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Ultrafast Energy Relaxation Dynamics of C_{120}, a [2+2]-bridged C_{60} Dimer

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The energy relaxation dynamics of the photoexcited [2+2]-bridged C_{60} dimer in *o*-dichlorobenzene has been investigated by the time-resolved fluorescence and transient absorption techniques. The absorption and fluorescence spectra of the C_{60} dimer show that the monomeric moieties of C_{60} are only weakly interacting with each other, indicating that the C_{60} dimer can be considered as a nearly decoupled bichromophoric molecular system in the ground state. The lowest emitting state of the C_{60} dimer is formed with ∼60-ps time constant, while its fluorescence decays nearly as fast (∼1.22 ns) as in the C_{60} monomer (∼1.17 ns). The 60-ps decay component was suggested to be due to a transition from an optically nonemissive state to an emissive state in the C_{60} dimer. It was also found that the overall photophysical properties of the C_{60} dimer have much more to do with the disruption of the π-bond system than any bichromophoric interaction between the individual C_{60} units.

1. Introduction

The C_{60} dimer linked by [2+2]-cycloaddition bonds is a system of considerable interest as it is often viewed as a basic building block of C_{60}-based molecular networks, which can be used as 1-, 2-, or 3-dimensional arrays for molecular electronic devices.[1−4] It can also serve as a good model system for bichromophoric interaction between two spherical molecular moieties. Molecular networks of fullerenes have often been observed under light irradiation or high pressure and high-temperature conditions in various crystalline phases such as rhombohedral, pseudotetragonal, and orthorhombic structures.[1−3]

There have been theoretical studies on the isomeric C_{60} dimers of various geometries. The electronic structures and vibrational modes were studied by MNDO, density functional theory, and ab initio methods.[5−8] The C_{60} dimer linked by two single bonds, which was predicted to be the most likely dimeric form among the possible isomers, was recently synthesized mechanochemically via a [2+2] cycloaddition reaction in solid phase by employing a high-speed vibration milling method.[9,10] The C_{60} dimer is known to be relatively stable under light illumination, but dissociates into two C_{60} monomers upon heating or reduction in solution.[9−11] The photophysical properties of C_{60} in solution and solid have been extensively studied,[12−15] but those of the C_{60} dimer have been little explored, even after the synthesis of C_{60} dimer became possible. Recently, Sun et al. for the first time studied the photophysical properties of this interesting molecule. They reported that the absorption and fluorescence spectra of the C_{60} dimer are similar to those of the C_{60} derivatives from 1,2-addition reaction, involving diverse functional groups such as 1,2-amino, methano, and pyrrolidino groups.[11] Their time-resolved fluorescence measurement indicated that the lifetime of C_{60} dimer in solution is 1.3 ns, which is slightly longer than that of the C_{60} (1.2 ns).

In this work we report a measurement on relaxation dynamics of the photoexcited C_{60} dimer, obtained in a time scale much shorter than in the previous study. In particular, a rise time of an unknown origin was detected with a 60-ps time constant in our time-resolved fluorescence, which was also manifest in the rise and fall components of the transient absorption. The difference in the energy relaxation dynamics between the monomeric and dimeric C_{60} is discussed as well as the electronic character of the C_{60} dimer.

2. Experimental Section

Spectroscopic grade *o*-dichlorobenzene (*o*-DCB) was used as solvent in this experiment. The C_{60} dimer was synthesized by a mechanochemical solid-state reaction using the high-speed vibration milling method.[9,10] The sample was fully characterized by IR, UV−vis, and ^{13}C NMR spectroscopies as well as FTICR mass spectrometry, cyclic voltammetry, differential scanning calorimetry, and X-ray crystallography.

The absorption spectra were obtained by using a Cary-3

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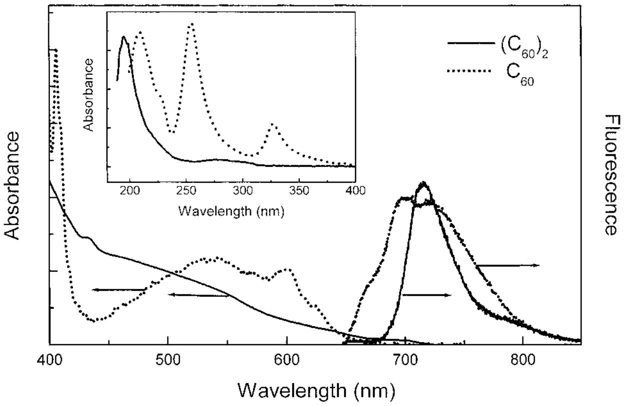

Figure 1. (a) Absorption (indicated by left arrows) and fluorescence (right arrows) spectra of C_{60} and the C_{60} dimer in *o*-dichlorobenzene. The inset shows the absorption spectra in the ultraviolet region in *n*-hexane. The dotted and solid lines represent the spectra of C_{60} and the C_{60} dimer, respectively.

spectrophotometer. An Ar-ion laser was used as the excitation source of fluorescence at 514.5 nm. The emission was collected by an f/1.2 camera lens and focused onto a 1 m double monochromator (Jobin-Yvon U-1000) using a plano convex lens ($f = 30$ cm), and detected by a photomultiplier tube (Hamamatsu R943−02) cooled to −20 °C.

The picosecond time-resolved fluorescence experiment was carried out by using the time correlated single photon counting (TCSPC) method. The excitation pulse of 10 μJ/cm^2 at 400 nm was obtained from a femtosecond Ti:sapphire laser (Coherent, Mira) with an average power of 500 mW at 800 nm. The pump pulse at a desired wavelength was generated by frequency doubling with a β-BBO crystal. The excitation pulse at 600 nm was from a cavity-dumped dye laser (Coherent 702) synchronously pumped by a mode-locked Nd:YAG laser (Coherent, Antares). The fluorescence was detected by a microchannel plate photomultiplier tube (Hamamatsu R2809U).[13]

The dual beam femtosecond time-resolved transient absorption spectrometer consisted of a self-mode-locked femtosecond Ti:sapphire laser (Clark), a Ti:sapphire regenerative amplifier (Clark, CPA-1000) pumped by a Q-switched Nd:YAG laser, a pulse stretcher/compressor, and an optical detection system.[16] The output had a pulse width of ~100 fs at 800 nm and an average power of 1 W at 1 kHz repetition rate. Optical pulses were separated by a 1:1 beam splitter, and one of them was used to generate the pump beam by frequency doubling with a β-BBO crystal. The other beam was focused onto a flowing water cell to generate a white light continuum, which was again split into two parts for probe and reference beams. The monitoring wavelength was selected by an appropriate interference filter (fwhm = 10 nm). By chopping the pump pulse at 41 Hz, the modulated probe and reference pulses were detected by two separate photodiodes. The output current was amplified by a homemade fast preamplifier, and then time-integrated by a boxcar averager. The resultant signal modulated by a chopper was measured by a lock-in amplifier and then fed into a computer for further signal processing.

3. Results and Discussion

Figure 1 shows the absorption spectra of C_{60} and C_{60} dimer in *o*-DCB. The absorption band edge of the C_{60} dimer is slightly red-shifted compared to C_{60}. This could indicate the modification of electronic structure resulting from the loss of one π-bond by the addition of two single bonds,[11] thereby lifting the degeneracy of certain degenerate levels. On the other hand, this may be due to a weak, yet nonnegligible interaction between the two C_{60} moieties. Because the absorption and fluorescence bands are similar to those of the various C_{60} derivatives substituted by 1,2-amino-, methano-, and pyrrolidino-functional groups,[11] the former seems to be a more plausible model to explain the observed red-shift in the C_{60} dimer. From this perspective, we note that the C_{60} dimer is considered as the dimeric form of a 1,2-substituted C_{60} monomer. The absorption band in the visible region is much less structured than that of C_{60}. On the other hand, in the UV region (inset of Figure 1) only a single strong absorption band is observed at ~190 nm, with a much weaker band at ~280 nm. The overall feature of the absorption spectrum in the UV region appears to be generally blue-shifted compared to that of C_{60}. This may be due to the partial loss of π-orbital delocalization caused by the breakage of the π-conjugation system upon 1,2-addition. In the fullerene family, we note that the absorption band in the UV region tends to show a gradual red-shift as the cage-size becomes larger, which results from the enhanced π-conjugation in larger fullerenes due to the reduced surface curvature in molecular geometry.

The fluorescence spectrum of the C_{60} dimer also exhibits a slight red-shift with a maximum at ~715 nm (Figure 1). The 490-cm^{-1} splitting observed in the fluorescence spectrum of C_{60} disappears in the case of the C_{60} dimer because this splitting is usually regarded as due to the totally symmetric Raman active breathing mode (A_g, 496 cm^{-1}) in the ground state. The [2+2] dimerization with the two linkage bonds results in a change in the molecular symmetry from I_h to D_{2h}. In the various 1,2-substituted C_{60} derivatives whose symmetry is likewise reduced, it was also found that this vibronic structure vanishes as in the present case of C_{60} dimer.[11] A previous nonresonant FT Raman experiment for the C_{60} dimer has reported that several new peaks caused by symmetry perturbation and mixing of vibrational modes appear near the nondegenerate A_g breathing mode of C_{60}.[17]

The comparison of both the absorption and fluorescence spectra between C_{60} and the C_{60} dimer suggests that no significant interaction exists between the two C_{60} moieties in the dimer in the ground state. In addition, any difference in the absorption and emission spectra between C_{60} and the C_{60} dimer is due mainly to the partial breakage of the π-orbital system. In the excited states, however, bichromophoric interactions between the two C_{60} moieties may need to be considered, especially in relation to the dynamics of energy relaxation.

The fluorescence decay profiles of C_{60}, the C_{60} dimer, and pyrrolidino-C_{60} at 720 nm following the photoexcitation at 400 nm are shown in Figure 2a. In the case of C_{60}, a single-exponential decay (with a decay time of 1.17 ns) was observed, as already established by many studies.[12−15] This decay time is identified to be the lifetime of the S_1 state, which is mainly governed by the intersystem crossing to the triplet state. In the cases of the C_{60} dimer and pyrrolidino-C_{60}, however, a distinct rise component with a time constant of ~60 ps was observed along with a slightly longer decay time (1.22 and 1.2 ns, respectively). This suggests that the lowest excited emitting state of these molecules is formed from higher excited states with ~60-ps time constant. On the contrary, in the case of C_{60}, the internal conversion to the S_1 emitting state is too fast to exhibit a rise component in fluorescence decay profile. The existence of such high-lying “dark” states is supported by the fact that no rise time was observed when we changed the photoexcitation wavelength to 600 nm (Figure 2b). It appears that the dark state

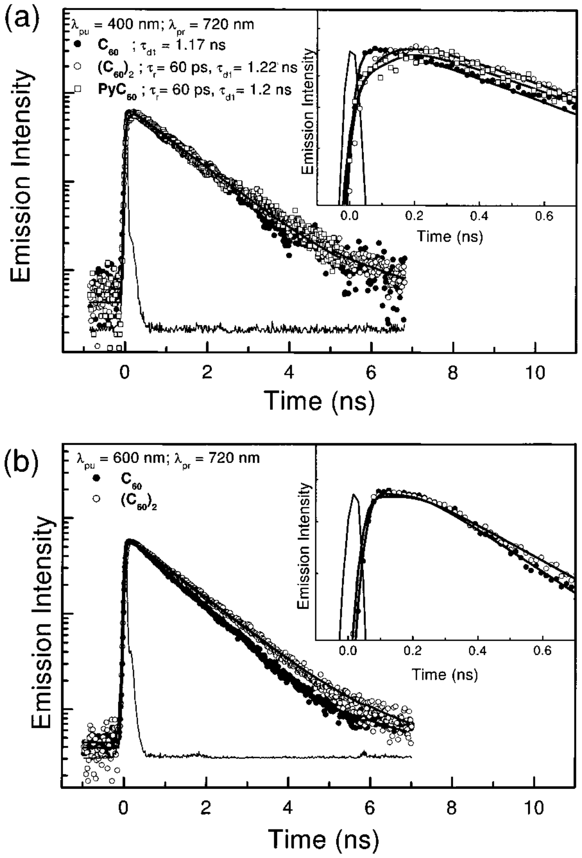

Figure 2. Fluorescence decay profiles of C_{60} (●), the C_{60} dimer (○) and pyrrolidino-C_{60} (□) measured at 720 nm after the photoexcitation at (a) 400 nm and (b) 600 nm. The inset shows the fluorescence rise component of the C_{60} dimer and pyrrolidino-C_{60} in a short time window.

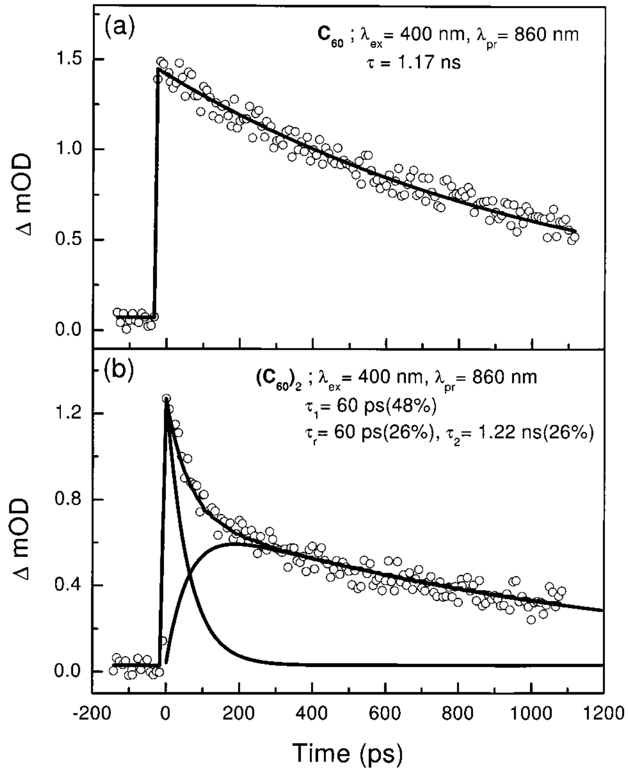

Figure 3. Transient absorption decay profiles of (a) C_{60} and (b) the C_{60} dimer measured at 860 nm following a photoexcitation at 400 nm. The fitting curves were obtained from the consecutive reaction model.

exists between ca. 2 eV (~600 nm) and ca. 3 eV (~400 nm) above the ground state.

At this point, the origin of the 60-ps rise time in the C_{60} dimer fluorescence needs to be considered. First, we can think of the possibility that the rise component is associated with the formation of other species (possibly C_{60}) by photochemical reactions. The C_{60} dimer, however, was found to be quite stable in solution medium to the irradiation by the femtosecond mode-locked Ti:sapphire laser used in this experiment.[18] No detectable change was observed in the absorption or fluorescence spectra, even after extended runs. Another possibility would be that the C_{60} dimers aggregate to form an intermolecular excimer whose formation could give rise to the rise component. In our experiments, however, we could not observe any change in absorption that could indicate aggregate formation, nor could we identify any signs of excimer emission, all as a function of concentration. Furthermore, we note that no rise component was observed by the 600-nm photoexcitation. Formation of an intermolecular excimer can be difficult between two C_{120} molecules due to the little intermolecular $\pi-\pi$ interactions arising from the surface curvature of the molecule. In contrast, the C_{70} molecule, which possesses two nearly planar, pyrene-like units, is known to form an intermolecular excimer in the triplet state.[19] As still another possibility, intramolecular interaction leading to *intra*molecular excimer formation or twisted intramolecular charge transfer can also be considered. But both of these are respectively excluded because of the aforementioned weakness of the $\pi-\pi$ interaction or the structural rigidity around the two single bonds at the bridge. Having exhausted all of these possibilities, we came to consider the existence of an optically nonemissive (dark) state with a lifetime of ~60 ps. In both C_{120} and pyrrolidino-C_{60}, the reduction of one π-bond would remove the degeneracy of electronic states, generating new electronic states not observed in C_{60}. We postulate that there exists a new electronic state with a relatively long lifetime (~60 ps) that is optically nonemissive. It should be located between the emissive S_1 state at ca. 2 eV (~600 nm) and another state at ca. 3 eV (~400 nm) above the ground state because the rise component of fluorescence was observed by photoexcitation at 400 nm but not at 600 nm.

Figure 3a and b show respectively the temporal profile of the transient absorption for the C_{60} monomer and the dimer at 860 nm following the photoexcitation at 400 nm. The latter exhibits a fast multiexponential decay that is clearly different from the former, which is a purely single-exponential decay with a slow time constant of 1.17 ns, as known from earlier studies.[13,15] No apparent rise component was explicitly observed in the transient absorption of the C_{60} dimer, possibly because the absorption bands of the emissive and nonemissive states may significantly overlap and thus become indistinguishable from each other over a wide wavelength range. However, when we tried to fit the overall decay profile of the C_{60} dimer, we came to learn that the best fit could be obtained with three time constants ($\tau_r = 60$ ps for rise; $\tau_1 = 60$ ps for fast decay; $\tau_2 = 1.22$ ns for slow decay). This is consistent with the results obtained from our TCSPC measurement.

The overall electronic energy relaxation process can be represented in the following way, employing a kinetic model for consecutive reactions: The initial photoexcitation at 3 eV or a higher energy will quickly bring the system down to an optically nonemissive excited state, which decays with a time constant of 60 ps. With its decay, an emissive state is simultaneously formed with a rise time of the same magnitude, 60 ps. This state then decays with a relatively long time constant of 1.22 ns, which is basically the intrinsic lifetime of the lowest excited state of the dimer. The 60-ps time constant seems to be quite slow for an energy relaxation process in a large molecule such as the pyrrolidino-substituted C_{60} or the C_{60} dimer. The common occurrence of the same rise time for both molecules, however, seems to indicate that such a feature results from the disruption of the π-orbital system rather than bichromophoric interaction between two monomeric units.[11] The origin of the optically nonemissive (dark) electronic state remains to be further investigated.

In conclusion, we examined the energy relaxation dynamics of the C_{60} dimer in the picosecond time scale. The fluorescence decay profile exhibited a rise component of ∼60 ps for the C_{60} dimer, in contrast to the case of C_{60} with no such rise time. The rise time was mainly due to the formation of an optically emissive excited state evolving from the initially prepared nonemissive state. The optically nonemissive state with a rather long lifetime of 60 ps appears to lie between ∼2 and 3 eV above the ground state. The S_1 state lifetime of the C_{60} dimer in *o*-DCB was found to be 1.22 ns, which is only slightly longer than that of C_{60}. The 60-ps rise component in the fluorescence decay of the C_{60} dimer was verified by the transient absorption temporal profile as well. The photophysical properties of the C_{60} dimer are mainly characterized by the partial disruption of the π-bond system rather than by any bichromophoric interaction between the individual C_{60} units.

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References and Notes

(1) Rao, A. M.; Zhou, P.; Wang, K.-A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W.-T.; Bi, X.-X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955.

(2) Iwasa, Y.; Fukawa, T.; Ozaki, T.; Mitani, T.; Yagi, T.; Arima, T. *Appl. Phys. A* **1997**, *64*, 251.

(3) Rachdi, F.; Goze, C.; Hajji, L.; Their, K. F.; Zimmer, G.; Mehring, M.; Núñez-Regueiro, M. *Appl. Phys. A* **1997**, *64*, 295.

(4) Segura, J. L.; Martin, N. *Chem. Soc. Rev.* **2000**, *29*, 13.

(5) Pederson, M. R.; Quong, A. A. *Phys. Rev. Lett.* **1995**, *74*, 2319.

(6) Scuseria, G. E. *Chem. Phys. Lett.* **1996**, *257*, 583.

(7) Patchkovskii, S.; Thiel, W. *J. Am. Chem. Soc.* **1998**, *120*, 556.

(8) Porezag, D.; Jungnickel, G.; Frauenheim, Th.; Seifert, G.; Ayuela, A.; Pederson, M. R. *Apply. Phys. A* **1997**, *64*, 321.

(9) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583.

(10) Komatsu, K.; Wang, G.-W.; Murata, Y.; Tanaka, T.; Fujiwara, K.; Yamamoto, K.; Saunders, M. *J. Org. Chem.* **1998**, *63*, 9358.

(11) Ma, B.; Riggs, J. E.; Sun, Y.-P. *J. Phys. Chem. B* **1998**, *102*, 5999.

(12) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, J. P., Jr.; Smith, A. B., III.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075.

(13) Kim, D.; Lee, M.; Suh, Y. D.; Kim, S. K. *J. Am. Chem. Soc.* **1992**, *114*, 4429.

(14) Ebbeson, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett.* **1991**, *181*, 501.

(15) Lee, M.; Song, O.-K.; Seo, J.-C.; Kim, D.; Suh, Y. D.; Jin, S. M.; Kim, S. K. *Chem. Phys. Lett.* **1992**, *196*, 325.

(16) Cho, H. S.; Yang, S. I.; Kim, S. K.; Shin, E.-J.; Kim, D. *J. Phys. Chem. B* **1999**, *103*, 6504.

(17) Lebedkin, S.; Gromov, A.; Giesa, S.; Gleiter, R.; Renker, B.; Rietschel, H.; Krätschmer, W. *Chem. Phys. Lett.* **1998**, *285*, 210.

(18) In the transient absorption experiments, however, the absorption signals of C_{60} and the C_{60} dimer were observed to decrease and eventually disappear as they were irradiated by increasingly higher laser fluence (more than ∼200 $\mu J/cm^2$). This could be due to the photochemical reactions with the solvent, *o*-dichlorobenzene. To avoid such sample degradation, the sample solution was circulated in a flowing cell (path length = 1 mm), and a weaker pump pulse (much less than ∼100 $\mu J/cm^2$) was employed.

(19) Etheridge, H. T., III.; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 2782.