

Self-Assembly of Rectangles and Prisms via a Molecular “Clip”

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Aromatic molecular “clips” bearing two symmetrically bound platinum moieties have been prepared. The molecular “clip” **4** readily self-assembled with linear linkers such as 4,4'-bipyridyl, 1,4-bis[2-(4-isocyano-3,5-diisopropylphenyl)-ethynyl]benzene, and nicotinic acid to form molecular rectangles. The overall dimensions of the rectangle **7** were 7.3 Å × 15.3 Å. The molecular “clip” also self-assembled with tritopic pyridyl and isocyanide ligands to form trigonal prismatic frameworks. The characterization of the supramolecules by multinuclear NMR, electrospray mass spectrometry, and X-ray crystal structures is also reported.

Introduction

The directed assembly of supramolecular entities from discrete molecular building units has received considerable attention.¹ The continuing interest arises from the multitude of assemblies, both two- and three- dimensional, that have been reported in the recent literature. An attractive aspect of this methodology is the rational design of structures of diverse shapes, sizes, and symmetries. Such assemblies are formed by the noncovalent or reversible dative interactions between building units. By employment of a rational transition-metal-mediated approach, many finite and nanoscopic supramolecules have been prepared.²

Of the geometric shapes accessible through the directional-bonding approach, tetranuclear squares have been the most widely reported.³ Other high-symmetry structures, such as triangles,⁴ hexagons,⁵ and dodecahedrons,⁶ have also been documented. As lower symmetry hosts can be expected to

show enhanced guest selectivity, especially toward planar aromatic guests,⁷ rectangles represent a crucial geometrical model in the development of this area. Despite their relative simplicity, molecular rectangles are much less common.⁸ Recently, the Hupp,⁹ Sullivan,¹⁰ and Süss-Fink groups¹¹ have reported the preparation of a series of rhenium-, ruthenium-, and manganese-based molecular rectangles. The most noteworthy were built by Stang and co-workers¹² from a ligand-directed approach to molecular rectangles. They have described the self-assembly reactions of a molecular “clip”-

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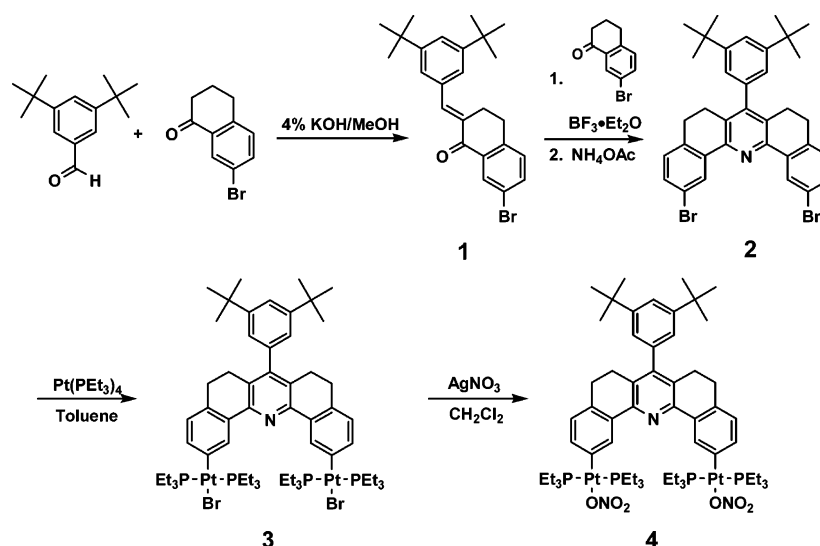
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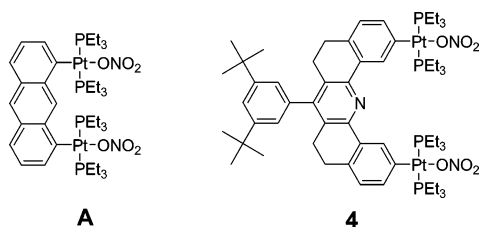
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Scheme 1



(A) as an efficient entry into the rectangular shape. 1,8-Bis-[*trans*-Pt(PEt₃)₂(NO₃)]anthracene possesses two labile coordination sites directed in a nearly parallel fashion. To get a variety of rectangles with different sizes and shapes, more molecular “clips” with the above shape are required.



Accordingly, we envisioned that if we could synthesize a building unit with two parallel coordination sites facing in the same direction such as **4**, such a subunit would offer another entry into new rectangles and trigonal prismatic frameworks. Here we report the self-assembly reactions and characterization of the members of a family of molecular rectangles and supramolecular coordination cages with trigonal prismatic frameworks via a new type of subunit (**4**).

Results and Discussion

Synthesis of a Molecular “Clip”. Our strategy for the synthesis of self-assembled supramolecules of molecular rectangles utilizes the molecular “clip” with two parallel coordination sites facing in the same direction. The synthesis of such molecular clip (**4**) followed many of the procedures described previously for analogous compounds.¹³ The synthetic procedures are outlined in Scheme 1.

The synthesis of **4** is conveniently prepared in four steps from the 7-bromo-1-tetralone: 7-bromo-1-tetralone reacted

with a slightly excess of 3,5-di-*tert*-butylbenzaldehyde in the presence of KOH to give **1**. Reaction of tetralone with **1** in boron trifluoride etherate gave **2** in 31% yield. The molecular clip was easily synthesized by a double oxidative addition. An oxidative addition reaction of 2.5 equiv of Pt(PEt₃)₄ with **2** gave the diplatinum species **3**. Subsequent reaction with silver nitrate resulted in formation of **4**. Molecular clip **4** is a crystalline solid that is stable in air and soluble in CH₂Cl₂, toluene, diethyl ether, and THF. Spectroscopic data for **4** are completely consistent with its proposed structure. Five distinct resonances at 8.40–6.75 ppm in the ¹H NMR spectrum and 13 peaks at 151.7–121.2 ppm for the aromatic region in the ¹³C NMR spectrum are observed. The ³¹P NMR spectrum of **4** shows a singlet at 12.2 ppm with concomitant ¹⁹⁵Pt satellites (*J*_{Pt} = 2894 Hz). This value is comparable to that observed for the 1,8-bis[*trans*-Pt(PEt₃)₂(NO₃)]anthracene.¹² The structure of **4** was established by single-crystal X-ray analysis and is shown in Figure 1. Crystals of **4** were grown by the layering of hexane in a toluene solution of the complex. Each unit contains one disordered toluene molecule. The crystallographic data and processing parameters are given in Table 1. The compound crystallizes in the triclinic system *P* $\bar{1}$ with six molecules in a unit cell. Therefore, there are three molecules in an asymmetric unit. In Figure 1, only one molecule of them is shown. All of the atoms in the spacer (except for the triethylphosphine ligands and two oxygen atoms of nitrate anions) lie approximately in the same plane. The coordination planes of both platinum atoms are perpendicular to the plane of spacer. The dihedral angle between the spacer and the 3,5-di-*tert*-butyl-phenyl group is –14.3°, possibly because of steric hindrance with neighboring ethylene units. Two platinum fragments are nearly parallel with the distance of 7.34 Å.

Synthesis of Bridging Ligands with Isocyanide Units, **5 and **6**.** The construction of many supramolecules has been

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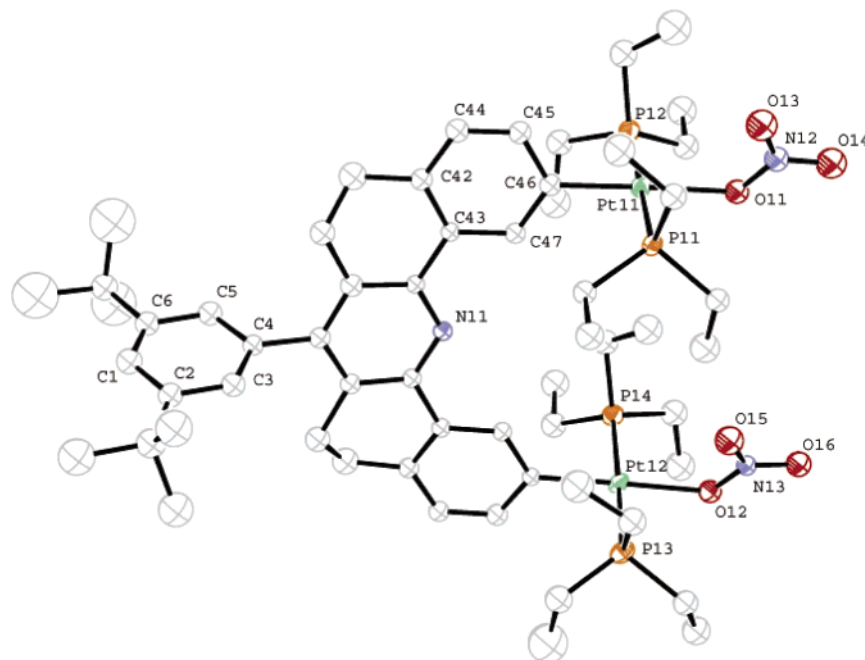


Figure 1. ORTEP drawing³⁵ of molecular “clip” **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and toluene are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(11)–C(46) 1.983(17), Pt(11)–O(11) 2.159(11), Pt(11)–P(11) 2.307(4), Pt(11)–P(12) 2.299(5); C(46)–Pt(11)–O(11) 175.1(6), P(11)–Pt(11)–P(12) 178.86(17).

Table 1. Crystal and Structure Refinement Data for **4** and **7**

param	4	7
empirical formula	C ₁₉₈ H ₃₀₉ N ₉ O ₁₈ P ₁₂ Pt ₆	C ₁₃₈ H ₂₀₆ N ₁₀ O ₁₂ P ₈ Pt ₄ ·12H ₂ O
fw	4645.72	3429.34
cryst syst	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.922(2)	13.979(3)
<i>b</i> (Å)	27.176(4)	17.444(3)
<i>c</i> (Å)	28.000(4)	18.672(3)
α (deg)	85.828(3)	73.179(3)
β (deg)	76.420(3)	71.998(3)
γ (deg)	76.017(3)	80.578(3)
<i>V</i> (Å ³)	10 708(3)	4131.0(13)
<i>Z</i> value	2	1
<i>D</i> _{calc} (g/cm ³)	1.441	1.378
<i>F</i> (000)	4704	1740
μ (Mo K α) (mm ^{−1})	4.052	3.514
2 θ range (deg)	1.50–56.98	2.38–57.12
no. of reflns measd	134 907	51 729
no. of observns (<i>I</i> > 2 σ (<i>I</i>))	53 205	20 466
<i>R</i>	0.0963	0.0763
<i>R</i> _w	0.1987	0.2014
goodness of fit	0.904	0.956

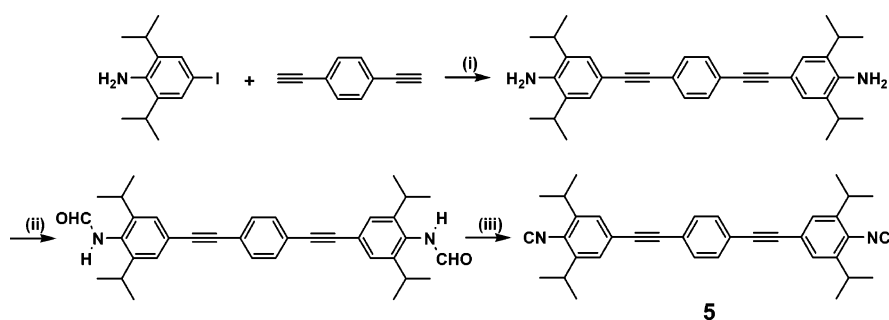
based on the coordination bonding motif between M(II) (M = Pd, Pt) acceptor units and nitrogen donor ligands or a few examples of oxygen donor linkers.¹⁴ To synthesize macrocycles via a new class of isocyanide-based carbon donors, we decided to prepare the di- and triisocyanide bridging ligands. Such ligands can be easily synthesized in three steps, as shown in Schemes 2 and 3. In each step, the reaction proceeds smoothly and the products can be obtained in high yield. In the first step, substitution of the iodide in 4-iodo-2,6-diisopropylaniline by the ethynyl group to afford 1,4-bis- and 1,3,5-tris[(4-amino-3,5-diisopropylphenyl)ethy-

nyl]benzene is achieved by Sonogashira cross-coupling reaction in the presence of catalytic amounts of Pd(PPh₃)₄ and copper iodide. Formylation of such amino compounds with formic acid and acetic anhydride affords the formamides. Di- and triisocyanide ligands were prepared by the dehydration reaction with triphosgene/triethylamine. A similar preparation of functionalized derivatives of 2,6-diisopropylphenyl isocyanide has been reported by the Mayr group.¹⁵ Ligands **5** and **6** are crystalline white solids that are stable in air and soluble in toluene, THF, and CH₂Cl₂. Spectroscopic data for **5** and **6** are completely consistent with their proposed structures. The ¹H NMR spectrum of **5** contained a methine resonance (3.38 ppm) and a methyl resonance (1.30 ppm). Two singlets (7.54 and 7.33 ppm) in the ¹H NMR spectrum and six resonances (145.4–123.1 ppm) in the ¹³C NMR spectrum could be assigned to the aromatic groups. The ¹³C NMR resonance of isocyanide group (170.3 ppm) is generally of low intensity. The alkynyl group in **5** gives rise to characteristic ¹³C NMR resonances at 91.0 and 90.2 ppm. These values are comparable to these observed for the aryl isocyanides.¹⁶

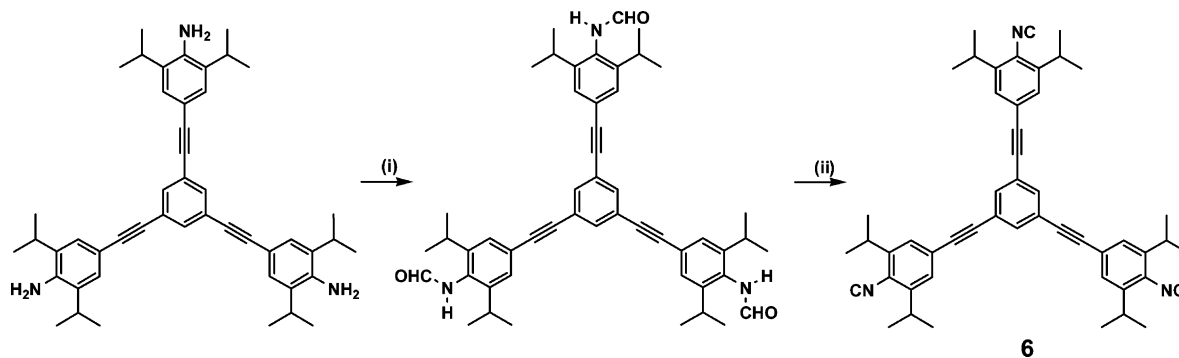
Self-Assembly of Molecular Rectangles. Molecular clip **4** was found to be a good scaffold to assemble a variety of donor ligands. For example, the new molecular rectangle **7** was readily self-assembled in almost quantitative yield when **4** was combined with an equimolar amount of 4,4'-dipyridyl in an acetone/H₂O mixture (Scheme 4). ³¹P NMR of **7** indicated the formation of a singlet with ¹⁹⁵Pt satellites, shifted 5.1 ppm upfield (−Δδ) relative to **4** (ΔJ_{Pt–P} = −300

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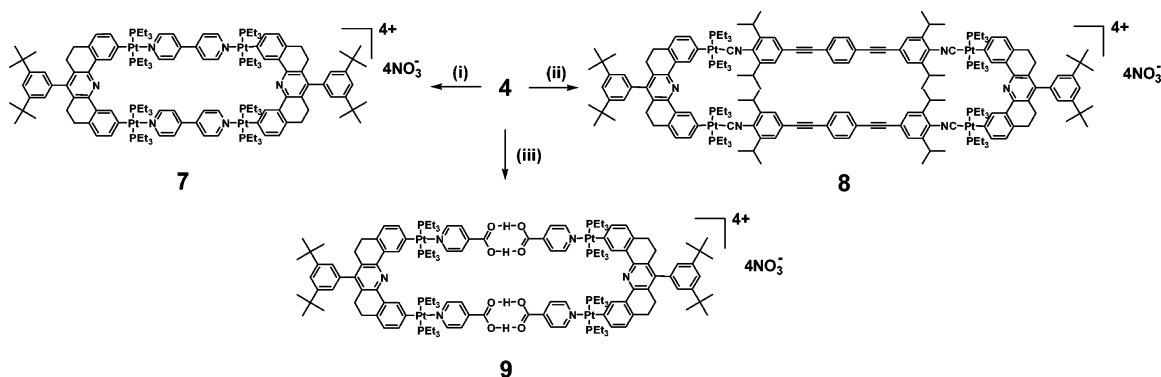
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Scheme 2^a

^a Key: (i) Pd(PPh₃)₄, CuI, Et₃N, THF; (ii) acetic anhydride, formic acid; (iii) triphosgene, Et₃N, THF.

Scheme 3^a

^a Key: (i) acetic anhydride, formic acid; (ii) triphosgene, Et₃N, THF.

Scheme 4^a

^a Key: (i) 4,4'-bipyridyl, acetone-H₂O; (ii) **5**, acetone-H₂O; (iii) isonicotinic acid, acetone-H₂O.

Hz). In a similar manner, reaction of **4** with bridging ligands 1,4-bis[2-(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene (**5**) afforded the rectangle **8** with different size and bonding mode. The ¹H NMR spectrum of **7** also indicated the formation of highly symmetrical structure and displayed spectroscopic differences from its monomeric subunit. The protons in the positions α and β to the bridging pyridine exhibit downfield shifts (~0.45 ppm) due to the loss of electron density upon coordination. As a result of increased back-donation from the platinum to the phosphine moiety, the protons of the methylene groups bonded to phosphorus showed slightly upfield shift, 0.18 ppm. Of note is that four sets of resonances from the pyridyl protons became inequivalent in the molecular rectangle. As revealed in the crystal structure of **7**, adjacent two bridging bipyridyl groups are situated in the perpendicular to the coordination plane to the platinum moiety. Clearly, rotation of bipyridyl rings is restricted once the rectangle is formed. Therefore, the

bipyridyl protons positioned toward the interior of the rectangle experience an environment different from those of periphery. A similar pattern was observed in the molecular rectangle based on the 1,8-bis[*trans*-Pt(PEt₃)₂(NO₃)]anthracene.^{12a} Additional evidence for the formation of the rectangle **7** was obtained from electrospray ionization mass spectroscopy. Peaks attributable to the consecutive loss of nitrate counterions, [M - 2NO₃]²⁺ (*m/z* = 1549.5), [M - 3NO₃]³⁺ (*m/z* = 1012.3), and [M - 4NO₃]⁴⁺ (*m/z* = 743.8), where M represents the intact rectangle, were detected.

The structure of **7** was unambiguously established by single-crystal X-ray analysis and is shown in Figure 2. The crystallographic data and processing parameters are given in Table 1. The crystal structure of **7** shows a rectangle with an inversion center located at the midpoint of the two bipyridine moiety. The entire aromatic framework appears to be nearly coplanar with a slight dihedral angle (28°) between the pyridyl planes of 4,4'-bipyridyl. As a conse-

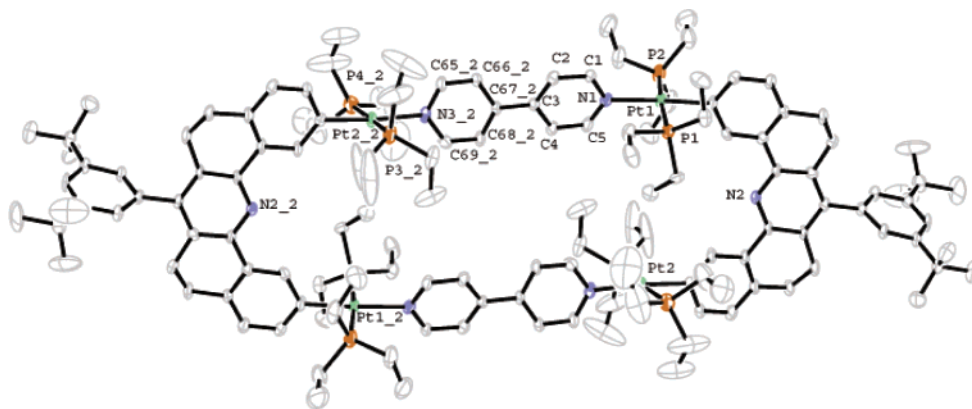
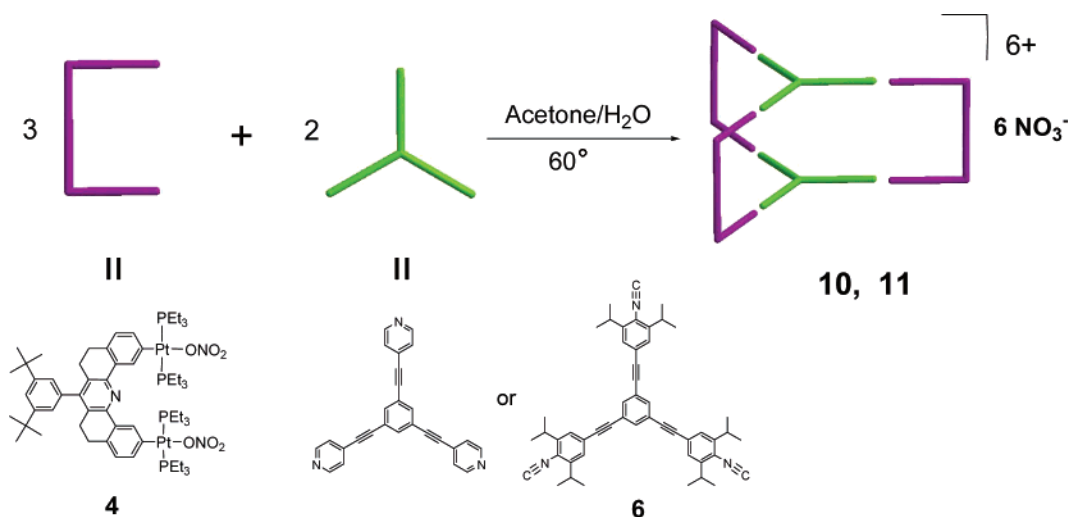


Figure 2. ORTEP drawing of rectangle **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms, counterions, and H₂O are omitted for clarity. Selected bond distances (Å) and angles (deg): Pt(1)–C(18) 2.031(12), Pt(1)–N(1) 2.126(10), Pt(1)–P(1) 2.318(4), Pt(1)–P(2) 2.301(5); C(18)–Pt(1)–N(1) 177.1(5), P(1)–Pt(1)–P(2) 173.51(13).

Scheme 5



quence, the fixed planar arrangement may be related to the rotational barrier found less around platinum–nitrogen bonds.¹⁷ The N(1)–Pt(1)–P(1) and P(1)–Pt(1)–P(2) angles in **7** of 90.7(3) and 173.51(13)°, respectively, are consistent with other slightly distorted square planar Pt(II) complexes. The overall dimension of the rectangle, as defined by the platinum corners, is 7.3 Å × 19.8 Å for **7**. No solvent molecules or counterions were not located in the cavity.

As the hydrogen-bond-mediated self-assembly of cyclic arrays from bis(platinum) complexes containing nicotinamide, nicotinic acid, and isonicotinic acids were reported,¹⁸ we attempted a similar reaction to check whether such methodology would be applied for the formation of a rectangle using the molecular clip (**4**). The self-assembly process was performed in the same general manner. Addition of isonicotinic acid to **4** in an acetone/H₂O mixture resulted in the quantitative formation of a highly symmetrical rectangle. The ³¹P NMR spectrum of this product exhibited a singlet with concomitant ¹⁹⁵Pt satellite indicating the

formation of a highly symmetrical species. Direct evidence for the formation of rectangle **9** arises from the ^1H NMR spectrum, appearing as four sets of resonances from the bridging pyridyl protons and a characteristic resonance at δ 12.70, assigned to a hydrogen-bonded carboxylic acid. The appearance of four sets of resonances demonstrates that the pyridyl protons positioned toward the interior of the rectangle experience an environment different from those of the periphery. ^1H NMR titration studies demonstrates its self-association to afford a hydrogen-bonded dimer in CDCl_3 solution at 298 K. At low concentrations ($< 0.05 \text{ mol dm}^{-3}$), molecular clip coordinated to isonicotinic acid self-associates to form **9** with $K_2 = 118.4 \pm 1.6 \text{ mol}^{-1} \text{ dm}^3$ according to the method of Saunders and Hyne.¹⁹ The value of the dimerization constant is comparable to that of *trans*-(4,4'-benzophenone)bis[(nicotinic acid)bis(triphenylphosphine)]-diplatinum(II) bis(triflate) ($K_2 = 98.2 \pm 1.1 \text{ mol}^{-1} \text{ dm}^3$ at 298 K).¹⁸ Additional proof of **9** is obtained using mass spectrometry. In the mass spectrum of **9**, peaks attributable to the consecutive loss of nitrate ions, $[\text{M} - \text{NO}_3]^+$ ($m/z = 1640.7$) and $[\text{M} - 2\text{NO}_3]^{2+}$ ($m/z = 789.3$), were observed.

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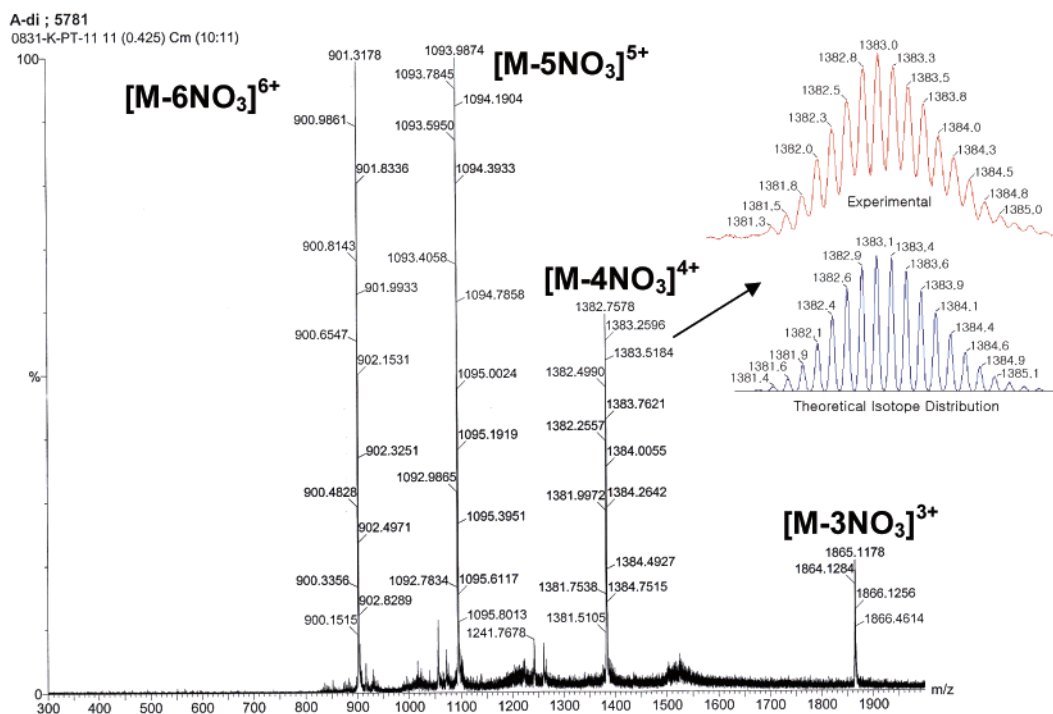


Figure 3. Experimental (top) and calculated (bottom) isotopic distribution pattern of $M - 4NO_3$ for **11**.

The isotopic distributions matched well with the theoretical isotopic ones. This mass data furnishes another evidence for **9**.

Self-Assembly of Trigonal Prisms. Although M_3L_2 prismatic frameworks remain relatively uncommon due to the scarcity of a predesigned unit,²⁰ Stang and co-workers²¹ recently reported the self-assembly of molecular prisms from planar tritopic ligands, directed by a molecular clip. Molecular clip **4** was also shown to be a good unit to assemble the trigonal prisms. A trigonal prism **10** can be prepared by the self-assembly from 2 equiv of tritopic 120° angular 1,3,5-tris(4-ethynylpyridyl)benzene and 3 equiv of ditopic 0° angular **4**. In the ^{31}P NMR spectrum of **10**, a sharp singlet at 7.1 ppm indicates the formation of a highly symmetric assembly. The upfield shift of this resonance ($-\Delta\delta = 5.1$ ppm), together with the change in J_{PtP} for the flanking ^{195}Pt satellites ($\Delta J_{PtP} = -197$ Hz), is indicative of coordination of platinum to pyridine unit. The 1H NMR data for **10** are consistent with the proposed trigonal prism. Of note is that four sets of resonances for the bridging pyridyl protons appear due to the restricted rotation of the bridging pyridine unit.

Further proof for the trigonal prism is obtained using mass spectroscopy. The ESI-mass spectrum of **10** showed prominent peaks attributable to the consecutive loss of nitrate ions. $[M - 3NO_3]^{3+}$ ($m/z = 1649.2$), $[M - 4NO_3]^{4+}$ ($m/z =$

1221.6), and $[M - 5NO_3]^{5+}$ ($m/z = 965.1$), where M represents the intact prismatic cage, were detected.

To demonstrate the versatility of **4** as a useful ditopic clip, a large trigonal prism **11** was synthesized, using the bridging ligand 1,3,5-tris[2-(4-isocyanato-3,5-diisopropylphenyl)ethynyl]benzene. We chose the isocyanide ligand as a bridging ligand because (i) the facile formation of adducts from Pt complexes by isocyanide²² and (ii) the facile synthesis of a variety of predesigned isocyanides. We also envisioned that this ligand containing an alkynyl unit would have the advantage of free rotating central rings. The self-assembly of **11** proceeds quantitatively as shown in Scheme 5. The 3:2 stoichiometric addition of **4** with tritopic isocyanide ligand **6** readily afforded the supramolecule **11**. The ^{31}P signal with ^{195}Pt satellites is shifted upfield by 3.2 ppm relative to **4** ($\Delta J_{PtP} = -463$ Hz). Of special note is that in the 1H NMR spectrum seven resonances in the aromatic region appear. This indicates that all the tritopic units are equivalent, due to rapid rotation. This result is completely different from the supramolecule **10**. The mass spectrum of **11** gave $[M - 3NO_3]^{3+}$ ($m/z = 1865.1$), $[M - 4NO_3]^{4+}$ ($m/z = 1382.8$), $[M - 5NO_3]^{5+}$ ($m/z = 1094.0$), and $[M - 6NO_3]^{6+}$ ($m/z = 901.3$), confirming the proposed structure. The isotopic distribution patterns matched well with the calculated ones. The calculated and experimental isotope distribution patterns of the $M - 4NO_3$ peak of **11** are depicted in Figure 3. This mass data, together with NMR data, provide strong evidence for the proposed structure.

As suitable quality crystals for X-ray crystallographic data could not be obtained, a calculation is required to visualize

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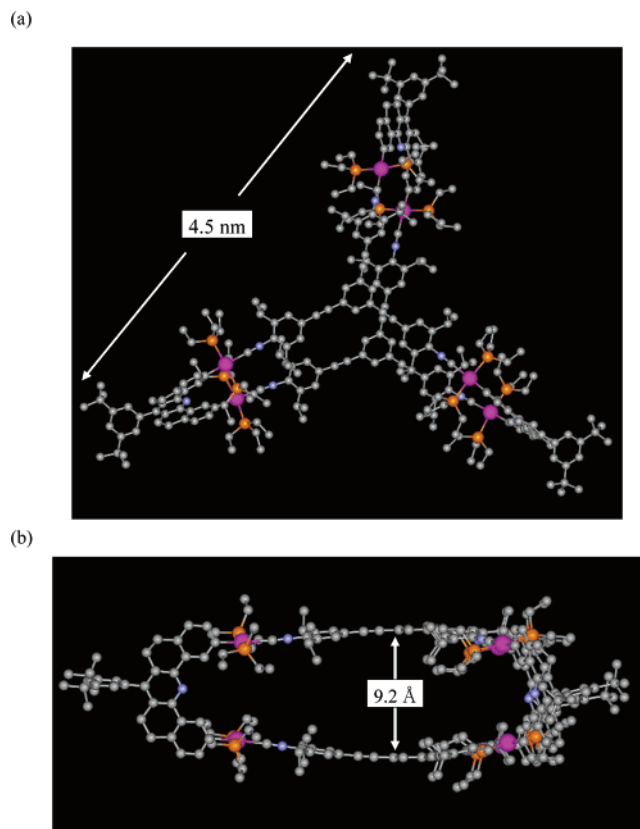


Figure 4. Ab initio calculation of optimized trigonal prism **11**: (a) overall figure; (b) side view for **11**. The molecule seems to have a C_3 symmetry or a modified C_{3h} symmetry. H atoms are omitted for clarity.

the size and shape of the molecule. A force field calculation such as MM2 is often used for this purpose;²³ however, it is inconvenient to handle the molecular charges in such calculations. In other words, it is almost impossible to differentiate the molecular structures with different charges in force field calculations. As the molecule **11** has a molecular charge of +6, we carried out ab initio calculations to obtain reliable structural information. The geometry of **11** was optimized by the calculations at the Hartree–Fock (HF) theory using a suite of Gaussian 98 program.²⁴ A shape consistent effective core potential (ECP) of CRENBS²⁵ was used as a basis set for platinum (Pt), and minimal STO-3G basis sets were used for all the other atoms. The optimized structure shows that the molecule **11** has a center cavity with a diameter of about 9.2 Å and has three arms with arm-to-arm distance of about 4.5 nm as shown in Figure 4.

Conclusion

A novel molecular “clip” **4** was prepared. The molecular clip was found to be an effective one to assemble various bridging ligands. Supramolecular rectangles (**7–9**) was readily prepared via self-assembly through the use of **4**. X-ray crystallography, NMR, and mass spectral data unambigu-

ously established the proposed structure. The molecular clip **4** also self-assembles with tritopic 120° angular bridging ligands to afford trigonal prisms (**10**, **11**). In particular, the use of isocyanide-containing linkers toward a Pt acceptor has potential to expand the range of the directional bonding modes in self-assembly. Work will involve the synthesis of various predesigned ligands and their self-assembly.

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques. THF, toluene, ether, and hexane were distilled from sodium benzophenone. Methylene chloride, CHCl_3 , MeOH, and EtOH were distilled under nitrogen from P_2O_5 . The ^1H , ^{13}C , and ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00, 75.44, and 121.44 MHz, respectively. IR spectra were recorded on a Biorad FTS-165 spectrometer. ESI-MS spectra were recorded on a Micromass QTOF2 mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer. Boron trifluoride ethyl etherate, formic acid, triphosgene, 4,4'-dipyridyl, and isonicotinic acid were purchased from Aldrich Chemical Co. 2,6-Diisopropyl-4-iodoaniline,^{15a} 7-bromo-1-tetralone,²⁶ 3,5-di-*tert*-butylbenzaldehyde,²⁷ 1,4-diethynylbenzene,²⁸ 1,3,5-triethynylbenzene,²⁹ 1,3,5-tris(4-ethynylpyridyl)benzene,³⁰ and $\text{Pt}(\text{PEt}_3)_4$ ³¹ were prepared according to literature methods.

7-Bromo-2-(3,5-di-*tert*-butylbenzylidene)-7-bromo-3,4-dihydro-2*H*-naphthalen-1-one (1). A 250 mL Schlenk flask was charged with 7-bromo-1-tetralone (4.00 g, 17.8 mmol) and 3,5-di-*tert*-butylbenzaldehyde (5.16 g, 23.6 mmol). This was dissolved in warm tetrahydrofuran (10 mL), and to this yellow solution was slowly added a 4 wt % solution of KOH in methanol (80 mL). The reaction was stirred for 36 h at room temperature. The solvent was then removed under reduced pressure, and it was poured into 100 mL of water and extracted with methylene chloride. The organic extract was dried over magnesium sulfate and filtered, and the solvent was removed at reduced pressure. The residue was chromatographed (1:2 benzene–hexane) to afford 5.53 g (73%) as yellow oil. ^1H NMR (CDCl_3): δ 8.25 (s, 1H), 7.93 (s, 1H), 7.57 (d, 1H, $J = 8.1$ Hz), 7.45 (s, 1H), 7.30 (s, 2H), 7.14 (d, 1H, $J = 8.1$ Hz), 3.15 (t, 2H, $J = 6.0$ Hz), 2.91 (t, 2H, $J = 6.0$ Hz), 1.36 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR(CDCl_3): δ 186.8, 151.0, 141.9, 139.1, 136.1, 135.8, 135.2, 134.9, 134.0, 131.1, 124.8, 124.1, 123.4, 123.0, 121.1, 35.0, 31.5, 28.5, 27.1. Anal. Calcd for $\text{C}_{25}\text{H}_{29}\text{BrO}$: C, 70.58; H, 6.87. Found: C, 70.32; H, 6.64.

2,12-Dibromo-[7-(3,5-*tert*-butylphenyl)-5,6,8,9-tetrahydro-dibenzo[*c,h*]acridine] (2,12-dibromo-DTDA) (2). A 500 mL flask was flame dried under a continuous stream of argon. The flask was charged with **1** (3.24 g, 7.62 mmol) and 7-bromo-1-tetralone (1.71 g, 7.62 mmol). These solids were mixed before $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (17.0 mL, 135 mmol) was added to form a brown-colored mixture. The reaction was then slowly heated to 115 °C and was maintained at this temperature for 8 h. This solution was cooled to 0 °C. To this was carefully added an ammonium acetate–ethanol solution (130 mL, 3.00 M) for 45 min. The mixture was refluxed for 24 h.

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During this time, the color changed from red to a pale yellow. After cooling of the mixture to room temperature, the solvent was removed under reduced pressure, 100 mL water was added, and the sample was extracted into methylene chloride. The organic extract was dried over magnesium sulfate and filtered, and the solvent was removed at reduced pressure. The residue was chromatographed (1:10 CH₂Cl₂–hexane) to afford 1.52 g (31.2%) as a white crystal. Mp: 220 °C. ¹H NMR (CDCl₃): δ 8.65 (s, 2H), 7.47 (s, 1H), 7.42 (d, 2H, *J* = 7.8 Hz), 7.08 (d, 2H, *J* = 7.8 Hz), 7.02 (s, 2H), 2.78 (m, 4H), 2.70 (m, 4H), 1.36 (s, 18H). ¹³C{¹H} NMR (CDCl₃): δ 151.1, 149.1, 137.3, 136.7, 136.4, 131.8, 131.3, 129.8, 128.4, 128.1, 123.6, 122.4, 121.1, 35.1, 31.6, 27.7, 25.8. Anal. Calcd for C₃₅H₃₅Br₂N: C, 66.78; H, 5.60. Found: C, 66.36; H, 5.42.

2,12-Bis[*trans*-Pt(PEt₃)₂Br]DTDA (3). A 100 mL Schlenk flask was charged under nitrogen with 2,12-dibromo-DTDA (0.41 g, 0.65 mmol) and Pt(PEt₃)₄ (1.09 g, 1.63 mmol). Freshly distilled toluene (30 mL) was added to the flask under nitrogen by syringe, and the resulting bright red solution was stirred for 60 h at 60 °C. The solvent was then removed in vacuo. The white microcrystalline residue was washed with methanol (3 × 50 mL) and dried in vacuo. Yield: 89%. Mp: 270 °C. ¹H NMR (CDCl₃): δ 8.47 (s, 2H, *J*_{H–Pt} = 65.4 Hz), 7.43 (s, 1H), 7.26 (d, 2H, *J*_{H–Pt} = 68.4 Hz, *J* = 7.8 Hz), 7.06 (s, 2H), 6.76 (d, 2H, *J* = 7.8 Hz), 2.72–2.66 (m, 8H), 1.71 (m, 24H), 1.35 (s, 18H), 1.11 (t, 36H, *J* = 6.9 Hz). ¹³C{¹H} NMR (CDCl₃): δ 151.2, 150.8, 148.2, 147.5, 137.6, 137.3, 136.8, 134.8, 131.8, 128.5, 126.8, 125.4, 124.0, 35.0, 31.6, 28.1, 26.7, 14.4, 8.2. ³¹P{¹H} NMR (CDCl₃): δ 6.04 (*J*_{Pt–P} = 2782 Hz). Anal. Calcd for C₅₉H₉₅Br₂N₄Pt₂: C, 47.49; H, 6.42. Found: C, 47.32; H, 6.34.

2,12-Bis[*trans*-Pt(PEt₃)₂NO₃]DTDA (4). 2,12-Bis[*trans*-Pt(PEt₃)₂Br]DTDA (0.139 g, 0.0093 mmol) and AgNO₃ (0.16 g, 0.93 mmol) in methylene chloride (30 mL) were placed in a Schlenk flask. The reaction was stirred in the dark at room temperature for 24 h. A clear solution with a heavy creamy precipitate was formed; the precipitate was filtered off, and the solvent was removed under a flow of nitrogen. The residue was redissolved in a minimal amount of methylene chloride, and then pentane was carefully added to precipitate the residual AgNO₃. The cloudy solution was filtered, and the product was precipitated by the addition of pentane. The crystals were obtained by layering hexane on the product dissolved in toluene. Yield: 98%. Mp: 286 °C. ¹H NMR (CDCl₃): δ 8.40 (s, 2H, *J*_{H–Pt} = 67.2 Hz), 7.43 (s, 1H), 7.23 (d, 2H, *J* = 7.8 Hz), 7.04 (s, 2H), 6.75 (d, 2H, *J* = 7.8 Hz), 2.66 (br, 8H), 1.58 (m, 24H), 1.34 (s, 18H), 1.15 (t, 36H, *J* = 7.8 Hz). ¹³C{¹H} NMR (CDCl₃): δ 151.7, 150.8, 148.3, 137.2, 134.8, 132.3, 128.7, 127.5, 125.9, 123.9, 123.4, 122.6, 121.2, 35.0, 31.6, 27.3, 26.7, 13.3, 7.8. ³¹P{¹H} NMR (CDCl₃): δ 12.2 (*J*_{Pt–P} = 2894 Hz). Anal. Calcd for C₅₉H₉₅N₃O₆P₄Pt₂: C, 48.65; H, 6.57. Found: C, 48.87; H, 6.72.

1,4-Bis[2-(4-amino-3,5-diisopropylphenyl)ethynyl]benzene. To a mixture of 1,4-diethynylbenzene (0.50 g, 4.03 mmol) and 4-iodo-2,6-diisopropylaniline (3.06 g, 10.09 mmol) in Et₃N (20 mL) and THF (20 mL) were added Pd(PPh₃)₄ (0.28 g, 0.24 mmol) and CuI (0.05 g, 0.24 mmol). The reaction mixture was stirred at 60 °C for 20 h under nitrogen. Then the solvent was removed under reduced pressure. The residue was extracted with diethyl ether and purified by chromatography on silica gel using CH₂Cl₂–hexane (1:1, v/v) as the eluent to afford orange powder. Yield: 86%. Mp: 257 °C. ¹H NMR (CDCl₃): δ 7.56 (s, 4H), 7.31 (s, 4H), 3.96 (br, 4H), 2.91 (heptet, 4H, *J* = 6.60 Hz), 1.33 (d, 24H, *J* = 6.60 Hz). ¹³C{¹H} NMR (CDCl₃): δ 141.2, 132.1, 131.2, 126.6, 123.1, 111.9, 93.0, 86.9, 27.8, 22.2. Anal. Calcd for C₃₄H₄₀N₂: C, 85.67; H, 8.46. Found: C, 85.32; H, 8.28.

1,4-Bis[2-(4-formamido-3,5-diisopropylphenyl)ethynyl]benzene. A mixture of acetic anhydride (3.0 mL) and formic acid (3.0 mL) was heated for 2 h at 50–60 °C with stirring. The solution was cooled to room temperature. 1,4-Bis[2-(4-amino-3,5-diisopropylphenyl)ethynyl]benzene (0.46 g, 0.66 mmol) dissolved in ether (20 mL) was slowly added to this solution. The resulting solution was stirred at room temperature for 24 h and neutralized to pH 7 with 10% aqueous sodium carbonate. The organic phase was dried over magnesium sulfate. After filtration and evaporation of the solvent, the product was obtained as a white solid which can be recrystallized from diethyl ether. Yield: 70%. Mp: 213 °C. ¹H NMR (CDCl₃): δ 8.49 (s, 2H), 8.03 (d, 2H, *J* = 11.7 Hz), 7.54 (s, 2H), 7.37 (s, 2H), 7.26 (s, 2H), 6.88 (d, 2H, *J* = 11.7 Hz), 3.20 (heptet, 4H, *J* = 6.9 Hz), 1.23 (d, 24H, *J* = 6.9 Hz). ¹³C{¹H} NMR (CDCl₃): δ 176.7, 146.6, 131.8, 130.3, 127.8, 127.2, 123.5, 91.1, 89.3, 27.8, 23.6. Anal. Calcd for C₃₆H₄₀N₂O₂: C, 81.17; H, 7.57. Found: C, 80.88; H, 7.36.

1,4-Bis[2-(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene (5). To a stirred mixture of 1,4-bis[2-(4-formamido-3,5-diisopropylphenyl)ethynyl]benzene (0.53 g, 1.00 mmol) and Et₃N (5.0 mL) in THF (15 mL) was added a solution of triphosgene (0.35 g, 1.20 mmol) in THF (15 mL) at –78 °C. The mixture was allowed to warm slowly to room temperature and stirred for 12 h. The mixture was evaporated under reduced pressure to remove THF and Et₃N. The reaction mixture was extracted with CHCl₃. The compound **5** was purified by chromatography on silica gel using *n*-hexane–methylene chloride (1:1, v/v) as the eluent to afford a white crystalline solid. Yield: 78%. Mp: 229 °C. ¹H NMR (CDCl₃): δ 7.54 (s, 4H), 7.33 (s, 4H), 3.38 (heptet, 4H, *J* = 6.9 Hz), 1.30 (d, 24H, *J* = 6.9 Hz). ¹³C{¹H} NMR (CDCl₃): δ 170.3, 145.4, 132.0, 127.2, 126.5, 124.1, 123.1, 91.0, 90.2, 29.4, 22.5. IR (KBr pellet, cm^{–1}): 2110 (ν(C≡N)). Anal. Calcd for C₃₆H₃₆N₂: C, 87.05; H, 7.31. Found: C, 86.86; H, 7.18.

1,3,5-Tris[(4-amino-3,5-diisopropylphenyl)ethynyl]benzene. This compound was prepared using the same procedure as that described for 1,4-bis[2-(4-amino-3,5-diisopropylphenyl)ethynyl]benzene. Yield: 72%. Mp: 165 °C. ¹H NMR (CDCl₃): δ 7.58 (s, 3H), 7.22 (s, 6H), 3.92 (br, 6H, NH₂), 2.88 (h, 6H, *J* = 6.6 Hz, CH), 1.29 (d, 36H, *J* = 6.6 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 141.8, 132.3, 130.6, 124.6, 117.4, 112.2, 93.8, 86.0, 28.3, 22.5. Anal. Calcd for C₄₈H₅₇N₃: C, 85.28; H, 8.50. Found: C, 85.15; H, 8.37.

1,3,5-Tris[(4-formamido-3,5-diisopropylphenyl)ethynyl]benzene. This compound was prepared using the same procedure as that described for 1,4-bis[2-(4-formamido-3,5-diisopropylphenyl)ethynyl]benzene. Yield: 85%. Mp: 208 °C. ¹H NMR (CDCl₃): δ 8.49 (s, 3H, CHO), 7.71 (s, 3H), 7.31 (s, 6H), 6.74 (s, 3H, NH), 3.21 (h, 6H, *J* = 6.6 Hz, CH), 1.24 (d, 36H, *J* = 6.6 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 163.8, 147.1, 130.5, 129.2, 127.8, 124.2, 123.4, 90.4, 88.3, 28.6, 23.4. IR (KBr pellet: cm^{–1}): 1684 (ν(CO)). Anal. Calcd for C₅₁H₅₇N₃O₃: C, 80.60; H, 7.56. Found: C, 80.38; H, 7.45.

1,3,5-Tris[(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene (6). Compound **6** was prepared using the same procedure as that described for **5**. Yield: 72%. Mp: 236 °C. ¹H NMR (CDCl₃): δ 7.71 (s, 3H), 7.32 (s, 6H), 3.36 (h, 6H, *J* = 6.9 Hz, CH), 1.31 (d, 36H, *J* = 6.9 Hz, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 170.3, 145.5, 130.8, 123.9, 123.0, 118.3, 116.8, 90.3, 89.2, 28.2, 22.5. IR (KBr pellet: cm^{–1}): 2109 (ν(C≡N)). FAB-MS: *m/z* 705 [M⁺]. Anal. Calcd for C₅₁H₅₁N₃: C, 86.77; H, 7.28. Found: C, 86.33; H, 7.14.

General Procedure for the Preparation of Supramolecules 7–11. A 50 mL flask was charged with 2,12-bis[*trans*-Pt(PEt₃)₂NO₃]DTDA (0.10 mg, 0.068 mmol) and 4,4'-dipyridyl (0.01 mg,

0.068 mmol) (1:1 molar ratio). A 12 mL volume of an acetone–H₂O mixture (2:1) was added to the flask, and the solution was then heated overnight at 50–55 °C with stirring. The pure product **7** was obtained by recrystallization with CH₂Cl₂–hexane as a colorless crystalline solid in 98% yield.

cyclo-Bis[(2,12-bis(trans-Pt(PEt₃)₂DTDA))(4,4'-dipyridyl)]-(NO₃)₄ (7**).** Mp: 301 °C. ¹H NMR (CDCl₃): δ 9.14 (d, 4H, *J* = 5.7 Hz), 8.82 (d, 4H, *J* = 5.4 Hz), 8.74 (d, 4H, *J* = 5.4 Hz), 8.57 (d, 4H, *J* = 5.7 Hz), 8.51 (s, 4H), 7.44 (s, 2H), 7.29 (d, 4H, *J* = 7.2 Hz), 7.04 (s, 4H), 6.91 (d, 4H, *J* = 7.2 Hz), 2.69 (br, 16H), 1.40 (m, 48H), 1.34 (s, 36H), 1.18 (t, 72H, *J* = 7.5 Hz). ¹³C{¹H} NMR (CDCl₃): δ 154.0, 152.1, 151.0, 150.7, 148.8, 145.9, 137.3, 136.7, 135.8, 133.8, 131.9, 129.4, 128.8, 127.1, 125.9, 121.6, 35.0, 31.8, 28.1, 26.5, 12.9, 8.0. ³¹P{¹H} NMR (CDCl₃): δ 7.1 (*J*_{Pt–P} = 2594 Hz). ESI-MS (*m/z*): 1549.5, [M – 2NO₃]²⁺; 1012.3, [M – 3NO₃]³⁺; 743.7, [M – 4NO₃]⁴⁺. Anal. Calcd for C₁₃₈H₂₀₆N₁₀O₁₂P₈Pt₄: C, 51.39; H, 6.44. Found: C, 51.02; H, 6.28.

cyclo-Bis[(2,12-bis(trans-Pt(PEt₃)₂DTDA)[1,4-bis[2-(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene]](NO₃)₄ (8**).** Mp: 191 °C. ¹H NMR (CDCl₃): δ 8.25 (s, 4H), 7.58 (s, 2H), 7.50 (d, 4H, *J* = 7.2 Hz), 7.44 (d, 4H, *J* = 7.6 Hz), 7.38 (s, 8H), 7.22 (s, 4H), 7.06 (d, 4H, *J* = 7.2 Hz), 7.02 (d, 4H, *J* = 7.6 Hz), 3.22 (septet, 8H, *J* = 6.9 Hz), 2.70 (br, 16H), 1.87 (br, 48H), 1.34 (s, 36H), 1.30 (d, 48H, *J* = 6.9 Hz), 1.19 (t, 72H, *J* = 7.5 Hz). ¹³C{¹H} NMR (CDCl₃): δ 166.3, 150.9, 150.5, 148.8, 147.5, 146.7, 145.3, 137.0, 136.4, 134.9, 132.2, 132.0, 131.8, 129.6, 128.0, 127.5, 126.4, 122.9, 122.7, 92.6, 92.5, 90.3, 31.5, 30.7, 29.7, 23.3, 15.7, 15.5, 8.6, 8.2. ³¹P{¹H} NMR (CDCl₃): δ 9.1 (*J*_{Pt–P} = 2439 Hz). IR (KBr pellet, cm^{–1}): 2148 (ν(C≡N)). ESI-MS (*m/z*): 1892.1, [M – 2NO₃]²⁺; 1240.4, [M – 3NO₃]³⁺; 914.4, [M – 4NO₃]⁴⁺. Anal. Calcd for C₁₉₀H₂₆₂N₁₀O₁₂P₈Pt₄: C, 58.42; H, 6.76. Found: C, 58.04; H, 6.58.

cyclo-Bis[(2,12-bis(trans-Pt(PEt₃)₂DTDA)(isonicotinic acid)₂](NO₃)₄ (9**).** Mp: 311 °C. ¹H NMR (CDCl₃): δ 12.70 (br, 4H, COOH), 9.24 (d, 4H, *J* = 5.1 Hz), 8.80 (d, 4H, *J* = 5.4 Hz), 8.51 (s, 4H), 8.49 (d, 4H, *J* = 5.1 Hz), 8.22 (d, 4H, *J* = 5.4 Hz), 7.45 (s, 2H), 7.32 (d, 4H, *J* = 7.5 Hz), 7.06 (s, 4H), 6.91 (d, 4H, *J* = 7.5 Hz), 2.70 (br, 16H), 1.65 (br, 48H), 1.36 (s, 36H), 1.22 (t, 72H, *J* = 7.5 Hz). ¹³C{¹H} NMR (CDCl₃): δ 169.2, 164.9, 152.8, 151.0, 150.7, 147.7, 142.6, 137.3, 136.6, 135.4, 133.7, 132.2, 129.4, 128.7, 126.6, 124.8, 122.2, 35.0, 31.6, 30.3, 12.9, 9.3, 8.3. ³¹P{¹H} NMR (CDCl₃): δ 6.8 (*J*_{Pt–P} = 2710 Hz). ESI-MS (*m/z*): 1640.7, [M – NO₃]⁺; 789.3, [M – 2NO₃]²⁺. Anal. Calcd for C₇₁H₁₀₅N₅O₁₀P₄Pt₂: C, 50.08; H, 6.22. Found: C, 49.74; H, 6.08.

Bicyclo{tris[2,12-bis(trans-Pt(PEt₃)₂DTDA)]bis[1,3,5-tris(4-ethynylpyridyl)benzene]}(NO₃)₆ (10**).** Mp: 207 °C. ¹H NMR (CDCl₃): δ 9.04 (d, 6H, *J* = 5.4 Hz), 8.67 (d, 6H, *J* = 5.7 Hz), 8.44 (s, 6H), 8.04 (d, 6H, *J* = 5.4 Hz), 7.75 (s, 6H), 7.72 (d, 6H, *J* = 5.7 Hz), 7.44 (s, 3H), 7.25 (d, 6H, *J* = 7.8 Hz), 7.05 (s, 6H), 6.90 (d, 6H, *J* = 7.8 Hz), 2.69 (m, 24H), 1.47 (m, 72H), 1.35 (s,

54H), 1.21 (m, 108H). ¹³C{¹H} NMR (CDCl₃): δ 150.9, 150.7, 150.0, 148.6, 137.1, 136.6, 135.5, 134.4, 133.8, 132.1, 131.4, 130.6, 129.3, 128.3, 126.3, 125.1, 123.4, 122.9, 95.9, 87.2, 35.0, 31.6, 29.1, 12.9, 8.2, 7.8. ³¹P{¹H} NMR (CDCl₃): δ 7.1 (*J*_{Pt–P} = 2697 Hz). ESI-MS (*m/z*): 1649.2, [M – 3NO₃]³⁺; 1184.4, [M – 4NO₃]⁴⁺; 964.2, [M – 5NO₃]⁵⁺. Anal. Calcd for C₂₃₁H₃₁₅N₁₅O₁₈P₁₂Pt₆: C, 54.06; H, 6.19. Found: C, 53.78; H, 6.04.

Bicyclo{tris[2,12-bis(trans-Pt(PEt₃)₂DTDA)]bis[1,3,5-tris[2-(4-isocyano-3,5-diisopropylphenyl)ethynyl]benzene]}(NO₃)₆ (11**).** Mp: 199 °C. ¹H NMR (CDCl₃): δ 8.27 (s, 6H), 7.79 (s, 3H), 7.74 (s, 6H), 7.43 (d, 6H, *J* = 7.8 Hz), 7.39 (s, 6H), 7.07 (s, 12H), 7.05 (d, 6H, *J* = 7.8 Hz), 3.19 (septet, 12H, *J* = 6.6 Hz), 2.71 (m, 24H), 1.83 (br, 72H), 1.35 (s, 54H), 1.30 (d, 72H, *J* = 6.6 Hz), 1.19 (m, 108H). ¹³C{¹H} NMR (CDCl₃): δ 165.8, 156.4, 150.9, 150.4, 148.9, 147.5, 145.3, 142.6, 136.9, 136.4, 135.0, 132.4, 131.6, 129.7, 128.1, 127.6, 126.2, 123.5, 122.7, 121.8, 91.0, 89.6, 35.1, 31.6, 30.9, 29.8, 29.5, 23.3, 15.7, 8.4. ³¹P{¹H} NMR (CDCl₃): δ 9.03 (*J*_{Pt–P} = 2431 Hz). IR (KBr Pellet; cm^{–1}): 2146 (ν(C≡N)). ESI-MS (*m/z*): 1865.1, [M – 3NO₃]³⁺; 1382.8, [M – 4NO₃]⁴⁺; 1094.0, [M – 5NO₃]⁵⁺; 901.3, [M – 6NO₃]⁶⁺. Anal. Calcd for C₂₇₉H₃₈₇N₁₅O₁₈P₁₂Pt₆: C, 57.96; H, 6.75. Found: C, 57.64; H, 6.62.

X-ray Crystallography. Suitable crystals of **4** and **7** were grown by toluene–hexane and CH₂Cl₂–hexane, respectively. All X-ray intensity data for compounds **4** and **7** were collected on a Bruker SMART 1000 CCD diffractometer³² with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). The collected data were processed for integration; an empirical absorption correction was made on the basis of the symmetry-equivalent reflection intensities (SAD-ABS).³³ Structures were solved by direct methods and refined by full-matrix least-squares procedures against *F*² using SHELXL97.³⁴ All non-hydrogen atoms in compounds **4** and **7** were refined anisotropically. All hydrogen atoms were included in the calculated positions.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinates and *U*(eq) values, bond distances and angles, anisotropic displacement parameters, and torsion angles and crystallographic data in CIF format for **4** and **7** (CCDC reference nos. 278206 and 278207). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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