Supplementary Information

Molecular insights into the sensitivity detection mechanism of fluorescent 2D Zr-BTB for 2,4-dinitrophenol

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Figure S1. (a) PXRD patterns of as-synthesized product and simulated 2D and 3D Zr-BTB. (b) FTIR spectra of ligand H₃BTB and as-synthesized 2D Zr-BTB nanosheets.
Figure S2. TGA of as-synthesized 2D Zr-BTB nanosheets.
Figure S3. UV-vis absorption spectra of ligand H$_3$BTB and 2D Zr-BTB nanosheets.
Figure S4. (a) The emission spectrum of H$_3$BTB, and excitation and emission spectra of 2D Zr-BTB nanosheets. (b) Emission spectra of Zr-BTB dispersed in various solvents. (c) Normalized intensity of Zr-BTB in H$_2$O, MeOH, and DMF.
Figure S5. Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water for 0-5 days.
Figure S6. (a-c) Fluorescence emission spectra of 2D Zr-BTB nanosheet suspension with various concentrations (0.8, 0.5, 0.2 mg/mL) by adding different volumes of 1.0 mM of 2,4-DNP. (d) Normalized fluorescence intensity of Zr-BTB suspension in the presence of a different concentration of 2,4-DNP (0-8 μM) at room temperature.
**Figure S7.** Fluorescence emission of Zr-BTB suspension before and after adding 2,4-DNP of 0.2 μM at 10, 20, 40, and 60 s.
Figure S8. (a) Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon incremental addition of 2,4-DNP (1mM, 0-20 μL). (b) Corresponding S-V plots of MOF suspension toward 2,4-DNP (0-8 μM).
Figure S9. (a) Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon incremental addition of 2-NP (1mM, 0-20 μL). (b) Corresponding S-V plots of MOF suspension toward 2-NP (0-8 μM).
Figure S10. (a) Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon incremental addition of TNT (1mM, 0-20 μL). (b) Corresponding S-V plots of MOF suspension toward TNT (0-8 μM).
Figure S11. (a) Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon adding 1,4-DNB (1mM, 0-20 μL). (b) Corresponding S-V plots of MOF suspension toward 1,4-DNB (0-8 μM).
Figure S12. (a) Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon incremental addition of NB (1mM, 0-20 μL). (b) Corresponding S-V plots of MOF suspension toward NB (0-8 μM).
Figure S13. Fluorescence emission spectra of 2D Zr-BTB nanosheets dispersed in water (0.2 mg/mL) upon incremental addition of 20 μL of 2,4-DNP in tap water (1.0 mM).
The as-synthesized Zr-BTB-F shows an ultrathin morphology with a smooth surface, which is consistent with the morphology of 2D Zr-BTB. The PXRD patterns of both also greatly match well, indicating the same phase. Therefore, Zr-BTB-F is analogous to Zr-BTB. However, the quenching efficiency of Zr-BTB-F towards 2,4-DNP of 8 μM is only 68.5%, significantly lower than that of Zr-BTB (87.5%) under the same conditions. Additionally, the quenching constant $K_{sv}$ for Zr-BTB is 4.8 times higher than that of Zr-BTB-F ($K_{sv}=9.52 \times 10^5$, $1.97 \times 10^5$ M$^{-1}$, respectively).
Figure S15. (a) Fluorescence emission spectra, and (b) corresponding fluorescence intensity- analyte concentration (2,4-DNP) plot of MOF suspension (0.2 mg/mL) upon incremental addition of 2,4-DNP (1 mM, 0-5 μL).

Limit of Detection (LOD) for 2,4-DNP with 2D Zr-BTB nanosheets in the aqueous phase:

\[ \text{LOD} = \frac{3\sigma}{\text{slope}}^2 \]

\[ = 3 \times 1.38/317.50 \]

\[ = 13.04 \text{ nM (2.40 ppb)} \]

Multiple fluorescence spectra (n = 10) were recorded for the blank sample of Zr-BTB suspension. The sample standard deviation \( \sigma \) for the blank probe, without adding 2,4-DNP, was calculated to be 1.38.
Figure S16. Fluorescence emission spectra of ligand H$_3$BTB solution (0.2 mg/mL) upon addition of 2,4-DNP (1mM, 0-20 μL).
Figure S17. PXRD patterns spectra of Zr-BTB before and after treatment with 8 μM of 2,4-DNP.
Figure S18. Fluorescence decay curves of Zr-BTB suspension before and after adding 2,4-DNP of 10 μM.
Figure S19. UV-vis absorption spectra of 2,4-DNP (0.1 mM, 2.0 mL) before and after interaction with Zr-BTB (1 mg).
Figure S20. The theoretical modeling of the adsorption I: a π-π stacking interaction of the benzene rings between 2,4-DNP and 2D Zr-BTB.
Figure S21. The theoretical modeling of the adsorption II: oxygen atoms from electron-deficient -NO₂ groups coordinated with electron-rich Zr⁺.
**Figure S22.** Potential energy surface of NO$_2$-Ph- NO$_2$ (2,4-DNP) converted to NH$_2$-Ph-NO$_2$. 
Figure S23. The differential charge density of Zr-BTB after treatment with 2,4-DNP. (Green: Zr; Red: O; Brown: C; Blue: N; White: H. Yellow isosurface: electron accumulation; Cyan isosurface: electron depletion)
Figure S24. Zr3d of XPS spectrum in pristine Zr-BTB and after treatment with 2,4-DNP of 20 μM.
**Table S1.** Bader charge of C13-C18 of the benzene ring in Zr-BTB before and after the π-π stacking interaction of MOF with the analyte.

<table>
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<tr>
<th>Atomic Number</th>
<th>Pristine Zr-BTB/ Bader Charges</th>
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References
