Supporting Information

Thermally Activated Delayed Fluorescence in a Y₃N@C₈₀ Endohedral Fullerene: Time-Resolved Luminescence and EPR Studies

Michal Zalibera, Denis S. Krylov, Dimitrios Karagiannis, Paul-Anton Will, Frank Ziegs, Sandra Schiemenz, Wolfgang Lubitz, Sebastian Reineke, Anton Savitsky, and Alexey A. Popov

anie_201710637_sm_miscellaneous_information.pdf
**Supporting information**

| Section                                                      | Page |
|--------------------------------------------------------------|------|
| Materials                                                   | S2   |
| Luminescence measurements                                   | S2   |
| Light-induced CW EPR                                        | S3   |
| Light-induced pulsed EPR                                    | S4   |
| Determination of the sign of ZFS parameter D                | S5   |
| W-band field dependent ENDOR                                | S7   |
| Spin Hamiltonian parameters of $\text{Y}_3\text{N} @ \text{C}_{80}$ excited triplet state | S9   |
| Computational details                                       | S9   |
| References                                                  | S10  |
Materials

Arc-discharge synthesis and chromatographic separation of \( Y_3N@C_{80} \) (\( I_h \) cage isomer) were described earlier.\(^{1,2}\)

Luminescence measurements

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. Variable temperature measurements of \( Y_3N@C_{80} \) dispersed on polystyrene film were performed with fluorescence microscope of local design and Janis ST-500 microscopy cryostat (temperatures down to 4 K).

Quantum yields were determined in solution using tetraphenylporphyrin as a standard (QY = 10\%). To ensure correct determination of fluorescence intensities, the detector was calibrated with an Avantes AvaLight-DH-CAL certified halogen lamp.

Luminescence lifetimes were measured by time-correlated single photon counting (TCSPC) technique based on PicoQuant TimeHarp counter/timer and the FluoFit software. Luminescence was excited by Omicron PhoxX diode laser modulated up to the frequency of 80 MHz (allowing the measurement of lifetimes longer than ~0.7 ns), time-resolved detection was performed by a PMT PMA 192 (PicoQuant).
Light-induced CW EPR

CW EPR measurements were performed with Bruker EMX Micro X-band CW spectrometer equipped with Eurotherm temperature control unit and helium cryostat. The measurements were performed in a Bruker ER 4104OR optical EPR cavity allowing simultaneous EPR and optical measurements. For light-induced EPR measurements, the samples (frozen toluene solution or polystyrene film) were illuminated by 488 nm Omicron PhoX diode laser.

![EPR spectrum](image)

Figure S1. CW X-band EPR spectrum of Y$_3$N@C$_{80}$ in frozen toluene solution at 7 K under illumination by 488 nm laser. Half-field signal corresponding to $\Delta m_S = 2$ transition can be clearly seen near 1707 G. In the $\Delta m_S = 1$ range, the spectrum exhibits absorption/emission pattern. The fine structure in the spectrum is presumably due to the different molecular sites in the frozen toluene.
Light-induced pulsed EPR

Saturated solutions of Y₃N@C₈₀ were prepared in toluene or toluene-d₈ (Sigma-Aldrich) at ambient conditions (without degassing), filled in the X/W-band quartz tubes, and flash frozen by immersing into the N₂(l) before insertion into the microwave cavity of the spectrometer.

Sample illumination in EPR/ENDOR experiments

The continuous irradiation in both X-band and W-band EPR/ENDOR experiments was achieved with the Power Technology Inc. IQ1C laser (510 nm, 40 mW). 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.

X-band pulsed EPR measurements

X-band pulse EPR measurements were performed at 10-60 K using a Bruker ELEXSYS II E580 X-band EPR spectrometer equipped with a EN4118X-MDS microwave cavity and a Oxford-CF935 liquid helium cryostat. Electron spin echo-detected (ESE) field-swept spectra were measured using the Hahn pulse sequence: \( t_\text{p} - \tau - 2t_\text{p} - \tau \)-echo. The length of the π/2 microwave pulse was generally set to \( t_\text{p} = 20 \text{ ns} \) and the interpulse distance to \( \tau = 400 \text{ ns} \). Under continuous irradiation (510 nm, 40 mW), 20 echo traces integrated over 180 ns around maximum were accumulated at each field position. The pulse repetition time was set to 5 ms. In time-resolved EPR measurements, the Hahn echo sequence was preceded by a laser flash (8 ns, 3 mJ/pulse at 488 nm, 2.5 s laser pulse repetition time) and a variable delay \( t_\text{DAF} \). A single echo was integrated at each field position. Decay of the polarized ESE signals was followed by incrementing the delay after laser pulse \( t_\text{DAF} \) in the range of 1 μs - 900 ms.

W-band pulsed EPR measurements

W-band measurements were performed at 10-60 K using a Bruker ELEXSYS E680 spectrometer operating at about 94 GHz. All experiments were carried out with a homebuilt ENDOR microwave cavity. Electron spin echo-detected (ESE) field-swept spectra were measured using the pulse sequence \( t_\text{p} - \tau - 2t_\text{p} - \tau \)-echo with \( t_\text{p} = 20 \text{ ns} \) and \( \tau = 300 \text{ ns} \). In continuous irradiation experiments (510 nm, 40 mW), 20 echos were accumulated and integrated over 140 ns around their maximum at each field position. The pulse repetition time was set to 1 ms. In the time-resolved EPR measurements single echo per field point was recorded with repetition time of 2.5 s (laser repetition time). Decay of the polarized ESE signals was followed by incrementing the delay after laser flash \( t_\text{DAF} \) in the range of 1 μs-900 ms. The ENDOR spectra were measured at 20 K under continuous irradiation of the sample (510 nm, 40 mW) using the Mims-type ENDOR sequence \( t_\text{p} - 2t_\text{p} - 7 - t_\text{p} - \tau \)-echo, with a RF pulse applied during the time interval \( T \). The experimental conditions were \( t_\text{p} = 20 \text{ ns} \), \( t_\text{RF} = 48 \text{ μs} \) or 60 μs, and \( \tau = 400 \text{ ns} \). All ENDOR spectra were recorded using the stochastic acquisition mode with two shot for each point, and the total number of scans was varied in the range 100–200 depending on the S/N.
Determination of the sign of ZFS parameter D

One of the advantages of the high-field EPR in the investigation of triplet states is the possibility to determine the sign of the ZFS D parameter by utilizing a effect thermal spin polarization at low temperatures. The approach is schematically sketched in Fig. S2.

Figure S2. Schematic illustration of the thermal polarization of triplet energy levels for a) positive and b) negative sign of ZFS parameter D. c) Contributions of the individual electron transitions to the EPR spectrum of $^3$Y$_3$N@C$_{80}^*$ at 10 K considering D of +128 MHz and −128 MHz, respectively.

Lowering of the experimental temperature in the range about the Boltzmann temperature $T_z = \frac{h\nu_m}{k}$ (4.5 K for 94 GHz W-band vs. 0.45 K for 94 GHz X-band) results in a progressive depopulation of the $T_+$ and $T_0$ levels and is connected with a smaller contribution of the $T_0 \leftrightarrow T_+$ transition in the EPR spectrum. Spectral contributions of the $T_0 \leftrightarrow T_+$ and $T_{-1} \leftrightarrow T_0$ transitions calculated using the spin Hamiltonian parameters from Table 1 and assuming $D>0$ or $D<0$, respectively, are shown in Fig. S2c. In the present case, a decrease of the EPR intensity at the edges of the spectrum is expected if $D > 0$, while a drop of the signal in the center of the spectrum should be observed for $D < 0$. Figure S3a compares the EPR spectra of $^3$Y$_3$N@C$_{80}^*$ recorded under continuous irradiation at 10 K and 20 K. A decrease of the signal intensities at the edges of the spectrum is observed at 10 K and is thus compatible with the positive sign of D for $^3$Y$_3$N@C$_{80}^*$. Indeed, a spectrum calculated for temperature of 10 K using $D$ of +128 MHz matches well with obtained experimental trace (Fig. S3b).
Figure S3. a) Normalized W-band ESE detected EPR spectra of $^{3}\text{Y}_3\text{N}@\text{C}_{80}^*$ at 10 K (solid line) and 20 K (dashed line); b) Experimental spectrum (solid line) at 10 K and spectra calculated using $D = +128$ MHz (dashed line) and $D = -128$ MHz (dotted line).
W-band field dependent ENDOR

Some estimate of the unpaired electron spin density distribution of the triplet can be obtained from the magnitude and symmetry of ZFS tensor. However, a more detailed information about spin density distribution is encoded in the hyperfine interactions of the electron spin with the nearby nuclei. Unfortunately, a common characteristic of the EPR spectra of random oriented triplet molecules, in the most often studied frozen solution form, is that the EPR spectrum lacks resolved small hyperfine splittings as a result of the anisotropy of the ZFS. In order to resolve the hyperfine couplings, one has to reach for hyperfine spectroscopy methods such as Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy (including Hyperfine Sub-level Correlation-HYSCORE) or Electron Nuclear Double Resonance (ENDOR) spectroscopy. While the ESEEM methods are more useful at lower microwave frequencies (X-band, 9.5 GHz) the ENDOR technique, similar to NMR, benefits considerably both in sensitivity and resolution from the use of higher magnetic fields and microwave frequencies (e.g. W-band, 94 GHz and higher). In the endohedral fullerene field ESEEM based methods were successfully used to characterize the paramagnetic N@C$_{60}$,$^6$ Y@C$_{82}$,$^7$ La@C$_{82}$,$^8$ while ENDOR proofed very powerful in investigations of La@C$_{82}$,$^{8-10}$ N@C$_{60}$,$^{11,12}$ and the triplet excited state of H$_2$@C$_{60}$.$^{13}$

![Figure S4. a) Frequency-field contour plot of the W-band Mims ENDOR spectra of $^3$Y$_3$N@C$_{80}$* recorded under continuous illumination (510 nm) at 20 K. Top panel shows the corresponding ESE detected EPR (blue line) and the pseudo-modulated EPR trace (green line). b) ENDOR spectra calculated using the spin Hamiltonian parameters from Table S1. * in a) marks the frequency position of an artefact line](image_url)

Twenty one Mims ENDOR traces were acquired at equidistant field positions covering the whole field range of the EPR spectrum and are shown in a contour plot presentation in Fig S4a. A pair of lines at 5.98 and 8.02 MHz respectively can be assigned to the hyperfine coupling of the $^{89}$Y nuclear spin. The orientation selection achieved in the W-band ENDOR spectra, together with the independence of signal positions on the field position, reveal a predominantly isotropic character of the $^{89}$Y hyperfine coupling and $A_{iso}(^{89}$Y) value of 1.02±0.2 MHz. The three $^{89}$Y nuclei in the endohedral cluster can thus be considered magnetically equivalent. With the positive value of D a positive sign of $A_{iso}(^{89}$Y) is additionally determined from the calculated ENDOR spectra in Fig. S4b. The ENDOR patterns in the range from 8.5 to 13.0 MHz in Fig. S4a originate from the $^{14}$N hyperfine and quadrupole couplings. Simulations indicate the presence of a small positive axial
hyperfine coupling $A_\parallel = +0.62$ MHz and $A_\perp = +0.15$ MHz and a larger quadrupole. From the well resolved features in Fig. S4a the $|\epsilon^2 Qq/h|$ value of 1.46 MHz and negligible asymmetry parameter $\eta \sim 0$ MHz are estimated but the orientation of the quadrupole tensor with respect to the ZFS and $g$ tensors could not be determined.
Spin Hamiltonian parameters of Y$_3$N@C$_{80}$ excited triplet state

Table S1. Spin Hamiltonian parameters used for the simulation of the EPR/ENDOR spectra of the $^{3}$Y$_3$N@C$_{80}$" (exp) and computed by DFT with PBE and PBE0 functionals

|       | g       | ZFS parameters, MHz | Hyperfine coupling, MHz | Nuclear quadrupole coupling, MHz |
|-------|---------|---------------------|--------------------------|---------------------------------|
| exp   | $g_z$   | 2.0004              | $D$ +128                 | $A_{iso}^{89\text{Y}}$ +1.02   | $|e^2Qq/h|$ 1.46 $\eta$ 0       |
|       | $g_y$   | 2.0008              | $E$ 0                    | $A_i$, $A_L^{(14\text{N})}$ +0.62, +0.15 |                               |
|       | $g_z$   | 2.0030              |                          |                                  |                               |
| PBE   | $g_x$   | 2.0004              | $D_{SS}$ +103            | $A^{(89\text{Y})}$ +1.74, +1.82, +2.15 | $|e^2Qq/h|$ 1.29 $\eta$ 0       |
|       | $g_y$   | 2.0008              | $E_{SS}$ 0               | $A^{(89\text{Y})}$ +1.90        |                               |
|       | $g_z$   | 2.0030              |                          | $A^{(14\text{N})}$ +0.09, -0.09, +0.83 |                               |
| PBE0  | $g_x$   | 2.0001              | $D_{SS}$ +53             | $A^{(89\text{Y})}$ +1.96, +2.05, +2.43 | $|e^2Qq/h|$ 1.36 $\eta$ 0       |
|       | $g_y$   | 2.0001              | $E_{SS}$ 0               | $A^{(89\text{Y})}$ +2.15        |                               |
|       | $g_z$   | 2.0028              |                          | $A^{(14\text{N})}$ -0.07, -0.07, +0.78 |                               |

Computational details

Molecular structures in the singlet and triplet states were first optimized at the PBE$^{14}$/TZ2P level using Priroda code.$^{15,16}$ The basis set for Y atoms used SBK-type core effective potential. The structure of the $S_1$ state was optimized at the time-dependent (TD) PBE/TZ2P level, the structure of the $T_1$ state was optimized with conventional DFT in triplet spin configuration.

More refined calculations of the spin properties were performed with Orca suite$^{17}$ with GGA PBE and hybrid PBE0 functionals, ZORA scalar-relativistic correction, and ZORA-tailored versions$^{18}$ of def2-TZVP basis set.$^{19}$ Table S1 lists DFT-computed g-tensors, A-tensors, zero-field splitting parameters and electric field gradient for N. Computations of zero-filed splitting resulted in unrealistically large spin-orbit terms (several orders of magnitude larger than experimental values), so only spin-spin terms are listed in the Table S1. In agreement with experimental results, DFT predicts small values of $hfc$ constants, quasi-isotropic $A^{(89\text{Y})}$ tensor, and substantial anisotropy of the $A^{(14\text{N})}$ tensor. Predicted spin-spin contributions to ZFS tensor are also in agreement with experiment (positive $D$ value in the range of 100 MHz and negligible $E$ value).
References

1. A. A. Popov, L. Zhang and L. Dunsch, ACS Nano, 2010, 4, 795–802.
2. S. Yang, A. A. Popov and L. Dunsch, Angew. Chem.-Int. Edit. Engl., 2008, 47, 8196-8200.
3. N. Cox, W. Lubitz and A. Savitsky, Molecular Physics, 2013, 111, 2788-2808.
4. A. Nalepa, K. Möbius, W. Lubitz and A. Savitsky, Journal of Magnetic Resonance, 2014, 242, 203-213.
5. L. Rapatskiy, N. Cox, A. Savitsky, W. M. Ames, J. Sander, M. M. Nowaczyk, M. Rögner, A. Boussac, F. Neese, J. Messinger and W. Lubitz, Journal of the American Chemical Society, 2012, 134, 16619-16634.
6. J. J. Morton, A. M. Tyryshkin, A. Ardavan, K. Porfyrakis, S. A. Lyon and G. A. Briggs, J Chem Phys, 2005, 122, 174504.
7. S. Knorr, A. Grupp, M. Mehring, U. Kirbach, A. Bartl and L. Dunsch, Applied Physics A: Materials Science & Processing, 1998, 66, 257-264.
8. K.-P. Dinse and T. Kato, 2006, 684, 185-207.
9. V. K. Koltover, V. P. Bubnov, Y. I. Estrin, V. P. Lodygina, R. M. Davydov, M. Subramoni and P. T. Manoharan, Physical Chemistry Chemical Physics, 2003, 5, 2774.
10. N. Weiden, T. Kato and K.-P. Dinse, The Journal of Physical Chemistry B, 2004, 108, 9469-9474.
11. A. M. Tyryshkin, J. J. Morton, A. Ardavan and S. A. Lyon, J Chem Phys, 2006, 124, 234508.
12. C. Knapp, N. Weiden and K. P. Dinse, Magnetic resonance in chemistry : MRC, 2005, 43 Spec no., S199-204.
13. V. Filidou, S. Mamone, S. Simmons, S. D. Karlen, H. L. Anderson, C. W. Kay, A. Bagno, F. Rastrelli, Y. Murata, K. Komatsu, X. Lei, Y. Li, N. J. Turro, M. H. Levitt and J. J. Morton, Philosophical transactions. Series A, Mathematical, physical, and engineering sciences, 2013, 371, 20120475.
14. J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865-3868.
15. D. N. Laikov and Y. A. Ustynuk, Russ. Chem. Bull., 2005, 54, 820-826.
16. D. N. Laikov, Chem. Phys. Lett., 1997, 281, 151-156.
17. F. Neese, WIREs Comput. Mol. Sci., 2012, 2, 73-78.
18. D. A. Pantazis, X.-Y. Chen, C. R. Landis and F. Neese, J. Chem. Theory Comput., 2008, 4, 908-919.
19. F. Weigend and R. Ahlrichs, Phys. Chem. Chem. Phys., 2005, 7, 3297-3305.