Coordination driven self-assembly of four new molecular boats using a flexible imidazole-containing donor linker†‡

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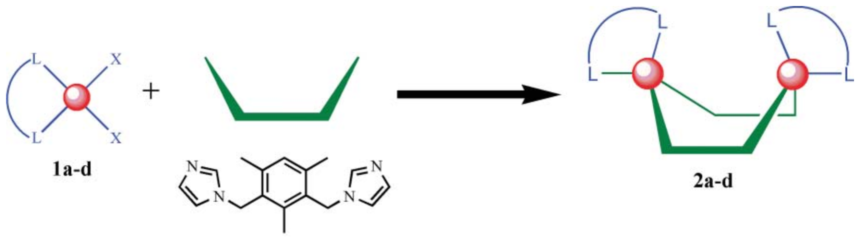
Received 7th September 2007, Accepted 19th December 2007
First published as an Advance Article on the web 6th February 2008
DOI: 10.1039/b713783d

Using a metal–ligand coordination bonding approach, the self-assembly of four new metallamacrocycles from Pd(II)-based 90° acceptors and a diimidazole donor ligand 1,3-bis(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene (**L**) has been achieved. The assemblies are characterized fully by NMR and electrospray ionization-mass spectroscopic (ESI-MS) analysis and in two cases the X-ray single-crystal structure analysis established the gross structures. The selective formation of a diimidazole-based linker (**L**) containing macrocycle $[(en)Pd(\mu\text{-L})_2Pd(en)]^{4+}$ from a 1 : 1 : 1 mixture of *cis*-$Pd(en)(NO_3)_2$, **L** and 1,2-bis(4-pyridyl)ethane is also established. Measuring the binding constants established the stronger Pd–**L** binding force compared to traditional Pd–N(pyridyl linker) interaction, which reveals the possibility of using imidazole donor ligands as potential linkers or even better ligands compared to the widely used pyridyl donor ligands in the construction of metal-based large supramolecular assemblies.

Introduction

From the beginning of the first organic chemistry reaction, enormous efforts have been made to discover of large and complicated synthetic molecules. During the last decades, chemists have shown particular interest in the directional self-assembly approach as an alternative way to build larger and more complex molecules.[1] This synthetic self-assembly may be guided by a range of interactions like: H-bonding, π–π interaction, van der Waals forces or by metal–ligand coordination. We are mainly interested in the self-assembly *via* coordination.[2] Coordination self-assembly has been demonstrated to be a useful and powerful alternative for the construction of predefined and well-organized architectures. Several discrete assemblies including extended polymeric frameworks have been reported in the last few years.[1,3] The important requirement for this process is the use of rigid precursors of appropriate shapes and symmetries. Square planar Pt(II) and Pd(II) have long been used as favorite acceptors in this area. In a majority of the cases, symmetrical and rigid polypyridyl ligands have been used as donors for this purpose with a few recent exceptions where we used oxygen-donor linkers.[4] On the other hand, flexible linkers are less predictable in self-assembly and have a tendency to form undesired polymers. However, flexible linkers may generate pseudo-rigid assemblies[5] that can distort their shapes to obtain a more thermodynamically stable conformation for host–guest interactions. As the use of pyridyl-donor ligands dominates the present literature, our interest was in incorporating a different kind of imidazole-type donor linker as well as the flexibility into Pd(II)-based metallasupramolecules.

Here we report the self-assembly of four new molecular boats (Scheme 1) of general formula $[(AA)_2Pd_2(\mu\text{-}\mathbf{L})_2](NO_3)_4$ (**2a–d**) using a flexible diimidazole donor ligand 1,3-bis(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene (**L**) and the corresponding *cis*-blocked acceptors $(AA)Pd(NO_3)_2$ (**1a–d**) [where AA = 1,2-ethanediamine (**1a**); 1,2-propanediamine (**1b**); 2,2′-bipyridyl (**1c**)



2a: LL = en; X = NO_3^-
2b: LL = 1,2-diaminopropane; X = NO_3^-
2c: LL = 2,2′-bipyridyl; X = NO_3^-
2d: LL = N^1, N^1, N^2, N^2-tetramethylethane-1,2-diamine; X = NO_3^-

Scheme 1 Self-assembly of **2a–d** from the analogous acceptors **1a–d** and the donor **L**.

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† CCDC reference numbers 659976 and 659977. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713783d

‡ Electronic supplementary information (ESI) available: ^1H NMR spectra of **2b–d**. See DOI: 10.1039/b713783d

and *N*,*N*,*N′*,*N′*-tetramethylethanediamine (**1d**)]. All these assemblies are characterized by NMR, mass spectrometry and in two cases (**2a** and **2b**), X-ray crystallography.† A preliminary investigation established that imidazole donor linkers could also be used as potential bridging ligands in directed self-assembly and this could be even better than the widely used pyridyl linkers. Despite the possibility of forming a bpe-bridged [bpe = 1,2-bis(4-pyridyl)ethane] macrocycle $[(en)Pd(\mu\text{-bpe})_2Pd(en)](NO_3)_4$, the self-selection of **2a** $[(en)Pd(\mu\text{-}\mathbf{L})_2Pd(en)](NO_3)_4$ was exclusively achieved by treating a 1 : 1 mixture of **L** and 1,2-bis(4-pyridyl)ethane (bpe) with one equivalent *cis*-$[(en)Pd(NO_3)_2]$ (**1a**).

Experimental

Synthesis

1a–d were synthesized from the corresponding dichlorides by treating with two equivalents of $AgNO_3$ in distilled water.[6] The corresponding dichlorides were prepared using the published procedure.[6b–c] All solvents were received from commercial sources and distilled prior to use. Deuterated solvents and 1,2-bis(4-pyridyl)ethane (bpe) were purchased from Aldrich. The elemental analyses were done using a Thermo Finnigan Flash EA 1112 CHNSO analyzer. NMR spectra were recorded on a Bruker 400 spectrometer and ^1H NMR chemical shifts (**2a–d**) are reported relative to the residual protons of deuterated methanol (δ 3.3 ppm). Mass spectra were obtained using an electrospray ionization (ESI) source. UV-visible spectra were recorded on a Perkin-Elmer spectrophotometer.

Synthesis of the ligand L

Imidazole (0.4 g, 6.0 mmol) and potassium hydroxide (1.4 g, 25 mmol) were dissolved in dimethylsulfoxide (DMSO) (15 ml) and the solution was stirred for 2 h at room temperature, then 1,3-bis(bromomethyl)-2,4,6-trimethylbenzene (0.84 g, 3.0 mmol) was added. After stirring for another 3 h at room temperature, an equivalent volume of water was added to the mixture. The aqueous solution was extracted with chloroform (4 × 10 ml) and the chloroform solution was dried over anhydrous sodium sulfate and filtered. Solvent was removed on a rotary evaporator and excess diethyl ether was added to the residue. After standing overnight at −10 °C, the white powder was filtered, washed with diethyl ether and dried in a vacuum desiccator. Yield: 73%. ^1H NMR ($CDCl_3$, ppm): δ 2.19 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 5.15 (s, 4H, CH_2), 6.74 (s, 2H, imidazole-H), 7.02 (s, 2H, imidazole-H), 7.04 (s, 1H, Ar-H), 7.30 (s, 2H, imidazole-H).

General procedure for the synthesis of assemblies 2a–d

To a stirred solution of the appropriate corner linker (**1a–d**) (0.06 mmol) in methanol was added a solution of **L** [**L** = 1,3-bis(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene] (16.82 mg, 0.06 mmol) in methanol and it was kept under stirring for 4 h. Precipitating out by ether addition isolated the products.

2a: ^1H NMR (MeOH-d_4, 400 Mz): δ 7.68 (s, 4H, imidazole-H), 7.44 (s, 4H, imidazole-H), 7.1 (s, 4H, imidazole-H); 7.05 (s, 2H, ArH); 5.28 (s, 8H, CH_2); 4.5(broad, 8H, NH_2); 2.76 (s, 8H, CH_2); 2.23 (s, 6H, CH_3); 2.13 (s, 12H, CH_3); Yield: 94%. Anal. calcd for $C_{38}H_{56}O_{12}N_{16}Pd_2$: C 39.97%; H 4.97%; N 19.63%. Found: C, 39.71; H, 4.88; N, 19.40%.

2b: ^1H NMR (MeOH-d_4, 400 MHz): δ 7.7 (dd, 4H, imidazole-H), 7.43 (s, 4H, imidazole-H), 7.08 (s, 4H, imidazole-H), 7.05 (s, 2H, ArH), 5.28 (s, 8H, CH_2), 3.34 (s, 4H, CH_2), 2.75 (m, 2H, CH), 2.21 (s, 6H, CH_3), 2.14 (d, 6H, CH_3), 1.2 (d, 12H, CH_3); Yield: 96%. Anal. calcd for $C_{40}H_{60}N_{16}O_{12}Pd_2$: C 41.07%; H 5.17%; N 19.16%. Found: C, 40.91; H, 4.86; N, 19.32%

2c: ^1H NMR (MeOH-d_4, 400 MHz): 8.31 (m, 4H, bpy-H), 8.22 (m, 4H, bpy-H), 8.04 (s, 4H, imidazole-H), 7.6 (s, 4H, imidazole-H), 7.49 (m, 8H, bpy-H), 7.31 (s, 4H, imidazole-H), 7.1 (s, 2H, Ar-H), 5.37 (s, 8H, CH_2), 2.4 (s, 6H, CH_3), 2.14 (s, 12H, CH_3); ESI-MS: $[M\text{-}2NO_3]^{2+}$ [m/z = 604.2 (calcd 604.12)] and $[M\text{-}4NO_3]^{4+}$ [m/z = 271.1 (calcd 271.06)]. Yield: 90%. Anal. calcd for $C_{54}H_{56}N_{16}O_{12}Pd_2$: C 48.62%; H 4.23%; N 16.80%. Found: C, 48.69; H, 4.83; N, 16.49%.

2d: ^1H NMR (MeOH-d_4, 400 MHz): 8.18 (s, 4H, imidazole-H), 7.5 (s, 8H, imidazole-H), 7.06 (s, 2H, Ar-H), 5.29 (s, 8H, CH_2), 2.95 (s, 8H, CH_2), 2.61 (s, 24H, NCH_3), 2.41 (s, 6H, CH_3), 1.95 (s, 12H, CH_3); ESI-MS: $[M\text{-}2NO_3]^{2+}$ [m/z = 564 (calcd 564.18)]; $[M\text{-}3NO_3]^{3+}$ [m/z = 355.5 (calcd 355.45)] and $[M\text{-}4NO_3]^{4+}$ [m/z = 251.3 (calcd 251.09)]. Yield: 93%. Anal. calcd for $C_{46}H_{72}N_{16}O_{12}Pd_2$: C 44.06%; H 5.79%; N 17.87%. Found: C, 44.39; H, 5.53; N, 17.65%.

X-Ray data collection† and refinements

Colorless crystals of **2a** and **2b** were mounted on glass fiber with traces of viscous oil and then transferred to a Bruker SMART APEX CCD diffractometer, equipped with a fine-focus sealed-tube Mo Kα X-ray source. SMART was used for data acquisition, and SAINT was used for data extraction. The crystals were positioned at 50 mm from the goneometer. Data for **2a** were collected at 150 K while for **2b** data were collected at 293 K. The structures were solved by a combination of direct methods and heavy atom using SIR 97.[7] All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, $U(H) = 1.2U(C)$ or $1.5U$(C-methyl), and their coordinates were allowed to ride on their respective carbons using SHELXL97.[8] The refinement converged to $R_1 = 0.0859$ (**2a**) and 0.0999 (**2b**); $wR_2 = 0.2250$ (**2a**) and 0.2580 (**2b**). The completeness of data as well as the quality of the structure of **2b** was not very satisfactory because of the very poor quality of the crystals. However, the gross connectivity and the dimeric nature of the molecule were clear from the present data set, which was also corroborated from other spectroscopic data.

Results and discussion

Synthesis and spectroscopic characterizations

When the methanolic solution of the ligand **L** [**L** = 1,3-bis(imidazole-1-ylmethyl)-2,4,6-trimethylbenzene] was treated with an equivalent amount of the linker **1a** in methanol, the [2 + 2] self-assembly of the metallamacrocycle **2a** occurred. A 0.38 ppm downfield shift of the proton signal of the C–H proton between the imidazole nitrogens indicated the loss of electron density from the donor **L** to palladium. A similar downfield shift of the other protons of the ligand was also observed upon the self-assembly reaction. ^{1}H NMR of the product also indicated the formation of a symmetrical product by the appearance of all the expected peaks in the product (Fig. 1). Similar treatment of **L** with the corresponding acceptors **1b–d** yielded analogous macrocycles **2b–d**, which were also identified by ^{1}H NMR. Despite the possibility of formation of a mixture of isomeric products (*syn* and *anti*) due to the presence of non-symmetric chelating amine in **1b**, a single isomeric product **2b** was formed exclusively.

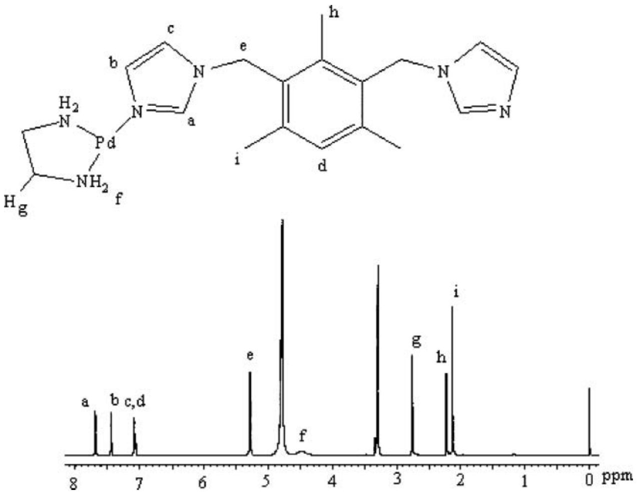


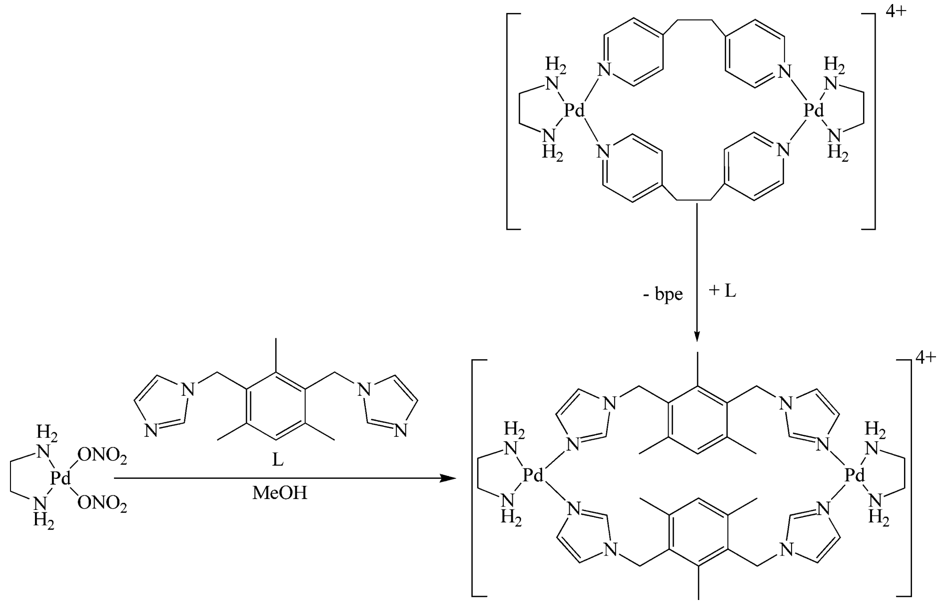
Fig. 1 ^{1}H NMR spectrum of the macrocycle **2a** in d$_4$-MeOH.

Moreover, when a methanolic slurry of the stable known macrocycle **3** [**3** = (en)$_2$Pd$_2$(μ-bpe)$_2$(NO$_3$)$_4$, where bpe = 1,2-bis(4-pyridyl)ethane] was treated with **L** in a 1 : 2 molar ratio, the macrocycle **2a** was immediately formed exclusively along with the release of ligand bpe (Scheme 2). The formation of **2a** and the free bpe was established by the solution-state NMR analysis. Although the ^{1}H NMR is not much informative in this case, the determination of binding constants by the UV-vis spectroscopic method in case of formation of **3** and **2a** corroborated the result.

Structure descriptions

Diffusion of ether into the methanolic solution of **2a** yielded a feather-shaped crystalline material which was not suitable for X-ray crystallography. The methanolic solution of the product was treated with four equivalents of Et$_4$NClO$_4$ to precipitate out the perchlorate salt of the product. Diffraction-quality single crystals of **2a** were grown by ether diffusion into the nitromethane solution of the perchlorate salt of **2a**. However, **2b** was crystallized directly by diffusing ether into the methanol solution of the product. Fig. 2 shows the molecular structures of **2a** and **2b**. Crystallographic parameters are assembled in Table 1. The structure of **2a** looks like a molecular boat with a Pd–Pd distance of 6.6 Å. The geometry around each palladium is square planar with N–Pd(1)–N bond angles in the range of 85.2(4)–94.3(3)° and N–Pd(2)–N angles are in the range of 85.2(4)–93.1(3)°. The distance between the centroids of the opposite benzene rings in **2a** is 7.44 Å. The boat accommodated a nitrate anion and a water molecule inside its belly. The nitrate anion and the water molecule are H-bonded to the NH$_2$ protons. H-bonding between the counter anions, lattice waters and the neighboring macrocyles helps to form an H-bonded supramolecular polymeric network in the solid state.

Similarly, the crystal structure of **2b** shows an identical boat-shaped macrocycle. The geometry around each palladium was almost square planar with the N–Pd(1)–N angles in the range of 85.4(4)–93.3(4)° and N–Pd(2)–N angles in the range of 86.9(5)–92.8(5)°. 1,3,5-Trimethylbenzene groups in the macrocycle are aligning in *anti*-fashion to minimize the steric interactions among the methyl groups. Similarly, the methyl groups of the 1,2-diaminopropane ligands are also oriented in *anti*-fashion. The distance between the centroids of two opposite benzene rings in case of **2b** is 7.52 Å while the intramolecular Pd–Pd distance is 6.6 Å. The packing diagram of **2a** along the crystallographic



Scheme 2 Formation of **2a** from **1a** as well as from **3** [(en)$_2$Pd$_2$(μ-bpe)$_2$]$^{4+}$.

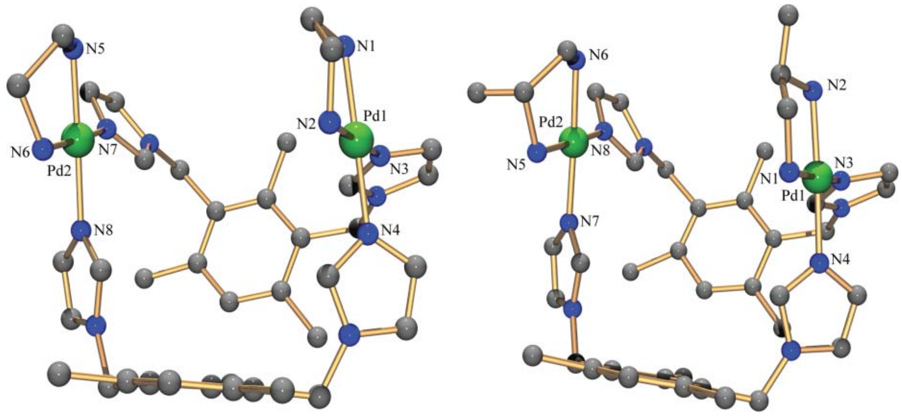


Fig. 2 View of the molecular structures of **2a** (left) and **2b** (right) with atom numbering. Green = Pd; blue = N; grey = C.

Table 1 Crystallographic data and refinement parameters of **2a** and **2b**†

Identification code	**2a**	**2b**
Formula	$C_{39.25}H_{62.75}Cl_3N_{13.25}O_{17.5}Pd_2$	$C_{41}H_{52}N_{16}O_{14}Pd_2$
F_w	1308.59	1205.79
Temp./K	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
λ/Å (Mo-Kα)	0.71073	0.71073
a/Å	14.786(2)	14.723(5)
b/Å	17.297(3)	17.227(6)
c/Å	21.718(3)	22.223(7)
β/°	101.913(3)	99.959(7)
V/Å^3	5434.6(14)	5552(3)
Z	4	4
ρ_{calcd}/mg m^{-3}	1.599	1.426
μ/mm^{-1}	0.888	0.719
$F(000)^a$	2653	2428
Total reflections	37941	39278
Unique data	9561 [R_{int} = 0.0635]	9772 [R_{int} = 0.1200]
R_1	0.0859	0.0999
$wR_2{}^b$	0.2250	0.2580

^{a} $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{b} $R_w = [\sum\{w(F_o{}^2 - F_c{}^2)^2\}/\sum\{w(F_o{}^2)^2\}]^{1/2}$.

c-axis showed the formation of a zigzag chain which is formed by the weak interaction of the counter anions with the bowls. One counter anion as well as a water molecule is entrapped inside the bowl through the weak H-bond among them *via* the amine groups of the 1,2-diaminopropane (Fig. 3). Selected bond parameters for both **2a** and **2b** are assembled in Table 2.

NMR spectroscopy generally provides a preliminary idea of the metal–ligand coordination, the progress of the reaction and the relative ratios of the reacting components. However, it does not provide any information about the molecular weight and the probable shape of this kind of product. ESI mass spectrometry has proven to be a potential tool in the corroboration of structural assignments for these kinds of self-assemblies.[9] ESI mass spectrometry clearly confirmed the $\mathbf{1c_2L_2}$ and $\mathbf{1d_2L_2}$ compositions with the molecular weight of 1332.24 and 1252.36 for **2c** and **2d** respectively. These compositions are analogous to the other two assemblies, which are characterized fully by NMR and single-crystal structure analysis.†

The ESI mass spectrum (Fig. 4) of **2c** showed the signals corresponding to the consecutive loss of nitrate counter anions $[M\text{-}2NO_3]^{2+}$, $[M\text{-}4NO_3]^{4+}$; while **2d** showed signals corresponding to the consecutive loss of counter anions $[M\text{-}2NO_3]^{2+}$, $[M\text{-}3NO_3]^{3+}$ and $[M\text{-}4NO_3]^{4+}$ (M = molecular weight based on the $\mathbf{1c_2L_2}$ and $\mathbf{1d_2L_2}$ compositions). For **2c**: $[M\text{-}2NO_3]^{2+}$ [m/z = 604.2 (calcd 604.12)] and $[M\text{-}4NO_3]^{4+}$ [m/z = 271.1 (calcd 271.06)]. For **2d**: $[M\text{-}2NO_3]^{2+}$ [m/z = 564 (calcd 564.18)]; $[M\text{-}3NO_3]^{3+}$ [m/z = 355.5 (calcd 355.45)] and $[M\text{-}4NO_3]^{4+}$ [m/z = 251.3 (calcd 251.09)]. These molecular compositions are fully consistent with the other dimeric assemblies (**2a** and **2b**). Several attempts to obtain single crystals yielded only powder materials in the cases of **2c** and **2d**.

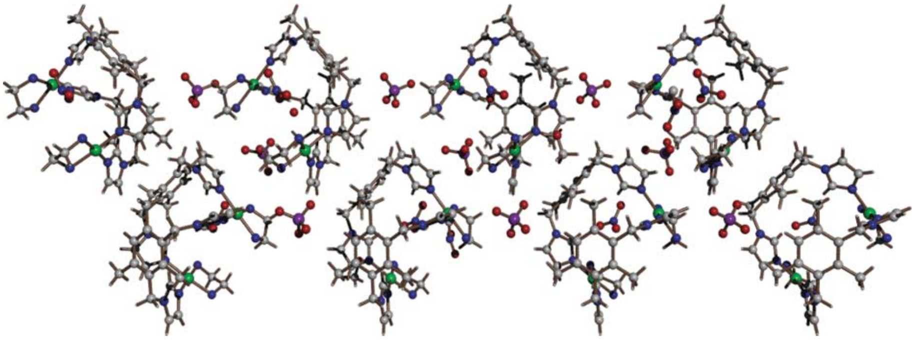


Fig. 3 Packing diagram of **2a** along the crystallographic *c*-axis.

Table 2 Selected bond angles (°) and bond distances (Å) of **2a** and **2b**†

2a					
Pd(1)–N(1)	2.036(8)	N(4)–Pd(1)–N(2)	92.9(4)	N(4)–Pd(1)–N(3)	87.6(3)
Pd(1)–N(2)	2.021(10)	N(2)–Pd(1)–N(3)	179.4(4)	N(4)–Pd(1)–N(1)	178.1(4)
Pd(1)–N(3)	2.027(8)	N(2)–Pd(1)–N(1)	85.2(4)	N(3)–Pd(1)–N(1)	94.3(3)
Pd(1)–N(4)	2.020(8)	N(7)–Pd(2)–N(8)	92.0(3)	N(7)–Pd(2)–N(5)	93.1(3)
Pd(2)–N(5)	2.031(9)	N(8)–Pd(2)–N(5)	174.9(3)	N(7)–Pd(2)–N(6)	177.6(3)
Pd(2)–N(6)	2.036(8)	N(8)–Pd(2)–N(6)	89.8(3)	N(5)–Pd(2)–N(6)	85.2(4)
Pd(2)–N(7)	2.002(8)				
Pd(2)–N(8)	2.027(8)				
2b					
Pd(1)–N(1)	2.029(11)	N(3)–Pd(1)–N(1)	178.0(4)	N(3)–Pd(1)–N(4)	88.3(4)
Pd(1)–N(2)	2.042(9)	N(1)–Pd(1)–N(4)	92.9(4)	N(3)–Pd(1)–N(2)	93.3(4)
Pd(1)–N(3)	2.020(11)	N(1)–Pd(1)–N(2)	85.4(4)	N(4)–Pd(1)–N(2)	177.7(5)
Pd(1)–N(4)	2.033(10)	N(8)–Pd(2)–N(7)	92.8(5)	N(8)–Pd(2)–N(6)	92.1(5)
Pd(2)–N(5)	2.057(12)	N(7)–Pd(2)–N(6)	175.0(5)	N(8)–Pd(2)–N(5)	177.7(5)
Pd(2)–N(6)	2.048(11)	N(7)–Pd(2)–N(5)	88.1(5)	N(6)–Pd(2)–N(5)	86.9(5)
Pd(2)–N(7)	2.036(11)				
Pd(2)–N(8)	1.989(14)				

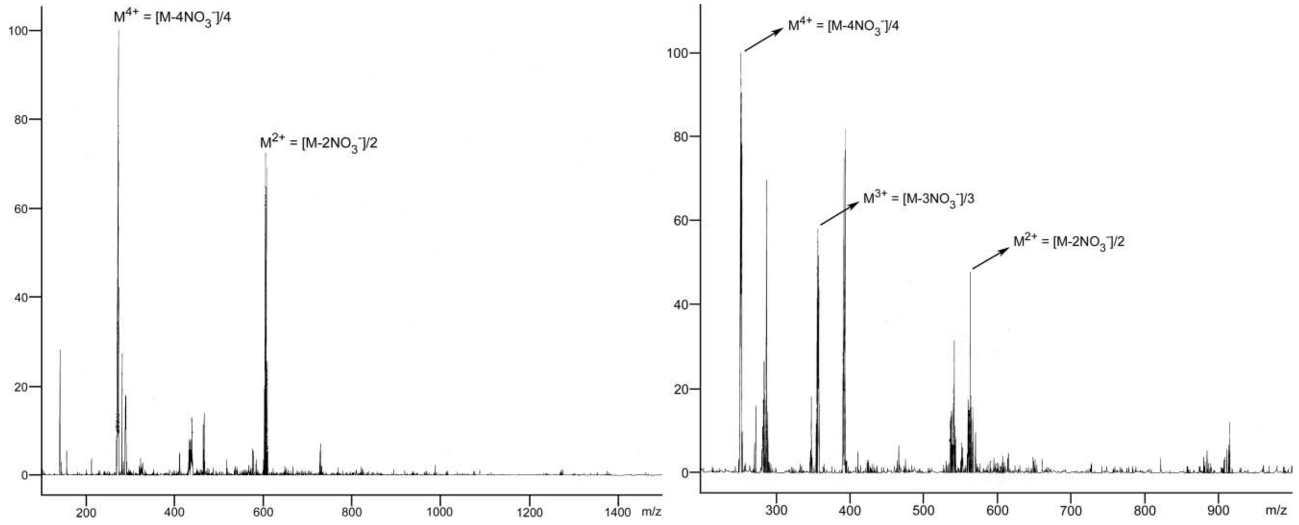


Fig. 4 ESI mass spectra of the complexes **2c** (left) and **2d** (right).

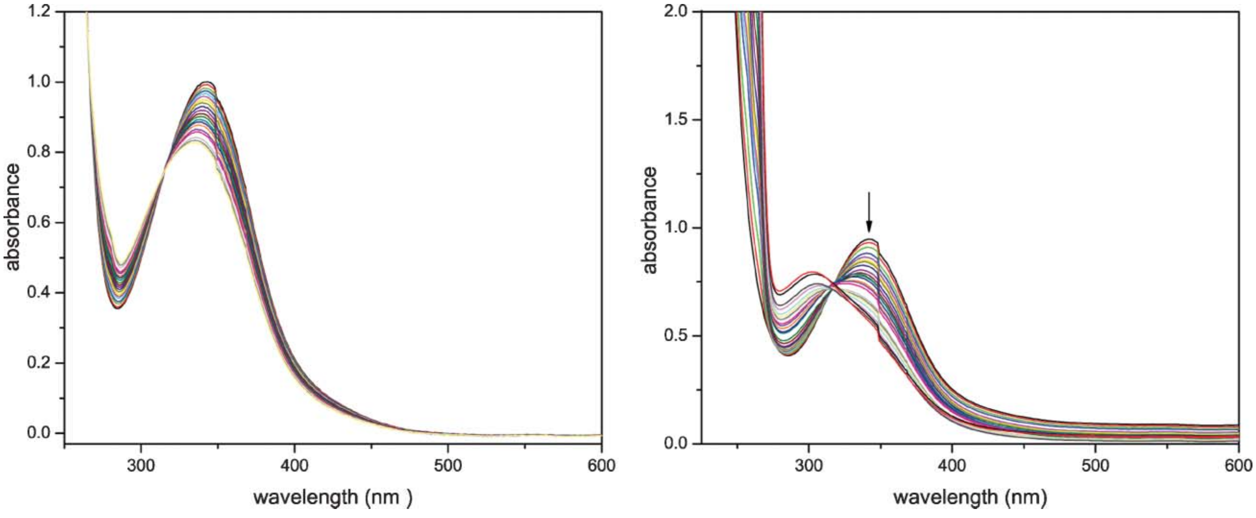


Fig. 5 Plots of optical density *vs.* wavelength for the formation of **2a** (left) and **3** (right).

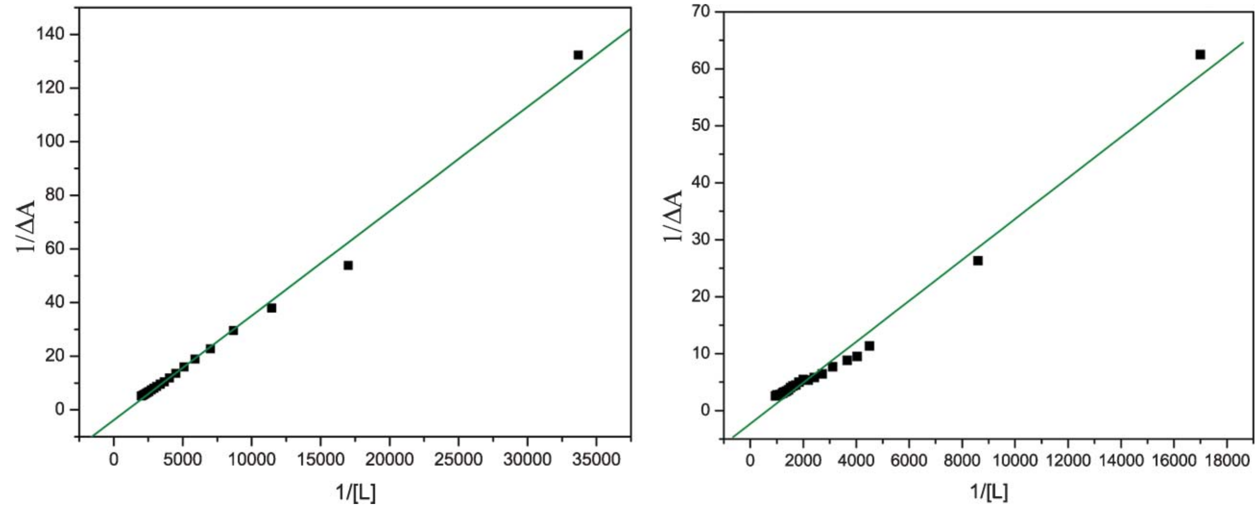


Fig. 6 Plots of $1/\Delta A$ *vs.* $1/[\mathbf{L}]$ for the formations of **2a** (left) and **3** (right).

UV-Visible spectroscopic studies and binding constants determination for 2a and 3

The binding constants for the formation of **2a** and **3** were measured separately by UV-visible spectroscopy. In both the cases the ligand solution was added in small portions to a 3.0×10^{-3} M concentrated solution of $(en)Pd(NO_3)_2$. The plots of optical density *vs.* wavelength for the corresponding titrations are shown in Fig. 5. The isosbestic points at 320 nm in both cases are due to 1 : 1 binding for **2a** and **3**. Binding constants were determined [976.55 and 608.34 M^{-1} for **2a** and **3** respectively] by applying the binding isotherm equation, and plotting $1/\Delta A$ *vs.* $1/[\mathbf{L}]$ as shown in Fig. 6. It was found that the binding constant for the formation of **2a** is 1.6 times greater than that of **3**. This may be due to the stronger binding of the imidazole ligand than the widely used pyridyl ligand with palladium.

In conclusion, we report here the synthesis and the spectral and structural characterizations of a series of metallamacrocycles derived from *cis*-blocked 90° Pd(II) acceptors and a diimidazole-donor flexible ligand (**L**). NMR, ESI mass spectrometry and single-crystal structure determination in two cases† clearly established the formation of pseudo-boat-shaped macrocycles (**2a–d**). Binding constants measurements as well as the facile formation of **2a** from the stable dipyridyl analogue **3** revealed the possibility of using the imidazole donor ligand as a potential linker or an even better ligand compared to the widely used pyridyl donor ligands in the construction of large metal-based supramolecular assemblies.

Acknowledgements

We thank the Department of Science and Technology, New Delhi (under the fast track scheme); and the Council for the Scientific and Industrial Research (CSIR), New Delhi, India, for financial support.

References

1 (*a*) J.-M. Lehn, *Supramolecular Chemistry, Concept and Perspectives*, VCH, NewYork, 1995; (*b*) S. R. Seidel and P. J. Stang, *Acc. Chem. Res.*, 2002, **35**, 972; (*c*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; (*d*) U. N. Nehete, G. Ananthraman, V. Chandrasekhar, R. Murugavel, H. W. Roesky, D. Vidovic, J. Mgull, K. Samwer and B. J. Sass, *Angew. Chem., Int. Ed.*, 2004, **43**, 3832; (*e*) F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; (*f*) V. Maurizot, M. Yoshizawa, M. Kawano and M. Fujita, *Dalton Trans.*, 2006, 2750; (*g*) S. J. Cantrill, K. S. Chichak, A. J. Peters and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 1; (*h*) G. F. Swiegers and T. J. Malefetse, *Coord. Chem. Rev.*, 2002, **225**, 91; (*i*) J. D. Badjic, A. Nelson, S. J. Cantrill, W. B. Turnbull and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 723; (*j*) S. J. Cantrill, K. S. Chichak, A. J. Peters and J. F. Stoddart, *Acc. Chem. Res.*, 2005, **38**, 1; (*k*) M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; (*l*) E. Uller, I. Demleitner, I. Bernt and R. W. Saalfrank, *Synergistic Effect of Serendipity and Rational Design in Supramolecular Chemistry: Structure and Bonding*, Springer, Berlin, 2000, vol. 96, p. 149; (*m*) D. L. Caulder and K. N. Raymond, *J. Chem. Soc., Dalton Trans.*, 1999, 1185; (*n*) D. L. Caulder and K. N. Raymond, *Acc. Chem. Res.*, 1999, **32**, 975; (*o*) P. N. W. Baxter, J. M. Lehn, G. Baum and D. Fenske, *Chem.–Eur. J.*, 1999, **5**, 102; (*p*) M. Fujita, *Chem. Soc. Rev.*, 1998, **27**, 417.

2 (*a*) S. Ghosh and P. S. Mukherjee, *J. Org. Chem.*, 2006, **71**, 8412; (*b*) P. S. Mukherjee, N. Das and P. J. Stang, *J. Org. Chem.*, 2004, **69**, 3526; (*c*) S. Ghosh, S. R. Batten, D. Turner and P. S. Mukherjee, *Organometallics*, 2007, **26**, 3252; (*d*) S. Ghosh and P. S. Mukherjee, *Organometallics*, 2007, **26**, 3362; (*e*) K. C. Mondal, M. G. B. Drew and P. S. Mukherjee, *Inorg. Chem.*, 2007, **46**, 5625; (*f*) S. Ghosh and P. S. Mukherjee, *Tetrahedron Lett.*, 2006, **47**, 9297; (*g*) S. Ghosh and P. S. Mukherjee, *Dalton Trans.*, 2007, 2542; (*h*) S. Ghosh, D. Turner, S. R. Batten and P. S. Mukherjee, *Dalton Trans.*, 2007, 1869; (*i*) K. C. Mondal, Y. Song and P. S. Mukherjee, *Inorg. Chem.*, 2007, **46**, 9736; (*j*) P. S. Mukherjee, K. S. Min, A. M. Arif and P. J. Stang, *Inorg. Chem.*, 2004, **43**, 6345; (*k*) K. C. Mondal, O. Sengupta, M. Nethaji and P. S. Mukherjee, *Dalton Trans.*, 2008, DOI: 10.1039/b715460g; (*l*) O. Sengupta, R. Chakrabarty and P. S. Mukherjee, *Dalton Trans.*, 2007, 4514; (*m*) P. S. Mukherjee, N. Lopez, A. M. Arif, F. Cervantes-Lee and J. C. Noveron, *Chem. Commun.*, 2007, 1433.

3 (*a*) S. Koner, E. Zangrando, F. Lloret and N. Ray Chaudhuri, *Angew. Chem., Int. Ed.*, 2002, **42**, 1562; (*b*) A. K. Ghosh, D. Ghoshal, J. Ribas, G. Mostafa and N. Ray Chaudhuri, *Cryst. Growth Des.*, 2006, **6**, 36; (*c*) T. K. Maji, S. Sain, G. Mostafa, T. H. Lu, J. Ribas and N. Ray Chaudhuri, *Inorg. Chem.*, 2003, **42**, 709; (*d*) K. W. Chi, C. Addicott, A. M. Arif, N. Das and P. J. Stang, *J. Org. Chem.*, 2003, **68**, 9798; (*e*) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 7740; (*f*) F. M. Tabellion, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2001, **123**, 11982; (*g*) S. Hiraoka and M. Fujita, *J. Am. Chem. Soc.*, 1999, **121**, 10239–10240; (*h*) M.-C. Brandys and R. J. Puddephatt, *J. Am. Chem. Soc.*, 2001, **123**, 4839; (*i*) Z. Qin, M. C. Jennings and R. J. Puddephatt, *Inorg. Chem.*, 2001, **40**, 6220; (*j*) J. W. Steed, D. R. Turner and K. J. Wallace, *Core Concepts in Supramolecular Chemistry and Nanochemistry*, John Wiley & Sons, Ltd., New York, 2007; (*k*) C. H. M. Amijs, G. P. M. van Klink and G. van Koten, *Dalton Trans.*, 2006, 308; (*l*) M. S. Vickers and P. D.

Beer, *Chem. Soc. Rev.*, 2007, **2**, 211; (*m*) K. Y. Ng, A. R. Cowley and P. D. Beer, *Chem. Commun.*, 2006, 3676; (*n*) D. Curiel and P. D. Beer, *Chem. Commun.*, 2005, 1909; (*o*) A. S. R. Chesman, D. R. Turner, D. J. Price, B. Moubaraki, K. S. Murray, G. B. Deacon and S. R. Batten, *Chem. Commun.*, 2007, 3541; (*p*) A. S. R. Chesman, D. R. Turner, E. I. Izgorodina, S. R. Batten and G. B. Deacon, *Dalton Trans.*, 2007, 1371.

4 (*a*) Y. K. Kryschenko, S. R. Seidel, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 5193; (*b*) P. S. Mukherjee, N. Das, Y. Kryeschenko, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2004, **126**, 2464; (*c*) S. J. Lee, A. Hu and W. Lin, *J. Am. Chem. Soc.*, 2002, **124**, 12948; (*d*) N. Das, P. S. Mukherjee, A. M. Arif and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 13950.

5 (*a*) S. Hiraoka, Y. Kubota and M. Fujita, *Chem. Commun.*, 2000, 1509; (*b*) D. K. Chand, M. Fujita, K. Biradha, S. Sakamoto and K. Yamaguchi, *Dalton Trans.*, 2003, 2750, and references therein; (*c*) H. K. Liu and K. Tong, *Chem. Commun.*, 2002, 1316.

6 (*a*) Y. Liu, *Tetrahedron Lett.*, 2007, **48**, 3871; (*b*) M. Chas, E. Pia, R. Toba, C. Peinadar and J. M. Quintela, *Inorg. Chem.*, 2006, **45**, 6117; (*c*) M. Chas, I. C. Platas, C. Peinadar and J. M. Quintela, *Tetrahedron Lett.*, 2006, **47**, 3119, and references therein.

7 *SIR97 (Release 1.02)*—a program for automatic solution and refinement of crystal structure: A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

8 G. M. Sheldrick, *SHELX97 [includes SHELXS97, SHELXL97, CIFTAB]. Programs for crystal structure analysis (Release 97-2)*, University of Göttingen, Germany, 1997.

9 (*a*) H. Jude, H. Disteldorf, S. Fischer, T. Wedge, A. M. Hawkridge, A. M. Arif, M. F. Hawthorne, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2005, **127**, 12131; (*b*) H. Jude, D. J. Sinclair, N. Das, M. S. Sherburn and P. J. Stang, *J. Org. Chem.*, 2006, **71**, 4155; (*c*) H. B. Yang, K. Ghosh, B. H. Northrop and P. J. Stang, *Org. Lett.*, 2007, **9**, 1561; (*d*) H. B. Yang, K. Ghosh, A. Arif and P. J. Stang, *J. Org. Chem.*, 2006, **71**, 9464; (*e*) H. B. Yang, K. Ghosh, N. Das and P. J. Stang, *Org. Lett.*, 2006, **8**, 3991; (*f*) M. Tominaga, K. Suzuki, T. Murase and M. Fujita, *J. Am. Chem. Soc.*, 2005, **127**, 11950.