ORGANOMETALLICS

Construction of Supramolecular Pyrene-Modified Metallacycles via Coordination-Driven Self-Assembly and Their Spectroscopic Behavior

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S Supporting Information

ABSTRACT: The design and self-assembly of novel multipyrene hexagonal metallacycles via coordination-driven self-assembly is described. By employing newly designed 120° dipyridine donor and di-Pt(II) acceptor linkers substituted with pyrene, a variety of tris- and hexakis(pyrene) hexagonal metallacycles with well-defined shape and size were prepared via [3 + 3] and [6 + 6] self-assembly, respectively, under mild conditions in high yields. The structures of these novel metallacycles were well characterized by multinuclear NMR



(³¹P and ¹H) spectroscopy, cold-spray ionization time-of-flight mass spectrometry (CSI-TOF-MS), electrospray ionization timeof-flight mass spectrometry (ESI-TOF-MS), and elemental analysis. The shape and size of all hexagonal metallacycles were investigated by the PM6 semiempirical molecular orbital method. The preliminary study of their spectroscopic behavior was also carried out. It was found that these pyrene-modified metallacycles displayed different optical behaviors, which might be caused by the structural effects.

INTRODUCTION

Self-assembly is an essential process for many key activities of living cells, such as the formation of proteins (protein folding), nucleic acid complexes, and plasma membranes, cytoskeleton assembly, etc.¹ Generally, biological systems are entirely driven by self-assembly and capable of performing physiological activities by taking advantage of a range of reversible noncovalent interactions such as hydrogen bonding, chargecharge, donor-acceptor, $\pi-\pi$ stacking, and van der Waals.² Additionally, many examples have demonstrated that nature utilizes the self-assembly approach to construct biologically relevant materials, in which the function of the self-assembled whole is greater than the sum of its individual parts.³ Inspired by nature, chemists have devoted to utilizing noncovalent interactions to build abiological self-assembly, which has not only furthered our understanding of the self-assembly process itself but also opened the door to the construction of a variety of complicated supramolecular architectures.⁴

Among various self-assembly protocols, coordination-driven self-assembly has emerged as a powerful tool to construct polygons and polyhedra with well-defined shapes, sizes, and geometries,^{2d,5} since the metal–ligand bonds are highly directional and relatively strong. During the past few years, the groups of Stang,⁶ Fujita,⁷ Mirkin,⁸ Raymond,⁹ Lehn,¹⁰ and others¹¹ have extensively explored the directional-bonding coordination-driven approach to the self-assembly of compli-

cated metallosupramolecular structures. In comparison to the traditional covalent synthesis strategy, the coordination-driven self-assembly protocol offers considerable synthetic advantages such as fewer steps, fast and facile construction of the final products, and inherently self-correcting and defect-free assembly. Furthermore, as the rigid molecular precursors present a number of different locations where functional moieties can be attached, a variety of functionalized polygons have been successfully designed and prepared, which can be potentially employed as precursors of electronic, catalytic, and photophysical materials or used for molecular recognition and encapsulation.¹² For example, we have demonstrated that the introduction of functional groups, such as crown ether, ferrocene, and Fréchet-type dendrons, at the vertex of 120° building blocks enabled the construction of novel functionalized two-dimensional metallacycles.¹³

The list of polygons synthesized to date includes the molecular square, rectangle, triangle, pentagon, and hexagon.¹⁴ Among these polygons, the hexagon has attracted considerable attention, since it is one of the most common patterns in nature, such as the honeycomb structure of a beehive and the micrograph of a snowflake.¹⁵ Thus, there has been an increasing interest in the construction of supramolecular hexagonal

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architectures through self-assembly in recent years.¹⁶ According to the "directional bonding" and "symmetry interaction" models,^{5a,b} the shape of an individual 2-D hexagon is usually determined by the value of the turning angle within its angular components. Moreover, the hexagonal supramolecular systems can be self-assembled in two different ways. For example, discrete hexagonal entities of the type $A_6^2L_6^2$ can be selfassembled from a combination of six shape-defining and directing corner units A^2 with six appropriate linear linker units L^2 . An alternative route for the assembly of hexagonal supermolecular systems involves the combination of two complementary ditopic building blocks, A^2 and X^2 , each incorporating 120° angles between the active coordination sites, allowing for the formation of hexagonal structures of type $A_3^2X_3^2$.

Pyrene is one of most useful fluorophores, which has received significant attention because of its interesting optical properties such as relatively long excited-state lifetimes and exceptional distinction of the fluorescence bands for monomers and excimers.¹⁷ Recently, the incorporation of multiple pyrene subunits into a single scaffold to construct multipyrene materials, such as polymers and dendrimers, has evolved to be one of the most attractive subjects within materials science.¹⁸ It provides an efficient approach to amplify and modulate the fluorescence response because the multipyrene materials often absorb light more effectively and usually exhibit excimer fluorescence. However, the preparation of multipyrene polymers and dendrimers often requires considerable synthetic effort and can be plagued by low yields and largely amorphous final structures. Thus, the introduction of multiple pyrene groups onto/into discrete supramolecular systems in a controlled manner is still a major challenge.

As mentioned above, previous studies indicated that coordination-driven self-assembly featured considerable synthetic advantages to construct multifunctional assemblies. By employing such an approach, many functionalized assemblies, such as tris(crown ether) hexagons and multiferrocenyl hexagons, have been successfully prepared.^{13c,19b} Moreover, we have previously realized well-controlled self-assembly on a large scale based on platinum–acetylide complexes as well.²⁰ Inspired by these successful examples, we envisioned that the construction of multipyrene functionalized hexgons would be realized via the coordination-driven self-assembly strategy, which would avoid elaborate synthesis work. More importantly, this strategy allows for precise control over the shape and size of the final construction as well as the distribution and total number of incorporated pyrene moieties.

Herein, we employ the newly designed 120° building blocks (5 and 6) decorated with one pyrene functional group (Figure 1) with the corresponding building blocks to construct a new family of multipyrene hexagons via [3 + 3] and [6 + 6]



Figure 1. Molecular structure of pyrene-modified ligands 5 and 6.

coordination-driven self-assembly, respectively. It should be noted that, by synthesizing a diverse library of donor and acceptor building blocks, two complementary strategies have been investigated in order to construct "isomeric" supramolecular multipyrene hexagons possessing the same geometry. A similar reasoning has been applied in the construction of nanoscopic cages such as cuboctahedra, truncated tetrahedra, and supramolecular M₂L₂ prisms.²¹ Moreover, it was found that a combination of the complementary donor units and acceptors allowed for the formation of novel multipyrene hexagons with precisely controlled shapes, sizes, and geometries via coordination-driven self-assembly. The structures of all multipyrene hexagonal metallacycles were characterized by multinuclear NMR (1H and 31P), CSI-TOF-MS and ESI-TOF-MS, and elemental analysis. Their primary spectroscopic behavior has been investigated.

RESULTS AND DISCUSSION

Synthesis of 120° Pyrene-Modified Acceptor Ligand 5 and Donor Ligand 6. The linear geometry of the alkynyl unit together with its π -unsaturated nature have made the rigid alkynyl moieties ideal building blocks for the construction of molecular wires, organometallic oligomers, and polymeric materials.²² Herein we utilized the coupling reaction of trans- $[PtI_2(PEt_3)_2]$ or 4-bromopyridine with C–H bonds in alkynes as the key steps in the synthesis of novel 120° building units (Figure 1). The new 120° pyrene-modified ligands 5 and 6 can be easily synthesized in a few steps, as shown in Scheme 1. The functional pyrene moiety was introduced by a Sonogashira coupling reaction of compound 1 with 1-bromopyrene, affording 2 in a good yield (93%). The key intermediate 3 was obtained by the deprotection reaction of 2 with K_2CO_3 . Compound 3 was then reacted with 4 equiv of trans- $[PtI_2(PEt_3)_2]$ to give diiodometal complex 4. Subsequent halogen abstraction with AgNO₃ resulted in the isolation of bis(nitrate) salt 5 in reasonable yield (66%). The second Sonogashira coupling reaction of compound 3 with 4bromopyridine in the presence of $Pd(PPh_3)_4$ afforded the desired pyrene-modified 120° donor ligand 6 in 45% yield.

The molecular structures of the newly designed precursors 5 and 6 were well characterized by using multiple-nuclei NMR (¹H, ³¹P, and ¹³C), mass spectrometry, and elemental analysis. The ³¹P{¹H} NMR spectrum of diplatimum acceptor 5 displayed a singlet at 20.6 ppm, accompanied by flanking ¹⁹⁵Pt satellites (Figure S4B in the Supporting Information). Single crystals of precursor 4 that were suitable for X-ray diffraction were grown by slow evaporation of the precursor in dichloromethane/methanol solution (3/1 v/v) at ambient temperature for 2–3 days. An ORTEP of complex 4 (Figure 2) showed that all of the atoms (except for the triethylphosphine ligands) approximately lay in the same plane. The platinum atoms in compound 4 were found to adopt a slightly distorted trans square planar geometry (C-Pt-I and P-Pt-P bond angles of 175.8 and 173.4°, respectively), which might be caused by the steric demands of the bulky triethylphosphine ligands. It also showed that precursor 4 was indeed a suitable candidate for a 120° building unit, with the angle between the two platinum coordination planes being approximately 124°. The distance between the two Pt centers in precursor 4 was ~1.0 nm.

Self-Assembly of Pyrene-Acceptor Ligand 5 into Hexagonal Tris(pyrene) Metallacycle 8a and Hexakis-(pyrene) Metallacycle 8b. According to the "directional Scheme 1. Synthesis of 120° Pyrene-Modified Ligands 5 and 6





Figure 2. Crystal structure of precursor 4. Selected bond lengths (Å) and angles (deg): Pt(1)-C(26) = 1.952, Pt(1)-I(1) = 2.648, Pt(1)-P(1) = 2.309, Pt(1)-P(2) = 2.307, C(25)-C(26) = 1.187; P(2)-Pt(1)-P(1) = 173.44, C(26)-Pt(1)-I(1) = 175.8, P(2)-Pt(1)-I(1) = 91.07, P(1)-Pt(1)-I(1) = 94.95, C(26)-Pt(1)-P(2) = 90.1, C(26)-Pt(1)-P(1) = 83.7.

bonding" model and the "symmetry interaction" model, ^{Sa,b} the shape of an individual 2-D polygon is usually determined by the value of the turning angle within its angular components. As discussed above, hexagonal assemblies can be self-assembled from a combination of three 120° building blocks with three complementary 120° building blocks or six 120° building blocks with linear building blocks. With the 120° pyrene-modified acceptor precursor **5** in hand, the self-assembly of two multipyrene hexagons of different sizes and with different numbers of pyrene groups were investigated. As shown in Scheme 2, the hexagonal tris(pyrene) metallacycle **8a** was prepared by mixing the di-Pt(II) acceptor ligand **5** with 120°

Scheme 2. Coordination-Driven Self-Assembly of Multipyrene Hexagons 8a,b



donor 7a via [3 + 3] self-assembly in a 1:1 stoichiometric ratio in an acetone/water mixed solvent (10/1 v/v) for 8 h. A more dramatic extension of functionalization by means of coordination-driven self-assembly is manifested in the construction of molecular hexagons with six pyrenes, where each pyrene moiety is on each of the vertices of the hexagon. The hexakis(pyrene) hexagonal metallacycle **8b** was prepared by mixing the di-Pt(II) acceptor ligand **5** with 180° linear donor 7b via [6 + 6] selfassembly by employing a procedure similar to that in the construction of **8a**.

The self-assembly progress was easily monitored with ${}^{31}P{}^{1}H{}$ and ${}^{1}H$ NMR (Figures 3 and 4; see sections 2 and 3 in the Supporting Information). The ${}^{31}P{}^{1}H{}$ NMR spectra of **8a,b** displayed a sharp singlet (17.3 ppm for **8a** and 17.2 ppm



Figure 3. ³¹P{¹H} NMR spectra (161.9 MHz, 298 K) of the 120° di-Pt(II) acceptor **5** in CD_2Cl_2 (A), the [3 + 3] hexagon **8a** in acetone- d_6 (B), and the [6 + 6] hexagon **8b** in acetone- d_6 (C).



Figure 4. Partial ¹H NMR spectra (400 MHz, 298 K) of the 120° donor ligand 7a in CD_2Cl_2 (a), [3 + 3] hexagon 8a in acetone- d_6 (b), 180° donor ligand 7b in $CDCl_3$ (c), and [6 + 6] hexagon 8b in acetone- d_6 (d).

for **8b**), which suggests the formation of a discrete, highly symmetric supramolecular assembly. It was found that the peak is shifted upfield from the starting platinum acceptors **5** by approximately 3.3 and 3.4 ppm, respectively. This change, as well as a decrease in coupling of flanking ¹⁹⁵Pt satellites ($\Delta J_{PPt} = -161.9$ Hz for **8a,b**), is consistent with back-donation from the platinum atoms. Additionally, the protons of the pyridine rings (α -H and β -H) exhibited shifts 0.2–0.4 ppm downfield, resulting from the loss of electron density upon coordination of the pyridine N atom with the Pt(II) metal center.

Mass spectrometric investigation of multipyrene hexagonal metallacycles was performed by the CSI-TOF-MS technique, which allows the assemblies to remain intact during the ionization process in order to obtain the high resolution required for unambiguous determination of individual charge states.²³ In the CSI-TOF-MS spectrum of **8a** (Figure S10 in the Supporting Information), for example, peaks at m/z 1636.39 and 1191.09, related to $[M - 3PF_6]^{3+}$ and $[M - 4PF_6]^{4+}$, respectively, were observed. These peaks were isotopically

resolved, and they agree very well with their theoretical distribution. Given the significantly larger molecular weight (10446 Da) of **8b**, it is more difficult to get strong mass signals even under CSI-TOF-MS conditions. With considerable efforts, the peak at m/z 1512.42 was observed in the CSI-TOF-MS spectrum, which corresponds to the $[M - 6PF_6]^{6+}$ charge state. The peak was isotopically resolved and agrees with the theoretical distribution, although overlap with the signal of a very minor unknown fragment, which could not be attributed to any alternative polygonal supramolecules, was also observed.

Self-Assembly of Pyrene-Donor Ligand 6 into Hexagonal Tris(pyrene) Metallacycle 10a and Hexakis-(pyrene) Metallacycle 10b. As mentioned above, by employing a diverse library of donor and acceptor building blocks, the construction of "isomeric" supramolecular multipyrene hexagons possessing the same geometry can be realized by two complementary strategies. Thus, from the 120° pyrenemodified donor precursor 6, another series of multipyrene hexagons were also obtained.

As shown in Scheme 3, the [3 + 3] molecular hexagon 10a was prepared by mixing the donor ligand 6 with 120° di-Pt(II)





acceptor 9a in a 1:1 stoichiometric ratio in aqueous acetone (acetone/water, 10/1 v/v) overnight. The PF₆ salts of **10a** were synthesized by dissolving the yellow NO3 salts of 10a in acetone/water and adding saturated aqueous solution of KPF₆ to precipitate the product, which was collected by vacuum filtration. ³¹P{¹H} NMR analysis (Figure 5A) of the reaction mixture of 10a is consistent with the formation of asingle, highly symmetric species, as indicated by the appearance of a sharp singlet (ca. 14.6 ppm) with concomitant ¹⁹⁵Pt satellites, shifted upfield by ca. 5.1 ppm in comparison to the signal for the starting platinum acceptor 9a. This change, as well as the decrease in coupling of the flanking ¹⁹⁵Pt satellites ($\Delta J = -199$ Hz), is consistent with back-donation from the platinum atoms. In the ¹H NMR spectrum of **10a**, the hydrogen atoms of the pyridine rings exhibited obvious shifts downfield (α -H, 0.48 ppm; β -H, 0.60 ppm) due to the loss of electron density that occurs upon coordination of the pyridine N atom with the Pt(II) metal center (Figure 6).

As indicated in Scheme 3, the [6 + 6] hexagon 10b can be self-assembled from six 180° acceptor units 9b and six of the 120° pyrene donor 6, each derivatized with one pyrene moiety.



Figure 5. ³¹P{¹H} NMR spectra (161.9 MHz, acetone- d_{6} , 298 K) of the 120° di-Pt(II) acceptor **9a** and the [3 + 3] hexagon **10a** (A) and ³¹P{¹H} NMR spectra (400 MHz, acetone- d_{6} , 298 K) of the 180° di-Pt(II) acceptor **9b** and the self-assembled [6 + 6] hexagon **10b** (B).



Figure 6. Partial ¹H NMR spectra (400 MHz, 298 K) of the pyrenemodified 120° donor ligand 6 in $CDCl_3$ (a), [3 + 3] hexagon 10a in acetone- d_6 (b), and [6 + 6] hexagon 10b in acetone- d_6 (c).

The reaction mixture was stirred at ambient temperature for 4 h to yield a cloudy yellow solution. As a result of the coordination of the pyridine moiety with the Pt center, only one sharp ³¹P NMR peak at 13.3 ppm was observed for **10b** (Figure 5B), shifted upfield by almost 6.2 ppm in comparison with the signal

for the starting acceptor ligand **9b** (δ 19.5 ppm). As expected, in the ¹H NMR spectra, the α -H of the pyridine rings shifted slightly from 8.6 ppm in the free donors to 8.7 ppm in the assemblies and β -H exhibited approximately 0.4 ppm downfield shifts (Figure 6) because of the loss of electron density that occurs upon coordination of the pyridine N atom with the Pt(II) metal center. All of the multiple NMR analyses above are in agreement with the formation of discrete and highly symmetric multipyrene hexagonal metallacycles.

Mass spectrometric studies of both assemblies were performed using the CSI-TOF-MS and ESI-TOF-MS techniques. The CSI-TOF-MS spectra of hexagon **10a** exhibited two charged states at m/z 1233.4 and 957.4, corresponding to $[M - 4PF_6]^{4+}$ and $[M - 5PF_6]^{5+}$, respectively. These peaks were isotopically resolved, and they agree well with their theoretical distribution (Figure S11 in the Supporting Information). Moreover, in the ESI-TOF-MS spectra of **10b**, a peak at m/z1940.52 corresponding to $[M - 5PF_6]^{5+}$ was observed. This peak was isotopically resolved, and it is in good agreement with its theoretical distribution. Thus, the obtained analysis data ensure that only the [3 + 3] and [6 + 6] multipyrene hexagons **10a,b**, respectively, were formed in each self-assembly.

Molecular Modeling Studies. Unfortunately, all attempts to grow X-ray-quality single crystals of hexagonal multipyrene metallacycles **8a,b** and **10a,b** have proven to be unsuccessful to date. Thus, the PM6 semiempirical molecular orbital method was employed to optimize the geometry of all multipyrene metallacycles. The optimized structure of each multipyrene hexagon featured a very similar, roughly planar hexagonal ring decorated with multiple pyrene groups at the exterior surface (Figure 7). Moreover, the sizes of these novel hexagonal metallacycles were determined as well. For instance, the [3 + 3]hexagons **8a** and **10a** have internal radii of approximately 1.4 and 1.5 nm, respectively, while the [6 + 6] hexagons **8b** and **10b** have larger internal radii of 2.1 and 2.5 nm, respectively. Additionally, it was found that the [3 + 3] hexagons **8a** and **10a** have external radii of approximately 2.8 and 2.9 nm,



Figure 7. Simulated molecular models of the pyrene-modified [3 + 3] hexagon **8a** (A), the [6 + 6] hexagon **8b** (B), the [3 + 3] hexagon **10a** (C), and the [6 + 6] hexagon **10b** (D).



Figure 8. Emission spectra of 5 (10^{-5} M), 6 (10^{-5} M), 8a (0.33×10^{-5} M), 8b (0.17×10^{-5} M), 10a (0.33×10^{-5} M), and 10b (0.17×10^{-5} M) in CH₂Cl₂.



Figure 9. Normalized absorbance and emission titration spectra of 10a (a, c) and 10b (b, d) in CH₂Cl₂.

respectively, while larger external diameters of 3.5 and 3.9 nm for the [6 + 6] hexagons **8b** and **10b** were observed. This indicated that the size of hexagonal cavities in the final assemblies can be controlled by using different sizes of donors and acceptors.

Thus the obtained analysis data including the singularity of each ${}^{31}P$ NMR signal ensures that the desired multipyrene hexagons **8a,b** and **10a,b** were formed in the self-assembly. The sharp NMR signals in both the ${}^{31}P{}^{1}H$ and ${}^{1}H$ NMR spectra along with the solubility of these species ruled out the formation of oligomers. This means that multiple pyrene derivatives with predesigned shapes and sizes can be easily prepared through coordination-driven self-assembly, which

avoids the time-consuming procedures and lower yields often encountered in covalent synthetic protocols. Furthermore, the synthesis is straightforward and the yield is quantitative, which eliminates the need for purification.

UV–Visible Absorption and Fluorescence Studies of the Building Blocks and Metallacycles. The pyrene moiety is one of the most useful fluorophores due to its efficiency in excimer formation and subsequent changes in its emission properties. With pyrene-containing building blocks 5 and 6 along with the novel multipyrene hexagons 8a,b and 10a,b in hand, an investigation of their spectroscopic behavior was carried out. As shown in Figure S12 (Supporting Information), the absorption spectrum of di-Pt(II) acceptor 5 $(1.0 \times 10^{-5} \text{ M})$

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in CH₂Cl₂ exhibited broad and structureless bands around 230-290 and 300-400 nm. On the basis of a previous spectroscopic invesitgation on platinum-acetylide complexs,² the low-energy absorption bands were described as an admixture of intraligand (IL) $(\pi - \pi^*(C \equiv CR))$ and metal-toligand charge transfer (MLCT) (d(Pt) $\pi - \pi^*(C \equiv CR)$) transitions. Moreover, the higher energy absorption bands were likely due to $\pi - \pi^*$ transitions localized on the pyrene ring. Likewise, dipyridyl donor 6 (1.0×10^{-5} M) in CH₂Cl₂ exhibited a similar pattern, which was dominated by the $\pi - \pi^*$ transition of aromatic pyrene rings and intraligand (IL) charge transfer.²⁵ The fluorescence emission of 5 and 6 with the ethynyl-pyrene moieties appeared at λ_{max} 405 nm with a shoulder band at 425 nm in CH₂Cl₂ (Figure 8). This result corresponded to the monomer emission of the pyrene chromophore. In comparison to those of the typical pyrenecontaining compounds without ethynylene groups, in which the emission peaks were at 375 and 395 nm,²⁶ the fluorescence emission spectra of 5 and 6 were red-shifted about 30 nm. The bathochromic shift of the emission wavelength might be due to the extended π -conjugation systems resulting from the introduction of an ethynylene group.²⁷

In comparison to the precursor **5**, the absorption coefficients (ε) of assemblies **8a,b** were enhanced, since the effective concentration of the pyrene moiety increased.²⁸ A similar feature was found in the assemblies **10a,b** (Table S1 in the Supporting Information). However, complexes **8a** ($\Phi_F = 0.030$) and **8b** ($\Phi_F = 0.013$) have a quantum yield much lower than that of compound **5** ($\Phi_F = 0.87$). Similarly, complexes **10a** ($\Phi_F = 0.0097$) and **10b** ($\Phi_F = 0.0032$) featured a quantum yield much lower than that of their precursor **6** ($\Phi_F = 0.12$). The fluorescence quenching of these assembles might be caused by the aggregation of themselves in CH₂Cl₂.²⁹

It should be noted that these novel multipyrene hexagons displayed dramatically different emission behaviors. The assemblies 8a,b showed weak emissions at 405 and 425 nm (Figure 8a). Notably, there was almost no emission band beyond 500 nm, indicating the absence of excimer formation of pyrene.³⁰ Interestingly, different from 8a,b, which showed typical monomeric emission of the pyrene, metallacycles 10a $(0.33 \times 10^{-5} \text{ M})$ and **10b** $(0.17 \times 10^{-5} \text{ M})$ in CH₂Cl₂ displayed a longer fluorescence emission band at λ_{max} 550 nm (Figure 8b), which corresponded to the excimer emission of the pyrene chromophore.³¹ It should be noted that at the same concentration as that of 10a,b, metallacycles 8a (0.33 \times 10⁻⁵ M) and **8b** (0.17 \times 10⁻⁵ M) were not able to form excimers, which might be attributed to the relatively lower charge densities of 8a,b in comparison to that of $10a,b^{32}$ (Table S2 in the Supporting Information). This means that the combination mode of building blocks can influence the excimer formation of the resulting pyrene-containing self-assemblies.

The effects of concentration on the absorption and fluorescence emission of **10a,b** are shown in Figure 9. When the concentrations of **10a** and **10b** were increased, a decrease of the absorbance at around 285 nm with a concomitant increase of the absorbance around 325 nm was observed. Likewise, a significant decrease of the emission at 405 nm and a hypochromic shift (145 nm) of the emission spectra were observed as well, which were in agreement with the formation of pyrene excimers.³³ Notably, dipyridyl donor **6** featured a concentration-dependent emission in CH₂Cl₂ (Figure S13, Supporting Information) as well. For example, it was found that the high-energy emission spectrum with a maximum of 393 nm

at 1.0×10^{-9} M disappeared, with the emission maximum redshifted to 530 nm at 3.0×10^{-2} M. It should be noted that, in comparison to metallacycles **10a,b**, the formation of pyrene excimers of **6** was observed at much higher concentration, which is indicative of the notion that the metallacycles **10a,b** have a tendency stronger than that of **6** to form excimers under similar conditions. These results indicated that structural effects played important roles during the formation of pyrene excimers.

CONCLUSION

In conclusion, the work presented here provided a simple and highly efficient approach to the construction of multipyrene hexagons possessing structurally well-defined cavities of varying diameter and shape via coordination-driven self-assembly. The covalent attachment of a pyrene to both 120° di-Pt(II) acceptor and 120° bipyridyl donor units allowed for the formation of a diverse library of new functionalized donor and acceptor building blocks, from which a series of "isomeric" supramolecular multipyrene hexagons possessing the same geometry were obtained via two complementary strategies. All of these assemblies were characterized by multinuclear NMR (³¹P and ¹H) spectroscopy, CSI-TOF-MS and ESI-TOF-MS, elemental analysis, and molecular modeling. These resultant multipyrene assemblies are unique in that the number and arrangement of their pendant macrocycles can be precisely controlled, owing to the conserved rigidity of their core 2-D polygonal scaffolds. The primary spectroscopic behavior of these newly designed assemblies was investigated. An interesting result was that these novel multipyrene hexagons displayed dramatically different emission behaviors, although they possessed the same geometry, which indicated that structural effects played important roles during the formation of pyrene excimers in this study. All of these findings enrich the library of functionalized supramolecular metallacycles and demonstrate again the power and scope of the coordination-driven self-assembly.

EXPERIMENTAL SECTION

General Information. All solvents were dried according to standard procedures, and all of them were degassed under N₂ for 30 min before use. Reagents were used as purchased. All air-sensitive reactions were carried out under an argon atmosphere. ¹H NMR, ¹³C NMR, and ³¹P NMR spectra were recorded on a Bruker 400 MHz spectrometer (¹H, 400 MHz; ¹³C, 100 MHz; ³¹P, 161.9 MHz) at 298 K. The ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent signals, and ³¹P NMR resonances are referenced to an internal standard sample of 85% H₃PO₄ (δ 0.0). Coupling constants (*J*) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad.

Synthesis of Compound 5. Diiodine complex 4 (184 mg, 0.13 mmol) and AgNO₃ (64 mg, 0.39 mmol) were placed in a 25 mL Schlenk flask followed by 3 mL of dichloromethane. The reaction mixture was stirred in the dark at room temperature for 24 h. A clear solution with a heavy creamy precipitate resulted; the precipitate was filtered off, and the solvent was removed in vacuo. The residue was redissolved in a minimal amount of dichloromethane, and then diethyl ether was carefully added to precipitate the product. The product **5** was obtained as a light yellow solid and dried in vacuo: yield 106 mg, 66%; ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.67 (d, *J* = 9.2 Hz, 1H), 8.29–8.07 (m, 8H), 7.35 (s, 2H), 7.09 (s, 1H), 2.00–1.95 (m, 24H), 1.28–1.20 (m, 36H); ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ 8.58 (s, *J*_{Pt-P} = 2470.6 Hz); MALDI HRMS *m*/*z* calcd for C₅₂H₇₂N₂O₆P₄Pt₂: C, 46.78; H, 5.44; N, 2.10. Found: C, 46.52; H, 5.59; N, 2.22.

Synthesis of Compound 6. Under an atmosphere of nitrogen, 20 mL of THF and 20 mL of i-Pr $_2NH$ were added to a mixture of compound 3 (494 mg, 1.41 mmol), 4-bromopyridine hydrochloride (1.10 g, 5.64 mmol), Pd(PPh₃)₄ (81 mg, 0.070 mmol), and CuI (13 mg, 0.070 mmol) in a 100 mL Schlenk flask. The mixture was stirred at 65 °C for 12 h. After that, insoluble materials were filtered through filter paper and the solvent was removed by evaporation on a rotary evaporator. Column chromatography with dichloromethane/acetone (5/1 v/v) as eluent afforded a yellow solid of compound 6 in a yield of 45%: $R_f = 0.58$ (dichloromethane/acetone, 5/1 v/v); mp 198 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.66–8.63 (m, 5H), 8.27–8.04 (m, 8H), 7.91 (s, 2H), 7.75 (s, 1H), 7.45 (d, J = 4.8 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.74, 134.89, 134.23, 131.92, 131.51, 131.05, 130.82, 130.69, 129.56, 128.49, 128.39, 127.06, 126.23, 125.73, 125.46, 125.10, 124.64, 124.43, 124.26, 124.06, 123.03, 116.64, 92.77, 91.84, 90.58, 87.86; MS (EI) m/z (%) 504 (M⁺, 1.75); HRMS calcd for C38H20N2 504.1626, found 504.1633.

Self-Assembly of Hexagon 8a. A mixture of bipyridyl donor ligand 7a (2.92 mg, 10.04 μ mol) and pyrene-modified acceptor 5 (13.92 mg, 10.04 μ mol) was placed in a glass vial. Then water (0.5 mL) and acetone (5.0 mL) were added into the bottle with continuous stirring (10 min). The reaction mixture was stirred for 8 h at 55 °C, upon which the starting materials completely dissolved and the reaction mixture attained a light yellow color. The PF₆ salts of 8a were synthesized by dissolving the yellow NO3 salts of 8a in acetone/water and adding a aqueous solution of KPF₆ to precipitate the product, which was collected by vacuum filtration: yield 98%; yellow solid; ¹H NMR (acetone- d_{6} , 400 MHz) δ 9.07 (d, J = 5.2 Hz, 12H), 8.69 (d, J =9.2 Hz, 3H), 8.40-8.13 (m, 27H), 7.98-7.82 (m, 18H), 7.69 (t, J = 7.6 Hz, 3H), 7.55 (s, 6H), 7.28 (s, 3H), 2.06-2.02 (m, 72H), 1.32-1.26 (m, 108H); ³¹P NMR (acetone- d_6 , 161.9 MHz) δ 17.32 (s, $J_{\text{Pt-P}}$ = 2852.0 Hz); CSI-TOF-MS $[M - 3PF_6]^{3+}$ 1636.39, $[M - 4PF_6]^{4+}$ 1191.09, $[M - 5PF_6]^{5+}$ 923.84. Anal. Calcd for $C_{216}H_{252}F_{36}N_6P_{18}Pt_6$: C, 48.54; H, 4.75; N, 1.57. Found: C, 48.23; H, 4.54; N, 1.77.

Self-Assembly of Hexagon 8b. A mixture of bipyridyl donor precursor 7b (1.04 mg, 6.66 μ mol) and pyrene-modified acceptor 5 (8.90 mg, 6.66 μ mol) was placed in a glass vial. Then water (0.5 mL) and acetone (5.0 mL) were added into the bottle with continuous stirring (10 min). The reaction mixture was stirred overnight at 55 °C, upon which starting materials completely dissolved and the reaction mixture attained a light yellow color. The PF₆ salt of 8b was synthesized by dissolving the yellow NO₃ salt of 8b in acetone/water and adding a aqueous solution of KPF₆ to precipitate the product, which was collected by vacuum filtration: yield 98%; yellow solid; ¹H NMR (acetone-*d*₆, 400 MHz) δ 9.21 (d, *J* = 5.2 Hz, 24H), 8.70 (d, *J* = 9.2 Hz, 6H), 8.40–8.13 (m, 72H), 7.56 (s, 12H), 7.29 (s, 6H), 2.06–2.02 (m, 144H), 1.32–1.24 (m, 216H); ³¹P NMR (acetone-*d*₆, 161.9 MHz) δ 17.28 (s, *J*_{Pt-P} = 2856.0 Hz); CSI-TOF-MS [M – 6PF₆]⁶⁺ 1512.42. Anal. Calcd for C₃₇₂H₄₈₀F₇₂N₁₂P₃₆Pt₁₂: C, 44.93; H, 4.87; N, 1.69. Found: C, 44.99; H, 4.95; N, 1.60.

Self-Assembly of Hexagon 10a. A mixture of bipyridyl donor ligand 6 (3.00 mg, 5.94 μ mol) and the 120° nitrate 9a (6.94 mg, 5.94 μ mol) was placed in a glass vial. Then water (0.5 mL) and acetone (5.0 mL) were added into the bottle with continuous stirring (10 min). The reaction mixture was stirred overnight at 55 °C, upon which the starting materials completely dissolved and the reaction mixture attained a yellow color. The PF₆ salt of 10a was synthesized by dissolving the yellow NO3 salt of 10a in acetone/H2O and adding a saturated aqueous solution of KPF₆ to precipitate the product, which was collected by vacuum filtration: yield 97%; yellow solid; ¹H NMR (acetone- d_{6} , 400 MHz) δ 9.14 (d, J = 5.6 Hz, 12H), 8.77 (d, J = 9.2 Hz, 3H), 8.42–8.17 (m, 30H), 8.04–8.00 (m, 15H), 7.72 (d, J = 8 Hz, 12H), 7.60 (d, J = 8 Hz, 12H). 1.52 (br, 72H), 1.28–1.18 (m, 108H); ³¹P NMR (acetone- d_6 , 161.9 MHz) δ 14.55 (s, J_{Pt-P} = 2648.7 Hz); CSI-TOF-MS [M - 4PF₆]⁴⁺ 1233.4, [M - 5NO₃]⁵⁺ 957.5. Anal. Calcd for C225H264N6F36O3P18Pt6: C, 49.02; H, 4.83; N, 1.52. Found: C, 48.75; H, 5.19; N, 1.74.

Self-Assembly of Hexagon 10b. The dipyridyl donor ligand 6 (2.50 mg, 4.95 μ mol) and the organoplatinum 180° acceptor 9b (6.13 mg, 4.95 μ mol) were weighed accurately into a glass vial. In the vial

was added CD₂Cl₂ (0.7 mL) solvent, and the reaction solution was then stirred at room temperature for 4 h to yield a cloudy yellow solution. The solution was then transferred into an NMR tube to collect ¹H and ³¹P NMR spectra. The solid product was obtained by removing the solvent under vacuum: yield 96%; yellow solid; ¹H NMR (CD₂Cl₂, 400 MHz) δ 8.71–8.69 (m, 30H), 8.33–8.02 (m, 66H), 7.87 (d, *J* = 5.6 Hz, 24H), 7.07 (s, 24H), 1.36 (br, 144H), 1.18–1.12 (m, 216H); ³¹P NMR (CD₂Cl₂, 161.9 MHz) δ 13.30 (s, *J*_{Pt-P} = 2736.1 Hz). Anal. Calcd for C₄₂₀H₅₀₄F₃₆N₁₂O₃₆P₂₄Pt₁₂S₁₂: C, 48.27; H, 4.86; N, 1.61; found: C, 48.32; H, 4.98; N, 1.72.

ASSOCIATED CONTENT

Supporting Information

Text, tables, figures, and a CIF file giving details of synthesis and characterization of the compounds and supplementary experimental data, as well as the crystal structure of **4**. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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