Supporting Information

High Blocking Temperature of Magnetization and Giant Coercivity in the Azafullerene Tb$_2$@C$_{79}$N with a Single-Electron Terbium–Terbium Bond

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Supporting Information

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Synthesis and HPLC separation of Tb$_2$@C$_{79}$N

Tb$_2$@C$_{79}$N was synthesized by a 3-phase electric arc discharge evaporation of graphite rods with Tb$_4$O$_7$ powder (Jiayuan Advanced Materials Co., Ltd) by injection into the 3-phase electric arc zone in a N$_2$ atmosphere. A HPLC trace of the product mixture after a usual amino functionalized silica chemical separation step is shown in Figure S1. The sample was then subjected to multiple collection passes with 100 μL injections with a PBB column (4.5 mm I.D. x 250 mm); λ = 390 nm; flow rate 1.0 mL/min; 1:1 toluene as eluent. The chromatographic trace after this separation stage is shown in Figure S2. At this stage, the desired Tb$_2$@C$_{79}$N still contains ~10% Tb$_2$N@C$_{80}$ as well as TbC$_{81}$N and Tb$_2$C$_{80}$N$_2$ as illustrated in the mass spectrum (Figure S3). In a final step, recycling HPLC with a Buckyprep column was used to obtain pure Tb$_2$@C$_{79}$N (Figure S4).

![Figure S1 HPLC trace of Tb$_2$@C$_{79}$N after the amino functionalized silica chemical separation step. PBB column (4.5 mm I.D. x 250 mm); λ = 390 nm; flow rate 1.0 mL/min; 1:1 toluene 25 °C; 100 μL injection.](image-url)
Figure S2. HPLC traces of purified Tb$_2$@C$_{79}$N. PBB column (4.5 mm I.D. x 250 mm); $\lambda = 390$ nm; flow rate 1.0 mL/min; toluene eluent; 25 °C; 100 UL injection.

Figure S3. Mass spectrum of new fullerenes: TbC$_{81}$N (1145 amu) and Tb$_2$C$_{80}$N$_2$ (1306 amu).
**Figure S4a.** Recycling HPLC separation of Tb$_2$@C$_{79}$N (Buckyprep column). Fraction F4 contains the target compound, Tb$_2$@C$_{79}$N, and is separated further to obtain Tb$_2$@C$_{79}$N in a pure form.

**Figure S4b.** Recycling HPLC separation of the fraction F4. Fraction F4-4 contains the target compound, Tb$_2$@C$_{79}$N.
**Figure S5a.** LDI mass-spectra of the fraction **F4-2**, positive (red) and negative (black) ion modes (Bruker autoflex mass-spectrometer). The peak at 1306 is assigned to Tb$_2$C$_{80}$N$_2$ (presumably, Tb$_2$CN@C$_{79}$N).

**Figure S5b.** LDI mass-spectra of the fraction **F4-4**, positive (red) and negative (black) ion modes (Bruker autoflex mass-spectrometer). The peak at 1280 is assigned to Tb$_2$@C$_{79}$N.
DFT calculations

Optimization of molecular structures of Tb$_2$@C$_{79}$N conformers were performed at the PBE-D level using VASP code (version 5.0) with PAW pseudopotentials. To screen many possible orientations of the Tb$_2$ dimer inside the C$_{79}$N cage, 120 initial configurations were prepared by fixing the cage coordinates (with nitrogen atom at the pentagon/hexagon/hexagon junction, 5/6/6) and rotating the Tb$_2$ dimer around Fibonacci sphere. Optimization for all structures resulted in several unique minima listed in Table S1. Additionally, C$_{79}$N cage with nitrogen at the hexagon/hexagon/hexagon (6/6/6) position was also considered, but with a smaller amount of initial Tb$_2$ orientations. The calculations proved that 5/6/6 position of nitrogen is much more energetically favourable. Inside the cage, Tb$_2$ cluster has at least five low-energy conformations, which likely to coexist in the real sample.

Table S1. Relative energies and molecular structures of DFT-optimized conformers of Tb$_2$@C$_{79}$N

| Conformer, $\Delta E$ | $\Delta E$ | N: 5/6/6 |
|-----------------------|------------|----------|
| **Conf. 1**           | $\Delta E = 0.0$ kJ/mol | N: 5/6/6 |
| **Conf. 2**           | $\Delta E = 1.8$ kJ/mol | N: 5/6/6 |
| **Conf. 3**           | $\Delta E = 1.9$ kJ/mol | N: 5/6/6 |
| Conf. | ΔE | N:   |
|-------|----|------|
| 4     | 2.2 kJ/mol | 5/6/6 |
| 5     | 5.3 kJ/mol  | 5/6/6 |
| 6     | 10.4 kJ/mol  | 5/6/6 |
| 7     | 51.4 kJ/mol  | 6/6/6 |
Conf. 8
$\Delta E = 51.8$ kJ/mol
N: 6/6/6

Conf. 9
$\Delta E = 53.2$ kJ/mol
N: 6/6/6

Conf. 9
$\Delta E = 79.5$ kJ/mol
N: 6/6/6
Relaxation times of Tb$_2$@C$_{70}$N in zero field determined by DC magnetometry

DC magnetic measurements were performed using a Quantum Design VSM MPMS3 magnetometer. The samples were drop-casted from Cs$_2$ solution into a standard powder sample holder.

Below 24 K, average magnetization relaxation times of Tb$_2$@C$_{70}$N were determined by DC magnetometry. The sample was first magnetized to saturation, then the field was swept to 0 T with the highest possible sweep rate, and then decay of magnetization of recorded, and the decay curve was then fitted with stretched exponential function:

$$M(t) = M_{eq} + (M_0 - M_{eq}) \exp\left[-\left(\frac{t}{\tau_m}\right)\beta\right]$$

(S1)

Where $M_{eq}$ and $M_0$ are the equilibrium and initial magnetizations, respectively, $\tau_m$ is a characteristic relaxation time and $\beta$ is an additional parameter that corresponds to the time-dependent decay rate. The need of the stretched exponential (instead of single exponential decay, $\beta = 1$) is caused by the change of the relaxation rate over the time, presumably caused by redistribution of local dipolar fields when magnetization of the sample is changing (in our measurements, $\beta$ is found to be between 0.7 and 0.8, see Table S2). Hence, stretched exponential fit gives an average relaxation time. Reliable estimation of $\tau_m$ for such values of $\beta$ requires recording of the decay for ca 3 times $\tau_m$ or longer. For low temperature measurements, this requirement cannot be properly fulfilled because relaxation times are too long. If decay time is considerably shorter than 3 $\tau_m$, the fit with equation S1 gives rather ambiguous results because $\tau_m$ strongly depends on $M_{eq}$, which is not well defined. Although $M_{eq}$ should be equal zero for a paramagnet in zero field, the small remnant magnetization is usually present even in zero field (e.g., diamagnetic contribution, small magnetization caused by deviation of the field from zero, etc). To avoid these ambiguities, $M_{eq}$ values were determined in separate measurements. Namely, the temperature was increased above blocking temperature to cause complete relaxation of magnetization, and then decreased again to the required temperature. Magnetization of the demagnetized sample was then measured over certain time, giving estimation of the $M_{eq}$ parameter. Using $M_{eq}$ values determined this way eliminates ambiguity in $M_{eq}$ and gives reliable estimation of relaxation times even when the measurement time is considerably shorter than $\tau_m$. Detailed discussion of the determination of long magnetization relaxation times is given in Ref. 4.
Figure S6. Selected magnetization decay curves, red lines are fits with stretched exponential function.
Table S2. Relaxation times of Tb$_2$@C$_{70}$N in zero field determined by DC magnetometry

| $T$, K | $\tau_m$, s | St. Dev. $\tau_m$, s | $\beta$ |
|-------|-------------|----------------|---------|
|  3.5  |  16302      |  14.5          |  0.72   |
|   6   |  16648      |  10.3          |  0.72   |
|  15   |  10843      |   9.1          |  0.73   |
|  17   |   9905      |  13.9          |  0.70   |
|  18   |   8930      |   5.2          |  0.75   |
|  19   |   7990      |   9.8          |  0.74   |
|  20   |   6564      |   5.7          |  0.77   |
| 20.5  |   6035      |   6.3          |  0.79   |
|  21   |   3815      |   1.8          |  0.79   |
| 21.3  |   2995      |   0.6          |  0.81   |
| 21.5  |   2493      |   0.5          |  0.81   |
| 21.8  |   1863      |   0.8          |  0.81   |
|  22   |   1340      |   1.0          |  0.79   |
| 22.4  |    967      |   1.7          |  0.79   |
| 22.7  |    687      |   1.5          |  0.81   |
|  23   |    338      |   2.3          |  0.73   |
| 23.4  |    282      |   1.5          |  0.80   |
| 23.7  |    185      |   1.7          |  0.73   |
Relaxation times of Tb$_2$@C$_{79}$N determined by AC magnetometry

A small oscillating magnetic field is used to drive spins in the sample with the frequencies between 0.1 and 1000 Hz (MPMS XL magnetometer is used for these measurements). The frequency $\omega$ of the oscillating magnetic field is scanned, and in-phase ($\chi'$) and out-of-phase ($\chi''$) magnetic susceptibilities are measured. The relaxation time is then calculated by fitting the $\chi'$ and $\chi''$ with the following formula (generalized Debye model):

$$
\chi'(\omega) = \chi_S + (\chi_T - \chi_S) \frac{1 + (\omega \tau_m)^{1-\alpha} \sin(\pi \alpha / 2)}{1 + 2 (\omega \tau_m)^{1-\alpha} \sin(\pi \alpha / 2) + (\omega \tau_m)^{2-2\alpha}}
$$

$$
\chi''(\omega) = (\chi_T - \chi_S) \frac{(\omega \tau_m)^{1-\alpha} \cos(\pi \alpha / 2)}{1 + 2 (\omega \tau_m)^{1-\alpha} \sin(\pi \alpha / 2) + (\omega \tau_m)^{2-2\alpha}}
$$

where $\alpha$ is the parameter, accounting for a distribution of the relaxation times ($\alpha=0$ when only one process is present), and $\chi_S/\chi_T$ are adiabatic and isothermal susceptibilities. Table S3 lists relaxation times, their standard deviations (from the fit) and $\alpha$ parameters, whereas Figure S7 shows frequency dependence of $\chi'$ and $\chi''$ at different temperatures and corresponding Cole-Cole (Agrand) plots.

Table S3. Relaxation times of Tb$_2$@C$_{79}$N in zero DC field determined by AC magnetometry

| $T$, K | $\tau_m$, s | St. Dev. $\tau_m$, s | $\alpha$ |
|-------|-------------|----------------------|------|
| 31    | 9.07·10$^{-2}$ | 1.69·10$^{-3}$ | 0.09 |
| 32    | 4.99·10$^{-2}$ | 8.00·10$^{-4}$ | 0.18 |
| 33    | 2.47·10$^{-2}$ | 4.41·10$^{-4}$ | 0.30 |
| 34    | 1.22·10$^{-2}$ | 3.47·10$^{-4}$ | 0.30 |
| 35    | 6.00·10$^{-3}$ | 1.93·10$^{-4}$ | 0.19 |
| 37    | 1.84·10$^{-3}$ | 8.12·10$^{-5}$ | 0.09 |
| 38    | 9.02·10$^{-4}$ | 7.77·10$^{-5}$ | 0.13 |
| 39    | 5.65·10$^{-4}$ | 4.27·10$^{-5}$ | 0.10 |
Figure S7. In-phase ($\chi'$) and out-of-phase ($\chi''$) magnetic susceptibility of Tb$_2$@C$_{29}$N and corresponding Cole-Cole plots. Dots are experimental values, lines are fits.
**Ab initio calculations**

*Ab initio* energies and wave functions of ligand field multiplets for the TbY@C\textsubscript{79}N\textsuperscript{−} molecules were calculated at the CASSCF/SO-RASSI level of theory using MOLCAS 8.0. The single ion LF-parameters were calculated based on *ab initio* data with the use of SINGLE_ANISO module. Figure S8 shows orientation of quantization axes for each Tb ion in different conformers, and Tables S4-S7 lists the energies and composition of ligand-field multiplets in $m_J$ basis.

Fig. S8 Orientation of quantization axes for individual Tb ions in Tb\textsubscript{2}@C\textsubscript{79}N conformers determined by *ab initio* calculations for TbY@C\textsubscript{79}N\textsuperscript{−} (for more details on the molecular structures of conformers, see Table S1). Analysis in the main manuscript is based on the results for **Conf 2**, but as can be seen, all other conformers have similar properties.
Table S4. Energies and composition in $|m_j\rangle$ basis of the ligand-field states of two Tb ions in Conf 1 of TbY@C$_{75}$N$^\circ$.  

| pKD | $E$, cm$^{-1}$ | Composition, % | $E$, cm$^{-1}$ | Composition, % |
|-----|---------------|----------------|---------------|----------------|
| 1   | 0.00          | 99.9|±6             | 0.00          | 100.0|±6         |
|     | 0.01          | 99.9|±6             |               | 100.0|±6         |
| 2   | 277.60        | 99.8|±5             | 252.74        | 99.9|±5         |
|     | 277.76        | 99.8|±5             | 252.87        | 99.9|±5         |
| 3   | 510.17        | 99.3|±4             | 510.25        | 99.4|±4         |
|     | 510.88        | 99.5|±4             | 511.67        | 99.8|±4         |
| 4   | 706.83        | 96.6|±3             | 711.11        | 99.2|±3         |
|     | 711.81        | 97.7|±3             | 730.60        | 98.1|±3         |
| 5   | 848.08        | 85.7|±2 + 12.9|0      | 852.54        | 89.4|±2 + 10.2|0    |
|     | 884.80        | 96.5|±2 + 2.1|1      | 875.38        | 99.4|±2         |
| 6   | 942.05        | 94.1|±1 + 3.0|±3 + 2.4|±2          | 924.23        | 97.8|±1         |
|     | 1042.23       | 93.3|±1 + 4.2|0       | 991.72        | 99.3|±1         |
| 5   | 1051.15       | 82.1|0 + 12.2|±2 + 4.6|±1          | 997.96        | 89.4|0 + 10.4|±2 |

“pKD” stands for pseudo-Kramers doublet, “S” denotes a singlet state. The contribution for the “$|±X\rangle$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ functions.

Table S5. Energies, composition in $|m_j\rangle$ basis of the ligand-field states, and $g_z$-components of Tb ion in Conf 2 of TbY@C$_{75}$N$^\circ$. Simulations of magnetic properties were performed using LF parameters and orientation of magnetic moment for this structure.

| pKD | $E$, cm$^{-1}$ | Composition, % | $g_z$ |
|-----|---------------|----------------|-------|
| 1   | 0.00          | 99.9|±6           | 17.9310 |
|     | 0.01          | 99.9|±6           |       |
| 2   | 264.65        | 99.5|±5           | 14.6411 |
|     | 264.96        | 99.6|±5           |       |
| 3   | 510.51        | 98.8|±4           | 11.4294 |
|     | 511.32        | 99.0|±4           |       |
| 4   | 709.49        | 97.1|±3           | 8.2938  |
|     | 717.69        | 98.4|±3           |       |
| 5   | 845.22        | 87.4|±2 + 12.0|0      | 5.6293  |
|     | 874.74        | 98.7|±2           |       |
| 6   | 926.19        | 96.6|±1           | 3.5958  |
|     | 1006.85       | 94.9|±1 + 3.3|0       |       |

“pKD” stands for pseudo-Kramers doublet, “S” denotes a singlet state. The contribution for the “$|±X\rangle$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ functions.
Table S6. Energies and composition in $|m_f\rangle$ basis of the ligand-field states of two Tb ions in Conf 4 of TbY@C$_{70}$N$^-$. 

| pKD | $E$, cm$^{-1}$ | Composition, % | $E$, cm$^{-1}$ | Composition, % |
|-----|---------------|----------------|---------------|----------------|
| 1   | 0.00          | 100.0±6        | 0.00          | 99.9±6         |
|     | 0.04          | 100.0±6        | 0.01          | 99.9±6         |
| 2   | 255.14        | 99.9±5         | 272.21        | 99.7±5         |
|     | 255.22        | 99.9±5         | 272.37        | 99.8±5         |
| 3   | 516.16        | 99.2±4         | 508.84        | 99.4±4         |
|     | 518.09        | 99.7±4         | 509.13        | 99.5±4         |
| 4   | 722.15        | 98.8±3         | 704.87        | 97.1±3         |
|     | 741.08        | 97.3±3         | 710.00        | 98.6±3         |
| 5   | 864.37        | 87.5±2 + 11.9| 87.2          | 97.1±2         |
|     | 894.22        | 98.9±2         | 875.07        | 97.1±2         |
| 6   | 941.12        | 96.8±1 + 2.5| 931.31        | 94.6±1         |
|     | 1019.80       | 99.0±1         | 1019.67       | 93.3±1         |
| 5   | 1025.35       | 87.3±2 + 12.3| 1028.58       | 83.1±0 + 10.8| 6.0±1 |

“pKD” stands for pseudo-Kramers doublet, “S” denotes a singlet state. The contribution for the “$|\pm X\rangle$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ functions.

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Table S7. Energies and composition in $|m_f\rangle$ basis of the ligand-field states of two Tb ions in Conf 5 of TbY@C$_{70}$N$^-$. 

| pKD | $E$, cm$^{-1}$ | Composition, % | $E$, cm$^{-1}$ | Composition, % |
|-----|---------------|----------------|---------------|----------------|
| 1   | 0.00          | 99.9±6         | 0.00          | 100.0±6        |
|     | 0.01          | 99.9±6         | 0.01          | 100.0±6        |
| 2   | 269.77        | 99.7±5         | 266.59        | 99.7±5         |
|     | 270.02        | 99.8±5         | 266.63        | 99.7±5         |
| 3   | 515.93        | 99.5±4         | 504.88        | 99.2±4         |
|     | 516.04        | 99.6±4         | 505.98        | 99.5±4         |
| 4   | 719.32        | 99.0±3         | 700.75        | 98.7±3         |
|     | 726.12        | 99.5±3         | 707.90        | 97.0±3         |
| 5   | 868.01        | 92.8±2 + 6.3| 843.45        | 90.1±2 + 8.6| 0.0 |
|     | 887.41        | 99.2±2         | 868.98        | 95.7±2 + 2.7| 1.0 |
| 6   | 953.65        | 97.4±1         | 933.23        | 94.6±1 + 3.0| 2.0 |
|     | 1015.84       | 97.6±1         | 994.66        | 89.6±1 + 7.1| 0.0 + 2.6| 2.0 |
| 5   | 1028.39       | 91.1±0 + 6.3| 1008.00       | 83.8±0 + 9.2| 1.0 + 6.9| 2.0 |

“pKD” stands for pseudo-Kramers doublet, “S” denotes a singlet state. The contribution for the “$|\pm X\rangle$” state means a sum of contributions for $|+X\rangle$ and $|-X\rangle$ functions.
Table S8. Ligand-field parameters $B(q,k)$ for Tb$^{3+}$ in Conf 2 of TbY@C$_{79}$N$_{3}$, in cm$^{-1}$.

| $k$ | $q$ | $B(q,k)$     |
|-----|-----|------------|
| 2   | -2  | 1.5176E+00 |
| 2   | -1  | 6.7233E-01 |
| 2   | 0   | -9.2482E+00|
| 2   | 1   | 3.2467E-02 |
| 2   | 2   | -4.8422E-01|
| 4   | -4  | -1.1344E-03|
| 4   | -3  | 1.0435E-02 |
| 4   | -2  | -7.8399E-03|
| 4   | -1  | -6.1057E-04|
| 4   | 0   | 3.6536E-03 |
| 4   | 1   | -1.7994E-03|
| 4   | 2   | 3.3407E-04 |
| 4   | 3   | 5.7437E-03 |
| 4   | 4   | 2.6048E-04 |
| 6   | -6  | 2.5033E-05 |
| 6   | -5  | -9.0669E-04|
| 6   | -4  | -6.8064E-05|
| 6   | -3  | 2.2052E-04 |
| 6   | -2  | 4.8932E-05 |
| 6   | -1  | -2.8774E-04|
| 6   | 0   | 5.3912E-06 |
| 6   | 1   | 5.2105E-05 |
| 6   | 2   | -8.4812E-05|
| 6   | 3   | 1.0418E-04 |
| 6   | 4   | -1.6245E-04|
| 6   | 5   | 9.7781E-04 |
| 6   | 6   | 1.0813E-04 |
Table S9. The lowest energy spin states of Tb$_2$@C$_{79}$N computed for $K^\text{eff}$ of 45 cm$^{-1}$

| G-tensor of states | 1 and | 2; Energies | 0 cm$^{-1}$ |
|--------------------|-------|-------------|-------------|
| $g_x$              | 0.0000| -0.29449381 | -0.95565043 | 0.00237939 |
| $g_y$              | 0.0000| 0.95565332  | -0.29449378 | 0.00037117 |
| $g_z$              | 37.7890| 0.00034601  | 0.00238317  | 0.99999710 |

| G-tensor of states | 3 and | 4; Energies | 250.9 cm$^{-1}$ |
|--------------------|-------|-------------|----------------|
| $g_x$              | 0.0000| 0.31208230  | 0.94982881     | 0.0207353  |
| $g_y$              | 0.0000| -0.95004851 | 0.31192471     | 0.01052626 |
| $g_z$              | 34.7375| 0.00353084  | -0.02298291    | 0.99972962 |

| G-tensor of states | 5 and | 6; Energies | 309.5 cm$^{-1}$ |
|--------------------|-------|-------------|----------------|
| $g_x$              | 0.0000| -0.34102890 | -0.93978022    | -0.02263704|
| $g_y$              | 0.0000| 0.94004606  | -0.34083626    | -0.01200255|
| $g_z$              | 34.8049| 0.00356424  | -0.02537308    | 0.99967170 |

| G-tensor of states | 7 and | 8; Energies | 410.2 cm$^{-1}$ |
|--------------------|-------|-------------|----------------|
| $g_x$              | 0.0000| -0.02159229 | -0.99770009    | -0.06425180|
| $g_y$              | 0.0000| -0.0047522  | -0.06425653    | 0.99793330 |
| $g_z$              | 11.6098| 0.00195919  | 0.02157820     | 0.00091331 |

| G-tensor of states | 9 and | 10; Energies | 493.6 cm$^{-1}$ |
|--------------------|-------|-------------|----------------|
| $g_x$              | 0.0001| -0.95112414 | 0.30864424     | 0.01007942 |
| $g_y$              | 0.0001| -0.30880256 | -0.95080532    | -0.02470279|
| $g_z$              | 31.6919| 0.00195919  | -0.02660797    | 0.99964403 |

| G-tensor of states | 11 and | 12; Energies | 504.9 cm$^{-1}$ |
|--------------------|-------|-------------|----------------|
| $g_x$              | 0.0001| 0.28054875  | -0.95926646    | 0.03316999 |
| $g_y$              | 0.0018| 0.00477010  | 0.03595082     | 0.99934218 |
| $g_z$              | 0.7853| -0.95982792 | -0.28020598    | 0.01466175 |
| G-tensor of states | Energies |  |
|--------------------|----------|---|
| States 13 and 14; Energies 541.3 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0000 | -0.98304726 | 0.18333791 | -0.00230284 |
| $g_y$ | 0.0001 | -0.18333060 | -0.98304654 | -0.00306403 |
| $g_z$ | 31.7492 | -0.00282555 | -0.00258990 | 0.99999265 |
| States 15 and 16; Energies 609.4 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0000 | -0.51851284 | -0.85465114 | -0.02675541 |
| $g_y$ | 0.0000 | 0.85506629 | -0.51816665 | -0.01910413 |
| $g_z$ | 31.8120 | 0.00246360 | -0.03278339 | 0.99945944 |
| States 17 and 18; Energies 643.4 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0001 | 0.06632526 | 0.98111745 | 0.18168519 |
| $g_y$ | 0.0003 | 0.11606094 | -0.18843594 | 0.97520344 |
| $g_z$ | 7.2187 | -0.99102513 | 0.04359407 | 0.12636748 |
| States 19 and 20; Energies 650.0 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0001 | -0.18676315 | 0.16761892 | 0.96799970 |
| $g_y$ | 0.0001 | -0.03997520 | -0.98581730 | 0.16299151 |
| $g_z$ | 4.6583 | 0.98159132 | -0.00825518 | 0.19081494 |
| States 21 and 22; Energies 719.7 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0001 | -0.80776547 | 0.58949974 | 0.00223508 |
| $g_y$ | 0.0001 | -0.58948684 | -0.80770728 | -0.01068733 |
| $g_z$ | 28.6612 | -0.00449489 | -0.00995041 | 0.99994039 |
| States 23 and 24; Energies 746.9 cm$^{-1}$ | x | y | z |
| $g_x$ | 0.0010 | 0.25956885 | 0.96562988 | -0.01352609 |
| $g_y$ | 0.0012 | -0.96568195 | 0.25940028 | -0.01303316 |
| $g_z$ | 28.6907 | -0.00907654 | 0.01644490 | 0.99982358 |
| G-tensor of states   | Energies     |
|---------------------|--------------|
| 25 and 26; Energies | 766.8 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0008         | 0.00220737   | -0.20606456  | -0.97853591 |
| gᵧ = 0.0015         | 0.00658407   | -0.97851409  | 0.20607481  |
| gᵣ = 7.3829         | 0.99997589   | 0.00689763   | 0.00080320  |

| G-tensor of states   | Energies     |
|---------------------|--------------|
| 27 and 28; Energies | 809.2 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0040         | 0.17809702   | 0.98400643   | 0.00357735  |
| gᵧ = 0.0042         | -0.98398614  | 0.17811782   | -0.00673147 |
| gᵣ = 28.6580        | -0.00726100  | -0.00232121  | 0.99997094  |

| G-tensor of states   | Energies     |
|---------------------|--------------|
| 29 and 30; Energies | 829.0 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0289         | -0.02373457  | -0.99659905  | 0.07891136  |
| gᵧ = 0.0631         | 0.39889423   | -0.08181871  | -0.91333953 |
| gᵣ = 5.8715         | 0.191668973  | 0.00979957   | 0.39947954  |

| G-tensor of states   | Energies     |
|---------------------|--------------|
| 31 and 32; Energies | 832.9 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0286         | 0.11447602   | 0.98637658   | 0.11813757  |
| gᵧ = 0.0971         | -0.38492155  | 0.15367083   | -0.91006630 |
| gᵣ = 5.6006         | -0.91582239  | 0.05870708   | 0.39726923  |

| G-tensor of states   | Energies     |
|---------------------|--------------|
| 33 and 34; Energies | 845.4 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0038         | 0.26915233   | -0.85686321  | -0.43970725 |
| gᵧ = 0.0058         | -0.01248011  | 0.45341385   | -0.89121273 |
| gᵣ = 1.3396         | 0.96301675   | 0.24535958   | 0.11134364  |

| G-tensor of states   | Energies     |
|---------------------|--------------|
| 35 and 36; Energies | 895.1 cm⁻¹   |
| x                   | y            | z            |
| gₓ = 0.0003         | -0.89027280  | -0.45519218  | -0.01464296 |
| gᵧ = 0.0003         | 0.45536538   | -0.89022249  | -0.01209457 |
| gᵣ = 28.5855        | -0.00753014  | -0.01743537  | 0.99981964  |
Table S10. Electrostatic potential distribution inside charged fullerene cages.\(^a\)

| plane \(^b\) | C\(_{70}\)N\(^{5-}\) | C\(_{80}\)(CH\(_2\)Ph)\(^{5-}\) | C\(_{80}\)\(^{6-}\) |
|---|---|---|---|

\(^a\) DFT calculation at the PBE/TZVP level with the Orca package;

\(^b\) nitrogen atom in C\(_{70}\)N\(^{5-}\) or benzyl-bearing C-sp\(^3\) carbon atom in C\(_{80}\)(CH\(_2\)Ph)\(^{5-}\) are shown in blue, other carbons – gray, cutting planes are shown in dark red;

\(^c\) the absolute scale is different for different species, but the relative scale is the same
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