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H-bonded and metal(II)-organic architectures assembled from an unexplored aromatic tricarboxylic acid: Structural variety and functional properties

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This study reports the application of an aromatic tricarboxylic acid, 2,5-di(4carboxylphenyl)nicotinic acid (H₃dcna) as a versatile and unexplored organic building block for assembling a new series of metal(II) (M = Co, Ni, Zn, Fe, and Mn) complexes and coordination ¹⁰ polymers, namely [M(Hdcna)(phen)₂(H₂O)]·H₂O (M = Co (1), Ni (2)), [Zn(μ -Hdcna)(phen)]_n (3), [Co(μ -Hdcna)(bipy)(H₂O)₂]_n·nH₂O (4), [Zn₂(μ -Hdcna)₂(bipy)₂(H₂O)₄]·6H₂O (5), [Zn(μ ₃-

- Hdcna)(H₂biim)]_n (**6**), $[Ni_2(Hdcna)_2(\mu-bpb)(bpb)_2(H_2O)_4]$ (**7**), $[Fe(\mu_4-Hdcna)(\mu-H_2O)]_n \cdot nH_2O$ (**8**), and $[Mn_3(\mu_5-dcna)_2(bipy)_2(H_2O)_2]_n \cdot 2nH_2O$ (**9**). Such a diversity of products was hydrothermally prepared from the corresponding metal(II) salts, H₃dcna as a principal multifunctional ligand, and
- ¹⁵ N-donor mediators of crystallization (1,10-phenanthroline, phen; 2,2'-bipyridine, bipy; 2,2'-biimidazole, H₂biim; or 1,4-bis(pyrid-4-yl)benzene, bpb). The obtained products 1–9 were fully characterized by standard methods (elemental analysis, FTIR, TGA, PXRD) and the structures were established by single-crystal X-ray diffraction. These vary from the discrete monomers (1, 2) and dimers (5, 7) to the 1D (3, 4, 6) and 2D (8, 9) coordination polymers (CPs). Structural and
- ²⁰ topological characteristics of hydrogen-bonded or metal-organic architectures in **1–9** were highlighted, revealing that their structural multiplicity depends on the type of metal(II) source and crystallization mediator. Thermal stability as well as luminescent, magnetic, or catalytic properties were explored for selected compounds. In particular, the zinc(II) derivatives **3**, **5**, and **6** were applied as efficient heterogeneous catalysts for the cyanosilylation of aldehydes with trimethylsilyl
- 25 cyanide at room temperature. The catalytic reactions were optimized by tuning the different reaction parameters (solvent composition, time, catalyst loading) and the substrate scope was also explored. Compound 5 revealed superior catalytic activity leading to up to 75% product yields, while maintaining its original performance upon recycling for at least four reaction cycles. Finally, the obtained herein products represent the unique examples of coordination compounds derived

³⁰ from H₃dcna, thus opening up the use of this multifunctional tricarboxylic acid for generating complexes and coordination polymers with interesting structures and functional properties.

Introduction

- ³⁵ The design of new first-row transition metal complexes and coordination polymers (CPs) has seen an enormous development in the last two decades.^{1–4} This is principally associated with a fascinating structural diversity of such compounds and their remarkable applications in diverse research fields which, among
- ⁴⁰ many other areas, include gas storage and separation,⁵⁻¹¹ catalysis,^{12–15} luminescence,^{16–21} and magnetism.^{22–25} However, even after years of comprehensive studies and numerous synthetic methodologies developed, it is still not easy to foresee structures of the resulting metal-organic architectures, since a
- ⁴⁵ diversity of factors may impact their synthesis and crystallization. The most common factors include the structural features of principal and supporting organic ligands,^{26–30} coordination requirements of metal ions,^{28,31,32} solvent composition,^{33–36} reaction temperature,^{37–39} and pH value.^{40,41} Among these, the

⁵⁰ type of main ligand represents a particularly interesting variable to modify, allowing the generation of potentially desired products. In this regard, polycarboxylic acids containing several aromatic rings with variable positions of the –COOH functionalities represent one of the most compelling classes of organic ligands,
 ⁵⁵ especially when dealing with the synthesis of new coordination polymers (CPs) or metal-organic frameworks (MOFs). The popularity of such aromatic carboxylic acids as building blocks for generating metal-organic architectures can be explained by their coordination versatility and an ability to act as multiple
 ⁶⁰ linkers, a high thermal stability, a tunable deprotonation of – COOH groups, remarkable physicochemical properties, as well

- as an ability to function as hydrogen bond donors and acceptors thus facilitating the formation of intricate H-bonded networks.^{12,14,28,41-44}
- 65 As an extension of our research on the hydrothermal synthesis of new first-row transition metal CPs and complexes driven by polycarboxylate blocks, herein we have centered our attention on a novel aromatic tricarboxylic acid, namely 2,5-di(4carboxylphenyl)nicotinic acid (H₃dcna, Scheme 1), as an

unexplored building block in coordination chemistry. Hence, the principal goal of the present work has been the exploration of H₃dcna as a multifunctional ligand for the assembly of new metal(II)-organic architectures under hydrothermal conditions, s along with the investigation of their structural features and properties. The selection of H₂dcna can be explained by a number

- properties. The selection of H_3 dcna can be explained by a number of features. (1) It is an organic ligand with three aromatic rings in a linear arrangement that are decorated with three carboxylic acid groups and a pyridyl site. (2) H_3 dcna thus features seven possible
- ¹⁰ sites for coordination, namely six O carboxylate atoms and one N donor of the nicotinate ring. (3) This building block is thermally stable and can be fully or partially deprotonated to produce soluble species under hydrothermal conditions. (4) H₃dcna can function as a multiple hydrogen bond acceptor and/or donor and ¹⁵ support the generation of H-bonded networks. (5) According to a
- search of the Cambridge Structural Database, coordination chemistry of H₃dcna remains unexplored.^{38,45}

Thus, with all this motivation in mind, we report in this work the hydrothermal generation, full characterization, 20 crystal structures, topological and H-bonding features, thermal stability, luminescent, magnetic, and catalytic properties of a new series of nine metal(II)-organic architectures assembled from H₃dcna as a principal ligand in the presence of some N-donor crystallization mediators 25 (Scheme 1). The hydrothermally generated products have been formulated as $[M(Hdcna)(phen)_2(H_2O)] \cdot H_2O$ (M = Co (2)), $[Zn(\mu-Hdcna)(phen)]_n$ (1),Ni (3), [Co(µ-Hdcna)(bipy)(H₂O)₂]_n $\cdot n$ H₂O (4), $[Zn_2(\mu Hdcna)_2(bipy)_2(H_2O)_4] \cdot 6H_2O$ (5), $[Zn(\mu_3-Hdcna)(H_2biim)]_n$ $_{30}$ (6), $[Ni_2(Hdcna)_2(\mu-bpb)(bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)(\mu-bpb)_2(H_2O)_4]$ (7), $[Fe(\mu_4-Hdcna)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bpb)(\mu-bp$ $H_2O)_n \cdot nH_2O$ (8), and $[Mn_3(\mu_5-dcna)_2(bipy)_2(H_2O)_2]_n \cdot 2nH_2O$ (9).

Apart from representing the unique examples of coordination compounds derived from H₃dcna, this study has also explored ³⁵ the thermal stability as well as luminescent, magnetic, or catalytic properties of selected products. In particular, zinc(II) derivatives **3**, **5**, and **6** have been applied as efficient heterogeneous catalysts for the cyanosilylation of aldehydes, including the optimization of different reaction parameters ⁴⁰ and investigation of substrate scope.



Scheme 1 Structures of H₃dcna and N-donor crystallization mediators.

45 Experimental section

General methods

All chemicals and solvents were obtained from commercial suppliers. 2,5-Di(4-carboxylphenyl)nicotinic acid (H₃dcna)

was acquired from Jinan Henghua Sci. & Tec. Co., Ltd. ⁵⁰ C/N/H analyses were run on an Elementar Vario EL elemental analyzer. Bruker EQUINOX 55 spectrometer was used for recording the FTIR spectra (potassium bromide discs). LINSEIS STA PT1600 thermal analyzer was used for thermogravimetric (TGA) measurements (heating rate: 10 ⁵⁵ °C/min; inert N₂ atmosphere). PXRD (powder X-ray diffraction) analyses were carried out on a Rigaku-Dmax 2400 diffractometer (Cu-K α radiation, $\lambda = 1.54060$ Å). Solid-state excitation and emission spectra were measured on an Edinburgh FLS920 fluorescence spectrometer under ambient ⁶⁰ temperature. Magnetic susceptibility data were collected

using a Quantum Design SQUID Magnetometer MPMSXL-7 (2–300 K, field of 0.1 T); diamagnetic contribution correction was performed prior to the analysis of data. Solution ¹H NMR spectra were recorded on a JNM ECS 400M spectrometer.

Synthesis of compounds 1–9

All products were assembled via a hydrothermal synthetic procedure, in which the reaction mixtures of different composition (Table 1) were treated in H₂O at 160 °C for three ⁷⁰ days, followed by a gradual cooling down and crystallization (10 °C per hour). Complete synthetic procedures and analytical data for compounds **1–9** are given in ESI.

 Table 1 Hydrothermal synthesis of 1-9: composition of the reaction mixtures.

Product formula	Metal(II)	Crystalliza-	M ²⁺ /H ₃ dena/
	precursor	tion media-	CM/NaOH
		tor (CM)	molar ratio
[Co(Hdcna)(phen) ₂ (H ₂ O)]·H ₂ O (1)	CoCl ₂ ·6H ₂ O	phen	1/1/1/2
[Ni(Hdcna)(phen) ₂ (H ₂ O)]·H ₂ O (2)	NiCl ₂ ·6H ₂ O	phen	1/1/1/2
$[Zn(\mu-Hdcna)(phen)]_n$ (3)	ZnCl ₂	phen	1/1/1/2
$[Co(\mu-Hdcna)(bipy)(H_2O)_2]_n \cdot nH_2O (4)$	CoCl ₂ ·6H ₂ O	bipy	1/1/1/2
[Zn ₂ (µ-Hdcna) ₂ (bipy) ₂ (H ₂ O) ₄]·6H ₂ O (5)	ZnCl ₂	bipy	1/1/1/2
$[Zn(\mu_3-Hdcna)(H_2biim)]_n$ (6)	ZnCl ₂	H ₂ biim	1/1/1/2
$[Ni_{2}(Hdcna)_{2}(\mu-bpb)(bpb)_{2}(H_{2}O)_{4}]$ (7)	NiCl ₂ ·6H ₂ O	bpb	1/1/1/2
$[Fe(\mu_4-Hdcna)(\mu-H_2O)]_n \cdot nH_2O (8)$	FeSO ₄ ·7H ₂ O	-	1/1/-/2
$[Mn_3(\mu_5-dcna)_2(bipy)_2(H_2O)_2]_n \cdot 2nH_2O$ (9)	MnCl ₂ ·4H ₂ O	bipy	1/0.67/1/2

75 "Synthesis under hydrothermal conditions: stainless steel reactor (Teflon-lined, 25 mL volume), water as solvent (10 mL), 160 °C, 3 days.

Single crystal X-ray diffraction and topological analysis

X-ray data for single crystals of 1–9 were obtained using ⁸⁰ either a Bruker Smart CCD or an Agilent SuperNova diffractometer (graphite-monochromated Mo K_{α} radiation, λ = 0.71073 Å). Semiempirical absorption corrections were performed with SADABS. SHELXS-97 and SHELXL-97⁴⁶ were used for structure solution by direct methods and ⁸⁵ refining by full-matrix least-squares on F^2 . All the non-H atoms were refined anisotropically by full-matrix leastsquares methods on F^2 . All the CH hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations at the ⁹⁰ final stage of full-matrix least-squares refinement. H atoms of H₂O/COOH functionalities were positioned by difference maps and constrained to ride on their parent O atoms. In structures **7–9**, as it was not possible to see clear electron-

density peaks in difference maps which would correspond to acceptable locations for the H atoms of water oxygen O7, the refinement was completed with no allowance for these H atoms in the model. Summary of crystal data for 1–9 is given in Table 2. Selected bond distances (Table S1) and parameters of H-bonding (Table S2) are listed in ESI.

Metal-organic or H-bonded networks in 1-9 were also analyzed from a topological perspective by applying the concept of underlying net.^{47,48} Simplified nets were

- ¹⁰ constructed by reducing the bridging ligands (when analyzing metal-organic networks) or discrete metal complexes (when analyzing hydrogen-bonded networks) to corresponding centroids while preserving their connectivity. The analysis of hydrogen-bonded networks was restrained to considering only ¹⁵ strong H-bonds D-H···A: D···A < 3.50 Å, H···A < 2.50 Å, and
- \angle (D-H···A) > 120°; D/A are the donor/acceptor atoms.^{47,48} CCDC-1984462–1984470 contain the supplementary crystallographic data for 1–9.

Catalytic cyanosilylation of aldehydes

²⁰ In a typical test, a suspension of an aromatic aldehyde (0.50 mmol, 4-nitrobenzaldehyde as a model substrate), trimethylsilyl cyanide (1.0 mmol), and catalyst (typically 3 mol%) in dichloromethane (2.5 mL) was stirred at room temperature. After a desired reaction time, the catalyst was
²⁵ removed by centrifugation, followed by an evaporation of the solvent from the filtrate under reduced pressure to give a crude solid. This was dissolved in CDCl₃ and analyzed by ¹H NMR spectroscopy for quantification of products (Fig. S5, ESI). To perform the recycling experiment, the catalyst was
³⁰ isolated by centrifugation, washed with dichloromethane, dried at room temperature, and reused. The subsequent steps were performed as described above.

35 Results and discussion

Hydrothermal preparation of 1–9. Despite commercial availability and the presence of seven potential coordination sites, 2,5-di(4-carboxylphenyl)nicotinic acid (H₃dcna) still remains unexplored as an aromatic building block for ⁴⁰ generating coordination compounds. To fill this gap, in this study we attempted a considerable number of hydrothermal reactions at 160 °C between transition metal(II) cations (i.e., Co²⁺, Ni²⁺, Zn²⁺, Fe²⁺, and Mn²⁺) and H₃dcna, also in the presence of sodium hydroxide (deprotonating agent) and ⁴⁵ different *N*-donor crystallization mediators (Scheme 1). The latter were selected from 1,10-phenanthroline (phen), 2,2'-bipyridine (bipy), 2,2'-biimidazole (H₂biim), or 1,4-bis(pyrid-

4-yl)benzene (bpb). Within the synthetic attempts performed, nine reactions were successful and well reproducible, leading
to the formation of pure microcrystalline products (Table 1) along with single crystals suitable for X-ray diffraction. The cobalt(II) compounds 1 and 4 were generated under equal conditions, except using different crystallization mediators (phen for 1 or bipy for 4), but led to distinct structures.
Likewise, structural differences between the Ni(II) derivatives 2 and 7 are also regarded to the use of distinct mediators of crystallization. Products 1 and 3 were also obtained under similar conditions, except for the type metal(II) chloride (CoCl₂·6H₂O for 1 and ZnCl₂ for 3). The differences observed ⁶⁰ in the structures of 1–9 show that their formation is primarily

dependent on the type of crystallization mediator and metal(II) source. All compounds were fully characterized and their crystal structures were confirmed by single-crystal X-ray diffraction (Table 2).

65

Compound	1	2	3	4	5
Chemical formula	C44H21C0N2O	C44H21NiN5O	C22H10ZnN2O4	C20H25C0N2O0	$C_{40}H_{50}Zn_2N_2O_{22}$
Formula weight	816 67	816.45	606.87	630.46	1345.86
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P-1	$P2_1/n$	P-1	P-1
a/Å	11 3259(8)	113784(7)	17.6863(4)	6 9985(6)	9 0097(4)
h/Å	13 2252(9)	13 1996(8)	17.2313(3)	9.2423(13)	12 2876(5)
c/Å	14.6526(13)	14 5453(9)	17.2313(3) 18 2480(3)	21235(2)	14 0100(7)
a/°	67 349(7)	67 404(6)	90	91 236(10)	98 691(4)
R/0	76175(7)	76.007(5)	109 196(2)	01.002(8)	102 242(4)
p_{\prime}	(0.173(7))	(0.097(3))	108.180(2)	91.092(0) 105.276(10)	105.242(4)
<i>γ</i> /	03.391(7)	03.830(0)	90	103.276(10)	94.700(3)
V/A ³	1836.1(3)	1831.5(2)	5283.43(18)	1324.2(3)	1481.23(12)
7/K	293(2)	293(2)	293(2)	293(2)	293(2)
Z	2	2	8	2	1
$D_c/\mathrm{g}~\mathrm{cm}^{-3}$	1.477	1.481	1.526	1.581	1.509
μ/mm^{-1}	0.533	1.314	1.745	0.713	1.738
F(000)	842	844	2480	650	696
Refl. measured	6511	5990	8814	4682	4851
Unique refl. (R_{int})	4370 (0.0438)	4684 (0.0315)	6899 (0.0343)	2258 (0.0848)	4355 (0.0224)
GOF on F^2	1.050	1.018	1.024	1.022	1.053
$R_1[I > 2\sigma(I)]^a$	0.0582	0.0388	0.0486	0.0868	0.0340
$wR_2[I \geq 2\sigma(I)]^b$	0.1121	0.0940	0.1338	0.1597	0.0972
Compound	6	7	8	9	
Compound Chemical formula	6 C ₂₆ H ₁₇ ZnN ₅ O ₆	7 $C_{88}H_{66}Ni_2N_8O_{16}$	8 C ₂₀ H ₁₅ FeNO ₈	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆	
Compound Chemical formula Formula weight	6 C ₂₆ H ₁₇ ZnN ₅ O ₆ 560.82	$7 \\ C_{88}H_{66}Ni_2N_8O_{16} \\ 1608.90$	8 C ₂₀ H ₁₅ FeNO ₈ 453.18	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆ 1269.83	
Compound Chemical formula Formula weight Crystal system	6 C ₂₆ H ₁₇ ZnN ₅ O ₆ 560.82 Triclinic	7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆ 1269.83 Triclinic	
Compound Chemical formula Formula weight Crystal system Space group	6 $C_{26}H_{17}ZnN_5O_6$ 560.82 Triclinic <i>P</i> -1	7 C ₈₈ H ₆₆ Ni ₂ N ₈ O ₁₆ 1608.90 Triclinic <i>P</i> -1	8 $C_{20}H_{15}FeNO_8$ 453.18 Triclinic P-1	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆ 1269.83 Triclinic <i>P</i> -1	
Compound Chemical formula Formula weight Crystal system Space group <i>a</i> /Å	6 C ₂₆ H ₁₇ ZnN₅O ₆ 560.82 Triclinic <i>P</i> −1 9.1466(7)	7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic <i>P</i> -1 6.1632(4)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8)	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆ 1269.83 Triclinic <i>P</i> -1 9.4017(13)	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å	6 C ₂₆ H ₁₇ ZnN₅O ₆ 560.82 Triclinic <i>P</i> −1 9.1466(7) 9.5909(7)	7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8)	9 C ₆₀ H ₄₄ Mn ₃ N ₆ O ₁₆ 1269.83 Triclinic <i>P</i> -1 9.4017(13) 10.8041(18)	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9)	9 $C_{60}H_{44}Mn_3N_6O_{16}$ 1269.83 Triclinic P-1 9.4017(13) 10.8041(18) 14.5350(16)	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å $a/^\circ$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6)	9 $C_{60}H_{44}Mn_3N_6O_{16}$ 1269.83 Triclinic P-1 9.4017(13) 10.8041(18) 14.5350(16) 105.013(12)	
Compound Chemical formula Formula weight Crystal system Space group <i>a</i> /Å <i>b</i> /Å <i>c</i> /Å <i>a</i> /° β/°		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5)	8 $C_{20}H_{15}FeNO_8$ 453.18 Triclinic P-1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7)	9 $C_{60}H_{44}Mn_3N_6O_{16}$ 1269.83 Triclinic P-1 9.4017(13) 10.8041(18) 14.5350(16) 105.013(12) 99.708(11)	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $y/^{\circ}$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8)	$\begin{array}{c} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn}_3\textbf{N}_6\textbf{O}_{16} \\ 1269.83 \\ \text{Triclinic} \\ P-1 \\ \textbf{9.4017(13)} \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ \textbf{99.708(11)} \\ 107.961(14) \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $\gamma/^{\circ}$ $\gamma/Å$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2)	8 $C_{20}H_{15}FeNO_8$ 453.18 Triclinic P-1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8) 916.87(15)	$\begin{array}{c} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn}_3\textbf{N}_6\textbf{O}_{16} \\ 1269.83 \\ \textbf{Triclinic} \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $\gamma/Å$ $\gamma/Å$ $\gamma/Å$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2)	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8) 916.87(15) 293(2)	$\begin{array}{l} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn}_{3}\textbf{N}_{6}\textbf{O}_{16} \\ 1269.83 \\ \textbf{Triclinic} \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $V/Å^3$ T/K Z		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic <i>P</i> -1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8) 916.87(15) 293(2) 2	$\begin{array}{c} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn}_{3}\textbf{N}_{6}\textbf{O}_{16} \\ 1269.83 \\ \textbf{Triclinic} \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $V/Å^3$ T/K Z $D_{r}/g cm^{-3}$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic <i>P</i> -1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481	8 C ₂₀ H ₁₅ FeNO ₈ 453.18 Triclinic <i>P</i> -1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8) 916.87(15) 293(2) 2 1.642	$\begin{array}{c} \textbf{9} \\ C_{60}H_{44}Mn_3N_6O_{16} \\ 1269.83 \\ Triclinic \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $V/Å^3$ T/K Z $D_c/g \text{ cm}^{-3}$ u/cm^{-1}		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315		$\begin{array}{l} \textbf{9} \\ C_{60}H_{44}Mn_3N_6O_{16} \\ 1269.83 \\ Triclinic \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \\ 6.518 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $V/Å^3$ T/K Z $D_c/g cm^{-3}$ μ/mm^{-1} F(000)		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830		$\begin{array}{c} \textbf{9} \\ C_{60}H_{44}Mn_3N_6O_{16} \\ 1269.83 \\ Triclinic \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \\ 6.518 \\ 645 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $V/Å^{3}$ T/K Z $D_c/g \text{ cm}^{-3}$ $\mu/\text{ mm}^{-1}$ F(000) Refl. measured		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971		$\begin{array}{c} \textbf{9} \\ C_{60}H_{44}Mn_3N_6O_{16} \\ 1269.83 \\ Triclinic \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \\ 6.518 \\ 645 \\ 4266 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å $a/^{\circ}$ $\beta/^{\circ}$ $\gamma/^{\circ}$ $V/Å^{3}$ T/K Z $D_c/g cm^{-3}$ μ/mm^{-1} F(000) Refl. measured Unique refl. (R_{w})	6 $C_{26}H_{17}ZnN_5O_6$ 560.82 Triclinic <i>P</i> -1 9.1466(7) 9.5909(7) 13.2159(10) 84.013(6) 78.778(7) 77.986(7) 1109.82(15) 293(2) 2 1.678 2.041 572 3709 3320 (0.0185)	7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971 3865 (0.0802)	8 $C_{20}H_{15}FeNO_8$ 453.18 Triclinic P-1 6.9066(8) 9.3698(8) 14.8244(9) 74.751(6) 85.796(7) 82.493(8) 916.87(15) 293(2) 2 1.642 0.874 460 3236 2585 (0.0353)	9 $C_{60}H_{44}Mn_3N_6O_{16}$ 1269.83 Triclinic P-1 9.4017(13) 10.8041(18) 14.5350(16) 105.013(12) 99.708(11) 107.961(14) 1306.0(3) 293(2) 1 1.615 6.518 645 4266 3493 (0.0591)	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $V/Å^3$ T/K Z $D_c/g \text{ cm}^{-3}$ μ/mm^{-1} F(000) Refl. measured Unique refl. (R_{int}) GOF on F^2		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971 3865 (0.0802) 1.064		$\begin{array}{c} 9\\ C_{60}H_{44}Mn_3N_6O_{16}\\ 1269.83\\ Triclinic\\ P-1\\ 9.4017(13)\\ 10.8041(18)\\ 14.5350(16)\\ 105.013(12)\\ 99.708(11)\\ 107.961(14)\\ 1306.0(3)\\ 293(2)\\ 1\\ 1.615\\ 6.518\\ 645\\ 4266\\ 3493\ (0.0591)\\ 1.001\\ \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ V/Å3 T/K Z $D_c/g \text{ cm}^{-3}$ μ/mm^{-1} F(000) Refl. measured Unique refl. (R_{int}) GOF on F^2 $R_1[Z \ge 2\sigma(D)]^a$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic P-1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971 3865 (0.0802) 1.064 0.0736		$\begin{array}{l} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn_3}\textbf{N}_6\textbf{O}_{16} \\ 1269.83 \\ \textbf{Triclinic} \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \\ 6.518 \\ 645 \\ 4266 \\ 3493(0.0591) \\ 1.001 \\ 0.0826 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $\gamma/°$ $\gamma/°$ $\gamma/°$ $\gamma/Å$ T/K Z $D_c/g cm^{-3}$ μ/mm^{-1} F(000) Refl. measured Unique refl. (R_{int}) GOF on F^2 $R_1 [L^> 2\sigma(I)]^a$ $wR_5 [L^> 2\sigma(I)]^b$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic <i>P</i> -1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971 3865 (0.0802) 1.064 0.0736 0.1989		$\begin{array}{l} \textbf{9} \\ \textbf{C}_{60}\textbf{H}_{44}\textbf{Mn_3}\textbf{N}_6\textbf{O}_{16} \\ 1269.83 \\ \textbf{Triclinic} \\ P-1 \\ 9.4017(13) \\ 10.8041(18) \\ 14.5350(16) \\ 105.013(12) \\ 99.708(11) \\ 107.961(14) \\ 1306.0(3) \\ 293(2) \\ 1 \\ 1.615 \\ 6.518 \\ 645 \\ 4266 \\ 3493 (0.0591) \\ 1.001 \\ 0.0826 \\ 0.2070 \end{array}$	
Compound Chemical formula Formula weight Crystal system Space group a/Å b/Å c/Å a/° $\beta/°$ $\gamma/°$ $\gamma/°$ $\gamma/°$ $\gamma/Å$ T/K Z $D_c/g \text{ cm}^{-3}$ μ/mm^{-1} F(000) Refl. measured Unique refl. (R_{int}) GOF on F^2 $R_1 [I> 2\sigma(I)]^a$ $wR_2 [I> 2\sigma(I)]^b$		7 $C_{88}H_{66}Ni_2N_8O_{16}$ 1608.90 Triclinic <i>P</i> -1 6.1632(4) 12.2650(7) 24.6163(17) 95.914(5) 93.921(5) 101.777(5) 1804.3(2) 293(2) 1 1.481 1.315 830 5971 3865 (0.0802) 1.064 0.0736 0.1989		9 $C_{60}H_{44}Mn_3N_6O_{16}$ 1269.83 Triclinic P-1 9.4017(13) 10.8041(18) 14.5350(16) 105.013(12) 99.708(11) 107.961(14) 1306.0(3) 293(2) 1 1.615 6.518 645 4266 3493 (0.0591) 1.001 0.0826 0.2070	

Table 2 Crystal data summary for 1–9

Structural description

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- $[M(Hdcna)(phen)_2(H_2O)] \cdot H_2O \ (M = Co \ (1), Ni \ (2)).$ Since mononuclear complexes 1 and 2 are isomorphous (Table 2), the structure of 1 is described as an example (Fig. 1). It comprises a Co(II) center, a terminal monodentate Hdcna²⁻ block (mode I, Sheme 2), two phen and one water ligands,
- 10 along with a crystallization H₂O molecule (Fig. 1a). The Co1 atom is 6-coordinate forming a distorted {CoN₄O₂} octahedral

geometry. The $[M(Hdcna)(phen)_2(H_2O)]$ units are hydrogenbonded between each other and involving water molecules of crystallization. As a result, an H-bonded 1D double chain is 15 generated (Fig. 1b). It can be topologically described as a **SP** 1-periodic net (3,6)(1,2) with the $(3^3.4^2.5)$ point symbol (Fig. 1c).

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Scheme 2 Different modes of coordination for Hdcna²⁻ and dcna³⁻ ligands in compounds 1-9.

 $[Zn(\mu-Hdcna)(phen)]_n$ (3). This compound is a 1D zigzag s coordination polymer (Fig. 2), wherein an asymmetric unit bears two Zn atoms (Zn1/Zn2), two μ -Hdcna²⁻ blocks, and two phen ligands (Fig. 2a). The 6-coordinate Zn1 and Zn2 centers display the distorted octahedral {ZnN₂O₄} environments. These are filled by four carboxylate oxygen 10 atoms of two μ -Hdcna²⁻ linkers and a pair of nitrogen atoms from phen moiety. The Zn–O [2.004(3)–2.480(4) Å] and Zn– N [2.105(3)–2.131(3) Å] bonds are within typical values.^{9,28,49} The Hdcna²⁻ ligand acts as a μ -linker (mode II, Scheme 2) with both COO⁻ groups in a bidentate mode. The μ -Hdcna²⁻ ¹⁵ linkers repeatedly connect the adjacent Zn1 and Zn2 centers to generate a 1D zigzag chain (Fig. 2b) of the 2C1 topological type (Fig. 2c). Besides, such 1D metal-organic chains are additionally interconnected by H-bonds to form a 2D H-bonded layer (Fig. S1, ESI).



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Fig. 1 Crystal structure of 1. (a) Molecular unit; CH atoms are omitted. (b) 1D H-bonded double chain; view along the *a* axis. (c) Topological representation of 1D H-bonded chain with a SP 1-periodic net (3,6)(1,2) topology; centroids of $[M(Hdcna)(phen)_2(H_2O)]$ molecular nodes (magenta), centroids of H₂O linkers (red).



Fig. 2 Crystal structure of **3**. (a) Coordination environment and connectivity of Zn centers; CH atoms are omitted. Symmetry code: i = x, y, z + 1. (b) 1D zigzag metal-organic chain; view along the *a* axis. Symmetry codes: i = x, y, z + 1; ii = x, y, z - 1. (c) Topological representation of two 1D chains with a 5 2C1 topology; Zn centers (cyan balls), centroids of μ -Hdcna²⁻ blocks (gray).

 $[Co(\mu-Hdcna)(bipy)(H_2O)_2]_n \cdot nH_2O \qquad (4).$ this 1D In coordination polymer (Fig. 3), an asymmetric unit is composed of a Co(II) center, a µ-Hdcna²⁻ linker, one bipy and 10 two terminal H₂O ligands, in addition to a lattice water molecule (Fig. 3a). The Co1 atom is 6-coordinate forming a distorted octahedral $\{CoN_2O_4\}$ environment. It is occupied by two oxygen atoms from two µ-Hdcna²⁻ linkers, two H₂O ligands, and two nitrogen atoms from bipy. The Co-O 15 [2.034(5)-2.197(4)Å] and Co-N [2.095(6)-2.124(6) Å] bond distances well agree with related literature data.41,43,44 The Hdcna²⁻ ligand functions as a µ-linker with two monodentate COO⁻ groups (mode III, Scheme 2). The µ-Hdcna²⁻ linkers connect neighboring Co1 centers to give a linear 1D metal-20 organic chain (Fig. 3b) of the 2C1 topological type (Fig. 3c). A number of hydrogen bonds between adjacent chains lead to the formation of 2D H-bonded layers (Fig. S2).

 $[Zn_2(\mu-Hdcna)_2(bipy)_2(H_2O)_4]\cdot 6H_2O$ (5). This structure reveals a cyclic Zn(II) dimer (Fig. 4). Its asymmetric unit 25 contains a Zn1 atom, a μ -Hdcna²⁻ linker, a bipy moiety, and 45

two H₂O ligands, in addition to three crystallization water molecules. The 6-coordinate Zn1 atom has a distorted $\{ZnN_2O_4\}$ octahedral environment. It is occupied by two carboxylate oxygen atoms from two µ-Hdcna²⁻ ligands, two 30 bipy N donors, and a pair of H₂O ligands (Fig. 4a). The Hdcna²⁻ ligand is bridging bidentate and functions as an internal µ-linker (mode IV, Scheme 2), namely by interconnecting the Zn1 atoms into a cyclic dizinc(II) molecular unit with a Zn…Zn distance of 13.312(2) Å. 35 Interestingly, crystallization water molecules are arranged into cyclic (H₂O)₄ clusters of the R4 type⁵⁰⁻⁵² (Fig. S3, ESI) that can grow into (H₂O)₆ aggregates if water ligands are taken into consideration. Numerous hydrogen-bond interactions between these water clusters and [Zn2(µ-⁴⁰ Hdcna)₂(bipy)₂(H₂O)₄] dimers lead to a complex 3D Hbonded framework (Fig. 4b). After simplification, this can be classified within the **fsc** topological type, revealing a binodal 4,6-connected net with the $(4^4.6^{10}.8)(4^4.6^2)$ point symbol (Fig. 4c).



⁵⁰ Fig. 3. Crystal structure of 4. (a) Coordination environment and connectivity of Co1 centers; CH atoms are omitted. Symmetry code: i = x, y+1, z. (b) Linear 1D metal-organic chain; view along the *a* axis. (c) Topological representation of two 1D chains with a 2C1 topology; Co centers (magenta balls), centroids of μ -Hdcna²⁻ blocks (gray).



Fig. 4 Crystal structure of **5**. (a) Cyclic dimer unit; CH atoms are omitted. Symmetry code: i = -x + 2, -y + 1, -z + 2. (b) 3D H-bonded network; view s along the *a* axis; 2,2'-bipy ligands are omitted. (c) Topological representation of a simplified 3D H-bonded net with a **fsc** topology; view along the a axis; centroids of $[Zn_2(\mu-Hdcna)_2(bipy)_2(H_2O)_4]$ molecular units (cyan balls), centroids of $(H_2O)_4$ clusters (red).

 $[Zn(\mu_3-Hdcna)(H_2biim)]_n$ (6). Coordination polymer 6 shows a 1D ladder structure (Fig. 5). An asymmetric unit contains a ¹⁰ Zn1 center, a μ_3 -Hdcna²⁻ linker, and a terminal H₂biim ligand. The Zn1 atom is 5-coordinate and reveals a distorted trigonal bipyramidal {ZnN₂O₃} geometry (Fig. 5a), which is formed by three oxygen atoms from three μ_3 -Hdcna²⁻ moieties and two N donors from H₂biim. The Zn–O [1.951(2)–2.142(2)Å] ¹⁵ and Zn–N [2.066(2)–2.145(2)Å] bonds are within standard values.^{28,49,53} The Hcpia²⁻ ligand functions as a tridentate μ_3 - linker (mode V, Scheme 2), with its central ring carboxylate group bridging two zinc centers to form a Zn₂ subunit with a Zn1…Zn1 separation of 3.276(5) Å (Fig. 5b). These Zn₂ ²⁰ subunits are joined together via remaining COO⁻ group of μ_3 -Hdcna²⁻ to produce a 1D metal-organic ladder (Fig. 5b). A topology of this ladder (Fig. 5c) can be described as an uninodal 3-connected chain of a SP 1-periodic net (4,4)(0,2) type. It contains the 3-connected Zn1 and μ_3 -Hdcna²⁻ nodes ²⁵ and has a point symbol of (4².6).



³⁰ Fig. 5 Crystal structure of 6. (a) Coordination environment and connectivity of Zn1 center; CH atoms are omitted. Symmetry codes: i = -x + 1, -y + 2, -z + 1; ii = x, y + 1, z. (b) 1D metal-organic ladder; view along the *a* axis; H₂biim ligands are omitted. (c) Topological representation of a 1D ladder with a SP 1-periodic net (4,4)(0,2) topology; view along the *a* axis; Zn nodes (cyan balls), centroids of μ_3 -Hdcna²⁻ nodes (gray).

 $[Ni_2(Hdcna)_2(\mu-bpb)(bpb)_2(H_2O)_4]$ (7). This compound features a discrete dimeric structure (Fig. 6), with an asymmetric unit holding a Ni1 center, a terminal Hdcna²⁻ ligand, one and a half of 1,4-bpb moieties, and a pair of terminal H₂O ligands. The half of 1,4-bpb moiety lies on an inversion center. The Ni1 center is 6-coordinate and unveils an octahedral {NiN₂O₄} environment. It is occupied by two to carboxylate oxygen atoms two N donors from two 1.4-bpb

⁴⁰ carboxylate oxygen atoms, two N donors from two 1,4-bpb moieties, and two H₂O ligands (Fig. 6a). The Ni–O [2.033(3)–

2.180(4) Å] and Ni–N [2.085(4)–2.094(4) Å] distances are within expected values.^{38,53,54} While Hdcna²⁻ is acting as a terminal ligand (mode VI, Scheme 2), the Ni1 centers are ⁴⁵ bridged by a μ -bpb linker to form a dimeric molecular unit (Fig. 6a). These Ni₂ units are further organized into a 3D Hbonded network trough the O–H···O/N hydrogen bonds (Fig. 6b). The resulting network is topologically classified (Fig. 6c) as an uninodal 8-connected net with the **hex** (hexagonal ⁵⁰ primitive) topology and the point symbol of (3⁶.4¹⁸.5³.6).



Fig. 6 Crystal structure of 7. (a) Molecular unit; CH atoms are omitted. Symmetry code: i = -x + 1, -y + 2, -z + 1. (b) 3D H-bonded network; view along 5 the *a* axis. (c) Topological representation of a simplified 3D H-bonded net with a **hex** topology; view along the a axis; centroids of [Ni₂(Hdcna)₂(μ -bpb)(bpb)₂(H₂O)₄] molecular units (green balls).

[$Fe(\mu_4$ -Hdcna)(μ -H₂O)]_n·nH₂O (8). This compound is a 2D CP (Fig. 7) and its asymmetric unit encloses two Fe(II) ¹⁰ centers (Fe1 and Fe2 with half occupancy, lie on independent inversion centers), one μ_4 -Hdcna²⁻ block, one μ -H₂O ligand, and one lattice water molecule (Fig. 7a). Both Fe1 and Fe2 centers are 6-coordinate and assume a distorted octahedral {FeO₆} geometry, which is occupied by four carboxylate ¹⁵ oxygen atoms from four μ_4 -Hdcna²⁻ ligands as well as two μ -H₂O ligands. The lengths of the Fe–O bonds are within the 1.955(2)–2.055(2) Å range.^{54–56} The Hdcna²⁻ block functions

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as a tetradentate μ_4 -bridging ligand with two COO⁻ groups being bridging bidentate (mode VII, Scheme 2). These ²⁰ carboxylate functionalities as well as the μ -H₂O linkers unite the Fe(II) centers to form a decorated 1D chain motif (Fig. 7b). Such 1D motifs are further connected by the remaining COO⁻ groups to produce a 2D metal-organic layer (Fig. 7c). Such a layer can be classified as a binodal 4,6-linked net with ²⁵ a 4,6L26 topology. It is described by the $(3^2.4^2.5^2)(3^4.4^4.5^4.6^3)$ point symbol wherein the $(3^2.4^2.5^2)$ and $(3^4.4^4.5^4.6^3)$ indices refer to the μ_4 -Hdcna²⁻ and Fe1/Fe2 nodes, respectively.







Fig. 7. Crystal structure of **8**. (a) Coordination environment around the Fe1 and Fe2 centers; CH atoms are omitted. Symmetry codes: i = -x + 1, -y + 1, -z + 1; ii = -x + 1, -y, -z + 1; iii = x, y + 1, z; iv = x + 1, y, z; v = x + 1, y + 1, z; vi = -x + 2, -y + 1, -z + 1. (b) 1D chain motif. (c) 2D metal-organic layer (view along the *c* axis). (c) Topological representation of a 2D metal-organic layer with a 4,6L26 topology; view along the *c* axis; Fe1/Fe2 nodes (green balls), centroids of μ_4 -HL²⁻ nodes (gray), centroids of μ -H₂O linkers (red).

[$Mn_3(\mu_5$ - $dcna)_2(bipy)_2(H_2O)_2]_n$ · $2nH_2O$ (9). This compound has an intricate 2D metal-organic layer structure (Fig. 8). An asymmetric unit contains two Mn(II) centers (a full ¹⁰ occupancy Mn1 and a half occupancy Mn2; Mn2 lies on an inversion center), a μ_5 - $dcna^{3-}$ block, a bipy moiety, a terminal H₂O ligand, as well as a water molecule of crystallization. The Mn1 center is 7-coordinate and assumes a distorted pentagonal bipyramid {MnN₂O₅} environment, which is ¹⁵ populated by five O atoms from three μ_5 - $dcna^{3-}$ blocks and a pair of bipy nitrogen atoms (Fig. 8a). The Mn2 center is 6coordinate revealing a distorted octahedral {MnO₆} geometry, which is completed by four O atoms from four μ_5 - $dcna^{3-}$ moieties and two terminal H₂O ligands. The Mn–O [2.147(3)– ²⁰ 2.495(4) Å] and Mn–N [2.258(4)–2.280(4)Å] bonds show

typical distances.^{28,41,57} The dcna³⁻ block functions as an overall heptadentate μ_5 -spacer (mode VIII, Scheme 2), in which three COO⁻ groups are terminal bidentate, μ -bridging bidentate or tridentate. Three adjacent Mn(II) atoms are ²⁵ joined via four carboxylate groups from four μ_5 -dcna³⁻ blocks to form Mn₃ subunits with a Mn1···Mn2 distance of 3.936(4) Å (Fig. 8b). These trimanganese(II) subunits are further joined together through the remaining carboxylate groups of μ_5 -dcna³⁻ into an intricate 2D metal-organic layer (Fig. 8c). ³⁰ After being simplified, topological analysis of this layer (Fig. 8d) discloses a trinodal 3,4,5-linked net of the 3,4,5L47 type. It is defined by the (4.6²)₂(4³.6⁷)₂(4⁴.6²) point symbol with the (4.6²), (4³.6⁷)₂, and (4⁴.6²) notations corresponding to the Mn1, μ_5 -dcna³⁻, and Mn2 nodes, respectively.



Fig. 8 Crystal structure of **9**. (a) Coordination environment and connectivity of Mn1 and Mn2 centers; H atoms are omitted. Symmetry codes: i = x + 1, y + 1, z; ii = x + 2, y + 1, z; iii = -x + 2, -y + 2, -z; iv = -x + 1, -y + 1, -z. (b) Trinuclear Mn(II) subunit. Symmetry code: i = x + 1, y + 1, z. (c) 2D metalorganic layer; view along the *ab* plane. (c) Topological representation of a simplified 2D layer with a 3,4,5L47 topology; view along the *c* axis; Mn1/Mn2 nodes (turquoise balls), centroids of μ_5 -dcna³⁻ nodes (gray).

45 Structural comparison of 1-9

2,5-Di(4-carboxylphenyl)nicotinic acid (H₃dcna) acts as Hdcna²⁻ or dcna³⁻ ligand in 1-9 with eight distinct coordination modes (Scheme 2). In all products, the N site at the central ring of Hdcna²⁻/dcna³⁻ remains uncoordinated ⁵⁰ what can be associated with a steric factor. The COO⁻ groups of Hdcna²⁻/dcna³⁻ show different denticity that varies from monodentate, bidentate, µ-bridging bidentate or tridentate. Despite considering H₃dcna as a rigid ligand, there is some

rotation between the central and outer aromatic rings along ⁵⁵ the C–C bonds in Hdcna^{2–}/dcna^{3–}, as attested by the dihedral angles in the 8.65–55.76° range. This gives some flexibility for fitting the coordination preference of metal centers in the course of hydrothermal generation of **1–9**. Apart from H₃dcna, the type of metal cation and crystallization mediator ⁶⁰ significantly influence the structure of the resulting product. In fact, similar synthetic strategies (Table 1) led to the generation of coordination compounds of distinct composition, nuclearity and dimensionality which range from mono- (1, 2) and dinuclear (5, 7) complexes to 1D (3, 4, 6) and 2D (8, 9) coordination polymers.

PXRD and TGA

- ⁵ PXRD (powder X-ray diffraction) patterns of 1–9 were recorded at room temperature using the microcrystalline samples (Fig. S4, ESI). In brief, the experimentally obtained diffractograms well agree with ones calculated on the basis of single-crystal X-ray diffraction data. This comparison testifies ¹⁰ a phase purity of the as-synthesized samples 1–9.
- TGA was used to study the thermal stability of compounds 1– 9 under nitrogen atmosphere (Fig. 9). Compound 1 shows a release of two H₂O molecules between 58 and 146 °C (exptl, 4.6%; calcd, 4.4%), followed by a decomposition of the 15 dehydrated sample above 243 °C. For 2, a loss of two water moieties is detected in the 79–196 °C interval (exptl, 4.3%; calcd, 4.4%), while a dehydrated solid is then stable until 317 °C. TGA data indicate that the zinc(II) products 3 and 6 are stable up to 301 and 266 °C, respectively. For compound 4, 20 there is a release of three H₂O molecules between 41 and 207 °C (exptl, 8.5%; calcd, 8.6%), followed by a decomposition above 271 °C. For 5, a thermal effect in the 82–155 °C range is associated with a loss of ten H₂O molecules (exptl, 13.1%;
- calcd, 13.4%); the remaining solid maintains stability until 25 306 °C. In compound 7, the release of four H₂O ligands (exptl, 4.3%; calcd, 4.5%) is detected in the 177–230 °C interval, whereas the decomposition of a dehydrated solid starts at 275 °C. TGA trace of CP 8 reveals a release of two water moieties (exptl, 8.0%; calcd, 7.9%) in the 256–288 °C ³⁰ range; the decomposition is then observed above 327 °C. For CP 9, a mass loss corresponding to four H₂O molecules occurs in the 90–122 °C interval (exptl, 5.5%; calcd, 5.7%). However, the dehydrated metal-organic network remains stable up to 378 °C.





Fig. 9 TGA plots of 1-9 (10 °C/min, 25-800 °C, N₂ atmosphere)

Luminescent properties

The emission spectra of zinc(II) derivatives (**3**, **5**, and **6**) and ⁴⁰ H₃dcna were recorded in the solid state at room temperature (Fig. 10). The spectrum of H₃dcna discloses a weak emission band centered at 401 nm. In contrast to H₃dcna, zinc(II) derivatives feature bands of a more pronounced intencity with maxima in the 364–388 nm range, namely 388 nm for **3**, 364 ⁴⁵ nm for **5**, and 379 nm for **6**. These bands are associated with an intraligand π – π * or n– π * transitions of main carboxylate ligand.^{28,49,53} An enhanced luminescence of **3**, **5**, and **6** vs. H₃dcna is likely due to the coordination of ligands to Zn(II), which may strengthen the rigidity of ligands and diminish a ⁵⁰ loss of energy from radiationless decay.^{53,54,57}



Fig. 10 Solid-state emission spectra of 3, 5, 6, and H₃dcna at room temperature (λ_{ex} = 326 nm).

Magnetic properties

⁵⁵ Magnetic behavior was investigated for the 2D Mn(II) coordination polymer **9** (Fig. 11). The $\chi_M T$ value at 300 K (13.02 cm³·mol⁻¹·K) is close to that (13.11 cm³·mol⁻¹·K) expected for three magnetically isolated high-spin Mn(II) centers ($S_{Mn} = 5/2$, g = 2.0). A monotonous decline of $\chi_M T$ on ⁶⁰ decreasing the temperature shows that there is a prevailing antiferromagnetic interaction (Fig. 11). In the 10–300 K range, the magnetic susceptibility obeys the Curie–Weiss law with C= 13.31 cm³·mol⁻¹·K and $\theta = -10.14$ K. A negative θ and a decrease of $\chi_M T$ are ascribed to an overall antiferromagnetic ⁶⁵ coupling between the Mn(II) centers in Mn₃ subunits, which feature two sets of magnetic exchange pathways involving different carboxylate bridges (Fig. 8b). As an attempt to fit

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the magnetic data of 9 (2–300 K), we applied the following expression^{58,59} for linear trinuclear Mn(II) derivatives:

$$\hat{H} = -2\sum_{i=1}^{n} \sum_{j=i}^{n} J_{ij} \vec{S}_{i} \vec{S}_{j}$$

$$\hat{H} = -2J_{12}\vec{S}_{1} \vec{S}_{2} - 2J_{23}\vec{S}_{2} \vec{S}_{3} - 2J_{13}\vec{S}_{1} \vec{S}_{3}$$

$$\chi_{t} = \frac{N\beta^{2}g^{2}}{3kT} \times \frac{\sum_{S} S_{T}(S_{T} + 1)(2S_{T} + 1)e^{-E(S_{T})/kT}}{\sum_{S} (2S_{T} + 1)e^{-E(S_{T})/kT}}$$

$$\chi_{m} = \frac{\chi_{t}}{1 - (2zJ'/Ng^{2}\beta^{2})\chi_{t}}$$

where $J_{12} = J_{23} = J_1$ and $J_{13} = J_2$. The parameters J_{12} and J_{23} s are the exchange interactions between the "central" Mn(II) and the two "outer" Mn(II) atoms, whereas J_2 is the interaction between the "outer" Mn(II) centers within the Mn₃ subunit (Fig. 8b); zJ' refers to the intercluster coupling constant in the 2D CPs. This model produced reasonable results with the following exchange parameters: $J_1/k_B = -2.45$ K, $J_2/k_B = 0.41$ K, $zJ'/k_B = -0.26$ K, and g = 2.01 (the agreement factor, $R = \sum (\chi_m T_{exp} - m T_{calc})^2 / \sum (\chi_m T_{exp})^2$ was 5.73×10^{-5}). These parameters confirm an antiferromagnetic interaction between the Mn centers within the trimanganese(II) subunits. The inercluster magnetic interaction (zJ') is small, thus indicating a very weak exchange interaction among two Mn₃ subunits. This can be explained by a long separation (10.804(3) Å) of the adjacent Mn₃ subunits.



²⁰ Fig. 11 Temperature dependence of $\chi_M T$ (O) and $1/\chi_M(\Box)$ vs. *T* for compound 9. The blue line represents the best fit to the equation in the text. The red line displays the Curie-Weiss fitting.

Catalytic cyanosilylation of aldehydes

- Given the potential of zinc(II) coordination compounds to ²⁵ catalyze the cyanosilylation of aldehydes,^{60–62} we explored the application of **3**, **5**, and **6** as heterogeneous catalysts in the cyanosilylation of 4-nitrobenzaldehyde as a model substrate to give 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile. Typical tests were carried out by reacting a mixture of 4-³⁰ nitrobenzaldehyde, trimethylsilyl cyanide (TMSCN), and a Zn
- catalyst in dichloromethane at room temperature (Scheme 3, Table 3). Such effects as reaction time, catalyst loading, solvent composition, catalyst recycling, and finally substrate scope were investigated.



Scheme 3 Zn-catalyzed cyanosilylation of 4-nitrobenzaldehyde (model substrate).

The dizinc(II) compound 5 appears to be the most active among the tested catalysts, resulting in an efficient conversion 4-nitrobenzaldehyde 2-(4-nitrophenyl)-2-40 of to [(trimethylsilyl)oxy]acetonitrile (Table 3). The latter is accumulated with an yield growth from 25 to 73% on extending the reaction time from 1 to 12 h (Table 3, entries 1-7; Fig. S6). An effect of catalyst loading was also studied, 45 showing that the product yield increases from 56 to 75% on rising the catalyst amount from 2 to 4 mol% (entries 7-9). Apart from dichloromethane, other solvents were explored but appeared to be less efficient with the following the trend in product yields (entries 7, 10–13): CH_2Cl_2 (73%) > CH_3Cl_3 $_{50}$ (69%) > CH₃OH (67%) > CH₃CN (63%) > THF (56%). In comparison with 5, the compounds 3 and 6 are slightly less active producing the maximum yields of 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile in the 55-60% range (entries 14, 15, Table 3). Although a relationship between structure 55 and catalytic activity can not be clearly seen, the highest efficiency shown by 5 may eventually be associated to its dimer structure or favorable packing arrangement with better accessible metal sites. It is also important to mention that the cvanosilvlation of 4-nitrobenzaldehyde almost does not 60 proceed in the absence of catalyst (only 3% product yield) or when using H₃dcna (5% yield) or ZnCl₂ (8% yield) as catalysts (Table 3, entries 16-18). Moreover, in the presence of 5, no other reaction products were detected thus indicating an excellent selectivity.

Table 3 Zn-catalyzed cyanosilylation of 4-nitrobenzal dehyde with TMSCN.^a

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Entry	Catalyst	Time, h	Catalyst loading, mol%	Solvent	Yield, % ¹
1	5	1	3.0	CH_2Cl_2	25
2	5	2	3.0	CH_2Cl_2	47
3	5	4	3.0	CH_2Cl_2	55
4	5	6	3.0	$\mathrm{CH}_2\mathrm{Cl}_2$	62
5	5	8	3.0	CH_2Cl_2	67
6	5	10	3.0	CH_2Cl_2	70
7	5	12	3.0	$\mathrm{CH}_2\mathrm{Cl}_2$	73
8	5	12	2.0	CH_2Cl_2	56
9	5	12	4.0	CH_2Cl_2	75
10	5	12	3.0	CH ₃ CN	63
11	5	12	3.0	THF	56
12	5	12	3.0	CH ₃ OH	67
13	5	12	3.0	CH ₃ Cl	69
14	3	12	3.0	CH_2Cl_2	55
15	6	12	3.0	$CH_2Cl_2 \\$	60
16	blank	12	-	$CH_2Cl_2 \\$	3
17	ZnCl	12	3.0	CH ₂ Cl ₂	8

The substrate scope was also investigated on other substituted aromatic aldehydes, namely by reacting them with trimethylsilyl cyanide under optimized conditions (3.0 mol% 5, CH₂Cl₂, 12 h). The corresponding cyanohydrin products ¹⁰ were produced in yields ranging from 50 to 69% (Table 4). Aryl aldehydes bearing strong electron-withdrawing substituents (e.g., nitro and chloro groups) exhibited the best reactivity (Table 4, entries 2–5), which might be related to an increase in the substrate electrophilicity. As expected, the ¹⁵ aldehyde substrates bearing electron-donating functionalities (e.g., methyl or methoxy groups) showed lower reaction

yields (Table 4, entries 7 and 8). Finally, to examine the stability of 5 in the present cyanosilylation process, we tested the recyclability of this 20 heterogeneous catalyst. For this purpose, upon completion of a reaction cycle, we separated the catalyst by centrifugation, washed it with CH₂Cl₂ and dried at room temperature before its use in a subsequent cycle. The obtained results (Fig. S7, ESI) indicate that the catalyst 5 essentially maintains its 25 activity for at least four consecutive reaction cycles as attested by similar product yields. According to the PXRD data (Fig. S8), the structure of 5 is essentially preserved after four catalytic cycles, despite the presence of some additional peaks or broadending of several signals. These changes are 30 associated with the presence of some impurities or decreased crystallinity, which might be expected after several catalytic runs. Hence, reusability of this catalyst for a number of additional runs might not be very efficient.

³⁵ **Table 4.** Cyanosilylation of various aldehydes with TMSCN catalyzed by **5**.^a



Entry	Substituted Benzaldehyde	Product
	Substrate (R-C ₆ H ₄ CHO)	Yield, % ^b
1	R = H	57
2	$R = 2-NO_2$	63
3	$R = 3-NO_2$	69
4	$R = 4-NO_2$	73
5	R = 4-Cl	66
6	R = 4-OH	62
7	$R = 4-CH_3$	54
8	R = 4-OCH ₃	50

^aReaction conditions: aldehyde (0.5 mmol), TMSCN (1.0 mmol), catalyst 5 (3.0 mol.%), CH₂Cl₂ (2.5 mL), solvent (2.5 mL), room
⁴⁵ temperature (~25 °C). ^bYields based on ¹H NMR analysis: [moles of product per mol of aldehyde substrate]×100%.

Conclusions

- ⁵⁰ In this study we explored the use of H₃dcna (2,5-di(4carboxylphenyl)nicotinic acid) as a novel tricarboxylic aromatic acid for assembling nine new metal(II) coordination compounds **1–9**, which were completely characterized by standard methods including single-crystal X-ray diffraction.
- ⁵⁵ Besides, structural and topological characteristics of the hydrogen-bonded or metal-organic architectures in 1-9 were highlighted, disclosing that their structural multiplicity is associated to the type of metal(II) center and *N*-donor crystallization mediator, along with the coordination modes of
- ⁶⁰ the Hdcna²⁻/dcna³⁻ ligands. In fact, the dimensionality of the obtained products ranges from discrete monomers (1 and 2) and dimers (5 and 7) to 1D chains (3, 4, and 6) and 2D metalorganic layers (8 and 9).

Thermal stability as well as luminescent, magnetic, or 65 catalytic properties were also investigated for selected compounds. In particular, the dizinc(II) complex **5** was shown to efficiently catalyze the cyanosilylation of aldehydes with trimethylsilyl cyanide under ambient conditions. The selective conversion of 4-nitrobenzaldehyde to 2-(4-nitrophenyl)-2-

- 70 [(trimethylsilyl)oxy]acetonitrile was explored as a model reaction, for which various parameters were optimized (solvent composition, time, catalyst loading), resulting in up to 75% product yields. Besides, this heterogeneous catalyst can be recycled for up to four times maintaining its original 75 catalytic activity. The substrate scope of the reaction was also extended to other substituted benzaldehydes, revealing their reactivity dependence on the electron-withdrawing or donating properties of functional groups.
- Moreover, the obtained herein products represent the unique ⁸⁰ examples of coordination compounds derived from H₃dcna, thus opening up the use of this tricarboxylic aromatic acid for generating complexes and coordination polymers with interesting structures and functional properties. We believe the present work will stimulate the use of H₃dcna and related ⁸⁵ multicarboxylic acids for designing new coordination compounds toward applications as functional molecules.

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2,5-di(4-carboxylphenyl)nicotinic acid was explored as a novel building block for assembling nine metal(II) coordination compounds; these were fully characterized and their structural features and functional properties were investigated.