Supplementary Material for PCCP

Supplementary Information

Controlling Intermolecular Spin Interactions of La@C_{82} in Empty Fullerene Matrices

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	in C_{60}			in C_{70}			in C_{78}		
Concentration (mol%)	0.1	0.5	1	0.1	0.5	1	0.1	0.5	1
FWHM LW (mT)	0.098	0.102	0.102	0.076	0.088	0.090	0.075	0.088	0.090
Exchange frequency (Hz)	4.5×10^5	9.0×10^6(58 %) 4.5×10^5 (42 %)	9.0×10^6(58 %) 4.5×10^5 (42 %)	4.5×10^5			4.5×10^5		
	in C_{82}			in C_{84}					
Concentration (mol%)	0.1	0.5	1	0.1	0.5	1			
FWHM LW (mT)	0.050	0.072	0.075	0.073	0.081	0.082			
Exchange frequency (Hz)	4.5×10^5			4.5×10^5					

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.

C_{2n} matrices	Concentration	k_1 (μT)	τ_r (ns)
C_{60}	0.1 mol%	-1.14	0.25
	0.5 mol%	-0.986	0.22
	1 mol%	-2.70	0.59
C_{70}	0.1 mol%	-1.96	0.43
	0.5 mol%	-1.37	0.30
	1 mol%	-2.24	0.49
C_{78}	0.1 mol%	-8.91	0.19
	0.5 mol%	-1.36	0.30
	1 mol%	-1.29	0.28
C_{82}	0.1 mol%	-0.640	0.14
	0.5 mol%	-1.02	0.22
	1 mol%	-1.45	0.31
C_{84}	0.1 mol%	-0.784	0.17
	0.5 mol%	-0.645	0.14
	1 mol%	-0.700	0.52

Table S2 Numerical data of k_1 parameter and the rotational correlation time τ_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 τ_r can be calculated by the equation S1:

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

where μ_B, B_0, $\hbar$, ω 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 $\Delta g = g_{\parallel} - g_{\perp} = 0.007$ and $\Delta a = a_{\parallel} - a_{\perp} = 5$ MHz.[2]

1 P. Jakes, A. Gembus, K. P. Dinse, and K. Hata, *J. Chem. Phys.*, 2008, **128**.
2 M. Rubsam, P. Schweitzer, and K. P. Dinse, *J. Phys. Chem.*, 1996, **100**, 19310.

Sample	Lattice	*a* (hex)	*c* (hex)	Volume (hex)	*a* (fcc)	*a*' (rhom)	*α* (rhom)	Volume (rhom)	*c*/*a*
C_{60}+0.1mol%La	fcc	1.000	2.444	2.12	1.413	0.9984	60.1	0.706	2.444
C_{60}+1mol%La	hcp	1.001	1.638	1.42					1.637
C_{78}+0.1mol%La	rhombohedral	1.248	3.204	4.32		1.288	57.9	1.44	2.568
C_{78}+1mol%La									
C_{82}+0.1mol%La	hcp	1.120	1.836	1.99					1.645
C_{82}+1mol%La	rhombohedral	1.297	3.335	4.86		1.340	57.9	1.62	2.571
C_{84}+0.1mol%La	rhombohedral	1.310	3.422	5.09		1.369	57.2	1.70	2.611
C_{84}+1mol%La									

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.

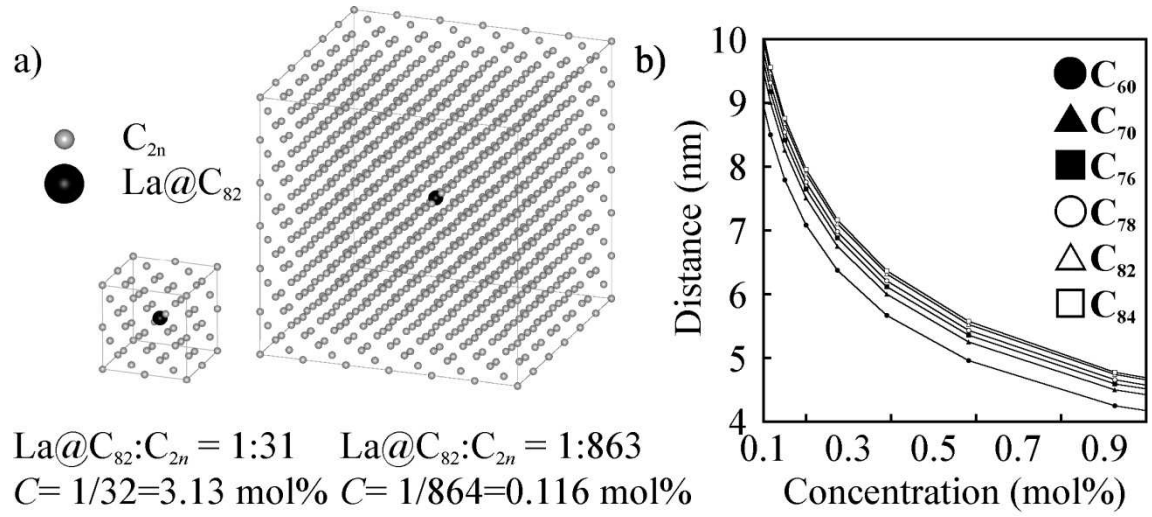

Fig. S1 a)Schematic model of La@C_{82} in C_{2n} fcc-crystals; b)Concentration dependence of the distance between La@C_{82} molecules in C_{2n} fcc-crystals.

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]

$$L = a \times (c / 25)^{1/3} \quad \text{(S2)}$$

$$a = 1.31 \times d(C_{2n}) + 0.492 \quad \text{(S3)}$$

$$d(C_{2n}) = 0.71 \times (2n / 60)^{1/2} \quad \text{(S4)}$$

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 → 1 mol% is chosen because in this range, a small variation in the concentration leads to a large change in the inter-fullerene distance.

3 Y. Saito, N. Fujimoto, K. Kikuchi, and Y. Achiba, *Phys. Rev. B*, 1994, **49**, 14794.

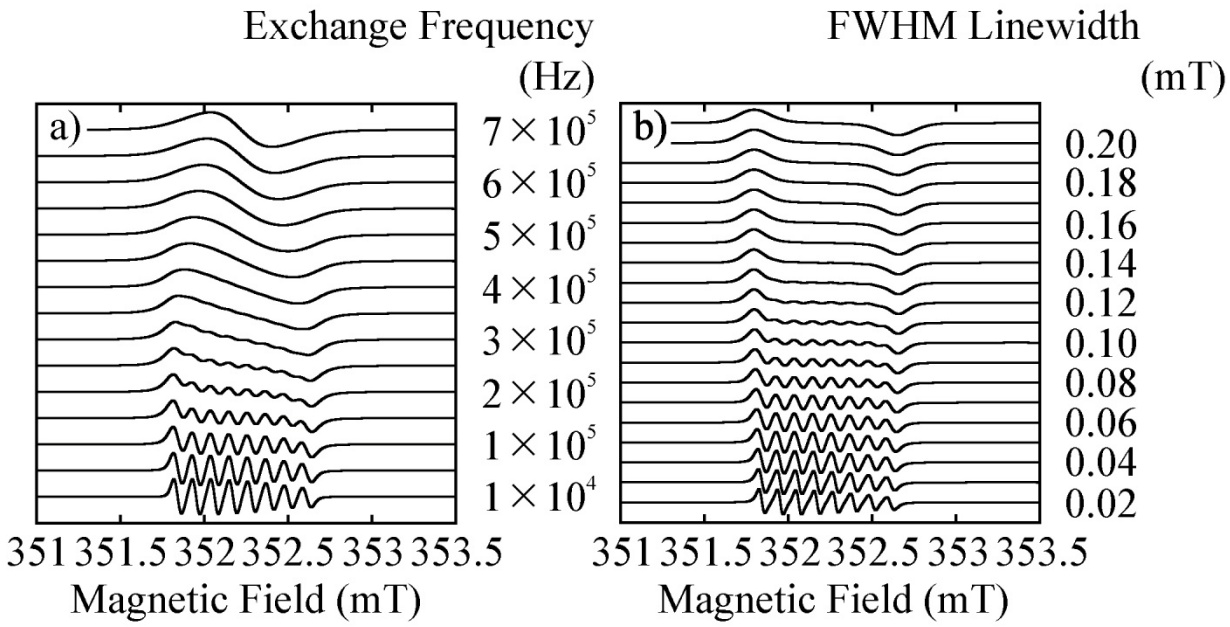

Fig. S2 a)Exchange frequency; and b)FWHM linewidth dependences of the hyperfine structure of La@C_{82}. These spectra are simulated by EasySpin software.[4]

4 S. Stoll and A. Schweiger, *J. Mag. Res.*, 2006, **178**, 42.

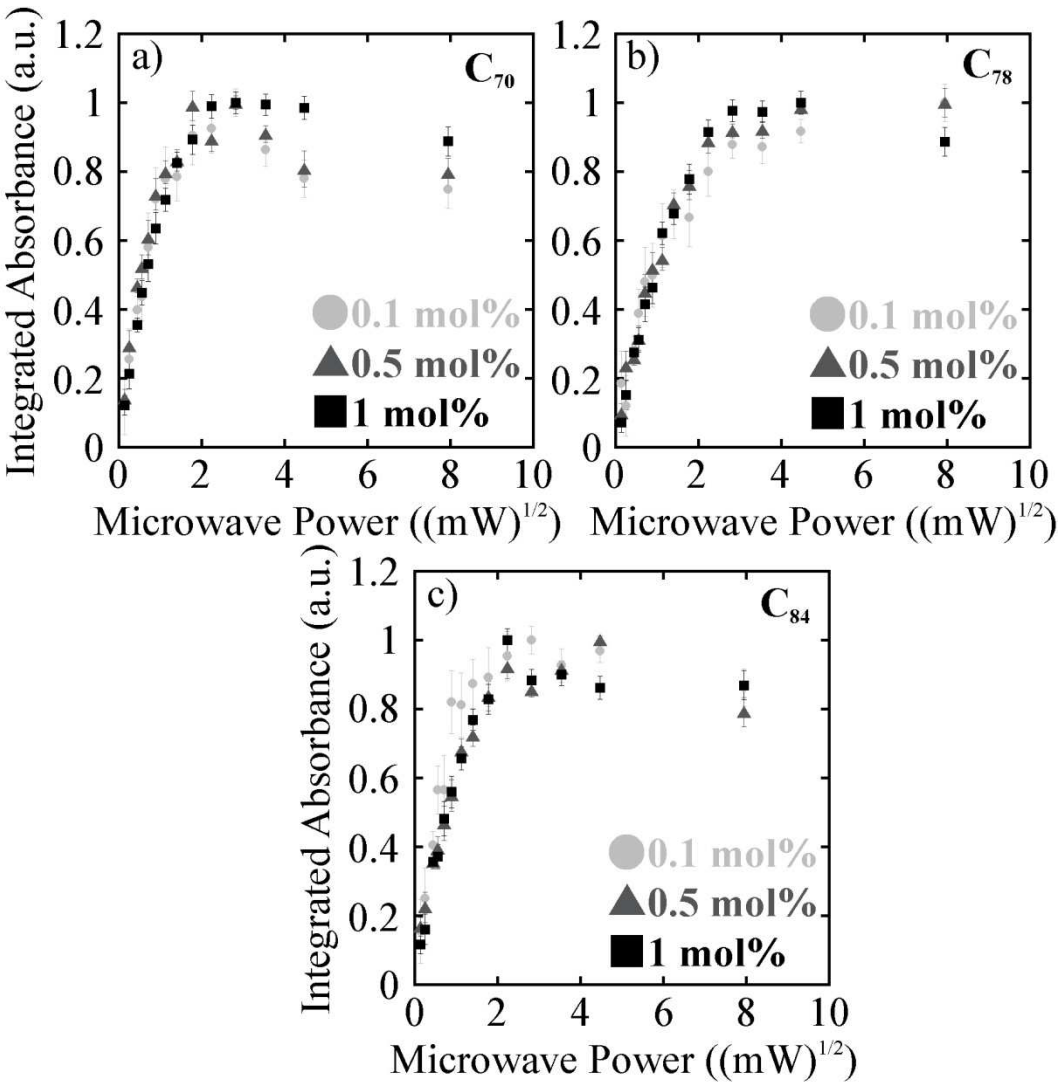

Fig. S3 Saturation curves of La@C_{82} in 0.1, 0.5 and 1 mol% in a)C_{70}; b)C_{78}; and c)C_{84} matrices at room temperature. Microwave frequency and modulation amplitude are 9.867 GHz and 0.025 mT, respectively.

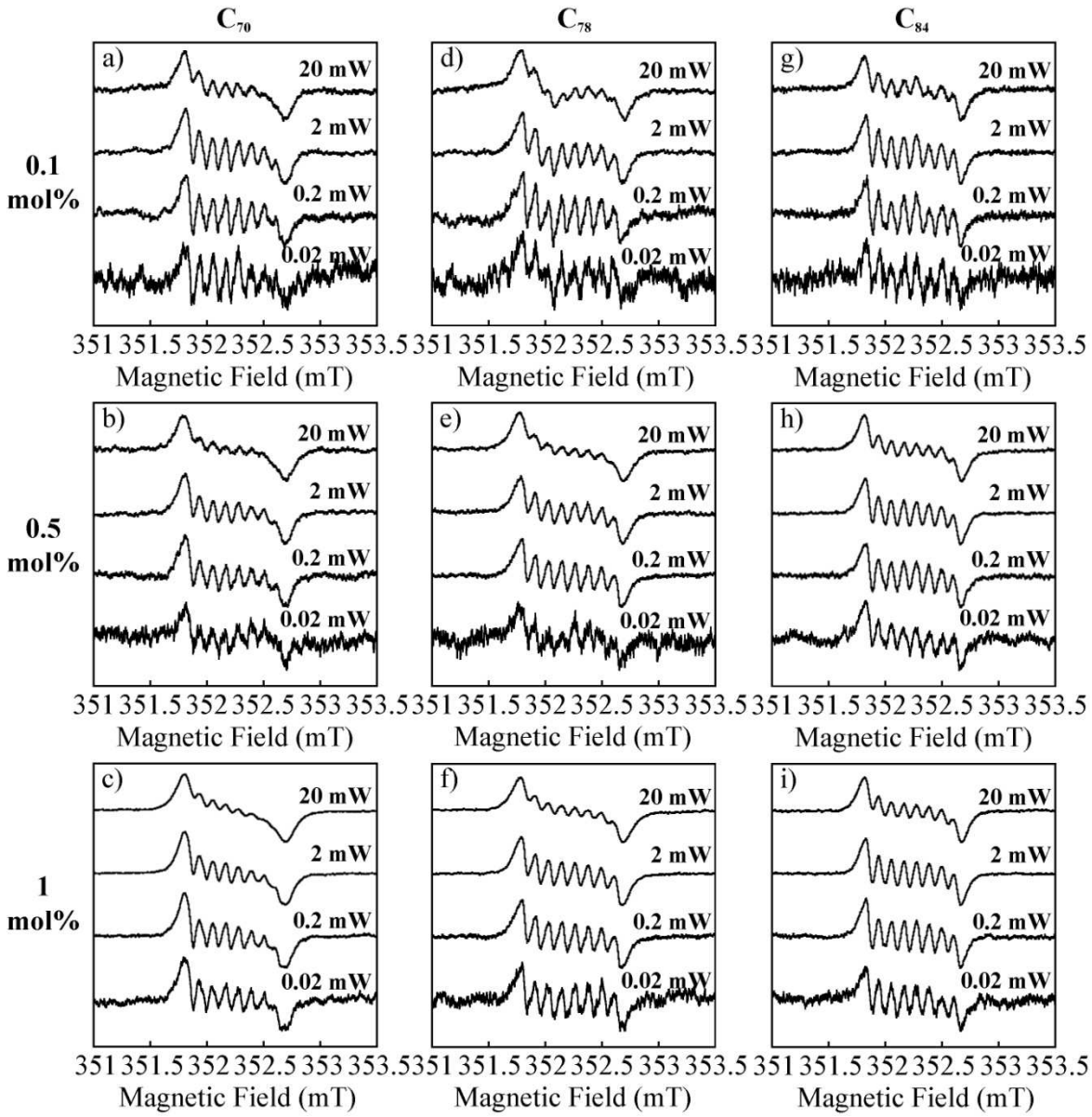

Fig. S4 Microwave power dependence of the ESR spectra of La@C_{82} in a)0.1; b)0.5; c)1 mol% in C_{70} matrix; d)0.1; e)0.5; f)1 mol% in C_{78} matrix; g)0.1; h)0.5; i)1 mol% in C_{84} matrix at room temperature. Microwave frequency and modulation amplitude are 9.867 GHz and 0.025 mT, respectively.