Supplementary Information

Controlling Intermolecular Spin Interactions of La@C$_{82}$ in Empty Fullerene Matrices

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Table S1 Numerical data of the simulated ESR spectra of La@C_{82} in C_{2n} matrices. Anisotropic g and a tensor, rotational correlation time are (2.0021  2.0013  2.0010), (2.15  2.25  4.85) and 4 ns, respectively.
Table S2 Numerical data of $k_1$ parameter and the rotational correlation time $\tau_r$ calculated by the equation S1.

The linear $m_i$ contribution (equation 1) is determined avoiding contribution from inhomogeneous broadening and other unspecified interactions.\(^1\) The rotational correlation time $\tau_r$ can be calculated by the equation S1:

$$k_1 = \frac{1}{15} \frac{2}{3} \Delta g \frac{\mu_B B_0}{h} \cdot \frac{2}{3} \Delta a \cdot \left[ 4\tau_r + \frac{3\tau_r}{1 + (\omega \tau_r)^2} \right]$$  \hspace{1cm} (S1)

where $\mu_B$, $B_0$, $h$, $\omega$ are Bohr magneton, the magnetic field, Planck's constant and the microwave frequency of measurements, respectively. Differences of principle values of the $g$ matrix and the hfi tensor have been determined previously as $\Delta g = g_1 - g_1 = 0.007$ and $\Delta a = a_1 - a_1 = 5$ MHz.\(^2\)

**Table S3** Numerical data of crystal structures for C$_{2n}$ powder with La@C$_{82}$. All dimensions are in nm, the angles in degrees and the volume in nm$^3$. The $a$ and $c$ axes of the corresponding hexagonal unit cells are given for easier comparison of the respective amount of distortion from the ideal lattices, i.e. from $c/a=1.633$ for hcp and $c/a=2.449$ for fcc lattice. The error of the experimental measurements is less than 0.5 percent.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice</th>
<th>$a$ (hex)</th>
<th>$c$ (hex)</th>
<th>Volume (hex)</th>
<th>$a'$ (fcc)</th>
<th>$\alpha$ (rhom)</th>
<th>Volume (rhom)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$+0.1mol%La</td>
<td>fcc</td>
<td>1.000</td>
<td>2.444</td>
<td>2.12</td>
<td>1.413</td>
<td>0.9984</td>
<td>60.1</td>
<td>0.706</td>
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<tr>
<td>C$_{60}$+1mol%La</td>
<td>hcp</td>
<td>1.001</td>
<td>1.638</td>
<td>1.42</td>
<td></td>
<td></td>
<td></td>
<td>1.637</td>
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<tr>
<td>C$_{78}$+0.1mol%La</td>
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<td>1.248</td>
<td>3.204</td>
<td>4.32</td>
<td>1.288</td>
<td>57.9</td>
<td>1.44</td>
<td>2.568</td>
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<tr>
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<td>3.335</td>
<td>4.86</td>
<td>1.340</td>
<td>57.9</td>
<td>1.62</td>
<td>2.571</td>
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<tr>
<td>C$_{82}$+0.1mol%La</td>
<td>hcp</td>
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<td>1.836</td>
<td>1.99</td>
<td></td>
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<td>1.645</td>
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<tr>
<td>C$_{82}$+1mol%La</td>
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<td>3.422</td>
<td>5.09</td>
<td>1.369</td>
<td>57.2</td>
<td>1.70</td>
<td>2.611</td>
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Fig. S1 a) Schematic model of La@C_{82} in C_{2n} fcc-crystals; b) Concentration dependence of the distance between La@C_{82} molecules in C_{2n} fcc-crystals.

In order to determine the range at concentrations to be examined, we calculated the change in average inter-fullerene distance as a function of the concentration. If it is assumed that La@C_{82} molecules are dispersed completely by empty fullerene (C_{2n}) matrices, that is, La@C_{82} molecules are located at the center of C_{2n} fcc-crystals (Fig. S1a), the distance $L$ between La@C_{82} molecules is calculated by follows.$^3$

$$L = a \times \left( \frac{c}{25} \right)^{1/3}$$  \hspace{1cm} (S2)

$$a = 1.31 \times d(C_{2n}) + 0.492$$  \hspace{1cm} (S3)

$$d(C_{2n}) = 0.71 \times \left( \frac{2n}{60} \right)^{1/2}$$  \hspace{1cm} (S4)

where $C$, $a$ and $d(C_{2n})$ are concentration of La@C_{82} (mol%), lattice constant of C_{2n} fcc-crystals and diameter of empty fullerenes, respectively. A concentration range between 0.1 $\rightarrow$ 1 mol% is chosen because in this range, a small variation in the concentration leads to a large change in the inter-fullerene distance.

Fig. S2 a) Exchange frequency; and b) FWHM linewidth dependences of the hyperfine structure of La@C$_{82}$. These spectra are simulated by EasySpin software.$^4$

**Fig. S3** Saturation curves of La@C_{82} in 0.1, 0.5 and 1 mol% in a) C_{70}; b) C_{78}; and c) C_{84} matrices at room temperature. Microwave frequency and modulation amplitude are 9.867 GHz and 0.025 mT, respectively.
**Fig. S4** Microwave power dependence of the ESR spectra of La@C_{82} in a)0.1; b)0.5; c)1 mol% in C_{70} matrix; d)0.1; e)0.5; f)1 mol% in C_{78} matrix; g)0.1; h)0.5; i)1 mol% in C_{84} matrix at room temperature. Microwave frequency and modulation amplitude are 9.867 GHz and 0.025 mT, respectively.