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Title: Comprehensive Structural and Microscopic Characterization of an Azine–Triazine-Functionalized

Highly Crystalline Covalent Organic Framework and Its Selective Detection of Dichloran and 4-

Nitroaniline

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Abstract:

In recent years, luminescent covalent organic frameworks (COFs) constructed with nitrogen-rich building units have been the target for selective detection of electron-deficient pollutants to serve for a clean environment. In order to contribute to these imperative applications, an azine-triazinebased COF (ANCOF) has been solvothermally synthesized and structurally characterized by a variety of analytical methods for comprehensive studies. ANCOF possesses micropores with a rare ABAB stacking, high thermal and chemical stabilities, and a Brunauer-Emmett-Teller surface area of 565 m2 g-1. On the other hand, ANCOF exhibits excellent luminescent property in the presence of different solvents marked by the wavelength shift due to polarity. Exploiting the bluish-white emission of ANCOF in aqueous medium, it has been found to be an excellent probe for the discriminative and selective detection of dichloran (DCNA) and 4-nitroaniline (4-NA) with detection limits of 142 and 89 ppb, respectively. A distinguishable color change for DCNA and 4-NA has been reflected by UV illumination, fluorescence microscopy, and a handy paper strip method. Timeresolved fluorescence studies, spectral overlap, density functional theory, and configurational bias Monte Carlo molecular simulation have been utilized to understand the mechanism of action and interaction of DCNA and 4-NA with the host ANCOF. The selectivity of ANCOF toward DCNA and 4-NA in the presence of other analytes and the recyclability after sensing experiments have been successfully demonstrated. Furthermore, the stability of ANCOF has been confirmed by powder Xray diffraction and field emission scanning electron microscopy with good retention of crystallinity and morphology. To the best of our knowledge, this is the first COF employed for the detection of amine derivatives in aqueous solution combining both experimental and computational studies.

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