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

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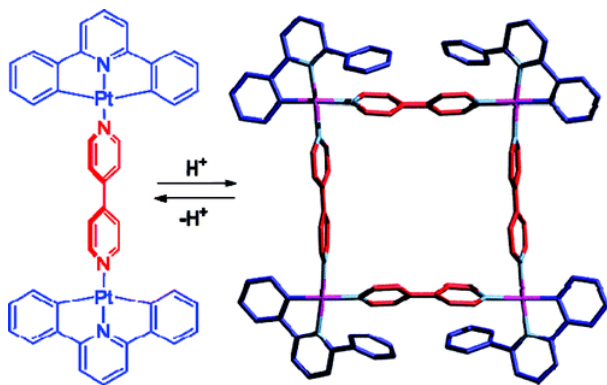
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Supporting information:

Experimental procedures and spectroscopic data for all new compounds; full crystallographic details for [[LPt(DMAP)], [HLPt(DMAP)OTs] and [(HLPt)₄(4,4'-bipy)₄](PF₆)₄. This material is available free of charge via the Internet at <http://pubs.acs.org>

Graphical abstract:



Abstract

The discovery of interconvertible platinum coordination modes, which reveals/masks *cis* coordinating groups upon addition of acid and base respectively, has been exploited to facilitate stimuli-responsive assembly and disassembly of both two and three-dimensional metallocsupramolecular architectures. By treating a binuclear platinum complex with acid and either a ditopic or a tritopic donor ligand, both a molecular square and a trigonal prism have been generated in good to high yield. These complexes have been unambiguously identified using electrospray mass spectrometry, ^1H NMR spectroscopy and X-ray crystallography. Both assemblies can be disassembled into their constituent parts by simply treating with base and the prism cycled between assembled and disassembled states by the alternate addition of base and acid.

Main text

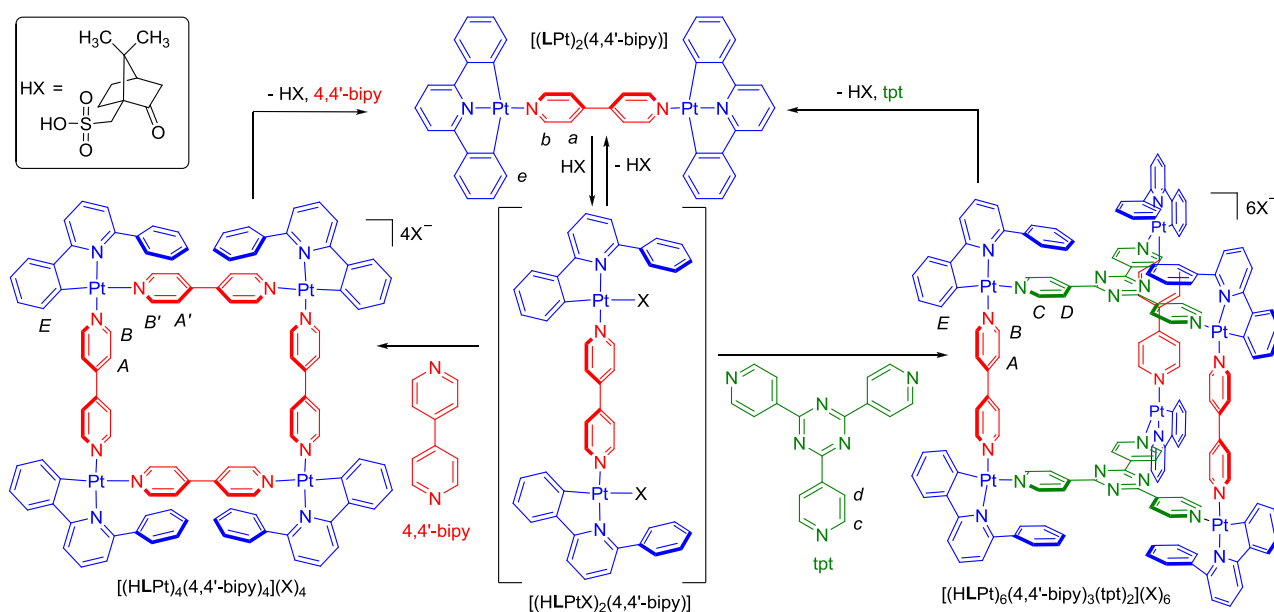
In the last 20 years, supramolecular chemistry has witnessed an explosion in discrete nanoscale self-assembled cages and capsules.¹⁻³ Nonetheless, many of these artificial systems lack the dynamic function which often defines their naturally occurring biological counterparts, such as the ability to spontaneously assemble (and then disassemble) in response to a specific stimulus or a subtle change in the local environment (e.g. pH change).⁴ The demonstration of stimuli-responsive dynamic function in metallocsupramolecular 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 cyclometallation reaction, which has been exploited to create stimuli-responsive metallocsupramolecular architectures that disassemble upon reaction with base and re-assemble through a proton-activated process.

This research was initiated by a study of the neutral pseudo-square planar carboplatinum complex [LPt(DMAP)] (H_2L = 2,6-diphenylpyridine, DMAP = 4-dimethylaminopyridine). Rather unexpectedly, when this complex was treated with one equivalent or an excess of *p*-toluenesulfonic acid (TsOH) clean and immediate formation of [HLPt(DMAP)OTs] was observed, where TsOH had effectively added across one of the Pt-C bonds. The structure of [HLPt(DMAP)OTs] was confirmed by X-ray crystallography (see 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 [LPt(DMAP)] to 1.95 Å for [HLPt(DMAP)OTs] (see Supporting Information), at the expense of the added chelate.

Nonetheless, the energetics of this process appear finely balanced as simply treating [HLPt(DMAP)OTs] with base, either heterogeneously using K_2CO_3 or in solution with the phosphazene base $\text{P}_1\text{-}^t\text{Bu}$,⁶ resulted in rapid conversion back to the starting material i.e. [LPt(DMAP)]. This process could be monitored using ^1H NMR spectroscopy and studies in different deuterium labeled solvents indicated that the TsO^- anion of [HLPt(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) centre, a process we therefore reasoned could be used to reversibly assemble metallosupramolecular architectures, similar to those previously reported by Stang² and Fujita³.

To explore this concept, $[(\text{LPt})_2(4,4'\text{-bipy})]$ was prepared by stirring two equivalents of the known complex⁷ $[\text{LPt}(\text{DMSO})]$ with 4,4'-bipy in dichloromethane. The product possessed relatively low solubility which facilitated the isolation of an orange solid through filtration. Despite the low solubility, treating $[(\text{LPt})_2(4,4'\text{-bipy})]$ 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 ^1H NMR spectrum of the resulting solution indicated the rapid formation of a predominantly single species, which did not appear to change over time. As well as sequential addition, treating $[(\text{LPt})_2(4,4'\text{-bipy})]$ directly with the CSA salt of 4,4'-bipy, i.e. 4,4'-bipy \cdot 2CSA gave the same ^1H NMR spectrum. To aid 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 several peaks between 500-1500 m/z units but a closer inspection of the peak at 823.5 m/z (Figure 1b) revealed a third of a unit peak separation and compared well to the predicted isotopic distribution (Figure 1c) for the tricationic molecular square⁸ $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_3^{3+}$. The peak at 1307 m/z showed half unit separation and although this was consistent with the 2+ molecular square ($[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_2^{2+}$) it overlapped with the singly charged half-molecular square fragment ($[(\text{HLPt})_2(4,4'\text{-bipy})_2](\text{PF}_6)^+$) and thus prohibited further predicted isotope comparison. Virtually all the peaks within the 500-1500 m/z region could be readily assigned to fragments of $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$.



Scheme 1. Stimuli-responsive assembly and disassembly of two and three dimensional metallosupramolecular architectures.

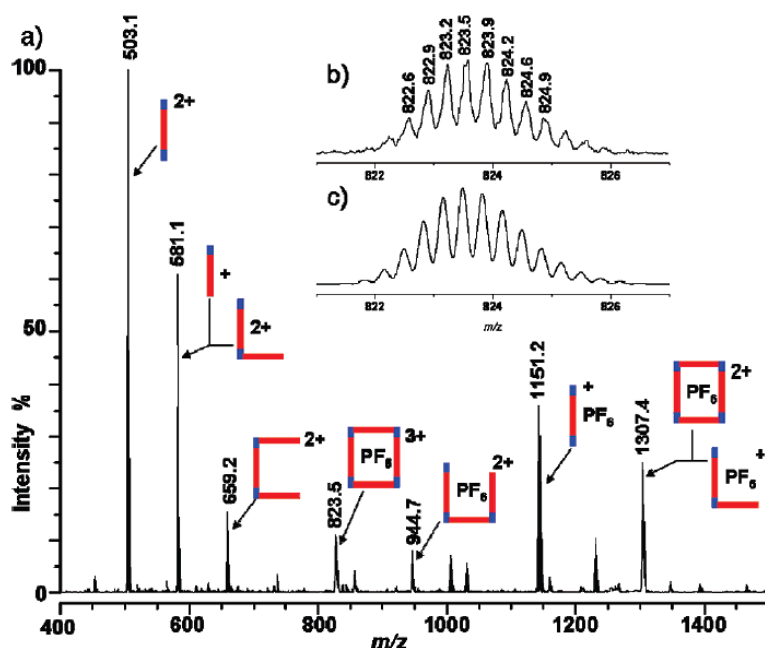


Figure 1. a) Electrospray mass spectrum of $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$; with insets b) experimental isotope pattern for tricationic molecular square $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)^{3+}$ and c) predicted isotopic distribution for molecular square $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)^{3+}$.

$[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$ could potentially adopt several different isomeric forms. However, the ^1H NMR spectrum of $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$ in CD_3NO_2 (Figure 2) indicated a single product with 14 different proton environments (for full assignment, see 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 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 between two acceptor and two donor components and explains the absence of any entropically favored triangular species.¹⁰

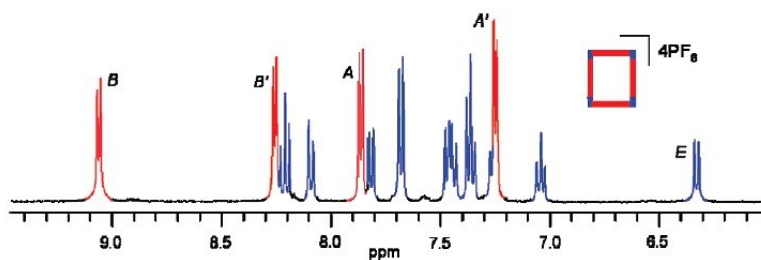


Figure 2. ^1H NMR spectrum (CD_3NO_2 , 400 MHz, 300 K) of molecular square $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$. The assignments correspond to the lettering shown in Scheme 1.

Single crystals of $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$ suitable for analysis by X-ray crystallography were grown from nitromethane and diethyl ether. The solid state structure (Figure 3) confirmed a tetrameric molecular square arrangement and also the connectivity of the kinetic D_{2h} product. However, when viewed along the plane of the square it can clearly be observed 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 which lie *trans* to the nitrogen donor of HL 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 non-planar orientation (torsion angle = 46°) such that two hydrogen atoms from each constituent pyridine moiety point slightly towards the centre of the square. The adoption of this conformation appears to be caused by π - π interactions between these constituent pyridine groups and the non-coordinating phenyl moiety of HL (centroid-centroid distances of between 3.41 and 3.52 Å).¹¹ In addition, the non-coordinating phenyl groups of HL are oriented either above or below the plane of the four platinum ions, presumably to avoid unfavorable steric interactions between adjacent sites.

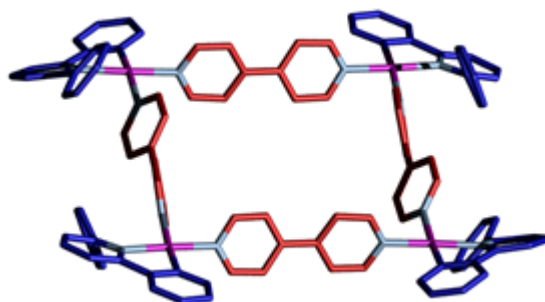


Figure 3. X-ray crystal structure of molecular square $[(\text{HLPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$. The carbon atoms of 4,4'-bipy are shown in red, the carbon atoms of HL in blue, platinum in magenta and nitrogen in pale blue. The PF_6 counter anions and five nitromethane solvent molecules have been removed for clarity.

To explore the stimuli-responsive disassembly process, a dichloromethane solution of $\text{P}_1\text{-}^t\text{Bu}$ was added to $[(\text{LPt})_4(4,4'\text{-bipy})_4](\text{PF}_6)_4$ (Scheme 1). Almost immediately, a darkening of the solution was observed and after stirring overnight at room temperature an orange solid was filtered off, which showed identical spectroscopic properties to the material already assigned as $[(\text{LPt})_2(4,4'\text{-bipy})]$. Unsurprisingly this base-induced disassembly of the tetramer is slow in comparison to the reaction of the mononuclear complex $[(\text{HLPt}(\text{DMAP})\text{OTs})] \rightarrow [\text{LPt}(\text{DMAP})]$ which under similar conditions is complete by the time an NMR spectrum can be recorded (less than five minutes).

To take this chemistry from two to three dimensions, the switchable self-assembly with the triazine ligand tpt ¹² has also been investigated, both by sequential addition of CSA and tpt to $[(\text{LPt})_2(4,4'\text{-bipy})]$ (Scheme 1)

and by direct addition of the salt. Again, formation was rapid at room temperature and after exchange of the counter anions 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 1359 and 2112 m/z compared well to the predicted isotopic distribution for the intact 3+ and 2+ species respectively (see Supporting Information), thus supporting the formation of the molecular trigonal prism $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$. In addition, the ^1H NMR 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 those of HL (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) compared to the free triazine ligand are likely caused by π - π interactions with the non-coordinating phenyl group of HL, which further supports the formation of a single product isomer from what is in effect a kinetically-controlled, five-component self-assembly process between three ditopic acceptors and two tritopic donor units.

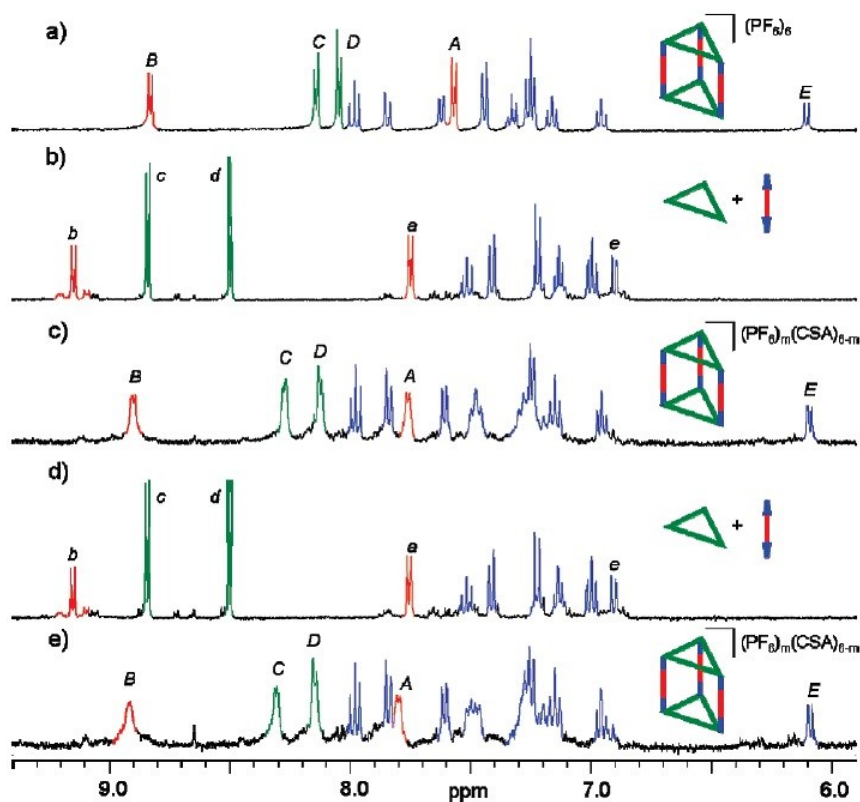


Figure 4. ^1H NMR spectra (CD_2Cl_2 , 400 MHz, 300 K) showing solution switching between assembled and disassembled states of trigonal prism $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2]^{6+}$. a) $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$; b) recorded 2 h after the addition of 12 eq. $\text{P}_1\text{-}^t\text{Bu}$ to $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$; c) 30 min after subsequent addition of 12 eq. CSA; d) 2 h after subsequent addition of $\text{P}_1\text{-}^t\text{Bu}$; e) 30 min after subsequent addition of 12 eq. CSA. The assignments correspond to the lettering shown in Scheme 1.

The increased solubility of the prism $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$ in dichloromethane, in comparison to the square, has allowed the stimuli-responsive switching to be monitored in solution using ^1H NMR spectroscopy (Figure 4). This experiment was initiated by the addition of 12 equiv. of $\text{P}_1\text{-}^t\text{Bu}$ (2 equiv. per Pt ion) to a CD_2Cl_2 solution of $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$. After 2 h, complete disappearance of the signals assigned to $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$ (H_{A-E}) and the emergence of new resonances which correspond to the disassembled components tpt (H_c and H_d) and $[(\text{LPt})_2(4,4'\text{-bipy})]$ (H_a , H_d , 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 $[(\text{LPt})_2(4,4'\text{-bipy})]$ and the appearance of a new set of signals (Figure 4c). This spectrum showed a striking similarity to the spectrum of $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$ (Figure 4a) indicating that the addition of CSA effects the re-assembly of the trigonal prism in solution. The subtle differences and slight broadening in the spectrum of the CSA re-assembled species are likely caused by a mixture of different counter anions present in solution, e.g. $[(\text{HLPt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_m(\text{CSA})_{6-m}$. A second addition of 12 equiv. of $\text{P}_1\text{-}^t\text{Bu}$ (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 by simply alternating the addition of base and acid.

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-assembly 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 treating 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.

Notes and references

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