Supporting Information

Reversible transformation of self-assemblies and fluorescence by protonation-deprotonation in pyrimidinylene–phenylene macrocycles

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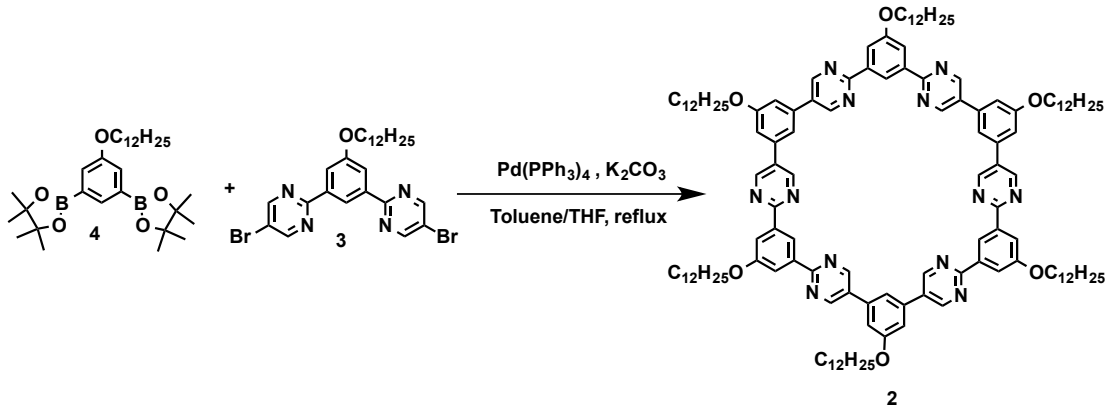
1. Measurements

^{1}H NMR spectra were recorded on a Bruker model Bruker AV-400 spectrometer, operating at 400 MHz. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI–TOF mass) was performed on an AB Sciex model AB Sciex 4800 Plus MALDI TOF/TOF Analyzer, using dithranol as a matrix. Gel permeation chromatography (GPC) analyses were performed on JAI model LC-9201 recycling preparative HPLC, using $CHCl_3$ as eluent. Fluorescence spectroscopy was conducted using a quartz cell of 1-cm path length on a HORIBA model Fluoromax-4 spectrophotometer. TEM microscopy was recorded on a JEOL model JEM-2100 electron microscope operating at 200 kV. Atomic force microscopy (AFM) was performed on a Bruker model Dimension Icon microscope. The ESI-TOF mass sepectra were acquired using an Agilent 6210 TOF mass spectrometer. The STM measurements were performed with a Nanoscope IIIa scanning probe microscope system (Bruker, USA).

2. Materials

Unless otherwise noted, all commercial reagents were used as received. Tetrahydrofuran (THF) was refluxed over a mixture of Na and benzophenone ketyl under argon and distilled just before use. DMF was dried over CaH_2 under argon and freshly distilled prior to use. CH_2Cl_2 was dried over CaH_2 under argon and freshly distilled prior to use. $CHCl_3$ was dried over molecular sieve and freshly distilled under argon before use.

3. Synthetic Procedure



Scheme S1. Synthesis of macrocycle **2**

Macrocycle 2. A THF/toluene solution (5 mL/2.5 mL) of a mixture of **4**[S1] (90 mg, 0.17 mmol, 1 eq.) and **3**[S1] (100 mg, 0.17 mmol, 1 eq.) were successively added $Pd(PPh_3)_4$ (30 mg, 0.019 mmol, 11% eq.) and an aqueous solution of K_2CO_3 (2 M, 1 mL) under argon, and the resulting suspension was refluxed at 80 °C for 48 h. After cooling to room temperature, the resulting mixture was extracted with chloroform. The organic phase was washed with water, dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was subjected to column chromatography on silica gel, giving the product as a white solid. The solid obtained were subjected to preparative GPC (gel permeation chromatography, $CHCl_3$ as eluent solution) to purify, **2** was given as white solid after several cycles.

2: Yield: 8.7 %. ^{1}H NMR (400 MHz, THF-d_8, 55 °C) δ (ppm) 8.97 (s, 3H), 8.86 (s, 12H), 7.79 (s, 6H), 7.37 (s, 3H), 6.94 (s, 6H), 4.08-3.97 (t, 12H), 1.85 (dd, J = 7.2 Hz, 12H), 1.21 (m, J = 18.7 Hz, 108H), 0.81 (t, J = 6.7 Hz, 18H). MALDI-TOF Mass: calcd. for $C_{132}H_{180}N_{12}O_6$ $[M]^+$: m/z = 2029.41; found: 2029.6699.

4. Supporting Reference

(S1) D. Xie, R. Li, D. Zhang, J. Hu, D. Xiao, X. Li, Y. Xiang, W. Jin, *Tetrahedron*, 2015, **71**, 8871.

5. Supporting Figures

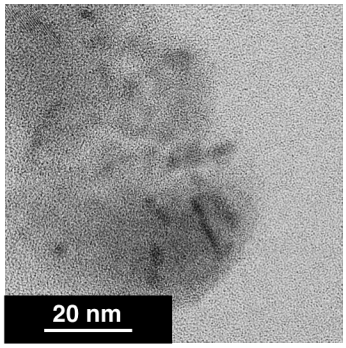


Figure S1. TEM image of $\mathbf{1_p}$ from CH_2Cl_2 in the presence of TFA.

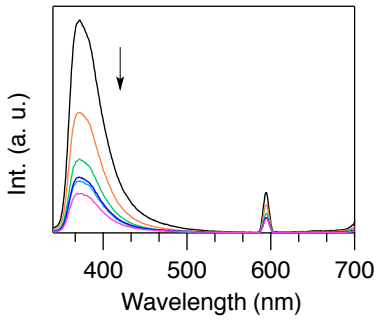
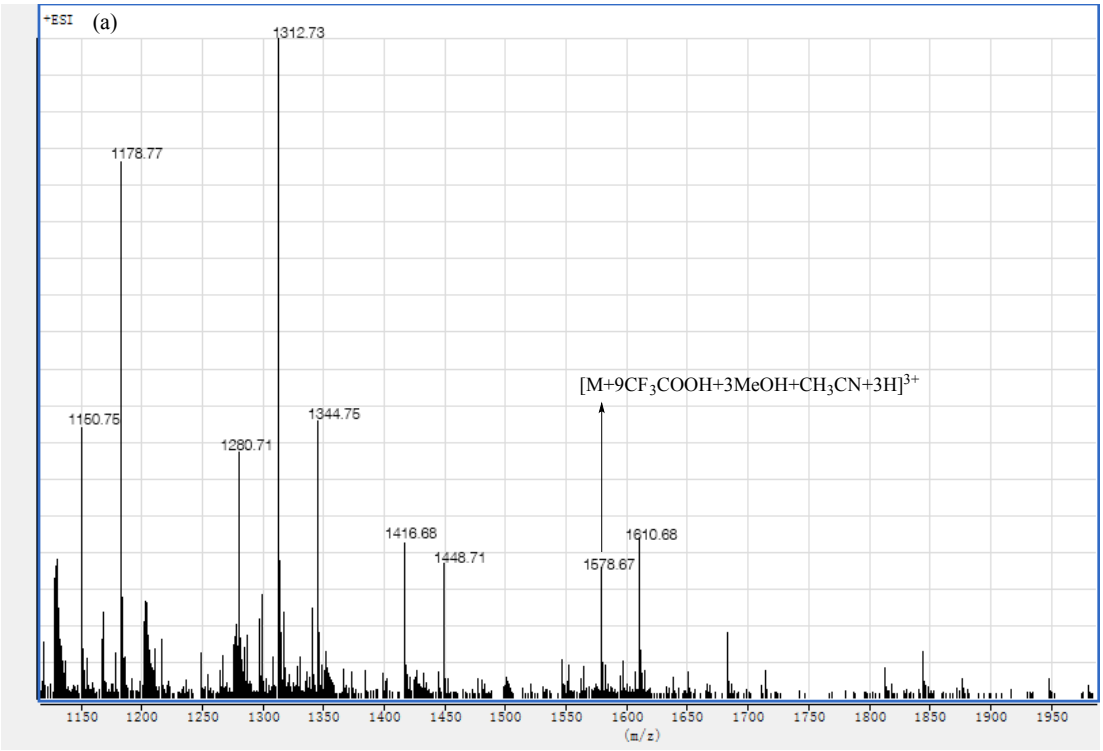
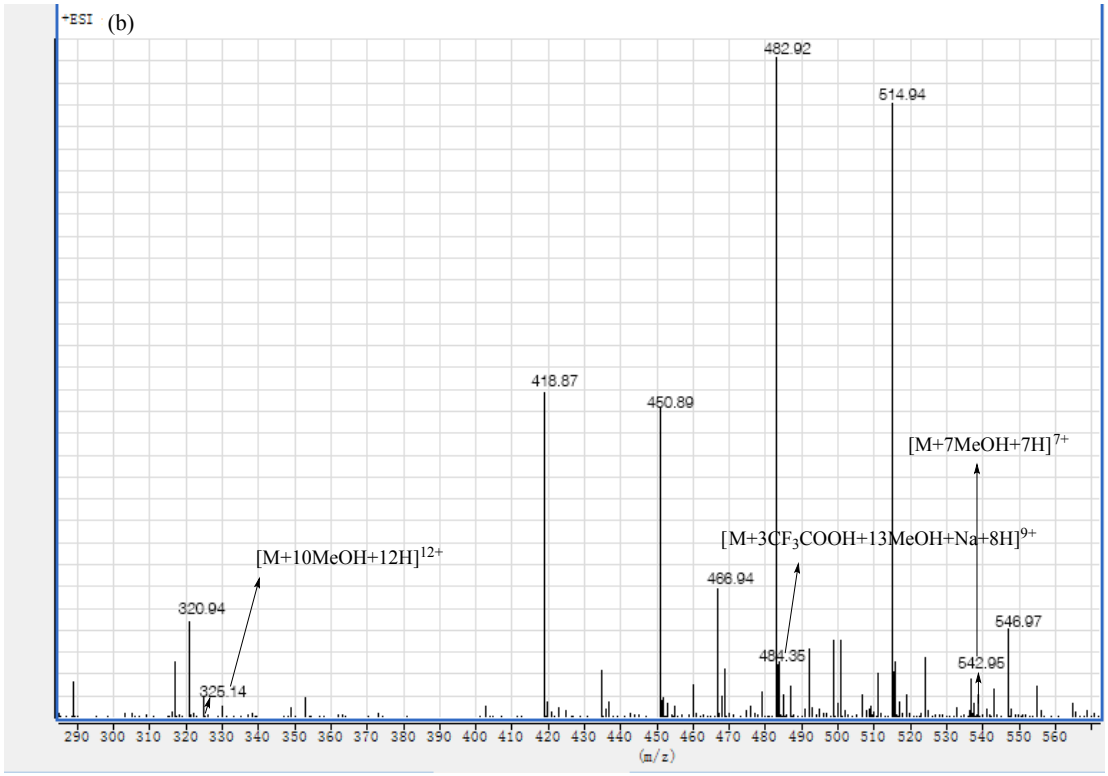
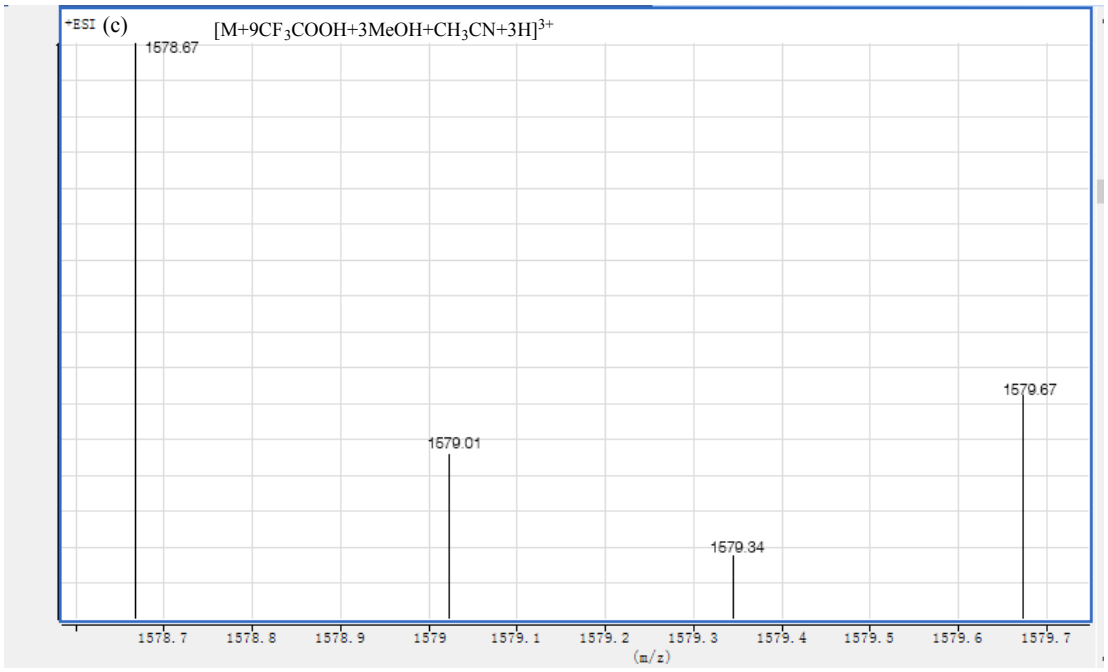
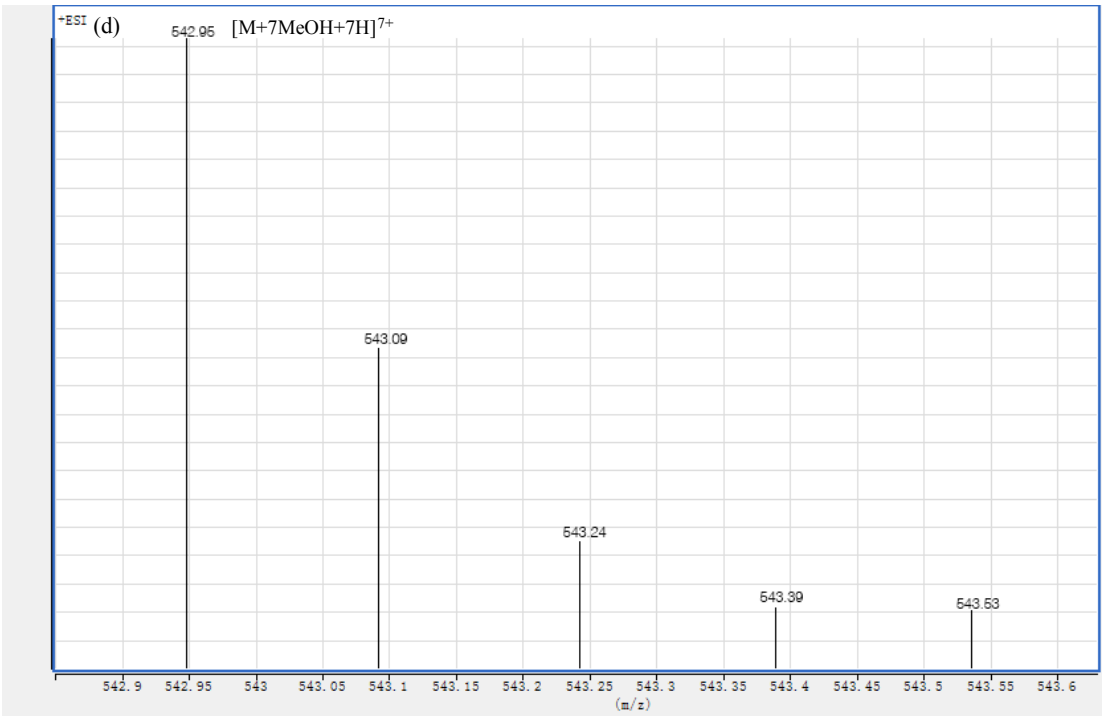


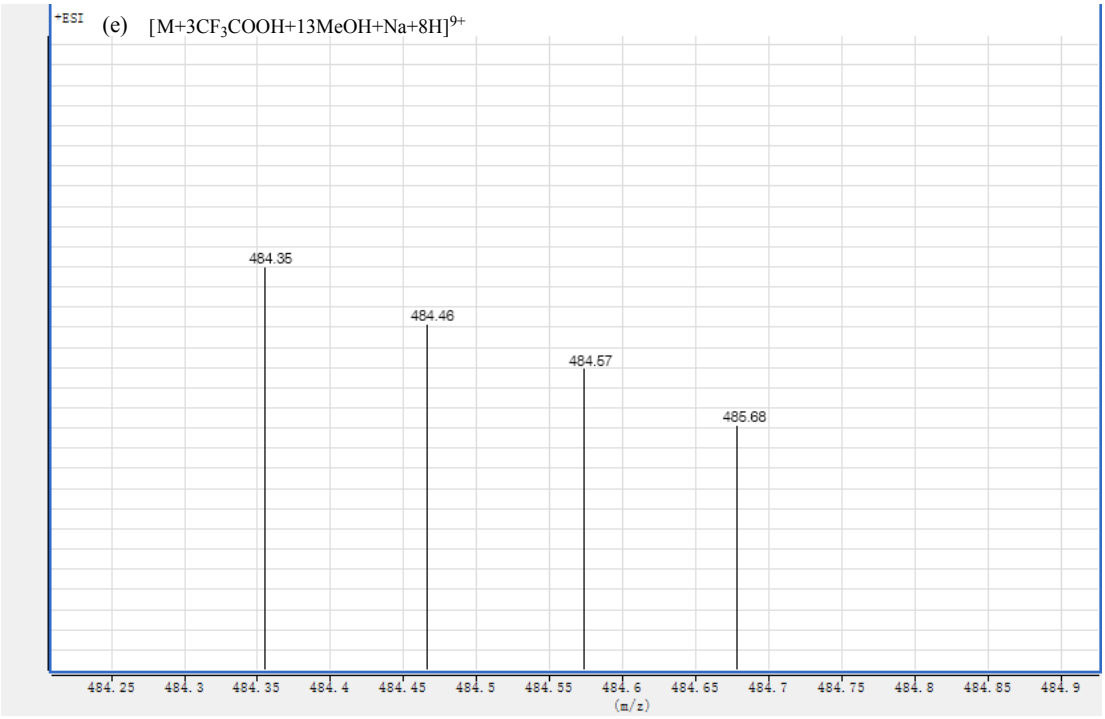
Figure S2. Fluorescence spectral changes of $\mathbf{1}_{NT}$ (5×10^{-6} M) upon titration with $CF_3COOCH_2CH_3$ in DCM at 25 °C. $CF_3COOCH_2CH_3$ = 0-200 eq. (0-1 mmol/L)




+ESI (b)
482.92
514.94
418.87
450.89
[M+7MeOH+7H]7+
[M+3CF3COOH+13MeOH+Na+8H]9+
[M+10MeOH+12H]12+
466.94
320.94
546.97
484.35
542.95
325.14
290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500 510 520 530 540 550 560
(m/z)


+ESI (c)
[M+9CF3COOH+3MeOH+CH3CN+3H]3+
1578.67
1579.67
1579.01
1579.34
1578.7 1578.8 1578.9 1579 1579.1 1579.2 1579.3 1579.4 1579.5 1579.6 1579.7
(m/z)


+ESI (d)
542.96 [M+7MeOH+7H]7+
543.09
543.24
543.39
543.53
542.9 542.95 543 543.05 543.1 543.15 543.2 543.25 543.3 543.35 543.4 543.45 543.5 543.55 543.6
(m/z)


+ESI (e) [M+3CF3COOH+13MeOH+Na+8H]9+
484.35
484.46
484.57
486.68
484.25 484.3 484.35 484.4 484.45 484.5 484.55 484.6 484.65 484.7 484.75 484.8 484.85 484.9
(m/z)

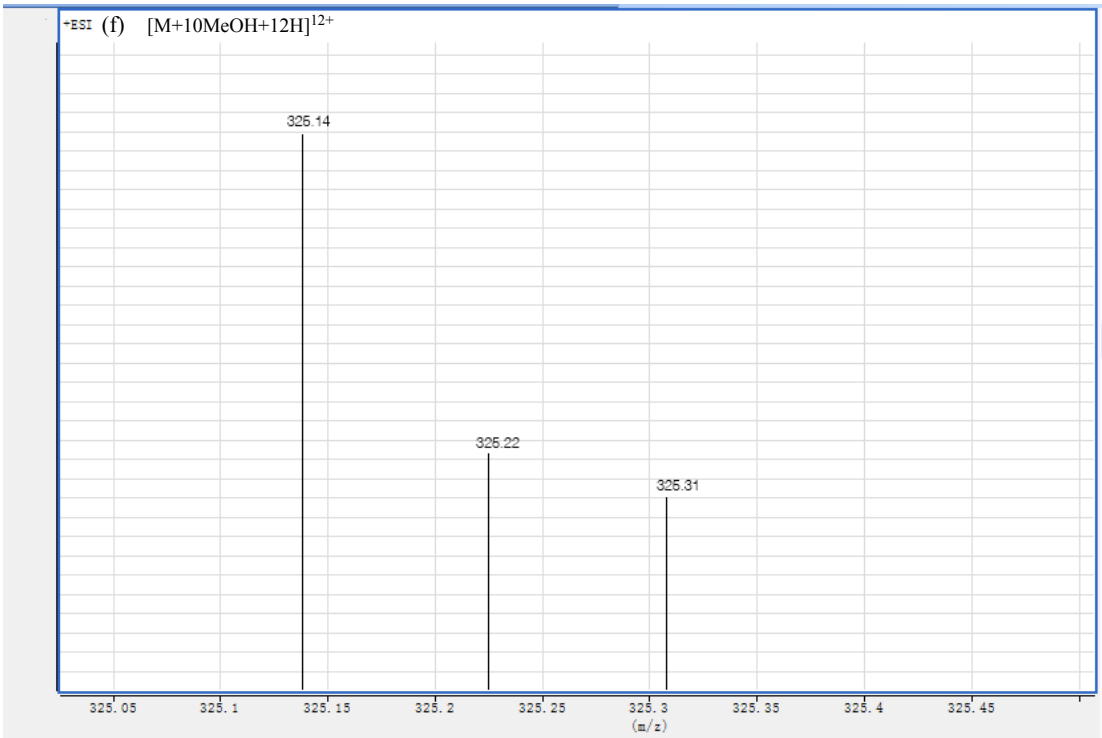


Figure S3. (a), (b) ESI-TOF mass spectra of $\mathbf{1_p}$ in the presence of TFA in MeOH/CH_3CN. (c), (d), (e), (f) experimental isotopic distirbutions for the different charged species.

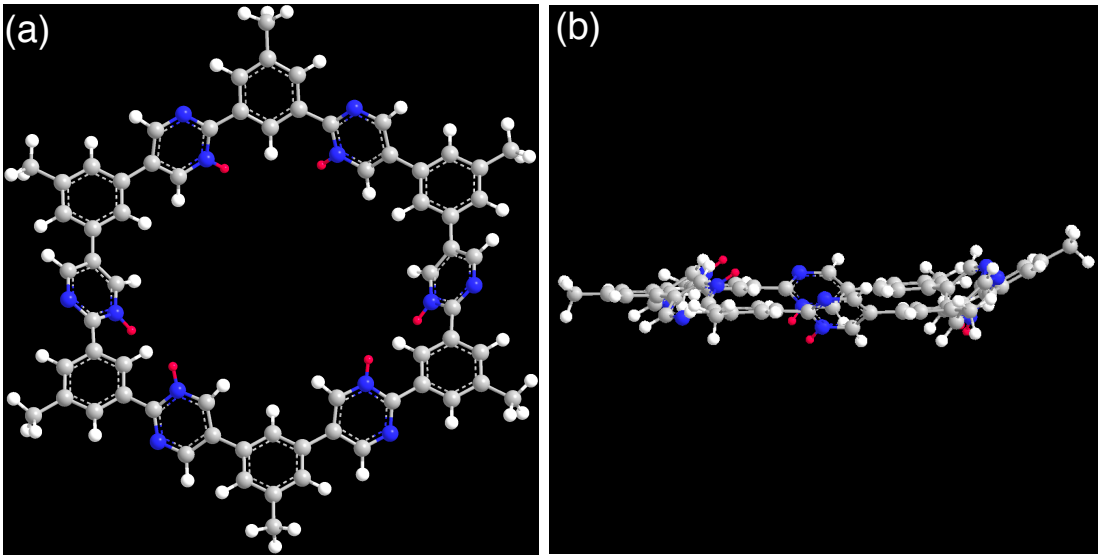


Figure S4. Optimized model structure of $\mathbf{1_p}$ with six proton (in red). (a) top view and (b) side view.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.639513	3.581747	-0.047125
2	6	0	-7.424849	2.864770	-0.103136
3	6	0	-6.198638	3.556533	-0.063541
4	6	0	-6.203548	4.964310	-0.012563
5	6	0	-7.427920	5.665885	-0.051541
6	6	0	-8.660119	4.987978	-0.048968
7	6	0	-7.483649	1.400239	-0.206838
8	6	0	-4.960570	5.738460	0.103441
9	7	0	-8.436011	0.697924	0.428162
10	6	0	-8.440524	-0.644193	0.372681
11	6	0	-7.459652	-1.404229	-0.333188
12	6	0	-6.541900	-0.644293	-1.054249
13	7	0	-6.569820	0.720206	-0.977484
14	7	0	-4.826552	6.932961	-0.495981
15	6	0	-3.664778	7.603782	-0.421998
16	6	0	-2.516332	7.109060	0.265901
17	6	0	-2.715639	5.911709	0.948436
18	7	0	-3.912965	5.259758	0.855450
19	6	0	1.202021	-9.048757	0.867493
20	6	0	1.216438	-7.801230	0.202342
21	6	0	-0.000419	-7.179499	-0.147487
22	6	0	-1.217359	-7.801086	0.202293
23	6	0	-1.203119	-9.048616	0.867448
24	6	0	-0.000595	-9.699509	1.187429
25	6	0	2.523234	-7.166668	-0.010946
26	6	0	-2.524071	-7.166368	-0.011045
27	7	0	3.556409	-7.476006	0.792694
28	6	0	4.727196	-6.831858	0.682629
29	6	0	4.947040	-5.768819	-0.242763
30	6	0	3.900534	-5.540619	-1.130213
31	7	0	2.729485	-6.240888	-1.007312
32	7	0	-2.730182	-6.240581	-1.007426
33	6	0	-3.901146	-5.540168	-1.130372
34	6	0	-4.947700	-5.768226	-0.242947
35	6	0	-4.728000	-6.831263	0.682488
36	7	0	-3.557302	-7.475561	0.792585
37	6	0	-6.220994	-5.003440	-0.284444
38	6	0	-6.220218	-3.596784	-0.351036
39	6	0	-7.439648	-2.887647	-0.329809

40	6	0	-8.650523	-3.605437	-0.269853
41	6	0	-8.676145	-5.010182	-0.221206
42	6	0	-7.447534	-5.692887	-0.213339
43	6	0	7.428591	5.665039	-0.051864
44	6	0	6.204125	4.963620	-0.012769
45	6	0	6.199030	3.555845	-0.063660
46	6	0	7.425153	2.863919	-0.103279
47	6	0	8.639908	3.580742	-0.047385
48	6	0	8.660696	4.986978	-0.049317
49	6	0	4.961253	5.737931	0.103286
50	6	0	7.483767	1.399373	-0.206879
51	7	0	4.827323	6.932399	-0.496220
52	6	0	3.665628	7.603358	-0.422197
53	6	0	2.517177	7.108807	0.265811
54	6	0	2.716401	5.911488	0.948425
55	7	0	3.913651	5.259401	0.855409
56	7	0	6.569819	0.719392	-0.977418
57	6	0	6.541752	-0.645111	-1.054110
58	6	0	7.459478	-1.405103	-0.333076
59	6	0	8.440491	-0.645123	0.372665
60	7	0	8.436120	0.696993	0.428074
61	6	0	1.222360	7.832792	0.298335
62	6	0	7.439318	-2.888516	-0.329615
63	6	0	6.219799	-3.597526	-0.350834
64	6	0	6.220414	-5.004169	-0.284214
65	6	0	7.446887	-5.693757	-0.213069
66	6	0	8.675562	-5.011198	-0.220926
67	6	0	8.650100	-3.606438	-0.269619
68	6	0	1.205745	9.241263	0.336930
69	6	0	0.000566	9.964571	0.357462
70	6	0	-1.204681	9.241380	0.336994
71	6	0	-1.221444	7.832910	0.298392
72	6	0	0.000424	7.130673	0.283043
73	6	0	-9.963605	5.744167	-0.063035
74	6	0	-9.983240	-5.762356	-0.202664
75	6	0	-0.000680	-11.049956	1.855400
76	6	0	9.982614	-5.763445	-0.202315
77	6	0	9.964314	5.742937	-0.063473
78	6	0	0.000667	11.472426	0.395281
79	1	0	-9.573890	3.031335	-0.031598
80	1	0	-5.258568	3.009261	-0.068061
81	1	0	-7.411827	6.750231	-0.049026
82	1	0	-9.240550	-1.132763	0.917369
83	1	0	-5.813008	-1.075967	-1.726679

84	1	0	-3.640533	8.559012	-0.934697
85	1	0	-1.976602	5.474926	1.606324
86	1	0	2.147240	-9.503154	1.140937
87	1	0	-0.000353	-6.174948	-0.565295
88	1	0	-2.148403	-9.502897	1.140858
89	1	0	5.513391	-7.155078	1.356569
90	1	0	3.972094	-4.857355	-1.966253
91	1	0	-3.972594	-4.856911	-1.966427
92	1	0	-5.514264	-7.154391	1.356391
93	1	0	-5.276372	-3.058558	-0.329892
94	1	0	-9.598592	-3.077144	-0.286597
95	1	0	-7.458713	-6.778131	-0.179432
96	1	0	7.412636	6.749384	-0.049408
97	1	0	5.258887	3.008697	-0.068067
98	1	0	9.574215	3.030206	-0.031877
99	1	0	3.641451	8.558552	-0.934967
100	1	0	1.977362	5.474841	1.606402
101	1	0	5.812768	-1.076740	-1.726468
102	1	0	9.240501	-1.133744	0.917329
103	1	0	5.276016	-3.059189	-0.329733
104	1	0	7.457942	-6.779001	-0.179152
105	1	0	9.598236	-3.078259	-0.286372
106	1	0	2.137697	9.795737	0.384760
107	1	0	-2.136563	9.795962	0.384857
108	1	0	0.000369	6.048726	0.181182
109	1	0	-10.755925	5.190523	0.447874
110	1	0	-10.298995	5.917583	-1.094270
111	1	0	-9.869048	6.722163	0.415844
112	1	0	-9.886268	-6.730595	0.295593
113	1	0	-10.334278	-5.956066	-1.224850
114	1	0	-10.768192	-5.197445	0.307639
115	1	0	-0.000517	-11.851801	1.104969
116	1	0	-0.886388	-11.191096	2.480422
117	1	0	0.884810	-11.191044	2.480745
118	1	0	10.335211	-5.954557	-1.224452
119	1	0	9.884915	-6.732916	0.293368
120	1	0	10.766799	-5.199798	0.310588
121	1	0	10.301115	5.913815	-1.094670
122	1	0	10.755869	5.190348	0.449787
123	1	0	9.869313	6.722066	0.412970
124	1	0	-0.884247	11.864775	0.903502
125	1	0	0.002533	11.886310	-0.621797
126	1	0	0.883907	11.864558	0.906611
127	1	0	2.019624	-6.125147	-1.724016

128	1	0	-2.020291	-6.124938	-1.724117
129	1	0	-5.948322	1.256982	-1.576062
130	1	0	-4.068097	4.437246	1.431700
131	1	0	4.068738	4.436922	1.431719
132	1	0	5.948324	1.256194	-1.575975

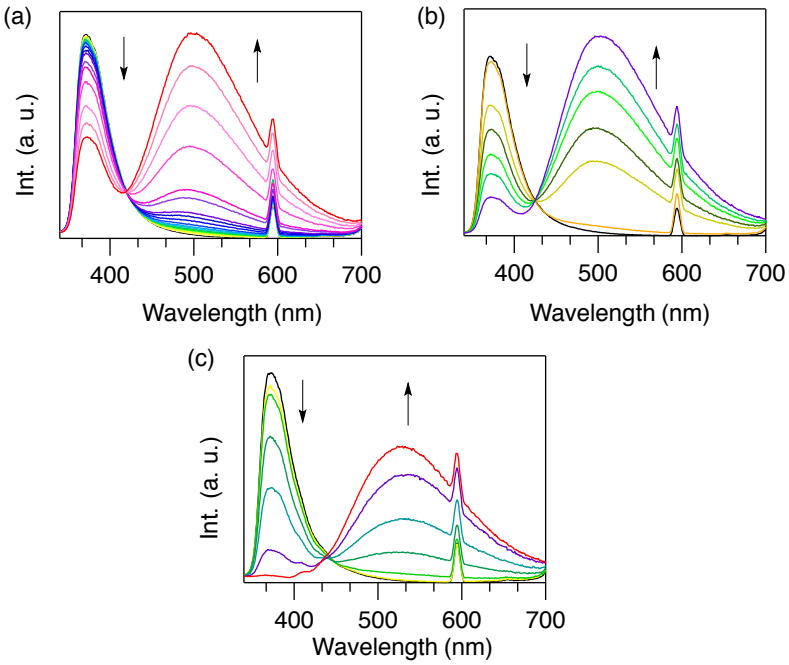


Figure S5. Fluorescence spectral changes of $\mathbf{1}_{NT}$ (5×10^{-6} M) upon titration with (a) CSA, (b) *p*-TSA, and (c) TfOH in DCM at 25 °C. CSA = 0-500 eq. (0-2.5 mmol/L), *p*-TSA = 0-40 eq. (0-0.2 mmol/L), TfOH = 0-9 eq. (0-0.045 mmol/L).

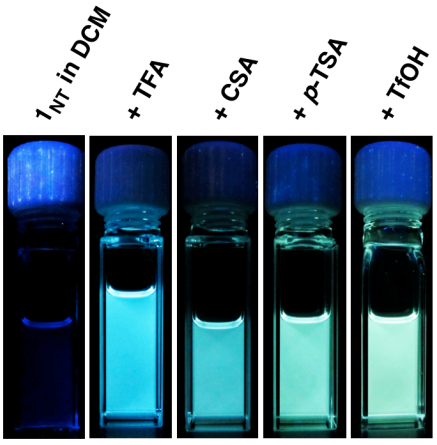


Figure S6. Fluorescence photographs of $\mathbf{1}_{NT}$ in DCM in the absence and presence of acid.

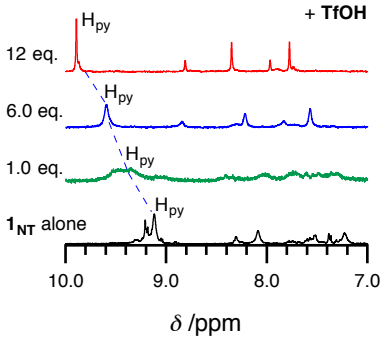


Figure S7. ^{1}H NMR (400 MHz) spectral changes of $\mathbf{1_{NT}}$ in CD_2Cl_2 at 25 °C in aromatic region upon titration with TfOH.

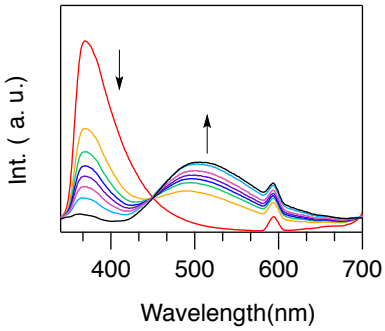


Figure S8. Fluorescence spectral changes of $\mathbf{1_{NT}}$ (5×10^{-6} M) upon titration with HCl (in THF). [HCl] = 0-200 eq. (0-1 mmol/L).

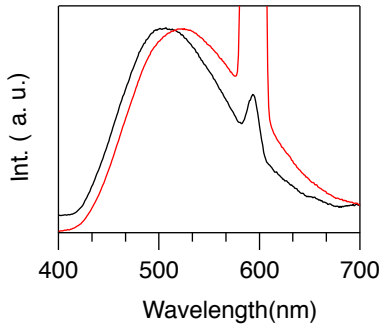


Figure S9. Fluorescence spectra of $\mathbf{1_{NT}}$ (5×10^{-6} M) upon titration with HCl ((black) and then with the THF solution of CF_3SO_3Ag (red).

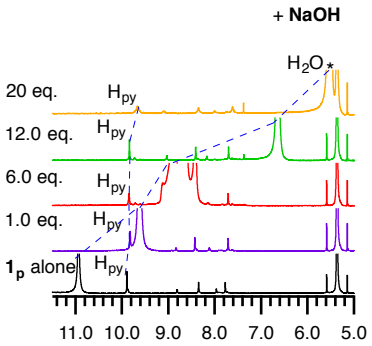


Figure S10. ^{1}H NMR (400 MHz) spectral changes of $\mathbf{1_p}$ in the presence of TfOH in CD_2Cl_2 in aromatic region upon titration with NaOH at 25 °C.

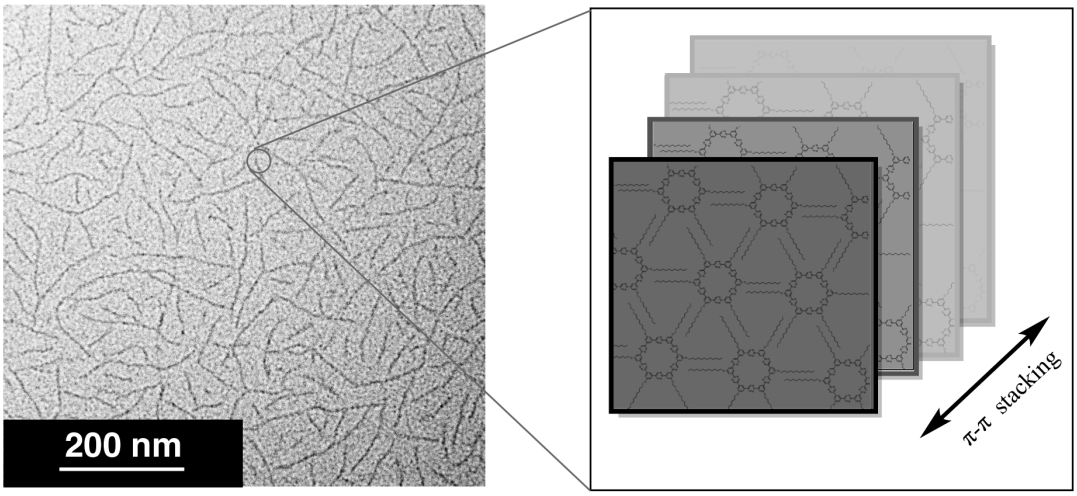


Figure S11. Schematic illustration showing the columnar molecular stacking of macrocycle **2** within the nanofibers ($\mathbf{2_{NF}}$).

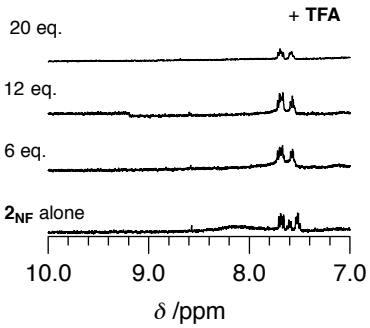


Figure S12. ^{1}H NMR (400 MHz) spectral changes of $\mathbf{2_{NF}}$ in CD_2Cl_2 at 25 °C in aromatic region upon titration with TFA.

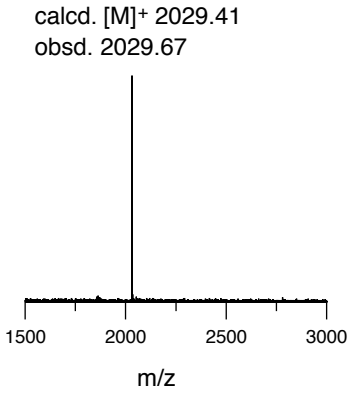


Figure S13. MALDI-TOF mass of macrocycle **2**.

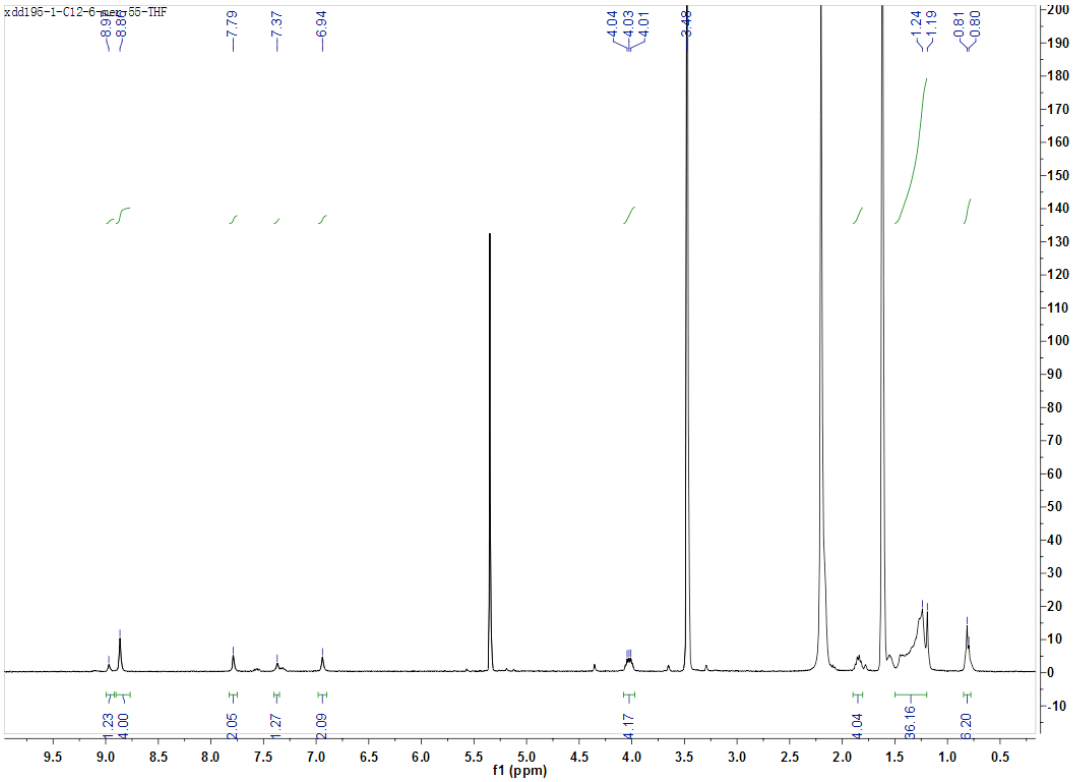


Figure S14. ^{1}H NMR spectrum of macrocycle **2** in THF-d_8 (55 °C).