

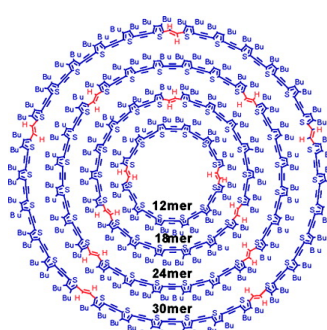
Communication

Giant Thienylene-Acetylene-Ethylene Macrocycles with Large Two-Photon Absorption Cross Section and Semishape-Persistence

Michele Williams-Harry, Ajit Bhaskar, Guda Ramakrishna, Theodore Goodson, Mika Imamura, Akane Mawatari, Kazumi Nakao, Hideo Enozawa, Tohru Nishinaga, and Masahiko Iyoda

J. Am. Chem. Soc., **2008**, 130 (11), 3252-3253 • DOI: 10.1021/ja078246s

Downloaded from <http://pubs.acs.org> on February 8, 2009



12mer:	$\delta_{\max} = 15,100 \text{ GM}$
18mer	$\delta_{\max} = 66,700 \text{ GM}$
24mer	$\delta_{\max} = 82,600 \text{ GM}$
30mer	$\delta_{\max} = 107,800 \text{ GM}$

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Giant Thienylene-Acetylene-Ethylene Macrocycles with Large Two-Photon Absorption Cross Section and Semishape-Persistence

Michele Williams-Harry,[†] Ajit Bhaskar,[†] Guda Ramakrishna,[†] Theodore Goodson, III,^{*,†} Mika Imamura,[‡] Akane Mawatari,[‡] Kazumi Nakao,[‡] Hideo Enozawa,[‡] Tohru Nishinaga,[‡] and Masahiko Iyoda^{*,‡}

Department of Chemistry and Department of Macromolecular Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109, and Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

Received October 28, 2007; E-mail: tgoodson@umich.edu; iyoda@tmu.ac.jp

Recently, the search for new organic materials with enhanced nonlinear optical effects has been driven by the formation of novel building block motifs.¹ Redox-active nanorings have attracted considerable attention for their single-molecule electronics, nano-fabrication, and unusual electronic and optical properties.¹ Among them, giant macrocycles composed of thiophene, acetylene, and ethylene building blocks are regarded as an infinite π -conjugated system with a large inner cavity, and hence their physical properties are strongly affected by their structures in solution and in the solid state.² Macrocyclic thiophene n -mers **1–4** ($n = 12, 18, 24,$ and $30,$ respectively) have both moderate molecular rigidity and flexibility with $21\text{--}60$ Å inner diameters^{3,4} and can change their conformation according to an external parameter.⁵ Since these π -expanded oligothiophenes possess similar molecular shape, important information can be obtained related to their ring size and functional properties, including evidence of cooperative enhancement in their nonlinear optical responses. In this contribution we investigate the two-photon properties of cyclic thiophenes **1–4** with varying sizes and number of building block chromophores.

The synthesis of large cyclic thiophenes **1–4** was carried out by a McMurry coupling reaction of **5** with low-valent titanium (Scheme 1). Cyclic oligomers **1–4** obtained as a mixture can be separated easily by gel permeation chromatography on polystyrene with toluene or chloroform as an eluent. All the giant macrocycles presented possess key stability and oxidative characteristics⁶ necessary for use in molecular electronics as a result of being very stable in the crystalline state in air at room temperature and having fairly low oxidation potentials ($E^{1/2} = 0.31\text{--}0.33$ V; $E^{2/2} = 0.50\text{--}0.52$ V vs Fc/Fc⁺), denoting low-lying HOMO–LUMO band gaps and therefore inherent conductivity.

As seen in Table 1, the longest absorption maxima of giant cycles **1–4** show an expected⁷ red shift and increasing extinction coefficient, ϵ , with an increasing number of thiophene units. There is a nonlinear relationship between the longest absorption maxima (eV) and $1/n$ (Supporting Information), suggesting considerable cyclic conjugation in **1–4** with saturation of the absorption maxima in rings **3** and **4** and therefore an effective conjugation limit (ECL)⁸ of 18 thiophene units. Coincidentally, with a 2.5-fold increase in chromophore density from **1** to **4** there is a 2.1-fold increase in the one-photon absorbance efficiency, ϵ , corresponding to the decreasing energy of the $\pi\text{--}\pi^*$ excitation energy gap. Similar to giant macrocycles previously reported,² one-photon fluorescence emission spectra of **1–4** show a nearly identical emission with two major emission bands and possess fluorescence quantum efficiencies (Φ_F)

Scheme 1. Synthesis of Thiophene $[n]$ Mers **1–4**

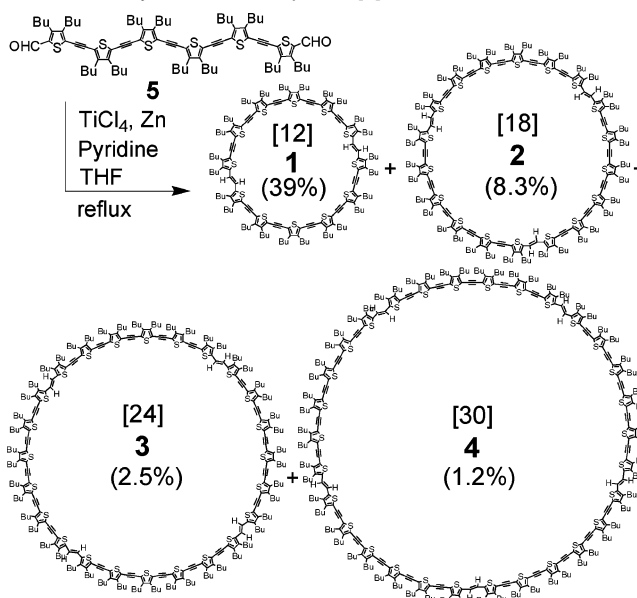


Table 1. Absorption Coefficients, Fluorescence Quantum Yields, and Relative Two-Photon Cross Sections of **1–4** in Dichloromethane

compd [n]mer	absorption		fluorescence		TPACS ^b δ_{\max} [GM]
	λ_{\max} [nm]	ϵ [M ⁻¹ cm ⁻¹]	λ_{\max} [nm]	Φ_F^a $\times 10^{-2}$	
1 [12]	452	295 000	562, 606	11	15 100
2 [18]	473	418 000	560, 603	8.5	66 700
3 [24]	478	528 000	559, 600	10	82 600
4 [30]	480	618 000	559, 600	9.5	107 800

^a Fluorescence quantum yields (Φ_F) were determined by comparison with quinine sulfate in 0.5 M H₂SO₄ ($\Phi_F = 0.51$). ^b TPA cross sections (δ) were measured in tetrahydrofuran; 1 GM = 10^{-50} cm⁴ s photon⁻¹.

of approximately 10%, which is much lower than the 30% efficiency reported for the linear α,α' -bisphenyl end-capped derivative of **5**.²

A single crystal of **1** suitable for X-ray analysis was obtained from chloroform-decane. The X-ray structure is shown in Figure 1.⁹ In our previous study,² the corresponding macrocycle composed of ten thiophene units showed a nearly round shape structure with all thiophene units in cisoid form, and the solvent heptane molecules were incorporated in the central cavity. In the present case, however, two thiophene units are in a transoid form to fill the center of the cycle. The resultant two small cavities are occupied with butyl

[†] University of Michigan.

[‡] Tokyo Metropolitan University.

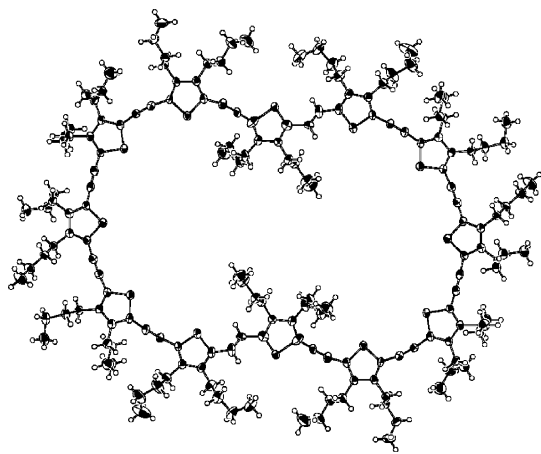


Figure 1. ORTEP drawing showing an X-ray structure of **1**.

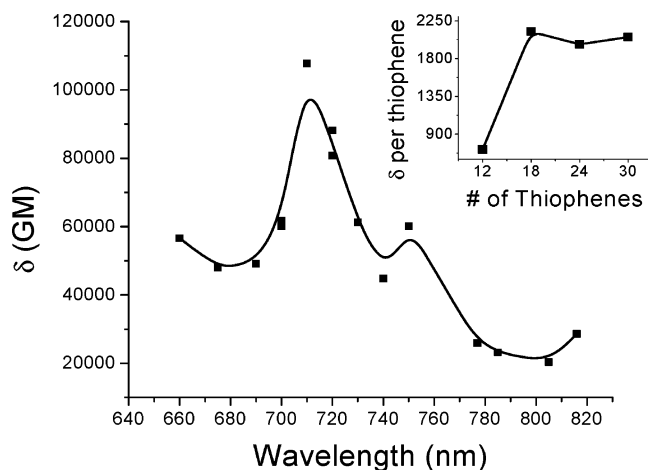


Figure 2. Two-photon cross-section spectrum of **4** with maximum TPACS values of **1–4** per thiophene shown at 710 nm (inset).

groups of adjacent molecules. As a result, the single crystal does not involve any solvent molecules, and **1** has a slightly bent chairlike structure.

The two-photon properties for the four macrocycles were investigated. Increasing ring size and π -character from **1** (72π) to **2** (108π), **1–3** (144π), and **1–4** (180π) show a 4.4-, 5.5-, and 7.1-fold amplification of the maximum two-photon absorption cross section (TPACS), δ , respectively (Table 1) which were measured according to the two-photon excited fluorescence (TPEF) method using femtosecond-pulses.¹⁰ These large increases in δ with an incremental addition of monomer unit **5** are clear evidence of intramolecular interactions¹¹ among these giant macrocycles. The maximum TPACS observed per thiophene unit is shown in the inset of Figure 2. The largest cross-section enhancement relative to **1** was observed in **2**. Further π -conjugation beyond the 108π ring size reveals a saturated maximum δ -value for rings **3** and **4**.

The excitation laser wavelength dependence, as shown for **4** in Figure 2, shows that the maxima are in the visible spectral region in the range from 710 to 750 nm. **1–4** have the largest known cross sections for an all-thiophene system compared to those observed for the C[nT-DA] cyclic series of compounds ($\delta_{\max} = 1470$ GM)¹² previously studied by our group and for poly-¹² ($\delta_{\max} = 38$ GM) and oligothiophenes¹³ ($\delta_{\max} = 181$ GM) presented in recent studies by others at approximately 800 nm.

Efficient delocalization gives rise to the immense magnitude of the TPA cross sections for macrocycles **1** and **2**. Saturation in one-photon absorbance and TPACS reveal macrocycle **2** as the optimal thienylene-acetylene-ethylene ring for both effective conjugation

and efficient electronic coupling. Besides the number of thiophene, acetylene, and ethylene units within this entry of a new class of TPA materials, **1–4** also have different molecular symmetry with D₂, D₃, D₄, and D₅ respective symmetries. Interestingly, macrocycle **2** is the only D₃ symmetrical ring and has shown the most enhancement of the two-photon cross section.

Transoid arrangement of **1** in its crystal structure is a consequence of ring strain since cisoid arrangement is observed in the less congested 10-thiophene derivative previously reported.² The D₂ symmetry of **1** conveniently allows a “ring flip” of the thiophenes adjacent to flexible double bonds to relieve strain. Macrocycles **3** and **4** should therefore be more flexible due to the availability of more degrees of freedom from additional double bonds and larger spatial arrangement, resulting in less effective π -overlap throughout the rings possibly due to a loss in planarity. Macrocycle **2** remains strained yet does not have the required symmetry for rapid “ring flip” of all available inflection points. Transient absorption measurements (Supporting Information) confirm that upon excitation enough energy enters into the ring system of **2** for the essential rotation and achievement of planarity resulting in a growth in stimulated emission. The addition of strong donor and acceptor groups on **2** would further optimize these optical properties and provide octupolar-type enhancement of the two-photon properties as a result of the molecular symmetry in the 108π conjugated system.^{11a}

Acknowledgment. This work was partly supported by the Ministry of Education, Culture, Sports and Technology, Japan. We thank Prof. Hitoshi Miyasaka and Dr. Yoshiyuki Kuwatani for the X-ray analysis of **1**. T.G. thanks the Army Research Office (Materials) and National Science Foundation (Polymers).

Supporting Information Available: Details of the synthesis and characterization of **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Krömer, L.; Rios-Carreras, I.; Fuhrmann, G.; Musch, C.; Wunderlin, M.; Debaerdemaeker, T.; Mena-Osteritz, E.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3481–3486. (b) Fuhrmann, G.; Krömer, L.; Bäuerle, P. *Synth. Met.* **2001**, *119*, 125–126. (c) Mena-Osteritz, E.; Bäuerle, P. *Adv. Mater.* **2001**, *13*, 243–246. (d) Fuhrmann, G.; Debaerdemaeker, T.; Bäuerle, P. *Chem. Commun.* **2003**, 948–949. (e) Sly, J.; Kasák, P.; Gomar-Nadel, E.; Rovira, C.; Górriz, L.; Thordarson, P.; Amabilino, D. B.; Rowan, A. E.; Nolte, R. J. M. *Chem. Commun.* **2005**, 1255–1257. (f) Enozawa, H.; Hasegawa, M.; Takamatsu, D.; Fukui, K.; Iyoda, M. *Org. Lett.* **2006**, *8*, 1917–1920. (g) Bhaskar, A.; Ramakrishna, G.; Hagedorn, K.; Varnavski, O.; Mena-Osteritz, E.; Bäuerle, P.; Goodson, T., III. *J. Phys. Chem. B* **2007**, *111*, 946–954.
- Nakao, K.; Nishimura, M.; Tamachi, T.; Kuwatani, Y.; Miyasaka, H.; Nishinaga, T.; Iyoda, M. *J. Am. Chem. Soc.* **2006**, *128*, 16740–16747.
- The inner diameters of **1–4** were estimated based on PM3 calculations.
- ¹H NMR spectra of **1–4** in CDCl₃ at -60 °C were similar to those at room temperature (Figures S6–S9, Supporting Information).
- Höger, S. Shape-Persistent Acetylenic Macrocycles for Ordered Systems. In *Acetylenic Chemistry*; Diederich, F., Stang, P. J., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, Germany, 2005.
- Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377.
- Bednarz, M.; Reineker, P.; Mena-Osteritz, E.; Bäuerle, P. *J. Lumin.* **2004**, *110*, 225–231.
- Meier, H.; Stalmach, U.; Kolshorn, H. *Acta Polym.* **1997**, *48*, 379–384.
- For the X-ray parameters, see the Supporting Information.
- Xu, C.; Webb, W. W., Jr. *J. Opt. Soc. Am. B* **1996**, *13*, 481–491.
- (a) Wang, Y.; He, G. S.; Prasad, P. N.; Goodson, T., III. *J. Am. Chem. Soc.* **2005**, *127*, 10128–10129. (b) Bhaskar, A.; Ramakrishna, G.; Lu, Z.; Twieg, R.; Hales, J. M.; Hagan, D. J.; Van Stryland, E.; Goodson, T., III. *J. Am. Chem. Soc.* **2006**, *128*, 11840–11849.
- Stabo-Egg, F.; Lindgren, M.; Nilsson, K. P. R.; Inganäs, O.; Hammarström, P. *Chem. Phys.* **2007**, *336*, 121–126.
- Feng, Y.; Yan, Y.; Wang, S.; Zhu, W.; Qian, S.; Tian, H. *J. Mater. Chem.* **2006**, *16*, 3685–3692.

JA078246S