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Unusual binding selectivity with non-selective homoditopic pillar[5]arene oxime: serendipitous discovery of a unique approach to heterobinuclear metalation in solution

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Supplementary Information

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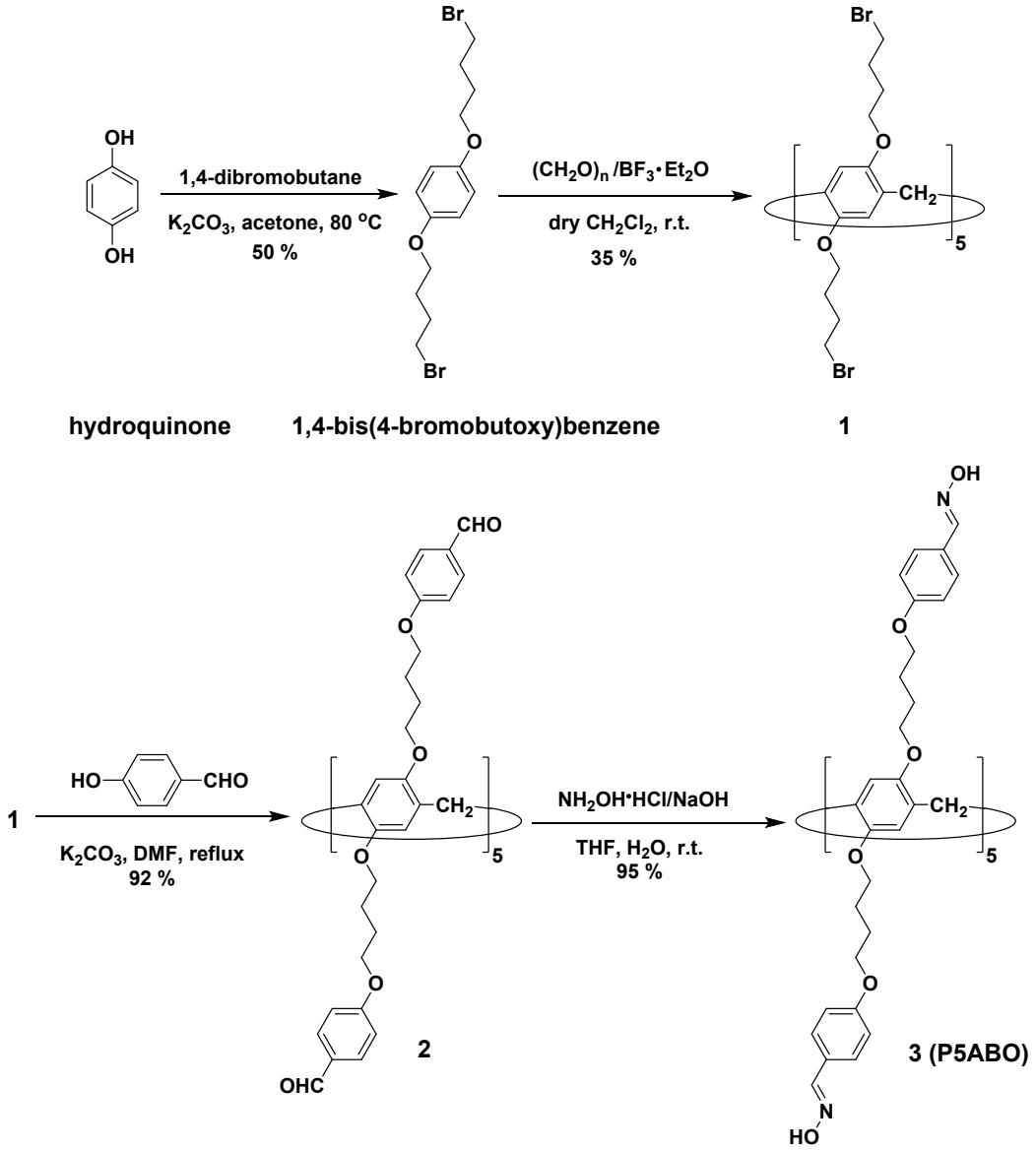
1. General information

Acetone and acetonitrile were used in HPLC grade. Acetonitrile-d_3 and acetone-d_6 were from Cambridge Isotope Laboratories (CIL). All chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE AV II-400 MHz (^{1}H: 400 MHz; ^{13}C: 100 MHz). Chemical shifts are reported in δ values in ppm using tetramethlysilane (TMS) and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = double doublet and m = multiplet. High resolution mass (HRMS) data were obtained by WATERS Q-TOF Premier. UV-vis absorption spectra were recorded on SHIMADZU UV-2450. Scanning electron micrographs were collected with a Hitachi S-450 instrument. Transmission electron microscopy (TEM) experiments were carried out in JEOL–2010 electron microscope operating at 200 kV. Atomic force microscopy (AFM) was carried out on Nanoscope IIIA microscopy (Digital Instruments) in tapping mode. The fluorescent images were obtained with an inverted fluorescence microscope (Olympus IX53) equipped with a 10× ocular lens and a 40× objective and the Image-Pro Plus acquisition software.

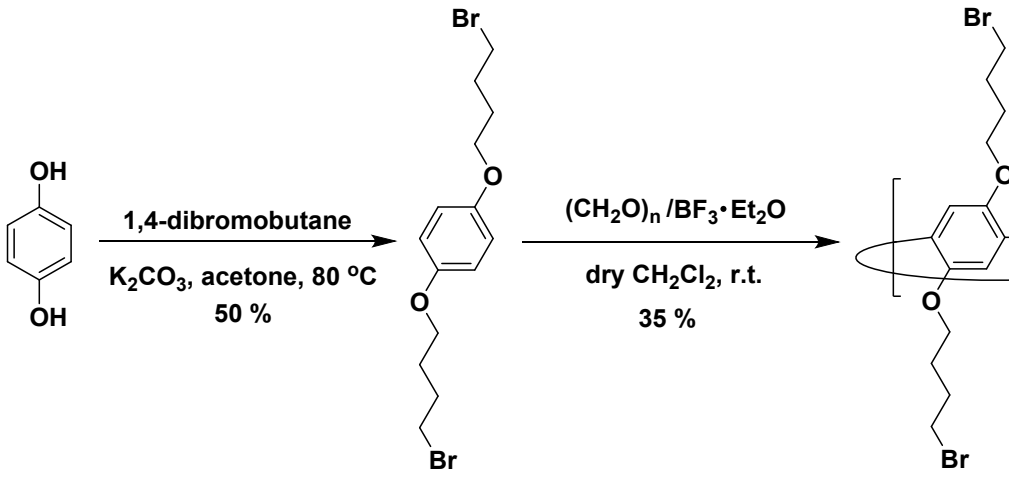
2. Synthesis and characterization

2.1 Synthetic route



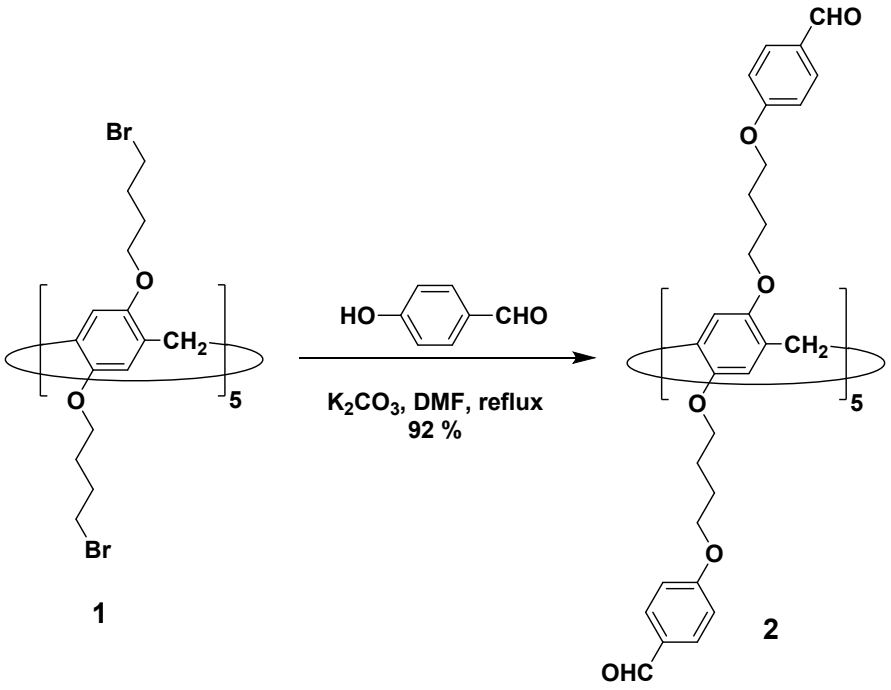
Scheme S1 Synthetic route of pillar[5]arene based benzaldehyde oxime **P5ABO 3**

2.2 Synthesis of 1,4-bis(4-bromobutoxy)benzene



The preparation experiments of 1,4-bis(4-bromobutoxy)benzene and compound **1** were carried out according to our previous reported work.[S1]

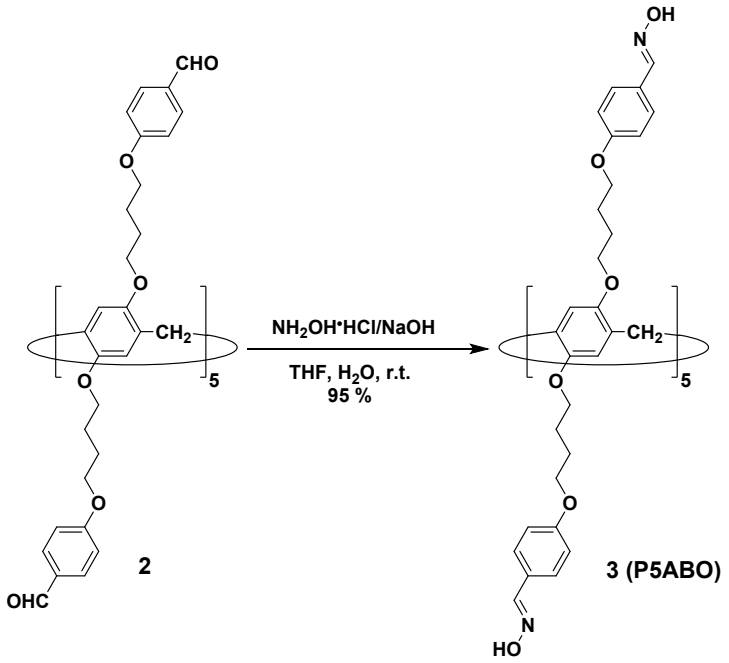
2.3 Synthesis of compound **2**



To a solution of 4-hydroxybenzaldehyde (925 mg, 7.25 mmol) and compound **1** (1.00 g, 0.50 mmol) in dry DMF (40 mL) was added sodium carbonate (1.66 g, 12 mmol) under nitrogen atmosphere. The mixture was stirred under refluxing for 12 h and filtered immediately, cooled to room temperature. After slow addition of ice water to the solution, the precipitate was collected by filtration and washed with distilled water (2×100 mL) and methanol (2×100 mL) to afford compound **2** as a white solid (850 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 5 H), 6.82 (s, 5 H), 4.00 (t,

J = 5.7 Hz, 10 H), 3.86 (t, *J* = 6.5 Hz, 10 H), 3.79 (s, 10 H), 3.55 (t, *J* = 5.7 Hz, 10 H), 1.78 (m, 10 H), 1.51 (m, 10 H), 0.98 (t, *J* = 7.4 Hz, 15 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.65, 163.88, 162.54, 149.85, 131.94, 129.91, 128.51, 115.29, 114.68, 68.08, 67.91, 26.38, 26.06.

2.4 Synthesis of compound **3**



A mixture of NaOH (506 mg, 12.65 mmol) and hydroxylamine hydrochloride (493 mg, 6.32 mmol) was dissolved in redistilled water (20 mL) and THF (40 mL) at room temperature. To the above solution, compound **2** (500 mg, 0.21 mmol) was added and the reaction mixture was stirred for 8 h at room temperature. Dilute hydrochloric acid (0.1 M) was added to adjust the pH to neutral and THF was removed under reduced pressure, the precipitated product was filtered off. Recrystallization in acetone afforded product **3** (503 mg, 95%) as white solid. ^{1}H NMR (400 MHz，CD_3COCD_3) δ = 10.10 (s，10 H), 8.07 (s, 10 H), 7.56 (d, 20 H, J=8.0 Hz), 7.00 (s, 10 H), 6.96 (d, 20 H, J=8.0 Hz), 4.10 (s，30 H), 3.92 (s，10 H), 3.80 (s, 10 H), 2.06 (m, 40 H). ^{13}C NMR (101 MHz, CD_3COCD_3) δ: 26.24, 26.55, 67.70, 68.02, 114.47, 114.64, 125.85, 128.05, 128.50, 148.07, 149.68, 160.17, 205.31. ESI-HRMS (m/z) calcd. for $C_{145}H_{160}N_{10}O_{30}$ $[M+H]^+$ 2523.1408; found $[M+H]^+$ 2523.1433.

3. NMR, UV-vis and ESI-MS spectra

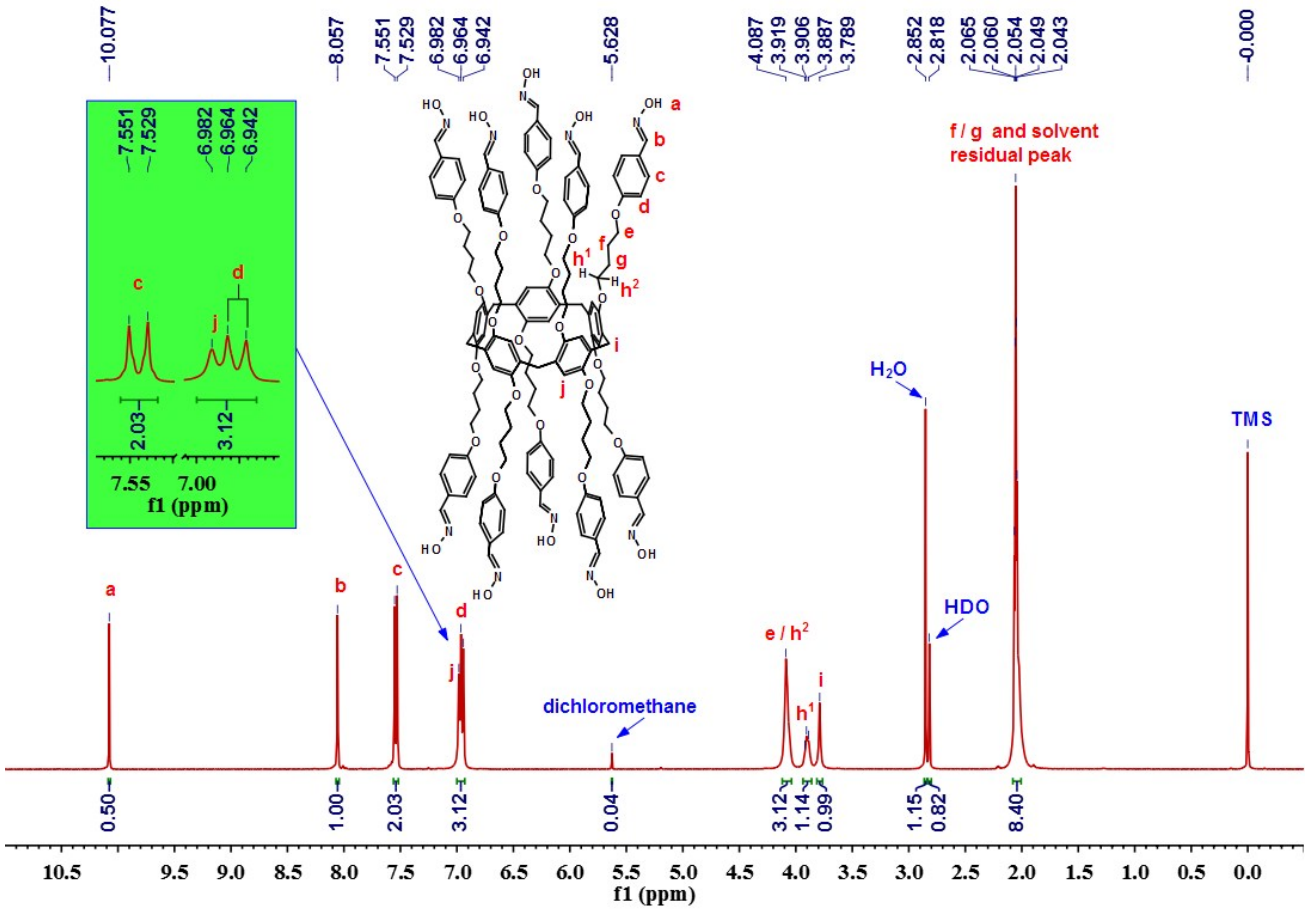


Fig. S1 ^{1}H NMR spectrum of **P5ABO** (400 MHz, acetone-d_6, 298 K)

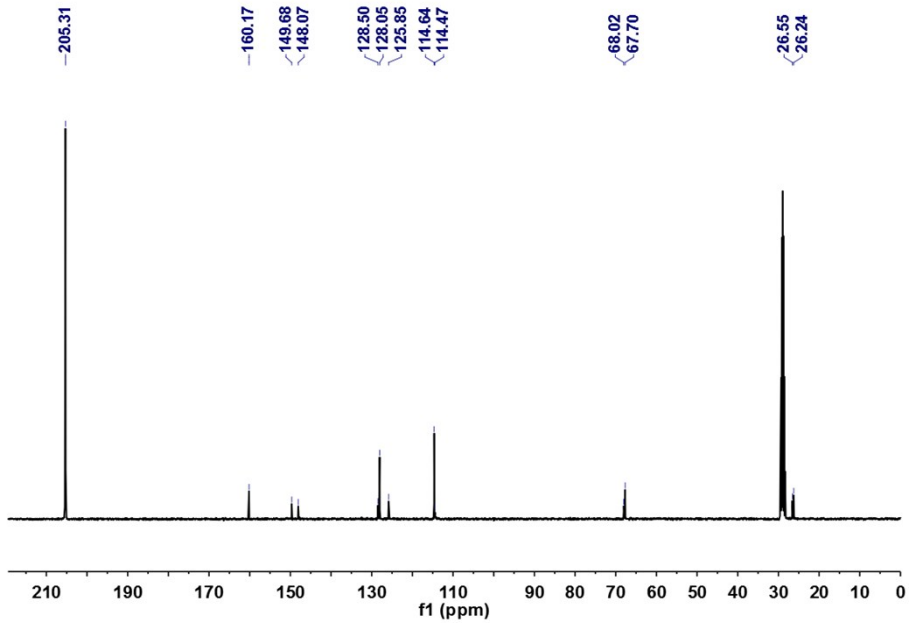


Fig. S1a. ^{13}C NMR spectrum of **P5ABO** (acetone-d_6, 101 MHz, 298 K).

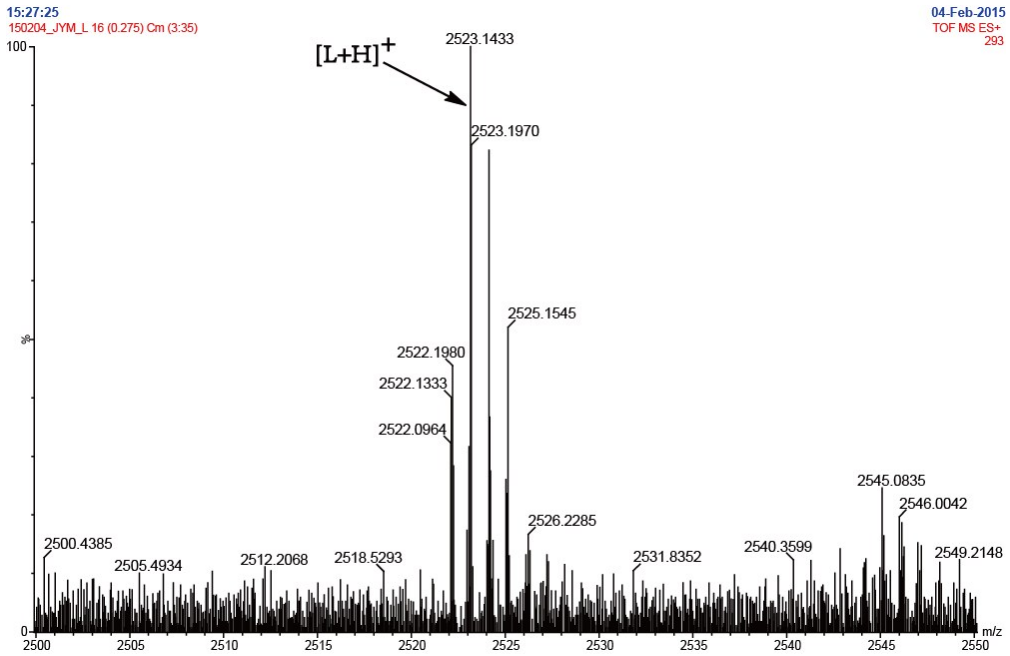


Figure S1b. ESI-HRMS spectrum of **P5ABO**.

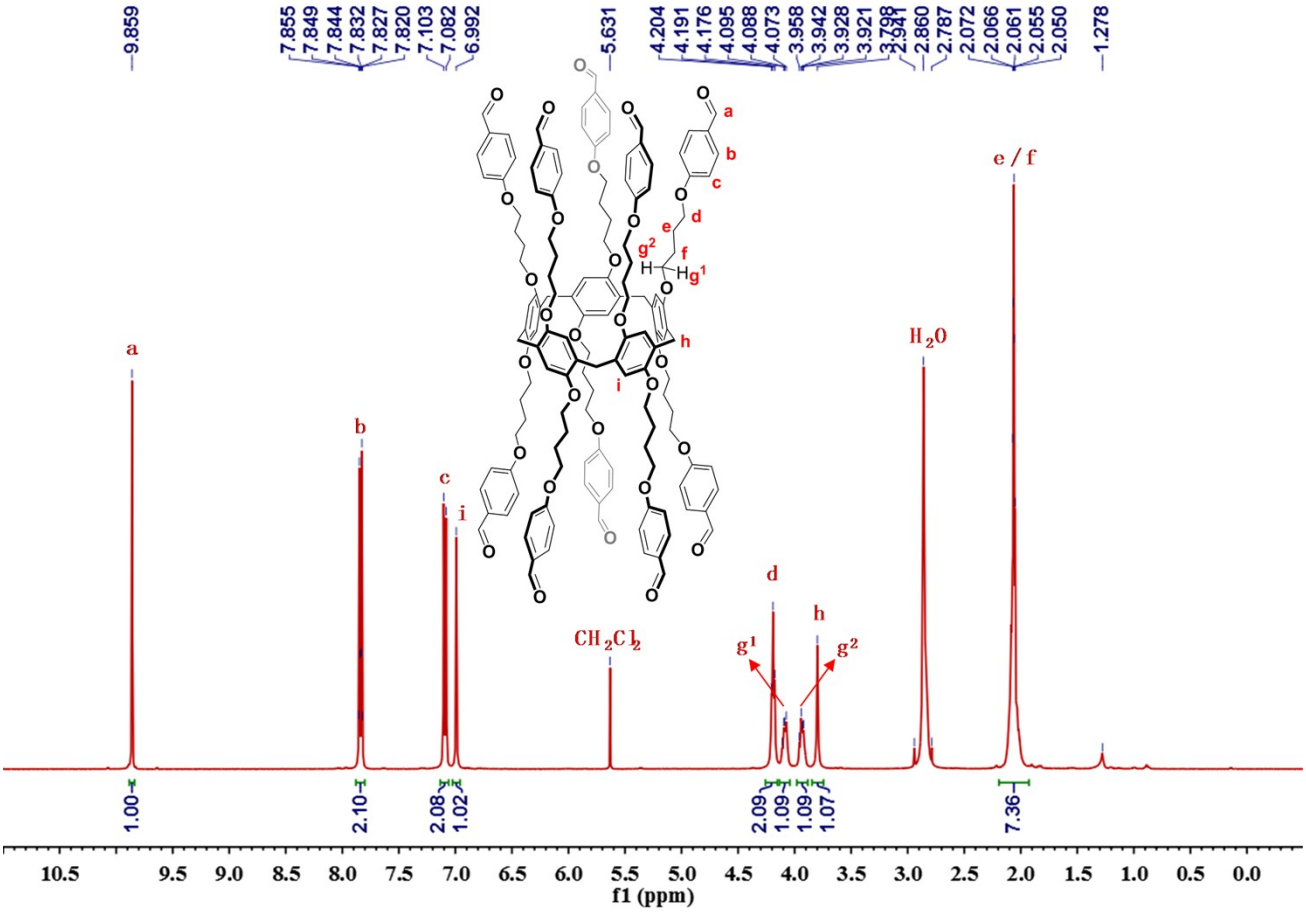


Fig. S2 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **P5ABO** at 298 K.

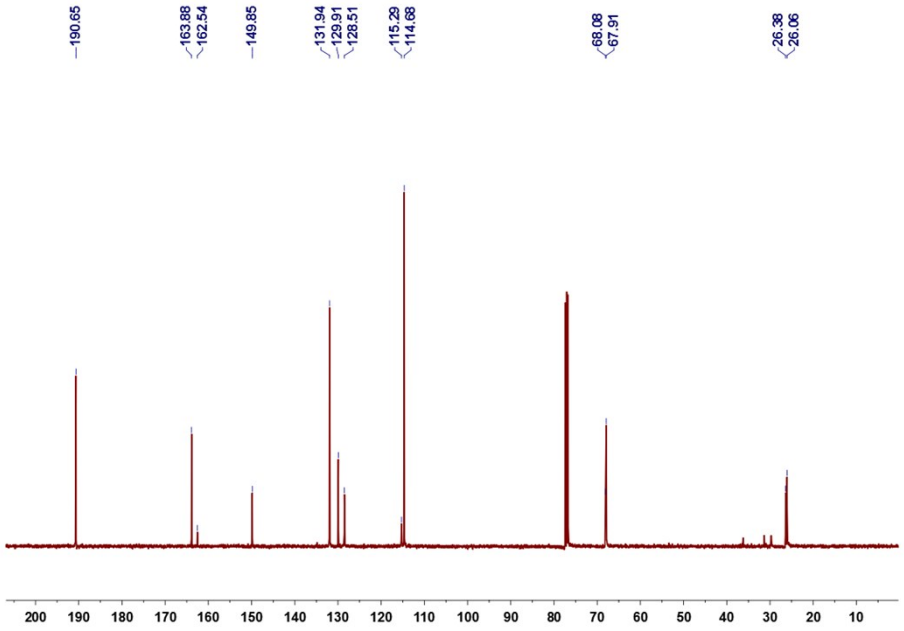


Fig. S2a ^{13}C NMR spectrum of **P5ABO** ($CDCl_3$, 101 MHz, 298 K).

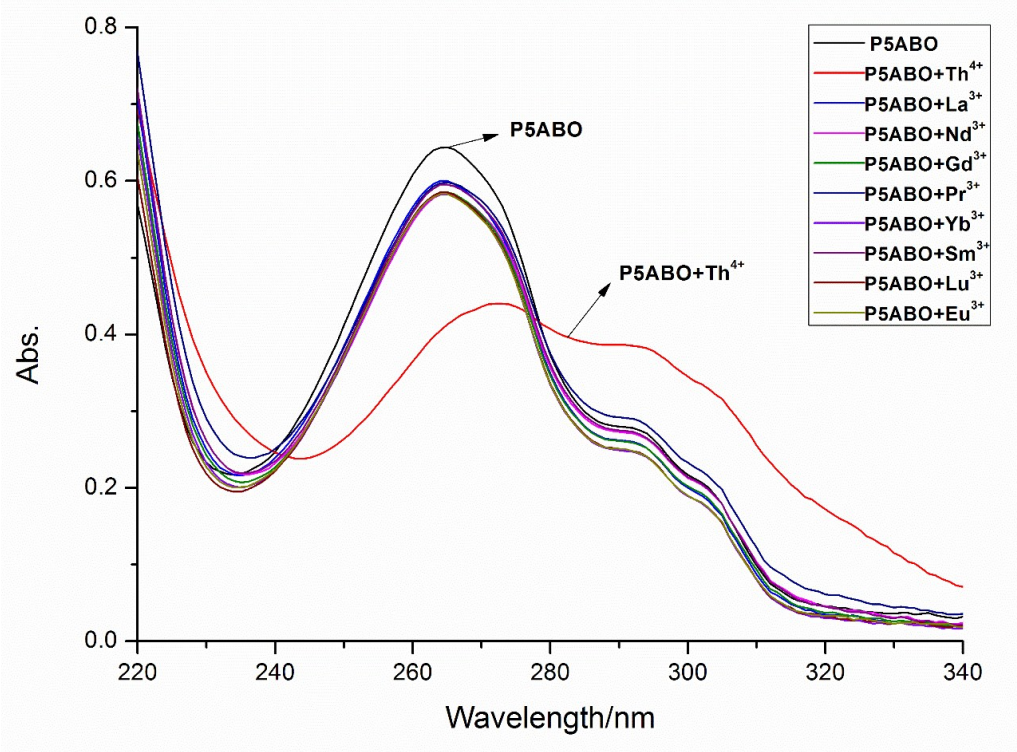


Fig. S3 UV-vis spectra of **P5ABO** (5.0 μM) upon addition of metal nitrate salts (5 equiv. for Th^{4+}, La^{3+}, Nd^{3+}, Gd^{3+}, Pr^{3+}, Er^{3+}, Yb^{3+}, Sm^{3+}, Lu^{3+} and Eu^{3+}) in acetonitrile.

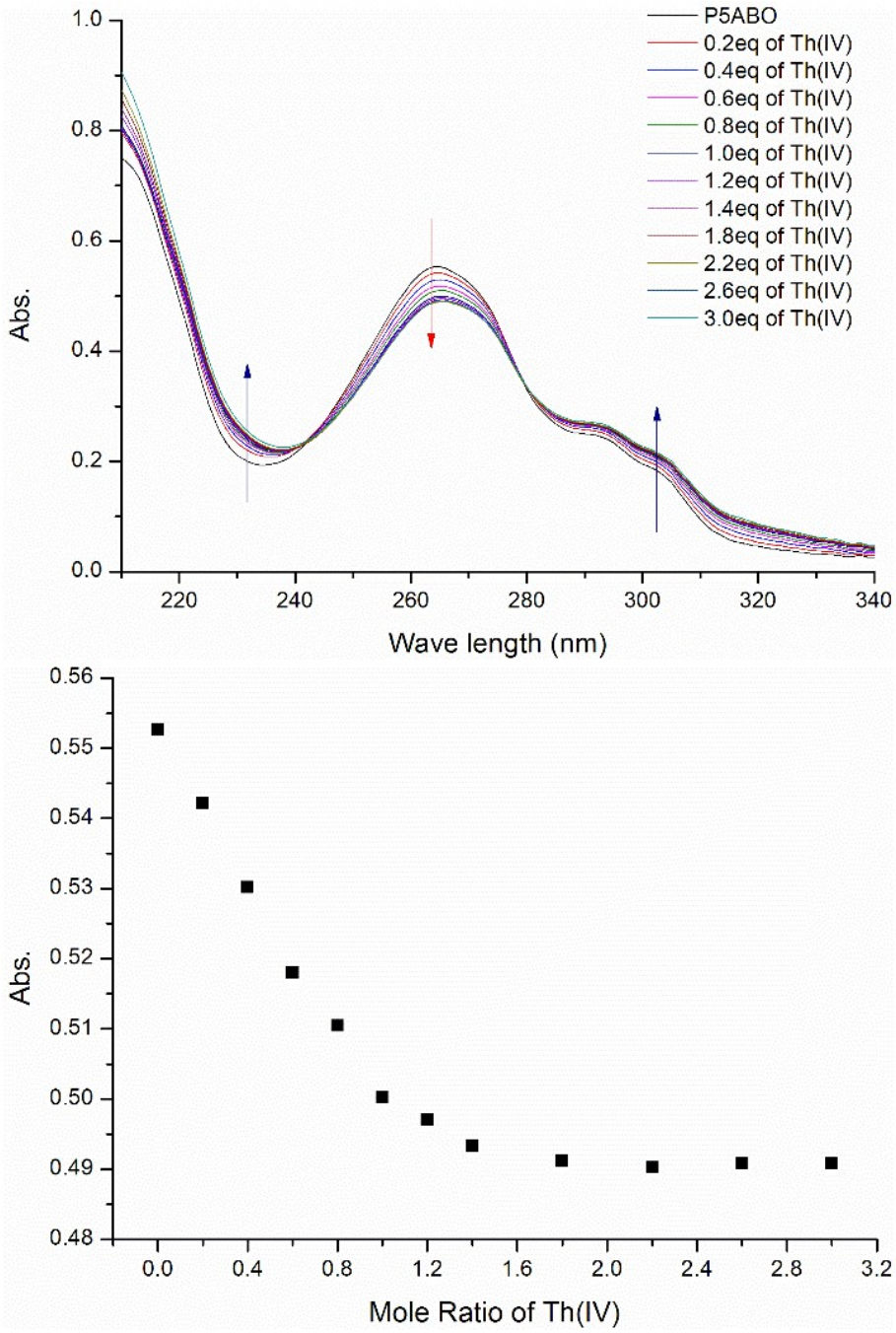


Fig.S4 UV-vis spectra of **P5ABO** (2.5 μM) with continuous equivalent of Th(IV) ($Th(NO_3)_4 \cdot 6H_2O$) in acetonitrile at 20 °C. (top); Plot of the normalized absorbance of **P5ABO** (2.5 μM) in acetonitrile at 264 nm with increasing equivalents of Th(IV) at 20 °C (bottom).

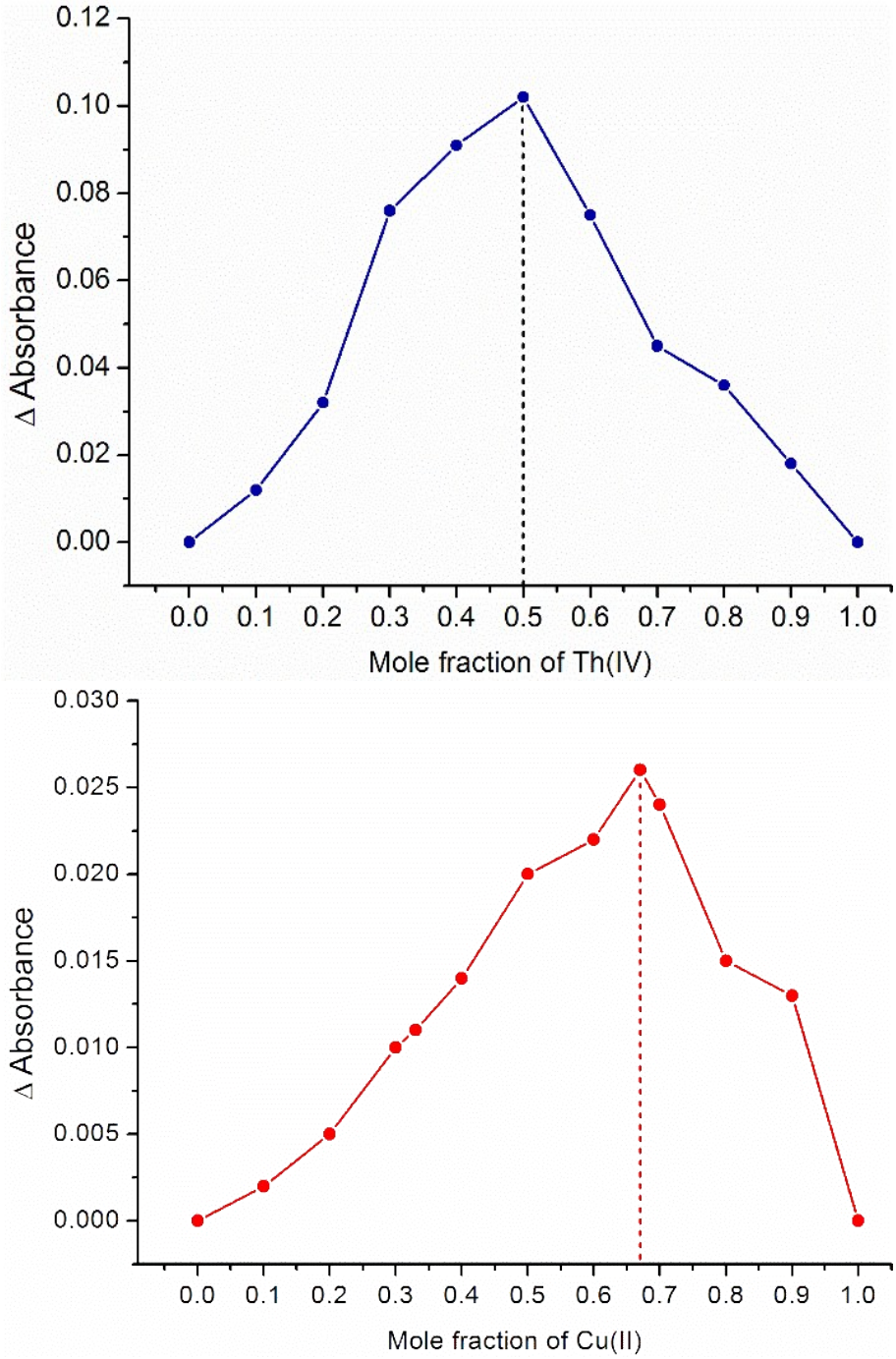


Fig. S5 Job plot of **P5ABO** upon complexation with Th(IV) (top) and Cu(II) ($Cu(NO_3)_2 \cdot 3H_2O$) (bottom) in acetonitrile at 20 °C (mole fraction of metal salts varied by 0.1 from 0.0. to 1.0)

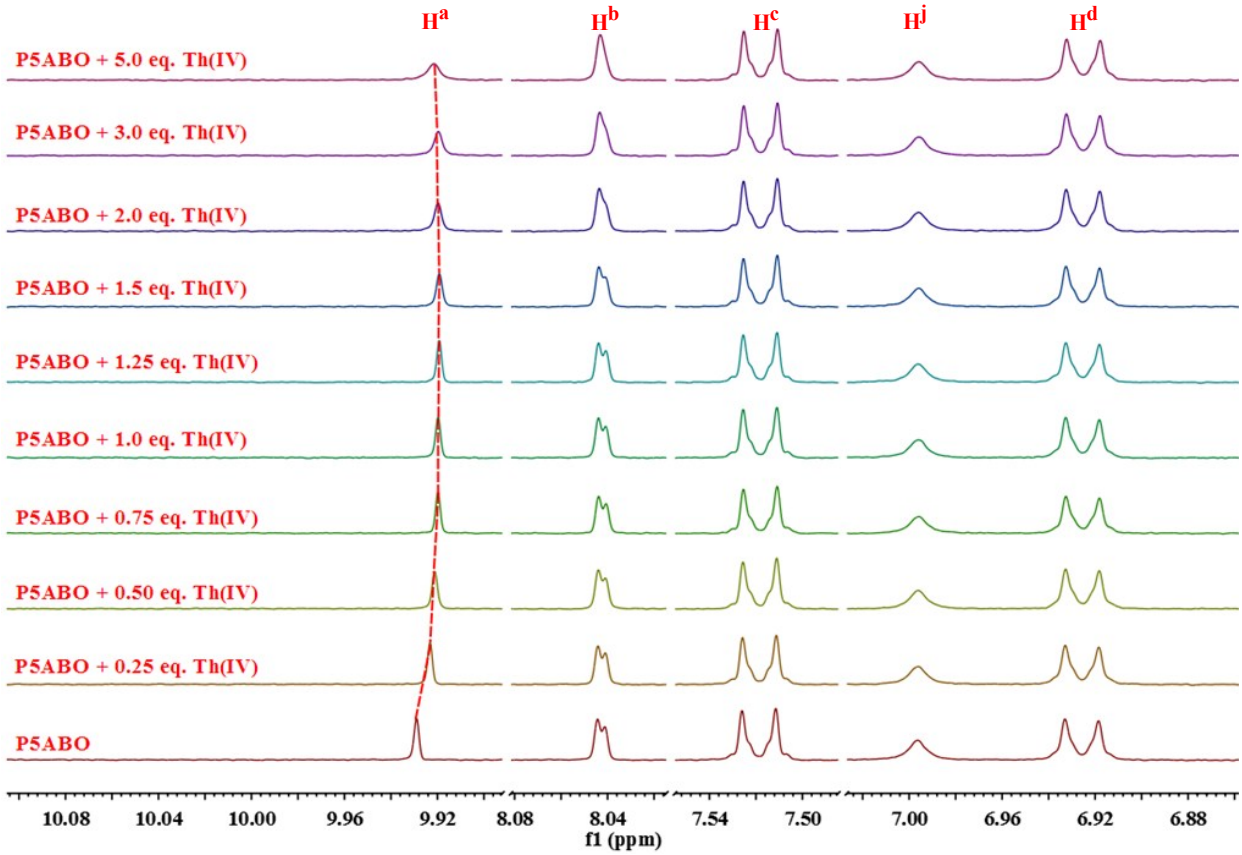


Fig. S6 Partial ^{1}H NMR (600 MHz, 298K) spectra of **P5ABO** (0.25 mM) with different eq. of Th(IV) in deuterated acetone : acetonitrile = 4 : 1 (v/v) mixture

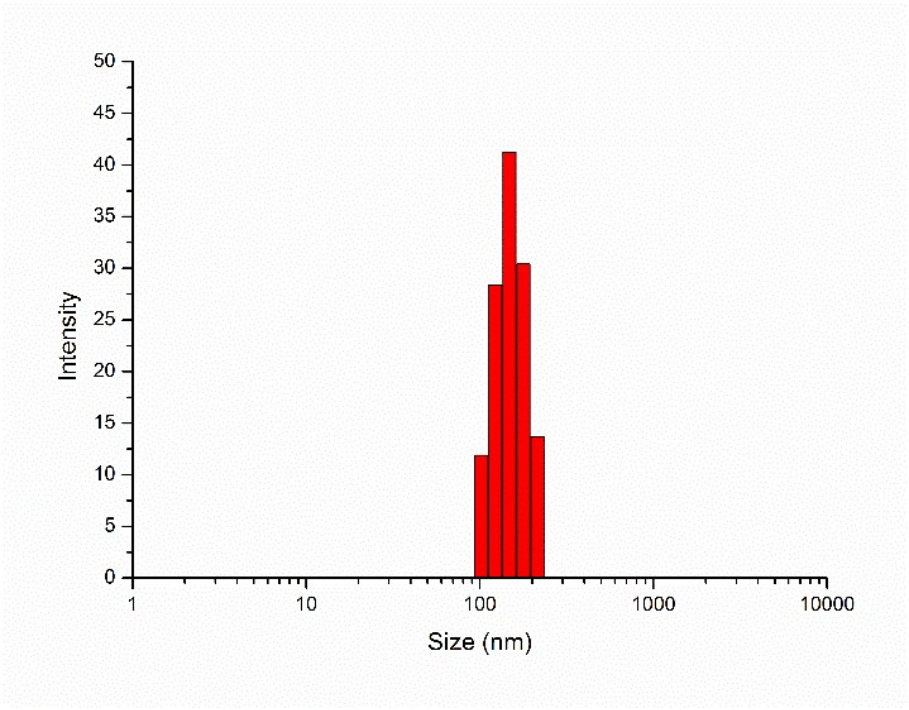


Fig. S7 Particle size distribution of **3**⊃Th(IV) in acetone by dynamic light scattering (DLS) at 20 °C

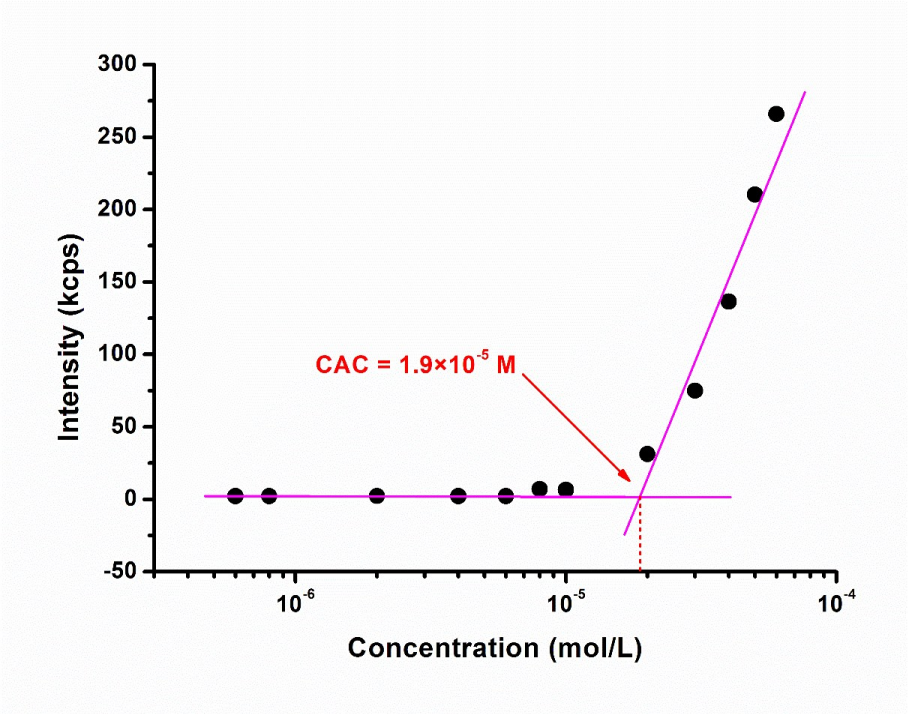


Fig. S8 Critical aggregation concentration (CAC) of **3**⊃Th(IV) in acetone detected by dynamic light scattering (DLS) at 20 °C

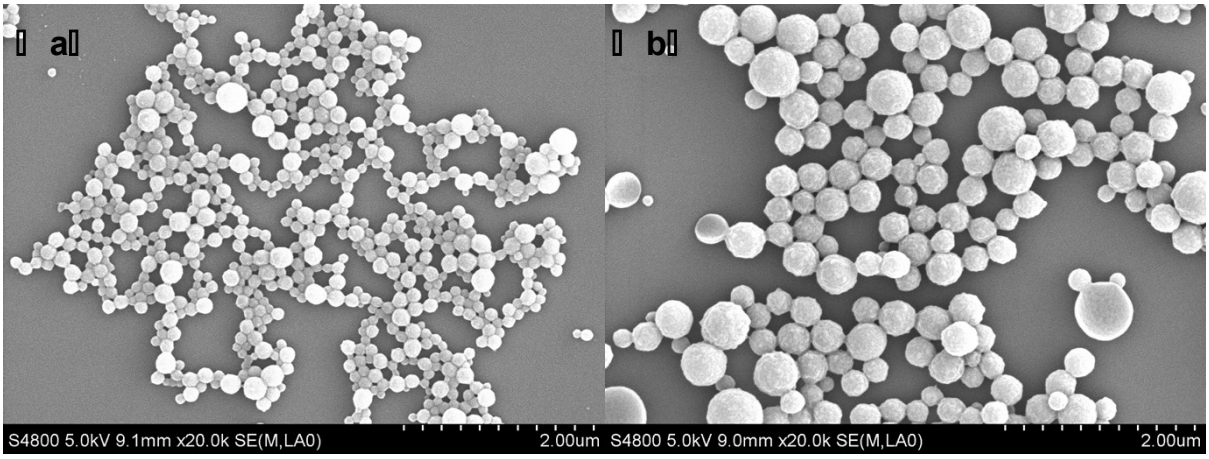


Fig. S9 SEM images of **3**⊃Th(IV) vesicular aggregates in (a) acetone (mean diameter: 138 nm) and (b) acetone-water (1:1, v/v) mixture (mean diameter: 305 nm)

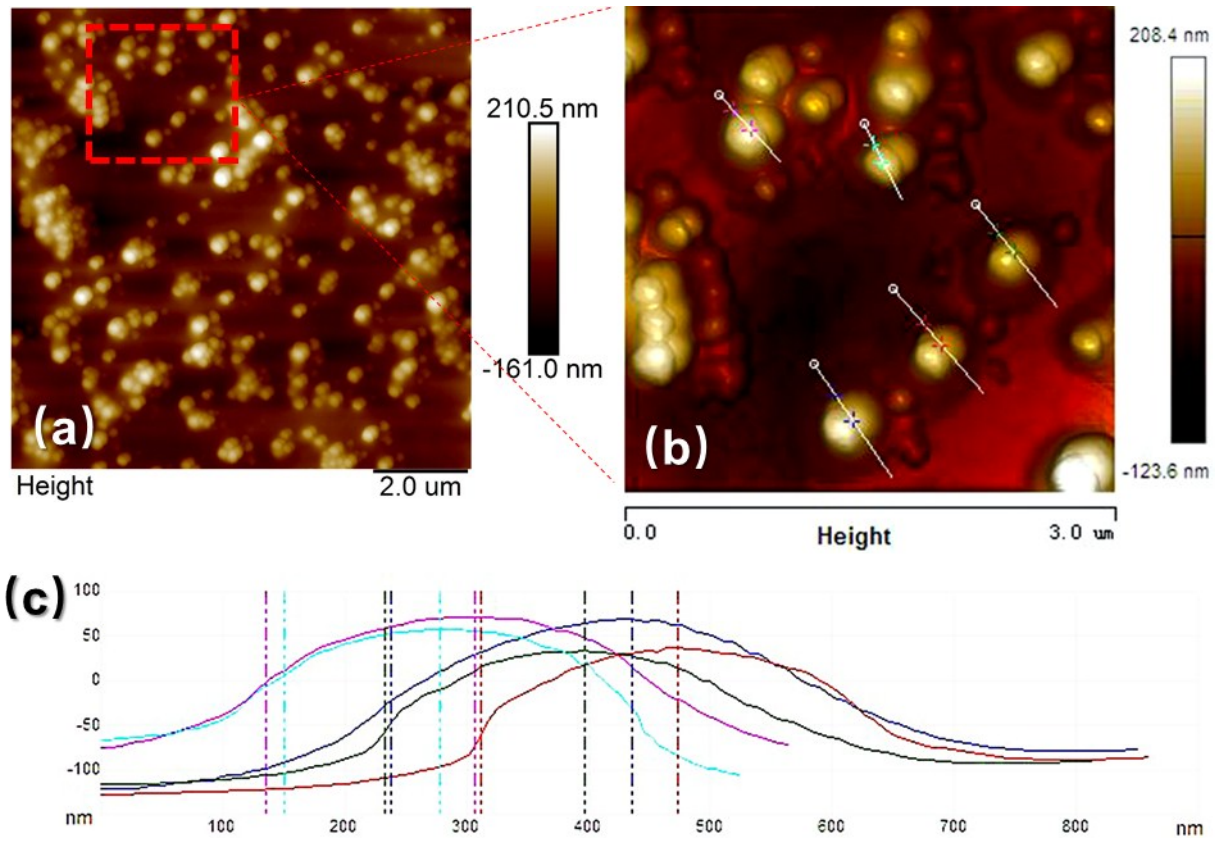


Fig.S10 AFM images of **3**⊃Th(IV) aggregates dried on silica basal laminae in air at 20 °C. (a) typical AFM topographic images; (b) 3D top view image of selected area in red dashed block of (a); (c) Height profile image of (b).

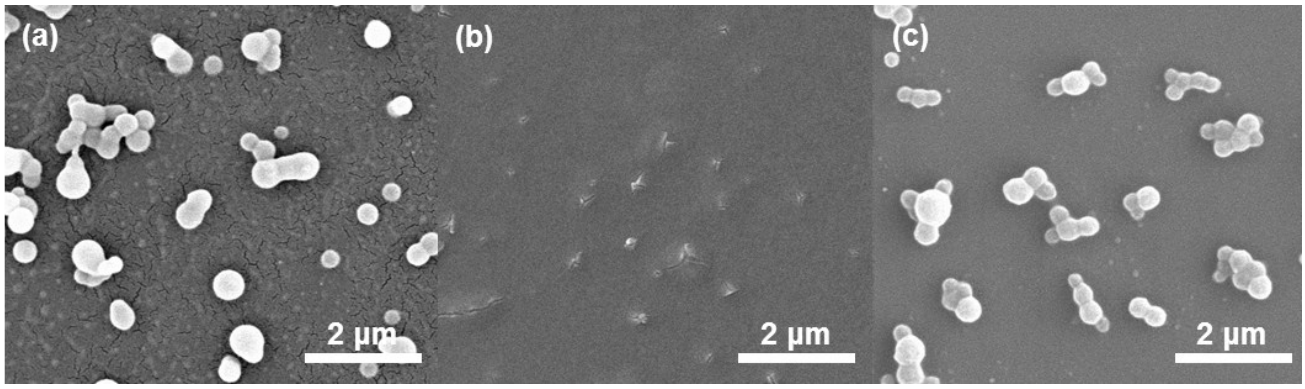


Fig. S11 SEM images of (a) **3**⊃Th(IV) vesicles, (b) **3**⊃Th(IV) with 4.2 equiv. of NaF added (c) **3**⊃Th(IV) with 1 equiv. of Th(IV) after 4.2 equiv. of NaF was added.

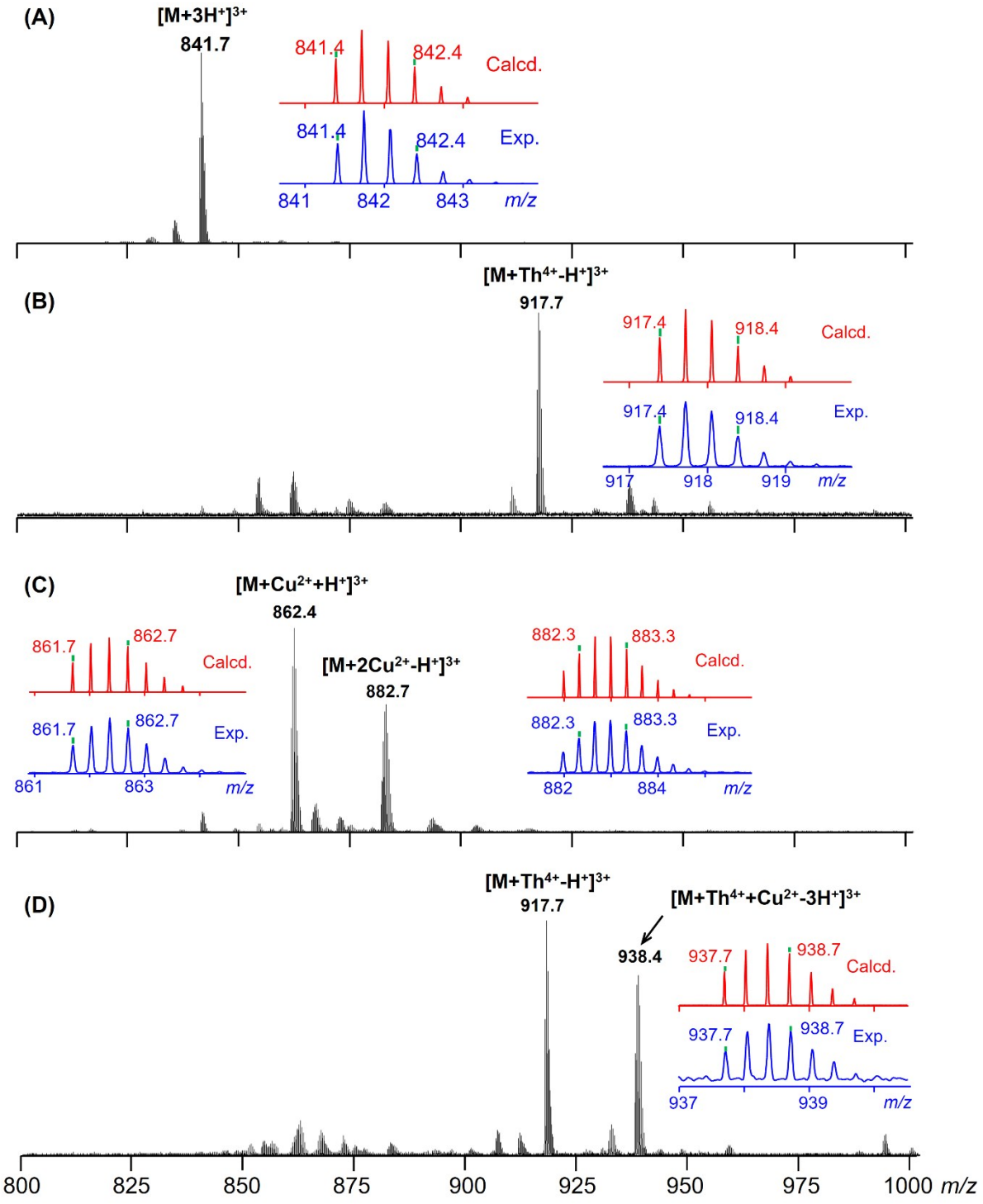


Fig.S12 HRESI-MS spectra of (A) **3**, (B) **3**⊃Th(IV), (C) **3**⊃Cu(II), (D) Th(IV)⊂**3**⊃Cu(II) complex. (Insert spectra are experimental (blue) and calculated (red) isotope distribution of related peaks)

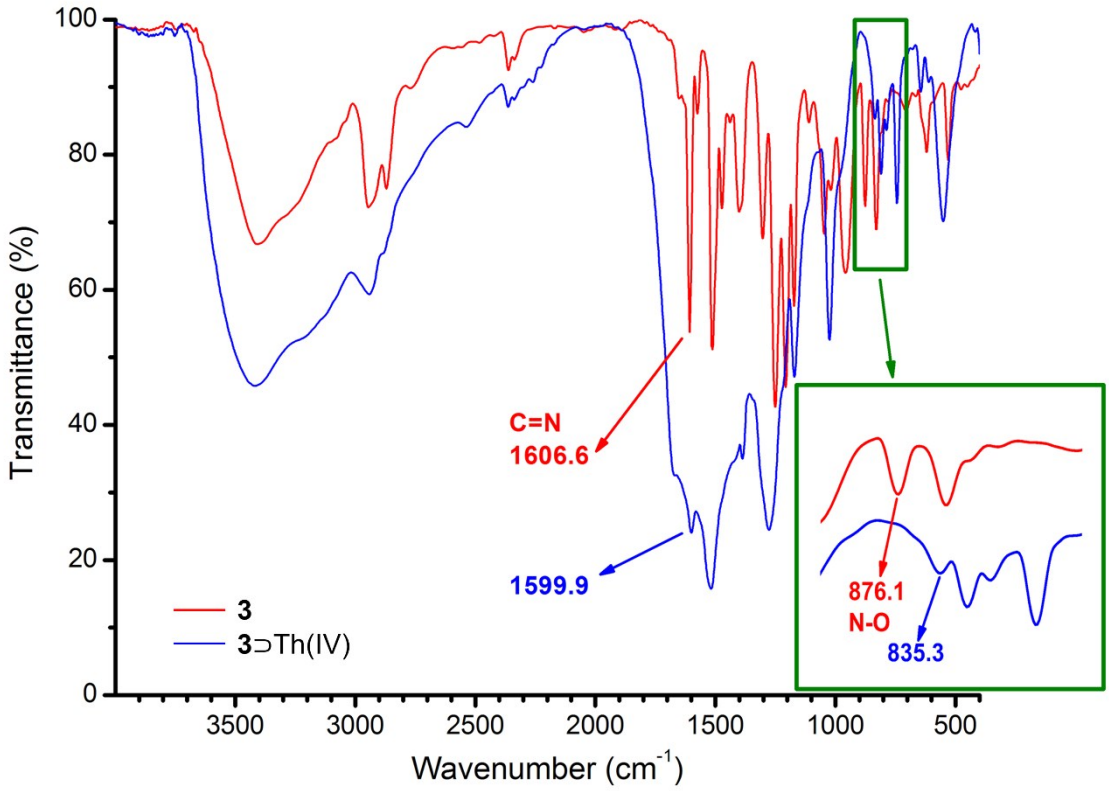


Fig. S13 Infrared spectra of **3** and **3**⊃Th(IV) complex in solid state. The spacing of inserted partial spectra has been adjusted for better view.

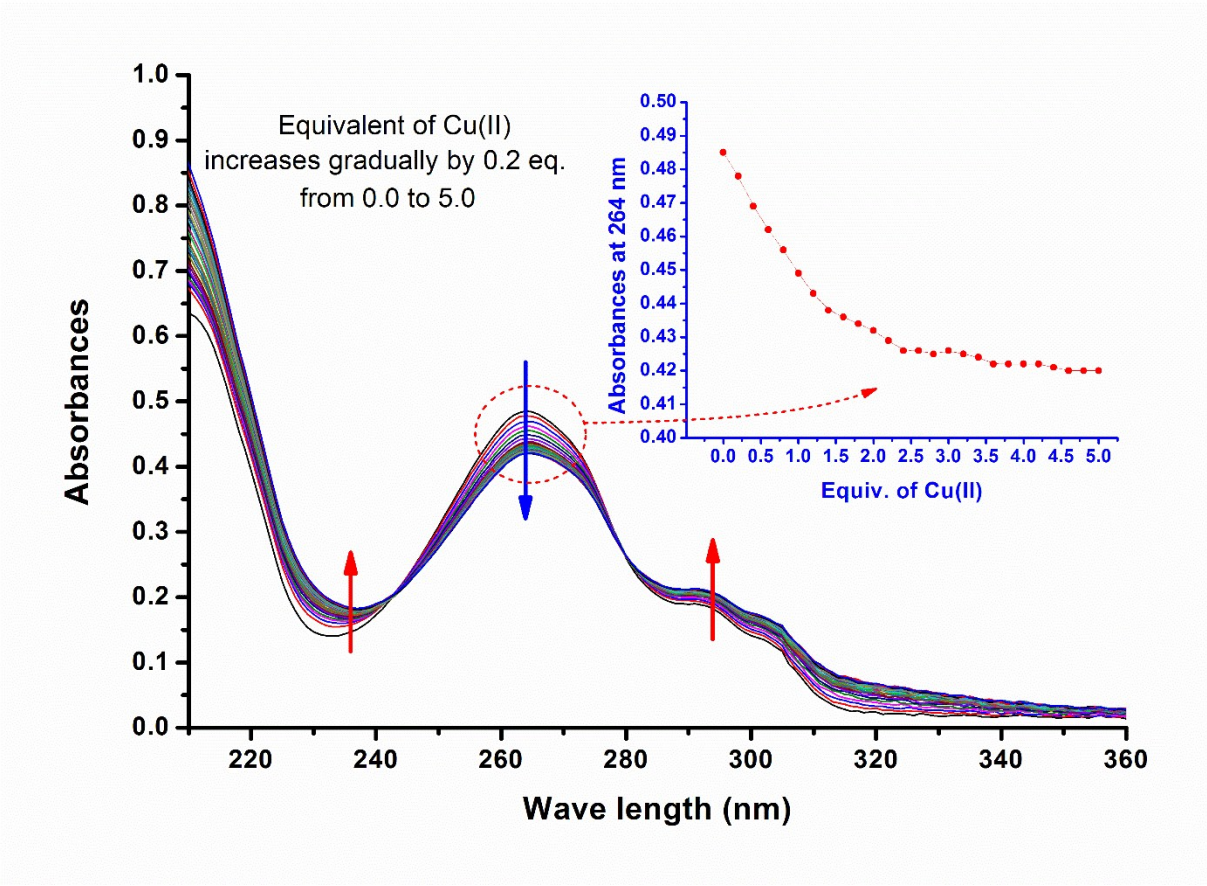


Fig. S14 UV-vis spectra of **P5ABO** with different equivalent of Th(IV) in acetonitrile at 20 °C. Equivalent of Cu(II) ion increases gradually by 0.2 from 0.0 to 5.0.

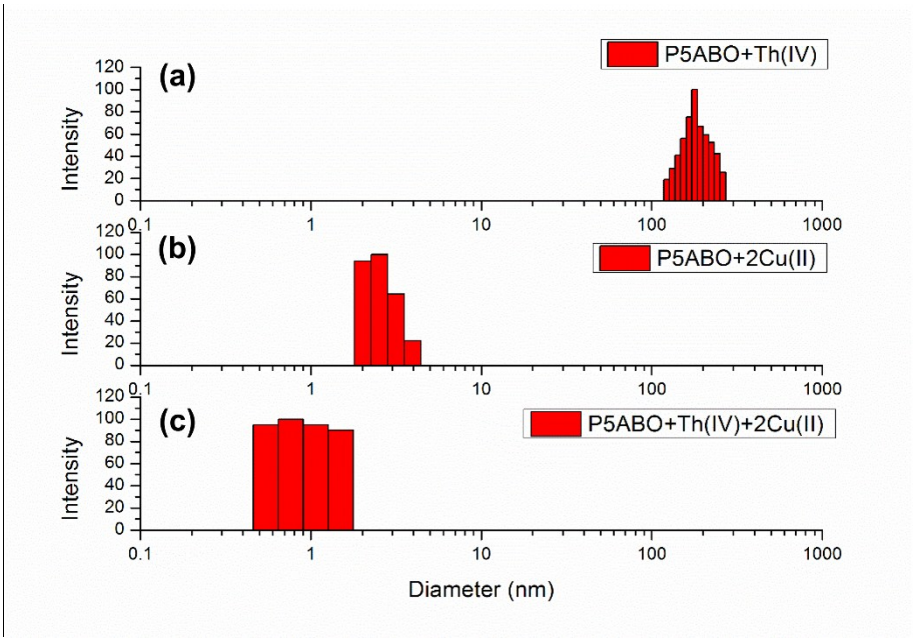


Fig. S15 DLS results of **P5ABO**-metal ion solutions in acetone at 20 °C. (a) **P5ABO** with 1 equiv. of Th(IV) ion added; (b) **P5ABO** with 2 equiv. of Cu(II) ions; (c) Solution (a) added with 2 equiv. of Cu(II) ions.

4. Encapsulation of rhodamine B

A rhodamine B solution (10 mM) was added to an acetone/water (1/1, v/v) solution of **P5ABO** (0.2 mM) with 1.0 equiv. of thorium nitrate hexahydrate and was allowed to stand for 48 h for completion of aggregation. Then the solution was centrifugalized for 30 min, 1/3 volume of the clear supernatant liquid was removed and acetone/water (1/1, v/v) mixture was added to the original volume. The solution was shacked genteelly for 5 min and then was centrifugalized for 30 min again. The clear supernatant liquid was removed again, also to 1/3 volume, one drop of the residuum solution was dropped on a microscope slide for observation.

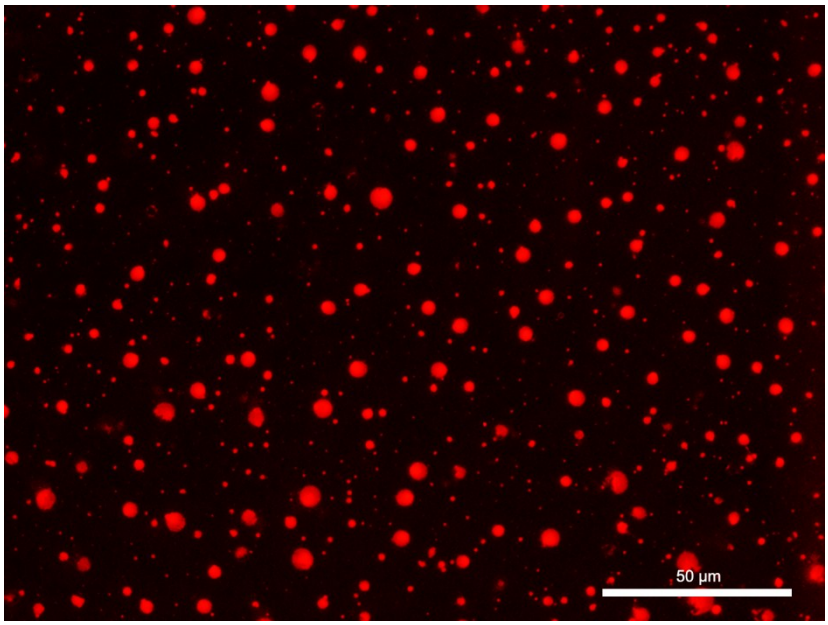


Fig. S16 Florescence image of rhodamine B loaded vesicle aggregates constructed by **3**⊃Th(IV) complex in water/acetone = 1/1 (v/v) mixture under fluorescence microscope at room temperature.

5. Density functional theory (DFT) calculation

The structure of model compound of **3**, whose linkers were replaced with shorter alkyl chains (-CH_2CH_2-), was optimized by the density functional theory (DFT) method at the B3LYP/6-31G level by employing the Gaussian 09 program. [S2]

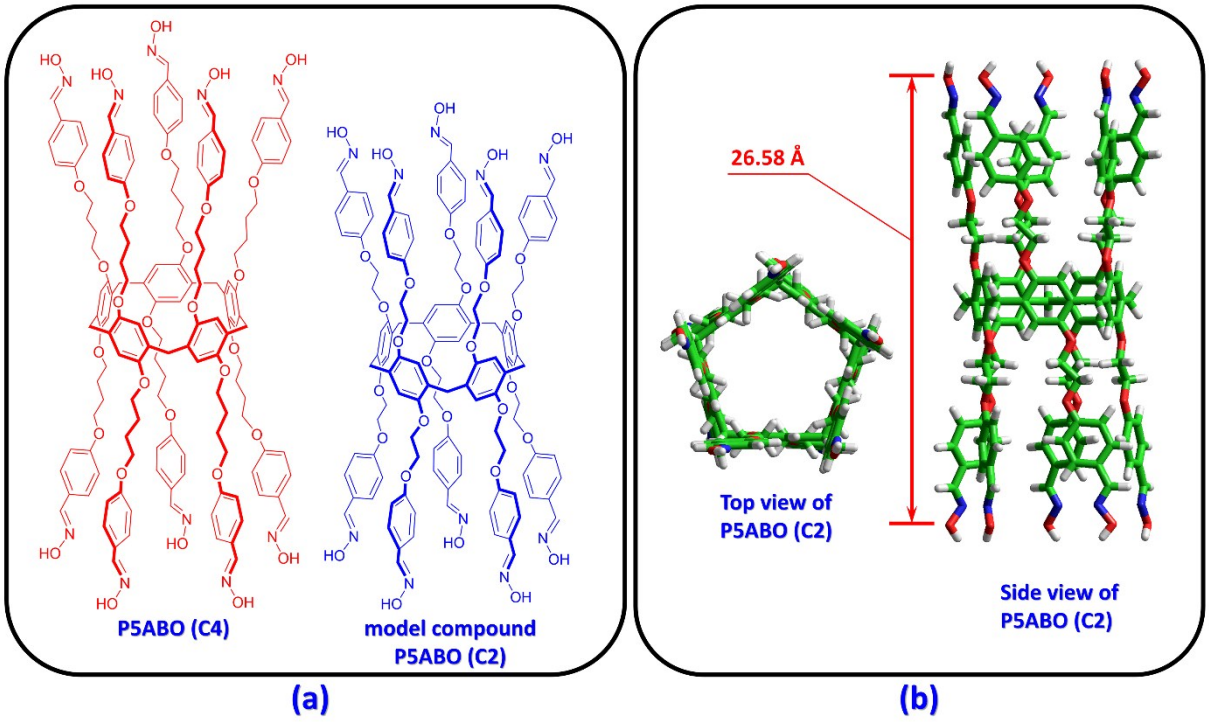


Fig. S17 Chemical structure of **P5ABO (C4)** (compound **3**) and its model compound **P5ABO (C2)** with geometry optimized molecular model at the B3LYP/6-31G level.

Table S1 Atomic coordinates for the optimized structure of **P5ABO (C2)**.

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.200976	-4.134558	0.611386
2	6	0	-0.003724	-4.357367	-0.068808
3	6	0	-1.202859	-4.139842	0.630770
4	6	0	-1.188288	-3.701894	1.958842
5	6	0	0.016135	-3.465147	2.634529
6	6	0	1.215440	-3.696220	1.939352
7	8	0	2.407022	-3.457466	2.648580
8	8	0	-2.394717	-4.381828	-0.076778
9	6	0	3.667475	-3.752259	1.994048
10	6	0	4.757438	-3.488871	3.018431
11	8	0	5.998434	-3.797608	2.325965
12	6	0	7.210352	-3.665925	2.996597
13	6	0	-3.654162	-4.229107	0.626604
14	6	0	-4.745625	-4.629170	-0.350666
15	8	0	-5.985303	-4.464107	0.391470
16	6	0	-7.198125	-4.758035	-0.223781
17	6	0	-7.317557	-5.243248	-1.531408
18	6	0	-8.591250	-5.513258	-2.044846
19	6	0	-9.747760	-5.304656	-1.274874

20	6	0	-9.601571	-4.808817	0.041441
21	6	0	-8.343671	-4.538877	0.561492
22	6	0	7.328416	-3.273767	4.335228
23	6	0	8.601514	-3.185069	4.909921
24	6	0	9.758613	-3.479660	4.169566
25	6	0	9.613853	-3.867699	2.817396
26	6	0	8.356635	-3.960097	2.237384
27	6	0	11.066321	-3.379273	4.815629
28	6	0	-11.056101	-5.607432	-1.852897
29	7	0	-12.148030	-5.444170	-1.181067
30	8	0	-13.293627	-5.824547	-1.998340
31	7	0	12.158574	-3.650658	4.180227
32	8	0	13.303607	-3.469712	5.064106
33	6	0	0.010126	-2.930009	4.059849
34	6	0	0.001061	-4.776331	-1.532446
35	6	0	1.199552	-0.687406	4.113181
36	6	0	-0.002013	-1.408294	4.109902
37	6	0	-1.204459	-0.680899	4.113768
38	6	0	-1.195931	0.717440	4.107351
39	6	0	0.005552	1.438246	4.097686
40	6	0	1.207981	0.711036	4.107728
41	8	0	2.396397	1.464583	4.109113
42	8	0	-2.392914	-1.433946	4.121616
43	6	0	3.659321	0.755040	4.185689
44	6	0	4.744954	1.813887	4.268670
45	8	0	5.988530	1.063623	4.342820
46	6	0	7.197135	1.745319	4.444071
47	6	0	-3.655779	-0.723658	4.191424
48	6	0	-4.741514	-1.781690	4.282363
49	8	0	-5.985188	-1.030968	4.351511
50	6	0	-7.193717	-1.712564	4.455919
51	6	0	-7.305051	-3.106077	4.530474
52	6	0	-8.574846	-3.683615	4.643896
53	6	0	-9.735395	-2.892825	4.682162
54	6	0	-9.597609	-1.487788	4.599232
55	6	0	-8.343625	-0.904024	4.487451
56	6	0	7.308984	3.139019	4.512423
57	6	0	8.579106	3.716449	4.622701
58	6	0	9.739362	2.925375	4.664009
59	6	0	9.600958	1.520051	4.587292
60	6	0	8.346681	0.936449	4.478873
61	6	0	11.043707	3.574323	4.787035
62	6	0	-11.039433	-3.541738	4.808586
63	7	0	-12.134681	-2.857408	4.860225

64	8	0	-13.274798	-3.756680	4.988659
65	7	0	12.138663	2.889727	4.841484
66	8	0	13.279254	3.788969	4.965684
67	6	0	-0.005830	2.959129	4.034167
68	6	0	1.190819	3.714095	1.925989
69	6	0	-0.012994	3.481945	2.604295
70	6	0	-1.213000	3.705558	1.907787
71	6	0	-1.199803	4.132413	0.576353
72	6	0	0.004168	4.350861	-0.106440
73	6	0	1.204070	4.140945	0.594421
74	8	0	2.395106	4.378890	-0.115589
75	8	0	-2.404034	3.472927	2.619677
76	6	0	3.655096	4.232977	0.588008
77	6	0	4.745174	4.629709	-0.392086
78	8	0	5.985597	4.471640	0.350448
79	6	0	7.197593	4.766793	-0.266034
80	6	0	-3.664381	3.758474	1.960907
81	6	0	-4.755002	3.510650	2.988412
82	8	0	-5.995152	3.809441	2.290123
83	6	0	-7.208025	3.688882	2.961097
84	6	0	-7.327949	3.320139	4.306174
85	6	0	-8.601742	3.241870	4.880760
86	6	0	-9.757754	3.523642	4.133793
87	6	0	-9.611146	3.888294	2.775307
88	6	0	-8.353174	3.970312	2.195339
89	6	0	7.315791	5.245632	-1.576138
90	6	0	8.588522	5.519346	-2.090039
91	6	0	9.745311	5.321108	-1.317853
92	6	0	9.600542	4.830922	0.000743
93	6	0	8.343610	4.557024	0.521099
94	6	0	11.052773	5.627705	-1.895849
95	6	0	-11.066365	3.434612	4.779702
96	7	0	-12.157799	3.695062	4.138233
97	8	0	-13.304029	3.529554	5.023644
98	7	0	12.144762	5.473185	-1.221836
99	8	0	13.289545	5.855615	-2.039376
100	6	0	-0.002240	4.757730	-1.573713
101	6	0	1.194337	2.980032	-2.936507
102	6	0	-0.009254	3.557317	-2.510387
103	6	0	-1.209611	2.967926	-2.942442
104	6	0	-1.197235	1.832438	-3.758697
105	6	0	0.006365	1.246186	-4.172662
106	6	0	1.206776	1.844326	-3.752585
107	8	0	2.397364	1.237099	-4.192394

108	8	0	-2.400206	3.578359	-2.506776
109	6	0	3.658587	1.859463	-3.837225
110	6	0	4.746286	1.045073	-4.515515
111	8	0	5.989020	1.699511	-4.138493
112	6	0	7.198949	1.197572	-4.607567
113	6	0	-3.662187	3.044083	-2.982390
114	6	0	-4.747641	3.953154	-2.432839
115	8	0	-5.992554	3.385954	-2.925860
116	6	0	-7.200109	3.997221	-2.603123
117	6	0	-7.308751	5.167393	-1.842508
118	6	0	-8.577792	5.699772	-1.587850
119	6	0	-9.740217	5.081968	-2.078525
120	6	0	-9.605002	3.897607	-2.839477
121	6	0	-8.351826	3.361295	-3.099143
122	6	0	7.312704	0.093990	-5.461237
123	6	0	8.583769	-0.317396	-5.878301
124	6	0	9.743216	0.354105	-5.455695
125	6	0	9.602910	1.462344	-4.588500
126	6	0	8.347657	1.879830	-4.169346
127	6	0	11.048851	-0.108374	-5.923649
128	6	0	-11.043479	5.679502	-1.792042
129	7	0	-12.140278	5.155782	-2.231524
130	8	0	-13.279164	5.956863	-1.800014
131	7	0	12.142872	0.483139	-5.572216
132	8	0	13.285187	-0.183808	-6.184857
133	6	0	-0.001502	-0.024470	-5.011458
134	6	0	1.194973	-1.868880	-3.741572
135	6	0	-0.008966	-1.285621	-4.158730
136	6	0	-1.209026	-1.879325	-3.731918
137	6	0	-1.195881	-3.008176	-2.906469
138	6	0	0.008013	-3.583117	-2.478116
139	6	0	1.208089	-2.997318	-2.915682
140	8	0	2.398883	-3.603679	-2.475316
141	8	0	-2.399659	-1.275613	-4.176361
142	6	0	3.660174	-3.076588	-2.960562
143	6	0	4.746236	-3.976917	-2.398014
144	8	0	5.990233	-3.421550	-2.906498
145	6	0	7.198075	-4.027969	-2.575772
146	6	0	-3.661162	-1.892764	-3.813458
147	6	0	-4.749067	-1.084293	-4.498625
148	8	0	-5.991659	-1.733813	-4.113103
149	6	0	-7.201717	-1.236475	-4.586594
150	6	0	-7.315344	-0.144784	-5.455372
151	6	0	-8.586690	0.262403	-5.875895

152	6	0	-9.746295	-0.401196	-5.441496
153	6	0	-9.605946	-1.497740	-4.559489
154	6	0	-8.350482	-1.911146	-4.137010
155	6	0	7.308082	-5.181039	-1.789720
156	6	0	8.577322	-5.710682	-1.529950
157	6	0	9.738501	-5.106753	-2.040600
158	6	0	9.601955	-3.938980	-2.826476
159	6	0	8.348601	-3.405565	-3.091422
160	6	0	11.041929	-5.701200	-1.748558
161	6	0	-11.052146	0.056768	-5.913352
162	7	0	-12.146449	-0.528108	-5.551438
163	8	0	-13.289129	0.131838	-6.170986
164	7	0	12.137580	-5.189897	-2.205451
165	8	0	13.276966	-5.984276	-1.762941
166	1	0	2.120599	-4.284000	0.061683
167	1	0	-2.108186	-3.504827	2.492776
168	1	0	3.808928	-3.108982	1.117363
169	1	0	3.701794	-4.799901	1.672684
170	1	0	4.749148	-2.441171	3.341985
171	1	0	4.627646	-4.134790	3.894533
172	1	0	-3.795866	-3.190001	0.946793
173	1	0	-3.686125	-4.878291	1.509512
174	1	0	-4.739118	-3.981254	-1.235309
175	1	0	-4.616252	-5.670187	-0.668697
176	1	0	-6.445415	-5.413460	-2.150235
177	1	0	-8.683961	-5.895733	-3.057286
178	1	0	-10.488481	-4.639258	0.640728
179	1	0	-8.218694	-4.154513	1.567071
180	1	0	6.455878	-3.039174	4.931982
181	1	0	8.693203	-2.886902	5.950401
182	1	0	10.501276	-4.090982	2.236761
183	1	0	8.232591	-4.252385	1.201171
184	1	0	11.106250	-3.068794	5.860172
185	1	0	-11.096691	-5.981701	-2.876299
186	1	0	-14.053304	-5.661373	-1.404329
187	1	0	14.063514	-3.694694	4.490936
188	1	0	-0.871450	-3.312710	4.580989
189	1	0	0.896947	-3.296419	4.583801
190	1	0	0.884600	-5.390852	-1.724852
191	1	0	-0.883919	-5.385856	-1.733460
192	1	0	2.121710	-1.252555	4.090355
193	1	0	-2.118113	1.282394	4.079610
194	1	0	3.807309	0.129852	3.297105
195	1	0	3.691488	0.116363	5.076179

196	1	0	4.737821	2.456990	3.380534
197	1	0	4.609168	2.435062	5.161571
198	1	0	-3.689030	-0.077652	5.076576
199	1	0	-3.802825	-0.105812	3.297543
200	1	0	-4.605597	-2.396409	5.179728
201	1	0	-4.735005	-2.431361	3.399023
202	1	0	-6.429660	-3.742717	4.502669
203	1	0	-8.661331	-4.764484	4.707943
204	1	0	-10.487947	-0.870291	4.621659
205	1	0	-8.224861	0.170981	4.418026
206	1	0	6.433800	3.775840	4.482114
207	1	0	8.666023	4.797571	4.681829
208	1	0	10.491025	0.902256	4.612193
209	1	0	8.227343	-0.138821	4.414998
210	1	0	11.078680	4.663128	4.835518
211	1	0	-11.073926	-4.630320	4.861907
212	1	0	-14.037461	-3.144944	5.015393
213	1	0	14.041634	3.176985	4.994870
214	1	0	0.876760	3.345338	4.551047
215	1	0	-0.891712	3.331055	4.555814
216	1	0	2.111243	3.521890	2.460945
217	1	0	-2.119732	4.275564	0.025406
218	1	0	3.799112	3.196173	0.914635
219	1	0	3.686355	4.887763	1.466767
220	1	0	4.739582	3.976921	-1.273143
221	1	0	4.613414	5.668720	-0.715682
222	1	0	-3.698159	4.801420	1.624561
223	1	0	-3.805772	3.102759	1.093515
224	1	0	-4.625619	4.170002	3.854512
225	1	0	-4.747197	2.468057	3.328122
226	1	0	-6.456165	3.096245	4.908160
227	1	0	-8.694827	2.962013	5.926199
228	1	0	-10.497784	4.101984	2.189874
229	1	0	-8.227657	4.245259	1.154574
230	1	0	6.443449	5.408589	-2.196531
231	1	0	8.680170	5.896909	-3.104434
232	1	0	10.487810	4.669280	0.601709
233	1	0	8.219644	4.177881	1.528763
234	1	0	11.092773	5.997069	-2.921041
235	1	0	-11.107671	3.142177	5.829381
236	1	0	-14.063151	3.744629	4.445660
237	1	0	14.049313	5.698789	-1.443767
238	1	0	0.882386	5.365845	-1.780303
239	1	0	-0.886123	5.370365	-1.770447

240	1	0	2.115163	3.427247	-2.586401
241	1	0	-2.118017	1.356830	-4.069000
242	1	0	3.802533	1.851727	-2.750207
243	1	0	3.692329	2.896712	-4.190681
244	1	0	4.737454	0.006525	-4.163758
245	1	0	4.613846	1.055390	-5.603615
246	1	0	-3.694658	3.042482	-4.078189
247	1	0	-3.809232	2.018531	-2.623056
248	1	0	-4.613136	4.977868	-2.798211
249	1	0	-4.737191	3.960285	-1.336420
250	1	0	-6.431833	5.666547	-1.449707
251	1	0	-8.662150	6.611088	-1.002810
252	1	0	-10.496700	3.410828	-3.216889
253	1	0	-8.235145	2.451927	-3.677060
254	1	0	6.438227	-0.445002	-5.803615
255	1	0	8.672038	-1.170012	-6.545544
256	1	0	10.492372	1.982363	-4.252445
257	1	0	8.227004	2.725080	-3.501800
258	1	0	11.085622	-0.973262	-6.586726
259	1	0	-11.076014	6.590460	-1.193599
260	1	0	-14.043248	5.476970	-2.177482
261	1	0	14.046845	0.333178	-5.854436
262	1	0	-0.885731	-0.021726	-5.654481
263	1	0	0.882830	-0.034654	-5.654156
264	1	0	2.115403	-1.396311	-4.057635
265	1	0	-2.116149	-3.452302	-2.551063
266	1	0	3.807663	-2.045603	-2.617490
267	1	0	3.691246	-3.092209	-4.056343
268	1	0	4.739472	-3.963156	-1.301606
269	1	0	4.608591	-5.008115	-2.743478
270	1	0	-3.696855	-2.933354	-4.156678
271	1	0	-3.803555	-1.874031	-2.726426
272	1	0	-4.617877	-1.106336	-5.586695
273	1	0	-4.739212	-0.042045	-4.157985
274	1	0	-6.440596	0.387836	-5.807002
275	1	0	-8.675055	1.105520	-6.555054
276	1	0	-10.495435	-2.011945	-4.214627
277	1	0	-8.229755	-2.747156	-3.457988
278	1	0	6.432096	-5.669123	-1.381201
279	1	0	8.662762	-6.609087	-0.925382
280	1	0	10.492818	-3.462844	-3.219102
281	1	0	8.230849	-2.508846	-3.688613
282	1	0	11.075728	-6.599101	-1.130763
283	1	0	-11.088913	0.912241	-6.588540

284	1	0	-14.050778	-0.379563	-5.831917
285	1	0	14.040091	-5.514498	-2.154774

The total electronic energy is calculated to be -7636.90856653 a.u.

[S1] Y. Fang, L. Wu, J. Liao, L. Chen, Y. Yang, N. Liu, L. He, S. Zou, W. Feng and L. Yuan, *RSC Advances*, 2013, **3**, 12376-12383.

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