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Developing a catalyst with the uniform and well-defined crystal structure is very important to establish a catalytic sensing system with high efficiency. In this work, Cu-BTC metal-organic frameworks (MOFs) without crystalline CuO or Cu<sub>2</sub>O phase were successfully synthesized by using a low temperature synthesis method, and the as-prepared Cu-BTC MOFs were found to have outstanding catalytic activity towards the traditional oxidase substrate, *o*-phenylenediamine (OPD), to generate a colored and fluorescent product. The results of kinetic analysis revealed that the catalytic behavior of Cu-BTC MOFs towards OPD could well follow the typical Michaelis-Menten equation, indicative of a strong affinity between Cu-BTC MOFs and OPD. On the basis of these findings, taken together the condensation reaction between the -CHO group of formaldehyde and the -NH<sub>2</sub> group of OPD to form Schiff base compounds, a novel Cu-BTC MOFs-based catalytic sensing system of detecting gaseous formaldehyde could be successfully established.

# Introduction

Enzymes are very critical for sustaining life operation because they can accurately manipulate various complex and functional chemical reactions in life systems. Natural enzymes not only can act as the catalyst role in life, but also can be utilized to develop bio-/chemosensing platforms due to their highly catalytic efficiency. However, most of used natural enzymes have some shortcomings including complex and tedious procedures of purification, high cost of producing, and harsh conditions of storage and usage, which are unfavourable for their practical applications such as establishing bio-/chemosensing systems. Therefore. developing various kinds of artificial enzyme mimics to replace the natural enzymes is attracting tremendous attentions in recent years mainly due to the high stability and facilely producing of artificial enzyme mimics.<sup>1-3</sup> In particular, some metal/metal oxide/metal sulfide nanomaterials, including Au,  $^4$  Ag,  $^5$  CeO,  $^6$  Fe $_3O_4, ^7$  CoFe $_2O_4, ^8$  FeS,  $^9$  and CdS,  $^{10}$ were found to have intriguing enzyme-like catalytic activity. These nanomaterials have been employed to establish a series of bio-/chemosensing systems and to even catalyse the decomposition reactions of environmental organic

pollutants.<sup>11, 12</sup> However, it should be pointed out that most of these nanomaterials used as artificial enzyme mimics in the field of bio-/chemosensing were short of uniform and well-defined crystal structures. Developing artificial enzyme mimics with well-defined crystal structures are very important for further understanding their catalytic mechanisms and establishing the relationship between catalytic activity and crystal structure, which are also beneficial to obtain excellent catalysts for establishing highly sensitive catalytic sensing systems. However, quite a few works involving in this aspect have been reported at present. This lack can be considered to result from the difficulty of preparing these enzyme-like nanomaterials with uniform and well-defined crystal structures.

Metal-organic frameworks (MOFs), a novel kind of porous materials, have been widely used in the fields of gas storage/separation,<sup>13-17</sup> catalysis,<sup>18</sup> drug delivery,<sup>19</sup> and sensing.<sup>20-25</sup> Compared with traditional metal/metal oxide/metal sulfide nanomaterials, MOFs can show several advantages: (i) MOFs with varied and tunable structures can be synthesized by employing various metal ions and organic linkers as building blocks;<sup>26</sup> (ii) MOFs have uniform and welldefined crystal structures which can ensure the uniformity of their pore and channel size, and large surface area, also resulting in improving the catalytic selectivity; (iii) Most of MOFs possess highly thermal and mechanical stability which are beneficial to the repeatable usage, in particular under some extremely operation conditions.<sup>27</sup> Therefore, these advantages can ensure that MOFs should be ideal catalysts which are useful for establishing excellent catalytic sensing systems. However, hitherto the established catalytic sensing systems involving in MOFs used as the catalysts are fairly



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scarce.<sup>28-30</sup> The reasons for this shortage likely include: (i) for limited kinds of metal ions which have excellent catalytic activity towards the traditional substrates to trigger the fluorogenic or chromogenic reactions, it is not easy to obtain their corresponding MOFs which have single crystal structures with high quality. It should be noted that some reported works of catalytic sensing involving in MOFs are lack of the detailed characterization of crystal structures;<sup>31-33</sup> (ii) although some metal ions have excellent catalytic activity towards these substrate molecules, the catalytic activity of their corresponding MOFs are greatly lowered or even disappear, due to the strong binding between metal ions and ligands.<sup>34</sup> Therefore, looking for one kind of metal ions with excellent catalytic activity to prepare the corresponding MOFs which can retain their partially or largely catalytic activity, is the prerequisite for establishing highly sensitive MOFs-based catalytic sensing systems. In 2016, our group found that Cu<sup>2+</sup> ions have extremely highly catalytic activity towards the oxidation reaction of o-phenylenediamine (OPD) which is a traditional enzyme substrate molecule to generate a fluorescent compound.<sup>35</sup> Therefore, we considered that whether Cu<sup>2+</sup> ions can serve as the good candidate to prepare MOFs capable of retaining partially or largely its original catalytic activity. If Cu2+-based MOFs possessing good catalytic activity for the fluorogenic reactions could be successfully prepared, it could not only offer an opportunity to establish novel highly sensitive MOFs-based catalytic sensing systems, but also lead to structural diversity of catalysts compared with that of metal ions.



Scheme 1. The draft illumination of the catalytic sensing mechanism in this work.

Therefore, in this work, by employing 1,3,5-benzene tricarboxylic acid (H<sub>3</sub>BTC) and Cu<sup>2+</sup> ions as the building blocks, Cu-BTC MOFs could be successfully prepared by using a low temperature synthesis method . The data of single crystal X-ray crystallographic diffraction (SCXRD) revealed that the asprepared Cu-BTC MOFs adopt a cubic structure, and powder X-ray powder diffraction (PXRD) experiments indicated that no CuO or Cu<sub>2</sub>O phase could be observed in the as-prepared Cu-BTC MOFs, different from that of Cu-BTC MOFs prepared under high temperature of above 100 °C. The surface area of the as-prepared Cu-BTC MOFs was estimated to 1554.835

m<sup>2</sup>/g, which is indicative of its good porous structure. It was found that Cu-BTC MOFs have the outstanding catalytic activity towards the traditional enzyme substrate OPD which could be catalysed to generate a fluorescent species. Considering the condensation reaction of forming Schiff base compounds between the -CHO group of formaldehyde and the -NH<sub>2</sub> group of OPD, a catalytic sensing platform for detecting gaseous formaldehyde was expected to be well established (Scheme 1). When a certain amount of gaseous formaldehyde was introduced into the solution containing OPD and the as-prepared Cu-BTC MOFs, the catalytic fluorogenic reaction was found to be gradually suppressed, due to the condensation reaction between formaldehyde and OPD. However other tested common gases like N<sub>2</sub>, CO<sub>2</sub>, and air did not produce observable effects on this catalytic reaction. Therefore, a novel, sensitive and selective catalytic sensing system of detecting gaseous formaldehyde could be successfully established.

## **Experimental section**

## Materials and instruments

Materials. KCl (99.5%, AR), methanol (99.5%, AR), ethanol (99.7%. AR), glacial acetic acid (99.5%, AR). N.N-Dimethylformamide (99.5%, AR), hydrochloric acid (36-38%, AR), acetonitrile (99%, AR), dichloromethane (99.5%, AR), and tris(hydroxymethyl)aminomethane (Tris, 99%, BR) were purchased from GuoYao (Shanghai, China). 1,3,5-benzene tricarboxylic acid (H<sub>3</sub>BTC) (98%), 3,3',5,5'-tetramethyl benzidine (TMB, 99%), and p-acetamidophenol (99%, AR) were purchased from Aladdin (Shanghai, China). Copper nitrate trihydrate (99%, AR) was obtained from Xiya Reagent (Shandong, China). Nafion solution (5%) was obtained from Sigma-Aldrich (Darmstadt, Germany). OPD (99.5%) was obtained from Macklin (Shanghai, China). Standard gases of CO<sub>2</sub>, N<sub>2</sub>, air and formaldehyde (100 ppm) were purchased from Putian Tongchuang Biotechnology Co. Ltd. (Beijing, China). Ultrapure water were purified by a Milli-Q system.

Instruments. Photoluminescence (PL) spectra were recorded with a FS5 fluorescence spectrophotometer (Edinburgh, UK). UV-vis absorption (UV) spectra were recorded with a UV-2600 spectrophotometer (Shimadzu, Japan). PXRD experiments were performed by using a Rigaku/SmartLa analyzer with Cu K $\alpha$  radiation ( $\lambda$ = 1.5406 Å) with the  $2\vartheta$  range from 5° to 60°. SCXRD data were collected by using a Gemini ECCD diffractometer with Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) (Aglient Technologies, Poland Sp.ZO.O). X-ray photoelectron spectroscopy (XPS) experiments were conducted by using an EscaLab 250Xi X-ray photoelectron spectrometer with the excitation of an Al Ka X-ray radiation source at 1486.6 eV (Thermo Scientific, USA). Fourier transform infrared (FT-IR) spectra were recorded with a Nicolet iS 50 instrument (Thermo Scientific, USA). The experiments of electrospray ionization mass spectrometry (ESI-MS) were performed on an infinity ultrahigh pressure

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liquid chromatography (UHPLC) system with a quadrupole (Q-TOF) mass time-of-flight spectrometer (Agilent Technologies, USA). Nuclear magnetic resonance (NMR) experiments were conducted with a 500 MHz/AVANCE III system (Bruker, Switzerland). Cyclic voltammetry curves were obtained on a CHI760E electrochemical workstation Chenhua Instrument Co., Ltd, (Shanghai China). Scanning electronic microscopy (SEM) experiments were performed with a Hitachi S-3500N system (Japan). Brunauer-Emmett-Teller (BET) test was conducted with an Autosorb-iQ automatic surface area and pore size distribution analyzer (Quantachrome Instruments, USA). Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) curves were measured with a DTG-60H thermos-gravimetricanalyzer (Shimadzu, Japan).

## **Experimental procedures**

Synthesis of Cu-BTC MOFs. After a sires of optimized experiments were conducted, a low temperature synthesis method was chosen to prepare  $Cu_3(BTC)_2$  MOFs, the single crystals.<sup>36</sup> 0.49 g  $Cu(NO_3)_2$ ·  $3H_2O$  was dissolved in 6 mL water-DMF mixed solvent of 1:1 (v/v) , and 0.24 g H<sub>3</sub>BTC was dissolved in 3 mL ethanol. Then,  $Cu(NO_3)_2$  solution and 12 mL glacial acetic acid were added to H<sub>3</sub>BTC solution. The resulting solution was then sealed in a small glass vial and placed in a heating oven at 55 °C for 3 days. After the solution was naturally cooled to room temperature, the blue Cu-BTC MOF crystals appeared on the inner wall of the glass vial. All crystals were collected, and carefully washed by ethanol for three times, for solvent exchange. Then, all crystals were dried in vacuum at 60 °C for 2 h, and stored in a common dyer for further experiments.

The catalytic activity of the as-prepared Cu-BTC MOFs. In order to investigate the catalytic activity of the asprepared Cu-BTC MOFs, PL spectrum of the oxidation product of OPD catalysed by Cu-BTC MOFs in 50 mM Tris-HCl buffer solution of pH 7.4 was monitored by a FS5 fluorescence spectrophotometer with the excitation wavelength of 415 nm. For a typical catalytic reaction experiment, the experimental procedure was followed: 300  $\mu$ L 0.8 mM OPD solution and 2.0 mg Cu-BTC MOFs were added into 2.7 mL 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile (by volume). Then, the reaction solution was heated in water bath at 60  $^{\circ}\mathrm{C}$  for 35 min. PL spectrum was immediately recorded, after the solution was guickly cooled to the room temperature. For the experiments of the effect of experimental parameters on this catalytic reaction, only the checked experimental parameter was changed yet other parameters were fixed to be same in this tested group. For the checked experimental parameters, the reaction time was changed from 0 min to 35 min, pH was adjusted from 4.2 to 10.2, temperature was set from 30 °C to 80 °C, OPD concentration was ranged from 4  $\mu$ M to 0.2 mM, Cu-BTC MOFs concentration was altered from 0.23 mg·mL<sup>-1</sup> to 1.0 mg·mL<sup>-1</sup>, and the content of acetonitrile was varied from 0 to 30%. The error bars could be obtained by measuring three parallel solutions.

Kinetic analysis of the catalytic activity of the as-prepared Cu-BTC MOFs towards OPD as the substrate was carried out by varying OPD concentration, such as 0.004, 0.01, 0.02, 0.04, 0.08, 0.14 and 0.20 mM. According to Michaelis-Menten equation,  $V = V_{max} \times [S]/(K_m + [S])$ , which is derived at the condition assuming in the presence of a steady-state reaction conditions, we could calculate the apparent kinetic parameters. In this equation, V is the initial velocity,  $K_{\rm m}$  is called as the Michaelis constant,  $V_{max}$  is the reaction velocity when the catalyst is saturated with the substrate, and [S] is the substrate concentration. The initial catalytic velocity was calculated from the initial slopes of curves of PL intensity at 564 nm wavelength vs time. The reaction velocity was measured in 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile, 0.67 mg·mL<sup>-1</sup> Cu-BTC MOFs and varied OPD concentration at 60 °C. The error bars could be obtained by measuring three parallel solutions.

Electrochemical measurements. A typical three electrode system was employed. The working electrode was a modified glassy carbon electrode with a diameter of 3 mm, the reference electrode was an Ag/AgCl electrode, and counter electrode was platinum wire electrode. First, the bare glassy carbon electrode was polished by using the polishing powder with the size of 1.0, 0.3, and 0.05  $\mu$ m, in turn, and then was sequentially put in ethanol and water for ultrasonic washing of 3 min. Cyclic voltammogram (CV) experiment of OPD was recorded in 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile, 1% KCl and 50 mM OPD. Before the measurement, the buffer solution was bubbled with nitrogen gas for 30 min for removing the dissolved oxygen. The applied potential was ranged from -1.5 to 1.2 V, and the scan rate was set to 50 mV·s<sup>-1</sup>. CV and differential pulse voltammetry (DPV) of the as-prepared Cu-BTC MOFs were also conducted. First, 5 mg ground powder of the asprepared Cu-BTC MOFs was weighted and added into 0.8 mL water-isopropanol mixed solution(v/v = 3:1). Then, 20  $\mu$ L 5% Nafion solution was added to the above solution, and the mixed solution was put in an ultrasonic cleaner by ultrasound for 10 min to obtain a homogeneous ink. 10  $\mu$ L ink was dropped into the working electrode to form a uniform film after the electrode was dried. 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile was employed as the electrolyte after the solution was bubbled with nitrogen gas for 30 min for removing the dissolved oxygen. For CV scanning, the potential was changed from -0.4 to 0.4 V, and the scan rate was set to 50 mV·s<sup>-1</sup>. For DPV scanning, the potential was ranged from 0.4 to -0.4 V, and the scan rate was set to 50 mV·s<sup>-1</sup>.

**Repeatability experiments of Cu-BTC MOFs.** To investigate the reusability and catalytic stability of the as-prepared Cu-BTC MOFs towards OPD, the experiments of cycling catalytic oxidation reaction were performed. The detailed experimental procedure as the follow: 300 µL 0.8 mM OPD

solution and 2.0 mg Cu-BTC MOFs were added into 2.7 mL 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile, and the mixed solution was placed into water bath at 60 °C for 35 min, and then PL spectrum was measured by using the excitation wavelength of 415 nm. After the measurement of PL spectrum was completed, the reaction solution was filtered to recover solid crystals. The collected crystals were carefully washed by ethanol for three times, and then placed in a vacuum dryer at 60 °C for 2 h. The resulting solid crystals were reused in next cycle of the catalytic reaction of OPD under the same experimental conditions. The experiment of the catalytic reaction of OPD was cycled for 5 times.

Detection of gaseous formaldehyde. For detecting gaseous formaldehyde by using the fluorogenic reaction of OPD catalysed by the as-prepared Cu-BTC MOFs, the experimental procedure was followed: The flow rate of standard formaldehyde gas was fixed as 40 mL·min<sup>-1</sup>, and a series of exposure times, such as 0 s, 5 s, 15 s, 30 s, 1 min, 2 min, 4 min, 6 min, 8 min, 10 min and 15 min, were tested. After 100 ppm standard formaldehyde gas was flowed to 5 mL 8 mM oxygen-free OPD solution with various exposure times, the resulting solution was sealed and heated in a water bath at 50 °C for 30 min. Then, 2 mg Cu-BTC MOFs were added into 30  $\mu$ L above reaction solution which was mixed with a certain volume of 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile, resulting in a total volume of 3 mL. After that, the mixed solution was sealed and heated in a water bath at 60 °C for 35 min. Then, the PL spectrum of the catalytic reaction solution was measured by a FS5 fluorescence spectrophotometer with excitation an wavelength of 415 nm. The error bars could be obtained by measuring three parallel solutions.

# **Results and discussion**

In this work, Cu-BTC MOFs were prepared by using a low temperature synthesis method. The SEM and optical microscope images of the as-prepared Cu-BTC MOFs were shown in Fig. S1a-d. The cubic geometry structure of blue Cu-BTC MOFs could be observed, and the average diameter was estimated to ca. 600 µm. SCXRD experiments can further confirm that the as-prepared Cu-BTC MOFs adopt the cubic structure. The diffraction peaks were refined by using the space group Fm-3m, affording the lattice parameters of a = 26.3805(3) Å, b = 26.3805(3) Å, c = 26.3805(3) Å, and  $\alpha$ ,  $\beta$ ,  $\gamma$  = 90°. As shown in Fig. 1a, the minimum repeating unit contains three Cu<sup>2+</sup> and two deprotonated H<sub>3</sub>BTC ligands. Every Cu<sup>2+</sup> can coordinate with four carboxylate groups, resulting in forming a square structure in the bottom position, and one oxygen atom can fill on the top position to offer a paddle wheel-like secondary building unit. The distance between two neighboring Cu<sup>2+</sup> is 2.634 Å. The inside views of the structure of Cu-BTC MOFs from both [100] (b) and [111] (c) axis directions were shown in Fig. 1b and Fig. 1c, respectively, indicated that the building units direct to form a symmetrical three-dimensional framework. The water and ethanol molecules were found in the channel as guest molecules to stabilize the porous structure. The crystal data were deposited in Table S1 (referring to CCDC No. CCDC reference number 1854611, which has been supplemented at Cambridge Crystallographic Data Centre). The results of PXRD experiments were shown in Fig. 2. The XRD pattern of Cu-BTC MOFs can well match that of the previous report.<sup>36</sup> It should be pointed out that, Cu-BTC MOFs synthesized by this method is somewhat different from those synthesized by the conventional hydrothermal synthesis method under high temperature, and the temperature used in other reported case was higher than 55 °C used in this work.37 The XRD reflection peaks of CuO ( $2\vartheta$  = 35.5° and 38.7°) or Cu<sub>2</sub>O ( $2\vartheta$  = 36.43°) can't be observed in the as-prepared Cu-BTC MOFs in this work yet appeared in the reported case which used the hydrothermal synthesis method under high temperature of over 100 °C (inset of Fig. 2).<sup>38</sup> Therefore, it can be believed that the reaction temperature has an important effect on whether forming CuO or Cu<sub>2</sub>O phase in Cu-BTC MOFs.



Fig. 1 Schematic view of the coordination environment of (a)  $Cu^{2+}$  and views inside of the structure of the as-prepared Cu-BTC MOFs from the [100] (b) and [111] (c) axis direction.



Fig. 2 PXRD patterns of the simulated (1), as-prepared (2), reused (3), and after sensing tested (4) Cu-BTC MOFs. Inset: local enlarged view of PXRD from 30  $^{\circ}$  to 42  $^{\circ}$ .

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FT-IR spectrum of the as-prepared Cu-BTC MOFs reveals that, the peak of 488 cm<sup>-1</sup> can be ascribed to the stretching vibration of Cu-O bond, and 1371 cm<sup>-1</sup> and 1450 cm<sup>-1</sup> can be attributed to the stretching vibration of C-O in the carboxylate group and the bending vibration of O-H, respectively (Fig. 3a). The peak of 1639 cm<sup>-1</sup> can be assigned to the stretching vibration of C=O, different from the peak of 1720 cm<sup>-1</sup> in H<sub>3</sub>BTC, likely because that the oxygen atom in the carboxyl group could coordinate with  $Cu^{2+}$ , resulting in a red shift.<sup>39</sup> Considering the porous structure of Cu-BTC MOFs, the surface area was measured. Before the N<sub>2</sub> adsorption isotherm was measured, 27.3 mg Cu-BTC MOFs was dried at 40 °C by vacuum for overnight. BET surface area was calculated by taking the  $p/p_0$  range from 0.05 to 0.2 of the isotherm. The surface area was estimated to 1554.835  $m^2/g$  (Fig. 3c), which is higher than those of Cu-based MOFs synthesized by other ways,<sup>40-42</sup> and pore size distribution of Cu-BTC MOFs was shown in Fig. 3d, supportive of its good porous structure.



Fig. 3 (a) FT-IR spectra of reused (1), as-prepared (2) Cu-BTC MOFs, and ligand  $H_3BTC$  (3). TGA (red) and DTG (blue) curves (b),  $N_2$  adsorption-desorption isotherm (c) and pore size distribution (d) of the as-prepared Cu-BTC MOFs.

To probe the thermal stability of the as-prepared Cu-BTC MOFs, TGA with heating rate of 5 °C per min was used. As shown in Fig. 3b, Cu-BTC MOFs have two weightless intervals. First, Cu-BTC MOFs lost water and ethanol guest molecules from the pores with a weight loss of 36.14% when temperature was enhanced from 50 °C to 200 °C. Then, a platform appeared from 200 °C to 325 °C, indicated that the framework could maintain a stable state in this temperature range. When the temperature was increased to be higher than 325 °C, the crystal structure would collapse, resulting in a sharp drop of the weight with loss ratio of *ca*. 24.18%. These observations can support that Cu-BTC MOFs have good thermal stability below 325 °C. It is beneficial to develop a thermal stable catalyst in the field of catalytic sensing.

The experiments of XPS and energy dispersive spectrum (EDS) were employed to evaluate the chemical components of the as-prepared Cu-BTC MOFs. EDS result reveals that Cu element exists in Cu-BTC MOFs, and its content was 7.47% (Fig. S2). The XPS peak of C1s can be observed at 285.07 eV

and 288.82 eV (Fig. 4), resulting from  $Cu_2(O_2CR)_4$ . The binding energy of O1s is 532.06 eV, originating from the lattice oxygen  $O^{2^-}$ . The peaks with the binding energies of 935.09 eV and 954.89 eV can be assigned to  $Cu2p_{3/2}$  and  $Cu2p_{1/2}$ , respectively. The peaks of the binding energies of 940.47, 944.59 eV and 963.15 eV belong to the satellite peaks of  $Cu2p_{3/2}$  and  $Cu2p_{1/2}$ , indicative of predominant  $Cu^{2^+}$  form in the catalyst.<sup>43</sup> This observation reveals that no crystalline  $Cu_2O$  exists in Cu-BTC MOFs, also supportive of obtaining Cu-BTC MOFs without crystalline  $Cu_2O$  phase by using this low temperature synthesis method.

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Fig. 4 XPS spectra of the as-prepared Cu-BTC MOFs: (a) the total spectrum, (b) O 1s spectrum, (c) C 1s spectrum and (d) Cu 2p spectrum.



**Fig. 5** PL spectra of OPD (red line,  $\lambda_{ex}$ =415 nm) and *p*-acetamidophenol (blue line,  $\lambda_{ex}$ =330 nm), and UV-vis absorption spectrum of TMB (black line) catalysed by the as-prepared Cu-BTC MOFs (a). Typical PL photographs of OPD catalysed by the as-prepared Cu-BTC MOFs (b), and of original OPD without catalysis (c), illuminated by 365 nm UV lamp in dark room. Experimental conditions: OPD, *p*-acetamidophenol and TMB concentrations were set to 0.08 mM, respectively; the temperature was 60 °C; Cu-BTC MOFs concentration was set to 0.67 mg·mL<sup>-1</sup>; the reaction time was 35 min; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile content was used.

The catalytic activity of the as-prepared Cu-BTC MOFs was investigated by employing OPD as the substrate. When 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile, 0.67 mg.mL<sup>-1</sup> Cu-BTC MOFs, and 0.08 mM OPD was heated in the water bath at 60 °C for 35 min, the resulting solution was found to become yellow color and emit yellow light under the irradiation of 365 nm UV lamp, yet its origin solution was non-fluorescent and colorless (Fig. 5b-c). The PL spectrum was recorded with maximum emission peak at 564 nm by using the excitation wavelength of 415 nm (Fig.

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5a). This result reveals that the as-prepared Cu-BTC MOFs likely possess outstanding catalytic activity towards OPD and the catalytic reaction can generate a fluorescent product. To further confirm the role of Cu-BTC MOFs, the experiments of removing dissolved oxygen and with or without the illumination of light were conducted. When dissolved oxygen in the buffer solution was largely removed by bubbling N<sub>2</sub> for 30 min or Cu-BTC MOFs were not added into the buffer solution, the PL intensity was found to be greatly lowered or even disappear, that means, the reaction could be greatly suppressed or even not occur (Fig. S3). Similarly, it was found that the illumination of room light has not significant effect on the fluorogenic reaction, indicated that the catalytic effect of light on this reaction could be excluded for the observable fluorogenic reaction (Fig. S3). Therefore, it could be deduced that the dissolved oxygen is the oxidant and Cu-BTC MOFs are the catalysts in this fluorogenic reaction. The electrochemical experiments were also employed to further support the catalyst role of Cu-BTC MOFs. Theoretically, if Cu-BTC MOFs can directly oxidize OPD, the Gibbs free energy of this assumed redox reaction should have a negative value. According to the CV curves of Cu-BTC MOFs and OPD, the half-wave potential ( $\varphi_{\rm h}$ ) of the cathodic peak of Cu-BTC MOFs and the half-wave potential ( $\varphi_h$ ) of the anodic peak of OPD could be estimated to 0.055 V and 0.368 V, respectively (Fig. S4-S5). Therefore, the difference between the two potentials  $(\Delta \phi_{\rm h})$  was calculated to be -0.313 V, and the Gibbs free energy  $\Delta G$  could be further calculated to 30.199 kJ·mol<sup>-1</sup>, according to the equation of  $\Delta G = -n\Delta \varphi F$ . Because the calculated value of the Gibbs free energy is positive value, it could be concluded that Cu-BTC MOFs did not directly oxidize OPD. This result could substantially support the catalyst role of Cu-BTC MOFs. In order to fully study the catalytic performance of Cu-BTC MOFs, other traditional enzyme substrates like TMB and p- acetamidophenol were chosen as the substrates in this catalytic fluorogenic reaction, respectively, to check whether Cu-BTC MOFs can catalyse their oxidation reaction. However, no colored or fluorescent product could be observed (Fig. 5a). Therefore, the asprepared Cu-BTC MOFs can be considered to have high catalytic selectivity towards OPD as the substrate.



Fig. 6 (a) Time-dependent change of PL intensity at 564 nm wavelength of the catalytic reaction of the as-prepared Cu-BTC MOFs towards OPD under various reaction temperatures. (b) The relationship between PL intensity at 564 nm wavelength and the reaction temperature when the reaction time was chosen as 35

min. Experimental conditions: Cu-BTC MOFs concentration was 0.67 mg mL<sup>-1</sup>; [OPD] = 0.08 mM; 50 mM Tris-HCl buffer solution of pH 7.4 containing 15% acetonitrile content was used.



**Fig. 7** pH-dependent change of the catalytic activity of the as-prepared Cu-BTC MOFs towards OPD (a). The relationships between the PL intensity at 564 nm wavelength and OPD concentration (b), Cu-BTC MOFs concentration (c), and the content of acetonitrile (d), respectively. Experimental conditions: Cu-BTC MOFs concentration was 0.67 mg mL<sup>-1</sup> (a, b, and d); [OPD] = 0.08 mM (a, c, and d); the reaction temperature was 60 °C (a-d); the reaction time was 35 min (a-d); 50 mM Tris-HCl buffer solution of pH 7.4 (b-d) was used; the acetonitrile content was 15% (a-c).

To further probe the catalytic reaction of the as-prepared Cu-BTC MOFs towards OPD, the effects of temperature, pH, OPD concentration, Cu-BTC MOFs concentration, acetonitrile content and reaction time on this catalytic fluorogenic reaction were detailedly investigated. When the temperature was enhanced from 40 °C to 80 °C, the catalytic activity was generally increased and showed a platform after the temperature was extended up to 60 °C (Fig. 6b). The reaction time effects on the catalytic reaction under various tested reaction temperatures were found to have an increase tendency on the PL intensity at 564 nm wavelength with increasing the reaction time from 0 to 35 min (Fig. 6a). For 70 °C and 80 °C, when the reaction time was increased up to 20 min, the catalytic reaction nearly reached a platform. The experimental results of pH effect reveals that, when pH was changed from 4.2 to 10.2, the catalytic activity first increased and then decreased (Fig. 7a). With increasing OPD concentration from 4  $\mu$ M to 0.2 mM, the PL intensity at 564 nm wavelength was found to gradually increase and reach a platform when OPD concentration was set to be higher than 0.08 mM (Fig. 7b). For Cu-BTC MOFs concentration effect, it was found that the tendency of the PL intensity at 564 nm wavelength first increased and then decreased with increasing Cu-BTC MOFs concentration from 0.23 mg·mL<sup>-1</sup> to 1.0 mg·mL<sup>-1</sup> (Fig. 7c). Considering that acetonitrile can promote the catalytic activity of Cu<sup>2+</sup> ions,<sup>35</sup> the effect of acetonitrile content on the catalytic reaction of Cu-BTC MOFs towards OPD was also investigated. With increasing acetonitrile content from 0 to 30%, the catalytic activity was found to be first enhanced and then have a platform (Fig. 7d). Therefore, after the experiments of the effects of experimental parameters were performed, 50 mM Tris-HCl

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buffer solution of pH 7.4 containing 15% acetonitrile, 0.67 mg.mL<sup>-1</sup> Cu-BTC MOFs, and 0.08 mM OPD, the reaction temperature of 60 °C and the reaction time of 35 min were chosen for further experiments.

On the basis of these above experimental results, the investigation on the reaction kinetics of the as-prepared Cu-BTC MOFs towards OPD as the substrate was further conducted. The initial rate method was employed to measure the apparent steady-state kinetic parameters of this catalytic reaction.<sup>44</sup> As shown in Fig. 8a, the catalytic reaction of Cu-BTC MOFs towards OPD could follow the traditional Michaelis-Menten equation. Furthermore, a doublereciprocal curve was obtained with a good linear relationship (Fig. 8b).  $V_{\text{max}}$  and  $K_{\text{m}}$  were calculated by using the doublereciprocal curve (Table 1). Obviously, the small  $K_m$  value of this catalytic system indicated that the affinity between OPD and Cu-BTC MOFs was stronger than that of other catalyst systems such as HRP,  $^{45}$  MnO<sub>2</sub>,  $^{45}$  Ag<sub>3</sub>PO<sub>4</sub> and Ag@Ag<sub>3</sub>PO<sub>4</sub> microcubes (MCs)<sup>46</sup> when OPD was used as the substrate. Furthermore, the maximum reaction velocity could reach the level of those of HRP and MnO<sub>2</sub>. These results can also further support that Cu-BTC MOFs did play the catalyst role in this fluorogenic reaction.



**Fig. 8** Steady-state kinetic analysis of the fluorogenic reaction of OPD catalysed by Cu-BTC MOFs on the basis of the Michaelis–Menten equation (a), and its double-reciprocal plot (b).

 Table 1. Comparison of apparent kinetic parameters of the as-prepared Cu-BTC MOFs in this work and other reported catalysts.

Catalyst	Substr ate	<i>K</i> <sub>m</sub> (mM)	V <sub>max</sub> (M·s <sup>-1</sup> )	Ref.
HRP	OPD	0.59	4.65×10 <sup>-8</sup>	45
MnO <sub>2</sub>	OPD	0.31	8.21×10 <sup>-8</sup>	45
$Ag_3PO_4MCs$	OPD	3.31	2.77×10 <sup>-6</sup>	46
Ag@Ag <sub>3</sub> PO <sub>4</sub> MCs	OPD	1.23	5.18×10 <sup>-6</sup>	46
Cu-BTC MOFs	OPD	0.0567	1.53×10 <sup>-8</sup>	This work

Considering that the reusability is one of advantage of MOFs, repeating the usage of the as-prepared Cu-BTC MOFs in the catalytic fluorogenic reaction of OPD was further investigated. It was found that under the tested experimental

conditions the as-prepared Cu-BTC MOFs could be repeatedly used at least 5 times to catalyse the fluorogenic reaction of OPD, without significantly decreasing its original catalytic activity (Fig. 9). Furthermore, the XRD peaks of the reused Cu-BTC MOFs after the cycle of 5 times was found to be identical to those of the as-prepared Cu-BTC MOFs (Fig.2), and IR result of the reused Cu-BTC MOFs is similar to that of the as-prepared Cu-BTC MOFs (Fig. 3a). These observations indicate that after the cycle experiments the component and valence state of Cu-BTC MOFs did not significantly change, which also confirm the catalyst role of the as-prepared Cu-BTC MOFs. Therefore, the as-prepared Cu-BTC MOFs could be viewed as the excellent potential catalysts for establishing repeatable sensing platforms, which is expected to be able to overcome the shortcoming of uncyclable usage in the case of Cu<sup>2+</sup> ions as the catalyst.<sup>35</sup>

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Fig. 9 Repeatability tests of 5 cycles on the catalytic fluorogenic reaction of the asprepared Cu-BTC MOFs towards OPD as the substrate.



**Fig. 10** ESI-MS result of the purified oxidation product of OPD catalysed by the as-prepared Cu-BTC MOFs. The main peak of m/z of 211.0980 can be ascribed to 2,3-diaminophenazine ([M + H]<sup>+</sup>, calcd. m/z is 211.0978). The raw product was extracted from the reaction aqueous solution by using CH<sub>2</sub>Cl<sub>2</sub>, and the organic solvent was removed by using rotary evaporation. Then, the product was put in a vacuum freeze-drying equipment for overnight. Finally, the purified product was obtained for performing ESI-MS experiment.

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To further study the fluorogenic reaction of OPD catalysed by the as-prepared Cu-BTC MOFs, the product of this catalytic reaction was probed by using ESI-MS and <sup>1</sup>H NMR. After the purification procedure was performed, the experimental result of ESI-MS of the product reveals that the recorded m/z peak value of 211.0978 can be assigned to 2,3-diaminophenazine (Fig. 10). The result of <sup>1</sup>H NMR can further confirm this main product (Fig. 11). Therefore, these results can well support our proposed catalytic mechanism (Scheme 1).



**Fig. 11** <sup>1</sup>H NMR result (500 MHz, DMSO- $d_6$ ) of the purified oxidation product of the fluorogenic reaction of OPD catalysed by Cu-BTC MOFs.  $\delta$  7.90-7.88 ppm (m, 2H), 7.56-7.54 ppm (m, 2H), 6.91 ppm (s, 2H), 6.26 ppm (s, 4H). The marked "\*" peaks are unknown peaks. The purification of product was the same as the above mentioned procedure.

Formaldehyde gas, generally released from various artificial boards in home, office and public buildings, is considered as a highly dangerous indoor pollutant. Taking into account that the -CHO group of formaldehyde can easily react with the -NH<sub>2</sub> group of OPD to form Schiff base compounds, a detection method of gaseous formaldehyde based on the catalytic fluorogenic reaction of Cu-BTC MOFs towards OPD as the substrate is thus expected to be developed. When the buffer solution containing OPD was bubbled with a certain amount of formaldehyde gas, the catalytic reaction in the presence of Cu-BTC MOFs was found to be suppressed. To detailedly study the feasibility of sensing gaseous formaldehyde, the flow rate of formaldehyde gas was fixed as 40 mL·min<sup>-1</sup> and various exposure times were set, before the buffer solution was sealed and heated under various temperatures. To study the optimum temperature and time of the reaction between OPD and formaldehyde, a series of temperatures (30, 40, 50, and 60 °C) and reaction times (15, 30, 60, 90, and 120 min) were tested, respectively (Fig S6). Therefore, after checking a series of experiments, 50 °C and 30 min were chosen as the reaction temperature and reaction time, respectively, in this condensation reaction. Further catalytic reaction experiments reveal that, with increasing exposure time of introducing formaldehyde gas, the PL intensity at 564 nm wavelength was found to have two kinds of decrease (Fig. 12). Two different response curves likely indicate that two different reactions between formaldehyde and OPD could occur, that is, with increasing formaldehyde it would generate the products containing one -C=N- or even two -C=N- bonds in the same OPD molecule due to OPD bearing two  $-NH_2$  groups. Two linear relationships between the PL intensity at 564 nm wavelength and the exposure time of formaldehyde could also be obtained from the PL response curves of formaldehyde (Fig. 12b). The limit of detection (LOD) of gaseous formaldehyde could be calculated to 0.358 s (3*s*/*k*, *n* = 9, in which *k* is the slope of the relationship curve in the exposure time ranging from 0 to 60 s).

To transform the exposure time of formaldehyde into formaldehyde concentration (ppm), the following equation (1) could be used,  $^{47}$ 



**Fig. 12** The effect of exposure time of gaseous formaldehyde on the PL spectra of OPD solution catalysed by the as-prepared Cu-BTC MOFs (a) and the relationship between PL intensity at 564 nm wavelength and the exposure time of formaldehyde (b). The error bars represent the standard deviation of three measurements.

$$C = w \frac{v t V_1 C_0}{V_0 V_2} \dots \dots (1)$$

where C is formaldehyde concentration (ppm), v is the flow rate of formaldehyde gas (mL·min<sup>-1</sup>), t is exposure time of formaldehyde gas (s), and  $V_0$  is the volume of OPD solution bubbled by formaldehyde gas (mL).  $V_1$  is the added volume of the forming Schiff base solution to this catalytic system (mL),  $V_2$  is the total volume of catalytic system solution (mL). w is the maximum solubility of formaldehyde (40%) in water,<sup>48</sup>  $C_0$ is the concentration of used standard formaldehyde gas (ppm). Therefore, LOD of formaldehyde could also be calculated to 18.67 ppb (3s/k, n = 9, k is the slope of)relationship curve in the exposure time ranging from 0 to 60 s), according to the equation (1) of gaseous formaldehyde concentration. This LOD is much lower than those of nonsystems for detecting catalytic sensing gaseous formaldehyde,<sup>49-51</sup> indicative of high sensitivity of this sensing systems due to introducing catalytic fluorogenic reaction.

The selectivity of this catalytic sensing platform towards other common gases such as  $N_2$ ,  $CO_2$ , and air were also investigated. Under the similar experimental conditions, it was found that individual these tested gases did not have a significant inhibitory effect on this catalytic system, even if the concentrations of these tested gases were set to be much

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higher than that of formaldehyde (Fig. 13). Therefore, this result reveals that this catalytic sensing system has good selectivity for gaseous formaldehyde. The forming product of the condensation reaction between formaldehyde and OPD was further probed by using ESI-MS. According to the result of ESI-MS, it was deduced that this condensation reaction could form 1-methylbenzimidazole and benzimidazole (Scheme 1), because the recorded m/z peak of 133.0762 and 119.0606 could be assigned to 1-methylbenzimidazole ([M + H]<sup>+</sup>, calcd. m/z is 133.0760) and benzimidazole ([M + H]<sup>+</sup>, calcd. m/z is 119.0604), respectively (Fig. S7). It should be pointed out that PXRD result of after sensing tested Cu-BTC MOFs was found to be almost same with that of unused Cu-BTC MOFs (Fig.2), substantially supportive of its catalyst role.



**Fig. 13** The selectivity of the catalytic fluorogenic system of the as-prepared Cu-BTC MOFs towards OPD as the substrate for individual N<sub>2</sub>, CO<sub>2</sub>, air and formaldehyde gas under various exposure times. The error bars represent the standard deviation of three measurements.  $F_0$  represents the PL intensity at 564 nm wavelength of the OPD solution catalyzed by Cu-BTC MOFs in the absence of formaldehyde or other common tested gases; *F* represents the PL intensity at 564 nm wavelength of the OPD solution catalyzed by Cu-BTC MOFs in the presence of formaldehyde or other common tested gases.

# Conclusions

In summary, in this work Cu-BTC MOFs without crystalline CuO or Cu<sub>2</sub>O phase could be successfully synthesized by using a low temperature synthesis method, exhibiting the outstanding catalytic activity towards the traditional enzyme substrate OPD to generate a fluorescent product. It is first time for reporting that Cu-based MOFs with uniform and well-defined structural characterization have excellent catalytic fluorogenic activity. The effects of experimental parameters on this catalytic reaction were detailedly investigated. The catalytic kinetic investigations reveal that this catalytic fluorogenic reaction of Cu-BTC MOFs towards OPD as the substrate could be followed by traditional Michaelis-Menten equation. On the basis of these findings, and taken together with the fact that the -CHO group of formaldehyde can react with the -NH<sub>2</sub> group of OPD to form Schiff bases, a novel, highly selective and sensitive catalytic sensing platform was thus successfully developed for detecting gaseous formaldehyde. Several intriguing enlightenments could be summarized in this catalytic sensing system, for example, (i) it is helpful for developing novel catalysts with uniform and well-defined crystal structures to establish highly sensitive catalytic sensing systems; (ii) Cu-BTC MOFs with high specific surface area show high catalytic fluorogenic activity, similar to that of Cu<sup>2+</sup> ions; (iii) the structural diversity and alterability of ligands, and diverse

coordination models of Cu<sup>2+</sup> ions can endow Cu MOFs with a

great promise in the field of artificial enzymatic mimics,

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# **Conflicts of interest**

There are no conflicts to declare.

compared with that of Cu<sup>2+</sup> ions.

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