Electronic Supplementary Information

From anion complexes to anion coordination polymers (ACPs): assembly with a 1,5-naphthylene bridged bis-bisurea ligand

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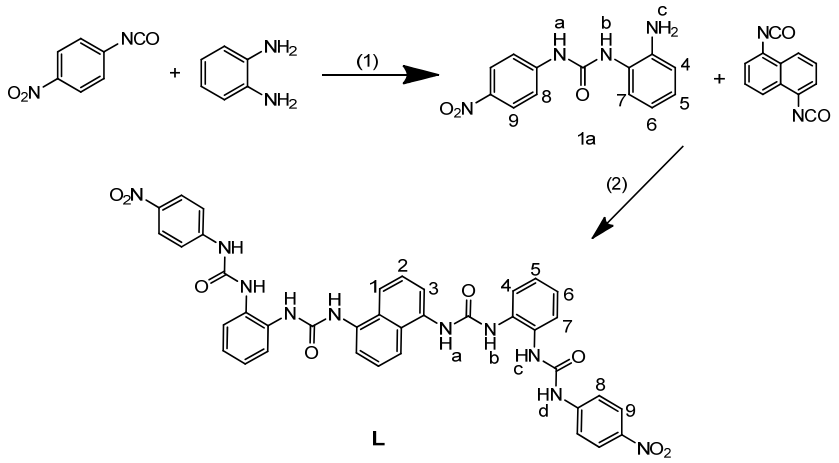
General

Tetrabutylammonium sulfate ($[(Bu)_4N]_2SO_4$) (50% water solution) and other tetrabutylammonium salts, p-nitro-phenylisocyanate and 1,5-naphthylisocyanate were purchased from Alfa Aesar and used as received. Tetrabutylammonium terephthalate was prepared according to the literature.[1] ^{1}H and ^{13}C NMR spectra were recorded on a Mercury plus-400 spectrometer at 400 MHz and 100 MHz, respectively, using TMS as an internal standard. All ^{1}H NMR titrations were performed in DMSO-d_6. UV-vis spectra were recorded on an HP845 spectrometer in DMSO. Fluorescence spectra were obtained on a Hitachi F7000 spectrophotometer (1-cm quartz cell). Elemental analyses were performed on a VarioEL instrument from Elementar Analysensysteme GmbH. IR spectra were measured using a Bruker IFS 120HR spectrometer as KBr disks. X-ray powder diffraction data were recorded with an X'Pert PRO instrument. TG analysis was carried out with a Pyris diamond instrument under N_2 atmosphere.

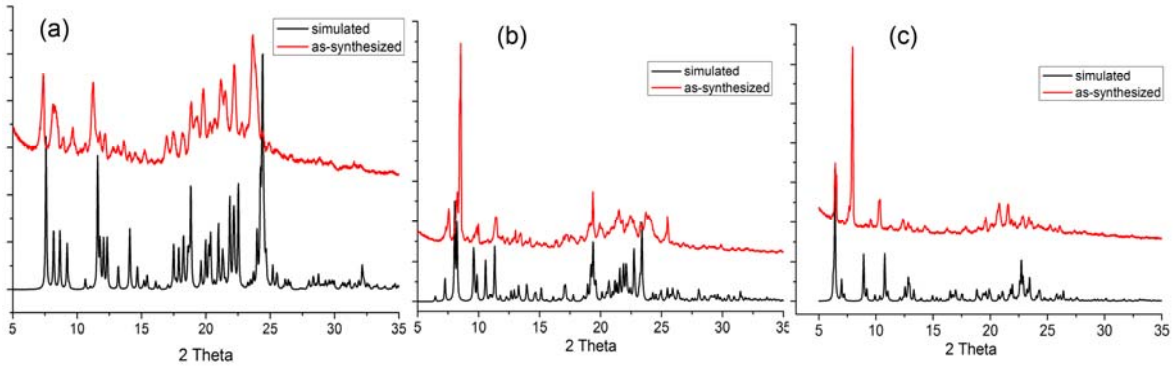
X-ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical adsorption correction using SADABS was applied for the data. The structures were solved by direct methods using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL-97, and hydrogen atoms were included in idealized positions with thermal parameters equivalents to 1.2 times those of the atom to which they were attached.

In complex **1**, the sulfate ion is disordered over two positions, with the eight half-occupied O atoms defining the corners of a cube. Besides, C25 atom of the TBA^+ countercation is disordered and displays unusual thermal parameters. In **2**, N1 atom of the ligand is disordered into two positions with occupancy rates of 60% and 40% and O2 and C38 are possibly disordered. Besides, C50 and C51 atoms of the TBA^+ cation have been refined isotropically due to their large ADPs. One acetone solvent was removed by SQUEEZE in complex **3** and some atoms (the carbon atoms of TBA^+ cations and N1, O1 of L) are disordered and display unusual thermal parameters. The SQUEEZE calculations showed a total solvent accessible area volume of 152 $Å^3$ in **3** and the residual electron density amounted to 38 e per unit cell, corresponding to nearly one acetone molecule (about 0.25 acetone per asymmetric unit). In complex **4**, one carbon atom (C29) of the TBA^+ cation is disordered into two positions with half-occupancy rate each. In complex **5**, C33 and C34 atoms of the TBA^+ cation are possibly disordered and display large ADPs. In complex **6**, some atoms (C100, C108, C114, C115 and C116 of the TBA^+ cations) are disordered and display unusual thermal parameters. Crystallographic data are provided in Table S1.



Scheme S1. Synthesis of L: (1) Toluene/THF; (2) THF.



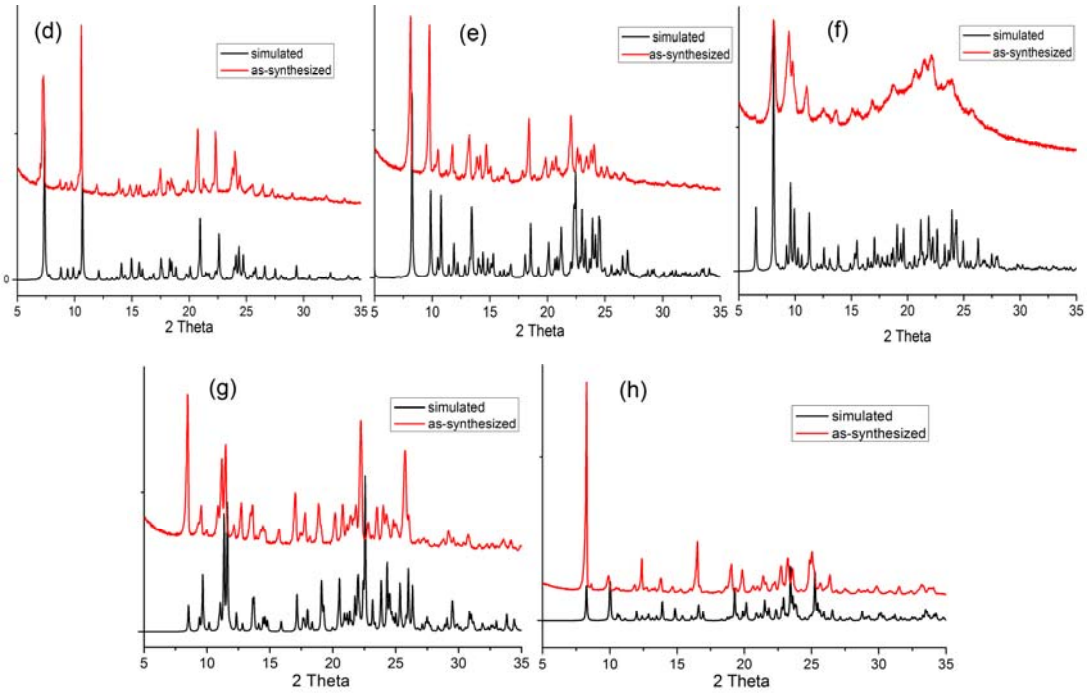


Fig. S1 Powder X-ray diffraction patterns for the anion complexes: as-synthesized (red) and simulated from the single-crystal diffraction data (black), (a) **1**; (b) **2**; (c) **3**; (d) **4**; (e) **5**; (f) **6**; (g) **7**; (h) **8**.

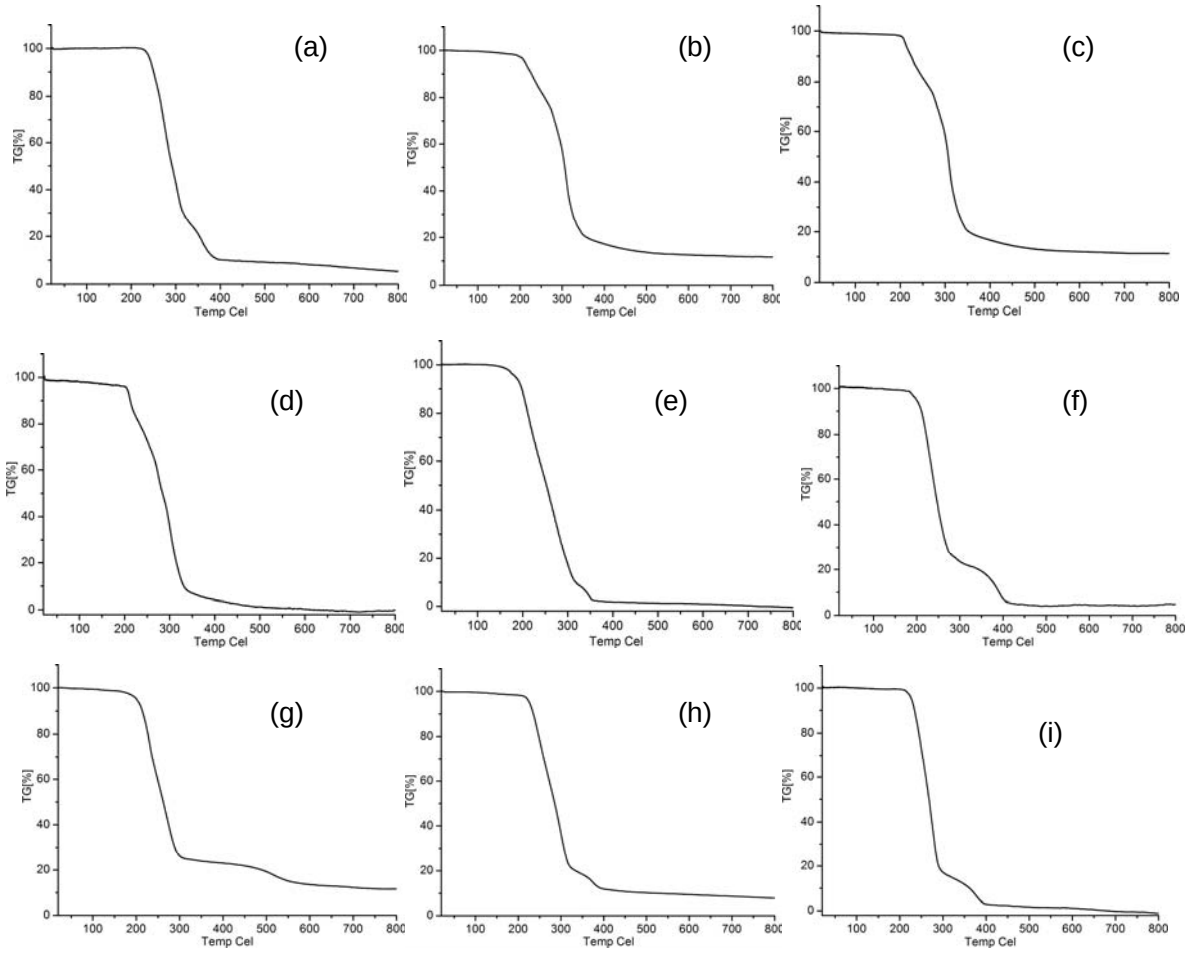


Fig. S2 TGA curves of the ligand L and complexes **1**–**8** (a–h).

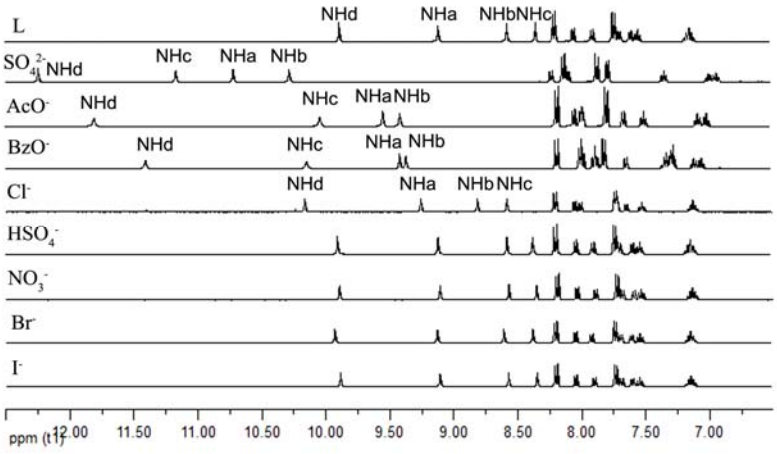


Fig. S3 ^{1}H NMR spectra of L (5 mM) in the presence of 2.0 equiv. of various anions (added as TBA^{+} salts, DMSO-d_6, 400 MHz).

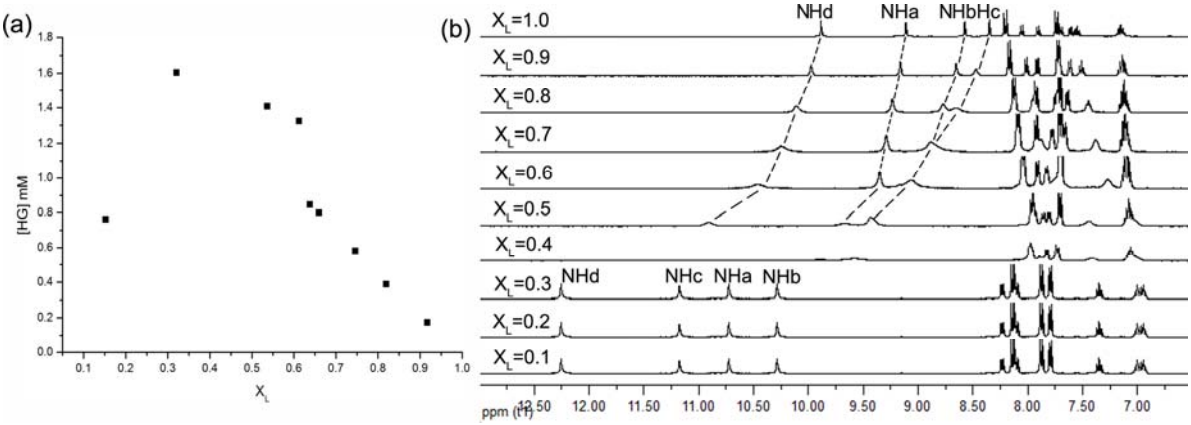


Fig. S4 (a) Job's plot of L with SO_4^{2-}; (b) the corresponding ^{1}H NMR spectra (added as TBA^{+} salt, DMSO-d_6, 400 MHz).

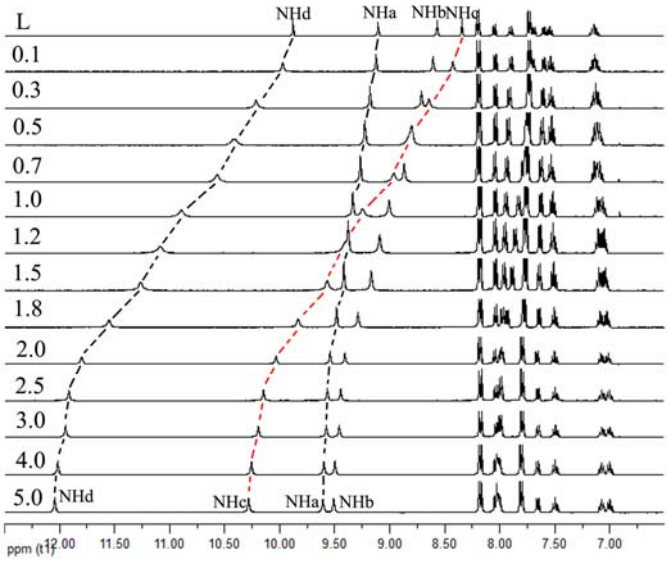


Fig. S5 ^{1}H NMR titration of L (5 mM) with AcO^{-} (as TBA^{+} salt) in DMSO-d_6.

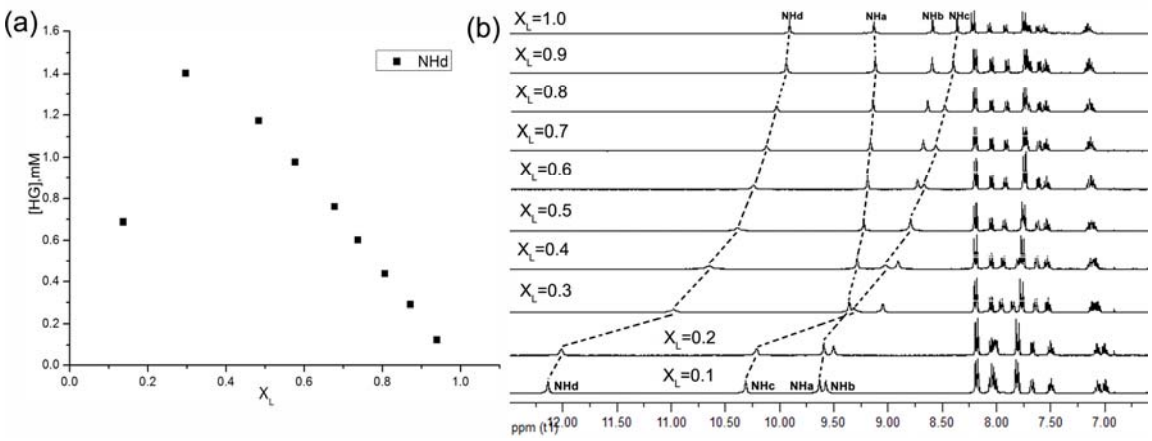


Fig. S6 (a) Job's plot of L with AcO^- and possible binding pattern; (b) the corresponding ^1H NMR spectra (added as TBA^+ salt, DMSO-d_6, 400 MHz).

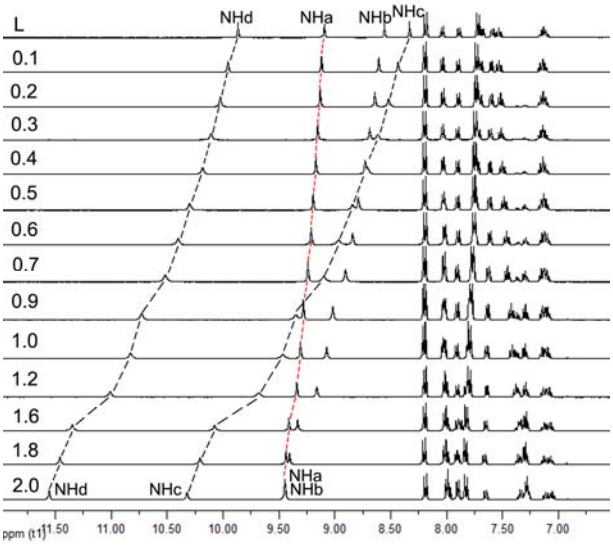


Fig. S7 ^1H NMR titration of **L** (5 mM) with BzO^- (as TBA^+ salt) in DMSO-d_6.

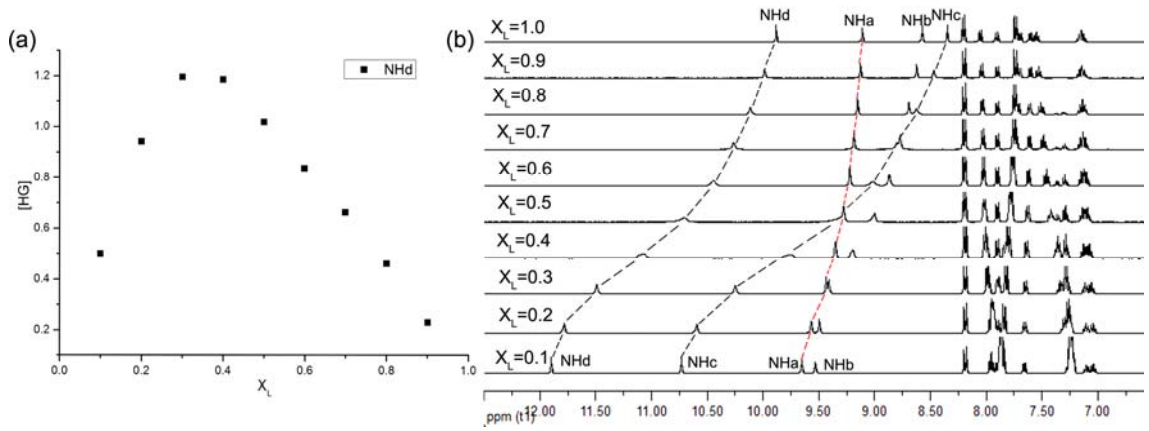


Fig. S8 (a) Job's plot of L with BzO^- and possible binding pattern; (b) the corresponding ^1H NMR spectra (added as TBA^+ salt, DMSO-d_6, 400 MHz).

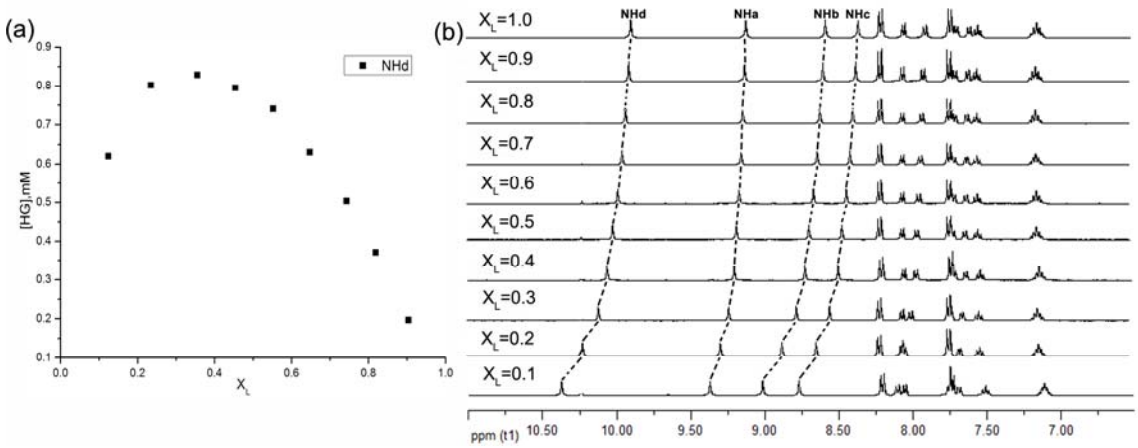


Fig. S9 (a) Job's plot of L with Cl^- and possible binding pattern; (b) the corresponding ^1H NMR spectra (added as TBA^+ salts, DMSO-d_6, 400 MHz).

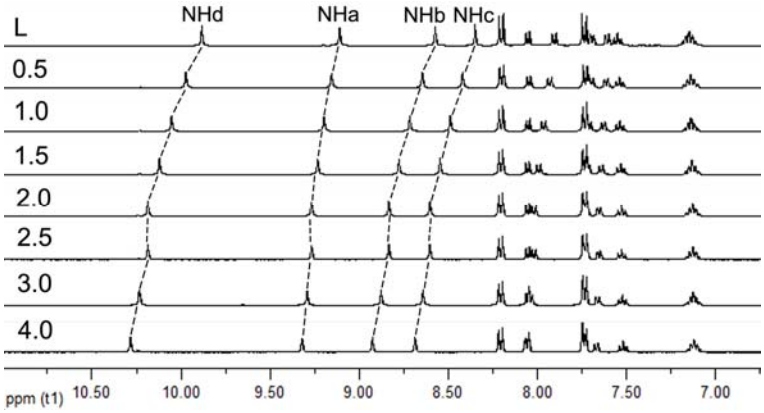


Fig. S10 ^1H NMR titration of **L** with Cl^- (added as TBA^+ salt, DMSO-d_6, 400 M Hz).

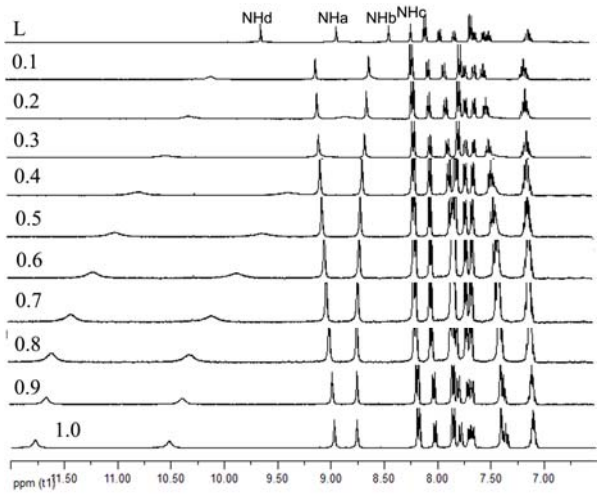


Fig. S11 ^1H NMR titration of **L** with *p*-$[COO\text{-}C_6H_4\text{-}COO]^{2-}$ (added as Na^+ salt, DMSO-d_6/H_2O, 400 MHz).

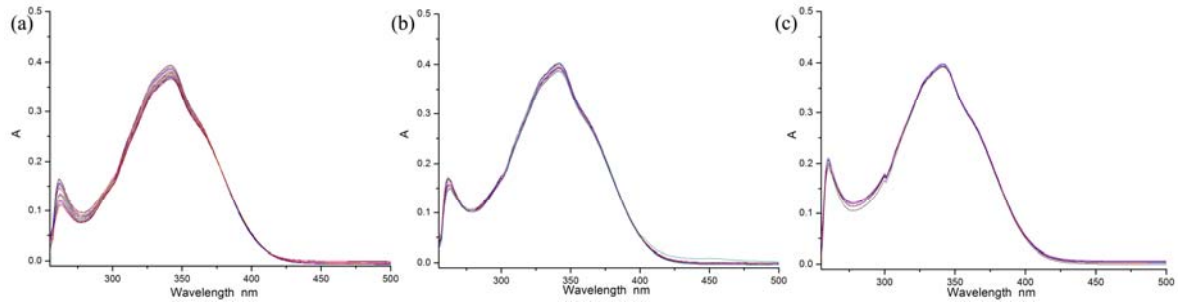


Fig. S12 UV-vis titration of **L** (1.0×10^{-5} M) with anions (as TBA^+ salts) in DMSO. (a) AcO^-; (b) BzO^-; (c) Cl^-.

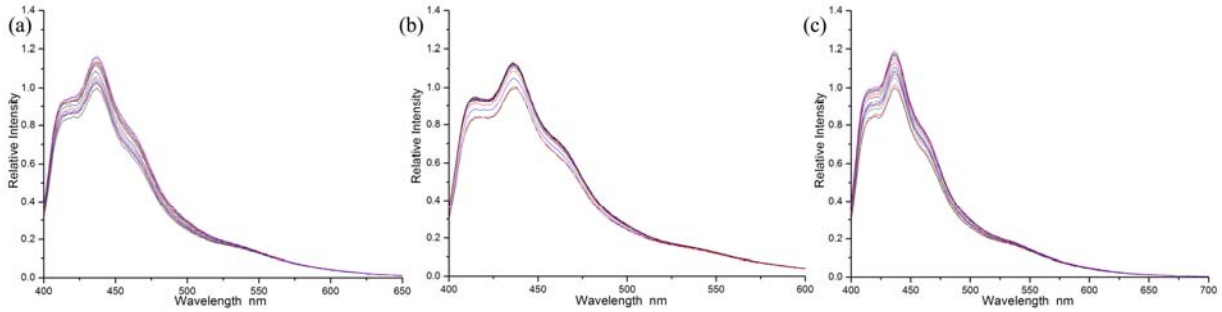


Fig. S13 Fluorescence titration of **L** (5.0×10^{-6} M) with anions (as TBA^+ salts) in DMSO. (a) AcO^-; (b) BzO^-; (c) Cl^-.

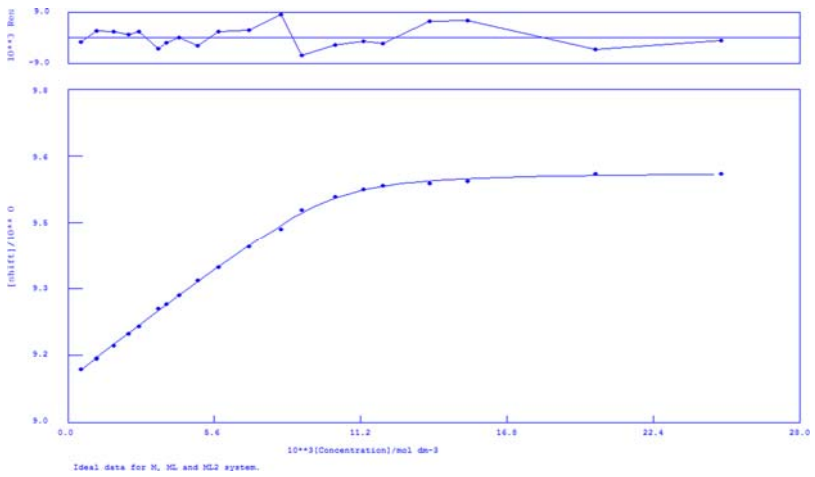


Fig. S14 ^{1}H NMR titration of L with AcO^- (as TBA^+ salt) in DMSO-d_6.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 20:34:45 on 11/22/2012

Ideal data for M, ML and ML2 system.
IDEAL DATA TAKEN FROM ACTUAL FIT of JIMMY1.FIT
Reactions: M + L = ML (beta1 = K1); M + 2L = ML2 (beta2 = K1K2)
Theoretical: k1=3900, k1k2 =11000000 del ML = 9.340, del ML2 = 9.542

File prepared by M.J. Hynes October 22 2000

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
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2	1	1.10000E+07	2.000E+00	0.000E+00	0.000E+00	BETA2
3	1	9.10236E+00	5.000E-02	3.645E-03	2.754E+00	M SHIFT
4	1	9.35357E+00	5.000E-03	6.456E-03	3.252E+00	ML SHIFT
5	1	9.60209E+00	1.000E-03	2.948E-03	3.492E+00	ML2 SHIFT

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RESIDUALS SQUARED = 2.60E-04
RFACTOR = 0.0384 PERCENT

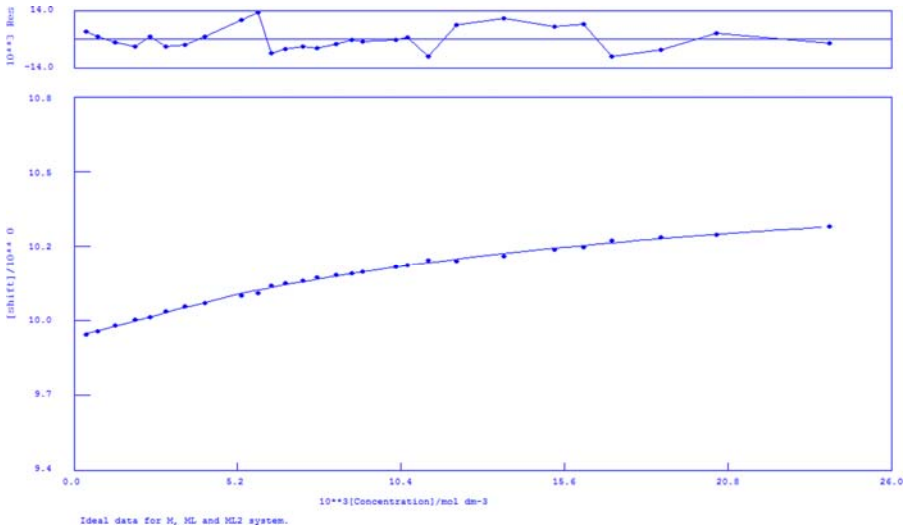

Fig. S15 ^{1}H NMR titration of L with Cl^{-} (as TBA^{+} salt) in DMSO-d_6.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 20:47:01 on 11/22/2012

Ideal data for M, ML and ML2 system.
IDEAL DATA TAKEN FROM ACTUAL FIT of JIMMY1.FIT
Reactions: M + L = ML (beta1 = K1); M + 2L = ML2 (beta2 = K1K2)
Theoretical: k1=9430, k1k2 =541157 del ML = 10.0523, del ML2 = 10.1623
File prepared by M.J. Hynes October 22 2000

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
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2	1	5.26253E+05	2.000E+00	8.704E+03	2.212E+00	BETA2
3	1	9.89671E+00	5.000E-03	3.770E-03	1.249E+00	M SHIFT
4	1	1.00616E+01	5.000E-03	2.900E-03	2.944E+00	ML SHIFT
5	1	1.05712E+01	1.000E-03	2.977E-02	3.313E+01	ML2 SHIFT

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RFACTOR = 0.0545 PERCENT

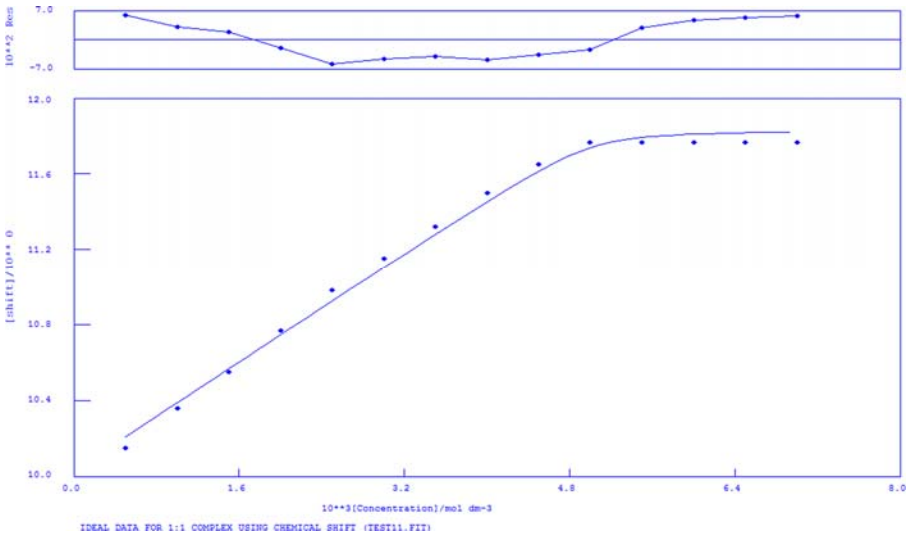

Fig. S16 ^{1}H NMR titration of L with terephthalate (as Na^{+} salt) in DMSO-d_6.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 09:59:30 on 07/26/2012

IDEAL DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (TEST11.FIT)
Reaction: M + L = ML
FILE: TEST11.FIT
IDEAL DATA: K1 = 40000; DELTA M = 9.8827; DELTA ML = 11.7648
File prepared by M. J. Hynes, October 22 2000

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	6.84042E+04	2.000E-01	8.469E+03	1.223E+00	K1
2	1	1.00280E+01	2.000E-01	3.119E-02	1.199E+00	SHIFT M
3	1	1.18330E+01	1.000E+00	2.098E-02	1.428E+00	SHIFT ML

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RFACTOR = 0.3808 PERCENT

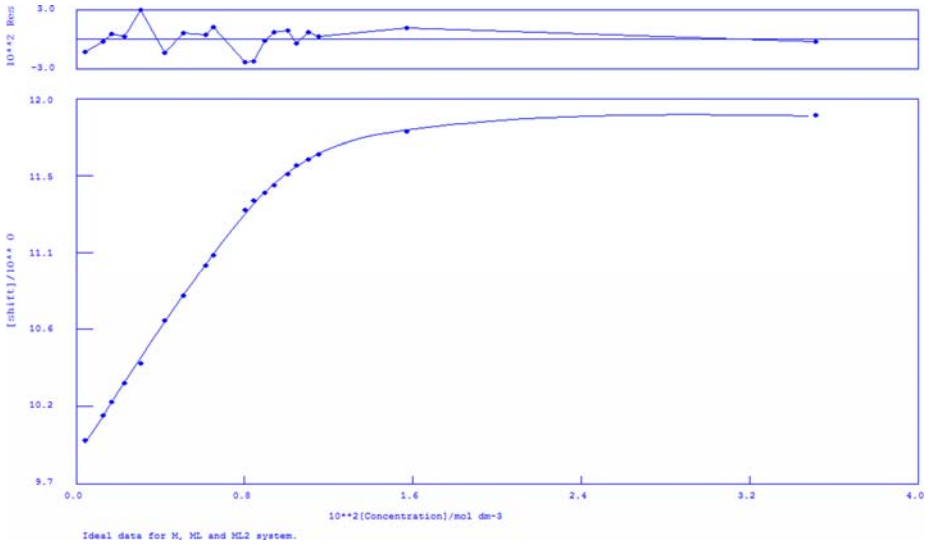

Fig. S17 ^{1}H NMR titration of L with BzO^{-} (as TBA^{+} salt) in DMSO-d_6.

Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 20:05:06 on 11/22/2011

Ideal data for M, ML and ML2 system.
IDEAL DATA TAKEN FROM ACTUAL FIT of JIMMY1.FIT
Reactions: M + L = ML (beta1 = K1); M + 2L = ML2 (beta2 = K1K2)
Theoretical: k1=2421, k1k2 =3687000 del ML = 10.818, del ML2 = 11.553
File prepared by M.J. Hynes October 22 2000

NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
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3	1	9.85711E+00	5.000E-02	1.186E-02	2.124E+00	M SHIFT
4	1	1.08923E+01	5.000E-03	2.090E-02	3.626E+00	ML SHIFT
5	1	1.19220E+01	1.000E-03	1.621E-02	7.370E+00	ML2 SHIFT

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RESIDUALS SQUARED = 2.84E-03
RFACTOR = 0.1103 PERCENT

Table S1. Crystallographic data and refinement details for ligand L and complexes **1**–**8**.

Compound	**L**	**1**	**2**	**3**	**4**
Formula	$C_{46}H_{54}N_{10}O_{12}S_4$	$C_{70}H_{102}N_{12}O_{12}S$	$C_{102}H_{174}N_{14}O_{16}S_2$	$C_{102}H_{174}N_{14}O_{16}S_2$	$C_{74}H_{108}N_{12}O_{12}$
M	1067.23	1335.70	1916.67	1916.67	1357.72
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*P*-1	$P2_1/c$	*P*-1	*C*2/*c*	*P*2(1)/*n*
a /Å	9.189(3)	12.501(6)	9.538(12)	27.889(4)	12.430(5)
b /Å	16.271(6)	19.167(9)	13.957(17)	16.427(2)	14.615(6)
c /Å	19.010(7)	16.971(6)	22.00(3)	24.753(3)	21.187(9)
α /°	114.021(5)	90	94.690(15)	90	90
β /°	98.024(5)	120.12(2)	100.617(17)	98.540(2)	97.784(6)
γ /°	94.551(6)	90	99.018(16)	90	90
V /Å^3	2541.3(16)	3517(3)	2824(6)	11215(3)	3813(3)
Z	2	2	1	4	2
T /K	153(2)	153(2)	153(2)	153(2)	153(2)
F(000)	1120	1436	1044	4176	1646
D_{calc} /g cm^{-3}	1.395	1.261	1.127	1.135	1.182
μ /mm^{-1}	0.26	0.12	0.11	0.11	0.08
R_{int}	0.085	0.097	0.068	0.054	0.074
GOF	1.13	1.20	1.12	1.00	1.04
R_1 [$I > 2\sigma(I)$]	0.0892	0.1266	0.0790	0.1040	0.0827
wR_2 [$I > 2\sigma(I)$]	0.1754	0.2498	0.1506	0.1741	0.1650

Compound	**5**	**6**	**7**	**8**
Formula	$C_{84}H_{112}N_{12}O_{12}$	$C_{78}H_{106}N_{12}O_{12}$	$C_{70}H_{102}Cl_2N_{12}O_8$	$C_{70}H_{102}Br_2N_{12}O_8$
M	1481.86	1403.75	1310.54	1399.46
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*C*2/*c*	*P*-1
a /Å	8.627(3)	23.764(5)	41.951(7)	8.9484(19)
b /Å	35.844(11)	17.225(4)	8.8842(15)	9.473(2)
c /Å	13.660(4)	20.791(5)	19.048(3)	21.594(5)
α /°	90	90	90	83.826(3)
β /°	102.017(4)	113.214(3)	99.546(2)	84.847(2)
γ /°	90	90	90	80.815(3)
V /Å^3	4131(2)	7822(3)	7001(2)	1791.6(7)
Z	2	4	4	1
T /K	153(2)	153(2)	296(2)	293(2)
F(000)	1592	3016	2816	740
D_{calc} /g cm^{-3}	1.191	1.192	1.243	1.297
μ /mm^{-1}	0.08	0.08	0.16	1.19
R_{int}	0.065	0.132	0.062	0.036
GOF	1.06	1.17	1.03	1.13
R_1 [$I > 2\sigma(I)$]	0.0837	0.1378	0.0540	0.0479
wR_2 [$I > 2\sigma(I)$]	0.1944	0.1693	0.1511	0.1412

Table S2. Hydrogen bonds around the SO_4^{2-} ion in complex **1**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···O5	0.860	2.033(9)	2.890(1)	174.0
N2[a]–H2A[a]···O8[a]	0.860	2.100(9)	2.808(1)	139.1
N3[a]–H3A[a]···O6[a]	0.860	1.975(8)	2.828(9)	171.5
N3–H3A···O7	0.860	2.271(9)	2.934(1)	134.1
N4[a]–H4A[a]···O6[a]	0.860	2.224(9)	3.055(1)	162.8
N4–H4A···O7	0.860	2.044(8)	2.735(9)	136.8
N5[a]–H5A[a]···O5	0.860	2.445(1)	3.304(1)	178.0
N5–H5A···O7	0.860	2.291(1)	2.946(1)	133.2
C3[a]–H3[a]···O8[a]	0.950	2.439(7)	3.207(9)	137.9

Symmetry code: [a] 1 – *x*, 1 – *y*, 1 –*z*.

Table S3. Hydrogen bonds around the SO_4^{2-} ion in complex **2**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···O5	0.880	2.668(4)	3.338(5)	133.8
N2–H2A···O7	0.880	1.907(4)	2.753(5)	160.7
N3–H3A···O5	0.880	2.076(3)	2.914(5)	159.0
N3–H3A···O7	0.880	2.698(4)	3.353(5)	132.2
N4–H4A···O5	0.880	1.990(3)	2.856(4)	168.0
N5–H5A···O5	0.880	2.462(4)	3.206(5)	142.5
N5–H5A···O6	0.880	2.357(4)	3.136(6)	147.5
C5–H5···O7	0.950	2.714(4)	3.431(6)	132.9

Table S4. Hydrogen bonds around the SO_4^{2-} ion in complex **3**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠ (DHA) (º)
N2–H2A···O7	0.880	1.956(2)	2.784(4)	156.0
N3–H3A···O5	0.880	1.978(3)	2.852(4)	171.5
N4–H4A···O5	0.880	1.930(3)	2.803(5)	171.0
N5–H5A···O6	0.880	1.984(3)	2.797(5)	152.8
C3–H3···O5	0.950	2.465(4)	3.240(5)	138.7

Table S5. Hydrogen bonds around the AcO^- ion in complex **4**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠ (DHA) (º)
N2–H2···O6	0.880	2.001(3)	2.874(5)	171.7
N3–H3···O5	0.880	1.837(3)	2.712(5)	173.0
N4[a]–H4[a]···O6	0.880	2.115(3)	2.925(5)	152.8
N5[a]–H5[a]···O6	0.880	1.923(3)	2.774(5)	162.2

Symmetry code: [a] – 1 – *x*, – *y*, – *z*.

Table S6. Hydrogen bonds around the BzO^- ion in complex **5**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···O5	0.880	1.958(3)	2.808(4)	162.0
N3–H3A···O5	0.880	2.169(3)	2.916(4)	142.3
N4–H4A···O6	0.880	1.968(3)	2.799(4)	156.7
N5–H5A···O6	0.880	2.038(30	2.852(4)	153.7

Table S7. Hydrogen bonds around the terephthalate ion in complex **6**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···O18	0.860	2.086(4)	2.866(6)	150.7
N3–H3A···O18	0.860	2.076(4)	2.873(7)	153.9
N4–H4A···O17	0.860	1.965(4)	2.777(6)	156.8
N5–H5A···O17	0.860	2.084(3)	2.869(5)	151.6
$N7^a$–$H7A^a$···O19	0.860	2.071(6)	2.732(9)	133.1
$N8^a$–$H8A^a$···O19	0.860	1.999(6)	2.771(8)	149.0
$N9^a$–$H9A^a$···O20	0.860	2.180(5)	2.959(7)	150.4
$N10^a$–$H10A^a$···O20	0.860	2.030(4)	2.834(6)	155.5

Symmetry code: [a] x, $1 + y$, z.

Table S8. Hydrogen bonds around the Cl^- ion in complex **7**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···Cl	0.860	2.501(6)	3.249(2)	145.8
N3–H3A···Cl	0.860	2.701(5)	3.290(2)	127.0
N4–H4A···Cl	0.860	2.427(5)	3.206(2)	150.8
N5–H5A···Cl	0.860	2.490(5)	3.296(1)	156.3

Table S9. Hydrogen bonds around the Br^- ion in complex **8**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (º)
N2–H2A···Br	0.880	2.765(6)	3.517(3)	144.3
N3–H3A···Br	0.880	2.513(5)	3.321(3)	152.9
N4–H4A···Br	0.880	2.483(5)	3.355(3)	171.1
N5–H5A···Br	0.880	2.873(6)	3.694(3)	156.0

References:

1. Z.-M. Shi, S.-G. Chen, X. Zhao, X.-K. Jiang and Z.-T. Li, *Org. Biomol. Chem.*, 2011, **9**, 8122-8129.