

## Microporous structures having phenylene fin: Significance of substituent groups for rotational linkers in coordination polymers



Ryotaro Matsuda<sup>a,b,\*</sup>, Wataru Kosaka<sup>c</sup>, Ryo Kitaura<sup>d,1</sup>, Yoshiki Kubota<sup>e</sup>, Masaki Takata<sup>b,f</sup>, Susumu Kitagawa<sup>a,b,d,\*</sup>

<sup>a</sup> Institute for Integrated Cell-Material Sciences, Kyoto University, Nishikyo-ku, Katsura, Kyoto 615-8510, Japan

<sup>b</sup> Harima Institute, RIKEN SPring-8 Center, Sayo-gun, Hyogo 679-5148, Japan

<sup>c</sup> Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

<sup>d</sup> Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

<sup>e</sup> Department of Physical Science, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

<sup>f</sup> Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan

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### ABSTRACT

Microporous coordination polymers having various shaped apertures were synthesized and crystallographically characterized using substituted terephthalate ligands. The substituents exert a notable influence on the channel size and shape depending on the orientations and disordering of the phenylene units such as a fin. This is a new aspect of porous coordination polymers, which would provide important information for a precise design of the micropore.

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### 1. Introduction

A new class of microporous materials known as porous coordination polymers that are constructed from metal ions and organic bridging ligands, has recently attracted a great deal of attention.[1–8] because of wide potential application ranging from gas storage,[9–16] molecular recognition and separation,[17–27] and heterogeneous catalysis [28–30] as multifunctional crystalline materials.[31–35] Now, they are gaining an important position in porous materials and adding a new category to a conventional classification. One of the advantages of microporous coordination polymers is highly designable framework in terms of pore shapes and surface property; even in topologically similar frameworks, sophisticatedly functionalized building units (i.e. organic ligands with functional groups) could provide a variety of porous proper-

ties. In these two decades, a large number of coordination polymers have been synthesized, most of which contain organic linkers having a fused hydrocarbon or heterocyclic rings for the sake of framework rigidity, affording a regular well-defined structures. Because the size of micropore is comparable to that of linkers and guest molecules, even a slight modification of the linker would impact on the sorption behavior of guest molecules. In a sense, size and shape of substituent group have important effect more than we expected. However, to date are sparse reports on analysis and examination of channel surfaces for microporous coordination polymers, where linkers are modified by substituents with the retention of topology. This is ascribed to the difficulty in systematic work that the crystal structure determination and examination of porous properties are simultaneously performed for all the compounds, whose linkers are systematically modified by substituent groups.

Recently, a series of 3-D grid-type frameworks have been constructed from M(II)/dicarboxylate/pillar ligand (where M = Cu(II) or Zn(II), pillar ligand = 1,4-diazabicyclo[2,2,2]octane (dabco), 4,4'-bipyridine or ligands with bis(4-pyridyl) group), which exhibit a high gas storage capacity.[13,21,36–67] These compounds have a

\* Corresponding authors at: Institute for Integrated Cell-Material Sciences, Kyoto University, Nishikyo-ku, Katsura, Kyoto 615-8510, Japan. Tel./fax: +81 75 383 2103.

E-mail addresses: [ryotaro.matsuda@gmail.com](mailto:ryotaro.matsuda@gmail.com) (R. Matsuda), [kitagawa@icems.kyoto-u.ac.jp](mailto:kitagawa@icems.kyoto-u.ac.jp) (S. Kitagawa).

<sup>1</sup> Current address: Department of Chemistry, Nagoya University, Nagoya 464-8602, Japan.

Jungle-gym-Analogue Structure, hereafter, this family is denoted as JAST, rationally obtained using various dicarboxylate building units. To gain a better understanding of chemical modification, namely substituent effect, on pore walls, and to establish guidelines in the design and synthesis of microporous coordination polymers, we focus on the influence of the introduction of substituents in linking ligands both on size and shape of the channel structures and on sorption properties (Scheme 1).

## 2. Experimental section

### 2.1. Syntheses

**2,3-Difluoro-1,4-benzenedicarboxylic acid (H<sub>2</sub>DFBDC):** To 2,3-difluorobenzoic acid (12.0 g, 76.1 mmol) in anhydrous tetrahydrofuran (THF) (230 mL) was added 1.6 M *n*-buthyllithium in hexane (110 mL, 176 mmol) at  $-78^{\circ}\text{C}$ . After stirring 2 h at  $-78^{\circ}\text{C}$ , excess dry ice was added then the temperature was gradually allowed to rise to room temperature. The suspension was stirred for 1 h. Following acidification with 1 N HCl solution (200 mL) at  $0^{\circ}\text{C}$ , the organic phase was extracted with diethyl ether. The extracts were washed with water and dried over Na<sub>2</sub>SO<sub>4</sub> then evaporated to dryness under reduced pressure (3.65 g, 18.1 mmol, 24% yield). Mass: *m/e* (%) 203 [M + 1<sup>+</sup>, (88)], 185 [M-OH, (100)], 158 [M-COOH, (6)].

**2,3-Dimethoxy-1,4-benzenedicarboxylic acid (H<sub>2</sub>DMBDC):** To 1,2-dimethoxybenzene (1.91 mL, 15.0 mmol) and N,N,N',N'-tetramethylethylenediamine (TMEDA) (36.6 mL, 60.0 mmol) in anhydrous diethyl ether (Et<sub>2</sub>O) (100 mL) was added dropwise 1.6 M *n*-buthyllithium in hexane (10.6 mL, 70.0 mmol) at  $-78^{\circ}\text{C}$ . After stirring 2.5 h at  $-78^{\circ}\text{C}$ , the temperature was allowed to rise to room temperature then the suspension was stirred for 3 days. After the temperature was allowed to decrease to  $-78^{\circ}\text{C}$ , excess dry ice was added then the temperature was gradually allowed to rise to room temperature and the mixture was stirred at room temperature. The Following acidification with 1 N HCl solution (100 mL)

at  $0^{\circ}\text{C}$ , the organic phase was extracted with diethyl ether. The extracts were washed with water and dried over Na<sub>2</sub>SO<sub>4</sub> then evaporated to dryness under reduced pressure (583 mg, 2.58 mmol, 17% yield). <sup>1</sup>H-NMR (CD<sub>3</sub>OD):  $\delta = 7.41$  (s, 2H),  $\delta = 3.83$  (s, 6H). Mass: *m/e* (%) 226 [M<sup>+</sup>, (100)], 151 [M-OCH<sub>3</sub>-COO, (68)], 134 [M-(COOH)<sub>2</sub>, (25)].

JAST-1, -2, -3-4 and -5: JAST-1 was prepared by using the literature [36,37] method, with some modifications. A solution of Cu(HCOO)<sub>2</sub>·4H<sub>2</sub>O (0.21 g, 1.00 mmol) dissolved in methanol (100 mL) and formic acid (2 mL) was slowly added to the methanol solution (100 mL) containing 1,4-benzenedicarboxylic acid (0.21 g, 1.00 mmol) at room temperature. After stirring for 3 day, the blue resultant precipitate were separated by centrifugation from mother liquor then transferred to stainless sealed Teflon reaction vessel. A toluene/methanol (1/1) solution of 1,4-diazabicyclo[2,2,2]octane (dabco) was added to the vessel. After reaction at 413 K for 12 h, the resultant yellow-green precipitate was filtered, washed with methanol and dried under reduced pressure. JAST-2, -3, -4 and -5 was prepared in the same way as described for JAST-1 by using H<sub>2</sub>DFBDC, H<sub>2</sub>NDC, H<sub>2</sub>TfBDC and H<sub>2</sub>DMBDC instead of H<sub>2</sub>BDC, respectively.

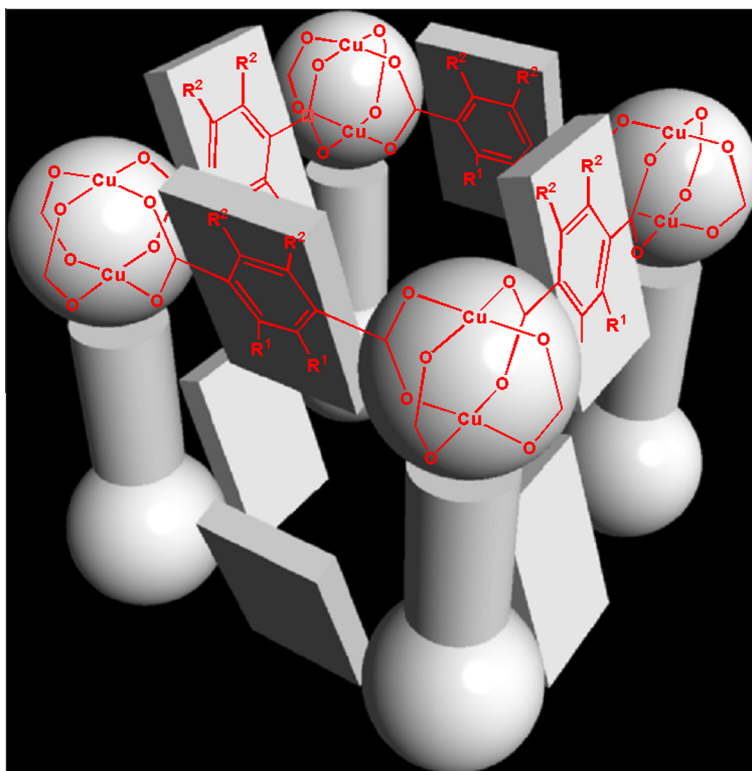
### 2.2. Adsorption measurements

The adsorption isotherms nitrogen at 77 K were measured with BELSORP18 volumetric adsorption equipment from Bel Japan. Nitrogen gas of high purity (99.9999%) were used. Prior to the adsorption measurements, all samples were obtained by treating under reduced pressure ( $<10^{-2}$  Pa) at 393 K for more than 10 h.

### 2.3. Dubinin–Radushkevich (DR) analysis [68]

The DR equation is given by

$$\ln W = \ln W_0 - (A/\beta E_0)^2 \quad (1)$$



**Scheme 1.** Representation of the “phenylene fin” in a microporous coordination polymer.

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