ORGANIC LETTERS

2008
Vol. 10, No. 21
4979−4982

First Triazole-Linked Porphyrin−Fullerene Dyads

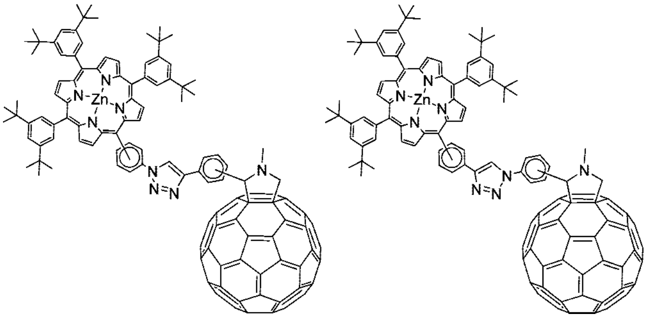
Michael A. Fazio,* Olivia P. Lee, and David I. Schuster*

Department of Chemistry, New York University, New York, New York 10003

m.fazio@nyu.edu; david.schuster@nyu.edu

Received September 2, 2008

ABSTRACT



A general procedure for the synthesis of 1,2,3-triazole-linked porphyrin−fullerene dyads is described. Four of these compounds have been prepared and characterized.

Porphyrin−fullerene dyads have been studied extensively with respect to photoinduced energy or electron transfer rates and mechanisms.[1] Face-to-face distances and the nature of the bridge that links the two chromophores have been subjects of investigation since these properties have such a large influence over the dynamics of electron and energy transfer processes.[2] The bridging unit in porphyrin−fullerene dyads performs two functions: it acts as a conduit through which electron transfer is facilitated, and it serves to orient the two chromophores at set distances and bond angles. In this paper, we report the use of a 1,4-diphenyl-1,2,3-triazole linker to connect a porphyrin and fullerene. The recent popularity of “click” reactions[3] has led to examples of porphyrin triazoles[4] and fullerene triazoles,[5] but to the best of our knowledge, no examples of triazole-linked porphyrin−fullerene dyads have been reported.

Imahori et al.[2b] demonstrated that in dyads with conjugated linkers electron transfer (ET) is promoted upon photoexcitation through bonds via a superexchange interaction, and they investigated the effect of ortho, meta, and para connectivity on the dynamics of photoinduced ET. Our triazole linker has two phenyl groups through which the chro-

---

(1) (a) Guldi, D. M. *Chem. Soc. Rev.* **2002**, *31*, 22. and references cited therein. (b) Bracher, P. J.; Schuster, D. I. *Fullerenes: From Synthesis to Optoelectronic Properties*; Guldi, D. M., Martin, N., Eds.; Kluwer Academic Publishers: Dordrecht, 2002; pp 163−212. (c) Xiao, S.; Li, Y.; Li, Y.; Zhuang, J.; Wang, N.; Liu, H.; Ning, B.; Liu, Y.; Lu, F.; Fan, L.; Yang, C.; Li, Y.; Zhu, D. *J. Phys. Chem. B* **2004**, *108*, 16677.

(2) (a) Guldi, D. M.; Luo, C.; Prato, M.; Troisi, A.; Zerbetto, F.; Scheloske, M.; Dietel, E.; Bauer, W.; Hirsch, A. *J. Am. Chem. Soc.* **2001**, *123*, 9166. (b) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771.

(3) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596. (b) Appukkuttan, P.; Dehaen, W.; Fokin, V. V.; Van der Eycken, E. *Org. Lett.* **2004**, *6*, 4223. (c) Díez-Gonzáles, S.; Correa, A.; Cavallo, L.; Nolan, S. P. *Chem.−Eur. J.* **2006**, *12*, 7558. (d) Wu, P.; Fokin, V. V. *Aldrichimica Acta* **2007**, *40*, 7.

(4) (a) Genady, A. R.; Gabel, D. *Tetrahedron Lett.* **2003**, *44*, 2915. (b) Tuncel, D.; Cindir, N.; Koldemir, Ü. *J. Inclusion Phenom. Macrocycl. Chem.* **2006**, *55*, 373. (c) Meudtner, R. M.; Ostermeier, M.; Goddard, R.; Limberg, C.; Hecht, S. *Chem.−Eur. J.* **2007**, *13*, 9834. (d) Punidha, S.; Sinha, J.; Kumar, A.; Ravikanth, M. *J. Org. Chem.* **2008**, *73*, 323. (e) Maeda, C.; Yamaguchi, S.; Ikeda, C.; Shinokubo, H.; Osuka, A. *Org. Lett.* **2008**, *10*, 549.

(5) (a) Chen, X.; Liu, C.-Y.; Jen, T.-H.; Chen, S.-A.; Holdcroft, S. *Chem. Mater.* **2007**, *19*, 5194. (b) Isobe, H.; Cho, K.; Solin, N.; Werz, D. B.; Seeberger, P. H.; Nakamura, E. *Org. Lett.* **2007**, *9*, 4611. (c) Zhang, W.-B.; Tu, Y.; Ranjan, R.; Van Horn, R. M.; Leng, S.; Wang, J.; Polce, M. J.; Wesdemiotis, C.; Quirk, R. P.; Newkome, G. R.; Cheng, S. Z. D. *Macromolecules* **2008**, *41*, 515.

10.1021/ol802053k CCC: $40.75

mophores connect. By varying the position of attachment of the phenyl linkers at both ends of the linker, it is possible to systematically alter the connectivity and the interchromophoric distance (defined here as the distance between the center of the porphyrins and the nearest carbon on C_{60}), both of which affect the dynamics of intramolecular electronic communication following photoexcitation of the porphyrins.

Imahori has also presented data for two porphyrin−fullerene dyads in which the identical porphyrin is connected to the fullerene through an amide linker.[6] The rate of charge recombination (CR) is drastically reduced for the amide with the carbonyl moiety closer to the porphyrin. The triazole unit at the middle of our linker can be positioned in one of two orientations, which may affect CR in a way similar to the Imahori system.

Using this approach, a large variety of structures for such dyads can be envisaged, depending upon whether the alkynyl and azido groups used in the triazole synthesis are attached to the porphyrin or to the fullerene, as well as the substitution pattern on the intervening phenyl groups. Several of these possibilities are illustrated in Figure 1, where for clarity the 3,5-di-*tert*-butylphenyl groups, present at the porphyrin meso positions to enhance solubility, are not shown.

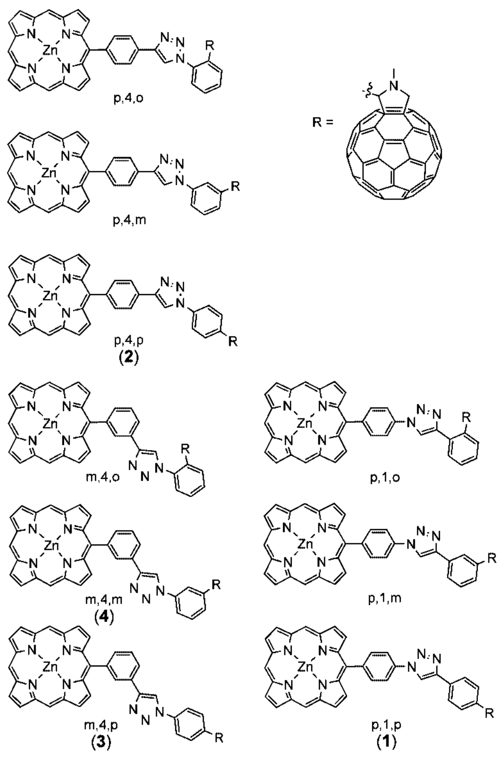


Figure 1. Porphyrin−triazole−fullerene dyads. For clarity, the 3,5-di-*tert*-butylphenyl groups on the porphyrin have been removed.

In naming these compounds, the first letter designates the connection of the alkyne or azide group to the phenyl ring on the porphyrins, the number indicates whether the porphyrin is attached to the 1 or 4 position on the triazole ring, and the second letter indicates the orientation of substituents on the phenyl ring on the fulleropyrrolidine. To date the p,1,p (**1**); p,4,p (**2**); m,4,p (**3**) and m,4,m (**4**) dyads have been prepared and characterized.

Molecular modeling using the program Materials Studio 4.2 indicates that the porphyrin and C_{60} moieties may be in close spatial proximity, in which case electronic communication following photoexcitation may occur through space (see Figure 2 for the energy-minimized model of **4**) rather than through the bonds.

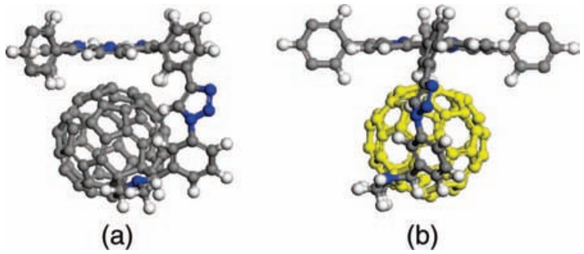


Figure 2. Molecular models of **4**. Energy was minimized with *tert*-butyl groups present on the phenyl rings which were then removed for clarity. Diagrams (a) and (b) are the same molecular model viewed from different perspectives. The C_{60} in diagram (b) is highlighted to distinguish it from the linker. The interchromophoric distance in this system is 2.84 Å.

The alkynyl porphyrins were made by a Lindsey mixed-aldehyde condensation using either 3-(TMS-ethynyl)benzaldehyde or 4-(TMS-ethynyl)benzaldehyde (TMS = trimethylsilyl) and 3,5-di-*tert*-butylbenzaldehyde (see Supporting Information for detailed procedures).[7]

The *meta*- and *para*-azidobenzaldehydes were made by reacting the corresponding bromobenzaldehydes with sodium azide, copper iodide, sodium ascorbate, and *N,N′*-dimethylethylenediamine according to a published procedure.[8] The progress of the reaction was monitored by appearance of the characteristic azide absorption band near 2100 cm^{-1} in the IR spectrum.

Porphyrin triazoles were then made by combining the alkynyl porphyrin and azidobenzaldehyde components using copper iodide and sodium ascorbate in a microwave-assisted reaction.[3b] The reactions were run in a DMSO/H_2O mixture in a small sealed flask under argon in a microwave reactor at a power setting of 50 W and a temperature setting of 80 °C for 30 min, giving 9% to quantitative yields. The porphyrin triazoles were characterized by ^1H NMR and MALDI-TOF mass spectrometry. The characteristic NMR changes are the appearance of a singlet between 8.3 and 8.6 ppm for the proton on the triazole ring and the disappearance

---

(6) Imahori, H.; Yamada, H.; Guldi, D. M.; Endo, Y.; Shimomura, A.; Kundu, S.; Yamada, K.; Okada, T.; Sakata, Y.; Fukuzumi, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2344.

(7) (a) Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941. (b) Li, F.; Yang, K.; Tyhonas, J. S.; MacCrum, K. A.; Lindsey, J. S. *Tetrahedron* **1997**, *53*, 12339.

(8) Andersen, J.; Madsen, U.; Björkling, F.; Liang, X. *Synlett* **2005**, 2209.

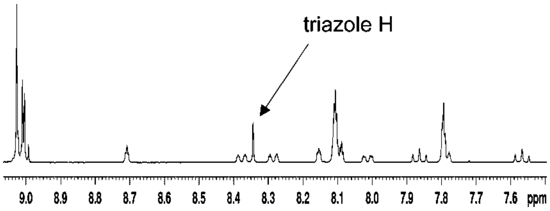


Figure 3. Partial ^{1}H NMR spectrum of m,4,m-ZnP-Tri.

of the 3.1–3.3 ppm singlet of the alkynyl proton (see Figure 3). Mass spectra show peaks for the molecular ion and M-28 for loss of nitrogen from the triazole ring (see Figure 4).

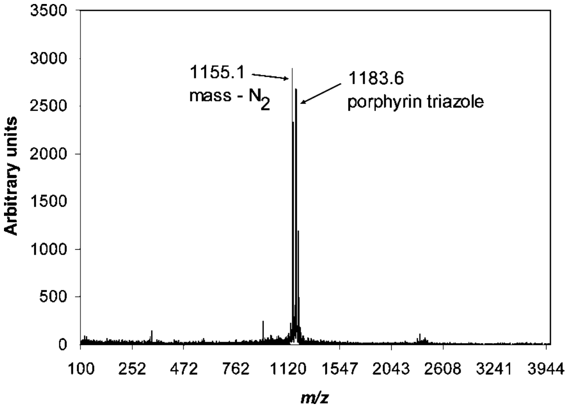
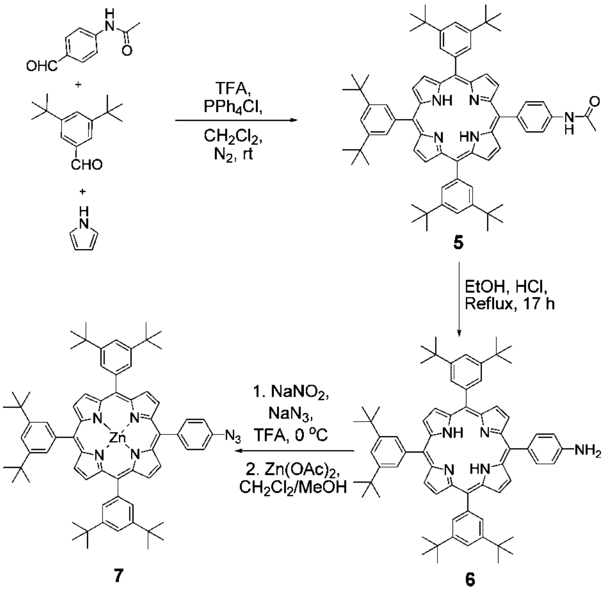


Figure 4. MALDI-TOF mass spectrum of m,4,m-ZnP-Tri.

As shown in Scheme 1, azidophenylporphyrins[9] were made from the corresponding amidophenylporphyrins,[10] followed by hydrolysis[11] and reaction with sodium nitrite and sodium azide in trifluoroacetic acid (TFA). Alkynyl benzaldehydes were made by deprotection of the commercially available trimethylsilyl-protected analogues.[12] Triazole formation using microwave-assisted “click” chemistry was carried out using the above conditions plus the addition of tris(benzyltriazolylmethyl)amine (TBTA)[13] for 90 min, affording product in 84% yield.

Finally, porphyrin–fullerene dyads were made by the Prato 1,3-dipolar cycloaddition to C_{60} of azomethine ylides derived from the porphyrinic aldehyde and sarcosine.[9] The MALDI-TOF mass spectra show a peak for the dyad minus N_2 and a peak for the porphyrin fragment in the positive ion mode (see Supporting Information). The ^{1}H NMR spectrum of **4** is shown in Figure 5. The results of our triazole and Prato syntheses are summarized in Table 1.

Scheme 1. *p*-Azidoporphyrin Synthetic Procedure



Figures 6 and 7 show the UV–vis absorption spectra and the steady-state fluorescence spectra of the zinc porphyrins (ZnP), porphyrin triazoles (ZnP–Tri), and the dyads (ZnP–Tri–Ful) in tetrahydrofuran (THF). The UV–vis spectra indicate no ground-state interaction between the

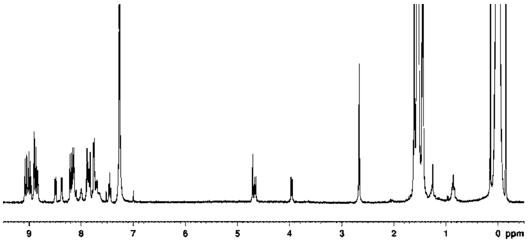


Figure 5. ^{1}H NMR spectrum of **4** in $CDCl_3$.

.

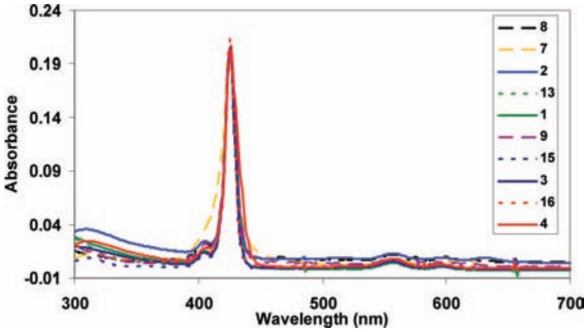


Figure 6. UV–vis spectra in THF.

---

(9) Séverac, M.; Le Pleux, L.; Scarpaci, A.; Blart, E.; Odobel, F. *Tetrahedron Lett.* **2007**, *48*, 6518.

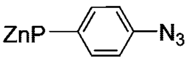
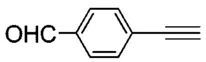
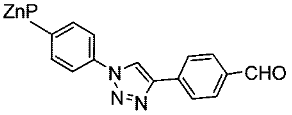
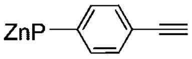
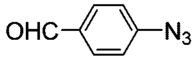
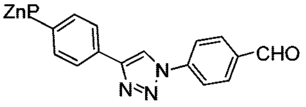
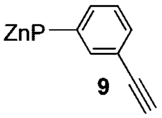
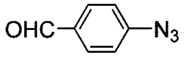
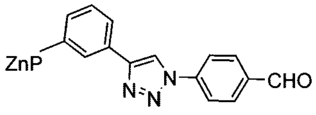
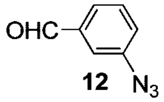
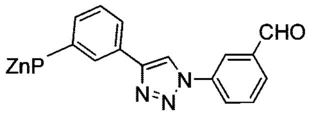
(10) Lindsey, J. S.; Brown, P. A.; Siesel, D. A. *Tetrahedron* **1989**, *45*, 4845.

(11) Imahori, H; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771.

(12) Wautelet, P.; Le Moigne, J.; Videva, V.; Turek, P. *J. Org. Chem.* **2003**, *68*, 8025.

(13) Chan, T. R.; Hilgraf, R.; Sharpless, K. B.; Fokin, V. V. *Org. Lett.* **2004**, *6*, 2853.

Table 1. Triazole and Dyad Synthesis Conditions and Yields[e]

porphyrin	aldehyde	triazole product	yield (%)	Prato product	yield (%)
 **7**	 **10**	 **13**	84^{a}	**1**	35^{c}
 **8**	 **11**	 **14**	9^{b} 40^{a}	**2**	23^{d}
 **9**	 **11**	 **15**	Quant.^{b}	**3**	31^{c} 65^{d}
	 **12**	 **16**	29^{b}	**4**	30^{c} 70^{d}

[a] 30 mol % of TBTA added to "click" reaction brew. [b] No TBTA added to "click" reaction brew. [c] Synthesized with 2 equiv of aldehyde, 2 equiv of sarcosine, and 1 equiv of C_{60}. [d] Synthesized with 1 equiv of aldehyde, 2 equiv of sarcosine, and 2 equiv of C_{60}. [e] ZnP = 5,10,15-tris(3,5-di-*tert*-butylphenyl)-Zn-porphyrin.

porphyrin and C_{60} moieties. The fluorescence spectra for the four dyads show strong quenching of the porphyrin fluorescence, demonstrating efficient electronic communication in the excited state between the porphyrin and fullerene moieties. Similar spectra were observed in toluene.

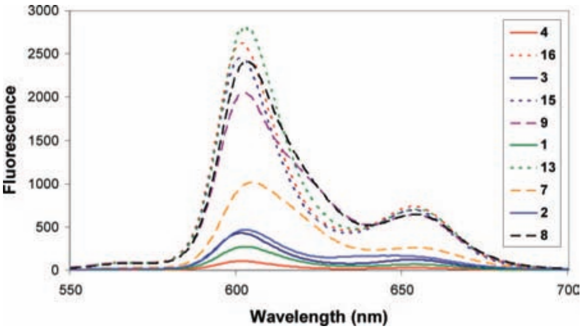


Figure 7. Steady-state fluorescence spectra in THF.

Work continues on synthesizing the other dyads in this series. Electrochemical analysis, measurement of fluorescence lifetimes, and detection and identification of short-lived transients produced upon photoexcitation will be carried out in the near future.

Acknowledgment. We are grateful to the National Science Foundation for support of the research under grant CHE-0647334. We are also grateful for support from the Camille and Henry Dreyfus Foundation under the Senior Mentor Program. We also thank Professor Phil Baran at Scripps for helpful comments regarding preparation of this manuscript.

Supporting Information Available: Detailed experimental procedures along with ^{1}H NMR spectra and mass spectra of all materials. This material is available free of charge via the Internet at http://pubs.acs.org.

OL802053K