

Supporting Information

Cycloaddition Reactivity of Yb@*D*_{3h}-C₇₄: the Carbon Cage Size

Matters

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1. Computational Method:

Geometry optimizations were conducted by using the PBE0 functional^[1] in conjunction with the standard 6-31G* all-electron basis set for the H, C, N and Cl atoms^[2], and the Stuttgart/Dresden quasi-relativistic effective core potential (ECP) and corresponding basis set (SDD) for the Yb atom.^[3] Such a level of theory is denoted here as PBE0/6-31G*~SDD for simplicity. All the DFT calculations were carried out by using the Gaussian 16 software package.^[4] The Mercury^[5] program was employed to visualize the results.

2. Separation, purification and mass spectrum of Yb@D_{3h}-C₇₄.

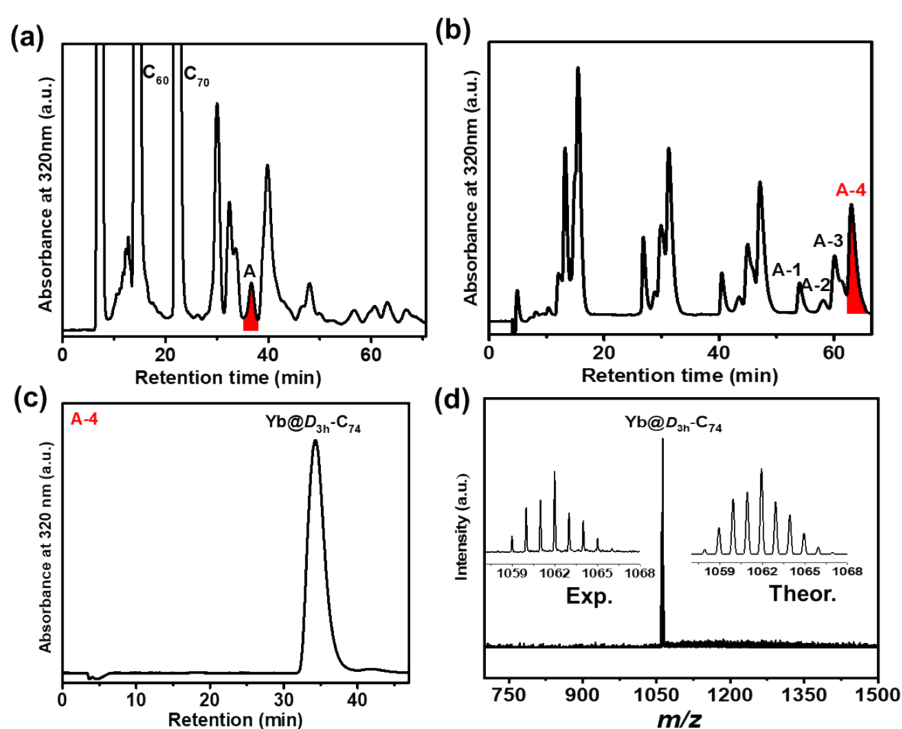


Figure. S1 (a) The HPLC profiles of the raw solution extracted from the carbon soot. Conditions: BP column (20 mm×250 mm); flow rate 10.0 mL min⁻¹; injection volume 10.0 mL; toluene as the eluent. (b) The HPLC profile of the toluene solution containing Yb@D_{3h}-C₇₄ in second-step separation. Conditions: BPM column (20 mm×250 mm); flow rate 15.0 mL min⁻¹; injection volume 5.0 mL; toluene as the eluent. (c) The HPLC profile of the toluene solution containing Yb@D_{3h}-C₇₄ in third-step separation. Conditions: 5PBB column (10 mm×250 mm); flow rate 5.0 mL min⁻¹; injection volume 5.0 mL; toluene as the eluent. (d) MALDI-TOF mass spectrum of Yb@D_{3h}-C₇₄ collected by three-step HPLC purification.

3. The HPLC purification and MALDI-TOF MS characterization of 2a-2c.

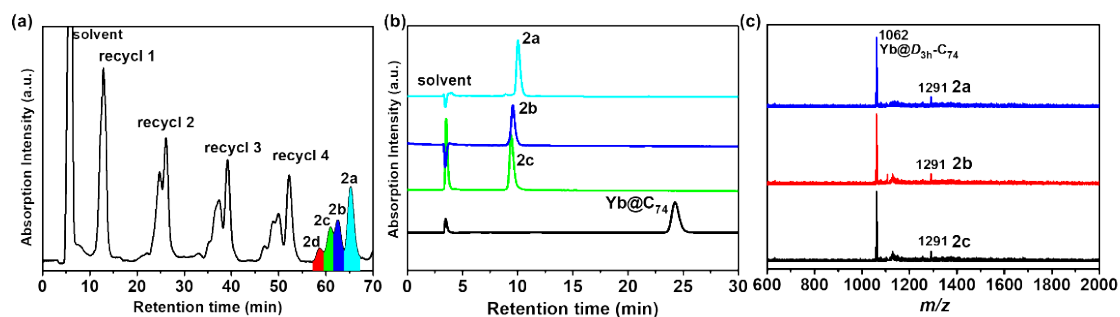


Figure. S2 (a) The prepared HPLC profiles of Yb@D_{3h}-C₇₄ derivatives using a BP column (10 mm×250 mm); flow rate 5.0 mL min⁻¹; injection volume 5 mL; toluene as the eluent. (b) The analytical HPLC profile of pure isomeric adducts **2a**, **2b**, **2c**. Conditions: BP column (2.5 mm×250 mm); flow rate 1.0 mL min⁻¹; injection volume 20 μL; toluene as the eluent. (c) MALDI-TOF mass spectrum of pure isomeric adducts **2a**, **2b**, **2c**.

4. Metal atom disorders and the relative position of major Yb site and center of carbon cage in Yb@D_{3h}-C₇₄ and 2a

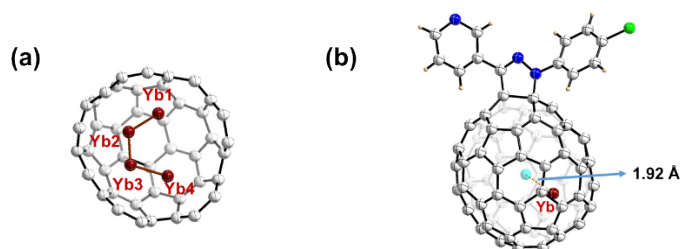


Figure S3. The position disorders of the encapsulated Yb ion in (a) **2a**, the grafted moiety was omitted for clarity; (b) the relative position between the major Yb site and the geometric center of carbon cage (shallow blue point) in **2a**.

5. Crystal data of 2a

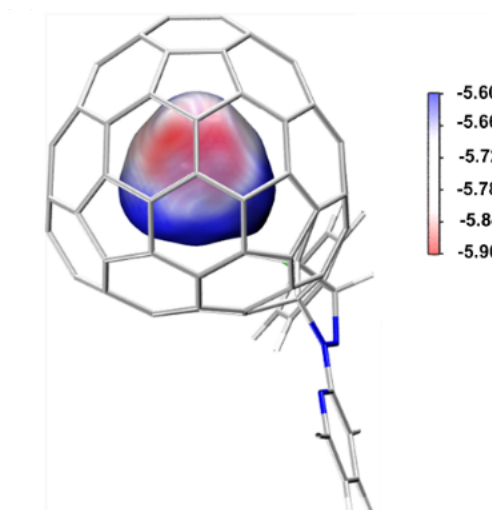
Table S1. Crystal data and structure refinement for **2a**

Identification code	2a
Empirical formula	C ₂₈₇ H ₁₅₃ ClN ₃₃ Yb
Formula weight	4270.61
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	21.677
b/Å	30.619
c/Å	29.418
$\alpha/^\circ$	90
$\beta/^\circ$	98.57
$\gamma/^\circ$	90
Volume/Å ³	19307.4
Z	4
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.469
μ/mm^{-1}	0.573
F(000)	8770.0
Crystal size/mm ³	0.08 × 0.07 × 0.07
Radiation	synchrotron ($\lambda = 0.710$)
2 θ range for data collection/ $^\circ$	1.93 to 38.668
Reflections collected	115764
Independent reflections	15764 [$R_{\text{int}} = 0.038$, $R_{\text{sigma}} = 0.0922$]
Data/restraints/parameters	15764/4173/4185
Goodness-of-fit on F^2	0.964
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0567$, $wR_2 = 0.1388$
Final R indexes [all data]	$R_1 = 0.1207$, $wR_2 = 0.1707$
Largest diff. peak/hole / e Å ⁻³	0.38/-0.30

Table S2. The comparison of these Di-EMFs with different carbon cage sizes.

Crystal of Di-EMFs	Encaged Yb disorders	Distance between main Yb and cage	Addition pattern
Yb@ D_{3h} -C ₇₄ derivative (2a)	Yb1(0.37), Yb2(0.30), Yb2(0.26), Yb4(0.07)	Yb1-C1 (1.96 Å), Yb1-C2 (2.09 Å)	[6,6]-closed addition
Yb@C _{2v} (3)-C ₈₀ -Ad	Yb1(0.43), Yb2(0.18), Yb3(0.14), Yb4(0.14), Yb5(0.04), Yb6(0.04), Yb7(0.03)	Yb1-C1 (2.43 Å), Yb1-C2 (2.48 Å)	[5,6]-open addition
Yb@C ₂ (13)-C ₈₄ -Ad	Yb1(0.32), Yb2(0.29), Yb2(0.22), Yb4(0.09), Yb5(0.08)	Yb1-C1 (2.29 Å), Yb1-C2 (2.34 Å)	[5,6]-closed addition

6. Theoretical calculation of Yb@ D_{3h} -C₇₄ and **2a**

**Figure S4.** The electrostatic potential of the 2⁻ charged outer cage of **2a**.

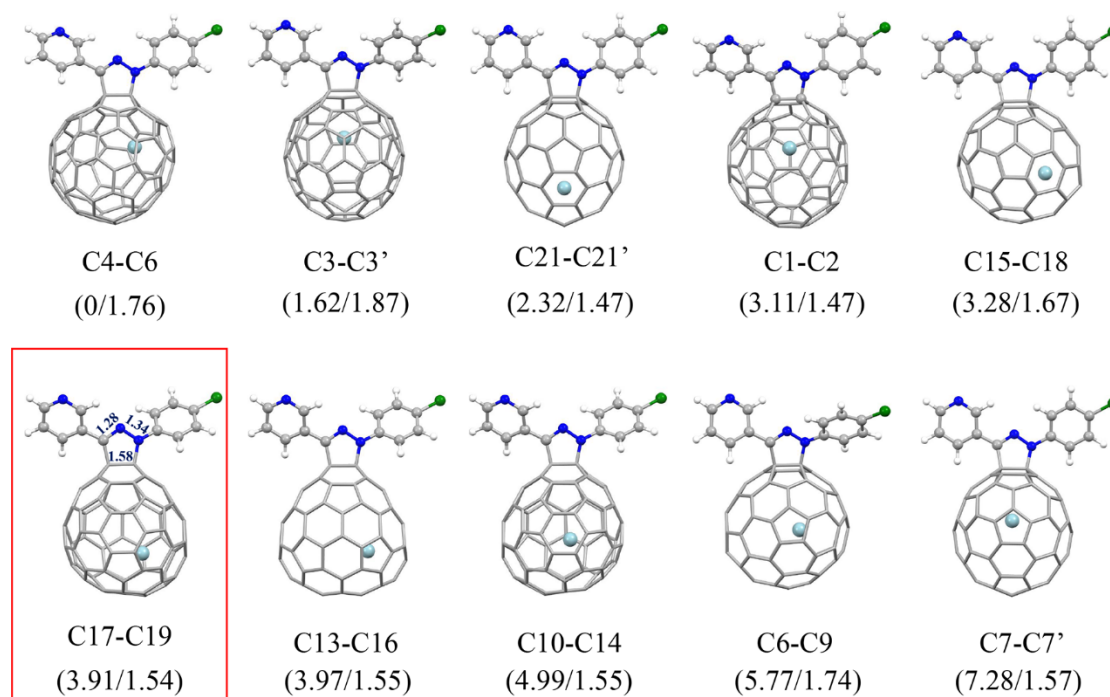


Figure S5. Optimized structures of ten low-energy $\text{Yb}@D_{3h}\text{-C}_{74}$ adducts with relative energies (kcal/mol)/HOMO-LUMO gap energies (eV) in parenthesis. The selected distances are given in Å. C: gray, N: blue, H: white, Cl: green, Yb: light blue. The single crystal structure is highlighted in red box.

Table S3 Relative energies(kcal/mol) and HOMO-LUMO gap energies(eV) of different Yb@D_{3h}-C₇₄(C₁₂N₃H₈Cl) adducts obtained at different levels of theory.

Addition site	Bond type	PBE0		M06-2X	
		ΔE	Gap	ΔE	Gap
4-6	[5,6]	0	1.76	0	2.99
3-3'	[5,6]	1.62	1.87	0.53	3.11
21-21'	[5,6]	2.32	1.47	1.68	2.65
1-2	[5,6]	3.11	1.47	4.37	2.65
15-18	[5,6]	3.28	1.67	2.48	2.88
17-19	[6,6]	3.91	1.54	3.82	2.72
13-16	[6,6]	3.97	1.55	-	-
10-14	[6,6]	4.99	1.55	-	-
6-9	[5,6]	5.77	1.74	-	-
7-7'	[5,6]	7.28	1.57	-	-

7. Electrochemical data of Yb@D_{3h}-C₇₄ and 2a.

Table S4. Redox potentials (V vs. Fc⁺/Fc)^[a] and electrochemical gaps(ΔE_{EC}) of Yb@D_{3h}-C₇₄ and **2a**.

Compound	^{ox} E ₂ (eV)	^{ox} E ₁ (eV)	^{red} E ₁ (eV)	^{red} E ₂ (eV)	^{red} E ₃ (eV)	^{red} E ₂ (eV)	HOMO/ LUMO	ΔE_{EC} (eV)	
Yb@D _{3h} -C ₇₄	-	+0.26	-0.81	-1.28	-	-	5.06/3.99	1.07	Ref. 15
2a	+0.62	+0.15	-0.78	-1.18	-1.89	-2.04	4.95/4.02	0.93	This work
Yb@C _{2v} (3)-C ₈₀	+0.78	+0.34	-0.89	-1.27	-1.87	-2.13	5.14/3.91	1.23	Ref. 9
2	+0.66	+0.13	-0.81	-1.34	-1.76	-2.13	4.93/3.99	0.94	Ref. 9
Yb@C ₂ (13)-C ₈₄	-	+0.45	-0.95	-1.16	-1.50	-1.76	5.25/3.85	1.40	Ref. 19
2b	+0.84	+0.34	-1.11	-1.44	-1.74	-2.19	5.14/3.69	1.45	Ref. 19

[a] DPV values on a Pt-working electrode in 1,2-dichlorobenzene; HOMO and LUMO values calculated according to the equation of E_{LUMO}= -e (E_{red}^{onset} +4.8 V); E_{HOMO}= -e (E_{ox}^{onset} +4.8 V).

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