Abstract: The endohedral fullerene $\text{Y}_3\text{N@C}_{80}$ exhibits luminescence with reasonable quantum yield and extraordinary long lifetime. By variable-temperature steady-state and time-resolved luminescence spectroscopy, it is demonstrated that above 60 K the $\text{Y}_3\text{N@C}_{80}$ exhibits thermally activated delayed fluorescence with maximum emission at 120 K and a negligible prompt fluorescence. Below 60 K, a phosphorescence with a lifetime of 192 ± 1 ms is observed. Spin distribution and dynamics in the triplet excited state is investigated with X- and $W$-band EPR and ENDOR spectroscopies and DFT computations. Finally, electroluminescence of the $\text{Y}_3\text{N@C}_{80}/\text{PFO}$ film is demonstrated opening the possibility for red-emitting endohedral fullerene-based organic light-emitting diodes (OLEDs).

Fullerenes usually exhibit low quantum yields (QY) of fluorescence (in the range of $10^{-4}$) owing to the slow radiative decay and a fast and efficient inter-system crossing (ISC), leading to an almost quantitative formation of triplet states with slow non-radiative decay. Exohedral fullerene derivatization can substantially modify the π-system of fullerenes and produce highly luminescent multi-adducts. Another way to enhance the quantum yield of luminescence of fullerenes is based on the thermal repopulation of the $S_1$ state, via the $T_1$ state, if the $S_1-T_1$ gap is sufficiently small. This process is known as thermally activated delayed fluorescence (TADF) and has been found to increase the fluorescence quantum yield of $\text{C}_{60}$ up to 0.08 at high temperatures. TADF is currently an extensively examined phenomenon in the field of organic light-emitting diodes (OLEDs) as it allows to harvest up to 100% of electrically formed excitons.

With the exception of several Er- and Tm-based endohedral metallofullerenes (EMFs), with metal-based emission, EMFs are also non-luminescent. The internal heavy-atom effect leads to even faster ISC in EMFs than in empty fullerenes. The lifetime of the $S_1$ state in $\text{ScN@C}_{80}$ is only 48 ps. Surprisingly, $\text{Y}_3\text{N@C}_{80}$ exhibits luminescence with reasonable quantum yield of ca 1% or even 8% in a cyclo- adduct, and an unusually long luminescence lifetime of 200–800 ns at room temperature. Herein, we explore the photo-emission mechanism of $\text{Y}_3\text{N@C}_{80}$ with variable-temperature time-resolved luminescence spectroscopy and EPR spectroscopy. The former reveals the evolution of the emission spectra and lifetimes with temperature, whereas the latter provides information on relaxation dynamics and spin density distribution in the triplet state of $\text{Y}_3\text{N@C}_{80}$. We show that efficient photoemission of $\text{Y}_3\text{N@C}_{80}$ is caused by the small $S_1-T_1$ gap leading to TADF above 60 K. In a blend with polyfluorene (PFO), $\text{Y}_3\text{N@C}_{80}$ exhibits electroluminescence, which suggests that after suitable optimization and boost of the QY, $\text{Y}_3\text{N@C}_{80}$ may be used for red or NIR-emitting OLEDs.

In deoxygenated toluene solution, $\text{Y}_3\text{N@C}_{80}$ exhibits luminescence with a QY of 1.7% and lifetime of 0.95 μs at 296 K. Saturation with air leads to a 30-fold reduction of the QY and appearance of singlet oxygen emission at 1270 nm. In iodobenzene, which dramatically reduces the fluorescence QY of fullerenes due to the external heavy-atom effect, only a small decrease of the QY of $\text{Y}_3\text{N@C}_{80}$ was found. The very long luminescence lifetime, dependence of the QY on oxygen, and negligible effect of the heavy atom all indicate that emission of $\text{Y}_3\text{N@C}_{80}$ is not a standard fluorescence.

Luminescence was then measured in toluene solution or in a polystyrene film at different temperatures down to 10 K. Cooling the sample from 296 K to 120 K increased the integral emission intensity (that is, the luminescence QY) more than 20-fold, but did not change the shape of the spectrum, comprising the main band at 701 nm and lower-energy vibronic bands (Figure 1a). With further cooling, a drop of the emission intensity at 701 nm was observed, and the band disappeared below 60 K (Figure 1b). At the same time, the band at 739 nm increased and became the main emission signal at low temperatures. The spectral pattern observed at 60 K remained unaltered down to 10 K (Figure 1c). The luminescence lifetime of $\text{Y}_3\text{N@C}_{80}$ dispersed in a polystyrene is gradually increasing with cooling from 1.08 μs

Thermally Activated Delayed Fluorescence in a $\text{Y}_3\text{N@C}_{80}$ Endohedral Fullerene: Time-Resolved Luminescence and EPR Studies

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which gives $\Delta E_{ST} = 0.08 \pm 0.01$ eV, intrinsic phosphorescence lifetime $\tau_S = 192 \pm 1$ ms, and $\tau_T = 1.7 \pm 1.3$ ms.

TADF has been described for empty fullerenes, and is particularly well studied for $C_{60}$.[2,9] In comparison to $Y_N@C_{60}$, empty fullerenes have much higher $\Delta E_{ST}$ values (0.25–0.30 eV), which result in higher temperatures, at which TADF is efficient (for example, above 250 K in $C_{60}$).

To understand the origin of the small $\Delta E_{ST}$ gap in $Y_N@C_{60}$, we performed DFT calculations.[10] In the lowest energy configuration of $Y_N@C_{60}$, Y atoms coordinate cage hexagons in $\eta^2$-manner (Figure 2). The HOMO of the molecule is localized on the poles, whereas the LUMO has the largest contributions near the Y-coordinated hexagons.

Time-dependent DFT calculations show that $S_0 \rightarrow S_1$ excitation is predominantly the HOMO–LUMO transition and can be described as the intramolecular electron transfer from the poles to the equator (see the difference electron density in Figure 2c). The spatial separation of the “donor” and “acceptor” parts causes the low $S_0 \rightarrow T_1$ gap (0.079 eV at the TD-PBE/TZ2P level). Importantly, $Y_N$ cluster has a negligible contribution to the $S_0 \rightarrow S_1$ excitation. Likewise, the spin density in the $T_1$ triplet state is localized on the carbon cage with very small spin populations on Y and N (Figure 2d).

$Y_N@C_{60}$ was further studied by electron paramagnetic resonance (EPR) spectroscopy. The long triplet lifetime enables the use of light-induced EPR to study the spin density distribution and relaxation dynamics of the triplet $Y_N@C_{60}$. Under continuous laser illumination below 120 K in frozen toluene or polystyrene film, a continuous wave (CW) EPR signal of the $Y_N@C_{60}$ triplet is measured (Supporting Information, Figure S1), which also features...
a half-field signal at helium temperatures (Supporting Information, Figure S1).

A further characterization of $^1\text{Y},\text{N}@\text{C}_{80}^+$ was achieved in a multifrequency pulsed EPR study. Figure 3 shows the time-resolved electron spin echo detected EPR (TR-ESE-EPR) spectra of the $\text{Y},\text{N}@\text{C}_{80}$ triplet at X- and W-band microwave frequencies. Shortly after the laser flash (Figure 3a,d) the spectra exhibit polarized character owing to the non-equilibrium population of the triplet energy levels generated during the intersystem crossing from the $S_1$ state. The polarization pattern is described as EE/AA at both microwave frequencies (emission/absorption). The polarization pattern is opposite to that observed for the empty fullerene excited triplets $^3\text{C}_{80}^+$, $^3\text{C}_{70}^+$ (AA/EE). The equilibrium population of the triplet energy levels is accomplished via spin lattice relaxation approximately 500 μs after the laser flash at 20 K (Figure 3g, $T_1$ of 74 μs and 91 μs at X- and W-band, respectively). EPR spectra recorded with longer delay after flash ($t_{\text{delay}}$) correspond to the Boltzmann population at the corresponding temperature (Figure 3b,e), and are reproduced in a simulation with a rhombic g tensor ($g_x = 2.0004$, $g_y = 2.0008$, $g_z = 2.0030$) and an axially symmetric zero field splitting tensor (ZFS, $D = +128$ MHz, $E = 0$). The positive sign of $D$ is determined by utilizing the enhanced thermal spin polarization in W-band EPR (Supporting Information, Figures S2, S3). The g tensor of $^3\text{Y},\text{N}@\text{C}_{80}^+$ is more asymmetric and the ZFS is smaller than in the case of the empty fullerene $^3\text{C}_{80}^+$ ($D(E = -340/ +15$ MHz)), $^3\text{C}_{70}^+$ ($D(E = +153/ +5–42$ MHz)) and monometallo endohedral fullerenes $^3\text{Sr}@\text{C}_{80}^+$ ($D(E = 260/35$ MHz), $^3\text{Ba}@\text{C}_{80}^+$ ($D(E = 250/47$ MHz)) and non-metal endofullerene $^3\text{H}_2@\text{C}_{80}^+$ ($D(E = -340/ +15$ MHz)). The small ZFS in $^3\text{Y},\text{N}@\text{C}_{80}^+$ points to a negligible impact of the spin orbit coupling and is thus in line with the dominant spin density distribution on the carbon cage (Figure 2d). It also reflects the larger size of the cage and thus formally longer spin-spin distribution between the unpaired electrons.

TR-ESE-EPR shows that the $^3\text{Y},\text{N}@\text{C}_{80}^+$ exhibits a long lifetime ($\tau_1$) depending on the deuteration level of toluene (Figure 3h; 240 ms in [D$_8$]toluene and 180 ms in [H$_8$]toluene at 20 K). Thus, the $\tau_1$ values determined by TR-ESE-EPR are in good agreement with the lifetime obtained from the luminescence (192 ms in polystyrene). Owing to the long lifetime of the $T_1$ at 20 K, the pulsed EPR spectra obtained under continuous irradiation (Figure 3e,f) correspond to the signals with equilibrium population of the triplet energy levels, and can be well simulated using the spin Hamiltonian parameters derived above. The X-band spectra (Figure 3b,c) exhibit an additional narrow hole in the centre of the spectrum, which can be traced back to the simultaneous excitation of both allowed electron spin transitions of the triplet($T_2\rightarrow T_1$ and $T_2\rightarrow T_3$) as described for $^3\text{C}_{80}^+$.12c

The detailed image of the spin density distribution in the $T_1$ state is encoded in the hyperfine interactions of the electrons with the nearby nuclei, and can be extracted using hyperfine spectroscopy methods such as electron nuclear double resonance (ENDOR).15 ENDOR proved very powerful in investigations of paramagnetic endohedral fullerenes La@C$_{80}$,16 $^3\text{Na}@\text{C}_{80}$17 $^3\text{N}@\text{C}_{70}$18 and the triplet excited state of H$_2@\text{C}_{80}$.14 For light excited triplets ENDOR studies are scarce and often hampered by the short $T_1$ and/or short $T_2$ relaxation times. Here, the long $\tau_2$ of $^3\text{Y},\text{N}@\text{C}_{80}^+$ allowed for a detailed ENDOR investigation. W-band ENDOR spectra recorded at different field positions corresponding to the turning points of the ZFS pattern, are shown in Figure 4. The trace in Figure 4a shows intense sharp lines around 7 MHz, 21.9 MHz and 35.9 MHz, at the Larmor frequencies of the $^{85}\text{Y}$, $^{2}$H and $^{13}$C nuclei. These signals are characteristic for the triplet states and originate from degenerate NMR transitions within the zero level electron spin manifold $m_S = 0$. The additional broader lines at frequencies below 13.0 MHz reflect the hyperfine and quadrupole couplings of the cluster nuclei, $^{85}$Y and $^{14}$N (Figure 4c,d; Supporting Information, Figure S4). The orientation selection achieved in the W-band ENDOR spectra reveal a predominantly isotropic character of the $^3\text{Y}$ hyperfine interaction, with a small positive $A_{\text{iso}}(^{85}\text{Y})$ hyperfine coupling (hfc) constant of $+1.02$ MHz, (for details, see the Supporting Information). The three Y nuclei in the cluster are magnetically equivalent. A small positive axial hfc with $A_i(^{14}\text{N}) = +0.62$ MHz, $A_i(^{13}\text{C}) = +0.15$ MHz ($A_{\text{iso}}(^{14}\text{N}) = +0.46$ MHz), and a somewhat larger nuclear quadrupole coupling of $\left| \frac{eQ}{\hbar} \right| = 1.46$ MHz (asymmetry $\eta \approx 0$), is found for the central $^{13}$N atom. Experimental hfc values are in reasonable agreement with the results of DFT calculations in the Supporting Information.
The isotropic hfc constants translate to about 0.082 \% s-spin population at each Y atom and 0.025 \% s-spin population on the nitrogen, respectively, in line with the negligible spin density delocalization on the cluster (Figure 2d). In the family of Y-containing EMF-radicals a similar situation is found for Y@C_{29} with $A_{\text{iso}}(^{3}Y)$ of 1.33 MHz (0.1 \% s-spin pop.).\(^{[19]}\)

Somewhat larger metal contributions are found in the radical anion of Y,N@C_{30} (32 MHz) and its pyrrolidine adduct (17.5 and 2.6 MHz).\(^{[20]}\) A strikingly different situation is found for the unpaired electron delocalized between two Y atoms in Y,N@C_{29}-N and Y,N@C_{29}(CH\_2C\_H\_2) with $A_{\text{iso}}(^{3}Y)$ close to 220 MHz (17.6 \% s-spin pop. for each Y).\(^{[21]}\) $A_{\text{iso}}(^{3}N)$ values reported earlier for nitride clusterfullerenes are 3.7 MHz in the anion radical of Y,N@C_{30} and 1.4 MHz in its pyrrolidine adduct.\(^{[20]}\)

TADF has recently been proposed as third generation emitter concept since it allows all triplets to be harvested radiatively and thus the internal quantum efficiency approaches 100 \%. To verify the applicability of EMFs such as Y,N@C_{30} in TADF-OLEDs, we prepared a simple solution-processed device using Y,N@C_{30} embedded in a polyfluorene (PFO) as an active material (Figure 5). The poly(3,4-ethyleneoxythiophene) polystyrene sulfonate (PEDOT:PSS) and PFO:Y,N@C_{30} layers were prepared sequentially by spin-coating onto indium tin oxide (ITO) electrodes. The device was then transferred into a vacuum chamber for Al deposition. Figure 5 shows that PFO with 10 \% mass of Y,N@C_{30} has a new band at 708 nm owing to the electroluminescence of Y,N@C_{30}, which is absent in the device made from pure PFO. The quantum yield of Y,N@C_{30} is rather low at room temperature for an efficient application, but a further increase of the QY may be achieved via derivatization,\(^{[22]}\) by changing the temperature (Figure 1), or by supramolecular assemblies.\(^{[23]}\) A co-existence of PFO fluorescence and Y,N@C_{30} luminescence in Figure 5 also indicates that the energy transfer in this device is not very efficient and needs further optimization.

To summarize, we have discovered that Y,N@C_{30} has a small $S_{T_{1}}$ gap of 0.08–0.09 eV and exhibits thermally activated delayed fluorescence above 60 K, with a quantum yield increasing from about 1 \% at room temperature to the maximum value of about 22 \% at 120 K. Below 60 K, phosphorescence with a long lifetime of 192 ± 1 ms is exclusively observed. The triplet state of Y,N@C_{30} is extensively characterized by time-resolved EPR and ENDOR spectroscopy, providing information on the dynamics, hyperfine structure, and spin density distribution in the T_{1} state.

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Conflict of interest

The authors declare no conflict of interest.

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