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Palladium Induced Macrocyclic Preorganization for Stabilization of a Tetrathiafulvalene Mixed-Valence Dimer

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ABSTRACT

Ditopic metalation of a flexible "Pacman"-like tetrathiafulvalene (TTF) modified Schiff-base-calixpyrrole results in the stabilization upon oxidation of an otherwise difficult-to-access mixed-valence TTF radical dimer. EPR and optical spectroscopies were used to characterize the mixed-valence species.

Flexible ligands and macrocycles, such as calixarenes,[1] foldamers,[2] and molecular capsules,[3] have garnered considerable attention for their ability to stabilize otherwise fragile supramolecular constructs via substrate-induced conformational changes. The Schiff-base calixpyrrole[4] **1** is emerging as a noteworthy dynamic macrocycle capable of stabilizing novel coordination environments through its ability to undergo changes in its geometry so as to accommodate various transition metals,[5] lanthanides,[6a] or actinides.[6a−c] The underlying metal-mediated conformational changes have also been exploited to preorganize the

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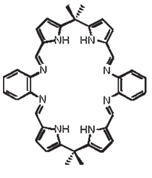
macrocyclic cleft for oxygen reduction catalysis,[7] uranyl reduction,[8] and encapsulation of magnesium hydroxide cubanes.[9] However, as of yet, this macrocycle has not been exploited to stabilize unstable or difficult-to-access organic species. Here we report the synthesis of a new tetrathiafulvalene (TTF) annulated derivative of **1** (compound **2**) and its use in stabilizing the mixed-valence (MV) radical dimer $[TTF_2]^{\bullet+}$.

Recently, efforts have been made to control the weakly associated electronic communication between tetrathiafulvalene (TTF) π-faces. One motivation for this work is the appreciation that an appropriate organization of two disparate TTF subunits may allow access to, and stabilization of, the organic MV radical species $[TTF_2]^{\bullet+}$ formed through partial oxidation. These MV dimers, which mimic the active species implicated in solid-state TTF-based conductive materials,[10] may provide a stepping stone toward the development of advanced organic conducting materials or complex supramolecular switches.[11]

To date, several strategies have been developed in an effort to make and study the MV state produced through oxidation of interacting TTF moieties. Elegant examples include the use of self-assembled clips,[12] cages acting as hosts,[13] the covalent attachment of TTF moieties to appropriate cyclophanes or scaffolds,[14] as well as a combination of these strategies via the use of a "molecular flask" to mechanically stabilize the radical dimer.[15] Our group has recently shown that by using a fluxional TTF-calix[4]pyrrole, an appropriate electron acceptor, and simple tetrabutylammonium anions it is possible to assemble a capsule-like complex wherein internal electron transfer and stabilization of a MV state is favored.[11c] As described below, we have now discovered that complexation of Pd(II) cations can be used to control the conformation of a TTF modified Schiff-base calixpyrrole and thus bring together two TTF moieties to the point where the MV state is stabilized upon oxidation. The MV species produced in this way was characterized using both optical and EPR spectroscopies.



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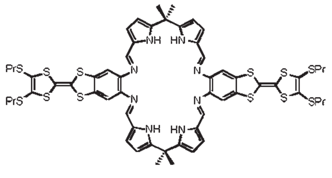

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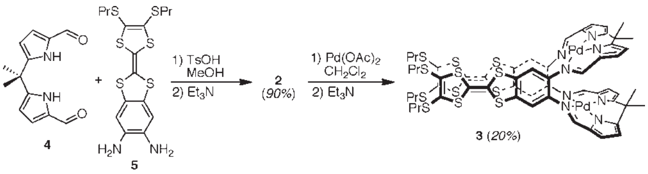
Scheme 1. Synthesis of TTF-Schiff-base Calixpyrrole **2** and bis-Pd(II) Complex **3**



The metal-free form of the TTF-Schiff-base calixpyrrole **2** was synthesized by condensing the known TTF phenylenediamine **4**[16] with diformyldipyrromethane **5** in the presence of *para*-toluenesulfonic acid (Scheme 1). Treatment of the suspended macrocyclic salt with triethylamine gave the free base Schiff-base macrocycle **2** as an orange precipitate in 90% yield. Reacting **2** with two equiv of palladium acetate in the presence of triethylamine then afforded complex **3** in a 20% yield.

It is well-known that upon formation of a binuclear complex with selected transition metal cations, such as Pd(II), the parent compound **1** switches its conformation from a flattened structure to a "Pacman"-like conformation in which the two o-aryl groups are π-stacked in a face-to-face fashion.[5g] It was anticipated that an analogous conformational "switching" would be observed as the free ligand **2** was converted to the corresponding bis-Pd(II) complex. Moreover, we envisioned that the extent of π-overlap would be greater in **3** as compared to the previously reported binuclear palladium complex of **1** due to the expanded nature of the π-surface.

Initial evidence for this conversion of **2** to **3** and the "Pacman"-like conformation of the latter species came from ^1H NMR spectroscopic measurements. In the spectrum of metal-free ligand **2**, recorded in $CDCl_3$ at room temperature, only one set of signals is visible for the propyl group hydrogen atoms, as would be expected for a species of high inherent symmetry. In contrast, the spectrum of **3** recorded under analogous conditions revealed the presence of a set of nonequivalent signals at 2.86 and 2.75 ppm corresponding to the propyl hydrogens (cf. Supporting Information). This latter nonequivalence is consistent with the presence of TTF subunits whose π-faces are proximate.

Support for this structural assignment came from a single crystal X-ray structure determination of **3**. The resulting structure (Figure 1) confirms that **3** does indeed

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adopt the expected “Pacman”-like cleft structure, at least in the solid state. In comparison to the parent compound **1**-Pd(II), the TTF-modified complex shows high coplanarity of the aryl planes and a small offset angle of 2.9° between the two aryl hinges. The intraplanar distance between the two TTF mean planes is a relatively short 3.65 Å. This latter observation led us to consider that in complex **3** these subunits would be preorganized for interaction in the form of a MV state following partial oxidation.

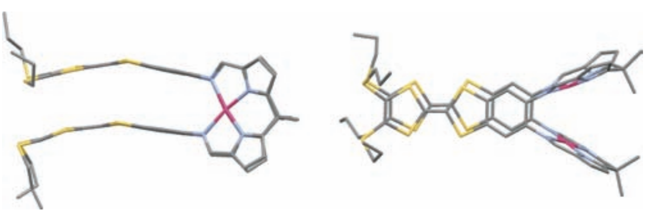

Figure 1. X-ray structure of $\mathbf{3}\cdot CH_2Cl_2$ (top and side views). Solvent and hydrogen atoms are omitted for clarity. Sulfur atoms are shown in yellow, nitrogen atoms in blue, carbon in gray and the palladium centers in magenta.

To determine if palladium coordination and the attendant TTF preorganization would enhance the stabilization of a putative MV state, the electrochemical behavior of **2** and **3** were compared in dichloromethane (0.25 mM) using cyclic voltammetry (CV). As can be seen from an inspection of Figure 2, the CV of the free-ligand **2** shows two reversible redox waves at 590 and 990 mV, respectively. On this basis, we infer that there is little if any interaction between the two donor TTF moieties. In contrast, the CV of **3**, also shown in Figure 2, reveals three reversible redox waves at 490, 600, and 1130 mV, respectively. Analysis of the peak heights leads us to infer that the first two-electron oxidation of **2** at 590 mV is split into two one-electron oxidations in **3**. To the extent that this assignment is correct, it is most easily rationalized in terms of a stabilizing interaction between the two TTF planes that is made possible by their proximity, which is in turn enforced by the “Pacman”-like conformation of this particular binuclear Pd(II) complex. More specifically, we propose that electronic communication between the two TTF moieties allows for stabilization of the first-formed radical and reduces the potential of the first oxidation step. The third sharp oxidation seen in the CV of **3** at 1130 mV is ascribed to a two-electron process that yields two dicationic TTF units. This oxidation process induces a destabilizing Coloumbic repulsion between the two doubly charged π-faces. This repulsion is enhanced due to the rigidly-enforced proximity of the oxidized TTF moieties in **3** and accounts for the fact that the potential for this two-electron oxidation process is higher in the binuclear Pd(II) complex **3** than it is in the free ligand **2**. Considered in concert, the remarkable differences between the electrochemical signatures of **2** and **3** provide support for the proposed stabilization of the MV state. They also serve to underscore the benefit of preorganization in stabilizing intramolecular TTF interactions.

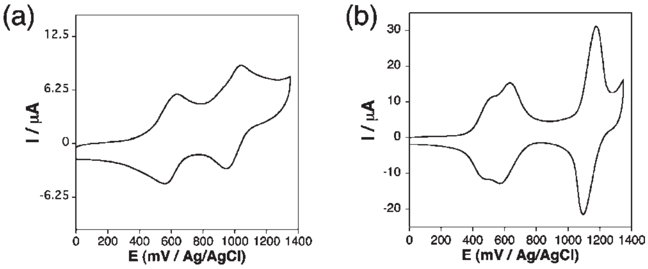

Figure 2. Cyclic voltammograms of (a) **2** and (b) **3** (0.25 mM) measured in CH_2Cl_2 using $TBA\cdot PF_6$ (0.2 M) as the supporting electrolyte, glassy carbon and Pt as the working and counter electrodes, respectively. Potentials were measured against a Ag/AgCl reference electrode at 100 mV/s.

To provide further support for the proposal that the two TTF moieties interact in **3** but not in **2**, room-temperature EPR titrations were carried out using the chemical oxidant tris(4-bromophenyl)aminium hexachloroantimonate (“Magic Blue”) (cf. Figure 3). Upon titration with oxidant, we observed marked differences between the two compounds. While the maximum EPR signal intensity is only seen after the free ligand **2** is treated with 2.0 equiv of oxidant (cf. Supporting Information), only 1.0 equiv of oxidant is required to reach this same maximum in the case of the Pd complex **3** (Figure 3a).

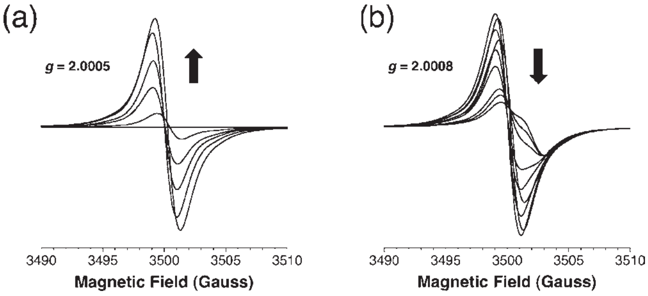

Figure 3. EPR spectra of **3** (0.2 mM in CH_2Cl_2, 295 K) recorded upon oxidation with (a) 0−1.0 equiv and (b) 1.0−4.0 equiv of “Magic Blue”.

We rationalize the above differences between **2** and **3** in structural terms. In **2**, the TTF units do not interact appreciably. Therefore, neither one is oxidized preferentially, and a full two equiv of oxidant are required to reach signal saturation. Addition of oxidant beyond 2.0 equiv leads to a reduction in the EPR signal intensity as the two TTF units are increasingly converted to the corresponding dicationic species, which are EPR silent.

In contrast, the EPR signal of **3** saturates after the addition of only 1.0 equiv of oxidant. We ascribe this result to the proximity between the TTF subunits, which allows for the preferential oxidation of only one TTF and the concomitant formation of a stabilized MV state. Addition of more oxidant equivalents, from 1.0 to 2.0 equiv, to **3** leads to a decrease in the TTF-radical signal, as would befit formation of the corresponding EPR silent spin-paired π-dimer $(TTF^{\bullet+})_2$.[14] Adding further oxidant, up to first 3.0 and then 4.0 equiv leads to further modifications in the EPR signal intensity as would be expected for the initial formation and then further oxidation of nonpaired radical species. However, as would be inferred from the CV analysis, which reveals a third redox process that is not split into two clear one-electron steps, the EPR changes induced by the addition of > 2.0 equiv of oxidant are not "clean" and thus difficult to interpret via a simple first-order analysis. Nevertheless, the key point, namely that a MV radical $(TTF_2)^{\bullet+}$ state is stabilized upon the addition of 1.0 equiv of oxidant, is fully supported by the EPR analyses of complex **3**.

It is well-known that the MV radical of TTF displays a characteristic absorbance centered between 1500 and 2500 nm.[17] Such an optical feature was thus expected when complex **3** was subject to oxidation but not when **2** was treated in the same way. The UV–vis–NIR spectra of both compounds were recorded upon titration with Magic Blue as was done in the case of the EPR titrations discussed above. As expected, when 0 to 1.0 equiv of this oxidant were added to a solution of **3** strong absorption features were seen to emerge at 925 and 2000 nm, respectively (cf. Figure 4). Further addition beyond 1.0 equiv led to a systematic disappearance of the absorption at 2000 nm ascribed to the MV state but continued growth of the peak at 925 nm. The continued growth of this latter signal and literature precedent[11c] leads us to assign the peak at 925 nm to the simple $TTF^{\bullet+}$ cation radical, which is in equilibrium with the MV state. In accord with this latter assignment, the spectrum of the free ligand **2** recorded in the presence of increasing quantities of oxidant is also characterized by a continued growth in the feature centered at 927 nm. However, in the case of this metal-free species, no MV signal is observed in the near-IR region.

More detailed examination of the electronic absorption spectra of **2** and **3** recorded in the presence of Magic Blue reveals slight differences in the 925 nm spectral region for the two species. Specifically, a broadening and slight splitting of this signal is seen in the case of palladium complex **3** but not for the free ligand **2**. Such a finding is in accord with the formation of a π –dimer, $(TTF^{\bullet+})_2$, in the case of **3**. This species, which has been shown to absorb between 740 and 1000 nm,[17] presumably exists in equilibrium with the monomeric radical cation, $TTF^{\bullet+}$, at appropriate oxidant concentrations. In contrast, in the case of **2**, it is the monomeric radical cation, $TTF^{\bullet+}$, that is formed under all conditions.

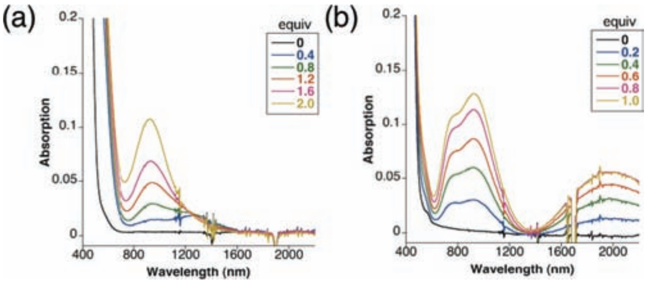

Figure 4. UV–vis–NIR spectra of (a) **2** and (b) **3** (0.20 mM in CH_2Cl_2) recorded upon stepwise addition of Magic Blue.

The absorption analysis of **2** and **3** were also measured in situ using spectroelectrochemistry (cf. Supporting Information). The free ligand and metal complex were subjected to gradual electrochemical oxidation from 0 to 850 mV at room temperature in dichloromethane. In this way, it proved possible to observe directly the absorbance change that occurs as the neutral TTF species are oxidized to ones that have undergone a loss of 2.0 electrons. The resulting UV–vis–NIR spectra show similar features as produced under the conditions of chemical oxidation processes shown in Figure 4. Specifically, the oxidized form of **2** produced in this way displays spectral features that are ascribable only to the production of a $TTF^{\bullet+}$ radical cation (absorbance centered around 925 nm). In contrast, electrochemical oxidation of **3** gives rise to a spectrum characterized by features at 2000 nm, ascribable to the expected MV state, as well as absorbances at ca. 925 nm characteristic of the $TTF^{\bullet+}$ and $(TTF^{\bullet+})_2$ radicals.

In summary, via ditopic metalation of a flexible macrocycle, **2**, we were able to bring together two otherwise independent TTF units and arrange them in such a manner that an MV radical state is stabilized upon oxidation. The remarkable difference in electronic structure between **2** and **3** that occurs upon the metalation-induced change in macrocyclic conformation was borne out via CV, EPR, and UV–vis–NIR studies. Work is currently underway in our laboratory to study the effect of varying the metal on the inter-TTF interactions and also developing more rigid aryl hinges that might allow for the stabilization of other, non-TTF derived MV states.

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Supporting Information Available. Experimental procedures and the characterization data for all new compounds and X-ray data for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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