Post synthetic modification of isomorphic coordination layers: exchange dynamics of metal ions in single crystal to single crystal fashion

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Supporting Information

FESEM images, IR spectra, TGA, and DSC curves, Metal and Anion Exchange Studies, Powder XRD patterns and crystallographic information of compounds and experimental details.

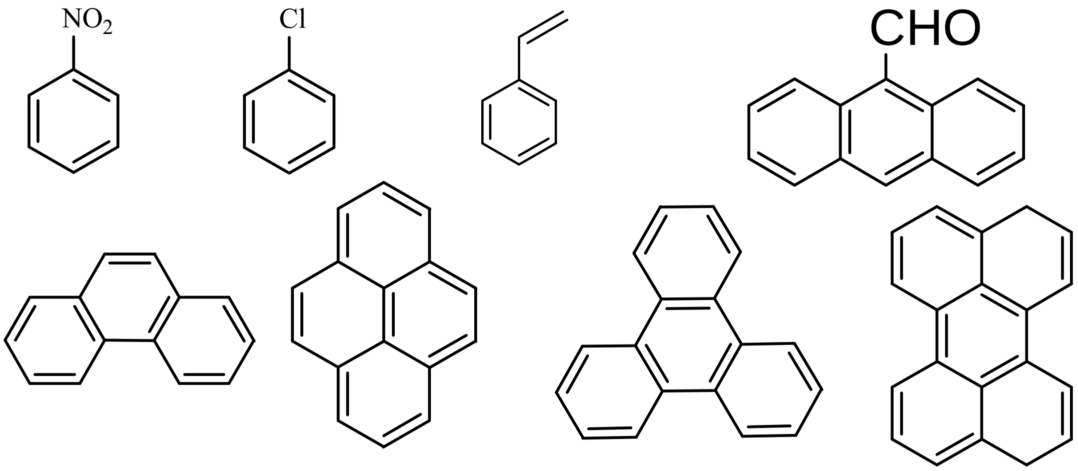
General. Fourier transform IR (FTIR) spectra, Atomic Absorption Spectra (AAS) were recorded with an Perkin-Elmer instrument. Elemental analyses were obtained with a Perkin-Elmer instrument, series II, CHNS/O analyzer 2400. Thermogravimetric analysis (TGA) data were recorded under an Ar atmosphere at a heating rate of 5ºCmin^{-1} with a Perkin-Elmer instrument, Pyris Diamond TG/DTA. Powder X-ray diffraction (XRD) data were recorded with a Bruker APEX-2 diffractometer. FESEM analysis was performed with a supra 40, Carl Zeiss Pvt. Ltd instrument.

The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ =0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2 using SHELX-97.[1] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. However, in 3a’ the guest pyrene molecules are refined in isotropically as the anisotropic refinement leading to severe distortions in pyrene and high thermal parameters. PLATON was used for the calculation of guest available volumes and squeeze option was used for as the free water molecules could not be located.[2]

Benzene-1,3,5-triyltriisonicotinate (BTTP4)

The BTTP4 ligand was prepared according to the previously reported method.[3]

Scheme S1. Chemical structures of the guests included in the layer reported here.



Synthesis of Complex by Direct Reactions:

Complex **2a**: Methanolic solution (1 mL) of $Zn(PF_6)_2$·(0.01 mmol, prepared by mixing methanolic solution of $Zn(NO_3)_2$ in $(NH_4)_2PF_6$ in 1:1 ratio) was added to a stirred solution of ligand (0.009 g, 0.02 mmol) and pyrene (0.004 g, 0.02 mmol) in 5 mL of $CHCl_3$. This solution was filtered after stirring of few minutes and kept for slow evaporation. Crystals were formed after few hours. In the case of solid guest molecules, 2 equiv of guest was used for 1 equiv of metal salt, whereas for liquid aromatic guest molecules, 2 mL of the solvent was used.

All the complexes were prepared in a similar way by using the ligand, corresponding metal salts, and guest molecules. In case of Cu(II) salts, addition of methanolic solution of Cu(II) salts to the chloroform solution of ligand and guests resulted in the formation of a blue precipitate. After 5-10 min of stirring, few drops of water was added. The blue precipitate became soluble, and a clear solution was obtained.

1. $\{[Zn(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot\text{pyrene}\cdot 2(H_2O)\}_{n,}$ **(2a)**
2. $\{[Cu(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot\text{pyrene}\cdot 2(H_2O)\}_n$, (**3a)**
3. $\{[Cu(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot\text{phenanthrene}\cdot 2(H_2O)\}_n$, (**3b**)
4. $\{[Cd(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot\text{pyrene}\cdot 2(H_2O)\}_n$, (**4a**)

5. $\{[Cd(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot$triphenelene$\cdot 2(H_2O)\}_n$, (**4b**)
6. $\{[Cd(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot$perylene$\cdot 2(H_2O)\}_n$, (**4c**)
7. $\{[Cd(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot$9-anthraldehyde$\cdot 2(H_2O)\}_n$, (**4d**)
8. $\{[Co(L)_2(H_2O)_2]\cdot 2(PF_6)\cdot$pyrene$\cdot 2(H_2O)\}_n$, (**5a)**
9. $\{[Cd(L)_2(H_2O)_2]\cdot 2(ClO_4)\cdot$pyrene$\cdot 2(H_2O)\}_n$, (**6a**)
10. $\{[Cd(L)_2(H_2O)_2]\cdot 2(ClO_4)\cdot$styrene$\cdot 2(H_2O)\}_n$, (**6b**)
11. $\{[Cd(L)_2(H_2O)_2]\cdot 2(ClO_4)\cdot$chlorobenzene$\cdot 2(H_2O)\}_n$, (**6c**)
12. $\{[Cu(L)_2(H_2O)_2]\cdot 2(ClO_4)$ pyrene$\cdot 2(H_2O)\}_n$, (**7a**)
13. $\{[Cu(L)_2(H_2O)_2]\cdot 2(ClO_4)$ phenanthrene$\cdot 2(H_2O)\}_n$,(**7b**)
14. $\{[Cu(L)_2(H_2O)_2]\cdot 2(ClO_4)$ nitrobenzene$\cdot 2(H_2O)\}_n$, (**7c**)
15. $\{[Cd(L)_2(H_2O)_2]\cdot 2(SbF_6)\cdot$pyrene$\cdot 2(H_2O)\}_n$, (**8a**)

The crystal structures of **2a**, **3a**, **4a** and **3a'** are included in the present manuscript with CIF files; all other structures will be published elsewhere.

Table S1:

Complex	**Yield (%)**	**Calculated % of C, H, N**	**Experimental % of C, H, N**
2a	83.3	C 50.76, H 3.33, N 5.55	C 50.59, H 3.26, N 6.03
3a	78.4	C 50.82, H 3.33, N 5.56	C 50.76, H 3.75, N 6.00
3b	78.7	C 50.09, H 3.25, N 5.65	C 50.15, H 3.22, N 5.98
4a	83.7	C 49.23, H 3.23, N 5.38	C 49.21, H 3.15, N 5.88
4b	81.6	C 50.00, H 3.18, N 5.30	C 50.19, H 3.07, N 5.64
4c	65.2	C 50.74, H 3.13, N 5.22	C 50.66, H 3.19, N 5.28
4d	76.7	C 48.34, H 3.22, N 5.37	C 48.36, H 3.02, N 5.83
5a	79.6	C 50.97, H 3.34, N 5.57	C 50.90, H 3.82, N 5.81
6a	80.5	C 52.28, H 3.43, N 5.72	C 52.31, H 3.40, N 6.12
6b	56.1	C 49.08, H 3.38, N 6.13	C 49.97, H 3.15, N 6.67
6c	73.8	C 47.04, H 3.14, N 6.10	C 47.65, H 3.44, N 6.85
7a	83.4	C 54.07, H 3.55, N 5.91	C 54.27, H 3.90, N 6.43
7b	85.6	C 53.36, H 3.47, N 6.02	C 53.77, H 3.45, N 6.31
7c	64.8	C 48.39, H 3.23, N 7.31	C 48.59, H 3.22, N 7.94
8a	50.0	C 44.10, H 2.89, N 4.82	C 44.17, H 3.09, N 5.37

Table S2:

Compounds	**2a**	**3a**	**3a'**	**4a**
Formula	$C_{64}H_{48}N_6O_{16}ZnF_{12}P_2$	$C_{64}H_{48}N_6O_{16}CuF_{12}P_2$	$C_{64}H_{48}N_6O_{16}CuF_{12}P_2$	$C_{64}H_{48}N_6O_{16}CdF_{12}P_2$
Mol.Wt.	1512.33	1510.56	1510.56	1561.45
T (K)	293(2)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	10.294(2)	10.224(2)	10.213(3)	10.484(3)
b(Å)	19.025(3)	18.934(4)	18.938(5)	19.181(5)
c(Å)	16.509(3)	16.667(4)	16.619(4)	16.381(4)
α(°)	90	90	90	90
β(°)	98.204(5)	96.438(7)	96.744(9)	99.553(8)
γ(°)	90	90	90	90
V (Å3)	3200.1(9)	3205.9(1)	3192.3(1)	3248.5(1)
Z	2	2	2	2
D(Mg/m^3)	1.570	1.565	1.572	1.594
R_1 (I>2σ(I))	0.0732	0.0830	0.1113	0.0759
wR_2 (on F^2, all data)	0.2308	0.2246	0.2936	0.2370
independent reflns	5201	3835	2957	2850
reflns used[I>2σ(I)]	6712	5798	5928	5667
R_{int}	0.0388	0.0632	0.1711	0.1673

Compounds	**4a'**	**3b**	**4b**	**4c**
Formula	$C_{64}H_{48}N_6O_{16}CdF_{12}P_2$	$C_{62}H_{48}N_6O_{16}CuF_{12}P_2$	$C_{66}H_{48}N_6O_{16}CdF_{12}P_2$	$C_{66}H_{50}N_6O_{16}CdF_{12}P_2$
Mol.Wt.	1561.45	1486.55	1585.47	1609.49
T (K)	293(2)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	10.466(3)	10.272(5)	10.415(1)	10.443(3)
b(Å)	19.148(5)	18.932(9)	19.071(2)	19.108(6)
c(Å)	16.347(4)	16.590(8)	16.975(2)	17.289(6)
α(°)	90	90	90	90
β(°)	100.704(8)	96.446(15)	99.838(3)	99.586(1)
γ(°)	90	90	90	90
V (Å3)	3218.93	3205.9	3321.98	3401.89

Compounds	**4d**	**5a**	**6a**	**6b**	**6c**
Formula	$C_{63}H_{50}N_6O_{17}CdF_{12}P_2$	$C_{64}H_{50}N_6O_{16}CoF_{12}P_2$	$C_{64}H_{50}N_6O_{24}CdCl_2$	$C_{56}H_{46}N_6O_{24}CdCl_2$	$C_{54}H_{43}N_6O_{24}CdCl_3$
Mol.Wt.	1565.44	1507.97	1470.42	1370.31	1378.71
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	10.4790(19)	10.279(1)	10.448(3)	10.411(4)	10.4311(2)
b(Å)	19.157(4)	18.975(2)	18.987(5)	18.888(8)	18.939(3)
c(Å)	16.893(3)	16.461(2)	16.960(4)	17.095(7)	17.326(3)
α(°)	90	90	90	90	90
β(°)	100.074(6)	98.611(3)	101.447(7)	101.817(12)	101.096(5)
γ(°)	90	90	90	90	90
V (Å3)	3338.93	3174.42	3297.32	3290.55	3358.92

Compounds	**7a**	**7b**	**7c**	**8a**
Formula	$C_{64}H_{50}N_6O_{24}CuCl_2$	$C_{62}H_{48}N_6O_{24}CuCl_2$	$C_{54}H_{43}N_6O_{26}CuCl_2$	$C_{64}H_{50}N_6O_{16}CdF_{12}Sb_2$
Mol.Wt.	1421.56	1395.52	1340.40	1743.02
T (K)	293(2)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	10.229(3)	10.2449(1)	10.2477(1)	10.535(6)
b(Å)	18.797(5)	18.667(2)	18.550(2)	19.350(1)
c(Å)	16.537(4)	16.777(2)	17.226(2)	16.334(9)
α(°)	90	90	90	90
β(°)	98.882(5)	99.323(4)	99.535	96.637(2)
γ(°)	90	90	90	90
V (Å^3)	3141.57	3166.15	3229.31	3307.5

TGA and DSC curves.

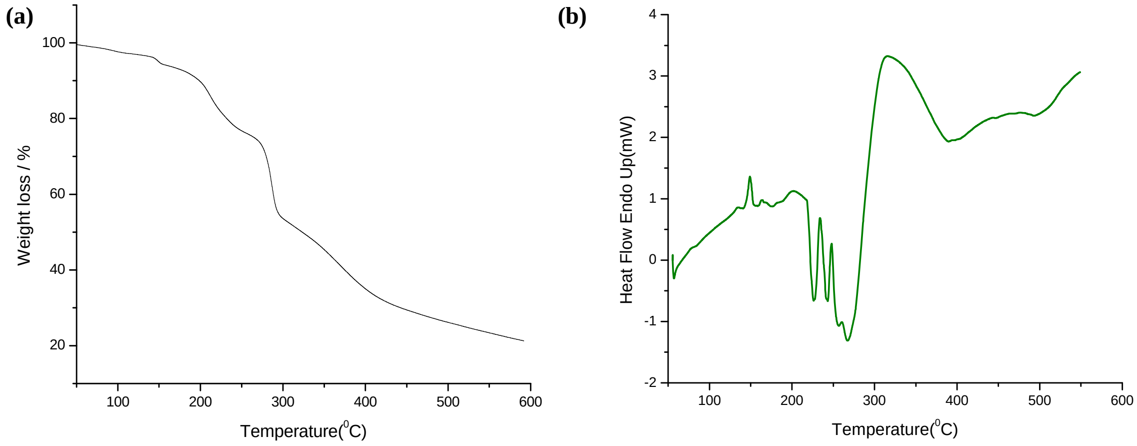


Figure S1. (a) TGA and (b) DSC curves of **2a**

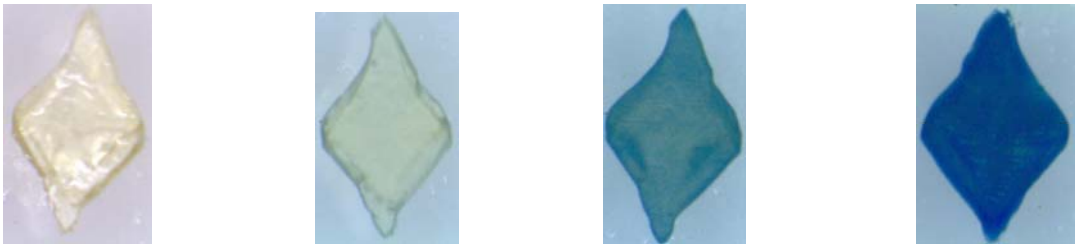
Metal and anion Exchange Procedure.

Crystals of as-synthesized complexes were immersed in 0.1 (M) methanolic solutions of targeted metal salts. After two days, the crystals were removed from the solution, kept in methanol for three days.

To study the metal exchange dynamics, crystals of as-synthesized complexes were crushed and immersed in 0.1 (M) methanolic solutions of targeted metal salts. A certain amount of sample was removed at a regular time intervals, thoroughly washed with methanol, dried, digested in concentrated nitric acid, and analyzed by AAS.

For anion exchange, crystals of **6a** complexes were soaked in 0.1(M) methanolic solutions of NH_4PF_6. Upon decanting the NH_4PF_6 solutions, the anion-exchanged crystals were rinsed in methanol, and dried.

2a to **3a'**



As synthesized

0 min

60 min

240 min

Figure S2. Microscopic images of **2a** to **3a'** metathesis.

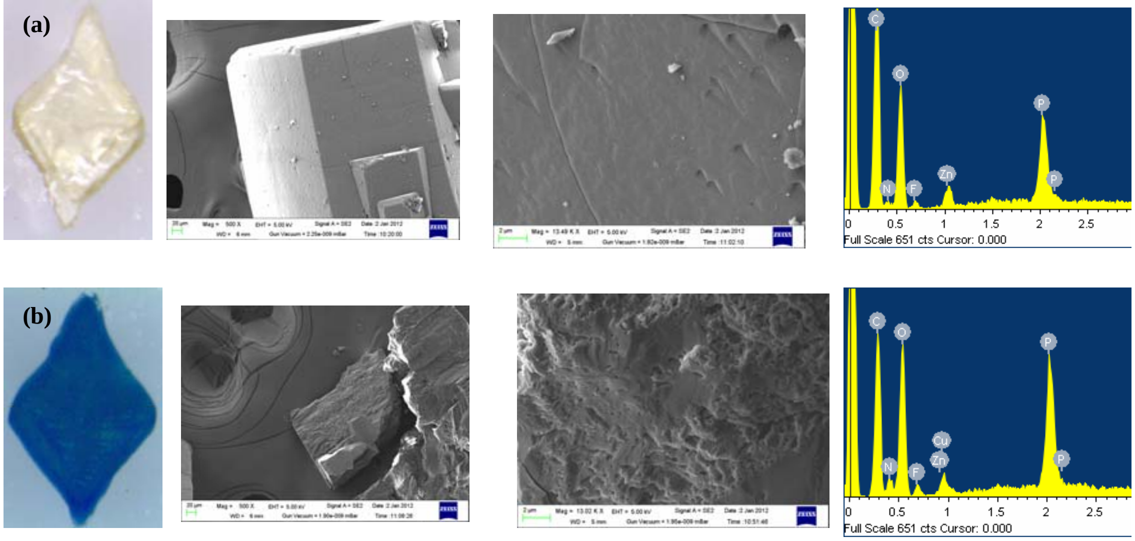


Figure S3. Microscopic images, FESEM images, and EDX spectra of **2a** before (a) and after (b) metal exchange by immersion in 0.1(M) methanolic solution of $Cu(PF_6)_2$.

4a to **3a'**

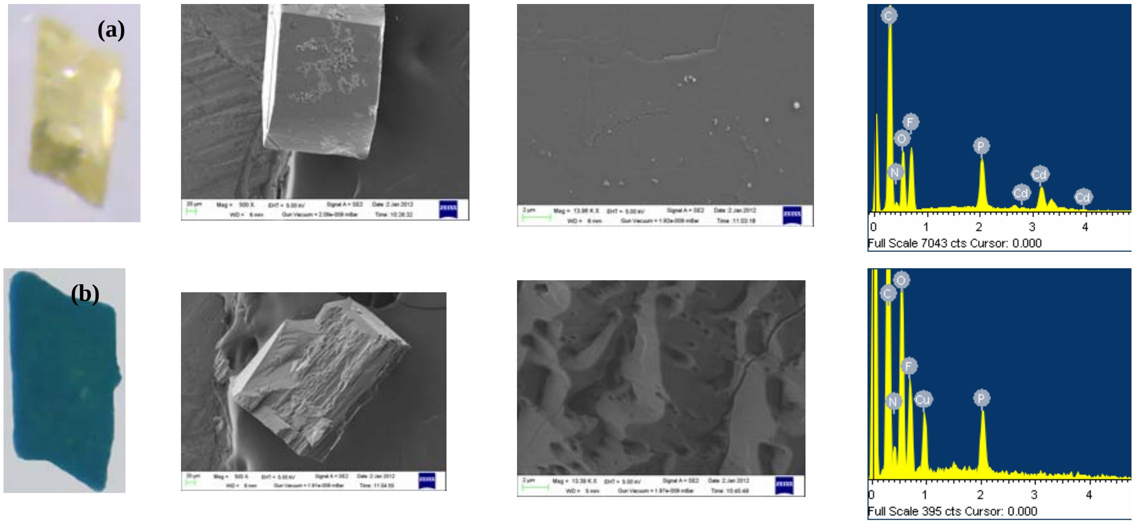


Figure S4. Microscopic images, FESEM images, and EDX spectra of **4a** before (a) and after (b) metal exchange by immersion in 0.1(M) methanolic solution of $Cu(PF_6)_2$.

3a to **4a'**

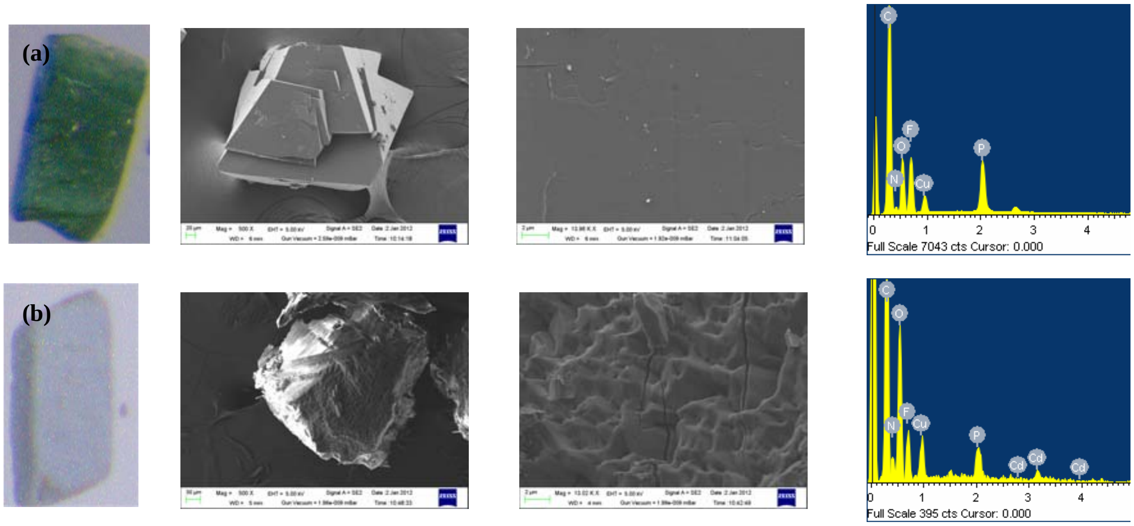


Figure S5. Microscopic images, FESEM images, and EDX spectra of **3a** before (a) and after (b) metal exchange by immersion in 0.1(M) methanolic solution of $Cd(PF_6)_2$.

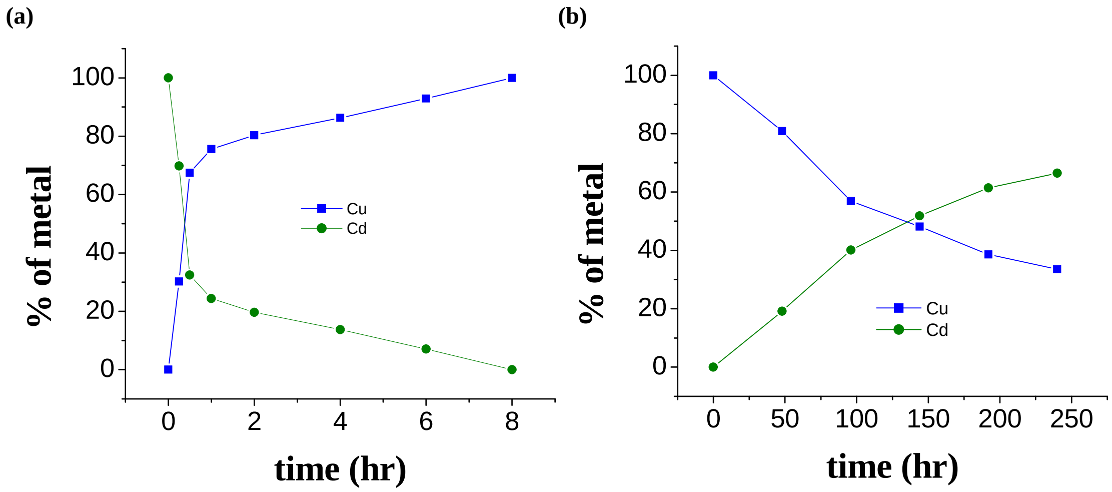


Figure S6. Metal ion exchange kinetics of (a) Cd(II) with Cu(II) in **4a** and (b) Cu(II) with Cd(II) in **3a**.

FT-IR Spectra:

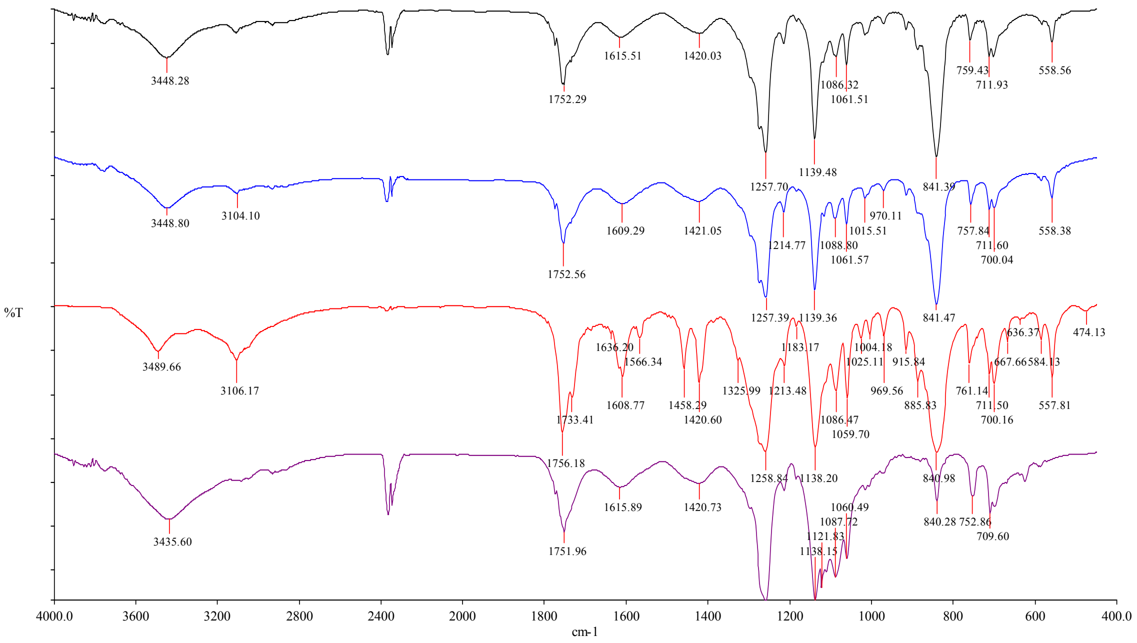


Figure S7. FT-IR spectra for as-synthesized **2a** (blue), **3a** (red), **4a** (black), **6a** (violet).
3106 cm^{-1} (aromatic C-H str); 1752-1756 cm^{-1} (ester C=O); 1608- 1420 cm^{-1}(C=C, C=N pyridine ring str); 840, 557 cm^{-1} (PF$_6$); 970-915, 757-567 cm^{-1}(pyrene).
3106 cm^{-1} (aromatic C-H str); 1751 cm^{-1} (ester C=O); 1615, 1420 cm^{-1}(C=C, C=N pyridine ring str); 1110-1141 cm^{-1} (ClO$_4$).752-567 cm^{-1} (pyrene).

Anion exchange

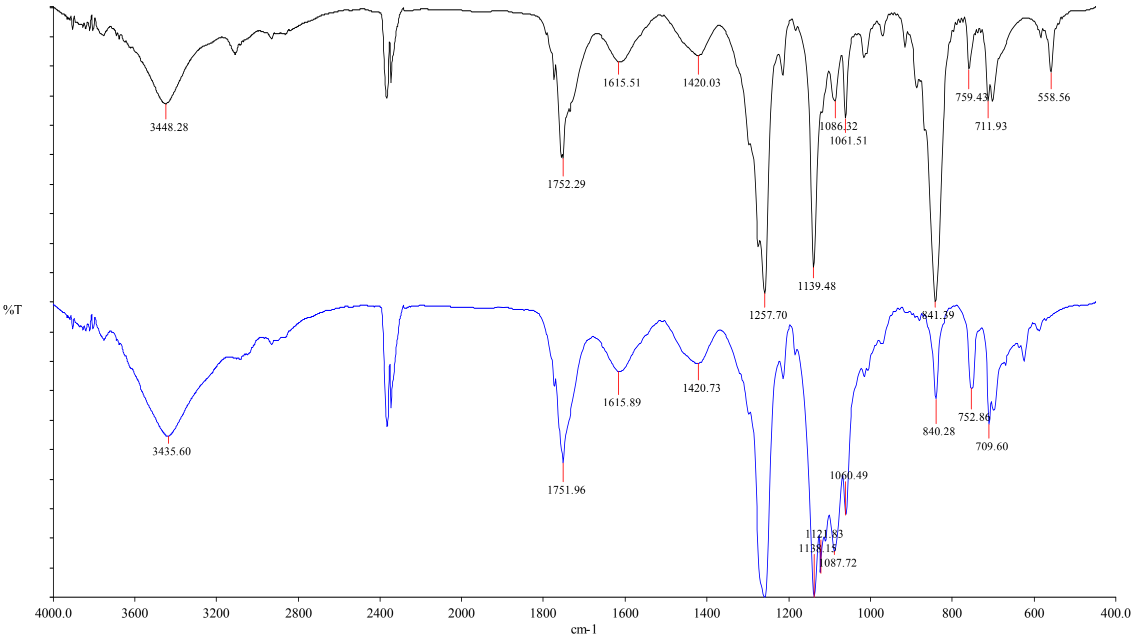


Figure S8. FT-IR spectra for as-synthesized **6a** (blue), and **4a'** (black) synthesized by anion exchange from **6a**.
1121 cm^{-1} (ClO_4) peak disappeares; the hollowness of the peak at 840 increased very significantly and a new peak at 557 cm^{-1} (PF_6) appears.

Anion Exchange in SCSC:

The exchange of ClO_4^- anion in complex **6a** was achieved by immersing as-synthesized crystals of **6a** in 0.1(M) methanolic solution of NH_4PF_6. From the X-ray analysis it was observed that the exchange of anion also proceeds in SCSC manner and the exchanged crystals **4a'** also isostructural with **4a**, for example the *c*-axes of **4a** and **4a'** are identical. The crystal structure of **4a'** shows the presence of PF_6 but contains high thermal parameters for F-atoms and distortion in pyrene. It is interesting to note here that the reverse exchange, that is the transformation of **4a** to **6a** was observed to be unsuccessful even after one month of immersion.

Table S3:

	a(Å)	*b*(Å)	*c*(Å)	*β*(°)	V (Å^3)
4a	10.484(3)	19.181(5)	16.381(4)	99.553(8)	3248.49
4a'	10.466(3)	19.148(5)	16.347(4)	100.704(8)	3218.93
6a	10.448(3)	18.987(5)	16.960(4)	101.447(7)	3297.32

Table S4:

Complex	**Calculated % of C, H, N**	**Experimental % of C, H, N**
4a	C 49.23, H 3.23, N 5.38	C 49.21, H 3.15, N 5.88
4a'	C 49.23, H 3.23, N 5.38	C 50.05, H 3.20, N 5.76
6a	C 52.28, H 3.43, N 5.72	C 52.31, H 3.40, N 6.12

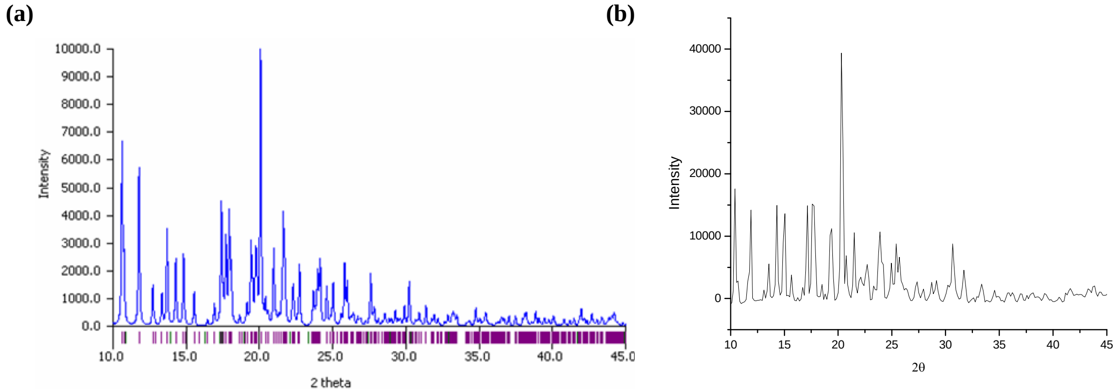


Figure S9. (a) Calculated and (b) experimental PXRD pattern of **2a**.

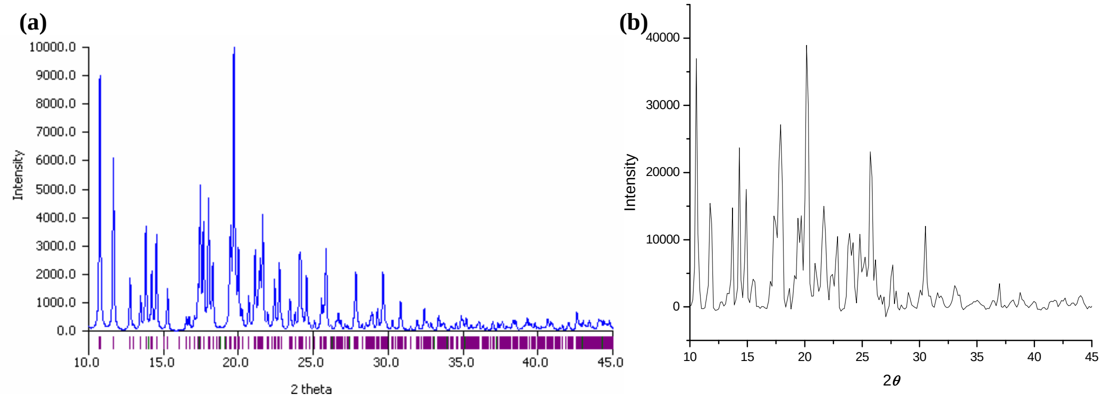


Figure S10. (a) Calculated and (b) experimental PXRD pattern of **3a**.

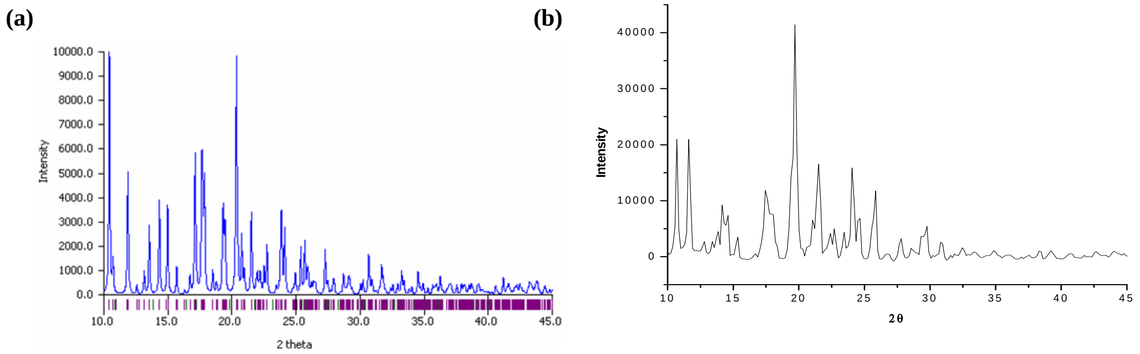


Figure S11. (a) Calculated and (b) experimental PXRD pattern of **4a**.

References:

(1) G. M. Sheldrick, SHELX-97, *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.

(2) A. L. Spek, *PLATON-A Multi Purpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002.

(3) Noh, T. H.; Kim, S. A.; Lee, S. Y; Jung, O. –S. *Eur. J. Inorg. Chem.* **2009**, 4518.