Electronic Supplementary Material (ESI) for ChemComm.

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

Jerico R. Piper, Lewis Cletheroe, Christopher G. P. Taylor, Alexander J. Metherell, Julia A. Weinstein, Igor V. Sazanovich and Michael D. Ward

Electronic supporting information

1. Experimental details

Picosecond transient absorption measurements were performed on the ULTRA apparatus (main text, ref. 17) at the Central Laser Facility (STFC Rutherford Appleton Laboratories, Harwell, UK). For the measurements, part of the titanium:sapphire laser output beam was used to generate a white light continuum (WLC) in a CaF_2 plate. The crystal plate was continuously rastered to avoid colour centre formation and to improve pulse-to-pulse stability in the probe. The WLC was dispersed through the grating spectrograph and detected using a linear silicon array (Quantum Detectors). In front of the spectrograph, a UV long-pass filter was placed in order to remove scatter from the excitation beam. The polarization of the pump pulses at the sample was at the magic angle relative to the probe, with an energy of 1 μJ and a spot size ca. 100-150 mm. The spectra were calibrated using the WCT-2065 calibration standard.

Fluorescence titrations were carried out by preparing a stock solution of $[Cd_8L_{12}](NO_3)_{16}$ (**H**: concentration of 1 or 10 μM) in de-ionised water. Guest solutions (usually 0.05-5 mM) were made up using this stock solution of host to avoid dilution of host as guest is added during the titration. 1500 μL of host solution was added to a standard 1 cm fluorescence cuvette, to which portions of guest solution were then added, leaving 15 minutes after each addition to allow the host / guest mixture to equilibrate. Fluorescence spectra were recorded on a Horiba-Jobin Yvon Fluoromax-4 spectrophotometer, with excitation at 280 nm and emission spectra recorded between 300 nm and 550 nm. For fluorescence-based assays aliquots of the stock cage solution (0−100 μL) and the guest solution (0−100 μL) were added to 24 wells of a Griener Bio-one μClear black 384-well plate in different proportions to a total volume of 100 μL in each well. The fluorescence emission at 420 nm, using 280 nm excitation, was measured for each well using a BMG FLUOstar Omega plate reader equilibrated at 298 K. Binding constants given in the main text calculated form luminescence titrations (see, for example, Fig. S3) are the average of at least three repeat measurements for each guest.

Crystallographic data for $[Cd_8L_{12}](NO_3)_{16}\bullet(dmf)_{13}\bullet(H_2O)_2$: $C_{399}H_{407}Cd_8N_{101}O_{87}$, M = 8908.43 g mol^{-1}, triclinic, space group P–1, a = 23.1625(3), b = 23.7759(4), c = 24.2858(3) Å, a = 108.5500(10), b = 101.7820(1), g = 90.4160(10)°, U = 12374.8(3) Å^3, Z = 1, r_{calc} = 1.195 g cm^{-3}, T = 100(2) K, l (Mo-Ka) = 0.71075 Å, μ = 0.413 mm^{-1}. 186901 reflections with $2q_{max}$ = 50° were merged to give 43696 independent reflections with R_{int} = 0.0458. Final R_1 [for data

with $I > 2s(I)] = 0.0925$; wR_2 (all data) = 0.333. The data collection was performed by the EPSRC National Crystallgraphy Service at the University of Southampton (ref. S1). Data were corrected for absorption using SADABS (ref. S2); the structure was solved and refined using the SHELX suite of programmes (ref. S3). The asymmetric unit contains one half of the cage either side of the inversion centre.

S1 S. J. Coles and P. A. Gale, *Chem. Sci.,* 2012, **3**, 683.

S2 G. M. Sheldrick, SADABS: A program for absorption correction with the Siemens SMART system, University of Göttingen, Germany, 2008.

S3 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2008, **64**, 112.

2. Additional figures

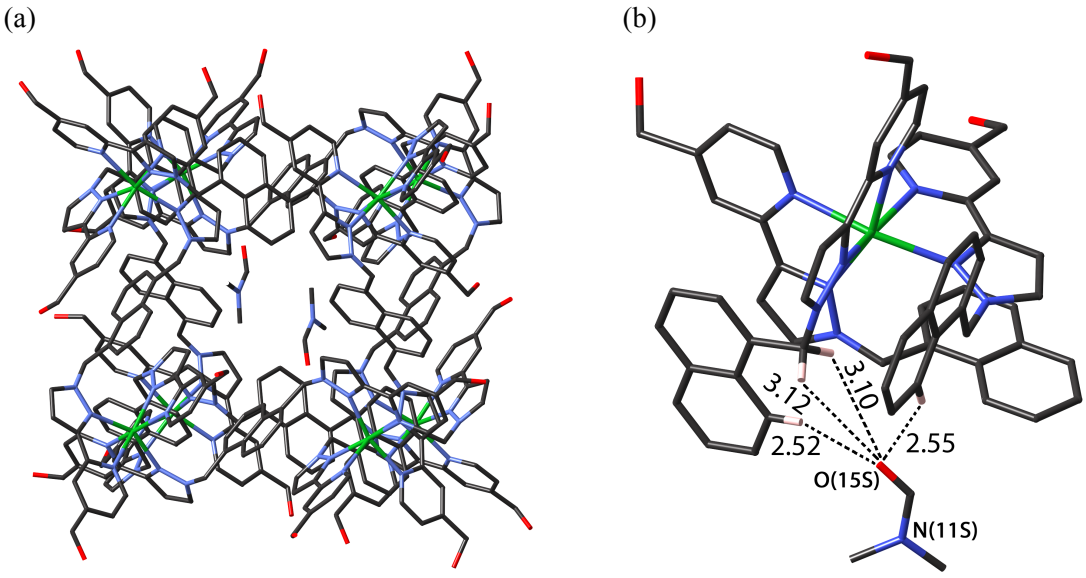
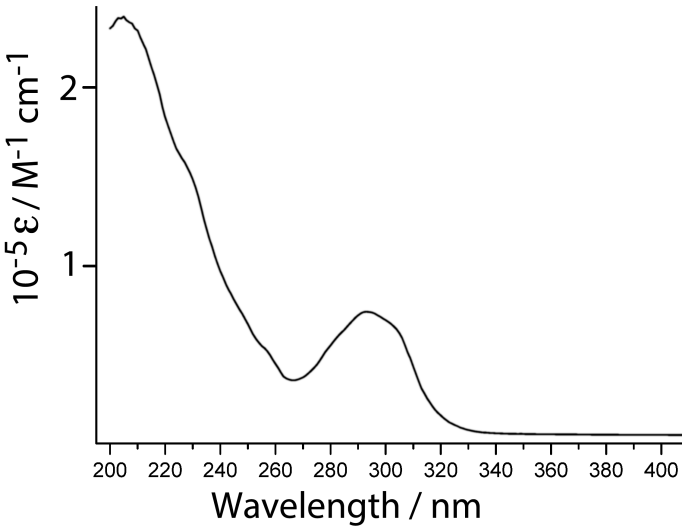


Fig. S1. Two additional views of the crystal structure of $[Cd_8L_{12}](NO_3)_{16}\bullet(dmf)_{13}\bullet(H_2O)_2$ illustrating guest inclusion. (a): The complete cage in wire-frame view, showing the two dmf guest molecules in the central cavity. (b) A close-up of one bound dmf guest molecules adjacent to one of the two *fac* tris-chelate vertices, with the four shortest CH•••O contacts shown [distances of the C•••O(1S) separations are in Å]..

(a)



(b)

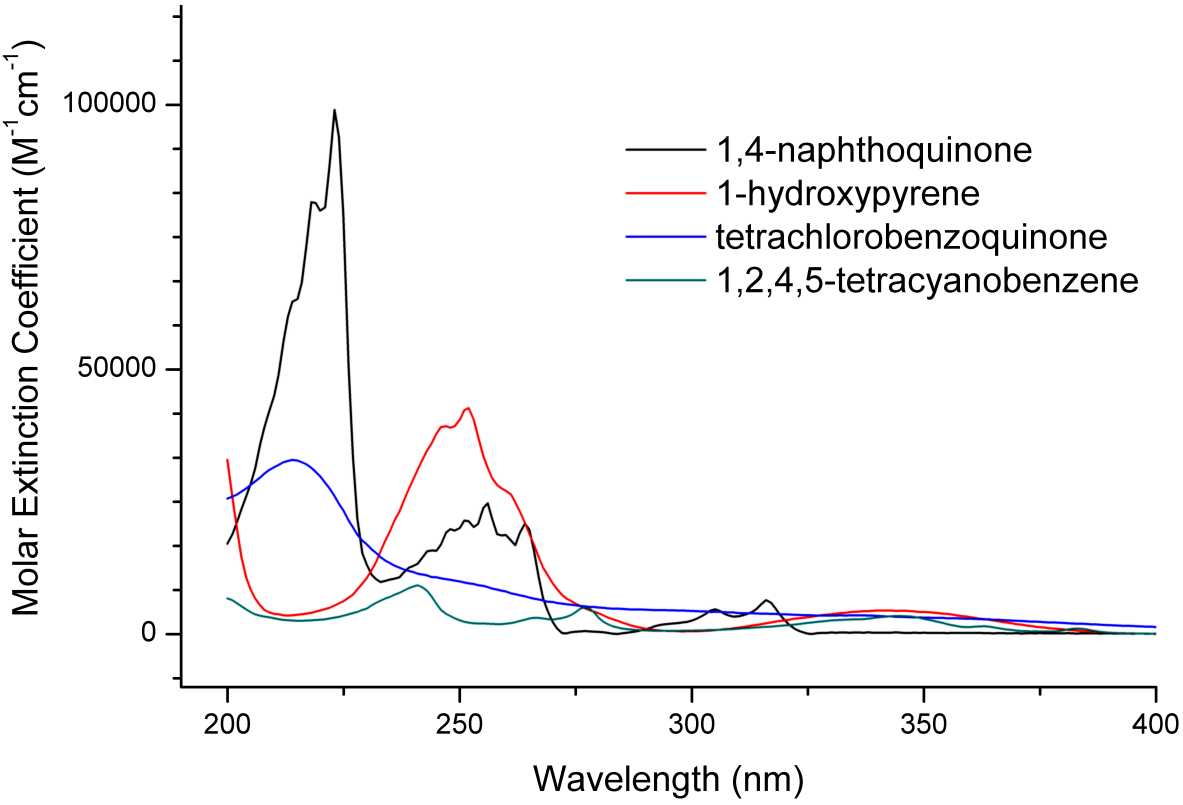


Fig. S2. (a) UV/Vis absorption spectrum of **H** in H_2O. (b) UV/Vis absorption spectra of guests **3** – **6** in H_2O.

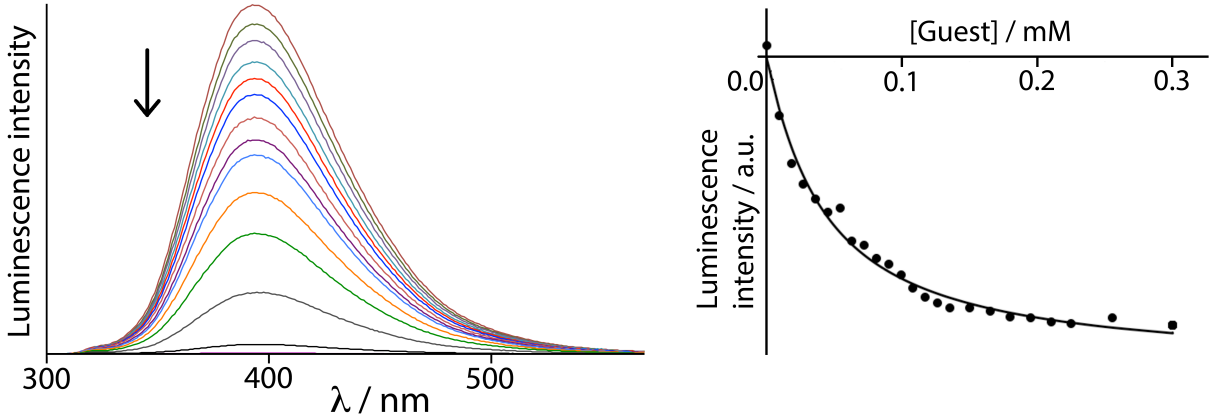


Fig. S3. **Left:** Luminescence titration of **H** (10 μM) with guest **5** in water showing quenching of cage fluorescence as the complex **H•5** forms. Similar results were obtained with guest **4**. **Right:** Luminescence intensity as a function of guest concentration, using the same data; this was fitted to a 1:1 binding isotherm (solid line) to give the binding constant of 2.9(5) x 10^4 M^{-1} given in the main text.

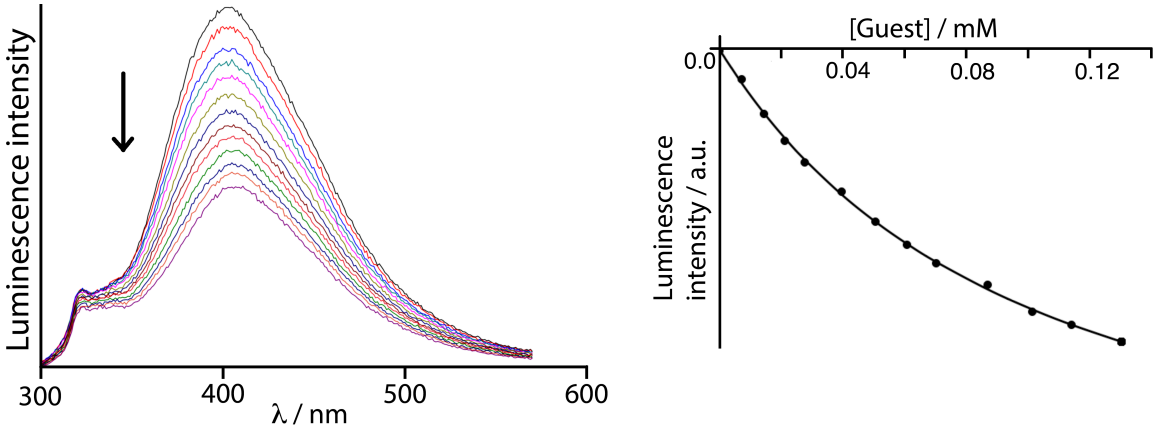


Fig. S4. **Left:** Luminescence titration of **H** (10 μM) with guest **6** in water showing quenching of cage fluorescence as the complex **H•6** forms. **Right:** Luminescence intensity as a function of guest concentration, using the same data; this was fitted to a 1:1 binding isotherm (solid line) to give the binding constant of 1.3(5) x 10^4 M^{-1} given in the main text.

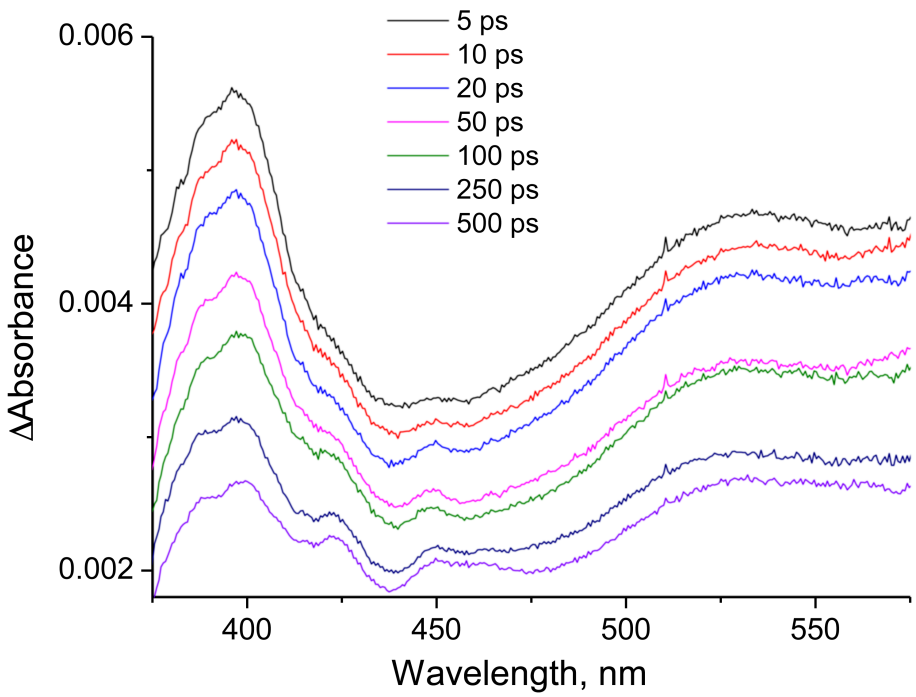


Fig. S5. Transient absorption spectra at a series of time delays form 5 ps to 500 ps following excitation of a *ca.*10 μM solution of the complex **H•6** (290 nm excitation, 40 fs pulse) in H_2O.