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A Terthiophene-Containing Alkynylplatinum Terpyridine Pacman Complex: Controllable Folding/Unfolding Modulated by Weak Intermolecular Interactions

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Supporting Information

ABSTRACT: Folded and unfolded solid-state structures of a bimetallic alkynylplatinum terpyridine complex with a flexible terthiophene linker have been obtained. Weak intermolecular interactions including $\pi-\pi$ stacking and C−H···O and C−H···Cl interactions as well as Cl−π interactions stabilize the folded structure. In solution, folding is studied by electronic absorption spectroscopy and ^{1}H and NOESY NMR experiments.

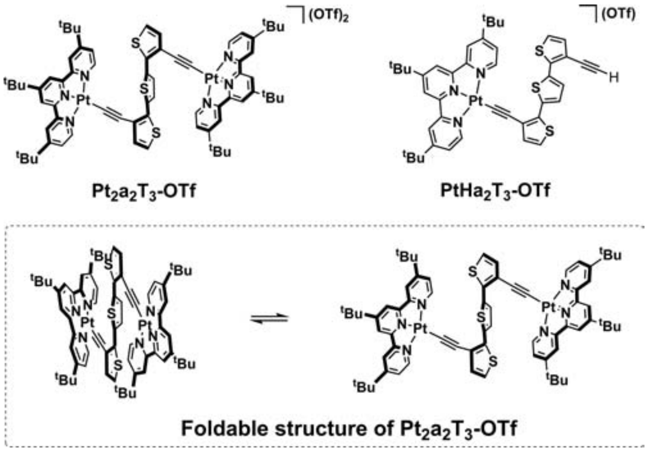
Functional oligothiophenes have attracted attention for their application in organic light-emitting devices, organic photovoltaic cells, and chemical/biological sensors.[1] Conformational control of the conjugated backbone is critical to the functionality of these molecules because the effective π-conjugation length is determined by torsion along the backbone.[2] Stimuli-responsive torsion of oligothiophene backbones is interesting because it allows access to variable conjugation lengths in the backbone, thus providing control over the electronic and photophysical properties. Photoisomerizable moieties,[3] cation binding sites,[4] and switchable transition-metal centers[5] have all been introduced to oligothiophene backbones to alter the conformation in different physical or chemical environments. Approaches that utilize supramolecular interactions to achieve this, however, have scarcely been explored, with only a few reported cases to date.[6] Differing molecular packing modes as a result of altered oligothiophene backbone conformation have rarely been studied, even though packing can have a profound impact on the performance of bulk optoelectronic molecular materials.[7]

Recently, planar alkynylplatinum terpyridine complexes have been explored as tools to encourage reversible aggregation via their $\pi-\pi$ stacking propensities. The aggregate-dependent spectroscopic (NMR, UV−vis, and luminescence) properties of these complexes can be used to report aggregation.[8] Attaching alkynylplatinum terpyridine end groups to flexible organic ligands such as *m*/*o*-phenyleneethynylene oligomers, Yam et al.[9] and Che et al.[10] were able to obtain solvent-dependent and temperature-responsive materials that form folded/helical structures under certain conditions. Other metal groups have been previously used to template the folding of oligoamides[11] and other systems.[12]

Herein, we report a foldable oligothiophene-containing metal complex based on a terthiophene ligand that tethers two alkynylplatinum terpyridine moieties. Solid-state crystal structures with the coplanar alkynylplatinum terpyridine moieties folded and unfolded, leading to torsion of the flexible terthiophene linker, are obtained. The "Pacman-like" behavior of this complex is studied in solution by ^{1}H and NOESY NMR and UV−vis absorption spectroscopy.

The bimetallic and monometallic complexes shown in Scheme 1 were synthesized in good yields from terthiophene-based ligand $H_2a_2T_3$ and [(^{t}Bu$_3$tpy)PtCl](OTf) [see the Supporting Information (SI) for details]. Two crystal structures of the bimetallic complex were obtained: one from acetonitrile ($Pt_2a_2T_3$-OTf·3CH$_3$CN) and a second from a chloroform solution ($Pt_2a_2T_3$-OTf·5CHCl$_3$) (Figure 1).

Scheme 1. Structures of $Pt_2a_2T_3$-OTf and $PtHa_2T_3$-OTf



In the structure of the folded complex crystallized from acetonitrile (Figure 1a), the thiophene rings adopt S−C−C−S torsion angles of 172.35° and 153.70°, slightly twisted from an all-trans conformation. The spatial proximity of the two terminal alkynes allows the two alkynylplatinum terpyridine moieties to be almost parallel to each other with a small dihedral angle of only 1.89° between planes (Figure 1a). The bulkiness of the peripheral *tert*-butyl groups on the pyridine rings prevents the terpyridine planes from strongly π-stacking (interplane distance = 3.62−4.06 Å); however, the pyridine rings interact strongly with the closest alkynyl groups (distance = 3.34 and 3.52 Å), suggesting that the latter contributes to stronger $\pi-\pi$ interactions in this folded structure. The side

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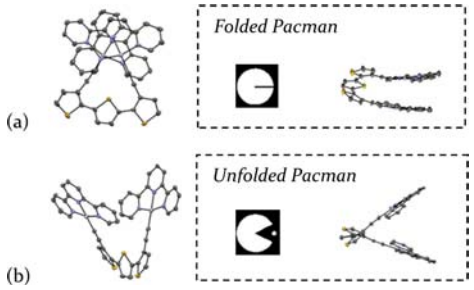

Figure 1. (a) Structure of one of the "folded" $Pt_2a_2T_3$-OTf molecules in the crystal obtained from acetonitrile. (b) Structure of "unfolded" $Pt_2a_2T_3$-OTf obtained from chloroform. Hydrogen atoms, *tert*-butyl groups, and solvent molecules have been omitted for clarity in both cases. Thermal ellipsoids are drawn at 50% probability.

view of this structure resembles a closed Pacman figure (Figure 1a, right). By contrast, the structure obtained from chloroform is similar to an open Pacman (Figure 1b, right). The thiophene rings in the unfolded $Pt_2a_2T_3$-OTf·$5CHCl_3$ structure are further twisted from the all-trans conformation with S−C−C−S torsion angles of 144.82° and 143.76°. The two terpyridine planes in the molecule open up in the unfolded structure, resulting in a dihedral angle of 58.98°. As a result, no intramolecular $\pi-\pi$ interaction is observed in this case, and an open cavity is created between the terpyridine planes (Figure 1b).

Interestingly, one of the $CHCl_3$ molecules in the $Pt_2a_2T_3$-OTf·$5CHCl_3$ structure is captured in the open cavity of the Pacman structure and anchored to the cation by the triflate counterion with C−H···O hydrogen bonds (Figure 2a).[13] The remaining four solvent molecules form a network of weak C−H···Cl hydrogen bonds,[14] with two of them connected to the triflate counterion by C−H···O hydrogen bonds.[15] Two different modes of Cl−π interactions are present in the structure,[16] an edge-on mode with Cl···C contacts and a face-on mode with a short Cl-to-centroid distance (Figure 2b).[17] Some disorder is found in the $Pt_2a_2T_3$-OTf·$3CH_3CN$ structure in both solvent molecules and the *tert*-butyl groups. By contrast, in the $Pt_2a_2T_3$-OTf·$5CHCl_3$ structure, there are five $CHCl_3$ molecules surrounding each bimetallic cation, and all of the solvent molecules, cations, and anions are highly ordered (Figure 2a). The open Pacman structure appears to be stabilized by these weak intermolecular C−H···O and C−H···Cl hydrogen bonds and Cl−π interactions. Together, these weak interactions are sufficient to overwhelm the tendency of terthiophene to maintain coplanarity between rings and the $\pi-\pi$ interactions that keep the structure closed in the $Pt_2a_2T_3$-OTf·$3CH_3CN$ crystals. Recently, Cl−π interactions have been recognized as important in biology;[16,18] however, we present here a case where this interaction is shown to be involved in the conformation of a synthetic foldable structure.

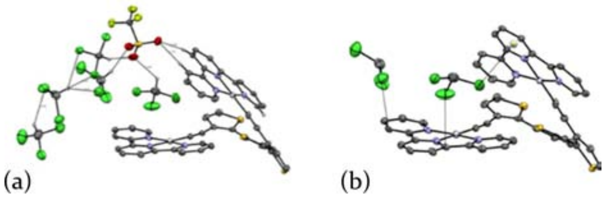

Figure 2. (a) C−H···O and C−H···Cl hydrogen bonds in the crystal structure of $Pt_2a_2T_3$-OTf·$5CHCl_3$. (b) Cl−π interactions in the same structure.

The two different conformations of the Pacman molecules also result in changes in molecular packing. In the $Pt_2a_2T_3$-OTf·$3CH_3CN$ structure (Figure S1a,b in the SI), identical molecules form chiral helical columns, in which each molecule is rotated 120° about the *c* axis with respect to the one above it. Moreover, columns with the same chirality organize into a hexagonal packing arrangement, in which only one of the stereoisomers of the bimetallic complex is found. In the $Pt_2a_2T_3$-OTf·$5CHCl_3$ structure, however, the bimetallic complex forms infinite zigzag chains with racemic molecules (Figure S1c,d in the SI). This may be driven by intermolecular $\pi-\pi$ interactions between head-to-tail-stacked alkynylplatinum pyridine moieties (shortest interplane distance ~3.35 Å), which are weaker in the helical structure.

The monometallic complex $PtHa_2T_3$-OTf is bright orange in an acetonitrile solution. The UV−vis absorption spectra in $CHCl_3$, to which an increasing amount of CH_3CN is added (Figure 3a), show an intense absorption feature at 300−350 nm assigned to intraligand $\pi \rightarrow \pi^*$ transitions of the terpyridyl and alkynyl moieties. Features between 350 and 450 nm are attributed to $\pi \rightarrow \pi^*$ transitions of terthiophene. The low-energy band between 450 and 600 nm is assigned as a MLCT/LLCT (mixed metal-to-ligand charge-transfer and alkynyl-to-terpyridine ligand-to-ligand charge-transfer) transition. This band blue-shifts as increasing amounts of CH_3CN are added to the $CHCl_3$ solution. This negative solvatochromism is typically observed in alkynylplatinum(II) terpyridine complexes because the excited state is less polar than the ground state.[9,10,19]

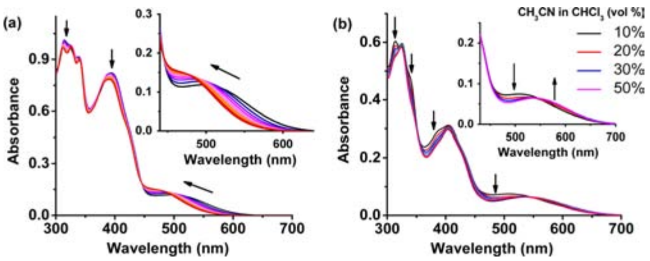

Figure 3. (a) UV−vis absorption spectra of $PtHa_2T_3$-OTf in $CHCl_3$ with increasing percentage of CH_3CN added (from 0% to 100%, 5×10^{-5} M). The inset shows the shift in the low-energy MLCT/LLCT absorbance band. (b) UV−vis absorption spectra of $Pt_2a_2T_3$-OTf in $CHCl_3$ with increasing percentage of CH_3CN added (from 0% to 100%, 2×10^{-5} M). The inset shows the change in the low-energy absorbance band with an isosbestic point at ~550 nm.

The absorption spectra of the bimetallic complex $Pt_2a_2T_3$-OTf show significantly different behavior as a function of the solvent composition. With increasing amounts of acetonitrile added to $CHCl_3$, the MLCT/LLCT absorption at 510 nm decreases while a new feature grows in at 530 nm, showing a clear isosbestic point (inset, Figure 3b). Interestingly, this feature still shows subtle negative solvatochromism when the percentage of CH_3CN present is greater than 50% (Figure S2 in the SI), indicating that this new feature still maintains its MLCT/LLCT character. Intermolecular aggregation can be ruled out as an explanation for this behavior because the extinction coefficient of this absorbance remains constant from 1.14 to 100 μM (Figure S3 in the SI). Similar phenomena have also been reported in other diplatinum complexes with flexible linkages,[9,10] and this behavior is consistent with the formation of a folded structure in solution. The absorbance of the $\pi \rightarrow \pi^*$ (alkynyl) shoulder at 340 nm, and the $\pi \rightarrow \pi^*$ (terthiophene) transition at 380 nm, decreases with the addition of increasing amounts of CH_3CN to $CHCl_3$. Both of these changes are not observed in the monometallic complex and are consistent with conformational changes of the ligand resulting from the formation of the closed Pacman structure in solution. No emission was observed in solution from $Pt_2a_2T_3$-OTf or $PtHa_2T_3$-OTf, possibly because of energy-transfer quenching from a low-lying, ligand-based triplet state on the terthiophene moiety.

^1H NMR experiments were carried out to further investigate the molecular behavior in solution. The pyridine protons on the bimetallic complex appear at a lower chemical shift compared to those of the monometallic complex. They are also shifted upfield in CD_3CN relative to the signals in $CDCl_3$ (Figure S4 in the SI). This is typically observed in systems with $\pi-\pi$ interactions.[9,20] Furthermore, variable-temperature NMR experiments with the bimetallic complex showed no significant shift or broadening in $CDCl_3$. In CD_3CN, however, the pyridine protons are broadened and shifted upfield at lower temperatures, while the thiophene proton signals are only slightly altered (Figure S5 in the SI). These changes are consistent with the restricted rotation of the alkynylplatinum terpyridine moieties and stronger $\pi-\pi$ stacking. NOESY experiments of $Pt_2a_2T_3$-OTf show cross peaks between the *tert*-butyl protons and the thiophene protons in CD_3CN (Figure S6 in the SI), indicating the spatial proximity of these protons, which are absent in $CDCl_3$ (Figure S7 in the SI). An intermolecular origin of these cross peaks can be excluded because $PtHa_2T_3$-OTf does not show any of these cross peaks (Figure S8 in the SI). These results are consistent with the unfolding of the molecule in $CDCl_3$ and folding in CD_3CN, analogous to the conformations observed in the solid-state structures obtained from the respective solvents.

In conclusion, we have prepared a novel terthiophene-based alkynylplatinum terpyridine Pacman complex that exhibits reversible folding in both solution and the solid state. Reversible torsion of the flexible terthiophene backbone in response to changes in the solvent environment have been successfully achieved via the introduction of alkynylplatinum terpyridine moieties. Cl−π interactions, along with weak C−H hydrogen bonding, play a role in the folding/unfolding behavior of this synthetic foldable structure, one of the first observations of this behavior in a nonprotein structure.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic details, UV−vis absorption, variable-temperature ^1H and NOESY NMR spectra, crystallographic details, molecular packing diagrams, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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