Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Photochemical and computational studies of inclusion complexes between β-cyclodextrin and 1,2-dihydroxyanthraquinones

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Scheme S1. Chemical structure of 1,2-DHAQ

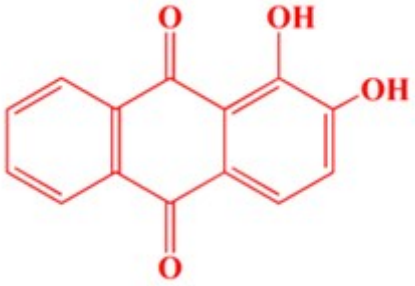


Table S1. Various prototropic maxima in (absorption and fluorescence) pKa and pKa* values of 1,2-DHAQ in aqueous and β-CD medium.

Species	Aqueous medium			β-CD medium		
	λ_{abs} (nm)	log ε	λ_{flu} (nm)	λ_{abs} (nm)	log ε	λ_{flu} (nm)
Neutral	434.0	3.43	516.5	435.0	3.67	517.5
	283.0	3.46	472.0	285.0	3.82	473.0
	243.0	3.49		245.0	3.94	
Monoanion	531.0	3.52	564.5	534.0	4.02	566.0
	328.0	3.56	516.0	329.0	4.29	517.0
	260.0	3.98		262.5	4.52	
Dianion	608.0	3.51	633.5	610.0	4.15	628.0
	562.5	3.62	510.2	566.0	4.24	514.5
	327.5	3.87		328.0	4.48	
	266.0	3.95		268.0	4.63	
Neutral f Monoanion pKa and pKa* (FT)	5.7		5.7	6.5		6.5
Monoanion f Dianion pKa and pKa* (FT)	9.2		9.4	10.1		10.2

FT – Fluorescence titration

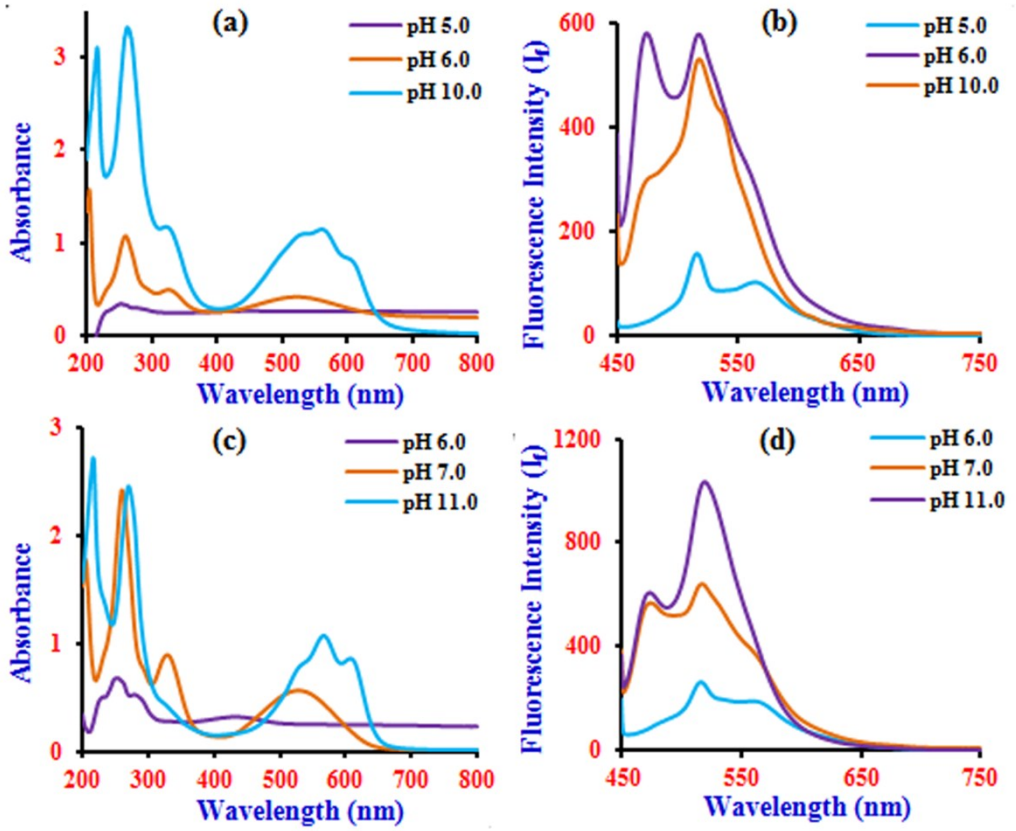


Figure S1. Absorption and fluorescence spectra in various prototropic species of 1,2-DHAQ (1 x10^{-4} M) at 303K; (a and b) aqueous and (c and d) β-CD medium (12 x10^{-3} M).

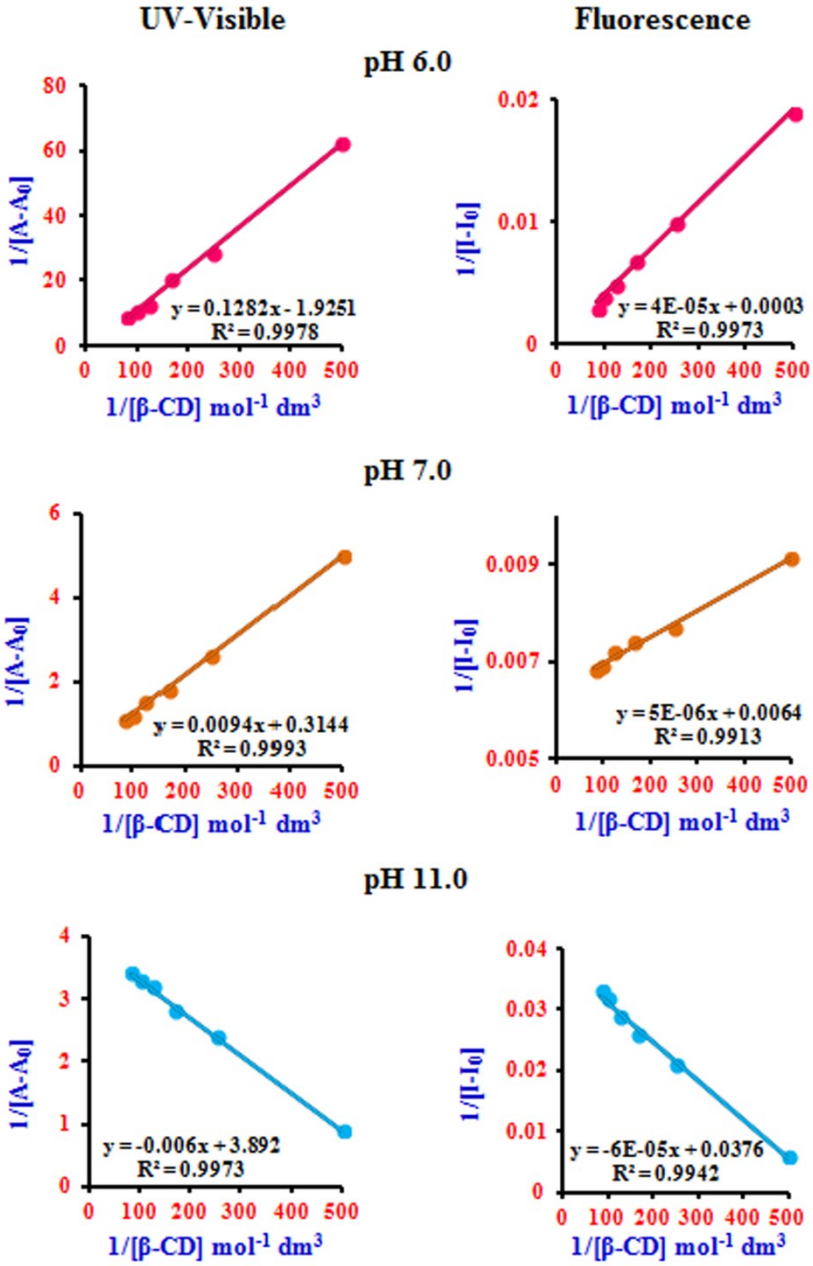


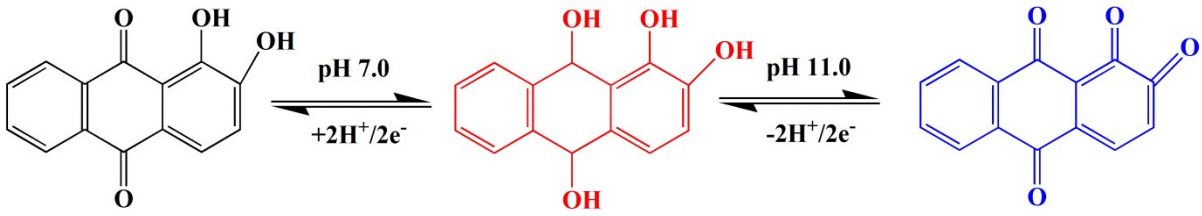
Figure S2. Benesi-Hildebrand plot of $1/[A-A_0]$ vs. $1/[\beta\text{-CD}]$ and $1/[I-I_0]$ vs. $1/[\beta\text{-CD}]$.

Table S2. Absorption and fluorescence maxima of 1,2-DHAQ at different concentrations of β-CD in pH 6.0, 7.0 and 11.0 solutions.

S.No.	Conc. of β-CD (M)	pH 6.0			pH 7.0			pH 11.0		
		λ_{abs} (nm)	log ε	λ_{flu} (nm)	λ_{abs} (nm)	log ε	λ_{flu} (nm)	λ_{abs} (nm)	log ε	λ_{flu} (nm)
1	0.000	434.0	3.41	516.5	531.0	3.37	564.5	608.0	3.87	633.5
		283.0	3.47	472.0	328.0	3.58	516.0	562.5	4.05	
		243.0	3.48		260.0	4.02		327.5	4.04	
								266.0	4.55	
2	0.002	435.0	3.46	516.5	534.0	3.77	566.0	608.5	3.82	633.0
		285.0	3.56	472.0	329.0	3.94	517.0	563.0	3.97	
		245.0	3.64		262.5	4.38		328.0	3.98	
								268.0	4.48	
3	0.004	435.0	3.47	516.5	534.0	3.82	566.0	608.5	3.73	631.0
		285.0	3.61	472.0	329.0	3.97	517.0	563.5	3.89	
		245.0	3.68		262.5	4.40		328.0	3.90	
								268.0	4.39	
4	0.006	435.0	3.50	516.5	534.0	3.91	566.0	609.0	3.72	630.5
		285.0	3.66	472.0	329.0	4.12	517.0	564.0	3.86	
		245.0	3.71		262.5	4.52		328.0	3.82	
								268.0	4.33	
5	0.008	435.0	3.51	516.5	534.0	3.92	566.0	609.0	3.71	629.0
		285.0	3.73	472.0	329.0	4.15	517.0	565.0	3.84	
		245.0	3.80		262.5	4.57		328.0	3.77	
								268.0	4.29	
6	0.010	435.0	3.52	516.5	534.5	3.93	566.0	609.5	3.65	628.5
		285.0	3.75	472.0	329.0	4.15	517.0	566.0	3.75	
		245.0	3.86		262.5	4.58		328.0	3.61	
								268.0	4.17	
7	0.012	435.0	3.56	516.5	534.5	3.94	566.0	610.0	3.45	628.0
		285.0	3.77	472.0	329.0	4.16	517.0	566.0	3.66	
		245.0	3.89		262.5	4.60		328.0	3.59	
								268.0	4.17	
Binding constant (M^{-1})		72.3		84.7	161.7		129.0	192.0		203.1
ΔG (kJ mol^{-1})		-10.7		-11.1	-12.8		-12.2	-13.2		-13.3

Table S3. Cyclic voltammetric study of 1,2-DHAQ at different concentrations of β-CD in pH 6.0, 7.0 and 11.0 buffer solutions. 1,2-DHAQ (1 x10^{-5} M); β-CD (12 x10^{-3} M). Scan rate 100 mVs^{-1}.

Buffers	Conc. of β-CD (M)	Epa (V)	Ipa (μA)	Epc (V)	Ipc (μA)	Epa - Epc /2mV
pH 6.0	0.000	0.121	9.14E-06	-1.102	-1.19E-05	611.6
	0.002	0.133	8.98E-06	-1.092	-1.22E-05	612.7
	0.004	0.148	8.84E-06	-1.083	-1.19E-05	610.5
	0.006	0.189	9.01E-06	-1.069	-1.14E-05	604.2
	0.008	0.196	9.03E-06	-1.055	-1.36E-05	610.9
	0.010	0.197	9.47E-06	-1.036	-1.28E-05	616.6
	0.012	0.199	9.95E-06	-1.031	-1.25E-05	615.3
	Binding constant (M^{-1})		34.71		59.34	
pH 7.0	0.000	0.123	8.03E-06	-0.921	-1.18E-05	522.4
	0.002	0.120	7.79E-06	-0.921	-1.18E-05	513.9
	0.004	0.118	7.71E-06	-0.921	-1.16E-05	511.5
	0.006	0.115	7.59E-06	-0.921	-1.13E-05	505.3
	0.008	0.113	6.93E-06	-0.921	-1.11E-05	512.7
	0.010	0.111	6.49E-06	-0.922	-1.08E-05	515.1
	0.012	0.110	6.35E-06	-0.922	-1.07E-05	517.6
	Binding constant (M^{-1})		80.21		40.37	
pH 11.0	0.000	0.101	5.32E-06	-0.943	-9.23E-06	522.4
	0.002	0.106	4.88E-06	-0.926	-9.2E-06	516.3
	0.004	0.108	4.54E-06	-0.916	-8.88E-06	512.6
	0.006	0.111	4.51E-06	-0.889	-8.58E-06	500.5
	0.008	0.113	4.49E-06	-0.884	-8.34E-06	499.2
	0.010	0.114	4.44E-06	-0.879	-8.01E-06	497.0
	0.012	0.114	4.38E-06	-0.867	-7.77E-06	489.5
	Binding constant (M^{-1})		373.64		110.27	



Scheme S2. Possible oxidation and reduction processes

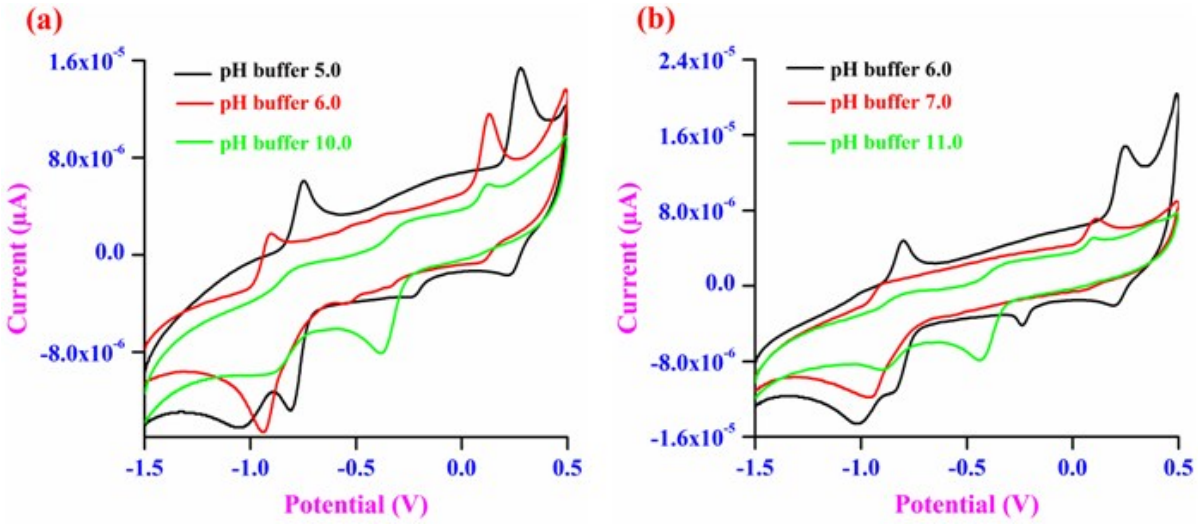


Figure S3. Cyclic Voltammetric study of 1,2-DHAQ (1 x10^{-5} M) in different pH buffers at 303K; (a) aqueous and (b) β-CD (12 x10^{-3} M) medium.

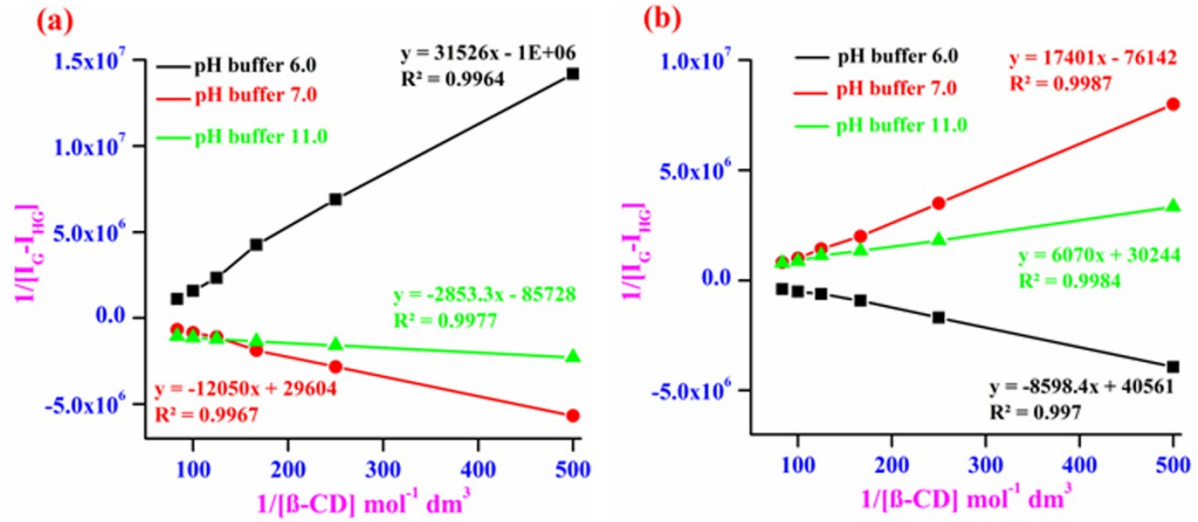


Figure S4. Benesi–Hildebrand plot of (a) oxidation and (b) reduction peak current at pH 6.0, pH 7.0 and pH 11.0 buffers in $1/[I_G-I_{HG}]$ vs. $1/[\beta\text{-CD}]$.

Table S4. ^{1}H NMR chemical shifts of β-CD in free and complexed β-CD:1,2-DHAQ state determined in D_2O at 303 K.

Protons	β-CD δ (ppm)	β-CD: 1,2-DHAQ δ (ppm)	Δδ	Protons	1,2-DHAQ δ (ppm)	β-CD: 1,2-DHAQ δ (ppm)	Δδ
H_1	4.966	4.812	-0.154	H_a	5.002	4.882	-0.120
H_2	3.624	3.281	-0.343	H_b	5.014	4.899	-0.115
H_3	3.977	3.894	-0.083	H_c	6.632	6.392	-0.240
H_4	3.612	2.723	-0.889	H_d	7.124	6.752	0.372
H_5	3.845	3.495	-0.350	H_e	7.512	7.102	- 0.410
H_6	3.897	3.762	-0.135	H_f	7.534	7.157	-0.377
				H_g	7.865	7.412	-0.453
				H_h	7.889	7.459	-0.430

Table S5. Computed using PatchDock and FireDock servers scores of the top 10 docked models of β-CD:1,2-DHAQ inclusion complex.

S.No.	Patchdock server			FireDock server			
	Score[a]	Area[b] (Å^2)	ACE[c] kcal/mol	Global Energy[d] kcal/mol	Attractive VdW[e] kcal/mol	Repulsive VdW[e] kcal/mol	ACE[f] kcal/mol
1	3002	361.70	-272.86	-44.75	-16.94	2.62	-13.56
2	2956	364.70	-266.90	-42.81	-16.85	4.62	-13.33
3	2952	362.10	-260.88	-42.64	-16.61	3.75	-13.00
4	2926	353.00	-264.15	-42.47	-16.07	2.20	-12.68
5	2888	352.20	-265.34	-42.37	-16.47	3.59	-12.98
6	2842	355.50	-268.71	-41.04	-16.48	4.48	-13.07
7	2746	295.00	-262.52	-40.72	-16.08	4.29	-12.98
8	2724	287.40	-254.45	-40.34	-15.72	2.92	-12.56
9	2718	347.90	-260.98	-39.34	-16.09	4.06	-11.85
10	2588	324.90	-209.39	-39.16	-16.15	4.33	-11.98

[a]Geometric shape complementarity score
[b]Approximate interface area size of the complex
[c]Atomic contact energy
[d]Indicating binding energy of the solution.
[e]Representing contribution of the van der Waals forces to the global binding energy.
[f]ACE shows contribution of the atomic contact energy (ACE) to the global binding energy.

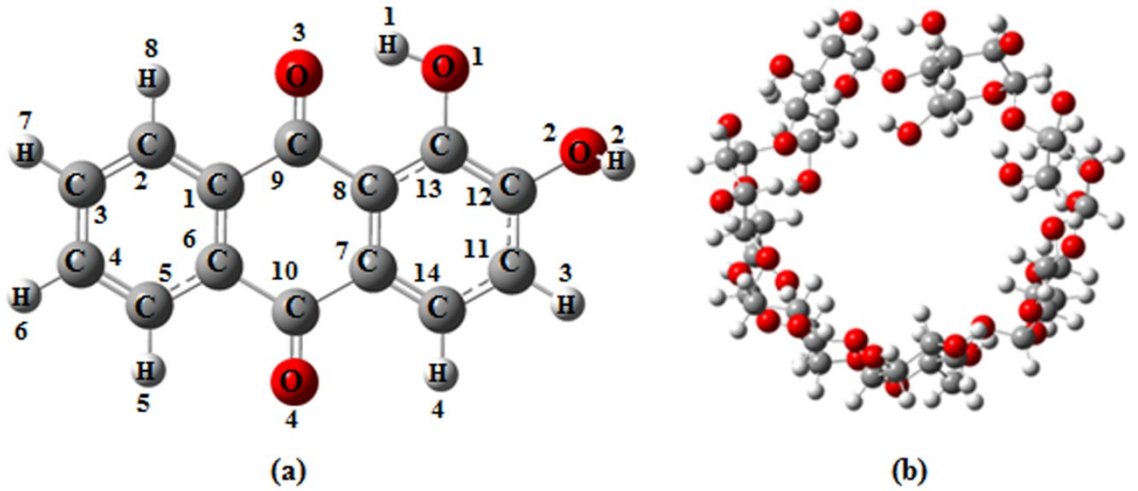


Figure S5. The optimized structure of (a) 1,2-DHAQ and (b) β-CD. The O, C, H atoms are shown as red, grey and white balls.

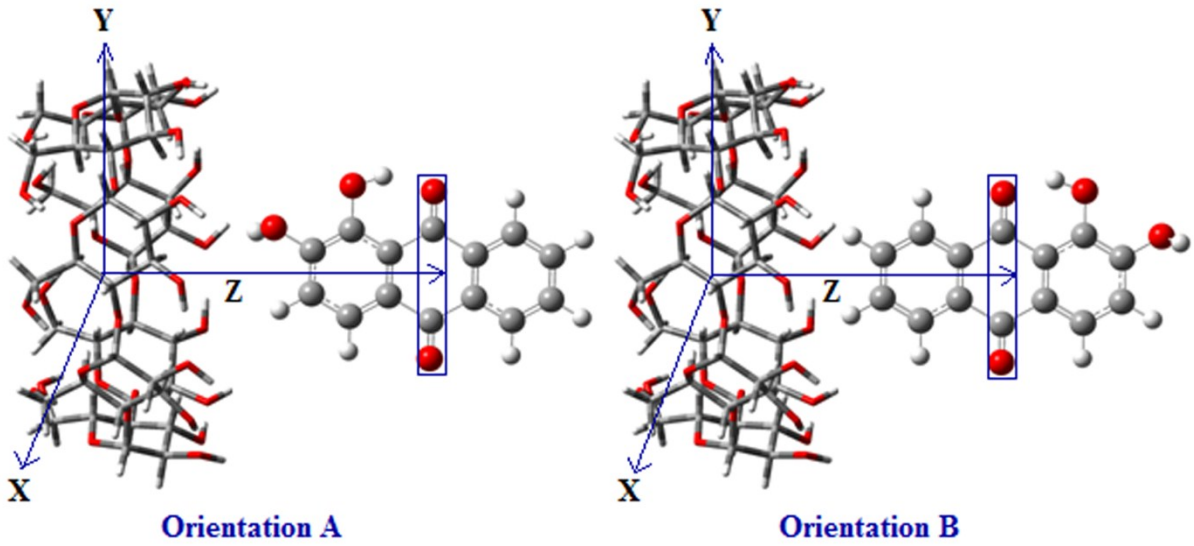


Figure S6. The coordinate systems used to define the process complexation for A and B orientations of β-CD:1,2-DHAQ. The O, C, H atoms are shown as red, grey and white balls and sticks.

Table S6. Selected bond distances (Å), bond angles (°) and dihedral angles (°) in 1,2-DHAQ and β-CD:1,2-DHAQ orientations A and B.

Properties	1,2-DHAQ	β-CD:1,2-DHAQ (A)	β-CD:1,2-DHAQ (B)
Bond distances (Å)			
C3-C4	1.38	1.35	1.33
C3-H1	5.86	5.55	5.79
C3-H2	9.26	8.70	8.47
C3-O1	6.61	6.37	6.35
C3-O2	8.71	8.61	8.48
C3-O3	4.22	4.25	4.25
C4-O4	4.22	4.28	4.26
Bond angles (°)			
C3-C4-O4	117.9	116.3	117.5
C3-O2-H2	121.0	91.2	86.5
C3-H1-O1	136.0	134.8	115.8
C4-C3-O3	117.9	116.6	116.9
C4-C3-O2	94.6	94.9	95.0
C4-C3-O1	108.5	108.7	109.0
C4-C3-H1	114.5	115.6	115.0
C4-C3-H2	93.0	100.7	102.4
Dihedral angles (°)			
C4-C3-O2-H2	108.2	143.1	-172.0
O3-C3-O2-H2	106.9	1.2	-33.7
O1-C3-O2-H2	106.2	102.6	169.9
H1-C3-O2-H2	106.3	-41.3	-17.5
C4-C3-O1-H1	-178.7	173.5	-133.8
O3-C3-O1-H1	-176.6	-104.3	151.1
O2-C3-O1-H1	179.5	162.4	-147.4
H2-C3-O1-H1	-162.0	131.7	-152.6

Table S7. Binding energies, HOMO-LUMO band-gap and calculated chemical properties of 1,2-DHAQ before and after β-CD complexation by PM3 method.

Properties	1,2-DHAQ	β-CD	β-CD: 1,2-DHAQ (A)	β-CD: 1,2-DHAQ(B)
E* ($kcalmol^{-1}$)	-86.29	-1458.32	-1568.09	-1557.10
ΔE* ($kcalmol^{-1}$)			-23.48	-12.49
Dipole moment (D)	2.61	7.03	8.05	7.16
E_{HOMO} (eV)	-9.37	-4.83	-9.07	-9.13
E_{LUMO} (eV)	-1.17	-1.53	-1.10	-1.35
μ (eV)	-5.27	-3.18	-5.08	-5.24
η (eV)	-4.10	-1.64	-3.98	-3.89
S (eV)	-0.24	-0.60	-0.25	-0.25
ω (eV)	-3.38	-3.08	-3.23	-3.52