Electronic Supplementary Information (ESI)

A robust and luminescent covalent organic framework as a highly sensitive and selective sensor for detection of Cu$^{2+}$ ion

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Section 1. Materials and Methods

The paraformaldehyde, 2-tert-butylphenol, silicon tetrachloride, hydrazine hydrate were obtained from Aldrich. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

$^1$H spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. The infrared spectra were recorded from 400 to 4000 cm$^{-1}$ on an Avatar FT-IR 360 spectrometer by using KBr pellets. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer by depositing powder on glass substrate, from 2θ = 4.0° to 45° with 0.02° increment at 25 °C. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer within the wavelength range 200–700 nm. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min$^{-1}$ from room temperature to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the NLDFT method was applied for the estimation of pore size distribution. The absolute fluorescence quantum yields were measured on Edinburgh FLS920 by using an integrating sphere. Photoluminescence measurements at room temperature were taken on a Cary Eclipse Fluorescence Spectrophotometer.

Luminescence Quenching Experiments: COF-JLU3 was readily dispersed in THF and the obtained suspension was almost transparent. Moreover, the fluorescence spectra of the native COF-JLU3 in THF solutions was recorded immediately. After
adding to 2eq metal ions (Li\(^+\), Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), Al\(^{3+}\), Zn\(^{2+}\), Pb\(^{2+}\), Ag\(^+\), Cr\(^{3+}\), Cd\(^{2+}\), Fe\(^{3+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\)) about 0.5 h, the fluorescence spectra was observed. Luminescence spectra of COF-JLU3 at 601 nm in the present of Cu\(^{2+}\) ion was also provided after mixing in other metal ions. Subsequently Besides, luminescence intensity of COF-JLU3 in different pH solution was observed at first, and the solution added Cu\(^{2+}\) ion was recorded subsequently. On the other hand, the absolute quantum yield and lifetimes of the original COF-JLU3 in THF were tested at first and these data with Cu\(^{2+}\) were obtained subsequently. Each test was repeated for three times to get average values with the measurements that were excited at \(\lambda_{\text{ex}} = 400\) nm and the corresponding emission wavelength was tested from \(\lambda_{\text{em}} = 550\) to 750 nm.
Section 2. Syntheses and Characterization

Scheme S1: Synthetic route for monomer

![Synthetic route for monomer](image)

Synthesis of 3-tert-butyl-4-hydroxyacetophenone (1)

Anhydrous aluminium chloride (4.0 g, 30 mmol) and toluene (100 mL) were added to a 250 mL round-bottom flask, and stirred at −45 °C for 5 min. 2-tert-butylphenol (4.0 mL, 26 mmol) was added slowly and the mixture was stirred at −45 °C for 3 h. And then acetyl chloride (2 mL, 28 mmol) was added to the flask and the mixture was stirred for 5 h. After heating to room temperature, the mixture was poured into the ice water, the white precipitate was filtered and washed with a large amount of water. The white powder was collected and dried in an oven to yield the target compound (3.7 g, 74%). 1H NMR (300 MHz, CDCl3) δ: 1.43 (s, 9H, C(CH3)3), 2.56 (s, 3H, CH3), 5.87 (s, 1H, OH), 6.75 (d, J = 8.4 Hz, 1H, Ph-H), 7.73 (dd, J = 2.1, 8.4 Hz, 1H, Ph-H), 7.96 (d, J = 2.1 Hz, 1H, Ph-H) ppm.

Synthesis of 1,3,5-tris(3’-tert-butyl-4’-hydroxyphenyl)benzene (2)

3-tert-butyl-4-hydroxyacetophenone (4.6 g, 24 mmol) and dry ethanol (50 mL) were added to a 250 mL round-bottom flask, and stirred at 0 °C for 15 min. Then silicon tetrachloride (13.8 mL, 120 mmol) was added dropwisely at same temperature. The reaction mixture was slowly up to room temperature and stirred overnight. The cool water (150 mL) was added into the flask, and extracted with methylene chloride (3×30 mL). The organic layer was washed with water, dried over Na2SO4, and concentrated in vacuum. The crude product was purified by column chromatography.
on silica by using a mixture of petroleum ether and methylene chloride to give target product as a white solid (3.36 g, 81%). $^1$H NMR(300 MHz, CDCl$_3$) $\delta$: 1.46 (s, 27H, C(CH$_3$)$_3$), 4.84 (s, 3H, OH), 6.77 (d, 3H, Ph-H), 7.39 (dd, 3H, $J = 9.6$ Hz, Ph-H), 7.58 (d, 3H, Ph-H), 7.61 (s, 3H, Ph-H) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 24.4, 29.5, 111.7, 118.9, 120.7, 128.8, 131.2, 137.2, 148.7 ppm.

**Synthesis of 1,3,5-tris(3’-tert-butyl-4’-hydroxy-5’-formylphenyl)benzene (3)**

1,3,5-tris(3’-tert-butyl-4’-hydroxyphenyl)benzene (2.2 g, 4.2 mmol), anhydrous magnesium dichloride (2.4 g, 25 mmol) and paraformaldehyde (1.2 g, 40 mmol) and dry tetrahydrofuran (50 mL) were added to a 250 mL round-bottom flask. Triethylamine (4.1 mL, 29 mmol) is added dropwise by syringe and the reaction mixture was refluxed for 8 h. The reaction mixture was cooled to room temperature and 90 mL of ethyl acetate was added. And then the resulting organic phase was separated and washed with 2 N HCl (3 × 20 mL) and water (3 × 20 mL), dried over MgSO$_4$, and concentrated in vacuum. The crude product was purified by column chromatography on silica by using petroleum ether as eluent to give target product as a light yellow solid (1.83 g, 72%). $^1$H NMR(300 MHz, CDCl$_3$) $\delta$: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 1.49 (s, 27H, C(CH$_3$)$_3$), 7.63 (s, 3H, Ph-H), 7.68 (d, 3H, Ph-H), 7.82 (d, 3H, Ph-H), 10.00 (s, 3H, CHO), 11.85 (s, 3H, OH) ppm. $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$: 29.2, 35.1, 120.7, 124.4, 130.3, 132.1, 133.2, 139.1, 141.8, 160.9, 197.1 ppm.

**Scheme S2**: Synthetic route for model compound.

**Synthesis of model compound**

3-Tert-butyl-hydroxybenzaldehyde (1.05 g, 5.9 mmol) was dissolved in 50 mL of ethanol. And then hydrazine hydrate (0.18 mL, 2.95 mmol) was added dropwise and
the reaction mixture was refluxed for 24 h. After cooling to room temperature, the yellow precipitate was collected by filtration, washed with cool ethanol, and dried under vacuum to give a yellow solid in 79% yield (0.8 g). ¹H NMR (300 MHz, CDCl₃) δ: 1.47 (s, 18H, C(CH₃)₃), 6.91 (t, 2H, Ph-H), 7.21 (d, 2H, Ph-H), 7.41 (d, 2H, Ph-H), 8.75 (s, 2H, CH=N), 12.02 (s, 2H, OH) ppm. IR (KBr, ν; cm⁻¹): 686, 752, 817, 846, 984, 1037, 1233, 1286, 1340, 1440, 1464, 1553, 1577, 1612 and 3058. UV-Vis (λ; nm): 362 and 401.

**Scheme S3**: Synthetic route for COF-JLU3

**Synthesis of COF-JLU3.**

A 10 mL pyrex tube was charged with 1,3,5-tris(3’-tert-butyl-4’-hydroxy-5’-formylphenyl)benzene (80 mg, 0.13 mmol), hydrazine hydrate (12 μL, 0.20 mmol), N,N-formdimethylamide (2.0 mL) and AcOH (0.4 mL, 3 M), the mixture was sonicated for 3 minutes, degassed through three freeze–pump–thaw cycles, sealed under vacuum. The reaction was heated at 120 °C for 72 h yielding a yellow solid at the bottom of the tube which was isolated by centrifugation and washed with anhydrous tetrahydrofuran and anhydrous acetone, and dried under vacuum at 120 °C for 10 h to afford red powder in 77% isolated yield. For other solvent conditions, such as mesitylene, tetrahydrofuran, methanol, mesitylene/dioxane (1/1 by vol), dioxane followed the same experimental procedure to obtain the covalent polymers. Elemental analysis for the calculated C (76.43%), H (8.88%), N (6.86%) and observed C (75.72%), H (6.99%), N (6.68%).
Figure S1. PXRD profiles of COF-JLU3 under variable reaction conditions.

Figure S2. FT-IR spectra of COF-JLU3 under variable reaction conditions.
Figure S3. N₂ adsorption (●) and desorption (○) isotherm profiles of COF-JLU3 measured at 77K.
**Figure S4.** The FT-IR spectra of monomer (red line), model compound (green line) and COF-JLU3 (black line).
Figure S5. Solid state $^{13}$C NMR spectra of the COF-JLU3 under N,N-dimethylformamide (black line), dioxane (blue line) and mesitylene/dioxane (green line). The COF-JLU3 samples obtained from the different solvent possess the same signal peaks.
Figure S6. SEM (A, B, C) and TEM (D) images of COF-JLU3. SEM images show that COF-JLU3 assumed belt morphology with lengths of several tens of micrometers and widths of about 100-300 nm and COF-JLU3 formed consisted of crystalline porous structure. Besides, TEM image reveals the presence of a porous texture and confirms this parallel multilayer structure further.
**Figure S7.** TGA curves of the COF-JLU3 samples obtained from N,N-dimethyformamide (black line), dioxane (blue line) and mesitylene/dioxane (green line).
**Figure S8.** The sample of COF-JLU3 was heated for 2 h at 300 °C and 400 °C under nitrogen, and after heating samples were labeled as COF-JLU3@300 and COF-JLU3@400, respectively. (a) Images of COF-JLU3@300 and COF-JLU3@400 in the solid state and under a UV-light irradiation of 360 nm. (b) XRD patterns and (c) FT-IR spectra of COF-JLU3, COF-JLU3@300, and COF-JLU3@400.
Figure S9. FT-IR spectra of the COF-JLU3 upon 6 h treatment in different conditions.
Figure S10. The excitation (○) and emission (●) spectra of COF-JLU3 samples obtained from DMF (black point), dioxane (blue point) and mesitylene/dioxane (green point). Inset: images of COF-JLU3 in the solid state and under a UV-light irradiation of 365 nm. These COF-JLU3 samples have similar luminescent properties.
Figure S11. The absorption spectra of COF-JLU3 (black line), 1,3,5-tris(3′-tert-butyl-4′-hydroxy-5′-formylphenyl)benzene (red line) and model compound (green line).

Figure S12. The fluorescence emission spectra of COF-JLU3 and M@COF-JLU3 in the presence of different metal ions. [COF-JLU3] = $10^{-4}$ M; [metal] = $2 \times 10^{-4}$ M
Figure S13. PL intensity of COF-JLU3 solution as a function of Cu$^{2+}$ concentration. 
LOD = 3 × 1.18/ 11.6 ×10$^6$= 0.31 μM
The detection limit = 3 × S.D./k where k is the slope of the curve equation, and S.D. Represents the standard deviation for the COF-JLU3 solution intensity in the absence of cooper ion.

Figure S14. Plot of PL quenching efficiency ($I_0/I$) as a function of Cu$^{2+}$ concentration.
Figure S15. The XPS spectrum of the Cu 3d orbital in Cu@COF-JLU3.

Figure S16. Nitrogen adsorption/desorption isotherm of Cu@COF-JLU3.
Figure S17. Effect of pH on luminescence intensity of COF-JLU3 at 601 nm in the present of Cu$^{2+}$ ion. [COF-JLU3] = 10$^{-4}$ M, [Cu$^{2+}$] = 2 × 10$^{-4}$ M

Figure S18. Fluorescence spectra of COF-JLU3 in THF.
Figure S19. PXRD profiles of COF-JLU3 and Cu$^{2+}$ metal ions incorporated Cu@COF-JLU3.

Figure S20. The luminescent emission spectra of COF-JLU3 in the absence (black) and presence (red line) of mix-metal solution containing Ni$^{2+}$, Co$^{2+}$, Fe$^{3+}$ and Cu$^{2+}$. We prepared the stock solution containing Cu, Ni, Co and Fe, and determined the metal contents after immersing the COF-JLU3 to the mix-metal solution by ICP. The results show that Cu$^{2+}$, Ni$^{2+}$, Fe$^{3+}$ and Co$^{2+}$ loading on the framework account for 11%, 2%, 5% and 1%, respectively. This indicates that COF-JLU3 is more selective towards Cu$^{2+}$ better than other ions. The deep understanding of such enhancing and quenching effects is still unclear. \([\text{COF-JLU3}] = 10^{-4} \text{ M, } [\text{Ni}^{2+}] = [\text{Co}^{2+}] = [\text{Fe}^{3+}] = [\text{Cu}^{2+}] = 2 \times 10^{-4} \text{ M.}\)
Table S1. Synthesis of the COF-JLU3 under variable solvothermal conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Temperature (°C)</th>
<th>Reaction Time (h)</th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesitylene (2 ml)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>223</td>
<td>78</td>
</tr>
<tr>
<td>Dioxane (2 mL)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>334</td>
<td>71</td>
</tr>
<tr>
<td>Dioxane (1 mL)/Mesitylene (1 mL)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>197</td>
<td>61</td>
</tr>
<tr>
<td>Methanol (2 ml)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>434</td>
<td>61</td>
</tr>
<tr>
<td>THF (2 ml)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>385</td>
<td>65</td>
</tr>
<tr>
<td>DMF (2 mL)/AcOH (6M, 0.4 mL)</td>
<td>120</td>
<td>72</td>
<td>570</td>
<td>77</td>
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