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Energy Harvesting in a Bodipy-Functionalized Rotaxane

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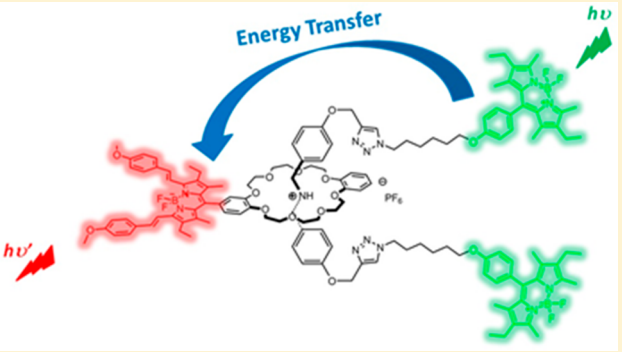
Supporting Information

ABSTRACT: A rotaxane composed of two separate Bodipy-functionalized units can be synthesized with a high yield. The resulting structure shows a very efficient through-space energy transfer (FRET), acting as an energy funnel. Thus, maximum solar output in the visible region can be collected and converted into red light, which can be transformed efficiently with a fine-tuned photovoltaic device. The versatility of the synthetic pathway demonstrates the potential utility of rotaxane-based energy harvesting supramolecules assemblies.



INTRODUCTION

Organic solar concentrators continue to attract attention.[1] Dendritic energy funnels with two or more distinct chromophores are an established approach[2] for obtaining a molecular solar concentrator producing a monochromic emission, which could then be coupled to a high-end photovoltaic device for enhanced efficiency. A promising alternative is to make use of mechanical interlocking,[3] thus quickly assembling multiple chromophores in close proximity for through -space energy transfer.[4]

Bodipy dyes, on the other hand, proved themselves to be very attractive chromophores in very diverse fields of applications[5] due to their high photostability and chemical stability coupled with large extinction coefficients in the visible region and impressive quantum yields. Not surprisingly, they attracted attention in various solar cell designs, as well.[6] Bodipy dyes are also very amenable to modification,[7] yielding dyes with absorbance peaks covering essentially the entire visible spectrum, and even near IR. Our goal in this work was to assemble a [2]rotaxane making use of dibenzo-fused [24]-crown-8 and dibenzyl ammonium modules. The affinity of this crown unit and the dibenzyl ammonium cation is well-established in the literature.[8]

RESULTS AND DISCUSSION

Our synthesis of the energy funnel rotaxane starts with tosylation of the commercially available oligoethylene glycol **1**, followed by the closure of the crown ring, yielding formyl-substituted dibenzo-fused 24-crown-8 (**3**, Scheme 1). Then, *meso*-substituted Bodipy (**4**) was synthesized by a well-established protocol in Bodipy synthesis.[9] The next step is the transformation of the green emitting light into a red emitting dye (**5**) by a reaction with *p*-methoxybenzaldehyde under conditions optimized in our laboratory.[10] The synthesis of the axle component of the rotaxane starts with *p*-hydroxybenzaldehyde (**6**), which can easily be reacted with propargyl bromide. Reductive amination using compound **8** in methanol yields dibenzylamine derivative **9** in a high yield. Protonation is followed by ion exchange with NH_4PF_6, which yields organic soluble ammonium salt **10**. Green emitting absorbing Bodipy modules were synthesized starting from previously reported[10b] compound **11**; its reaction with sodium azide in DMSO at 100 °C yields Bodipy compound **12**. The final assembly reaction of the rotaxane makes use of the affinity of dibenzylammonium cation for dibenzo-fused [24]-crown-8, which is followed by the click attachment of the chromophore/stoppers yielding the target supramolecular assembly **13** (Scheme 1 and Figure 1).

In order to assess energy transfer characteristics of the rotaxane, we acquired absorption spectra of the rotaxane and the related modules separately, and as a mixture.

In the absorbance spectrum, the changes are relatively minor (Figure 2). More revealing is the emission spectra of the [2]-rotaxane **13** and the modules **5** and **12**, separately and as a mixture, Figure 3. The green emission module is highly fluorescent either alone (**12**) or in the mixture. However, in the mixture, excitation at 500 nm yields no detectable emission at 675 nm. The energy funneling rotaxane, however, at the same concentrations, yields a very minor peak around 530 nm, while most of the emission is centered around 675 nm when excited at 500 nm. This is a very clear evidence for energy transfer in rotaxane **13**. An excitation spectrum was also acquired in Figure 4. As expected, it shows two peaks when the emission is collected at 673 nm. Energy transfer efficiencies are

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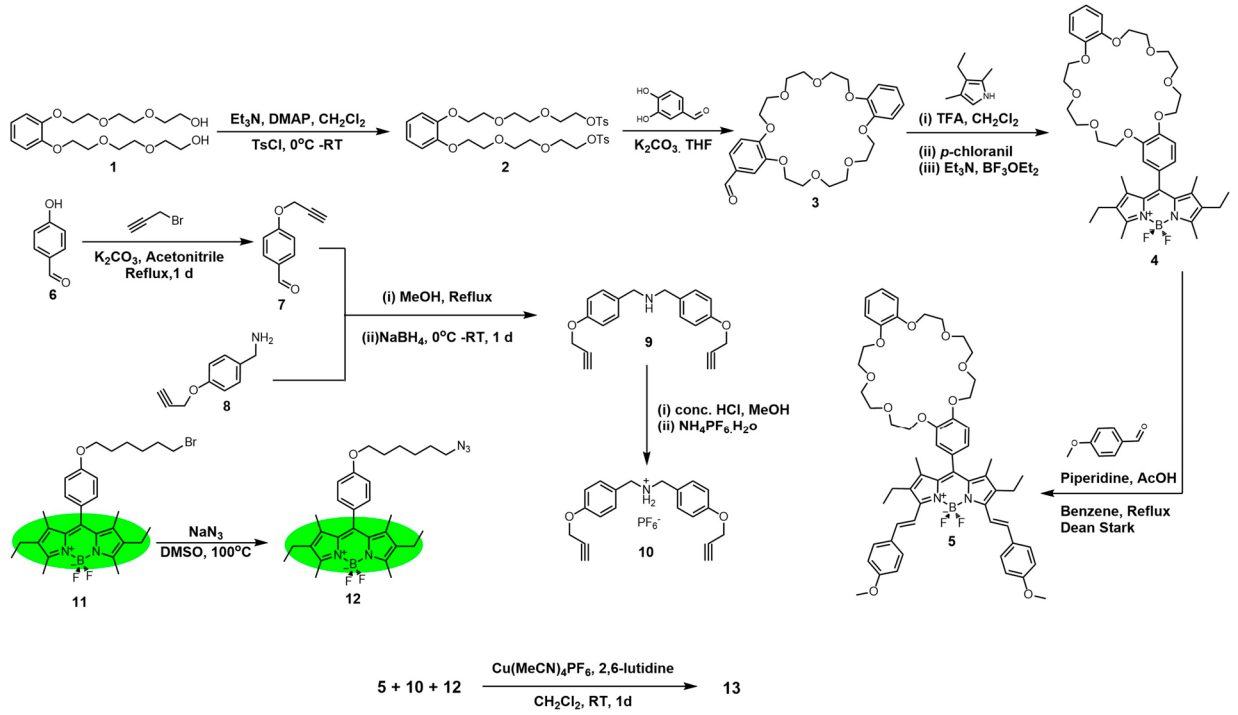
Scheme 1. Synthesis of the Rotaxane-Based Energy Funnel 13



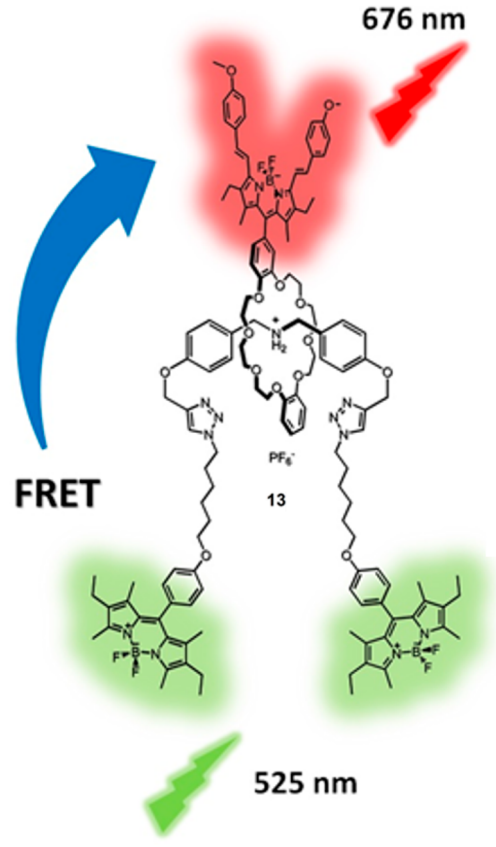


Figure 1. Structure of the target [2]-rotaxane **13** and the direction of energy transfer and conversion.

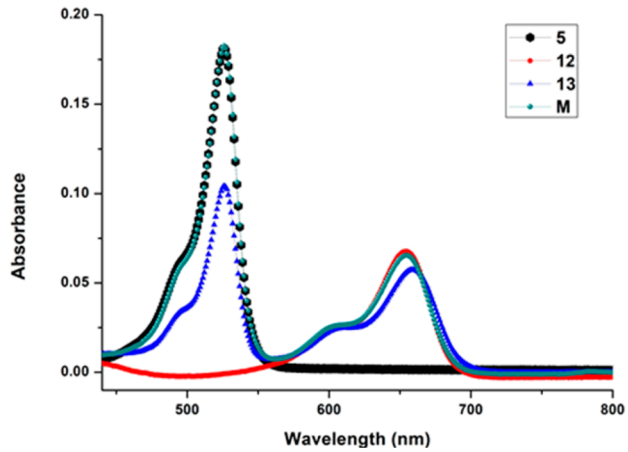


Figure 2. Absorption spectra of [2]rotaxane **13** (1.0×10^{-6} M), compound **5** (1.0×10^{-6} M), compound **12** (2.0×10^{-6} M), and mixture **M** (a mixture of **5** and **12** in a molar ratio of 1:2) in chloroform.

often reported with large over estimations[11] based on the decrease in the quantum yield of the donor chromophore. Thus, a change in the quantum yields of the donor suggests an efficiency of 97%, but a more reliable estimate of energy transfer as a function of wavelength can be obtained by the normalizing absorption spectrum and excitation spectrum of the energy transfer cassette, at the peak of the acceptor absorption.[12] This yields an approximate energy transfer of 40−50% between 475 and 550 nm.

Modular synthesis of energy-funneling supramolecular systems is likely to find practical applications in organic solar concentrators. In this work, we presented a concise approach for the assembly of a trichromophoric system; however, the idea presented here is fully transferable to a more elaborate multichromophoric assembly, with higher conversion efficiencies. Our work toward that goal is in progress.

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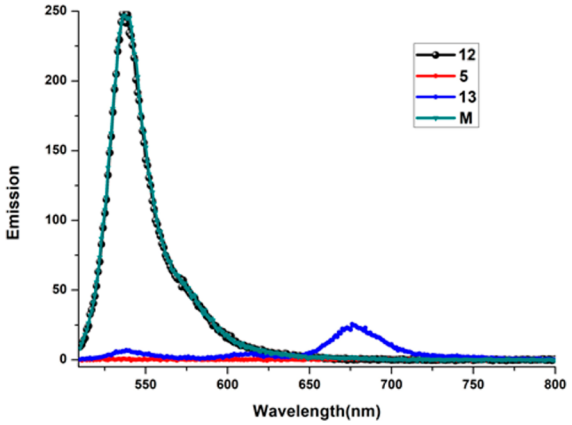

Figure 3. Emission spectra of [2]rotaxane **13** (1.0×10^{-6} M), compound **5** (1.0×10^{-6} M), compound **12** (2.0×10^{-6} M), and mixture **M** (a mixture of **5** and **12** in a molar ratio of 1:2) in chloroform. The excitation wavelength of the fluorescent spectra is 500 nm.

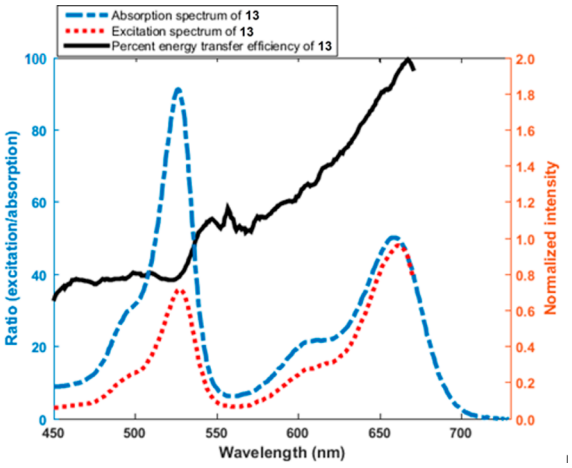

Figure 4. Percent energy transfer efficiency of **13** (solid line) as a function of wavelength of excitation. Excitation spectrum of **13** (dotted line) and absorption spectrum of **13** (dash-dotted line), normalized at 660 nm. (Emission data were collected at 673 nm.)

EXPERIMENTAL SECTION

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 (operating at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) in $CDCl_3$ with tetramethylsilane as an internal standard. All spectra were recorded at 25 °C, and coupling constants (J values) were given in hertz (Hz). Chemical shifts were given in parts per million (ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and p (pentet). All of the ^{13}C spectra were recorded with simultaneous decoupling of proton nuclei. Melting points were determined with an Electrochemical 9100 apparatus. Mass spectra were recorded on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS system. Absorption spectra were performed by using a Varian Cary-100 spectrophotometer. Fluorescence measurements were conducted on a Varian Eclipse spectrofluometer. Reactions were monitored by thin-layer chromatography using Merck TLC silica gel 60 F_{254}. Silica gel column chromatography was performed over Merck silica gel 60 (particle size: 0.040−0.063 mm, 230−400 mesh ASTM). All other reagents and solvents were purchased from Aldrich and used without further purification. Compounds **1**[13] and **8**[8b] were synthesized according to the literature.

Synthesis of Compound **2**. Compound **1** (5.6 g, 15 mmol), triethylamine (8.7 mL, 62 mmol), and 4-dimethylamino pyridine (10 mg, 0.15 mmol) were mixed in DCM (60 mL) at 0 °C in an ice bath. 4-Toluenesulfonyl chloride (7.2 g, 38 mmol) dissolved in DCM (150 mL) was added dropwise to the reaction mixture with vigorous stirring. After the temperature was kept at 0 °C for 1 h, the ice bath was removed. The reaction mixture was stirred at room temperature overnight. The reaction mixture was washed with 0.1 M HCl (twice) and saturated NaCl solutions (twice). The organic layer was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified by column chromatography (silica gel, EtOAc/hexane 1:6 (v/v)). Compound **2** was obtained as a colorless oil (6.68 g, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 4H), 7.34 (d, J = 8.0 Hz, 4H), 6.93 (s, 4H), 4.18−4.14 (q, J = 4.0 Hz, 8H), 3.84 (t, J = 4.0 Hz, 4H), 3.72−3.68 (m, 8H), 3.64−3.61 (m, 4H), 2.45 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 144.8, 133.1, 129.8, 128.0, 121.7, 115.0, 70.8, 70.8, 69.8, 69.3, 68. 9, 68.7, 21.6 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{32}H_{42}O_{12}S_2Na$, 705.2010; found, 705.1977.

Synthesis of Compound **3**. Under an argon atmosphere, 3,4-dihydroxybenzaldehyde (1.38 g, 10 mmol) and K_2CO_3 (16.3 g, 50 mmol) were mixed in THF (300 mL). The mixture was heated under reflux for 1 h, and then compound **2** (6.83 g, 10 mmol) in THF (100 mL) was added. The reaction mixture was heated under reflux for 24 h. After the reaction cooled to room temperature, the solvent was removed by evaporation. The residue was dissolved in DCM (200 mL) and washed with 1 M HCl and saturated NaCl aqueous solutions. The organic layer was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified by column chromatography (silica gel, EtOAC/MeOH 10:1). Compound **3** was obtained as an off-white solid (2.88 g, 60% yield). Mp: 95.0−97.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.77 (s, 1H), 7.40−7.33 (m, 2H), 6.92−6.82 (m, 5H), 4.19−4.11 (m, 8H), 3.92−3.78 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 154.3, 149.2, 148.9, 148.9, 130.2, 126.7, 121.4, 121.4, 114.1, 112.0, 111.2, 71.5, 71.4, 71.3, 69.9, 69.7, 69.5, 69.4, 69.4, 69.3 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{25}H_{32}O_9Na$, 499.1939; found, 499.1922.

Synthesis of Dibenzocrown-Substituted Bodipy **4**. CH_2Cl_2 (300 mL) was purged with argon for 30 min. Compound **3** (500 mg, 1.04 mmol) and 3-ethyl-2,4-dimethyl pyrrole (0.33 mL, 2.41 mmol) were added. The color of the solution turned to red after the addition of 2 drops of trifluoroacetic acid. The reaction mixture was stirred at room temperature overnight. Then, *p*-chloranil (283 mg, 1.15 mmol) was added, and the reaction mixture was stirred at room temperature for 2 h. Then triethyl amine (1.3 mL) and boron trifluoride diethyl etherate (1.3 mL) were added sequentially. After the mixture was stirred at room temperature for 30 min, the reaction mixture was extracted with water. The organic layer was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified by column chromatography (silica gel, EtOAC/hexane 2:1 (v/v)). Compound **4** was obtained as a red wax (0.33 g, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98−6.90 (m, 5H), 6.82 (d, J = 8.0 Hz, 2H), 4.24−4.17 (m, 6H), 4.15−4.11 (m, 2H), 3.87−4.02 (m, 16H), 2.54 (s, 6H), 2.32 (q, J = 8.0 Hz, 4H), 1.38 (s, 6H), 1.00 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 149.6, 149.3, 149.0, 139.9, 138.4, 132.7, 131.0, 128.5, 121.5, 121.4, 114.2, 114.1, 113.9, 71.5, 71.4, 71.3, 69.98, 69.91, 69.87, 69.6, 69.5, 69.4, 69.3, 17.1, 14.6, 12.5, 11.8 ppm. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{41}H_{53}BF_2N_2O_8Na$, 772.3792; found, 772.3793.

Extended-Conjugation Chromophore **5**. Compound **4** (259 mg, 0.345 mmol) and 4-methoxy benzaldehyde (105 μL, 0.862 mmol) were dissolved in benzene (40 mL). Piperidine (0.32 mL) and acetic acid (0.32 mL) were added to the reaction mixture. The reaction mixture was refluxed using a Dean−Stark apparatus until all of the aldehyde was consumed. After the reaction was completed, it was extracted with DCM and water. The organic layer was dried over Na_2SO_4 and concentrated by evaporation. The crude product was purified by silica gel column chromatography (first DCM/MeOH 95:5 then EtOAC/hexane 2:1 (v/v)). Compound **5** was obtained as a green solid (0.18 g, 54% yield). Mp: 212.2−214.1 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 16.8 Hz, 2H), 7.59 (d, J = 7.6 Hz, 4H), 7.23 (d, J = 16.0 Hz, 2H), 7.01−7.91 (m, 9H), 6.85 (d, J

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= 10.0 Hz, 2H), 4.29−4.12 (m, 10H), 4.01−3.91 (m, 14H), 3.88 (s, 6H), 4.02 (q, J = 8.0 Hz, 4H), 1.43 (s, 6H), 1.18 (t, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 150.4, 149.6, 149.4, 138.8, 137.7, 135.3, 133.5, 130.4, 128.8, 121.5,121.5, 118.2, 114.2, 71.5, 71.4, 71.3, 71.3, 70.0, 69.9, 69.9, 69.6, 69.5, 69.4, 69.4, 55.4, 29.7, 18.4, 14.0, 11.6 ppm. HRMS (ESI-TOF) m/z: $[M + K]^+$ calcd for $C_{57}H_{65}BF_2N_2O_{10}K$, 1024.4368; found, 1024.4389.

Synthesis of 4-Propargyloxybenzaldehyde ***7***. To a solution of K_2CO_3 (1.50 g, 7.3 mmol) in acetonitrile (100 mL) were added 4-hydroxybenzaldehyde (0.1 g, 0.82 mmol) and propargyl bromide (0.11 g, 0.90 mmol), and the mixture was refluxed for 2 days under an argon atmosphere. Then, the reaction mixture was cooled and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL), filtrated, and then washed with water (100 mL) three times. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent $CHCl_3$) to afford a white solid (0.98 g, 74% yield). Mp: 82.0−84.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 4.78 (s, 2H), 2.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6, 162.4, 132.3, 130.59, 115.16, 77.58, 76.40, 56.11. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_9O_2$, 161.0597; found, 161.0569.

Synthesis of the Dibenzylamine Compound ***9***. Compound **7** (0.43 g, 2.67 mmol) and compound **8** (0.43 g, 2.67 mmol) were mixed in methanol (20 mL), and the mixture was refluxed for 24 h. Then, the reaction mixture was cooled to 0 °C, and $NaBH_4$ (1.0 g, 26.4 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 24 h. Water was added to the reaction. and the mixture was concentrated under vacuum pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and was washed with water (100 mL) three times. The organic phase was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent 100:1 DCM/MeOH) to afford a yellow oil (0.50 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 8.5 Hz, 4H), 4.69 (d, J = 2.3 Hz, 4H), 3.76 (s, 4H), 2.56 (t, J = 2.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 133.4, 129.4, 114.9, 78.8, 75.65, 55.9, 52.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{20}NO_2$, 306.1489; found, 306.1517.

Synthesis of Compound ***10***. Compound **9** (0.50 g, 1.61 mmol) was dissolved in methanol (15 mL), and concentrated HCl was added to adjust the pH lower than 2; then, the solvent was removed in vacuo. The reaction residue was dissolved in acetone (15 mL), and a saturated solution of NH_4PF_6 was added dropwise until the reaction mixture became clear. The solvent was removed under reduced pressure, and water was added to the residue. The resulting mixture was filtered, and the residue was washed with water several times and dried to give a white solid (0.68 g, 94% yield). Mp: 238.0−240.0 °C. ^{1}H NMR (400 MHz, MeOD): δ 7.44 (d, J = 8.7 Hz, 4H), 7.07 (d, J = 8.8 Hz, 4H), 4.77 (d, J = 2.4 Hz, 4H), 4.18 (s, 4H), 2.95 (t, J = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, MeOD): δ 158.6, 131.2, 123.7, 115.2, 78.1, 75.7, 55.3, 50.0. HRMS (ESI-TOF) m/z: $[M - PF_6]^+$ calcd for $C_{20}H_{20}NO_2$, 306.1494; found, 306.1510.

Synthesis of Compound ***12***. Compound **11** (0.40 g, 0.72 mmol) and NaN_3 (0.12 g, 1.79 mmol) were dissolved in DMSO (20 mL), and the reaction mixture was heated to 100 °C for 2 h. The reaction was controlled by TLC. When the reaction was complete, it was cooled to room temperature and $CHCl_3$ (100 mL) was added and washed with water (100 mL) six times. The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was used without further purification. A dark red solid (0.35 g, 97% yield) was afforded. Mp: 102.0−103.0 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 4.04 (t, J = 6.4 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H), 2.55 (s, 6H), 2.32 (q, J = 7.5 Hz, 4H), 1.94−1.80 (m, 2H), 1.71−1.64 (m, 2H), 1.61−1.49 (m, 4H), 1.36 (s, 6H), 1.00 (t, J = 7.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 153.5, 140.4, 138.4, 132.6, 131.2, 129.4, 127.8, 115.0, 67.9, 51.4, 29.1, 28.8, 26.6, 25.7, 17.1, 14.6, 12.5, 11.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{29}H_{38}BF_2N_5ONa$, 543.3066; found, 543.3039.

Synthesis of Rotaxane ***13***. A solution of compound **5** (326 mg, 0.33 mmol) and compound **10** (100 mg, 0.22 mmol) was dissolved in degassed DCM (15 mL) and stirred at room temperature for 4 h. Then, compound **12** (252 mg, 0.48 mmol) in 5 mL of DCM and $Cu(CH_3CN)_4PF_6$ (74 mg, 0.20 mmol) and 2,6-lutidine (5 μL, 0.107 mmol) were added. The resulting mixture was stirred at room temperature for 1 day. After 1 day, DCM (25 mL) was added to the reaction mixture and it was washed with water (30 mL). The organic layer was dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified with column chromatography over silica gel (9:1 DCM/MeOH). Compound **13** was afforded as a dark purple solid (175 mg, 32% yield). Mp: 204.0−206.0 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$): δ H 7,83 (s, 2H), 7.66 (d, J = 16.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 4H), 7.38 (J = 1.2 Hz, 4H), 7.25 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.4 Hz, 4H), 7.05 (d, J = 8.0 Hz, 2H), 7 (s, 2H), 6.97 (d, J = 4.8 Hz, 4H), 6.94 (d, J = 4.8 Hz, 4H), 6.90 (d, J = 8.0 Hz, 4H), 6.82 (s, 1H), 6.78−6.73 (m, 2H), 5.19 (s, 4H) 4.50 (m, 2H), 4.41 (t, J = 7.2 Hz), 4.31−4.26 (m, 2H), 4.19−4.16 (m, 2H), 4.11−4.10 (m 2H), 4.05−4.04 (m, 2H), 4.01 (t, J = 6.4 Hz, 4H), 3.95−3.93 (m, 2H), 3.90−3.88 (m, 2H), 3.87 (s, 6H, Ar-OCH3), 3.73−3.69 (m, 2H), 3.67−364 (m, 2H), 3.52−3.42 (m, 6H), 3.37−3.34 (m, 2H), 2.54 (s, 12H), 2.31 (q, J_1 = 7.2 Hz, J_2 = 7.6 Hz, 10H), 2.04−1.95 (m, 6H), 1.88−1.80 (m, 6H), 1.47−1.44 (m, 4H), 1.35 (s, 12H), 1.25 (s, 6H), 1.13 (t, J = 7.2 Hz, 6H), 1.00 (t, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 159.5, 159.0, 153.4, 150.6, 148.5, 148.4, 147.2, 143.2, 140.4, 138.5, 138.3, 135.6, 133.7, 132.6, 130.7, 130.2, 129.4, 128.8, 128.3, 127.7, 123.9, 123.5, 121.9, 118.0, 115.1, 114.9, 114.3, 70.7, 67.8, 61.6, 55.4, 52.01, 50.3, 30.2, 29.7, 29.7, 29.1, 26.3, 25.6, 22.7, 18.4, 17.1, 14.6, 14.0, 12.49, 12.46, 12.44, 11.9, 11.4. HRMS (ESI-TOF) m/z: $[M-PF_6]^+$ calcd for $C_{135}H_{161}B_3F_6N_{13}O_{14}$, 2333.2651; found, 2333.2310.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b01928.

Spectral data and copies of ^{1}H and ^{13}C spectra for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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