Molecular Switches

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A [2]Rotaxane Flip Switch Driven by Coordination Geometry**

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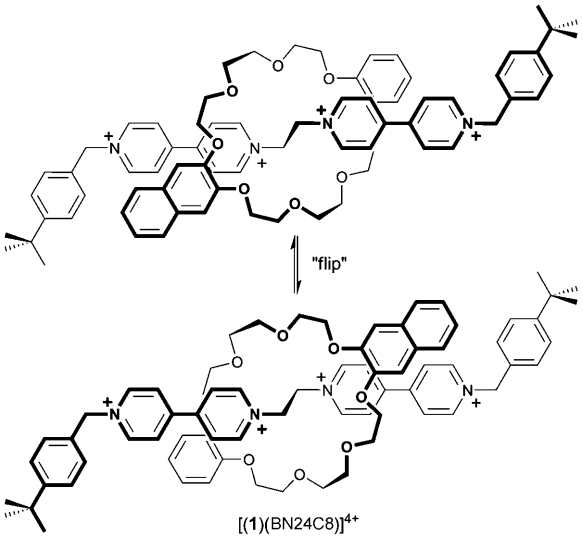
A molecular switch that is derived from a mechanically interlocked molecule (MIM) can exist in two distinct molecular arrangements: the ground-state co-conformation (GSCC) and a metastable co-conformation (MSCC), which are in equilibrium.[1] Ideally, these co-conformers are easily identifiable by using a spectroscopic technique, their relative populations are quantifiable, and the position of the equilibrium can be controlled by some external perturbation.[1,2] Probably the most well understood MIM switches are the bistable [2]rotaxane,[3] or molecular shuttle, and the bistable [2]catenane,[4] both pioneered by Stoddart and co-workers. In these systems, two different recognition sites are present on one component for the binding of a single macrocycle. The two states of the switch are co-conformers that are related by the relative positioning of the two interlocked components. In a related set of MIMs, we recently reported the first examples of a molecular "flip switch" that operates at a single recognition site on a simple [2]rotaxane.[5] In this system, the stability of the GSCC and MSCC are related to the degree of π stacking between the axle and the wheel, and the position of the co-conformational equilibrium was shown to be sensitive to the structure of the pyridinium component or the nature of the solvent.

The flip-switch [2]rotaxane is built around the templating motif of [24]crown-8 macrocycles and 1,2-bis(pyridinium)-ethane axles.[6] This motif has been successfully used in creating a variety of unique rotaxanes[7] and catenanes,[8] and has been incorporated into metal–organic frameworks (MOFs).[9] The concept of a flip-switch [2]rotaxane is shown in Scheme 1. In the [2]rotaxanes $[(\mathbf{1})(N24C8)]^{4+}$ and $[(\mathbf{1})(BN24C8)]^{4+}$, although the axle $\mathbf{1}^{4+}$ is symmetrical, the two ends of the molecules are different because the crown ethers contain two different aromatic rings. This result is clearly shown by low-temperature ^{1}H NMR spectra in CD_2Cl_2, which show eight distinct sets of pyridinium protons for $[(\mathbf{1})(N24C8)]^{4+}$ and six sets for $[(\mathbf{1})(BN24C8)]^{4+}$ because the pyridinium protons experience different amounts of shielding from the presence or absence of a naphtho or benzo ring. Each pair of exchanging resonances is separated by approximately 0.35 ppm, which is consistent with the effects of shielding that arise from π stacking. The rate of end-to-end exchange or "flipping" was determined to be on the order of $10^3\ s^{-1}$ at room temperature.



Scheme 1. [2]Rotaxanes such as $[(\mathbf{1})(N24C8)]^{4+}$ or $[(\mathbf{1})(BN24C8)]^{4+}$ (shown) with a single recognition site but containing a crown ether with two different aromatic groups (BN24C8 = [24]crown-8 bearing naphtho and benzo units; N24C8 = [24]crown-8 bearing only naphtho units). The crown ether undergoes a dynamic reorientation, reminiscent of a mechanical flip switch.

Since the flip-switch equilibrium is dictated by the degree of π stacking and thus the structural composition of the pyridinium component, it was of interest to use this principle to control the switching process. Herein, we report that the relative co-conformational stabilities can be controlled by manipulating the coordination geometry of an appended chelating group. The pioneering work of Sauvage and co-workers on Cu^I/Cu^{II} rotaxane systems,[10] and Leigh and co-workers on Cu^{II} and Pd^{II} molecular shuttle systems[11] are examples in which co-conformational switching of interlocked molecules has been shown to be dependent on metal–ligand coordination.

This new [2]rotaxane flip switch system incorporates a terpyridine (terpy) group on one end of the axle (see Scheme 2). The [2]rotaxane ligands $[(\mathbf{3})(BN24C8)]^{3+}$ and $[(\mathbf{3})(N24C8)]^{3+}$ were prepared by stoppering the 1,2-bis(pyridinium) axle $\mathbf{2}^{2+}$ with *tert*-butylbenzylbromide in the presence of an excess of the appropriate crown ether. The products were purified by column chromatography on silica and the anion was exchanged to the triflate ($CF_3SO_3^-$; OTf) salt to maintain solubility in organic solvents. The Pt^{II} and Ru^{II} complexes of these ostensibly terpy ligands were then prepared using standard conditions and appropriate starting materials (Scheme 2).

We chose to prepare the square-planar complexes $[PtMe(\mathbf{3})(BN24C8)]^{4+}$ and $[PtMe(\mathbf{3})(N24C8)]^{4+}$ as well as

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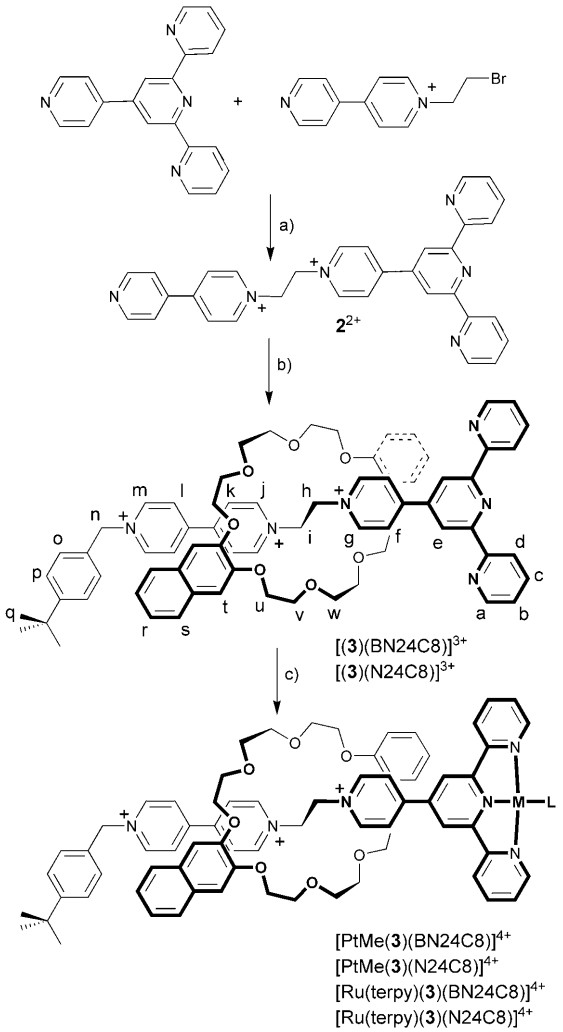
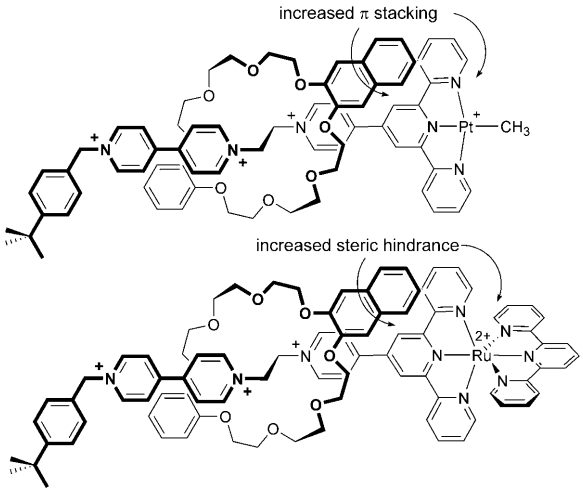


Scheme 2. a) MeCN, reflux, 7 days; anion exchange with NaOTf. b) *tert*-Butylbenzylbromide (2 equiv), crown ether (6 equiv), MeCN, RT, 7 days; anion exchange with NaOTf. c) For Pt complexes: [PtClMe-(Me_2S)$_2$] and AgOTf (1 equiv of each), MeOH, 50 °C, 24 h; for Ru complexes: [$RuCl_3$(terpy)], reflux in EtOH/H_2O, 12 h; labels refer to NMR spectral assignments. All anions are OTf^-.

the octahedral complexes [Ru(terpy)(**3**)(BN24C8)]$^{5+}$ and [Ru(terpy)(**3**)(N24C8)]$^{5+}$ as Pt^{II} and Ru^{II} provide robust, inert complexes for which metal–ligand exchange hardly occurs in a noncompetitive solvent such as $MeNO_2$.[12] It was rationalized that coordination of Pt^{II} would lock the pyridine rings of the terpy chelate into a single aromatic surface and the presence of an electropositive metal would create a large electron-poor surface for π stacking with the larger naphtho group on the crown ether. In contrast, we envisioned that the chelation of two orthogonally positioned terpy groups at an octahedral Ru^{II} center would present a significant steric barrier to the π stacking of the longer naphtho group on the crown ether (Scheme 3).[13] Ideally, it would be possible to record the limiting low-temperature ^{1}H NMR spectra for each flip-switch [2]rotaxane and integrate the peaks that represent the most affected pyridyl protons in order to determine the relative populations of the GSCC and MSCC. Unfortunately, because exchange was still rapid at the lowest



Scheme 3. Association between axle and wheel is dependent on the coordination geometry. A square-planar PtMe complex provides a large electron-poor surface for π stacking with the naphtho ring (top). An octahedral Ru(terpy) complex causes steric interactions between the ancillary terpy ligand and the naphtho unit (bottom).

temperatures that were accessible in CD_3CN, this measurement was not possible. Instead, the positions of the resonances that represent the exchanging protons m(BN) and m(N) in [(**3**)(BN24C8)]$^{3+}$ and [(**3**)(N24C8)]$^{3+}$ at room temperature (300 K) were compared to the limiting shifts for these protons, m(DB) and m(DN), in the analogous rotaxanes [(**1**)(DB24C8)]$^{4+}$ and [(**1**)(DN24C8)]$^{4+}$ in order to determine the ratio of co-conformers for all six [2]rotaxanes studied (Figure 1 and Table 1). It should be noted that this method

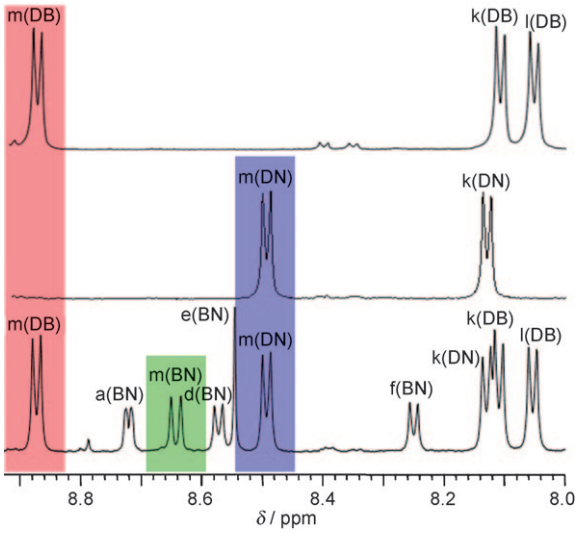


Figure 1. Partial ^{1}H NMR spectra (500 MHz, 300 K, CD_3CN, 2.0×10^{-3} M) comparing the shifts of pyridyl proton labeled m. Top: the model [2]rotaxane [(**1**)(DB24C8)]$^{4+}$ (red); middle: the model [2]rotaxane [(**1**)(DN24C8)]$^{4+}$ (blue); bottom: the flip-switch [2]rotaxane [(**3**)-(BN24C8)]$^{4+}$ (green) and model compounds [(**1**)(DB24C8)]$^{4+}$ (red) and [(**1**)(DN24C8)]$^{4+}$ (blue). The ratio of co-conformers was determined by comparing the chemical shift value of the flip switch to the limiting shifts of the two reference rotaxanes in the fast-exchange regime.

Table 1: Ratios of co-conformations for various flip-switch [2]rotaxanes.[a]

[2]Rotaxane	Co-conformer ratio (N/DP:N/TP)[b]
[(**3**)(BN24C8)]$^{3+}$	61:39
[PtMe(**3**)(BN24C8)]$^{4+}$	26:74
[Ru(terpy)(**3**)(BN24C8)]$^{5+}$	62:38
[(**3**)(N24C8)]$^{3+}$	59:41
[PtMe(**3**)(N24C8)]$^{4+}$	12:88
[Ru(terpy)(**3**)(N24C8)]$^{4+}$	59:41

[a] Determined by ^{1}H NMR spectroscopy in CD_3CN (2.0×10^{-3} M) at 298 K. [b] N/DP indicates naphtho π stacked with 4,4′-dipyridinium and N/TP naphtho π stacked with terpyridine. Errors for ratios are estimated to be < 5%.

was successfully employed with the original system shown in Scheme 1. In particular, the use of [(**1**)(DB24C8)]$^{4+}$ and [(**1**)(DN24C8)]$^{4+}$ as internal standards eliminated the introduction of small errors that arise from differences in solvent, temperature, and NMR measurements that would be inherent in any external comparisons.

Solution-based studies (Table 1) show that our original hypothesis of controlling the relative stabilities of the co-conformations by changing the coordination geometry at the terpy site was realized. In both ligand [2]rotaxanes, [(**3**)(BN24C8)]$^{3+}$ and [(**3**)(N24C8)]$^{3+}$, the naphtho ring of the crown ether prefers to π stack with the more electron-poor, doubly charged bipyridinium unit rather than the terpyridine unit to give co-conformational preference ratios of 61:39 and 51:49, respectively (Table 1). This result is consistent with previously observed trends from [2]pseudorotaxane studies which showed that axles that bear this paraquat-like group preferred DN24C8 > DB24C8 > 24C8.[14] The introduction of a PtMe unit and the enforcement of a square-planar geometry completely reverses this trend and greatly increases the population of the co-conformer that positions the naphtho group over the metal coordination site, thus favoring this site by a factor of approximately 3 for BN24C8 and a factor greater than 7 for N24C8. The rationale for this reversal is straightforward: the naphtho group of BN24C8 or N24C8 extends far enough that it can be influenced by the [Pt(terpy)Me]$^+$ coordination environment, while this is not the case for the benzo group in BN24C8, and for N24C8 there is no competing aromatic group. The presence of the Pt^{II} fragment provides a larger, rigid, and more electron-poor surface, which results in increased π-stacking interactions.

Single crystals suitable for X-ray crystallography were grown by slow evaporation of a solution of the complex [PtMe(**3**)(BN24C8)][OTf]$_4$ in $CHCl_3$. Figure 2a shows a ball-and-stick representation of the cationic portion of [PtMe(**3**)(BN24C8)]$^{4+}$. As expected, the thread adopts an *anti* conformation at the central NCH_2CH_2N unit while the BN24C8 wheel exhibits a typical S-shaped conformation. These conformations complement each other such that the two aromatic groups of the crown ether wheel are oriented over the aromatic portions of the axle. Not surprisingly, in the solid state, [PtMe(**3**)(BN24C8)]$^{4+}$ adopts the co-conformation favored in solution where the naphtho ring π stacks with the {PtMe(terpy)} fragment and the benzo group with the 4,4′-dipyridinium unit of the axle.

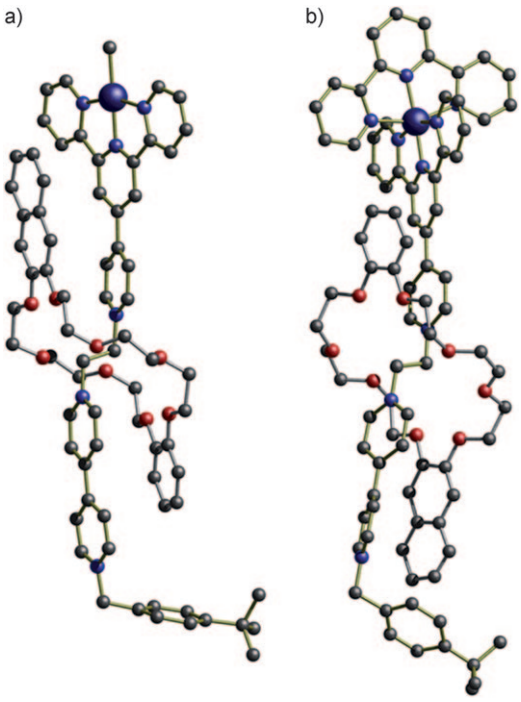


Figure 2. a) Ball-and-stick representation of the X-ray structure of [PtMe(**3**)(BN24C8)]$^{4+}$. The naphtho group is π stacked over the PtMe coordination site. b) Ball-and-stick representation of the X-ray structure of [Ru(terpy)(**3**)(BN24C8)]$^{5+}$. The naphtho group is π stacked over the 4,4′-bipyridinium site. Oxygen = red, nitrogen = blue, carbon = black, metal = dark blue, axle = gold bonds, wheel = silver bonds.

Conversely, for the octahedral Ru^{II} complexes, the presence of a second terpy ligand at right angles to the rotaxane ligand effectively eliminates the possibility of π stacking with the terpy portion of the axle. Instead, coordination creates a steric barrier between the crown ether naphtho ring and the ancillary terpy ligand, thus lowering the stability of this orientation. From the ratios in Table 1, 62:38 and 59:41 for [Ru(terpy)(**3**)(BN24C8)]$^{5+}$ and [Ru(terpy(**3**)(N24C8)]$^{5+}$, respectively, it is clear that the naphtho group prefers to π stack with the 4,4′-bipyrdinium site rather than the terpyridine.

Single crystals of [Ru(terpy)(**3**)(BN24C8)][OTf]$_4$ were grown by diffusion of *iso*propyl ether into a solution of the complex in $MeNO_2$. Figure 2b shows a ball-and-stick representation of the cationic portion of the complex [Ru(terpy)(**3**)(BN24C8)]$^{5+}$. Again, the complex adopts the lower energy co-conformation observed in solution, in which the naphtho ring π stacks with the 4,4′-dipyridinium unit, thus allowing the smaller benzo ring to π stack with the terpyridine unit of the thread.

Interestingly, the co-conformational preferences for the Ru^{II} complexes (62:38 and 59:41) are practically the same as those found in the absence of the Ru(terpy) coordination (61:39 and 59:41 for BN24C8 and N24C8, respectively). This similarity occurs because the Ru(terpy)$_2$ unit can rotate away from the naphtho group, which mitigates much of the negative

effects of the introduction of a steric barrier. This effect can been seen clearly in the previously reported structure of [Ru(terpy)(**3**)(DN24C8)][OTf]$_4$ in which both aromatic rings are naphtho.[15] In this complex, the naphtho group lies between the two sets of perpendicular terpyridine planes that have rotated approximately 38° from the position that would normally result in π stacking. In the absence of this steric problem, there is no rotation and the two sets of rings (benzo and pyridinium) are essentially coplanar as in [Ru(terpy)(**3**)-(BN24C8)]$^{5+}$.

From the results obtained from solutions and the behavior in the solid state, it was concluded that the coordination of PtMe and the creation of an enhanced electron-poor surface for π stacking is a much better strategy for influencing co-conformational preference than attempting to create a steric barrier by introducing an octahedral center through the addition of Ru(terpy).

With the effect of coordination geometry established by using inert Ru^{II} and Pt^{II} complexes, it was of interest to apply this principle to more labile metals in order to allow for interconversion between the two states of the flip switch by exchanging metal ions and their coordination geometry. Since the position of the co-conformational equilibrium was not significantly altered upon coordination of the octahedral Ru^{II} center, we chose to focus on the coordination chemistry of a square-planar metal center as the driving force to control switching. To this end, we prepared the Ag^{I} complex [Ag-(MeCN)(**3**)(BN24C8)]$^{4+}$ as a labile analogue of [PtMe(**3**)-(BN24C8)]$^{4+}$.[16] ^{1}H NMR spectroscopy was then used to determine the position of the equilibrium in the presence and absence of Ag^{I}. The ^{1}H NMR spectrum of the ligand [(**3**)(BN24C8)]$^{3+}$ and that of [Ag(MeCN)(**3**)(BN24C8)]$^{4+}$, which results from the addition of AgOTf to a solution of the ligand, are compared in Figure 3. After subsequent treatment with nBu$_4$NCl and filtration, the solution spectrum was essentially identical to that recorded before the addition of Ag^{I}. This cycle was repeated five times without significant degradation in the quality of the NMR spectrum. Using the same solution NMR methodology shown in Figure 1 and summarized in Table 1, it was possible to show that the co-conformer ratio switches from 39% naphtho π stacked with terpyridine (N/TP) in the absence of Ag^{I} to 62% N/TP in the presence of Ag^{I}.

In summary, it has been demonstrated that our original design of a flip-switch [2]rotaxane is versatile enough to be incorporated into a molecular switch, which can be controlled by the addition and removal of an external perturbation. The use of a ligating (terpy) component on the axle provides a simple way to modulate the interaction between axle and wheel by changing coordination geometry. Moreover, this compact flip-switch [2]rotaxane, which requires only a single recognition site, has major advantages over more complex and larger molecular shuttles. In particular, the simpler flip switch should be significantly easier to incorporate into materials or surface applications because of its size. As has been demonstrated for many types of molecular shuttles, control of the switching by using electrochemical and photochemical means should also be possible.

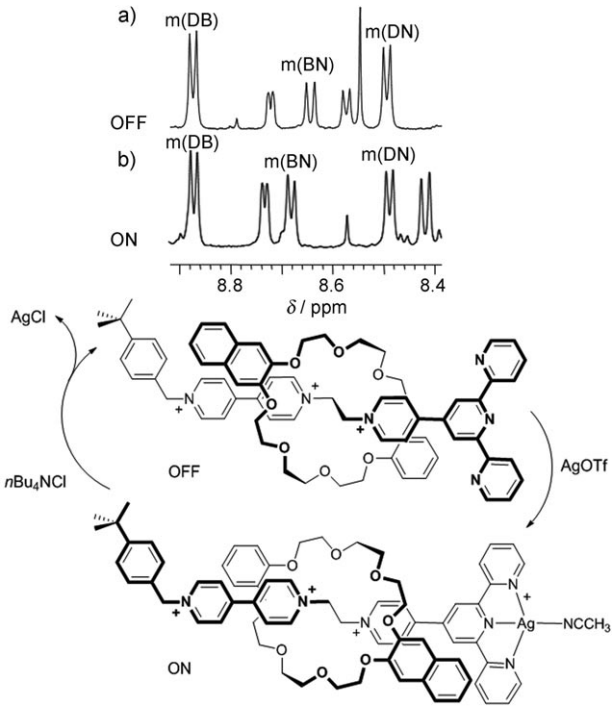


Figure 3. Partial ^{1}H NMR spectra (500 MHz, 300 K, CD_3CN, 2.0×10^{-3} M) comparing the shifts of pyridyl proton labeled m (green). a) Ligand [(**3**)(BN24C8)]$^{4+}$; b) after addition of AgOTf. The ratio of co-conformers was determined by comparing the chemical shift value of the flip switch to the limiting shifts of the two reference rotaxanes in the fast-exchange regime.

Experimental Section

The axle **2**[OTf]$_2$ was prepared as described previously.[17] DB24C8 was purchased from Aldrich Chemicals and used as received. DN24C8, BN24C8, and N24C8 were prepared by a slight modification of the reported procedure;[18] see the Supporting Information for details. Complexes [PtMeCl(Me_2S)$_2$][19] and [$RuCl_3$(terpy)][20] were prepared by following reported procedures. All NMR experiments were recorded on a Bruker AMX 500 MHz NMR spectrometer.

Crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer with a CCD detector. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL program library[21] and figures were drawn with DIAMOND software.[22] Crystal data for [PtMe(**3**)-(BN24C8)][OTf]$_4$·$(CHCl_3)_2(H_2O)_4$ $C_{78}H_{96}Cl_6F_{12}N_6O_{24}PtS_4$; M_r = 2257.6; yellow prisms ($0.20\times0.16\times0.14$ mm); monoclinic; $P2_1/n$, a = 16.933(3), b = 13.034(2), c = 41.590(6) Å; β = 93.701(3)°; U = 9160(2) Å^3; Z = 4; ρ_{calcd} = 1.637 g cm^{-3}; μ = 0.190 mm^{-1}; min/max trans. = 0.7430; $Mo_{K\alpha}$ λ = 0.71073 Å; T = 173.0(2) K; 16128 total reflections (R(int) = 0.0609); $R1$ = 0.0883, $wR2$ = 0.2275 [$I > 2\sigma I$]; $R1$ = 0.1090, $wR2$ = 0.2409 (all reflections); GoF(F^2) = 1.132, data/variables/restraints = 16128/1180/18. Crystal data for [Ru(terpy)(**3**)-(BN24C8)]·$Cl_{4.2}(OTf)_{5.8}(H_2O)_{12}$: $C_{88.9}H_{98}Cl_{2.1}F_{8.8}N_9O_{22.8}RuS_{2.9}$; M_r =

2091.5; red prisms (0.24 × 0.22 × 0.16 mm); triclinic; $P\bar{1}$, $a = 21.195(4)$, $b = 22.269(4)$, $c = 27.002(5)$ Å; $\alpha = 105.750(3)$, $\beta = 95.199(3)$, $\gamma = 112.865(3)°$; $U = 11023(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.260$ g cm^{-3}; $\mu = 0.329$ mm^{-1}; min/max trans. = 0.7824; $Mo_{K\alpha}$ $\lambda = 0.71073$ Å; $T = 173.0(2)$ K; 22885 total reflections (R(int) = 0.1048); $R1 = 0.1206$, $wR2 = 0.3227$ [$I > 2\sigma I$]; $R1 = 0.2078$, $wR2 = 0.3827$ (all reflections); GoF(F^2) = 1.233, data/variables/restraints = 22885/2671/487. Disorder between $CF_3SO_3^-$ and Cl^- ions resulted in a model containing 5.83 triflate ions and 4.17 chloride ions. A total of 12 water molecules were also located and refined. Both Ru ions in the asymmetric unit were well-behaved. CCDC-769124 and 769125 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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