Supporting Information

pH-Controlled Enantioselectivity Switching of Irregular Photodimers in Photocyclodimerization of 2-Anthracenecarboxylic acid-mediated with β-cyclodextrin Derivatives

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TABLE OF CONTENTS

1. General information……..…...……....S1

2. Synthesis and characterization of CDx derivatives…….……....…….....S3

3. Conformation analysis of hosts **9-11**……..……..….S14

4. Binding constant of hosts **7**, **8** and **10** with AC……..…….....S21

5. Photocyclodimerization of AC mediated by native and modified CDxs……..……....S29

6. Calculation of pK_a values……..…….....S34

7. UV-vis., Fluorescence, and CD spectral studies.……...…….....S37

8. NMR spectral studies……...S41

9. Theoretical calculation studies……..……..……...…S47

10. References……...……..……....S48

1. General Information

1.1 Experimental

Materials

β-Cyclodextrin (CDx, **7**) (Junsei, Japan), and 8-bromomethylquinoline (Adamas, China) were purchased and are used as received without further purification. 2-Anthracenecarboxylic acid (AC) was purchased from Aladdin (China) and used as received without further purification. Double distilled water (which was free from ions) and HPLC grade solvents has used for all spectral measurements. All other chemicals and solvents were purchased from Adamas-beta, Amethyst, and Oceanpak and used as received without further purification.

1.2 Methods

Reverse-phase chromatography was used to separate the CDx derivatives and water-soluble compounds through ODS-SM-50C column and water - 90% EtOH/MeOH (v/v) (linear elution) in water as eluent.

Nuclear magnetic resonance spectroscopy (NMR) was acquired on a Bruker Ascend 400 (400 MHz) instrument using TMS as an internal standard at 298 K. Coupling constants were reported in Hz and chemical shifts (δ) in ppm [relative to TMS or residual solvent peaks [for ^{1}H ($CDCl_3$: 7.26, DMSO-d_6: 2.50, D_2O: 4.79, CD_3CN: 1.94, CD_3OD: 3.31) and ^{13}C ($CDCl_3$: 77.16, DMSO-d_6: 39.52, CD_3CN: 1.32, 118.26, CD_3OD: 49.00)].[S1] Multiplicities were assigned as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and brs (broad singlet).

Ultraviolet-visible absorption spectroscopy (UV-Vis.) measurements were recorded using a JASCO V-650 double beam spectrophotometer with PMT detector. UV-vis. Analyses were done using JASCO-Spectral manager, and the calculations were done in Microsoft Origin software. Fluorescence spectroscopy was recorded using JASCO FP-8500 or Fluoromax-4 (attached with TCSPC) spectrofluorometer (HORIBA JOBIN YVON) with excitation slit set at 5.0 nm band pass and emission at 5.0 nm band pass in 1 x 1 cm quartz cell. Emission calculations were done using Microsoft Origin software. Circular dichroism spectroscopy (CD) has measured on a JASCO J-1500 spectropolarimeter with PMT detector in the wavelength range 190-900 nm. For these studies, solutions were of less or higher concentration than those for spectrophotometric studies. Sample cell temperature was controllable in the range from -90 °C to 100 °C.

Mass-spectral data were obtained using Electrospray Ionization Mass Spectrometry (ESI-MS) and Matrix-Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) mass spectrometry. MALDI mass analysis has performed in the positive ion mode on a MALDI-TOF mass spectrometer (BRUKER-AUTO FLEX III, USA). The samples were introduced into the ion source through a multi-sample probe (microtiter format with 384/1536 samples) coated with CHCA(NACL) (α-cyano-4-hydroxy cinnamic acid) or DHAP (2',6'-dihydroxyacetophenone) matrixes. The data were collected based on TOF, through reflection (REF) or linear (LIN) mode. Detector: multichannel plate; vacuum method: Turbomolecular pumps/mechanical pumps; scan rate (amu/sec): 20 / 50 Hz laser; data

acquisition (data analysis system): Flex analysis. ESI-MS analysis has performed in the positive/negative ion mode on a liquid chromatography-ion trap mass spectrometer (Waters® Q-Tof Premier™, Waters Corporation, USA). The samples were introduced into the ion source by the direct nanoflow method at different flow rates. The high-resolution *m/z* rang up to 100,000. Isothermal titration calorimetry (ITC) data were recorded by using VP-ITC MicroCalorimeter.

1.3 Preparation of stock solutions

Preparation of PBS buffer solution: The pH 4-9 buffer solutions were prepared by mixing the different volumes of separately prepared 66.7 mM NaH_2PO_4 and 66.7 mM Na_2HPO_4 solution. The pH 2 and 3 buffer solutions were prepared by the addition of 1 M HCl solution to 66.7 mM NaH_2PO_4 solution. The pH 10-buffer solution has prepared by the addition of 66.7 mM NaOH solution to 66.7 mM Na_2HPO_4 solution.

Preparation of AC solution: 0.004 M AC solution was prepared by dissolving the 88.89 mg of AC in 0.01 M NaOH solution and sonicated for 2 hrs at room temperature. The diluted AC solutions of different pH were prepared dilution of the above stock using respective PBS buffers and used for measurements.

Preparation of host solution: Hosts solution of different pH were prepared by dissolving the respective quantity of solid hosts **7**, **8**, **9, 10** and **11** in PBS buffers and used for measurements.

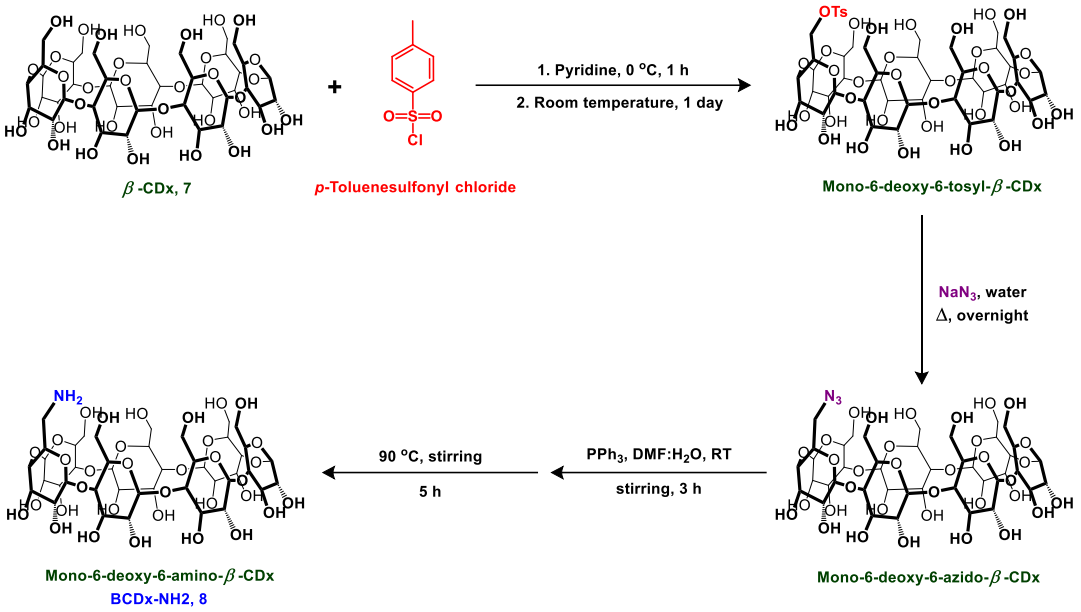
1.4 Photoreaction

Photoirradiation has performed in a temperature-controlled water/ethylene glycol bath. Solutions containing 0.2 mM AC and 2.0 mM CDx host derivatives **7**, **8**, **9, 10** and **11** were irradiated at 365 nm in a borosilicate glass tube under an N_2 atmosphere with an LED lamp (Zhuhai haoyun optoelectronic technology co. LTD, and model: HY-UV0003) with a diameter of 1 cm and an intensity of 200 mW/cm^2 for an appropriate time.

The resulting photolyzed solution was filtered using membrane and analyzed by analytical chiral HPLC, performed on a tandem column of Inertsil ODS-2 (GL Sciences Inc.) and CHIRALCEL® OJ-RH (Daicel), and operated at 35 ºC using 0.1% trifluoroacetic acid (TFA) dissolved in water and acetonitrile (62:38, volume ratio), at a flow rate of 0.5 mL/min. The relative chemical yield and *ee* value of photoproducts were determined from the peak area of HPLC chromatogram.

2. Synthesis and characterization of CDx derivatives

2.1 Synthesis and characterization of mono-6-deoxy-6-amino-*β*-CDx (BCDx-NH2, **8**)



Scheme S1. Synthesis of mono-6-deoxy-6-amino-*β*-CDx derivative (BCDx-NH2, **8**).

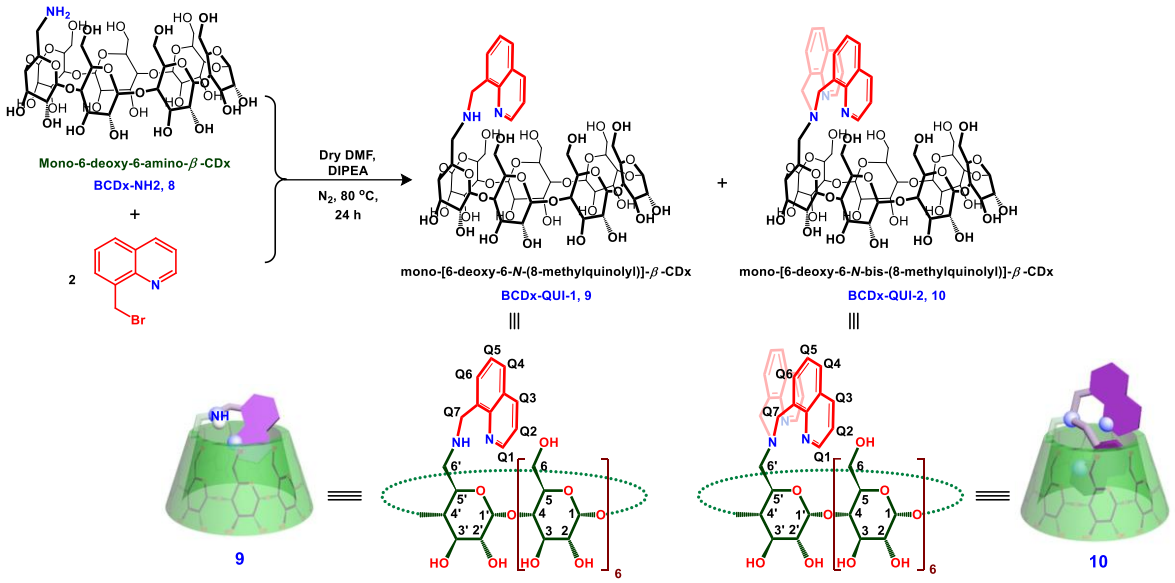
Mono-6-amino-*β*-CD$_X$ (BCDx-NH2, **8**) was synthesized and purified according to the procedure described in the literature with a small modification (Scheme S1).[S2] The product was dried for 24 h under vacuum at 60 °C and then stored in a vacuum desiccator and are characterized by ^{1}H and ^{13}C-NMR, and MS analysis, which were in accordance with literature reports.[S2]

Mono-6-deoxy-6-amino-*β*-cyclodextrin (BCDx-NH2, **8**), **^{1}H NMR (400 MHz, D$_2$O, δ ppm):** 5.02 (s, 8H), 4.79 (s, 70H), 4.01 – 3.68 (m, 32H), 3.68 – 3.44 (m, 16H), 3.44 – 3.04 (m, 2H), 2.88 (dt, *J* = 16.5, 8.3 Hz, 1H), 0.00 (d, *J* = 12.9 Hz, 1H), 0.00 (s, 8H), 2.95 – 2.79 (m, 1H). **^{13}C NMR (101 MHz, D$_2$O, δ ppm):** 101.81, 101.53, 81.08, 80.82, 73.02, 72.01, 71.75, 60.23, 41.06. **HRMS (ESI)** *m/z* calcd. for $C_{42}H_{72}NO_{34}$ $[M+H]^+$ 1134.3936, found 1134.3852; calcd. for $C_{42}H_{73}NO_{34}$ $[M+2H]^+$ 1135.4014, found 1135.3772; calcd. for $C_{42}H_{71}NO_{34}Na$ $[M+Na]^+$ 1156.3755, found 1156.3614.

2.2 Synthesis and characterization of mono-*N*-bis-(8-methylquinolyl) tethered *β*-CDx derivatives (BCDx-QUI-2, **9**)

To a dry DMF solution (10 mL) of BCDx-NH2, **8** (1.134 g, 1 mmol), 8-bromomethylquinoline (0.489 g, 2.2 mmol) and DIPEA (0.2 mL) were added drop-wise. The reaction mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere, and then the solvent was removed under a vacuum. The residue was dissolved in a small amount of DMF and then added drop-wise to acetone (300 mL). The resulting white precipitate was filtered and washed successively with acetone (20 mL x 4) to give the crude product. The crude product was loaded onto the preparative reverse phase column (ODS-SM-

50C) and eluted with a linear gradient ranging from water to 40% (v/v) methanol-water. The desired fraction has collected, and the eluent was evaporated/lyophilized to yield the desired products as white powders.



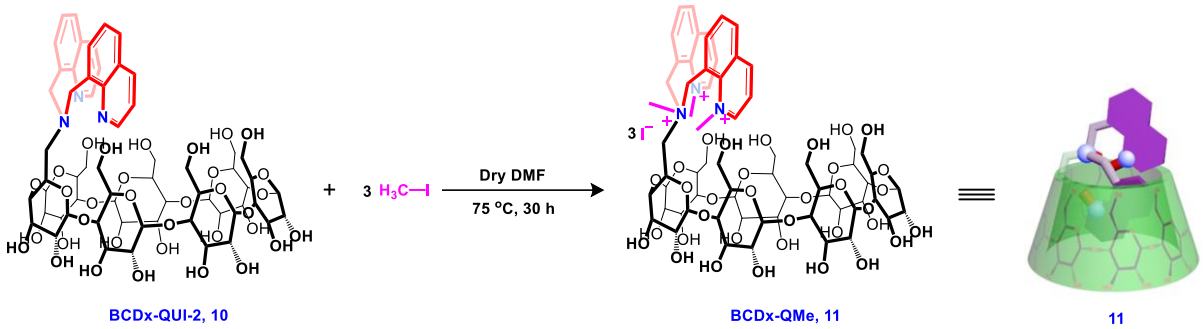
Scheme S2. Synthesis of *β*-CDx appended mono-*N*-(8-aminomethylquinoline) and mono-*N*-bis-(8-aminomethylquinoline) derivative (BCDx-QUI-1, **9**; BCDx-QUI-2, **10**).

Mono-[6-deoxy-6-*N*-(8-methylquinolyl)]-*β*-cyclodextrin (BCDx-QUI-1, 9) (yield 30%) **^{1}H NMR (400 MHz, D_2O, δ ppm):** 8.96 (d, *J* = 4.0 Hz, 1H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 13.0, 7.8 Hz, 1H), 7.63 – 7.53 (m, 1H), 5.07 (d, *J* = 3.1 Hz, 1H), 5.03 (d, *J* = 3.5 Hz, 1H), 5.01 – 4.96 (m, 1H), 4.92 (d, *J* = 3.4 Hz, 1H), 4.89 (d, *J* = 3.6 Hz, 1H), 4.81 (d, *J* = 3.5 Hz, 1H), 4.22 – 4.16 (m, 1H), 4.08 – 4.01 (m, 1H), 4.01 – 3.94 (m, 1H), 3.94 – 3.84 (m, 2H), 3.78 (t, *J* = 15.1 Hz, 3H), 3.70 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.64 (ddd, *J* = 13.7, 9.3, 4.1 Hz, 2H), 3.60 – 3.53 (m, 2H), 3.53 – 3.44 (m, 2H), 3.41 (dd, *J* = 9.3, 3.7 Hz, 1H), 3.38 – 3.27 (m, 2H), 3.27 – 3.20 (m, 1H), 3.19 – 3.07 (m, 1H), 3.06 – 2.97 (m, 1H), 2.76 – 2.68 (m, 1H), 2.48 (s, 1H). **^{13}C NMR (101 MHz, CD_3OD, δ ppm):** 154.83, 150.65, 141.96, 138.13, 132.98, 130.75, 129.15, 126.66, 122.50, 122.38, 101.82, 84.21, 81.08, 73.06, 72.03, 71.75, 70.08, 60.24, 59.16, 54.13, 42.58, 38.76. **HRMS (ESI)** *m/z* calcd. for $C_{52}H_{79}N_2O_{34}H$ $[M + H]^+$ 1275.4514, found 1275.4409.

Mono-[6-deoxy-6-*N*-bis(8-methylquinolyl)]-*β*-cyclodextrin (BCDx-QUI-2, 10) (yield 90%) **^{1}H NMR (400 MHz, D_2O, δ ppm):** 8.67 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 6.1 Hz, 1H), 7.52 – 7.40 (m, 2H), 5.24 (d, *J* = 14.2 Hz, 1H), 5.04 (d, *J* = 3.5 Hz, 1H), 5.02 (s, 1H), 4.97 (d, *J* = 3.7 Hz, 1H), 4.96 – 4.87 (m, 2H), 4.07 – 3.99 (m, 1H), 3.98 – 3.87 (m, 2H), 3.80 (dt, *J* = 12.8, 8.8 Hz, 2H), 3.74 – 3.67 (m, 1H), 3.66 – 3.46 (m, 7H), 3.44 – 3.33 (m, 2H), 3.32 – 3.22 (m, 3H), 3.21 – 3.09 (m, 2H), 3.05 (d, *J* = 8.9 Hz, 1H), 2.98 (s, 1H). **^{13}C NMR (101 MHz, CD_3OD, δ ppm):** 149.37, 144.89, 137.35, 132.17, 130.07, 127.42, 126.41, 126.24, 121.95, 101.43, 100.77, 82.44, 80.98, 73.19, 72.71, 72.00, 71.69, 71.38, 67.51, 60.31, 58.73, 56.29. **HRMS (ESI)** *m/z* calcd. for

$C_{62}H_{85}N_3O_{34}Na$ $[M + Na]^+$ 1438.4912, found 1438.4788; $C_{62}H_{86}N_3O_{34}$ $[M + H]^+$ 1416.5093, found 1416.4975; $C_{62}H_{84}N_3O_{34}$ $[M - H]^+$ 1414.4936, found 1414.4892.

2.3 Synthesis and characterization of *N*-methyl derivative of BCDx-QUI-2 (BCDx-QMe, 11)



Scheme S3. Synthesis of BCDx-QMe derivative (**11**).

The oven-dried round-bottom flask was charged with dry DMF (5 mL), BCDx-QUI-2, **10** (1 mmol, 1.0 equiv), CH_3I (3.5 mmol, 3.5 equiv). The reaction mixture was stirred at 75 °C for 24 h under a nitrogen atmosphere, and then the solvent was removed under vacuum. The residue was dissolved in a small amount of DMF and then added drop-wise to acetone (300 mL). The resulting white precipitate was filtered and washed successively with acetone (20 mL x 4) to give the crude product. The crude product was loaded onto the preparative reverse phase column (ODS-SM-50C) and eluted with a linear gradient ranging from water to 35% (v/v) methanol-water. The desired fraction has collected, and the eluent was evaporated/lyophilized to yield the desired products as white powders.

BCDx-QMe, 11 (yield 97%) **^{1}H NMR (400 MHz, D_2O, δ ppm):** 8.59 (s, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.63 (s, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.38 (dd, *J* = 7.6, 4.2 Hz, 1H), 5.20 (d, *J* = 13.0 Hz, 1H), 5.07 – 5.00 (m, 2H), 4.99 – 4.94 (m, 2H), 4.90 (dd, *J* = 8.8, 3.3 Hz, 2H), 4.01 (t, *J* = 9.4 Hz, 1H), 3.90 (dd, *J* = 17.1, 8.3 Hz, 2H), 3.86 – 3.73 (m, 5H), 3.72 – 3.65 (m, 2H), 3.65 – 3.46 (m, 11H), 3.41 (dd, *J* = 17.3, 8.5 Hz, 2H), 3.31 (dt, *J* = 32.6, 13.2 Hz, 4H), 3.19 – 2.96 (m, 3H). **^{13}C NMR (101 MHz, D_2O, δ ppm):** 149.70, 145.29, 137.37, 132.51, 129.93, 127.77, 126.70, 126.25, 122.07, 101.85, 101.41, 83.64, 80.58, 73.07, 72.66, 71.99, 71.88, 71.37, 68.32, 60.28, 59.49, 57.29, 46.32, 30.90. **HRMS (MALDI-TOF)** *m/z* calcd. for $C_{65}H_{94}I_2N_3O_{34}$ $[M+2I]^+$ 1714.3808, found 1714.3806.

2.4. ^{1}H and ^{13}C NMR and HRMS spectra

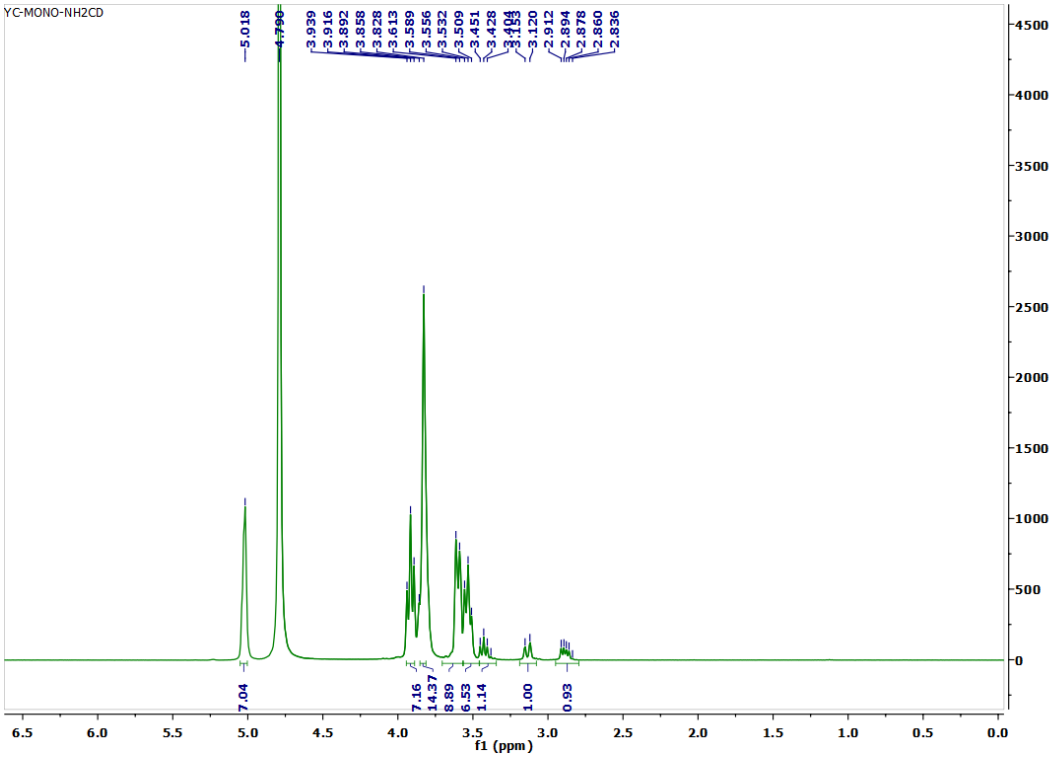


Figure S1. ^{1}H NMR spectrum of mono-6-deoxy-6-amino-*β*-CDx (BCDx-NH_2, **8**) (D_2O, 400 MHz, 25 °C).

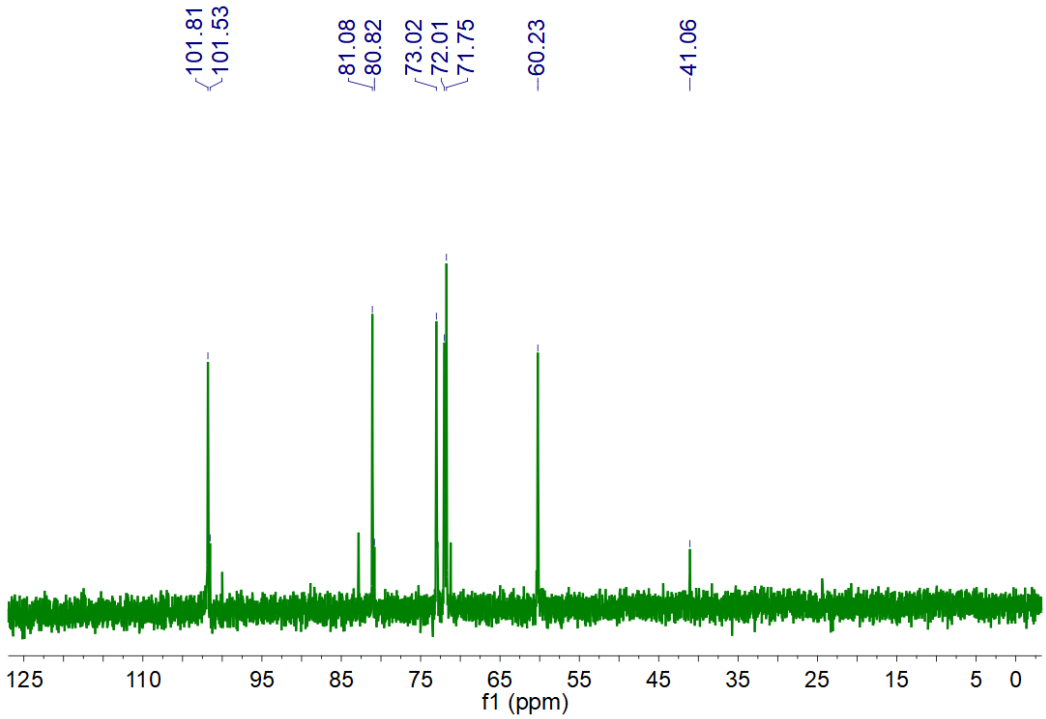


Figure S2. ^{13}C NMR spectrum of mono-6-deoxy-6-amino-*β*-CDx (BCDx-NH_2, **8**) (D_2O, 101 MHz, 25 °C).

BCDx-NH2, ESI+

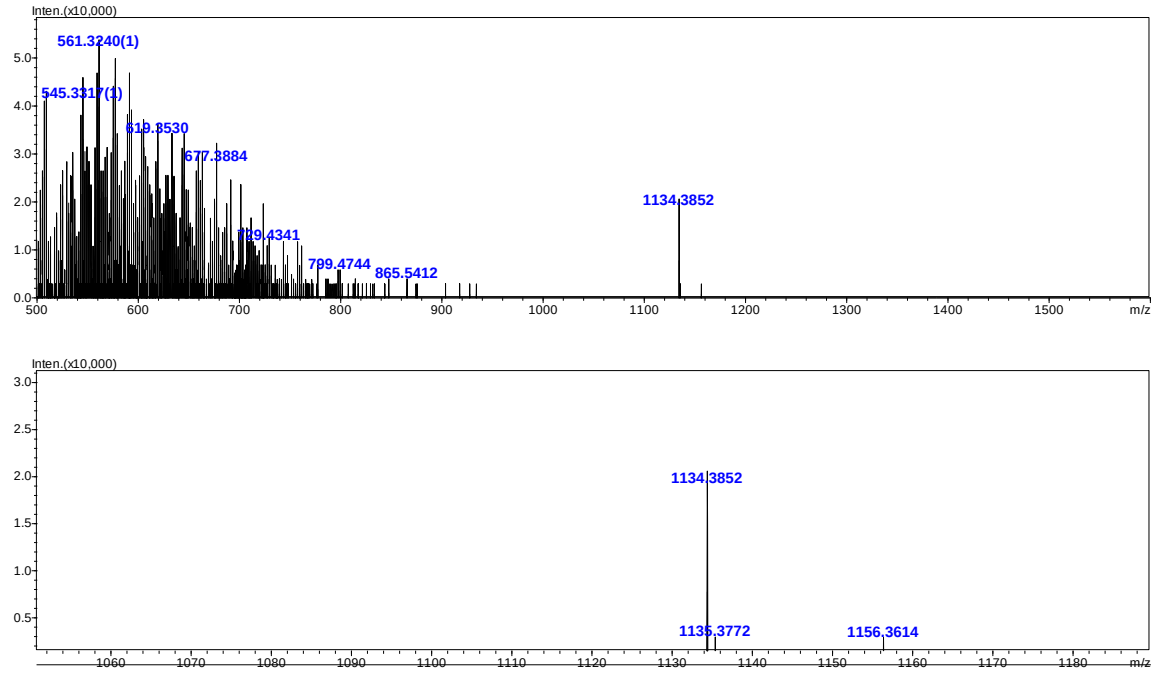


Figure S3. HRMS (ESI) Spectrum of BCDx-NH2, **8**.

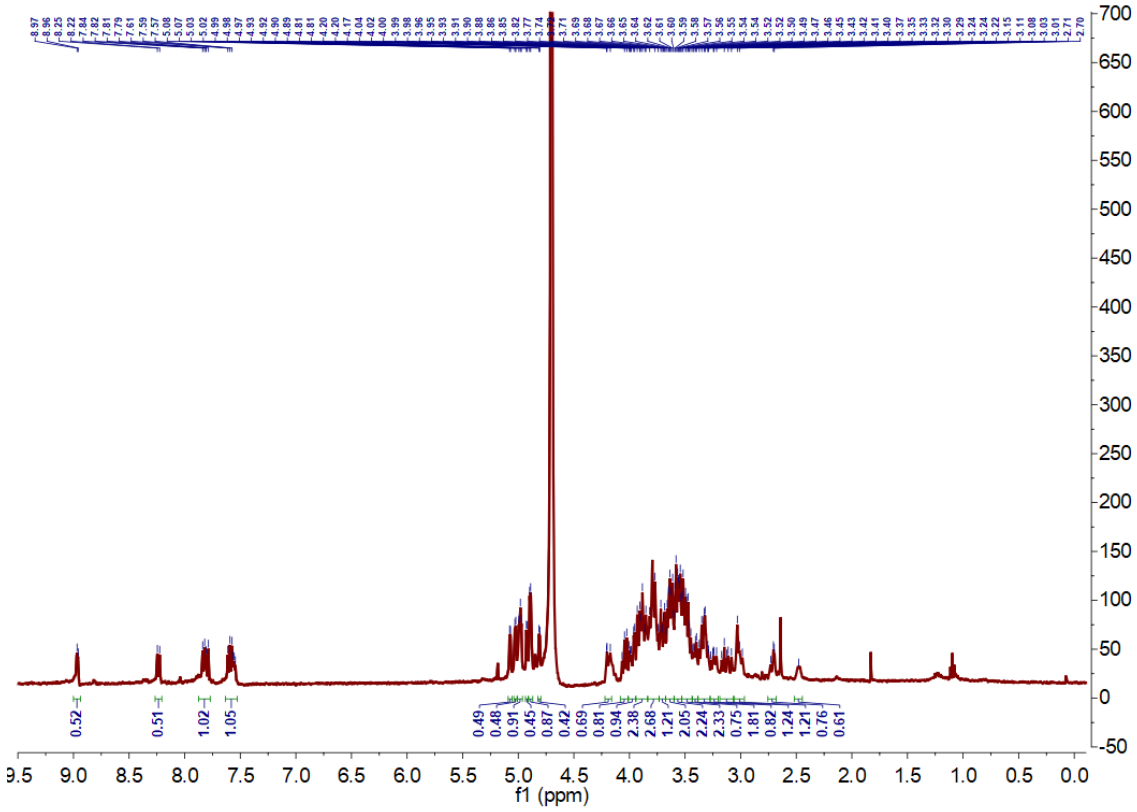


Figure S4. ^{1}H NMR Spectrum of **9** (D_2O, 400 MHz, 25 °C).

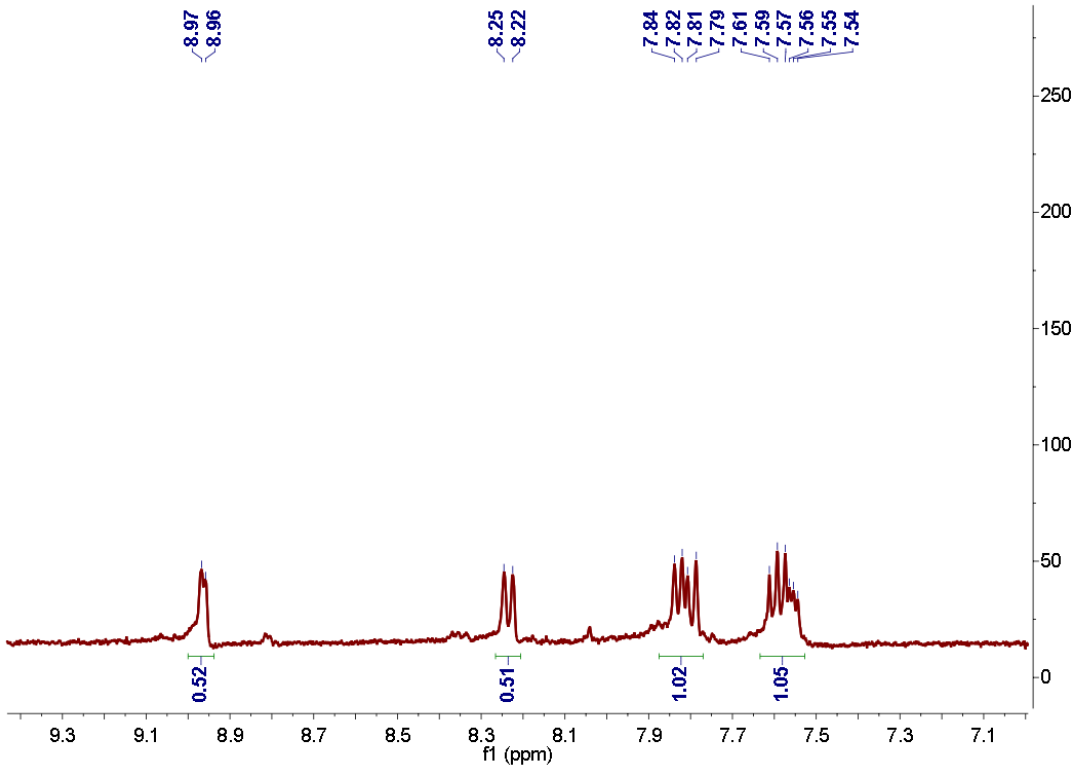


Figure S5. Expanded ^{1}H NMR spectrum of **9** in the aromatic proton region (D_2O, 400 MHz, 25 °C).

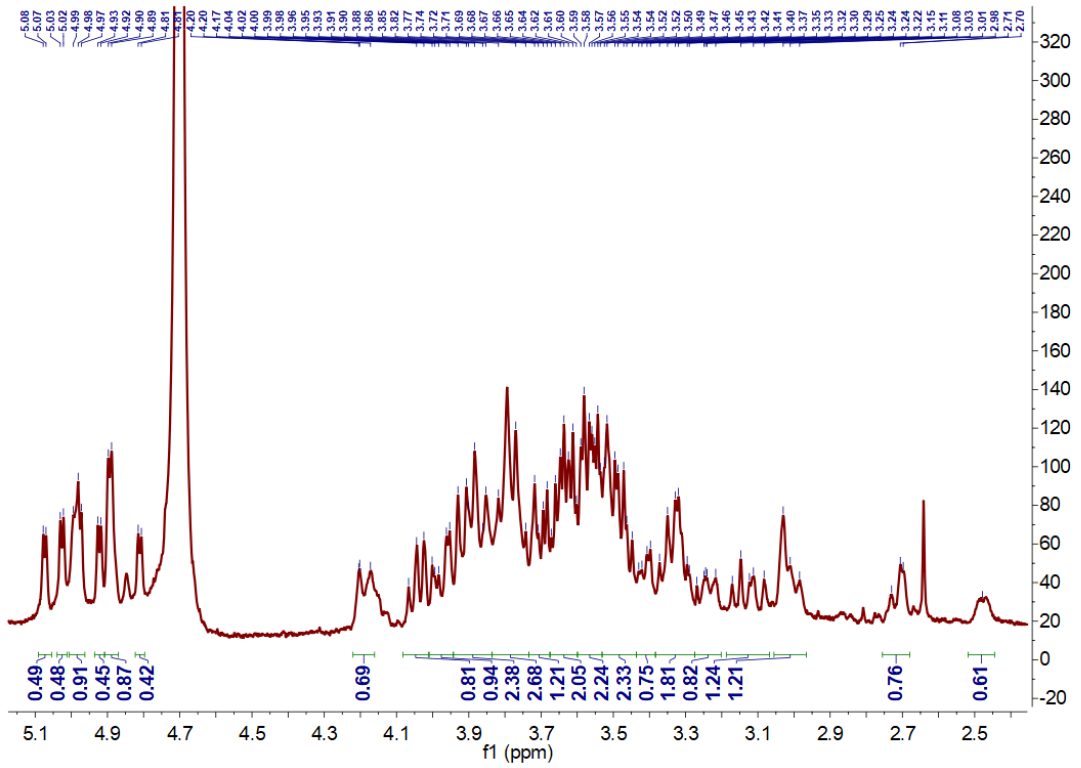


Figure S6. Expanded ^{1}H NMR spectrum of **9** in the CDx proton region (D_2O, 400 MHz, 25 °C).

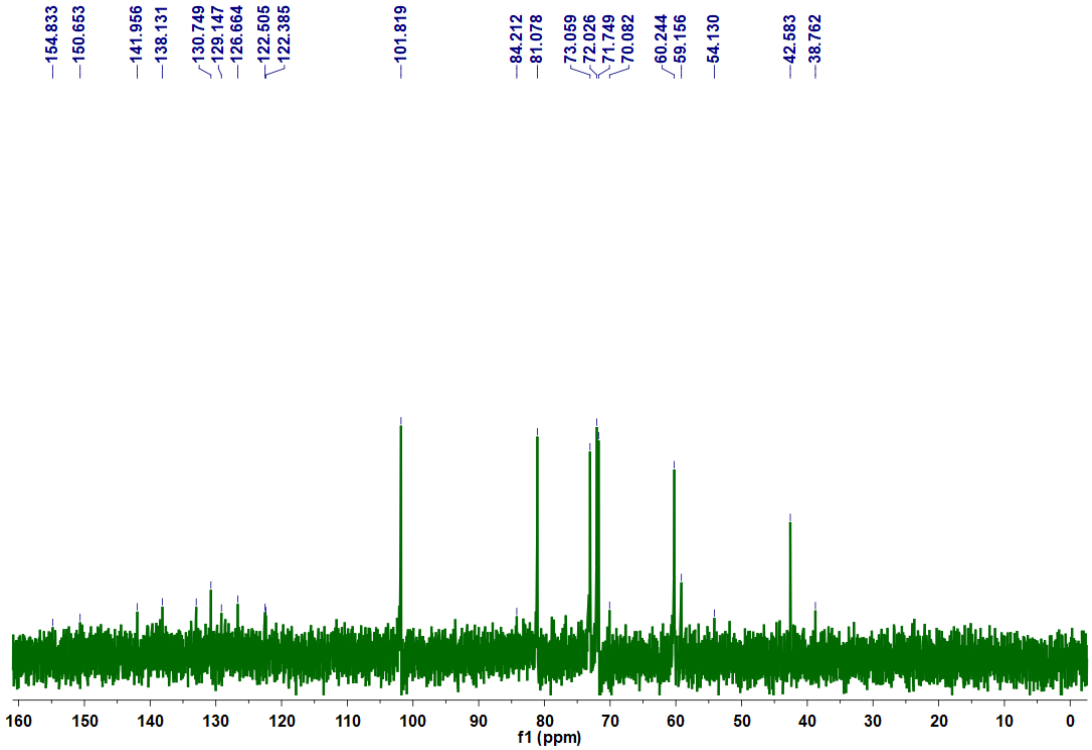


Figure S7. ^{13}C NMR spectrum of **9** (CD_3OD, 101 MHz, 25 °C).

BCD-QUI-1 ESI+

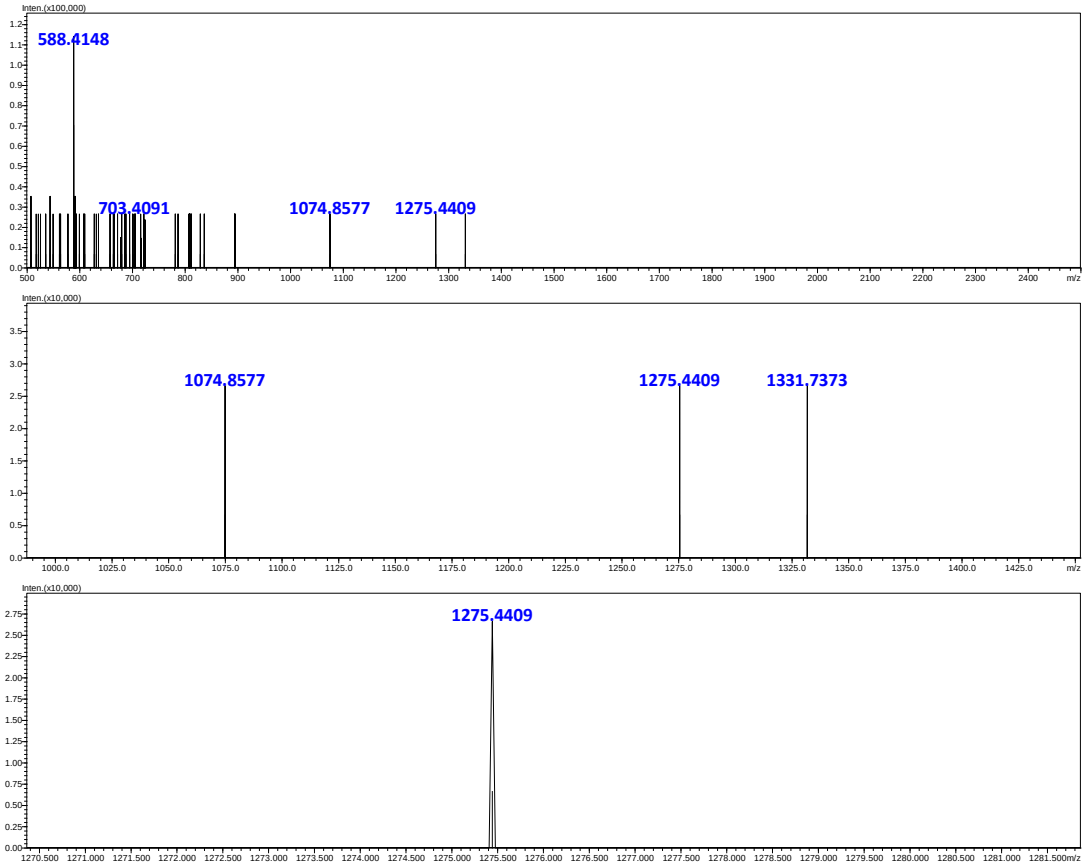


Figure S8. HRMS (ESI) spectrum of **9**.

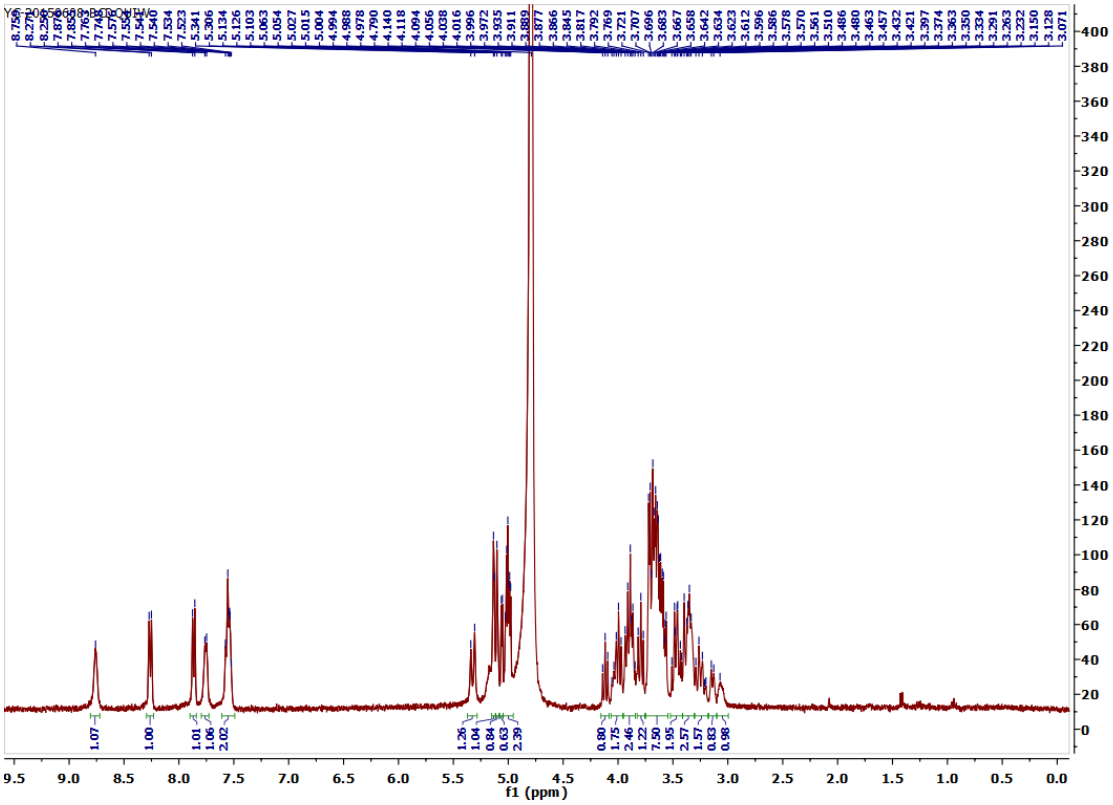


Figure S9. ^{1}H NMR spectrum of **10** (D_2O, 400 MHz, 25 °C).

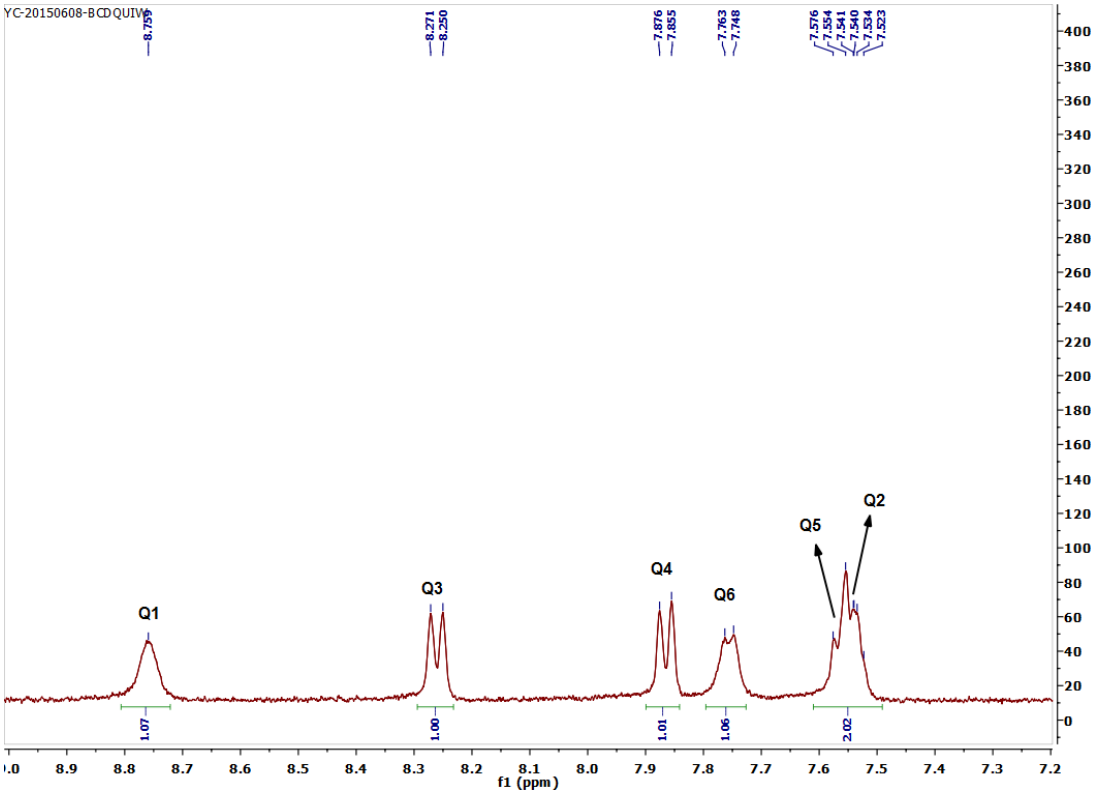


Figure S10. Expanded ^{1}H NMR spectrum of **10** in the aromatic proton region (D_2O, 400 MHz, 25 °C).

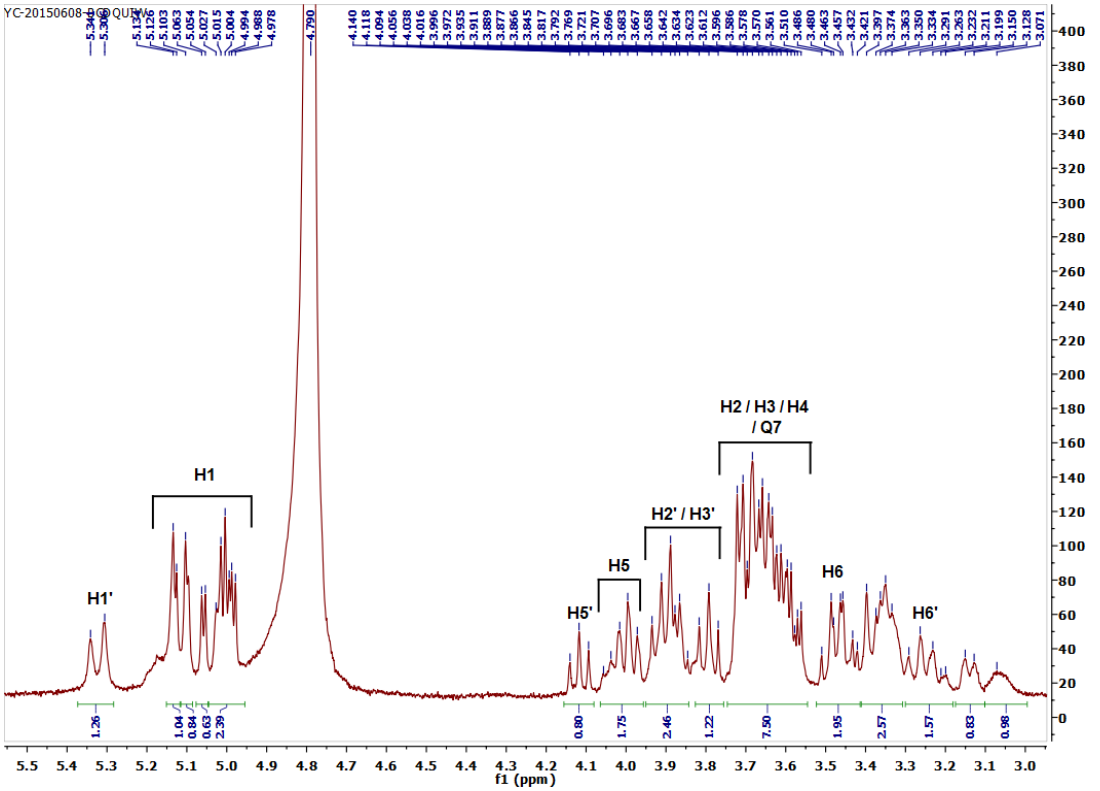


Figure S11. Expanded ^{1}H NMR spectrum of **10** in the CDx proton region (D_2O, 400 MHz, 25 °C).

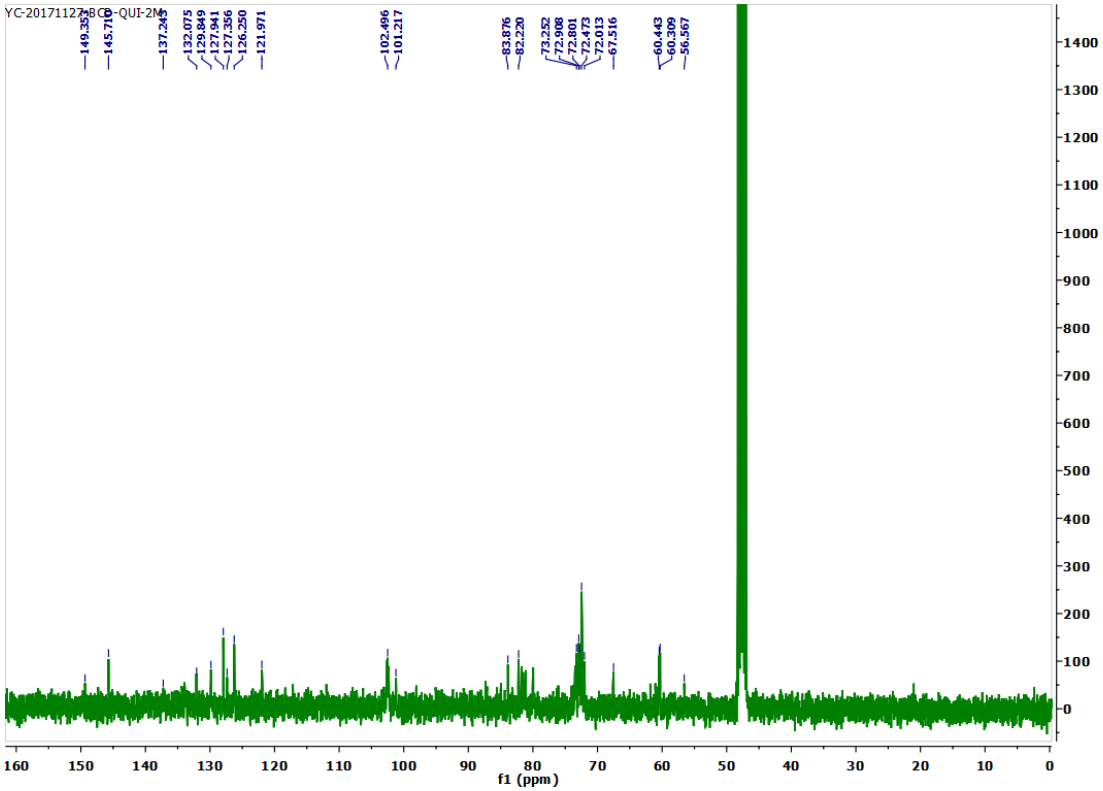


Figure S12. ^{13}C NMR spectrum of **10** (CD_3OD, 101 MHz, 25 °C).

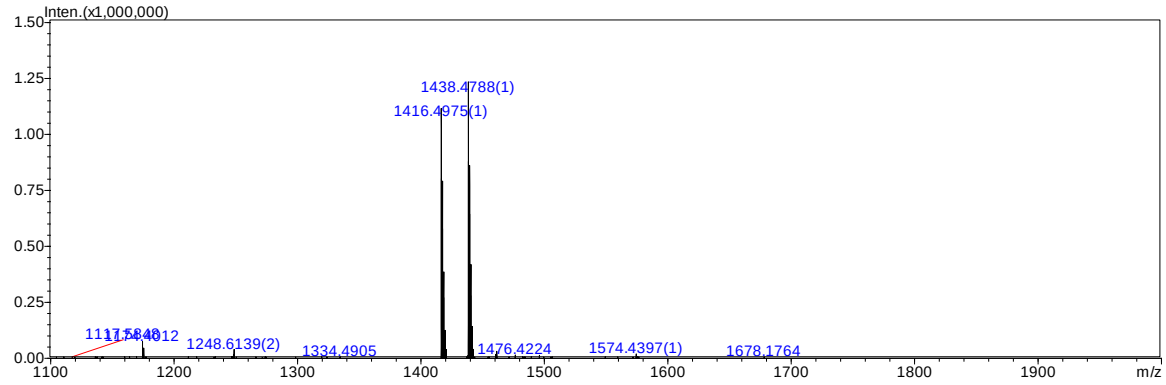


Figure S13. HRMS (ESI) spectrum of **10**.

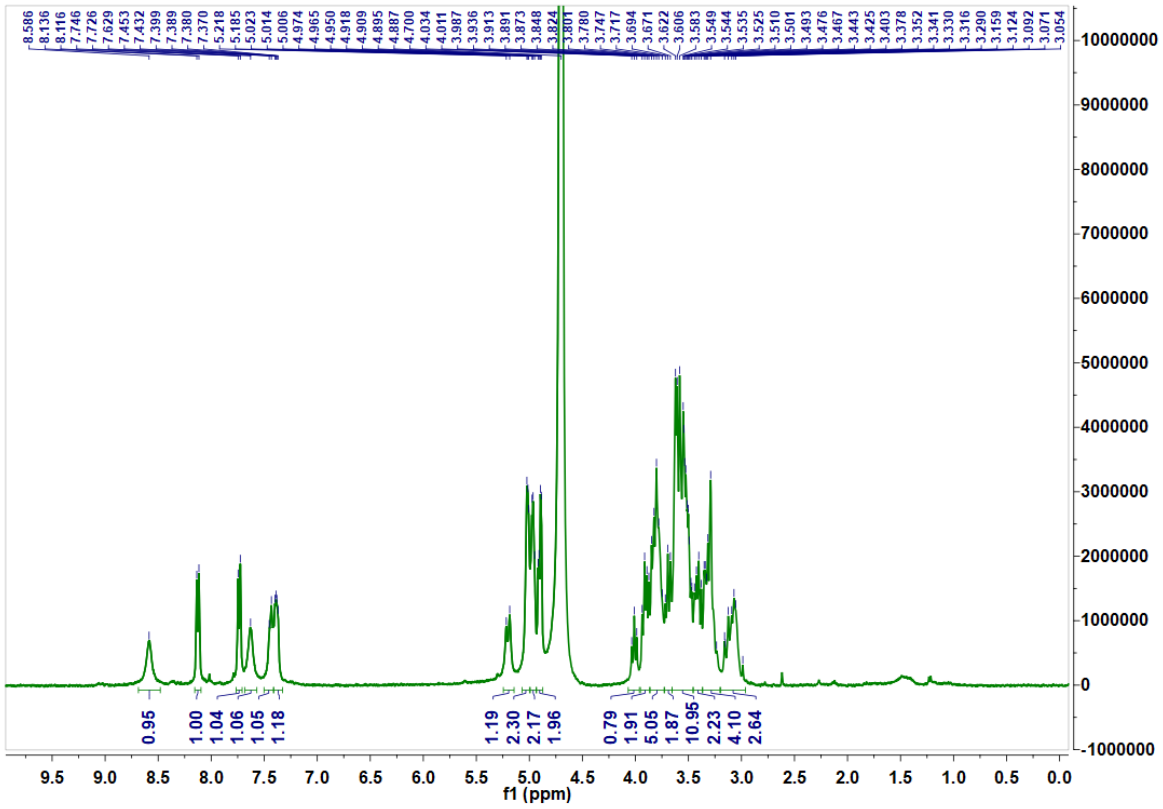


Figure S14. ^{1}H NMR spectrum of **11** (D_2O, 400 MHz, 25 °C).

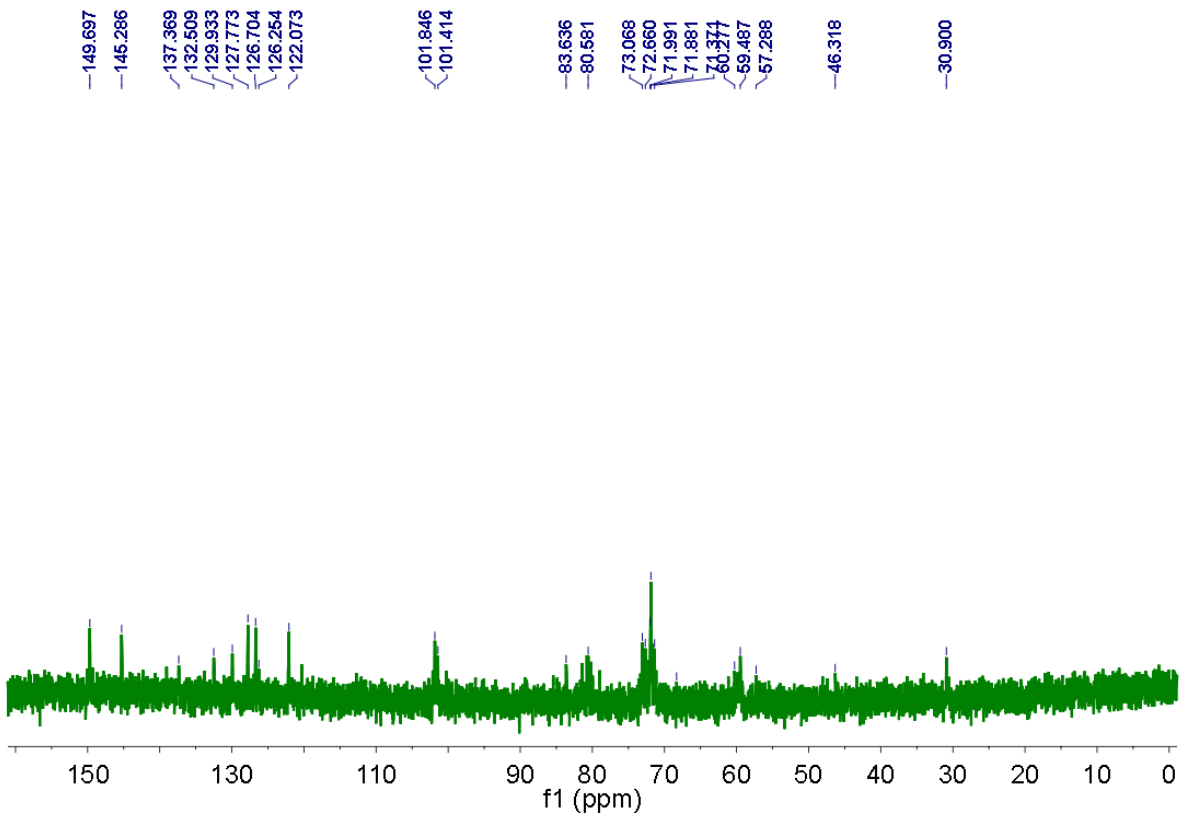


Figure S15. ^{13}C NMR spectrum of **11** (D_2O, 101 MHz, 25 °C).

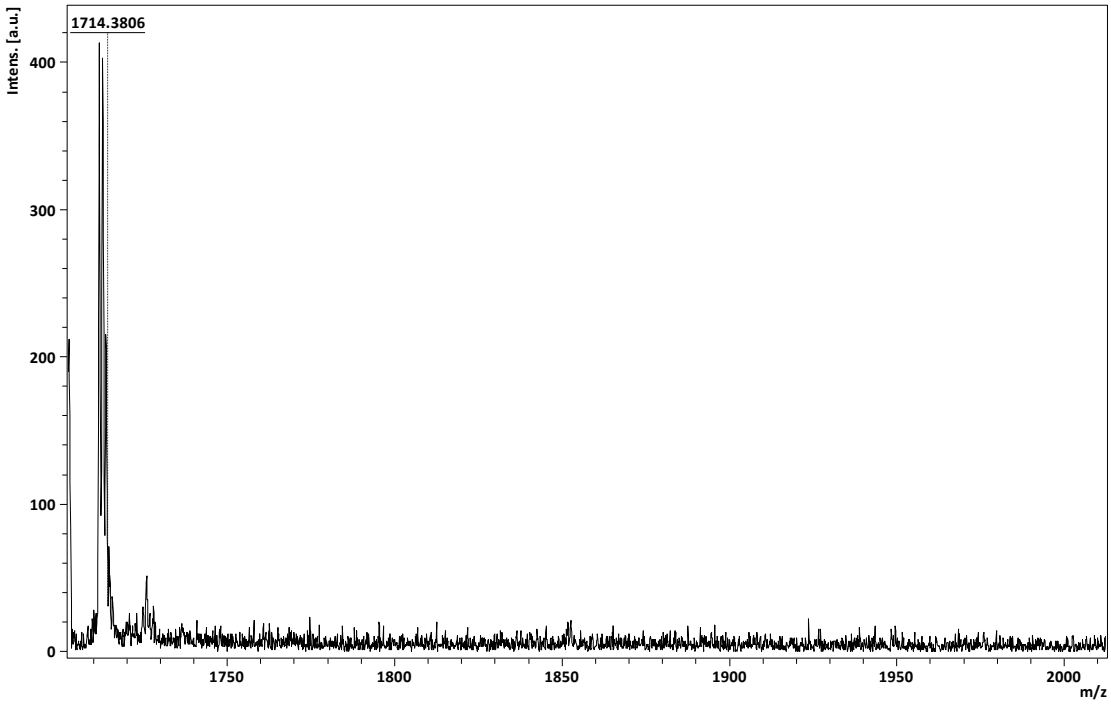


Figure S16. HRMS (MALDI-TOF) spectrum of **11**.

3. Conformation analysis of host 9-11

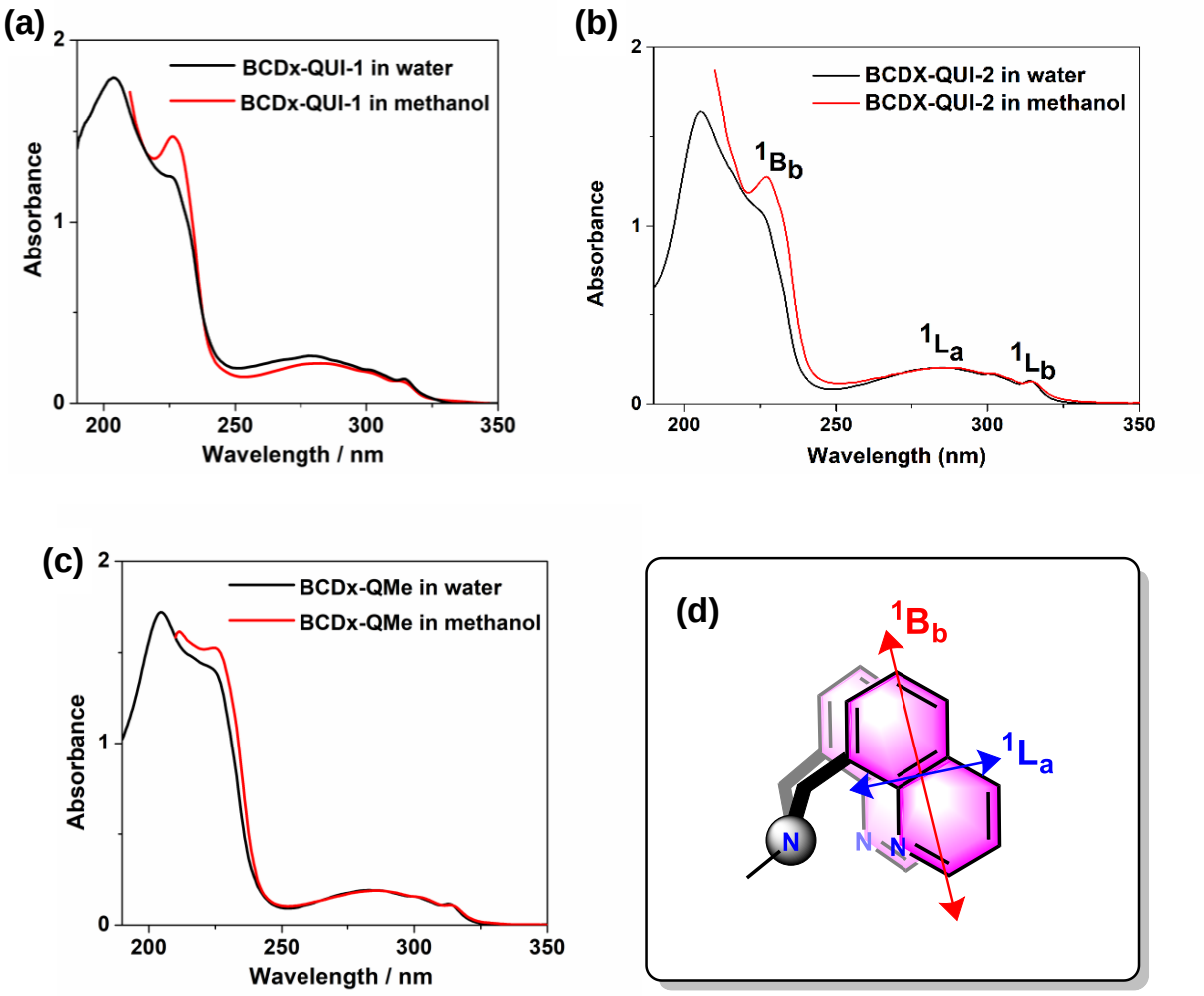


Figure S17. Absorption spectra of (a) **9** (63.4 μM), (b) **10** (36.8 μM) and (c) **11** (31.2 μM) in water and methanol. (d) The orientations of the absorption transition moments for both ^1B_b and ^1L_a absorption bands of quinoline chromophore.

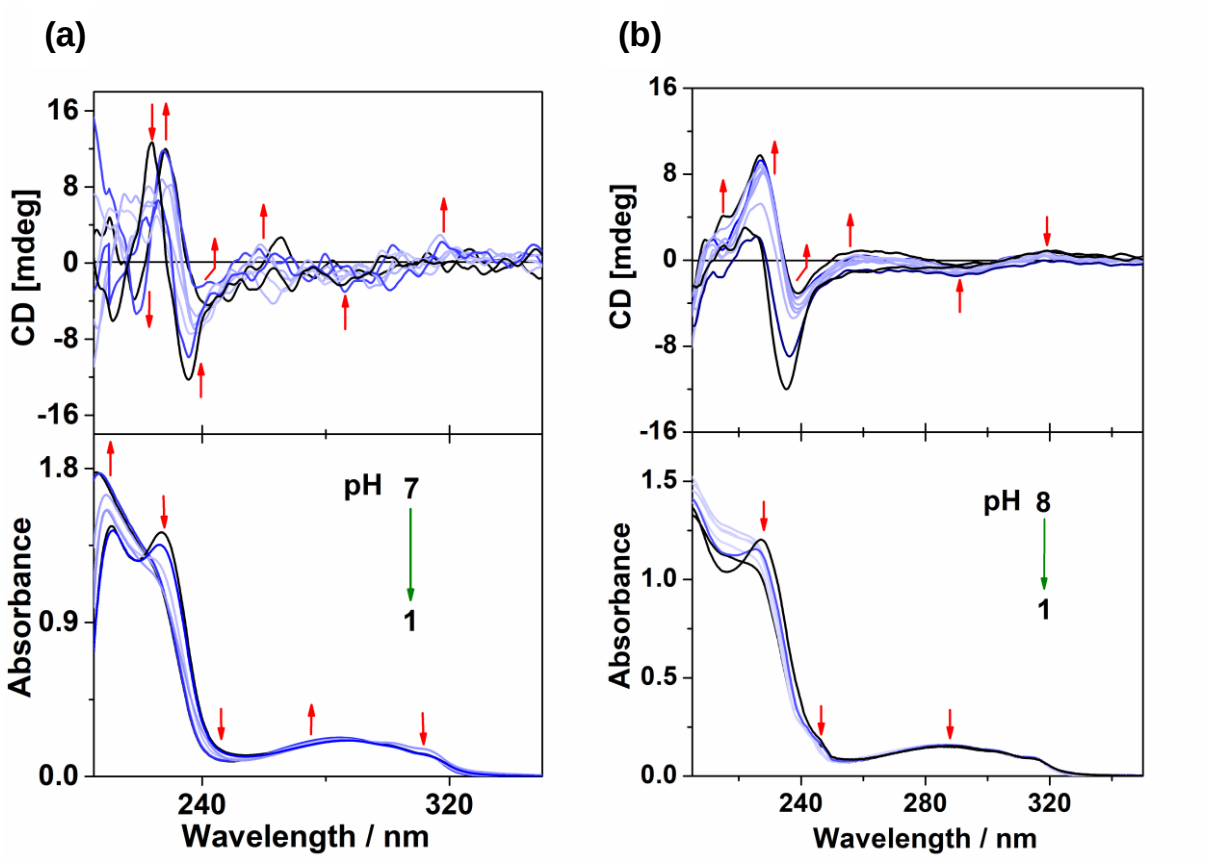


Figure S18. Circular dichroism (upper panel) and UV-vis absorption (lower panel) spectral changes of (a) **10** (4.28 x 10^{-5} M) and (b) **11** (2.72 x 10^{-5} M) in different PBS buffers with pH 1-8, at 25 °C.

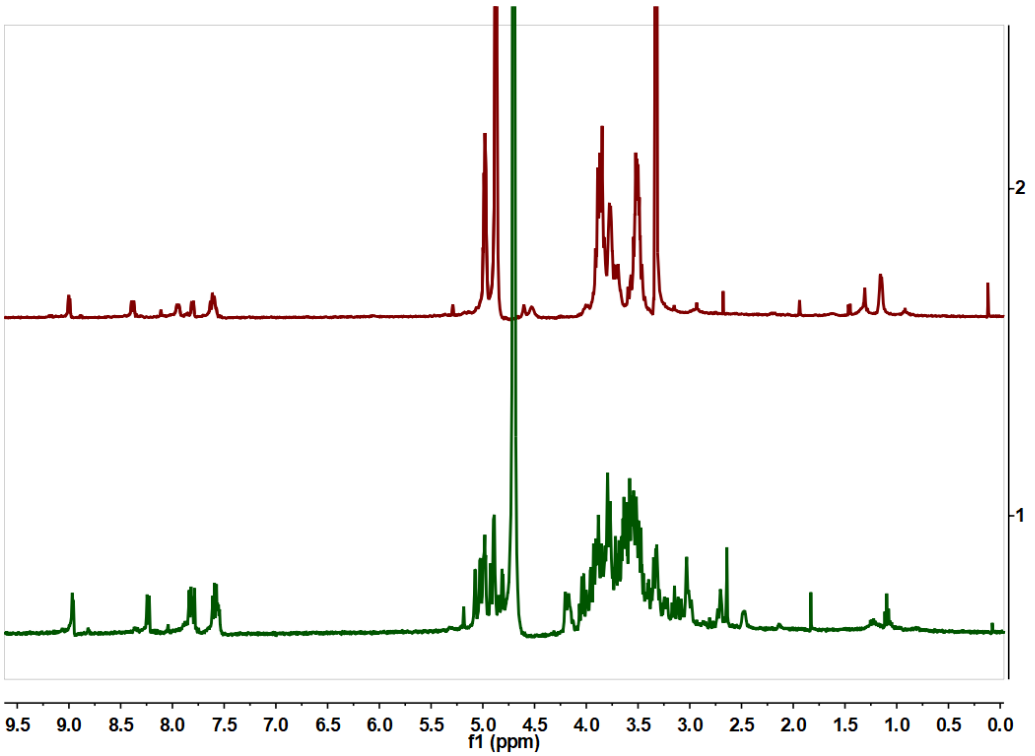


Figure S19. Comparison of ^{1}H NMR spectra (400 MHz, 25 °C) of **9** in CD_3OD (top) and D_2O (bottom).

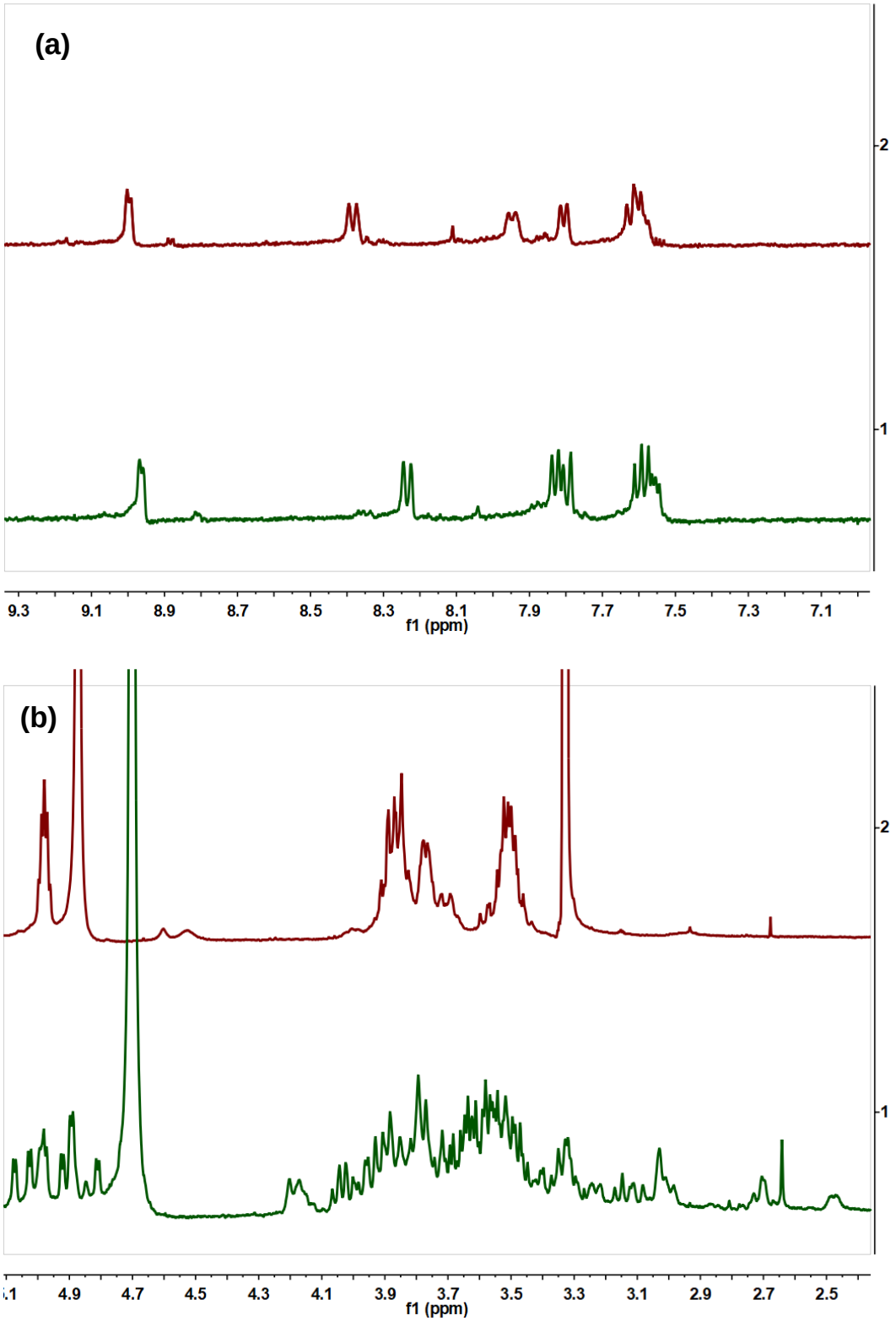


Figure S20. Expansion spectra of Figure S19 in the (a) aromatic proton region and (b) CDx proton region.

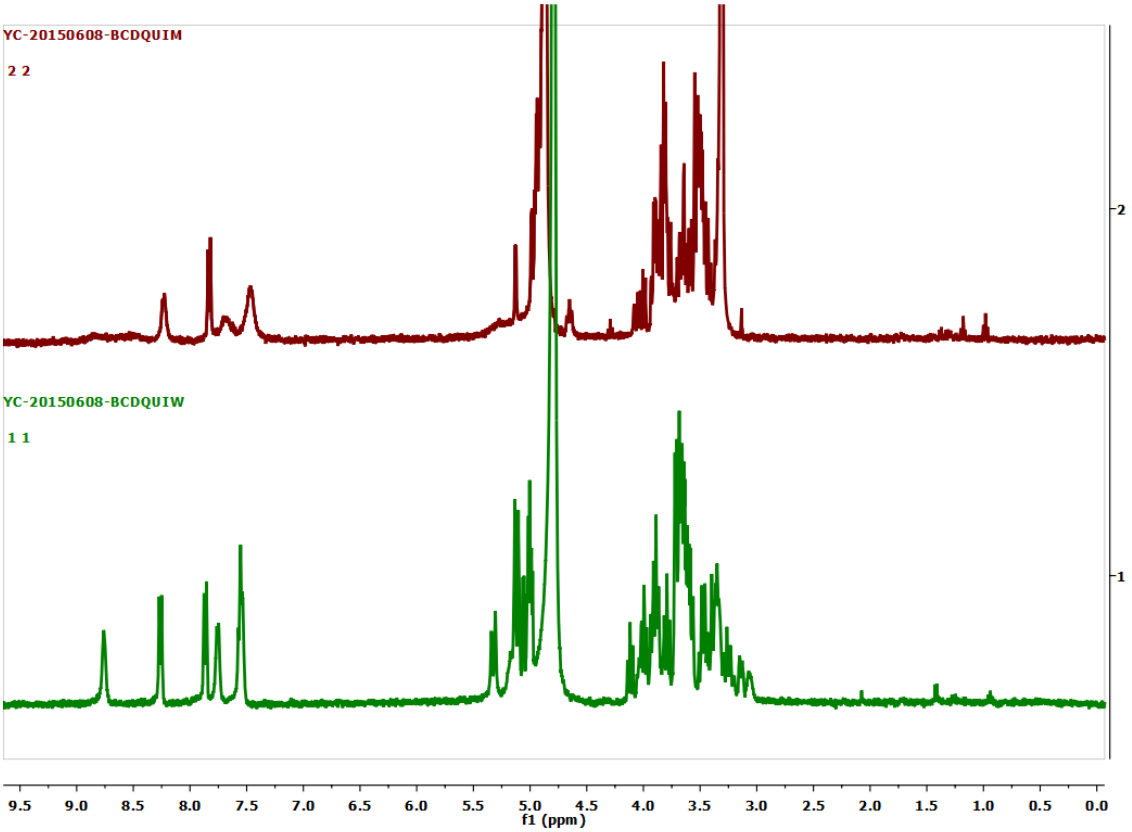


Figure S21. Comparison of ^{1}H NMR spectrum (400 MHz, 25 °C) of **10** in CD_3OD (top) and D_2O (bottom).

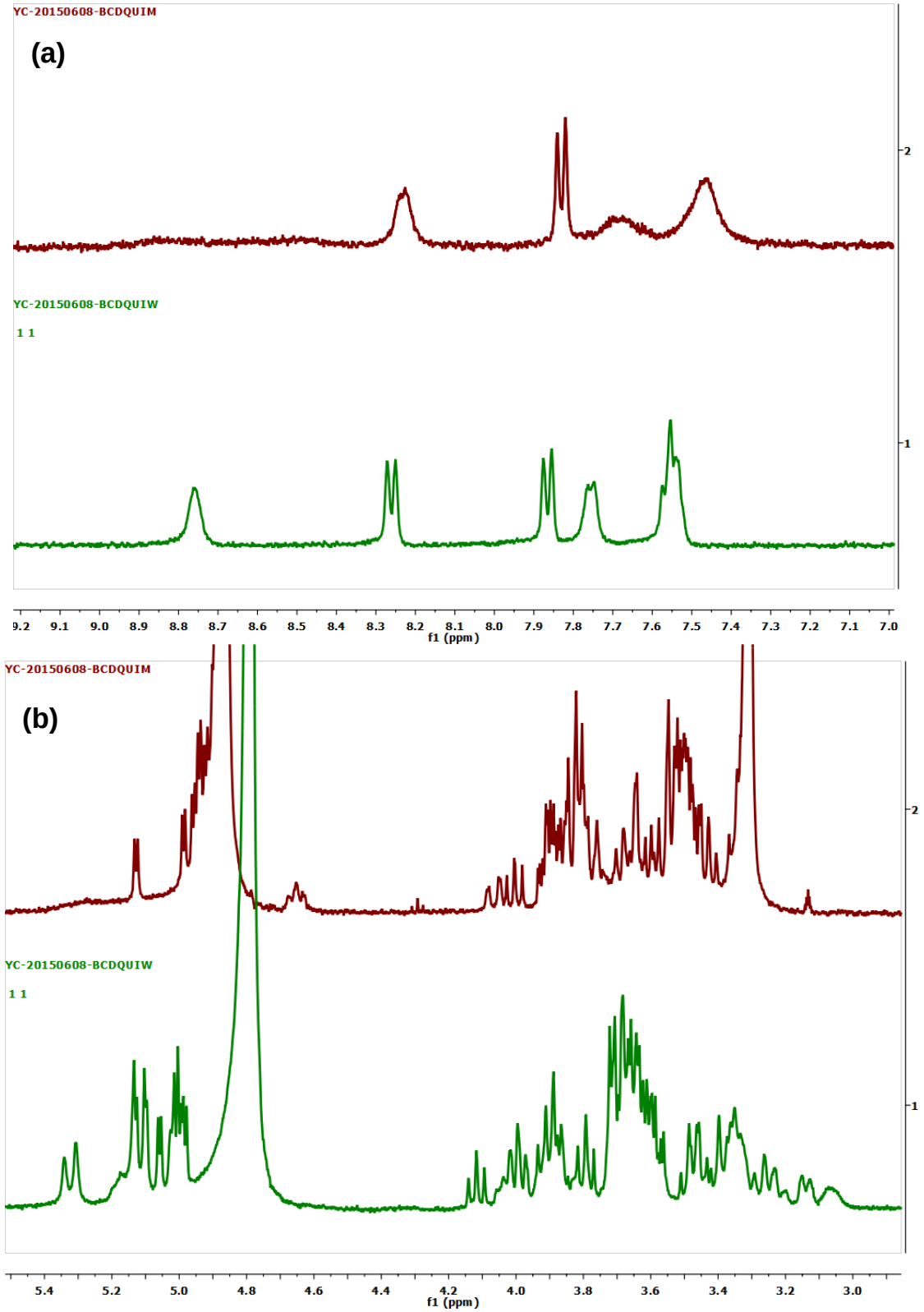


Figure S22. Expansion spectra of Figure S21 in the (a) aromatic proton region and (b) CDx proton region.

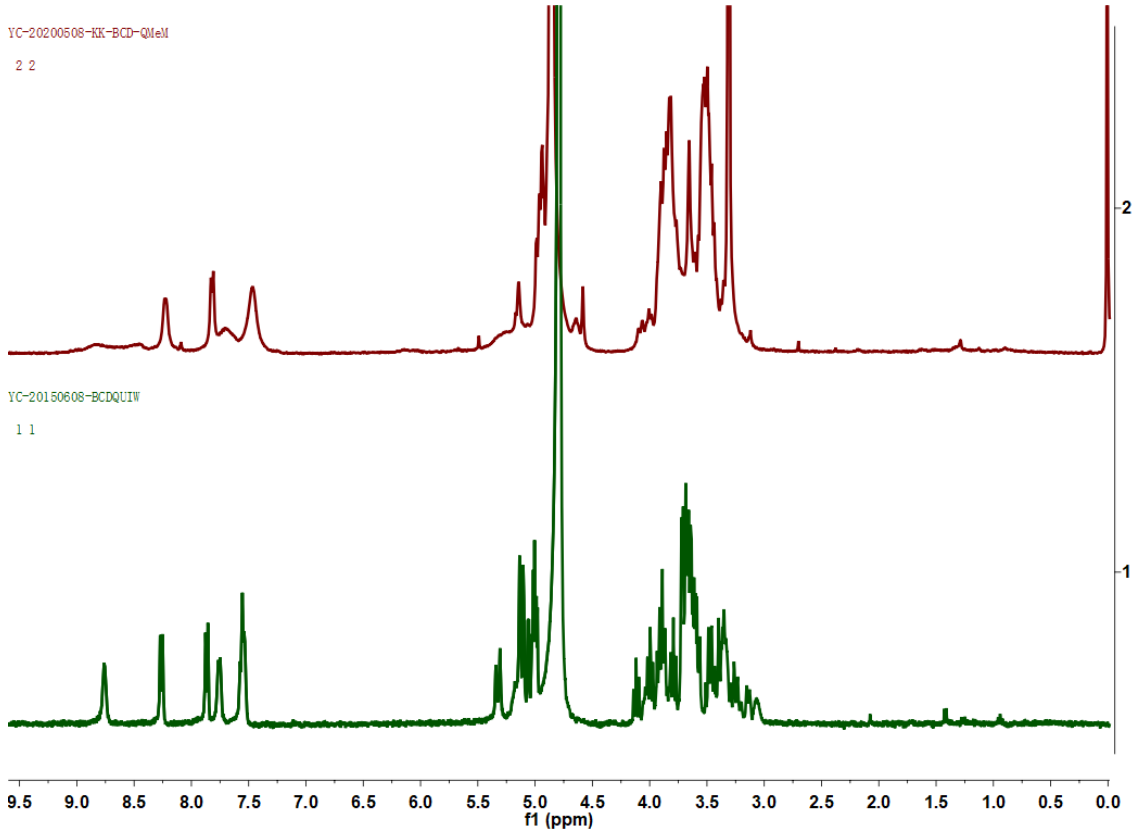


Figure S23. Comparison of ^{1}H NMR spectra (400 MHz, 25 ^{o}C) of **11** in CD_3OD (top) and D_2O (bottom).

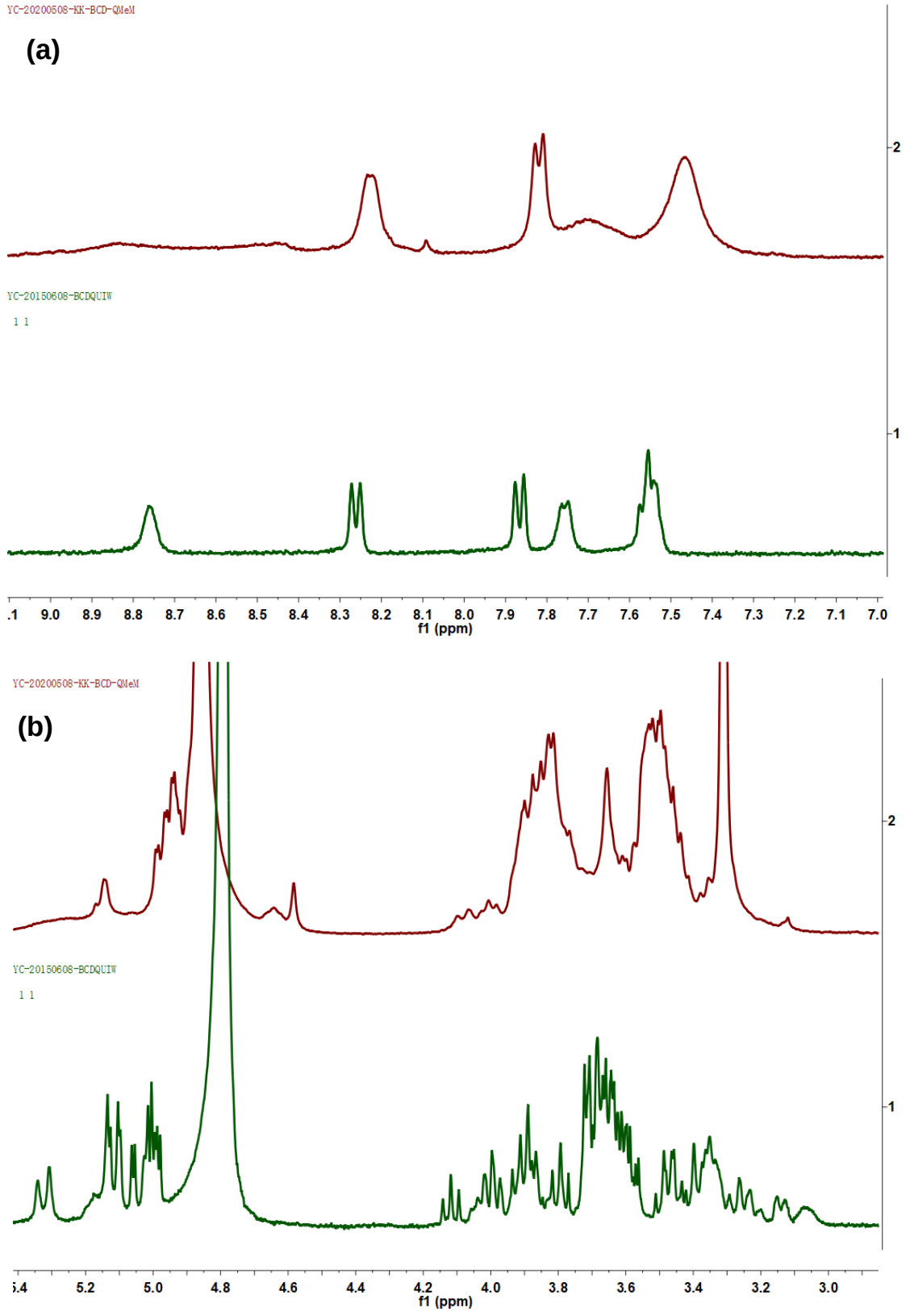


Figure S24. Expansion spectra of Figure S23 in the (a) aromatic proton region and (b) CDx proton region.

4. Association constants of hosts 7, 8, and 10 with AC

Table S1. Calculated association constants and thermodynamic parameters for the 1:1 and 1:2 complexation of AC with **7** at different pH at 25 ºC.[a]

pH	Association constant / M^{-1}		$K_1 K_2$ / x 10^5 M^{-2}	K_2 / K_1
	K_1	K_2		
9 [b]	3800 ± 50	150 ± 30	5.7	0.04
[a]calculated using ITC measurements, [AC] = 0.2 mM, [**7**] = 4 mM in PBS buffer. [b]T = 298 K. [c]reported in ref. S3, binding constants are calculated in PBS (pH 9.0) buffer using circular dichroism titrations at 25 °C, ellipticity changes ($\Delta\theta$) at 258 nm.				

Table S2. Calculated association constants for the 1:1 and 2:2 host-guest complexation of **8** with AC at different pH at 25 ºC [a]

pH	Association constant / M^{-1}		$K_1 K_2$ / x 10^7 M^{-2}	K_2 / K_1
	K_1	K_2		
7	44400 ± 1200	1830 ± 81	8.13	0.04
8	30100 ± 800	2400 ± 54	7.22	0.08
9	14100 ± 370	3510 ± 86	4.95	0.25
10	13200 ± 420	5240 ± 140	6.92	0.40
[a]calculated using ITC measurements, [AC] = 0.2 mM, [**6**] = 4 mM in PBS buffer.				

Table S3. Calculated association constant for the 1:1 and 2:2 host-guest complexation of **10** with AC at different pH at 25 ºC.[a]

pH	Association constant / M^{-1}		$K_1 K_2$ / x 10^8 M^{-2}	K_2 / K_1
	K_1	K_2		
6 [b]	58300 ± 1400	16400 ± 1200	9.56	0.28
7	64800 ± 1100	11130 ± 800	7.21	0.17
8	73700 ± 1800	5100 ± 150	3.75	0.07
9	76800 ± 1370	3220 ± 98	2.47	0.04
10	75300 ± 1420	3550 ± 100	2.67	0.05
[a]calculated using ITC measurements, [AC] = 0.2 mM, and [**7**] = 4 mM in PBS buffer. [b]estimated [AC] = 0.02 mM by UV-vis. absorption spectra and [**7**] = 4 mM.				

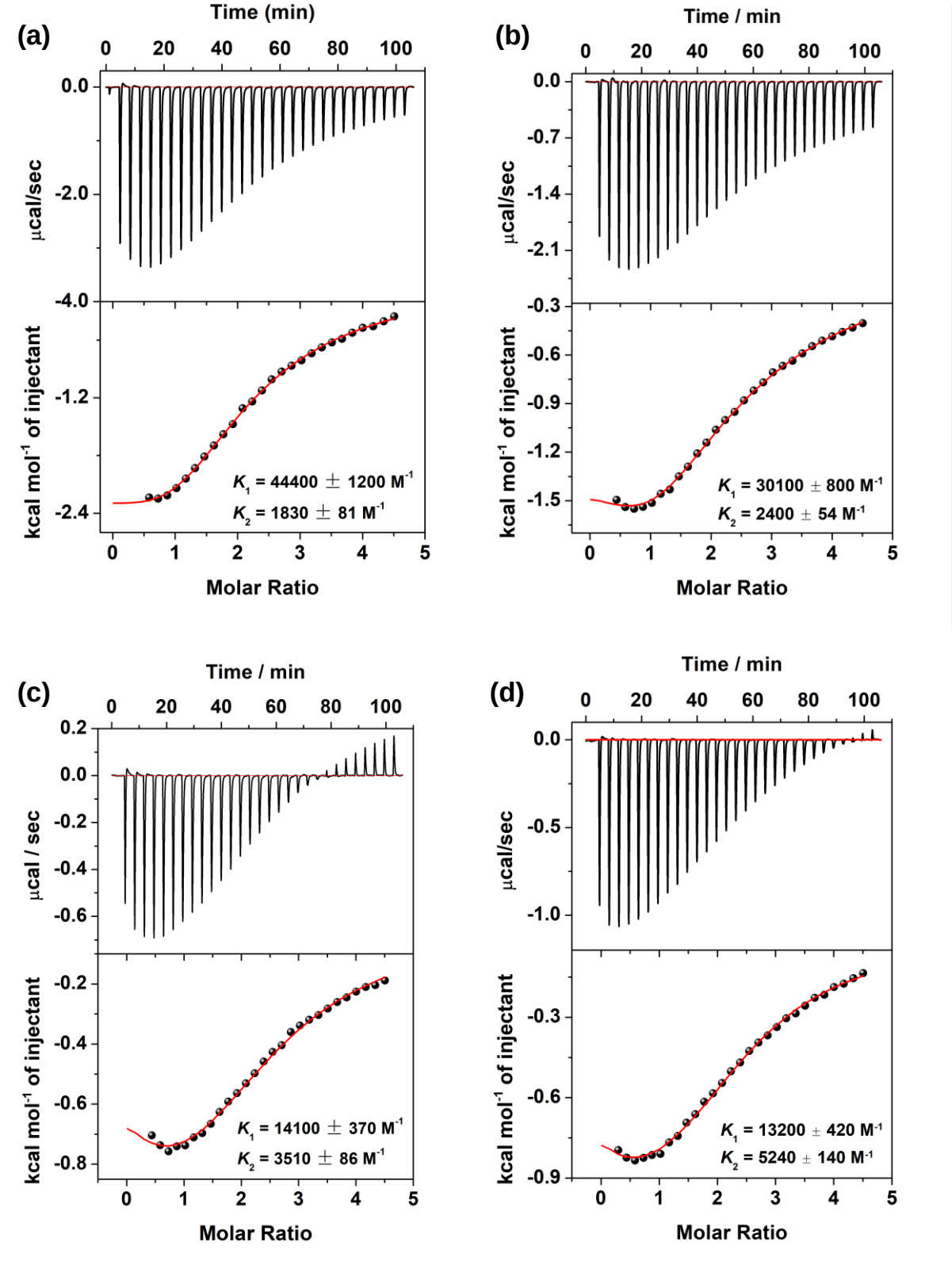


Figure S26. ITC titration data for the complexation of host **8** with AC in aqueous PBS buffer solution (a) pH7, (b) pH8, (c) pH9, and (d) pH10 at 25 °C, which gave the 1:1 association constant (K_1) and the 2:2 association constant (K_2).

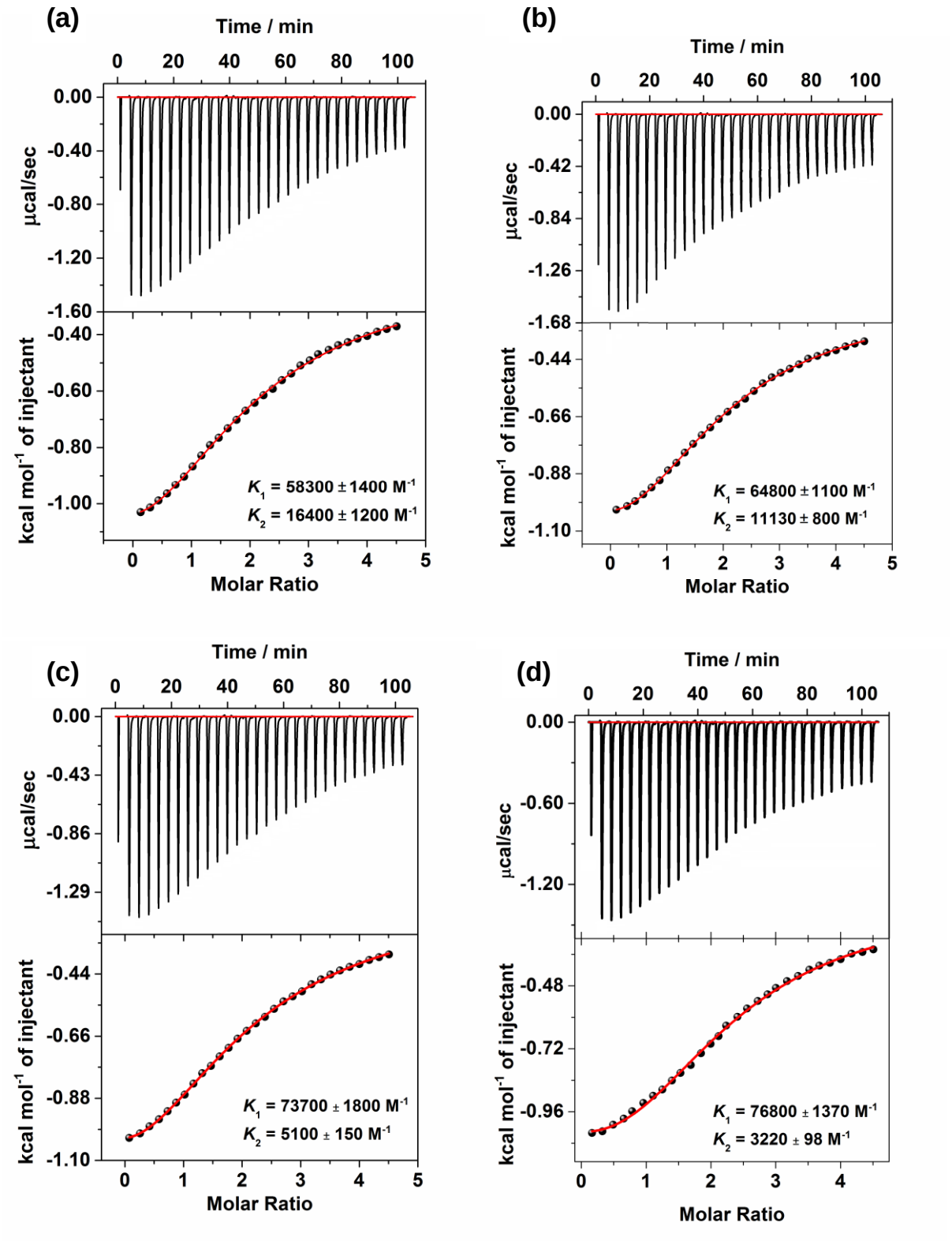


Figure S27. ITC titration data for the complexation of host **10** with AC in aqueous PBS buffer solution (a) pH7, (b) pH8, (c) pH9, and (d) pH10 at 25 °C, which gave the 1:1 association constant (K_1) and the 2:2 association constant (K_2).

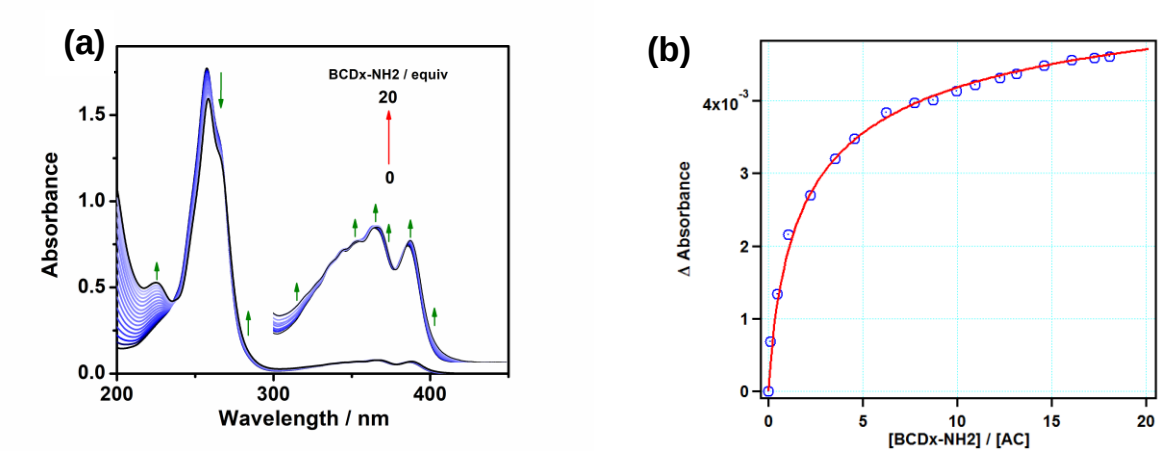


Figure S28. (a) UV-Vis absorption spectral changes of AC upon addition of **8** in pH 7 PBS buffer, [AC] = 0.02 mM; [**8**] = 0 - 4 mM. (b) Calculated 1:1 association constant (K_1) is 44538 ± 280 M^{-1} and the 2:2 association constant (K_2) is 1939 ± 23 M^{-1}.

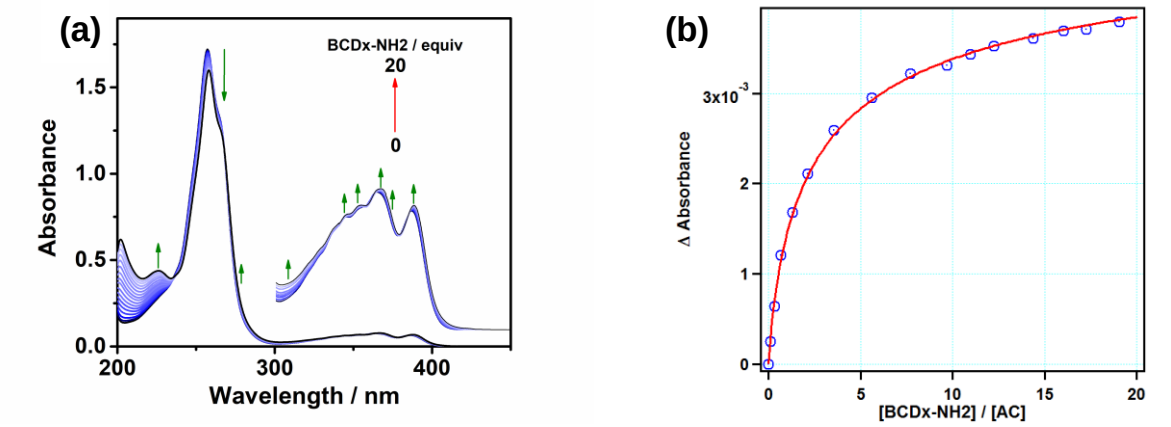


Figure S29. (a) UV-Vis absorption spectral changes of AC upon addition of **8** in pH 8 PBS buffer, [AC] = 0.02 mM; [**8**] = 0 - 4 mM. (b) Calculated 1:1 association constant (K_1) is 30156 ± 177 M^{-1} and the 2:2 association constant (K_2) is 2586 ± 16 M^{-1}.

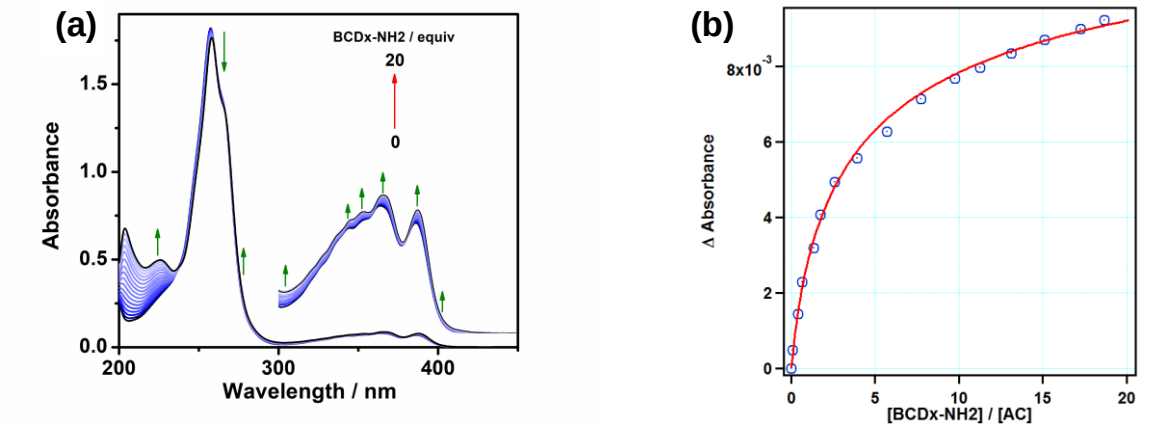


Figure S30. (a) UV-Vis absorption spectral changes of AC upon addition of **8** in pH 9 PBS buffer, [AC] = 0.02 mM; [**8**] = 0 - 4 mM. (b) Calculated 1:1 association constant (K_1) is 14292 ± 139 M^{-1} and the 2:2 association constant (K_2) is 3544 ± 40 M^{-1}.

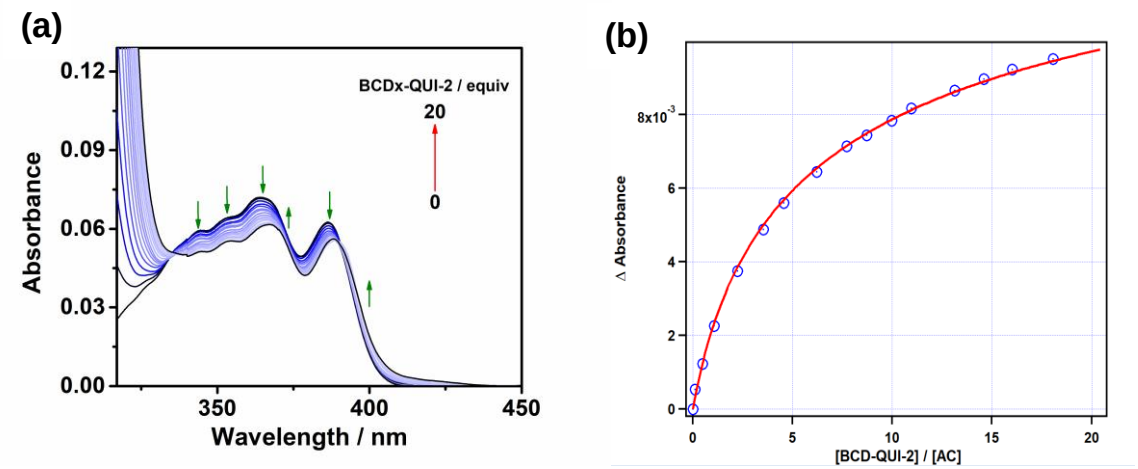


Figure S31. (a) UV-Vis absorption spectral changes of AC upon addition of **10** in pH 6 PBS buffer, calculated [AC] = 0.019 mM; [**10**] = 0 - 4 mM. (b) Calculated 1:1 association constant (K_1) is 58711 ± 1145 M^{-1} and the 2:2 association constant (K_2) is 16884 ± 1228 M^{-1}.

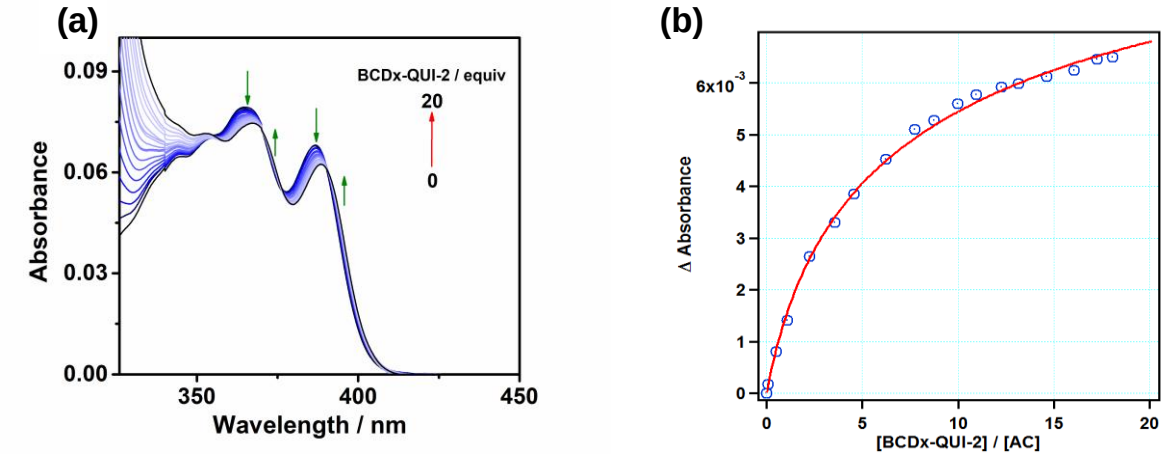


Figure S32. (a) UV-Vis absorption spectral changes of AC upon addition of **10** in pH 7 buffer, [AC] = 0.02 mM; [**10**] = 0 - 0.4 mM. (b) Calculated 1:1 association constant (K_1) is 64474 ± 1367 M^{-1} and the 2:2 association constant (K_2) is 11677 ± 715 M^{-1}.

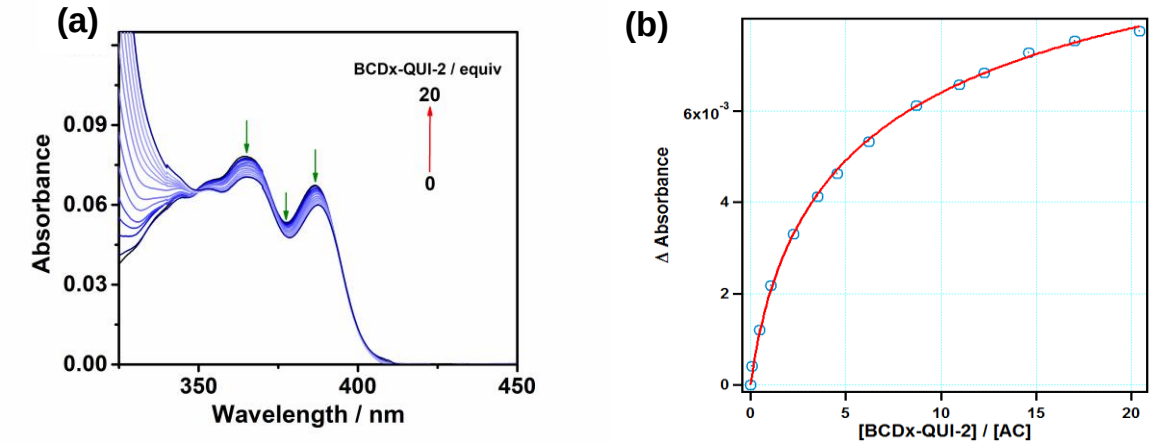


Figure S33. (a) UV-Vis absorption spectral changes of AC upon addition of **10** in pH 8 PBS buffer, [AC] = 0.02 mM; [**10**] = 0 - 4 mM. (b) Calculated 1:1 association constant (K_1) is 73615 ± 817 M^{-1} and the 2:2 association constant (K_2) is 5327 ± 115 M^{-1}.

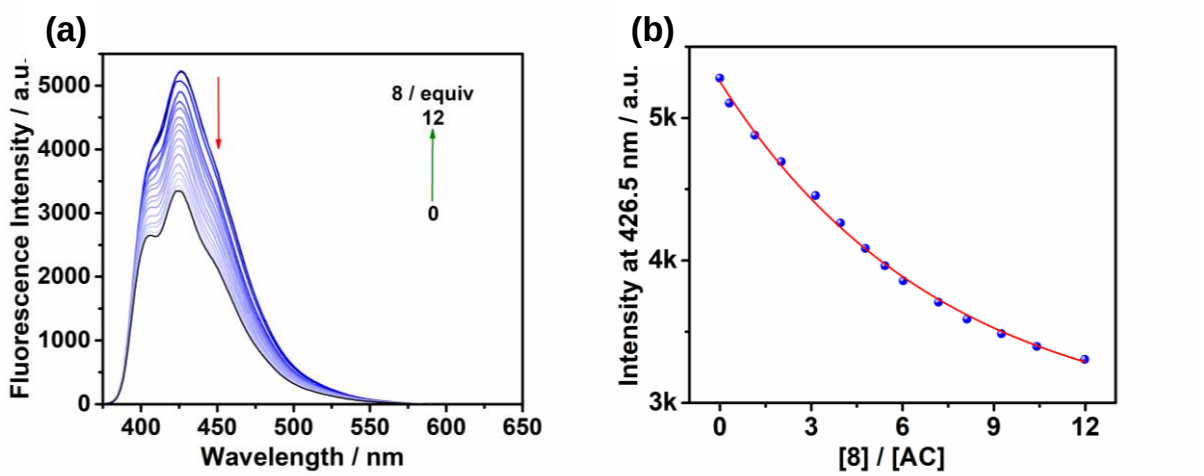


Figure S34. (a) Fluorescence emission spectral changes of AC upon addition of **10** in pH 7 PBS buffer, [AC] = 0.2 mM; [**8**] = 4 mM. (b) A plot of the fluorescence intensity at 426.5 nm versus the host [**8**].

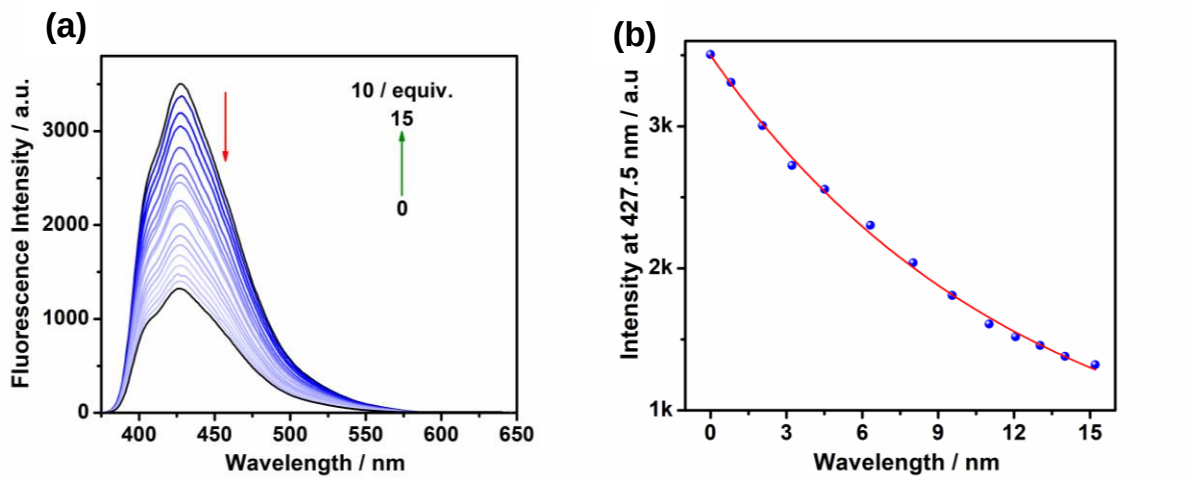


Figure S35. (a) Fluorescence emission spectral changes of AC upon addition of **10** in pH 8 PBS buffer, [AC] = 0.2 mM; [**10**] = 4 mM. (b) A plot of the fluorescence intensity at 427.5 nm versus the host [**10**].

Table S4. Estimated populations of the free AC and complex species (AC:**10**) in the solution used for the photoreaction.[a]

pH	[AC] /mM	[10] /mM	H/G ratio	Population of AC / %		
				Free AC	1:1 complex	2:2 complex
6	0.2	0	0.0	100	0	0
	0.2	0.2	1	16	29	55
	0.2	0.6	3	1.3	32	66.7
	0.2	1	5	0.7	32	67.3
	0.2	2	10	0.3	32.1	67.6
	0.2	**4.5**	**22.5**	**0.1**	**32.2**	**67.7**
	0.2	6	30	0.1	32.1	67.8
	0.02	6	300	0.2	68.8	31.0
7	**0.2**	**4.5**	**22.5**	**0.1**	**37.5**	**62.4**
	0.2	6	30	0.1	37.5	62.4
8	**0.2**	**4.5**	**22.5**	**0.2**	**49.6**	**50.2**
	0.2	6	30	0.1	49.7	50.2
9	0.2	0.2	1	18	49.9	32.1
	0.2	0.6	3	1.8	56.7	41.5
	0.2	1	5	0.9	57.2	41.9
	0.2	2	10	0.4	57.3	42.3
	0.2	4	20	0.2	57.4	42.4
	0.2	**4.5**	**22.5**	**0.2**	**57.4**	**42.4**
	0.2	6	30	0.1	57.4	42.5
	0.02	6	300	0.2	89.5	10.3
10	**0.2**	**4.5**	**22.5**	**0.2**	**55.7**	**44.1**
	0.2	6	30	0.1	55.8	44.1

[a] calculated using binding constant data from ITC measurements, pH 6 (K_1 =58300 ± 1400 and K_2 = 16400 ± 1200), pH 7 (K_1 = 64800 ± 1100 and K_2 = 11130 ± 800) pH 8 (K_1 = 73700 ± 1800 and K_2 = 5100 ± 150) pH 9 (K_1 = 76800 ± 1370 and K_2= 3220 ± 98) and pH (K_1 = 75300 ± 1420 and K_2 = 3550 ± 100).

5. Photocyclodimerization of AC mediated by native and modified CDxs

Table S5. Photocyclodimerization of AC mediated by native *β*-CDx, **7** in PBS buffer (1-10).[a]

Solvent	Added salt	*T* /° C	Conv. /%	Yield / %						*ee*[b] /%				5/1	6/2	(1+5)/ (2+6)
				1	2	3	4	5	6	2	3	5	6			
pH 1	none	0.5	67.4	56.1	27.2	3.9	0.7	0.9	11.2	26.3	-7.9	45.7	40.0	0.016	0.41	1.48
pH 1 [c]	none	0.5	86.9	57.5	23.7	7.2	*d*	2.2	9.4	24.7	-8.1	49.6	26.2	0.038	0.40	1.80
pH 2	none	0.5	73.2	57.9	26.8	3.3	*d*	1.4	10.6	20.4	-7.6	41.9	36.1	0.024	0.40	1.59
pH 2 [c]	none	0.5	87.2	61.5	20.5	6.5	*d*	2.6	8.9	19.6	-8.3	44.6	26.9	0.042	0.43	2.18
pH 3	none	0.5	72.0	60.4	24.5	2.7	*d*	1.9	10.5	7.4	-7.4	43.1	35.3	0.032	0.42	1.78
pH 3 [c]	none	0.5	86.7	61.9	20.2	5.2	*d*	4.2	8.5	10.6	-7.8	40.5	25.7	0.068	0.42	2.30
pH 4	none	0.5	75.9	68.6	18.1	0.9	*d*	2.5	9.9	5.0	-7.8	46.8	33.0	0.036	0.55	2.54
pH 4 [c]	none	0.5	86.2	61.1	19.3	4.1	*d*	7.5	8.0	5.3	-7.9	38.2	22.4	0.12	0.42	2.51
pH 5	none	0.5	81.7	72.2	9.0	*d*	*d*	9.2	9.6	-25.3	*e*	44.5	27.2	0.13	1.07	4.38
pH 5 [c]	none	0.5	95.1	65.1	12.9	2.5	*d*	12.3	7.2	-19.8	-6.3	33.1	20.5	0.19	0.56	3.85
pH 5.1[g]	none	0.5	94.6	99.2	0.8	*d*	*d*	*d*	*d*	-20.6	*e*	*e*	*e*	*e*	*e*	124
pH 6	none	0.5	83.9	73.8	5.4	*d*	*d*	13.8	7.0	-24.6	*e*	38.4	26.2	0.19	1.30	7.07
pH 6 [c]	none	0.5	86.5	68.2	9.4	1.1	*d*	15.2	6.1	-25.6	-6.2	30.7	20.6	0.22	0.65	5.38
pH 7	none	0.5	78.0	68.1	3.2	*d*	*d*	20.6	8.1	-20.8	*e*	43.0	20.7	0.30	2.53	7.85
pH 7.1 [g]	none	0.5	94.0	49.0	1	1	*d*	35.0	14.1	8	-5	46	12	0.71	14	5.6
pH 8	none	0.5	82.3	63.0	2.4	*d*	*d*	25.6	9.0	-19.1	*e*	43.3	19.9	0.41	3.75	7.77
pH 9	none	0.5	85.0	61.1	1.1	*d*	*d*	28.3	9.5	-16.1	*e*	42.8	15.9	0.46	8.64	8.43
		50	-	60.0	4	3	1	23.0	9.0	-8	-1	41	31	0.38	2.25	6.39
	none	25	-	65.0	1	1	*d*	25.0	8.0	-10	-1	47	24	0.39	8.0	10.0
		0.5	-	65.0	1	*d*	*d*	26.0	8.0	-18	*e*	43	16	0.4	8.0	10.11
pH 9 [h]		40	-	16.0	*d*	*d*	*d*	59.0	25.0	*e*	*e*	32	10	3.7	*f*	3.0
	CsCl	20	-	13.0	*d*	*d*	*d*	59.0	28.0	*e*	*e*	23	-4	4.5	*f*	2.57
		0.5	-	14.0	*d*	*d*	*d*	55.0	31.0	*e*	*e*	10	-16	3.9	*f*	2.23
		-20	-	20.0	*d*	*d*	*d*	49.0	31.0	*e*	*e*	-7	-36	2.5	*f*	2.23
pH 9.4 [g]	none	0.5	84.4	43.3	0.7	0.9	*d*	40.3	14.8	-10.3	-34.6	43.0	6.8	0.93	21.1	5.39
pH 10	none	0.5	86.1	59.5	1.0	*d*	*d*	29.6	9.9	-20.6	*e*	43.1	14.1	0.50	9.9	8.17

[a] [AC] = 0.2 mM, [**7**] = 4.5 mM; irradiated at 365 nm for 30 min with a LED at 0.5 °C, unless stated otherwise. [b] Enantiomeric excess determined by chiral HPLC, where the first-eluted enantiomer is given a positive sign for all of the chiral products, *i.e.*, **2**, **3**, **5**, and **6**. [c] filtrate. [d] Yield < 0.5%. [e] Not determined because of the low yield. [f] Larger than 1000 because of the low yield of **2**. [g] From reference [S7]. [h] From reference [S3] presence of 6M CsCl.

Table S6. Photocyclodimerization of AC mediated by native BCDx-NH2, **8** in PBS buffer (1-10).[a]

Solvent	Added salt	*T* / °C	Conv. /%	Yield / %						*ee*[b] /%				5/1	6/2	(1+5)/(2+6)
				1	2	3	4	5	6	2	3	5	6			
pH 1	none	0.5	75.6	26.6	21.5	*d*	*d*	18.4	33.5	-27.6	*e*	37.6	13.2	0.69	1.56	0.82
pH 1 [c]	none	0.5	82.3	23.2	22.3	*d*	*d*	20.1	34.4	-22.3	*e*	32.8	24.2	0.87	1.54	0.76
pH 2	none	0.5	74.8	36.1	19.5	*d*	*d*	13.6	30.8	-21.8	*e*	34.2	12.7	0.38	1.58	0.99
pH 2 [c]	none	0.5	80.6	28.5	21.8	*d*	*d*	14.1	35.6	-18.2	*e*	31.2	13.2	0.50	1.63	0.74
pH 3	none	0.5	72.0	39.9	16.8	*d*	*d*	9.4	33.9	-19.9	*e*	32.0	10.1	0.24	2.02	0.97
pH 3 [c]	none	0.5	77.0	32.5	17.6	*d*	*d*	12.6	37.3	-17.6	*e*	28.1	9.8	0.39	2.12	0.82
pH 4	none	0.5	72.2	42.4	11.0	*d*	*d*	11.1	35.5	-18.8	*e*	29.5	5.6	0.26	3.23	1.15
pH 4 [c]	none	0.5	70.5	36.2	13.5	*d*	*d*	13.5	36.8	-12.9	*e*	20.1	2.9	0.37	2.73	0.99
pH 5	none	0.5	66.7	37.4	10.3	*d*	*d*	17.1	35.2	-11.3	*e*	31.0	-9.7	0.46	3.42	1.20
pH 5 [c]	none	0.5	60.9	32.1	13.1	*d*	*d*	18.3	36.5	-11.9	*e*	28.6	-10.5	0.57	2.79	1.02
pH 6	none	0.5	61.8	32.6	8.7	*d*	*d*	25.5	33.2	-12.5	*e*	30.2	-12.4	0.78	3.81	1.39
pH 6 [c]	none	0.5	61.5	26.5	11.2	*d*	*d*	24.2	38.1	-8.9	*e*	31.8	-12.9	0.91	3.40	1.03
pH 7	none	0.5	54.5	25.5	5.1	*d*	*d*	31.2	38.2	-20.0	*e*	29.7	-14.8	1.22	7.49	1.31
pH 8	none	0.5	49.7	14.3	3.2	*d*	*d*	43.1	39.4	-36.7	*e*	30.7	-17.9	3.01	12.31	1.35
pH 9	none	0.5	45.2	11.8	0.7	*d*	*d*	45.4	42.1	-35.9	*e*	32.3	-19.9	3.85	60.14	1.34
pH 9 [f]	CsCl	40	32	17.0	*d*	*d*	*d*	55.0	28.0	*e*	*e*	30	5	3.24	*g*	2.57
		20	39	15.0	*d*	*d*	*d*	52.0	33.0	*e*	*e*	21	-10	3.47	*g*	2.03
		0.5	43	11.0	*d*	*d*	*d*	49.0	40.0	*e*	*e*	10	-28	4.46	*g*	1.50
		-20	49	7.0	*d*	*d*	*d*	48.0	45.0	*e*	*e*	-1	-44	6.86	*g*	1.22
pH 10	none	0.5	45.9	9.9	0.9	0.7	*d*	46.1	42.4	-37.1	22	33.2	-20.2	4.66	47.11	1.29

[a] [AC] = 0.2 mM, [**8**] = 4.5 mM; irradiated at 365 nm for 30 min with a LED at 0.5 °C, unless stated otherwise. [b] Enantiomeric excess determined by chiral HPLC, where the first-eluted enantiomer is given a positive sign for all of the chiral products, *i.e.*, **2**, **3**, **5**, and **6**. [c] filtrate, estimated [AC] = 0.039 μM (pH1), 0.24 μM (pH2), 1.18 μM (pH3), 1.52 μM (pH4) and 4.12 μM (pH5), by HPLC. [d] Yield < 0.5%. [e] Not determined because of the low yield. [f] From reference [S3] in the presence of 6M CsCl. [g] Larger than 1000 because of the low yield of 2.

Table S7. Photocyclodimerization of AC mediated by BCDx-QUI-1, **9** in PBS buffer (1-10) at various temperatures (*T*) and in the presence or absence of salts.[a]

Solvent	Added salt	*T* / °C	Conv. /%	Yield / %						*ee*[b] /%				5/1	6/2	(1+5)/ (2+6)
				1	2	3	4	5	6	2	3	5	6			
pH 1	none	0.5	74.8	7.9	15.3	3.1	2.1	40.4	31.2	9.6	-7.8	38.8	12.7	5.11	2.04	1.04
pH 1 [c]	none	0.5	79.2	2.4	17.5	1.2	1.1	44.6	33.2	7.2	-6.9	30.7	15.8	18.58	1.90	0.93
	CsCl [d]	0.5	24.6	15.9	1.7	*f*	*f*	39.8	42.6	12.6	*g*	19.7	9.1	2.50	25.06	1.26
		-20	28.6	20.2	6.1	*f*	*f*	39.2	34.5	19.9	*g*	22.8	34.5	1.94	5.66	1.46
pH1/ MeOH[e]	none	0.5	56.2	15.6	21.4	4.8	3.2	41.9	23.1	1.6	-11.2	11.0	9.7	7.48	1.08	1.07
		-20	61.8	0.8	26.5	1.9	2.2	44.8	23.8	2.5	-9.9	20.1	16.1	56	0.90	0.91
pH 2	none	0.5	67.9	17.2	10.3	3.7	1.3	36.1	31.4	9.4	-6.9	32.1	9.7	2.10	3.05	1.28
pH 2 [c]	none	0.5	68.4	22.2	9.8	1.2	*f*	38.6	28.2	6.2	-7.2	30.5	14.9	1.74	2.88	1.60
pH 3	none	0.5	55.3	20.3	7.2	5.7	1.5	34.6	30.7	8.5	-6.8	32.0	7.7	1.70	4.26	1.45
pH 3 [c]	none	0.5	51.6	22.8	7.8	0.6	*f*	36.6	32.2	5.2	-5.2	29.2	9.7	1.61	4.13	1.49
pH 4	none	0.5	46.5	34.2	5.5	4.5	2.3	14.1	39.4	9.4	-6.3	24.6	2.7	0.41	7.16	1.08
pH 4 [c]	none	0.5	50.2	39.5	4.6	*f*	0.6	20.2	35.1	3.6	*g*	25.4	3.1	0.51	7.63	1.50
pH 5	none	0.5	27.4	33.7	2.3	4.2	1.3	17.1	41.8	5.5	-7.2	25.1	-9.7	0.51	18.17	1.14
pH 5 [c]	none	0.5	26.6	37.1	3.5	*f*	*f*	16.9	42.5	1.9	*g*	22.3	-12.2	0.46	12.14	1.17
pH 6	none	0.5	32.8	31.2	2.3	4.3	1.2	20.9	40.1	-2.1	-6.9	23.7	-17.2	0.67	17.44	1.23
pH 6 [c]	none	0.5	32.4	32.3	1.4	*f*	*f*	24.7	41.6	-0.7	*g*	20.0	-19.7	0.77	29.71	1.33
pH 7	none	0.5	52.5	23.8	1.8	3.1	3.0	26.2	42.1	-11.9	-7.0	21.3	-29.5	1.10	23.39	1.14
pH 8	none	0.5	60.2	20.9	1.9	3.6	3.1	30.3	40.2	-17.9	-6.8	22.5	-33.9	1.45	21.16	1.22
pH 9	none	0.5	63.6	18.3	1.8	2.8	3.5	32.3	41.3	-20.5	-6.3	19.8	-37.7	1.77	22.94	1.17
pH 9	CsCl [d]	0.5	22.6	14.9	9.4	*f*	1.3	38.2	36.2	-7.5	*g*	19.1	-28.5	2.56	3.85	1.17
		-20	32.3	3.9	15.5	*f*	*f*	46.2	34.4	-14.6	*g*	26.9	-39.2	11.85	2.22	1.00
pH9/ MeOH[e]	none	0.5	36.9	7.9	1.1	*f*	*f*	37.7	53.3	-31.5	*g*	5.6	-39.8	4.77	48.46	0.84
		-20	45.6	1.2	2.1	*f*	*f*	40.4	56.3	-41.9	*g*	11.6	-51.5	33.67	26.81	0.71
pH 10	none	0.5	66.9	23.2	1.8	1.6	3.2	31.1	39.1	-21.2	-5.7	19.9	-39.2	1.34	23.00	1.33

[a] [AC] = 0.2 mM, [**9**] = 4.5 mM; irradiated at 365 nm for 30 min with a LED at different temperatures. [b] Enantiomeric excess determined by chiral HPLC, where the first-eluted enantiomer is given a positive sign for all of the chiral products, *i.e.*, **2**, **3**, **5**, and **6**. [c] filtrate, estimated [AC] = 0.028 μM (pH1), 0.39 μM (pH2), 1.08 μM (pH3), 1.92 μM (pH4) and 4.36 μM (pH5), by HPLC. [d] Presence of 6M CsCl. [e] ratio of solvent is 1:1 (V/V). [f] Yield < 0.5%. [g] Not determined because of the low yield.

Table S8. Photocyclodimerization of AC mediated by BCDx-QUI-2, **10** in PBS buffer (1-10) at various temperatures (*T*) and in the presence or absence of salts.[a]

Solvent	Added salt	*T* / °C	Conv. /%	Yield / %						*ee*[b] /%				5/1	6/2	(1+5)/ (2+6)
				1	2	3	4	5	6	2	3	5	6			
pH 1	none	25	61.2	5.2	8.1	1.2	*g*	51.3	34.2	8.2	25.3	48.2	21.3	9.87	4.22	1.34
		0.5	78.8	6.2	5.3	0.9	*g*	55.5	32.1	12.7	30.8	59.7	25.7	8.95	6.06	1.65
pH 1 [c]	none	25	77.4	2.8	4.8	*g*	*g*	51.5	40.9	16.6	*h*	39.7	25.7	18.39	8.52	1.19
		0.5	89.4	7.2	5.1	*g*	*g*	59.2	28.5	19.8	*h*	51.2	31.2	8.22	5.59	1.98
	LiCl [d]	0.5	19.1	1.2	1.2	*g*	0.8	62.5	34.3	9.2	*h*	15.4	40.8	52.08	28.58	1.79
		-20	10.2	1.6	5.2	*g*	*g*	64.8	28.4	12.5	*h*	22.4	48.7	40.50	5.46	1.98
	CsCl [e]	25	34.5	8.2	13.5	1.2	3.2	46.3	27.6	2.2	9.2	42.1	37.2	5.65	2.04	1.33
		0.5	48.9	8.5	12.2	*g*	1.2	45.7	32.4	7.6	*h*	54.6	40.2	5.38	2.66	1.22
		-20	66.5	6.9	9.6	*g*	*g*	48.3	35.2	15.8	*h*	64.2	45.8	7.00	3.67	1.23
pH1/ MeOH[f]	none	0.5	43.2	7.5	5.2	*g*	*g*	55.2	39.1	22.2	*h*	46.2	28.5	7.36	6.17	1.68
		-20	57.9	0.6	6.5	*g*	0.6	64.1	28.2	19.2	*h*	47.8	35.7	106.83	4.34	1.87
pH 2	none	0.5	77.4	7.6	6.4	1.7	*g*	52.5	31.8	9.4	26.9	54.5	19.6	6.91	4.97	1.57
pH 2 [c]	none	0.5	79.7	8.2	7.8	*g*	*g*	50.8	33.2	11.2	*h*	52.1	23.2	6.20	4.26	1.44
pH 3	none	0.5	55.3	14.9	5.2	1.7	*g*	48.1	30.1	8.5	16.8	52.3	16.2	3.23	5.79	1.79
pH 3 [c]	none	0.5	50.8	17.3	6.4	*g*	*g*	51.2	25.1	9.2	*h*	54.5	20.7	2.96	3.92	2.18
pH 4	none	0.5	36.5	29.5	4.1	*g*	0.9	38.1	27.4	9.4	*h*	53.4	13.0	1.29	6.68	2.15
pH 4 [c]	none	0.5	42.1	24.2	8.1	*g*	*g*	38.4	29.3	8.4	*h*	48.9	9.8	1.59	3.62	1.67
pH 5	none	0.5	47.4	34.5	3.7	*g*	*g*	36.9	24.9	7.5	*h*	45.7	-6.8	1.07	6.73	2.50
pH 5 [c]	none	0.5	48.5	32.1	5.5	*g*	*g*	32.7	29.7	6.9	*h*	43.1	-4.2	1.02	5.40	1.84
pH 6	none	0.5	52.2	31.6	2.9	*g*	*g*	37.8	27.7	2.6	*h*	43.5	-7.9	1.20	9.55	2.27
pH 6 [c]	none	0.5	56.7	30.5	4.8	*g*	*g*	32.1	32.6	0.9	*h*	39.3	-19.8	1.05	6.79	1.67
pH 7	none	0.5	62.8	26.6	2.1	*g*	*g*	51.1	20.2	-4.9	*h*	39.8	-34.1	1.92	9.62	3.48
pH 8	none	0.5	72.2	16.6	1.7	*g*	*g*	50.5	31.2	-7.7	*h*	39.7	-44.5	3.04	18.35	2.04
pH 9	none	25	63.2	12.5	2.2	1.8	2.2	53.2	28.1	-2.4	13.8	34.6	-29.9	4.26	12.77	2.17
		0.5	76.6	20.6	1.4	*g*	*g*	56.3	21.7	-10.9	*h*	39.2	-47.8	2.73	15.50	3.33
		15	19.6	17.1	3.4	*g*	*g*	39.2	40.3	-1.7	*h*	32.4	-35.0	2.29	11.85	1.29
	LiCl [d]	0.5	22.2	15.8	2.6	*g*	*g*	35.4	46.2	-4.5	*h*	48.1	-35.2	2.24	17.77	1.05
		-20	27.4	18.2	*g*	*g*	*g*	44.3	37.5	-15.2	*h*	56.9	-39.8	2.43	*i*	1.67
pH 9		15	36.1	12.3	*g*	*g*	*g*	66.6	21.1	-7.2	*h*	45.2	-45.0	5.42	*i*	3.74
	CsCl [e]	0.5	42.8	5.2	*g*	*g*	*g*	70.2	24.6	-15.6	*h*	48.9	-52.5	13.50	*i*	3.07
		-20	46.6	3.4	*g*	*g*	*g*	75.5	21.1	-19.2	*h*	52.6	-68.2	22.21	*i*	3.74
pH9/ MeOH[f]	none	0.5	32.2	14.2	2.2	*g*	1.2	50.2	32.2	-29.8	*h*	43.2	-46.2	3.54	14.64	1.87
		-20	36.1	12.5	2.8	*g*	2.2	51.3	31.2	-32.2	*h*	52.0	-51.2	4.10	11.14	1.88
pH 10	none	0.5	76.7	9.3	1.5	*g*	0.7	52.2	36.3	-14.6	*h*	39.5	-51.3	5.61	24.20	1.63

[a] [AC] = 0.2 mM, [**10**] = 4.5 mM; irradiated at 365 nm for 30 min with a LED at different temperatures. [b] Enantiomeric excess determined by chiral HPLC, where the first-eluted enantiomer is given a positive sign for all of the chiral products, *i.e.*, **2**, **3**, **5**, and **6**. [c] filtrate, estimated [AC] = 0.042 μM (pH1), 0.47 μM (pH2), 1.24 μM (pH3), 2.74 μM (pH4) and 5.79 μM (pH5), by HPLC. [d] Presence of 1M LiCl. [e] Presence of 6M CsCl. [f] ratio of solvent is 1:1 (V/V). [g] Yield < 0.5%. [h] Not determined because of the low yield. [i] Larger than 1000 because of the low yield of **2**.

Table S9. Photocyclodimerization of AC mediated by BCDx-QMe, **11** in PBS buffer at various temperatures (*T*) and in the presence or absence of salts.[a]

Solvent	Added salt	T /°C	Conv. /%	Yield / %						*ee*[b] /%				5/1	6/2	(1+5)/(2+6)
				1	2	3	4	5	6	2	3	5	6			
pH 1	none	0.5	80.4	12.8	*g*	*g*	*g*	56.1	31.1	*h*	*h*	62.0	41.2	4.38	*i*	2.22
pH 1 [c]	none	0.5	84.6	20.2	1.2	*g*	*g*	50.9	27.7	21.6	*h*	64.2	40.9	2.52	23.08	2.46
	LiCl [d]	0.5	24.3	8.8	*g*	0.9	*g*	44.6	45.7	*h*	5.2	48.2	25.6	5.07	*i*	1.17
		-20	16.6	1.2	*g*	0.7	*g*	51.6	46.5	*h*	12.3	58.8	39.8	43.0	*i*	1.14
	CsCl [e]	0.5	46.8	2.5	*g*	1.2	*g*	55.9	40.4	*h*	5.6	51.3	39.1	23.36	*i*	1.45
		-20	53.4	0.6	*g*	1.6	*g*	71.7	26.1	*h*	10.2	68.1	54.8	119.5	*i*	2.77
pH1/MeOH[f]	none	0.5	36.7	9.9	9.6	*g*	*g*	41.6	38.9	25.6	*h*	32.2	52.7	4.20	4.05	1.06
		-20	55.9	0.8	1.2	*g*	*g*	56.8	41.2	35.2	*h*	48.9	64.2	71.0	34.33	1.36
pH 2	none	0.5	79.2	13.2	*g*	*g*	*g*	50.7	36.1	*h*	*h*	61.6	32.4	3.84	*i*	1.77
pH 2 [c]	none	0.5	81.3	15.3	2.3	1.2	*g*	42.3	38.9	22.3	5.2	60.8	36.9	2.77	16.91	1.40
pH 3	none	0.5	74.6	10.1	*g*	2.9	*g*	45.8	41.2	*h*	5.0	59.0	11.3	4.54	*i*	1.36
pH 3 [c]	none	0.5	77.7	3.1	3.9	2.3	*g*	49.2	41.5	17.0	6.5	59.2	19.3	15.87	10.64	1.15
pH 4	none	0.5	62.3	10.2	*g*	1.7	*g*	48.0	40.1	*h*	6.7	56.5	7.4	4.71	*i*	1.45
pH 4 [c]	none	0.5	60.6	11.8	8.6	3.6	*g*	37.1	38.9	7.6	7.9	56.3	9.2	3.14	4.52	1.03
pH 5	none	0.5	36.4	32.3	17.1	2.6	*g*	13.2	34.8	-3.2	7.0	52.2	-19.3	0.41	2.04	0.88
pH 5 [c]	none	0.5	35.9	29.6	12.9	6.2	*g*	15.3	36.0	-2.7	8.9	50.7	-12.2	0.52	2.79	0.92
pH 6	none	0.5	48.8	14.2	9.4	3.0	*g*	27.3	46.1	-9.2	8.2	48.2	-28.3	1.92	4.90	0.75
pH 6 [c]	none	0.5	42.8	5.6	14.1	3.9	1.1	31.2	44.1	-7.9	9.3	49.3	-30.6	5.57	3.13	0.63
pH 7	none	0.5	72.1	8.3	10.6	1.2	1.1	24.5	54.3	-12.2	9.5	45.6	-44.7	2.95	5.12	0.51
pH 8	none	0.5	80.4	15.1	11.2	3.1	1.3	18.2	51.1	-15.4	10.4	20.4	-56.6	1.21	4.56	0.54
	LiCl [d]	0.5	20.9	13.2	1.4	*g*	2.3	21.5	61.6	-6.8	*h*	36.8	-42.2	1.63	44.00	0.55
		-20	27.6	12.2	1.5	*g*	5.1	16.4	64.8	-19.2	*h*	41.2	-61.4	1.34	43.20	0.43
	CsCl [e]	0.5	44.8	7.6	1.2	*g*	0.9	38.2	52.1	-21.6	*h*	24.6	-51.3	5.03	43.42	0.86
		-20	51.4	0.7	2.5	*g*	1.4	21.2	74.2	-36.3	*h*	32.7	-81.2	30.29	29.68	0.29
pH9/MeOH[f]	none	0.5	22.1	19.6	6.2	7.2	0.8	35.1	31.1	-20.5	15.5	9.4	-32.5	1.79	5.02	1.47
		-20	26.5	28.2	18.7	3.3	1.2	37.4	11.2	24.8	21.2	16.2	-36.1	1.33	0.60	2.19
pH 9	none	0.5	83.3	14.6	11.2	3.2	1.3	17.4	52.3	-19.0	11.7	33.3	-59.2	1.19	4.67	0.50
pH 10	none	0.5	81.2	4.4	10.4	3.7	1.4	28.2	51.9	-18.1	12.4	54.9	-61.7	6.41	4.99	0.52

[a] [AC] = 0.2 mM, [**9**] = 4.5 mM; irradiated at 365 nm for 30 min with a LED at 0.5 °C, unless stated otherwise. [b] Enantiomeric excess determined by chiral HPLC, where the first-eluted enantiomer is given a positive sign for all of the chiral products, *i.e.*, **2**, **3**, **5**, and **6**. [c] filtrate, estimated [AC] = 0.098 μM (pH1), 0.43 μM (pH2), 2.06 μM (pH3), 3.22 μM (pH4) and 6.46 μM (pH5), by HPLC. [d] Presence of 1M LiCl. [e] Presence of 6M CsCl. [f] ratio of solvent is 1:1 (V/V). [g] Yield < 0.5%. [h] Not determined because of the low yield. [i] Larger than 1000 because of the low yield of 2.

6. Calculation of p*K*a values

Table S10. Calculated p*K*a values of host and its AC complexes at 25 ºC.[a]

	Calculated p*Ka*		Reported p*Ka*
	UV-vis.	Fluorescence	
AC (pK_a^{AC})	-	-	4.35 [S4]
β-CDx, **7** (pK_a^{7}) [b]			12.202,[S5a-d] 12.1,[S5e] 12.201,[S5f] 13.5[S5g]
Quinoline (p$K_a^{Qui.}$)	-	-	4.85 [S6]
BCDx-QUI-1, **9** (pK_a^{9}) [c]	-	4.84	
BCDx-QUI-2, **10** (pK_a^{10}) [d]	-	4.18	-
7:AC complex (p$K_a^{7:AC}$) [e]	5.1	-	-
8:AC complex (p$K_a^{8:AC}$) [f]	4.72	4.81	-
9:AC complex (p$K_a^{9:AC}$) [g]	5.20	5.12	
10:AC complex (p$K_a^{10:AC}$) [h]	5.58	5.68	-

[a]calculated using UV-vis and fluorescence spectral measurements, pH was adjusted using 66.7 mM, NaOH and 1 M HCl solution. [b]determined by pH potentiometry (25 °C) and ^{1}H and ^{13}C NMR study. [c][**9**] = 0.039 mM. [d][**10**] = 0.105 mM. [e] Ref. S7. [f] [AC] = 0.02 mM, [**8**] = 0.4 mM. [g][AC] = 0.02 mM, [**8**] = 0.4 mM. [h][AC] = 0.02 mM, [**10**] = 0.25 mM.

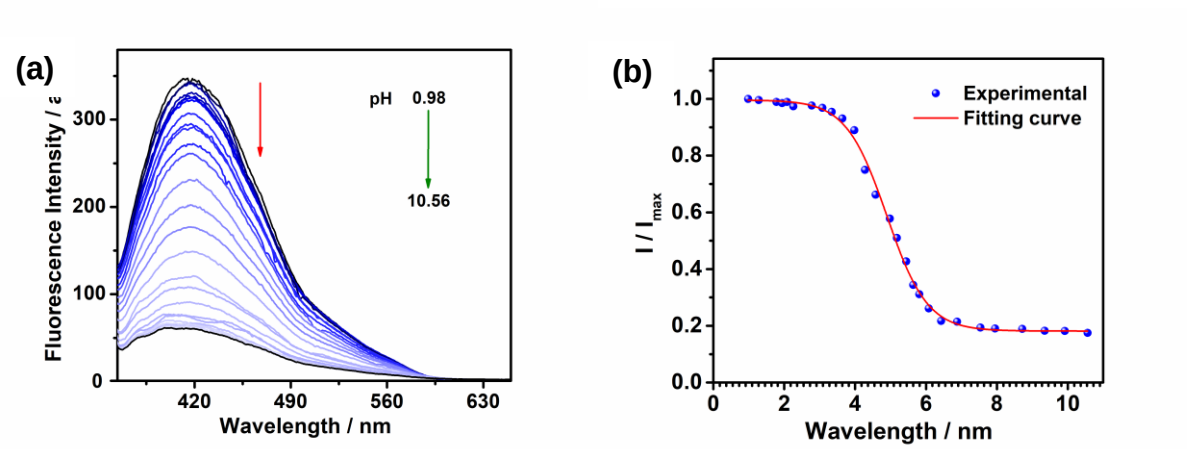


Figure S35. (a) Fluorescence spectral changes of **9** (0.039 mM) in different PBS buffers with pH ranging from 0.98 – 10.56, at 25 ºC (λ_{exc} = 315 nm), and (b) the relative fluorescence intensity changes with pH and the calculated p*K*a of **9** is 4.84.

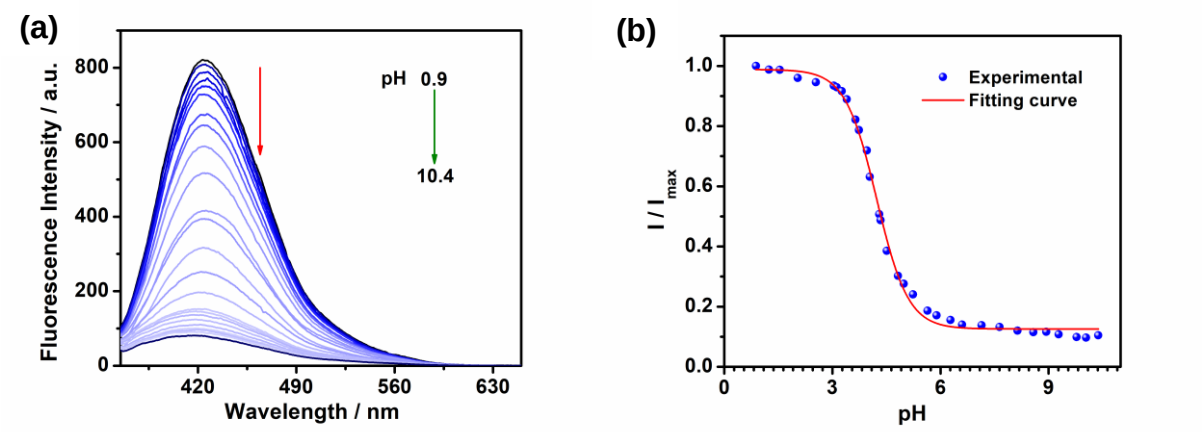


Figure S36. (a) Fluorescence spectral changes of **10** (0.105 mM) in different PBS buffers with pH ranging from 0.9 – 10.4, at 25 ºC (λ_{exc} = 315 nm), and (b) the relative fluorescence intensity changes with pH and the calculated p*K*a of **10** is 4.18.

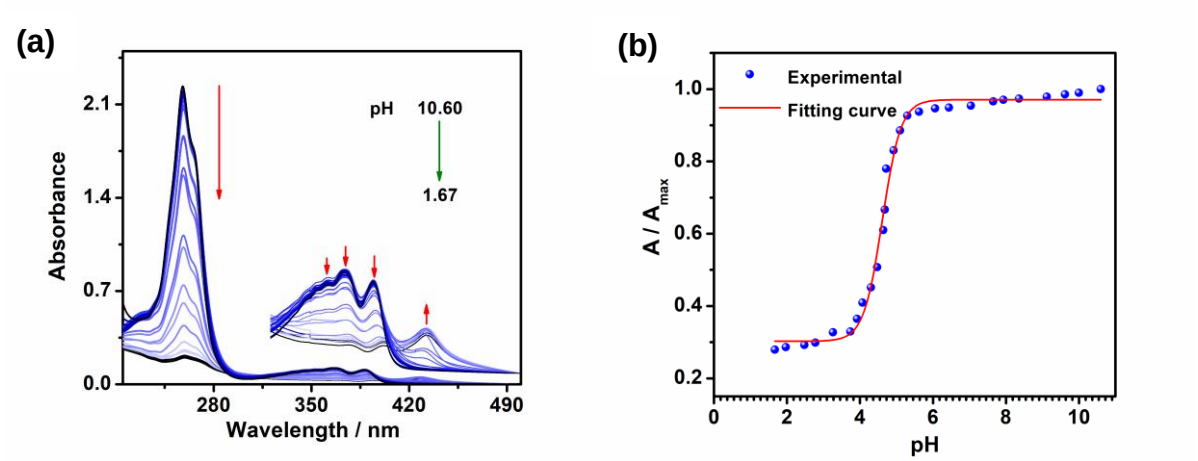


Figure S37. (a) Absorption spectral changes of **8** (0.4 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 1.67 – 10.60, at 25 °C, and (b) the relative absorption changes with pH and the calculated pK_a of **8**:AC complex is 4.72.

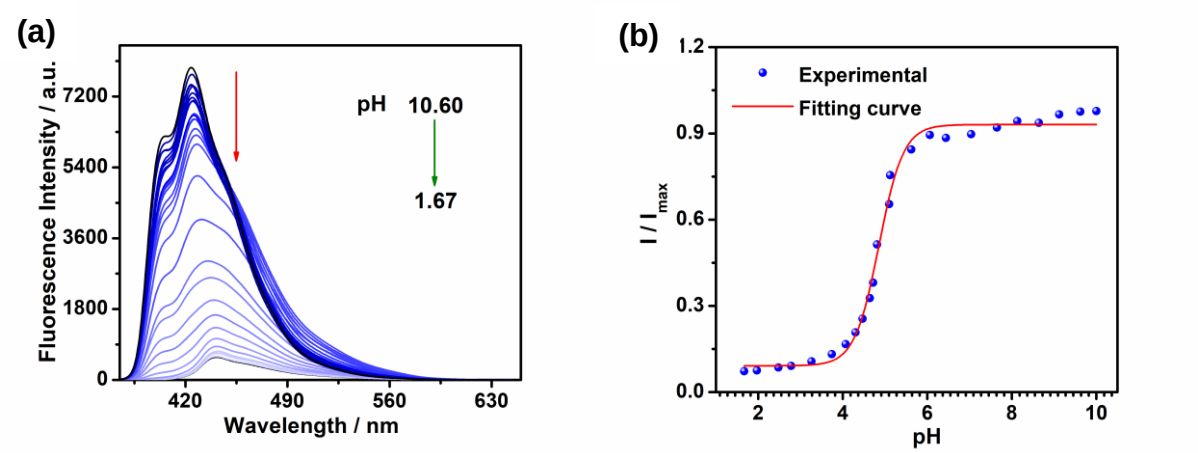


Figure S38. (a) Fluorescence spectral changes of **8** (0.4 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 1.67 – 10.60, at 25 °C (λ_{exc} = 365 nm), and (b) the relative fluorescence changes with pH and the calculated pK_a of **8**:AC complex is 4.81.

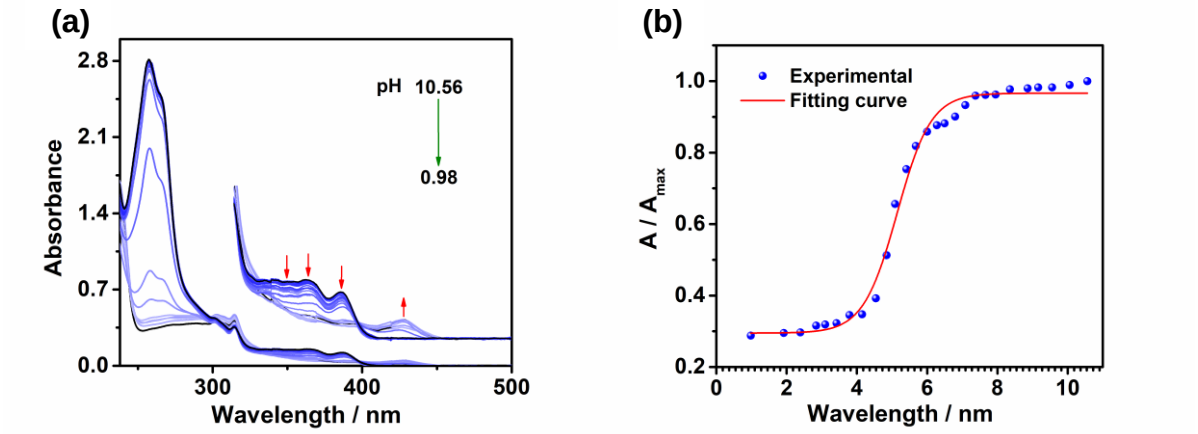


Figure S39. (a) Absorption spectral changes of **9** (0.4 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 0.98 – 10.56, at 25 °C, and (b) the relative absorption changes with pH and the calculated pK_a of **9**:AC complex is 5.20.

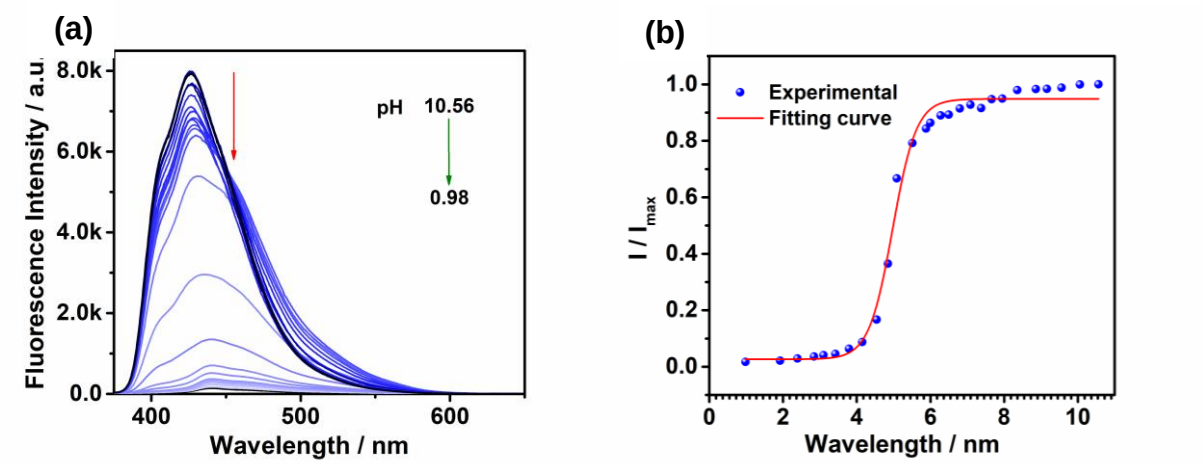


Figure S40. (a) Fluorescence spectral changes of **9** (0.4 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 0.98 – 10.56, at 25 °C (λ_{exc} = 365 nm), and (b) the relative fluorescence changes with pH and the calculated pK_a of **9**:AC complex is 5.12.

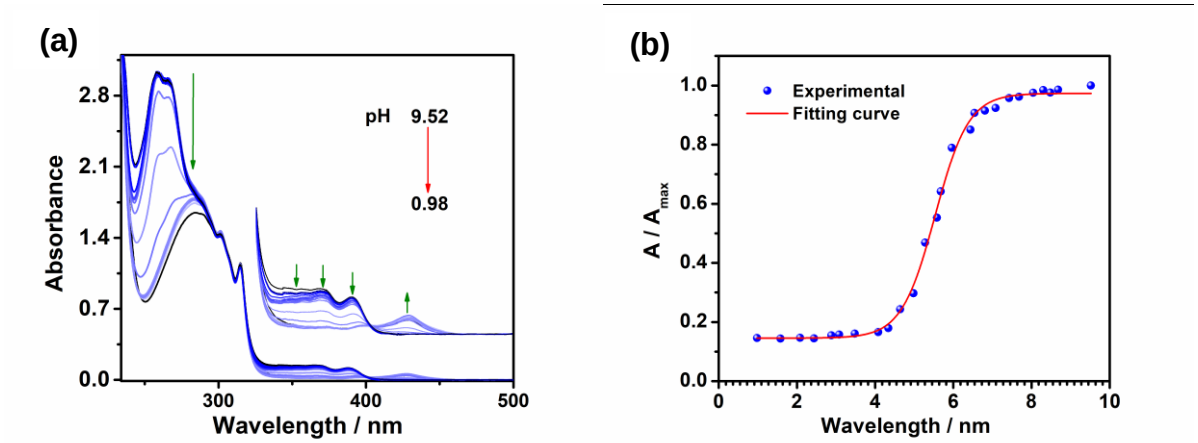


Figure S41. (a) Absorption spectral changes of **10** (0.25 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 0.98 – 9.52, at 25 °C, and (b) the relative absorption changes with pH and the calculated pK_a of **10**:AC complex is 5.58.

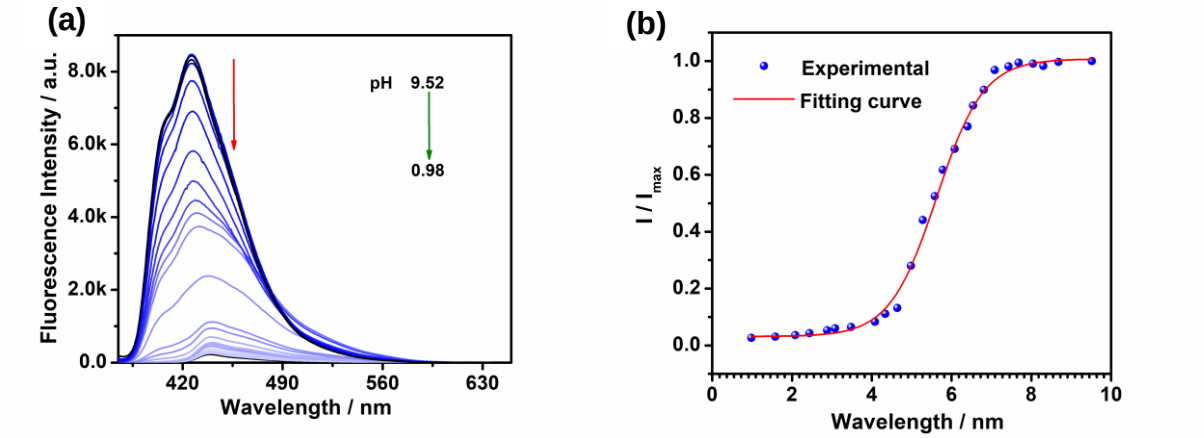


Figure S42. (a) Fluorescence spectral changes of **10** (0.25 mM) - AC (0.02 mM) complex in different PBS buffers with pH ranging from 0.98 – 9.52, at 25 °C (λ_{exc} = 365 nm), and (b) the relative fluorescence changes with pH and the calculated pK_a of **10**:AC complex is 5.68.

7. UV-vis., Fluorescence, and CD spectral studies

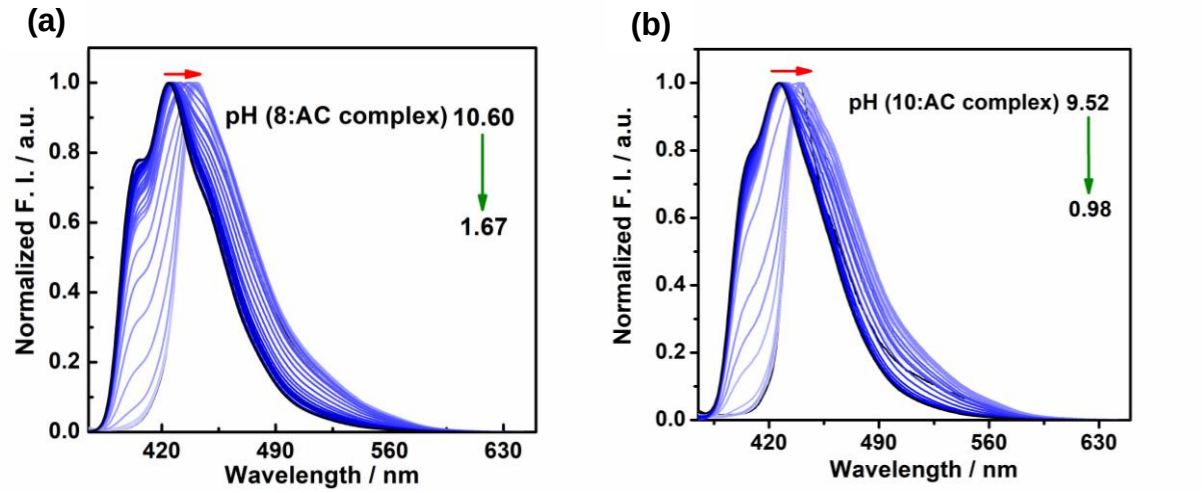


Figure S43. Normalized fluorescence spectra of **8** (0.4 mM)-AC (0.02 mM), and **10** (0.25 mM)-AC (0.02 mM) complex in different PBS buffers with pH range from ~1 - ~10, at 25 °C.

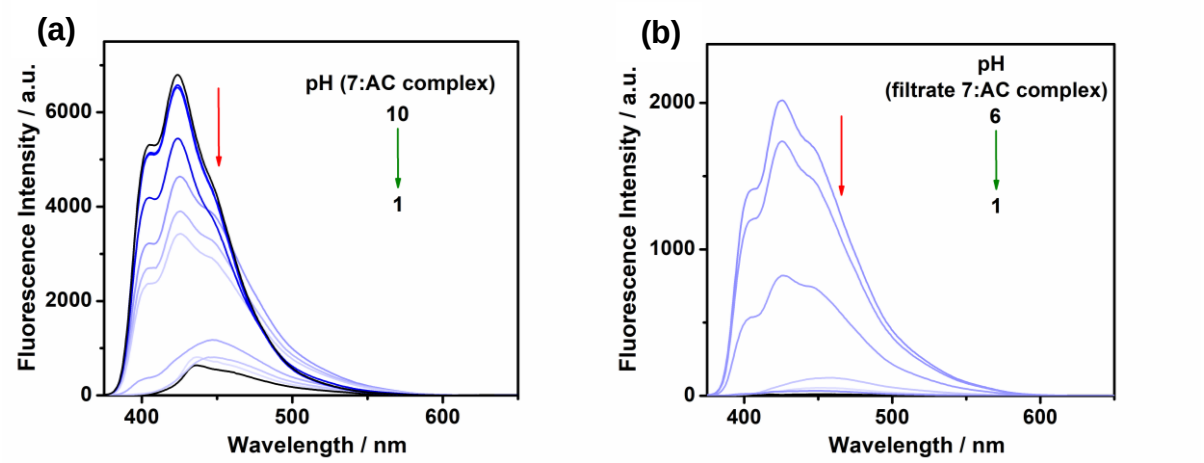


Figure S44. Fluorescence spectra of **7** (0.4 mM)-AC (0.02 mM) complex, in different PBS buffer with the pH ranging from 1 – 10, and (b) its complex filtrate solution at 25 °C (λ_{exc} = 365 nm).

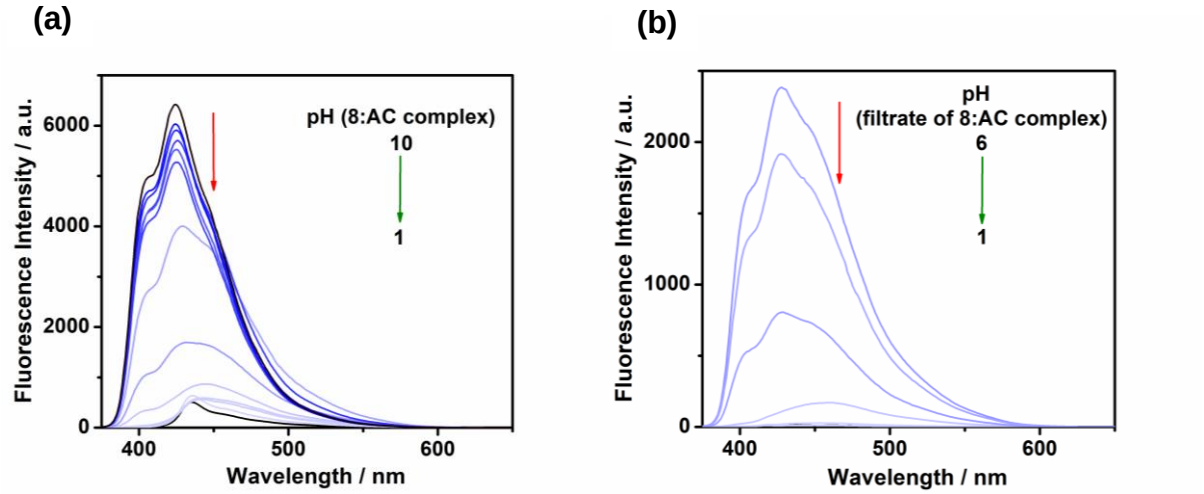


Figure S45. Fluorescence spectra of **8** (0.4 mM)-AC (0.02 mM) complex in different PBS buffer with the pH ranging from 1 – 10, and (b) its complex filtrate solution at 25 °C (λ_{exc} = 365 nm).

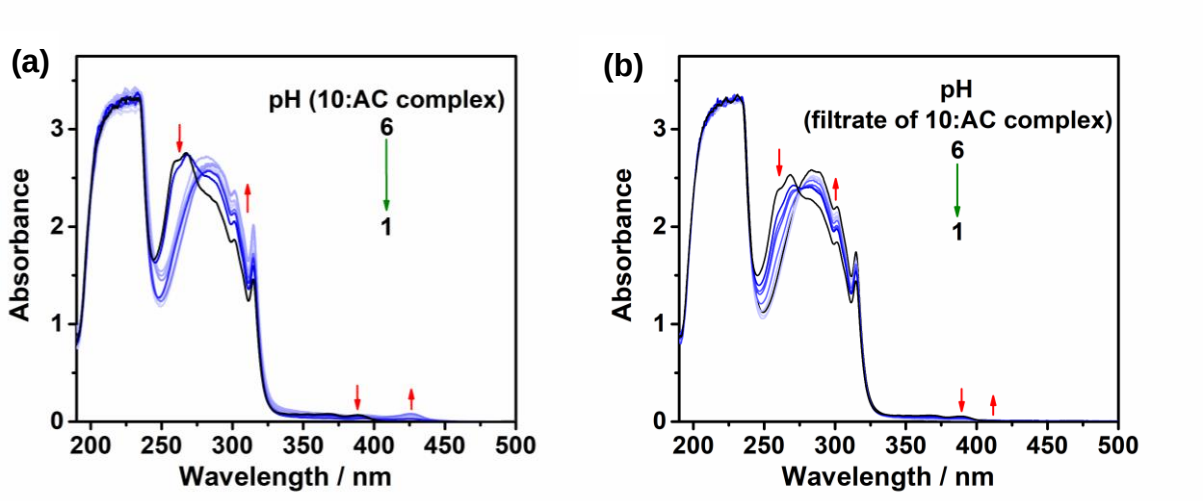


Figure S46. UV-Vis. absorbance spectra of (a) **10** (0.4 mM)-AC (0.02 mM) complex in different PBS buffer with the pH ranging from 1 – 6, and (b) its complex filtrate solution at 25 °C.

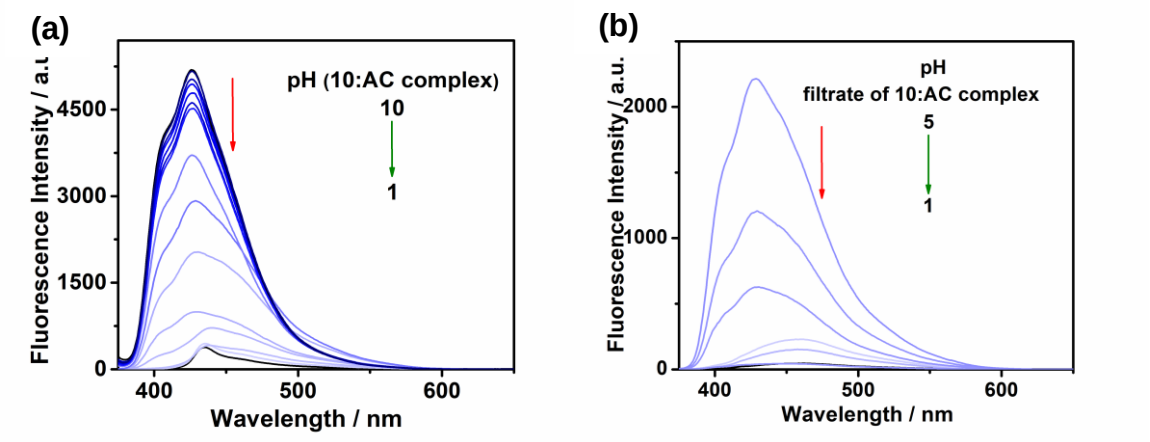


Figure S47. Fluorescence spectra of (a) **10** (0.4 mM)-AC (0.02 mM) complex in different PBS buffer with the pH ranging from 1 – 6, and (b) its complex filtrate solution at 25 °C (λ_{exc} = 365 nm).

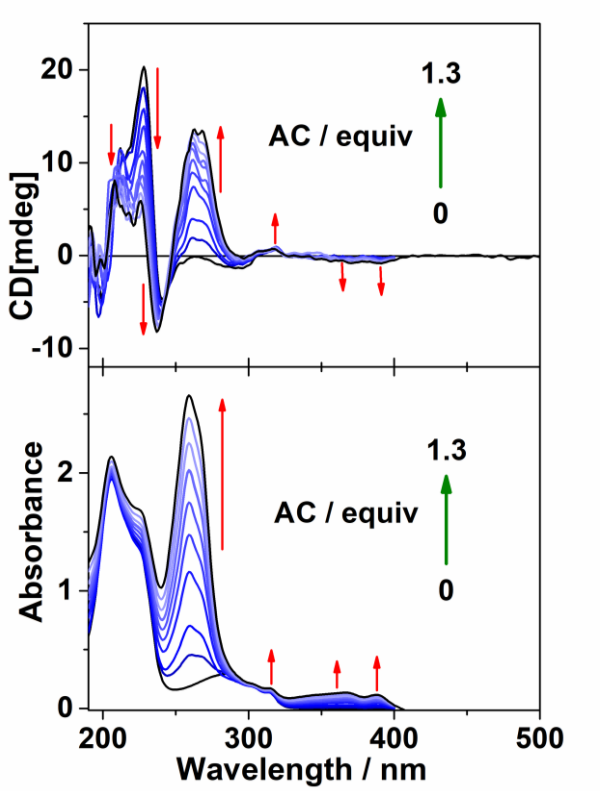


Figure S48. Circular dichroism spectra (upper panel) and UV-vis. (lower panel) of host **10** (0.18 mM) in a pH 7 (PBS, 66.7 mM) with increasing the concentration of AC at 25 ºC.

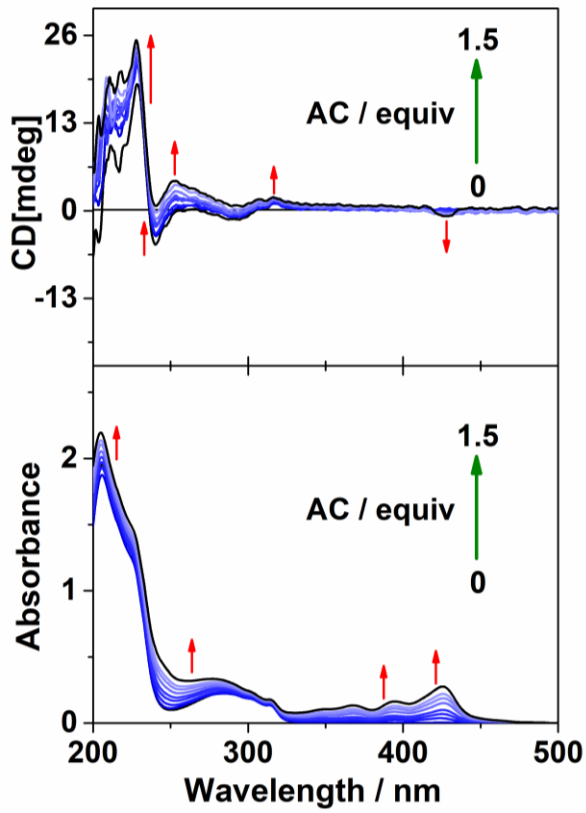


Figure S49. Circular dichroism spectra (upper panel) and UV-vis. (lower panel) of host **10** (0.18 mM) in a pH 2 (PBS, 66.7 mM) with increasing the concentration of AC at 25 ºC.

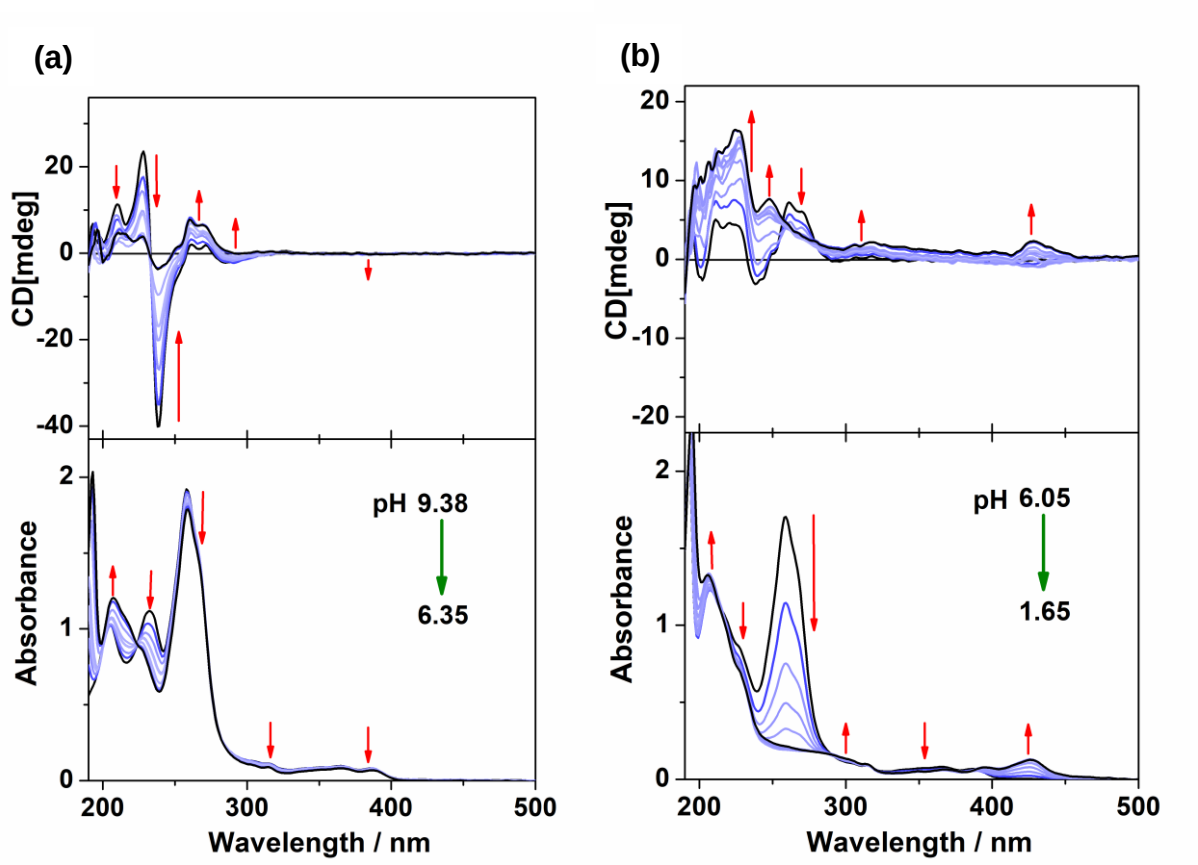


Figure S50. Circular dichroism spectra (upper panel) and UV-vis. (lower panel) of host **10** (0.2 mM) - AC (0.2 mM) complex in different PBS buffers with pH (a) 9.38–6.35 and (b) 6.05-1.65 at 25 ºC.

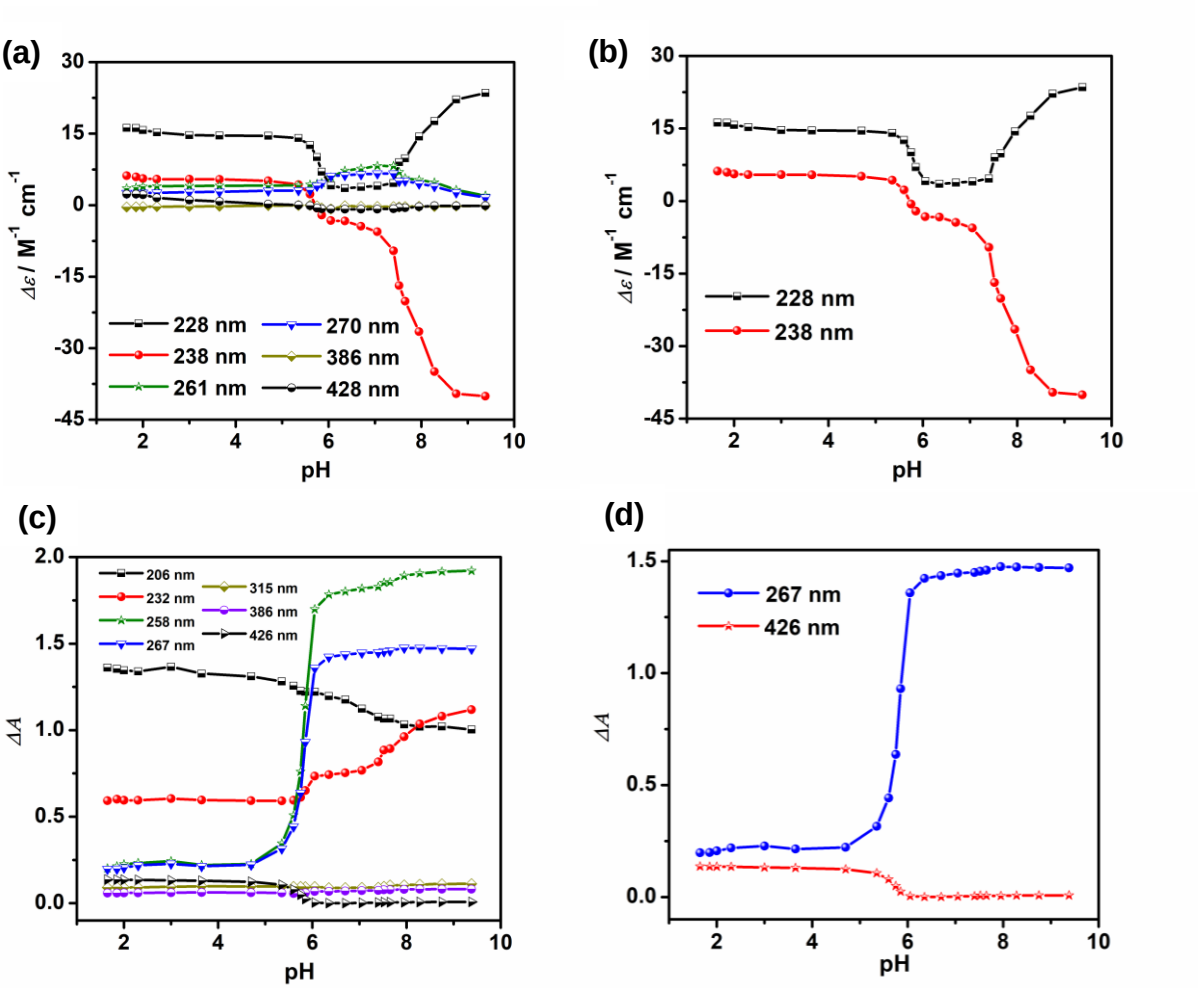


Figure S51. (a) and (b) Circular dichroism changes, (c) and (d) UV-Vis. absorption spectral changes of host **10** (0.2 mM) - AC (0.2 mM) complex in different PBS buffers with pH at different wavelengths (at 25 ºC).

8. NMR spectral studies

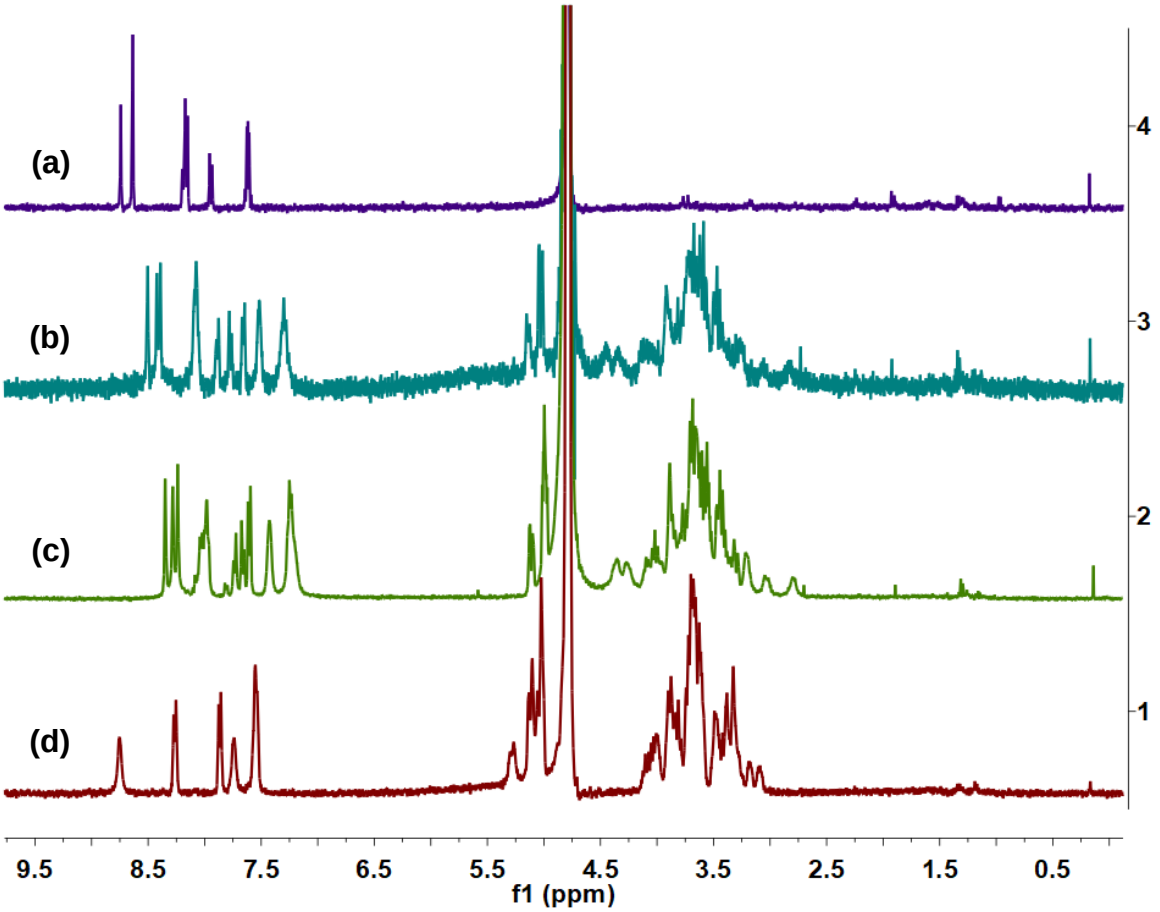


Figure S52a. ^{1}H NMR spectrum of (a) AC (0.4 mM) in D_2O (pD 9.0); (b) AC (0.9 mM) in D_2O (pD 9.0) in the presence of **10** (3.0 mM); (c) AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); and (d) **10** (3.0 mM) in D_2O (D_2O, 400 MHz, 25 ºC).

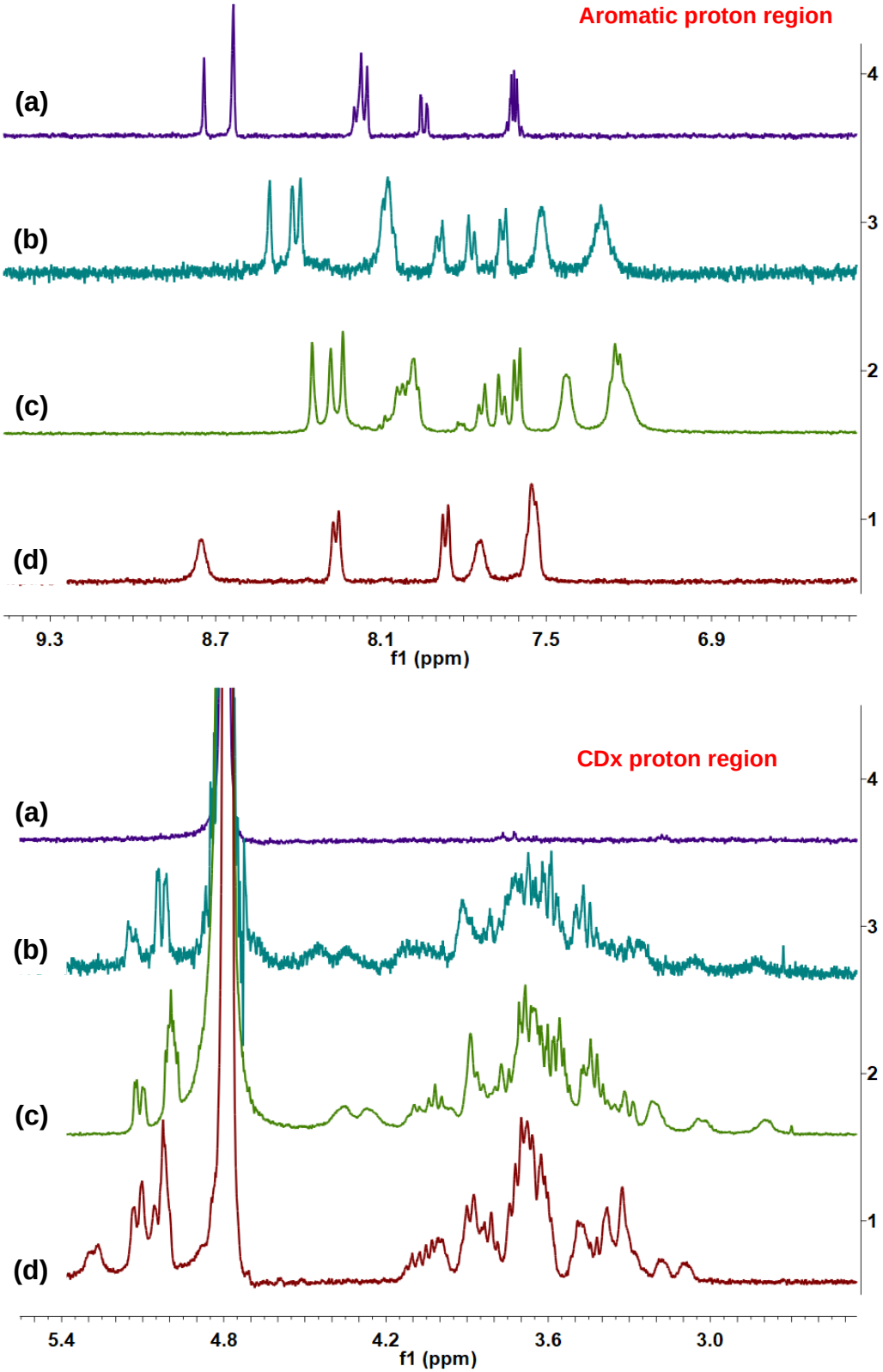


Figure S52b. ^{1}H NMR spectrum of (a) AC (0.4 mM) in D_2O (pD 9.0); (b) AC (0.9 mM) in D_2O (pD 9.0) in the presence of **10** (3.0 mM); (c) AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); and (d) **10** (3.0 mM) in D_2O (D_2O, 400 MHz, 25 ºC).

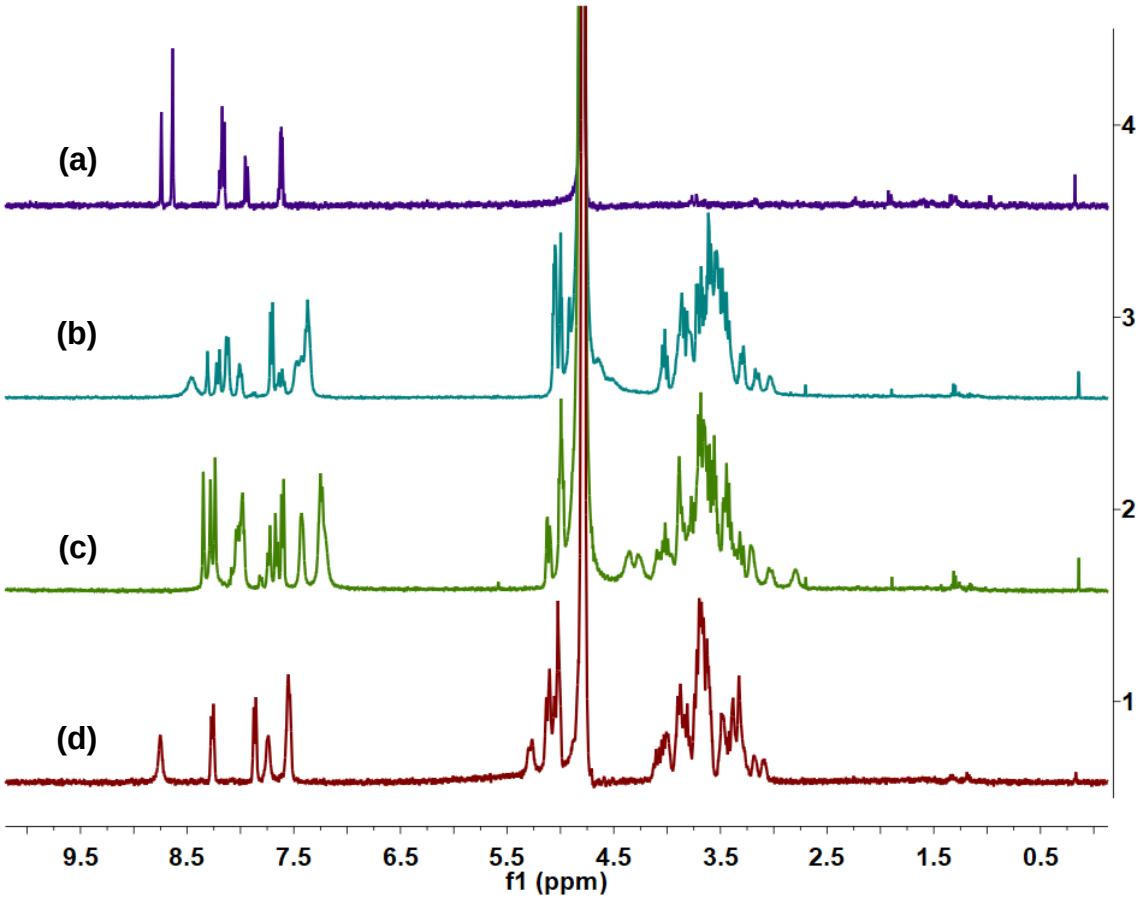


Figure S53a. ^{1}H NMR spectrum of (a) AC (0.4 mM) in D_2O (pD 9.0); (b) AC (0.2 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); (c) AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); and (d) **10** (3.0 mM) in D_2O (D_2O, 400 MHz, 25 ºC).

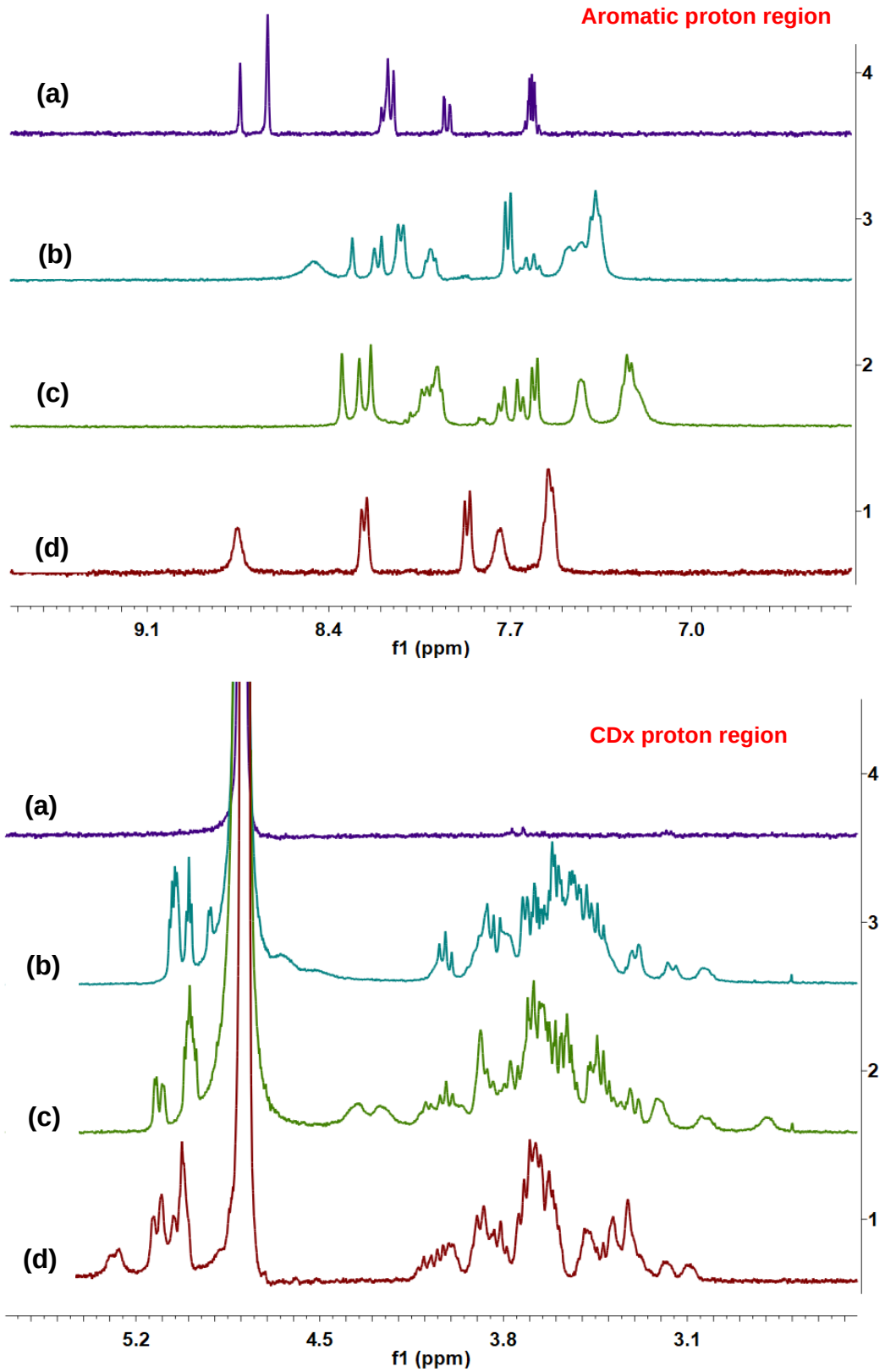
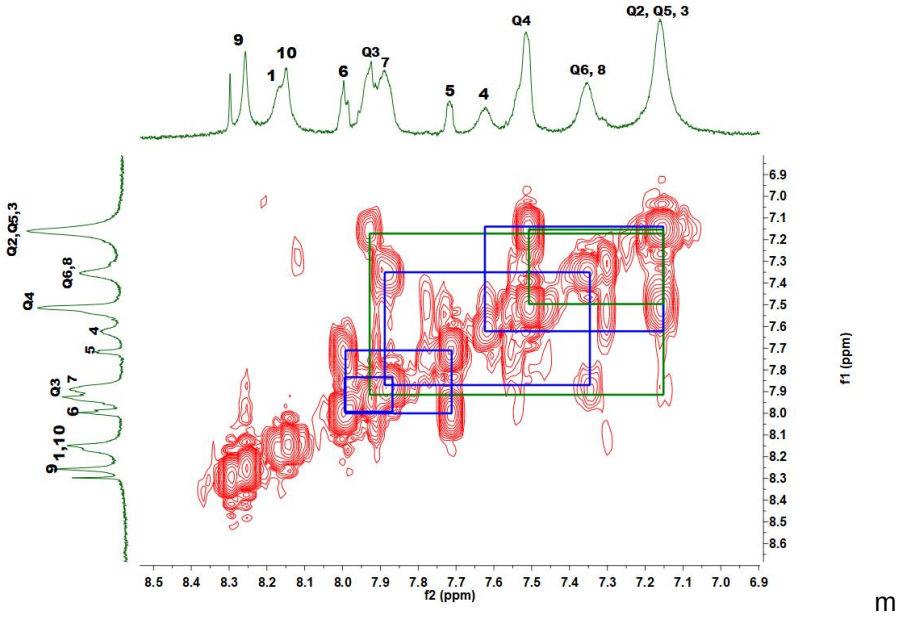


Figure S53b. ^{1}H NMR spectrum of (a) AC (0.4 mM) in D_2O (pD 9.0); (b) AC (0.2 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); (c) AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM); and (d) **10** (3.0 mM) in D_2O (D_2O, 400 MHz, 25 ºC).



m

Figure S54a. ^{1}H-^{1}H COSY spectrum of AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM) (D_2O, 700 MHz, 25 ºC).

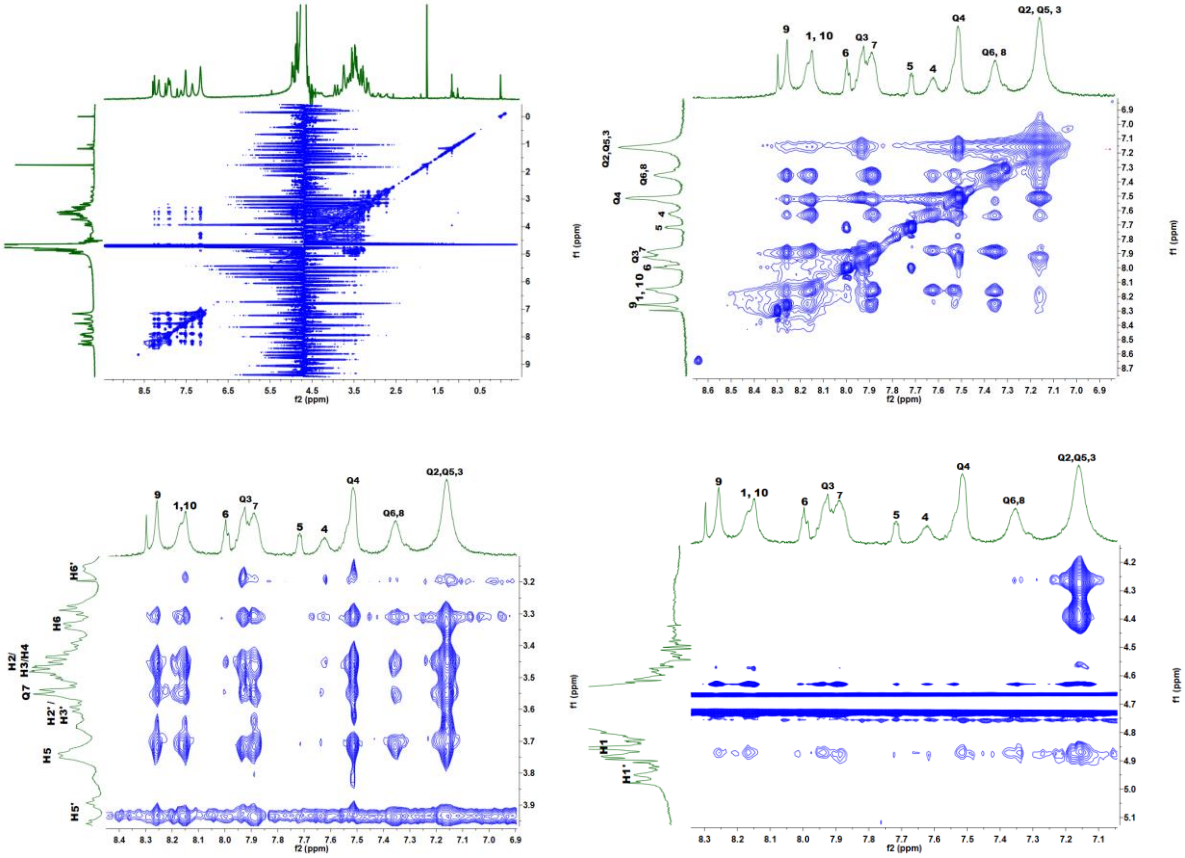


Figure S54b. NOESY spectrum of AC (0.4 mM) in D_2O (pD 6.0) in the presence of **10** (3.0 mM) (D_2O, 700 MHz, 25 ºC).

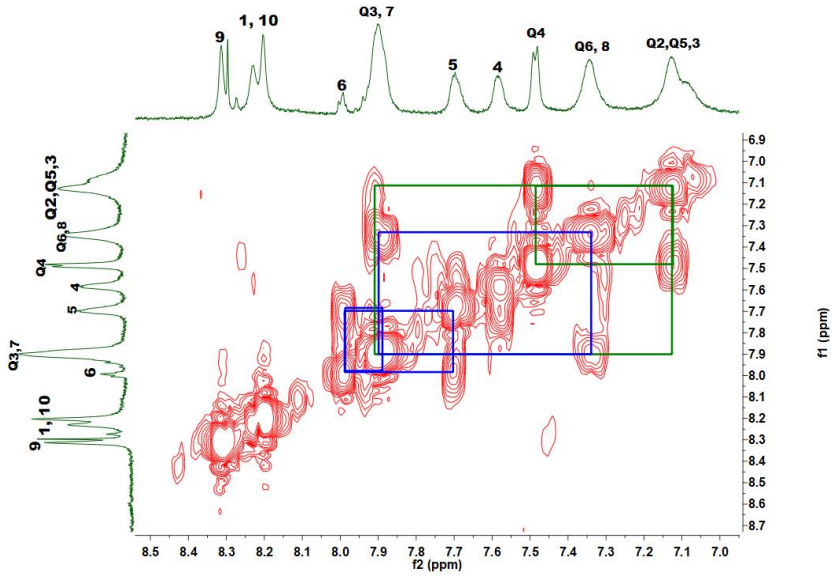


Figure S55a. ^{1}H-^{1}H COSY spectrum of AC (0.9 mM) in D_2O (pD 9.0) in the presence of **10** (3.0 mM) (D_2O, 400 MHz, 25 ºC).

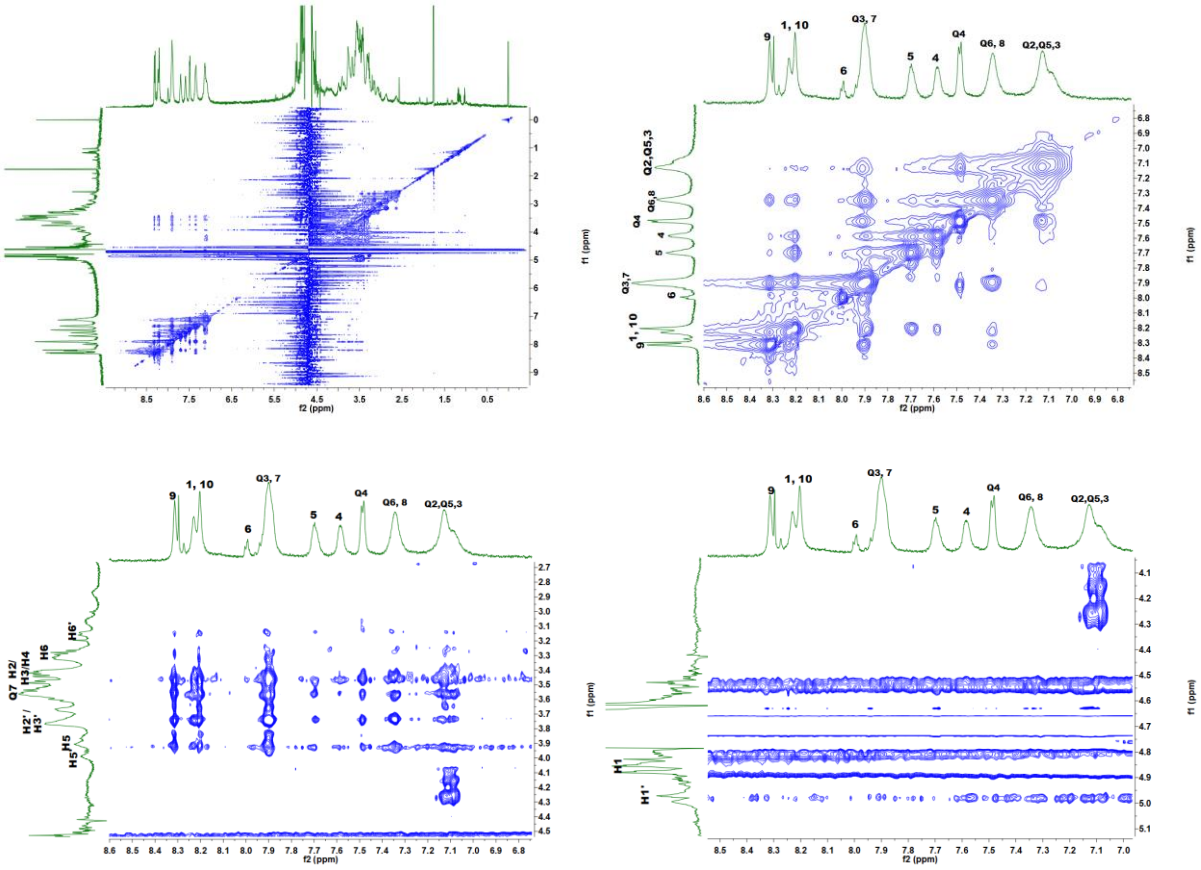
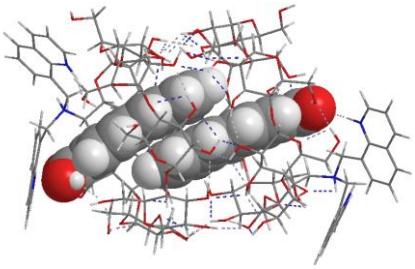


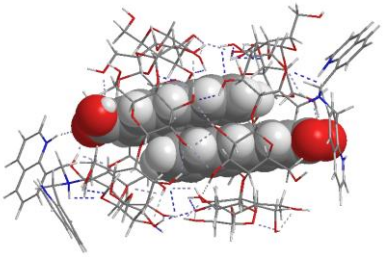
Figure S55b. NOESY spectrum of AC (0.9 mM) in D_2O (pD 9.0) in the presence of **10** (3.0 mM) (D_2O, 400 MHz, 25 ºC).

9. Theoretical calculation studies

pH1

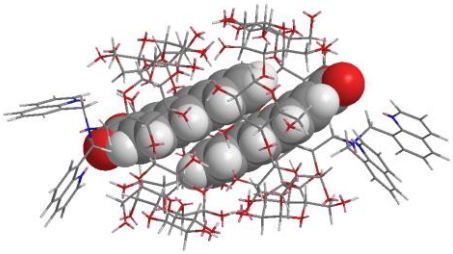


pro-**6**$_{+}$ / **6**$_{M}$ complex
E = 1568.2452 kJ mol^{-1}
ΔE = 0 kJ mol^{-1}

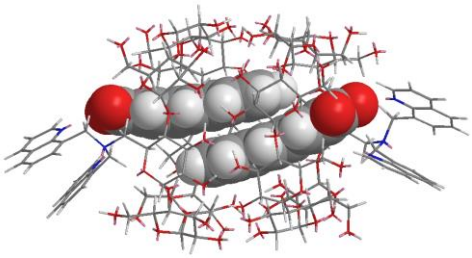


pro-**6**$_{-}$ / **6**$_{P}$ complex
E = 1589.9376 kJ mol^{-1}
ΔE = 21.6924 kJ mol^{-1}

pH9



pro-**6**$_{+}$ / **6**$_{M}$ complex
E = 287.8960 kJ mol^{-1}
ΔE = 66.2465 kJ mol^{-1}



pro-**6**$_{-}$ / **6**$_{P}$ complex
E = 221.6495 kJ mol^{-1}
ΔE = 0 kJ mol^{-1}

Figure S56. MM2-optimized structures and energies (E) of the stereoisomeric 2:2 complexes of AC with **BCD-QUI-2**, **10** at pH9 and pH1: at pH9 (a) *pro*-**6**$_{+}$ / **6**$_{M}$ and (b) *pro*-**6**$_{-}$ / **6**$_{P}$ and at pH1 (c) *pro*-**6**$_{+}$ / **6**$_{M}$ and (d) *pro*-**6**$_{-}$ / **6**$_{P}$, which are precursors to dimers (*M*)-**6** and (*P*)-**6**, respectively; ΔE: relative energy against at *pro*-**6**$_{+}$ / **6**$_{M}$ pH9. **Color code:** white for hydrogen, grey for carbon, red for oxygen, blue for nitrogen, dotted line for hydrogen bond. **Stability order complexes:** at pH1 *pro*-**6**$_{-}$ / **6**$_{P}$ complex < *pro*-**6**$_{+}$ / **6**$_{M}$ complex and at pH9 *pro*-**6**$_{+}$ / **6**$_{M}$ complex < *pro*-**6**$_{-}$ / **6**$_{P}$ complex.

10. References

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