A supramolecular system of tetrathiafulvalene, assembled by hydrogen bonding, ionic coordination bonding and topological cooperation†

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Solid state and solution chemistry of a supramolecular system, a sodium complex with ligands of tetrathiafulvalene (TTF) dicarboxylate and benzotriazole molecules, have been studied. The well characterized host–guest response in H_2O–CH_3CN (1 : 1 v/v) was monitored by electronic spectra and cyclic voltammetry. The host–guest reaction occurred immediately under the experimental conditions, which took only about 15 min to form high quality and large scale crystals. By the coordination of sodium cations and the water bridges, an unusual one dimensional structure formed. The compound is a coordination bonding, hydrogen-bonding assembled and, especially, topological cooperated supramolecule. The reaction selectivity of the TTF-dicarboxylate with small organic molecules has also been discussed.

The tetrathiafulvalene (TTF) unit can exist in three stable redox-states ($TTF/TTF^{\bullet+}/TTF^{2+}$) and therefore TTF derivatives are widely used in supramolecular chemistry as functional bricks and redox-active centers. Modern-day progress in construction of new TTF systems with applications in different areas, such as electroactive sensors, molecular shuttles and molecular switches, has revealed great potential for this molecular system.[1] The host–guest chemistry of TTF-crown ethers first received attention in the context of ion recognition.[2] New pyrrolo-TTFs are also being explored and used for applications in cation and anion sensors.[3] These types of TTF derivatives are based on the macrocyclic structures, and are mostly used for the recognition of inorganic guests. Lately, a TTF derivative with calixarene moiety has been synthesized for supramolecular study.[4] However, up to now few studies have been concerned with the ion recognition using acyclic TTF-based systems.[5] Supramolecular interactions through multiple hydrogen bonding are of major importance for natural systems such as base pairing in nucleic acids. Some TTF derivatives with amide, imidazole and carboxylate groups have been reported for hydrogen bonding assembly of materials.[6] However, attempts on TTF host–guest systems for small organic molecules incorporated with multiple hydrogen bondings are relatively scarce.[7] Recently, cyclic voltammetric responses of TTF compounds with aminopyridine derivative and acetamide, through multi-hydrogen-bonds, have been reported by Cooke[7a] and Goldenberg,[7b] respectively. A theoretical model was used for the investigation of the role and efficiency of the H-bonding. However, the studies on these kinds of host–guest systems or on molecular recognition of small organic units are just beginning.

Herein we report a new supramolecular system, a sodium(I) salt of dimethylthio-TTF dicarboxylate (**1**) (**1** = $C_{10}H_6O_4S_6Na_2$) reacting with benzotriazole molecules (bzta). It is a new host–guest system constructed by multiple hydrogen-bonding. Ionic coordination of sodium(I) ion also takes an important part in the formation of the TTF complex. The host–guest responses in solution were monitored by electronic spectra and electrochemical measurements. The selectivity of the TTF derivative in reaction with small molecules is also discussed.

Experimental

The TTF-dicarboxylate salt $C_{10}H_6O_4S_6Na_2\cdot 3H_2O$ ($\mathbf{1}\cdot 3H_2O$) was prepared and characterized as previously reported.[6] Solvents were dried and distilled by a standard method before use. The other analytical pure chemicals were used as purchased without further purification. Elemental analysis of C, H and N were performed using a MOD 1106 elemental analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Magna 550 FT-IR spectrometer. UV–Vis spectra were recorded using Shimadzu UV-240 and UV-3150 spectrometer. Cyclic voltammetry (CV) was performed on a CHI660 electrochemistry workstation in a three-electrode system, a single-compartment cell equipped with a platinum working electrode (*ca.* 0.25 cm^2), a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference. HPLC grade acetonitrile and ultra purified water were used as solvents, and tetrabutylammonium perchlorate was used as electrolyte.

Synthesis of the compound and the solution measurements

Synthesis of $\mathbf{1}\cdot 2bzta\cdot 2H_2O$. To a solution of $\mathbf{1}\cdot 3H_2O$ (48.2 mg, 0.1 mmol) in H_2O (2 mL) was added benzotriazole ($C_6H_5N_3$, bzta, 23.9 mg, 0.2 mmol). The yellow color of the solution turned to orange immediately and red crystals of large size were obtained after about 15 min. (49.2 mg, Yield: 70%),

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Anal. calc. for $C_{22}H_{20}N_6Na_2O_6S_6$: C, 37.60; H, 2.87; N, 11.96, Found: C, 37.31; H, 2.74; N, 11.86%.

All the measurements in solution (UV–Vis spectra and cyclic voltammetry) were conducted in the mixed solvent of H_2O–CH_3CN (1 : 1 v/v). The purpose of the added acetonitrile is to increase the solubility of the product and the electrolyte.

X-ray crystallography

A red crystal of **1** · 2bzta · $2H_2O$ with dimension of 0.60 × 0.40 × 0.17 mm was mounted on a Rigaku Mercury CCD area detector with graphite monochromated Mo-Kα (λ = 0.710 73 Å) radiation. The data were collected at 193 ± 1 K and processed using CrystalClear (Rigaku). A total 21 243 reflections were collected, of which 5165 were independent. The structure was solved by direct methods using SHELXS-97[11] and refined using SHELXL-97.[12]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model except the H(3)–H(6) atoms which bond to the nitrogen and oxygen atoms of water were located from the map. The final refinement was based on all the independent reflections and 406 variable parameters. Reflections, 4657 ($I > 2\sigma I$) were used only for calculating R(gt)-factor. A summary of the crystallographic data and experimental details are listed following. Crystal structure determination of **1** · 2bzta · $2H_2O$, $C_{22}H_{20}N_6Na_2O_6S_6$: M_w = 702.78, monoclinic, space group $P\ 2_1/n$, a = 10.3953(19), b = 6.5823(12), c = 43.283(8) Å, β = 93.228(5)°, V = 2956.9(9) Å^3. Z = 4, $D_{calc.}$ = 1.579 g cm^{-3}, $F(000)$ = 1440. R/R (gt) [$I > 2\sigma(I)$] = 0.0451/0.0531, wR/R (gt) = 0.0891/0.0921, GOF 1.182 (CCDC reference number 279396).†

Results and discussion

The TTF-dicarboxylate salt $C_{10}H_6O_4S_6Na_2 \cdot 3H_2O$ (**1** · $3H_2O$) was prepared and characterized as previously reported.[8] The redox active salt forms a mono-protonated anion at pH range of 2 ∼ 5 and a redox coupled association–dissociation of the proton was observed. Recently, during our study on the supramolecular properties of the TTF salt, we found that wondrously the salt **1** reacted with benzotriazole (bzta) very quickly and crystals of the complex **1** · 2bzta · $2H_2O$ grew up immediately under the experiment conditions. It took only about 15 min to form high quality and large scale crystals, about 0.60 × 0.40 × 0.20 mm, suitable for X-ray determination. Generally, it takes one or two days longer than this for good quality crystals of coordination compounds to form. The higher speed of crystallization indicates that: (1) the intermolecular interactions between **1** and bzta are very effective; (2) the crystals of the compound show certain ionic properties.

Is this only a phenomenon of co-crystallization with hydrogen bonds, and do the interactions only exist in the solid state? To answer these questions, the reaction of the salt **1** with bzta in H_2O–CH_3CN (1 : 1 v/v) was monitored by electronic spectra, ranging from 320 nm to 700 nm (Fig. 1). The spectrum of **1** shows a maximum absorption peak at 380 nm (line a), which gradually disappears with the increase of bzta concentration. At the same time, a new peak appears at 470 nm, and finally an unconverted spectrum of the product is achieved (line f). Since the small molecule bzta does not show any absorption in this region, the appearance of an isosbestic point at 427 nm reveals that there is a two-species equilibrium associated with the TTF moiety in this system. They are the starting compound **1** and the product, the molecular addition complex (Scheme 1). The curve a (salt **1** only) deviates somewhat from the isobestic point, which is due to the partial hydrolysis of the anion. It has been discussed in our previous paper that there is a small quantity of mono-protonated anion of TTF-dicarboxylate in solution.[8] In order to understand the exact stoichiometry of the complex in solution (H_2O–CH_3CN), the concentration change method was also carried out in a higher concentration of the same magnitude order as that in preparation of the compound (10^{-2} M), because at lower concentration of **1** the turning point of the absorbance–concentration (bzta) curve is not so obvious. The resulting curves in this case gave an obvious turning at about 1 : 1.7 mole ratio of **1** *vs.* bzta at different wavelength.† The result is evidence for suggesting a 1 : 2 supramolecular complex in solution (with partial dissociation). Therefore, the host–guest compound not only exists in the solid state, but is also stable to some extent in solution, though the exact structure in the solution state might have some changes compared with that in the solid state.

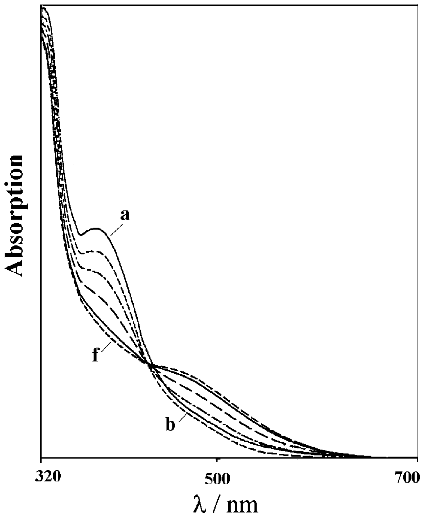
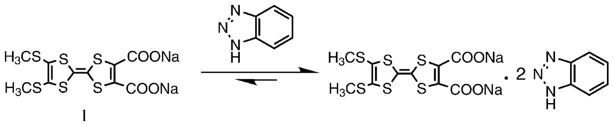


Fig. 1 Electronic spectra of the salt **1** (1.0×10^{-3} M) in H_2O–CH_3CN (1 : 1 v/v) with increasing concentration of bzta: (a) 0; (b) 1.0×10^{-3} M; (c) 2.0×10^{-3} M; (d) 4.0×10^{-3} M; (e) 8.0×10^{-3} M; (f) 1.0×10^{-2} M.



Scheme 1

Now the problem is what are the forces between the TTF-dicarboxylate salt and the neutral benzotriazole. Fortunately, the X-ray crystal structure determination of the compound, **1** · 2bzta · $2H_2O$, was successful. The ORTEP presentation with

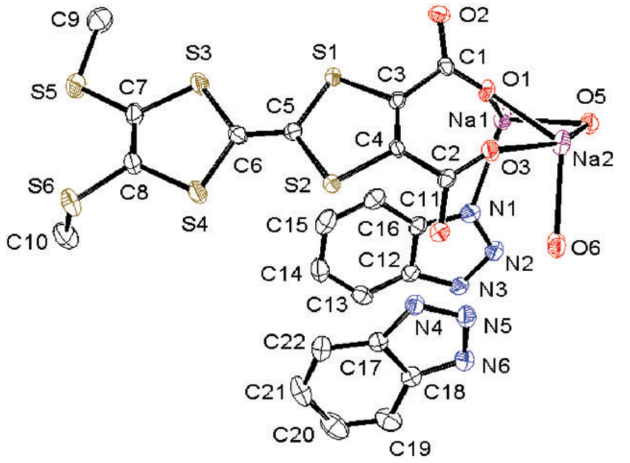


Fig. 2 ORTEP structure of **1** · 2bzta · $2H_2O$, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 40% probability level and, the H atoms have been omitted for the sake of clarity. Bond distances: Na(1)–O(1) 2.414(2), Na(1)–N(1) 2.527(3), Na(1)–O(5) 2.345(2), Na(2)–O(1) 2.383(2), Na(2)–O(3) 2.400(2), Na(2)–O(5) 2.446(2) and Na(2)–O(6) 2.434(2).

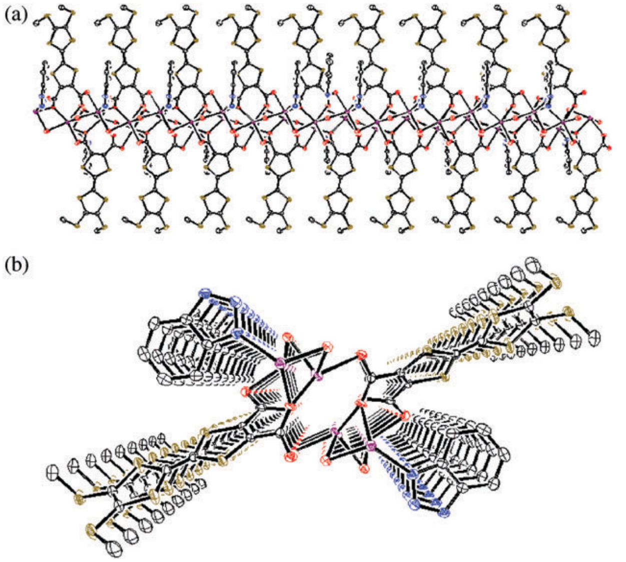


Fig. 3 The side view (a) and top view (b) of the one-dimensional structure of **1** · 2bzta · $2H_2O$.

atom labeling is shown in Fig. 2. The compound is composed of tetrathiafulvalene dicarboxylate anion, sodium cations and neutral benzotriazole molecules at 1 : 2 : 2 molar ratios. Water molecules, O(5) and O(6), also participate in the structure through coordination and multiple hydrogen bonding. The TTF-dicarboxylate anions coordinate to sodium cations using both the carboxylate groups. Atom O(1) bridges Na(1) and Na(2) with distances 2.414(2) and 2.383(2) Å, respectively, and O(3) only bonds Na(2) with distance 2.400(2) Å. One of the benzotriazole molecules (bzta-1) coordinates to sodium cation by N(1)–Na(1) coordination bond, 2.527(3) Å. These distances are compatible with those reported in the literature.[9] As with most compounds having coordinated sodium cations, the bonding is to some extent ionic. Instead of coordinating directly to the metal centers, the second benzotriazole molecule (bzta-2) is sandwiched between the two bzta-1 planes and is only stabilized by hydrogen bonding.

The sodium atoms Na(1) and Na(2) are not only coordinated by carboxylates of the TTF salt and by bzta molecules, but also bridged by two water molecules, O(5) and O(6). Through the coordination of carboxylate groups and the water bridges, the components, anions, cations and molecules, further assemble to form a one-dimensional structure. Fig. 3 presents the side view (a) and the top view (b), respectively. The one dimensional $(–CO_2)–Na(I)–H_2O$ coordination core is surrounded by TTF moieties and bzta molecules, which gives a column structure (Fig. 3(b)). The nearest S···S distance between two TTF neighbors (4.241 Å) is larger than the sum of the van der Waals radii of two S atoms (3.60–3.70 Å) indicating no significant S···S contact within the crystal. However, the intramolecular hydrogen bonds play an important role in the supramolecular assembling. Among the carboxyl group (cb), benzotriazol (bzta) and the water molecules there are three types of hydrogen-bonds, one is a $N_{bz}–H\cdots O_{cb}$ interaction and the other two are water bridged hydrogen bonds, $N_{bz}\cdots H–O–H\cdots N_{bz}$ and $O_{cb}\cdots H–O–H\cdots N_{bz}$. Details of the hydrogen bonds are listed in Table 1. The host–guest compound is therefore constructed by ionic coordination bonding and hydrogen bonding.

The redox properties of the salt **1** have been reported previously.[8] The salt shows two quasi-reversible redox waves in $H_2O–CH_3CN$ (1 : 1 v/v) corresponding to the two-step one-electron oxidations, $TTF^{\bullet+}/TTF$ and $TTF^{2+}/TTF^{\bullet+}$, respectively. Fig. 4 describes the CV curves of **1** with the increased concentration of bzta. The values of the first and the second $E_{1/2}$ potentials of **1** are at 0.30 and 0.56 V *versus* SCE. The first oxidation wave is broadened due to the overlap of a shoulder peak at about 0.40 V which arises from the partial hydrolysis of the salt, a mono-protonated anion of **1**.[8] Since the solutions used for CV measurements are the same as those for electronic spectra measurements (Fig. 1) except that electrolyte Bu_4NClO_4 is added to the CV solution, it is reasonable that the CV curves change successively in redox currents with constant current points, which is in accordance with the change in UV–Vis spectra (Fig. 1). Although the shifts in

Table 1 Selected bond lengths (Å), bond angles (°) of the hydrogen bonds

D–H···A	Distance D–H	Distance H···A	Distance D···A	Angle D–H···A
N(3)–H···O(2^a)	0.86(3)	1.88(3)	2.737(3)	169(3)
N(4)–H···O(4)	0.88(4)	1.93(4)	2.742(3)	153(3)
O(5)–H···N(6^b)	0.89(4)	2.02(4)	2.908(3)	175(3)
O(5)–H···O(3^c)	0.83(4)	1.99(4)	2.762(3)	154(4)
O(6)–H···N(5)	0.88(4)	2.04(4)	2.914(3)	169(4)
O(6)–H···N(2^d)	0.80(4)	2.08(4)	2.875(3)	174(4)

[a] $x + 1, y, z$; [b] $x - 1, y, z$; [c] $-x + 1/2, y - 1/2, -z + 1/2$; [d] $-x + 3/2, y + 1/2, -z + 1/2$.

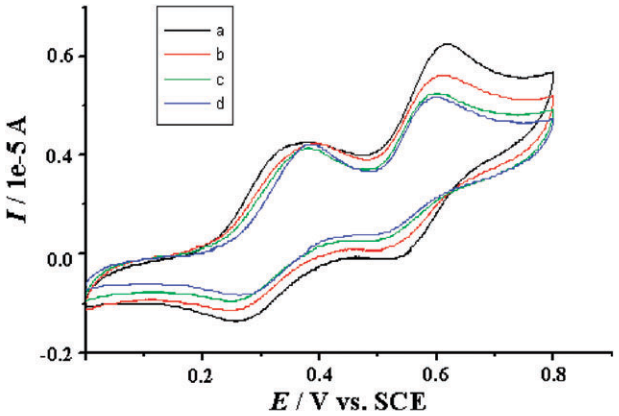
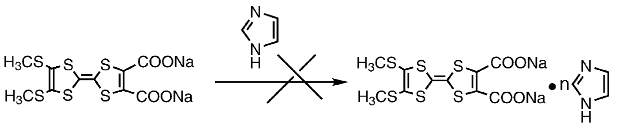


Fig. 4 Cyclic voltammograms of the salt **1** (1.0 × 10^{-3} M) in H_2O–CH_3CN (1 : 1 v/v) with increasing concentration of bzta: (a) 0; (b) 2.0 × 10^{-3} M; (c) 4.0 × 10^{-3} M; (d) 8.0 × 10^{-3} M.



Scheme 2

$E_{1/2}$ of CV are not too large, the results also reveals that there is an equilibrium of compound **1** with the bzta complex of **1**.

The most interesting thing we found is the selectivity of the addition reaction. When the organic base imidazole (im) was used in place of benzotriazol (bzta) in these experiments, no response was found as that observed in the **1**-bzta system, although im is an analog of bzta and has the same –NH– and =N– sites (Scheme 2). Challenges on preparing crystals or even powder of **1**-im complex did not succeed and the influences of the im on the spectra and CV results of **1** were not observed. Fig. 5(a) and (b) show the color change of **1** in H_2O–CH_3CN (1 : 1 v/v) before and after adding bzta or im. The TTF moiety is a chromophore and its color is able to be changed according to the electronic state of the quasi conjugated system.[1,10] On the other hand, both the guest molecules are colorless, and therefore only bzta interacts with **1** and changes its electronic state. Since im is also able to hydrogen bond with **1** and has a coordination site, it is difficult to explain the different phenomena. On the other hand, no $\pi\cdots\pi$ interaction between **1** and the benzene plane of bzta has been found even in the solid state of **1** · 2bzta · $2H_2O$. Therefore, topological cooperation might be one of the most important reasons for the formation of the stable addition complex. It should be remembered that the addition compound **1** · 2bzta · $2H_2O$ grew very quickly in about 15 min to form large crystals. This is a primary example of selectivity for molecular recognition.

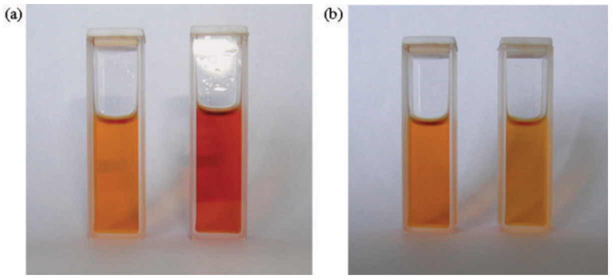


Fig. 5 Photos of the color of **1** in H_2O–CH_3CN (1 : 1 v/v), left cell in (a) and (b), and the color change after the addition of bzta or im, right cell in (a) and (b), respectively.

In conclusion, a supramolecular system, a sodium coordination compound with ligands of TTF dicarboxylate and benzotriazole, has been studied. Electronic spectra show that there are strong interactions between the salt **1** and bzta. The crystal structure of the supramolecular compound **1** · 2bzta · $2H_2O$ has been obtained, showing an unusual one-dimensional structure with a carboxyl–sodium–water core, which is surrounded by TTF and bzta moieties. Cyclic voltammetric measurements also reveal the response of **1** to the added bzta molecules. When imidazole (im) was used instead of the benzotriazol (bzta) in these experiments, no response as that observed in the **1**-bzta system was found. Coordination bonding (ionic), hydrogen-bonding and, especially, topological cooperation in the structure are the important forces forming the stable addition compound. The reaction selectivity for small organic molecules found in this TTF–dicarboxylate system is significant for further studying molecular sensors using TTF derivatives.

Acknowledgements

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