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Guest responsivity of a two-dimensional coordination polymer incorporating a cholesterol-based co-ligand†

Kazuki Kajitani,[a] Tomomi Koshiyama,[a] Akihiro Hori,[b] Ryo Ohtani,[c] Akio Mishima,[a] Kohei Torikai,[a] Makoto Ebine,[a] Tohru Oishi,[a] Masaki Takata,[b] Susumu Kitagawa[b,c,d] and Masaaki Ohba*[a,b]

To implement specific guest responsivity, a hydrophobic cholesterol-based co-ligand, cholest-5-en-3-yl-4-isonicotinate (Cholpy), was incorporated into a two-dimensional Hofmann-type Co(II)Ni(II) coordination polymer. The chemically programmed structure successfully demonstrated the unique guest response with remarkable chromatic changes.

The design strategy to produce functional coordination polymers (CPs, or metal–organic frameworks (MOFs)), formed by alternate arrays of mono- or polynuclear metal building units and organic ligands as linkers, has made remarkable progress in recent years.[1] The structural diversity of CPs exceeds that of the parental coordination compounds, and CPs can inherit and merge the original characteristics of the constituent coordination compounds depending on an appropriate molecular design. CPs provide one promising platform to programme the desired functions and properties. In the past decade, CPs providing uniform pores within their structure have been developed and are called porous coordination polymers (PCPs), which have emerged as a new class of porous materials that represent an evolved form of CPs.[1] PCPs provide a flexible and designable framework with highly regular pores. It is expected that they will find applications as general use porous solids[2] (*e.g.*, for gas storage, separation materials, ion exchange and heterogeneous catalysts) and as new multifunctional materials that combine porous properties with physical properties[3] (*e.g.*, magnetic, proton conductive and optical properties). To achieve such specific functions, a well-designed coordination programme of frameworks that closely links host–guest interactions with their properties is essential.

Hofmann-type CPs $\{M(L)_2[M'(CN)_4]G\}$ (M = Co, Mn, Fe, Ni *etc.*; M'^{II} = Ni, Pd and Pt; L = axial co-ligand; G = guest molecule) are some of the most attractive compounds to provide a multifunctional platform.[4] The Hofmann-type CPs have a two-dimensional (2-D) layer structure extended by M–CN–M′ linkages of six coordinated octahedral M^{II} ions and accommodate guest molecules between the layers. Our group has investigated 3-D Hofmann-type PCPs $\{Fe(pz)[M(CN)_4]\}$ (pz = pyrazine; M^{II} = Ni, Pd and Pt).[4c–j] The compounds have pillared layer structures linking 2-D layers of $\{Fe[M(CN)_4]\}_\infty$ through Fe–pz–Fe bridges and show spin transition around room temperature. The framework provides important interactive sites on the pz pillar ligands and the coordinatively unsaturated M^{II} centres. The spin states of the Fe^{II} ion switch between the high-spin (HS) and low-spin (LS) states, depending on the guest molecule. By contrast, the 2-D Hofmann-type CPs $\{Fe(L)_2[M^{II}(CN)_4]\}$ (L = pyridine, *etc.*) respond to no guest molecules because of their closely packed interlayer structure, which results from the stronger interaction between the axial co-ligands.[4b,k] To use the 2-D structure for delivering specific guest responsivity, we contrived to incorporate hydrophobic co-ligands between the layers as additional guest-responsive sites. From the perspective of the hydrophobic area, we focused on an amphiphilic cholesterol molecule having a steroid ring, an alkyl group and a reactive hydrophilic hydroxyl group.[5] We found that the cholesterol derivatives could act as an axial co-ligand for the 2-D Hofmann-type structure (Scheme 1). Here, we report on a new 2-D Hofmann-type CP, $\{Co(Cholpy)_2[Ni(CN)_4]\}$ (Cholpy = cholest-5-en-3-yl isonicotinate; **1**), which incorporated a hydrophobic area, and its guest responsivity, which was associated with chromatic changes.

The cholesterol-based co-ligand Cholpy‡ was prepared by modification of a method reported in the literature.[6] The crystal structure of Cholpy is shown in Fig. S1.† $\{Co(Cholpy)_2[Ni(CN)_4]H_2O\}$ (**1**·H_2O)‡ was obtained as orange

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[a] Department of Chemistry, Faculty of Science, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, Japan. E-mail: ohba@chem.kyushu-univ.jp; Fax: +81-92-642-2570; Tel: +81-92-642-2570

[b] Quantum Order Research Group, RIKEN SPring-8 Center, Koto 1-1-1, Sayo-cho, Sayo, Hyogo, Japan

[c] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto, Japan

[d] Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto, Japan

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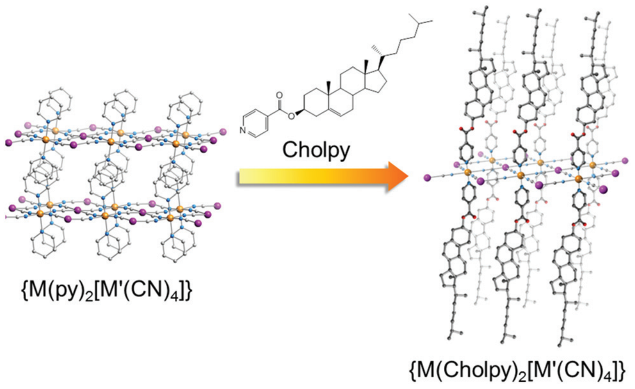


Scheme 1

microcrystals by the reaction of a tetrahydrofuran (THF) solution of $Co(NO_3)_2{\cdot}6H_2O$ and Cholpy, and an aqueous MeOH solution of $K_2[Ni(CN)_4]{\cdot}H_2O$.

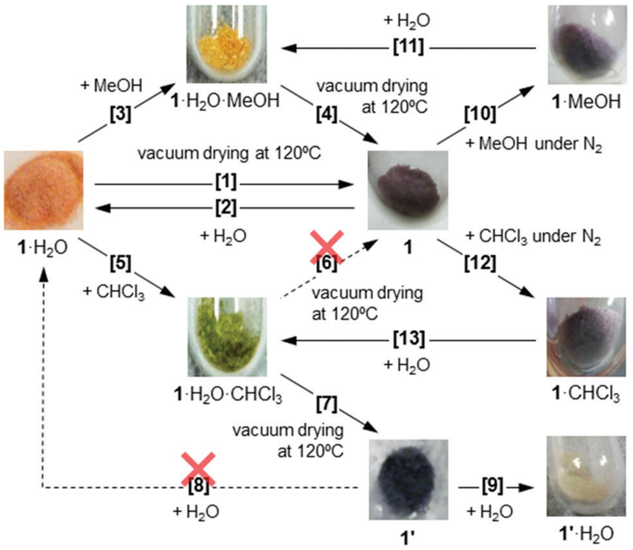
Infrared (IR) spectra of **1**·H_2O and Cholpy are shown in Fig. S2.† Compound **1**·H_2O showed typical bands attributed to Cholpy and a strong single C≡N stretching band at 2165 cm^{-1}. The formation of Ni–C≡N–Co bridges in **1**·H_2O was confirmed by the upshift of the ν_{CN} band from that of $K_2[Ni(CN)_4]$ (2122 cm^{-1}).

Microcrystals of **1**·H_2O showed a broad X-ray powder diffraction (XRPD) pattern indicating low crystallinity of **1**·H_2O (Fig. S3†). The low-angle region XRPD pattern of **1**·H_2O resembled the simulation pattern of $\{Fe(pep)_2[Pt(CN)_4]\}$ (**2**; pep = 4-(2-phenylethyl) pyridine).[4k] Compound **2** had an interdigitated 3-D network, linking the 2-D Hofmann-type layers by weak π–π interactions between the relatively large co-ligands pep. Several peaks were indexed based on the structure of **2**, in which in-plane peaks upshifted because the atomic radius of Ni is shorter than that of Pt, and because the out-of-plane (interlayer) peaks downshifted. These results and the single ν_{CN} band in the IR spectrum suggested that **1**·H_2O formed a 2-D Hofmann-type framework with an elongated interlayer structure by the large co-ligand Cholpy. The large interlayer separation should explain the low crystallinity.

The monohydrate **1**·H_2O adsorbed various guest molecules in the gas phase or in solution and retained the lattice water molecule. A change in colour of **1**·H_2O accompanied the guest adsorption (Table 1). Guest molecules were grouped into two classes according to their effect on the sample colour. Most of the solvents gave yellow products, as observed for MeOH. By contrast, with $CHCl_3$ and CH_2Cl_2 the colour changed to green. Here, MeOH and $CHCl_3$ were selected as representative guest molecules. The compositions of guest clathrates **1**·H_2O·G were estimated by thermogravimetric analysis (Fig. S4†). Magnetic measurements showed the Co^{II} ion in the HS state at room temperature in all clathrates.

Table 1 Summary of the guest responsivity of **1**·H_2O

Colour	Guest molecules (G)
Yellow	MeOH, EtOH, 1-PrOH, 2-PrOH, MeCN, $MeNO_2$, Et_2O, THF, hexane, benzene, toluene and CS_2
Green	$CHCl_3$ and CH_2Cl_2



Scheme 2

Compound **1**·H_2O showed unique guest responses with chromatic changes through somewhat complicated processes (Scheme 2). The guest responsivity was detected by solid-state reflectance spectra measured under guest vapour (Fig. S5†). The initial state **1**·H_2O was changed to guest-free **1** by vacuum drying at 120 °C for 12 h (process [1] in Scheme 2). During dehydration, the sample colour changed to purple and new adsorption bands appeared around 540 and 580 nm. In process [2], the colour of guest-free **1** was returned to orange (**1**·H_2O) by rehydration. The colour of **1**·H_2O was changed to yellow by absorption of MeOH (**1**·H_2O·MeOH) with decreasing intensity of an absorption band around 550 nm (process [3]). Compound **1**·H_2O·MeOH was changed to **1** by desolvation (process [4]) and was returned to the initial state **1**·H_2O by rehydration (process [2]). The three-step colour change between orange, purple and yellow was reversible through guest adsorption and desorption processes [3] → [4] → [2]. By contrast, the colour of **1**·H_2O was changed to green by adsorption of $CHCl_3$ (**1**·H_2O·$CHCl_3$; process [5]), and new absorption bands appeared around 600 and 650 nm. Vacuum drying (process [6]) did not change the colour of **1**·H_2O·$CHCl_3$ to purple but to dark blue (**1′**) and produced a new absorption band around 550 and 580 nm (process [7]). The desolvated **1′** was not returned to the initial state **1**·H_2O by rehydration (process [8]) but changed to a light-yellow solid (**1′**·H_2O). Compound **1′**·H_2O showed a reflectance spectrum similar to that of **1**·H_2O·MeOH with additional weak bands around 650 and 680 nm. The three-step colour change between orange, green and light yellow through processes [5] → [7] → [9] was irreversible, and the guest-free **1** exhibited different guest responsivities under a N_2 atmosphere. In processes [10] and [12], **1** adsorbed MeOH (**1**·MeOH) and $CHCl_3$ (**1**·$CHCl_3$), respectively,

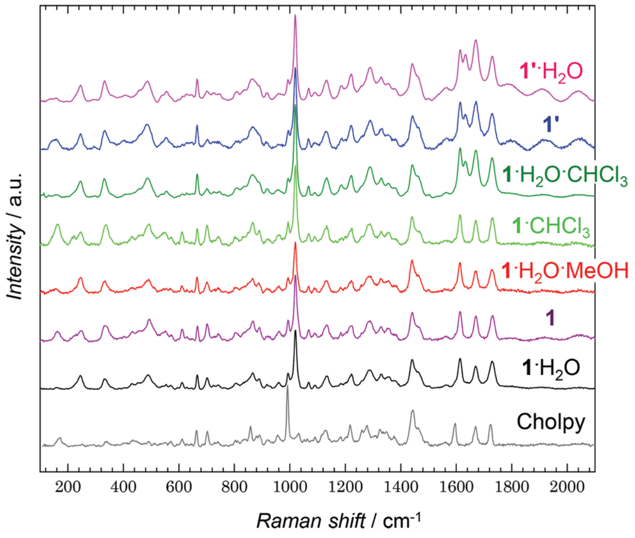
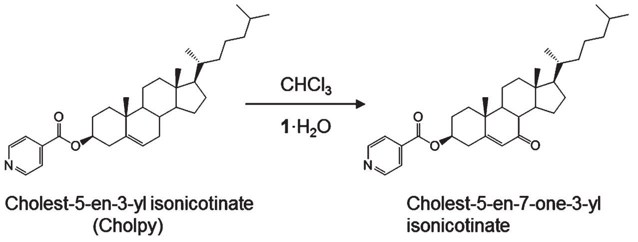


Fig. 1 Raman spectra of **1**·H_2O, Cholpy and the resulting compounds through the guest adsorption and desorption processes.

after exposure to the guest vapour under N_2, but without changing colour. Compounds **1**·MeOH and **1**·$CHCl_3$ were converted to **1**·H_2O·MeOH and **1**·H_2O·$CHCl_3$ by hydration processes [11] and [13], respectively. The responses of **1** through the processes [10] → [11] and [12] → [13] suggest that H_2O plays an important role in guest responsivity.

Raman spectra of Cholpy, **1**·H_2O, **1**, **1**·H_2O·MeOH, **1**·$CHCl_3$, **1**·H_2O·$CHCl_3$, **1′** and **1′**·H_2O are shown in Fig. 1 and S6.† Compared with the Raman spectrum of **1**·H_2O, the guest-free **1** prepared by process [1] showed a new band that could be attributed to the coordination bond around Co^{II} at 246 cm^{-1}. The band was also observed in **1**·$CHCl_3$ prepared by process [12] under N_2. The appearance of the new band suggested that the symmetry around Co^{II} was reduced with elongation of the axial Co–N bond by dehydration and that the reduced symmetry was not recovered without the lattice H_2O. The reduced symmetry allows the d–d transition with lifting of the Laporte-forbidden transition, which explained the strong absorption band around 580 nm in the solid-state reflectance spectra of **1** and **1**·$CHCl_3$. Compound **1**·H_2O and Cholpy showed three characteristic Raman bands that could be attributed to a steroid ring around 610, 665 and 703 cm^{-1}. In the case of **1**·H_2O·$CHCl_3$ compared with **1**·H_2O, two of the bands around 610 and 703 cm^{-1} disappeared and a new band appeared at 1633 cm^{-1} but without symmetry changes around Co^{II}. The latter band was attributed to a structural change in Cholpy. A similar spectrum pattern was also observed in desolvated **1′** (process [7]) and rehydrated **1′**·H_2O (process [9]), whereas **1**·$CHCl_3$ (process [12]) showed no change around 610, 703 and 1633 cm^{-1}.

IR spectra of **1**·H_2O and the resulting compounds (**1**, **1**·H_2O·MeOH, **1**·H_2O·$CHCl_3$, **1**·MeOH, **1**·$CHCl_3$, **1′** and **1′**·H_2O) are shown in Fig. S7.† The spectrum patterns of **1**, **1**·MeOH, **1**·H_2O·MeOH and **1**·$CHCl_3$ showed no remarkable changes compared with **1**·H_2O. In the cases of **1**·H_2O·$CHCl_3$, **1′** and **1′**·H_2O, a new peak appeared at 1672 cm^{-1}. The spectrum changes corresponded well to the structural changes in Cholpy as indicated by the Raman spectra.



Scheme 3

To confirm the structural change in Cholpy, the co-ligand was extracted from **1**·H_2O·$CHCl_3$ (see ESI†). After an isolation treatment of **1**·H_2O·$CHCl_3$ with a solution of disodium ethylenediaminetetraacetate, a white precipitate was obtained from the organic phase. IR spectra of the extracts showed that a peak appeared at 1672 cm^{-1} as shown for **1**·H_2O·$CHCl_3$, **1′** and **1′**·H_2O. ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) and MALDI-TOF-MS spectra of the extracts revealed that Cholpy was changed to Cholest-5-en-7-one-3-yl isonicotinate (calcd for $C_{33}H_{48}NO_3$ ($[M + H]^+$) m/z 506.3, found 507.4) during the absorption process of $CHCl_3$ (Scheme 3, Fig. S8 and S9†), which corroborated the irreversible changes observed in IR and Raman spectra. The allylic oxidation of steroid is explained by a radical reaction involving $Cl^{\cdot}$ and $^{\cdot}OH$ species.[7]

These guest responses emphasize the following two points: (a) the chromatic changes through processes [3], [5], [11] and [13] were assisted by lattice water, and (b) the origin of the chromatic change induced by $CHCl_3$ uptake (process [5]) was different from that induced by MeOH (process [3]). Such chromatic changes were not observed in the analogous 2-D Hofmann-type compounds {$Co(L)_2[Ni(CN)_4]$} (L = pep, 4-styrylpyridine and pyridine derivatives), which highlights the effect of the co-ligand Cholpy on the guest responsivity (Fig. S10†). In addition, another analogue {$Ni(Cholpy)_2[Ni(CN)_4]\cdot nH_2O$} (**3**·$H_2O$) did not exhibit a notable colour change when exposed to MeOH and $CHCl_3$ vapour (Fig. S11†). These results suggest that both Co^{II} and Cholpy are essential factors for the specific guest responsivity.

Conclusions

The guest-responsive 2-D Hofmann-type coordination polymer {$Co(Cholpy)_2[Ni(CN)_4]H_2O$} (**1**·$H_2O$) was prepared successfully by incorporating a hydrophobic cholesterol-based co-ligand, Cholest-5-en-3-yl isonicotinate (Cholpy). Compound **1**·H_2O showed a unique guest response with remarkable chromatic changes assisted by lattice water molecules. This article discussed the complicated guest responsivity of **1**·H_2O as shown by solid-state reflectance, Raman, IR and NMR spectroscopic studies. The colour changes were classified into three patterns: (i) a reversible change between orange and purple induced by dehydration and hydration (processes [1] and [2]), (ii) a reversible change between orange and yellow induced by adsorption–desorption of MeOH and various other solvents (processes [3], [4] and [2]), and (iii) an irreversible change from orange to green induced by adsorption of $CHCl_3$ and CH_2Cl_2 (process [5]). The origin of the deep colour observed for **1**, **1′**, **1**·MeOH and **1**·$CHCl_3$ was attributed to the allowed d–d transition under low-symmetric Co^{II}. The chromatic change in (ii) would stem from slight structural changes caused by an additional guest molecule. In the case of (iii), the chromatic change is associated with the oxidation of Cholpy by the interplay of H_2O and $CHCl_3$. Spectroscopic studies revealed that the incorporated Cholpy was an essential component for the unique guest responsivity. This framework design should contribute to the creation of novel functional CPs that can respond to external stimuli and to the application of unique reaction spaces based on CPs.

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Notes and references

‡Cholest-5-en-3-yl 4-isonicotinate (Cholpy): isonicotinic acid (1.23 g, 10 mmol) and 1,1′-carbonyl-bis(1*H*-imidazole) (1.62 g, 10 mmol) were dissolved in dry THF (15 mL) and stirred for 10 min. The THF solution was evaporated to dryness, and dry benzene (20 mL) and cholesterol (3.86 g, 10 mmol) were added to the solid. The mixture was refluxed for 4 h, then cooled to room temperature, washed with brine twice and dried by $MgSO_4$. After filtration, the filtrate was evaporated to dryness to give a white solid dried *in vacuo*. Yield: 4.23 g (86%). Elemental analysis (%) calcd for Cholpy ($C_{33}H_{49}NO_2$): C, 80.60; H, 10.04; N 2.85. Found: C, 80.66; H, 10.14; N, 2.69. IR (cm^{-1}): 2953–2868(ν_{CH}), 1724(ν_{CO}).

$\{Co(Cholpy)_2[Ni(CN)_4]H_2O\}$ (**1**·H_2O): to a solution (30 mL) of $Co(NO_3)_2 \cdot 6H_2O$ (0.076 g, 0.26 mmol) and Cholpy (0.256 g, 0.52 mmol) in THF, a solution of $K_2[Ni(CN)_4] \cdot H_2O$ (0.067 g, 0.26 mmol) in H_2O and MeOH (30 mL, H_2O–MeOH = 1 : 9 v/v) was added dropwise. The mixture solution was stirred at room temperature for 2 days to give orange microcrystals. The microcrystals were collected by centrifugal separation, washed with THF, H_2O and MeOH and dried *in vacuo*. Yield: 0.21 g (66%). Elemental analysis (%) calcd for **1**·H_2O ($C_{70}H_{100}N_6O_5CoNi$): C, 68.73; H, 8.24; N, 6.87. Found: C, 68.45; H, 8.08; N, 6.97. X-ray fluorescence analysis: Ni/Co = 0.96. IR (cm^{-1}): 2951–2868(ν_{CH}), 2160(ν_{CN}), 1728(ν_{CO}).

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