ORGANIC LETTERS

2008
Vol. 10, No. 11
2215−2218

Thiophene Donor−Acceptor [2]Rotaxanes

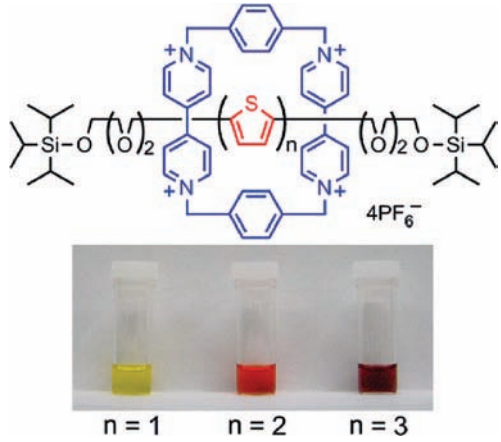
Taichi Ikeda,*,† Masayoshi Higuchi,† Akira Sato,† and Dirk G. Kurth†,‡

Functional Modules Group, Organic Nanomaterials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044 Japan, and Max Plank Institute of Colloids and Interfaces, Research Campus Golm, D-14424, Potsdam, Germany

ikeda.taichi@nims.go.jp

Received March 18, 2008

ABSTRACT



A series of the thiophene donor−acceptor [2]rotaxanes have been synthesized based on the inclusion complexes of cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) with thiophene, bithiophene, and terthiophene. The maximum wavelength of the charge-transfer band strongly depends on the number of thiophene units, while the association constant does not. These donor−acceptor pairs will be fascinating constituents for optoelectronic and electromechanical materials.

Inclusion complexation between electron-deficient (acceptor) cyclophanes, i.e., cyclobis(paraquat-*p*-phenylene) (**$CBPQT^{4+}$**),[1] and electron-rich (donor) aromatic compounds, e.g., 1,4-hydroxybenzene,[2] 1,5-dioxynaphthalene,[3] biphenol,[4] benzidine,[4,5] and tetrathiafulvalene derivatives,[6] has attracted much attention. The combination of donor−acceptor host−guest pair results in the formation of the charge-transfer (CT) complexes with fascinating electrochemical[7] and optical[8]

† National Institute for Materials Science.
‡ Max Plank Institute of Colloids and Interfaces.

(1) Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1547.
(2) Ashton, P. R.; Odell, B.; Reddington, M. V.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1550.
(3) Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 630.
(4) Córdva, E.; Bissel, R. A.; Spencer, N.; Ashton, P. R.; Stoddart, J. F.; Kaifer, A. E. *J. Org. Chem.* **1993**, *58*, 6440.
(5) Ikeda, T.; Aprahamian, I.; Stoddart, J. F. *Org. Lett.* **2007**, *9*, 1481.
(6) (a) Philp, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1548. (b) Anelli, P.-L.; Asakawa, M.; Ashton, P. R.; Bissell, R. A.; Clavier, G.; Górski, R.; Kaifer, A. E.; Langford, S. J.; Mattersteig, G.; Menzer, S.; Philip, D.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Tolly, M. S.; Williams, D. J. *Chem. Eur. J.* **1997**, *3*, 1113. (c) Jeppesen, J. O.; Becker, J. *Eur. J. Org. Chem.* **2003**, 3245.
(7) (a) Bissell, R. A.; Córdova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (b) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamrs, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 333.
(8) (a) Steuerman, D. W.; Tseng, H.-R.; Peters, A. J.; Flood, A. H.; Jeppesen, J. O.; Nielsen, K. A.; Stoddart, J. F.; Heath, J. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 6486. (b) Ikeda, T.; Saha, S.; Aprahamian, I.; Leung, K. C.-F.; Williams, A.; Deng, W.-Q.; Flood, A. H.; Goddard, W. A., III; Stoddart, J. F. *Chem. Asian J.* **2007**, *2*, 76.

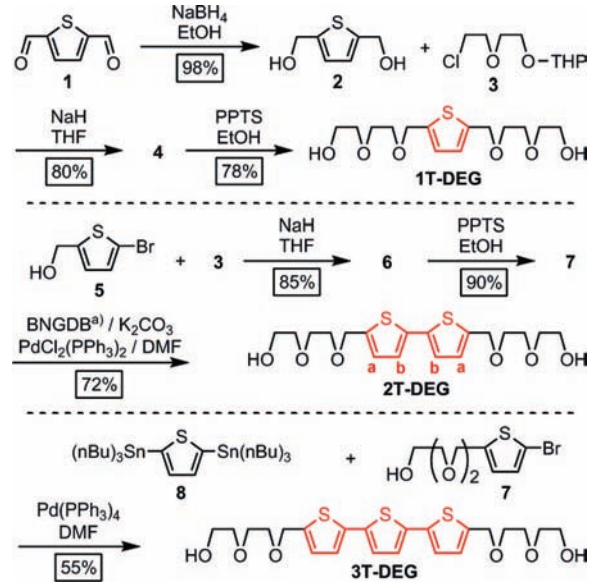
10.1021/ol800624c CCC: $40.75
Published on Web 05/03/2008

properties. Therefore, the interlocked donor−acceptor compounds have been used to fabricate molecular electronic devices[9] and nanoelectromechanical systems.[10] Despite extensive studies over two decades, inclusion complexation of **CBPQT**$^{4+}$ with thiophene derivatives has not been reported so far. The oligo- and polythiophene derivatives have been widely applicable to optoelectronic devices and sensors[11] because of their well-established chemical modification protocols.[12] Although some groups have reported thiophene [*n*]rotaxanes,[13] the formation of CT complexes as in the host−guest pair **CBPQT**$^{4+}$−thiophene has not been explored. We expect the donor−acceptor interlocked compounds, consisting of **CBPQT**$^{4+}$ and thiophene, to be attractive candidates for optoelectronic and electromechanical materials.

Here, we describe the synthesis of a series of new guest compounds, diethyleneglycol-substituted thiophenes (***n*T-DEG**, $n = 1-3$), for the host **CBPQT**$^{4+}$, as well as a series of thiophene donor−acceptor [2]rotaxanes (***n*T-Rx**, $n = 1-3$) using ***n*T-DEG** as precursors for the dumbbells.

First, we synthesized the diethyleneglycol-substituted thiophene derivatives (***n*T-DEG**). The routes employed in the synthesis of ***n*T-DEG** ($n = 1-3$) are summarized in Scheme 1. 2,5-Dihydroxymethylthiophene (**2**) was synthesized by the reduction of 2,5-thiophenedicarboxaldehyde (**1**) with $NaBH_4$. THP-protected diethyleneglycol-substituted thiophene (**4**) was prepared by alkylation of two hydroxyl groups in **2** with 2-(2-(2-chloroethoxy)ethoxy)tetrahydro-2*H*-pyran **3**. [8b] **1T-DEG** was obtained by deprotection of the terminal THP groups with pyridinium *p*-toluenesulfonic acid (PPTS).[14] Mono(diethyleneglycol)-substituted thiophene bromide **7** was prepared through alkylation of 5-bromo-2-hydroxymethylthiophene (**5**)[15] with **3**, followed by the deprotection of **6**. **2T-DEG** was synthesized via a one-pot tandem Miyaura boronic ester formation and Suzuki coupling[16] with the base (K_2CO_3) and the boron reagent [bis(neopentylglycolato)diboron]. **3T-DEG** was synthesized using the palladium-catalyzed Stille coupling with 2,5-stannylated thiophene (**8**) and **7**.[17] In the synthesis of **3T-DEG**, a small amount of **2T-DEG** was also obtained as a side product. Thus, we purified the product using preparative HPLC.

Scheme 1. Synthesis of Diethyleneglycol-Substituted Thiophene Derivatives and Labeling Scheme for **2T-DEG**



[a]BNGDP: bis(neopentylglycolato)diboron.

When **CBPQT**·4PF_6—a white powder—was added to a solution of ***n*T-DEG** in MeCN, the color of the solution changed immediately, indicating the formation of the pseudorotaxane.[2−6] This new absorption band arises from the CT band between the electron-rich thiophene unit and the electron-deficient bipyridinium units (Table 1). We confirmed that the maximum wavelengths of the CT bands correlate well with those of the ***n*T-DEG** $\pi-\pi^*$ bands (Table 1). From the Job plot using UV−vis absorption measurements,[18a] the stoichiometry of inclusion complex was confirmed to be 1:1 in all cases (Figure 1a).

Table 1. Maximum Absorption Wavelength (λ_{max}) in UV−vis Spectra for $\pi-\pi^*$ and CT Bands and Association Constants (K_a)

guest	λ_{max}, nm $\pi-\pi^*$ band [a]	λ_{max}, nm CT band[b]	K_a M^{-1}
1T-DEG	230	~400[c]	1900
2T-DEG	302	467	2800
3T-DEG	352	507	2200

[a] $\pi-\pi^*$ transition band of the thiophene derivatives. [b] Charge-transfer band of the complex. [c] CT band overlaps the absorption peak of **CBPQT**$^{4+}$.

A series of the [2]rotaxanes ***n*T-Rx**·4PF_6 were prepared through the capping reaction of the terminal hydroxyl groups of the [2]pseudorotaxanes with TIPS triflate in MeCN laced with 2,6-lutidine (Scheme 2).[19] **1T-**, **2T-**, and **3T-Rx**·4PF_6 were obtainable as yellow, red, purple solids, respectively.

(9) (a) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172. (b) Green, J. E.; Choi, J. W.; Boukai, A.; Bunimovich, Y.; J-Halperin, E.; Delonno, E.; Luo, Y.; Sheriff, B. A.; Xu, K.; Shin, Y. S.; Tseng, H. R.; Stoddart, J. F.; Heath, J. R. *Nature* **2007**, *445*, 414.

(10) (a) Huang, T. J.; Brough, B.; Ho, C.-M.; Liu, Y.; Flood, A. H.; Bonvallet, P. A.; Tseng, H.-R.; Stoddart, J. F.; Baller, M.; Magonov, S. *Appl. Phys. Lett.* **2004**, *85*, 5391. (b) Saha, S.; Leung, L. C.-F.; Nguyen, T. D.; Stoddart, J. F.; Zink, J. I. *Adv. Funct. Mater.* **2007**, *17*, 685.

(11) (a) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571. (b) Murphy, A. R.; Freshet, M. J. *Chem. Rev.* **2007**, *107*, 1066. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

(12) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93.

(13) (a) Vögtle, F.; Jäger, R.; Händel, M.; Ottens-Hildebrandt, W.; Schmidt, W. *Synthesis* **1996**, 353. (b) Sakamoto, K.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Org. Chem.* **2007**, *72*, 459.

(14) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

(15) Hagen, S. E.; Domagala, J.; Gajda, C.; Lovdahl, M.; Tait, B. D.; Wise, E.; Holler, T.; Hupe, D.; Nouhan, C.; Urumov, A.; Zeikus, G.; Zeikus, E.; Lunney, E. A.; Pavlovsky, A.; Gracheck, S. J.; Saunders, J.; Roest, S. V.; Brodfuehrer, J. *J. Med. Chem.* **2001**, *44*, 2319.

(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(17) Wei, Y.; Yang, Y.; Yeh, J.-M. *Chem. Mater.* **1996**, *8*, 2659.

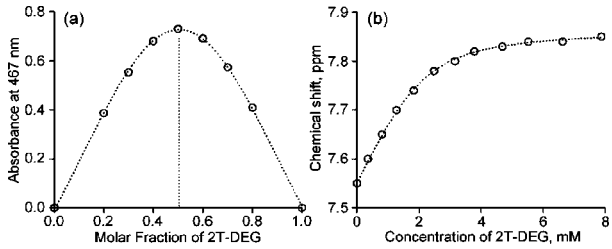
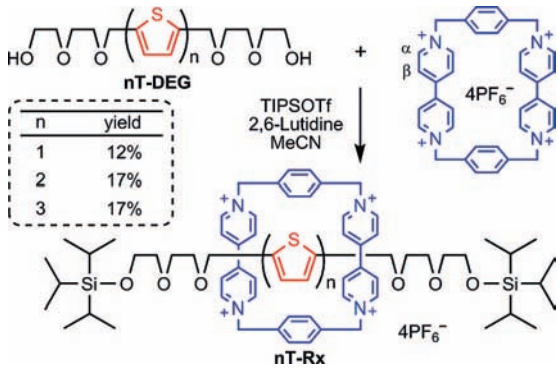


Figure 1. (a) Job plot for inclusion complexation of **2T-DEG** and **CBPQT**·4PF_6 (MeCN, rt). (b) Chemical shift change in ^{1}H NMR titration (**2T-DEG** vs **CBPQT**·4PF_6, MeCN, 288 K, concentration of **CBPQT**·4PF_6: 2.1 mM). The curve fit is depicted as dot line (K_a = 2800).

The absorption maximum of the CT band of each [2]rotaxane ***n*T-Rx** is identical to the observed value of the corresponding [2]pseudorotaxane (Table 1).

Scheme 2. Synthesis of the Thiophene [2]Rotaxanes



n	yield
1	12%
2	17%
3	17%

Figure 2 shows the ^{1}H NMR spectra of (a) 1:1 mixture of the dumbbell (**2T-DEG** capped with the TIPS groups) and **CBPQT**·4PF_6, (b) 1:1 mixture of the thread (**2T-DEG**) and **CBPQT**·4PF_6, and (c) the thiophene [2]rotaxane **2T-Rx**·4PF_6. In the first case (Figure 2a), the bulky end groups of the dumbbell hinder inclusion complexation. We confirmed that the chemical shifts of the peaks in Figure 2a are identical to those obtained from the dumbbell and the macrocycle independently. Figure 2b shows single broad peak for each proton on the thread, especially proton b, suggesting that the complexed and uncomplexed species are in fast exchange on the ^{1}H NMR time scale. Since the chemical shift change of the *p*-phenylene protons depends on the molar ratio of the thread and the macrocycle, we could calculate the association constant (K_a) of the inclusion complex (Figure 1b).[18b]

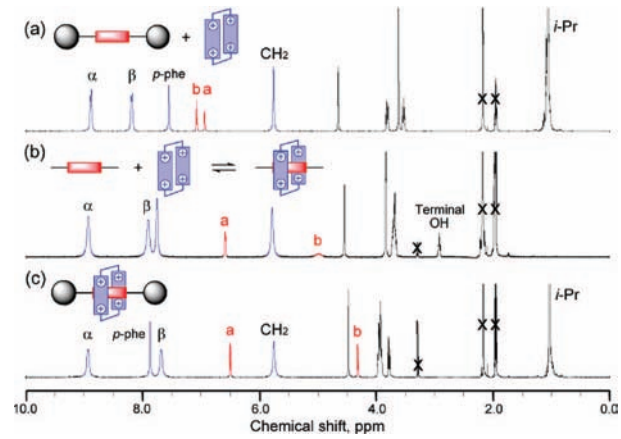


Figure 2. ^{1}H NMR spectra of (a) 1:1 mixture of **2T-DEG** capped with TIPS groups and **CBPQT**·4PF_6, (b) 1:1 mixture of **2T-DEG** and **CBPQT**·4PF_6, (c) [2]rotaxane **2T-Rx**·4PF_6. CD_3CN, 300 MHz, 288 K, X: solvent peaks.

Table 1 summarizes the association constants obtained from ^{1}H NMR titration. Stoddart et al. pointed out that the electrostatic interaction and the hydrogen bond between the ether oxygen atoms and the cationic bipyridinium unit play important roles in stabilizing the complex.[19] In addition, Kaifer reported[20] a drastic change in the K_a values in response to the extension of the aromatic repeating units. For example, the K_a values of the diethyleneglycol-substituted 1,4-dihydroxybenzene[19] and 4,4′-biphenol[4] are 2200 and 140 M^{-1}, respectively. In the cases of ***n*T-DEG** (n = 1−3), we detected no dramatic change in the K_a values. Although the longer thiophene moiety pushes its arms away from the cavity, the diethyleneglycol can wrap around and interact with the positive bipyridinium unit even in the case of **3T-DEG**.

Interestingly, the observed K_a value for **2T-DEG** (K_a = 2800) is much smaller than that reported for the diethyleneglycol-substituted tetrathiafulvalene derivatives (**TTF-DEG**, K_a = 380000).[21] Before the experiment, we expected that these two aromatic units (**2T** and **TTF**) should arrange their ethyleneglycol chains in a similar manner around the bipyridinium units and would have comparable binding affinities because of their similar molecular shapes. The most important factor in differentiating the binding affinities is considered to be the bond order of the inter-ring bond. In the case of **TTF-DEG**, the inter-ring double bond inhibits the free rotation of the binding unit. On the other hand, the free rotation between two thiophene rings should be suppressed after inclusion complexation. This entropically unfavorable process is attributable to the smaller K_a value for **2T-DEG** in comparison with **TTF-DEG**. The weaker electron-donating property of **2T** compared to **TTF** may also contribute to reducing the binding affinity. It is interesting

(18) (a) Schneider, H.-J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; John Wiley & Sons: Chichester, West Sussex, 2000; p 148. (b) Reference 18a, p 142.

(19) Anelli, P. L.; Ashton, P. R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M. T.; Goodnow, T. T.; Kaifer, A. E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vicent, C.; Williams, D. J. *J. Am. Chem. Soc.* **1992**, *144*, 93.

(20) Castro, R.; Nixon, K. R.; Evanseck, J. D.; Kaifer, A. E. *J. Org. Chem.* **1996**, *61*, 7298.

(21) Choi, J. W.; Flood, A. H.; Steuerman, D. W.; Nygaard, S.; Braunschweig, A. B; Moonen, N. N. P.; Laursen, B. W.; Luo, Y.; DeIonno, E.; Peters, A. J.; Jeppesen, J. O.; Xu, K.; Stoddart, J. F.; Heath, J. R *Chem. Eur. J.* **2006**, *12*, 261.

that such a small structural difference between **2T** and **TTF** aromatic rings gives rise to such a large difference in K_a.

In the ^{1}H NMR spectrum of the [2]rotaxane **2T-Rx**·4PF_6 (Figure 2c), we confirmed the sharp resonances of the thiophene protons. Compared to the free dumbbell (Figure 2a), the signals for the thiophene protons in the [2]rotaxane **2T-Rx**·4PF_6 are shifted to higher field. In particular, a dramatic upfield shift was observed for the protons b (6.99 → 4.32 ppm). This upfield shift is attributed to the shielding effect on the guest protons situated within the **CBPQT**$^{4+}$ cavity.[2–7] Of the protons associated with the **CBPQT**$^{4+}$ ring, the chemical shifts for the α and CH_2 protons are almost identical (cf. parts a and c of Figure 2), while the β and *p*-phenylene protons are shifted to higher and lower fields, respectively. These observations strongly suggest that the plane of the thiophene rings is parallel to the bipyridinium units and perpendicular to the *p*-phenylene aromatic rings present in the **CBPQT**$^{4+}$. The [2]rotaxanes **1T-Rx**·4PF_6 and **3T-Rx**·4PF_6 show similar results.

An X-ray analysis[22] revealed the interlocked structure of the [2]rotaxane **2T-Rx**·4PF_6 (Figure 3). The bithiophene unit,

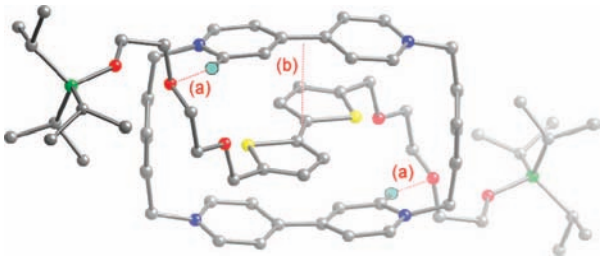


Figure 3. X-ray crystallographic structure of the donor−acceptor thiophene [2]rotaxane **2T-Rx**·4PF_6. The counterions and the hydrogen atoms not participating in the hydrogen bonds are omitted for clarity. (a) hydrogen bond (C···O), (H···O) distances and C−H···O angle: 3.18, 2.27 Å and 165°. (b) $\pi-\pi$ stacking distance: 3.43 Å.

in which the sulfur atoms possess an anti orientation, is inserted centrosymmetrically through the center of the tetracationic cyclophane. While the bipyridinium units are distorted from the normal planar geometries (dihedral angle between two pyridine ring mean planes: 15°), the π-system in the bithiophene unit is completely planarized (dihedral angle between two thiophene ring mean planes: 0°). The tilt angle of the central C−C vector between two thiophene rings relative to the bipyridinium N^+-N^+ vector is 71°. This value is close to the tilt angle observed in the X-ray structure of the **TTF**-included [2]catenane (74°).[7b] The dihedral angles of the mean planes of the *p*-phenylene and the bipyridinium units with respect to the mean plane of the thiophene units are 3° and 85°, respectively. These results are in good agreement with the molecular orientation deduced from the ^{1}H NMR result. The complex is stabilized by the [C−H ··· O] hydrogen bonds between the ether oxygen and α-bipyridinium hydrogen (Figure 3a) as well as $\pi-\pi$ stacking interactions (Figure 3b). However, no T-type CH-π interaction, which has been usually observed for the **CBPQT**$^{4+}$ inclusion complex,[2,3,19] is detectable between the thiophene hydrogen atom and the *p*-phenylene aromatic ring ([H ··· π] distance:[23] 4.21 Å).

In conclusion, we have synthesized a series of new guest compounds containing the thiophene units for the **CBPQT**$^{4+}$ host (***n*T-DEG**, $n = 1-3$). We confirmed inclusion complexation between ***n*T-DEG** and **CBPQT**$^{4+}$. Furthermore, we have obtained a series of the thiophene donor−acceptor [2]rotaxanes. The maximum wavelength of the CT band strongly depends on the number of thiophene unit, while the association constant does not. Increasing the number of thiophene units ($n > 3$) will further induce red shift of the CT band. In addition, extended thiophene moiety will afford a long, rigid, and multidentate binding site. The thiophene [2]rotaxanes reported herein have demonstrated that the thiophene derivatives will be fascinating constituents of functional interlocked molecules. The synthesis of the oligothiophene rotaxanes (***n*T-Rx**, $n > 3$) and the characterization of electromechanical properties are now in progress.

Acknowledgment. The authors thank Dr. Tadateru Nishikawa (Bruker BioSpin K.K.) for the 2D NMR measurement. This work was financially supported by the Iketani Science and Technology Foundation.

Supporting Information Available: Experimental procedures, full spectroscopic data for all new compounds, ^{1}H NMR titration results, and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL800624C

(22) The single crystals of the [2]rotaxane **2T-Rx**·4PF_6 were grown by vapor diffusion of *i*-Pr_2O into a MeCN solution of **2T-Rx**·4PF_6. Crystal data for [**2T-Rx**·4PF_6·6MeCN]: $C_{72}H_{98}N_4O_6S_2Si_2$·4$PF_6$·6MeCN, M = 2062.07, triclinic, a = 11.323(4) Å, b = 11.942(4) Å, c = 20.512(7) Å, α = 91.128(5)°, β = 101.002(5)°, γ = 114.600(5)°, V = 2460.2(15) Å^3, space group $P\bar{1}$, $Z = 1$, r_{calcd} = 1.392 g cm^{-3}, μ(Mo Kα) = 2.43 cm^{-1}, $F(000)$ = 826.0, T = 120 K, red plate crystal, 0.60 × 0.30 × 0.10 mm, R_1 = 0.0650, $wR_2(F_2)$ = 0.1648, goodness of fit = 1.045.

(23) The distance between the proton b of the thiophene unit and the centroid of the *p*-phenylene unit.