Coordination Chemistry Reviews 335 (2017) 28–43

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Recent advances in guest effects on spin-crossover behavior in Hofmann-type metal-organic frameworks

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ARTICLE INFO

Article history:
Received 25 October 2016
Accepted 5 December 2016
Available online 18 December 2016

Keywords:
Spin-crossover
Host-guest interaction
Hofmann-type
Metal-organic frameworks

ABSTRACT

The incorporation of spin-crossover (SCO) properties into metal-organic frameworks (MOFs) is an appealing subclass of multifunctional MOFs with potential applications in molecular sensing. This review focuses on the design of SCO Hofmann-type MOFs, with emphasis on the guest effect on their SCO properties. The influences of guest size, dielectric constant, $\pi\cdots\pi$ interaction, hydrogen bonding interactions, weak X···M′ covalent bonding, and chemical reaction on the SCO properties of Hofmann-type MOFs are systematically explored. Further enhancements of sensing properties are also illustrated.

Contents

Abbreviations: azpy, *trans*-4,4′-azopyridine; pz, pyrazine; py, pyridine; 3-Fpy, 3-fluoropyridine; 3-NH_2py, 3-aninopyridine; phpy, 4-phenylpyridine; bpac, bis(4-pyridyl) acetylene; bpeben, 1,4-bis(4-pyridylethynyl)-benzene; dpsme, 4,4′-di(pyridylthio)methane; bipytz, 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine; bpmp, 1,4-bis(pyridin-4-ylmethyl) piperazine; bpp, 2,5-bis(pyrid-4-yl)pyridine; dpb, 1,4-di(pyridin-4-yl)benzene; bz, benzene; Ac, acetone; Acn, acetonitrile; IBz, iodobenzene; MeOH, methanol; EtOH, ethanol; Tol, toluene; fur, furan; pyr, pyrrole; thio, thiophene; Mal, maleic anhydride; HMal, Maleic acid; bpbd, 2,3-bis(4′-pyridyl)-2,3-butanediol; *n*-PrOH, 1-propanol; C_6H_{12}, cyclohexane; *s*-BuOH, *sec*-butanol; *i*-BuOH, isobutanol; *i*-PrOH, isopropanol; naph, naphthalene; anth, anthracene; TClBz, 1,2,4-trichlorobenzene; ClBz, chlorobenzene; BrBz, bromobenzene; dpe, 1,2-di(4-pyridyl)ethylene; dpa, 1,2-di(4-pyridyl)ethane; bbz, bibenzyl; stb, stilbene; bpb, bis(4-pyridyl)butadiyne; bipydz, 3,6-bis(4-pyridyl)-1,2-diazine; C_7H_8, 2,5-norbornadiene.

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http://dx.doi.org/10.1016/j.ccr.2016.12.002
0010-8545/

1. Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are a class of porous crystalline material consisting of metal ions and organic linkers [1–3]. Due to their designable and tunable composition, structure, porosity and functionality, MOFs have attracted great attention during the past two decades. In addition to the continuous optimization of porous properties for gas storage [4–11] and separation [12–16], promising functionalities such as luminescence [17–22], conductivity [23,24], magnetism [25–28], catalytic activity [29–34] and chirality [35,36] were also widely explored by the incorporation of the corresponding functional building blocks or guests. The potential applications of MOFs have been extensively investigated in many fields such as gas storage [4–11], molecular separation [12–16,37,38], catalysis [29–34], sensing [19–21,39,40], biomedicine [41–45] and energy storage [46–51].

Among the functional MOFs, incorporation of the spin-crossover (SCO) property into MOFs yields undoubtedly an appealing subclass of MOFs [52–56], in which the switching between high-spin (HS) and low-spin (LS) states of $d^4–d^7$ transition-metal ions can be triggered by external perturbations such as temperature, pressure, light, or guest [57,58]. Along with the change of spin states, dramatic physical responses in structure, colour and polarizability appear simultaneously, which provides many useful outputs. Its potential application in the area of molecular sensing was well illustrated in the SCO MOFs $[Fe(azpy)_2(NCS)_2]$ by Kepert and co-workers in 2002 [59]. Hereafter, this family of $[Fe(L)_2(NCS)_2]$ (L = bis-monodentate ligand) was rapidly developed, which was structurally characterized as the double interpenetration of two-dimensional (2D) rhombic grids leading to 1D channels [60–66]. Unfortunately, their spin transition temperatures were always lower than room temperature. Once the cooperative SCO property near room temperature was revealed in the 3D Hofmann-type MOFs $[Fe(pz)M'(CN)_4]$ (**pzM′**, M′ = Ni^{2+}, Pd^{2+}, or Pt^{2+}) [67], they immediately attracted great attention [68–75]. Especially, their guest-dependent SCO properties were excitedly explored, in which the guest adsorption and desorption served as the perturbation [76,77]. In these Hofmann clathrates, the host can be interacted with the guest through van der Waals interactions, $\pi\cdots\pi$ interactions, hydrogen bonding and even coordination bonding. Most interestingly, the guest-dependent memory effect was observed, which added a unique functionality to molecular sensing [78,79]. In this review, we highlight the details of guest effects on the SCO properties in these appealing Hofmann-type coordination polymers $[Fe(L)_nM'(CN)_4]\cdot G$ (n = 1 or 2 for the bridging or unidentate ligands, respectively; and M′ = Ni^{2+}, Pd^{2+}, or Pt^{2+}; G = guest) and $[Fe(L)_n\{M'(CN)_2\}_2]\cdot G$ (M′ = Ag^+ or Au^+) abbreviated by **LM′·G** (Fig. 1).

1.1. Spin-crossover

SCO materials are typical molecular switching species, which can switch between two well-defined HS and LS states. It offers potential applications in data storage, displays, switches and sensors [80–83]. The occurrence of SCO phenomenon is fundamentally rationalized by the ligand-field theory [84]. Since the energy of the d orbitals splits into t_{2g} and e_g sets for octahedral coordination compounds, transition metal ions with $d^4–d^7$ electronic configurations may exist in either HS or LS state depending on the ligand field strength. For example, in the case of iron(II) ion, $t_{eg}^4e_g^2$ ($^5T_{2g}$) and $t_{eg}^6e_g^0$ ($^1A_{1g}$) configurations correspond to the HS and LS states, respectively. When the strength of ligand field is suitable, the energy difference of the zero point energies for the HS and LS states, $\Delta E_{HL}^0 = E_{HS}^0 - E_{LS}^0$, can decrease to a small value close to the thermal energy k_BT. Thus, a thermally induced SCO phenomenon can be observed [85–87].

Since the nature of e_g orbitals is antibonding, the population and depopulation of two electrons in e_g orbitals provokes obvious structural changes in the coordination sphere around iron(II). Therefore, the average Fe—N bond distance can be shortened by 0.2 Å, which corresponds to about 10% of the Fe—N bond length or 5% of the unit cell volume [85]. These dramatic changes can be transmitted cooperatively in the solid state through elastic interactions [88]. When the cooperativity is weak, only gradual SCO behavior is observed. On the contrary, when the cooperativity is strong, abrupt or even hysteretic SCO behavior can occur, which is important for the practical application of SCO materials [85,86,89]. To get strong SCO cooperativity, two kinds of approaches have been widely investigated. One is the introduction of effective intermolecular interactions, such as $\pi\cdots\pi$ interactions and hydrogen bonding [87,90–92]. The other is the introduction

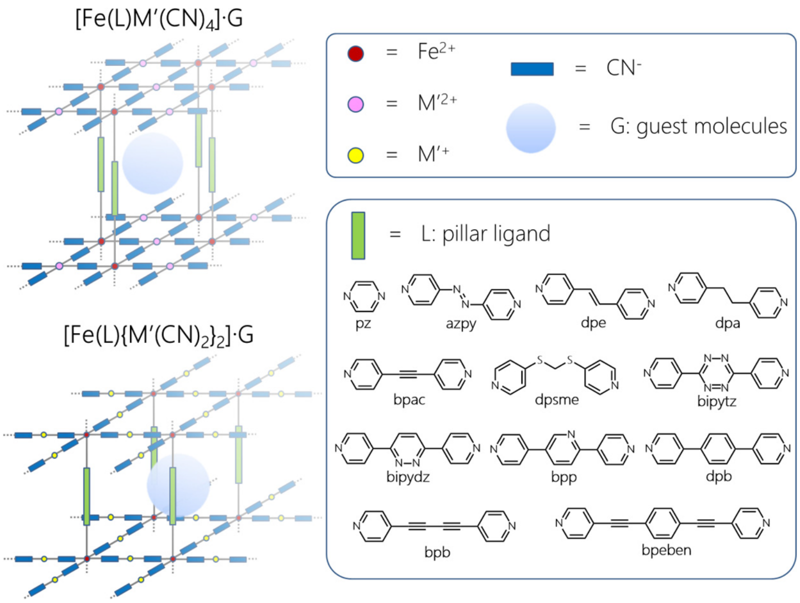

Fig. 1. Schematic illustration of 3D Hofmann-type MOFs $[Fe(L)M'(CN)_4]\cdot G$ (M′ = Ni^{2+}, Pd^{2+}, or Pt^{2+}) and $[Fe(L)\{M'(CN)_2\}_2]\cdot G$ (M′ = Ag^+ or Au^+).