Supporting Information for

Highly regioselective complexation of tungsten with Eu@C$_{82}$/Eu@C$_{84}$:
interplay between endohedral and exohedral metallic units induced by electron transfer

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Crystal data of Eu@C_2(5)-C$_{82}$·Ni(OEP)·2(C$_6$H$_6$). black block, 0.20 × 0.20 × 0.17 mm, monoclinic, space group $C2/m$, a = 25.236(2) Å, b = 15.0375(14) Å, c = 19.8277(19) Å, β = 94.3850(10) °, V = 7502.3(12) Å^3, Fw = 1884.45, λ = 0.65250 Å, Z = 4, D_{calc} = 1.668 Mg m^{-3}, μ = 0.913 mm^{-1}, T = 100 K, R_1[8461 reflections with $I > 2\sigma(I)$] = 0.0873, wR_2 (all 62921 data) = 0.2663, GOF (on F^2) = 1.036. The maximum residual electron density is 1.480 eÅ^{-3}. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1579794).

Crystal data of Eu@C_2(13)-C$_{84}$·Ni(OEP)·1.61(C$_6$H$_6$)·0.39(CS$_2$). black block, 0.30 × 0.24 × 0.24 mm, monoclinic, space group $C2/m$, a = 25.3346(8) Å, b = 15.1339(5) Å, c = 19.9751(6) Å, β = 95.6590(10) °, V = 7621.4(4) Å^3, Fw = 1907.70, λ = 0.65250 Å, Z = 4, D_{calc} = 1.663 Mg m^{-3}, μ = 0.915 mm^{-1}, T = 100 K, R_1[8432 reflections with $I > 2\sigma(I)$] = 0.0795, wR_2 (all 58740 data) = 0.2028, GOF (on F^2) = 1.021. The maximum residual electron density is 1.789 eÅ^{-3}. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1851767).

Crystal data of 2a·CS$_2$. black plate, 0.30 × 0.20 × 0.04 mm, monoclinic, space group $P2_1/n$, a = 22.367(2) Å, b = 11.2378(10) Å, c = 27.520(3) Å, β = 112.0420(10) °, V = 6411.8(10) Å^3, Fw = 1879.17, λ = 0.65250 Å, Z = 4, D_{calc} = 1.947 Mg m^{-3}, μ = 2.343 mm^{-1}, T = 100 K, R_1[15400 reflections with $I > 2\sigma(I)$] = 0.0448, wR_2 (all 111667 data) = 0.1248, GOF (on F^2) = 1.042. The maximum residual electron density is 2.677 eÅ^{-3}. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1579799).

Crystal data of 2b·CS$_2$. black plate, 0.10 × 0.08 × 0.02 mm, monoclinic, space group $P2_1/n$, a = 22.3565(8) Å, b = 11.4569(4) Å, c = 27.6560(10) Å, β = 112.8190(10) °, V = 6529.3(4) Å^3, Fw = 1903.20, λ = 0.65250 Å, Z = 4, D_{calc} = 1.936 Mg m^{-3}, μ = 2.302 mm^{-1}, T = 100 K, R_1[13446 reflections with $I > 2\sigma(I)$] = 0.0592, wR_2 (all 96159 data) = 0.1609, GOF (on F^2) = 1.062. The maximum residual electron density is 2.563 eÅ^{-3}. Crystallographic data has been deposited in the Cambridge Crystallographic Data Center (CCDC number: 1579800).
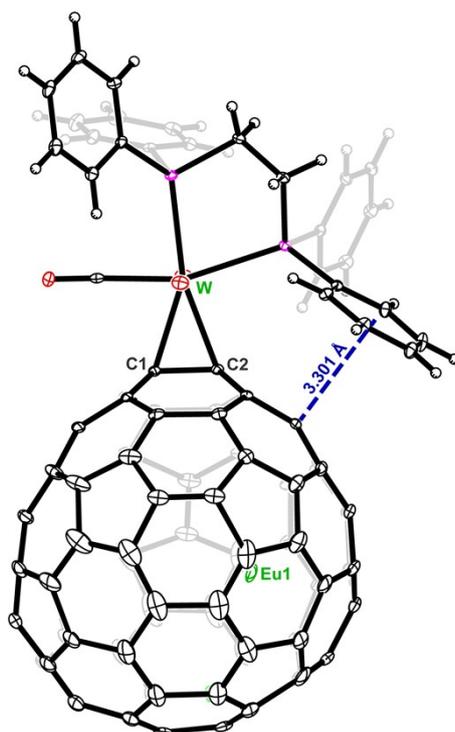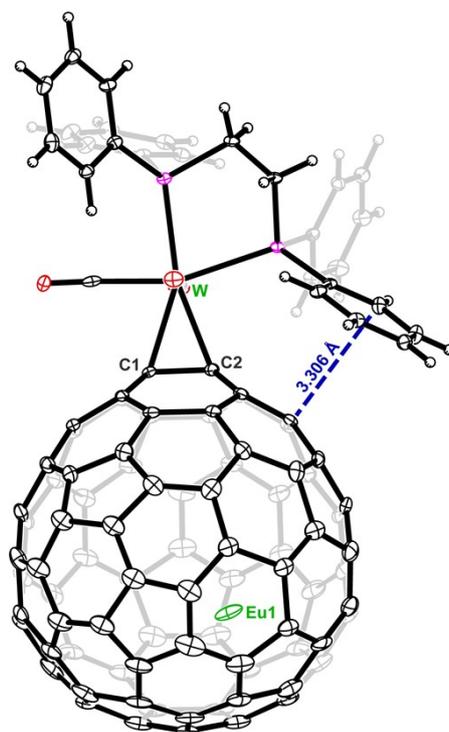
Fig. S1. Ortep drawing of **2a** with thermal ellipsoids set at the 20% probability level. Only one cage orientation and the major metal sites are shown. Solvent molecules and the minor metal sites are omitted for clarity.

Table S1. The experimentally observed and calculated POAV values of C1 and C2 and the bond lengths of C1-C2 (the site of addition) in Eu@C_2(5)-C$_{82}$, **2a**, Eu@C_2(13)-C$_{84}$ and **2b**.

	POAV angles (°)				C1-C2 bond length (Å)	
	C1$_{exp}$	C1$_{cal}$	C2$_{exp}$	C2$_{cal}$	Experimental	Calculated
Eu@C_2(5)-C$_{82}$	10.65	11.60	10.66	11.40	1.36(2)	1.38
2a	15.10	15.80	15.99	15.90	1.47(6)	1.48
Eu@C_2(13)-C$_{84}$	11.44	11.70	9.31	11.50	1.38(2)	1.37
2b	15.40	15.50	16.83	16.40	1.49(1)	1.47

Table S2. Natural Population Analysis (NPA) Charges and Natural Electron Configuration Populations of the Eu Atom in Eu@C_2(5)-C$_{82}$, **2a**, Eu@C_2(13)-C$_{84}$ and **2b**.

| species	Charge (e)	population
Eu@C_2(5)-C$_{82}$	1.41	$6s^{0.06}4f^{7.00}5d^{0.38}6p^{0.13}6d^{0.02}7p^{0.01}$
2a	1.42	$6s^{0.06}4f^{7.00}5d^{0.37}6p^{0.13}6d^{0.02}7p^{0.01}$
Eu@C_2(13)-C$_{84}$	1.41	$6s^{0.06}4f^{7.00}5d^{0.37}6p^{0.13}6d^{0.02}7p^{0.01}$
2b	1.42	$6s^{0.06}4f^{7.00}5d^{0.37}6p^{0.13}6d^{0.02}7p^{0.01}$

Fig. S2. Ortep drawing of **2b** with thermal ellipsoids set at the 20% probability level. Only one cage orientation and the major metal sites are shown. Solvent molecules and the minor metal sites are omitted for clarity.
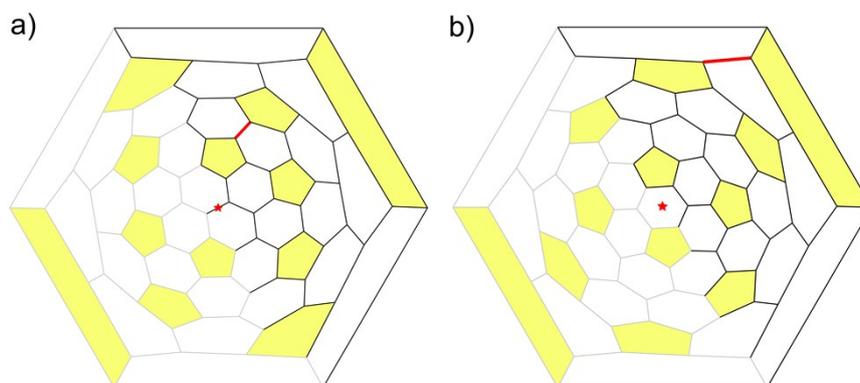

Fig. S3. Schlegel diagrams showing a) 62 nonequivalent C-C bonds on $C_2(5)$-C_{82} and b) 63 nonequivalent C-C bonds on $C_2(13)$-C_{84}. The C-C bonds and pentagons at equivalent sites are displayed in light color. The C-C bonds at the site of addition are highlighted in red. The pentagons are highlighted in yellow. The red star in each diagram indicates the position of the C_2 axis which is perpendicular to the paper plane.
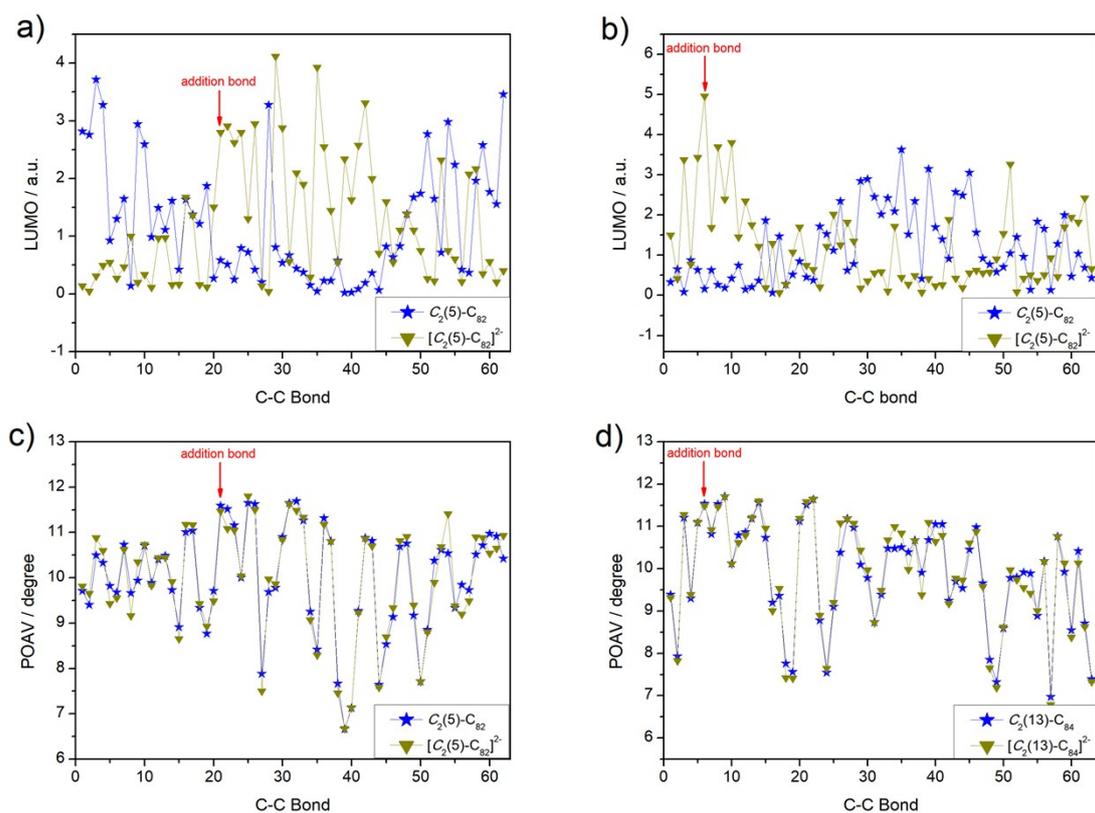
Fig. S4. The average LUMO distributions of two bonded cage carbons on a) neutral and di-anionic $C_2(5)\text{-}C_{82}$ and b) neutral and di-anionic $C_2(13)\text{-}C_{84}$. The average π-orbital axis vector (POAV) values of two bonded cage carbons on c) neutral and di-anionic $C_2(5)\text{-}C_{82}$ and d) neutral and di-anionic $C_2(13)\text{-}C_{84}$. The bonds at the site of coordination reaction are marked with red arrows. Equivalent C-C bonds on the cage are omitted according to cage symmetry.
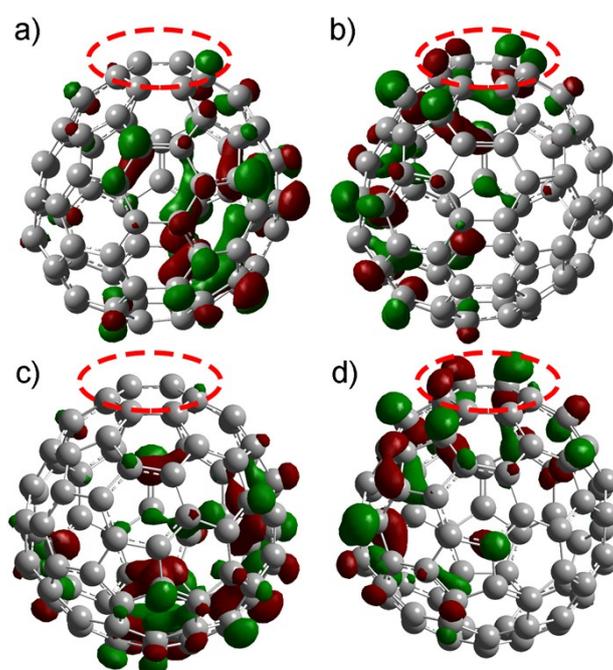
Fig. S5. LUMO distributions of a) $C_2(5)\text{-}C_{82}$, b) $[C_2(5)\text{-}C_{82}]^{2-}$, c) $C_2(13)\text{-}C_{84}$ and d) $[C_2(13)\text{-}C_{84}]^{2-}$. The sites of addition are highlighted by red dashed circles.
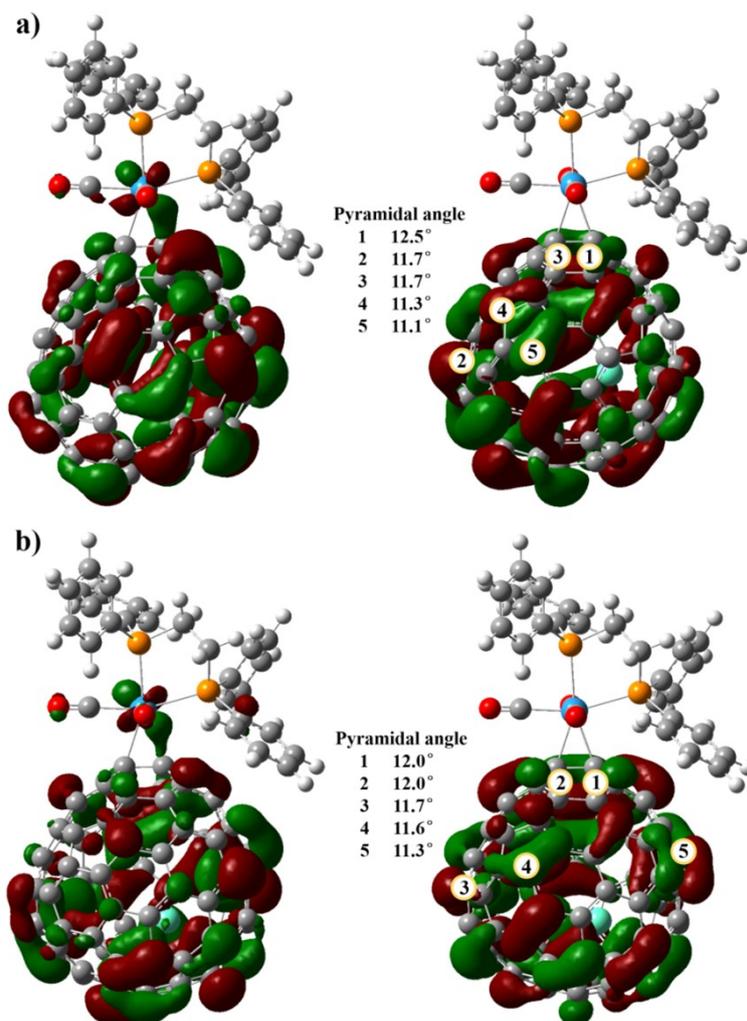
Fig. S6. HOMO (left) and LUMO (right) plots of a) **2a** and b) **2b**. The five carbon sites holding both large LUMO distributions and high POAV values are labeled.
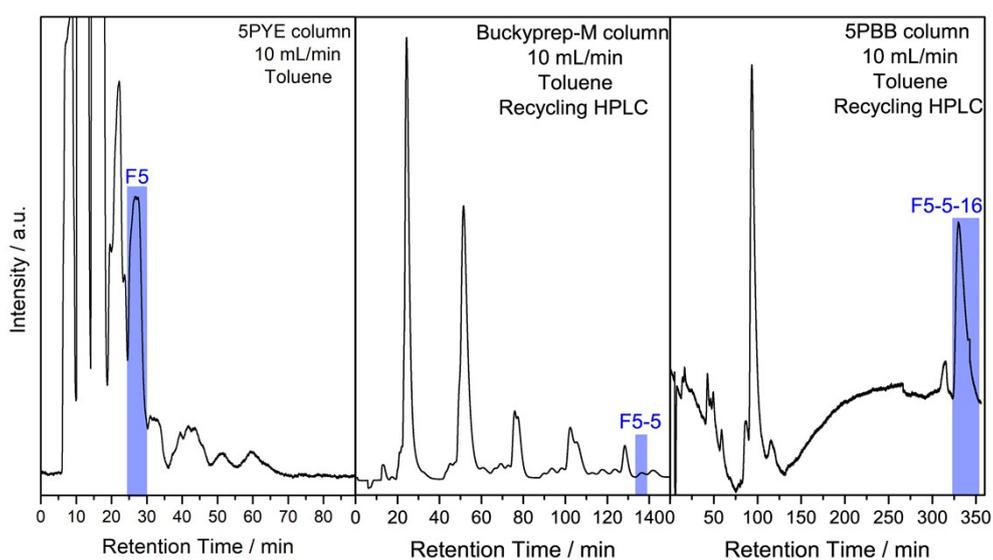
Fig. S7. Multi-stage preparative HPLC profiles of the separations of Eu@C_2(5)-C_{82}. HPLC conditions: toluene flow; 40 °C; 330 nm detection wavelength.