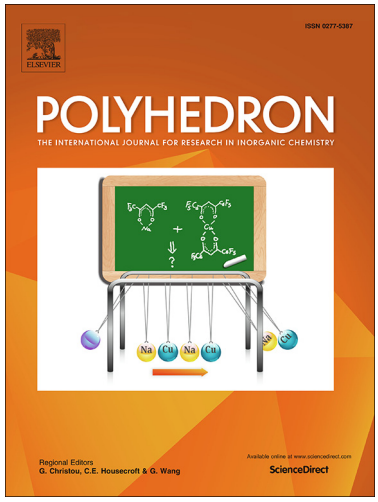


Self-assembled Pd_3L_2 cages having flexible tri-imidazole donors

Atul Kumar, Ennio Zangrando, Partha Sarathi Mukherjee

PII: S0277-5387(19)30180-9
DOI: https://doi.org/10.1016/j.poly.2019.03.014
Reference: POLY 13815

To appear in: *Polyhedron*

Received Date: 31 January 2019
Revised Date: 4 March 2019
Accepted Date: 9 March 2019

Please cite this article as: A. Kumar, E. Zangrando, P.S. Mukherjee, Self-assembled Pd_3L_2 cages having flexible tri-imidazole donors, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.03.014

Self-assembled Pd_3L_2 cages having flexible tri-imidazole donors

Atul Kumar,[a] Ennio Zangrando,[b] Partha Sarathi Mukherjee[a]*

[a] *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560 012, India.*

[b] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34127 Italy.*

*Corresponding author: P. S. Mukherjee, E-mail: psm@iisc.ac.in; Tel.: +91-80-22933352;

Fax: +91-80-23601552.

Abstract

Four new M_3L_2 molecular cages (CA1 – CA4) have been synthesized in excellent yield via coordination driven self –assembly of flexible tri-imidazole donors based on triazine (L1) and tri-phenyl benzene (L2) core with 90º cis-blocked metal acceptors of Pd(II). Two of them CA1 and CA2 are highly soluble in water. All the cages were characterized by spectroscopic studies and ESI-MS; CA3 and CA4 also by X-ray diffraction. Selective formation of two separate cages CA3 and CA4 was noticed instead of a hetero-ligand cage, when the metal acceptor (dppf)$Pd(OTf)_2$ was treated with a mixture of ligands L1 and L2.

Keywords: *palladium(II), cage compounds, self-assembly, supramolecular chemistry, X-ray structure determination*

1. Introduction

Inspired from biological systems, where small molecules interact and self-organize to form well organized functional systems,[1-12] chemists have developed metal−ligand coordination driven self-assembly an as alternative protocol that helps to design large molecular structures with diverse shapes and sizes in facile manner.[13-17] Over last few decades, coordination driven self-assembly established itself as a well-defined methodology in constructing molecular architecture from two dimensional 2-D polygons to three dimensional 3-D cages, prism, polyhedral species, tubes and capsules which possesses diverse functionality.[18-53] Non-covalent cages are preferred over its covalent analogues as they avoid multistep synthesis which is obligatory in latter one.[54,55] Declining use of templates and enthralling features of an imidazole donor over a pyridyl donor has prompted synthetic chemists to design functionalized supramolecules without a template based on polyimidazole ligands.[56-87]

Designing of supramolecular coordination complexes requires rigid molecular building blocks and correct orientation of the coordination site/s on metal acceptor.[31-33,38] However, building molecular architectures based on flexible donors is a risky task due to diverse orientation of the donors around the metal centres that leads to the formation of undesired structures. Herein, we design two flexible tri-imidazole ligands (L1 and L2) based on electron deficient triazine and moderate electron rich triphenyl benzene cores, respectively. Both L1 and L2 are similar in size and metal binding site. Template-free synthesis of water-soluble M_3L_2 bifacial molecular cages CA1 and CA2 was achieved through two-component self-assembly of triazine and triphenyl benzene functionalized tri-imidazole donor L1 and L2 respectively, with cis blocked 90º acceptor cis-(tmen)Pd$(NO_3)_2$ [tmen = N,N,N'N'-tetramethylethane-1,2-diamine]. In a similar way, CA3 and CA4 were prepared by two-component self-assembly of L1 and L2 separately with cis-(dppf)Pd$(OTf)_2$. Multicomponent self-assembly of cis-(dppf)Pd$(OTf)_2$ with L1 and L2 resulted in the formation of a mixture CA3 and CA4 instead of any multicomponent cage comprising of both the ligands.

2. Experimental

2.1 Material and methods

All the reagents were purchased from different commercial sources and used without further purification. NMR (1D and 2D) spectra were recorded on Bruker 400 MHz spectrometer and the chemical shifts (δ) in the ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the solvents $CDCl_3$ (7.26 ppm), CD_3CN (1.94 ppm) and D_2O (4.79 ppm). Electrospray ionization mass spectrometry (ESI-MS) experiments were carried out in Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer using standard spectroscopic-grade solvents.

2.2 Synthesis of the ligands

2.2.1 *Synthesis of 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (1A)*

4-Bromomethylbenzonitrile (2 g, 10.2 mmol) was added to trifluoromethanesulfonic acid (2.6 mL, 10.2 mmol) in small portion at 0ºC. After addition, the mixture was warmed to room temperature and stirred for further 24 h, then poured into ice, neutralized by ammonium hydroxide. The solid phase was collected by filtration to afford white powder (1.82 g, 91%).

m.p. 195 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (6H, d, *J* = *8* Hz), 7.60 (6H, d, *J* = *8* Hz), 4.59 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.5, 142.7, 136.5, 129.9, 129.8, 33.1. FTIR (KBr), ν (cm^{-1}): 2922, 2852, 1584, 1518, 1415, 1371, 1226, 1178, 1018, 866, 814, 606. ESI MS (m/z): Calcd. For $[M+Na]^+$ 609.81, found 609.80 for $[M+Na]^+$,

2.2.2 *Synthesis of 2,4,6-tris(4-((1H-imidazol-1-yl)methyl)phenyl)-1,3,5-triazine (L1)*

Imidazole (0.38 g, 5.61 mmol) and potassium hydroxide KOH (0.57 g, 10.2 mmol) were taken in 50 mL round bottom flask, with addition of 25 mL of acetonitrile and the reaction mixture was stirred for 2 h at room temperature. Then compound 1A (1 g, 1.7 mmol) was added and stirring was continued for further 12 h. Next the solvent was evaporated and washed several times with water to give desired product as white solid. (0.84 g, 90%). m.p. >250 °C. δ: 8.72 (6H, d, *J* = *8* Hz), 7.62 (3H, s), 7.33 (6H, d, *J* = *8* Hz), 7.14 (3H, s), 6.95 (3H, s), 5.25 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.1, 140.8, 137.5, 136.0, 130.0, 129.6, 127.45, 119.3, 50.5. FTIR (KBr), ν (cm^{-1}): 3392, 3106, 1584, 1524, 1420, 1368, 1290, 1232, 1178, 1020, 814, 752, 656, 600. ESI MS (m/z): Calcd. For $[M+H]^+$ 550.24, found 550.24 for $[M+H]^+$, For $[M+Na]^+$ 572.24, found 572.26 for $[M+Na]^+$.

2.2.3 *Synthesis of 4,4''-dimethyl-5'-(p-tolyl)-1,1':3',1''-terphenyl (2A)*

4-Methylacetophenoe (2 g, 14.9 mmol) and p-toluenesulfonic acid (PTSA) (0.25 g, 1.5 mmol) were taken in 50 mL flask and heated under nitrogen atmosphere for 16 h at 146 ℃. The reaction mixture was allowed to warm to room temperature and then excess PTSA was neutralized with sodium hydrogen carbonate. Then the reaction mixture was extracted with dichloromethane. Crude product was purified by column chromatography using silica 60 – 120 (hexane/ethyl acetate : 98/2) (white solid, yield =1.38 g, 80%). m.p. 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (3H, s), 7.60 (6H, d, *J* = *8* Hz), 7.29 (6H, d, *J* = *8* Hz), 2.42 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.7, 138.9, 137.7, 130.0, 127.7, 125.1, 21.6. FTIR (KBr), ν (cm^{-1}): 3022, 2961, 2921, 2865, 1512, 1450, 1366, 1186, 1113, 1060, 1039, 1019, 809, 734, 720. ESI MS (m/z): Calcd. For $[M+Na]^+$ 371.18, found 371.19 for $[M+Na]^+$.

2.2.4 *Synthesis of 2.2.3 Synthesis of 4,4''-dimethyl-5'-(p-tolyl)-1,1':3',1''-terphenyl (2B)*

Compound 2A (1 g, 2.86 mmol), N-bromosuccinimide (1.68 g, 9.46 mmol), benzoyl peroxide (69 mg, 0.28 mmol) and CCl_4 (30 mL) were taken in 100 mL round bottom flask and heated to reflux for 14 h. The reaction mixture was then cooled to ambient temperature and filtered to remove by-product. Crude product was purified by column chromatography using silica 60 –

120 (hexane/ethyl acetate: 90/10) as white solid product. (1.49 g, 89%). m.p. 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (3H, s), 7.66 (6H, d, *J = 8* Hz), 7.51 (6H, d, *J = 8* Hz), 4.58 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.2, 141.4, 137.7, 130.1, 128.2, 125.7, 33.8. FTIR (KBr), ν (cm^{-1}): 3108, 1646, 1588, 1506, 1438, 1388, 1282, 1076, 1028, 910, 820, 744, 658. ESI MS (m/z): Calcd. For $[M+Na]^+$ 606.91, found 606.92 for $[M+Na]^+$.

2.2.5 *Synthesis of 1,1'-((5'-(4-((1H-imidazol-1-yl)methyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-diyl)bis(methylene))bis(1H-imidazole) (L2)*

Imidazole (0.38 g, 5.64 mmol) and potassium hydroxide KOH (0.575 g, 10.25 mmol) were taken in a 50 mL round bottom flask with addition of 25 mL of acetonitrile and the reaction mixture was stirred for 2 h at room temperature. Then compound 2B (1 g, 1.71 mmol) was added and stirring continued for further 12 h. Subsequently, solvent was evaporated and washed several times with water to give desired product as white solid. (0.8 g, 85%). m.p. 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71(3H, s), 7.64 (6H, d, *J = 8* Hz), 7.58 (3H, s), 7.25 (6H, d, *J = 8* Hz), 7.10 (3H, s), 6.93 (3H, s), 5.17 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.2, 141.3, 137.8, 136.1, 130.3, 128.36, 128.35, 125.7, 119.7, 50.9. FTIR (KBr), ν (cm^{-1}): 3110, 1686, 1652, 1594, 1508, 1448, 1394, 1282, 1230, 1078, 1024, 910, 820. ESI MS (m/z): Calcd. For $[M+Na]^+$ 569.25, found 569.26 for $[M+Na]^+$.

2.3 Synthesis of the cages

2.3.1 General procedure for the synthesis of CA1 to CA2

M1 (5 mg, 3 equivalents) was dissolved in H_2O (1 mL) and the yellow clear solution was added to solid ligand L (2 equivalents) and heated at 60ºC with stirring for 12 h. The solution turned colourless with the consumption of the donor. Upon completion of the reaction, the mixture was filtered, concentrated under reduced pressure, and the pure form of cage CA was obtained as an off-white powder by trituration with acetone.

2.3.1.1 Synthesis of CA1

Isolated yield: 8.92 mg (92%). m.p. >250 °C. ^{1}H NMR (400 MHz, D_2O) δ: 8.46 (6H), 7.31 (6H), 6.75 (18H), 6.29 (18H), 5.02 (12H), 2.70 – 2.78 (48H). ESI MS (m/z): 651.05 $[(CA1) - 3NO_3]^{3+}$, 1007.58 $[(CA1) - 2NO_3]^{2+}$.

2.3.1.2 Synthesis of CA1_PF6

M.p. 210 °C. CA1 (10.0 mg, 0.0023 mmol) in 1mL H_2O was treated with excess KPF_6 (8.00 mg, 0.046 mmol) and stirred at room temperature for 6 h. Then solid precipitate was filtered

and washed several times with H_2O and dried under reduce pressure to get the product as white powder. Isolated yield: 11.2 mg (91%). ^{1}H NMR (400 MHz, CD_3CN) δ: 8.34 (6H), 7.86 (12H, d, *J* = *8* Hz), 7.43 (6H), 7.32 (18H), 6.89 (6H, d, *J* = *8* Hz), 3.01 (12H), 2.73 (36H).

2.3.1.3 Synthesis of CA2

Isolated yield: 8.7 mg (89%). m.p. >250 °C. ^{1}H NMR (400 MHz, D_2O) δ: 8.38 (6H), 7.21 (12H), 6.67 (30H), 3.03 (12H), 2.65 – 2.68 (36H). ESI MS (m/z) 649.73 $[(CA2) - 3NO_3]^{3+}$, 1005.60 $[(CA2) - 2NO_3]^{2+}$.

2.3.2 General procedure for the synthesis of CA3 and CA4

Cis-protected phosphine blocked acceptor M2 (10.0 mg, 3 equivalents) and ligand L (2 equivalents) were dissolved in CH_3NO_2 followed by subsequent stirring at room temperature for 24 h. The resulting clear solution was triturated with diethyl ether to obtain pure product.

2.3.2.1 Synthesis of CA3

Isolated yield: 11.2 mg (81%). m.p. 160 °C ^{1}H NMR (400 MHz, CD_3CN) δ: 7.65 – 7.92 (78H), 6.69 – 6.97 (24H), 4.95 (12H), 4.66 (24H). $^{31}P\{^1H\}$ NMR (CD_3CN, 121.4 MHz) δ: 32.37 (s). ESI MS (m/z): 645.94 $[(CA3) – 5OTf]^{5+}$, 844.69 $[(CA3) – 4OTf]^{4+}$,1175.94 $[(CA3) – 3OTf]^{3+}$, 1838.45 $[(CA3) – 2OTf]^{2+}$.

2.3.2.2 Synthesis of CA4

Isolated yield: 11.0 mg (80%). m.p. 157 °C. ^{1}H NMR (400 MHz, CD_3CN) δ: 7.59 – 7.90 (78H), 6.71 – 6.96 (30H), 4.82 (12H), 4.65 (24H). $^{31}P\{^1H\}$ NMR (CD_3CN, 121.4 MHz) δ: 32.24 (s). ESI MS (m/z): 844.25 $[(CA4) – 4OTf]^{4+}$,1837.57 $[(CA4) – 2OTf]^{2+}$.

2.4 Single crystal X-ray crystallography

Single crystal X-ray data of CA3 and CA4 were collected on X-ray diffraction beamline XRD1 of the ELETTRA Synchrotron, Trieste (Italy), using the rotating crystal method with a monochromatic wavelength of 0.7000 Å, on a Dectris Pilatus 2M detector. Measurements were performed at 100(2) K using a nitrogen stream cryo-cooler. The structure was solved by intrinsic phasing method with ShelXT[(88)] and refined by the full-matrix least-squares method based on F^2 with all observed reflections using the Olex2 program.[(89)] All non-hydrogen atoms were refined with an isotropic displacement coefficients. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In addition, the

structure contains a huge void of disordered solvent molecules therefore, solvent mask incorporated in the program was applied to account for embedded solvent molecules.[90] Crystallographic data and refinement parameter are given in Table 1.

Table 1: Crystallographic Data and Refinement Parameters of Cage

	CA3	**CA4**
empirical formula	$C_{168}H_{138}Fe_3N_{18}P_6Pd_3$	$C_{174}H_{144}Fe_3N_{12}P_6Pd_3$
Fw	3677.81	3373.71
T (K)	100(2)	100(2)
crystal system	triclinic	hexagonal
space group	*P-1*	*R-3*
a/Å	23.615(5)	67.121(10)
b/Å	23.634(5)	67.121(10)
c/Å	23.775(5)	30.088(6)
α/deg	61.87(3)	90
β/deg	63.99(3)	90
γ/deg	74.92(3)	120
V/Å^3	10493(5)	117393(41)
Z	2	18
ρ_{calcd} (g cm^{-3})	1.164	0.859
μ (Mo Kα) (mm^{-1})	0.571	0.436
λ/Å	0.700	0.700
F (000)	3740	31032.0
collected reflns	38086	48128
unique reflns	24599	23000

GOF (F^2)	1.05	1.171
R_1[a]	0.1021	0.1068
wR_2[b]	0.3123	0.3600

[a]$R_1=\Sigma\big|\,|F_o|-|F_c|\,\big|/\Sigma|F_o|$, [b]$wR_2=[\Sigma\{w(F_o^2-F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

3. Result and discussion

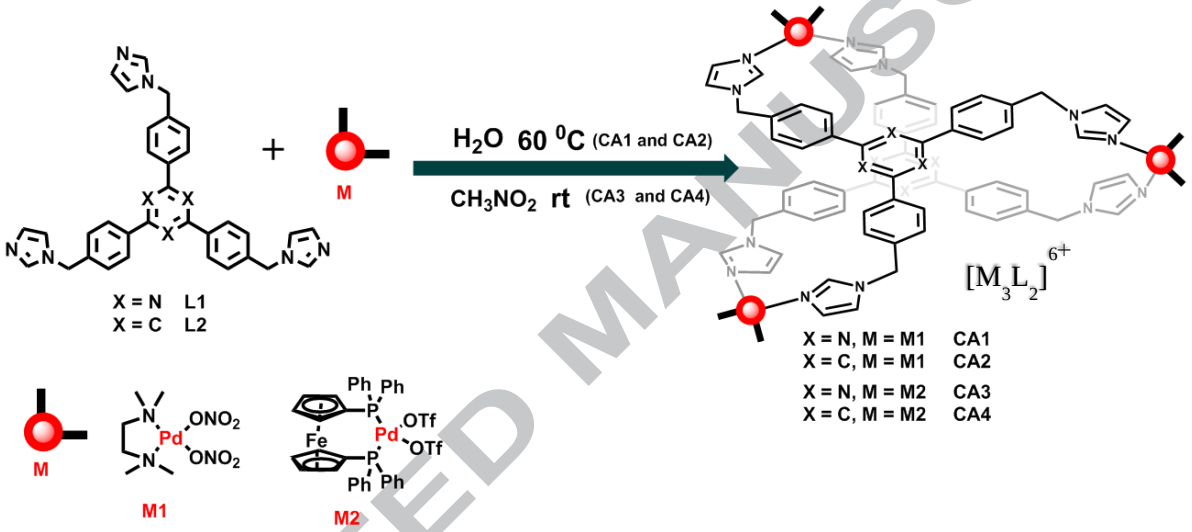
Ligand L1 was synthesized in two steps (Scheme S1, supporting information) by cyclotrimerization of 4-(bromomethyl)benzonitrile, using catalytic amount of trifluoro-methane sulfonic acid, followed by allylic coupling in presence of base. While ligand L2 was synthesized in three steps (Scheme S2) first by cyclotrimerization of 4-methylacetophenone followed by allylic bromination and then allylic coupling in presence of base. Both ligands were fully characterized by ^{1}H and ^{13}C NMR, ESI-MS and IR spectroscopy.

M_3L_2 self-assembled molecular cages CA1 and CA2 were obtained by two-component self-assembly. Synthesis of CA1 and CA2 was carried out by adding an aqueous solution of cis-(tmen)Pd$(NO_3)_2$ (M1) into the solid tritopic donor L1 or L2 in 3:2 molar ratio followed by subsequent stirring at 60ºC for 12 h. The resulting clear solution was triturated with acetone to obtain [3+2] self-assembled M_3L_2 molecular cage CA as an off-white precipitate in pure form. CA3 and CA4 were synthesized by mixing the acceptor cis-Pd(dppf)$(OTf)_2$ {dppf=1,1'-Bis(dipheylphosphino) ferrocene} (M2) and ligand L1 or L2 in 3:2 molar ratio followed by subsequent stirring at room temperature for 24 h. The resulting clear solution was triturated with diethyl ether to obtain pure self-assembled molecular cage CA M_3L_2.

Complexes CA1 and CA2 were characterize by ^{1}H NMR spectroscopy, DOSY, COSY and ESI-MS, while CA3 and CA4 were characterized by ^{1}H and ^{31}P NMR spectroscopy, DOSY, COSY, ESI-MS and single crystal XRD diffraction.

^{1}H NMR spectroscopic analysis of CA1 in D_2O (Figure1) exhibited sharp distinct peaks with noticeable downfield shift as compared to ligand L1, which is expected because of the coordination of ligand L1 to Pd^{II}. Diffusion-ordered NMR spectroscopy (DOSY) corroborated the formation of a single species by the appearance of a clear single band for complex CA1 at logD = -10.40 and CA2 at -10.38. ESI-MS spectra showed peaks at m/z = 651.05 for $[CA1\text{-}3NO_3]^{3+}$, 1007.58 for cage $[CA1\text{-}2NO_3]^{2+}$ (Figure 2), 649.73 for $[CA2\text{-}3NO_3]^{3+}$and at 1005.60 for $[CA2\text{-}2NO_3]^{2+}$ (Figure S15) with isotopic patterns consistent with the charge states. Several

attempts were made to crystallize CA1 and CA2 by vapour diffusion and slow evaporation, but any attempt failed. Therefore we change the acceptor from cis-(tmen)Pd(NO_3)$_2$ to cis-Pd(dppf)(OTf)$_2$. Formation of single product in this case was confirmed from the appearance of a single peak in ^{31}P NMR, which showed up-field shift [32.37 ppm for CA3 and 32.24 ppm for CA4] compared to corresponding acceptor peak (Figures S9 and S11). Formation of single M_3L_2 system for CA3 and CA4 is also supported from ^{1}H, COSY and DOSY NMR (Figures S9-S12). Finally, diffraction quality single crystals were obtained by slow vapour diffusion of diethyl ether into nitromethane solutions of complexes CA3 and CA4 at room temperature for four days.



Scheme 1 Schematic representation of the formation of 3D molecular cages.

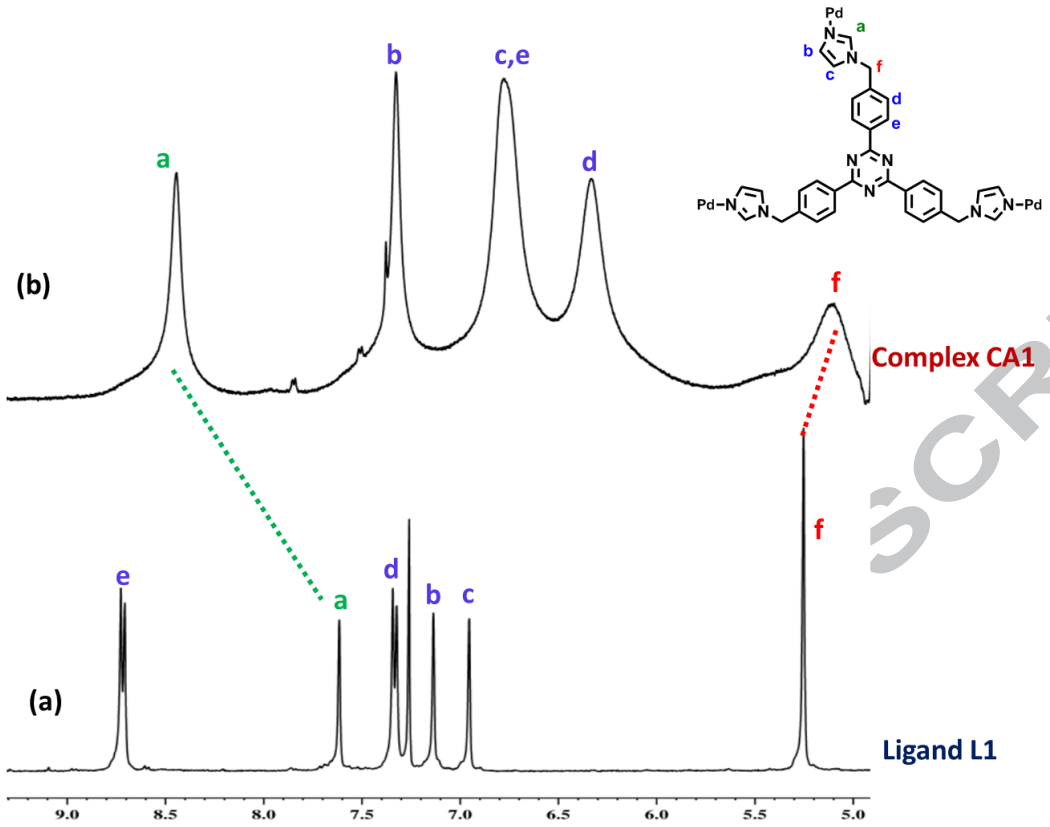


Figure 1: Partial ^{1}H NMR spectra of a) ligand L1 recorded in $CDCl_3$, and b) complex CA1 recorded in D_2O.

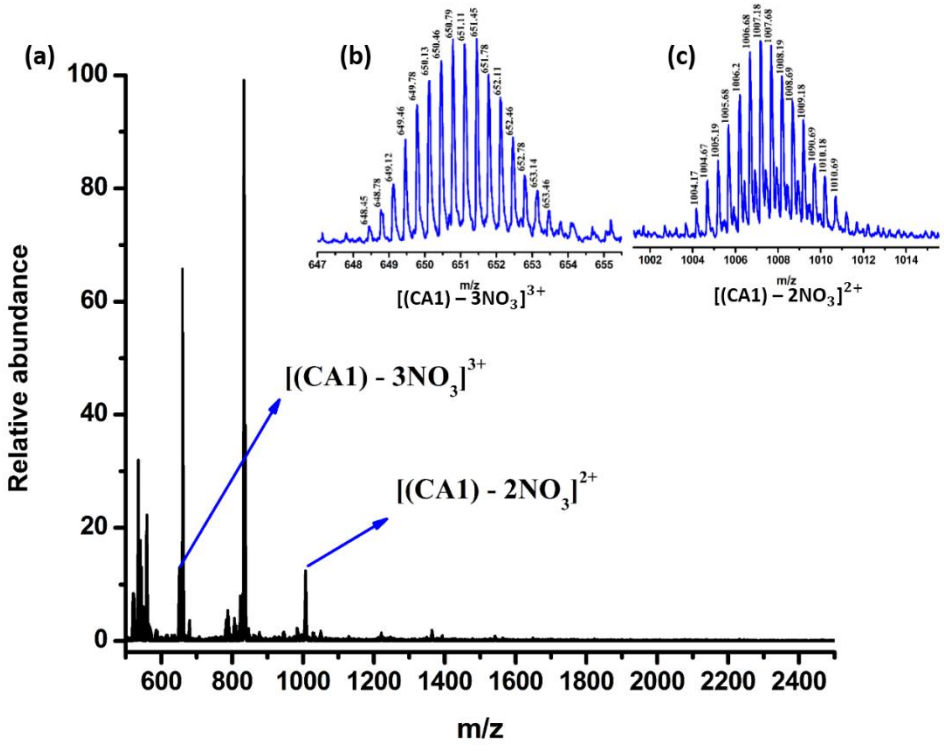


Figure 2: ESI-MS spectrum of (a) cage CA1 recorded in H_2O. Inset: isotopic distributions for the fragments (b) $[CA1\text{-}3NO_3]^{3+}$and (c) $[CA1\text{-}2NO_3]^{2+}$.

3.1 Crystal structure details

Complex CA3 (Figure 3a) crystallizes in triclinic system with space group $P\bar{1}$ (CCDC: 1894555). The asymmetric unit consists of three independent Pd(II) ions and two ligands L1. The coordination environment of each Pd centre is almost square planar where Pd-N bond distances range from 2.05 - 2.09 Å. The closest distance between two central triazine is 3.14 Å Bent angle of flexible CH_2 group between benzene and imidazole varies from 107.34º to 113.85º. Complex CA4 (Figure 3b) crystallizes in trigonal system with space group $R\bar{3}$ (CCDC: 1894704) Its asymmetric unit also consists of three independent Pd(II) ions and two ligands L2. The closest distance between two central benzene cores is 3.44 Å. Bent angle of flexible CH_2 group between benzene and imidazole varies from 107.44 to 113.65°. Distances of 3.14 and 3.44 Å between two triazine (CA3) and two benzene cores (CA4), respectively, fall in the range of π-π interactions, which strongly favoured the self-assembly of complexes as M_3L_2 system. Flexibility of CH_2 group, as evident from bent angle measured in crystal structure of both cages, helps in the formation of M_3L_2 cages. Space-filled model of the cages suggests a highly reduced cavity size, which makes it difficult for any guest encapsulation.

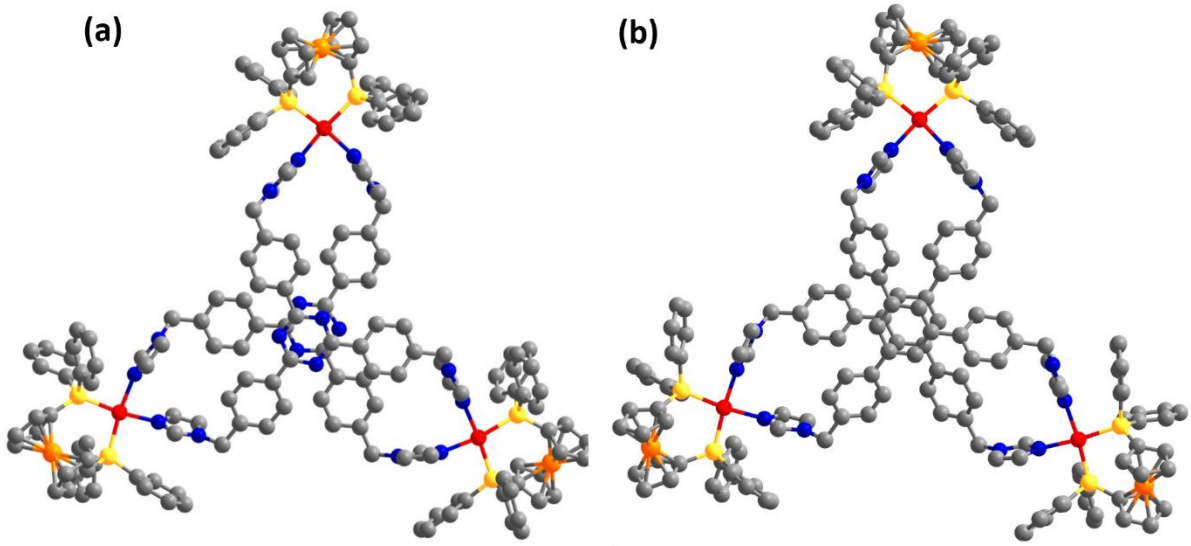
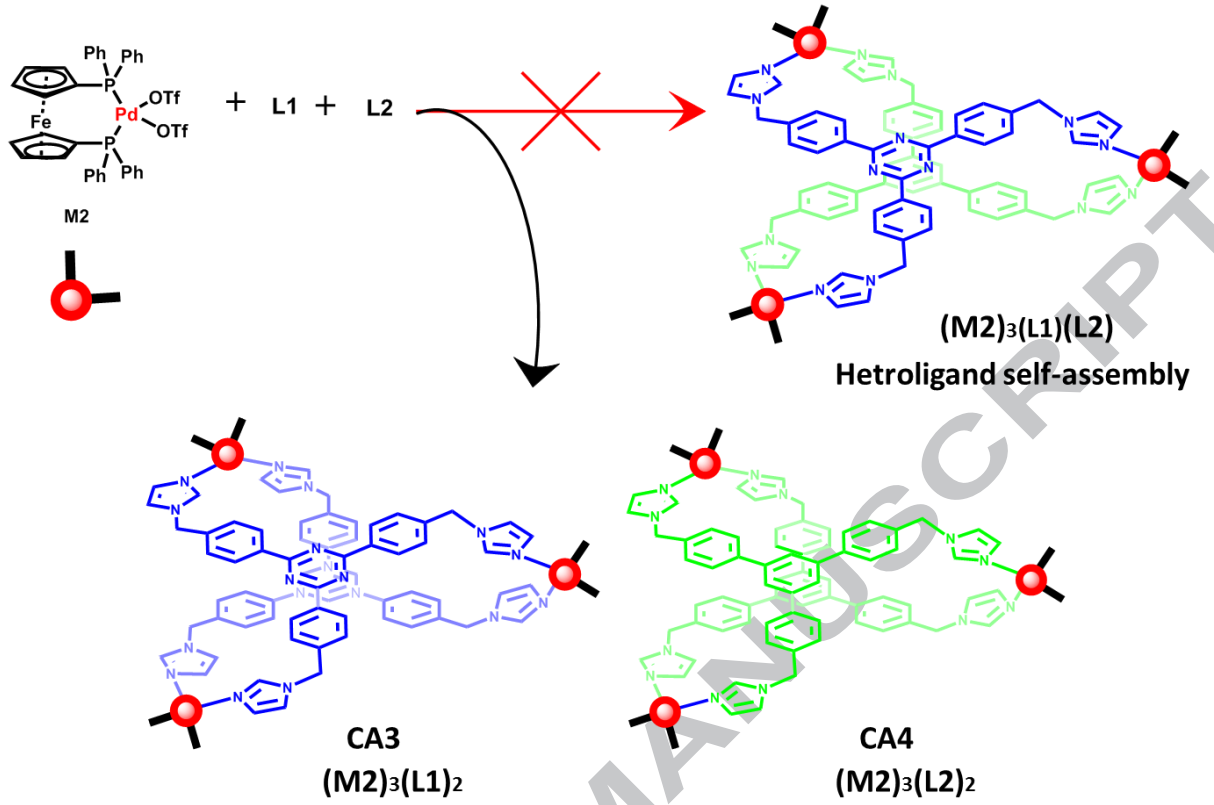


Figure 3. Single crystal XRD structures of the cages (a) CA3; and (b) CA4. Colour codes: red – Pd, yellow-P, blue-N, grey-C, orange - Fe.

3.2 Self-sorting experiment of CA3 and CA4

As both the ligands L1 and L2 have similar geometry and form cages of almost equivalent shape and size with complementary building unit, we were curious to know whether (in presence of L1 and L2) the same metal acceptor would lead to the formation of a multicomponent cage comprising both the ligands. As L1 has an electron deficient central core (triazine) and L2 has a relatively electron rich core, we assumed that multicomponent cage formation would be straightforward. For this experiment, we have used cis-Pd(dppf)$(OTf)_2$ as metal acceptor as it is easier to determine the number of products formed by simply ^{31}P NMR. To investigate this, reaction of cis-Pd(dppf)$(OTf)_2$ with L1 and L2 in 3:1:1 ratio respectively in CH_3NO_2 was done by stirring at room temperature for 24 h. Final product was isolated and characterized.

Appearance of two peaks at 32.37 and 32.34 ppm in ^{31}P NMR indicated the formation of a mixture of CA3 and CA4 (Figure 4) instead of the expected multicomponent cage (Scheme 2). ^{1}H NMR (Figure S14) also indicates the formation of two products as two different CH_2 peaks appear at 4.96 and 4.84 which correspond to CA3 and CA4, respectively. Also, from ESI-MS (Figure S19) two overlapping isotopic distribution patterns are observed at m/z = 1176 for charge +3, which suggests the formation of mixture of cages CA3 and CA4. The formation of complexes as M_3L_2 is favoured by strong π-π interaction between two central cores of triazine and benzene of CA3 and CA4, respectively. The formation of two different self-assembly in self-sorting suggests the π-π interaction is more favourable between two central triazine in case of CA3 and between two central benzene in case of CA4 than π-π interaction between benzene and triazine.



Scheme 2 Self-sorting reaction between *cis*-Pd(dppf)$(OTf)_2$ with L1 and L2 in CH_3NO_2 shows the formation of two different self-assembly

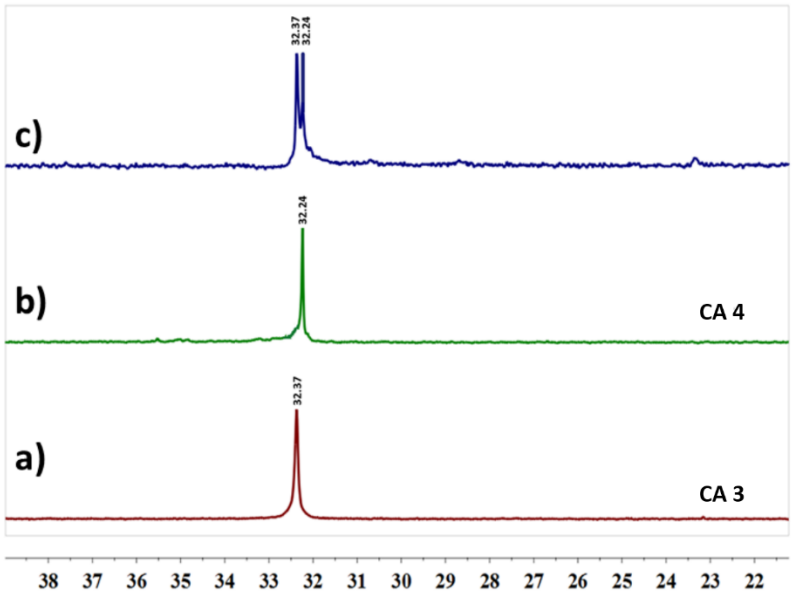


Figure 4 Partial ^{31}P NMR spectra of **a)** cage CA3, **b)** cage CA4 and **c)** self-sorting reaction of CA3 and CA4 recorded in CD_3CN.

4. Conclusion

In this article we report the synthesis of bifacial M_3L_2 nanocage via coordination-driven self-assembly without using any template. All cages were fully characterized by spectroscopic techniques and we were successful in obtaining single crystals of CA3 and CA4. The formation of M_3L_2 self-assembly in all cases is favoured by a strong π-π interaction between two electron deficient cores of ligands. All cages show a much reduced cavity size, which makes them unfavourable for any guest encapsulation. Both types of cage with ligand L1 and L2 are highly stable and do not lose their identity as evident from self-sorting reaction.

Acknowledgments

P.S.M thanks the Council of Scientific and Industrial Research (CSIR-India), India, for financial support. Authors sincerely thank Dr. Prodip Howlader for his kind help in structure analysis.

Appendix A. Supplementary Information

Schemes of synthesis of the ligands, ^{1}H NMR, ^{13}C NMR and ESI-MS of two cages. CCDC numbers [CCDC: 1894555(CA3); 1894704(CA4)] carry the crystallographic details of the structures.

References

[1] J. M. Grimes et al., Nature. 395 (1998) 470-478.

[2] W. R. Wikoff et al., Science. 289 (2000) 2129-2133.

[3] D. L. D. Caspar, A. Klug, Cold Spring Harbor Symp. Quant. Biol. 27 (1962) 1-24.

[4] L. Liljas, T. Unge, T. A. Jones, K. Fridborg, S. Lo¨vgren, U. Skoglund and B. Strandberg, J. Mol. Biol. 159 (1982) 93–108.

[5] R. W. Horne, Virus Structure (Academic Press, New York, 1974).

[6] S. Casjens, Virus Structure and Assembly (Jones and Bartlett, Boston, 1985).

[7] G. C. Ford, P. M. Harrison, D. W. Rice, J. M. A. Smith, A. Treffry, J. L. White and J. Yariv, Philos. Trans. R. Soc. London, Ser. B. 304 (1984) 551–565.

[8] D. M. Lawson, P. J. Artymiuk, S. J. Yewdall, J. M. A. Smith, J. C. Livingstone, A. Treffry, A. Luzzago, S. Levi, P. Arosio, G. Cesareni, C. D. Thomas, W. V. Shaw and P. M. Harrison, Nature. 349 (1991) 541–544.

[9] B. V. Prasad, S. Yamaguchi and P. Roy, J. Virol. 66 (1992) 2135–2142.

[10] J. A. Speir, S. Munshi, G. J. Wang, T. S. Baker and J. E. Johnson, Structure. 3 (1995) 63–78.

[11] J. M. Grimes, J. N. Burroughs, P. Gouet, J. M. Diprose, R. Malby, S. Zie´ntara, P. P. C. Mertens and D. I. Stuart, Nature. 395 (1998) 470–478.

[12] Matthew, C. T.; Stoddart, J. F. Synthetic Supramolecular Chemistry. Acc. Chem. Res. 30 (1997) 393–401.

[13] Pedersen, C. J. J. Am. Chem. Soc. 89 (1967) 7017-7036.

[14] Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. *Science*. 295 (2002) 2418–2421.

[15] Lindsey, J. S. Self-Assembly in Synthetic Routes to Molecular Devices. Biological Principles and Chemical Perspectives: A Review. New. J. Chem. 15 (1991) 153– 180.

[16] Lehn, J. M. Supramolecular Chemistry: Concept and Perspectives; VCH: New York, 1995.

[17] A. H. Clever, M. Shionoya, Coord. Chem. Rev. 254 (2010) 2391 –2402.

[18] R. Chakrabarty, P. S. Mukherjee, P. J. Stang, Chem. Rev. 111 (2011) 6810 –6918.

[19] S. Liu, Y.-F. Han, G.-X. Jin, Chem. Soc. Rev. 36 (2007) 1543 –1560.

[20] Y.-F. Han, G.- X. Jin, Acc. Chem. Res. 47 (2014) 3571 –3579.

[21] A. Castilla, W. Ramsay, J. R. Nitschke, Acc. Chem. Res. 47 (2104) 2063 –2073.

[22] J. R. Nitschke, Acc. Chem. Res. 40 (2007) 103– 112.

[23] M. Han, D. M. Engelhard, G. H. Clever, Chem. Soc. Rev. 43 (2014) 1848 – 1860.

[24] M. D. Pluth, K. N. Raymond, Chem. Soc. Rev. 36 (2007) 161 –171.

[25] Y. Takezawa, M. Shionoya, Acc. Chem. Res. 45 (2012) 2066 –2076.

[26] T. R. Cook, Y. Zheng, P. J. Stang, Chem. Rev. 113 (2013) 734 –777.

[27] P. Wang, C. N. Moorefield, G. R. Newkome, Angew. Chem. Int. Ed. 44 (2005) 1679–1683.

[28] J. Heo, C. A. Mirkin, Angew. Chem. Int. Ed. 45 (2006) 941 –944.

[29] M. Wang, C. Wang, X.-Q. Hao, X. Li, T. J. Vaughn, Y.-Y. Zhang, Y. Yu, Z.-Y. Li, M.-P. Song, H.-B. Yang, X. Li, J. Am. Chem. Soc. 136 (2014) 10499–10507.

[30] C. S. Wood, T. K. Ronson, A. M. Belenguer, J. J. Holstein, J. R. Nitschke, Nat. Chem. 7 (2015) 354 –358.

[31] M. Fujita, J. Yazaki, K. Ogura, J. Am. Chem. Soc. 112 (1990) 5645 –5647.

[32] P. J. Stang, D. H. Cao, J. Am. Chem. Soc. 116 (1994) 4981 –4982.

[33] C. J. Kuehl, Y. K. Kryschenko, U. Radhakrishnan, S. R. Seidel, S. D. Huang, P. J. Stang, Proc. Natl. Acad. Sci. USA. 99 (2002) 4932 – 4936.

[34] A. M. Brown, M. V. Ovchinnikov, C. L. Stern, C. A. Mirkin, J. Am. Chem. Soc. 126 (2004) 14316 – 14317.

[35] K. Nakabayashi, M. Kawano, M. Yoshizawa, S. Ohkoshi, M. Fujita, J. Am. Chem. Soc. 126 (2004) 16694 – 16695.

[36] B. Olenyuk, J. A. Whiteford, A. Fechtenkotter, P. J. Stang, Nature. 398 (1999) 796 – 799.

[37] B. Olenyuk, M. D. Levin, J. A. Whiteford, J. E. Shield, P. J. Stang, J. Am. Chem. Soc. 121 (1999) 10434 – 10435.

[38] S. J. Lee, W. Lin, J. Am. Chem. Soc. 124 (2002) 4554 – 4555.

[39] V. M. Dong, D. Fiedler, B. Carl, R. G. Bergman, K. N. Raymond, J. Am. Chem. Soc. 128 (2006) 14464 –14465.

[40] K. Harano, S. Hiraoka, M. Shionoya, J. Am. Chem. Soc. 129 (2007) 5300 –5301.

[41] A. K. Bar, R. Chakrabarty, G. Mostafa, P. S. Mukherjee, Angew. Chem. Int. Ed. 47 (2008) 8455 – 8459.

[42] W. Meng, J. K. Clegg, J. D. Thoburn, J. R. Nitschke, J. Am. Chem. Soc. 133 (2011) 13652– 13660.

[43] M. Wang, C. Wang, X.-Q. Hao, X. Li, T. J. Vaughn, Y.-Y. Zhang, Y. Yu, Z.-Y. Li, M.-P. Song, H.-B. Yang, X. Li, J. Am. Chem. Soc. 136 (2014) 10499–10507.

[44] C. S. Wood, T. K. Ronson, A. M. Belenguer, J. J. Holstein, J. R. Nitschke, Nat. Chem. 7 (2015) 354 –358.

[45] P. Das, A. Kumar, P. Howlader, P. S. Mukherjee, Chem. Eur. J. 23 (2017) 12565-12574.

[46] M. Mastalerz, I. M. Oppel, Angew. Chem. Int. Ed. 51 (2012) 5252 –5255.

[47] L.-J. Chen, S. Chen, Y. Qin, L. Xu, G.-Q. Yin, J.-L. Zhu, F.-F. Zhu, W. Zheng, X. Li, H.-B. Yang, J. Am. Chem. Soc. 140 (2018) 5049–5052.

[48] C.-B. Huang, L. Xu, J.-L. Zhu, Y.-X. Wang, B. Sun, X. Li, H.-B. Yang, J. Am. Chem. Soc. 139 (2017) 9459–9462.

[49] S. Datta, M.L. Saha, P.J. Stang, Acc. Chem. Res. 51 (2018) 2047–2063.

[50] C.-W. Zhang, B. Ou, S.-T. Jiang, G.-Q. Yin, L.-J. Chen, L. Xu, X. Li, H.-B. Yang, Polym. Chem. 9 (2018) 2021–2030.

[51] W.-J. Fan, B. Sun, J. Ma, X. Li, H. Tan, L. Xu, Chem. Eur. J. 21 (2015) 12947–12959.

[52] L. Xu, Y.-X. Wang, H.-B. Yang, Dalt. Trans. 44 (2015) 867–890.

[53] L. Xu, L.-J. Chen, H.-B. Yang, Chem. Commun. 50 (2014) 5156–5170.

[54] T. S. Koblenz, J. Wassenaar, J. N. H. Reek, Chem. Soc. Rev. 37 (2008) 247– 262.

[55] C. A. Wiley, L. R. Holloway, T. F. Miller, Y. Lyon, R. R. Julian, R. J. Hooley, Inorg. Chem. 55 (2016) 9805– 9815.

[56] A. M. Johnson, R. J. Hooley, Inorg. Chem. 50 (2011) 4671– 4673.

[57] A. M. Johnson, O. Moshe, A. S. Gamboa, B. W. Langloss, J. F. K. Limtiaco, C. K. Larive, R. J. Hooley, Inorg. Chem. 50 (2011) 9430 –9442.

[58] L. R. Holloway, H. H. McGarraugh, M. C. Young, W. Sontising, G. J. O. Beran, R. J. Hooley, Chem. Sci. 7 (2016) 4423 – 4427.

[59] B. Sun, M. Wang, Z. Lou, M. Huang, C. Xu, X. Li, L.-J. Chen, Y. Yu, G. L. Davis, B. Xu, H.-B. Yang, X. Li, J. Am. Chem. Soc. 137 (2015) 1556– 1564.

[60] B. Song, Z. Zhang, K. Wang, C.-H. Hsu, O. Bolarinwa, J. Wang, Y. Li, G.-Q. Yin, E. Rivera, H.-B. Yang, C. Liu, B. Xu, X. Li, Angew. Chem. Int. Ed. 56 (2017), 5258 –5262.

[61] W. Zheng, L.-J. Chen, G. Yang, B. Sun, X. Wang, B. Jiang, G.-Q. Yin, L. Zhang, X. Li, M. Liu, G. Chen, H.-B. Yang, J. Am. Chem. Soc.138 (2016) 4927 –4937.

[62] M. Wang, K. Wang, C. Wang, M. Huang, X.-Q. Hao, M.- Z. Shen, G.-Q. Shi, Z. Zhang, B. Song, A. Cisneros, M.-P. Song, B. Xu, X. Li, J. Am. Chem. Soc. 138 (2016) 9258 – 9268.

[63] Y. Li, Z. Jiang, M. Wang, J. Yuan, D. Liu, X. Yang, M. Chen, J. Li, X. Yan, P. Wang, J. Am. Chem. Soc. 138 (2016) 10041 –10046.

[64] A. M. Johnson, M. C. Young, X. Zhang, R. R. Julian, R. J. Hooley, J. Am. Chem. Soc. 135 (2013) 17723 – 17726.

[65] X. Lu, X. Li, Y. Cao, A. Schultz, J.-L. Wang, C. N. Moorefield, C. S. Wesdemiotis, Z. D. Cheng, G. R. Newkome, Angew. Chem. Int. Ed. 52 (2013) 7728 – 7731.

[66] Z. Zhao, Y.-R. Zheng, M. Wang, J. B. Pollock, P. J. Stang, Inorg. Chem. 49 (2010) 8653 – 8655.

[67] M. Wang, Y.-R. Zheng, K. Ghosh, P. J. Stang, J. Am. Chem. Soc.132 (2010) 6282 – 6283.

[68] Y.-R. Zheng, Z. Zhao, M. Wang, K. Ghosh, J. B. Pollock, T. R. Cook, P. J. Stang, J. Am. Chem. Soc. 132 (2010) 16873 – 16882.

[69] D. Samanta, P. S. Mukherjee, Chem. Commun. 49 (2013) 4307– 4309.

[70] T. K. Ronson, B. S. Pilgrim, J. R. Nitschke, J. Am. Chem. Soc. 138 (2016) 10417 – 10420.

[71] W. Brenner, T. K. Ronson, J. R. Nitschke, J. Am. Chem. Soc. 139 (2017) 75–78.

[72] Z. J. Wang, C. J. Brown, R. G. Bergman, K. N. Raymond, F. D. Toste, J. Am. Chem. Soc. 33 (2011) 7358 –7360.

[73] M. D. Pluth, R. G. Bergman, K. N. Raymond, Science 316 (2007) 85–88.

[74] S. Wang, T. Sawada, M. Fujita, Chem. Commun. 52 (2016) 11653 – 11656.

[75] M. Schmittel, B. He, P. Mal, Org. Lett. 10 (2008) 2513 –2516.

[76] K. Ono, M. Yoshizawa, T. Kato, M. Fujita, Chem. Commun. 0 (2008) 2328 – 2330.

[77] J. Lee, K. Ghosh, P. J. Stang, J. Am. Chem. Soc. 131 (2009) 12028 –12029.

[78] D. Samanta, S. Shanmugaraju, S. A. Joshi, Y. P. Patil, M. Nethaji, P. S. Mukherjee, Chem. Commun. 48 (2012) 2298 – 2300.

[79] A. K. Bar, S. Raghothama, D. Moon, P. S. Mukherjee, Chem. Eur. J. 8 (2012) 3199 – 3209.

[80] X. Ji, J. Chen, X. Chi, F. Huang, ACS Macro Lett. 3 (2014) 110–113.

[81] D. Xia, G. Yu, J. Li, F. Huang, Chem. Commun. 50 (2014) 3606 – 3608.

[82] X. Yan, B. Jiang, T. R. Cook, Y. Zhang, J. Li, Y. Yu, F. Huang, H.-B. Yang, P. J. Stang, J. Am. Chem. Soc. 135 (2013) 16813 – 16816.

[83] X. Yan, S. Li, T. R. Cook, X. Ji, Y. Yao, J. B. Pollock, Y. Shi, G. Yu, J. Li, F. Huang, P. J. Stang, J. Am. Chem. Soc. 135 (2013) 14036 –14039.

[84] D. Samanta, S. Mukherjee, Y. P. Patil, P. S. Mukherjee, Chem. Eur. J. 18 (2102) 12322–12329.

[85] P. Wei, X. Yan, F. Huang, Chem. Soc. Rev. 44 (2015) 815 –832.

[86] X.-Y. Hu, T. Xiao, C. Lin, F. Huang, L. Wang, Acc. Chem. Res. 47 (2014), 2041–2051.

[87] P. Wei, T. R. Cook, X. Yan, F. Huang, P. J. Stang, J. Am. Chem. Soc. 136 (2014), 15497 –15500.

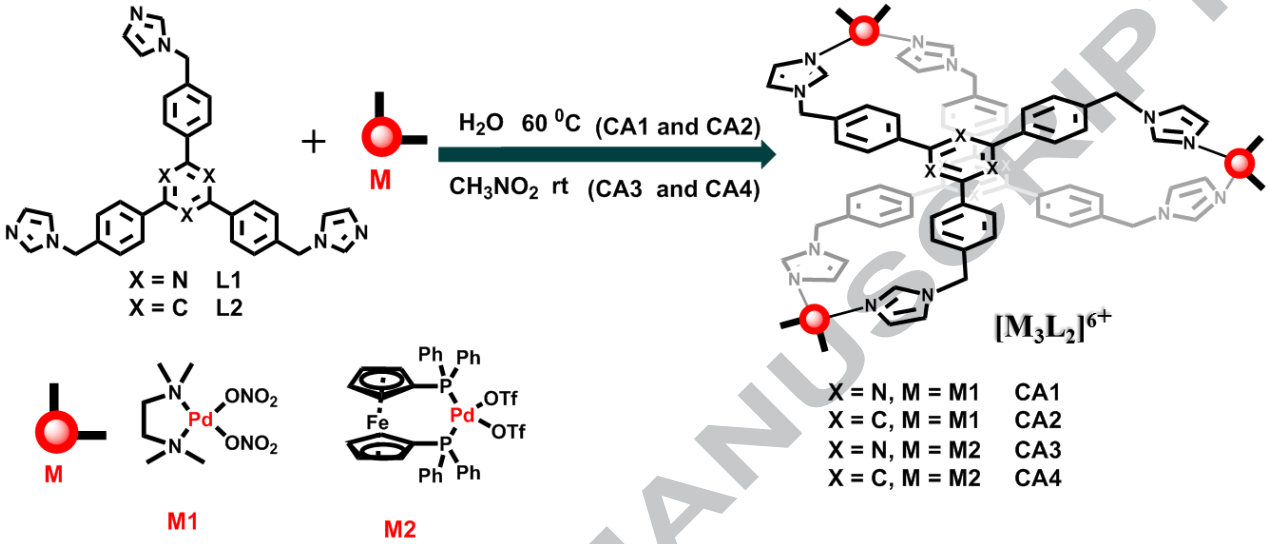
[88] G. Sheldrick,Acta Crystallogr. Sect. A. 71 (2015) 3–8.

[89] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H.Puschmann,J. Appl. Crystallogr. 42 (2009) 339–341.

[90] A. Spek,Acta Crystallogr. Sect. C. 71 (2015) 9–18.

Self-assembled Pd_3L_2 cages having flexible tri-imidazole donors

Atul Kumar, Ennio Zangrando, Partha Sarathi Mukherjee*



Four new Pd_3L_2 self-assembled molecular cages consisting of flexible tri-imidazole donors have been synthesized and characterized. Two of such cages are soluble in water, while the other two are soluble in organic solvents.