

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

COMMUNICATION

Halogen-Bonding for Visual Chloride Ion Sensing: A Case Study Using Supramolecular Poly(aryl ether) Dendritic Organogel System

Received 00th January 20xx,
Accepted 00th January 20xx

Zhi-Xiong Liu,^a Yihua Sun,^b Yu Feng,^{*a} Hui Chen,^b Yan-Mei He,^a and Qing-Hua Fan^a

DOI: 10.1039/x0xx00000x

www.rsc.org/

A convenient and straightforward method for the visual recognition of chloride anion has been established through a chloride-responsive dendritic organogel. The specificity was largely attributed to the higher binding affinity of the dendritic gelator for chloride than other anions through halogen bonding interactions.

Recognition and sensing of biological anions such as chloride has been a topic of interest for years on account of their important role in clinical diagnosis, environmental monitoring and industrial applications.¹ During the past decade, significant progress in chloride anion recognition and detection has been achieved by means of spectroscopic instruments, such as NMR, UV/Vis and fluorescence spectroscopy.² The development of straightforward and convenient visual detection protocol for chloride detection, however, is still a major challenge. Only very limited examples of visual chloride detection via color changing and precipitate formation have been achieved to date.³ In recent years, the responsive gel systems have been regarded as intriguing visual sensor platforms for a variety of analytes via gel formation and collapsing.⁴ Despite advances in application of gels in visual detection of molecules, anions, metal ions, and chiral compounds,⁵ the visual detection of chloride has remained unsuccessful to date.⁶ Herein, we wish to report the first example of employing supramolecular gel systems for visual specific detection of chloride.

Halogen bonding (XB) is a specific non-covalent interaction occurring between a Lewis-acidic halogen atom and a neutral or negatively charged Lewis base, which has been exploited successfully in the crystal engineering, liquid crystals, nanomaterials catalysis, structural biology and medicinal chemistry.⁷ Importantly, halogen bonding has recently emerged as a useful method for selective anion recognition processes.⁸⁻¹⁰ For example, Taylor and

coworkers recently reported a series of bi- and tridentate receptors based on ortho-substituted iodoperfluoroarenes that were able to bind halogen anions through XB interactions.⁹ Beer et al. designed a bidentate bromimidazoliophane receptor and found its selectivity for bromide recognition.¹⁰

Following our continuing pursuit of developing efficient functional dendritic organogels,¹¹⁻¹² in this work, we present the construction of new dendritic organogels based on poly(aryl ether) dendrons **1-2** with multiple halogen bond donors (ortho-substituted iodoperfluoroarenes) at the tether termini (Scheme 1). Remarkably, these hierarchically self-assembled supramolecular gels can specifically recognize chloride through XB interactions accompanied with gel-sol phase transition. The dendritic molecules **1** and **2** were designed with the following rationales: (1) peripheral multiple iodoperfluoroarene units to enhance gelation ability due to the strong $\pi-\pi$ stacking interactions;^{11,13} (2) the strong XB interactions between terminal iodoperfluoroarenes and chloride might result in a large conformational change throughout the dendron,⁹ which is expected to induce a collapse of the gel network owing to disrupted intermolecular $\pi-\pi$ stacking between dendrons.

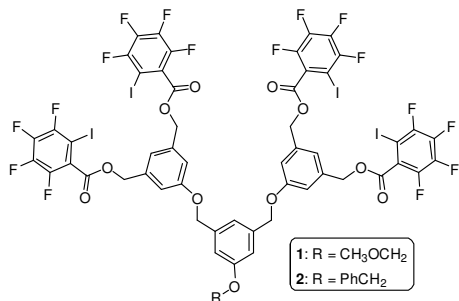
The dendritic gelators were synthesized as a white solid via divergent strategy modified from our previous method.¹⁴ The synthetic details and characterization of **1** and **2** are given in the Supporting Information (SI). Their purities and chemical structures were confirmed by ¹H NMR, ¹³C NMR, ¹⁹F NMR, and HRMS-ESI mass spectroscopy as well as elemental analysis.

The gelation properties of these dendrons were evaluated in various organic solvents and mixed solvents, and the critical gelator concentrations (CGCs) were collected in Table S1 of SI. It was found that the sonication exhibited an intriguing effect on the gelation efficiency.^{15,12c} Upon the heated solutions cooling to room temperature, suspension instead of stable gel was observed. But when ultrasound was applied to this suspension or its hot solution for minutes with a sonicator (0.4 w/cm², 40 KHz), a translucent gel was formed rapidly (Figure S2 in SI). Notably, the dendron **1** exhibited excellent gelation abilities in a wide variety of organic solvents including 4 alcoholic solvents and 8 mixed solvents upon ultrasonic treatment (Figures S1 in SI). For example, 3.3 mg of gelator **1**

^a Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P. R. China. E-mail: fengyu211@iccas.ac.cn

^b Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China

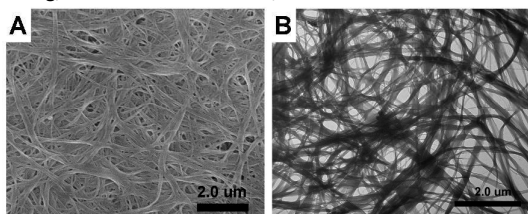
Electronic Supplementary Information (ESI) available: Synthetic and experimental details, additional characterization data, computational details, and Cartesian coordinates of DFT-optimized structure (PDF). See DOI: 10.1039/x0xx00000x

Scheme 1. Chemical structure of dendritic organogelators

can cause the gelation of 1 mL of methanol, suggesting that 1.3×10^4 methanol molecules are immobilized per molecule of dendron **1**. In contrast to dendron **1**, dendron **2** turned out to be a poor gelator, no gelation was observed in all tested solvents.

The thermal stability of the gels increased with increasing concentration, as established for the series of **1**/dichloroethane-*n*-hexane and **1**/toluene-*n*-hexane gels formed with the gelator concentrations varying from 7–24 mg/mL (Figure S3). Furthermore, the elastic property of dendritic gel **1** was also estimated using rheological measurements. As shown in Figure S4 in SI, the storage modulus G' is larger than the loss modulus G'' , and a pronounced plateau region of these moduli plotted against the frequency in range of 0.1–100 rad/s, which is a characteristic feature of gels. More interestingly, these dendritic gels from most tested organic solvents possessed thixotropic properties, which exhibited reversible sol-gel transformations upon exposure to external mechanical stress (Figures S5–S6 in SI).

The aggregation structures of the dendritic xerogels **1** were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 1 and Figures S7–8). As shown in Figure 1 and Figure S1, fiberlike or ribbonlike morphologies in different organic solvents were observed. For example, the xerogels of **1** from methanol exhibited an entangled network of thin solid fibers with diameters smaller than 150 nm and lengths of several micrometers (Figure 1A). The morphological properties were further confirmed by TEM (Figures 1B and S8). To gain further insight into the assembly process, the structure and dimensions of the xerogel networks of **1**/toluene-*n*-hexane (20 mg/mL) was studied by small-angle X-ray scattering (Figure S9 in SI). The diffraction patterns were observed at d -spacing values of 5.46, 3.85, 2.78, 2.52, 1.71, 1.32, and 1.23 nm, which are in the ratio of $1 : 1/\sqrt{2} : 1/2 : 1/\sqrt{5} : 1/\sqrt{10} : 1/4 : 1/\sqrt{20}$. This pattern is reasonably assigned to a columnar square structure whose diameter of the column is 5.43 nm. Taking a typical stacking distance (ca. 3.7 Å) between two closely packed dendrons in the column and a density of $d = 1.6 \text{ g/cm}^3$ into consideration,¹⁵ we can calculate the average

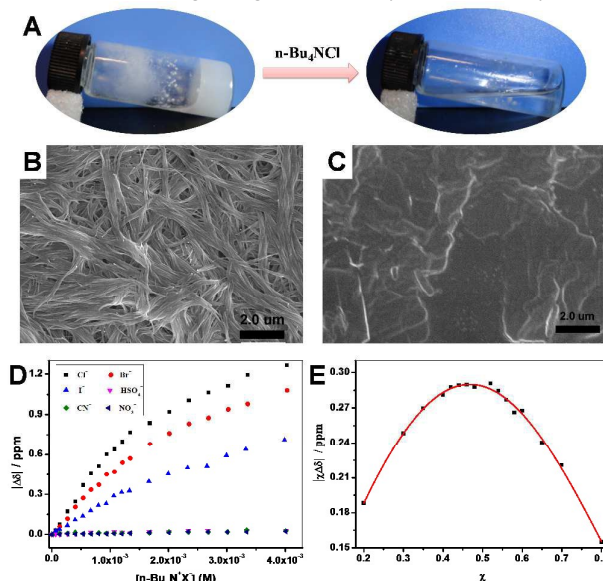
**Figure 1.** (A) SEM and (B) TEM images of **1** xerogel from methanol.

number of dendritic molecules in a single slice of the cylinders is approximately six.

In order to further investigate the gel behaviors and the assembly mechanism of these nanostructures, concentration-dependent (CD) and temperature-dependent (TD) ^1H NMR spectroscopy studies were measured. In the CD- ^1H NMR experiments performed in 0.00993–2.53 mM solutions of **1** in methanol- d_4 , the increase in the concentration resulted in the slight upfield shifts of the resonance signals for the aromatic protons (Figure S10). TD- ^1H NMR experiments of 4.0 mg/mL gel **1**, showed slight downfield shifts of the resonance signals for the aromatic protons with increasing temperature from 5 to 70 °C (Figure S11). In addition, the π - π interactions were further evidenced by solvent titration experiments and powder X-ray diffraction studies (Figures S12–S13 in SI). Based on all the above experimental evidences and our previous study,¹¹ multiple strong π - π stacking and solvophobic interactions might be the key factors guiding the self-assembly processes.

Since π - π stacking and solvophobic interactions are considered as key contributions to the gel formation, the molecular conformation and solubility change of the dendritic gelator will obviously affect these non-covalent interactions, which are expected to allow a control over formation and collapse of the gel. Therefore, the introduction of halogen anion in dendritic gel **1** was expected to induce a collapse of the gel network owing to the disrupted intermolecular π - π stacking between dendrons.

Aiming at a simple approach to visual discrimination of halogen anions, the anion recognition experiment was first conducted by adding 0.8 equivalent selected target anions (Cl^- , Br^- , I^- , HSO_4^- , NO_3^- , and CN^- as tetrabutylammonium salts, 50 μL in acetone) onto the stable turbid dendritic gels. Figure S14 clearly shows that only the

**Figure 2.** (A) Photographs of the dendritic gel **1** in acetone-*n*-hexane mixed solvent (1:8, v/v , 12.0 mg/mL) before and after the addition of chloride anion. SEM images of (B) the xerogel of **1** and (C) the aggregate from sol state after the addition of chloride anion. (D) ^{19}F NMR titration of dendron **1** (acetone- d_6 , 298 K; changes in chemical shift $|\Delta\delta|$ (in ppm) vs $[\text{n-Bu}_4\text{N}^+\text{X}^-]$ (in M)). Curves represent the fit of a 1:1 binding isotherm. (E) Job plot ($[\text{dendron } \mathbf{1} + \text{n-Bu}_4\text{N}^+\text{Cl}^-] = 2.0 \text{ mM}$, $|\chi\Delta\delta|$ vs mole fraction χ).

Cl^- successfully triggered the gel-sol phase transition and finally the gel was completely transformed into solution in approximate ten minutes. However, only a small amount of the organogel was broken upon the addition of Br^- even after overnight, other anions, such as I^- , HSO_4^- , NO_3^- , and CN^- caused no significant effect on the gels. Moreover, it should be noted that only more than 2.0 equivalent Br^- or 5.0 equivalent I^- could induce the organogel collapsed. The visual chloride anion selective recognition was further confirmed by an SEM study (Figures 2B-C). Compared to the entangled 3D fibrillar network of the xerogel in acetone/n-hexane, the SEM image of the dried according solution showed no sign of fibers. The difference in superstructure may be responsible for the chloride collapse of the gel network. The addition of chloride anions might disrupt the molecular packing of the dendron **1** and resulted in dissociation of the fibers and the 3D network of the gel, accompanied by visible gel-sol phase transition.

The ^{19}F NMR titration study of dendron **1** in acetone- d_6 in the presence of tetrabutylammonium counterion further confirmed the chloride anion selective recognition results and the difference in the SEM morphologies. According to the ^{19}F NMR titration experiments (Figure 2D), upon gradual addition of Cl^- (0 to 20 equiv) to the solution of dendron **1** (6.72×10^{-4} M) in acetone- d_6 at 298 K, the downfield shifts of the ^{19}F NMR spectra were observed. Moreover, in Job's plots (Figure 2E), the chemical shifts of ^{19}F NMR approached the maximum when the molar fraction of dendron **1** was 0.5, which demonstrated the formation of a 1:1 complex between dendron **1** and Cl^- . In addition, the high-resolution mass spectrometry (HRMS-ESI) provided additional support for the formation of a 1- Cl^- complex of 1:1 stoichiometry. When using mixture of dendron **1** and 5 equivalent $n\text{-Bu}_4\text{N}^+\text{Cl}^-$ in acetonitrile, the highest intensity peak in the mass spectrum was detected at m/z 1712.70671, corresponding to the complex $[\text{1-Cl}]^-$ (Figure S19 in SI). By the nonlinear least-squares analysis of the chemical shift vs the Cl^- concentration,¹⁶ the association constant K_a of dendron **1** and Cl^- was calculated to be $6.5 \times 10^2 \text{ M}^{-1}$ (Figure S16). Furthermore, the other halogen anions like Br^- and I^- showed lower association constant K_a with dendron **1** (Figures S17 and S18 in SI). In contrast, it shows negligible affinity for the other anions such as NO_3^- , HSO_4^- and CN^- . The binding constants of dendron **1** to the anions are

summarized in Table 1, and the affinities decrease in the order $\text{Cl}^- > \text{Br}^- > \text{I}^- \gg \text{NO}_3^-, \text{HSO}_4^-, \text{CN}^-$.

Table 1. Association constants (K_a) of dendron **1** with $n\text{-Bu}_4\text{N}^+\text{X}^-$

X^-	Cl^-	Br^-	I^-	HSO_4^-	NO_3^-	CN^-
$K_a [\text{M}^{-1}]^a$	6.5×10^2	3.9×10^2	1.4×10^2	<10	<10	<10

^aBinding constants K_a were determined by curve-fitting 1:1 binding isotherms to ^{19}F NMR titration data in acetone- d_6 at 298K. Each reported binding constant reflects an average of two or three independent determinations, with an estimated error less than $\pm 10\%$. See the SI.

To comprehend the chloride anion recognition event from a microscopic view, extensive DFT modelings (PBE0-D3/def2-SVP) were carried out for 1- Cl^- complex system. Our calculations revealed that the geometry of the 1- Cl^- complex was characterized by an average of $\text{I} \cdots \text{Cl}^-$ distances of 3.08 Å, and C-I- Cl^- angles of about 170° (Figure 3A). The computed electrostatic potential surface of **1** in its chloride-bound conformation illustrates the extended region of partial positive charge created by the four electron-deficient iodo groups (Figure 3B). Thus, the results of the calculation provide a partial explanation for chloride anion recognition in the gels.

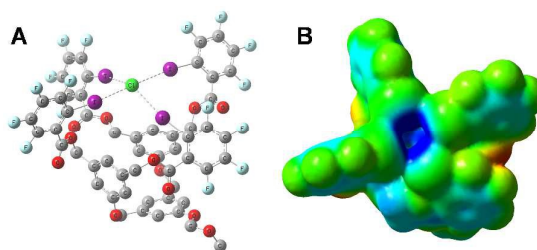


Figure 3. (A) Calculated structure of the 1- Cl^- complex and (B) electrostatic potential surface of **1** (chloride-bound conformation, blue indicates sites of partial positive charge and red sites of partial negative charge).

The dendritic gel **1** assembly and recognition event may involve a two-stage process: a) gel assembly through π - π stacking interactions, and b) collapse of the gel caused by Cl^- through XB interactions (Figure 4). For the gel hierarchical assembly process, upon cooling the clear solution of dendron **1**, the individual dendron is able to form the columnar slice that is arranged in a coplanar geometry, in which six molecules comprise a single stratum of the cylinder. And such self-assembled units can arrange

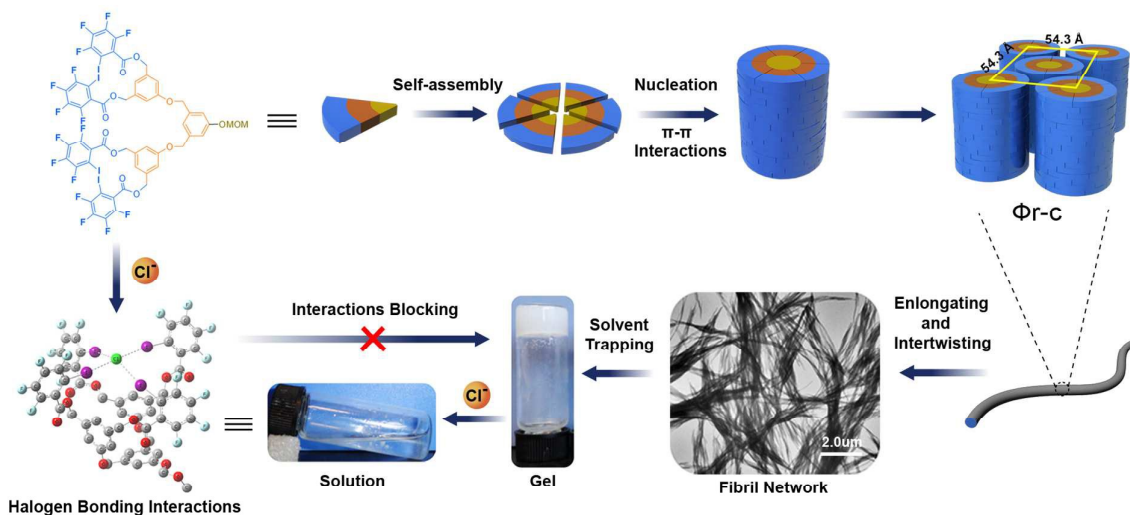


Figure 4. Representation of the dendritic gel **1** self-assembly and Cl^- induces the collapse of the gel.

one over the other in a columnar fashion, through π - π stacking between the dendron units. Eventually, a three-dimensional fibril network was formed with the ability to gelate solvent molecules. For the gel collapse process, upon the chloride anion added, a complex between dendron **1** and Cl^- through XB interactions was formed due to the stronger binding capability. It is likely that the nonplanar conformation of **1**- Cl^- complex prevents the occurrence of efficient π - π stacking between dendrons, thus leading to significantly less aggregation and the gel-sol conversion.

In summary, a convenient and straightforward method for the visual recognition of chloride anion has been established through an chloride-responsive dendritic organogel prepared from a novel poly(aryl ether) dendritic gelator **1** with multiple halogen bond donors at the periphery. The specific discrimination of chloride anion observed was largely attributed to the higher binding affinity of the dendron **1** for chloride than for the other anions through halogen-bonding interactions. To the best of our knowledge, this work represents the first example employing supramolecular gel systems for visual specific detection of chloride anion through halogen-bonding interactions, which provides new possibility for the development of novel visual anion sensors.

We thank the National Basic Research Program of China (973 program, No. 2013CB932800) and the National Natural Science Foundation of China (No 91027046, 21290194 and 21221002) for financial support.

Notes and references

- For selected reviews and examples, see: (a) F. Davis, S. D. Collyer, and S. P. J. Higson, *Top. Curr. Chem.* **2005**, 255, 97-124; (b) L. D. Lavis, and R. T. Raines, *ACS Chem. Biol.* **2008**, 3, 142-155; (c) P. A. Gale, *Chem. Commun.* **2008**, 4525-4540; (d) N. P. Illsley, and A. S. Verkman, *Biochemistry* **1987**, 26, 1215-1219; (e) A. Martin, and R. Narayanaswamy, *Sens. Actuators, B* **1997**, 39, 330-333; (f) I. H. A. Badr, M. Diaz, M. F. Hawthorne, and L. G. Bachas, *Anal. Chem.* **1999**, 71, 1371-1377; (g) B. Schazmann, N. Alhashimy, and D. Diamond, *J. Am. Chem. Soc.* **2006**, 128, 8607-8614; (h) U. I. Kim, J. M. Suk, V. R. Naidu, and K. S. Jeong, *Chem. Eur. J.* **2008**, 14, 11406-11414.
- For selected examples, see: (a) Y. Li, and A. H. Flood, *Angew. Chem. Int. Ed.* **2008**, 47, 2649-2652; (b) N. H. Evans, C. J. Serpell, and P. D. Beer, *Chem. Eur. J.* **2011**, 17, 7734-7738; (c) W. Zhang, E. Rozniecka, E. Malinowska, P. Parzuchowski, and M. E. Meyerhoff, *Anal. Chem.* **2002**, 74, 4548-4557; (d) A. Dorazco-Gonzalez, *Organometallics* **2014**, 33, 868-875; (e) S. Madhu, R. Kalaiyarasi, S. K. Basu, S. Jadhav, and M. Ravikanth, *J. Mater. Chem. C* **2014**, 2, 2534-2544.
- For selected examples, see: (a) R. B. P. Elmes, P. Turner, and K. A. Jolliffe, *Org. Lett.* **2013**, 15, 5638-5641; (b) C. G. Collins, E. M. Peck, P. J. Kramer, and B. D. Smith, *Chem. Sci.* **2013**, 4, 2557-2563.
- For selected reviews, see: (a) G. O. Lloyd, and J. W. Steed, *Nat. Chem.* **2009**, 1, 437-442; (b) X. Yang, G. Zhang, and D. Zhang, *J. Mater. Chem.* **2012**, 22, 38-50; (c) S. S. Babu, V. K. Praveen, and A. Ajayaghosh, *Chem. Rev.* **2014**, 114, 1973-2129.
- For selected reviews and examples, see: (a) T. Tu, W. Fang, and Z. Sun, *Adv. Mater.* **2013**, 25, 5304-5313; (b) K. K. Kartha, A. Sandeep, V. K. Praveen, and A. Ajayaghosh, *Chem. Rec.* **2015**, 15, 252-265; (c) P. Mukhopadhyay, Y. Iwashita, M. Shirakawa, S. Kawano, N. Fujita, and S. Shinkai, *Angew. Chem. Int. Ed.* **2006**, 45, 1592-1595; (d) X. Chen, Z. Huang, S.-Y. Chen, K. Li, X.-Q. Yu, and L. Pu, *J. Am. Chem. Soc.* **2010**, 132, 7297-7299; (e) T. Tu, W. Fang, X. Bao, X. Li, and K. H. Dötz, *Angew. Chem. Int. Ed.* **2011**, 50, 6601-6605; (f) P. Rajamalli, and E. Prasad, *Org. Lett.* **2011**, 13, 3714-3717; (g) K. K. Kartha, S. S. Babu, S. Srinivasan, and A. Ajayaghosh, *J. Am. Chem. Soc.* **2012**, 134, 4834-4841; (h) G. Z. Zhao, L. J. Chen, W. Wang, J. Zhang, G. Yang, D. X. Wang, Y. Yu, and H. B. Yang, *Chem. Eur. J.* **2013**, 19, 10094-10100; (i) J. Liu, Y. Feng, Z. X. Liu, Y. M. He, and Q. H. Fan, *Chem. Asian J.* **2013**, 8, 572-581; (j) W. Miao, L. Zhang, X. Wang, H. Cao, Q. Jin, and M. Liu, *Chem. Eur. J.* **2013**, 19, 3029-3036; (k) Y. He, M. Xu, R. Gao, X. Li, F. Li, X. Wu, D. Xu, H. Zeng, and L. Yuan, *Angew. Chem. Int. Ed.* **2014**, 53, 11834-11839; (l) W. Fang, X. Liu, Z. Lu, and T. Tu, *Chem. Commun.* **2014**, 50, 3313-3316.
- There is only one example of chloride-responsive gel, see: H. Maeda, Y. Haketa, and T. Nakanishi, *J. Am. Chem. Soc.* **2007**, 129, 13661-13674. However, this gel system could not specifically recognize chloride ion.
- (a) P. Metrangolo, and G. Resnati, *Halogen Bonding I: Impact on Materials Chemistry and Life Sciences (Topics in Current Chemistry)*; Springer: Heidelberg, **2015**; (b) P. Metrangolo, and G. Resnati, *Halogen Bonding: Fundamentals and Applications (Structure and Bonding)*; Springer: Heidelberg, **2010**.
- G. Cavallo, P. Metrangolo, T. Pilati, G. Resnati, M. Sansotera, and G. Terraneo, *Chem. Soc. Rev.* **2010**, 39, 3772-3783.
- (a) M. G. Sarwar, B. Dragisic, S. Sagoo, and M. S. Taylor, *Angew. Chem. Int. Ed.* **2010**, 49, 1674-1677; (b) M. G. Sarwar, B. Dragisic, L. J. Salsberg, C. Gouliaras, and M. S. Taylor, *J. Am. Chem. Soc.* **2010**, 132, 1646-1653.
- (a) N. L. Kilah, M. D. Wise, C. J. Serpell, L. Amber, A. L. Thompson, G. Nicholas N. G. White, K. E. Christensen, and P. D. Beer, *J. Am. Chem. Soc.* **2010**, 132, 11893-11895; (b) M. J. Langton, S. W. Robinson, I. Marques, V. Félix, and P. D. Beer, *Nat. Chem.* **2014**, 6, 1039-1043.
- (a) Y. Feng, Z. T. Liu, J. Liu, Y. M. He, Q. Y. Zheng, and Q. H. Fan, *J. Am. Chem. Soc.* **2009**, 131, 7950-7951; (b) Y. Feng, Z. X. Liu, H. Chen, Z. C. Yan, Y. M. He, C. Y. Liu, and Q. H. Fan, *Chem. Eur. J.* **2014**, 20, 7069-7082; (c) Y. Feng, Z. X. Liu, L. Y. Wang, H. Chen, Y. M. He, and Q. H. Fan, *Chin. Sci. Bull.* **2012**, 8, 4289-4295.
- (a) Y. Feng, Y. M. He, and Q. H. Fan, *Chem. Asian J.* **2014**, 9, 1724-1750; (b) Q. Chen, Y. Feng, D. Q. Zhang, G. X. Zhang, and Q. H. Fan, S. N. Sun, and D. B. Zhu, *Adv. Funct. Mater.* **2010**, 20, 36-42; (c) Z. X. Liu, Y. Feng, Z. C. Yan, Y. M. He, C. Y. Liu, and Q. H. Fan, *Chem. Mater.* **2012**, 24, 3751-3757; (d) Z. X. Liu, Y. Feng, Z. Y. Zhao, Z. C. Yan, Y. M. He, X. J. Luo, C. Y. Liu, and Q. H. Fan, *Chem. Eur. J.* **2014**, 20, 533-541; (e) H. Chen, Y. Feng, G. J. Deng, Z. X. Liu, Y. M. He, and Q. H. Fan, *Chem. Eur. J.* **2015**, 21, 11018-11028.
- Halogen atom can promote the gelation ability due to the strong π - π interactions, see: (a) A. F. M. Kilbinger, and R. H. Grubbs, *Angew. Chem. Int. Ed.* **2002**, 41, 1563-1566; (b) S. S. Babu, V. K. Praveen, S. Prasanthkumar, and A. Ajayaghosh, *Chem. Eur. J.* **2008**, 14, 9577-9584; (c) D. M. Ryan, S. B. Anderson, F. T. Senguen, R. E. Youngman, and B. L. Nilsson, *Soft Matter* **2010**, 6, 475-479; (d) S. -M. Hsu, Y. -C. Lin, J. -W. Chang, Y. -H. Liu, and H. -C. Lin, *Angew. Chem. Int. Ed.* **2014**, 53, 1921-1927.
- Y. Feng, Y. M. He, L. W. Zhao, Y. Y. Huang, and Q. H. Fan, *Org. Lett.* **2007**, 9, 2261-2264.
- For selected review, see: G. Cravotto, P. Cintas, *Chem. Soc. Rev.* **2009**, 38, 2684-2697, and references therein.
- Powder of **1** was immersed in several calibrating organic solvents. We decided that the approximate density of **1** was the point at which the powder neither floated nor sank.
- S. Freye, R. Michel, D. Stalke, M. Pawliczek, H. Frauendorf, and G. H. Clever, *J. Am. Chem. Soc.* **2013**, 135, 8476-8479.