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Role of 4,4'-bipyridine versus longer spacers 4,4'-azobipyridine, 1,4-bis(4-pyridyl)ethylene, and 1,2-bis(pyridin-3-ylmethylene)hydrazine in the formation of thermally labile metallophosphate coordination polymers

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One dimensional metallophosphate coordination polymers $\{[M(dtbp)_2(azopy)(H_2O)_2]\cdot(azopy)\}_x$ (M = Mn (**1**); Co (**2**); Cu (**3**); Cd (**4**)) have been synthesized from the reaction of a suitable metal precursor with di-*tert*-butylphosphate (dtbp-H) in the presence of ditopic linker 4,4′-azobipyridine (azopy) in a 1:2:2 stoichiometric ratio. Isostructural compounds **1**-**4** have been characterized by analytical and spectroscopic methods and single crystal X-ray diffraction studies. Single crystal X-ray diffraction measurements further reveal that compounds **1**-**3** (all C2/c) and **4** (P-1) are linear 1D coordination polymers. The uncoordinated 4,4′-azobipyridine in the lattice is responsible for the conversion of these 1D coordination polymers into 3D supramolecular assemblies through O-H···N hydrogen bonding interactions between coordinated water and N-centers of azopy ligand. Similar reactions carried out using 1,4-bis(4-pyridyl)ethylene (bpe) as linker yielded compounds having formula $\{[M(dtbp)_2(bpe)(H_2O)_2]\cdot(bpe)\}_x$ (M = Mn (**5**); Co (**6**); Cu (**7**); Ni (**8**)). Compounds **5**-**8** have been characterized by analytical and spectroscopic methods. Preliminary single crystal X-ray diffraction studies carried out on poorly diffracting crystals of **5** and **6** establish their isostructural nature to **1**-**4**, also displaying similar supramolecular aggregation behaviour. A longer ditopic N,N'-donor ligand, 1,2-bis(pyridin-3-ylmethylene)hydrazine (bph), has been used in place of bpe/azoby to synthesize 1-dimensional coordination polymers $[\{M(bph)(H_2O)_4\}\{(dtbp)_2\}]$ (M = Ni (**9**) and M = Co (**10**)) and $[Cd(bph)_3(dtbp)_2]n$ (**11**) which have completely different structural motifs compared to **1**-**4**.

Introduction

The growing interest in supramolecular chemistry of transition-metal complexes and coordination polymers (CPs) exhibiting different types of network or cage topologies can be traced to potential applications of these materials arising out of solvent-inclusion, gas-adsorption, electronic, or nonlinear optical properties.[1,2] While majority of CPs and metal-organic- frameworks (MOFs) are based on the coordination of multitopic carboxylate ligands with transition metal ions,[3] recent research has established the importance of both phosphonic acids[4,5] and phosphate esters[4] as building blocks for rationally designed CPs and MOFs. Metal phosphates have in particular been studied in much detail as they appear in nature as minerals or as constituents of living animals and also play an important role in energy conversion cycles, apart from being similar to silicates from a structural point of view.[6] The other reasons which have made metallophosphate chemistry very relevant in recent times are their usefulness as models for secondary building units (SBUs) of zeolites[7] and their ability to function as single-source precursors

for the preparation of ceramic materials,[8] apart from the facile structural transformations metal phosphates undergo under mild conditions.[9] Our earlier studies, which were initially directed towards use of di-*tert*-butylphosphate derived one-dimensional coordination polymers $[M(dtbp)_2]_n$ as ceramic precursors for $M(PO_3)_2$,[8] have been later extended to studies on structural transformations effecting facile dimensionality changes at room temperature. For example, $[M(dtbp)_2]_n$ (M = Mn, Co, Cu, Cd) can readily be transformed to two-dimensional grid structures by the addition of 4,4-bipyridine at room temperature as schematically depicted in Scheme 1.[9] Subsequently, a variety of supra-molecular structures and coordination polymers exhibiting different types of network topologies have been prepared in our laboratory to understand the formation of these superstructures and the dimensionality changes.[10,11] In order to probe whether other types of CPs can be formed by dtbp ligand in the presence of other ditopic spacers, we have employed in the present study not only longer but also functional ditopic N-donor spacers 4,4'-azobipyridine (azopy), 1,4-bis(4-pyridyl)ethylene (bpe) and 1,2-bis(pyridin-3-
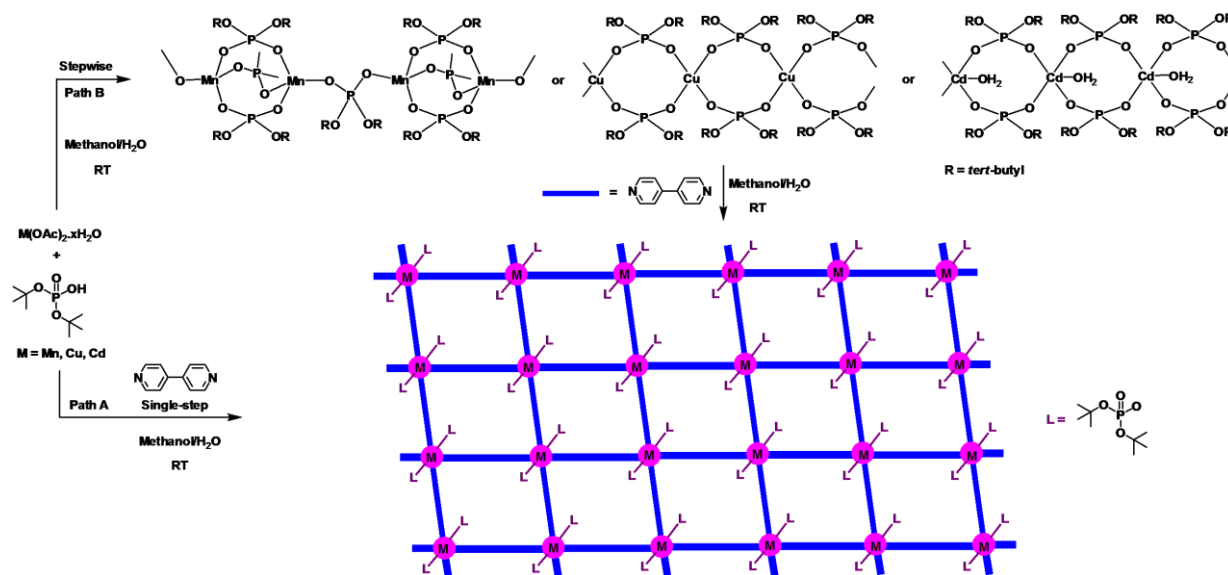
Scheme 1 One-pot (path A) and stepwise (path B) synthesis of two-dimensional 4,4'-bipyridine derived metallophosphate polymers $[M(dtbp)_2(bpy)_2]_x$ exhibiting a grid architecture.

ylmethylene)hydrazine (bph) to prepare newer metallophosphate coordination polymers exhibiting completely different supramolecular aggregation compared to those observed for 4,4'-bipyridine.[9]

Results and discussion

A. Synthesis and characterization of coordination polymers 1-4 using 4,4'-azobipyridine. Metallophosphates of the formula $\{[M(dtbp)_2(azopy)(H_2O)_2]\cdot(azopy)\}_x$ (M = Mn (**1**); Co (**2**); Cu (**3**); Cd (**4**)) have been synthesized by the reaction of metal acetates or perchlorates with dtbp-H and azopy in methanol and DMF (Scheme 2). Alternatively the compounds can also synthesized from the dtbp polymers $[M(dtbp)_2]_n$ by mixing azopy at room temperature. The products, that are air and moisture stable and soluble in polar organic solvents, have been characterized by elemental analysis, FT-IR, UV-Vis, NMR and EPR spectroscopy and TG-DTA analysis.
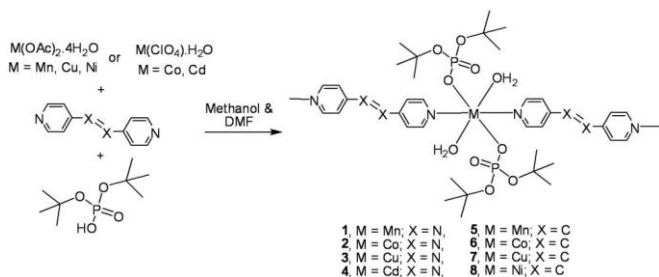
Scheme 2 Synthesis of metallophosphate polymers **1-8**.

Elemental analysis values obtained for **1-4** are consistent with the formula $\{[M(dtbp)_2(azopy)(H_2O)_2](azopy)\}$, which has been later verified by single crystal X-ray diffraction studies (vide infra). The FT-IR spectrum of **1** shows characteristic absorptions at 2977, 1184 and 1069 cm^{-1} corresponding to the $\nu_{asy(C-H)}$, $\nu_{(P-O-O)}$ and ν_{M-O-P} vibrations. The presence of a broad ν_{O-H} absorption at 3388 cm^{-1} is indicative of the presence of water either in the coordination sphere of the metal or in the lattice. The FT-IR spectra of **2-4** are similar to that of **1** (Fig. S9-S12). While compounds **1-3** are paramagnetic, the diamagnetic **4** yields a single resonance in the ^{31}P NMR spectrum at

-5.87 ppm indicating the presence of only one type of phosphorus in the complex (Fig. 1). The ^{1}H NMR spectrum of **4** shows well seperated peaks for the protons of azopy and dtbp ligands (Fig. 2). Two doublets appearing at 7.91 and 8.85 ppm correspond to the C-H protons of the azopy ligand. The *tert*-butyl protons of dtbp appear as a singlet at 1.38 ppm.
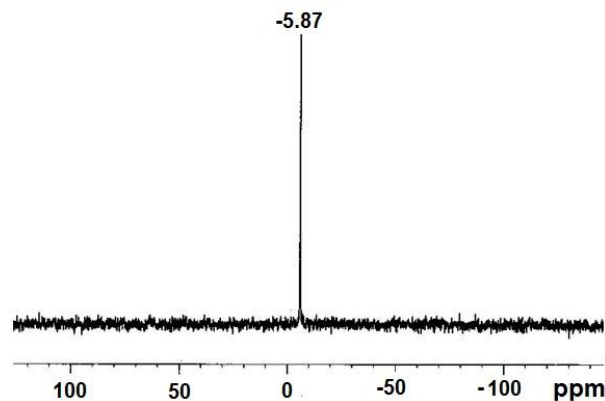

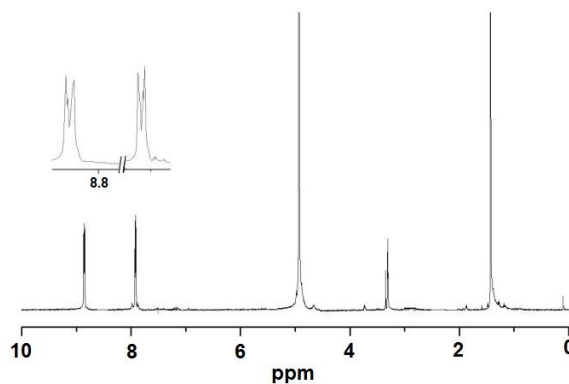**Fig. 1** ^{31}P NMR spectrum of **4** in CD$_3$OD.

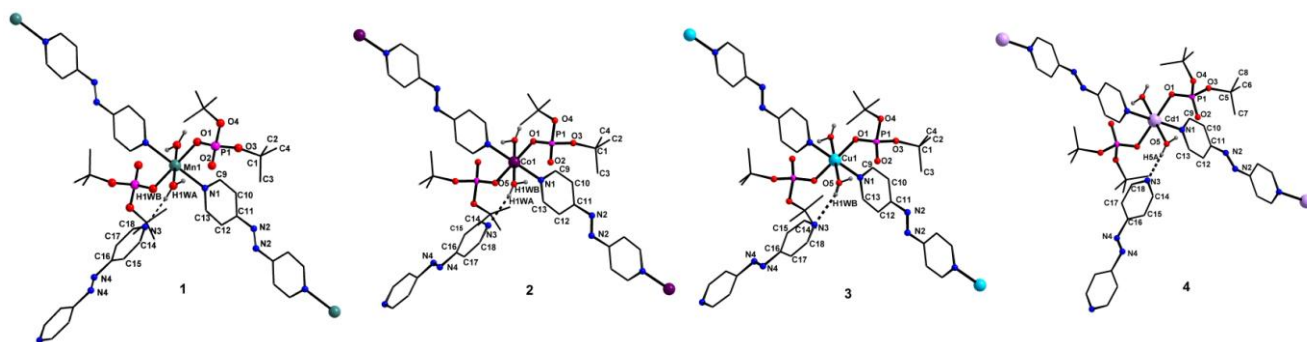**Fig. 2** ^{1}H NMR spectrum of **4** in CD$_3$OD.

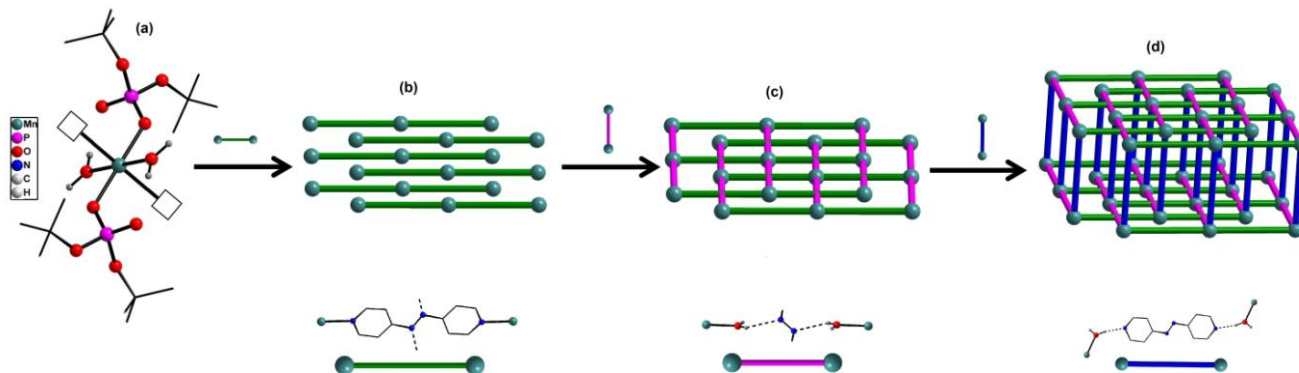**Fig. 3** Repeating units in the molecular structure of compounds **1-4**.

Fig. 4 Evolution of a 3-D framework structure in compounds **1-4** through coordination and hydrogen bonding interactions.

Molecular structures of 1-4. Isomorphous compounds **1-3** crystallize in the monoclinic *C2/c* space group. Cadmium phosphate **4**, which crystallizes in triclinic P-1 space group, is also isostructural to compounds **1-3**. The coordination environment around the central metal ion for compounds **1-4** is shown in Fig. 3. Selected structural parameters for compounds **1-4** are listed in Table 1. The hydrogen bond parameters for **1-4** are given in Table S1. Due to the close resemblance of structures of **1-4**, a detailed description of the structure of compound **1** alone is presented here. The electronic supporting information contains other details. The asymmetric part of the unit cell in **1** contains one manganese ion, two metal bound terminal unidentate dtbp ligands, two coordinated water molecules and two azopy ligands (of which only one is coordinated to the metal and the other remains uncoordinated). Both the azopy ligands are found in trans configuration in all the four crystal structures.

The central manganese adopts a nearly ideal octahedral geometry as shown in Fig. 3 as can been seen from the bond angles listed in Table 1. The M-N, M-OH$_2$, and M-OP distances found for compounds **1-4** are very similar those observed other metal phosphate complexes that have similar set of ligands, especially those with the grid framework structures formed by dtbp ligand.[7] It is of interest to examine in detail the formation of the final framework in the structure of **1**. For a better understanding of the framework formation, the various interactions present within the crystal are hierarchically and pictorially depicted in Fig. 4, making use of final atomic coordinates obtained for the fully refined structure of **1**. As Fig. 4a reveals, two terminal dtbp ligands and two water molecules, in an all *trans* configuration, occupy four of the total six coordination sites around the metal. The remaining two coordination sites are occupied by the nitrogen terminals of two different azopy ligands in a trans fashion, eventually leading to the formation of a linear 1-D polymer as shown in Fig. 4b (the azopy ligands coordinately linking the metals are shown by green rods) (cf. also Fig. S1-S3). It is obvious from Fig. 4b that several such polymers run parallel to each other, with every adjacent polymeric chain displaced from the first by half of the length of the azopy ligand. The next step in the structure evolution of **1-4** is the interaction of water molecules on the metal with the azo (N=N) fragment of the coordinated azopy ligand through O-H⋯N hydrogen bonding (pink linker in Fig. 4c; O5⋯N2 2.981 Å), leading to the formation of a tightly woven 2D sheet (Fig. 4c). Thus the coordinated azobpy ligand uses all its four nitrogen centers to form the 2-D grid structure (Fig. 4 and 5).
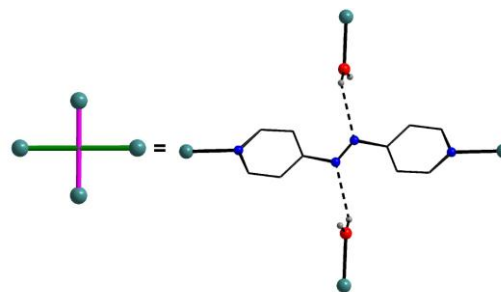
Fig. 5 The role of coordinate azopy ligand in the crystal lattice; two-fold coordination and two-fold H-bond formation.

In the final step, the second molecule of azopy molecule present in the asymmetric part of the unit cell plays a significant role, by engaging itself in hydrogen bonding interaction between the 2-D grid sheets (purple rod) as shown in Fig. 4d. This interaction between the pyridinic nitrogen of uncoordinated azopy and the coordinated water is extremely strong (N(3)⋯H(1WB)-O(5): 2.979 Å, 168.5°), thereby forming a three-dimensional robust framework
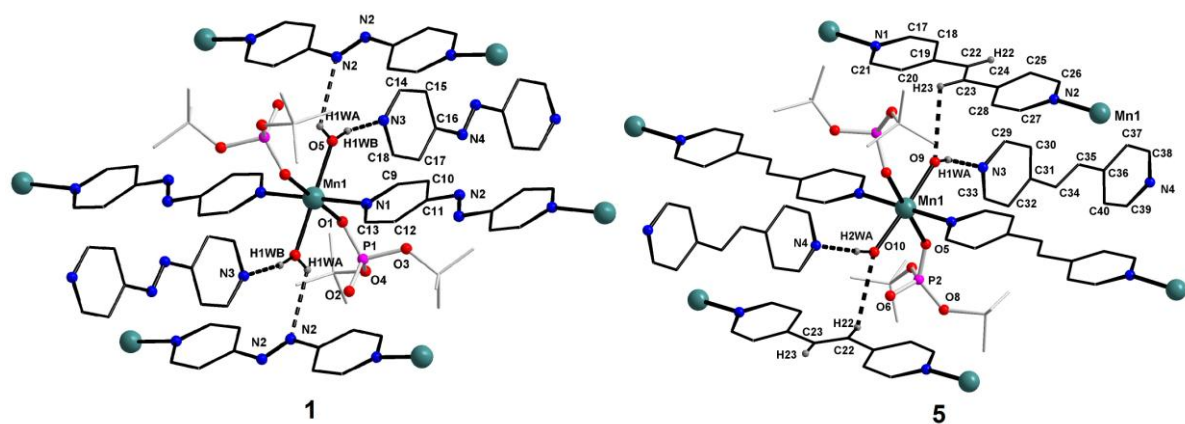
Fig. 6 Difference in the structures and hydrogen-bonding pattern of **1** and **5**.

structure. In addition to the above-described H-bonding interactions that lead to framework building, there are additional intramolecular H-bonding interactions involving phosphate oxygen atoms of dtbp with water hydrogen atoms (not depicted in Fig. 3 or 4) (see also ESI).

B. Synthesis and characterization of coordination polymers 5-8 using 1,4-bis(4-pyridyl)ethylene (bpe) spacer. In terms of end-to-end (N to N) distance, both azopy and bpe ligands are essentially similar. However, it can be anticipated that the replacement of –N=N– central unit by a –CH=CH– unit would bring about significant changes in the hydrogen bonding pattern and hence a different kind of supramolecular aggregation. The reaction of transition metal acetates with dtbp-H was carried out in the presence of ditopic bpe in a 1:2:2 ratio of the reactants in methanol at room temperature. The products obtained analyzed as {[M(dtbp)$_2$(bpe)(H$_2$O)$_2$]·(bpe)}$_x$ (M = Mn (**5**); Co (**6**); Cu (**7**); Ni (**8**)) for the four metals used in this reaction are similar to **1-4** in composition. Compounds **5-8**, which are air and moisture stable and are soluble in polar organic solvents, have been characterized by elemental analysis, FT-IR, TG-DTA analysis, UV-Vis and EPR spectroscopic methods. The IR spectra of **5-8** show broad absorption in the range 3214-3376 cm^{-1} assignable for ν_{O-H} of the coordinated water molecules. Strong absorption bands observed around 1184 and 1071 cm^{-1} are characteristic for $\nu_{(P-O-O)}$ and ν_{M-O-P} vibrations (Fig. S13-S16).

Molecular structures of 5 and 6. Unlike compounds **1-4**, compounds **5-8** do not crystallize well and hence it has been extremely difficult to grow diffraction quality single crystals for these compounds. Hence X-ray diffraction studies were carried out with the best possible crystals for compounds **5** and **6**, while it was not possible to obtain crystals of any quality for **7** and **8**. Compounds **5** and **6** are isomorphous (P2$_1$/c) and are, to a large extent, also isostructural to **1-4**. The major difference between the two classes compounds lies in the hydrogen bonding details. As it is evident from Fig. 6, although the overall framework structure observed in **1** is also maintained in **5**, the coordinated water molecules behave both as hydrogen bond donor (N···H-O) and acceptor (O···C-H). Thus the O-H···N hydrogen bonds in **1** are replaced by O···H-C hydrogen bonds (O9···H23-C23: 2.809 Å) in **5**. This minor difference in hydrogen bonding details however does not change the structure of the overall supramolecular aggregate (Fig. S7).

4,4'-Bipyridine as ditopic spacer versus 4,4'-azobipyridine and 1,4-bis(4-pyridyl)ethylene. In contrast to the formation of a three

dimensional framework structures in **1-8** aided by a combination of both coordination and hydrogen bonding interactions (Fig. 4 and 6), the previously investigated spacer ligand 4,4'-bipyridine produces only a regular two-dimensional grid structure (Fig. 7).[7b,c]

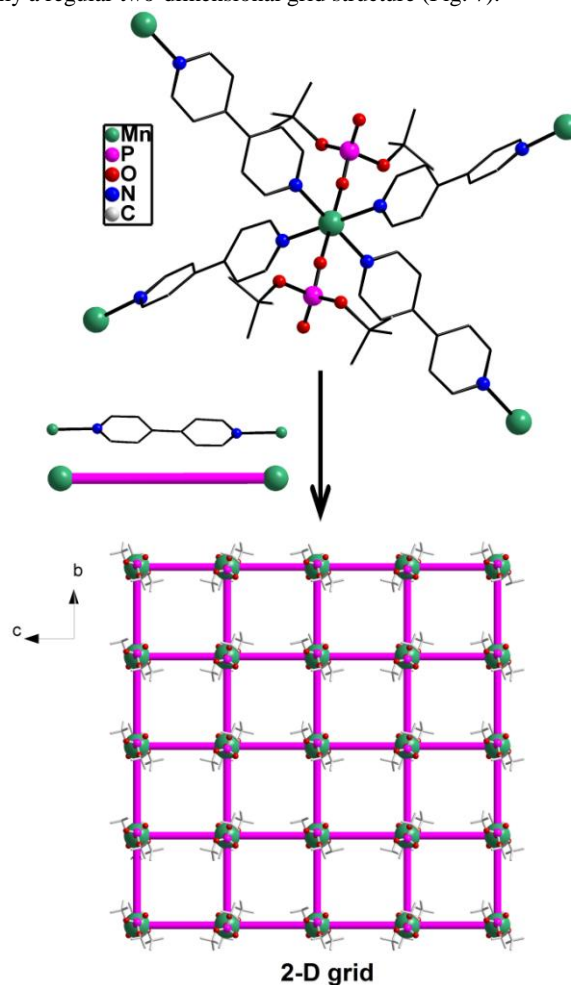**Fig. 7** Formation of 2-D grid structures by orthogonally bound 4,4'-bipyridine ligands in [M(dtbp)$_2$(4,4'-bpy)$_2$]$_n$.

The structure evolution in metal-dtbp-4,4'-bpy complexes [M(dtbp)$_2$(4,4'-bpy)$_2$]$_n$(2H$_2$O)$_n$ depicted in Fig. 7 clearly shows that both the bpy ligands present in the asymmetric part of the unit cell are fully bound to the metal, which in turn does not leave room for

Table 1 Selected structural parameters for compounds **1**-**5**.

Parameters	1 (M = Mn)	2 (M = Co)	3 (M = Cu)	4 (M = Cd)	5 (M = Mn)
M-N, Å	2.313(2)	2.078(4)	2.090(2)	2.3617(18)	2.239(12), 2.297(11)
M-O (P), Å	2.1136(18)	1.938(3)	1.931(2)	2.2504(15)	2.136(8), 2.143(6)
M-OH$_2$, Å	2.1882(19)	2.406(4)	2.406(2)	2.2931(15)	2.167(6), 2.186(7)
H$_2$O-M-OH$_2$, °	180.0	180.0	180.0	180.0	177.0(3)
PO-M-OP, °	180.0	180.0	180.0	180.0	178.6(4)
N-M-N, °	180.0	180.0	180.0	180.0	179.2(4)
O-M-N, °	86.95(7)	92.21(14)	87.70(9)	85.43(6)	91.0(4), 87.7(3)
	93.05(7)	87.79(14)	92.30(9)	94.57(6)	90.3(4), 91.9(4)
	90.29(7)	90.78(13)	90.81(9)	91.33(6)	88.8(4), 92.5(3)
	89.71(7)	89.22(13)	89.19(9)	88.67(6)	90.5(3), 87.3(4)
H$_2$O-M-OP, °	90.29(7)	88.15(14)	91.86(9)	91.69(6)	89.2(3), 90.5(2)
	89.71(7)	91.85(14)	88.14(9)	88.31(6)	92.8(3), 87.6(3)

water to coordinate to the metal. Since the polymer growth along two directions at the metal center is orthogonal, a two-dimensional grid decorated with dtbp ligands above and below the grid plane is the final result. It is important to note here that all the three series of compounds (bpy, azopy, and bpe) were prepared under almost identical conditions starting from one equivalent of metal source, two equivalents of dtbpH ligands, and two equivalents of ditopic spacer ligand.

It is unclear why both the equivalents of 4,4'-bipyridine used in the reaction manage to enter the coordination sphere of the metal in [M(dtbp)$_2$(4,4'-bpy)$_2$]$_n$(2H$_2$O)$_n$ while only one equivalent of azopy or bpe ligand enters the metal coordination sphere in **1**-**4** or **5**-**8**, leaving the second equivalent of azopy or bpe in the lattice. This is mode of coordination in **1**-**8** however provides the required room for two water molecules to enter the metal coordination sphere and complete a 3-D framework structure. The differing roles of 4,4-bipyridine vis-à-vis azopy or bpe can be visualized by comparing the distances between the adjacent metal centers (manganese taken as common example) in the 2-D grid lattice as shown in Fig. 7. Two observations are obvious from this comparison: (1) the insertion of additional two atoms (–N=N– or –CH=CH–) in between the two pyridyl rings results in larger Mn···Mn separation in the structures (case of **1** and **5**); (2) the presence of a water molecule between the ditopic spacer and metal along one of the two grid axes results in unequal Mn…Mn separations along the two directions (13.647 and 17.510 Å). Due to these reasons, a M$_4$ fragment of [M(dtbp)$_2$(4,4'-bpy)$_2$]$_n$ appears to be nearly a square in Fig. 8, while those of **1** and **5** appear to be a distorted rectangle.
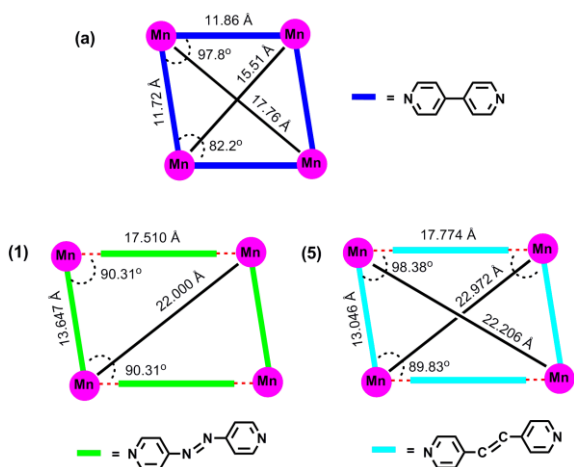

Fig. 8 Comparison of the molecular structure of [Mn(dtbp)$_2$(bpy)$_2$](H$_2$O)$_2$ with [Mn(dtbp)$_2$(azopy)(H$_2$O)$_2$](azobpy) (**1**) and [Mn(dtbp)$_2$(bpe)(H$_2$O)$_2$](bpe) (**5**).

One of the original objectives of choosing spacer with azo and ethylene units has been to investigate the resultant products for any photoisomerization (azo group) or photodimerization (ethylene unit), in view of well established photoactive units containing molecules undergoing structural changes (one form to other) by photoirradiation.[12] The incorporation of photoactive azo groups in **1**-**4** and ethylene group in **5**-**8** indeed can offer such possibilities in the present case. However, due to the formation of fairly dense 3-D structures, such processes do not take place in compounds **1**-**8**. Further, from the discussions above, it is clear that the adjacent ethylene groups are not properly aligned for any light induced dimerization reactions to take place in **5**-**8**.

C. Synthesis and characterization of coordination polymers 9-11 using 1,2-bis(pyridin-3-ylmethylene)-hydrazine (bph) spacer. To study the role of the length of N,N'-ditopic donor ligand on the final structures of the coordination polymers isolated, a relatively new spacer ligand that contain a four atom chain in between the two pyridyl ligands, viz. 1,2-bis(pyridin-3-ylmethylene)hydrazine (bph), has been used in place of bpe/azoby ligands described above. One-dimensional coordination polymers [{M(bph)(H$_2$O)$_4$}{(dtbp)$_2$}] (M = Ni (**9**) and M = Co (**10**)) and [Cd(bph)$_3$(dtbp)$_2$]$_n$ (**11**) (Scheme 3) have been isolated as the products from the reaction of the respective metal perchlorate salts with dtbp-H and spacer bph in methalol / DMF medium. The crystals obtained for these compounds are air and moisture stable and are soluble in polar organic solvents such as DMSO.
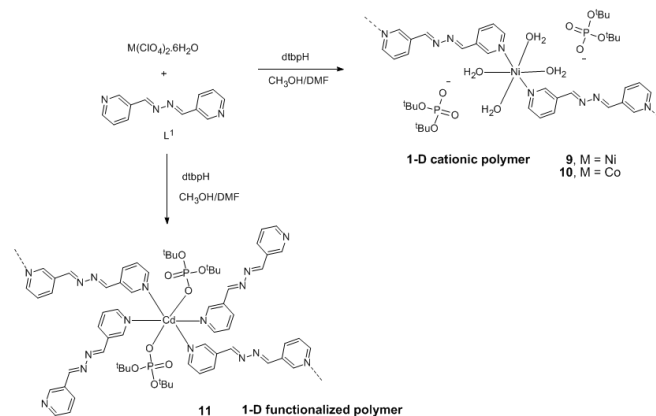
Scheme 3 Synthesis of various types of 1-D coordination polymers **9**-**11**.

Elemental analysis values obtained for **9**-**11** are consistent with the calculated formula, which has later been verified by single

crystal X-ray diffraction studies (vide infra). The FT-IR spectra of **9-11** show characteristic absorptions around 2970, 1190 and 1060 cm^{-1} corresponding to the $\nu_{asy(C-H)}$, $\nu_{(P-O-O)}$ and ν_{M-O-P} vibrations. The presence of a broad ν_{O-H} absorption around 3400 cm^{-1} is indicative of the presence of water either in the coordination sphere of the metal or in the lattice in **10** and **11** (Fig. S17-S19). While compounds **9** and **10** are paramagentic, the diamagnetic **11** yields a single resonance in the ^{31}P NMR spectrum at -6.93 ppm indicating the presence of only one type of phosphorus in the complex (Fig. S8). The ^{1}H NMR spectrum of **11** shows well separated peaks for the protons of L^1 and dtbp ligands in a 4:2 ratio. A doublet and three multiplets appear at 9.034, 8.718, 8.290 and 7.569 ppm correspond to the C-H pyridine protons of the bph ligand and a singlet at 8.794 ppm corresponds to the CH-N protons. The *tert*-butyl protons of dtbp appear as a singlet at 1.33 ppm.

Molecular structures of 9 and 10. Isomorphous compounds **9** and **10** crystallize in the triclinic *P-1* space group. The immediate coordination environment around the central metal ion for compounds **9-10** is shown in Fig. 9. Due to the close resemblance of structures of **9** and **10**, a detailed description of the structure of compound **9** alone is presented here. The asymmetric part of the unit cell in **9** contains one nickel ion, four coordinated water molecules and one bph ligand, apart from the two deprotonated dtbp$^-$ anions in the lattice (Fig. 9). The metal ion adopts distorted octahedral geometry with $-N_2O_4$ coordination environments and metal ion is coordinated by four O-atoms of four water molecules and two N-atoms of two bph.

Another terminal N-atom of bph is linked to other metal ions and leads to the formation of 1-dimentional coordination polymer (Fig. 10).
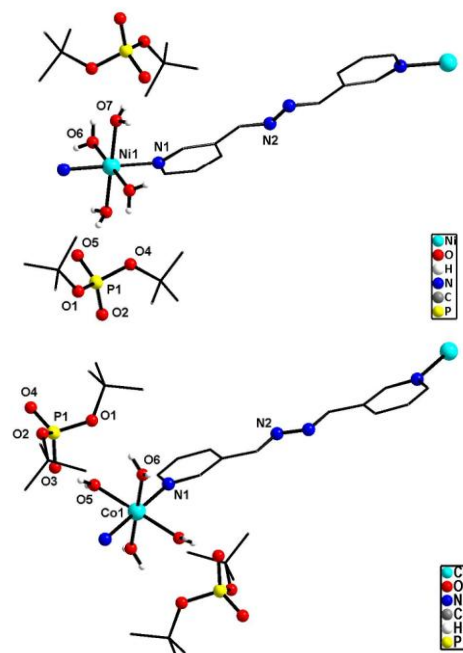

Fig. 9 Repeating units in 1-D polymeric structure of **9** (top) and **10** (bottom) (hydrogen atoms on carbon are omitted for clarity).
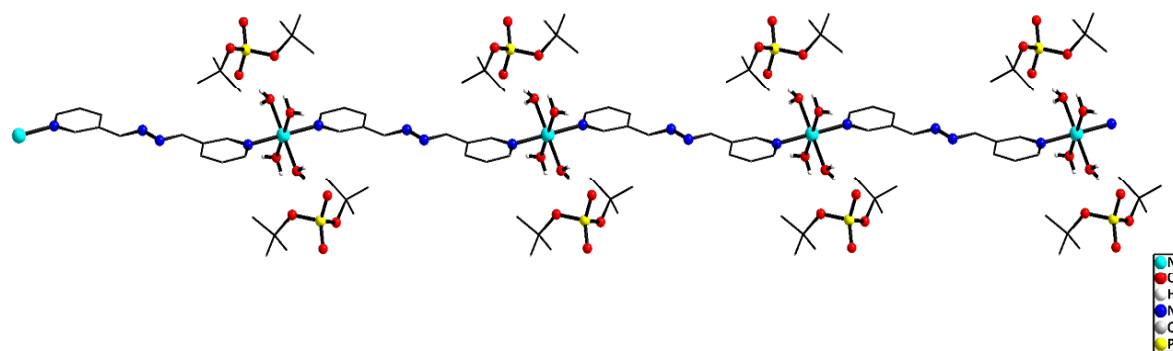

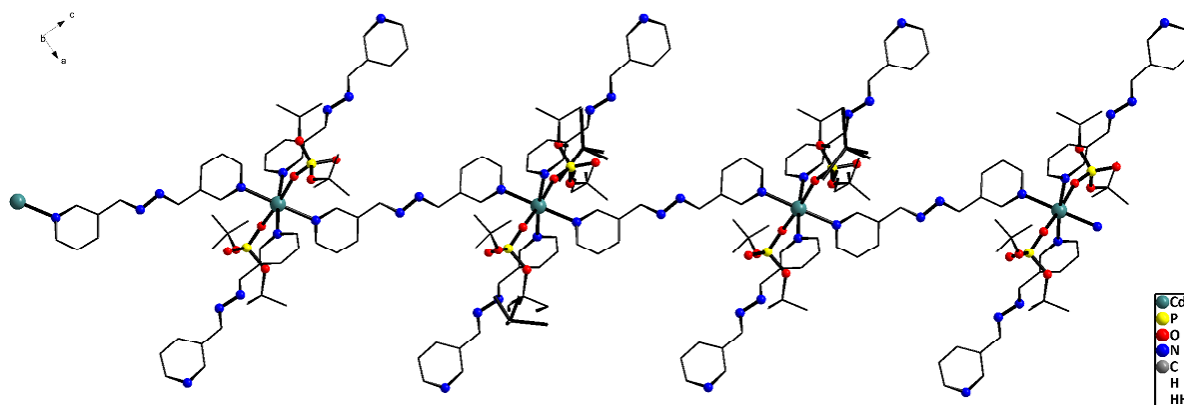**Fig. 10** 1-dimensional polymeric view of **10** (hydrogen atoms on carbon are omitted for clarity).

Fig. 11 1-dimensional polymeric view of **11** (hydrogen atoms are omitted for clarity).

Table 2 Crystal data for compounds **1-5** and **9-11**.

Compound	1	2	3	4	5*	9	10*	11
Formula	$C_{36}H_{56}MnN_8O_{10}P_2$	$C_{36}H_{56}CoN_8O_{10}P_2$	$C_{36}H_{56}CuN_8O_{10}P_2$	$C_{36}H_{56}CdN_8O_{10}P_2$	$C_{40}H_{60}MnN_4O_{10}P_2$	$C_{28}H_{54}N_4NiO_{12}P_2$	$C_{28}H_{44}CoN_4O_{12}P_2$	$C_{52}H_{68}CdN_{12}O_9P_2$
Formula weight	877.77	881.76	886.37	935.23	873.80	759.40	749.54	1179.52
Temperature (K)	293(2)	150(2)	295(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength, (Å)	0.71073	0.71073	1.54178	0.71073	0.71075	0.71075	0.71075	0.71075
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	C2/c	C2/c	C2/c	P-1	P21/c	P-1	P-1	P21/c
a (Å)	29.7719(17)	28.612(5)	28.527	8.7071(3)	14.296(7)	7.026(3)	7.23(2)	9.877(4)
b (Å)	13.6473(6)	13.113(5)	13.224	8.8842(3)	13.946(6)	10.737(5)	11.02(4)	23.870(9)
c (Å)	11.1274(7)	11.789(5)	11.761	14.3210(3)	22.881(11)	13.782(6)	14.09(4)	24.139(9)
α (°)	90	90.000(5)	90	91.155(2)	90	104.485(5)	104.67(4)	--
β (°)	109.043(7)	91.344(5)	91.26	92.669(2)	93.456(8)	96.215(8)	96.20(2)	97.363(9)
γ (°)	90	90.000(5)	90	102.119(2)	90	103.909(3)	104.44(7)	--
Volume (Å³)	4273.7(4)	4422(3)	4435.7	1081.44(6)	4554(4)	961.3(7)	1033(6)	5644(4)
Z	4	4	4	1	4	1	1	4
D(calcd), Mg/m³	1.364	1.324	1.327	1.436	1.275	1.312	1.205	1.388
Cryst. size, mm³	0.2 x 0.2 x 0.2	0.24 x 0.22 x 0.17	0.38 x 0.22 x 0.12	0.31 x 0.28 x 0.23	0.20 x 0.09 x 0.04	0.04 x 0.12 x 0.24	0.12 x 0.21 x 0.32	0.08 x 0.21 x 0.32
abs coeff, mm⁻¹	0.447	0.521	1.904	0.641	0.416	0.646	0.547	0.508
Data/restraints/parameters	3753 / 3 / 259	3882 / 15 / 274	4460 / 69 / 298	3801 / 0 / 265	7966 / 113 / 514	3351/ 2/ 227	3519/ 0/ 214	9350/ 0/ 685
Goodness-of-fit on F^2	0.946	0.997	1.010	1.080	1.064	1.259	1.366	1.047
R_1 [$I>2\sigma(I)$]	0.0474	0.0754	0.0800	0.0234	0.1636	0.0372	0.1067	0.0750
R_2 [$I>2\sigma(I)$]	0.1265	0.2169	0.2314	0.0617	0.3587	0.1286	0.3254	0.1957

* Poor quality crystals-repeated attempts failed to improve the diffraction quality (R_1 [$I>2\sigma(I)$] = 0.1636 (**5**) and 0.1067 (**10**).

Four equatorial coordination sites of metal ions are coordinated by water molecules through O-atoms (Ni1-O6: 2.070(2) and Ni-O7: 2.061(2) Å) and remaining two axial sites are coordinated by bph through N-atoms (Ni1-N1: 2.095(2) Å). Two deprotonated dtbp units are sitting in lattice through strong hydrogen bonding with the coordinated water molecules (O6-H6B···O1: 2.16(4) and O7-H7D···O5: 1.88(3) Å). The distance between P and O atoms (P1-O5: 1.503(2) and P1-O2: 1.487(2) Å) reveals that the deprotonated oxygen exhibits strong hydrogen bonding interactions with water molecules. Selected bond lengths and angles of **9** and **10** are given Table S9 and S10.

Molcular structure of 11. Green crystals of **11** have been obtained from the reaction mixture containing methanol and dimethylformamide solvents at 25° C after standing for several days. Compound **11** crystallizes in the monoclinic P21/c space group. Asymmetric unit of **11** contains a cadmium metal ion, three Schiff base ligands (bph) , two dtbp molecules. A water molecule is present in the lattice. Central cadmium ion adopts distorted octahedral geometry with –N4O2 coordination environment, coordinated by four N-atoms of four different bph ligands and two oxygen atoms of deprotonated two dtbp molecules. Two of the four bph ligands at each metal bridge metal ions at the other end, leading to the formation of 1-dimensional polymer (Fig. 11). Two of the bph ligands surprisingly remain unidentate at each metal. The presence of these free N-donor sites along the length of the polymer may find valuable use in supporting other metal ions which are catalytically active, e.g. palladium or rhodium ions. The Cd-N distances (Cd1-N9: 2.354(5), Cd1-N1: 2.432(5) and Cd1-N5: 2.427(5) Å) are very similar and consistent with values found in complex **4**. The M-O distance between metal ions and two dtbp molecules are same (Cd1-O1: 2.253(5) and Cd1-05: 2.242(5) Å). A water molecule is present in the lattice through strong hydrogen bonding with P=O units of two adjacent molecules (O2···H17A-O17: 2.003(2) Å). Other bond lengths and angles of **11** are listed in Table S11.

D. Thermal studies. The presence of highly thermally labile dtbp groups on the framework structures **1-8** prompted a detailed

investigation of their thermal decomposition behavior (see ESI; Fig. S20-S30). The thermo gravimetric analysis of **1** reveals that the first weight loss observed in the range of 85-130 °C (9.5 %) corresponds to the loss of two H_2O molecules. The second major weight loss beyond 130 °C corresponds to the loss of four isobutene and two azopy moieties in succession to result in the formation of $Mn(PO_3)_2$ (Fig. S20). Similarly, the TGA of **3** reveals the first weight loss of 4% in the temperature range 100-135°C for the loss of coordinated H_2O molecules. The second major weight loss occurring until 205 °C corresponds to the loss of four isobutene molecules while third weight loss which sets in beyond this temperature is responsible for the loss two 4,4'- azobipyridine moiety to yield $Cu(PO_3)_2$ after a further water loss. The TGA data for all complexes are listed in the Table S2. Similarly, TGA of **9** and **10** reveal that the first weight loss occur around 100-135 °C due to the loss of coordinated H_2O molecules. The weight loss in the range of 150-300 °C corresponds to the loss of organic groups in **9-11** (Fig. 12).
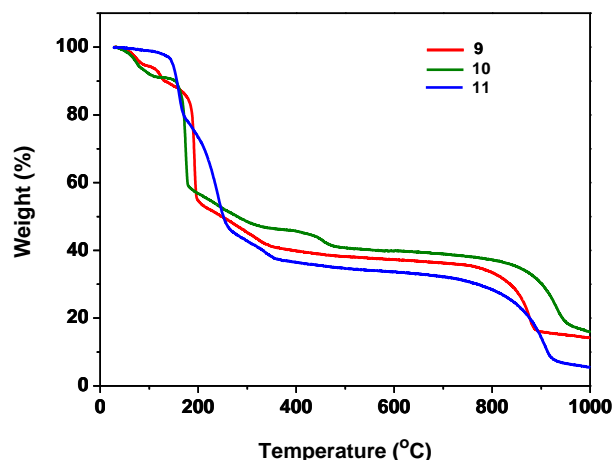

Fig. 12 TGA curve for compound **9-11** (N_2, 10 °C/min).

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Experimental Section

Materials and Methods. Commercial grade solvents have been purified by employing conventional procedures and distilled prior to their use. Starting materials such as Mn(OAc)$_2$·4H$_2$O (E.Merck), Cu(OAc)$_2$·H$_2$O (E.Merck), Cd(ClO$_4$)$_2$·H$_2$O (Aldrich), 4-aminopyridine (Aldrich), Ni(OAc)$_2$·6H$_2$O (E.Merck), 1,4-bis(4-pyridyl)ethylene (bpe) (Aldrich) and Co(OAc)$_2$·4H$_2$O(Aldrich) used have been purchased from commercial sources and used without any further purification. 4,4'-Azobipyridine (azopy) has been synthesized from 4-aminopyridine and 1,2-bis(pyridin-3-ylmethylene)hydrazine following previously reported methods.[13]

Elemental analyses have been performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer at IIT-Bombay. Infrared spectra have been recorded on a Perkin Elmer FT-IR spectrometer as KBr diluted discs. The ^{1}H and ^{31}P NMR spectra are obtained on a Bruker AS 300 and Varian 400S spectrometers using Me$_4$Si (external) as a reference for ^{1}H NMR and 85 % H$_3$PO$_4$ (external) as a reference for ^{31}P NMR spectral measurements. UV-vis spectra are obtained on Shimdzu UV-260 and UV-160A spectrophotometers. The EPR measurements have been performed on a Varian 109C E-line X-band EPR spectrometer fitted with a quartz Dewar for measurements at 77 K. The EPR spectra have been calibrated using tetracyanoethylene (tcne). Thermal analyses have been carried out on a Perkin Elmer Pyris Diamond thermal analysis system.

Synthesis of 1. To a methanol solution (30 mL) of dtbp-H (0.105 g, 0.5 mmol) and Mn(CH$_3$COO)$_2$·4H$_2$O, (0.030 g, 0.125 mmol), a N,N-dimethylformamide solution (2 mL) of azopy (0.092 g, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for 24h. The clear solution was obtained by filtration and kept for crystallization at room temperature. Brown single crystals of **1** were obtained after 4 days. M.p. 120 ºC. Yield 0.18 g (42 % based on dtbp-H). IR data (KBr, cm^{-1}): 3388(br), 2977(m), 2928(m), 1590(w), 1415(s), 1184(m), 1069(s), 982(m), 852(w). Anal. Calcd. for C$_{36}$H$_{56}$MnN$_8$O$_{10}$P$_2$ (%): C, 49.26, H 6.43, N 12.77. Found. C 48.7, H 6.5, N 11.6. TGA [temp range, ºC (% weight loss)]: 85-130 (9.5, -H$_2$O); 131-230 (68, -isobutene, - azobipyridine).

Synthesis of 2. To a methanol solution (10 mL) of [Co(dtbp)$_2$]$_n$ (0.091 g, 0.189 mmol), DMF solution (5 mL) of 4,4'-azobipyridine (0.0695 g, 0.378 mmol) was added and heated at reflux for 12 h. The resulting solution was filtered and kept for crystallization at room temperature. Single crystals of **2** were obtained after 72 h. M.p. > 250 ºC. Yield 0.11 g (35 % based on azopy). IR data (as KBr dics, cm^{-1}): 3410(br), 2980(s), 1595(br), 1415(s), 1365(m), 1182(w), 1066(vs), 983(vs), 852(s), 709(w). Anal. Calcd. for C$_{36}$H$_{52}$CoN$_8$O$_8$P$_2$ (%): C, 51.1, H 6.2, N 13.25. Found. C 49.7, H 6.2, N 13.52. TGA [temp range, ºC (% weight loss)]; 75-122 (8, -H$_2$O); 122-200 (60, -isobutene); 200-900 (-bpe and -P$_2$O$_5$).

Synthesis of 3. To a methanol solution (30 mL) of dtbp-H (0.105 g, 0.5 mmol) and Cu(CH$_3$COO)$_2$·H$_2$O (0.0515 g, 0.25 mmol), a N,N-dimethylformamide solution (2 mL) of azobpy (0.092 g, 0.5 mmol) was added. The reaction mixture was stirred for 12 h and heated in water bath till dryness. The green colored residue obtained was dissolved in 30 mL acetonitrile and left for crystallization at room temperature. Light yellowish green single crystals of **3** were obtained after 2 days. M.p. 130 ºC. Yield 0.19 g (40 % based on azopy). IR data (as KBr disc, cm^{-1}): 3466(br), 2978(m), 1598(w), 1417(m), 1187(m), 1066(s), 1013(w), 979(m), 850(w). Anal. Calcd. for C$_{40}$H$_{68}$CuN$_8$O$_{12}$P$_2$ (%): C, 49.10, H 7.00, N 11.45. Found. C 51.2, H 6.5, N 10.04. TGA [temp range, ºC (% weight loss)]; 131 (7.0, -H$_2$O); 131-800 (73, -isobutene, -azopy).

Synthesis of 4. To a methanol solution (10 mL) of Cd(ClO$_4$)$_2$.H$_2$O (0.0374 g, 0.122 mmol), DMF solution (5 mL) of azopy (0.0372 g, 0.244 mmol) and dtbp-H (0.0448 g, 0.244 mmol) was added. The reaction mixture was heated at reflux for 12 h. The resulting solution was filtered and kept for crystallization at room temperature. Crystals of **4** were obtained after 72 h. M.p. > 250 ºC. Yield 0.073 g (40 % based on 4,4'-azobipyridine). IR data (as KBr dics, cm^{-1}): 3390(br), 2976(m), 1597(m), 1415(m), 1364(m), 1184(w), 1067(vs), 979(vs), 853(m), 715(w). Anal. Calcd for C$_{36}$H$_{54}$CdN$_8$O$_9$P$_2$ (%): C, 47.12, H 5.93, N 12.26. Found. C 46.10, H 5.89, N 12.15. ^{1}H NMR (CD$_3$OD, 400 MHz, ppm): δ 1.38 (s, 36H, ^{t}Bu), 7.91 (dd, 4H, C$_3$H, C$_3$'H, $^2J_{HH}$ = 3 Hz), 8.85 (dd, C$_4$H, C$_4$'H, $^2J_{HH}$ = 4 Hz). ^{31}P NMR (CD$_3$OD, 160 MHz, ppm): δ -5.87 ppm. TGA [temp range, ºC (% weight loss)]; 80-136 (10, -H$_2$O); 136-203 (55, -isobutene); 203-900 (-bpe and -P$_2$O$_5$).

General procedure for 5-8. To a methanolic solution (10 mL) of dtbp-H (0.2 mmol, 0.042 g), 0.1 mmol of M(OAc)$_2$.nH$_2$O (M =Mn/Co/Cu/Ni) was added and stirred for 30 minutes. To this reaction mixture, methanol solution (5 mL) of bpe (0.2 mmol, 0.0364 g) was added and stirred for 3 h at room temperature. The clear solution obtained by filtration on crystallization yielded **5-8**.

Synthesis of 5. M.p. 200 ºC. Yield 0.0733 g (84 % based on dtbp-H). IR data (KBr, cm^{-1}): 3390(br), 2976(m), 1605(s), 1424(m), 1184(s), 1073(vs), 980(m), 828(w). Anal. Calcd. for C$_{40}$H$_{60}$MnN$_4$O$_{10}$P$_2$ (%): C, 54.9, H 6.9, N 6.4. Found. C 55.1, H 7.1, N 6.0. TGA [temp range, ºC (% weight loss)]; 80-150 (5, -H$_2$O); 150-232 (58, -isobutene, -bpe); 232-472 (6,-azopy); 472-950 (10,azopy); 850-1027 (-P$_2$O$_5$).

Synthesis of 6. M.p. 230 ºC. Yield 0.069 g (80 % based on dtbp-H). IR data (KBr, cm^{-1}): 3376(br), 2972(m), 1604(s), 1424(m), 1186(s), 1071(vs), 979(m), 828(w). Anal. Calcd. for C$_{40}$H$_{60}$CoN$_4$O$_{10}$P$_2$ (%): C, 54.7, H 6.9, N 6.7. Found. C 54.7, H 7.1, N 7.1. TGA [temp range, ºC (% weight loss)]; 75-150 (8, -H$_2$O); 150-225 (44, -isobutene); 225-450 (6, -azoby), 450-940 (-bpe and -P$_2$O$_5$).

Synthesis of 7. M.p. 211 ºC. Yield 0.074 g (85 % based on dtbp-H). IR data (KBr): 3399(br), 2977(m), 1612(s), 1433(m), 1252(m), 1186(s), 1074(vs), 974(s), 834(s). Anal. Calcd. for C$_{40}$H$_{60}$CuN$_4$O$_{10}$P$_2$ (%): C, 54.4, H 6.8, N 6.3. Found. C 54.44, H 6.75, N 6.34. TGA [temp range, ºC (% weight loss)]; 55-170 (8, -H$_2$O); 170-220 (25, -isobutene); 220-455 (20,-isobutene and bpe); 450-900 (-P$_2$O$_5$).

Synthesis of 8. M.p. 190 ºC. Yield 0.0067 g (75 % based on dtbp-H). IR data (KBr): 2973(m), 1609(s), 1425(m), 1184(s), 1071(s), 977(s), 829(s). Anal. Calcd. for C$_{40}$H$_{60}$NiN$_4$O$_{10}$P$_2$ (%): C, 54.4, H 6.8, N 6.3. Found. C 53.59, H 6.74, N 5.66. TGA [temp range, ºC (% weight loss)]; 100-149 (10, -H$_2$O and isobutene); 150-350 (50,-isobutene and bpe); 400-800 (-P$_2$O$_5$).

General procedure for 9-11. Methanol solution (20 mL) of metal perchlorate and dtbp-H was stirred for 1h. Ligand bph in DMF (5 mL) was added to that reaction mixture and allowed to stir at 70°C for 10h. The solution was filtered and the clear solution was kept for crystallization at 25°C.

Synthesis of [{Ni(bph)(H$_2$O)$_4$}{(dtbp)$_2$}]$_n$ (9). Green crystals have been obtained from Ni(ClO$_4$)$_2$.4H$_2$O (96 mg, 0.025 mmol), dtbp-H (100 mg, 0.5 mmol) and bph (105 mg, 0.5 mmol). Yield 0.164 g (86 % based on nickel perchlorate). IR data (KBr, cm^{-1}): 3424 (br), 2974(m), 2926(m), 1636(s), 1425(m), 1194(s), 1063(s), 962(s), 827(m). Anal. Calcd. for C$_{28}$H$_{54}$NiN$_4$O$_{12}$P$_2$ (%): C, 44.29, H 7.17, N 7.38. Found. C 44.30, H 8.06, N 7.26. TGA [temp range, ºC (% weight loss)]; 80-100 (7, -2H$_2$O); 100-165 (8, -2H$_2$O); 165-400 (46, L^1 and isobutene); 400-900 (-P$_2$O$_5$).

Synthesis of [{Co(bph)(H$_2$O)$_4$}{(dtbp)$_2$}]$_n$ (10). Purple crystals of **10** have been obtained from Co(ClO$_4$)$_2$.4H$_2$O (96 mg,

0.025 mmol), dtbp-H (100 mg, 0.5 mmol) and bph (105 mg, 0.5 mmol). Yield 0.147 g (56 % based on cobalt perchlorate). IR data (KBr, cm^{-1}): 3424 (br), 2974(m), 2930(m), 1636(s), 1424(m), 1191(s), 1063(w), 965(m), 828(m). Anal. Calcd. for C$_{28}$H$_{54}$CoN$_4$O$_{12}$P$_2$ (%): C, 44.27, H 7.17, N 7.38. Found. C 44.30, H 8.06, N 7.26. TGA [temp range, ºC (% weight loss)]; 80-145 (10, H$_2$O); 145-181 (30, - isobutene); 181-600 (20, L^1); 600-950 (-P$_2$O$_5$).

Synthesis of [Cd(bph)$_3$(dtbp)$_2$]$_n$ (11). Yellow crystals have been obtained from Cd(ClO$_4$)$_2$.6H$_2$O (102 mg, 0.025 mmol), dtbp-H (100 mg, 0.5 mmol) and bph (105 mg, 0.5 mmol). Yield 0.169 g (58 % based on metal perchlorate). IR data (KBr, cm^{-1}): 3400 (br), 2976(m), 2931(m), 1629(s), 1419(m), 1188(s), 1076(s), 973(s), 827(m). Anal. Calcd. for C$_{52}$H$_{66}$CdN$_{12}$O$_8$P$_2$ (%): C, 53.77, H 5.73, N 14.47. Found. C 53.34, H 5.87, N 13.91. ^{1}H NMR (DMSO-d_6, 500 MHz, ppm): δ 9.03 (d, J = 1 Hz, 2H, H^1, pyridine), 8.79 (s, 2H, H^5, CH=N), 8.71 (m, 2H, H^4, pyridine), 8.29 (m, 2H, H^3, pyridine), 7.56 (m, 2H, H^2, pyridine) and 1.33 (s, 9H, C(CH$_3$)$_3$). ^{31}P NMR (DMSO-d_6, 202 MHz, ppm): δ -6.93 ppm. TGA [temp range, ºC (% weight loss)]; 140-260 (50, -isobutene); 240-600 (21, L^1); 600-920 (-P$_2$O$_5$).

Crystal structure determination. A suitable crystal of **1** was mounted on a Oxford Xcalibur diffractometer equipped with Sapphire-III CCD camera for unit cell determination and three dimensional intensity data collection. Data integration and indexing using CrysAlisPro[14] followed by structure solution using SIR 92[15] and refinement using Shelxl-97[16] resulted in the complete structure determination of **1.** The final refinement converged at R value of 0.0474 (I>2σ(I)). A similar procedure on suitably selected crystal of **2** mounted on the same diffractometer yielded the final structure (R = 0.0754 (I>2σ(I)). In the final refinement, a residual electron density near azobipyridine ligand amounting roughly to half of a carbon atom could not be meaningfully assigned. The data collection for **3** was carried out on a Oxford Xcalibur Gemini diffractometer. A residual peak (electron density) near azobipyridine moiety once again could not be assigned. The final refinement converged to R value of 0.080 (I>2σ(I)). A suitable crystal of **4** measured on Oxford Xcalibur diffractometer with Sapphire-III CCD camera yielded a final R value of 0.0234 (I>2σ(I)). Crystallization of the crude product of **5** from methanol at room temperature yields single crystals of **5**. A suitable crystal of size 0.2 x 0.09 x 0.04 mm^3 was mounted on a Rigaku Saturn 724+ CCD diffractometer for unit cell determination and three dimensional intensity data collection. 800 frames in total were collected at 150 K with the exposure time of 20 s per frame. Unit cell determination using both high and low angle reflections reveal that compound **5** crystallizes in monoclinic P2$_1$/c space group. The final refinement of the solved structure converged at the final R value of 0.1636 (I>2σ(I)). Data collection and structure solution for **6** carried out in the same way reveals that it is iso-structural to **5**. However, the structure refinement in this case did not converge or yield good R value. Suitably selected crystals of **9-11** were mounted on Rigaku Saturn 724+ CCD diffractometer yielded the final structure (R$_1$ = 0.0372 for **9**, R$_1$ = 0.1067 for **10** and 0.0750 for **11**). The final coordinates along with the thermal parameters and other refinement details have been deposited as cif file in CCDC. Crystallographic data are listed in Table 2. The selected bond length and angles of **1-6** and **9-11** are listed in Tables S3-S11. PXRD pattern for crystalline samples of **2-6** and **9-11** are included in Fig. S54-S61.

Conclusions

It has been shown in this contribution that both azopy and bpe behave very differently compared to 4,4'-bipyridine in the metallophosphate coordination polymer chemistry involving the

thermally labile diester dtbp-H. The major structural difference in **1-8** is induced by the introduction of two coordinated water molecules around each metal, which in turn forces the second ditopic spacer out of the coordination sphere of the metal. This in turn facilitates very interesting hydrogen bonding interactions, that are often geometrically orthogonal, leading to the formation of an highly periodic 3-D coordination polymeric framework. The use of a longer spacer ligand bph yields one-dimensional coordination polymers which are either cationic or surface N-functionalized. Among these the surface functionalized polymer **11** which contains two free N-donor sites at each repeating unit may served as a useful starting point for building higher dimensional coordination polymers or even loading catalytically active metal ions such as palladium. Further, it is highly likely that other carefully chosen ditopic (and even tritopic) spacers in metal-dtbp chemistry will offer newer forms of coordination polymers which are hitherto unknown. We are currently investigating these possibilities.

Notes and references

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