Acceleration of Photoinduced Charge Separation in Porphyrin-C_{60} Dyad with an Acetylene Spacer

Koji Yamada, Hiroshi Imahori,* Yoshinobu Nishimura,† Iwao Yamazaki,*† and Yoshiteru Sakata*
The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihoga-oka, Ibaraki, Osaka 567-0047
†Department of Molecular Chemistry, Graduate School of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628

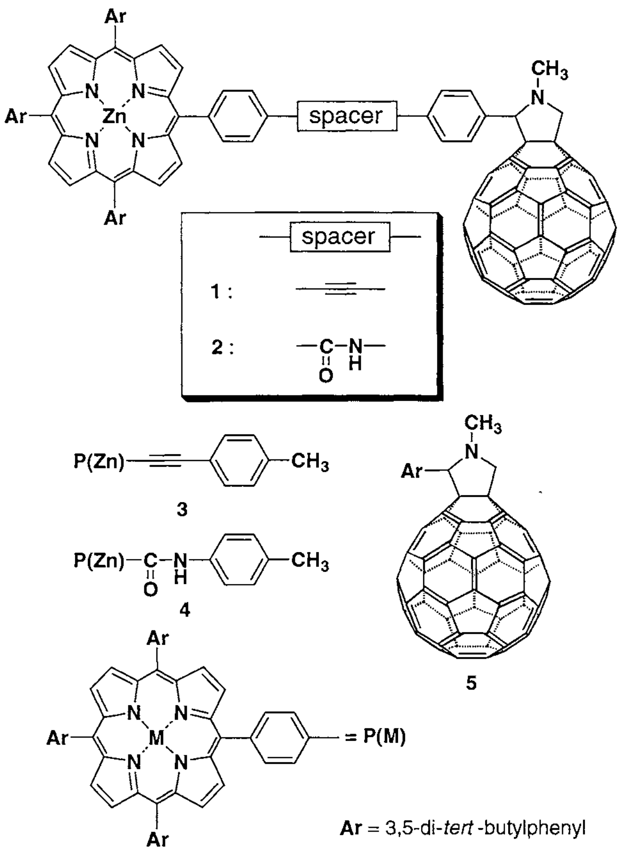
(Received May 28, 1999; CL-990441)

A porphyrin-C_{60} dyad with an acetylene spacer has been synthesized for the first time. The rate constant for charge separation in the dyad is larger by a factor of about three compared with a porphyrin-C_{60} dyad with an amide spacer, showing that the triple bond is a good electron transfer mediator.

Much attention has been devoted to "molecular wire", for the realization of molecular electronics and photonics.[1] Utilization of "molecular wire" for a spacer in donor-bridge-acceptor systems is a promising strategy to facilitate efficient electron transfer (ET) over a long distance. So far several examples using polyenes, polyynes, and others have appeared.[2,3] In our previous study, we first prepared porphyrin-quinone dyad with a diacetylene spacer.[4] However, further studies have been hampered owing to the unstability. Recently, it has been revealed that fullerenes are good, robust electron acceptors in ET.[5,6] We have shown that fullerenes accelerate photoinduced charge separation (CS) and slow down charge recombination (CR) in donor-linked fullerenes due to the small reorganization energies of fullerenes.[7,8] Therefore, a combination of fullerenes and "molecular wire" seems to be a good strategy to construct artificial photosynthesis and molecular photonics. Here we report the first synthesis and photophysical properties of porphyrin-C_{60} dyad with an acetylene spacer **1** (Figure 1). The ET-mediating properties of the acetylene spacer in **1** are expected to be evaluated accurately by comparing those of an amide spacer in porphyrin-C_{60} dyad **2**.[9]

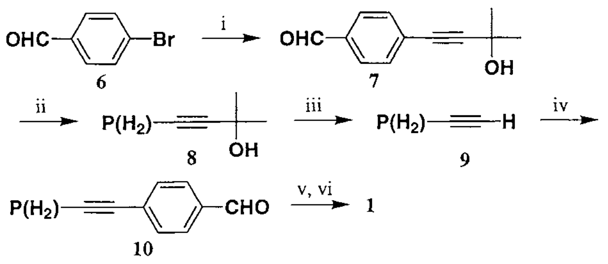
The synthesis of **1** was carried out as shown in Scheme 1. Lindsey's method of mixed-aldehyde condensations with pyrrole afforded a mixture of six porphyrins, which could not be separated easily with column chromatography.[10] To overcome the tedious separation, 4-(3-hydroxy-3-methyl-1-butynyl)-benzaldehyde **7**, where the ethynyl group is protected by a polar protecting group, was employed for the condensation. Thus, BF_3-catalyzed condensation of **7** and 3,5-di-*tert*-butylbenzaldehyde with pyrrole gave a mixture of several porphyrins. As expected, the desired porphyrin **8** was easily separated from the mixture of porphyrins by flash column chromatography. Deprotection of **8** was carried out under the basic conditions. The coupling reaction of **9** and 4-iodobenzaldehyde with tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) and triphenylarsine ($AsPh_3$) in toluene afforded porphyrin aldehyde **10** in 55% yield. The desired dyad **1** was obtained in 34% yield by 1,3-dipolar cycloaddition with **10**, *N*-methylglycine, and C_{60} in toluene and subsequent treatment with $Zn(OAc)_2$.[11] Porphyrin-C_{60} dyad **2** as well as single-chromophore references **3**-**5** were also prepared. Their structures were verified by spectroscopic analyses.[12]

Electronic absorption spectra of **1** and **2** in THF and DMF



Ar = 3,5-di-*tert*-butylphenyl

Figure 1.



Scheme 1. Synthesis of **1** : i) 2-methyl-3-butyn-2-ol, $Pd(OAc)_2$, PPh_3, Et_3N, 100%; ii) pyrrole, 3,5-di-*tert*-butylbenzaldehyde, $BF_3 \cdot Et_2O$, NaCl, $CHCl_3$, 12%; iii) KOH, 2-propanol/toluene, 72%; iv) 4-iodobenzaldehyde, $Pd_2(dba)_3$, $AsPh_3$, toluene/Et_3N, 55%; v) C_{60}, *N*-methylglycine, toluene, 34%; vi) $Zn(OAc)_2$, $MeOH/CHCl_3$, 100%.

were essentially a linear combination of the spectra of the corresponding chromophores **3**-**5**, indicating that there is no appreciable interaction between the porphyrin and C_{60} in the ground state. The redox potentials of **1**-**5** were measured by a differential pulse voltammetry in CH_2Cl_2 using 0.1 M *n*-Bu_4NPF_6 as a supporting electrolyte. The potentials of **1** and **2** (**1**: −1.52, −1.15, +0.33 V; **2**: −1.51, −1.12, +0.32 V vs. Fc/Fc^+) can be explained by the sum of **3** and **4** (**3**: +0.33 V; **4**: +0.34 V vs. Fc/Fc^+) and **5** (-1.54, -1.15 V vs. Fc/Fc^+), respectively.

Steady-state fluorescence spectra of **1**-**4** were taken in THF and DMF with the same concentration exciting at the Soret band where the porphyrin parts absorb mainly. The emissions of **1** and **2** were very weak compared with those of **3** and **4** (relative intensities: 0.012 for **1**, 0.037 for **2** in THF; 0.039 for **1**, 0.069 for **2** in DMF), showing the rapid quenching of the excited singlet state of the porphyrin ($^1ZnP^*$) by the C_{60}. The emissions of **1** and **2** (550-750 nm) were observed only from the porphyrin, with no detectable emission from the C_{60} (700-750 nm). Therefore, there is no evidence for the existence of the singlet-singlet energy transfer from $^1ZnP^*$ to the C_{60}. It is well established that in ZnP-C_{60} dyads photoinduced CS occurs efficiently from $^1ZnP^*$ to C_{60} in polar solvents such as THF and DMF.[5,7,8] Based on the energy diagram shown in Figure 2, CS from $^1ZnP^*$ to the C_{60} is energetically feasible (Table 1).[13] From these results, we can conclude that CS from $^1ZnP^*$ to C_{60} is a main pathway for the emission quenching in THF and DMF.

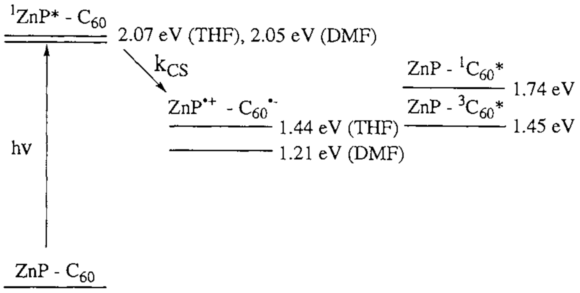


Figure 2. Energy Diagram for **1**.

The fluorescence lifetimes of **1**-**4** were measured by a picosecond single photon counting technique with excitation at 425 nm where the porphyrin absorbs mainly and monitoring at 605 nm where the fluorescence is due to only the porphyrin. The fluorescence decays of **1** and **2** in THF and DMF were analyzed to give one major component (τ=27 ps for **1**, τ=75 ps for **2** in THF; τ=33 ps for **1**, τ=75 ps for **2** in DMF). Based on the data we can calculate the CS rates, k_{CS} (= $\tau^{-1} - \tau_{ref}^{-1}$; τ_{ref} =2.0 ns for **3**, τ_{ref}=2.1 ns for **4** in THF; τ_{ref}=1.9 ns for **3**, τ_{ref}=2.0 ns for **4** in DMF). In THF and DMF the k_{CS} of **1** is larger by a factor of about three than that of **2**. Considering that the driving forces for the photoinduced CS, the separation distances, and the reorganization energies are quite similar in **1** and **2**, the acceleration effect can be explained by the larger electronic coupling between the porphyrin and the C_{60} *via* the acetylene spacer compared with the amide spacer.

Table 1. Free energy changes ($-\Delta G_{CS}$) and rate constants (k_{CS}) for charge separation.

Compounds	THF		DMF	
	$-\Delta G_{CS}$ / eV	k_{CS} / s^{-1}	$-\Delta G_{CS}$ / eV	k_{CS} / s^{-1}
1	0.63	3.72×10^{10}	0.84	3.01×10^{10}
2	0.67	1.28×10^{10}	0.88	1.28×10^{10}

In conclusion, the zincporphyrin-C_{60} dyad with the acetylene spacer has been prepared for the first time. It is shown that photoinduced CS from $^1ZnP^*$ to the C_{60} is accelerated *via* the triple bond spacer. The facile synthetic accessibility from the ethyne to polyyne spacer as well as the well-defined linear structure will allow us to extend the present system toward more refined donor-"molecular wire"-acceptor systems. The extended systems, in addition to the detailed photodynamics, are in progress.

This work was supported by the Grant-in Aids for COE Research and Scientific Research (No. 10131246 (Priority Area of Electrochemistry of Ordered Interfaces) and No. 09740471 to H. I. and No. 10146103 (Priority Area of Creation of Delocalized Conjugated Electronic Systems) to Y. S.) from the Ministry of Education, Science, Sports and Culture, Japan. Y. S. thanks the Mitsubishi Foundation for financial support.

References and Notes

1 "Molecular Electronics," ed by J. Jortner and M. Ratner, Blackwell, Oxford (1997).
2 A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki, and Y. Nishimura, *J. Org. Chem.*, **60**, 7177 (1995).
3 W. B. Davis, W. A. Svec, M. A. Ratner, and M. R. Wasielewski, *Nature*, **396**, 60 (1998).
4 H. Imahori, Y. Tanaka, T. Okada, and Y. Sakata, *Chem. Lett.*, **1993**, 1215.
5 H. Imahori and Y. Sakata, *Adv. Mater.*, **9**, 537 (1997).
6 N. Martín, L. Sánchez, B. Illescas, and I. Pérez, *Chem. Rev.*, **98**, 2527 (1998).
7 H. Imahori, K. Hagiwara, M. Aoki, T. Akiyama, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *J. Am. Chem. Soc.*, **118**, 11771 (1996).
8 H. Imahori, K. Hagiwara, T. Akiyama, M. Aoki, S. Taniguchi, T. Okada, M. Shirakawa, and Y. Sakata, *Chem. Phys. Lett.*, **263**, 545 (1996).
9 M. Fujitsuka, O. Ito, H. Imahori, K. Yamada, H. Yamada, and Y. Sakata, *Chem. Lett.*, in press.
10 R. W. Wagner, T. E. Johnson, and J. S. Lindsey, *J. Am. Chem. Soc.*, **118**, 11166 (1996).
11 M. Maggini, G. Scorrano, and M. Prato, *J. Am. Chem. Soc.*, **115**, 9798 (1993).
12 **1**: ^1H NMR (270 MHz, $CDCl_3$): δ 1.53 (s, 54H), 2.77 (s, 3H), 3.91 (d, *J* = 10 Hz, 1H), 4.58 (s, 1H), 4.71 (d, *J* = 10 Hz, 1H), 7.71 (m, 4H), 7.79 (m, 3H), 7.91 (d, *J* = 8 Hz, 2H), 8.07 (m, 6H), 8.17 (d, *J* = 8 Hz, 2H), 9.00 - 8.90 (m, 8H); MS (FAB) m/z 1889 ($M+H^+$) and 720 (C_{60}^+); UV/Vis λ_{max} (THF) 426, 557, 597 nm.
13 $-\Delta G_{CR} = E_{ox} - E_{red} + \Delta G_s$, $-\Delta G_{CS} = \Delta E_{0\text{-}0} - (-\Delta G_{CR})$, $\Delta G_s = e^2/(4\pi\varepsilon_0)[(1/(2R^+) + 1/(2R^-) - 1/R_{cc})(1/\varepsilon_s) - (1/(2R^+) + 1/(2R^-))(1/\varepsilon_r)]$ where $\Delta E_{0\text{-}0}$ is energy of the 0-0 transition between the S_1 and S_o states for the porphyrin, E_{ox} and E_{red} are the first oxidation potential of the porphyrin and the first reduction potential of the C_{60} in CH_2Cl_2, respectively, R^+ and R^- are radii of donor and acceptor, respectively, R_{cc} is center-to-center distance between the two moieties, and ε_s and ε_r are static dielectric constants of solvent used and when measured the redox potentials, respectively: R^+= 5.0 Å for the porphyrin, R^-= 4.4 Å for the C_{60}, R_{cc}=18.3 Å for **1** and R_{cc}=18.0 Å for **2**. See A. Weller, *Z. F. Phys. Chem. N. F.*, **113**, 93 (1982).