Supporting Information

Designed Self-assemblies Based on Cooperative Noncovalent Interactions Including Anion-π, Lone-pair Electron-π and Hydrogen Bonding

Wei Liu, Qi-Qiang Wang, Yuanyuan Wang, Zhi-Tang Huang, and De-Xian Wang*

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

Email: dxwang@iccas.ac.cn

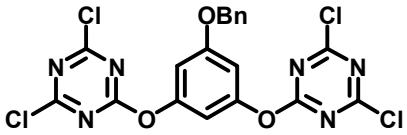
Table of Contents

1. General information

^{1}H and ^{13}C NMR spectra were recorded on 300MHz, 400MHz and 600MHz NMR spectrometers. Chemical shifts are reported in ppm with either tetramethylsilane or the residual solvent used as an internal standard. Melting points are uncorrected. All solvents were dried according to standard procedures prior to use. All other major chemicals were obtained from commercial sources and used without further purification.

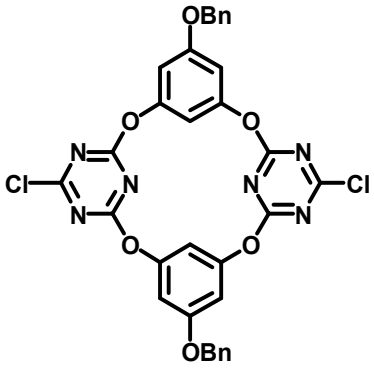
2. Experimental details

Synthesis of 3



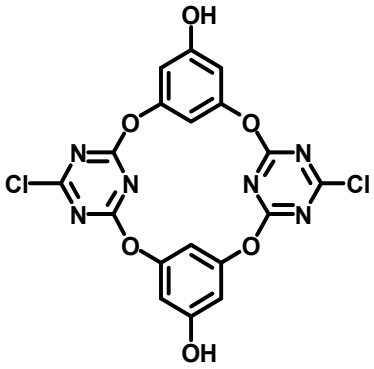
To an ice-bath cooled flask containing cyanuric chloride (1.62 g, 8.8 mmol) in tetrahydrofuran (30 mL) was added dropwise a mixture of 5-(benzyloxy)-benzene-1,3-diol **1** (0.86 g, 4 mmol) and diisopropylethylamine (1.30 g, 10 mmol) in tetrahydrofuran (40 mL) within 1 h. The reaction mixture was stirred for another 2 hour. After filtration, the filtrate was concentrated and chromatographed on a silica gel column with a mixture of petroleum ether and ethylacetate (15:1) as an eleunt to give pure compound **3** as white solid (1.34 g, 65 %): mp 157-158 °C; IR (KBr) ν 1629, 1600, 1554, 1532 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.43-7.34 (m, 5H), 6.81 (d, J=2.1 Hz, 2H), 6.70 (t, J=2.1 Hz, 1H), 5.08 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 170.7, 160.6, 152.0, 135.5, 128.8, 128.5, 127.6, 107.3, 106.9, 70.9; MS (EI) m/z (%) 514 (0.6), 512 (1), 510 (M+0.8), 92 (10), 91 (100), 65 (7). Anal. Calcd. For $C_{19}H_{10}N_6O_3Cl_4$: C, 44.56; H, 1.97; N, 16.41. Found: C, 44.89; H, 1.97; N, 16.30.

Synthesis of 4b



At room temperature, monomer 5-(benzyloxy)-benzene-1,3-diol **1** (2.30 g, 10.6 mmol) and trimer **3** (5.50 g, 10.6 mmol) was dissolved in acetone (250 mL), respectively and the mixture was added dropwise simultaneously to a solution of diisopropylethylamine (5.2 g, 40 mmol) in acetone (1000 mL) within 3 hours. The mixture was stirred for another 24 h. After removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethylacetate (15:1) as an eluent to give pure compound **4b** as white solid (3.60 g, 52%): mp 186-187°C; IR (KBr) *v* 1628, 1598, 1550 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm 7.37-7.28 (m,10H), 6.56 (d, *J*=2.0 Hz, 4H), 6.34 (t, *J*=2.0 Hz, 2H), 4.96 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 172.3, 160.7, 152.1 ,135.5, 128.7, 128.4, 127.3, 108.2, 106.6, 70.8; MS (MALDI-TOF) m/z (%) 655.0 (M+1, 100), 656.0 (44), 657.0 (78), 658.0 (24),659.0 (16), 677.0 (M^++Na, 20), 678.0 (9), 679.0 (16), 680.0(5). Anal. Calcd. For $C_{32}H_{20}N_6O_6Cl_4$: C, 58.64; H, 3.08; N, 12.82. Found: C, 58.62; H, 3.17; N, 12.67.

Synthesis of 4a



To the solution of $AlCl_3$ (1.99 g, 15 mmol) in 40 mL of $CHCl_3$ was added compound **4b** (0.98 g, 1.5 mmol). The solution was refluxed for 3 hours under argon atmosphere. The

reaction was quenched by 50 mL ice-water. The resulting solution was extracted with ethylacetate (120 mL × 2)and the organic phase was dried with anhydrous sodium sulphate. After removal of the solvent, the residue was chromatographed on a silica gel column with a mixture of petroleum ether and ethylacetate (3:1) as an eleunt to give pure **4a** as white solid (0.15 g, 21%): mp >300 ^{o}C; IR (KBr) ν 3225, 1551, 1440 cm^{-1}; ^{1}H NMR (300 MHz, d_6-acetone) δ ppm 9.19 (s, 2H), 6.57 (d, J=1.8 Hz, 2H), 6.54 (d, J=1.8 Hz, 4H); ^{13}C NMR (150 MHz, d_6-acetone) δ 173.5, 172.5, 159.4, 152.6, 107.0, 106.6; MS (ESI, neg.) *m/z* 473.1 (M-H). Anal. Calcd. for $C_{18}H_8Cl_2N_6O_6$·EA: C, 46.91; H, 2.86; N, 14.92. Found: C, 46.85; H, 2.66; N, 15.19.

Methods to get the single crystal fitted to X-ray analysis.

Et_4N^+(4a·Cl)$^-$ ($C_{26}H_{28}Cl_3N_7O_6$). 4a (6 mg) and tetraethylammonium chloride (4 mg) was dissolved in acetone and methanol, respectively. The two solutions were mixed together and diethyl ether was allowed to evaporate into the mixture slowly to afford colorless single crystals. Same procedures were applied to obtaine single crystals of **Et_4N^+(4a·Br)$^-$** and **Et_4N^+(4a·NO_3)$^-$**.

4a ($C_{44}H_{34}Cl_4N_{12}O_{17}$). 4a (10 mg) was dissolved in a mixture of ethyl acetate and petroleum ether. The solution was allowed to evaporate slowly at room temperature to afford colorless single crystals.

NMR titrations.

The ^{1}H NMR titration was performed at ambient temperature. The concentration of **4a** (1.26×10^{-2} M, 0.5ml, d_6-acetone) was kept constant, batch of anions (chloride, bromide and nitrate) in tetrabutylammonium salts were added and the ^{1}H NMR spectra were recorded. The titration data was fitted with a HyperNMR program.

Diffusion-ordered NMR spectroscopy.

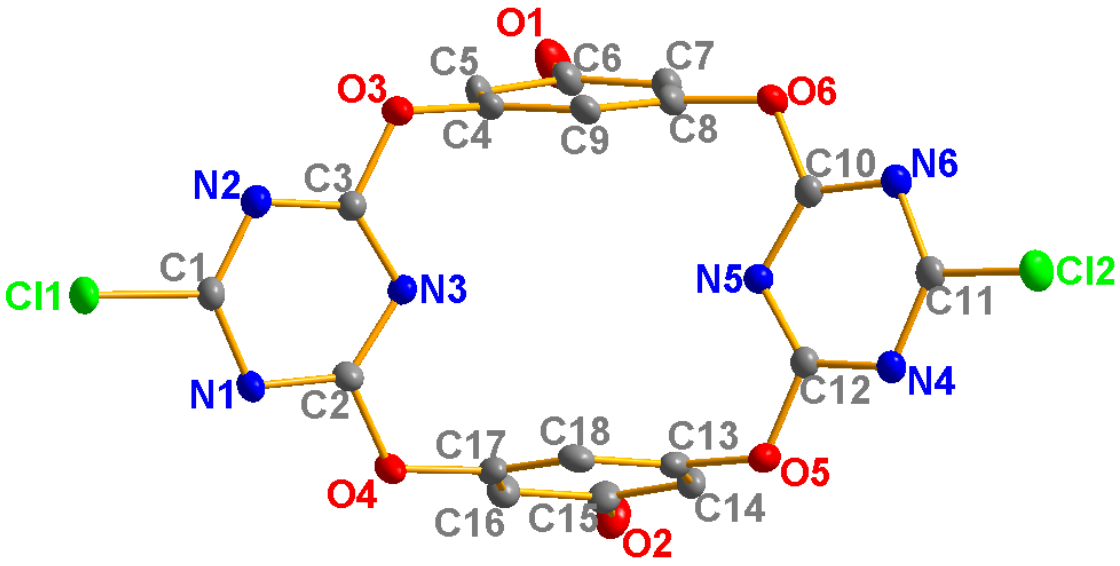
Diffusion ordered spectroscopy (DOSY) was performed at 213 K. The method applied was a pulse sequence employing stimulated echo, longitudinal eddy current delay, bipolar gradients during a recycle delay of 1.5 seconds. For 16 gradient amplitudes that were incremented in steps of gradient squared between 0.68 and 32.35 G cm^{-1}, 8 transients of 32768 complex data points (acquisition time 911 ms) were acquired using a diffusion

delay Δ=100 ms. The gradient pulse durations of δ=1.7 ms for Bu_4NCl (2.76×10^{-2} M), δ=2.1 ms for **4a** and δ=2.6 ms for the mixture of **4a** and Bu_4NCl were used, respectively. To obtain the diffusion coefficients of the host and guest, the weight average of diffusion coefficients of all the aryl and alkyl protons was calculated, respectively.

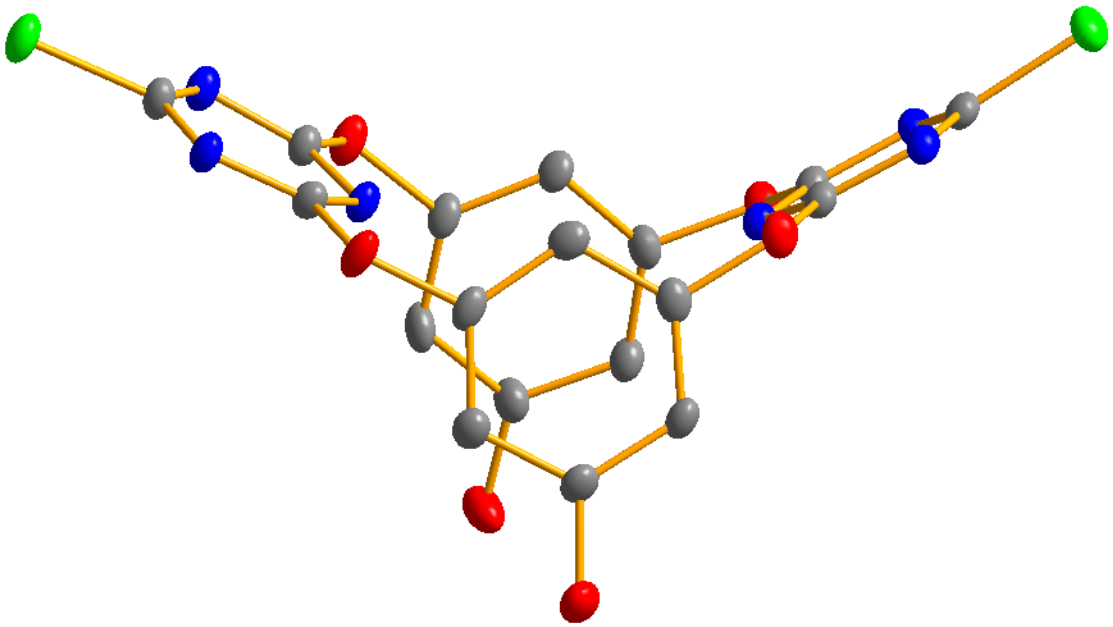
3. X-ray Structures

Table S1 Crystallographic data for **4a** and complexes of **4a** and anions.

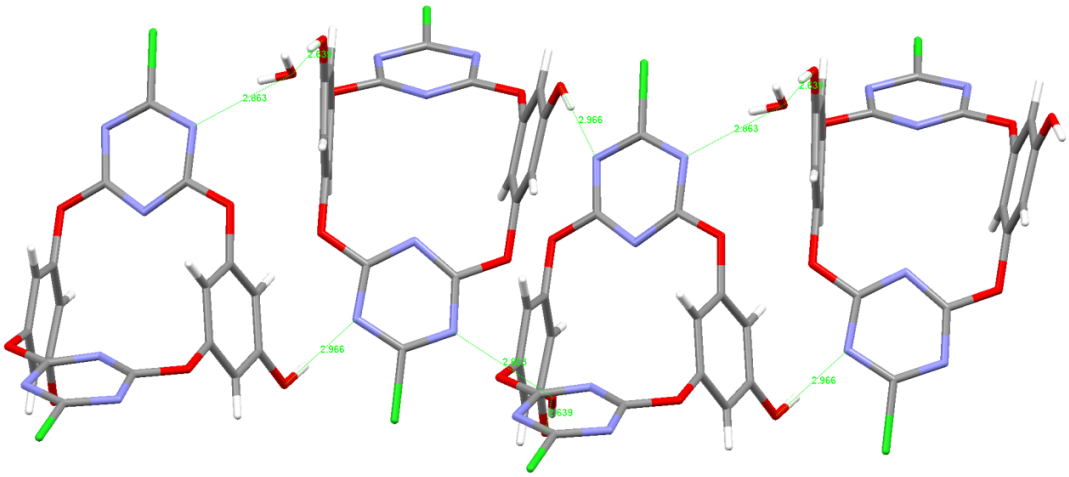
Complex	Et_4N^+(**4a**·Cl^-)	Et_4N^+(**4a**·Br^-)	Et_4N^+(**4a**·NO_3^-)	**4a**
empirical formula	$C_{26}H_{28}Cl_3N_7O_6$	$C_{26}H_{28}BrCl_2N_7O_6$	$C_{26}H_{28}Cl_2N_8O_9$	$C_{44}H_{34}Cl_4N_{12}O_{17}$
M_r	640.90	685.36	667.46	1144.63
crystal size [mm^3]	0.50×0.45×0.36	0.44×0.26×0.24	0.46×0.21×0.19	0.50×0.20×0.12
crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	Pbca	Pbca	Pbca	P2(1)/n
a [Å]	17.004(3)	17.077(3)	17.539(4)	13.470(3)
b [Å]	18.042(3)	17.927(4)	17.744(4)	12.046(2)
c [Å]	19.082(5)	19.393(4)	19.730(4)	30.738(6)
α [deg]	90.00	90.00	90.00	90.00
β [deg]	90.00	90.00	90.00	92.59(3)
γ [deg]	90.00	90.00	90.00	90.00
V [$Å^3$]	5854(2)	5937(2)	6140(2)	4982.6(17)
d [g/cm^3]	1.454	1.534	1.444	1.526
Z	8	8	8	4
T [K]	173(2)	173(2)	173(2)	173(2)
R factor [I>2σ(I)]	0.1154	0.1483	0.2288	0.1180
R factor (all data)	0.1244	0.1808	0.2533	0.1316
quality of fit	1.262	1.300	1.325	1.279
CCDC	968607	968608	968609	968610



A



B



C

Figure S1 Crystal structure of **4a** (A) top view, (B) side view and (C) self assembly through intermolecular hydrogen bonding. Selected bond lengths [Å]: C3-O3 1.351, O3-C4 1.420, C8-O6 1.423, O6-C10 1.343, C12-O5 1.343, O5-C13 1.424, C17-O4 1.409, O4-C2 1.347. Selected distances [Å]: C1···C11 9.218, N3···N5 4.556, C9···C18 4.460, C6···C15 5.373. The probability is 25 percentage. Hydrogen atoms were omitted for clarity.

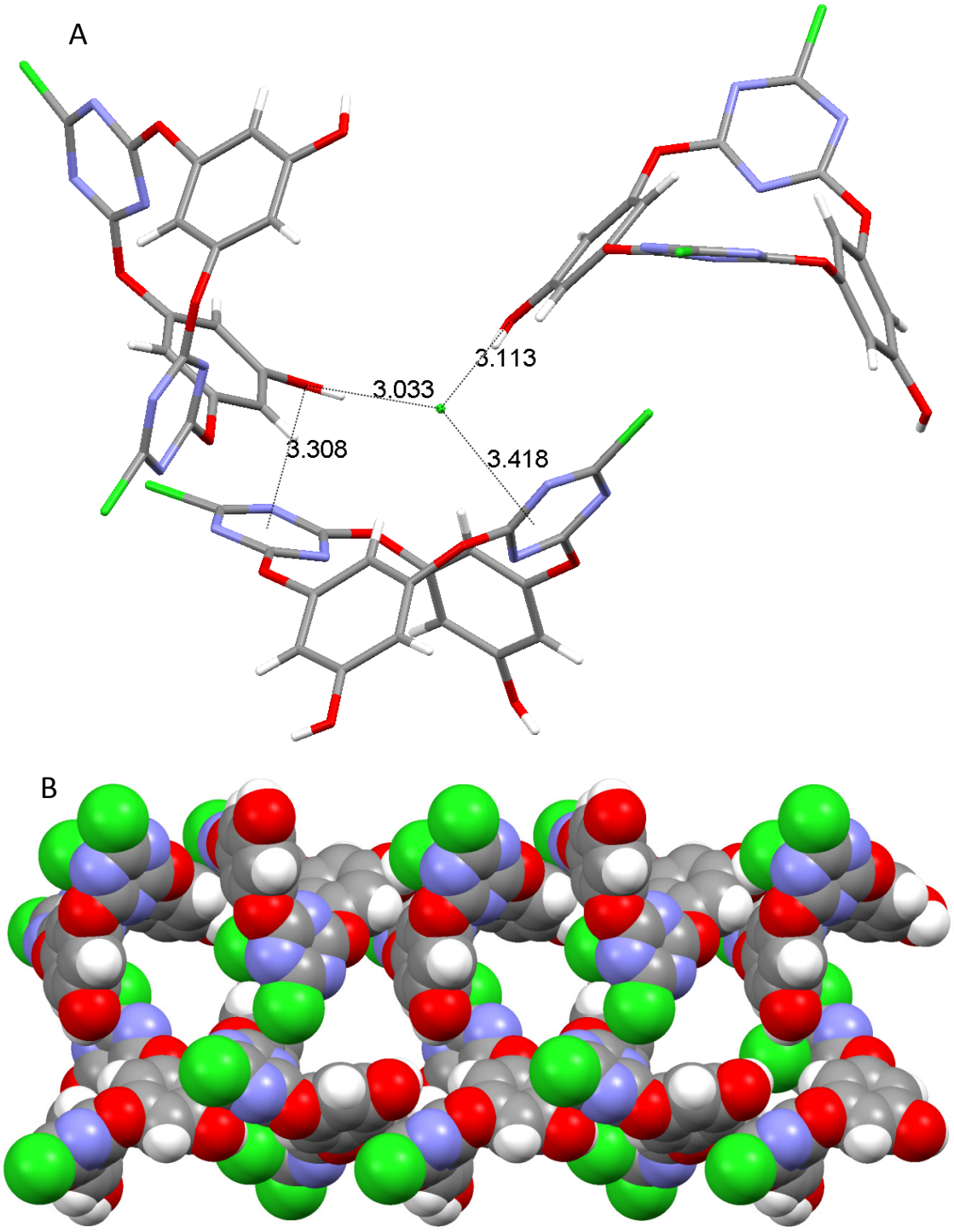
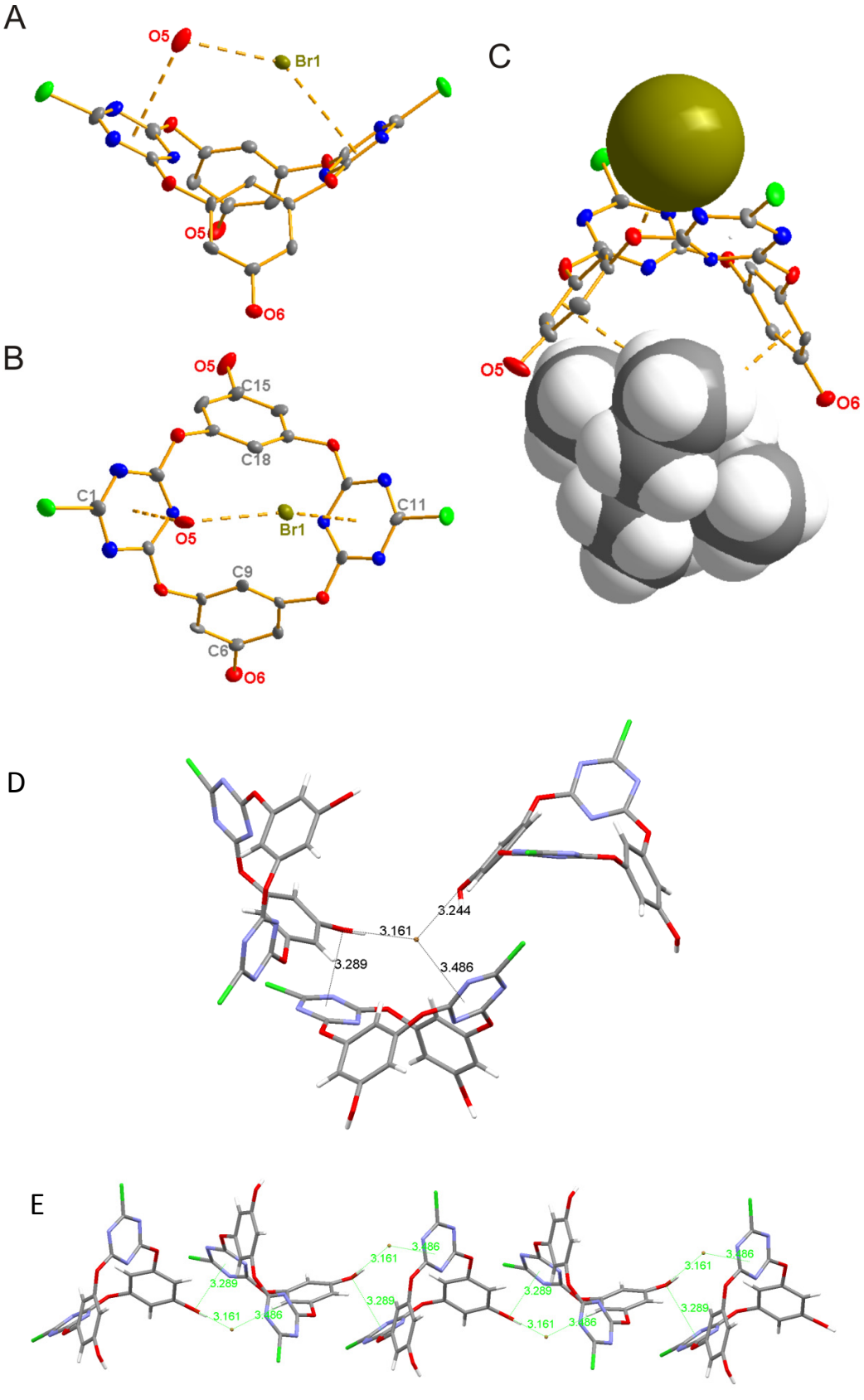


Figure S2 **(A)** Intra- and intermolecular interactions in complex of **4a** and chloride and (B) Infinite meshy assembly



F

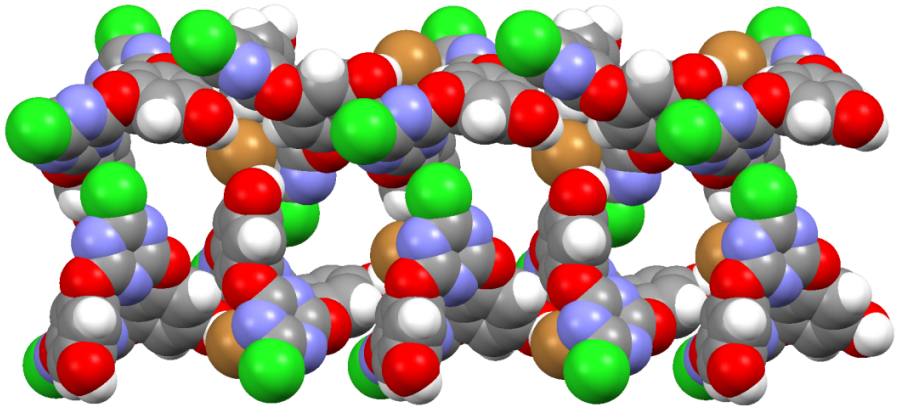
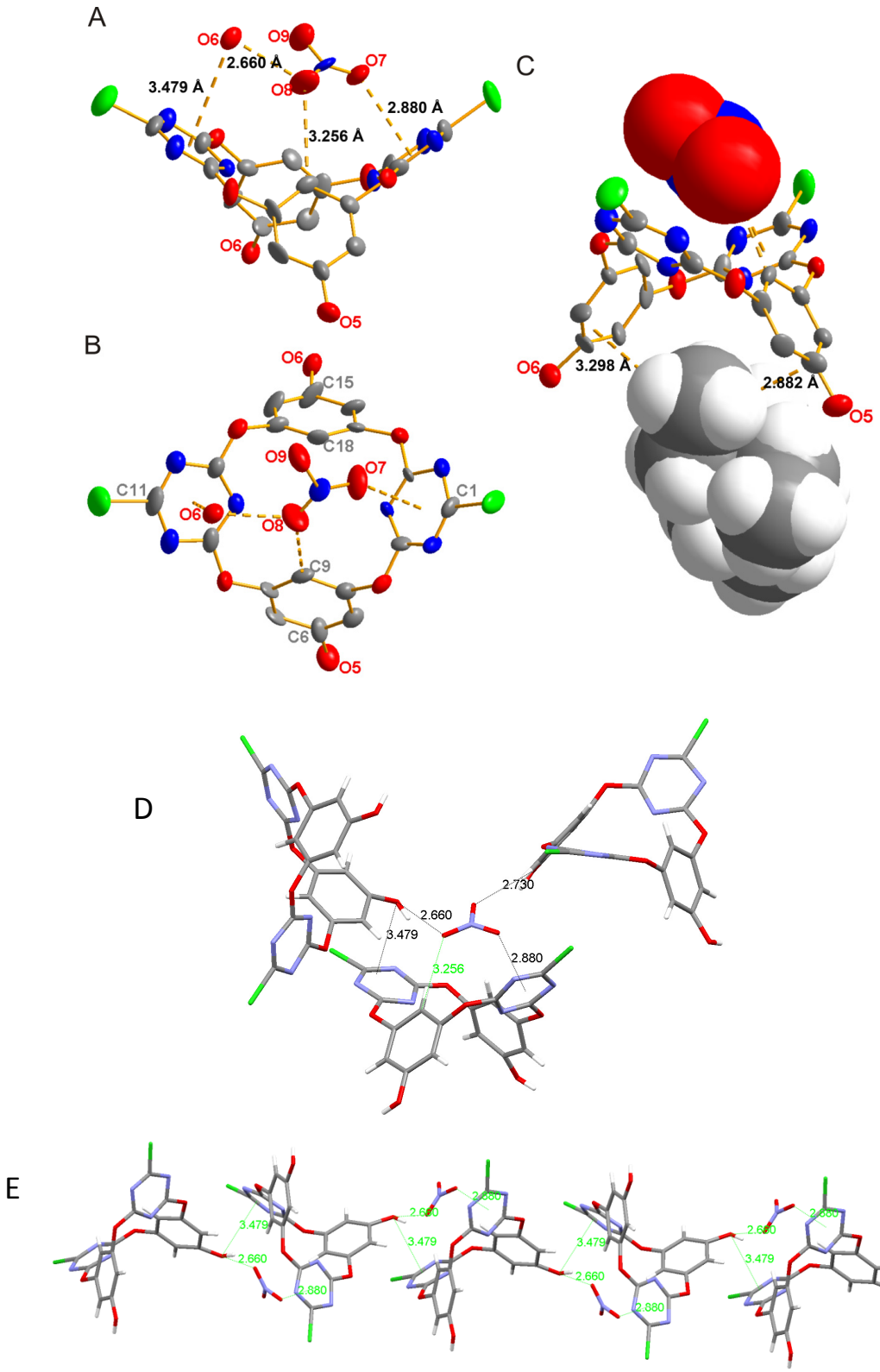


Figure *S3* Crystal structure of complex Et_4N^+(**4a**·Br^-) (A) side view, (B) top view, (C) ion pair complex, (D) intra- and intermolecular interactions of the complex, (E) and (F) infinite linear and meshy self-assemblies. Selected distances (Å): 3.486 [Br(1)···triazine(1) plane], 3.161 [Br(1)···O(5)], 3.289 [O(5)···triazine(2) plane], 8.901 [C(1)···C(11)], 4.123 [C(9)···C(18)], 7.428 [C(6)···C(15)].


A
O6
O9
2.660 Å
O7
3.479 Å
O8
2.880 Å
3.256 Å
O6
O5
B
O6
C15
C18
O9
O7
C11
C1
O6
O8
C9
C6
O5
C
O6
3.298 Å
2.882 Å
O5
D
2.730
2.660
3.479
2.880
3.256
E
3.479
2.660
2.880
2.660
3.479
3.479
2.660
2.880
2.660
3.479
2.880

F

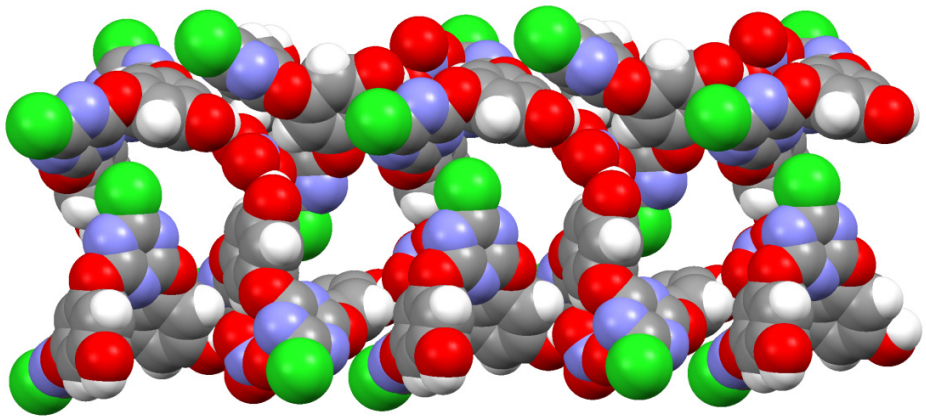
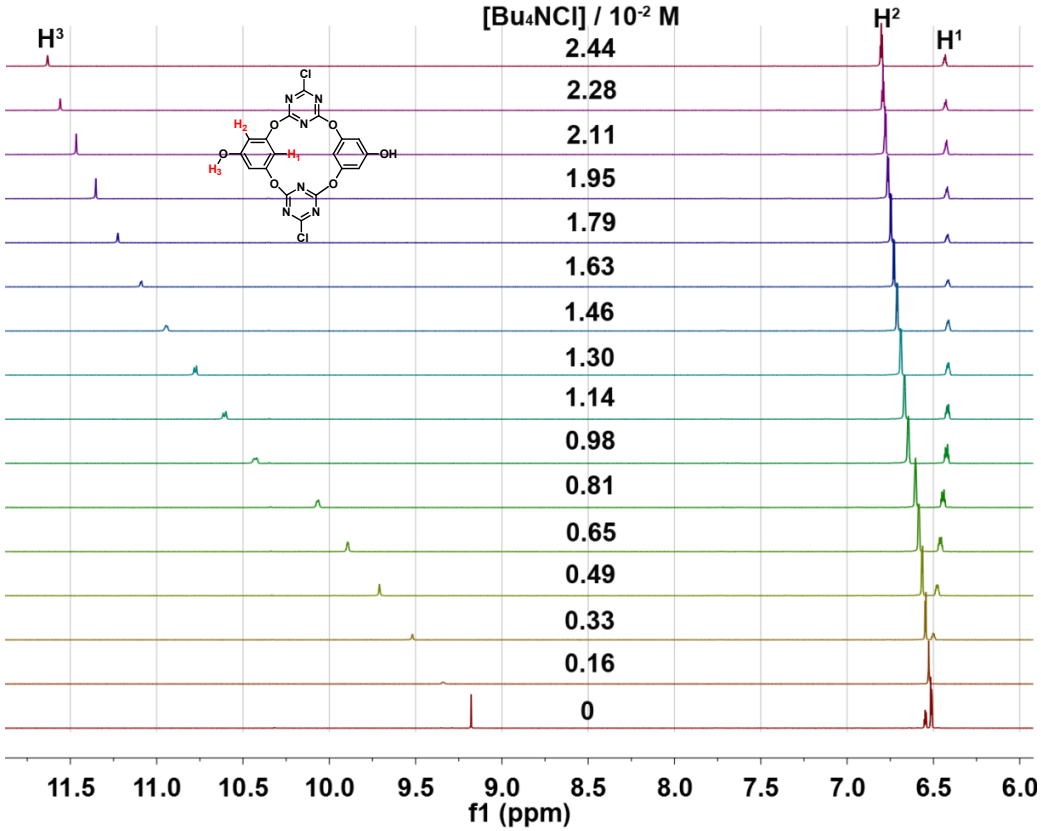


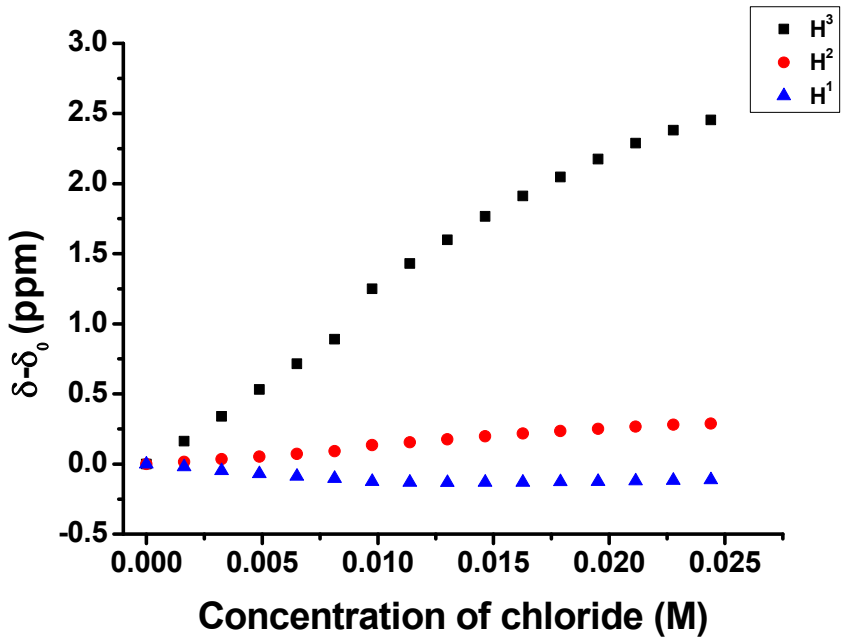
Figure S4 Crystal structure of complex Et_4N^+(**4a**·NO_3^-) (A) side view, (B) top view, (C) ion pair complex, (D) intra- and intermolecular interactions in complex of **4a** and nitrate, (E) and (F) infinite linear and meshy self-assemblies. Selected distances (Å): 2.880 [O(7)···triazine(1) plane], 2.660 O(8)···O(6), 3.256 O(8)···C(9), 3.479 [O(6)···triazine(2) plane], 8.908 C(1)···C(11), 4.164 C(9)···C(18), 7.024 C(6)···C(15).

4. NMR titration, DOSY and 1-D Selective NOESY results

A



B



C

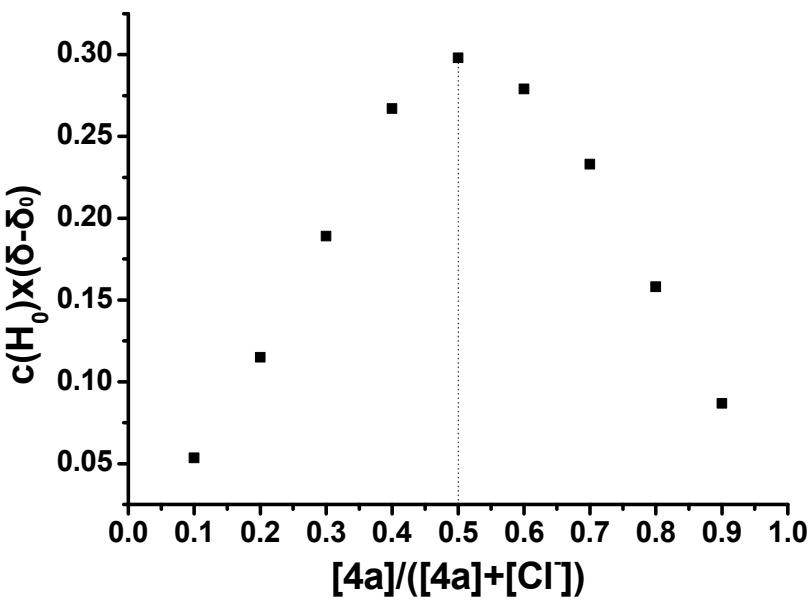
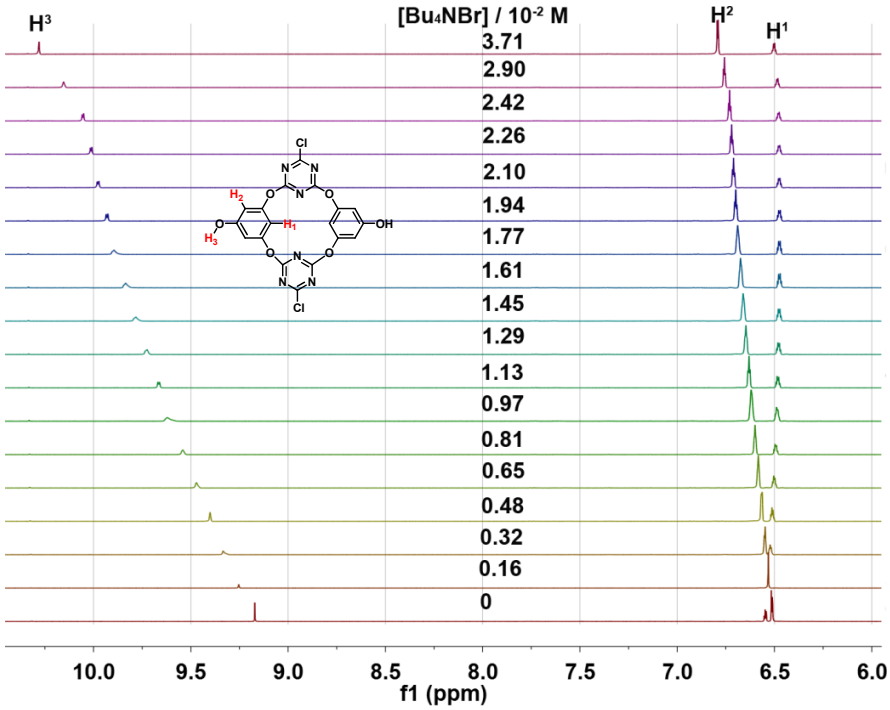
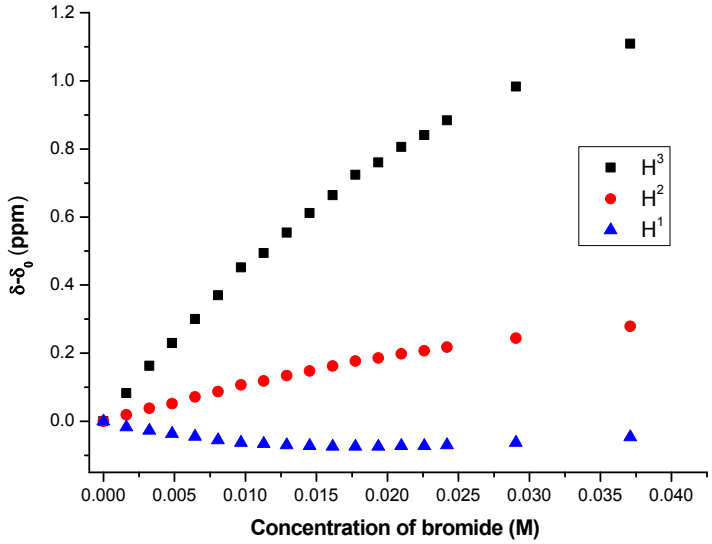


Figure S5 ^{1}H NMR titrations of **4a** (1.26×10^{-2} M) with the addition of tetrabutylammonium chloride in d_6-acetone at room temperature: (A) spectra of titrations with the increasing of anions. (B) Job's plot of the complex with total concentrations being 1.10×10^{-2} M and (C) ^{1}H NMR titration isotherm.

A



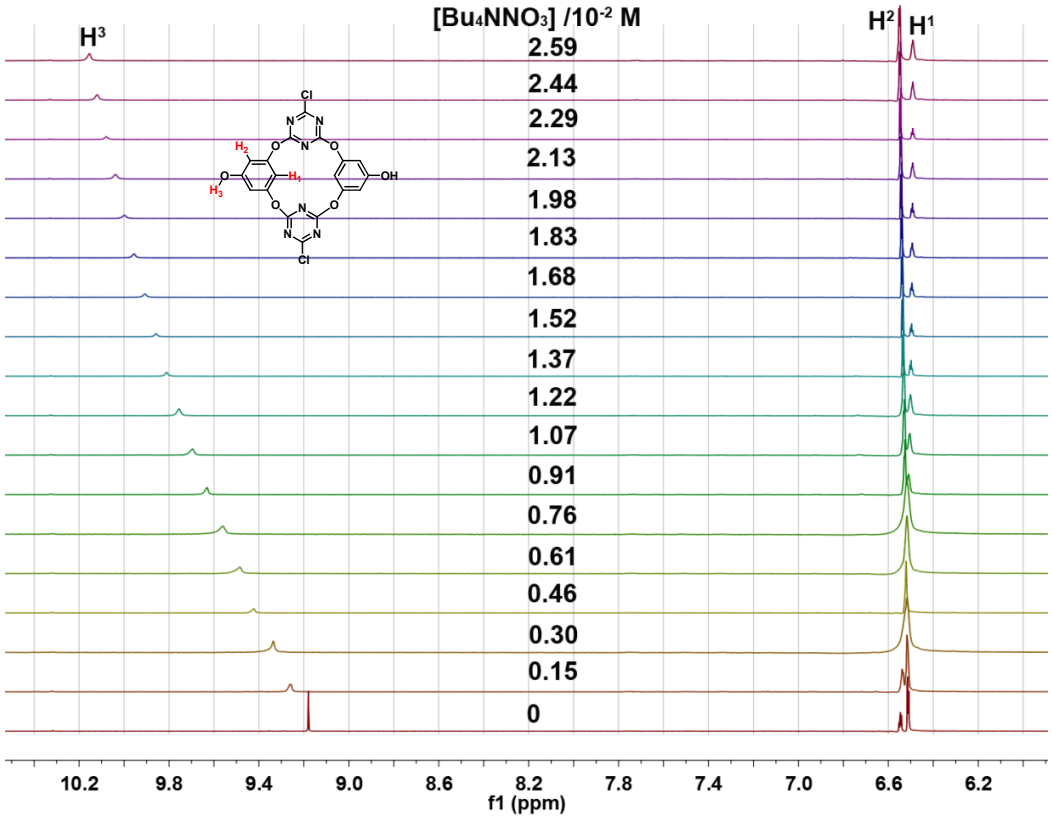
B



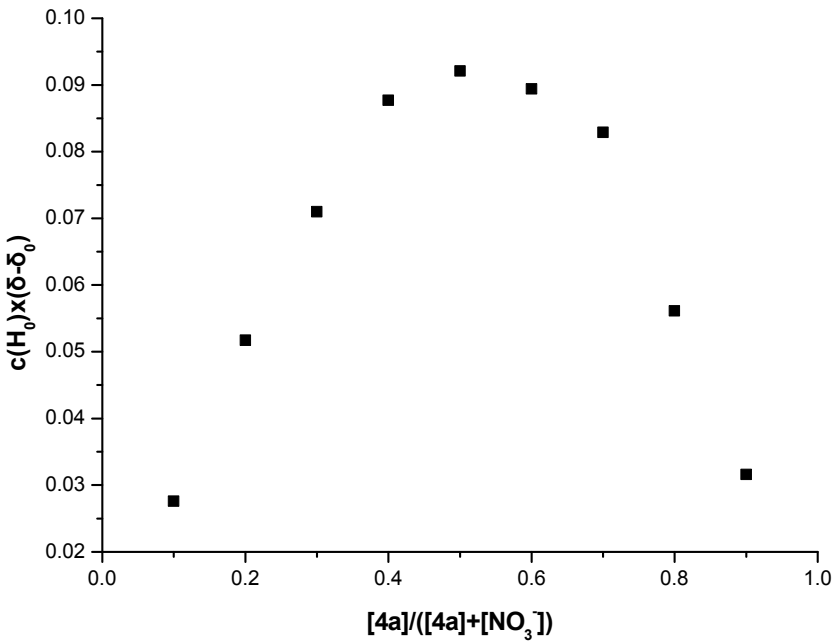
B

Figure S6 ^{1}H NMR titrations of **4a** (1.26×10^{-2} M) with the addition of tetrabutylammonium bromide in d_6-acetone at room temperature: (A) spectra of titrations with the increasing of anions. (B) ^{1}H NMR titration isotherm.

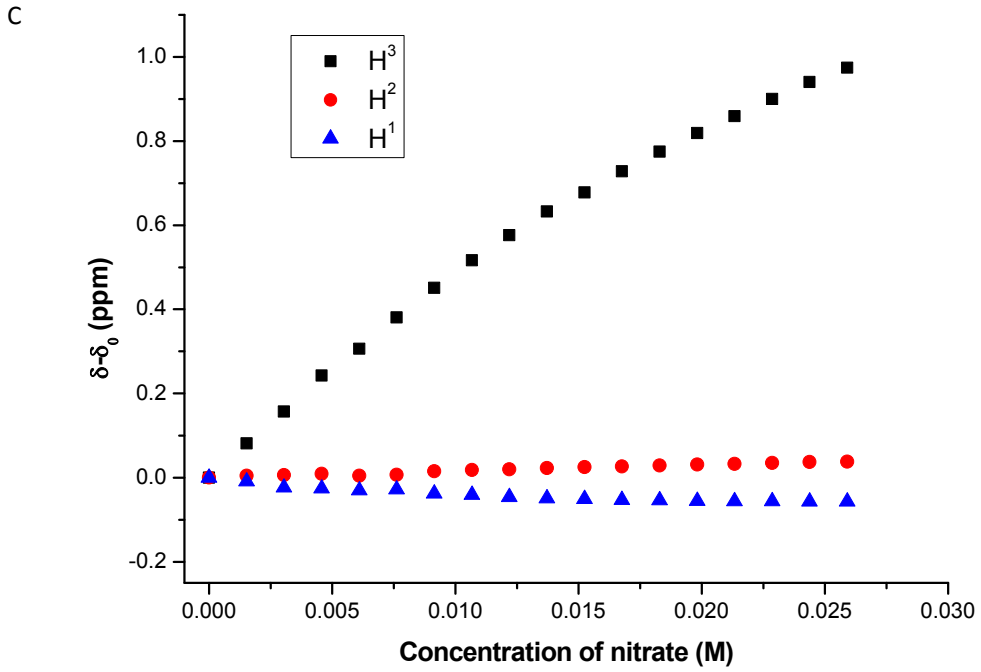
A



B



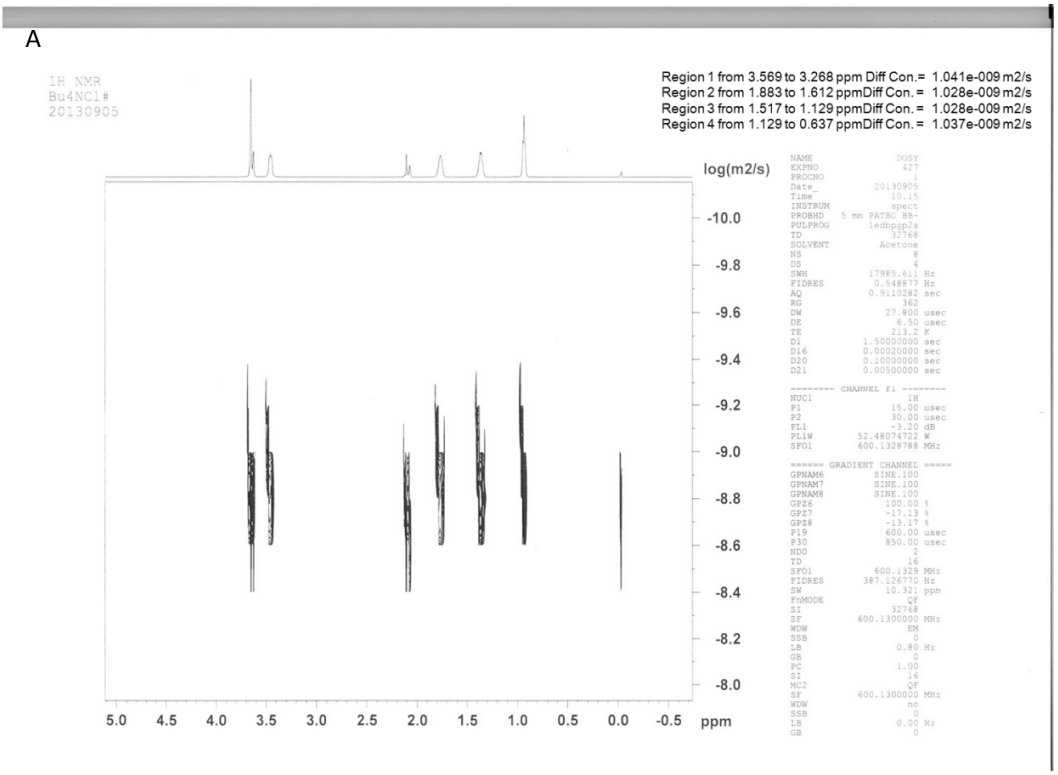
C



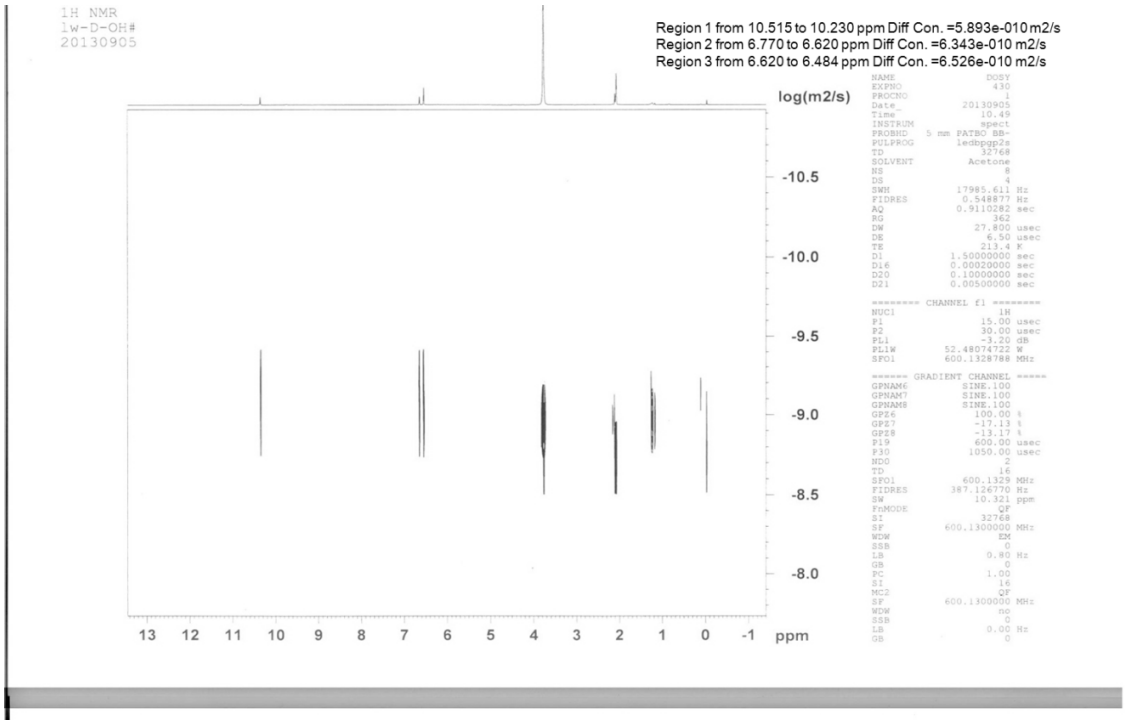
C

Figure S7 ^{1}H NMR titrations of **4a** (1.26×10^{-2} M) with the addition of tetrabutylammonium nitrate in d_6-acetone at room temperature: (A) spectra of titrations with the increasing of anions. (B) Job's plot of the complex with total concentrations being 1.10×10^{-2} M and (C) ^{1}H NMR titration isotherm.

A


1H NMR
Bu4NCl#
20130905
Region 1 from 3.569 to 3.268 ppm Diff Con.= 1.041e-009 m2/s
Region 2 from 1.883 to 1.612 ppmDiff Con. = 1.028e-009 m2/s
Region 3 from 1.517 to 1.129 ppmDiff Con. = 1.028e-009 m2/s
Region 4 from 1.129 to 0.637 ppmDiff Con. = 1.037e-009 m2/s
log(m2/s)
-10.0
-9.8
-9.6
-9.4
-9.2
-9.0
-8.8
-8.6
-8.4
-8.2
-8.0
5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm

B


1H NMR
1w-D-OH#
20130905
Region 1 from 10.515 to 10.230 ppm Diff Con. =5.893e-010 m2/s
Region 2 from 6.770 to 6.620 ppm Diff Con. =6.343e-010 m2/s
Region 3 from 6.620 to 6.484 ppm Diff Con. =6.526e-010 m2/s
log(m2/s)
-10.5
-10.0
-9.5
-9.0
-8.5
-8.0
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 ppm

C

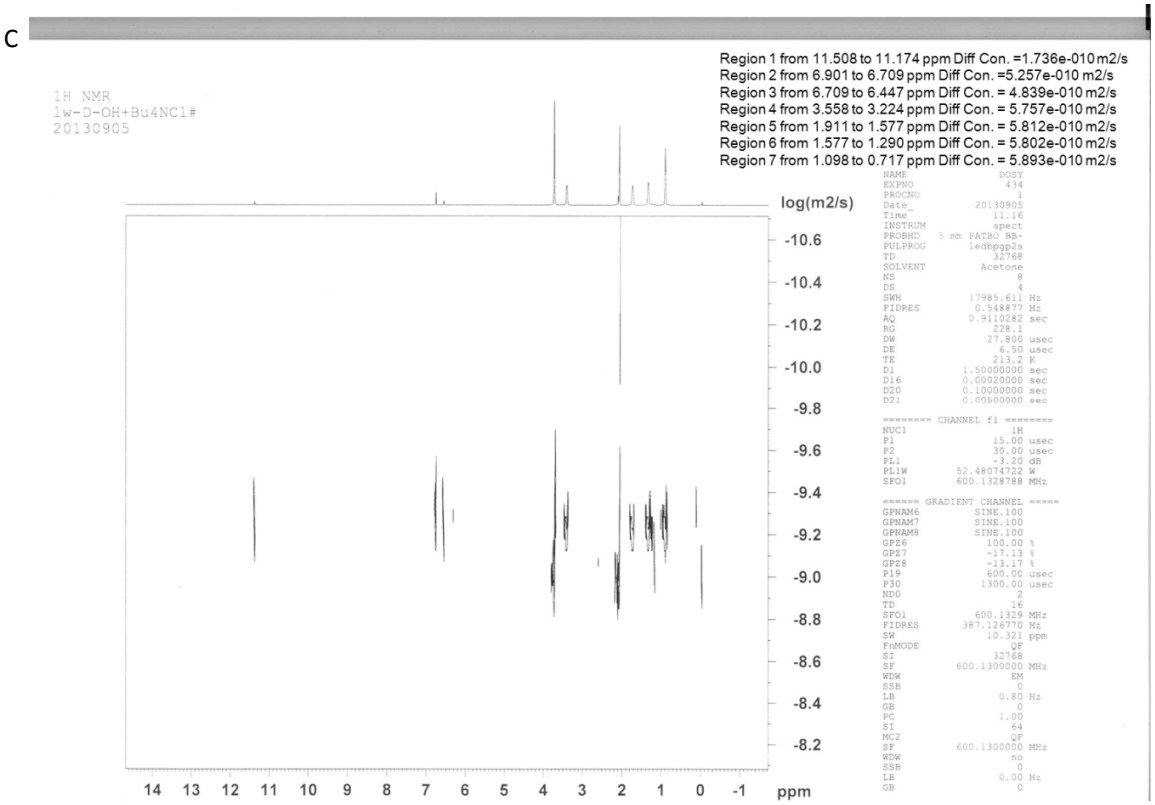
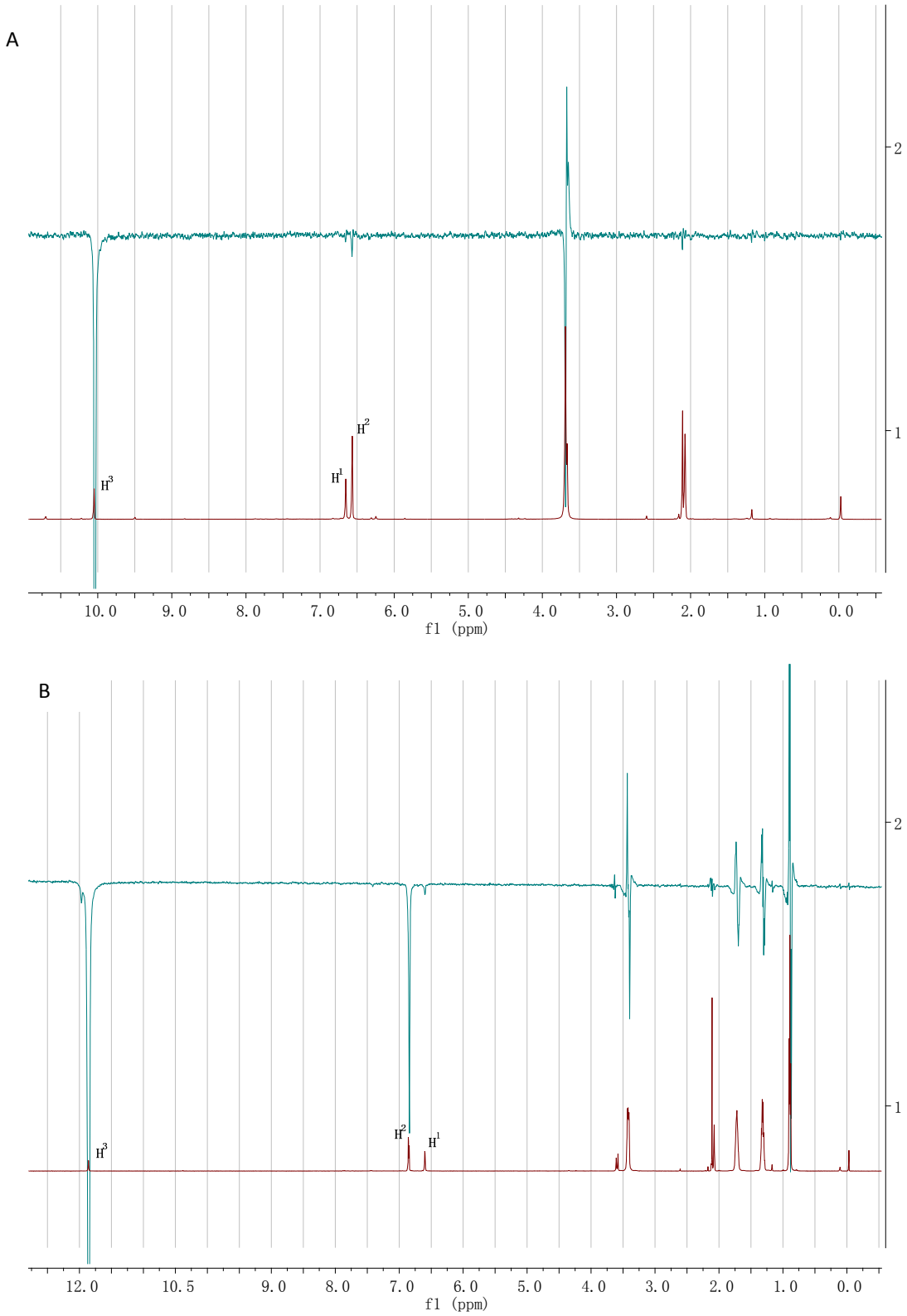


Figure S8 DOSY NMR spectra of (A) Bu_4NCl (2.76×10^{-2} M), (B) **4a** (1.37×10^{-2} M) and (C) mixture of **4a** (1.37×10^{-2} M) and Bu_4NCl (2.76×10^{-2} M) in d_6-acetone. The temperature is 213 K. To obtain the diffusion coefficients of the host and guest, the weight average of diffusion coefficients of all the aryl and alkyl protons was calculated, respectively.



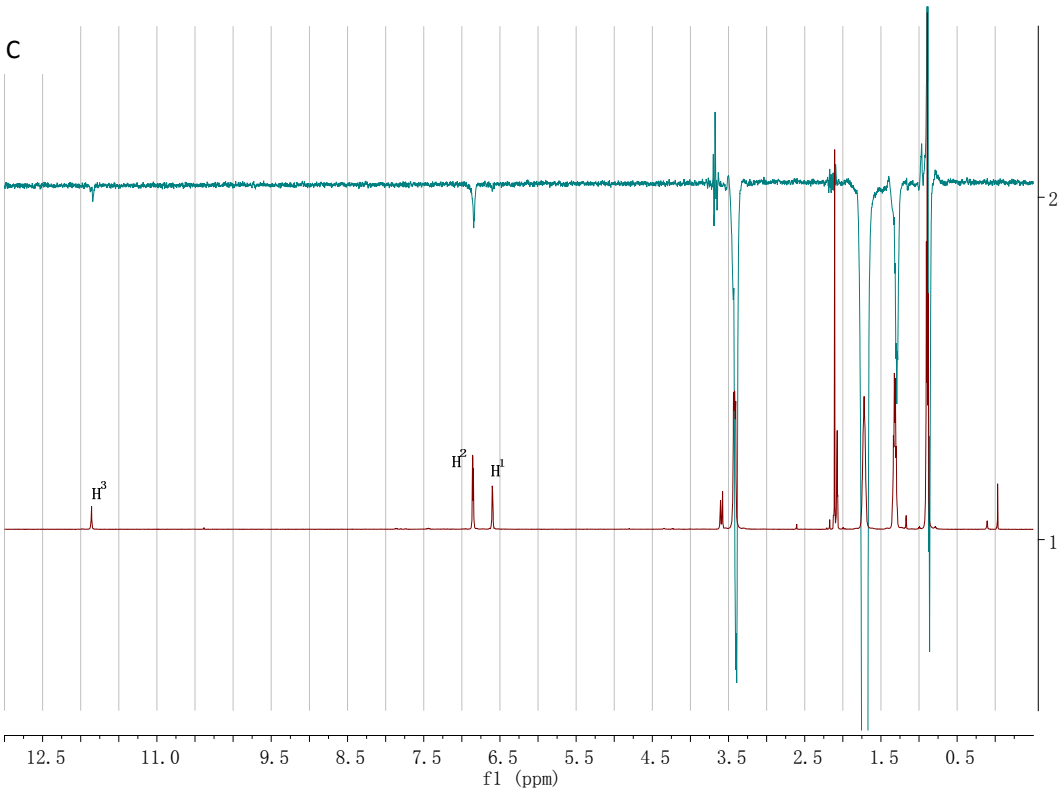


Figure S9 ^{1}H NMR spectra of (A) **4a** alone with selective excitation of H^3, (B) **4a** in the presence of Bu_4NCl with selective excitation of H^3 and (C) **4a** in the presence of Bu_4NCl with selective excitation of protons of Bu_4NCl.

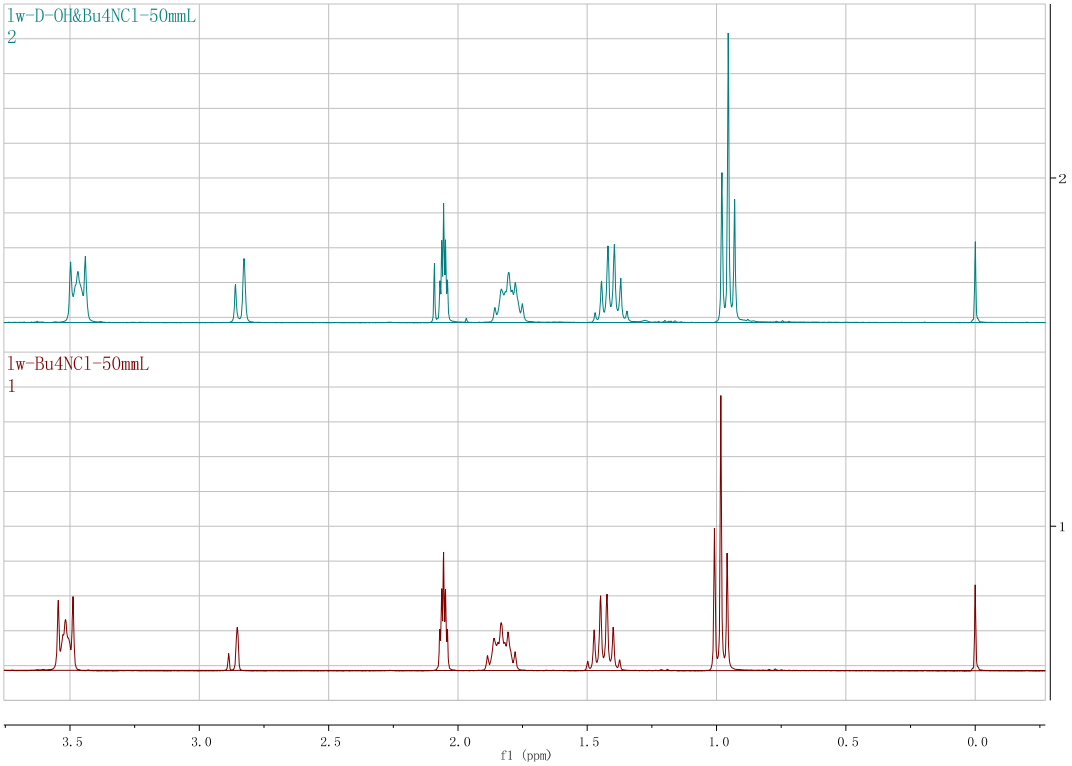


Figure S10 ^{1}H NMR of tetrabutylammonium chloride (0.87×10^{-2} M) without (up) and with (down) the presence of **4a** (0.96×10^{-2} M) in d_6-acetone at room temperature.

5. ESI-MS spectra

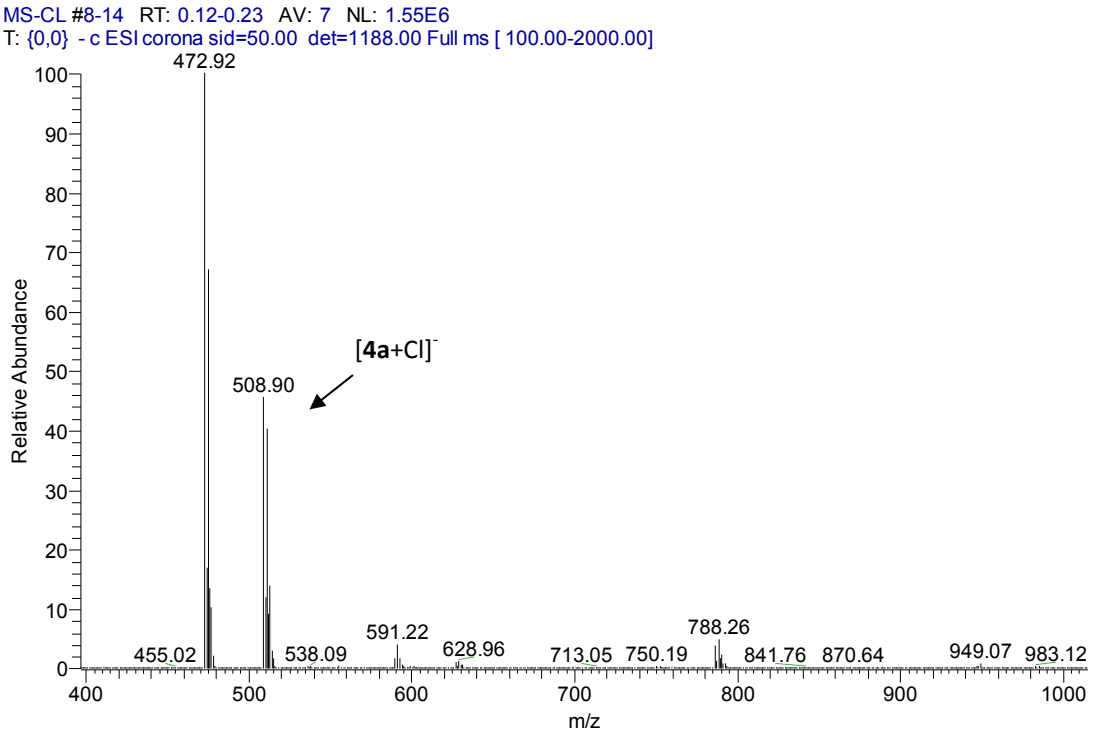


Figure S11 ESI-MS spectra of the complex of **4a** and chloride.

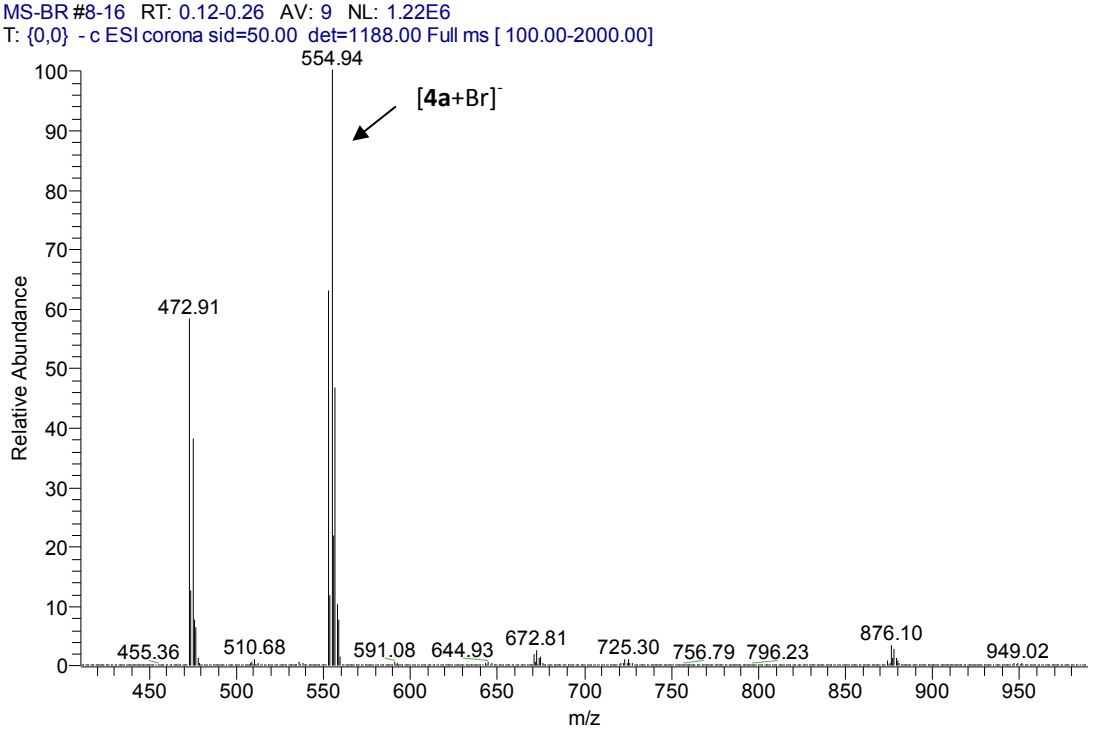


Figure S12 ESI-MS spectra of the complex of **4a** and bromide.

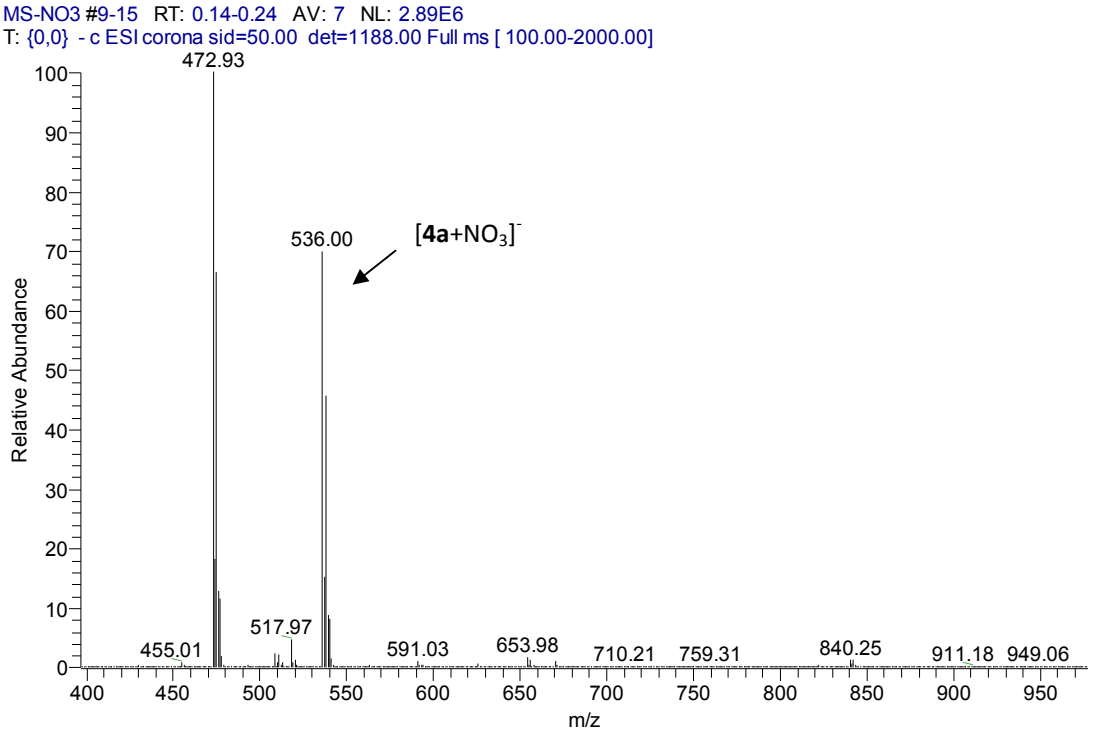
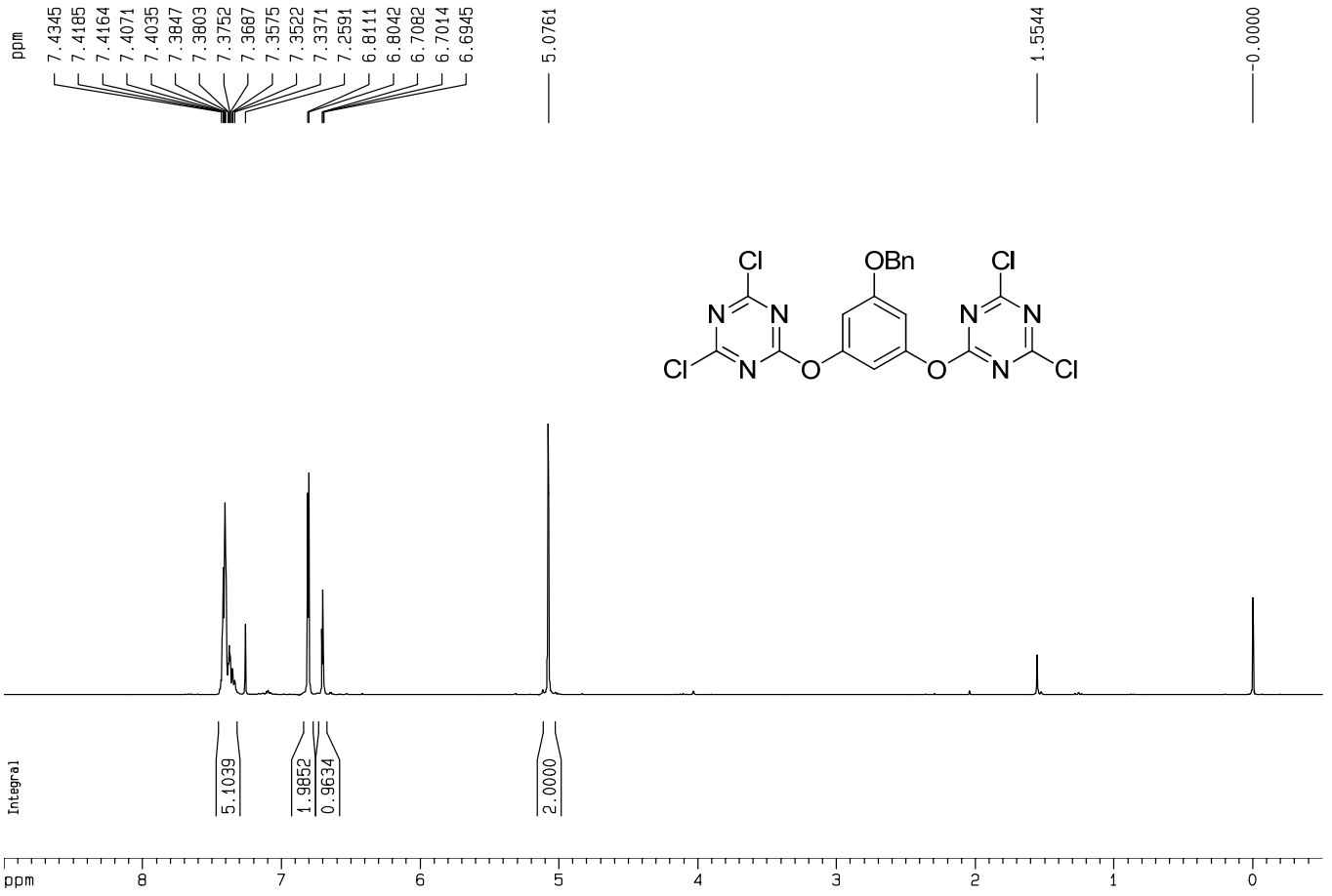


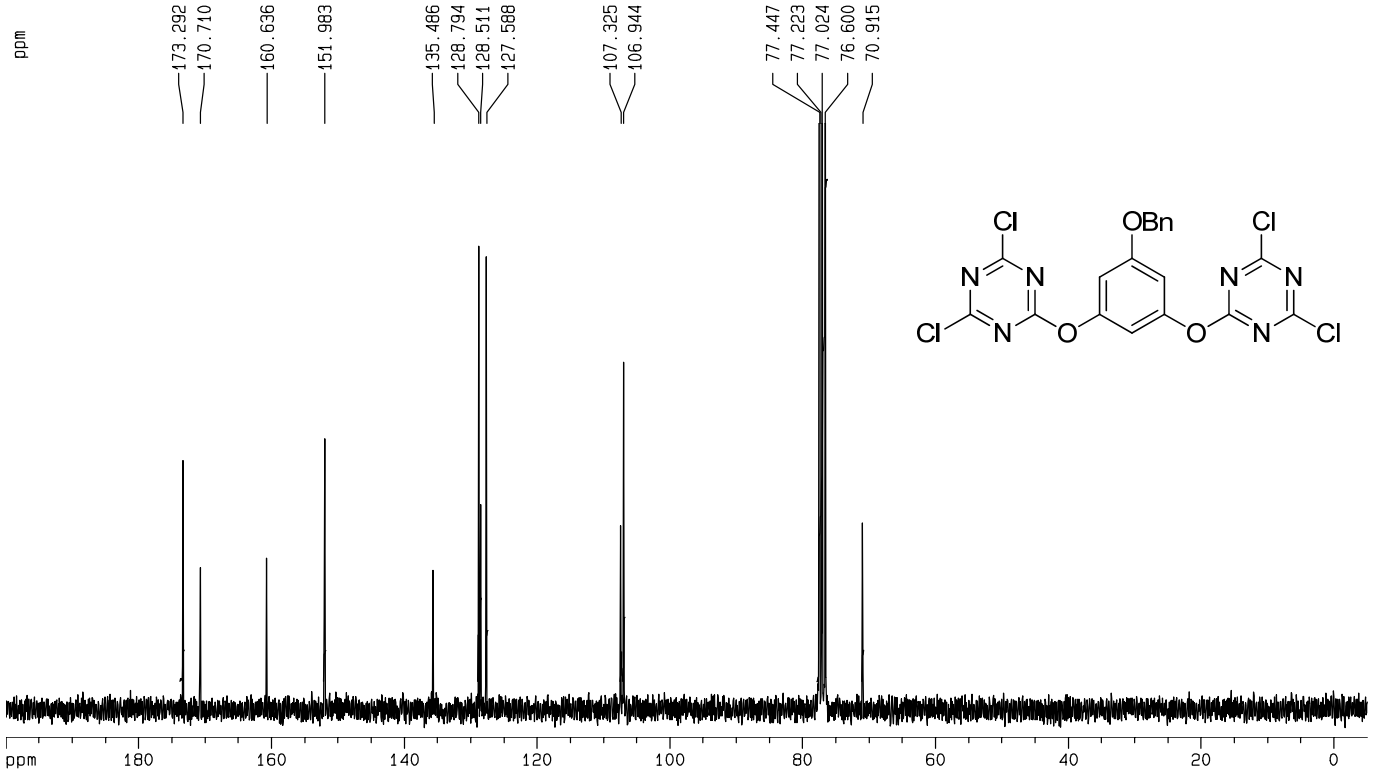
Figure S13 ESI-MS spectra of the complex of **4a** and nitrate.

6. NMR spectra



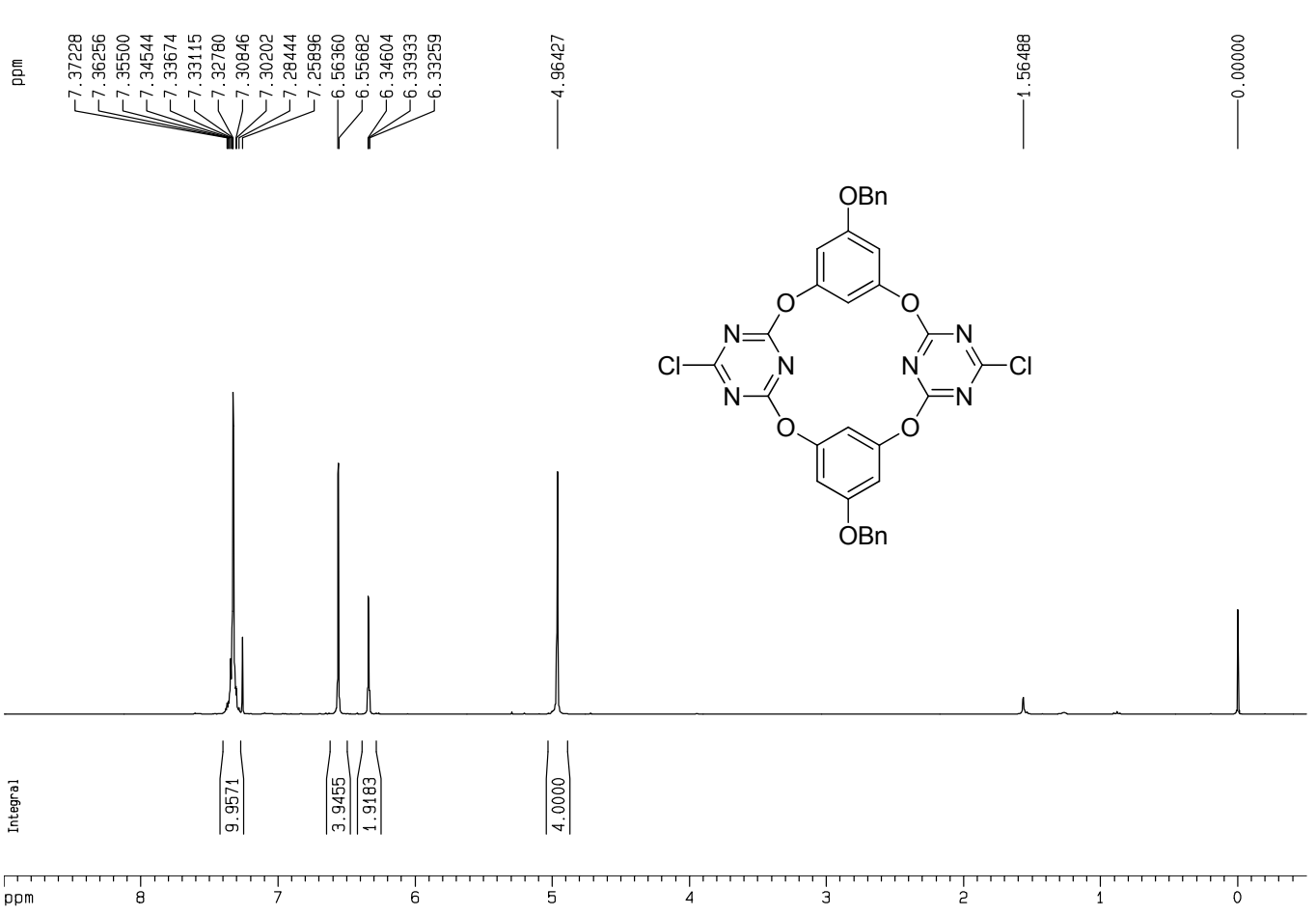

```
Current Data Parameters
NAME            wqq3-33a
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060607
Time                8.27
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                   362
DW                81.000 usec
DE                 6.00 usec
TE                300.3 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 9.30 usec
PL1               -1.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300066 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 22.00 cm
CY                  5.00 cm
F1P                9.000 ppm
F1              2701.17 Hz
F2P                -0.500 ppm
F2              -150.07 Hz
PPMCM           0.43182 ppm/cm
HZCM          129.60159 Hz/cm
```

Figure S14 ^{1}H NMR spectrum of **3**.



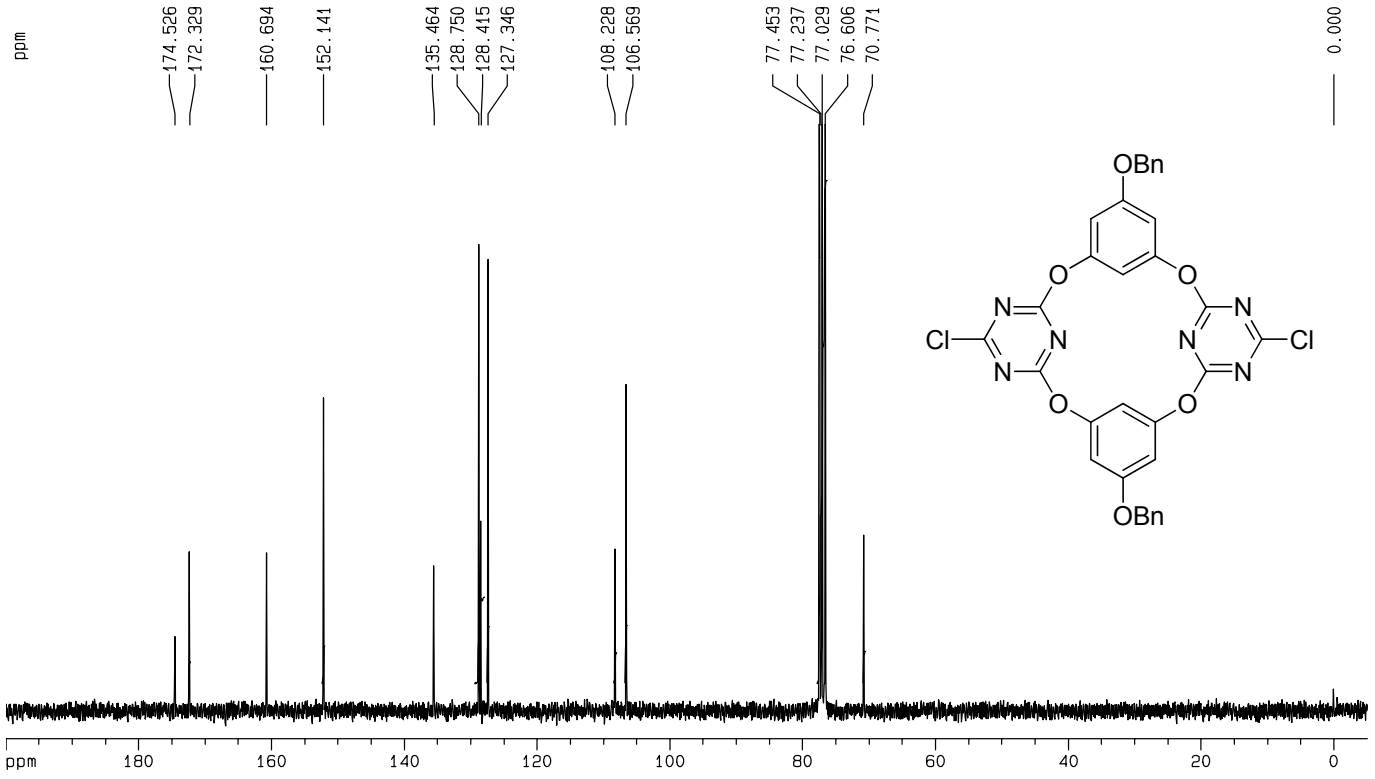

```
Current Data Parameters
NAME            wqq3-33a
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060607
Time                8.30
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  235
DS                    4
SWH           17985.611 Hz
FIDRES        0.274439 Hz
AQ            1.8219508 sec
RG                  512
DW               27.800 usec
DE                6.00 usec
TE               300.6 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                9.40 usec
PL1              -1.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2            80.00 usec
PL2              -1.00 dB
PL12             18.00 dB
PL13             18.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                32768
SF           75.4677490 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

1D NMR plot parameters
CX                22.00 cm
CY                15.00 cm
F1P              200.000 ppm
F1             15093.55 Hz
F2P               -5.000 ppm
F2              -377.34 Hz
PPMCM           9.31818 ppm/cm
HZCM          703.22217 Hz/cm
```

Figure S15 ^{13}C NMR spectrum of **3**.




```
Current Data Parameters
NAME                  wqq3-35a
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_               20060606
Time                     8.26
INSTRUM                 av300
PROBHD   5 mm DUL 13C-1
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                          11
DS                           2
SWH                 6172.839 Hz
FIDRES              0.094190 Hz
AQ                  5.3084660 sec
RG                       287.4
DW                    81.000 usec
DE                     6.00 usec
TE                     299.0 K
D1                  2.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       9.30 usec
PL1                     -1.00 dB
SFO1              300.1318534 MHz

F2 - Processing parameters
SI                      32768
SF                300.1300067 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00

1D NMR plot parameters
CX                      22.00 cm
CY                       6.00 cm
F1P                      9.000 ppm
F1                    2701.17 Hz
F2P                     -0.500 ppm
F2                    -150.07 Hz
PPMCM                 0.43182 ppm/cm
HZCM                129.60159 Hz/cm
```

Figure S16 ^{1}H NMR spectrum of **4b**.




```
Current Data Parameters
NAME            wqq3-35a
EXPNO                 12
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060606
Time                8.36
INSTRUM            av300
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   310
DS                     4
SWH            17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 322.5
DW                27.800 usec
DE                 6.00 usec
TE                299.1 K
D1            2.00000000 sec
d11           0.03000000 sec
d12           0.00002000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                 9.40 usec
PL1               -1.00 dB
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2             80.00 usec
PL2               -1.00 dB
PL12              18.00 dB
PL13              18.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF            75.4677490 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX                 22.00 cm
CY                 13.00 cm
F1P               200.000 ppm
F1              15093.55 Hz
F2P                -5.000 ppm
F2               -377.34 Hz
PPMCM             9.31818 ppm/cm
HZCM            703.22217 Hz/cm
```

Figure S17 ^{13}C NMR spectrum of **4b**.

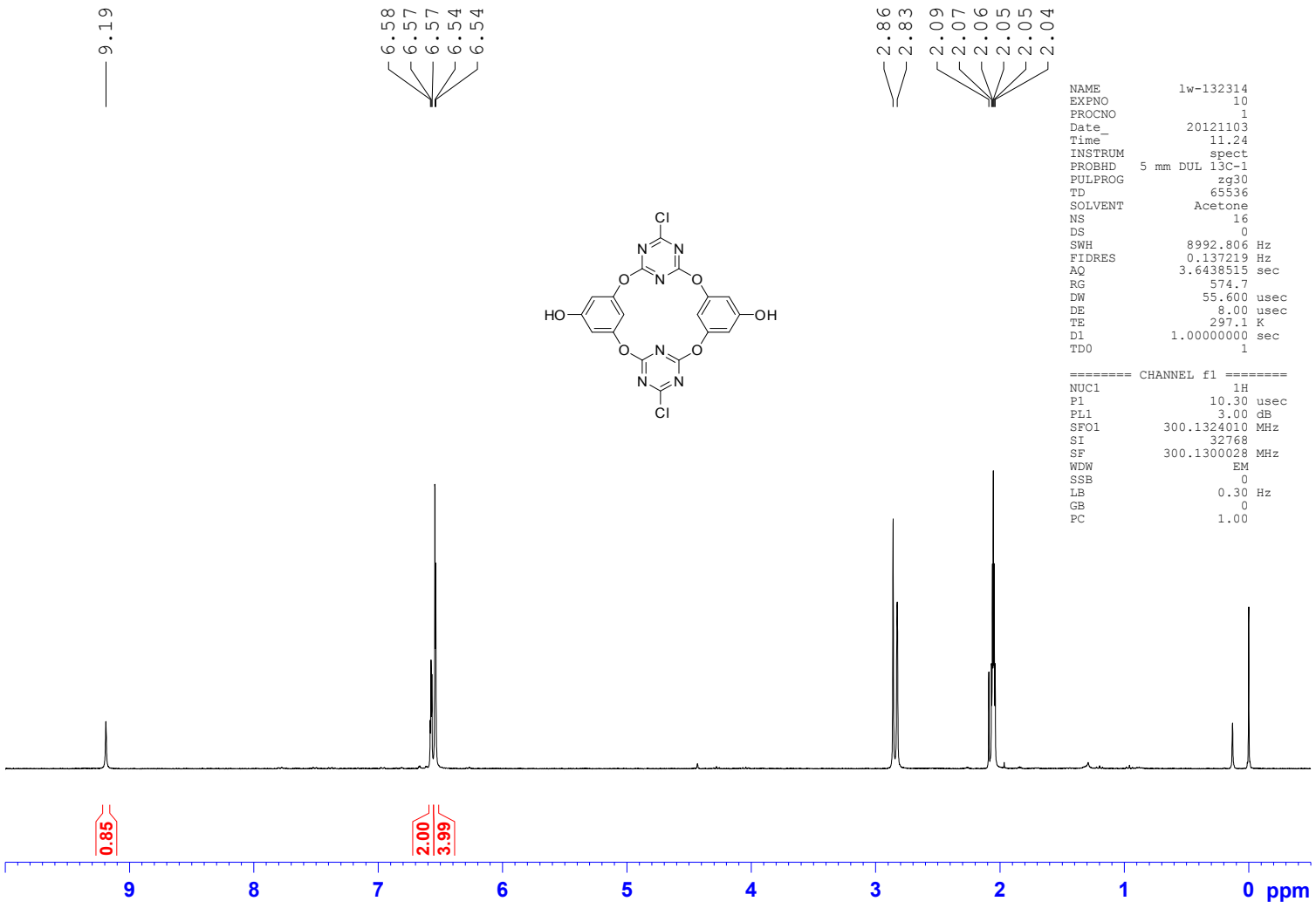
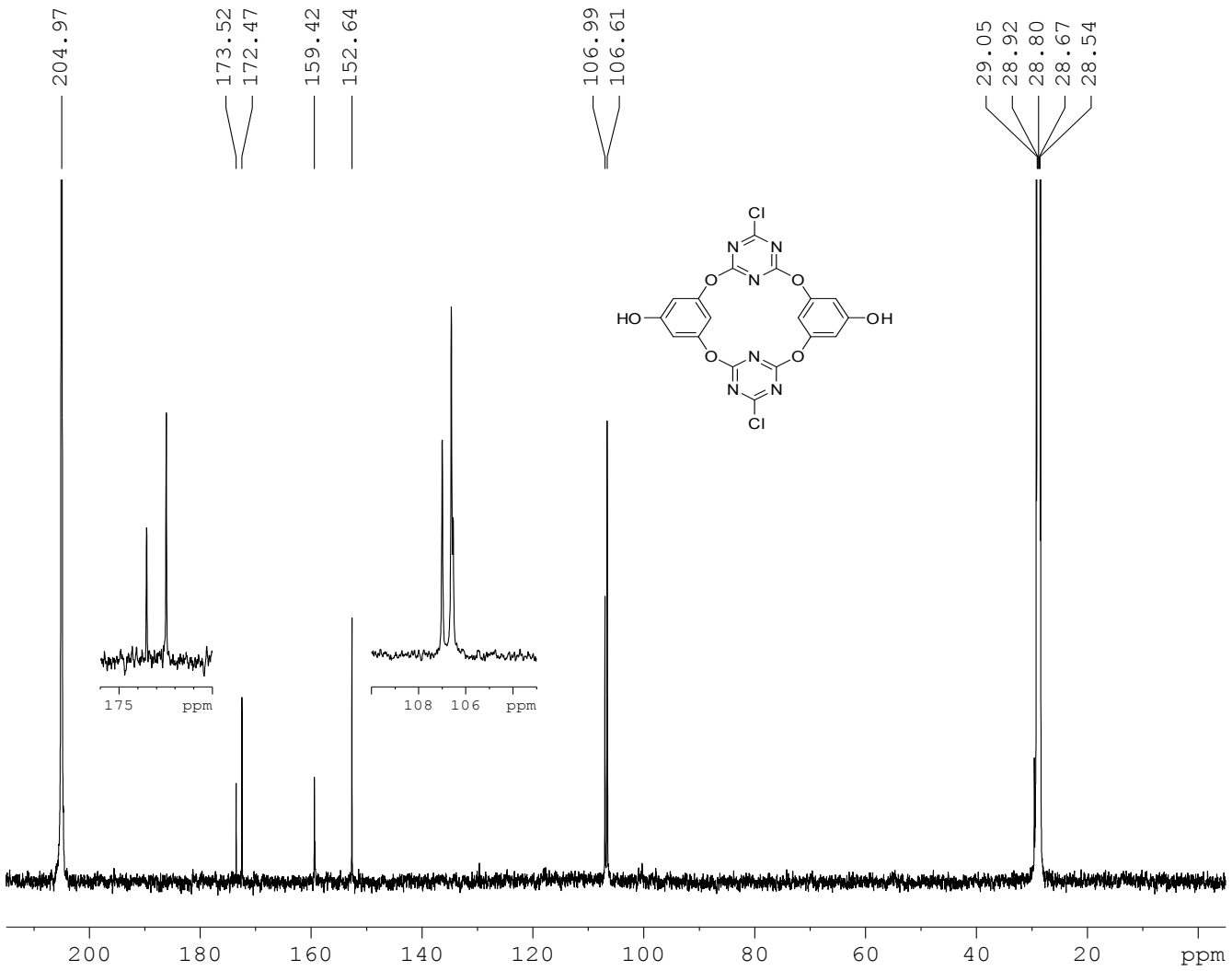


Figure S18 ^{1}H NMR spectrum of **4a**.



NAME	13C
EXPNO	143
PROCNO	1
Date_	20130719
Time	10.40
INSTRUM	spect
PROBHD	5 mm PATBO BB-
PULPROG	zgpg30
TD	32768
SOLVENT	Acetone
NS	1620
DS	0
SWH	37593.984 Hz
FIDRES	1.147277 Hz
AQ	0.4358777 sec
RG	32768
DW	13.300 usec
DE	6.50 usec
TE	323.3 K
D1	1.50000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	12.00 usec
PL1	3.00 dB
PL1W	37.76776123 W
SFO1	150.9178988 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	70.00 usec
PL2	-3.20 dB
PL12	10.18 dB
PL13	15.78 dB
PL2W	52.48074722 W
PL12W	2.40990520 W
PL13W	0.66374314 W
SFO2	600.1324005 MHz
SI	32768
SF	150.9028090 MHz
WDW	EM
SSB	0
LB	5.00 Hz
GB	0
PC	1.40

Figure S19 ^{13}C NMR spectrum of **4a**.