Electronic Supplementary Information

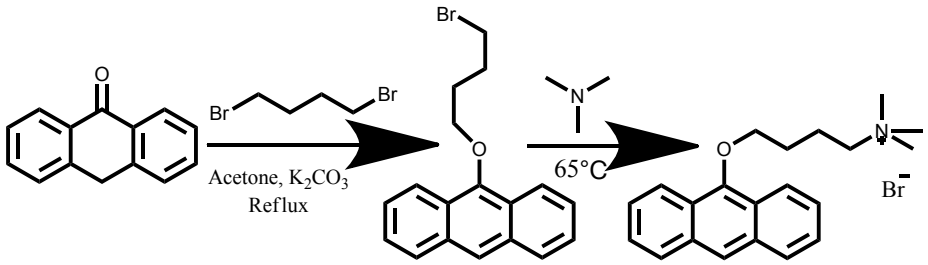
Multi-charged Macrocycle as Platform for Rapid and Broad Spectral Photodecomposition of Aromatic Dye

*Xin-Ran Guan, Yong Chen, Peng Guo, Pei-Yu Li, and Yu Liu**

College of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China; Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.

Experimental Section.

Materials. Anthrone and 1,4-dibromo butane were purchased from Energy Chemical. Potassium carbonate was purchased from Adamas Reagent. Trimethylamine was purchased from TCI. Anthraquinone was purchased from HEOWNS. Cucurbit[8]uril (CB[8]) was purchased from HWRK CHEM. Sulfatocyclodextrin (SCD, sulfated sodium salt extent of labeling: 12-15 mol per mol β-CD) was purchased from Sigma-Aldrich. All of them were used without further purification. p-Sulfonatocalix[6]arene and DNC sodium salt were prepared according to literature methods.[1,2] All aqueous solutions were prepared with distilled water. The mixing concentration for the amphiphilic assembly was 0.01 mM for SCD and 0.10 mM for AnQA throughout the work, unless mentioned otherwise.



Scheme S1. Synthesis of AnQA.

Synthesis of AnQA. 9-(4-Bromobutoxy)anthracene[11] (600 mg, 1.8 mmol) was dissolved in trimethylamine (20 mL), and the solution was heated to 65 °C overnight. After cooling to room temperature, the mixture was poured into anhydrous diethyl ether (200 mL) with vigorous stirring. The precipitates produced were filtered and washed with diethyl ether and acetone. The product was dried under vacuum (yield: 450 mg, 65%). ^{1}H NMR (400 MHz, D_2O, δ): 8.00 (d, J = 8.7 Hz, 2H), 7.78 (s, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.35 (dt, J = 14.9, 7.0 Hz, 4H), 3.74 (s, 2H), 3.07 (d, J = 7.0 Hz, 2H), 2.90 (s, 9H), 1.63 (s, 4H); ^{13}C NMR (101 MHz, D_2O, δ): 150.18, 131.76, 128.06, 125.78, 125.69, 124.16, 122.03, 74.63, 65.71, 52.68, 26.25, 18.98; HRMS (ESI) *m/z*: $[AnQA - Br]^+$ calcd for $C_{21}H_{26}NO^+$, 308.2009; found, 308.2013.

Preparation of the supramolecular aggregate. 0.1mM CB[8] stock solution, 1 mM SC6A stock solution, 1 mM DNC stock solution, 1 mM SCD stock solution and 1 mM AnQA stock solution were prepared with distilled water. Then the corresponding volume of macrocycle stock solution and the AnQA stock solution were mixed, and then distilled water was added until the total volume reached 3 mL.

Irradiation. The samples were placed in a quartz cell and further exposed to light sources (high-pressure mercury lamp with a power of 400 W or sunlight at 10 am on September 24, 2019) in air at room temperature.

UV/Vis spectroscopy

The optical transmittance of the aqueous solution was measured in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller.

Fluorescence Spectroscopy

Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path, 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell Peltier accessory to control the temperature.

TEM experiments

High-resolution TEM images were acquired using a Tecnai 20 high-resolution transmission electron microscope operating at an accelerating voltage of 200 keV. The sample for high-resolution TEM measurements was prepared by dropping the solution onto a copper grid, and the grid was then air-dried.

DLS measurements

The sample solution for DLS measurements was prepared by filtering the solution through a 450 nm Millipore filter into a clean scintillation vial. The samples were examined on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (TurboCorr) at 636 nm at a scattering angle of 90°.

Zeta (ζ) Potential Measurement

Zeta potential values were determined at 25 °C on a Brookhaven ZetaPALS (Brookhaven Instrument, USA). The instrument utilizes the phase analysis light scattering to provide an average over multiple particles. Doubly distilled water was used as the background electrolyte for ζ potential measurements.

NMR Spectroscopy

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer at 25 °C.

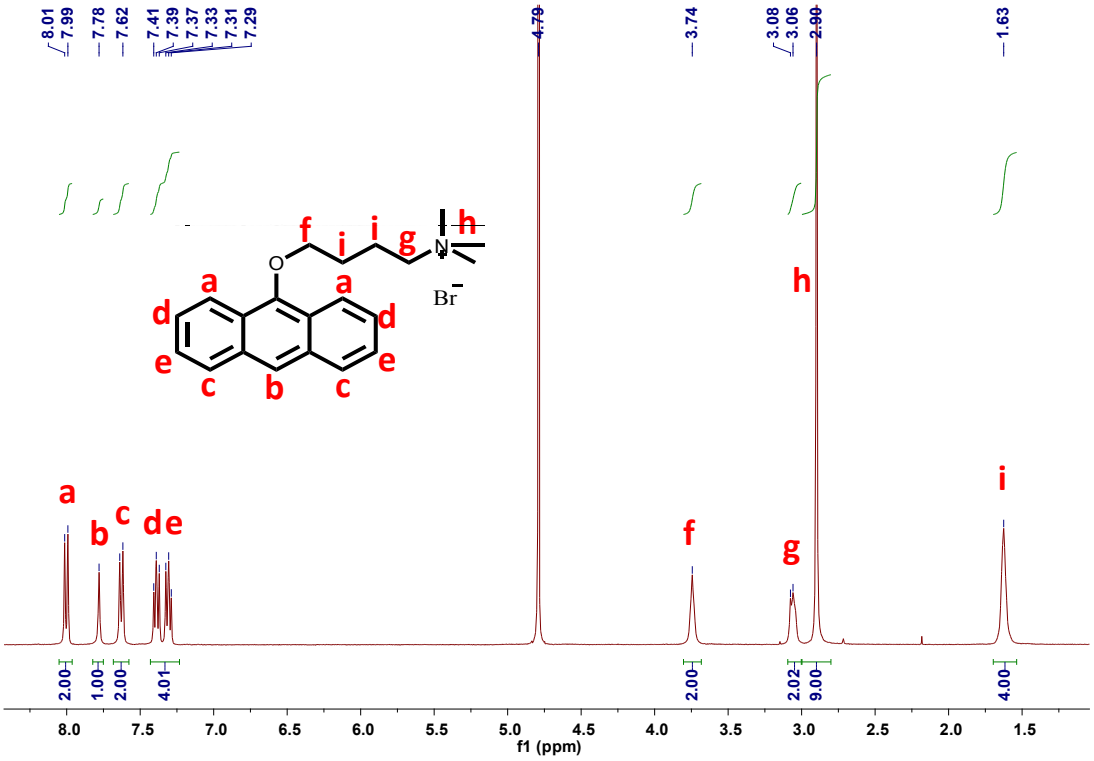


Figure S1. ^{1}H NMR spectrum (400 MHz, D_2O, 25°C) of AnQA.

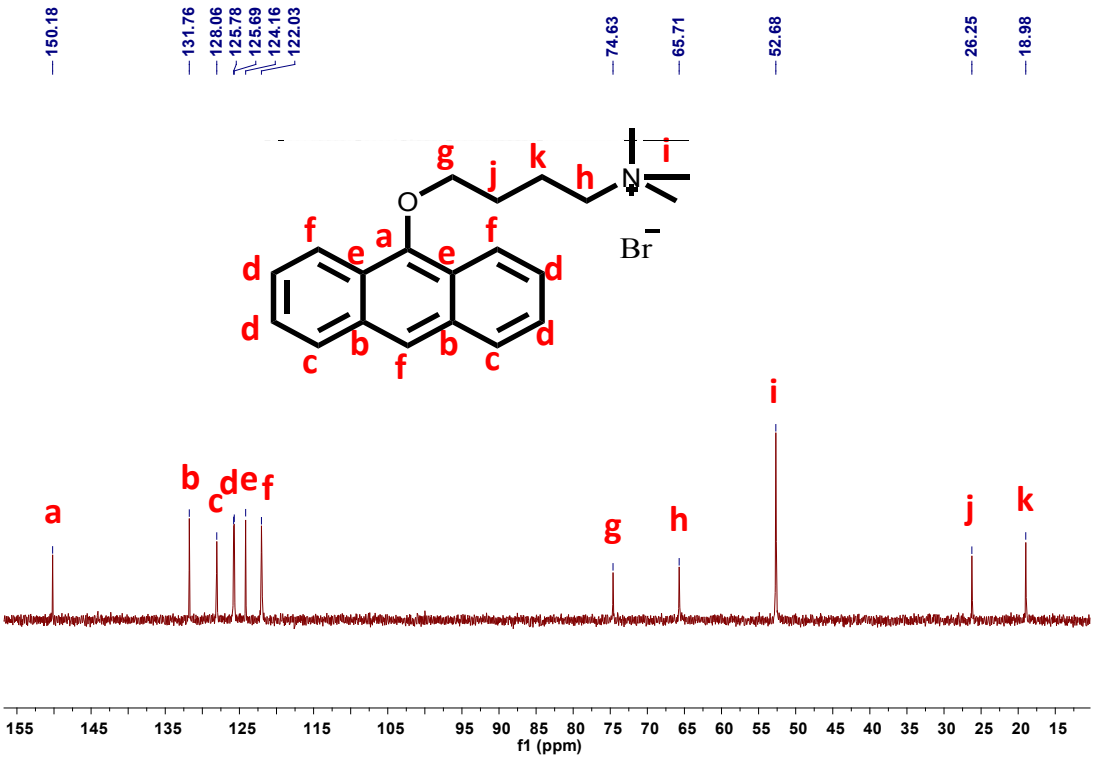


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 25°C) of AnQA.

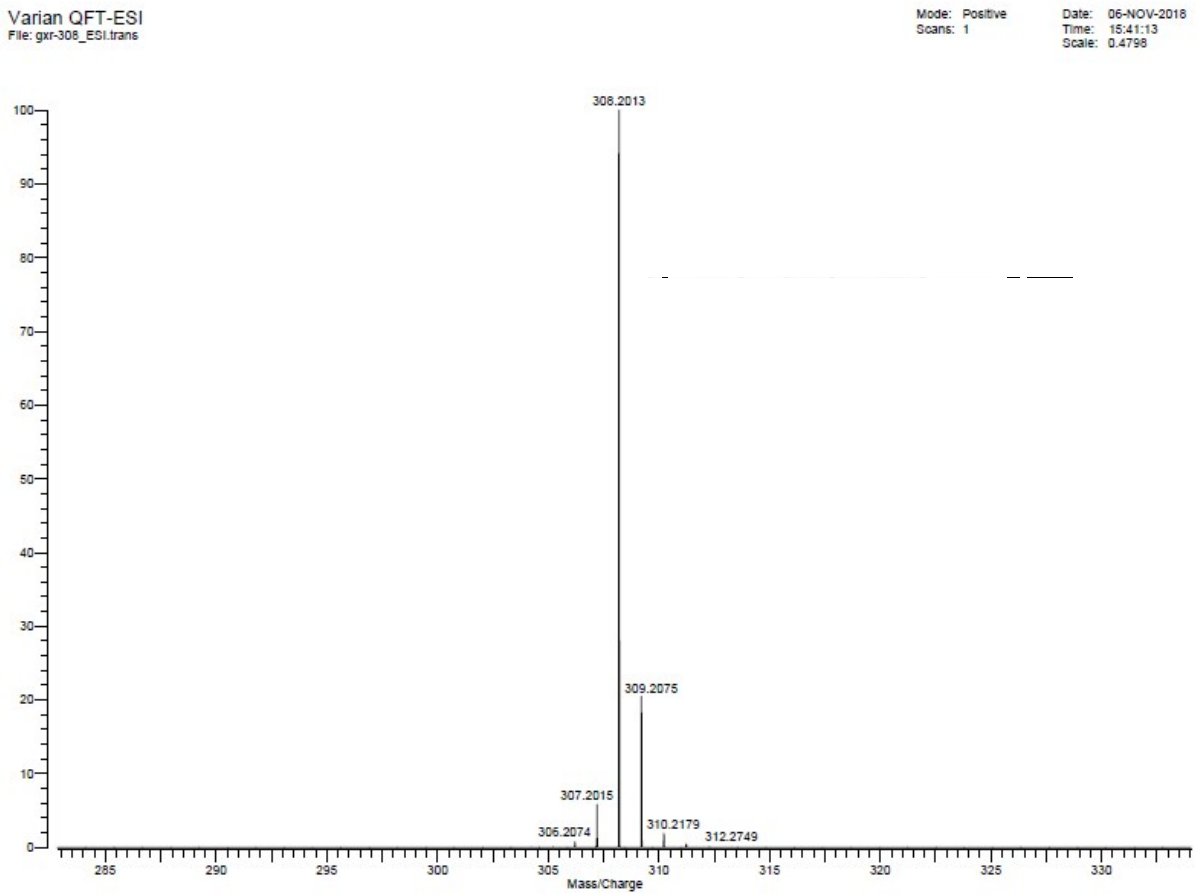


Figure S3. HRMS spectra of AnQA. Assignment of the main peak: m/z 308.2013 ([AnQA − Br]$^+$, calcd for $C_{21}H_{26}NO^+$, 308.2009).

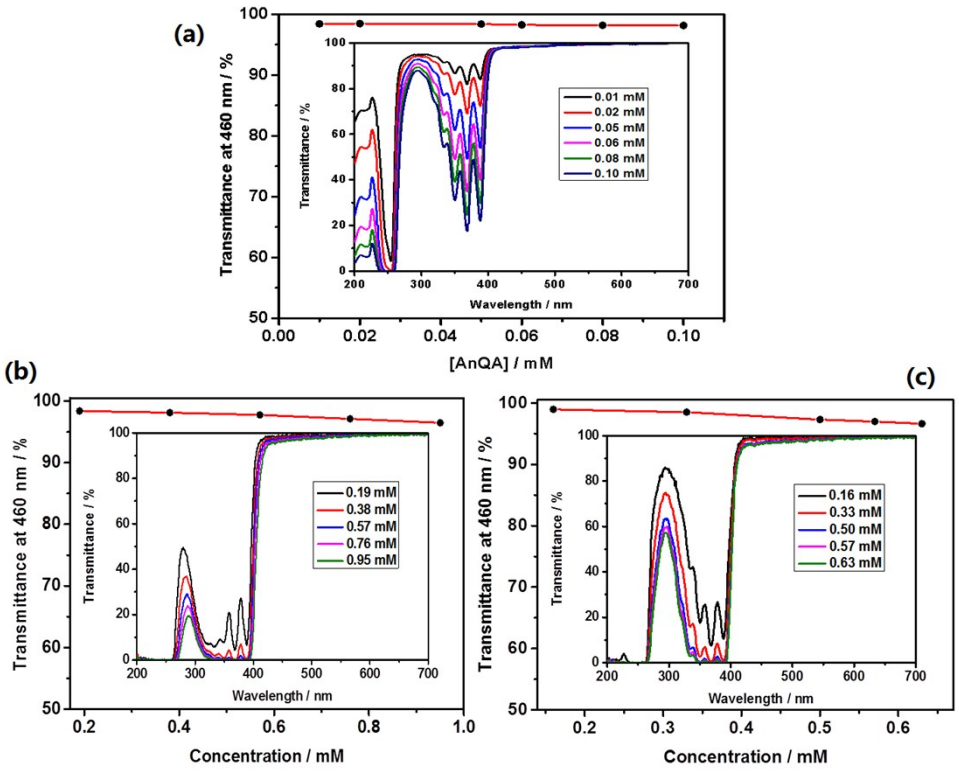


Figure S4. (a) Dependence of the optical transmittance at 460 nm on AnQA concentration. Inset: optical transmittance of aqueous solutions of AnQA at different concentrations at 25 °C. (b, c)Dependence of the optical transmittance at 460 nm on AnQA concentration in the presence of 0.05 mM DNC (b), CB[8] (c). Inset: optical transmittance of AnQA at different concentrations in the presence of 0.05 mM DNC (b), CB[8] (c) at 25 °C.

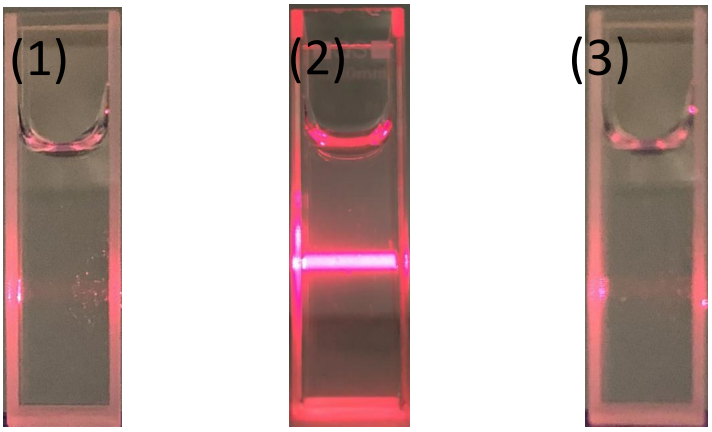


Figure S5. Tyndall effect of free SCD (1), SCD/AnQA assembly (2), free AnQA (3); [SCD] = 0.01 mM, [AnQA] =0.10 mM

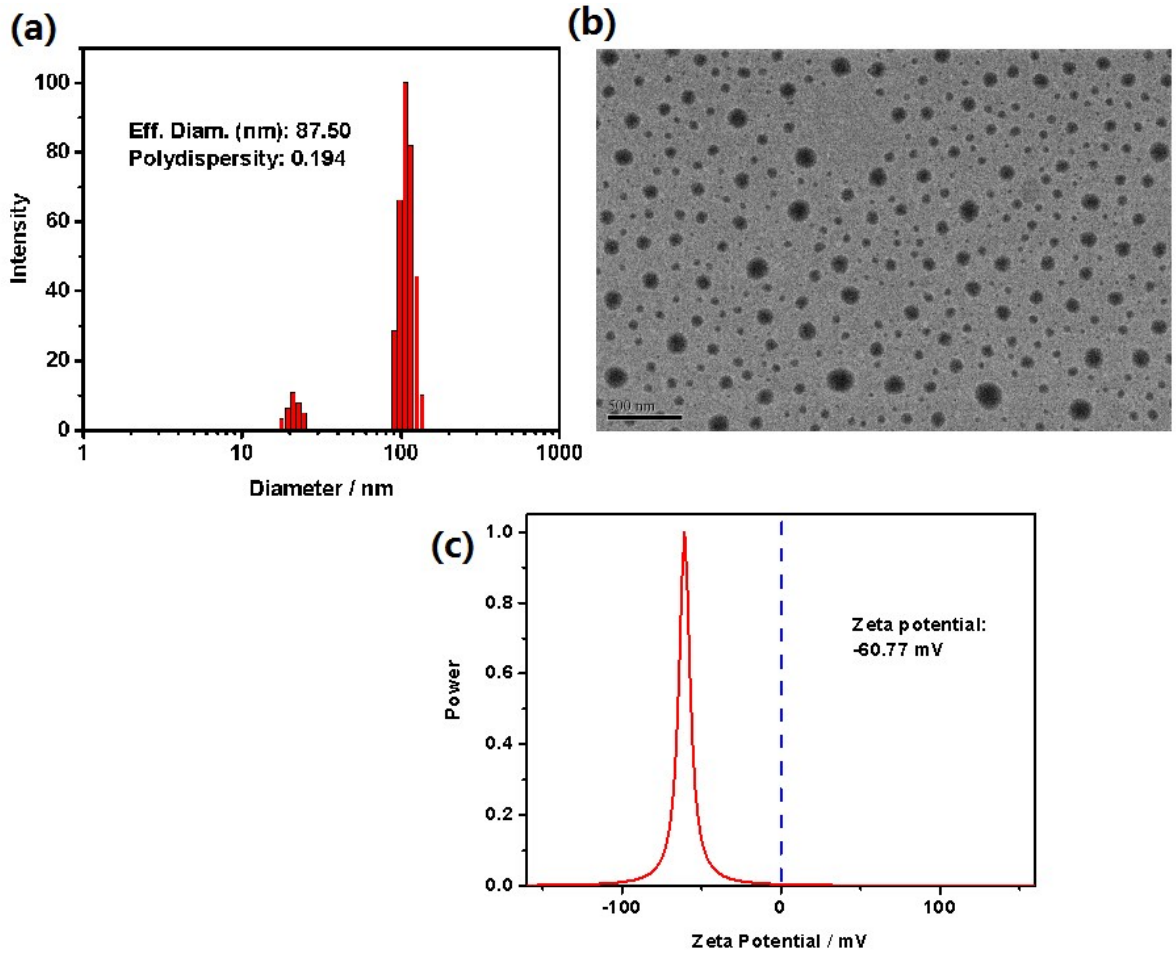
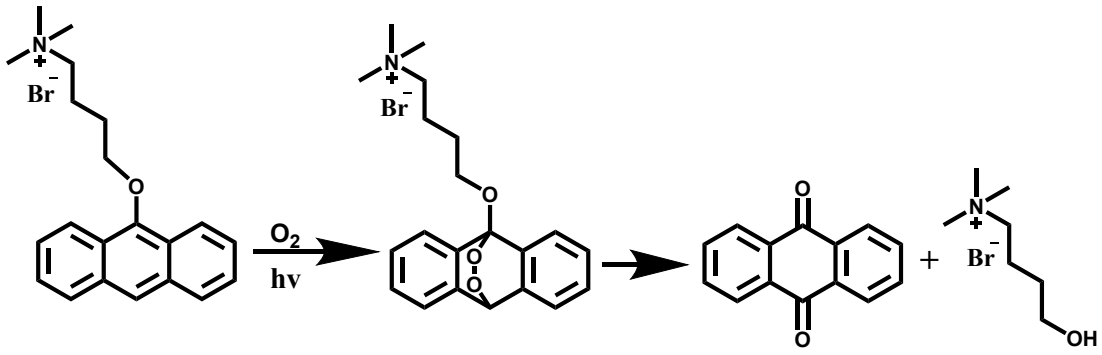


Figure S6. (a) DLS data of the SCD/AnQA assembly at 25 °C. (b) TEM image of the SCD/AnQA assembly (scale bar = 200 nm). (c) Zeta potential data of the SCD/AnQA assembly in water at 25 °C.



Scheme S2. Mechanism of photo-oxidation and further decomposition of AnQA.

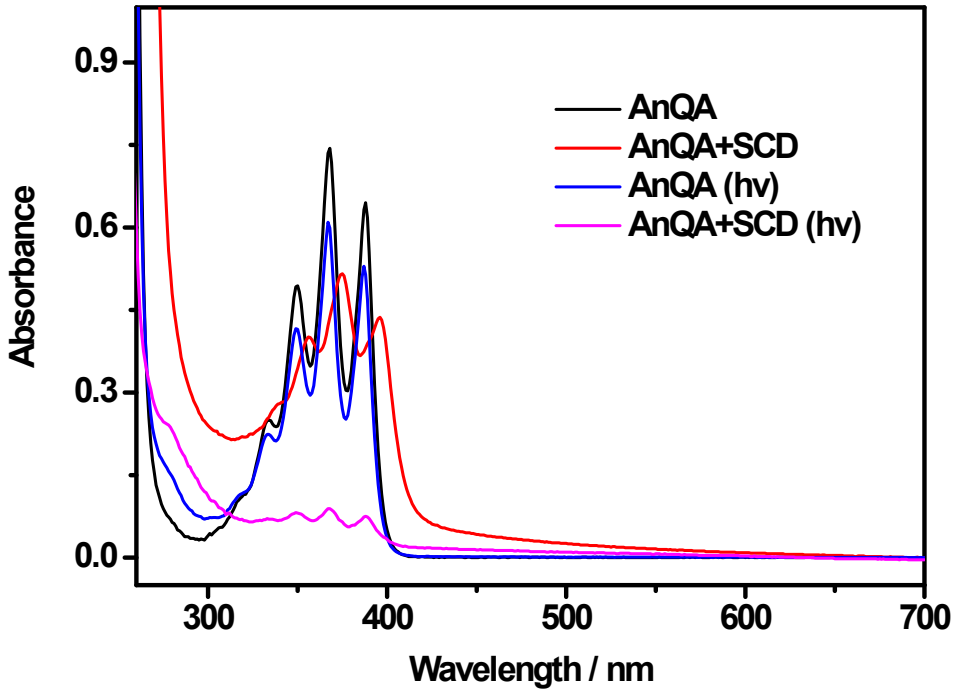


Figure S7. UV/Vis absorption spectra of AnQA (0.10 mM), SCD/AnQA assembly, AnQA after UV irradiation at 365 nm for 20 min, SCD/AnQA assembly after UV irradiation at 365 nm for 20 min.

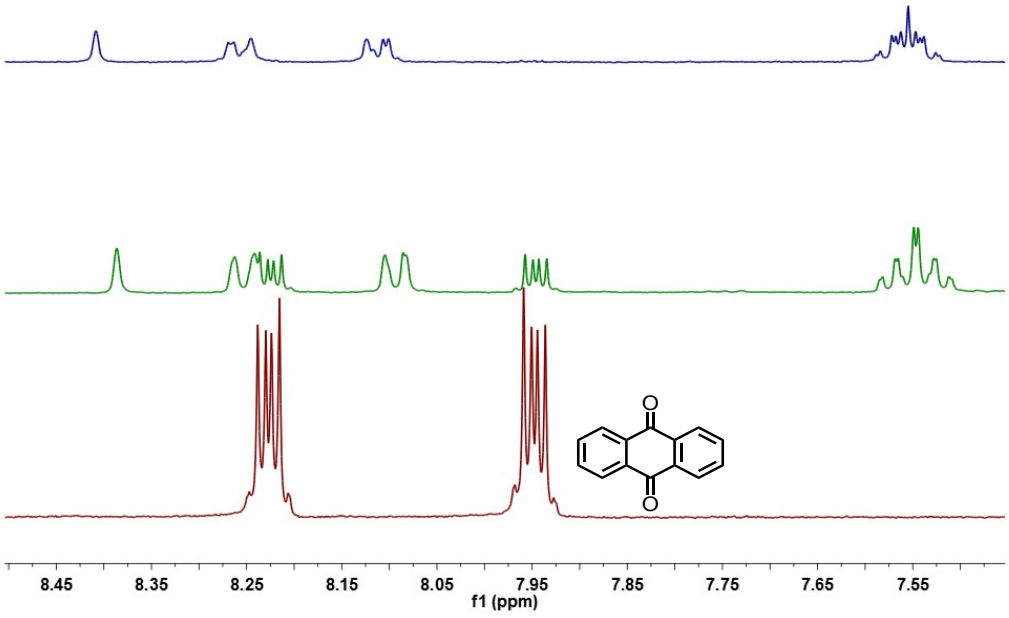


Figure S8. ^{1}H NMR spectra of AnQA (0.1mM, blue line), the SCD/AnQA assembly after UV irradiation at 365 nm for 10 min ([SCD] = 0.24 mM and [AnQA] = 2.4 mM, green line) and anthraquinones (red line) in DMSO-d_6.

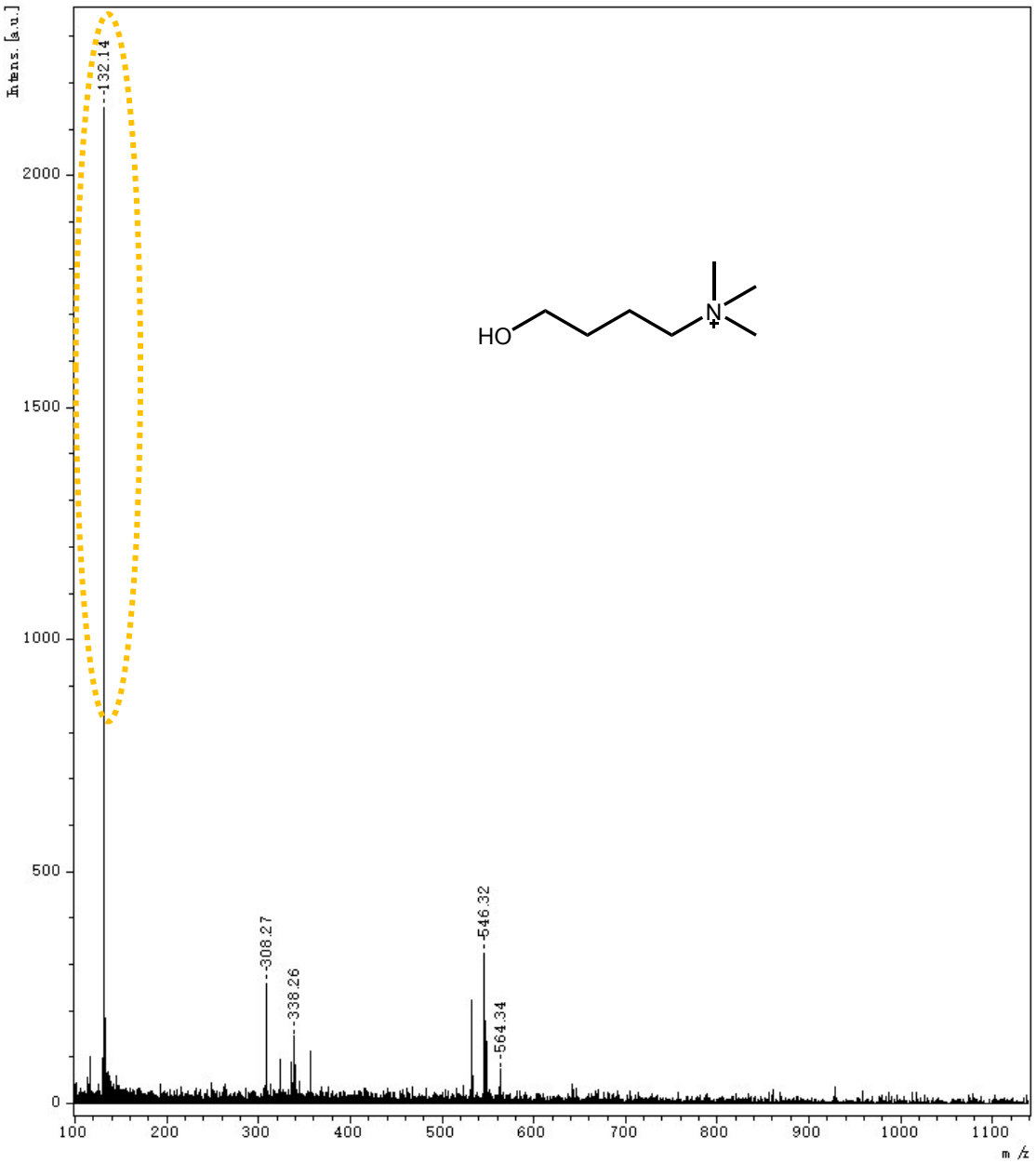


Figure S9. MALDI-TOFMS spectra of the SCD/AnQA assembly after UV irradiation at 365 nm for 10 min. Assignment of the main peak: m/z 132.14 ($[M - Br]^+$, calcd for $C_7H_{18}NO^+$, 132.14).

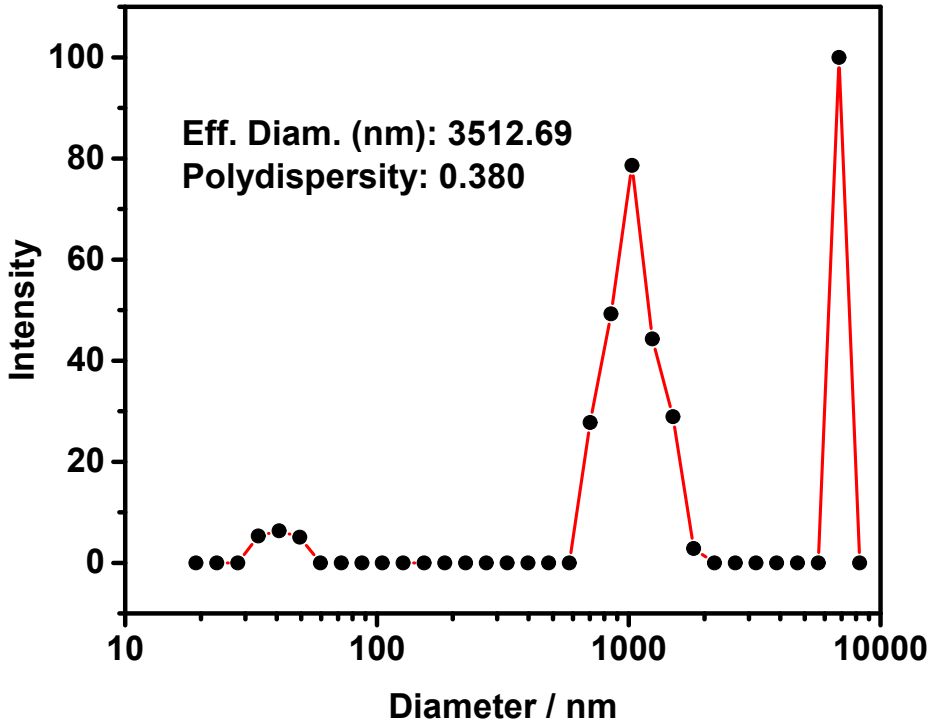


Figure S10. DLS data of the SCD-AnQA assembly upon UV irradiation at 365 nm for 20 min.

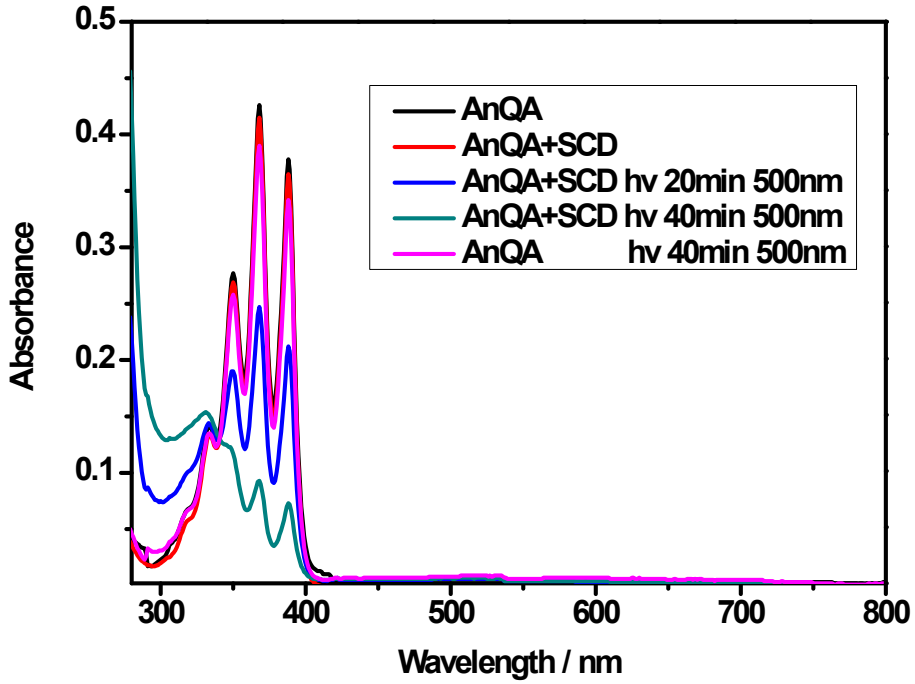


Figure S11. UV/Vis absorption spectra of AnQA (0.10 mM), SCD/AnQA assembly, SCD/AnQA assembly after irradiation at 500 nm for 20 min, 40min and AnQA after irradiation at 500 nm for 40 min. Note that: before UV/Vis absorption tests were performed, an equal volume ethanol solution is added to the sample solution to eliminate the scattering error from the assemblies and facilitate quantitative analysis.

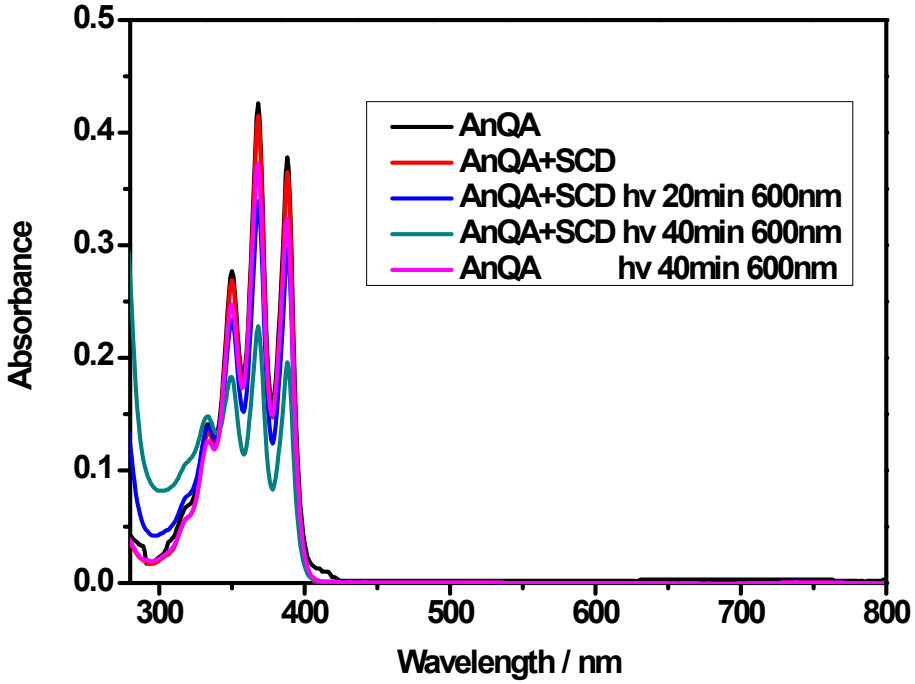


Figure S12. UV/Vis absorption spectra of AnQA (0.10 mM), SCD/AnQA assembly, SCD/AnQA assembly after irradiation at 600 nm for 20 min, 40min and AnQA after irradiation at 600 nm for 40 min. Note that: before UV/Vis absorption tests were performed, an equal volume ethanol solution is added to the sample solution to eliminate the scattering error from the assemblies and facilitate quantitative analysis.

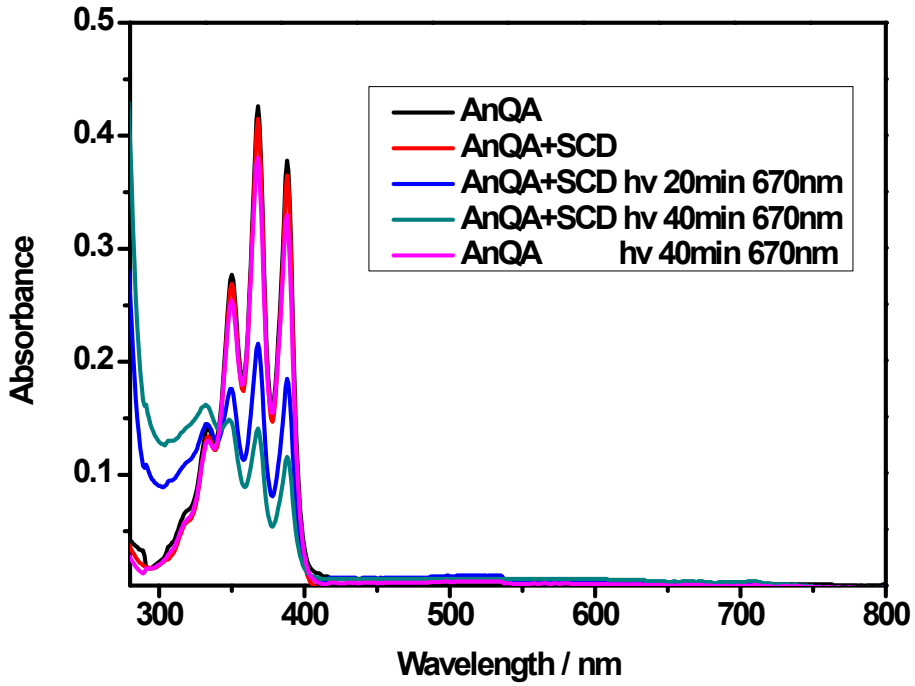


Figure S13. UV/Vis absorption spectra of AnQA (0.10 mM), SCD/AnQA assembly, SCD/AnQA assembly after irradiation at 670 nm for 20 min, 40min and AnQA after irradiation at 670 nm for 40 min. Note that: before UV/Vis absorption tests were performed,

an equal volume ethanol solution is added to the sample solution to eliminate the scattering error from the assemblies and facilitate quantitative analysis.

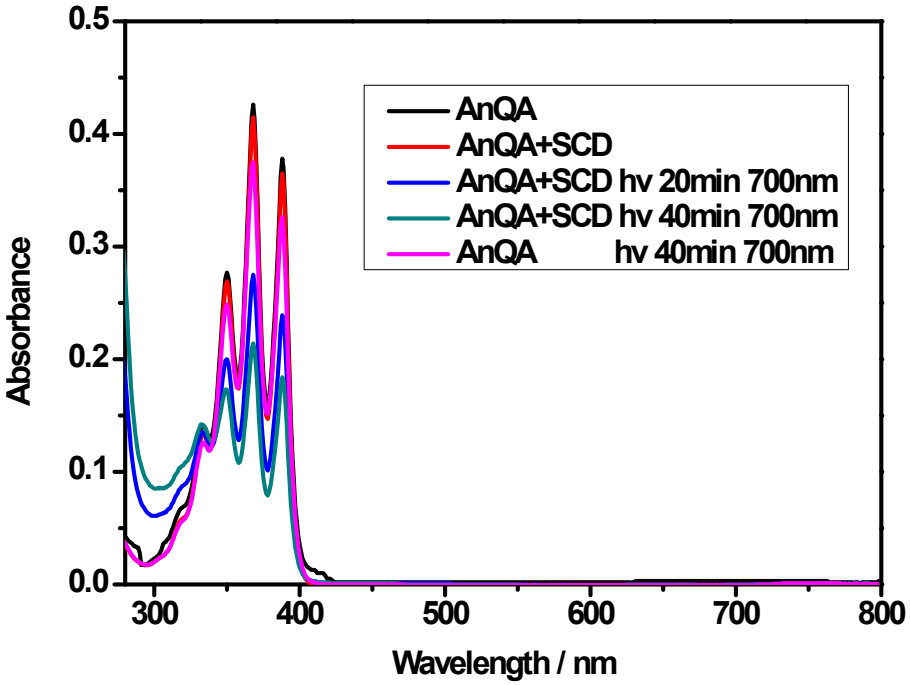


Figure S14. UV/Vis absorption spectra of AnQA (0.10 mM), SCD/AnQA assembly, SCD/AnQA assembly after irradiation at 700 nm for 20 min, 40min and AnQA after irradiation at 700 nm for 40 min. Note that: before UV/Vis absorption tests were performed, an equal volume ethanol solution is added to the sample solution to eliminate the scattering error from the assemblies and facilitate quantitative analysis.

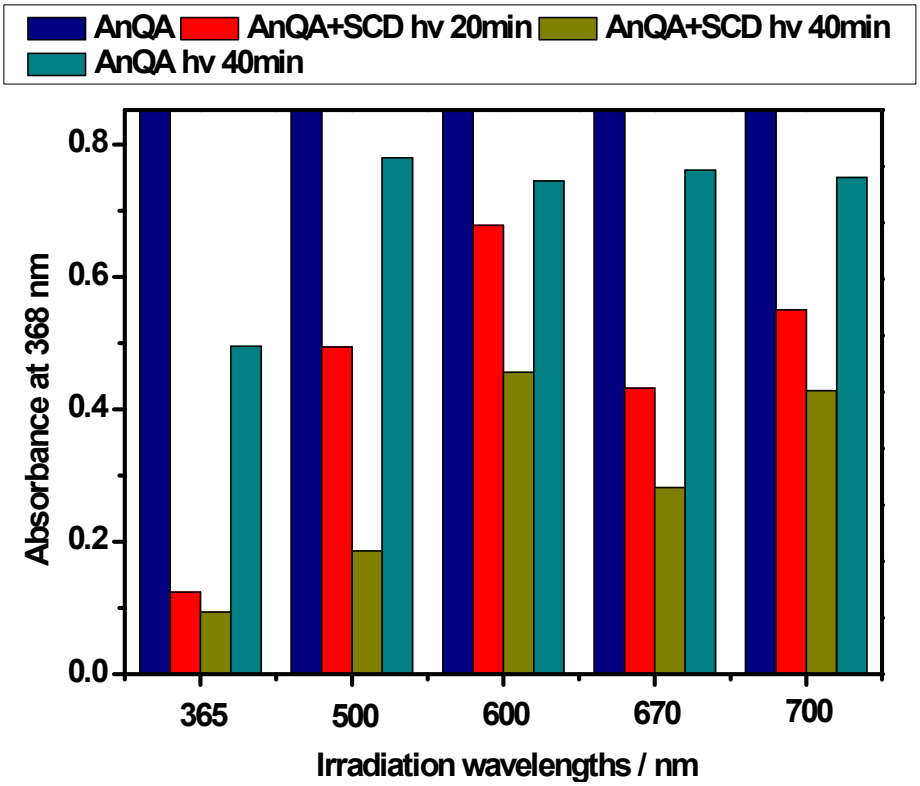
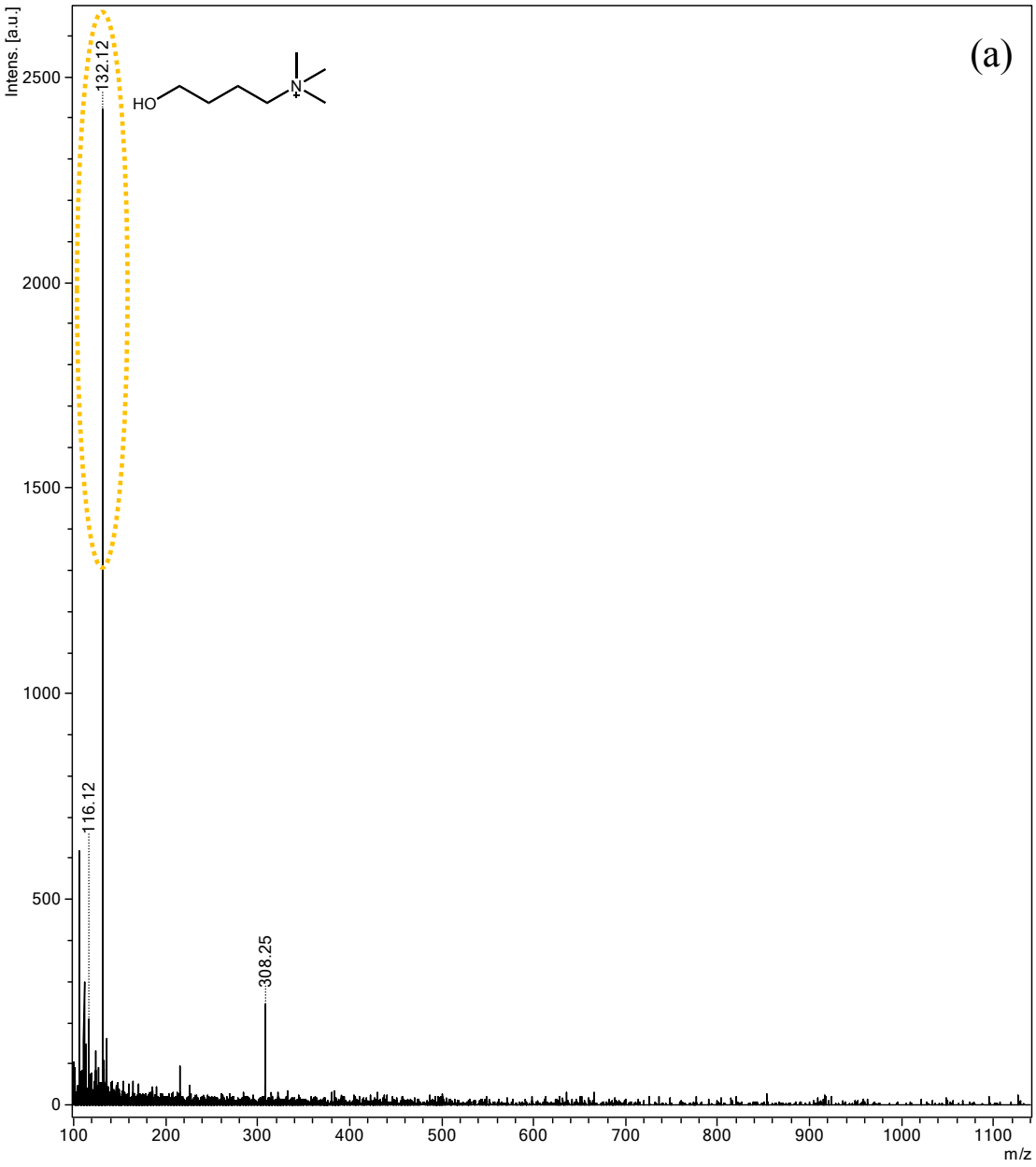
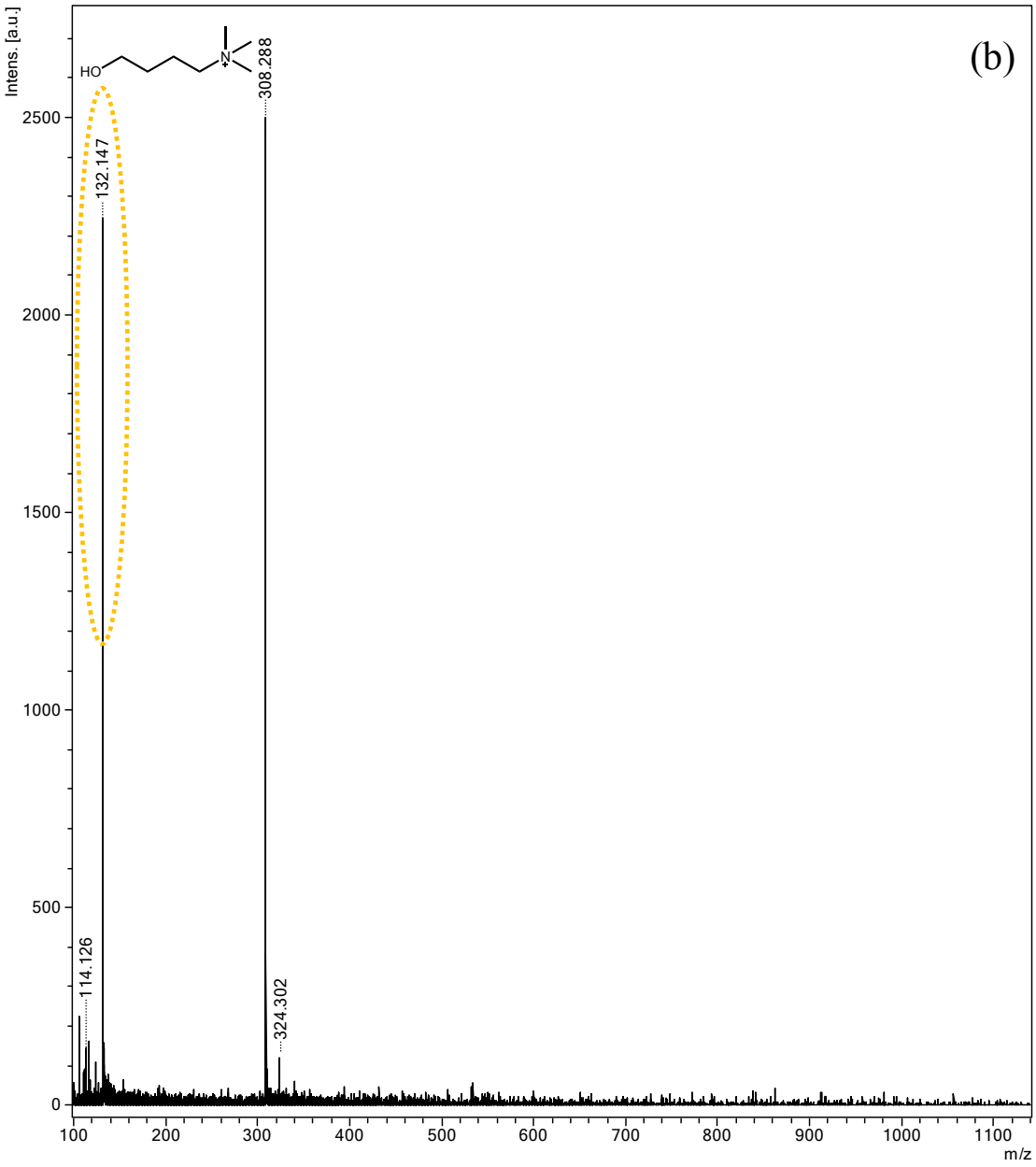
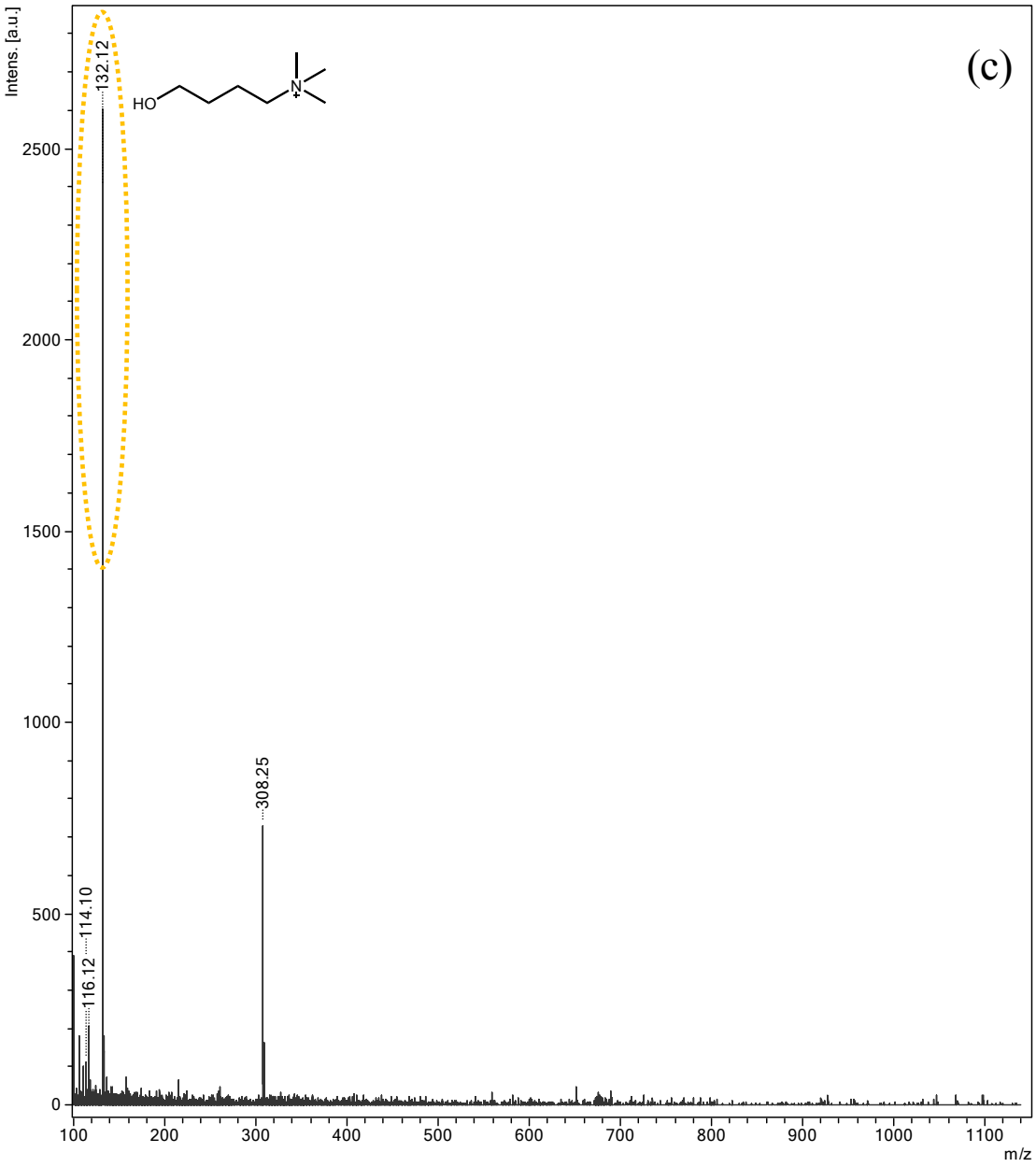


Figure S15. Absorbance of AnQA and the SCD-AnQA assembly at 368 nm upon irradiation at different light wavelengths for different amounts of time.


(a)
Intens. [a.u.]
2500
2000
1500
1000
500
0
132.12
116.12
308.25
HO
N
100
200
300
400
500
600
700
800
900
1000
1100
m/z


(b)
Intens. [a.u.]
HO
N+
308.288
132.147
114.126
324.302
2500
2000
1500
1000
500
0
100
200
300
400
500
600
700
800
900
1000
1100
m/z


(c)
Intens. [a.u.]
2500
2000
1500
1000
500
0
132.12
308.25
114.10
116.12
HO
N+
100
200
300
400
500
600
700
800
900
1000
1100
m/z

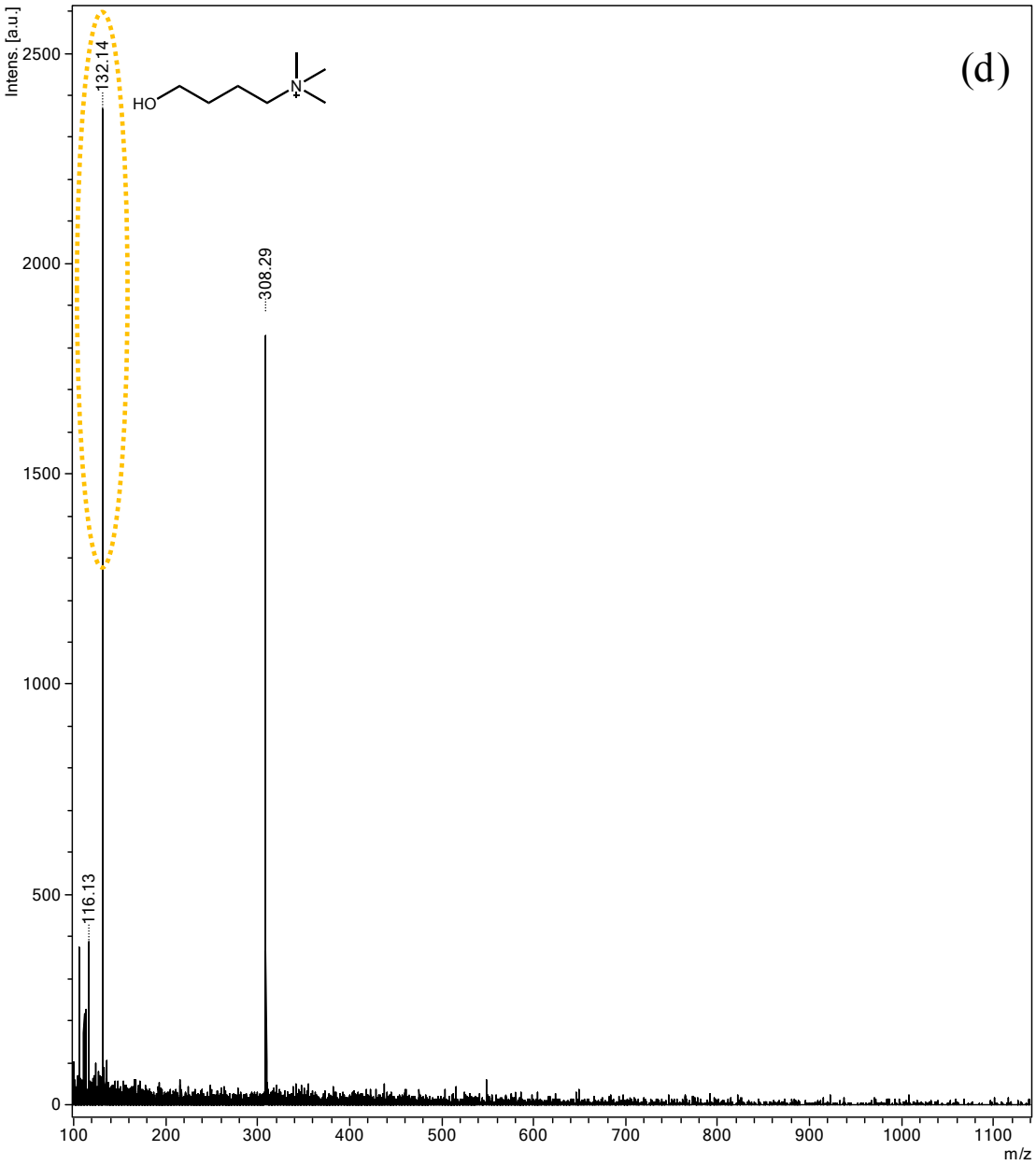


Figure S16. MALDI-TOFMS spectra of the SCD/AnQA assembly after irradiation at 500 nm (a), 600 nm (b), 670 nm (c), 700 nm (d) for 40 min.

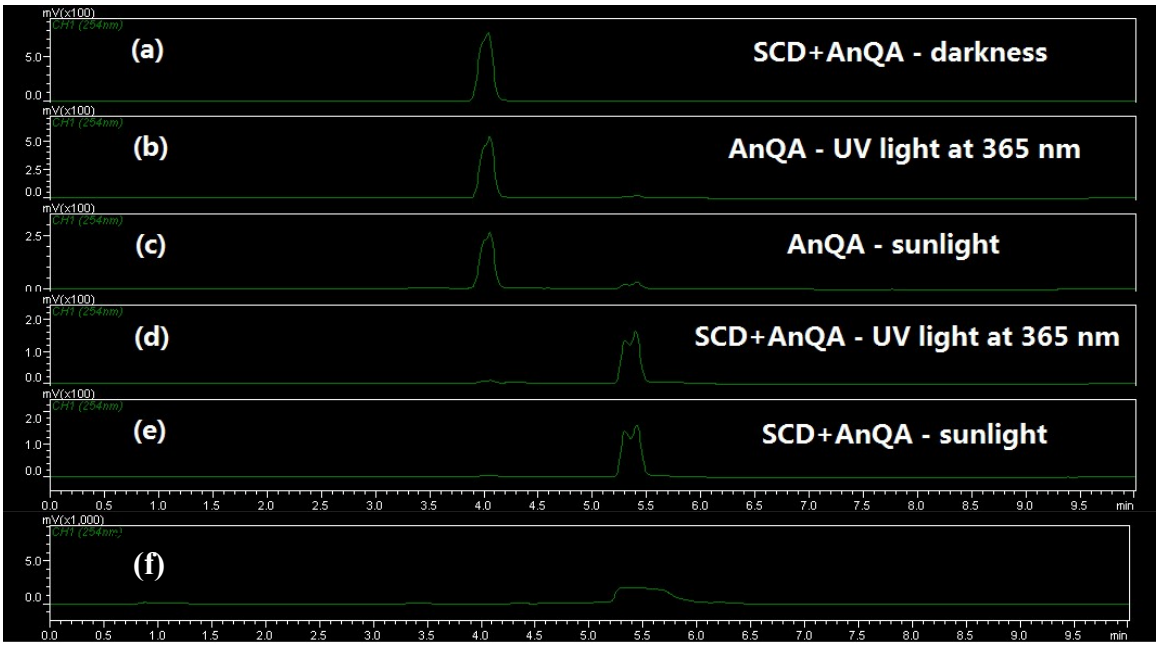


Figure S17. Typical HPLC chromatogram of anthraquinone (f), the SCD/AnQA assembly placed in darkness (a), free AnQA after irradiation with UV light at 365 nm (b), free AnQA after irradiation with sunlight (c), the SCD/AnQA assembly after irradiation with UV light at 365 nm (d), the SCD/AnQA assembly after irradiation with sunlight (e) for 20 minutes. Peaks in the chromatograms were detected by monitoring the absorption at 254 nm.

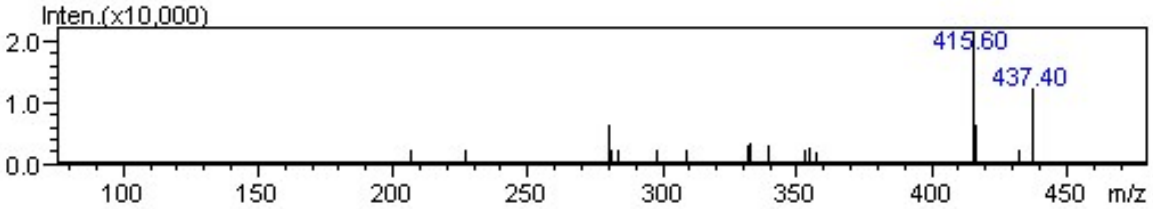


Figure S18. MS spectra of anthraquinone. Assignment of the main peak: m/z 415.60 ([M − Br]$^+$, calcd for $C_{28}H_{16}O_4$, 416.10).

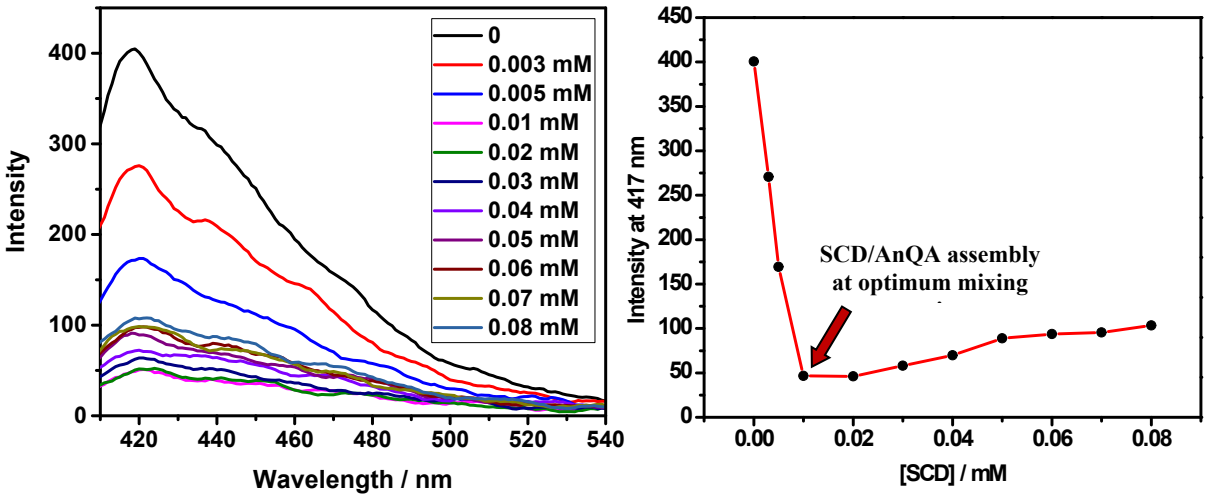


Figure S19. Emission spectra (a) and trend chart of fluorescence emission intensity of SCD/AnQA assembly solution at 417 nm with increasing the concentration of SCD. [AnQA] = 0.10 mM

Host	DNC[2]		
Outer size / Å	14.32 × 10.17 × 6.52		
Inner size / Å	10.45 × 6.88 × 6.52		
Height / Å	6.52		
Host	β-cyclodextrin[3]	Calix[6]arene[4]	Cucurbit[8]uril[5]
Outer diameter / Å	15.4	-	17.5
Cavity diameter / Å	6.0-6.5	4.96	8.8
Height / Å	7.9	16.24	9.1
Cavity volume / Å^3	262	-	479

Table S1. All host molecules with their size.

References

[1] a) G. Arena, A. Contino, G. G. Lombardo, D. Sciotto, *Thermochim. Acta*, **1995**, 264, 1; b) S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki, O. Manabe, *J. Am. Chem. Soc.*, **1986**, 108, 2409.

[2] L. Chen, H. Y. Zhang, Y. Liu, *J. Org. Chem.*, **2012**, 77, 9766.

[3] E. M. Martin Del Valle, *Process Biochem.*, **2004**, 39, 1033.

[3] E. Da Silva, A.N. Lazar, A.W. Coleman, *J. Drug Del. Sci. Tech.*, **2004**, 14, 3.

[4] Khaleel I. Assaf and Werner M. Nau, *Chem. Soc. Rev.*, **2015**, 44, 394.