

A novel porous molecular crystal that varies its color in response to the change in surrounding humidity

Sensors that detect the content of a certain molecule are of fundamental importance in many industrial processes. To ensure safety and reproducible operations, facilities often need to monitor the feed or drain gases. Along with organic or inorganic gases, water plays a crucial role in such chemical processes. Water molecules are ubiquitous in the environment, but they are not always preferable for chemical or physical processing, especially when delicate reactive compounds or substrates are treated.

An established way of monitoring the water content in the atmosphere is to use an electrical capacitor whose capacitance changes in response to the surrounding humidity. However, electricity and physically connected circuits are necessary for these types of electric sensor, which limits the applicable situations of these devices. Namely, these devices cannot be implanted in physically and electrically isolated chambers.

Colorimetric humidity sensors are advantageous in this context. Colorimetric sensors, or constituent hydrochromic compounds, alter their absorption color in response to the surrounding humidity. Although the color change is not easy to detect precisely, it is beneficial in various situations because of the setup simplicity and the electricity-free working mechanism. Cobalt complexes, for instance, change their absorption color from blue to pink upon the adsorption of humidity. Since the color change is readily visible and requires no additional equipment, these colorimetric compounds are frequently utilized in the food industry.

The color change of these compounds commonly relies on the adsorption of water molecules onto the constituent organic or inorganic molecules. Therefore, porous crystals featuring extremely large surface areas and uniform pore morphology are advantageous for enhancing the color change and response speed. However, organic porous crystals are unstable under humid conditions. Representative porous organic crystals, such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), or hydrogen-bonded organic frameworks (HOFs), are built up via coordination bonds, dynamic covalent bonds, or hydrogen bonds, which are all susceptible to water molecules. Elaborate and complex molecular design is necessary to make these materials tolerant to water.

A much simpler and straightforward way of circumventing this issue is to grow porous crystals with less-polar bonds such as van der Waals forces,

π - π stacking, and C–H \cdots X bonds [1,2]. The attractive nature of these less-polar bonds originates mostly from the dispersion forces, whose bonding strength is independent of the polarity of the surrounding medium. Therefore, porous crystals grow with these less-polar bonds (van der Waals porous molecular crystals, VPCs) survive even in highly polar solvents including water. However, the design strategy for porous molecular crystals has yet to be established because of the difficulty in predicting and controlling these weak bonds.

In this study, we newly synthesized a porous molecular crystal from a novel aromatic dendrimer and examined its hydrochromic behavior (Fig. 1) [3]. The constituent organic molecule **1** is a second-generation fully aromatic dendrimer featuring six carbazole (Cz) moieties at the periphery and a dibenzophenazine (DBPHZ) core (Fig. 1(a)). The carbazole dendron and dibenzophenazine act as an electron donating group and an electron accepting group, respectively, providing a charge transfer (CT) nature to **1**. The Lippert–Mataga plot, as well as the E_{30} plot, of **1** based on electronic absorption and photoluminescence spectra confirms the CT character of **1**.

Despite its sterically bulky morphology, **1** formed crystalline powder (VPC-1) upon thermal annealing in a binary mixture of CHCl_3 and MeOH. The N_2 adsorption isotherm of VPC-1 measured at 77 K exhibits a marked uphill profile in the low relative pressure range, indicating that VPC-1 is a microporous crystal. This finding itself is of fundamental importance because VPC-1 is a molecular crystal sustained totally by weak van der Waals forces. Despite the weak intermolecular bonding network, VPC-1 maintains its porous framework even after the evacuation of the crystallization solvent.

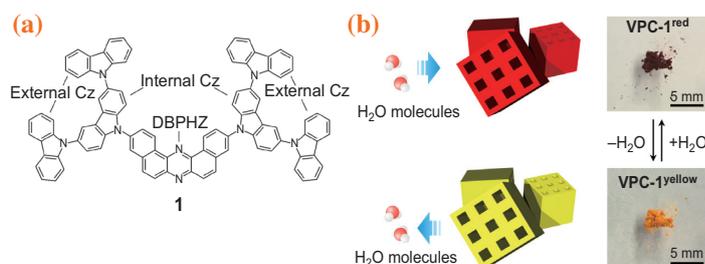


Fig.1. (a) Molecular structure of **1**. (b) Schematic representation of the hydrochromic behavior of VPC-1 upon adsorption and desorption of H_2O molecules together with their photographs.

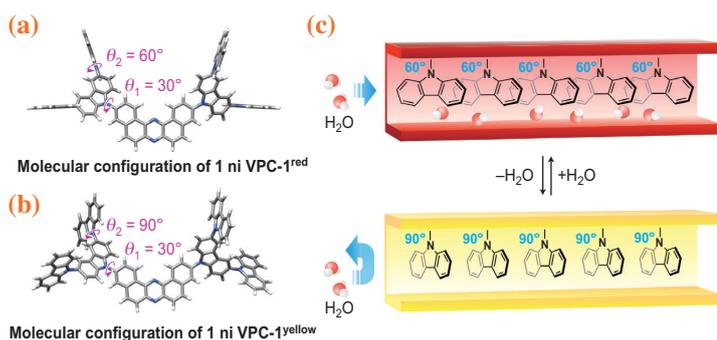


Fig. 2. (a) Computational models for **1** in VPC-1^{red} and VPC-1^{yellow}. (b) Schematic representation of the flipping of carbazole dendrons in VPC-1 upon adsorption and desorption of H₂O molecules.

The powdery specimen of VPC-1 exhibited a yellow color (VPC-1^{yellow}) just after drying under vacuum but became red (VPC-1^{red}) upon exposure to humid air. The color change was investigated in detail by means of IR (infrared), Raman, and diffuse reflection measurements under controlled humidity at SPring-8 BL43IR, where a series of spectroscopic or diffractometric apparatuses equipped with humidifier is available. These facilities can also enable us to investigate the molecular structure in detail when needed. Therein, microscopic measurements were also available and beneficial for the kinetic study of the hydration and dehydration processes.

This color change process is fully reversible upon decreasing the humidity. The K-M values of VPC-1 at 570 nm plotted against the relative humidity (RH) of

the surrounding atmosphere show a sigmoidal curve with a clear threshold at around 50 RH% without hysteresis.

The color change of VPC-1 is attributed to the prompt uptake/removal of the H₂O molecules accompanied by the flipping of the outer carbazole moieties (Fig. 2). Molecular vibrational bands corresponding to C–N stretching, pyrrole breathing, C–H bending, and O–H stretching modes in the IR spectra exhibit analogous abrupt changes upon increasing or decreasing the surrounding humidity (Fig. 3). According to the results of our computational analysis, the IR spectral change indicates the rotational motion of carbazole. The H₂O adsorption isotherm measured at 20°C also shows a sigmoidal curve.

The heat of adsorption profile and computational analysis shed light on the possible molecular mechanism of how VPC-1 responds to the humidity. At a low humidity, the carbazole dendrons of **1** have a lower affinity to H₂O molecule. When the surrounding humidity surpasses a certain threshold, the carbazole dendrons flip and undergo a dipole–dipole interaction with the guest H₂O and accelerates the adsorption of H₂O (Fig. 2(b)).

The sigmoidal H₂O adsorption and following color change of VPC-1 are of practical value, especially for H₂O detection in an isolated chamber. Fundamentally, the thermal stability of VPC-1 with the sigmoidal flipping of carbazole dendrons in response to H₂O is intriguing, since it combines seemingly incompatible features, namely, structural rigidity and flexibility.

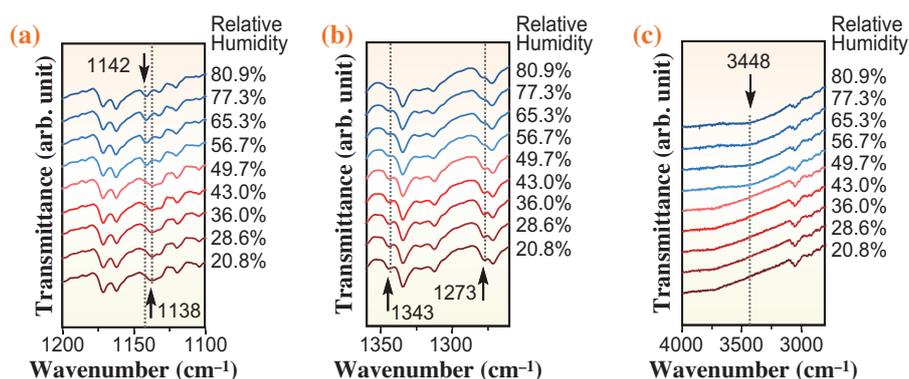


Fig. 3. Magnified IR spectra that correspond to the C–N stretching, pyrrole breathing, and C–H bending (a, b) and O–H stretching modes (c) of **1** in VPC-1 upon increasing the surrounding humidity from 20.8 to 80.9%.

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