CHEMISTRY
AN ASIAN JOURNAL
ACES
FULL PAPER

DOI: 10.1002/asia.201402789

Efficient Intramolecular Energy Transfer between Two Fluorophores in a Bis-Branched [3]Rotaxane

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Abstract: A bis-branched [3]rotaxane, with two [2]rotaxane arms separated by an oligo(*para*-phenylenevinylene) (OPV) fluorophore, was designed and investigated. Each [2]rotaxane arm employed a difluoroboradiaza-*s*-indacene (BODIPY) dye-functionalized dibenzo[24]crown-8 macrocycle interlocked onto a dibenzylammonium in the rod part. The chemical structure of the [3]rotaxane was confirmed and characterized by ^{1}H and ^{13}C NMR spectroscopy and high-resolution ESI mass spectrometry. The photophysical properties of [3]rotaxane and its reference systems were investigated through UV/Vis absorption, fluorescence, and time-resolved fluorescence spectroscopy. An efficient energy-transfer process in [3]rotaxane occurred from the OPV donor to the BODIPY acceptor because of the large overlap between the absorption spectrum of the BODIPY moiety and the emission spectrum of the OPV fluorophore; this shows the important potential of this system for designing functional molecular systems.

Keywords: click chemistry · energy transfer · fluorophores · FRET · rotaxanes

Introduction

The photosynthetic proteins are efficiently produced through natural light-harvesting systems that convert solar energy into chemical energy.[1] In these systems, excitation energy transfer (ET), which attracts much attention from biologists and chemists, is an essential process.[1d,2] Recently, several light-harvesting systems, mainly those using shape-persistent π-conjugated dendrimers and well-defined tree-like macromolecules, have been developed to imitate natural photosynthetic systems.[3] In these light-harvesting systems, the donor and acceptor moieties are usually connected in close proximity by covalent bonds;[1b,4] however, noncovalent interactions exhibit the advantages of more versatility and tenability[5] in comparison with covalent bonds, as occurs in naturally occurring light-harvesting systems.

On the other hand, mechanically interlocked molecules (MIMs) have been extensively studied with the development of supramolecular chemistry owing to their excellent functional properties and potential applications in molecular switches and molecular machinery.[6,7] Meanwhile, MIMs can easily achieve specific functions by introducing active units on the axle or ring components.[8] Moreover, the components in MIMs can be located at an appropriate distance, which is ideal for controlling intercomponent interactions, such as ET processes between donor and acceptor units, so MIMs should be good candidates for the construction of novel light-harvesting systems.[9] At present, light-harvesting systems in which efficient and unidirectional ET processes occur from the outer chromophores to the core chromophores are mainly dendrimers.[3] Thus, designing similar intramolecular ET molecular systems in MIMs has attracted our interest.

Herein, we report a bis-branched [3]rotaxane that contains two chromophoric units, namely, an oligo(*para*-phenylenevinylene) (OPV) in the middle of the axis unit and two difluoroboradiaza-*s*-indacene (BODIPY) dyes in two dibenzo[24]crown-8 (DB24C8) rings, and possesses efficient ET processes from the central OPV chromophore to the outer BODIPY chromophores. As shown in Scheme 1, [3]rotaxane **1** has a symmetrical structure that contains two mechanically interlocked [2]rotaxane arms, each of which employs BODIPY-functionalized DB24C8 as a macrocycle and two distinguishable stations, namely, dibenzylammonium (DBA)[10] and a *N*-methyltriazolium (MTA)[11] recognition stations, for the DB24C8 ring in the molecular thread component. An OPV derivative as a donor fluorophore was introduced as a bridge to separate the two [2]rotaxane arms in the middle part of the thread because of its tunable photophysical properties in the UV/Vis spectral region, as well as its stability and relatively high fluorescence quantum yield.[12] Meanwhile, a BODIPY fluorophore was introduced into each of the two DB24C8 macrocycles as an acceptor, not only owing to its relatively high fluorescence quantum yield, high photostability, and high chemostability, but also owing to its strong UV/Vis absorption with a high molar extinction coefficient.[13] Furthermore, owing to the large overlap between the absorption spectrum of the BODIPY moiety and the emission spectrum of the OPV axis, efficient

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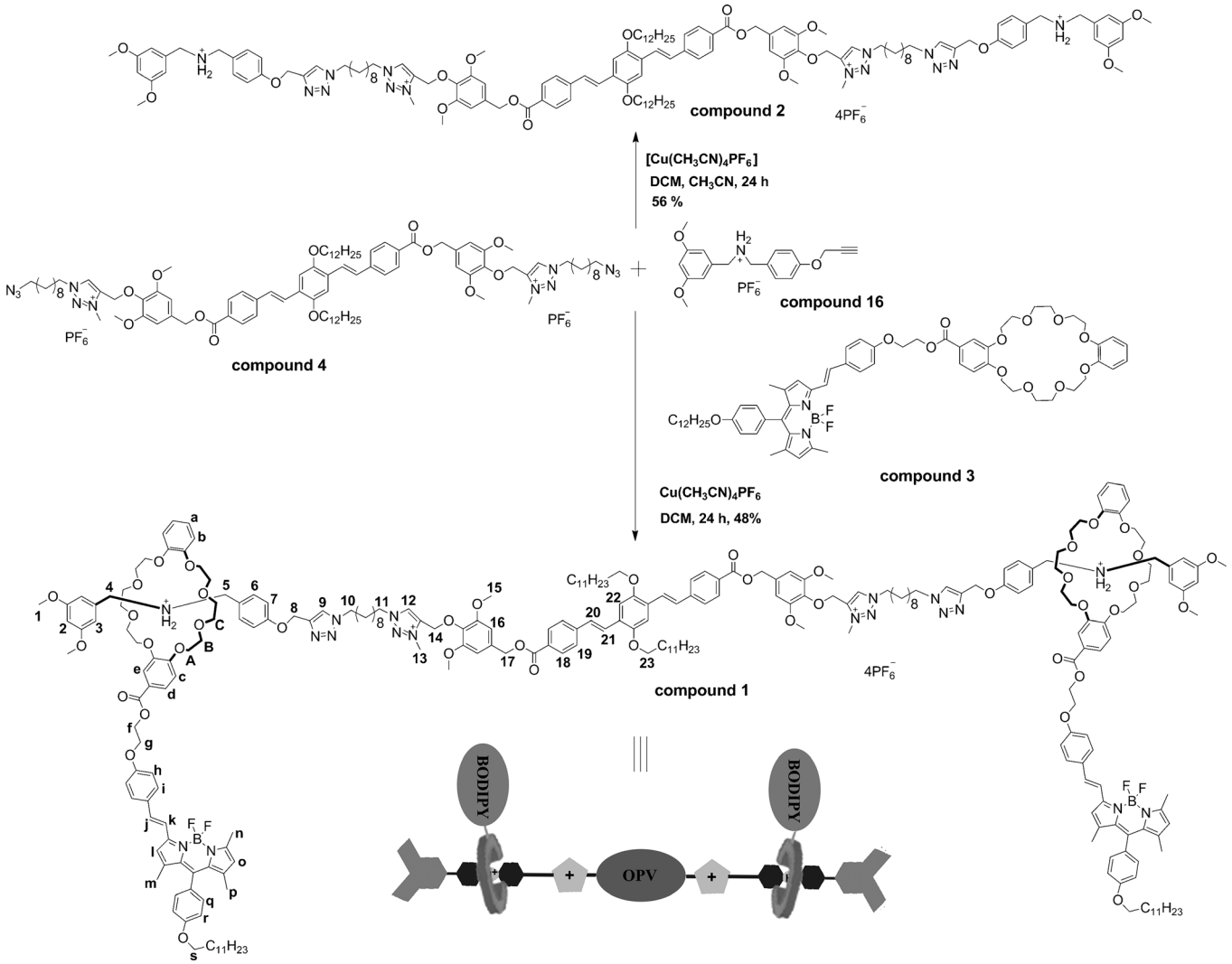
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201402789.



Scheme 1. The synthetic procedure for the preparation of [3]rotaxane **1**, dumbbell compound **2**, and key intermediate compounds **3** and **4**. DCM = dichloromethane.

ET from the OPV fluorophore on the axle to the BODIPY fluorophore on the DB24C8 macrocycle occurred. In addition, the BODIPY-functionalized DB24C8 macrocycle in the [3]rotaxane can also reversibly shuttle between two distinguishable recognition sites in response to external acid–base stimuli. This can pave the way for the design and construction of functional molecular systems based on MIMs.

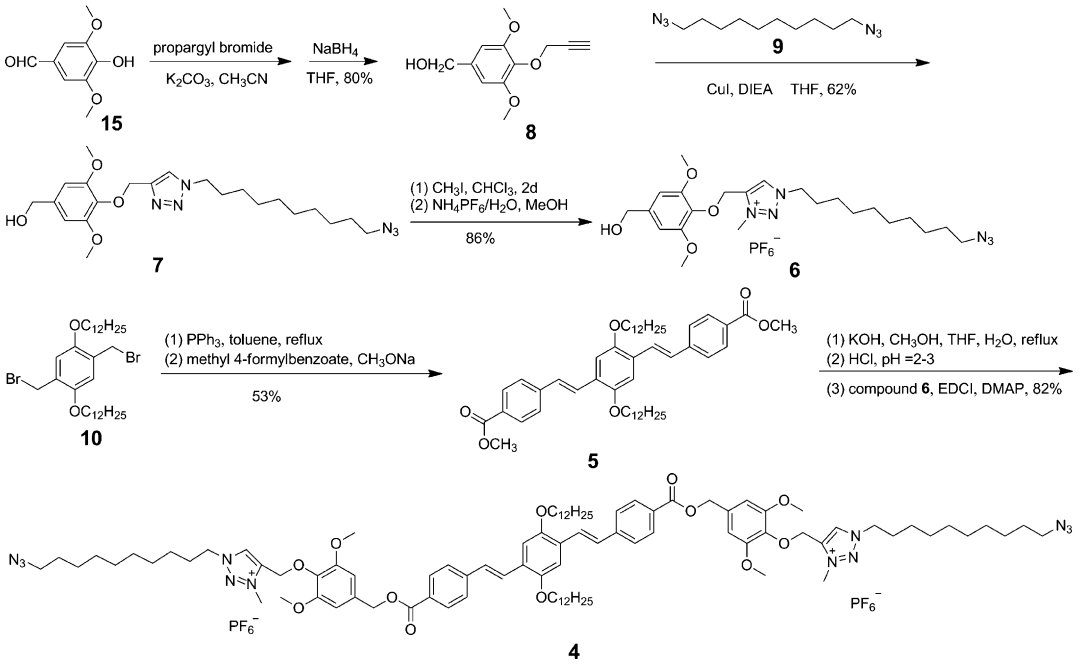
Results and Discussion

Synthesis and Characterization

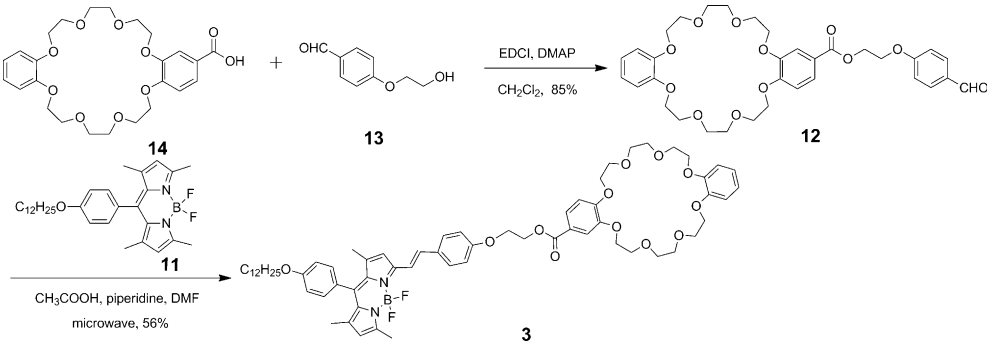
The syntheses, chemical structures, model diagrams of [3]rotaxane **1**, dumbbell compound **2**, and intermediate compounds **3** and **4** are shown in Scheme 1.

The synthetic approach to one key intermediate, compound **4**, which contains an OPV core is shown in Scheme 2. Starting from syringaldehyde (**15**), Williamson etherification with propargyl bromide and subsequent reduction with $NaBH_4$ resulted in the formation of **8** in 80% yield over two steps. The copper-catalyzed click reaction[11c,14] between **8** and **9** in the presence of CuI and DIEA gave **7** in 62% yield. Subsequent methylation of the 1,2,3,-triazole unit in **7**, followed by anion exchange with a saturated solution of NH_4PF_6 in MeOH afforded **6** in 86% yield. To obtain OPV derivative **5**, compound **10** was heated at reflux in toluene for 6 h in the presence of PPh_3, followed by a Witting reaction with methyl 4-formylbenzoate in methanol to give compound **5** in moderate yield (53%). Compound **5** was hydrolyzed with KOH, acidified with hydrochloric acid, and, following esterification with **6** in the presence of EDCI and DMAP, produced key intermediate **4** in 82% yield.

BODIPY-functionalized DB24C8 macrocycle **3** was also prepared, as shown in Scheme 3. The etherification reaction between **13** and **14** in the presence of EDCI and DMAP in dry CH_2Cl_2 resulted in the formation of **12** in 85% yield. The Knoevenagel reaction of **12** with BODIPY derivative **11** under microwave conditions generated **3** in moderate



Scheme 2. Synthetic procedure for the preparation of key intermediate **4**. THF = tetrahydrofuran, DIEA = *N*,*N*-diisopropylethylamine, EDCI = 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, DMAP = 4-dimethylamiopryidine.



Scheme 3. Synthetic procedure for the preparation of key intermediate **3**. DMF = *N*,*N*-dimethylformamide.

yield (56%; Scheme 3).The other intermediate compounds, **9**, **10**, **11**, **13**, **14**, and **16**, were synthesized according to previous reports.[14b,15] As shown in Scheme 1, a mixture of **16** and **3** can form a predominantly [2]pseudorotaxane in CH_2Cl_2, then the click reaction with key intermediate **4** in the presence of $[Cu(CH_3CN)_4]PF_6$ as a catalyst can give the target compound [3] rotaxane **1** in 48% yield. Without the presence of **3**, the click reaction between **16** and **4** in the presence of $[Cu(CH_3CN)_4]PF_6$ results in dumbbell compound **2** in moderate yield (56%). The target [3] rotaxane **1**, dumbbell compound **2**, and intermediate compounds **3** and **4** were all characterized by ^1H and ^{13}C NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry. The reversible acid–base-driven mechanical movement of **1** was also investigated by ^1H NMR spectroscopy.

The ^1H NMR spectrum of **1** in $CDCl_3$ is shown in Figure 1. We analyzed the ^1H NMR spectrum of **1** in comparison with our previously reported rotaxanes,[14b,c,15a,16] and found that the BODIPY-functionalized DB24C8 macrocycles predominately resided on the DBA recognition sites in **1**. The chemical shifts at $\delta = 8.34$, 8.05, and 7.12 ppm indicated the existence of the OPV moiety in **1**. Meanwhile, the signals at $\delta = 6.00$, 6.59, and 2.57 ppm demonstrated the existence of the BODIPY fluorophore. The protons on the crown ether with chemical shifts from $\delta = 3.3$ to 4.5 ppm were separated into three groups, which indicated that BODIPY-functionalized DB24C8 interlocked onto the axis. Moreover, the chemical shift of the protons on the triazole rings at $\delta = 7.86$ ppm indicated the success of the click reaction. The chemical structure of **1** was also confirmed by HR-ESI mass spectrometry. The mass spectrum of **1** possesses a major peak at m/z 1128.1349, which corresponds to species that have lost four PF_6^- counterions, that is, $[M-4PF_6]^{4+}$.

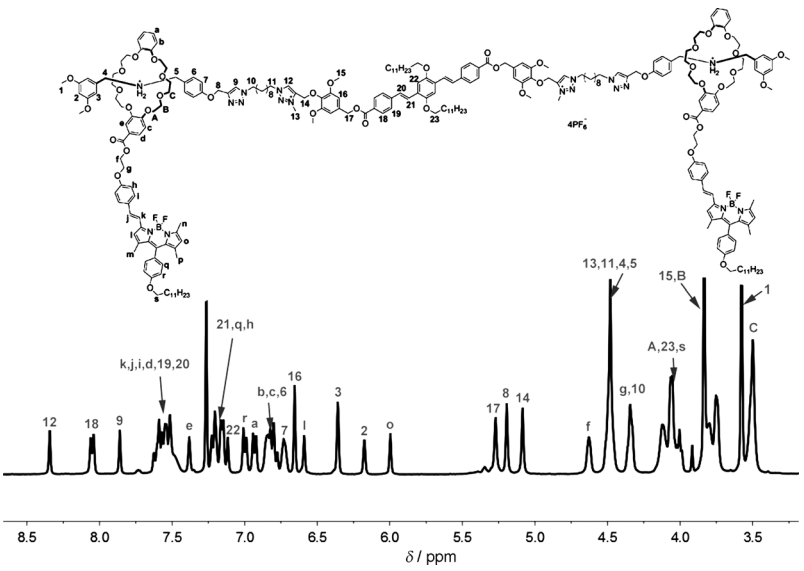


Figure 1. Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of [3]rotaxane **1**.

Photophysical Properties of [3]Rotaxane 1

Next, we focused on the photophysical properties of **1** and reference compounds **2** and **3**. First, the absorption spectra of these three compounds were investigated in CH_2Cl_2. As shown in Figure 2, compound **2** exhibited two absorption

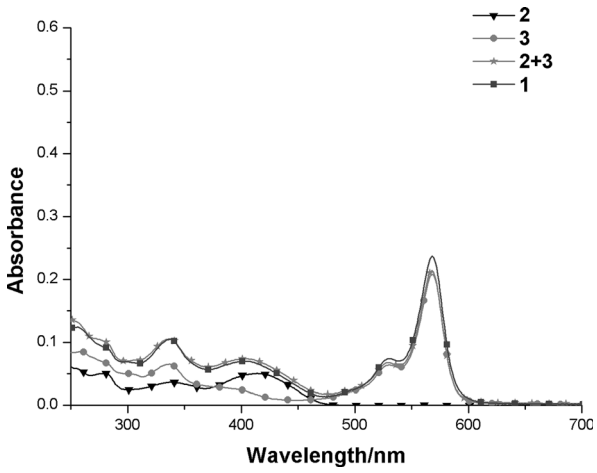


Figure 2. The absorption spectra of [3]rotaxane **1** (1×10^{-6} M), compound **2** (1×10^{-6} M), compound **3** (2×10^{-6} M) and system **M** (a mixture of **2** and **3** in a molar ratio of 1:2).

bands with λ_{max} at 340 and 415 nm, which were characteristic of OPV chromophore, and macrocycle **3** also exhibited two absorption bands of BODIPY derivatives with λ_{max} at 531 and 569 nm and a large molar extinction coefficient. At the same time, the absorption spectrum of a reference system **M** (a mixture of compounds **2** and **3** with a molar ratio of 1:2) was measured, and it was found that the absorption spectrum of system **M** was almost the same as that of [3]rotaxane **1**, which could be constructed by the addition of the absorption spectra of **2** and **3**. From this phenomenon, we can infer that there are no ground-state interactions for either system **M** or [3]rotaxane **1**.

Meanwhile, the emission spectra of **1**, **2**, **3**, and as system **M** in CH_2Cl_2 at room temperature were also investigated. As shown in Figure 3, the fluorescence spectra of **2** and **3** showed emission peaks at $\lambda_{max}=485$ nm and $\lambda_{max}=585$ nm, respectively, when excited at $\lambda=415$ nm. Notably, there is a large overlap between the absorption spectrum of **3** and the emission spectrum of **2** (Figure 4); this is ideal for

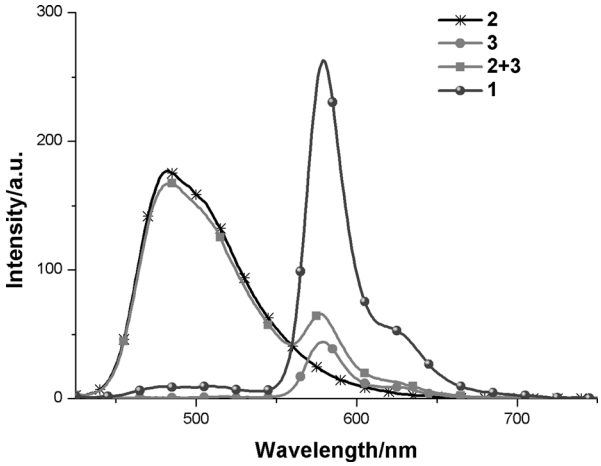


Figure 3. The emission spectra of [3]rotaxane **1** (1×10^{-6} M), compound **2** (1×10^{-6} M), compound **3** (2×10^{-6} M), and system **M** (a mixture of **2** and **3** in a molar ratio of 1:2). The excitation wavelength of the fluorescent spectra is the absorption maximum of **2** at $\lambda=415$ nm.

fluorescence resonance energy transfer (FRET) through interactions between transition dipoles.[9b,17]

Moreover, the emission spectrum of system **M** was almost the weighted addition of the emission spectra of compounds **2** and **3**, when excited at the absorption maximum of OPV at $\lambda=415$ nm. Therefore, in the simple mixed system **M**, the two fluorophores **2** and **3** acted independently as noninteracting chromophores in a simple mixture of **2** and **3**.[9b,18] However, a remarkable change was observed in the emission spectrum of **1**, compared with that of system **M**: the emission intensity of **1** at $\lambda_{max}=585$ nm became stronger than that of **3**, whereas the characteristic emission peak of the OPV moiety with λ_{max} at $\lambda=485$ nm almost disappeared. Meanwhile, the emission spectrum of **1** was still strong upon excitation at $\lambda=450$ nm, at which wavelength the absorb-

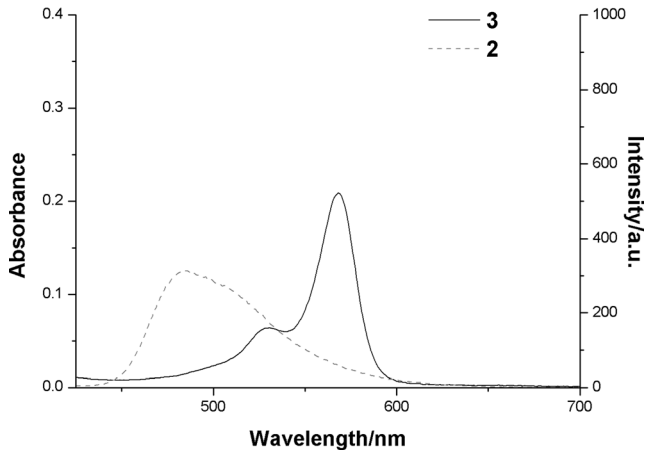


Figure 4. The UV/Vis absorption spectrum of **3** (2×10^{-6} M) and the emission spectrum of **2** (1×10^{-6} M) in CH_2Cl_2.

ance of BODIPY was negligible (Figure S1 in the Supporting Information). From these phenomena, we can speculate that in **1** there is an efficient FRET process ($E=95.5\%$; see the Supporting Information) from the OPV moiety to the BODIPY fluorophores because of the suitable distance between the donor and acceptor in **1**.

To further investigate the FRET process in **1**, the time-resolved fluorescence of **1**, reference compounds **2** and **3**, and system **M** were also measured. As shown in Table 1, when monitored at $\lambda=585$ nm, the time-resolved fluorescence of **M** showed a single exponential decay with a lifetime of 3.40 ns (Figure S2 in the Supporting Information); this was consistent with the lifetime of **3** (Figure S3 in the Supporting Information), and characteristic of BODIPY derivatives.[19] However, a biexponential decay of mixture **M** with lifetimes of 1.33 (42.1) and 3.31 ns (57.9%) were observed (Figure S4 in the Supporting Information) when monitored at $\lambda=$ 558 nm; this phenomenon can be explained in that the lifetime of 1.33 ns should be the intrinsic lifetime of compound **2**, for which a single exponential decay with a lifetime of 1.59 ns was detected (Figure S5 in the Supporting Information) that was consistent with the OPV derivatives.[12c,20] The longer lifetime (3.31 ns) should be the intrinsic lifetime of **3**. Furthermore, the proportion of the two lifetimes of the two fluorophores in mixture **M** was very similar, which was consistent with our previous deduction that the two fluorophores in mixture **M** were independent in solution. However, a single exponential decay with the lifetime of **1** was obtained when monitored at $\lambda=558$ or 585 nm (Figures S6 and S7 in the Supporting Information), which was similar to the lifetime of **3**. In addition, the contribution from OPV moiety, which could be observed clearly in the mixture, disappeared entirely. This phenomenon indicated that, before the excited states of OPV underwent radiative decay, another faster process occurred in **1**, for instance, a FRET process to the ring. Because the FRET process was much faster than the lifetimes of these two fluorophores, a single exponential decay lifetime was obtained for **1**, rather than the biexponential decay found in many simple kinetic models.[9b,21]

Shuttling Movement of [3]Rotaxane 1

At present, a number of FRET rotaxanes have been researched,[9b,18b,22] but using a molecular shuttle to modulate the FRET effect is still very rare and this attracted our interest. First, we investigated the reversible acid–base-driven mechanical motions of BODIPY-functionalized DB24C8 macrocycles between two kinds of distinguishable recognition sites of **1** by ^{1}H NMR spectroscopy. After the addition of 2.4 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to the solution of **1** in $CDCl_3$, remarkable changes to the ^{1}H NMR spectrum (Figure 5b) were observed compared with the original spectrum (Figure 5a). The chemical shift of protons H_4 and H_5 close to the DBA station moved upfield by 0.98 ppm. At the same time, the chemical shift of protons H_{11}, H_{12}, H_{13}, and H_{14} adjacent to the MTA recognition site also shifted by 0.45, 0.88, −0.27, and −0.15 ppm, respectively. These above-mentioned changes revealed that the ammonium recognition sites were deprotonated to generate free secondary amines successfully and DB24C8 macrocycles subsequently shuttled toward the secondary MTA stations. Meanwhile, the ammonium recognition sites could be regenerated after introducing 5.0 equivalents of CF_3COOH; the ^{1}H NMR spectrum was completely recovered (Figure 5c).

With the introduction of secondary MTA stations, the BODIPY-functionalized DB24C8 macrocycle can shuttle toward the secondary MTA stations after the addition of DBU; this is expected to alter the distance between two fluorophores, and, as a result, change the efficiency of the FRET process. Molecular dynamics (MD) simulations were performed to determine the distance between the two fluorophores in the two states. As shown in Figure S8 in the Supporting Information, the average distance between the OPV and BODIPY fluorophores is about 38.4 Å and the two fluorophores are almost parallel in the initial state. From Equation (1), R_0 (R_0 is the distance at which ET between a given

Table 1. The maximal absorption wavelength (λ_{max}), molar extinction coefficient (ε), maximal emission wavelength (λ_{em}), fluorescent quantum yield (Φ_f), and fluorescence lifetime (τ) of **1**, **2**, **3**, and **M**.

	λ_{max} [nm]	ε (10^4)	λ_{em} [nm]	Φ_f [%]	τ [ns]	χ^2
2	415	5.4	485	0.96	1.59[a]	1.006
3	531, 569	3.1, 10.3	585	0.81	3.50[c]	1.006
1	338, 531, 569	24.8, 7.62, 10.7	585	0.60	3.28[b]	1.004
					3.88[c]	1.106
M	338, 531, 569		585		1.33 (42.1%), 3.31 (57.9%)[b]	0.984
					3.40[c]	1.043

[a] Fluorescence lifetime monitored at $\lambda=485$ nm. [b] Fluorescence lifetime monitored at $\lambda=558$ nm. [c] Fluorescence lifetime monitored at $\lambda=585$ nm.

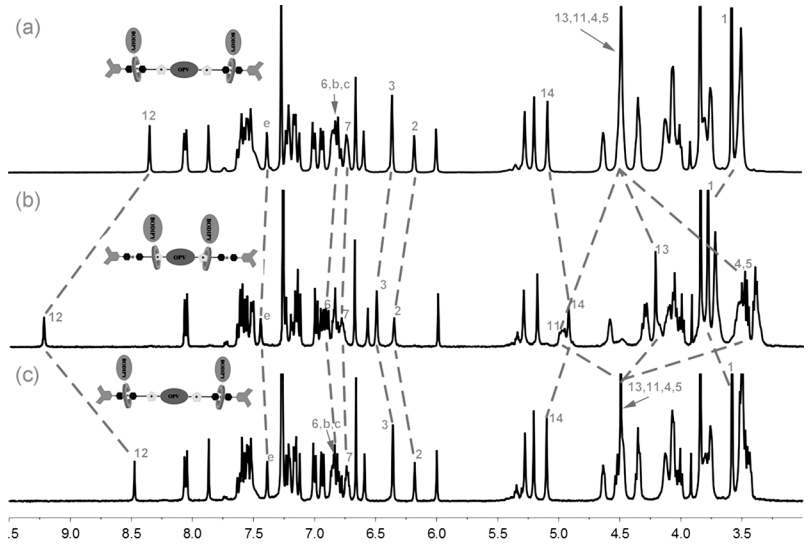


Figure 5. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 298 K) of a) [3]rotaxane **1**, b) deprotonation with the addition of 2.4 equivalents of DBU to sample a), and c) reprotonation with the addition of 5.0 equivalents of CF_3COOH to sample b).

donor–acceptor pair is 50 %)[23] was calculated to be 62.7 Å. After the addition of DBU, as shown in Figure S9 in the Supporting Information, the distance between the two fluorophores changed from 38.4 to 18.3 Å, and the efficiency of the FRET process was calculated to be 99.9 % from Equation (1). There was no clear change compared with that of the original state.

$$E_{FRET} = R_0^6/(R_0^6 + R^6) \quad (1)$$

Meanwhile, we measured the UV/Vis absorption and fluorescence emission spectra of **1** in response to acid–base stimuli. As shown in Figures S10 and 11 in the Supporting Information, no clear changes in the spectra were observed, and the efficiency of the FRET process between the donor and acceptor fluorophores in **1** had no clear changes. These phenomena are consistent with results from theoretical calculations. Although the distance between the two fluorophores changed, the efficiency of the FRET process had no clear change mainly because the distance between the two fluorophores was not big enough and the efficiency was in a high level in the initial state. Although modulation of the FRET efficiency is not good as expected, this result can help us to improve the molecular design in the future work, such as introducing more rigid chains and enlarging the distance between the two recognition states to achieve better modulation of FRET efficiency.

Conclusion

We successfully constructed and characterized a bis-branched [3]rotaxane. By introducing an OPV fluorophore as a donor into the axle component and two BODIPY fluorophores as acceptors in the macrocycle components, an efficient ET process from the OPV fluorophore to the BODIPY moieties occurred, owing to the appropriate distance between the two fluorophores in the rotaxane. The BODIPY-functionalized DB24C8 rings could reversibly shuttle between the distinguishable recognition sites through external acid–base stimuli. Meanwhile, this work shows important potential in the design and construction of functional molecular systems based on MIMs. In future work, we will introduce more rigid structures and enlarge the distance between the fluorophores and two recognition sites to modulate the FRET effect.

Experimental Section

General Methods and Materials

^{1}H and ^{13}C NMR spectroscopy were measured on a Brüker AV-400 spectrometer. The ESI mass spectra were recorded on a LCT Premier XE mass spectrometer. The UV/Vis absorption spectra and fluorescence spectra were also recorded on Varian Cary 100 and Varian Cary Eclipse spectrometers (1 cm quartz cell used), respectively. The fluorescence lifetime measurements were performed by using the time-correlated single-photon-counting (TCSPC) technique following excitation by means of a nanosecond flash lamp. All solvents were of reagent grade and were dried and distilled prior to use according to standard procedures. The quantum yields of fluorescence were measured by using a Fluoromax-4 fluorescence spectrophotometer equipped with a quantum yield measuring accessory and report generator program. The molecular structures were confirmed by using ^{1}H and ^{13}C NMR spectroscopy and high-resolution ESI mass spectrometry. Compounds **9**, **10**, **11**, **13**, **14**, and **16** were synthesized and purified according to previously reported procedures.[14b,15]

*Compound **12***

A mixture of compound **13** (0.492 g, 1 mmol) and **14** (0.200 g, 1.2 mmol) was dissolved in dry CH_2Cl_2 (6 mL), then EDCI (0.768 g, 4 mmol) and DMAP (0.122 g, 1 mmol) were added and the mixture was stirred overnight at room temperature under an argon atmosphere. The reaction mixture was then washed with water and extracted with CH_2Cl_2 (3× 50 mL), the organic layer was dried over anhydrous Na_2SO_4 and evaporated, and the residue was purified by chromatography on silica gel with CH_2Cl_2/MeOH (200:1) as the eluent to give **12** as a white solid (0.54 g, 85 %). M.p. 118–119 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 9.90 (s, 1H), 7.85 (d, J = 8.8 Hz, 2H), 7.66 (dd, J = 8.4, 1.6 Hz, 1H), 7.52 (d, J = 2.0 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 6.97–6.81 (m, 5H), 4.66 (t, J = 4.8 Hz, 2H), 4.38 (t, J = 4.8 Hz, 2H), 4.21–4.13 (m, 8H), 3.96–3.90 (m, 8H), 3.86–3.81 ppm (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 190.8, 166.2, 163.6, 153.2, 148.9, 148.3, 132.0, 130.3, 124.2, 122.3, 121.4, 114.9, 114.4, 113.9, 111.9, 71.5, 71.4, 71.3, 70.0, 69.8, 69.6, 69.5, 69.4, 69.3, 66.3, 62.8 ppm; HRMS (ESI): m/z calcd for $C_{34}H_{40}NaO_{12}$: 633.2417 $[M+Na]^+$; found: 633.2409.

Compound ***3***

Compound **11** (128 mg, 0.2 mmol) was dissolved in anhydrous DMF (20 mL) in a 50 mL three-necked, round-bottomed flask, then acetic acid (0.5 mL), piperidine (0.5 mL), and **12** (102 mg, 0.2 mmol) were added under an argon atmosphere. After reaction under microwave conditions (8 min, 150 °C), the reaction mixture was cooled to room temperature and extracted with EtOAc (3×50 mL). The organic layer was combined and concentrated in vacuo, and the product was further purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 120:1), to yield **3** as a purple solid (127 mg, 56%). M.p. 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.64 (dd, J = 8.4, 1.6 Hz, 1H), 7.59–7.49 (m, 4H), 7.21–7.12 (m, 3H), 6.97 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 6.88–6.81 (m, 5H), 6.57 (s, 1H), 5.99 (s, 1H), 4.62 (t, J = 4.0 Hz, 2H), 4.38 (t, J = 4.0 Hz, 2H), 4.19–4.10 (m, 8H), 3.99 (t, J = 6.4 Hz, 2H), 3.94–3.87 (m, 8H), 3.84–3.79 (m, 8H), 2.58 (s, 3H), 1.86–1.76 (m, 2H), 1.52–1.42 (m, 8H), 1.40–1.23 (m, 16H), 0.88 ppm (t, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.2, 159.7, 159.4, 154.6, 153.1, 153.0, 148.9, 148.2, 142.7, 142.5, 140.4, 135.7, 133.2, 132.2, 132.0, 129.8, 129.4, 129.0, 126.9, 124.2, 122.4, 121.4, 121.1, 117.4, 115.0, 114.9, 114.4, 114.0, 111.9, 71.5, 71.4, 71.3, 70.0, 69.8, 69.6, 69.5, 69.4, 69.3, 68.2, 66.2, 63.2, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.9, 14.7, 14.6, 14.2 ppm; HRMS (ESI): m/z calcd for $C_{65}H_{81}N_2F_2BNaO_{12}$: 1153.5748 $[M+Na]^+$; found: 1153.5747.

Compound ***5***

A mixture of **10** (3.15 g, 5 mmol) and PPh_3 (2.882 g, 11 mmol) was dissolved in toluene under an argon atmosphere. The reaction mixture was heated at reflux for 6 h. After termination of the reaction, a white solid was precipitated and filtered. Then, the generated solid was transferred to a Schlenk tube and methyl 4-formylbenzoate (1.97 g, 12 mmol) was added, and the mixture was dissolved in methanol under an argon atmosphere. Sodium methoxide (0.81 g 15 mmol) in methanol (15 mL) was injected into the mixture slowly and the mixture became yellow. Later, the precipitate formed. After being stirred for another 4 h, the reaction was quenched with water (20 mL), and the yellow solid was filtered and washed with methanol. The crude product was heated at reflux in toluene with a catalytic amount of iodine for 1 h, and the solvent was evaporated. The pure product was obtained after column chromatography (SiO_2, petroleum ether (PE)/EtOAc = 5:1), followed by recrystallization from dichloromethane and methanol, to yield **5** as a yellow solid (2.03 g, 53%). M.p. 120–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.02 (d, J = 8.4 Hz, 4H), 7.62–7.56 (m, 6H), 7.18 (d, J = 16.4 Hz, 2H), 7.13 (s, 2H), 4.07 (t, J = 6.4 Hz, 3H), 3.93 (s, 6H), 1.94–1.85 (m, 4H), 1.57–1.51 (m, 4H), 1.43–1.26 (m, 32H), 0.88 ppm (t, J = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.9, 151.3, 142.4, 130.0, 128.7, 128.0, 126.8, 126.3, 126.0, 110.7, 69.5, 52.1, 32.0, 30.2, 29.7, 29.5, 29.4, 26.3, 22.7, 14.2 ppm; HRMS (ESI): m/z calcd for $C_{50}H_{71}O_6$: 767.5251 $[M+H]^+$; found: 767.5244.

Compound ***8***

A mixture of **15** (5.0 g, 0.027 mol), propargyl bromide (6.04 g, 0.055 mmol), and K_2CO_3 (7.59 g, 0.055 mol) were dissolved in acetone (150 mL) in a 250 mL flask, then the mixture was heated at reflux overnight under an argon atmosphere. The reaction mixture was washed with water and extracted with CH_2Cl_2 (3×50 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated before THF (100 mL) was added. After the solution was cooled to 0 °C, $NaBH_4$ (2.05 g, 0.054 mol) was added slowly and stirred overnight at room temperature. The reaction was quenched with water and the resulting aqueous solution was extracted with CH_2Cl_2 (3×50 mL). The solvent was removed under reduced pressure to obtain the crude product, which was purified by column chromatography with CH_2Cl_2/PE (2:1) as the eluent to give **8** as a white solid (4.795 g, 80%). M.p. 99–100 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.59 (s, 2H), 4.69 (d, J = 2.4 Hz, 2H), 4.64–4.60 (m, 2H), 3.85 (s, 6H), 2.44–2.41 (m, 2H), 1.97–1.91 ppm (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 153.6, 137.4, 134.7, 103.7, 79.4, 74.8, 65.4, 59.9, 56.1 ppm; HRMS (ESI): m/z calcd for $C_{12}H_{15}O_4$: 223.0970 $[M+H]^+$; found: 223.0976.

Compound ***7***

In a 50 mL flask, compound **9** (1.92 g, 8.66 mmol), CuI (1.67 g, 1.73 mmol), DIEA (2.24 g, 17.3 mmol), and compound **8** (3.89 g, 17.3 mmol) were mixed in dry THF (30 mL), and the reaction mixture was stirred overnight under an argon atmosphere. After the mixture was poured into water (200 mL) and stirred for another half an hour, the aqueous layer was extracted with CH_2Cl_2 (3×25 mL). After the combined organic layers were concentrated in vacuo, purification was performed by column chromatography (SiO_2, CH_2Cl_2/MeOH = 200:1) to give **7** as a yellow oil (2.40 g, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 7.69 (s, 1H), 6.58 (s, 2H), 5.15 (s, 2H), 4.62 (s, 2H), 4.32 (t, J = 8.0 Hz, 2H), 3.82 (s, 6H), 3.25 (t, J = 8.0 Hz, 2H), 1.92–1.84 (m, 2H), 1.62–1.53 (m, 2H), 1.36–1.24 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 153.3, 145.0, 137.7, 137.6, 135.2, 122.8, 103.6, 66.4, 65.0, 56.0, 51.4, 50.7, 50.3, 30.3, 29.7, 29.3, 29.2, 29.0, 28.9, 28.8, 26.6, 26.4 ppm; HRMS (ESI): m/z calcd for $C_{22}H_{34}N_6NaO_4$: 469.2539 $[M+Na]^+$; found: 469.2537.

Compound ***6***

Compound **7** was dissolved in iodomethane (6 mL), then the mixture was stirred at 40 °C for 4 days. After removing excess iodomethane, the clear yellow fluid was dissolved in methanol (30 mL). Then a saturated solution of NH_4PF_6 (10 mL) was added and the mixture was stirred at room temperature for 4 h. The reaction mixture was extracted with CH_2Cl_2 (3×25 mL), and the organic layer was dried and evaporated. The crude product was purified by chromatography on silica gel by using CH_2Cl_2/MeOH (100:1) as the eluent to give **6** as a yellow oil (1.17 g, 86%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.23 (s, 1H), 6.57 (s, 2H), 5.14 (s, 2H), 4.60 (s, 2H), 4.50–4.42 (m, 5H), 3.79 (s, 6H), 3.25 (t, J = 8.0 Hz, 2H), 1.97–1.90 (m, 2H), 1.62–1.55 (m, 2H), 1.36–1.24 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 152.9, 139.9, 139.1, 133.0, 129.6, 103.4, 64.9, 60.7, 55.8, 54.1, 51.4, 38.4, 29.3, 29.2, 29.1, 29.0, 28.8, 28.7, 26.6, 25.9 ppm; HRMS (ESI): m/z calcd for $C_{23}H_{37}N_6O_4$: 461.2876 $[M-PF_6]^+$; found: 461.2873.

Compound ***4***

Compound **5** (153 mg, 0.2 mmol), KOH (224 mg, 4 mmol), methanol (6 mL), THF (6 mL), and water (4 mL) were added to a flask and the mixture was heated at reflux for 10 h. After the reaction mixture was cooled to room temperature, water (10 mL) was added. Then, 1 N HCl was added to adjust the pH to 2–3, and the resulting yellow precipitate was filtered and washed with dichloromethane/methanol (1:10). After drying, the crude intermediate was transferred to a flask and **6** (267 mg, 0.44 mmol), EDCI (307 mg, 1.6 mmol), and DMAP (49 mg, 0.4 mmol) were added and dissolved in dichloromethane (4 mL). The reaction mixture was stirred for 10 min and became clear. The mixture was stirred overnight. After termination of the reaction, the solvent was removed by using a rotary evaporator to give the crude product, which was purified by column chromatography with CH_2Cl_2/EtOAc (10:1) as the eluent to afford **4** as a yellow solid (314 mg, 82%). M.p. 107–109 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.32 (s, 2H), 8.05 (d, J = 8.4 Hz, 4H), 7.60–7.54 (m, 6H), 7.16 (d, J = 16.4 Hz, 2H), 7.11 (s, 2H), 6.68 (s, 4H), 5.29 (s, 4H), 5.20 (s, 4H), 4.55–4.47 (m, 10H), 4.05 (t, J = 6.4 Hz, 4H), 3.86 (s, 12H), 3.26 (t, J = 6.8 Hz, 4H), 2.04–1.95 (m, 4H), 1.92–1.83 (m, 4H), 1.63–1.49 (m, 8H), 1.43–1.23 (m, 60H), 0.89 ppm (t, J = 2.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 166.2, 153.1, 151.3, 142.7, 139.9, 134.1, 133.9, 130.2, 129.7, 128.4, 127.9, 126.8, 126.4, 126.2, 105.1, 69.4, 66.6, 60.8, 56.0, 54.1, 51.5, 38.6, 31.9, 29.7, 29.6, 29.4, 29.3, 29.0, 28.8, 28.7, 26.7, 26.3, 26.0, 22.7, 14.2 ppm; HRMS (ESI): m/z calcd for $C_{94}H_{136}N_{12}O_{12}/2$: 813.0217 $[M-2PF_6]^{2+}$; found: 813.0208.

Compound ***2***

In a 25 mL flask, compounds **4** (50 mg, 0.026 mmol) and **16** (48 mg, 0.105 mmol) were dissolved in dichloromethane (2 mL) and acetonitrile (2 mL), then $[Cu(CH_3CN)_4]PF_6$ (19.4 mg, 0.052 mmol) was added and the solution was stirred at room temperature for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 120:1) to give **2** as a yellow solid (41 mg, 56%).

^{1}H NMR (CD_3COCD_3, 400 MHz, 298 K): δ = 8.79 (s, 2H), 8.09–8.01 (m, 6H), 7.74–7.66 (m, 6H), 7.51–7.39 (m, 8H), 7.05 (d, J = 8.8 Hz, 4H), 6.88 (s, 4H), 6.70 (d, J = 2.0 Hz, 4H), 6.50–6.44 (m, 2H), 5.38 (s, 4H), 5.31 (s, 4H), 5.16 (s, 4H), 4.75 (t, J = 7.2 Hz, 4H), 4.61 (s, 6H), 4.40 (t, J = 7.2 Hz, 4H), 4.20 (d, J = 6.0 Hz, 8H), 4.15 (t, J = 6.4 Hz, 4H), 3.85 (s, 12H), 3.77 (s, 12H), 1.93–1.83 (m, 8H), 1.62–1.53 (m, 4H), 1.48–1.40 (m, 4H), 1.37–1.21 (m, 56H), 0.85 ppm (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_3COCD_3, 298 K): δ = 170.7, 166.5, 164.1, 158.6, 156.6, 148.1, 145.5, 139.6, 139.2, 136.3, 135.9, 135.2, 133.9, 133.3, 132.0, 131.6, 131.3, 129.0, 120.1, 116.2, 112.4, 110.4, 107.6, 105.4, 74.3, 71.5, 66.7, 66.2, 60.8, 60.1, 59.0, 55.0, 43.4, 36.9, 35.3, 31.4, 30.9, 27.7, 18.7 ppm; HRMS (ESI): m/z calcd for $C_{132}H_{180}N_{14}O_{18}$/4: 562.5909 $[M-4PF_6]^{4+}$; found: 562.5909.

Compound ***1***

In a 25 mL flask, compounds **3** (88 mg, 0.078 mmol) and **16** (30 mg, 0.066 mmol) were dissolved in dichloromethane (3 mL), the mixture was stirred for half an hour, and then **4** (50 mg, 0.026 mmol) and $[Cu(CH_3CN)_4]PF_6$ (19.4 mg, 0.052 mmol) were added and the solution was stirred at room temperature for 24 h. After removal of the solvent, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH = 120:1) to give **1** as a purple solid (64 mg, 48%). M.p. 82–84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 8.34 (s, 2H), 8.05 (d, J = 8.0 Hz, 4H), 7.86 (s, 2H), 7.65–7.47 (m, 16H), 7.38 (s, 2H), 7.24–7.18 (m, 5H), 7.17–7.14 (m, 5H), 7.12 (s, 2H), 7.00 (d, J = 8.0 Hz, 4H), 6.93 (d, J = 8.4 Hz, 4H), 6.87–6.69 (m, 14H), 6.66 (s, 4H), 6.59 (s, 2H), 6.36 (s, 4H), 6.18 (s, 2H), 6.00 (s, 2H), 5.27 (s, 4H), 5.19 (s, 4H), 5.08 (s, 4H), 4.63 (t, J = 4.0 Hz, 4H), 4.53–4.42 (m, 18H), 4.38–4.30 (m, 8H), 4.17–3.97 (m, 24H), 3.58 (s, 12H), 3.54–3.38 (m, 16H), 2.57 (s, 3H), 2.05–1.78 (m, 8H), 1.71–1.58 (m, 8H), 1.52–1.42 (m, 20H), 1.41–1.21 (m, 92H), 0.91–0.83 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ = 165.2, 164.9, 159.8, 158.7, 158.4, 157.9, 153.6, 152.1, 151.9, 150.5, 150.3, 146.1, 146.0, 142.1, 141.7, 141.6, 139.4, 138.8, 134.6, 133.1, 132.8, 132.7, 132.2, 131.1, 130.1, 129.8, 129.1, 128.8, 128.6, 128.3, 128.0, 127.9, 127.4, 126.9, 125.7, 125.4, 125.1, 123.3, 122.8, 122.6, 121.8, 120.6, 120.1, 116.4, 116.2, 114.0, 112.1, 111.4, 110.7, 109.7, 105.6, 104.0, 98.8, 69.6, 69.1, 68.9, 68.4, 67.3, 67.2, 66.9, 65.6, 65.1, 62.3, 60.4, 59.8, 55.0, 54.2, 53.1, 52.5, 51.7, 51.2, 49.8, 37.5, 30.9, 30.5, 30.4, 29.2, 29.0, 28.7, 28.6, 28.4, 28.3, 28.1, 27.6, 27.5, 27.4, 27.3, 26.2, 25.2, 25.1, 25.0, 24.6, 24.5, 21.7, 13.8, 13.7, 13.6, 13.1 ppm; HRMS (ESI): m/z calcd for $C_{262}H_{342}B_2F_4N_{18}O_{42}$/4: 1128.1342 $[M-4PF_6]^{4+}$; found: 1128.1349.

Acknowledgements

We thank the NSFC/China (21272073, 21190033) and the National Basic Research 973 Program (2011CB808400), the Fundamental Research Funds for the Central Universities, and the Innovation Program of Shanghai Municipal Education Commission, and the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry for financial support. This work is partially supported by the Science Fund for Creative Research Groups (No. 21421004). Meanwhile, we thank Dr. X. Li for help with the molecular dynamics (MD) simulations.

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Received: July 5, 2014
Revised: July 21, 2014
Published online: September 18, 2014