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Redox active [Pd$_2$L$_4$]$^{4+}$ cages constructed from rotationally flexible 1,1′-disubstituted ferrocene ligands†

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Two new ferrocene-containing [Pd$_2$(L$_{Fc}$)$_4$]$^{4+}$(X$^−$)$_4$ (where X$^−$ = BF$_4^−$
or SbF$_6^−$) self-assembled cages (C·BF$_4$ and C·SbF$_6$) were synthesised
from the known, rotationally flexible, 1,1′-bis(3-pyridylethynyl)ferrocene
ligand (L$_{Fc}$), and characterised by ^{1}H, ^{13}C and diffusion ordered (DOSY)
NMR and UV-visible absorption spectroscopies, high resolution electro-
spray ionisation mass spectrometry (HR-ESI-MS), elemental analysis,
X-ray crystallography and cyclic voltammetry (CV). The molecular
structures confirmed that cage-like systems (C·BF$_4$ and C·SbF$_6$) were
generated. Similar to related [Pd$_2$L$_4$]$^{4+}$(X$^−$)$_4$, C·SbF$_6$ was able to interact
with a range of neutral and anionic guests, with *p*-toluenesulfonate
showing the strongest association constant. Cyclic voltammetry studies
revealed that the cage systems were redox active. However, the redox
potential of the cage was unperturbed upon the addition of guests.

Interest in self-assembled metallosupramolecular architectures
has erupted over recent years due to the myriad of potential
applications that these systems display.[1] The host–guest
properties[2] of these architectures have been exploited for storage,[3]
catalysis,[4] electrochemical[5] and photochemical[6] sensing and drug
delivery.[7] Additionally, these types of systems have displayed bio-
logical activity.[8]

Discrete [Pd$_2$L$_4$]$^{4+}$ cage-like structures, first reported by McMorran
and Steel,[9] have been particularly well studied, presumably
because the di-heterocycle containing ligands used to assemble
the architectures are readily accessible.[10] While more and more
of these self-assembled architectures are being synthesised, the
vast majority contain ligands featuring rigid backbones, reliably
creating either macrocycles or cage structures through the pre-
organization of ligand geometry.[11] On the other hand, using more
flexible linking units tends to lead to reduced control over what

architecture will be generated. Some [Pd$_2$L$_4$]$^{4+}$ cages have been
generated with semi-flexible ligands. For example, McMorran and
Steel[9] observed the formation of discrete [Pd$_2$L$_4$]$^{4+}$ cage-like
architectures upon complexation of ether linked dipyridyl ligands.
The flexibility of the ligand backbone enabled the modulation of
the Pd–Pd distance (from 7.4 Å to 8.8 Å) when different sized
anions were encapsulated. Similarly, Clever and co-workers have
used semi-flexible dithienylethene ligands to generate [Pd$_2$L$_4$]$^{4+}$
cages that display interesting light driven switching behaviour.[12]
However, when the spacer between the heterocyclic donors is
too flexible mononuclear spiro-[PdL$_2$]$^{2+}$ complexes are obtained
instead of [Pd$_2$L$_4$]$^{4+}$ cage-like structures.[13] For example, Chand
and co-workers[13a] examined the self-assembly of polyethylene
glycol linked dipyridyl ligands with Pd(ɪɪ). The inherent flexibility
lead to the formation of the entropically favoured mononuclear
[PdL$_2$]$^{2+}$ loops.

Ferrocene (Fc), provides an interesting combination of
rigidity coupled with rotational flexibility (*syn* to *anti* rotation,
Fig. 1). Additionally, Fc is well-known to be redox active, and
thus provides extra functionality to any self-assembled system.
In fact, Fc has been widely exploited as a pendant or peripheral
part of ligands used to generate redox active architectures.[5,14]
However, while quite common,[15] 1,1′-disubstituted Fc ligands
have scarcely been used to generate cavity containing metallo-
supramolecular architectures.[16] Most often, metallomacrocycles,[17]
where the 1,1′-disubstituted Fc ligands adopt the *syn* conformation
with the aromatic "arms" π-stacked, or coordination polymers,[15]
with the Fc ligands in the *anti* conformation, are obtained.
Raymond and co-workers examined the self-assembly of a
1,1′-disubstituted bis-bidentate catecholamide Fc ligand, with
germanium(ɪᴠ) ions. Nuclear magnetic resonance (NMR) and
high resolution electrospray ionisation mass spectrometry
(HR-ESI-MS) data indicated that the entropically favoured
M$_2$L$_3$ helicate formed in preference to the cavity containing
M$_4$L$_6$ tetrahedron.[18] Attempts to crystallize the helicate lead
instead to the isolation of a M$_2$L$_2$ metallomacrocycle complex,
with the Fc units adopting the *syn* π-stacked orientation of the
catechol "arms". Others[19] have also generated M$_2$L$_3$ helicates

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a)

L_{Fc}

L_{dipy} (Y = CH)
L_{tripy} (Y = N)

b)

ΔE = -90 kJ/mol

+2 kJ/mol
−2 kJ/mol
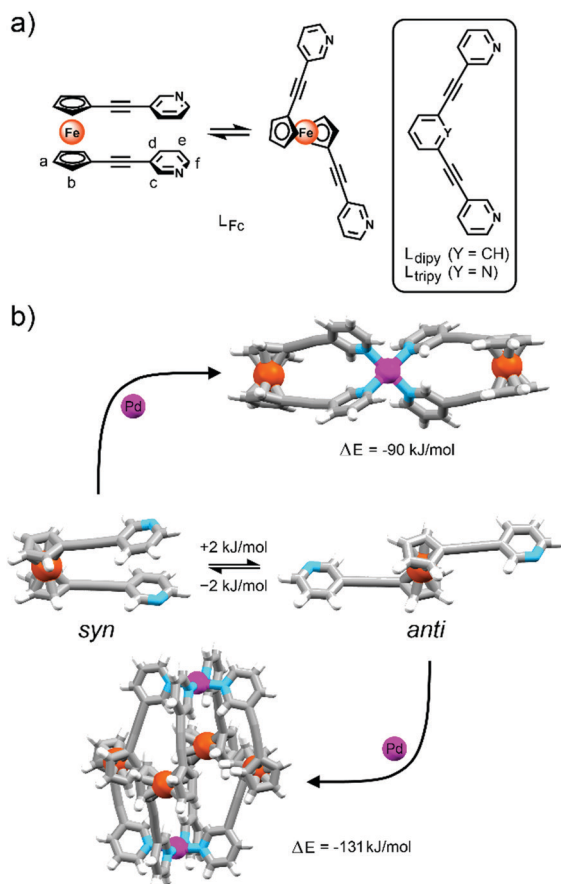
syn   *anti*

ΔE = -131 kJ/mol

Fig. 1 (a) The 1,1′-bis(3-pyridylethynyl)ferrocene, L_{Fc}, ligand in the *syn* and *anti* conformations shown alongside the structurally similar L_{dipy} and L_{tripy} ligands; (b) molecular structures, calculated using DFT, (BP86, def2-SVP, CH_3CN solvent field), of L_{Fc} and *cis*-$[Pd(L_{Fc})_2]^{2+}$ and $[Pd_2(L_{Fc})_4]^{4+}$, along with the associated energies of formation (ΔE).

using 1,1′-disubstituted Fc ligands but to the best of our knowledge no host–guest chemistry has been observed with these systems. Lindner and co-workers synthesised 1,1′-bis(3-pyridylethynyl)ferrocene, L_{Fc}, (Fig. 1a) and the related 1,1′-bis(4-pyridylethynyl)ferrocene and studied their coordination chemistry with silver(I), palladium(II) and nickel(II).[20] In all cases [2:2] metallomacrocycles where the ligands maintained the *syn* π-stacked conformation were observed. Given the structural similarity of L_{Fc} to the known L_{dipy}[21] and L_{tripy}[22] ligands (Fig. 1a) we postulated that the rotationally flexible ferrocene ligand could potentially assemble into $[Pd_2L_4]^{4+}$ cage-like structures, when exposed to "naked" Pd(II) ions, if the ligand adopted the *anti* conformation. Herein we investigate the self-assembly of L_{Fc} with Pd(II) ions. Additionally, the redox properties and host–guest chemistry of the Fc containing metallosupramolecular architectures are examined.

Initially, the conformational preference of the ligand L_{Fc} and the energies of formation of $[Pd(L_{Fc})_2]^{2+}$ (*cis* and *trans*) and the $[Pd_2(L_{Fc})_4]^{4+}$ cage were examined using density functional theory calculations (DFT, BP86, def2-SVP, CH_3CN solvent field, Fig. 1b and ESI†). The *syn* and *anti* forms were found to be rather close in energy, with the *syn* π-stacked conformation being 2 kJ mol^{-1} more stable, as expected from the previous literature.[17,23] This was

also supported by ^{1}H NMR experiments (ESI†), the proton signals associated with the 3-pyridyl ($H_{c–f}$) arms of L_{Fc} were shifted upfield relative to those of the model compound 3-pyridylethynyl-ferrocene, indicating that L_{Fc} ligand adopts a stacked (*syn*) conformation in solution.

The formation energy of the *trans*-$[Pd(L_{Fc})_2]^{2+}$ complex was calculated to be +42 kJ mol^{-1} higher in energy than the starting materials indicating that it was unlikely to form, presumably due to the severe bond angle strain observed in the calculated structure (ESI†). In contrast, the DFT calculations indicated that both *cis*-$[Pd(L_{Fc})_2]^{2+}$ (ΔE = −90 kJ mol^{-1}) and $[Pd_2(L_{Fc})_4]^{4+}$ (ΔE = −131 kJ mol^{-1}) complexes were significantly lower in energy than the starting materials. However, the formation of the cage architecture was found to be the most favoured. Encouraged by the computational results the orange (λ_{max} = 455 nm) ferrocene ligand L_{Fc} (2 equiv.) was suspended in acetonitrile and treated with either 1 equiv. of $[Pd(CH_3CN)_4][BF_4]_2$ or 1 equiv. of $[(CH_3CN)_2Pd(Cl)_2]$ and $AgSbF_6$ (2 equiv.) to give darker orange solutions (λ_{max} = 464 nm) indicative of complex formation (ESI†). Precipitation with diethyl ether followed by filtration resulted in the formation of orange-red solids in excellent yields (78–99%). The ^{1}H NMR spectra (CD_3CN, 298 K) of the isolated materials displayed a single set of resonances indicative of the formation of the highly symmetric coordination complexes $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ (where X^- = BF_4^- or SbF_6^-) **C·BF$_4$** or **C·SbF$_6$** (ESI†). The resonances of the α-pyridyl protons (H_c and H_f) have shifted downfield relative to the "free" ligand (*e.g.* $\Delta\delta$ = 0.75 and 1.00 ppm for **C·SbF$_6$** and **C·BF$_4$**, respectively). ^{1}H diffusion ordered NMR spectroscopy (DOSY, CD_3NO_2 or CD_3CN) also provided evidence for the formation of larger discrete architectures. The diffusion coefficients (D) for **C·SbF$_6$** and **C·BF$_4$** were found to be D = 5.4 × 10^{-10} m^2 s^{-1} and 6.3 × 10^{-10} m^2 s^{-1}, respectively, in CD_3NO_2. The diffusion coefficient of L_{Fc} in CD_3NO_2 was higher (D = 10.9 × 10^{-10} m^2 s^{-1}) suggesting that the complexes are significantly larger than the free ligand. Similarly, the diffusion coefficients (D) for **C·SbF$_6$** and **C·BF$_4$** were found to be D = 7.16 × 10^{-10} m^2 s^{-1} and 7.12 × 10^{-10} m^2 s^{-1}, respectively, in CD_3CN, these values were similar to those observed for related $[Pd_2L_4]^{4+}$ cages in the same solvent (ESI†), consistent with the formation of complexes with the $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ formulation.[22,24] HR-ESI-MS provided additional support for the $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ stoichiometry of the complexes; the dominant isotopically resolved palladium-containing species present in the mass spectrum occurred at m/z = 617.6927 and 666.9897, respectively, which were attributed to $[Pd_2(L_{Fc})_4](BF_4)^{3+}$ and $[Pd_2(L_{Fc})_4](SbF_6)^{3+}$ ions. There were also a series of other ions that were consistent with the $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ formulation (ESI†).

The molecular structures of the **C·BF$_4$** and **C·SbF$_6$** metallosupramolecular architectures were determined unequivocally using X-ray crystallography. X-ray quality single crystals of **C·BF$_4$** and **C·SbF$_6$** were obtained *via* vapour diffusion of diethyl ether into acetonitrile solutions of the respective complexes. The X-ray data revealed that lantern-shaped $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ cages (Fig. 2) were generated.[22,24] The structure of **C·BF$_4$** was solved in the triclinic space group $P\bar{1}$, with two half-cages, four BF_4^- counterions and two acetonitrile solvent molecules in the asymmetric unit. There were two crystallographically independent cage complexes in the

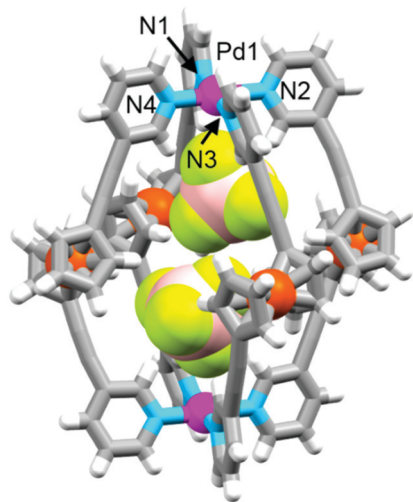Fig. 2 Tube representation of X-ray structure of **C·BF₄** with encapsulated BF_4^- counterions shown as spacefilling. Solvent molecules and other BF_4^- counterions omitted for clarity. Colours: carbon grey, hydrogen white, nitrogen blue, palladium magenta, iron orange, boron salmon, fluorine yellow/green. Pd–N bond lengths range: 2.01(1)–2.07(1) Å; Pd1–Pd1′ = 13.090(2) Å.

unit cell with the Pd1–Pd1′ distance being 13.090(2) Å and the Pd2–Pd2′ distance 13.410(2) Å. These are longer than the Pd–Pd distances of previous crystallographically characterised cages, which range from 11.49 to 12.51 Å.[21,22,24] All four Fc units in the ligands adopted a lower-energy "eclipsed" orientation, and the ligands themselves are in the *anti* conformation (average angle between the alkyne "arms" θ = 150.38°; ranging from 144.28°–154.21°). Each cage contains two tetrafluoroborate counterions in its cavity, oriented in such a way that there is a hydrogen-bonding network between the fluorine atoms of the counterions and the internally directed α-pyridyl protons of the ligands, as has been observed in other $[Pd_2L_4]^{4+}(BF_4^-)_4$ cage systems.[25] While the X-ray data obtained for the **C·SbF₆** was modest, due to weaker diffraction and disorder in the counter anions and solvents of crystallisation, the cationic portion of the structure was well defined and showed unequivocally that a $[Pd_2(L_{Fc})_4]^{4+}$ system was obtained with an SbF_6^- counter anion located within the cavity of the cage (ESI†). The Pd1–Pd2 bond distance was 13.397(1) Å. Interestingly, both cages (**C·BF₄** and **C·SbF₆**) are *meso*-systems with two **L_Fc** ligands in the *M* configuration and two in the *P* configuration (ESI†).

Related $[Pd_2L_4]^{4+}$ cages have been shown to bind neutral inorganic,[22,24] and organic[26] guests and anions[27] in a variety of solvents. Therefore, we examined the interaction of the cages (**C·SbF₆** and **C·BF₄**) with cisplatin (CP), 9-methylanthracene (9-MA),[28] 2,4-dinitrotoluene (DNT), 1,4-benzoquinone (BQ),[26a,b] 2,4,7-trinitrofluorenone (TNF) and sodium *p*-toluenesulfonate (TOS)[24c,27b,29] guest molecules (in acetonitrile solutions due to solubility limitations, ESI†). The **C·BF₄** system displayed only very modest complexation induced shifts (CIS) of the H_c proton of the cage in the presence of the guest molecules (ESI†). Larger CIS were observed with **C·SbF₆** suggesting that the guest molecules interact more strongly with that cage. That was consistent with observations of Lusby and co-workers who showed that anion competition for the cage cavity in related $[Pd_2L_4]^{4+}$ systems affects the strength of the host guest interaction

with neutral guests.[26b] ^{19}F NMR spectroscopy (CD₃CN, CD₃NO₂ or d_6-acetone) suggested that the BF_4^- anions were interacting with the cage, in a similar fashion to that observed in the X-ray structure, as the resonance due to the BF_4^- anions of **C·BF₄** was shifted and broadened relative to that of NaBF₄ (ESI†). With **C·SbF₆**, only very small CIS were observed with DNT and 9-MA and while CP induced a larger shift ($\Delta\delta(H_c)_{CP}$ = 0.08 ppm) of the H_c proton of the cage we could not carry out a titration due to the poor solubility of CP in CD₃CN. The association constants (K_a) for the other guests (BQ, TNF and TOS) with **C·SbF₆** were determined using ^{1}H NMR titrations (ESI†). The largest CIS, in each case, were those of the cage H_c protons (*e.g.* $\Delta\delta(H_c)_{TOS}$ = 0.43 ppm), consistent with guest binding within the cage cavity (ESI†). The ^{1}H NMR titration data was curve fitted using Bindfit (supramolecular.org).[30] The 1:1 host:guest model gave the best fit, similar to what has been observed with other related $[Pd_2(L)_4]^{4+}$ cages.[26] The anionic TOS (K_a = 900 ± 100 M⁻¹) guest had the strongest interaction with the cage presumably due the stronger electrostatic interaction between the cationic cage and the anionic guest supplementing the hydrogen bonding interaction between H_c and the sulfonate's oxygen atoms. The neutral organic guests had weaker interactions with the **C·SbF₆** (BQ (K_a = 50 ± 4 M⁻¹) and TNF (K_a = 350 ± 30 M⁻¹)) but also seem to interact through hydrogen bonding between the acidic internal α-pyridyl protons of the cage and the carbonyl and nitro oxygen atoms on the guests (ESI†). Presumably, the larger association constant for the TNF-cage adduct reflects the presence of additional C–H···π and van der Waals interactions with the Fc units of the cage.

The redox behaviour of **L_Fc**, **C·BF₄** and **C·SbF₆** was probed through cyclic voltammetry (CV) experiments in nitromethane solution (Table 1 and ESI†).[31] **L_Fc** exhibited the expected single reversible oxidation of the Fc unit with $E°$ = 0.77 V, (*vs.* decamethylferrocene; $E°$ = 0.00 V) in agreement with previous reports (albeit in different solvents).[20,32] CV experiments also revealed that both **C·BF₄** and **C·SbF₆** are redox active, giving a single oxidation process, at $E°$ = 0.86 V, indicating that there was no electronic communication between the four Fc units of the cages ($\Delta E = E_{pc} - E_{pa}$ = 110 mV, for both systems). CV experiments with **C·BF₄** in the presence of 10 equiv. of the guest molecules BQ, TNF, and TOS were also carried out. Disappointingly, no shift (within experimental uncertainty) of the redox potential of the cage was observed, suggesting that under these conditions the cages cannot be used as electrochemical sensors of guest binding (Table 1).[33]

We have herein reported the synthesis, characterisation and host–guest chemistry of two new, redox active $[Pd_2(L_{Fc})_4]^{4+}(X^-)_4$ (where X^- = BF_4^- or SbF_6^-) cages containing rotationally flexible ferrocene ligands. Host–guest studies with **C·SbF₆** and three different guests (TOS, TNF and BQ) revealed that the anionic sulfonate guest exhibits the largest association constant in CD₃CN. Unfortunately, while the cages were redox active, CV experiments suggested that the guests did not have any effect on the redox potentials of the ferrocene cages. Future work will examine generating analogous cages with larger non-interacting anions such as tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (BArF⁻) as this should lead to enhanced host–guest interactions and enable the cages to be exploited as electrochemical sensors[33] or for redox catalysis.[34]

Table 1 Formal electrode potentials $(E^\circ)^a$ exhibited by **L$_{Fc}$**, **C·BF$_4$**, **C·SbF$_6$**, and **C·BF$_4$** in the presence of 10 equiv. of each of the three guests (TOS, TNF, and BQ), in nitromethane solution

Compound	$E_{1/2}$ (Fc/Fc★) (V)
L$_{Fc}$	0.77
C·BF$_4$	0.86
C·SbF$_6$	0.86
TNF ⊂ C·BF$_4$	0.87
TOS ⊂ C·BF$_4$	0.85
BQ ⊂ C·BF$_4$	0.86

^{a} $E^\circ = (E_{pc} + E_{pa})/2$, conditions: nitromethane solvent, 0.1 M Bu$_4$NPF$_6$ as supporting electrolyte, $\sim$1 mM concentration of electroactive analyte, potentials referenced to the [Fc★]$^{+/0}$ = 0.00 V of decamethylferrocene, 100 mV s^{-1}.

Conflicts of interest

There are no conflicts to declare.

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