A multifunctional Ni(II) coordination polymer: synthesis, crystal structure and applications as luminescence sensor, electrochemical probe, and photocatalyst

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Scheme S1 Simplified photocatalytic reaction mechanism of dye solutions.

Table S1 The comparison about photocatalytic activities of CP 1 under different experimental conditions.

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Fig. S1 PXRD patterns of CP 1 ((a) for simulated from single-crystal X-ray data, (b) for as-synthesized bulk sample, (c) for CP 1 suspended in the water solution for 24 h, (d) for CP 1 in detecting Fe$^{3+}$ ions over five repeated cycles, (e) for CP 1 after the photocatalytic reactions).

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Fig. S3 (a) Coordination mode of the (TPA-Cl$_2$)$^{2-}$ anion; (b) 1D infinite chain
constructed by the (TPA-Cl₂)²⁻ anion; (c) Coordination mode of the 1,4-bib-1 ligand; (d) 1D zigzag chain constructed by the 1,4-bib-1 ligand; (e) Coordination mode of the 1,4-bib-2 ligand.

Fig. S4 Thermogravimetric (TG) analysis curve of CP 1.

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Fig. S6 (a) Comparation of the luminescent intensity of CP 1 in aqueous solution by gradual addition of different metal ions (10⁻⁴ M); (b) Luminescent intensity of CP 1 in aqueous solution by gradual addition of mixed metal ions (10⁻⁴ M); (c) Comparation of the luminescent intensity of CP 1 after five recycles; (d) Quenching efficiency CP 1 after five recycles; (e) UV-vis absorption spectra of different metal ions in aqueous solution and the excitation for CP 1.

Fig. S7 (a) Dependence of the reduction peak (I) and oxidation peak (I') on scan rates; (b) Dependence of the reduction peak (II) and oxidation peak (II') on scan rates; (c) Linearity relationship between the response current and the nitrite concentration at different potentials; (d) The reproducibility of six modified electrodes based on CP 1 towards 1.0 mM nitrite ions; (e) The repeatability of six modified electrodes based on CP 1 towards 1.0 mM nitrite ions; (f) The long-term stability of six modified electrodes based on CP 1 towards 1.0 mM nitrite ions.

Fig. S8 Absorption spectra of the MB solution during the catalytic reaction in a dark environment.

Fig. S9 (a) Absorption spectra of the MB solution during the photodegradation reaction for 0 mg CP 1 under 500 W UV light; (b) Absorption spectra of the MB solution during the photodegradation reaction for 10 mg CP 1 under 500 W UV light; (c) Absorption spectra of the MB solution during the photodegradation reaction for 20 mg CP 1 under 500 W UV light; (d) Absorption spectra of the MB solution during the photodegradation reaction for 30 mg CP 1 under 500 W UV light; (e) Absorption spectra of the MB solution during the photodegradation reaction for 50 mg CP 1 under 500 W UV light.

Fig. S10 (a) Comparation of the UV-vis absorption spectra of CP 1 after five recycles;
(b) Photocatalytic efficiency CP 1 after three recycles.
**S1 Luminescence quenching experiment**

The luminescent sensing measurements were collected by a Edinburgh FS5 spectrofluorometer at room temperature. The powder samples of CP 1 (4 mg) were suspended in 3.6 mL of water solution containing 0.4 mL of M(NO$_3$)$_x$ solution ($10^{-4}$ M) (M = Mg$^{2+}$, Ag$^+$, Na$^+$, Li$^+$, Cd$^{2+}$, Cu$^+$, Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Fe$^{3+}$, Ca$^{2+}$, Zn$^{2+}$, K$^+$, Mn$^{2+}$, Sn$^{2+}$ and Ba$^{2+}$, respectively) and then sonicated about 30 min. The mixtures were then used for luminescent sensing measurements.
S2 Electrochemical experiment

The electrochemical analysis was carried out using a CHI 660E electrochemical workstation (Chenhua Instrument, Shanghai, China). A conventional three-electrode system was used at room temperature. The CPs chemically bulk-modified carbon paste electrodes (1-CPE) were used as the working electrodes. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrodes, respectively. The 1-CPE was fabricated as follows: 0.5 g graphite powder and 0.04 g complex were mixed and ground together by agate mortar and pestle to achieve an even, dry mixture; and then 0.2 mL paraffin oil was added to the mixture and stirred with a glass rod. The homogenized mixture was used to pack a 3 mm inner diameter PTFE tube to a length of 1 cm, and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode. The same procedure was used for the preparation of the bare CPE.
S3 Photocatalytic experiment

The photocatalytic performance of CP 1 was investigated for the degradation of different dyes (MB, RhB, and MO) through a typical process as follows: different amount of crystal sample of each title coordination polymer (0 mg, 10 mg, 20 mg, 30 mg, 40 mg and 50 mg) was mixed with 100 mL of dye solution (10 mg/L). The mixture was magnetically stirred for half an hour in a dark environment to get a uniform working solution. Then a high-pressure mercury lamp (300 W or 500 W) was used as the UV light source to irradiate the above solution, which was continuously stirred during the photodegradation. Aliquots (3.5 mL) of the suspension were taken at given time intervals, separated through centrifugation and then subsequently analyzed by using a UV-visible spectrometer at a specific wavelength. In addition, the control experiment for MB photodegradation was also performed under the same condition without any catalyst. The stability of the CPs after the photocatalytic process has been tested by PXRD.
Scheme S1 Simplified photocatalytic reaction mechanism of dye solutions.
**Table S1** The comparison about photocatalytic activities of CP 1 under different experimental conditions.

<table>
<thead>
<tr>
<th>Dye</th>
<th>The power of UV light (W)</th>
<th>The amount of photocatalysts (mg)</th>
<th>The photocatalytic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>500</td>
<td>0</td>
<td>8.8</td>
</tr>
<tr>
<td>MB</td>
<td>500</td>
<td>10</td>
<td>72.4</td>
</tr>
<tr>
<td>MB</td>
<td>500</td>
<td>20</td>
<td>76.8</td>
</tr>
<tr>
<td>MB</td>
<td>500</td>
<td>30</td>
<td>83.6</td>
</tr>
<tr>
<td>MB</td>
<td>500</td>
<td>40</td>
<td>92.1</td>
</tr>
<tr>
<td>MB</td>
<td>500</td>
<td>50</td>
<td>88.2</td>
</tr>
<tr>
<td>MB</td>
<td>300</td>
<td>40</td>
<td>74.3</td>
</tr>
<tr>
<td>MB</td>
<td>0</td>
<td>40</td>
<td>4.0</td>
</tr>
<tr>
<td>RhB</td>
<td>500</td>
<td>40</td>
<td>85.7</td>
</tr>
<tr>
<td>MO</td>
<td>500</td>
<td>40</td>
<td>86.2</td>
</tr>
</tbody>
</table>
Table S2 The comparison about the structures and photocatalytic properties between CP 1 and the related previous reported MOFs.

<table>
<thead>
<tr>
<th>The related CPs</th>
<th>Crystal structure</th>
<th>Topology</th>
<th>Dye</th>
<th>The photocatalytic efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>{Ni(1,4-bib)1.5(TPA-Cl2)·H2O}n (1)</td>
<td>Three-fold interpenetration 3D framework</td>
<td>sqc12</td>
<td>MB</td>
<td>92.1 in 120 min</td>
<td>This work</td>
</tr>
<tr>
<td>{[Ni(tptc)0.5(1,3-bimb)]·H2O}n (2)</td>
<td>2D layer</td>
<td>kgm</td>
<td>MB</td>
<td>66.8 in 120 min</td>
<td>27</td>
</tr>
<tr>
<td>{[Ni(H2L)(bip)(H2O)·0.5H2O]n (3)</td>
<td>2D layer</td>
<td></td>
<td>MB</td>
<td>100 in 120 min</td>
<td>28</td>
</tr>
<tr>
<td>[Ni(dpdb)(bimb)(H2O)]n (4)</td>
<td>2D layer</td>
<td></td>
<td>MB</td>
<td>88.1 in 90 min</td>
<td>105</td>
</tr>
<tr>
<td>{[Ni2(bib)(adc)2]·0.5H2O}n (5)</td>
<td>1D chain</td>
<td>Not provided</td>
<td>MO</td>
<td>No obvious photocatalytic activity</td>
<td>106</td>
</tr>
<tr>
<td>[Ni(bib)(hip)]n (6)</td>
<td>2D layer</td>
<td>Not provided</td>
<td>MO</td>
<td>No obvious photocatalytic activity</td>
<td>106</td>
</tr>
<tr>
<td>[Ni(L)1.5(2-CMSN)(H2O)·2H2O (7)</td>
<td>1D chain</td>
<td>Not provided</td>
<td>MB</td>
<td>20.0 in 180 min</td>
<td>107</td>
</tr>
<tr>
<td>[Ni(2-CMSN)(biim-4)0.5(H2O)2 ] (8)</td>
<td>2D layer</td>
<td>Not provided</td>
<td>MB</td>
<td>No obvious photocatalytic activity</td>
<td>108</td>
</tr>
<tr>
<td>[Ni(bix)2][VW12O40]·(H2bix)·H2O (9)</td>
<td>3D framework</td>
<td>Not provided</td>
<td>RhB</td>
<td>86.7 in 7 h</td>
<td>109</td>
</tr>
</tbody>
</table>

For CP 1: 1,4-bib = 1,4-bis(1H-imidazol-1-yl)benzene, H2TPA-Cl2 = 2,5-dichloro-terephthalic acid;
For CP 2: 1,3-bimb = 1,3-bis(imidazol-1-ylmethyl)benzene, Hatptc =
terphenyl-3,3”,5,5”-tetracarboxylic acid;
For CP 3: bibp = 4,4′-bis(imidazolyl)biphenyl, H₄L = 5,5’-(1,3-phenylenebis(methoxy))diisophthalic acid;
For CP 4: bimb = 1,4-bis(imidazol-1-ylmethyl)benzene, H₂dpb = 3,5-di(4’-carboxyl-phenyl)benzene acid;
For CP 5: bib = 1,4-bis(2-methyl-imidazol-1-yl)butane, adc = 1,3-adamantanedicarboxylate;
For CP 6: bib = 1,4-bis(2-methyl-imidazol-1-yl)butane, hip = 5-hydroxyisophthalate;
For CP 7: L = 1,4-bis(imidazol-1-ylmethyl)benzene, 2-H₂CMSN = 2-carboxymethylsulfanyl nicotinic acid;
For CP 8: biim-4 = 1,1’-(1,4-butanediyl)bis(imidazole), 2-H₂CMSN = 2-carboxymethylsulfanyl nicotinic acid;
For CP 9: bix = 1,4-bis(imidazol-1-ylmethyl)-benzene.
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(a)

(b)
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