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Coordination-directed self-assembly of a simple benzothiadiazole-fused tetrathiafulvalene to low-bandgap metallogels

Coordination-driven gelation of a benzothiadiazole-fused tetrathiafulvalene (TTF) is demonstrated. This is the first work reporting highly stable metallogels based on a donor-acceptor conjugate with such a simple structure for the construction of new low-bandgap materials with various functional properties and novel nanostructures.

Molecular gels have applicability in a wide variety of interesting mechanical, electrical, and biological systems. They can potentially form highly ordered self-assembled structures in a bottom up strategy, facilitating fast and easy fabrication of molecular electronic devices. Potential application in organic electronics has driven research into new molecular materials containing electron donors, acceptors, or combined donor-acceptor moieties. The interaction between donor and acceptor allows the specification and control of energy levels, critical aspects that dramatically influence performance. There has been a relative dearth, however, of donor-acceptor compounds incorporated into metallogels that assemble through π–π stacking or metal-ligand interactions.

Our interest in both electron donor-acceptor materials and supramolecular systems motivated us to explore the possibility of supramolecular organization created from a benzothiadiazole (BTD)-fused tetrathiafulvalene (TTF), as shown in Figure 1. To our surprise, we found that 1 acts as a low molecular weight gelator (LMWG) in the presence of certain transition metal halide salts. This self-assembly process is mainly driven by coordination ability of the BTD moiety to metal ions. Although TTF-based LMWGs as well as supramolecular self-assembled structures of TTF ligands with some transition metal ions have been reported in the literature, no metallogels of them are known. On the other hand, all of the reported TTF gelators have specific structural characteristics that are frequently employed to drive gelation; for example, the inclusion of amide or other hydrogen-bonding moieties as well as long fatty chains to increase van der Waals interactions. The present work represents the first example of low-bandgap metallogels based on a TTF gelator with a very simple structure. We describe various microscopic and spectroscopic techniques used to characterize these metallogels, which are both more pure and more facile to synthesize than metallopolymers formed through covalent bonds.

The gelator 1 was obtained by a phosphite-mediated cross-coupling reaction of 4,5-bis(propylsulfanyl)-1,3-dithiol-2-thione and 1,3-dithiolato[4,5-f]-2,1,3-benzothiadiazole-6-one in 61% yield. Complexes with MX₂ (M(II) = Cu, Cd, Co; X = Cl and Br) to give solvents forming multi-component supramolecular metallopolymers. As illustrated in Figure 1, gelation occurred in less than five minutes upon mixing an ethanol solution of copper chloride (1 equiv.) to a solution of 1 in CHCl₃; the gel is very stable to inversion and is self-supporting.
sustaining. Upon gelation, a dramatic colour change from clear red to dark blue was observed. The effect of solvent on gelation was tested. The critical gel concentration of I in different solvents when combined with CuCl₂ in ethanol is as follows: chloroform, 0.02 M; dichloromethane, 0.04 M; chlorobenzene, 0.03 M; and o-dichlorobenzene, 0.04 M. The gelation was not effective in non-halogenated solvents.

To further explore the role of metal salts, different metal cations (Table S1) and counterions (Table S2) were chosen for the gelation studies. The result was that MX₄ with M(II) = Cu, Cd, Co (X = Cl, Br) can form dark blue gels, but not in the cases of Zn(II), Mn(II) and Fe(II). The anion clearly plays a role on the gelation, as fluoride and perchlorate copper salts do not form gels. The halide ions show high propensity to form gels, very probably ascribed to their ability to form metal clusters via halide bridge, and here we focus on these salts.

It has to be noted that the metallogel exhibit high stability as evidenced by the fact that the sol-gel transformation cannot be tuned by external chemical stimuli. For example, differential scanning calorimetry (DSC) measurements of the CuCl₂ xerogel (Figure S1) indicate three irreversible endothermic transitions, very probably due to the loss of solvents and the solid-state-like phase transition. It appears that the gel is thermo-reversible as it remains intact when heated up to 70 °C while it is gradually fragmented with increasing of the temperature, finally leading to a dark blue precipitate in solution. It is neither responsive to a metal trapping reagent - such as ethylene diamine tetraacetic acid (EDTA) - nor to oxidation. Additionally, the reversibility of the gelation process did not occur through mechanical stimuli either. When shaking breaks a gel, the appearance of the system becomes one that is composed of fibres dispersed in solvent. This effect is irreversible. All these results demonstrate that metallogel possess a rigid rather than flexible suprastructure.

The UV-visible absorption spectra of I in CHCl₃ solution and as a film as well as of a CuCl₂ gel are shown in Figure 2. According to our previous results of analogues, the intense absorption band peaking at 488 nm in solution corresponds to an intramolecular charge-transfer transition from the HOMO localized on the TTF core to the LUMO localized on the BTD moiety. A slight red-shift of this optical absorbance in the film is attributed to strong intermolecular interactions. The copper chloride gel shows an even larger red-shift extending into the near-IR region giving rise to a low bandgap (< 1.2 eV), indicative of the coordination of Cu(II) by the nitrogen atoms on the BTD portion of I. These results are consistent with the ¹H NMR data of the CdBr₂ gel (Figure S2). Upon gelation, the signals due to the benzene ring and propyl groups of I become broad and are shifted upfield. Additionally, FTIR spectra of I and its MCl₂ xerogels (Figure S3) indicate slight shifts of the vibration frequencies for the BTD aromatic ring in a range of 1200 cm⁻¹ and 1500 cm⁻¹ upon gelation. All these observations imply that the coordination bonds are primary driving forces to form the fibers while the π-π stacking between BTD-fused TTF units and non-covalent van der Waals interactions play an important role in the entanglement of fibers and the capture of solvent.

Powder X-ray diffraction patterns of a xerogel from CuCl₂ and I as well as of monomer I on its own are shown in Figure S4. The gel shows some amorphous as well as crystalline character, as evidenced by the presence of both broad and sharp peaks. The gel spectrum exhibits some similarity to I but also new features that do not correspond to either pure CuCl₂ or I, indicating that the self-organization in the gel is not simply precipitated monomer, but a new hybrid of both metal ions and I.

Magnetic susceptibility (SQUID) measurements (Figure S5) also determined that there was 8.3% of copper(II) in the xerogel, which is close to the expected value of 11% for a 1:1 ratio of I to copper(II) in the bulk gel. Moreover, the magnetic susceptibility data show that there is a pronounced antiferromagnetic coupling between neighboring Cu(II) ions. These results indicate that the Cu(II) is involved in the gelation and not just a precipitate dispersed in the gel matrix.

Scanning electron microscopy (SEM) was used to visualize the morphology of the xerogels formed under different conditions. As depicted in Figure S6, the gels have a wavy suprastructure in less polar solvents, such as chloroform and chlorobenzene, and more flat structures in more polar solvents, such as o-dichlorobenzene and dichloromethane. The 3-D network has a waven appearance with belt like fibers of about 50 nm in diameter, which shows some alignment over several tens of microns. Similar features, albeit with some subtle differences, were observed in the SEM images of other metallogels (Figure S7).

![Fig. 2 UV-vis spectra of I in solution, film, and as a CuCl₂ gel.](image-url)
pressed together to blend the green gelatinous particulates (visible under optical microscope) into an amorphous green film. The glass slides were then slid laterally apart. The resulting films were allowed to dry, whereupon they darkened. When viewed under a polarizing optical microscope, a homogeneous film of uniform alignment responded to the polarized light, indicating the parallel alignment of the chromophoric units. A SEM image of the resulting film (Figure S11) shows that there are features on the scale of 500 nm to 1 μm.

A doped thin film of the CuCl xerogel was prepared after exposure to iodine vapors for two minutes and further investigated as a conductor. Electron paramagnetic resonance (EPR) spectroscopy is useful for exploring the electronic characteristics of this kind of material. As illustrated in Figure S12, the undoped xerogel exhibits a clear EPR signal with a peak-to-peak linewidth (∆Hpp) of 30 G. This EPR signal was observed when doped samples were heated up to 200 °C and subsequently cooled down to room temperature. Interestingly, a peak-to-peak linewidth of 6 G is characteristic of oxidized TTF-based organic conductors. Therefore, four-probe DC resistance measurements on doped CuCl xerogels were carried out to study the electrical properties of the two phases and, further, to control the change of the electrical properties during the phase transition. In a typical experiment, a freshly doped xerogel sample was introduced into an oven that was previously set at 200 °C while a four-probe DC measurement of the sample resistance was conducted at the same time. Clearly, we observed typical semiconductor behaviour in the doped xerogel sample, as the resistance decreased with increasing temperature (Figure 3). However, around 150 °C, a change in the slope of the resistance versus temperature curve was observed, hence underpinning the phase transition studied with EPR spectroscopy.

The electrical properties of the doped film of the CuCl xerogel of 1 were also studied by current sensing atomic force microscopy (CS-AFM). Typical images show regions of high conductivity that have an acicular shape (Figure 4). These features do not necessarily coincide with the points of greatest height in the film of the xerogel, a feature that rules out any topographic anomaly. In general, scaly features can be appreciated in the topography and the conducting regions are approximately 300 nm wide and up to a micron long, although it is clear that the bulk material is a conductor, otherwise no imaging would be possible. (The contact is made through the graphite substrate.) The I/V sweeps at different locations show the clear presence of a gap, characteristic of a semiconducting material.
In summary, we have investigated gelation behaviour of a simple BTD-fused TTF primarily through coordination bonds of MX₂ (M(II) = Cu, Cd, Co; X = Cl⁻ and Br⁻) with the BTD moiety. Among the tested transition metal ions, Cu(II) is most likely to undergo self-sustaining gelation. The morphologies of the metallo-gels depend upon the solvent used to dissolve I. Furthermore, EPR and four-probe DC resistance measurements confirm that these doped CuCl xerogels can undergo a high-temperature phase transition to a new phase with similar electronic properties to the as-prepared conducting xerogels. This is the first work reporting TTF-based metallo-gels and opens up an avenue for the construction of new low-bandgap materials with various functional properties and novel nanostructures. It is envisaged that such intensely coloured metallo-gels represent a promising class of materials for photovoltaic applications.

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Notes and references


