Electronic Supplementary Information (ESI)

An electron-transfer induced conformational transformation: From noncofacial "sofa" to cofacial "boat" in cyclotetraveratrylene (CTTV) and formation of charge transfer complexes

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Table of contents

S1. General methods and Synthesis	2
S2. Variable Temperature ¹ H-NMR of CTTV	7
S3. Electrochemistry characterization of CTTV and model complexes	10
S4. Generation of CTTV ^{+*} by redox titrations	11
S5. Electron donor-acceptor (EDA) complexes of CTTV	12
S6. X-ray crystallography of EDA complexes	14
S7. Computational details	15
S8. References	18

S1. General methods and Synthesis

General methods: All reactions were performed under an argon atmosphere unless otherwise noted. All commercial reagents were used without further purification unless otherwise noted. Dichloromethane (Aldrich) was repeatedly stirred with fresh aliquots of concentrated sulfuric acid (~10 % by volume) until the acid layer remained colorless. After separation, CH₂Cl₂ layer was washed successively with water, 5% aqueous sodium bicarbonate, water, and saturated aqueous sodium chloride and dried over anhydrous calcium chloride. The CH₂Cl₂ was distilled twice from P₂O₅ under an argon atmosphere and stored in a Schlenk flask equipped with a Teflon valve fitted with Viton O-rings. NMR spectra were recorded on Varian 400 MHz NMR spectrometers. UV-vis absorption spectra were collected with an Agilent 8453 diode array spectrometer, and infrared (IR) spectra were measured using a Nicolet Magna-IR 560 spectrometer. Electronic absorption (UV-Vis/NIR) measurements were made on a Cary 5000 instrument. Cyclic and square-wave voltammograms were measured under inert atmosphere with an epsilon EC potentiostat (iBAS) at a scan rate of 100 mV/s with 0.1 M [NBu₄]PF₆ electrolyte. The three electrode cell consisted of an Ag/AgCl reference electrode, a platinum auxiliary electrode, and a glassy carbon working electrode.

Synthesis of cyclotetraveratrylene (CTTV)



Method A^1 : A solution of 3,4-dimethoxy benzyl alcohol (1.68 g, 10 mmol) in glacial acetic acid (20 mL) containing five drops of concentrated sulfuric acid, After heated to 90 °C for 15 minutes, large amount of precipitate formed in the solution. Solid crude product was collected by filtration and washed with large amount of water, which was further purified by many times recrystallization from chloroform/benzene and chloroform to give cyclotriveratrylene (CTV, 0.88 g, yield 58%) and cyclotetraveratrylene (CTTV, 0.18 g, yield 12%).



Method B: Veratrole (0.69g, 5 mmol) and paraformaldehyde (0.3g, 10 mmol) were dissolved into 9 ml of dichloromethane at room temperature. Then methanesulfonic acid (1 mL) was added drop wisely into reaction mixture. The color slowly changed to dark brown. After 3 hours stirring at room temperature, the reaction was quenched with addition of 40 ml of water. The mixture was filtered and solid residue was washed several times with water to give brownish color crude product, which was further washed with 20 ml of methanol to give white powder as pure cyclotriveratrylene (**CTV**, 0.63 g, yield 85%). ¹H NMR (CDCl₃ at 22 °C) δ : 3.57 (d, 3H), 3.84 (s, 18H), 4.78 (d, 3H), 6.83 (s, 6H).

Cyclotriveratrylene (0.54g, 1.2 mmol) was added into 18 ml of dichloromethane solution containing 2 ml of methanesulfonic acid. Then 3,4-dimethoxybenzyl alcohol (0.6g, 3.6 mmol) in 5 ml of dichloromethane solution was dropwisely added into the mixture and stirred for 3 hours at room temperature. After quenched with addition of 40 ml of water, the mixture was filtered and washed several times with water to give brownish crude product, which was further washed with 20 ml of methanol and easily recrystallized from chloroform to give colorless crystal as pure cyclotetraveratrylene (**CTTV**, 0.76 g, yield 70 %). ¹H NMR (CD₂Cl₂ at 22 °C) δ : 3.72 (broad, 32 H), 6.60 (broad, 8H). ¹H NMR (CD₂Cl₂ at -80 °C) δ : 3.18 (d, 4H), 3.48 (s, 12H), 3.77 (d, 4H), 3.85 (s, 12H), 6.22 (s, 4H), 6.82 (s, 4H). ¹H NMR (CDCl₃ at 22 °C) δ : 3.78 (broad, 32 H), 6.58 (broad, 8H). ¹³C NMR (CDCl₃ at 22 °C) δ : 34.99, 54.08, 111.31 (broad), 115.67 (broad), 131.66 (broad), 147.30.

NMR Spectroscopy

¹H NMR spectrum of cyclotriveratrylene at 22°C in CDCl₃



¹H NMR spectrum of CTTV at -80 °C in CD₂Cl₂



 1H NMR spectrum of CTTV at 20 $^\circ C$ in CD_2Cl_2



¹H NMR spectrum of CTTV at 20 °C in CDCl₃



¹³C NMR spectrum of CTTV at 20 °C in CDCl₃



S2. Variable Temperature ¹H-NMR of CTTV

Variable temperature NMR data were recorded on Varian 400 MHz NMR spectrometers. Sample were prepared by dissolving 5 mg of **CTTV** in 0.5 mL of CD_2Cl_2 and $CDCl_3$ separately. The results were showed in **Fig. S1** (in CD_2Cl_2 from 20 to -80 °C) and **Fig. S2** (in $CDCl_3$ from 20 to 60 °C). Details on the parameters of the NMR experiments: Acquisition time (at): 2.556 s; Relaxation Delay (d1): 1.000 s; Number of scan: 8; Pulse: 45°; Spectral width (SW): -2 to 14 ppm.



Fig. S1. Variable temperature (VT) NMR of **CTTV** in CD_2Cl_2 in the range from 20 to -80 °C. The activation energy for the interchange between four conformers (shown in **Fig. S3** below) was estimated to be 14.9 kcal mol⁻¹.



Fig. S2. Variable temperature (VT) NMR of CTTV in CDCl₃ in the range from 20 to 60 °C.



Fig. S3. Four interconverted structures of open CTTV

The activation energy was calculated² as $\Delta G = a T_c [9.972 + \log(\frac{T_c}{\Delta v})]$, where *a* equals to 4.575×10^{-3} kcal/mol; Δv is the separation in Hz between the two signals at slow-exchange limit, $\Delta v = 21$ Hz between peaks at 6.26 and 6.32 ppm; $T_c = 20$ °C is coalescence temperature.

S3. Electrochemistry characterization of CTTV and model complexes

Cyclic and square-wave voltammograms were measured under inert atmosphere with an epsilon EC potentiostat (iBAS) at a scan rate of 100 mV/s with 0.1 M [NBu₄]PF₆ electrolyte at -30 °C. The three electrode cell consisted of an Ag/AgCl reference electrode, a platinum auxiliary electrode, and a glassy carbon working electrode. Ferrocene was used as internal reference.



Fig. S4. Cyclic voltammograms (CVs, solid lines) and square waves (SWs, dashed lines) of 2 mM **M** (top, green color), **CTV** (middle, blue color) and **CTTV** (bottom, red color) in CH_2Cl_2 (0.1 M n-Bu₄NPF₆) at a scan rate 100 mV s⁻¹.

S4. Generation of CTTV^{+•} by redox titrations

Electronic absorption spectra of **CTTV**^{+•} in CH₂Cl₂ at 22 °C were obtained by quantitative redox titrations using robust aromatic oxidant, i.e. [**THEO**^{+•}SbCl₆⁻] (1,4,5,8-dimethano-1,2,3,4,5,6,7,8-octahydro-9,10-dimethoxyanthracene hexachloroantimonate; $E_{red1} = 0.67$ V vs Fc/Fc⁺, $\lambda_{max} = 518$ nm, $\lambda_{max} = 7300$ cm⁻¹ M⁻¹).³



Fig. S5. Chemical structures of aromatic oxidant THEO used in redox titrations.

The redox titration experiment was carried out by an incremental addition of **CTTV** to the solution of **THEO**⁺⁺ where the 1- e^- oxidation of **CTTV** and reduction of **THEO**⁺⁺ can be described by equilibrium equation:

THEO^{+•} + **CTTV**
$$\rightleftharpoons$$
 THEO + **CTTV**^{+•} (eq. 1)

Numerical deconvolution^{4, 5} of the absorption spectrum at each increment produced mole fractions of **THEO**⁺⁺ and **CTTV**⁺⁺ against the added equivalents of **CTTV** and confirmed a 1:1 stoichiometry of the redox reaction (**Fig. S6** below reproduced from **Fig. 5** in the main text). The experimental plots of mole fraction vs equivalent of added donor were fitted by varying $\Delta G_1 =$

 $E_{ox1}^{CTTV} - E_{red}^{THEO^{+\bullet}}$.



Fig. S6. A: Spectral changes observed upon the reduction of 0.051 mM THEO⁺⁺ in CH₂Cl₂ (3 mL) of 1.49 mM solution of CTTV in CH₂Cl₂ at 22 °C. Inset: the isovalue plot of spin density distribution in CTTV⁺⁺. B: Plot of the mole fractions of THEO⁺⁺ (red) and CTTV⁺⁺ (black) against the added equivalents of neutral CTTV. Symbols represent experimental points, while the solid lines show best-fit to experimental points using $\Delta G = E_{ox}(CTTV) - E_{red}(THEO^{++}) = 25$ mV.⁴

S5. Electron donor-acceptor (EDA) complexes of CTTV

The quantitative intermolecular association was evaluated in the form of the K_{DA} and ecr values for the formation and visualization, respectively, of various tweezer/acceptor complexes; and the quantitative analysis of the spectrophotometric absorption changes was treated by the Benesi-Hilderbrand method using the eq. 2: ⁶

$$\frac{[A]}{A_{CT}} = \frac{1}{\varepsilon_{CT}} + \frac{1}{K_{DA}\varepsilon_{CT}} \frac{1}{[D]} \quad (eq. 2)$$

In eq. 2, A_{CT} is the molar absorbance and ε_{CT} is the extinction coefficient of the charge transfer band at the monitoring wavelength. The concentration of the electron acceptor was kept at least 10 times greater than that of tweezer donors, and a plot of [A]/ACT versus the reciprocal donor concentration was found to be linear in all tweezer/acceptor complexation measurements. From the slope $[K_{DA}\varepsilon_{CT}]^{-1}$ and the intercept $[\varepsilon_{CT}]^{-1}$, the values of association constant (K_{DA}) and extinction coefficient (ε_{CT}) were readily calculated.



Fig. S7. Spectral changes attendant upon the incremental addition of **CTTV** (1.08×10^{-3} M) to chloranil (0.022 M) in DCM (left) and Benesi-Hildebrand plot (right). $K_{DA} = 15 \text{ M}^{-1}$, $\varepsilon_{CT} = 347 \text{ M}^{-1} \text{ cm}^{-1}$



Fig. S8. Spectral changes attendant upon the incremental addition of **CTTV** (6.0×10^{-5} M) to **DDQ** (0.011 M) in DCM (left) and Benesi-Hildebrand plot (right). $K_{DA} = 591$ M⁻¹, $\varepsilon_{CT} = 2066$ M⁻¹ cm⁻¹

S6. X-ray crystallography of EDA complexes

	CTTV~DDQ	CTTV~CA
Empirical formula	C49.55H48.65Cl11.68N2O10	C50H44Cl12O12
Formula weight	1246.2	1262.25
Temperature/K	100.15	100(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	10.0667(4)	9.0593(2)
b/Å	16.1954(7)	12.1761(2)
c/Å	19.0021(8)	12.5506(2)
α/°	111.109(4)	74.4930(10)
β/°	94.141(4)	89.5790(10)
γ/°	100.255(4)	84.4840(10)
Volume/Å ³	2812.4(2)	1327.60(4)
Z	2	1
$\rho_{calc}g/cm^3$	1.472	1.579
μ/mm^{-1}	5.743	6.256
F(000)	1277	644
Crystal size/mm ³	$0.286 \times 0.103 \times 0.017$	$0.26\times0.16\times0.10$
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)	$CuK\alpha$ ($\lambda = 1.54178$)
2Θ range for data collection/°	9.028 to 141.55	7.32 to 134.32
Index ranges	$\begin{array}{c} \text{-12} \leq h \leq 12, \text{-19} \leq k \leq 19, \text{-23} \leq l \leq \\ 23 \end{array}$	$\begin{array}{c} \text{-10} \leq h \leq 10, \text{-13} \leq k \leq 14, 0 \leq l \leq \\ 14 \end{array}$
Reflections collected	52221	11087
Independent reflections	10686 [Rint = 0.0954, Rsigma = 0.0660]	4379 [Rint = 0.0134, Rsigma = 0.0133]
Data/restraints/parameters	10686/129/760	4379/0/423
Goodness-of-fit on F ²	0.955	1.069
Final R indexes [I>= 2σ (I)]	R1 = 0.0664, wR2 = 0.1840	R1 = 0.0245, wR2 = 0.0633
Final R indexes [all data]	R1 = 0.0995, wR2 = 0.2048	R1 = 0.0252, wR2 = 0.0637
Largest diff. peak/hole / e Å ⁻³	2.13/-0.49	0.24/-0.29

Table S1. Summary of X-ray crystallographic data collection and structure refine.



Fig. S9. A. Bond length analysis of veratryl ring on complex CTTV~CA; B. Bond length analysis of veratral ring on complex CTTV~DDQ.

S7. Computational details

All electronic structure calculations of were performed in Gaussian 09 package.⁷ It is well known that accurate description of the electronic structure of the cation radicals of piconjugated and pi-stacked systems is challenging for many DFT functionals due to the selfinteraction error that causes artificial hole delocalization and leads to underestimated oxidation potentials and incorrect nature of the excited states.⁸⁻¹⁰ It was shown¹¹ that B1LYP¹² with 40% of the HF exchange provides a balanced description of the electronic structure of the poly-pphenylene cation radicals. Accordingly, in this manuscript, we performed electronic structure calculations using B1LYP-40-D3/6-31G(d) level of theory. In order to account for dispersion interactions within B1LYP-40 functional we have utilized D3 version of Grimme's dispersion¹³ parameters SR6=1.3780 and S8=1.2170. In recent studies we have shown^{14, 15} that such a modification provided a balanced description of the neutral and cation radical states of various pi-stacked systems. Solvent effects were included using the implicit integral equation formalism polarizable continuum model (IEF-PCM)¹⁶⁻²⁰ with dichloromethane solvent parameters ($\varepsilon =$ 8.93). In all DFT calculations, ultrafine Lebedev's grid was used with 99 radial shells per atom and 590 angular points in each shell. In cation radical calculations, wave function stability test²¹ was performed to ensure absence of solutions with lower energy. Tight cutoffs on forces and atomic displacement were used to determine convergence in geometry optimization procedure. Harmonic vibrational frequency calculations were performed for the optimized structures to confirm absence of imaginary frequencies. Free energies were computed within harmonic

oscillator approximation for T = 298.15 K and P = 1 atm. NMR shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method.²²



Fig. S10 Conformations of CTTV calculated using B1LYP40-D3/6-31G(d)

Table S2. Relative free energies of **CTTV** conformers calculated using B1LYP40-D3/6-31G(d) and M062X/6-31G(d) in dichloromethane

	B1LYP40-D3/6-31G(d)	M062X/6-31G(d)
1(open)	0.00	0.00
2(closed)	1.37	1.21
3	6.31	6.88
4	15.97	16.01

Table S3. Relative free energies of **CTTV** conformers calculated in various solvents using B1LYP40-D3/6-31G(d)

	Dichloromethane	Acetonitrile	Acetone	Methanol	Toluene
1(open)	0.00	0.00	0.00	0.00	0.00
2(closed)	1.37	1.31	1.32	1.31	1.90
3	6.31	5.83	5.98	5.85	6.89
4	15.97	15.87	15.90	15.88	16.14



Fig. S11 Correlation plot between isotropic ¹H magnetic shieldings calculated using B1LYP40-D3/6-31G(d) and M062X/6-31G(d) in dichloromethane.

Table S4. Relative free energies of $CTTV^{+}$ conformers calculated using B1LYP40-D3/6-31G(d) and M062X/6-31G(d) in dichloromethane

	B1LYP40-D3/6-31G(d)	M062X/6-31G(d)
1(open)	5.64	5.62
2(closed	0.00	0.00
3	12.57	18.82
4	20.37	21.31

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