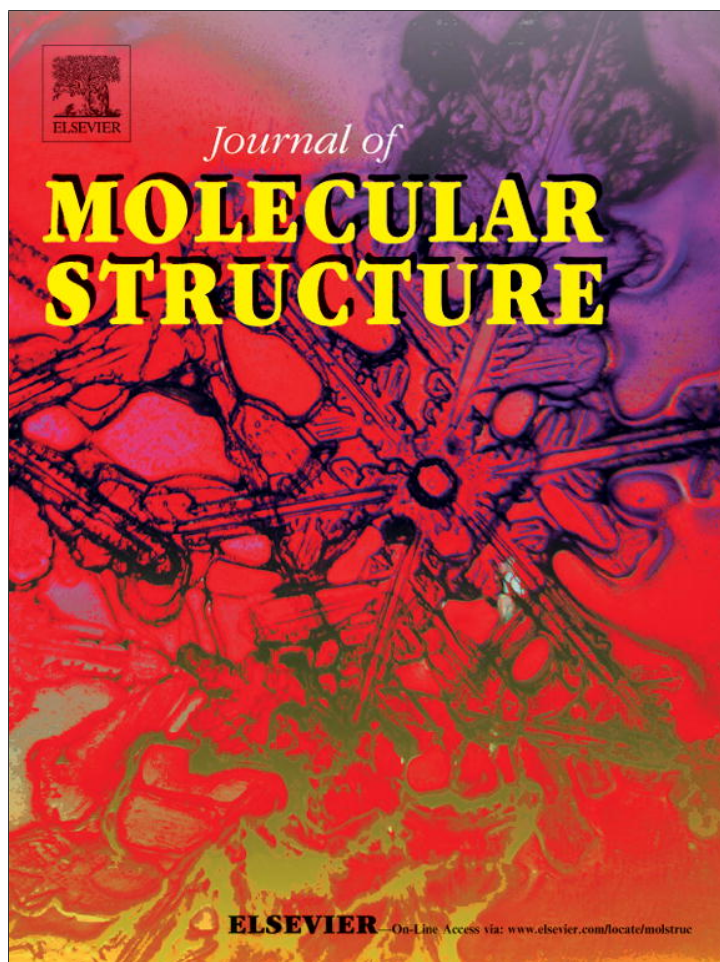


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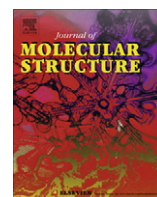
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Time-of-diffusion dependent structural diversity in the M^{II} -phen-tetracyanometalates ($M = Zn, Mn$) supramolecular system

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HIGHLIGHTS

- ▶ Three series of supramolecular assemblies were crystallized at different periods.
- ▶ A time-of-diffusion dependent structural diversity was involved.
- ▶ Chelated ligands contribute to isolations of low-dimensional cyanide-based systems.

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ABSTRACT

The mononuclear molecules, ionic compounds and cyanide-based layers were isolated at different periods from one-pot crystallization in the M^{II} -phen-tetracyanometalates ($M = Zn, Mn$) system, in which a time-of-diffusion dependent structural diversity was involved.

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1. Introduction

Molecule-based materials have received much attention in recent years due to their tremendous potential applications [1]. Cyanometalate anions such as $[M(CN)_4]^{2-}$ ($M = Ni, Pd, Pt$), $[M(CN)_6]^{3-}$ ($M = Fe, Co, Cr$) and $[M(CN)_8]^{4-}$ ($M = Mo, W, n = 3, 4; M = Nb, n = 4$) have been extensively used as building blocks to construct multi-functional assemblies with intriguing structural features and fascinating properties [2–4]. In the process of the construction of molecule-based materials, as is well known, the chelated aromatic ligands (e.g., bpy, phen, tmphen) are usually employed to block coordination sites on metal ions, hence restricting the growth of the structure to finite dimensions rather than extended networks [5,6]. Continuing with this research line and one of the themes pursued in our laboratory of investigating the impacts on the formation of cyanide-based assemblies with low-dimensional structures [7,8], we reported in this contribution the self-organization of transition

metal ions M^{2+} ($M = Zn, Mn$), the bidentate chelated ligand phen and $[M'(CN)_4]^{2-}$ ($M' = Ni, Pd, Pt$) precursors.

Slow diffusion of the solutions resulted in the generations of mononuclear molecules $Zn(phen)(H_2O)_3(SO_4) \cdot H_2O$ (**1**) or $Mn(phen)(H_2O)_4 \cdot (SO_4) \cdot 2H_2O$ (**2**), ionic compounds $M(phen)_2(H_2O)_2 \cdot M'(CN)_4 \cdot 4H_2O$ ($M = Zn, M' = Ni$ (**1a**), **1b**), **1c**); $M = Mn, M' = Ni$ (**2a**), **2b**), **2c**) and metal cyanide layers $M(phen)M'(CN)_4$ ($M = Zn, M' = Ni$ (**1d**), **1e**), **1f**); $M = Mn, M' = Ni$ (**2d**), **2e**), **2f**) after the reaction system was allowed to stand for 3, 6 and 10 days, respectively. Although the temperature-, pH- and ligand concentration-dependent self-organizations have been documented previously [9–11], we present in this contribution a time-of-diffusion dependent structural transformation in cyanide-based systems.

2. Experimental

2.1. Materials and methods

All reagents, unless otherwise stated, were obtained from commercial sources and were used without further purification.

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Elemental analyses for C, H and N were performed with a Perkin–Elmer 240C elemental analyzer. IR spectra were measured on a Nicolet FT 1703X spectrophotometer in the form of KBr pellets in the 4000–400 cm^{-1} region.

2.2. Syntheses

Single crystals of all compounds were prepared by slow diffusion method at room temperature. A small glass vial (2 mL) containing the solids of $\text{MSO}_4 \cdot n\text{H}_2\text{O}$ ($M = \text{Zn, Mn}$) (0.05 mmol) and phen (0.05 mmol) was placed into a big glass vial (20 mL) containing the solid of $\text{K}_2[\text{M}'(\text{CN})_4]$ ($M' = \text{Ni, Pd, Pt}$) (0.05 mmol). The two vials were filled slowly with the $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solvent ($V/V = 1/1$). The big vial was sealed and then allowed to stand at room temperature for three days, whereupon plate-like crystals (**1**, **2**) were formed at the bottom of the small vial. After allowing the solution to stand for further three days, rod-like crystals (**1a**, **1b**, **1c**, **2a**, **2b**, **2c**) appeared on the bottom and inner wall of the small vial, and then polyhedral crystals (**1d**, **1e**, **1f**, **2d**, **2e**, **2f**) generated on the bottom and inner wall of the small vial after further four days. Yield for compound **1d**: 26% based on the Zn salt. The other compounds (**1e**, **1f**, **2d**, **2e**, **2f**) have similar mass yields.

Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{NiZn}$ (**1d**): C 47.06, H 1.97, N 20.58. Found: C 47.15, H 1.90, N 20.51; Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{PdZn}$ (**1e**): C 42.13, H 1.77, N 18.43. Found: C 42.08, H 1.65, N 18.21; Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{PtZn}$ (**1f**): C 35.28, H 1.48, N 15.43. Found: C 35.12, H 1.60, N 15.29. Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{NiMn}$ (**2d**): C 48.30, H 2.03, N 21.12. Found: C 48.21, H 2.09, N 21.19; Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{PdMn}$ (**2e**): C 43.12, H 1.81, N 18.86. Found: C 42.99, H 1.86, N 18.73; Elem. anal. calcd for $\text{C}_{16}\text{H}_8\text{N}_6\text{PtMn}$ (**2f**): C 35.97, H 1.51, N 15.73. Found: C 36.01, H 1.56, N 15.62.

IR (KBr) for compound **1a**, $\nu_{\text{C}\equiv\text{N}}$: 2169, 2131 cm^{-1} , $\nu(\text{O}-\text{H})$: 3436 cm^{-1} ; compound **1b**, $\nu_{\text{C}\equiv\text{N}}$: 2181, 2142 cm^{-1} , $\nu(\text{O}-\text{H})$: 3428 cm^{-1} ; compound **1c**, $\nu_{\text{C}\equiv\text{N}}$: 2177, 2139 cm^{-1} , $\nu(\text{O}-\text{H})$: 3444 cm^{-1} ; compound **1d**, $\nu_{\text{C}\equiv\text{N}}$: 2169, 2131 cm^{-1} ; compound **1e**, $\nu_{\text{C}\equiv\text{N}}$: 2181, 2142 cm^{-1} ; compound **1f**, $\nu_{\text{C}\equiv\text{N}}$: 2178, 2140 cm^{-1} ; compound **2a**, $\nu_{\text{C}\equiv\text{N}}$: 2162, 2129 cm^{-1} , $\nu(\text{O}-\text{H})$: 3436 cm^{-1} ; compound **2b**, $\nu_{\text{C}\equiv\text{N}}$: 2173, 2140 cm^{-1} , $\nu(\text{O}-\text{H})$: 3425 cm^{-1} ; compound **2c**, $\nu_{\text{C}\equiv\text{N}}$: 2168, 2136 cm^{-1} , $\nu(\text{O}-\text{H})$: 3447 cm^{-1} ; $\nu_{\text{C}\equiv\text{N}}$ for compound **2d**: 2164, 2131 cm^{-1} ; $\nu_{\text{C}\equiv\text{N}}$ for compound **2e**: 2173, 2141 cm^{-1} ; $\nu_{\text{C}\equiv\text{N}}$ for compound **2f**: 2169, 2139 cm^{-1} .

Table 1
Crystallographic data and structural refinement for compounds **1**, **1a**, **1b**, **1c**, **1d**, **1e** and **1f**.

Compound	1	1a	1b	1c	1d	1e	1f
Formula	$\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_8\text{SZn}$	$\text{C}_{28}\text{H}_{28}\text{N}_8\text{O}_6\text{NiZn}$	$\text{C}_{28}\text{H}_{28}\text{N}_8\text{O}_6\text{PdZn}$	$\text{C}_{28}\text{H}_{28}\text{N}_8\text{O}_6\text{PtZn}$	$\text{C}_{16}\text{H}_8\text{N}_6\text{NiZn}$	$\text{C}_{16}\text{H}_8\text{N}_6\text{PdZn}$	$\text{C}_{16}\text{H}_8\text{N}_6\text{PtZn}$
M_r	413.70	696.67	744.40	833.07	408.36	456.05	544.74
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
a (Å)	8.0382(4)	17.2605(12)	17.344(2)	17.390(18)	6.5685(19)	6.6180(4)	6.6152(5)
b (Å)	8.6318(5)	13.5098(9)	13.6818(18)	13.561(14)	19.240(6)	19.5275(12)	19.6642(14)
c (Å)	11.5887(6)	14.0210(10)	14.2169(19)	14.065(15)	11.502(3)	11.7969(7)	11.9098(8)
α (°)	92.0780(10)	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	92.1200(10)	108.1040(10)	108.721(2)	108.510(11)	90.696(3)	91.4790(10)	91.2020(10)
γ (°)	103.7640(10)	90.00	90.00	90.00	90.00	90.00	90.00
$V/\text{Å}^3$	779.61(7)	3107.6(4)	3195.2(7)	3145(6)	1453.5(7)	1524.04(16)	1548.92(19)
Z	2	4	4	4	4	4	4
ρ (g cm^{-3})	1.762	1.472	1.531	1.742	1.866	1.988	2.336
μ (mm^{-1})	1.755	1.431	1.365	5.258	2.955	2.763	10.579
Total, unique	6024, 2984	11846, 3045	11292, 2816	8935, 2788	5472, 1410	5887, 1574	5985, 1572
Observed [$I > 2\sigma(I)$]	2879	2567	2546	2189	1305	1546	1478
GOF on F^2	1.051	1.043	1.040	1.048	1.118	1.189	1.103
$R_1, \omega R_2$ [$I > 2\sigma(I)$]	0.0177, 0.0490	0.0270, 0.0747	0.0214, 0.0564	0.0327, 0.1019	0.0190, 0.0478	0.0133, 0.0361	0.0144, 0.0351
$R_1, \omega R_2$ (all data)	0.0185, 0.0497	0.0360, 0.0775	0.0257, 0.0581	0.0543, 0.1395	0.0218, 0.0487	0.0137, 0.0363	0.0159, 0.0358

2.3. Crystallographic data collection and structure determination

Diffraction data for all compounds were collected on a Bruker Smart APEX II diffractometer equipped with Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation. Diffraction data analysis and reduction were performed within SMART, SAINT, and XPREP [12]. Correction for Lorentz, polarization, and absorption effects were performed within SADABS [13]. Structures were solved using Patterson method within SHELXS-97 and refined using SHELXL-97 [14–16]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms of phen were calculated at idealized positions and included in the refinement in a riding mode. The H atoms bound to coordinated water molecule were located from difference Fourier maps and refined as riding mode. The crystallographic data and experimental detail for structural analysis are summarized in Tables 1 and 2.

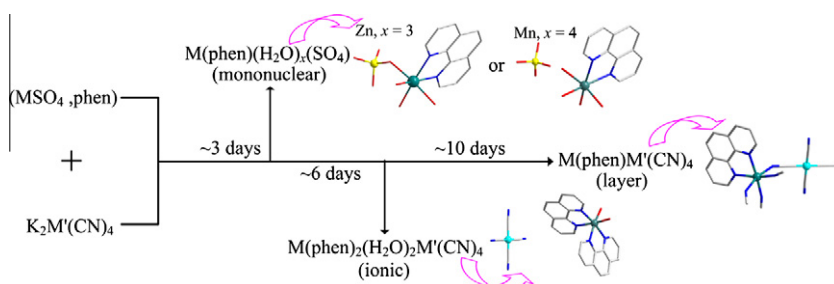
3. Results and discussion

The solution chemistry in our case may be roughly elucidated as shown in Scheme 1, taking the Zn-phen-Ni(CN)₄ system as an example. The generation of time-dependent products can be explained reasonably in terms of the setup, the concentration gradients and stoichiometries. The self-assembly between Zn^{2+} ions and phen ligands occurred with the dissolution of starting materials ZnSO_4 and phen on the bottom of the small vial, isolating the plate-like cyanometalate-free crystals with mononuclear molecule **1**. The amount of plates gradually increased as the zinc salt and phen dissolved. No precipitates generated in the solution at initial time if the metal chlorides were used instead of the metal sulfates. Although plate-like crystals formed when the metal nitrates were employed, any effort to determine the unit cell was unsuccessful because the crystals were fragile and degraded upon removed from the mother liquid. It should be noted here that the intermediate-time and final products still formed in both cases.

The concentration gradient in the small vial changed upon the slow dissolve and diffusion of the precursor $\text{K}_2[\text{Ni}(\text{CN})_4]$, and at this time the $[\text{Ni}(\text{CN})_4]^{2-}$ units begin to participate in the self-assembly process, accompanied by the single-crystal-to-single-crystal transformation from mononuclear molecule **1** to ion-pair rod-like compound **1a**. Obviously, the $\text{Ni}^{\text{II}}/\text{Zn}^{\text{II}}$ stoichiometry in intermediate-time product **1a** was different from that in **1**. The plates converted exclusively to rods over time, and

Table 2
Crystallographic data and structural refinement for compounds **2**, **2a**, **2b**, **2c**, **2d**, **2e** and **2f**.

Compound	2	2a	2b	2c	2d	2e	2f
Formula	C ₁₂ H ₂₀ N ₂ O ₁₀ SMn	C ₂₈ H ₂₈ N ₈ O ₆ NiMn	C ₂₈ H ₂₈ N ₈ O ₆ PdMn	C ₂₈ H ₂₈ N ₈ O ₆ PtMn	C ₁₆ H ₈ N ₆ NiMn	C ₁₆ H ₈ N ₆ PdMn	C ₁₆ H ₈ N ₆ PtMn
<i>M_r</i>	439.30	686.20	733.93	822.59	397.93	445.62	534.31
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	C2/c	C2/c	C2/c	C2/c	C2/c	C2/c
<i>a</i> (Å)	8.8683(18)	17.099(4)	17.128(2)	17.196(5)	6.672(3)	6.6928(8)	6.6503(9)
<i>b</i> (Å)	18.491(4)	13.711(4)	13.9380(19)	13.882(4)	19.487(7)	19.748(2)	19.904(3)
<i>c</i> (Å)	22.081(4)	14.284(4)	14.401(2)	14.426(4)	11.805(4)	12.0134(14)	12.0716(17)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	90.00	108.126(4)	109.250(2)	108.965(3)	91.736(4)	92.9750(10)	93.229(2)
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00	90.00
<i>V</i> (Å ³)	3620.9(13)	3182.5(14)	3245.8(8)	3256.7(16)	1534.1(10)	1585.7(3)	1595.4(4)
<i>Z</i>	8	4	4	4	4	4	4
ρ (g cm ⁻³)	1.612	1.415	1.485	1.661	1.723	1.867	2.225
μ (mm ⁻¹)	0.898	1.040	0.994	4.729	2.059	1.939	9.559
Total, unique	26475, 3553	12144, 3129	12211, 3181	12413, 3188	6575, 1758	6830, 1829	6814, 1835
Observed [<i>I</i> > 2 σ (<i>I</i>)]	2521	1664	2853	2787	1548	1650	1645
GOF on <i>F</i> ²	1.006	0.930	1.085	1.082	1.087	1.060	1.056
<i>R</i> ₁ , ωR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0344, 0.0745	0.0502, 0.1124	0.0235, 0.0655	0.0186, 0.0430	0.0261, 0.0714	0.0195, 0.0470	0.0139, 0.0339
<i>R</i> ₁ , ωR ₂ (all data)	0.0643, 0.0835	0.1356, 0.1614	0.0277, 0.0677	0.0238, 0.0448	0.0313, 0.0750	0.0243, 0.0492	0.0168, 0.0354



Scheme 1. Time-of-diffusion dependent structural diversity in the M-phen-M'(CN)₄ system.

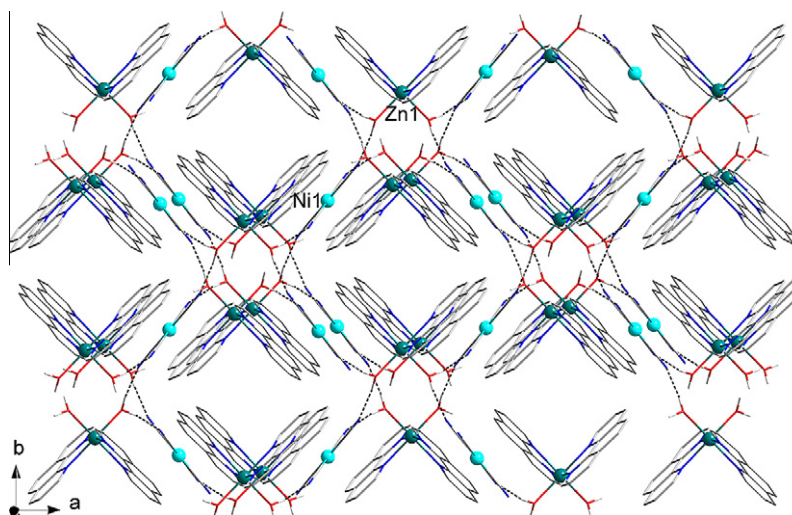


Fig. 1. The 3D supramolecular network constructed through O—H...N hydrogen bonds (black dotted lines) of compound **1a**. Crystallized water molecules and hydrogen atoms of phen ligands were omitted for clarity.

then the Ni^{II}/Zn^{II} concentration ratio further increased upon the continuous diffusion of [Ni(CN)₄]²⁻ units, resulting in the formation of polyhedral crystals with metal cyanide layer **1d** generated on the bottom and the inner wall of the small vial. Similarly, rods transformed exclusively to polyhedrons at the end, indicating that compound **1d** was the most kinetically favored product in the ternary Zn-phen-Ni(CN)₄ system. In fact, powder X-ray diffraction analysis revealed that only final products was obtained if solutions of three starting materials (M²⁺, phen, [M'(CN)₄]²⁻) were simply mixed immediately.

Single-crystal X-ray diffraction analysis revealed that the structure of compounds **1** and **2** has been reported previously and comprised of monomers without any M'(CN)₄ units strongly interlinked by hydrogen bonds, generating a three-dimensional (3D) supramolecular network, in which the M(II) center adopts an octahedral {MN₂O₄} geometry [17–19]. However, the initial-time products **1** and **2** are not isostructural, which can be attributed to the difference of starting material metal sulfates.

The two structure types (**1a–1c** and **2a–2c**) are all isostructural, as are **1d–1f** and **2d–2f**, although the starting materials changed

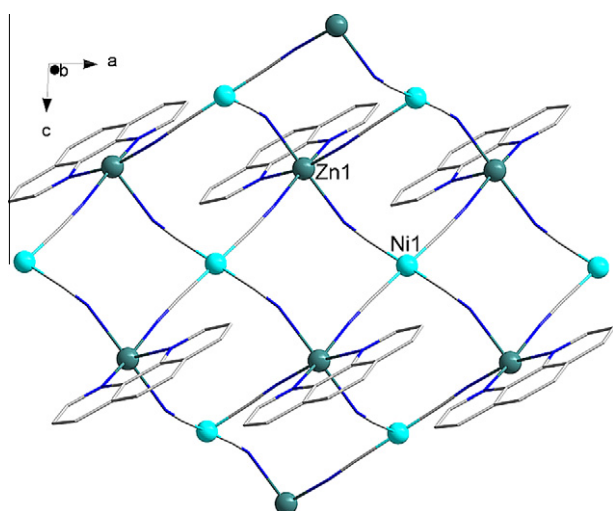


Fig. 2. The metal cyanide layer of compound **1d**. Hydrogen atoms were omitted for clarity.

upon altering Zn for Mn, and Ni for Pd for Pt. For the ionic compounds **1a**, **1b**, **1c**, **2a**, **2b** and **2c**, the structure consists of cation $[M(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$ and anion $[M'(\text{CN})_4]^{2-}$ units, which are linked through the O–H \cdots N hydrogen bonds (O1–H1A \cdots N5ⁱⁱⁱ and O1–H1B \cdots N1 for compound **1a**, symmetry code: (iii) $-0.5-x$, $0.5+y$, $0.5-z$), forming a 3D supramolecular network (Fig. 1). The M(II) center was coordinated by four nitrogen atoms of two phen ligands and two water molecules, exhibiting an octahedral $\{\text{MN}_6\}$ geometry.

In the structure of isostructural compounds **1d**, **1e**, **1f**, **2d**, **2e** and **2f**, the M(II) center exhibits an octahedron $\{\text{MN}_6\}$ geometry, where the equatorial sites are occupied by four nitrogen atoms from one phen ligand and two bridging cyano groups, and other two bridging cyano-nitrogen atoms are in the axial positions. As a result, the M(II) and M'(II) centers are linked alternatively through cyano groups to form metal cyanide layers, where phen ligands are located in both sides of the sheets (Fig. 2). Adjacent layers are further packed through π – π interactions (face–face distance of 3.299 Å) of the phen aromatic rings into a 3D supramolecular network and no hydrogen bonds or other weak interactions were found.

4. Conclusion

In summary, three series of supramolecular assemblies were crystallized from one-pot reaction at different periods in the M(II)–phen–M'(CN)₄ system, and a time-of-diffusion structural

transformation occurred. In addition, the presence of chelated ligand has played a crucial role in the construction of low-dimensional cyanide-based systems. The studies on this line are underway.

Supplementary material

CCDC numbers: 897783 (**1**), 897784 (**1a**), 897785 (**1b**), 897786 (**1c**), 897787 (**1d**), 897788 (**1e**), 897789 (**1f**), 897790 (**2**), 897791 (**2a**), 897792 (**2b**), 897793 (**2c**), 897794 (**2d**), 897795 (**2e**) and 897796 (**2f**). This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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