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Complete List of Authors:	Wang, Denan; Marquette University, Department of Chemistry Ivanov, Maxim; Marquette University, Department of Chemistry Mirzaei, Saber; Marquette University, Department of Chemistry Lindeman, Sergey; Marquette University, Department of Chemistry Rathore, Rajendra; Marquette University, Department of Chemistry



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## An Electron-Transfer Induced Conformational Transformation: From Non-Cofacial "Sofa" to Cofacial "Boat" in Cyclotetramertrylene (CTTV) and Formation of Charge Transfer Complexes

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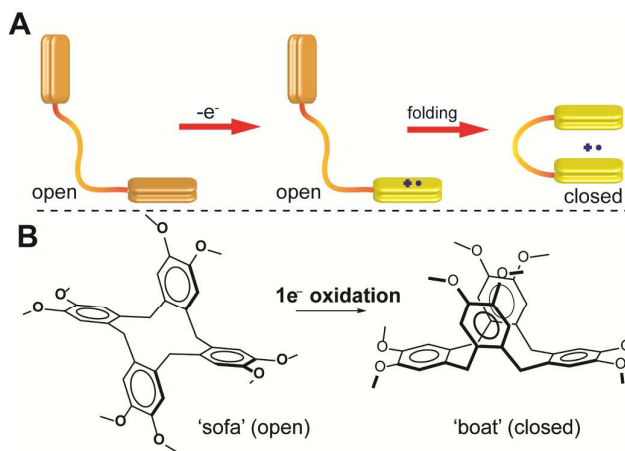
Denan Wang<sup>\*a</sup>, Maxim V. Ivanov<sup>a</sup>, Saber Mirzaei<sup>a</sup>, Sergey V. Lindeman<sup>a</sup> and Rajendra Rathore<sup>b</sup>

**Electro-active polychromophoric assemblies that undergo clam-like electromechanic actuation represent an important class of organic functional materials. Here, we show that the readily available cyclotetramertrylene (CTTV) undergoes oxidation-induced folding, consistent with interconversion from a non-cofacial "sofa" conformation to a cofacial "boat" conformer. It is found that the non-cofacial "sofa" conformer of CTTV forms stable electron donor-acceptor complexes with chloranil and DDQ. Electron-transfer induced conformational transformation in CTTV provides a framework for the rational design of novel organic functional molecules.**

The design and synthesis of organic functional molecules is critically important for numerous practical applications, such as molecular sensors, molecular switches, nonlinear optical materials, etc.<sup>1-10</sup> Among the various classes of functional materials, molecular actuators have attracted significant attention. Typically, a molecular actuator exhibits dramatic conformational changes when triggered by an external stimulus (e.g., heat, light, metal ion binding, or electron transfer), leading to a modulation in their physical properties (e.g. color, spin, electrical conductivity, and optical properties).

Among various external stimuli, electron transfer is of particular importance, especially in the case conformationally mobile bichromophores that can adopt a  $\pi$ -stacked arrangement of its chromophores. Extensive studies have established that upon ionization, charge-resonance stabilization of the cationic charge (i.e., hole) is dependent on the orbital overlap between the aromatic moieties of two chromophores.<sup>11,12</sup> Because orbital overlap is maximal when the chromophores are perfectly sandwiched,<sup>11</sup> many conformationally mobile chromophores undergo oxidation-induced actuation from "open" to "closed" conformation as schematically depicted in Fig. 1A.

Many examples of molecular actuators are available in the literature<sup>5-7, 13-15</sup> and here we seek to identify whether readily available<sup>16-19</sup> cyclotetramertrylene (CTTV, Fig. 1B) can undergo oxidation-induced actuation. Past studies have established that conformationally mobile CTTV at the neutral state prefers "sofa" conformation and not "boat" or "crown" conformations. Considering that the closed conformation of CTTV contains a pair of cofacially-arrayed aromatic rings well-suited for the efficient hole stabilization, in this work we question whether CTTV would undergo oxidation-induced actuation from the (open) "sofa" to (closed) "boat" conformation.



**Fig. 1.** A. Schematic illustration of the electron-transfer-induced conformational transformation. B. Illustration of the oxidation-induced folding from (open) 'sofa' or (closed) 'boat' CTTV.

Accordingly, here we demonstrate with the aid of electrochemistry, generation of CTTV cation radical, and DFT calculations that in solution CTTV indeed undergoes (electro)chemical actuation as depicted in Fig. 1B. Furthermore, we show that CTTV effectively binds chloranil (i.e., CA) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (i.e., DDQ), forming electron donor-acceptor (EDA) complexes as shown via optical spectroscopy and X-ray crystallography. The latter showed that in the crystal structures of both EDA complexes, the CTTV molecule exists in open conformation, which allows a maximum number of cofacial  $\pi$ - $\pi$  contacts between the

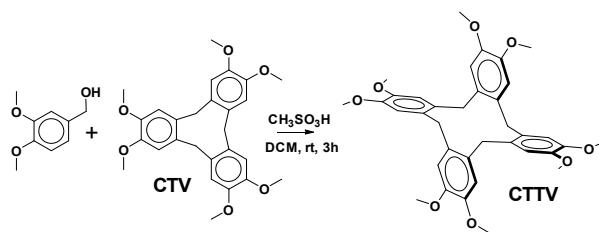
<sup>a</sup> Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, WI 53201-1881. E-mail: denan.wang@marquette.edu.

<sup>b</sup> Deceased February 16, 2018

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aromatic moieties of **CTTV** and the aromatic acceptors. These findings underscore the importance of local environment in promoting oxidation-induced actuation and contribute to the design of novel organic functional molecules based on oxidation-induced mechanical actuation.

As first reported by White and Gesner, starting with veratryl alcohol in glacial acetic acid containing a few drops of concentrated sulfuric acid as catalyst, a mixture of cyclotrimeratrylene (**CTV**, 68%) and **CTTV** (16%) can be generated by the cyclo-oligomerization reaction.<sup>19</sup> With the aim of selective production of **CTTV**, we employed (Scheme 1) methanesulfonic acid as catalyst and stirred the reaction mixture containing one equivalent of cyclotrimeratrylene (**CTV**) and three equivalent of veratryl alcohol at room temperature for 3 hours, which afforded **CTTV** in excellent yield (>70%); see ESI for full experimental details and complete characterization data.



Scheme 1. Synthesis of cyclotetrameratrylene (**CTTV**).

Past studies using X-ray crystallography and variable temperature <sup>1</sup>H NMR (VT-NMR) have shown that **CTTV** and its derivatives prefer open conformation, although the closed conformation may be energetically similar.<sup>16, 18-23</sup> Here, in order to confirm these findings we performed VT-NMR experiment in CD<sub>2</sub>Cl<sub>2</sub> solution. As shown in Fig. 2A the NMR spectrum at 20 °C displays two broad signals at 6.60 and 3.72 ppm with the ratio of integration 1:4, respectively. Upon cooling to -80 °C, the aromatic signal separated into two equivalent sharp singlet signals at 6.82 and 6.22 ppm, while the peak from the methylene proton split into two doublets at 3.18 and 3.77 ppm. In addition, two sharp singlet signals at 3.48 and 3.85 were observed that were assigned to the methoxy groups. Simulation of the <sup>1</sup>H NMR spectra of open and closed conformations using DFT calculations confirmed that positions of the experimental peaks are consistent with the open conformation (Fig. 2B). Thus, broadening of the signals at room temperature corresponds to the interchange between multiple equivalent conformers of open **CTTV** via pseudo rotation of the methylene carbons (Fig. 2A). Note that temperature increase up to 60 °C did increase sharpness of the peaks without adding any new features (Fig. S2 in the ESI) suggesting that only one conformer of **CTTV** is present in solution.

In order to further confirm that open conformation is the most stable, we performed a conformational analysis of neutral **CTTV** using density functional theory (DFT) calculations. First, we note that the accurate description of the oxidation-induced actuation in such systems as **CTTV** presents a challenge for DFT.<sup>24</sup> Many standard density functionals do not include long-range dispersion interactions and therefore total energy of the closed conformation of an actuator may be overestimated.<sup>25</sup> In addition, self-interaction error often leads

to the underestimated oxidation potentials and artificially delocalized cation radical states.<sup>26, 27</sup> Finally, basis set superposition error is expected to be dependent on the conformation of the actuator.<sup>28</sup>

Recent benchmarking studies have demonstrated that standard B1LYP functional with 40% of Hartree-Fock exchange (i.e., B1LYP40) accurately reproduce oxidation potentials and the cation radical excitation energies of a variety of  $\pi$ -conjugated systems.<sup>29, 30</sup> Furthermore, another recent study showed that B1LYP40 accurately reproduces experimental binding energies of the van der Waals fluorene dimers, if the missing dispersion interactions are accounted for using the empirical Grimme's D-3 term.<sup>31</sup> Therefore, in this work we employed B1LYP40-D3/6-31G(d) level of theory with the solvent effects accounted via polarizable continuum model (PCM) with CH<sub>2</sub>Cl<sub>2</sub> parameters.

The calculations showed that among four different conformations, open **CTTV** is the lowest energy structure, lying 1.4 kcal/mol lower than the closed conformer (Fig. S10 and Table S2 in the ESI). While the energetic difference is small, this corresponds to 95.6% contribution of open **CTTV** at 22 °C according the Boltzmann distribution if entropic factor is included.

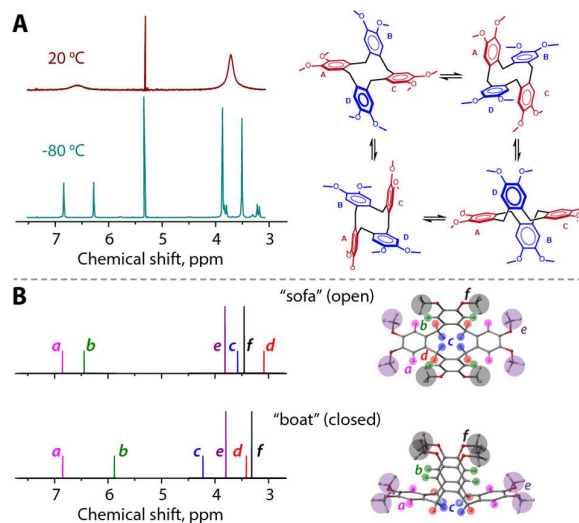
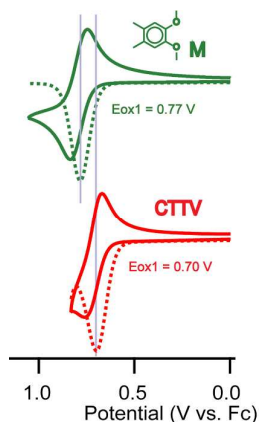


Fig. 2. A. <sup>1</sup>H NMR spectra of **CTTV** at 20 and -80 °C. Representative interconverting structures of open **CTTV** are shown on the right. B. <sup>1</sup>H NMR spectra of open and closed **CTTV** calculated using B1LYP40-D3/6-31G(d)+PCM(CH<sub>2</sub>Cl<sub>2</sub>).

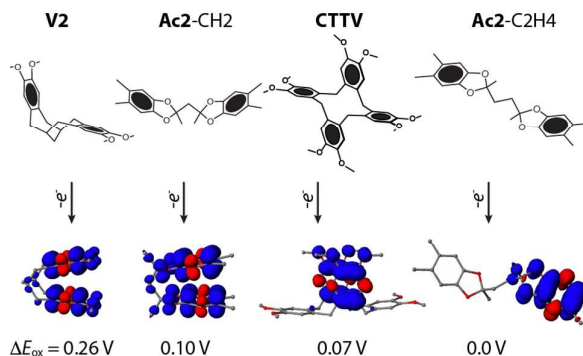
The electron donor strengths of **CTTV** and model monochromophoric compound 1,2-dimethoxy-4,5-dimethylbenzene (**M**) were evaluated by electrochemical oxidation at a platinum electrode as a 2.0×10<sup>-3</sup> M solution in dichloromethane containing 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte. The cyclic voltammogram (CV) of model compound **M** showed (Fig. 3) one reversible oxidation wave with the oxidation potential  $E_{ox} = 0.77$  V vs Fc/Fc<sup>+</sup>, while oxidation potential of **CTTV** was found to be 70 mV lower than **M**, i.e.,  $E_{ox}[\text{CTTV}] = 0.70$  V vs Fc/Fc<sup>+</sup>, signifying that structural and conformational reorganization occurs leading to the stabilization of the cationic charge.



**Fig. 3.** Cyclic voltammograms (CVs, solid lines) and square waves (SWs, dashed lines) of 2 mM **CTTV** (red color) and **M** (green color) in  $\text{CH}_2\text{Cl}_2$  (0.1 M  $n\text{-Bu}_4\text{NPF}_6$ ) at a scan rate  $100 \text{ mV s}^{-1}$ .

It has been established that at the cation radical state of a polyaromatic electron donor, charge-resonance stabilization is maximal when aromatic moieties adopt a perfect “sandwich-like” arrangement that allows for the maximal orbital overlap between the aromatic moieties.<sup>11,12</sup> Thus, many conformationally mobile actuators have been reported to undergo electromechanical actuation that is driven by the charge-resonance interactions. Yet, observed hole stabilization of 0.07 V in **CTTV** (i.e.,  $\Delta E_{\text{ox}} = E_{\text{ox}}[\text{M}] - E_{\text{ox}}[\text{CTTV}]$ ) is relatively small, especially considering that in *rigid* cofacially arrayed bichromophores hole stabilization may reach 0.35 V.<sup>32,33</sup> One has to note that although the enthalpy gain of a cofacial arrangement of two aromatic moieties may be indeed significant, the overall free energy gain depends also on the entropic contribution.<sup>1</sup> For example, a series of veratrole- and acetal-based actuators showed a varied hole stabilization from  $\Delta E_{\text{ox}} = 0.26 \text{ mV}$  to 0.0 V, underscoring the important role of the linker connecting two chromophores (Fig. 4).<sup>5,7,13</sup>

While actuators **V2** and **Ac2-CH2** shown in Fig. 4 show a significant hole stabilization with the hole delocalization over both chromophores, compound **Ac2-C2H4** does not display any stabilization with the hole localized on a single chromophore. In the case of **CTTV**, entropic penalty required to freeze (pseudo) rotation of the C-C bonds at four methylene groups upon its actuation, leads to a modest yet appreciable 70 mV stabilization with the hole delocalization over both chromophores. Finally, DFT calculations further confirmed that closed conformation is the global minimum structure at the cation radical state that lies 5.6 kcal/mol lower than open **CTTV**<sup>+</sup> (Table S4 in the ESI).

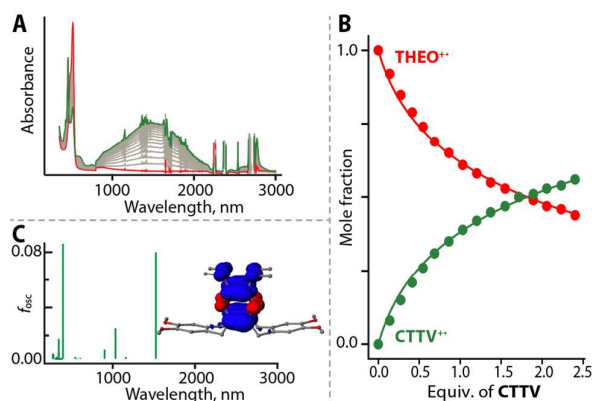


**Fig. 4.** Examples of the actuators<sup>5,7,13</sup> with varied hole stabilization ( $\Delta E_{\text{ox}}$ ) as indicated. Calculated [B1LYP40-D3/6-31G(d)+PCM( $\text{CH}_2\text{Cl}_2$ )] spin-density plots show extent of hole delocalization in each case.

In order to further support that **CTTV** undergoes oxidation-induced folding, we generated the cation radicals of **CTTV** via quantitative<sup>34</sup> redox titrations using stable cation-radical salt [**THEO**<sup>•+</sup>SbCl<sub>6</sub><sup>-</sup>] (1,4,5,8-dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxyanthracene hexachloroantimonate;  $E_{\text{red}} = 0.67 \text{ V vs Fc/Fc}^+$ ,  $\lambda_{\text{max}} = 518$ ,  $\epsilon = 7300 \text{ M}^{-1} \text{ cm}^{-1}$ , Fig. S3 in ESI) as one-electron aromatic oxidants in dichloromethane.<sup>32</sup> The redox titration experiment was carried out by an incremental addition of sub-stoichiometric amounts of the electron donor (i.e., **CTTV**) to the solution of an oxidant cation radical (i.e., **THEO**<sup>•+</sup>). The one-electron oxidation of **CTTV** to **CTTV**<sup>•+</sup> and reduction of **THEO**<sup>•+</sup> to **THEO** can be described by an equilibrium shown in eq. 1.



Treatment of the orange-red solution of **THEO**<sup>•+</sup> with increments of **CTTV** led to disappearance of the absorption bands of **THEO**<sup>•+</sup> at 518 nm and concomitant growth of a new sharp band at 460 nm and a broad featureless band at  $\sim 1500 \text{ nm}$  (Fig. 5A). Numerical deconvolution<sup>34</sup> of the absorption spectrum at each increment produced mole fractions of **THEO**<sup>•+</sup> and **CTTV**<sup>•+</sup> against the added equivalents of **CTTV** (Fig. 5B), confirming the redox reaction follows 1:1 stoichiometry as shown in eq. 1 without formation of **CTTV** dication or any biproducts. Unfortunately, repeated attempts to generate crystal of **CTTV**<sup>•+</sup> were unsuccessful due to the overnight decomposition of **CTTV**<sup>•+</sup> even at  $-30 \text{ }^\circ\text{C}$ .

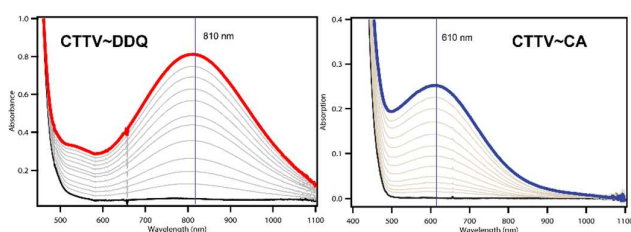


**Fig. 5.** A: Spectral changes observed upon the reduction of 0.051 mM **THEO**<sup>•+</sup> in  $\text{CH}_2\text{Cl}_2$  (3 mL) with sub-stoichiometric addition of 1.49 mM solution of **CTTV** in  $\text{CH}_2\text{Cl}_2$  at  $22 \text{ }^\circ\text{C}$ . B: Plot of the mole fractions of **THEO**<sup>•+</sup> (red) and **CTTV**<sup>•+</sup> (green)

against the added equivalents of neutral **CTTV**. Symbols represent experimental points, while the solid lines show best-fit to experimental points using  $\Delta G = E_{ox}(\text{CTTV}) - E_{red}(\text{THEO}^+) = 25 \text{ mV}$ . C. Electronic transitions of closed **CTTV**<sup>•+</sup> calculated using TD-B1LYP40-D3/6-31G(d)+PCM(CH<sub>2</sub>Cl<sub>2</sub>). Inset shows the isovalue plot of the spin-density distribution in **CTTV**<sup>•+</sup> calculated at B1LYP40-D3/6-31G(d) level of theory.

The presence of the intense absorption band at the near-IR region in **CTTV**<sup>•+</sup> indicates extensive through-space hole delocalization, suggesting that **CTTV**<sup>•+</sup> exists in the (cofacial) closed conformation. Indeed, a similar band at ~1500 nm has been previously reported in various other rigid veratrole-based cofacially-arrayed bichromophores.<sup>1, 5</sup> Furthermore, TD-DFT calculations confirmed that closed **CTTV**<sup>•+</sup> contains a strong transition at 1525 nm in full agreement with the experimental spectrum (Fig. 5C).

As the isolation of the **CTTV** cation radical was not feasible, we questioned whether the partial oxidation upon interaction with an acceptor molecule might lead to the interconversion into a closed conformation. Thus, next we examined the electron donor-acceptor (EDA) complexes of **CTTV** with acceptors of varied strength, i.e., chloranil (**CA**,  $E_{red} = 0.02 \text{ V}$  vs SCE)<sup>35</sup> and **DDQ** ( $E_{red} = 0.56 \text{ V}$  vs SCE)<sup>36, 37</sup>. Mixing of **CTTV** with **CA** or **DDQ** in dichloromethane solvent produced a yellowish or brownish colored solution, respectively, indicative of the formation of the EDA complex. Indeed, the UV-vis absorption spectra of the **CTTV**~**CA** and **CTTV**~**DDQ** EDA complexes showed a charge-transfer band at  $\lambda_{CT} = 610$  and  $810 \text{ nm}$ , respectively (Fig. 6). The quantitative analysis of the binding of **CA** and **DDQ** with **CTTV** in solution was carried out by spectrophotometric analysis, with absorbance data treated according to the Benesi-Hildebrand procedure<sup>38, 39</sup> (Fig. S3 in the ESI) to derive the values of association constants ( $K$ ), extinction coefficient ( $\epsilon_{CT}$ ), and the “effective absorbance” ( $K_{DA}\epsilon_{CT}$ ) of the EDA complexes (Table 1). Interestingly, the **CTTV**~**DDQ** EDA complex displays a high association constant  $K = 591 \text{ M}^{-1}$ , which is about 40 times higher than that of **CTTV**~**CA** complex, and is consistent with the varied electron acceptor strength of **DDQ** and **CA**.<sup>40</sup>



**Fig. 6.** Left: Spectral changes recorded upon the incremental addition of **CTTV** ( $6.0 \times 10^{-5} \text{ M}$ ) to **DDQ** ( $0.011 \text{ M}$ ) in dichloromethane. Right: Spectral changes recorded upon the incremental addition of **CTTV** ( $1.08 \times 10^{-3} \text{ M}$ ) to **CA** ( $0.022 \text{ M}$ ) in dichloromethane.

**Table 1.** Compilation of wavelength of CT band, association constants, extinction coefficient and “effective absorbance”

Acceptor	$\lambda_{CT}$ (nm)	$K_{DA}$ ( $\text{M}^{-1}$ )	$\epsilon_{CT}$ ( $\text{M}^{-1} \text{ cm}^{-1}$ )	$K_{DA}\epsilon_{CT}$
<b>DDQ</b>	810	591	2066	1,221,000
<b>CA</b>	610	15	347	5,205

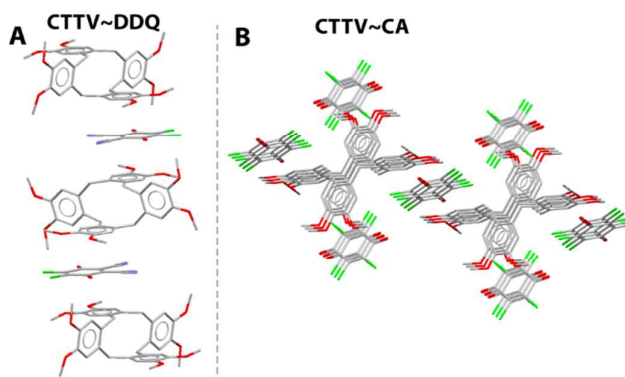
Large quantities of the EDA complexes **CTTV**~**DDQ**/**CTTV**~**CA** can be easily prepared by mixing the **CTTV** with **DDQ**/**CA** in chloroform or dichloromethane at room temperature. After careful layering with hexane and a slow

evaporation, X-ray quality single crystals were generated in good yield. Availability of the EDA complexes of **CTTV** with varied acceptors allowed a detailed elucidation of the role of acceptor on the structure of the EDA complex.

First, we note that the relative arrangement between **CTTV** and acceptor is distinct in **CTTV**~**DDQ** and **CTTV**~**CA** crystal structures (Fig. 7). In **CTTV**~**DDQ** crystal, **CTTV** and **DDQ** form one-dimensional arrays with 1:1 stoichiometry (Fig. 7A). Noteworthy, the mean plane of **DDQ** is almost parallel to two adjacent veratrole planes of the two neighbouring **CTTV** molecules. The short distances between the **DDQ** mean plane and centroids of the veratrole rings of 3.17 and 3.13 Å reflect the strength of the donor-acceptor interactions. Importantly, the distances of C<sub>Ar</sub>-O in the veratrole units that form contacts with **DDQ** are 0.8-1.1 pm shorter than those that are free from any contact, indicating an appreciable charge-transfer character in the formation of the EDA complexes.

Remarkably, the **CTTV**~**CA** complex exhibits completely different packing (Fig. 7B). Analysis of the crystal structure shows that multiple CH- $\pi$  interaction and  $\pi$ - $\pi$  interactions are established in the full net of the crystal. The crystal structure shows that each **CTTV** molecule is surrounded by four **CA** molecules, i.e., each **CA** molecule interacts with two **CTTV** molecules, which corresponds to a 1:2 stoichiometry. The **CA** molecules are tilted by 20.9°-14.2° towards the veratrole rings due to the C-H...Cl hydrogen-bond and C-H- $\pi$  interactions.

Finally, we note that open conformation of **CTTV** was found in both donor-acceptor complexes, as it allows a maximum number of cofacial  $\pi$ - $\pi$  contacts between the veratroles of **CTTV** and the aromatic moiety of the acceptors. According to Mulliken theory,<sup>35, 41</sup> the redox potential of the acceptor directly affects the strength of the interaction in the charge-transfer complex,<sup>20,25</sup> thereby explaining the difference in the acceptor-to-donor stoichiometry in the crystal structures of **CTTV**~**CA** and **CTTV**~**DDQ**.



**Fig. 7.** Packing diagrams of EDA complexes **CTTV**~**DDQ** (A) and **CTTV**~**CA** (B). (Thermal ellipsoids drawn at 50% probability, solvent molecules and hydrogen atoms removed for clarity).

## Conclusions

Motivated by the interest in identification of novel redox-controlled actuators, in this manuscript, we sought to identify whether readily available **CTTV** molecule undergoes a conformational reorganization from (open) “sofa” into a (closed) “boat” conformation upon electron ejection. Synthesis of **CTTV** via an improved synthetic approach followed by

electrochemical, spectroscopic and computational analyses showed that in the neutral state **CTTV** exists in the “sofa” conformation and upon oxidation undergoes interconversion into a “boat” conformation where a pair of cofacially-arrayed veratrole rings effectively stabilizes cationic charge via charge-resonance.

We further examined the electron donor-acceptor (EDA) complexes of **CTTV** with **CA** and **DDQ** using optical spectroscopy and X-ray crystallography. In the solid state, **CTTV** exists in a “sofa” conformation that is stabilized by the charge-transfer interaction with four and two acceptor molecules of **CA** and **DDQ**, respectively. We believe that these findings can be applied to the design and synthesis of novel organic functional molecules based on oxidation-induced mechanical actuation.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

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### Notes and references

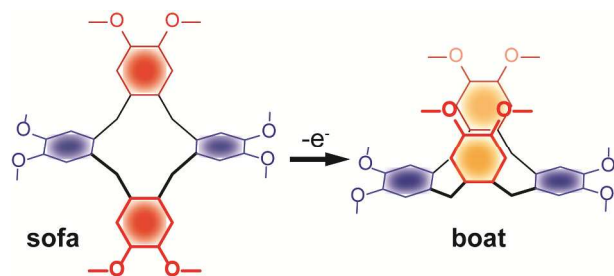
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## Table of Contents Entry



Cyclotetraveratrylene (CTTV) undergoes oxidation-induced folding, consistent with interconversion from a non-cofacial "sofa" conformation to a cofacial "boat" conformer.