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Spatial and Surface Design of Porous Coordination Polymers

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A significant challenge in the development of porous coordination polymers (PCP's), beyond control of pore size, is control of the shape and chemical nature of the pores. This short review presents some compounds that illustrate these features and general approaches to their preparation.

Keywords: Coordination polymers; Crystal engineering; Porosity

INTRODUCTION

In the last decade considerable efforts have been made to create porous coordination polymers (PCPs) with diverse functions, such as storage, exchange, separation, and catalysis [1–15]. These functions are responsible for properties characteristic of space accompanying metal-organic frameworks, which are composed of organic ligand(s) and metal ion(s) by using coordination bonds. PCPs are distinguished from conventional materials such as zeolites and activated carbons regarding two features; framework flexibility and designable pore surface. The formation of framework structures can be achieved by enthalpy gain and entropy loss. Therefore, enthalpy gain is necessary as much as possible, to prevent densely packed frameworks with all the sites occupied. Against the propensity that nature dislikes vacuum, numerous efforts have been devoted to usable porous frameworks to date, providing size- and shape-controlled pores well-suited for guest molecules. Therefore, these pore walls are able to exert van der Waals type effects on the guest–surface interaction. Still lacking are functional pores with acidic sites and/or basic sites open for guest molecules. The spatial and electronic structures

of pores are a pair of gears, namely, control of both size/shape of porous frames and surface functionality are inseparable. This article gives an overview of the functional pores based on spatial and surface designed PCPs (Fig. 1), which are categorized as acidic, basic, and chiral pores.

SYNTHETIC STRATEGIES OF FUNCTIONALIZED PCPs

Lewis-Acidic Surface

Most PCPs have pore surfaces with their functional groups coordinatively saturated. The introduction of Lewis-acidic sites into the pore, however, requires coordinatively unsaturated metal cation(s) (open metal site(s)) in the pore surface. Taking into account that the coordinative saturation of metal ions in PCPs tends to occur in usual frameworks, a clue to create open metal sites is to use volatile solvent molecules bound to metal ions, such as a water molecule, functionalizing the surface towards guest molecules. The removal of the volatile molecules by heating under vacuum results in Lewis-acidic pore surfaces.

One-pot synthesis often creates porous frameworks with volatile solvent molecules bound to familiar dicopper paddlewheel units (Fig. 2a) [16,17]. For instance, the solvothermal reaction of Cu^{2+} and trimesic acid in $\text{H}_2\text{O}/\text{EtOH}$ forms $[\text{Cu}_3(\text{tma})_2(\text{H}_2\text{O})_3]$ with a three-dimensional channel [16], in which H_2O molecules are bound to Cu^{2+} cluster as removable molecules. Recently, Lewis-acid sites of this PCP have been used for catalysis [18] and hydrogen storage material [19].

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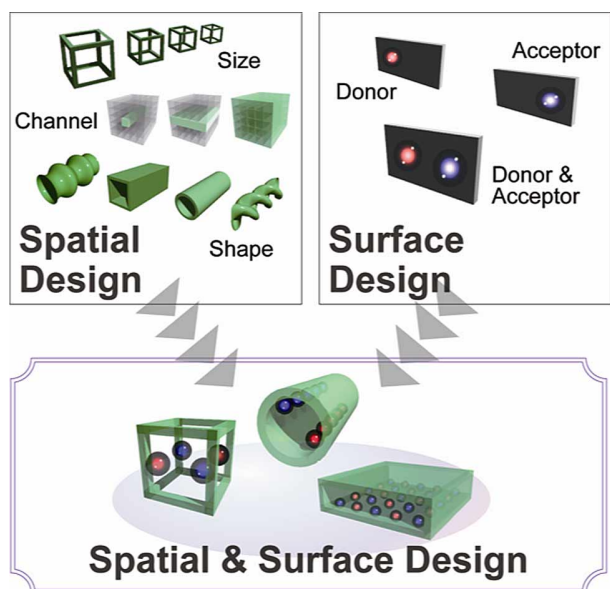


FIGURE 1 Spatial & Surface Design of Porous Coordination Polymers (PCPs).

Also, the solvothermal reaction of Cu^{2+} ion and 3,3',5,5'-biphenyltetracarboxylic acid (H_4bptc) in DMF/EtOH/ H_2O forms $[\text{Cu}_2(\text{bptc})(\text{H}_2\text{O})_2(-\text{DMF})_3(\text{H}_2\text{O})]$ with paddlewheel units, in which the effect of an open metal site to hydrogen storage have been expected [17].

Unlike the one-pot synthesis, a utilization of pre-organized metalloligand intrinsically gives rise to open metal sites. There are various kinds of metalloligands reported previously [20]. For instance, macrocyclic porphyrin ligands with an open metal site at the central metal ion have been

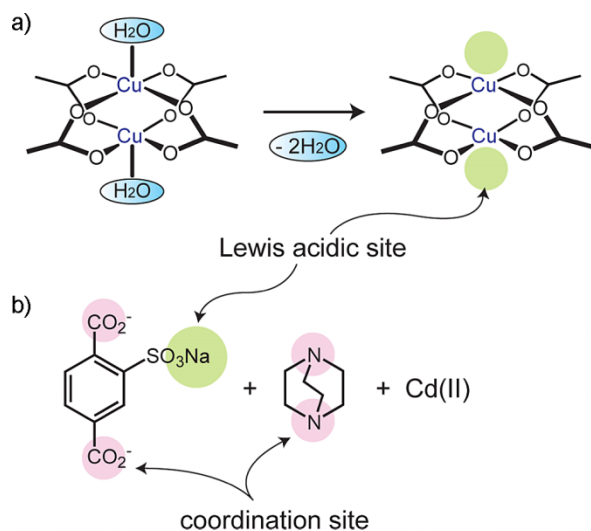


FIGURE 2 Schematic representation of (a) Lewis-acidic site of dicopper cluster, (b) elements of PCPs containing Na^+ as Lewis-acidic site.

utilized to create PCPs [21,22], which show different guest selectivity responsible for a difference in porosity of the central metal ion.

Another approach for an open metal site is an organic ligand with alkali cation. $[\text{CdNa}(2\text{-stp})(\text{dabco})_{0.5}(\text{H}_2\text{O})]2\text{H}_2\text{O}$ (2-stp = 2-sulfonylterephthalate, dabco = 1,4-diazabicyclo[2,2,2]octane, Fig. 2b), has been prepared by the reaction of Cd^{2+} with 2-stpNa and dabco in $\text{H}_2\text{O}/\text{EtOH}$ media under basic conditions using NaOH [23]. The Na^+ ions are densely immobilized at the 1D pore surface and shows strong adsorbate/adsorbent interaction for acetone and benzene. In this case, the $-\text{CO}_2^-$ coordinates to Cd^{2+} to form open framework, whereas $-\text{SO}_3^-$ groups bind to Na^+ as active Lewis-acidic sites [24].

Lewis-Basic Surface

The basic functional sites contribute essentially to superior characteristics of metal-organic frameworks. In spite of their great importance, reports on PCPs with basic porous surfaces have been rare because basic groups are preferentially bound by metal ions as connectors during the assembly. The most quoted examples of robust PCPs are constructed using transition metal cations with either an anionic multi-carboxylate or a neutral bipyridyl linker, whose coordination sites are used to form available pore structures. On the other hand, the creation of free base-functionalized channels is a difficult target as the coordination strength of these ligands increases.

To construct the pore walls with nitrogen donor sites, several attempts have been reported utilizing a ligand with multiple pyridyl groups. For example, pyrimidine-containing ligands such as 2,6-Bis(trans-4-styrylpyridyl)pyridine or 1-(4-pyridyl)-2-(4-pyrimidyl)ethene provide the porous frameworks with the basic functionality (Fig. 3a) [25,26]. In these examples, the ligands containing both coordinated and uncoordinated pyridyl sites were prepared, with which $\text{Co}(\text{SCN})_2$ forms a 2D square grid sheet.

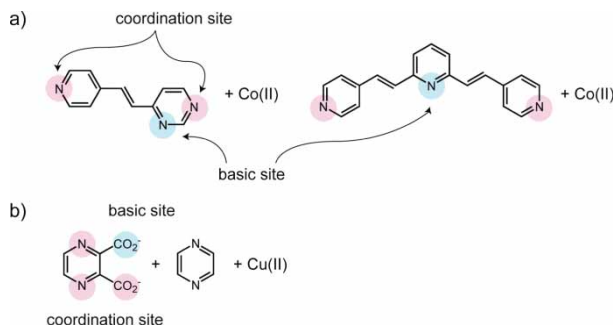


FIGURE 3 Schematic representation of elements of PCPs containing Lewis-basic site.

The uncoordinated pyridyl groups remain inside the network and the PCP consists of Co(II) and 1-(4-pyridyl)-2-(4-pyrimidyl)ethene shows alcohol adsorption with hydrogen-bonding interaction at basic sites.

On the other hand, by employing the multicarboxylate ligands with the aid of other co-ligands, the basic pore environment with oxygen donors can also be synthesized (Fig. 3b). The Cu(II) pillared-layer type PCPs, which consists of Cu(II), pyrazine-2,3-dicarboxylate, and pyrazine has micropore walls with basic oxygen atoms. This compound is synthesized by one-pot reaction of each component at room temperature and atmospheric pressure and shows type I adsorption isotherms for gas molecules (N_2 , CO_2 , O_2 , ...) and solvents (methanol, water, ...). The basic oxygen sites located at the pore interior provide fascinating sorption and reaction prospects. In case of acetylene as adsorbate, the basic micropore accommodate the gas molecules from low pressure even at 300 K via hydrogen bonding between H ($HC\equiv CH$) and basic O atoms [27]. Consequently, the guests are aligned within the 1D pores in a completely ordered fashion and the density of adsorbed C_2H_2 inside the pore is 200 times larger than the value of the compression limit for the safe use of C_2H_2 at RT. These studies indicate that the basic sites in micropores play an important role in guest recognition/reaction with unprecedented molecular accommodation.

Chiral Space

The PCPs with either helical or chiral structures on the pore surface are of intense interest in chemistry and such porous solids are potentially useful to find applications in enantioselective sorption/separation and catalysis. Compared with conventional adsorbents such as activated carbon or zeolites or mesoporous silicas, PCPs have an advantage for construction of chiral open structures because of their high structural diversity and designability. Three kinds of synthetic approaches to construct the homochiral PCPs are proposed; (1) from only achiral ligands, (2) by the combination of chiral co-ligand and connector ligands, (3) from only chiral ligands [28]. The third strategy has been most reliable and a number of attractive chiral PCP structures have been reported.

Recently, the homochiral PCPs constructed from mixed-ligand system or lanthanide metals have emerged by hydrothermal techniques [29], but there are a few reports about adsorption/catalytic functions based on the pore chirality. For instance, a combination of Cd(II) and (*R*)-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl-4,4'-bipyridine (Fig. 4a) forms a threefold interpenetrated 3D chiral porous framework by slow diffusion method into a mixture

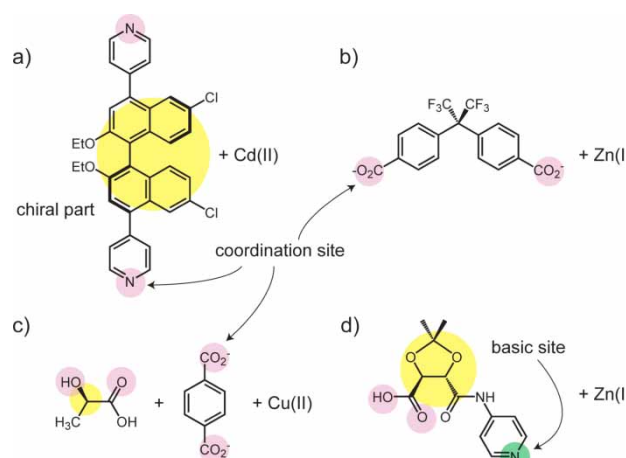


FIGURE 4 Schematic representation of elements of PCPs containing chiral space.

of DMF/ethyl acetate/EtOH. Although multiply interpreted, by employing the longer size of chiral ligand, 1D micropores with diameter of ~ 15 Å are formed and the compound represents the enantiomeric sorption ability for (*R*)-enantiomer of 1-phenylethanol [30].

Other chiral PCPs with adsorption property have also been observed [31], and the further studies on crystalline chiral PCP suggests future opportunities for enantioselective adsorption or catalysis with high enantiomeric excess (ee).

Lewis-Acidic Chiral Space or Lewis-Basic Chiral Space

There have been a couple of reports about PCP containing either Lewis acidic chiral surfaces or Lewis basic chiral surfaces. One example of Lewis acidic chiral PCP has been synthesized from hydrothermal reaction of Zn(II) and a chiral 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (Fig. 4b) [32]. This framework containing 1D chiral channels ($8 \times 8 \text{ \AA}^2$) shows acidic catalytic activity for acetalization of (*R,S*)-2-phenylpropionaldehyde and enantiomeric acetals were obtained with ee of 30%. According to the second synthetic approach to create a chiral framework, the reaction of Zn(II) and L-lactic acid and 1,4-benzenedicarboxylic acid (bdc) (Fig. 4c) under the DMF solution at 110°C for 2 days also provides a chiral microporous structure [33]. The chiral 2D sheets consisting of Zn(II) and L-lactic acid are linked by bdc to form a 3D open framework and represents oxidation of thioethers to sulfoxides by urea hydroperoxide or H_2O_2 with good yield even though these mechanisms of the catalytic activity are not yet clear.

The Lewis basic chiral PCPs are hardly observed, except for one example reported [34]. In this case, the chiral ligand which also contains basic pyridyl ring is synthesized from D-tartaric acid (Fig. 4d). According

to the third synthetic approach, the ligand reacts with Zn(II) in H₂O/MeOH media, 1D channels with the dimension of ~13 Å are created. This structure has coordination-free pyridyl groups on the pore surface acting as basic sites, and shows transesterification of esters to ethyl acetate with ~8% ee. The key point to achieve the construction of this Lewis basic chiral structure is the introduction of SBU (secondary building block) of Zn(II)–O clusters to extend the 3D structure while retaining the chiral and basic sites.

Lewis-Acidic and Basic Surface

At present it is still a challenging topic to synthesize PCPs with either Lewis-acidic or basic pore surface, as mentioned above, and their properties and possibilities are intensively studied. There have been sparse reports about PCPs with both properties, that are Lewis-acidic and basic surfaces to date because it is expected to be difficult to put closely both of Lewis-acidic and basic sites in the achiral/chiral pores due to the interaction between them. When that kind of PCPs in these categories could be synthesized, the unique properties of gas separation or catalysis, such as the enantioselective acid–base enhanced reaction, are expected.

SUMMARY

Since the discovery of robust, permanent porous metal-organic coordination polymer frameworks and their gas/solvent adsorption properties, the structural modification and their sorption studies have been extensively developed during the last decade along with the progress of X-ray analysis techniques. The functionalization of the pore structure of PCPs via self-assembly requires high ordering and density of guest-accessible sites with excellent yield and this point is quite different from a post-synthetic approach, which is popular for mesoporous materials.

Moreover, the sophisticated assembly of these functional groups in a nanospace would make the precise confinement of desired guests and selective catalytic reaction possible. The combination of organic ligands, metal ions, and/or synthetic conditions allows one to control PCPs properties rationally and to optimize them for desired application, and the higher activity of the synthesized

compounds may contribute to the new generation of functional porous materials.

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