Title: Electron Donor Coordinated Metal-Organic Framework to Enhance Photoelectrochemical Performance

Authors: Weisu Kong, Da Zhu, Yong Zhang, Rengan Luo, Jing Ma, Jianping Lei, and Huangxian Ju

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 2023, e202308514

Link to VoR: https://doi.org/10.1002/anie.202308514
COMMUNICATION

Electron Donor Coordinated Metal-Organic Framework to Enhance Photoelectrochemical Performance


Abstract: To enhance photoelectrochemical (PEC) performance, additional electron donor/acceptor is generally required to inhibit the electron-hole recombination. However, the enhancement is limited due to the long-distance diffusion. Herein a self-supplying electron strategy is designed for PEC enhancement by coordinating an electron donor 1,4 diazabicyclo[2.2.2]octane (Dabco) in metal-organic framework (MOF). The intrareticular photogenerated electron transfer mechanism in mixed-ligand MOF (m-MOF) is experimentally revealed and verified by density functional theory calculations. The presence of Dabco efficiently inhibits the electron-hole recombination due to the self-supplying electrons and longer electron lifetime in the framework, and thus leads to 23.2-fold enhancement of photocurrent. As proof of concept, a simple PEC method is constructed with the designed m-MOF to demonstrate its application in sensitive bioanalysis. This work provides a new avenue for improving the PEC performance of nanomaterials.

The photoelectrochemistry (PEC) process involves the generation of the electron-hole (e-h+) pair under light irradiation and subsequent energy transfer between electron donor/acceptor and photactive material. Usually, the charge separation and transport of photactive materials determine the photoelectric conversion efficiency. Therefore, many strategies have been devoted to the construction of PEC materials for enhancing the efficiency of photovoltaic conversion. For example, the enhancement of photocurrent has been achieved by trapping plasmonic nanoparticles (Au NPs) and an electron donor (ascorbic acid) in the photactive material TiO2. Charge separation has also been facilitated through multi-media transfer of photogenerated electrons driven by electrochemical potential gradients at an integrated system consisting of BiVO4 photoanode and organic polymer-based photocathode. However, it is hard to understand the electron transfer pathway since the conventional PEC platform frequently has flaws like an uncontrollable structure, short electron-hole pair lifetime, and unclear electron transfer paths. Hence, the discovery of PEC materials with tunable structures and efficient photovoltaic properties is highly essential for the verification of PEC electron transfer mechanism and the development of highly efficient PEC bioanalytical methods.

Metal-organic frameworks (MOFs) with multiple functionalities and controllable structures are gaining popularity in optoelectric fields including photoelectrochemical catalysis, electrochemiluminescence (ECL), and PEC. In particular, electroactive MOFs have been developed for PEC research due to the precise net structure. Typically, ZnO@ZIF-8 nanorods exhibit the confinement of the pore size of ZIF-8 shell to selectively detect electron donors of different sizes. The host-guest interaction has been used to regulate the excited behaviors in semiconductive MOFs by inducing conductive ligands and heterojunction structures, which results in efficient energy transfer from MOF skeleton to molecular acceptors for improving optoelectronic performance. However, the post-modified guest molecules are limited by the pore size and bandgap matching of MOFs, so it is necessary to develop intrinsic MOFs with electron donor for the construction of efficient PEC systems.

To improve the ECL performance of MOFs, a flexible and hydrophobic Zn-based MOF with two types of electroactive ligands has been studied to demonstrate the luminescence, coreactant, and self-enhanced ECL functions of 9,10-di(p-carboxyphenyl)anthracene (DPA), 1,4 diazabicyclo[2.2.2]octane (Dabco), and metal node, respectively. The dual intrareticular oxidation and the charge transfer between two oxidized ligands to generate the excited DPA* for enhanced ECL emission. Inspired by the intrareticular charge transfer, this work used Dabco as an electron donor for inhibiting the electron-hole recombination to investigate the PEC performance of the mixed-ligand MOF (m-MOF). In m-MOF, [Zn(COO)4]2- paddlewheel unit acted as metal node, and DPA ligand acted as a light-absorbing unit (Figures 1a, 1b, and 1c). Each filling of d orbitals (3d10) made Zn2+ redox inactive and thus blocked the charge transfer between ligand and metal.[13] which highlighted the importance to study photoinduced ligand-ligand electron transfer, and provided an excellent model for the verification of electron donor-mediated PEC electron transfer mechanism. Compared to single-ligand MOF (s-MOF, only DPA as ligand, Figures 1a, 1c, and 1d), m-MOF showed 23.2-fold increase of the photocurrent, which was attributed to the presence of electron donor and the longer electron lifetime in the m-MOF. The electron transfer mechanism could be well verified by density functional theory (DFT) calculations, and the
application of the enhanced PEC performance was also demonstrated by using the m-MOF to construct a simple PEC biosensing method for sensitive detection of cell membrane protein tyrosine kinase-7 (PTK7) as an analyte model.

The high-resolution transmission electron microscopic (HR-TEM) image of m-MOF indicated a clear nanosheet shape and a lattice of 1.38 nm corresponding to (020) crystal facet (Figure 1d). Similarly, the lattice spacing of s-MOF with rodlike structure was 1.22 nm, which was assigned to (002) crystal facet (Figure S2). Moreover, the Brunauer-Emmett-Teller surface areas of m-MOF and s-MOF were measured by nitrogen adsorption-desorption isotherms to be 673.04 m² g⁻¹ (Figure 1e) and 5.43 m² g⁻¹ (Figure S3), respectively. The large specific surface area is favorable for the redox reaction to promote the electron transfer. The X-ray photoelectron spectroscopy survey spectrum of s-MOF and m-MOF confirmed the presence of C, N, O, and Zn elements (Figure S4). Compared with s-MOF (Figure S4a-d), two strong peaks at 1044.43 and 1021.25 eV in Zn 2p region of m-MOF were negatively shifted by ~0.15 eV, indicating the increase in electron density on Zn⁴⁺ of m-MOF.¹⁴ which could be assigned to the coordination effect of electron donor Dabclo. In addition, m-MOF carried more negative charges than s-MOF and DPA, indicating the successful coordination of electron-rich Dabclo ligand in m-MOF (Figure S5).

To verify the semiconducting properties of the MOFs, the densities of states (DOS) were calculated by DFT method. The direct bandgap width of 2.11 and 1.96 eV for m-MOF and s-MOF respectively (Figures 2a and S6) indicated that the coordination of Dabclo presents a less important on the forbidden bandwidth of the MOFs. The onset levels (E_onset) of s-MOF (Figure S7a) and m-MOF (Figure 2b) were 17.34 and 17.73 eV, respectively. The work functions (Φ, the relative energy gap between the vacuum level and the Fermi level, E_F - E_v) of the s-MOF and m-MOF were 3.88 and 3.49 eV, which were calculated with Φ = hv - E_onset (hv = 21.22 eV).¹⁶ Furthermore, relative electronic binding energies between the valence band maximum and Fermi level (E_vbf - E_v) of s-MOF and m-MOF were 2.92 (Figure S7b) and 2.96 eV (inset in Figure 2b), from which their E_vbf were calculated to be -6.80 and -6.45 eV, respectively.¹⁶ The band structures of s-MOF and m-MOF could be precisely determined by combining the ultraviolet photoelectron spectrum (UPS) and Tauc plots (Figure S9).¹³⁴ The conduction band minimum (E_cm) was obtained with E_cm = E_CBM - E_onset, where E_onset is the optical bandgap.¹⁷ According to the above results, the energy band diagrams of the s-MOF and m-MOF were provided (Figure 2c). The position of the energy band of m-MOF was negatively shifted compared with s-MOF, which could be attributed to the coordination of electron-rich ligand Dabclo to enhance the reducibility of MOFs.

The positive slope of Mott-Schottky curves (Figure S9) indicated that both s- and m-MOF were N-type semiconductors,¹⁸ and their Hall coefficients were consistent (Table S1).¹⁹ The broad UV-Vis absorption (350-420 nm) was attributed to DPA ligand (Figure S10), which proved that the site of the generated electronic transition was the DPA ligand under light radiation. In addition, the excited state calculated by DFT was dominant in the DPA unit (Figure S11), confirming that the photo-excited electron transfer profiled from π-π* electron transition of the DPA unit.²⁰ Time-resolved photoluminescence (PL) spectral measurements and multi-exponential fitting calculations (Figure 2d and Table S2) gave the average lifetimes of 1.13 ns for DPA, 3.09 ns for s-MOF, and 5.02 ns for m-MOF. The prolongation of PL lifetime of m-MOF indicated that electron-hole pair recombination was suppressed, which was beneficial to the improvement of charge separation efficiency after introducing electron-rich Dabclo ligand.²¹

The cyclic voltammetric (CV) test with equivalent MOFs and ligands coated glassy carbon electrodes (GCEs) demonstrated the significantly enhanced current of m-MOF (Figures 3a and S12). The enhanced photocurrents of DPA (Figure S13a) and s-MOF (Figure S13b) with increasing Dabclo concentration indicated that the heightened electrochemical signal of m-MOF was attributed to the Dabclo ligand. In optimal PEC measurement conditions (Figure S14), the photocurrents of s-MOF and m-MOF modified indium tin oxide (ITO) electrodes were -3.7 and -456.6 nA, respectively (Figure 3b), which resulted from the reduction of dissolved oxygen by photogenerated electrons of the MOFs, and were obviously different from the background of 10.4 nA at bare ITO (Figure S15). The photocurrent of m-MOF was 23.2 fold that of s-MOF, and its intensity was very stability upon successive irradiation (Figure S16), indicating that the electron donor coordinated MOF possessed excellent PEC properties. After N₂ bubbling for 30 min, the photocurrent of s-MOF
role of metal node, which showed the PXRD pattern as expected (Figure S22a). The photocurrent of m-MOF(Cu) was much higher than that of m-MOF(Zn) (Figure S22b) due to the exciton trap of Cu²⁺ node, which resulted from its 3d electronic arrangement to drive recombination of electron-hole pairs,²⁵² indicating that the redox inactivity of Zn²⁺ favored PEC performance.

To prove the generation of free radicals in PEC process, the EPR spectra were recorded using DMPO as a spin-trapping agent under light irradiation,²⁶ which showed the characteristic signals of both the DMPO-hydroxyl radical (‘OH) and the DMPO-superoxide radical (O₂⁻) (Figures 3c and 3d). In the presence of Dabco the PEC process of s-MOF did not show the signal of ‘OH (Figure 3c), indicating that Dabco hindered the generation of ‘OH by consuming the photogenerated hole, which could improve the PEC performance. This result was consistent with the significantly enhanced DMPO–O₂⁻ peak of m-MOF (Figure 3d). Subsequently, the charge density difference of m-MOF between the lowest exciton excitation and original ground state clearly revealed the electron transfer process of reticular m-MOF in photocexcitation. Moreover, the photogenerated electron transfer site of m-MOF was mainly on the DPA ligand as light collector (Figures 3e and 3f).

The frontier orbitals calculations of two ligands in m-MOFs demonstrated the matching HOMO of Dabco with that of DPA (Figure 4a), facilitating electron transfer from Dabco to DPA. Thus, the photogenerated carrier transfer process of m-MOF was shown in Figure 4b. Under the photoexcitation of 410 nm, the electrons could be easily excited from the HOMO to the LUMO of DPA ligand, while Dabco as electron donor effectively consumed the holes to inhibit the recombination of electron-hole pairs, resulting in enhanced photocurrent. In the presence of dissolved oxygen (O₂) the electrons at the LUMO level could be transferred to O₂ to form O₂⁻,²⁷² leading to the increased photocurrent at acidic pH (Figure S23) due to the promoted protonation of O₂⁻.

Under continuous illumination, both the powder X-ray diffraction (PXRD) patterns and the morphology of s- and m-MOFs did not show obvious change (Figure S20), indicating their excellent photo-stability. The m-MOFs showed higher room temperature conductivity than the s-MOFs (Figure S21 and Table S3), indicating that the introduction of Dabco into the framework enhanced the electro-conductivity. The m-MOF(Cu) was also synthesized with the same ligands to examine the
COMMUNICATION

MOF (m-MOF-aptamer), whose preparation was characterized in Figures S24 and S25. The photocurrent or electrochemical impedance spectroscopic measurements demonstrated the coating of m-MOF and m-MOF-aptamer on ITO or GCE respectively and the recognition of the biosensor to PTK7 as a model target (Figure S26). Under optimal conditions (Figure S27), the photocurrent of the PEC biosensor significantly increased with the increasing concentration of PTK7 from 0.001 to 50 nM (Figure 4c). The photocurrent intensity and the logarithm of PTK7 concentration showed favorable linearity from 0.005 to 10 nM (Figure 4d). The detection limit was obtained at S/N=3 to be 3.3 pM, which was lower than those of fluorescence approaches (Table S4). Although two previously reported differential pulse voltammetric methods for PTK7 detection gave lower detection limits than this work,[15] they needed a tedious and highly expensive procedure for obtaining amplified signal. The specificity and practical application of the proposed method were demonstrated by comparing the response of PTK7 with those of Muc.[16]

In summary, the PEC electron transfer mechanism of electron donor coordinated MOF has been revealed for the first time by DFT calculations and a series of experimental characterizations, which demonstrates a self-supplying electrons strategy for greatly enhancing the PEC performance. In m-MOF, DPA ligand acts as a light collector to achieve the photo-excited electron transfer and charge separation, and its HOMO level can well match that of Dabco, which facilitates the electron transfer from Dabco to DPA. The presence of Dabco as an excellent electron donor prolongs the electron lifetime in the framework, and can thus efficiently suppress electron-hole recombination of DPA. The practicality of the self-supplying electrons PEC strategy has been demonstrated with a simple PEC biosensing method, indicating a promising way to improve the PEC performance of nanomaterials and extend the application of MOFs in PEC bioanalysis.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (21827812, 21890741), and the Science and Technology Project of Nanjing City (202110023).

Conflict of interest

The authors declare no conflict of interest.

Keywords: photoelectrochemistry • metal-organic frameworks • electron donor • intrareticular photoelectron transfer • biosensors

For electron donor coordinated metal-organic frameworks, the photoelectrochemical electron-transfer mechanism is revealed by density functional theory calculations and experiments, which show a self-supplying electrons strategy. The matching HOMO levels of the light collector and electron-donor ligands facilitate electron transfer which efficiently suppresses electron-hole recombination, greatly enhancing the photoelectrochemical performance.