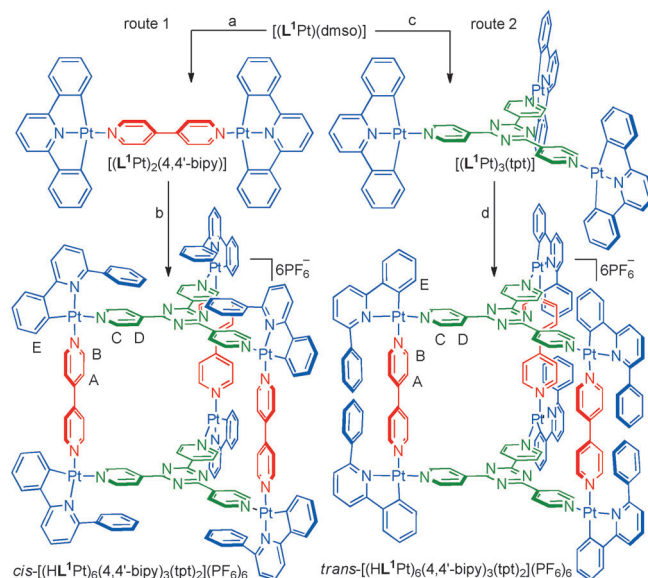


Sequential, Kinetically Controlled Synthesis of Multicomponent Stereoisomeric Assemblies**

Oleg Chepelin, Jakub Ujma, Perdita E. Barran,* and Paul J. Lusby*

The reversibility of noncovalent and metal–ligand interactions has widely been exploited to synthesize a plethora of supramolecular and coordination-based assemblies under thermodynamic control.^[1] Occasionally, entrapment in local energy minima leads to the formation of metastable products, which are often converted into lower-energy products upon prolonged reaction times.^[2] In contrast, self-assembled products in nature almost always arise according to the most expedient reaction pathway, that is, the kinetically selected.^[3] Herein we demonstrate a kinetically controlled approach to self-assembly, in which the sequence of addition^[4] of molecular structural units leads to the stereoselective formation of metallosupramolecular isomers.

The use of platinum(II) (and other third-row transition metals) is particularly well-suited to a kinetic approach to self-assembly, not just because Pt–ligand bonds can be kinetically inert, but also because the metal ion can be conveniently tuned to produce a vast range of different ligand-exchange labilities. For instance, assemblies that utilize bis(phosphine) ligands as corner protecting groups often readily assemble at room temperature,^[5] while those that exploit neutral N-donor bidentate ligands, such as ethylene diamine, typically require several hours at elevated temperature to reach equilibrium.^[6] Furthermore, the mechanism of labilization, that is, the trans effect, is such that it is possible for a single metal center to possess *cis* exchangeable sites with dramatically different kinetic properties. We have recently prepared a metallosupramolecular trigonal prism that possesses an unsymmetrical cyclometalated CN corner protecting group, which was assembled in two steps by treating $[\text{L}^1\text{Pt}(\text{dms})]$ (where $\text{H}_2\text{L}^1 = 2,6\text{-diphenylpyridine}$) sequentially with 4,4'-bipy and tpt.3CSA (Scheme 1, steps a and b).^[7] The isolation of a single isomeric product from a possible fourteen products, as indicated by the ^1H NMR spectrum of the hexa- PF_6 salt (see the Supporting Information, Figure S1a), led us to ask, was this selectivity a result of each Pt center possessing one labile and one inert exchangeable site, or was the selectivity thermodynamic in origin?



Scheme 1. Sequence-specific control over the formation of metallosupramolecular stereochemical isomers. a) 4,4'-bipy, CH_2Cl_2 , RT, 18 h, 77%; b) (i) tpt.3CSA, CH_2Cl_2 , RT, 1 h; (ii) NH_4PF_6 , 97%; c) tpt, CH_2Cl_2 , 18 h, 85%; d) (i) 4,4'-bipy.2CSA, CH_2Cl_2 , RT, 3 h; (ii) NH_4PF_6 , 99%. bipy = bipyridine, CSA = camphorsulfonic acid, dms = dimethylsulfoxide, tpt = tris(4-pyridyl)triazine.

To answer this question, the sequence in which 4,4'-bipy and tpt were added to $[\text{L}^1\text{Pt}(\text{dms})]$ was reversed. $[\text{L}^1\text{Pt}(\text{dms})]$ was first treated with a third of an equivalent of tpt at room temperature in CH_2Cl_2 to give $[\text{L}^1\text{Pt}]_3(\text{tpt})$ (Scheme 1, step c), which was then treated with 4,4'-bipy.2CSA, and after metathesis with NH_4PF_6 , the hexa- PF_6 salt was isolated in 99% yield (Scheme 1, step d). The ^1H NMR spectrum of this product (see the Supporting Information, Figure S1b) also indicated the formation of a single species, yet there were clear differences between the spectra of the two isomers, in particular, for resonances $\text{H}_{\text{A-E}}$. The product from route 1 was assigned as *cis*- $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$, in which the tpt ligand is coordinated *cis* to the nitrogen of the 2,6-diphenylpyridine ligand, and the product from route 2 was assigned as *trans*- $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_6$, in which the tpt ligand is coordinated *trans* to the nitrogen of the 2,6-diphenylpyridine ligand. This absolute assignment was made on the basis that a) the resonance of the *ortho* proton of tpt (H_{C}) is more deshielded in the *trans*-to-nitrogen coordination site in comparison to the *ortho* proton 4,4'-bipy (H_{B}), and b) the large and small relative separations between the resonances of H_{A} and H_{B} , and between the resonances of H_{C} and H_{D} .

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To corroborate the structure assignment of the isomers in solution, analysis was undertaken using nano-electrospray mass spectrometry (nESI). While samples of the presumed *cis* and *trans* isomers both showed peaks that matched the predicted isotope pattern for the intact 3+ and 2+ charged cages (1360 and 2114 *m/z*, respectively), their collision-induced dissociation (CID) pathways differed significantly. For instance, MS–MS experiments showed that with increasing kinetic energy, the isolated intact 3+ charged cage $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_3^{3+}$ of the *cis* isomer initially fragments to give ions at 1308 and 1464 *m/z*, which then fragment further to a dominant species at 1152 *m/z* (Figure 1a). Although the singly charged peak at 1152 *m/z* unambiguously corresponds to $[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})]\text{PF}_6^+$, and thus supports the assignment of the *cis* isomer, in which

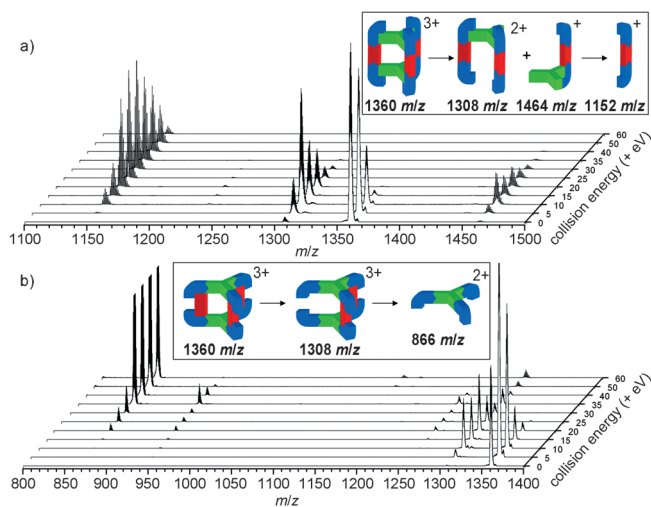
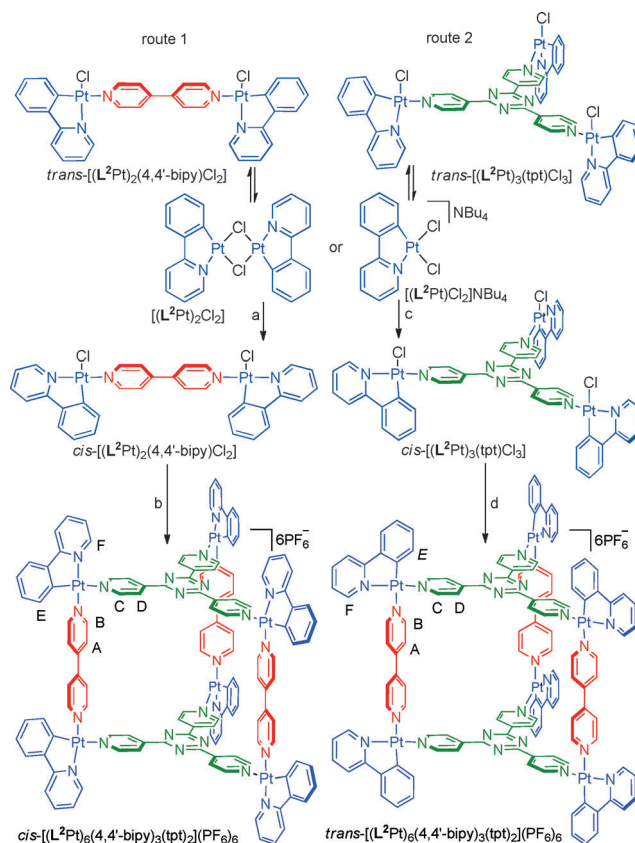


Figure 1. Partial nESI spectra with increasing collisional energy of the +3 charged intact prism (1360 *m/z*) to illuminate the CID pathways (see insets) for a) *cis*- and b) *trans*- $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_3(\text{tpt})_2](\text{PF}_6)_3^{3+}$.

the weaker *trans*-to-phenylato Pt–tpt bond undergoes selective dissociation at lower potential, the peaks at both 1308 (+2) and 1464 (+1) *m/z* could correspond to more than one different structure with the formulas of $[(\text{HL}^1\text{Pt})_4(4,4'\text{-bipy})_2(\text{tpt})_2](\text{PF}_6)_2^{2+}$ and $[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})(\text{tpt})]\text{PF}_6^+$, respectively. However, MS³ experiments of both the species at 1308 and 1464 *m/z* showed the predominant appearance of the +1 ion at 1152 *m/z* ($[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})]\text{PF}_6^+$). This finding suggests that the ions at 1308 and 1464 *m/z* correspond to tpt coordinated with two and one $[(\text{HL}^1\text{Pt})_2(4,4'\text{-bipy})]$ unit(s), respectively, and that initial fragmentation of the cage results from cleavage of Pt–tpt bonds from adjacent panels (Figure 1a, inset). When the isolated 3+ ion from the *trans* isomer was subjected to the same CID experiment, a signal at 1308 *m/z* was also observed at low voltage (Figure 1b), yet the different charge state (+3) indicates that the initial fragmentation involves the loss of a single 4,4'-bipy ligand to give $[(\text{HL}^1\text{Pt})_6(4,4'\text{-bipy})_2(\text{tpt})_2](\text{PF}_6)_3^{3+}$ (Figure 1b, inset). At higher potential, this peak diminishes with a concomitant appearance of a +2 ion at 866 *m/z*, which unequivocally corresponds to $[(\text{HL}^1\text{Pt})_3(\text{tpt})]^{3+}$. This fits with a preferential,

low-energy dissociation of the weaker Pt–4,4'-bipy bond from the *trans* isomer (Figure 1b, inset).

To ascertain whether a kinetic self-assembly strategy could be used if the labile coordination site isn't initially masked, we have investigated the sequential addition of tpt and 4,4'-bipy to both $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ and $[(\text{L}^2\text{Pt})\text{Cl}_2]\text{NBu}_4$, where HL^2 is the bidentate CN ligand 2-phenylpyridine (Scheme 2). The ¹H NMR spectrum of a mixture of $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ and 0.5 equivalents of 4,4'-bipy (Scheme 2, route 1, step a) showed



Scheme 2. Kinetically controlled synthesis using an “unmasked” corner protecting ligand. a) 4,4'-bipy, $\text{C}_2\text{H}_2\text{Cl}_4$, 45 °C, 24 h; b) (i) AgCSA, $\text{C}_2\text{H}_2\text{Cl}_4$, RT, 3 h; (ii) tpt, $\text{C}_2\text{H}_2\text{Cl}_4$, RT, 24 h; (iii) NH_4PF_6 , 98 % (starting from $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$); c) tpt, $\text{C}_2\text{H}_2\text{Cl}_4$, 45 °C, 24 h; d) (i) AgCSA, $\text{C}_2\text{H}_2\text{Cl}_4$, RT, 3 h; (ii) 4,4'-bipy, $\text{C}_2\text{H}_2\text{Cl}_4$, RT, 24 h; (iii) NH_4PF_6 , 77 % (starting from $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$).

the appearance of several new peaks after 5 minutes (see the Supporting Information, Figure S2b); these peaks differed from those of the $[(\text{L}^2\text{Pt})_2\text{Cl}_2]$ starting material (see the Supporting Information, Figure S2a). However, the gradual disappearance of these initial peaks and the concomitant appearance of a new set of signals, which converged to a single species after 24 hours at 45 °C, was observed (see the Supporting Information, Figure S2c). Based on the relative chemical shifts, and in particular the significant differences of H_E and H_F in the initial and final compounds (which is caused by shielding by the coordinated 4,4'-bipy ligand), it appears that *trans*- $[(\text{L}^2\text{Pt})_2(4,4'\text{-bipy})\text{Cl}_2]$ is the initial kinetic product, which rearranges into the thermodynamically (and kineti-

cally) more-stable *cis*-[(L^2Pt)₂(4,4'-bipy)Cl₂] (Scheme 2, route 1, step a).^[8] After halide extraction using AgCSA, treatment with tpt, and then anion exchange with NH₄PF₆, *cis*-[(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆ was isolated in virtually quantitative yield (Scheme 2, route 1, step b). The ¹H NMR spectrum of this product (see the Supporting Information, Figure S2d) again suggested the formation of a single isomer. When the sequence of addition of 4,4'-bipy and tpt to [(L^2Pt)₂Cl₂] was switched (Scheme 2, route 2) a single, yet different product was obtained. A comparison of the ¹H NMR spectra of the two isomers showed significant differences (see Supporting Information, Figure S2d and S2e), particularly in resonances H_{A-P}.

The nESI mass spectra of *cis* and *trans*-[(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆ showed identical peaks at 1208 and 1884 *m/z*, which matched the predicted isotope patterns for the intact +3 and +2 charged prisms, respectively (not shown). However, in contrast to the analogous experiments with *cis* and *trans*-[(HL¹Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆, the CID of the *cis* and *trans* isomers of [(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆ showed mainly peaks that did not correspond to any sensible combinations of L^2Pt , 4,4'-bipy, tpt, and PF₆. Instead, the dominant CID pathway for both *cis* and *trans*-[(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₃³⁺ involves fluoride abstraction from the PF₆ counteranions. With the *cis* isomer, the disappearance of the 1208 *m/z* peak is initially accompanied by a dominant species at 1093 *m/z*, which corresponds to the formula [(L^2Pt)₄(4,4'-bipy)₂(tpt)F]PF₆²⁺ (Figure 2a). In an analogous manner to *cis* isomer of [(HL¹Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆, it appears that the initial fragmentation pathway involves the cleavage of the weaker Pt–tpt bonds from adjacent panels (also supported by a smaller intensity ion at 1311 *m/z*, which corresponds to [(L^2Pt)₂(4,4'-bipy)(tpt)]PF₆⁺), a route that is either promoted or stabilized by abstraction of fluoride from

one of the PF₆ counteranions (Figure 2a, inset). MS³ experiments show that the disappearance of this 1093 *m/z* ion results from the dissociation into a low-intensity ion at 873 *m/z*, which matches [(L^2Pt)₂(4,4'-bipy)F]⁺, and subsequent MS⁴ experiments show that this fragments into a singly charged ion at 505 *m/z*, by loss of the neutral [(L^2Pt)F] from [(L^2Pt)₂(4,4'-bipy)F]⁺. For the *trans* isomer, the fragmentation pathway appears to first involve loss of a single 4,4'-bipy, again either promoted or stabilized by fluoride abstraction from the counter anion, to give [(L^2Pt)₆(4,4'-bipy)₂(tpt)₂F]-(PF₆)₂³⁺ (1114 *m/z*), which subsequently loses another 4,4'-bipy by a fluoride promoted/stabilized route to produce [(L^2Pt)₆(4,4'-bipy)(tpt)₂F₂](PF₆)₂³⁺ (1020 *m/z*). Again, the selective loss of 4,4'-bipy ligands from the weaker *trans*-to-phenylato coordination sites supports the formation of *trans*-[(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆.

The four metallocsupramolecular stereochemical isomers do not undergo isomerization, or reassemble to generate other assemblies (e.g. Pt₄ squares or Pt₆(tpt)₄ cages) at room temperature in solution.^[9] We attribute this stability to the unlabile Pt–N bonds *trans* to the nitrogen donors of HL¹/L²; although these bonds form readily at room temperature (or just above in the case of L²) from the corresponding solvato/halide complexes, the activation barrier for de-coordination is such that this step is essentially irreversible under ambient conditions. Therefore the sequence in which the N-donor bridging ligands are added to the starting platinum complexes determines the stereochemical outcome of the reaction. In this regard, the synthesis of these metallocsupramolecular isomers combines elements of covalent (irreversible) synthesis and noncovalent (reversible) thermodynamically controlled assembly. It could also be expected that the isomers would show some thermodynamic bias towards either the *cis* or the *trans* form, however, heating samples of either *cis* or *trans*-[(HL¹/L²Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆ at 80 °C for 24 hours results in a complex mixture with no obvious preference for a single species. This is perhaps unsurprising as to gain greater than 95 % selectivity for a single species, an energy difference greater than 1.74 kcal mol^{−1} would be required. This is in marked contrast to the sequential, kinetically controlled syntheses described herein; these syntheses give greater than 95 % selectivity for single stereochemical isomers, thus highlighting the potential benefits of exploiting differences in rates of assembly, rather than simply considering ground-state energies, for the preparation of multicomponent systems.

The vast difference in labilities of *cis* exchangeable platinum coordination sites have been exploited to selectively synthesize multicomponent stereoisomeric assemblies using a template-free, sequential, kinetically controlled approach. We anticipate that this approach to noncovalent, and in particular coordination driven self-assembly will facilitate the generation of multicomponent, ultimately functional systems.

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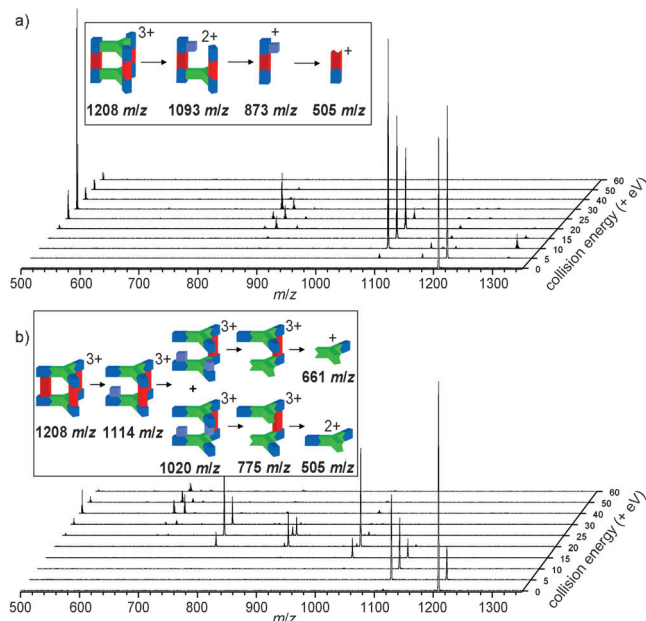


Figure 2. Partial nESI mass spectra with increasing collisional energy of the +3 charged intact prism (1208 *m/z*) to illuminate the fluoride-induced CID pathways (see insets) for a) *cis*- and b) *trans*-[(L^2Pt)₆(4,4'-bipy)₃(tpt)₂](PF₆)₆.

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