Supporting Information

Binding of $HgCl_2$ by Tripodals Controlled by $AgPF_6$: Receptors of the PF_6^- Anion par excellence

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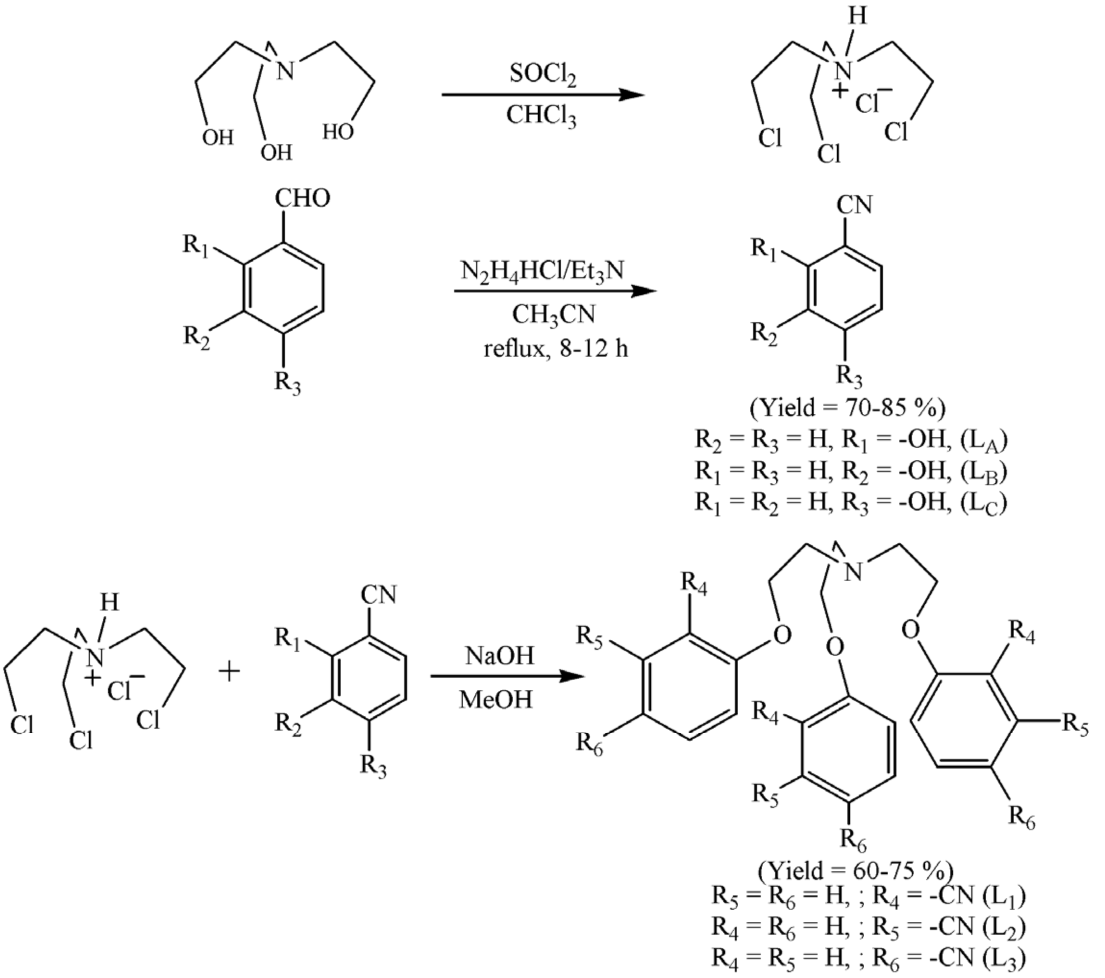
SYNTHETIC SCHEME:

Schematic diagram for synthesis of ligands **L_1-L_5** is shown below. The synthesis of ligands **L_1-L_5** was accomplished by simple SN$_2$ substitution with corresponding alcohols in dry DMF. The ligands **L_1-L_3** were made from corresponding hydroxybenzaldehyde in dry acetonitrile using hydroxylamine hydrochloride, triethylamine and phthalic anhydride over a period of 7-8 h. These ligands **L_1-L_5**, has been characterized by ^{1}H-NMR, ^{13}C-NMR and IR-spectra.



Synthesis of tris (2-chloroethyl) amine hydrochloride:

This was prepared by the following literature method. [1] Triethanolamine (4.6 g; 30 mmol) was dissolved in chloroform (10 mL) and added drop wise with constant stirring to a solution of thionyl chloride (14.7 g; 120 mmol) in chloroform (10 mL). After the addition was complete, the reaction mixture was stirred for another 1 h and the volatile components were distilled off. The crystalline product left behind was recrystallized from acetone.

Yield: 6.6 g (92%); mp 128^{0}C (lit. 127-130^{0}C).

General Procedure for synthesis of hydroxybenzonitrile:

To a cold solution of hydroxylamine hydrochloride (0.38 g, 5.5 mmol) in anhydrous acetonitrile (50 mL), triethylamine (freshly distilled from KOH) (0.77 mL, 5.5 mmol) and hydroxybenzaldehyde (5 mmol) were added and stirred for about 30 min. Phthalic anhydride (0.75 g, 5.05 mmol) was successively added under nitrogen atmosphere. The resulting mixture was heated under reflux for about 7-8 h (reaction was monitored through TLC plate). The solution was concentrated under reduced pressure, and the resulting residue was added and stirred with cold DCM (30 mL x 3) and then filtered. The filtrate was washed with 5% NH_3-H_2O to remove phthalic acid completely. The separated organic layer was dried with $MgSO_4$ and then evaporated under reduced pressure, finally the residue was recrystallized from n-hexane/ethyl acetate to get the pure product.

Synthesis of N-OTN (L_1):

To a solution of 2-hydroxybenzonitrile (7.4 g, 62.2 mmol) in DMF (35 mL) was added K_2CO_3 (12.9 g, 93.3 mmol) and stirred at RT for 30 min. To the resulting suspension, tris(2-chloroethyl)amine hydrochloride (5 g, 20.7 mmol) was added at once and the mixture was stirred at RT (25-30^{0}C) for 24 h. Thereafter ochre brown color solution was allowed to cool at RT and poured into 100 mL cold water. The expected product was extracted from this mixture, with 3x 100 mL of $CHCl_3$. The organic layer was washed with water, dried over Na_2SO_4 and all solvents were removed under reduced pressure. The crude product was purified by column chromatography with 75% ethyl acetate in petroleum ether as the eluent. The resulting compound was milky white solid. Yield 75% ; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.35 (t, 6H, *J* = 4.76 Hz), 4.27 (t, 6H, *J* = 4.76 Hz), 6.91-7.03 (m, 6H), 7.46-7.50 (m, 6H) (Figure 1); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.1 (x3C), 69.8 (x3C), 101.4 (x3C), 112.2 (x3C), 116.7 (x3C), 120.6 (x3C), 133.3 (x3C), 134.4 (x3C), 160.8 (x3C) (Figure 2); IR (KBr) cm^{-1} 3111, 3072, 2878, 2222, 1596, 1493, 1449, 1290, 1248, 1166, 1109, 1038, 760 (Figure 3); Anal. Calcd. for $C_{27}H_{24}N_4O_3$: C 71.67, H 5.35, N 12.38%. Found: C 70.47, H 5.55 N 12.78%.

Synthesis of N-MTN (L_2):

This ligand was prepared in same way as that of $\mathbf{L_1}$. Yield 60%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.15 (t, 6H, *J* = 5.48), 4.08 (t, 6H, *J* = 5.48), 7.08 (m, 3H), 7.23 (dd, 3H), 7.32-7.36 (m, 6H) (Figure 4); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 54.20 (x3C), 67.25 (x3C), 113.06 (x3C), 117.30 (x3C), 118.53 (x3C), 119.62 (x3C) 124.59 (x3C), 130.33 (x3C), 158.59 (x3C), (Figure 5); IR (KBr) cm^{-1} 3056, 2828, 2230, 1724, 1597, 1581, 1484, 1433, 1284, 1148, 1040, 704 (Figure 6); Anal. calcd for $C_{27}H_{24}N_4O_3$: C 71.67, H 5.35, N 12.38%. Found: C 70.47, H 5.55 N 12.78%.

Synthesis of N-PTN (L_3):

This ligand was prepared in same way as that of $\mathbf{L_1}$. Yield 70%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.15 (t, 6H, J = 5.24 Hz), 4.10 (t, 6H, J = 5.24 Hz), 6.87 (d, 6H, J = 8.8 Hz), 7.53 (d, 6H, J = 8.8 Hz), (Figure 7); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 54.1 (x3C), 67.2 (x3C), 104.1 (x3C), 115.1 (x6C), 118.9 (x3C), 133.9 (x6C), 161.8 (x3C), (Figure 8); ESI-MS $[M+1]^+$ 453 (Figure 9). IR (KBr) cm^{-1} 2874, 2224, 1727, 1605, 1510, 1255, 1174, 1043, 834, (Figure 10); Anal. Calcd. for $C_{27}H_{24}N_4O_3$: C 71.67, H 5.35, N 12.38%. Found: C 71.07, H 5.65, N 12.08%.

Synthesis of N-PTNO$_2$ (L_4):

To a solution of 4-hydroxynitrobenzene (7.4 g, 62 mmol) in DMF (35 mL) was added K_2CO_3 (12.9 g, 93 mmol) and stirred at RT for 30 min. To the resulting suspension, tris(2-chloroethyl)amine hydrochloride (5 g, 20.7 mmol) was added at once and the mixture was stirred at RT (25-30^{0}C) for 24 h. Thereafter ochre brown color solution was allowed to cool at RT and poured into 100 mL cold water. The expected product was extracted from this mixture, with 3x 100 mL of $CHCl_3$. The organic layer was washed with water, dried over anhydrous Na_2SO_4 and solvents were removed under reduced pressure. The crude product was purified by column chromatography with 75% ethyl acetate (in petroleum ether) as the eluent. The desired compound was a pale yellow solid.

Yield 70%; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 3.20 (t, 6H, J = 5.48 Hz), 4.16 (t, 6H, J = 5.48 Hz), 6.89 (d, 6H, J = 4.88 Hz), 7.53 (d, 6H, J = 4.88 Hz), (Figure 11); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 54.2 (x3C), 67.7 (x3C), 114.3 (x3C), 125.9 (x6C), 141.6 (x3C), 163.5 (x6C) (Figure 12); IR (KBr) cm^{-1} 3113, 3083, 2826, 1596, 1500, 1335, 1259, 1169, 1109, 1033, 848 (Figure 13); Anal. Calcd. for $C_{27}H_{24}N_4O_9$: C 56.25, H 4.72, N 10.93%. Found: C 55.05, H 5.02, N 10.83%.

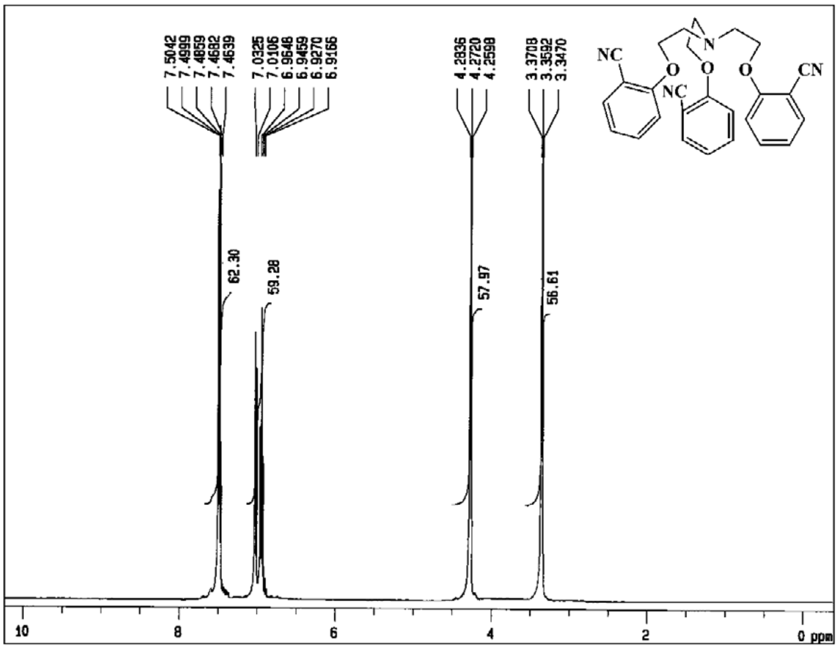


Figure 1 ^{1}H-NMR spectrum of N-OTN (**L_1**) in $CDCl_3$.

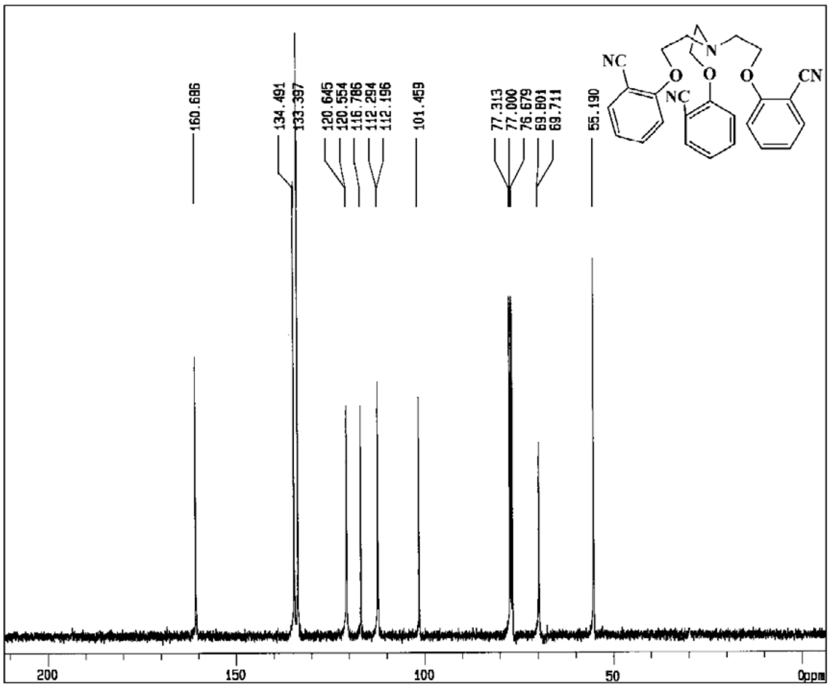


Figure 2 ^{13}**C**-NMR spectra of N-OTN (**L_1**) in $CDCl_3$.

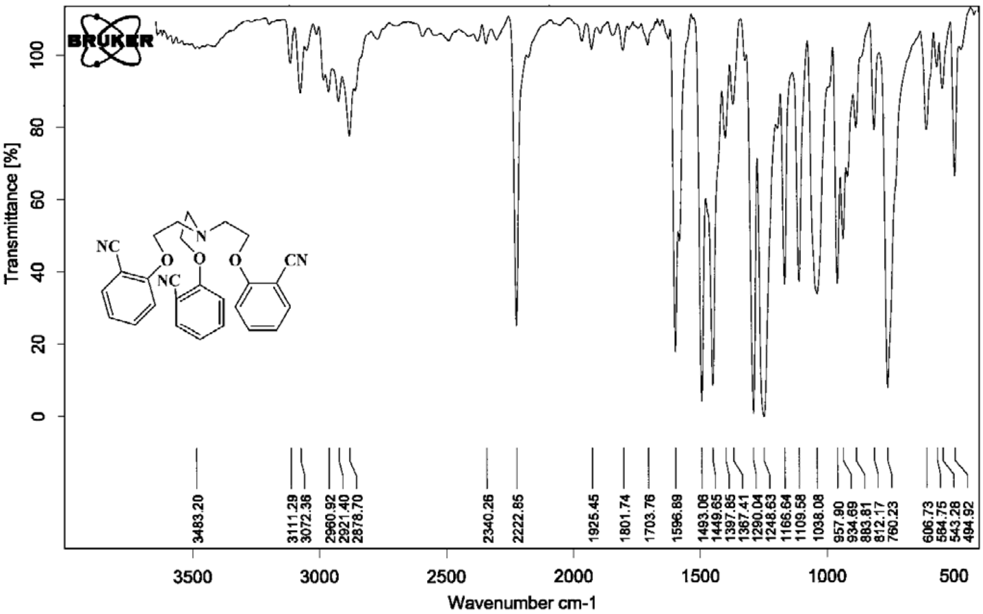


Figure 3 FT-IR spectrum of N-OTN (**L₁**).

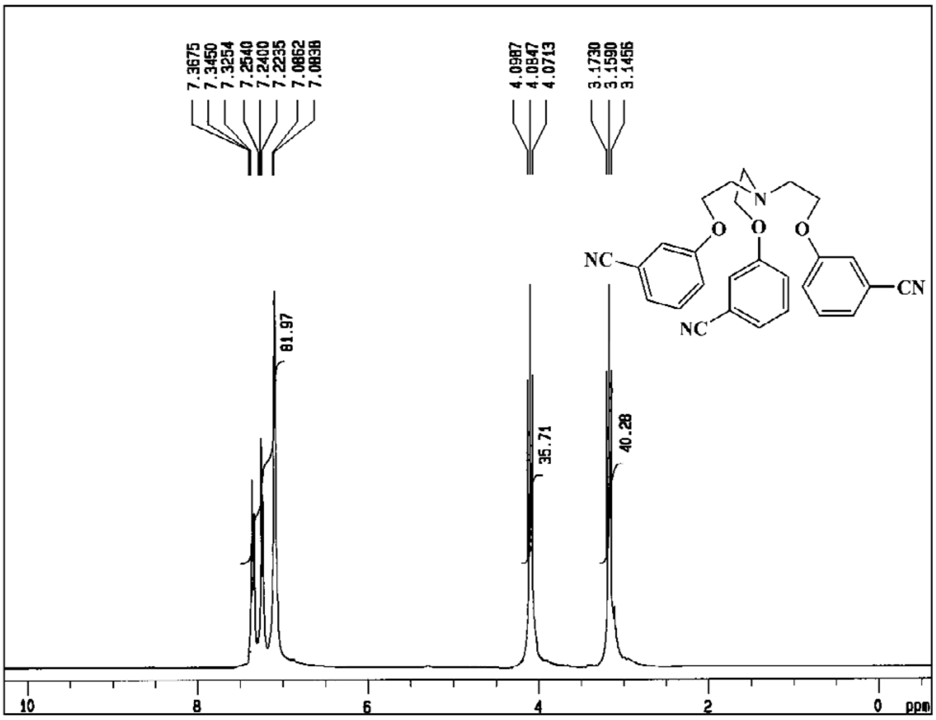


Figure 4 ^{1}H-NMR spectrum of N-MTN (**L₂**) in $CDCl_3$.

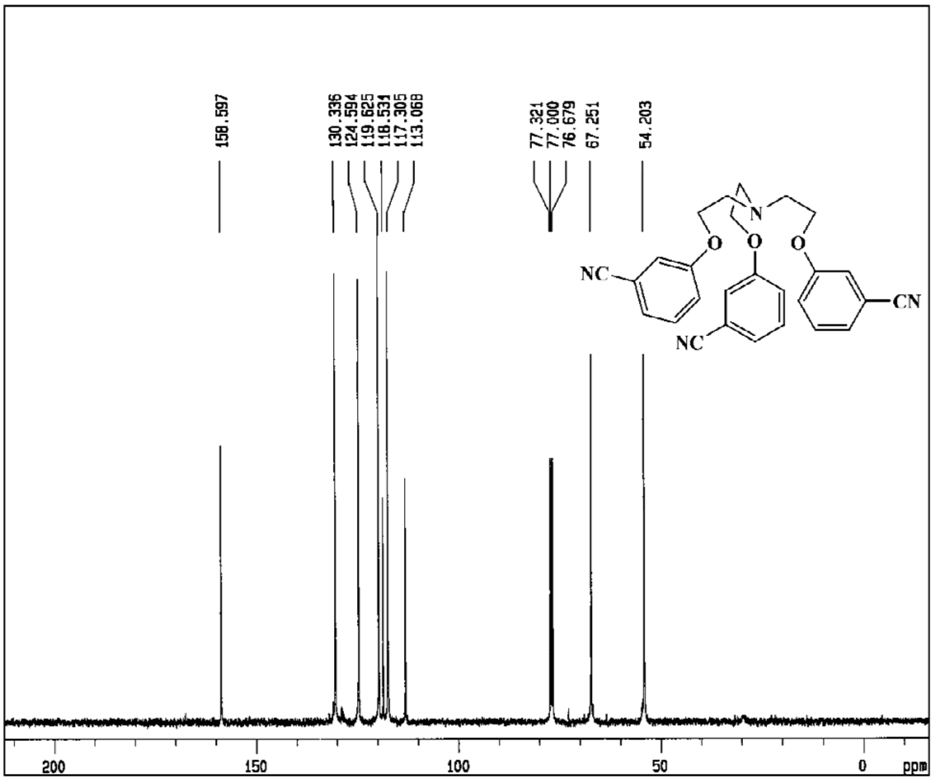


Figure 5 ^{13}C-NMR spectrum of N-MTN (**L_2**) in $CDCl_3$.

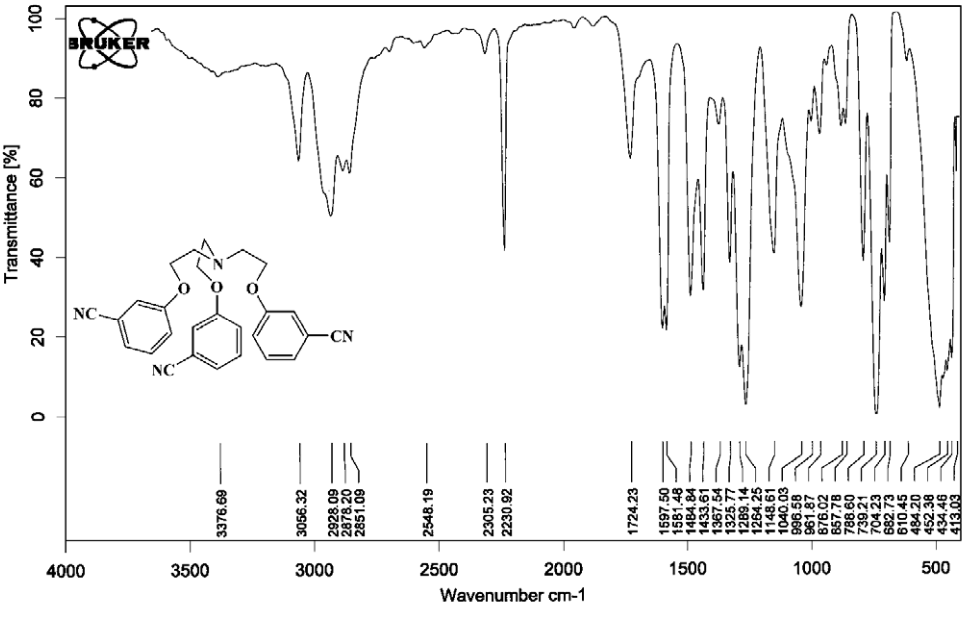


Figure 6 IR-spectrum of N-MTN (**L_2**).

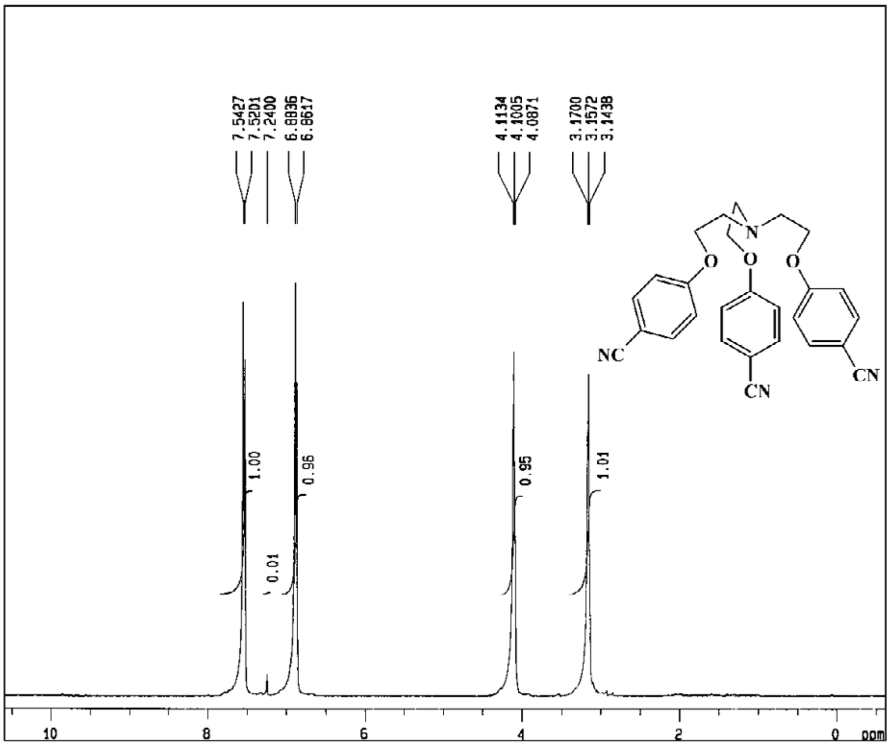


Figure 7 ^{1}H-NMR spectrum of N-PTN (**L$_3$**) in CDCl$_3$.

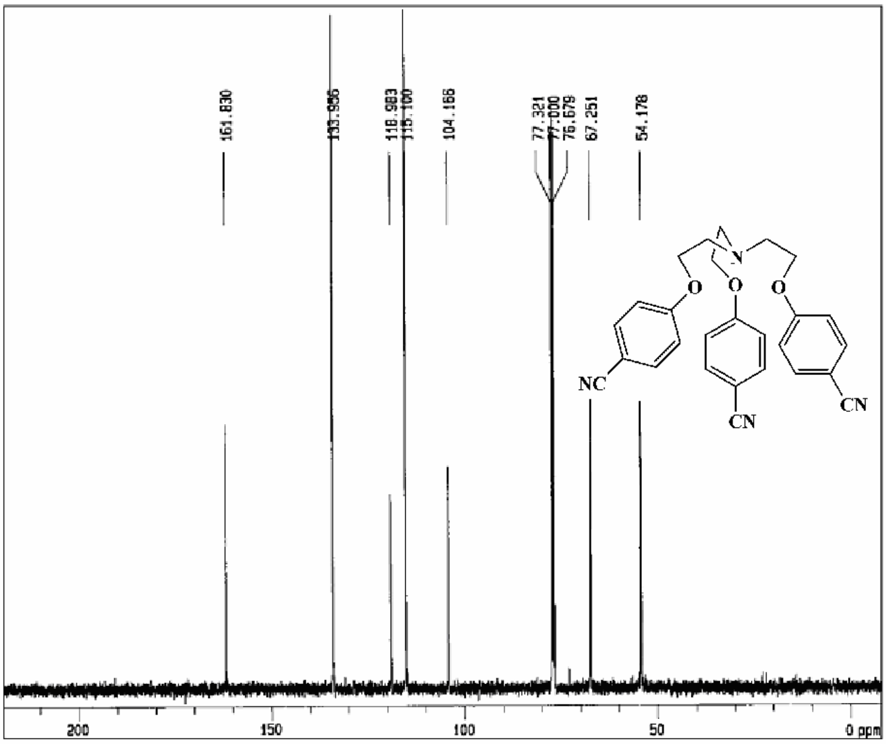


Figure 8 ^{13}C-NMR spectrum of N-PTN (**L$_3$**) in CDCl$_3$.

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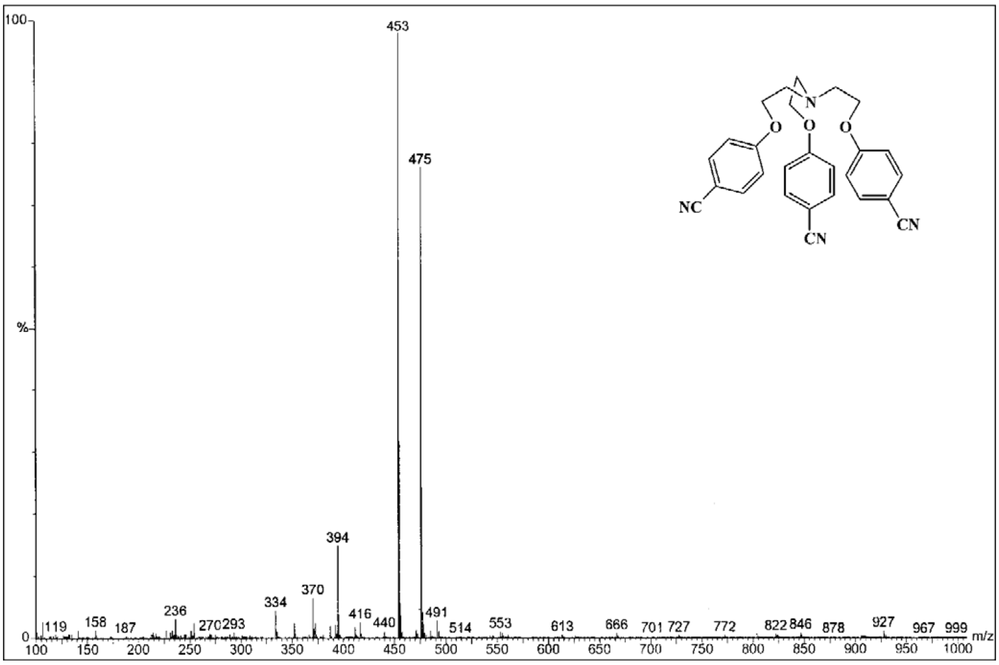


Figure 9 ESI-mass spectrum of N-PTN ($\mathbf{L_3}$).

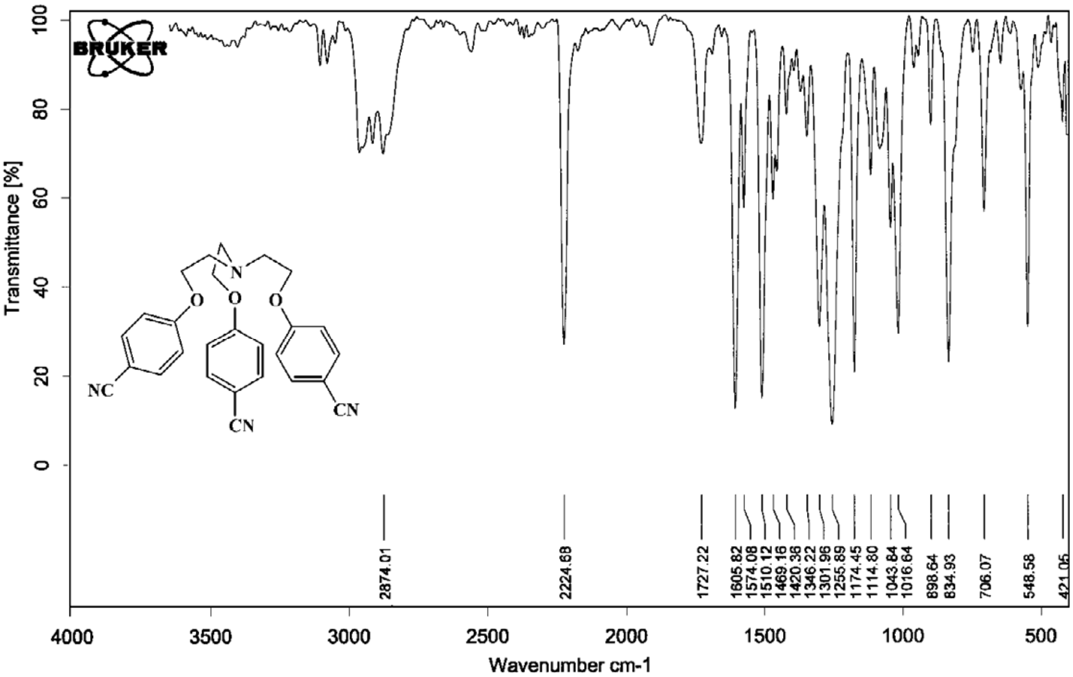


Figure 10 IR-spectrum of N-PTN ($\mathbf{L_3}$).

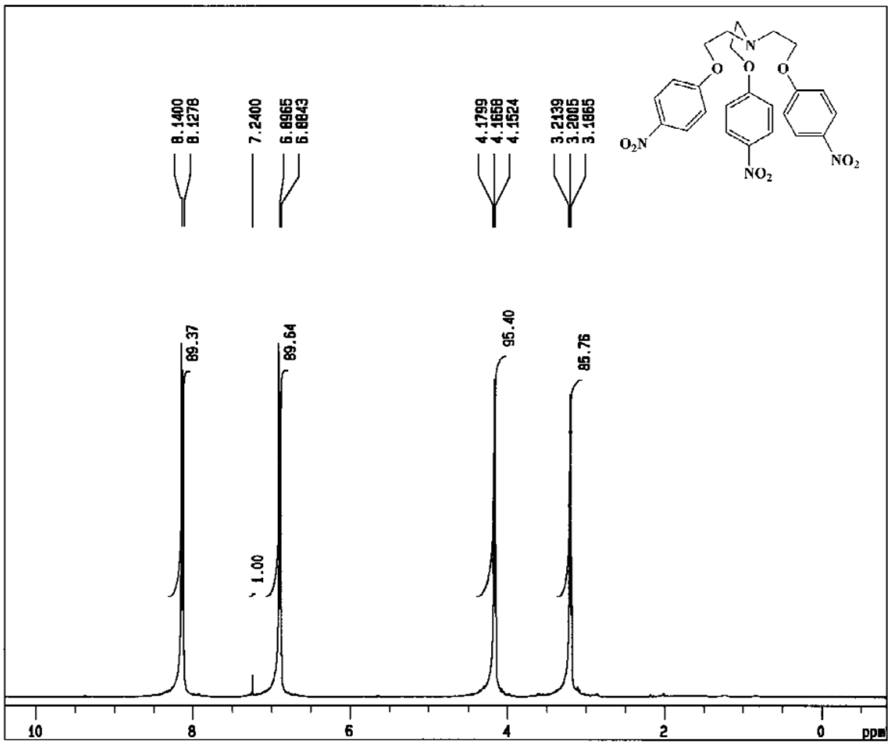


Figure 11 ^{1}H-NMR spectrum of N-PTNO$_2$ (**L$_4$**) in CDCl$_3$.

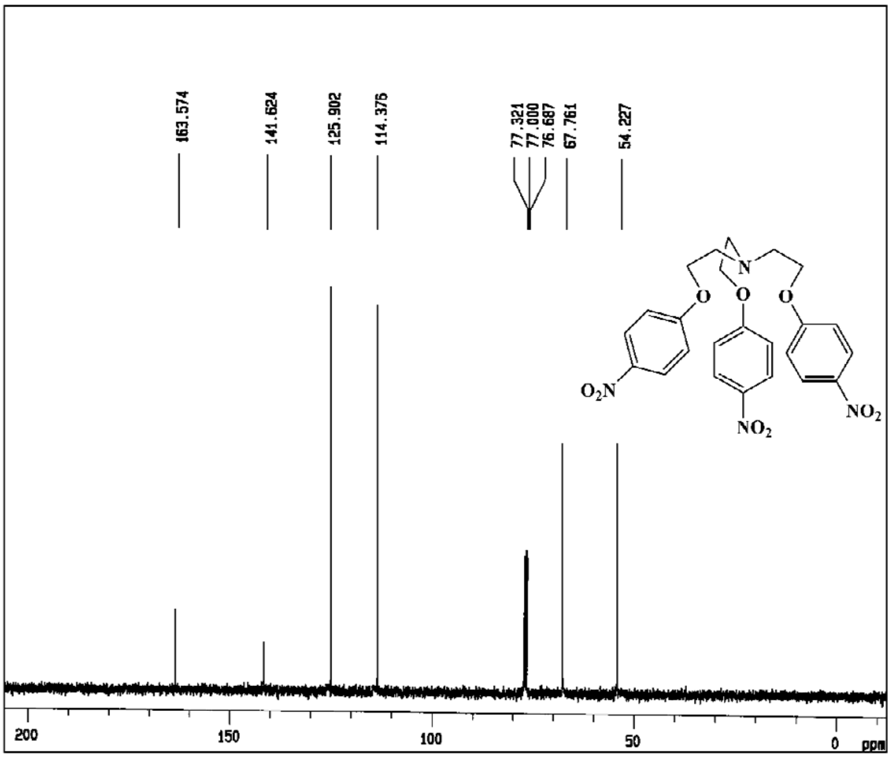


Figure 12 ^{13}C-NMR spectrum of N-PTNO$_2$ (**L$_4$**) in CDCl$_3$.

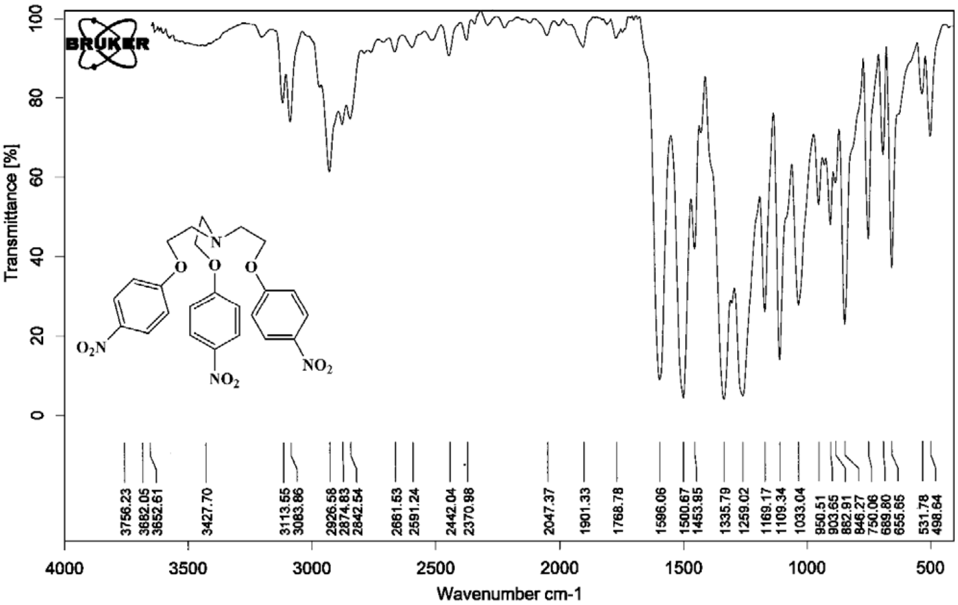


Figure 13 IR-spectrum of N-PTNO$_2$ (**L$_4$**).

Synthesis of N-OTN.HgCl$_2$ (1):

To the ligand **L$_1$** (0.45g; 1 mmol) in 10 mL MeOH was added a solution of HgCl$_2$ (0.27 g; 1 mmol) dissolved in 10 mL MeOH in a dropwise manner over a period of 30 min. at RT and then filtered. The filtrate was allowed to evaporate at RT for 2-3 days, when colorless crystals obtained in ~92% yield. Anal. calcd. for $C_{27}H_{24}N_4O_3Cl_2Hg$: C, 44.79; H, 3.34; N, 7.74%. Found: C, 44.97; H, 3.56; N, 7.49%.

Synthesis of N-MTN.HgCl$_2$ (2):

This complex was prepared in a similar manner as above. Yield ~ 94%. Anal. calcd for $C_{27}H_{24}N_4O_3Cl_2Hg$: C, 44.79; H, 3.34; N, 7.74%. Found: C, 44.54; H, 3.46; N, 7.57%.

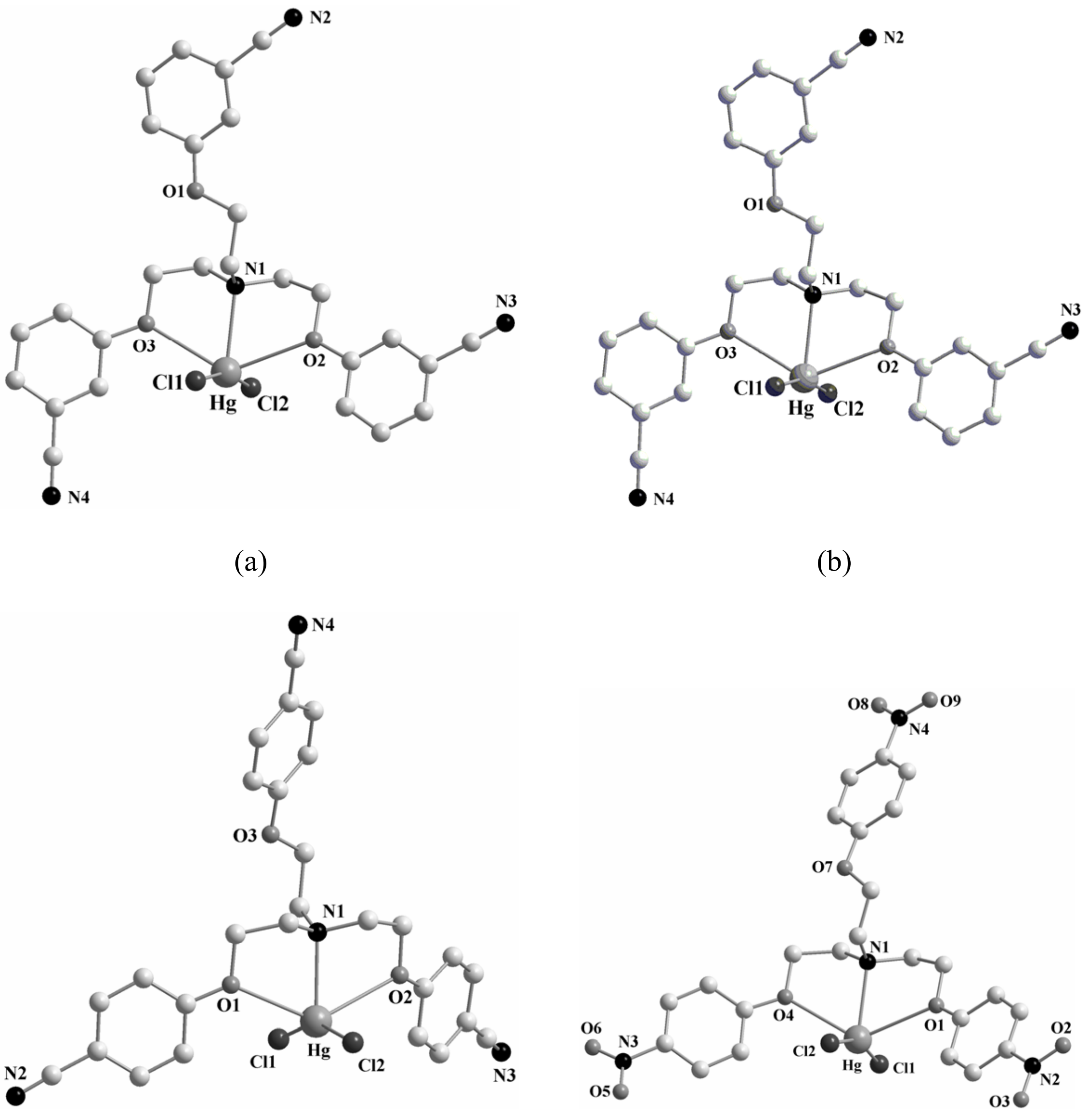
Synthesis of N-PTN.HgCl$_2$ (3):

This complex was also prepared as above. Yield ~92%. Anal. calcd for $C_{27}H_{24}N_4O_3Cl_2Hg$: C, 44.79; H, 3.34; N, 7.74%. Found: C, 44.41; H, 3.39; N, 7.56%.

Synthesis of N-PTNO$_2$.HgCl$_2$ (4)

This complex was also prepared as above. Yield ~95%. Anal. calcd for $C_{24}H_{24}N_4O_9Cl_2Hg$: C, 36.77; H, 3.09; N, 7.15%. Found: C, 36.21; H, 3.17; N, 7.07%.

Description of Crystal Structures obtained from podand L_1-L_4 with HgCl$_2$



(a) (b)

(c) (d)

Figure 14 Crystal Structure of adduct of L_1 with HgCl$_2$ (a); adduct of L_2 with HgCl$_2$ (b); adduct of L_3 with HgCl$_2$ (c) adduct of L_4 with HgCl$_2$ (d).

Table 1. Selected bond distances (A^{o}) and bond angles (^{o}) for **1-4**

1

Hg–N1	2.583(6)	N1–Hg–Cl1	98.86(15)
Hg–Cl1	2.312(2)	N1–Hg–Cl2	92.68(15)
Hg–Cl2	2.318(2)	Cl1–Hg–Cl2	167.91(8)
Hg–O1	2.987(2)	N1–Hg–O1	67.24(3)
		O1–Hg–Cl1	97.76(2)
		O1–Hg–Cl2	97.76(4)

2

Hg–N1	2.540(8)	N1–Hg–Cl1	99.1(2)
Hg–Cl1	2.303(3)	Cl1–Hg–Cl2	162.22(10)
Hg–Cl2	2.323(3)	O2–Hg–N1	64.8(3)
Hg–O2	2.818(2)	N1–Hg–Cl2	98.4(2)
Hg–O3	2.811(2)	O2–Hg–O3	129.9(1)
		O2–Hg–Cl1	97.7(8)
		O2–Hg–Cl2	92.2(6)
		O3–Hg–N1	65.2(4)
		O3–Hg–Cl1	88.2(4)
		O3–Hg–Cl2	96.7(2)

3

Hg–N1	2.486(5)	N1–Hg–Cl1	99.09(13)
Hg–Cl1	2.329(2)	N1–Hg–Cl2	107.48(12)
Hg–Cl2	2.315(2)	Cl1–Hg–Cl2	153.40(6)
Hg–O1	2.774(3)	O1–Hg–O2	131.8(4)
Hg –O2	2.839(2)	O1–Hg–Cl2	91.5(2)
		O1–Hg–Cl1	97.76(3)
		O1–Hg–N1	67.24(5)

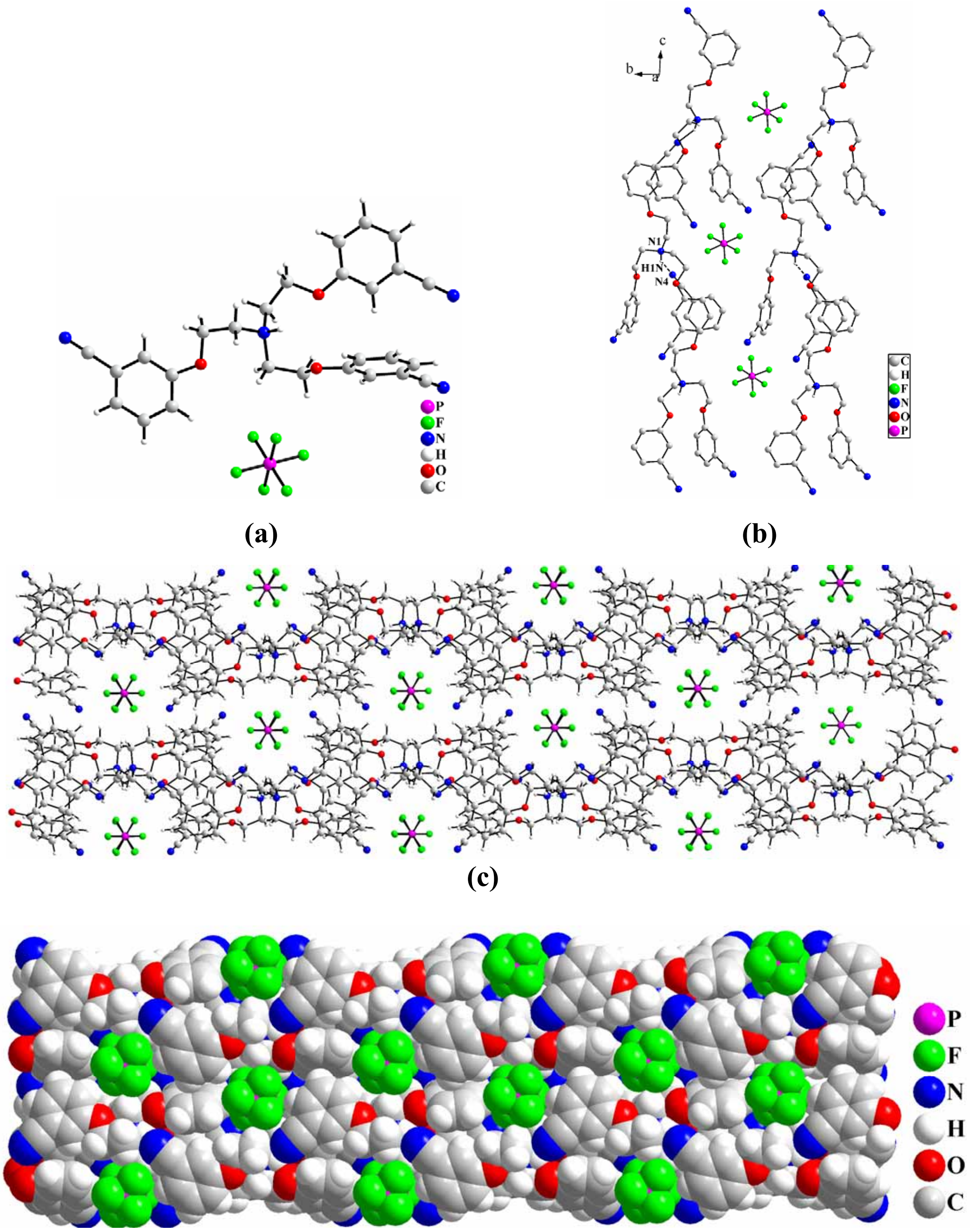
4

Hg–N1	2.487(8)	N1–Hg–Cl1	99.52(19)
Hg–Cl1	2.317(3)	N1–Hg–Cl2	102.92(19)
Hg–Cl2	2.305(3)	N1–Hg–O1	64.50 (10)
Hg–O1	2.840(3)	N1–Hg–O4	65.76(4)
Hg–O4	2.791(2)	Cl1–Hg–Cl2	157.38(10)
		O1–Hg–Cl1	99.09(3)
		O1–Hg–O4	129.61(2)
		O4–Hg–Cl2	90.28(3)

Table 2. Crystal Lattices and Refinement Data for the complexes **1-4**

	N-OTN.$HgCl_2$ **1**	**N-MTN.$HgCl_2$** **2**	**N-PTN.$HgCl_2$** **3**	**N-PTNO$_2$.$HgCl_2$** **4**
Empirical Formula	$C_{27}H_{24}Cl_2HgN_4O_3$	$C_{27}H_{24}Cl_2HgN_4O_3$	$C_{27}H_{24}Cl_2HgN_4O_3$	$C_{24}H_{24}Cl_2HgN_4O_9$
Formula weight	723.99	723.99	723.99	783.96
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71069	0.71073	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\ 2_1/n$	$P\ 2_1/c$	P -1	P -1
a, Å	7.828(5)	11.6156(9)	8.338(5)	8.190(5)
b, Å	24.454(5)	16.1637(13)	8.372(5)	8.396(5)
c, Å	14.274(5)	14.9583(12)	20.101(5)	20.920(5)
α (°)	90.00(5)	90	92.608(5)	80.781(1)
β (°)	102.386(5)	107.491(1)	92.608(5)	88.390(1)
γ(°)	90.00(5)	90	106.888(5)	73.641(1)
V, $Å^3$	2669(2)	2678.6(4)	1338.7(12)	1362.2(12)
Z	4	4	2	2
ρ_{calc} Mg/m^3	1.802	1.795	1.796	1.911
μ, mm^{-1}	6.004	5.982	5.984	5.905
F (000)	1408	1408	704	764
T (min.)	0.4662	0.4673	0.4672	0.4920
T (max.)	0.6141	0.6151	0.6149	0.6186
Data / parameter	17724/ 334	17,500 / 314	8871/ 334	9141/ 354
Reflection (Unique)	6596	6631	6254	6441
GOOF on F^2	1.046	1.266	1.101	1.243
R_{Final} R1 =	0.0501	0.0507	0.0434	0.0478
$I > 2\sigma(I)$ wR2 =	0.0895	0.0982	0.1017	0.1080
R_{all} R1 =	0.0852	0.0767	0.0494	0.0656
(all data) wR2 =	0.1164	0.1546	0.1127	0.1638

Description of Crystal Structure 5, obtained from adduct 2 with $AgPF_6$



(a) (b)

(c)

(d)

Figure 15 Crystal structure of (a) anion receptor $(\mathbf{L_2+H})^+$ with PF_6^- anion; (b) packing diagram of **5** where protonated N-bridgehead of one podand is H-bonded with N-atom of -CN group of another podand forming a chain and PF_6^- anion occupies the cavity formed by two neighboring chain (c) and its space-filled diagram (d).

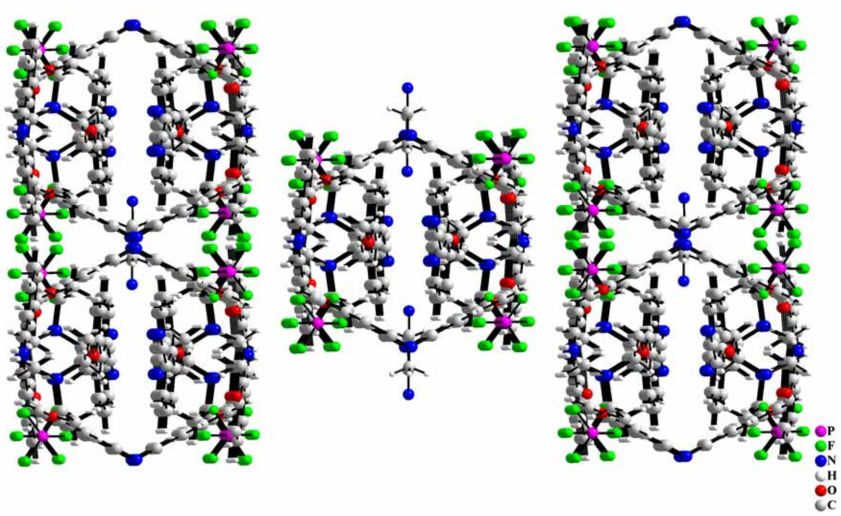
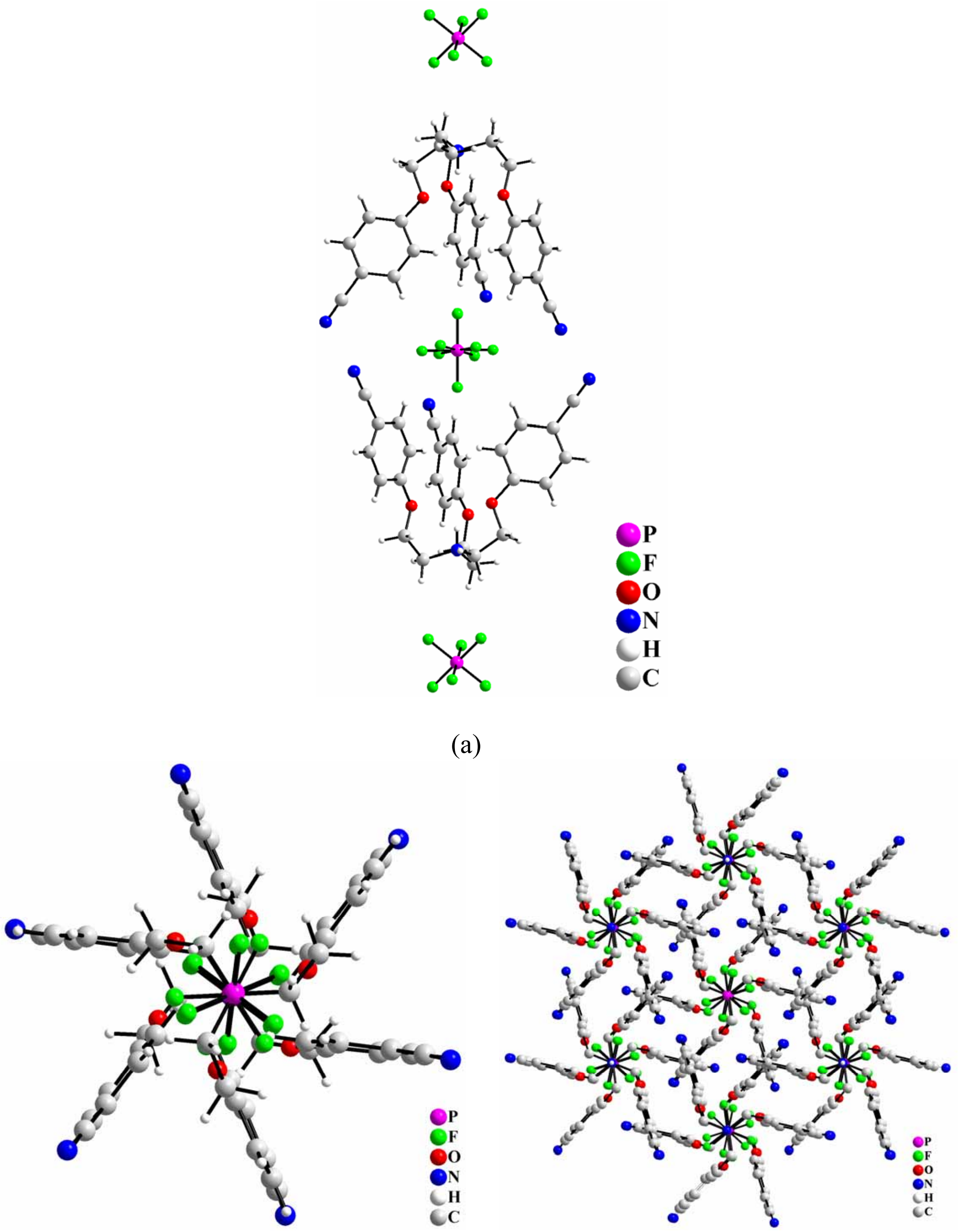


Figure 16 Packing diagram of **5** showing 3D-architecture in its solid state.

Description of Crystal Structure 6, obtained from adduct 3 with $AgPF_6$

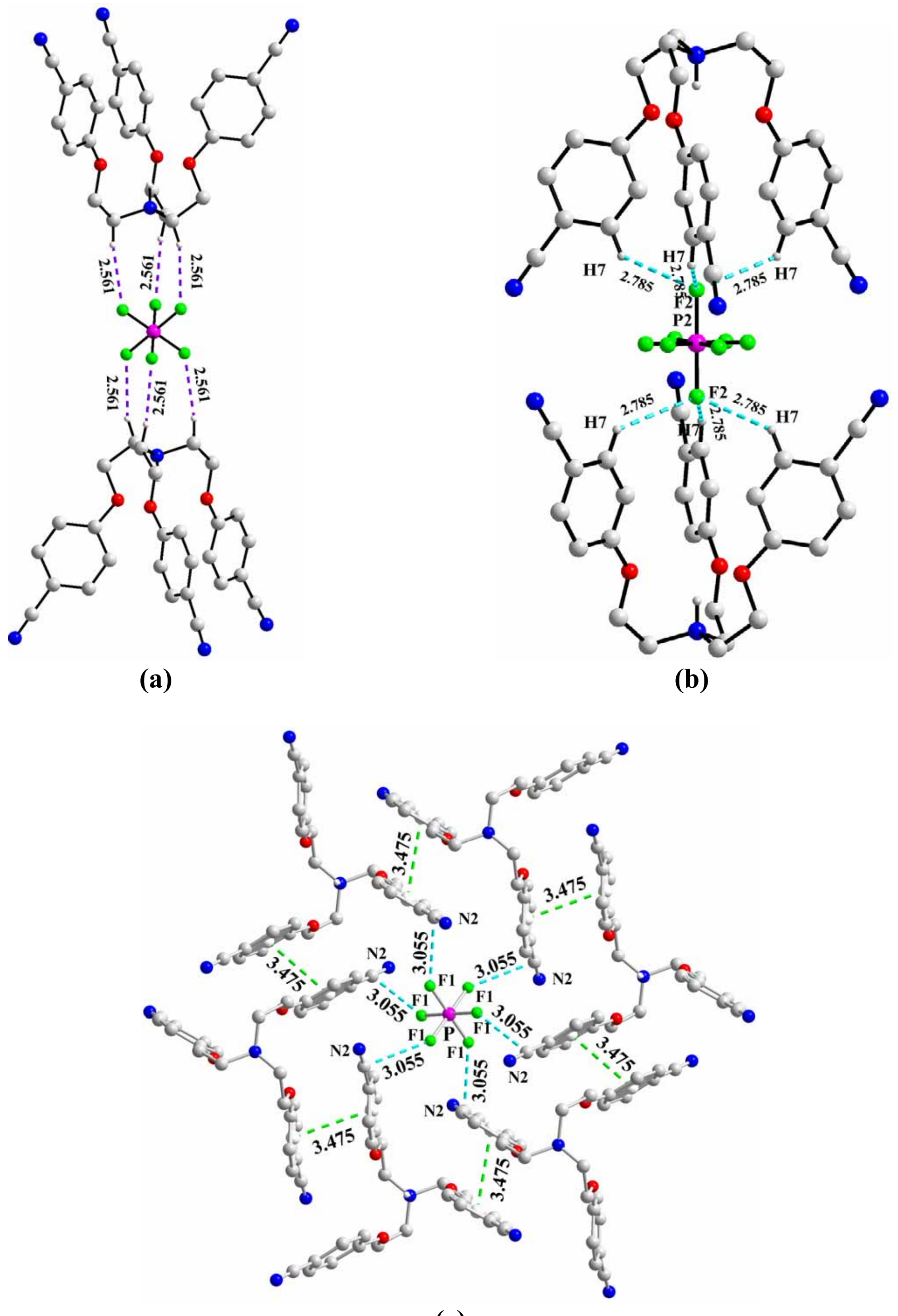


(a)

(b)

(c)

Figure 17 Crystal Structure of anion receptor $(\mathbf{L_3{+}1})^+$ for PF_6^- (a); arms of podand, encapsulating PF_6^- are in gauche conformation (b) and its 3D-network (c).



(a) **(b)**

(c)

Figure 18 Crystal structure of (a) H-bonded self-assembly of PF_6^- anion with **$(L_3+H)^+$**, bringing two podand **$(L_3+H)^+$** unit together; (b) encapsulated PF_6^- anion between two podand **$(L_3+H)^+$** unit, F···H interactions between F-atom of encapsulated PF_6^- anion and *meta* H-atom of aromatic ring; (c) Encapsulation of PF_6^- anion through anion···π interactions (cyan colored broken lines, P-F···π 3.055 Å) inside the cavity formed by π···π stacking (green colored broken lines, 3.475 Å), between two **$(L_3+H)^+$** unit and F-atom of encapsulated PF_6^- anion.

Table 3. Crystal Lattices and Structure Refinement Data for **5** and **6**

	5	**6**
Empirical Formula	$C_{29}H_{28}F_6N_5O_3P$	$C_9H_{8.33}N_{1.33}OP_{0.33}F_2$
Formula weight	639.53	208.88
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Trigonal
Space group	C 2/c	R-3
a, Å	29.780(4)	13.3330(17)
b, Å	10.3967(11)	13.3330(17)
c, Å	21.165(3)	26.773(4)
α (°)	90.00	90.00
β (°)	120.922(4)	90.00
γ(°)	90.00	120
V, $Å^3$	5621.6(13)	4121.8(10)
Z	4	3
ρ_{calc} Mg/m^3	1.463	1.493
μ, mm^{-1}	0.177	0.185
F (000)	2552	1902
T (min.)	0.9554	0.9586
T (max.)	0.9672	0.9745
Data / parameter	6929/ 387	1564 / 129
Reflection (Unique)	18407	6983
GOOF on F^2	1.073	1.143
R_{Final} R1 =	0.0638	0.0577
$I > 2\sigma(I)$ *w*R2 =	0.1239	0.1501
R_{all} R1 =	0.1106	0.0664
(all data) *w*R2 =	0.1614	0.1548

Table 4. Important non-bonding distances (Å) and angles (^{o})

	5		
C(11)…F(4)	3.465(3)	C(11)-H(11A)… F(4)	159.02
C(15)…F(2)	3.248(2)	C(15)-H(15)…F(2)	144.92
C(16)…F(1)	3.538(2)	C(16)-H(16)…F(1)	153.58
C(20)…F(1)	3.496(3)	C(20)-H(20A)…F(3)	166.16
C(15)…F(2)	3.248(2)	C(15)-H(15)…F(2)	144.92
C(10)…F(5)	3.268(3)	C(10)-H(10B)…F(5)	128.91
C(19)…F(3)	3.485(2)	C(19)-H(19B)…F(3)	174.62
C(2)…F(3)	3.802(2)	C(2)-H(2B)…F(3)	161.59
	6		
C(5)…F(1)	3.275	C(5)-H(5)…F(1)	130.45
C(1)…F(1)	3.521	C(1)-H(1A)…F(1)	163.52
C(7)…F(2)	3.487	C(7)-(H7)…F(2)	131.33
C(7)…F(3)	3.487	C(7)-H(7)…F(3)	143.95

References:

[1] Ward, Jr., K. *J. Am. Chem. Soc.* **1935**, 57, 914.