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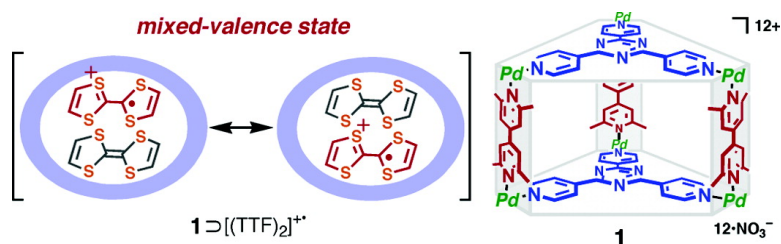
Room-Temperature and Solution-State Observation of the Mixed-Valence Cation Radical Dimer of Tetrathiafulvalene, [(TTF)], within a Self-Assembled Cage

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Room-Temperature and Solution-State Observation of the Mixed-Valence Cation Radical Dimer of Tetrathiafulvalene, [(TTF)₂]⁺•, within a Self-Assembled Cage

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Whereas mixed-valence states are often observed for metal−metal-bonded or metal-conjugated compounds,[1] they are much less common for fully organic systems. Since the first report in 1965 on the mixed-valence state of two aggregated aromatic compounds,[2] there have appeared several intense studies on fully organic mixed-valence state.[3−5] They are, however, weakly associated species and are commonly observed only at low temperatures in solid state unless covalently linked.[6] We report here the room-temperature and solution-state observation of the mixed-valence dimer [(TTF)₂]⁺• (TTF = tetrathiafulvalene) that is generated within a self-assembled coordination cage. TTF is a strong electron donor and apt to generate the stable cation radical TTF⁺• upon oxidation. Although the formation of a cation radical dimer in organic hosts has been reported,[7,8] the mixed-valence dimer [(TTF)₂]⁺• has, to the best of our knowledge, never been described. The cage we employ here has an organic-pillared framework (**1** in Scheme 1) in which two

Scheme 1
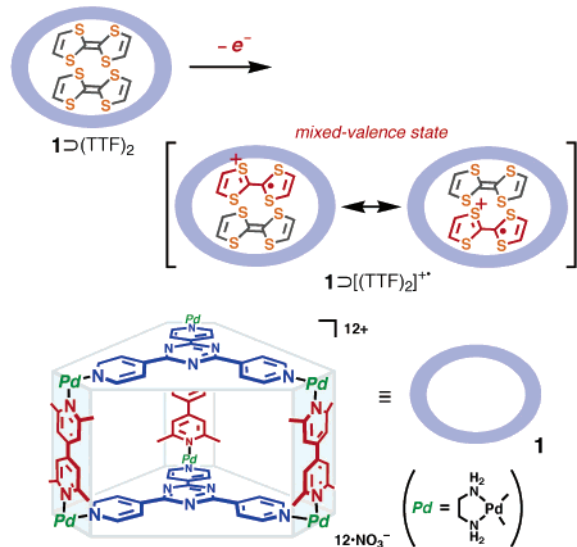
tris(4-pyridyl)triazine ligands are situated in parallel with an interplane separation of ∼10 Å.[9] The two TTF molecules are bound by the cage so that they stack on each other. Therefore, despite the absence of any covalent or noncovalent bonds between the TTF molecules, they are smoothly oxidized into the mixed-valence dimer [(TTF)₂]⁺• by electrochemical oxidation (Scheme 1).

When excess TTF (0.08 mmol) was suspended in a H₂O solution (1.0 mL) of **1** (0.02 mmol) at room temperature for 30 min under an argon atmosphere, the colorless solution quickly turned deep green. CSI-MS measurement revealed the formation of **1**⊃(TTF)₂, with a series of clear peaks corresponding to the formula of [**1**⊃(TTF)₂−n(NO₃⁻)+2M]$^{n+}$ (n = 5−7, M denotes an aromatic-
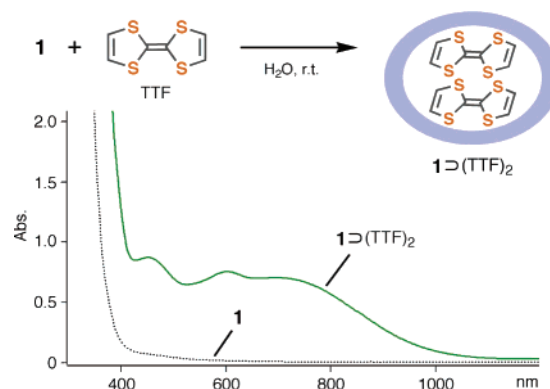
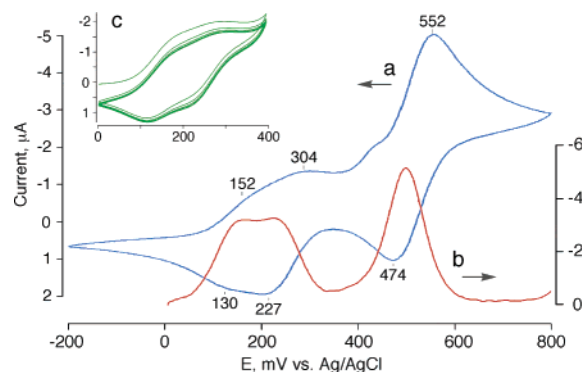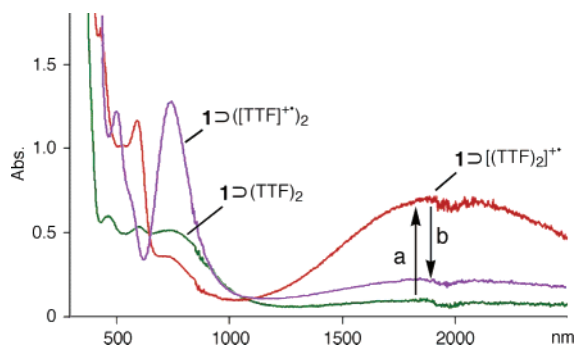**Figure 1.** UV−vis spectra (H₂O, room temperature) of **1** and **1**⊃(TTF)₂.

Figure 2. Cyclic voltammogram of **1**⊃(TTF)₂ at a scan rate of 100 mV/s in the range of (a) −200 to 800 mV, and (c) 0 to 400 mV (the first five cycles); (b) square-wave voltammogram (ΔE = 1 mV, E_{sw} = 5 mV, f = 5 Hz) of **1**⊃(TTF)₂ (glassy carbon disk electrode vs Ag/AgCl, 30 mM NaNO₃ in H₂O, room temperature).

cored matrix[10]). The UV−vis spectrum (Figure 1) of the colored solution showed a new absorption band around 740 nm, which is attributed to the CT interaction between electron-rich TTF and the electron-deficient triazine ligand of **1**.[9,11] Due to the strong CT interaction, TTF seems to possess a radical cationic nature. Hence, in the ¹H NMR, the signal of TTF appearing at δ = 5.5 ppm was considerably broadened.[12]

Electrochemical studies showed the unique behavior of accommodated TTF molecules. The cyclic voltammogram of **1**⊃(TTF)₂ was recorded in aqueous NaNO₃ solution at a scan rate of 100 mV/s in the range of −200 to 800 mV (Figure 2a). Roughly two oxidation waves were observed around 200 and 500 mV, which are attributed to the formation of the cation radical TTF⁺• and the dication TTF²⁺, respectively.
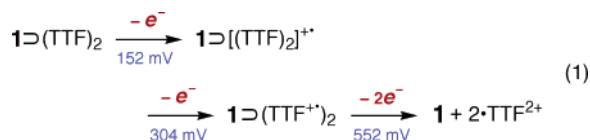
A striking feature was that the former oxidation wave around 200 mV could be resolved into two waves at the peak potentials of

Figure 3. In situ electronic absorption spectra of $\mathbf{1}\supset(TTF)_2$ at various applied potentials. Electrochemical oxidation of $\mathbf{1}\supset(TTF)_2$ at constant voltage of (a) 180 and (b) 400 mV. ITO electrode vs Ag/AgCl, 30 mM $NaNO_3$ in H_2O, room temperature.

152 and 304 mV (Figure 2a), as clearly revealed by the square-wave voltammogram (Figure 2b). This indicated the oxidation of half of TTF at 152 mV,[11,12] implying the generation of the mixed-valence dimer $[(TTF)_2]^{+\bullet}$. This species was subsequently oxidized into the cation radical dimer $(TTF^{+\bullet})_2$ at 304 mV. The potential was positively shifted as compared with that of free $TTF/TTF^{+\bullet}$ oxidation (178 mV; $\Delta E_{1/2} = 126$ mV), presumably due to cationic repulsion between the host and the guest.[13] The two-electron oxidation/reduction of $(TTF)_2$ within $\mathbf{1}$ occurred reversibly in the range of 0−400 mV (Figure 2c), showing the stability of $[(TTF)_2]^{+\bullet}$ and $(TTF^{+\bullet})_2$ as well as the absence of guest declathration during the redox.

The cation radical was further oxidized at the peak potential of 552 mV (half-wave potential $E_{1/2}^{ox2} = 513$ mV) into the dication TTF^{2+}. The potential was comparable to that of free $TTF^{2+}/TTF^{+\bullet}$ oxidation (555 mV; $\Delta E = 3$ mV), suggesting that TTF^{2+} was liberated from the cage because of cationic repulsion among the host and the two guest molecules. In these sequential oxidations, the most probable transformations are summarized in eq 1.

$$\mathbf{1}\supset(TTF)_2 \xrightarrow[152\text{ mV}]{-e^-} \mathbf{1}\supset[(TTF)_2]^{+\bullet}$$

$$\xrightarrow[304\text{ mV}]{-e^-} \mathbf{1}\supset(TTF^{+\bullet})_2 \xrightarrow[552\text{ mV}]{-2e^-} \mathbf{1} + 2\cdot TTF^{2+} \quad (1)$$

The proposed transformations were strongly supported by electronic absorption spectroscopy. We succeeded in the direct observation of the mixed-valence dimer $[(TTF)_2]^{+\bullet}$ by electrochemical oxidation within $\mathbf{1}$ at room temperature in solution. Thus, the in situ absorption analysis of $\mathbf{1}\supset(TTF)_2$ during electrolysis at a constant voltage of 180 mV, which is below $[(TTF^{+\bullet})_2/(TTF)_2^{+\bullet}]$ oxidation potential, showed a new broad absorption band in the near-infrared region ($\lambda_{max} = \sim 2000$ nm), as shown in Figure 3. This broad band is characteristic of the mixed-valence state of two TTF molecules.[5,6,11] Surprisingly, the mixed-valence species thus generated was remarkably stable, and the spectrum decayed very slowly ($t_{1/2} = \sim 1$ day) at room temperature even under air. Of course, such a mixed-valence species was not observed in the absence of the cage. The remarkable stability of the mixed-valence dimer is ascribed to the efficient stacking of two TTF molecules in the cage.

Further oxidation at 400 mV generated $\mathbf{1}\supset(TTF^{+\bullet})_2$. New absorption bands appeared in the UV−visible region (758, 534,

and 406 nm). These bands are characteristic of the cation radical dimer $(TTF^{+\bullet})_2$.[7,8] Interestingly, the absorption of the cation radical dimer gradually disappeared within 2 h. Probably, $\mathbf{1}\supset(TTF^{+\bullet})_2$ is a metastable species and the cationic guest is liberated from the cationic cage.

In summary, through the accommodation in a self-assembled cage, we succeeded in the generation and observation of a mixed-valence dimer $[(TTF)_2]^{+\bullet}$. It is particularly interesting that a weak dimeric species, which typically cannot be generated unless covalently linked, is observed in cage $\mathbf{1}$. This is because cage $\mathbf{1}$ possesses a large electron-deficient cavity that provides an ideal interplane distance for binding two planar electron-rich molecules. By utilizing such a unique cavity, observation of various weak interactions between molecules (for example, metal−metal interactions or spin−spin interactions) is currently being studied in our laboratory.[14]

Supporting Information Available: Experimental details and spectroscopic data of $\mathbf{1}\supset(TTF)_2$ and $\mathbf{2}\supset TTF^{11}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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