Supporting Information

A Cyclodextrin-Insulated Anthracene Rotaxane with Enhanced Fluorescence and Photostability

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Experimental Procedures

General. Unless otherwise noted, all starting materials were obtained from commercial suppliers and were used without further purification. All air- or moisture-sensitive reactions were done under an atmosphere of dry nitrogen. Thin layer chromatography (TLC) was performed using aluminum-foil backed plates precoated with Kieselgel 60 F_{254}. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from Aldrich. ^{1}H NMR and ^{13}C NMR spectra were recorded on Brucker DPX 200, DPX 400, and AV 500 with $^{13}C\{^{1}H\}$ cryoprobe. NOESY was performed on Bruker DRX500. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as an internal standard. Coupling constants, *J*, are reported in Hertz (Hz), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Mass spectra were obtained through the Mass Spectrometry Facility, Chemistry Research Laboratory, University of Oxford. Electrospray ionization (ESI) mass spectra were obtained out on a Micromass LCT platform. Field ionization (FI) and electron impact ionization (EI) mass spectra were obtained out on a Micromass GCT. UV-vis spectra were performed on a Perkin Elmer Lamda-6. Fluorescence data were recorded with a fluoromax-2 fluorimeter (Horiba Jobin Yuon).

HPLC analyses were carried out on an Agilent HP 1100 series workstation. The analytes were eluted using a timetabled two-solvent gradient system and monitored using a diode array detector as shown in the graph below where CHAPS is 0.25 % w/v dicyclohexylammonium phosphate in ultra-pure water and MeOH is methanol (Figure S1). Analytical HPLC was carried out using a Zorbax Eclipse XDB C8 analytical column (4.6 x 15 mm, 5 micron) at a flow rate of

1 mL min^{-1}. Preparative HPLC was carried out using a Zorbax Eclipse XDB C8 semi-preparative column (9.4 x 250 mm, 5 micron) at a flow rate of 4 mL min^{-1}.

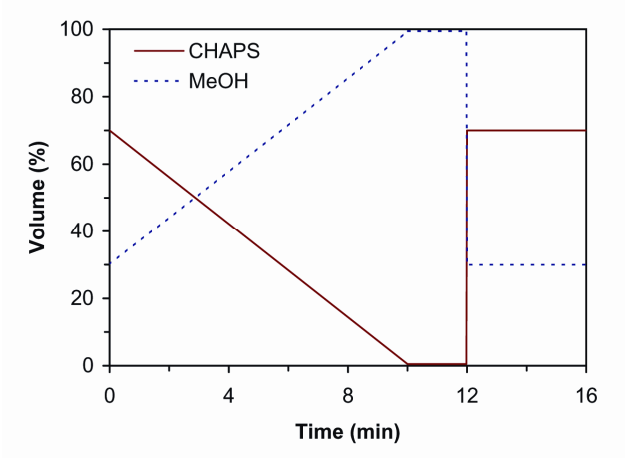
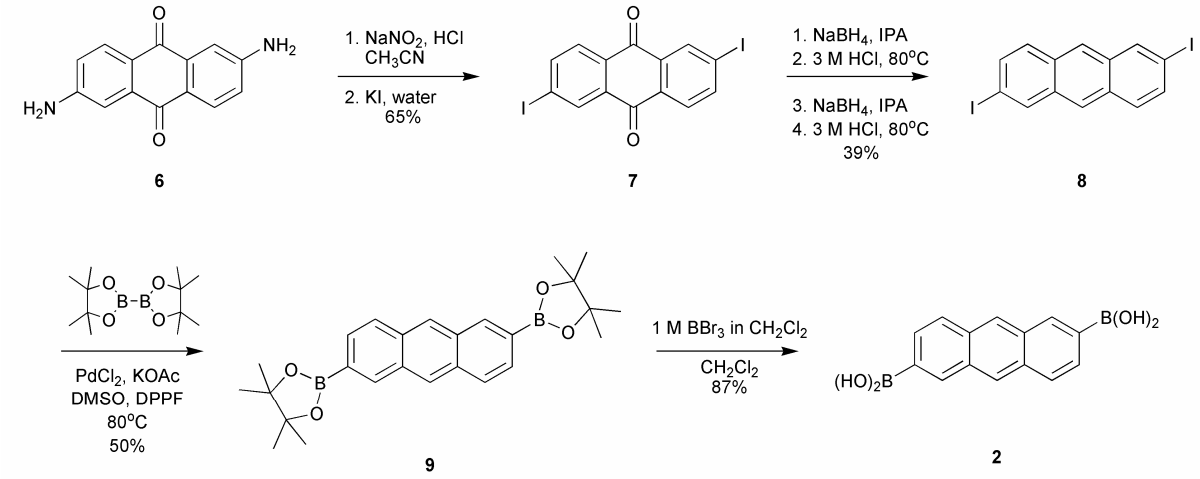


Figure S1. HPLC timetabled two-solvent gradient system.

Synthesis. Synthesis of 2,6-anthracene-bis-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **9** has been reported by Meng and coworkers from 2,6-dibromoanthracene.[1] To our knowledge compounds **3**, **6**, and **8** have not been previously prepared and procedures for compounds were adapted from cited references.



Scheme S1. Synthesis of anthracene-2,6-diboronic acid **2**.

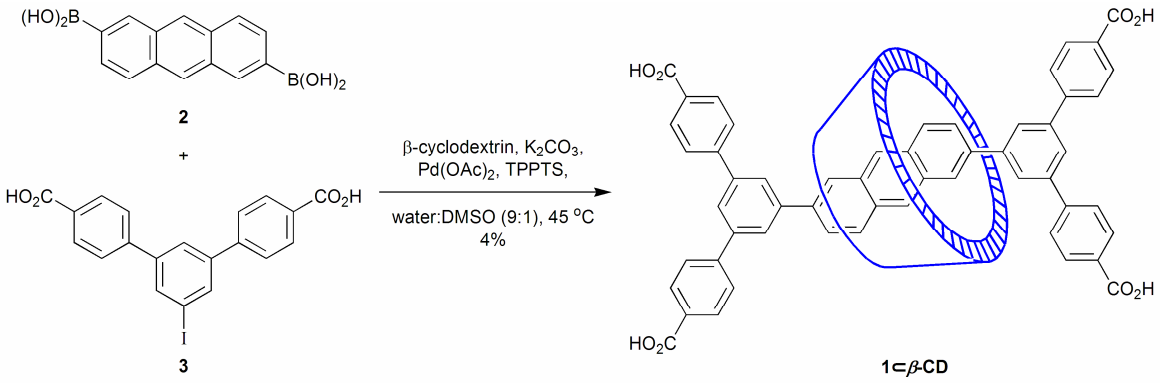
2,6-Diiodo-9,10-anthraquinone (7).[2] To a 1 L round bottom flask was added 2,6-diaminoanthraquinone **6** (10.0 g, 42.2 mmol), acetonitrile (300 mL), and hydrochloric acid (160 mL of 1.5 M). The resulting slurry was cooled to 0 °C in an ice bath and then a solution of sodium nitrite (6.95 g, 101 mmol) in water (15 mL) also at 0 °C was slowly added. The reaction mixture was then stirred for 30 min at 0 °C and then added to a second 1 L round bottom flask containing a solution of potassium iodide (35.6 g, 214 mmol) in water (50 mL) cooled to 0 °C. Then the solution was allowed to warm to room temperature with stirring for 1 h and then it was heated to 60 °C for another hour. The product was then recovered by filtration and washing with copious amounts of water and then methanol. The product was purified by stirring the solid in dichloromethane (200 mL) until a fine suspension was formed, filtered, washed with an additional amount of dichloromethane (100 mL), and then dried under vacuum to give 12.6 g (27.3 mmol, 65%) of pure **7** as a light brown semicrystaline solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8. 66 (d, J = 2 Hz, 2H), 8.19 (dd, J = 8, 2 Hz, 2H), 7.99 (d, J = 8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) 181.6, 143.4, 136.3, 133.8, 132.1, 128.8, 102.8; HRMS (FI) *m/z* $[M]^+$ calcd for $C_{14}H_6I_2O_2$ 459.8451; found, 459.8463.

2,6-Diiodoanthracene (8).[3] To a 500 mL round bottom flask were added 2,6-diiodo-9,10-anthraquinone **7** (8.04 g, 18.7 mmol) and isopropanol (200 mL) to give a suspension. Sodium borohydride (2.84 g, 75.1 mmol) was added and the mixture was stirred for 15 h at room temperature, then poured over ice water, and filtered to give a solid. The solid was added to a 500 mL round bottom flask along with hydrochloric acid (200 mL, 3.0 M) and was heated to 80 °C for 6 h. Then the solution was cooled and filtered to give a solid. The solid was placed in a 500 mL round bottom flask along with isopropanol (250 mL) and then sodium borohydride (3.95 g, 104 mmol) was added. The reaction mixture was refluxed for 18 h then allowed to cool to room temperature and then added to hydrochloric acid (400 mL, 3.0 M). Product was recovered by filtration and was washed with copious amounts of water and methanol. The product was purified by stirring the solid in dichloromethane (100 mL) until a fine suspension was formed, filtered, washed with additional dichloromethane (100 mL), and then dried under vacuum to give 3.14 g (7.30 mmol, 39%) of pure **7** as a light brown solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.42 (d, J = 1 Hz, 2H), 8.26 (s, 2H), 7.74 (d, J = 9 Hz, 2H), 7.69 (dd, J = 9, 1 Hz, 2H); ^{13}C NMR (125

MHz, $CDCl_3$) 136.9, 134.4, 133.1, 130.2, 129.7, 125.3, 91.8; HRMS (EI) *m/z* $[M]^+$ calcd for $C_{14}H_8I_2$ 429.8716; found, 429.8722.

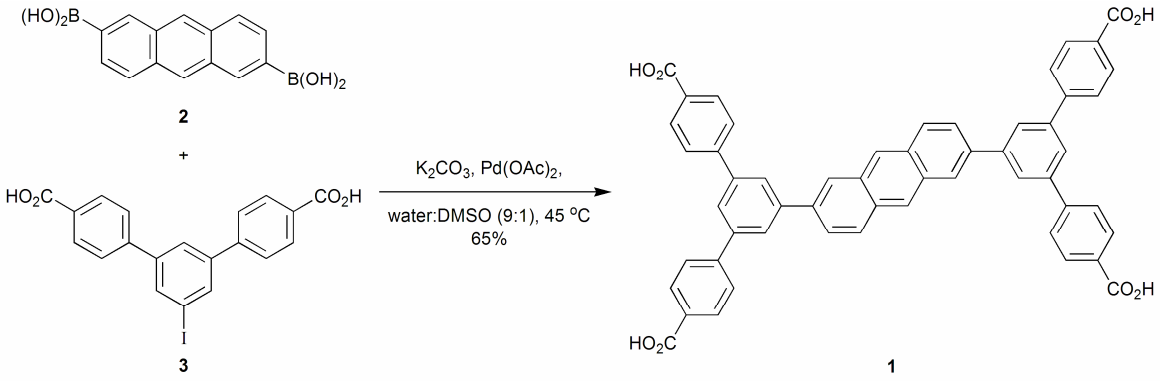
2,6-Anthracene-bis-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9).[1] To a 100 mL round bottom flask was added 2,6-diiodoanthracene **8** (1.00 g, 2.32 mmol), bis(pinacolato)diboron (1.20 g, 4.71 mmol), palladium (II) dichloride (34.3 mg, 0.195 mmol), 1,1'-bis(diphenylphosphino)ferrocene (131 mg, 0.236 mmol), and potassium acetate (1.13 g, 11.5 mmol). The flask was evacuated and filled with nitrogen three times and then dry dimethyl sulfoxide (30 mL) was added and the solution was degassed under vacuum three times. The solution was heated to 60 °C for 16 h, then it was allowed to cool to room temperature, poured into ice water (100 mL), and then extracted with dichloromethane (3 × 30 mL). The combined organic layer was washed with water, dried with magnesium sulfate, filtered, concentrated *in vacuo*, and purified by silica gel column chromatography (petroleum ether/dichloromethane, 1/1, 0/1) to give 0.504 g (1.17 mmol, 50%) of pure **9** as light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 2H), 8.45 (s, 2H), 8.00 (d, J = 8 Hz, 2H), 7.79 (d, J = 9, 2H), 1.42 (s, 24H); ^{13}C NMR (50 MHz, $CDCl_3$) 137.3, 132.7, 131.8, 129.6 129.1, 127.4, 127.1, 84.0, 24.9; HRMS (FI) *m/z* $[M]^+$ calcd for $C_{26}H_{32}B_2O_4$ 430.2487; found, 430.2471; TLC R_f = 0.24 (chloroform/hexanes, 3/2).

Anthracene-2,6-diboronic acid (2). To a 50 mL round bottom flask was added 2,6-anthracene-bis-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **9** (333 mg, 0.775 mmol) and dichloromethane (10 mL). The solution was cooled to 0 °C and then a solution of boron tribromide in dichloromethane (4 mL, 1.0 M) was added under a nitrogen atmosphere. The ice bath was removed and the solution was stirred for 1 h. The reaction was quenched with ice water (20 mL), the resulting precipitate was washed with dilute hydrochloric acid (0.1 M) and water, and then dried under vacuum to give 180 mg (0.675 mmol, 87%) of **2** as a pale brown solid and the material was used for the next reaction without any further purification: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 2H), 8.54 (s, 2H), 8.25 (bs, 4H), 8.04 (d, J = 9 Hz, 2H), 7.84 (d, J = 9 Hz, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) 135.6, 131.9, 131.7 (broad), 131.3, 129.6, 126.7, 126.3; MS (ESI) *m/z* $[M - H]^-$ calcd for $C_{14}H_{11}B_2O_4$ 265.0843; found, 265.0839.



Scheme S2. Synthesis of *β*-cyclodextrin anthracene rotaxane **1**⊂*β*-CD.

***β*-Cyclodextrin anthracene rotaxane (1⊂*β*-CD).** To a 50 mL round bottom flask was added anthracene-2,6-diboronic acid **2** (82.6 mg, 0.310 mmol), iodoterphenylenedicarboxylic acid **3** (273 mg, 0.613 mmol), potassium carbonate (496 mg, 3.59 mmol), *β*-cyclodextrin (2.11 g, 1.86 mmol), and trisodium triphenylphosphine-3,3′,3′′-trisulfonate (20 mg, 0.035 mmol). The flask was evacuated and filled with nitrogen three times and then degassed water (18 mL) was added. The solution was degassed three times under vacuum and a solution of palladium acetate (6.9 mg, 0.031 mmol) in dimethylsulfoxide (2 mL) was added. The solution was then heated to 45 °C for 18 h. The product was precipitated with hydrochloric acid (1.0 M) and separated from the supernatant by centrifugation. The product was extracted from the precipitate several times with methanol and concentrated *in vacuo*. The product was then purified by preparative reverse phase high performance chromatography to give 22.1 mg (0.0113 mmol, 4%) of pure **1**⊂*β*-CD as pale white solid: λ_{max} (phosphate buffer pH 11.4) 300 nm (ε = 152,000); ^{1}H NMR (400 MHz, CD_3OD) δ 8.86 (s, 1H), 8.83 (s, 1H), 8.57 (1H), 8.46 (d, J = 9 Hz, 1H), 8.32 (1H), 8.31 (d, J = 10, 2H), 8.26-8.01 (m, 10H), 8.13-8.01 (m, 14H) 4.90 (d, J = 4 Hz, 7H), 3.80 (t, J = 9 Hz, 7H), 3.69 (dd, J = 12, 3 Hz, 7H), 3.57 (m, 14H), 3.48 (d, J = 9 Hz, 7H), 3.48 (dd, J = 10, 3 Hz, 7H); HRMS (ESI) *m/z* $[M - H]^-$ calcd for $C_{96}H_{104}O_{43}$ 1944.59; found, 1944.59.



Scheme S3. Synthesis of anthracene dumbbell **1**.

Anthracene dumbbell (1). To a 25 mL round bottom flask was added anthracene-2,6-diboronic acid **2** (30.7 mg, 0.115 mmol), iodoterphenylenedicarboxylic acid **3** (107 mg, 0.403 mmol), and potassium carbonate (185 mg, 1.34 mmol). The flask was evacuated and filled with nitrogen three times and then degassed water (5 mL) was added. The solution was degassed three times under vacuum and a solution of palladium acetate (2.6 mg, 0.012 mmol) in dimethyl sulfoxide (0.5 mL) was added. The solution was then heated to 45 °C for 18 h. The product was precipitated with hydrochloric acid (1.0 M), separated by centrifugation, and washed with methanol, then purified by repeated precipitation from dimethyl sulfoxide with methanol to give 60.4 mg (0.0745 mmol, 65%) of pure **4** as waxy yellow solid: λ_{max} (phosphate buffer pH 11.4) 298 nm (ε = 127,000); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 2H), 8.71 (s, 2H), 8.29 (d, J = 9 Hz, 2H), 8.27 (d, J = 1 Hz, 2H), 8.17-8.09 (m, 20H); ^{13}C NMR (125 MHz, DMSO-d_6) 167.2, 144.1, 141.6, 140.8, 136.6, 131.7, 131.0, 130.00 129.98, 129.0, 127.5, 126.6, 126.1, 125.7, 125.6, 125.0; HRMS (ESI) *m/z* [M – H]$^-$ calcd for $C_{54}H_{33}O_8$ 809.2170; found, 809.2166.

^{1}H NMR NOESY. Spectra of rotaxane **1**⊂*β*-CD were collect at 500 MHz in CD_3OD at 298 K with a mixing time of 400 ms.

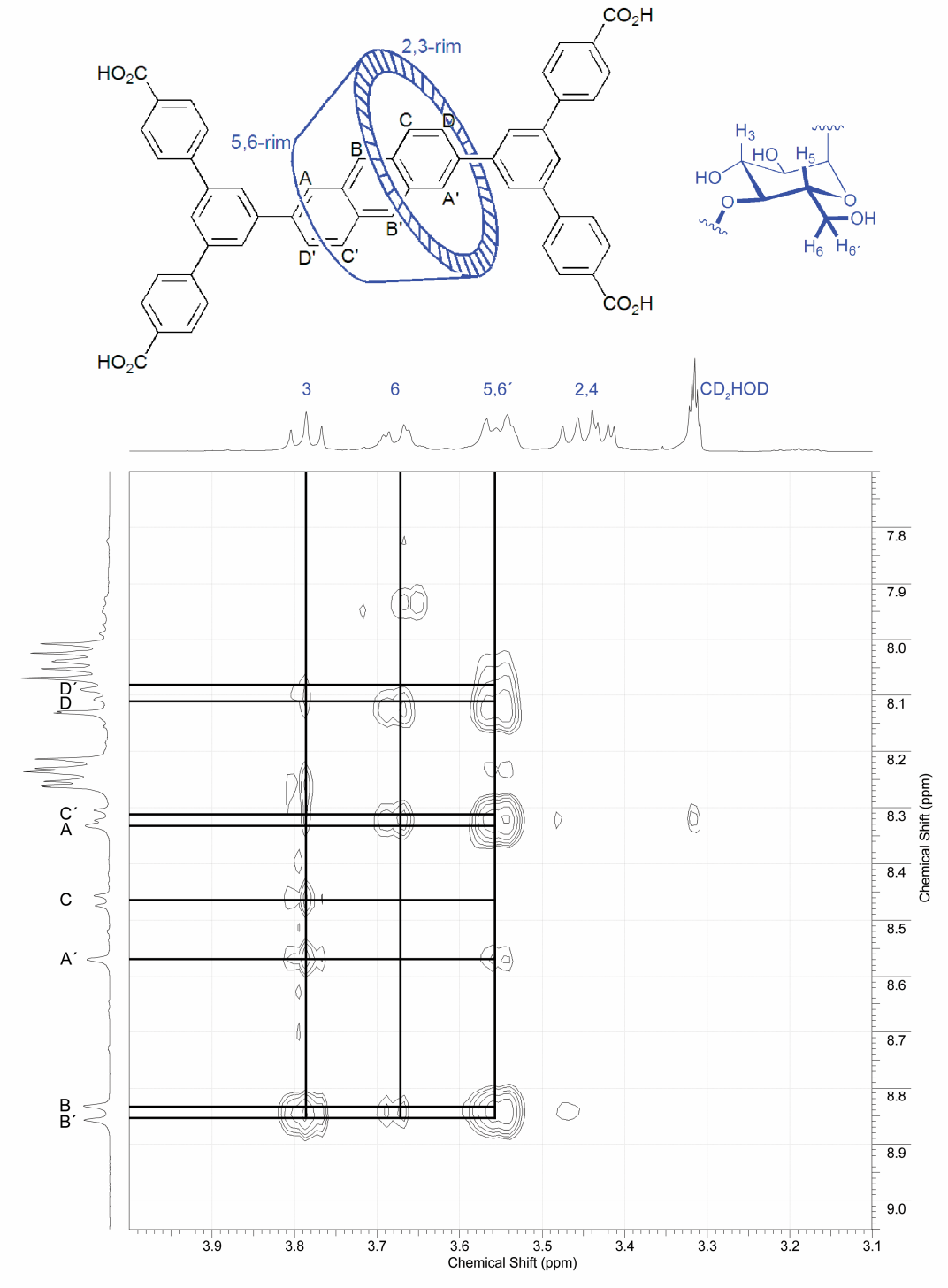


Figure S2. Selected region of the ^{1}H NMR NOESY of rotaxane **1**⊂*β*-CD.

Mass spectrum of 1⊂*β*-CD.

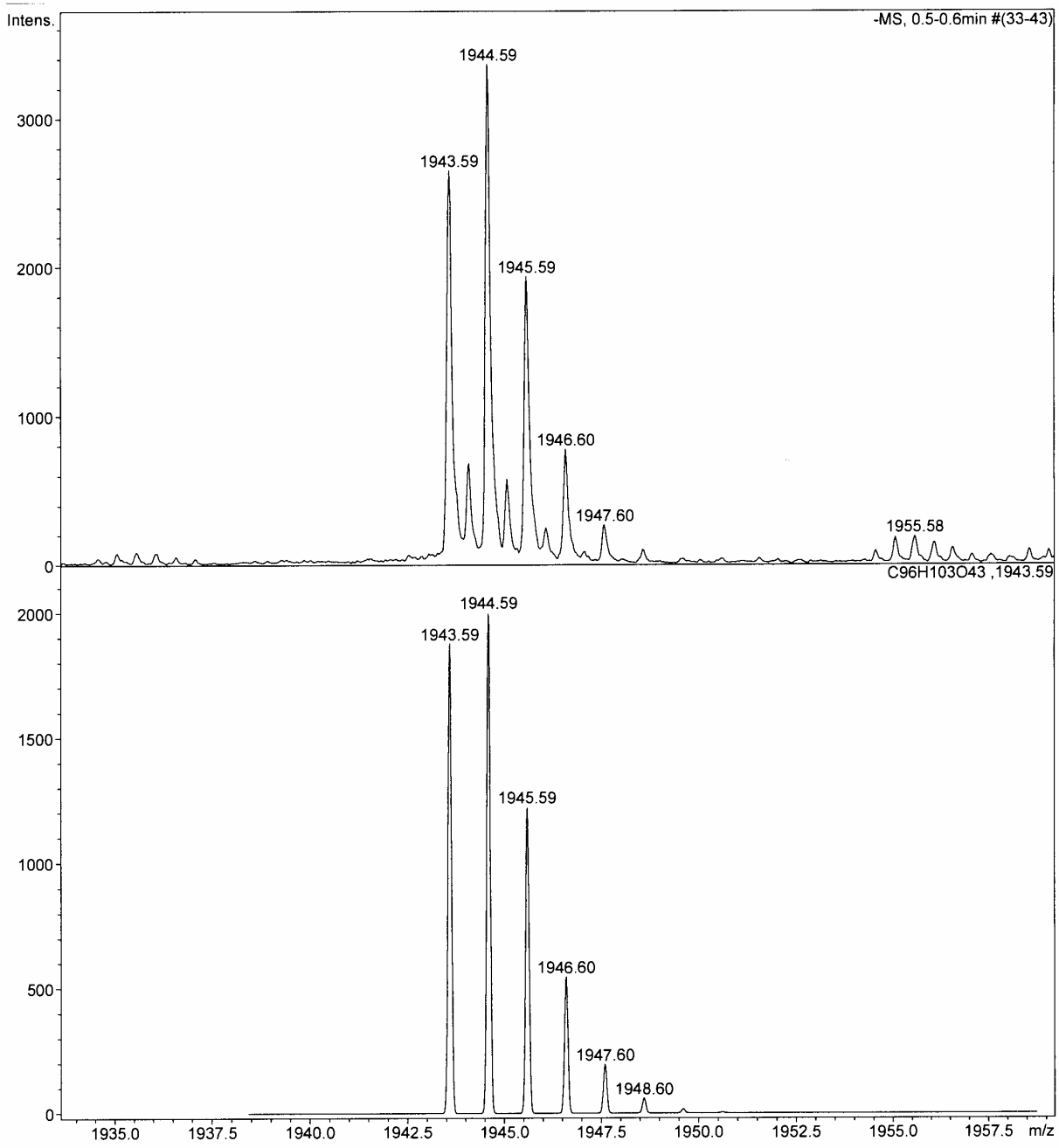
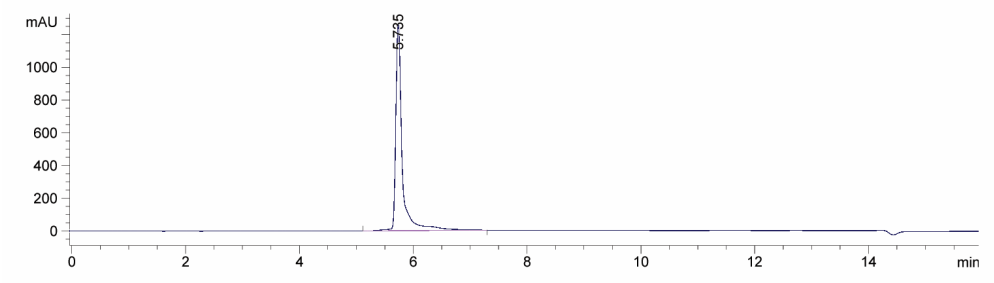


Figure S3. High resolution mass spectrum of rotaxane **1**⊂*β*-CD (top) and calculated isotopic pattern (bottom).

Analytical HPLC. Chromatograms below were monitored at 280 nm as a function of time and were collected according to the method outlined in the general experimental procedures.

Rotaxane **1**⊂*β*-CD



Dumbbell **1**

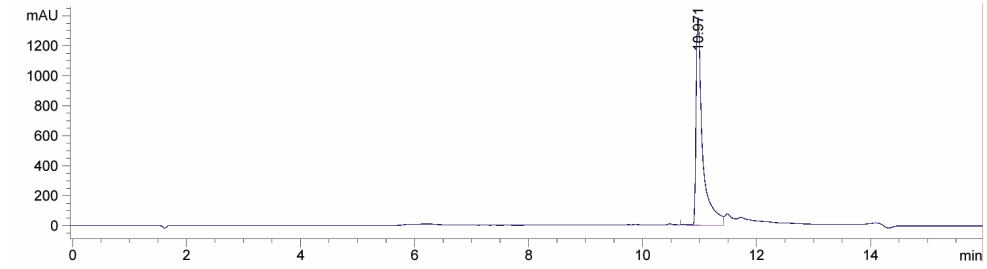


Figure S4. Chromatograms of rotaxane **1**⊂*β*-CD and dumbbell **1**.

UV absorption spectra. Spectra of rotaxane **1**⊂*β*-CD and dumbbell **1** were collected at ca. 7 μM in pH 11.4 buffered solutions at room temperature.

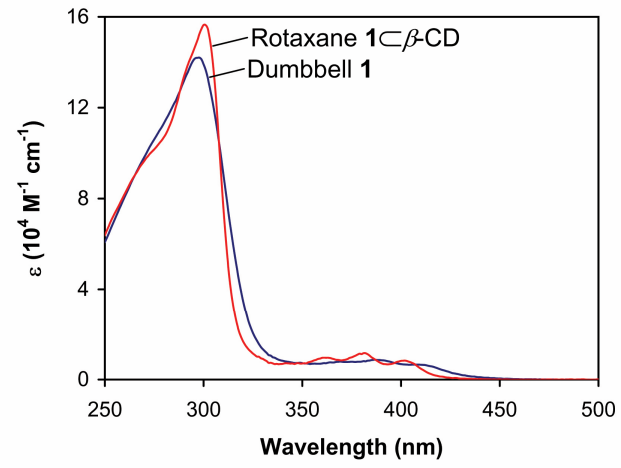


Figure S5. UV spectrum of rotaxane **1**⊂*β*-CD and dumbbell **1**.

UV Dilution. Solutions of rotaxane **1**⊂*β*-CD and dumbbell **1** in pH 11.4 buffered solutions at room temperature were recorded at various concentrations.

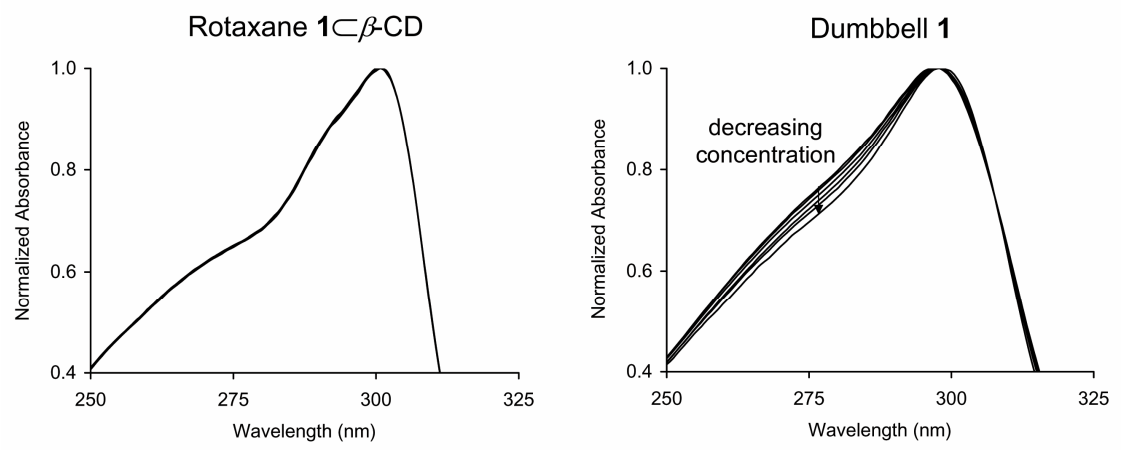


Figure S6. UV absorbance spectra of rotaxane **1**⊂*β*-CD at 11, 8.9, 6.7, 4.5, and 2.2 μM and dumbbell **1** at 8.8, 7.3, 5.9, 4.3, 2.9, and 1.5 μM. Spectra were normalized to their maximum absorbance for comparison of their shape.

Measurement of fluorescence quantum yield. Fluorescence spectra were collected in ~5 mM sodium hydroxide at room temperature and were excited at 350 nm. The spectra were collected from 365 nm to 685 nm. The absorbance of a stock solution was measured and the absorbances of individual solutions were then calculated according the Beer-Lambert law. The fluorescence quantum yields of rotaxane **1**⊂*β*-CD (Φ_F = 0.39) and dumbbell **1** (Φ_F = 0.38) were calculated by referencing quinine in 0.1 M sulfuric acid (Φ_F = 0.50) reported by Dawson and Windsor.[4]

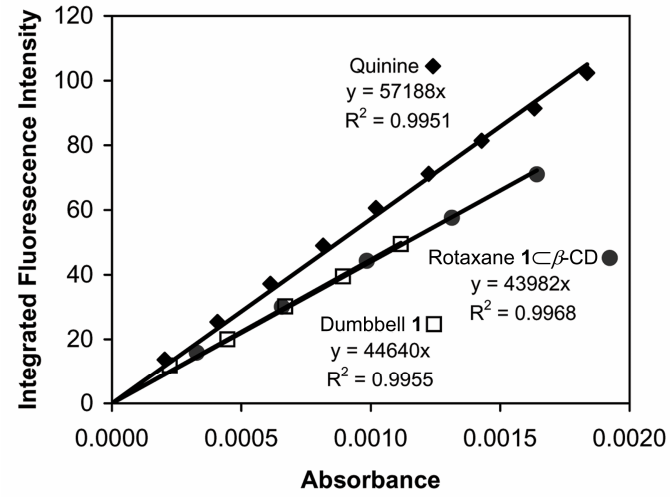


Figure S7. Integrated fluorescence intensity as a function of the absorbance at 350 nm where rotaxane **1**⊂*β*-CD, dumbbell **1**, and a quinine standard were excited.

Photobleaching kinetics. Solutions of rotaxane **1**⊂*β*-CD and dumbbell **1** were prepared at 6.7 μM and 8.1 μM in phosphate buffered aqueous solutions, respectively. A 2 mL portion of each solution was irradiated at 380 nm in a quartz fluorescence cuvette in a fluorimeter. The spectra were fit to a pseudo first-order rate equation using SPECFIT software.

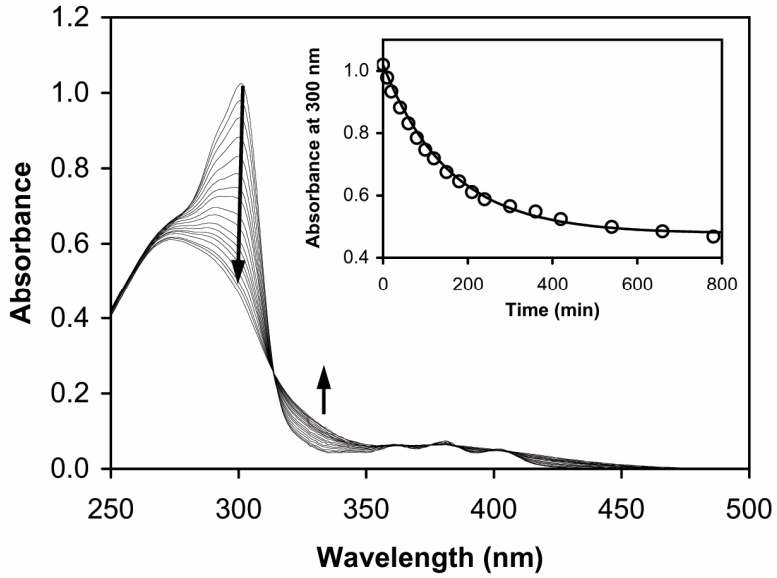


Figure S8. UV spectra of rotaxane **1**⊂*β*-CD as the time irradiated is increased. The inset shows data was fit to a pseudo first order rate constant ($t_{½}$ = 109 ± 4 min, k = 0.00634 ± 0.00024 min^{-1}).

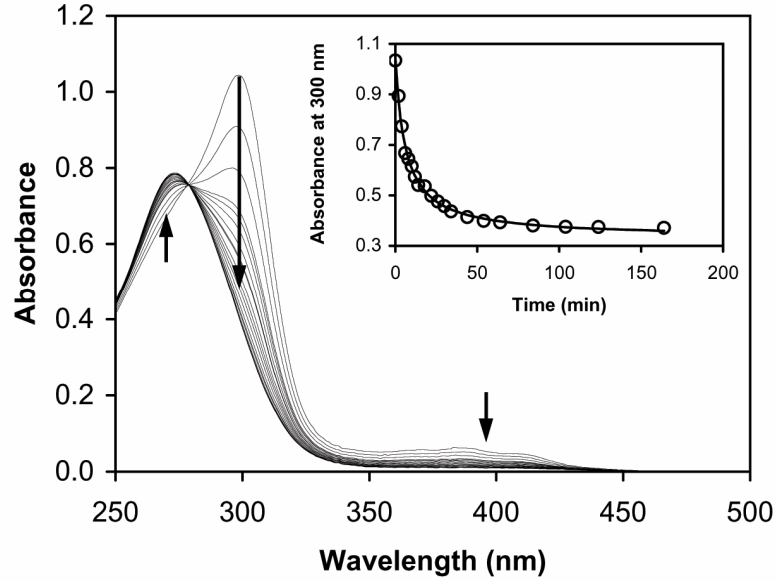


Figure S9. UV spectra of dumbbell **1** as the time irradiated is increased. The inset shows data was fit to a second order rate constant ($t_{½}$ = 13 ± 0.4 min at 8.1 μM, k = 9800 ± 350 M^{-1} min^{-1})

Mass spectrum of rotaxane 1⊂β-CD after photoirradiation for 18 hours.

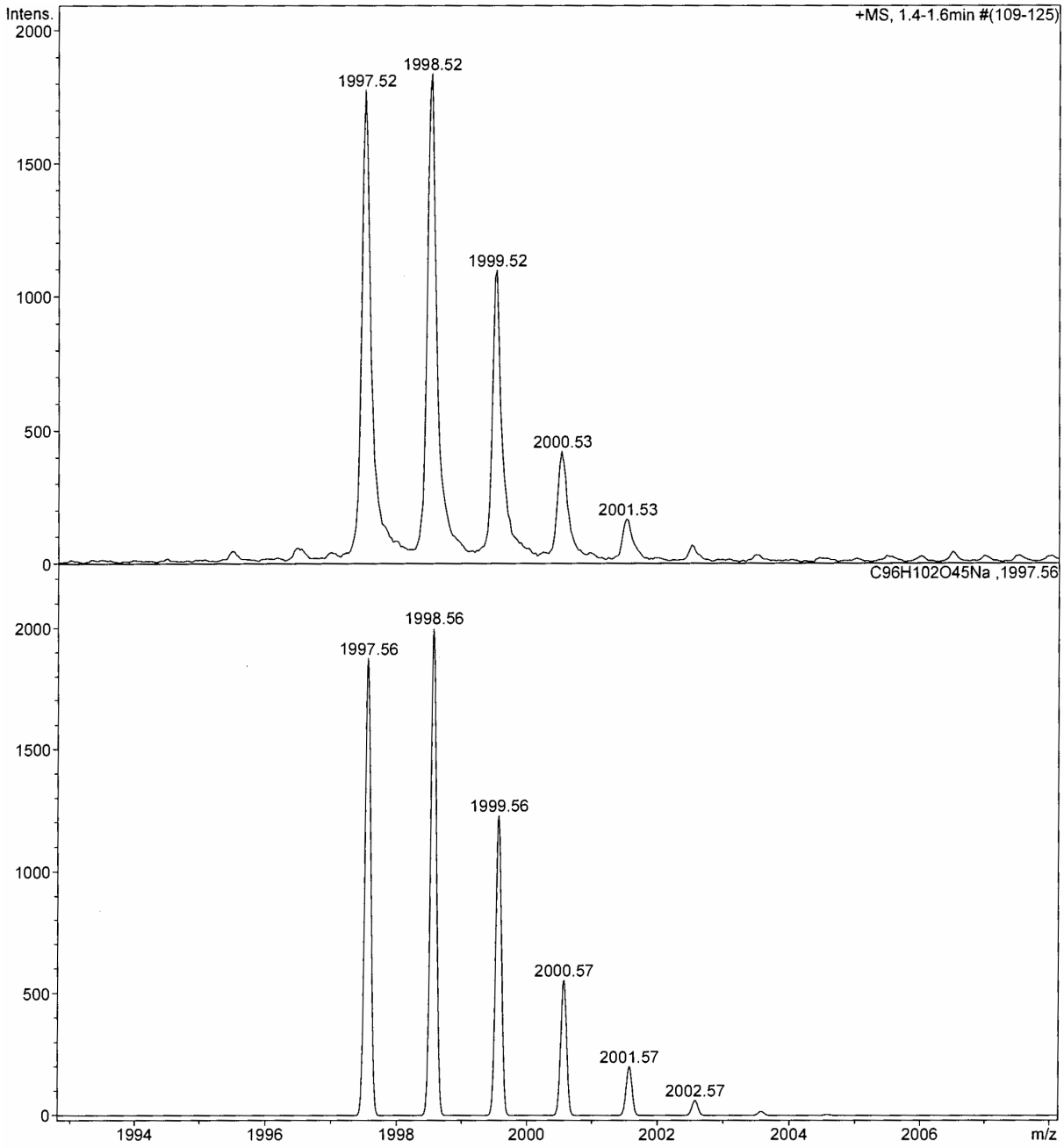


Figure S10. High resolution mass spectrum of endopeperoxide (M^{-2} + Na) formed after photoirradiation of rotaxane **1**⊂β-CD (top) and calculated isotopic pattern (bottom).

Mass spectrum of Dumbbell 1 after photoirradiation for 18 hours.

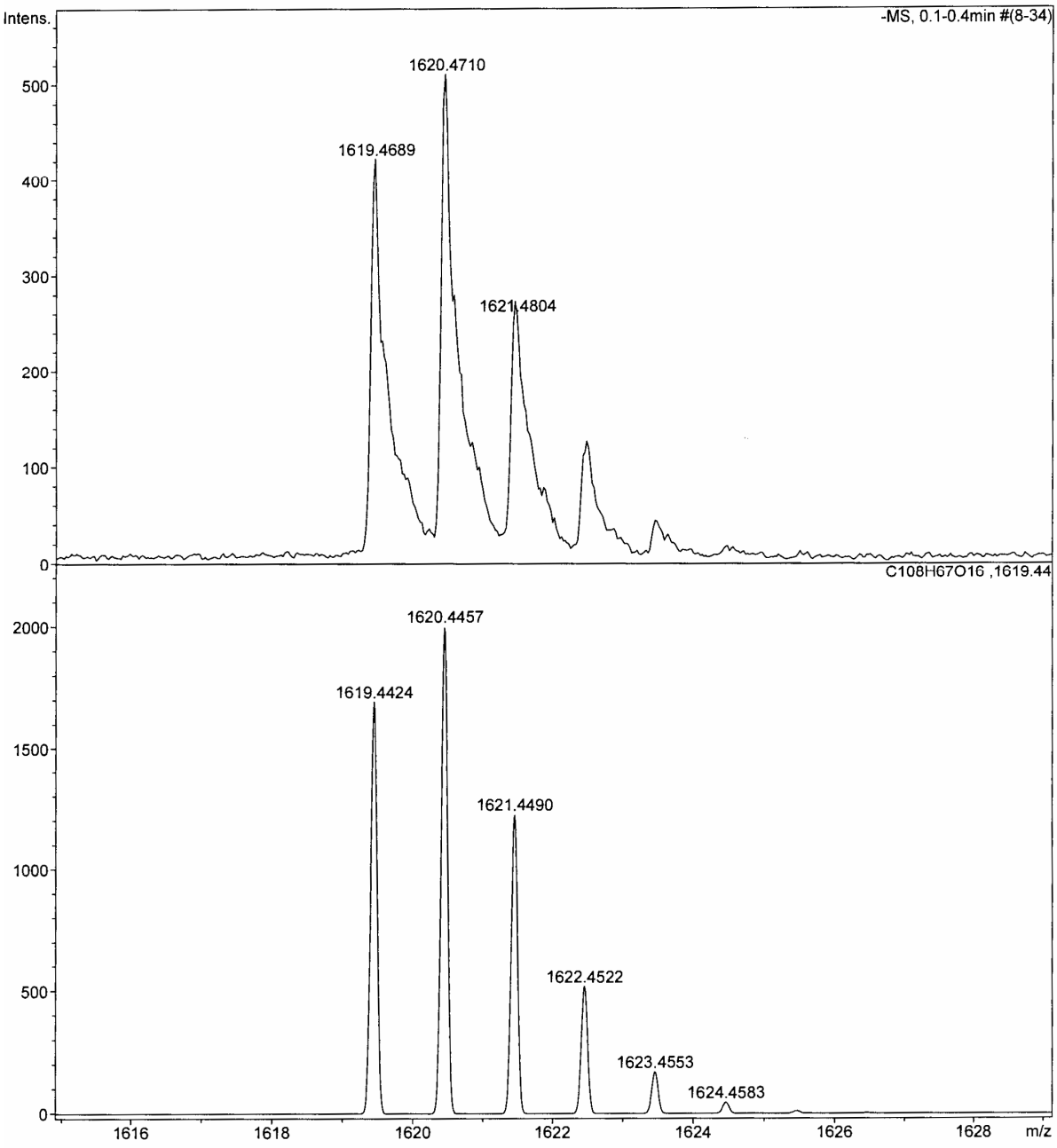


Figure S11. High resolution mass spectrum of photodimer (M^{-1}) formed after photoirradiation of dumbbell **1** (top) and calculated isotopic pattern (bottom).

Notes and references:

1 H. Meng, F. P. Sun, M. B. Goldfinger, G. D. Jaycox, Z. G. Li, W. J. Marshall and G. S. Blackman, *J. Am. Chem. Soc.*, 2005, **127**, 2406-2407.
2 S. K. Lee, W. J. Yang, J. J. Choi, C. H. Kim, S. J. Jeon and B. R. Cho, *Organic Letters*, 2005, **7**, 323-326.
3 R. S. Coleman and M. A. Mortensen, *Tetrahedron Lett.*, 2003, **44**, 1215-1219.
4 W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, 1968, **72**, 3251-3260.