Diastereoselectively self-sorted low-symmetry binuclear metallomacrocycle and trinuclear metallocage†

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A pyridine/aniline appended unsymmetrical bis-monodentate ligand N-(3-aminophenyle)nicotinamide, L\textsuperscript{un}\textsuperscript{a} is synthesized via condensation of nicotinic acid with excess m-phenylene diamine. A low-symmetry binuclear complex of the Pd\textsubscript{n}L\textsubscript{2}L\textsuperscript{m}\textsubscript{2} type and an extremely rare trinuclear complex of the Pd\textsubscript{n}L\textsuperscript{m}\textsubscript{2} type are produced by self-assembly of the ligand L\textsuperscript{un}\textsuperscript{a} with cis-protected palladium\textsuperscript{ii} (i.e., Pd\textsubscript{L}) and palladium\textsuperscript{ii}, respectively. Two isomers (i.e. [(2,0), (2,0)] and [(1,1), (1,1)]-forms) are theoretically possible for the Pd\textsubscript{n}L\textsubscript{2}L\textsuperscript{m}\textsubscript{2} type complex whereas nine isomers can be envisaged in the case of the Pd\textsubscript{n}L\textsuperscript{m}\textsubscript{2} type arrangement. However, one of the isomers of the Pd\textsubscript{2}L\textsubscript{2}L\textsuperscript{m}\textsubscript{2} type complex as well as the one for the Pd\textsubscript{n}L\textsuperscript{m}\textsubscript{2} type complex are experimentally obtained. The exclusive formation of specific isomers could be predicted from the 1D/2D NMR study in the solution state and the DFT calculations in the gas phase/implicit solvent media. The formation of the predicted all-[(L1)-(Pd\textsubscript{2}[en])L\textsuperscript{m}\textsubscript{2}][NO\textsubscript{3}\textsubscript{3}] has been confirmed by a single-crystal XRD study. DFT calculations for the isomers of the Pd\textsubscript{n}L\textsuperscript{m}\textsubscript{2} type arrangement show that a cis(2,2), cis(2,2), cis(2,2)) isomer is energetically favourable than the alternatively predicted (trans(2,2), trans(2,2), trans(2,2)) isomer. Conformational changes within the build of the exclusively formed isomers are proposed on the basis of NMR study.

Introduction

Palladium\textsuperscript{ii}-based self-assembled bi/poly-nuclear complexes of Pd\textsubscript{n}L\textsubscript{2}L\textsubscript{2} and Pd\textsubscript{n}L\textsubscript{2n} compositions containing the non-chelating bis-monodentate ligand L in their frameworks are members of an eminent class of compounds (L’ stands for a cis-protecting bidentate ligand).\textsuperscript{1-7} The equimolar combination of cis-Pd(L’)(monoanion)\textsubscript{2} and the selected non-chelating bis-monodentate ligand L is known to produce self-assembled metallomacrocycles of Pd\textsubscript{n}L\textsubscript{2}L\textsubscript{2} composition (x ranges from 2 to 4) which finds application in host–guest chemistry. Similarly, the complexation of palladium\textsuperscript{ii} with the non-chelating bis-monodentate ligand L is known to produce metallocages of Pd\textsubscript{n}L\textsubscript{2n} composition where the value of n ranges usually from 2 to 6. However, complexes having the value of n>6 are also known and the highest value of n is 48. These Pd\textsubscript{n}L\textsubscript{2n}–type cage molecules are well explored for various applications such as molecular recognition,\textsuperscript{8} supramolecular catalysis,\textsuperscript{9} and biomedical applications.\textsuperscript{10} Most of the discrete self-assembled complexes of the abovementioned varieties are of high symmetry architecture, prepared using pseudo C\textsubscript{2}-symmetric ligands and well reviewed.\textsuperscript{1-7} However, the preparation of low-symmetry self-assembled coordination complexes is a recent development.\textsuperscript{11-16} Low-symmetry complexes of the types (Pd\textsubscript{L})\textsubscript{n}(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2}) and Pd\textsubscript{n}(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2})(L\textsuperscript{2}\textsubscript{2}) can be achieved by combining a suitable palladium\textsuperscript{ii} component with two types of complementary ligands (L\textsuperscript{a} and L\textsuperscript{b}).\textsuperscript{14-16} Another approach to prepare low-symmetry complexes has been combining a metal component with one type of unsymmetrical ligand (L\textsuperscript{un}\textsuperscript{a}).\textsuperscript{11-13} Unsymmetrical ligands may generate a isomeric mixture of complexes due to the random arrangement of the binding sites of the ligand strands around the metal centres. Thus, the preparation of self-assembled coordination complexes of Pd\textsubscript{L}L\textsubscript{un}\textsuperscript{a} and Pd\textsubscript{n}L\textsubscript{un}\textsubscript{2n} formulations with exclusive diastereoselectivity is quite challenging. Binding site complementarity offered by the ligand and the geometrical preference of all the components involved play an important role in the intricate arrangement observed in low-symmetry complexes.

Although the preparation of Pd\textsubscript{2}L\textsubscript{2}L\textsuperscript{un}\textsubscript{2} type complexes using an unsymmetrical bis-monodentate ligand was introduced some time ago,\textsuperscript{17,18} so far only a few reports are available in the literature. Two diastereomeric arrangements are possible for such binuclear complexes due to the two possible
orientations of the ligand-pair around cis-palladium(II). As described, the Pd₄L₂₀₃₅ type complexes prepared using symmetrical ligands are well explored, whereas the Pd₄(L¹μ)₂₀₃₅ type complexes have caught the attention of researchers in recent times. Our group and other groups have demonstrated the preparation of binuclear Pd₂L¹μ₄ cages using low-symmetry bis-monodentate ligands.¹⁹–²⁴ Four diastereomers are possible for the Pd₂L¹μ₄ variety; nevertheless certain ligand systems favour one of the isomers exclusively. As the nuclearity of the low-symmetry self-assembled complex increases, the number of possible diastereomers also increases. Severin et al. used the “orbit-stabilizer” method to calculate the number of possible isomers for the Pd₃L¹μ₆-, Pd₄L¹μ₈- and Pd₆L¹μ₁₂-type low-symmetry self-assembled complexes.²⁵ Exclusive isomers of the Pd₂L¹μ₆- and Pd₄L¹μ₈-type low-symmetry complexes, out of a vast pool of potential isomers, are prepared by Severin’s group using unsymmetrical bis-monodentate dipyridyl ligands. Recently Wang et al. showed the synthesis of a series of low-symmetry Pd₄L¹μ₈-type complexes and a Pd₆L¹μ₁₂-type complex using unsymmetrical bis-monodentate dipyridyl ligands with varied spacers.²⁶ They observed that an increase in ligand dissymmetry improves conformational control, providing selective self-assembled products. Although some Pd₄L¹μ₈-type complexes were reported in the recent past, there are only a handful of reports for higher nuclearity low-symmetry complexes. There is no report on the use of any given ligand for the exclusive diastereoselective synthesis of both Pd₂L¹′₂L¹μ₂- and Pd₃L¹μ₆-type assemblies.

Herein, we report the exclusive diastereoselective synthesis of Pd₂L¹′₂L¹μ₂- and Pd₃L¹μ₆-type self-assembled complexes by combining an unsymmetrical bis-monodentate ligand with cis-protected and naked palladium(II) components, respectively. Two and nine diastereomers, not including the conformers, are possible for the Pd₂L¹′₂L¹μ₂- and Pd₃L¹μ₆-type complexes (Fig. 1) However, only one diastereomer is selectively formed for each type.

Results and discussion

The unsymmetrical bis-monodentate ligand N-(3-aminophenyl)nicotinamide, L¹μ (Scheme 1) investigated in this work has pyridine and aniline moieties as coordination sites. A carboxylic spacer unit interconnects the two metal binding moieties by utilizing the meta positions of pyridine and aniline as the points of attachment. The ligand L¹μ was prepared by the condensation of nicotinic acid with excess m-phenylene diamine. It was characterized by various spectroscopic techniques, including ¹H NMR, ¹³C NMR, 2D NMR and ESI-MS (Fig. S1–S6†). The trans-isomer of the ligand L¹μ has four planar conformers (i.e. anti-anti, syn-syn, anti-syn and syn-anti), as shown in Fig. 2. All four conformers can participate to generate the Pd₂L¹′₂L¹μ₂-type complex, where the pair of bound ligands are required to have the same conformation for geometrical compatibility. The pair of ligands can orient together, either in the [(2,0), (0,2)] manner or in the [(1,1), (1,1)] manner around the metal centres. Thus, eight supramolecular isomers of the Pd₂L¹′₂L¹μ₂-type complexes are possible for the chosen L¹μ (Fig. 3). However, in the Pd₄L¹μ₈-type arrangement, only two conformers of L¹μ (i.e. syn-syn and anti-anti) can fit the requirement where the conformations of all the six ligand units of the molecular triangle are also expected to be the
same. Thus, eighteen diastereomers (nine are shown in Fig. 1) of the Pd$_3$L$_{12}^{4-}$-type low-symmetry complexes can be imagined.

Equimolar combination of Pd(en)(NO$_3$)$_2$ and the ligand L$_{12}^{4-}$ (2.5 mM each) in DMSO-$d_6$ yielded a single discrete binuclear complex within 5 min. The complex is designated as all-(1,1)-[Pd$_2$(en)$_2$(L$_{12}^{4-}$)$_2$](NO$_3$)$_4$, 1 (Scheme 1), on the basis of NMR spectral analysis and confirmed from the single crystal structure. The $^1$H NMR spectrum of 1 in DMSO-$d_6$ shows a single set of peaks (Fig. 4), corresponding to the bound ligand components, suggesting the exclusive formation of a single diastereomer. The formation of a binuclear complex is probably due to the favourable entropy and geometric reasons.

The appreciable downfield shift of the signals of Py$_a$ alpha protons (H$_b$) and aryl-amine protons (H$_j$) with $\Delta \delta = 0.1$ and 2.0 ppm, respectively, indicates the metal–ligand coordination. However, the signal of other Py$_a$ protons (H$_a$) was found to be upfield shifted by 0.4 ppm, in contrast to the expected complexation induced downfield shift. The complexation reaction was also successful in H$_2$O (Fig. S7†), and quantitative isolation of the complex 1 could be carried out by simply evapor-
ating the solvent. The isolated complex 1 was characterized by various spectroscopic techniques including $^1$H NMR, $^{13}$C NMR, COSY, HSQC, NOESY, and single crystal XRD techniques (Fig. S8–S12, Table S1, Fig. S13† and Fig. 5). Notably, two sets of protons were observed for the ethylene diamine (en) moieties of 1; one of the sets is designated as $H_\alpha$, $H_\beta$ and the other as $H_\gamma$, $H_\delta$. The overall environment of one of the coordinated en moieties should be different from the other en in the case of the (2,0) diastereomer. Thus, the pseudo $C_2$-symmetry with respect to the coordination environment is retained for each bound en moiety. Although the overall environment of a bound en unit is comparable with the other en unit for the all-(1,1) diastereomer, for a given en moiety the $C_2$-symmetry is lost. This means, for the all-(1,1) isomer, the amine protons on one nitrogen are inequivalent to the protons on the other nitrogen and the methylene protons on one carbon are inequivalent to the protons on the other carbon.

The 2D COSY NMR analysis of 1 shows that one set of methylene protons in the ethylene diamine unit (say $H_\alpha$) displays correlation with the other set (say $H_\beta$), which is only possible in the (1,1) isomer (Fig. 4b). In addition, the splitting pattern of the methylene protons (multiplet instead of singlet) suggests the formation of the all-(1,1) isomer in the solution state (Fig. 4b and S8†). X-ray diffraction-quality single crystals of 1 were obtained by the slow evaporation of an aqueous solution of 1, and the crystal structure confirms the head-to-tail arrangement of the binuclear complex all-(1,1)-[Pd$_2$(en)$_2$(L$^{\text{mm}}$)$_2$](NO$_3$)$_4$, 1 (Fig. 5 and Table S1, Fig. S13†), where both the bound ligands have the $\text{anti-syn}$ conformation.

Density functional theory (DFT) calculations at the B3LYP-D3(SDD,6-31G(d) level of theory were performed on all possible eight isomers of 1 in the gas phase and the implicit DMSO phase. The study suggested that the all-(1,1) diastereomer (chair, $\text{syn-anti}$) is the energetically preferred structure as compared with the other isomers of 1 (Fig. 3) in the gas phase. The $E_{\text{rel}}$ values of three of the conformers of the all-(1,1)-diastereomer, i.e. (chair, $\text{syn-anti}$), (boat, $\text{syn-syn}$), and (chair, $\text{anti-anti}$) are within a span of 1.74 kcal mol$^{-1}$, while the fourth one (i.e. boat, $\text{anti-anti}$) has a relatively higher energy in the gas phase (Fig. 3 and Table S2†). However, in the implicit DMSO phase, the (chair, $\text{anti-syn}$) conformer of the all-(1,1)-diastereomer of 1 is found to be energetically preferred and the $E_{\text{rel}}$ values of all four conformers are within a span of 2.85 kcal mol$^{-1}$ (Fig. S14 and Table S3†). Notably, the chair, $\text{anti-syn}$ conformer is observed in the crystal structure of 1. Since the energy difference among the conformers of the all-(1,1) diastereomer is relatively small, we assume that conformational changes occur in the backbone of the bound ligand strands in the architecture of the all-(1,1) diastereomer of 1. The observation of the intriguing NOE coupling of the amide proton ($H_\epsilon$) of 1 with two types of pyridyl protons ($H_\delta$ and $H_\alpha$) of the complex experimentally supports the proposed conformational changes.

Combination of Pd(NO$_3$)$_3$ and ligand L$^{\text{mm}}$ in a 1:2 ratio in DMSO-$d_6$ at 2.5 mM concentration with respect to palladium (n) at ambient temperature spontaneously yielded a single discrete structure as concluded from the $^1$H NMR spectrum of the product (Fig. 4a). A single set of new peaks in the spectrum as compared with that of the free ligand (Fig. 4) indicated the formation of only one diastereomer in an exclusive manner that is proposed as either an all-$\text{trans}(2,2)$ or an all-$\text{cis}(2,2)$-isomer (Fig. 1. structures H and I), as described below. The ESI-MS study of [Pd$_2$(L$^{\text{mm}}$)$_2$](BF$_4$)$_6$, 2, prepared in DMSO-$d_6$, supports the formation of a trinuclear structure (discussed later). As debated before, eighteen isomers are possible for the Pd$_3$L$^{\text{mm}}$ arrangement of 2. Complex 2 exhibited an appreciable down-field shift of the signals of $\alpha/\alpha'$-pyridyl ($H_\delta$/$H_\delta'$) and aryl-amine ($H_\epsilon$) protons with $\Delta\delta$ = 0.4, 0.2 and 2.4 ppm, respectively. Interestingly, the signal due to the aryl-amine protons of 2 appeared as a doublet of doublet, unlike the singlet observed in L$^{\text{mm}}$ or 1. This can be considered as a signature of a specific diastereomer of 2. A single set of peaks in the $^1$H NMR spectrum of 2 suggests that all three palladium(n) centres have a similar coordination environment in the trinuclear complex. This rules out the possibility of seven of the diastereomers (i.e. structures A–G) out of the nine shown in Fig. 1. These seven diastereomers possess a dissimilar coordination environment around palladium(n) centres and each isomer is expected to show more than one set of peaks in the $^1$H NMR spectrum, unlike the all-$\text{cis}(2,2)$ and all-$\text{trans}(2,2)$ diastereomers. The doubling of doublet for the aryl-amine protons indicates that the protons experience unequal magnetic environments and are thus diastereotopic in nature. This is expected for all-$\text{cis}(2,2)$-[Pd$_2$(L$^{\text{mm}}$)$_2$](NO$_3$)$_4$, 2, where all three palladium(n) centres are coordinated by two NH$_2$ and two pyridine moieties in the cis manner, making the two protons of aryl-NH$_2$ diastereotopic in nature. However, the formation of the all-$\text{trans}(2,2)$ diastereomer cannot be completely ruled out as the amine protons in this isomer may possibly experience unequal magnetic environments. All our attempts to grow single crystals of complex 2 proved unsuccessful.

Density functional theory (DFT) calculations at the B3LYP-D3(SDD,6-31G(d) level of theory were carried out to understand the energetics of the possible isomers in the gas phase (Fig. 6 and Fig. S15, Table S4†). We propose that the all-$\text{cis}(2,2)$ diastereomer (syn-syn for all L$^{\text{mm}}$) is energetically favoured compared to the other diastereomers on the basis of the relative energies of the optimized structures. However, conformational changes in the build of 2 are proposed on the
basis of the NOE study. Energy optimisation of the all-cis(2,2) and all-trans(2,2) isomers of [Pd₃(Lun)₆]⁶⁺ in implicit DMSO was not successful.

Cage 2 could be successfully isolated from the DMSO medium using the precipitation method by adding excess EtOAc. The isolated complex was characterized by various spectroscopic techniques including ¹H NMR, ¹³C NMR, COSY, HSQC, and NOESY (Fig. S16–S20†). The assignment of aryl-amine (Hj) protons could be explicitly made only after analysing the NOESY data. Consequently, the peak positions of a few other protons could be reconfirmed. The baseline of the ¹H NMR spectrum of 2 is found to be not so smooth but it smoothens when the spectrum is recorded at an elevated temperature (Fig. S21†). However, by increasing the concentration of 2, another set of peaks (minor) could be clearly observed in the ¹H NMR spectra (Fig. S22 and Table S5†). Two sets of signals can be attributed to the existence of either a dynamic mixture of diastereomerically pure complexes but of different nuclearities (e.g. Pd₃Lun⁶⁻ and Pd₄Lun⁸⁻ type complexes) or a mixture of cis(2,2)- and trans(2,2)-Pd₃Lun⁶⁻ type complexes of the same nuclearity. The intensities of the minor signals were lowered when the spectra were recorded as a function of elevated temperature or time (Fig. S23 and 24†). The result of the ¹H NMR study is supportive of the formation of a species of higher nuclearity. The formula of the minor product is proposed as [Pd₄(Lun)₈](NO₃)₈ (3) and confirmed by the ESI-MS study.

We also observed ligand exchange reactions around the metal centres of the complexes all-(1,1)-[Pd₂(en)₂(Lun)₂](NO₃)₄ (1) and all-cis(2,2)-[Pd₃(Lun)₆](NO₃)₆ (2). When a DMSO-d₆ solution of complex 1 was allowed to stand at ambient temperature for 14 d, it showed a dynamic equilibrium of 1 with the ensuing 2 (35% with respect to ligand) along with concomitant Pd(en)₂(NO₃)₂ (4) (Scheme 2 and Fig. S27†). The combination of complex 2 with 4 in a 1:3 ratio resulted in a similar dynamic equilibrium (Fig. S28†). Interestingly, complexes 1 and 2 evolved as the ligand exchange reactions also exhibited diastereoselectivity, parallel to that observed when these are synthesized by the complexation of the metal components with the ligand. Such kinds of ligand exchange reactions for PdₓLₓ⁺Lunₓ⁻ and PdₓLₓ⁻ type binuclear complexes containing another unsymmetrical bis-monodentate ligand were observed in our previous work.²³

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Fig. 6 Optimized geometries and relative energies of the possible isomers of [Pd₃(Lun)₆]⁶⁺ in the gas phase (DFT[B3LYP-D3/SDD,6-31G(d)]).


Experimental section

Materials and instruments

PdCl₂, AgBF₄, and m-phenylenediamine were obtained from Sigma-Aldrich whereas nicotinic acid, AgNO₃, ethylenediamine, N-Ethyl-N′-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), 4-dimethylaminopyridine (DMAP), and common solvents were obtained from Spectrochem, India. All the chemicals were used as received without further purification. Dichloromethane (DCM) was distilled over CaH₂ prior to use. The deuterated solvent DMSO-d₆ was obtained from Sigma-Aldrich. Nuclear magnetic resonance (NMR) spectra were recorded in DMSO-d₆ at room temperature using Bruker AV400 and AV500 spectrometers at 400 MHz and 500 MHz for ¹H, COSY, and NOESY spectra and at 100 MHz and 125 MHz for ¹³C NMR spectra. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent protons (2.50 ppm for DMSO-d₆ in ¹H NMR and 39.52 ppm in ¹³C NMR). The ESI mass spectra were recorded using an Agilent Q-TOF mass spectrometer. The crystal structure was obtained using a Bruker AXS Kappa Apex III PHOTON II dual source diffractometer. The cis-protected palladium(II) component, i.e., Pd(en)(NO₃)₂, was prepared by following a known procedure.²⁷

Synthesis of the ligand L\textsuperscript{un}

To a suspension of nicotinic acid (0.500 g, 4.061 mmol) in 50 mL of dry DCM maintained at 0–5 °C, m-phenylenediamine (0.658 g, 6.091 mmol) and dimethylaminopyridine (DMAP) (0.248 g, 2.03 mmol) were added followed by N-ethyl-N′-(dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) (0.775 g, 4.061 mmol). The reaction mixture was stirred for 12 h under a nitrogen atmosphere. In order to neutralize the acid, NaHCO₃ solution (10% w/v) was added slowly to the reaction mixture until the evolution of CO₂ had ceased. The mixture was cooled to room temperature. The addition of an excess amount of ethyl acetate (15 mL) and then centrifuged to separate the precipitated AgCl to obtain complex 1.

Synthesis of complexes [Pd\textsubscript{2}(en)\textsubscript{2}(Lun)\textsubscript{2}](NO₃)\textsubscript{4} (1)

Method 1. To a yellow-coloured clear solution of Pd(en)(NO₃)₂ (0.3 mg, 0.001 mmol) in DMSO-d₆ (0.4 mL), ligand L\textsuperscript{un} (0.21 mg, 0.001 mmol) was added. The resulting solution was stirred for 5 min at room temperature to obtain a clear solution. Then the reaction mixture was centrifuged, as a precaution, and the supernatant was used to record the ¹H NMR spectrum.

¹H NMR (400 MHz, DMSO-d₆): δ = 10.27 (s, 1H, Hₐ), 8.82 (d, 1H, J = 5.5 Hz, Hₕ), 8.73 (d, 1H, J = 1.5 Hz, Hₙ), 8.48 (d, 1H, J = 8.1 Hz, Hₐ), 7.70 (t, 1H, J = 6.9 Hz, Hₗ), 7.32, 7.31 (m, 2H, J = 8.3 Hz, Hₗ), 7.26 (t, 1H, Hₙ), 7.14 (s, 1H, Hₕ), 7.01 (d, 2H, J = 8.1 Hz, Hₖ), 5.41 (s, 2H, Hₖ), 5.31 (s, 2H, Hₗ), 2.70 (m, 2H, Hₖ) ppm. ¹³C NMR (125 MHz, DMSO-d₆): 161.27, 154.38, 151.62, 140.88, 139.21, 138.33, 131.84, 129.91, 125.04, 117.38, 116.29, 112.66, 47.49, 46.11 ppm.

Method 2. To a yellow-coloured solution of Pd(en)(NO₃)₂ (11.6 mg, 0.04 mmol) in H₂O (4 mL), the ligand, L\textsuperscript{un} (8.5 mg, 0.04 mmol) was added. The resulting solution was stirred for 1 h at 50 °C and then the reaction mixture was centrifuged. The supernatant was evaporated and the resulting sample was dried under vacuum to obtain complex 2 as a dark brown powder (yield: 18 mg, 90%). Melting point: 180 °C decomposition. The isolated complex 1 was re-dissolved in D₂O to record the ¹H NMR spectrum of the sample. The isolated complex 1 was also dissolved in DMSO-d₆ and the ¹H NMR spectrum of the isolated complex was found to be comparable with that prepared by the in situ method in DMSO-d₆.

¹H NMR (400 MHz, D₂O): δ = 8.87 (s, 1H, Hₐ), 8.84 (s, 1H, Hₕ), 8.27 (d, 1H, J = 8.1 Hz, Hₔ), 7.65 (m, 1H, Hₕ), 7.59 (d, 1H, J = 8.1 Hz, Jₖ = 5.6 Hz, Hₗ), 7.13 (d, 1H, J = 8.3 Hz, Hₘ), 7.06 (t, 1H, J = 7.95 Hz, Hₕ), 6.64 (d, 2H, J = 8.1 Hz, Hₗ) ppm.

Synthesis of [Pd\textsubscript{2}(Lun\textsuperscript{un})\textsubscript{2}](NO₃)\textsubscript{2} (2) and [Pd\textsubscript{2}(Lun\textsuperscript{un})\textsubscript{3}](NO₃)\textsubscript{2} (3)

A mixture of PdCl₂ (10.6 mg, 0.06 mmol) and AgNO₃ (20.4 mg, 0.12 mmol) was taken in 6 mL of DMSO and stirred at 70 °C for 30 minutes. The mixture was cooled to room temperature and then centrifuged to separate the precipitated AgCl to afford a brown-coloured solution of Pd(NO₃)₂. Ligand L\textsuperscript{un} (25.6 mg, 0.12 mmol) was added to a clear solution of Pd(NO₃)₂ and the reaction mixture was stirred for 10 min at room temperature. The addition of an excess amount of ethyl acetate (20 mL) to the resulting solution precipitated a pale-yellow solid which was separated by centrifugation. The solid was washed with acetone and dried under vacuum to afford a pale-yellow solid, 2 + 3 (yield: 36 mg, 83%). Melting point: 248 °C decomposition.

¹H NMR (500 MHz, DMSO-d₆): δ = 10.39 (s, 1H, Hₐ), 10.22 (s, 1H, Hₕ), 9.45 (s, 1H, Hₕ), 9.27 (s, 1H, Hₕ), 9.25 (bs, 1H, Hₛ), 8.96 (d, 1H, J = 5.3 Hz, Hₕ), 8.63 (d, 1H, J = 8.2 Hz, Hₖ), 8.50 (d, 1H, J = 7.6 Hz, Hₕ), 7.98 (s, 2H, Hₕ), 7.67 (t, 2H, J = 6.8 Hz, Hₙ), 7.10 (t, 2H, J = 7.6 Hz, Hₕ), 6.93 (t, 2H, J = 7.6 Hz, Hₕ), 6.78 (t, 2H, J = 7.6 Hz, Hₕ), 6.26 (t, 2H, J = 8.1 Hz, Hₕ), 5.98 (s, 2H, Hₕ), 5.26 (s, 2H, Hₔ), 3.91 (s, 2H, Hₕ), 3.80 (s, 2H, Hₕ), 3.57 (s, 2H, Hₕ), 3.35 (s, 2H, Hₕ), 3.15 (s, 2H, Hₕ), 2.82 (s, 2H, Hₕ), 2.71 (s, 2H, Hₕ), 2.49 (s, 2H, Hₕ), 2.05 (s, 2H, Hₕ), 1.74 (s, 2H, Hₕ), 1.58 (s, 2H, Hₕ), 1.27 (s, 2H, Hₕ), 1.20 (s, 2H, Hₕ), 1.03 (s, 2H, Hₕ), 0.98 (s, 2H, Hₕ), 0.89 (s, 2H, Hₕ), 0.84 (s, 2H, Hₕ).
Hz, Hz, Hz, Hz), 7.44 (dd, 2H, J1 = 57.4 Hz, J2 = 9.3 Hz, Hz, Hz), 7.28 (m, 2H, Hz, Hz, Hz), 7.09 (m, 2H, Hz, Hz), 6.87 (s, 1H, Hz), 6.62 (s, 1H, Hz) ppm. 13C NMR (125 MHz, DMSO-d6): δ 161.44, 161.20, 156.72, 155.46, 153.45, 151.98, 141.05, 140.82, 139.21, 138.02, 137.81, 131.50, 131.24, 129.70, 129.50, 125.25, 124.93, 117.34, 116.73, 116.40, 113.86, 113.16.

Synthesis of [Pd2(Lum)]2[BF4]6 (2') and [Pd4(Lum)]2[BF4]6 (3')

A sample of Pd(BF4)2 was prepared in 0.4 mL of DMSO-d6 by stirring a mixture of PdCl2 (0.17 mg, 0.0009 mmol) and AgBF4 (0.37 mg, 0.0019 mmol) at 60 °C for 30 min. The precipitated AgCl was separated by centrifugation and the supernatant containing Pd(BF4)2 was transferred using a syringe. The ligand Lum (0.42 mg, 0.0019 mmol) was added to the solution of Pd(BF4)2 that was prepared in 0.4 mL of DMSO-d6 to get a clear solution within 5 min. The 1H NMR spectrum of complex 2 was recorded, which was found to be closely comparable with the data of complex 1. ESI-MS: m/z calculated for [2'-2F4]15+, 972.6382; observed, 972.6360; calculated for [2'-3BF4]15+, 619.7543; observed, 619.7561; and calculated for [3'-3BF4]15+, 855.1151; observed, 855.1204 (data collected for 20 mM concentration with respect to palladium). The initial geometries of the [Pd2(en)2(Lum)]3+ and [Pd4(Lum)]3+ complexed cations (multiplicity = singlet), constructed using GaussView 6.0 and pre-optimized with the semi-empirical PM6 method, were further optimized using density functional theory (DFT) in the gas phase. The B3LYP (Becke’s three-parameter hybrid functional using the LYP correlation) functional, with the SDD Effective Core Potential (ECP) and the basis set for Pd, and the 6-31G* basis set for hydrogen, carbon, nitrogen, and oxygen were employed. For calculations in which Pd was represented with the Stuttgart–Dresden (SDD) ECP and basis set, Grimme’s D3 empirical dispersion corrections were added. The optimized geometries were subjected to frequency calculations at the same level of theory to confirm the absence of any imaginary frequencies. The polarizable continuum model (PCM) was used to perform the geometry optimizations followed by frequency calculations for [Pd2(en)2(Lum)]3+ in DMSO. All these quantum chemical calculations were carried out using Gaussian 16 packages.

Conclusions

In conclusion, we have shown the exclusive formation of (1,1)-Pd2L2Lum2- and all-cis(2,2)-Pd4Lum6-type self-assembled complexes using a common unsymmetrical bis-monodentate ligand. Eight isomers and eighteen isomers can be envisaged for the Pd2L2Lum2-type and the Pd4Lum6-type complexes, respectively. Out of the several possibilities, only one isomer is solely formed for each case. Presumably, the selectivity is controlled by the enthalpic factor. Low-symmetry Pd4Lum6-type complex is extremely rare and we expect more such examples in the future. The proposed all-cis(2,2)-isomer of the Pd4Lum6 complex could be made by careful analysis of the 1H NMR spectral data of the complex and DFT study.

Author contributions

D. K. C. and S. S. M. conceptualized the work, carried out the research and analysed the data. S. S. M was involved in analysing the 1D and 2D NMR data, DFT calculations, and the single crystal growth of the metallamacrocycle and contributed to composing the manuscript. D. K. C is the principal investigator of the project. Both authors discussed the work and edited the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

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Notes and references