

Vapochromic behaviors of organic crystals: A convenient and versatile chemical sensor for sick house gas detection

The development of highly sensitive and selective detection colorimetric reagents for volatile organic compounds (VOPs) including so-called sick house syndrome gases has been one of the urgent social demands. A variety of transition-metal-based colorimetric reagents have been reported for VOP detection. The large *d*-orbitals of an electron-rich metal can interact effectively with VOP molecules to provide a highly sensitive and versatile color change toward the adsorption/desorption of VOP molecules. However, some of the heavy metals used for colorimetric reagents are environmentally unfriendly and expensive. The development of metal-free organic colorimetric reagents with sustainability is becoming an urgent social demand, which motivated and guided us.

Recently, our research group has found that the organic crystal of the PI-NDI molecule, in which 1,4,5,8-naphthalenetetracarboxylic diimide (NDI) is connected to two 4-*t*-butylpyrroleimine (PI) tethers, shows remarkable sensing ability for VOP detection, including typical sick house syndrome gases such as methanol, toluene, and formaldehyde (Fig. 1) [1]. The red-purple powder crystal of PI-NDI changed to orange upon exposure to methanol vapor. Vapochromism, a reversible color change upon absorption/desorption of VOP vapor, was observed on the PI-NDI system, as shown in Fig. 1. The methanol-absorbed orange powder crystal reverts to the original red-purple powder under vacuum condition where the vapochromic process can be repeated without crystal decomposition. The visible detection of typical sick house syndrome gases that are emitted from building materials, which cause chronic health problems and allergy symptoms such as headache, chills, and eye, nose, throat irritation, was demonstrated upon exposure of PI-NDI to toluene, DMSO, THF, and formaldehyde. The distinct and wide range of color

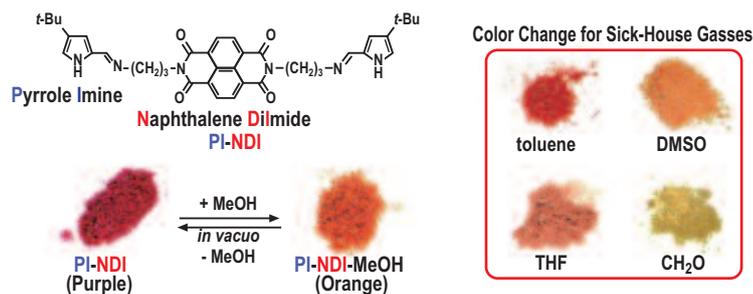


Fig. 1. PI-NDI molecule and colorimetric changes for VOP detection.

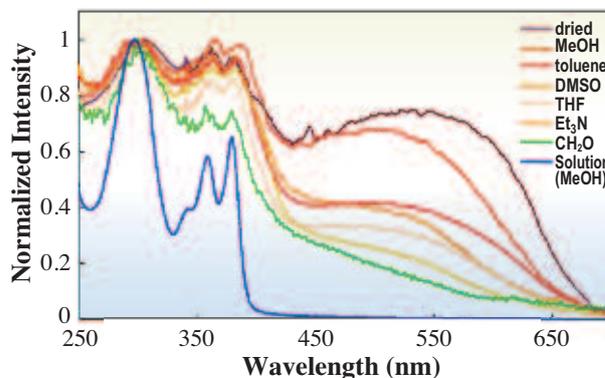


Fig. 2. Solid-state UV-vis spectra of PI-NDI exposed to various VOPs.

change from the original red-purple to orange to yellow guarantee the effectiveness and usefulness of PI-NDI as an organochemical sensor.

The mechanistic investigation of the vapochromic color change of PI-NDI was carried out by solid-state UV-vis spectroscopy in BaSO₄ as matrix (Fig. 2). The significant change of the 400-650 nm region ascribed to the charge transfer of the PI unit to the NDI unit suggested that the gas molecules introduced into the crystalline PI-NDI affect the charge transfer interaction. The lack of solvation-induced color change in methanol solution (blue line in Fig. 2) supports the fact that the molecular structure and assembly formed in the crystal state are keys for the vapochromic behavior.

The molecular structure of PI-NDI in crystal was unequivocally determined by synchrotron X-ray powder diffraction at beamline **BL19B2**. The X-ray structure of the methanol absorbed PI-NDI definitely demonstrated that methanols trapped in the crystal lattice occupy the interstitial cavity between the PI and NDI units affecting the perturbation of PI-NDI charge-transfer interactions (Fig. 3). The molecular structure of guest-VOP-free PI-NDI was also obtained from the powder X-ray structure analysis at the same beamline. The S-shaped sandwich structure of PI-NDI well retained with the cavity for VOP trap and detection. The interspatial distance of PI and NDI unit shortened from 3.319 Å of PI-NDI·2MeOH to 3.292 Å of guest-free PI-NDI qualifies as evidence for VOP-inclusion-induced perturbation change of PI-NDI interaction. The relationship of color change and PI-NDI geometry was confirmed by DFT calculation based on these X-ray structures within

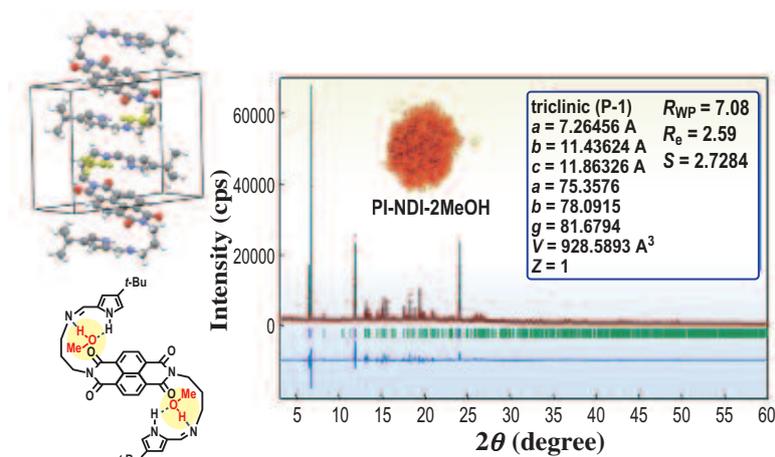


Fig. 3. Molecular structure of methanol absorbed PI-NDI.

periodic boundary condition using GGA-PBE pseudopotential. The DFT-based simulation clearly exhibits the decrease in the 450-650 nm signal intensity corresponding to the color change from red-purple to orange as observed in the methanol absorption of PI-NDI. The calculated changes in the interspatial distances of PI-NDI were 3.322 Å for PI-NDI·2MeOH and 3.296 Å for guest-free PI-NDI, being in good agreement with the results of powder

X-ray structure analysis. The combination of strong electron donor and acceptor of PI and NDI would lead to the observed susceptibility to microenvironmental change in the PI-NDI crystal lattice and molecular geometry to afford a versatile color change dependent on various VOP molecules. These results clearly indicate the effectiveness of the molecular design based on the charge transfer system for the creation of metal-free organochemical sensors.

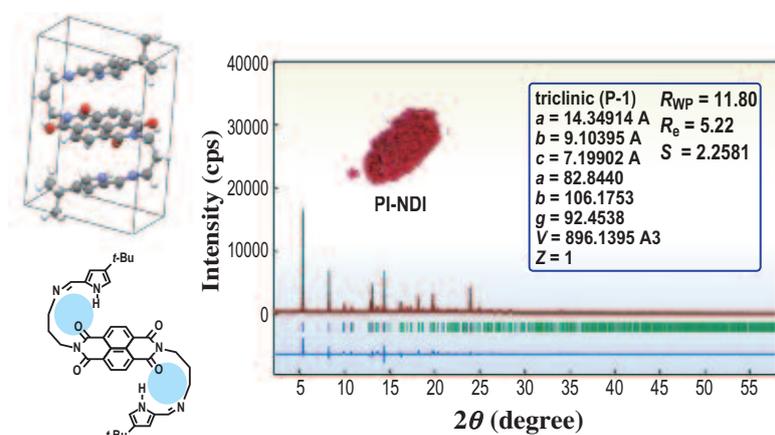


Fig. 4. Molecular structure of guest-free PI-NDI.

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References

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