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Stimuli-Responsive Reversible Assembly of 2D and 3D Metallosupramolecular Architectures

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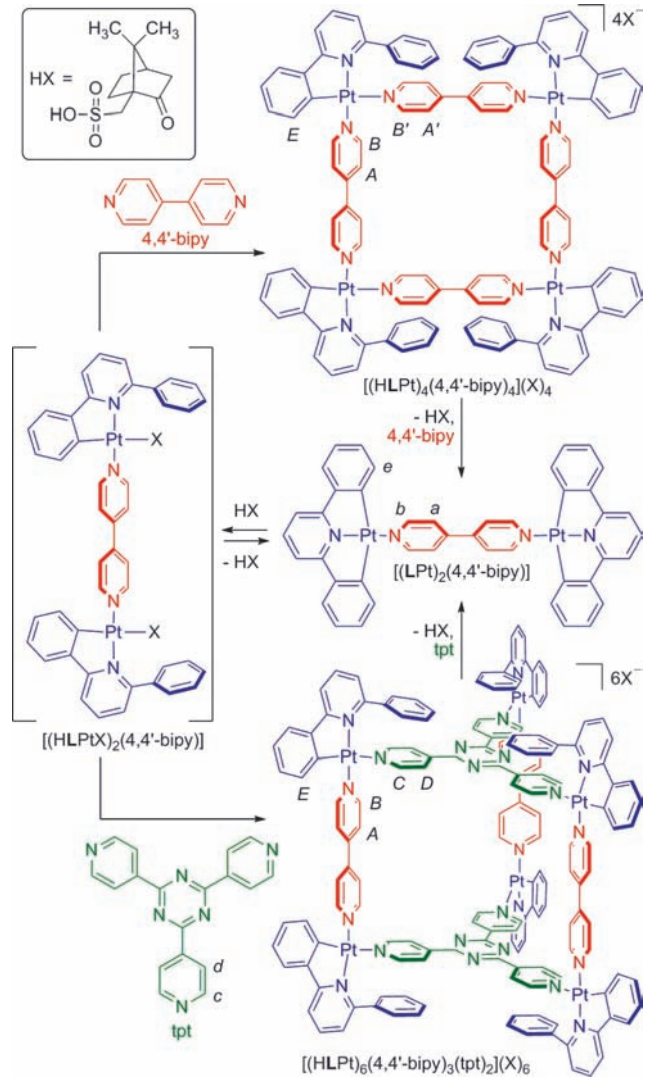
In the last 20 years, supramolecular chemistry has witnessed an explosion in discrete nanoscale self-assembled cages and capsules.[1−3] Nonetheless, many of these artificial systems lack the dynamic function that often defines their naturally occurring biological counterparts, such as the ability to spontaneously assemble (and then disassemble) in response to a specific stimulus or a subtle change in the local environment (e.g., a pH change).[4] The demonstration of stimuli-responsive dynamic function in metallosupramolecular systems, such as reversible switching between different assemblies in solution, remains rare.[5] In this communication, we report the discovery of a reversible, acid−base-switchable platinum cyclometalation reaction, which has been exploited to create stimuli-responsive metallosupramolecular architectures that disassemble upon reaction with base and reassemble through a proton-activated process.

This research was initiated by a study of the neutral pseudo-square-planar carboplatinum complex [**L**Pt(DMAP)] (H_2**L** = 2,6-diphenylpyridine, DMAP = 4-dimethylaminopyridine). Rather unexpectedly, when this complex was treated with 1 equiv or an excess of *p*-toluenesulfonic acid (TsOH), clean and immediate formation of [H**L**Pt(DMAP)OTs] was observed, where TsOH had effectively added across one of the Pt−C bonds. The structure of [H**L**Pt(DMAP)OTs] was confirmed by X-ray crystallography (see the Supporting Information) using crystals grown from diisopropyl ether and chloroform. It appears that this process is driven by a slight shortening of the remaining Pt−C bond, from 2.06 Å in [**L**Pt(DMAP)] to 1.95 Å in [H**L**Pt(DMAP)OTs] (see the Supporting Information), at the expense of the added chelate. Nonetheless, the energetics of this process appear to be finely balanced, as simply treating [H**L**Pt(DMAP)OTs] with base, either heterogeneously using K_2CO_3 or in solution with the phosphazene base P_1-^{t}Bu,[6] resulted in rapid conversion back to the starting material, [**L**Pt(DMAP)]. This process could be monitored using ^{1}H NMR spectroscopy, and studies in different deuterium-labeled solvents indicated that the TsO^- anion of [H**L**Pt(DMAP)OTs] is readily displaced by better ligands such as pyridine and even acetonitrile. In effect, this protonation/deprotonation event reveals/masks cis coordinating groups at a square-planar Pt(II) center, a process we therefore reasoned could be used to reversibly assemble metallosupramolecular architectures, similar to those previously reported by Stang[2] and Fujita.[3]

To explore this concept, [(**L**Pt)$_2$(4,4′-bipy)] was prepared by stirring 2 equiv of the known complex[7] [**L**Pt(DMSO)] with 4,4′-bipyridine in dichloromethane. The product possessed relatively low solubility, which facilitated the isolation of an orange solid through filtration. Despite the low solubility, treatment of [(**L**Pt)$_2$(4,4′-bipy)] with a dichloromethane solution of (+)-camphor-10-sulfonic acid (CSA) resulted in dissolution within minutes to give a pale-yellow solution, after which time a second equivalent of 4,4′-bipy was added (Scheme 1). The ^{1}H NMR spectrum of the resulting solution indicated the rapid formation of predominantly a single species that did not appear to change over time. As an alternative to sequential addition, treatment of [(**L**Pt)$_2$(4,4′-bipy)] directly with the CSA salt of 4,4′-bipyridine (i.e., 4,4′-bipy·2CSA) gave the same ^{1}H NMR spectrum. To aid in the isolation, NH_4PF_6 was added to the solution, and following recrystallization from nitromethane and diethyl ether, the product was obtained as a yellow solid. The electrospray mass spectrum of this sample (Figure 1a) showed

Scheme 1. Stimuli-Responsive Assembly and Disassembly of 2D and 3D Metallosupramolecular Architectures



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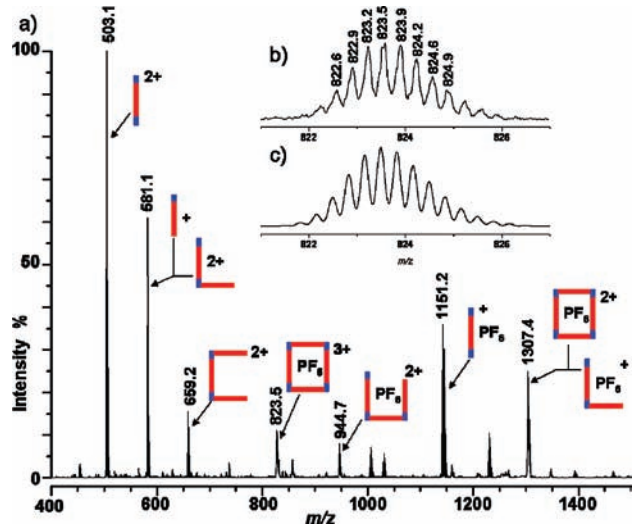

Figure 1. (a) Electrospray mass spectrum of $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$. The insets show (b) the experimental isotope pattern and (c) the predicted isotopic distribution for the tricationic molecular square $[[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)]^{3+}$.

several peaks between *m/z* 500 and 1500, but a closer inspection of the peak at *m/z* 823.5 (Figure 1b) revealed a third of a unit peak separation, and the peak pattern compared well to the predicted isotopic distribution (Figure 1c) for the tricationic molecular square[8] $[[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)]^{3+}$. The peak at *m/z* 1307 showed a half-unit separation, and although this was consistent with the 2+ molecular square $[[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_2]^{2+}$, the peak overlapped with that for the singly charged half-molecular-square fragment $[(H\mathbf{L}Pt)_2(4,4'\text{-bipy})_2](PF_6)]^{+}$, prohibiting further predicted isotope comparison. Virtually all of the peaks within the *m/z* 500−1500 region could be readily assigned to fragments of $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$.

$[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$ could potentially adopt several different isomeric forms. However, the ^{1}H NMR spectrum of $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$ in CD_3NO_2 (Figure 2) indicated a single product with 14 different proton environments (for the full assignment, see the Supporting Information), which eliminated lower-symmetry isomers and suggested that the product was one of two possibilities: either the D_{2h}-symmetric isomer shown in Scheme 1 or the C_{4h} isomer in which the Pt corner pieces all point in a clockwise direction. Further NMR analysis revealed an nuclear Overhauser effect (NOE) cross-signal between the different ortho bipy protons (H_B and $H_{B'}$) but not between the meta bipy protons (H_A and $H_{A'}$), which eliminated the C_{4h} isomer.[9] In effect, the formation of the D_{2h} metallocycle in methylene chloride at room temperature is a kinetically controlled four-component self-assembly process involving two acceptor and two donor components, which explains the absence of any entropically favored triangular species.[10]

Single crystals of $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$ suitable for analysis by X-ray crystallography were grown from nitromethane and diethyl

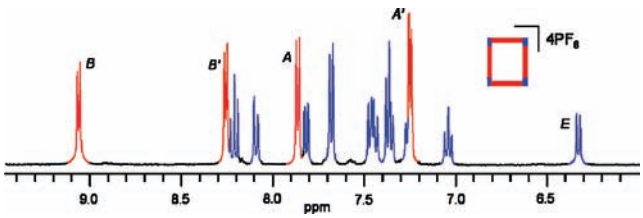

Figure 2. ^{1}H NMR spectrum (CD_3NO_2, 400 MHz, 300 K) of the molecular square $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$. The assignments correspond to the lettering shown in Scheme 1.

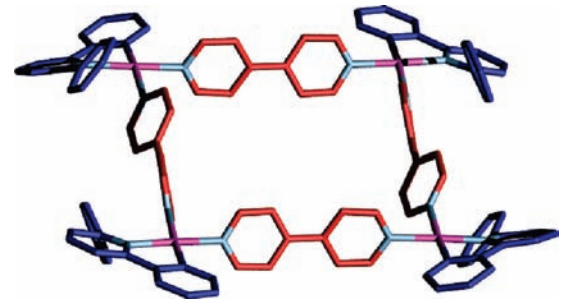

Figure 3. X-ray crystal structure of the molecular square $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$. The carbon atoms of 4,4′-bipy are shown in red, carbon atoms of H**L** in blue, platinum atoms in magenta, and nitrogen atoms in pale-blue. The PF_6 counteranions and five nitromethane solvent molecules have been removed for clarity.

ether. The solid-state structure (Figure 3) confirmed a tetrameric molecular-square arrangement and also the connectivity of the kinetic D_{2h} product. However, the view along the plane of the square clearly shows that the product adopts a lower-symmetry arrangement in the solid state due to quite different 4,4′-bipy conformations. The 4,4′-bipy units that lie trans to the nitrogen donor of H**L** adopt an essentially planar conformation (torsion angle = 9°) and lie perpendicular to the plane of the four platinum ions. In contrast, the other bipy units adopt a nonplanar orientation (torsion angle = 46°) in which two hydrogen atoms from each constituent pyridine moiety point slightly toward the center of the square. The adoption of this conformation appears to be caused by $\pi-\pi$ interactions between these constituent pyridine groups and the noncoordinating phenyl moiety of H**L** (centroid−centroid distances of between 3.41 and 3.52 Å).[11] In addition, the noncoordinating phenyl groups of H**L** are oriented either above or below the plane of the four platinum ions, presumably to avoid unfavorable steric interactions between adjacent sites.

To explore the stimuli-responsive disassembly process, a dichloromethane solution of P_1-^{t}Bu was added to $[(\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$ (Scheme 1). Almost immediately, a darkening of the solution was observed, and after the solution was stirred overnight at room temperature, an orange solid was filtered off and showed spectroscopic properties identical to those of the material already assigned as $[(\mathbf{L}Pt)_2(4,4'\text{-bipy})]$. Unsurprisingly, this base-induced disassembly of the tetramer is slow in comparison to the reaction of the mononuclear complex [H**L**Pt(DMAP)OTs] to give [**L**Pt(DMAP)], which under similar conditions is complete by the time an NMR spectrum can be recorded (less than 5 min).

To take this chemistry from two to three dimensions, the switchable self-assembly with the triazine ligand tpt[12] was also investigated, both by sequential addition of CSA and tpt to $[(\mathbf{L}Pt)_2(4,4'\text{-bipy})]$ (Scheme 1) and by direct addition of the salt. Again, formation was rapid at room temperature, and after exchange of the counteranions by treatment with NH_4PF_6, a yellow solid was isolated in 97% yield. The electrospray mass spectrum of this product showed several peaks, many of which could be assigned to fragments of the cage, but those at *m/z* 1359 and 2112 compared well to the predicted isotopic distribution for the intact 3+ and 2+ species, respectively (see the Supporting Information), thus supporting the formation of the molecular trigonal prism $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$. In addition, the ^{1}H NMR spectrum of this product (Figure 4a) showed the correct ratio of triazine signals (H_C and H_D), bipy signals (H_A and H_B), and signals from H**L** (e.g., H_E), and the NOE spectrum showed a cross-peak between H_B and H_C. The large upfield shifts of the triazine pyridyl signals (H_C and H_D) relative to those for the free triazine ligand are likely caused by $\pi-\pi$ interactions with the noncoordinating phenyl group of H**L**, which further supports

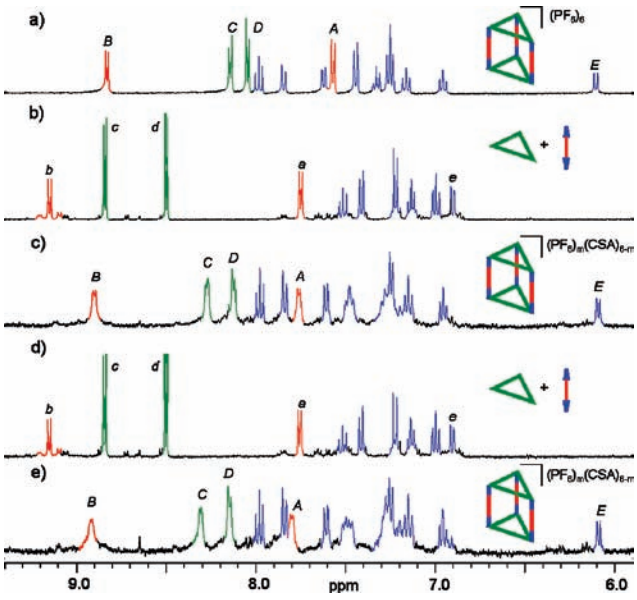

Figure 4. ^{1}H NMR spectra (CD_2Cl_2, 400 MHz, 300 K) showing solution switching between assembled and disassembled states of the trigonal prism $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2]^{6+}$: (a) spectrum of $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$; spectra recorded (b) 2 h after the addition of 12 equiv of P_1-^{t}Bu to $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$; (c) 30 min after subsequent addition of 12 equiv of CSA; (d) 2 h after subsequent addition of 12 equiv of P_1-^{t}Bu; and (e) 30 min after subsequent addition of 12 equiv of CSA. The assignments correspond to the lettering shown in Scheme 1.

the formation of a single product isomer via what is in effect a kinetically controlled, five-component self-assembly process involving three ditopic acceptors and two tritopic donor units.

The increased solubility of the prism $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$ in dichloromethane, relative to that of the square, allowed the stimuli-responsive switching to be monitored in solution using ^{1}H NMR spectroscopy (Figure 4). This experiment was initiated by the addition of 12 equiv of P_1-^{t}Bu (2 equiv per Pt ion) to a CD_2Cl_2 solution of $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$. After 2 h, complete disappearance of the signals assigned to $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$ (H_A−H_E) and the emergence of new resonances corresponding to the disassembled components tpt (H_c and H_d) and $[(\mathbf{L}Pt)_2(4,4'\text{-bipy})]$ (H_a, H_b, and H_e) was observed. Addition of 12 equiv of CSA to the same sample resulted in the disappearance of the signals due to free tpt and $[(\mathbf{L}Pt)_2(4,4'\text{-bipy})]$ and the appearance of a new set of signals (Figure 4c). This spectrum showed a striking similarity to the spectrum of $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_6$ (Figure 4a), indicating that the addition of CSA effects the reassembly of the trigonal prism in solution. The subtle differences and slight broadening in the spectrum of the CSA-reassembled species are likely caused by a mixture of different counteranions present in solution to give $[(H\mathbf{L}Pt)_6(4,4'\text{-bipy})_3(tpt)_2](PF_6)_m(CSA)_{6-m}$. A second addition of 12 equiv of P_1-^{t}Bu (Figure 4d) followed by 12 equiv of CSA (Figure 4e) indicate these metallosupramolecular architectures can be efficiently cycled between assembled and disassembled states in solution simply by alternating the addition of acid and base.

In conclusion, the discovery of a pH-switchable platinum coordination mode has been exploited to switch on the self-assembly of two- and three-dimensional metallosupramolecular architectures. The efficacy of this self-asssembly process was demonstrated through the formation of single species in good to excellent yields, and in both cases, the self-assembly process could be simply reversed in full by treatment with a slight excess of base. We are currently looking at ways to link this responsive behavior to other functions such as transport, catalysis, and sensing.

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Supporting Information Available: Experimental procedures and spectroscopic data for all new compounds; full crystallographic details for [**L**Pt(DMAP)], [H**L**Pt(DMAP)OTs], and $[(H\mathbf{L}Pt)_4(4,4'\text{-bipy})_4](PF_6)_4$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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