VIP Self-Assembly

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Mechanical Bond Formation by Radical Templation**

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One of the more promising entries into molecular nanotechnology has followed in the wake of the advent of the mechanical bond[1] in chemistry. Mechanically interlocked molecules[2] (MIMs), such as bistable [2]catenanes[3] and [2]rotaxanes,[4] have been integrated into nanoelectromechanical systems[5] (NEMs) in the context of, for example, molecular electronic devices[6] (MEDs) with a future generation of computers in mind, and mechanized silica nanoparticles[7] (MSNPs) with finely tuned and precisely targeted drug delivery capsules in prospect. The initial forays into the making of the mechanical bond relied on either statistical events[8] intervening during the course of classical chemical reactions or on the meticulously scripted and synthetically demanding use of covalent templation[9] in the midst of multistep reaction sequences. These approaches to the synthesis of MIMs are often limited in their practical utility on account of low yields of products and the tedious nature of the synthetic protocols, not to mention the close to total absence of any discrete and potentially useful intramolecular intercomponent interactions existing between their mechanically interlocked components.

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The emergence of noncovalent templates, which rely upon metal–ligand coordination,[10] donor–acceptor interactions, involving both charged[11] and neutral[12] recognition sites, hydrophobic forces[13] expressed in aqueous solutions, hydrogen bonding also operative in neutral[14] as well as charged[15] settings, electrostatic forces,[16] and anion binding[17] to provide[18] the supramolecular assistance[19] to covalent and hence mechanical bond formation, have transformed the chemical landscape and brought mechanostereochemistry[20] to the forefront as a means of introducing integrated nanosystems based on "smart" molecules into nano- and biotechnology. These templation processes, which make use of noncovalent bonding interactions, however, have not relied previously upon the remarkable stabilization which can ensue from the radical-pairing interactions.

In the domain of donor-acceptor MIMs, viologen—(1,1′-dialkyl-4,4′-bipyridinium) dications[21] $\mathbf{V}^{2+}$—and cyclobis(paraquat-*p*-phenylene) ($\mathbf{CBPQT}^{4+}$)[22] have been investigated[23] extensively as examples of π-electron-deficient guests and hosts, respectively. Recently, we have demonstrated[24] that viologen radical cations ($\mathbf{V}^{\bullet+}$) form strong inclusion complexes with the tetracationic cyclophane in its reduced diradical dicationic state ($\mathbf{CBPQT}^{2(\bullet+)}$) as a consequence of radical-pairing interactions. In view of the remarkable stabilization[25] associated with this supramolecular entity containing three [π···π]-stacked bipyridinium radical cations ($BIPY^{\bullet+}$),[26] we set out to assemble a [2]rotaxane incorporating a viologen derivative and the tetracationic cyclophane in its dumbbell and ring components, respectively, by means of a radical template-directed protocol. Assuming this objective can be met, we can contemplate a [2]rotaxane existing in a relatively high energy state, following the aerial oxidation of the $BIPY^{\bullet+}$ radical cation in the dumbbell component, together with oxidation of the two $BIPY^{\bullet+}$ radical cations in the ring component. The [2]rotaxane will be devoid of stabilizing intercomponent intramolecular binding interactions as a consequence of Coulombic repulsion between the two positively charged mechanically interlocked components. The synthesis of such a compound adds an additional strategy to the options available for the construction of mechanically interlocked compounds characterized by little to no binding affinities in their isolated forms.[27] Herein, we report the preparation of a [2]rotaxane, composed of positively charged ring and dumbbell components, which, upon reduction, forms a highly stable intermediate, involving radicals which serve as effective template for its construction.

The successful template-directed synthetic strategy for the assembly of the [2]rotaxane $\mathbf{R}\cdot 6PF_6$ is illustrated in Figure 1. The viologen derivative $\mathbf{T}^{2+}$ with two terminal azide functions was prepared (see the Supporting Information) in high overall

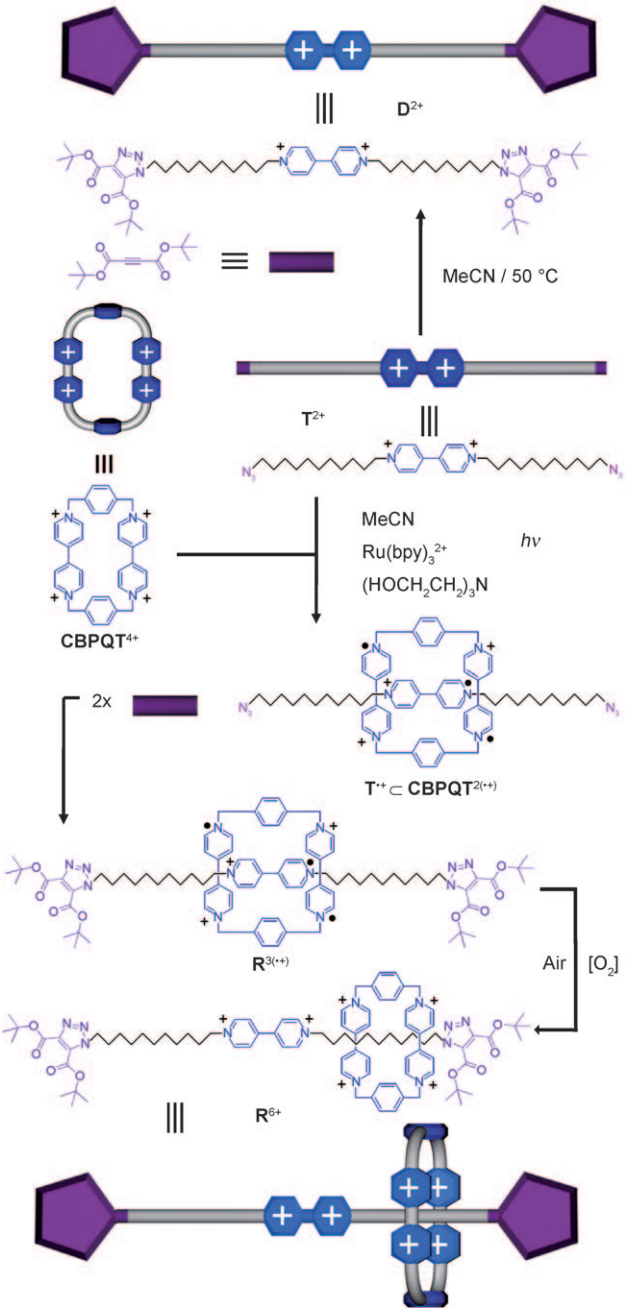

Figure 1. The radically promoted, template-directed synthesis of the [2]rotaxane **R**·6PF$_6$ via the intermediacy of the highly stable [2]pseudorotaxane [**T**$^{\bullet+}$⊂**CBPQT**$^{2(\bullet+)}$] which affords the [2]rotaxane **R**$^{3(\bullet+)}$, prior to its subsequent aerial oxidation to give **R**·6PF$_6$ during its purification and isolation. The PF_6^- counterions are omitted for the sake of clarity. The graphical representations of the structural formulas have been introduced to aid and abet the presentations of molecular structures in Figure 2–4.

yield in three steps from 11-bromo-1-undecanol and 4,4′-bipyridine. The template-directed synthesis of the [2]rotaxane **R**·6PF$_6$ was achieved using a copper-free azide–alkyne 1,3-dipolar cycloaddition[28,29] after the BIPY^{2+} dications in both **CBPQT**$^{4+}$ and **T**$^{2+}$ had been reduced to BIPY$^{\bullet+}$ radical cations to promote the formation of the **T**$^{\bullet+}$⊂**CBPQT**$^{2(\bullet+)}$ inclusion complex.[30] In order to effect the reduction of all three BIPY^{2+} units simultaneously to their respective radical cations in both **T**$^{\bullet+}$ and **CBPQT**$^{2(\bullet+)}$, the well-known [Ru(bpy)$_3$]$^{2+}$ reducing system (bpy = 2,2′-bipyridine),[31] which can be activated by visible light, was chosen because of its highly efficient reduction of BIPY^{2+} units by photoinduced charge transfer. Triethanolamine (TEOA), which was employed as the sacrificial electron donor, prevents back electron transfer from the BIPY$^{\bullet+}$ radical cation to the [Ru(bpy)$_3$]$^{3+}$ species.[32] In order to complete the template-directed synthesis of the [2]rotaxane by a threading-followed-by-stoppering strategy, a 1,3-dipolar cycloaddition between di-*tert*-butyl acetylenedicarboxylate[33]—the precursor to the two stoppers—and the terminal azide groups on the thread component of the inclusion complex was performed. The [2]rotaxane **R**·6PF$_6$ was isolated in 35% yield after a workup during which time all the BIPY$^{\bullet+}$ radical cations were oxidized back to BIPY^{2+} dications by atmospheric oxygen.

The ^{1}H NMR spectrum of the [2]rotaxane **R**·6PF$_6$ is compared with those of the dumbbell and ring components in Figure 2. The assignments were confirmed by two-dimensional NMR techniques (Figures S1 and S2 in the Supporting Information). In the ^{1}H NMR spectrum (Figure 2b) recorded in CD_3CN, a majority of the resonances for the oligomethylene protons $H_{a–k}$ located on the side of the dumbbell component occupied by the CBPQT^{4+} ring undergo dramatic upfield shifts (see Table 1 for a listing of $\Delta\delta$ values). By contrast, all the methylene protons $H_{a'-k'}$ located on the side of the dumbbell component not occupied by the CBPQT^{4+} ring undergo effectively no shifts (Figure 2b and Table 1), compared with their counterparts in the free dumbbell **D**·2PF$_6$ (Figure 2a). In particular, the observation of upfield shifts for the protons of the seven methylene groups $H_{b–h}$ indicates that they are threaded through the CBPQT^{4+} ring and hence are spending significant amounts of time under the influence of

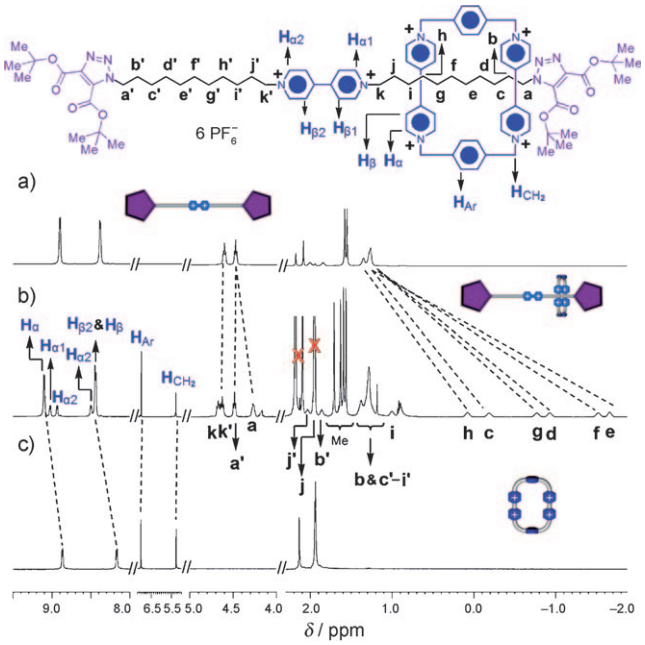

Figure 2. Partial ^{1}H NMR spectra (600 MHz, CD_3CN, 298 K) of a) the dumbbell **D**·2PF$_6$, b) the [2]rotaxane **R**·6PF$_6$ and c) **CBPQT**·4PF$_6$.

Table 1: The relative chemical shift changes ($\Delta\delta$) for the methylene groups in the oligomethylene chain in the [2]rotaxane **R**·6PF$_6$ in CD$_3$CN at 298 K with reference to their counterparts in the dumbbell **D**·2PF$_6$.

Proton[b]	$\Delta\delta$[a] [ppm]	Proton[b]	$\Delta\delta$[a] [ppm]
H_a	−0.21	$H_{a'}$	−0.02
H_b	−0.60	$H_{b'}$	−0.02
H_c	−1.45	$H_{c'}$	0.00
H_d	−2.19	$H_{d'}$	0.00
H_e	−2.93	$H_{e'}$	0.00
H_f	−2.79	$H_{f'}$	0.00
H_g	−2.03	$H_{g'}$	0.00
H_h	−1.29	$H_{h'}$	0.00
H_i	−0.37	$H_{i'}$	0.00
H_j	−0.06	$H_{j'}$	0.00
H_k	0.07	$H_{k'}$	−0.01

[a] $\Delta\delta$ is defined as : $\Delta\delta = \delta_{rotaxane} - \delta_{dumbbell}$. $\delta_{rotaxane}$ and $\delta_{dumbbell}$ are defined as the chemical shifts of an assigned proton of the [2]rotaxane **R**·6PF$_6$ and the dumbbell **D**·2PF$_6$, respectively. [b] See Figure 2 for the proton assignment of the [2]rotaxane **R**·6PF$_6$.

the bipyridinium and paraphenylene units of the CBPQT^{4+} ring. The resonances for the protons of the BIPY^{2+} unit in both the dumbbell-shaped component and the ring-shaped component of the [2]rotaxane **R**·6PF$_6$ (Figure 2b) undergo only minor changes in their chemical shifts, compared with their counterparts in the free components, namely **D**·2PF$_6$ (Figure 2a) and **CBPQT**·4PF$_6$ (Figure 2c). These observations can be attributed to Coulombic repulsions between the BIPY^{2+} units of the dumbbell component of **R**·6PF$_6$ and these same units in the CBPQT^{4+} ring, which conspire to force the tetracationic cyclophane away from the BIPY^{2+} unit in the dumbbell component. The methylene protons H_i, H_j, H_k, as well as H_a, exhibit modest changes in their chemical shifts (Table 1) compared to their counterparts in the free dumbbell **D**·2PF$_6$, an observation which indicates that these four methylene units reside outside the influence of the CBPQT^{4+} ring, on account of their proximity to the BIPY^{2+} unit of the dumbbell component in **R**·6PF$_6$ (H_i, H_j, H_k) or the bulky stopper (H_a), respectively. These results reveal that the oligomethylene chain in the [2]rotaxane **R**·6PF$_6$ serves as a "pseudo-station" for the tetracationic cyclophane—even although it presumably does not express any binding affinity—on account of the presence of the mechanical bond and the Coulombic repulsion dictated by the BIPY^{2+} unit in the dumbbell component.

In order to shed further light on the mechanism of rotaxanation employing radical templation, we have investigated the electrochemistry and spectroelectrochemistry (SEC) of the [2]rotaxane **R**·6PF$_6$, as well as of its separate free components (**CBPQT**·4PF$_6$ and **D**·2PF$_6$). The cyclic voltammograms (CVs) of the dumbbell **D**·2PF$_6$, **CBPQT**·4PF$_6$, and the [2]rotaxane **R**·6PF$_6$ are illustrated in Figure 3. The dumbbell **D**·2PF$_6$ containing only one BIPY^{2+} unit undergoes two consecutive reversible one-electron processes (Figure 3a) relative to the redox couples **D**$^{2+}$/**D**$^{+\bullet}$ (−0.48 V peak potential) and **D**$^{+\bullet}$/**D** (−0.90 V peak potential), while the **CBPQT**·4PF$_6$ with its two BIPY^{2+} units undergoes two consecutive reversible two-electron processes (Figure 3b) relative to the redox couples **CBPQT**$^{4+}$/**CBPQT**$^{2(+\bullet)}$ (−0.32 V peak potential) and **CBPQT**$^{2(+\bullet)}$/**CBPQT** (−0.76 V peak potential). No significant intermolecular interactions occur during the reduction of a 1:1 mixture of these free components (see Figure S5 in the Supporting Information).

The CV of the [2]rotaxane **R**·6PF$_6$ reveals (Figure 3c) four consecutive reversible redox processes. The reduction peak at −0.16 V, which corresponds to a two-electron process, can be assigned to two one-electron reductions—one electron being transferred to one of the BIPY^{2+} units of the CBPQT^{4+} ring (CBPQT^{4+}/CBPQT$^{(2+)(+\bullet)}$), and the other to the BIPY^{2+} unit of the dumbbell component (D^{2+}/D$^{+\bullet}$). This reduction potential is shifted positively compared to those of the free dumbbell **D**·2PF$_6$ and **CBPQT**·4PF$_6$ as a consequence of the stability of the radical cation dimers compared with their monomeric forms. The reduction peak observed at −0.27 V corresponding to a one-electron process, can be attributed to the further reduction of the CBPQT$^{(2+)(+\bullet)}$ monoradical trication to its diradical dicationic state (CBPQT$^{(2+)(+\bullet)}$/CBPQT$^{2(+\bullet)}$). The reason why this reduction peak is not shifted as much, compared with the first reduction process, is that the radical cation (BIPY$^{+\bullet}$) subunit is not strongly engaged in the radical pairing interactions. Further evidence (see Figure S7 in the Supporting Information) of these assignments was provided by SEC. In line with assignments to a previously studied[24] pseudorotaxane, the third reduction peak (−0.74 V) observed for the rotaxane can be assigned to the one-electron reduction of one of the two BIPY$^{+\bullet}$ units in the CBPQT$^{2(+\bullet)}$ ring (CBPQT$^{2(+\bullet)}$/CBPQT$^{+\bullet}$), which is not as strongly engaged in radical paring interactions with the BIPY$^{+\bullet}$ radical cation of the dumbbell component of **R**·6PF$_6$. The fourth reduction peak, which can be attributed to two simultaneous one-electron reductions (CBPQT$^{+\bullet}$/CBPQT and D$^{+\bullet}$/D), are shifted to a substantially more negative value (−1.01 V), compared with the second reduction peaks of the free **CBPQT**·4PF$_6$ and free dumbbell **D**·2PF$_6$ at −0.76 V and −0.90 V, respectively. This negative shift can be attributed to the stabilizing influence of the radical-pairing interaction, which renders further reduction more difficult

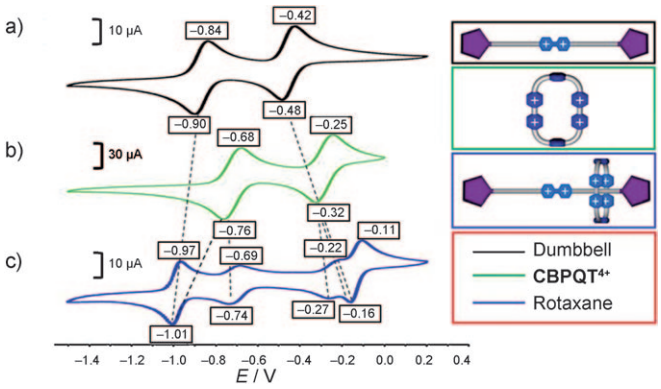

Figure 3. Second scans of the cyclic voltammograms (CVs) for a) the dumbbell **D**·2PF$_6$, b) **CBPQT**·4PF$_6$, and c) the [2]rotaxane **R**·6PF$_6$. All the CVs were recorded under the same conditions of temperature (298 K), solvent (argon-purged MeCN), concentrations (1 mM) and tetrabutylammonium hexafluorophosphate electrolyte (0.1 M **TBA**·PF$_6$). The scan rate was set at 200 mV s^{-1}.

and is characteristic of the encirclement of the $CBPQT^{2(\bullet+)}$ around the $BIPY^{\bullet+}$ unit of the dumbbell component.

The first two reduction processes leading to the formation of the trisradical species of the [2]rotaxane **R**·6PF_6 were also examined by UV/Vis spectroscopy using SEC. The absorption spectra for **CBPQT**·4PF_6, the dumbbell **D**·2PF_6, a 1:1 mixture of **D**·2PF_6 and **CBPQT**·4PF_6 and the [2]rotaxane **R**·6PF_6 were recorded (Figure 4), upon application of a reductive voltage

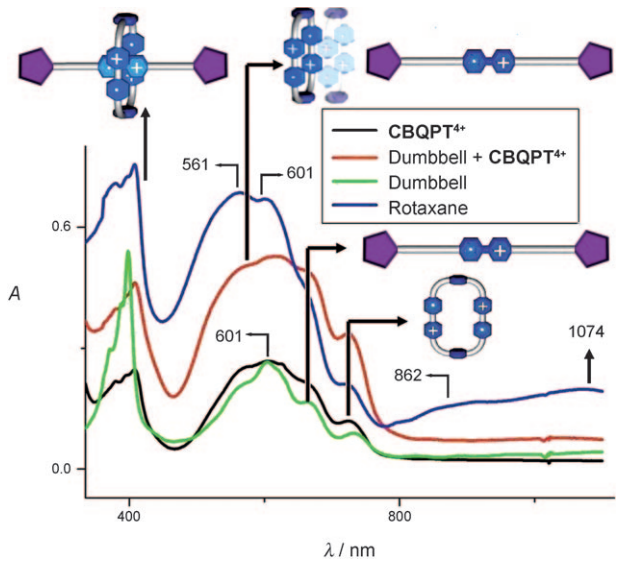

Figure 4. The outcomes of spectroelectrochemistry (SEC) carried out on the dumbbell **D**·2PF_6 (green trace), **CBPQT**·4PF_6 (black trace), a 1:1 mixture of **D**·2PF_6 and **CBPQT**·4PF_6 (red trace), and the [2]rotaxane **R**·6PF_6 (blue trace). All the spectra were recorded in argon-purged MeCN in a 2 mm cell path length, under the same conditions of temperature (298 K), concentration (1 mM), electrolyte (0.1 M **TBA**·PF_6) and voltage (−700 mV).

of −700 mV. Both **CBPQT**·4PF_6, the dumbbell **D**·2PF_6 as well as their 1:1 mixture exhibit a characteristic maximum absorption band (λ_{max}) for a typical viologen radical monomer centered on 601 nm, in keeping with the data published previously[24] on viologen radical cations. These data indicate that the $\mathbf{CBPQT}^{2(\bullet+)}$ and $\mathbf{D}^{\bullet+}$ do not interact significantly with each other if not mechanically interlocked, an observation which supports the results of the CV investigations. By contrast, after applying a potential of −700 mV, **R**·6PF_6 displays a maximum absorption ($\lambda_{max} = 561$ nm) band, accompanied by the appearance of a distinctive set of broad bands ($\lambda_{max} = 862$ nm, 1074 nm), consistent with the absorption spectra of the $BIPY^{\bullet+}$ radical cations in their dimerized form, as well as our previously studied pseudorotaxane and rotaxane systems.[24] These characteristic maximum absorptions support the conclusions drawn from the CV data, that is, the encirclement of $CBPQT^{2(\bullet+)}$ component around the $BIPY^{\bullet+}$ radical cation unit of the dumbbell component occurs after reduction. These CV and SEC experiments show that the radical interactions employed as the template in the synthesis live on in the rotaxane, after having supported the radical templation mechanism.

In summary, an unlikely [2]rotaxane **R**·6PF_6 composed only of electron-deficient $CBPQT^{4+}$ and $BIPY^{2+}$ units with no complementary electron-rich components has been prepared and fully characterized. Radical dimer interactions have been utilized as a recognition motif to generate this mechanically-interlocked compound. Upon oxidation of this rotaxane forged in its trisradical tricationic form to its fully oxidized state, a combination of Coulombic repulsion and the mechanical bonding forces the oligomethylene chain to play the role of a "pseudo-station" for the $CBPQT^{4+}$ ring. This synthetic strategy, which takes advantage of the marriage between templation and radical-pairing interactions, promises to help chemists overcome the reliance on the traditional template-directed protocols, and can be utilized as a general synthetic procedure for preparing MIMs composed of components with little or no binding affinities characterizing their ground states.[27]

Experimental Section

R·6PF_6: **T**·2PF_6 (167 mg, 0.2 mmol), **CBPQT**·4PF_6 (110 mg, 0.1 mmol), and tris(2,2′-bipyridine)dichlororuthenium(II) hexahydrate (74.8 mg, 0.1 mmol) were dissolved in MeCN (20 mL). The mixture was purged with Ar whilst stirring for 30 min, and then triethanolamine (1.49 g, 10 mmol) and di-*tert*-butyl acetylenedicarboxylate (226 mg, 1 mmol) were added. The reaction mixture was stirred under an Ar atmosphere in visible light for 3 days. The solvent was evaporated off and the residue was purified by column chromatography (SiO_2: MeOH and then 0.1% NH_4PF_6 in Me_2CO). Yellow fractions were collected, concentrated to a minimum volume, from which the product was precipitated on addition of H_2O, before being collected by filtration to afford **R**·6PF_6 (80 mg, 35%) as a light-yellow powder. ^{1}H NMR (500 MHz, CD_3CN): $\delta = 9.10$ (d, $J = 6.0$ Hz, 8H), 9.02 (d, $J = 6.5$ Hz, 2H), 8.93 (d, $J = 6.5$ Hz, 2H), 8.50 (d, $J = 6.5$ Hz, 2H), 8.44 (m, 10H), 7.55 (s, 8H), 5.78 (m, 8H), 4.68 (t, $J = 8.0$ Hz, 2H), 4.63 (t, $J = 8.0$ Hz, 2H), 4.49 (t, $J = 8.0$ Hz, 2H), 4.27 (m, 2H), 2.02 (br, 2H), 1.86 (br, 2H), 1.70 (s, 9H), 1.62 (s, 9H), 1.59 (s, 9H), 1.57 (s, 9H), 1.39–1.23 (m, 16H), 0.99 (br, 2H), 0.07 (br, 2H), −0.19 (br, 2H), -0.78 (br, 2H), −0.93 (br, 2H), −1.53 (br, 2H), −1.67 ppm (br, 2H). ^{13}C NMR (125 MHz, CD_3CN): $\delta = 159.4$, 159.4, 157.7, 157.6, 149.7, 149.6, 147.7, 145.4, 145.2, 140.8, 140.2, 135.7, 130.9, 130.8, 123.0, 128.4, 126.9, 126.8, 126.7, 85.4, 84.7, 83.0, 82.3, 67.4, 64.4, 61.8, 61.7, 49.8, 49.3, 38.3, 30.9, 30.6, 29.8, 29.6, 29.4, 29.1, 28.9, 28.8, 28.6, 28.3, 28.2, 28.0, 27.0, 26.9, 26.8, 25.8, 25.6, 25.2, 23.2, 22.4, 13.0, 10.0 ppm. ESI-HRMS calcd for $m/z = 1050.3951$ $[M-2PF_6]^{2+}$, found $m/z = 1050.3962$.

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