

Supporting Information
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**Theoretical insights into the atomic and electronic structures of
polyperyleneimide: On the origin of photocatalytic oxygen
evolution activity**

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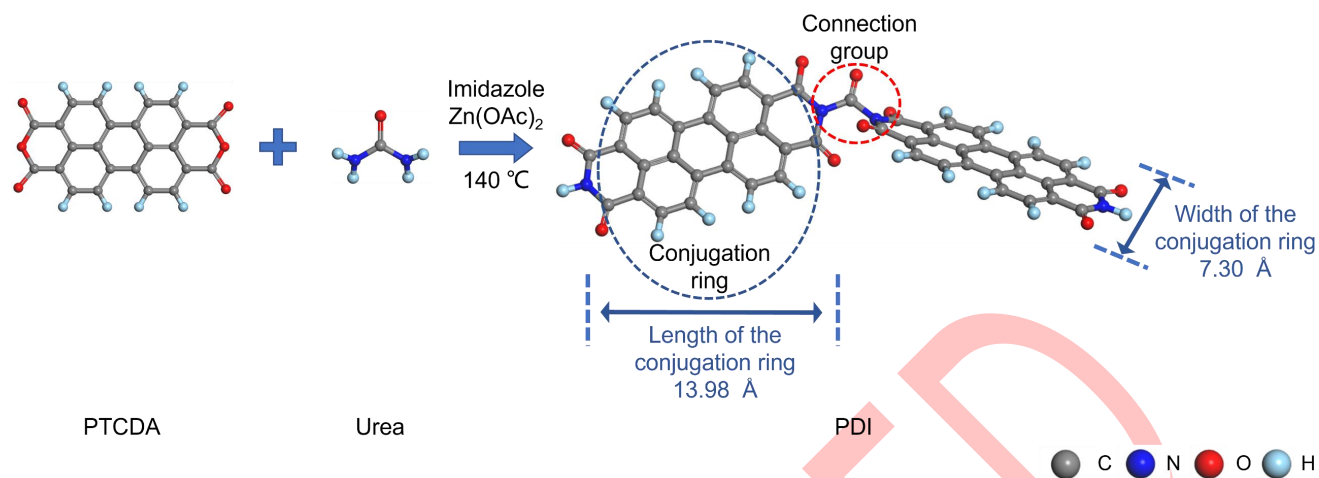


Figure S1. Synthetic process of PDI with PTCDA and urea as starting materials.

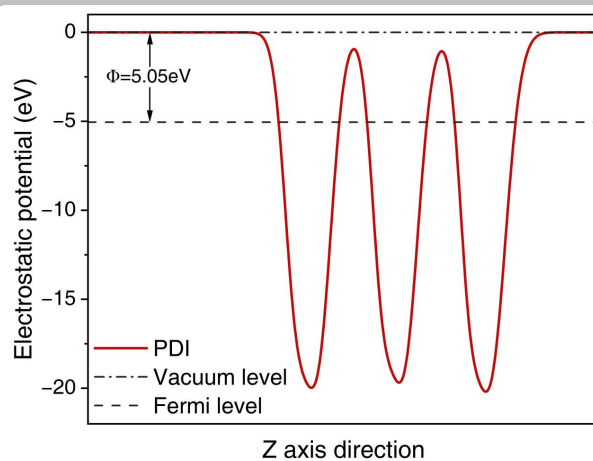


Figure S2 Electrostatic potentials of PDI.

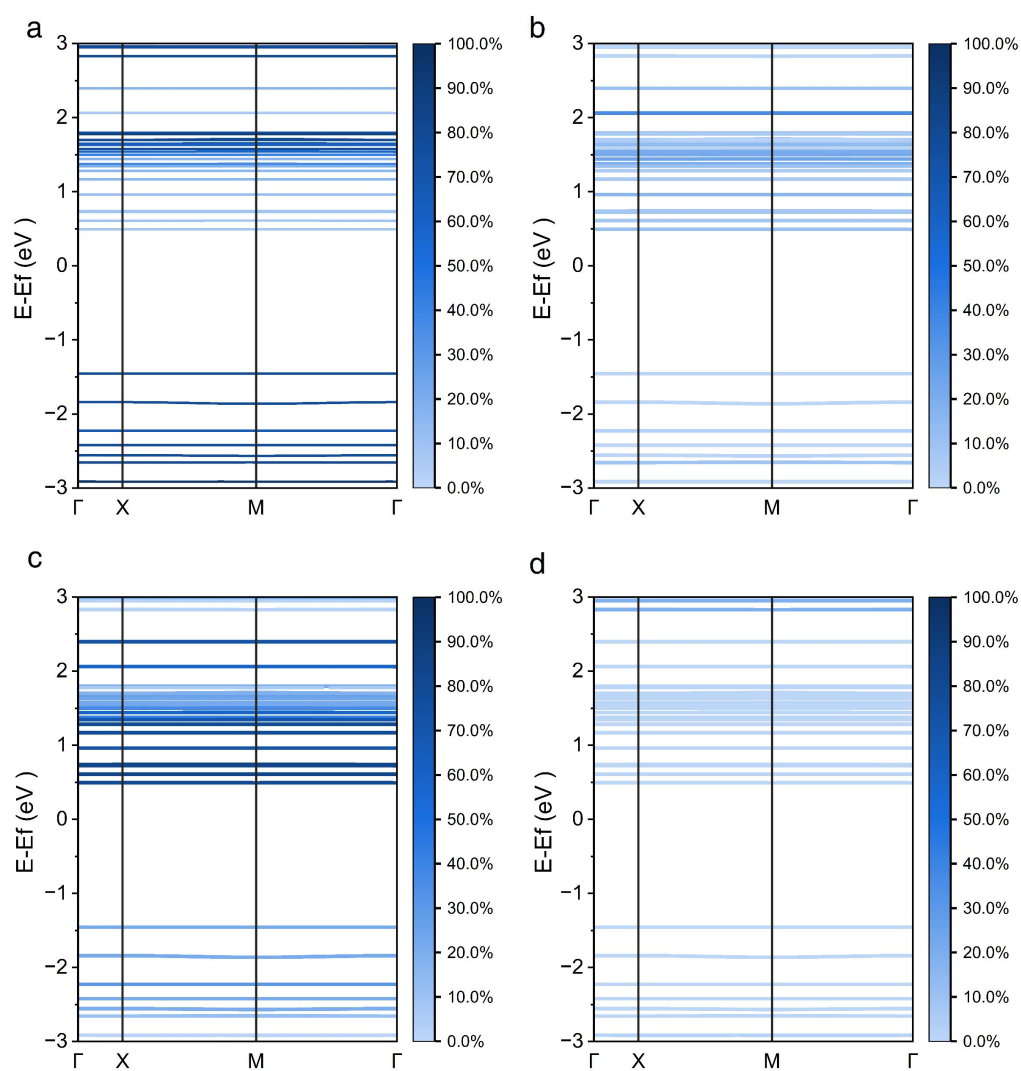


Figure S3. Projected band structure of PDI for (a) C atoms, (b) N atoms, (c) O atoms, (d) H atoms.

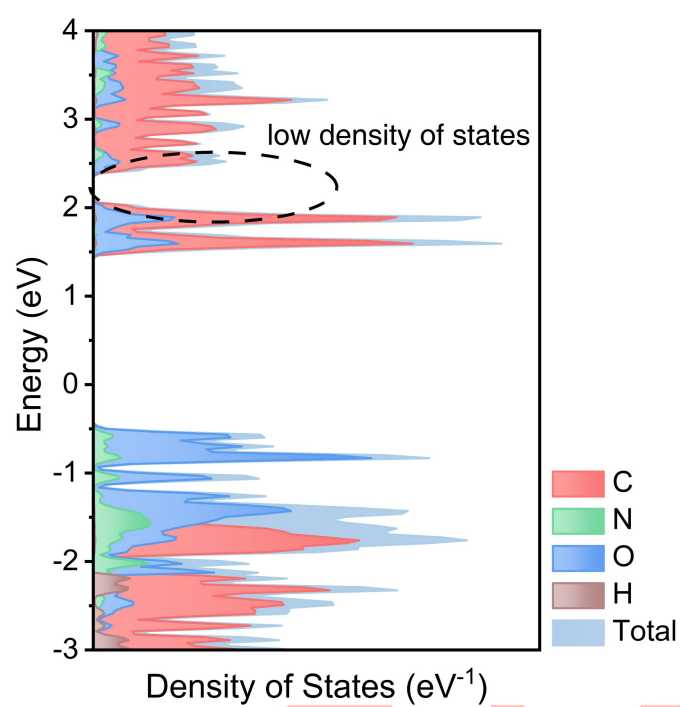


Figure S4 Calculated density of states of PDI.

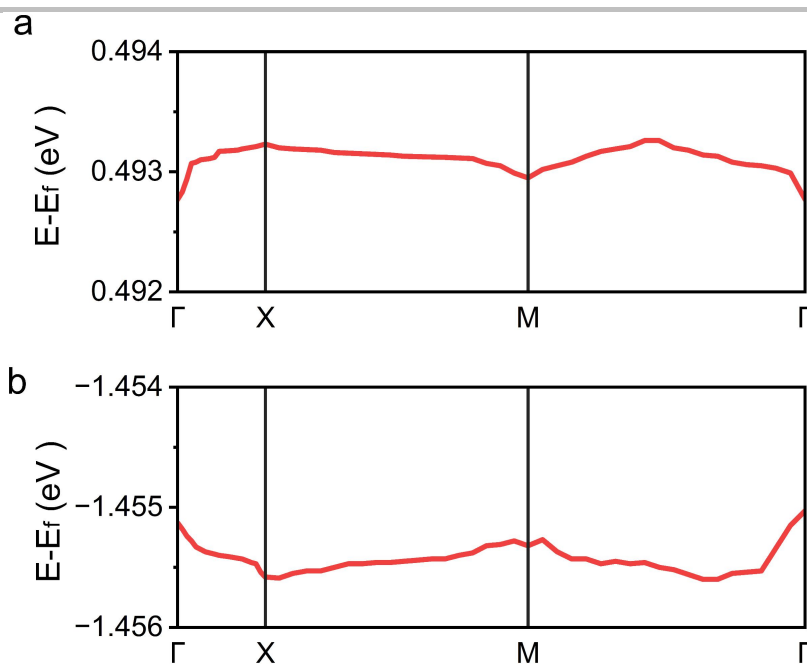


Figure S5 Calculated band structures of PDI at (a) CBM and (b) VBM. The effective masses of electrons and holes are related to the second differential of energy band structure at the VBM and CBM, which satisfies the equation $\frac{1}{m_a^*} = \frac{1}{\hbar^2} \frac{\partial^2 E(k)}{\partial k^2}$.

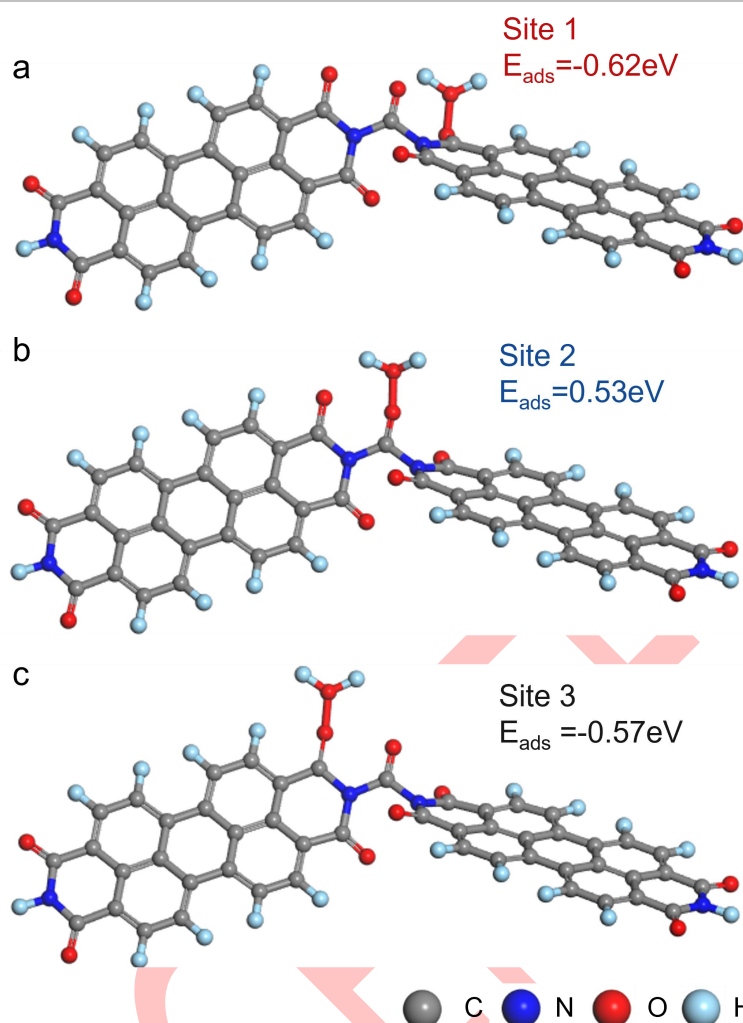


Figure S6 Structure of water molecule adsorbed at different oxygen atoms as different active sites, (a) Site 1, (b) Site 2, and (c) Site 3, with corresponding adsorption energy (E_{ads}) calculated for each site.

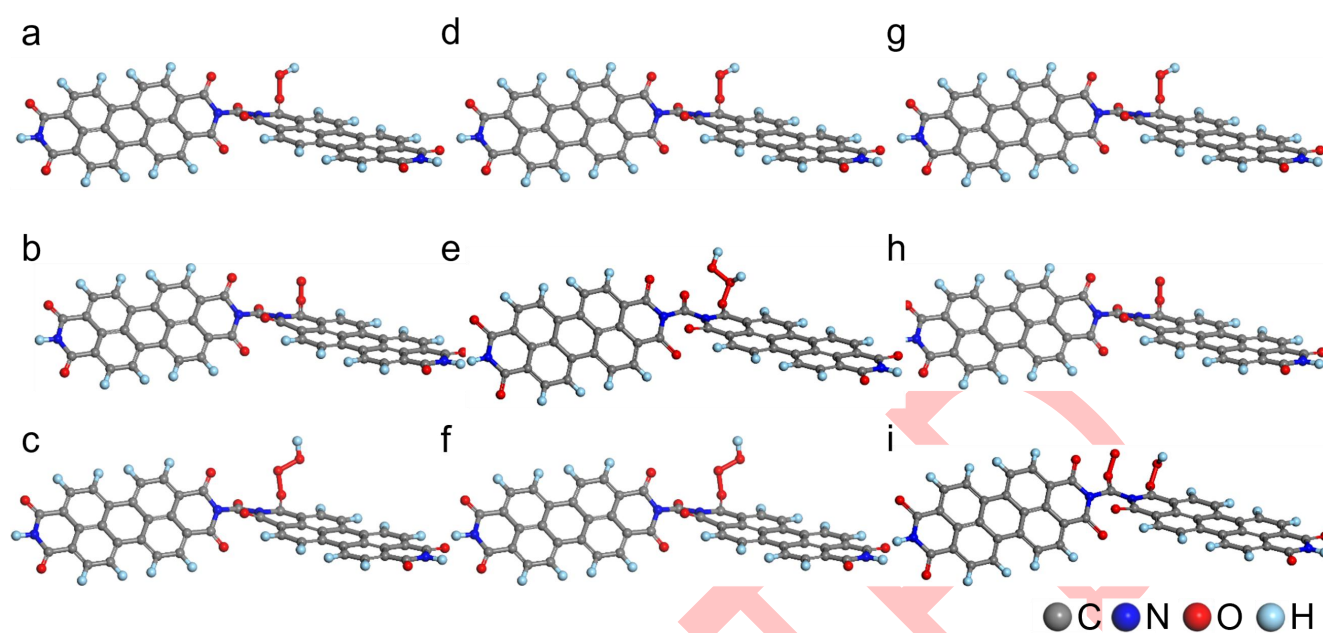


Figure S7 Proposed mechanisms for OER over PDI. Pathway 1: $\text{H}_2\text{O} \rightarrow ^*\text{OH} \text{ (a)} \rightarrow ^*\text{O} \text{ (b)} \rightarrow ^*\text{OOH} \text{ (c)} \rightarrow \text{O}_2$. Pathway 2: $\text{H}_2\text{O} \rightarrow ^*\text{OH} \text{ (d)} \rightarrow ^*\text{HOOH} \text{ (e)} \rightarrow ^*\text{OOH} \text{ (f)} \rightarrow \text{O}_2$. Pathway 3: $\text{H}_2\text{O} \rightarrow ^*\text{OH} \text{ (g)} \rightarrow ^*\text{O} \text{ (h)} \rightarrow ^*\text{OOH} \text{ (i)} \rightarrow \text{O}_2$.

Table S1. Atomic coordinates of PDI.

atom	X coordinate	Y coordinate	Z coordinate	atom	X coordinate	Y coordinate	Z coordinate
C	0.11614	0.38408	0.09275	C	0.7287	0.19919	0.2277
C	0.12067	0.45715	0.31937	C	0.77876	0.15676	0.14349
C	0.1697	0.49196	0.41652	C	0.81889	0.29961	0.1703
C	0.21426	0.45378	0.28558	C	0.80843	0.48387	0.28319
C	0.20968	0.37736	0.05937	C	0.8485	0.625	0.31177
C	0.1607	0.34278	-0.03692	C	0.83855	0.81024	0.42533
C	0.26324	0.49629	0.37888	C	0.78871	0.85476	0.50677
C	0.2677	0.57587	0.60366	C	0.8984	0.58182	0.22652
C	0.22329	0.60997	0.73674	C	0.86921	0.25956	0.08461
C	0.17415	0.56787	0.64305	H	0.2425	0.34626	-0.03716
C	0.1293	0.60504	0.77279	H	0.15741	0.28656	-0.20435
C	0.08034	0.56962	0.67522	H	0.13237	0.65886	0.94134
C	0.0759	0.49686	0.44711	H	0.04735	0.59729	0.77191
C	0.31651	0.62876	0.6917	H	0.38901	0.50315	0.23177
C	0.36032	0.60772	0.55502	H	0.3049	0.39962	0.0823
C	0.35624	0.5231	0.33235	H	0.19579	0.7119	1.06271
C	0.30777	0.46531	0.2454	H	0.28076	0.80589	1.21245
C	0.22832	0.69136	0.96076	H	0.54716	0.23504	0.47079
C	0.27727	0.74506	1.04718	H	0.63319	0.1525	0.32057
C	0.3216	0.71678	0.91082	H	0.71847	1.05499	0.68032
C	0.40759	0.68365	0.63609	H	0.63221	1.13804	0.81888
C	0.37024	0.78465	0.99134	H	0.69947	0.09257	0.20749
C	0.06707	0.35328	-0.00479	H	0.78623	0.01925	0.06096
C	0.02694	0.46443	0.34615	H	0.86804	0.91506	0.44954
C	0.46411	0.81801	0.9185	H	0.78151	0.99232	0.5897
C	0.54982	0.90286	0.80771	H	-0.01218	0.37171	0.04801
C	0.59904	0.85558	0.72096	H	0.94445	0.37374	0.04912
C	0.60825	0.66751	0.61527	N	0.41437	0.75315	0.85719
C	0.56741	0.52835	0.59607	N	0.0228	0.39376	0.12084
C	0.51788	0.57722	0.68923	N	0.50946	0.76453	0.79808
C	0.57699	0.33953	0.48735	N	0.90872	0.40101	0.11161
C	0.62668	0.29168	0.40115	O	0.06333	0.28319	-0.22864
C	0.6677	0.43135	0.42338	O	-0.01683	0.50342	0.47282
C	0.65808	0.61965	0.53137	O	0.87897	0.07837	-0.02703
C	0.69848	0.76075	0.55655	O	0.93722	0.72187	0.2576
C	0.68887	0.94974	0.66186	O	0.47912	0.43432	0.68085
C	0.63927	0.99737	0.74267	O	0.54202	1.09164	0.90528
C	0.74844	0.71404	0.47667	O	0.44647	0.74594	0.50745
C	0.7583	0.5274	0.36645	O	0.36961	0.89319	1.19562
C	0.71801	0.38546	0.33923	O	0.47129	0.96615	1.08331

Author Contributions

For author contributions, Yiqing Wang, Zhi Lin, Shaohua Shen proposed the conceptualisation of the project, Yiqing Wang, Mingtao Li proposed the specific methodology, Yiqing Wang, Zhi Lin completed the experimental investigations, Yiqing Wang completed the visualisation, Shaohua Shen, Yiqing Wang funded the project, Shaohua Shen completed the management of the project and supervised the project, Yiqing Wang, Shaohua Shen completed the original drafts of the write-ups and the reviewing and editing. All the authors discussed the results and commented on the manuscript.

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