Solvent induced rapid modulation of micro/nano structures of metal carboxylates coordination polymers: mechanism and morphology dependent magnetism

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Rational modulation of morphology is very important for functional coordination polymers (CPs) micro/nanostructures, and new strategies are still desired to achieve this challenging target. Herein, organic solvents have been established as the capping agents for rapid modulating the growth of metal-carboxylates CPs in organic solvent/water mixtures at ambient conditions. Co-3,5-pyridinedicarboxylate (pydc) CPs was studied here as the example. During the reaction, the organic solvents exhibited three types of modulation effect: anisotropic growth, anisotropic growth/formation of new crystalline phase and the formation of new crystalline phase solely, which was due to the variation of their binding ability with metal cations. The following study revealed that the binding ability was critically affected by their functional groups and molecular size. Moreover, their modulation effect could be finely tuned by changing volume ratios of solvent mixtures. Furthermore, they could be applied for modulating other metal-carboxylates CPs: Co-1,3,5-benzenetricarboxylic (BTC), Zn-pydc and Eu-pydc etc. Additionally, the as-prepared Co-pydc CPs showed a fascinating morphology-dependent antiferromagnetic behavior.

Coordination polymers (CPs), formed by metal cations linking with organic bridging ligands, are well known due to their potential applications in catalysis, nonlinear optics, gas storage and medicine delivery etc.1–6. Recently, downsizing the CPs to micro- and nano-regime has gained growing attention owing to their highly tailorable morphology and versatile compositions7–25. For example, Maspoch and his coworkers have developed a general spray-drying strategy to fabricate hollow superstructures assembled by kinds of CPs nanocrystals25. Moreover, the micro- or nanoscale CPs have also shown promising functionalities, such as optical properties4, ion exchange6, drug delivery20, or magnetism14,23. Very recently, highly conductive [Pt2I(S2CCH3)4]n CPs nanoribbons have been reported, which could be candidate materials for applications in molecular electronics26,27. To date, although remarkable progress has been made for CPs micro- and nanostructures, general methods for effective modulation of their morphology are still desired.

At molecular level, downsizing the CPs could be regarded as the suppression of infinite extension for coordination framework28–30. To achieve this target, some reports focused on the modulation growth in confined location such as microemulsion7,16, microfluidic chip31 or surface of substrate32. While others offered another effective blocking strategy by using capping agents such as pyridine molecules33, modulating ligands29,34 or surfactants35–37. The key point is that the capping agent must be able to suppress the growth of certain crystal facet by binding with metal cations or organic ligands in the coordination framework. These works have opened an avenue for effective morphology modulation of CPs, and inspired us to further find other capping agents with more versatile control effect. Besides that, in-depth study of the modulation mechanism of capping agents is another challenging task and critical for their applications28,29. It is known that many organic solvents could bind
with metal cations and form stable complexes\textsuperscript{38}, which is coincided with the requirement of capping agents. Recently, Schröder et al. have demonstrated that the binding ability between organic solvents and metal cations could obviously affect the dissolution-recrystallization process of CPs\textsuperscript{39}. These clues motivated us to exploit the organic solvents as capping agents for modulating the crystal growth of CPs. Although several reports have mentioned the intriguing morphology control of CPs in mixed solvents\textsuperscript{40–44}, the solvents played auxiliary roles compared with other reaction parameters, and seldom of them recognized the solvents as the capping agents and fully discussed their modulating effects.

In this article, we have selected series of organic solvents such as EtOH, THF, DMF, MeCN and DMSO etc. as the capping agents to modulate metal-carboxylates CPs in organic solvent/water mixtures at ambient conditions. As an example, cobalt(II)-3,5-pyridinedicarboxylate (pydc) CPs (including: Co(Pydc)(H\textsubscript{2}O)\textsubscript{2}) \textsubscript{2}H\textsubscript{2}O, {Co(Pydc)(H\textsubscript{2}O)}\textsubscript{4} \textsubscript{2}H\textsubscript{2}O and Co(Pydc)\textsubscript{2}(OH)\textsubscript{6} \textsubscript{2}H\textsubscript{2}O-1.2DMSO) was carefully studied here, and kinds of interesting micro- and nanostructures have been prepared within 20 minutes. It is shown that the modulation effect could be divided into three types: anisotropic growth, anisotropic growth/formation of new crystalline phase and the formation of new crystalline phase solely. Detailed analysis proved that it was decided by the binding ability of organic solvents with cobalt cations. The following study further demonstrated that this binding ability was crucially affected by the functional groups and molecular size of organic solvents. Time dependent study displayed the modulation kinetics of CPs, indicating that the organic solvents played their roles originated from the nucleation stage. Moreover, the exquisite modulation growth of CPs could be achieved by changing the volume ratios of organic solvents in binary mixtures. Furthermore, this strategy could be facially applied to fabricate other metal-carboxylates CPs micro- and nanostructures at ambient conditions, including Co-BTC, Zn-pydc as well as Eu-pydc etc.. Additionally, the as-prepared Co-pydc CPs displayed an interesting morphology-dependent antiferromagnetic behavior.

**Results**

Several organic solvents such as EtOH, THF, MeCN, DMF and DMSO have been selected as the capping agents, and the modulation growth of Co-pydc CPs were carefully studied here as an example. Briefly, the metal cations and pydc ligands were firstly dissolved in certain organic solvent-water mixtures, respectively. Then the reactions terminated within 1–20 minutes once they mixed at ambient conditions (Table S1–S3). Rapid precipitation usually resulted in irregularly shaped and randomly aggregated CPs particles due to the simultaneously occurrence of nucleation and crystal growth\textsuperscript{46}. However, in our synthesis, the as-prepared CPs showed well-defined morphology by using organic solvents as the capping agents (Fig. 1).

In the control experiment, Co-pydc CPs obtained in pure water were nanofibers with the length of 5–10 \textmu m and the diameter of 200–500 nm (Fig. S1, denoted as S-H\textsubscript{2}O). When using EtOH as the capping agent, the as-prepared CPs was multi-pod microrods with the diameter of 500 nm–1 \textmu m (Fig. 1, a1–a3, denoted as S-EtOH). When using THF, the products featured as microtubes with the length of more than 20 \textmu m and the diameter of 2–5 \textmu m (Fig. 1b1, denoted as S-THF). The magnified SEM highlighted a typical microtube, which showed a rectangular cross section (Fig. 1b2). Moreover, their TEM image also confirmed the tube nature by displaying a pale inner part (Fig. 1b3). While for DMF, the size of the CPs obviously decreased, and hierarchical nanoblades-assembly were produced (Fig. 1, c1–c3, denoted as S-DMF), which contained nanoblades as subunits with thickness of less than 300 nm (Fig. 1c2 and 1c3). When using MeCN, the size of the CPs was further decreased. The microspheres (2–4 \textmu m in diameter) assembled by uniform nanopolyhedrons dominated the products (Fig. 1, d1–d3, denoted as S-MeCN). The magnified SEM image showed the size of nanopolyhedron was ~50 nm (Fig. 1d2) indicating a strong suppression of crystal growth by MeCN. While for DMSO, uniform rhombic lamellas were obtained (Fig. S2, denoted as S-DMSO), and it is shown that the lamella had a major axis of ~5 \textmu m and minor axis of ~3 \textmu m with a blade-like edge (~200 nm) (Fig. S2). Above all, using organic solvents as the capping agents contributed us five kinds of CPs micro- and nanostructures. Moreover, according to the morphology evolution of CPs, it could be preliminarily proposed that as the capping agents, DMF, MeCN and DMSO had stronger suppression effect for crystal growth than EtOH and THF. However, the morphology evolution of CPs is not adequate for discovering the modulation effect of organic solvents, and careful study for their structure and composition is necessary.

Therefore, PXRD, FT-IR, elemental analysis (EA) and thermogravimetric analysis (TGA) were performed here to resolve the structure and compositions of Co-pydc CPs. The PXRD patterns showed that all the Co-pydc CPs were well-crystallized (Fig. 2, Fig. S3) in spite of the moderate reaction condition, and they were divided into three groups. The first group consisted of S-H\textsubscript{2}O, S-EtOH and S-THF, which were indexed to the bulk Co(pydc)(H\textsubscript{2}O)\textsubscript{2} (simulated curve of Co-pydc CPs prepared in organic solvent/water mixture (v:v = 15:10), (a1–a3) EtOH, (b1–b3) THF, (c1–c3) DMF, (d1–d3) MeCN, the total volume was 25 mL.

![Figure 1](https://example.com/figure1.png)
ing vibrations of carboxylate groups, respectively. It evidenced the chemical compositions (details see Fig. S8 and Table S5). Notably, the S-DMSO had higher weight loss (nearly 40%) than other CPs (Table S4). For CPs in the first and second group, their EA results were agreed with their chemical formulas, which confirmed the accuracy of EA analysis. It is known from the FT-IR experimental values were agreed with their chemical formulas, which confirmed their chemical compositions (details see Fig. S5). The PXRD pattern of S-DMSO was different from other CPs and could not be assigned to any known crystals (Fig. S3), thus we assigned this sample as the third group. Therefore, from the PXRD patterns, it is suggested that DMF, MeCN and DMSO should have stronger binding ability with metal cations than EtOH and THF due to the induced formation of new crystalline phase, which was consistent with the size changing of CPs shown in SEM images.

The FT-IR spectra of Co-pydc CPs resembled to each other providing their similar chemical compositions and chemical bonding (Fig. S6). The broad band at 3430 cm⁻¹ could be assigned to coordinated water and hydrogen bond, which confirmed the presence of water in the samples. The strong bands centered at 1610 cm⁻¹ and 1380 cm⁻¹ were ascribed to the asymmetric and symmetric stretching vibrations of carboxylate groups, respectively. It evidenced the presence of pydc ligands in these compounds. The band at 500 cm⁻¹ could be assigned to Co-O and symmetric C-C-O, indicating the coordination of Co cations and carboxylates ligands.

The chemical compositions of Co-pydc CPs were determined by EA results (Table S4). For CPs in the first and second group, their experimental values were agreed with their chemical formulas, which confirmed the accuracy of EA analysis. It is known from the FT-IR spectra that cobalt cations coordinated with pydc ligands and water molecules in the CPs frameworks (Fig. S6). Hence, for the third groups, the empirical formulas of CPs could be proposed as Co(pydc)₀.₇(OH)₀.₆·H₂O·1.2DMSO. The S-DMSO showed special chemical composition by containing DMSO molecules, which was evidenced by XPS S2p spectrum (Fig. S7). TGA analysis further confirmed their chemical compositions (details see Fig. S8 and Table S5). Notably, the S-DMSO had higher weight loss (nearly 40%) than other CPs (~20%) after 300 °C, which further proved the intercalating of DMSO molecules in its coordination framework. As a result, it is found that: i) the first group of CPs were further confirmed to have the same chemical composition; ii) DMF and MeCN induced the formation of new compound by changing the number of coordinated water in the CPs framework; iii) DMSO intercalated in the coordination framework and thus formed a new crystalline phase, which suggested its stronger binding ability than other organic solvents.

**Discussion**

Based on the morphology, structure and composition analysis of Co-pydc CPs, the organic solvents used here could be divided into three types as follow (Fig. 3, coincided with three groups of CPs referred above):

**Type I (EtOH and THF):** They had relative weak binding ability with metal cations, so S-EtOH and S-THF had the same crystalline phase and compositions to S-H₂O. However, they could selectively absorb on certain crystalline facet of the CPs, and induce the anisotropic growth of CPs, which resulted in the formation of multi-pod microrods and microtubes.

**Type II (DMF and MeCN):** They had medium binding ability with metal cations, which resulted in the size decreasing of CPs and the formation of new crystalline phase. It is proposed that this type of organic solvent could bind with metal cations and compete with pydc ligands simultaneously, which greatly perturbed the crystal growth of CPs and finally changed their crystalline phase. However, the coordinating numbers of pydc ligands in S-DMF and S-MeCN were identical with ones obtained using type I solvents, and their binding ability with metal cations was not strong enough to make them intercalate in the coordination frameworks.

**Type III (DMSO):** DMSO had the strongest binding ability with metal cations owing to its intercalation in the coordination frameworks.

As a result, it is demonstrated that for the binding ability with metal cations, there existed: Type I (EtOH, THF) < Type II (DMF, MeCN) < Type III (DMSO). However, this clue was not enough for their further applications. So discussion at molecular level is necessary. One crucial factor is the functional groups of organic solvents. It is known that the nucleophilicity of functional groups could greatly affect their binding ability with metal cations. Hence the organic solvents used here could be distinguished by analyzing their nucleophilicity. The functional groups for type I solvents are -OH and ether oxygen, their nucleophilicity was weaker than the C=O and -CN groups in type II solvents. While for DMSO, the -S=O was easier to donate lone pair electrons of oxygen atoms to the empty d orbits of Co²⁺, which is responsible for its strongest binding ability with cobalt cations. Moreover, the correlation of functional groups and binding ability were also evidenced by the experiments. For this purpose, several samples were obtained using kinds of alcohols with different “R” groups (Table S6), and they showed similar rod-like morphology as well as identical PXRD patterns. It suggested functional groups of organic solvents were crucial in deciding the morphology and crystalline phase of the CPs (Fig. S9 and Fig. S10).

However, when using MeOH as the capping agent, its product displayed different morphology from those obtained using other alcohols (Fig. S11a and S11b). Moreover, its PXRD pattern showed that it had the same crystalline phase to S-MeCN, which belonged to the type II solvents (Fig. S11e). Considering MeOH had the smallest “R” group among the alcohols, the molecular size might be another structural factor. It is known that smaller molecular size would bring less steric effect for organic molecules when binding with metal cations, and vice versa. Hence, when the molecular size became smaller, the binding ability of organic solvent with metal cations would be increased. That is why MeOH resulted in the similar product compared with type II solvents (medium strong). Another example of molecular size effect is N,N-dimethylacetamide (DMA), which possessed the same functional group to DMF but with larger molecular size. As shown in Fig. S11c and S11d, the CPs obtained using DMA were mixtures of microrods/multi-pod microrods, which closely resembled those obtained using alcohols (Fig. 2, a1–a3 and Fig. S9). Moreover, its PXRD pattern was identical with S-EtOH (Fig. S11f), which further confirmed increasing of the
molecular size would weaken the binding ability of solvent molecules with metal cations. As a result, it is demonstrated that i) the organic solvents used here were divided into three types according to their binding ability with metal cations, which decided the morphology and crystalline phase of the CPs; ii) this binding ability was crucially affected by the nucleophilicity of their functional groups; iii) the molecular size of organic solvents could also affect their binding ability with metal cations. When it was smaller, the binding ability would be increased, and vice versa.

To study the modulation kinetics of organic solvents, time-dependent experiments were performed using THF, MeCN and DMSO as the capping agents, respectively. It is found that the CPs could get their embryonic form within a short time (1 min), which suggested that organic solvents played their roles early in the nucleation stage, and decided the morphology and structure of CPs during subsequent crystal growth process (details see Fig. S12–Fig. S15).

It is a challenging task to precisely control the morphology of CPs micro/nanostructures. Herein, by varying the volume ratios of solvent-water mixtures, the morphology of CPs could be finely controlled. THF, DMF and DMSO were carefully studied here as examples. When using THF and the volume ratio was 10:15 (THF/H₂O), the final products were short microrods with the diameter of 1–3 μm and length of 5–10 μm (Fig. S16a). When its volume ratio was 5:20, the main products were nanofibers with a high aspect ratio (diameter: 200 nm, length: 5–10 μm, Fig. S16b). The PXRD patterns showed that all these CPs had the same crystalline phase (Fig. S17a). When using DMF and the volume ratios was 10:15 and 5:20, respectively (Fig. S16c and S16d), and these samples also had the same crystalline phase (Fig. S17b). The morphology control using other solvents was also studied here such as ethanol and DMA (Fig. S18). Results showed that varying of their volume ratios could also change the morphology of as-prepared CPs, but the change was not so obvious like other solvents did. Above description elucidated that the morphology of CPs were highly dependent on the quantity of organic solvents, which further confirmed their roles as the capping agents. Additionally, when the quantity of organic solvents decreased, the reaction time was greatly prolonged (Table S2). For example, when the volume ratio was 5:20 (DMSO: H₂O), its reaction time was 60 min, which meant that only the volume ratio of organic solvent was high enough, the rapid formation of CPs could be achieved.

As the versatile capping agents, the organic solvents could be applied to modulate other metal-carboxylates CPs such as Co-BTC (Co₃(BTC)₂·12H₂O and Co₃(BTC)₂·4DMSO, Fig. 4, a1–a5, Fig. S19a, Fig. S20a), Zn-pydc (Zn(pydc)·2H₂O, Fig. 4, b1–b5, Fig. S19b, Fig. S20b) and Eu-pydc ([Eu(pydc)₂(H₂O)]·3H₂O, Fig. 4, c1–c5, Fig. S19c, Fig. S20c). All the CPs products were obtained at ambient conditions, and exhibited diverse morphologies (Fig. 4). Moreover, it is found that the modulation effect of organic solvents for each kind of CPs might be different from each other. For example, type I solvent and type II solvents for Co-pydc CPs induced the formation of same crystalline phase for Co-BTC CPs (Co₃(BTC)₂·12H₂O). However, DMSO was still intercalated into the coordination framework and induced the formation of Co₃(BTC)₂·4DMSO, which further confirmed its stronger binding ability with metal cations than other solvents. This interesting phenomenon was ascribed to the variation of binding ability for metal-organic solvent pairs and would be discussed in future.

Recently, coordination polymer magnets and magnetostructural relationship have attracted considerable attention due to their unusual molecular structures and physical properties. However, there was very few reports discussed the magnetic properties of...
Herein, the magnetic measurements were carried out and analyzed for Co-pydc CPs. As shown in Fig. 5, the magnetic susceptibility of S-MeCN, S-MeOH and S-DMF were measured at 1 kOe and the temperature range of 2–300 K. The $\chi_m T$ curves of the three samples displayed similar trend and decreased gradually from 300 K to 2 K. The $\chi_m$ vs $T$ plots in the temperature range of 50–300 K (Fig. 6) gave the $C = 3.59$ cm$^3$ K mol$^{-1}$, $3.49$ cm$^3$ K mol$^{-1}$, $3.18$ cm$^3$ K mol$^{-1}$ and $\theta = -8.11$ K, $-16.02$ K, $-8.51$ K for the S-MeCN, S-MeOH and S-DMF, respectively, according to the Curie-Weiss law. The negative value of $\theta$ indicated the antiferromagnetic coupling between the metal centres and/or the spin-orbit coupling effect of Co(II) cations. Their magnetization curves at 2 K (Fig. 5, inset) also demonstrated the antiferromagnetic coupling. Interestingly, the CPs displayed morphology dependent magnetic properties (Fig. 5). For one thing, it is known that the size of CPs existed: S-MeCN, S-MeOH or S-DMF, so the smallest CPs had the largest $C$ and $\theta$ values. For another, S-MeOH and S-DMF had the same crystalline structure but different morphology, and it is shown that their magnetic curves and related parameters are distinct from each other.

In summary, a solvent induced rapid modulation growth for metal carboxylates coordination polymers micro/nanostructures have been demonstrated here. All the synthesis were performed in organic solvent/water mixtures at ambient conditions and terminated within 20 minutes. For example, cobalt (II)-3,5-pyridinedicarboxylate (including: Co(Pydc)$\cdot$$2$H$_2$O, {Co(Pydc)(H$_2$O)$_4$$\cdot$$2$H$_2$O and Co(Pydc)$_{0.7}$(OH)$_{0.6}$2H$_2$O.1.2DMSO} CPs was carefully studied, and various micro- and nanostructures were obtained. Based on analysis of these products, the modulation effect of organic solvents was summarized as three types: anisotropic growth, anisotropic growth/formation of new crystalline phase and the formation of new crystalline phase solely. The binding ability of organic solvents with metal cations was proved crucial for their modulation effect, which was closely associated with their functional groups and molecular size. This strategy exhibited an exquisite modulation effect for CPs and could be facially expanded to many other metal carboxylates. Additionally, morphology dependent antiferromagnetic behaviour was also observed here. Our research established a kind of simple but versatile capping agents for fabrication of CPs micro/ nanostructures. Moreover, the detailed discussion of modulation effect would bring more CPs with well controlled shape and size by consciously selected proper organic solvents as the capping agents.

**Methods**

All the reagents were commercially available.
Synthesis of metal-carboxylates CPs. In a typical synthesis, 1 mL of 0.1 M Co(NO$_3$)$_2$·6H$_2$O aqueous solution was added into a mixture of organic solvent (15 mL) and deionized water (8 mL) at room temperature. After stirring for a few minutes, a clear solution was obtained. Then 1 mL of 0.1 M Na$_2$pydc aqueous solution was added dropwise into aforementioned solution under vigorous stirring, and a reddish suspension was obtained immediately. After reaction for 1 min to 20 h (Table S1), the precipitate was collected via centrifugation, washed with ethanol for several times, and dried at 70°C for 6 h. The organic solvents used here included absolute ethanol (EOH), tetrahydrofuran (THF), acetonitrile (MeCN), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), n-propanol, n-butanol, phenylcarbinol, methanol (MeOH) and N,N-dimethylethamide (DMEA), respectively.

- Morphology control of Co-pydc CPs was achieved by changing the volume ratios of organic solvents in the binary mixtures while kept other reaction parameters unchanged, and their reaction time was also recorded (Table S2).

For the preparation of Co-BTC, Zn-pydc and Eu-pydc CPs, similar synthesis procedures were employed, except that the organic ligands or metal salts were changed, respectively. To study the modulation kinetics of the organic solvents, time-dependent experiments were carried out. The procedures were similar with the preparation of CPs referred above. However, certain time intervals were selected depending on the different organic solvents.

Characterization. Scanning electron microscope (SEM) were performed with the JEOL, JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before SEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before SEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before TEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before TEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before SEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before SEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope. Before SEM test, the sample powder was placed on the conductive belt using the JEOL JSM-7500F, Shimadzu SS-550 and JEOL-6700F scanning electron microscope.
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Acknowledgments
This work was financially supported by the 973 Program of China (2014CB845600), the NNSF of China (21031002, 21303118) and MOE Innovation Team (IRT13022) of China.

Author contributions
Z.R.S. and K.L. designed the experiment. K.L. performed the experiment. Y.L. contributed to the data analysis. S.D.H. assisted the magnetism measurement. T.L.H. and D.S.Z. assisted the analysis of crystal structure. The manuscript was prepared by K.L. and Z.R.S. X.H.B. and W.J.R. directed the whole work.

Additional information
Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Liu, K. et al. Solvent induced rapid modulation of micro/nano structures of metal carboxylates coordination polymers: mechanism and morphology dependent magnetism. Sci. Rep. 4, 6023; DOI:10.1038/srep06023 (2014).

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