Preparation and Photochemical Properties of Polyisocyanides with Regularly Arranged Porphyrin Pendants

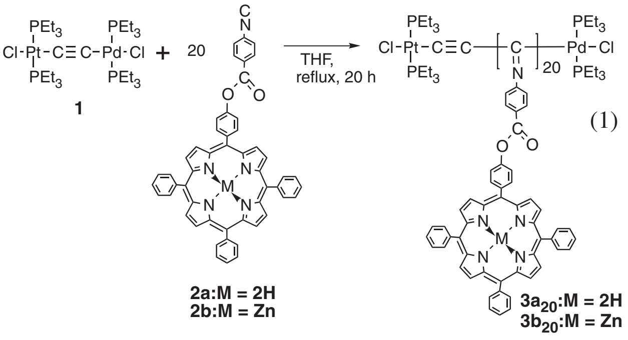
Fumie Takei, Sugiko Nakamura, Kiyotaka Onitsuka, Akito Ishida, Sachiko Tojo, Tetsuro Majima, and Shigetoshi Takahashi*
The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047

(Received February 25, 2003; CL-030158)

A novel triblock polyisocyanide having free-base- and zinc-porphyrins as pendants was prepared by living polymerization with a Pt-Pd μ-ethynediyl complex as an initiator, and irradiated at 420 or 556 nm in a THF solution to cause intramolecular energy transfer from the zinc-porphyrin to the free-base-porphyrin.

Porphyrin has a wide range of potential applications in the fields of optoelectronics, fluorescent materials and catalysts.[1] Recently, to develop new materials incorporating some of the prominent properties of porphyrin, there has been an increasing interest in the design of nano-sized macromolecules[2] in which porphyrin moieties are regularly arranged. We previously reported an attractive method for preparing polyisocyanides bearing porphyrin as a pendant group by the polymerization of porphyrin-isocyanide **2** with Pt-Pd μ-ethynediyl complex **1**.[3–5] This method offers a precise synthesis of definite oligomers and polymers with a polymerization degree (*DP*) of 2 to 100 or greater. Polyisocyanides with bulky groups on the nitrogen atoms are known to adopt a 4_1 helical structure with a pitch of ca. 4 Å.[6,7] In fact, the porphyrin-isocyanide polymers showed characteristic absorption spectra[4] due to electronic coupling between porphyrins attached to the nitrogen atoms through phenyl groups in the helical structure, suggesting that porphyrin pendants are regularly arranged along the helical main chain. Based on the structural characteristics of the polymers, this polymerization method may be extended for the synthesis of electronically heterogeneous structures using two kinds of chromophores, in which an increase in the excitation level is expected to offer an antenna effect.[8] In this paper, we report the synthesis of block copolymers using free-base porphyrin- and zinc porphyrin-isocyanides, and the photochemical properties of the novel copolymers.

Isocyanide monomers (**2a** and **2b**) bearing tetraphenylporphyrin (TPPH) and zinc tetraphenylporphyrin (TPPZn) were prepared and polymerized using initiator **1** to give respective homopolymers **3a** and **3b**[4] (Eq 1). In the UV-vis absorption spectra, polymers **3a** showed a split Soret band at around 420 nm, indicating regular face-to-face orientation of the porphyrin chromophores.[4,9] The fluorescence spectra of polymer **3a$_{20}$** ($DP = 20$, $M_n = 6000$, $M_w/M_n = 1.05$) with excitation at 420 nm (Soret band) and 556 nm (Q band) showed bands at 654 and 725 nm, respectively, which are characteristic of TPPH (Figure 1). Polymers **3b** showed a broad Soret band at around 420 nm in the UV-vis absorption spectra. The fluorescence spectra of **3b$_{20}$** ($DP = 20$, $M_n = 5600$, $M_w/M_n = 1.05$) with excitation at 420 and 556 nm showed bands at 604 and 656 nm (Figure 2).



(1)

The present polymerization system has an almost ideal living nature[5] and multi-block copolymers can be prepared by a usual technique.[3] Thus, 10 equiv. of **2b** as the first monomer were added to a solution of initiator **1** in THF and reacted under reflux to give polymer **3b$_{10}$** ($M_n = 4200$). After complete consumption of monomer **2b**, 2 equiv. of **2a** as the second monomer were added to give a diblock copolymer ($M_n = 4500$), followed by 10 equiv. of **2b** to give triblock copolymer **4** in 95% isolated yield ($M_n = 6100$; $M_w/M_n = 1.04$) (Eq 2). A trace experiment with GPC analysis indicated an expected increase in molecular

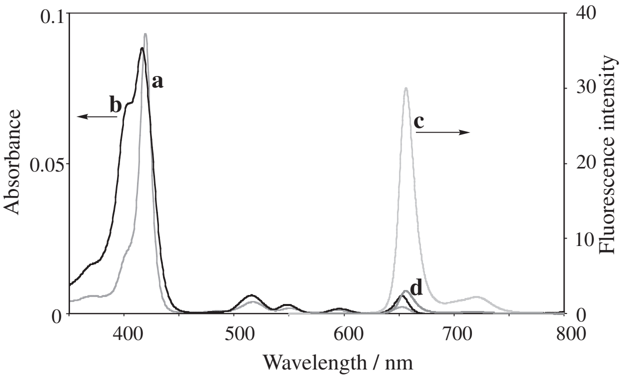


Figure 1. Absorption spectra of **2a** (**a**) and **3a$_{20}$** (**b**), and fluorescence spectra of **3a$_{20}$** excited at 420 nm (**c**) and 556 nm (**d**) at room temperature.

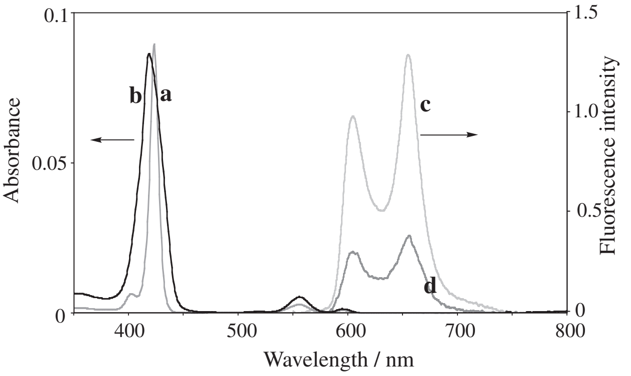
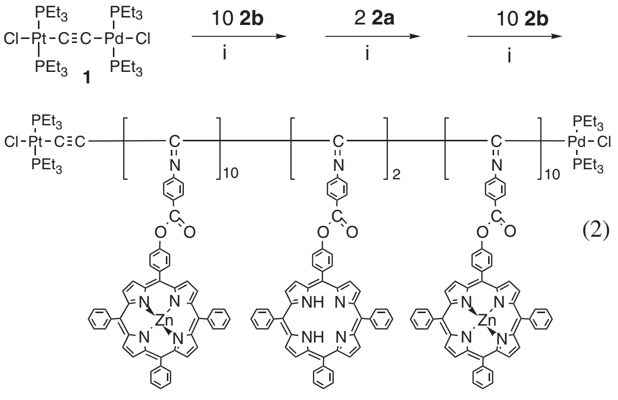


Figure 2. Absorption spectra of **2b** (**a**) and **3b$_{20}$** (**b**), and fluorescence spectra of **3b$_{20}$** excited at 420 nm (**c**) and 556 nm (**d**) at room temperature.



(2)

4

i) THF, reflux, 20 h

weights at the each step, and resulting polymer **4** was identified by spectral and elemental analyses. The UV-vis absorption spectrum of **4** showed clear maxima at 420, 556, and 596 nm along with weak bands at 513 and 650 nm. The spectrum was very similar to that of a 10:1 mixture of homopolymers **3b**$_{20}$ and **3a**$_{20}$. The Q-bands of **4** indicate the existence of TPPZn and TPPH as pendant groups in a ratio of 10:1 in the polymer molecule. The ratio of TPPZn to TPPH was confirmed by a quantitative analysis with UV-vis spectra and ICP analysis, the latter of which indicated that the ratio of platinum to zinc in the polymer molecule was 1:20.[10]

In polymer **4**, we can consider that the pendant groups of TPPZn and TPPH are almost regularly stacked along the main chain with a spacing of ca. 4 Å. Since the emission spectrum of TPPZn fortunately overlaps the absorption spectrum of TPPH, intramolecular fluorescence resonant energy transfer (FRET) from the former to the latter porphyrin moieties can be expected. When a 10:1 mixture of homopolymers **3b**$_{20}$ and **3a**$_{20}$ in THF was excited at 556 nm tuned to the absorption of TPPZn, three bands appeared at 604, 654, and 725 nm. The intensity of each band was consistent with the superimposition of the emission spectra of **3b**$_{20}$ and **3a**$_{20}$, undoubtedly indicating that intermolecular energy transfer does not occur between homopolymers **3a** and **3b** in solution. The fluorescence spectrum (Figure 3) of **4** excited at 556 nm also showed three bands at 604, 654, and 725 nm. These three bands indicate that both TPPZn and TPPH emit fluorescence because TPPZn shows fluorescence bands at 604 and 656 nm, while TPPH shows bands at 654 and 725 nm. The intensity of the emission at 604 nm due to TPPZn decreased by half compared to that for a mechanical mixture of homopolymers **3a** and **3b**, while the intensities of the emissions at 654 and 725 nm due to TPPH were greatly increased in the spectrum of **4**. This increase in emission clearly suggests energy transfer from TPPZn to TPPH in **4** in the excited state.

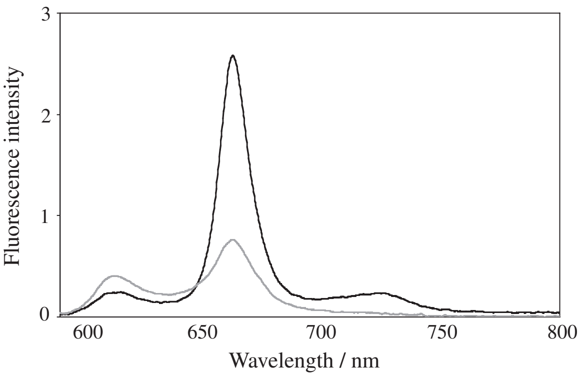


Figure 3. Fluorescence spectra of polymer **4** (—) and a mixture of **3a** and **3b** (—) excited at 556 nm.

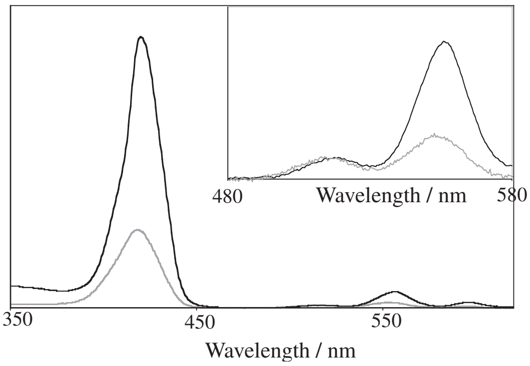


Figure 4. Absorption spectrum (—) and excitation spectrum of **4** monitored at 725 nm (—).

Intramolecular energy transfer was also confirmed by the fluorescence excitation spectrum (Figure 4) in comparison with the absorption spectrum. Based on the close similarity of both spectra and especially the appearance of absorption at 556 nm due to TPPZn in the excitation spectrum, efficient intramolecular energy transfer from TPPZn to TPPH can be concluded. Using both spectra, the energy transfer quantum yield was calculated to be about 35%.[11] This observation suggests that helical polyisocyanides provide a suitable nano-sized frame for aligning small functional molecules.

This work was supported in part by a Grant-in-Aid for COE Research and Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology. F. T. thanks the Mitsubishi Chemical Corporation Fund. We are grateful to Prof. N. Kobayashi (Tohoku University) for assignment of UV spectra and Mr. S. Tamiya (General Workshop, Osaka University) for assistance with the ICP analysis.

References and Notes

1 K. M. Kadish, K. M. Smith, and R. Guild, in "The Porphyrin Handbook," Academic Press, San Diego (1999).

2 For recent reviews, see: a) A. K. Burrell, D. L. Officer, P. G. Plieger, and D. C. W. Reid, *Chem. Rev.*, **101**, 2751 (2001). b) N. Aratani and A. Osuka, *Macromol. Rapid Commun.*, **22**, 725 (2001). c) D. Holten, D. F. Bocian, and J. S. Lindsey, *Acc. Chem. Res.*, **35**, 57 (2002).

3 K. Onitsuka, K. Yanai, F. Takei, T. Joh, and S. Takahashi, *Organometallics*, **13**, 3852 (1994).

4 a) F. Takei, K. Onitsuka, N. Kobayashi, and S. Takahashi, *Chem. Lett.*, **2000**, 916. b) F. Takei, H. Hayashi, K. Onitsuka, N. Kobayashi, and S. Takahashi, *Angew. Chem., Int. Ed. Engl.*, **40**, 4092 (2001).

5 F. Takei, K. Yanai, K. Onitsuka, and S. Takahashi, *Chem.—Eur. J.*, **6**, 983 (2000).

6 For reviews, see: a) F. Millich, *Adv. Polym. Sci.*, **19**, 117 (1975). b) W. Drenth and R. J. M. Nolte, *Acc. Chem. Res.*, **12**, 30 (1979). c) R. J. M. Nolte, *Chem. Rev.*, **94**, 11 (1994).

7 a) A. J. M. Van Beijmen, R. J. M. Nolte, W. Drenth, and A. M. F. Hezemans, *Tetrahedron*, **32**, 2017 (1976). b) J. J. L. M. Cornelissen, J. J. J. M. Donners, R. Gelder, W. S. Graswinckel, G. A. Metselaar, A. E. Roman, N. A. J. M. Sommerdijk, and R. J. M. Nolte, *Science*, **293**, 676 (2001).

8 a) S. E. Webber, *Chem. Rev.*, **90**, 1469 (1990). b) B. Hong and M. A. Fox, *Can. J. Chem.*, **73**, 2101 (1995). c) D. J. Kiserow, Y. Itoh, and S. E. Webber, *Macromolecules*, **30**, 2934 (1997).

9 A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, **110**, 4454 (1988).

10 Analysis with ICP Calcd for: Pt:Pd:Zn = 1.0:1.0:20; found: Pt:Pd:Zn = 1.0:0.99:19.6.

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

Published on the web (Advance View) May 13, 2003; DOI 10.1246/cl.2003.506