), 4.82 (dd, *J* = 12.9, 7.0 Hz, 1H), 4.23–4.09 (m, 1H), 3.89 (q, *J* = 7.0 Hz, 1H), 3.66 (s, 3H), 3.29 (dd, *J* = 14.5, 5.2 Hz, 1H), 3.06 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.27 (t, *J* = 7.4 Hz, 2H), 1.63 (m, 4H), 1.32 (m, 12H); ¹³C NMR (100 MHz, CDCl₃): δ 174.45, 165.32, 164.45, 163.83, 159.91, 154.89, 134.14, 132.84, 131.93, 130.49, 129.73, 128.60, 127.73, 126.56, 125.90, 125.66, 123.97, 122.72, 120.87, 116.68, 110.64, 77.44, 77.12, 76.80, 53.12, 51.54, 40.48, 35.02, 34.20, 29.54, 29.47, 29.43, 29.30, 29.21, 28.22, 27.21, 25.04. MS(EI): *m/z* calculated for C₃₉H₄₃N₂O₆ [M+H]⁺: 635.3, found: 635.7.

Synthesis of compound 2: LiOH (5.8 g, 241.66 mmol) in 50 mL water was added to a THF solution (50 mL) of **2b** (5.0 g, 8.06 mmol). The mixture was stirred for 3 days and organic solvent was removed by evaporation. The water phase was acidified to pH 2-3 with HCl. The slurry was filtrated and the solid was washed by ether to give **2** as a white powder. Yield 77%, m.p. 86–88 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.69 (ddd, *J* = 8.4, 7.8, 1.1 Hz, 1H), 8.46 (d, *J* = 8.3 Hz, 1H), 7.78 (dd, *J* = 8.3, 7.4 Hz, 1H), 7.57–7.41 (m, 1H), 7.38–7.09 (m, 9H), 6.91 (d, *J* = 8.3 Hz, 1H), 5.94 (d, *J* = 7.5 Hz, 1H), 4.87 (dd, *J* = 13.3, 6.0 Hz, 1H), 4.23–4.07 (m, 1H), 3.73 (q, *J* = 7.0 Hz, 1H), 3.42 (s, 1H), 3.25 (dd, *J* = 14.1, 5.6 Hz, 1H), 3.14 (dd, *J* = 14.0, 6.2 Hz, 1H), 2.16 (t, *J* = 7.3 Hz, 1H), 1.92 (d, *J* = 12.7 Hz, 1H), 1.71 (d, *J* = 9.3 Hz, 2H), 1.64–1.46 (m, 2H), 1.46–1.01 (m, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 173.57, 165.10, 164.52, 163.93, 159.97, 154.86, 132.95, 132.00, 130.43, 129.71, 129.42, 128.55, 127.06, 126.53, 125.62, 123.97, 122.63, 120.79, 116.57, 110.67, 77.34, 77.22, 77.02, 76.71, 53.17, 49.64, 40.53, 36.49, 33.58, 29.20, 29.08, 28.04, 27.06, 25.52, 25.49, 24.79. MS (EI): *m/z* calculated for C₃₈H₄₁N₂O₆ [M+H]⁺: 621.3, found: 621.2; Anal. Calcd for C₃₈H₄₀N₂O₆: C, 73.53; H, 6.50; N, 4.51. Found: C, 73.63; H, 6.50; N, 4.43.

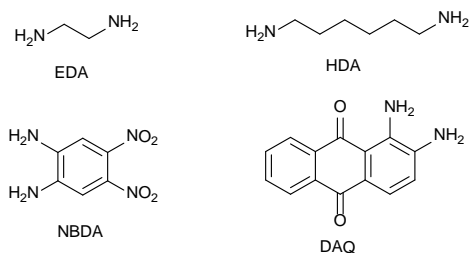
Gelation test of organic fluids

When **1** or **2** mixed with diamines as shown in Scheme 2, dissolved in some organic solvent, the complexes show the character of gelation. For example, when 0.1 g (0.21 mmol) **1** and 7.35 μL (0.11 mmol) 1,2-diamineoethane were dissolved in chloroform, the two component gelator **1**+EDA was obtained after removing chloroform. Generally, the molar proportion of compound **1** or **2** with diamine is 2: 1. The gelator (5 mg) and the solvent (200 μL) were put in a hermetic test tube (1.5 mL) and heated (> 75 °C) until the solid was dissolved. Then the sample vial was cooled to 25 °C (prepared sample). Qualitatively, gelation was considered successful if no sample flowed upon

inverting the container at room temperature. The critical gelation concentrations (CGC) were tested using dilution method after the gels were formed (Table 1). For example, to a 200 μL gel sample in test tube, additional 50 μL solvent was added, followed by a heating-cooling process to see whether it could form a gel again. This process was repeated until the gel came to flow, and this concentration was recorded as a CGC.

Techniques

UV-visible spectra were recorded on an UV-vis 2550 spectroscopy (Shimadzu). Fluorescent spectra were tested on an Edinburgh Instruments FLS 900 with Xe lamp as the excitation source. Fourier transform infrared (FT-IR) spectra were performed using an IRPRESTIGE-21 spectroscopy (Shimadzu) with KBr pellets. SEM images of the xerogels were obtained using a SSX-550 (Shimadzu) with an accelerating voltage of 15 kV. Samples were prepared by diluting the gel and dropping it on the surface of a mica flake, and then freeze dried and coating with Au. Powder X-ray diffractions were generated by using a Philips PW3830 sealed-tube X-ray generator (Cu target, $\lambda = 0.1542$ nm) with a power of 40 kV and 50 mA. Samples were prepared by freeze dried gels. Freezing dry was performed in a FDU-1200 Freeze Dryer (Tokyo Rikakikai, Japan) with the trap temperature of -45 $^{\circ}\text{C}$.



Scheme 2 Structures and abbreviations of different amines checked for gelation.

Results and discussion

Gel formation and characterization

Naphthalimide undecane acids **1** and **2** are used as the fundamental gel composition. These two compounds have no capability to form gels by themselves. After mixed with various kinds of diamines (Scheme 2, details for preparation are given in the Experimental Section), the two component complexes can gel in a variety of organic solvents. Gelation property of the complexes was checked in 14 kinds of organic solvents with the molar ratio of **1**/amine or **2**/amine of 2: 1 (Table 1). It was observed that the complexes of **1** and amines were more capable of gelation than that of **2**. **1** could form gel in alcohols, cyclohexane, acetonitrile and toluene with both aliphatic and aromatic amines. **2** could only gelate long chain alcohols in the presence of aliphatic amines. It was also found that the complexes with aliphatic amines, such as EDA and HDA can gelate more kinds of solvents, especially in alcohol. On the contrary, the complexes with aromatic amines such as NBDA and DAQ make compounds more soluble in most of tested solvent. Hereinto, **1**+DAQ has better gelation property in acetonitrile and ethanol, with a critical gelation concentration of 12.5 and 7.7 mg/mL, respectively.

Table 1 Gelation ability of **1** and **2** with several amines

Solvent	EDA		HDA		NBDA		DAQ	
	1	2	1	2	1	2	1	2
n-Octanol	G (10)	G (12.5)	G (5)	G (12.5)	S	S	S	S
n-Pentanol	G (10)	S	G (5)	G (25)	S	S	S	S
Methanol	G (9)	P	G (5)	P	G (10)	P	G (10)	S
Ethanol	G (9)	P	G (5)	P	G (7.7)	S	G (7.7)	S
1,4-Dioxane	PG	G (14.3)	PG	S	S	S	S	S
DMSO	P	S	S	S	S	S	S	S
Chloroform	S	S	S	S	I	I	S	I
Acetone	G (10)	P	P	I	S	P	S	S
Cyclohexane	G (12)	I	G (7.7)	I	G (10)	I	G (12.5)	I
Acetonitrile	G (10)	I	G (5)	I	G (10)	G (10)	G (12.5)	P
Ethyl acetate	PG	P	PG	P	S	G (25)	S	P
Toluene	G (7.1)	G (12.5)	PG	I	I	G (12.5)	S	P
1-Methyl-2-pyrrolidone	S	S	S	S	S	S	S	S
Tetrahydrofuran	S	S	PG	P	S	S	S	S

G = Gel; PG = Partial Gel; P = Precipitation; S = Solution; I = Insoluble. Molar ratio of acid: amine = 2: 1, concentration = 25 mg/mL. The critical gelation concentration was in the bracket (mg/mL). Gels were made by heating-cooling process from 75 $^{\circ}\text{C}$ to 25 $^{\circ}\text{C}$.

The viscoelastic behaviour of gels of **1** with both aliphatic (**1**+HDA) and aromatic diamines (**1**+DAQ) (**1**/amine = 2: 1, 25 mg/mL in ethanol) was studied by dynamic oscillatory measurements. The linear viscoelastic region (LVR), as a function of increasing amplitude of deformation due to shearing, was determined with strain amplitude in the range 0.005–1000% at an angular frequency of 6.28 rad s^{-1} (Fig. 1a). The two gels show similar viscoelastic behaviour. The strength (storage modulus, G') of the gel is around 150 Pa with a small strain of 0.01%, which indicates that these gels were relatively weak compared to other gels in the field.¹⁰ With the small strain amplitudes, the storage modulus (G') is larger than the loss modulus (G'') in both gels, and G' and G'' remain nearly constant (LVR) up to approximately 0.3% and 2% of strain, respectively. At larger strain amplitudes, the gels showed a catastrophic disruption accompanied by a step decrease in the values of both moduli and the reversal of the viscoelastic signal ($G' < G''$) is 15% in **1**+DAQ and 20% in **1**+HDA. The implementation of a frequency sweep between 0.3 and 100 rad s^{-1} at a strain of 0.2% shows $G' > G''$ in both gels, which confirms that the gels have a predominantly elastic character (Fig. 1b). The elasticity of the gels was further evident from the facts that the G' and G'' values are minimally sensitive to frequency (ω), which indicated that the gel system formed a stable network structure.¹⁸

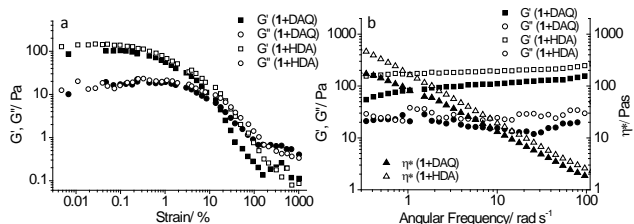


Fig. 1 Dynamic oscillatory data for gel **1**+DAQ and **1**+HDA (25 mg/mL in ethanol) at 20 °C. (a) Strain sweep of the gels at a frequency of 6.28 rad s⁻¹. (b) Frequency sweep of the gel at a strain of 0.2%.

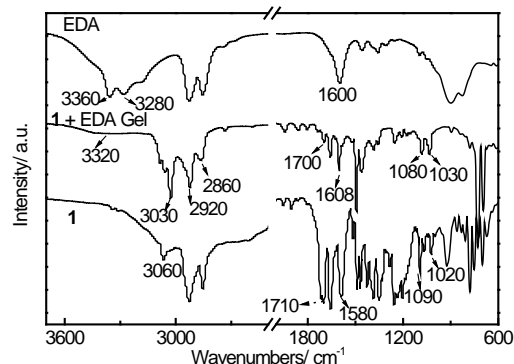


Fig. 3 IR spectra of powder of **1**, EDA and xerogel of **1**+EDA formed in toluene (25 mg/mL).

The network morphologies of the freeze-dried gels derived from gelators of compound **1** and **2** mixed with kinds of amines in organic solvent were investigated by scanning electron microscopy (SEM) (Fig. 2). From the images, it can be seen that the architectures from gels of **1** with variety amines are similar in appearance. Those gels show ribbon structure with the width from 2~ 5 μm (Fig. 2a – 2d). As for compound **2** with aliphatic amines, the morphologies show networks interweaved by fine flexible fibers with diameter smaller than 100 nm (Fig. 2e, 2f and Fig. S1 in the ESI[†]).

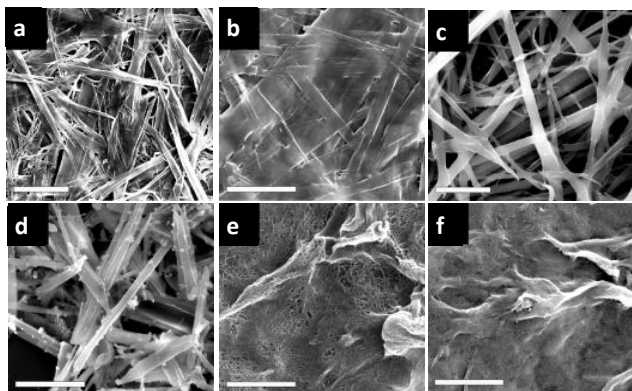


Fig. 2 SEM images of self-assembled complexes: (a) **1**+EDA in ethanol, (b) **1**+HDA in ethanol, (c) **1**+NBDA in ethanol, (d) **1**+DAQ in ethanol, (e) **2**+EDA in octanol, (f) **2**+HDA in octanol, scale bars for a, b, c, d, e and f are 20, 20, 20, 50, 5 and 10 μm , respectively.

To investigate the interactions between **1** and amines, IR analysis of **1** and the complexes of **1**+EDA and **1**+DAQ were taken. As shown in Fig. 3, the characteristic peak of the stretching vibration of C=O of **1** at around 1710 cm^{-1} attributed to carboxylic acid drastically decreased and shifted to 1700 cm^{-1} when interacted with EDA and DAQ in the gel formation (also see Fig. S2 in the ESI[†]). The stretching vibration of C-O of **1** at 1090 and 1020 cm^{-1} was shifted to 1080 and 1030 cm^{-1} , which also suggested the strong interaction between carboxylic acid and amines. The disappearance of the strong vibration at 1600 cm^{-1} of EDA (belonging to N-H bond) and the appearance of the peak at 1608 cm^{-1} in **1**+EDA are attributable to the complex formation between -NH₂ of diamine and -COOH of **1**. Moreover, the peaks of stretching vibration of N-H at 3360 and 3280 cm^{-1} almost vanished in **1**+EDA gel, and the presence of multi peaks in the range of 3000~3100 cm^{-1} strongly suggested the formation of ammonium ions. All these data were indicative of carboxylate salt formation between **1** and amines.

X-ray diffractions (XRD) can provide structure information for the self-assembly in the gel state. Here XRD were recorded for powder of **1**, DAQ and xerogels of the complexes from ethanol (Fig. 4A). The molar ratio of **1** and diamines in the complex gelator is 2: 1, just like all the above. The X-ray diffraction profiles of the xerogels of the complexes are quite different with sole compound of **1** or DAQ, indicating the formation of the complex. The X-ray diffraction profile of the xerogel of **1** with aromatic amines showed a series of peaks of 24.35, 12.30, 8.43 \AA for **1**+DAQ, and 25.14, 12.58, 8.42 for **1**+NBDA (Fig. S3 in ESI[†]), with a ratio of 1: 1/2: 1/3, a character of lamellar packing of the complexes. The distance of 24.35 \AA for **1**+DAQ is in agreement with the length of the joint body of molecules **1** (16 \AA) and DAQ (9 \AA). The dimensions of about 4.1 \AA in the complexes may suggest π - π interactions. The existence of π - π stacking in **1**+DAQ was also supported by spectral study discussed in the following part. The proposed aggregation mode of **1**+DAQ is shown in Fig. 4B, in which the complexes of **1**+DAQ are formed by acid base interaction and then the complexes further aggregate to a layer structure. The X-ray diffraction in the gels of **1** with aliphatic amines, such as EDA and HDA was much weaker and broader than that with aromatic amines, indicating the less ordered structure in those gels (Fig. S3).

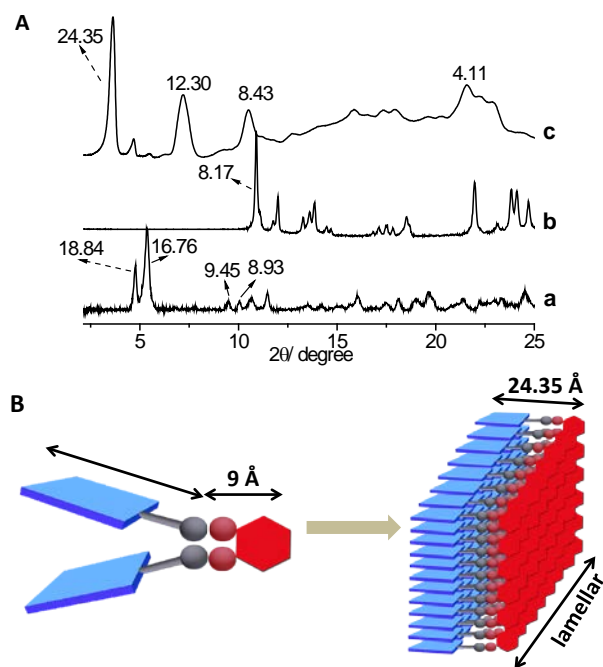


Fig. 4 (A) XRD spectra of **1** (a), DAQ (b), and the xerogels of **1**+DAQ (c). Numbers marked on the peaks of XRD stands for value of distance (Å).

(B) Proposed interaction mode of **1** and DAQ (left) and the supposed stacking method (right).

The spectroscopic study also supports the formation of π - π stacking between gelators. The maximum absorption and emission of compound **1** in CH_3CN (1×10^{-5} M) is located at 360 nm and 429 nm, respectively (Fig. S4 in ESI[†]). The fluorescent quantum yield (ϕ) of **1** was 0.1366 using quinine sulfate as a reference. DAQ solution has an absorption band at 500 nm in visible range and an emission band at 625 nm ($\phi = 0.0061$). To investigate the fluorescence character in the aggregation state, emission spectra of gels (25 mg/mL) and related sols (5×10^{-4} M) were studied and are shown in Fig. 5a, 5b and Fig. S5 in ESI[†]. It is clear that all emission spectra have a red shift from sol to gel state. In case of **1**+EDA in toluene, the emission band of naphthalimide group was modulated from 420 nm in sol to 478 nm in the gel. While for **1**+DAQ in acetonitrile, this peak shifted from 421 to 434 nm. The weak emission band at 625 nm of **1**+DAQ belongs to DAQ in the gel state, by comparison with pure DAQ solution (Fig. S4 in ESI[†]). A red shift of the absorption band from sol to gel state could also be observed that the absorption peak for naphthalimide group shifted from 359 to 401 nm in **1**+EDA and from 359 to 364 nm in **1**+DAQ, respectively (Fig. 5c and 5d). This indicates that the π - π interaction between naphthalimide groups has great contribution to the gel formation in complex gels.

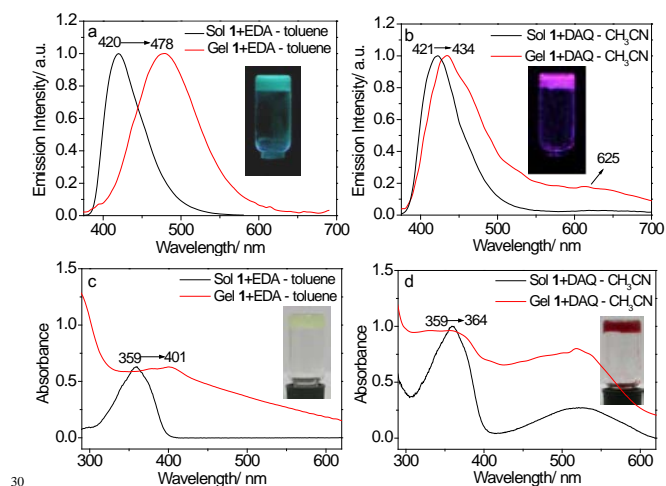


Fig. 5 Emission and absorption spectra of the sols and gels of (a, c) **1**+EDA in toluene and (b, d) **1**+DAQ in acetonitrile; respectively. Insets are pictures of gels in 365 UV-light (a and b) or in natural light (c and d). Molar ratio of acid: amine = 2: 1, the concentration for sols are 5×10^{-4} M and for gels are 25 mg/mL.

Response to NO_2^-

Gel **1**+DAQ was found sensitive to NO_2^- as we imagined (Fig. 6). The original colour of the two component gel was red as shown in Fig. 6a due to a strong absorption of DAQ at 517 nm. With the addition of aqueous solution of NaNO_2 , the gel was collapsed to a suspension and the colour of the gel was gradually faded. Quantitatively, when 100 equiv of NaNO_2 aqueous solution was added to the top surface of the gel of **1** + DAQ (25 mg/mL in acetonitrile, molar ratio of **1**: DAQ = 2: 1), in two hours which equals the average level of using DAQ to sense nitrite anion in the literature,¹⁹ the colour of the broken gel was completely faded with an obvious decrease of the absorption at 517 nm (Fig. 6b and 6d). What's more, the fluorescence emission of **1** at 434 nm quenched to 40% of its original intensity and fluorescence emission of the DAQ at 639 nm fell to nearly zero because of the existence of colourless triazole formed from the reaction of DAQ and NO_2^- (Fig. 6c and 6e). Results of LC-MS demonstrate this reaction. After reaction, the peak for DAQ ($m/z = 239$) in mass spectra was totally changed into benzotriazole ($m/z = 249$), but the peak for compound **1** ($m/z = 474$) was unchanged (Fig. S6 in ESI[†]). The mechanism is shown in Fig. 6f. These facts indicate that the complex **1**+DAQ can serve as an indicator of NO_2^- that is visible to the naked eye. It should be pointed out that pure water or other solution of salt can also destroy the gel, but the colour and emission character would not be changed (Fig 6b and 6c).

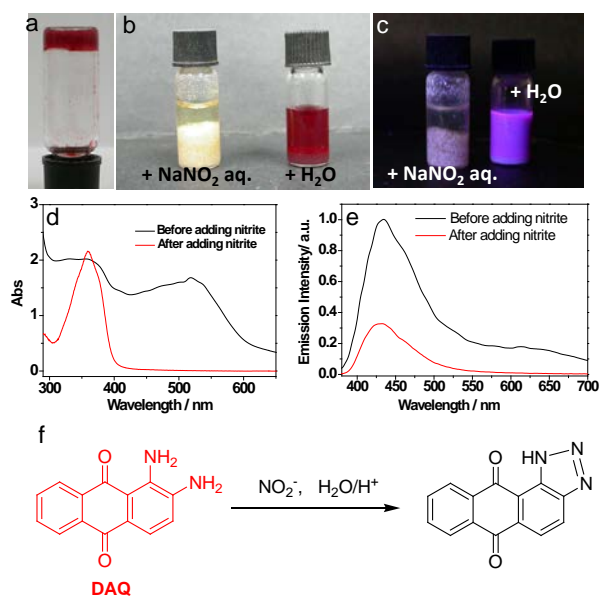


Fig. 6 Photos of gel **1**+DAQ (a, 25 mg/mL in acetonitrile), and the gel added with NaNO₂ solution (left) and pure water (right) in natural light (b) and with 365 nm light irradiation (c). (d) Absorption and (e) emission spectra of gel **1**+DAQ before and after treated with NO₂⁻. (f) The scheme of the reaction between DAQ and NO₂⁻.

As for the practical application and recycle consideration, the quantitative change of detecting of Gel **1** + DAQ for both pure water and different concentration of NO₂⁻ (0 ~ 200 eq of DAQ) were checked. After reaction, the mixture consists of two parts: the liquid part (L) mainly including solvent, triazole product of DAQ or remaining DAQ, and the precipitation part mainly including **1** (P), as **1** could hardly dissolve in acetonitrile or water. The liquid part was taken out by filter membrane and diluted by 4 mL THF solutions to make sure that the proportion stayed unchanged. The precipitation part was also dissolved in 4 mL of THF to see how much **1** remained that could be taken for reuse by means of absorption spectrum. As we observed from the absorption and emission spectra of the liquid part of the broken gel treated with nitrite (**1**+DAQ+NaNO₂) (L) in Fig. 7, the gel mixture of **1**+DAQ quickly faded after addition of 5 eq of NaNO₂ (40% of absorbance quenched), and gradually decreased after further addition of NaNO₂. The reaction was complete within two hours after 200 eq NaNO₂ (relative to DAQ) was added (98% of the absorbance quenched, Fig. 7a). Fig. 7b shows the absorbance change of **1** + DAQ (liquid part) with the addition of different molar ratio of NaNO₂, from which we can see that the **1**+DAQ gel is very sensitive to NO₂⁻. Besides, because **1** hardly dissolved in the gelling solvent CH₃CN, it was easily called back and reused. As shown in Fig. S7 in the ESI[†], the comparison of the absorbance at 359 nm belonging to **1** from the liquid part and the precipitation part of **1**+DAQ+NaNO₂ solution in THF shows that only 9% of **1** remains in the liquid part, which means the majority of **1** could be reused.

High-level selectivity is of paramount importance for an excellent chemosensor. In the present work, the common environment salts such as NaF, NaHCO₃, Na₂SO₃ and Na₃PO₄ were checked with **1**+DAQ by means of absorption spectroscopy. A gel of **1**+DAQ (20 μM) has little variation of absorption upon the addition of excess anions (100 eq), such as NaF, NaHCO₃,

Na₂SO₃, Na₃PO₄ (Fig. 7c). This indicates a high selectivity of **1**+DAQ towards NO₂⁻ compared with other anions.

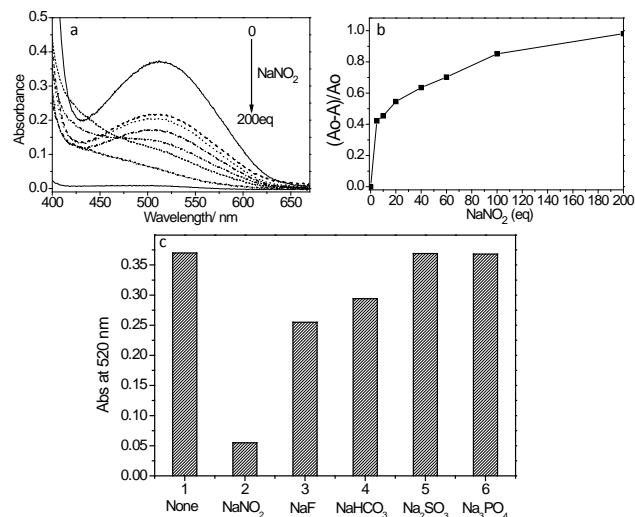


Fig. 7 (a) UV-visible absorption spectra of the liquid part of gel **1**+DAQ treated with pure water and different equivalences of NaNO₂ aqueous solution (cell: 1 mm); (b) The absorbance change at 520 nm with the addition of different molar ratio of NaNO₂. (c) The absorbance at 520 nm with the addition of different kinds of anions (100 eq of DAQ). Samples all dilute in THF.

Compared with the previous reported NO₂⁻ probe, the main advantages of this kind of two-component low molecular weight organogel are as follows: (1) it affords an easy way for sensing NO₂⁻ with obvious colour and emission change through self-assembly of an organic acid and DAQ; (2) additional HCl is no need in the sensing process, as reported in some previous work,⁶ because **1** provides necessary proton for the reaction between DAQ and NO₂⁻; (3) the two component gel is decomposable and the part of organic acid **1** could be called back and used as a circulative material, showing environmental-friendly.

Conclusions

In conclusion, we made a kind of two-component low molecular weight organogels from naphthalenediimide undecane acid mixed with several aliphatic and aromatic diamines. The spectroscopic and morphological properties of the gels could be tuned by changing the associated amines. Besides, this conveniently prepared two-component gel containing diaminoanthraquinone can be used as a new kind of probe for sensing NO₂⁻ in neutral environment. What's outstanding is that, besides the colorimetric change, this gel state probe has a fluorescence emission response towards NO₂⁻, which expands the field for more practically applications.²⁰ After sensing, the organic acid could be recycled. This two component gel is thus an ideal platform for the design of supramolecular visually sensing system with tuneable optical properties.

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