Mechanochemical Synthesis of Phosphonate-based Proton Conducting Metal Organic Frameworks

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Abstract:
The rational design of new type of water stable metal–organic frameworks (MOFs) as promising proton-conductors has attracted great attention owing to their applications in proton-exchange membrane fuel cells (PEMFC). Herein, we report the mechanochemical gram scale synthesis of three new mixed ligand phosphonate-based MOFs, {Co(H$_2$PhDPA)(4,4’-Bipy)(H$_2$O)-2H$_2$O}$\_n$ (BAM-1), {Fe(H$_2$PhDPA)(4,4’-Bipy)(H$_2$O)-2H$_2$O}$\_n$ (BAM-2) and {Cu(H$_2$PhDPA)(Dpe)$_2$(H$_2$O)$_2$·2H$_2$O}$\_n$ (BAM-3) [where H$_2$PhDPA = Phenylendiphosphonate 4,4’-Bipy = 4,4’-Bipyridine, and Dpe = 1,2-Di(4-pyridyl)ethylene]. Single crystal X-ray diffraction measurements revealed that BAM-1 and BAM-2 are isostructural and possess a three-dimensional (3D) network structure comprising 1D channels filled with guest water molecules. Whereas BAM-3 displays a one-dimensional (1D) network structure extended to 3D supramolecular structure by hydrogen-bonding bridging and π-π interactions. In all three structures, guest water molecules are interconnected with uncoordinated acidic hydroxylgroups of the phosphonate moieties and coordinated water molecules by means of extended hydrogen-bonding interactions. BAM-1 and BAM-2 showed gradual increase of proton conductivities with increasing temperature and reached to 4.9 × 10$^{-5}$ and 4.4 × 10$^{-5}$ S cm$^{-1}$ at 90 ºC and 98% RH. In case of BAM-3, the highest proton conductivity recorded was 1.4 × 10$^{-5}$ S cm$^{-1}$ at 50 ºC and 98% RH. Upon further heating, BAM-3 undergoes dehydration followed by phase transition to another crystalline form which largely effects the performance. All compounds exhibited a proton hopping (Grotthuss model) mechanism as suggested by their low activation energy.
Introduction

The consumption of nonrenewable fossil fuels has caused severe environmental damage. Correspondingly, the need for alternative green energy sources is more urgent than ever before. In this regard, proton exchange membrane fuel cell (PEMFC) based on hydrogen and methanol are very promising technologies. By harnessing the controlled conversion of hydrogen into electrical energy, such fuel cells generate power while producing environmentally benign water as by product. The proton conductivity of proton exchange membrane (PEM) is one of the parameter contributing to the overall efficiency of a PEMFC. The research on materials suitable for use as PEMs is therefore a dynamic field aiming to make PEMFC technologies a reality.

Materials being used as PEMs must exhibit high proton conductivity at working conditions of the targeted PEMFC. To date, Nafion and Nafion-like polymers with acidic functionality are widely used as membrane materials due to their high proton conductivity in the range of $10^{-1}$ to $10^{-2}$ S cm$^{-1}$ at higher relative humidity. However, these materials suffer from high costs, hazardous production process, and poor performance at high temperature, limiting their versatility. For further developments of PEMFC a broader range of materials is needed to extent the scope of their applications.

Recent efforts have identified crystalline porous metal organic frameworks (MOFs) as a promising class of materials for use as PEMs due to their diverse and tunable framework structures, high porosity, and physicochemical properties. Furthermore, the high crystallinity of MOFs offers an excellent opportunity to understand the proton conducting mechanism by investigating the proton transfer pathway and the structure-property relationships by using diffraction techniques and theoretical calculation. Two main approaches exist for the performance improvement of the MOF-based proton-conductive electrolytes. The first approach is based on including proton carrier guest molecules (ammonium-based cations, N-heterocycle-based molecules) into the MOFs pores. In the second approach, organic linkers with acidic functionalities (sulfono- or phosphono-groups) are included into the MOF structure. In this regard, phosphonate-based MOFs are gaining interest for designing potential proton conductor. Aryl phosphonic acid linkers provide extremely rich and robust metal-binding modes, resulting in a great variety of possible structures with unique thermal and chemical stability. Moreover, the uncoordinated oxygen atoms of phosphonic acid participate in the formation of H-bond networks with the lattice water (solvent) molecules, which facilitate the proton conduction.
Conventionally, MOFs are prepared under hydro- or solvothermal conditions which require large volume of solvents and long reaction time. These methods also suffer from poor scalability. Mechanochemical synthesis (i.e. co-grinding dry solid reagents or with negligible amount of solvents) are an attractive alternative to conventional solution-based synthesis. This environmentally benign technique has been extensively applied for rapid and high-yielding synthesis of wide range of molecules and materials including cocrystal, organometallic complexes, MOFs, and composites. Recently, mechanochemical syntheses have been utilized for preparation of porous MOFs for different functional applications, while proton conductive MOFs are still scarce.

Here, we report the synthesis of three novel MOFs of Co(II), Fe(II), and Cu(II) based on 1,4-phenylenediphosphonic acid with bipyridine-based auxiliary linkers by mechanochemical grinding using small amounts of water. Structure analysis revealed that all the frameworks consist of a defined hydrogen-bonded network formed between phosphonate and guest water molecules. These MOFs exhibit significant vapor sorption abilities. These structural features represent the conventional criterions for proton conductivity in framework materials. All three MOFs displayed high proton conductivity under humidity and over a wide temperature range. Furthermore, detailed investigations of the proton-conducting mechanisms have been presented.

**Result and Discussion**

Block shaped crystals of \{Co(H$_2$PhPA)(4,4’-Bipy)(H$_2$O)-2H$_2$O\}$_n$ (BAM-1), \{Fe(H$_2$PhPA)(4,4’-Bipy)(H$_2$O)-2H$_2$O\}$_n$ (BAM-2), and \{Cu(H$_2$PhPA)(Dpe)$_2$(H$_2$O)$_2$·2H$_2$O\} (BAM-3) were obtained at room temperature by slow diffusion technique of aqueous solutions of disodium salt of 1,4-Phenylenediphosphonic acid (Na$_2$H$_2$PhPA) and methanolic solution of 4,4’-Bipyridine (4,4’-Bipy) or 1,2-Di(4-pyridyl)ethylene (Dpe) with corresponding metal(II) solution [Co(II), Fe(II), and Cu(II)]. Single crystal X-ray analysis revealed that BAM-1 and BAM-2 are isostructural, differing only in the metal species [Co(II) or Fe(II)], hence the structure is described using BAM-1 as an example. BAM-1 crystallizes in the monoclinic space group $P2_1$ and the asymmetric unit contains one Co(II) ion, one H$_2$PhPA dianion, one 4,4’-Bipy molecule, one coordinated water molecule and two molecules of lattice water. Here, each Co(II) ion is coordinated in a slightly distorted octahedron by two nitrogen atoms (N1 and N2) from two different bridging 4,4’-Bipy, three oxygen atoms (O1, O2$^a$ and O5$^b$) from three different H$_2$PhPA dianions and one water molecule (O7) (Figure 1a). The selected bond lengths and bond angles are reported in Table S2. In each H$_2$PhPA dianion, one phosphono...
group binds to a Co(II) ion in a monodentate binding mode and the second phosphono group binds two Co(II) ions in a bridging bidentate fashion, resulting in the formation of sheets in the crystallographic bc plane (Figure 1b). The sheets are pillared by 4,4'-Bipy linkers into a three-dimensional (3D) structure with 1D channel along the b-axis that are filled with water molecules (Figure 1c). In 1D channels, the water molecules are hydrogen bonded with uncoordinated acidic OH groups of phosphonate moieties and the coordinated water (Figure 1d). Structural analysis with TOPOS reveals that BAM-1 exhibits a (3,5)-connected binodal network with Schlafli symbol $\{6^3\}{6^9.8}$ (Figure 1e). A detailed structural description of BAM-2 is provided in the supporting information (Figure S1 and Table S3).

**Figure 1.** Crystal structure of BAM-1. (a) Coordination environment around the octahedrally coordinated Co(II) center; here, Co (purple), O (red), N (blue), P (orange), and C (black). (b) View of metal phosphonate zig zag sheets along the crystallographic bc-plane. (c) Three-dimensional network structure filled with water channels along crystallographic b-axis. (d) View of well-defined hydrogen bonding interaction (green dotted lines) between lattice water, uncoordinated acidic OH of phosphonate group and the coordinated water molecules. (e) The simplified (3,5)-connected binodal network net of BAM-1. Some hydrogen atoms are omitted for clarity.

BAM-3 crystallizes in the triclinic $\bar{P}1$ space group with the Cu(II) ion is located in special position (half-occupied) along with one monodentate pendant Dpe ligand, one half H$_2$PhDPA dianion, one coordinated water and one lattice water. Here, each Cu(II) ion is coordinated in a slightly distorted octahedron by two nitrogen atoms (N1 and N1$^a$) from two monodentate
Figure 2. Crystal structure of BAM-3. (a) Coordination environment around the octahedrally coordinated Cu(II) center; here, Cu (cyan), O (red), N (blue), P (orange), and C (black). (b) View of extended 1D chain connected by bridging monodentate H₂PhDPA and pendent monodentate Dpe ligand with Cu(II) along the crystallographic b-axis. (c) Supramolecular 3D network constructed by hydrogen bonding interactions. (d) View of well-defined hydrogen bonding interaction (green dotted lines) between lattice water, uncoordinated acidic OH of phosphonate group and the coordinated water molecules. Pendent Dpe, two oxygen atoms (O1 and O1") from two different H₂PhDPA dianions and two water molecules (O5 and O5") (Figure 2a). The selected bond lengths and bond angles are reported in Table S4. Here, each H₂PhDPA dianion connects two different Cu(II) centres via bridging monodentate fashion to form 1D chain with pendent monodentate Dpe ligands along the crystallographic b-axis (Figure 2b). In the crystal packing, these 1D chains are connected to each other by hydrogen bonding interaction between the nitrogen atom (N2) of the pendent Dpe ligand and OH of phosphonate group to form three-dimensional (3D) supramolecular
arrangement (Figure 2c) with 1D channel filled with lattice water molecules along the crystallographic $a$-axis. The supramolecular structure is also stabilized by interchain $\pi-\pi$ interactions (4.2 Å). The lattice water molecules are also hydrogen-bonded with O and OH of phosphonate group in a complicated fashion (Figure 2d). It is interesting to note that in the three structures, the lattice water molecules are hydrogen-bonded with uncoordinated acidic OH of phosphonate group and the coordinated water to complicated hydrogen bonded supramolecular structures, which are the key element for proton conduction.

MOF materials are generally used in their powder state for practical applications. We therefore focused the bulk synthesis of **BAM-1** and **BAM-2** by environmentally benign mechanochemical synthesis using water as a liquid assisted grinding (LAG) liquid in custom-made acrylic jars along with one stainless steel balls. Mechanochemical grinding of Co(OAc)$_2$·4H$_2$O with 4,4’-Bipy and H$_4$PhDPA for 30 min produces **BAM-1**. The acetate ion acts as a base, deprotonating H$_4$-PhDPA, yielding volatile acetic acid. The evaporation of the acetic acid along the second byproduct water effectively pushes the equilibrium to the products side, leaving compound **BAM-1** as the only solid phase (Scheme 1). The milling reaction was conducted first at a 100 mg scale. Analysis of the PXRD pattern revealed excellent agreement with the simulated PXRD pattern, thus the synthesis was upscaled tenfold and the PXRD was still in excellent agreement with the simulated pattern (Figure 3). In case of mechanochemical synthesis of **BAM-2**, FeCl$_2$·4 H$_2$O was reacted with 4,4’-Bipy and H$_4$PhDPA instead of

**Scheme 1**: Mechanochemical syntheses of **BAM-1** (top), **BAM-2** (middle) and **BAM-3** (bottom). The grinding conditions are summarized above the reaction arrow after ref. 40.
Fe(OAc)$_2$ because of its air instability. Starting from FeCl$_2$·4H$_2$O we added two equivalents of NaHCO$_3$ as a base to deprotonate the H$_2$-PhDPA, forming NaCl as the second solid product of the reaction (Scheme 1). After 30 min milling, the product shows reflection of BAM-2 as well as NaCl (Figure S5). Consecutive washing of the milled powder with water, pure form BAM-2 is instead achieved (Figure S3 and Figure S5). BAM-3 has mechanochemically been synthesized by the same procedure as BAM-1 using Cu(OAc)$_2$·H$_2$O instead Co(OAc)$_2$·4H$_2$O. A blue powder was obtained after 30 min of grinding (Scheme 1). The PXRD pattern is also well corroborated with the simulated PXRD pattern (Figure 3).

![PXRDs of mechanochemically synthesized BAM-1 (black), BAM-2 (red) and BAM-3 (blue) in 100 mg and 1 g scale compared to their simulated pattern from single crystal.](image)

**Figure 3.** PXRDs of mechanochemically synthesized BAM-1 (black), BAM-2 (red) and BAM-3 (blue) in 100 mg and 1 g scale compared to their simulated pattern from single crystal.

To study the thermal stability of all three MOFs, thermogravimetric analyses (TGAs) have been performed in a temperature range of 25–1000 °C under a N$_2$ atmosphere with 10 °C/min heating rate. BAM-1 showed first weight loss 3.63% of its initial mass at 95°C, which corroborates the removal of one guest water molecules (calc. 3.56%) (Figure 4). The partial dehydrated framework of BAM-1 is stable up to 95°C. The second step was observed when heated until 198°C with weight loss 6.91%, indicating the loss of both lattice water molecules (calc. 6.56%). A subsequent weight loss takes place upon further heating and is difficult to assign to a specific weight loss step, signifying framework decomposition. *In situ* variable-temperature powder X-ray diffraction (VT-PXRD) studies also revealed that the diffraction pattern of BAM-1
remained almost unchanged except lowering the intensity below 190°C (Figure S6). Upon further heating, the crystallinity of the framework is highly reduced and transformed to an unidentified non crystalline product after the loss of all coordinated and guest water molecules. Similarly, **BAM-2** shows a first weight loss of 3.73% mass at 105°C, which can be attributed to the loss of one guest water molecule (calc. 3.59%) (Figure 4). A subsequent weight loss takes place upon further heating and the framework displays 7.40% mass loss at 175°C (calc. 7.17%), which corresponds to release of another guest water molecules, followed by to decomposition to unidentified product. VT-PXRD studies also showed that **BAM-2** retains its good crystalline nature until 130 °C, and then decrease in intensity with disappearing of some peaks of the PXRD patterns were observed, signify the decomposition of the framework at high temperature (~190 °C) (Figure S7). In case of **BAM-3**, it has interesting stepwise thermal profile. First weight loss was started at 90 °C and the framework loses 9.88% mass at 140 °C (calc. 9.78%), which corresponds to the two guest and two coordinated water molecules. Then the dehydrated framework is stable up to 190 °C (Figure 4). The VT-PXRD studies showed that many new reflections in the PXRD pattern appeared compared to the pristine pattern at 90 °C. A complete structural change was observed at 100 °C, owing to the removal of guest and coordinated water molecules from the framework (Figure S8). At 180 °C, another crystalline phase transition began and ended at 200 °C. The composition of this structures needs further investigation.

![Thermogravimetric analysis of BAM-1, BAM-2, and BAM-3.](image)

**Figure 4.** Thermogravimetric analysis of **BAM-1**, **BAM-2**, and **BAM-3**.
To study the porous nature of all three frameworks, N₂ sorption studies at 77 K were carried out on partially dehydrated frameworks. Due to the decomposition of the frameworks, as evident from thermal and VT_PXRD studies, the complete dehydration of all these compounds is not possible. The N₂ isotherms of BAM-1, BAM-2 and BAM-3 show type II profiles with the final uptakes of 45, 111, and 59 cc g⁻¹, respectively, suggesting only surface adsorptions, Figure S9. The BET surface areas are determined and show relatively low with 14.0403 m² g⁻¹ and 26.1758 m² g⁻¹ for BAM-1 and BAM-2, respectively. Furthermore, to check the water affinity of all three frameworks, dynamic vapor sorption (DVS) using water have been carried out at room temperature (Figure 5). BAM-1 showed an uptake of ~45 cm³ g⁻¹ at very low pressure (P/P₀ ≈ 0.025), which suggests very high-water affinity of the framework. After that, the H₂O adsorption profile of BAM-1 displays a gate opening type profile P/P₀ ≈ 0.25 and the final uptake reaches up to 163 cm³ g⁻¹ which corresponds to 3.7 molecule of H₂O per formula. BAM-2 also exhibit high water affinity towards water at very low pressure and adsorbs ~62 cm³ g⁻¹ at P/P₀ ≈ 0.05. After that, a steep uptake was noticed and the final uptake amount reaches up to 163 mL g⁻¹, which also corresponds to 3.7 water molecules per formula. In case of BAM-3, water adsorption isotherm exhibits gate-opening at P/P₀ values of 0.15 and the final uptake amounts of 150 cm³ g⁻¹, which correspond to 3.4 molecules of H₂O per formula. The desorption curves of all three compound did not follow the adsorption pathway and exhibited large hysteresis with kinetic trapping of water molecules due to the small pore windows in the frameworks.

![Figure 5](image-url)  
*Figure 5. Water uptake of BAM-1, BAM-2 and BAM-3 measured at 298 K; filled and empty symbols represent the adsorption and desorption isotherms, respectively.*
The well-defined hydrogen bonded water channels in the structure, their good thermal stability and strong water affinity of BAM-1, BAM-2, and BAM-3, prompted us to study their proton conductivity. Measurements were performed by alternating current (AC) impedance spectroscopy, using pelleted powder samples over a large range of temperatures (25-90 °C) and relative humidity (RH) levels (68-98%) as shown in Figure 6 and Figures S10-S12. The EIS results were represented in Nyquist form where \( Z'' \) (imaginary component of the impedance) is plotted as the function of \( Z' \) (real component of impedance). All the Nyquist plots showed a semicircle at the high frequency region followed by an elongated tail at the low frequency region. The Nyquist plots were fitted to a suitable equivalent circuit ((R1/Q1) + (R2/Q2) + Q3), where R1 and R2 represent resistance and Q1, Q2 and Q3 represent constant phase elements as shown in the inset figure. On fitting, the Nyquist plots resolved into a well fitted high frequency semicircle with lower radius and a low frequency semicircle with a high radius, representing the resistance of the material analogous to the proton conductivity and the contact resistance respectively. The conductivities were calculated from the fitted high frequency semicircle of the Nyquist plots and were found to be highly dependent on the relative humidity (Figures S10-S12). The strongly hydrogen bonded guest water molecules are poorly labile at low humidity. However, their mobility increases with RH, resulting in enhanced proton conductivity performance. For instance, all the frameworks reported here, showed very poor proton conductivity at 25 °C and low RH. When the RH was increased, keeping the temperature constant, the conductivity of BAM-1, BAM-2 and BAM-3 increased with 2-fold order and reached \( 2.1 \times 10^{-6}, 3.4 \times 10^{-6} \) and \( 5.1 \times 10^{-6} \) S cm\(^{-1} \), respectively at 98% RH (Figures S10-S12). Moreover, on gradually increasing the temperature (at constant RH of 98%), the conductivities of BAM-1 and BAM-2 have been observed to increase, which is a typical proton conductivity behavior.\(^{9,10} \) At 90 °C and 98% RH, the conductivity of BAM-1 and BAM-2 reached maximum values of \( 4.9 \times 10^{-5} \) (Figure 6a) and \( 4.4 \times 10^{-5} \) S cm\(^{-1} \) (Figure 6b), respectively. In case of BAM-3, with increasing temperature the conductivity also increased and reached a maximum value of \( 1.4 \times 10^{-5} \) S cm\(^{-1} \) at 50 °C and 98% RH (Figure 6c). The proton conductivity remains almost constant with further increase in temperature, but suddenly drops at 90 °C to \( 7.6 \times 10^{-6} \) S cm\(^{-1} \). This is consistent with the phase transition observed by VT-PXRD in which lattice water, and hence the hydrogen bonding network, is lost, Figure S8. Following conductivity measurements, PXRD patterns indicate no irreversible structural transition in any of the reported compounds.
The activation energy ($E_a$) is the key parameter to understand the proton transport mechanism. For example, proton conduction in materials with $E_a$ less than 0.4 eV proceeds by transferring protons between the H-donor and acceptor, i.e., Grotthuss mechanism. In contrast, for material with $E_a$ greater than 0.4 eV, proton conduction proceeds through the vehicle mechanism wherein protons transfer via the diffusion of protonated carriers. At 98% RH, the $E_a$ extracted from Arrhenius plots were 0.37 eV for BAM-1, 0.23 eV for BAM-2 and 0.10 eV for BAM-3, respectively (Figure 6d). These values suggest that proton conduction proceeds by the Grotthuss mechanism in all three compounds. This is presumably facilitated by the well-defined hydrogen bonding between guest waters with uncoordinated OH groups of the phosphonates and coordinate water molecules.

![Figure 6](image.png)

**Figure 6.** Nyquist plot for (a) BAM-1, (b) BAM-2, and (c) BAM-3, respectively, at different temperatures and at 98% RH. (d) ln($\sigma$T) vs 1000T$^{-1}$/K plots at 98% RH for BAM-1, BAM-2, and BAM-3, respectively. The solid lines signify the best fit of the data.

**Conclusion**

In summary, we have synthesized three novel proton-conductive MOFs, \{Co(H$_2$PhDPA)(4,4'-Bipy)(H$_2$O)$_2$·2H$_2$O\}$_n$ (BAM-1), \{Fe(H$_2$PhDPA)(4,4'-Bipy)(H$_2$O)$_2$·2H$_2$O\}$_n$ (BAM-2), and \{Cu(H$_2$PhDPA)(Dpe)$_2$(H$_2$O)$_2$·2H$_2$O\}$_n$ (BAM-3) in gram scale by environmentally benign
mechanochemical methods using minimum amount of added water. In all the framework structures, extended hydrogen-bonding interactions were identified between uncoordinated acidic OH of phosphonate group and coordinated water molecule in the 1D channels. These hydrogen-bonding could facilitate the proton hopping mechanism. The proton conductivities were recorded to be $4.9 \times 10^{-5}$ and $4.4 \times 10^{-5}$ S cm$^{-1}$ at 90 °C and 98% RH for the 3D isostructural BAM-1 and BAM-2, respectively. In contrast, BAM-3 recorded highest proton conductivity $1.4 \times 10^{-5}$ S cm$^{-1}$ at 50 °C and 98% RH, and after that it underwent dehydration followed by crystalline phase transition, which largely effects the proton conductivity.

The present work highlights the fact that green mechanochemical synthesis could be an alternative method to conventional solvent assisted synthesis of designing proton conductive MOFs with appropriate organic linkers for the generation of green energy.

Experimental Section

Growth of single crystals

\{Co(H$_2$PhDPA)(4,4'-Bipy)(H$_2$O).2H$_2$O\}$\_n$ (BAM-1). An aqueous solution (10 ml) of the disodium salt of 1,4-Phenylenediphosphonic acid (Na$_2$H$_2$PhDPA;1 mmol, 282.04 mg) was added to a methanolic solution (10 ml) of 4,4'-Bipyridine (4,4'-Bipy;1 mmol, 156.19 mg) and stirred for 30 minutes to ensure even mixing. In a separate beaker an aqueous solution (10 ml) of Co(NO$_3$)$_2$·6H$_2$O (1 mmol, 291.03 mg) was prepared. Hereafter, 6 ml of the above mixed linkers solution was slowly and carefully layered over 3 ml of the metal salt solution. Pink needle-shaped crystals were obtained from the interface of the two layers after one week. After extraction the crystals were washed with methanol and air dried.

\{Fe(H$_2$PhDPA)(4,4'-Bipy)(H$_2$O).2H$_2$O\}$\_n$ (BAM-2). The synthesis of compound BAM-2 is similar to compound 1, except for the metal salt, which was changed to FeCl$_2$·4H$_2$O (1 mmol, 198.81 mmol). Dark brown needle-shaped crystals were obtained at the junction of both solutions after one week.

\{Cu(H$_2$PhDPA)(Dpe)$_2$(H$_2$O)$_2$.2H$_2$O\}$\_n$ (BAM-3). Here also same method was adopted as BAM-1 using 1,2-Di(4-pyridyl)ethylene (Dpe; 1 mmol, 182.23 mg) and Cu(NO$_3$)$_2$·6H$_2$O (1 mmol, 291.04 mg) instead of 4,4'-Bipyridine and Co(NO$_3$)$_2$·6H$_2$O, respectively. Blue colored plate single crystals were extracted, washed with methanol and air dried after one week.

Mechanochemical synthesis by liquid assisted grinding (LAG)

BAM-1. In a typical grinding experiment Co(OAc)$_2$·4H$_2$O (0.155 mmol, 38.7 mg), H$_4$-PhDPA (0.155 mmol, 37.0 mg) and 4,4'-Bipyridine (0.155 mmol, 24.3 mg) were placed into an acrylic
milling jar with polyoxymethylene caps (4 ml approximate volume) alongside one stainless steel milling ball (7 mm diameter). After adding 20 µL of milliQ water, the closed milling jar was placed into a Pulverisette 23 vertical ball mill (Fritsch GmbH, Germany). The mixture was ground at a frequency of 50 Hz for 30 mins and the obtained damp, pink powder was washed three times with water and air-dried subsequently.

**BAM-2.** It was synthesized by same water assisted milling method as that for **BAM-1** using FeCl$_2$·4H$_2$O (0.131 mmol, 26.1 mg) and NaHCO$_3$ (0.263 mmol, 22.1 mg) instead of Co(OAc)$_2$·4H$_2$O. The obtained dark brown powder was washed five times with water and air-dried.

**BAM-3.** It was synthesized similar to **BAM-1** using Cu(OAc)$_2$·2H$_2$O (0.125 mmol, 22.6 mg) and 1,2-Di(4-pyridyl)ethylene (0.249 mmol, 45.4 mg) instead of Co(OAc)$_2$·4H$_2$O and 4,4’-Bipyridine. The obtained blue powder was washed three times with water and air-dried.

For the mechanochemical synthesis of all three compounds in 1 g scale the reactants masses are increased tenfold, using a stainless-steel milling jar (10 mL volume) and two stainless-steel milling balls (10 mm, 4g each), while keeping a frequency of 50 Hz and milling time of 30 min.

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**Conflict of interest**

There are no conflicts of interests from the authors.

**References**


TOC

Mechnochemical synthesis

Metal(II) + \[\text{Phosphoric acid} \rightarrow \text{BAM-1/BAM-2} \]

BAM-3