

Macrocycle-assisted tunable carbon dots from single organic precursors in water

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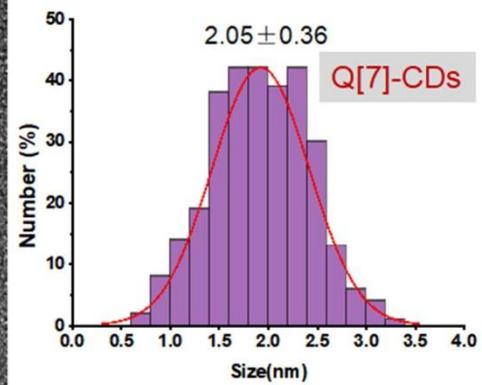
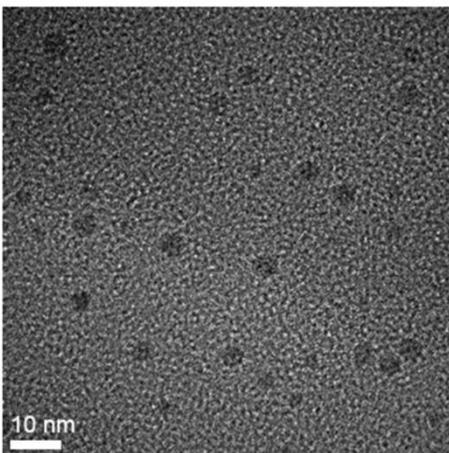
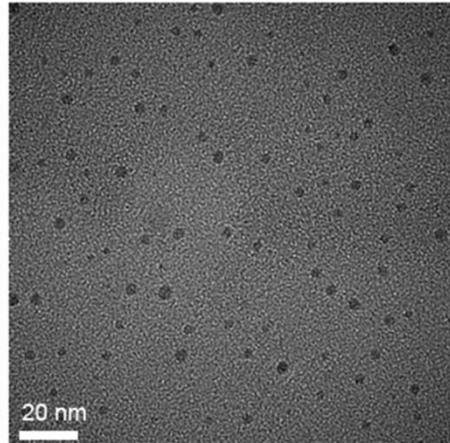
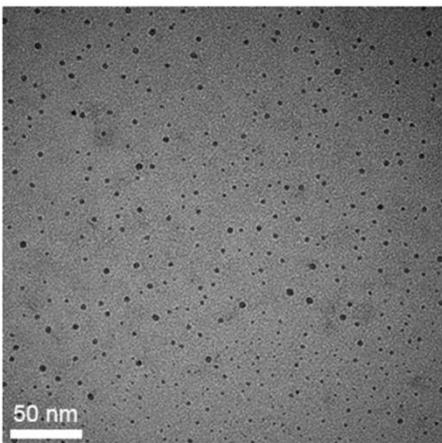
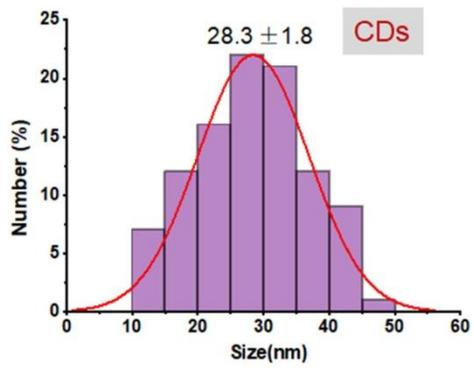
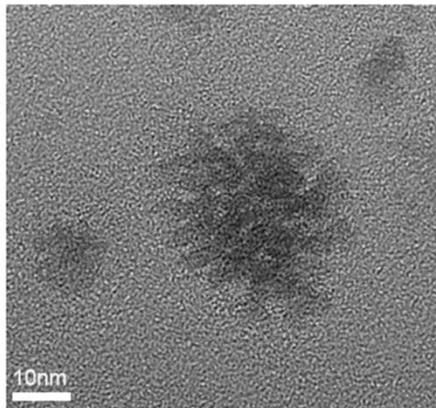
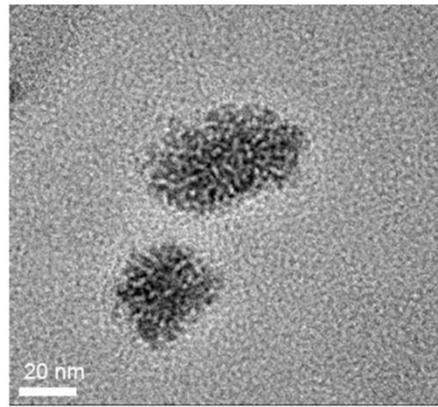
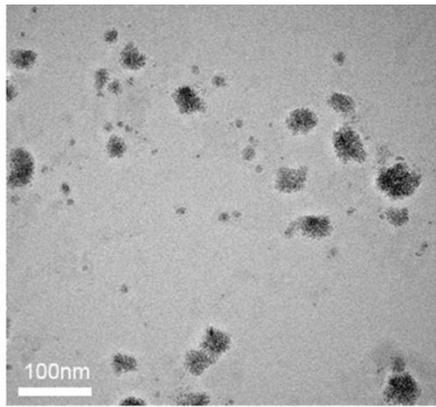
Materials

Reagents purchased from commercial suppliers were used as received. Tobias acid (TBA) and 1-adamantanamine were purchased from TCI (Shanghai). Q[7] and Q[8] were prepared according the reported literatures.¹ Cell culture of Dulbecco's modified eagle medium (DMEM) and Fetal bovine serum (FBS) were purchased from Thermo Fisher Scientific. All reagents were direct used without any further purification. Deionized (DI) water was used throughout the whole process.

Characterization

¹H NMR spectra were measured on JNM-ECZ400 MHz nuclear magnetic resonance (NMR) spectrometer. UV-vis spectra were recorded on an Agilent-8453 spectrophotometer. Fluorescence spectra measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer equipped with a xenon discharge lamp. Fluorescence lifetime and quantum yield were obtained with an Edinburgh Instrument FLS 980 fluorospectrometer. Fourier transform infrared (FTIR) spectra recorded on a Bruker Vertex with KBr pellets. Powder X-ray diffraction (XRD) pattern was performed on a D/max 82400 Xray powder diffractometer (Rigaku, Japan) by using CuK α ($\lambda = 0.154056 \text{ \AA}$) as the incident radiation. Transmission electron microscopy (TEM) was carried out on a Hitachi H-8100 EM (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV.

1. A. Day, A. P. Arnold, R. J. Blanch and B. Snushall, *J. Org. Chem.* **2001**, *66*, 8094–8100.



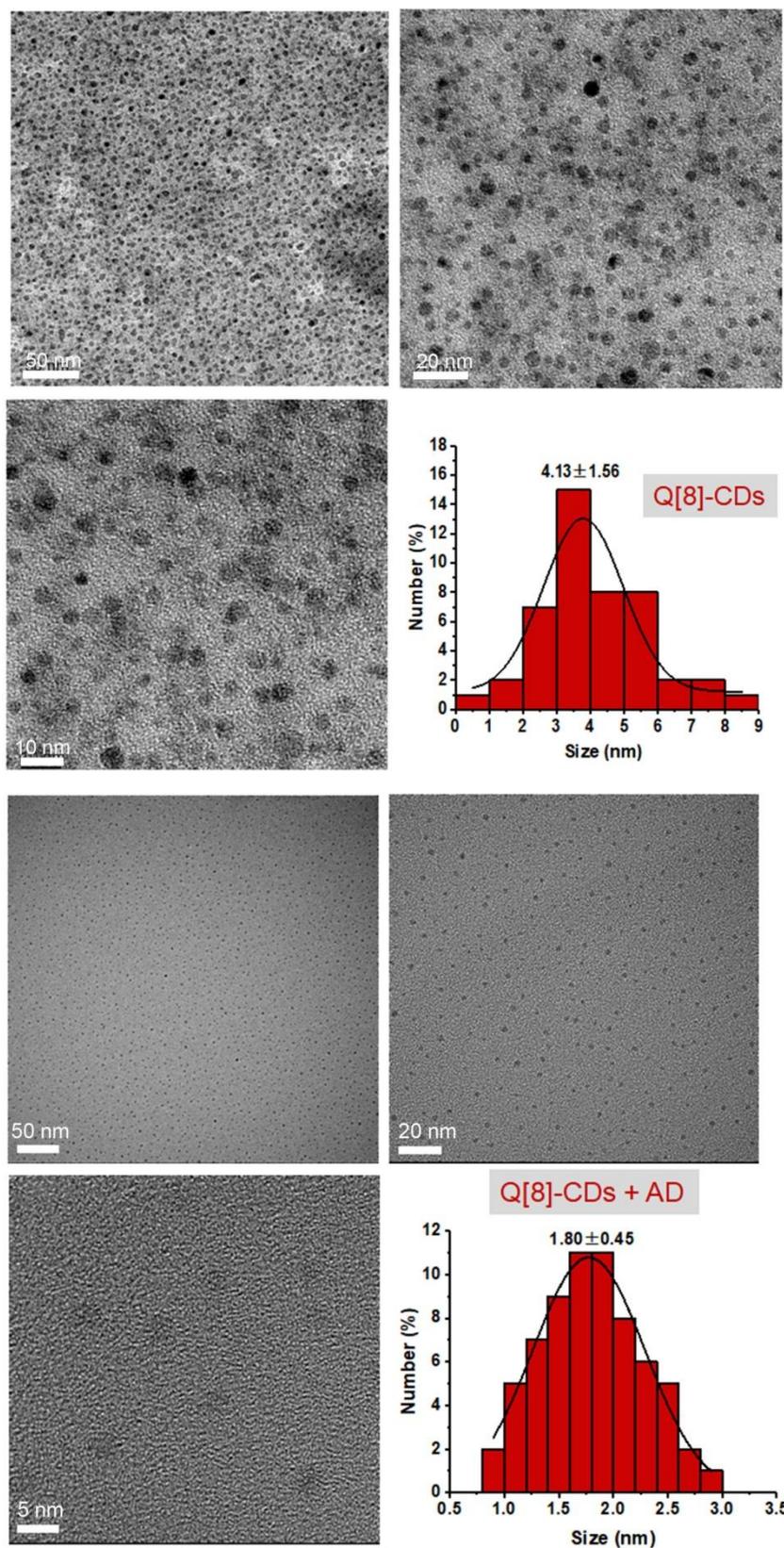


Figure S1. TEM images of CDs, Q[7]-CDs, Q[8]-CDs, and Q[8]-CDs (20.0 $\mu\text{g/mL}$) upon the addition of 50.0 μM of AD in water.

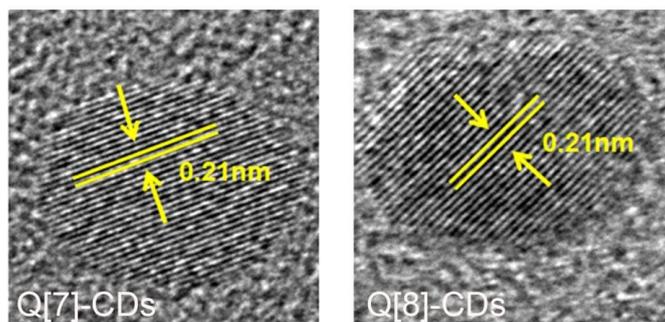


Figure S2. High resolution TEM images obtained for Q[7]-CDs and Q[8]-CDs.

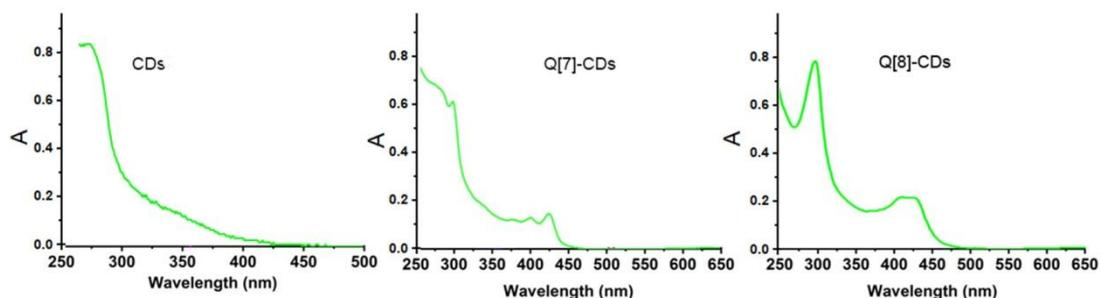


Figure S3. UV-vis absorption spectra of CDs, Q[7]-CDs, and Q[8]-CDs (each of 20.0 $\mu\text{g/mL}$ in neutral water, pH 7.1).

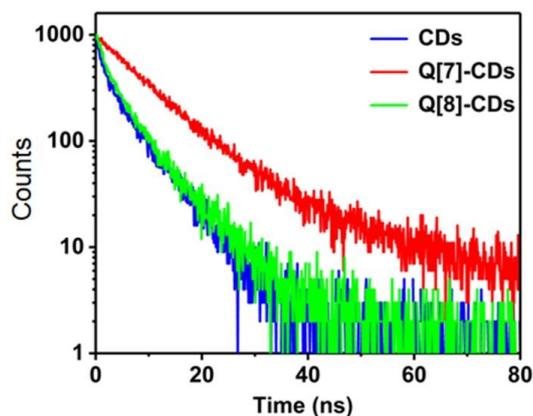


Figure S4. Fluorescence decay traces of CDs, Q[7]-CDs, and Q[8]-CDs (each of 20.0 $\mu\text{g/mL}$ in neutral water, pH 7.1) ($\lambda_{\text{ex}} = 400 \text{ nm}$).

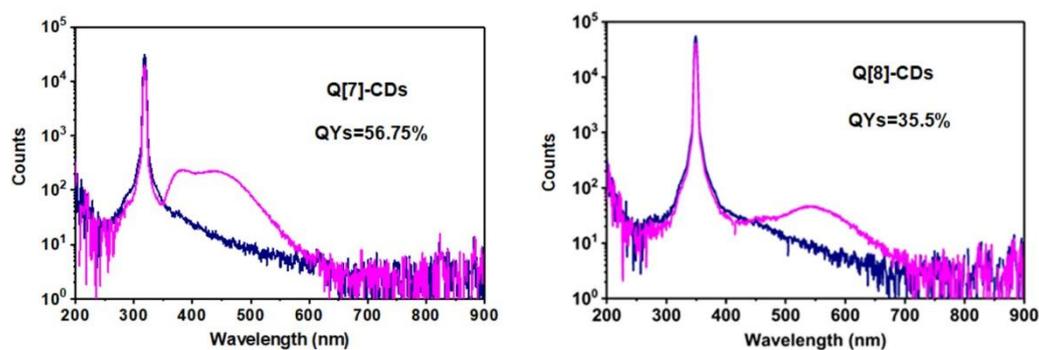


Figure S5. Absolute fluorescence quantum yield of Q[7]-CDs, and Q[8]-CDs (each of 20.0 $\mu\text{g/mL}$ in neutral water, pH 7.1) ($\lambda_{\text{ex}} = 400 \text{ nm}$).

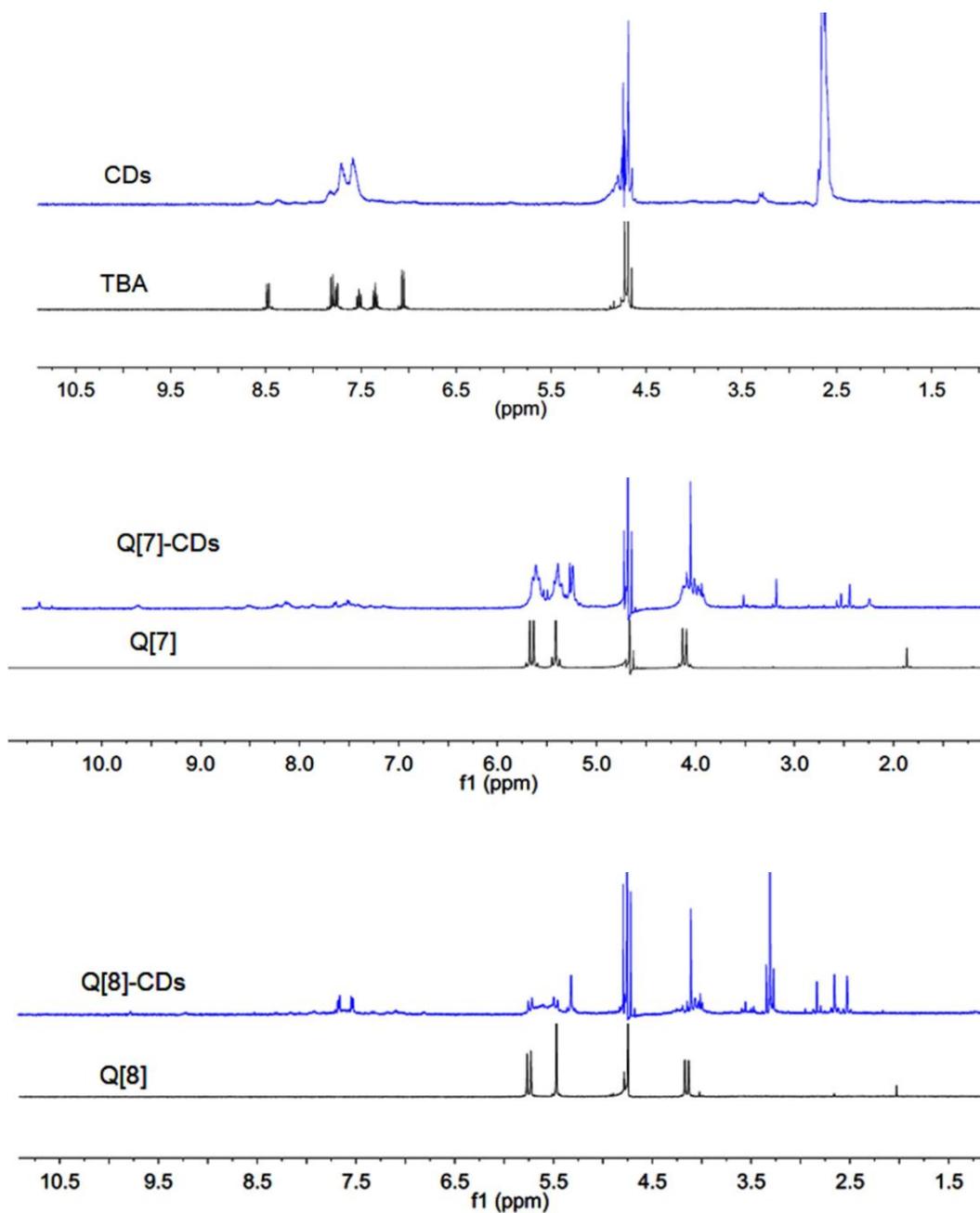


Figure S6. Blue color: ¹H NMR spectra of CDs, Q[7]-CDs, and Q[8]-CDs in D₂O at 25 °C; black color: ¹H NMR spectra of TBA, pristine Q[7], and pristine Q[8] in D₂O at 25 °C, (where TBA was used directly from commercial sample, pristine Q[7] and pristine Q[8] were obtained by dissolving their pure samples in DI water in Teflon autoclave and heated at 180 °C for 2 h).

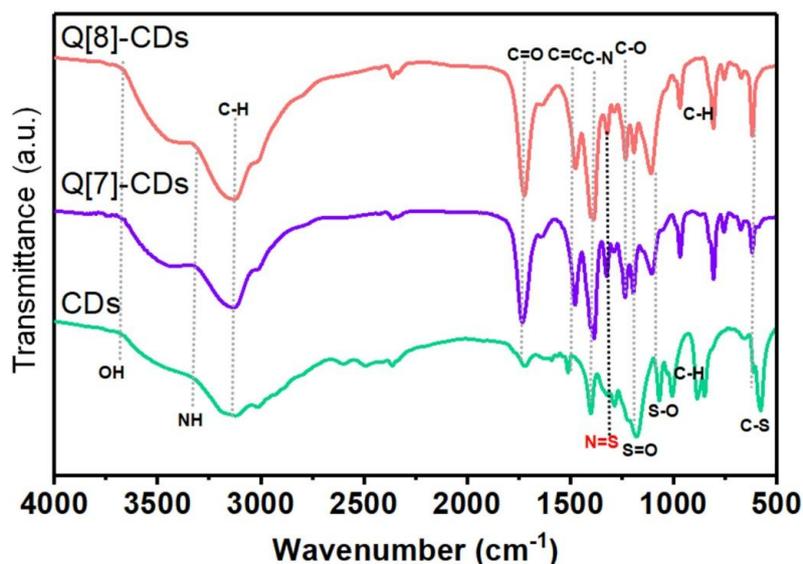


Figure S7. FT-IR of the CDs, Q[7]-CDs, and Q[8]-CDs.

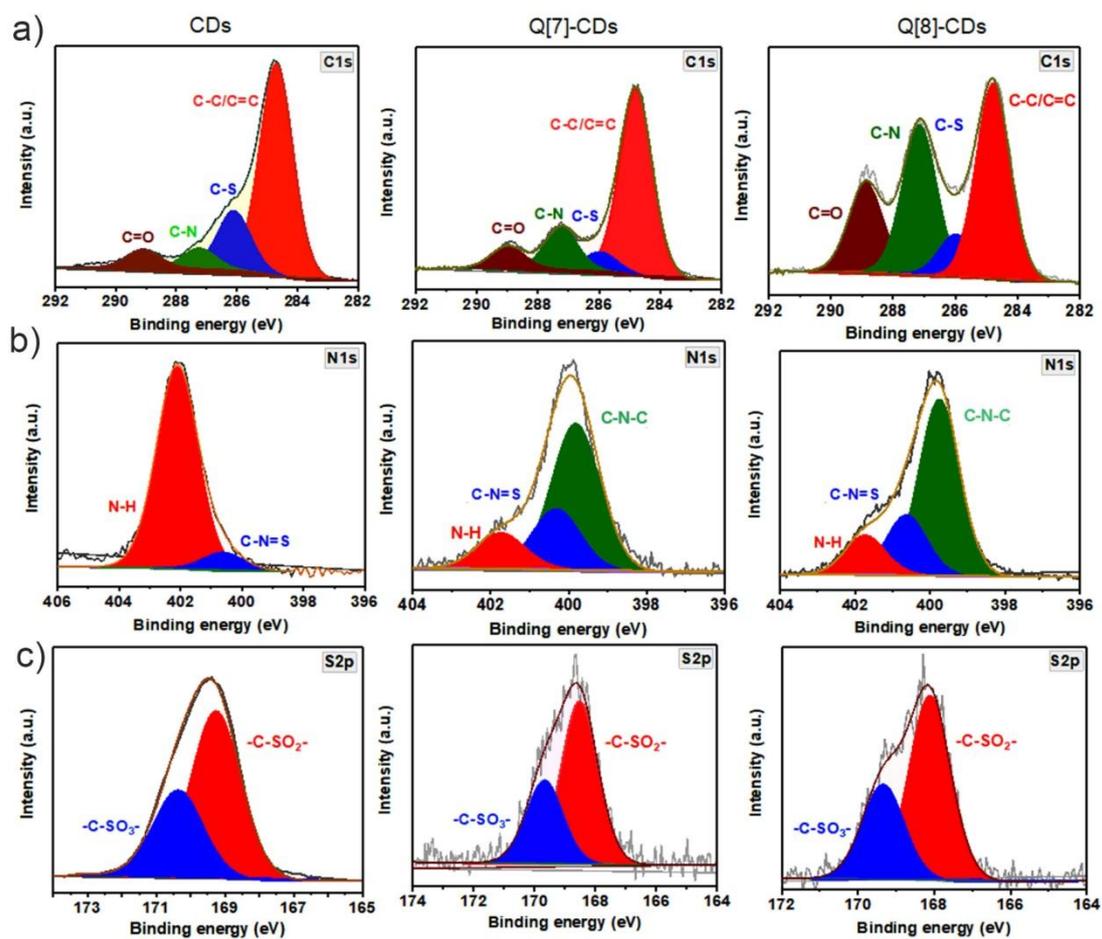


Figure S8. (a) High resolution XPS spectra of C1s of CDs, Q[7]-CDs, and Q[8]-CDs; (b) High resolution XPS spectra of N1s of CDs, Q[7]-CDs, and Q[8]-CDs; (c) High resolution XPS spectra of S2p of CDs, Q[7]-CDs, and Q[8]-CDs.

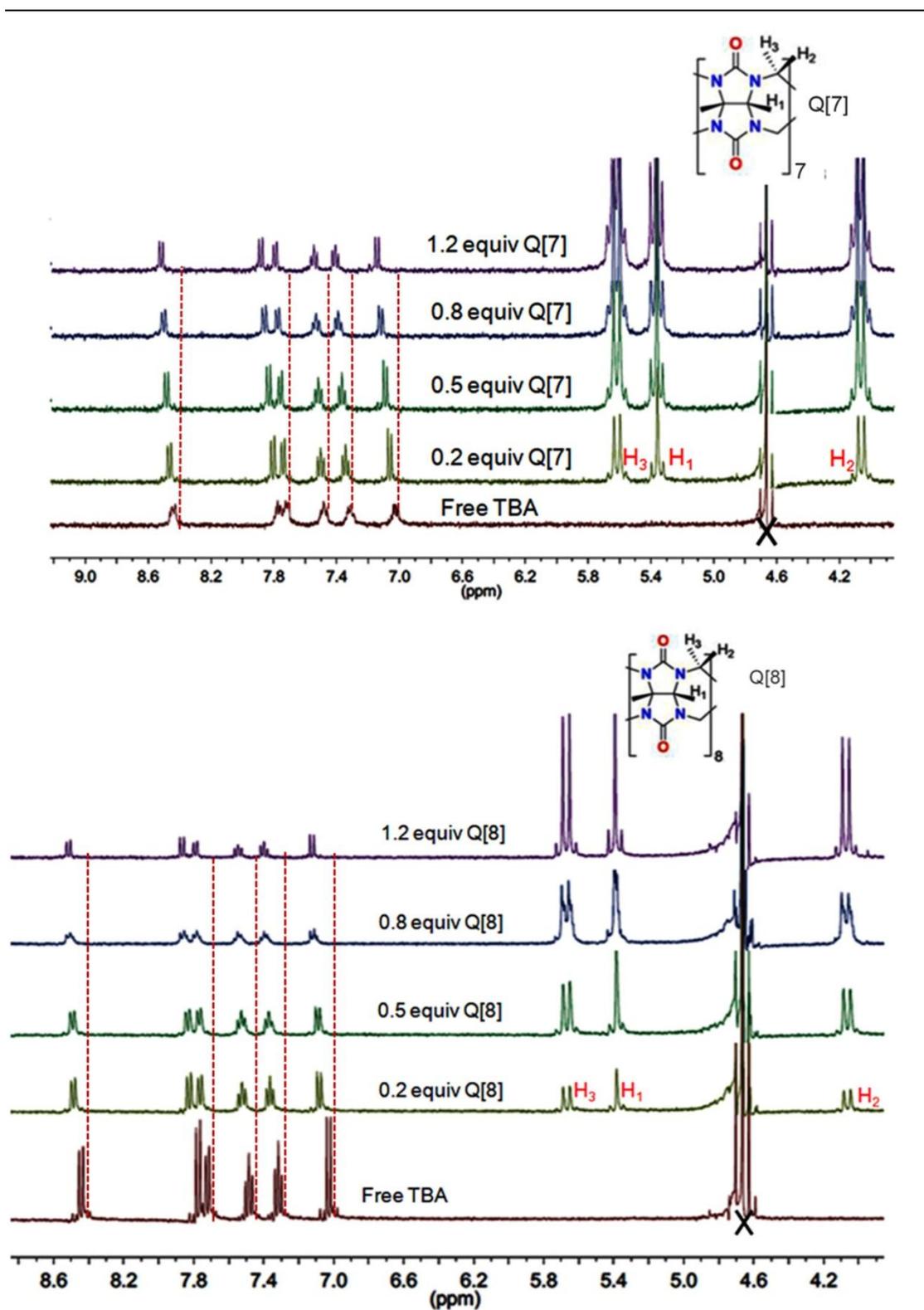


Figure S9. ^1H NMR spectra of TBA (1.0 mM in D_2O , pD, 2.5) in the absence and presence of increasing concentrations of Q[7] and Q[8], respectively, at 25 $^\circ\text{C}$. The peak of solvent was marked as (X).

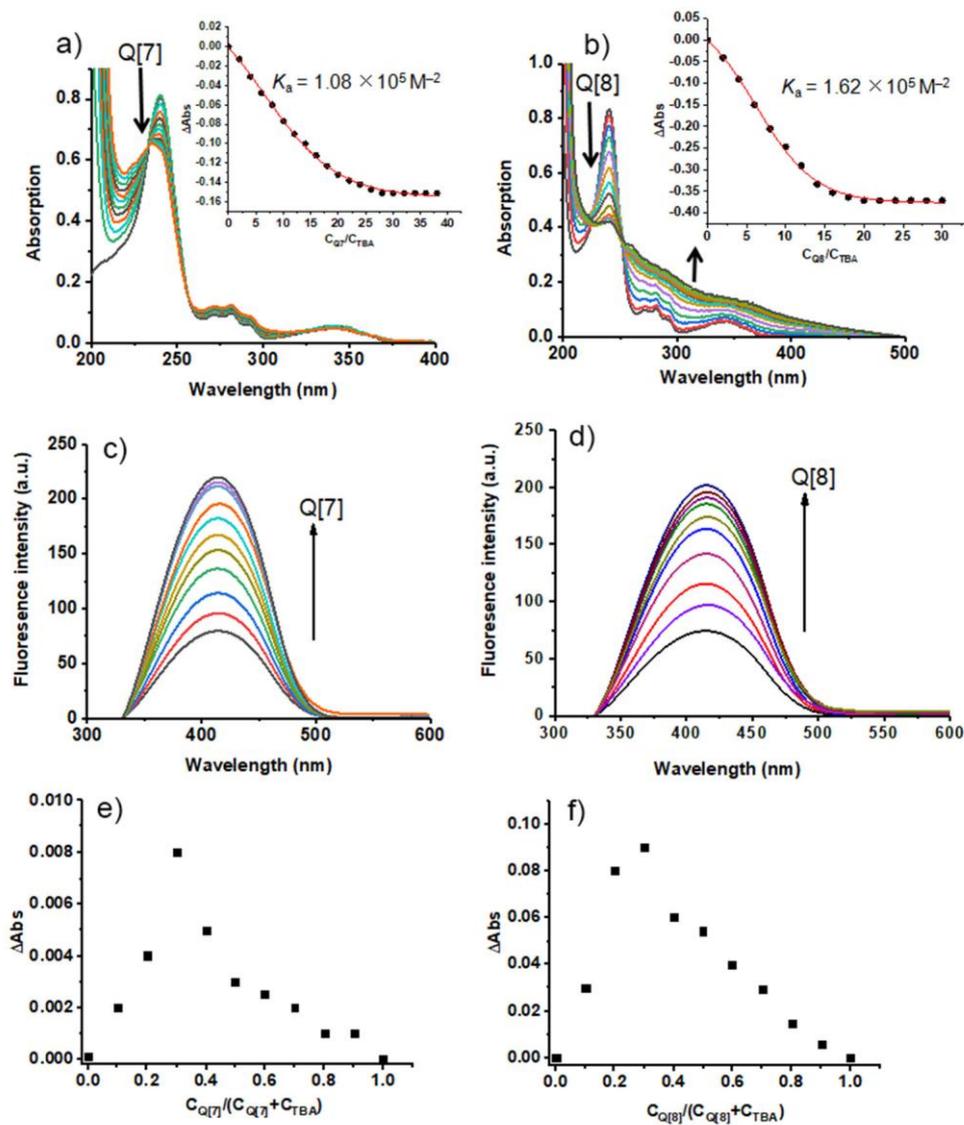


Figure S10. UV-vis absorption (a, b) and fluorescence spectra (c, d) of TBA (10.0 μM in aqueous solution, pH 2.5) in the presence of increased concentrations of Q[7] and Q[8], respectively. ($\lambda_{\text{ex}} = 241 \text{ nm}$); (e, f) Job plot of Q[7] and Q[8] with TBA guest. Insert (a, b), binding constant of Q[7] and Q[8] with TBA guest.

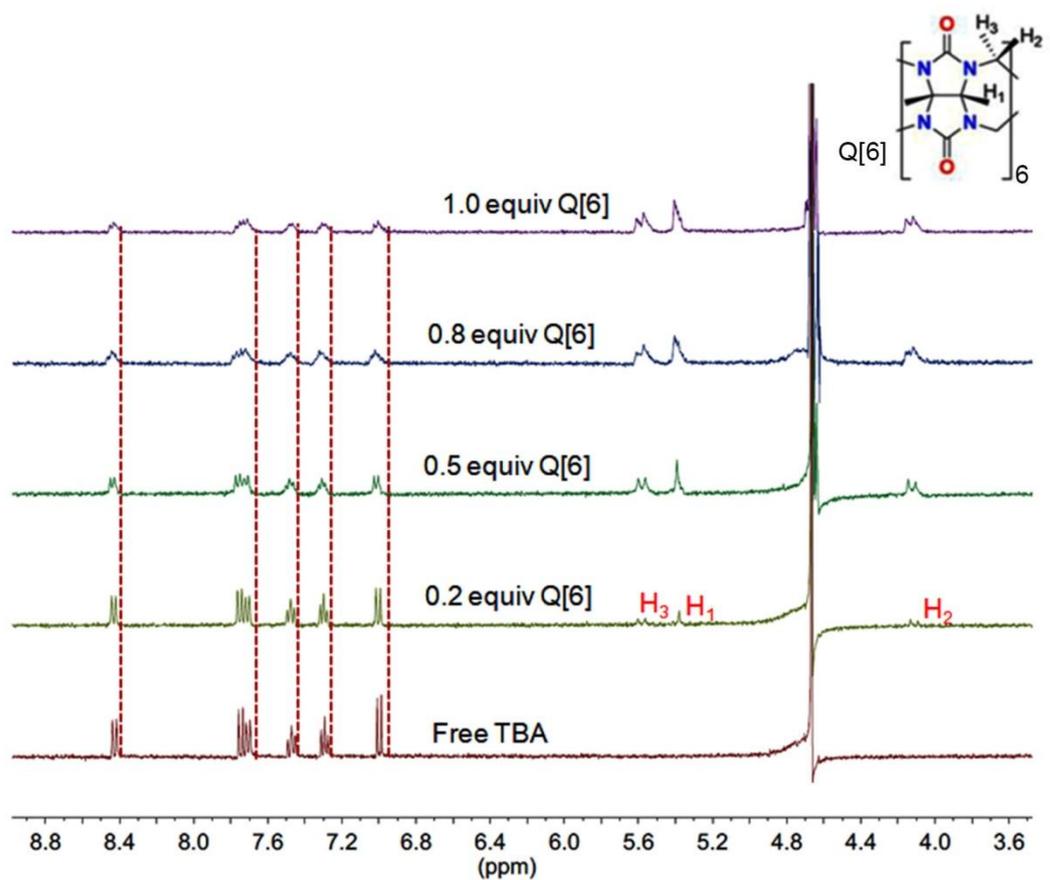


Figure S11. ^1H NMR spectra of TBA (1.0 mM in D_2O , pD 2.5) in the absence and presence of increasing concentrations of Q[6] at 25 $^\circ\text{C}$.

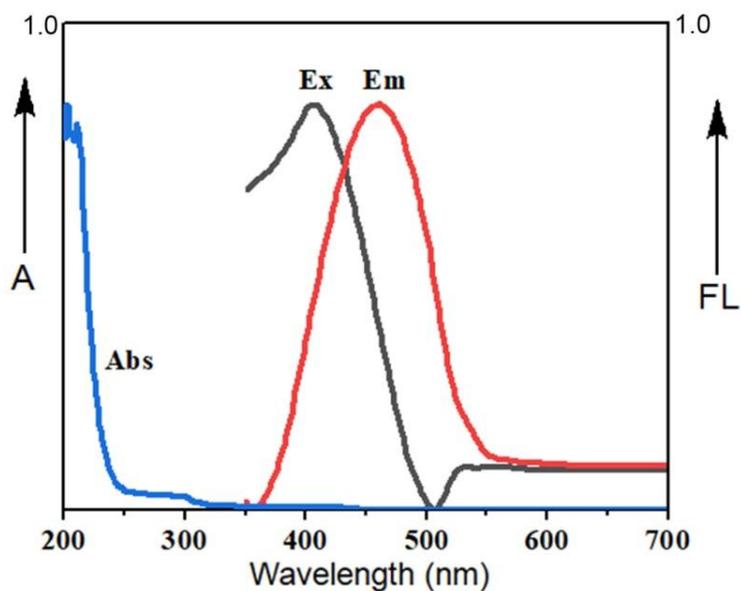


Figure S12. Normalized absorption and emission spectra of Q[6]-CDs (20.0 $\mu\text{g}/\text{mL}$ in neutral aqueous solution, pH 7.1).

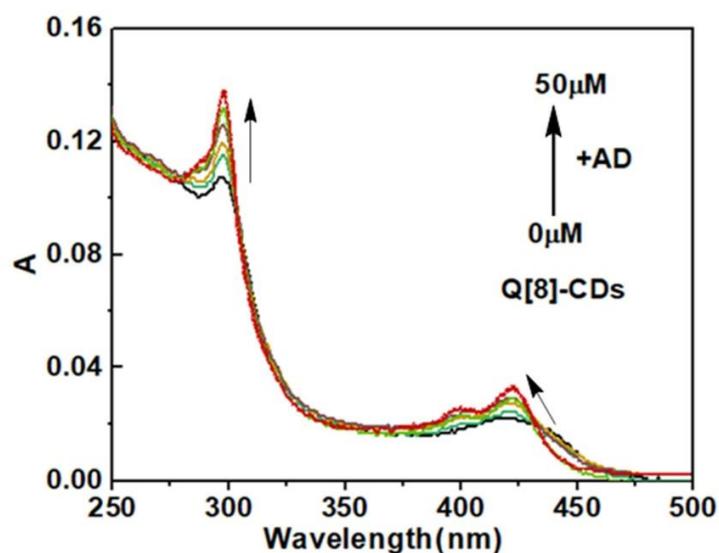


Figure S13. UV-vis absorption spectra obtained for Q[8]-CDs (20.0 $\mu\text{g}/\text{mL}$ in neutral water, pH 7.1) upon increasing the concentration of AD in water.

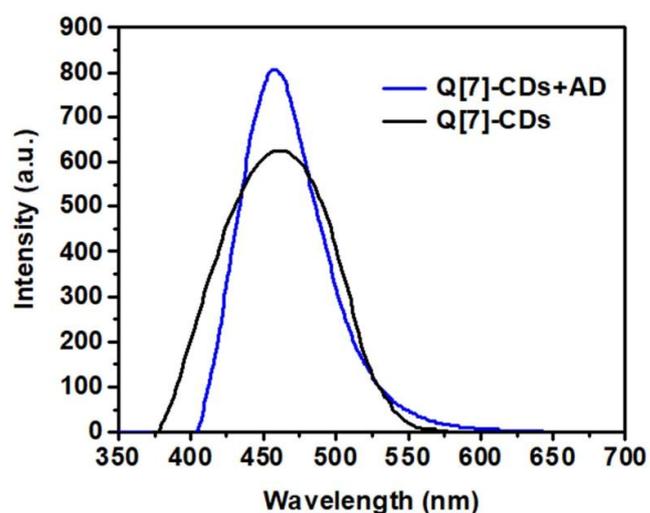


Figure S14. Fluorescence spectra obtained for Q[7]-CDs (20.0 $\mu\text{g}/\text{mL}$) in neutral water (pH 7.1) upon addition of 50.0 μM AD.

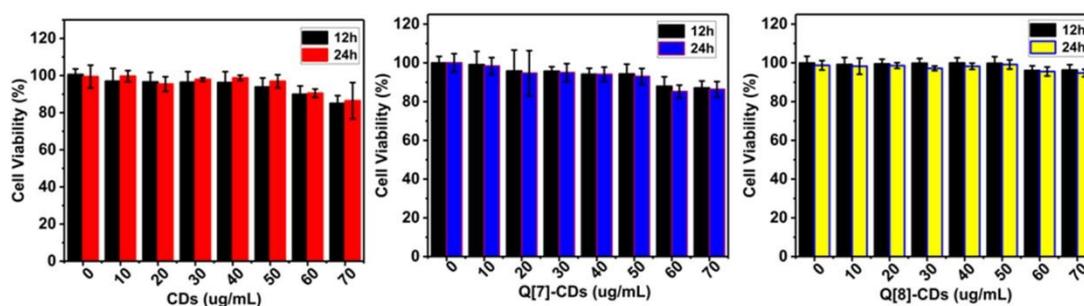


Figure S15. Percentage of MCF-7 cell viability remaining after cell treatment with CDs, Q[7]-CDs and Q[8]-CDs, respectively, at different times (untreated cells were considered to have 100% survival). Cell viability was assayed by the MTT method.

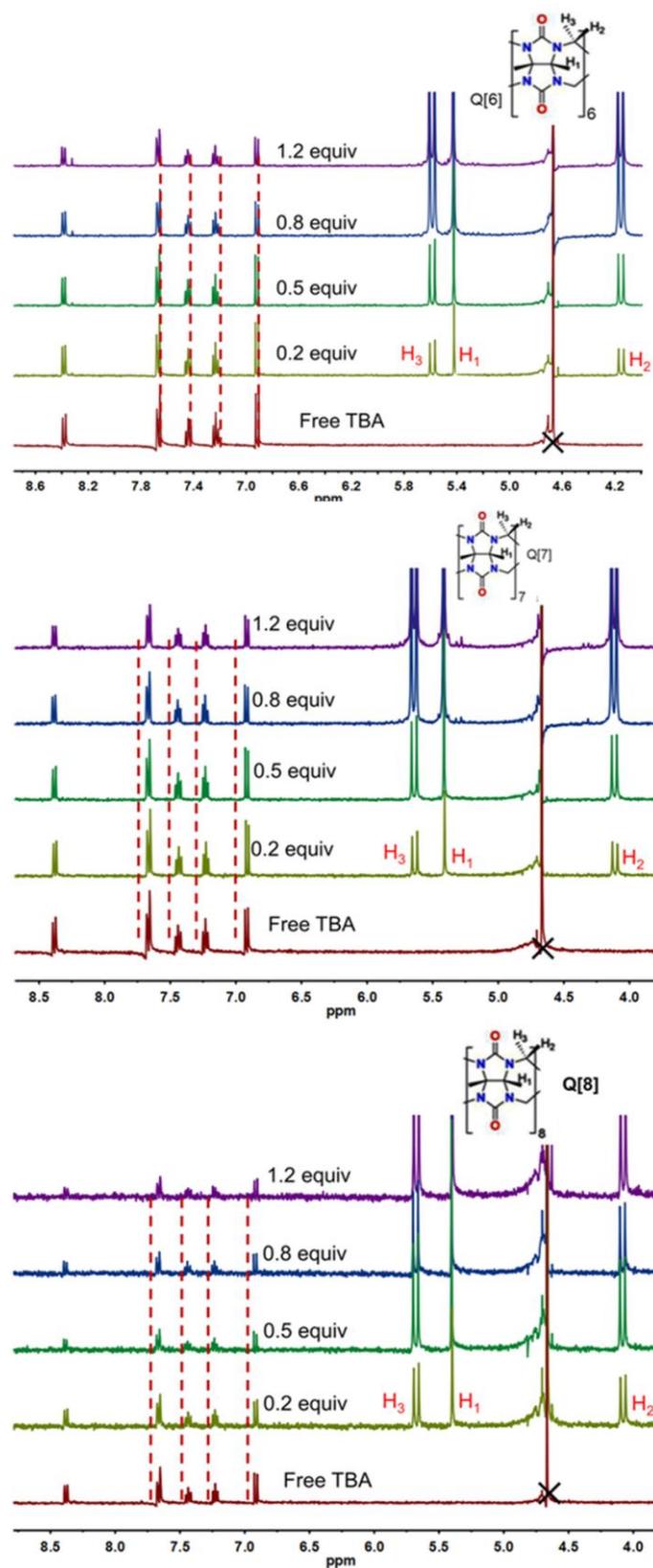


Figure S16. ^1H NMR spectra of TBA (1.0 mM in D_2O , pD 8.0) in the absence and presence of increasing concentrations of Q[6], Q[7] and Q[8], respectively, at 25 $^\circ\text{C}$. The peak of solvent was marked as (X).