Inorganic Chemistry Communications 61 (2015) 35–40

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Short communication

Construction and structural diversity of Cd-MOFs with pyrazole based flexible ligands and positional isomer of naphthalenedisulfonate

Udai P. Singh [a,*], Neetu Singh [a], Suman Chandra [b]

[a] Department of Chemistry, Indian Institute of Technology, Roorkee, Roorkee 247 667, Uttarakhand, India
[b] Physical/Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India

ARTICLE INFO

Article history:
Received 15 June 2015
Received in revised form 8 August 2015
Accepted 14 August 2015
Available online 20 August 2015

Keywords:
Cadmium(II)
Coordination polymers
Conformation
Naphthalenedisulfonate
Thermal stability
Photophysical properties

ABSTRACT

In the present communication, we have reported the construction of a series of Cd(II)-MOFs using conformationally flexible ligand (CFL); 3,3′,5,5′-tetramethyl-4,4′-bipyrazolyl (H_2BPz), flexible bent ligand (FBL); methylenebis-(3,5-dimethylpyrazole) (H_2MBPz) and positional isomer of naphthalene disulfonic acid salt ligands (1,5-NDS, 2,6-NDS). By using these ligands, four new coordination polymers namely $[Cd(H_2MBPz)_2{\cdot}1,5\text{-}NDSA]_n$ (NDS-MOF-1), $[Cd(H_2BPz){\cdot}1,5\text{-}NDSA]_n$ (NDS-MOF-2), $\{[Cd(H_2MBPz)_2]^{2+}{\cdot}2,6\text{-}NDSA^{2-}\}_n$ (NDS-MOF-3) and $\{[Cd(H_2BPz)_2]^{2+}{\cdot}2,6\text{-}NDSA^{2-}\}_n$ (NDS-MOF-4) have been synthesized. The crystal structure analysis revealed that the employment of positional isomeric naphthalene disulfonic acid salts resulted in different architectures ranging from one dimensional chain to two dimensional grid network and further connected into a three dimensional supramolecular structure through intermolecular hydrogen bonds, π···π and C–H···π interactions. In addition, the photophysical properties and thermal stability studies for all the NDS-MOFs 1–4 were also investigated.

During the past several years, metal-organic frameworks (MOFs) have gained huge attraction to become one of the most rapidly developing research areas in chemical and material sciences and emerged as an important ancestor of porous materials. This is not only because of their intriguing network [1] topologies, but also due to their exploitable properties for potential applications including gas adsorption and separation, catalysis, luminescence, sensing, and proton conduction [2–6].

In literature, as there is a prolific production of MOFs based on rigid ligands, the design, synthesis and applications of MOFs based on flexible ligands have so far attracted peerless attention [7]. Therefore, the construction of flexible ligands based MOFs has been found to be difficult due to the flexibility of ligands that can adopt different conformations via bending, twisting, or rotating and thus lead to distinct symmetries during self-assembly process [8]. Although various azoles based flexible ligands have been used for the construction of one, two and three dimensional coordination polymers [9]. In the category of flexible ligands, H_2BPZ and H_2MBPz have received considerable attention as a better linker and both serve as a neutral bridging, bidentate ligand to connect two metal ions [10–15]. The extensive work has been carried out using these attractive and structurally simple ligands from which several porous and the helical nature of coordination polymer has been reported [16].

In comparison to carboxylates and even phosphonates, sulfonate coordination polymer is still very unexplored because of the spherical and poor ligating in the nature of the SO_3 group but conventionally, dynamic behavior of sulfonate framework is more dominant than the robustness of sulfonate coordination. Many literatures are available in the different coordination modes of sulfonate by changing the substituent on the arenesulfonate [17]. Here we report the change in coordination behavior of the sulfonate group to the metal center by changing the position of sulfonate group from α to β of the naphthalene. Cai et al. prepared aqua metal sulfonate salts from the aqueous solution of metal sulfonate and reported the tunable coordination behavior of arenedisulfonate in metal sulfonate with the addition of amino acid [18]. Also on introducing the other auxiliary ligands to the metal center, the sulfonate anion and water compete for the coordination with the metal center [19].

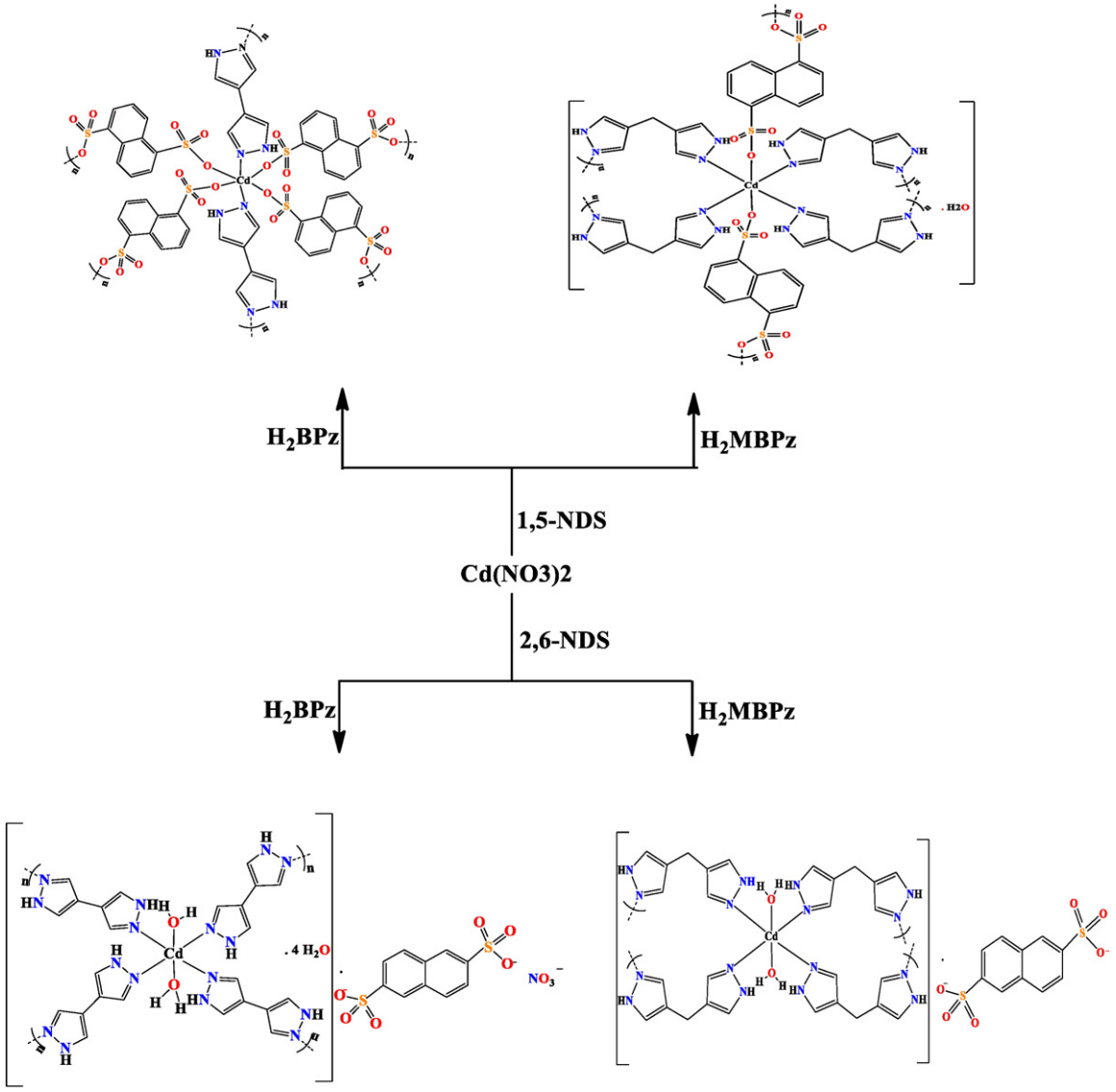
The tridentate sulfonate anions have received significant interest as they may give intricate and diverse supramolecular architecture [20]. In general, the use of multifunctional sulfonates such as arenedisulfonates has been directed toward the formation of pillared layer metal sulfonates, microporous and nanoporous solids, etc. [21]. In recent years, various flexible N-donor azole based ligand MOFs together with aromatic and aliphatic carboxylates have been reported [22]. However, coordination polymers based on these flexible azoles and sulfonates are very limited [23].

In this report, we have synthesized and structurally analyzed a series of MOFs, derived from a mixed ligand system viz. H_2Bpz and H_2MBPz as well as various isomeric disulfonates i.e. 1,5-NDS and 2,6-NDS (Scheme 1).

The implementation of a methodical approach has extended researchers to understand the effect of positional isomer of

* Corresponding author.
E-mail address: udaipfcy@iitr.ernet.in (U.P. Singh).

http://dx.doi.org/10.1016/j.inoche.2015.08.009
1387-7003/



Scheme 1. Synthesis of MOFs 1–**4**.

naphthalenedisulfonate on the coordination behavior of sulfonate and conformation of H_2BPz and H_2MBPz ligands. Although the exploitation of structural diversity of sulfonates and pyrazole has been performed separately, to the best of our knowledge, there are no reports in literature about the effect of the change in conformation of H_2BPz and H_2MBPz with different isomers of naphthalenedisulfonates.

Single crystal X-ray diffraction analysis revealed that NDS-MOF-1 crystallizes in the monoclinic crystal system with *P2/n* space group

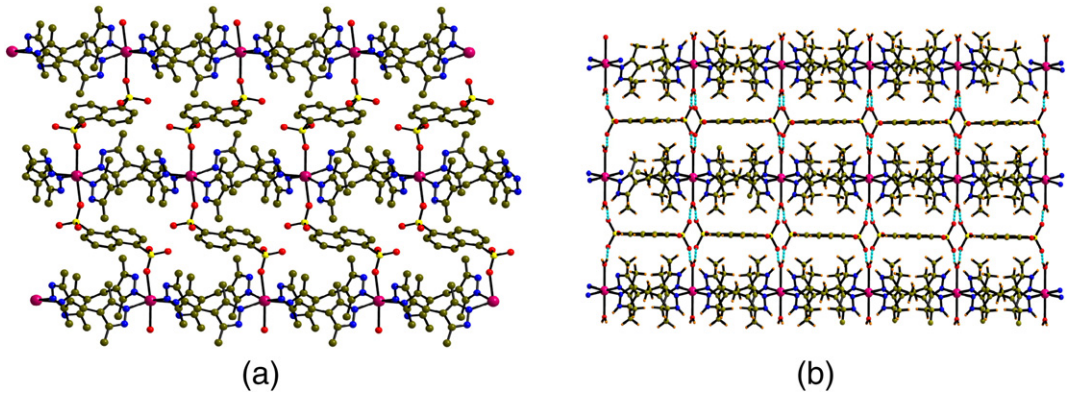


Fig. 1. View of 2D sheet representing the interaction of positional isomer of sulfonates with the 1D tape of metal and H_2MBPz.