Electronic Supplemental Information for

**Stabilizing Three-Center Single-Electron Metal-Metal Bond in a Fullerene Cage**

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**Table of Contents**

| Section                                                                 | Page |
|------------------------------------------------------------------------|------|
| S1. Experimental Section                                               | S2   |
| S2. Isolation of Dy₃C₂@I₇-C₈₀                                         | S3   |
| S3. Estimation of the relative yield of Dy₃C₂@I₇-C₈₀.                   | S4   |
| S4. X-ray single crystal data of Dy₃C₂@I₇-C₈₀.                         | S5   |
| S5. Computational analysis of molecular srtucture and bonding in Dy₃C₂@I₇-C₈₀. | S7   |
| S6. Calculated MO levels and charged states of Dy₃C₂@C₈₀ and Sc₃C₂@C₈₀| S18  |
| S7. UV-vis-NIR spectroscopic data and cyclic voltammograms of Dy₃C₂@I₇-C₈₀ in different scanning regions | S19  |
| References                                                             | S21  |
**S1. Experimental Section**

**Materials**

All materials including dry solvents were obtained from commercial suppliers and used without further purification. Dy_2O_3 (99.99%) was purchased from Suzhou Rare Earth New Materials Co., Ltd, TiO_2 (99.99%) were obtained from Sinopharm Chemical Reagent Co., Ltd, Graphite rods (SP) were purchased from Sinosteel Shanghai New Graphite Material Co., Ltd.

**Synthesis, isolation and spectroscopic characterizations of Dy_3C_2@h(7)-C_{80}.**

Dy_3C_2@h(7)-C_{80} were synthesized in a modified Krätschmer-Huffman fullerene generator by vaporizing composite graphite rods (Ø 8 × 100 mm) containing a mixture of Dy_2O_3, TiO_2 and graphite powder (molar ratio of Dy : Ti : C = 1 : 1 : 15) with the addition of 10 mbar N_2 into 200 mbar He. The as-produced soot was Soxhlet-extracted by CS_2 for 24 h, and the resulting brown-yellow solution was distilled to remove CS_2 and then immediately re-dissolved in toluene and subsequently passed through a 0.2 μm Telflon filter (Sartorius AG, Germany) for HPLC separation.

The isolation of Dy_3C_2@h(7)-C_{80} was successfully isolated from fraction A which was isolated running in a 20 x 250 mm 5PYE column (Figure S1a) from Dy_2O_3/TiO_2/N_2 extracts (mixed with a small number of Dy_2O_3/TiO_2/Fe_3N extracts) (flow rate 15.0 ml/min; inject volume 15 ml; toluene as eluent; 40 °C) by the following two-step HPLC. In the first-step HPLC isolation running in a 20 × 250 mm Buckyprep-M column and the chromatogram is shown in Figure S1b (flow rate 15.0 ml/min; inject volume 15 ml; toluene as eluent; 40 °C), Fraction A-3 was collected and then subjected to the second-step HPLC running in a 10 × 250 mm 5PBB column and the chromatogram is shown in Figure S1c (flow rate 5.0 ml/min; inject volume 5 ml; toluene as eluent; 25 °C). Pure Dy_3C_2@h(7)-C_{80} (fraction A-3-3) was obtained, for which the purities of the isolated Dy_3C_2@h(7)-C_{80} were further checked by laser desorption/ionization time-of-flight (LD-TOF) mass spectroscopic (MS) analysis (Biflex III, Bruker Daltonics Inc., Germany) shown in Figure 1a.

UV-vis-NIR spectra were recorded on a UV-vis-NIR 3600 spectrometer (Shimadzu, Japan) using a quartz cell of 1 mm layer thickness and 1 nm resolution with the samples dissolved in toluene.

**Electrochemical Study.** Electrochemical study was performed in o-dichlorobenzene (o-DCB, anhydrous, 99%, Aldrich). The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF_6, puriss. electrochemical grade, Fluka), which was dried under reduced pressure at 340 K for 24 h and stored in glovebox prior to use. Cyclic voltammogram experiments were performed with a CHI 660 potentiostat (CH Instrument, USA) at room temperature in a glovebox. A standard three-electrode arrangement of a platinum (Pt) wire as working electrode, a platinum coil as counter electrode, and a silver wire as a pseudoreference electrode was used. In a comparison experiment, ferrocene (Fc) was added as the internal standard and all potentials are referred to the Fc/Fc^+ couple.
X-ray crystallographic studies. Crystal growth was accomplished by a mixing solution of clusterfullerenes and DPC. After the two solutions diffused together over a period of one-two weeks, small black crystals suitable for X-ray crystallographic study formed upon a slow evaporation of solvent. The crystallographical characterization was performed at 100 K in beamline station BL17B at Shanghai Synchrotron Radiation Facility. The structure was refined using all data (based on F²) by SHELX 2014 within Olex2. And a part of the solvent disorder was dealt with using Program SQUEEZE if needed. Crystallographic data of Dy₃C₂@I₇-C₈₀-2(DPC)-3(C₇H₈) can be obtained free of charge from the Cambridge Crystallographic Data Center (CCDC number: 2057452).

S2. Isolation of Dy₃C₂@I₇-C₈₀

Figure S1. Isolation scheme of Dy₃C₂@I₇-C₈₀. (a) HPLC profile of the Dy₂O₃/TiO₂/N₂ fullerene extract mixture (20×250 mm 5PYE column; flow rate: 15 mL·min⁻¹; injection volume: 15 mL; toluene as eluent; 40 °C). Fraction A was collected and then subjected to the next-step HPLC isolation. Fraction B contains C₈₀, DyCN@C₂n (2n=76, 82) and Dy₃N@C₈₀. (b) HPLC profile of fraction A (20 × 250 mm Buckyprep-M column, flow rate: 15 mL·min⁻¹; injection volume: 15 mL; toluene as eluent; 40 °C), Subfractions A-1, A-2 correspond to C₈₀, Dy₂C₉₀+DyC₉₂, respectively. (c) HPLC profile of fraction A-3 (10 × 250 mm 5PBB column, flow rate: 5 mL·min⁻¹; injection volume: 5 mL; toluene as eluent; 25 °C). Subfractions A-3-1, A-3-2, A-3-4, A-3-5, A-3-6, A-3-7, A-3-8 correspond to DyC₇₄, Dy₂C₈₂, DyC₈₀, DyC₉₀, DyC₉₂(I), DyC₉₂(II), DyC₉₄+Dy₃N@C₈₈.
S3. Estimation of the relative yield of Dy\textsubscript{3}C\textsubscript{2}@I\textsubscript{h}(7)-C\textsubscript{80}.

Table S1. Assignment of each (sub)fraction and their relative abundance.

| Fraction | Sub-fraction | Major component | Relative abundance |
|----------|--------------|-----------------|--------------------|
| B        | B-1          | C\textsubscript{86} | 63.38 %            |
|          | B-2          | DyCN@C\textsubscript{76/82} | 17.51 %            |
|          | B-3          | Dy\textsubscript{3}N@C\textsubscript{80} | 19.11 %            |
| A        | A-1          | C\textsubscript{94} | 64.12 %            |
|          | A-2          | Dy\textsubscript{2}C\textsubscript{90}+DyC\textsubscript{92} | 33.65 %            |
|          | A-3          | DyC\textsubscript{92/94}+Dy\textsubscript{3}N@C\textsubscript{88} | 2.23 %             |
| A-3      | A-3-1        | DyC\textsubscript{84} | 3.73 %             |
|          | A-3-2        | Dy\textsubscript{2}C\textsubscript{82} | 6.88 %             |
|          | A-3-3        | Dy\textsubscript{3}C\textsubscript{2}@C\textsubscript{80} | 6.69 %             |
|          | A-3-4        | DyC\textsubscript{90} | 7.52 %             |
|          | A-3-5        | Dy\textsubscript{2}C\textsubscript{90} | 3.55 %             |
|          | A-3-6        | DyC\textsubscript{92(I)} | 4.82 %             |
|          | A-3-7        | DyC\textsubscript{92(II)} | 11.39 %            |
|          | A-3-8        | DyC\textsubscript{94}+Dy\textsubscript{3}N@C\textsubscript{88} | 55.23 %            |

Given that relative yield of fraction A:B is \textasciitilde2:5, the relative yield of Dy\textsubscript{3}C\textsubscript{2}@I\textsubscript{h}(7)-C\textsubscript{80} to Dy\textsubscript{3}N@C\textsubscript{80} can be calculated as:

\[
\text{Dy}_3\text{C}_2@I_h(7)-\text{C}_{80} : \text{Dy}_3\text{N}@\text{C}_{80} = (6.69 \times 2.23\%) : (19.11\% \times 2.5) \approx 1 : 320.2
\]
### S4. X-ray single crystal data of Dy₃C₂@I₈(7)-C₈₀.

**Table S2.** Crystal and structure data of Dy₃C₂@I₈(7)-C₈₀ at 100 K.

| Crystal                | Dy₃C₂@I₈(7)-C₈₀ |
|------------------------|-----------------|
| Formula weight         | 3550.76         |
| Wavelength (λ, Å)      | 0.71073         |
| Temperature/K          | 100(2)          |
| Crystal system         | monoclinic      |
| Space group            | P2₁/c           |
| a, Å                   | 14.761          |
| b, Å                   | 32.102          |
| c, Å                   | 32.240          |
| α, deg                 | 90              |
| β, deg                 | 101.88          |
| γ, deg                 | 90              |
| Volume, Å³             | 14949.9         |
| Z                      | 4               |
| Unique data (R_{int})  | 25480(0.069)    |
| Parameters             | 2371            |
| Restraints             | 1083            |
| Observed data (I > 2σ(I)) | 20088           |
| R1 (observed)          | 0.0907          |
| wR2 (all data)         | 0.2709          |

*a* For data with I > 2σ(I), R1 = 1/|Σ [F_o] - |F_c|/|Σ |F_o|.  
*b* For all data, wR2 = [Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)²]]^{1/2}.  

55
Figure S2. All disordered dysprosium sites in Dy$_3$C$_2$@h$_6$-C$_{80}$ relative to cage orientation. The fractional occupancies are 0.482(2), 0.501(2), 0.429(3), 0.175(2), 0.205(2), 0.138(2), 0.1174(19), 0.073(2), 0.238(3), 0.138(3), 0.051(2), 0.139(3), 0.188(3), 0.126(2) for Dy1, Dy2, Dy3, Dy4, Dy5, Dy6, Dy7, Dy8, Dy9, Dy10, Dy11, Dy12, Dy13, and Dy14, respectively.

Figure S3. The molecular packing of Dy$_3$C$_2$@h$_6$(7)-C$_{80}$-2DPC. Only the major Dy$_3$C$_2$ site is shown. Solvent molecules and H atoms are omitted for clarity.
S5. Computational analysis of molecular structure and bonding in Dy$_3$C$_2@I_8(7)$-C$_{80}$.

1) DFT calculations of molecular structures:
A reliable description of molecules with partially-filled 4f-shell requires expensive multiconfigurational approaches and is hardly possible for a molecule like Dy$_3$C$_2@C_{80}$ at this moment. Single-determinant DFT calculations with explicit consideration of 4f electrons are not very reliable, and to avoid this problem we therefore preferred to use 4f-in-core effective core potential with ECP55MWB-II basis set to treat Dy atoms. For Sc and carbon atoms, def2-TZVPP basis was used. Number of basis functions and contraction schemes are listed below in \{s/p/d/f/g\} form. Calculations were performed with Orca package using PBE functional.

C: \{62111/411/11/1\}
Sc: \{842111/63111/4111/11/1\}
Dy: \{311111/31111/21111/111/1\}

In addition to limited Dy calculations used for property evaluation, we also performed a broader search of rotational conformers for Y$_3$C$_2@C_{80}$ using Priroda code with implemented basis set of TZ2P quality for carbon and SBKJC-type effective core potential for Y. Calculations showed several conformers different in the relative orientation of the Y$_3$C$_2$ cluster within the fullerene cage. The structure of the cluster remains almost intact, relative energies of such rotational conformers are close within few kJ/mol. Priroda code was also used to locate the transition state between bat ray and trifoliate configurations.

Table S3. Relative energies (kJ mol$^{-1}$) of different cluster configurations in Y$_3$C$_2@C_{80}$ and Dy$_3$C$_2@C_{80}$

|          | bat ray | trifoliate | transition state |
|----------|---------|------------|------------------|
| Y$_3$C$_2@C_{80}$ | 0.0     | 60.2       | 105.6            |
| Dy$_3$C$_2@C_{80}$/Y$_3$C$_2@C_{80}$[a] | 0.0     | 89.4       | 139.8 [b]        |
| Dy$_3$C$_2@C_{80}$ | 0.0     | 89.9       |                  |

[a] Single-point energy calculation for Dy$_3$C$_2@C_{80}$ in geometry optimized for Y$_3$C$_2@C_{80}$
[b] Figure 3 uses this value for the relative energy of TS configuration
Figure S4. (a,b) DFT optimization of Y₃C₂@C₈₈ with different starting configurations of the Y₃C₂ cluster, leading to flattened bat ray configuration after optimization. (c) Spin-density distribution in DFT-optimized Dy₃C₂@C₈₈ with flattened bat ray configuration of Dy₃C₂ cluster.
2) Canonical molecular orbitals:

Figure S5. Canonical Kohn-Sham molecular orbitals of Dy$_3$C$_2$@C$_{80}$ in selected energy range. Occupation of a given orbital (1 for occupied and 0 for unoccupied) is given in parentheses followed by the orbital energy in eV. For SOMO and some low-energy unoccupied orbitals, $\alpha$ and $\beta$ orbital are shown as they have somewhat different energies and shapes because of the spin polarization. For other orbitals, $\beta$ orbitals are not shown as they are similar to $\alpha$ counterparts.
Figure S5. (continued) Canonical Kohn-Sham molecular orbitals of Dy$_3$C$_2$@C$_{80}$ in selected energy range. Occupation of a given orbital (1 for occupied and 0 for unoccupied) is given in parentheses followed by the orbital energy in eV. For SOMO and some low-energy unoccupied orbitals, $\alpha$ and $\beta$ orbital are shown as they have somewhat different energies and shapes because of the spin polarization. For other orbitals, $\beta$ orbitals are not shown as they are similar to $\alpha$ counterparts.
Figure S5. (continued) Canonical Kohn-Sham molecular orbitals of Dy$_2$C$_2$@C$_{80}$ in selected energy range. Occupation of a given orbital (1 for occupied and 0 for unoccupied) is given in parentheses followed by the orbital energy in eV. For SOMO and some low-energy unoccupied orbitals, $\alpha$ and $\beta$ orbital are shown as they have somewhat different energies and shapes because of the spin polarization. For other orbitals, $\beta$ orbitals are not shown as they are similar to $\alpha$ counterparts.
Figure S5. (continued) Canonical Kohn-Sham molecular orbitals of Dy$_3$C$_2$@C$_{80}$ in selected energy range. Occupation of a given orbital (1 for occupied and 0 for unoccupied) is given in parentheses followed by the orbital energy in eV. For SOMO and some low-energy unoccupied orbitals, α and β orbital are shown as they have somewhat different energies and shapes because of the spin polarization. For other orbitals, β orbitals are not shown as they are similar to α counterparts.
Figure S5. (continued) Canonical Kohn-Sham molecular orbitals of Dy$_3$C$_2$@C$_{80}$ in selected energy range. Occupation of a given orbital (1 for occupied and 0 for unoccupied) is given in parentheses followed by the orbital energy in eV. For SOMO and some low-energy unoccupied orbitals, $\alpha$ and $\beta$ orbital are shown as they have somewhat different energies and shapes because of the spin polarization. For other orbitals, $\beta$ orbitals are not shown as they are similar to $\alpha$ counterparts.
3) Localized molecular orbitals:
For a more illustrative analysis of the bonding, we performed localization of molecular orbitals with Pipek-Mezey approach.\textsuperscript{[58]} Localized orbitals give more condensed representation of the orbital than (delocalized) canonical orbitals. Figures S4 and S5 show PM-localized orbitals for the two configurations of Dy\textsubscript{3}C\textsubscript{2} cluster in Dy\textsubscript{3}C\textsubscript{2}@C\textsubscript{80}.

\textbf{Figure S6.} PM-localized orbitals of the bat ray configuration of Dy\textsubscript{3}C\textsubscript{2} cluster in Dy\textsubscript{3}C\textsubscript{2}@C\textsubscript{80}. One σ-bonding and two π-bonding orbitals of C\textsubscript{2} unit are two-fold occupied (both α and β components are present). The only singly-occupied cluster-based orbital (only α component is present) is the 3-center Dy–Dy–Dy bonding MO (it has similar shape to the canonical MO).

\textbf{Figure S7.} PM-localized orbitals of the trifoliate configuration of Dy\textsubscript{3}C\textsubscript{2} cluster in Dy\textsubscript{3}C\textsubscript{2}@C\textsubscript{80}. The σ-bonding orbitals of C\textsubscript{2} unit is two-fold occupied (both α and β components are present). π-bonding orbitals of C\textsubscript{2} unit are more complex. One can see two β orbitals and one α orbital with clear π-bonding character. There are two other α orbitals with mixed C\textsubscript{2}-π-bonding/5d-π bonding character.
4) Spin density distribution:

Figure S8. DFT-computed spin density distribution in Dy$_3$C$_2$@C$_{80}$ with bat ray (left) and trifoliate (right) cluster configurations. Note that the use of 4f-in-core potential limits the spin density to the valence part only, whereas 4f-shell is not represented.
5) QTAIM analysis of charge distribution and bonding:

Topological analysis of the electron density was performed using Bader Quantum Theory of Atoms in Molecules (QTAIM).

QTAIM of the electron density required full-electron calculations, whereas the use of ECP basis may lead to artefacts. Among rare-earth metals of comparable ionic radius, Y and Gd analogs can be described by a single-determinant wavefunction and can be therefore reliably treated with full-electron DFT calculations. We thus performed QTAIM analysis of Y$_3$C$_2$@C$_{80}$ and Gd$_3$C$_2$@C$_{80}$ using DFT-optimized Dy$_3$C$_2$@C$_{80}$ geometry. Electron density was computed at the PBE level with DKH scalar-relativistic correction as implemented in Orca with def2-SVP basis set for carbon, and SARC-DKH-TZVP basis sets for Gd and Y.

QTAIM calculations were performed with the AIMAll package. From the large set of parameters provided by QTAIM, we focus here on atomic charges and delocalization indices (the number of electron pairs shared between two atoms aka QTAIM bond orders). Figure S7 compares bat ray and trifoliate cluster configurations for Y$_3$C$_2$@C$_{80}$ and Gd$_3$C$_2$@C$_{80}$ along with the atomic charges and delocalization indices. For Y analog, calculations predict more ionic nature (more positive/negative atomic charges of metals/carbon, and smaller metal–carbon bond orders), but the overall bonding situation in Y$_3$C$_2$@C$_{80}$ and Gd$_3$C$_2$@C$_{80}$ is similar. The bat ray configuration has less positive/negative atomic charges of metals/carbons than in the trifoliate configuration. It points to the higher covalency in the bat ray configuration. The C–C bond order in the bay ray structure (2.35 for Y and 2.31 for Gd) is higher than in the trifoliate one (2.03 for Y and 1.95 for Gd), agreeing with a smaller formal negative charge (C$_2$^2− versus C$_2$^3−).

In the trifoliate configuration, each metal is bonded to the C$_2$ group in η$^2$-manner. Note however that two of three metals have somewhat higher M–C bond orders, which also corresponds to the shape of localized MOs, which have large contributions from two metals (Fig. S5). Metal-metal interactions in the trifoliate configuration are negligible (delocalization indices 0.03–0.04 for Y and 0.04–0.05 for Gd). In the bat ray configuration, two metals also have η$^1$-bonding (M–C bond orders near 0.35–0.41/0.21–0.24), whereas one shows η$^1$-bonding to only one carbon (M–C bond order 0.47 for Y and 0.52 for Gd). Most importantly, QTAIM analysis reveals considerable M–M delocalization indices in the bat ray configuration. M–M bond orders of 0.12/0.14/0.16 for Y and 0.14/0.15/0.17 for Gd sum up to 0.41 (Y) or 0.45 (Gd) electron pairs shared between three metal atoms, perfectly corresponding to the three center-one electron bond.
Figure S9. QTAIM atomic charges and delocalization indices (bond orders) in Gd$_3$C$_2$@C$_{80}$ and Y$_3$C$_2$@C$_{80}$ with bat ray (upper row) and trifoliate (bottom row) cluster configurations (atomic coordinates are optimized for Dy$_3$C$_2$@C$_{80}$).
S6. MO levels and charged states of Dy$_3$C$_2$@C$_{80}$ and Sc$_3$C$_2$@C$_{80}$

Frontier MO energies of Dy$_3$C$_2$@C$_{80}$ and Sc$_3$C$_2$@C$_{80}$ are compared in Table S5. Note that both HOMO and LUMO here correspond to the occupied and unoccupied components of the SOMO (see Fig. 3 in the main text for MO levels of other orbitals). The HOMO-LUMO gap of Dy$_3$C$_2$@C$_{80}$ is higher than in Sc$_3$C$_2$@C$_{80}$, which may be also reflected in their electrochemical properties, i.e. the electrochemical gap of Dy$_3$C$_2$@C$_{80}$ is higher than in Sc$_3$C$_2$@C$_{80}$. However, considering only MO energies, one might expect that the oxidation potential of Sc$_3$C$_2$@C$_{80}$ should be more positive than in Dy$_3$C$_2$@C$_{80}$, which does not agree with the experimental observation. However, experimental redox processes in fact correspond not to the arbitrary orbital energies but to the energy differences between the charged state. Thus, we performed DFT optimization of Dy$_3$C$_2$@C$_{80}$ and Sc$_3$C$_2$@C$_{80}$ in their cation and anionic states, and then also performed single-point energy calculations in o-DCB modeled as polarized continuum (C-PCM model). Table S5 also compares electron affinities (EA) and ionization potential (IP) of the two molecules in gas phase and their values with solvation correction (which correspond to redox potentials). Calculations in the gas phase show that although HOMO level of Sc$_3$C$_2$@C$_{80}$ is lower in energy than in Dy$_3$C$_2$@C$_{80}$, IP of Sc$_3$C$_2$@C$_{80}$ is smaller than that of Dy$_3$C$_2$@C$_{80}$. In agreement with earlier results,[512] we also found that the Sc$_3$C$_2$ cluster in Sc$_3$C$_2$@C$_{80}^+$ attains the trifoliate configuration. With solvation correction, computed electrochemical gap of Dy$_3$C$_2$@C$_{80}$ is 1.10 V (versus experimental 1.18 V) and 0.61 V in Sc$_3$C$_2$@C$_{80}$ (versus experimental 0.47 V).

Table S4. DFT-computed MO energies, ionization potential (IP), and electron affinities (EA) of Dy$_3$C$_2$@C$_{80}$ and Sc$_3$C$_2$@C$_{80}$ in gas phase and in o-DCB (eV).

|                        | Dy$_3$C$_2$@C$_{80}$ | Sc$_3$C$_2$@C$_{80}$ |
|------------------------|----------------------|----------------------|
| $E_{\text{ox}}$(exp), V | +0.19                | −0.03                |
| $E_{\text{red}}$(exp), V | −0.99                | −0.50                |
| $\Delta E_{\text{EC}}$(exp), V | 1.18                | 0.47                |
| SOMO(occ)              | −4.878               | −4.998               |
| SOMO(unocc)            | −4.030               | −4.500               |
| $\Delta E_{\text{MO}}$ | 0.848                | 0.498                |
| $EA$ (gas)             | 2.786                | 3.221                |
| $IP$ (gas)             | 6.129                | 5.954                |
| $\Delta (IP-EA)$       | 3.343                | 2.733                |
| $\Delta E_{\text{solv}}$(0) | −0.066              | −0.097               |
| $\Delta E_{\text{solv}}$ (−1) | −1.047              | −1.047               |
| $\Delta E_{\text{solv}}$ (+1) | −1.329              | −1.277               |
| $EA$(oDCB) $\equiv E_{\text{red}}$[b] | 3.768                | 4.162                |
| $IP$(oDCB) $\equiv E_{\text{ox}}$[v] | 4.865                | 4.774                |
| $\Delta E_{\text{EC}}$(oDCB) | 1.098                | 0.612                |

[a] redox potentials in o-DCB versus Fe(Cp)$_2$+/0 pair;
[b] absolute potentials
Table S5. DFT-optimized bond lengths (Å) in bat ray configuration of Dy₃C₂@C₈₀ in cation, neutral, and anionic states.

|                | q = +1 | q = 0 | q = -1 |
|----------------|--------|-------|--------|
| Dy₁–Dy₂        | 3.542  | 3.408 | 3.320  |
| Dy₁–Dy₃        | 3.668  | 3.441 | 3.363  |
| Dy₂–Dy₃        | 3.472  | 3.382 | 3.366  |
| Dy₁–C₈₁        | 2.545  | 2.686 | 2.692  |
| Dy₁–C₈₂        | 2.372  | 2.357 | 2.361  |
| Dy₂–C₈₁        | 2.314  | 2.325 | 2.334  |
| Dy₃–C₈₁        | 2.608  | 2.677 | 2.666  |
| Dy₃–C₈₂        | 2.350  | 2.365 | 2.370  |
| C₈₁–C₈₂        | 1.260  | 1.256 | 1.256  |

Comparison of the bond lengths in Dy₃C₂ cluster in different charge state of the molecule (Table S5) shows that Dy–Dy distances are most affected. In the anion, the distances become shorter whereas in the cation they are longer than in the neutral state. Changes of Dy–C and C–C bond are less pronounced. These changes agree well with the population and depopulation of the Dy–Dy–Dy bonding orbital.

S7. UV-vis-NIR spectroscopic data and cyclic voltammograms of Dy₃C₂@I₈₋(7)-C₈₀ in different scanning regions.

Table S6. Redox Potentials (V vs. Fc/Fc⁺), electrochemical gaps (ΔE_EC) of Dy₃C₂@I₈₋(7)-C₈₀ and other reported M₃C₂@I₈₋(7)-C₈₀ (M=Sc, Ti).

| sample                  | E₁/₂ (V vs Fc/Fc⁺) | ΔE_EC / V [a] | Absorption onset (λ_onset, nm) | ΔE_optical / eV [b] | Ref.   |
|-------------------------|---------------------|---------------|--------------------------------|---------------------|--------|
|                         | Reduction steps (E_red) | Oxidation step (E_ox) |                           |                      |        |
|                         | first   | second  | third  | first   |                      |        |
| Dy₃C₂@I₈₋(7)-C₈₀       | -0.99   | -1.65   | [c]   | /       | +0.19               | 1.18   | 835  | 1.49 | This work |
| Sc₃C₂@I₈₋(7)-C₈₀       | -0.50   | -1.64   | /      | /       | -0.03               | 0.47   | 900  | 1.38 | S13     |
| Dy₃TiC₂@I₈₋(7)-C₈₀     | -1.14   | -1.58   | -2.29  | +0.47   | 1.61                | 1.13   | 1100 | 0.89 | S14     |
| Sc₂TiC₂@I₈₋(7)-C₈₀     | -0.76   | -1.01   | -1.96  | +0.53   | 1.26                | 1.26   | 1400 | 0.89 | S15     |

*a ΔE_EC = E₁/₂, ox - E₁/₂, red.  
b ΔE_optical = 1240/onset.  
c irreversible, d established from ref. S13.
Figure S10. Cyclic voltammograms of Dy$_3$C$_2$I$_h$(7)-C$_{80}$ measured in o-DCB solution in different scanning regions showing the correlation of each reduction step with the corresponding reoxidation step. Scan rate: 100 mV·s$^{-1}$, TBAPF$_6$ as supporting electrolyte. Each redox step is marked with a number and a solid dot to aid comparison. The asterisk labels the oxidation peak of ferrocene.
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