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Photoinduced energy- and electron-transfer from a photoactive coordination cage to bound guests†

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In a coordination cage which contains an array of twelve naphthyl chromophores surrounding a central cavity, photoinduced energy or electron-transfer can occur from the chromophore array to the bound guest in supramolecular host/guest complexes.

The ability to perform multiple photoinduced energy- or electron-transfer processes in a single assembly, with several light-harvesting units interacting with a single energy- or electron-accepting unit, is of fundamental importance for applications from solar energy harvesting to photocatalysis. For photoinduced energy-transfer (PEnT), the antenna effect is a well-understood way of ensuring that (i) as much light as possible is absorbed, and (ii) the resulting excitation energy is channelled in a predictable way down an energy gradient to the ultimate acceptor, which may be a photosynthetic reaction centre¹ or a dye-sensitised solar cell.² For photoinduced electron transfer (PET), being able to induce multiple electron-transfer events in a single assembly is key to the ongoing search for artificial catalysis for both photochemical water splitting and harvesting the energy from sunlight to make highly reduced solar fuels.³

There is accordingly a need for simple synthetic strategies that will allow a single component – the ultimate user of the absorbed light energy – to interact with multiple chromophores. Covalent connection of multiple components in one molecule may allow precise control of structure, but each individual compound is necessarily limited in scope and probably challenging to prepare. Nature exploits supramolecular methods to achieve self-assembled arrays of the necessary components for photo-synthesis,⁴ and the use of the methodology of supramolecular chemistry to assemble photophysically active components into arrays with desirable properties is now well-established.⁵

Against this background the recent emergence of self-assembled coordination cages offers possibilities that are only just beginning to be exploited. Many such cages are photophysically unremarkable and are of interest purely for their structures and ability to act as containers for small-molecule guests.⁶ However, a minority have been prepared containing photophysically active components, and these provide possibilities for interaction of a large number of chromophoric units – either at the metal vertices⁷ or in the organic ligands⁸ – in the cage assembly with a single bound guest. Such cages present an ideal way to prepare an assembly in which a very high local concentration of chromophores in a known orientation can be brought into close proximity to a substrate bound in the cage cavity, which can therefore interact with the chromophore array *via* photoinduced energy- or electron-transfer.⁹ It is becoming clear from these recent examples that the relatively mature field of coordination cage self-assembly offers barely-exploited possibilities for photo-induced reactions between bound guests and the surrounding array of chromophores in a nice fusion of self-assembly and photophysics.⁹

Here we report studies on the photophysical consequences of binding different guest types in the cavity of an octanuclear cubic coordination cage in which an array of twelve naphthyl chromophores surrounds the central cavity.^{10,11} We demonstrate examples of both PET and PEnT between cage and guest, including the dynamic behaviour of a short-lived charge-separated cage^{•+}/guest^{•-} excited state. The cage that we use in this work is [Cd₈L₁₂](NO₃)₁₆ (hereafter abbreviated as 'H' for 'Host') which has an approximately cubic structure with a Cd(II) ion at each vertex, and a bis(pyrazolopyridine) bridging ligand incorporating a fluorescent naphthyl spacer spanning each edge (Fig. 1a). It is isostructural to the [Co₈L₁₂]¹⁶⁺ analogue which we have studied for its outstanding guest binding properties,¹⁰ but it contains non-quenching Cd(II) ions at the vertices to allow the fluorescence from the array of naphthyl units to be retained. We reported the preparation of [Cd₈L₁₂](NO₃)₁₆ recently.¹¹

We start by reporting the crystal structure of H (Fig. 1b–d; see also Fig. S1, ESI†); it is, as expected, essentially identical to that of the Co(II) analogue reported earlier.^{10b} Despite slightly longer metal–N distances associated with the larger ionic

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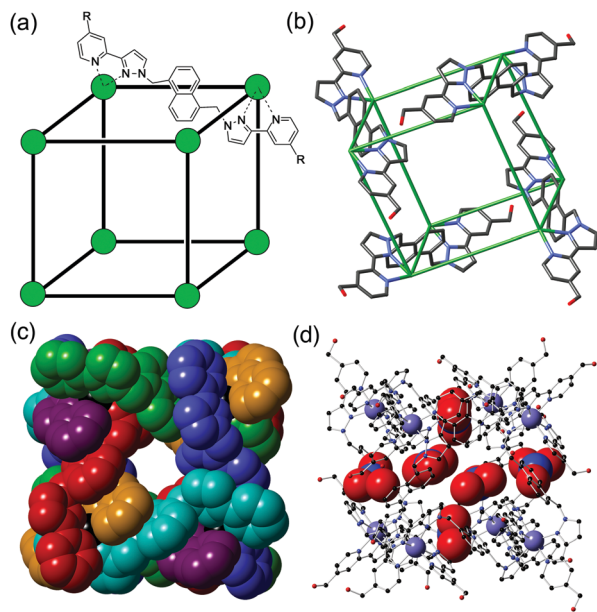


Fig. 1 The host cage $[\text{Cd}_8\text{L}_{12}](\text{NO}_3)_{24}$, **H**. (a) A sketch emphasising the cubic array of $\text{Cd}(\text{II})$ ions and the disposition of a bridging ligand **L** ($\text{R} = \text{CH}_2\text{OH}$); (b) a view of the complex cation from the crystal structure showing only four of the bridging ligands; (c) space-filling view of the complex cation with ligands coloured separately for clarity; (d) view of the complex emphasising the positions of some of the nitrate anions (shown space-filling) which occupy the portals on the faces of the cube. Additional figures showing the inclusion of **dmf** guest molecules and their interactions with the interior cage surface are in ESI.†

radius of $\text{Cd}(\text{II})$ compared to $\text{Co}(\text{II})$, the $\text{Cd}\cdots\text{Cd}$ separations along the edges are comparable to those of $\text{Co}\cdots\text{Co}$ separations in the $\text{Co}(\text{II})$ -based cubes.^{10d,b} The central cavity contains two **dmf** guest molecules whose $\text{C}=\text{O}$ groups are directed into the H-bond donor pockets that are associated with the internal surface of the cage around each of the two *fac* tris-chelate metal vertices (Fig. S1, ESI†).¹² Every face of the cube has a nitrate anion associated with the window in the face centre, with the anion forming a set of $\text{CH}\cdots\text{O}$ interactions with the cage surface (Fig. 1d).

H has the ability to act as an energy or electron-donor from its excited state. The singlet excited state of naphthalene has an energy content of *ca.* 4 eV¹³ and can therefore act as an energy-donor to any species with lower energy excited states. The relative ease of oxidation of naphthalene to its radical cation^{13a} means that its excited state is also a powerful electron donor, capable of effecting PET to a range of electron-acceptor quenchers.¹⁴ The steady-state fluorescence spectrum of host cage **H** is shown in Fig. 2; the properties of the naphthyl units are perturbed from those of free naphthalene due to their π -stacking interactions with electron-deficient pyrazolyl-pyridine units on either side of them.^{8a,10a} **H** displays, in solution, a broad and unstructured fluorescence centred at 400 nm from the array of twelve naphthyl groups around the cage periphery, which resembles that of a naphthalene excimer.¹⁵ At 77 K in MeOH/EtOH glass this is blue-shifted to 350 nm, indicating an available excited-state energy of *ca.* 28 500 cm^{-1} .

The guests (generally denoted **G**) that we investigated for their ability to bind in the cavity of **H** are shown in Scheme 1. These include some aliphatic ketones (**1** and **2**) which are non-chromophoric and

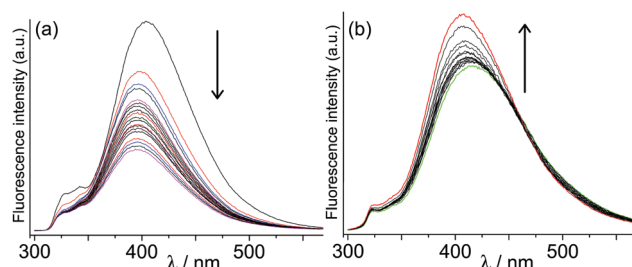
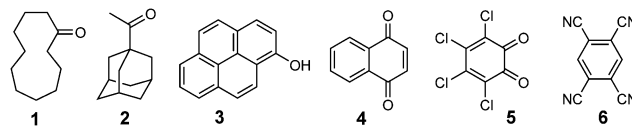


Fig. 2 Effect of non-chromophoric guests on fluorescence of the host. (a) Decrease in fluorescence of **H** on titration with the flexible guest **1** to form **H-1**; (b) increase in fluorescence of **H** on titration with the rigid guest **2** to give **H-2**.



Scheme 1 Structural formulae of guests used in this work.

therefore not expected to participate in PET or PEnT with the naphthyl groups: these can be considered as controls. The remaining guests are rigid aromatic species whose ability to be accommodated in the cage cavity was confirmed by molecular modelling and/or a calculation using molecular docking software.^{10c} These are the substituted pyrene **3** which is expected to be a good energy acceptor from the cage based on relative excited state energies of **H** and **3**; and three good electron-acceptors (quinones **4** and **5**, and tetracyanobenzene **6**).

Initially we investigated the effect on cage fluorescence of binding the non-chromophoric and non redox-active guests **1-2**, by conventional luminescence titrations in which portions of guest were added stepwise to a 0.01 mM aqueous solution of **H**. In each case a change in luminescence intensity was observed, with the cyclic ketone **1** resulting in a partial loss of luminescence intensity, but the more rigid guest **2** affording a slight increase in intensity (Fig. 2). We ascribe these changes to mechanical effects associated with differing degrees of rigidity of these guests: the flexible guest **1** provides sufficient additional vibrational modes to facilitate non-radiative deactivation, whereas the much more rigid guest **2** has the opposite effect by stiffening the cage and making non-radiative deactivation less likely. Importantly, the binding constants for these guests calculated from fitting the observed intensity changes to a 1 : 1 binding isotherm [**1**, $1.1(1) \times 10^6 \text{ M}^{-1}$; **2**, $3(1) \times 10^4 \text{ M}^{-1}$] agree well with what we previously observed for binding the same guests in the isostructural $\text{Co}(\text{II})$ cage measured by NMR titrations.^{10d}

Next, we investigated the effect of guest **3** on the cage fluorescence. Given that naphthyl \rightarrow pyrenyl photoinduced energy transfer has been demonstrated,¹⁶ we would expect the **H-3** complex to provide an example of PEnT from the array of chromophores in the host to the bound pyrene guest, possibly resulting in sensitised luminescence. This was confirmed by a luminescence titration in which small portions of **3** were added to a solution of **H** in water (1 μM). The high binding constant for formation of **H-3** in water [$1.3(1) \times 10^6 \text{ M}^{-1}$, from this data, in good agreement with previous observations]^{10c} means that by the end of the titration, **H-3** should be *ca.* 80% formed under the conditions used. As **3** binds in the



Excitation of the complex **H-6** under the same conditions produced the set of difference spectra shown in Fig. S5 (ESI[†]). These spectra look superficially similar to those observed for free **H**, as (i) there is only one guest per many naphthalene units and (ii) there is a small amount of free **H** in the equilibrium mixture. However, there are clear differences in the shape of the TA spectra of **H-6** vs. **H**: namely, an increased absorbance in the 380–460 nm region; an additional narrow band at *ca.* 450 nm; and pronounced additional fine structure in the ~ 400 nm band (Fig. 4b). The region of new absorbance in the range 380–410 nm matches what is expected from the presence of both tetracyanobenzene radical anion, $6^{\bullet-}$,¹⁹ and a naphthyl radical cation from $H^{\bullet+}$.^{14b,20} The naphthyl radical cation has a characteristic comparatively sharp absorption band at 382 nm with a shoulder at 366 nm, which explains the increased absorbance in the TA spectrum of **H-6** compared to **H**. The clear, relatively sharp feature at 450 nm in the TA spectrum of **H-6** matches the most intense feature in the absorption spectrum of $6^{\bullet-}$,¹⁹ this feature did not appear in a control experiment using just **6**.

The features in the TA spectrum of **H-6** that are absent in the spectrum of **H** alone (Fig. 4b) are therefore consistent with the occurrence of cage \rightarrow guest PET to generate the $H^{\bullet+}/6^{\bullet-}$ charge-separated pair. Both of the excited state features attributed to $H^{\bullet+}/6^{\bullet-}$ decay synchronously with a first-order time constant of $\approx 160(25)$ ps, which can be ascribed to charge recombination by back electron transfer. The features of the transient spectrum of **H-6** which correspond to ¹Naph* persist over longer time scales, decaying with the same dynamics as the free cage.

In conclusion, we have demonstrated that the array of 12 naphthyl fluorophores built into the self-assembled cage **H** is capable of acting as an antenna group, effecting photoinduced energy or electron transfer to a guest that is bound in the central cavity in supramolecular **H-G** complexes. This opens up extensive possibilities for use of these cages in both single- and multi-electron photocatalysis.

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Notes and references

‡ For collisional (dynamic) quenching a standard Stern–Volmer analysis applies: $I_0/I = 1 + k[\text{guest}]\tau_0$, where $\tau_0 \approx 2$ ns (lifetime of naphthalene excited state). Even assuming a diffusion-limited rate constant for collisions of 10^{10} s^{-1} , and a huge excess of guest (4 mM), the maximum possible fluorescence quenching would be just 8% – so quenching is associated with guest binding in the cage cavity.

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