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A Photochemical On−Off Switch for Tuning the Equilibrium Mixture of H_2 Nuclear Spin Isomers as a Function of Temperature

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S *Supporting Information*

ABSTRACT: The photochemical interconversion of the two allotropes of the hydrogen molecule [*para*-H_2 (pH_2) and *ortho*-H_2 (oH_2)] incarcerated inside the fullerene C_{70} ($pH_2@C_{70}$ and $oH_2@C_{70}$, respectively) is reported. Photoexcitation of $H_2@C_{70}$ generates a fullerene triplet state that serves as a spin catalyst for pH_2/oH_2 conversion. This method provides a means of changing the pH_2/oH_2 ratio inside C_{70} by simply irradiating $H_2@C_{70}$ at different temperatures, since the equilibrium ratio is temperature-dependent and the electronic triplet state of the fullerene produced by absorption of the photon serves as an "on−off" spin catalyst. However, under comparable conditions, no photolytic pH_2/oH_2 interconversion was observed for $H_2@C_{60}$, which was rationalized by the significantly shorter triplet lifetime of $H_2@C_{60}$ relative to $H_2@C_{70}$.

Spin chemistry is a field that is concerned with the nuclear and electronic spin control of the rates of elementary chemical and physical steps of thermal and photochemical reactions. The field has been dominated by investigations of spin control of photophysical steps involving electronic singlet−triplet (and triplet−singlet) intersystem crossing (ISC) transitions. Although nuclear-spin ISC is also subject to spin control, as a rule there are very few examples that have proven to be useful for experimental study. The outstanding exception to this rule is the ISC of the two nuclear spin isomers of H_2, *ortho*-H_2 (oH_2) and *para*-H_2 (pH_2). oH_2 (↑↑) is a nuclear triplet and NMR-active, whereas pH_2 (↑↓) is a nuclear singlet and NMR-silent. The pH_2/oH_2 ratio is temperature-dependent, with values of ∼33% at 300 K, ∼50% at 77 K, and ∼100% below 20 K.[1] Thus, if equilibrium could be achieved, the ^1H NMR signal of H_2 would disappear as the temperature approaches 20 K!

However, the equilibrium between pH_2 and oH_2 takes months or longer to achieve in the absence of a "spin catalyst". A spin catalyst is often in the form of an electronic or nuclear spin that can interact more strongly with one of the nuclear spins of H_2 than the other and, in effect, induce a selective flip of one spin.[2−5] We have reported that the nuclear spin isomers of $H_2@C_{60}$ (Figure 1) can be interconverted by dispersing the fullerene on the surface of NaY zeolite at room temperature and exposing the $H_2@C_{60}$@zeolite solid to liquid oxygen for 30 min at 77 K.[6,7]

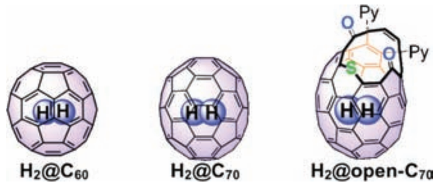

Figure 1. Structures of endofullerenes (Py = 2-pyridyl).

Although this method is effective and serves as a proof of principle for the spin conversion of the H_2 nuclear spin isomers of $H_2@C_{60}$, one limitation of the method is that only the equilibrium pH_2/oH_2 ratio of ∼50% can be achieved at 77 K. Clearly, the invention of an effective method that would allow forward ISC conversion ($oH_2 \rightarrow pH_2$) and back ISC conversion ($pH_2 \rightarrow oH_2$) to be initiated at the experimenter's convenience at any temperature is highly desirable. An ideal system would enable the experimenter to "switch" the spin catalyst on and off at will at any temperature. The temperature of the experiment would "tune" the equilibrium concentration of nuclear spin isomers, and the switch would determine whether the spin catalyst is active or inert. This was partially achieved with covalently bound nitroxide radicals; however, these catalysts are either generally too fast or too slow to finely control the oH_2/pH_2 ratio inside.[8,9]

An elegant possibility for such a spin catalyst on−off switch exists as an inherent electronic feature of the fullerene skeleton. Absorption of a photon by C_{60} and C_{70} produces a very short lived electronically excited singlet state that undergoes ISC to a triplet state in less than 1 ns.[10−12] While the fullerene skeleton is in the electronic triplet state, its paramagnetism might serve as a means of causing ISC of the nuclear spin isomers of $H_2@C_{60}$ and $H_2@C_{70}$. In other words, the "paramagnetic skin" of the fullerene in the triplet state serves as a potential spin catalyst for ISC of the nuclear spin isomers of H_2 in the fullerene (Figure 2). If the photoactive

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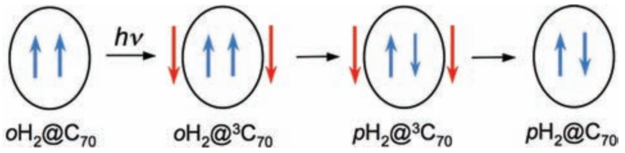

Figure 2. Using the photoinduced electronic triplet state of C_{70} (red arrows) to convert oH_2 to pH_2 inside the cage (blue arrows).

paramagnetism of the "cage" triplet state could catalyze a spin transformation of the "guest" inside, promoting the conversion of oH_2 to pH_2 inside could be as simple as changing the temperature of the system and flipping a light switch. Furthermore, the nonuniform distribution of spin density in the triplets of both fullerenes, as determined by electron paramagnetic resonance spectroscopy,[13−15] could provide the magnetic field gradient needed to induce ortho/para conversion.

We report experimental examples of the achievement of a photochemical on−off switch for tuning the equilibrium mixture of nuclear spin isomers of H_2 incarcerated in a fullerene. We also report here that while $H_2@C_{60}$ does not effectively work as such a switch, $H_2@C_{70}$ is an excellent one. A simple rationale of the difference between these two systems is presented.

The endofullerenes $H_2{}^*@C_{60}$ and $H_2{}^*@C_{70}$ ($H_2{}^*$ represents a mixture of ^{1}H-NMR-active H_2 and HD) were prepared [see the Supporting Information (SI)].[16−21] The equilibrium mixture of pH_2 and oH_2 is conveniently followed by ^{1}H NMR spectroscopy: since pH_2 is NMR-silent, the depletion of the oH_2 singlet resonance in the ^{1}H NMR spectrum can be used to quantify the composition of the nuclear spin isomers in the equilibrium mixtures as follows. The NMR spectra were normalized to the ^{1}H NMR triplet from endohedral HD, which does not have ortho and para states. Approximately 0.2 mg each of $H_2{}^*@C_{60}$ and $H_2{}^*@C_{70}$ were dissolved together in 300 μL of toluene-d_8 and added to a quartz tube. This solvent is known to form transparent glasses at low temperatures (~160 K) and can serve as an NMR solvent at room temperature. The quartz tube was degassed via several freeze−pump−thaw cycles and flame-sealed. The sample of mixed $H_2{}^*@C_{60}$ and $H_2{}^*@C_{70}$ was then placed in a quartz optical dewar filled with liquid N_2 and irradiated with a 300 W xenon lamp fitted with a water filter for 4 h. Following irradiation, the sample tube remained sealed and was inserted into a 5 mm NMR tube.

Figure 3 shows the ^{1}H NMR spectra of $H_2{}^*@C_{60}$ and $H_2{}^*@C_{70}$ taken before and after the irradiation. Both spectra have been normalized to the $HD@C_{70}$ NMR lines. The same normalization factor sufficed for both sets of HD peaks, indicating that irradiation did not change the ratio of the two fullerenes in the sample. While the resonances for $oH_2@C_{60}$, $HD@C_{60}$, and $HD@C_{70}$ were essentially unchanged after irradiation, the oH_2 inside C_{70} was clearly depleted. While the HD signals should not change, the disparity in the signals from oH_2 inside C_{60} and C_{70} is striking and significant. Quantitative analysis of the results showed that the irradiated $H_2{}^*@C_{60}$ sample at 77 K showed essentially no change in the equilibrium composition at room temperature. On the other hand, the irradiated $H_2{}^*@C_{70}$ at 77 K exhibited a 33% reduction in the oH_2 signal at room temperature, corresponding to the value for the expected 50:50 ratio of the equilibrium mixture of nuclear spin isomers of H_2 at 77 K. Enrichment beyond 50% pH_2 was achieved by cooling $H_2{}^*@C_{70}$ in toluene in a He cryostat and irradiating for 7 h, which gave a mixture containing ~60% pH_2. The temperature of the system could not be determined accurately, but an equilibrium containing 60% pH_2 would correspond to a temperature of 65 K, suggesting that under the conditions employed, the irradiation produced substantial warming of the frozen sample.

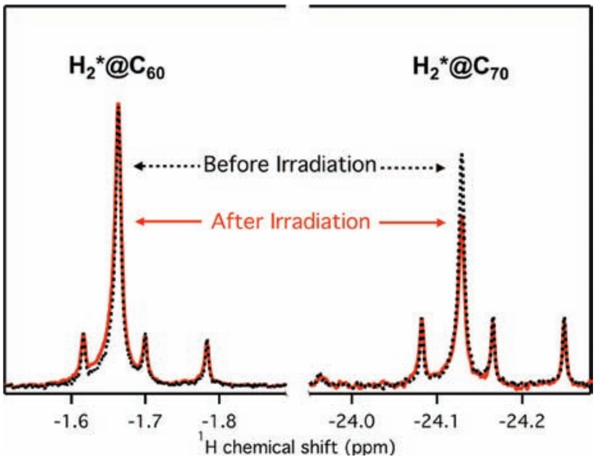

Figure 3. ^{1}H NMR spectra of a mixture of $H_2{}^*@C_{60}$ and $H_2{}^*@C_{70}$ in toluene-d_8 before (black, dotted) and after (red, solid) irradiation at 77 K.

To ensure that the signal depletion illustrated in Figure 3 was indeed a result of pH_2 enrichment inside C_{70}, thermally induced spin conversion was performed using liquid O_2 as a spin catalyst. Approximately 3 mg each of $H_2@C_{70}$ and $H_2{}^*@C_{60}$ dissolved in 1 mL of CS_2 were added to a slurry of 2 g of NaY zeolite in 30 mL of hexanes. After the solution was stirred at room temperature for 1 h, the color changed from red to colorless and the zeolite was colored instead, indicating dispersion of the fullerene. Next, the fullerene@NaY was added to a glass vessel, which was evacuated and cooled to 77 K. Several milliliters of liquid O_2 was then condensed into the vessel. After 30 min, the O_2 was removed via dynamic vacuum while the vessel was still immersed in liquid nitrogen. The vessel was then warmed to room temperature, and the fullerenes were extracted from the zeolite with excess CS_2. After removal of CS_2 under vacuum, the ^{1}H NMR spectrum was taken in 1,2-dichlorobenzene-d_4.

The oH_2 singlet inside *both* fullerenes was reduced in intensity relative to the $HD@C_{60}$ triplet, similar to the photoconverted $oH_2@C_{70}$, indicating that the *thermally induced spin-conversion method is effective for both $H_2@C_{60}$ and $H_2@C_{70}$, whereas the photoinduced method is effective only for $H_2@C_{70}$*. The solution was maintained at room temperature and monitored regularly via ^{1}H NMR spectroscopy as the oH_2/pH_2 ratio slowly increased to 3:1 over the course of several days with lifetimes of 6.8 ± 0.7 and 2.7 ± 0.3 days for $H_2@C_{60}$ and $H_2@C_{70}$, respectively. The irradiated sample of $H_2{}^*@C_{70}$ was also monitored in this way, and the oH_2 signal returned with a similar lifetime of 2.8 ± 0.7 days, indicating that in both cases an excess of pH_2 was initially present at room temperature and then slowly relaxed to equilibrium at the same rate (Figure 4).

We next address the issue of why the $H_2{}^*@C_{60}$ sample did not undergo conversion upon photolysis whereas the $H_2{}^*@C_{70}$ sample did, although *both* samples do undergo *thermally induced* conversion to the expected 50:50 equilibrium mixtures of spin isomers using the previously established method. Thus, the failure of $H_2{}^*@C_{60}$ to undergo nuclear-spin ISC under photolysis at 77 K while $H_2{}^*@C_{70}$ undergoes full conversion is most

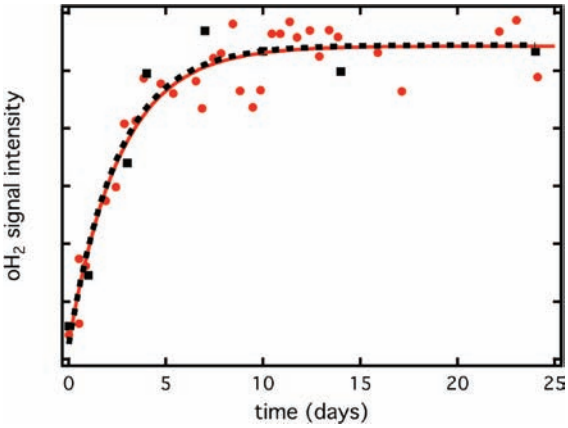

Figure 4. Restoration of the $oH_2@C_{70}$ NMR signal, indicating room-temperature back conversion of pH_2 generated thermally (red) and photochemically (black) to the equilibrium amount of oH_2.

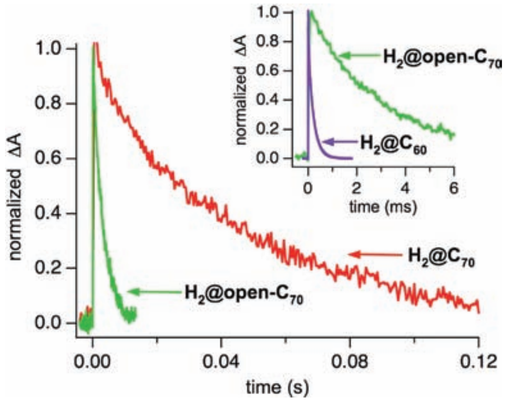

Figure 5. Transient absorption decay traces of fullerene triplet states at 77 K in 3:1 (v/v) decalin/cyclohexane monitored at 785 nm after excitation with laser pulses at 532 nm.

likely due to differences between the $H_2^*@C_{60}$ and $H_2^*@C_{70}$ triplet systems.

We hypothesized that the difference between the two systems under photoinduced conversion is the lifetime of the electronic triplet state of $H_2^*@C_{70}$ relative to that of $H_2^*@C_{60}$. We therefore measured the triplet lifetimes of $H_2^*@C_{60}$ and $H_2^*@C_{70}$ at 77 K. The samples were prepared in 3:1 (v/v) decalin/cyclohexane glass at a concentration of 100 μM, and the triplet absorption decay was measured by probing at 785 nm. The triplet lifetimes were found to be 0.21 ± 0.01 and 46 ± 2 ms for $H_2@C_{60}$ and $H_2@C_{70}$, respectively (Figure 5). These compare favorably with values reported in the literature for C_{60} and C_{70} at room temperature.[22] The value for $H_2@C_{70}$ was confirmed by a phosphorescence measurement as 49 ± 2 ms (see the SI). Thus, we conclude that the ~100-fold longer lifetime of triplet $H_2^*@C_{70}$ relative to triplet $H_2^*@C_{60}$ allowed the paramagnetism of the former to operate as a spin catalyst more effectively with respect to the conversion of the spin isomers. The long lifetime of the C_{70} triplet state also accounts for the effectiveness of the triplet self-quenching in toluene ($k = 1.2 \times 10^8$ M^{-1} s^{-1}) via short-lived triplet excimers;[22] however, in a glassy matrix this quenching mechanism is not active and thus does not affect the spin conversion by lowering the steady-state concentration of the C_{70} triplet. This quenching would reduce the C_{70} triplet lifetime to less than 100 μs at the experimental concentration of ~1 mM.

The lifetime hypothesis was confirmed by comparing the conversion of dihydrogen inside an open-cage C_{70} (H_2@open-C_{70}) to that of $H_2@C_{70}$ at 77 K. H_2@open-C_{70} (Figure 1) is a synthetic precursor to $H_2@C_{70}$ that contains a 13-membered-ring orifice through which H_2 is inserted at high pressure and temperature (the H_2 remains inside upon cooling to room temperature). With the same procedure as above, enrichment of pH_2 inside open-C_{70} was detected with a 20% signal reduction and pH_2/oH_2 = 40:60 after 4 h of irradiation. However, the enrichment of pH_2@open-C_{70} was observed only when a focusing lens was employed to increase the photon flux through the glassy sample. In the case of photoconversion of $H_2@C_{70}$, a focusing lens was not necessary.

The triplet lifetime of H_2^*@open-C_{70} (3.2 ± 0.2 ms) was measured to be ~10 times shorter than that of triplet $H_2^*@C_{70}$, and this species is apparently much less efficient in conversion, by at least an order of magnitude. Since triplet $H_2^*@C_{60}$ is an additional ~10 times shorter-lived than triplet H_2^*@open-C_{70}, its efficiency seems to be negligible under our conditions. The major differences in triplet lifetimes (Figure 5) speak against the different structural symmetry of $H_2^*@C_{60}$ versus $H_2^*@C_{70}$ as the sole mechanistic basis for the difference in the photochemical efficiencies of $H_2^*@C_{60}$ and $H_2^*@C_{70}$.

Now we consider the photochemical back conversion (nuclear-spin ISC of enriched $pH_2@C_{70}$ to $oH_2@C_{70}$) at room temperature. Surprisingly, we found that irradiation of the enriched sample at room temperature in liquid toluene did not lead to any back conversion within detection limits after substantial photolysis. Having determined that triplet lifetimes are critical in determining the efficiency of forward conversion, we concluded that this result was due to the shortened lifetime of triplet $pH_2@C_{70}$ in fluid solution at room temperature. As stated above, the triplet lifetime of C_{70} is shortened to values on the order of tens of microseconds as a result of various quenching processes such as self-quenching and triplet−triplet annihilation. Thus, the short triplet lifetime was hypothesized as an explanation for the failure to observe back conversion in fluid solution. A test of this hypothesis would be to remove the lifetime-reducing factors by carrying out the photolysis at a temperature low enough that the solvent remains frozen but sufficiently high that the equilibrium pH_2/oH_2 ratio differs from that in the enriched sample.

To test the hypothesis, $pH_2@C_{70}$ was enriched to pH_2/oH_2 = 50:50 by irradiating $H_2^*@C_{70}$ at 77 K as described above. Next, the sample was thawed and the solution warmed to 300 K and irradiated again. As noted above, no change in the NMR signal was seen in a comparison of the spectra before and after this second irradiation. The procedure was then repeated, but this time the sample was held at 155 K using a liquid nitrogen evaporator and irradiated for 2 h. At that temperature, the expected equilibrium pH_2/oH_2 ratio is 28:72. Photolysis caused a 15% increase in the oH_2 signal relative to the HD ^{1}H NMR triplet (i.e., a pH_2/oH_2 ratio of 38:62), indicating some, though not complete, conversion. Still, this result confirmed that the triplet lifetime is the critical feature in determining the effectiveness of both forward and back conversion via the photolysis of $H_2^*@C_{70}$.

We have shown that spin conversion of H_2 inside C_{70} can be driven in either direction by absorption of a photon, with the requirement that the solvent is a glass during the irradiation to produce a long lifetime of the $H_2^*@C_{70}$ triplet. The constraint that the C_{70} must be in a glass supports the hypothesis that the photoinduced triplet state serves as a spin catalyst for this reaction because in a thawed solution, triplet−triplet annihilation or other quenching processes eliminate the paramagnetism of the cage.

In summary, we have demonstrated that under the proper conditions, the nuclear-spin ISC of $H_2@C_{70}$ can be turned on or off with a photon switch and that the composition of the equilibrium mixture of nuclear spin isomers of $H_2@C_{70}$ can be tuned with temperature with the triplet $H_2@C_{70}$ produced by photon absorption providing the paramagnetism for spin catalysis. In contrast, $H_2@C_{60}$ does not undergo significant conversion under similar photolysis conditions because of its much shorter triplet lifetime.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and phosphorescence data. This material is available free of charge via the Internet at http://pubs.acs.org.

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