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Fluoride-responsive organogel containing azobenzyl and cholesterol units

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ABSTRACT

In this paper, two new cholesterol-based compounds **O1** and **O2** were designed and synthesized. The compound **O2** could selectively gel in 1,4-dioxane with porous ribbon structure. The aggregation mode of **O2** molecules were characterized by SEM, IR, UV–vis and XRD experiments. Interestingly, the gel of **O2** was also fluoride-responsive. The addition of TBAF on the gel surface would trigger the gel–sol transition, and the collapse time could be controlled by amount of fluoride ions. The response process was also accompanied by dramatic color changes from orange to purple. From the NMR titration experiments, it was deduced that the hydrogen bonding competition between the anion-receptor and self-assembly of the receptor played an important role for the gel–sol transition.

1. Introduction

LMOGs (Low Molecular-mass Organic Gelators) have attracted increasing attention in the material chemistry due to their merits such as stimulus responsibility, reversibility, as well as self-healing properties, which make them play important roles in the filed of drug controlled release, molecular devices, biological issue, and intelligent materials [1–8]. These organogels are constructed by non-covalent interactions such as hydrogen bonding, π–π stacking, van der Waals interaction, which are very sensitive to external stimuli such as ions, sonication, heat, pH, as well as biological molecules [9–18]. In particular, anion-responsive gels have drawn special attention in recent years [19,20]. The introduction of anions could change the gel state in micro/macrolevels depending on the interaction between anions and gelator molecules [21–23].

The design and preparation of fluoride receptors have received considerable attention due to their important roles in the field of biology, chemistry, and environment [24,25]. It is well-known that the NH units such as amides, (thio)ureas, ammonium, imidazole units could be served as hydrogen bonding sites for anions in the diluted solution [26–32]. However, most of the recognition events are performed in solution, which restricted them from potential application.

In the past decades, fluoride-ion-responsive LMOGs are beginning to attract particular attention [33–35]. Although many kinds of fluoride-ion-responsive LMOGs were designed and studied, few of them was able to sense fluoride anions with high selectivity among fluoride and other anions [36]. So far, design of the anion receptors with high selectivity toward fluoride in organogel issue is still a challenge. In this paper, two new cholesterol-based compounds with azo units as the chromophore and imidazole group as the anion acceptor were designed and synthesized. Compound **O2** was able to aggregate in 1,4-dioxane to form stable and red color gel. Further study showed that compound **O2** could selectively recognize fluoride anion either in solution or gel state, accompanied by dramatic color and phase changes.

2. Results and discussion

The synthesis and characterization of **O1** and **O2** could be seen from Scheme 1 and supporting information. From Table 1, with the concentration of 25 mg/mL, **O2** could selectively gel in 1,4-dioxane to form red and opaque organogel by classic heating-cooling process. Without the $-NO_2$ group, **O1** displayed poor solubility in the test organic solvents. By heating-cooling process, molecules of **O1** precipitated in 1,4-dioxane. SEM images revealed that they

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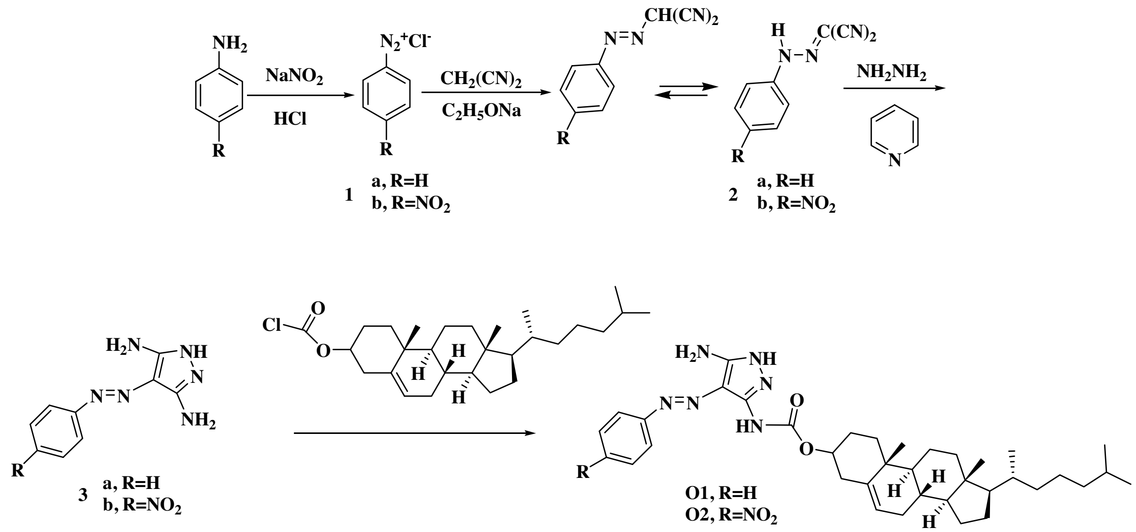

Scheme 1. Chemical structure and synthesis route of **O1** and **O2**.

Table 1
The gelation properties of **O1** and **O2** (25 mg/mL).

	O1	O2
THF	P	P
Methanol	I	I
Ethanol	I	I
1,4-Dioxane	P	OG
Xylene	I	I
Ethyl acetate	I	I
n-Propanol	I	I
Cyclohexane	I	I
n-Hexane	I	I

I: insoluble; P: precipitate; OG: opaque gel.

assembled to microsphere structure with diameters ranged from 5 to 10 μm. From the magnified image (Fig. 1a–c), it was observed that the spheres were with nanoporous surface. While ribbons with porous surface were formed by **O2** molecules in the gel issue (Fig. 3d–f).

From the UV–vis spectra (Fig. 2a), the absorption band of **O2** in the solution exhibited one peak at 421 nm with yellow color, which was attributed to conjugated π system of azobenzyl and imidazole groups. In the gel state, the peak became broad with a new shoulder at 532 nm, which displayed red shift, indicating the enhanced π conjugated system in gel state. FT-IR experiment confirmed that the hydrogen bonding played an important role for the gelation and molecular assembly. From Fig. 2b, the –NH stretching bands of **O2** in gel state from 1,4-dioxane were positioned at 3477, 3435, 3366 cm^{-1}, indicating the existence of multiple hydrogen bondings; the bands at 1720, 1637, were ascribed to the corresponding C=O vibrations, and the peak at 1565 cm^{-1} was ascribed to amino II band.

To gain a deeper insight into the molecular assembly mechanism, XRD experiments were also performed. From Fig. 3, the peak of the gel for **O2** at 2.5 nm was ascribed to the d value of single molecule. The peaks at 2.5, 1.25, 0.6 were with the ratio of 1:1/2:1/4, reflecting the lamer structure of the aggregation.

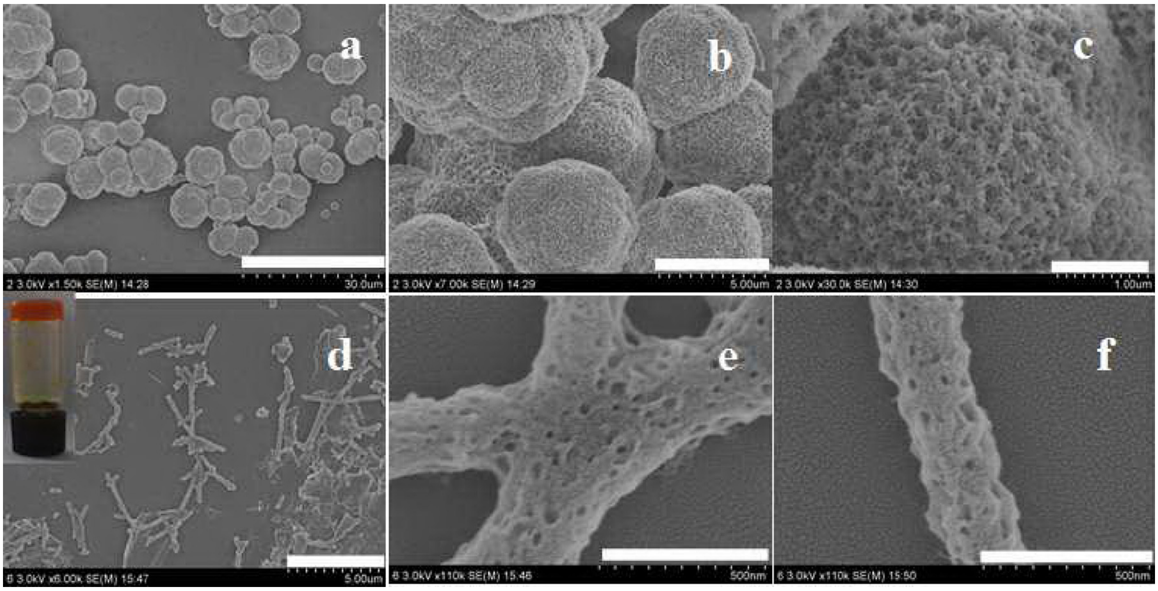

Fig. 1. SEM images of the precipitate of **O1** (a–c) and the gel of **O2** (d–f). (b) The magnified picture of (a), (c) the magnified picture of (b); (e) the magnified picture of (d), (f) the magnified picture of (e); Scale bar: (a) 30 μm; (b) 5 μm; (c) 1 μm; (d) 5 μm; (e) 500 nm; (f) 500 nm.

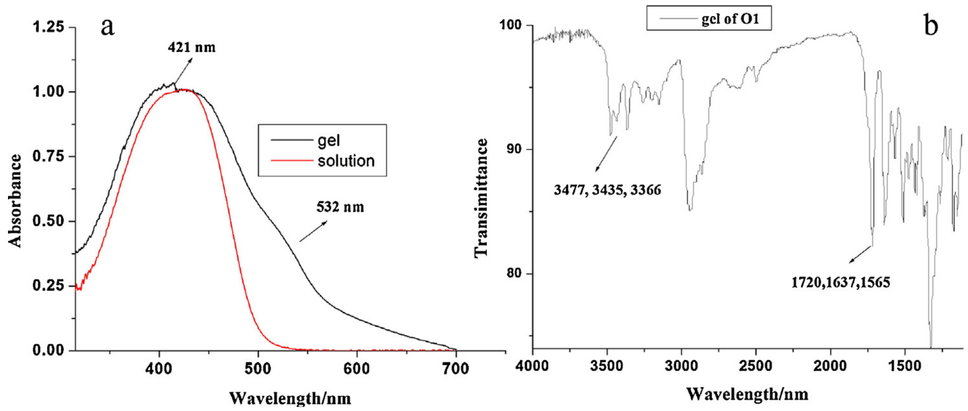

Fig. 2. (a) Absorption spectra of **O2** in the solution of 1,4-dixane (10^{-4} M) and the gel (25 mg/mL); (b) IR spectrum of the gel of **O2**.

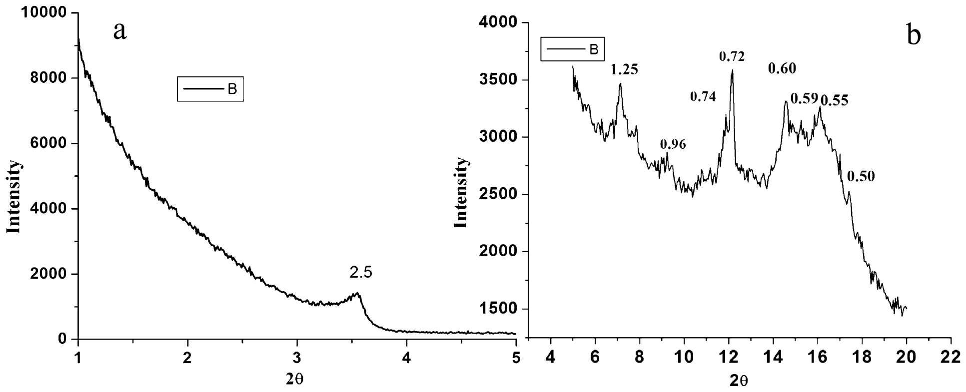

Fig. 3. XRD data of Xerogel of **O2** in 1,4-dioxane.

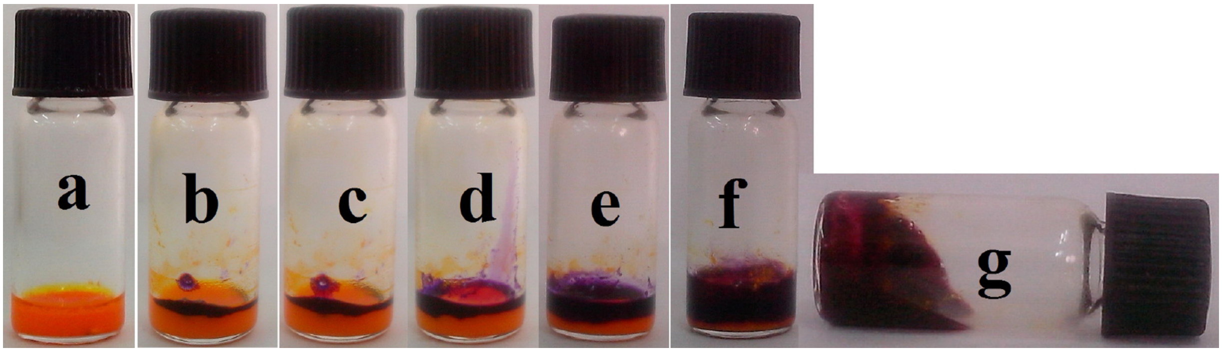

Fig. 4. The gel phase changes after the addition of fluoride. (a) Gel; (b) treated with F^- instantly; (c) after 70 min; (d) after 90 min; (e) after 120 min; (f) after 150 min; (g) after 170 min.

Generally speaking, hydrogen bonding plays an important role in either gel assembly or anion recognition events. Therefore, the addition of anions into gels would change the gel assembly in molecular level due to the hydrogen bonding competition. Seen from Fig. 4a, by classic heating-cooling process, the **O2** formed stable gel in 1,4-dioxane with red color. Upon addition of 20 equiv. of fluoride anion (solid) on the gel surface, the interface became purple instantly. The gradually collapse process could be seen from Fig. 4c–f. After staying for 3 h, the gel corrupted and became purple wholly (Fig. 4g). Also, the corruption rate could be controlled by the equivalent of fluoride anions ranging from minutes to days (Table 2).

To further examine the color changes and the selectivity of **O2** toward anions. The UV–vis experiments in the solution state were carried out to study the host–guest interaction. From Fig. 5, upon the addition of 20 equiv. of fluoride anions, the peak of **O2** (5×10^{-5} M) in solution at 443 nm disappeared, while a new strong peak at 563 nm appeared and increased, accompanied with the obvious color changes from yellow to blue, indicating formation of the complex **O2** + F^-. Other anions such as AcO^-, Cl^-, Br^-, I^- and $HSO_4{}^-$ did not triggered any obvious color or spectral changes (Fig. 5). The above results suggested the high selectivity of the organogelator **O2** toward tested anions. As expected, addition of these anions event at 50 equiv. on the gel surface, there was no obvious color or phase changes.

Table 2
The collapse time controlled by the amount of F^-.

Equiv. of fluoride	2	5	20	50	100
Collapse time	1 day	18 h	4 h	1 h	10 min

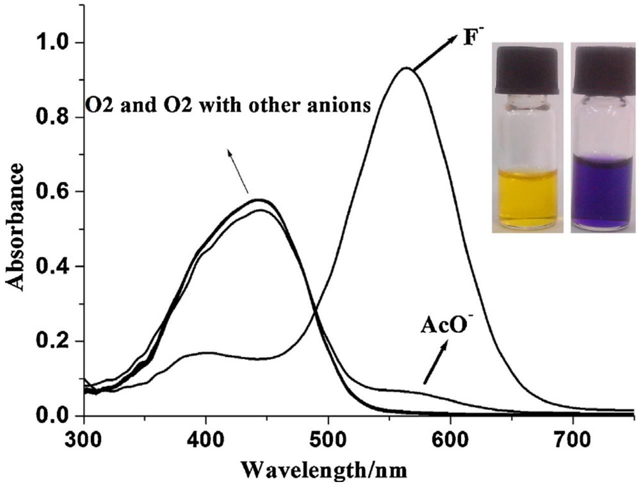

Fig. 5. UV–vis titrations of **O2** (5×10^{-5} M) with different anions (100 equiv.).

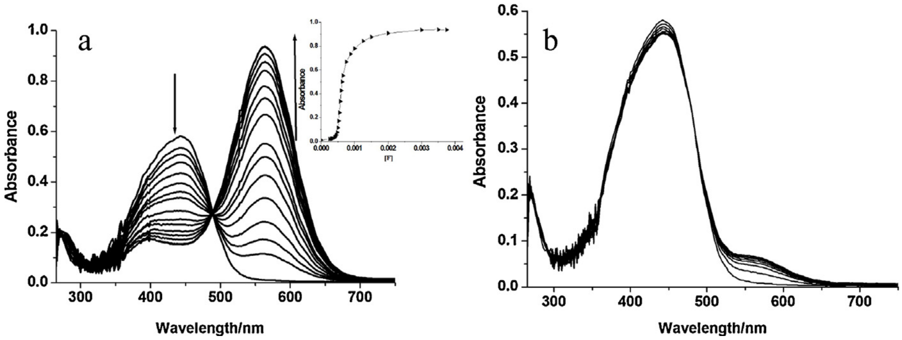

Fig. 6. UV–vis titrations of **O2** solution (5×10^{-5} M). (a) Upon the addition of fluoride anions; (b) upon the addition of AcO⁻ anions.

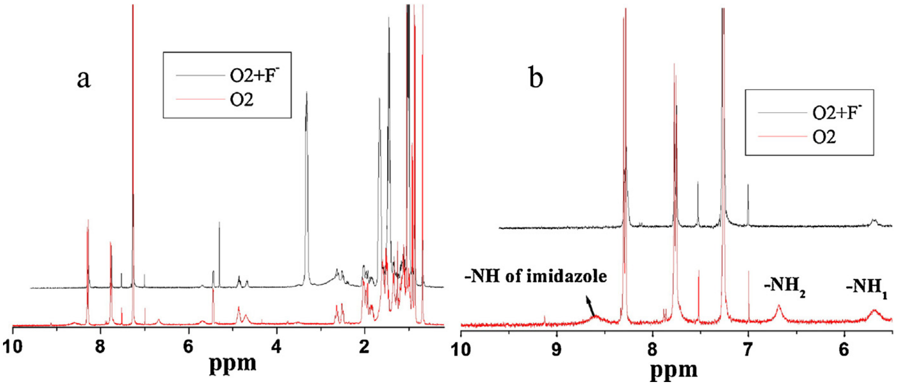

Fig. 7. The NMR titrations of **O2** with F⁻ (30 equiv.).

By a precise study, addition of fluoride (0–80 equiv.) resulted in remarkable and regular decrease of peak at 443 nm and increase of the peak at 563 nm, indicating the strong and stable interaction among **O2** with F⁻ via hydrogen bonding among –NHs as the anion acceptor (Fig. 6a). While AcO⁻ triggered very weaker changes compared with that of fluoride (0–100 equiv.). NMR titrations were also performed to confirm the bonding properties of **O2** with F⁻. From Fig. 7, the addition of fluoride anions triggered the complete disappearance of the –NH, indicating a deprotonation process. KOH as a kind of a strong base was added into the solution of **O2** in order to further check the binding mechanism. UV–vis experiment revealed that KOH triggered very similar spectrum changes of **O2** just like that of F⁻ (Fig. S1), which was in accordance with the NMR titration experiment.

3. Conclusion

Two new kinds of cholesterol-based compounds were designed and synthesized. The structural modification on the benzyl unit had great impact on the gelaion properties. The gel was characterized by SEM, XRD, IR as well as UV–vis measurements. Interestingly, the gel was selectively fluoride-responsive among test anions, expressing gel–sol transition and red-purple color changes for easily nake-eye detection. Multiple interactions such as hydrogen bonding, hydrophobic interaction, as well as π–π stacking were essential for the gel formation. It was deduced that addition of fluoride anions destroyed the balance among organogelator molecules, resulting in the gel–sol transition due to the hydrogen bonding competition.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.12.005.

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