Supporting Information

Experimental and theoretical exploration of supramolecular interactions and photoresponse properties of two Ni(II) complexes

Samit Pramanik[a], Sudipta Pathak[b], Sumanta Jana[a], Monotosh Mondal[b], Antonio Frontera*[,c], Subrata Mukhopadhyay*[,a]

[a]Department of Chemistry, Jadavpur University, Kolkata 700032, India

[b]Department of Chemistry, Haldia Government College, Debhog, Purba Medinipur, West Bengal, India

[c]Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain

Table of Contents:

Table S1. Crystal Data and Structure Refinement Parameters for Complex 1 and 2

Complex	**1** (2052738)	**2** (2052737)
Empirical formula	$C_{32}H_{22}N_8NiClO_9$	$C_{36}H_{28}N_{12}NiF_{24}OP_4$
Formula Weight	757.72	1283.27
Temperature (K)	273(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
space group	*P* -1	*P* -1
a, b, c (Å)	8.4334(14), 13.968(2), 18.311(3)	9.0874(14), 9.5574(16), 28.115(4)
α, β, γ (°)	102.822(5), 101.380(5), 94.631(4)	83.970(4), 86.039(4), 88.258(4)
Volume ($Å^3$)	2044.3(6)	2421.8(7)
Z / Density (calc.) (Mg/m^3)	2 / 1.231	2 / 1.760
Absorption coefficient (mm^{-1})	0.595	0.673
F(000)	776	1280
Crystal size (mm^3)	0.18 × 0.25 × 0.3	0.18 × 0.25 × 0.3
θ range for data collection	2.122 to 27.170	2.143 to 27.133
Completeness to θ (%)	100%	100%
Absorption correction	EMPIRICAL	EMPIRICAL
Max. and min. transmission	0.898 and 0.837	0.886 and 0.817
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	9047 / 465	10688 / 706
Goodness-of-fit on F^2	1.089	1.049
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0715$, $wR_2 = 0.2167$	$R_1 = 0.0883$, $wR_2 = 0.2395$
R indices (all data)	$R_1 = 0.0897$, $wR_2 = 0.2294$	$R_1 = 0.1171$, $wR_2 = 0.2647$
Largest diff. peak and hole ($e.Å^{-3}$)	0.931 and -0.920	0.901 and -0.876

$R_1=\sum|| F_o|-|F_c||/\sum|F_o|$, $wR_2 = [\sum\{(F_o^2-F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$ $w = 1/\{\sigma^2(F_o^2) + (aP)^2 + bP\}$ where, $P = (F_o^2 + 2F_c^2)/3$,
a = 0.1176; b = 2.4644 for complex **1** and a = 0.1206; b = 7.4829 for complex **2**

Table S2. Selected Bond Distances [Å] for Complex 1 and 2

	Bonds	**Distance (Å)**	**Bonds**	**Distance (Å)**
Complex **1**	Ni1−O1	2.170(3)	Ni1−N13	2.140(3)
	Ni1−O12	2.109(3)	Ni1−N30	1.974(3)
	Ni1−N9	1.960(3)	Ni1−N36	2.117(3)
Complex **2**	Ni1−N1	2.156(5)	Ni1−N25	2.159(5)
	Ni1−N18	1.995(4)	Ni1−N36	1.990(4)
	Ni1−N24	2.177(4)	Ni1−N47	2.149(5)

Table S3. Selected Bond Angles [°] for Complex 1 and 2

	Bond angles	**Value (°)**	**Bond angles**	**Value (°)**
Complex **1**	O1−Ni1−O12	155.94(11)	N13−Ni1−N36	154.40(13)
	O1−Ni1−N9	77.42(12)	N30−Ni1−N36	77.29(13)
	O1−Ni1−N13	91.92(11)	Ni1−O1−C2	112.4(3)
	O1−Ni1−N30	102.46(12)	Ni1−O12−C10	114.1(3)
	O1−Ni1−N36	92.71(11)	Ni1−N9−C8	118.7(3)
	O12−Ni1−N9	78.52(12)	Ni1−N9−C4	119.5(2)
	O12−Ni1−N13	94.04(12)	Ni1−N13−C14	128.0(3)
	O12−Ni1−N30	101.59(12)	Ni1−N13−C18	114.5(3)
	O12−Ni1−N36	91.91(13)	Ni1−N30−C19	121.0(3)
	N9−Ni1−N13	103.44(13)	Ni1−N30−C29	120.5(3)
	N9−Ni1−N30	179.41(14)	Ni1−N36−C31	114.1(2)
	N9−Ni1−N36	102.14(13)	Ni1−N36−C35	127.7(3)
	N13−Ni1−N30	77.13(13)		
Complex **2**	N1−Ni1−N18	76.84(17)	N36−Ni1−N47	76.65(18)
	N1−Ni1−N24	152.65(16)	Ni1−N1−C2	128.0(4)
	N1−Ni1−N25	92.41(16)	Ni1−N1−C6	113.8(3)
	N1−Ni1−N36	103.10(17)	Ni1−N18−C17	121.3(3)
	N1−Ni1−N47	92.73(18)	Ni1−N18−C7	120.1(3)
	N18−Ni1−N24	75.86(15)	Ni1−N24−C19	114.5(3)
	N18−Ni1−N25	106.29(17)	Ni1−N24−C23	128.4(3)
	N18−Ni1−N36	177.48(18)	Ni1−N25−C26	127.9(4)
	N18−Ni1−N47	100.83(18)	Ni1−N25−C30	114.4(3)
	N24−Ni1−N25	93.64(16)	Ni1−N36−C31	121.7(4)
	N24−Ni1−N36	104.24(16)	Ni1−N36−C41	121.0(4)
	N24−Ni1−N47	93.93(17)	Ni1−N47−C46	127.8(4)
	N25−Ni1−N36	76.23(17)	Ni1−N47−C42	114.3(4)
	N25−Ni1−N47	152.86(17)		

Table S4. Geometrical Parameters for the Hydrogen Bonds of Complex 1 and 2

	D–H···A	D–H [Å]	H···A	D···A [Å]	D–H···A [°]	Symmetry
Complex **1**	N27−H27···O49	0.8600	2.3100	3.111(6)	155.00	x, y, -1+z
	O37−H37···O11	0.8200	1.8000	2.598(6)	164.00	−
	O49−H49B···Cl1	0.8500	2.2100	3.010(6)	157.00	−
	C5−H5···O48	0.9300	2.4300	3.286(7)	154.00	-1+x, 1+y, z
	C14−H14···O39	0.9300	2.5100	3.212(7)	133.00	1-x, 1-y, 1-z
	C23−H23···Cl1	0.9300	2.3900	3.230(7)	150.00	-1+x, y, -1+z
	C25−H25···O47	0.9300	2.2900	3.127(6)	149.00	-1+x, y, -1+z
	C26−H26···O1	0.9300	2.5400	3.325(8)	142.00	1-x, 1-y, -z
	C35−H35···N45	0.9300	2.4900	3.362(5)	157.00	2-x, 1-y, 1-z
	C43−H43···O3	0.9300	2.5800	3.412(7)	149.00	1+x, -1+y, z
Complex **2**	O2−H2B···F10	0.8500	2.4100	2.995(8)	127.00	−
	O2−H2B···F12	0.8500	2.3700	2.990(8)	130.00	−
	N15−H15···O2	0.8600	1.9200	2.717(8)	154.00	−
	C2−H2···F6	0.9300	2.5300	3.444(13)	167.00	1-x, 1-y, 1-z
	C13−H13···F13	0.9300	2.5400	3.166(8)	124.00	-x, -y, 1-z
	C14−H14···F18	0.9300	2.4900	3.286(9)	143.00	-x, -y, 1-z
	C38−H38···F1	0.9300	2.2000	3.08(2)	157.00	x, y, -1+z
	C39−H39···F4	0.9300	2.5400	3.252(16)	133.00	x, y, -1+z
	C44−H44···F6	0.9300	2.5100	3.400(14)	161.00	-x, 1-y, 1-z
	C45−H45···F17	0.9300	2.4500	3.089(10)	126.00	−
	C46−H46···F15	0.9300	2.5300	3.431(8)	164.00	−

Table S5. Geometrical Parameters (Å, °) for the π-Stacking Interactions for the Title Complexes

	Cg(i)···Cg(j)	Cg(i)···Cg(j) [Å]	α (°)	β (°)	γ (°)	Cg(i)–perp[Å]	Cg(j)–perp[Å]	Symmetry
Complex **1**	Cg(5)[1]···Cg(10)	3.764(3)	7.54	27.86	23.34	3.456	3.327	2-x, 1-y, 1-z
	Cg(6)[1]···Cg(9)	3.715(3)	2.46	18.70	19.80	3.495	3.519	-1+x, y, z
	Cg(8)[1]···Cg(9)	3.561(3)	2.35	13.85	15.89	3.425	3.458	1-x, 1-y, -z
	Cg(9)[1]···Cg(6)	3.715(3)	2.46	19.80	18.70	3.518	3.495	1+x, y, z
	Cg(9)[1]···Cg(8)	3.561(3)	2.35	15.89	13.85	3.458	3.425	1-x, 1-y, -z
	Cg(10)[2]···Cg(5)	3.765(3)	7.54	23.34	27.86	3.328	3.456	2-x, 1-y, 1-z
Complex **2**	Cg(7)[1]···Cg(7)	3.635(4)	0.04	14.69	14.69	3.516	3.516	1-x, -y, 1-z
	Cg(9)[1]···Cg(12)	3.957(3)	4.24	29.07	24.83	3.591	3.458	1+x, y, z
	Cg(12)[1]···Cg(9)	3.956(3)	4.24	24.83	29.07	3.458	3.591	-1+x, y, z

Table S6. Geometrical Parameters (Å,°) for the C−H···π Interactions for the Complex 2

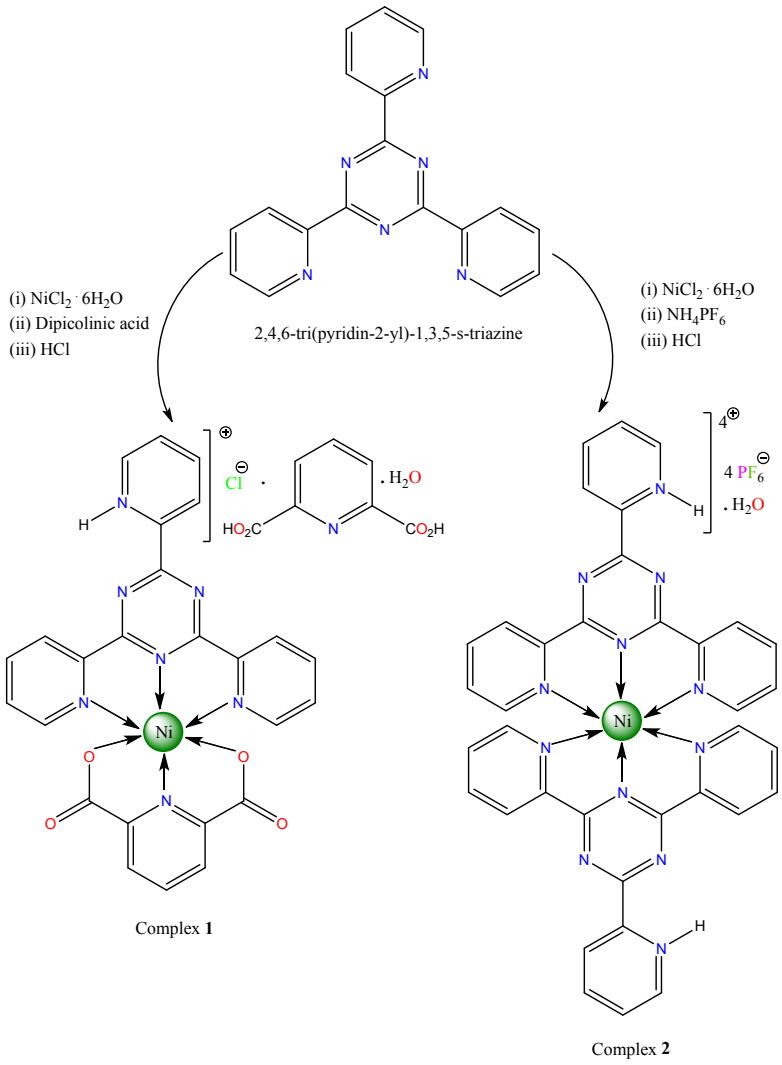
	X–H(I)···Cg(J)	H···Cg	X···Cg	X–H···Cg	Symmetry
Complex **2**	C(4)−H(4)[1]···Cg(9)	2.82	3.738(7)	169	x, -1+y, z

For complex **2**: Cg(9) is the centroid of [N25/C26/C27/C28/C29/C30] ring.

Table S7 Geometrical Parameters (Å, °) for the Anion···π Interactions for the Title Complexes

	Y–X(I)···Cg(J)	X···Cg [Å]	Y···Cg [Å]	Y–X ···Cg (°)	Symmetry
Complex **1**	C(10)−O(11)[1]···Cg(5)	3.493(4)	4.090(5)	110.2(3)	1-x, 1-y, 1-z
	C(38)−O(39)[2]···Cg(1)	3.989(6)	4.734(5)	123.1(5)	1-x, 1-y, 1-z
	C(38)−O(39)[2]···Cg(5)	3.918(7)	4.152(6)	93.2(4)	1-x, 1-y, 1-z
	C(46)−O(47)[2]···Cg(1)	3.546(5)	4.031(5)	105.4(3)	2-x, 1-y, 1-z
Complex **2**	P(2)−F(9)[3]···Cg(8)	3.329(8)	4.462(3)	128.0(4)	1-x, 1-y, 1-z
	P(3)−F(15)[4]···Cg(6)	2.999(5)	4.337(2)	140.6(3)	x, y, z
	P(3)−F(17)[4]···Cg(1)	3.743(6)	4.693(3)	118.3(3)	-1+x, y, z
	P(3)−F(17)[4]···Cg(5)	3.316(6)	4.419(3)	125.9(3)	-1+x, y, z
	P(3)−F(18)[4]···Cg(7)	3.282(7)	4.611(3)	142.6(4)	x, y, z
	P(4)−F(19)[5]···Cg(5)	3.747(9)	4.485(3)	108.3(4)	x, 1+y, z
	P(4)−F(22)[5]···Cg(5)	3.636(8)	4.485(3)	112.7(3)	x, 1+y, z
	P(4)−F(22)[5]···Cg(10)	3.012(7)	4.086(3)	122.9(3)	x, y, z
	P(4)−F(23)[5]···Cg(12)	3.203(7)	4.203(3)	119.7(4)	x, 1+y, z
	P(4)−F(24)[5]···Cg(10)	3.454(7)	4.086(3)	102.2(3)	x, y, z

Cg(j) denotes centroid of j^{th} ring of the title complexes. For complex **1**: Cg(1) is the centroid of [Ni1/O1/C2/C4/N9] ring; and Cg(5) is the centroid of [N9/C4/C5/C6/C7/C8] ring. For complex **2**: Cg(1) is the centroid of [Ni1/N1//C6/C7/N18] ring; Cg(5) is the centroid of [N1/C2/C3/C4/C5/C6] ring; Cg(6) is the centroid of [N8/C7/N18/C17/N16/C9] ring; Cg(7) is the centroid of [N15/C10/C11/C12/C13/C14] ring; Cg(8) is the centroid of [N24/C19/C20/C21/C22/C23] ring; Cg(10) is the centroid of [N32/C31/N36/C41/N40/C33] ring; and Cg(12) is the centroid of [N47/C42/C43/C44/C45/C46] ring.



Scheme 1 Schematic representations of the synthesis of complex **1** and **2**

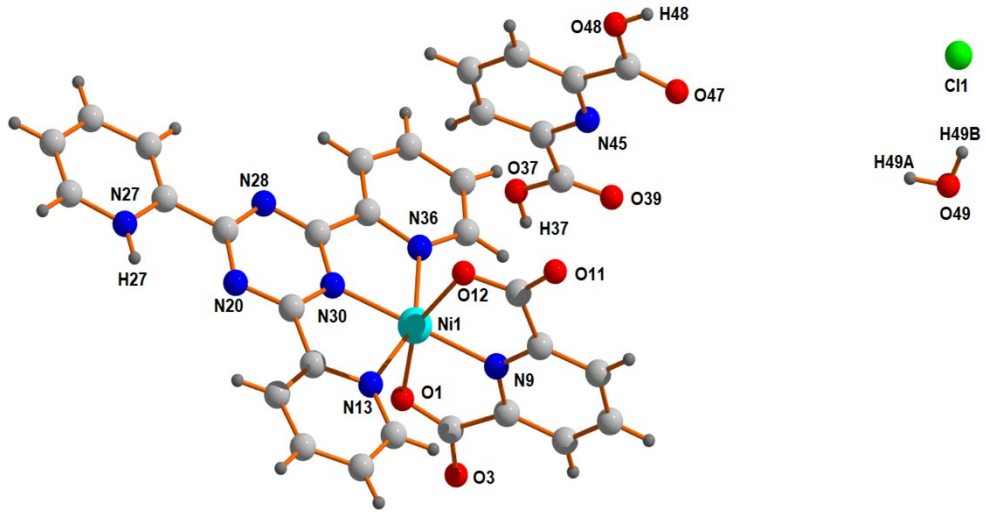


Fig. S1. Asymmetric unit of complex **1**

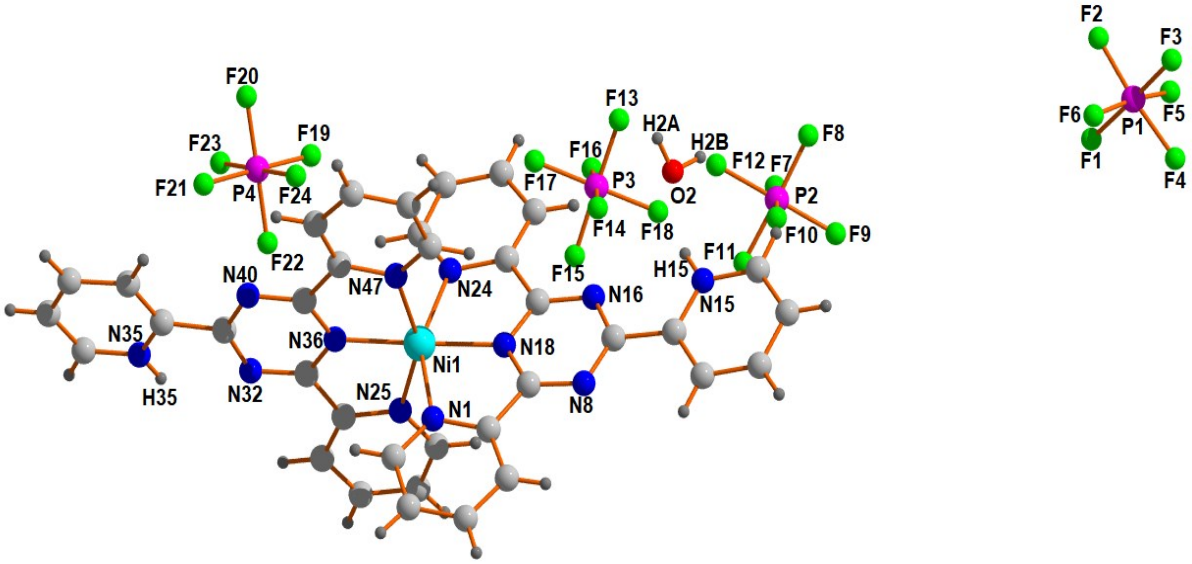


Fig. S2 Asymmetric unit of complex **2**

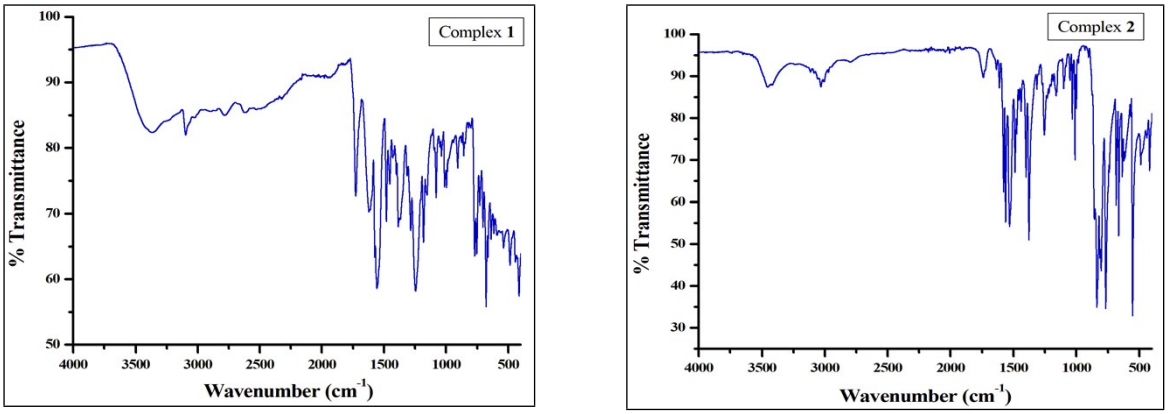


Fig. S3. FT-IR spectra for Complex **1** and Complex **2**

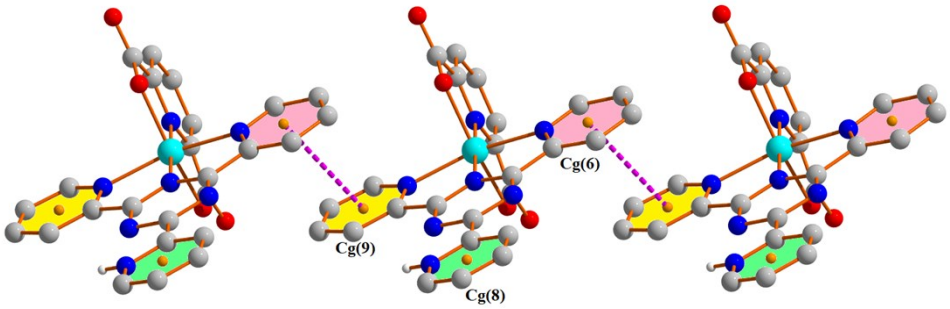


Fig. S4 1D polymeric chain through a π···π interaction (aromatic hydrogen atoms have been omitted for clarity).

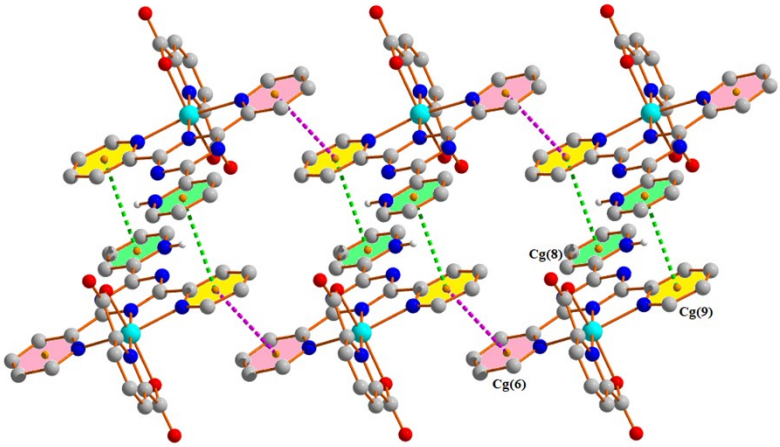


Fig. S5 Perspective view of the extended supramolecular networks in complex **1** through π···π and π···π+ interactions (aromatic hydrogen atoms have been omitted for clarity).

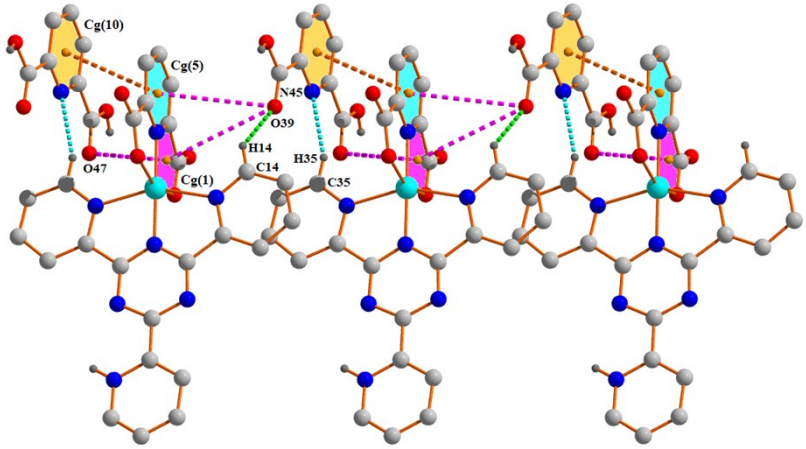


Fig. S6 Propagation 1-D of polymeric chain through π···π / lone pair···π / hydrogen bonding interactions in complex **1**(other aromatic hydrogen atoms have been omitted for clarity).

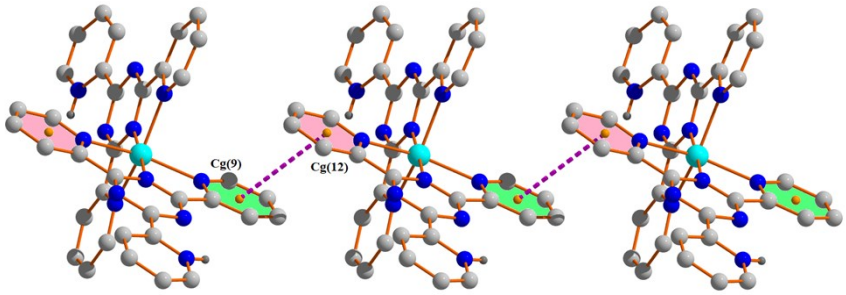


Fig. S7 1-D polymeric chain through a π···π interaction in complex **2** (aromatic hydrogen atoms have been omitted for clarity).

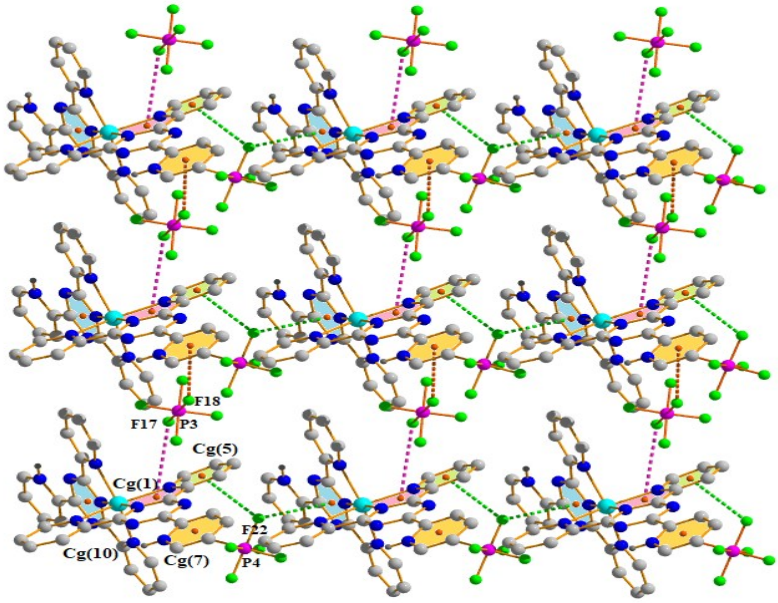


Fig. S8 Perspective view of 2-D layer incorporating anion···π and anion···π+ interactions in complex **2**(aromatic hydrogen atoms have been omitted for clarity).

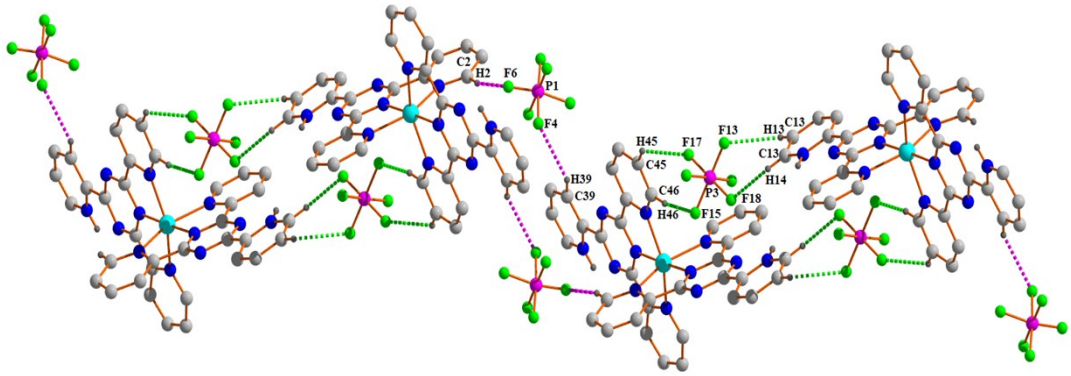


Fig. S9 One-dimensional (1-D) zigzag polymeric chain through hydrogen bonding interactions in complex **2** (other aromatic hydrogen atoms have been omitted for clarity).

Table S8 Device parameter for **1**

condition	on /off	conductivity δ(S cm^{-1})	ideality factor η	dv/dlnI Rs (k ohm)	H Rs (k ohm)	barrier height Φ_B	transit time t×10^{-9} (s)	D ×10^{-6}	L_D ×10^{-7}	Mobility μ_{eff} ×10^{-5} (cm^2 V^{-1} s^{-1})
Dark	2.95	2.45×10^{-3}	2.81	9.63	9.40	0.64	8.31	3.69	2.476	7.14
Light	31.31	6.06×10^{-3}	1.79	5.58	5.18	0.70	6.3	18.45	2.584	14.30

Table S9 Device parameter for **2**

condition	On /off	conductivity δ (S cm^{-1})	ideality factor η	dv/dlnI Rs (k ohm)	H Rs (k ohm)	barrier height Φ_B	transit time t×10^{-9} (s)	D ×10^{-6}	L_D×10^{-7}	Mobility μ_{eff} ×10^{-4} (cm^2 V^{-1} s^{-1})
Dark	31.21	1.54×10^{-2}	2.53	3.11	2.64	0.73	7.2	8.25	3.447	3.19
Light	54.93	3.24×10^{-2}	1.44	2.58	2.17	0.60	5.7	13.86	3.976	5.36

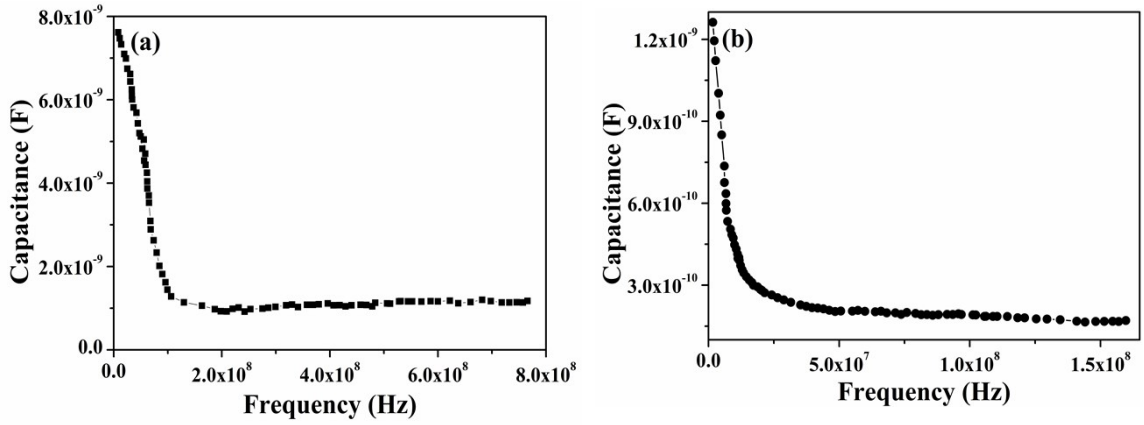


Fig. S10 Capacitance *vs*. Frequency plot of (a) device 1 and (b) device 2

Table 10 Conductivity data reported for single crystals of Ni-based complexes at room temperature

Ni(II) complex	Electrical conductivity (S cm^{-1})	Reference
$[Ni_2(C_4N_2H_3S)_4]_n$	5×10^{-3}	(1)
$C_{20}H_{10}N_4NiHg_2S_4$	2.18×10^{-10}	(2)
$Ni_2(C_{22}H_{20}N_6O_4)_n$	2.15×10^{-11}	(3)
$C_{10}H_{23}N_4O_8SClNi$	2.14×10^{-9}	(4)
$C_{60}H_{54}Br_4N_4Ni_2O_{13}$	3.57×10^{-4}	(5)
$Ni(BzO_4[16]octaeneN_4)](ClO_4)_2$	6.97×10^{-4}	(6)
$C_{52}H_{40}F_2N_8NiS_2$	9.81×10^{-9}	(7)
$C_{32}H_2N_8NiClO_9$ (Complex **1**)	6.0×10^{-6}	Present work
$C_{36}H_{28}N_{12}NiOF_{24}P_4$ (Complex **2**)	3.24×10^{-5}	Present work

References

1. Y. Zhao, M. Hong, Y. Liang, R. Cao, W. Li, J. Weng and S. Lu, *Chem. Commun.*, 2001, 1020−1021.
2. N. Singh and V. K. Singh, *Transition Met. Chem.*, 2001, **26**, 435−439.
3. J. T. Makode, A. R. Yaul, S. G. Bhadange, and A. S. Aswar, *Russ. J. Inorg. Chem.*,2009, **54**, 1372−1377.
4. M. S. Refat, I. M. ElDeen, M. A. Zein, A. M. A. Adam, M. I. Kobeasy, *Int. J. Electrochem. Sci.*, 2013, **8**, 9894−9917.
5. İ. Gönül, *Inorg. Chim. Acta*, 2019, **495**, 119027−119034.
6. M. E. Sánchez-Vergaraa, B. Molinab, A. Hernández-Garcíaa, J. R. Álvarez-Badaa, and R. Salcedoc, *Semiconductors*, 2020, **54**, 441−449.
7. U. M. Osman, S. Silvarajoo, K. H. Kamarudin, M. I. M. Tahir, H. C. Kwong, *J. Mol. Struct.*, 2021, **1223**, 128994−129003.