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Pyrazine-Based Donor Tectons: Synthesis, Self-Assembly and Characterization

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Abstract

Two new supramolecular building blocks derived from pyrazine are introduced. These molecules, having pendant pyridine units covalently linked to central pyrazine ring, are structurally rigid with pre-defined bite angles. Therefore they can act as donor tectons in design of supramolecular hexagons using coordination driven self-assembly protocol. Multinuclear NMR (including ^{1}H DOSY) and mass spectrometry have been utilized to confirm the purity and stoichiometry of these self assembled hexagonal ensembles. PM6 molecular modeling studies corroborate their hexagonal shape and nanoscalar dimensions.

Introduction

Supramolecular chemistry utilizes non-covalent interactions for design of complex architectures.[1] These complex frameworks often utilize several multidentate ligands of two or more types as that bind with each other using non-covalent interactions. Coordination driven self assembly of finite supramolecular architectures has emerged as a popular field of research in modern supramolecular chemistry.[1] Among others, one important feature of this synthetic protocol is the yield of finite two and three dimensional frameworks in a single step reaction.[2] This methodology however necessitates design of new building blocks (tectons) for construction of supramolecular architectures.[3,1a,b,k,l] In this context, two types of supramolecular building blocks are utilized, namely donor and acceptor ligands.[4,5] While Pd(II) and Pt(II) based inorganic or organometallic complexes are most popular acceptor tectons, donor tectons are predominantly organic molecules that contain two or more pyridine units as pendant functional groups.[5,6] In the context of two dimensional metallamacrocycles, polygonal frameworks of various shapes and sizes have been designed over the past two decades.[7,1a,b] Interestingly, there are less literature reports of higher polygons (pentagons, hexagons, etc.) than smaller ones (such as molecular rhomboids, triangles, rectangles and squares).[8] This is because, design of higher polygons generally requires self-assembly of a relatively larger number of donor and acceptor building blocks in comparison to the self-assembly event of smaller polygonal macrocycles. Therefore synthesis of higher polygons (pentagons, hexagons, etc.) is more complex and challenging than relatively smaller polygons such as square, rhomboid or triangles.

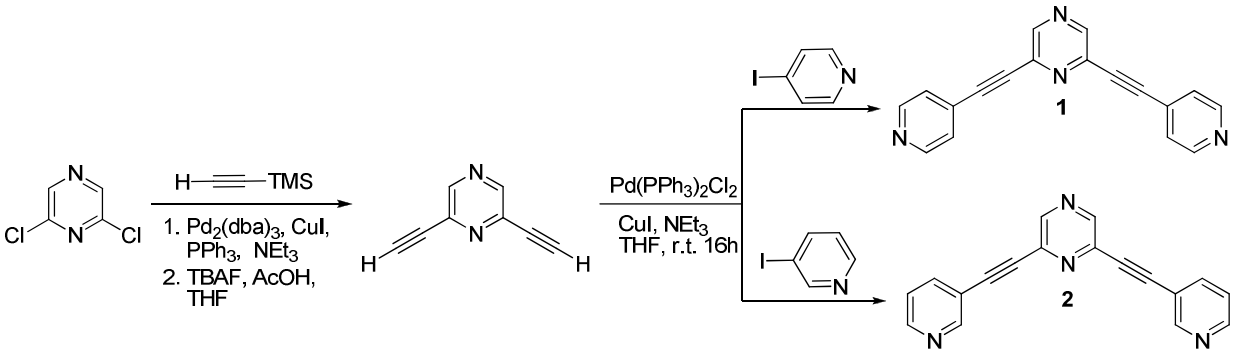
More recently, we have reported in literature a new acceptor tecton derived from pyrazine.[9] This pyrazine based ditopic organometallic complex contains platinum ethynyl motifs. Continuing our research interest to enrich the existing literature with new tectons and their application in self assembly of supramolecular frameworks, herein we describe synthesis and characterization of two new ditopic pyrazine based donor tectons that contain two pyridyl rings covalently connected to a central pyrazine ring. These donor tectons are interesting because they contain several N centers (in pyridine or pyrazine rings) that can potentially coordinate with metal centers. Therefore, these ligands qualify to act as donor building blocks in the self assembly of finite metallamacrocycles. To illustrate this point, synthesis and self assembly of two new

platinum(II)-based molecular polygons is reported herein. These metallamacrocycles were characterized by multinuclear NMR spectroscopy including ^{1}H DOSY, ESI-TOF mass spectrometry and elemental analyses techniques. Further insight into the shape and size of these hexagonal macrocycles was obtained by employing molecular simulation using PM6 semiempirical molecular orbital method. Our studies suggest that the resulting metallamacrocycles are in nanoscalar dimensions.

Result and Discussion

Synthesis and characterization of the pyrazine based organic donor linker 1 and 2.

Using 2,6-dichloropyrazine as a synthon, synthesis of two new pyrazine based donor linkers (**1** and **2**) were achieved in two steps (Scheme 1). Sonogashira cross coupling reaction of 2,6-dichloropyrazine with (trimethylsilyl)acetylene, followed by deprotection of trimethylsilyl group yielded 2,6-diethynylpyrazine. Subsequent coupling of 4- or 3-iodopyridine with 2,6-diethynylpyrazine in presence of Pd(0) catalyst and CuI co-catalyst resulted in the formation of desired organic linkers **1** and **2** respectively in reasonably high yields (> 80%). Both ligands **1** and **2**, obtained as white solids, are stable in air/moisture and have high solubility in common organic solvents. These molecules were fully characterized by FT-IR and NMR (^{1}H and ^{13}C) spectroscopy, mass spectrometry and elemental analyses. In FT-IR spectra of **1** and **2**, the presence of a strong band at 2111 cm^{-1} and 2217 cm^{-1} (ν C≡C str.) respectively, indicates the presence of ethynyl moiety in final products. In ^{1}H NMR spectra of **1** and **2** (supporting information S2 and S3), presence of sharp singlet at 8.75 ppm and 8.86 ppm respectively, were assigned to the aromatic protons of the pyrazine ring present in these molecules. In the ^{1}H NMR spectrum of **1**, the two sets of signals in the range of 8.69 to 8.68 ppm and 7.48 to 7.47 ppm are attributed to the pyridyl protons in the product. In case of **2**, as expected additional four sets of signal were observed in the ^{1}H NMR due to the four different kind of chemically inequivalent protons and this suggests the formation of **2**. The ^{13}C{^{1}H} NMR spectrum of both **1** and **2** exhibited all the characteristic peaks corresponds to pyrazine, pyridine and ethynyl units in expected region (supporting information S2 and S3). In addition, the molecular structure of **1** was further confirmed unambiguously by single crystal X-ray analysis.



Scheme 1. Synthesis of pyrazine based organic donor linkers **1** and **2**.

X-ray crystallography analysis of ligand 1.

Single crystals of **1** was obtained by slow vapor diffusion of acetone into a chloroform solution of ligand **1** at ambient temperature. Compound **1** was crystallized in a monoclinic system with

C*2*/c space group. The asymmetric unit of compound **1** is shown in Figure 1. X-Ray crystallographic analysis of ligand **1** indicated presence of various C─H···N short interactions in its crystal lattice (supporting information S17).

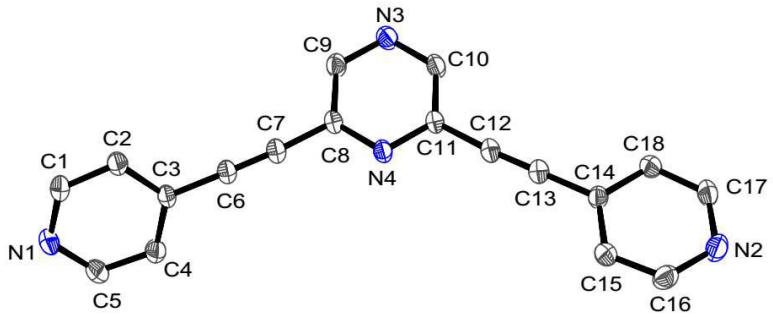
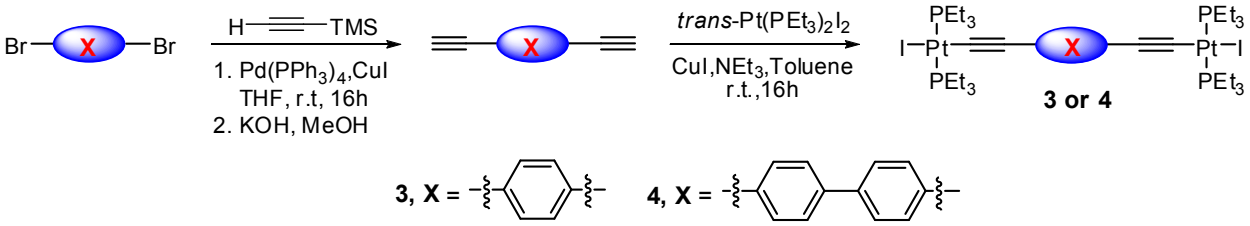


Figure 1: ORTEP diagram for compound **1** with 50% thermal ellipsoid probability.

Improved synthesis and characterization of the linear organometallic acceptor 3 and 4. There are few reports in the literature wherein Pd(II)/Pt(II) containing symmetrical and ditopic ligands have been prepared and subsequently utilized as linear (180°) acceptor tectons in the self assembly of supramolecular polygonal ensembles. Ligands **3** and **4** are examples of such kind of linear diplatinum ditopic acceptor tectons, first reported by Mukherjee and co-workers.[4b,6g] Using anhydrous diethylamine as base, stirring the reaction mixture for 36 hours, and purification of crude product using column chromatography, compounds **3** and **4** were obtained in 36 and 42 % yields. In this context, we report herein improved synthesis of **3** and **4**, wherein our synthetic protocol requires lesser reaction time. Moreover the yields of the reaction are considerably higher than that reported previously. In the improved synthesis being reported herein, *trans*-$PtI_2(PEt_3)_2$ was reacted with the respective terminal dialkynes in presence of CuI (catalyst), and triethylamine (base) in toluene (solvent) at room temperature for 16h (Scheme 2). The yield of reaction in either case was above 60%. The binuclear linear organometallic acceptors (**3** and **4**) were characterized by ^{1}H , ^{31}P NMR and ^{13}C NMR spectroscopy (supporting information S4, S5 and S6). The diplatinum acceptors (**3** and **4**), in their respective ^{31}P NMR spectrum, exhibited a singlet at δ = 8.41 ppm and 8.50 ppm with accompanying ^{195}Pt satellites ($^{1}J_{PPt}$ = 1164 Hz and $^{1}J_{PPt}$ = 1163 Hz). The ^{1}H NMR spectrum of compound (**3**) exhibited a sharp singlet at δ = 7.14 ppm corresponding to the phenyl protons in the aromatic region, in addition to the other expected signals due to the ethyl group of PEt_3 group. As expected, in the ^{1}H NMR spectrum of compound **4**, two sets of signal in the range of 7.46 to 7.31ppm were observed and these correspond to the phenyl protons in the aromatic region.



Scheme 2. Synthesis of organometallic acceptor linkers **3** and **4**.

Design strategies towards self assembly of supramolecular hexagons.

As per the "directional bonding approach", two strategies are reported in literature for the synthesis of convex hexagonal discrete supramolecular ensembles (Chart 1). In the first method, six ditopic angular tectons (bearing 120° angles between the two binding sites) react with six complimentary linear tecton (bearing 180° angles between the two binding sites) to yield [6 + 6] molecular hexagons (Chart 1a).[10] In the second method, three donor ditopic 120° units react with three acceptor ditopic 120° units to yield [3 + 3] molecular hexagons (Chart 1b).[11] Herein, we propose a third strategy that also yields molecular hexagons albeit involving lesser number of self-assembling units. Unlike the previously reported self assembled molecular hexagons where the individual tectons occupy a single vertex or edge, in the third strategy, the tecton is designed in such a way so that it simultaneously occupies two vertices defining the polygon upon self assembly (Chart 1c).[12] The hexagon depicted in Chart 1c may be described as a [2+2] molecular hexagon. In case of the "hexameric" and "trimeric" hexagonal frameworks (1a and 1b in Chart 1), the resulting polygons are regular hexagons that are equiangular having equilateral edges. However, the "dimeric" hexagon (Chart 1c) is isogonal (equal angles) but it may not be equilateral. Ligand **2** is an example of such a ditopic donor tecton that upon self assembly with an appropriate complimentary linear (180°) acceptor tecton would yield a dimeric ensemble that is anticipated to have a irregular hexagonal shape.

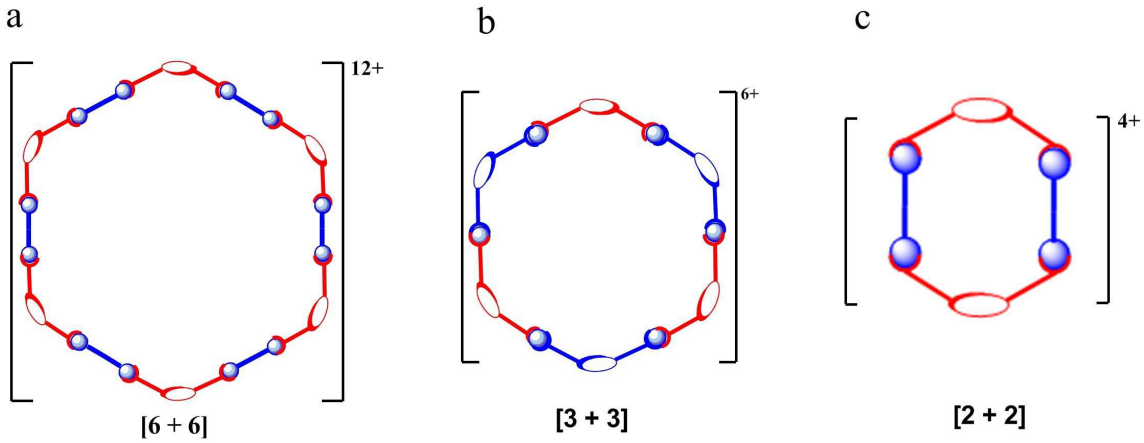
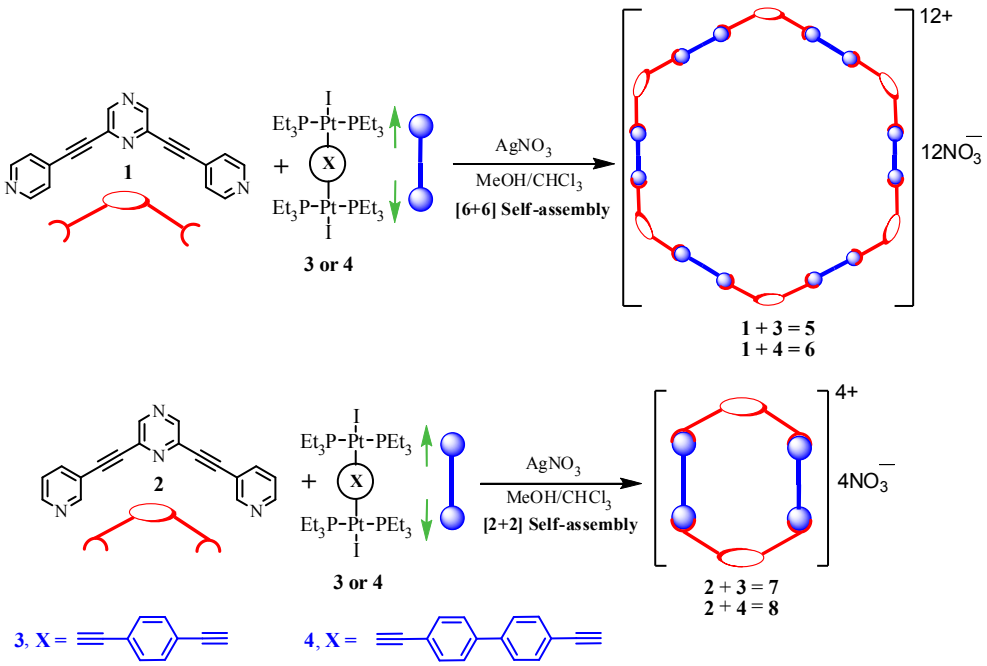


Chart 1. Schematic representation of (a) [6 + 6] (b) [3 + 3] and (c) [2 + 2] hexagon.

Application of 1 and 2 as tectons in self assembly of supramolecular hexagons.

To illustrate this point, self assembly and characterization of four cationic hexagons employing two different synthetic strategies have been described herein (Scheme 3). **1** and **2** are ditopic donor tectons since these have two pendant pyridine moieties. In ligand **1**, the two pyridyl groups are oriented in such a manner so that this molecule has 120° directionality. On the other hand, in ligand **2** the two pyridyl donor sites are oriented such that the resulting coordination vectors are parallel with respect to each other and pointing in the same direction. Thus **1** is an angular donor tecton while **2** can be described as a donor "molecular clip". According to the "directional-bonding" approach, it is anticipated that the self assembly of **1** with suitable linear ditopic acceptor linker in an equimolar stoichiometric ratio will yield a [6+6] hexagonal metallamacrocycle, whereas in case of linker **2,** a similar reaction with a 180° linear ditopic donor tecton would result in the self assembly of a [2+2] discrete ensemble also having a hexagonal shape.



Scheme 3. Self assembly of [**6** + **6**] macrocycles (**5** and **6**) and [**2** + **2**] macrocycles (**7** and **8**) using the pyrazine based organic donor linkers (**1** and **2**) and organometallic Pt^{II}_2-linear acceptor tectons (**3** and **4**).

The 120º donor linker **1** was treated separately with two different linear Pt^{II}_2 organoplatinum acceptor complexes **3** and **4**. Iodide units (attached to the platinum center) of acceptor complexes (**3** and **4**) were abstracted via salt metathesis reaction with 2 equiv. silver nitrate (in chloroform) and subsequently reacted with methanolic solution of donor linker **1** in 1:1 stoichiometric ratio. This resulted into the self assembly of corresponding macrocycles **5** and **6** in high yields. Solubility tests revealed that these self assembled products had high solubility in green solvents like methanol and ethanol but poor solubility in halogenated solvents such as chloroform and

dichloromethane. **5** and **6** were completely characterized by multinuclear NMR spectroscopy, ESI-MS spectrometry and elemental analyses. The $^{31}P\{^{1}H\}$ NMR spectra of these products (**5** and **6**) exhibited sharp singlet [15.57 ppm and 15.61 ppm] along with an accompanying pair of platinum satellites [($^{1}J_{PPt}$ = 1157 Hz and $^{1}J_{PPt}$ = 1160 Hz]. This clearly suggested the formation of a highly symmetrical architecture in each case, wherein all phosphorous nuclei are chemically equivalent in the product. Additionally, a significant decrease in the magnitude of coupling constant of concomitant Pt-satellites in the product (**5** and **6**) relative to the precursor organoplatinum complexes (**3** and **4**) was indicative of new metal-ligand coordination at platinum centers. Similarly, the ^{1}H NMR spectra of **5** and **6** also suggested the incorporation of both **1** and **3/4** in the respective final products. In the ^{1}H NMR spectrum of **5** (Figure 2), the sharp singlet at 8.88 ppm is due to the aromatic protons of pyrazine, whereas the two sets of signal at 8.83 to 8.79 ppm and 7.83 ppm to 7.82 ppm correspond to the pyridyl protons. The aromatic proton of Pt^{II}_2 acceptor unit appears as sharp singlet at 7.08 ppm. The peaks in the range 1.08 to 1.81 ppm are due to the PEt_3 groups attached to the Pt(II)-centers.

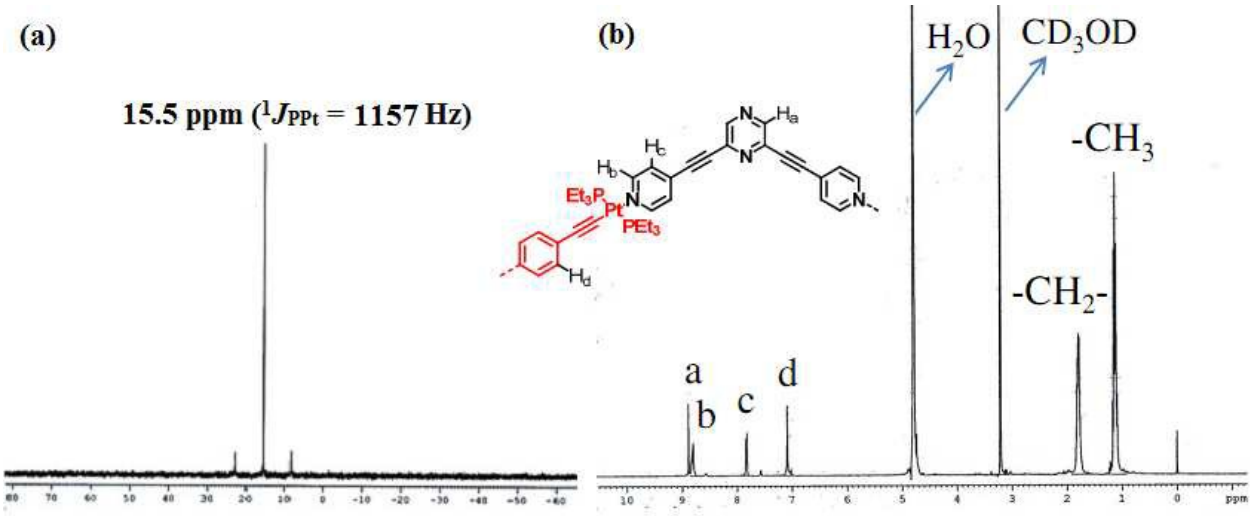


Figure 2. (a) $^{31}P\{^{1}H\}$ NMR and (b) ^{1}H NMR spectra of macrocycle **5** recorded in CD_3OD.

Similarly in case of **6**, all proton signals are assigned precisely. In both cases (**5** and **6**), the integration of peaks due to the pyrazine donor unit (**1**) and Pt^{II}_2 acceptor units suggested their self assembly in 1:1 stoichiometric ratio. Therefore, multinuclear NMR (^{1}H, ^{13}C and ^{31}P) spectra of **5** and **6** (supporting information S7, S8 and S9) hinted at the formation of discrete supramolecular assemblies. Furthermore, the purity of both products (**5** and **6**) was checked by ^{1}H DOSY NMR spectroscopy, wherein a single trace in the DOSY NMR (supporting information S13), ratified the formation of a single product and simultaneously disapproves the possibility of presence of other macrocycles or oligomers as byproduct. The mass spectrometric analysis (ESI-TOF-MS) of **5** and **6** also confirmed that reaction of pyrazine donor linker **2** and the Pt^{II}_2 acceptor units (**3** or **4**) indeed resulted in the self assembly of desired [6+6] molecular ensembles over other oligomeric/polymeric products (supporting information S15). The ESI-TOF-MS spectrum of **5** showed signals due the consecutive loss of nitrate counter anions from expected [6+6] macrocycle at m/z = 2026.59 [**5**-4NO_3]$^{4+}$, 1330.40 [**5**-6NO_3]$^{6+}$, 982.30 [**5**-8NO_3]$^{8+}$, 866.27 [**5**-9NO_3]$^{9+}$, 773.44 [**5**-10NO_3]$^{10+}$ and 634.20 [**5**-12NO_3]$^{12+}$. Similarly, in case of **6**, the observed charge states at 2140.64 [**6**-4NO_3]$^{4+}$, 1406.43 [**6**-6NO_3]$^{6+}$, 1196.65 [**6**-7NO_3]$^{7+}$, 1039.32 [**6**-

$8NO_3]^{8+}$, 916.95 [**6**-$9NO_3]^{9+}$, 819.06 [**6**-$10NO_3]^{10+}$, 738.96 [**6**-$11NO_3]^{11+}$ and 672.22 [**6**-$12NO_3]^{12+}$ in ESI-TOF-MS spectrum confirms the formation of [6+6] macrocyclic architecture. Both the linkers (**1** and **2**) contain a pyrazine moiety in the core and are connected with two peripheral pyridine motifs. However, unlike the former (**1**), in case of the latter (**2**) the 0º bite angle between two nitrogen donor sites of pyridine moiety renders it as a "clip" donor tecton. The self assembly of linker **2** with linear Pt^{II}_2 ditopic acceptor complexes (**3** and **4**) proceeds in a similar manner as described for linker **1**, with the formation of corresponding self assembled products (**7** and **8**). The ^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra of assemblies **7** and **8** (supporting information S10, S11 and S12) suggested the incorporation of both the molecular subunits (pyrazine based organic donor **2** and Pt^{II}_2 acceptor unit: **3** or **4**). The formation of highly symmetrical products was also evident from the sharp ^{31}P singlet at 15.53 ppm and 15.56 ppm with concomitant platinum satellites ($^1J_{PPt}$ = 1156 Hz and $^1J_{PPt}$ = 1159 Hz) for **7** and **8** respectively. Moreover, ^1H DOSY NMR spectra of **7** and **8** also supported the formation of single species in these self assembly reactions (supporting information S14). These self assembled products (**7** and **8**) were also analyzed using ESI-TOF-MS to identify the number of each unit (donor/acceptor) present (supporting information S16). The ESI-TOF-MS analysis of **7** confirmed the formation of a self assembled product with M_2L_2 stoichiometry [M = Pt^{II}_2 acceptors **3** or **4**, L = linker **2**] with the appearance of charge state at m/z = 2722.84 [**7**-$NO_3]^+$, 1330.42 [**7**-$2NO_3]^{2+}$, 866.28 [**7**-$3NO_3]^{3+}$ and 634.21 [**7**-$4NO_3]^{4+}$ (Figure 3 and supporting information S16). Similarly for **8**, mass signals corresponding to [**8**-$2NO_3]^{2+}$ at m/z = 1406.43, [**8**-$3NO_3]^{3+}$ at m/z = 916.95 and [**8**-$4NO_3]^{4+}$ at m/z = 672.22 clearly suggests the self assembly of a [2+2] macrocyclic ensembles (supporting information S16). The peaks corresponding to species [**6**-$11NO_3]^{11+}$, [**7**-$NO_3]^+$, [**7**-$3NO_3]^{3+}$ and [**8**-$3NO_3]^{3+}$ peaks were isotopically resolved and were found to match well with the theoretically predicted distribution (Figure 3 and supporting information S15 and S16).

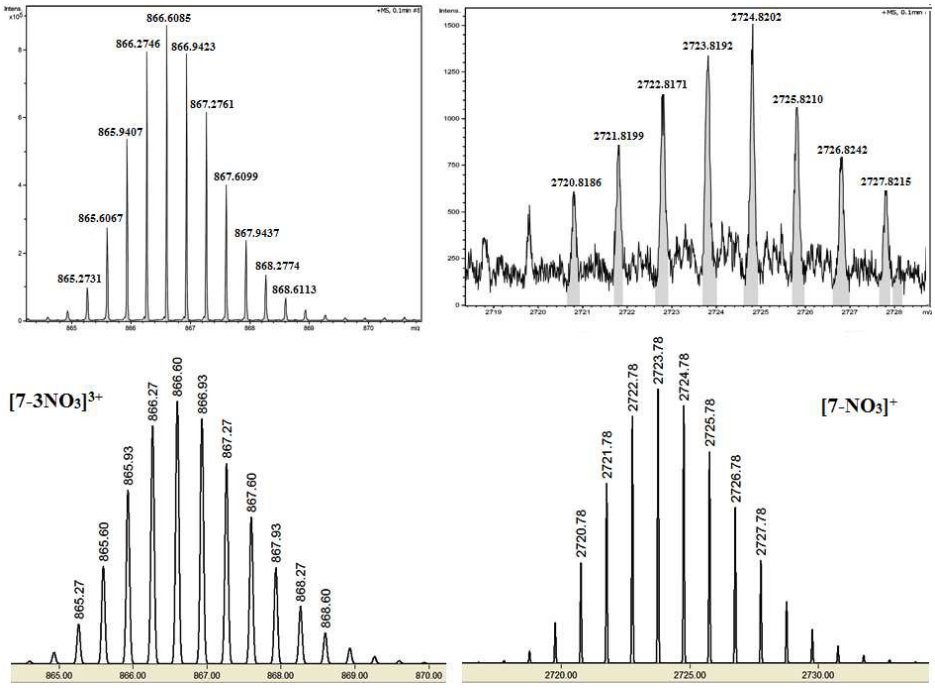


Figure 3. Experimental (top) and theoretical (bottom) ESI-mass spectrum of the macrocycle **7**.

PM6 Molecular modeling of self assembled ensembles 5−8.

Our unsuccessful attempts to structurally characterize these newly synthesized molecular hexagons (by single crystal X-ray diffraction studies) prompted us to employ PM6 semiempirical molecular orbital method to obtain useful information regarding the shape and size of the macrocycle and cavity within it. The presence of hexagonal cavity in these macrocycle is clearly evident from the space filling molecular models of the energy-minimized structures of macrocycles **5**-**8**. Thus molecular modelling supports the formation of hexagonal shape as predicted considering the tenets of directional bonding approach (Chart 1). In case of macrocycles **7** and **8**, the [2+2] self assembly of pyrazine based donor **2** and a linear acceptor (**3** or **4**) results in the formation of an irregular molecular hexagon (Figure 4) which is isogonal but not equilateral (all edges are not equal in length). In these well-defined hexagonal supramolecular macrocycles (**7** and **8**), two edges are relatively longer (1.87 nm for **7**, and 2.3 nm for **8**), whereas the other four edges are relatively shorter (0.67 nm for both **7** and **8**). On the other hand, the [6+6] self assembled ensembles (**5** and **6**) are regular hexagons (Figure 5) in which each side is of equal length (3.23 nm for **5** and 3.66 for **6**). The distance between two diagonally opposite endocyclic nitrogen atoms is estimated to be 2.19 nm and 2.62 nm respectively for macrocycle **7** and **8**, while in case of [6+6] molecular hexagons **5** and **6** the distance is relatively larger and found to be 6.19 nm and 7.05 nm respectively. The average distance between two furthest platinum centers of macrocycles **5**-**8** are found to be 1.76 nm, 2.07 nm, 5.76 nm and 6.49 nm respectively.

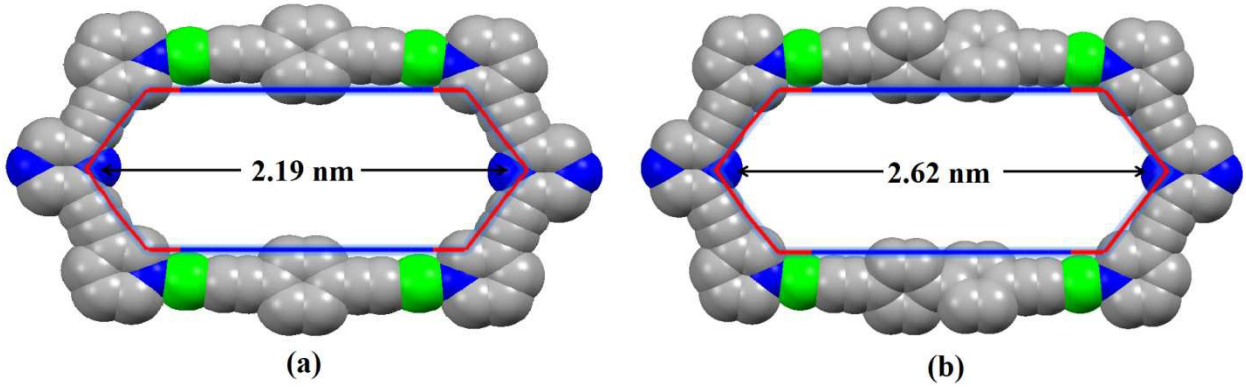


Figure 4. Simulated space filling molecular model of (a) macrocycle **7** and (b) macrocycle **8** optimized by PM6 semiempirical molecular orbital methods (light gray: C, green: Pt, blue: N). (Phosphine ligands and H atoms are omitted for clarity).

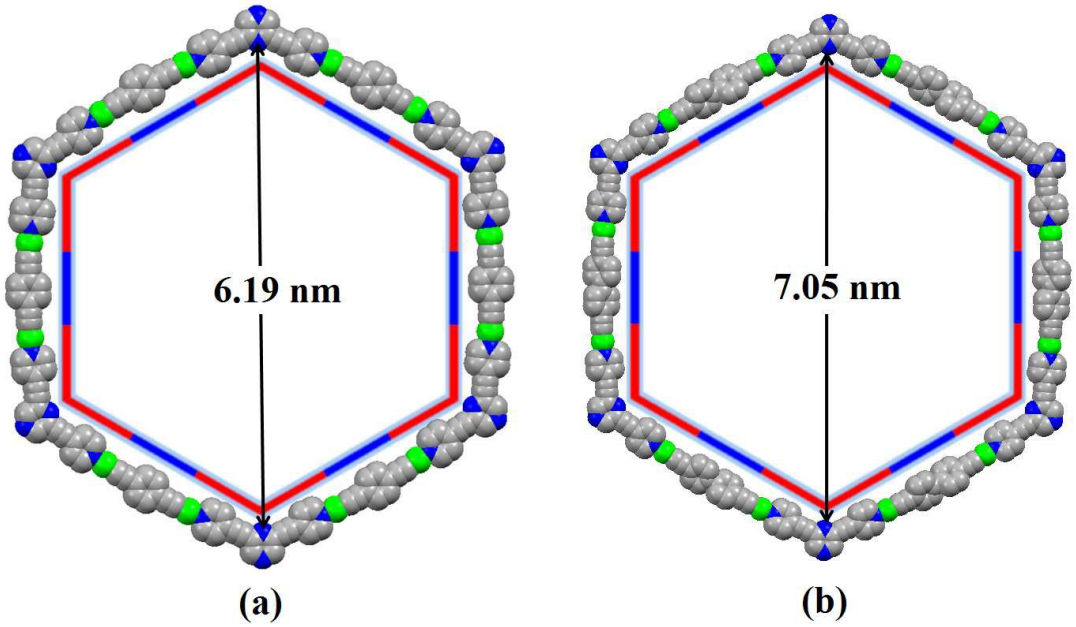


Figure 5. Simulated space filling molecular model of (a) macrocycle **5** and (b) macrocycle **6** optimized by PM6 semiempirical molecular orbital methods (light gray: C, green: Pt, blue: N). (Phosphine ligands and H atoms are omitted for clarity).

In conclusion, we report herein syntheses of two new molecules (**1** and **2**) in which a central pyrazine ring is covalently linked to a pyridine unit on either site via ethynyl bridges. The presence of two pendent pyridine units in **1** and **2** qualifies them to act as donor tectons in coordination driven self assembly reactions. In conjugation with linear acceptor tectons (**3** and **4),** self assembly of discrete hexagonal metallamacrocycles (**5**-**8**) have been conveniently achieved. Although all macrocycles obtained have a hexagonal cavity, as suggested by their respective PM6 molecular modeling, **5** and **6** are regular hexagons while **7** and **8** have irregular hexagonal shape.

Experimental Section

General details

All chemicals and anhydrous solvents used in this work were purchased from commercial sources and used without further purification. 2,6-diethynyl pyrazine was prepared by following the reported literature procedures.[13] FTIR spectra were recorded in a PerkinElmer Spectrum 400 FT-IR spectrophotometer. ^{1}H NMR spectra and ^{31}P NMR spectra were recorded on Bruker 400/500 MHz spectrometers. Elemental analyses were carried out using a Thermo Scientific Flash 2000 Organic Elemental Analyzer. ESI-MS spectra of the compounds were recorded using a Bruker UltrafleXtreme™ ESI mass spectrometer. DOSY NMR measurements were performed on a Bruker AV 500 NMR spectrometer using a 5 mm gradient probe at 298 K. DOSY spectra were recorded using a standard Bruker pulse sequence (ledbpgp2s) with longitudinal eddy current delay.

General procedure for the synthesis of organic molecules 1 and 2.

2,6-diethynylpyrazine (100 mg, 0.78 mmol), 4-iodopyridine (320 mg, 1.561 mmol), CuI (15 mg, 0.078 mmol) and bis(triphenylphosphine)palladium(II) dichloride (55 mg, 0.078 mmol) were charged in a 50 ml Schlenk flask in the glove box. Subsequently, 20 ml dry THF and freshly distilled triethylamine (0.5 ml, 3.122 mmol) were added under nitrogen. The reaction mixture was stirred overnight at room temperature. After overnight stirring, the dark brown reaction mixture was filtered through a bed of celite. The filtrate obtained was evaporated to dryness on a rotary evaporator to get crude product which was purified by column chromatography on silica gel by eluting with 35% ethyl acetate in hexane to isolate the desired product (**1** and **2**) as off white solid.

Organic linker (1). Yield: 0.192 g, 87%; mp 185-190 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 2H, Ar-H), 8.69 (dd, J = 1.52 Hz, 1.52 Hz, 4H, Ar-H), 7.48 (dd, J = 1.56 Hz, 1.56 Hz, 4H, Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.0, 146.4, 138.9, 129.3, 125.7, 90.4, 88.1. IR (ATR): 3015, 2925, 2859, 2223, 1593, 1510, 1403, 1304, 1166, 1010, 894, 820 cm^{-1}. Anal. Calcd. For $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.84; H, 3.76; N, 19.97.

Organic linker (2). Yield: 0.2 g, 91%; mp 145-150 ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (s, 2H, Ar-H), 8.72 (s, 2H, Ar-H), 8.65 (dd, J = 1.48 Hz, 1.48 Hz, 2H, Ar-H). 7.93-7.90 (m, 2H, Ar-H), 7.37-7.33 (m, 2H, Ar-H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 152.7, 149.9, 145.9, 139.2, 123.2, 118.5, 90.1, 88.3. IR (ATR): 3031, 2924, 2856, 2217, 1559, 1510, 1477, 1420, 1304, 1149, 1123, 1001, 811 cm^{-1}. Anal. Calcd. For $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.88; H, 3.72; N, 19.93.

General procedure for the synthesis of organometallic complexes 3 and 4.

1,4-Diethynylarene (0.238 mmol) and *trans*-$(PEt_3)_2PtI_2$ (490 mg, 0.714 mmol) were charged in a 25 mL Schlenk flask inside a glovebox. Subsequently, 10 mL of dry toluene and 5 mL of freshly distilled triethylamine were added under nitrogen. The solution was stirred for 10 min at room temperature before CuI (7 mg, 0.035 mmol) was added in one portion. After overnight stirring at room temperature, triethylammonium iodide precipitated from solution, which was separated by filtration. Toluene was evaporated on a rotary evaporator and the resulting yellow residue was purified by column chromatography on silica gel, eluting initially with 3% ethyl acetate in hexane and subsequently increasing polarity of the eluting solvent by using 6% ethyl acetate in hexane to isolate the desired complexes (**3** or **4**) as a white solid.

1,4-bis[trans-Pt(PEt_3)$_2$I(ethynyl)]benzene (3). Yield: 180 mg, 61%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.14 (s, 4H, Ar-H), 2.25-2.17 (m, 24H, -CH_2-), 1.20-1.12 (m, 36H, -CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 8.41 ($^{1}J_{PPt}$ = 1164 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 131.5, 130.3, 125.4, 100.4, 29.4, 16.6, 8.4. IR (ATR): 2118 cm^{-1} for ethynyl group. For $C_{34}H_{64}I_2P_4Pt_2$: C, 32.91; H, 5.20. Found: C, 32.85; H, 5.27.

4,4-Bis[trans-Pt(PEt_3)$_2$I(ethynyl)]biphenyl (4). Yield: 125 mg, 64%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.44 (d, J = 8.32 Hz, 4H, Ar-H), 7.34-7.31 (d, J = 8.32 Hz, 4H, Ar-H), 2.27-2.20 (m, 24H, -CH_2-), 1.22-1.14 (m, 36H, -CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 8.50 ($^{1}J_{PPt}$ = 1163Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 137.8, 131.0, 127.4, 126.4, 100.1, 90.6, 16.6, 8.3. IR (ATR): 2135 cm^{-1} for an ethynyl group. $C_{40}H_{68}I_2P_4Pt_2$: C, 36.48; H, 5.20. Found: C, 36.61; H, 5.35.

General procedure for the self assembly of macrocycles 5, 6, 7 and 8.

To the solution of respective organometallic complex (**3** or **4**, 0.024 mmol) in chloroform (5ml), was added methanolic solution (3ml) of $AgNO_3$ (0.048 mmol) and the reaction mixture was stirred for 4h in the dark at room temperature. The precipitated AgI was filtered off over a bed of celite. To the filtrate thus obtained, was added (dropwise) a methanolic solution (3ml) of a pyrazine based linker (**1** or **2**, 0.024 mmol). The reaction mixture was stirred overnight at room temperature, and subsequently solvents were removed under reduced pressure to obtain a yellowish solid that was washed twice with diethyl ether and finally dried in vacuum. This product thus obtained was recrystallized from a mixture of chloroform and methanol to obtain the desired macrocycles as yellowish microcrystalline solid.

Macrocycle 5. Yield: 26 mg, 86%; ^{1}H NMR (400 MHz, MeOD): δ 8.88 (s, 12H, Ar-H), 8.83-8.79 (m, 24H, Ar-H), 7.83-7.82 (d, J = 6.16 Hz, 24H, Ar-H), 7.08 (s, 24H, Ar-H), 1.81-1.75 (m, 144H, -CH_2-), 1.16-1.08 (m, 216H, -CH_3). ^{31}P{^{1}H} NMR (162 MHz, MeOD): δ 15.57 ($^1J_{PPt}$ = 1157 Hz). ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ 152.9, 148.1, 147.5, 138.3, 131.8, 131.0, 129.7. 128.1, 126.1, 98.3, 92.9, 86.1, 29.1, 13.8, 6.8. IR (ATR): 2974, 2932, 2883, 2127, 1609, 1510, 1453, 1330, 1149, 1042, 828 cm^{-1}. Anal. Calcd. For $C_{312}H_{444}N_{36}O_{36}P_{24}Pt_{12}$: C, 49.21; H, 5.88; N, 4.41. Found: C, 49.28; H, 5.93; N, 4.44. MS (ESI) m/z: 2026.59 [**5**-4NO_3]$^{4+}$, 1330.40 [**5**-6NO_3]$^{6+}$, 982.30 [**5**-8NO_3]$^{8+}$, 866.27 [**5**-9NO_3]$^{9+}$, 773.44 [**5**-10NO_3]$^{10+}$ and 634.20 [**5**-12NO_3]$^{12+}$.

Macrocycle 6. Yield: 25mg, 81%; ^{1}H NMR (400 MHz, MeOD): δ 8.88 (s, 12H, Ar-H), 8.83-8.81 (m, 24H, Ar-H), 7.84-7.82 (d, J = 5.92 Hz, 24H, Ar-H), 7.49-7.46 (d, J = 8.36 Hz, 24H, Ar-H), 7.25-7.23 (d, J = 8.04 Hz, 24H, Ar-H), 1.82-1.75 (m, 144H, -CH_2-), 1.18-1.10 (m, 216H, -CH_3). ^{31}P{^{1}H} NMR (162 MHz, MeOD): δ 15.61 ($^1J_{PPt}$ = 1160 Hz). ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ 152.9, 149.2, 147.1, 139.6, 137.9, 132.8, 130.3, 129.7, 128.4, 100.7, 94.3, 91.6, 87.8, 13.8, 6.7. IR (ATR): 2974, 2941, 2883, 2118, 1609, 1502, 1460, 1337, 1149, 1033, 1009, 820 cm^{-1}. Anal. Calcd. For $C_{348}H_{468}N_{36}O_{36}P_{24}Pt_{12}$: C, 51.78; H, 5.84; N, 4.16. Found: C, 51.95; H, 5.98; N, 4.32. MS (ESI) m/z: 2140.64 [**6**-4NO_3]$^{4+}$, 1406.43 [**6**-6NO_3]$^{6+}$, 1196.65 [**6**-7NO_3]$^{7+}$, 1039.32 [**6**-8NO_3]$^{8+}$, 916.95 [**6**-9NO_3]$^{9+}$, 819.06 [**6**-10NO_3]$^{10+}$, 738.96 [**6**-11NO_3]$^{11+}$ and 672.22 [**6**-12NO_3]$^{12+}$.

Macrocycle 7. Yield: 28mg, 90%; ^{1}H NMR (400 MHz, MeOD): δ 9.06 (s, 4H, Ar-H), 9.04 (s, 4H, Ar-H), 8.99-8.79 (m, 4H, Ar-H), 8.30-8.26 (m, 4H, Ar-H), 7.74-7.71 (m, 4H, Ar-H), 7.08 (s, 8H, Ar-H), 1.81-1.75 (m, 48H, -CH_2-), 1.23-1.09 (m, 72H, -CH_3). ^{31}P{^{1}H} NMR (162 MHz, MeOD): δ 15.53 ($^1J_{PPt}$ = 1156 Hz). ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ 154.6, 153.0, 146.8, 138.3, 131.4, 130.4, 128.4, 125.0, 122.6, 93.6, 89.8, 86.1, 29.1, 13.9, 6.8. IR (ATR): 2965, 2908, 2875, 2120, 1584, 1444, 1411, 1370, 1247, 1033, 836 cm^{-1}. Anal. Calcd. For $C_{104}H_{148}N_{12}O_{12}P_8Pt_4$: C, 49.21; H, 5.88; N, 4.41. Found: C, 49.25; H, 5.91; N, 4.46. MS (ESI) m/z: 2722.84 [7-NO_3] $^+$, 1330.42 [7-2NO_3]$^{2+}$, 866.28 [7-3NO_3]$^{3+}$ and 634.21 [7-4NO_3]$^{4+}$.

Macrocycle 8. Yield: 27mg, 87%; ^{1}H NMR (400 MHz, MeOD): δ 9.07 (s, 4H, Ar-H), 8.87 (s, 4H, Ar-H), 8.86-8.79 (m, 4H, Ar-H), 8.29-8.27 (d, J = 8Hz, 4H, Ar-H), 7.75-7.71 (m, 4H, Ar-H), 7.48-7.46 (d, J = 8.2Hz, 8H, Ar-H), 7.25-7.23 (d, J = 8.12Hz, 8H, Ar-H), 1.83-1.75 (m, 48H, -CH_2-), 1.21-1.10 (m, 72H, -CH_3). ^{31}P{^{1}H} NMR (162 MHz, MeOD): δ 15.56 ($^1J_{PPt}$ = 1159 Hz). ^{13}C{^{1}H} NMR (CD_3OD, 100 MHz): δ 154.6, 153.0, 147.5, 146.8, 138.3, 137.8, 131.0, 128.7, 127.7, 126.1, 122.6, 89.8, 86.1, 83.6, 82.0, 13.9, 6.8. IR (ATR): 2974, 2932, 2883, 2115, 1617, 1477, 1411, 1337, 1149, 1042, 828 cm^{-1}. Anal. Calcd. For $C_{116}H_{156}N_{12}O_{12}P_8Pt_4$: C, 51.78; H,

5.84; N, 4.16. Found: C, 51.88; H, 5.95; N, 4.29. MS (ESI) m/z: 1406.43 $[8\text{-}2NO_3]^{2+}$, 916.95 $[8\text{-}3NO_3]^{3+}$ and 672.22 $[8\text{-}4NO_3]^{4+}$.

Single-Crystal Structure Determination for compound 1.

A suitable single crystal of compound **1** was carefully selected under a polarizing microscope and mounted at the tip of the thin glass fiber using cyanoacrylate (super glue) adhesive. Single crystal X-ray data was collected on a Bruker Smart Apex II diffractometer equipped with an Oxford Cryostream low-temperature device and a fine-focus sealed-tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromated) operating at 50 kV and 30 mA. Raw data collection and refinement were done using SMART. Data reduction was performed using SAINT[14] and corrected for Lorentz and polarization effects. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS.[15] The structure was solved by direct methods using SHELXS-97,[16] which enabled us to locate the non-hydrogen (C, N) positions from the difference Fourier maps. For the final refinement, hydrogen atom of compound **1** was placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS[17] package of programs. Details of the structure determination and final refinements of **1** listed below.
Crystal Data of 1 : $C_{18}H_{10}N_4$, M = 282.30, Monoclinic, space group C2/c, a = 22.8914(8)Å, b = 5.7531(2)Å, c = 23.2380(7)Å , β = 113.464(4)° , V = 2807.30(16) Å^3 , T = 296 K, Z= 8, D_{calc} = 1.336 Mgm^{-3}, μ = 0.083 mm^{-1}, 29111 reflections measured , 4277 unique [R_{int} = 0.0386], R1 [I > 2σ(I)] = 0.0431, wR2 (F , all data) = 0.1214, GOF(F^2) = 1.053, CCDC 1032260.

ASSOCIATED CONTENT

Supporting Information
^{1}H and ^{13}C{^{1}H} NMR spectra of organic molecules **1** and **2**, ^{1}H and ^{31}P{^{1}H} NMR spectra of organometallic complexes **3** and **4**, ^{1}H, ^{31}P{^{1}H} and ^{1}H DOSY NMR spectra of the metallamacrocycles **5**-**8**, ESI-TOF-MS of **5**-**8**, X-ray crystallography analysis of ligand 1 and detailed simulation protocol. CCDC contains the supplementary crystallographic data for this paper with a deposition number of CCDC 1032260 (**1**). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK. [Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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Author Contributions
N.D. conceived the research and supervised the experimental work. S.B. synthesized all compounds reported in this manuscript. S.C. optimized the energy-minimized geometry of the metallacycles **5**-**8**. J.N.B. and S.R.M collected XRD data and refined structure of **1**.
Notes

The authors declare no competing financial interest.

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Table of Contents Synopsis and Graphic

Pyrazine-Based Donor Tectons: Synthesis, Self-Assembly and Characterization

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Two supramolecular donor tectons, wherein a central pyrazine unit is covalently linked to two pyridine moieties, have been synthesized. In conjugation with Pt^{II}_2 acceptor units, these ligands have been used to self-assemble four ionic nanoscalar metallamacrocycles, each having a convex hexagonal cavity.