Stable π-dimer of a tetrathiafulvalene cation radical encapsulated in the cavity of cucurbit[8]uril

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The first stable π-dimer of a tetrathiafulvalene (TTF) cation radical encapsulated in the cavity of cucurbit[8]uril has been isolated at room temperature and fully characterized; it shows absorption bands at 400, 540 and 760 nm, characteristic of the TTF cation radical dimer.

Because of their strong electron donor ability, tetrathiafulvalene (TTF)[1] and its derivatives have been extensively employed in the development of electrical,[1a,b] magnetic,[1c] and optical materials,[1d] and more recently utilized as building blocks for the construction of supramolecular structures including molecular machines.[1f,i] The one-electron oxidized species, TTF cation radical is known to exist as a paramagnetic monomer in solution at room temperature,[2] and its π-dimer formation is observed only at low temperatures or in the solid state.[3] Although the broad band near 800 nm observed in oligomeric TTF derivatives such as dendrimers has been attributed to the intra- and intermolecular π–π interaction between TTF cation radicals,[4] TTF cation radical dimers that are stable at room temperature have not been isolated and characterized.[2]

The host family cucurbit[n]uril (CB[n], n = 5–8) comprising n glycoluril units, have a hydrophobic cavity and two identical carbonyl-laced portals, which allow them to form stable inclusion complexes with a wide variety of guest molecules.[5–8] In particular, CB[8], which has a cavity comparable with that of γ-cyclodextrin, exhibits remarkable host–guest properties including the encapsulation of two identical or two different guest molecules inside the cavity to form a stable ternary complex.[7a,b] Furthermore, by encapsulation, the molecular host can stabilize otherwise unstable species.[7d–f] For example, methylviologen cation radical forms a stable π-dimer in the cavity of CB[8] as evidenced by spectroelectrochemistry.[7d] This discovery prompted us to study the stabilization of TTF cation radical dimers by encapsulation in the molecular host. Herein we report the first stable π-dimer of a TTF cation radical encapsulated in the cavity of cucurbit[8]uril, which has been isolated at room temperature and fully characterized.

The water soluble TTF derivative **1** (Scheme 1) is synthesized in two steps;† TTF is first converted to 4-(hydroxymethyl)tetrathiafulvalene[9] which is then reacted with monotosyl-penta-(ethylene glycol) to yield **1** as an air-stable yellow oil. The ^{1}H NMR spectrum of **1** in D_2O (Fig. 1) taken in an inert atmosphere shows the signals for the TTF moiety at 6.35 ppm and those for the side-chain in the range of 3.3–4.3 ppm.‡ The UV-visible spectrum of **1**

(Fig. 2) in aqueous solution exhibits a characteristic absorption band of TTF at 300 nm. The oxidation of **1** by $Fe(ClO_4)_3$ produces the corresponding TTF radical cation (**1**+·) which exists as a paramagnetic monomer as evidenced by UV-visible[10] (Fig. 2) and EPR spectroscopy (Fig. 3).[11]

When CB[8] is added to an aqueous solution of **1**, the color of the solution slowly turns from yellow to pink upon stirring in air. After removing unreacted CB[8] by filtration, the filtrate is concentrated and allowed to stand in a refrigerator to yield **2** as a red precipitate (Scheme 1).§ When the synthesis is carried out in an inert atmosphere, however, no formation of **2** is observed. Furthermore, **2** can be synthesized by adding 0.5 equiv. of CB[8] into a solution
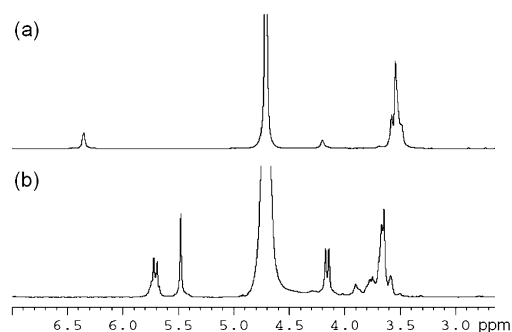

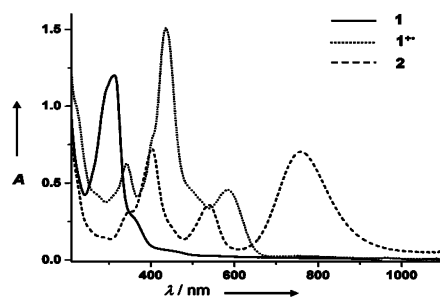**Fig. 1** ^{1}H NMR spectra of (a) **1** and (b) **2** in D_2O (1 mM).

Fig. 2 Absorption spectra of **1**, **1**+· and **2** in H_2O (0.1 mM).
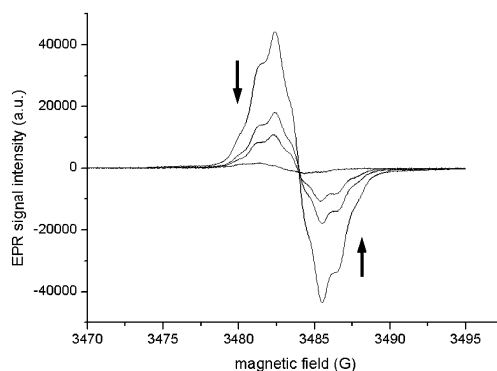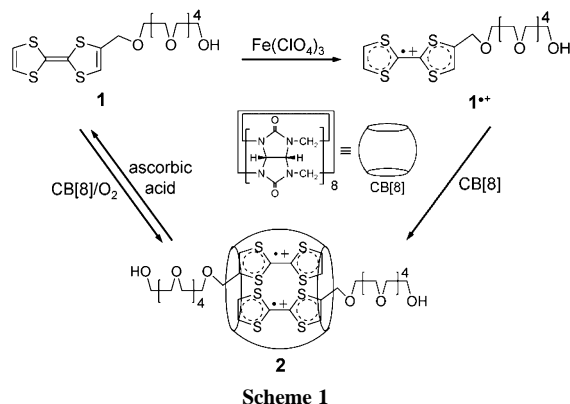

Fig. 3 EPR spectral changes observed for **1**+· (0.5 mM) in H_2O upon addition of CB[8].

Scheme 1

containing $1^{+\cdot}$ generated by oxidation of **1** using Fe(ClO$_4$)$_3$. The complex **2** is indefinitely stable in the solid state and no sign of decomposition is observed in aqueous solution over a month. No signal for the TTF unit is observed in the ^{1}H NMR spectrum of **2** taken in D$_2$O, but those for the host and the ethylene glycol unit are seen (Fig. 1). The signal integration establishes **2** as a 1 : 2 complex between CB[8] and **1**. The down-field shift of the signal for the ethylene glycol unit indicates that the polar unit is located outside CB[8] in **2**. The hydrodynamic volume of **2** estimated by the diffusion NMR technique is almost 2 times as large as that of CB[8]. The parent ion peak at 2236 in the MALDI-TOF mass spectrum of **2** confirms the formation of a 1 : 2 complex between CB[8] and **1**. Most importantly, the UV-visible spectrum of **2** (Fig. 2) in aqueous solution displays absorption bands at 400, 540 and 760 nm, characteristic of the π-dimer of TTF cation radical.[3] Taken together, these spectroscopic data indicate that **2** is a 1 : 2 host–guest complex of CB[8] and $1^{+\cdot}$, which is generated by air oxidation of **1**. In **2**, the TTF cation radical units form a stable π-dimer in the cavity of CB[8] while the polar ethylene glycol units reside outside the CB[8] cavity. The formation of the π-dimer in the cavity of CB[8] is further evidenced by EPR spectroscopy. Upon addition of excess CB[8] into the solution containing $1^{+\cdot}$ at room temperature, the EPR signal of $1^{+\cdot}$ slowly decreases and finally almost disappears (Fig. 3); the final EPR spectrum is essentially the same as that of **2** in water at room temperature. The quenching of the EPR signal in **2** is due to the strong coupling between the two cation radical units residing inside CB[8]. The markedly enhanced stability of the π-dimer by encapsulation in the host may be attributed to the interaction between the TTF cation radical dimer and the hydrophobic cavity which exhibits slightly negative electrostatic potential.[6a] Upon addition of ascorbic acid, the solution of **2** becomes turbid and the UV-visible spectrum becomes similar to that of **1**, which indicates that the reduction of **2** generates **1** and free CB[8] which is sparingly soluble in water (Scheme 1).

In conclusion, the first stable π-dimer of a TTF cation radical encapsulated in the cavity of cucurbit[8]uril has been isolated at room temperature and fully characterized. This work once again demonstrates the effectiveness of the cucurbituril host family in stabilizing otherwise unstable species by encapsulation. Since the reduction of the host stabilized guest π-dimer regenerates the free TTF molecule and host, one can design electrochemically controllable molecular machines based on this observation, in a similar way to the viologen case.[7f] We are currently working along these lines.

Notes and references

† To a suspension of sodium hydride (0.043 g (60% in oil), 1.2 mmol) in dry THF (5 ml) a solution of 4-(hydroxymethyl)tetrathiafulvalene (0.25 g, 1 mmol) in dry THF (10 ml) was added slowly under an argon atmosphere. The reaction mixture was refluxed for 1 h. A solution of monotosyl-penta(ethylene glycol) (0.5 g, 1.2 mmol) in dry THF (20 ml) was added dropwise and the reflux was continued for two days. After addition of wet THF (1 ml) to quench unreacted sodium hydride, the solvent was removed in vacuum. Column chromatography (silica gel, eluent diethyl ester : methanol, 10 : 1) gave **1** as a yellow oil (0.28 g, 60%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.25 (s, H), 3.66 (m, 20H), 4.30 (s, 2H), 6.23 (s, H), 6.30 (s, 2H). HRFAB-MS: calcd: 454.0612 [M$^+$], 455.0690 [MH$^+$]; found 454.0634, 455.0690.

‡ No signal for the TTF moiety is observed in the ^{1}H NMR spectrum of **1** in D$_2$O taken *in air*, which is presumably due to the presence of a small amount of the TTF radical cation ($1^{+\cdot}$) generated by air oxidation; a similar

behavior has been reported before.[12] It also indicates that the radical cation of **1** is generated by air oxidation, but the equilibrium is in favor of the neutral species in the absence of CB[8]. However, in the presence of CB[8], the facile formation of the stable π-dimer of $1^{+\cdot}$ inside CB[8] shifts the equilibrium toward the radical cation species.

§ A mixture of CB[8]·H$_2$SO$_4$·16H$_2$O (68 mg, 40 μmol) and **1** (26 mg, 56 μmol) in water (20 ml) was stirred at room temperature overnight. After the undissolved solid was filtered off, the volume of the filtrate was reduced to 2 ml under a reduced pressure. It was then allowed to stand in a refrigerator overnight to produce a red precipitate which was filtered, washed and dried to afford **2** (54 mg, 70%). ^{1}H NMR (500 MHz, D$_2$O): δ = 3.72 (m, 40H), 4.26 (d, J = 15 Hz, 16H), 5.56 (s, 16H), 5.80 (d, J = 15 Hz, 16H); MALDI-MS: 2236 [M$^+$]; elemental analysis, calcd (%) for (C$_{48}$H$_{48}$N$_{32}$O$_{16}$)·(C$_{17}$H$_{26}$O$_6$S$_4^+$)$_2$·(SO$_4^{2-}$)·24H$_2$O; C, 35.60; H, 5.39; N, 16.20; found: C, 35.25; H, 5.10; N, 16.54%.

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