Metallofullerene photoswitches driven by photoinduced fullerene-to-metal electron transfer

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Samples

Nitride clusterfullerenes $Y_xSc_{3-x}N@C_{80}$ ($x = 0–3$) were synthesized in our group earlier, using the protocol similar to the described in ref. 1, but employing NH$_3$ as a source of nitrogen. 2

Photophysical studies

Absorption spectra were measured with Shimadzu dispersive spectrophotometer.

Steady-state emission spectra were excited with Omicron PhoxX diode lasers (405 and 488 nm lines) and detected with Avantes AvaSpec HS1024x122TEC high-sensitivity fiber-optic spectrometer with TE-cooled backthinned CCD detector. To get over the detector limits of Si-based CCDs for Sc$_3$N@C$_{80}$, AvaSpec NIR 256 1.7 spectrometer (Avantes) was used. The measurement in the NIR range beyond 1000 nm did not reveal new features in the luminescence spectra of Sc$_3$N@C$_{80}$.

Variable temperature measurements of fullerenes dispersed in polystyrene film were performed with fluorescence microscope of local design and Janis ST-500 microscopy cryostat (temperatures down to 4 K) or an Oxford Instruments MO2 cryostat. At temperatures below liquid nitrogen, a certain temperature gradient evolves inside a contact cryostat between the cold finger and a sample. Besides, the laser irradiation also results in local heating of the sample (the effect is however diminished in time-resolved measurements with long waiting time between laser pulses). These effects may lead to a temperature difference between a sample and the cold finger up to 5–8 K. The temperature values listed in Table S2-S4 and the main text are recordings of the controller, and the real temperature at the sample may be somewhat higher.

Additional variable-temperature measurements were performed for Y$_3$N@C$_{80}$ in degassed toluene solution. The sample was sealed in the glass tubed and cooled using a nitrogen-flow cryostate of home design.

Luminescence lifetimes were measured by time-correlated single-photon counting (TCSPC) method. Luminescence was excited by a digitally modulated Omicron PhoxX diode laser, time-resolved detection was performed by a PMT PMA 192 (PicoQuant) or an ID230 NIR single-photon counter (ID Quantique) and acquired by a time-correlated single-photon counting system (TCSPC) based on TimeHarp 260 counter/timer (PicoQuant) and the FluoFit software. When emission was intense enough, the emitted light was passed through a 9030 compact monochromator (Sciencetech) ($\approx$20 nm maximal bandwidth) to the detector. For week emission intensities, a broadband regime was used either with long-pass ($> 650$ nm) or band-pass filters (820–880 nm). The ID230 detector and the scanning monochromator together with the SciSpec software was used to record continuous and time-resolved luminescence of Sc$_3$N@C$_{80}$ at wavelengths longer than 900 nm. Note that chosen detection range not necessarily corresponds to the maximum PL intensity but was chosen for optimal measurement in a broader temperature range.

Examples of decay curves measured for Y$_3$N@C$_{80}$ are shown in Fig. S1. Tables S1–S4 list determined luminescence lifetimes together with the detection range.
Figure S1. Selected PL decays curves recorded for Y$_3$N@C$_{60}$ at room temperature, 78 K, and 25 K, and their fits with exponential decay, and residual. Right bottom corner shows PL lifetimes in linear scale.
Table S1. Luminescence lifetimes of Y$_3$N@C$_{80}$ in polystyrene films and edgassed toluene solution measured at different temperatures

| $T$, K | $\tau$, ms, polymer | $\tau$, ms, toluene | detection |
|--------|---------------------|---------------------|-----------|
| 14     | 189                 |                     | monochromator @740 nm |
| 14.5   | 196                 |                     | monochromator @740 nm |
| 18.5   | 194                 |                     | monochromator @740 nm |
| 23.5   | 197                 |                     | monochromator @740 nm |
| 28.5   | 200                 |                     | monochromator @740 nm |
| 28.5   | 196                 |                     | monochromator @740 nm |
| 33.5   | 197                 |                     | monochromator @740 nm |
| 38.5   | 197                 |                     | monochromator @740 nm |
| 40     | 193                 |                     | monochromator @740 nm |
| 48.5   | 194                 |                     | monochromator @740 nm |
| 50     | 192                 |                     | monochromator @740 nm |
| 60     | 189                 |                     | monochromator @740 nm |
| 63.5   | 183                 |                     | monochromator @740 nm |
| 70     | 167                 |                     | monochromator @740 nm |
| 78     | 143                 |                     | monochromator @740 nm |
| 78.5   | 127                 |                     | monochromator @740 nm |
| 78.5   | 131                 |                     | monochromator @740 nm |
| 100    | 30                  |                     | monochromator @701 nm |
| 120    | 5                   |                     | monochromator @701 nm |
| 140    | 1.05                |                     | monochromator @701 nm |
| 165    | 0.878               | 0.620               | monochromator @706 nm |
| 175    | 0.528               | 0.405               | monochromator @706 nm |
| 200    | 0.165               | 0.0954              | monochromator @706 nm |
| 225    | 0.0265              | 0.0247              | monochromator @706 nm |
| 250    | 0.0072              | 0.0065              | monochromator @706 nm |
| 296    | 0.00108             | 0.00095             | monochromator @706 nm |
| 325    | 0.00045             |                     | monochromator @706 nm |
| 335    | 0.00035             |                     | monochromator @706 nm |
### Table S2. Luminescence lifetimes of Y₂ScN@C₈₀ in polystyrene films measured at different temperatures

| T, K | τ, ms | detection                  |
|------|-------|----------------------------|
| 4    | 78    | Filter long-pass 650 nm    |
| 10   | 77.7  | Filter long-pass 650 nm    |
| 15   | 76    | Filter long-pass 650 nm    |
| 25   | 74    | Filter long-pass 650 nm    |
| 40   | 68.6  | Filter long-pass 650 nm    |
| 50   | 61.5  | Filter long-pass 650 nm    |
| 60   | 47.6  | Filter long-pass 650 nm    |
| 65   | 21.5  | monochromator @770 nm      |
| 78   | 6.27  | monochromator @753 nm      |
| 90   | 2.17  | monochromator @753 nm      |
| 120  | 0.429 | monochromator @753 nm      |
| 150  | 0.125 | monochromator @753 nm      |
| 200  | 0.044 | monochromator @753 nm      |
| 250  | 0.018 | monochromator @753 nm      |
| 270  | 0.015 | monochromator @753 nm      |
| 296  | 0.0105| monochromator @750 nm      |
| 396  | 0.003 | monochromator @740 nm      |

### Table S3. Luminescence lifetimes of YSc₂N@C₈₀ in polystyrene films measured at different temperatures

| T, K | τ, ms | detection                  |
|------|-------|----------------------------|
| 4    | 26    | Filter long-pass 650 nm    |
| 15   | 26    | Filter long-pass 650 nm    |
| 25   | 26.5  | Filter long-pass 650 nm    |
| 30   | 25    | Filter long-pass 650 nm    |
| 35   | 24    | Filter long-pass 650 nm    |
| 40   | 12    | Filter long-pass 650 nm    |
| 50   | 7.2   | Filter long-pass 650 nm    |
| 60   | 2.5   | monochromator @800 nm      |
| 70   | 1.1   | monochromator @800 nm      |
| 78   | 0.77  | monochromator @800 nm      |
| 120  | 0.049 | monochromator @800 nm      |
| 180  | 0.0068| monochromator @800 nm      |
| 240  | 0.0022| monochromator @800 nm      |
| 296  | 0.0012| monochromator @800 nm      |
Table S4. Luminescence lifetimes of Sc\textsubscript{3}N@C\textsubscript{80} in polystyrene films measured at different temperatures

| $T$, K | $\tau$, $\mu$s | $\tau'$, $\mu$s | $\tau''$, $\mu$s | detection$^a$ |
|--------|----------------|----------------|----------------|--------------|
| 4      | 400            | 1800           | 0.0014         | band-pass 820–880 nm |
| 7      | 400            | 1640           |                | band-pass 820–880 nm |
| 10     | 410            | 1360           |                | band-pass 820–880 nm |
| 15     | 240            | 1000           |                | band-pass 820–880 nm |
| 25     | 160            | 510            |                | band-pass 820–880 nm |
| 35     | 120            | 340            | 0.0017         | band-pass 820–880 nm |
| 50     | 64             | 250            |                | band-pass 820–880 nm |
| 65     | 13             |                |                | band-pass 820–880 nm |
| 78     | 5              |                |                | band-pass 820–880 nm |
| 100    | 2.55           |                | 0.0028         | band-pass 820–880 nm |
| 150    | 0.66           |                | 0.0070         | band-pass 820–880 nm |
| 200    | 0.24           |                | 0.0088         | band-pass 820–880 nm |
| 225    | 0.13           |                |                | band-pass 820–880 nm |
| 296    | 0.3            |                |                | band-pass 820–880 nm |

$^a$ In addition to the measurements in the 820–880 nm range with PMT PMA 192, test PL lifetime measurements of Sc\textsubscript{3}N@C\textsubscript{80} were also performed at $\lambda$>1000 nm with ID230 NIR single photon counter. These measurements did not reveal processes with different lifetimes and are thus not discussed.
DFT calculations

Computational details. Each structure was optimized in the S₀ and T₁ electronic states at the PBE level using the Priroda code with the implemented basis set of TZ2P quality with an effective core potential for Sc and Y atoms. Each unique conformer found in this screening was verified to be a true minimum by a Hessian calculation. Optimized coordinates of unique T₁ conformers were then re-optimized in the S₁ state at the TD-DFT level. Single point energy calculations at the PBE/def2-TZVPP level with ZORA scalar-relativistic corrections were then performed for all unique conformers in S₀, S₁, and T₁ states using ORCA suite, which was also used for calculations of hyperfine tensors and g-factors in the triplet state.

Relative energies of all computed conformers in S₀, T₁, and S₁ states are listed in Table S5, whereas Figures S2-S3 show isosurfaces of HOMO, LUMO, difference density Δρ(S₀→S₁), and spin density ρ_{spin}(T₁) for selected conformers

Table S5. Relative energies of Y₂Sc₃N@C₈₀ conformers in S₀, S₁, and T₁ electronic states (in eV)

|        | S₀   | S₀(S₁) | S₀(T₁) | S₁   | S₁(S₀) | T₁   | T₁(S₀) | ΔST | ρ_{spin}(T₁) |
|--------|------|--------|--------|------|--------|------|--------|-----|--------------|
| Y₃N@C₈₀ | conf 1 | 0.000  | 0.067  | 0.068 | 1.554  | 1.599 | 1.451  | 1.498| 0.104  | 0.08 |
|        | conf 2 | 0.062  | 0.144  | 0.131 | 1.568  | 1.649 | 1.494  | 1.569| 0.073  | 0.17 |
|        | conf 3 | 0.069  | 0.150  | 0.138 | 1.568  | 1.665 | 1.492  | 1.583| 0.076  | 0.18 |
| Y₂ScN@C₈₀ | conf 1 | 0.000  | 0.082  | 0.077 | 1.516  | 1.576 | 1.424  | 1.483| 0.092  | 0.15 |
|        | conf 2 | 0.044  | 0.145  | 0.131 | 1.463  | 1.548 | 1.389  | 1.477| 0.074  | 0.28 |
|        | conf 3 | 0.138  | 0.128  | 1.438 | 1.375  | 1.063 | 0.30   |      |      |
|        | conf 4 | 0.299  | 0.245  | 1.553 | 1.471  | 0.082 | 0.23   |      |      |
|        | conf 5 | 0.224  | 0.224  | 1.466 | 1.445  | 0.021 | 0.41   |      |      |
| YSc₂N@C₈₀ | conf 1 | 0.000  |        |      |        | 1.564 |        | 1.488|        |      |
|        | conf 2 | 0.001  |        |      |        | 1.544 |        | 1.458|        |      |
|        | conf 3 | 0.012  | 0.111  | 0.100 | 1.312  | 1.436 | 1.249  | 1.366| 0.062  | 0.42 |
|        | conf 4 | 0.028  | 0.080  | 0.075 | 1.444  | 1.489 | 1.359  | 1.401| 0.084  | 0.23 |
|        | conf 5 | 0.041  | 0.120  | 0.118 | 1.350  | 1.443 | 1.296  | 1.379| 0.054  | 0.43 |
|        | conf 6 | 0.320  | 0.284  | 1.408 | 1.335  |        | 0.073 | 0.43 |
|        | conf 7 | 0.329  | 0.263  | 1.426 | 1.359  | 0.067  | 0.35 |
|        | conf 8 | 0.193  | 0.185  | 1.336 | 1.302  | 0.034  | 0.56 |
|        | conf 9 | 0.350  | 0.227  | 1.445 | 1.422  | 0.022  | 0.38 |
| Sc₃N@C₈₀ | conf 1 | 0.000  | 0.133  | 0.081 | 1.430  | 1.503 | 1.356  | 1.421| 0.074  | 0.29 |
|        | conf 2 | 0.024  | 0.127  | 0.111 | 1.239  | 1.357 | 1.195  | 1.302| 0.044  | 0.56 |
|        | conf 3 | 0.068  | 0.161  | 0.151 | 1.178  | 1.267 | 1.148  | 1.234| 0.030  | 0.67 |
|        | conf 4 | 0.071  |        | 1.501 |        | 1.425 |        | 0.58 |      |
|        | conf 5 | 0.305  | 0.287  | 1.264 | 1.238  | 0.025  | 0.41 |
|        | conf 6 | 0.227  | 0.188  | 1.381 | 1.324  | 0.056  | 0.35 |
|        | conf 7 | 0.187  | 0.174  | 1.430 | 1.368  | 0.062  | 0.46 |
|        | conf 8 | 0.361  | 0.334  | 1.443 | 1.380  | 0.063  | 0.29 |

Relative energies are referred to the lowest-energy conformers of the ground electronic state; “S₀” denotes the energy of the S₀ state in optimized S₀ geometry, “S₀(S₁)” is the energy of the S₀ state in the optimized S₁ geometry, and “S₀(T₁)” is the energy of the S₀ state in the optimized T₁ geometry; ΔST is the adiabatic energy difference between S₁ and T₁, and ρ_{spin}(T₁) is net Mulliken spin population of the M₂N cluster in the triplet state.
Table S6. Relative adiabatic energies of Sc$_3$N@C$_{80}$ conformers in $T_1$ and monoanionic state (in eV)

|       | $T_1$, Δ-SCF |       |       | $T_1$, TD-DFT |       |       |       | Sc$_3$N@C$_{80}^-$ |
|-------|--------------|-------|-------|--------------|-------|-------|-------|-----------------|
|       | ΔE vs conf 1, $S_0$ | ΔE vs conf 3, $T_1$ | ΔE vs conf 1, $S_0$ | ΔE vs conf 3, $T_1$ | ΔE vs conf 1, $S_0$ | $EA$ | ΔE       |
| conf 3 | 1.220        | 0.000 | 1.148 | 0.000        | 2.683 | 0.000 |       |
| conf 2 | 1.245        | 0.025 | 1.195 | 0.046        | 2.660 | 0.023 |       |
| conf 5 | 1.313        | 0.092 | 1.238 | 0.090        | n/a   | n/a   |       |
| conf 6 | 1.384        | 0.164 | 1.324 | 0.176        | 2.495 | 0.187 |       |
| conf 1 | 1.386        | 0.166 | 1.356 | 0.208        | 2.500 | 0.183 |       |
| conf 7 | 1.405        | 0.185 | 1.368 | 0.220        | 2.480 | 0.203 |       |
| conf 8 | 1.433        | 0.213 | 1.380 | 0.231        | 2.459 | 0.224 |       |

Δ-SCF denotes computations of the triplet state by ground-state DFT with spin multiplicity $2S+1 = 3$. TD-DFT denotes computations of the triplet state energy with TD-DFT, using geometry optimized with Δ-SCF approach. The energies are referenced versus conf 1 in its $S_0$ state (which gives excitation energies), or versus conf 3 in its $T_1$ state (which gives relative energies of conformers). For the anions, electron affinity $EA$ is computed as the energy difference of the optimized anion of a given conformer and the neutral Sc$_3$N@C$_{80}$, conf 1 in $S_0$ state.
Figure S2a. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0 \rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for $Y_3N@C_{80}$, conf 1

Figure S2b. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $Y_2ScN@C_{80}$, conf 1

Figure S2c. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $Y_2ScN@C_{80}$, conf 2
Figure S2d. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0 \rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for $Y_2\text{ScN@C}_{80}$, conf 3

Figure S2e. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $\text{YS}C_2\text{N@C}_{80}$, conf 1

Figure S2f. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $\text{YS}C_2\text{N@C}_{80}$, conf 2
Figure S2g. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0\rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for YSc$_2$N@C$_{80}$, conf 3

Figure S2h. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0\rightarrow S_1)$ computed for YSc$_2$N@C$_{80}$, conf 4

Figure S2i. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0\rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for YSc$_2$N@C$_{80}$, conf 5
Figure S2j. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $\text{Sc}_3\text{N}@\text{C}_{80}$, conf 1

Figure S2k. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0 \rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for $\text{Sc}_3\text{N}@\text{C}_{80}$, conf 2

Figure S2l. Isosurfaces of HOMO, LUMO, difference density $\Delta \rho(S_0 \rightarrow S_1)$, and spin density $\rho_{\text{spin}}(T_1)$ computed for $\text{Sc}_3\text{N}@\text{C}_{80}$, conf 3
Figure S2m. Isosurfaces of HOMO, LUMO, and difference density $\Delta \rho(S_0 \rightarrow S_1)$ computed for $\text{Sc}_3\text{N} @ \text{C}_{80}, \text{conf} \ 4$

Figure S3. Isosurfaces of spin density $\rho_{\text{spin}}(T_1)$ of the lowest-energy $T_1$ conformers
Figure S4. The relation between the total spin population of the endohedral cluster in the triplet state and the $S_1$–$T_1$ energy gap according to DFT and TD-DFT calculations. The dashed line is shown to guide the eye only.
Table S7. DFT-computed EPR parameters of selected $Y_3Sc_3\cdot N@C_{80}$ conformers in the triplet state

|                      | $A_x/g_x$ | $A_y/g_y$ | $A_z/g_z$ | $A_{iso}/g_{iso}$ | $|e^2Qg/h|$ | $\eta$ |
|----------------------|-----------|-----------|-----------|-------------------|-------------|-------|
| $Y_3N@C_{80}$, conf 1 |           |           |           |                   |             |       |
| PBE, ZORA            |           |           |           |                   |             |       |
| Y                    | 1.74      | 1.82      | 2.15      | 1.90              | 1.359       | 0.00  |
| N                    | -0.09     | -0.09     | 0.82      | 0.21              | 1.431       | 0.00  |
| g                    | 2.0024    | 2.0024    | 2.0042    | 2.0030            |             |       |
| PBE0, ZORA           |           |           |           |                   |             |       |
| Y                    | 1.96      | 2.05      | 2.42      | 2.14              |             |       |
| N                    | -0.07     | -0.07     | 0.78      | 0.22              | 1.431       | 0.00  |
| g                    | 2.0001    | 2.0001    | 2.0028    | 2.0010            |             |       |
| $Y_2ScN@C_{80}$, conf 3 |           |           |           |                   |             |       |
| PBE, ZORA            |           |           |           |                   |             |       |
| Sc                   | 9.10      | 13.65     | 16.61     | 13.12             | 82.5        | 0.06  |
| Y                    | -0.91     | -1.36     | -1.37     | -1.22             |             |       |
| Y                    | -5.72     | -6.20     | -6.31     | -6.08             |             |       |
| N                    | -0.11     | -0.20     | -0.35     | -0.22             | 1.247       | 0.17  |
| g                    | 1.9974    | 1.9994    | 2.0032    | 2.0000            |             |       |
| PBE0, ZORA           |           |           |           |                   |             |       |
| Sc                   | 16.15     | 20.81     | 23.61     | 20.19             | 82.90       | 0.07  |
| Y                    | -0.97     | -1.35     | -1.42     | -1.25             |             |       |
| Y                    | -5.67     | -6.06     | -6.31     | -6.01             |             |       |
| N                    | -0.28     | -0.44     | -0.69     | -0.47             | 1.311       | 0.18  |
| g                    | 1.9978    | 1.9986    | 2.0007    | 1.9990            |             |       |
| $Y_2ScN@C_{80}$, conf 2 |           |           |           |                   |             |       |
| PBE, ZORA            |           |           |           |                   |             |       |
| Sc                   | 13.57     | 19.57     | 20.95     | 18.03             | 84.47       | 0.06  |
| Y                    | -1.22     | -1.55     | -1.67     | -1.48             |             |       |
| Y                    | -2.67     | -3.01     | -3.26     | -2.98             |             |       |
| N                    | -0.07     | -0.20     | -0.40     | -0.22             | 1.235       | 0.20  |
| g                    | 1.9971    | 2.0011    | 2.0024    | 2.0002            |             |       |
| PBE0, ZORA           |           |           |           |                   |             |       |
| Sc                   | 20.53     | 27.03     | 27.86     | 25.14             | 85.05       | 0.07  |
| Y                    | -1.20     | -1.56     | -1.57     | -1.45             |             |       |
| Y                    | -3.56     | -3.85     | -4.17     | -3.86             |             |       |
| N                    | -0.24     | -0.50     | -0.77     | -0.50             | 1.296       | 0.20  |
| g                    | 1.9972    | 1.9998    | 2.0013    | 1.9994            |             |       |
| $YSc_2N@C_{80}$, conf 3 |           |           |           |                   |             |       |
| PBE, ZORA            |           |           |           |                   |             |       |
| Sc                   | 23.83     | 28.27     | 31.36     | 27.82             | 79.5        | 0.06  |
| Sc                   | 19.41     | 25.44     | 26.59     | 23.81             | 81.2        | 0.05  |
| Y                    | -2.21     | -2.64     | -2.72     | -2.52             |             |       |
| N                    | -0.17     | -0.31     | -0.40     | -0.29             | 1.217       | 0.17  |
| g                    | 1.9987    | 2.0006    | 2.0016    | 2.0003            |             |       |
| PBE0, ZORA           |           |           |           |                   |             |       |
| Sc                   | 25.88     | 31.03     | 32.64     | 29.85             | 82.0        | 0.05  |
| Sc                   | 35.78     | 40.91     | 42.95     | 39.88             | 80.3        | 0.07  |
| Y                    | -2.20     | -2.56     | -2.62     | -2.46             |             |       |
| N                    | -0.28     | -0.49     | -0.75     | -0.51             | 1.261       | 0.18  |
| g                    | 1.9983    | 1.9993    | 2.0002    | 1.9993            |             |       |
Theory: PBE or PBE0 functional with ZORA scalar-relativistic correction, the basis set is SARC or ZORA-adapted version of def2-TZVP.\textsuperscript{7,8,12} Computed parameters are: Principal values of A-tensor (A_x, A_y, A_z) and their average (A_{iso}) in MHz, principal values of g-tensor (g_x, g_y, g_z) and their average (g_{iso}), nuclear quadrupolar coupling $|e^2Qq/h|$ in MHz, and asymmetry parameter $\eta$.

Comparison of experimental and computed $^{45}\text{Sc}$ hfc constants shows a systematic underestimation of the experimental values by theory. Similar underestimation was also observed for the $^{45}\text{Sc}$ hfc constants in $\text{Sc}_3\text{N}@\text{C}_{80}^-$ anion in the exhaustive study,\textsuperscript{13} which used various density functional and basis sets. A possible reason of this underestimation is the influence of the dynamic effects on the experimental values,\textsuperscript{14} but the failure of DFT approach to correctly describe the polarization of core $s$-electrons in Sc atoms is also a possibility.
Photoelectron spectroscopy

Photoelectron spectra of Sc$_3$N@C$_{80}^-$ were obtained using a size-selective cryogenic photoelectron spectroscopy apparatus that couples an electrospray ionization (ESI) source and a temperature-controlled ion trap to a magnetic-bottle time-of-flight photoelectron spectrometer.$^{15}$ A small sample of Sc$_3$N@C$_{80}$ was dissolved in toluene and reduced by adding dilute tetrakis(dimethylamino)ethylene (TDAE) in CH$_3$CN under a nitrogen-filled glovebox. The resulting ESI solution was ca. 5x10$^{-4}$ M. Sc$_3$N@C$_{80}^-$ anions were directed by two rf-only quadrupoles into the cryogenic ion trap, where the ions were accumulated and cooled down to 12 K in order to eliminate vibrational hot bands and achieve optimal spectral resolution. The Sc$_3$N@C$_{80}^-$ anions were mass-selected and then maximally decelerated (to minimize Doppler Broadening) before being photodetached with 266 nm (4.661 eV) or 355 nm (3.496 eV) photons. The laser was operated at a 20 Hz repetition rate with the ion beam off on alternating laser shots for background subtraction. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 5.2 m long electron flight tube. TOF photoelectron spectra were collected and converted to kinetic energy spectra calibrated using the known spectra of I$^-$ (ref 16) and OsCl$_6^{2-}$ (ref 17). The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the detachment photon energies used. The gas-phase electron affinity was directly measured from the 0–0 transition in the corresponding photoelectron spectrum.
Light-induced pulsed EPR

Saturated solutions of \( \text{Y}_3\text{N}@\text{C}_{80} \), \( \text{Y}_2\text{ScN}@\text{C}_{80} \), \( \text{YSc}_2\text{N}@\text{C}_{80} \) and \( \text{Sc}_3\text{N}@\text{C}_{80} \) were prepared in toluene-d\(_8\) (Sigma-Aldrich) at ambient conditions (without degassing), filled in the W-band quartz tubes, and flash-frozen by immersing into the liquid nitrogen before insertion into the microwave cavity of the spectrometer.

Sample illumination in EPR/ENDOR experiments

The continuous irradiation in W-band EPR/ENDOR experiments was achieved with the Power Technology Inc. IQ1C laser (510 nm, 40mW). A pulsed Nd-YAG Innolas SpitLight Compact 400 laser equipped with OPO (1.5 mJ/pulse for W-band, 3 mJ/pulse for X-band at 488 nm) was used in time-resolved measurements.

W-band pulsed EPR measurements

W-band measurements were performed at 20 K using a Bruker ELEXYS E680 spectrometer operating at about 94 GHz. All experiments were carried out with a homebuilt ENDOR microwave cavity.\(^{18-20}\) Electron spin echo-detected (ESE) field-swept spectra were measured using the Hahn echo pulse sequence \( tp-\tau-2tp-\tau-echo \) with \( tp = 20 \) ns and \( \tau = 300 \) ns. In continuous irradiation experiments (510 nm, 40 mW), 20-100 echoes were accumulated depending on the S/N and integrated over 140 ns around their maximum at each field position. The pulse repetition time was set to 2 ms. In the time-resolved EPR measurements, 12 ns laser pulse and a 500 ns delay after laser flash (\( t_{\text{DAF}} \)) preceded the Hahn echo sequence. Four echoes per field point were recorded with a repetition time of 2.5 s (laser repetition time). The decay of the polarized ESE signals was followed by incrementing the \( t_{\text{DAF}} \) in the range of 0.5\( \mu \)s-900 ms.

The Mims-type ENDOR spectra were measured at 20 K under continuous irradiation of the sample (510 nm, 40 mW) using the Mims-type ENDOR sequence \( tp-\tau-tp-\tau_{\text{RF}}-tp-\tau-echo \), with an RF pulse applied during the time interval \( t_{\text{RF}} \). The experimental conditions were \( tp = 40 \) ns, \( t_{\text{RF}} = 48 \) \( \mu \)s or 60 \( \mu \)s, and \( \tau = 564 \) ns. All ENDOR spectra were recorded using the stochastic acquisition mode with two shots for each point, and the total number of scans was varied in the range 100-400 depending on the S/N.

The Davies-type ENDOR spectra were measured at 20 K under continuous irradiation of the sample (510 nm, 40 mW) using the ENDOR sequence \( t_{\text{inv}}-t_{\text{RF}}-tp-\tau-2tp-\tau-echo \). The experimental conditions were \( t_{\text{inv}} = 100 \) ns, \( tp = 40 \) ns, \( t_{\text{RF}} = 10 \) \( \mu \)s and \( \tau = 1000 \) ns. Davies-type ENDOR spectra were recorded using the stochastic acquisition mode with two shots for each point, and the total number of scans was varied in the range 500-1000 depending on the S/N.

The EPR and ENDOR spectra were analyzed by computer simulation within the Spin Hamiltonian framework sketched in the manuscript using the EasySpin\textsuperscript{21} package running under Matlab.
Figure S5. W-band (94 GHz) time-resolved ESE EPR spectra of the EMF triplets from a) Y$_3$N@C$_{80}$, b) Y$_2$ScN@C$_{80}$, d) YSc$_2$N@C$_{80}$ and d) Y$_3$N@C$_{80}$. The pale lines show the polarized spectra recorded directly after the laser flash while the full colors represent records after $t_{\text{DAF}}$ of few ms when the polarization already relaxed. The polarized spectra (pale lines) reflect the non-equilibrium population of triplet energy levels built during the intersystem crossing and include absorptive (A) and emissive (E) signals. The “relaxed” spectra (full colors) correspond to the thermal Boltzmann population of the triplet levels and are purely absorptive.
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