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$N@C_{60}$–Porphyrin: A Dyad of Two Radical Centers

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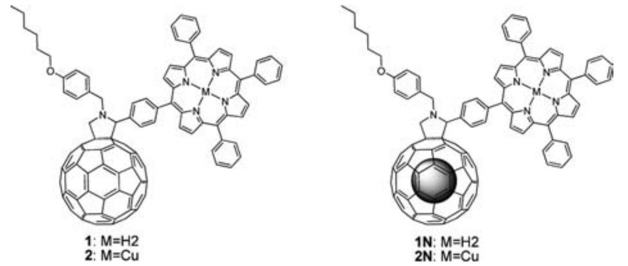
Ⓢ *Supporting Information*

ABSTRACT: Dyads of endohedral nitrogen fullerene and porphyrin have been synthesized. In the two-radical-center dyad, the copper(II) tetraphenylporphyrin suppressed the electron spin resonance (ESR) signal of $N@C_{60}$ through intramolecular dipolar coupling with a strength of 27.0 MHz. Demetalation of the metalloporphyrin moiety of the dyad, which effectively turned the two-radical-center dyad into a single-radical-center dyad, recovered 82% of the ESR signal of $N@C_{60}$. Such mechanism of switching a spin state on and off could find use in molecular spintronics applications.

In the search for molecular materials for quantum technologies, endohedral fullerenes are leading candidates.[1,2] $N@C_{60}$, with a nitrogen atom trapped inside the C_{60} cage,[3−6] exhibits the longest electron spin coherence time of any molecular radical.[7] Single-qubit operations and coherent quantum state transfer between the electron spin and nuclear spin of $^{15}N@C_{60}$ have been demonstrated.[8,9] To fulfill the scalability requirement, much effort has been dedicated to the synthesis of dimers of endohedral fullerenes. Initial progress was made in the synthesis of fullerene dimers of the type $N@C_{60}$–C_{60}, in which one fullerene moiety is spin-active and the other is spin-silent,[10−12] but recently we succeeded in synthesizing $N@C_{60}$–$N@C_{60}$.[13] At the same time, dyads of C_{60} and porphyrin have been widely explored in the interests of photovoltaic energy conversion.[14,15] Some of the reaction schemes have been successfully transferred to endohedral fullerenes such as $M_3N@C_{80}$ (M = Y, Sc) and $La@C_{82}$.[16,17] If both the porphyrin and endohedral fullerene in the dyad are paramagnetic, a two-radical-center system can be constructed using this approach. A recent investigation reported ferromagnetic spin coupling between copper porphyrin and the metallofullerene $La@C_{82}$ in a porphyrin-based inclusion complex.[18] Herein we have synthesized two covalently linked $N@C_{60}$–porphyrin dyads and demonstrated intramolecular spin–spin coupling between the copper porphyrin and the endohedral fullerene. The two $N@C_{60}$–porphryin dyads **1N** and **2N** (Chart 1), as well as their C_{60}–porphyrin counterparts **1** and **2**, were synthesized following the Prato reaction procedure.[19] Complete separation of dyad **1N** (or **1**) from dyad **2N** (or **2**) was achieved using recycling-mode HPLC (Figure 1). The removal of residual dyad **1N** was essential when the electron spin resonance (ESR) spectrum of dyad **2N** was measured because of the high sensitivity of ESR spectroscopy.

Chart 1. C_{60}–H_2TPP (1), C_{60}–CuTPP (2), $N@C_{60}$–H_2TPP (1N), and $N@C_{60}$–CuTPP (2N) (TPP = Tetraphenylporphyrin)



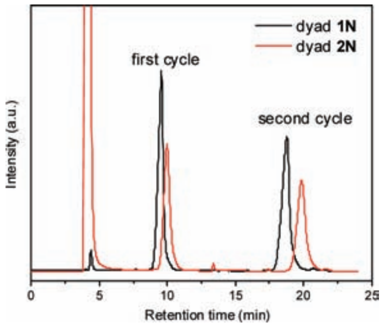


Figure 1. HPLC traces of dyads **1N** (black) and **2N** (red) (5PBB column, toluene as eluent, 18 mL/min).

The UV–vis absorption spectra of these dyads are combinations of the spectra of the constituent fullerenes and porphyrins, consistent with previous reports on other fullerene–porphyrin dyads.[20−22] A sample containing dyad **1N** (a mixture of **1N** and **1**) exhibited ESR spectra similar to those of other pyrrolidine derivatives of $N@C_{60}$.[23,24] As shown in Figure 2, zero-field splitting (ZFS) features (D = 16.3 MHz and E = 0.4 MHz) were observed in the frozen-solution ESR spectrum of dyad **1N**. This finding confirms a negligible effect of the free-base porphyrin on the electron spins in the $N@C_{60}$ moiety.

Copper(II) tetraphenylporphyrin (CuTPP) and dyad **2** exhibit similar g factors and hyperfine interaction patterns, indicating a negligible effect of the empty fullerene cage on the

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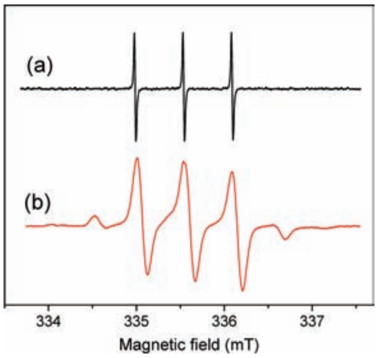


Figure 2. ESR spectra of dyad **1N** in toluene at (a) 295 and (b) 77 K.

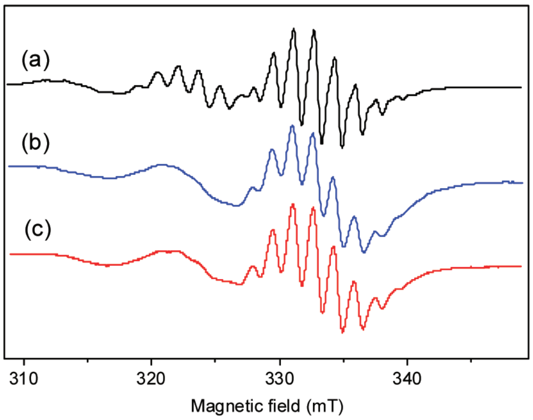


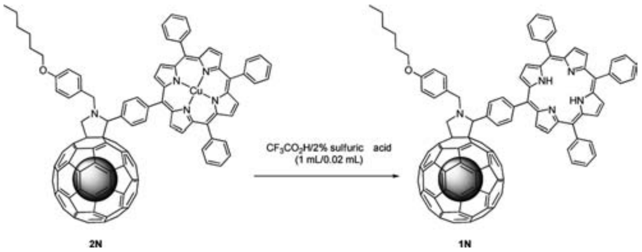
Figure 3. ESR spectra of (a) CuTPP, (b) dyad **2**, and (c) dyad **2N** in CS_2.

electron spin located on the copper center (Figure 3). The splitting of nine lines in the highest-field component indicates that the four nitrogen atoms in the porphyrin macrocycle are magnetically equivalent. The differences in the line shapes of the two spectra are caused by the different molecular correlation times (79 ps for CuTPP and 355 ps for dyad **2**).[25] The incorporation of a fullerene cage in dyad **2** increases the molecular size and slows the tumbling rate of the molecule significantly.

Unexpectedly, the dyad **2N** sample (a mixture of **2N** and **2**) showed ESR spectra similar to those of dyad **2**, containing only features of the CuTPP moiety (Figure 3). The characteristic ESR signal of N@C_{60} was detected in neither the room-temperature solution nor the frozen solution of the dyad **2N** sample. The disappearance of the N@C_{60} signal could be caused either by an interaction with the copper spin or decomposition of N@C_{60} during the reaction, leaving only dyad **2** in the sample.[26] Therefore, it was indispensible to be able to demonstrate the presence of dyad **2N** in the sample.

Demetalation[27] was employed to convert dyad **2N** into dyad **1N** (Scheme 1), from which the ESR signal of N@C_{60} could be determined. The acidification process was monitored by UV−vis spectroscopy. As shown in Figure 4a, after the copper ion was removed, the absorption peaks ascribed to CuTPP disappeared and peaks ascribed to free-base porphyrin emerged. Accordingly, the ESR signal of N@C_{60} was recovered (Figure 4b). The recovered N@C_{60} signal was 82 ± 4% of that of the previous dyad **1N** sample with the same concentration. Given the possibility of decomposition of N@C_{60} during the acidification, it is reasonable to expect that the fraction of endohedral species in the dyad **2N** sample is similar to that in the dyad **1N** sample (approximately 0.014%).

Scheme 1. Demetalation of Dyad 2N



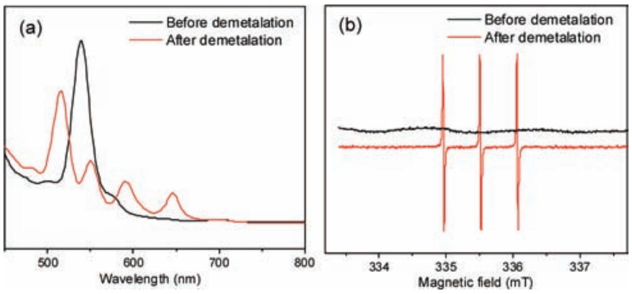


Figure 4. (a) UV−vis absorption and (b) ESR spectra of a dyad **2N** sample before and after demetalation. The UV−vis spectra were recorded in a CH_2Cl_2 solution, and ESR spectra were recorded in a CS_2 solution.

Because every N@C_{60} is bound to CuTPP in the dyad, the complete suppression of the ESR signal of N@C_{60} indicates strong spin−spin interactions between the unpaired electrons of the nitrogen and the copper. In the weak-coupling regime, there are two kinds of spin−spin interactions between the two separated radical centers, namely, dipolar coupling and exchange coupling. Exchange coupling normally requires overlap of the electron density distributions, but such overlap could be excluded in dyad **2N** on the basis of our DFT calculations.[25] First, both the theoretical calculations and previous experimental results confirmed that approximately 98% of the nitrogen spin is localized on the endohedral nitrogen atom in N@C_{60}.[6,15] Second, the copper spin is exclusively distributed on the porphyrin moiety, as also indicated by the similarity between the ESR spectra of dyad **2** and CuTPP (Figure 3). Third, the interaction between the porphyrin moiety and the fullerene moiety is negligible in the electronic ground states of the fullerene−porphyrin dyads on the basis of their UV−vis absorption spectra. Therefore, dipolar coupling must be the dominant mechanism of spin−spin interaction in dyad **2N**.

In solution samples of dyad **2N**, both intermolecular and intramolecular dipolar coupling are present. Whereas the intermolecular coupling is sensitive to the sample concentration, the intramolecular coupling is independent of the concentration. Therefore, the effects of the two types of dipolar coupling can be distinguished by the concentration-dependence studies of the ESR spectra. In a simple mixture of N@C_{60} with CuTPP, where intermolecular dipolar coupling exists exclusively, an increase in sample concentration led to both line width broadening[25] and a decrease in the signal amplitude (Figure 5a). The ESR signal of N@C_{60} disappeared only in samples with very high concentrations (e.g., 4.1×10^{-3} M).

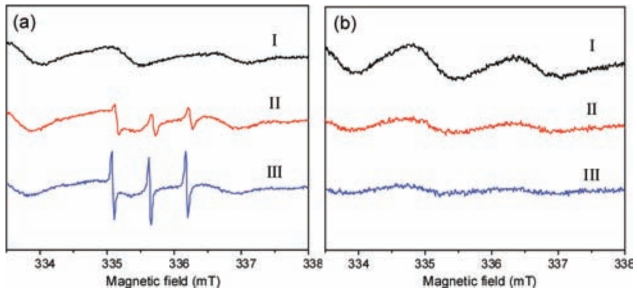


Figure 5. ESR spectra of (a) an N@C_{60}/CuTPP mixture (molar ratio 1:1) and (b) a dyad **2N** sample at (I) 4.1×10^{-3} M, (II) 1.6×10^{-3} M, and (III) 8.0×10^{-4} M. Measurements were taken at room temperature in CS_2, and the parameters were set to best demonstrate the signal of N@C_{60}.

However, for dyad **2N**, no ESR signal of N@C_{60} was observed at any of the experimental concentrations (Figure 5b). Since the intermolecular dipolar coupling is negligible in samples with low concentrations (e.g., 8.0×10^{-4} M), we deduce that the intramolecular dipolar coupling plays the dominant role in the suppression of N@C_{60} signal.

To calculate the intramolecular dipolar coupling strength, we used a distance of 1.26 nm between the two radical centers, which was determined on the basis of the optimized geometry of dyad **2**, assuming that the nitrogen atom occupies the center of the fullerene cage.[25] The coupling strength (D_{dip}) was therefore found to be 2.7×10^7 Hz following the classical point-dipole approximation. Because the spin−lattice relaxation rate of the copper ion in solution (1×10^9 to 3.3×10^9 Hz)[28] is higher than D_{dip}, the main consequence of dipolar coupling is expected to be line width broadening rather than any AB splitting pattern.[29,30] Furthermore, the molecular tumbling rate of 2.8×10^9 Hz for dyad **2N** in CS_2, which falls in the intermediate molecular motion regime, cannot effectively counteract the line width broadening effect. In view of the extremely narrow line width of N@C_{60} (<9 kHz),[2] the broadening effect should dramatically reduce the signal amplitude of N@C_{60}. Such a decrease in signal amplitude, as well as the low endohedral nitrogen percentage in the dyad, could explain the disappearance of the N@C_{60} signal in the ESR spectrum of the dyad **2N** sample.

In summary, two dyads of N@C_{60} and porphyrin have been synthesized. The free-base porphyrin imposes a negligible effect on N@C_{60} in dyad **1N**. In the two-radical-center dyad **2N**, the ESR signal of N@C_{60} disappears. The concentration dependence demonstrated strong intramolecular dipolar coupling between the two radicals, and the dipolar coupling strength was calculated to be 27.0 MHz. The line width broadening and amplitude decrease resulting from dipolar coupling explain the suppression of the ESR signal of N@C_{60} in dyad **2N**. Removal of the copper ion from the metalloporphyrin moiety, which led to recovery of approximately 82% of the N@C_{60} signal, proved the existence of dyad **2N** in the sample. The demetalation, which changed the two-radical-center system (dyad **2N**) into a single-radical system (dyad **1N**), provides a strategy for switching spin states on and off. This may have applications in molecular spintronics devices. Additionally, these dyads may provide a system in which the electron spins of N@C_{60} interact with the electron pair resulting from photon-induced charge separation in photoactive adducts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization of dyads **1** and **2**, simulation of ESR spectra, demetalation process of dyads **2** and **2N**, and DFT calculation results for dyads **2** and **2N**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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