

# Supporting Information

## A Mixed-Valence Superstructure Assembled from A Mixed-Valence Host-Guest Complex

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## 1. General Methods

All reagents were purchased from commercial suppliers and used without further purification. Methyl viologen (paraquat) bis(hexafluorophosphate) ( $MV \cdot 2PF_6$ ) and cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) ( $CBPQT \cdot 4PF_6$ ) were prepared<sup>1</sup> according to literature procedures. Bis(cyclopentadienyl)cobalt(II) (cobaltocene,  $CoCp_2$ ) was purchased from Sigma-Aldrich and stored in an Ar-filled glovebox. Prior to experiments,  $CoCp_2$  was assayed in dried and degassed MeCN using a colorimetric method.<sup>2</sup> All experiments were performed in MeCN solutions, previously degassed, in a glovebox under an Ar atmosphere. Thin layer chromatography (TLC) was performed on silica gel 60 F254 (E. Merck). Column chromatography was carried out on silica gel 60F (Merck 9385, 0.040–0.063 mm). UV/Vis Spectra were recorded at room temperature on a Shimadzu UV-3600 spectrophotometer in a quartz cell with an optical path-length of 2 mm containing the solution of interest. Samples were prepared immediately prior to use and the solutions were sealed under Ar with Teflon stoppers. Experimental error: absorption maxima,  $\pm 1$  nm. Electron paramagnetic resonance (EPR) measurements at X-band (9.5 GHz) were performed with a Bruker Eleksys E580, equipped with a variable Q dielectric resonator (ER-4118X-MD5-W1). All samples were prepared in an Ar-filled atmosphere. Samples were loaded into quartz 1.4 mm tubes and sealed with a clear ridged UV doming epoxy (IllumaBond 60-7160RCL) and used immediately after preparation. Steady-state solution CW EPR spectra were collected with a 0.25 G modulation amplitude 2.56 ms time constant, and 10.24 ms conversion time, averaging 100 sweeps 50 G wide, centered around 2465 G. Steady-state solid continuous-wave EPR spectra were measured with the same parameters with a modulation amplitude of 0.05 G on a sample of several crystals of complex  $[MV \subset (CBPQT)_2]_3 \cdot (PF_6)_2$ —which was confirmed by single-crystal X-ray diffraction—in a quartz 1.4 mm tube in Ar. Single-crystal data was measured on a Bruker Kappa APEX2 CCD diffractometer using Cu-K $\alpha$  radiation. Data collection and structure refinement details can be found in the CIF file. CCDC 985866 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 2. Solution-State Characterization of the 1:1 Mixture of CBPQT and MV

### 2.1. UV–Vis–NIR Spectroscopy

A solution of the reduced equimolar mixture of CBPQT and MV in MeCN was prepared by the chemical reduction of a fully oxidized equimolar mixture of CBPQT•4PF<sub>6</sub> and MV•2PF<sub>6</sub> using 6.0 equiv of CoCp<sub>2</sub>. The reduction was carried out under Ar in a glovebox. First of all, a CBPQT•4PF<sub>6</sub>/MV•2PF<sub>6</sub> solution (1:1, 80 μM, 5 mL) and a CoCp<sub>2</sub> solution (1.7 mM, 1 mL) in degassed MeCN were prepared. Then a solution with 1:6 molar ratio of the 1:1 mixture CBPQT•4PF<sub>6</sub>/MV•2PF<sub>6</sub> : CoCp<sub>2</sub> in a final volume of 1.00 mL was prepared by adding the CoCp<sub>2</sub> solution into the CBPQT•4PF<sub>6</sub>/MV•2PF<sub>6</sub> solution. The UV–Vis–NIR spectra were recorded on solutions with 1:0 and 1:6 molar ratios of the 1:1 mixture CBPQT•4PF<sub>6</sub>/MV•2PF<sub>6</sub> : CoCp<sub>2</sub> in a final volume of 1.00 mL in the wavelength window of 275–2200 nm using a 2-mm quartz cuvette.

### 2.2. EPR Spectroscopy

Samples for EPR investigations were prepared as described for the UV–Vis spectroscopy with the exception that the concentration of the stock solution of the equimolar mixture of CBPQT•4PF<sub>6</sub> and MV•2PF<sub>6</sub> was maintained at 250 μM. The EPR spectra of CBPQT•4PF<sub>6</sub>/MV•2PF<sub>6</sub> and its reduced product were recorded at 298 K after the chemical reduction with 6 equiv of CoCp<sub>2</sub>.

## 3. Crystallographic Characterization

Crystallographic data are available free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### 3.1. Method

Single crystals of  $[\text{MV}(\text{CBPQT})_2]_3 \cdot (\text{PF}_6)_2$  were grown under inert (Ar) atmosphere at 0 °C by slow vapor diffusion of  $i\text{Pr}_2\text{O}$  into a MeCN /  $\text{CH}_2\text{Cl}_2$  solution containing an equimolar mixture of CBPQT and MV prepared by the chemical reduction of an equimolar mixture of  $\text{CBPQT} \cdot 4\text{PF}_6$  and  $\text{MV} \cdot 2\text{PF}_6$  using 6.0 equiv of  $\text{CoCp}_2$ . A black single crystal suitable for crystallographic analysis was selected and mounted in inert oil and transferred to the cold gas stream of a Bruker Kappa APEX2 CCD area detector equipped with a Cu-K $\alpha$  microsource with MX optics. SADABS-2008/1 (Bruker, 2008) was used for absorption correction.  $wR_2(\text{int})$  was 0.0748 before and 0.0585 after correction. The ratio of minimum to maximum transmission is 0.8704. The  $\lambda/2$  correction factor is 0.0015.

### 3.2. Crystal Structure Determination of $[\text{MV}(\text{CBPQT})_2]_3 \cdot (\text{PF}_6)_2$

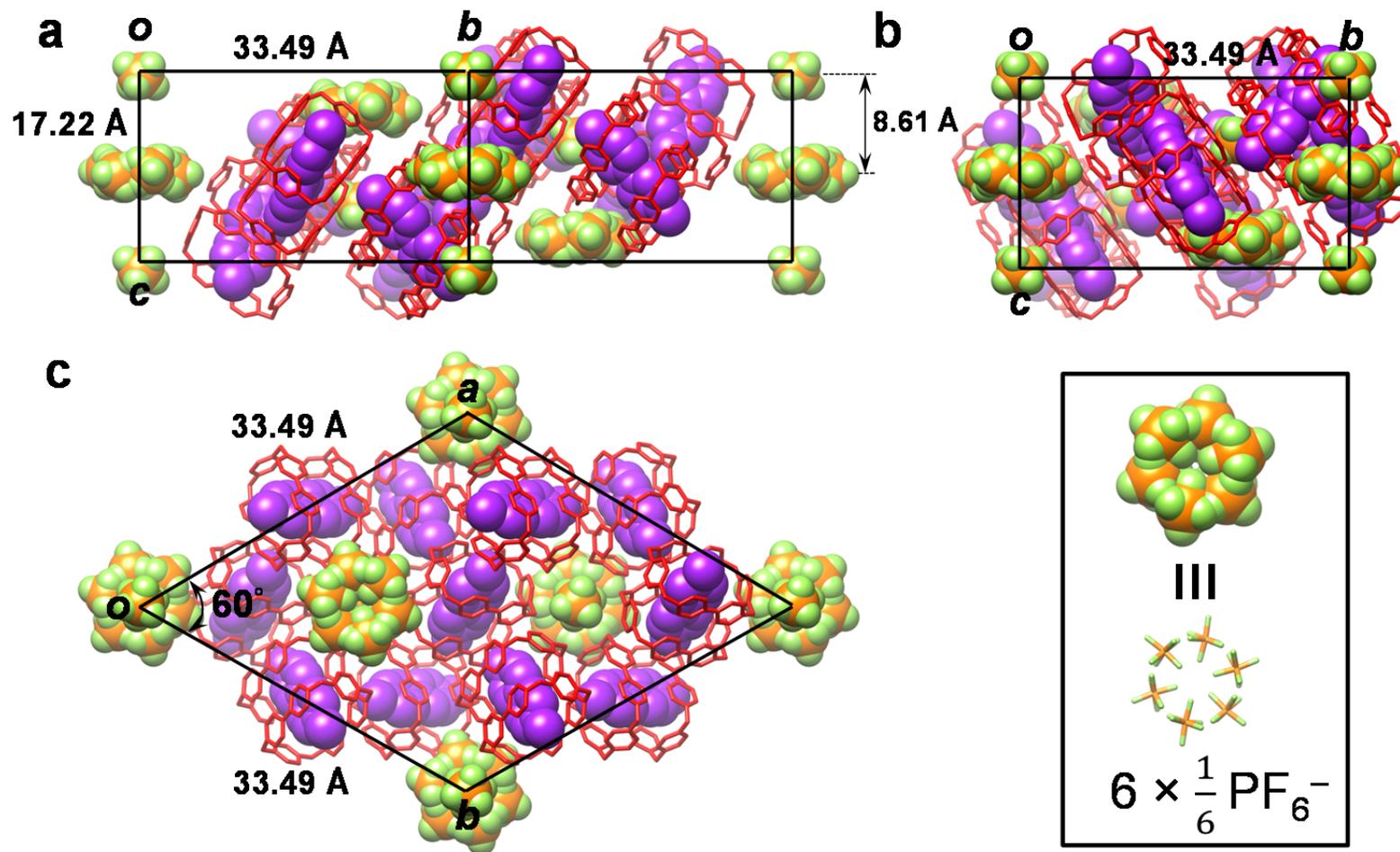
**Crystal Data of  $[\text{MV}(\text{CBPQT})_2]_3 \cdot (\text{PF}_6)_2$ :**  $M = 3972.68$ , trigonal, space group  $R\bar{3}$  (no. 148),  $a = 33.494$  (3),  $c = 17.2240$  (17) Å,  $U = 16734$  (4) Å<sup>3</sup>,  $T = 100.01$  K,  $Z = 3$ ,  $\mu$  (Cu-K $\alpha$ ) = 0.786 mm<sup>-1</sup>. A total of 32335 reflections were collected, of which 5902 ( $R_{\text{int}} = 0.0414$ ) were unique and used in all calculations. The final  $wR$  ( $F_2$ ) was 0.1809 (all data).

### 3.3. Refinement Details.

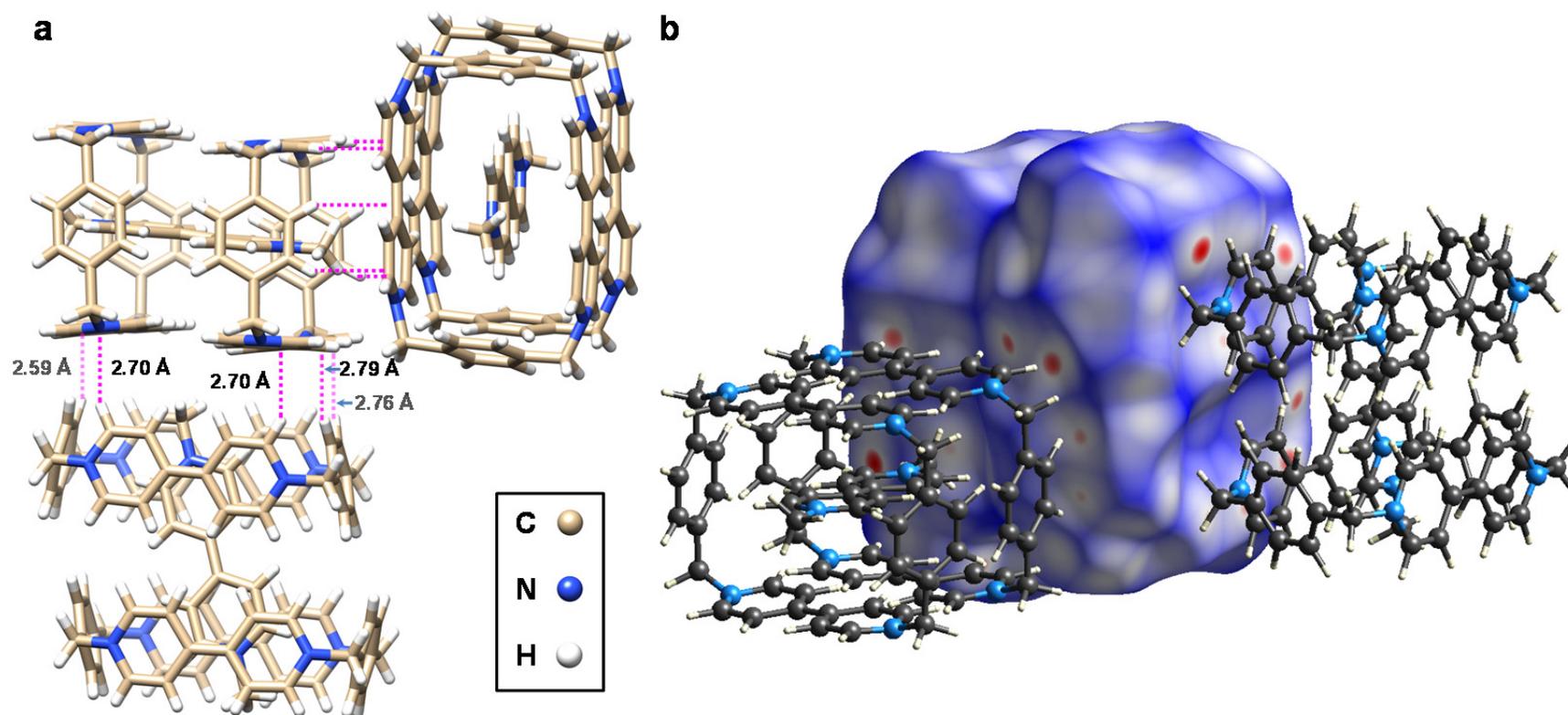
One  $\text{PF}_6^-$  counteranion is disordered about a six-fold crystallographic axis. Displacement parameters of the P and F atoms were refined with rigid bond (DELU) and similarity (SIMU) restraints. P–F and F–F distances were refined with SADI restraints to keep the octahedral geometry reasonable.

**Table S1. Crystal Data and Structure Refinement for [MV<sub>3</sub>(CBPQT)<sub>2</sub>]<sub>3</sub>•(PF<sub>6</sub>)<sub>2</sub>**

Empirical Formula	[MV <sub>3</sub> (CBPQT) <sub>2</sub> ] <sub>3</sub> •(PF <sub>6</sub> ) <sub>2</sub>
CCDC Number	985866
Formula Weight	3972.68
<i>T</i> / K	100.01
Crystal System	Trigonal
Space Group	<i>R</i> $\bar{3}$
<i>a</i> , <i>b</i> , <i>c</i> / Å	33.494 (3), 33.494 (3), 17.2240 (17)
$\alpha$ , $\beta$ , $\gamma$ / °	90, 90, 120
<i>V</i> / Å <sup>3</sup>	16734 (4)
<i>Z</i>	3
$\rho_{\text{calc}}$ / mg mm <sup>-3</sup>	1.256
$\mu$ / mm <sup>-1</sup>	0.786
<i>F</i> (000)	6678
Crystal Size / mm <sup>3</sup>	0.161 × 0.109 × 0.086
2 $\theta$ Range for Data Collection	9.146 to 124.7°
Index Ranges	-38 ≤ <i>h</i> ≤ 38, -38 ≤ <i>k</i> ≤ 38, -13 ≤ <i>l</i> ≤ 19
Reflections Collected	32335
Independent Reflections	5902 [ <i>R</i> <sub>int</sub> = 0.0414]
Data / Restraints / Parameters	5902 / 189 / 527
Goodness-of-Fit on <i>F</i> <sup>2</sup>	1.096
Final <i>R</i> Indexes [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0534, <i>wR</i> <sub>2</sub> = 0.1722
Final <i>R</i> Indexes [all data]	<i>R</i> <sub>1</sub> = 0.0600, <i>wR</i> <sub>2</sub> = 0.1809
Largest diff. peak / hole / e Å <sup>-3</sup>	0.631 / -0.321



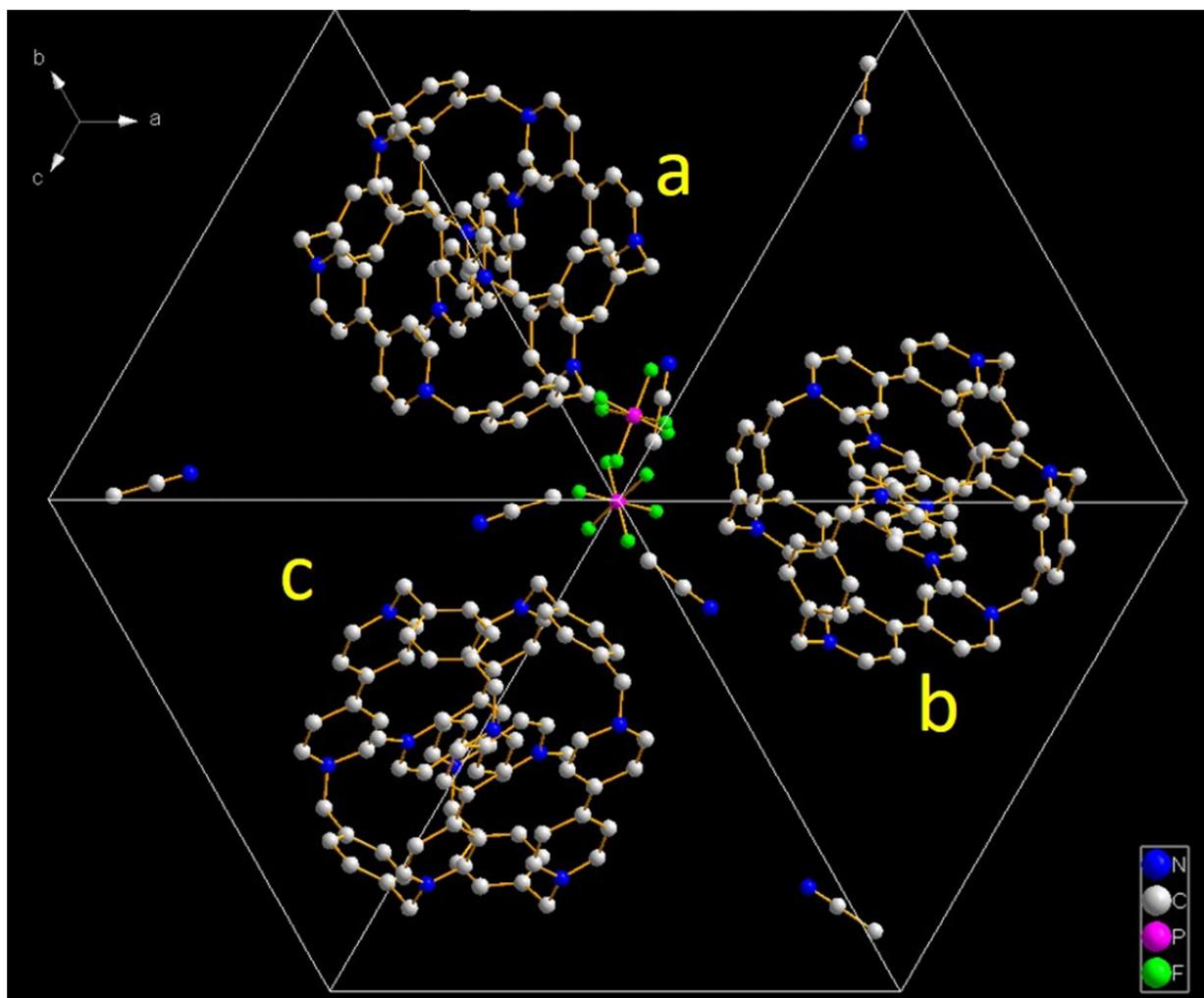
**Figure S1.** Three views of the single-crystal X-ray superstructure of the complex  $[\text{MV}\subset(\text{CBPQT})_2]_3 \cdot (\text{PF}_6)_2$ . a) Front, b) side, and c) top views. When viewing down along the *c* crystallographic axis, hexagonal channels—which are filled (Figure 4d) with  $\text{PF}_6^-$  anions of  $8.61 \text{ \AA}$  apart from each other—can be observed to pack into trigonal arrangements. One of the  $\text{PF}_6^-$  anion pairs is disordered about a 6-fold crystallographic *c*-axis. CBPQT is depicted as a tubular representation, while MV, and  $\text{PF}_6^-$  are depicted as space-filling representations. CBPQT, red; MV, purple; F, green; P, orange yellow. Hydrogen atoms and solvent molecules are omitted for the sake of clarity.



**Figure S2.** (a) A perspective view showing 10 complementary [C–H···π] interactions ranging from 2.59 to 2.79 Å between BIPY planes and the H atoms on CBPQT rings of three adjacent and orthogonally oriented complexes. (b) The Hirshfeld<sup>3</sup> surface plot of MV<sub>C</sub>(CBPQT)<sub>2</sub>. Dark-red spots in the  $d_{norm}$  surface mapping are the result of [C–H···π] interactions between BIPY planes and the H atoms on CBPQT rings of three adjacent but orthogonally oriented complexes. On account of the C<sub>2</sub> symmetry of the MV<sub>C</sub>(CBPQT)<sub>2</sub> complex, another 10 two-fold symmetry-related complementary [C–H···π] interactions exist between the opposite BIPY planes and the H atoms on the opposite CBPQT rings of each complex. The reciprocal [C–H···π] / [π···H–C] interactions are the most significant inter-complex interactions which contribute 79.8% to the Hirshfeld surface.

## 4. DFT Calculations

All the periodic calculations were carried out with CRYSTAL14<sup>4</sup> at the level of M06-HF/6-31G\*. In order to establish an initial geometry, the  $R\bar{3}$  symmetry was removed from the single-crystal XRD (super)structure and from the six symmetry-equivalent positions for the  $\text{PF}_6^-$  anions, i.e., one was selected. The initial broken symmetry guess was employed so that electrons with different spins were allowed to populate different orbitals.



**Figure S3.** The DFT-optimized structure with the single-crystal structure as the initial geometry. Two  $\text{MV}^{+\cdot} \subset (\text{CBPQT}^0)_2$  complexes are labeled as **a** and **b**, while one neutral  $\text{MV}^0 \subset (\text{CBPQT}^0)_2$  complex is labeled as **c**. Hydrogen atoms were omitted for the sake of clarity.

**Table S2. Mulliken-Charge and Spin-Population of Each Complex and MV Unit as well as the Length of Bond C4–C4' in MV in the Periodic Calculation**

Complex	Fragment	Charge	Spin	Length of Bond C4–C4' in MV / Å
<b>a</b>	MV⊂(CBPQT) <sub>2</sub>	0.74	-1.00	
	MV	0.78	-0.98	1.42
<b>b</b>	MV⊂(CBPQT) <sub>2</sub>	0.73	1.00	
	MV	0.79	0.98	1.42
<b>c</b>	MV⊂(CBPQT) <sub>2</sub>	-0.09	-0.00	
	MV	-0.06	-0.00	1.36

## 5. References

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