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Photophysical Studies of 1,2-$C_{70}H_2$

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Photophysical measurements have been made on 1,2-$C_{70}H_2$, the most stable isomer of the simplest C_{70} derivative. This dihydride's electronic absorption spectrum is more diffuse than that of C_{70}. Red shifts in the fluorescence and phosphorescence emission spectra show that excitations to the lowest singlet and triplet electronic states require approximately 8% less energy in 1,2-$C_{70}H_2$ than in C_{70} and that the S_1-T_1 gap of 1,2-$C_{70}H_2$ is ca. 310 cm^{-1} smaller than that of the parent fullerene. The dominant peak in the dihydride's $T_n \leftarrow T_1$ near-infrared absorption spectrum falls at 1050 nm. Compared to the corresponding transition of C_{70}, this absorption feature is broadened, red-shifted by 75 nm, and reduced in peak molar absorptivity by a factor of 2. Derivatization of C_{70} to form 1,2-$C_{70}H_2$ accelerates T_1 decay by more than an order of magnitude, giving an intrinsic triplet lifetime of 2.0 ms at room temperature. The rate constant for triplet deactivation through ground state self-quenching is near 7.6×10^7 M^{-1} s^{-1}, or approximately twice that of C_{70}.

Introduction

The photophysical properties of fullerenes have attracted continuing attention since the first isolation of C_{60}. For basic researchers, fullerenes form an intriguing new class of compounds to investigate and understand, while applied researchers hope to find or enhance special properties that may lead to improved photodynamic therapy, solar energy harvesting, optical limiting, or other uses. In both of these pursuits, chemical derivatization is an important tool. It is therefore necessary to study the effects of chemical modifications on fullerene photophysics.

Although a number of C_{60} derivatives have now been photophysically characterized,[1−3] very little is known about the changes in basic photophysical properties caused by derivatizing higher fullerenes. To investigate this area, we have studied $C_{70}H_2$, the simplest adduct of C_{70} and the prototype of a large class of C_{70} derivatives. In the 1,2-isomer of this dihydride, which is found to be the most stable by experiment and ab initio calculations,[4] hydrogen atoms are added to adjacent carbon atoms at a fusion of two of the six-membered rings that surround a five-membered ring at the C_{70} molecule's "pole". C_{70} has 10 equivalent [6,6] bonds of this type. The remaining three types of [6,6] bonds in C_{70} are in local environments with less curvature and show lower reactivities.[5] For samples of the 1,2-isomer of $C_{70}H_2$, we have measured the ground state absorption spectrum, quantum yield for singlet oxygen generation, fluorescence and phosphorescence spectra, transient absorption spectrum, and triplet kinetics data. The results indicate that the triplet quantum yield of 1,2-$C_{70}H_2$ remains nearly unchanged compared with the C_{70} parent compound, some of its excited state energies are markedly lowered, and its T_1 decay is strongly accelerated.

Experimental Section

To synthesize the samples, the general procedure described previously for the reduction of C_{60} by anhydrous hydrazine[6] was applied to C_{70}. A solution of C_{70} (23 mg, 0.027 mmol) in freshly distilled benzene (30 mL) was degassed by bubbling argon through it for 1 h. A 10-fold molar excess of anhydrous hydrazine (8.8 mg, 0.27 mmol) in methanol (10% v/v) was added in four portions over 36 h while the mixture was stirred under argon. The crimson C_{70} solution gave way to a dark brown product mixture within 24 h of the initial hydrazine addition. After 48 h reaction time, the mixture was extracted with water (3×100 mL) and brine (3×100 mL) and the organic layer was then dried over Na_2SO_4. Evaporation of the solvent gave 20 mg of a dark reddish-brown solid.

Analysis and purification of the product mixture was accomplished by HPLC with a Regis Buckyclutcher I stationary phase,[7] 70:30 toluene:hexane isocratic mobile phase, and UV detection at 330 nm. The major product of the reaction appeared as a single band with a small leading shoulder. These products were collectively separated from the crude reaction mixture and identified as C_{70} dihydrides by FD-MS. Analysis by ^1H NMR (toluene-d_8, 250 MHz) confirmed their isomeric identities (1,2-$C_{70}H_2$: AB quartet at 4.25, 4.17, 3.73, and 3.65 ppm; 5,6-$C_{70}H_2$: singlet at 3.86 ppm).[4] The isomeric mixture was separated by further HPLC runs to give a pure sample of the major 1,2-$C_{70}H_2$ product.

For studies in toluene solution, the collected HPLC fraction was evaporated at room temperature and then redissolved in toluene that had been purified by sequential distillation from $LiAlH_4$ and P_2O_5. Benzene-d_6 (Cambridge Isotope Laboratories, 99.6%) was used without further purification as a solvent for induced absorption measurements in the near-infrared, where its freedom from C−H stretching overtones gave adequate transparency. Oxygen was removed from fluid solutions by approximately 12 cycles of freeze−pump−thaw degassing with agitation. To prepare solid film samples, a solution of 1,2-$C_{70}H_2$ in toluene was mixed with a toluene solution of poly-methyl methacrylate (PMMA). After the resulting viscous mixture was applied to a glass substrate, the solvent was evaporated by exposure to air for 1 or 2 days (in darkness) followed by 1 h of vacuum-drying at room temperature. Films produced in this way

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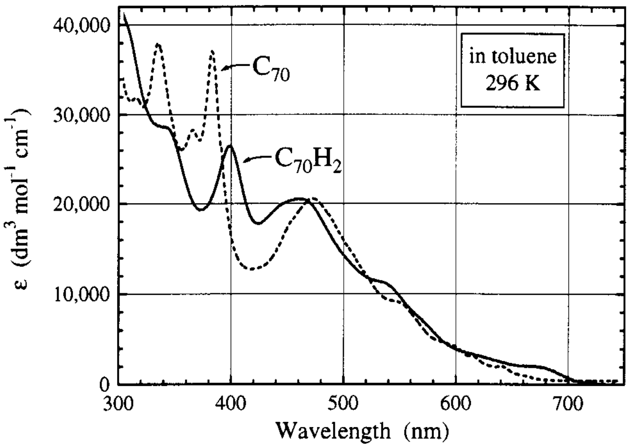

Figure 1. Ground state absorption spectra of 1,2-$C_{70}H_2$ (solid line) and C_{70} (dottted line) in toluene solution at 296 K. The absorptivities in the C_{70} spectrum are taken from ref 8.

had thicknesses in the 100−200 μm range and showed UV−visible absorption spectra very similar to that in fluid toluene solution. For low-temperature measurements, film samples were mounted in a cryostat (Oxford Optistat-DN) whose sample chamber was evacuated and back-filled with dry nitrogen gas. A digital controller (Oxford ITC-601) stabilized the sample at selected temperatures within the range from 77 to 320 K.

Ground state UV−visible absorption spectra were recorded on a Cary 4 or GBC 918 spectrophotometer set for 1 nm resolution. We determined molar absorptivities by taking the spectrum of a sample solution and then weighing the solute that remained after evaporating a measured volume to dryness. For samples that are unstable to heating, such as $C_{70}H_2$, this procedure avoids concentration errors that would occur when preparing standard solutions by weighing out solid samples that contain residual solvent. For luminescence and induced absorption measurements, our samples were optically excited by nanosecond-scale 532 nm pulses from a Nd:YAG laser system (New Wave MiniLase II). The pulse energy incident on the samples was between 0.1 and 1 mJ, and the irradiated area varied between 0.1 and 1.0 cm^2. Sample luminescence was collected at 90° with lenses, spectrally selected by a monochromator (ISA Triax 180) containing gratings with 600 and 1200 grooves/mm, and detected with a biased silicon photodiode. After preamplification, the detected signals were averaged over multiple excitation pulses by a digitizing oscilloscope (Tektronix TDS-430A). An IBM-compatible computer controlled the oscilloscope and monochromator through a GPIB interface. The detection system's time resolution was limited by the preamplifier to 0.7 μs. For induced absorption measurements, the same detection system was used in conjunction with probe light from a tungsten−halogen lamp driven by a highly regulated power supply. In this configuration, the excitation and probe beams were aligned collinearly through sample cells of 1 or 5 cm path length.

Results and Discussion

Figure 1 shows the visible and near-ultraviolet absorption spectrum of ground state 1,2-$C_{70}H_2$ in toluene solution. For comparison, we also plot a spectrum of C_{70} in which the absorptivities have been scaled to match values from a careful study that used solvent-free C_{70} crystals.[8] The two compounds show transitions with similar molar absorptivities throughout this range. However, the ultraviolet absorption spectrum of 1,2-$C_{70}H_2$ is noticeably broader than that of C_{70}, probably reflecting greater line broadening from accelerated $S_n \rightarrow S_1$ internal conversion. The dihydride spectrum shows maxima at 399 and 461 nm plus shoulders near 342, 537, and 680 nm. These features are consistent with an earlier, lower resolution spectrum lacking absorptivity calibration that was included as Supporting Information in a paper by Spielmann et al.[9] The peaks in our spectrum are blue-shifted by ca. 7 nm compared to those shown by Henderson et al. for 1,2-$C_{70}H_2$ in a toluene/hexane mixed solvent.[4] We also note that our spectrum is very similar in shape to that reported for the *o*-quinodimethane 1,2-monoadduct,[5] suggesting that major features of C_{70} adduct electronic spectra depend only weakly on the addend's chemical properties.

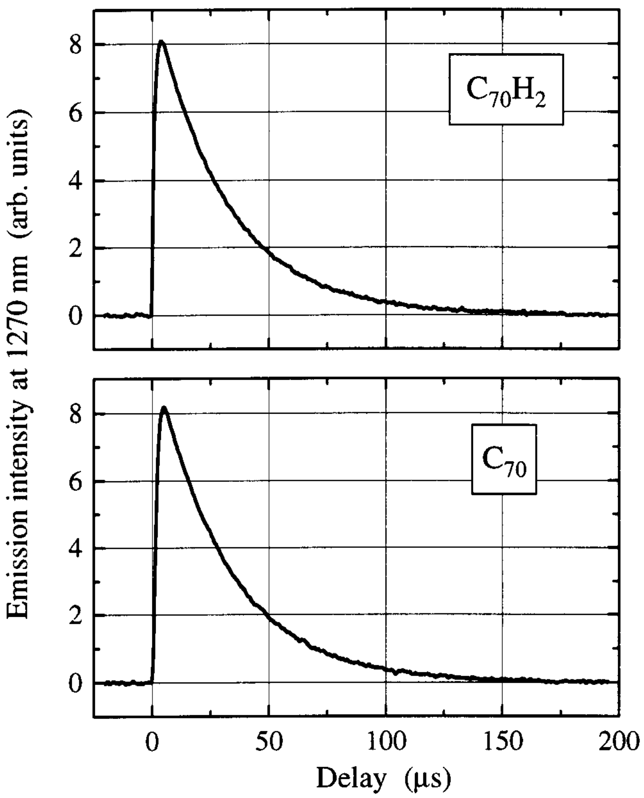

Figure 2. Time-resolved 1270 nm oxygen luminescence from optically excited, air-saturated solutions of 1,2-$C_{70}H_2$ and C_{70} in toluene at 296 K. The traces have been vertically scaled to compensate for absorption differences at the excitation wavelength.

As is the case for C_{60},[10] many of its derivatives,[11] and C_{70},[12] optical excitation of 1,2-$C_{70}H_2$ leads to the efficient population of the lowest-lying triplet state (T_1). In the presence of dissolved oxygen, these triplet states (like those of most organic molecules) are efficiently quenched by an energy transfer process that leaves the oxygen molecules in low-lying excited singlet states.[13] From the very short (300 ns) triplet lifetimes of C_{70} and 1,2-$C_{70}H_2$ in air-saturated toluene solutions, it is clear that oxygen quenching completely dominates all other triplet decay channels under these conditions. The concentration of excited $^1\Delta_g$ O_2 molecules is therefore proportional to the initial concentration of fullerene triplet states. The excited oxygen concentration may be monitored through the intensity of luminescence near 1270 nm. Figure 2 shows such time-resolved oxygen luminescence signals, adjusted for the relative sample absorptions at 532 nm, measured from air-saturated solutions of C_{70} and 1,2-$C_{70}H_2$ under the same conditions. From the very similar emission intensities, and taking the quantum yield of triplet formation to be 1.00 for C_{70},[12] we deduce that ϕ_T for 1,2-$C_{70}H_2$ is 0.99 ± 0.02.

Luminescence spectra were measured for 1,2-$C_{70}H_2$ and C_{70} samples in PMMA films at and below room temperature. The

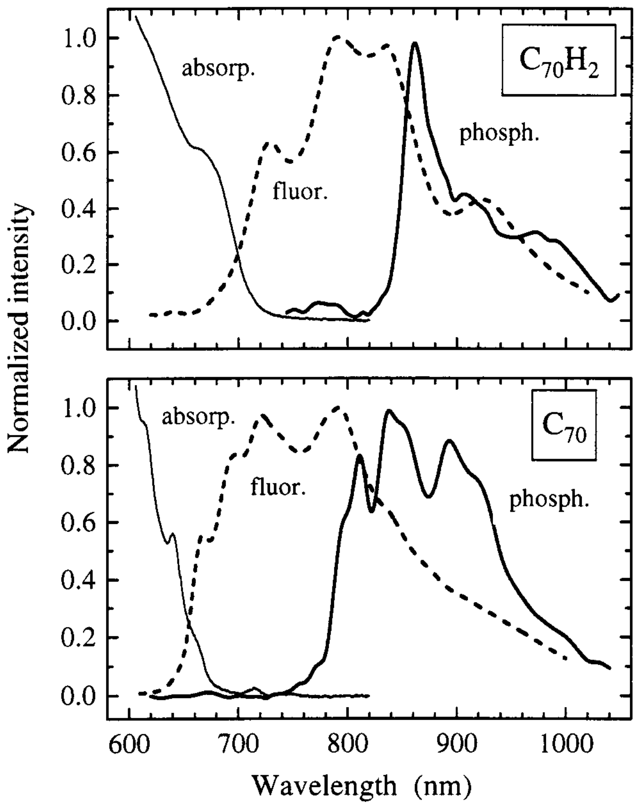

Figure 3. Emission and absorption spectra of 1,2-$C_{70}H_2$ (top frame) and C_{70} (bottom frame). Emission samples were in oxygen-free PMMA films at 140 and 200 K, respectively; absorption samples were in toluene solution at 296 K. Dotted curves show prompt emission (fluorescence), thick solid curves show delayed emission (phosphorescence), and thin solid curves show absorption. The emission spectra have been normalized to the same peak height for comparison, but their shapes have not been corrected for wavelength-dependent instrumental sensitivity. Absorption spectra have been scaled to show their relation to fluorescence spectra.

TABLE 1: Energies (in cm^{-1}) of the Lowest Excited Singlet and Triplet States of 1,2-$C_{70}H_2$ and C_{70}, As Found from Emission Spectra (exp) and Quantum Chemical Calculations (calc)

compound	$\Delta E_{exp}(S_1 - S_0)$	$\Delta E_{calc}(S_1 - S_0)$	$\Delta E_{exp}(T_1 - S_0)$	$\Delta E_{calc}(T_1 - S_0)$
1,2-$C_{70}H_2$	13 725 ± 20	14 434	11 610 ± 20	11 486
C_{70}	15 015 ± 20	15 298	12 590 ± 45	12 488
difference	−1290 ± 30	−864	−980 ± 50	−1002

dotted curves in Figure 3 show the emission spectra detected promptly (within our instrumental time resolution) after 532 nm excitation. We identify this emission as $S_1 \rightarrow S_0$ fluorescence. In cooled samples at longer delays, we observe a much weaker emission whose time dependence matches the induced absorption kinetics described below. We assign these delayed emissions to $T_1 \rightarrow S_0$ phosphorescence and plot their spectra as solid curves in Figure 3. All emission spectra are uncorrected for instrumental response and have been normalized to the same peak height in the figure. At higher sample temperatures, we also observe thermally activated delayed fluorescence. Those findings will be described in a separate report.[14]

Taking the shortest-wavelength distinct feature of each luminescence spectrum to represent the origin transition, we obtain energies of the S_1 and T_1 states of 1,2-$C_{70}H_2$ and C_{70} relative to the corresponding electronic ground states. These excitation energies are shown in Table 1. Both the S_1 and T_1 energies of 1,2-$C_{70}H_2$ are lowered significantly, by ca. 1290 and 980 cm^{-1}, respectively, compared to those of the parent fullerene. These changes represent approximately 8% of the excited states' energies. In addition, the gap between T_1 and S_1 origins is reduced by ca. 13% to approximately 2115 cm^{-1} in 1,2-$C_{70}H_2$.

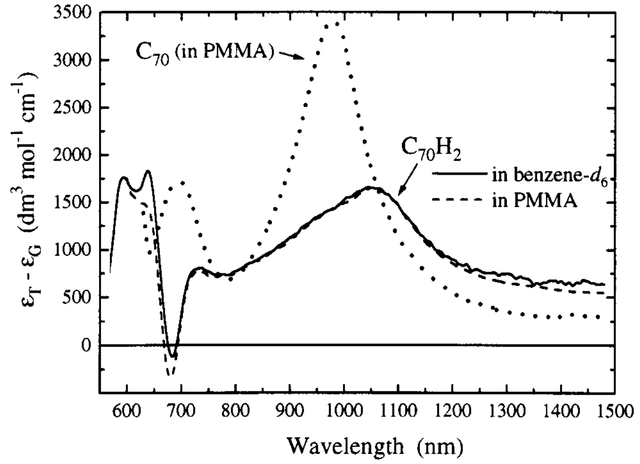

Figure 4. Induced absorption spectra of samples of 1,2-$C_{70}H_2$ dissolved in benzene-d_6 (solid line) and solid PMMA (dashed line) at 296 K, following 532 nm excitation. The corresponding induced spectrum of C_{70} in solid PMMA is drawn for comparison (dotted line). Peak absorptivities for the film samples were assumed to match those measured in solution.

Also included in Table 1 are the results of semiempirical quantum chemical calculations of the vertical T_1 and S_1 transition energies. These calculations were performed using the PM3 module of Hyperchem 5.1. After full optimization of the ground state geometry, a CI calculation using 14 occupied and 14 unoccupied orbitals gave the energies of electronically excited states. The computed transition energies to T_1 and S_1 differ from the experimental values by only 1−5%, and they correctly reflect our observation that these energies decrease by approximately 1000 cm^{-1} in going from C_{70} to 1,2-$C_{70}H_2$. This decrease seems to result from the shape of the LUMO, which, unlike the HOMO or most nearby orbitals, is concentrated near the equator, away from the derivatization sites. Derivatization to form the dihydride therefore raises the LUMO energy much less than that of the HOMO, resulting in a smaller HOMO−LUMO gap and lower excitation energy. However, these PM3-CI calculations (in contrast to CI results using ZINDO/S) do not predict the reduced gap between S_1 and T_1 that is observed in the dihydride.

Further information about the energies of excited states can be obtained from transient absorption spectra. Figure 4 shows induced absorption spectra, as measured at delays of many microseconds, in room-temperature 1,2-$C_{70}H_2$ samples dissolved in solid PMMA and in benzene-d_6. Little difference in spectral shape is seen between these two solvents. The data, which are uncorrected for ground state depopulation, show a superposition of positive-going $T_n \leftarrow T_1$ absorptions and negative-going $S_1 \leftarrow S_0$ bleaching features. In particular, the sharp dip at 680 nm matches the longest-wavelength transition seen in the ground state absorption spectrum. Features to the red of 700 nm therefore arise only from triplet−triplet absorptions. The dominant band in this region is the broad feature peaking at 1050 nm. Presuming that this transition correlates with the 975 nm peak in the $T_n \leftarrow T_1$ spectrum of C_{70}, formation of the dihydride shifts the dominant red triplet−triplet band 75 nm to longer wavelengths. This 8% reduction in transition energy, which matches that found in fluorescence and phosphorescence, implies that the upper triplet electronic state of the dihydride is lowered in energy by 785 cm^{-1} relative to T_1 and by 1765 cm^{-1}

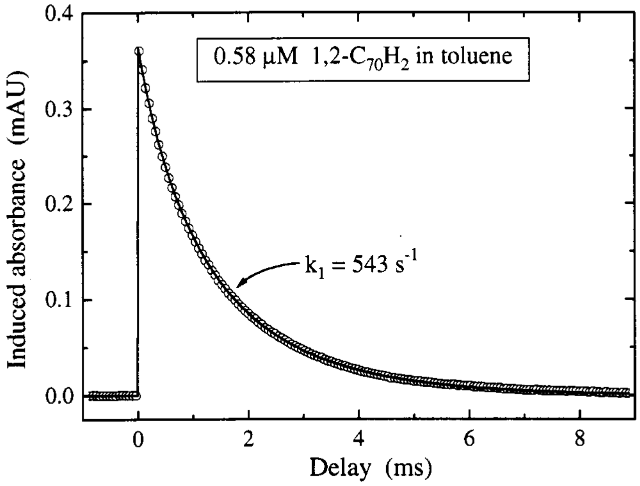

Figure 5. Induced absorbance kinetics measured at 1050 nm for a 0.58 μM solution of 1,2-$C_{70}H_2$ in toluene at 296 K following 532 nm excitation. The path length was 5 cm. Points show measured data (thinned for clarity), and the solid curve shows a best-fit kinetic simulation representing concurrent first- and second-order decay. In the simulation, the initial decay was 41% second-order and the first-order decay constant was 543 s^{-1}.

relative to S_0. We note that analogous derivatization of C_{60} causes the dominant triplet−triplet absorption band to shift in the opposite direction.[11,15] The 1050 nm $T_n \leftarrow T_1$ band of 1,2-$C_{70}H_2$ is noticeably broader than the 975 nm band of C_{70}, and comparative measurements show that its peak molar absorptivity is reduced by approximately 50% from that of C_{70}, to 1650 $dm^3\ mol^{-1}\ cm^{-1}$ in 296 K toluene solution.

We studied the triplet state decay kinetics of 1,2-$C_{70}H_2$ through induced absorption measurements at 1050 nm. Figure 5 shows results for a 0.58 μM solution in toluene at 296 K. The solid curve through the data points is a kinetic best-fit simulation using mixed first- and second-order decay with a first-order rate constant of 543 s^{-1}. Even at very modest excitation energies and sample concentrations, the long intrinsic lifetime allows a substantial amount of second-order decay from triplet−triplet annihilation. We determined the corresponding k_{TT} value to be $8 \times 10^9\ M^{-1}\ s^{-1}$ in room-temperature toluene solution. By measuring the variation of first-order rate constant with sample concentration, we found that the T_1 state of 1,2-$C_{70}H_2$ undergoes bimolecular self-quenching (through encounters with ground state molecules) with a rate constant $k_{sq} = 7.6\ (\pm 1.5) \times 10^7\ M^{-1}\ s^{-1}$. This is roughly twice the revised value of $3 \times 10^7\ M^{-1}\ s^{-1}$ found in this laboratory for k_{sq} of C_{70},[3] which is in turn approximately twice that of C_{60}.[16] The intrinsic triplet state lifetime of 1,2-$C_{70}H_2$ at 296 K is 1.98 ± 0.06 ms, as determined both from the zero-concentration intercept of the self-quenching plot and by measurements in rigid PMMA films. Derivatization to form the 1,2-dihydride thus shortens the triplet state's intrinsic lifetime by a factor of 12 relative to that of C_{70} under the same conditions.[14] We note that in the C_{60} family, simple [6,6]-closed derivatization has also been found to shorten the intrinsic triplet state lifetime, although typically by more modest relative factors in the range 1.8−3.2 at room temperature.[17]

Conclusions

Several photophysical properties of the dominant $C_{70}H_2$ isomer have been examined and compared to those of pristine C_{70}. We find that the electronic absorption spectrum is more diffuse for the dihydride. Both the fluorescence and phosphorescence spectra of the dihydride show red shifts relative to C_{70}, indicating that the lowest singlet and triplet electronic excitations require approximately 8% less energy in 1,2-$C_{70}H_2$ than in C_{70}. Semiempirical quantum calculations suggest that this reduction arises from the lower electron density of the LUMO than the HOMO at the derivatization sites. The spectroscopic S_1−T_1 gap is ca. 310 cm^{-1} smaller in 1,2-$C_{70}H_2$. We find the quantum yield for triplet state formation in 1,2-$C_{70}H_2$ to be nearly 1.0, the same as for C_{70}. Triplet−triplet absorption measurements reveal a dominant near-infrared transition peaked at 1050 nm. Compared to the corresponding triplet transition of C_{70}, this feature is much broader, reduced by ca. 50% in peak molar absorptivity, and red-shifted by 75 nm. These effects are similar to those observed on forming [6,6] adducts of C_{60}, except that their $T_n \leftarrow T_1$ spectral shifts occur in the opposite direction. The intrinsic lifetime for triplet state decay of room-temperature 1,2-$C_{70}H_2$ is 2.0 ms, more than an order of magnitude shorter than that of C_{70}. This acceleration of triplet decay on derivatization is several times greater than typically observed for analogous adducts of C_{60}. We also find that the rate constant for triplet self-quenching is approximately twice as large in 1,2-$C_{70}H_2$ as in C_{70}. Further experimental and theoretical research will be needed to explore the variations in C_{70} photophysical properties with adduct properties and derivatization site, and to systematically understand these properties on the basis of molecular electronic structure.

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