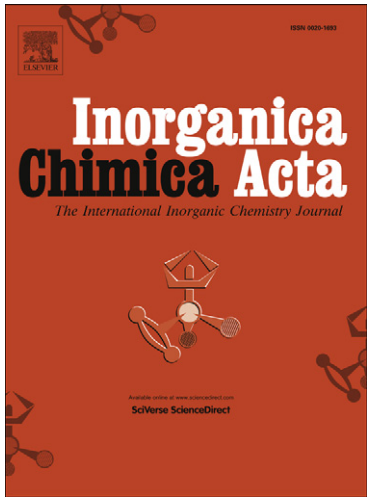

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Self-assembled mononuclear palladium(II) based molecular loops

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Abstract: The *meta*-pyridine appended bidentate ligands $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$, crafted with flexible polyether spacer, are prepared by condensation of nicotinoyl chloride hydrochloride with di, tri-, and tetra-ethylene glycol, respectively. Self-assembled palladium(II) based mononuclear molecular loops of general formula *cis*-[Pd(N-N)(**L**)]$(NO_3)_2$ are obtained exclusively by combining one equivalent of a ligand **L** with one equivalent of a *cis*-protected palladium(II) component, *cis*-[Pd(N-N)$(NO_3)_2$]. Complexation of two equivalents of **L** with one equivalent of palladium(II) nitrate also resulted mononuclear complexes, i.e. [Pd(**L**)$_2$]$(NO_3)_2$. The ligands used in the complexation reactions are $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_3}$ where as the *cis*-protecting units N-N employed are ethylenediamine (*en*), 2,2′-bipyridine (*bpy*), and 1,10-phenanthroline (*phen*). Thus twelve number of mononuclear complexes are prepared using all possible combination of above mentioned three number of ligands and four variety of palladium(II) components. Large chelate rings are realized irrespective of the spacer length or type of palladium(II) component used. All the resulted compounds are characterized by NMR and ESI-MS techniques and the structure of *cis*-[Pd(*en*)($\mathbf{L_1}$)]$(NO_3)_2$, *cis*-[Pd(*bpy*)($\mathbf{L_1}$)]$(NO_3)_2$ and [Pd($\mathbf{L_3}$)$_2$]$(NO_3)_2$ are confirmed by single crystal X-ray diffraction. The binding abilities of *cis*-[Pd(*phen*)($\mathbf{L_1}$)]$(NO_3)_2$, *cis*-[Pd(*phen*)($\mathbf{L_2}$)]$(NO_3)_2$ and *cis*-[Pd(*phen*)($\mathbf{L_3}$)]$(NO_3)_2$ with DNA has been investigated by ethidium bromide displacement assay and gel electrophoresis.

Keywords: palladium, self-assembly, bidentate ligands, molecular loops

1. Introduction

The design, synthesis and application of metal driven self-assembly continue to be an area of great activity and interest among chemists.[1] The shape, size, denticity, electronic environment, steric behaviour and directionality of the ligand unit along with the coordination behaviour of metal component are important factors to determine the final structure of the self-assembled metallomacrocycle.[2] However, the solvent of choice, presence of guest molecules and change of concentration may alter the structures.[3] The area of metal driven or coordination driven self-assembly has witnessed the use of a variety of rigid, well directional multidentate non-chelating ligands; in particular non-chelating bidentate ligands have been widely used to construct discrete structures.[4] The directionality of these non-chelating bidentate ligands lead to various discrete structures; non-chelating bidentate ligands with non-rigid or flexible spacer have also been used to construct metallosupramolecules and in many cases, it forms higher nuclear self-assembled molecules.[5,2b] However, formation of mononuclear compounds with a flexible non-chelating bidentate ligands and a Pd(II) center is not widely reported.[6] Ros group[7] reported a few mononuclear Pd(II) compounds with pyrazole appended bidentate ligands.

Herein, we report synthesis of discrete mononuclear metallocycles or molecular loops achieved from the combination of simple and flexible pyridine appended bidentate ligands (**L_1-L_3**) with various Pd(II) components (i.e. *cis*-[Pd(en)(NO_3)$_2$], *cis*-[Pd(bpy)(NO_3)$_2$], *cis*-[Pd(phen)(NO_3)$_2$], and Pd(NO_3)$_2$). Out of the series of molecular loops obtained a few selected assemblies containing 1,10-phenanthroline in the superstructure have been screened for the interaction with plasmid DNA *pBR 322*. The π-surface present as phen unit in the complexes is expected to facilitate intercalation and hence binding with DNA. Structure of the ligands and the complexes are given in Fig. 1-3.

2. Results and discussion

Ligand $\mathbf{L_1}$ has been prepared by following a reported method;[8] nicotinoyl chloride hydrochloride was reacted with diethyleneglycol in presence of triehtylamine in dry dichloromethane to obtain $\mathbf{L_1}$. Ligand $\mathbf{L_2}$and $\mathbf{L_3}$ are also reported [9,10] and have been prepared by using same procedures as that of $\mathbf{L_1}$.

2.1 Complexation of ligands with Pd(II) units

Reaction of ligand $\mathbf{L_1}$ with *cis*-[Pd(en)$(NO_3)_2$] in water at 1:1 ratio gave a colorless solution at room temperature which upon evaporation resulted a colorless solid. The ^{1}H NMR of the obtained solid suggests formation of a single compound. The ESI MS and single crystal X-ray studies confirmed the product as a mononuclear complex i.e. *cis*-[Pd(en)($\mathbf{L_1}$)]$(NO_3)_2$, **1**. Similarly, the reaction of *cis*-[Pd(bpy)$(NO_3)_2$] with $\mathbf{L_1}$ in acetonitrile at 1:1 ratio produced yellowish white precipitate which was also found to be mononuclear and represented as *cis*-[Pd(bpy)($\mathbf{L_1}$)]$(NO_3)_2$, **2**. X-ray quality crystals were obtained by slow evaporation of a solution of **2** in water whose analysis confirmed the structure. In a similar procedure, reaction of $\mathbf{L_1}$ with *cis*-[Pd(phen)$(NO_3)_2$] in acetonitrile at 1:1 ratio also gave the mononuclear compound *cis*-[Pd(phen)($\mathbf{L_1}$)]$(NO_3)_2$, **3** which is characterized by proton NMR and ESI MS spectrometry. When ligand $\mathbf{L_1}$ was treated with Pd$(NO_3)_2$ in acetonitrile at 2:1 ratio the mononuclear compound [Pd($\mathbf{L_1}$)$_2$]$(NO_3)_2$, **4** was formed (Fig. 1).

In a similar method, complexation of ligand $\mathbf{L_2}$ with *cis*-[Pd(en)$(NO_3)_2$] in water at 1:1 ratio yielded the mononuclear complex *cis*-[Pd(en)($\mathbf{L_2}$)]$(NO_3)_2$, **5**, and the reaction of *cis*-[Pd(bpy)$(NO_3)_2$] with $\mathbf{L_2}$ in actonitrile at 1:1 ratio produced the mononuclear compound *cis*-[Pd(bpy)($\mathbf{L_2}$)]$(NO_3)_2$, **6**. Reaction of $\mathbf{L_2}$ with *cis*-[Pd(phen)$(NO_3)_2$] in acetonitrile resulted compound *cis*-[Pd(phen)($\mathbf{L_2}$)]$(NO_3)_2$, **7** and when ligand $\mathbf{L_2}$ was treated with Pd$(NO_3)_2$ in acetonitrile at 2:1 ratio, the mononuclear compound [Pd($\mathbf{L_2}$)$_2$]$(NO_3)_2$, **8** was obtained (Fig. 2).

Ligand $\mathbf{L_3}$ forms *cis*-[Pd(en)($\mathbf{L_3}$)]$(NO_3)_2$, **9**; *cis*-[Pd(bpy)($\mathbf{L_3}$)]$(NO_3)_2$, **10** and *cis*-[Pd(phen)($\mathbf{L_3}$)]$(NO_3)_2$, **11** when reacted with *cis*-[Pd(en)$(NO_3)_2$], *cis*-[Pd(bpy)$(NO_3)_2$] and *cis*-[Pd(phen)$(NO_3)_2$], respectively at 1:1 ratio. Mononuclear compound [Pd($\mathbf{L_3}$)$_2$]$(NO_3)_2$, **12** was obtained when ligand $\mathbf{L_3}$ was treated with Pd$(NO_3)_2$ in acetonitrile at 2:1 ratio (Fig. 3).

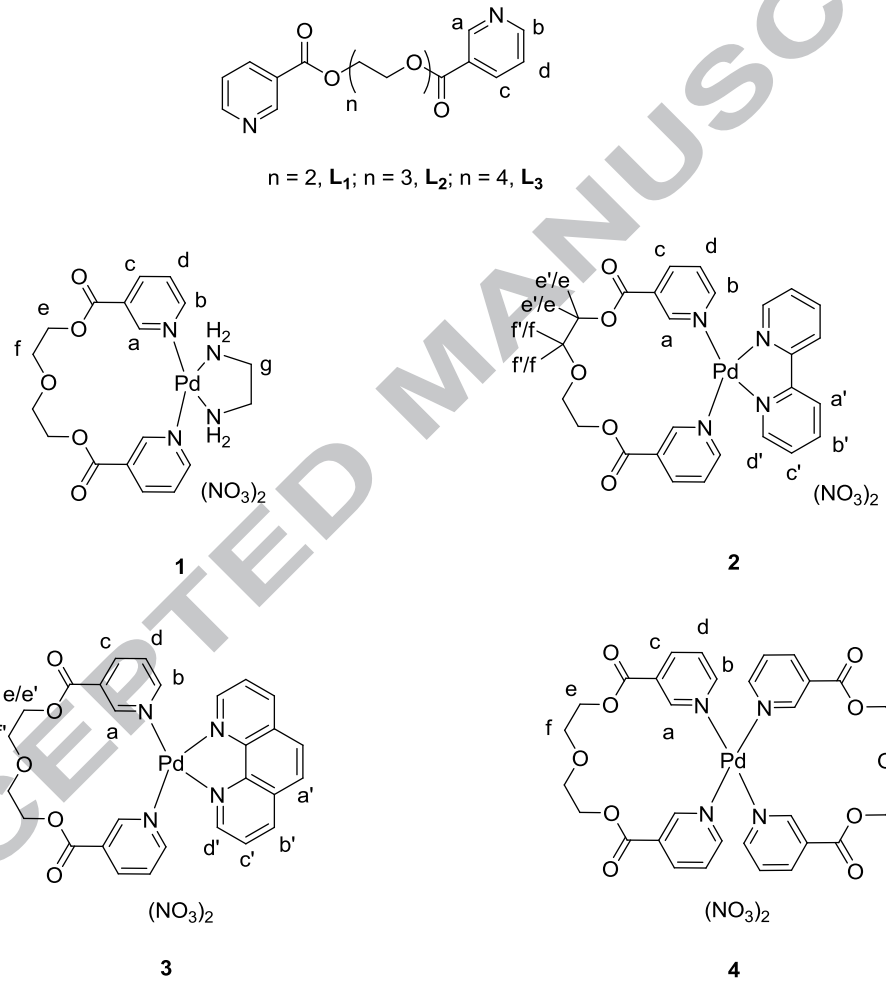
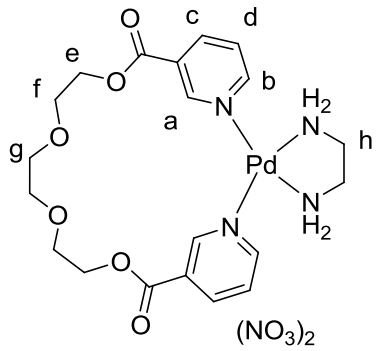


Figure 1. Ligands $\mathbf{L_1}$-$\mathbf{L_3}$ crafted with flexible spacers; structures of *cis*-[Pd(en)($\mathbf{L_1}$)]$(NO_3)_2$, **1**; *cis*-[Pd(bpy)($\mathbf{L_1}$)]$(NO_3)_2$, **2**; *cis*-[Pd(phen)($\mathbf{L_1}$)]$(NO_3)_2$, **3** and [Pd($\mathbf{L_1}$)$_2$]$(NO_3)_2$, **4**.



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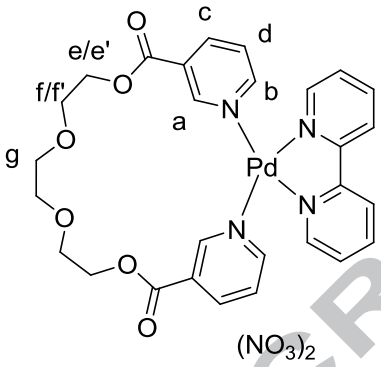

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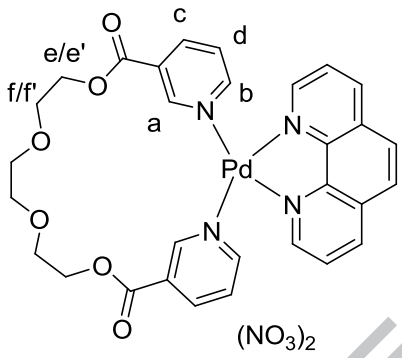

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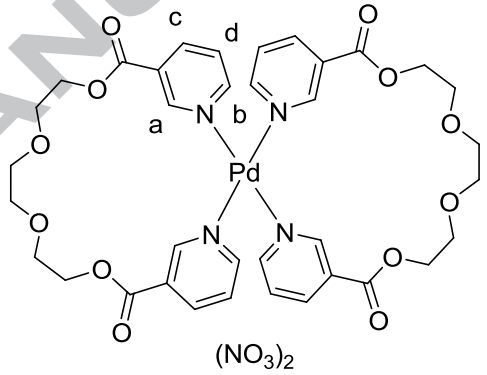

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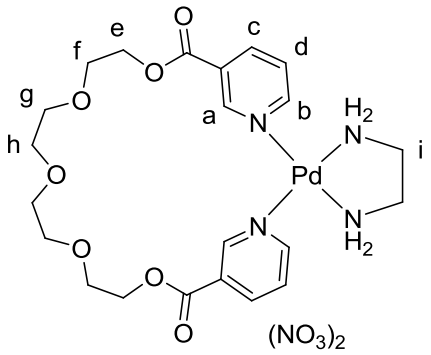
Figure 2. Structures of the complexes *cis*-[Pd(en)(**L₂**)](NO₃)₂, **5**; *cis*-[Pd(bpy)(**L₂**)](NO₃)₂, **6**; *cis*-[Pd(phen)(**L₂**)](NO₃)₂, **7** and [Pd(**L₂**)₂](NO₃)₂, **8**.



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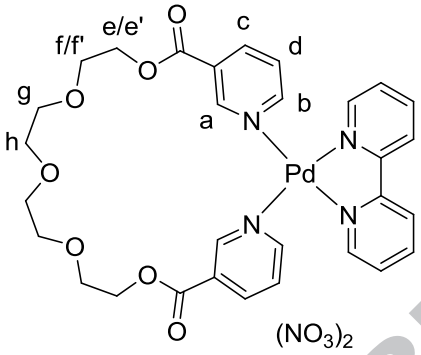

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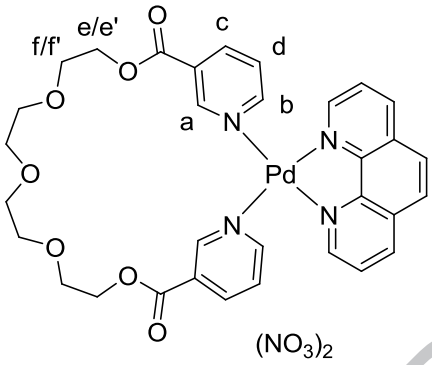

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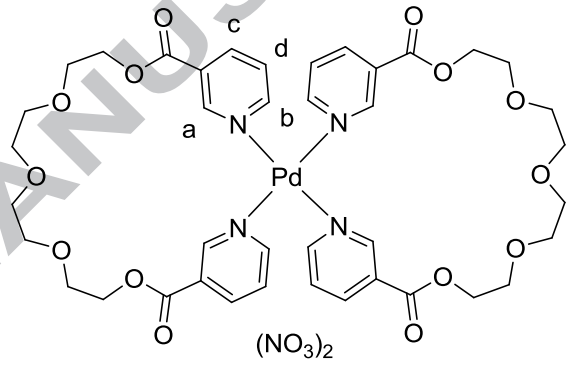

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Figure 3. Structures of the complexes *cis*-[Pd(en)(**L$_3$**)]$(NO_3)_2$, **9**; *cis*-[Pd(bpy)(**L$_3$**)]$(NO_3)_2$, **10**; *cis*-[Pd(phen)(**L$_3$**)]$(NO_3)_2$, **11** and [Pd(**L$_3$**)$_2$]$(NO_3)_2$, **12**.

2.2 Characterization of compounds

The impressively simple nature of the ^{1}H NMR spectrum for compound **1** shows the presence of a single entity in the solution state. Four signals in aromatic region correspond to the protons of the pyridine ring of the ligand and are consistent with highly symmetric nature of the complex. The pyridine-α protons are down field shifted when compared with free ligand suggests metal-ligand interaction. Proton *a* is most deshielded by the metal ligand interaction and downfield shifted (Δδ = 1.0 ppm) as compared to free ligand. Similar downfield shift is

observed for protons *b*, *c* and *d*; the shifts are found to be Δδ = 0.55, 0.47 and 0.42 ppm, respectively. The aliphatic protons e and f are also marginally (Δδ = 0.13 and 0.14 ppm, respectively) downfield shifted (Fig. 4).

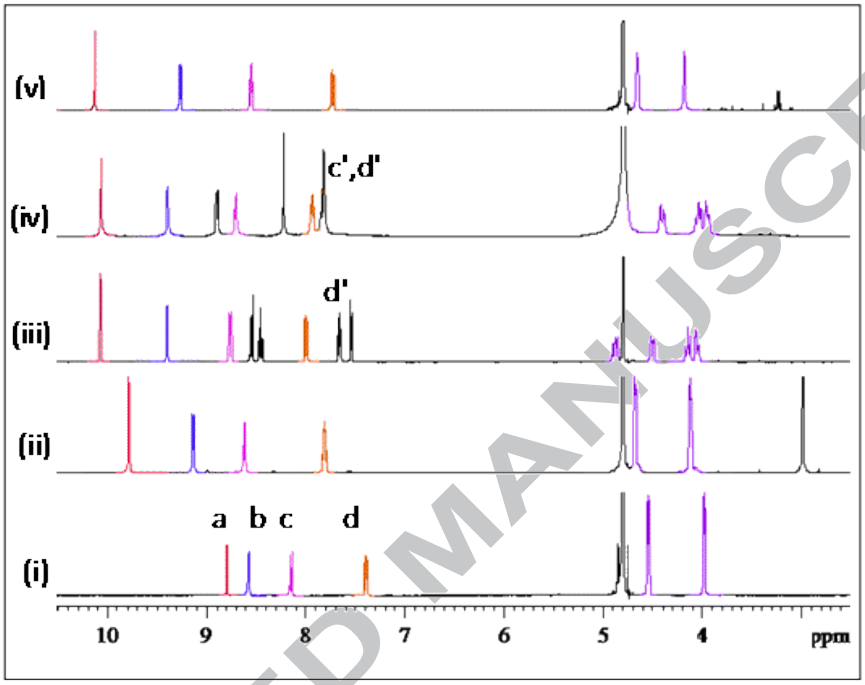

Figure 4. 400 MHz ^{1}H NMR spectra in D_2O for (i) ligand $\mathbf{L_1}$; (ii) *cis*-[Pd(en)($\mathbf{L_1}$)]$(NO_3)_2$, **1**; (iii) *cis*-[Pd(bpy)($\mathbf{L_1}$)]$(NO_3)_2$, **2**; (iv) *cis*-[Pd(phen)($\mathbf{L_1}$)]$(NO_3)_2$, **3** and (v) [Pd($\mathbf{L_1}$)$_2$]$(NO_3)_2$, **4**.

For compounds **2-12,** the signals corresponding to the pyridine protons displayed similar kind of down field shift due to metal ligand interaction (Δδ values are given in table-1) (also see supporting information). The appreciable upfield shift of *d′* proton in case of compounds **2**, **6** and **10** when compared to the same in free *bpy* or *cis*-[Pd(bpy)$(NO_3)_2$] is evident of through space Pd(bpy)-py interaction for such type of complexes.[11] Similar upfield shift for the *d′* proton of *phen* unit is also observed in compounds **3**, **7** and **11.** In such compounds the proton *d′* is situated above the ring current created by the *py* ring of the bound ligand. The methylene protons of the ligand moiety in compound **2** show a different behavior as that of

compound **1** in ^{1}H NMR spectrum. The four protons *e*, *e′* and *f*, *f′* show four signals and thus are different from each other unlike compound **1**. These four protons are presumably in different magnetic environment, thus are diastereotopic in nature. The H-H COSY spectrum shows each proton correlated to other three protons of the neighbor (one proton from *geminal* carbon and other two are from the *vicinal* carbon). The C-H COSY spectrum shows a set of two protons correlated to one carbon atom only (Fig. S11 and S12 of supporting info). A similar trend is also observed for signals corresponding to protons *e, e′* and *f, f′* methylene protons in compounds **3**, **6**, **7**, **10** and **11**.

Table 1. Change in chemical shift (Δδ) values in ppm for pyridine protons in the complexes **1-12** as compared to corresponding ligands $\mathbf{L_1}$-$\mathbf{L_3}$.

Complex	Δδ(H_a)	Δδ (H_b)	Δδ (H_c)	Δδ (H_d)
1	1.0	0.55	0.47	0.42
2	1.28	0.82	0.61	0.60
3	1.30	0.85	0.60	0.60
4	1.34	0.69	0.41	0.34
5	0.71	0.43	0.32	0.29
6	1.09	0.79	0.51	0.51
7	1.11	0.80	0.48	0.49
8	0.91	0.68	0.38	0.37
9	0.33	0.36	0.29	0.28
10	0.63	0.64	0.31	0.32
11	0.82	0.82	0.46	0.48
12	0.36	0.45	0.30	0.26

The ESI mass spectra of **1-12** show peaks confirming isotopic pattern for fragments which contain one palladium centre, however, with varied charges due to loss of the counter anion(s). For compound **1** the peak at 542 corresponds to $[\mathbf{1}\text{-}NO_3]^+$ which shows each isotopic peak separated by one unit whereas the peak at 241 corresponds to $[\mathbf{1}\text{-}2NO_3]^{2+}$, each mass unit exhibits two isotopic peaks. For compound **2**, the ESI MS shows peak at 640 and 289 which correspond to $[\mathbf{2}\text{-}NO_3]^+$, and $[\mathbf{2}\text{-}2NO_3]^{2+}$ respectively. Peaks at 664 and 301 confirms $[\mathbf{3}\text{-}NO_3]^+$ and $[\mathbf{3}\text{-}2NO_3]^{2+}$ respectively, for the fragments of compound **3**. Similarly,

the ESI MS of compound **4** shows peaks at 800 correspond to $[\mathbf{4}\text{-}NO_3]^+$ and at 369 corresponds to $[\mathbf{4}\text{-}2NO_3]^{2+}$. ESI MS spectra and analysis of data for all compounds **1**-**12** are described in supporting information.

*2.3 Crystal structure of compounds **1**, **2** and **8***

Attempts were made to grow single crystals for all of the above discussed compounds; however, X-ray quality crystals were successfully obtained only for compounds **1**, **2** and **8**. Compounds **1** and **2** were crystallized from their respective aqueous solutions at room temperature by slow evaporation. Compound **8** was crystallized out from acetonitrile by standing at 0-5 °C. Crystallographic details for the compounds are given in table S1 (see supporting info).

A perspective view of the metal coordination environment of $[cis\text{-}Pd(en)(\mathbf{L_1})](NO_3)_2\cdot 2H_2O$ is shown in Fig. 5. The geometry around the metal is square planner and the square plane is comprised of the two pyridyl nitrogen of ligand unit disposed in a *cis* manner to each other whereas other two *cis* positions are occupied by two nitrogen atoms of ethylenediamine unit. The metal center sits almost at the bisector of both diagonals of the square. Compound **1** has two water molecules of crystallization. The atoms N1N2N3N4 form a square plane; the two pyridyl rings of the ligand are not coplanar.

The Pd-N distances are 2.02(3) and 2.028(4) Å for N(en)-Pd bonds whereas 2.025(1) and 2.044(2) Å for N(py)-Pd bonds. In the plane bond angle of N1-Pd-N2 containing ethylenediamine nitrogens is 84.06° and N3-Pd-N4 containing pyridyl nitrogen is 91.70°; the other angles N2-Pd-N3 and N1-Pd-N4 are 91.76° and 92.50°, respectively. Two nitrate anions stay outside the cavity and are planner. In compound **2**, atoms N1N2N3N4 form a square plane and the palladium atom is at the bisector of the diagonal N1N4 and N2N3. The Pd-N distances are 1.997(1) Å and 2.013(3) Å for N(bpy)-Pd bonds and 2.031 Å for both the N(py)-Pd bonds. In the plane bond angel N-Pd-N are in the range from 80.58-97.54°. The

two pyridyl rings from the ligands are perfectly orthogonal to the square plane and two units of the molecule present in a crystallographic cell (see supporting info).

The X-ray crystal structure of compound **8** shows the two ligand units bonded to the metal centre where each ligand describes a *cis*-chelating orientation. The molecule appears as a perfect chair and the two rings of the ligands are parallel and opposite to each other and shown in different colours. The molecule has a center of inversion and crystallizes in P21/n space group. It has one water molecule of crystallization and out of two nitrates only one nitrate is found in the solved structure. Four pyridyl rings are perfectly orthogonal to the square plane and each of two *trans* positioned pyridyl rings are in one plane (Fig. 5). In compound **8**, atoms N1N2N1N2 form the square plane and two *trans* positioned pyridyl units are coplanar. The Pd-N distances are 2.016 and 2.038 Å for both the Npy-Pd bonds. The in plane bond angle of N1-Pd1-N2 for the angles of palladium and both the pyridyl nitrogen atoms are 89.2 and 90.8°. Crystallographic details for **8** are given in table S1 (see supporting info).

The molecular loops presented in this work are formed immediately in water whereas for the reported loops the solvents used were DMSO, DMF or DMF-H_2O. In literature, mononuclear molecular loop consisting of Pd(II)/Pt(II) and 4-pyridyl appended rigid ligands are studied.[6a] The mononuclear compounds **1-12** have discrete structures which are prepared from the combination of a 3-pyridyl appended flexible bidentate ligands (**L_1-L_3**) with a *cis*-protected Pd(II) or simple Pd(II) component. Consequently, few of these loops contain a *cis*-protected Pd(II) unit and a ligand unit and the rest of the loops obtained from simple Pd(II) possess two units of ligands bound around a Pd(II) in a *cis*-chelating fashion. Ligands **L_1-L_3** are convergent in directionality due to *meta* substituted pyridines and the chain length in the backbone favors the formation of chelated compounds / molecular loops.

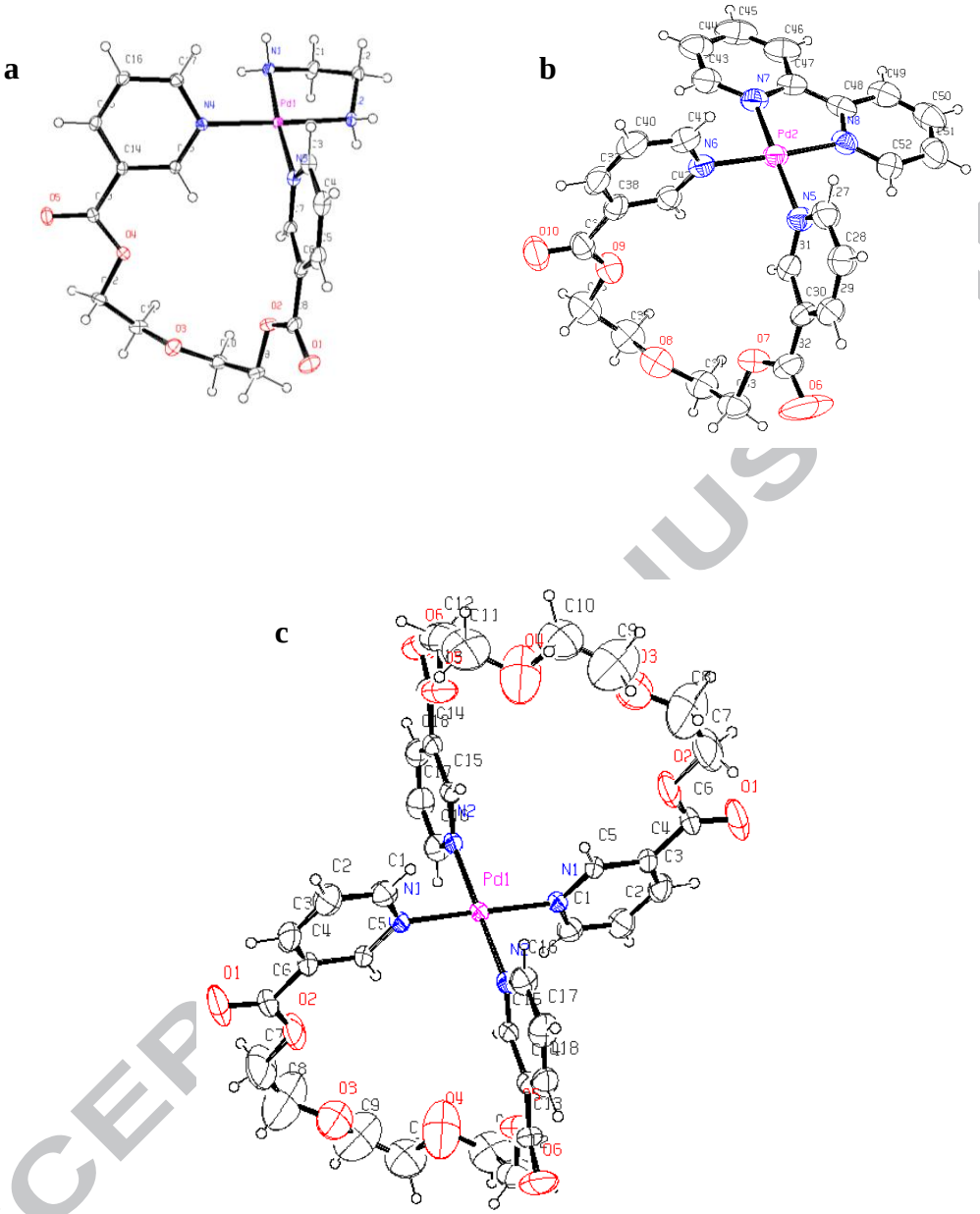

Figure 5. ORTEP diagram for the cationic part of the complexes (a) **1**, (b) **2** and (c) **8**. Anions and solvent molecules are removed for clarity. Thermal ellipsoids are shown in 30% probability level.

2.4 Interaction of complexes with DNA

Ethidium bromide displacement assay: Competitive binding to DNA of the complexes with ethidium bromide (EtBr) could provide rich information regarding DNA binding nature and relative DNA binding affinity. The competitive DNA binding of complexes has been studied by monitoring changes in emission intensity of EtBr bound to CT-DNA as a function of added complex concentration. EtBr shows reduced emission intensity in a buffer because of quenching by solvent molecules and a significant enhancement of the intensity when bound to DNA.[12-14] Binding of the second molecule to EtBr bound DNA decreases the emission intensity and the extent of the reduction of the emission intensity gives a measure of the DNA binding propensity of the complexes.

The complexes **2**, **3**, **7** and **11** were selected for DNA interaction studies based on the structures of the complexes. When complexes **2**, **3**, **7** and **11** are added to DNA pretreated with EtBr {[DNA]: [EtBr] = 1:1}, the DNA induced emission intensity of EtBr decreases (Fig. 6, also Fig. S55 of supp info). The addition of the complexes **2**, **3**, **7** and **11** to the DNA bound EtBr solutions, caused obvious reduction in emission intensities, indicating that the complexes competitively bound to DNA with EtBr. The apparent binding constant (K_{app}) has been calculated from the relation [15] $K_{EtBr}[EtBr] = K_{app}[complex]$. Where, $K_{EtBr}$is 1×10^{7} M^{-1} and the concentration of EtBr is 20 μM. The concentration of the complex is taken for observing 50% reduction of the emission intensity of DNA bound EtBr. The K_{app} values for the complexes are 1.6×10^{6}, 2.5×10^{6}, 1.4×10^{6} for compounds **3**, **7** and **11** respectively (see supporting info).

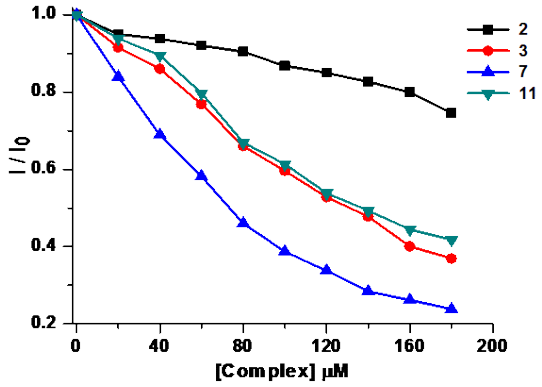

Figure 6. Plots of relative integrated emission intensity versus [complex].

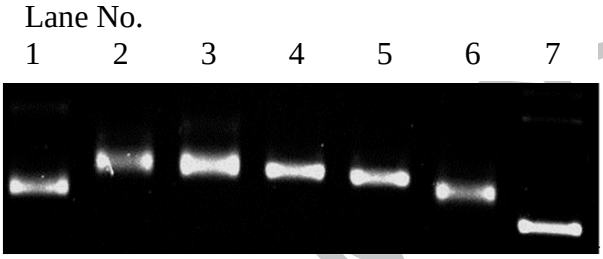

Figure 7. Agarose gel electrophoresis of pBR 322DNA, [complex] = 2–20 μM, [DNA] = 200 ng, incubation time = 30 min, at 37°C. TBE buffer, pH 8.2, Lanes 1-6: DNA + **2**, 2, 4, 8, 10, 14, 20 μM respectively, Lane 7: DNA control.

Electrophoretic mobility study of the complexes: The influence of the compounds on the structure of DNA was determined by their ability to modify the electrophoretic mobility of the super coiled (SC) form of pBR 322 DNA. Different concentration of complexes **2**, **3**, **7** and **11** were incubated with pBR 322 DNA at 37º C for 30 min. The representative gels obtained for complexes **2**, **3**, **7** and **11** are shown in Fig 7 and Fig S56 of Supporting Info. The study shows concentration dependent change in electrophoretic mobility of DNA in presence of complexes. The behaviour observed for the electrophoretic mobility of super coiled (SC) form of pBR 322 DNA in the presence of complexes indicates that some conformational changes occurred by alteration in the degree of superhelicity of the DNAmolecules. These

change in mobility of DNA may be due to the formation of DNA-complex adduct by hydrogen bonding between complex and DNA base pairs.

3. Conclusion

Flexible bidentate non-chelating ligands have been employed to form self-assembled Pd(II) compounds and visualized as mononuclear loops. These compounds represent one of the few examples where bidentate ligands with well separated donor atoms act as chelating ligands to give mononuclear Pd(II) complexes. Both spectroscopic and X-ray studies demonstrates the mononuclear nature of these compounds. A novel shape, molecular chair is reported in this work. In earlier reports, the mononuclear chelated Pd(II) compound form catenanes in aqueous solution, however, our chosen ligands form single compounds in water and these compounds represent one of the few examples where bidentate ligands with well separated donor atoms act as chelating ligands to give mononuclear Pd(II) complexes. Interaction of few of these molecular loops with DNA has been studied.

4. Experimental Section

4.1 General

NMR spectra were obtained at room temperature with a BRUKER AVANCE-400 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively at 25 °C if not stated otherwise. Calibrations were made by using TMS in $CDCl_3$as external standard. Mass spectra were recorded on a MICROMASS Q-TOF mass spectrometer equipped with standard electrospray source. The samples were dissolved in water and introduced into the ESI source through a syringe pump at the rate of 5 μL per minute. The ESI capillary was set at 3.5 kV, the cone voltage was 5 – 15 V. Steady-state

emission experiments were carried out on a Shimadzu RF-5301 spectrofluorometer at room temperature.

Ethidium Bromide Displacement Assay. The apparent binding constants (K_{app}) of the complexes were determined by a fluorescence spectral technique using ethidium bromide (EtBr) bound CT DNA solution in phosphate buffer (pH 7.2). The changes in fluorescence intensities at 600 nm (546 nm excitation) of EtBr bound to DNA was recorded with an increasing concentration of the palladium complexes **2**, **3**, **7** and **11**. EtBr was non–emissive in phosphate buffer (pH 7.2) medium due to fluorescence quenching of the free EtBr by the solvent molecules. In the presence of DNA, EtBr showed enhanced emission intensity due to its intercalative binding to DNA. A competitive binding of the palladium complexes to CT DNA resulted in the displacement of the bound EtBr decreasing its emission intensity.

Electrophoretic Mobility Study.The electrophoretic mobility experiments were carried out by gel electrophoresis as described earlier.[16] The electrophoretic mobility experiments were carried out by agarose gel electrophoresis on a 10 μL total sample volume in 0.5 mL transparent Eppendorfmicrocentrifuge tubes containing *pBR322* DNA (200 ng). For the Gel–electrophoresis experiments, supercoiled *pBR322* DNA was treated with the palladium complexes (2–120 μM) and the mixtures were incubated in the dark for 30 min/37 °C. The samples were analyzed by 1% agarose gel electrophoresis (Tris–Boric acid–EDTA (TBE) buffer, pH=7.8) for 3 h at 60 V. The gel was stained with a 0.5 μg/mL ethidium bromide and visualized by UV light and photographed for analysis using the Alpha Innotech Gel documentation system (AlphaImager 2200).

4.2 Preparation of nicotinoyl chloride hydrochloride.

Nicotinic acid (0.732 g, 5.95 mmol) was taken in a 100 mL round bottom flask and thionyl chloride (6 mL) was added to it at once at room temperature. This mixture was stirred and refluxed (appx. at 80 ^{o}C) for 30 min and the resulted clear solution was evaporated to dryness

under vacuum to get white shiny crystals as the product (m.p. 425 K). The prepared nicotinoyl chloride hydrochloride was immediately used for further reactions.

4.3 Synthesis of ligand ***L₁***.

Nicotinoyl chloride hydrochloride (758 mg, 4.26 mmol) was taken in a 100 mL round bottom flask and of dichloromethane (15 mL) was added to it under nitogen atmosphere. The suspension was stirred vigorously for 10 min followed by addition of diethylene glycol (0.20 mL, 218 mg, 2.10 mmol) in dichloromethane (15 mL). The mixture was kept in an ice bath and triethylamine (1 mL) was added dropwise over a period of 30 min. The resulting mixture was stirred at room temperature for 24 h under nitrogen atmosphere. To this mixture $NaHCO_3$ solution (10% w/v) was added slowly to neutralize the acid until the evolution of CO_2 has ceased. The organic layer was washed with distilled water, separated and dried over anhydrous sodium sulfate. Evaporation of the solvent gave a yellowish solid as the product, 539 mg (79%). m.p. 416 K; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.21 (s, 2H, H_a), 8.75 (d, J = 4.0 Hz, 2H, H_b), 8.26 (d, J = 8.0 Hz, 2H, H_c), 7.41 (t, J = 6.2 Hz, 2H, H_d), 4.52-4.51 (m, 4H, H_2), 3.88-3.87 (m, 4H, H_f) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.17, 153.51, 150.95, 137.06, 125.90, 123.27, 69.06, 64.25 ppm; MS (ESI): *m/z* = 317 (100%) $[(\mathbf{L_1}+H)]^+$; Anal.Calcd for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10; N, 8.86. Found: C, 60.78; H, 5.03; N, 8.98.

^{1}H NMR (400 MHz, D_2O) δ = 8.79 (d, J = 1.6 Hz, 2H, H_a), 8.58 (dd, J = 5.0 and 1.4 Hz, 2H, H_b), 8.15 (td, J = 8.0 and 1.6 Hz, 2H, H_c), 7.39 (dd, J = 6.2 and 4.8 Hz, 2H, H_d), 4.56-4.53 (m, 4H, H_e), 3.99-3.97 (m, 4H, H_f) ppm.

4.4 Synthesis of ***L₂***.

Similar procedure was adopted as ligand $\mathbf{L_1}$ to synthesize ligand $\mathbf{L_2}$, triethylene glycol was used in place of diethyleneglycol. Evaporation of the solvent after work up gave yellowish oil as the product, 712 mg (95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.24 (dd, J = 2.0 and 0.8 Hz, 2H, H_a), 8.77 (dd, J = 4.8 and 1.6 Hz, 2H, H_b), 8.30 (td, J = 7.6 and 2.0 Hz, 2H, H_c), 7.38 (dd,

J = 7.8 and 3.4 Hz, 2H, H_d), 4.52 – 4.49 (m, 4H, H_e), 3.86 – 3.84 (m, 4H, H_f), 3.72 (s, 4H, -H_g) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.23, 153.51, 151.02, 137.13, 126.03, 123.28, 70.78, 69.17, 64.46 ppm; MS (ESI): *m/z* = 361 (100%), [(**L₂**+H)] $^+$; Anal. Calcd for $C_{18}H_{20}N_2O_6$: C, 59.99; H, 5.59; N, 7.77. Found: C, 59.83; H, 5.64; N, 7.83.

^{1}H NMR (400 MHz, D_2O) δ = 8.93 (s, 2H, H_a), 8.63 (dd, *J* = 4.0, 1.6 Hz, 2H, H_b), 8.25 (dd, *J* = 7.0, 2.0 Hz, 2H, H_c), 7.48 - 7.45 (m, 2H, H_d), 4.49 – 4.48 (m, 4H, H_e), 3.95 – 3.94 (m, 4H, H_f), 3.82 (s, 4H, H_g) ppm.

4.5 Synthesis of ***L₃***

Similar procedure was adopted to synthesize ligand **L₃** as described for ligand **L₁**, tetraethyleneglycol was used in place of diethyleneglycol. Evaporation of the solvent after work up gave yellowish oil as the product, 2.23 g (55%). m. p. 325 K; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.24 (d, *J* = 2.0 Hz, 2H, H_a), 8.77 (dd, *J* = 4.8 and 1.6 Hz, 2H, H_b), 8.31 (td, *J* = 8.0 and 2.0 Hz, 2H, H_c), 7.39 (dd, *J* = 8.0 and 4.8 Hz, 2H, H_d), 4.52 – 4.49 (m, 4H, H_e), 3.85 – 3.82 (m, 4H, H_f), 3.71-3.68 (m, 8H, $H_{g,h}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.32, 153.56, 151.09, 137.26, 126.13, 123.38, 70.82, 70.79, 69.16, 64.59 ppm; MS (ESI): *m/z* = 405 (100%), [(**L₃**+H)] $^+$; Anal. Calcd for $C_{20}H_{24}N_2O_7$: C, 59.40; H, 5.98; N, 6.93. Found: C, 59.63; H, 5.68; N, 7.33.

^{1}H NMR (400 MHz, D_2O) δ = 9.04 (s, 2H, H_a), 8.71 (dd, *J* = 4.8, 1.2 Hz, 2H, H_b), 8.36 (d, *J* = 7.2 Hz, 2H, H_c), 7.57 (dd, *J* = 8.0, 5.2 Hz, 2H, H_d), 4.52 – 4.50 (m, 4H, H_e), 3.93 – 3.90 (m, 4H, H_f), 3.77-3.73 (m, 8H, $H_{g,h}$) ppm.

4.6 Synthesis of complexes

*Synthesis of cis-[Pd(en)(**L₁**)](NO₃)₂,* ***1***.

cis-[Pd(en)$(NO_3)_2$] (28.9 mg, 0.099 mmol) was dissolved in water (5 mL), to this solution ligand **L₁** (31.7 mg, 0.1 mmol) was added. The solution was stirred for half an hour at room temperature to get a clear solution which was centrifuged and evaporated to get a colourless

solid as the product, 51.4 mg (85%). m. p. 516 K (decomposed); ^{1}H NMR (400 MHz, D_2O) δ = 9.79 (s, 2H, H_a), 9.13 (d, J = 5.6 Hz, 2H, H_b), 8.62 (d, J = 8.4 Hz, 2H, H_c), 7.81 (dd, J = 7.8 and 5.8 Hz, 2H, H_d), 4.68 (m, 4H, H_e), 4.12 (m, 4H, H_f), 2.99 (s, 4H, H_g) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 164.08, 155.20, 151.45, 141.29, 129.22, 126.86, 67.88, 64.92, 46.87 ppm; MS (ESI): *m/z* = 544 [**1**-NO_3]$^+$, 241 [**1**-2NO_3]$^{2+}$; Anal. Calcd for $C_{18}H_{24}N_6O_{11}Pd$: C, 35.63; H, 3.99; N, 13.85. Found: C, 35.69; H, 4.12; N, 13.65.

*Synthesis of cis-[Pd(bpy)(**L$_1$**)](NO$_3$)$_2$, **2**.*

Ligand **L$_1$** (32.5 mg, 0.102 mmol) was dissolved in acetonitrile (5 mL), to this *cis*-[Pd(bpy)(NO_3)$_2$] (39.4 mg, 0.102 mmol) was added. The solution was stirred for three hour and the yellowish solution was centrifuged. The clear solution was evaporated at room temperature to get a yellowish white powder as the pure product, 68.3 mg (95%). m. p. 540 K (decomposed); ^{1}H NMR (400 MHz, D_2O) δ = 10.07 (s, 2H, H_a), 9.40 (d, J = 5.6 Hz, 2H, H_b), 8.76 (d, J = 8.0 Hz, 2H, H_c), 8.55 (d, J = 8.0 Hz, 2H, $H_{a'}$), 8.46 (t, J = 7.6 Hz, 2H, $H_{b'}$), 7.99 (dd, J = 8.0 and 6.0 Hz, 2H, H_d), 7.66 (t, J = 6.6 Hz, 2H, $H_{c'}$), 7.54 (d, J = 5.2 Hz, 2H, $H_{d'}$), 4.88 (tt, J = 9.4 and 2.4 Hz, 2H, $H_{e/e'}$), 4.51 (qd, J = 12.6 and 2.0 Hz, 2H, $H_{e/e'}$), 4.15 (tt, J = 9.8 and 1.6 Hz, 2H, $H_{f/f'}$), 4.05 (qd, J = 12.8 and 2.1 Hz, 2H, $H_{f/f'}$) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.68, 156.73, 154.90, 151.75, 149.89, 142.89, 142.20, 129.89, 128.52, 128.09, 124.44, 67.95, 65.07 ppm; MS (ESI): *m/z* = 640 [**2**-NO_3]$^+$, 289 [**2**-2NO_3]$^{2+}$; Anal. Calcdfor $C_{26}H_{24}N_6O_{11}Pd$: C, 44.43; H, 3.44; N, 11.96. Found: C 44.59, H 3.62, N, 12.12.

*Synthesis of cis-[Pd(phen)(**L$_1$**)](NO$_3$)$_2$, **3**.*

Ligand **L$_1$** (12.1 mg, 0.038 mmol) was dissolved in acetonitrile (4 mL), *cis*-[Pd(phen)(NO_3)$_2$] (16.4 mg, 0.04 mmol) was added to it. The solution was stirred for twelve hour to obtain an yellowish white precipitate as the product, 26.7 g (92%). m. p. 513 K; ^{1}H NMR (400 MHz, D_2O) δ = 10.09 (s, 2H, H_a), 9.43 (d, J = 5.6 Hz, 2H, H_b), 8.94 (d, J = 7.6 Hz, 2H, $H_{b'}$), 8.75 (d, J = 8.0 Hz, 2H, H_c), 8.27 (s, 2H, $H_{a'}$), 7.99 (dd, J = 8.0 and 6.0 Hz, 2H, H_d), 7.90-7.84 (m,

4H, $H_{c'}$ and $H_{d'}$), 4.80 ($H_{e/e'}$), 4.07 (t, J = 5.6 Hz, 2H, $H_{f/f'}$), 3.84 (d, J = 11.2 Hz, 2H, $H_{f/f'}$) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.56, 155.03, 151.88, 150.38, 147.00, 142.15, 141.74, 131.16, 129.78, 128.38, 128.01, 125.95 67.83, 64.95 ppm; MS (ESI): *m/z* = 664 [**3**-NO_3]$^+$, 301 [**3**-$2NO_3$]$^{2+}$; Anal. Calcd for $C_{28}H_{24}N_6O_{11}Pd$: C, 46.26, H, 3.33; N, 11.56. Found: C, 46.48; H, 3.61; N, 11.82.

*Synthesis of [Pd(**L₁**)$_2$](NO$_3$)$_2$, **4**.*

Ligand **L₁** (40 mg, 0.13 mmol) was added to a 10 mM $Pd(NO_3)_2$ solution in acetonitrile (6 mL, 0.06 mmol) at room temperature, the solution was stirred for six hour at same temperature to get a white precipitate. This precipitate was centrifuged and dried, the white powder was again dissolved in water (5 mL) and stirred for one hour at room temperature, it was centrifuged and the colourless solution was decanted and evaporated at room temperature to get a colourless solid as the product, 43.6 mg (79%). m. p. 469 K (decomposed); ^{1}H NMR (400 MHz, D_2O) δ = 10.13 (d, J = 1.2 Hz, 4H, H_a), 9.27 (dd, J = 5.8 and 0.8 Hz, 4H, H_b), 8.56 (td, J = 8.0 and 1.5 Hz, 4H, H_c), 7.73 (dd, J = 8.2 and 5.8 Hz, 4H, H_d), 4.67 - 4.65 (m, 8H, H_e), 4.19 - 4.17 (m, 8H, H_f) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.69, 154.47, 151.16, 141.68, 129.68, 127.37, 68.00, 65.22 ppm; MS (ESI): *m/z*= 800 [**4**-NO_3]$^+$, 369 [**4**-$2NO_3$]$^{2+}$; Anal. Calcd for $C_{32}H_{32}N_6O_{16}Pd$: C, 44.53; H, 3.74; N, 9.74. Found: C, 44.67; H, 3.63; N, 9.82.

*Synthesis of cis-[Pd(en)(**L₂**)](NO$_3$)$_2$, **5**.*

cis-[Pd(en)(NO_3)$_2$] (30 mg, 0.10 mmol) was dissolved in water (5 mL); ligand **L₂** (38 mg, 0.10 mmol) was added to it. The mixture was stirred for half an hour at room temperature to get a clear solution which was centrifuged and evaporated to get a colorless solid as the product, 55 mg (82%). m. p. 440 K (decomposed); ^{1}H NMR (400 MHz, D_2O) δ = 9.64 (d, J = 1.6 Hz, 2H, H_a), 9.06 (dd, J = 5.2 and 0.8 Hz, 2H, H_b), 8.57 (dd, J = 7.2 and 1.6 Hz, 2H, H_c), 7.76 (dd, J = 8.2 and 5.8 Hz, 2H, H_d), 4.59 – 4.58 (m, 4H, H_e), 3.98 – 3.96 (m, 4H, H_f), 3.86

(s, 4H, H_g), 2.93 (s, 4H, H_h) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 164.28, 154.78, 152.33, 141.40, 128.99, 127.02, 70.11, 68.49, 65.47, 46.86 ppm; MS (ESI): *m/z*= 263 [**5**-2NO_3]$^{2+}$; Anal. calcd for $C_{20}H_{28}N_6O_{12}Pd$: C, 36.91; H, 4.34; N, 12.91. Found: C, 36.98; H, 4.31; N, 12.85.

*Synthesis of cis-[Pd(bpy)(**L₂**)](NO₃)₂, **6**.*

Ligand **L₂** (39.3 mg, 0.10 mmol) was dissolved in acetonitrile (5 mL), to this solution *cis*-[Pd(bpy)$(NO_3)_2$] (40.2 mg, 0.10 mmol) was added at room temperature. The resulting solution was stirred for three hour at the same temperature and the yellowish solution was centrifuged, the clear solution was evaporated at room temperature to get a yellowish white solid as the pure product, 73.8 mg (95%). m. p. 429 K; ^{1}H NMR (400 MHz, D_2O) δ = 10.02 (s, 2H, H_a), 9.42 (dd, *J* = 5.2 and 0.8 Hz, 2H, H_b), 8.76 (d, *J* = 8.0 Hz, 2H, H_c), 8.52 (d, *J* = 8.0 Hz, 2H, $H_{a'}$), 8.42 (dt, *J* = 7.9 and 0.9 Hz, 2H, $H_{b'}$), 7.98 (dd, *J* = 8.2 and 5.8 Hz, 2H, H_d), 7.61 (dt, *J* = 6.7 and 1.0 Hz, 2H, $H_{c'}$), 7.39 (d, *J* = 5.6 Hz, 2H, $H_{d'}$), 4.74 (t, *J* = 10.2 Hz, 2H, $H_{e/e'}$), 4.49 (dd, *J* = 12.2 and 3.0 Hz, 2H, $H_{e/e'}$), 4.05 (t, *J* = 9.6 Hz, 2H, $H_{f/f'}$), 3.89 (d, *J* = 2.8 Hz, 2H, $H_{f/f'}$), 3.84 (s, 4H, H_g) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.92, 156.67, 154.56, 152.33, 149.75, 142.88, 142.39, 130.20, 128.33, 128.08, 124.45, 70.03, 68.37, 65.62 ppm; MS (ESI): *m/z*= 684 [**6**-NO_3]$^+$, 311 [**6**-2NO_3]$^{2+}$; Anal. Calcd for $C_{28}H_{28}N_6O_{12}Pd$: C, 45.02; H, 3.78; N, 11.25. Found: C, 45.14; H, 3.96; N, 11.19.

*Synthesis of cis-[Pd(phen)(**L₂**)](NO₃)₂, **7**.*

Ligand **L₂** (22 mg, 0.045 mmol) was dissolved in acetonitrile (5 mL), *cis*-[Pd(phen)$(NO_3)_2$] (25 mg, 0.06 mmol) was added to it. The solution was stirred for tweleve hour to obtain an yellowish solution which upon evaporation gives yellowish solid as the product, 44.6 mg (95%). m. p. 549 K; ^{1}H NMR (400 MHz, D_2O) δ = 10.04 (s, 2H, H_a), 9.43 (d, *J* = 5.6 Hz, 2H, H_b), 8.89 (d, *J* = 8.4 Hz, 2H, $H_{b'}$), 8.73 (d, *J* = 8.4 Hz, 2H, H_c), 8.23 (s, 2H, $H_{a'}$), 7.96 (dd, *J* = 7.2 and 6.0 Hz, 2H, H_d), 7.82 (dd, *J* = 8.0 and 5.2 Hz, 2H, $H_{c'}$) 7.69 (d, *J* = 5.2 Hz, 2H, $H_{d'}$),

4.70-4.65 (m, 2H, $H_{e/e'}$), 4.43-4.40 (m, 2H, $H_{e/e'}$), 3.99-3.94 (m, 2H, $H_{f/f'}$), 3.80-3.76 (m, J = 8.4 Hz, 2H, $H_{f/f'}$), 3.75 (s, 4H, H_g) ppm; ^{13}C NMR (100 MHz, D_2O): δ = 164.10, 155.00, 152.82, 150.57, 147.20, 142.58, 141.98, 131.41, 130.35, 128.46, 128.27, 126.23, 70.21, 68.54, 65.76 ppm; MS (ESI): *m/z* = 708 [**7**-NO_3]$^+$, 323 [**7**-$2NO_3$]$^{2+}$; Anal. calcd $C_{30}H_{28}N_6O_{12}Pd$: C, 46.73; H, 3.66; N, 10.09. Found: C, 46.67; H, 3.97; N, 10.38.

*Synthesis of [Pd(**L₂**)₂](NO₃)₂, **8**.*

Ligand **L₂** (43.4 mg, 0.12 mmol) was added to a $Pd(NO_3)_2$ solution in acetonitrile (6 mL of 10 mM, 11 mmol) at room temperature, the color of $Pd(NO_3)_2$ faded away immediately and the solution was stirred for three hour at same condition. The yellowish solution was centrifuged and evaporated to give a colorless solid as the product, 52.1 mg (92%). m. p. 507 K (decomposed); ^{1}H NMR (400 MHz, D_2O) δ = 9.84 (s, 4H, H_a), 9.31 (d, J = 5.2 Hz, 4H, H_b), 8.63 (d, J = 8.0 Hz, 4H, H_c), 7.84 (t, J = 6.8 Hz, 4H, H_d), 4.66 (s, 8H, H_e), 4.07 (s, 8H, H_f), 3.96 (s, 8H, H_g) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.71, 154.09, 151.72, 141.98, 129.65, 127.58, 70.80, 68.37, 65.46 ppm; MS (ESI): *m/z*= 888 [**8**-NO_3]$^+$, 413 [**8**-$2NO_3$]$^{2+}$; Anal. Calcd for $C_{36}H_{40}N_6O_{18}Pd$: C, 45.46; H, 4.24; N, 8.84. Found: C, 45.36; H, 4.32; N, 8.97.

*Synthesis of cis-[Pd(en)(**L₃**)](NO₃)₂, **9**.*

cis-[Pd(en)$(NO_3)_2$] (10 mg, 0.034 mmol) was dissolved in water (4 mL) to this ligand **L₃** (13.9 mg, 0.034 mmol) was added. The mixture was stirred for six hour at room temperature to get a clear solution which was centrifuged and evaporated to get a colorless solid as the product, 18.6 mg (78%). m. p. 343 K; ^{1}H NMR (400 MHz, D_2O) δ = 9.37 (d, J = 1.2 Hz, 2H, H_a), 9.07 (dd, J = 6.0 and 1.2 Hz, 2H, H_b), 8.65 (dd, J = 8.0 and 1.2 Hz, 2H, H_c), 7.85 (dd, J = 8.0 and 5.6 Hz, 2H, H_d), 4.65 – 4.63 (m, 4H, H_e), 3.99 – 3.97 (m, 4H, H_f), 3.84 – 3.79 (m, 8H, $H_{g,h}$), 2.99 (s, 4H, H_i) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 164.44, 154.92, 152.36, 141.73, 129.30, 127.31, 70.09, 69.99, 68.88, 65.67, 47.06 ppm; MS (ESI): *m/z*= 632 [**9**-NO_3]$^+$ and285

[**9**-2NO_3]$^{2+}$; Anal. calcd for $C_{22}H_{32}N_6O_{13}Pd$: C, 38.02; H, 4.64; N, 12.09. Found: C, 38.35; H, 4.31; N, 12.43.

*Synthesis of cis-[Pd(bpy)(**L₃**)](NO₃)₂,* ***10***.

Ligand **L₃** (12.6 mg, 0.031 mmol) was dissolved in acetonitrile (3 mL), to this solution *cis*-[Pd(bpy)(NO_3)$_2$] (12 mg, 0.031 mmol) was added at room temperature. The resulting solution was stirred for six hour at the same temperature and the yellowish solution was centrifuged, the clear solution was evaporated at room temperature to get a yellowish white solid as the pure product, 22.4 mg (91%). m. p. 353 K; ^{1}H NMR (400 MHz, D_2O) δ = 9.67 (s, 2H, H_a), 9.35 (d, J = 5.6 Hz, 2H, H_b), 8.67 (d, J = 8.0 Hz, 2H, H_c), 8.43 (d, J = 8.0 Hz, 2H, $H_{a'}$), 8.33 (t, J = 6.8 Hz, 2H, $H_{b'}$), 7.89 (t, J = 6.8 Hz, 2H, H_d), 7.51 (t, J = 6.8 Hz, 2H, $H_{c'}$), 7.33 (d, J = 5.6 Hz, 2H, $H_{d'}$), 4.65 – 4.63 (m, 2H, $H_{e/e'}$), 4.49 – 4.44 (m, 2H, $H_{e/e'}$), 3.92 – 3.85 (m, 4H, $H_{f/f'}$), 3.72 (s, 4H, H_g), 3.64 (s, 4H, H_h) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 164.07, 156.87, 154.84, 152.22, 149.97, 143.01, 142.68, 130.61, 128.48, 128.24, 124.61, 70.04, 69.89, 68.89, 65.83 ppm; MS (ESI): *m/z*= 333 [**10**-2NO_3]$^{2+}$; Anal. Calcd for $C_{30}H_{32}N_6O_{13}Pd$: C, 45.55; H, 4.08; N, 10.62. Found: C, 45.14; H, 3.92; N, 11.05.

*Synthesis of cis-[Pd(phen)(**L₃**)](NO₃)₂,* ***11***.

Ligand **L₃** (14.8 mg, 0.035 mmol) was dissolved in acetonitrile (4 mL), to this 15 mg of *cis*-[Pd(phen)(NO_3)$_2$] (0.036 mmol) was added. The solution was stirred for fifteen hour to obtain an yellowish solution which upon evaporation gave pale yellow solid as the product, 27.1 mg (91%). m. p. 483 K; ^{1}H NMR (400 MHz, D_2O) δ = 9.86 (s, 2H, H_a), 9.53 (d, J = 4.8 Hz, 2H, H_b), 8.98 (d, J = 8.4 Hz, 2H, $H_{b'}$), 8.82 (d, J = 8.4 Hz, 2H, H_c), 8.31 (s, 2H, $H_{a'}$), 8.05 (d, J = 6.4 Hz, 2H, H_d), 7.91 (dd, J = 8.0 and 5.6 Hz, 2H, $H_{c'}$), 7.81 (s, 2H, $H_{d'}$), 4.75 - 4.72 (m, 2H, $H_{e/e'}$), 4.61 - 4.56 (m, 2H, $H_{e/e'}$), 3.95 (bs, 4H, $H_{f/f'}$), 3.77 (bs, 4H, H_g), 3.70 (bs, 4H, H_h) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 164.08, 155.12, 152.49, 150.60, 147.20, 142.71, 141.94, 131.40, 130.61, 128.45, 128.29, 126.22, 69.99, 69.86, 68.89, 65.77 ppm; MS (ESI): *m/z* =

345 [**11**-2NO_3]$^{2+}$; Anal. calcd for $C_{32}H_{32}N_6O_{13}Pd$: C, 47.16; H, 3.96; N, 10.31. Found: C, 47.34; H, 4.16; N, 10.68.

*Synthesis of [Pd(**L**$_3$)$_2$](NO$_3$)$_2$, **12**.*

Ligand **L**$_3$ (32 mg, 0.08 mmol) was added to a $Pd(NO_3)_2$ solution in acetonitrile (4 mL of 10 mM, 0.04 mmol) at room temperature, the color of $Pd(NO_3)_2$ faded away immediately and the solution was stirred for three hour at same condition. The yellowish solution was centrifuged and evaporated to give a colorless solid as the product, 34.2 mg (83%). m. p. 458 K; ^{1}H NMR (400 MHz, D_2O) δ = 9.40 (d, J = 1.2Hz, 4H, H_a), 9.16 (d, J = 5.2 Hz, 4H, H_b), 8.66 (td, J = 8.0 and 1.6 Hz, 4H, H_c), 7.83 (dd, J = 7.6 and 5.6 Hz, 4H, H_d), 4.63 – 4.61 (m, 4H, H_e), 4.03 – 3.96 (m, 4H, H_f), 3.83 – 3.81 (m, 8H, $H_{g,h}$) ppm; ^{13}C NMR (100 MHz, D_2O) δ = 163.98, 154.72, 151.98, 142.46, 129.95, 127.88, 70.08, 69.98, 68.82, 65.69 ppm; MS (ESI): *m/z*= 457 [**12**-2NO_3]$^{2+}$; Anal. calcd for $C_{40}H_{48}N_6O_{20}Pd$: C, 46.23; H, 4.66; N, 8.09. Found: C, 46.66; H, 4.31; N, 8.37.

Supporting Information: Electronic Supplementary Information (ESI) available: NMR, ESI MS and crystallographic data. CCDC (compound no.) 775746 (**1**); 775747(**2**); 775748(**8**).

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Water soluble mononuclear self-assembled Pd(II) based molecular loops

Molecular chair like structure demonstrated via crystallographic study.

Binding of few molecular loops with DNA

Self-assembled mononuclear palladium(II) based molecular loops

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Graphical abstract

Synopsis

Mononuclear self-assembled palladium(II) based molecular loops are prepared by combining *meta*-pyridine appended bidentate ligands crafted with flexible polyethylene glycol spacers with a variety of palladium(II) components. A family of twelve compounds with large chelate rings has been realized both in solution and a few in solid states. All the molecules are water soluble and exclusively mononuclear in nature.