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Title: A dual-functionalized, luminescent and highly crystalline covalent organic framework: molecular

decoding strategies for VOCs and ultrafast TNP sensing

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Keywords: Covalent organic frameworks

Nuclear magnetic resonance spectroscopy

Volatile organic compounds

Naphthalene

Issue Date: 2018

Publisher: Royal Society of Chemistry

Citation: Journal of Materials Chemistry A, 6(33), pp. 16246-16256

Abstract:

Luminescent and robust covalent organic frameworks (COFs) with desired crystallinity and properties are rarely obtained due to synthetic challenges in combining the molecular building blocks required to adopt a structure that prevents aggregation-caused quenching (ACQ) of π - π stacked layers. In this work, we have designed and developed a novel COF bearing a π -electron deficient triazine core and a π-electron rich core containing phenyl and naphthalene rings connected with -O and -N donor Lewis basic sites in hexagonal honeycomb layers with three different kinds of pore, which is rare for COFs, and this was confirmed using an N2 sorption study and via observation of strong (100) diffraction at $2\theta = 1.75^{\circ}$ using SAXS. The synthesis involves an imine condensation reaction between a triazine-based trialdehyde with three-fold symmetry and naphthalene diamine without the need for an acid catalyst and under inert conditions in 80% yield, making it easy to scale up to gram quantities. The formation of the -CN- bond in 1 was confirmed using FTIR and 13C CP MAS solid state NMR spectroscopy. The surface morphology was confirmed using FESEM, HRTEM, STEM, SAX and AFM analyses. Utilizing its dual functionality, herein we report the first example of molecular decoding of both π -electron rich and π -electron deficient volatile organic compounds (VOCs) with similar structures and physical properties using a COF based on a dual-readout identification scheme constructed from its lifetime or emission intensity and quantum yield responses toward the VOC accommodation. Similarly, the electrondeficient triazine core in 1 allows the selective uptake of a π-electron rich unsaturated moiety (benzene) over its saturated congener (cyclohexane), an industrially important separation of two C6 cyclic congeners. On the other hand, the electron-rich core in 1 is very efficient for the selective and ultra-low detection of highly explosive TNP in water at 68 ppb. In all cases, 1 supersedes the previously reported examples.

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