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The Diversity of Zn(II) Coordination Networks Composed of Multi-Interactive Ligand TPHAP$^-$ via Weak Intermolecular Interaction

Tatsuhiro Kojima,$^a$ Tomofumi Yamada,$^b$ Yumi Yakiyama,$^a$ Eri Ishikawa,$^c$ Yasushi Morita,$^d$ Masahiro Ebihara,$^b$ and Masaki Kawano*$^a$

Kinetic state networks can be trapped by multi-interactive ligands via weak intermolecular interactions. Self-assembly of a tripyridyl multi-interactive ligand K$^+$TPHAP$^-$ (potassium 2,5,8-tri(4′-pyridyl)-1,3,4,6,7,9-hexaazaphenalene) and ZnI$_2$ produced seven types of networks depending on the solvent systems (MeOH/additive solvent): [ZnI(TPHAP)] 3.5CH$_3$OH (1) (from MeOH/DMA), [ZnCl$_0.5$I$_0.5$(TPHAP)H$_2$O] 7H$_2$O (2) (from MeOH/DMA+water), [ZnI(TPHAP)] 3PhOH 2CH$_3$OH (3) (from MeOH/phenol (<33%)), [ZnI(TPHAP)] 5PhOH 2.5CH$_3$OH (4) (from MeOH/phenol (>50%)), [ZnI(TPHAP)] 2PhNO$_2$ 6CH$_3$OH (from MeOH/nitrobenzene) (5), [ZnI$_2$(TPHAP)CH$_3$OH] 3PhNH$_2$ (6) (from MeOH/aniline), and [[ZnI$_2$(TPHAP)(HCON(CH$_3$)$_2$)$_3$(CH$_3$OH)$_2$]][(ZnI$_2$)$_2$(TPHAP)(HCON(CH$_3$)$_2$)] (HCON(CH$_3$)$_2$) 4CH$_3$OH (7) (from MeOH/DMF). All structures were characterized by single crystal X-ray structure determination. Each topology was analyzed by TOPOS. The structures were categorized into two- or three-periodic structure. The structural features of each network were explained by the weak intermolecular interactions between TPHAP$^-$ and guest molecules. We demonstrated the multi-interactivity of TPHAP$^-$ which can recognize the slight difference of weak intermolecular interactions.

Introduction

Coordination network is one of representative subjects of crystal engineering.$^1$ Network topology is based on the coordination geometry of metal ions and the shape of organic ligands. A combination of metal ions and organic ligands can form a number of unique networks.$^2$ Furthermore, weak intermolecular interactions like hydrogen bond and π-π interactions play a crucial role in networking.$^3$ Even same components of metal ions and organic ligands can produce several kinds of networks depending on an energy landscape directed by experimental conditions, e.g. solvent, guest molecule, temperature, reaction speed, and so on.$^4$ Although various topologies were reported, the number of porous networks composed of the same combination of metal ions and ligands is generally limited. To demonstrate the importance of intermolecular interactions in network formation, we focused on a hexaazaphenalenyl (HAP) skeleton to introduce weak intermolecular interactions.$^5$ We synthesized a multi-interactive ligand, potassium 2,5,8-tri(4′-pyridyl)-1,3,4,6,7,9-hexaazaphenalene (K$^+$TPHAP$^-$), which is sensitive to weak intermolecular interactions (Scheme 1).$^6$ TPHAP$^-$ has mainly three significant features: i) multi-dentate coordination sites, ii) a large aromatic plane, iii) six hydrogen bond accepter sites.

These interactive sites can induce weak intermolecular interactions during self-assembly. Therefore, this ligand can trap various kinetic states because weak intermolecular interactions deepen local potential energy minima.$^7$ Indeed, the TPHAP$^-$ ligand can form a variety of networks depending on the slightly different experimental conditions. We reported coordination networks composed of TPHAP$^-$ and Co$^{2+}$ and the dynamic structure transformation depending on temperature.$^6$ In this study, we investigated solvent effects on networking. Solvent effects sometime make crystal engineering more difficult, especially in polymorph.$^8$ A large number of polymorphs obtained from various solvents were reported. Here, we report seven kinds of coordination networks using the
same starting materials of K\textsuperscript{+}TPHAP\textsuperscript{–} and ZnI\textsubscript{2} in various solvents: [ZnI(TPHAP)] 3.5CH\textsubscript{3}OH (1), [ZnCl\textsubscript{0.3}I\textsubscript{0.7}(TPHAP)H\textsubscript{2}O] 7H\textsubscript{2}O (2), [ZnI(TPHAP)] 3PhOH 2CH\textsubscript{3}OH (3), [ZnI(TPHAP)] 5PhOH 2.5CH\textsubscript{3}OH (4), [ZnI(TPHAP)] 2PhNO\textsubscript{2} 6CH\textsubscript{3}OH (5), [ZnI(TPHAP)CH\textsubscript{3}OH] 3PhNH\textsubscript{2} (6), [(ZnI\textsubscript{2}(TPHAP)(HCON(CH\textsubscript{3})\textsubscript{2})(CH\textsubscript{3}OH)\textsubscript{2}]\textsuperscript{+}[(ZnI\textsubscript{2})(TPHAP)(HCON(CH\textsubscript{3})\textsubscript{2})\textsuperscript{+}(HCON(CH\textsubscript{3})\textsubscript{2})] 4CH\textsubscript{3}OH (7) (Scheme 2).

This diversity of Zn\textsuperscript{2+}-TPHAP coordination networks exemplifies the multi-interactivity of TPHAP\textsuperscript{–} via weak intermolecular interaction.

Table 1 Experimental conditions and structural features

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<th>Additive solvent\textsuperscript{a}</th>
<th>Point symbol</th>
<th>Vertex symbol</th>
<th>RCSR</th>
<th>Type of network\textsuperscript{b}</th>
<th>Coordination geometry</th>
<th>% of pore space against the unit cell volume\textsuperscript{c}</th>
<th>Volume for a pore / Å\textsuperscript{3}</th>
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\textsuperscript{a} See experimental section. \textsuperscript{b} Analyzed by TOPOS. \textsuperscript{c} Calculated on 3.1. Mercury.
**Fig. 1** Crystal structure and schematic view of 1. a) Zn$^{2+}$ tetrahedral coordination environment by three tridentate TPHAP$^-$ and I$^-$. Orange, violet, blue, and gray spheres represent Zn, I, N and C atoms. H atoms are omitted for clarity. b) Zigzag sheet structure composed of Zn(TPHAP). Zn$^{2+}$ ion acts as a trident junction. c) 3-c net schematic structure of zigzag sheet. d) Interpenetrating zigzag sheet structure viewed from the a axis, showing one-dimensional channels. e) Schematic view of interpenetrating zigzag sheet structure from top. f) Interpenetrating zigzag sheet structure viewed from the b axis, showing no space for guest-encapsulation between TPHAP$^-$. g) Schematic view of interpenetrating zigzag sheet structure from side, showing stacking ABABAB.

**Fig. 2** Crystal structure and schematic view of 2. a) Zn$^{2+}$ trigonal bipyramidal molecular geometry by three tridentate TPHAP$^-$, water and I$^-$ (or Cl$^-$). Colour codes are the same as those in Fig. 1 and red and green spheres represent O and Cl, respectively. b) Planar sheet structure composed of Zn$_{0.5}$Cl$_{0.5}$(TPHAP)H$_2$O. Zn$^{2+}$ ion acts as a trident junction. c) 3-c net schematic structure of planar sheet. d) Top view of planar sheet stacking structure, showing one-dimensional channel. e) Schematic view of planar sheet stacking structure from top. f) Side view of planar sheet stacking structure, showing no space for guest-encapsulation between TPHAP$^-$. g) Schematic view of planar sheet stacking viewed from side, showing stacking ABABAB.

**Results**

**Syntheses and Characterization**

The layering diffusion method of a methanol solution of ZnI$_2$ into a MeOH–guest solution of K$^+$(TPHAP)$^-$. Totally seven types of different network crystals were obtained depending on solvent and the mixing ratio (Table 1).

**Crystal structure**

**1 [ZnI(TPHAP)] 3.5CH$_3$OH**

1 was obtained from methanol/additive solvent which has no hydrogen bond donor site such as DMA, DMSO, 1,4-dioxane and THF (Fig. 1). The network of 1 consists of TPHAP$^-$, I$^-$ and Zn$^{2+}$. The Zn$^{2+}$ centre has a tetrahedral geometry coordinated by three tridentate TPHAP$^-$s and I$^-$, forming zigzag sheet structure. Furthermore, two zigzag sheets interpenetrate each other. Because both of a ZnI$^+$ unit and a TPHAP$^-$ molecule can be regarded as a 3-connected node, 1 represents a uninodal 3-c net and TOPOS indicates that the zigzag sheet structure is 6$^3$-hcb (Fig. 1e). The interpenetrating networks stack each other via π-π interaction to form layers along the a axis (Fig. 1g) and 1D channels containing methanol. The interpenetrating structure 1 has a smaller void (27.4% against the unit cell volume) than do other networks which were obtained from aromatic solvent.

**2 [ZnCl$_{0.5}$I$_{0.5}$(TPHAP)H$_2$O] 7H$_2$O**

2 was obtained from water/DMA/methanol (Fig. 2). The Zn$^{2+}$ centre forms a five coordinate of a trigonal bipyramidal geometry composed of three tridentate TPHAP$^-$s, a water and I$^-$ or Cl$^-$ (I$^-$ and Cl$^-$ are disordered at a similar position and each occupancy factor was converged to 0.5 and 0.5, respectively) (Fig. 2a). In a similar way to 1, both a ZnI$^+$ unit and a TPHAP$^-$ molecule act as a 3-connected node. Therefore, 2 represents a uninodal 3-c net, but the trigonal coordination of three TPHAP$^-$s forms a planar sheet 6$^3$-hcb structure which is...
interaction. An iodide locates above the TPHAP, forming the iodine/TPHAP/phenol/TPHAP/iodine arrangement. The total void (68.0%) is larger than that of 2. Four phenols form hydrogen bonds to nitrogen atoms on two central TPHAP skeletons. 4 has more hydrogen bonds than does 3.

5 [Zn(TPHAP)] 2PhNO2 6CH3OH

Unexpected 3D network 5 was obtained from nitrobenzene/methanol (Fig. 5). The Zn2+ centre has a tetrahedral geometry coordinated by three tridentate TPHAP’s and I−. The component of network and the uninode 3-c net are the same as those of 1, 3 and 4. However, the network structure is different from those. TOPOS indicates that 5 has 2-fold interpenetration of 83-ef3 net. This classification of network topology is the first example in the database of TOPOS& RCSR. The network 5 has two kinds of 1D channels along the c axis, so-called, biporous structure. Each channel is surrounded by different characteristic environments, halogen space (surrounded by iodine) and π space (surrounded by TPHAP). Aromatic nitrobenzene prefers the π space via π−π interaction with TPHAP. Differently from other solvent systems, nitrobenzene can form π-stacking dimer, therefore quadruple π-stacking structure consists of two TPHAP and two nitrobenzene (TPHAP/nitrobenzene/nitrobenzene/TPHAP). Thanks to the nitrobenzene dimer, this network has a large void (66.9%).

6 [Zn(TPHAP)CH3OH] 3PhNH2

The combination of methanol/aniline produced the zigzag sheet structure [Zn(TPHAP)CH3OH] slightly different from 3 (Fig. 6). Although the Zn2+ centre has five coordinate by three TPHAP’s, I− and a methanol, the network connectivity is the same, a uninode 3-c net, as that of 3. Therefore, the network is described as zigzag sheet 63-hcb. However, because of methanol coordinatino to Zn2+, its dihedral angle between TPHAP planes slightly changed from 108.82(5)° in 2 to 91.03(2)° in 6 (Scheme 3). One aniline was encapsulated between TPHAP’s via π−π interaction.

7 [(ZnI2)(TPHAP)(HCON(CH3)2)(CH2OH)](HCON(CH3)2)4CH3OH
7 was obtained from methanol/DMF (Fig. 7). Two kinds of 1D networks interpenetrate each other via π−π interaction. One 1D network consists of a bidentate TPHAP and ZnI2, in which the remaining pyridyl group and a carbonyl oxygen of DMF coordinate to ZnI2, forming a negatively charged network, [(ZnI2)2(TPHAP)(HCON(CH3)2)]+. The other 1D network also consists of a bidentate TPHAP and ZnI2, in which, however, the remaining pyridyl group of TPHAP, three carbonyl oxygen of DMF and two methanol molecules coordinate to ZnI2, forming positively charged network [(ZnI2)2(TPHAP)(HCON(CH3)2)]+. To the best of our knowledge, this network is the first hybrid open framework composed of alternatively arrayed positively- and negatively-charged 1D chains.
Fig. 4 Crystal structure and schematic view of 4. a) Zn$^{2+}$ tetrahedral coordination environment by three tridentate TPHAP’s and I$^-$ in a similar way to 1 and 3. b) Encapsulation of phenols (orange) between TPHAP’s (blue and red) via π-π interaction and hydrogen bond. Iodide locates above the TPHAP$^-$. c) 3D network composed of Zn[TPHAP]. Zn$^{2+}$ ion acts as a trident junction. d) 3-c net schematic structure of 3D network. e) Interpenetrating 3D network. f) Schematic view of 2-fold interpenetrating 3D network.

Fig. 5 Crystal structure and schematic view of 5. a) Zn$^{2+}$ tetrahedral coordination environment by three tridentate TPHAP’s and I$^-$ in a similar way to 1, 3 and 4. Colour codes are the same as those in Fig. 1. b) Encapsulation of nitrobenzene dimer (orange) between TPHAP’s (blue and red) via π-π interaction. c) 3D network composed of Zn[TPHAP]. d) 3-c net schematic structure of 3D network. e) Interpenetrating biporous 3D network, showing two kinds of 1D channels which are surrounded by π planes and iodine atoms (violet). f) Schematic view of interpenetrating biporous 3D network viewed from the top.

Fig. 6 Crystal structure and schematic view of 6. a) Zn$^{2+}$ pseudo-tetrahedral coordination environment by three tridentate TPHAP’s, I$^-$ and methanol. Colour codes are the same as those in Fig. 2. b) Encapsulation of anilines (orange) between TPHAP’s via π-π interaction. c) Zigzag sheet structure composed of ZnI(TPHAP)(CH$_3$OH). d) 3-c net schematic structure of zigzag sheet. e) Zigzag sheet stacking structure without interpenetration viewed from the a axis. f) Schematic view of non-interpenetrating zigzag sheet stacking structure from top. g) Non-interpenetrating zigzag sheet stacking structure viewed from the c axis, showing spaces which can encapsulate anilines between TPHAP’s. h) Schematic view of planar sheet stacking viewed from the side, showing stacking ABABAB.

Fig. 7 Crystal structure of 7. a) Four types of Zn$^{2+}$ coordination environment. Upper left: tetrahedral ZnI$_2$(TPHAP)$_2$, upper right: tetrahedral Zn$_4$(TPHAP)$_4$, lower left: tetrahedral ZnI$_2$(TPHAP)(DMF) and lower right: octahedral ZnI(TPHAP)(DMF)$_2$(MeOH). Colour codes are the same as those in Fig. 2. b) An anionic 1D chain of [ZnI$_2$(TPHAP)(HCON(CH$_3$)$_2$)$_2$]$_n^-$. c) A cationic 1D chain of [ZnI$_4$(TPHAP)(HCON(CH$_3$)$_2$)$_2$(CH$_3$OH)$_2$]$_n^+$. d) Top view of alternative zigzag chain structure. e) Side view of alternative zigzag chain structure, showing no space for guest encapsulation between TPHAP’s.
Table 2 Crystal data and experimental conditions

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Discussion

Effect of solvent on network topology and coordination environment

We obtained four kinds of topology (interpenetrating $6^3$-hbcb, non-interpenetrating $6^3$-hbcb, interpenetrating $10^3$-srs, and interpenetrating $8^2$-etf) except for 7 (Table 1). All networks are composed of the same component, ZnI(TPHAP), in which both ZnI$^-$ and TPHAP$^-$ act as 3-connected nodes. Previously, Kawano, Fujita and co-workers reported 62 networks by using TPT (2,4,6-tris(4-pyridyl)-1,3,5-triazine) ligand and they were categorized into four topology ($10^3$-srs, $10^3$-ths, $4^2$-6, and $6^3$-hbcb). The topology consist of one kind of node, 3-connected TPT ligand, in which TPT ligand does not act as a C₃ symmetrical node because each TPT ligand is connected by lower symmetry of ZnI$_2$. Therefore, all TPT networks do not have the strong isotropic property. To form strong isotropic property, a higher symmetrical node is required. On the other hand, ZnI(TPHAP) networks consist of two kinds of C₃ symmetry nodes: TPHAP and ZnI$.^-$ Therefore, ZnI(TPHAP) may produce stronger isotropic property networks than ZnI$_2$(TPT). Further, we explain topological mechanism on the basis of symmetry of node and the weak intermolecular interactions between TPHAP$^-$ and guest molecules.

1) 2-periodic $6^3$-hbcb structures

1, 2, 3, and 6 are similar 2-periodic $6^3$-hbcb structures. It is worth noting that, in 1, 2, 3, and 6 networks, π-π interaction dominates intermolecular interactions within TPHAP molecules, forming a dimer of TPHAP’s. Especially, 1, 3, and 6 have the same $6^3$-hbcb zigzag sheet, however each stacking structure is different. While the $6^3$-hbcb zigzag sheets in 1 interpenetrate each other, those in 3 and 6 are stacked without interpenetration. Because 1 was obtained from the non-aromatic solvent system (methanol/DMA, DMSO, 1,4-dioxane or THF), π-π interaction may dominate intermolecular interactions within only TPHAP$^-$ molecules, followed by interpenetrating network formation with a 27.4% void. On the other hand, because 3 and 6 were obtained from aromatic solvent (methanol/phenol and methanol/aniline, respectively), the solvent molecules were encapsulated in a void via π-π interaction with TPHAP$^-$, leading to non-interpenetrating network. Therefore, the voids in 3 and 6 (54.6% and 47.4%, respectively) are larger than that of 1.

2) Interpenetrating $10^3$-srs structure

3-periodic interpenetrating $10^3$-srs structure, 4, was obtained from the same solvent system as in 3 (PhOH/MeOH). The different ratio of phenol (volumetric ratio < 33% or > 50%) generated totally different networks, $6^3$-hbcb (3) and $10^3$-srs (4), respectively. Among unimodal 3-c nets, hbcb and srs are well-known networks with 2445 and 307 examples in TOPOS&RCSR database. As Sunada mentioned, $10^3$-srs nets possesses strong symmetry. Especially, a pair of...
interpenetrating \(10^3\)-srs nets is similar to so-called gyroid structure with 84 examples.\(^{15}\) Among them, only 6 examples are the strong isotropic gyroid structures (Fig. 8b), which consist of organic ligands and metal connector as \(C_3\) symmetry of nodes.\(^{16}\) In this study, 4 forms gyroid structure thanks to \(C_3\) symmetry of both nodes, \(\text{Zn}^2+\) and TPHAP\(^−\) (Fig. 8a). The \(10^3\)-srs network 4 obtained from phenol-rich solution (> 50% volumetric ratio) has a large void occupied by solvent through hydrogen bond and \(\pi-\pi\) interaction, in which phenol prefers hydrogen bond to \(\pi-\pi\) interaction, probably preventing TPHAP dimer formation. Thanks to multi-interactive and highly symmetrical \(C_3\) TPHAP\(^−\) and metal connector, we successfully constructed the strong isotropic gyroid structure, 4.

3) Interpenetrating \(8^3\)-etf structure

5 forms 3-periodic 2-fold interpenetrating \(8^3\)-etf network composed of \(\text{Zn}^2+\) and TPHAP\(^−\). Network 5 has a larger void between TPHAP\(^−\) dimers. TPHAP\(^−\) and nitrobenzene form quadruple \(\pi-\pi\) stacking structure (TPHAP\(^−\)/nitrobenzene/nitrobenzene/TPHAP\(^−\)). Among all, thanks to nitrobenzene double layer, only 5 has a pore window large enough for guest molecules to enter. 

\[\text{Zn}^2+\] ions in 2, 6 and 7 have different coordination geometry. Network 2 and 7 were obtained from the solvent systems containing water and DMF which can coordinate to metal ions. Therefore, it is not surprising that they provided unique coordination geometry. However, in the case of 6, even though aniline did not coordinate to \(\text{Zn}^2+\) ions, the coordination geometry changed slightly from tetrahedral to pseudo-tetrahedral by additional methanol coordination thanks to the flexibility of coordination mode of \(\text{Zn}^2+\) ions (Scheme 3).

\[
\begin{align*}
\text{Scheme 3} & \text{ Dihedral angle between TPHAP}^−\text{ planes and trident junction part of } \\
\text{Zn}^2+: & \text{ a) in } 3 \text{ and b) in } 6.
\end{align*}
\]

**Networking mechanism through cation-assisted dimerization**

From the structural point of view, except for 4, it is noteworthy that a dimer of TPHAP\(^−\) can be regarded as one unit. This result indicates that in solution TPHAP\(^−\) s form a dimer, and that the dimerization helps networking (scheme 4). To check the species in solution state, we measured cold-spray ionization mass spectra (CSI-MS).\(^{17}\) A peak of \([\text{K(TPHAP)}_3]^−\) (m/z=843.219) species was observed in CSI-MS (Fig. 9). The crystal structure of \(\text{K}^+\text{TPHAP}^−\) suggests that this species forms a dimer not only with \(\text{K}^+\) ion bridging but also via \(\pi-\pi\) interaction. This result supports our assumption that dimerization assisted by \(\text{K}^+\) may help ligand exchange during networking. Even using smaller ionic cation salt such as \(\text{Li}^+\text{TPHAP}^−\) and \(\text{Na}^+\text{TPHAP}^−\), ESI-MS showed dimerization in solution, e.g. \([\text{Li(TPHAP)}_2]^−\) (m/z=810.252) and \([\text{Na(TPHAP)}_2]^−\) (m/z=827.240). Indeed, using those salts, we obtained 5. Furthermore, as a control experiment, we failed to form 5 using an organic cation salt, \(([(\text{C}_6\text{H}_5)_3\text{P}]^+\text{TPHAP}^-)\), which cannot assist dimerization. So far we also have never succeeded in networking with the same crystallization method using \(\text{H}^+\text{TPHAP}^−\). Even though dimer \(([(\text{H}^+\text{TPHAP}^-)\text{TPHAP}^-]\) (m/z=805.262) was detected by CSI-MS, it is likely that the strength of dimerization is weaker than the dimer assisted by
metal ion \([\text{M(TPHAP)}]_\text{2}^+\) (\(\text{M} = \text{Li}^+, \text{Na}^+, \text{and K}^+\)). Still other factors can be considered for the reasons that the TPHAP neutral form cannot produce any network yet. However, this cation-assisted dimerization can be an important factor for networking.

**Conclusions**

We showed the diversity of multi-interactivity of TPHAP via weak intermolecular interactions in coordination network formation. TPHAP and \(\text{Zn}^{2+}\) produced seven types of networks depending on the nature of solvent. Among them, 1, 3, 4 and 5 consist of the same component, Zn(TPHAP). Especially, although 3 and 4 were obtained from the same solvent system (PhOH/MeOH), different networks were formed due to the different solvent ratio. This fact indicates that a slight difference in experimental conditions makes a big difference in networking thanks to multi-interactivity of TPHAP to weak intermolecular interactions. Furthermore, this extreme multi-interactivity can generate two kinds of pores depending on coexisting molecules. This interactive ligand can be an excellent probe for weak intermolecular interactions and can form various networks depending on coexisting molecules. This interactive ligand can be useful for trapping kinetic state networks.

**Experimental**

**General procedures**

All reagents were purchased from commercial sources and used without further purification unless otherwise noted. The following reagents were used for crystallization: 99.5% dimethylacetamide (DMA), 99.8% dimethylsulfoxide (DMSO), 99.0% phenol, 99.0% nitrobenzene, 99.5% dimethylformamide (DMF), (SAMCHUN); 99.5% aniline (Sigma Aldrich). 99.0% phenol, 99.0% nitrobenzene, 99.5% dimethylformamide (DMA), 99.8% dimethylsulfoxide (DMSO), following reagents were used for crystallization: 99.5% methanol (SAMCHUN) was dried over 4 Å molecular sieves.

**Synthesis**

1 \([\text{ZnI(TPHAP)}] \cdot 5\text{CH}_\text{3} \text{OH}\)

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI\(_2\) (59.2 mM) as the top layer, 2 ml methanol as the middle layer, and 2 ml DMA / methanol solution (1.5 mM DMA + 0.5 mL methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Caled for \(\text{C}_{22}\text{H}_{26}\text{Cl}_6\text{I}_5\text{O}_6\text{Zn} (= (\text{C}_2\text{H}_2\text{H}_2\text{N}_2\text{O}_5\text{I}_2)(\text{CH}_3\text{O}_2\text{H}_2\text{O}_2)\)) (%): C, 43.21; H, 3.93; N, 18.90 %. Found: C, 43.04; H, 3.65; N, 18.88. IR (ATR, \(\nu_{\text{max}}/\text{cm}^{-1})\): 3360s, 1590vs, 1560s, 1505s, 1480w, 1420m, 1375w, 1325m, 1210vw, 1180w, 1075w, 1050w, 1030w, 930w, 845w, 755w, 740w, 690w.

2 \([\text{ZnCl}_2\text{I}_6\text{S}_2\text{(TPHAP)}] \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}\)

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI\(_2\) (59.2 mM) as the top layer, 2 ml methanol/water mixture (1.9 ml methanol + 0.1 ml water) as the middle layer, and 2 ml DMA/methanol solution (1.5 mM DMA + 0.5 mL methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Caled for \(\text{C}_{22}\text{H}_{26}\text{Cl}_6\text{I}_5\text{O}_6\text{Zn} (= (\text{C}_2\text{H}_2\text{H}_2\text{N}_2\text{O}_5\text{Zn})(\text{CH}_3\text{O}_2\text{H}_2\text{O}_2)\)) (%): C, 43.21; H, 3.93; N, 18.90 %. Found: C, 43.04; H, 3.65; N, 18.88. IR (ATR, \(\nu_{\text{max}}/\text{cm}^{-1})\): 3360s, 1590vs, 1560s, 1480w, 1420m, 1375w, 1325m, 1210vw, 1180w, 1075w, 1050w, 1030w, 930w, 840w, 755w, 740w, 695w, 680w.

3 \([\text{Zn(TPHAP)}] \cdot 3\text{H}_2\text{O} \cdot \text{C}_2\text{H}_3\text{OH}\)

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI\(_2\) (59.2 mM) as the top layer, 2 ml methanol/pheno1 mixture (1.5 mM methanol + 0.5 mL phenol) as the middle layer, and 2 ml phenol /methanol solution (1.5 mM phenol + 0.5 mL methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Caled for \(\text{C}_{22}\text{H}_{26}\text{I}_5\text{O}_6\text{N}_4\text{Zn} (= (\text{C}_2\text{H}_2\text{H}_2\text{N}_2\text{O}_5\text{I}_2)(\text{CH}_3\text{O}_2\text{H}_2\text{O}_2)\)) (%): C, 54.00; H, 3.56; N, 14.17 %. Found: C, 54.40; H, 3.48; N, 13.79. IR (ATR, \(\nu_{\text{max}}/\text{cm}^{-1})\): 3200s, 1590vs, 1560s, 1500w, 1480w, 1420m, 1380w, 1325w, 1300m, 1240w, 1170w, 1080w, 1050w, 1030w, 930w, 845w, 810w, 755w, 740w, 695w, 680w.

4 \([\text{Zn(TPHAP)}] \cdot 5\text{PhOH} \cdot 2\text{C}_2\text{H}_3\text{OH}\)

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI\(_2\) (59.2 mM) as the top layer, 2 ml methanol/pheno1 mixture (0.5 mL methanol + 1.5 mL phenol) as the middle layer, and 2 mL phenol /methanol solution (1.5 mM phenol + 0.5 mL methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Caled for \(\text{C}_{22}\text{H}_{26}\text{I}_5\text{O}_6\text{N}_4\text{Zn} (= (\text{C}_2\text{H}_2\text{H}_2\text{N}_2\text{O}_5\text{Zn})(\text{CH}_3\text{O}_2\text{H}_2\text{O}_2)\)) (%): C, 37.60; H, 3.44; N, 17.94. Found: C, 37.69; H, 3.37; N, 17.81. IR (ATR, \(\nu_{\text{max}}/\text{cm}^{-1})\): 3200s, 1595vs, 1560s, 1480w, 1420m, 1380w, 1330m, 1300s, 1180w, 1080w, 1055w, 1030w, 935w, 845w, 755w, 740w, 690w.
1300s, 1175w, 1080w, 1055w, 1030w, 935w, 845w, 810vw, 755w, 735w, 690w.

5 [Zn(TPHAP)] 2PhNO₂ 6CH₃OH

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI₂ (59.2 mM) as the top layer, 2 ml methanol as the middle layer, and 2 ml nitrobenzene/methanol solution (1.5 ml nitrobenzene + 0.5 ml methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Calcd for C₄₀H₄₂Cl₀.2IK₀.2N₁₁.4O₉.3Zn (%): C, 46.82; H, 2.77; N, 14.11. IR (ATR, νmax/cm⁻¹): 3230s, 1595vs, 1560s, 1520w, 1480w, 1420m, 1380w, 1325m, 1300s, 1175w, 1080w, 1055w, 1030w, 930w, 845w, 810vw, 755w, 735w, 690w.

6 [Zn(TPHAP)CH₃OH] 3PhNH₂

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI₂ (59.2 mM) as the top layer, 2 ml methanol as the middle layer, and 2 ml aniline/methanol solution (1.5 ml aniline + 0.5 ml methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, brown crystals were grown. Anal. Calcd for C₂₈H₂₅Cl₀.5IK₀.5N₁₀O₃Zn (%): C, 43.16; H, 3.23; N, 17.98. Found: C, 43.03; H, 2.87; N, 17.68. IR (ATR, νmax/cm⁻¹): 3200s, 1595vs, 1560s, 1520w, 1495w, 1480w, 1420m, 1380w, 1345vw, 1325m, 1300s, 1175w, 1080w, 1055w, 1030w, 930w, 845w, 810vw, 755w, 735w, 690w.

7 [(ZnI)₃(TPHAP)(HCON(CH₃)₂)₂(CH₂OH)₂][(ZnI)₂(TPHAP)(HCON(CH₃)₂)] [HCON(CH₃)₂] 4CH₃OH

The single crystals were grown from a triple-layered solution consisting of 2 ml methanol solution of ZnI₂ (59.2 mM) as the top layer, 2 ml methanol as the middle layer, and 2 ml DMF/methanol solution (1.5 ml DMF + 0.5 ml methanol) of K'TPHAP (9.5 mM) as the bottom layer at 14 °C. After a few days, pale yellow crystals were grown. Anal. Calcd for C₃₅H₃₀Cl₀.2IK₀.2N₁₆.8O₆.8Zn (%): C, 31.89; H, 2.77; N, 14.11. Found: C, 31.87; H, 3.09; N, 14.37. IR (ATR, νmax/cm⁻¹): 3330s, 1650w, 1595vs, 1560s, 1480w, 1420m, 1380w, 1325m, 1300s, 1175w, 1080w, 1055w, 1030w, 930w, 845w, 810vw, 755w, 740w, 690w.

Single Crystal X-ray Structure Determination

The diffraction data for 1, 2 and 4 were recorded with a Bruker APEX-II/CCD QUAZAR diffractometer equipped with a focusing mirror (MoKα radiation, λ = 0.71073 Å). Empirical absorption corrections were applied with the data using the program SADABS. The diffraction data for 5 was recorded with a RIGAKU/MSC Mercury CCD X-ray diffractometer with a synchrotron radiation (λ = 0.6889 Å) at PF-AR (NW2A beamline) of the High Energy Accelerator Research Organization (KEK). The diffraction images were processed by using HKL2000. Absorption correction was performed with the program PLATON. The diffraction data for 3, 6 and 7 were recorded with an ADSC Q210 CCD area detector with a synchrotron radiation at 2D beamline in Pohang Accelerator Laboratory (PAL). The diffraction images were processed by using HKL3000. Absorption correction was performed with the program PLATON.

Cold spray ionization mass spectra

Cold spray ionization mass spectrometry (CSI-MS) measurements were carried out with a microTOF time-of-flight mass spectrometer (Bruker Daltonics). A CSI unit was attached to the ESI-MS measurement system for the CSI-MS measurements. Negative mode was employed for all measurements (capillary voltage: 3.5 kV, capillary exit-skimmer potential difference: 30 V). CSI-MS spectrum was obtained by direct infusion of methanol solutions of K’TPHAP by using a syringe pump with a rate of 750 µL·h⁻¹. The desolvation temperature was set to 30 °C.

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Notes and references

a Division of Advanced Materials Science, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea.; Fax: (+82)-54-279-8739; Tel: (+82)-54-279-8740; E-mail: mkawano@postech.ac.kr
b Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido 1-1, Gifu, 501-1193, Japan
c Department of Applied Chemistry, Chubu University, Kasugai, Aichi 487-8501, Japan
d Department of Chemistry, Graduate School of Science, Osaka University, Machikaneyama 1-1, Toyonaka, Osaka 560-0043, Japan
† Electronic Supplementary Information (ESI) available: [CCDC 944048-944054 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.]
Centre via www.ccdc.cam.ac.uk/data_request/cif]. See DOI: 10.1039/b000000x/  
10  Terminology followed the recommendation by V. A. Blatov, D. M. Proserpio and M. O’Keeffe. V. A. Blatov, D. M. Proserpio and M. O’Keeffe, CrystEngComm, 2010, 12, 44.  
11  ‘Cl’ comes from a small amount of KCl contained as impurity which was not removed by purification of KTPHAP. Because of high solubility of KCl in water, KCl affected formation of compound 2 obtained from DMA/methanol/water.  
The Diversity of Zn(II) Coordination Networks Composed of Multi-Interactive Ligand TPHAP via Weak Intermolecular Interaction

Tatsuhiro Kojima, Tomofumi Yamada, Yumi Yakiyama, Eri Ishikawa, Yasushi Morita, Masahiro Ebihara, and Masaki Kawano

Seven types of different Zn(TPHAP) coordination networks were prepared thanks to the excellent multi-interactivity of TPHAP for weak intermolecular interaction.