Fabrication of Amine and imine-functionalized Isoreticular Pillared-layer Metal-Organic Frameworks for Highly Selective Detection of Nitro-aromatics

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Experimental Section

Materials and Physical Techniques

All starting materials, including Zinc (II) nitrate hexahydrate 1, 1’-Carbonyldiimidazole, 4, 4’-oxybis (benzoic acid) (H2OBA) were purchased from Aldrich and Merck Company and used as received. Melting points were measured on an Electrothermal 9100 apparatus. FT-IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of 10ºC.min⁻¹ in a static atmosphere of argon. X-ray powder diffraction (XRD) measurements were performed using a Philips X’pert diffractometer with monochromated Cu-Kα radiation. The ¹H-NMR spectrum was recorded on a Bruker AC-250 MHz spectrometer at ambient temperature in d₆- DMSO and D₂SO₄. The samples were also characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA with gold coating.

X-ray crystallography analysis

Single crystals of TMU-6(RL1) and TMU-21(RL2) were selected and mounted on a loop in inert oil and transferred to the cold gas stream of a Bruker APEX-II CCD diffractometer. The data was corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structures were solved by conventional methods and refined by full-matrix least-squares on all F² data using SHELX97 or SHELX2014 in conjunction with the X-Seed or Olex2 graphical user interface. Anisotropic thermal parameters were refined for non-hydrogen atoms and hydrogen atoms were calculated and refined with a riding model.

Crystallographic data: TMU-6(RL1): C₂₃H₁₇N₂O₅Zn, M= 466.75 g mol⁻¹, Monoclinic, C2/C, a= 14.953(6) Å, b= 23.994(9) Å, c= 15.975(6) Å, β= 112.674(2), V= 5289.2(4) Å³, Z=8, ρcalc= 1.172 g cm⁻³, λ= 1.54178, T=100 K, Rf= 0.0306, wR²= 0.0848, S= 1.049, ccdc= 1814568

Crystallographic data: TMU-21(RL2): C₂₅H₁₈N₂O₅Zn, M= 564.88 g mol⁻¹, Monoclinic, C2/C, a= 14.656(9) Å, b= 25.332(10) Å, c= 15.943(8) Å, β= 109.865(6), V= 5567.1(5) Å³, Z=8, ρcalc= 1.348 g cm⁻³, λ= 0.71073, T=293 K, Rf= 0.0428, wR²= 0.1110, S= 1.015, ccdc= 1814569
Figure S1. Binuclear Secondary Building Unit in TMU-6(RL1)
Figure S2. Binuclear Secondary Building Unit in TMU-21(RL2)
Figure S3. FT-IR spectra of TMU-6(RL1)

Figure S4. FT-IR spectra of TMU-21(RL2)
Figure S5. PXRD patterns of simulated, as-synthesized, stabilities in water solvent, after Sensing and activated form of **TMU-6(RL1)**

Figure S6. PXRD patterns of simulated, as-synthesized, stabilities in water solvent, after Sensing and activated form of **TMU-21(RL2)**
Figure S7. Thermogravimetric analysis of TMU-6(RL1) and TMU-21(RL2)
Figure S8. Solid state UV-vis spectroscopy of TMU-6(L1)

Figure S9. Solid state UV-vis spectroscopy of TMU-21(L2)
Figure S10. Solid state UV-vis spectroscopy of TMU-6(RL1)

Figure S11. Solid state UV-vis spectroscopy of TMU-21(RL2)
Fluorescence Measurements

The Fluorescence properties of TMU-6(RL1) and TMU-21(RL2) were measured in different solvent emulsions containing MOF using a PerkinElmer-LS55 fluorescence spectrometer at room temperature. In a typical procedure, 2 mg of an activated MOF was grinded down, and then immersed in different analyte a solution (3 ml) was tested in the emission mode. For fluorescence measurement in the presence of nitroaromatic compounds toluene was chosen as suitable solvent.
**Figure S12.** Fluorescence emission spectra of TMU-6(RL1) dispersed in different solvents

**Figure S13.** Fluorescence emission spectra of TMU-21(RL2) dispersed in different solvents
Figure S14. Fluorescence emission spectra of TMU-6(L1) dispersed in toluene solution at different concentrations of TNT.

Figure S15. Fluorescence emission spectra of TMU-6(L1) dispersed in toluene solution at different concentrations of 2,4-DNT.
Figure S16. Fluorescence emission spectra of TMU-6(L1) dispersed in toluene solution at different concentrations of 1,3-DNB.

Figure S17. Fluorescence emission spectra of TMU-6(L1) dispersed in toluene solution at different concentrations of NB.
$K_{SV} = 3412 \, M^{-1}$

(a)

$K_{SV} = 2715 \, M^{-1}$

(b)
Figure S18. Stern-Volmer (SV) plots in the presence of 2 mg of TMU-6(L1) in different TNT (a) 2,4-DNT (b) 1,3-DNB (c) NB (d) concentrations ([Q]) in toluene

K_{SV} = 2875 M^{-1}

K_{SV} = 2091 M^{-1}
Figure S19. Fluorescence emission spectra of TMU-21(L2) dispersed in toluene solution at different concentrations of TNT.

Figure S20. Fluorescence emission spectra of TMU-21(L2) dispersed in toluene solution at different concentrations of 2,4-DNT.
Figure S21. Fluorescence emission spectra of TMU-21(L2) dispersed in toluene solution at different concentrations of 1,3-DNB.

Figure S22. Fluorescence emission spectra of TMU-21(L2) dispersed in toluene solution at different concentrations of NB.
\[ K_{SV} = 4836 \text{ M}^{-1} \] (a)

\[ K_{SV} = 3075 \text{ M}^{-1} \] (b)
Figure S23. Stern-Volmer (SV) plots in the presence of 2 mg of TMU-21(L2) in different TNT (a) 2,4-DNT (b) 1,3-DNB (c) NB (d) concentrations ([Q]) in toluene.
Figure S24. Fluorescence emission spectra of TMU-6(RL1) dispersed in toluene solution at different concentrations of TNT.

Figure S25. Fluorescence emission spectra of TMU-6(RL1) dispersed in toluene solution at different concentrations of 2,4-DNT.
Figure S26. Fluorescence emission spectra of TMU-6(RL1) dispersed in toluene solution at different concentrations of 1,3-DNB.

Figure S27. Fluorescence emission spectra of TMU-6(RL1) dispersed in toluene solution at different concentrations of NB.
\( K_{SV} = 18729 \text{ M}^{-1} \)

(a)

\( K_{SV} = 10199 \text{ M}^{-1} \)

(b)
Figure S28. Stern-Volmer (SV) plots in the presence of 2 mg of TMU-6(RL1) in different TNT concentrations ([Q]) in toluene.

(a) 2,4-DNT (b) 1,3-DNB (c) NB (d) concentrations ([Q]) in toluene.
Figure S29. Fluorescence emission spectra of TMU-21(RL2) dispersed in toluene solution at different concentrations of TNT.

Figure S30. Fluorescence emission spectra of TMU-21(RL2) dispersed in toluene solution at different concentrations of 2,4-DNT.
Figure S31. Fluorescence emission spectra of TMU-21(RL2) dispersed in toluene solution at different concentrations of 1,3-DNB.

Figure S32. Fluorescence emission spectra of TMU-21(RL2) dispersed in toluene solution at different concentrations of NB.
$K_{SV} = 43874 \text{ M}^{-1}$

$K_{SV} = 19186 \text{ M}^{-1}$
Figure S33. Stern–Volmer (SV) plots in the presence of 2 mg of TMU-21(RL2) in different TNT (a) 2,4-DNT (b) 1,3-DNB (c) NB (d) concentrations ([Q]) in toluene.
Figures 34. Fluorescence emission spectra of TMU-21(RL2) dispersed in toluene solution at .01-.05 M concentration of TNT.

Figure S35. Stern-Volmer (SV) plots in the presence of 2 mg of TMU-21(RL2) in different TNT concentrations ([Q]) in toluene.

\[ k_{sv} = 107344 \text{ M}^{-1} \]
Figure S36. Contact angles of TMU-21(L2)

Figure S37. Contact angles of TMU-21(RL2)
Figure S38. Contact angles of TMU-6(RL1)

Figure S39. Contact angles of TMU-6(L1)
Figure S40. FE-SEM images of TMU-6(L1) as-synthesized particles (a) after sensing (b)

Figure S41. FE-SEM images of TMU-21(L2) as-synthesized particles (a) after sensing (b)
Figure S42. FE-SEM images of TMU-6(RL1) as-synthesized particles (a) after sensing (b)

Figure S43. FE-SEM images of TMU-21(RL1) as-synthesized particles (a) after sensing (b)
Figure S44. UV-vis spectra of different concentrations of TNT.
Figure S45. UV-vis spectra of different concentrations (μl) of TNT in the presence of TMU-6(L1).

Figure S46. UV-vis spectra of different concentrations (μl) of TNT in the presence of TMU-21(L2).
Figure S47. UV-vis spectra of different concentrations (μl) of TNT in the presence of TMU-6(RL1).

Figure S48. UV-vis spectra of different concentrations (μl) of TNT in the presence of TMU-21(RL2).
Figure S49. The changes in absorbance at 300 nm upon addition of different concentrations of TNT in the presence and absence of a) TMU-6(L1) and b) TMU-21(L2) in toluene.
Figure S50. The changes in absorbance at 300 nm upon addition of different concentrations of TNT in the presence and absence of a) TMU-6(RL1) and b) TMU-21(RL2) in toluene.
Table S1. Relative contributions of various non-covalent contacts to the Hirshfeld surface area in compounds TMU-6(L1), TMU-6(RL1), TMU-21(L2) and TMU-21(RL2).

<table>
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<tr>
<th>Compound</th>
<th>H···H</th>
<th>C···H</th>
<th>C···C</th>
<th>N···H</th>
<th>O···H</th>
<th>Zn···O</th>
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<tr>
<td>TMU-6 (L1)</td>
<td>44.8</td>
<td>18.5</td>
<td>7.5</td>
<td>4.8</td>
<td>12.7</td>
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<td>18.8</td>
<td>7.1</td>
<td>2.1</td>
<td>15.3</td>
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<td>2.1</td>
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<td>TMU-21 (RL2)</td>
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<td>14.0</td>
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**Extraction Procedure**

To approve diffusion of aromatic compounds to the frameworks' pores, at first 10 mL toluene solution including 300 ppb of TNT, was added to 3 mg of the MOFs as sorbent. After stirring for 20 min in order to enhance the speed of adsorption, the MOFs was separated from the samples by centrifugation and then washed with methanol to remove the physically adsorbed species on the MOFs surface. The analytes were desorbed from the sorbent with 1 mL of methanol by powerful vortex for 5 minutes. The extracts were further concentrated under a gentle stream of nitrogen gas to 100 μl prior to GC-MS analysis and analyzed by GC-MASS.
Table S2. Comparison of LOD and quenching constant of the proposed method and other techniques in determination of TNT

<table>
<thead>
<tr>
<th>Probes</th>
<th>Material</th>
<th>LDO  (nM)</th>
<th>$K_{sv}$ (M$^{-1}$)</th>
<th>Reference</th>
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<tr>
<td>Probes</td>
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<td>LDO (nM)</td>
<td>$K_{SV}$ (M$^{-1}$)</td>
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<td>Phenylethynylene calix[4]arenes -ANC</td>
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<td>$3.5 \times 10^4$</td>
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<td>(PCN-224) Zr$6$(OH)8 ,TCPC</td>
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<tr>
<td>Probes</td>
<td>Material</td>
<td>LDO (nM)</td>
<td>$K_{SV}$ (M$^{-1}$)</td>
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<td>This Work</td>
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Reference