J|A|C|S
COMMUNICATIONS

Excited-State Symmetry Breaking in Cofacial and Linear Dimers of a Green Perylenediimide Chlorophyll Analogue Leading to Ultrafast Charge Separation

Jovan M. Giaimo, Alexey V. Gusev, and Michael R. Wasielewski*

Department of Chemistry and Center for Nanofabrication and Molecular Self-Assembly, Northwestern University, Evanston, Illinois 60208-3113

Received April 4, 2002

Cofacial π-stacked arrangements of chromophores are found in many biologically important molecules such as DNA and the primary electron donor within photosynthetic reaction center proteins. In the latter case, it has been proposed that symmetry breaking within the photoexcited singlet state of the special pair dimer results in significant intradimer charge-transfer character.[1−4] However, photoexcitation of arene dimers constrained to a cofacial orientation usually leads to excimer formation.[5] In related conformationally flexible dianthrylethanes, symmetry breaking in the lowest excited singlet state produces ion pairs only in highly polar solvents, while excimer formation still dominates at low polarity.[6] Perhaps the most widely studied case of solvent-induced excited-state symmetry breaking in polar media is that of 9,9′-bianthryl, in which two anthracenes are bound in an edge-to-edge geometry with their π systems perpendicular to one another in the ground state.[7,8] Recent evidence indicates that geometry changes following excitation of 9,9′-bianthryl increase the electronic coupling between the two anthracenes leading to the formation of a significant dipole moment even in low polarity solvents.[9] However, charge separation between identical chromophores in a π-stacked configuration in low polarity media has not been reported. In an effort to develop more robust biomimetic electron donor−acceptor systems, we have synthesized 1,7-bis(pyrrolidin-1′-yl)perylene-3,4:9,10-bis(dicarboximide) (5PDI),[10] a green chromophore having properties that are remarkably similar to those of chlorophyll *a*.[11] Here we present data showing that a symmetric cofacial 5PDI dimer undergoes symmetry breaking following photoexcitation yielding complete charge separation between the two halves of the dimer in the relatively low polarity solvent toluene.

The cofacial dimer, *cof*-5PDI$_2$, was synthesized by reacting both amines of 2,7-di-*tert*-butyl-9,9-dimethyl-4,5-xanthene-diamine[12] with *N*-cyclohexyl-1,7-bis(pyrrolidin-1′-yl)-perylene-3,4-imide-9,10-anhydride.[11] Steric hindrance between the pyrrolidine rings produces a preference for the isomer shown in the drawing of *cof*-5PDI$_2$, which was isolated chromatographically and was used in this study. For comparison, a linear dimer, *lin*-5PDI$_2$, with a ground-state structure similar to that of 9,9′-bianthryl, was synthesized using established procedures.[11] The energy-minimized ground-state geometry of *cof*-5PDI$_2$, calculated using AM1,[13] places the two 5PDI chromophores in a nearly cofacial geometry with an average 3.7 Å interplanar distance. The AM1 structure of *lin*-5PDI$_2$ has a center-to-center distance between the two 5PDI chromophores of 12.7 Å with a dihedral angle of 84° between the average planes of the chromophores.

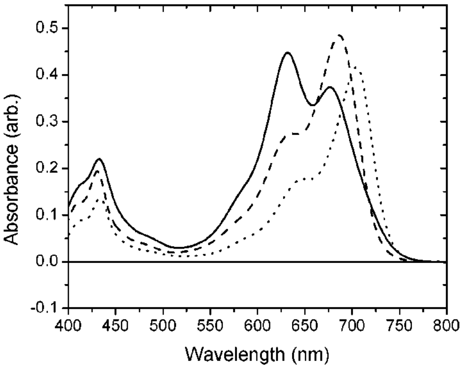
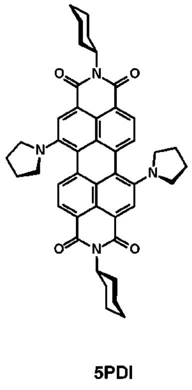
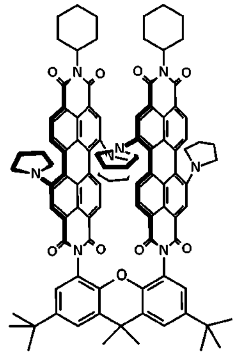


Figure 1. Ground-state absorption spectra for 5PDI (− − −), *cof*-5PDI$_2$ (−), and *lin*-5PDI$_2$ (····) in toluene.

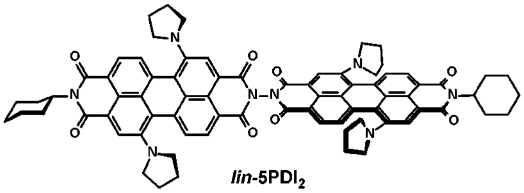
The ground-state absorption spectra of 5PDI, *cof*-5PDI$_2$, and *lin*-5PDI$_2$ in toluene are shown in Figure 1. The lowest energy absorption band of 5PDI occurs at 686 nm, while *cof*-5PDI$_2$ has two bands at 632 and 677 nm, and *lin*-5PDI$_2$ has a single band at 704 nm. The zero-order molecular exciton model[14] predicts that dipole−dipole coupling of the transition moments of the monomers will produce two electronic transitions upon dimer formation. For the parallel, stacked geometry, this model predicts that the higher-energy transition will have all of the oscillator strength. Extension of this model to include vibronic coupling in the exciton states of the dimer relieves the symmetry restrictions inherent to the simple model.[15,16] Thus, most likely the 632 nm band is the transition from the ground state to the $v = 0$ vibronic level of the upper exciton state, while the 677 nm band is the corresponding transition to the $v = 1$ vibronic level of the lower exciton state. The greater oscillator



5PDI



***cof*-5PDI$_2$**



***lin*-5PDI$_2$**

---

* To whom correspondence should be addressed. E-mail: wasielew@chem.northwestern.edu.

10.1021/ja026422l CCC: $22.00 © 2002 American Chemical Society

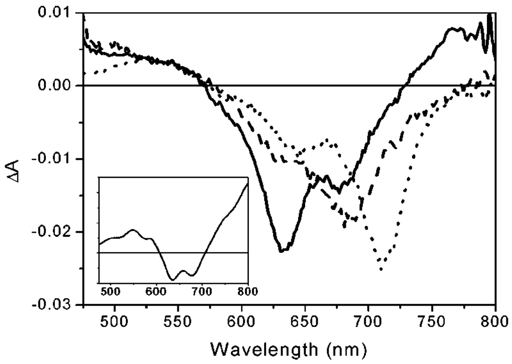


Figure 2. Transient absorption spectra of 5PDI (− − −), *cof*-5PDI$_2$ (−), and *lin*-5PDI$_2$(····) in toluene following excitation with a 400 nm, 80 fs laser pulse. Inset: The simulated transient absorption spectrum of 5PDI$^+$−5PDI$^-$ based on spectroelectrochemistry.

strength of the 632 nm transition in *cof*-5PDI$_2$ is consistent with the geometry of the dimer enforced by the xanthene spacer. The same model predicts that positioning two transition dipoles in an end-to-end fashion as they are in *lin*-5PDI$_2$ will result in a dominant transition to the lower energy exciton state, as is observed in Figure 1. However, the $1/r^3$ distance dependence of the exciton interaction results in a much weaker coupling between the 5PDI chromophores in *lin*-5PDI$_2$ relative to that of *cof*-5PDI$_2$ because of the larger 5PDI−5PDI distance in *lin*-5PDI$_2$.

Detailed ultrafast transient absorption studies of 5PDI in toluene and 2-methyltetrahydrofuran (MTHF) have been reported previously.[11] For comparison, the transient spectrum of 5PDI in toluene at 100 ps following a 400 nm, 80 fs laser flash is given in Figure 2 along with those of *cof*-5PDI$_2$ and *lin*-5PDI$_2$. The main transient spectral features for ^{1*}5PDI are ground-state bleaching at 686 nm and a positive absorption band located at 475−575 nm, and little or no absorbance change from 750 to 800 nm. These features decay with $\tau = 4.5$ ns in toluene and $\tau = 3.0$ ns in MTHF. In contrast, photoexcitation of *cof*-5PDI$_2$ in toluene shows a new absorption band at 725−800 nm in addition to ground-state bleaching at 632 and 677 nm. This band appears and decays with time constants of $\tau = 0.52$ and 222 ps, respectively. The decay time is identical to that for the recovery of the bleach at 632 and 677 nm. The transient absorption spectrum of *cof*-5PDI$_2$ in MTHF (not shown) shows the same spectral features observed in toluene with rise and decay times of $\tau = 0.33$ and 38 ps, respectively. Excitation of *cof*-5PDI$_2$ with 700 nm, 100 fs laser pulses shortens the rise time of these spectral features in both toluene and MTHF to 0.17 ps, while the decay times are the same.

The observed excited-state dynamics of *cof*-5PDI$_2$ cannot be explained in terms of exciton coupling, which predicts a long-lived lower exciton state for the parallel π-stacked geometry of *cof*-5PDI$_2$,[14] contrary to what is observed. The ultrafast dynamics and the appearance of new transient absorption features suggest that electron transfer is responsible for the observed behavior. To confirm this mechanism, spectroelectrochemistry was used to determine the optical absorption spectra of 5PDI$^+$ and 5PDI$^-$. The ground-state absorption spectrum of *cof*-5PDI$_2$ was subtracted from the sum of the measured spectra of 5PDI$^+$ and 5PDI$^-$ to simulate the transient spectrum expected from formation of the 5PDI$^+$−5PDI$^-$ radical ion pair, inset to Figure 2. The simulation shows that 5PDI$^+$−5PDI$^-$ within *cof*-5PDI$_2$ should have a ground-state bleaching between 610 and 710 nm, a broad positive absorption band between 475 and 610 nm corresponding to the absorption of both 5PDI$^+$ and 5PDI$^-$, and a sharper positive feature at 710−800 nm caused mostly from 5PDI$^-$, which exhibits an absorption maximum at 840 nm. The similarity between the spectrum of 5PDI$^+$−5PDI$^-$ determined using spectroelectrochemistry and the transient absorption spectrum of *cof*-5PDI$_2$ strongly indicates that intradimer photoinduced electron transfer occurs between the 5PDI chromophores in *cof*-5PDI$_2$ in both toluene and MTHF. A comparison of the formation times for the ion pair in toluene and MTHF relative to the respective nanosecond excited-state decay times of 5PDI in these solvents shows that ion pair formation in *cof*-5PDI$_2$ is quantitative.

The transient absorption spectrum of *lin*-5PDI$_2$ in toluene does not show significant absorption at 725−800 nm, Figure 2. Moreover, the excited-state dynamics of *lin*-5PDI$_2$ in toluene are similar to those of 5PDI with a decay time of $\tau = 3.3$ ns. These observations show that photoexcitation of *lin*-5PDI$_2$ in toluene does not produce 5PDI$^+$−5PDI$^-$. In contrast, the transient absorption spectrum of *lin*-5PDI$_2$ in MTHF displays the 725−800 nm band (not shown) because of 5PDI$^+$−5PDI$^-$, which appears with $\tau =$ 55 ps and decays with $\tau = 99$ ps. It is likely that solvent dipole fluctuations in the higher polarity solvent lead to symmetry breaking in the excited state of *lin*-5PDI$_2$ producing 5PDI$^+$−5PDI$^-$, similar to what is observed for 9,9′-bianthryl.[7,8]

Our results suggest that excited-state symmetry breaking in 5PDI dimers provides new routes to biomimetic charge separation and storage assemblies that can be more easily prepared and modified than those based on multiple tetrapyrrole macrocycles.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy (Grant DE-FG02-99ER14999).

Supporting Information Available: Synthetic and spectroscopic details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Lathrop, E. J. P.; Friesner, R. A. *J. Phys. Chem.* **1994**, *98*, 3056−3066.
(2) Won, Y.; Friesner, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 5511−5515.
(3) Parson, W. W.; Scherz, A.; Warshel, A. **1985**, *42*, 112−130.
(4) Laporte, L. L.; Palaniappan, V.; Kirmaier, C.; Davis, D. G.; Schenck, C. C.; Holten, D.; Bocian, D. F. *J. Phys. Chem.* **1996**, *100*, 17696−17707.
(5) Staab, H. A.; Riegler, N.; Diederich, F.; Krieger, C.; Schweitzer, D. *Chem. Ber.* **1984**, *117*, 246−259.
(6) Yao, H.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 7388−7394.
(7) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971−988.
(8) Kang, T. J.; Kahlow, M. A.; Giser, D.; Swallen, S.; Nagarajan, V.; Jarzeba, W.; Barbara, P. F. *J. Phys. Chem.* **1988**, *92*, 6800−6807.
(9) Piet, J. J.; Schuddeboom, W.; Wegewijs, B. R.; Grozema, F. C.; Warman, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5337−5347.
(10) Zhao, Y.; Wasielewski, M. R. *Tetrahedron Lett.* **1999**, *40*, 7047−7050.
(11) Lukas, A. S.; Zhao, Y.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2002**, *106*, 1299−1306.
(12) Hamann, B. C.; Branda, N. R.; Rebek, J. *Tetrahedron Lett.* **1993**, *34*, 6837−6840.
(13) AM1 calculations were performed using HyperChem, Hypercube, Inc., 1115 NW 1114th Street, Gainesville, FL 32601.
(14) Kasha, M.; Rawls, H. R.; El-Bayoumi, M. A. *Pure Appl. Chem.* **1965**, *11*, 371−392.
(15) Fulton, R. L.; Gouterman, M. *J. Chem. Phys.* **1964**, *41*, 2280−2286.
(16) Oddos-Marcel, L.; Madeore, F.; Bock, A.; Neher, D.; Ferencz, A.; Rengel, H.; Wegner, G.; Kryschi, C.; Trommsdorff, H. P. *J. Phys. Chem.* **1996**, *100*, 11850−11856.

JA026422L