1. Materials

Unless otherwise noted, all starting materials, reagents, and solvents were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on glass silica gel plates; visualization of products was performed with a handheld UV lamp. All aqueous solutions were prepared with deionized distilled water obtained from a Milli-Q water-purifying system (18 MΩ cm).

2. Instruments and Measurements

The ^{1}H and ^{13}C NMR spectra were recorded on a AVANCE III 400MHz spectrometer using the residual solvent proton signal for calibration. Electrospray mass spectra were obtained on a Bruker maXis 4G ESI-Q-TOF. For cryo-TEM, samples were prepared at room temperature by placing a droplet on a TEM grid, and then the grid was blotted to remove excess solution with a filter paper. Afterward, the grid was immediately plunged into precooled liquid ethane at its freezing point (-172°C). The TEM instrument used was a JEOL JEM-2010 equipped with a Gatan 832 CCD camera. Electronic absorption spectra were recorded on a JASCO model V–570 UV/VIS/NIR spectrophotometer. FTIR spectra were recorded at room temperature on a JASCO model FT/IR–660*Plus* Fourier transform infrared spectrometer.

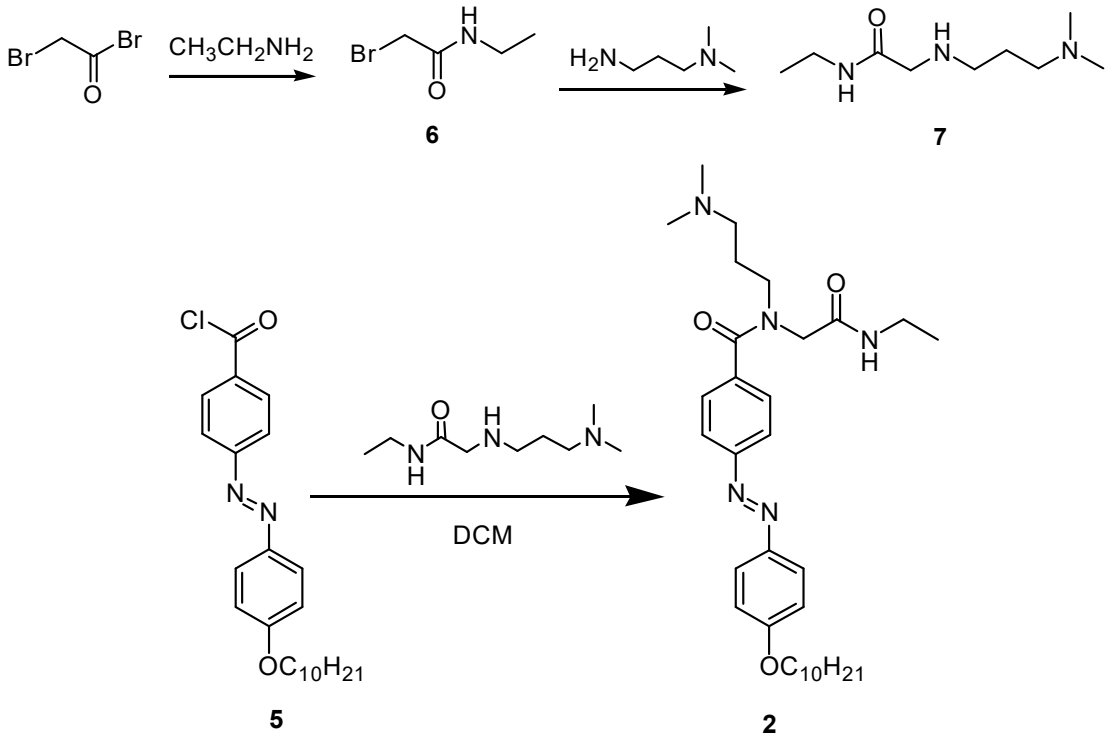


Figure S1. The scheme for the synthesis of compound 2.

3. Synthesis The compound **1** and **3** was synthesized according to the literature procedures.[S1] The synthesis of compound **2** was shown in Figure S1.

Compound 2. The compound **5** was synthesized according to the literature procedures.[S2] To a stirred solution of bromoacetyl bromide (220 mg, 1 mmol, 1.1 eq.) in 10 mL THF was added ethanamine (2mol/L in THF, 1.0 eq.) dropwise at -78℃. The mixture was allowed to warm to room temperature over 12 hours. After the reaction, the mixture was washed with saturated $NaHCO_3$ and extracted with EA. The resulting product (compound **6)** was taken directly to the next step without further purification.

A 50mL round bottom flask was charged with 3-(N,N-diethylamino)propylamine (1.1g, 11 mmol, 1.1eq.), H_2O (20 mL), $NaHCO_3$ (10eq.), then the mixture was cooled to 0℃. Compound **6** (1.66 g, 10 mmol, 1.0eq.) in 10 mL H_2O was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred for another 12 hours. After the reaction, the product was extracted with CH_2Cl_2, dried over $MgSO_4$, concentrated under vacuum to give the desired product (compound **7**) as colorless oil which was taken directly to the next step without purification.

Triethylamine (TEA, 0.075 mL, 1.1 eq.) was added dropwise to a stirred solution of compound **7** (206mg, 1.1 mmol, 1.1 eq.) in 20 mL CH_2Cl_2, then the mixture was cooled to 0℃. Compound **5** (400 mg, 1.0 mmol, 1.0 eq.) was dissolved in 10 mL CH_2Cl_2 and added to the mixture at 0℃. Then the mixture was warmed to room temperature and stirred for 2 hours. After the reaction, the mixture was washed with water, followed by saturated $NaHCO_3$ and brine. The organic phase was dried over $MgSO_4$ and concentrated in vacuo by rotary evaporation. Purification via column chromatography (CH_2Cl_2: TEA=25:1). Yield: 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, J = 8.4 Hz, 4H), 7.57 (s, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.20-3.97 (m, 4H), 3.74-3.31 (m, 4H), 2.51 (s ,2H), 2.12 (s, 6H), 1.84-1.08 (m, 21H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ:172.33, 169.09, 162.21, 153.42, 146.76, 136.84, 127.67, 125.07, 122.69, 114.79, 68.44, 56.30, 50.90, 49.50, 45.10, 34.44, 31.90, 31.44, 30.20, 29.70, 29.38, 29.32, 29.18, 26.47, 26.01, 22.69, 14.84, 14.12. MS (m/z): $[M+H]^+$ calcd for $[C_{32}H_{49}N_5O_3]$, 551.38; found: 552.57

4. Absorption

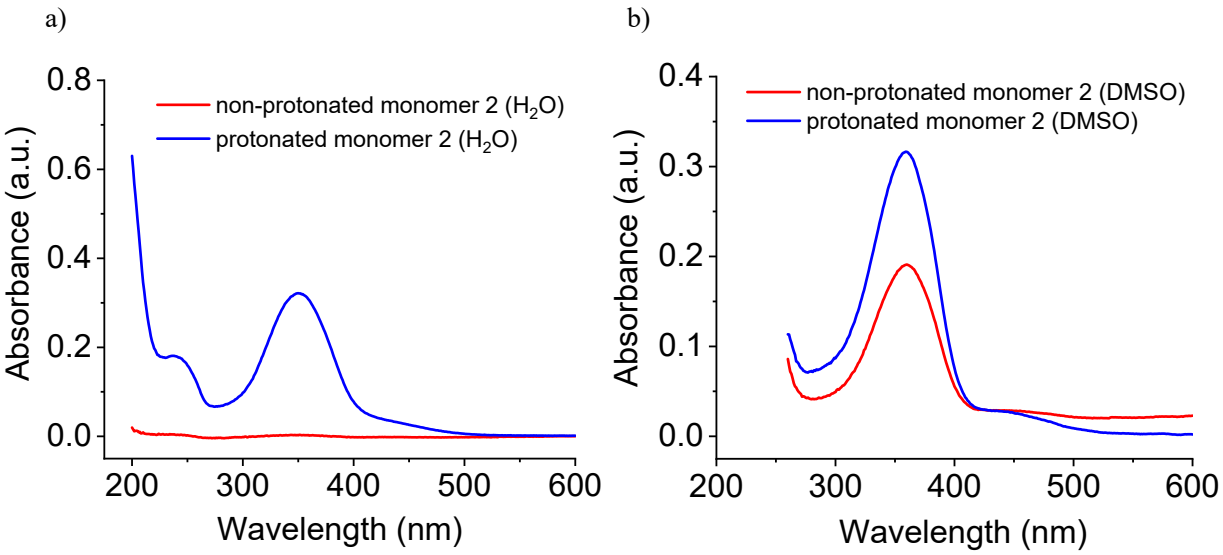


Figure S2. Absorption spectra of the non-protonated monomer (compound **2**, red**)** and the protonated monomer (cation **2**, blue**)** in water (a) and in DMSO (b).

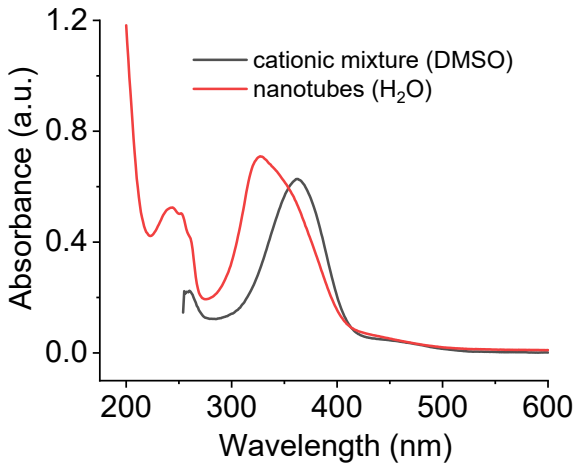
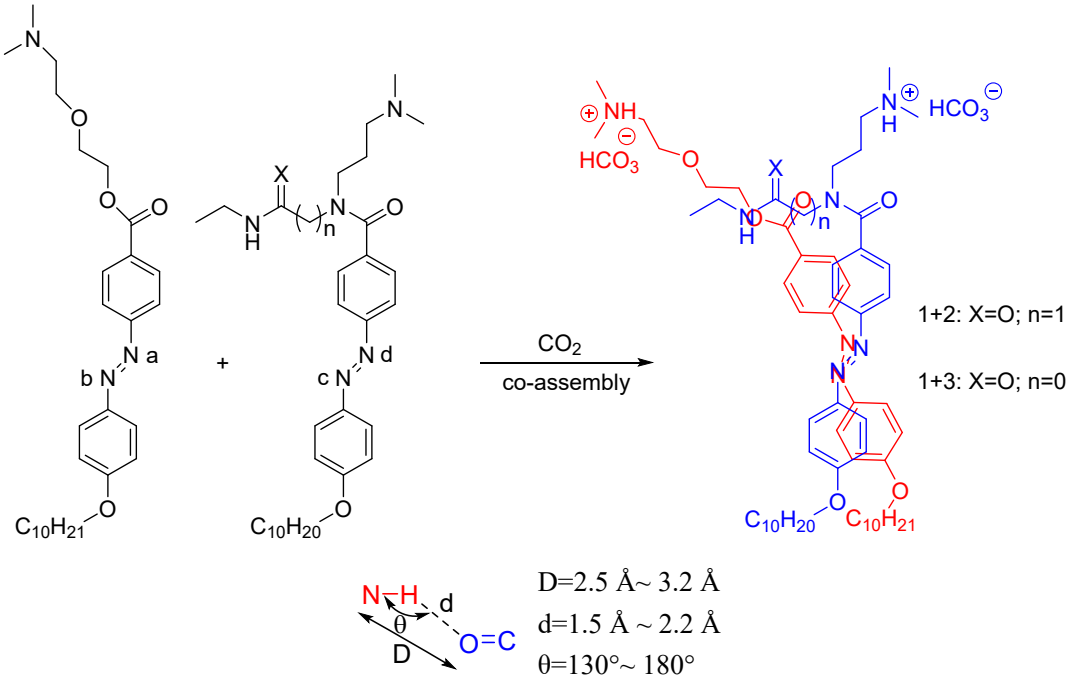


Figure S3. Absorption spectra of cations **1**+**2** in DMSO (black) and CO_2-triggered co-assembled nanotubes of cations **1**+**2** system prepared in water (red).

5. Computational Details



All the building blocks geometries were first optimized without geometry constraints using the B3LYP functional with the standard 6-31++G (d, p) basis set. The long hydrophobic chains of the building blocks are ignored to improve calculation efficiency. Based on the optimized building blocks geometries, dimers geometries of different systems were constructed separately according to the following methods. The π-π stacking distance between two azobenzene molecules is about 0.34 nm, and the dihedral angle (∠Na-Nb-Nc-Nd) were scanned based on the structural parameters of the N─H···O═C hydrogen bond. For the O and S systems, the dihedral angle (∠Na-Nb-Nc-Nd) was scanned from -27° to -19°, once every 2° for a total of 5 scans. For the CO system, the dihedral angle (∠Na-Nb-Nc-Nd) were scanned from 5° to 13°, once every 2° for a total of 5 scans. The dimers geometries were computed at the M06-2X/6-31G (d) level in aqueous solution (Polarizable continuum model, PCM) and in the gas phase. In addition, the calculation of the interaction energy in the gas phase takes into basis set superimposition error (BSSE). In all cases, analysis of vibrational frequencies ensures the found dimers geometries correspond to a local energy minimum. All calculations were done using Gaussian 09 program package [S3].

The standard orientation of **1+2** (5°) as follows, other angles (7°, 9°, 11° and 13°) can be obtained by adjusting the dihedral angle(∠N8-N7-N69-N70):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.287572	-1.959808	-0.581875
2	6	0	1.104138	-2.009468	-0.616542
3	6	0	1.832433	-1.066152	-1.352693
4	6	0	1.148578	-0.077982	-2.084837
5	6	0	-0.237074	-0.043894	-2.066296
6	6	0	-0.969325	-0.965635	-1.297370
7	7	0	3.241839	-1.208422	-1.304443
8	7	0	3.880220	-0.327383	-1.946933
9	6	0	5.283307	-0.462035	-1.918449
10	6	0	6.006415	0.516396	-2.621958
11	6	0	7.390173	0.479192	-2.667984
12	6	0	8.085177	-0.546929	-2.007096
13	6	0	7.371575	-1.529841	-1.296860
14	6	0	5.983820	-1.483335	-1.256547
15	8	0	9.438722	-0.504932	-2.113298
16	6	0	10.221337	-1.530740	-1.496487
17	6	0	-2.470725	-0.927914	-1.393326
18	8	0	-3.007512	-0.583146	-2.444415
19	7	0	-3.217546	-1.312775	-0.301549
20	6	0	-4.666585	-1.445900	-0.485682
21	6	0	-5.102785	-2.850913	-0.924824
22	6	0	-6.615106	-2.915289	-1.162460
23	7	0	-7.114268	-4.265270	-1.425278
24	6	0	-8.567054	-4.316763	-1.327059
25	6	0	-6.665349	-4.796705	-2.704876
26	1	0	-0.849189	-2.704648	-0.026570
27	1	0	1.652663	-2.778050	-0.081439
28	1	0	1.723725	0.635809	-2.662693
29	1	0	-0.778812	0.690514	-2.653575
30	1	0	5.450983	1.298808	-3.129032
31	1	0	7.961049	1.225941	-3.209139
32	1	0	7.892988	-2.326548	-0.779925
33	1	0	5.419616	-2.234583	-0.715830
34	1	0	10.060622	-1.514584	-0.438749
35	1	0	9.931374	-2.483886	-1.886787
36	1	0	-5.136417	-1.197554	0.467838
37	1	0	-4.974448	-0.689122	-1.215057
38	1	0	-4.560422	-3.134245	-1.835805

39	1	0	-4.829410	-3.566298	-0.143922
40	1	0	-7.119778	-2.553477	-0.258307
41	1	0	-6.895035	-2.213313	-1.977098
42	1	0	-8.884641	-3.981156	-0.334974
43	1	0	-8.909565	-5.347967	-1.460555
44	1	0	-9.082061	-3.689043	-2.081195
45	1	0	-5.574600	-4.858481	-2.735882
46	1	0	-7.055619	-5.810825	-2.835491
47	1	0	-6.999627	-4.190420	-3.571135
48	6	0	-2.719646	-1.380602	1.055189
49	1	0	-1.718675	-0.944395	1.102964
50	1	0	-3.358140	-0.767180	1.704532
51	6	0	-2.659235	-2.821819	1.599334
52	8	0	-2.809911	-3.793974	0.869885
53	7	0	-2.396166	-2.963292	2.932905
54	1	0	-2.296184	-2.075422	3.409010
55	6	0	-2.120635	-4.177833	3.693400
56	1	0	-2.596570	-4.072591	4.674829
57	1	0	-2.618786	-5.020337	3.207600
58	6	0	-0.626164	-4.467726	3.867685
59	1	0	-0.136770	-4.616025	2.900085
60	1	0	-0.124229	-3.636634	4.373007
61	1	0	-0.477762	-5.370256	4.469540
62	1	0	11.257561	-1.361252	-1.702431
63	6	0	-0.006728	-0.006367	2.520161
64	6	0	1.378847	0.038002	2.438877
65	6	0	2.002992	1.033567	1.684846
66	6	0	1.237782	1.992298	1.008894
67	6	0	-0.144683	1.946525	1.091283
68	6	0	-0.770844	0.947010	1.846287
69	7	0	3.427148	0.984926	1.669592
70	7	0	3.959979	1.875122	0.974736
71	6	0	5.374036	1.848664	0.944596
72	6	0	5.982002	2.830760	0.153475
73	6	0	7.359397	2.895590	0.050591
74	6	0	8.153799	1.972756	0.744751
75	6	0	7.552374	0.986400	1.541498
76	6	0	6.169488	0.929751	1.636398
77	8	0	9.488075	2.109057	0.588199
78	6	0	10.335322	1.201918	1.276713
79	6	0	-2.254153	0.861762	1.957116
80	8	0	-2.875973	1.822488	1.261798
81	8	0	-2.844863	0.021859	2.599622
82	6	0	-4.305312	1.806205	1.313128

83	6	0	-4.773086	2.964201	0.455644
84	8	0	-6.178942	2.952444	0.487080
85	6	0	-6.741128	4.015004	-0.256259
86	6	0	-8.252658	3.860266	-0.189462
87	7	0	-8.959274	5.020174	-0.713907
88	6	0	-10.382939	4.897693	-0.436059
89	6	0	-8.747467	5.173340	-2.147047
90	1	0	-0.508470	-0.773166	3.100834
91	1	0	1.997318	-0.691801	2.951350
92	1	0	1.738376	2.758619	0.428924
93	1	0	-0.746409	2.684516	0.572791
94	1	0	5.349693	3.537306	-0.375503
95	1	0	7.848282	3.648596	-0.558134
96	1	0	8.152828	0.266390	2.084556
97	1	0	5.693252	0.172118	2.248839
98	1	0	10.197636	1.280629	2.360107
99	1	0	10.150616	0.171147	0.956894
100	1	0	-4.679531	0.854098	0.926940
101	1	0	-4.640932	1.921041	2.347340
102	1	0	-4.377105	3.910667	0.853059
103	1	0	-4.399955	2.845873	-0.572559
104	1	0	-6.447681	4.985729	0.171777
105	1	0	-6.371955	3.974650	-1.291472
106	1	0	-8.546745	2.928895	-0.711025
107	1	0	-8.523296	3.742106	0.865669
108	1	0	-10.905295	5.788472	-0.796909
109	1	0	-10.832788	4.013079	-0.922973
110	1	0	-10.544083	4.814572	0.642700
111	1	0	-9.334307	6.021327	-2.511068
112	1	0	-9.051724	4.273299	-2.713139
113	1	0	-7.695651	5.377477	-2.363025
114	1	0	11.353410	1.487751	1.016455

The standard orientation of **1+3** (-19°) as follows, other angles(-21°, -23°, -25° and -27°) can be obtained by adjusting the dihedral angle(∠N8-N7-N66-N67):

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.193027	2.666627	-0.473793
2	6	0	-1.150268	2.374194	-0.665440
3	6	0	-1.529768	1.162391	-1.246069
4	6	0	-0.558390	0.245866	-1.662800

5	6	0	0.782987	0.549575	-1.488463
6	6	0	1.165402	1.746809	-0.874397
7	7	0	-2.933233	0.964328	-1.381654
8	7	0	-3.246582	-0.140255	-1.870523
9	6	0	-4.639139	-0.349905	-2.018087
10	6	0	-5.017218	-1.581927	-2.562770
11	6	0	-6.352512	-1.885347	-2.752384
12	6	0	-7.334691	-0.952718	-2.397148
13	6	0	-6.964373	0.283377	-1.849636
14	6	0	-5.621201	0.577704	-1.663354
15	8	0	-8.613102	-1.334607	-2.620874
16	6	0	-9.643402	-0.425422	-2.294164
17	6	0	2.633963	2.048237	-0.784527
18	8	0	3.383297	1.713650	-1.682806
19	7	0	3.100358	2.787229	0.296378
20	6	0	4.362716	3.515328	0.108510
21	6	0	4.161910	4.794179	-0.698490
22	6	0	5.494021	5.494569	-0.945844
23	7	0	5.347040	6.835336	-1.494539
24	6	0	6.638121	7.495931	-1.553892
25	6	0	4.733540	6.816828	-2.810943
26	7	0	2.393670	1.994845	2.390096
27	6	0	1.536112	2.053092	3.565642
28	6	0	2.171263	2.839129	4.706751
29	1	0	0.486209	3.612266	-0.024106
30	1	0	-1.928672	3.072163	-0.374680
31	1	0	-0.874384	-0.682289	-2.124581
32	1	0	1.558598	-0.127843	-1.832327
33	1	0	-4.237538	-2.287460	-2.832166
34	1	0	-6.669725	-2.832203	-3.175232
35	1	0	-7.713221	1.014835	-1.569806
36	1	0	-5.315722	1.528793	-1.241757
37	1	0	-9.644357	-0.194012	-1.222430
38	1	0	-9.548150	0.504610	-2.866980
39	1	0	4.753771	3.747130	1.100910
40	1	0	5.053246	2.837676	-0.399049
41	1	0	3.683431	4.527915	-1.648123
42	1	0	3.492926	5.464955	-0.149111
43	1	0	6.024900	5.591182	0.010512
44	1	0	6.127886	4.861134	-1.601314
45	1	0	7.076094	7.540622	-0.552144
46	1	0	6.511414	8.519786	-1.918261
47	1	0	7.353187	6.977847	-2.221530
48	1	0	3.713874	6.429085	-2.753343

49	1	0	4.681267	7.838340	-3.198825
50	1	0	5.301522	6.200646	-3.534540
51	1	0	2.835574	1.123630	2.139937
52	1	0	0.590053	2.518953	3.270848
53	1	0	1.323476	1.022955	3.864395
54	1	0	1.501104	2.869716	5.570898
55	1	0	3.115627	2.381312	5.014539
56	1	0	2.365892	3.862538	4.378382
57	6	0	2.415601	3.029773	1.515301
58	8	0	1.933433	4.121218	1.760478
59	1	0	-10.576711	-0.921317	-2.559416
60	6	0	0.536258	0.098992	2.018145
61	6	0	-0.846840	0.215186	2.048396
62	6	0	-1.645843	-0.817329	1.555784
63	6	0	-1.060147	-1.976075	1.032383
64	6	0	0.320078	-2.090727	1.003525
65	6	0	1.121618	-1.053685	1.494642
66	7	0	-3.050750	-0.593024	1.631857
67	7	0	-3.738867	-1.521905	1.162726
68	6	0	-5.138617	-1.318320	1.229353
69	6	0	-5.927192	-2.340354	0.690599
70	6	0	-7.306178	-2.243490	0.701602
71	6	0	-7.918752	-1.114326	1.258232
72	6	0	-7.136054	-0.086395	1.801609
73	6	0	-5.752466	-0.193209	1.784120
74	8	0	-9.271800	-1.103911	1.227128
75	6	0	-9.936367	0.010605	1.783900
76	6	0	2.609673	-1.131005	1.476841
77	8	0	3.056441	-2.282753	0.944468
78	8	0	3.345198	-0.265814	1.887154
79	6	0	4.476984	-2.419653	0.884631
80	6	0	4.744931	-3.769279	0.251390
81	8	0	6.137909	-3.912779	0.163966
82	6	0	6.521466	-5.156219	-0.378427
83	6	0	8.039519	-5.160284	-0.465427
84	7	0	8.576290	-6.471097	-0.794582
85	6	0	10.019527	-6.478414	-0.629060
86	6	0	8.227238	-6.875559	-2.146295
87	1	0	1.179975	0.887869	2.393129
88	1	0	-1.334356	1.099059	2.446908
89	1	0	-1.701233	-2.765037	0.656936
90	1	0	0.788761	-2.982204	0.601959
91	1	0	-5.428601	-3.206171	0.265996
92	1	0	-7.938022	-3.022439	0.289123

93	1	0	-7.596316	0.793294	2.235930
94	1	0	-5.130191	0.591806	2.199423
95	1	0	-9.706934	0.118257	2.850574
96	1	0	-9.669437	0.935788	1.259693
97	1	0	4.906659	-1.611360	0.286291
98	1	0	4.902257	-2.364146	1.890437
99	1	0	4.301023	-4.567570	0.866690
100	1	0	4.277670	-3.815178	-0.745014
101	1	0	6.188829	-5.985554	0.264929
102	1	0	6.056021	-5.286503	-1.367887
103	1	0	8.365247	-4.383391	-1.184313
104	1	0	8.419034	-4.869758	0.520083
105	1	0	10.406565	-7.481498	-0.831360
106	1	0	10.529559	-5.767942	-1.306477
107	1	0	10.274365	-6.213456	0.401123
108	1	0	8.681200	-7.847015	-2.362009
109	1	0	8.577755	-6.152625	-2.907713
110	1	0	7.144581	-6.986074	-2.248958
111	1	0	-11.001692	-0.181865	1.659717

Table S1. Relative energies (in kJ·mol^{-1}) of co-assemblies at different dihedral angles [a]

dihedral angle (°)	E_1[b]	Ex[c]	$E_{assemblies}$	ΔE[d]
1+2	-3260573.605 (-3260538.719)	-3660060.883 (-3660001.566)		
5	-	-	-6920695.929 (-6920575.754)	-61.440 (-35.469)
7	-	-	-6920659.319 (-6920578.523)	-24.831 (-38.238)
9	-	-	-6920650.609 (-6920617.804)	-16.120 (-77.518)
11	-	-	-6920695.929 (-6920617.840)	-61.440 (-77.555)
13	-	-	-6920707.274 (-6920617.804)	-72.785 (-77.518)
1+3	-3260573.605 (-3260538.719)	-3556942.231 (-3556893.931)		
-19	-	-	-6817583.457 (-6817517.347)	-67.621 (-84.697)
-21	-	-	-6817583.434 (-6817517.523)	-67.597 (-84.873)
-23	-	-	-6817582.935 (-6817517.523)	-67.098 (-84.873)
-25	-	-	-6817583.431 (-6817517.515)	-67.594 (-84.865)
-27	-	-	-6817583.444 (-6817517.528)	-67.607 (-84.878)

a The energies outside the brackets were obtained in the water phase at M06-2X/6-31G (d) level of theory, and the energies inside brackets were obtained after basis set superposition error (BSSE) correction in the gas phase with the equivalent theoretical level.

b E_1 represents the energies parameter of the monomer **1**.

c Ex represents the energies of **2**, and **3**, respectively.

dΔE represents interaction energies,$\Delta E = E_{\text{assemblies}} - (E_1 + Ex)$.

Notes and references

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