Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Host-Guest Interactions Induced Emission Enhancement of Amphiphilic AIEgens: A Computational Study

Junfang Yang,[a] Qian Peng,[b] Ruide Xue,[c] Zesheng Li,[a] Xiaoyan Zheng*[a]

[a]Key Laboratory of Cluster Science of Ministry of Education, Beijing Key laboratory of Photoelectronic/Electro-photonic Conversion Materials, School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing, 100081, China.

[b]b. School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing, 100049, P. R. China.

[c]Shanxi Recycle Environmental Protection Technology Company Limited, ShanXi, 030500, China.

E-mail: xiaoyanzheng@bit.edu.cn

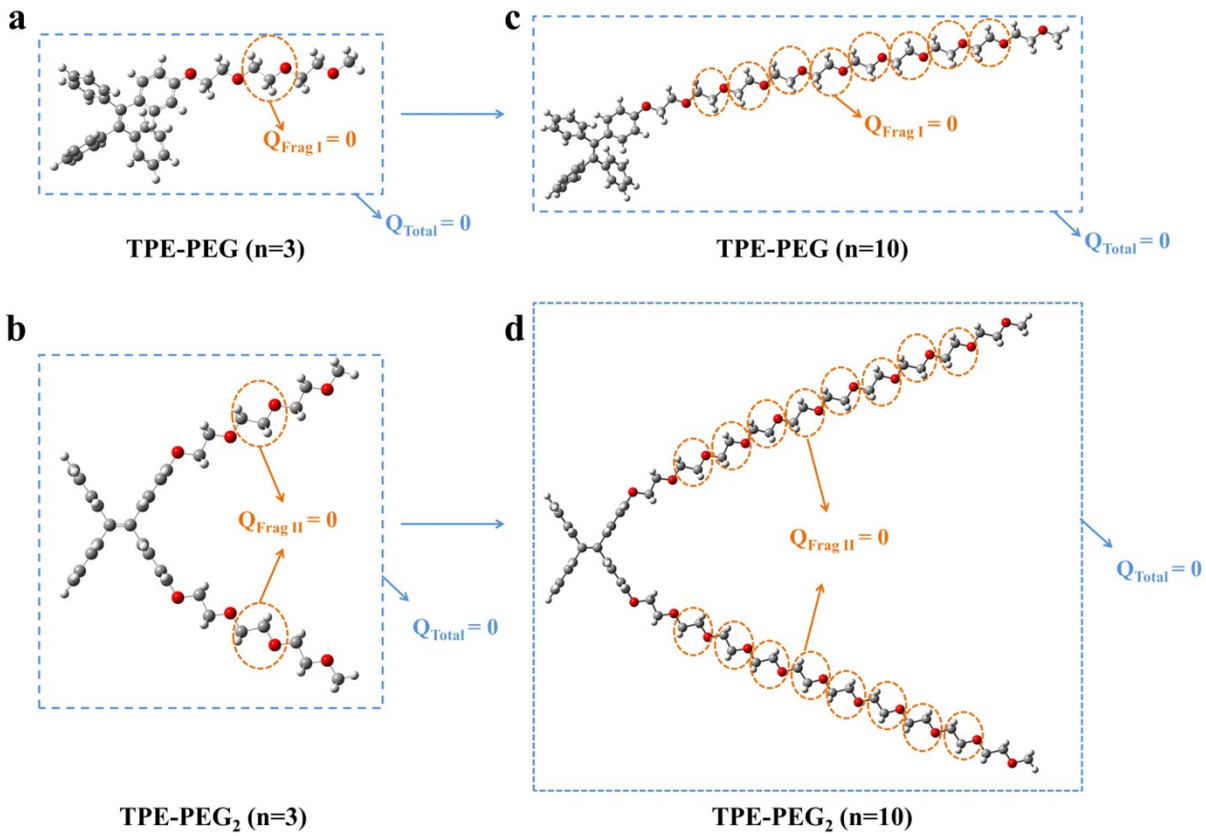

Fig. S1. The optimized structures of TPE-PEG and TPE-PEG$_2$ to obtain the partial charges of modeled guest molecules (G-1, G-2 and G-3) by using restrained electrostatic potential (RESP) fit method.

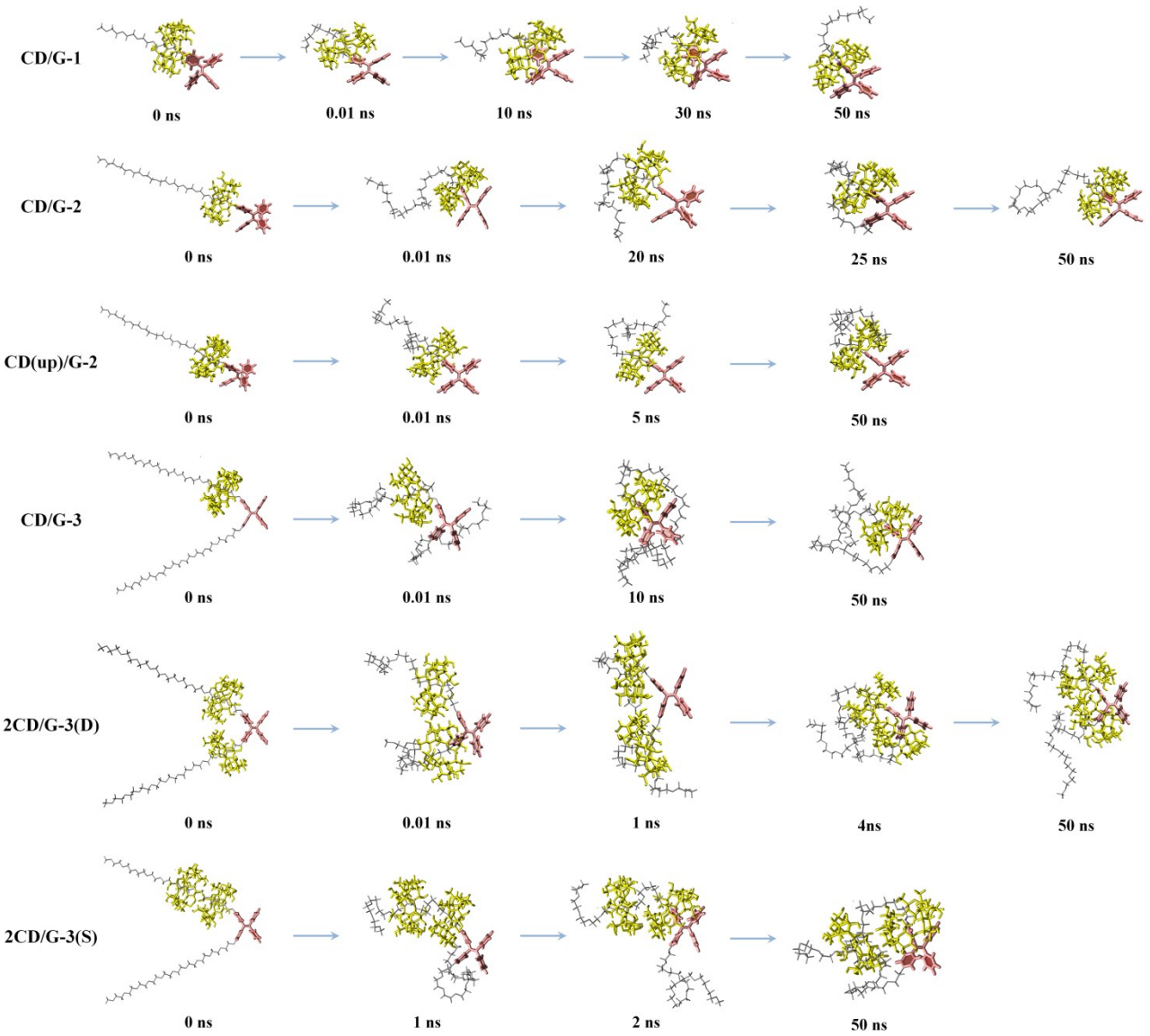

Fig. S2. Snapshots of the crucial phases in the progress of self-assembly between CD and guest molecules as a function of time during the MD simulations.

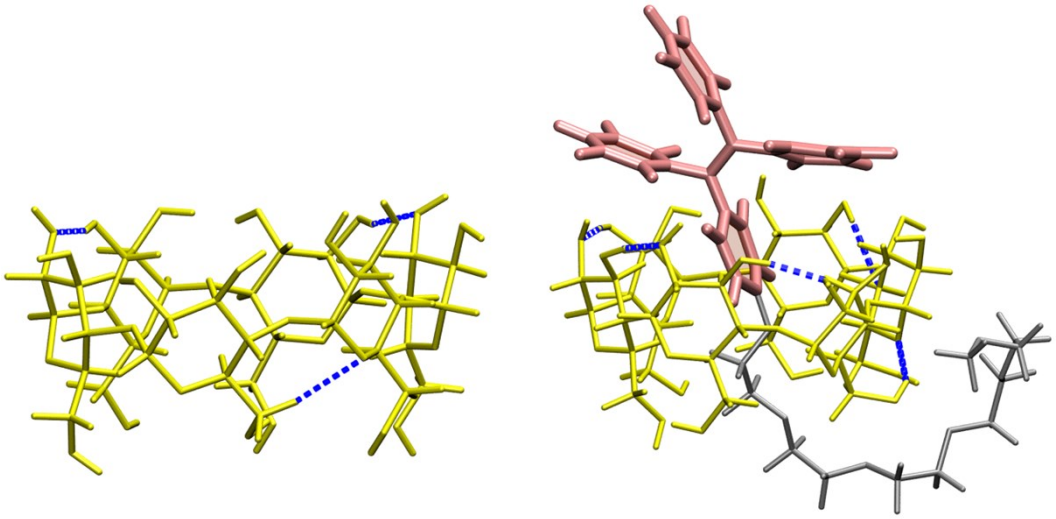

Fig. S3. The intramolecular H-bonds of free CD (left) and CD/G-1 host-guest inclusion (right), remarked by dashed blue line.

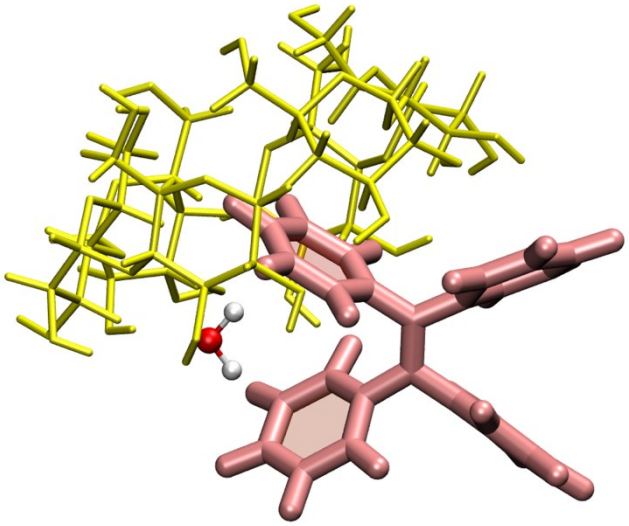

Fig. S4. Representative configuration of CD/TPE and one embedded water is shown in the cavity of CD.

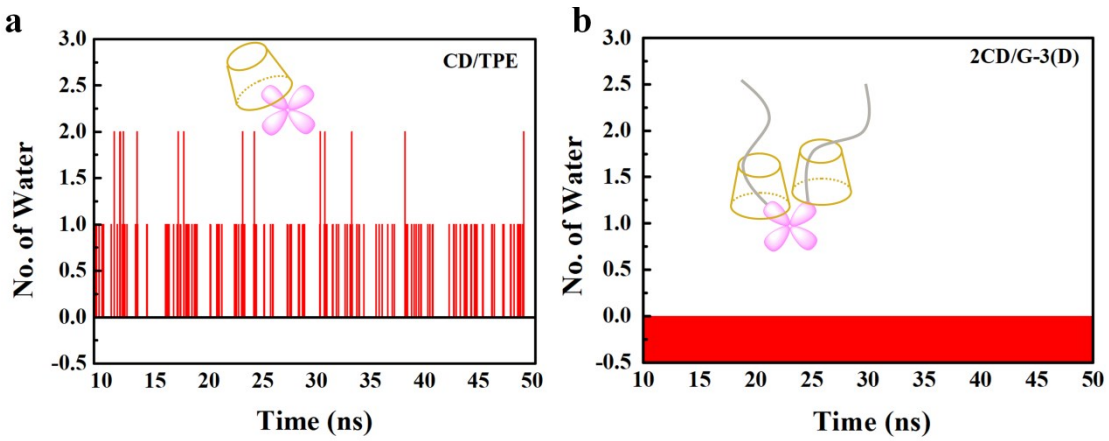

Fig. S5. Evolution of embedded water numbers in the cavity of CD in (a) CD/TPE inclusion and (b) 2CD/G-3(D) as a function of simulation time. CD/TPE is modelled system for comparison.

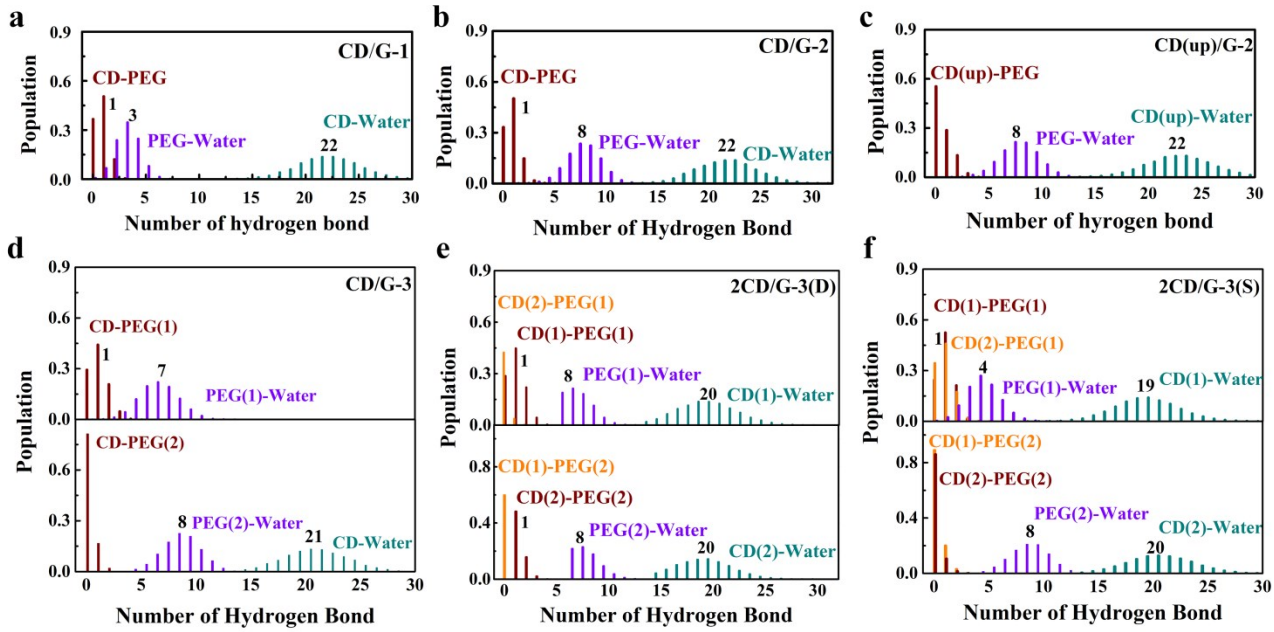

Fig. S6. Distributions of intermolecular H-bonds for six studied host-guest inclusions: (a) CD/G-1, (b) CD/G-2, (c) CD(up)/G-2, (d) CD/G-3, (e) 2CD/G-3(D) and (f) 2CD/G-3(S), respectively.

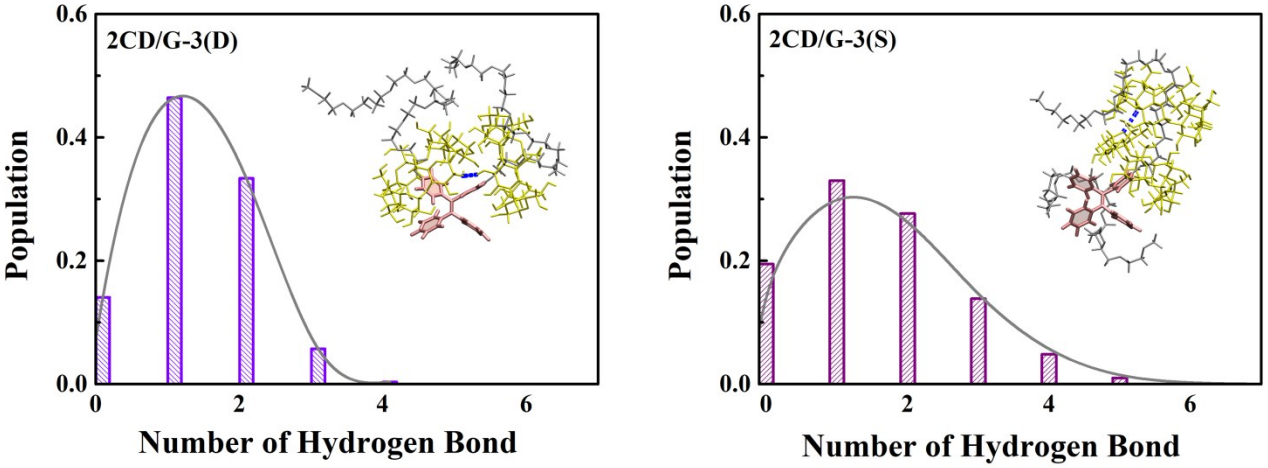

Fig. S7. The population of intermolecular H-bonds of neighboring two CDs in 2CD/G-3(D) (left) and 2CD/G-3(S) (right) inclusions. The representative snapshots of 2CD/G-3(D) and 2CD/G-3(S) were shown in the inset.

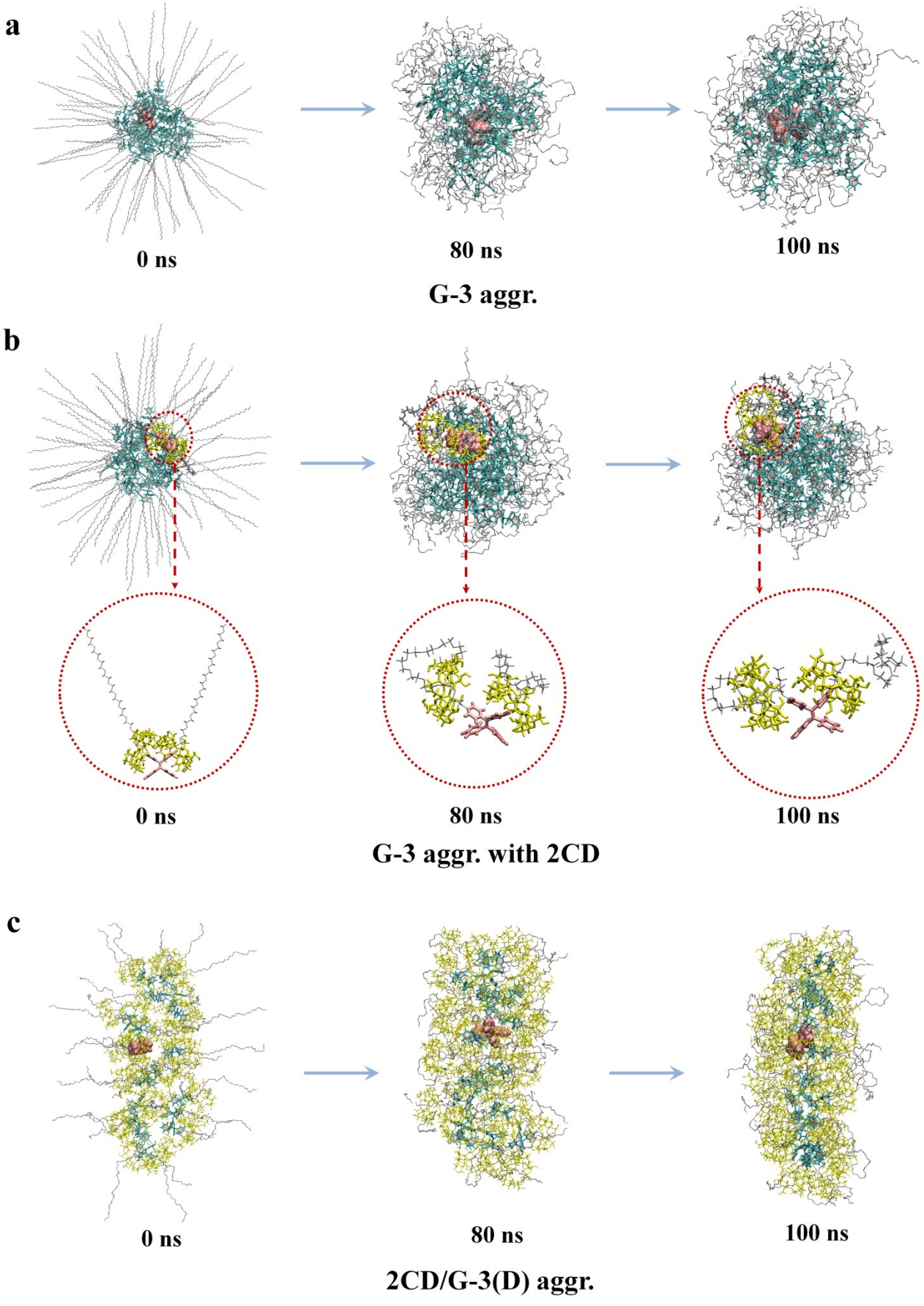

Fig. S8. Snapshots of the crucial phases in the progress of assembly of (a) G-3 aggregate, (b) G-3 aggregate with 2CD and (c) 2CD/G-3(D) aggregate as a function of time during the MD simulations.

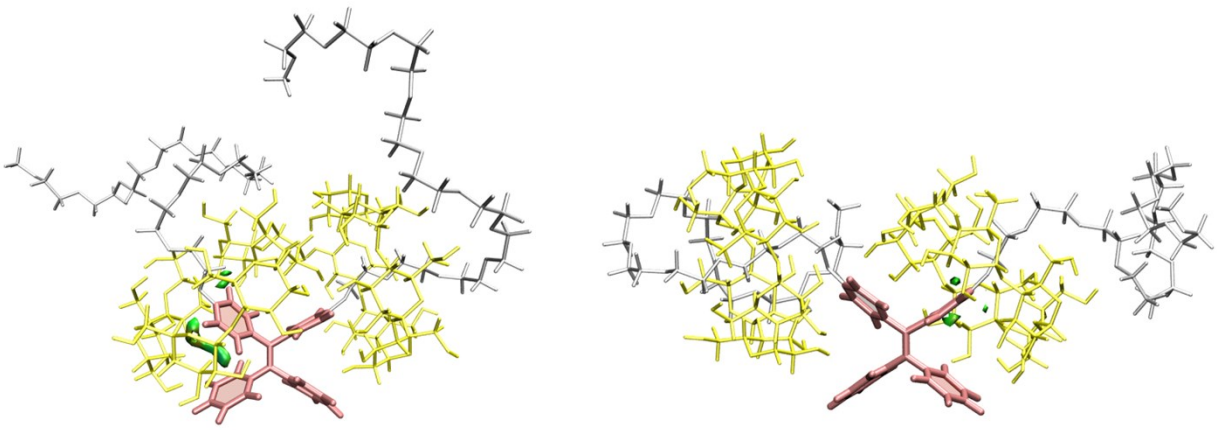

Fig. S9. The Independent Gradient Model (IGM) analysis for 2CD/G-3(D) (left) and one molecule with CD in G-3 aggregate with 2CD (right).

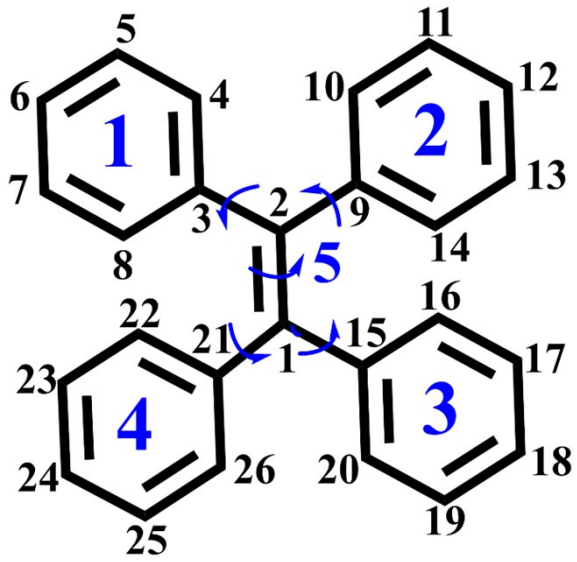

Chart S1. Chemical Structure of QM region of the representative monomers: G-2, G-3, 2CD/G-3(D), and assembled aggregates: G-3 aggregate, G-3 aggregate with 2CD and 2CD/G-3(D) aggregate.

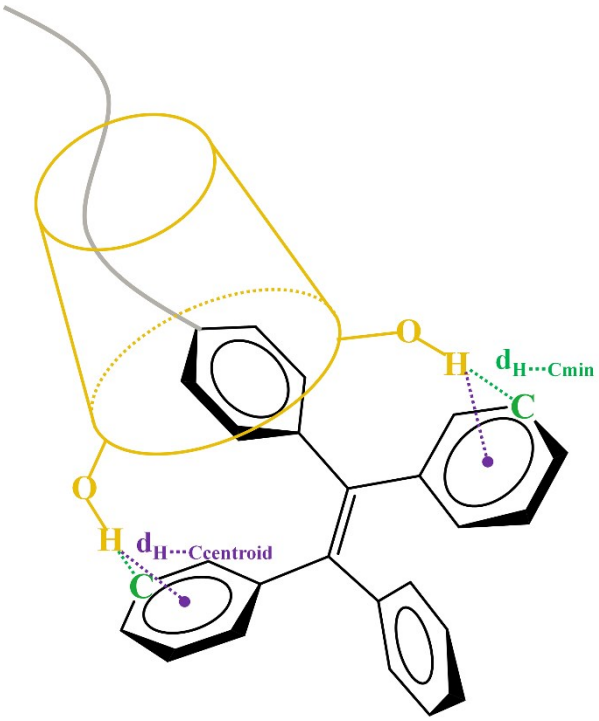

Chart S2. Definitions of distances measured in O−H···π interactions: $d_{H\cdots Cmin}$ = distance between the hydroxyl group of CD and the nearest aromatic carbon ($H_{hydroxyl}\cdots C_{aromatic}$ distance) at 2- or 4-position of TPE moiety of guests in host-guest inclusions (dashed green line); $d_{H\cdots Ccentroid}$ = distance between the hydroxyl group of CD and the centroid of the phenyl ring of TPE moiety of guests in host-guest inclusions (dashed purple line).

Table S1. Distances $d_{H\cdots Cmin}$ and $d_{H\cdots Ccentroid}$ measured in O−H$\cdots\pi$ interactions at 2- and 4-position of TPE moiety for CD/G-1, CD/G-2, CD(up)/G-2, CD/G-3, 2CD/G-3(D) and 2CD/G-3(S), respectively. The cutoff distance for O−H$\cdots\pi$ interactions are $d_{H\cdots Cmin}$ < 2.90 Å and $d_{H\cdots Ccentroid}$ < 3.60 Å, respectively. Distance larger than cutoff distance is marked in orange.

		$\mathbf{d_{H\cdots Cmin}}$(Å)	$\mathbf{d_{H\cdots Ccentroid}}$ (Å)
CD/G-1	2-position	2.187	2.760
	4-position	2.851	3.974
CD/G-2	2-position	2.433	2.502
	4-position	2.966	4.056
CD(up)/G-2	2-position	2.986	3.208
	4-position	3.972	4.735
CD/G-3	2-position	2.895	3.524
	4-position	2.080	2.876
2CD/G-3(D)	2-position	2.321	2.985
	4-position	2.548	3.266
2CD/G-3(S)	2-position	2.040	2.865
	4-position	2.511	3.049

Table S2. Calculated vertical excitation energy (VEE), electronic dipole moment (EDM), oscillator strength (*f*) and the assignment for S_1 of TPE and radiative decay rate constant (k_r).

S_1	VEE	EDM	f	assignment	k_r
G-2	2.02 eV (613 nm)	5.21 D	0.2081	HOMO → LUMO (98.0%)	3.70×10^7
G-3	2.06 eV (603 nm)	5.22 D	0.2124	HOMO → LUMO (97.8%)	3.90×10^7
2CD/G-3(D)	2.82 eV (439 nm)	4.64 D	0.2312	HOMO → LUMO (97.7%)	7.99×10^7
G-3 aggr.	2.73 eV (454 nm)	5.22 D	0.2824	HOMO → LUMO (99.4%)	9.14×10^7
G-3 aggr. with 2CD	3.50 eV (354 nm)	5.07 D	0.3409	HOMO → LUMO (98.0%)	1.81×10^8
2CD/G-3(D) aggr.	3.31 eV (375 nm)	4.19 D	0.2201	HOMO → LUMO (98.1%)	9.56×10^7

Table S3. The extracted key dihedral angles (in degree) of three monomers: G-2, G-3, 2CD/G-3(D) and three nanoaggregates: G-3 aggregate, G-3 aggregate with 2CD and 2CD/G-3(D) aggregate, respectively. S_0/S_1 and $|S_0-S_1|$ represent the geometric parameters extracted from the ground/excited states and the difference between them, respectively.

	G-2			G-3			2CD/G-3(D)			G-3 aggr.			G-3 aggr. with 2CD			2CD/G-3 aggr.		
	S_0	S_1	$\|S_0-S_1\|$	S_0	S_1	$\|S_0-S_1\|$	S_0	S_1	$\|S_0-S_1\|$	S_0	S_1	$\|S_0-S_1\|$	S_0	S_1	$\|S_0-S_1\|$	S_0	S_1	$\|S_0-S_1\|$
1-	134.8	153.2	**18.3**	136.0	152.8	**16.8**	102.8	104.0	**1.2**	125.3	148.1	**22.8**	77.8	62.5	**15.3**	82.6	62.7	**19.9**
2-	133.9	151.1	**17.2**	134.9	150.5	**16.6**	134.5	154.0	**19.5**	60.5	52.3	**8.2**	102.6	137.0	**34.4**	90.7	137.5	**46.8**
3-	47.5	23.2	**24.3**	47.5	24.0	**23.5**	60.7	26.1	**34.6**	127.7	140.9	**13.2**	78.9	89.7	**10.8**	69.4	25.5	**43.9**
4-	47.5	21.5	**26.0**	47.1	21.1	**26.0**	46.6	40.8	**5.8**	129.4	142.2	**12.8**	136.9	167.9	**31.0**	75.1	81.3	**6.2**
5-	170.2	129.0	**41.2**	168.5	130.0	**38.5**	3.6	20.5	**16.9**	175.2	145.5	**29.7**	178.8	179.9	**1.1**	2.6	28.2	**25.6**

Table S4. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of G-2 at S_0 (S_1) minimum and the difference between S_0 and S_1

structural parameters		G-2		
		S_0	S_1	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.354	1.465	0.111
	C_2-C_3	1.489	1.440	0.049
	C_2-C_9	1.491	1.447	0.044
	C_1-C_{15}	1.491	1.445	0.046
	C_1-C_{21}	1.491	1.444	0.047
bond angle				
	C_1-C_2-C_3	122.7	118.8	3.8
	C_1-C_2-C_9	122.4	118.4	4.0
	C_2-C_1-C_{15}	122.5	118.4	4.1
	C_2-C_1-C_{21}	122.6	118.8	3.8
dihedral angle				
1-	C_1-C_2-C_3-C_4	134.8	153.2	18.3
2-	C_1-C_2-C_9-C_{10}	133.9	151.1	17.2
3-	C_2-C_1-C_{15}-C_{16}	47.5	23.2	24.3
4-	C_2-C_1-C_{21}-C_{22}	47.5	21.5	26.0
5-	C_3-C_2-C_1-C_{15}	170.2	129.0	41.2

Table S5. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of G-3 at S_0 (S_1) minimum and the difference between S_0 and S_1

	structural parameters	G-3		
		S_0	S_1	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.355	1.465	0.110
	C_2-C_3	1.489	1.441	0.048
	C_2-C_9	1.489	1.446	0.043
	C_1-C_{15}	1.491	1.446	0.045
	C_1-C_{21}	1.490	1.443	0.047
bond angle				
	C_1-C_2-C_3	122.5	119.1	3.4
	C_1-C_2-C_9	122.4	118.4	4.0
	C_2-C_1-C_{15}	122.6	118.4	4.2
	C_2-C_1-C_{21}	122.5	118.9	3.6
dihedral angle				
1-	C_1-C_2-C_3-C_4	136.0	152.8	16.8
2-	C_1-C_2-C_9-C_{10}	134.9	150.5	16.6
3-	C_2-C_1-C_{15}-C_{16}	47.5	24.0	23.5
4-	C_2-C_1-C_{21}-C_{22}	47.1	21.1	26.0
5-	C_3-C_2-C_1-C_{15}	168.5	130.0	38.5

Table S6. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of 2CD/G-3(D) at S_0 (S_1) minimum and the difference between S_0 and S_1

	structural parameters	2CD/G-3(D)		
		S_0	S_1	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.346	1.437	0.091
	C_2-C_3	1.491	1.433	0.059
	C_2-C_9	1.490	1.467	0.023
	C_1-C_{15}	1.489	1.419	0.070
	C_1-C_{21}	1.489	1.481	0.008
bond angle				
	C_1-C_2-C_3	124.2	124.6	0.4
	C_1-C_2-C_9	123.3	122.0	1.3
	C_2-C_1-C_{15}	121.1	120.4	0.7
	C_2-C_1-C_{21}	122.9	120.8	2.1
dihedral angle				
1-	C_1-C_2-C_3-C_4	102.8	104.0	1.2
2-	C_1-C_2-C_9-C_{10}	134.5	154.0	19.5
3-	C_2-C_1-C_{15}-C_{16}	60.7	26.1	34.6
4-	C_2-C_1-C_{21}-C_{22}	46.6	40.8	5.8
5-	C_3-C_2-C_1-C_{15}	3.6	20.5	16.9

Table S7. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of G-3 aggregate at S_0 (S_1) minimum and the difference between S_0 and S_1

	structural parameters	G-3 aggr.		
		S_0	S_1	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.348	1.445	0.097
	C_2-C_3	1.493	1.435	0.058
	C_2-C_9	1.496	1.468	0.028
	C_1-C_{15}	1.494	1.455	0.038
	C_1-C_{21}	1.493	1.440	0.053
bond angle				
	C_1-C_2-C_3	122.1	120.8	1.3
	C_1-C_2-C_9	121.0	119.4	1.6
	C_2-C_1-C_{15}	121.8	119.6	2.2
	C_2-C_1-C_{21}	123.0	120.1	2.9
dihedral angle				
1-	C_1-C_2-C_3-C_4	125.6	148.1	22.5
2-	C_1-C_2-C_9-C_{10}	60.2	52.3	7.9
3-	C_2-C_1-C_{15}-C_{16}	127.7	140.9	13.2
4-	C_2-C_1-C_{21}-C_{22}	129.5	142.2	12.7
5-	C_3-C_2-C_1-C_{15}	174.9	145.5	29.4

Table S8. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of G-3 aggregate with 2CD at S_0 (S_1) minimum and the difference between S_0 and S_1

	structural parameters	G-3 aggr. with 2CD		
		S_0	S_1	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.341	1.430	0.089
	C_2-C_3	1.495	1.432	0.063
	C_2-C_9	1.499	1.482	0.017
	C_1-C_{15}	1.496	1.491	0.005
	C_1-C_{21}	1.493	1.425	0.068
bond angle				
	C_1-C_2-C_3	124.4	121.7	2.7
	C_1-C_2-C_9	122.5	121.1	1.4
	C_2-C_1-C_{15}	121.6	119.5	2.1
	C_2-C_1-C_{21}	125.7	123.1	2.6
dihedral angle				
1-	C_1-C_2-C_3-C_4	77.8	62.5	15.3
2-	C_1-C_2-C_9-C_{10}	102.6	137.0	34.4
3-	C_2-C_1-C_{15}-C_{16}	78.9	89.7	10.8
4-	C_2-C_1-C_{21}-C_{22}	136.9	167.9	31.0
5-	C_3-C_2-C_1-C_{15}	178.8	179.9	1.1

Table S9. Selected bond lengths (Å), bond angle (degree), and dihedral angle (degree) of 2CD/G-3(D) aggregate at S_0 (S_1) minimum and the difference between S_0 and S_1

	structural parameters	2CD/G-3(D) aggr.		
		S_0	S_0	$\|S_0-S_1\|$
bond lengths				
	C_1-C_2	1.339	1.436	0.097
	C_2-C_3	1.486	1.424	0.062
	C_2-C_9	1.492	1.485	0.007
	C_1-C_{15}	1.500	1.437	0.064
	C_1-C_{21}	1.487	1.479	0.008
bond angle				
	C_1-C_2-C_3	121.5	117.3	4.2
	C_1-C_2-C_9	122.3	122.0	0.3
	C_2-C_1-C_{15}	118.4	116.5	1.9
	C_2-C_1-C_{21}	126.0	126.9	0.9
dihedral angle				
1-	C_1-C_2-C_3-C_4	82.6	62.7	19.9
2-	C_1-C_2-C_9-C_{10}	90.7	137.5	46.8
3-	C_2-C_1-C_{15}-C_{16}	69.4	25.5	43.9
4-	C_2-C_1-C_{21}-C_{22}	75.1	81.3	6.2
5-	C_3-C_2-C_1-C_{15}	2.6	28.2	25.5

Table S10. Reorganization Energy of each configuration is showed by AP.

	λgs (eV)	λes (eV)	λ (eV)
G-2	1.06	0.92	1.98
G-3	1.02	0.89	1.91
2CD/G-3(D)	0.68	0.88	1.56
G-3 aggr.	0.63	0.98	1.61
G-3 aggr. with 2CD	0.48	0.99	1.47
2CD/G-3(D) aggr.	0.54	1.16	1.70