Supplementary Information for

# Single-atom loaded BTEA-COF for enhanced visible-light photocatalytic $H_2$ production: Insights from first-principles and real-time TDDFT calculations

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## I. Additional figures

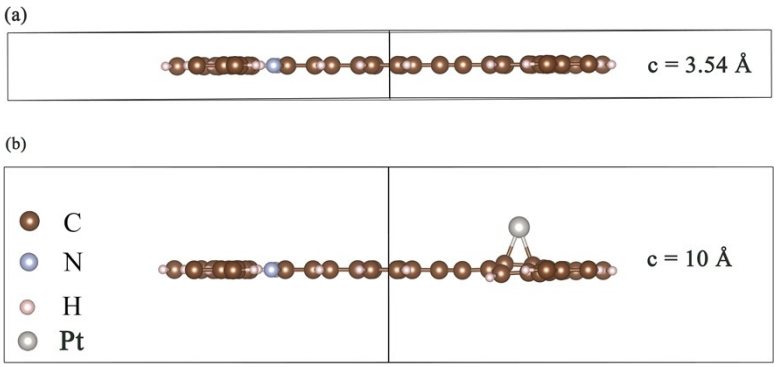


**Fig. S1** Side view of the geometric structure of (a) BTEA-COF and (b) Pt/BTEA-COF, respectively.

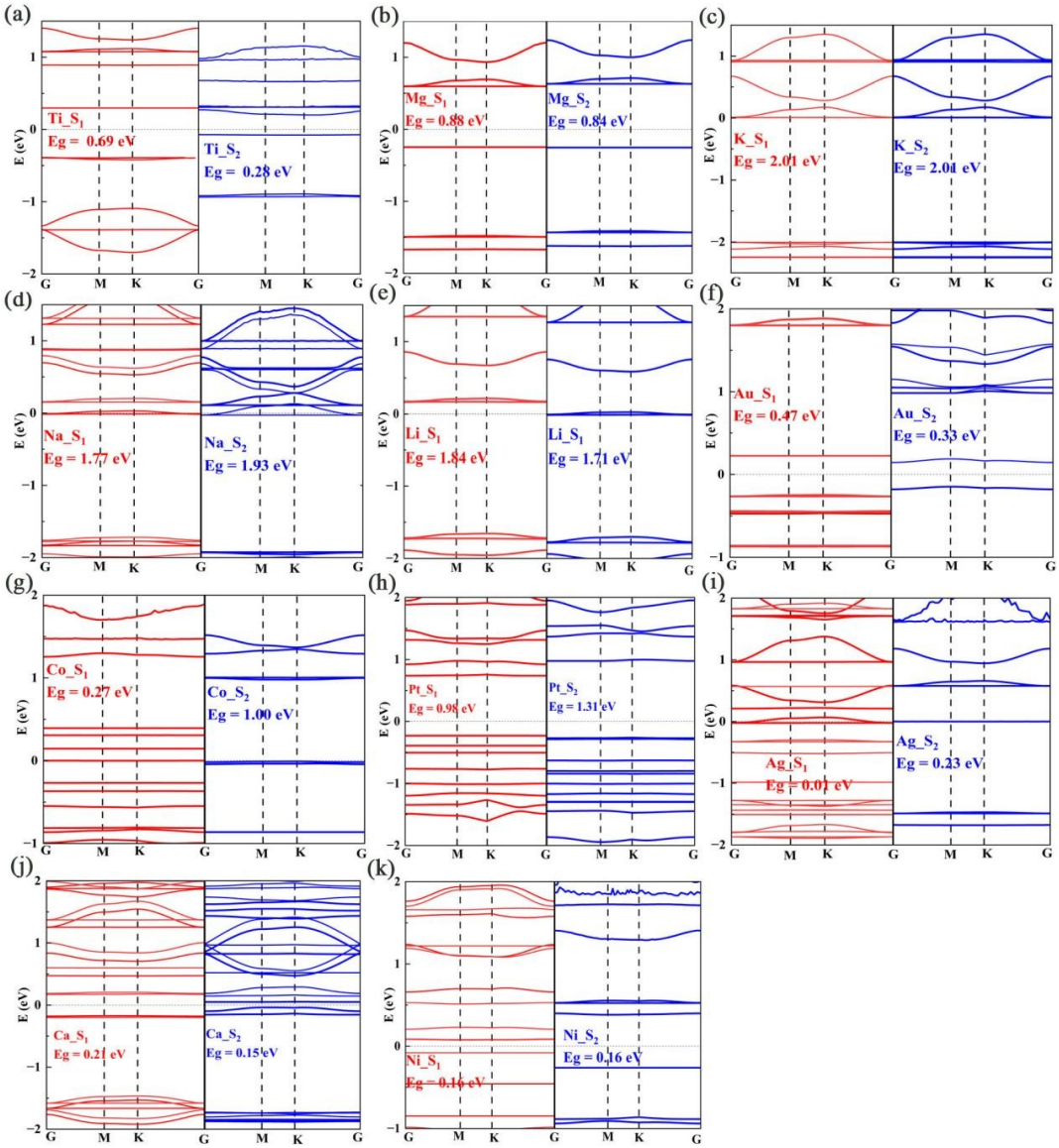


**Fig. S2** Band structure of Ti-, Mg-, K-, Na-, Li-, Au-, Co-, Pt-, Ag-, Ca-, and Ni- doping BETA-COF, respectively. $S_1$ and $S_2$ denote the two distinct doping sites.

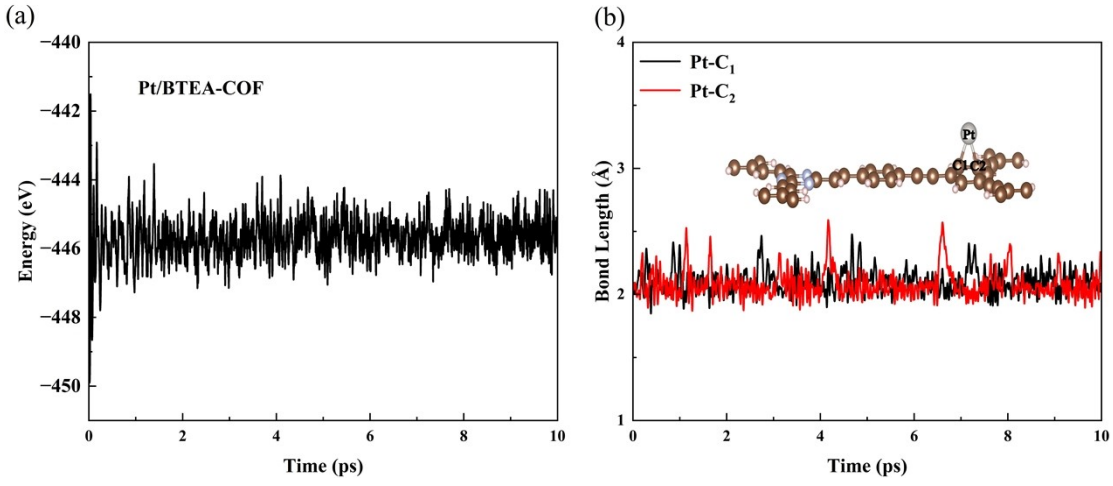

**Fig. S3** (a) Total energy and (b) evolution of Pt-C bond lengths with time for Pt/BTEA-COF at 500K.

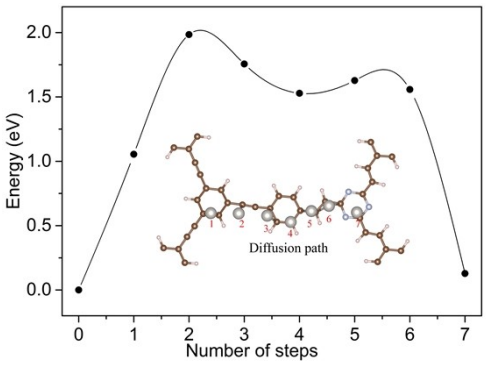


**Fig. S4** The diffusion path of Pt atom on the BTEA-COF surface.

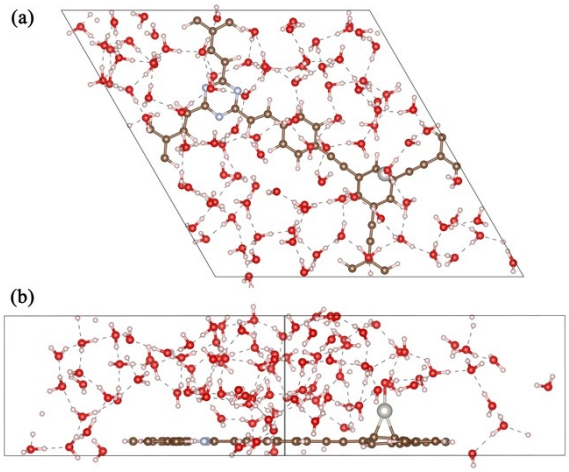


**Fig. S5.** (a)Top view and (b) side view of $H_2O$@Pt/BTEA-COF system.

## II. The calculation details of the Gibbs free energies of hydrogen adsorption.

The HER performance was evaluated through the calculation of the adsorption free energy ( $\Delta G_{H^*}$) in acidic media (pH = 0) , which was determined using the following equation[1]:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_{H^*} \quad (S1)$$

Where the term $\Delta E_{H^*}$ refers to the H adsorption energy, $\Delta E_{ZPE}$ and $\Delta S_{H^*}$ represents the difference in zero-point energy and entropy between the adsorbed H (H*) and the gaseous $H_2$ (1/2 $H_2$). The contributions from the catalyst for the two parameters are minimal and can be disregarded. Therefore, the $\Delta E_{ZPE}$ can be according to the following formula[2]:

$$\Delta E_{ZPE} = E_{ZPE}^{nH} - E_{ZPE}^{(n-1)H} - \frac{1}{2}E_{ZPE}^{H_2} \quad \text{(S2)}$$

where $E_{ZPE}^{nH}$ denotes the zero-point energy of n hydrogen atoms adsorbed on catalyst (BTEA-COF or Pt/BTEA-COF), excluding the influence of the catalyst, and $E_{ZPE}^{H_2}$ denotes the zero-point energy of $H_2$ molecule in the gas phase. The value of $\Delta E_{ZPE}$ can vary between -0.01 and 0.04 eV. The entropy of atomic hydrogen, denoted as $\Delta S_H$, is approximately -1/2$\Delta S_H^0$, where $\Delta S_H^0$ signifies the entropy of the $H_2$ molecule in the gas phase. At a temperature of 300 K, $\Delta S_H^0$is estimated to be 0.4 eV[3], which results in the expression $\Delta E_{ZPE} - T\Delta S_{H^*} = 0.24$ eV. Therefore, we simplify the Gibbs free energy as：

$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24 \quad \text{(S3)}$$

An ideal catalyst should have a $\Delta G_{H^*}$ value of zero. In this context, $\Delta E_{H^*}$ represents the hydrogen adsorption of hydrogen, which can be defined as follows:

$$\Delta E_{H^*} = E_{\text{monolayer + H}} - E_{\text{monolayer}} - 1/2E_{H_2,\text{isolated}} \quad \text{(S4)}$$

Where $E_{\text{monolayer + H}}$ and $E_{\text{monolayer}}$stand for the total energy of the total energy of the monolayer with and without hydrogen atom, respectively; $E_{H_2,\text{isolated}}$ is an isolated $H_2$ molecule.

## Notes and references


1 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and U. Stimming. J. Electrochem. Soc. 2005, **152**, J23 - I26.

2 G. Henkelman, A. Arnaldsson and H. Jónsson. Comput. Mater. Sci. 2006, **36**, 354-360.

3 C. Tsai, F. Abild-Pedersen and J. K. Nørskov. Nano Lett. 2014, **14**, 1381-1387.