JOC Article

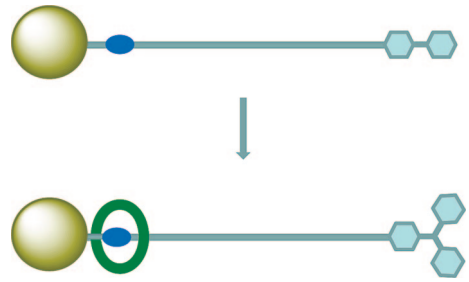
Charge Transfer Chromophore-Stopped [2]Rotaxane through [2 + 2] Cycloaddition

Weidong Zhou, Jialiang Xu, Haiyan Zheng, Huibiao Liu, Yuliang Li,* and Daoben Zhu

Beijing National Laboratory for Molecular Science (BNLMS), CAS Key Laboratory of Organic Solids Institute of Chemistry, Chinese Academy of Sciences and Graduate school of Chinese Academy of Sciences, Beijing 100190, P. R. China

ylli@iccas.ac.cn

Received July 6, 2008



Three charge-transfer chromophore-terminated [2]rotaxanes were synthesized, using a high-yield [2 + 2]cycloaddition reaction in apolar solvent at room temperature. Two solvent-driving molecular shuttles were constructed, which exhibit distinct conformations in different solvent as a result of the shuttling movement of the macrocycle.

Introduction

Biological molecular machines, such as the supramolecular system in photosynthesis, which are able to transform chemical energy into mechanical motion, have been well studied during the past few years. In order to simulate these biological machines with synthetic systems, many simple prototypes of artificial molecular motors, consisting of a few components capable of moving in a controllable way, have been proposed in recent years.[1] Mechanically interlocked molecules, such as catenanes and rotaxanes, have become typical candidates in the design of artificial molecular machines because some of their components have the ability of reversibly moving among two or more stations on application of external stimuli.[1] Various stimuli have been employed to induce such switches, ranging from illumination[2] and variation of the electrochemical potential[3] to solvent[4] or pH change.[5] Various methods for the preparation of such bistable rotaxanes are being pursued actively in order to facilitate the optimal realization of their applications. Threading followed by stopping and "clipping" are two efficient strategies for the construction of rotaxanes.[6] As for the method of threading followed by stopping methodology, many reactions have been employed for pseudorotaxanes, in order to form rotaxanes, such as click reaction[7] and reductive amination.[8] However, in

(1) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391. (b) Stoddart, J. F. *Acc. Chem. Res.* **2001**, *34*, 409–522. (c) Balzani, V.; Credi, A.; Venturi, M. *Molecular Devices and Machines: A Journey into the Nano World*; Wiley-VCH: Weinheim, Germany, 2003. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2006**, *41*, 72–191. (e) Credi, A.; Tian, H. *Adv. Funct. Mater.* **2007**, *17*, 671–840. (f) Tian, H.; Wang, Q.-C. *Chem. Soc. Rev.* **2006**, *35*, 361–374.

(2) (a) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G.W. H. *Science* **2001**, *291*, 2124–2128. (b) Balzani, V.; Clemente-Leon, M.; Credi, A.; Ferrer, B.; Venturi, M.; Flood, A. H.; Stoddart, J. F. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 1178–1183. (c) Wang, Q. C; Qu, D. H.; Ren, J; Chen, K. C.; Tian, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2661–2665. (d) Qu, D.-H.; Wang, Q.-C.; Tian, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5296–5299.

(3) (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433–444. (b) Altieri, A.; Gatti, F. G.; Kay, E. R.; Leigh, D. A.; Martel, D.; Paolucci, F.; Slawin, A. M. Z.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2003**, *125*, 8644–8654. (c) Mateo-Alonso, A.; Fioravanti, G.; Marcaccio, M.; Paolucci, F.; Rahman, G. M. A.; Ehli, C.; Guldi, D. M.; Prato, M. *Chem. Commun.* **2007**, 1945–1947. (d) Flood, A. H.; Nygaard, S.; Laursen, B. W.; Jeppesen, J. O.; Stoddart, J. F. *Org. Lett.* **2006**, *8*, 2205–2208.

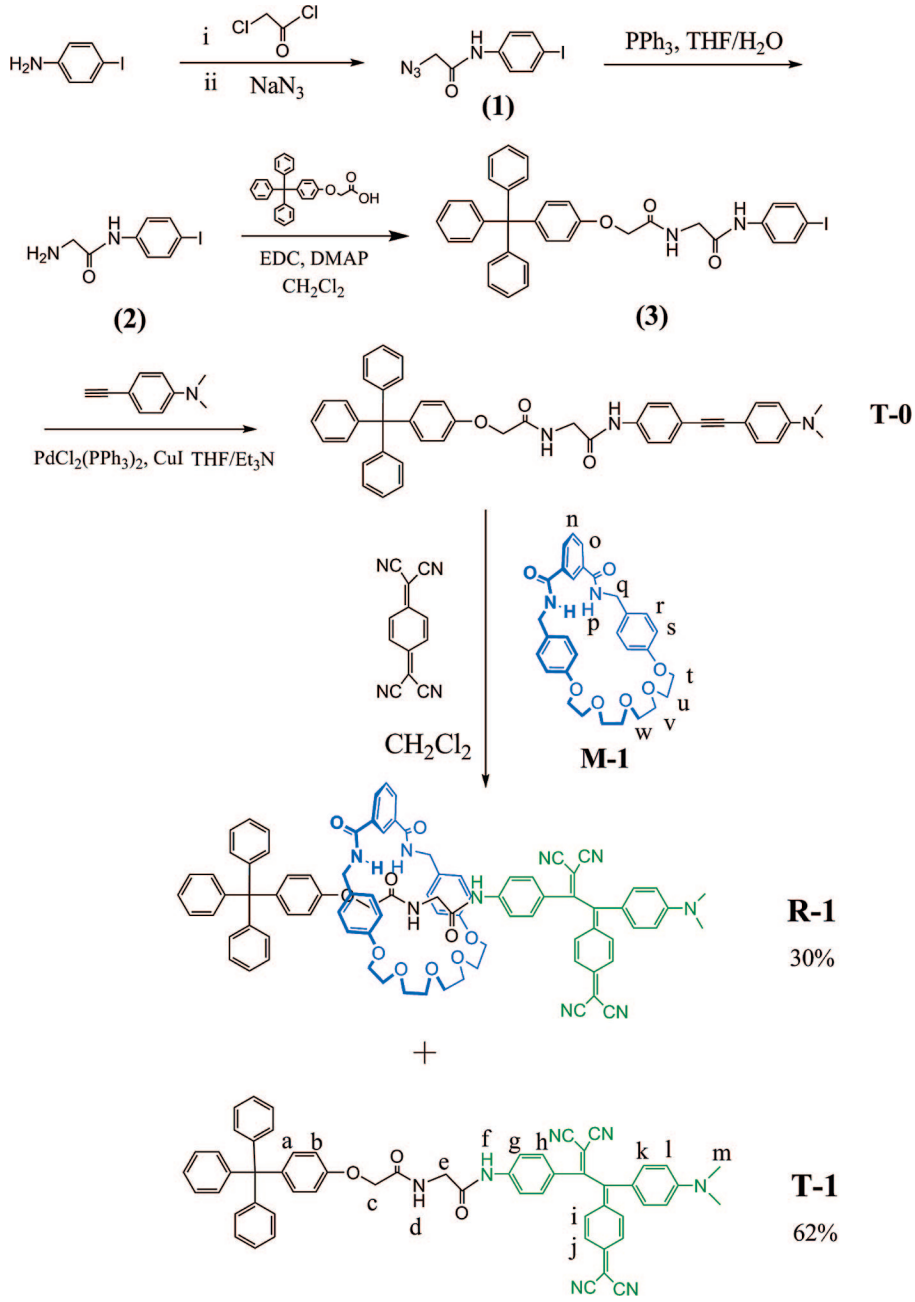
(4) (a) Lane, A. S.; Leigh, D. A.; Murphy, A. *J. Am. Chem. Soc.* **1997**, *119*, 11092–11093. (b) Da Ros, T.; Guldi, D. M.; Morales, A. F.; Leigh, D. A.; Prato, M.; Turco, R. *Org. Lett.* **2003**, *5*, 689–691. (c) Leigh, D. A.; Morales, M. A. F.; Perez, E. M.; Wong, J. K. Y.; Saiz, C. G.; Slawin, A. M. Z.; Carmichael, A. J.; Haddleton, D. M.; Brouwer, A. M.; Buma, W. J.; Wurpel, G.W. H.; Leon, S.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 3062–3067.

(5) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gomez-Lopez, M.; Martinez-Diaz, M.-V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 11932–11942. (b) Keaveney, C. M.; Leigh, D. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1222–1224. (c) Huang, F.; Nagvekar, D. S.; Slebodnick, C.; Gibson, H. W. *J. Am. Chem. Soc.* **2005**, *127*, 484–485.

(6) Amabilino, D. B.; Stoddart, J. F. *Chem. Rev.* **1995**, *95*, 2725–2828.

10.1021/jo8014566 CCC: $40.75
Published on Web 09/10/2008

SCHEME 1. Synthetic Route to T-1 and R-1



practice, the using of catalysts or molecular sieves sometimes limits their application. So, the search for a mild and high-yield reaction suitable for the construction of [2]rotaxane is still important to scientists in this field. [9]

Organic donor−acceptor molecules have been given much attention as promising compounds for molecular electronics, particularly in all optical computing and signal processing. Since interlocked compounds are believed to be superior scaffolds for molecular devices,[1] interlocked compounds containing donor−acceptor groups are of great interest. Herein, we describe three [2]rotaxanes containing a charge transfer chromophore stopper synthesized through a high efficiency [2 + 2] cycloaddition reaction. This cycloaddition reaction developed by Diederich occurs in apolar solvent at room temperature without the help of catalyst.[10] These conditions are ideal for strong hydrogen

(7) (a) Aucagne, V.; Hanni, K. D.; Leigh, D. A.; Lusby, P. J.; Walker, D. B. *J. Am. Chem. Soc.* **2006**, *128*, 2186–2187. (b) Aucagne, V.; Berna, J.; Crowley, J. D.; Goldup, S. M.; Hanni, K. D.; Leigh, D. A.; Lusby, P. J.; Ronaldson, V. E.; Slawin, A. M. Z.; Viterisi, A.; Walker, D. B. *J. Am. Chem. Soc.* **2007**, *129*, 11950–11963. (c) Dichtel, W. R.; Miljanić, O. S.; Spruell, J. M.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 10388–1039.

(8) (a) Glink, P. T.; Oliva, A. I.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1870–1875. (b) Williams, A. R.; Northrop, B. H.; Chang, T.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6665–6669. (c) Leung, K.C.-F.; Aricó, F.; Cantrill, S. J.; Stoddart, J. F *J. Am. Chem. Soc.* **2005**, *127*, 5808–5810.

(9) (a) Chiu, C.-W.; Lai, C.-C.; Chiu, S.-H. *J. Am. Chem. Soc.* **2007**, *129*, 3500–3501. (b) Hsueh, S.-Y.; Cheng, K.-W.; Lai, C.-C.; Chiu, S.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 4436–4439. (c) Hoffart, D. J.; Tiburcio, J.; Torre, A; de, la; Knight, L. K.; Loeb, S. J *Angew. Chem., Int. Ed.* **2008**, *47*, 97–101. (d) Mullen, K. M.; Gunter, M. J. *J. Org. Chem.* **2008**, *73*, 3336–3350.

(10) (a) Michinobu, T.; May, J. C.; Lim, J. H.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Biaggio, I.; Diederich, F. *Chem. Commun.* **2005**, *D*, 737–739. (b) Michinobu, T.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Frank, B.; Moonen, N. N. P.; Gross, M.; Diederich, F. *Chem. Eur. J.* **2006**, *12*, 1889–1905. (c) Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4731–4733.

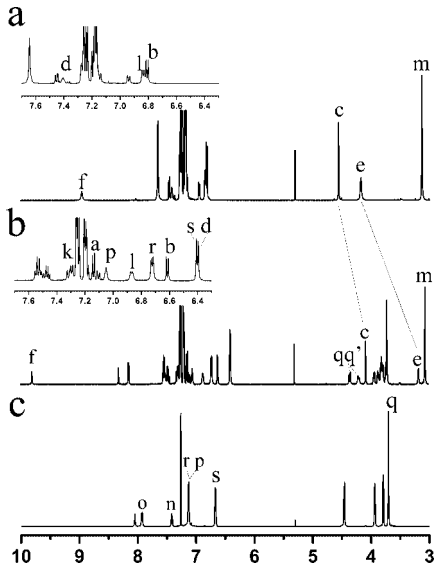


FIGURE 1. Partial ^{1}H NMR spectra (600 MHz, 298 K, $CDCl_3$, 1×10^{-3} M) of **T-1** (a), **R-1**(b), and macrocycle **M-1** (c).

bonding induced recognition between macrocycle and thread molecules containing amide.[11]

Results and Discussion

The shuttle was synthesized according to Scheme 1. Amide−amide hydrogen bonding of short peptide units with isophthalamide macrocycles has been well studied by the Leigh group for template-induced synthesis of rotaxanes.[11] In CH_2Cl_2, macrocycle **M-1** assembled with the monostoppered peptide thread **T-0**, forming a pseudorotaxane (Scheme 1). Covalent capture of the threaded intermediate compound by cycloaddition reaction with tetracyanoquinodimethane (TCNQ) afforded the free thread **T-1** and [2]rotaxane **R-1** in 62% and 30% yields, respectively. This cycloaddition reaction developed by Diederich occurs at room temperature and in apolar solvents without the help of catalyst.[10] All these conditions are ideal for strong hydrogen binding of macrocycle **M-1** with thread molecules containing amide.[11b,12] The synthesis of the intramolecular charge transfer (ICT) chromophore and the stopping of the pseudorotaxanes could be carried out in one step. This cycloaddition reaction exhibits some advantages over typical methods such as click reaction and reductive amination, where the introduction of metal catalyst or molecular sieve sometimes put limitations on their application.

Since the xylylene parts of the macrocycle shields encapsulated regions of the thread, the position of the macrocycle could be determined by comparing the chemical shift of the protons in rotaxane with those of the corresponding thread.[11,12] The ^{1}H NMR spectra (Figure 1) of thread **T-1** and rotaxane **R-1** confirm the interlocked nature of **R-1** and show that in **R-1** the macrocycle is localized on the peptide region of the thread (Scheme 1). The upfield shifts of the methylene resonances of the peptide station (H_e 1.00, H*c* 0.48) in **R-1** are characteristic[11,12] of aromatic shielding by the encapsulating macrocycle. The

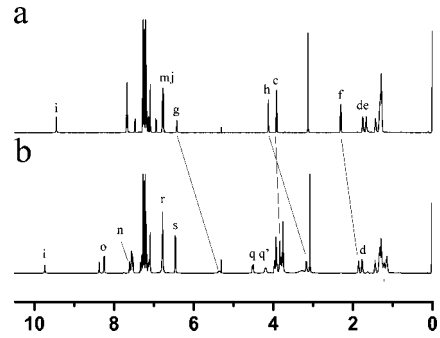


FIGURE 2. Partial ^{1}H NMR spectra (400 MHz, 1×10^{-3} M, $CDCl_3$) of **T-2** (a) and **R-2** (b).

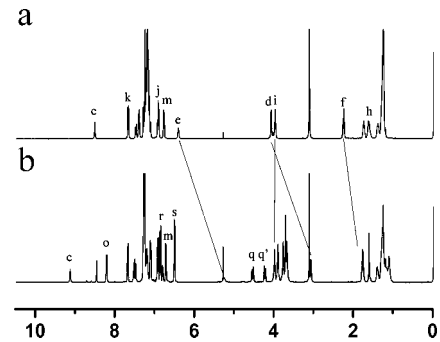


FIGURE 3. Partial ^{1}H NMR spectra (400 MHz, 1×10^{-3} M, $CDCl_3$) of **T-3** (a) and **R-3** (b).

signals corresponding to phenylene protons H_b exhibited substantial upfield shift of 0.23 ppm due to the shielding effect from the macrocycle. The signals for $H_{q/q'}$ separated into two different sets of signals as a consequence of losing their planes of symmetry orthogonal to the principal axis in [2]rotaxane.[5a,13] The amide resonance H_f shifted downfield by 0.84 ppm in the rotaxane as a result of the hydrogen bonding to the macrocycle polyether oxygens.[11b] The HRMS (N-SIMS NBA) of **R-1** revealed a high intensity signal at *m*/*z* 1407.600 and 1430.580 corresponding to **R-1** and **R-1**+Na (see Supporting Information).

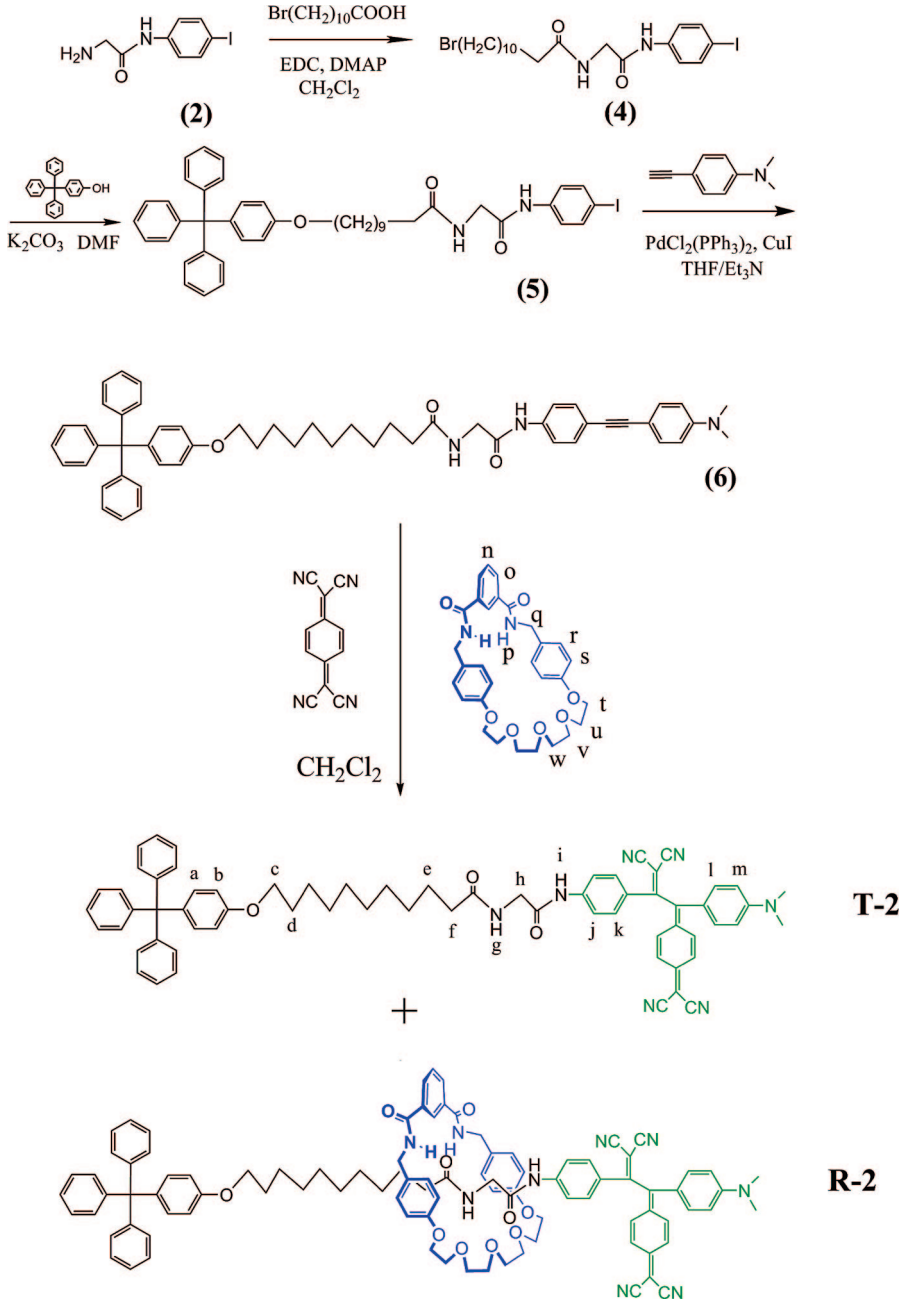
To put this synthesis strategy into the construction of molecular shuttle, two [2]rotaxanes **R-2** and **R-3** containing a C10-chain bridge between peptide and ICT chromophore were synthesized with similar reaction mechanism and process (Schemes 2 and 3). The ^{1}H NMR spectra (Figures 2 and 3) of [2]rotaxane **R-2** and **R-3** confirm their interlocked nature and show that in **R-2** and **R-3** the macrocycle is localized on the peptide region of the thread. The upfield shifts of the methylene resonances of the peptide station (H_f 0.45, H_h 0.96, Figure 2b) in **R-2** are characteristic of aromatic shielding by the encapsulating macrocycle. The amide proton resonance H_g in **R-2** experienced an upfield shift of 1.06 ppm as a result of the shield effect from the macrocycle. In addition, the alkyl-chain proton resonances H_c and H_d in **R-2** are still in the same station as those in **T-2**, which indicate the independence of macrocycle and alkyl-chain. All these features verify that the macrocycle stay in the peptide station in **R-2** in $CDCl_3$. In **R-3**, the two signals H_d and H_f adjacent to peptide group upfield shifted by 1.01 and 0.51 ppm, respectively, which indicates the shield effect

(11) (a) Leigh, D. A.; Murphy, A.; Smart, J. P.; Slawin, A. M. Z. *Angew. Chem., Int. Ed.* **1997**, *36*, 728–732. (b) Leigh, D. A.; Thomson, A. R. *Org. Lett.* **2006**, *8*, 5377–5379.

(12) (a) Li, Y.; Li, H.; Li, Y.; Liu, H.; Wang, S.; He, X.; Wang, N.; Zhu, D. *Org. Lett.* **2005**, *7*, 4835–4838. (b) Zhou, W.; Chen, D.; Li, J.; Xu, J.; Lv, J.; Liu, H.; Li, Y. *Org. Lett.* **2007**, *9*, 3929–3932.

(13) (a) Badjic, J. D.; Ronconi, C. M.; Stoddart, J. F.; Balzani, V.; Silvi, S.; Credi, A. *J. Am. Chem. Soc.* **2006**, *128*, 1489–1499. (b) Zhou, W.; Li, J.; He, X.; Li, C.; Lv, J.; Li, Y.; Wang, S.; Liu, H.; Zhu, D. *Chem. Eur. J.* **2008**, *14*, 754–763.

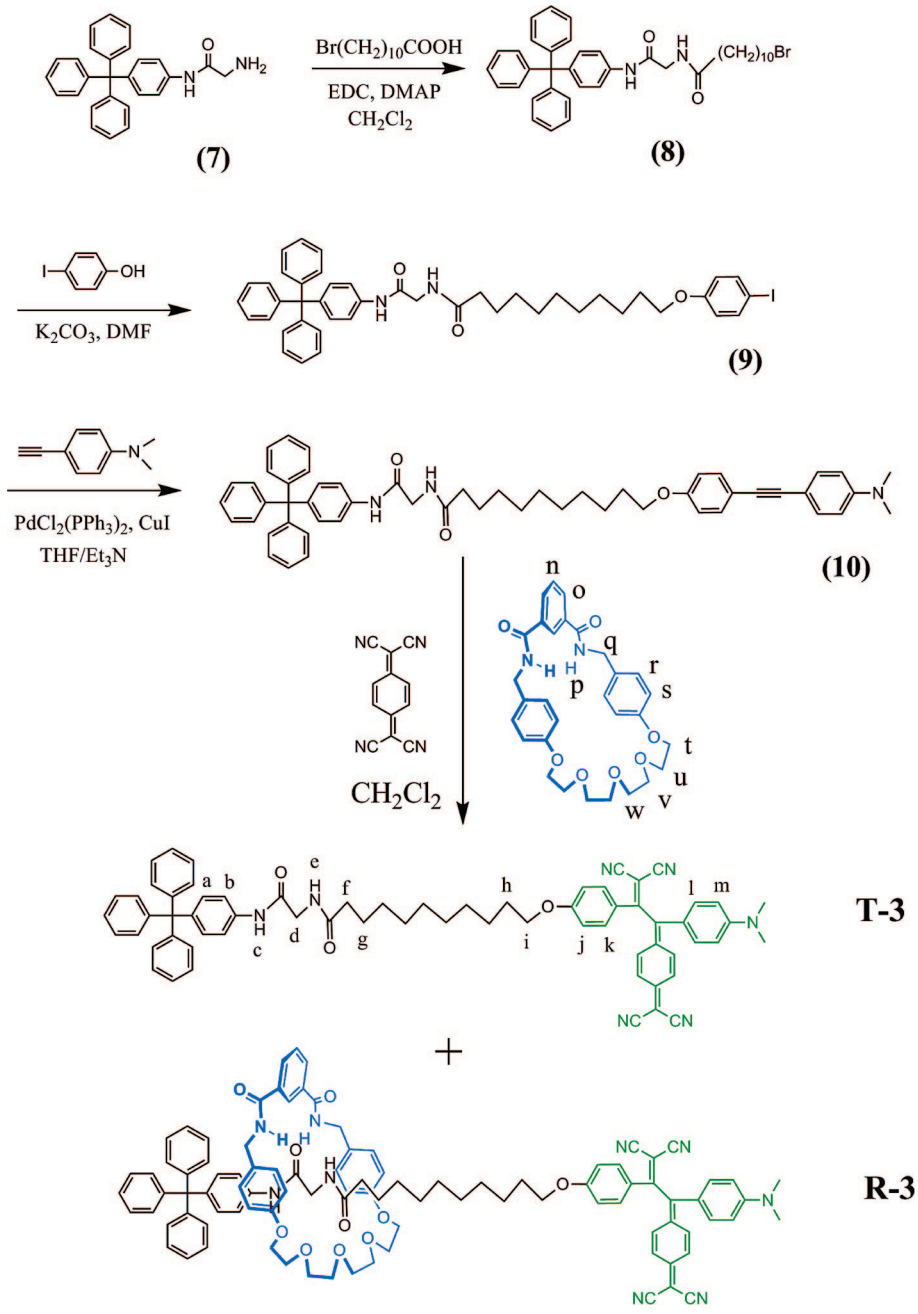
SCHEME 2. Synthetic Route to T-2 and R-2



from the macrocycle.(Figure 3b) The amide proton resonance H_e in **R-3** experienced an upfield of 1.12 ppm due to the shield effect from the macrocycle. Furthermore, the alkyl-chain proton resonance H_i did not exhibit obvious shift compared with that in free thread **T-3**. These features verify that the macrocycle stays in the peptide station in **R-3** in $CDCl_3$.

The macrocycle can be dissociated from the peptide by changing into a highly polar solvent, which solvates the hydrogen-bonding sites of the macrocycle and the peptide more strongly than they bind to each other.[4] In DMSO, a typical solvent that destroys hydrogen bonding, significant changes occurred in ^1H NMR spectra. The amide signal of H_g and the methylene resonance H_h in **R-2** exhibit shifts similar to those in free thread **T-2** (Figure 4), which can be attributed to the disappearance of the hydrogen bonds and the shield effect from the macrocycle when dissolved in DMSO, while the upfield shifts of the methylene resonance (H_c 0.32) in **R-2** are characteristic of aromatic shielding by the encapsulating macrocycle. The alkyl-chain proton signals in **R-2** experienced significant upfield shift compared with the free thread **T-2**, which can be attributed to the shield effect of the macrocycle. These features indicate the macrocycle in **R-2** moved toward the long alkyl chain and apart from the ICT chromophore unit in DMSO (Scheme 4a). In **R-3**, the amide signal of H_e and the methylene resonance H_d exhibited the same shift as in free thread **T-3** (Figure 5). The signal assigned to methylene H_i experienced an upfield shift of 0.44 ppm, which indicates the shield effect from the macrocycle. The proton signals assigned to the long alkyl chain exhibited obvious upfield shift compared to those in free thread **T-3**, which indicate the aromatic shielding from the encapsulating macrocycle. These features indicate the

SCHEME 3. Synthetic Route to T-3 and R-3



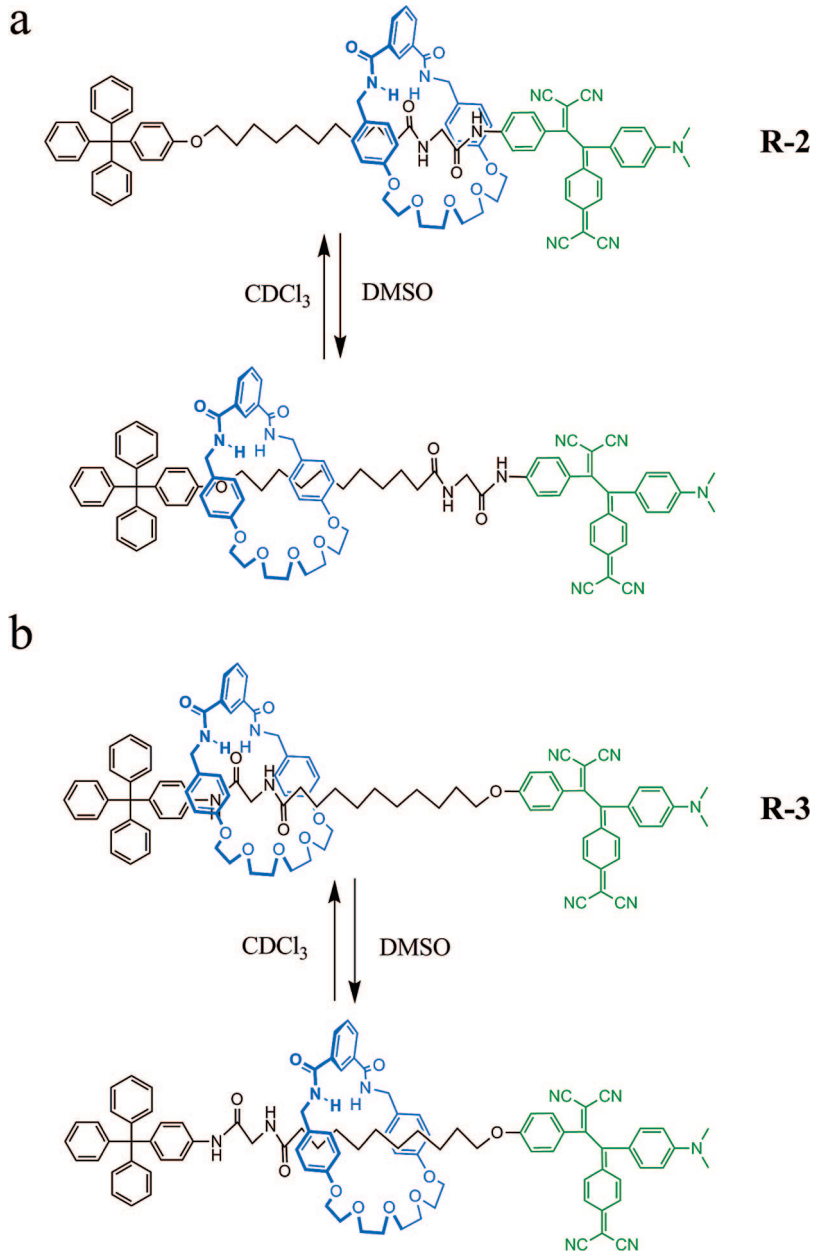
macrocycle in **R-3** moved toward the long alkyl chain and toward the ICT chromophore unit in DMSO (Scheme 4b). So, two solvent-driving molecular shuttles were successfully constructed through the [2 + 2] cycloaddition reaction, which exhibit distinct conformations in different solvents as a result of the shuttling movement of the macrocycle.

In conclusion, three charge transfer chromophore-terminated [2]rotaxanes were synthesized by virtue of a cycloaddition reaction. The mild condition of this reaction provides extensive opportunity for the construction of [2]rotaxane. The incorporation of the charge transfer chromophore to the molecular shuttle as a bulk stopper will introduce more understanding of the construction of future molecular shuttles.

Experimental Section

2-Azido-acetyl-4-iodobenzenamine (1). 2-Chloroacetyl chloride (0.67 g, 6mmol) was added to a solution of 4-iodobenzenamine (1.31 g, 6mmol) and Et_3N (1 mL) in $CHCl_3$ at 0 °C. Then the mixture was stirred at room temperature for 2 h and washed with distilled water (3 × 50 mL). The collected organic layers were dried over $NaSO_4$, and the chloroform was removed in vacuo to gain the product (1.55 g, 85%) which was used without further purification. The 2-chloroacetyl-4-iodobenzenamine (1.32 g, 4.5 mmol) was dissolved in DMF, and NaN_3 (1 g, 15 mmol) was added in one portion. The temperature of the solution was raised to 80 °C, and stirring was continued at 80 °C for 10 h. The reaction was cooled to room temperature, and solvent was then evaporated off. The residue was dissolved in $CHCl_3$, washed with water three times, and dried over $MgSO_4$. The crude product was purified by SiO_2

SCHEME 4. Shuttling Movment of the Macrocycle in R-2 and R-3 in Different Solvents



chromatography with CH_2Cl_2/*n*-hexane (2/1, v/v) to obtain pure 2-azido-acetyl-4-iodobenzenamine (1.2 g, 90% yield) as a white powder. ^{1}H NMR ($CDCl_3$) δ 8.00(s, 1H), 7.65(d, 2H, J = 8.5 Hz), 7.34(d, 2H, J = 8.5 Hz), 4.15(s, 2H). ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ 171.2, 143.1, 142.4, 126.7, 92.0, 56.9. MS (EI): 302 (M^+). Elemental Analysis for $C_8H_7IN_4O$: C, 31.81; H, 2.34; N, 18.55. Found: C, 31.87; H, 2.37; N, 18.41.

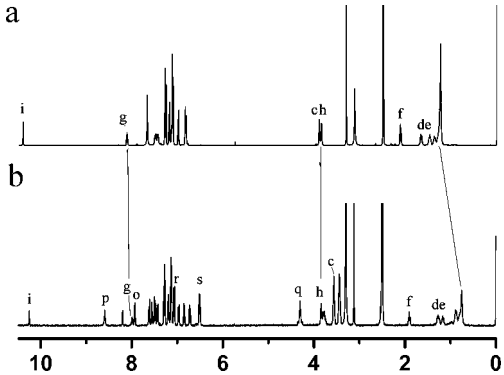


FIGURE 4. Partial ^{1}H NMR spectra (400 MHz, 1 × 10^{-3} M, DMSO-d_6) of **T-2** (a) and **R-2** (b).

2-Amino-*N*-(4-iodophenyl)acetamide (2). To a solution of 2-azido-acetyl-4-iodobenzenamine (1.0 g, 3.3 mmol) in tetrahydrofuran (60 mL) were added triphenylphosphine (2.6 g, 10 mmol) and water (3 mL). The reaction mixture was stirred at room temperature for 16 h, and solvent was then evaporated off. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/MeOH (50/1, v/v) to obtain pure 2-amino-*N*-(4-iodophenyl)acetamide (0.68 g, 75% yield) as white powder. Mp 155 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.46(s, 1H), 7.63(d, 2H, J = 8.55 Hz), 7.40(d, 2H, J = 8.55 Hz), 3.46(s, 2H). ^{13}C NMR (DMSO-d_6) δ 172. 8, 139.1, 137.8, 121.7, 86.9, 46.1. MS (EI): 275 (M^+). Elemental Analysis for $C_8H_9IN_2O$: C, 34.80; H, 3.29; N, 10.15. Found: C, 34.77; H, 3.23; N, 10.22.

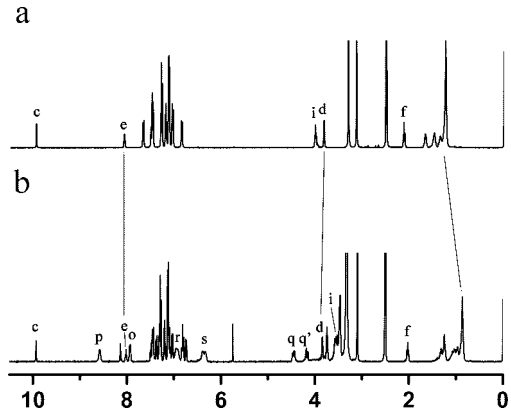


FIGURE 5. Partial ^{1}H NMR spectra (400 MHz, 1×10^{-3} M, DMSO-d_6) of **T-3** (a) and **R-3** (b).

***N*-(4-Iodophenyl)-2-(2-(4-tritylphenoxy)acetamido)acetamide (3).** To a stirred solution of compound **2** (600 mg, 2.19 mmol), **1** (866 mg, 2.2 mmol), and DMAP (305 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (200 mL) cooled on an ice bath was added EDCI·HCl (480 mg, 2.5 mmol). After 16 h the solution was washed with a saturated solution of citric acid (3 × 80 mL) and H_2O (3 × 50 mL), the organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate reduced in volume to obtain a white solid. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (100/1, v/v) to give **3** (1.11 g, 78%). Mp 253 °C. ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H), 7.60(d, 2H, J = 8.7 Hz), 7.4(s, 1H), 7.29(d, 2H, J = 8.7 Hz), 7.25−7.24(m, 5H), 7.20−7.16(m, 12H), 6.82(d, 2H, J = 8.9 Hz), 4.57(s, 2H), 4.169(d, 2H, J = 5.8 Hz). ^{13}C NMR (DMSO-d_6) δ 168.7, 168.1, 156.1, 147.1, 139.7, 139.2, 137.9, 132.1, 130.9, 128.2, 126.5, 121.9, 114.4, 87.3, 67.4, 64.4, 43.0. MS (TOF): 652 (M), 675 (M + Na). Elemental Analysis for $C_{35}H_{29}IN_2O_3$: C, 64.42; H, 4.48; N, 4.29. Found: C, 64.37; H, 4.41; N, 4.32.

T-0. To a stirred solution of 4-ethynyl-*N*,*N*-dimethylbenzenamine (224 mg, 1.55mol) and compound **3** (1.0 g, 1.53mmol) were added $PdCl_2(PPh_3)_2$ (10 mg) and CuI (10 mg) under nitrogen flow at room temperature. The reaction mixture was stirred for 2 h, and solvent was then evaporated off. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/MeOH (50/1, v/v) to obtain pure **T-0** (760 mg, 75% yield) as white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.27(s, 1H), 7.60(d, 1H, J = 8.5 Hz), 7.46−7.38(m, 5H), 7.25−7.23(m, 5H), 7.20−7.15(m, 12H), 6.82(dd, J = 8.9 and 2.58 Hz), 6.65(d, 2H, J = 8.9 Hz), 4.57(s, 2H), 4.19(t, 2H, J = 5.98 Hz), 2.99(s, 6H). ^{13}C NMR (DMSO-d_6) δ 168.6, 168.0, 156.1, 150.5, 147.1, 139.6, 139.1, 137.8, 132.7, 132.1, 130.9, 128.1, 126.4, 121.8, 119.5, 118.3, 114.3, 112.4, 109.2, 90.5, 87.6, 87.2, 67.3, 64.3, 42.9. MS (TOF): 669 (M), 692 (M + Na). Elemental Analysis for $C_{45}H_{39}N_3O_3$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.72; H, 5.91; N, 6.20.

T-1. Macrocycle **1** (270 mg, 0.5mmol) was added to a solution of **T-0** (334 mg, 0.5mmol) in CH_2Cl_2 (100 mL) at room temperature. The mixture was stirred under nitrogen flow for 30 min. Then, TCNQ (102 mg, 0.5mmol) was added, and the mixture was stirred for 12 h at 20 °C. The solvent was removed in vacuo, and the product was purified by SiO_2 chromatography with CH_2Cl_2/ MeOH (100/1, v/v) to obtain pure **T-1** (260 mg, 62% yield) and **R-1** (210 mg, 30%) as copper-like metallic solids. Mp 190 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.945(s, 1H), 7.645(s, 4H), 7.45(d, 2H, J = 9.5 Hz), 7.41(s, 1H), 7.27−7.20(m, 6H), 8.18−7.15(m, 14H), 6.94(d, 1H, J = 9.5 Hz), 6.84(d, 2H, J = 8.1 Hz), 6.81(d, 2H, J = 9.18 Hz), 4.56(s, 2H), 4.18(s, 2H), 3.14(s, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.3, 170.0, 167.1, 154.8, 154.1, 152.3, 151. 8, 146.7, 142. 7, 141.1, 135.6, 134.5, 132.6, 131.9, 131.3, 131.1, 130.1, 127.6, 126.1, 125.4, 125.0, 124.6, 119.9, 114.8, 114.7, 113.6, 113.5, 113.4, 113.1, 112. 6, 85.4, 72.0, 67.0, 64.3, 53.5, 44.6. 40.6. MS (TOF): 873 (M), 896 (M + Na). Elemental Analysis for $C_{57}H_{43}N_7O_3$: C, 78.33; H, 4.96; N, 11.22. Found: C, 78.41; H, 4.99; N, 11.16.

R-1. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.79(s, 1H), 8.31(s, 1H), 8.15(d, 2H, J = 7.7 Hz), 7.53(m, 4H), 7.47(m, 2H), 7.28(m, 3H), 7.25−7.24(m, 5H), 7.20−7.17(m, 10H), 7.14(d, 2H, J = 8.8 Hz), 7.10(d, 2H, J = 9.3 Hz), 7.05(s, 2H), 6.87(s, 2H), 6.72(d, 4H, J = 7.9 Hz), 6.61(d, 2H, J = 8.8 Hz), 6.40(d, 5H, J = 8.3 Hz), 4.35(d, 2H, J = 14.3 Hz), 4.20(d, 2H, J = 14.3 Hz), 4.08(s, 2H), 3.93(m, 2H), 3.87(m, 2H), 3.83−3.76(m, 6H), 3.73(m, 2H), 3.72(s, 4H), 3.17(d, 2H, J = 5.4 Hz), 3.06(s, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.4, 168.7, 168.3, 165.9, 157.6, 154.7, 154.2, 152.8, 152.1, 146.8, 142.9, 140.9, 134.5, 134.4, 134.3, 133.8, 132.5, 132.3, 131.9, 131.0, 129.9, 129.7, 129.3, 127.6, 126.0, 125.1, 123.4, 122.7, 119.5, 114.7, 113.9, 113.5, 112.7, 112.5, 112.4, 85.1, 77.3, 77.1, 76.9, 71.9, 70.6, 70.1, 69.9, 66.8, 66.7, 64.3, 53.5, 44.4, 40.3, 40.2. MS (TOF): 1431.5 (M + Na). Mp 210 °C. HRMS: 1408.6000 (M), 1431.5874 (M + Na).

Compound 4. To a stirred solution of compound **2** (630 mg, 2.3 mmol), 11-bromoundecanoic acid (610 mg, 2.3 mmol), and DMAP (305 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (200 mL) cooled on an ice bath was added EDCI·HCl (480 mg, 2.5 mmol). After 16 h the solution was washed with a saturated solution of citric acid (3 × 80 mL) and H_2O (3 × 50 mL), the organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was reduced in volume to obtain a white solid. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (100/1, v/v) to give compound **4** (920 g, 75%). Mp 146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 10.04(s, 1H), 8.11(t, 1H, J = 5.7 Hz), 7.64(d, 2H, J = 8.64 Hz), 7.43(d, 2H, J = 8.64 Hz), 3.85(d, 2H, J = 5.8 Hz), 3.51(t, 2H, J = 6.7 Hz), 2.14(t, 2H, J = 7.4 Hz), 1.78(m, 2H), 1.49(broad, 2H), 1.36(broad, 2H), 1.24(broad, 10H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.3, 168.7, 139.3, 137.9, 121.8, 87.1, 43.2, 35.7, 32.8, 29.6, 29.4, 29.3, 29.2, 29.0, 28.8, 28.6. EI-MS 536. Elemental Analysis for $C_{20}H_{30}BrIN_2O_2$: C, 44.71; H, 5.63; N, 5.21. Found: C, 44.77; H, 5.69; N, 5.31.

Compound 5. K_2CO_3 (1 g) was added to a DMF solution containing compound **4** (860 mg, 1.6mmol) and 4-tritylphenol (570 mg, 1.7 mmol) under nitrogen. The mixture was stirred at 80 °C for 10 h. The solvent was evaporated under vacuum and washed with water three times. The organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by column chromatography with CH_2Cl_2/CH_3OH (100/1, v/v). The white product was obtained with a yield of 89%. Mp 165 °C.^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.56(s, 1H), 7.57(d, 2H, J = 8.4 Hz), 7.35(d, 2H, J = 8.4 Hz), 7.19(broad, 15H), 7.08(d, 2H, J = 8.6 Hz), 6.96(s, 1H), 6.75(d, 2H, J = 8.7 Hz), 4.17(d, 2H, J = 4.12 Hz), 3.9(t, 2H, J = 6.4 Hz), 2.28(t, 2H, J = 7.3 Hz), 1.7(m, 2H), 1.63(m, 2H), 1.42(m, 2H), 1.27(broad, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.5, 167.4, 157.1, 147.1, 138.8, 137.8, 132.2, 131.2, 127.4, 125.8, 121.7, 113.3, 87.6, 67.9, 64.4, 53.5, 44.5, 36.3, 29.6, 29.4, 29.3, 26.2, 25.7. MS(MALDI-TOF) 801 (M + Na). Elemental Analysis for $C_{44}H_{47}IN_2O_3$: C, 67.86; H, 6.08; N, 3.60. Found C, 67.88; H, 6.09; N, 3.54.

Compound 6. To a stirred solution of 4-ethynyl-*N*,*N*-dimethylbenzenamine (220 mg, 1.5mol) and compound **5** (0.9 g, 1.15mmol) in THF/Et_3N (1/1, v/v) were added $PdCl_2(PPh_3)_2$ (20 mg) and CuI (20 mg) under a nitrogen flow at room temperature. The reaction mixture was stirred for 12 h, and solvent was then evaporated off. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/ MeOH (100/1, v/v) to obtain compound **6** (690 mg, 75% yield) as a white powder. The crude product was used for the next reaction directedly, because it was not stable enough for further purification.

Compound T-2 and R-2. Compounds **T-2** and **R-2** were synthesized from compunds **6**, TCNQ, and macrocycle with a similar method to the preparation of compounds **T-1** and **R-1**.

Compounds T-2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.6(S, 1H), 7.66(q, 4H, J = 5.4 Hz), 7.49(d, 1H, J = 8.6 Hz), 7.27−7.17(m, 16H), 7.08(d, 2H, J=8.8 Hz), 6.95(d, 1H, J = 8.4 Hz), 6.73(d, 2H, J = 8.8 Hz), 6.71(d, 2H, J = 9.1 Hz), 6.53(s, 1H), 4.13(d, 2H, J = 4.96), 3.90(t, 2H, 6.5 Hz), 3.11(s, 6H), 2.29(t, 2H, J = 7.59

Hz), 1.74(m, 2H), 1.65(m, 2H), 1.40(m, 2H), 1.28(broad, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 174.9, 171.5, 167.8, 157.2, 154.3, 152.9, 147.2, 143.1, 138.9, 134.6, 132.3, 131.8, 131.4, 131.2, 130.1, 127.5, 125.9, 125.4, 124.9, 124.0, 120.0, 114.9, 113.5, 113.3, 112.7, 85.4, 71.7, 67.9, 64.4, 45.1, 40.3, 36.5, 31.7, 29.6, 29.5, 29.3, 26.2, 25.7, 22.8. Mp 160 °C. MS (MALDI-TOF) 1022 (M + Na).Elemental Analysis for $C_{66}H_{61}N_7O_3$: C, 79.25; H, 6.15; N, 9.80. Found: C, 79.33; H, 6.19; N, 9.72.

Compounds R-2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.78(s, 1H), 8.37(s, 1H), 8.25(d, 2H, J = 7.73 Hz), 7.53(m, 5H), 7.29−7.17(m, 15H), 7.11(m, 5H), 6.75(m, 7H), 6.44(d, 4H, J = 8.3 Hz), 5.21(s, 1H), 4.48(d, 2H, J = 14.1 Hz), 4.16(d, 2H, J = 14.1 Hz), 3.94−3.90(m, 6H), 3.79−3.74(m, 12H), 3.13(s, 2H), 1.83(t, 2H, J = 7.6 Hz), 1.75(m, 2H), 1.42(m, 2H), 1.30−1.21(broad, 10H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ 173.4, 171.4, 169.5, 157.7, 157.2, 154.2, 152.7, 151.9, 147.2, 143.1, 138.8, 135.8, 134. 5, 134.4, 133.9, 132.4, 132.2, 131.9, 131.2, 131.1, 129.8, 129.5, 127.5, 125.9, 125.7, 125.3, 123.6, 123.1, 119.5, 114.7, 114.2, 113.5, 113.3, 112.7, 85.1, 72. 1, 70.7, 70.2, 70.1, 67.9, 66.9, 64.4, 44.4, 40.4, 36.2, 31.7, 29.6, 29.5, 29. 3, 26.2, 25.4, 22.7. MS (MALDI-TOF) 1533.5. Mp 185 °C. Elemental Analysis for $C_{96}H_{95}N_9O_{10}$: C, 75.12; H, 6.24; N, 8.21. Found: C, 75.20; H, 6.31; N, 8.11.

Compound 8. To a stirred solution of compound **7** (900 mg, 2.3 mmol), 11-bromoundecanoic acid (610 mg, 2.3 mmol), and DMAP (305 mg, 2.5 mmol) in anhydrous CH_2Cl_2 (200 mL) cooled on an ice bath was added EDCI·HCl (480 mg, 2.5 mmol). After 16 h the solution was washed with a saturated solution of citric acid (3 × 80 mL) and H_2O (3 × 50 mL), the organic layer was dried over anhydrous Na_2SO_4 and filtered, and the filtrate was reduced in volume to obtain a white solid. Purification was accomplished by column chromatography on silica with CH_2Cl_2/CH_3OH (100/1, v/v) to give compound **8** (1.14 g, 78%). Mp 107 °C. ^{1}H NMR ($CDCl_3$): δ 9.38(s, 1H), 7.47(d, 2H, J = 8.6 Hz), 7.23−7.13(broad, 17H), 6.99(s, 1H), 4.17(d, 2H, J = 4.72 Hz), 3.36(t, 2H, J = 6.85 Hz), 2.26(t, 2H, J = 7.5 Hz), 1.82(m, 2H), 1.64(m, 2H), 1.37(m, 2H), 1.22(broad, 10H). ^{13}C NMR ($CDCl_3$) δ 174.6, 167.6, 146.9, 143.0, 136.0, 131. 9, 131.3, 127.7, 126.2, 119.0, 64.8, 52.1, 44.7, 36.5, 34.2, 33.0, 29.5, 29.5, 29.4, 28.9, 28.4, 25.9. MS (TOF): 638 (M), 661 (M + Na). Elemental Analysis for $C_{38}H_{43}BrN_2O_2$: C, 71.35; H, 6.78; N, 4.38. Found C, 71.41; H, 6.81; N, 4.31.

Compound 9. K_2CO_3(450 mg, 3.2mmol) was added to a solution of 4-iodophenol (356 mg, 1.6mmol) and compound **8** (1 g, 1.5 mmol) in 30 mL of DMF. Then the mixture was stirred at 60 °C for 8 h, and the solvent was evaporated off. The residue was dissolved in $CHCl_3$, washed with water three times, and dried over Na_2SO_4. The crude product was purified by SiO_2 chromatography with CH_2Cl_2/MeOH (100/1, v/v) to obtain pure compound **9** (1 g, 86%) as a white solid. Mp 90 °C. ^{1}H NMR ($CDCl_3$) δ 9.26(s, 1H), 7.51(d, 2H, J = 8.51 Hz), 7.45(d, 2H, J = 8.41 Hz), 7.23−7.13(m, 17H), 6.87(s, 1H), 6.64(d, 2H, J = 8.57 Hz), 4.14(d, 2H, J = 4.59 Hz), 3.86(t, 2H, J = 6.6 Hz), 2.25(t, 2H, J = 7.81 Hz), 1.62(m, 4H), 1.39(m, 2H), 1.25(broad, 10H). ^{13}C NMR ($CDCl_3$) δ 174.5, 167.4, 159.2, 146.8, 142.9, 138.3, 135.8, 131.8, 131.2, 128.1, 126.0, 118.9, 117.1, 82.5, 68.2, 64.7, 44. 6, 36.4, 34.5, 29.8, 29.5, 29.4, 28.8, 28.7, 25.7. MS (TOF): 778 (M), 801 (M + Na). Elemental Analysis for $C_{44}H_{47}IN_2O_3$: C, 67.86; H, 6.08; N, 3.60. Found C, 67.88; H, 6.11; N, 3.55.

Compound 10. To a stirred solution of 4-ethynyl-*N*,*N*-dimethylbenzenamine (224 mg, 1.55mol) and compound **9** (0.8 g, 1.03mmol) were added $PdCl_2(PPh_3)_2$ (20 mg) and CuI (20 mg) under a nitrogen flow at room temperature. The reaction mixture was stirred for 12 h, and solvent was then evaporated off. The mixture was purified by SiO_2 chromatography with CH_2Cl_2/MeOH (100/1, v/v) to obtain pure compound **10** (600 mg, 75% yield) as a white powder. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.25(s, 1H), 7.47(d, 2H, J = 8.58 Hz), 7.40(q, 4H, J = 8.61 Hz), 7.25−7.18(m, 17H), 6.83(d, 2H, J = 8.61 Hz), 6.65(d, 2H, J = 8.73 Hz), 4.15(d, 2H, J = 4.81 Hz), 3.93(t, 2H, J = 6.45 Hz), 2.97(s, 6H), 2.27(t, 2H, J = 7.51 Hz), 1.75(m, 2H), 1.67(m, 4H), 1.42(m, 2H), 1.27(broad, 8H). ^{13}C NMR ($CDCl_3$) δ 174.6, 167.5, 158.9, 150.1, 146.9, 142.9, 136.0, 132.7, 131.9, 131.3, 130.2, 127.7, 126.1, 119.0, 116.3, 114.7, 112.1, 110.7, 89.2, 87.5, 68.2, 64.8, 44.7, 40.5, 36.5, 32.2, 29.9, 29.7, 29.7, 29.6, 29.5, 27.4, 26.2. MS (TOF): 795 (M), 818 (M+Na).

Compound T-3 and R-3. Compounds **T-3** and **R-3** were synthesized from compund **10**, TCNQ, and macrocycle with a similar method to the preparation of compounds **T-1** and **R-1**.

Compounds T-3. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53(s, 1H), 7.68(d, 2H, J = 8.76 Hz), 7.48(d, 1H, J = 8.5 Hz), 7.41(d, 2H, J = 8.48 Hz), 7.30−7.19(m, 15H), 6.92(m, 3H), 6.78(d, 2H, J = 8.8 Hz), 6.42(s, 1H), 4.08(d, 2H, J = 4.44 Hz), 3.98(t, 2H, J = 7.5 Hz), 3.12(s, 6H), 2.27(t, 2H, J = 7.4 Hz), 1.76(m, 2H), 1.63(m, 2H), 1.38(m, 2H), 1.26(broad, 10H). ^{13}C NMR ($CDCl_3$) δ 174.4, 171.5, 167.3, 163.9, 154.4, 153.0, 152.9, 146.8, 142.9, 135.7, 134.6, 132.4, 131.8, 131.4, 131.2, 127.6, 126.0, 125.2, 124.7, 123.9, 118.9, 115.7, 115.0, 114.9, 113.9, 113.0, 112.6, 83.4, 71.1, 68.8, 64.7, 44.5, 40.3, 36.4, 31.7, 29.5, 29.4, 29.3, 29.3, 29.3, 25.9, 25.7, 22.7. Mp 130 °C. MS (TOF): 1022 (M + Na). Elemental Analysis for $C_{66}H_{61}N_7O_3$: C, 79.25; H, 6.15; N, 9.80. Found: C, 79.29; H, 6.10; N, 9.51.

Compounds R-3. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.15(s, 1H), 8.47(s, 1H), 8.22(d, 2H, J = 7.7 Hz), 7.68(d, 2H, J = 8.92 Hz), 7.56(d, 1H, J = 8.0 Hz), 7.48(d, 1H, J = 8.6 Hz), 7.28−7.20(m, 15H), 7.13(m, 4H), 6.93(d, 2H, J = 8.68 Hz), 6.87(d, 4H, J = 8.24 Hz), 6.81(d, 1H, J = 8.0 Hz), 6.73(d, 2H, J = 8.8 Hz), 6.53(d, 4H, J = 8.28 Hz), 5.21(s, 1H), 4.57(d, 2H, J = 14.6 Hz), 4.26(d, 2H, J = 14.6 Hz), 3.99(t, 2H, J = 7.2 Hz), 3.91(m, 4H), 3.78(m, 4H), 3.71(m, 4H), 3.67(m, 4H), 3.12(s, 6H), 3.08(d, 2HHHH, J = 4.9 Hz), 1.78(m, 4H), 1.62(m, 2H), 1.28(m, 2H), 1.26(broad, 10H). ^{13}C NMR ($CDCl_3$) δ 172.8, 171.4, 168.3, 166.1, 163.9, 157.7, 154.3, 152.8, 152.7, 146.9, 142.7, 136.1, 135.8, 134.5, 133.8, 132.4, 131.9, 131.5, 131.3, 131.1, 129.9, 129.4, 129.3, 127.9, 127.7, 126.7, 126.1, 125.3, 124.8, 124.1, 123.2, 118.3, 115.7, 114.9, 114.8, 114.3, 83.4, 71.5, 70.7, 70.2, 70.1, 68.8, 66.8, 64.8, 53.5, 44.5, 41.9, 40.3, 36.2, 31.7, 29.5, 29.4, 29.3, 29.0, 25.9, 25.4, 22.7. Mp 151 °C. MS (TOF): 1556 (M + Na), 1572 (M + K). Elemental Analysis for $C_{96}H_{95}N_9O_{10}$: C, 75.12; H, 6.24; N, 8.21. Found C, 75.20; H, 6.19; N, 8.11.

Acknowledgment. This work was supported by the National Nature Science Foundation of China (20531060) and the National Basic Research 973 Program of China (2006CB932102, 2006CB806200 and 2007CB936401).

Supporting Information Available: Full experimental details pertaining to the preparation and characterization of all the compounds including the NMR and MS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO8014566