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

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Supporting Information Placeholder

ABSTRACT: Herein, we report an unprecedented mixed-valence crystal superstructure which consists of a 2:1 host-guest complex \([MV\subset(CBPQT)_2]^{2+}\) \([MV = \text{methyl viologen}, \text{CBPQT} = \text{cyclobis(paraquat-}\pi\text{phenylene})]\). One electron is distributed statistically between three \([MV\subset(CBPQT)_2]^{2+}\) comprised of a total of 15 viologen units. The mixed-valence state is validated by single-crystal X-ray crystallography which supports an empirical formula of \([MV\subset(CBPQT)_2]_2\pi(PF_6)_3\) for the body-centered cubic superstructure. Electron paramagnetic resonance provides further evidence of electron delocalization. Quantum chemistry calculations support the existence of mixed-valence state. Our findings demonstrate that precise tuning of the redox states in host-guest systems can lead to a promising supramolecular strategy for achieving long-range electron delocalization in solid-state devices.

Long-range electron delocalization involving noncovalently bonded assemblies plays a pivotal role in biological processes such as light-harvesting antenna complexes. A steadily improving understanding of electron delocalization at the molecular level has been assisted by the investigation of artificial model systems—invoking donor–acceptor assemblies and mixed-valence complexes—which have instigated the creation of optoelectronic devices. Indeed, tremendous advances have been made towards developing artificial systems composed of molecular frameworks and supramolecular architectures. The development of host-guest chemistry has opened the door to synthetic hosts being ideal systems for studying electron delocalization through noncovalent-bonding interactions. Since the late 1980s, we have investigated cyclobis(paraquat-\pi\text{phenylene}) (CBPQT4+). Figure 1a—composed of two 1,1’-dialkyl-4,4’-bipyridinium (BIPY2+) units—which is capable of forming inclusion complexes with neutral π-electron-rich guests through π–π and charge-transfer interactions. Recently, we discovered the ability of CBPQT4+, when reduced to CBPQT2(•+) to form a stable 1:1 inclusion complex BIPY2•+(CBPQT2(•+)) with appropriate guests containing BIPY2•+ because of favorable radical–radical interactions. By employing this 1:1 complex as a template, many high-energy mechanically interlocked molecules—(MIMs)—which would otherwise be difficult to synthesize—have been prepared. These MIMs exhibit intramolecular electron delocalization in their mixed-valence states thanks to the protection of the mechanical bond.

Herein, we demonstrate an unprecedented example of mixed-valence states in a crystal superstructure assembled from a unique 2:1 host-guest complex MV⊂(CBPQT)2 (MV = \text{methyl viologen})—namely, one MV entity encircled by two CBPQT rings—which bears evenly 2/3+ charge. In other words, two positive charges are distributed statistically among total 15 BIPY units as well as its unusual ratio of BIPY/charge have been confirmed as one neutral MV0⊂(CBPQT)2 and one neutral MV0⊂(CBPQT)2. The formation of this mixed-valence superstructure complex as well as its unusual ratio of BIPY/charge have been confirmed by single-crystal X-ray diffraction (XRD), which affords an empirical formula of \([MV\subset(CBPQT)_2]_2\pi(PF_6)_3\) for the body-centered cubic superstructure, while the existence of free radicals in the bulk sample has been proved by electron paramagnetic resonance (EPR) spectroscopy. Quantum chemistry calculations support the existence of mixed-valence state.

Figure 1. (a) Structural formulas of BIPY2+ and CBPQT4+. (b) UV-Vis-NIR Absorption and (c) EPR spectra of an equimolar mixture (deep blue) of CBPQT•4PF6 and MV•2PF6 and its reduced product (red) upon addition of 6 equiv of CoCp2. 
To understand the binding properties\textsuperscript{19} of CBPQT\textsubscript{2} towards 
neutral MV\textsubscript{0}, we investigated the reduction of an equimolar mixture 
of CBPQT•4PF\textsubscript{6} and MV•2PF\textsubscript{6} using cobaltocene (CoCp\textsubscript{2}). 
The UV-Vis-NIR spectrum (Figure 1b) of this mixture before 
reduction exhibits no Vis-NIR absorption bands and no EPR signals 
are observed (Figure 1c). Upon reducing this mixture with 6 
equiv of CoCp\textsubscript{2}, a new band appears at 367 nm with a shoulder at 
392 nm, observations which are in line with the spectra reported\textsuperscript{19-} 
20 for neutral CBPQT\textsubscript{0} and MV\textsubscript{0}, indicating the generation of both 
these neutral forms. We observed, however, a very weak broad 
NIR absorption band at \sim1178 nm, which is not really noticeable 
until it is magnified 20-fold. This characteristic NIR band, which 
de-rives from charge-resonance transitions, can be ascribed to the 
formation of complexes between BIPY\textsuperscript{0} and trace of the incompletely 
reduced BIPY\textsuperscript{+} radical cations. Consistent with the appearance 
of the NIR band, a non-negligible weak EPR signal is 
also evident for the reduced solution sample, confirming the presence 
of radical species. The existence of both weak NIR band and 
EPR signal indicates that, although most of this mixture is re-
duced to CBPQT\textsuperscript{0} and MV\textsuperscript{0}, trace amounts of BIPY in CBPQT or 
MV still remain as radical cationic BIPY\textsuperscript{+} which associates with 
its neutral counterpart BIPY\textsuperscript{0}. Thus, certain mixed-valence complexes 
are formed.

This observation encouraged us to assess the formation of complexes 
in the extreme case of a mixed-valence system. Despite the 
rapid disproportionation of BIPY\textsuperscript{+} radical cations, we were able 

to obtain black single crystals suitable for XRD from an equimolar 
mixture of CBPQT•4PF\textsubscript{6} and MV•2PF\textsubscript{6} reduced with 6 equiv 
of CoCp\textsubscript{2}. The resulting black crystals are strikingly different 
from the red crystals of CBPQT\textsuperscript{0} and MV\textsuperscript{0}. Single-crystal XRD 
analysis (Figure 2) shows that the superstructure is composed of a 
unique 2:1 host-guest complex MV⊂(CBPQT),—namely, a MV 
entity embraced by two CBPQT rings with a C\textsubscript{2} axis passing 
perpendicular (Figure 2c) through the center of the MV plane. Two 
isostructural CBPQT rings—adopting a slightly conical shape 
with two angles between the ring plane and two p-xylene planes 
of 100 and 104°—are held (Figure 2b) together head-to-head by 
six [H\cdots H] contacts of 2.33–2.39 Å. The “corner” angles of 
CBPQT are 112°, a value which is comparable with the 113° 
found in CBPQT\textsuperscript{0}. The mean distance between two BIPY planes 
of CBPQT is 6.83 Å, similar to the value reported\textsuperscript{19} for CBPQT\textsuperscript{0}. 
The MV entity is encapsulated through π–π interactions of 3.31 Å 
between MV and two CBPQT as well as by four [C–H\cdots π] interactions 
of 2.85–2.94 Å with a dihedral angle between MV and 
CBPQT of 70°. Somewhat unexpectedly, the positive charge car-
died by this complex is observed to be a non-integer less than 
even 2. We identified two CBPQT rings and (ii) a host-guest complex bear-
ing charges more than zero but less than one.

For the sake of simplicity, we used a model in which MV is 
shown in purple and CBPQT, in red. The bond lengths of BIPY 
in MV and CBPQT are 3.25 Å and 3.23 Å, respectively. The bond lengths for BIPY of 
CBPQT are 3.30 Å and 3.28 Å, similar to those reported for BIPY of CBPQT. 

Figure 2. Crystal (super)structure of MV⊂(CBPQT)\textsubscript{2}. (a) Front 
view showing the corner angles of CBPQT, torsional angle of 
BIPY in CBPQT, and [C–H\cdots π] interactions (pink dash lines). (b) Side view exhibiting the angles between xylene planes and 
CBPQT, the dihedral angle between MV and CBPQT, and [H\cdots H] 
interactions (blue dash lines) between two CBPQT. (c) Top view 
indicating the C\textsubscript{2} symmetrical axis and the width of CBPQT, and 
π–π interactions between MV and CBPQT. H, white; CBPQT, red; 
MV, purple. The bond lengths of BIPY in MV and CBPQT are 
portrayed in purple and red, respectively.

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of 2.85–2.94 Å with a dihedral angle between MV and 
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died by this complex is observed to be a non-integer less than 
even 2. We identified two CBPQT rings and (ii) a host-guest complex bear-
ing charges more than zero but less than one.

Despite the fact that torsional angles associated with BIPY 
change upon guest complexation, the change in the bond lengths 
can be used to establish\textsuperscript{19,21-22} the oxidation states of BIPY. To 
clarify the oxidation states of each BIPY of [MV⊂(CBPQT)\textsubscript{2}]\textsuperscript{2/3+}, 
we compared the bond lengths of two classes of BIPY units in this 
complex with those for BIPY reported\textsuperscript{19,23} present in CBPQT\textsubscript{0}, 
CBPQT\textsuperscript{2/3+}, and CBPQT\textsuperscript{0} as well as MV\textsuperscript{2+}, MV\textsuperscript{3+}, and MV\textsuperscript{0}. We 
were able to identify (Figure 3) a clear trend in the lengths of the 
bonds in BIPY at different redox states. In particular, the bond 
length for C4–C4’ undergoes a distinct change from \sim1.49 Å (2+), 
to \sim1.43 Å (2+), to \sim1.37 Å (0), in line with the nature of bond 
C4–C4’ changing from a single bond, a radical-delocalized bond,

Figure 3. Comparison of bond lengths of BIPY in MV and 
CBPQT for MV⊂(CBPQT)\textsubscript{2} with BIPY in CBPQT\textsuperscript{2+}, CBPQT\textsuperscript{2/3+}, 
CBPQT\textsuperscript{0}, MV\textsuperscript{2+}, MV\textsuperscript{3+}, and MV\textsuperscript{0}. Arrows indicate the changes in 
bond lengths of BIPY.

The existence of the unpaired electrons in the mixed-valence 
crystals was also confirmed by EPR spectroscopy. An EPR signal 
inhomogeneously broadened by many hyperfine splittings was
Figure 5. Crystal superstructure of $[\text{MV} \subset \text{CBPQT})_2]_{\text{PF}_6}$: (a) Octahedron assembled from six $\text{MV} \subset \text{CBPQT})_2$ surrounding two $\text{PF}_6$ and (e) its schematic representations. (b) Body-centered cubic superstructure assembled by adjacent octahedrons sharing $\text{MV} \subset \text{CBPQT})_2$ as linkers and (f and g) its schematic representations. (d) Hexagonal channels packing into (c) hexagonal arrangement as viewing along c-axis (the diagonal of the cube in b). (h) Schematic representation of body-centered cubic superstructure after removing all $\text{MV} \subset \text{CBPQT})_2$. Green balls represent $\text{PF}_6$ pairs in e-h. (i) A representation showing that every $\text{MV} \subset \text{CBPQT})_2$ is encircled by four $\text{MV} \subset \text{CBPQT})_2$ and two pairs of $\text{PF}_6$. (j) 20 Complementary [C–H···π] interactions (Figure S2) of 2.59–2.79 Å between BIPY planes and H atoms on $\text{CBPQT}$ of adjacent $\text{MV} \subset \text{CBPQT})_2$. (k) Schematic representation of an extended body-centered cubic framework wherein $\text{PF}_6$ pairs are omitted. $\text{CBPQT}$, red; $\text{MV}$, purple; F, green; P, yellow. H atoms in a–d and i and solvents are omitted.

Figure 4. Solid-state continuous-wave EPR spectrum of crystals of $[\text{MV} \subset \text{CBPQT})_2]_{\text{PF}_6}$. 

The X-ray crystal superstructure reveals that every two $\text{PF}_6$ anions—one of them disordered (Figure S1) about a six-fold c-axis—are surrounded by the $\text{para}$-xylylene planes of six $\text{MV} \subset \text{CBPQT})_2$ to form (Figure 5a and e) an octahedron wherein six $\text{MV} \subset \text{CBPQT})_2$ occupy the vertices, but they also serve as shared linkers in connecting these octahedrons together in a three-dimensional array which extends throughout the whole crystal. Thus, every octahedron has the empirical formula of $[\text{MV} \subset \text{CBPQT})_2]_{\text{PF}_6}$. The $[\text{MV} \subset \text{CBPQT})_2]_{\text{PF}_6}$ repeating motifs adopt (Figure 5b, f–g) an approximately body-centered cubic packing arrangement, wherein (i) $\text{PF}_6$ anion pairs represent (Figure 5h) the vertices and the center of the cube and (ii) each $\text{MV} \subset \text{CBPQT})_2$ is linked with two pairs of $\text{PF}_6$ through its two outward-pointing $\text{para}$-xylylene faces. As viewed along the c-axis (Figure 5b), hexagonal channels—which are filled (Figure 5d) up with $\text{PF}_6$ anions at 8.61 Å apart from each other and penetrate through every octahedron—can be observed to pack (Figures 4c and S1) into a hexagonal arrangement. In the superstructure every $\text{MV} \subset \text{CBPQT})_2$ is encircled (Figure 5i) by four adjacent $\text{MV} \subset \text{CBPQT})_2$ and two pairs of $\text{PF}_6$ generating an octahedron. Since every complex has three types of facets—namely, $\text{para}$-xylylene planes, BIPY planes, and $\text{CBPQT}$ ring planes—in which the $\text{para}$-xylylene planes interact with $\text{PF}_6$ anions, every $\text{MV} \subset \text{CBPQT})_2$ links (Figures 5 and S2) with four adjacent but orthogonally oriented $\text{MV} \subset \text{CBPQT})_2$ by means of 20 complementary [C–H···π] interactions ranging from 2.59 to 2.79 Å between the BIPY planes and H atoms on the $\text{CBPQT}$ rings, assembling (Figure 5k) into an extended body-centered cubic framework with $\text{PF}_6$ pairs as vertices and center of each cube. Hirshfeld surface analysis confirms (Figure S2b) that the reciprocal [C–H···π]/[π···H–C] interactions, which contribute 79.8%, are the most significant interactions between $\text{MV} \subset \text{CBPQT})_2$.
Quantum chemistry calculations were carried out to analyze the charge distribution within and beyond MV⊂(CBPQT)₂. XRD analysis indicates that every three MV⊂(CBPQT)₂ share statistically two positive charges to give a body-centered cubic superstructure with the empirical formula of [MV⊂(CBPQT)₂]₂(PF₆)₃. The calculated bond lengths (Table S2) for C4–C4’ in MV (1.36 Å) and MV’ (1.42 Å) agree well with the trend in Figure 3. The uneven distribution of positive charge attracts PF₆ anions, encouraging one of them to drift from the 3-fold axis to a position that is closer to the two MV⊂(CBPQT)₂. Such an outcome is in agreement with observations (from XRD) which show that one of the two PF₆ anions does not occupy one single position with equal distances between six MV⊂(CBPQT)₂, but is disordered over six symmetry-related positions with one-sixth occupancy. We have demonstrated that two CBPQT rings are able to encapsulate cooperatively one MV entity to form a mixed-valence 2:1 host-guest complex MV⊂(CBPQT)₂. XRD analysis indicates that every three MV⊂(CBPQT)₂ share statistically two positive charges to give a body-centered cubic superstructure with the empirical formula of [MV⊂(CBPQT)₂]₂(PF₆)₃. The fact that every MV⊂(CBPQT)₂ bears only a mean charge of 2/3+ suggests the distribution of every two positive charges over two MV⊂(CBPQT)₂ with one neutral MV₀⊂(CBPQT)₂. Quantum chemistry calculations confirm the mixed-valence state of the solid-state superstructure. This research highlights the potential of host-guest strategies for achieving long-range charge delocalization in solid-state devices by constructing host-guest complexes with precisely adjustable redox states.

ASSOCIATED CONTENT

Supporting Information
Detailed information regarding the experimental methods and procedures, X-ray crystallographic data, and supportive figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org. CIF file for [MV⊂(CBPQT)₂]₂(PF₆)₃ (CCDC 985866).

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Notes
The authors declare no competing financial interests.

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