Photoinduced Energy- and Electron- Transfer Between a Photoactive Cage Based on a Thermally Activate Delayed Fluorescence Ligand and Encapsulated Fluorescent Dyes

Diego Rota Martir, Antonella Pizzolante, Daniel Escudero, Denis Jacquemin,* Stuart L. Warriner, and Eli Zysman-Colman*

Abstract. The vast majority of polyhedral assemblies prepared by combining organic bent ligands and “photophysically innocent” palladium(II) metal ions are non-emissive. Here we report a simple strategy to switch on the luminescence properties of a polyhedral assembly by combining a Thermally Activated Delayed Fluorescence (TADF) organic emitter based on a dipyridylcarbazole ligand scaffold with Pd$^{2+}$ ions, giving rise to a luminescent Pd$_6$L$_{12}$ molecular cube. The assembly is capable of encapsulating within its cavity up to three molecules per cage of Fluorescein, in its neutral lactone form, and up to two molecules of Rose Bengal in its dianionic quinoidal form. Photoinduced electron Transfer (PeT) between the photoactive cage and the encapsulated Fluorescein and Photoinduced Energy Transfer (PET) from the cage to encapsulated Rose Bengal have been observed by steady-state and time-resolved emission spectroscopy.

Introduction.
Coordination cages, formed through the self-assembly of arrays of metal ions and bridging ligands, have been one of the main areas of interest in supramolecular chemistry during the last two decades.\textsuperscript{1-4} More recently, the focus has turned towards the functional properties of such cages.\textsuperscript{5-8} Small guest molecules have been shown to be sequestered inside the cavities of these cages and their host-guest interactions have been exploited in diverse applications such as in sensing,\textsuperscript{9} for gas storage and purification,\textsuperscript{10} and for catalysis.\textsuperscript{11-12}

In recent years, there has been an increasing exploration of the properties of photoactive supramolecular cages in which at least one component, either the metal ion\textsuperscript{13-15} or the bridging ligand,\textsuperscript{16-18} is luminescent. Such cages provide both a high concentration of luminophoric units in known relative orientations and dispositions, and restricted shape and size to govern the host-guest interactions. There are only a few examples of photoactive cages based on palladium(II) metal ions.\textsuperscript{19-21} More generally, incorporation of fluorescent emitters such as porphyrins,\textsuperscript{22} BODIPYs,\textsuperscript{23} and π-conjugated organic compounds,\textsuperscript{16-17} or phosphorescent complexes such as iridium(III),\textsuperscript{24-26} ruthenium(II),\textsuperscript{27-29} and platinum(II)\textsuperscript{30-31} metal complexes either into the ligand backbone or as coordinating vertices of the cage have all been previously explored. The luminescent properties of these assemblies have been primarily exploited for small molecules sensing,\textsuperscript{23,32-33} biological imaging,\textsuperscript{34} and photoresponsive guest uptake/release.\textsuperscript{35-36} However, the vast majority of cage structures composed of organic bridging ligands coordinated to Pd\textsuperscript{II} or Pr\textsuperscript{III} are non-emissive. For instance, the self-assembly of 3,6-bis(pyridin-4-ylethynyl)-carbazole ligand, L, with Pd\textsuperscript{II} ions gave rise to non-emissive cages of compositions [Pd\textsubscript{2}L\textsubscript{4}]\textsuperscript{4+} and [Pd\textsubscript{4}L\textsubscript{8}]\textsuperscript{8+}.\textsuperscript{37}

Depending on the nature of the emission, luminescence emanating from a single species can be broadly classified into three main categories: fluorescence, phosphorescence and thermally activated delayed fluorescence (TADF). Among these three mechanisms, purely organic TADF compounds have recently attracted attention as sustainable, inexpensive, and
efficient emitters in Organic Light-Emitting Devices (OLEDs).\textsuperscript{38-40} In the OLED, similar to phosphorescent organometallic emitters, TADF compounds can harvest both singlet and triplet excitons for light emission via a thermal upconversion of the triplet excitons to singlet excitons mediated by a reverse intersystem crossing (RISC). TADF relies on a small (< 0.2 eV) singlet-triplet energy gap, \( \Delta E_{ST} \), defined as the difference in energy between the lowest energy triplet state (\( T_1 \)) and the lowest energy singlet state (\( S_1 \)). These emitters are generally based on donor-acceptor structures in which the donor moieties are in a highly twisted conformation relative to the acceptors plane, resulting in reduced exchange integral between the HOMO and LUMO and therefore small \( \Delta E_{ST} \).\textsuperscript{41-42}

Herein we report the first example of self-assembly involving an organic TADF ligand, \textbf{4PyCzBP}, with \( \text{Pd}^{2+} \) ions, which gives rise to a luminescent cage of composition [(4PyCzBP)\(_{12}\)Pd\(_6\)](BF\(_4\))\(_{12}\). \textbf{4PyCzBP-Pd} (Figure 1). \textbf{4PyCzBP} itself is based on a 3,6-di(pyridin-4-yl)-9\( H \)-carbazole donor moiety and ligand scaffold functionalised with benzophenone as the acceptor unit. The photoactive cage \textbf{4PyCzBP-Pd} is capable of encapsulating two common xanthene-based dyes, Fluorescein, in its neutral lactone form, and Rose Bengal, in its dianionic quinoidal form. Photoinduced electron Transfer (PeT) between the photoactive cage and the encapsulated Fluorescein, and Photoinduced Energy Transfer (PET) from the cage to the encapsulated Rose Bengal have been observed by steady-state and time-resolved emission spectroscopy.

\textbf{Results and discussion.}

We recently reported the syntheses and the photophysical properties of \textbf{4PyCzBP} and \textbf{3PyCzBP } (4-(3,6-di(pyridin-3,4-yl)-9\( H \)-carbazol-9-yl)phenyl)(phenyl) methanone), the former of which was used to make two component supramolecular gels.\textsuperscript{43} The TADF nature of
4PyCzBP and 3PyCzBP was confirmed through a combination of steady-state and time-resolved emission spectroscopy measurements.\textsuperscript{43-44}

When 4PyCzBP and [Pd(NCMe)\textsubscript{4}](BF\textsubscript{4})\textsubscript{2} were heated in a 2:1 ratio in DMSO-\textit{d}\textsubscript{6} at 85°C for 12 h the proton resonances associated with 4PyCzBP broadened and shifted downfield (Figure 1a). The broad \textsuperscript{1}H NMR signals are indicative of the formation of a large structure, the motion of which being very slow on the NMR time scale (Figure 1b). Evidence for the formation of a single species was confirmed by \textsuperscript{1}H DOSY NMR spectroscopy where the diffusion coefficient, D, in DMSO-\textit{d}\textsubscript{6} was found to be 9.1 × 10\textsuperscript{-11} m\textsuperscript{2}/s. The magnitude of D correlates to the presence of a larger structure than the 4PyCzBP ligand, which shows a diffusion coefficient of 1.7 × 10\textsuperscript{10} m\textsuperscript{2}/s (Figure 1c).

The calculated hydrodynamic radius (r\textsubscript{s}) of the cage is 12.1 Å (Table S1). The compositions of the assembly 4PyCzBP-Pd has been unequivocally established to be [(4PyCzBP)_\textsubscript{12}Pd\textsubscript{6}(BF\textsubscript{4})\textsubscript{12}] by HR-ESI-MS spectrometry, showing isotopically resolved peaks for [(4PyCzBP-Pd)-(BF\textsubscript{4})\textsubscript{n}]\textsuperscript{\textsuperscript{+} n} (n = 5 - 8) (Figures 2 and S5–S8). The angle between the two 4-pyridyl coordinating motifs in 4PyCzBP is 93.5°, which is ideal for the formation of a Pd\textsubscript{6}L\textsubscript{12} cage (Figure S2). Indeed, Fujita \textit{et al.} previously reported that the formation of Pd\textsubscript{6}L\textsubscript{12} assemblies is only possible when the pyridine-based ligands have angles of approximately 90°.\textsuperscript{45-46} Under similar reaction conditions, the self-assembly of 3PyCzBP with [Pd(NCMe)\textsubscript{4}](BF\textsubscript{4})\textsubscript{2} produced multiple products including the assembly of composition [(3PyCzBP)\textsubscript{4}Pd\textsubscript{2}(BF\textsubscript{4})\textsubscript{4}], which was detected by ESI-HR-MS spectrometry (Figures S9-S12).
Figure 1. a) Self-assembly between 4PyCzBP, and Pd$^{2+}$ ions yielding cage 4pyCzBP-Pd. The geometries of 4pyCzBP-Pd has been determined in vacuo with DFT. b) $^1$H NMR of 4PyCzBP, in red and 4PyCzBP-Pd, in blue. c) $^1$H DOSY NMR of 4PyCzBP, in red and 4PyCzBP-Pd, in blue. The NMR spectra were collected in DMSO-$d_6$ at 298 K.
Figure 2. ESI-MS spectra of a DMSO solution containing cage 4PyCzBP-Pd. Inserts show the measured (in blue) and simulated (in red) isotope patterns for the 7+ (left) and 6+ (right) charge states. Additional data is given in the supporting information.

The structures of 4PyCzBP-Pd was modelled at the B3LYP-D3BJ/6-31G(d)/LanL2DZ level of theory (Figure 1a). The computed structure of Pd₆L₁₂ cube places the six Pd ions at the center of each face of the cube in a structure close to D₂ point group. Similar cubic assemblies of compositions M₆L₁₂ and M₁₂L₁₂ have been previously reported.⁴⁵,⁴⁷-⁴⁹ The dimension of the optimized structure of 4PyCzBP-Pd is ca. 4 x 4 x 4 nm, corresponding to a volume of ca. 6400 Å³. The diameter of 4PyCzBP-Pd, based on the Pd⋯Pd distance, is ca. 21.6 Å, whereas its diameter around the macrocyclic core across long axes of the structure is 47.8 Å (Figure S2). The dimensions of 4PyCzBP-Pd are comparable to those of the Pd₆L₁₂ nanocube of Fujita et al.,⁴⁵ and of the Cu₁₂L₁₂ truncated octahedron of Yaghi et al.,⁴⁷ which showed, respectively, diameters of 26.0 Å and 27.0 Å. The nanostructure of the cage was probed by Transmission Electron Microscopy (TEM) measurements upon deposition of a 1 x 10⁻⁶ M DCM solution of 4PyCzBP-Pd onto carbon-coated copper grids (Figure 3). The size of the nanostructures range between 4.5 – 5.0 nm and matches with the diameter of 4.78 nm obtained for the calculated structure (Figure S2).
Figure 3. TEM images of the nanostructures of 4PyCzBP-Pd.

The emission profile of 4PyCzBP-Pd in DCM (Figure 4a) is broader and red-shifted at 555 nm with a lower photoluminescence quantum yield, $\Phi_{PL}$, of 4% compared to that of 4PyCzBP ($\lambda_{max} = 477$ nm, $\Phi_{PL} = 52\%$). Similarly, the emission of 4PyCzBP-Pd in PMMA-doped film is red-shifted at 553 nm with a $\Phi_{PL}$ of 5% compared to the emission observed for 4PyCzBP ($\lambda_{max} = 447$ nm, $\Phi_{PL} = 21\%$). The emission decay profile of 4PyCzBP and 4PyCzBP-Pd collected in DCM solution and as PMMA-doped films at 298 K are illustrated in Figure 4b. As previously reported, the transient PL decay in DCM of 4PyCzBP is triexponential showing a short prompt fluorescence, $\tau_p$, of 15.1 ns and a longer two-component delayed fluorescence, $\tau_d$, of 0.69 $\mu$s and 9.80 $\mu$s. Similarly, in the PMMA doped film 4PyCzBP exhibits a $\tau_p$ of 33.5 ns and $\tau_d$ of 0.61 $\mu$s and 6.32 $\mu$s. The cage 4PyCzBP-Pd does not exhibit a delayed fluorescence either in DCM solution or as a PMMA-doped film. 4PyCzBP-Pd exhibits a bi-exponential fluorescence decay of 3 ns and 30 ns in DCM and 27 ns and 54 ns in the PMMA-doped film (Table S3). Therefore, 4PyCzBP-Pd does not emit via a TADF mechanism but only from singlet excited states. DFT calculations reveal that the HOMO of 4PyCzBP-Pd is mainly distributed over the twelve dipyridylcarbazolyl groups, as in the isolated dye (Figure 4c). However, the LUMO of 4PyCzBP-Pd is not localized on the benzophenone moiety as observed for the 4PyCzBP, but it is primarily distributed on the six palladium atoms and their vicinal pyridyl units (Figure 4d). As a result, the palladium ions act as electron acceptor units and quench the TADF nature of the 4PyCzBP chromophores assembled within the structure of 4PyCzBP-Pd.
Figure 4. a) Normalized emission spectra of 4PyCzBP collected in deaerated DCM (solid light-blue line) and as a 10 wt% PMMA-film (solid blue-line) and of 4PyCzBP-Pd collected in deaerated DCM (dotted red line) and as a 10 wt% PMMA-film (dotted orange line at 298 K. b) Emission decays of 4PyCzBP in deaerated DCM (light-blue line) and in 10 wt% PMMA-film (blue-line) and of 4PyCzBP-Pd collected in deaerated DCM (red line) and as a 10 wt% PMMA-film (orange line) at 298 K. DFT (CAM-B3LYP) calculated electron density distribution of c) HOMO level and d) LUMO level of 4PyCzBP-Pd. Note that the HOMO and LUMO are each degenerated due to the high symmetry of the cage, and that only one representative MO is shown.

Xanthene dyes are widely used as pH sensor as they exist as colored quinone dianions (open form) at high pH (typically pH = 8 – 12) and as colorless lactones (closed form) at pH lower than 7. Fujita et al. have recently demonstrated that the structural conversion of phthalein dyes can also be promoted through their encapsulation into the restricted cavity of cages, with
the spatial constraints pushing the equilibrium toward the formation of either the quinone dianions open form or the lactone closed form.\textsuperscript{52}

In order to better understand the interplay between photoactive hosts and guests, two common xanthene dyes, fluorescein (F) and rose bengal (RB), were employed as guests. Notably, Ward \textit{et al.} have recently demonstrated the encapsulation of F, Rhodamine and two other coumarin-based dyes into supramolecular polyhedral compartments of a crystalline zeolite framework, and have observed that the polyhedral cage prevented the dye monomers from aggregating.\textsuperscript{53} Therefore, even at very high concentration, the emission of the encapsulated dyes is consistent with the presence of isolated monomeric species without any evidence of self-quenching.
Figure 5. a) Representation of encapsulation in DMSO-$d_6$ at room temperature of two molecules of RB within the cavity of 4PyCzBP-Pd; including (top) the $^1$H DOSY NMR spectra of RB (in red), 4PyCzBP-Pd (in purple) and a 2:1 solution of RB and 4PyCzBP-Pd (4PyCzBP-Pd⊃(RB)$_x$, (in blue). b) $^1$H DOSY NMR spectra of F (in red), 4PyCzBP-Pd (in purple) and a 2:1 solution of F and 4PyCzBP-Pd (4PyCzBP-Pd⊃(F)$_x$, (in blue). The B3LYP-D3BJ/6-31G(d)/LANL2DZ optimized host-guest structure 4PyCzBP-Pd⊃(RB)$_2$ is shown.

The calculated internal volume of 4PyCzBP-Pd is suited to accommodate two guest RB molecules (Figure 5). The binding of F and RB into the cavity of 4PyCzBP-Pd was first examined. $^1$H DOSY NMR analysis of a room temperature DMSO-$d_6$ solution containing one equivalent of the cage and two equivalents of either F and RB revealed a significant reduction of the diffusion coefficients of the guest molecules [$D_{(F)} = 1.9 \times 10^{-10} \text{m}^2/\text{s}, D_{(RB)} = 1.8 \times 10^{-10} \text{m}^2/\text{s}$] after mixing with 4PyCzBP-Pd to form the host-guest assembly 4PyCzBP-Pd⊃(F)$_x$ and 4PyCzBP-Pd⊃(RB)$_x$ [D$_{(4PyCzBP-Pd⊃(F)_x)}$ = 9.7 $\times$ 10$^{-11}$ m$^2$/s, D$_{(4PyCzBP-Pd⊃(RB)_x)}$ = 9.4 $\times$ 10$^{-11}$ m$^2$/s, Figure 5], with diffusion coefficients similar to that of 4PyCzBP-Pd [D$_{(4PyCzBP-Pd)}$ = 9.1 $\times$ 10$^{-11}$ m$^2$/s]. The $^1$H NMR spectra of 4PyCzBP-Pd⊃(F)$_x$ and 4PyCzBP-Pd⊃(RB)$_x$ showed that the resonances associated with the encapsulated dyes were significantly broadened and shifted downfield (Figures S29-S30). Electrospray ionization mass spectrometry (ESI-HRMS) experiments showed the presence of 4PyCzBP-Pd⊃(F)$_{1,3}$ where one, two and three molecules of the neutral dye were encapsulated within the cavity of the cage (Figure S13-S21). The encapsulation of one and two molecules of RB into 4PyCzBP-Pd (4PyCzBP-Pd⊃(RB)$_{1,2}$) was also detected by ESI-MS. However, RB is encapsulated as its quinoid dianionic form (Figure S22-S26) and, as it is larger than F, the encapsulation of a third molecule of RB within the cavity of 4PyCzBP-Pd is sterically unfeasible. In order to ascertain whether 4PyCzBP-Pd demonstrated selectivity for the encapsulation of F or RB, we collected the ESI-MS spectra of...
a DMSO-$d_6$ mixture containing one equivalent of $4\text{PyCzBP-Pd}$ and two equivalents of both guests. The ESI-MS spectra revealed a complicated mixture of host-guest systems of composition $4\text{PyCzBP-Pd}⊃(\text{F})_{1,2}$, $4\text{PyCzBP-Pd}⊃(\text{RB})_{1,2}$, $4\text{PyCzBP-Pd}⊃(\text{F})_1(\text{RB})_1$ and $4\text{PyCzBP-Pd}⊃(\text{F})_2(\text{RB})_1$ (Figure S27-S28).

Having confirmed that the cavity of $4\text{PyCzBP-Pd}$ can accommodate F and RB, we turned our attention to the impact of encapsulation on the photophysical properties of the cage. UV-Visible spectra of F and RB in DMSO show, respectively, the yellow-green and pink colors characteristic of their dianion quinoid species.\textsuperscript{54-56} A solution of $4\text{PyCzBP-Pd}$ was added dropwise into the solutions of F and RB. Upon addition of $4\text{PyCzBP-Pd}$ (from 0.1 to 3.0 equiv.) to the solution of F, the absorption band of F with a maximum at 522 nm, characteristic of its open quinoid form, significantly decreased. When three equivalents of $4\text{PyCzBP-Pd}$ were added, the yellow-green solution became colorless (Figure 6a). Therefore, the restricted cavity of $4\text{PyCzBP-Pd}$ promotes the lactonization of F, which corroborates the presence of neutral fluorescein guest molecules by ESI-MS. Such behavior is analogous to that observed by Fujita et al.\textsuperscript{52} who investigated the encapsulation of phthalein dyes within a tetrahedral cage. By contrast, when $4\text{PyCzBP-Pd}$ (from 0.1 to 3.0 equiv.) was gradually added into a solution of RB, no change in intensity of the characteristic absorption band of this dye at 567 nm was observed (Figure 6b), implying that this dye remains in its open dianion quinoid form upon encapsulation.
Figure 6. a) UV-Vis titration of F (50 μM) after gradual addition of 4PyCzBP-Pd (from 0 to 150 μM) in DMSO. b) UV-Vis titration of RB (50 μM) after gradual addition of 4PyCzBP-Pd (from 0 to 150 μM) in DMSO. Photographs of solutions after addition of 4PyCzBP-Pd (left) and initial solutions of dyes (right) are shown in the insets of each figure.

Emission titration experiments of 4PyCzBP-Pd (from 0 to 150 μM) into a 50 μM degassed DMSO solution of either F or RB at 298 K were also carried out. When 4PyCzBP-Pd was gradually added into the solution of F, a gradual quenching of the dye emission at 545 nm was observed, regardless of whether photoexcitation occurred at 360 nm (Figure S37), where both F and 4PyCzBP-Pd both absorb, or at 480 nm (Figure S38), where only F absorbs. In both cases the emission of 4PyCzBP-Pd was completely quenched. The quenching of the emission of F is attributed to its structural conversion toward the closed lactone form upon encapsulation.\textsuperscript{52,55} However, the efficient quenching of the emission of 4PyCzBP-Pd is ascribed to the formation of a non-emissive charge-separated state following PeT in 4PyCzBP-Pd⊃(F)\textsubscript{1,3}. The emission titration data was fitted to a 1:2 sequential binding model (Figure S39) with binding constant of $K_b^*$ of $7.8 \times 10^3 \pm 0.1 \text{ M}^{-1}$ for the encapsulation of the first molecule of F, and $K_b^*$ of $9.1 \times 10^6 \pm 0.5 \text{ M}^{-1}$ for the encapsulation of the second and third guest molecule within the cavity of 4PyCzBP-Pd. Fujita \textit{et al.}\textsuperscript{52} obtained a similar binding constant, $K_b$, of
approximately $10^7$ M$^{-1}$ for the encapsulation of one molecule of F into the cavity of their tetrahedral cage.

The redox properties of 4PyCzBP-Pd and F were investigated by Cyclic Voltammetry (CV) and Differential Pulse Voltammetry (DPV) analyses (Figures S33 and S34), and combined with optical data were used to estimate the energetics of the PeT processes in 4PyCzBP-Pd⊃F (Figure S35 and Table S4). The oxidation and reduction potentials of 4PyCzBP-Pd are, respectively, at 1.76 and -1.63 V, whereas for F the oxidation potential is less positive at 0.67 V and the reduction potential is less negative at -1.08 V (Table S4). Therefore, the ground state electrochemical data suggests that for 4PyCzBP-Pd⊃F, F is a better electron donor than 4PyCzBP-Pd due to its higher ionization potential while 4PyCzBP-Pd acts as the electron acceptor moiety.$^{57}$ The free energy ($\Delta G_{cs}$) associated with the formation of the charge-separated state $[\text{F}]^+ \cdot [\text{4PyCzBP-Pd}]^-$ was estimated from the Rehm-Weller equation$^{57}$ (see the SI for details) and was found to be exergonic at -0.39 eV and accounts for the quenching of the emission of 4PyCzBP-Pd. Upon encapsulation of F into the cavity of a redox-active cobalt cage, Duan and et al. observed PeT from the excited state of F, there acting as the electron donor, to the redox-active cage.$^{58}$ By contrast, no optoelectronic communication was observed by Ward et al. between a F guest and a crystalline zeolite host.$^{53}$

Emission titration of RB (from 0 to 150 μM) into a 50 μM degassed DMSO solution of 4PyCzBP-Pd at 298 K resulted in a gradual quenching of the green emission of the donor 4PyCzBP-Pd together with a gradual enhancement of the orange RB emission at 582 nm, with an isosbestic point observed at 561 nm (Figure 7a). As a result, upon photoexcitation of 4PyCzBP-Pd⊃RB at 360 nm, PET from 4PyCzBP-Pd to RB is promoted. The binding constants determined from the emission titration study are $K_b$ of $9.2 \times 10^3 \pm 0.06$ M$^{-1}$ for the encapsulation of the first molecule of RB and $K_b$ of $1.8 \times 10^7 \pm 0.4$ M$^{-1}$ for the encapsulation
of the second molecule of guest dye within the cavity of the cage (Figure S40). As electrostatic as well as non-covalent forces govern the binding of RB within 4PyCzBP-Pd, the binding constants for the assembly 4PyCzBP-Pd⊃RB are greater than those obtained for 4PyCzBP-Pd⊃F. Our titration data also suggest that the encapsulation of two molecules of F is thermodynamically more favorable than the encapsulation of only one molecule of guest, which is consistent with the DFT computations (see the SI).

Stern-Volmer quenching analysis of 4PyCzBP-Pd⊃RB demonstrated that the energy transfer/quenching process is very efficient,\textsuperscript{59} with a calculated quenching rate constant (k\textsubscript{q}) of 4.07 x 10\textsuperscript{11} M\textsuperscript{-1}s\textsuperscript{-1} and a Stern-Volmer constant (K\textsubscript{SV}) of 1.22 x 10\textsuperscript{4} M\textsuperscript{-1} (Table S5). Due to the large spectral overlap (J = 1.41 x 10\textsuperscript{12} nm\textsuperscript{4} M\textsuperscript{-1} cm\textsuperscript{-1}) between the absorption of RB and the emission of 4PyCzBP-Pd (Figure S41), Förster energy transfer is the likely mechanism for the energy transfer in system. The Commission Internationale de l’Éclairage, CIE, diagram shown in Figure 7b illustrates the change in the emission colors observed during the emission titration. Importantly, by manipulating the concentration of the host 4PyCzBP-Pd and guest RB, we developed a white-light emitting assembly with CIE coordinates of (0.32, 0.34), which are close to coordinates of the pure white light (x: 0.31, y: 0.33).
Figure 7. a) Emission titrations of RB (from 0 μM to 150 μM) into a 50 μM solution of 4PyCzBP-Pd at 298 K in degassed DMSO. b) CIE diagram indicating the change of emission colors during the emission titration. Photograph of the white-emitting solution with CIE coordinates (x: 0.32, y: 0.34) is shown in the inset of the spectrum.

Conclusions.

In summary, a luminescent supramolecular [Pd₆L₁₂](BF₄)₁₂ cage has been prepared by self-assembly of Pd²⁺ ions with a TADF ligand 4PyCzBP. 4PyCzBP-Pd is able to encapsulate up to up to three molecules of fluorescein, in its closed lactone form, and up to two molecules of Rose Bengal, in its open quinoid form. Examples of efficient energy or electron transfer between luminescent guests and photoactive cages are rare. In the present study we showed that PeT between the encapsulated fluorescein and the cage 4PyCzBP-Pd and PET from 4PyCzBP-Pd to encapsulated Rose Bengal occur. These assemblies open up the possibility of exploiting these interactions in photocatalysis, examples of which are exceedingly rare.

Acknowledgements. We thank the Leverhulme Trust (RPG-2016-047) and EPSRC (EP/P010482/1) for financial support. DE thanks funding from the European Union's Horizon 2020 research and innovation programme under the Marie Sklodowska-Curie grant agreement No. 700961. We thank Umicore Ag for the gift of the Pd(II) salts. We thank the EPSRC UK National Mass Spectrometry Facility at Swansea University for analytical services. This work uses computational resources of the CCIPL installed in Nantes.

Supporting information. Experimental section, characterization of ligands and cages, supplementary optoelectronic data and supplementary computational details.

References.


**TOC Graphic.**