COMMUNICATION

Self-assembly of supramolecular triangles with neutral *trans*-PdCl$_2$ directing units†

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Pd(II)-directed self-assembly of homoleptic metal–polypyridyl complexes functionalized with 3-pyridyl groups gives rise to supramolecular metallo-triangles as confirmed by a combination of analytical techniques.
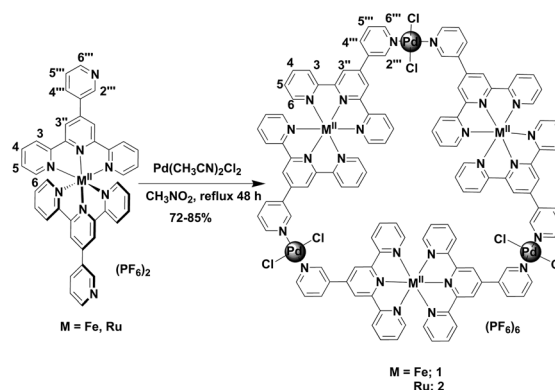
The self-assembly of building-blocks by carefully designed directing units is of continuing interest due to the growing applications of an ever-increasing number of supramolecular architectures.[1] Since the pioneering work by Lehn[2] and Sauvage[3] these assemblies find diverse applications in the encapsulation of guest molecules with unusual chemical activity,[4] supramolecular catalysis,[5] *functional* nano-architectures,[6] and material chemistry[7] due to their rich redox and photophysical properties. Luminescent polynuclear assemblies are of particular interest as they find potential application as sensors and probes in photonic devices.[8] The photophysical properties of these assemblies, especially their emission, which originates from a triplet metal-to-ligand charge transfer (^{3}MLCT) transition, can be fine-tuned by changing the nature of the coordinating ligands.[9] Since the first self-assembled molecular square, prepared by Fujita and co-workers, based on labile and cationic *cis*-Pd(II)-directing units,[10] much attention has been focused on Pd(II), Pt(II) and Re(I) based supramolecular architectures.[11] Interestingly, most examples of self-assembly are predominantly based on cationic metal complexes, while reported supramolecules with neutral metal complexes are comparatively few,[12] probably due to the poor solubility of the resulting assemblies. Nonetheless, the latter compounds have an advantage as they can act as both cation and anion-receptors in sensors.

In this context, we present herein the self-assembly of metallo-ligands, *i.e.*, using metal–polypyridyl complexes as bridging ligands with neutral metal complex, PdCl$_2$, to synthesize

hexanuclear metallo-triangles. The metallo-ligands used in this study are homoleptic Fe(II) and Ru(II)-complexes of 4-(3-pyridyl)-2,2′:6′,2″-terpyridine, (3-pytpy).

The syntheses of these Fe and Ru-metallo-ligands have been well documented elsewhere.[13] Metallo-triangles **1** and **2** of general formula, (PdCl$_2$[μ-(3-pytpy)$_2$M])$_3$(PF$_6$)$_6$, (where M = Fe, **1**; Ru, **2**) were synthesized by refluxing a mixture of the homoleptic Fe(II) and Ru(II)-complexes of 3-pytpy and a slight excess of Pd(CH$_3$CN)$_2$Cl$_2$ in nitromethane (Scheme 1). Subsequent isolation of the precipitate, induced by addition of diethylether to these concentrated reaction mixtures, followed by titration with acetone provided the complexes in analytically pure form.

The presence of a polar non-coordinating and non-reducing solvent, for *e.g.*, nitromethane, was essential to form the desired assembly compared to other solvents, such as acetonitrile, DMSO and alcohols, which were found to be competitive towards the coordination to [Pd]. This behaviour was observed during the high temperature syntheses of the complexes whereas attempts for low-temperature syntheses of the complexes always yielded a mixture of oligomers and solvent adducts. However, after the formation of the discrete supramolecules, the complexes are chemically robust and do not

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Scheme 1 Syntheses of complexes **1** and **2** also showing the labeling of different protons adopted for these complexes.
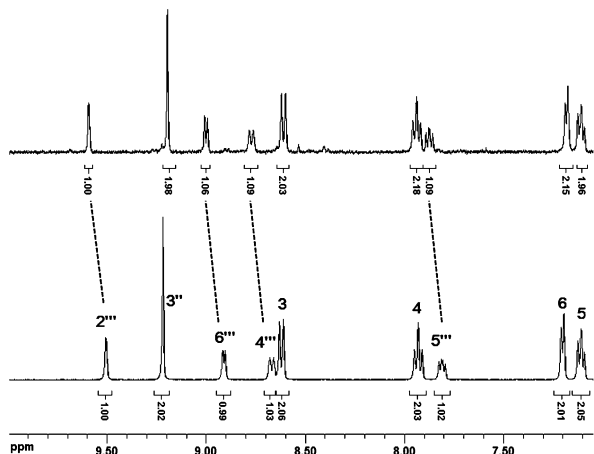
Fig. 1 ^{1}H NMR spectrum of complex **1** (top), recorded at r.t. in CD$_3$CN, showing the downfield shift of the most affected protons of Fe-met-alloligand (bottom) upon coordination.

undergo dissociation in the presence of coordinating solvents at room temperature.

The successful coordination to neutral PdCl$_2$ by the hetero-atom of the pendant pyridyl group in the metalloligands was demonstrated by the respective ^{1}H NMR spectra of **1** and **2**. The formation of metallo-triangles is very well supported by three principal features of these ^{1}H NMR spectra (Fig. 1), for *e.g.*, (i) the symmetric nature suggests formation of a closed-ring discrete species with 1 : 1 stoichiometry of the metallo-ligand and PdCl$_2$, (ii) well-defined integrations exclude the formation of long-chain metallo-polymer, (iii) most importantly, the downfield shift of pyridine (Py)-α (2′′′ and 6′′′) protons by ∼0.1 ppm and also similar shifts of β and γ (5′′′ and 4′′′) protons of the pendant 3-pyridyl unit upon coordination. The terpyridine core-protons, being distant from the coordination site, are barely affected. Unlike the downfield shift of Py-α protons by ∼1–2 ppm, as observed by Fujita *et al.* for coordination to cationic [Pd]-precursor,[14] the lower value of downfield-shifting (0.1–0.8 ppm) is typically indicative of the coordination to neutral-metal centres.[12c,15]

To verify the downfield-shift of the protons of the coordinated pyridyl units, three other model complexes, **3–5** (Chart 1), with electron-donating and electron-withdrawing functional groups were synthesized following literature procedures.[7d] The chemical shift values of different protons (in ppm) of these complexes are tabulated in comparison to those of their respective free ligands (Table 1).
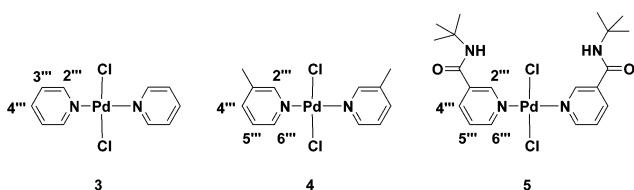
Chart 1 Model complexes **3–5** with proton labelling scheme.

Table 1 Comparison of chemical shifts (in ppm) of different protons in complexes **1–5** and that of their corresponding ligands

Compounds	Solvent	H2′′′	H4′′′	H5′′′	H6′′′
Fe-metallo-ligand	CD$_3$CN	9.51	8.67	7.81	8.91
1	CD$_3$CN	9.59	8.77	7.88	9.01
Ru-metallo-ligand	CD$_3$CN	9.41	8.56	7.80	8.87
2	CD$_3$CN	9.48	8.66	7.98	8.96
Pyridine	DMSO-d$_6$	8.58	7.79	—	—
3	DMSO-d$_6$	8.75	8.00	—	—
3-Picoline	CD$_3$CN	8.42	7.51	7.19	8.37
4	CD$_3$CN	8.60	7.72	7.32	8.56
[structure]	DMSO-d$_6$	8.93	8.12	7.46	8.66
5	DMSO-d$_6$	9.08	8.23	7.56	8.81
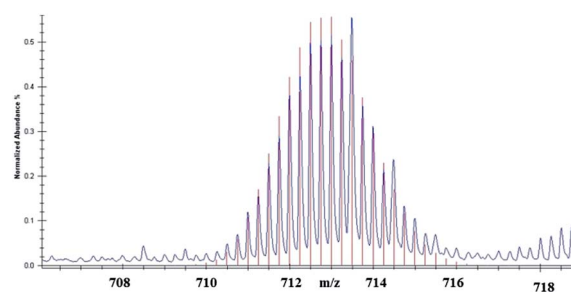
Fig. 2 Overlay of observed high-res LC-TOF MS of [C$_{120}$H$_{84}$N$_{24}$Fe$_3$Pd$_3$Cl$_3$ (PF$_6$)$_2$]$^{4+}$ (blue, outer trace) with simulated isotope pattern (red, inner trace).

Data in Table 1 clearly indicates that the downfield coordination induced shift (CIS) of 3-pyridyl protons of **1** and **2** fall in the same range (0.09–0.21 ppm) as observed with the model complexes, which supports for the formation of the cyclic metallo-triangle.

Elemental analyses of complexes **1** and **2** revealed a 1 : 1 stoichiometry of metallo-ligand and PdCl$_2$ and together with NMR spectroscopy; this data strongly supports the formation of discrete, cyclic trimers.

A common and powerful characterisation technique of supramolecular species is electrospray mass spectrometry (ESI-MS).[7c,15] The most abundant species in the TOF HR-ESI-MS for complexes **1** and **2** correspond to [M]$^{2+}$ species of the metallo-ligands. Molecular triangles at different charged states, for *e.g.*, [(Fe-metallo-ligand)$_3$(PdCl$_2$)$_3$(PF$_6$)$_z$]$^{(6-z)+}$; $z = 3$ ($m/z = 998.98427$), 2 (712.99702), 1 ($m/z = 541.40458$) were observed for complex **1** (Fig. 2 and S1 in ESI†). Similar species were also observed for complex **2** (Fig. S2–S5 in ESI†). More importantly, no signals that would correspond to other oligomers, such as dimers, tetramers, pentamers are present. Therefore, together with NMR spectroscopy and elemental analysis, mass spectrometry provides unambiguous evidence for the existence of the cyclic trimer as the only supramolecular oligomer formed in solid, solution and gas-phase.

Table 2 Redox data of complexes **1–4** and some benchmark complexes

Compound	$E_{1/2}^{\mathrm{Ox}\,a}$ (mV)	$E_{1/2}^{\mathrm{Red}\,a}$ (mV)
1	1.19 (60)	−0.76 (irr)[b], −1.14 (70), −1.26 (70), −1.87 (140)
2	1.37 (70)	−0.77 (irr)[b], −1.15 (80), −1.40 (70), −1.81 (70)
Fe-metallo-ligand[c]	1.22 (60)	−1.13 (85), −1.25 (74), −1.87 (122)
Ru-metallo-ligand[c]	1.35 (86)	−1.16 (61), −1.38 (88), −1.80 (104)
3	—	−0.53 (irr)[b]
4	—	−0.84 (irr)[b]

[a] Potentials are in volts *vs.* SCE for acetonitrile solutions, 0.1 M in TBAPF$_6$ recorded at 25 ± 1 °C at a sweep rate of 50 mV s^{-1}, using ferrocene as internal standard. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses. All the compounds are recorded as their hexafluorophosphate salts in their divalent states. [b] Irreversible; potential is given for the cathodic wave. [c] From ref. 12*a*.

Electrochemistry

The electrochemical behaviour of complexes **1** and **2** were investigated in dry, degassed acetonitrile using tetrabutyl-lammonium hexafluorophosphate as the supporting electrolyte and a glassy carbon electrode as working electrode and ferrocene as the internal standard. The data (reported *vs.* SCE) are gathered in Table 2.

At positive potentials, quasi-reversible metal-based oxidations are observed within 1.18–1.38 V range for complexes **1** and **2**, with the Ru(III)/Ru(II) oxidation in complex **2** being ∼180 mV more positive than that of Fe(III)/Fe(II) couple (Fig. 3 and S6 in ESI†). This trend is also observed in their corresponding metallo-ligands and their prototypes [M(tpy)$_2$]$^{n+}$.[16] This result also supports the observed red-shift of the lowest energy singlet metal-to-ligand charge transfer (^{1}MLCT) absorption maxima of complex **1** compared to the same of **2** in their respective electronic absorption spectra. The relative current intensity ratio of the oxidation peaks of either **1** or **2** and that of ferrocene was found to be 3 : 1, which suggests that the metal centres are redox independent in the final assemblies.[17a]
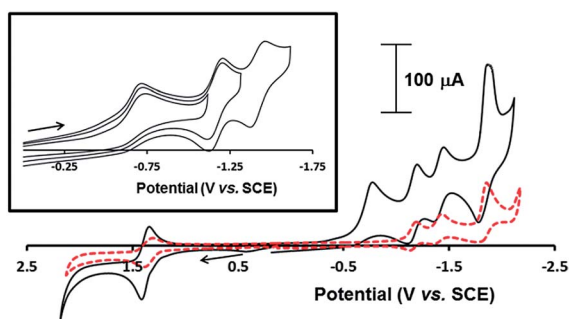

Fig. 3 Cyclic voltammograms of complex **2** (bold line) and Ru–metallo-ligand (dashed line). Inset shows the irreversible and quasi-reversible natures of individual reduction peaks of complex **2**.

The cathodic region is rich with several multi-electron reduction phenomena, with the first irreversible reduction being assigned to reduction of Pd(II) to Pd(0). Comparing this value with the irreversible reduction potentials of Pd(II) to Pd(0) in model complexes **3** and **4** reveals that the *meta*-substituted 3-pyridyl group is more electron donating than a free pyridyl group, but less donating compared to 3-picoline.[18] For complexes **1** and **2** two quasi-reversible ligand-based reductions are observed between −1.14 V to −1.40 V, whereas other ligand-based quasi-reversible reductions are also observed at relatively higher cathodic potentials. The relative current intensity ratio of the different reduction peaks was found to be 2 : 1 : 1 : 2, whereas with respect to equimolar amount of ferrocene, the relative current intensity ratio of the oxidation peak of ferrocene and the reduction peaks of complexes **1** and **2** was found to be 1 (Fc$^+$/Fc):6 : 3 : 3 : 6. This fact also supports the existence of a trimeric self-assembled oligomer in solution. All the ligand-based reductions in **1** and **2** appear more or less at the same potentials as observed for their respective metallo-ligands, suggesting that coordination of 3-pyridyl group to the neutral PdCl$_2$ has a minimal effect onto the electronic properties of the metal-tpy core.

Photophysical behaviour

The electronic absorption spectra (Fig. 4) of the complexes were recorded in dry, degassed acetonitrile solution at room temperature and the absorption data are gathered in Table 3. The electronic absorption profile of complexes **1**, **2** and their respective metallo-ligands are shown in Fig. 3. The UV-region of the electronic spectra of complexes **1**, **2** and their precursors are dominated by ligand centered (LC) $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, while the broad absorptions at visible energy region (400–700 nm) are assigned to ^{1}MLCT transitions. Although coordination induced bathochromic shifts of the absorption maxima are usually expected, the electronic transitions of **1** and **2** appear more or less at the same wavelengths compared to their corresponding metallo-ligands. This observation suggests that coordination of the 3-pyridyl ring to the neutral PdCl$_2$ does
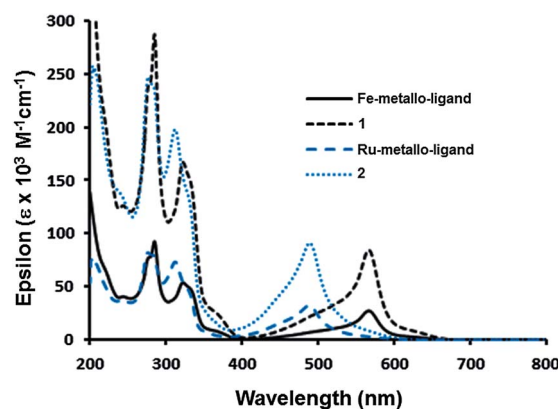

Fig. 4 Electronic absorption spectra of complexes **1**, **2** and their respective metallo-ligands.

Table 3 UV–vis absorption data of complexes **1**, **2** and model complex **4** with their respective precursors

Compound	λ_{max}, nm ($\varepsilon \times 10^3$, M^{-1} cm^{-1})
1	244 (126), 278 (243), 286 (289), 323 (167), 267 (25), 568 (85)
2	243 (136), 278 (248), 285 (240), 313 (199), 488 (91)
Fe-metallo-ligand	244 (40), 278 (77), 285 (92), 322 (53), 367 (7), 566 (27)
Ru-metallo-ligand	241 (38), 277 (80), 283 (78), 312 (70), 488 (28)
3-Picoline	234
4	237

not affect the π^* orbital localized on the pytpy ligand and hence no red-shift is observed. This fact is also supported by the negligible red-shift (3 nm) of LC transition in model complex **4** with respect to that of 3-picoline. Interestingly, for approximately similar molar concentration ($\sim 1.2 \times 10^{-5}$ M) of either of complexes **1** or **2** and their corresponding metallo-ligands, the absorption coefficient of the former was found be roughly 3 times higher than that of the latter, which supports the existence of the trimeric oligomer in dilute solution.

Complexes **1** and **2** were found to be non-luminescent at r.t. in dry, degassed acetonitrile, although the Ru-metallo-ligand emits at 695 nm under the same experimental conditions. The quenching of luminescence in Fe-metallo-ligand and **1** is attributed to the existence of non-emitting triplet ligand field (^{3}LF) state lower in energy than the triplet metal-to-ligand charge transfer (^{3}MLCT) state. The ^{3}MLCT excited state is thermally deactivated through the ^{3}LF states *via* an efficient nonradiative decay pathway.[17a] In contrast, the Ru-metallo-ligand is emissive due to the higher energy ^{3}LF state for Ru complexes as compared to Fe complexes. The Ru metallo-ligand ^{3}MLCT excited state is efficiently quenched in **2** by electron transfer to the easily-reduced [Pd] metal centre.[15]

Preliminary density functional theory (DFT) calculations for the geometry optimized structures of complexes **1** and **2** using B3LYP function and 6-31G(d,f) (for C, H and N atoms) and double-ζ quality LANL2DZ-ECP (for Fe, Ru and Pd atoms) basis sets also suggests the formation of the discrete triangular assemblies over open chain oligomeric structures (top figures in Fig. S7 in ESI†) without any significant over-tension for the formation of the discrete assemblies. Pseudo C3-symmetric cavities are observed in the metallo-triangles (bottom figure in Fig. S7 in ESI†). The radius of the central cavity is approximately 4–4.2 Å (volume of 268–310 Å^3), as suggested by DFT calculations, which may be suitable for recognition of molecules of similar size.

In conclusion it has been demonstrated that the judicious design of metallo-ligands with appropriate coordination vectors gives rise to predictable discrete supramolecular assemblies, such as metallo-triangles, which is unambiguously supported by various analytical techniques, especially, ^{1}H NMR, HR-MS and elemental analysis. The metallo-triangles exhibit multi-electronic redox process with negligible communication among

the metal centres. The photophysical properties of the assemblies are dominated by the individual chromophoric components with minimal effect from the neutral binder except the quenching of r.t. luminescence of complex **2**. The properties of these new assemblies, such as anion sensing and host–guest chemistry, will be reported in due course.

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