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Post-synthetic modification of coordination networks

Guest Editors: Andy Burrows and Seth Cohen

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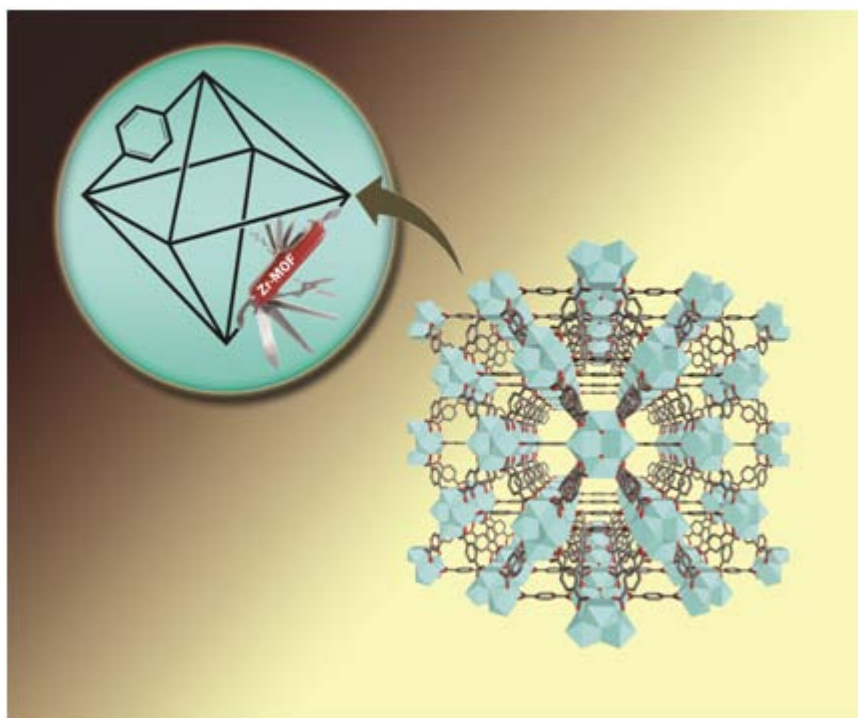


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PAPER

Syntheses of metal–organic frameworks with protected phosphonate ligands†

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Protected phosphonate groups were embedded onto isophthalic acid and reacted with zinc ion to synthesize metal–organic frameworks (MOFs). Single-crystal X-ray diffraction measurement revealed the crystal structures of obtained MOFs under various temperatures and solvent conditions. The isopropyl groups were left protected when the complexation reaction was executed at 60 °C, while they were partially deprotected in the sample prepared at 120 °C. When the reaction was carried out at 180 °C, the isopropyl groups were totally deprotected. This result provides us with information on the deprotection reaction in a post-synthetic method for constructing MOFs.

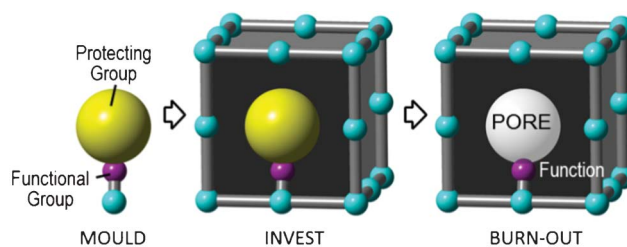
Introduction

Metal–organic frameworks (MOFs) have achieved impressive progress recently, and show specific gas adsorption behaviour, showing promise for smart gas separation for many different gases.^{1–10} MOFs can contain a wide variety of metal ions and bridging ligands, and their structures can be designed to specific pore sizes, dimensions, and configurations inside their frameworks. In the design of the inner environment of these frameworks, various functional groups have been modified, such as hydrophobic alkyl groups, fluorinated groups,¹¹ acidic groups and uncoordinated metal centres (UMCs). An analogy with heterogeneous catalysts provided us with the idea that uncoordinated metal centres^{12,13} or acidic groups would potentially act as active sites for catalytic reactions. However, UMCs or acidic groups have barriers towards their introduction into MOF frameworks, and one of these is that MOFs contain coordination bonds between the metal ions and bridging ligands, but UMCs have the ability to coordinate to ligands. Uncoordinated acidic sites also tend to coordinate to a metal site, for example, 2,5-dihydroxyterephthalic acid coordinates to the metal site in a bidentate fashion to construct the CPO-27 family,^{12,14} which has a different framework to an isorecticular MOF series.

A post-synthetic modification technique is a rational strategy for modifying acidic functional groups in a framework.¹⁰ Aldehyde or amino groups can be introduced into a framework before reacting with amino, acid anhydride,^{15–18} isocyanate,^{19,20} or carbonyl groups.^{21,22} Sada and co-workers have executed a click reaction on a framework.²³

The protection–complexation–deprotection (PCD) method is a sophisticated process for constructing MOFs containing reactive functional groups.^{24–26} This method is analogous to foundry work, as shown schematically in Scheme 1. Conventional foundry works consists of mould, invest and burn-out processes. The desired cavity shape is designed by figuring a mould and an object was constructed by investing before eliminating the mould to construct the desired shape. The PCD method also includes three reaction steps. The first step of the PCD method is a protection reaction where a reactive group in the ligand is modified by an unreactive organic group to prevent any unwanted reactions disrupting the pore structure in a framework, as preparing the mould in foundry works. A complexation reaction is then executed afterwards, and an MOF is constructed with the designed framework arrangement, and the prepared mould is inserted into the MOF matrix. Finally, the protecting groups are removed chemically, being comparable to a burn-out process in the foundry process, and the reactive groups reappear. Guest molecules can be inserted into the pores that have formed to interact with the functional groups. In this method, highly reactive groups do not have the chance to attack the metal site, and arbitrary functional groups can be introduced into the framework. Several types of group can be introduced, and thus, isostructural MOFs can be designed easily.

Here, we describe the reaction of protected phosphonate groups of 2-phosphoterephthalic acid with zinc ions. The



Scheme 1 A schematic representation of the PCD method.

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protected ligand was synthesized using a two-step complexation reaction. Single crystal X-ray diffractometry on the MOFs obtained revealed that the zinc ions assisted in the deprotection of the phosphonate groups, and novel MOFs were synthesized. This result provides us with a novel strategy for constructing secondary building units using known subunits.

Results and discussion

Syntheses and crystal structures

To investigate the reactivity of the protected ligand, we planned to synthesize diisopropyl 3,5-dicarboxylphenylphosphonate (H_2dppip , **2**) as described below. However, there was the suspicion that esterification of the phosphonate group of 3,5-dicarboxyphenylphosphonic acid (H_4pip) would result in the esterification of all the carboxyl groups as well as the phosphoxyl groups. Therefore, we applied another route, as shown in Scheme 2 for synthesizing H_2dppip .

The stability of the protecting group was evaluated using NMR measurements. H_2dppip was dissolved in deuterated water and/or deuterated DMF, and was kept at 60 °C to evaluate the deprotection ratio using 1H NMR spectroscopy. No peaks emerged up to a period of 11 days, and the ligand was found to be highly stable.

Synthesis of the MOFs was carried out using H_2dppip , 4,4'-bipyridine (bpy), and zinc ions with various solvents at several reaction temperatures. The crystal structure of **3** is shown in Fig. 1. Compound **3** consists of protected ligands (dppip), bpy, and zinc ions. The two carboxylate groups of dppip coordinate monodentately to the zinc ions, and the phosphonate group remains protected. Each zinc ion is coordinated by two coordination water molecules, two oxygen atoms from the two carboxylate groups, and one nitrogen atom of the bpy ligand, and has a trigonal bipyramidal structure. As a result, a one-dimensional framework is constructed along the *a*-axis. These chains make hydrogen bonds between each other constructing a void between them, and water and DMF are aligned in interchain as well as disordered isopropyl groups of the dppip ligand.

The crystal structure of **4** is shown in Fig. 2. From a reaction carried out in a mixture of water and ethanol at 120 °C, one of the isopropyl groups of each ligand becomes deprotected and the phosphonate groups coordinate to the zinc ions. Each zinc atom is coordinated by the nitrogen atom of a bpy ligand and three oxygen atoms from a phosphonate group, a carboxylate group, and a coordinating water molecule. The isopropyl 3,5-dicarboxylphenylphosphonate (Hppip) ligand bridges the zinc atoms *via* carboxylate

and phosphonate groups, and constructs a one-dimensional framework. One carboxylate group in each Hppip ligand does not take part in the coordination, but as it is protonated, forms a hydrogen bond with the crystalline water present.

The crystal structure of **5** is shown in Fig. 3. It is widely known that *N,N*-dimethylformamide undergoes hydrolysis to form a dimethylammonium ion, and the MOF obtained incorporates this as a counter ion. One isopropyl group is deprotected on each phosphonate group and the resulting phosphonate groups bridge two zinc atoms. Two carboxylate groups coordinate to two zinc atoms monodentately, and thus, each ligand bridges four zinc atoms. The zinc ions are coordinated by two oxygen atoms from two carboxylate groups, and the other two oxygen atoms from the phosphonate groups, giving a tetrahedral geometry. Therefore, a three-dimensional anionic framework is constructed by the stoichiometric divalent zinc cation and the trivalent anion ligand. The dimethylammonium cation is introduced inside the framework for charge compensation, and forms a hydrogen bond with the oxygen atoms of the carboxylate groups.

When the reaction was carried out in water at 180 °C, the phosphonate group was fully deprotected, as shown in Fig. 4. The three oxygen atoms of each phosphonate group of **6** bridge three zinc ions to form a one-dimensional ladder composed of zinc ions and phosphonate groups. These ladders are linked with the bpy ligands to construct a two-dimensional layer, shown by the colours in Fig. 4(c). The two carboxylate groups remain uncoordinated and protonated, and hydrogen bonds are formed between adjacent carboxylic acid sites and crystalline water.

Reaction mechanism

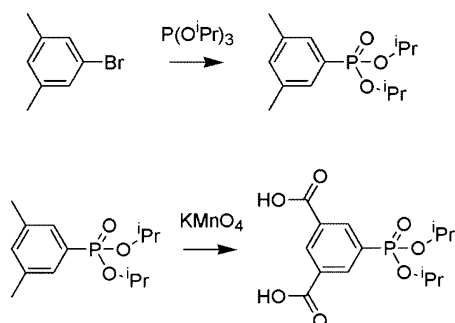
The pH of the reaction mixture of **3** changed from 3.6 to 3.1. This is rational because complexation or ester hydrolysis reactions release protons and the solution became more acidic. On the other hand, the other solutions became basic as a result of the reactions. This is probably due to the buffering effect of the ammonium released by the hydrolysis of DMF.

From the results of the NMR study, the protected ligand in **2** is itself stable under the conditions using a mixture of water and DMF at high temperature. The MOF obtained from the reaction carried out at 60 °C resulted in the complexation of the carboxylate groups and the zinc ions, while the phosphonate groups remained protected. Therefore, the complexation reaction at 60 °C was simple, as the carboxylate groups of the ligand and the bpy groups coordinated to the zinc ions to construct the MOF.

The complexation reaction at 120 °C was different. The complexation reaction occurred *via* the partial elimination of the isopropyl ligands, because these ligands become deprotected in a simple solution because of the existence of zinc ions. Metal ions can act as a Lewis acid, and thus, the deprotection occurred from the interaction of the oxygen atoms on the phosphoxyl groups with the zinc ions. The reaction at 180 °C resulted in the total deprotection of the ligand due to the high reaction temperature.

Conclusions

Diisopropylphosphoxisophthalic acid was reacted with zinc ions, and crystal structures of the compounds obtained were determined. The isopropyl groups were protected when the complexation reaction was carried out at 60 °C, while they were partially



Scheme 2 Synthesis scheme for **2**.

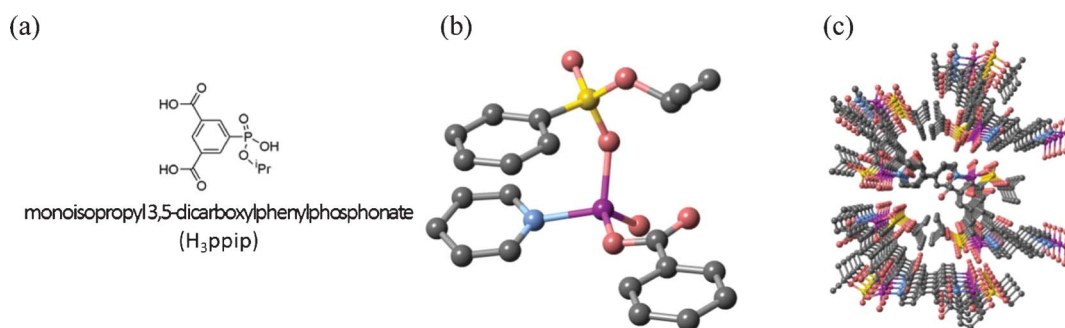
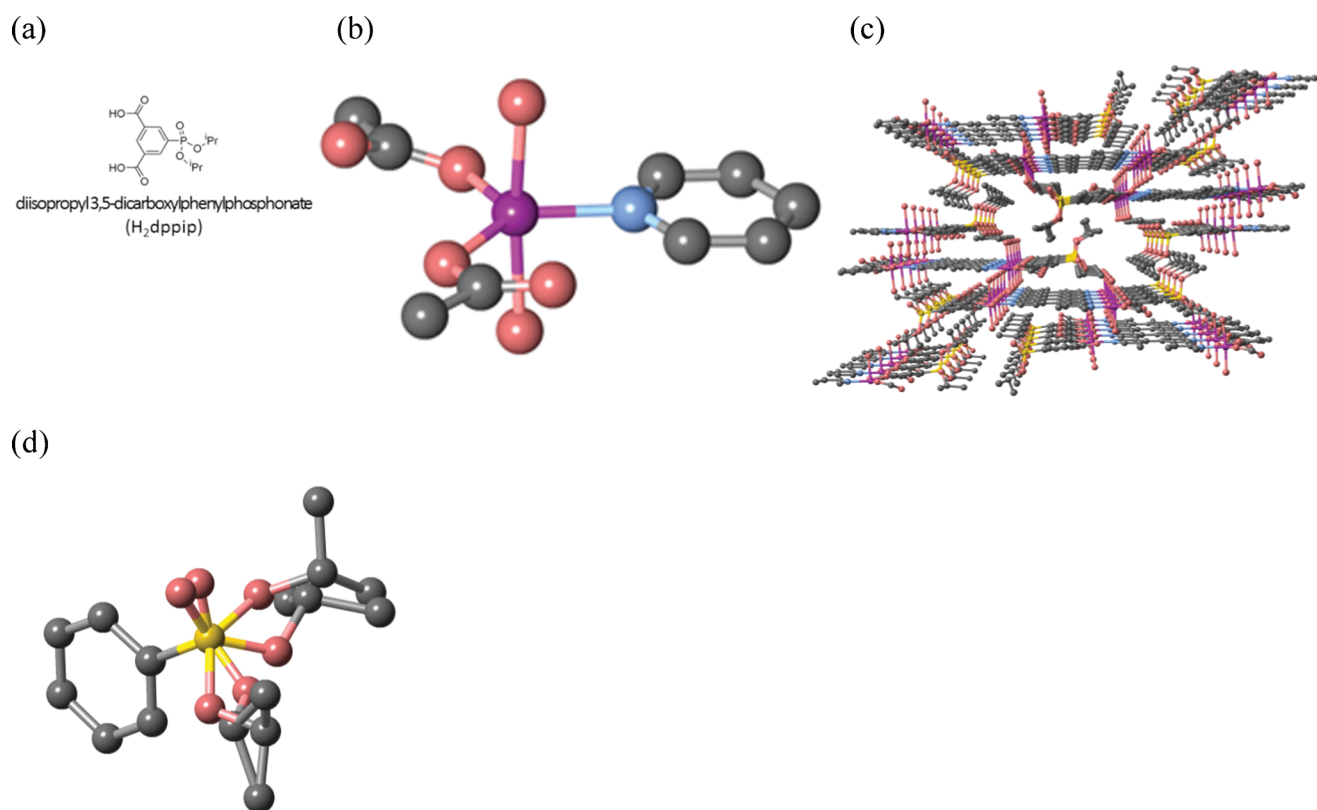


Fig. 2 (a) The chemical structure of H_3ppip and (b,c) the crystal structure of $[Zn_2(Hppip)_2(bpy)(H_2O)] \cdot 2H_2O$ (4). The white, grey, pink, blue, yellow, and purple spheres denote hydrogen, carbon, oxygen, nitrogen, phosphorus, and zinc atoms, respectively. Crystalline water and one of the disordered isopropyl branches are omitted for clarity.

deprotected in the sample prepared at $120^\circ C$. When the reaction was carried out at $180^\circ C$, the isopropyl groups were fully deprotected. From these results, four types of MOF were synthesized from the same starting materials under reactions carried out at different temperatures and in different solvents. This result provides us with information on deprotection reactions with metal ions.

Experimental

Synthetic procedure

Synthesis of diisopropyl-3,5-dimethylphosphonate (1). The reaction was executed according to a literature procedure.²⁷

Under argon atmosphere, triisopropyl phosphite (3.61 g, 17.3 mmol) was added dropwise to a suspension of 5-bromo-*m*-xylene (2.64 g, 14.3 mmol) and nickel bromide (0.61 g, 2.8 mmol) at $150^\circ C$. After a period of 3 h, the reactant was extracted with ethyl acetate and washed with water. The extract was dried using anhydrous magnesium sulfate and evaporated at 1 mmHg. Compound **1** was obtained quantitatively and used in further reactions without further purification.

Synthesis of H_2dppip (2). A mixture of **1** (1.93 g, 7.1 mmol), potassium permanganate (8.00 g, 50.6 mmol), potassium carbonate (2.22 g, 16.1 mmol) and Aliquat 336 (0.12 g) in water (70 mL) was refluxed for 3 h, and the resulting suspension

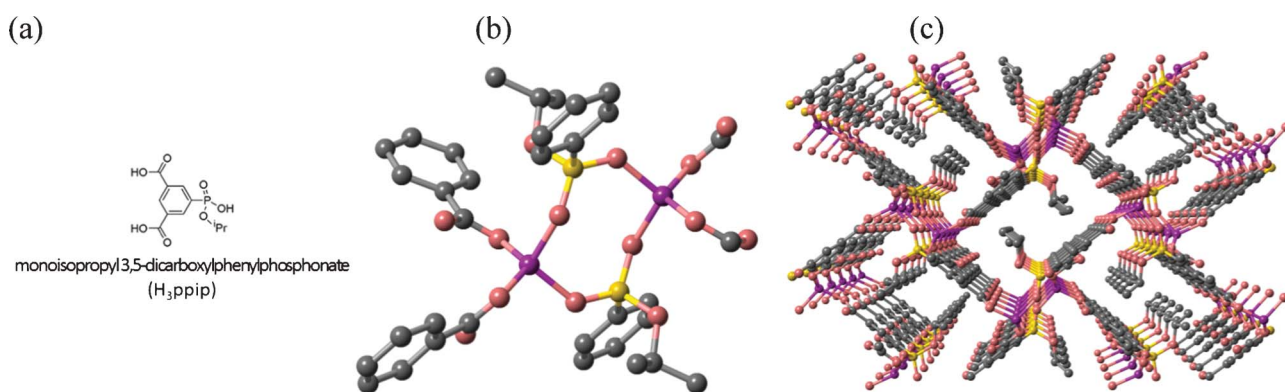


Fig. 3 (a) The chemical structure of H_3ppip and (b,c) the crystal structure of $(dma)[Zn(ppip)]$ (**5**). The white, grey, pink, blue, yellow, and purple spheres denote hydrogen, carbon, oxygen, nitrogen, phosphorus, and zinc atoms, respectively. The dma molecules and one of the disordered isopropyl branches are omitted for clarity.

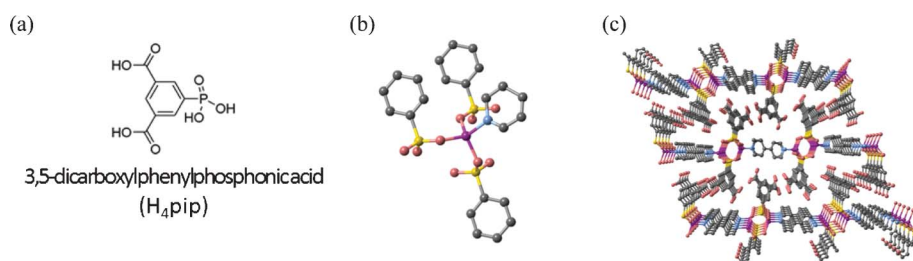


Fig. 4 (a) The chemical structure of H_4pip and (b,c) the crystal structure of $[Zn_2(H_2pip)_2(bpy)] \cdot 2H_2O$ (**6**). The white, grey, pink, blue, yellow, and purple spheres denote hydrogen, carbon, oxygen, nitrogen, phosphorus, and zinc atoms, respectively. The crystalline water are omitted for clarity.

filtered. The solution was neutralized with conc. hydrochloric acid and a white precipitate readily formed. The suspension was cooled, filtered, and dried, and a white powder is obtained. Yield = 1.55 g (66.1%). Elemental analysis calc. (found)% for $C_6H_3(COOH)_2(PO_3^iPr)_2$: C = 48.78 (48.88); H = 6.02 (5.87).

Synthesis of $[Zn_2(dppip)_2(bpy)(H_2O)_4] \cdot 2H_2O$ (3**).** Zinc nitrate hexahydrate (149 mg, 0.50 mmol), **2** (165 mg, 0.50 mmol), 4,4'-bipyridine (78 mg, 0.50 mmol), 4 mL of DMF, and 4 mL of water were placed in a screw vial and allowed to react at 60 °C for a period of one week. After cooling, colourless block crystals were obtained. The pH of the solution changed from 3.8 to 4.1 by the reaction. Yield = 31 mg (9.7%).

Synthesis of $[Zn_2(Hppip)_2(bpy)(H_2O)_2] \cdot 2H_2O$ (4**).** **4** was synthesized in almost the same procedure for **3** instead replacing DMF by ethanol under elevated temperature.

Zinc nitrate hexahydrate (149 mg, 0.50 mmol), **2** (165 mg, 0.50 mmol), 4,4'-bipyridine (78 mg, 0.50 mmol), 5 mL of ethanol, and 5 mL of water were placed in a Teflon-lined stainless autoclave and allowed to react at 120 °C for 48 h. After cooling, colourless block crystals were obtained. The pH of the solution changed from 3.6 to 3.1 by the reaction. Yield = 12 mg (5.0%).

Synthesis of $(dma)[Zn(ppip)]$ (5**).** **5** was synthesized in almost the same procedure for **3** under elevated temperature.

Zinc nitrate hexahydrate (149 mg, 0.50 mmol), **2** (165 mg, 0.50 mmol), 4,4'-bipyridine (78 mg, 0.50 mmol), 5 mL of DMF, and 5 mL of water were placed in a Teflon-lined stainless

autoclave and allowed to react at 120 °C for 48 h. After cooling, colourless block crystals were obtained. The pH of the solution changed from 3.8 to 5.5 by the reaction. Yield = 74 mg (37.3%). Elemental analysis calc. (found) for $ZnC_{13}H_{18}O_7NP$: C = 39.36 (39.09); H = 4.57 (4.53); N = 3.53 (3.53).

Synthesis of $[Zn_2(H_2pip)_2(bpy)] \cdot 2H_2O$ (6**).** **6** was synthesized in almost the same procedure for **3** under elevated temperature.

Zinc nitrate hexahydrate (149 mg, 0.50 mmol), **2** (165 mg, 0.50 mmol), 4,4'-bipyridine (78 mg, 0.50 mmol), and 10 mL of water were placed in a Teflon-lined stainless autoclave and allowed to react at 180 °C for 72 h. After cooling, colourless block crystals were obtained. The pH of the solution changed from 3.8 to 6.1 by the reaction. Yield = 149 mg (36.7%). Elemental analysis calc. (found) for $ZnC_{13}H_{11}O_8NP$: C = 38.50 (38.21); H = 2.73 (2.79); N = 3.45 (3.40).

Single-crystal X-ray diffraction measurements

The crystals under analysis were mounted on a glass fibre using silicone grease, and placed in flowing cold nitrogen gas. The diffraction data were collected using a SMART APEXII CCD area detector (Bruker) employing monochromated Mo-K α radiation (0.71073 Å) from a rotating anode source with a mirror focusing apparatus. The data were corrected for Lorentz and polarization effects and absorption using the SADABS software package. The structure was solved using direct methods and refined using the full-matrix least-squares method on F^2 using the Yadokari-2009 software package^{28,29} implemented in

Table 1 Crystallographic parameters of the compounds

Compound	3	4	5	6
Formula	C ₄₁ H ₆₀ N ₃ O ₂₂ P ₂ Zn ₂	ZnC ₁₆ H ₂₁ PNO ₁₀	C ₁₃ H ₁₈ NO ₇ PZn	Zn ₂ C ₂₆ H ₂₂ P ₂ O ₁₆ N ₂
Formula weight	1139.60	483.72	396.62	811.14
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$ (#2)	<i>P</i> $\bar{1}$ (#2)	<i>P</i> 2 ₁ / <i>n</i> (#14)	<i>P</i> $\bar{1}$ (#2)
<i>a</i> /Å	9.5545(12)	8.463(2)	9.7414(11)	5.1360(14)
<i>b</i> /Å	10.3457(13)	11.263(3)	16.0486(18)	12.264(3)
<i>c</i> /Å	13.7876(17)	11.774(3)	11.0596(12)	12.574(3)
α (°)	81.6150(10)	110.960(2)		69.555(3)
β (°)	82.8130(10)	96.523(3)	95.4460(10)	79.414(3)
γ (°)	70.7230(10)	108.941(2)		82.245(3)
<i>V</i> /Å ³	1268.4(3)	957.2(4)	1721.2(3)	727.3(3)
<i>Z</i>	1	2	4	1
Crystal size, μm^3	300 × 200 × 200	300 × 300 × 100	140 × 80 × 60	100 × 50 × 20
Unique reflections	5347	3348	3054	3259
Refined parameters	419	346	233	215
<i>D</i> _c /g cm ⁻³	1.492	1.678	1.531	1.852
<i>F</i> (000)	593	498	744	396
μ (Mo-K α)/cm ⁻¹	1.090	1.423	1.552	1.847
<i>R</i> ₁ [<i>I</i> > 2 σ]	0.0788	0.0262	0.0379	0.0384
<i>wR</i> ₂ [all reflections]	0.1709	0.0759	0.0968	0.0976
Goodness of fit	1.086	1.067	1.068	1.036
Max shift/Error	0.000	0.001	0.001	0.000
Max peak/e Å ⁻³	1.708	0.554	1.113	0.617
Min peak/e Å ⁻³	-1.200	-0.594	-0.655	-0.553
CCDC	869666	869667	869668	869669

the SHELXTL software package (Table 1).³⁰ Most atoms were refined anisotropically without any restraints; however disordered groups in compounds **3** (isopropyl groups) and **6** (pyridyl groups) were refined isotropically. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 869666–869669 for **3–6**, respectively.†

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