CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200800213

Direct Observation of Mixed-Valence and Radical Cation Dimer States of Tetrathiafulvalene in Solution at Room Temperature: Association and Dissociation of Molecular Clip Dimers Under Oxidative Control

Pinn-Tsong Chiang,[a] Nai-Chia Chen,[a] Chien-Chen Lai,*[b] and Sheng-Hsien Chiu*[a]

Abstract: We have observed the mixed-valence and radical cation dimer states of a glycoluril-based molecular clip with tetrathiafulvalene (TTF) sidewalls at low concentration (1 mM) at room temperature. This molecular clip has four consecutive anodic steps in its cyclic voltammogram, which suggests a sequential oxidation of these TTF sidewalls to generate species existing in several distinct charge states: neutral monomers, mixed-valence dimers, radical cation dimers, and fully oxidized tetracationic monomers. The observation of characteristic NIR spectroscopic absorption bands at approximately 1650 and 830 nm in spectroelectrochemistry experiments supports the presence of intermediary mixed-valence and radical cation dimers, respectively, during the oxidation process. The stacking of four TTF radical cations in the dimer led to the appearance of a charge-transfer band at approximately 946 nm. Nanoelectrospray ionization mass spectrometry was used to verify the tricationic state and confirm the existence of other different charged dimers during the oxidation of the molecular clip.

Keywords: cation radical dimer · mixed-valent compounds · molecular machines · supramolecular chemistry · tetrathiafulvalene

Introduction

Electronic communication between two (or more) associated species with different oxidation states (i.e., mixed-valence states) is an important feature of electronically active materials.[1] Although electronic communication had been well established to occur between metals and in metal-conjugated compounds,[2] electronic communication between mixed-valence states of purely organic compounds had not been observed prior to 1965.[3] Because the noncovalent interactions between most organic compounds are weak, organic mixed-valence states are generally hard to detect in solution at room temperature unless the components are linked covalently.[4] The stable radical cations and dications of tetrathiafulvalene[5] (TTF, Figure 1) and its derivatives have been widely employed in several applications, including organic superconductors[6] and electrochemically switchable materials.[7] Nevertheless, the observation of mixed-valence dimers $[(TTF)_2]^{\bullet+}$ and radical cation dimers $[(TTF)_2]^{2\bullet 2+}$ in solution at room temperature remains a challenging task unless suitable hosts (e.g., cucurbituril)[8] or self-assembled molecular cages[9] are used to bridge the TTF units noncovalently. Recently, an elegant approach was developed to meet this challenge through the formation of a unique $TTF^{+\bullet}CB^{-}$ salt (CB = permethylcarboranyl), which forms mixed-valence dimers with neutral TTF and dimerizes at high concentrations.[10] Mixed-valence dimers $[(TTF)_2]^{\bullet+}$ and radical cation dimers $[(TTF)_2]^{2\bullet 2+}$ exist in solution at low concentration only when the intermolecular interactions between the two constituents are sufficiently strong. Clip-shaped molecules form complexes efficiently with a range of aromatic guest units;[11] this feature endows them with the potential to dimerize (Figure 1).[12] Previously, we developed a glycoluril-based molecular clip with electron-rich TTF units as its sidewalls;[13] herein, we report that sequential ox-

---

[a] P.-T. Chiang, N.-C. Chen, Prof. S.-H. Chiu
Department of Chemistry
National Taiwan University
Taipei (Taiwan ROC)
Fax: (+886) 2-3366-1677
E-mail: shchiu@ntu.edu.tw

[b] Prof. C.-C. Lai
Institute of Molecular Biology
National Chung Hsing University and
Department of Medical Genetics
China Medical University Hospital
Taichung (Taiwan ROC)
Fax: (+886) 4-2285-8163
E-mail: lailai@dragon.nchu.edu.tw

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

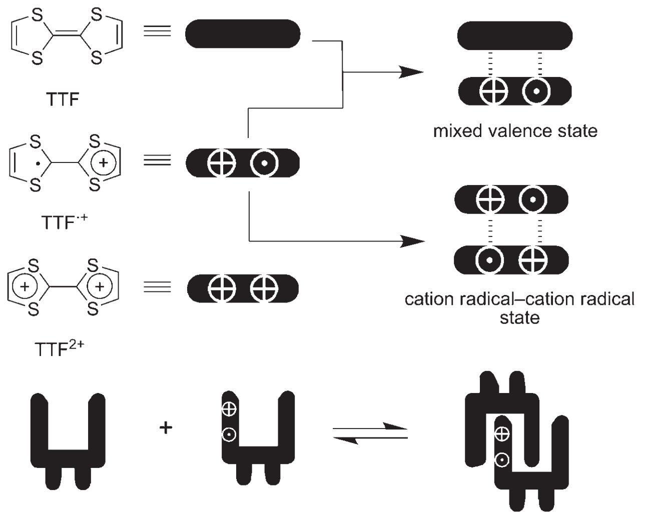
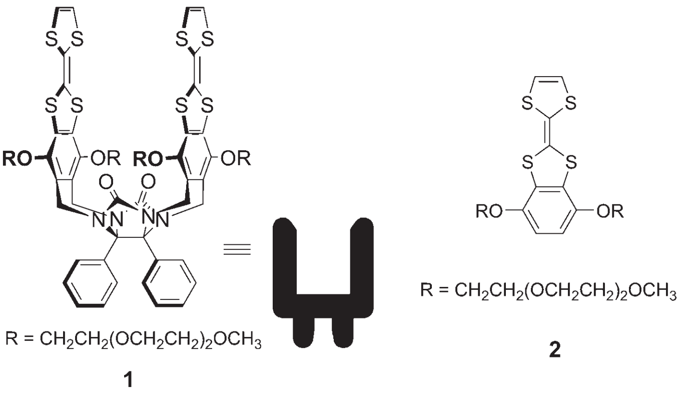


Figure 1. Cartoon representations of the mixed-valence and radical cation–radical cation dimers of TTF and molecular clips.

idation of these TTF sidewalls generates species in several distinct charge states: neutral monomers, mixed-valence dimers, radical cation dimers, and fully oxidized tetracationic monomers.

Results and Discussion

Electrochemistry: Previously, we reported that the TTF-sidewall molecular clip **1** (Scheme 1) can form quadruply controllable macrocycle/molecular clip complexes.[13a] Because the rich redox chemistry of TTF units provides a very efficient tool for controlling the switching of supramolecular assemblies between their different states, we were interested in examining the electrochemistry of molecular clip **1**. The distance between the two almost parallel TTF sidewalls in **1** is approximately 6.8 Å;[14] therefore, electronic communication between the pair of TTF units on each clip during the oxidation process is very unlikely. Thus, we expected to observe two two-electron oxidation processes in the cyclic voltammetry (CV) traces of **1**. Interestingly, the cyclic voltammogram of molecular clip **1** in CH_3CN (1 mM) had four consecutive anodic steps at peak potentials of 430, 562, 680, and 1020 mV, respectively, versus Ag/AgCl (Figure 2 and Table 1). The four peak currents are not equivalent: the second and third steps proceed with relatively low values of I_p. To understand this behavior, we synthesized TTF derivative **2** as a reference compound (Scheme 1); as expected, it has two successive oxidation steps in the CV trace. Thus, we suspect that the two extra oxidation peaks in the cyclic voltammogram of molecular clip **1** arose as a result of intermolecular interactions.



1

2

Scheme 1. Structures of molecular clip **1** and TTF derivative **2**.

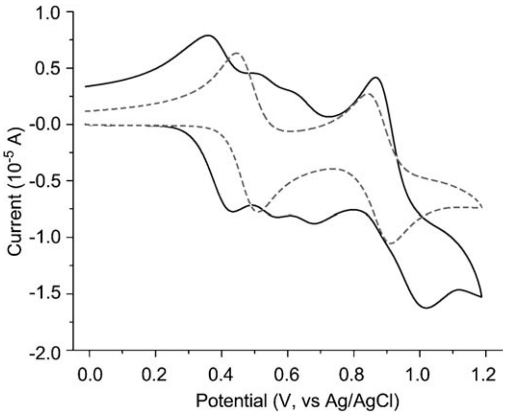


Figure 2. Cyclic voltammograms of 1 mM solutions of **1** (——) and **2** (-----) in CH_3CN. Supporting electrolyte: Bu_4NPF_6 (0.1 M), scan rate: 100 mV s^{-1}.

Table 1. Redox potential (mV, vs. Ag/AgCl) from CV.[a]

	E_{ox}^1	E_{ox}^2	E_{ox}^3	E_{ox}^4	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
1	430	562	680	1020	864	628	518	358
2	510	910	–	–	844	447	–	–

[a] E_{ox}^n are the *n*th oxidation peak potentials of the neutral compound and E_{red}^n are the *n*th reduction peak potentials of the fully oxidized species.

In Figure 3, we propose that the four consecutive oxidation potentials observed in the CV oxidation trace of molecular clip **1** were the result of the initial oxidation of **1** and subsequent oxidations of its various charged dimers. The distance (≈6.8 Å) between the two TTF sidewalls of **1** is ideal for intercalation (π stacking) of a guest molecule, especially for mixed-valence interactions with a complementary electron-poor radical cation TTF, so we might suspect the initial formation of a mixed-valence radical cation dimer $[\mathbf{1}\supset\mathbf{1}]^{\cdot+}$. It would be unlikely, however, for this mixed-valence dimer to exist as a fully aromatic stacked form because of the destabilizing effect of the stacking of two π-electron-rich TTF units. Thus, the oxidation potential for the removal of a second electron would most likely be indistinguishable from

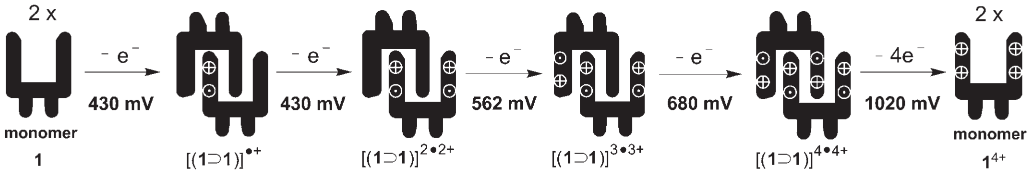


Figure 3. Graphical representation of the stepwise oxidation of the molecular clip dimer.

that of the first; indeed, we observed an initial single two-electron oxidation at 430 mV, which led to the formation of the diradical dication dimer $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$.[15] The favorable array of stabilizing intermolecular interactions within dimer $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$ would increase the potential required for the oxidation of its third TTF unit; indeed, the oxidation of $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$ to the triradical tricationic dimer $[\mathbf{1}\supset\mathbf{1}]^{3\cdot3+}$ occurred at a potential (562 mV) significantly higher than that for the oxidation of the first two TTF sidewalls.[16] Likewise, the subsequent oxidation to the tetraradical tetracation dimer $[\mathbf{1}\supset\mathbf{1}]^{4\cdot4+}$, which features only radical cation–radical cation interactions (i.e., no mixed-valence interactions), occurred at 680 mV. Finally, this dimer dissociated, which is represented by one broad peak at 1020 mV, upon removal of four electrons simultaneously from the four stacked TTF radical cations. The dissociation of the dimer is most likely to have been driven by charge repulsion, as has been proposed for other systems;[9] the dissociation of this molecular assembly into fully oxidized tetracationic monomers $\mathbf{1}^{4+}$ is evident by its reduction potential being similar to that of the fully oxidized dicationic TTF $\mathbf{2}^{2+}$. The low values of I_p for the second and third oxidation signals can be explained by the dynamic equilibrium of the monomers and dimers in solution.

Because the dimers $[\mathbf{1}\supset\mathbf{1}]^{\cdot+}$ and $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$ were stabilized in solution mainly through mixed-valence interactions, the dimer $[\mathbf{1}\supset\mathbf{1}]^{4\cdot4+}$ through radical cation–radical cation interactions, and the dimer $[\mathbf{1}\supset\mathbf{1}]^{3\cdot3+}$ through both radical cation and mixed-valence interactions, we suspected that their respective absorption spectra would reveal changes in the characteristic absorptions of their mixed-valence and radical cation dimer states during the sequential oxidation processes.

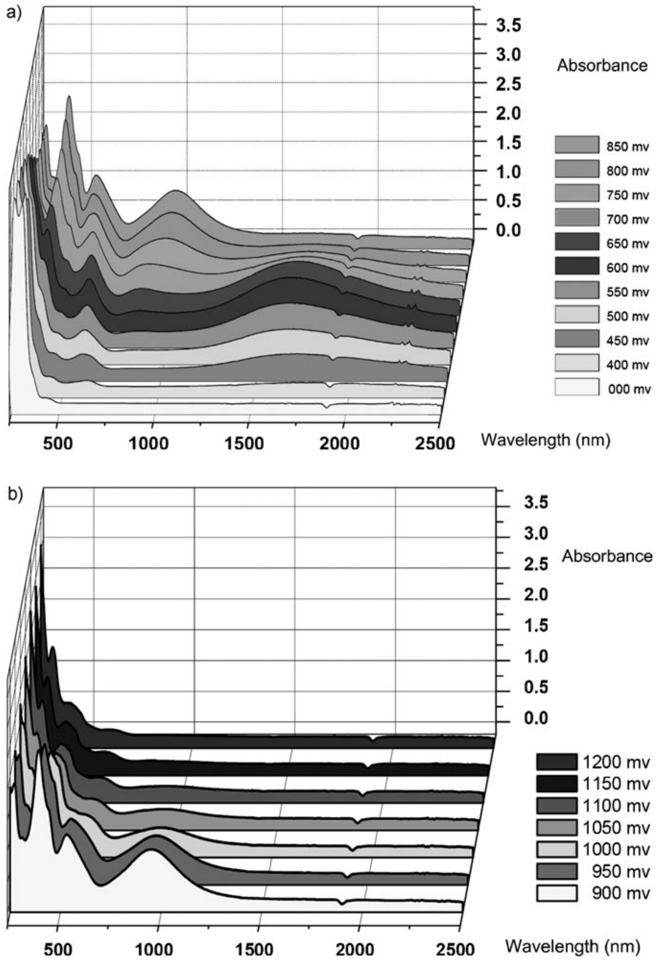


Figure 4. In situ electronic absorption spectra of molecular clip **1** (1 mM) at oxidation potentials in the ranges a) 0–850 and b) 900–1200 mV versus Ag/AgCl, 0.1 M Bu_4NPF_6 in CH_3CN, room temperature.

Spectroelectrochemistry: In situ absorption analysis of molecular clip **1** subjected to a gradual potential increase from 400 to 550 mV—the range in which we would expect oxidation to the dimer $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$—revealed the growth of a new broad absorption band in the near-infrared (NIR) region ($\lambda_{max} \approx 1650$ nm; Figure 4). We observed a growing absorption in the NIR ($\lambda_{max} \approx 830$ nm) region when the oxidation potential was extended beyond 600 mV. These NIR absorption bands are characteristic of mixed-valence and radical cation–radical cation dimer states, respectively, for pairs of stacked TTF units.[8–10,17] These spectra suggest the sequential formation of the tricationic dimer $[\mathbf{1}\supset\mathbf{1}]^{3\cdot3+}$ (see below) after the formation of the mixed-valence dimers $[\mathbf{1}\supset\mathbf{1}]^{\cdot+}$ and $[\mathbf{1}\supset\mathbf{1}]^{2\cdot2+}$. Increasing the oxidation potential to 800 mV enhanced the signal of the absorption of the radical cation–radical cation systems, with a decrease in the intensity of the absorption signal for the mixed-valence states. This behavior strongly supports our hypothesis that mixed-valence interactions transformed into radical cation–radical cation interactions upon increasing the oxidation potential. At 800 mV, the NIR absorption of the mixed-valence state became negligible, which suggested that the dimer $[\mathbf{1}\supset\mathbf{1}]^{4\cdot4+}$ was the predominant species at that point. We note that the characteristic absorption of the radical cation–radical cation state in dimer $[\mathbf{1}\supset\mathbf{1}]^{4\cdot4+}$ at a wavelength of 946 nm was considerably higher than the value observed for the $[\mathbf{1}\supset\mathbf{1}]^{3\cdot3+}$ dimer, which had fewer stacked TTF radical cations

(830 nm). This observation suggests that the stacking of more than two TTF radical cations in this dimer shifts the absorption band toward longer wavelengths; that is, the characteristic absorption of four continuously stacked TTF radical cations in this system is approximately 946 nm. To the best of our knowledge, such an absorption has never been observed before in solution at room temperature. Thus, these electronic absorption experiments strongly support our proposed sequential transformation of the neutral monomer into the mixed-valence dimers $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$ and $[\mathbf{1}\supset\mathbf{1}]^{2\bullet 2+}$, then into $[\mathbf{1}\supset\mathbf{1}]^{3\bullet 3+}$, and then into the tetracationic dimer $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$.

To extend the potential applications of this system to redox-switchable materials, we also examined the chemical oxidation of molecular clip **1**. When using $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$[18] to oxidize **1** in CH_3CN, we observed behavior in the resulting UV/Vis/NIR spectra similar to that in the spectroelectrochemistry experiments. The addition of $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ (1 equiv) to a solution of **1** in CH_3CN removed electrons (1 equiv) from the clip monomers to generate strong characteristic absorptions for the mixed-valence species at 1630 nm together with weak signals for radical cation–radical cation species at 830 nm (Figure 5). Increasing the amount of the oxidizing agent to 1.5 equiv converted the mixed-valence dimers $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$ and $[\mathbf{1}\supset\mathbf{1}]^{2\bullet 2+}$ to the radical cation dimers $[\mathbf{1}\supset\mathbf{1}]^{3\bullet 3+}$ and $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$, as evidenced by the decreased absorption maximum at approximately 1660 nm and the increased signal at approximately 830 nm. After adding 2 equiv of the oxidizing agent, the absorption at 1660 nm for the mixed-valence state disappeared completely and one at 946 nm appeared for tetraradical tetracationic $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$. These results suggest that both the chemical and electrochemical oxidations proceeded though the same four intermediary dimers.[19] As expected, when we added a large excess of $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ to the solution **1** in CH_3CN, the absorption at 946 nm for the radical cation–radical cation dimer state disappeared and the resulting spectrum, which had absorptions at 440 and 598 nm, was similar to that obtained after the oxidation of monomeric TTF derivative **2** under the same conditions (Figure 6).

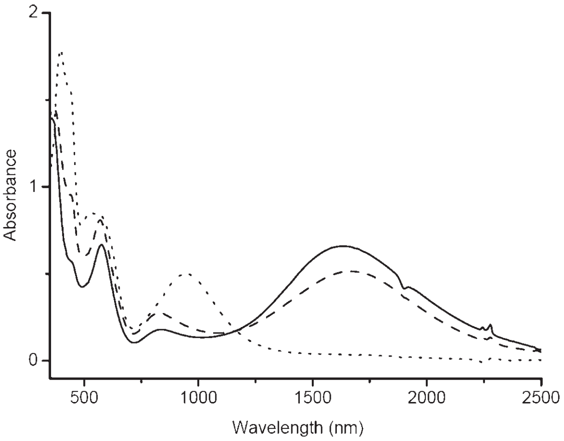


Figure 5. Electronic absorption spectra of the molecular clip **1** in CH_3CN (1 mM) in the presence of 1.0 (——), 1.5 (– – –), and 2.0 equiv (-----) of the oxidizing agent $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$.

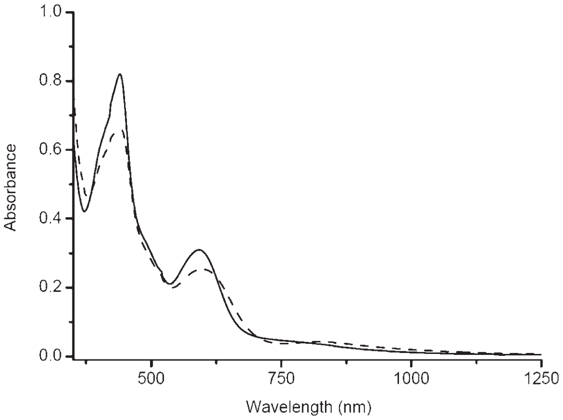


Figure 6. Electronic absorption spectra of the molecular clip **1** (——) and the monomeric TTF derivative **2** (– – –) in CH_3CN (1 mM) in the presence of excess amounts of the oxidizing agent $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$.

This finding is consistent with dissociation of the clip dimer $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$ into two tetracationic monomers $\mathbf{1}^{4+}$ upon oxidation of the four complexed TTF radical cation units into their corresponding dications, which is in good agreement with our observations from the CV experiments. Thus, the association and dissociation of these molecular clip dimers can be controlled through simple oxidation processes, for example, through judicious choice of the oxidation potential or the amount of oxidizing agent.

Nanoelectrospray mass spectrometry: We used nanoelectrospray ionization mass spectrometry (nanoESIMS) to confirm the sequential formation of the four different charged dimers from $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$ to $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$ during the oxidation of **1**. NanoESIMS analysis of a solution of **1** and $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ (20:1) in CH_3CN revealed a signal at m/z 2998.7 corresponding to the singly charged dimer $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$. Tandem mass spectrometric analysis (nanoESIMS/MS) of this signal gave two clear peaks at m/z 1498.3 and 2998.7, corresponding to the $\mathbf{1}^{\bullet+}$ and $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$ ions, respectively, which suggests that the dimer ion comprised one neutral and one singly charged unit of **1** (Figure 7). NanoESIMS analysis of an equimolar solution of **1** and $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ in CH_3CN displayed two doubly charged signals at m/z 749.3 and 1499.6; nanoESIMS/MS analyses of these signals suggested the existence of clip monomers $\mathbf{1}^{2\bullet 2+}$ and dimers $[\mathbf{1}\supset\mathbf{1}]^{2\bullet 2+}$ under these conditions (see the Supporting Information). Dimer $[\mathbf{1}\supset\mathbf{1}]^{3\bullet 3+}$ was identified through nanoESIMS analysis of a solution of **1** and $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ (1:1.5) in CH_3CN as a triply charged signal at m/z 999.9; nanoESIMS/MS analysis of this peak provided signals for the species $\mathbf{1}^{2\bullet 2+}$, $[\mathbf{1}\supset\mathbf{1}]^{3\bullet 3+}$, and $\mathbf{1}^{\bullet+}$ at m/z 749.2, 999.9, and 1498.3, respectively (Figure 8). We ob-

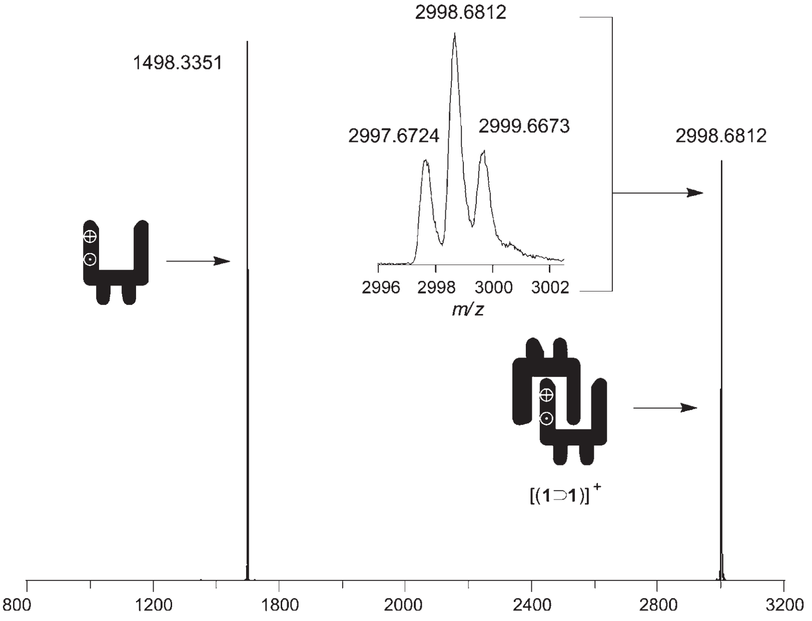


Figure 7. NanoESI-Q-TOF-MS/MS spectrum of the dimer $[\mathbf{1}\supset\mathbf{1}]^{\bullet+}$ (*m*/*z* 2998.7 in the singly charged state).

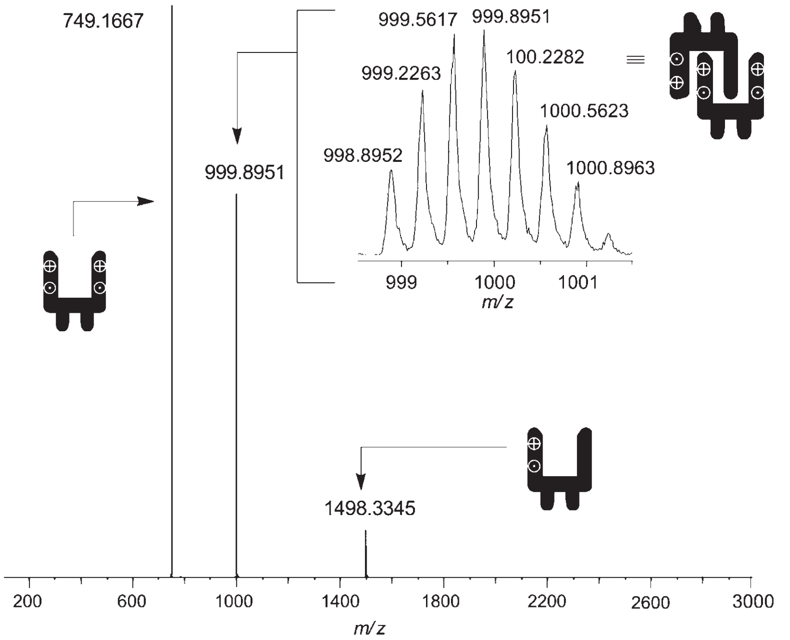


Figure 8. NanoESI-Q-TOF-MS/MS spectrum of the dimer $[\mathbf{1}\supset\mathbf{1}]^{3\bullet 3+}$ (*m*/*z* 999.9 in the triply charged state).

served overlapping tetracationic and dicationic signals at *m*/*z* 749.3 in the nanoESI mass spectrum of a solution of **1** and $[(2,4\text{-}Br_2C_6H_3)_3N][SbCl_6]$ (1:2) in CH_3CN, which confirmed the existence of the intermediate $[\mathbf{1}\supset\mathbf{1}]^{4\bullet 4+}$ (see the Supporting Information). Thus, nanoESIMS provided evidence for the presence of each of the four sequential intermediates during the oxidation of **1**.

Conclusion

We have demonstrated that the generally hard to observe mixed-valence and radical cation–radical cation states of TTF dimers can be prepared at room temperature and low concentrations through the oxidation of a molecular clip with two TTF sidewalls. Gradual oxidation of the TTF sidewalls of the molecular clips (neutral monomers) led to their dimerization into three successive oxidative states (mixed-valence dimers followed by radical cation–radical cation dimers) and then, ultimately, dissociation (fully oxidized monomers). Because the degree of dimerization of the molecular clip was under oxidative control, such molecular clips might be useful materials for the construction of unique supramolecular machinery, for example, molecular goalkeepers or fences formed from multiple molecular clips that prevent the passage of molecules of interest within porous materials.

Experimental Section

Electrochemistry: The oxidation potentials for molecular clip **1** and monomeric TTF derivative **2** were determined from CV. The electrochemical instrumentation used consisted of a commercially available electrochemical analyzer and a conventional personal computer. A three-electrode configuration was applied in which Pt wire was used as the counter electrode, a commercially available Ag/AgCl electrode was used as the reference electrode, and a Pt disk (area: 0.07 cm^2) was used as the working electrode. The reference electrode was calibrated by using Fc/Fc^+ before and after the experiments. The measurements were performed in anhydrous solutions that were freshly distilled prior to use. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$; Fluka, electrochemical grade). All samples were deoxygenated with nitrogen prior to measurement.

UV/Vis/NIR Spectroscopy: All solvents were freshly distilled and deoxygenated with nitrogen prior to use. The oxidant, tris-(2,4-dibromophenyl)ammonium hexachloroantimonate, and TTF derivatives **1** and **2** were carefully weighed in a glove box filled with nitrogen; these solutions were prepared simultaneously. A cell with a path length of 0.1 cm was used to acquire the spectra. All UV/Vis/NIR spectral measurements were performed by using a commercially available spectrometer and a personal computer.

Spectroelectrochemistry: Spectroelectrochemistry was performed on samples placed within a quartz cuvette with a path length of 0.1 cm. Pt gauze (100 mesh) was used as an optically transparent electrode. The reference and auxiliary electrodes were Ag/AgCl and a Pt wire, respectively. UV/Vis/NIR spectra were acquired by using the same instrument as that described above. Fixed-potential electrolysis was performed by using the same electrochemical analyzer as that employed for CV measurements. The sample used for spectroelectrochemistry was prepared in the same manner as those for CV.

Nanoelectrospray quadrupole time-of-flight tandem mass spectrometry (Nano-ESI-Q-TOF-MS/MS): High-resolution (HR) nano-ESI-Q-TOF-MS and tandem MS were performed by using a QSTAR^{XL} quadrupole time-of-flight (Q-TOF) mass spectrometer (Applied Biosystems/MDS Sciex, Foster City, CA) equipped with a nanospray source. Ionization (ionization potential: 1.0 kV) was performed by using a coated nanospray tip (ES380; Proxeon, Odense, Denmark). The optimum sprayer position was typically flush with or slightly inserted ($\approx$1 mm) into the curtain chamber. The temperature of the heated laminar flow chamber was set at 100° C. The potential of the curtain plate and the curtain gas flow rate were set at 250 V and $1.3\,\mathrm{L\,min^{-1}}$, respectively. All other potentials were optimized to provide maximum signal intensities and resolution. Tandem mass spectrometry employed collision-induced dissociation (CID) at variable kinetic energies, with nitrogen as the collision gas.

Acknowledgements

This study was supported by the National Science Council, Taiwan (NSC-95-2113-M-002-016-MY3).

---

[1] a) M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422; b) J. A. Kramer, F. H. Herbstein, D. N. Hendrickson, *J. Am. Chem. Soc.* **1980**, *102*, 2293–2301; c) K. Lahlil, A. Moradpour, C. Bowlas, C. Menou, P. Cassoux, J. Bonvoisin, J.-P. Launay, G. Dive, D. Dehareng, *J. Am. Chem. Soc.* **1995**, *117*, 9995–10002; d) R. Rathore, A. S. Kumar, S. V. Lindeman, J. K. Kochi, *J. Org. Chem.* **1998**, *63*, 5847–5856; e) J. K. Kochi, R. Rathore, P. Le Maguères, *J. Org. Chem.* **2000**, *65*, 6826–6836; f) M. M. Matsushita, T. Sugawara, *J. Am. Chem. Soc.* **2005**, *127*, 12450–12451.

[2] a) G. C. Allen, N. S. Hush, *Prog. Inorg. Chem.* **1967**, *8*, 357–389; b) K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655–2685.

[3] I. C. Lewis, L. S. Singer, *J. Chem. Phys.* **1965**, *43*, 2712–2727.

[4] a) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, P. E. Seiden, *Phys. Rev. B* **1979**, *19*, 730–741; b) H. Spanggaard, J. Prehn, M. B. Nielsen, E. Levillain, M. Allain, J. Becher, *J. Am. Chem. Soc.* **2000**, *122*, 9486–9494; c) M. Iyoda, M. Hasegawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase, G. Yamamoto, *Chem. Lett.* **2001**, 1146–1147; d) J. Lyskawa, M. Salle, J.-Y. Balandier, F. Le Derf, E. Levillain, M. Allain, P. Viel, S. Palacin, *Chem. Commun.* **2006**, 2233–2235; e) F. Biaso, M. Geoffroy, E. Canadell, P. Auban-Senzier, E. Levillain, M. Fourmigue, N. Avarvari, *Chem. Eur. J.* **2007**, *13*, 5394–5400.

[5] a) T. Jørgensen, T. K. Hansen, J. Becher, *Chem. Soc. Rev.* **1994**, *23*, 41–51; b) M. Nielsen, C. Lomholt, J. Becher, *Chem. Soc. Rev.* **2000**, *29*, 153–164; c) M. Iyoda, M. Hasegawa, Y. Kuwatani, H. Nishikawa, K. Fukami, S. Nagase, G. Yamamoto, *Chem. Lett.* **2001**, 1146–1147; d) M. Giffard, G. Mabon, E. Leclair, N. Mercier, M. Allain, A. Gorgues, P. Molinie, O. Neilands, P. Krief, V. Khodorkovsky, *J. Am. Chem. Soc.* **2001**, *123*, 3852–3853; e) V. Khodorkovsky, L. Shapiro, P. Krief, A. Shames, G. Mabon, A. Gorgues, M. Giffard, *Chem. Commun.*, **2001**, 2736–2737; f) M. Iyoda, M. Hasegawa, Y. Miyake, *Chem. Rev.* **2004**, *104*, 5085–5113; g) J. O. Jeppesen, M. B. Nielsen, J. Becher, *Chem. Rev.* **2004**, *104*, 5115–5131; h) D. V. Konarev, S. S. Khasanov, G. Saito, A. Otsuka, R. N. Lyubovskaya, *J. Mater. Chem.* **2007**, *17*, 4171–4177.

[6] a) M. R. Bryce, *Chem. Soc. Rev.* **1991**, *20*, 355–390; b) D. Jerome, *Chem. Rev.* **2004**, *104*, 5565–5591; c) R. Lortz, Y. Wang, A. Demuer, P. H. M. Bottger, B. Bergk, G. Zwicknagl, Y. Nakazawa, J. Wosnitza, *Phys. Rev. Lett.* **2007**, *99*, 187002.

[7] a) C. P. Collier, G. Mattersteig, E. W. Wong, Y. Luo, K. Beverly, J. Sampaio, F. M. Raymo, J. F. Stoddart, J. R. Heath, *Science* **2000**, *289*, 1172–1175; b) H. Yu, Y. Luo, K. Beverly, J. F. Stoddart, H.-R. Tseng, J. R. Heath, *Angew. Chem.* **2003**, *115*, 5884–5889; *Angew. Chem. Int. Ed.* **2003**, *42*, 5706–5711; c) J. W. Choi, A. H. Flood, D. W. Steuerman, S. Nygaard, A. B. Braunschweig, N. N. P. Moonen, B. W. Laursen, Y. Luo, E. DeIonno, A. J. Peters, J. O. Jeppesen, K. Xu, J. F. Stoddart, J. R. Heath, *Chem. Eur. J.* **2006**, *12*, 261–279; d) K. A. Nielsen, W.-S. Cho, J. Lyskawa, E. Levillain, V. M. Lynch, J. L. Sessler, J. O. Jeppensen, *J. Am. Chem. Soc.* **2006**, *128*, 2444–2451; e) S. Nygaard, B. W. Laursen, A. H. Flood, C. N. Hansen, J. O. Jeppesen, J. F. Stoddart, *Chem. Commun.* **2006**, 144–146; f) S. Nygaard, K. C.-F. Leung, I. Aprahamian, T. Ikeda, S. Saha, B. W. Laursen, S.-Y. Kim, S. W. Hansen, P. C. Stein, A. H. Flood, J. F. Stoddart, J. O. Jeppesen, *J. Am. Chem. Soc.* **2007**, *129*, 960–970; g) S. Nygaard, B. W. Laursen, T. S. Hansen, A. D. Bond, A. H. Flood, J. O. Jeppesen, *Angew. Chem.* **2007**, *119*, 6205–6209; *Angew. Chem. Int. Ed.* **2007**, *46*, 6093–6097; h) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi, A. Credi, *J. Am. Chem. Soc.* **2007**, *129*, 12159–12171.

[8] A. Y. Ziganshina, Y. H. Ko, W. S. Jeon, K. Kim. *Chem. Commun.* **2004**, 806–807.

[9] M. Yoshizawa, K. Kumazawa, M. Fujita, *J. Am. Chem. Soc.* **2005**, *127*, 13456–13457.

[10] S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2007**, *129*, 828–838.

[11] a) C.-W. Chen, H. W. Whitlock, *J. Am. Chem. Soc.* **1978**, *100*, 4921–4922; b) S. C. Zimmerman, K. W. Saionz, *J. Am. Chem. Soc.* **1995**, *117*, 1175–1176; c) O. A. Matthews, F. M. Raymo, J. F. Stoddart, A. J. P. White, D. J. Williams, *New J. Chem.* **1998**, *22*, 1131–1134; d) A. E. Rowan, J. A. A. W. Elemans, R. J. M. Nolte, *Acc. Chem. Res.* **1999**, *32*, 995–1006; e) H. Kurebayashi, T. Haino, S. Usui, Y. Fukazawa, *Tetrahedron* **2001**, *57*, 8667–8674; f) H. M. Colquhoun, Z. Zhu, D. J. Williams, *Org. Lett.* **2003**, *5*, 4353–4356; g) J. N. H. Reek, J. A. A. W. Elemans, R. de Gelder, P. T. Beurskens, A. E. Rowan, R. J. M. Nolte, *Tetrahedron* **2003**, *59*, 175–185; h) H. M. Colquhoun, Z. Zhu, *Angew. Chem.* **2004**, *116*, 5150–5155; *Angew. Chem. Int. Ed.* **2004**, *43*, 5040–5045; i) A. Wu, P. Mukhopadhyay, A. Chakraborty, J. C. Fettinger, L. Isaacs, *J. Am. Chem. Soc.* **2004**, *126*, 10035–10043; j) F.-G. Klaerner, B. Kahlert, R. Boese, D. Blaeser, A. Juris, F. Marchioni, *Chem. Eur. J.* **2005**, *11*, 3363–3374; k) G. Fukuhara, S. Madenci, J. Polkowska, F. Bastkowski, F.-G. Klaerner, Y. Origane, M. Kaneda, T. Mori, T. Wada, Y. Inoue, *Chem. Eur. J.* **2007**, *13*, 2473–2479.

[12] a) J. N. H. Reek, A. Kros, R. J. M. Nolte, *Chem. Commun.* **1996**, 245–247; b) J. N. H. Reek, A. E. Rowan, R. de Gelder, P. T. Beurskens, M. J. Crossley, S. de Feyter, F. de Schryver, R. J. M. Nolte, *Angew. Chem.* **1997**, *109*, 396–399; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 361–363; c) J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *Ind. Eng. Chem. Res.* **2000**, *39*, 3419–3428; d) Z.-G. Wang, B.-H. Zhou, Y.-F. Chen, G.-D. Yin, Y.-T. Li, A.-X. Wu, L. Isaacs, *J. Org. Chem.* **2006**, *71*, 4502–4508; e) Y. Chen, N. She, X. Meng, G. Yin, A. Wu, L. Isaacs, *Org. Lett.* **2007**, *9*, 1899–1902.

[13] a) P.-T. Chiang, P.-N. Cheng, C.-F. Lin, Y.-H. Liu, C.-C. Lai, S.-M. Peng, S.-H. Chiu, *Chem. Eur. J.* **2006**, *12*, 865–876; b) K.-W. Cheng, C.-C. Lai, P.-T. Chiang, S.-H. Chiu, *Chem. Commun.* **2006**, 2854–2856.

[14] a) A. P. H. J. Schenning, B. de Bruin, A. E. Rowan, H. Kooijman, A. L. Spek, R. J. M. Nolte, *Angew. Chem.* **1995**, *107*, 2288–2289; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2132–2134; b) P. R. Carlier, *Angew. Chem.* **2004**, *116*, 2654–2657; *Angew. Chem. Int. Ed.* **2004**, *43*, 2602–2605.

[15] Although there are three other dicationic dimers that can be drawn if the positive charges are considered as localized on specific TTF

units, the delocalized model was suggested by our subsequent experiments. Thus, we use the notation $[\mathbf{1}\supset\mathbf{1}]^{2\cdot 2+}$ to represent this state.

[16] There is one other tricationic dimer that can be drawn if the positive charges are considered as localized on specific TTF units.

[17] a) B. Badgaer, B. Brocklehurst, B. *Nature* **1968**, *219*, 263–265; b) J. B. Torrance, B. A. Scott, B. Welber, F. B. Kaufman, P. E. Seiden, *Phys. Rev. B* **1979**, *19*, 730–741; c) T. Kitahara, M. Shirakawa, S.-I. Kawano, U. Beginn, N. Fujita, S. Shinkai, *J. Am. Chem. Soc.* **2005**, *127*, 14980–14981.

[18] The oxidation of TTF derivatives has been performed by using $[(p\text{-BrPh})_3N][SbCl_6]$ as the oxidizing agent; see: a) E. Steckhan, *Top. Curr. Chem.* **1987**, *142*, 1–69; b) H.-R. Tseng, S. A. Vignon, J. F. Stoddart, *Angew. Chem.* **2003**, *115*, 1529–1533, *Angew. Chem. Int. Ed.* **2003**, *42*, 1491–1495; c) M. Guerro, T. Roisnel, P. Pellon, D. Lorcy, *Inorg. Chem.* **2005**, *44*, 3347–3355; in this study, however, we required a stronger oxidant, $[(2,4\text{-Br}_2C_6H_3)_3N][SbCl_6]$, to ensure that the TTF units could be oxidized to their dicationic states; for more details regarding this oxidizing agent, see: d) W. Yueh, N. L. Bauld, *J. Am. Chem. Soc.* **1995**, *117*, 5671–5676; e) N. G. Connelly, W. E. Geiger, *Chem. Rev.* **1996**, *96*, 877–910.

[19] We also performed these chemical oxidations in CH_2Cl_2 and THF; the mixed-valence absorptions shifted only slightly, to 1670 and 1630 nm, respectively. Because the NIR absorption is largely unaffected by the solvent polarity, the mixed-valence state of the clip dimers appears to belong to the delocalized model. For more details regarding the delocalization model, see: a) B. S. Brunschwig, N. Sutin, *Coord. Chem. Rev.* **1999**, *187*, 233–254; b) B. S. Brunschwig, N. Sutin in *Electron Transfer in Chemistry, Vol. 2* (Ed.: V. Balzani), Wiley, New York, **2001**, pp. 583–617; c) D. M. D'Alessandro, A. C. Topley, M. S. Davies, R. F. Keene, *Chem. Eur. J.* **2006**, *12*, 4873–4884.

Received: February 2, 2008