Supporting information

Photochemical Reaction Containers as Energy and Electron Transfer Agents

Pradeepkumar Jagadesan, Barnali Mondal, Anand Parthasarathy,

V. Jayathirtha Rao and V. Ramamurthy*

Department of Chemistry, University of Miami, Coral Gables, FL-33124, USA.

murthy1@miami.edu

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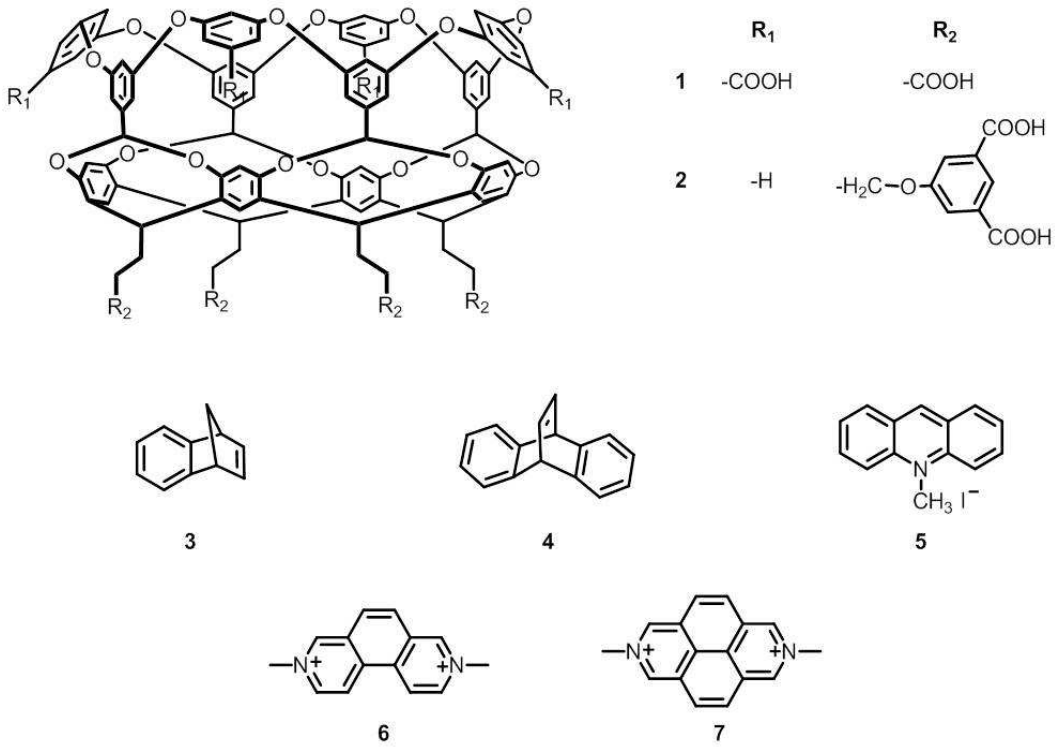

Chart S1: Structure of hosts, guests and cationic acceptors used for the study.

Experimental Section

Materials and Methods:

OA (**1**) was synthesized according to literature procedure [S1] and ROA (**2**) was synthesized as reported in previous publication.[S2] Benzonorbornadiene (**3**) and dibenzobarrelene (**4**) was synthesized following literature procedures [S3,S4,S5] respectively. Acceptors N-methylacridinium iodide (**5**), dimethyldiazaphenanthrenium iodide (**6**) and dimethyldiazapyrenium iodide (**7**) were synthesized and characterized following the literature procedures [S6,S7,S8] respectively. Di-methoxy benzoic acid (DMBA) was purchased from Sigma-Aldrich. All ^{1}H NMR spectra were recorded on a Bruker 500 / 400 MHz NMR spectrometer.

General protocol for the binding studies of guests with OA, ROA and NMR characterization: 600µL of a D_2O stock solution of hosts **OA** and **ROA** (1 mM in 10 mM $Na_2B_4O_7$) were added to two NMR tubes separately. To these tubes, aliquots of guest solution were added such that 0.25 equivalents were added upon each addition (2.5 µL of a 60 mM solution in DMSO-d_6). The complex formation was achieved by shaking the NMR tube for 5 min. Spectra were recorded after each addition of the guest solution under aerated conditions on a Bruker 500 MHz NMR spectrometer at 25 °C. Complete complexation was observed after the addition of 1 equivalent of **3** to the **OA**/**ROA** solution and 0.5 equivalents in the case of **4**. The addition of excess guest led to turbidity and NMR spectra demonstrated the formation of (2:2) (H:G) complex in the case of **3** and (2:1) (H:G) complex in the case of **4**. To confirm the (2:2) (H:G) complex formation between **3** and **OA**, a 2D DOSY NMR spectrum was recorded using 'stebpg1s' pulse sequence, pulsed field gradients were incremented linearly from 1.06 (2 % of field gradient strength) to 50.35 G/cm (95 % of field strength) in 16 steps with each step containing 8 scans. The data was processed by T_1/T_2 relaxation module in the TOPSIN 2.1 software.

Photolysis of guests inside OA capsule:

(**3**)$_2$@(**OA**)$_2$ and **4**@(**OA**)$_2$ were prepared by adding 10 µL of 60 mM solution of **3** in DMSO-d_6 to 600 µL of 1 mM **OA** solution in 10 mM $Na_2B_4O_7$ and 5 µL of 60 mM solution of **4** in DMSO-d_6 to 600 µL of 1 mM OA solution in 10 mM $Na_2B_4O_7$ respectively. The solutions were degassed for 20 min and irradiated with 450 W medium pressure mercury lamp for 30 min. All the solutions were prepared in a pyrex NMR tube. The irradiated samples were analyzed by ^{1}H NMR and also by GC after extracting into $CDCl_3$.

Extraction and analysis of photoproduct from OA:

After photolysis, reactants and products were extracted from the aqueous solution using $CHCl_3$, dried over anhydrous Na_2SO_4, concentrated and analyzed on a HP-6890 gas chromatograph fitted with a SPB-5 capillary column. The products were also identified by GC-MS.

Procedure for Fluorescence study:

Fluorescence emission spectra were recorded on a FS920CDT Edinburg steady-state fluorimeter and the lifetime measurements on FL900CDT fluorescence lifetime spectrometer. Required solution of cationic guests were prepared in 10 mM borate buffer and used for steady state fluorescence study and lifetime measurements. Calculated amounts of quencher solution (**1**, **2**, or **DMBA**) were added and mixed thoroughly and fluorescence spectra were recorded.

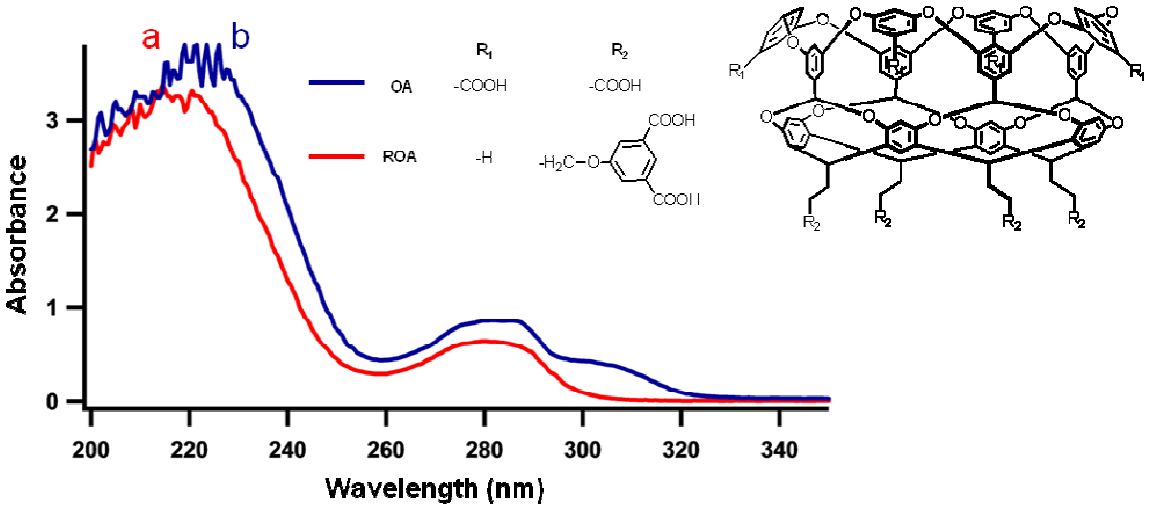

Figure S1. Absorption spectra of (a) **1** ([**1**] = 5 × 10^{-5} M in 10 mM $Na_2B_4O_7$ buffer solution) and (b) **2** ([**2**] = 5 × 10^{-5} M in 10 mM $Na_2B_4O_7$ buffer solution).

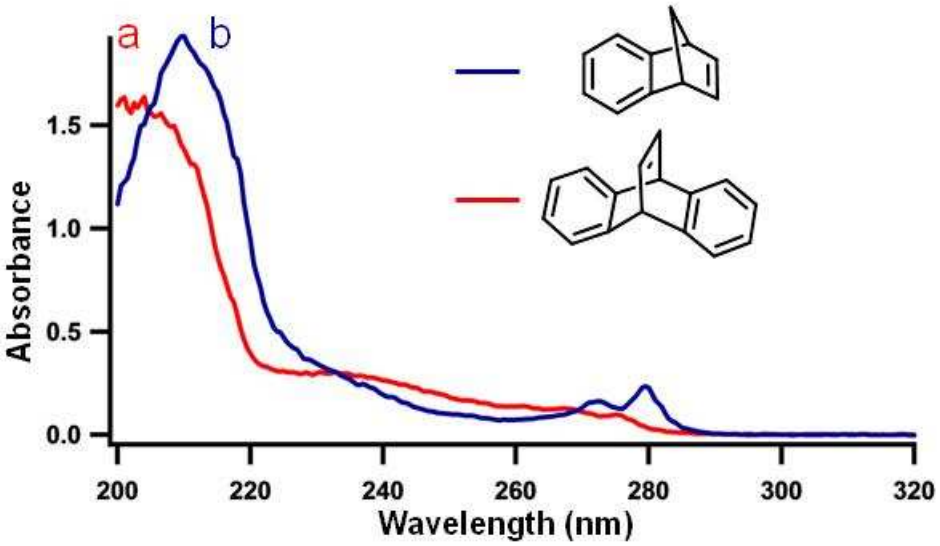

Figure S2. Absorption spectra of (a) **3** ([**3**] = 5 × 10^{-5} M) and (b) **4** ([**4**] = 5 × 10^{-5} M) in hexane.

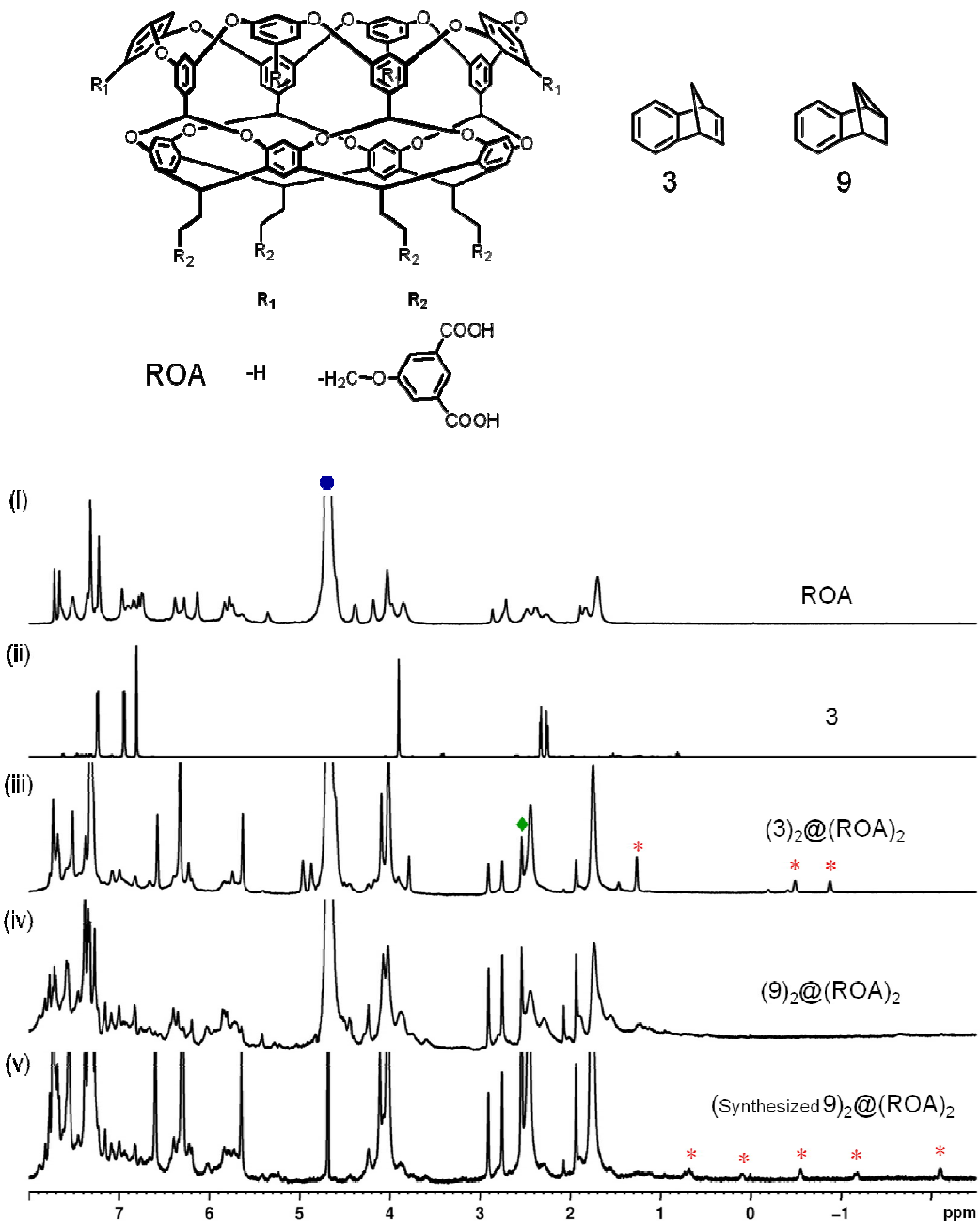

Figure S3. ^{1}H-NMR (500 MHz) spectra of (i) **ROA** (in 10 mM $Na_2B_4O_7$ buffer/D_2O), (ii) **3** in $CDCl_3$, (iii) (**3**)$_2$@(**ROA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O, (iv) (**3**)$_2$@(**ROA**)$_2$ (after 30 min irradiation) in 10 mM $Na_2B_4O_7$ buffer/D_2O and (v) (synthesized **9**)$_2$@(**ROA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O. [**ROA**] = [**3**] = [**9**] = 1 mM. '*' represents the bound guest proton resonance. '●' and '♦' represent the residual proton resonance from D_2O and DMSO-d_6 respectively.

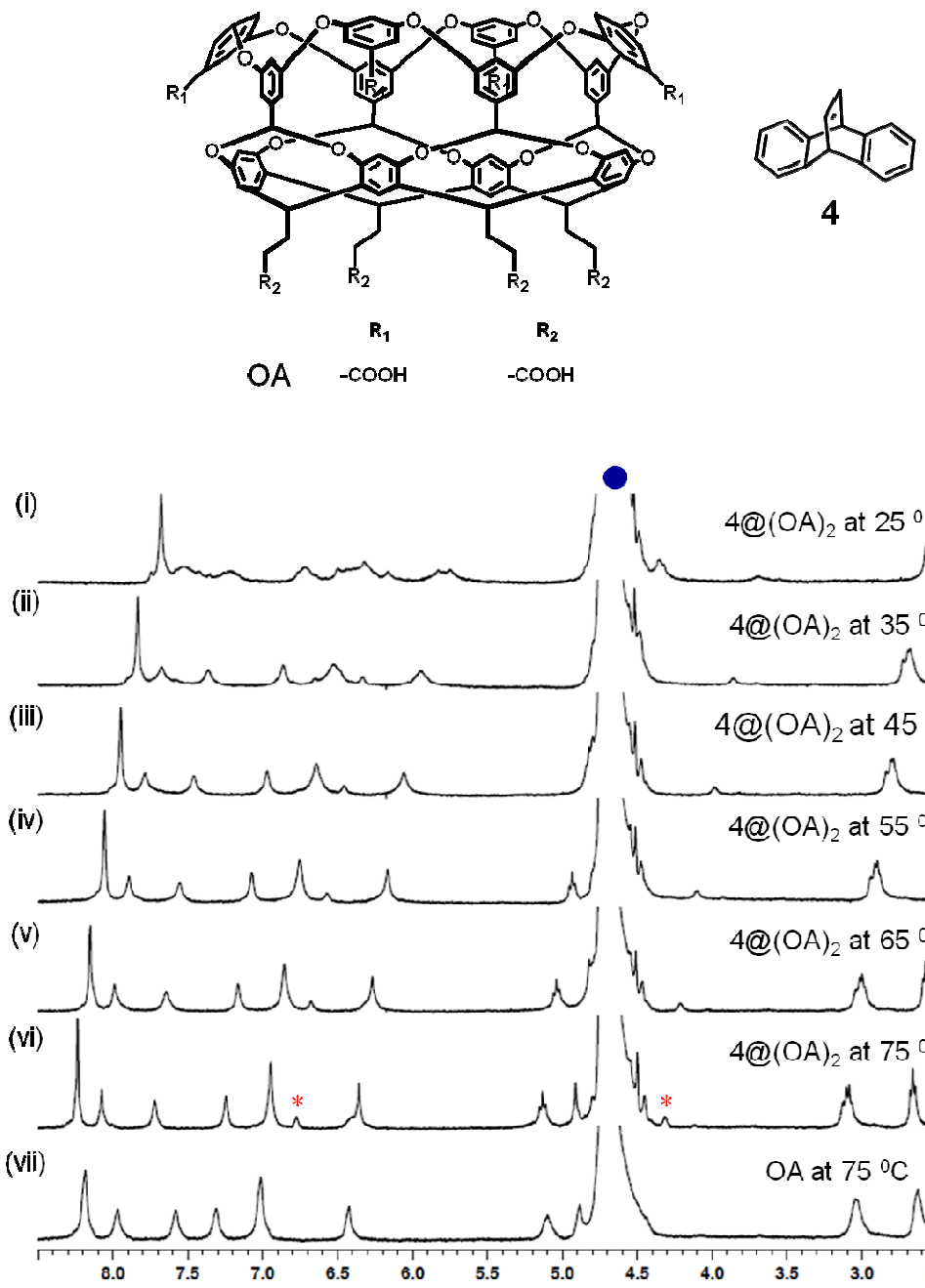

Figure S4. ^{1}H-NMR (400 MHz) spectra of (i) **4**@(**OA**)$_2$ at 25 ^{0}C, (ii) **4**@(**OA**)$_2$ at 35 ^{0}C, (iii) **4**@(**OA**)$_2$ at 45 ^{0}C, (iv) **4**@(**OA**)$_2$ at 55 ^{0}C, (v) **4**@(**OA**)$_2$ at 65 ^{0}C, (vi) **4**@(**OA**)$_2$ at 75 ^{0}C, (vii) **OA** at 75 ^{0}C. [**OA**] = 1 mM and [**4**] = 0.5 mM in 10 mM $Na_2B_4O_7$ buffer/D_2O '*' represents the bound guest proton peaks. '●' represents the residual proton resonance from D_2O respectively.

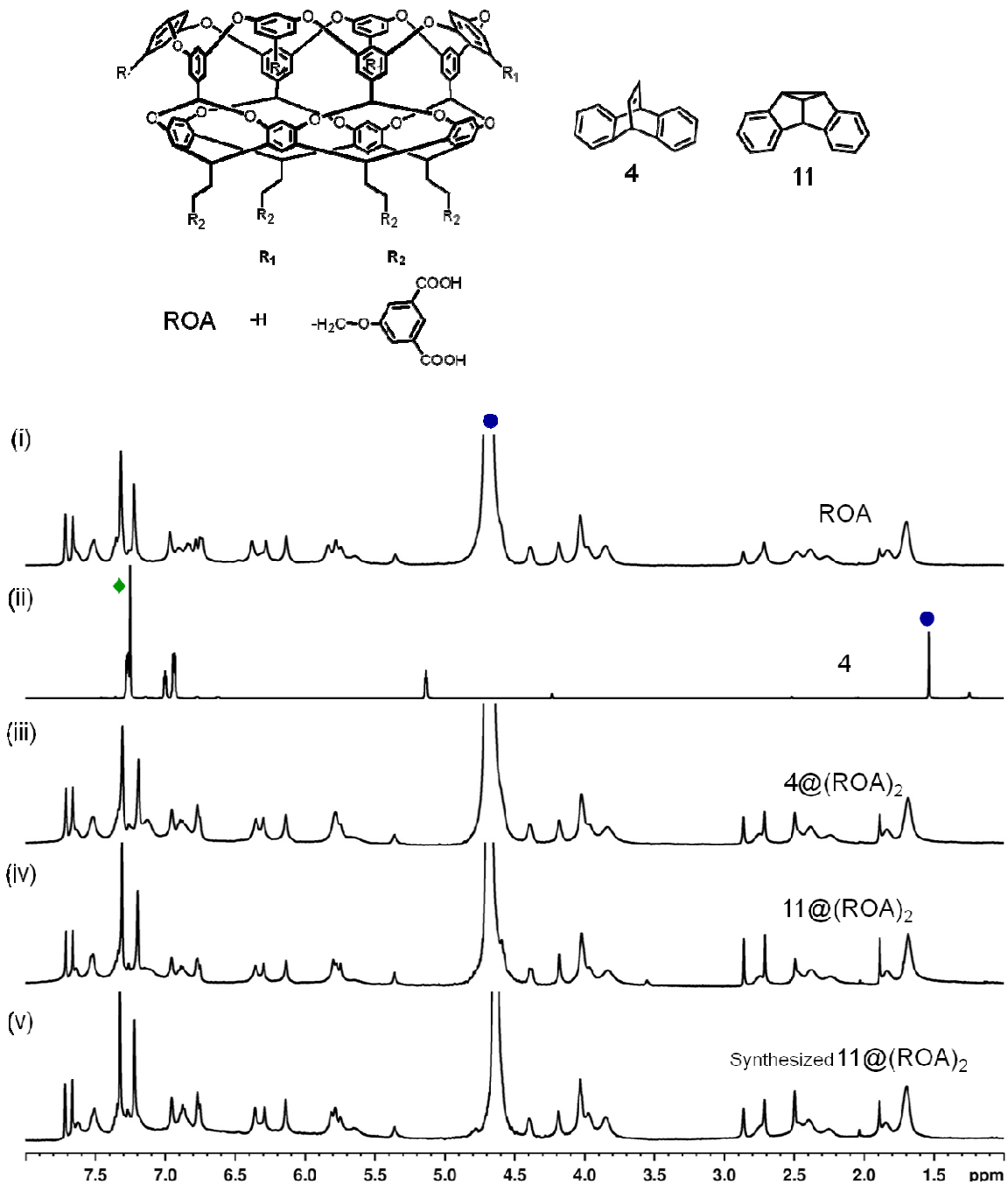

Figure S5. ^{1}H-NMR (500 MHz) spectra of (i) **ROA** ([**ROA**] = 1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, (ii) **4** in $CDCl_3$, (iii) **4**@(**ROA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O, (iv) **4**@(**ROA**)$_2$ (after 30 min irradiation) in 10 mM $Na_2B_4O_7$ buffer/D_2O and (v) synthesized **11**@(**OA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O. '●' and '♦' represent the residual proton resonance from D_2O and $CDCl_3$ respectively.

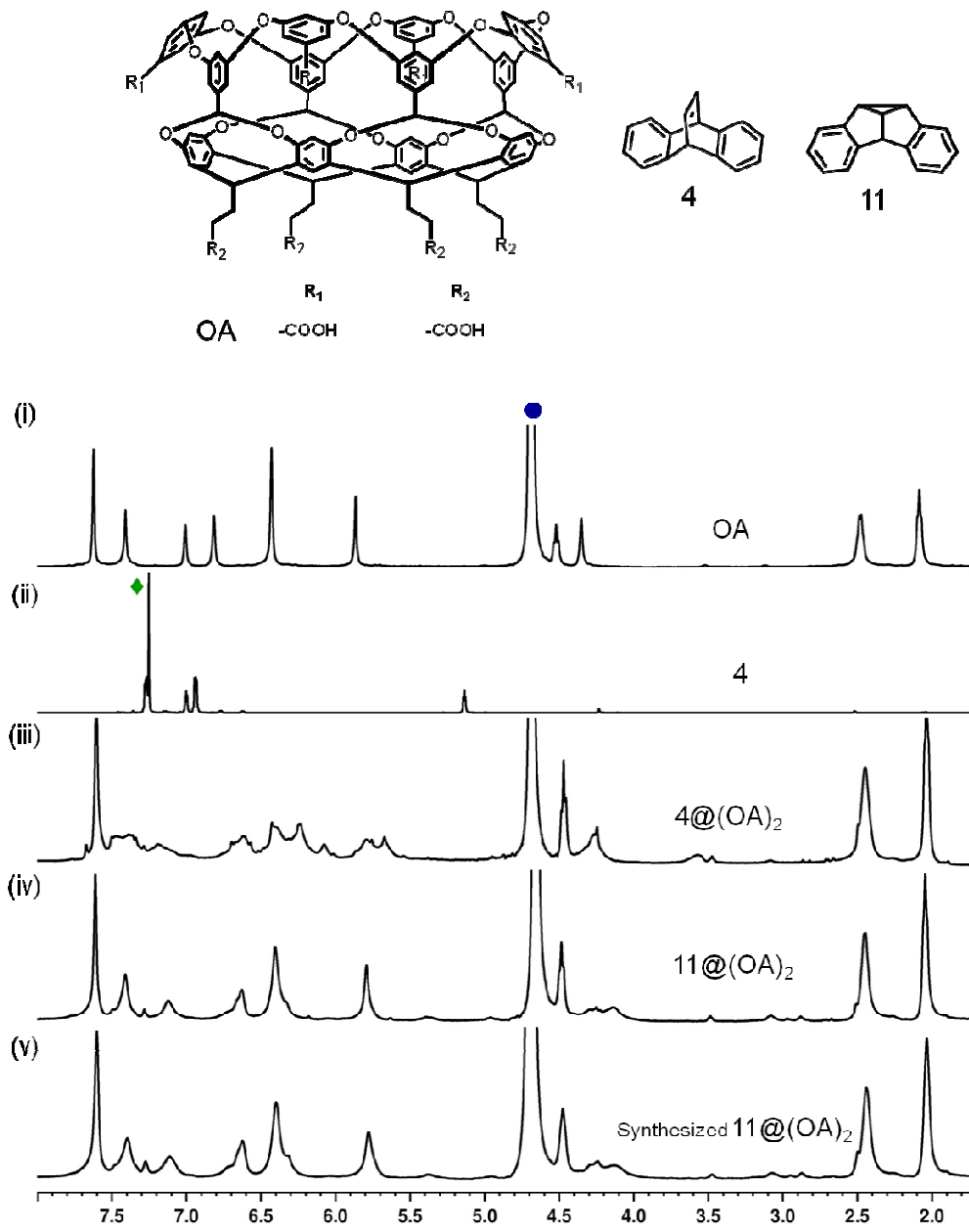

Figure S6. ^{1}H-NMR (500 MHz) spectra of (i) **OA** ([**OA**] = 1 mM) in 10 mM $Na_2B_4O_7$ buffer/D_2O, (ii) **4** in $CDCl_3$, (iii) **4**@(**OA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O, (iv) **4**@(**OA**)$_2$ (after 30 min irradiation) in 10 mM $Na_2B_4O_7$ buffer/D_2O and (v) synthesized **11**@(**OA**)$_2$ in 10 mM $Na_2B_4O_7$ buffer/D_2O. '*' represents the bound guest proton resonance. '●' and '♦' represent the residual proton resonance from D_2O and $CDCl_3$ respectively.

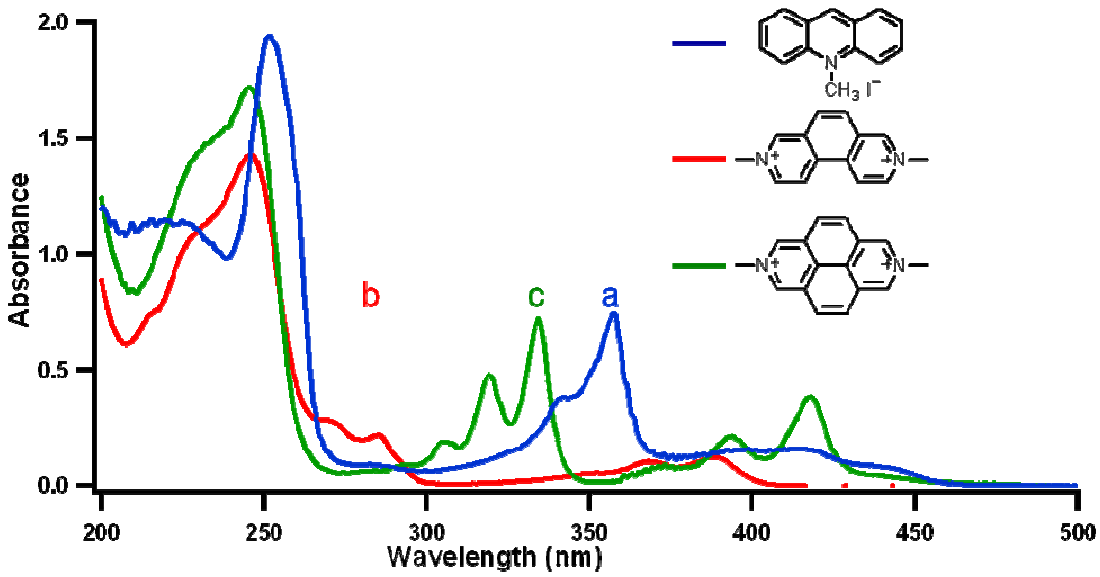

Figure S7. Absorption spectra of (a) **5** [**5**] = 2×10^{-5} M, (b) **6** [**6**] = 5×10^{-5} M, (c) **7** [**7**] = 4×10^{-5} M in 10 mM $Na_2B_4O_7$ buffer solution**.**

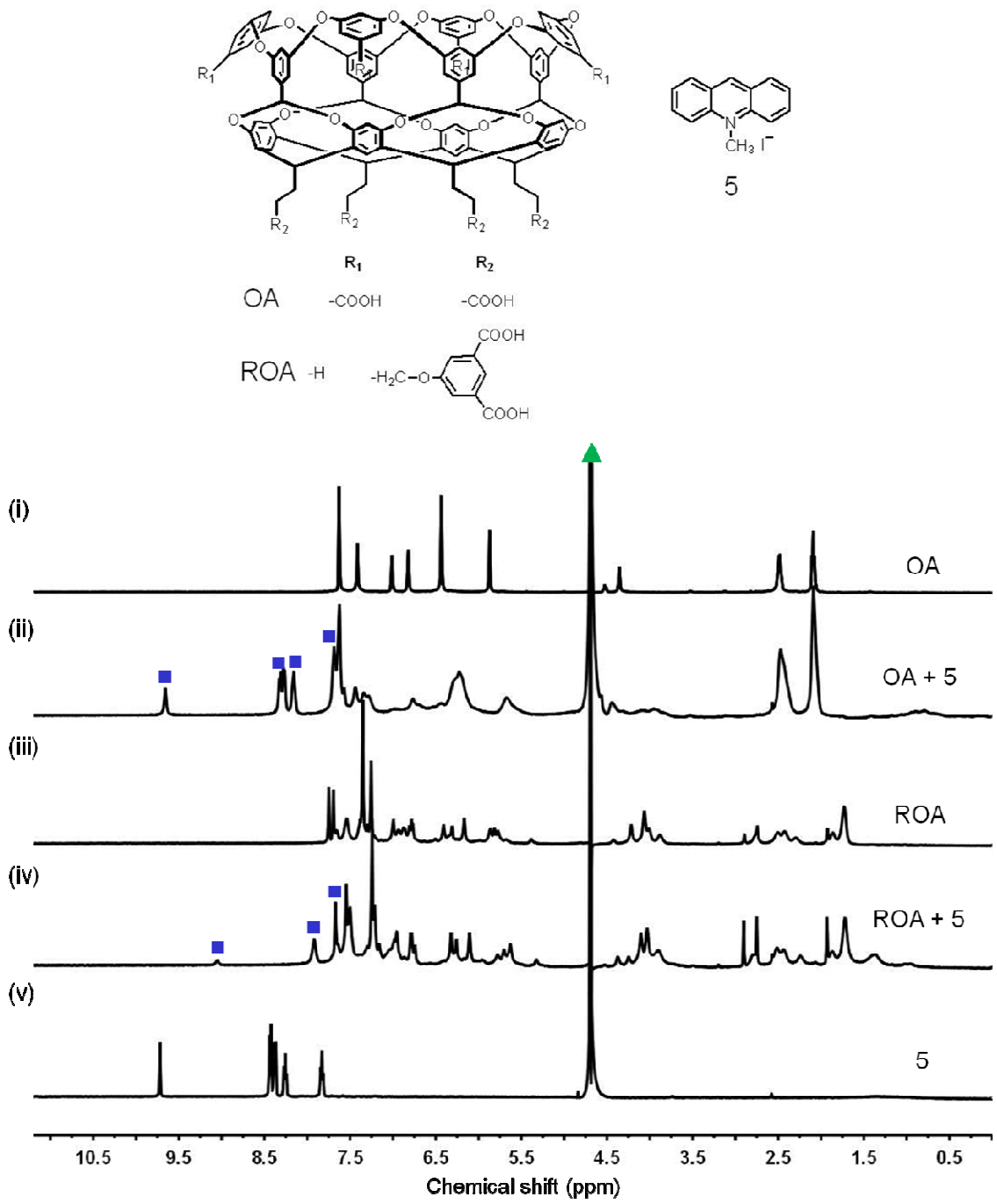

Figure S8. ^{1}H-NMR (500 MHz, 10 mM $Na_2B_4O_7$ buffer/D_2O) spectra of (i) **1** (ii) **5**@**1** (iii) **2** and (iv) **5**@**2**. (v) **5** . [**1**] = [**2**] = [**5**] = 1mM. '▲' represents the residual proton resonance from D_2O and '■' represents the unbound proton peaks of **5**.

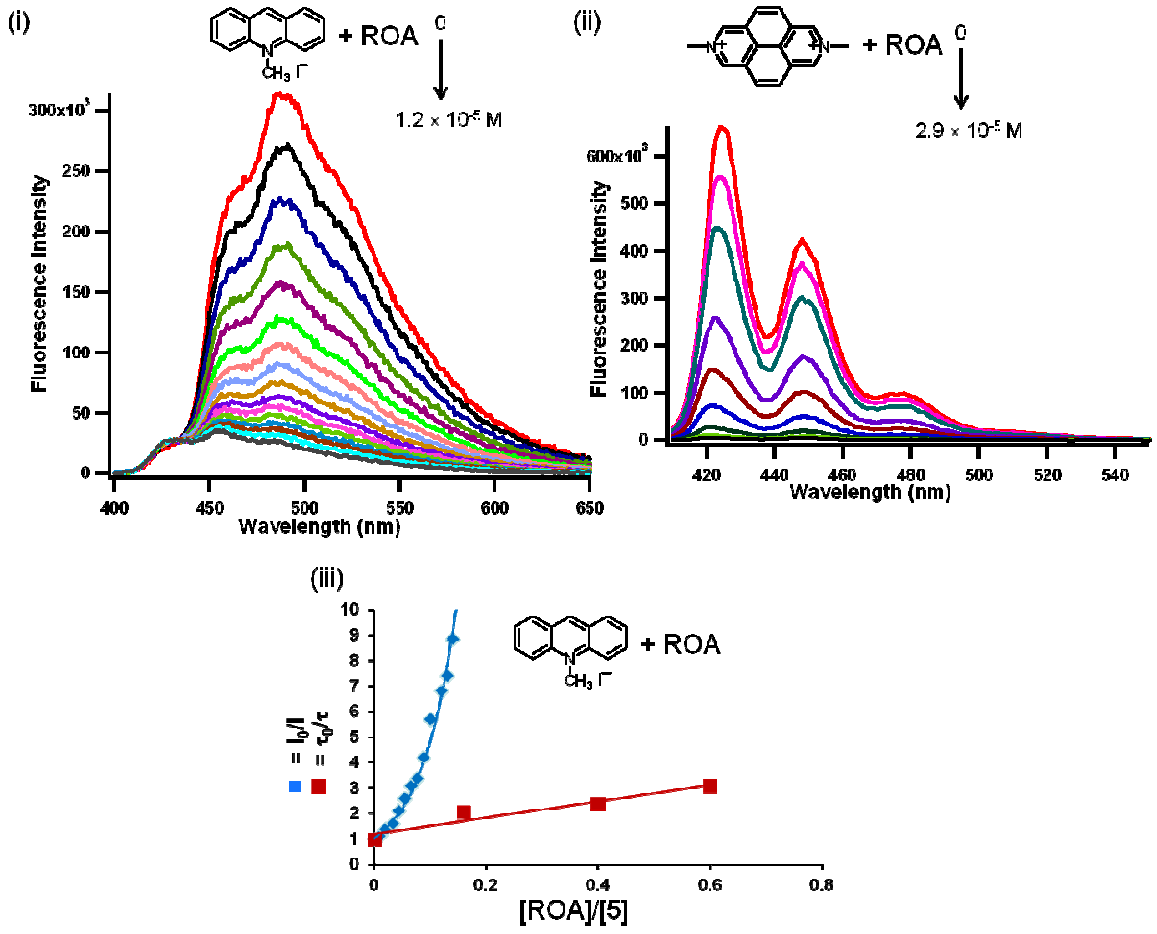

Figure S9. Fluorescence titration spectra of (i) **5** with **2**, [**5**] = 6 × 10^{-6} M (λ_{ex} = 380 nm) and [**2**] = 0 to 1.2 × 10^{-5} M, (ii) **7** with **2**, [**7**] = 4 × 10^{-5} M (λ_{ex} = 390 nm) and [**2**] = 0 to 2.9 × 10^{-5} M in 10 mM $Na_2B_4O_7$ buffer. (iii) Stern-Volmer plot for the quenching study of **5** with **2**. ('■'and '■' represent steady state and fluorescence lifetime data respectively).

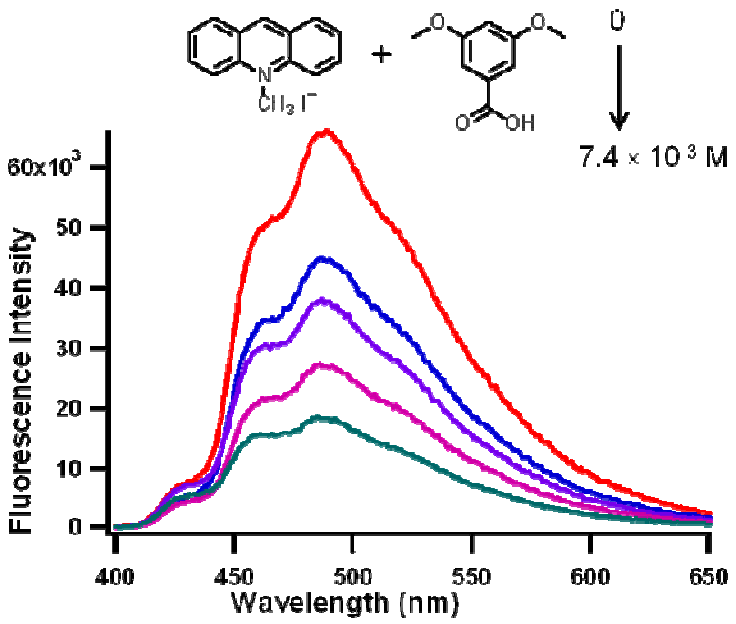

Figure S10. Fluorescence quenching titration of **5** with 3, 5-dimethoxy benzoic acid (**DMBA**), [**5**] = 6×10^{-6} M and **[DMBA]** = 0 to 7.4×10^{-3} M in 10 mM $Na_2B_4O_7$ buffer (λ_{ex}= 380 nm).

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