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Croconaine Rotaxane Dye with 984 nm Absorption: Wavelength-Selective Photothermal Heating

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Abstract

Croconaines are an emerging class of near-infrared dyes that are useful for various sensing, photothermal, optoelectronic, and photoacoustic applications. Previous work encapsulated a dumbbell-shaped croconaine dye whose structure contains two thiophene flanking units inside a tetralactam macrocycle and produced a croconaine rotaxane **1** with a narrow 824 nm absorption band. Herein, a new rotaxane **2** is reported that encapsulates a croconaine dye with two thienothiophene flanking units. The new croconaine rotaxane **2** exhibits a narrow 984 nm absorption band that is distinct from the 824 nm absorption of rotaxane **1**. Photothermal heating experiments showed that an 830 nm diode laser selectively heats a solution containing rotaxane **1**, with no heating of a solution containing rotaxane **2**. Conversely, a 980 nm diode laser selectively heats a solution containing rotaxane **2**, with no heating of a solution containing rotaxane **1**. The new croconaine rotaxane **2** shows no fatigue after four cycles of laser heating and cooling.

Graphical Abstract

Rotaxanes, Near-Infrared Dyes

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A rotaxane that encapsulates a croconaine dye with two flanking thienothiophene units exhibits a narrow 984 nm absorption band that is distinct from the 824 nm absorption of a related croconaine rotaxane. The minimal spectral overlap enables wavelength-selective heating of separate solutions using two diode lasers.

Keywords

Rotaxane; mechanically interlocked molecule; near-infrared dye; laser; photothermal heating

Introduction

For several decades there has been considerable research effort to develop new classes of dyes that can absorb near-infrared (NIR) light. A lot of work has involved dyes that absorb in the region of 650–1000 nm (NIR I) because there is relatively low background absorption by biological samples.^{[1] [2] [3]} In addition, there is increasing interest in dyes that absorb in the second region of 1000–1700 nm (NIR II) which is another window that has low biological absorption.^{[4] [5]} The chemical design of NIR dyes is a multifarious challenge. Not only must the chemical structures contain conjugated systems with the appropriately small HOMO-LUMO gaps,^[6] but the dyes must exhibit very specific photophysical and photochemical properties. For example, fluorescent dyes must have high fluorescence quantum yields, oxygen photosensitizers must undergo efficient intersystem crossing, and photothermal dyes must have high rates of non-radiative relaxation.^[7] In addition, there may be other dye performance requirements such as high chemical and photochemical stability, capacity for surface immobilization or bioconjugation, high solubility, and low (or high propensity) for dye self-aggregation. One experimental approach to this dye modification challenge is to pursue covalent refinements of the dye structure, whereas an alternative strategy is to modify the dye by supramolecular encapsulation.^{[8] [9] [10] [11]} For the last fifteen years we have pursued this latter idea by devising chemical methods of encapsulating pseudooxocarbon dyes, specifically squaraines and croconaines, within interlocked rotaxane structures.^{[12] [13] [14]}

This report describes an advance in our work on croconaine dyes, an emerging near-infrared chromophore system that is gaining increasing attention for various sensing, photothermal, optoelectronic, and photoacoustic applications.^{[15] [16] [17] [18]} In 2013, we showed that croconaine dyes, such as **C1** (Scheme 1), are very useful as near-infrared photothermal agents,^[14] and in the subsequent time period we and others have shown that they can be

used for clean photothermal heating of nanoparticles without producing singlet oxygen,^[19] photothermal switching of polymer morphology,^{[20] [21]} and laser ablation of tumors in living animals.^{[22] [23]} We have also shown that croconaines can be converted to rotaxane structures, such as **1**, that exhibit sharp absorption bands at 820 nm, even under conditions that aggregate the molecules. These croconaine rotaxanes have enabled pH sensing in living subjects using photoacoustic imaging^[24] and activated photothermal heating of nanoparticles.^[25] Croconaine rotaxanes exhibit unusually narrow absorption bands which raises the alluring idea of using them for multiplex heating or ratiometric photoacoustic detection.^[26] The key technical requirement is wavelength-selective excitation of two or more different croconaine rotaxanes, each with a narrow and distinct absorption wavelength. To reduce this idea to practice, we first needed to invent a new type of croconaine rotaxane with an absorption wavelength that was significantly removed from the 820 nm exhibited by rotaxane **1**.

While some croconaine dyes are known with absorption maxima between 900 – 1000 nm, none have been reported as an interlocked rotaxane.^[15] The chemical structure of croconaine **C1** has two flanking thiophene units and in a recent study of analogous squaraine dyes we found that synthetic substitution of the thiophenes with flanking thienothiophene units led to an increase in conjugation and a 100 nm red-shift in the squaraine absorption maxima band.^[27] Equally important, the flanking thienothiophene units still allowed threading of the tetralactam macrocycle **M**. With this precedence in mind we decided to prepare the new extended croconaine dye **C2** and determine if it could be used to thread **M2** and be converted into the new croconaine rotaxane **2**. Once **2** was in hand, we wanted to demonstrate wavelength-selective photothermal heating of separate solutions containing either **1** or **2**.

Results and Discussion

Synthesis

Shown in Scheme 2 is the synthetic pathway used to make croconaine rotaxane **2**. Croconic acid was condensed with two molar equivalents of the previously reported thienothiophene **3**,^[27] to give croconaine dye **C2** in 36% yield. As discussed further below, mixing **C2** with macrocycle **M** in chloroform solution, with heating by sonication over 6 hours, produced the threaded complex **MDC2** in near-quantitative yield. The threaded complex was purified by column chromatography (silica gel) and then converted into rotaxane **2** by conducting a copper-catalyzed azide/alkyne cycloaddition reaction that covalently attached a bulky stopper group to each end of the dye and produced the permanently threaded rotaxane in 82% yield.

Spectral Properties

In Figure 1 is a comparison of ¹H NMR spectra in CDCl₃ for separate samples containing **C2**, **MDC2**, or **M**. Inspection of the spectra reveals the expected changes in chemical shift that are diagnostic of macrocycle threading.^[25] Notably, the peaks for protons 1 and 2 on **C2** and protons E and F on **M** are shifted upfield due to changes in aromatic ring shielding caused by threading. In addition, the peaks for protons C and D on **M** are shifted downfield

due to hydrogen bonding interactions with the oxygens atoms on the encapsulated croconaine.^{[28][29]} Another expected feature of the NMR spectral pattern for **MDC2** is the appearance of many of the signals as multiple peaks.^[25] The spectral expansion in Figure 2 clearly shows that the signal for macrocycle protons B exists as three pairs of singlets in a population ratio is 6:3:1. Also shown in Figure 2 is a schematic rationalization for these three sets of peaks. The encapsulated **C2** can adopt three low-energy conformational isomers relative the central croconaine core, and the unsymmetric structure of each isomer induces the two macrocycle protons B to be inequivalent. The NMR data does not allow assignment of the NMR signals to a specific dye conformation

As expected, the ¹H NMR spectra for rotaxane **2** (Figure S5) is very similar to the spectrum above for **MDC2**. However, there is a difference in the peak shape for three protons on the encapsulated dye. As shown in Figure 3A, the spectrum for threaded complex **MDC2** at 20°C exhibits sharp peaks for dye protons 2, 3 and 5. In the case of rotaxane **2** at 20°C, the peaks for the same dye protons are very broad, but they separate and sharpen when the temperature is lowered. We know from previous dynamic NMR studies of squaraine rotaxanes that the C-N bond at each end of a pseudooxocarbon chromophore has partial double character that can restrict bond rotation.^[30] Thus, the difference in peak shape is very likely because rotation around the croconaine C-N bond (Figure 3B) at 20°C is rapid in **MDC2**, but more restricted in rotaxane **2**. The only difference between these two dye encapsulated structures is the identity of the terminal groups that flank the croconaine core. In the case of **2**, the terminal group is a large benzyltriazole derivative and we speculate that it interacts with surrounding macrocycle in way that increases the barrier to C-N bond. There is precedence for this type of interaction in analogous threaded complexes. For example, we have recently shown that the flanking chains on an encapsulated squaraine dye can undergo back-folding and form stabilizing interactions with the surrounding macrocycle.^[31] Similarly, work on structurally related tetralactam rotaxanes has reported evidence for interactions between the ends of the encapsulated thread and the surrounding macrocycle.^{[32] [28] [33]} It is worth noting that our previous study of rotaxane **1** also observed broad NMR peaks for dye protons 2, 3 and 5 but the published report did not offer a structural explanation.^[25] Presumably it is the same phenomenon.

The absorption properties of dyes **C1** and **C2** and rotaxanes **1** and **2** are listed in Table 1. The change in absorption maxima from 824 nm for **1** to 984 nm for **2** is even larger than the change observed with the analogous squaraine series.^[27] The 30–40 nm red shift in croconaine absorption upon encapsulation by **M** is consistent with our previous studies.^[14] As shown by the absorption spectra in Figure 4, the absorption maxima bands for **1** and **2** are quite sharp with little spectral overlap. Each dye exhibits very weak fluorescence which is typical for this class of croconaine dyes.^[14]

Photothermal Heating Experiments

To demonstrate wavelength-selective heating of rotaxanes **1** and **2**, two laser diodes were chosen with 830 and 980 nm beam lines that closely matched the respective λ_{max} values. Two separate plastic tubes (Eppendorf tubes) were charged with solutions of **1** or **2** (5 μM in CHCl_3), and the temperature in each tube was monitored using a thin thermocouple wire and

also an external thermal video camera. The first photothermal experiment irradiated the entirety of each tube with the 830 nm laser (6.25 W/cm^2) for 10 minutes and shown in Figure 5A-D is the change in temperature for each tube. After 10 minutes of 830 nm irradiation, the temperature of the tube containing rotaxane **1** increased by 6°C , while there was minimal change in the temperature of the tube containing **2**. The photothermal experiment was repeated using the 980 nm laser (5.00 W/cm^2). After 10 minutes of laser irradiation, the temperature of the tube containing rotaxane **2** increased by 7°C , while the temperature of the tube containing **1** was unchanged (Figure 5E-H). To test the photostability of rotaxane **2**, a sample ($5 \mu\text{M}$, CHCl_3) was irradiated with the 980 nm laser for 5 minutes and allowed to cool back to room temperature (Figure 6). This heating/cooling cycle was repeated four times on the same sample and the change in temperature was consistent, indicating no fatigue of the dye.

Conclusions

A new NIR croconaine dye **C2** with two thienothiophene flanking units was prepared and converted into rotaxane **2** by conducting a “clicked capping” reaction. Rotaxane **2** exhibits an intense and narrow absorption band at 984 nm which is greatly red-shifted compared to the 824 nm absorption maxima of known croconaine rotaxane **1** with two thiophene flanking units. The minimal spectral overlap of the two absorption bands enabled wavelength-selective heating of separate solutions using two diode lasers. An 830 nm laser selectively heated the sample of **1** and a 980 nm laser selectively heated the sample of **2**. The solution of rotaxane **2** showed no evidence of fatigue after four laser heating and cooling cycles. It should be possible to exploit wavelength-selective laser heating for a variety of applications such as polymer welding,^[34] heat reversible materials,^{[20] [21]} or photothermal therapy.^{[22] [23]} In addition, there is great potential for new approaches to ratiometric photoacoustic imaging.^{[24] [35]}

Experimental Section

Materials

Commercially available solvents and chemicals were purchased from Sigma-Aldrich, Alfa-Aesar, and VWR international and used without further purification unless otherwise stated. Thienothiophene **3** was prepared using a previously reported procedure.^[27] Flash column chromatography was performed using Biotage flash purification system with SNAP Ultra flash chromatography cartridges. ^1H and ^{13}C NMR spectra were recorded on 400 and 500 MHz spectrometers. Chemical shift was presented in ppm and referenced by residual solvent peak. Mass spectrometry (MS) was performed using a time-of-flight spectrometer.

Croconaine Dye **C2**

Croconic acid (559 mg, 0.0039 mol) and N-ethyl-N-(2-(prop-2-yn-1-yloxy)ethyl)thieno[3,2-b]thiophen-2-amine **3** (1.73 g, 0.0083 mol) were dissolved in 1:1 anhydrous toluene/1-butanol (30 mL) and heated at reflux for 1 h under Ar. After this time, the solution was allowed to cool to room temperature and the solvent removed *in vacuo*. The crude residue was purified by silica gel column chromatography using 0–10% acetone/dichloromethane to

elute the croconaine dye product **C2** as a black solid (80.4 mg, 36%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=8.74 (m, 2H; CH), 6.24 (s, 2H; CH), 4.12 (d, ³J(H,H)=4 Hz, 4H; CH), 3.73 (t, ³J(H,H)=4 Hz, 4H; CH₂), 3.61 (t, ³J(H,H)=4 Hz, 4H; CH₂), 3.61 (q, ³J(H,H)=8 Hz, 4H; CH₂), 2.39 (t, ³J(H,H)=4 Hz, 2H; CH), 1.26 ppm (t, ³J(H,H)=8 Hz, 6H;CH₃). Low solubility and dye-self-aggregation prevented ¹³C NMR analysis. MS-ESI *m/z* 636.0853 ([*M*]⁺, C₃₁H₂₈N₂O₅S₄, calcd 636.0876). λ_{abs,max} (CHCl₃): 941 nm, log ε (CHCl₃): 5.39.

Threaded Complex **MDC2**

Croconaine dye **C2** (25 mg, mmol) and anthracene macrocycle **M** (42mg, mmol) were dissolved in CHCl₃ (4 mL) and the solution was heated by sonication for 6 h. After this time, the solvent was removed *in vacuo* and the resulting residue purified by gradient silica gel column chromatography using 0–20% acetone/dichloromethane to elute the threaded complex product **MDC2** as a dark purple solid (35 mg, 62%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=9.16–9.69 (m, 2H, CH), 8.30–8.47 (m, 4H, CH), 7.81–8.30 (m, 4H, NH), 7.76–7.69 (m, 8H, CH), 7.22–7.40 (m, 2H, CH), 6.36–6.92 (m, 8H, CH), 5.90–6.02 (m, 2H, CH), 4.93–5.13 (m, 8H, CH₂), 4.21–4.22 (m, 4H, CH₂), 3.81–3.85 (m, 4H, CH₂), 3.67–3.71 (m, 4H, CH₂), 3.58–3.63 (m, 4H, CH₂), 2.46–2.47 (m, 2H, CH), 1.45–1.51 (m, 18H, CH₃), 1.36–1.40 ppm (m, 6H, CH₃). MS-ESI *m/z* 1480.4885 ([*M*]⁺, C₈₇H₈₀N₆O₉S₄, calcd 1480.4864). λ_{abs,max} (CHCl₃): 980 nm, log ε (CHCl₃): 5.30 M⁻¹cm⁻¹.

Croconaine Rotaxane **2**

Threaded complex **MDC2** (23 mg, 0.0155 mmol), 1-(azidomethyl)-3,5-di-tert-butylbenzene **4** (11 mg, 0.0466 mmol), Cu(I)TBTA Br (3 mg, 0.0047 mol) and DIPEA (6 μL, 0.0466 mmol) were dissolved in CHCl₃ (4 mL) and the solution was sonicated for 4 h. The solvent was removed *in vacuo* and the resulting residue purified by gradient silica gel column chromatography using 5–20% acetone/dichloromethane to elute the rotaxane product **2** as a purple/brown solid (25mg, 82%). ¹H NMR (400 MHz, CDCl₃, 25°C, TMS): δ=9.18–9.78 (m, 2H, CH), 8.34–8.48 (m, 4H, CH), 7.85–8.34 (m, 4H, NH), 7.50–7.72 (m, 10H, CH, CH), 7.44–7.48 (m, 2H, CH), 7.35 (m, H, 2CH), 7.04 (m, H, 4CH), 6.37–6.85 (m, 8H, CH), 5.44 (m, 4H, CH₂), 5.05–5.13 (m, 8H, CH), 4.67 (m, 4H, CH₂), 3.83 (m, 4H, CH₂), 1.46–1.53 (m, 18H, CH₃), 1.32 (m, 6H, CH₃), 1.22 (m, 36H, CH₃). ¹³C NMR (100 MHz, CDCl₃, 25°C, TMS): δ=184.4, 167.7, 167.7, 167.4, 167.3, 152.2, 152.1, 151.9, 144.3, 133.8, 133.5, 133.4, 133.3, 130.6, 130.5, 130.4, 130.2, 128.8, 128.7, 128.5, 128.3, 125.7, 125.6, 125.2, 124.9, 124.6, 124.3, 124.1, 123.8, 122.9, 122.6, 122.5, 77.3, 64.6, 54.9, 53.8, 38.6, 38.2, 35.4, 35.3, 34.9, 33.7, 31.9, 31.6, 31.6, 31.5, 31.5, 31.4, 30.2, 29.7, 29.4, 29.3, 29.0, 27.5, 26.7, 23.2, 22.7, 14.2, 14.2. MS-ESI *m/z* 1970.8613 ([*M*]⁺, C₁₁₇H₁₂₆N₁₂O₉S₄, calcd 1970.8648). λ_{abs,max} (CHCl₃): 984 nm, log ε (CHCl₃): 5.29 M⁻¹cm⁻¹.

Laser Heating Experiments

Separate 1 mL solutions of **1** or **2** in CHCl₃ (5.0 μM) were dispensed into two plastic Eppendorf tubes and an Omega hypodermic thermocouple (HYPO-33–31T-G-60-SMPW-M) was inserted into the solution. Each tube was irradiated from above by a continuous wave diode laser (ThorLabs Inc, 830 nm, 6.25 W/cm² or 980 nm, 5.00 W/cm²) and the change in solution temperature was monitored in real time using a USB calibrated thermal video

camera (Infrared Cameras Inc, 7320) and confirmed using the thermocouple. A dye fatigue study conducted four heating/cooling cycles. Each cycle irradiated a sample of **2** in CHCl₃ (5.0 μM) for 5 minutes using the 980 nm laser, followed by 5 minutes of dark to allow the solution to cool back to room temperature.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.
Chemical structures including croconaine rotaxanes.

Scheme 2.
Synthesis of **C2**, **MDC2**, and **2**.

Figure 1. Partial ^1H NMR (CDCl_3 , 400 MHz) spectra of separate samples containing (A) **C2**, (B) **MDC2**, and (C) **M**. Atom labels are provided in Scheme 2.

Figure 2.

(A) Expansion of ^1H NMR spectrum (CDCl₃, 400 MHz) for **MDC2** showing the peaks for proton B as three pairs of singlets in a ratio of 6:3:1. (B) The encapsulated croconaine **2** exists as three low energy conformational isomers that exchange slowly on the NMR time scale. The red ring is the surrounding **M** and the yellow circles are sulfur atoms in **2**.

Figure 3.

(A) ^1H NMR (CDCl_3 , 400 MHz) signals for dye protons 2, 3 and 5 in **MDC2** at 20°C, and the same protons in **2** at 20°C and -50°C. (B) Illustration of croconaine C-N bond rotation that exchanges the chemical shifts of protons 2, 3, and 5. The rotation is relatively rapid in **MDC2** but slow in rotaxane **2**.

Figure 4. Overlay of the absorption spectra for **1** and **2** (5 μ M in CHCl_3). The dotted lines indicate the relative absorption of 830 nm and 980 nm laser lines by each rotaxane.

Figure 5.

(A) Change in temperature of solutions containing **1** or **2** ($5\mu\text{M}$, CHCl_3) over 10 minutes of irradiation with 830 nm laser, (B) bright field view of a sample tube, (C) and (D) thermal images of tubes containing **1** or **2** after 10 minutes of irradiation with 830 nm laser. (E) Change in temperature of solutions containing **1** or **2** ($5\mu\text{M}$, CHCl_3) over 10 minutes of irradiation with 980 nm laser, (F) bright field view of a sample tube, (G) and (H) thermal images of tubes containing **1** or **2** after 10 minutes of irradiation with 980 nm laser.

Figure 6. Four heating/cooling cycles for a sample tube containing **2** that was irradiated each cycle at 980 nm (5.00 W/cm²) for five minutes.

Table 1.

Absorption maxima (λ_{max}) and molar extinction coefficients (ϵ) in CHCl_3 .

	C1	1	C2	2
λ_{max} (nm)	795	824	940	984
log ϵ	5.39	5.26	5.39	5.29