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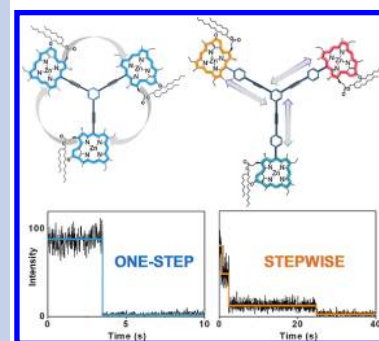
Fluorescence Dynamics of Chlorophyll Trefoils in the Solid State Studied by Single-Molecule Fluorescence Spectroscopy

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ABSTRACT We have comparatively investigated the single-molecule photophysical properties of two chlorophyll trefoils that feature distinctive electronic couplings induced by differences in linkage: one is an ethynyl-linked chlorophyll trefoil (**1**) in which relatively short and rigid linkage between the chromophores promotes effective electronic coupling, and the other is a phenyl–ethynyl-linked chlorophyll trefoil (**2**) in which the phenyl addition induces an orthogonal geometry impeding π -conjugation and provides a longer interchlorophyll distance reducing through-space interaction. By recording single-molecule fluorescence intensity trajectories and their corresponding lifetimes, we observed one-step photobleaching behaviors, less frequent on–off behaviors, a narrower fluorescence lifetime distribution, and higher photostability in **1** as compared with **2**. These results indicate that the performance of molecular photosynthetic systems in the solid state is strongly associated with electronic couplings and, thus, give insight into the construction of well-functioning artificial photosynthetic systems.

SECTION Kinetics, Spectroscopy



Photosynthetic antennae and reaction centers have served as important models for developing synthetic light-harvesting and photochemical charge separation systems.^{1,2} These natural organisms frequently use chlorophylls (Chls) as building block elements for both energy and charge transfer, and the specific tasks of Chls are differentiated largely by their interaction with other Chls. To mimic this versatility, we have prepared two Chl trefoil arrays **1** and **2**, in which three identical Chls are attached to a central benzene scaffold through ethynyl and phenyl–ethynyl linkers, respectively (Chart 1). These molecular arrays have been previously shown to exhibit distinctive electronic couplings and photophysical properties, because the Chl linkage controls the overall properties of the molecular structures.^{3–8}

In the previous ensemble study,³ the energy transfer processes occurring in Chl trefoils were characterized in a tetrahydrofuran solution by using femtosecond transient absorption (TA) spectroscopy. The excitation energy hopping time for **1** (1.8 ps) was determined to be 3 times faster than that for **2** (6.0 ps), while the calculated Förster energy transfer lifetimes for **1** (3 ps) and **2** (31 ps) predict a 10:1 ratio difference.^{9,10} The discrepancy between the experimentally observed lifetimes and their calculated lifetimes confirms that, in addition to through-space interaction, or Förster energy transfer, through-bond interaction between Chls contributes significantly to the energy transfer process. In addition, upon chemical reduction of one Chl unit per trefoil,

electron nuclear double resonance (ENDOR) spectroscopy shows unpaired electron sharing in **1** between all three Chl units, while no sharing is observed in **2**. This further supports the importance of through-bond electronic coupling and the differences in molecule behaviors.

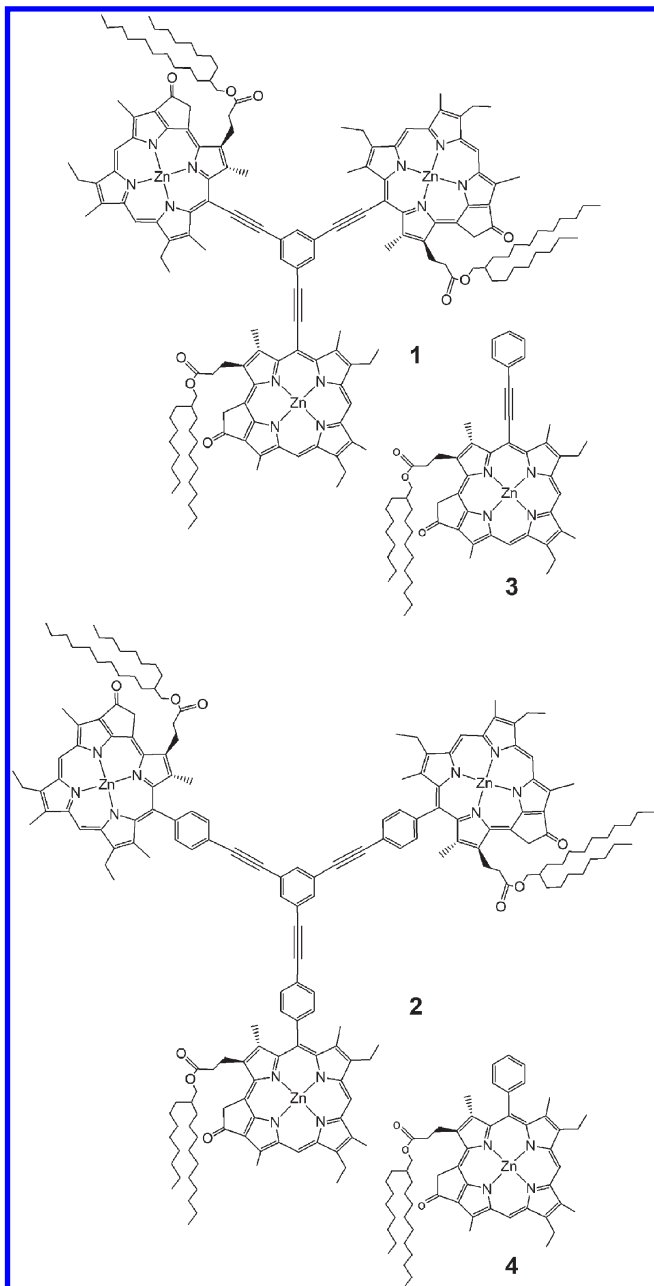
In this study, we have comparatively investigated the photophysical properties of Chl trefoils **1** and **2** in the solid state by using single-molecule fluorescence spectroscopy (SMFS).^{11–16} As spectroscopic investigation at the single-molecule level eliminates the averaging effect inherent in ensemble measurements, SMFS can provide unprecedented detailed information as well as conformational dynamics of individual molecules.^{17,18} Herein, we have examined the interchromophoric interactions and molecular properties of individual Chl trefoils that depend on the linkages between chromophores by measuring fluorescence intensity trajectories (FITs) and fluorescence lifetimes of single molecules, with a particular focus on the relationship between the linkage and electronic coupling in the solid state. To the best of our knowledge, our study is the first attempt to examine single-molecule fluorescence dynamics of Chl-based molecular systems, which are promising components for artificial photosynthetic systems.

Received Date: October 28, 2009

Accepted Date: November 19, 2009

Published on Web Date: December 01, 2009

Chart 1. Molecular Structures of the Chl Trefoils **1** and **2**, and the Reference Monomers **3** and **4**^a



^a In **1** and **2**, three identical Chls are attached to a central benzene scaffold through ethynyl and phenyl–ethynyl linkers, respectively.

The absorption spectra of the Chl trefoils show that both the Soret and Q bands of **1** are red-shifted by approximately 10 nm relative to those of **2** (Figure S1 in the Supporting Information). This feature results from the poor π -conjugation in **2**, arising from the nearly orthogonal geometry between Chls and the phenyls of phenyl–ethynyl linkages. In contrast, ethynyl linkages directly attached to Chls allow for effective π -conjugation, thus the absorption spectrum of **1** is more red-shifted than that of **2**.

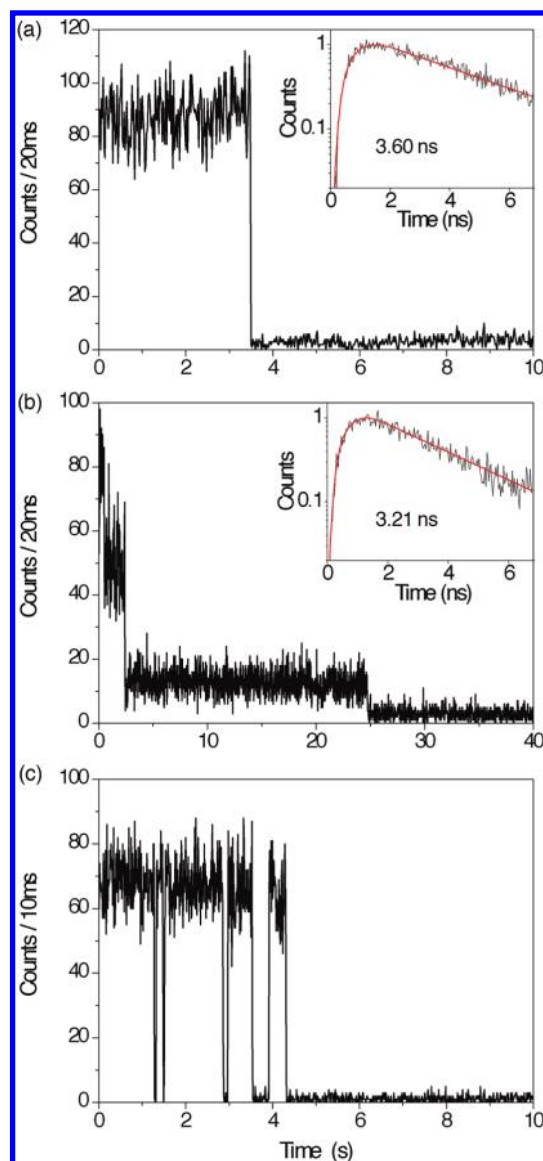


Figure 1. Representative FITs of the one-step photobleaching behavior of **1** (a), the stepwise photobleaching behavior of **2** (b), and the on–off behavior of **1** (c). FITs were recorded using an excitation wavelength of 405 nm. Insets in a and b show fluorescence decay profiles corresponding to the first emissive levels in the FITs, which were well fitted with a single exponential decay function.

To obtain in-depth information on the photophysical properties of Chl trefoils, we have recorded the FITs of single molecules embedded in a poly(methyl methacrylate) (PMMA) polymer matrix. The FITs of the reference monomers **3** and **4** exhibit one-step photobleaching behavior in accordance with the number of Chl units (Figure S2 in the Supporting Information). Unlike the FITs of the reference monomers, **1** and **2** exhibit distinctive photobleaching behaviors. The representative FITs of 140 single molecules of **1** and **2** are given in Figure 1. While 52 % (73/140) of the FITs of **1** show one-step photobleaching behavior (Figure 1a) with the remaining ones exhibiting two- (33 % (46/140)) or three-step

(15% (21/140)), the FITs of **2** primarily show stepwise photobleaching behavior (Figure 1b): 14% (19/140), 49% (69/140), and 37% (52/140) for three-, two-, and one-step photobleaching behaviors, respectively. This stepwise photobleaching observed for **2** is similar to the behavior seen in the FITs of other weakly interacting multichromophoric systems,^{17,19} which indicates that Chls in **2** maintain monomeric character. On the other hand, one-step photobleaching in the FITs of **1** suggests that **1** behaves like one quantum system.^{20,21}

To explain this feature, we need to consider the electronic couplings between Chl units in **1** and **2**. Intermolecular electronic interactions can be categorized into through-space (Förster-type) and through-bond (Dexter-type) mechanisms. As mentioned above, the calculated Förster energy transfer rate for **1** is about 10 times faster than that for **2**. This is a simple reflection of the significant change in the inter-Chl distance between **1** (15.1 Å) and **2** (21.5 Å), as the dipole–dipole interaction shows inverse sixth power dependence on the center-to-center distance.

In addition, it is expected that **1** exhibits stronger through-bond interaction than **2** due to the geometry of Chl π systems relative to the linkages. The large dihedral angles between Chls and the phenyls of the phenyl–ethynyl linkages in **2** that arise from steric hindrance lead to ineffective π -conjugation. On the other hand, in **1**, all Chls are in the same plane as the benzene core as a result of the rigidity of the ethynyl linkages, thereby resulting in π -conjugation from effective orbital overlap. Further support for through-bond interactions arises from the quantification of the through-bond energy transfer rates for **1** and **2**. Equation 1 shows that the overall energy transfer rates in multichromophoric systems can be expressed by the summation of through-bond and through-space energy transfer rates.²²

$$k_{\text{trans}} = k_{\text{TB}} + k_{\text{TS}} \quad (1)$$

Considering the experimentally observed and the calculated Förster energy transfer rates (vide supra), the through-bond energy transfer rate for **1** ((4.5 ps)^{−1}) is approximately 2 times faster than that for **2** ((7.5 ps)^{−1}).

Thus, we claim that both stronger through-space and through-bond interactions in **1** make this multichlorophyll system act as one quantum system.

Another interesting observation in the FITs is collective off-states, that is, a temporal drop of fluorescence intensity to the background level, which is one of the characteristic features in single molecule photodynamics. The respective frequencies of the FITs showing on–off behaviors are 35% (49/140) and 58% (81/140) for **1** and **2**. For example, in a representative FIT of **1** displayed in Figure 1c, the molecule exhibits four reversible intensity jumps at 1.26, 1.46, 2.84, and 3.52 s with duration times in the off-states of 80, 80, 140, and 420 ms, respectively. It has been suggested that the collective off-states seen in the FITs of multichromophoric systems are caused by efficient excitation energy transfer to fluorescence quenching sites existing in the system,^{17,23} because the possibility of all the chromophores simultaneously being in the nonemissive state is unlikely. Thus, the collective off-states observed for the Chl trefoils prove that there is effective

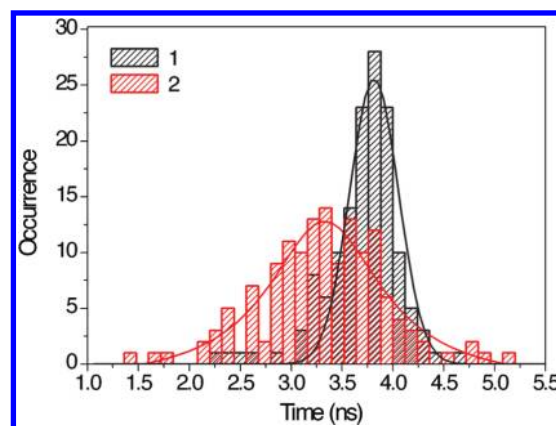


Figure 2. Single-molecule fluorescence lifetime distribution of 140 single molecules of **1** (gray) and **2** (red), where all the fluorescence decay profiles were constructed by fluorescence photons at the initial emissive level in the FITs and are well fitted by a single exponential function. The solid lines denote respective Gaussian fitting curves, and the average fluorescence lifetimes with their standard deviations for **1** and **2** are 3.66 ± 0.66 ns and 3.37 ± 1.16 ns, respectively.

electronic communication between Chls in both trefoils. We emphasize that, although both through-space and through-bond interactions in **2** are relatively weaker than those in **1**, their strength is still strong enough to show collective off-states in the FITs.

In most FITs showing on–off behaviors, the duration time of the off-states was found to vary from sub- to several seconds (Figure 1c). The long off-states have been observed in a variety of molecular systems composed of porphyrins and perylene derivatives, as well as polymers.^{18,19,24–27} The general agreement in explaining this behavior is that long off-states are induced by the intermolecular charge transfer between the excited state of molecule and the surrounding polymer matrix.²⁸ Particularly, our earlier study on the cyclic porphyrin arrays has shown that, as the conformational heterogeneity becomes larger, the molecular system goes to off-states more frequently.^{11,18} This tendency was also observed in the Chl trefoils. In **2**, placing additional phenyls in the linkages increases the degrees of freedom in the molecular system, which may contribute to the increase in conformational heterogeneity because more flexible structures are prone to be affected during the spin-coating process to prepare sample films. Thus, the higher occurrence of long off-states in **2** can be attributed to the generation of non-radiative decay channels in various conformational isomers, induced by the more flexible conformation of **2** as compared with **1**.

To examine the fluorescence dynamics of **1** and **2** in the excited state, we measured time-resolved fluorescence decays in bulk PMMA film and at the single-molecule level by using TCSPC method. All the fluorescence decay profiles for single molecules were constructed by fluorescence photons at the initial emissive level in the FITs and are well fitted by a single exponential function.

In the ensemble measurement, the fluorescence lifetime of **2** (3.40 ns) is shorter than that of reference monomer, **4** (3.95 ns), while the fluorescence lifetime of **1** (3.80 ns) is

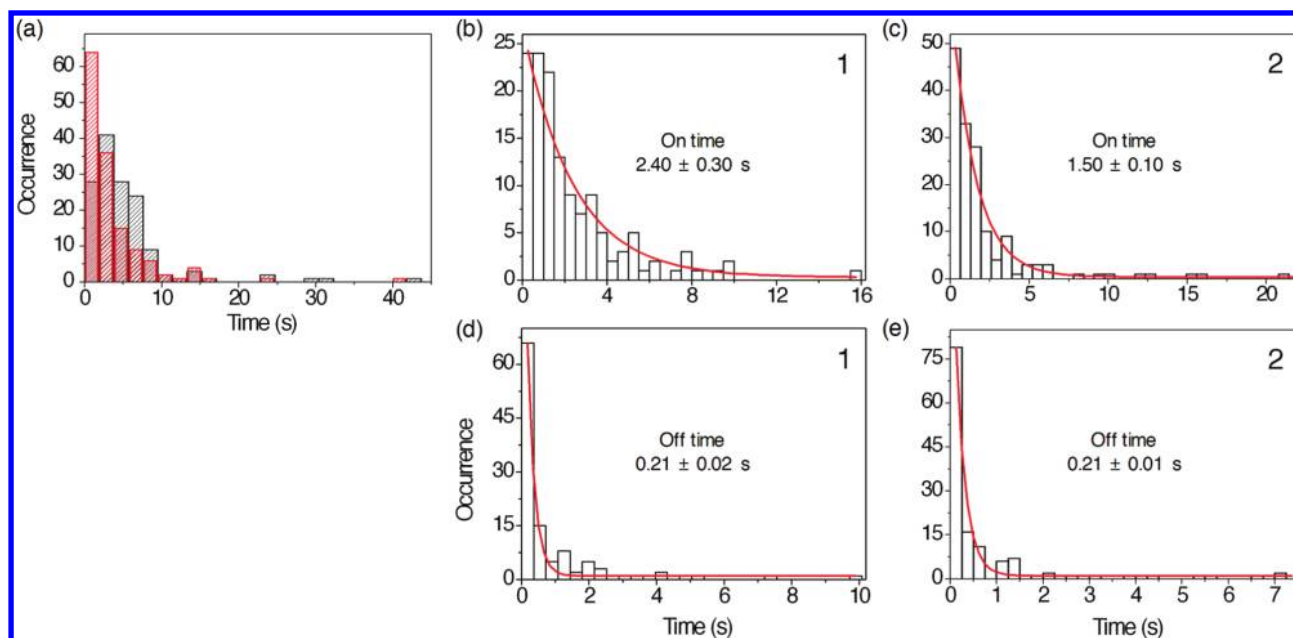


Figure 3. (a) Histograms of the duration times at the first emissive level in the FITs of **1** (gray) and **2** (red). The single exponential fitting results in duration times of 7.59 and 3.94 s for **1** and **2**, respectively. Histograms of the duration times at on-states for **1** (b) and **2** (c), and those at off-states for **1** (d) and **2** (e).

similar to that of **3** (3.90 ns) (Figure S3 in the Supporting Information). We also observed a similar trend in the single-molecule fluorescence lifetimes. As shown in the insets of Figure 1a,b and in Figure S2, the fluorescence lifetime becomes shorter only in the case of **2**: 3.60, 3.21, 3.70, and 3.68 ns in going from **1** to **4**. Since the long linkages in **2** increase the flexibility and structural inhomogeneity of the molecular system, the shortened fluorescence lifetime of **2** can be explained in terms of the increase in nonradiative decay rate. Figure 2 shows single-molecule fluorescence lifetime distribution for **1** and **2** with its Gaussian fitting curves. The average fluorescence lifetime of **2** (3.37 ns) is shorter than that of **1** (3.66 ns), which corroborates the above observation. Concurrently, **2** exhibits a broader distribution than **1**: the standard deviation of **2** (1.16 ns) is roughly two times larger than that of **1** (0.66 ns). This broader distribution obviously verifies that there are more conformational heterogeneities in **2**.

Finally, we have compared the photostability of **1** and **2** against repetitive photoexcitation. Since the initial emissive level in the FITs of single molecules reflects the pristine status of molecules prior to any photoinduced perturbation, the duration time at this level can be strongly correlated with the photostability.²⁵ Figure 3a shows a histogram of the duration times at the initial emissive levels for **1** and **2**. These histograms were fitted by an exponential decay function, and the resulting fitted duration time of **1** (7.59 s) is 2 times longer than that of **2** (3.94 s), which indicates that **1** is more photostable than **2** at the intact status. We attribute this result to the rigid and well-defined structure of **1** that is achieved by relatively rigid ethynyl linkages. Fewer nonradiative decay pathways in **1** as compared with **2**, as verified from the lower frequency of

the off-states and the longer fluorescence lifetimes, allowing **1** to be less susceptible to photoreactions.

In accordance with the above observation, for the molecules exhibiting on–off behaviors in the FITs, a histogram for the duration times at on-states exhibits analogous behavior. Figure 3b–e shows histograms of the duration times at on- and off-states. While the on-state duration times of **1** and **2** are 2.4 and 1.5 s, respectively, the off-state duration times are the same as 0.21 s. This implies that nonradiative decay channels in the molecular systems can expedite a transition from on- to off-state, thus **2** exhibits 1.6 times shorter duration time at on-states than **1**. Conversely, the same duration time at off-states infers that the relaxation of off-states, that is, the charge recombination process, is rather insensitive to nonradiative decay rates differentiated by the flexibility of Chl trefoils.

In conclusion, our studies on Chl trefoils at the single-molecule level have revealed fluorescence dynamics depending on the type of linkages. The one-step photobleaching behavior in the FITs implies that **1** behaves like one quantum system owing to both stronger through-space and through-bond electronic interactions than **2**, because the ethynyl linkages allow **1** to adopt well-defined coplanar geometry. On the contrary, relatively long phenyl–ethynyl linkages increase the flexibility of **2**, which produces more nonradiative decay pathways that lead to a shorter fluorescence lifetime with large heterogeneity and lower photostability than **1**. These results suggest that the performance of molecular photosynthetic systems in the solid state is strongly associated with both linkages and structural rigidities. Therefore, the design of structurally well-defined and robust molecular systems is highly important for the construction of efficient artificial photosynthetic systems.

Experimental Methods

The synthesis of the Chl trefoil arrays is described elsewhere. The spin-cast dilute film of the arrays embedded in PMMA was illuminated by a 405 nm picosecond-pulse diode laser with an irradiation power of 0.9 μ W at the sample. The fluorescence of the single molecules was detected using a confocal microscope equipped with an avalanche photodiode. More details on sample preparation, experimental method, and data analysis are provided in the Supporting Information.

SUPPORTING INFORMATION AVAILABLE Steady-state absorption and emission spectra, FITs of the Chl monomers, fluorescence lifetimes obtained from the ensemble measurement, and detailed description of experimental methods. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT This work was supported by the Star Faculty and World Class University (2008-8-1955) Programs from the Ministry of Education, Science, and Technology (MEST) of Korea and the AFSOR/AOARD Grant (FA4869-08-1-4097) (D.K.). J.-E.L. and J.-Y. acknowledge the fellowship of the BK21 program from the MEST. The work at Northwestern University was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, U.S. DOE under Grant No. DE-FG02-99ER14999 (M.R.W.).

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