Energy Harvesting in a Bodipy-Functionalized Rotaxane

Nisa Yesilgul, Ozlem Seven, Ruslan Guliyev, and Engin U. Akkaya

Department of Chemistry, Bilkent University, Ankara 06800, Turkey
UNAM-National Nanotechnology Research Center, Bilkent University, Ankara 06800, Turkey

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 approach2 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 applications5 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, 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, meta-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 NH₄PF₆, which yields organic soluble ammonium salt 10. Green emitting absorbing Bodipy modules were synthesized starting from previously reported10b 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 dibenzylationmonium 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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often reported with large over estimations\textsuperscript{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.\textsuperscript{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.
Further purifying the crude product was achieved by column chromatography (silica gel, EtOAc/hexane 1:6 (v/v)). Compound 2 was obtained as a colorless oil (6.68 g, 65% yield). 1H NMR (400 MHz, CDCl3): 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).

General Procedures. 1H NMR and 13C NMR spectra were recorded on a Bruker DPX-400 (operating at 400 MHz for 1H NMR and 100 MHz for 13C NMR) in CDCl3 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 13C spectra were recorded with simultaneous decoupling of proton nuclei. Melting points were determined with a 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 spectrophotometer. Reactions were monitored by thin-layer chromatography using Merck TLC silica gel 60 F254. 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 113 and 850 were synthesized according to the literature.

**Experimental Section**

**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 Na2SO4 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). 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ 149.0, 144.9, 143.1, 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 C15H14O12SNa, 705.1977; found, 705.1977.

**Synthesis of Compound 3.** Under an argon atmosphere, 3,4-dihydroxybenzaldehyde (1.38 g, 10 mmol) and K2CO3 (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 Na2SO4 and concentrated by evaporation. The crude product was purified by column chromatography (silica gel, EtOAc/hexane 1:6 (v/v)). Compound 3 was obtained as an off-white solid (2.88 g, 60% yield). Mp: 95.0–97.0 °C. 1H NMR (400 MHz, CDCl3): 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). 13C NMR (100 MHz, CDCl3): δ 190.8, 154.3, 149.2, 148.9, 148.9, 143.0, 126.7, 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 C32H42O12S2Na, 499.1939; found, 499.1922.

**Synthesis of Dibenzo crown-Substituted Bodipy 4.** CH3Cl (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 triethylamine (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 Na2SO4 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). 1H NMR (400 MHz, CDCl3): 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, 4H). 13C NMR (100 MHz, CDCl3): 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 C15H14O12SNa, 772.3972; found, 772.3973.

**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 Na2SO4 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). 1H NMR (400 MHz, CDCl3): 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
and NaN₃ (0.12 g, 1.79 mmol) were dissolved in DMSO (20 mL), and the reaction mixture was cooled to 0 °C, and propargyl bromide (0.11 g, 0.90 mmol), was added. The mixture was refluxed for 2 days under an argon atmosphere. Then, the reaction mixture was cooled, concentrated under reduced pressure, and the residue was dissolved in acetone (100 mL), filtrated, and then washed with water (100 mL) three times. The organic phase was dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent CHCl₃) to afford a white solid (0.98 g, 74% yield). Mp: 82.0−84.0 °C. 1H NMR (400 MHz, CDCl₃): δ 7.85 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 4.78 (s, 2H), 2.59 (s, 12H). 13C NMR (100 MHz, CDCl₃): δ 190.6, 162.4, 132.3, 135.9, 115.6, 77.58, 76.40, 56.11. HRMS (ESI-TOF) m/z: [M + H]^+ calcd for C₂₀H₂₀NO₂, 306.1494; found, 306.1517.

Synthesis of 4-Propargyloxybenzaldehyde 7. To a solution of K₂CO₃ (1.50 g, 7.3 mmol) in acetone (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, concentrated under reduced pressure, and the residue was dissolved in CH₂Cl₂ (100 mL) and was washed with water (100 mL) three times. The organic phase was dried with Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (eluent CHCl₃) to afford a white solid (0.35 g, 60% yield). Mp: 258.0−260.0 °C (decomp). 1H NMR (400 MHz, CDCl₃): δ 7.85 (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), 7.03 (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, 2H), 4.30 (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, 3H, 2H), 3.54−3.46 (m, 6H, 2H), 3.37−3.34 (m, 2H), 2.54 (s, 12H), 2.51 (q, J = 7.2 Hz, 2H), 7.10 (t, J = 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 2H). 13C NMR (100 MHz, CDCl₃): δ 160.3, 159.5, 159.0, 153.4, 150.6, 148.5, 148.7, 147.2, 143.2, 140.4, 138.5, 133.8, 133.7, 133.6, 130.7, 130.2, 129.8, 128.8, 127.7, 127.9, 123.9, 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, 14.4, 11.9, 11.4. HRMS (ESI-TOF) m/z: [M+PF₆]^− calcd for C₁₃₅H₁₆₁B₃F₆N₁₃O₁₄, 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 1H and 13C spectra for new compounds (PDF)

AUTHOR INFORMATION

Corresponding Author

Engin U. Akkaya:0000-0003-4720-7554

ORCID

Engin U. Akkaya: 0000-0003-4720-7554

AUTHOR DECLARATION

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