Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6022

www.rsc.org/obc

PAPER

Synthesis of a [2]rotaxane operated in basic environment†

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Received 9th May 2011, Accepted 6th June 2011
DOI: 10.1039/c1ob05726j

A tight [2]rotaxane with two chromophores as stoppers is described, in which the macrocycle is able to reversibly move by tuning of base. This moving process can result in intramolecular photo-induced electron transfer (PET), changing the photo-physical properties.

Introduction

During the past decade, scientists have developed new concepts and morphologies for synthesizing and characterizing many new supermolecular systems based on molecular machines. Rotaxanes have become typical candidates in the design of artificial molecular machines because some of their components are able to reversibly move between two or more stations on application of an external stimulus.[1] Various stimuli have been employed to induce such switching by illumination[2] and variation of the electrochemical potential,[3] solvent[4] and pH change.[5–7]

Synthetic rotaxanes are often used as analogues of natural systems, and such research has also led to the discovery of new applications of these systems, for example in ion and material transportation[8] or energy and electronic transfer that transform energy in both directions. The alteration of the relative positions of the interlocked components constitutes a basic kind of mechanical switch, which can vary the physical properties of the molecular rotaxane such as conductivity,[9] circular dichroism,[10] and fluorescence.[11] The use of fluorescent change as an output signal is preferable because it is easy to detect signals and is inexpensive. Recently, some rotaxanes that can switch between two or more fluorescent states (output) have been constructed.[12]

In the traditional rotaxanes, the stations were mostly linked by long alkyl chains, between which the macrocycle can reversibly move upon application of an external stimulus. The stations were far away from their adjacent stopper, and there was no steric hindrance between the macrocycle and the corresponding stopper when the macrocycle moved towards the station. Examples are the [2]rotaxanes driven by acid–base,[5] in which the macrocycle moved towards and resided around the other station when acid or base was added into the system. Normally, the acid–base driven [2]rotaxanes based on a crown–dialkylammonium interaction need to be protonated for the shuttling movement, that is, the [2]rotaxanes have to be in acidic and basic environment. However, [2]rotaxanes that work fully in a basic environment are rare.[13] Herein, we synthesized a tight [2]rotaxane with two stations linked by a short bridge, which is operated only in a basic environment and accompanied by fluorescent responses (Fig. 1).

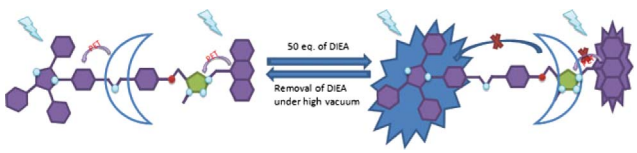

Fig. 1 Schematic of the DB24C8 movement and the fluorescent responses.

Results and discussion

The shuttle was synthesized according to Scheme 1. The already reported secondary dialkylammonium was chosen as the template moiety for the preparation of the [2]rotaxane **R-1-a**, and as one station for DB24C8 in the targeted molecular machine **R-2-a**. Another station, the cationic electron-poor aromatic ring *N*-methyltriazolium, was prepared by regioselective methylation of the [2]rotaxane **R-1-a**, which could interact with the DB24C8, either by π–π stacking with the electron-rich catechol ring, by ion–dipole interactions between the cationic charge and the oxygens of the macrocycle, or by hydrogen bonding between the vinylic hydrogen of the *N*-methyltriazolium and the oxygens of the macrocycle.[14]

The direct comparison of the ^{1}H NMR spectra (Fig. 2) of the thread **T-2-a**, the rotaxane **R-2-a** and the uncomplexed DB24C8 in CD_3CN readily confirms the interlocked nature of **R-2-a** and indicates the localization of the DB24C8. The ^{1}H NMR spectrum of the rotaxane **R-2-a** revealed well-resolved peaks (Fig. 2b), all of which could be assigned with the help of COSY-NMR spectroscopic measurements (Supporting Information Fig. S0†). The peaks arising from the -OCH_2CH_2O- repeating unit appear

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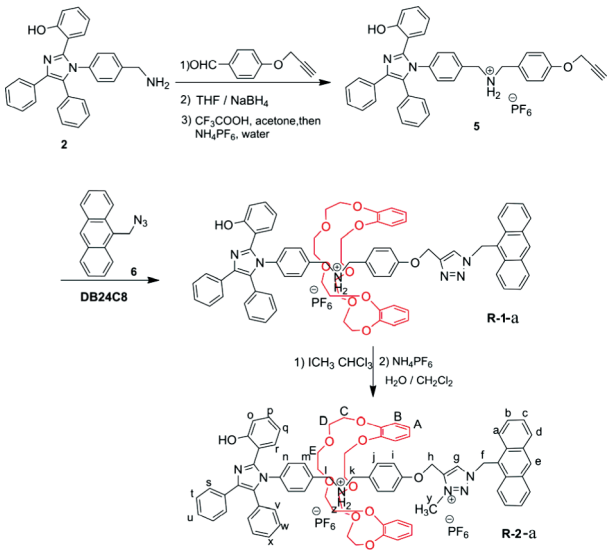
† Electronic supplementary information (ESI) available: Synthesis, 2D, NMR studies, UV/visible. See DOI: 10.1039/c1ob05726j



Scheme 1 Synthesis of **R-1-a** and **R-2-a**.

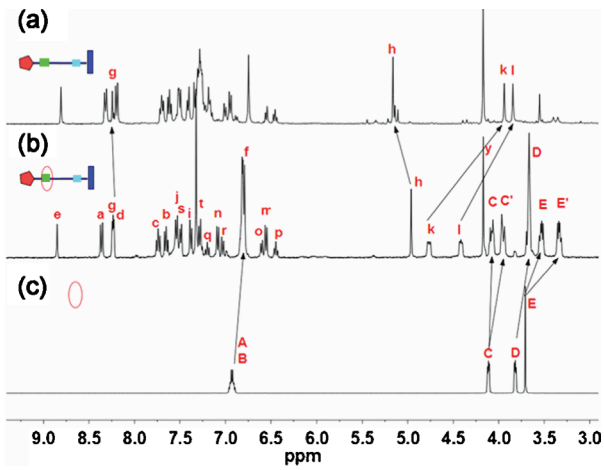
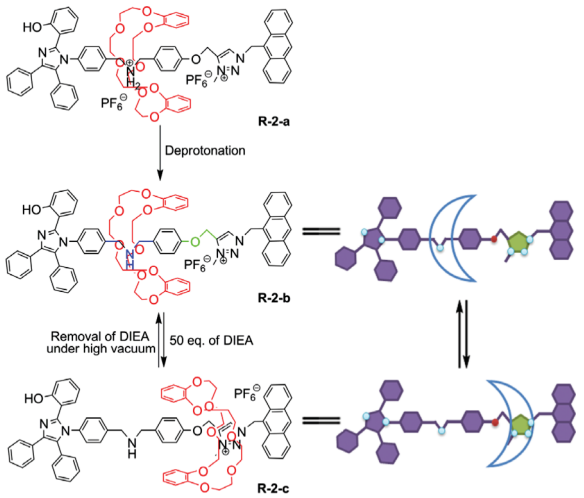


Fig. 2 ^{1}H NMR spectra (400 MHz, CD_3CN, 298 K) of a) **T-2-a**, b) **R-2-a**, and c) DB24C8. The letters corresponding to the protons are shown in Scheme 1.

in the region $\delta = 3.2$–4.2 ppm and are not individually resolved on account of the association of the DB24C8 ring with the -NH_2^+- center. In the rotaxane **R-2-a**, H_k and H_l adjacent to the -NH_2^+- center resonate (Fig. 2b) at $\delta = 4.77$ and 4.42 ppm (dramatically shifted downfield $\Delta\delta = 0.43$ and 0.22 ppm, respectively), and no significant variation in the chemical shift of H_g was noticed, indicating that the DB24C8 mainly resides around the ammonium station. In comparison with the free DB24C8, the signals of the oligo(ethylene glycol) moiety of the macrocycle experienced upfield shift due to a combination of C–H$\cdots$O and N^+–H$\cdots$O hydrogen bonds.[6] The chemical shifts of the complexed crown ether hydrogens H_C and H_E of the rotaxane **R-2-a** are split, indicating that they are facing the two non-symmetrical ends of the threaded.[15]

Actually, the DB24C8 may probably prefer to sit over the alkyl chain rather than over the sterically hindered spacer[14,15] and diisopropylethylamine (DIEA) is strong enough to deprotonate the NH_2^+ center.[16] The deprotonation of the [2]rotaxane **R-2-a** was carried out in acetone with a large excess of DIEA and purified



Scheme 2 Movement process of **R-2-b** under base-only stimulus.

through the method reported by Coutrot,[14] but the rotaxane **R-2-b** was obtained instead of **R-2-c** (Scheme 2), with the DB24C8 still sitting on the -NH- station (**R-2-b**), which is in contrast with the normal rotaxanes with these two stations.[6,14] This may be due to the greater flexibility of the -NH- moiety (blue, **R-2-b**) than the short bridge (green, **R-2-b**). However, when more DIEA was added to **R-2-b**, the DB24C8 could move towards the *N*-methyltriazolium station (**R-2-c**). This phenomenon was clearly observed from the ^{1}H NMR spectral titration of **R-2-b** (Fig. 3). When 1 equiv. of DIEA was add to the solution of **R-2-b**, the rotaxane partially adopted the **R-2-c** conformation and no evident change was found after 24 h standing; when more DIEA was continuously added, more rotaxane transformed from the **R-2-b** to **R-2-c** conformation. When 50 equiv. of DIEA was added, nearly all the rotaxane adopted the **R-2-c** conformation, which indicated that the DB24C8 had moved towards the *N*-methyltriazolium station almost quantitatively. This interpretation was supported by the following (from Fig. 3): 1) the peak for the *N*-methyltriazolium proton H_g is shifted downfield ($\Delta\delta = 1.04$ ppm) on association with the DB24C8 ring; 2) ^{1}H NMR signals for H_k and H_l are

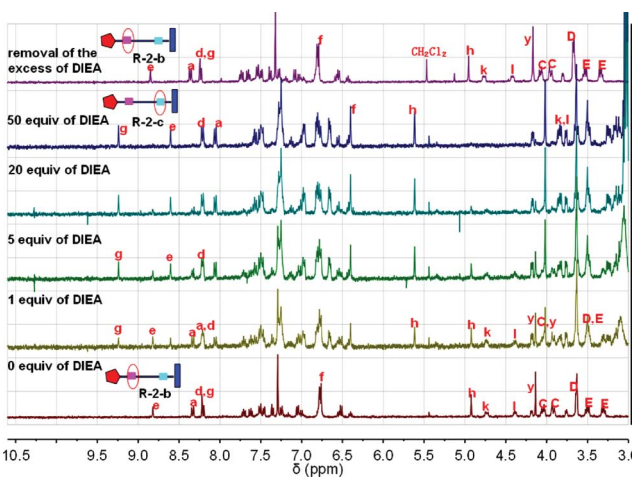


Fig. 3 ^{1}H NMR spectra of **R-2-b** (1.5 mM) in CD_3CN at 298 K upon titrational addition of DIEA.

shifted upfield ($\Delta\delta = 0.91$ and 0.53 ppm, respectively) as a result of both the deprotonation of the neighbouring ammonium and the shuttling of the macrocycle; 3) the signal for proton H_h is shifted downfield ($\Delta\delta = 0.7$ ppm) when the DB24C8 ring migrates to the *N*-methyltriazolium station, while H_f is shifted upfield ($\Delta\delta = 0.38$ ppm).

To our surprise, on removal of the excess of DIEA under vacuum, **R-2-b** is obtained which is shown in the middle part of Scheme 2, which may be due to the bulky anthracene stopper. The bulky anthracene substituent on the *N*-methyltriazolium enhanced the spatial limitation for the solvent to stabilize the *N*-methyltriazolium cations, so the disassociation of the *N*-methyltriazolium–PF_6 ion-pair was depressed,[17] and the macrocycle can not interact with the *N*-methyltriazolium in the ion-pair. With the addition of the strong Lewis base DIEA, which can solvate the cations,[18] the *N*-methyltriazolium–PF_6 ion-pair tended to dissociate to free ions, and the DB24C8 could interact with the *N*-methyltriazolium cation.

The absorption spectra of **T-1-a**, **R-1-a**, **T-2-a** and **R-2-a** showed superposition features of the hydroxylsubstituted tetraphenylimidazole (HPI) and anthracene moieties (Fig. 4a). After regioselective methylation of **T-1-a** and **R-1-a**, three absorption peaks arising from the anthracene unit experienced a red shift of 2 nm for **T-2-a** and **R-2-a** respectively, which can be ascribed to the interaction between the electron-deficient *N*-methyltriazolium station and the anthracene unit in the ground state. As shown in Fig. 4b, **T-1-a** exhibited an emission at 412 nm, while **R-1-a** exhibited a stronger emission around 413 nm. This enhancing effect can be attributed to the existence of DB24C8, which inhibited the aggregation of the rotaxane. The anthracene fluorescence of **R-2-a** was quenched completely due to the strong photo-induced electron transfer (PET) from anthracene to the *N*-methyltriazolium station, while **T-2-a** exhibited higher fluorescence emission because of the easier aggregation of the thread than the rotaxane.

Upon addition of 1 equivalent of DIEA to **R-2-b**, the emission of the anthracene moiety increased slightly; when an excess of base was added to it, the emission intensity was found to increase continuously (Fig. 5). The emission exhibited a linear growth with the increase of DIEA from 1 equiv. to 15 equiv. and tended to remain at equilibrium until 50 equiv. of DIEA was added (inset of Fig. 5). To the thread **T-2-b**, however, no evident fluorescence emission change was found with the addition of DIEA from 1 to 50 equiv (Fig. S4†). So, the fluorescence emission changes of **R-2-b** can be attributed to the movement of the DB24C8. When the DIEA was added to the **R-2-b**, the DB24C8 moved towards the *N*-methyltriazolium station, and the PET was restricted from anthracene to *N*-methyltriazolium because of the association between DB24C8 and *N*-methyltriazolium. After removal of the excess of DIEA under vacuum, the fluorescence intensity was recovered, indicating the DB24C8 was back to the -NH- station (Fig. S2†). A similar phenomenon can also be observed when the HPI unit was excited (Fig. S3†). The DB24C8 resides at the -NH- station and the HPI unit exhibited weak emission; this was due to the strong interaction between the HPI stopper and the DB24C8. With increasing DIEA, the DB24C8 moved towards the *N*-methyltriazolium station, the distance is longer between the HPI stopper and the DB24C8, leading to the interaction being weakened and the fluorescence emission of the HPI unit increased. All the observations in the fluorescence experiments were in accordance with the ^{1}H NMR spectra.

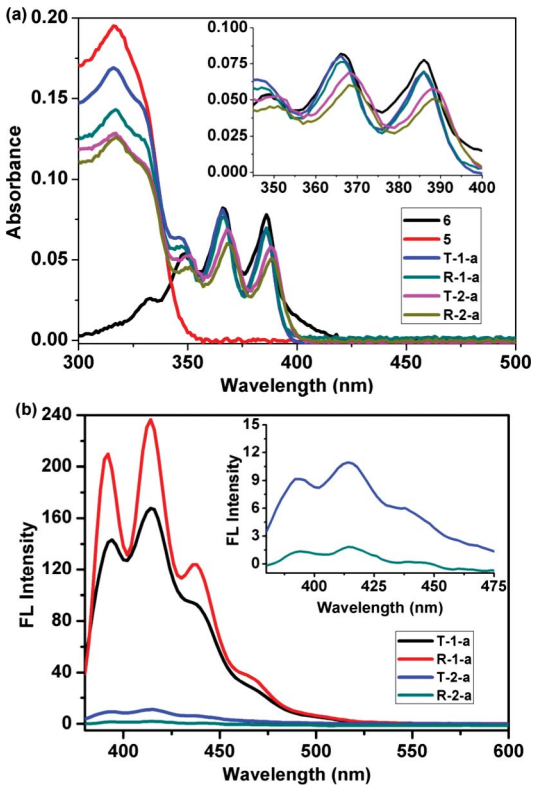


Fig. 4 Absorption and fluorencent specta of compound **T-1-a**, **T-2-a**, **R-1-a** and **R-2-a** (1×10^{-5} M, 298 K) in CH_3CN.

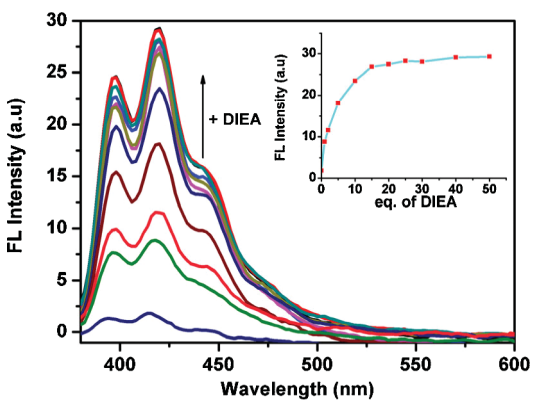


Fig. 5 Fluorescence spectra of **R-2-b** ($\lambda_{exc} = 370$ nm, 1×10^{-5} M) in CH_3CN with various equivalents of DIEA (0 to 50 equiv.).

Conclusion

In summary, we have presented a tight [2]rotaxane shuttling in a basic environment. The macrocycle could move towards the *N*-methyltriazolium station quantitatively in the presence of base, while the shuttling process can be inverted by removal of the base. The shuttling movement of the macrocycle was also accompanied by fluorescent responses, which can be used as a fluorescent switch in basic environments.

Experimental

Synthesis of compounds **5**, **R-1-a**, **R-2-a**, **R-2-b**

Compound **5**: A solution of the compound **2** (0.418 g, 1 mmol) and **3** (0.16 g, 1 mmol) in toluene (50 mL) was heated under reflux overnight by using a Dean–Stark apparatus. The solvent was removed under reduced pressure after the reaction was cooled to room temperature. The residue was dissolved in THF (50 mL), then $NaBH_4$ (0.4 g, 10.5 mmol) was added cautiously at 0 °C. The mixture was stirred at room temperature for a further 4 h. Water was added to quench the excess $NaBH_4$. The solvent was evaporated off, and the residue was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4. After concentrating *in vacuo*, the crude product compound **4** (300 mg, 0.53 mmol) was dissolved in acetone and a few drops of trifluoroacetic acid were added. After 0.5 h, the solvent was removed under vacuum. The residue was dissolved in a mixture of acetone and water. Then an aqueous solution of NH_4PF_6 (122 mg, 0.75 mmol) was added. The mixture was stirred for 1 h and then the acetone was evaporated off. The aqueous solution was extracted with CH_2Cl_2 several times. The collected organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo* to yield **5** as a yellow solid (600 mg, 85%). Mp = 115–116 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (m, 2 H), 7.46 (m, 2 H), 7.16–7.38 (m, 10 H), 6.95–6.99 (m, 4 H), 6.65 (m, 1 H), 6.45 (m, 1 H), 4.78 (s, 2 H), 3.81 (s, 2 H), 3.67 ppm (s, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 158.49, 157.03, 144.22, 136.5, 132.89, 132.22, 131.96, 131.62, 131.19, 130.69, 129.69, 128.75, 127.56, 122.7, 119.22, 117.89, 115.47, 114.98, 111.17, 78.06, 76.15, 55.77 ppm; MS (MALDI-TOF): *m/z* 562.3; elemental analysis (%) calcd for $C_{38}H_{31}N_3O_2$: C 81.26, H 5.56, N 7.48; found: C 81.59, H 5.53, N 7.51.

Rotaxane **R-1-a**: A mixture of compound **5** (354 mg, 0.50 mmol), compound **6** (117 mg, 0.50 mmol), macrocycle DB24C8 (211 mg, 0.48 mmol), and $[Cu(MeCN)_4]PF_6$ (175 mg, 0.47 mmol) was stirred in dry CH_2Cl_2 at room temperature under nitrogen for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO_2: CH_2Cl_2/MeOH 60 : 1) to afford rotaxane **R-1-a** (845 mg, 68%). Mp = 139–140 °C. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.56 (s, 1 H), 8.36 (m, 2 H), 8.06 (m, 2 H), 7.52 (m, 2 H), 7.19–7.46 (m, 17 H), 7.15 (m, 1 H), 7.01 (m, 1 H), 6.98 (m, 2 H), 6.88 (m, 4 H), 6.72 (m, 4 H), 6.68 (m, 2 H), 6.42 (m, 1 H), 6.27 (m, 1 H), 4.92 (s, 2 H), 4.61 (s, 2 H), 4.20 (s, 2 H), 4.08 (m, 4 H), 3.99 (m, 4 H), 3.59 (m, 8 H), 3.33 (m, 4 H), 3.28 ppm (m, 4 H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K) δ = 160.22, 159.75, 150.04, 148.83, 146.26, 144.78, 138.93, 136.22, 135.87, 134.58, 133.23, 132.94, 132.61, 132.5, 132.13, 131.85, 131.72, 131.35, 131.02, 130.81, 130.64, 130.43, 130.19, 129.92, 128.91, 127.82, 127.44, 126.96, 126.61, 124.94, 124.87, 124.75, 122.83, 116.56, 115.78, 114.43, 114.12, 71.94, 71.39, 69.46, 62.51, 53.67, 52.59, 47.49 ppm; MS (MALDI-TOF): *m/z*: 1243.5 $[M]^+$, 1275.5 $[M+O_2]^+$; elemental analysis (%) calcd for $C_{77}H_{75}N_6F_6O_{10}P$: C 66.56, H 5.44, N 6.05; found: C 66.78, H 5.42, N 6.09.

Rotaxane **R-2-a**: Rotaxane **R-1-a** (100 mg, 0.08 mmol) was dissolved in iodomethane (2 mL) and the mixture was stirred for 24 h at 40 °C. Then iodomethane was evaporated and the solid was washed with Et_2O to give an orange solid. Then, to a suspension of the previous solid in H_2O (10 mL) were added NH_4PF_6 (16.3 mg, 0.1 mmol) and CH_2Cl_2 (15 mL). Then the resulted bilayer solution was vigorously stirred for 1h. After separation, the aqueous layer was extracted with CH_2Cl_2 (×3). The organic layers were combined, dried over Na_2SO_4, and concentrated to obtain quantitatively the rotaxane **R-2-a** (123 mg) as a yellow solid. Mp = 128–129 °C. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.85 (s, 1 H), 8.36 (d, 2 H, *J* = 9.14 Hz), 8.24 (m, 3 H), 7.74 (t, 2 H, *J* = 6.81, 7.62 Hz), 7.65 (t, 2 H, *J* = 7.84, 6.81 Hz), 7.52–7.55 (m, 4 H), 7.49 (m, 2 H), 7.38 (d, 1 H, *J* = 8.33 Hz), 7.27–7.32 (m, 7 H), 7.19 (m, 1 H), 7.09 (d, 2 H, *J* = 8.65 Hz), 7.03 (m, 1 H), 6.78–6.84 (m, 10 H), 6.57 (m, 1 H), 6.54 (d, 2 H, *J* = 8.62 Hz), 6.44 (m, 1 H), 4.95 (s, 2 H), 4.75 (m, 2 H), 4.42 (m, 2 H), 4.16 (s, 3 H), 4.05–4.09 (m, 4 H), 3.93–3.96 (m 4 H), 3.65–3.68 (m, 8 H), 3.51–3.55 (m, 4 H), 3.31–3.35 ppm (m, 4 H); ^{13}C NMR (CD_3CN, 100 MHz, 298 K) δ = 159.20, 158.30, 149.52, 148.28, 148.15, 145.67, 140.53, 139.54, 132.64, 132.36, 132.18, 132.15, 131.21, 130.49, 130.17, 129.97, 129.58, 129.35, 129.07, 127.20, 126.68, 115.44, 115.25, 113.83, 113.63, 71.46, 71.29, 70.92, 70.74, 69.85, 69.52, 68.88, 58.77, 52.96, 52.19, 50.98, 39.60 ppm; MS (MALDI–TOF): *m/z*: 1257.6 $[M - H]^+$; elemental analysis (%) calcd for $C_{78}H_{78}N_6F_{12}O_{10}P_2$: C 60.46, H 5.07, N 5.42; found: C 60.69, H 5.04, N 5.44.

Rotaxane **R-2-b**: To a solution of the rotaxane **R-2-a** (1 equiv) in acetone was added a large excess of DIEA (100 equiv) and the mixture was stirred for 1 h. After evaporation, and in order to remove the diisopropylethylammonium hexafluorophosphate, the crude mixture was diluted with CH_2Cl_2 and water was added. The aqueous layer was extracted with CH_2Cl_2 (×3) then the organic layers were combined, dried over Na_2SO_4 and concentrated. Et_2O was added to dissolve the excess of DIEA then removed to obtain the rotaxane **R-2-b**. ^{1}H NMR (CD_3CN, 400 MHz, 298 K): δ = 8.85 (s, 1 H), 8.36 (d, 2 H, *J* = 9.0 Hz), 8.23 (m, 3 H), 7.74 (t, 2 H, *J* = 6.64, 8.88 Hz), 7.65 (t, 2 H, *J* = 8.0, 7.0 Hz), 7.52–7.55 (m, 3 H), 7.49 (m, 2 H), 7.38 (m, 2 H), 7.27–7.32 (m, 7 H), 7.19 (m, 1 H), 7.08 (d, 2 H, *J* = 8.4 Hz), 7.03 (m, 1 H), 6.78–6.84 (m, 10 H), 6.59 (m, 1 H), 6.55 (d, 2 H, *J* = 8.4 Hz), 6.44 (m, 1 H), 4.96 (s, 2 H), 4.77 (m, 2 H), 4.42 (m, 2 H), 4.17 (s, 3 H), 4.06–4.09 (m, 4 H), 3.93–3.97 (m 4 H), 3.65-3.68 (m, 8 H), 3.51–3.54 (m, 4 H), 3.33–3.36 ppm (m, 4 H).

Acknowledgements

We are grateful for financial support from the National Natural Science Foundation of China (21031006, 20831160507, 20721061, 20971127), NSFC-DFG joint fund (TRR 61) and the National Basic Research 973 Program of China.

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