Platinum(II) and palladium(II) metallomacrocycles derived from cationic 4,4′-bipyridinium, 3-aminopyrazinium and 2-aminopyrimidinium ligands†

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A series of cationic, ditopic *N*-donor ligands based on 4,4′-bipyridine (4,4′-bipy), 3-aminopyrazine (apyz) and 2-aminopyrimidine (apym), each incorporating two positively-charged *N*-heterocycles linked by a conformationally-flexible spacer unit, have been synthesised and treated with palladium(II) or platinum(II) precursors [M(2,2′-bipy)$(NO_3)_2$] (M = Pd(II) or Pt(II)) to form highly cationic metallocyclic species. Treatment of 1,6-bis(4,4′-bipyridinium)hexane nitrate with [M(2,2′-bipy)$(NO_3)_2$] in aqueous solution, followed by the addition of KPF_6, resulted in the formation of the [2+2] species [M_2(2,2′-bipy)$_2${4,4′-bipy$(CH_2)_6$4,4′-bipy}$_2$]$(PF_6)_8$. Treatment of [Pd(PhCN)$_2Cl_2$] with 1,3-bis(4,4′-bipyridinium)propane hexafluorophosphate in MeCN afforded [Pd_2Cl_4{4,4′-bipy$(CH_2)_3$4,4′-bipy}$_2$]$(PF_6)_4$. When the cationic apyz or apym ligands were used in aqueous solution, the analogous metallomacrocycles did not form. Instead, deprotonation of the exocyclic amino group occurred upon coordination of the ligand to afford a tetranuclear [4+2] species in the case of platinum(II), with Pt(II)···Pt(II) bonding supported by strong UV-vis absorption at $\lambda = 428$ nm which was assigned to a metal-metal-to-ligand charge transfer (MMLCT) band. Thus, treatment of 1,6-bis(3-aminopyrazinium)hexane nitrate with [Pt(2,2′-bipy)$(NO_3)_2$], followed by the addition of KPF_6, led to the formation of the red species [Pt_4(2,2′-bipy)$_4${apyz$(CH_2)_6$apyz–2H}$_2$]$(PF_6)_8$. No related products could be identified with palladium(II), consistent with the low propensity for this metal ion to form strong Pd(II)···Pd(II) bonding interactions.

Introduction

N-donor heterocyclic ligands such as 2,2′- and 4,4′-bipyridine (2,2′-bipy and 4,4′-bipy, respectively) have been an ubiquitous part of coordination chemistry[1] for many decades and, more recently, in the study of metallosupramolecular systems.[2] By comparison, the use of related cationic ligands is extremely limited, not surprisingly, due to the low stability of the resulting coordination complexes as a result of strong electrostatic repulsions between the charged ligand and the transition metal cation. In contrast, formally cationic ligands such as the cyclic conjugated tropylium,[3] cyclopropenyl[3] and triazolidene[4] species are well-documented in organometallic chemistry where low-valent metals can form stable complexes with these types of ligand systems.

Despite their paucity, several distinct classes of cationic ligands largely based on *N*- and/or *P*-donor atoms have been reported. These examples include hydrazinium salts which form, for example, complexes of the type M$(N_2H_5)_2(SO_4)_2$ (M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II));[5] related ligands such as the 1,1,1-trimethylhydrazinium cation are also known.[6] *P*-donor ligands including phosphenium[7] and phosphonium cations[8,9] can sometimes form stable complexes,[10] *e.g.* [NiCO(np$_3$H)]$^+$ which contains the protonated form of tris(2-(diphenylphosphino)ethyl)amine (np$_3$),[11] and a few hybrid *N*,*P*-donor ligand systems have also been reported.[12,13] Heterocyclic *N*-donor ligands and related imidazolium ionic liquids in which at least one nitrogen atom is protonated or, alternatively, quaternised with alkyl groups are the best represented examples of cationic ligands which have been reported to date.[14-19] These ligands, particularly the ionic liquids, are of interest in catalysis, environmental chemistry, studies of electron transfer phenomena, and in supramolecular systems.

Our interest in multinuclear metal complexes bearing high positive charges stems from the potential use of such complexes in new materials such as metal-organic frameworks which may be exploited for the selective trapping of anionic species and large metallomacrocycles that may be used to probe the structure and function of polyanionic biomolecules such as DNA.[20] The ability to synthesise a diverse range of cationic, bridging *N*-donor ligand derivatives would allow direct entry to highly water-soluble multinuclear complexes, with the properties of the complexes able to be tuned by the appropriate ligand design.

In this paper we report a family of ditopic ligands, each of which incorporate two positively-charged *N*-heterocycles linked by a conformationally flexible spacer unit. These compounds represent a family of ligands which can be engineered readily in terms of their size (by varying the spacer unit), solubility (by varying the nature of the counter-ion), and basicity (by varying the nature of the heterocyclic donor group, in this case 4,4′-bipy, 3-aminopyrazine

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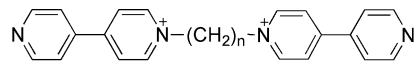
(apyz) or 2-aminopyrimidine (apym)). We also describe the reactions of selected ligands with palladium(II) and platinum(II) precursors to afford highly cationic metallomacrocycles, some of which undergo facile deprotonation in aqueous solution to afford new types of metallomacrocycles which possess unusual structures.

Results and discussion

Synthesis of the cationic ligands

The cationic bridging ligands **1-8** were conveniently prepared as their bromide salts by using an adaptation of the procedure described by Attalla and co-workers.[21] Originally used for the preparation of α,ω-bis(4,4′-bipyridinium)alkane bromide salts, this method was readily adapted with respect to the nucleophilic heterocyclic species as well as the alkyl bromides. For the preparation of the dicationic species, the nucleophile was typically used in excess (~4 equiv.) in order to promote di- rather than mono-substitution reactions. The crude products were readily crystallised from hot water to give satisfactory yields of the bromide salts. The bromide counter-ions were exchanged for nitrate and hexafluorophosphate in order to generate a suite of heterocyclic salts that were soluble in both organic and aqueous solutions. In addition, the bromide counter-ion was replaced in the ligands to avoid competition with the *N*-donor atoms for metal coordination sites.



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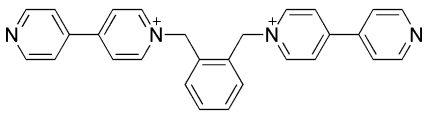
2 n = 4
3 n = 6



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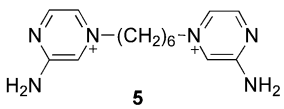

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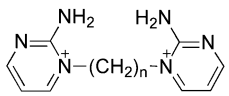
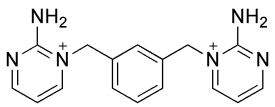


6 n = 4
7 n = 5



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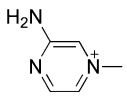

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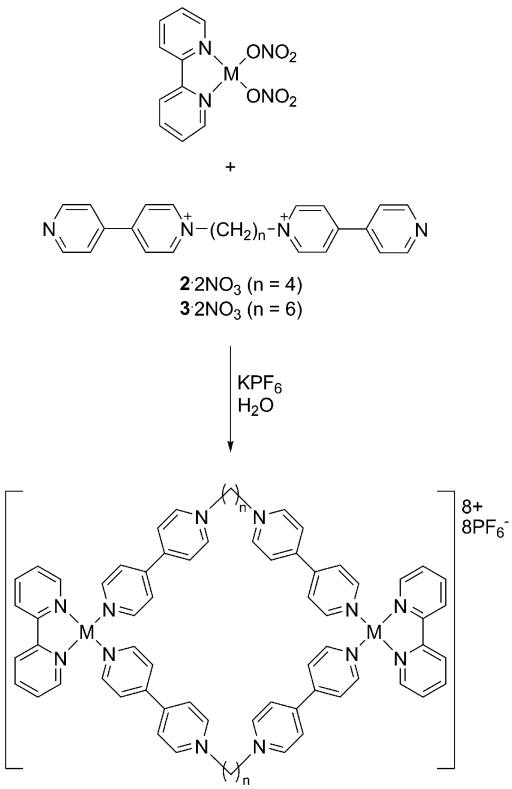
Platinum(II) and palladium(II) complexes containing 4,4′-bipyridinium derivatives

An equimolar mixture of the alkyl-bridged 4,4′-bipyridinium nitrate salts **2**·2NO_3 or **3**·2NO_3 and [M(2,2′-bipy)$(NO_3)_2$] (M = Pd, Pt) in D_2O solution was heated at 80 °C and the reaction mixture was monitored by ^{1}H NMR spectroscopy (Scheme 1). The NMR spectrum of all four metal complexes **10-13** exhibited a single set of resonances after 24 h or 48 h heating (for Pd(II) or Pt(II), respectively), consistent with the formation of a single product possessing high symmetry in each reaction. The complexes **10-13** were isolated as their hexafluorophosphate salts by the addition of saturated aqueous KPF_6 to the solution.



2·2NO_3 (n = 4)
3·2NO_3 (n = 6)

10 M = Pd; n = 4
11 M = Pt; n = 4
12 M = Pd; n = 6
13 M = Pt; n = 6

Scheme 1

The ^{1}H NMR spectra of **2**·2NO_3 and the corresponding palladium(II) complex **10** are shown in Fig. 1. The protons α- to the non-quaternary *N*-atoms resonated at lower field upon reaction with palladium(II) ($\Delta\delta = 0.48$). This change in chemical shift is diagnostic of coordination of $\mathbf{2}^{2+}$ to the electrophilic metal centre and is consistent with, but not necessarily indicative of, dinuclear complex formation. The NMR data for the other complexes (**11-13**) were also consistent with their proposed structures but while NMR analysis can often confirm the symmetry of

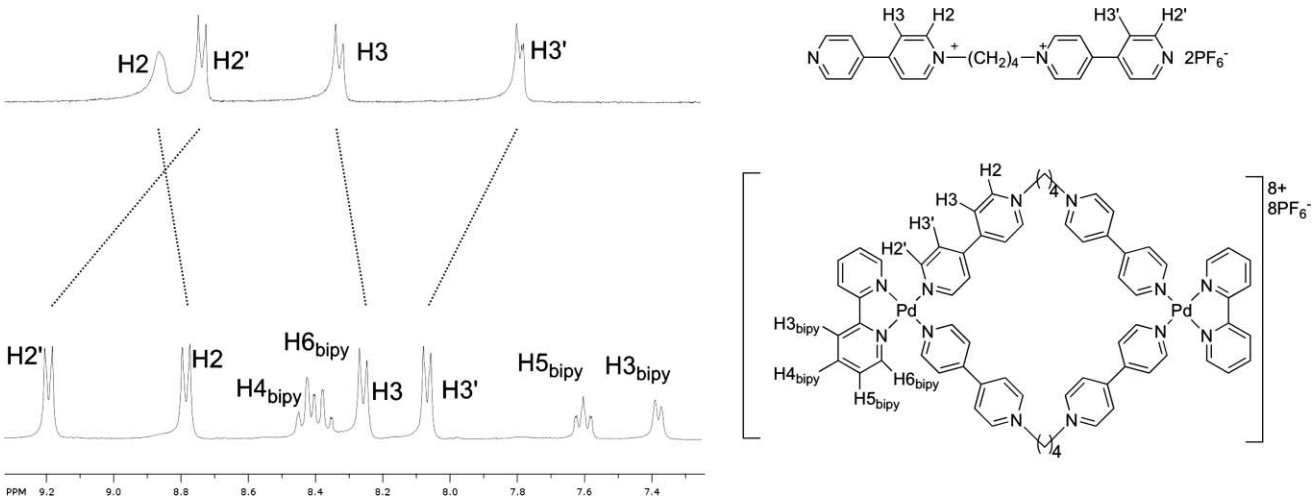
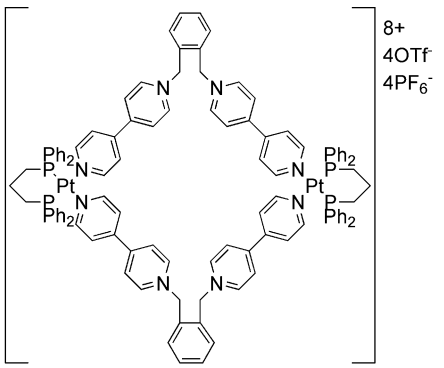


Fig. 1 Partial ^{1}H NMR spectra of **2**·2NO_3 (top) and **10** (bottom) recorded in CD_3CN at 300 MHz.

metallosupramolecular species, it provides no evidence regarding nuclearity.[23] ESI-MS analysis was used to provide some insight into the nuclearity of the complexes but was unsuccessful when the nitrate salts were used; only smaller cationic fragments were detected. In contrast, the hexafluorophosphate salts **10-13** which are soluble in Me_2CO or MeCN were more amenable to ESI-MS analysis and, in the case of **13**, the intact complex ions [**13**–2PF_6]$^{2+}$ (*m*/*z* 1182.153886, calcd 1182.156840) and [**13**–3PF_6]$^{3+}$ (*m*/*z* 739.781613, calcd 739.782983) were observed in the ESI-FTICR mass spectrum.

The organic soluble hexafluorophosphate salts of selected organocations (**1**·2PF_6 and **4**·2PF_6) were also combined with palladium(II) or platinum(II) precursors in order to determine whether related dinuclear species to **10-13** would form in non-aqueous solvents where ion-pairing would be expected to feature. The metal precursors employed were chosen based on their organic solubility and it was expected that the phosphine and chlorido ligands might labilise the weakly-bound ligands *trans* to these ligands (triflato and benzonitrile, respectively), resulting in rapid formation of the thermodynamic product in each case. Equimolar mixtures of **4**·2PF_6 and [Pt(dppp)(OTf)$_2$] (dppp = 1,3-bis(diphenylphosphino)propane) or **1**·2PF_6 and [Pd(PhCN)$_2$Cl$_2$] were heated in MeCN solution to afford the dinuclear metallomacrocycles **14** and **15**, respectively. Each of the metallomacrocycles was characterised by ^{1}H NMR spectroscopy, ESI-MS and microanalysis. Quintela and co-workers have recently reported the preparation of the closely-related metallacyclic complexes **16** and **17**,[24,25] which were integrated into catenane topologies, *via* interaction of the electron deficient metallomacrocycle with electron-rich organic macrocycles such as dibenzo-24-crown-8.



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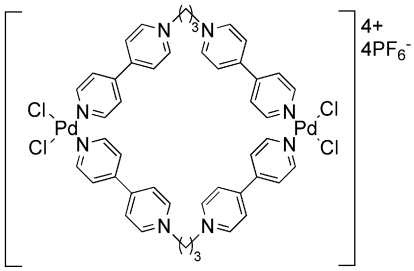

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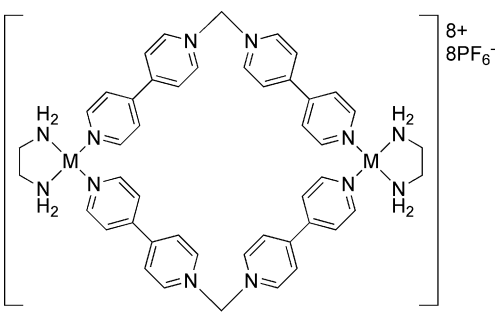
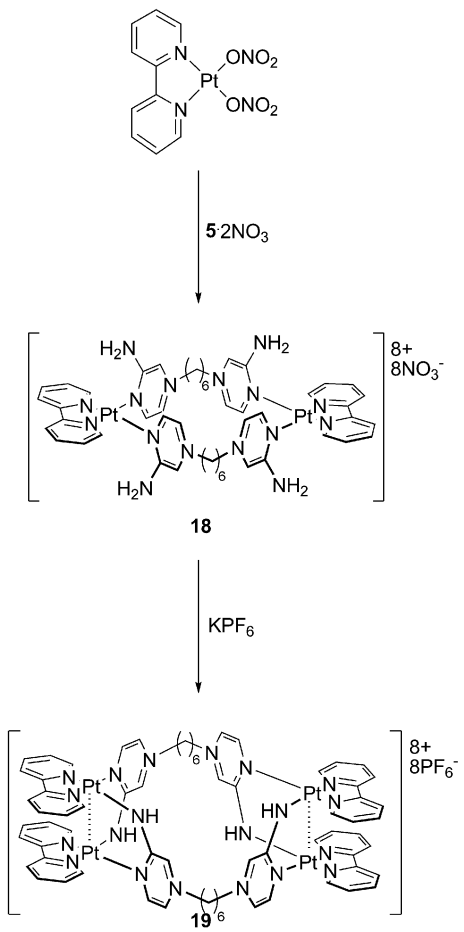


16 M = Pd
17 M = Pt

Platinum(II) complexes derived from 3-aminopyrazinium derivatives

The coordination chemistry of the bis(3-aminopyrazinium) derivative **5**·2NO_3 was investigated using platinum(II) and palladium(II). Heating an aqueous suspension of equimolar amounts of **5**·2NO_3 and [Pt(2,2′-bipy)(NO$_3$)$_2$] resulted in the formation of an

orange solution rather than the expected pale-yellow solution with the solution changing to red upon further heating. ESI-FTICR-MS analysis of the hexafluorophosphate derivative of this product was consistent with the presence of a tetranuclear species such as **19** (Scheme 2) incorporating two quadruply-bridging zwitterionic ligands (*m*/*z* 891.768992, calcd 891.768257 [M – $3PF_6$]$^{3+}$). Initial coordination of ligand **5**·$2NO_3$ to the metal centre followed by deprotonation of exocyclic amine allows coordination to four platinum(II) centres, each of which are equivalent. The ^{195}Pt NMR spectrum of **19** displays a single peak δ –2361, consistent with a PtN_4 coordination sphere.[26] The complexation of each platinum(II) centre by a pyrazine *N*-atom as well as an amido *N*-atom is necessary in order to satisfy the identical coordination spheres of the four metal centres. While one possible structure for **19** is presented in Scheme 2, another possible structure for this complex is a double helix, in which there is inversion of chirality at one of the metal centres thus resulting in a 'twist' in the bridging ligands. Unfortunately, numerous attempts to confirm the structure of **19** by X-ray diffraction studies failed as suitable single crystals could not be obtained.



Scheme 2

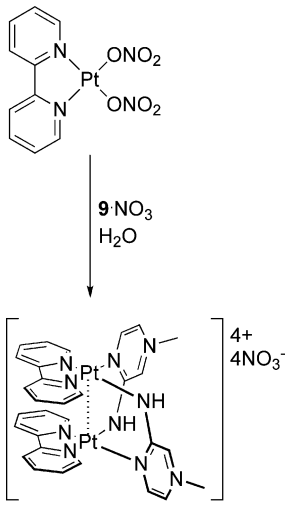
Further support for the tetranuclear nature of **19** was provided by the UV-visible spectrum of the metallomacrocycle which featured an absorption peak at 428 nm and is assigned to a metal-metal-to-ligand charge transfer (MMLCT) band.[27,28] The Pt(II)···Pt(II) and π–π interactions present within the complex give rise to this absorption and also result in its deep-red colour; such interactions would also help to stabilise the octacationic species. Each of the $[Pt_2(2,2'\text{-bipy})_2]^{4+}$ groups in **19** forms "head-to-tail" dimers as each platinum(II) centre is bound to nonequivalent atoms in the bridging ligands. As the formula of the tetranuclear complex suggests, it can be prepared using a 2:1 (Pt : ligand) molar ratio of the precursors. Under these conditions only one set of hexylene signals was observed in the ^{1}H NMR spectrum of the reaction mixture with no free ligand being present. It is also noteworthy that no reaction products could be identified when **5**·$2NO_3$ was treated with the palladium(II) precursor [Pd(2,2′-bipy)$(NO_3)_2$], perhaps indicating that metal-metal interactions involving the 5*d* rather than 4*d* metal ion may be required to stabilise the cationic metallomacrocycle **19**.[29] Similar results were observed when bis(2-aminopyrimidinium) salts were used (*vide infra*).

Metal-metal (metallophilic) interactions of the type which appear to be present in **19** are not uncommon for d^8 ions,[29-31] and certain arrangements of metal centres, including those involving the stacking of such metallodimers in infinite 1-D chains, can give rise to anisotropic materials with unique optical properties.[32] The formation of species incorporating $[Pt_2(2,2'\text{-bipy})_2]^{4+}$ fragments is well-documented, and several reports exist of these bridged structures. For example, Sakai and co-workers reported the preparation of [Pt(2,2′-bipy)(2-aminopyridine)$_2$]$(NO_3)_2$ from [Pt(2,2′-bipy)$(NO_3)_2$] and 2-aminopyridine.[33] However, this species decomposed in superheated H_2O (415 K) to afford the Pt(II)···Pt(II) bonded species $[Pt_2(2,2'\text{-bipy})_2(2\text{-aminopyridinato})_2](NO_3)_2$ and free 2-aminopyridinium.[34] This species, owing to the "head-to-tail" arrangement of ligands, is chiral and under the conditions employed would be expected to be formed as the racemate. In the present study, the increased acidity of the aminopyrazinium groups, relative to 2-aminopyridine, is the likely reason why supercritical conditions are not required for the reactions when these ligands are employed. As a consequence, we propose the facile formation of **19** from the intermediate **18** which was not detected spectroscopically (Scheme 2). This result is in contrast to the example reported by Sakai *et al.*,[33] in which the corresponding mononuclear intermediate species was isolated.

In order to compare the aqueous reactivity of the apyz ligands to that of 2-aminopyridine, the chemistry of a simple cationic ligand incorporating one (instead of two) heterocyclic rings was studied. Heating an equimolar suspension of [Pt(2,2′-bipy)$(NO_3)_2$] and **9**·NO_3 in D_2O gave rise to a red solution in which the dinuclear complex **20** was the major product (Scheme 3). Although the parent ions of **20** (or its hexafluorophosphate salt) could not be observed by ESI-MS, NMR and UV-visible spectroscopic and microanalytical data were consistent with the proposed structure. A very complex ^{1}H NMR spectrum, similar to that of **19**, was obtained and the structure presented for **20** represents only one of the isomers that may form (*vide supra*). Of particular interest are the almost identical λ_{MMLCT} and $\delta(^{195}\text{Pt})$ values measured for both the dinuclear **20** and tetranuclear **19** complexes.

Platinum(II) complexes derived from 2-aminopyrimidinium derivatives

Given that "head-to-tail" platinum(II) complexes of guanidinato derivatives have been previously reported,[32] it was of interest to

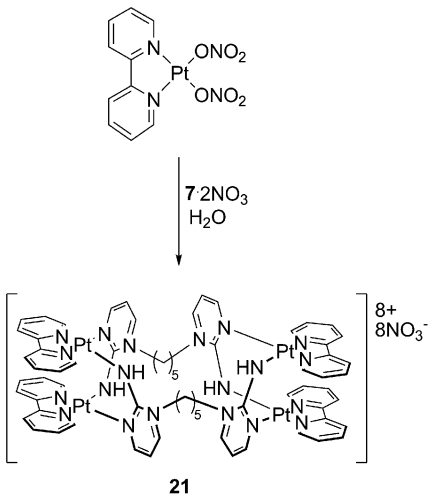


20

Scheme 3

prepare complexes of bis(2-aminopyrimidinium) nitrate salts. The apym fragments, each of which incorporates an aryl guanidinium moiety, were expected to behave in much the same way as the related apyz species discussed above.

Heating an aqueous suspension of **6**·2NO_3 and [Pt(2,2′-bipy)$(NO_3)_2$] (2 equiv.) afforded a clear red solution, suggesting formation of a Pt(II)···Pt(II) bonded species (*cf.* the apyz species **19**). However, NMR and ESI-MS data did not provide conclusive data to support the formation of a tetranuclear species as found in the reaction of the apyz ligand **5**·2NO_3 with the same precursor complex (Scheme 2). Extended heating of the mixture resulted in the precipitation of an intractable dark-red material. In contrast, using the same reaction conditions with the related salt **7**·2NO_3 resulted in formation of the dinuclear complex **21** (Scheme 4) which precipitated as an orange solid as the hexafluorophosphate salt. Complex **21** may also possess a chiral double-helicate structure, as discussed for the metallomacrocycle **19**.



21

Scheme 4

Analysis of complex **21** by ESI-FTICR-MS showed an ion distribution centred at *m*/*z* 1395.61458, which is assigned to [**21**–2PF_6]$^{2+}$. A second ion distribution centred at *m*/*z* 1395.11783, corresponding to the dinuclear fragment ion [$\frac{1}{2}$**21**–PF_6]$^+$, was superimposed on this envelope. In both cases, the difference between isotopologue *m*/*z* values for each species (~0.5 and ~1, respectively) is consistent with the proposed formula.

^{1}H NMR spectroscopic analysis of **21** showed the presence of one major product with trace amounts of another species, possibly a diastereomer of the major product (the dinuclear fragment is not expected to be stable in solution). A single ^{195}Pt NMR resonance at δ −2254 was observed, which is consistent with a PtN_4 core. However, the UV-visible spectrum of **21** lacks an absorption peak at ~450 nm which is often diagnostic of Pt(II)···Pt(II) interactions in similar systems (*vide supra*).[27,28]

As described above for the 4,4′-bipy cations **2**·2NO_3, **3**·2NO_3, **1**·2PF_6 and **4**·2PF_6, the reactivity of selected apyz and apym dications as the hexafluorophosphate salts towards labile platinum(II) complexes was also investigated in organic solvents. Both types of cationic heterocycles were found to be very poor ligands in non-aqueous solvents probably due to the formation of intimate ion-pairs which would possess a low propensity to undergo metal complexation. For example, the ligand **8**·2PF_6 was combined with an equimolar amount of [Pt(dppp)$(OTf)_2$] in CD_3CN solution. There was no evidence of any reaction from NMR or ESI-MS analyses but the ligand **8**·2PF_6 (as its mixed PF_6^-/OTf^- salt, **8**·PF_6/OTf) was crystallised from the solution and its structure was solved by X-ray diffraction (see Supplementary Information). Deprotonation of the conjugated amine groups in the apyz and apym dications by the addition of base, *e.g.* NEt_3, to the reaction mixtures failed to induce any complexation.

Conclusion

In this work we have described the preparation of a series of cationic *N*-donor ligands which were treated with labile palladium(II) and platinum(II) precursors to afford highly-charged, stable di- and tetra-nuclear species. The cationic 4,4′-bipy ligands preferentially form dinuclear metallomacrocycles with palladium(II) and platinum(II) but in the case of the apyz and apym ligands in aqueous solution, coordination followed by deprotonation of exocyclic amine groups resulted in the formation of tetranuclear metallomacrocycles with platinum(II), with strong spectroscopic evidence for Pt(II)···Pt(II) bonding in the case of one of the complexes. We are currently exploring the coordination chemistry of these ligands with other metal ions as well as the DNA-binding interactions of selected complexes. The results of this work will be reported in due course.

Experimental

General

Heterocycles, bromoalkyl precursors and other reagents were purchased from the Aldrich Chemical Co. and used without further purification. $K_2[PtCl_4]$ was obtained from Johnson Matthey. Compounds, **1**·2Br,[21] **2**·2Br,[21] **3**·2Br,[22] **4**·2Br,[22] **4**·2PF_6,[35] **9**·I,[36] [M(2,2′-bipy)$(NO_3)_2$][37] (M = Pd and Pt) and [Pt(dppp)$(OTf)_2$][38] were prepared by the literature methods.

All NMR spectra were recorded at 300 K on a Bruker AVANCE DRX400 spectrometer (^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz, and ^{195}Pt at 85.7 MHz). All NMR signals (δ) are reported in

ppm relative to TMS (δ 0.00). ^{1}H and ^{13}C{^{1}H} NMR data were referenced to the residual solvent peak. ^{195}Pt{^{1}H} NMR data were referenced to an external standard of 0.1 M $Na_2[PtCl_6]$ in D_2O (δ 0.00). ESI mass spectra were acquired in an appropriate solvent (flow rate 100 μL min^{-1}) on a Finnegan LCQ MS Detector. A spray voltage of 5 kV was applied with a heated capillary temperature of 200 °C and a nitrogen sheath gas pressure of 60 psi. High resolution ESI-FTICR-MS data was recorded on a Bruker 7.0 T mass spectrometer. Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago, New Zealand.

Syntheses

Synthesis of quaternary bromide salts. The syntheses of cationic ligands were performed by using adaptations of the procedure described by Attalla *et al.*[21] Unless otherwise specified, the *N*-heterocyclic nucleophile (12 mmol) and bis(alkyl bromide) derivative (3 mmol) were stirred overnight in DMF (10 mL) at 70 °C, over which time an off-white precipitate formed. After cooling to room temperature, the product was isolated by filtration, washed with DMF (2 mL) and Et_2O (5 mL) and crystallised from a small volume of hot H_2O to afford the desired ligand salt. Derivatives of apym did not require re-crystallisation.

1,6-Bis(3-aminopyrazinium)hexane bromide (5·2Br). The title compound was prepared from aminopyrazine and 1,6-dibromohexane (56%, yellow powder). ^{1}H NMR (D_2O) δ 8.59 (m, 3H, H5), 8.16 (m, 3H, H6), 7.96 (s, 3H, H2), 4.49 (t, 4H, $^{3}J_{H,H}$ = 7.5 Hz, $H_{hexylene\alpha}$), 2.04 (m, 4H, $H_{hexylene\beta}$), 1.46 (m, 4H, $H_{hexylene\gamma}$) ppm. ^{13}C{^{1}H} NMR (D_2O) δ 159.06, 149.38, 125.52, 123.58 (t, $^{1}J_{C,N}$ = 8.0 Hz), 62.64, 30.24, 25.20 ppm. ESI-MS: *m*/*z* 353.20 [M – Br]$^+$, 273.20 [M – H – 2Br]$^+$, 137.20 [M – 2Br]$^{2+}$. Anal. calcd for $C_{14}H_{22}N_6Br_2$: C, 38.73; H, 5.11; N, 19.36. Found: C, 38.89; H, 5.39; N, 19.16.

1,4-Bis(2-aminopyrimidinium)butane bromide (6·2Br). The title compound was prepared from 2-aminopyrimidine and 1,4-dibromobutane (76%, white powder). ^{1}H NMR (D_2O) δ 8.82 (dd, 2H, $^{3}J_{H,H}$ = 4.4 Hz, $^{4}J_{H,H}$ = 2.0 Hz, H4), 8.40 (dd, 2H, $^{3}J_{H,H}$ = 6.4 Hz, $^{4}J_{H,H}$ = 2.0 Hz, H6), 7.14 (dd, 2H, $^{3}J_{H,H}$ = 6.4 Hz, $^{3}J_{H,H}$ = 4.4 Hz, H5), 4.28 (m, 4H, $H_{butylene\alpha}$), 2.04 (m, 4H, $H_{butylene\beta}$). ^{13}C{^{1}H} NMR (100 MHz, D_2O) δ 166.3, 155.5, 149.8, 111.5, 53.8, 23.1. ESI-MS: *m*/*z* 245.07 [M – 2Br – H]$^+$, 123.07 [M – 2Br]$^{2+}$. Anal. calcd for $C_{12}H_{18}N_6Br_2{\cdot}3H_2O$: C, 31.32; H, 4.73; N, 18.26. Found: C, 31.00; H, 5.12; N, 17.81.

1,5-Bis(2-aminopyrimidinium)pentane bromide (7·2Br). The title compound was prepared from 2-aminopyrimidine and 1,5-dibromopentane (22%, colourless crystals). A significant loss of yield was due to crystallisation from H_2O. ^{1}H NMR (300 MHz, D_2O) δ 8.85 (m, 2H, H4), 8.43 (m, 2H, H6), 7.17 (m, 2H, H5), 4.25 (t, 4H, $^{3}J_{H,H}$ = 6.9 Hz, $H_{pentylene\alpha}$), 2.02 (m, 4H, $H_{pentylene\beta}$), 1.56 (m, 2H, $H_{pentylene\gamma}$). ^{13}C{^{1}H} NMR (D_2O) δ 166.52, 155.94, 150.26, 111.83, 54.71, 26.24, 22.60. ESI-MS: *m*/*z* 758.73 [2M – Br]$^+$, 678.67 [2M – 2Br – H]$^+$, 598.67 [2M – 3Br – 2H]$^+$, 520.00 [2M – 4Br – 3H]$^+$, 340.80 [M – Br]$^+$, 259.13 [M – 2Br$^-$–H]$^+$, 130.27 [M – 2Br]$^{2+}$. Anal. calcd for $C_{13}H_{20}N_6Br_2{\cdot}2H_2O$: C, 34.69; H, 5.22; N, 18.67. Found: C, 34.72; H, 5.36; N, 18.61.

1,3-Bis(1-methyl-2-aminopyrimidinium)benzene bromide (8·2Br). The title compound was prepared from 2-aminopyrimidine and 1,3-bis(bromomethyl)benzene (69%, white powder). ^{1}H NMR (D_2O) δ 8.88 (m, 2H, $H4_{apym}$), 8.63 (m, 2H, $H6_{apym}$), 7.63 (t, 1H, $^{3}J_{H,H}$ = 7.58 Hz, $H5_{xylylene}$), 7.47 (d, 4H, $^{3}J_{H,H}$ = 7.58 Hz, $H4_{xylylene}$), 7.23 (s, 1H, $H2_{xylylene}$), 7.17 (m, 2H, $H5_{apym}$), 5.47 (s, 4H, CH_2). Traces of DMF present. ^{13}C{^{1}H} NMR (D_2O) δ 167.2 ($C4_{apym}$), 156.5 ($C2_{apym}$), 150.2 ($C6_{apym}$), 132.5 ($C1_{xylylene}$), 131.3 ($C5_{xylylene}$), 129.7 ($C4_{xylylene}$), 127.9 ($C2_{xylylene}$), 112.3 ($C5_{apym}$), 57.3 (CH_2). ESI-MS: *m*/*z* 827.00 [2M – Br]$^+$, 746.67 [2M – 2Br – H]$^+$, 666.67 [2M – 3Br – 2H]$^+$, 584.87 [2M – 4Br – 3H]$^+$, 293.13 [M – 2Br – H]$^+$, 198.20 [M – apym – 2Br – H$^+$]$^+$, 147.20 [M – 2Br]$^{2+}$. Anal. calcd for $C_{16}H_{18}Br_2N_6$: C, 42.31; H, 3.99; N, 18.50. Found: C, 42.13; H, 3.97; N, 18.42.

Synthesis of nitrate salts. Typically, the halide salt (1 mmol) was dissolved in the minimum amount of warm H_2O, and treated with $AgNO_3$ (1 mmol/mmol halide ion) in H_2O (5 mL). The mixture was filtered and concentrated to ~3 mL on a hotplate (with further filtering through cellulose if required). The solvent was removed *in vacuo* and, if required, the solid was crystallised from H_2O to give the pure nitrate salt.

1,4-Bis(4,4′-bipyridinium)butane nitrate (2·2NO$_3$). The title compound was prepared from **2**·2Br (51%, colourless crystals). ^{1}H NMR (200 MHz, D_2O) δ 9.01 (d, 4H, $^{3}J_{H,H}$ = 6.0 Hz, H2′), 8.79 (d, 4H, $^{3}J_{H,H}$ = 4.3 Hz, H2), 8.46 (d, 4H, $^{3}J_{H,H}$ = 6.0 Hz, H3′), 7.85 (d, 4H, $^{3}J_{H,H}$ = 4.3 Hz, H3), 4.79 (obscured by HOD peak, m, 4H, $H_{butylene\alpha}$), 2.96 (m, 4H, $H_{butylene\beta}$). ESI-MS: *m*/*z* 430.0 [M – NO_3]$^+$, 184.2 [M – 2NO_3]$^{2+}$.

1,6-Bis(4,4′-bipyridinium)hexane nitrate (3·2NO$_3$). The title compound was prepared from **3**·2Br (53%, colourless crystals). ^{1}H NMR (D_2O) δ 8.98 (d, 4H, $^{3}J_{H,H}$ = 6.76 Hz, H2), 8.76 (d, 4H, $^{3}J_{H,H}$ = 5.37 Hz, H2′), 8.40 (d, 4H, $^{3}J_{H,H}$ = 6.76 Hz, H3), 7.89 (d, 4H, $^{3}J_{H,H}$ = 5.37 Hz, H3′), 4.70 (t, 4H, $^{3}J_{H,H}$ = 7.20 Hz, $H_{hexylene\alpha}$), 2.12 (m, 4H, $H_{hexylene\beta}$), 1.49 (m, 4H, $H_{hexylene\gamma}$). ^{13}C{^{1}H} NMR (D_2O) δ 154.24, 150.47, 125.15, 142.92, 126.41, 122.83, 61.922, 30.61, 25.33. ESI-MS: *m*/*z* 457.67 [M – NO_3]$^+$, 197.67 [M – 2NO_3]$^{2+}$. Anal. calcd for $C_{26}H_{26}O_6N_6$: C, 59.99; H, 5.42; N, 16.14. Found: C, 59.79; H, 5.44; N, 16.02.

1,6-Bis(3-aminopyrazinium)hexane nitrate (5·2NO$_3$). The title compound was prepared from **5**·2Br (96%, tan crystals). ^{1}H NMR (D_2O) δ 8.58 (m, 2H, H5), 8.15 (s, 2H, H6), 7.95 (d, 2H, $^{3}J_{H,H}$ = 2.8 Hz, H2), 4.48 (t, 4H,$^{3}J_{H,H}$ = 7.4 Hz, $H_{hexylene\alpha}$), 2.03 (m, 4H, $H_{hexylene\beta}$), 1.45 (m, 4H, $H_{hexylene\gamma}$). ^{13}C{^{1}H} NMR (D_2O) δ 159.09, 149.38, 125.52, 123.56, 62.65, 30.22, 25.19. ESI-MS: *m*/*z* 336.1 [M – NO_3]$^+$, 273.0 [M – H$^+$ – 2NO_3]$^+$, 137.2 [M – 2NO_3]$^{2+}$. Anal. calcd for $C_{14}H_{22}N_8O_6$: C, 42.21; H, 5.57; N, 28.13. Found: C, 42.28; H, 5.57; N, 27.86.

1,4-Bis(2-aminopyrimidinium)butane nitrate (6·2NO$_3$). The title compound was prepared from **6**·2Br (91%, white powder). ^{1}H NMR (D_2O) δ 8.82 (dd, 2H, $^{3}J_{H,H}$ = 3.3 Hz, $^{4}J_{H,H}$ = 1.5 Hz, H4), 8.38 (dd, 2H, $^{3}J_{H,H}$ = 5.0 Hz, $^{4}J_{H,H}$ = 1.6 Hz, H6), 7.13 (dd, 2H, $^{3}J_{H,H}$ = 5.0 Hz, $^{3}J_{H,H}$ = 3.4 Hz, H5), 4.26 (m, 4H, $H_{butylene\alpha}$), 2.03 (m, 4H, $H_{butylene\beta}$). ^{13}C{^{1}H} NMR (D_2O) δ 166.3, 155.5, 149.8, 111.4, 53.8, 23.0. ESI-MS: *m*/*z* 245.07 [M – 2NO_3 – H]$^+$, 123.13 [M – 2NO_3]$^{2+}$.

1,5-Bis(2-aminopyrimidinium)pentane nitrate (7·2NO$_3$). The title compound was prepared from **7**·2Br (78%, white powder). ^{1}H NMR (300 MHz, D$_2$O) δ 8.81 (dd, 2H, $^3J_{H,H}$ = 4.32 Hz, $^4J_{H,H}$ = 1.75 Hz, H4), 8.37 (dd, 2H, $^3J_{H,H}$ = 6.58 Hz, $^4J_{H,H}$ = 1.66 Hz, H6), 7.13 (dd, 2H, $^3J_{H,H}$ = 6.42 Hz, $^3J_{H,H}$ = 4.76 Hz, H4), 4.21 (t, 4H, $^3J_{H,H}$ = 7.34 Hz, H$_{pentylene\alpha}$), 1.97 (m, 4H, H$_{pentylene\beta}$), 1.51 (q, 2H, $^3J_{H,H}$ = 7.18 Hz, H$_{pentylene\gamma}$). ^{13}C{^{1}H} NMR (D$_2$O) δ 166.50, 155.94, 150.21, 111.77, 54.67, 26.20, 22.57. ESI-MS: *m/z* 259.07 [M – 2NO$_3^-$ – H$^+$]$^+$, 130.20 [M – 2NO$_3$]$^+$. Anal. calcd for C$_{13}$H$_{20}$O$_6$N$_8$·1.66H$_2$O: C, 37.69; H, 5.67; N, 27.05. Found: C, 37.38; H, 5.40; N, 27.16.

1-Methyl-3-aminopyrazinium nitrate (9·NO$_3$). The title compound was prepared from **9**·I (99%, colourless crystals). Slow evaporation of an aqueous solution of the title compound afforded single crystals suitable for X-ray crystallographic analysis (see Supplementary Information). ^{1}H NMR (D$_2$O) δ 8.56 (m, 1H, H5), 8.11 (m, 1H, H6), 7.12 (s, 1H, H2), 4.28 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (D$_2$O) δ 158.97, 149.10, 126.55 (t, $^1J_{C,N}$ = 11.18 Hz), 124.52 (t, $^1J_{C,N}$ = 8.85 Hz) 48.83 (t, $^1J_{C,N}$ = 5.1 Hz). ESI-MS: *m/z* 110.00 [M – NO$_3$]$^+$. Anal. calcd for C$_5$H$_8$O$_3$N$_4$: C, 34.17; H, 4.82; N, 31.88. Found: C, 34.10; H, 4.64; N, 31.77.

Synthesis of hexafluorophosphate salts. Typically, a bromide salt (0.5 mmol) was dissolved in the minimum amount of H$_2$O and was treated with KPF$_6$ (saturated aqueous solution, 50 mL). The mixture was allowed to stand overnight and the precipitate which formed was isolated by filtration, washed with H$_2$O (2 mL) and dried *in vacuo* to give the hexafluorophosphate salt as a white/off-white powder.

1,3-Bis(4,4′-bipyridinium)butane hexafluorophosphate (2·2PF$_6$). The title compound was prepared from **2**·2Br (51%, white powder). ^{1}H NMR (CD$_3$CN) δ 8.88 (d, 4H, $^3J_{H,H}$ = 5.4 Hz, H2), 8.83 (d, 4H, $^3J_{H,H}$ = 6.6 Hz, H2′), 8.40 (d, 4H, $^3J_{H,H}$ = 6.7 Hz, H3), 7.83 (d, 4H, $^3J_{H,H}$ = 4.6 Hz, H3′), 4.73 (t, 4H, $^3J_{H,H}$ = 7.7 Hz, H$_{propylene\alpha}$), 2.75 (qu, 2H, $^3J_{H,H}$ = 7.7 Hz, H$_{propylene\beta}$). ^{13}C{^{1}H} NMR (CD$_3$CN) δ 154.45, 150.94, 144.82, 140.75, 126.06, 121.50, 57.40, 31.42. ESI-MS: *m/z* 499.1 [M – PF$_6$]$^+$, 177.3 [M – 2PF$_6$]$^{2+}$. Anal. calcd for C$_{23}$H$_{22}$N$_4$P$_2$F$_{12}$: C, 42.87; H, 3.4444; N, 8.69. Found: C, 42.64; H, 3.55; N, 8.67.

1,3-Bis(1-methyl-2-aminopyrimidinium)benzene hexafluorophosphate (8·2PF$_6$). The title compound was prepared from **8**·2Br (51%, colourless crystals). ^{1}H NMR (CD$_3$CN) δ 8.85 (dd, 2H, $^3J_{H,H}$ = 4.33 Hz, $^4J_{H,H}$ = 1.95 Hz, H4), 8.10 (dd, 2H, $^3J_{H,H}$ = 6.66 Hz, $^4J_{H,H}$ = 1.95 Hz, H6), 7.58 (t, 1H, $^3J_{H,H}$ = 7.65 Hz, H5$_{xylylene}$), 7.41 (d, 4H, $^3J_{H,H}$ = 7.65 Hz, H4$_{xylylene}$), 7.22 (br, s, 4H, NH$_2$), 7.14 (s, 1H, H2$_{xylylene}$), 7.12 (dd, 2H, $^3J_{H,H}$ = 6.66 Hz, $^3J_{H,H}$ = 4.33 Hz, H5), 5.25 (s, 4H, CH$_2$). ^{13}C{^{1}H} NMR (CD$_3$CN) δ 167.88, 156.97, 150.23, 132.75, 131.57, 130.5, 129.00, 113.20, 57.36. ESI-MS: *m/z* 439.00 [M – PF$_6$]$^+$, 293.20 [M – 2PF$_6$ – H]$^+$, 198.27 [M – apym – 2PF$_6$ – H]$^+$, 147.12 [M – 2PF$_6$]$^{2+}$. Anal. calcd for C$_{16}$H$_{18}$P$_2$F$_{12}$N$_6$: C, 32.89; H, 3.11; N, 14.38. Found: C, 32.99; H, 2.89; N, 14.28.

Synthesis of metal complexes

[Pd$_2$(2,2′-bipy)$_2${4,4′-bipy(CH$_2$)$_4$4,4′-bipy}$_2$](PF$_6$)$_8$ (10). A solution of **2**·2NO$_3$ (9.85 mg, 20.0 μmol) in H$_2$O (1 mL) was treated with [Pd(2,2′-bipy)(NO$_3$)$_2$] (7.73 mg, 20.0 μmol) and the suspension stirred for 24 h at 80 °C. The mixture was filtered through cellulose, and the yellow solution treated with a saturated aqueous solution of KPF$_6$ (20 mL). The precipitate was isolated by filtration, washed with cold H$_2$O (0.5 mL) and dried *in vacuo* to give the product as an off-white solid (17.7 mg, 73%). ^{1}H NMR (CD$_3$CN) δ 9.22 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H2), 8.81 (d, 8H, $^3J_{H,H}$ = 6.7 Hz, H2′), 8.43 (m, 8H, H4$_{bipy}$, H6$_{bipy}$), 8.29 (d, 8H, $^3J_{H,H}$ = 6.7 Hz, H3′), 8.29 (d, 8H, $^3J_{H,H}$ = 6.7 Hz, H3), 7.63 (dd, 4H, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 1.4 Hz, H5$_{bipy}$), 7.41 (d, 4H, $^3J_{H,H}$ = 5.4 Hz, H3$_{bipy}$), 4.67 (m, 8H, H$_{butylene\alpha}$), 2.11 (m, 8H, H$_{butylene\beta}$). Anal. calcd for C$_{68}$H$_{64}$F$_{48}$N$_{12}$P$_8$Pd$_2$·3H$_2$O: C, 32.99; H, 2.85; N, 6.79. Found: C, 32.70; H, 2.81; N, 6.65.

[Pt$_2$(2,2′-bipy)$_2${4,4′-bipy(CH$_2$)$_4$4,4′-bipy}$_2$](PF$_6$)$_8$ (11). The title compound was prepared in a similar manner to **10**, using [Pt(2,2′-bipy)(NO$_3$)$_2$] instead of [Pd(2,2′-bipy)(NO$_3$)$_2$] and heating for 48 h (white powder, 19.4 mg, 74%). ^{1}H NMR (CD$_3$CN) δ 9.18 (d, 8H, $^3J_{H,H}$ = 5.1 Hz, H2), 8.79 (d, 8H, $^3J_{H,H}$ = 6.9 Hz, H2′), 8.46 (m, 8H, H4$_{bipy}$,H6$_{bipy}$), 8.29 (d, 8H, $^3J_{H,H}$ = 6.9 Hz, H3′), 8.28 (d, 8H, $^3J_{H,H}$ = 5.1 Hz, H3), 7.65 (m, 8H, H3$_{bipy}$,H5$_{bipy}$), 4.65 (m, 8H, H$_{butylene\alpha}$), 2.09 (m, 8H, H$_{butylene\beta}$). ^{1}H NMR (D$_2$O, of NO$_3^-$ salt) δ 9.40 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H2) 9.05 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H2′) 8.54 (m, 8H, H2$_{bipy}$,H6$_{bipy}$) 8.46 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H3′) 8.23 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H3) 7.71 (m, 8H, H3$_{bipy}$,H5$_{bipy}$) 4.65 (m, 8H, H$_{butylene\alpha}$) 2.09 (m, 8H, H$_{butylene\beta}$). Anal. calcd for C$_{68}$H$_{64}$F$_{48}$N$_{12}$P$_8$Pt$_2$·0.5H$_2$O: C, 31.31; H, 2.51; N, 6.44. Found: C, 31.85; H, 2.81; N, 6.45.

[Pd$_2$(2,2′-bipy)$_2${4,4′-bipy(CH$_2$)$_6$4,4′-bipy}$_2$](PF$_6$)$_8$ (12). The title compound was prepared in a similar manner to **10**, using **3**·2NO$_3$ instead of the butane derivative (white powder, 17.2 mg, 69%). ^{1}H NMR (CD$_3$CN) δ 9.17 (d, 8H, $^3J_{H,H}$ = 6.3 Hz, H2), 8.79 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H2′), 8.35 (m, 8H, H4$_{bipy}$,H6$_{bipy}$), 8.24 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H3′), 8.29 (d, 8H, $^3J_{H,H}$ = 6.3 Hz, H3), 7.58 (m, 4H, H5$_{bipy}$), 7.39 (d, 4H, $^3J_{H,H}$ = 5.1 Hz, H3$_{bipy}$), 4.54 (t, 8H, $^3J_{H,H}$ = 7.2 Hz, H$_{hexylene\alpha}$), 1.97 (m, 8H, H$_{hexylene\beta}$), 1.40 (m, 8H, H$_{hexylene\gamma}$). ESI-FTICR-MS: *m/z* calcd for C$_{72}$H$_{72}$F$_{36}$N$_{12}$P$_6$Pt$_2^{2+}$, [M – 2PF$_6$]$^{2+}$: 1182.6561. Found: 1182.6558, calcd for C$_{72}$H$_{72}$F$_{30}$N$_{12}$P$_5$Pt$_2^{3+}$, [M – 3PF$_6$]$^{3+}$: 739.782983. Found: 739.781613. Anal. calcd for C$_{72}$H$_{72}$F$_{48}$N$_{12}$P$_8$Pd$_2$·H$_2$O: C, 34.65; H, 2.99; N, 6.73. Found: C, 34.67; H, 3.22; N, 6.65.

[Pt$_2$(2,2′-bipy)$_2${4,4′-bipy(CH$_2$)$_6$4,4′-bipy}$_2$](PF$_6$)$_8$ (13). The title compound was prepared in a similar to **11**, using **3**·2NO$_3$ instead of the butane derivative (white powder, 20.9 mg, 79%). ^{1}H NMR (CD$_3$CN) δ 9.17 (d, 8H, $^3J_{H,H}$ = 6.4 Hz, H2), 8.78 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H2′), 8.38 (m, 8H, H4$_{bipy}$,H6$_{bipy}$), 8.24 (d, 8H, $^3J_{H,H}$ = 6.6 Hz, H3′), 8.06 (d, 8H, $^3J_{H,H}$ = 6.4 Hz, H3), 7.58 (m, 4H, H5$_{bipy}$), 7.39 (d, 4H, $^3J_{H,H}$ = 5.4 Hz, H3$_{bipy}$), 4.54 (t, 8H, $^3J_{H,H}$ = 4.5 Hz, H$_{hexylene\alpha}$), 1.97 (m, 8H, H$_{hexylene\beta}$), 1.40 (m, 8H, H$_{hexylene\gamma}$). ESI-FTICR-MS: *m/z* calcd for C$_{72}$H$_{72}$F$_{36}$N$_{12}$P$_6$Pt$_2^{2+}$, [M – 2PF$_6$]$^{2+}$: 1182.156840. Found: 1182.153886, calcd for C$_{72}$H$_{72}$F$_{30}$N$_{12}$P$_5$Pt$_2^{3+}$, [M – 3PF$_6$]$^{3+}$: 739.782983. Found: 739.781613. Anal. calcd for C$_{72}$H$_{72}$F$_{48}$N$_{12}$P$_8$Pt$_2$: C, 32.57; H, 2.73; N, 6.33. Found: C, 32.53; H, 2.99; N, 6.29.

[Pt$_2$(dppp)$_2${4,4′-bipy(*o*-xylylene) 4,4′-bipy}$_2$](PF$_6$)$_4$(OTf)$_4$ (14). Ligand **4**·2PF$_6$ (7.07 mg, 10.0 μmol) and [Pt(dppp)(OTf)$_2$] (9.06 mg, 10.0 μmol) were dissolved in MeCN (1 mL) and the solution was stirred for 24 h at 60 °C. The solvent was allowed to evaporate slowly, and the residue was dried *in vacuo* to give

the product as a white solid (16.41 mg, 99%). ^{1}H NMR (CD_3CN) δ 8.79 (m, 8H), 8.08 (m, 4H), 7.58 (m, 16H), 7.44 (m, 6H), 7.38 (m, 8H), 7.21 (m, 2H), 5.86 (m, 4H, NCH_2), 5.66 (m, 4H, NCH_2'; these protons become diastereotopic upon complexation due to restricted rotation of the coordinated ligand.), 3.19 (m, 8H, PCH_2), 2.23 (m, 4H, $PCH_2C\mathbf{H}_2$). ^{31}P{^{1}H} NMR (121 MHz, CD_3CN) δ–13.61 (s, $^1J_{PPt}$ = 3028 Hz, Pt-P), –143.40 (septet, $^1J_{P,F}$ = 707 Hz, PF_6^-). ESI-FTICR-MS: *m/z* calcd for $C_{111}H_{100}Pt_2F_{27}N_8O_3P_8S^{3+}$, $[M - 3OTf]^{3+}$: 928.48171. Found: 928.48223. Anal. calcd for $C_{114}H_{100}F_{36}N_8O_{12}P_8Pt_2S_4\cdot 5H_2O$: C, 41.32; H, 3.35; N, 3.38. Found: C, 41.20; H, 3.33; N, 3.39.

***cis*-[Pd$_2$Cl$_4${4,4′-bipy(CH$_2$)$_3$4,4′-bipy}$_2$](PF$_6$)$_4$ (15).** A solution of **1**·2PF_6 (6.44 mg, 10.0 μmol) in MeCN (1 mL) was treated with $[Pd(PhCN)_2Cl_2]$ (3.83 mg, 10.0 μmol) and the suspension stirred for 24 h at 60 °C. The solution was allowed to evaporate slowly, and the solid was washed with Et_2O (0.5 mL) and dried *in vacuo* to give the product as a yellow solid (8.29 mg, 94%). ^{1}H NMR (CD_3CN) δ 9.04 (d, 8H, $^3J_{H,H}$ = 5.9 Hz, H2), 8.82 (d, 8H, $^3J_{H,H}$ = 6.1 Hz, H2′), 8.34 (d, 8H, $^3J_{H,H}$ = 6.1 Hz, H3′), 7.86 (d, 8H, $^3J_{H,H}$ = 5.9 Hz, H3), 7.67 (m, 12H, H2,4$_{benzonitrile}$), 7.50 (m, 8H, H3$_{benzonitrile}$), 4.70 (m, 8H, H$_{propyleneα}$), 2.70 (m, 4H, H$_{propyleneβ}$). ESI-FTICR-MS: *m/z* 677.97932 $[M - 2PF_6]^{2+}$. Anal. calcd for $C_{46}H_{44}Cl_4F_{24}N_8P_4Pd_2\cdot PhCN\cdot H_2O$: C, 36.08; H, 2.91; N, 7.14. Found: C, 35.74; H, 3.02; N, 7.03.

[Pt$_4$(2,2′-bipy)$_4${apyz(CH$_2$)$_6$apyz–2H}$_2$](PF$_6$)$_8$ (19). A solution of **5**·2NO_3 (7.96 mg, 20.0 μmol) in H_2O (1 mL) was treated with [Pt(2,2′-bipy)$(NO_3)_2$] (19.01 mg, 40.0 μmol) and the suspension was stirred for 72 h at 80 °C. The red solution was treated with a saturated aqueous solution of KPF_6 (15 mL) and allowed to stand for 30 min. The precipitate was isolated by filtration, washed with cold H_2O (1 mL) and dried *in vacuo* to give the product as an orange-red solid (19.6 mg, 61%). ^{1}H NMR (D_2O, of NO_3^- salt) δ 8.80–7.20 (m, 44H, H$_{bipy,apyz}$), 4.36 (m, 8H, H$_{hexyleneα}$), 1.92 (m, 8H, H$_{hexyleneβ}$), 1.42 (m, 8H, H$_{hexyleneγ}$). ^{195}Pt NMR (D_2O, NO_3^- salt) δ–2361. ESI-FTICR-MS: *m/z* calcd for $C_{68}H_{72}F_{30}N_{20}P_5Pt_4^{3+}$, $[M - 3PF_6]^{3+}$: 891.768257. Found: 891.768992. Anal. calcd for $C_{68}H_{72}F_{48}N_{20}P_8Pt_4\cdot 6H_2O$: C, 25.38; H, 2.63; N, 8.71. Found: C, 25.57; H, 2.66; N, 8.49. UV-vis (0.014 mM in H_2O): λ = 305 nm, $\varepsilon = 6.82\times10^4$ $M^{-1}cm^{-1}$; λ = 428 nm, $\varepsilon = 8.36\times10^3$ $M^{-1}cm^{-1}$.

[Pt$_2$(2,2′-bipy)$_2$(Meapyz–H)$_2$](PF$_6$)$_4$ (20). A solution of **9**·NO_3 (6.88 mg, 40.0 μmol) in H_2O (1 mL) was treated with [Pt(2,2′-bipy)$(NO_3)_2$] (19.01 mg, 40.0 μmol) and the suspension was stirred for 72 h at 80 °C. The red solution was treated with a saturated aqueous solution of KPF_6 (15 mL) and allowed to stand for 30 min. The precipitate was isolated by filtration, washed with cold H_2O (1 mL) and dried *in vacuo* to give the product as an orange-red solid (19.44 mg, 64%). ^{1}H NMR (D_2O, of NO_3^- salt) δ 8.70-7.30 (m, 22H, H$_{bipy,apyz}$), 4.20 (m, 6H, CH_3). ^{195}Pt NMR (D_2O, NO_3^- salt) δ–2358. Anal. calcd for $C_{30}H_{30}F_{24}N_{10}P_4Pt_2\cdot H_2O$: C, 23.73; H, 2.12; N, 9.22. Found: C, 23.77; H, 2.42; N, 9.03. UV-vis (0.031 mM in H_2O): λ = 305 nm, $\varepsilon = 2.22\times10^4$ $M^{-1}cm^{-1}$; λ = 428 nm, $\varepsilon = 2.90\times10^3$ $M^{-1}cm^{-1}$.

[Pt$_4$(2,2′-bipy)$_4${apym(CH$_2$)$_5$apym–2H}$_2$](PF$_6$)$_8$ (21). A solution of **7**·2NO_3 (9.00 mg, 20.0 μmol) in H_2O (1 mL) was treated with [Pt(2,2′-bipy)$(NO_3)_2$] (19.01 mg, 40.0 μmol) and the suspension was stirred for 72 h at 80 °C. The orange solution was treated with a saturated aqueous solution of KPF_6 (15 mL) and allowed to stand for 30 min. The precipitate was isolated by filtration, washed with cold H_2O (1 mL) and dried *in vacuo* to give the product as an orange solid (21.57 mg, 70%). ^{1}H NMR (D_2O, NO_3^- salt) δ 9.48 (d, 4H, $^3J_{H,H}$ = 5.3 Hz, H6$_{apym}$), 8.74 (d, 4H, $^3J_{H,H}$ = 6.1 Hz, H4$_{apym}$), 8.70 (d, 4H, $^3J_{H,H}$ = 5.7 Hz, H$_{bipy}$), 8.4–8.15 (m, 12H, H$_{bipy}$), 8.13 (d, 4H, $^3J_{H,H}$ = 8.1 Hz, H$_{bipy}$), 7.67 (t, 4H, $^3J_{H,H}$ = 6.6 Hz, H$_{bipy}$), 7.28 (t, 4H, $^3J_{H,H}$ = 6.6 Hz, H$_{bipy}$), 7.12 (t, 4H, $^3J_{H,H}$ = 5.9 Hz, H5$_{apym}$), 4.75 (m, 4H, H$_{pentyleneα}$), 4.33 (m, 4H, H$_{pentyleneα}$′), 2.0–1.2 (m, 12H, H$_{pentyleneβ}$,H$_{pentyleneγ}$). ^{195}Pt NMR (D_2O, NO_3^- salt) δ–2254. ESI-FTICR-MS: *m/z* calcd for $C_{66}H_{68}F_{36}N_{20}P_6Pt_4^{2+}$, $[M - 2PF_6]^{2+}$: 1395.61755. Found: 1395.61458, calcd for $C_{33}H_{34}F_{18}N_{10}P_3Pt_2^+$, $[\frac{1}{2}M - PF_6]^+$: 1395.11721. Found: 1395.11783 (the intensities of both ions are comparable). Anal. calcd for $C_{66}H_{68}F_{48}N_{20}P_8Pt_4\cdot 6H_2O$: C, 25.73; H, 2.22; N, 9.09. Found: C, 25.97; H, 2.36; N, 9.16. UV-vis (0.120 mM in H_2O): λ = 358 nm, $\varepsilon = 1.72\times10^4$ $M^{-1}cm^{-1}$; λ = 433 nm, $\varepsilon = 4.91\times10^3$ $M^{-1}cm^{-1}$.

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