Supporting information for

Engineering design toward exploring the functional group substitution in 1D channels of Zn-organic frameworks upon nitro explosives and antibiotics detection

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Experimental section

Materials: 2,4,6-trinitrophenol (TNP), 4-nitrophenol (4-NP), 2-nitrophenol (2-NP), 2nitrophenol (3-NP), 2-nitrotoluene (2-NT), nitrobenzene (NB), 2,4-dinitrotoluene (2,4-DNT), and 1,3-dinitrobenzene (1,3-DNB) were provided by Shandong Asia Chemical Industry Co. Ltd. (China). All the antibiotics including nitro-furazon (NZF), furazolidone (FZD), nitrofurantoin (NFT), dimetridazole (DTZ), ronidazole (RDZ), ornidazole (ODZ), and metronidazole (MDZ) were purchased from Blue Gene (Shanghai, China). Zn(NO₃)₂, 5aminoisophthalic acid (H₂aip, L1), isophthalic acid (Hip, L2), and 1,3,5-benzenetricarboxylic acid (BTC, L3) were obtained by the Aladdin (Shanghai, China). N4, N4'-di(pyridine-4yl)biphenyl-4,4'-dicarboxamide) (L) was synthesized according to our previous reports¹⁻². All other reagents were purchased commercially and used without further purification.

Physical measurements: Scanning electron microscope images were measured using a Phenom Pure desktop scanning electron microscope. Ultraviolet-visible adsorption spectra were recorded at room temperature on a PerkinElmer Lambda 35 spectrophotometer. Infrared spectra on KBr pellets were obtained using a Bruker Equinox-55 spectrophotometer. Powder X-ray diffraction (PXRD) patterns were obtained using a D/Max-2500 X-ray diffractometer using Cu Ka ($\lambda = 1.54$ Å) radiation. Fluorescence spectra were obtained using a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Preparation of MOFs: Typically, $Zn(NO_3)_2$, L, and H_2aip (L1) / Hip (L2) / H_3BTC (L3) with a ratio of 1:1:1 were dissolved in 6 mL of DMF/ H_2O (5:1) solution, then the mixture was transferred into a Teflon reactor and heated at 393 K for 48 h. After cooling to room temperature, the mixture was centrifuged and washed with DMF twice to obtain the light-yellow powder.

Nitro explosives or antibiotics sensing experiments: MOFs (1, 2, or 3) were dispersed in pure water with the concentration of 50 μ g/mL, and treated via ultrasonication for 30 mins to form a stable emulsion. Then a series of nitro explosives or antibiotics solution with the various concentrations were respectively added to the emulsion of MOFs before carrying out the fluorescence studies.



Fig. S1 Emission spectra of the ligand L, L1, and 1 in solid powder.



Fig. S2 Emission spectra of the ligand L, L2, and 2 in solid powder.



Fig. S3 Emission spectra of the ligand L, L3, and **3** in solid powder.



Fig. S4 The normalize emission spectra of 1 (A) and 2 (B) in solid powder or in water.



Fig. S5 The normalize emission spectra of **3** in solid powder or in water.



Fig. S6 Emission spectra of 1 (50 μ g/mL) upon addition of 4-NP in water at concentrations from 0 to 140 ppm. Inset: Plot of I₀/I *vs.* the concentration of 4-NP.



Fig. S7 Emission spectra of 1 (50 μ g/mL) upon addition of 2-NP in water at concentrations from 0 to 120 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NP.



Fig. S8 Emission spectra of 1 (50 μ g/mL) upon addition of 3-NP in water at concentrations from 0 to 400 ppm. Inset: Plot of I₀/I *vs.* the concentration of 3-NP.



Fig. S9 Emission spectra of 1 (50 μ g/mL) upon addition of 2-NT in water at concentrations from 0 to 300 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NT.



Fig. S10 Emission spectra of **1** (50 μ g/mL) upon addition of NB in water at concentrations from 0 to 380 ppm. Inset: Plot of I₀/I *vs.* the concentration of NB.



Fig. S11 Emission spectra of **1** (50 μ g/mL) upon addition of 2,4-DNT in water at concentrations from 0 to 400 ppm. Inset: Plot of I₀/I *vs*. the concentration of 2,4-DNT.



Fig. S12 Emission spectra of **1** (50 μ g/mL) upon addition of 1,3-DNB in water at concentrations from 0 to 310 ppm. Inset: Plot of I₀/I *vs*. the concentration of 1,3-DNB.



Fig. S13 The UV absorption spectra of various nitro explosives (0.1 mM) and the emission spectrum of 1 in aqueous solution.



Fig. S14 Emission spectra of **2** (50 μ g/mL) upon addition of 4-NP in water at concentrations from 0 to 80 ppm. Inset: Plot of I₀/I *vs.* the concentration of 4-NP.



Fig. S15 Emission spectra of **2** (50 μ g/mL) upon addition of 2-NP in water at concentrations from 0 to 120 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NP.



Fig. S16 Emission spectra of **2** (50 μ g/mL) upon addition of 3-NP in water at concentrations from 0 to 200 ppm. Inset: Plot of I₀/I *vs.* the concentration of 3-NP.



Fig. S17 Emission spectra of **2** (50 μ g/mL) upon addition of 2-NT in water at concentrations from 0 to 200 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NT.



Fig. S18 Emission spectra of 2 (50 μ g/mL) upon addition of NB in water at concentrations from 0 to 280 ppm. Inset: Plot of I₀/I *vs.* the concentration of NB.



Fig. S19 Emission spectra of **2** (50 μ g/mL) upon addition of 2,4-DNT in water at concentrations from 0 to 260 ppm. Inset: Plot of I₀/I *vs*. the concentration of 2,4-DNT.



Fig. S20 Emission spectra of **2** (50 μ g/mL) upon addition of 1,3-DNB in water at concentrations from 0 to 240 ppm. Inset: Plot of I₀/I *vs*. the concentration of 1,3-DNB.



Fig. S21 Emission spectra of **3** (50 μ g/mL) upon addition of 4-NP in water at concentrations from 0 to 60 ppm. Inset: Plot of I₀/I *vs*. the concentration of 4-NP.



Fig. S22 Emission spectra of **3** (50 μ g/mL) upon addition of 2-NP in water at concentrations from 0 to 60 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NP.



Fig. S23 Emission spectra of **3** (50 μ g/mL) upon addition of 3-NP in water at concentrations from 0 to100 ppm. Inset: Plot of I₀/I *vs*. the concentration of 3-NP.



Fig. S24 Emission spectra of **3** (50 μ g/mL) upon addition of 2-NT in water at concentrations from 0 to 140 ppm. Inset: Plot of I₀/I *vs.* the concentration of 2-NT.



Fig. S25 Emission spectra of **3** (50 μ g/mL) upon addition of NB in water at concentrations from 0 to 160 ppm. Inset: Plot of I₀/I *vs.* the concentration of NB.



Fig. S26 Emission spectra of **3** (50 μ g/mL) upon addition of 2,4-DNT in water at concentrations from 0 to 180 ppm. Inset: Plot of I₀/I *vs*. the concentration of 2,4-DNT.



Fig. S27 Emission spectra of **3** (50 μ g/mL) upon addition of 1,3-DNB in water at concentrations from 0 to 200 ppm. Inset: Plot of I₀/I *vs*. the concentration of 1,3-DNB.



Fig. S28 Emission spectra of **1** (50 μ g/mL) upon addition of FZD in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of FZD.



Fig. S29 Emission spectra of **1** (50 μ g/mL) upon addition of NFT in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of NFT.



Fig. S30 Emission spectra of **1** (50 μ g/mL) upon addition of DTZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of DTZ.



Fig. S31 Emission spectra of **1** (50 μ g/mL) upon addition of RDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of RDZ.



Fig. S32 Emission spectra of **1** (50 μ g/mL) upon addition of ODZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs*. the concentration of ODZ.



Fig. S33 Emission spectra of **1** (50 μ g/mL) upon addition of MDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of MDZ.



Fig. S34 Emission spectra of **2** (50 μ g/mL) upon addition of FZD in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of FZD.



Fig. S35 Emission spectra of **2** (50 μ g/mL) upon addition of NFT in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of NFT.



Fig. S36 Emission spectra of **2** (50 μ g/mL) upon addition of DTZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of DTZ.



Fig. S37 Emission spectra of **2** (50 μ g/mL) upon addition of RDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of RDZ.



Fig. S38 Emission spectra of **2** (50 μ g/mL) upon addition of ODZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of ODZ.



Fig. S39 Emission spectra of **2** (50 μ g/mL) upon addition of MDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of MDZ.



Fig. S40 Emission spectra of **3** (50 μ g/mL) upon addition of NZF in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of NZF.



Fig. S41 Emission spectra of **3** (50 μ g/mL) upon addition of FZD in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of NZF.



Fig. S42 Emission spectra of **3** (50 μ g/mL) upon addition of NFT in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of NFT.



Fig. S43 Emission spectra of **3** (50 μ g/mL) upon addition of DTZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of DTZ.



Fig. S44 Emission spectra of **3** (50 μ g/mL) upon addition of RDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of RDZ.



Fig. S45 Emission spectra of **3** (50 μ g/mL) upon addition of ODZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of ODZ.



Fig. S46 Emission spectra of **3** (50 μ g/mL) upon addition of MDZ in water at concentrations from 0 to 100 ppm. Inset: Plot of I₀/I *vs.* the concentration of MDZ.



Fig. S47 The FT-IR of original sample and samples respectively immersed in organic solvents or the aqueous solution of aromatic nitro compounds for three days based on **1**.



Fig. S48 The FT-IR of original sample and samples respectively immersed in organic solvents or the aqueous solution of aromatic nitro compounds for three days based on **2**.



Fig. S49 The FT-IR of original sample and samples respectively immersed in organic solvents or the aqueous solution of aromatic nitro compounds for three days based on **3**.



Fig. S50 The XRD of simulated sample and samples respectively immersed in the aqueous solution of aromatic nitro compounds for three days based on **2**.



Fig. S51 The XRD of simulated sample and samples respectively immersed in the aqueous solution of aromatic nitro compounds for three days based on **3**.



Fig. S52 The XRD of simulated sample and samples respectively immersed in the aqueous solution of various antibiotics for three days based on 2.



Fig. S53 The XRD of simulated sample and samples respectively immersed in the aqueous solution of various antibiotics for three days based on 3.

S1. L.-F. Ma, X.-N. Wang, D.-S. Deng, F. Luo, B.-M. Ji, J. Zhang, J. Mater. Chem. A, 2015,
3, 20210-20217.

S2. F. Luo, M.-S. Wang, M.-B. Luo, G.-M. Sun, Y.-M. Song, P.-X. Lia, G.-C. Guo, *Chem. Commun.*, 2012, **48**, 5989-5991.