

# p-Type Dopant-Mediated Electron–Hole Recombineering to Tune the Electrochemiluminescence of Metal–Organic Frameworks

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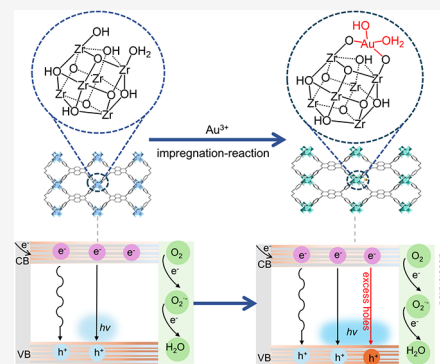


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**ABSTRACT:** Constructing high-performance electrochemiluminescence (ECL) emitters through rational structural engineering is pivotal to overcoming the intrinsic limitations of conventional systems and advancing their practical applications. This work reports an electron–hole recombination engineering strategy to enhance the ECL emission of metal–organic frameworks (MOFs) by p-type doping of metal single-atom sites. Using Zr-TBAPy as a model, the experimental data and theoretical calculations demonstrate that the doping of single-atom Au induces notable defect energy levels, thereby providing additional recombination channels for conduction-band (CB) electrons and valence-band (VB) holes. The defect level ultimately increases the electron–hole recombination efficiency. Compared to Zr-TBAPy, single-atom Au-doped Zr-TBAPy (Au@Zr-TBAPy) exhibits a 4-fold enhancement in cathodic ECL intensity with an ECL efficiency of up to 50.56%. An ECL immunoassay was used to demonstrate the ECL application of Au@Zr-TBAPy. This work not only proposes a rational metal single-atom doping strategy for engineering ECL emitters to achieve high performance but also provides fundamental insights into the dependence of ECL emission on metal single-atom sites, opening new avenues for advanced applications of MOFs in sensitive ECL biosensing.



## INTRODUCTION

Electrochemiluminescence (ECL) detection possesses low background, high sensitivity, and a wide detectable range of concentrations and has extensively been used for detecting low-abundance analytes.<sup>1–3</sup> Undoubtedly, the intrinsic performance of ECL luminophores is a foundational determinant of the sensitivity, reliability, and overall efficiency of ECL detection platforms.<sup>4,5</sup> Considerable efforts have been made to improve ECL emission by redistributing excess charge,<sup>6</sup> combining double-layered ECL luminophores with nanozymes,<sup>7</sup> or incorporating coreactant accelerators,<sup>8</sup> which realize relatively high ECL intensity and thus facilitate the development of ECL detection technology. Among these studies, the formation and subsequent recombination of conduction-band (CB) electrons with valence-band (VB) holes in semiconductor nanocrystals constitute the core mechanistic basis for ECL emission.<sup>6,9–11</sup> By molecular capacitance mediation, a spatiotemporally coordinated strategy has been proposed to facilitate electron accumulation for enhancing ECL efficiency.<sup>12</sup> This unique structure significantly increases the probability of electron–hole radiative recombination by modulating the electron distribution in bulk cyanogen nitride. The primary strategies for increasing electron–hole recombination efficiency ( $\eta_{re}$ ) involve tuning the electronic structure and surface defect states of the phosphor through precise engineering of the material structure.<sup>13–15</sup> However, these strategies commonly suffer from high costs and uncontrollable preparation processes,<sup>16,17</sup> while establishing precise depend-

ence of performance on the structure at the atomic level still remains a formidable challenge. Thus, developing a facile and controllable strategy to modulate the electronic structure of luminophores for enhancing the recombination of electron–hole pairs is of paramount importance in achieving high-performance ECL emission.

Metal–organic frameworks (MOFs), an emerging class of materials with ordered and tunable pores,<sup>18</sup> molecularly designable compositions,<sup>19</sup> and easily functionalized channels,<sup>20</sup> have been extensively synthesized for the construction of ECL emitters.<sup>21–24</sup> Although substantial efforts have been devoted to enhancing the ECL performance of MOFs,<sup>25–27</sup> the practical applications of MOF materials in ECL biosensing are severely constrained by their intrinsically poor electrical conductivity and low ECL intensity. To meet the demands of sensitive ECL detection, some coreactant promoters,<sup>28,29</sup> single-atom catalysts,<sup>30,31</sup> and electron traps<sup>32</sup> have been introduced into ECL systems to enhance the emission through accelerating the electron transfer, activating peroxydisulfate,<sup>31</sup> or regulating the electronic structure for accelerating electron–

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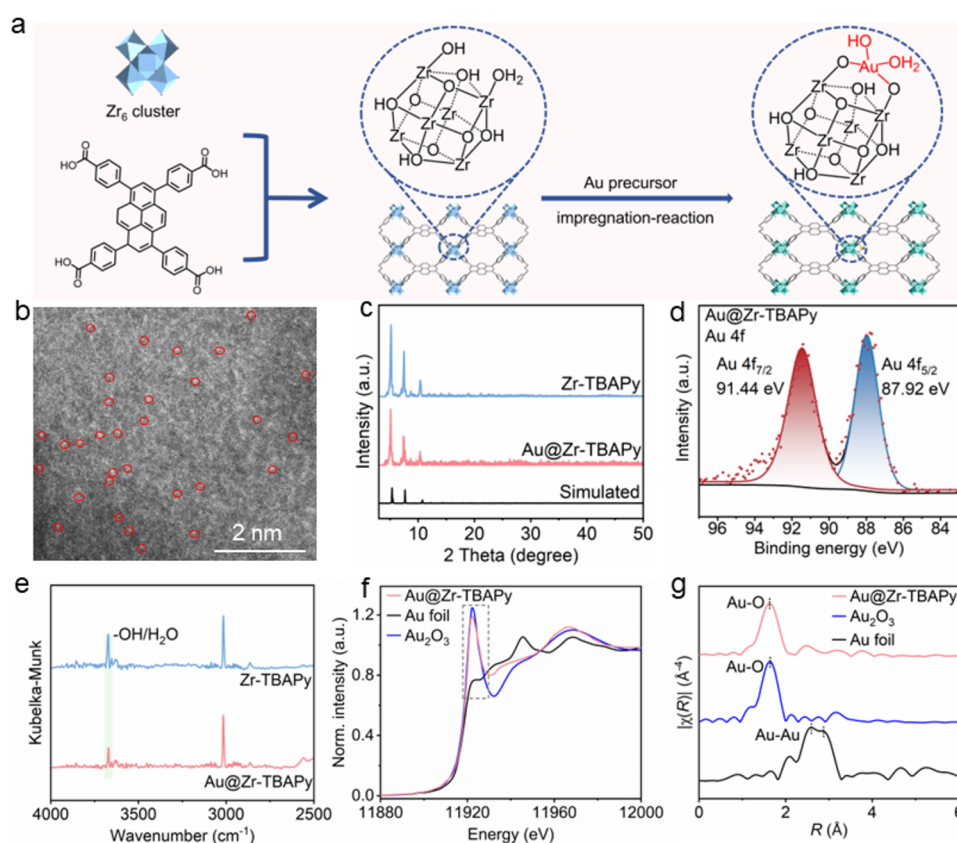


**Figure 1.** (a) Schematic illustration of Au@Zr-TBAPy synthesis. (b) Aberration-corrected high-angle annular dark-field TEM image of Au@Zr-TBAPy. (c) Powder X-ray diffraction (PXRD) patterns of Zr-TBAPy, Au@Zr-TBAPy, and simulated Zr-TBAPy. (d) Au 4f X-ray photoelectron spectra of Au@Zr-TBAPy. (e) Diffuse reflectance infrared Fourier transform spectra (DRIFTS) of Zr-TBAPy and Au@Zr-TBAPy. (f) X-ray absorption near-edge structure (XANES) spectra at the Au L<sub>3</sub>-edge of Au@Zr-TBAPy with Au foil and Au<sub>2</sub>O<sub>3</sub> as references. (g) *k*<sup>2</sup>-weighted Au L<sub>3</sub>-edge Fourier transform extended X-ray absorption fine structure (FT-EXAFS) spectra of the Au foil, Au<sub>2</sub>O<sub>3</sub>, and Au@Zr-TBAPy at the R-space.

hole recombination.<sup>32</sup> However, to date, both single-atom catalysts and the electron trap strategy have not been used to enhance the ECL of MOF materials; moreover, these systems need endogenous coreactants to trigger the ECL emission. Inspired by the structure modulation for boosting the  $\eta_{\text{re}}$  and ECL efficiency ( $\Phi_{\text{ECL}}$ ), this work designs an electron–hole recombineering strategy of MOFs to enhance their ECL emission through convenient p-type doping of single metal atoms in the MOF structure, which has been considered an effective strategy to enhance hole concentration and mobility<sup>33</sup> and modulate charge transfer dynamics and optical emission characteristics.<sup>34</sup>

Here, the p-type doping was performed via precisely anchoring single-atom Au at the Zr-oxo nodes of Zr-based MOFs with 1,3,6,8-tetra(4-carboxylphenyl) pyrene (TBAPy) as a ligand (Figure 1a). The prepared Au@Zr-TBAPy exhibited uniform distribution of Au species in the porous architecture of the MOF. The strong interaction between single-atom Au and TBAPy achieved the regulation of the electronic structure of Zr-TBAPy via the induced defect energy level, which provided additional recombination channels for CB electrons and VB holes, and thus led to 4-fold enhancement of the ECL intensity. In particular, the p-doping increased the  $\eta_{\text{re}}$  from 19.8% for Zr-TBAPy to 48.6% for Au@Zr-TBAPy and demonstrated an excellent cathodic ECL performance in the presence of dissolved oxygen as a coreactant. As a proof of concept, a sensitive immunosensing method was proposed for the detection of carcinoembryonic

antigen (CEA) down to 0.005 ng mL<sup>−1</sup> without any signal amplification. Therefore, the p-type dopant-mediated electron–hole recombineering strategy provides a new paradigm for boosting the ECL emission and advances the analytical applications of MOF-based ECL emitters.

## EXPERIMENTAL SECTION

### Synthesis of Zr-TBAPy

The synthesis of Zr-TBAPy was performed with a previously reported method.<sup>1</sup> Briefly, 1.50 mmol ZrOCl<sub>2</sub>·8H<sub>2</sub>O and 66 mmol BA were dissolved in 40 mL of DMF as solution A. 0.15 mmol TBAPy was dissolved in 40 mL of DMF as solution B. After solution A was poured into solution B, 10  $\mu$ L of TFA was added, and the mixture was placed into an oven at 100 °C for 1 h. After cooling to room temperature, the suspension was isolated by centrifugation at 10,000 rpm for 5 min. The product was washed thrice with DMF, twice with acetone, and vacuum-dried at 60 °C overnight.

### Synthesis of Au@Zr-TBAPy

Au@Zr-TBAPy was prepared with an impregnation method.<sup>2</sup> 10 mg of Zr-TBAPy was added to 9 mL of DMF solution containing 5 mg of AuCl<sub>3</sub> with sonication for 20 min. After heating in an isothermal oven at 85 °C for 24 h, the product was collected by centrifugation at 8000 rpm for 5 min. It was then washed three times with DMF (30 mL) and once with EtOH (30 mL), followed by vacuum drying at 60 °C overnight.

### Preparation of the Zr-TBAPy-MOF-Ab<sub>2</sub> Bioconjugate

After 1 mg of Zr-TBAPy-MOF, 10 mg of EDC, and 10 mg of NHS were successively added in 1 mL of PBS (pH 6.0), the obtained

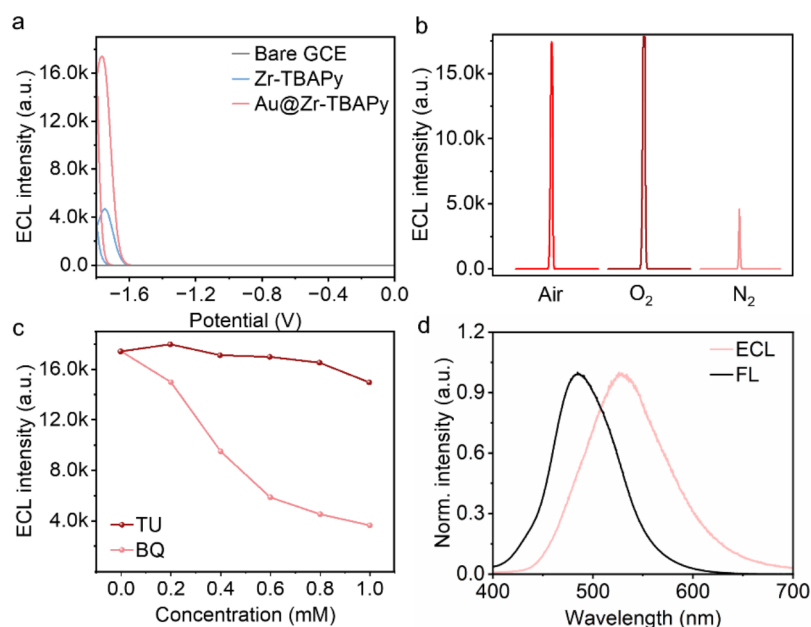


**Figure 2.** (a) ECL–potential curves of the bare GCE and Zr-TBAPy- and Au@Zr-TBAPy-modified GCEs in 0.1 M PBS (pH 7.4) containing 0.1 M KNO<sub>3</sub>. (b) Effect of dissolved O<sub>2</sub> on ECL intensity. (c) Effect of benzoquinone (BQ) and thiourea (TU) as radical scavengers on ECL intensity. Scan rate: 100 mV s<sup>−1</sup>, PMT: 500 V. (d) ECL spectrum of the Au@Zr-TBAPy-modified GCE and fluorescence (FL) spectrum of Au@Zr-TBAPy in H<sub>2</sub>O.

mixture was stirred for 30 min and subjected to centrifugation at 10,000 rpm for 5 min. The harvested product was repeatedly rinsed with 1 mL of PBS (pH 7.4). Afterward, the product was resuspended in 1 mL of PBS (pH 7.4) supplemented with 100  $\mu$ L of Ab<sub>2</sub> (1 mg mL<sup>−1</sup>) to stir at 37 °C for 30 min, which formed Au@Zr-TBAPy-Ab<sub>2</sub> bioconjugates. To prevent nonspecific binding, 100  $\mu$ L of 3% BSA solution was added to the mixture and stirred for 1 h. After centrifugation and dispersion, the resulting Au@Zr-TBAPy-Ab<sub>2</sub> was stored at 4 °C for subsequent applications.

### ECL Immunosensing

ECL immunosensing was performed with a typical sandwich immunoassay procedure using Au@Zr-TBAPy as a tag. Specifically, the glassy carbon electrode (GCE) was first electrodeposited with a layer of Au nanoparticles (AuNPs) by holding a freshly polished GCE at −0.3 V for 50 s in 0.1 M phosphate buffer solution (PBS, pH 7.4) containing 6 mM HAuCl<sub>4</sub> and 0.1 M KCl to form AuNPs/GCE. The AuNPs/GCE was then incubated with 10  $\mu$ L of 18  $\mu$ g mL<sup>−1</sup> carcinoembryonic antigen (CEA) capture antibody (Ab<sub>1</sub>) at 4 °C for 12 h to form Ab<sub>1</sub>/AuNPs/GCE by Au–S bonding. After removing physically absorbed Ab<sub>1</sub> by washing with PBS and blocking with a drop of 10  $\mu$ L of 3% BSA solution at 37 °C for 1 h, the immunosensor was obtained for the ECL immunoassay of CEA, which was performed by incubating the immunosensor with the CEA sample at 37 °C for 2 h and then 10  $\mu$ L of Au@Zr-TBAPy-Ab<sub>2</sub> conjugate at 37 °C for 2 h to measure the ECL signal in 0.1 M PBS (pH 7.4) containing 0.1 M KNO<sub>3</sub>.

## RESULTS AND DISCUSSION

### Synthesis and Structural Characterization of Au@Zr-TBAPy

Zr-TBAPy was first synthesized as a MOF model.<sup>35</sup> The thermogravimetric (TGA) analysis (Figure S1) disclosed its defects at the Zr-oxo nodes due to the lack of ligands. The Fourier transform infrared (FT-IR) spectrum indicated the presence of abundant −OH groups (Figure S2), which endowed the MOF structure with inherent capability to anchor exogenous metal ions.<sup>36,37</sup> Therefore, Au@Zr-TBAPy could be prepared via an impregnation method,<sup>38</sup> which led to

a relatively reducing FT-IR absorption of −OH groups (Figure S2). Both Au@Zr-TBAPy and Zr-TBAPy shared similar morphologies with a uniform rough-textured elliptical structure and the absence of nanoparticles and nanoclusters (Figures S3 and S4), indicating that the Au element was present as isolated atoms or tiny clusters, which led to the single bright dots of Au@Zr-TBAPy (Figure 1b). The energy dispersive spectra (EDS) of Zr-TBAPy and Au@Zr-TBAPy confirmed the uniform distribution of Au, Zr, O, and C elements (Figure S5). Their powder X-ray diffraction (PXRD) spectra showed the same 2 $\theta$  at 5.3, 7.7, and 10.7°, which were assigned to Zr-TBAPy (CCDC deposition number: 2088773), indicating the absence of Au oxides or nanoparticles (Figure 1c). The loading of the Au element in Au@Zr-TBAPy was measured with inductively coupled plasma-optical emission spectroscopy to be 1.77 wt %.

The X-ray photoelectron spectroscopic (XPS) survey spectra further confirmed the existence of the Au element in Au@Zr-TBAPy, which showed a weak peak attributed to Au 4f (Figure S6), split into two signals at ~87.92 and ~91.44 eV (Figure 1d), corresponding to the binding energies of Au 4f<sub>7/2</sub> and 4f<sub>5/2</sub> for Au<sup>3+</sup>, respectively.<sup>39</sup> The high-resolution XPS spectra of O 1s, C 1s, and Zr 3d (Figure S7) along with FT-IR (Figure S1) and UV–vis absorption spectra (Figure S8) illustrated that the doping of single-atom Au caused negligible disruption to the Zr-TBAPy. However, the diffuse reflectance infrared Fourier transform spectra (DRIFTS) exhibited an apparent decrease of peak intensity at 3670 cm<sup>−1</sup> upon doping (Figure 1e), which was attributed to the endmost −OH/OH<sub>2</sub> at Zr-oxo nodes, indicating that single-atom Au was precisely anchored to the −OH/H<sub>2</sub>O groups through covalent bonding rather than electrostatic attraction.<sup>40,41</sup>

The energy absorption intensity of Au@Zr-TBAPy was closer to that of Au<sub>2</sub>O<sub>3</sub> but much higher than that of the Au foil (Figure 1f), suggesting the presence of highly oxidized Au species, consistent with the XPS result (Figure 1d). This result

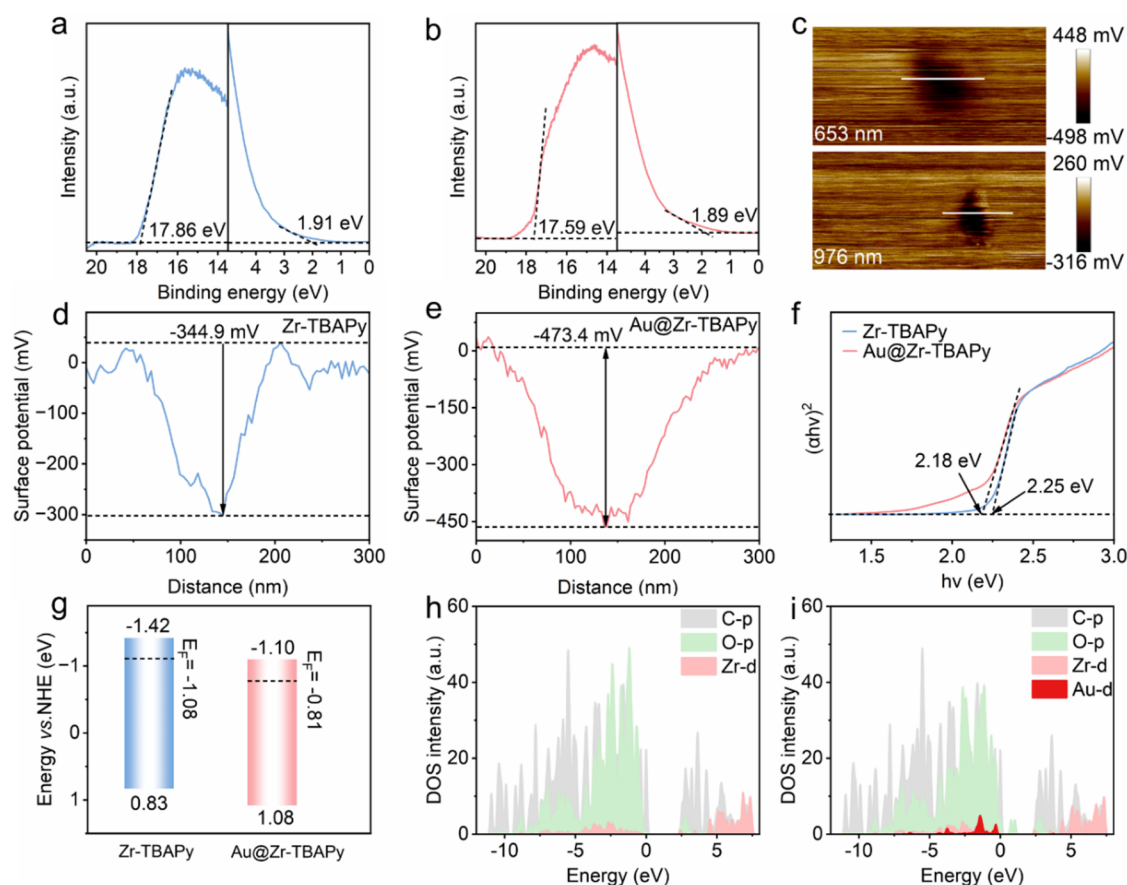


**Figure 3.** Magnified view of UPS spectra of (a) Zr-TBAPy and (b) Au@Zr-TBAPy at a bias of  $-5.0$  eV. (c) KPFM potential images of Zr-TBAPy (bottom) and Au@Zr-TBAPy (top). (d, e) Corresponding surface potential curves along the white lines in (c). (f) Tauc plots of Zr-TBAPy and Au@Zr-TBAPy at room temperature in air. (g) Band structure alignments. (h, i) Density of states (DOS) for Zr-TBAPy (h) and Au@Zr-TBAPy (i).

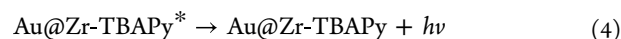
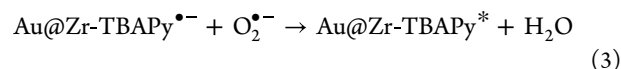
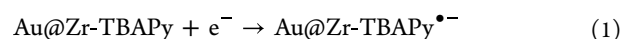
was also confirmed by the difference of their Fourier transform extended X-ray absorption fine structure (FT-EXAFS) fitting curves (Figure S9) and wavelet transform (WT) plots (Figure S10), which demonstrated a prominent peak of the Au–O band at  $1.63$  Å (Figure 1g) with a bond distance of  $\sim 2.00$  Å, shorter than the Au–Au distance in the Au foil (Figure S11 and Table S1). The coordination number of Au in Au@Zr-TBAPy was determined to be  $\sim 4.1$ , significantly lower than the value of 12 in the Au foil. Moreover, the WT profile of Au@Zr-TBAPy did not show a discernible signal attributable to the Au–Au interaction as observed from  $\text{Au}_2\text{O}_3$  and the Au foil (Figure S10), indicating the high dispersion of Au atoms.

### ECL Behaviors of Au@Zr-TBAPy

The Zr-TBAPy-modified glassy carbon electrode (GCE) showed a weak reduction peak of dissolved oxygen at  $-0.58$  V and a cathodic peak around  $-1.70$  V in  $0.1$  M PBS (pH 7.4) (Figure S12). The latter could be assigned to the reduction of pyrene moieties.<sup>42</sup> Upon single-atom Au doping, these peaks increased and became more obvious (Figures S12 and S13), indicating its promotion to the reduction processes, which also resulted in the decrease of electron transfer resistance ( $R_{ct}$ ) (Figure S14) and increased the ECL response by about 4-fold (Figure 2a).

To verify the ECL mechanism, the solution was bubbled with  $\text{N}_2$ , air, and oxygen, which showed the dependence of ECL intensity on dissolved oxygen concentration (Figure 2b), demonstrating the role of dissolved oxygen as a coreactant.

The ECL intensity of Au@Zr-TBAPy retained approximately 92.2% of its initial value after storage at  $4^\circ\text{C}$  for 10 days, demonstrating satisfactory long-term stability (Figure S15). The reduction of dissolved oxygen typically involves the generation of reactive oxygen species (ROS), including hydroxyl radicals ( $\text{OH}^\bullet$ ), superoxide radicals ( $\text{O}_2^{\bullet-}$ ), and other radical derivatives, which can serve as key intermediates in accounting for the luminescent phenomenon. To confirm the ROS intermediates in the ECL process, benzoquinone (BQ) as an  $\text{O}_2^{\bullet-}$  scavenger or thiourea (TU) as an  $\text{OH}^\bullet$  scavenger was added in this system, which induced a quick decrease of ECL intensity upon addition of BQ (Figure 2c), while the addition of TU exerted a much less impact, indicating that the  $\text{O}_2^{\bullet-}$  was the active intermediate to generate the ECL emission. The possible ECL mechanism of Au@Zr-TBAPy is described by eqs 1–4. The TBAPy unit was electrochemically reduced to form the Au@Zr-TBAPy $^{\bullet-}$  species, which was then oxidized by  $\text{O}_2^{\bullet-}$  to form the excited state of Au@Zr-TBAPy\* for ECL emission.



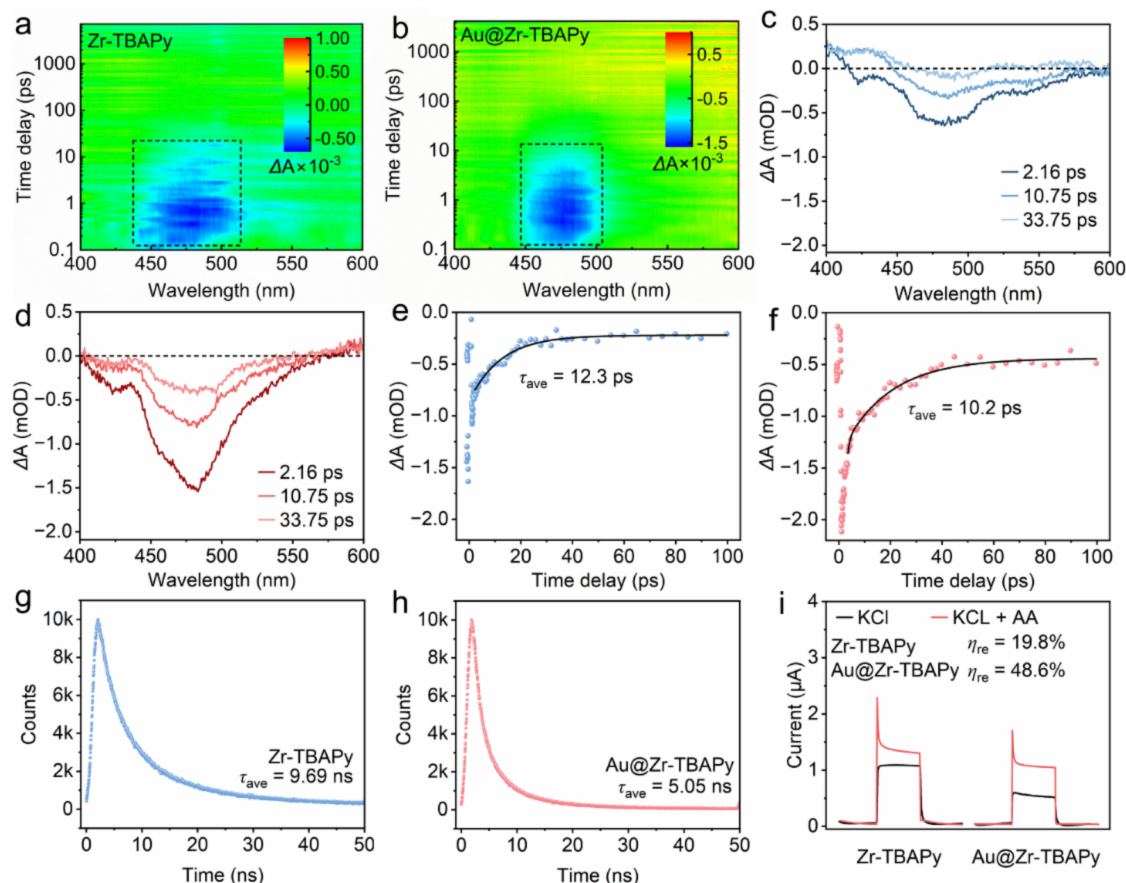


**Figure 4.** (a, b) Pseudocolor plots and (c, d) transient absorption spectra of Zr-TBAPy (a, c) and Au@Zr-TBAPy (b, d). (e, f) Representative ultrafast transient absorption kinetics at 480 nm and (g, h) time-resolved fluorescence spectra for Zr-TBAPy (e, g) and Au@Zr-TBAPy (f, h). (i) Transient photocurrent responses of Zr-TBAPy and Au@Zr-TBAPy in 0.1 M PBS containing 0.1 M KCl with and without 0.1 M AA at an applied potential of  $-0.3$  V.

Interestingly, the ECL intensity of the Au-doped MOF system showed a positive correlation with the metal content within a specific range, beyond which the content of Au species compromised the material performance (Figure S16), further supporting the promotion of single-atom Au. The ECL spectrum of Au@Zr-TBAPy showed a peak at approximately 530 nm, a significant red shift from its fluorescence (FL) peak at 484 nm (Figure 2d), indicating a typical surface state transition mechanism.<sup>43,44</sup> Furthermore, the FL emission of Au@Zr-TBAPy also showed a red shift compared to the 462 nm of Zr-TBAPy, along with greater emission intensity (Figure S17), indicating that the doping of single-atom Au facilitated the charge transfer and radiative recombination during the ECL process.<sup>45,46</sup> The weaker electron paramagnetic resonance (EPR) signal of Au@Zr-TBAPy further confirmed the facilitated recombination (Figure S18). From the ECL spectra and current–time curves (Figure S19), the  $\Phi_{ECL}$  of Zr-TBAPy and Au@Zr-TBAPy vs  $[Ru(bpy)_3]^{2+}$  was calculated to be 23.95 and 50.56%, respectively (Table S2).

#### Single-Atom Au-Induced p-Type Doping

To elucidate the origins of rapid electron transfer and radiative recombination, the electronic properties were examined with ultraviolet photoelectron spectroscopy (UPS), which showed a decreased VB edge of Au@Zr-TBAPy from 1.91 eV for Zr-TBAPy to 1.89 eV, while its work function ( $W_F$ ) increased from 3.36 eV for Zr-TBAPy to 3.63 eV (Figure 3a,3b), consistent with the expected p-type doping behavior.<sup>47,48</sup> This

result was consistent with the lower surface potential of Au@Zr-TBAPy, obtained from the Kelvin-probe force microscopy (KPFM) data (Figures 3c–e and S20). Typically, p-type doping increases the hole concentration in semiconductors by withdrawing electrons from the VB.<sup>49</sup> The electronic states in the low-binding energy region further confirmed the extraction of VB electrons (Figure S21). Au@Zr-TBAPy exhibited a lower UPS intensity than that of Zr-TBAPy within the low-binding energy regime (marked with a black circle), implying a diminished number of states near the valence band maximum (VBM) upon single-atom Au doping, which indicated that charge transfer occurred via electron extraction from the VBM of Au@Zr-TBAPy. The optical band gaps of 2.25 and 2.18 eV for Zr-TBAPy and Au@Zr-TBAPy (Figure 3f), respectively, suggested the regulation of Au doping on the energy level structure, from which the energy diagrams of Zr-TBAPy and Au@Zr-TBAPy are depicted in Figure 3g, and the band structures are listed in Table S3, revealing that single-atom Au doping effectively shifted the Fermi level ( $E_F$ ) toward the VBM and increased the hole concentration in Au@Zr-TBAPy.<sup>50</sup> Negative Hall coefficients ( $R_{Hh}$ , Table S4) and positive slopes of Mott–Schottky plots (Figure S22) collectively demonstrated that Zr-TBAPy and Au@Zr-TBAPy possessed n-type semiconducting properties, suggesting that the electrons served as the predominant carriers. Excess holes provided additional recombination channels, thereby increasing the probability of electron–hole recombination.

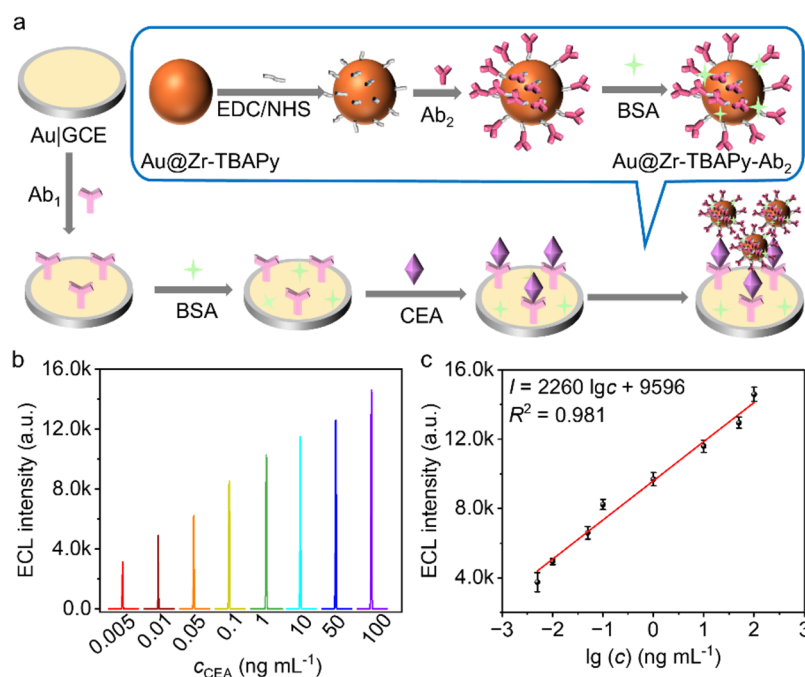


**Figure 5.** (a) Schematic diagram of immunosensor preparation for CEA detection. (b) ECL responses to 0.005, 0.01, 0.05, 0.1, 1.0, 10, 50, and 100  $ng\ mL^{-1}$  CEA in 0.1 M PBS containing 0.1 M  $KNO_3$ . (c) Corresponding calibration curve.

Density functional theory (DFT) calculations were conducted to probe the effect of single-atom Au on the hole concentration of Au@Zr-TBAPy. Models were constructed from the periodic framework of the MOF with appropriate modification and subsequently subjected to DFT-based energy optimization (Figure S23). The density of states (DOS) for Zr-TBAPy and Au@Zr-TBAPy is shown in Figure 3h,i. The VBM of Zr-TBAPy was primarily constructed from C 2p and O 2p orbitals, while the conduction band minimum (CBM) mainly originated from O 2p, C 2p, and Zr 3d orbitals. A similar DOS of the CBM was observed in Au@Zr-TBAPy, with negligible contribution from the Au 5d orbital, while the Au 5d, O 2p, and Zr 3d orbitals collectively formed the VBM. Surprisingly, a notable defect energy level from the O 2p orbital of Au@Zr-TBAPy was observed, which was generated by p-type doping and served as a critical mediator for enhancing hole concentration. More specifically, single-atom Au anchored at Zr-oxo nodes influenced the electronic structure of the O atoms, creating a new defect level and thereby potentially enhancing the surface hole concentration. Fewer available states in the DOS near the VBM of Au@Zr-TBAPy, in conjunction with more states approaching the VBM of the localized defect energy level around +0.85 eV (relative to the  $E_F$ ) of Au@Zr-TBAPy, provided compelling support for hole concentration enhancement.<sup>51</sup>

### Enhancement of Electron–Hole Recombination Efficiency

Excess hole concentration induced by p-type doping enhanced electron–hole recombination channels.<sup>49,52</sup> As a critical factor governing the ECL response,  $\eta_{re}$  of Au@Zr-TBAPy was assessed via femtosecond transient absorption spectroscopy (fs-TAS), time-resolved FL, and photoelectrochemical (PEC) measurements. The negative signal in the 450–500 nm range (Figure 4a,b) originated from electron–hole recombination.<sup>53</sup> Single-atom Au doping resulted in a drastic enhancement of the negative signal in the same wavelength range (Figure S24), suggesting that excess holes in Au@Zr-TBAPy boosted the  $\eta_{re}$ .

Both Au@Zr-TBAPy and Zr-TBAPy manifested broad negative absorption signals at 480 nm at different delay times (Figure 4c,d), corresponding to the ground-state bleaching, as observed from their UV–vis absorption spectra (Figure S8). Single-atom Au led to an obvious enhancement of the negative absorption signal, confirming the  $\eta_{re}$  increase of Au@Zr-TBAPy. To quantify the recombination efficiency of photoinduced electron–hole pairs, a two-exponential function was employed to analyze the time profiles of the TAS signal monitored at 480 nm under light irradiation (Figure 4e,f). Au@Zr-TBAPy exhibited an electron–hole recombination lifetime of 10.2 ps, which was shorter than that of 12.3 ps for Zr-TBAPy. This observation was consistent with its higher FL intensity, indicating faster electron–hole recombination. The FL decay lifetimes of Zr-TBAPy and Au@Zr-TBAPy were determined as 9.69 and 5.05 ns, respectively (Figure 4g,h and Table S5). Compared to the approximately 7-fold increase in FL intensity (Figure S17), the FL lifetime shortened by only 48%, which was obviously inconsistent with the defect passivation mechanism with decreasing nonradiative recombination rate.<sup>54</sup> The  $\eta_{re}$  calculated from the transient photocurrent responses increased from 19.8% for Zr-TBAPy to 48.6% for Au@Zr-TBAPy (Figure 4i). Therefore, engineering electronic structures with single-atom Au to induce the p-type doping effect and thereby construct additional electron–hole recombination channels is a promising strategy for the rational design of high-performance ECL materials and devices.

### Biosensing with the Engineered MOF

To demonstrate the practical application of Au@Zr-TBAPy, an ECL immunoassay method was proposed using CEA as a model analyte and Au@Zr-TBAPy as a labeling tag (Figure 5a). Upon layer-by-layer modification, the electron transfer resistance of the resulting electrode in 0.1 M KCl containing 5 mM  $K_3Fe(CN)_6/K_4Fe(CN)_6$  (1:1) gradually increased from 75.3  $\Omega$  for the bare GCE to 58.4  $\Omega$  for Au|GCE, 637.5  $\Omega$  for Ab1|Au|GCE, 871.4  $\Omega$  for the CEA immunosensor, 1053  $\Omega$  for

CEA-Ab1|AulGCE, and  $1403\ \Omega$  for Au@Zr-TBAPy-MOF-Ab2-CEA-Ab1|AulGCE (Figure S25). The sandwich-type immunoassay was demonstrated by the increasing  $R_{ct}$ . Under the optimal conditions (Figure S26), the ECL intensity increased with the increasing concentration of CEA from 0.005 to  $100\ \text{ng mL}^{-1}$  and a detection limit of  $1.6\ \text{pg mL}^{-1}$  (Figure 5b). The plot of ECL intensity vs the logarithm of CEA concentration exhibited favorable linearity (Figure 5c). The constructed immunosensor was comparable with previous reports (Table S6). This method showed excellent specificity (Figure S27). Thus, the p-type dopant-mediated electron–hole recombining advanced the ECL application of MOFs in sensitive biosensing.

## CONCLUSIONS

In conclusion, we have demonstrated the precise anchoring of highly dispersed single-atom Au at Zr-oxo nodes of Zr-based MOFs to modulate the electronic structure, which achieves electron–hole recombination engineering via p-type doping of single metal atoms in the MOF structure for significantly enhancing the ECL performance. The doping of single-atom Au not only facilitates the charge transfer but also induces a notable defect energy level and increased hole concentration to provide additional channels for radiative recombination of CB electrons and VB holes, which increases the  $\eta_{re}$  from 19.8 to 48.6%, enhances the ECL response by about 4-fold, and boosts the  $\Phi_{ECL}$  from 23.95 to 50.56%. The practical application of Au@Zr-TBAPy as a sensitive ECL-labeling tag has also been demonstrated. The proposed metal single-atom doping strategy establishes a generalizable paradigm for the functional regulation of metal-modified luminescent nanomaterials and holds great promise in interdisciplinary fields, including optoelectronic devices, clinical diagnosis, and bioimaging.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.6c03746>.

Materials and reagents, apparatus, ECL and PEC measurements, calculation of relative ECL efficiency and LOD, and computation details (Figures S1–S27 and Tables S1–S7) (PDF)

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## Notes

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