Supramolecular Cages

Homochiral Emissive $\Delta_8^-$ and $\Delta_8^-[\text{Ir}_8\text{Pd}_4]^{16+}$ Supramolecular Cages


Abstract: Synthetic self-assembly is a powerful technique for the bottom-up construction of discrete and well-defined polyhedral nanostructures resembling the spherical shape of large biological systems. In recent years, numerous Archimedean-shaped coordination cages have been reported based on the assembly of bent monodentate organic ligands containing two or more distal pyridyl rings and square-planar Pd$^+$ ions. The formation of photoactive Pd$^+$ metallamacrocycles and cages, however, remain rare. Here we report the first examples of emissive and homochiral supramolecular cages of the form $[\text{Ir}_8\text{Pd}_4]^{16+}$. These cages provide a suitably sized cavity to host large guest molecules. Importantly, encapsulation and energy transfer have been observed between the blue-emitting NBu$_4[\text{Ir}(\text{dFppy})_2\text{(CN)}]_3$ guest and the red-emitting $\Delta_8^-[\text{Ir}_8\text{Pd}_4]^{16+}$ cage.

Introduction

Chemists have often found inspiration from the spontaneous and precise self-assembly exhibited by biological systems into giant, well-defined and functional superstructures.[1] In natural photosynthesis, for instance, organisms optimise solar energy conversion through self-organised assemblies of photofunctional chromophores.[2] Similarly, catalysis is possible as a consequence of the secondary and tertiary structures of self-assembled proteins, providing well-defined local environments to mediate biochemical transformations.[3] Much effort has been devoted to the preparation of large artificial nanostructures to mimic the precise assembly of multiple protein subunits into giant, polyhedral functional structures.[4] Nowadays, the self-assembly between square-planar palladium(II) or platinum(II) metal ions and complementary bent ligands containing specifically positioned distal pyridine moieties, first demonstrated by Fujita et al.,[5] is one of the most popular and successful strategies to prepare molecular capsules or cages.[6] These nanostructures generally possess well-defined internal cavities that promote the ingress of guest molecules and have been exploited in sensing,[7] gas storage and purification,[8] and catalysis.[9] Usually the metal ions play solely a structural role within these supramolecular architectures; however, more recently, there has been increasing interest in the investigation of photophysically active supramolecular architectures. These have included systems that incorporate photophysically active metal ions as structural units within the architecture framework,[10] as well as those that employ ligand scaffolds decorated with photoactive units, including luminescent metal complexes.[11] Photocatalytic cages and metallamacrocycles provide restricted shape and size to govern host–guest interactions and, as a consequence of the optoelectronic communication between host and guest, distinct photophysical properties that are difficult to attain in conventional molecular materials can be achieved.[12]

Iridium(III) complexes possess a highly desirable set of optoelectronic and physical properties, including colour tunability across the visible spectrum, high photoluminescence quantum yields with short phosphorescence lifetimes and high chemical stability.[13] They have been used as integral components of sensors,[14] as luminescent biological probes[15] and as emitters in electroluminescent devices.[16] However, despite their desirable photophysical properties, there exist to date only a handful of examples of photoactive iridium(III) complexes in...
supramolecular architectures, including cages, coordination capsules and metallamacrocycles, coordination polymers and MOFs, discrete paddlewheel structures, and soft salts. These metallosupramolecular assemblies generally show red-shifted emission compared to their mononuclear analogues and, except for the coordination capsule reported by Lusby et al., decreased photoluminescence quantum yields, $\Phi_{PL}$, and shorter emission lifetimes, $\tau_e$.

Here we report the first examples of homochiral red-emitting supramolecular cages of the form of $[\text{IrPd}]^{16+}$ that are able to encapsulate large anionic guests, including a blue-emitting $\text{NBu}_2[N\text{Ir(dFppy)}_2\text{CN}]_2$ complex. Controlled photoinduced energy transfer from the donor anionic iridium complex guest to the acceptor iridium metalloligands in the $[\text{IrPd}]^{16+}$ cage is efficiently promoted. Such photoactive homochiral assemblies have the potential to mediate enantioselective photocatalytic reactions and act as single white-light emissive materials.

**Results and Discussion**

We report herein the first example of phosphorescent cages based on the self-assembly between two families of Ir metallopalladates of the form $[\text{Ir(C}^N\text{)}_2\text{qpy}]\text{BF}_4$ [where $C^N$ is mesppy = 2-phenyl-4-mesitylpypyridinato and dFmesppy = 2-(4,6-difluorophenyl)-4-mesitylpypyridinato, and qpy = 4,4′,2′,2′′-quaterpyridine] with Pd$^{2+}$ ions through $\text{N}_{Pd}$-Pd coordination (Figure 1a, b). Each family of metalloligands is easily accessed in racemic form in a five step synthesis, however, with the aim of assessing the impact of iridium-based chirality on the self-assembly, we also prepared the enantiopure metallocyclic analogues and, except for the coordination capsule reported by Lusby et al., increased photoluminescence quantum yields, $\Phi_{PL}$, and shorter emission lifetimes, $\tau_e$.

![Figure 1. Self-assembly between the metalloligands, and Pd$^{2+}$ ions yielding: a) for rac-1, $\Lambda$, $\Lambda$-1, $\Lambda$-1; racemic rac-C1, and homochiral $\Lambda$, $\Lambda$, $\Lambda$-C1 and $\Lambda$, $\Lambda$, $\Lambda$-C1 cages, respectively (for clarity, only the calculated structure of $\Lambda$, $\Lambda$-C1 obtained from $\Lambda$, $\Lambda$-1 is shown) and b) for rac-2, $\Lambda$, $\Lambda$-2, $\Lambda$, $\Lambda$-2; rac-C2, $\Lambda$, $\Lambda$, $\Lambda$-C2 and $\Lambda$, $\Lambda$, $\Lambda$-C2 cages (for clarity, only the calculated structure of $\Lambda$, $\Lambda$-C2 obtained from $\Lambda$, $\Lambda$-2 is shown). c) CD spectra collected in CH$_2$Cl$_2$ at 298 K; light-red lines: $\Lambda$, $\Lambda$-1 (left), $\Lambda$, $\Lambda$-1 (right); red lines: $\Lambda$, $\Lambda$-1 (left) and $\Lambda$, $\Lambda$-1 (right); orange lines: rac-1 (left) and rac-C1 (right). d) CD spectra collected in CH$_2$Cl$_2$ at 298 K; light-green lines: $\Lambda$, $\Lambda$, $\Lambda$-2 (left), $\Lambda$, $\Lambda$, $\Lambda$-2 (right); green lines: $\Lambda$, $\Lambda$, $\Lambda$-2 (left) and $\Lambda$, $\Lambda$, $\Lambda$-2 (right); light-blue lines: rac-2 (left) and rac-C2 (right). The CD spectra of 1 and 2 were collected at a concentration of $5 \times 10^{-3}$ M. e) $^1$H DOSY NMR of $\Lambda$, $\Lambda$-1, in red and $\Lambda$, $\Lambda$-1, in blue. f) $^1$H DOSY NMR of $\Lambda$, $\Lambda$-2, in red and $\Lambda$, $\Lambda$-2, in blue (left) and stacked $^1$F NMR spectra of $\Lambda$, $\Lambda$-2 in red, and $\Lambda$, $\Lambda$-2 in blue (right). The geometries of $\Lambda$, $\Lambda$-1 and $\Lambda$, $\Lambda$-2 have each been determined in vacuo at the HF/6-31G(d) level of theory.](https://example.com/fig1)
olute configurations of the enantiomers Δ-1, Δ-1, Λ-2 and Δ-2.23 The enantiomeric excess of the bulk samples was confirmed by CD spectroscopy (Figure 1c, d). We introduced the bulky mesityl substituent at the 4-position of the pyridine of C^N ligands of 1 and 2 to increase the solubility of the complexes in organic solvents and to reduce intramolecular interactions without interfering in the assembly process.24 The presence of fluorine atoms in 2 provides a useful tag for monitoring both the self-assembly process and the purity of the cage by 19F NMR spectroscopy and, by virtue of their electron-withdrawing nature, for promoting a blue-shift in the absorption and emission spectra concomitant with a stabilisation of the HOMO of the complex.25

When any of the metalloligands rac-1, Λ-1, Δ-1 and rac-2, Λ-2, Δ-2 and [Pd(NCMe)4][BF4]2 were heated in a 2:1 ratio in [D2]dimethyl sulfoxide ([D2]DMSO) at 85 °C for 12 h, the proton resonances associated with the metalloligand broadened and experienced downfield shifts (Figures S23 and S28 in the Supporting Information). The broad 1H NMR signals are indicative of the formation of very large assemblies, the tumbling motion of which is very slow on the NMR timescale.26 As expected, the proton resonances associated with the proton in ortho-position to the distal nitrogen of the pyridine moiety (H^t, H^p, in Figures S23 and S28) were most sensitive to the axial coordination of the pyridine ring to Pd. Evidence for the formation of a single species was confirmed by 1H DOSY NMR spectroscopy with a single diffusion coefficient (D) in [D2]DMSO of 5.2 × 10^{-11} m^2 s^{-1} and 4.9 × 10^{-11} m^2 s^{-1}, respectively, for C1 and C2 (Figure 1e, f, and Figures S26 and S30). These diffusion coefficients are indicative of much larger structures than either of the two metalloligands 1 and 2, which show nearly identical diffusion coefficients in [D2]DMSO of 1.3 × 10^{-10} m^2 s^{-1} and 1.2 × 10^{-10} m^2 s^{-1}, respectively (Figure 1e, f and Figures S27 and S31). The corresponding hydrodynamic radii (rH) of C1 and C2 are calculated to be 19.8 Å and 20.0 Å, respectively (Table S1 in the Supporting Information). 19F NMR spectroscopy further confirmed quantitative conversion from 2 to C2, with the fluoro resonances associated with the dFppy ligand shifted downfield from −106.33 ppm and −108.52 ppm in 2 to −106.09 ppm and −108.31 ppm in C2 (Figure 1f and Figure S29 in the Supporting Information). As the two doublets associated with the fluoro resonances of the dFppy ligands in 2 are maintained in the 19F NMR spectra of C2, the local C2 symmetry present around the iridium centre in 2 is maintained also in the cage. Furthermore, no differences in the 1H, 1H DOSY and 19F NMR spectra were observed when the enantipure metalloligands Λ-1 and Δ-1 or Λ-2 and Δ-2 were employed towards the self-assembly of the cages in lieu of the racemic analogues rac-1 and rac-2 (Figures S25–S29 in the Supporting Information).

The compositions of the assemblies C1 and C2 have been unequivocally established to be [1Pd4][BF4]14 and [2Pd4][BF4]14, respectively, by HR-ESI-MS spectrometry, showing iso- topically resolved peaks for [C1-(BF4)6]^{+} (n=4–8). For example, each of the ESI-MS spectra of rac-1, Λ-1 and Δ-1 reveal peaks at m/z = 2635.5650, 2067.2391, 1707.8640, 1451.5934 and 1259.2675, which are assigned to [C1-(BF4)4]^{+}, [C1-(BF4)5]^{+}, [C1-(BF4)6]^{+}, [C1-(BF4)7]^{+}, [C1-(BF4)8]^{+}, respectively (Figure S33 in the Supporting Information). Similarly, the charge states [C2-(BF4)6]^{+} (n = 5–8), were likewise observed in the MS spectra of each of rac-1, Λ-2 and Δ-2 at m/z = 2067.2391, 1707.8640, 1451.5934 and 1259.2765, respectively (Figure S38). The isotopically resolved distributions of these spectra closely match the simulated spectra. The ESI-MS spectra of all the cages can be found in Figures S33–S41 in the Supporting Information. Among supramolecular assemblies composed of ligands containing two or more pyridine units possessing divergent vectors and Pd^{2+} ions, the stoichiometry ([Li][Pd4]) is rare as this relative stoichiometry is only possible when the angle between the coordinating 4-pyridyl units is inferior to 90°.26

The CD spectra of Λ-C1, Δ-C1, Λ-C2 and Δ-C2 revealed that the Ir-centred stereochemistry of the eight metalloligands was maintained during the self-assembly, and homochiral cages of compositions Λs and Δs([1Pd4][BF4]14 and Δs and Δs[2Pd4][BF4]14] were formed (Figure 1c, d). When rac-1 and rac-2 were employed as the metalloligands, racemic mixtures of composition rac-[1Pd4][BF4]14 and rac-[2Pd4][BF4]14, respectively, were formed (orange and light-blue lines in Figure 1c, d), although this did not enable us to determine if these complexes were racemic cages, or racemic mixtures of enantiopure cages.

In order to ascertain the impact of the nature of the iridium-centred stereochemistry on the assembly of the cages, we examined the self-assembly, in [D2]DMSO, of Pd^{2+} ions with one equivalent of one of the isostructural and enantiopure metalloligands, Λ-1 or Δ-1, and one equivalent of Δ-2. There are three possibilities by which similarly shaped components can self-assemble in structures: 1) random mixing,27 2) well-defined mixing,28 or 3) self-sorting.29 ESI-MS of a [D2]DMSO solution containing either Λ-1 or Δ-1 with Δ-2 and [Pd(NCMe)4][BF4]2, stirred at 85 °C for 12 h, show a statistical mixture of cage species of composition ([Λ-1/Δ-1)_{n}[Δ-2]_{m}][Pd4][BF4]14 (n + m = 8), from Λ-1/Δ-1:Δ-2 = 7:1 to Λ-1/Δ-1:Δ-2 = 1:7, Figures S42 and S43 in the Supporting Information), indicating that our cages do not assemble by self-sorting with respect to either the chirality or identity of the metalloligands. Similarly, mixing the pre-formed cages Λ-C1 and Λ-C1 with Δ-C2 (Figure 2a) at 85 °C for 12 h resulted in a rapid exchange between ligands Λ-1, Δ-1, and Λ-2, and Δ-C2 (Figure 2b, cand Figures S44 and S45). As illustrated in Figures S45a, c, the isotopically resolved distributions of the 7+ charge states, ([Λ-C1+Δ-C1]+(Δ-C2)_{n}][BF4]^{+} closely match the simulated spectra. When homochiral cages of the same stereochemistry, Λ-C1 and Δ-C2, are mixed at 85 °C in [D2]DMSO, the formation of homochiral heteronuclear cages are observed by CD spectroscopy with a CD spectrum intermediate for the mixed cage assemblies (Figure S45h, dark-blue line). However, when homochiral cage Λ-C1 is mixed with Δ-C2 at 85 °C, which is of opposite stereochemistry, the formation of racemic heteronuclear cages is promoted (Figure S45h, light-blue line). This was expected considering that the chirality of the iridium core does not contribute directly to the overall self-assembly process. No metalloligand exchange is observed when either homochiral cage Λ-C1/Δ-C1 is mixed with Δ-C2.
at room temperature, and the cages show a high degree of kinetic inertness (Figures S45 e–S47). The structures of both C1 and C2 were modelled at the HF/6-31G(d) level of theory (Figure 1a), and were found to be very similar. They resemble metallamacrocyclic structures in which two ligands doubly bridge between adjacent Pd centres around the macrocycle, in a crown-like fashion. Of potential structures of [L8Pd4] cages, this particular arrangement is rare, only five examples of assemblies with this structural motif were reported to date. The calculated structure confirmed that the qpy vector of the metalloligands 1 and 2 is compatible to form the [Ir8Pd4]16+ cages identified by mass spectrometry (Figure S32 in the Supporting Information). The optimised cage exhibits a diameter of approximately 18.8 Å (corresponding to the Pd–Pd distance), an internal volume from the top to the bottom bounds of the structure of approximately 3480 Å3, and a distance between neighbouring Ir atoms bridging the same Pd–Pd edge of approximately 13.7 Å. The radius around the metallamacrocyclic core across long axes of the structure, measures 21.5 Å (Figure S32) and matches with the hydrodynamic radii obtained by 1H NMR DOSY analysis (rt = 19.8 Å). The cage structure can be seen to be approximately C4 symmetric.
about the Pd$_4$ square. Unfortunately, while single crystals of cages C1 or C2 could be grown, and were examined by X-ray diffraction, all crystals investigated showed extremely weak diffraction, with even synchrotron radiation not showing diffraction above 1.6 Å. Attempted structure solutions have given the positions of the metal cations and poorly ordered parts of the ligands, the data not, as yet, being amenable to refinement (Figure S62).

In CH$_2$Cl$_2$, the photophysical properties of the racemic metalloligands rac-1 and rac-2 and of the racemic cages rac-C1 and rac-C2 are identical to those of the respective homochiral analogues Λ-1/Δ-1, Λ-2/Δ-2, Λ-C1/Δ-C1, and Λ-C2/Δ-C2 (Table 1). The emission profiles of both families of cages C1 and C2 in CH$_2$Cl$_2$ are red-shifted, respectively, at 655 nm and 561 nm, relative to those of the corresponding metalloligands 1 (λ$_{max}$ = 620 nm) and 2 (λ$_{max}$ = 527 nm). Their photoluminescence quantum yields, $\Phi_{PL}$, and emission lifetimes, $\tau_e$, are correspondingly lower and shorter, respectively (e.g., rac-C1: $\Phi_{PL} = 5\%$, $\tau_e = 202$ ns; rac-C2: $\Phi_{PL} = 10\%$, $\tau_e = 825$ ns), compared to those of 1 and 2 (e.g., rac-1: $\Phi_{PL} = 14\%$, $\tau_e = 300$ ns; rac-2: $\Phi_{PL} = 34\%$, $\tau_e = 1000$ ns). These features are reflected in the excited-state decay kinetics. Indeed, both families of homochiral and racemic coordination cages C1 and C2 exhibit slightly smaller radiative rate constants ($k_r$, e.g., 2.47 × 10$^5$ s$^{-1}$ for rac-C1 and 1.21 × 10$^5$ s$^{-1}$ for rac-C2), and slightly larger non-radiative rate constants ($k_{nr}$, e.g., 4.66 × 10$^5$ s$^{-1}$ for rac-C1 and 1.09 × 10$^6$ s$^{-1}$ for rac-C2), relative to the corresponding metalloligands (e.g., rac-1: $k_r = 4.67 \times 10^5$ s$^{-1}$, $k_{nr} = 2.45 \times 10^5$ s$^{-1}$; rac-2: $k_r = 3.40 \times 10^5$ s$^{-1}$, $k_{nr} = 6.60 \times 10^5$ s$^{-1}$). The presence of the electron-withdrawing fluoride atoms in C2 induces a blueshift in the emission relative to the fluoride-free cage C1. Similar to that observed for 1 and 2, the emission profiles of C1 and C2 are broad and unstructured, an indication that the nature of the emission remains unchanged and is from mixed metal-to-ligand and ligand-to-ligand charge transfer (MLCT/LLCT) states (Figure 3 and Figures S64 and 65 in the Supporting Information).

The red-shifted emissions of the cages C1 and C2 in both CH$_2$Cl$_2$ and PMMA-doped films (PMMA = poly-(methyl methacrylate)) relative to those of the corresponding metalloligands can be interpreted as the result of coordination of the Lewis acidic Pd$^4$ to the iridium complex. By acting as a Lewis acid, the Pd$^4$ ions lower the LUMO levels of complexes 1 and 2 located on the qpy ligand, giving rise to smaller optical gaps.

In order to mitigate non-radiative vibrational motion, we spin-coated 5 wt% of 1, 2, C1 and C2 in PMMA, which serves as an inert matrix. As a result of the less polar environment

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Table 1. Photophysical properties of 1, C1, 2 and C2.

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[a] Measurements in degassed CH$_2$Cl$_2$ at 298 K (λ$_{max}$ = 360 nm). [b] Thin films formed by spin-coating on a pristine quartz substrate. [c] $\Phi_{PL}$, measurements were carried out in degassed CH$_2$Cl$_2$ under nitrogen (λ$_{max}$ = 360 nm) using quinine sulfate as the external reference ($\Phi_{PL} = 54.6\%$ in 0.5 M H$_2$SO$_4$ at 288 K). [d] Values obtained using an integrating sphere. [e] Values in parentheses are pre-exponential weighting factor, in relative % intensity, of the emission decay kinetics ($\lambda_{max}$ = 378 nm).

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Figure 3. Normalised emission spectra of a) Δ-1 and Δ-C1 and b) Λ-2 and Δ-C2. Dotted dark-blue lines: PMMA-doped film with 5 wt% of metalloligands Δ-1 and Δ-2 spin-coated on quartz substrates; Dotted light-blue lines: deaerated CH$_2$Cl$_2$ solution of Δ-1 and Δ-2; Solid orange lines: PMMA-doped film with 5 wt% of cages C1 and Δ-C2 spin-coated on quartz substrates; Solid red lines: deaerated CH$_2$Cl$_2$ solution of Λ-C1 and Δ-C2.
and the rigidification conferred by the PMMA host, the emissions of 1, 2, C1 and C2 in the thin films were blue-shifted, respectively at 564 nm, 518 nm, 643 nm and 531 nm (Figure 3, Figures S64 and 65 in the Supporting Information), with enhanced $\Phi_{PL}$ and longer multi-exponential $\tau_e$ (as representative examples: rac-1: $\Phi_{PL} = 28\%$, $\tau_{e} = 344$, 1045 ns, rac-2: $\Phi_{PL} = 41\%$, $\tau_{e} = 48$, 259, 1195 ns, rac-C1: $\Phi_{PL} = 11\%$, $\tau_{e} = 49$, 270, 715 ns, and rac-C2: $\Phi_{PL} = 17\%$, $\tau_{e} = 13$, 412, 1125 ns) relative to the photophysical behaviour in CH$_2$Cl$_2$ (Table 1).

The calculated cage structures, rac-C1, C1-C1, C1-C1 all show an internal pocket volume of approximately 3480 Å$^3$, which is sufficient to include large guest molecules, including mononuclear phosphorescent iridium complexes. Several studies have demonstrated that the photophysical properties of luminescent transition-metal complexes emitting from CT states strongly depend on the local environment.$^{18b,34}$ For example, Umakoshi et al.$^{18b}$ encapsulated an Ir$^{	ext{III}}$ complex, [Ir(bpy)$_2$(bpy)Cl] (bpy is 2,2'-bipyridine), within a hexameric resorcinarene hydrogen-bonded capsule and observed that the capsule effectively hampers the non-radiative decay thereby enhancing both the $\Phi_{PL}$ and the $\tau_e$ of the encapsulated iridium guest. We targeted the encapsulation of blue-emitting Ir$^{	ext{III}}$ guests within the confined cavity of our red-emitting cage C1 to study the nature of the energy-transfer process between donor guest and acceptor host cage. Importantly, by modulating the degree of energy transfer between the donor and the acceptor as a function of the choice of medium or concentration, emission of white light can also be achieved.$^{21a,35}$ In the context of iridium phosphors, this approach has been investigated in multi-metallic covalently linked complexes,$^{36}$ soft salts,$^{21a,34}$ or in MOFs containing emissive materials,$^{18b}$ but still unexplored in photo-active host–guest assemblies.$^{35}$

Preliminary $^1$H NMR studies on the interactions between a selected range of small organic guest compounds and C1 revealed that the cage interacts selectively with anionic guests in [D$_6$]DMSO. Interactions can be observed with ammonium tetryphenyl borate or ammonium pyrene-carboxylate (see $^1$H NMR spectra in Figures S48c and S49), but no interaction is observed for neutral guest compounds, such as pyrene or pyrene carboxylic acid (see $^1$H NMR spectra in Figure S48ab in the Supporting Information). A similar behaviour was observed for the interaction of guest molecules with a polycationic [Pd$_4$L$_4$]$_{12}^+$ cage (in which L are acridinium panels connected by a meta-phenylene spacers).$^{18b}$ Indeed, in the computed molecular electrostatic potential map of C1 (Figure 4), all regions are of positive potential, the most positive regions of C1 are present in the pocket of the cage (in the closest proximity to the Pd$^{	ext{II}}$ ions). Therefore, favourable interactions are only expected with negatively charged guests. We next turned our attention to investigate the interactions between the blue-emitting anionic [Ir(dfpppy)$_2$(CN)$_2$]$^-$ complex (IrCN)$^{27}$ with cage C1-C1 (Figure 5a). $^1$H DOSY NMR analysis of a room-temperature solution containing one equivalent of both C1-C1 and IrCN in [D$_6$]DMSO revealed a significant reduction of the diffusion coefficient of IrCN ($D_{\text{IrCN}} = 1.9 \times 10^{-10}$ m$^2$ s$^{-1}$) after mixing with cage C1 to form the host–guest system C1-C1$\cdot$IrCN ($D_{\text{C1-C1-IrCN}} = 4.9 \times 6.0 \times 10^{-11}$ m$^2$ s$^{-1}$).

Figure 4. Molecular electrostatic potential [HF/6-31G(d)] map of C1 with front (left) and central (right) views. The most positive potential regions are shown in deep blue.

Figure 5 a), with a diffusion coefficient similar to that of host C1 ($D_{\text{C1}} = 5.3 \times 10^{-11}$ m$^2$ s$^{-1}$). In addition, the $^1$H NMR spectra of C1$\cdot$IrCN revealed the binding of IrCN with cage C1 proceeds with significant broadening of the resonances associated with IrCN (Figure S50), confirming its slow tumbling motion on the NMR timescale. A downfield shift and a significant broadening of the fluoride resonances of IrCN in C1$\cdot$IrCN were also observed by $^{19}$F NMR spectroscopy (Figure S52). In contrast, when the cationic complex [Ir(dfpppy)$_2$(dmbypy)$] PF$_6$ (dmby = 4,4'-dimethyl-2,2'-bipyridine; Irdmbypy) was mixed with C1 in [D$_6$]DMSO at room temperature, no binding affinity was observed by $^1$H, $^{19}$F and $^1$H DOSY NMR spectroscopy (Figure 5b and Figures S55–S57).

The potential host–guest complexes, C1$\cdot$IrCN and C1$\cdot$Irdmbypy, were optimised at the HF/6-31G(d) level of theory in order to gain insights into the nature of the host–guest interactions. For the optimised C1$\cdot$IrCN host–guest structure, the IrCN complex is located in the pocket of the cage (Figure 5a), in agreement with the electrostatic potential map predictions for the cage. Its optimised structure reveals weak interactions between the cyano ligand of IrCN with one of the Pd$^{	ext{II}}$ ions (3.2 Å) and several C–H units of C1. By contrast, any attempts to optimise a C1$\cdot$Irdmbypy host–guest structure did not lead to a stable complex. Indeed, both units fall apart during the optimisation process, stressing that no favourable interactions between Irdmbypy and C1 could be found, and that this holds both in the pocket and on the exterior surface of the cage.

The anionic complex IrCN exhibits a blue $^1$LC emission in DMSO, with two maxima at 458 and 483 nm and a shoulder at 515 nm (blue line in Figure 6a), a $\Phi_{PL}$ of 52\% and a $\tau_e$ of 2915 ns. The same vibronic emission profile, with $\lambda_{\text{max}}$ at 460 nm and 485 nm, was observed in CH$_2$Cl$_2$ but with a higher $\Phi_{PL}$ of 80\% and a longer $\tau_e$ of 3280 ns.$^{27}$ Emission titration of cage C1 (from 0 to 120 μm) into a 100 μm degassed solution of IrCN in DMSO at 298 K results in a gradual quenching of the blue emission of the donor IrCN together with a gradual enhancement of the emission of the red-emitting cage at 666 nm with an isosbestic point observed at 565 nm (Figure 6a). At a concentration of 110 μm of C1 (titration 8 in Figure 6a), the emission of the IrCN was completely quenched and only emiss-
sion from $\Delta$-C1 was observed. Upon photoexcitation of $\Delta$-C1$\supset$IrCN at 360 nm, energy transfer from the blue-emitting IrCN to the red-emitting $\Delta$-C1 is therefore promoted. This emission titration data could be fitted to a 1:1 binding model (Figure S79 in the Supporting Information) with a binding constant $K_b$ of $3.9 \times 10^6 \pm 0.2 \text{ M}^{-1}$ for the formation of $\Delta$-C1$\supset$IrCN from $\Delta$-C1 and IrCN. This association constant is in the range reported for encapsulation of anionic guests into polycationic host cages.\textsuperscript{38}

To study the energy transfer between anionic IrCN and $\Delta$-C1 in $\Delta$-C1$\supset$IrCN, Stern-Volmer quenching analysis was carried out (Table S4 in the Supporting Information).\textsuperscript{32} Based on a bimolecular quenching model, the reciprocal of the lifetime of IrCN is linearly correlated to the concentration of the quencher.
Δ-C1 (Figure 6b). From this analysis, we calculated a quenching rate constant ($k_q$) of $1.44 \times 10^8$ M$^{-1}$ s$^{-1}$ and a Stern–Volmer constant ($K_{SV}$) of $4.20 \times 10^4$ M$^{-1}$, suggesting that the energy-transfer/quenching process in Δ-C1 ⇌ IrCN is very efficient.$^{21a, 29}$ Förster energy transfer is unlikely to be an efficient pathway for energy transfer due to the poor spectral overlap between the absorption of Δ-C1 and the emission of IrCN (Figure S81), therefore, Dexter energy transfer is the likely mechanism for the energy transfer in system.$^{21a}$ The CIE (Commission Internationale de l’Éclairage) diagram shown in Figure 6c illustrates the change in the emission colours observed during the emission titration. Titration 5 (Figure 6a) shows CIE coordinates of (0.36, 0.30), which are close to coordinates of the pure white light ($\chi$: 0.31, $\gamma$: 0.33). By contrast, emission titrations of Δ-C1 (from 0 to 120 μM) into a 100 μM solution of the cationic Irmدبpy complex at 298 K in DMSO did not show any evidence of quenching of the emission of Irmدبpy to the Δ-C1 cage (Figure S90); rather a superposition of the emission spectra of the two species was observed. These findings are consistent with our computational investigation of Δ-C1 ⇌ Irmدبpy, which did not lead to a stable complex. Both emission studies and host–guest simulations demonstrate that high binding affinity between the host and the guest is required to promote energy transfer.

**Conclusion**

Emissive and homochiral supramolecular Pd$_4$L$_4$ cages have been prepared by self-assembly between Pd$^{2+}$ ions and two families of enantiopure metallo ligands, $\Delta$- and $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$, and $\Lambda$- and $\Delta$-[Ir(dfmesppy)$_2$(qpy)]BF$_4$. The polycationic Cage $\Delta$-C1 selectively encapsulates anionic compounds. Strong binding and efficient energy transfer ($k_e = 1.44 \times 10^8$ M$^{-1}$ s$^{-1}$) between the anionic blue-emitting complex [Ir(dFppy)$_3$(CN)$_4$]$^-$ and the red-emitting cage $\Delta$-C1 has been observed. Examples of efficient energy transfer between luminescent guests and photостatic cages are rare. These cages are promising candidates as chiral photostatic containers capable of absorbing photons and transferring light energy to or from encapsulated guest acceptors. These assemblies open up the possibility of promoting stereoselective photocatalytic transformations, examples of which at present are exceedingly rare. On the materials front, the host–guest assemblies can serve as stable white-light emitting materials for solution-processed electroluminescent devices.

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**Conflict of interest**

The authors declare no conflict of interest.

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[32] The emission lifetimes of IrCN (monitored at $\lambda_{\text{em}} = 480$ nm in degassed DMSO, $\lambda_{\text{exc}} = 378$ nm) after addition of increasing amount of quencher $\Delta$-C1 were recorded. The concentration of IrCN was maintained constant at 1.00 mM, whereas the concentration of $\Delta$-C1 varied from 0 to 120 $\mu$M.


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