Photophysics of cage/guest assemblies: photoinduced electron transfer between a coordination cage containing Os(II) luminophores, and electron-deficient bound guests in the central cavity.

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Supporting information
**Fig. S1.** 400 MHz 1H NMR and DOSY spectra of Os•Zn (chloride salt) in D$_2$O at 298 K

**Fig. S2.** Cyclic voltammograms of Os•Zn (black), [Os(L$^{\text{nap}}$)$_3$]Cl$_2$ (red) and [Os(L$^{Me}$)$_3$]Cl$_2$ (blue), in H$_2$O, vs. an Ag/AgCl reference electrode.
Fig. S3. $^1$H NMR (400 MHz, CD$_3$CN) of [Os(L$^{Me}_3$)](PF$_6$)$_2$ showing the four environments for each type of proton arising from the mixture of fac and mer isomers.

Fig. S4. Time-resolved luminescence decay traces from aqueous solutions of (a) [Os(L$^{Me}_3$)]Cl$_2$, (b) [Os(L$^{nap}_3$)]Cl$_2$ and (c) Os•Zn. Measured data are black dots; best fit curves are shown by red lines, based on the parameters in Table 1 of the main text; residuals from the fits are shown in red at the bottom.
Fig. S5. 400 MHz $^1$H NMR spectra recorded during titration of (a) NN, (b) NQ and (c) TCNB (up to 16 equivalents of each) into [Co$_8$(L$^{nap}$)$_{12}$]Cl$_{16}$ (0.15 mM in D$_2$O). Some of the broad signals associated with the paramagnetic cage are split into separate signals for free host and host/guest species, but in addition much sharper new signals associated with bound guest are apparent in each case (labelled *).
Fig. S6. Top: UV/Vis spectra of the Os₄Cd₄ cage in the fully reduced Os(II) form (black), and the fully oxidised Os(III) form (red), taken from previous work (ref. 10a, main text). Bottom; difference between the two UV/Vis spectra showing spectroscopic changes associated with oxidation of Os(II) to Os(III) (compare with the TA spectra in Fig. 5, main text).
Fig. S7. Decay-associated spectra for the free cage Os•Zn in aqueous solution fitted to a 3-component sequential model. The top figure shows the normalised spectra, whereas the bottom figure is pre-normalisation and therefore reflects the relative intensities of the three components.
Fig. S8. Decay-associated spectra derived from TA spectroscopy of Os•Zn/NQ (top) and Os•Zn/NN (bottom) relating to the short time constant (ca. 200 ps, red trace, from the cage/guest complex) and the longer time constant (ca. 25 ns, black trace, from the free unquenched cage in the equilibrium mixture); the difference between these was used to calculate the absorption spectra of the transient charge-separated pairs shown in Fig. 7b of the main text (green and red spectra, respectively).
Fig. S9. Decay-associated spectra (DAS) derived from TA spectroscopic data of the Os•Zn/TCNB system showing the spectra associated with the four components of the global fit (see main text). Top left: normalised DAS with maximum positive and negative features fitting within a scale of $\Delta$OD $\pm$1. Top right: the same decay-associated spectra but not normalised. Bottom: observed single-point kinetics at 465 nm (black trace) with the result of the 4-component sequential global fit (red trace) superimposed, including on the right an expansion of the early-time data showing the grow-in of the charge-separated state.
Fig S10. Decay-associated spectra (DAS) derived from TA spectroscopic data of the Os•Zn/NQ system showing the spectra associated with the four components of the global fit (see main text). Top left: normalised DAS with maximum positive and negative features fitting within a scale of ΔOD ±1. Top right: the same decay-associated spectra but not normalised. Bottom: observed single-point kinetics at 550 nm (black trace) with the result of the 4-component sequential global fit (red trace) superimposed, including on the right an expansion of the early-time data showing the grow-in of the charge-separated state.
Fig. S11. Decay-associated spectra (DAS) derived from TA spectroscopic data of the Os•Zn/NN system showing the spectra associated with the four components of the global fit (see main text). Top left: normalised DAS with maximum positive and negative features fitting within a scale of ΔOD ±1. Top right: the same decay-associated spectra but not normalised. Bottom: observed single-point kinetics at 470 nm (black trace) with the result of the 4-component sequential global fit (red trace) superimposed, including on the right an expansion of the early-time data showing the grow-in of the charge-separated state.
**Fig. S12.** UV/Vis absorption data derived from a spectroelectrochemistry experiment showing neutral NN (black line) and the mono-reduced radical anion NN$^{•–}$ (red line) following reduction at a Pt grid working electrode in an OTTLE cell in MeCN at –20°C. Note the main absorption feature of NN$^{•–}$ at ca. 460 nm, which correlates with a feature in the TA spectra of the Os•Zn/NN (main text, Fig. 6b).
**Fig S13.** Transient absorption spectra (400 nm excitation, ca. 40 fs pulse, in water; for conditions see main text) obtained by subtracting the spectrum recorded at the longest time delay (7.5 ns) from the spectra at shorter time delays (1 ps to 1 ns). The top panel is for the Os•Zn/TCNB system and is the same as the top panel in Fig. 6 of main text; the bottom panel is for the [Os(L^{me}_3)]Cl_2 / TCNB system containing the same concentration of Os(II) chromophore units. The absence of the transient feature indicating the grow-in and then decay of TCNB^– in the bottom set of spectra is clear.
Table S1. Crystal data and structure refinement for Os•Zn (perchlorate salt)

Nominal formulation \[\text{Os}_4\text{Zn}_4(\text{L}^{\text{nap}})_{12}](\text{ClO}_4)_{16} \cdot 2\text{MeNO}_2 \cdot 4\text{H}_2\text{O}\]
Empirical formula \(\text{C}_{338}\text{H}_{278}\text{Cl}_{16}\text{N}_{74}\text{O}_{72}\text{Os}_4\text{Zn}_4\)
Formula weight 8117.80
Temperature 100(2) K
Wavelength 0.71073 Å
Crystal system Trigonal
Space group R-3
Unit cell dimensions \(a = 28.814(2) \text{ Å} \quad \alpha = 90^\circ\).
\(b = 28.814(2) \text{ Å} \quad \beta = 90^\circ\).
\(c = 52.971(4) \text{ Å} \quad \gamma = 120^\circ\).
Volume 38087(6) Å³
Z 3
Density (calculated) 1.062 Mg/m³
Absorption coefficient 1.328 mm⁻¹
Crystal size 0.32 x 0.21 x 0.16 mm³
Theta range for data collection 0.902 to 19.826°.
Index ranges \(-27 \leq h \leq 27, -24 \leq k \leq 27, -50 \leq l \leq 49\)
Reflections collected 86465
Independent reflections 7688 [R(int) = 0.1465]
Completeness to theta = 19.826° 99.6 %
Absorption correction Semi-empirical from equivalents
Refinement method Full-matrix least-squares on \(F^2\)
Data / restraints / parameters 7688 / 582 / 726
Goodness-of-fit on \(F^2\) 1.616
Final R indices \([I > 2\sigma(I)]\) \(R1 = 0.134, wR2 = 0.393\)
R indices (all data) \(R1 = 0.193, wR2 = 0.438\)

Data were collected at the University of Sheffield on a Bruker Apex II diffractometer with a CCD detector. One sixth of the complete cage is found in the asymmetric unit, with the Zn and Os atoms occupying the same sites such that these were refined as a 50/50 mixture of the two atom types. Fourteen of the required sixteen anions could be located from the data; the other two are presumably too badly disordered to locate but were included in the calculated formula. All anions were refined with isotropic displacement parameters; all anions, and the nitromethane molecule, needed weak DFIX restraints to keep their geometry sensible during the refinement. Weak global restraints were applied to all C, N, O atoms to achieve a chemically reasonable model (RIGU for the cage ligands, and SIMU/DELU commands for the solvents and anions). All hydrogen atoms were added in calculated positions, apart from those on the water molecules which were not located from the data but were included in the reported formula. After the cage and anions were located, a large solvent-accessible void containing diffuse electron density remained. This region of diffuse electron density was removed with the SQUEEZE command on PLATON; full details are given in the CIF.

Substantial regions of diffuse electron density that could not be meaningfully modelled were removed from the final refinement using the SQUEEZE function in PLATON;⁵¹ full details are in the CIF. We emphasise that the cage complex cations and the surface-bound perchlorate ions are well defined with acceptable thermal displacement parameters. CCDC deposition number: 1871131
### Table S2. Crystal data and structure refinement for [Co₈(L nap)₁₂](BF₄)₁₆•0.66(TCNB)

| Property                      | Value                                                                 |
|-------------------------------|----------------------------------------------------------------------|
| Nominal formulation           | [Co₈(L nap)₁₂](ClO₄)₁₆•(TCNB)₀.₆₆•(MeOH)₃₈(H₂O)₂                     |
| Empirical formula             | C₃₈₀.₄H₄₂₁.₃N₇₄.₆O₄₀B₁₆Co₈                                          |
| Formula weight                | 8538.07                                                              |
| Temperature                   | 100(2) K                                                            |
| Wavelength                    | 0.6889 Å (synchrotron)                                              |
| Crystal system                | Monoclinic                                                          |
| Space group                   | C2/c                                                                |
| Unit cell dimensions          | a = 32.99046(15) Å, α = 90°.                                        |
|                               | b = 29.89184(14) Å, β = 95.8843(4)°.                                |
|                               | c = 39.71423(18) Å, γ = 90°.                                        |
| Volume                        | 38957.7(2) Å³                                                       |
| Z                             | 4                                                                   |
| Density (calculated)          | 1.456 Mg/m³                                                          |
| Absorption coefficient        | 0.41 mm⁻¹                                                            |
| Crystal size                  | 0.80 x 0.70 x 0.16 mm³                                              |
| Theta range for data collection | 0.89 to 36.091°                                                      |
| Index ranges                  | -55<=h<=54, -50<=k<=49, -64<=l<=67                                  |
| Reflections collected         | 420787                                                              |
| Independent reflections       | 94621 [R(int) = 0.058]                                               |
| Completeness to theta = 36.091° | 92.8 %                                                            |
| Absorption correction         | Semi-empirical from equivalents                                     |
| Refinement method             | Full-matrix least-squares on F²                                     |
| Data / restraints / parameters | 94621 / 5859 / 2331                                                  |
| Goodness-of-fit on F²         | 0.974                                                               |
| Final R indices [I > 2σ(I)]   | R1 = 0.080, wR2 = 0.259                                              |
| R indices (all data)          | R1 = 0.132, wR2 = 0.292                                              |

Data were collected at beamline i-19 at the Diamond Light Source. The complex molecule lies astride an inversion centre such that half of it lies in the asymmetric unit. Rigid bond and similarity restraints were applied to the anisotropic and isotropic displacement parameters of all atoms in the structure (RIGU and SIMU). Methanol residues O21S, O41S, O51S and water residue O2W were refined with isotropic displacement parameters fixed at values of 0.1. All other non-hydrogen atoms in the structure were refined with isotropic displacement parameters. The anisotropic displacement parameters of tetrafluoroborate residue B31 were restrained to have more isotropic character (ISOR); a measure likely necessary as a result of un-modelled disorder in the partial occupancy residue.

The occupancies of cage encapsulated 1,2,4,5-tetracyanobenzene residue and methanol residue O11S were refined to values of 0.66(1) and 0.55(1) respectively. The occupancy of tetrafluoroborate residue B31 was allowed to refine to a value of 0.68(1). The occupancies of tetrafluoroborate residues B41 and B51 were constrained to sum to unity and refined to values of 0.33(1) and 0.67(1) respectively. The occupancies of methanol residues O21S, O41S, O51S and water residue O2W were refined to values of 0.71(1), 0.49(1), 0.43(1) and 0.42(2) respectively.

The geometries of methylene-pyrazolyl-pyridine and naphthyl moieties were restrained to have similar geometries (SAME). The geometries of all tetrafluoroborate residues were restrained to have similar geometries reflecting their tetrahedral shape (SADI). The C-O bond lengths of methanol residues O21S, O41S and O51S were restrained to a target value of 1.42 Å (DFIX). The pairs of chemically
equivalent cyano C-N and C-C distances were restrained to have similar bond lengths (SADI).

A short intermolecular distance 2.90(1) Å is observed between cage encapsulated methanol oxygen atom O11S and cage encased 1,2,4,5-tetracyanobenzene cyano carbon atom C14G. This distance and angle (O11s...C14G-N15G, 101.6(3)) are consistent with the Burgi-Dunitz angle describing the approach of a nucleophile to an unsaturated carbon atom.\textsuperscript{52}

The methyl H atoms of methanol residues O21S, O41S, O51S, hydroxy hydrogen atoms of all methanol residues and hydrogen atoms of water residue O2W were not observed in the electron density map and are not included in the model, however, all hydrogen atoms were included in the unit cell contents. All other hydrogen atoms in the structure were geometrically placed and refined with a riding model.

Disordered solvent molecules could not be sensibly modelled, so the structure was treated the SQUEEZE function in PLATON;\textsuperscript{51} full details are in the CIF. A total of 2178 electrons were accounted from the P1 cell in this way, equating to 30 methanol molecules per asymmetric unit, which have been included in the unit cell contents and calculation of derived parameters. \textbf{CCDC deposition number: 1884249.}

S1 (a) Spek, A. L. \textit{J. Appl. Crystallogr.} \textbf{2003, 36}, 7; (b) van der Sluis, P.; Spek, A. L. \textit{Acta Crystallogr., Sect. A: Found. Crystallogr.} \textbf{1990, 46}, 194.

S2 Burgi, H. B.; Dunitz, J. D.; Shefter, E. \textit{J. Am. Chem. Soc.} \textbf{1973, 95}, 5065.