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Self-Sorting

Integrative Self-Sorting Synthesis of a $Fe_8Pt_6L_{24}$ Cubic Cage**

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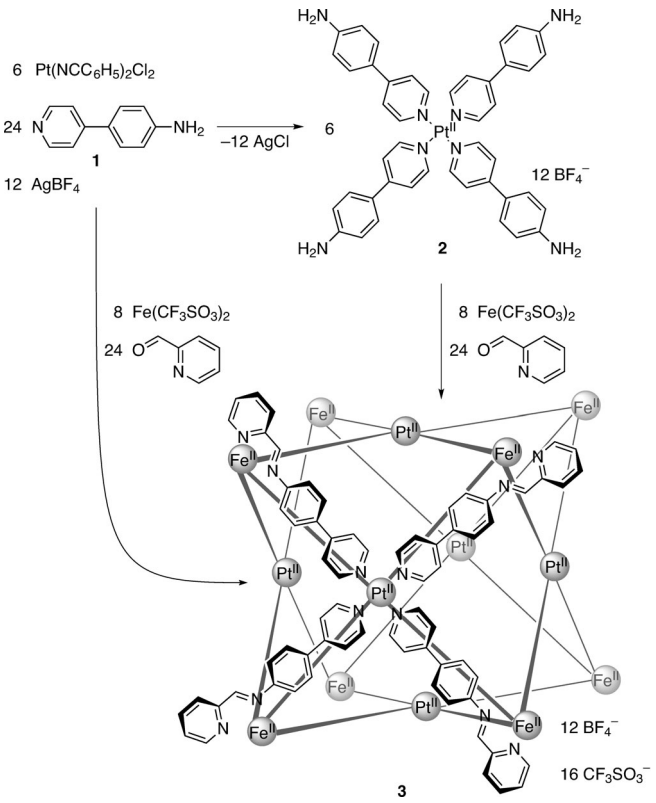
The many different chemical processes associated with life run in parallel within the cytoplasm of a cell. These processes are not spatially separated by membranes, yet they do not interfere with each other. The biomolecular agents of these processes can be said to undergo self-sorting,[1] which is defined as "the high-fidelity recognition of self from nonself", into the locally organized systems that achieve individual functions. The goal of creating synthetic self-sorting systems[2] is thus inspired in part by the prospect of synthesizing functional supramolecular systems that carry out different processes together in solution.

Self-assembled metal–organic capsules[3] have been shown to be useful for a variety of applications, including guest binding and separation,[4] cavity-controlled catalysis,[5] generation of unusual reaction products,[6] and stabilization of reactive intermediates.[7] New strategies have been explored to prepare more complex, metal–organic capsules so as to achieve new functions. The potential of self-sorting has only recently been acknowledged by researchers as a method for preparing such capsules.[8]

One strategy pursued by researchers to create progressively more-complex metal–organic architectures has been the preparation of heteroleptic species. This method relies on the combination of at least two types of homotopic ligands and a single metal ion for the construction of a metal–organic complex.[9] An alternative method to create complexity, employed herein, entails the use of a single heterotopic ligand and more than one metal ion, wherein the fidelity of the self-assembly relies on integrative self-sorting.[10] Our construction method relies on two different metal ions and coordination environments: in addition to the tris(pyridylimine)iron(II) moiety, widely employed in the subcomponent self-assembly[11] of complex structures,[12] we have introduced a second coordination motif, the tetrakis(pyridine)platinum(II) moiety.[9d,13] To this end, ditopic ligand **1** (Scheme 1), was selected as a ligand that can coordinate to both Fe^{II} (as a tris(pyridylimine) complex) and Pt^{II} ions (through its terminal pyridine group).



Scheme 1. The two-step synthesis of cube **3** via the square-planar Pt^{II} intermediate **2** and the one-pot synthesis of **3** starting from free subcomponents and metal ions. For clarity, the chemical structure of only one of the six faces of the cube is shown.

Based on the fourfold symmetry of the tetrakis(pyridine)platinum(II) moiety and the threefold symmetry of the tris(pyridylimine)iron(II) moiety, we envisioned the possibility of preparing a heterometallic cubic capsule:[4c,14] after synthesis of the square-planar Pt^{II} complex **2**, this intermediate could be incorporated into heterometallic cube **3** by formation of Fe^{II}-stabilized pyridylimine bonds (Scheme 1, right). Self-sorting could be validated within such a system by starting with the free subcomponents and metal ions, and allowing each to find its proper place within the final product structure (Scheme 1, left). For this self-assembly process to work, the two different kinds of sp^2-hybridized nitrogen donors must bind to the correct metal ions, without scrambling.

Herein we employ integrative self-sorting in the synthesis of the heterometallic $Fe_8Pt_6L_{24}$ cube **3** (Scheme 1). A one-pot synthesis of cube **3** from four different components, in which a total of 62 building blocks are brought together, was found to be possible, thus demonstrating both the potential of self-

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sorting in the fabrication of larger and more complex structures, as well as the dynamic nature of the employed self-assembly method. The dynamic nature of the linkages that knit the subcomponents of **3** together also enabled efficient cage-to-cage conversions: in a first transformation step, a tetrahedral Fe_4L_6 cage was converted into the $Fe_8Pt_6L_{24}$ cube, which in a subsequent step was converted into a second tetrahedral $Fe_4L'_6$ cage.

The square-planar tetrakis(pyridine)platinum(II) precursor **2** was prepared according to a modified literature procedure (Scheme 1):[15] $Pt(C_6H_5CN)_2Cl_2$ (1 equiv) was treated with ligand **1** (4 equiv) and $AgBF_4$ (2 equiv) in acetonitrile. After removal of the co-product AgCl by filtration, compound **2** was recrystallized by diffusion of diethyl ether vapor into an acetonitrile solution and was isolated in 71% yield. The formation and purity of **2** were confirmed by ^1H and ^{13}C NMR spectroscopy, electrospray mass spectrometry (ESI-MS), elemental analysis, and single-crystal X-ray diffraction (see the Supporting Information).

In contrast to a previously studied[4c] tetrakis(4-aminophenyl)porphyrin subcomponent, which was found only to undergo self-assembly in dimethylformamide because of its insolubility in other solvents, square-planar Pt^{II} ligand **2** was found to be sufficiently soluble in acetonitrile to allow for **3** to self-assemble in this solvent. The reaction of metallo-subcomponent **2** (6 equiv), iron(II) trifluoromethanesulfonate ($Fe(OTf)_2$, 8 equiv), and 2-formylpyridine (24 equiv) in acetonitrile resulted in the formation of cubic $Fe_8Pt_6L_{24}$ cage **3** (Scheme 1) as the unique product, as evidenced by NMR spectroscopy (78% yield of isolated product). In contrast to previously reported heterometallic cubes,[14] cage **3** displayed high solubility (in acetonitrile), which facilitated its characterization. The ^1H and ^{13}C NMR spectra of cage **3** displayed only one set of ligand resonances in solution, consistent with a chiral octahedral, *O*-symmetric structure (Figure 1 and Figure S3 in the Supporting Information). Two-dimensional NMR spectra, DOSY, ESI-MS, and elemental analysis also confirmed the formation of cube **3** (see the Supporting Information).

Numerous attempts to grow crystals of **3** of sufficient quality for single-crystal X-ray analysis were unsuccessful. We therefore constructed a MM2-optimized[16] molecular model

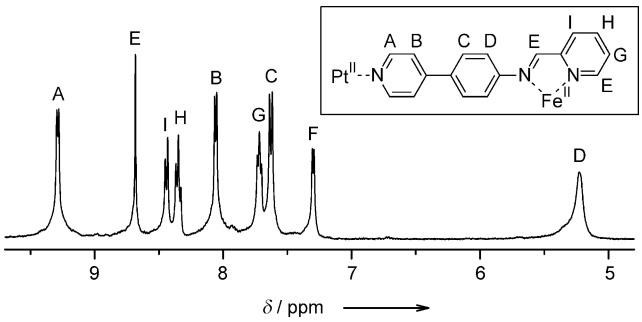


Figure 1. ^1H NMR spectrum of cube **3** in CD_3CN (1.1 mM). Only one set of ligand resonances is evident in solution, consistent with an *O*-symmetric structure. The signals were assigned with the aid of ^1H-^1H COSY and NOESY spectra (see Figures S5 and S6 in the Supporting Information).

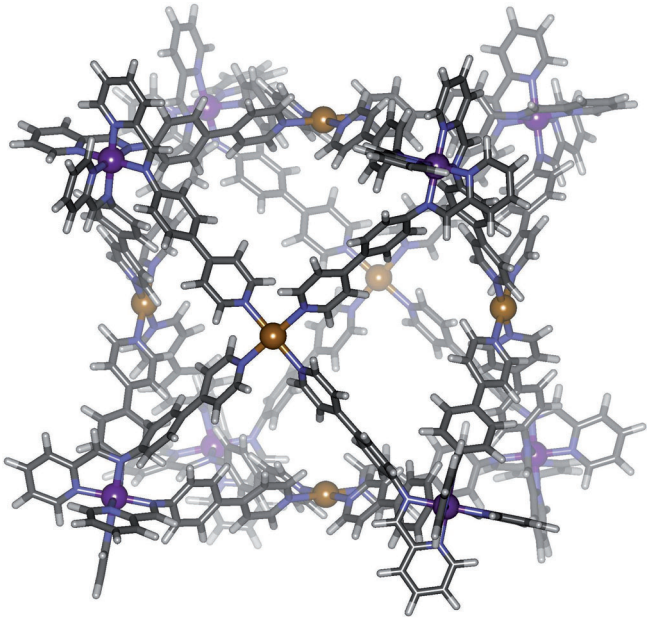


Figure 2. Energy-minimized molecular model of cube **3.** Color scheme: dark gray: C, light gray: H, blue: N, purple: Fe, orange: Pt (for details of the optimization, see the Supporting Information).

of cube **3** (Figure 2; see the Supporting Information). To reproduce the *O* symmetry deduced from ^1H NMR spectroscopy, we assigned the three bidentate pyridylimine ligands around each Fe^{II} center to have facial geometry, and the eight tris(pyridylimine)iron(II) corners to be either all Δ or all Λ.

The model shows how ligand **2** forms the faces of the cube, with the square-planar Pt^{II} ion residing in the middle of each face. Moreover, the model shows how the octahedral Fe^{II} ions define the vertices of the cube, and how heterotopic ligand **1** connects the two metal ions, thereby yielding the heterometallic $Fe_8Pt_6L_{24}$ cubic cage. No features of the model, or spectroscopic features of **3**, suggested apparent strain; nor were indicators of the strain observed in a previously reported Fe_8L_6 porphyrin-faced cube.[4c] These observations suggest that the ability to form a Fe_8L_6 assembly may be a general feature of fourfold-symmetric tetrakis(anilines).

The eight Fe^{II} ions define a cube with a volume that could allow encapsulation of a large guest. The shortest $Fe^{II}\cdots Fe^{II}$ distance in **3** is calculated to be approximately 17.6 Å along an edge, whereas the tetrakis(4-aminophenyl)porphyrin-based cubic cage reported previously[4c] is characterized by a metal-to-metal distance of 14.8 Å.[17] A range of molecules was investigated as potential guests (see Table S2 in the Supporting Information), but there was no evidence of the encapsulation of any of them within cage **3** by ^1H NMR spectroscopy and ESI-MS. From inspection of the structure of **3**, we inferred the absence of guest binding to be due to the open structure of the cage; the large pores along the cube's edges reduce the amount of solvent-accessible surface area that would be covered upon guest binding, a parameter which has been observed to correlate with binding strength.[18]

In addition to the two-step preparation of **3** involving the synthesis and isolation of square-planar Pt^{II} metallo-subcomponent **2** (Scheme 1), we also effected the one-pot synthesis of

3 (Scheme 1). To this end, ligand **1** (24 equiv), Pt(C_6H_5CN)$_2$Cl$_2$ (6 equiv), $AgBF_4$ (12 equiv), Fe(OTf)$_2$ (8 equiv), and 2-formylpyridine (24 equiv) were found to react overnight in acetonitrile at 338 K. The ^{1}H NMR spectrum (see Figure S8 in the Supporting Information) revealed that, apart from excess 2-formylpyridine, the major product in the reaction mixture was structure **3**; ESI-MS also confirmed the formation of cube **3** (see Figure S9 in the Supporting Information).

In this one-pot synthesis of the cube, 62 building blocks were brought together, ultimately forming a single self-assembled complex through the formation of 96 new bonds. The dynamic nature of the imine[19] and coordination bonds—in particular, the iron(II)–pyridylimine bonds—means that the synthesis of **3** is carried out under thermodynamic control, thus allowing for error-checking during the cage's assembly and ultimately leading to the formation of the energetically most favored structure, that is, cube **3**.[20]

In addition, the successful one-pot synthesis of **3** implies an efficient self-sorting between two different coordination motifs that both contain the pyridine moiety. In the synthesis of **3**, the terminal pyridine moiety present in subcomponent **1** was observed to preferentially coordinate to the Pt^{II} ion, whereas the subcomponent's amine moiety, after condensation with 2-formylpyridine, coordinated to the Fe^{II} ion. The ability of this system to self-sort is further supported by the observation that, in the absence of Fe^{II} ions and ligand **1**, 2-formylpyridine can coordinate to a Pt^{II} ion (see Figures S10 and S11 in the Supporting Information), while in the absence of Pt^{II} ions, ligand **1** can also coordinate to an Fe^{II} ion through the pyridine moiety (see Figure S12 in the Supporting Information).

The two-step synthesis of cube **3** starts from a tetrafunctional amine (i.e. compound **2**), which stands in contrast to the preparation of tetrahedral cages previously reported by our research group that relied either on bifunctional amine ligands[12d,21] or trifunctional amine ligands.[22] Since in all these metal–organic capsules the dynamic tris(pyridylimine)iron(II) moiety is present at the capsule's vertices, we set out to investigate whether a cage-to-cage conversion through amine residue exchange[23] was possible (Scheme 2).

To this end, tetrahedral cage **5** was prepared by reaction of the electron-poor diamine **4** (6 equiv), iron(II) bis(trifluoromethanesulfonimidate) (Fe(NTf$_2$)$_2$, 4 equiv), and 2-formylpyridine (12 equiv; see the Supporting Information). The addition of tetraamine **2** (4.1 equiv) to tetrahedral cage **5** (1 equiv) led to the formation of cubic cage **3** and diamine **4**, as evidenced by ^{1}H NMR spectroscopy (Figure 3b and Figure S21 in the Supporting Information), DOSY NMR spectroscopy (Figure S23 in the Supporting Information), and ESI-MS (Figure S22 in the Supporting Information). We infer that this cage-to-cage transformation is entropically favorable because for each tetraamine **2** that is incorporated in cube **3**, two equivalents of diamine **4** are released; overall, 8 moles of reagents are transformed into 13 moles of products in this transformation. This increase in entropy appears to offset the

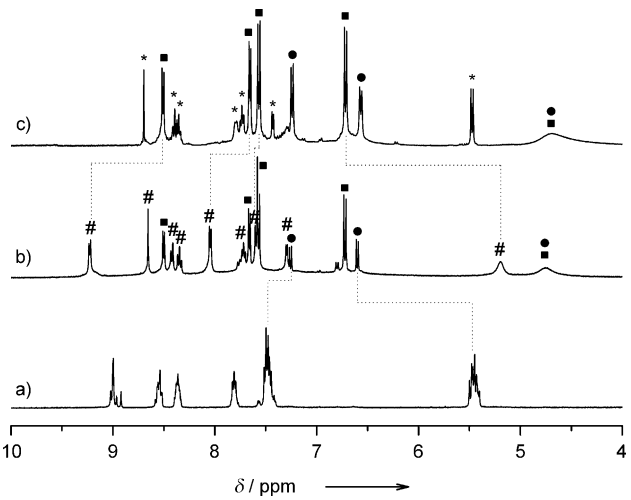
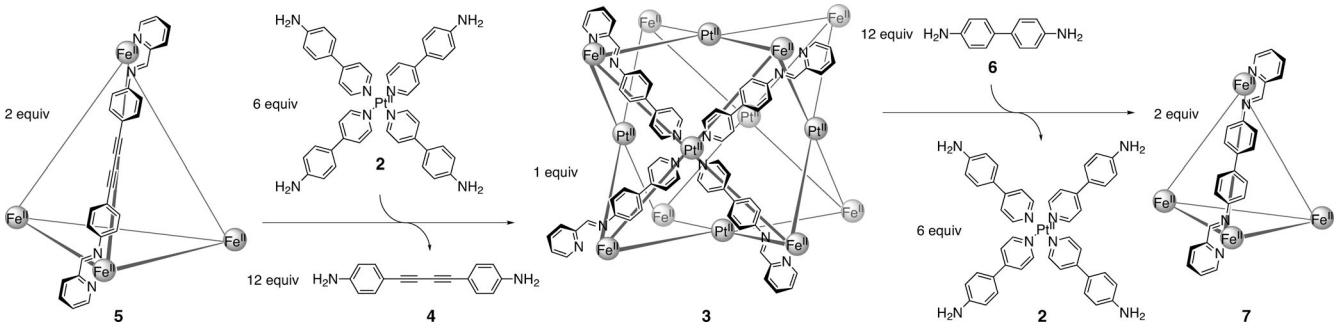


Figure 3. ^{1}H NMR spectrum of: a) tetrahedral cage **5** in CD_3CN; (b) cubic cage **3** (resonances marked with #), obtained after addition of ligand **2** to a solution of **5** in CD_3CN; c) tetrahedral cage **7** (resonances marked with *), obtained after addition of ligand **6** to the solution of **3** in CD_3CN. In (b) and (c) the resonances corresponding to liberated ligands **2** and **4** can also be observed. The dotted lines show how the chemical shifts of the protons on ligands **4** and **2** change as a result of the conversion from **5** into **3** and from **3** into **7**, respectively. Resonances corresponding to free **2** and **4** are marked by ■ and ●, respectively. The full assignment of the ^{1}H NMR spectra is given in the Supporting Information (see Figures S21 and S24).



Scheme 2. Schematic representation of the conversion of tetrahedral cage **5** into cubic cage **3** upon addition of square-planar metallo-subcomponent **2**, followed by the conversion of cubic cage **3** into tetrahedral cage **7** upon addition of **6**. For clarity, the chemical structure of only one of the ligands is shown for cages **3**, **5**, and **7**.

enthalpic cost associated with the incorporation of the more electron-poor tetraamine **2** compared to diamine **4** (Hammett σ_{para} values for the ethynyl and 4-pyridyl groups are +0.23 and +0.44, respectively).[24]

Subsequent addition of 4,4′-diaminobiphenyl (**6**; 12.9 equiv per equiv of capsule **3**) to cubic cage **3** (in the presence of the free ligand **4**) resulted in the formation of tetrahedral cage **7** and concomitant release of ligand **2** (Figure 3c; see Figures S24–S27 in the Supporting Information).[25] Although entropically disfavored, this transformation appears to be driven by the incorporation of diamine **6**, which is more electron-rich than tetraamine **2** (the Hammett value σ_{para} for the phenyl group is −0.01).[24] Also, ^{19}F NMR spectroscopy revealed that a BF_4^- ion resides inside the cavity of cage **7** (see Figure S25 in the Supporting Information), thus indicating that anion templation could provide a further driving force to the transformation of **3** to **7**.[26] We will treat the behavior of cage **7** in greater detail in a separate contribution.[27]

In conclusion, we have shown how, on the basis of integrative self-sorting, the formation of a soluble heterometallic cube starting from a heterotopic ligand and two different metal ions is possible. Self-sorting allowed a one-pot synthesis of the cubic complex, thus bringing together 62 building blocks through the formation of 96 new bonds. Even though bis(pyridylimine)platinum(II) complexes are known and stable, as are hexakis(pyridine)iron(II) complexes, efficient self-sorting during the reaction of ligand **1** in the presence of both an Pt^{II} and Fe^{II} salt ensures the preferential formation of the heterometallic cube **3**.

Few examples exist of metal–organic complexes prepared from such a large number of building blocks: Stang and co-workers have reported the formation of a dodecahedron from 50 components,[3j] while Fujita and co-workers recently reported a $M_{24}L_{48}$ polyhedron.[3i]

Finally, the results presented herein illustrate how the concept of self-sorting adds to the range of synthetic methods employed by chemists in their ongoing efforts to create evermore complex self-assembled metal–organic architectures, because of the useful functions these structures display.[5b]

Experimental Section

2: Dichlorobis(benzonitrile)platinum(II) (242 mg, 0.512 mmol), 4-(pyridin-4-yl)aniline (350 mg, 2.06 mmol), silver tetrafluoroborate (213 mg, 1.09 mmol), and acetonitrile (100 mL) were added to a 250 mL round bottom flask. The reaction was stirred for 24 h at 338 K, during which time a precipitate was observed to form (inferred to be AgCl). After allowing the reaction mixture to cool to room temperature, the precipitate was removed by filtration through celite. The filtrate was concentrated by partial removal of the acetonitrile in vacuo. Slow diffusion of diethyl ether vapor into the remaining acetonitrile solution resulted in the formation of yellow needlelike crystals of **2**. Yield: 380 mg (71%). ^{1}H NMR (400 MHz, 298 K, CD_3CN): δ = 8.52 (d, 2H), 7.65 (d, 2H), 7.57 (d, 2H) 6.72 (d, 2H) 4.75 ppm (s, 2H); ^{13}C NMR (126 MHz, 298 K, [D$_6$]DMSO) δ = 152.3, 151.0, 150.7, 128.7, 121.7, 119.8, 114.1 ppm; ESI-MS: 437.69 ([Pt($C_{11}H_{10}N_2$)$_4$]$^{2+}$) and 962.32 ([Pt($C_{11}H_{10}N_2$)$_4$$BF_4$]$^+$). Elemental analysis calcd for $C_{44}H_{40}B_2F_8N_8Pt{\cdot}0.9\,CH_3CN$: C 50.63, H 3.96, B 1.99, F 13.99, N 11.47, Pt 17.96; found: C 50.74, H 4.09, N 11.34.

3: Iron(II) triflate (22.1 mg, 62.4 μmol), **2** (49.1 mg, 46.7 μmol), 2-formylpyridine (17.8 μL, 187 μmol), and acetonitrile (8 mL) were added to a 25 mL Schlenk flask. The solution was purified of dioxygen by three vacuum/nitrogen fill cycles. The reaction was then stirred for 24 h at 343 K before cooling to room temperature. The BF_4^-/TfO^- salt of **3** was precipitated as a purple microcrystalline solid by the addition of diethyl ether. Yield: 68 mg (78%). ^{1}H NMR (400 MHz, 298 K, CD_3CN) δ = 9.29 (d, 48H), 8.68 (s, 24H), 8.44 (d, 24H), 8.35 (t, 24H), 8.06 (d, 48H), 7.72 (t, 24H), 7.63 (d, 48H), 7.30 (d, 24H), 5.23 ppm (br s, 48H); ^{13}C NMR (126 MHz, 298 K, CD_3CN) δ = 176.46, 158.93, 156.99, 153.08, 152.60, 151.62, 140.75, 136.36, 132.46, 131.01, 129.88, 126.34, 122.91 ppm; ESI-MS: the complex was obtained as the 28+ complex with a varying number of BF_4^- and OTf^- counterions. The assigned ESI mass spectrum is given in the Supporting Information (see Figure S4). Elemental analysis calcd for $C_{408}H_{312}N_{72}Fe_8Pt_6(BF_4)_{12}(F_3CSO_3)_{16}$: C 45.20, H 2.79, B 1.15, F 16.19, Fe 3.97, N 8.95, O 6.82, Pt 10.39, S 4.55; found: C 45.07, H 2.81, N 9.14.

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