Electronic Supplementary Information

Synthesis, structure, and anion binding of functional oxacalix[4]arenes

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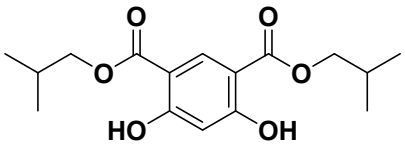
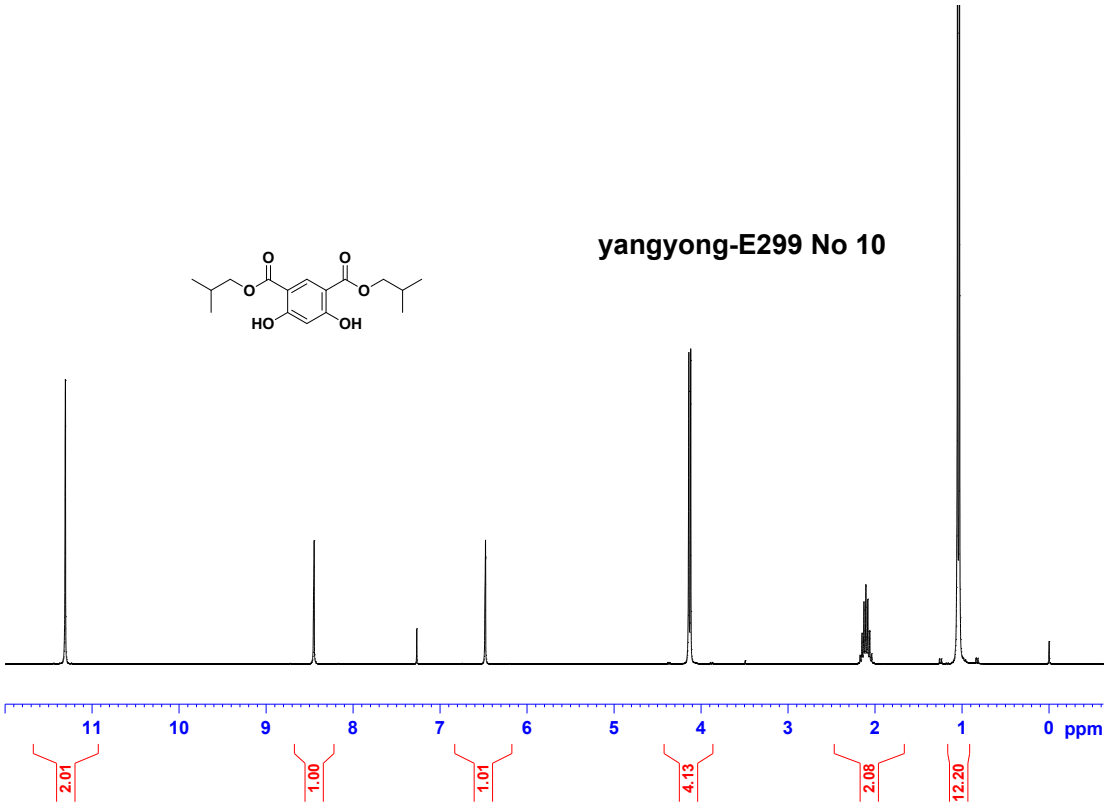
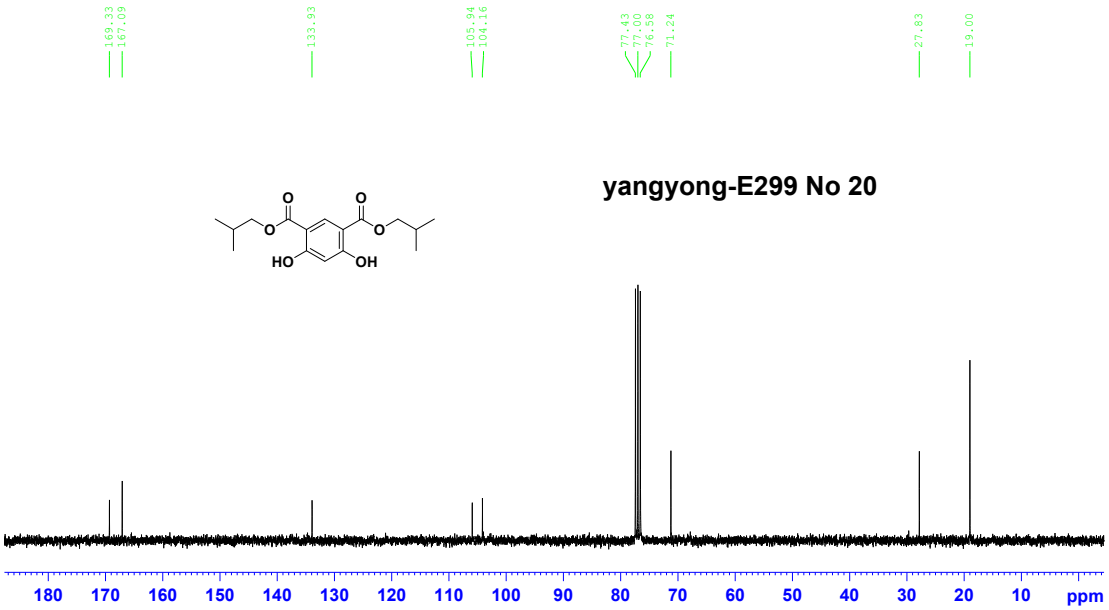
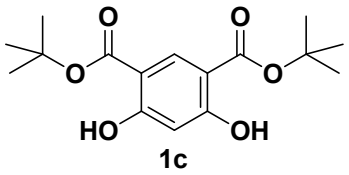


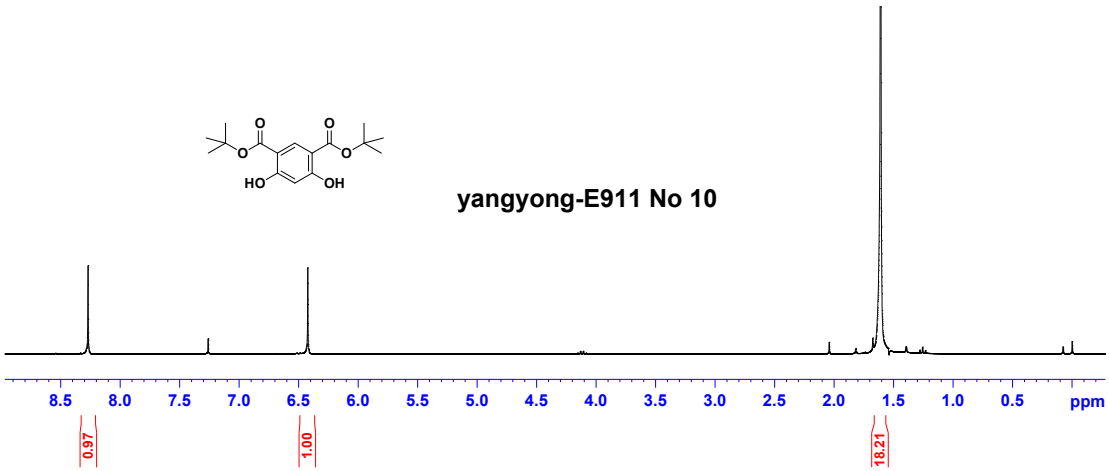
1b

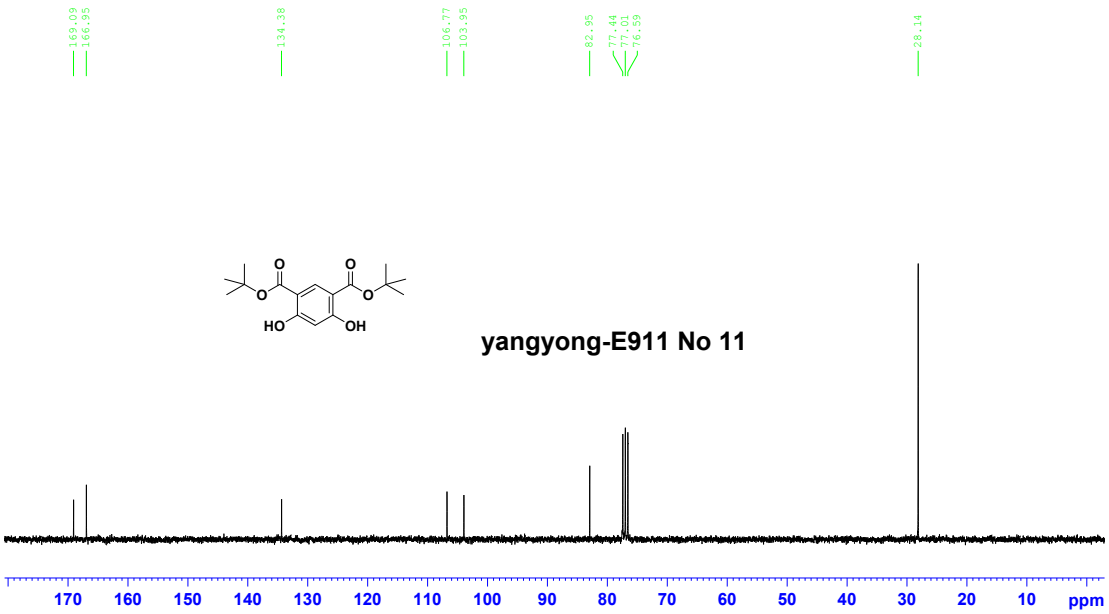


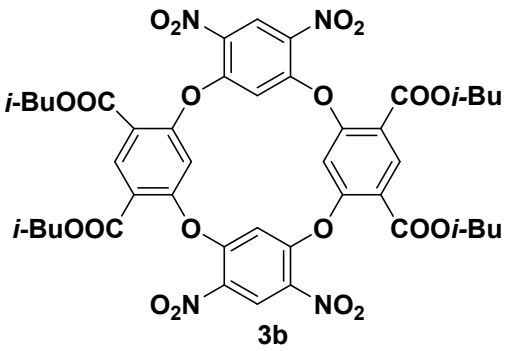

169.33
167.09
133.93
105.94
104.16
77.43
77.00
76.58
71.24
27.83
19.00
yangyong-E299 No 20
HO
OH
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


HO
OH

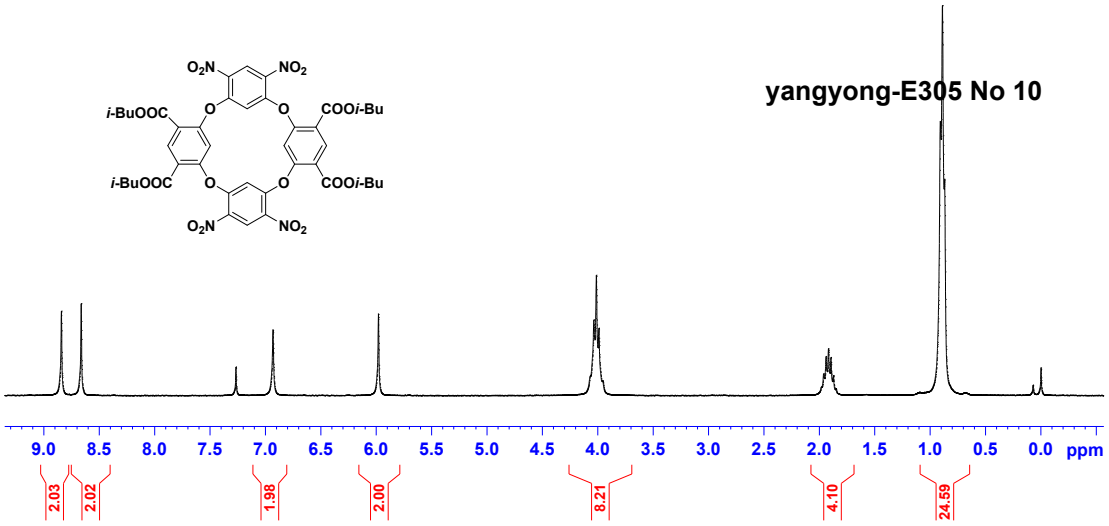
1c

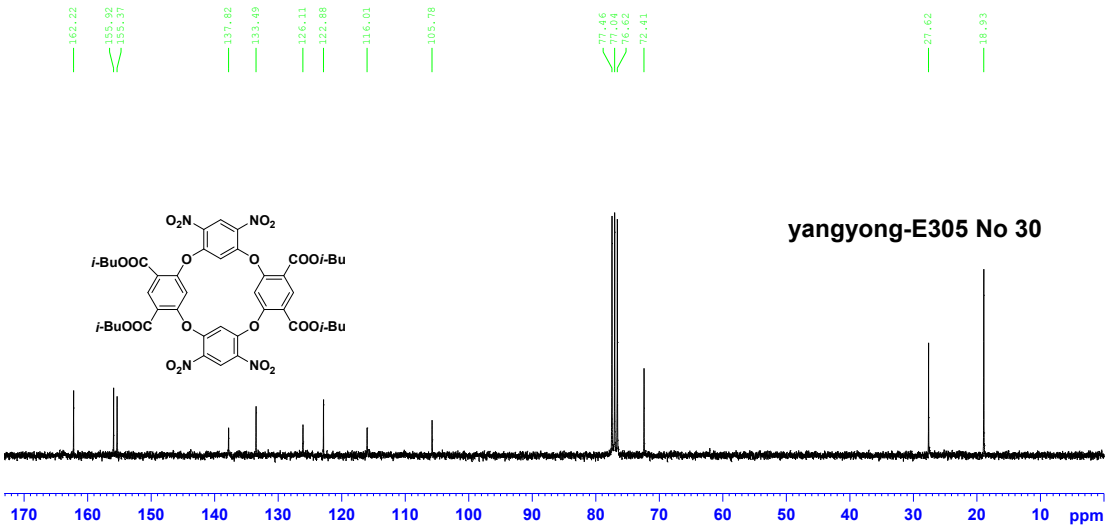

HO
OH
yangyong-E911 No 10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.97
1.00
18.21

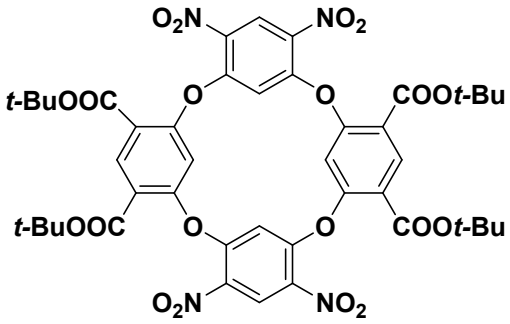

169.09
166.95
134.38
106.77
103.95
82.95
77.44
77.01
76.59
28.14
HO
OH
yangyong-E911 No 11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O_2N
NO_2
i-BuOOC
COO*i*-Bu
O

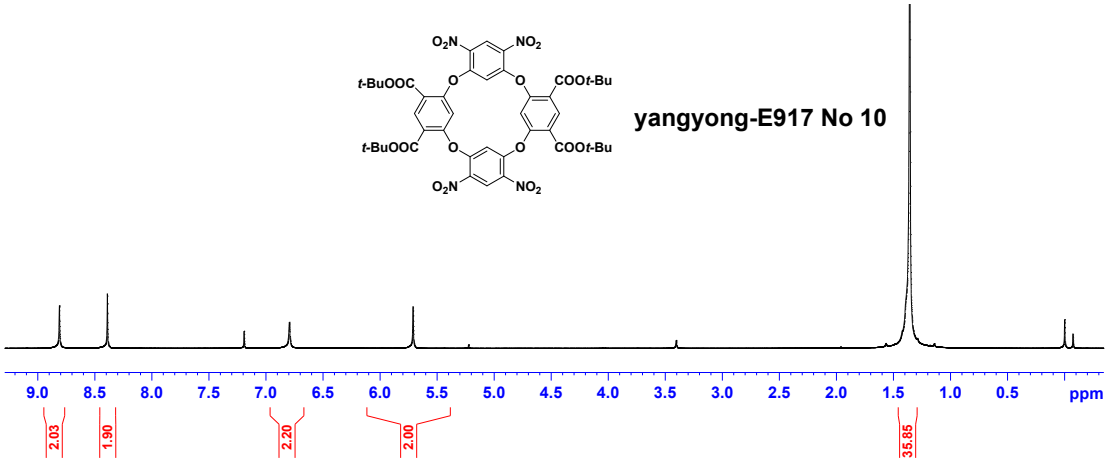
3b

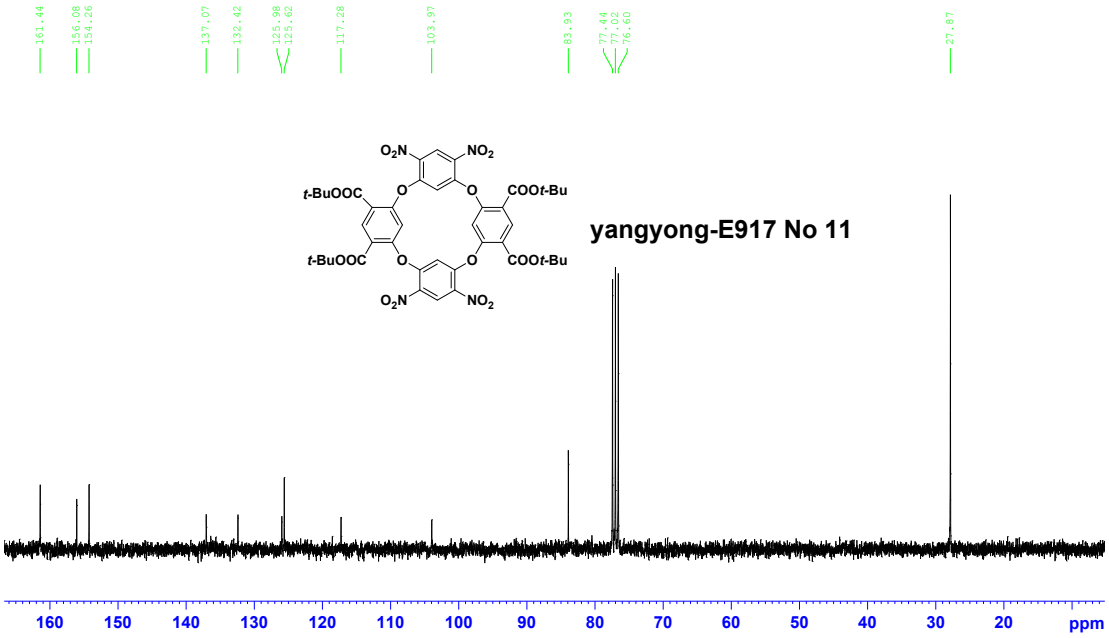

yangyong-E305 No 10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.03
2.02
1.98
2.00
8.21
4.10
24.59

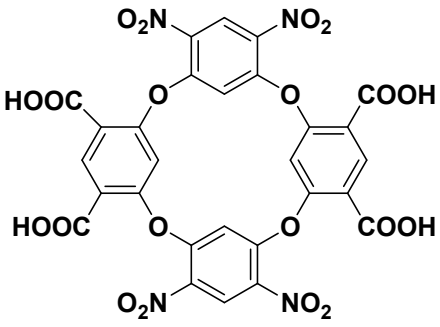

162.22
155.92
155.37
137.82
133.49
126.11
122.88
116.01
105.78
77.46
77.04
76.62
72.41
27.62
18.93
yangyong-E305 No 30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


t-BuOOC
COOt-Bu

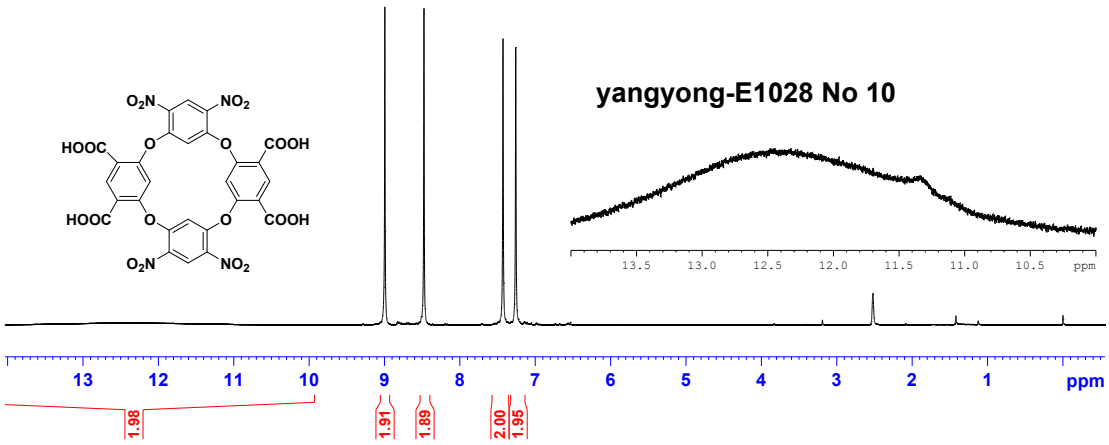
3c

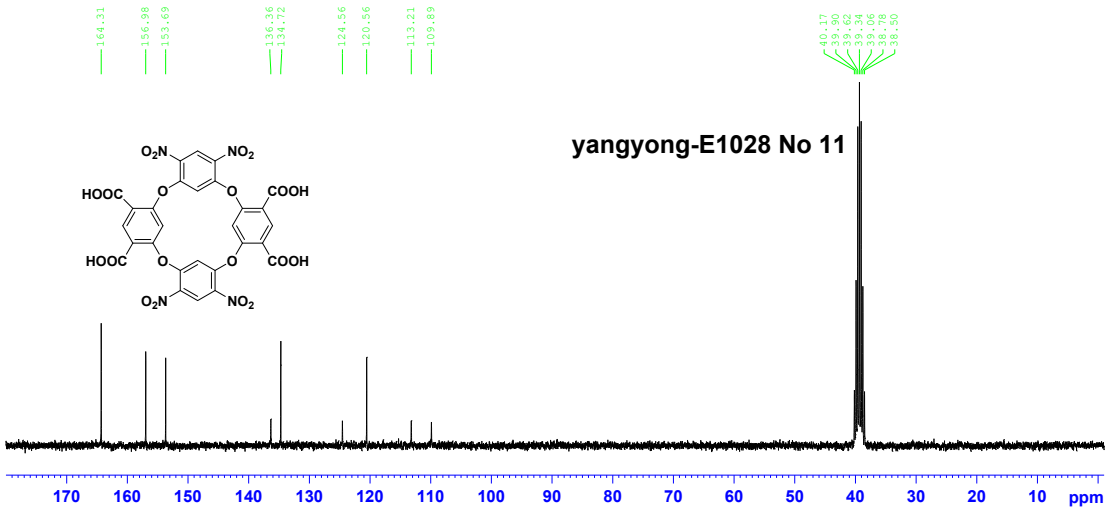

yangyong-E917 No 10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.03
1.90
2.20
2.00
35.85

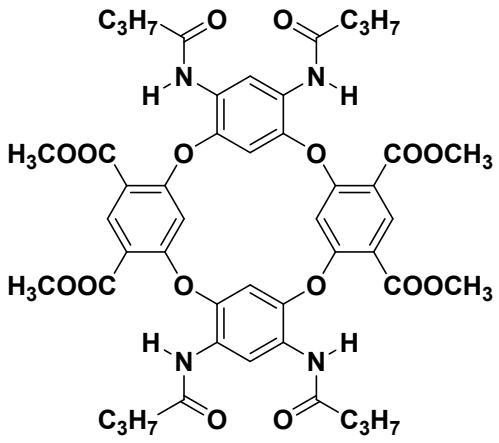

161.44
156.08
154.26
137.07
132.42
125.98
125.62
117.28
103.97
83.93
77.44
77.02
76.60
27.87
t-BuOOC
COOt-Bu
yangyong-E917 No 11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


HOOC
COOH

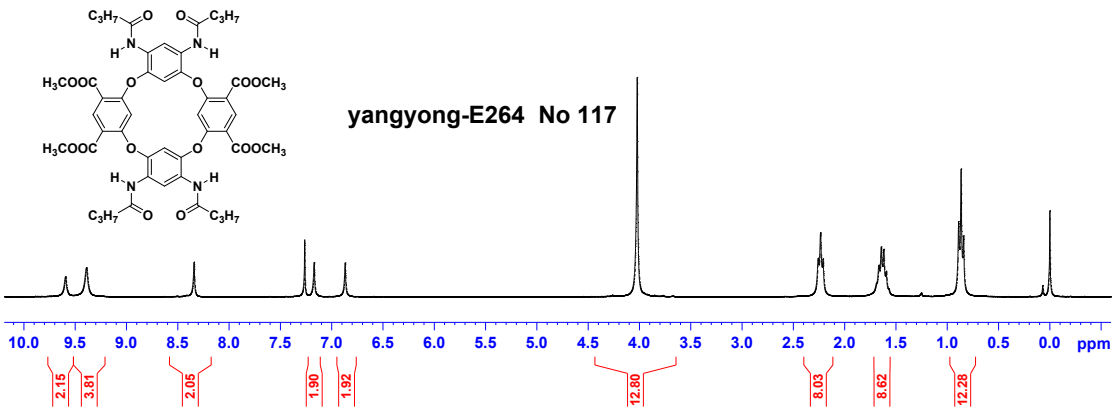
4

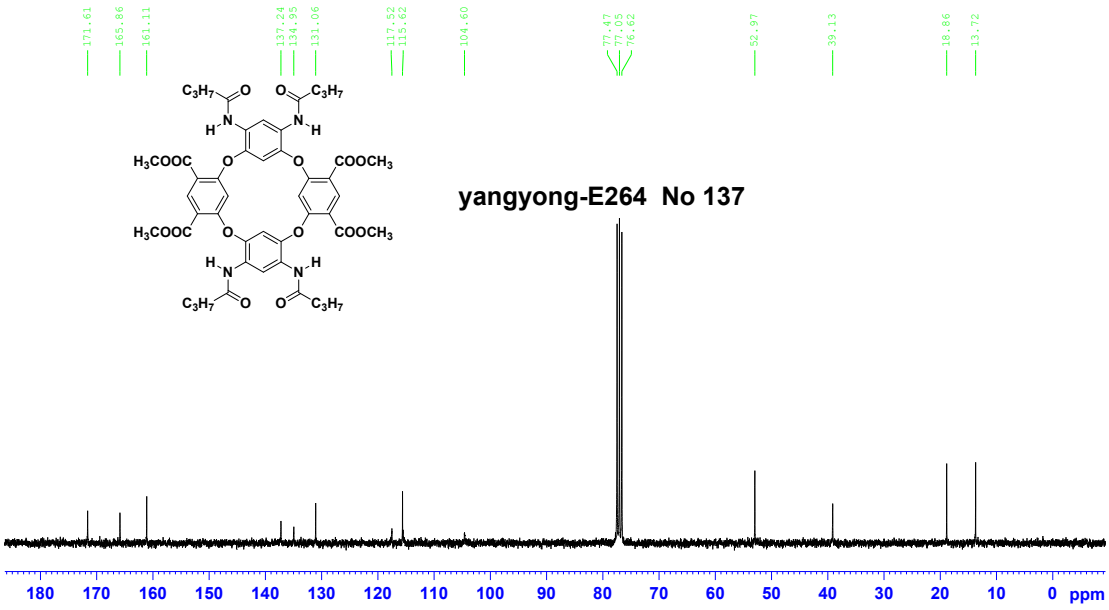

HOOC
COOH
yangyong-E1028 No 10
13.5
13.0
12.5
12.0
11.5
11.0
10.5
ppm
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.98
1.91
1.89
2.00
1.95

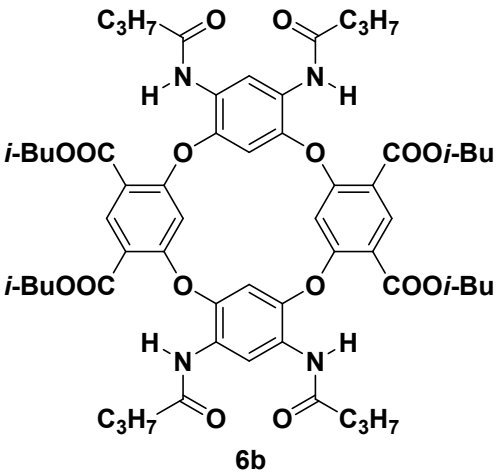

164.31
156.98
153.69
136.36
134.72
124.56
120.56
113.21
109.89
40.17
39.90
39.62
39.34
39.06
38.78
38.50
yangyong-E1028 No 11
HOOC
COOH
HOOC
COOH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

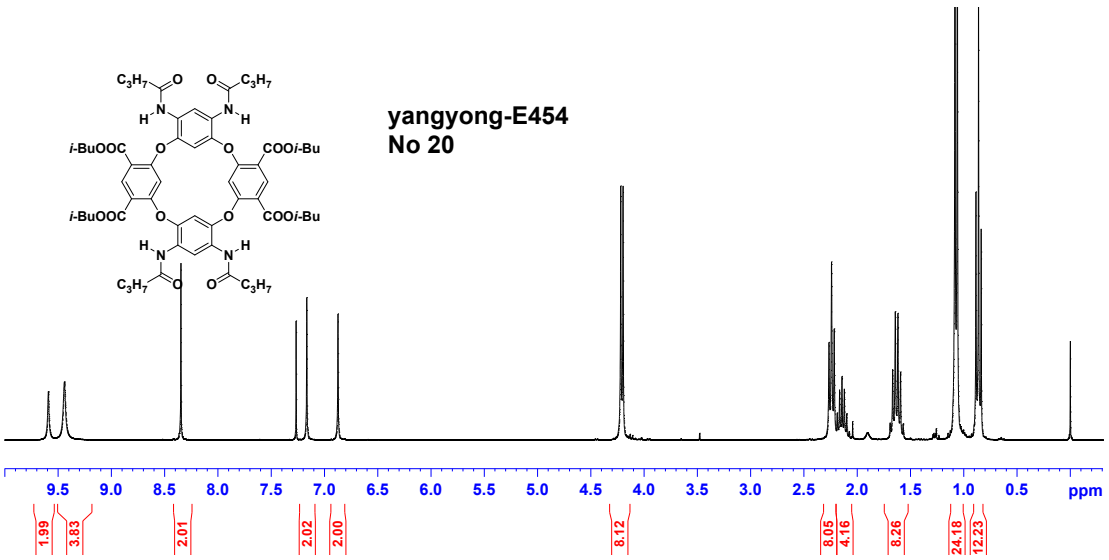


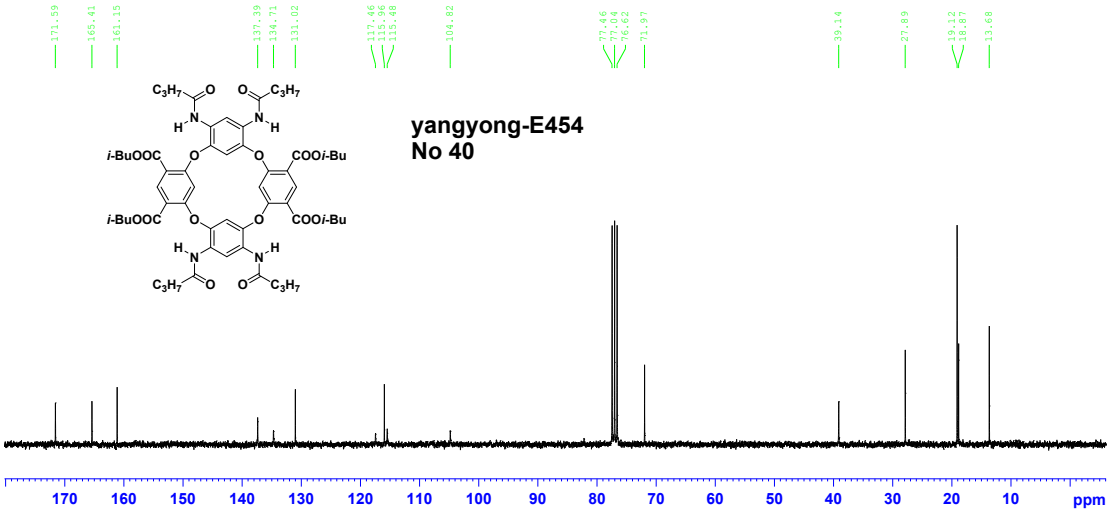
6a

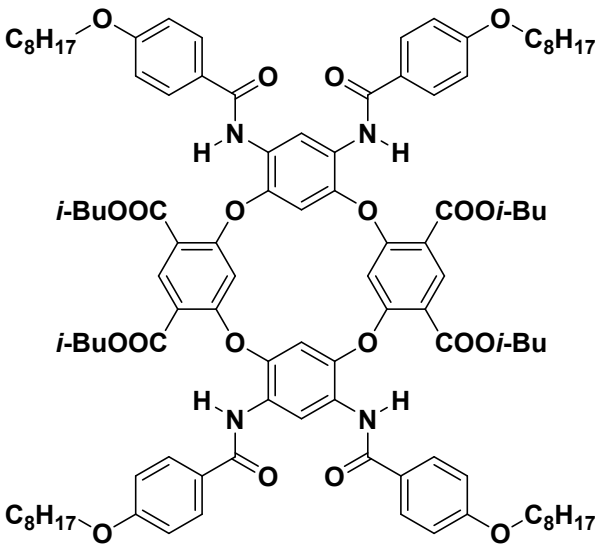

yangyong-E264 No 117
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.15
3.81
2.05
1.90
1.92
12.80
8.03
8.62
12.28


171.61
165.86
161.11
137.24
134.95
131.06
117.52
115.62
104.60
77.47
77.05
76.62
52.97
39.13
18.86
13.72
yangyong-E264 No 137
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

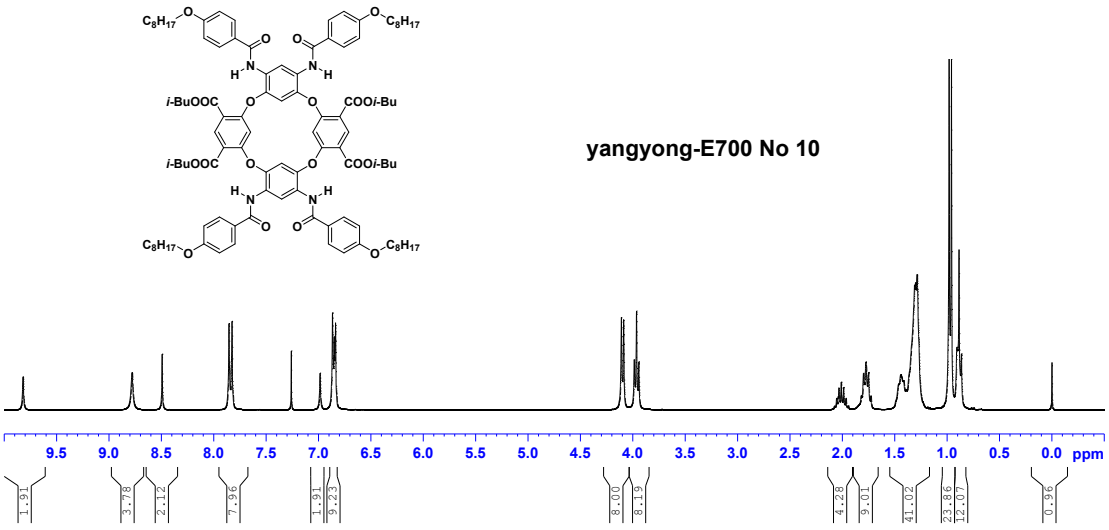

i-BuOOC
COOi-Bu
6b

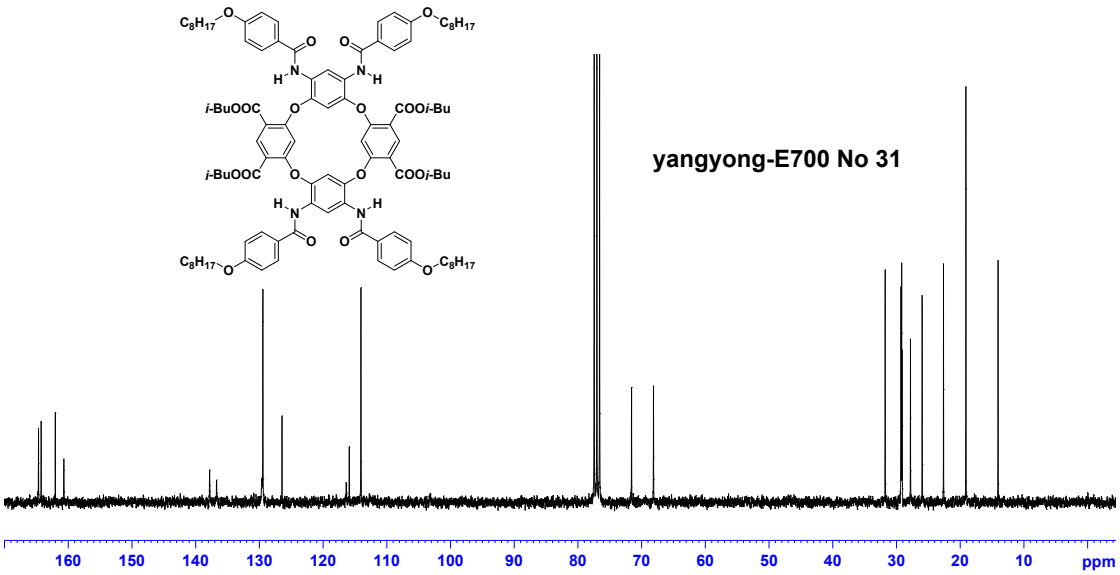

yangyong-E454
No 20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.99
3.83
2.01
2.02
2.00
8.12
8.05
4.16
8.26
24.18
12.23

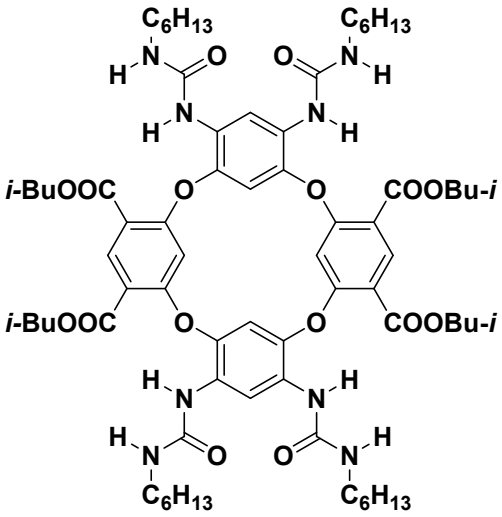

171.59
165.41
161.15
137.39
134.71
131.02
117.46
115.96
115.48
104.82
72.46
71.04
70.62
71.97
39.14
27.89
19.12
18.87
13.68
yangyong-E454
No 40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


C8H17
O
O
O
O
H
N
N
H
i-BuOOC
O
O
COOi-Bu
i-BuOOC
O
O
COOi-Bu
H
N
N
H
C8H17
O
O
C8H17

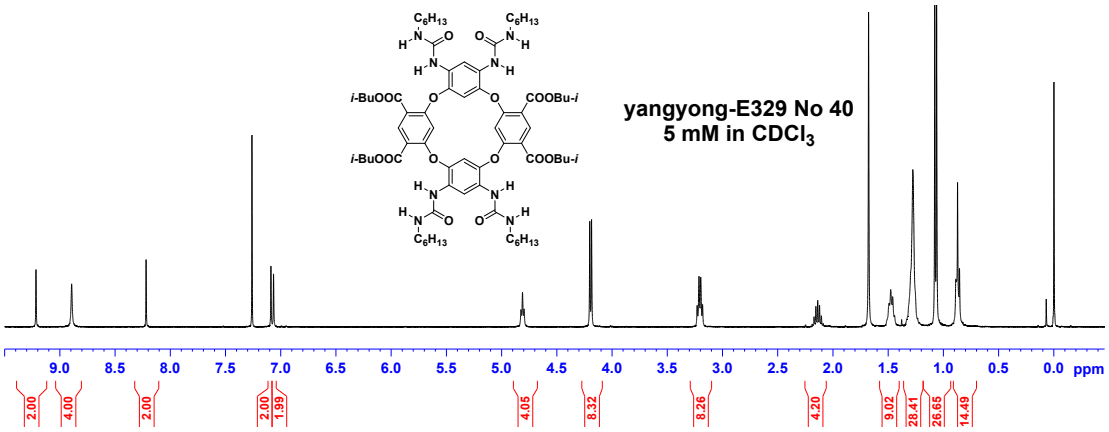
6c

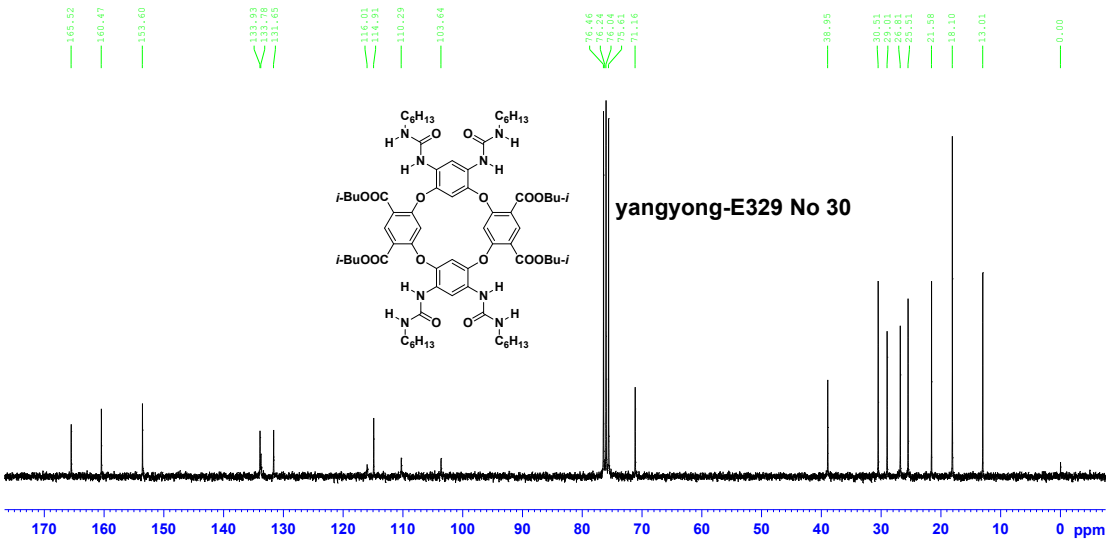

yangyong-E700 No 10
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.91
3.78
2.12
7.96
1.91
9.23
8.00
8.19
4.28
9.01
41.02
23.86
12.07
0.96

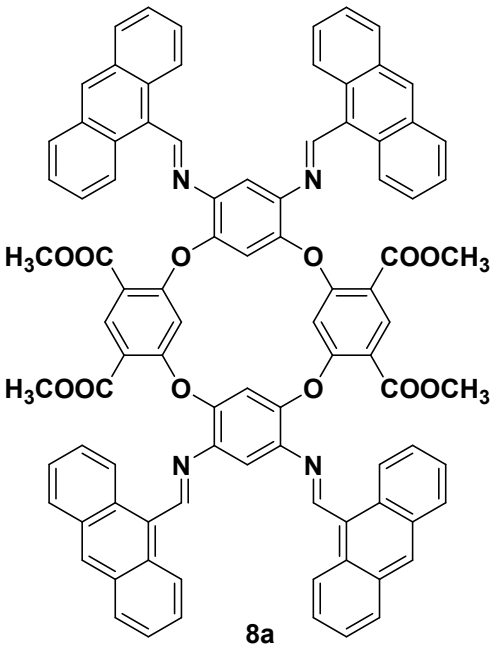

yangyong-E700 No 31
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



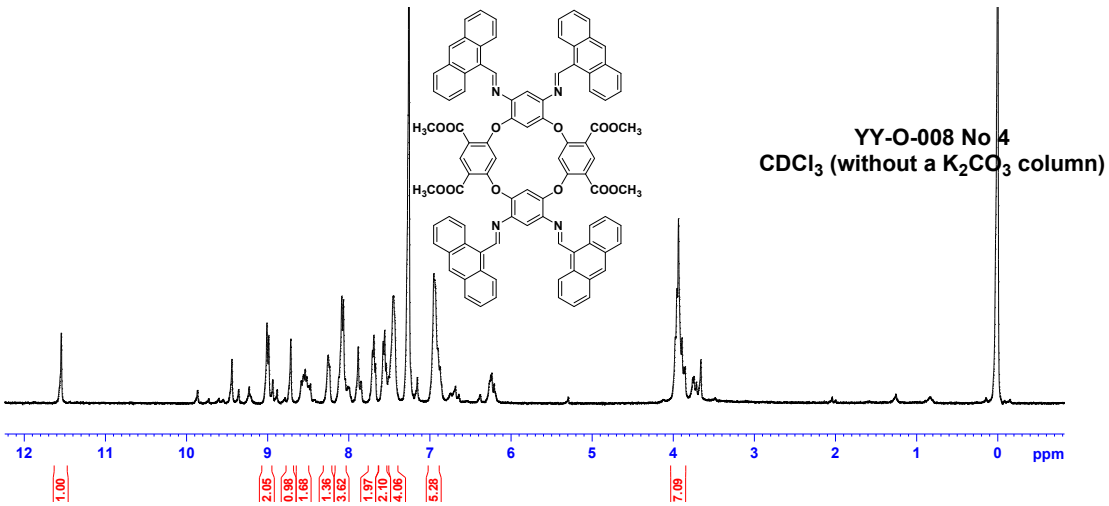
7

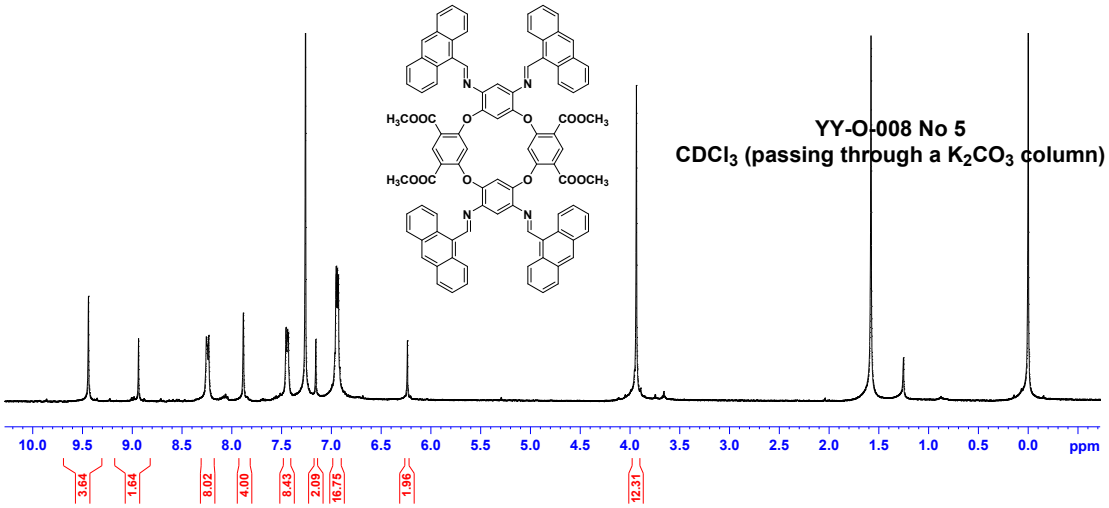

yangyong-E329 No 40
5 mM in CDCl3
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00 4.00 2.00 2.00 1.99 4.05 8.32 8.26 4.20 9.02 28.41 26.65 14.49

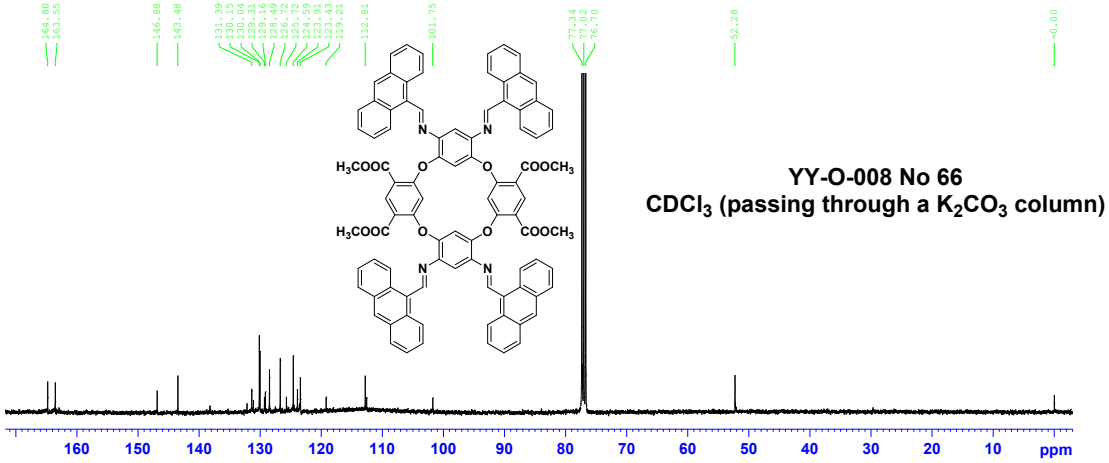

yangyong-E329 No 30
ppm

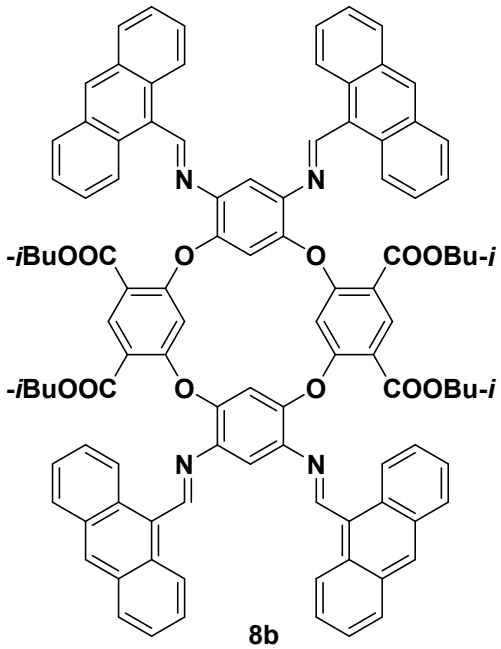


8a

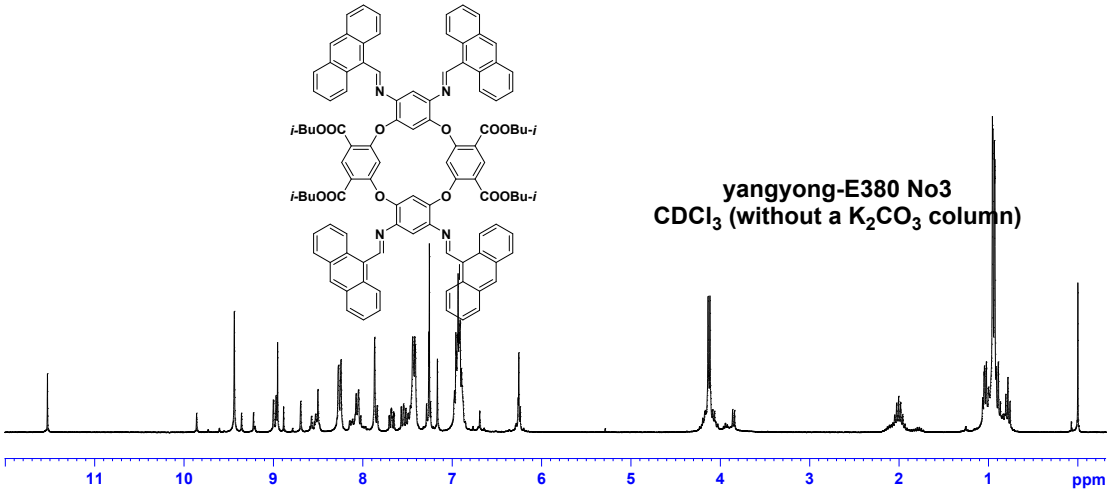

YY-O-008 No 4
CDCl3 (without a K2CO3 column)
ppm

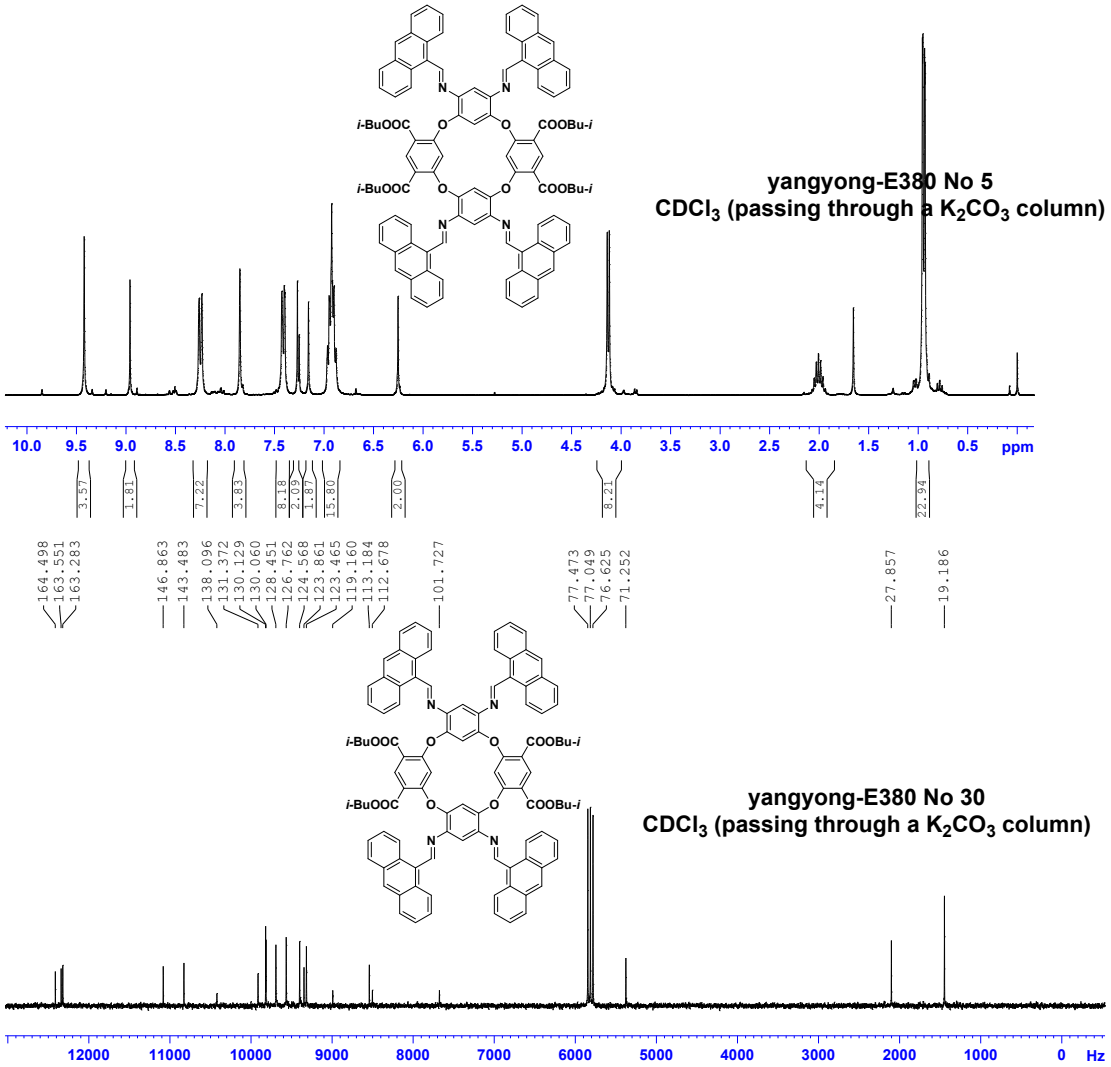

YY-O-008 No 5
CDCl3 (passing through a K2CO3 column)
H3COOC
COOCH3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.64
1.64
8.02
4.00
8.43
2.09
16.75
1.96
12.31


YY-O-008 No 66
CDCl3 (passing through a K2CO3 column)
H3COOC
COOCH3
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

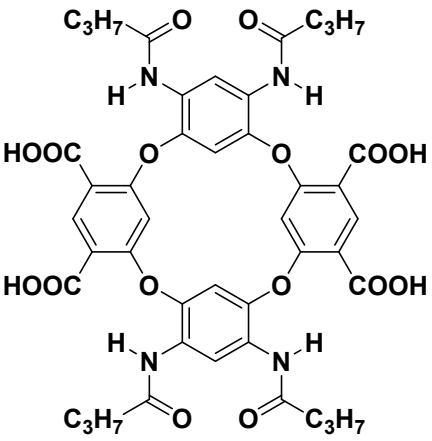

-iBuOOC
COOBu-i

8b

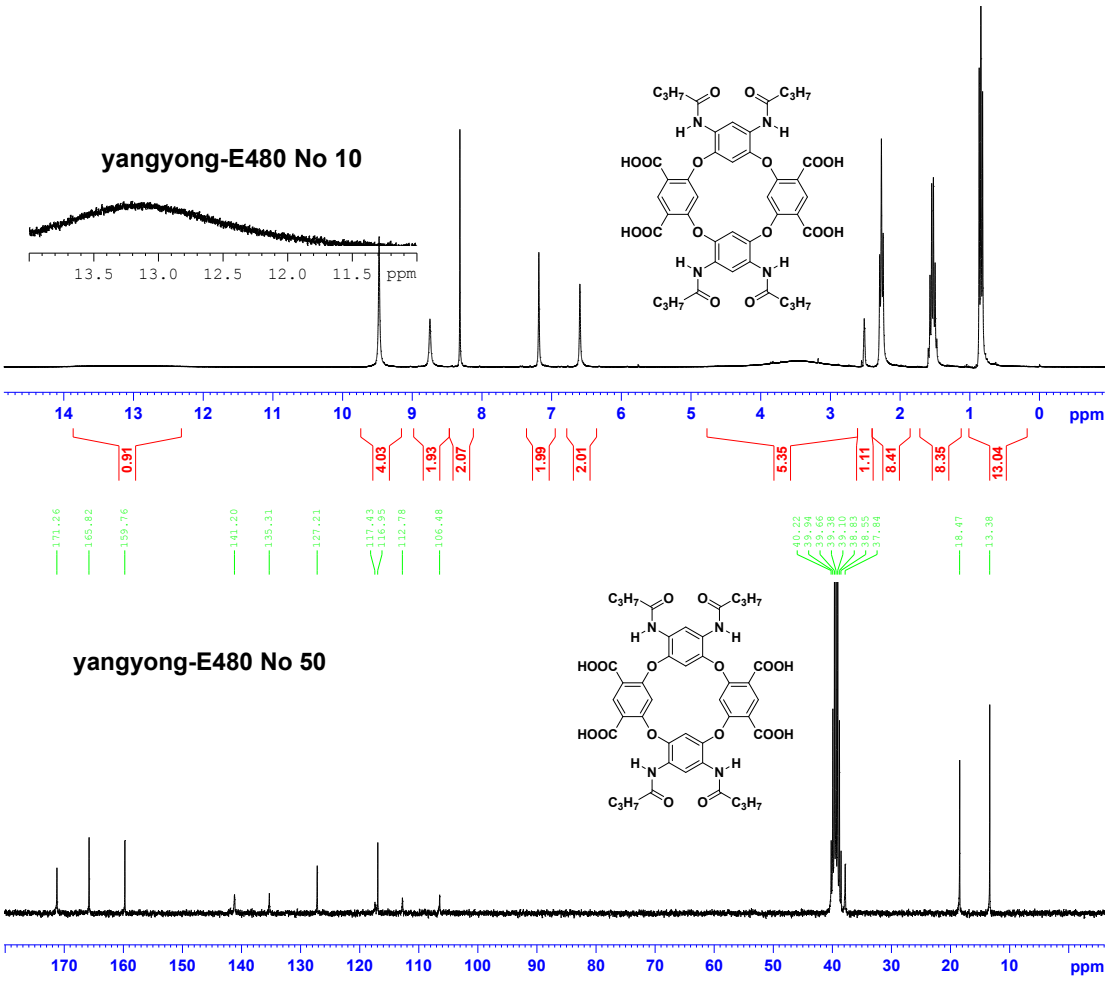

i-BuOOC
COOBu-i
yangyong-E380 No3
CDCl3 (without a K2CO3 column)
11
10
9
8
7
6
5
4
3
2
1
ppm

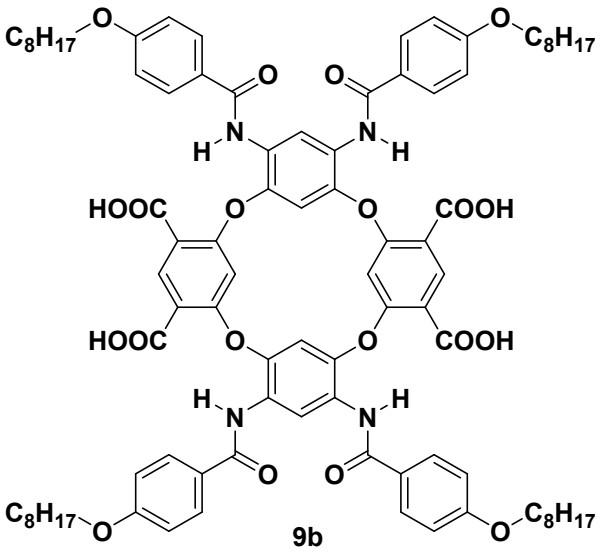

i-BuOOC
COOBu-i
yangyong-E380 No 5
CDCl3 (passing through a K2CO3 column)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.57
1.81
7.22
3.83
8.18
2.09
1.87
15.80
2.00
8.21
4.14
22.94
164.498
163.551
163.283
146.863
143.483
138.096
131.372
130.129
130.060
128.451
126.762
124.568
123.861
123.465
119.160
113.184
112.678
101.727
77.473
77.049
76.625
71.252
27.857
19.186

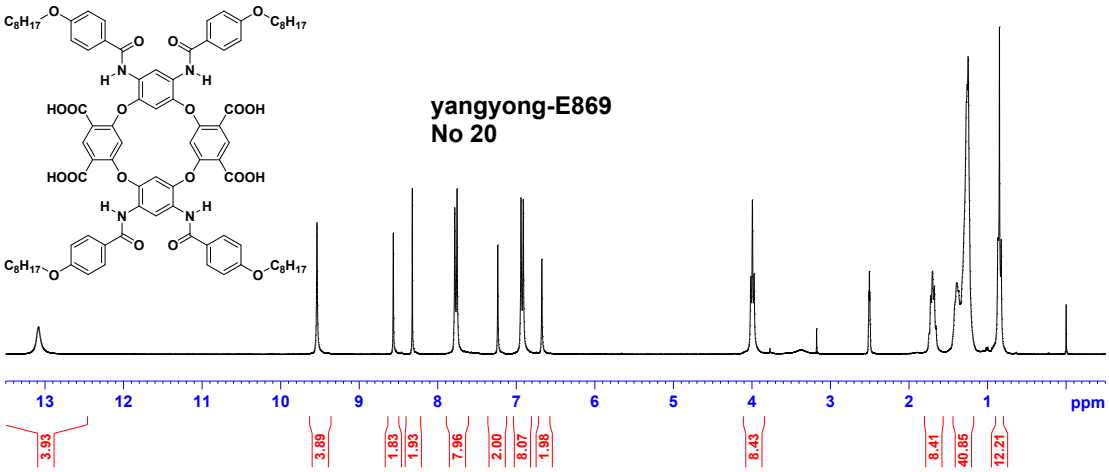
i-BuOOC
COOBu-i
yangyong-E380 No 30
CDCl3 (passing through a K2CO3 column)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Hz

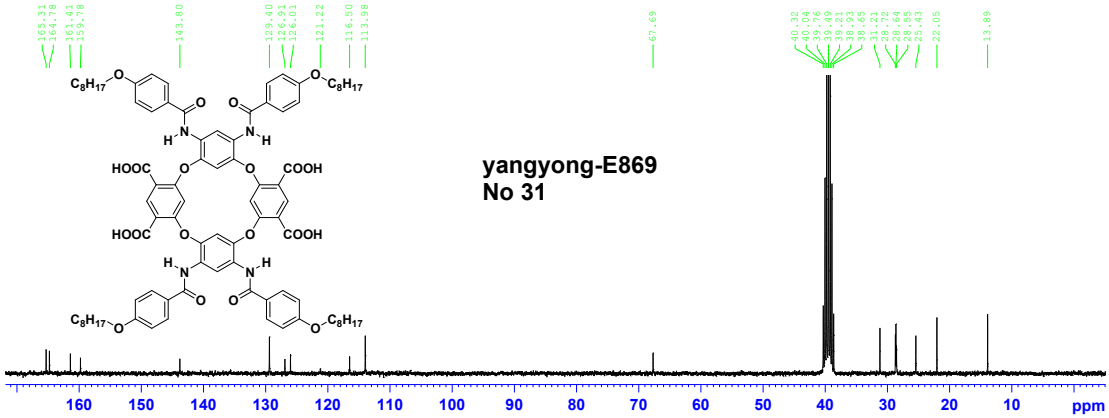


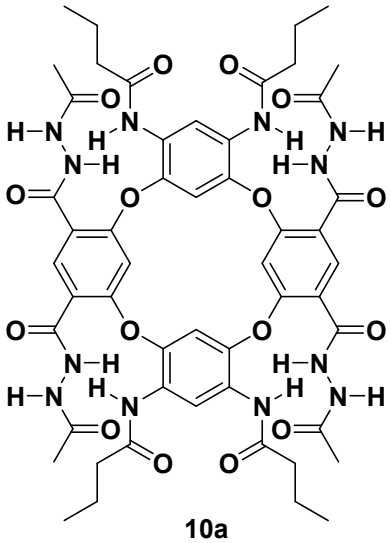
9a


yangyong-E480 No 10
13.5 13.0 12.5 12.0 11.5 ppm
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.91
4.03
1.93
2.07
1.99
2.01
5.35
1.11
8.41
8.35
13.04
171.26
165.82
159.76
141.20
135.31
127.21
117.43
116.95
112.78
106.48
40.22
39.94
39.66
39.38
39.10
38.83
38.55
37.84
18.47
13.38
yangyong-E480 No 50
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

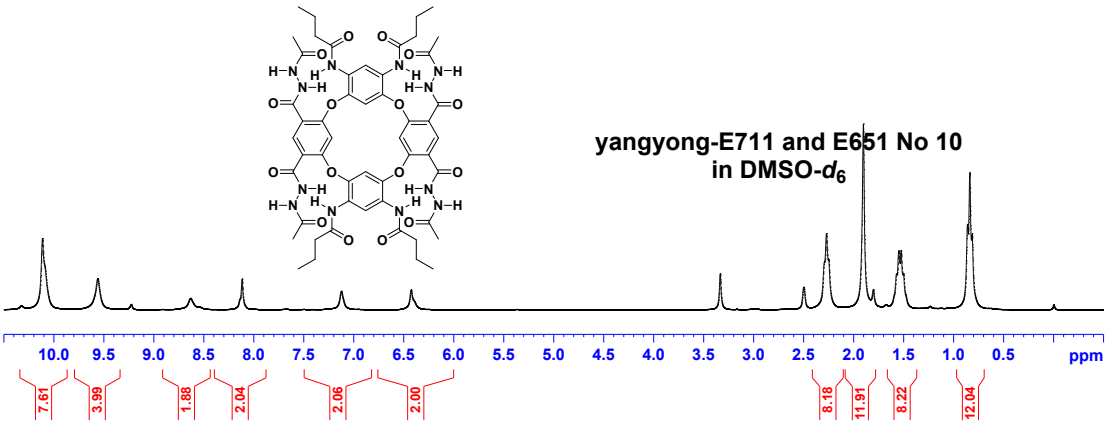

C8H17
HOOC
COOH
9b

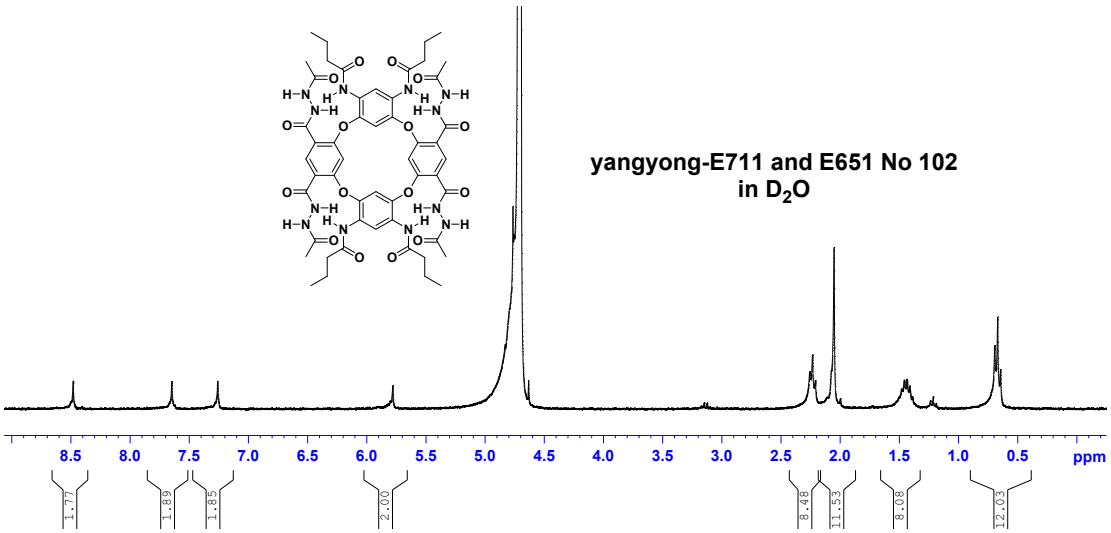

yangyong-E869
No 20
ppm

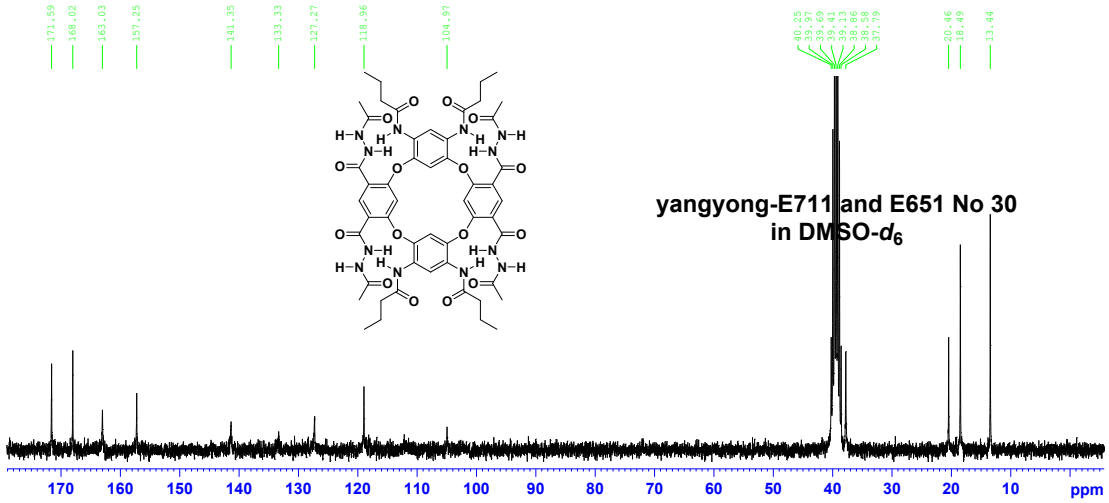

yangyong-E869
No 31
ppm

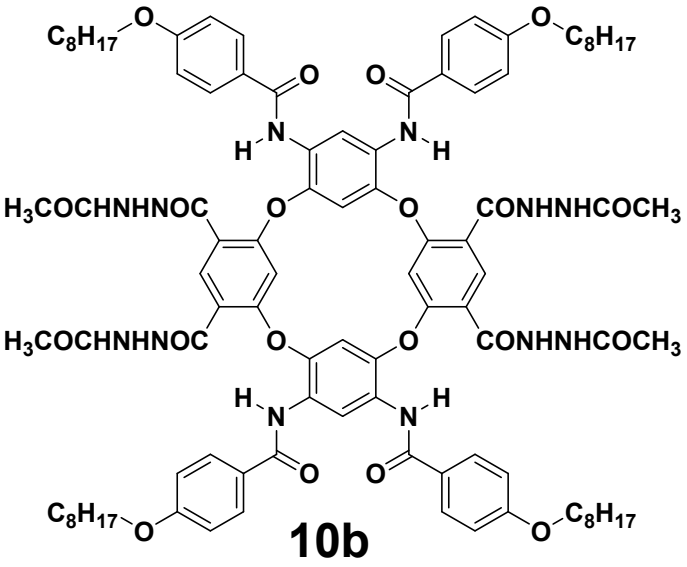


10a

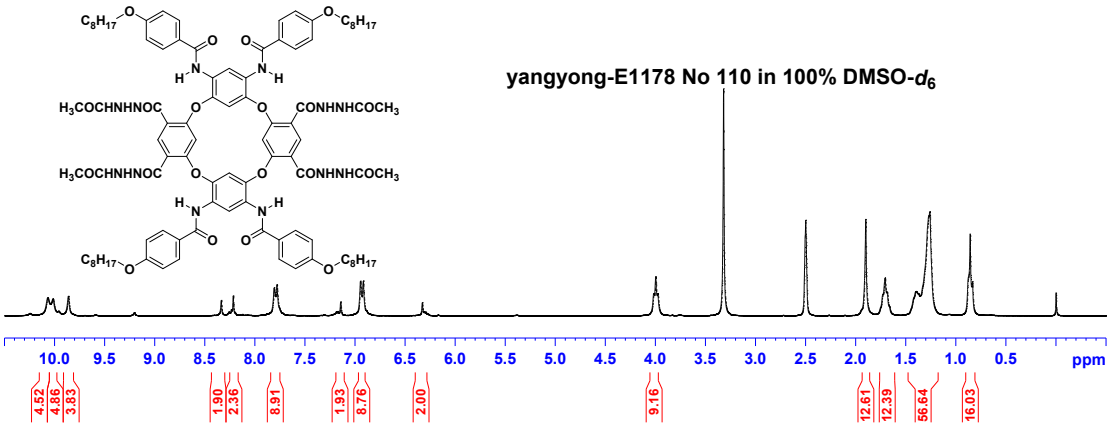

yangyong-E711 and E651 No 10
in DMSO-d_6
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
7.61 3.99 1.88 2.04 2.06 2.00 8.18 11.91 8.22 12.04

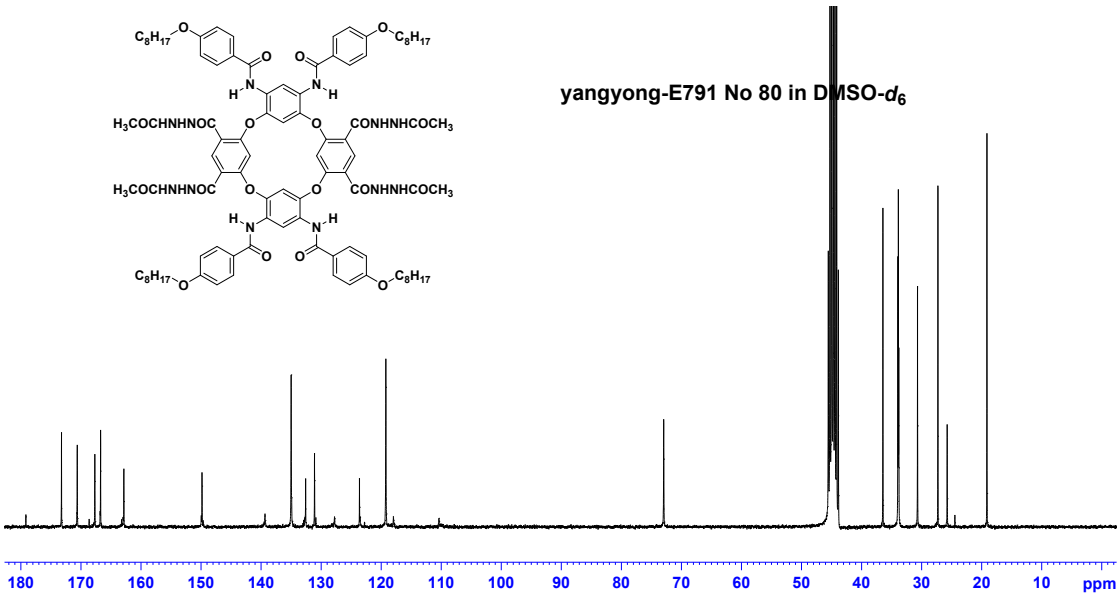

yangyong-E711 and E651 No 102
in D_2O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.77 1.89 1.85 2.00 8.48 11.53 8.08 12.03

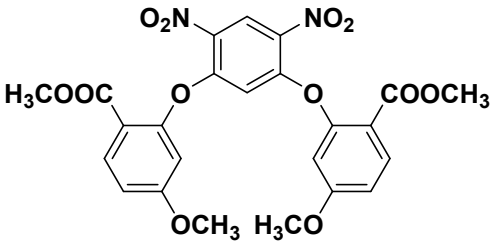

171.59
168.02
163.03
157.25
141.35
133.33
127.27
118.96
104.97
40.25
39.97
39.69
39.41
39.13
38.86
38.58
37.79
20.46
18.49
13.44
yangyong-E711 and E651 No 30
in DMSO-d6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


C8H17
O
H3COCHNHNOC
CONHNHCOCH3
H
N

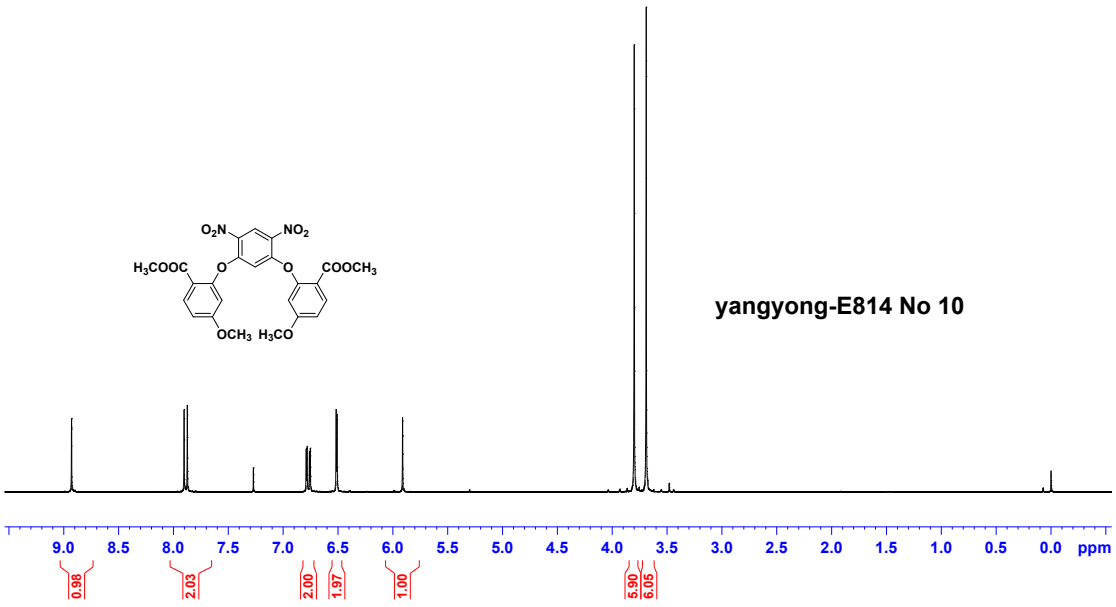
10b

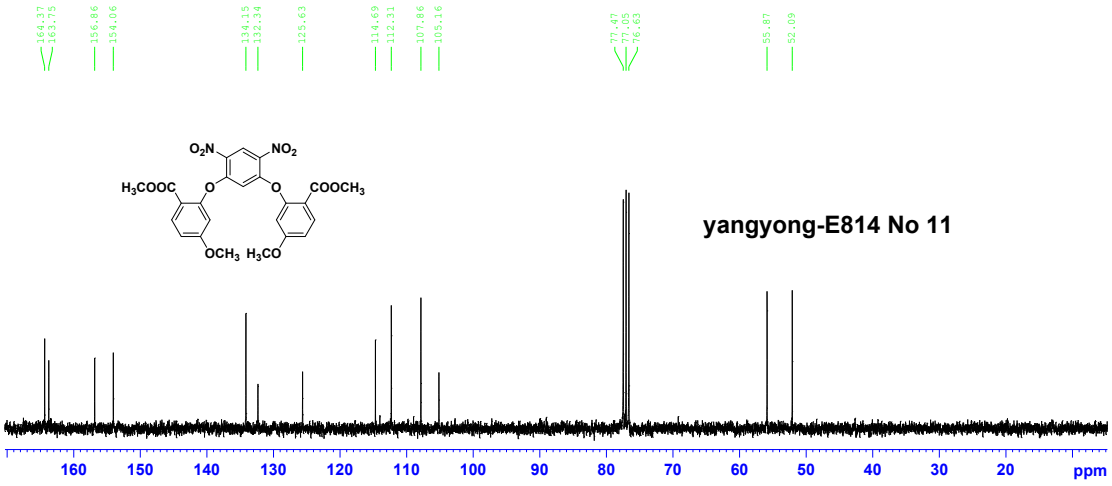

yangyong-E1178 No 110 in 100% DMSO-d6
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.52
4.86
3.83
1.90
2.36
8.91
1.93
8.76
2.00
9.16
12.61
12.39
56.64
16.03

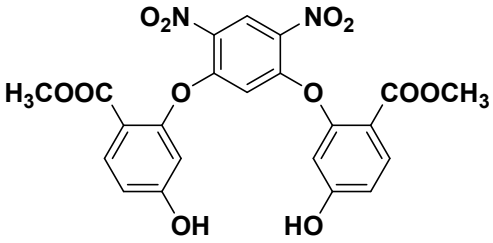

yangyong-E791 No 80 in DMSO-d_6
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



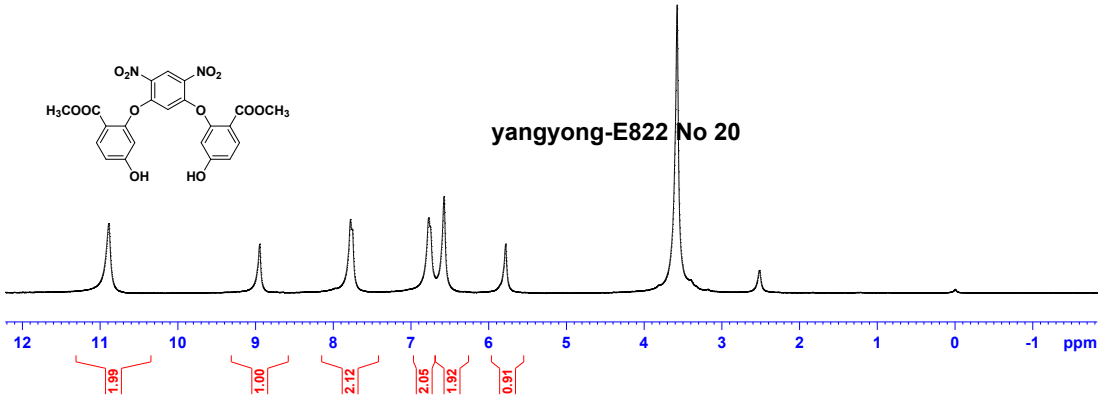
14

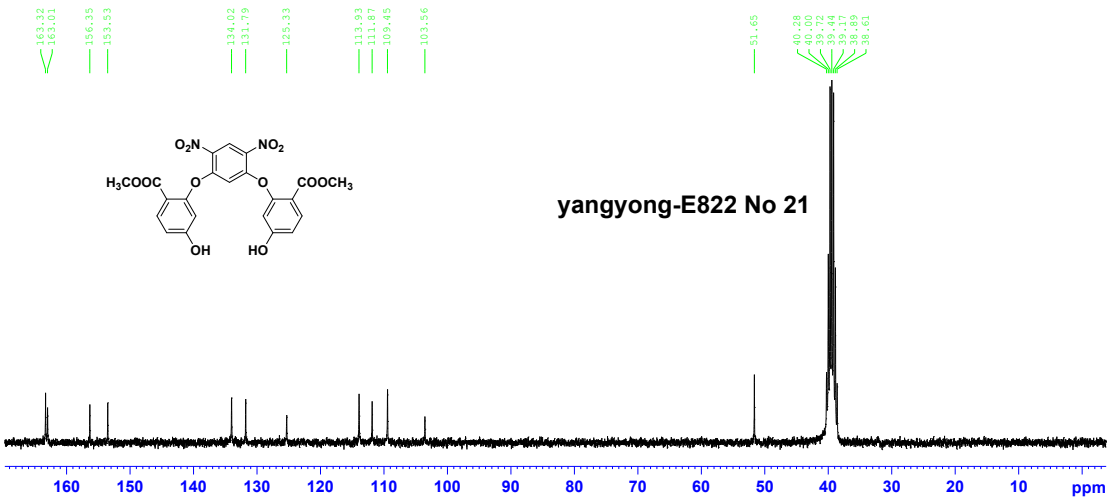

yangyong-E814 No 10
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
0.98 2.03 2.00 1.97 1.00 5.90 6.05


164.37
163.75
156.86
154.06
134.15
132.34
125.63
114.69
112.31
107.86
105.16
77.47
77.05
76.63
55.87
52.09
yangyong-E814 No 11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

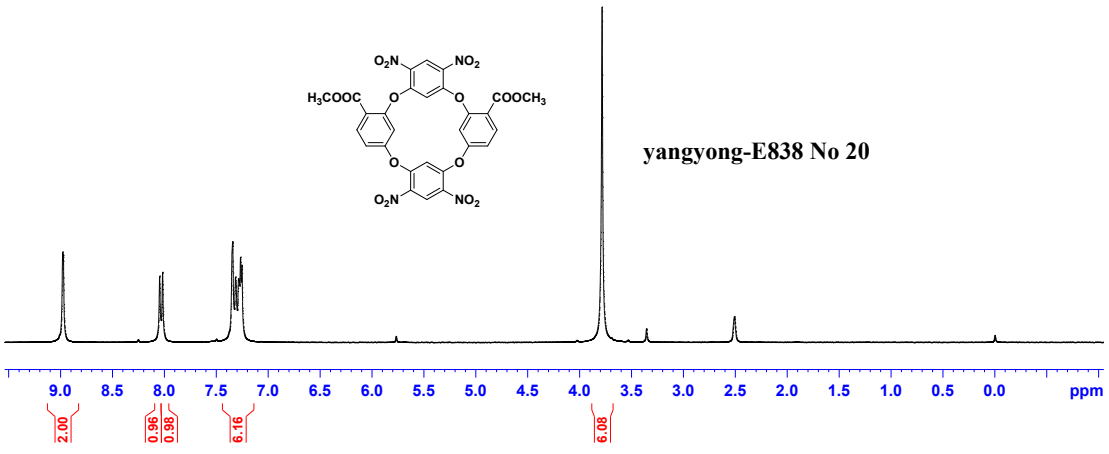

O2N
NO2
H3COOC
O
O
COOCH3
OH
HO

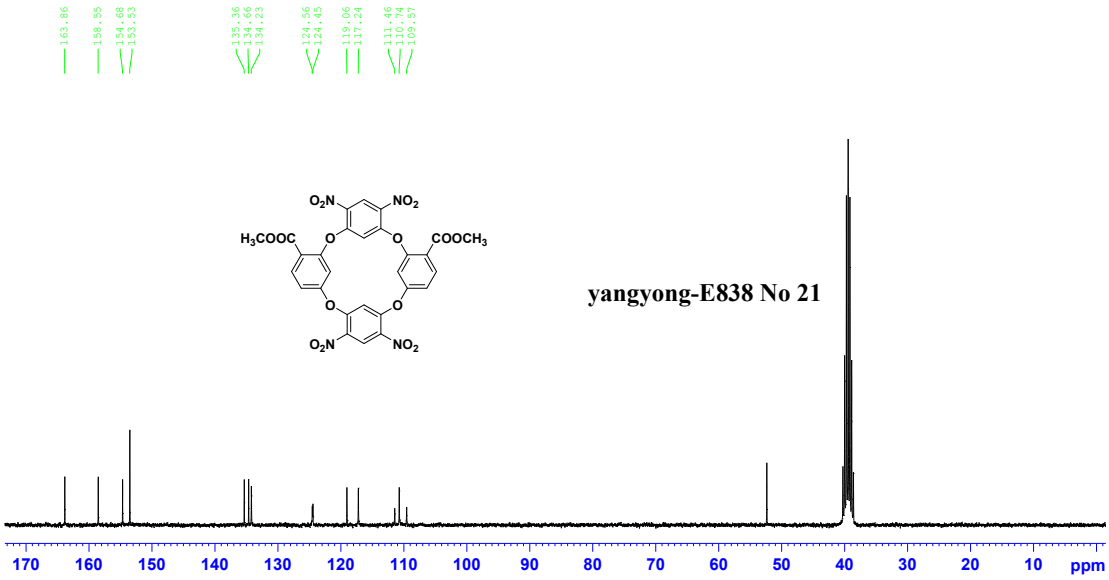
16

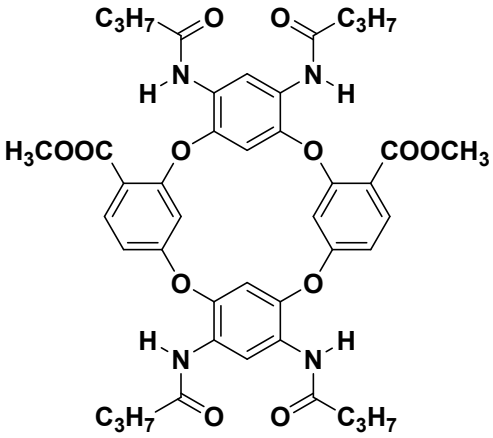

yangyong-E822 No 20
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.99
1.00
2.12
2.05
1.92
0.91



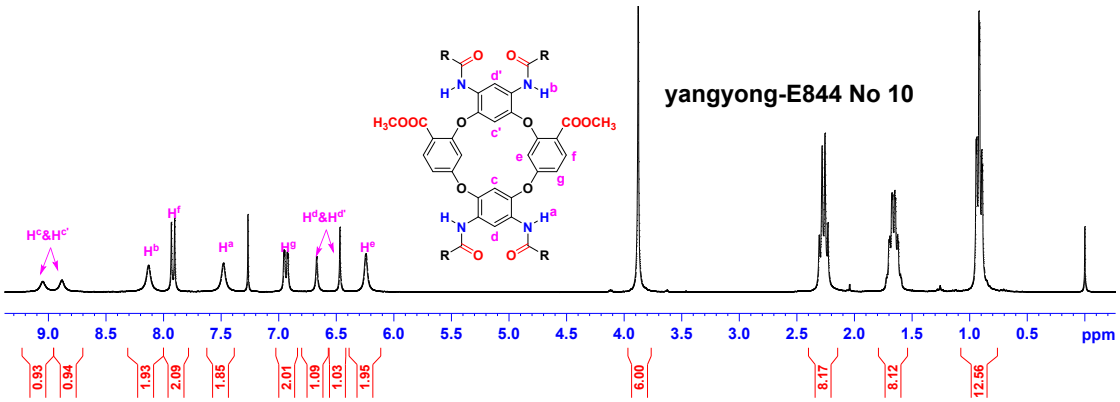
17

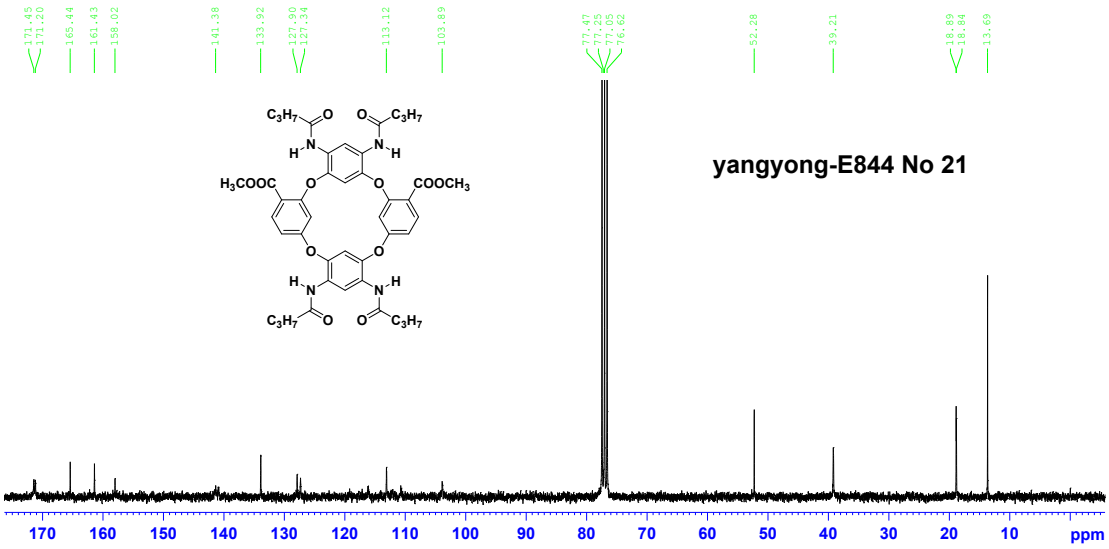


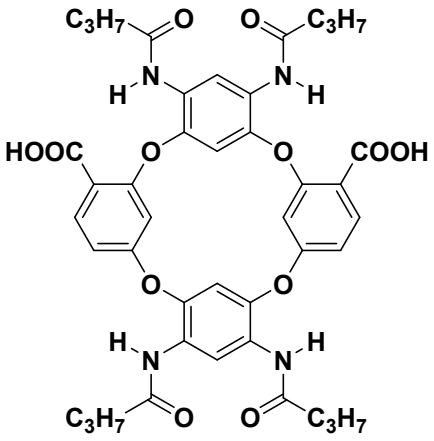

163.86
158.55
154.68
153.53
135.36
134.66
134.23
124.56
124.45
119.06
117.24
111.46
110.74
109.57
yangyong-E838 No 21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



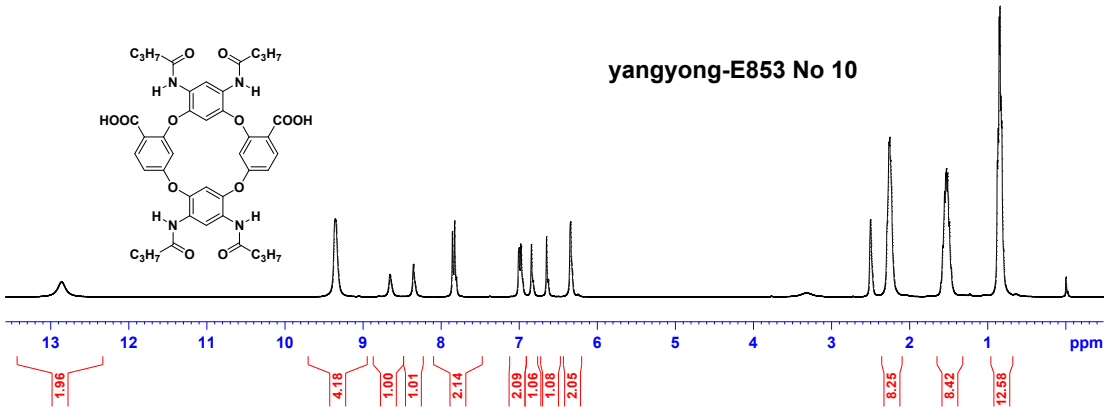
18

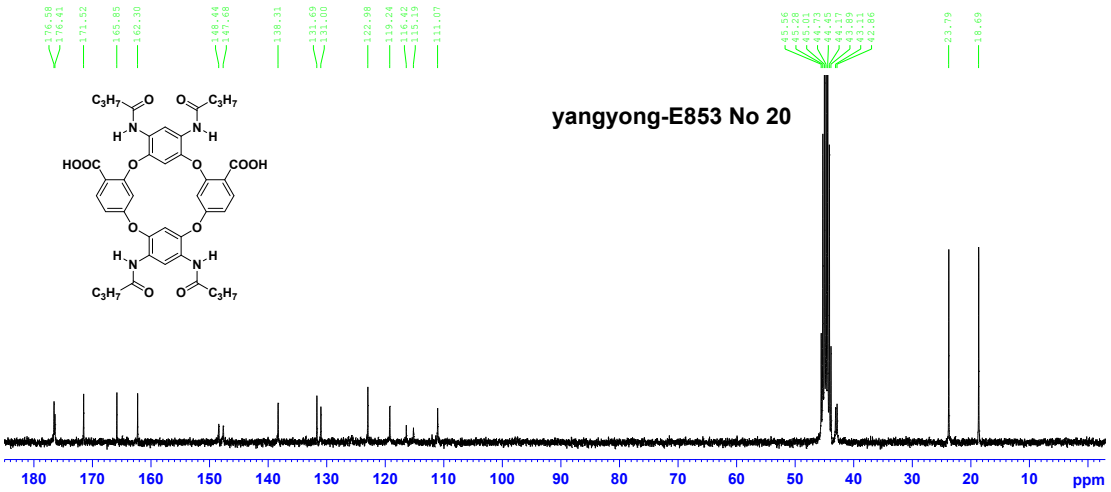

yangyong-E844 No 10
Hc&Hc'
Hb
Hf
Ha
Hg
Hd&Hd'
He
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.93
0.94
1.93
2.09
1.85
2.01
1.09
1.03
1.95
6.00
8.17
8.12
12.56

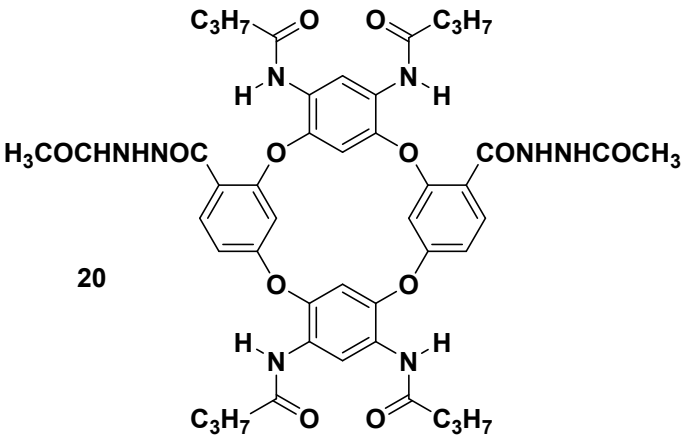

171.45
171.20
165.44
161.43
158.02
141.38
133.92
127.90
127.34
113.12
103.89
77.47
77.25
77.05
76.62
62.28
39.21
18.89
18.84
13.69
yangyong-E844 No 21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

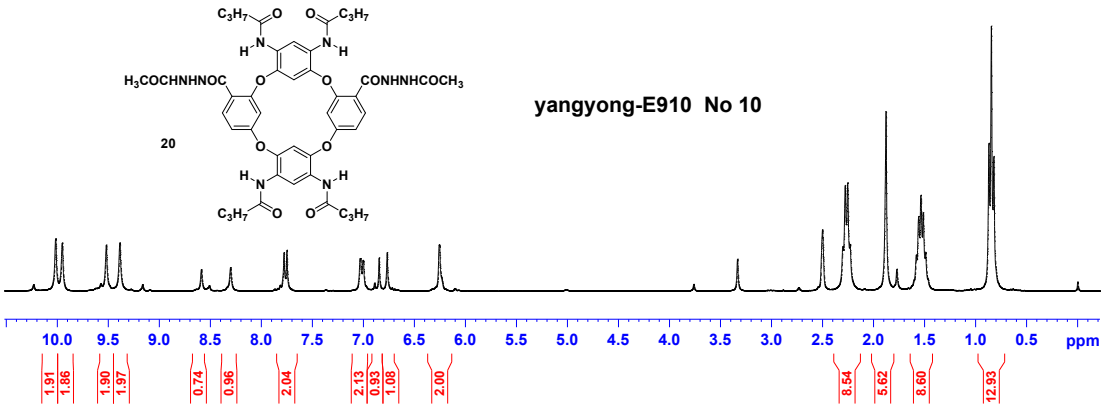


19


yangyong-E853 No 10
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.96
4.18
1.00
1.01
2.14
2.09
1.06
1.08
2.05
8.25
8.42
12.58


yangyong-E853 No 20
ppm


H3COCHNHNOC
CONHNHCOCH3
20


yangyong-E910 No 10
20
ppm

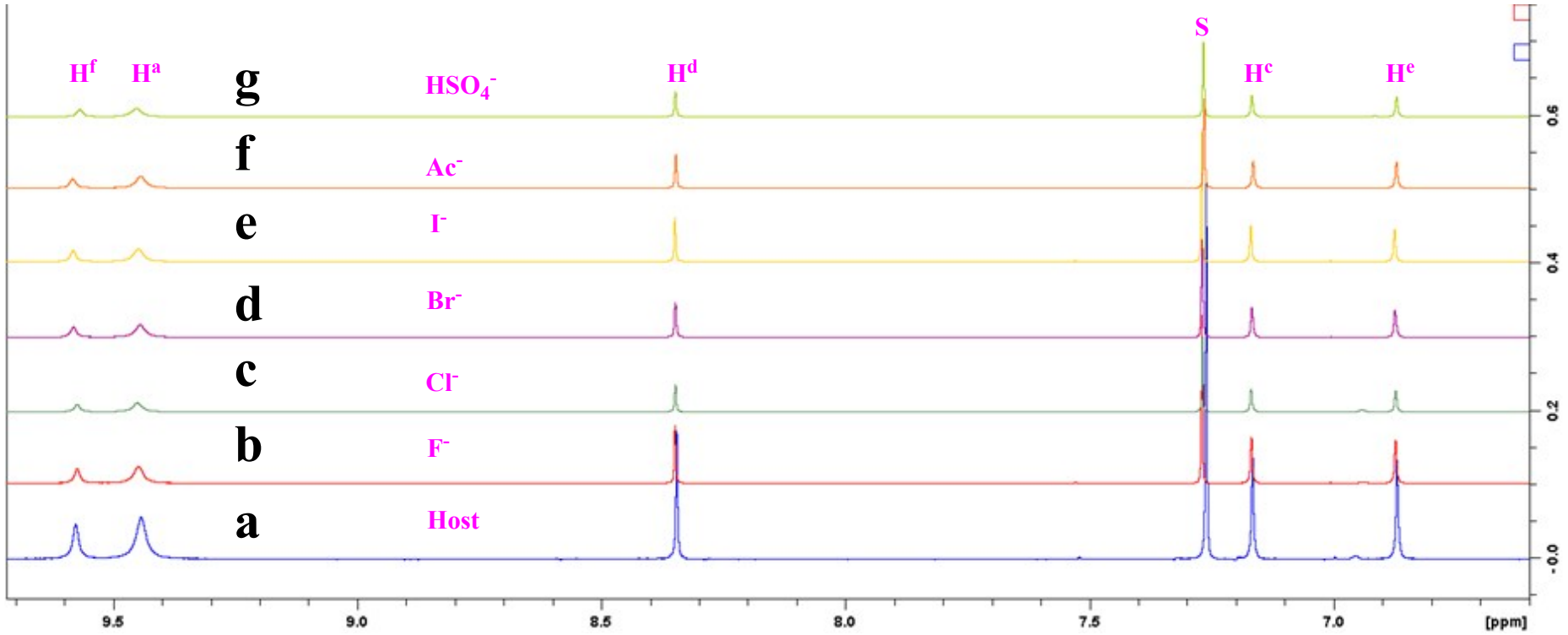


Fig. S1. Stacked partial spectra for 5 mM **6b** in $CDCl_3$ (a), with 15 mM $Bu_4N^+F^-$ (b), with 15 mM $Bu_4N^+Cl^-$ (c), with 15 mM $Bu_4N^+Br^-$ (d), with 15 mM $Bu_4N^+I^-$ (e), with 15 mM $Bu_4N^+Ac^-$ (f), with 15 mM $Bu_4N^+HSO_4^-$ (g), 298 K, 400 MHz.

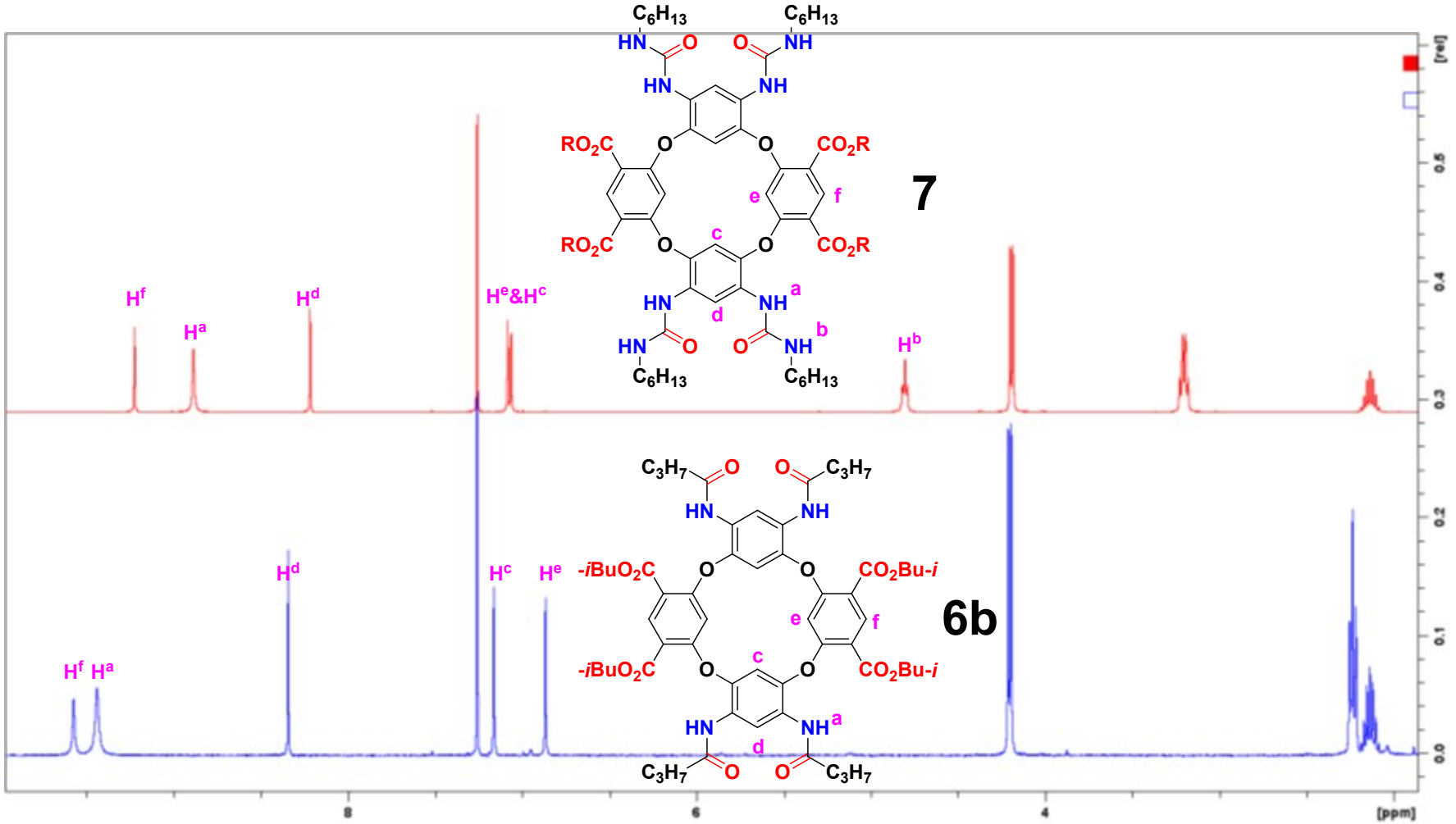


Fig. S2. Stacked partial spectra for 5 mM **6b** (bottom) and 5 mM **7** (up), $CDCl_3$, 298 K, 400 MHz.

Determination of association constant (K_a) of Tetraureido Oxacalix[4]arene **7** and the anion guests F^-, Cl^-, Br^-, I^-, Ac^-, and HSO_4^-, from UV-vis titration data was based on the following equation.[S1-S2]

$$H + G \rightleftharpoons HG$$

$$K_a = \frac{[HG]}{[H][G]}$$

$$[H] = [H]_0 - [HG]$$

$$[G] = [G]_0 - [HG]$$

$$[HG] = \frac{[G]_0 + [H]_0 + \frac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \frac{1}{K_a})^2 - 4[G]_0[H]_0}}{2}$$

$$A_{obs} = \varepsilon_1[H] + \varepsilon_2[HG]$$

$$= \varepsilon_1([H]_0 - [HG]) + \varepsilon_2[HG]$$

$$= \varepsilon_1[H]_0 + (\varepsilon_2 - \varepsilon_1)[HG] \qquad A_0 = \varepsilon_1[H]_0$$

$$A_{obs} - A_0 = (\varepsilon_2 - \varepsilon_1)[HG]$$

$$\Delta A = A_{obs} - A_0 \qquad C = \varepsilon_2 - \varepsilon_1$$

$$\Delta A = C\frac{[G]_0 + [H]_0 + \frac{1}{K_a} - \sqrt{([G]_0 + [H]_0 + \frac{1}{K_a})^2 - 4[G]_0[H]_0}}{2} \qquad \text{(Eq. S1)}$$

$[H]_0$: the initial concentration of Host

[H]: the concentration of free Host

$[G]_0$: the initial concentration of Guest

[G]: the concentration of free Guest

[HG]: the concentration of Host-Guest complex

K_a: association constant

ε_1: molar absorption coeffcient of Host

ε_2 : molar absorption coeffcient of Host-Guest complex HG

A_0: the initial absorption value of Host

A_{obs}: absorption value measured for each titration

ΔA : changes for absorption value

C : constant

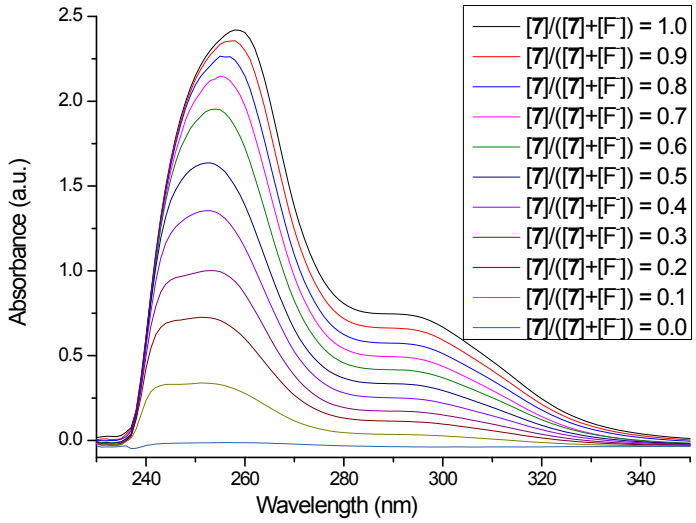


Fig. S3. UV-vis spectra of mixtures of host **7** and guest $Bu_4N^+F^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5×10^{-5} M.

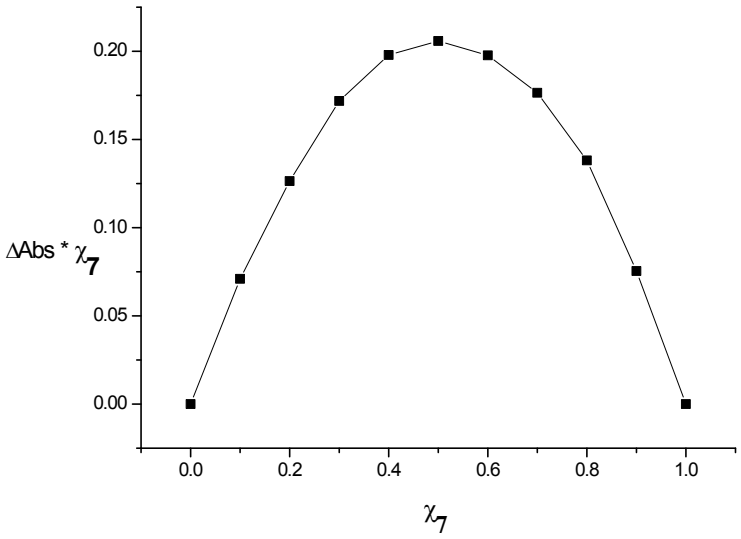


Fig. S4. Job-plot for the complex between host **7** and guest $Bu_4N^+F^-$ in $CHCl_3$ using UV-vis absorption values at $\lambda = 290$ nm, showing a 1:1 stoichiometry.

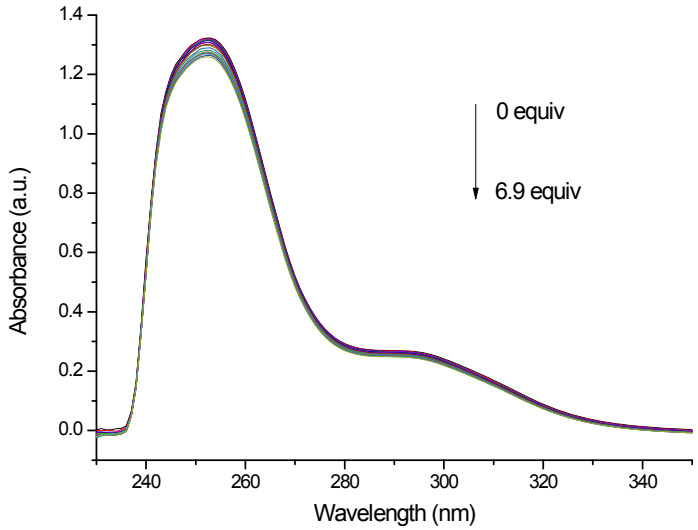


Fig. S5. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-6.9 equivalents of guest $Bu_4N^+F^-$, 298 K.

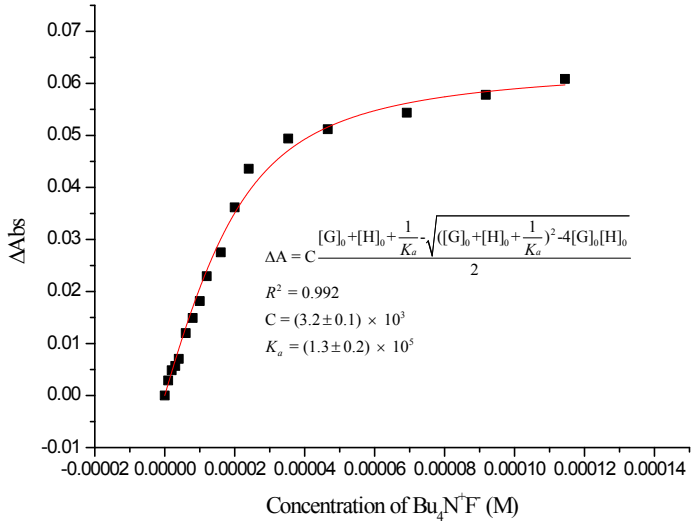


Fig. S6. Plot of the absorption intensity changes at λ = 254 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant $K_a = (1.3 \pm 0.2) \times 10^5$ M^{-1}.

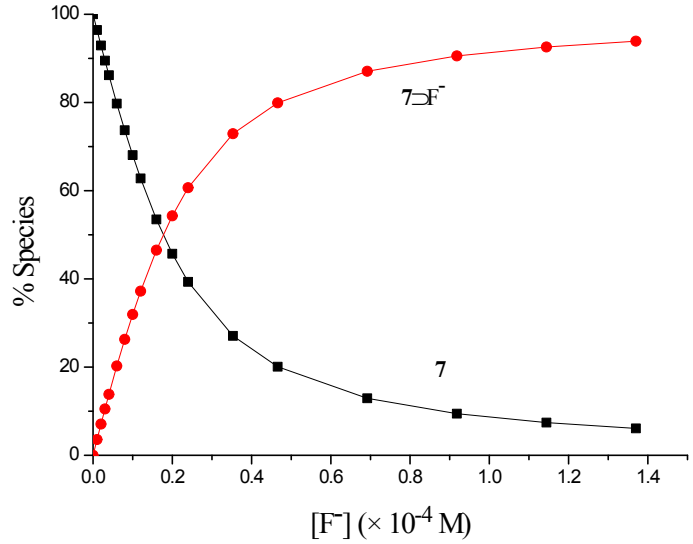


Fig. S7. Distribution diagram between **7** and **7**⊃F^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 254 nm.

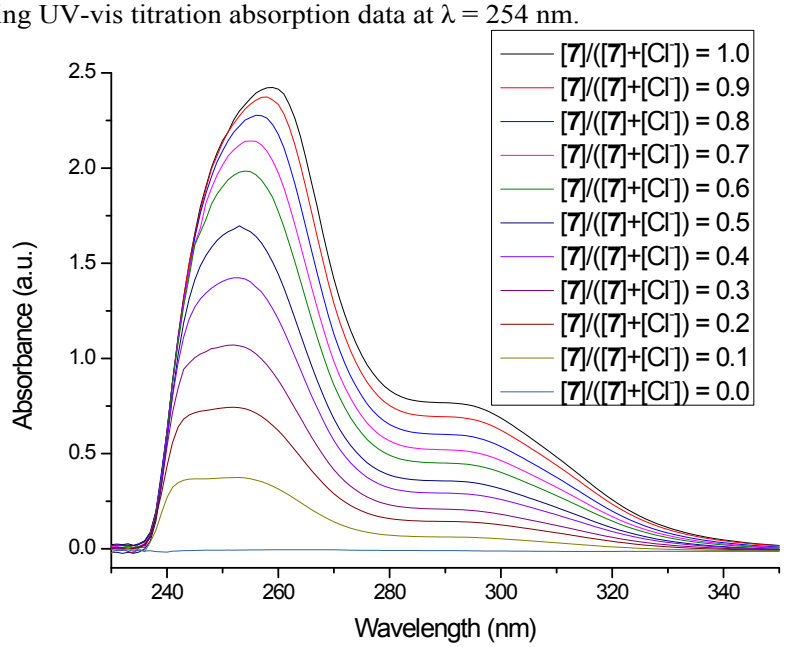


Fig. S8. UV-vis spectra of mixtures of host **7** and guest $Bu_4N^+Cl^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5 × 10^{-5} M.

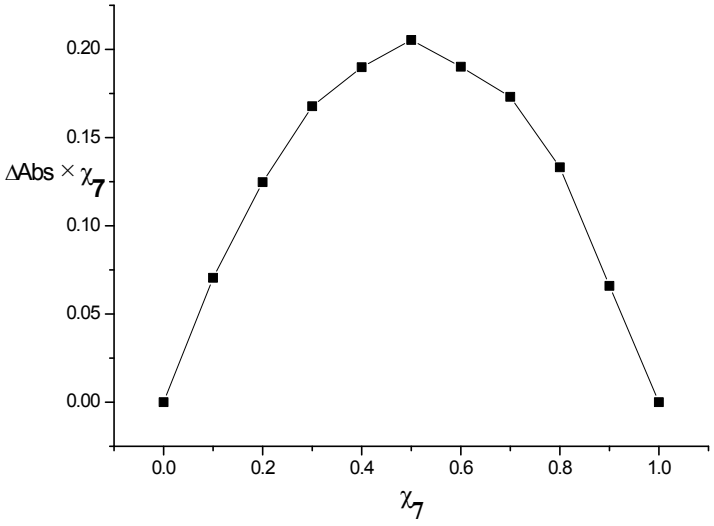


Fig. S9. Job-plot for the complex between host **7** and guest $Bu_4N^+Cl^-$ in $CHCl_3$ using UV-vis absorption values at $\lambda = 290$ nm, showing a 1:1 stoichiometry.

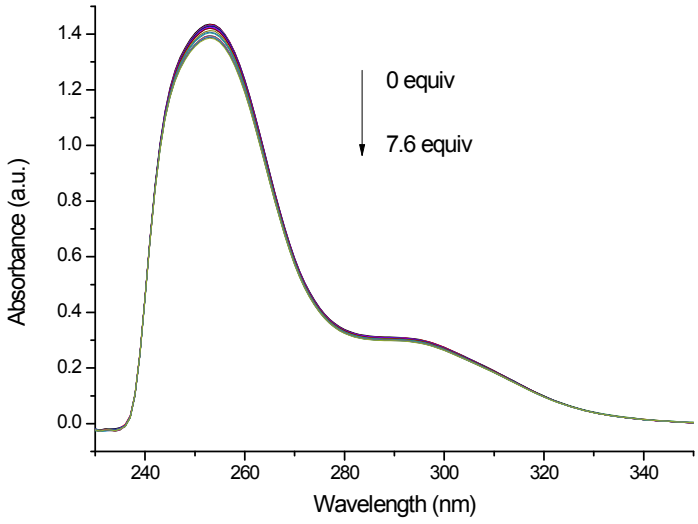


Fig. S10. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-7.6 equivalents of guest $Bu_4N^+Cl^-$, 298 K.

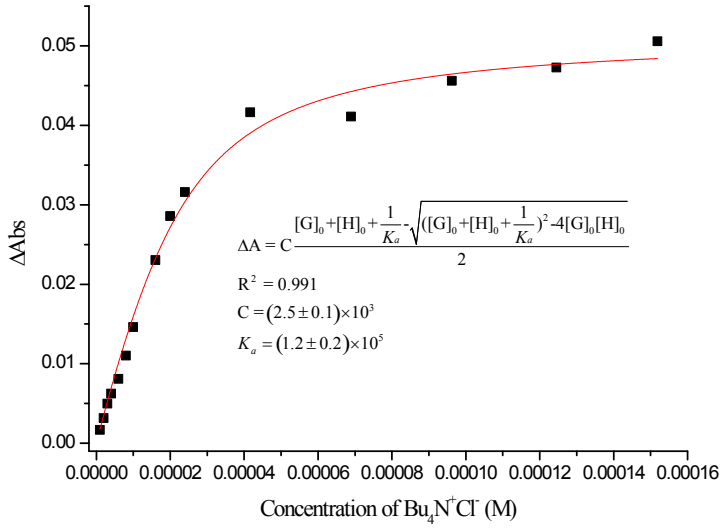


Fig. S11. Plot of the absorption intensity changes at λ = 253 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (1.2 ± 0.2) × 10^5 M^{-1}.

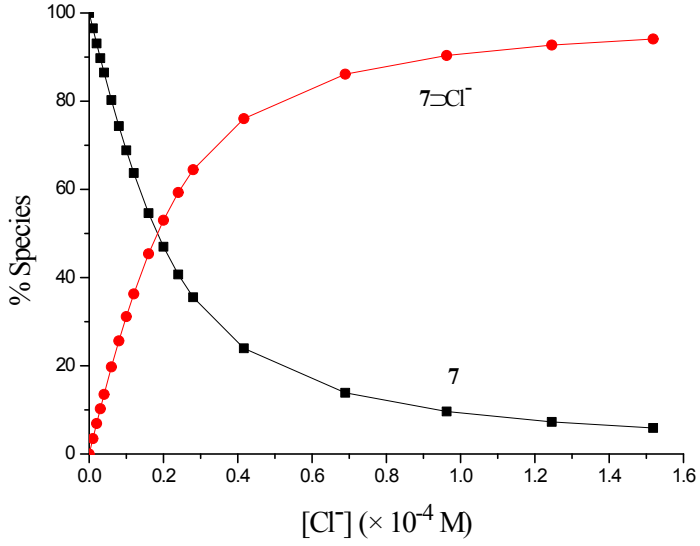


Fig. S12. Distribution diagram between **7** and **7**⊃Cl^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 253 nm.

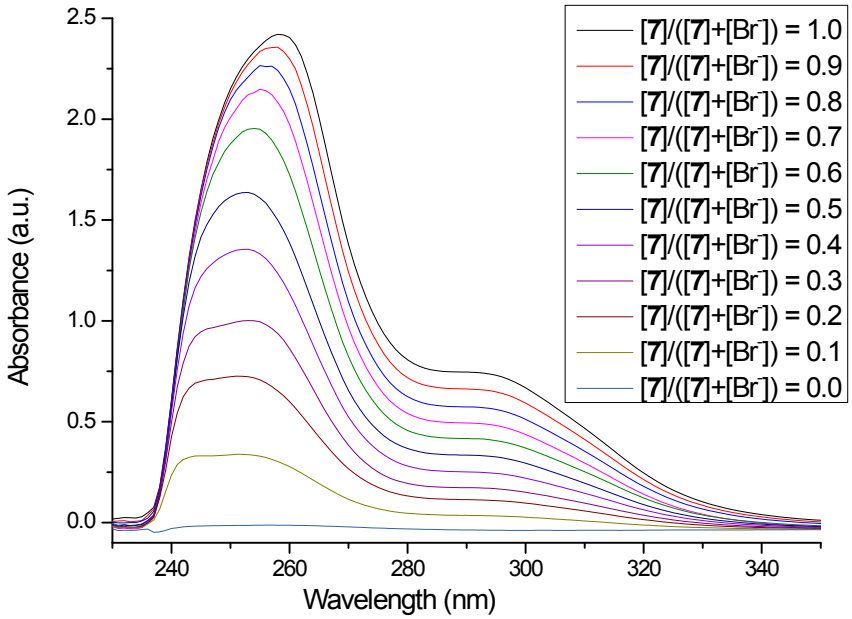


Fig. S13. UV-vis spectra of mixtures of host **7** and guest $Bu_4N^+Br^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5×10^{-5} M.

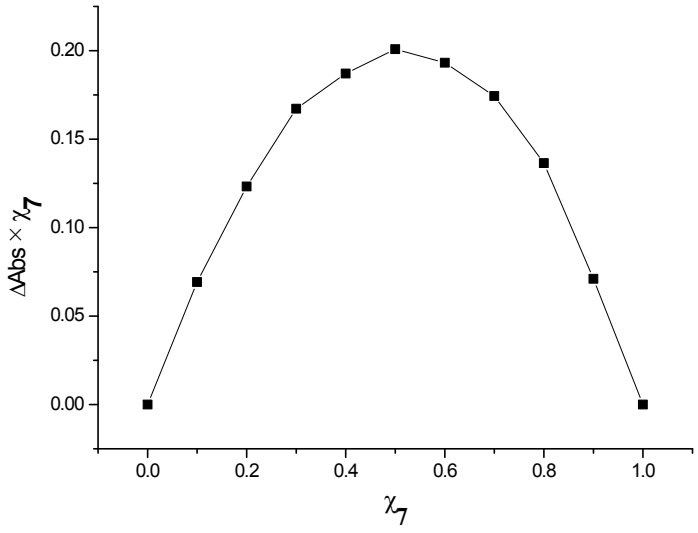


Fig. S14. Job-plot for the complex between host **7** and guest $Bu_4N^+Br^-$ in $CHCl_3$ using UV-vis absorption value at $\lambda = 290$ nm, showing a 1:1 stoichiometry.

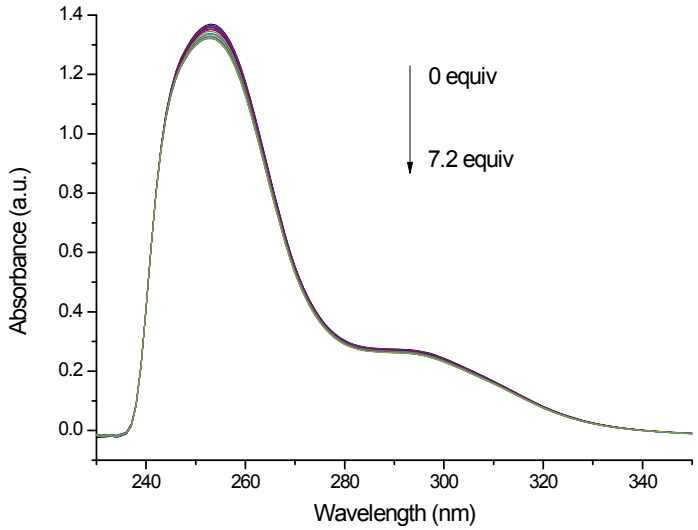


Fig. S15. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-7.2 equivalents of guest $Bu_4N^+Br^-$, 298 K.

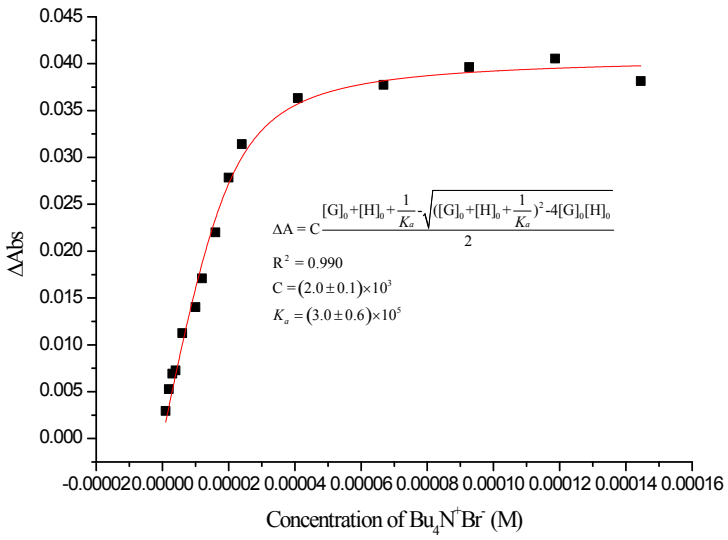


Fig. S16. Plot of the absorption intensity changes at λ = 250 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant $K_a = (3.0 \pm 0.6) \times 10^5$ M^{-1}.

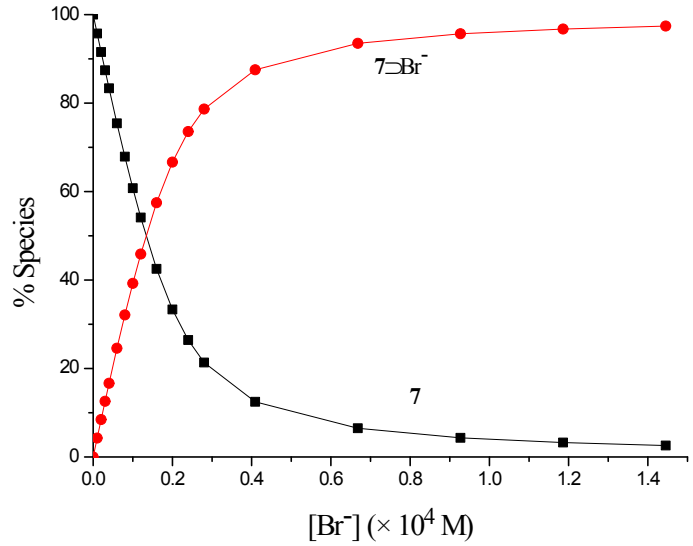


Fig. S17. Distribution diagram between **7** and **7**⊃Br^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 250 nm.

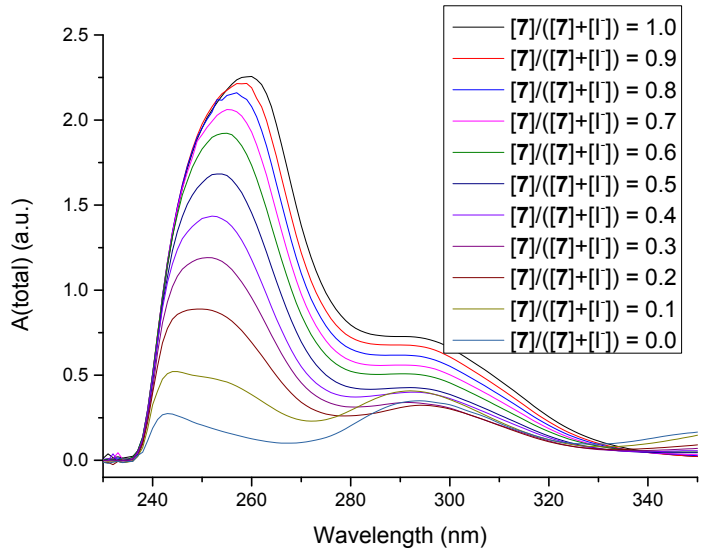


Fig. S18. UV-vis spectra of a mixture of host **7** and guest $Bu_4N^+I^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5×10^{-5} M.

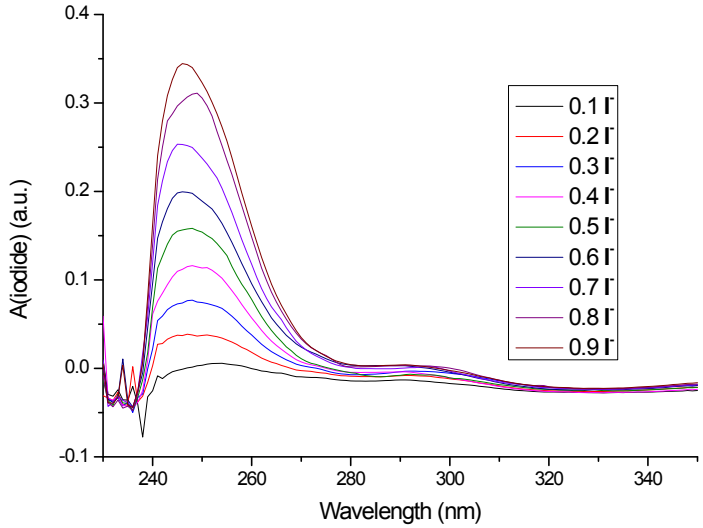


Fig. S19. UV-vis spectra of guest $Bu_4N^+I^-$ with the same concentrations in the above measurements.

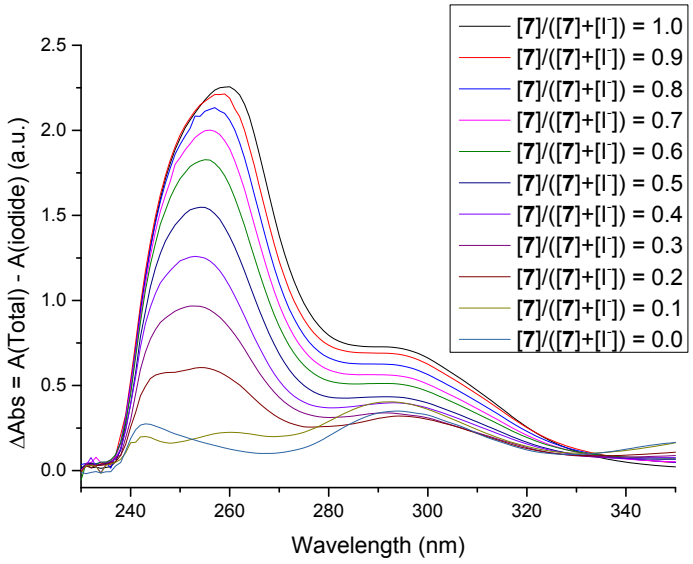


Fig. S20. UV-vis spectra, after deduction of I^- absorbance.

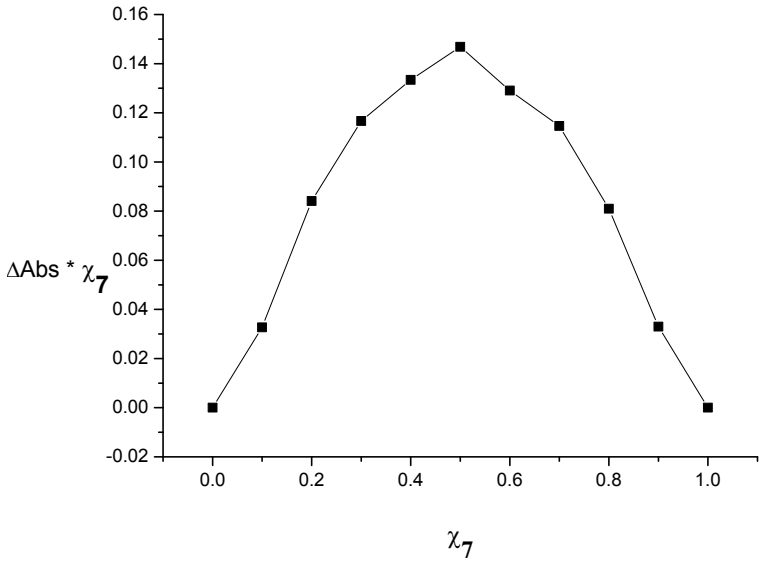


Fig. S21. Job-plot for the complex between host **7** and guest $Bu_4N^+I^-$ in $CHCl_3$ using UV-vis absorption value at λ = 290 nm, showing a 1:1 stoichiometry.

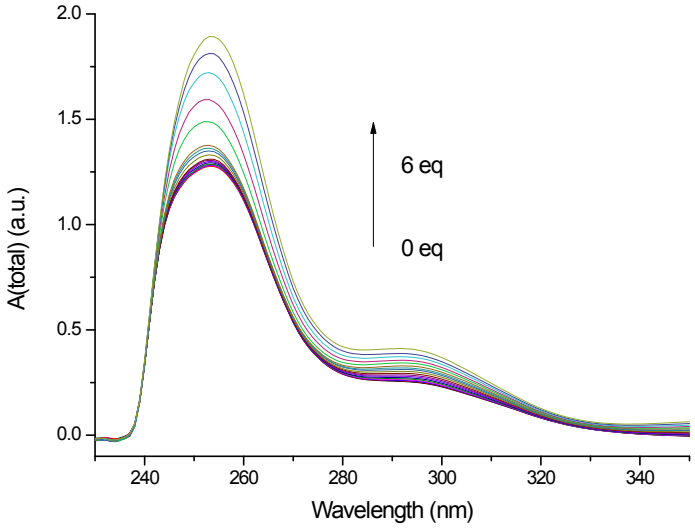


Fig. S22. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-6 equivalents of guest $Bu_4N^+I^-$, 298 K.

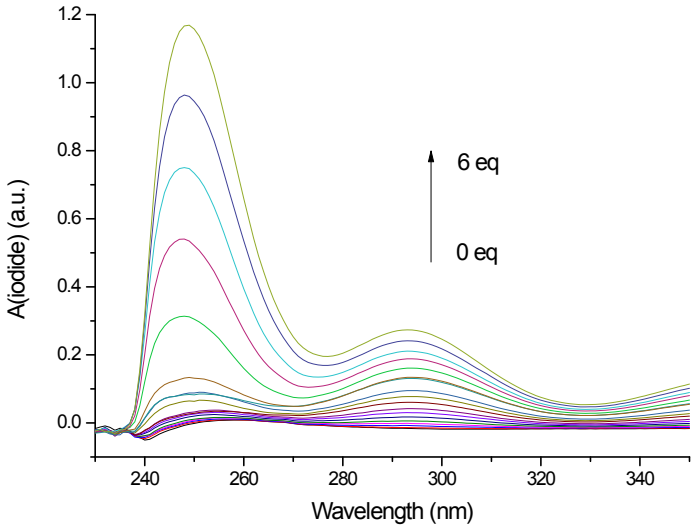


Fig. S23. UV-vis spectra of guest $Bu_4N^+I^-$ with the same concentrations in the above titration measurements.

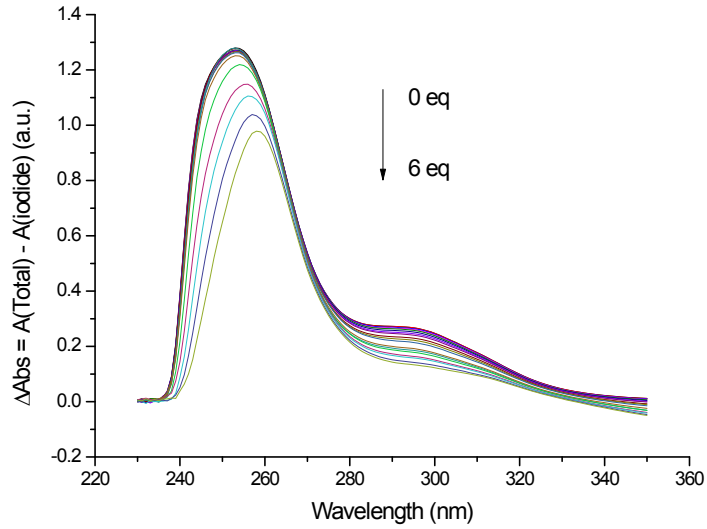


Fig. S24. UV-vis titration curves, after deduction of I^- absorbance.

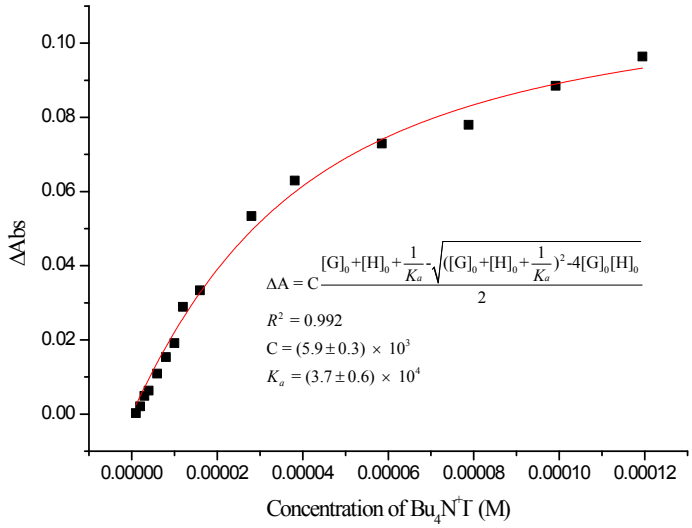


Fig. S25. Plot of the absorption intensity changes at λ = 282 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (3.7 ± 0.6) × 10^4 M^{-1}.

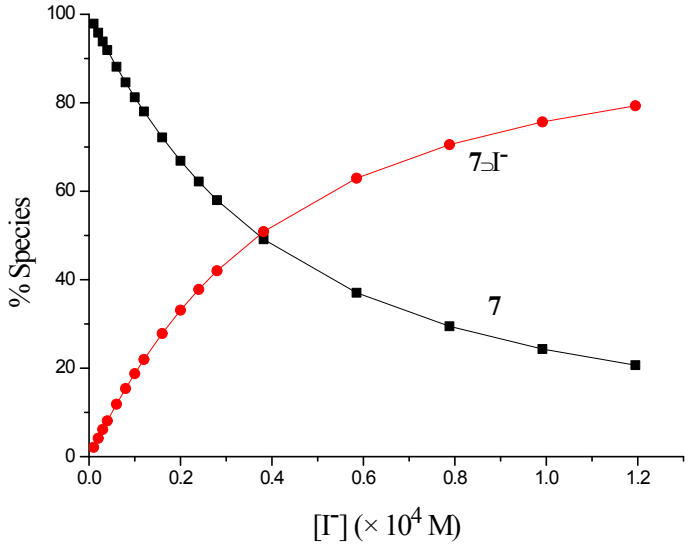


Fig. S26. Distribution diagram between **7** and **7**⊃I^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 282 nm.

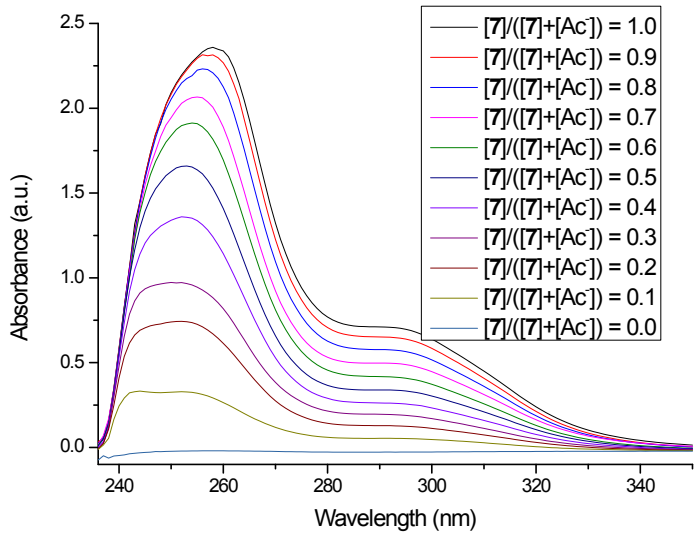


Fig. S27. UV-vis spectra of mixtures of host **7** and guest $Bu_4N^+Ac^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5×10^{-5} M.

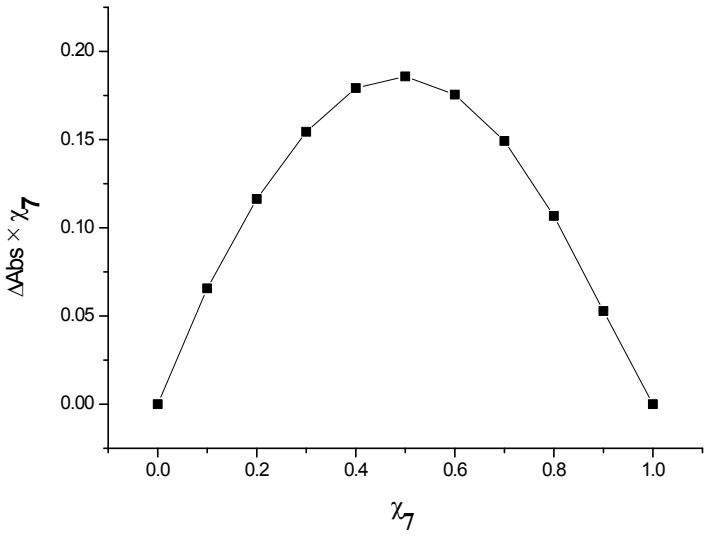


Fig. S28. Job-plot for the complex between host **7** and guest $Bu_4N^+Ac^-$ in $CHCl_3$ using UV-vis absorption value at $\lambda = 290$ nm, showing a 1:1 stoichiometry.

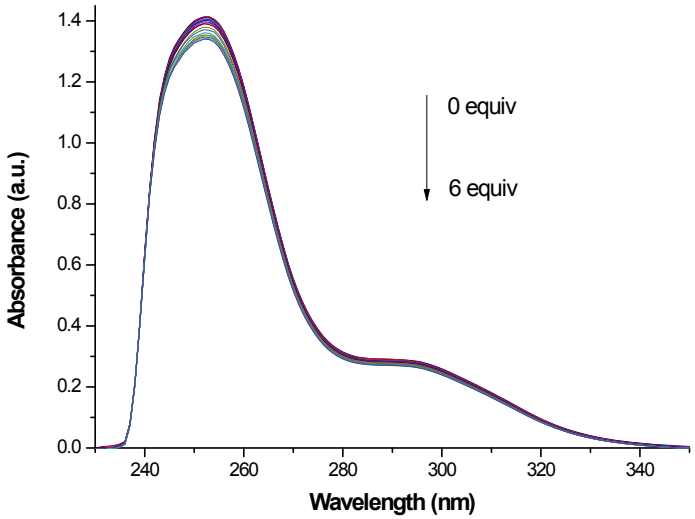


Fig. S29. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-6 equivalents of guest $Bu_4N^+Ac^-$, 298 K.

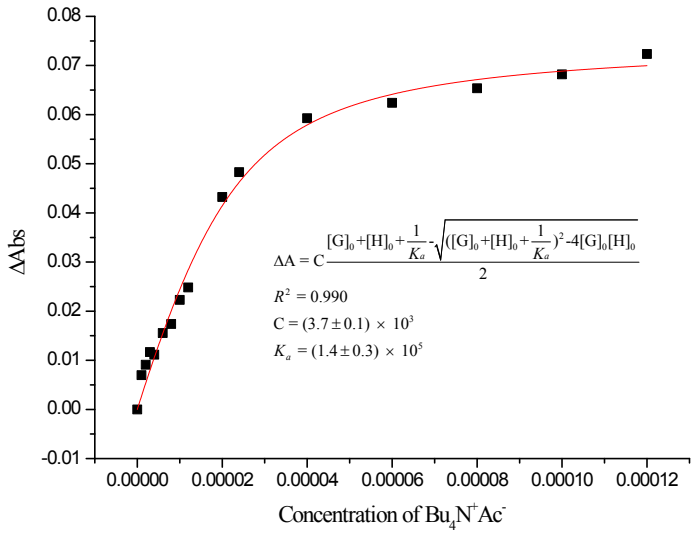


Fig. S30. Plot of the absorption intensity changes at λ = 255 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant $K_a = (1.4 \pm 0.3) \times 10^5$ M^{-1}.

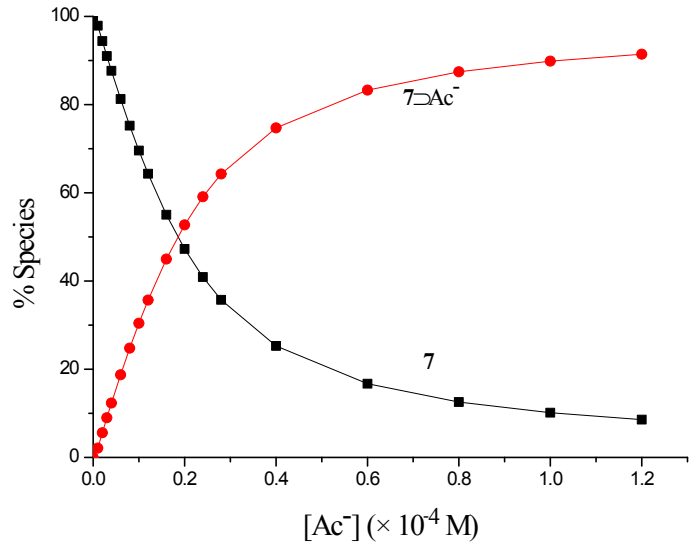


Fig. S31. Distribution diagram between **7** and **7**⊃Ac^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 255 nm.

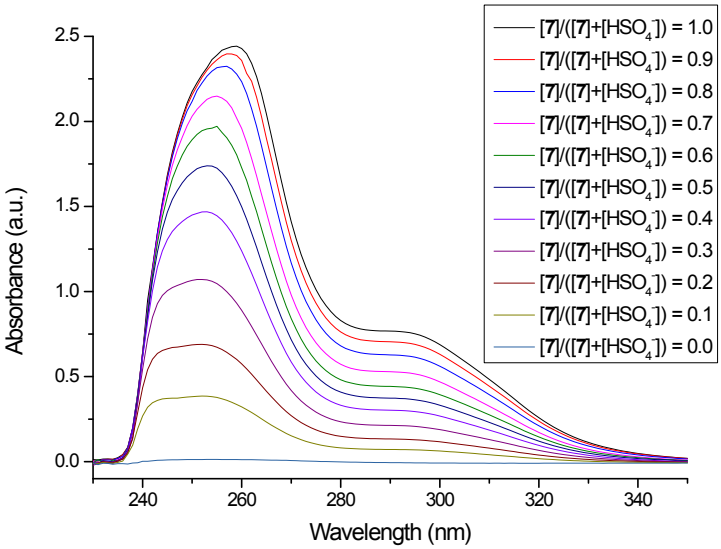


Fig. S32. UV-vis spectra of mixtures of host **7** and guest $Bu_4N^+HSO_4^-$ with different ratios in $CHCl_3$, with the total concentration fixed at 5×10^{-5} M.

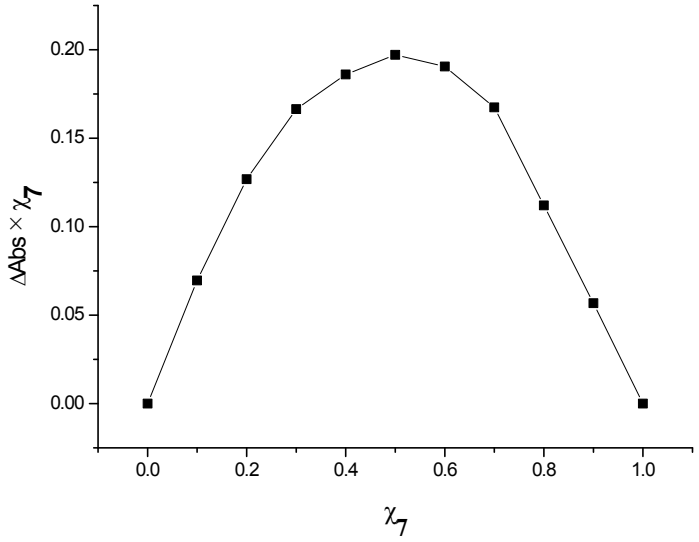


Fig. S33. Job-plot for the complex between host **7** and guest $Bu_4N^+HSO_4^-$ in $CHCl_3$ using UV-vis absorption value at λ = 290 nm, showing a 1:1 stoichiometry.

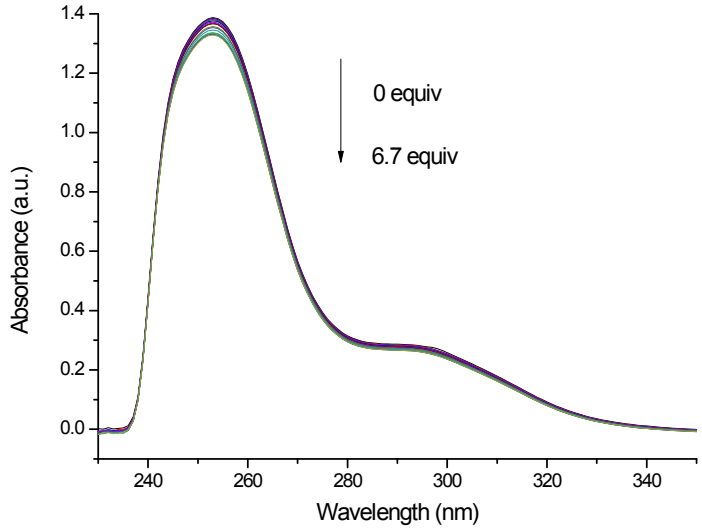


Fig. S34. Titration curves of host **7** (fixed at 2×10^{-5} M in $CHCl_3$) with 0-6.7 equivalents of guest $Bu_4N^+HSO_4^-$, 298 K.

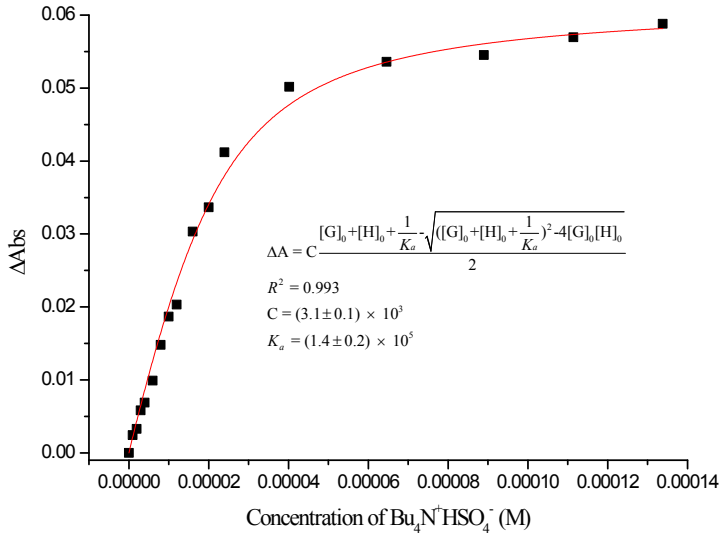


Fig. S35. Plot of the absorption intensity changes at λ = 254 nm *vs* the guest concentration. The red line was obtained from non-linear curve-fitting using Eq. S1, yielding an association constant K_a = (1.4 ± 0.2) × 10^5 M^{-1}.

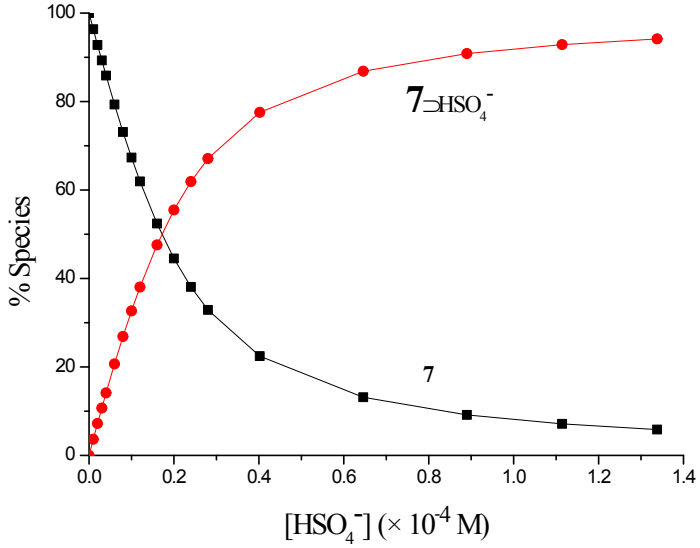


Fig. S36. Distribution diagram between **7** and **7**⊃HSO_4^- during the spectrophotometric titration, calculated using UV-vis titration absorption data at λ = 254 nm.

Reference

S1. K. A. Connors, *Binding Constants: The Measurement of Molecular Complex Stability*, Wiley, 1987

S2. K. Hirose, in *Analytical Methods in Supramolecular Chemistry*, ed. C. Schalley, Wiley-VCH, 2012, vol. 1, pp. 27-66.