Title:	Strategic Construction of Highly Stable Metal-Organic Frameworks Combining Both Semi-Rigid Tetrapodal and Rigid Ditopic Linkers: Selective and Ultrafast Sensing of 4-Nitroaniline in Water
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Abstract:	In this work, we have designed two new 3D metal–organic frameworks (MOFs), {Zn4(TPOM)(1,4-NDC)4}n (1) and {Ni2(TPOM)(1,4-NDC)2(H2O)2}n (2), utilizing both semi-rigid tetrapodal neutral linker, tetrakis(4-pyridyloxymethylene)methane (TPOM) and rigid ditopic anionic linker, 1,4-naphthalene dicarboxylic acid (H2(1,4-NDC)). On the basis of the single-crystal X-ray diffraction, 1 has a 3D structure with star-shaped pores arising from four-fold symmetry due to the presence of a paddle-wheel core [Zn2(O2CC12H6)4(C6H4N)2] as a subunit, whereas 2 consists of a zig-zag 3D framework with strong hydrogen bonding between the coordinated water molecules and coordinated carboxylate groups. Their thermogravimetric analysis indicates an extraordinary thermal stability: 1 up to 400 °C and 2 up to 350 °C. In addition to elemental microanalysis and spectroscopic characterization (UV–vis and infra-red spectroscopy), the bulk phase purity of 1 and 2 as well as hydrolytic stability of 1 are established by powder X-ray diffraction. Exploiting the luminescence nature of 1, both solvent-dependent fluorescence properties and sensing of various amines in aqueous medium are demonstrated. It exhibits good sensing ability toward 4-nitroaniline (4-NA) and 2,6-dichloro-4-nitroaniline (2,6-DCNA; a broad spectrum pesticide belonging to toxicity class III) with the lowest detection limit of 88 ppb and 0.28 ppm, respectively. The mechanism of action has been established through Stern–Volmer plots, time-resolved fluorescence studies, spectral overlap, and density functional theory calculations. The recyclability and stability of 1 after sensing experiments also reveal no change in its crystallinity. Furthermore, selectivity test and time-dependent detection for 4-NA have been successfully demonstrated. For practical applications, naked eye detection of 4-NA using test paper strips is also displayed.
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