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(dFppy)$_2$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, 7] 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 frameworks,[10] as well as those that employ ligand scaffolds decorated with photoactive units, including luminescent metal complexes.[11] Photofactive 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 metalloacryocycles, 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 $[\text{IrPd}]^+-$ that are able to encapsulate large anionic guests, including a blue-emitting NBu$_4$[Ir(dFmesppy)$_2$(CN)$_2$] complex. Controlled photoinduced energy transfer from the donor anionic iridium complex guest to the acceptor iridium metalloligands in the $[\text{IrPd}]^+$-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 III metalloligands of the form $[\text{Ir(CN)}_2(qpy)]$BF$_4$ (where C=NN is mesrapy = 2-phenyl-4-mesitylpyridinato and dFmesppy = 2-(4,6-difluorophenyl)-4-mesitylpyridinato, and qpy is 4,4′,2′,2″-tetrapyridine) with Pd$^{2+}$ ions through N$_{py}$–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 metalloligands $\Lambda$- and $\Delta$-[Ir(dFmesppy)$_2$(qpy)]BF$_4$ ($\Lambda$-1 and $\Delta$-1) and $\Lambda$- and $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$ ($\Lambda$-2 and $\Delta$-2) by using L- and D-serine as chiral auxiliaries, following the protocol illustrated in Scheme S1 in the Supporting Information. The absolute configuration for each of the enantiopure iridium dimers $\Lambda$, $\Delta$, $\Delta$-D1, $\Delta$, $\Delta$-D2 and $\Delta$, $\Delta$-D2 (Scheme S1) has been unambiguously determined by X-ray crystallography (Figure S59 in the Supporting Information) and used to ascertain the abso-
olute configurations of the enantiomers Λ-1, Δ-1, Λ-2 and Δ-2. 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. 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.

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 [D6]dimethyl sulfoxide ([D6]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. As expected, the proton resonances associated with the proton in ortho-position to the distal nitrogen of the pyridine moiety (H^t, H^h, 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 [D6]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 [D6]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 (r_h) 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 fluorine resonances associated with the dfppy ligand shifted downfield from −106.33 ppm and −108.52 ppm to −106.09 ppm and −108.31 ppm in [D6]DMSO (Figure 1f and Figure S29 in the Supporting Information). As the two doublets associated with the fluorine 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 1 is maintained also in the cage. Furthermore, no differences in the 1H, 1D 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]16 and [2Pd4][BF4]10, respectively, by HR-ESI-MS spectrometry, showing isotopically resolved peaks for [C1-(BF4)]n+ (n = 4–8). For example, each of the ESI-MS spectra of rac-1, Λ-C1 and Δ-C1 reveal peaks at m/z = 2635.5650, 2067.2391, 1707.8564, 1451.5934 and 1259.2675, which are assigned to [C1-(BF4)]m+n, [C1-(BF4)]2+ and [C1-(BF4)]3+ respectively (Figure S33 in the Supporting Information). Similarly, the charge states [C2-(BF4)]n+ (n = 5–8), were likewise observed in the MS spectra of each of rac-1, Λ-C2 and Δ-C2 at m/z = 2067.2391, 1707.8640, 1451.5934 and 1259.2765, respectively (Figure S38). The isolotopically 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 ([L]Pd4) is rare as this relative stoichiometry is only possible when the angle between the coordinating 4-pyridyl units is inferior to 90°.

The CD spectra of Λ-C1, Λ-C1, Δ-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 Λ-1 and 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, 2) well-defined mixing, or 3) self-sorting. ESI-MS of a [D6]DMSO solution containing either Λ-C1 or Λ-C1 with [Pd(NCMe)4][BF4]2 stirred at 85 °C for 12 h showed a statistical mixture of cage species of composition [(Λ-C1/Δ-C1)1/Δ-2]8Pd4 (n + m = 8), from Λ-1/Λ-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 preformed 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, Λ-1, and Δ-2 (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)](BF4)7+ closely match the simulated spectra. When homochiral cages of the same stereochemistry, Λ-C1 and Δ-C2, are mixed at 85 °C in [D6]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 1 a), 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. [30] Of potential structures of [L 8Pd4] cages, this particular arrangement is rare, only five examples of assemblies with this structural motif were reported to date. [30, 31] 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 ‘H NMR DOSY analysis (r_h = 19.8 Å). The cage structure can be seen to be approximately C4 symmetric.

Figure 2. a) Schematic representation of the exchange experiments carried out by mixing Δ-C1 or Δ-C1 (ppy ligand in red) with Δ-C2 (dfppy ligand in green). The mesityl substituents have been omitted for clarity. b) Illustration of the formation of statistical mixture of cage species of compositions [[(L−/D−)1]((L−/D−)2)Pd4[(BF4)4] (n + m = 8, from Δ−/Δ− = 7:1 to Δ−/Δ− = 1:7). c) ESI mass spectra of the 7+ charge states [(11n2m)(BF4)7]+= (n + m = 8, from 1:2 = 7:1 to 1:2 = 1:7) of Δ−/Δ−-1BF4+−/Δ−/Δ−-2BF4+ heated at 85°C for 12 h. In red are illustrated the simulated 7+ charge states of the heteroleptic cages. The same statistical distributions are observed for the 8+, 6+ and 5+ charge states.
about the Pd₄ 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 CH₂Cl₂, 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 Δ-1/Δ-1, Δ-2/Δ-2, Δ-C1/Δ-C1, and Δ-C2/Δ-C2 (Table 1). The emission profiles of both families of cages C1 and C2 in CH₂Cl₂ are red-shifted, respectively, at 655 nm and 651 nm, relative to those of the corresponding metalloligands 1 (λmax = 620 nm) and 2 (λmax = 527 nm). Their photoluminescence quantum yields, φPL, and emission lifetimes, τe, are correspondingly lower and shorter, respectively (e.g., rac-C1: φPL = 5%, τe = 202 ns; rac-2: φPL = 10%, τe = 825 ns), compared to those of 1 and 2 (e.g., Δ-C1: φPL = 14%, τe = 300 ns; Δ-C2: φPL = 34%, τe = 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 (kₑ, e.g., 2.47 × 10⁷ s⁻¹ for rac-C1 and 1.21 × 10⁷ s⁻¹ for rac-2), and slightly larger non-radiative rate constants (knr, e.g., 4.66 × 10⁷ s⁻¹ for rac-C1 and 1.09 × 10⁷ s⁻¹ for rac-2), relative to the corresponding metalloligands (e.g., rac-C1: kₑ = 4.67 × 10⁶ s⁻¹, knr = 2.45 × 10⁷ s⁻¹; rac-2: kₑ = 3.40 × 10⁶ s⁻¹, knr = 6.60 × 10⁷ s⁻¹). The presence of the electron-withdrawing fluorine atoms in C2 induces a blue-shift in the emission relative to the fluorine-free cage C1. Similarly 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 CH₂Cl₂ 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 Pd⁴⁺ to the iridium complex. By acting as a Lewis acid, the Pd⁴⁺ ions lower the LUMO levels of complexes 1 and 2 located on the qpy ligand, giving rise to smaller optical gaps.

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

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<tr>
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<th>1</th>
<th>C1</th>
<th>2</th>
<th>C2</th>
<th>1</th>
<th>C1</th>
<th>2</th>
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<td>14</td>
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<td>300</td>
<td>444</td>
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<td>28.7</td>
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<td>1044</td>
<td>(0.88)</td>
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<td>564</td>
<td>5</td>
<td>10.9</td>
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<td>49</td>
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<td>270</td>
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<tr>
<td>τe [ns]</td>
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<td>564</td>
<td>10</td>
<td>9.6</td>
<td>202</td>
<td>47</td>
<td>(0.12)</td>
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<td>563</td>
<td>13</td>
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<td>299</td>
<td>343</td>
<td>(0.12)</td>
<td>1044</td>
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<td>kₑ [%]</td>
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<td>518</td>
<td>35</td>
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<td>16.3</td>
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<td>kₑ [ns]</td>
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<td>11</td>
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<td>824</td>
<td>11</td>
<td>(0.13)</td>
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</table>

[a] Measurements in degassed CH₂Cl₂ at 298 K (λmax = 360 nm). [b] Thin films formed by spin-coating on a pristine quartz substrate. [c] φPL measurements were carried out in degassed CH₂Cl₂ under nitrogen (λmax = 360 nm) using quinine sulfate as the external reference (φPL = 54.6% in 0.5 w% H₂SO₄ at 298 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 (λmax = 378 nm).

Figure 3. Normalised emission spectra of: a) Δ-1 and Δ-1 and 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 CH₂Cl₂ solution of Δ-1 and Δ-2; Solid orange lines: PMMA-doped film with 5 wt% of cages Δ-C1 and Δ-C2 spin-coated on quartz substrates; Solid red lines: deaerated CH₂Cl₂ solution of Δ-C1 and Δ-C2.

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...
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 S65 in the Supporting Information), with enhanced $\Phi_R$ and longer multi-exponential $\tau_e$ (as representative examples: rac-1: $\Phi_R = 28\%$, $\tau_e = 344$, 1045 ns, rac-2: $\Phi_R = 41\%$, $\tau_e = 48$, 259, 1195 ns, rac-C1: $\Phi_R = 11\%$, $\tau_e = 49$, 270, 715 ns, and rac-C2: $\Phi_R = 17\%$, $\tau_e = 13$, 412, 1125 ns) relative to the photophysical behaviour in CH$_2$Cl$_2$ (Table 1).

The calculated cage structures, rac-C1, $\Lambda$-C1, $\Delta$-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$^{III}$ complex, [Ir(dp-py)$_2$(bpy)]Cl (bpy is 2,2'-bipyridine), within a hexameric resorcinarene-nanoporous-caged-bonded capsule and observed that the capsule effectively hampers the non-radiative decay thereby enhancing both the $\Phi_R$ and the $\tau_e$ of the encapsulated iridium guest. We targeted the encapsulation of blue-emitting Ir$^{III}$ guests within the confined cavity of our red-emitting cage $\Delta$-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 acceptor as a function of the choice of medium or concentration.

With guests within the confined cavity of our red-emitting cage $\Delta$-C1 and the rigidification conferred by the PMMA host, the emission of white light can also be achieved.$^{[21a, 35]}$ In the acceptor as a function of the choice of medium or concentration.

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$^{[21a, 35]}$ In the acceptor as a function of the choice of medium or concentration. The potential host–guest complexes, $\Delta$-C1–IrCN and $\Delta$-C1–Irdmppy, 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 $\Delta$-C1–IrCN host–guest structure, the IrCN complex is located in the pocket of the cage (Figure 5 a), 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$^{II}$ ions (3.2 Å) and several C–H units of $\Delta$-C1. By contrast, any attempts to optimise a $\Delta$-C1–Irdmppy 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 Irdmppy and $\Delta$-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 3LC emission in DMSO, with two maxima at 458 and 483 nm and a shoulder at 515 nm (blue line in Figure 6a), a $\Phi_R$ 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 $\Phi_R$ of 80% and a longer $\tau_e$ of 3280 ns.$^{[37]}$ Emission titration of cage $\Delta$-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 $\Delta$-C1 (titration 8 in Figure 6a), the emission of the IrCN was completely quenched and only emiss-
Upon photoexcitation of D-C1/C27IrCN at 360 nm, energy transfer from the blue-emitting IrCN to the red-emitting D-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 \( K_b = 3.9 \times 10^6 M^{-1} \) for the formation of D-C1\( \supset \)IrCN from D-C1 and IrCN. This association constant is in the range reported for encapsulation of anionic guests into polycationic host cages.\(^{38}\)

To study the energy transfer between anionic IrCN and D-C1 in D-C1\( \supset \)IrCN, Stern–Volmer quenching analysis was carried out (Table S4 in the Supporting Information).\(^{32}\) 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 (kₚ) of 1.44×10⁹ M⁻¹ s⁻¹ and a Stern–Volmer constant (Kₛᵥ) of 4.20×10⁴ M⁻¹, suggesting that the energy-transfer/quenching process in Δ-C1·IrCN is very efficient.²¹a,²² 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’Eclairage) diagram shown in Figure 6a shows CIE coordinates of (0.36, 0.30), which are close to coordinates of the pure white light (x: 0.31; y: 0.33). By contrast, emission titrations of Δ-C1 (from 0 to 120 µM) into a 100 µM solution of the cationic Ir(dFppy)₂(qpy)BF₄ complex at 298 K in DMSO did not show any evidence of quenching of the emission of Ir(dFppy)₂(qpy)BF₄, 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 Pd₄L₄ cages have been self-assembled by between Pd²⁺ ions and two families of enantiopure metalloligands, Δ- and Δ-[Ir(mesppy)₂(qpy)]BF₄ and Δ- and Δ-[Ir(dFmesppy)₂(qpy)]BF₄. The polycationic cage Δ-C1 selectively encapsulates anionic compounds. Strong binding and efficient energy transfer (kₚ = 1.44×10⁹ M⁻¹ s⁻¹) between the anionic blue-emitting complex [Ir(dFppy)₂(CN)]⁻ and the red-emitting cage Δ-C1 has been observed. Examples of efficient energy transfer between luminous guest and photoactive cages are rare. These cages are promising candidates as chiral photoactive 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.

**Keywords:** cage compounds · iridium · palladium · photochemistry · self-assembly

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[32] The emission lifetimes of IrCN (monitored at \( \lambda_{em} = 480 \) nm in degassed DMSO, \( \lambda_{exc} = 378 \) nm) after addition of increasing amount of quencher \( \Delta C1 \) were recorded. The concentration of IrCN was maintained constant at 100 \( \mu \)M, whereas the concentration of \( \Delta C1 \) varied from 0 to 120 \( \mu \)M.

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Homochiral Emissive $\Lambda_8^+$ and $\Delta_8^+ \text{[Ir}_8\text{Pd}_4\text{]}^{16+}$ Supramolecular Cages

Caged in: Emissive and homochiral supramolecular Pd$_4$L$_8$ cages have been prepared by self-assembly between Pd$^{2+}$ ions and two families of enantiopure metalloligands, $\Lambda$- and $\Delta$-[Ir(mesppy)$_2$(qpy)]BF$_4$ and $\Lambda$- and $\Delta$-[Ir(dFmesppy)$_2$(qpy)]BF$_4$ (mesppy = 2-phenyl-4-mesitylpyridinato and dFmesppy = 2-(4,6-difluorophenyl)-4-mesitylpyridinato, and qpy is 4,4':2',4'':4'':2''-quaterpyridine). These polycationic cages selectively encapsulate anionic compounds. These cages are promising candidates as chiral photoactive containers capable of absorbing photons and transferring light energy to or from encapsulated guest acceptors.