Supporting Information

Tunable covalent benzo-heterocyclic rings constructed two-dimensional conjugated polymers for visible-light-driven water splitting

Cong Wang,^{ab} Ying-Nan Zhao,^c Zhong-Ling Lang,^{d*} Yang-Guang Li,^c Zhong-Min

Suace and Hua-Qiao Tanc*

^{*a.*} School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, 130022, China.

^{b.} Engineering Research Center of Optoelectronic Functional Materials, Ministry of Education, Changchun 130022, China.

^{c.} Key Laboratory of Polyoxometalate and Reticular Material Chemistry of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, China.

^{d.} Centre for Advanced Optoelectronic Functional Materials Research, Key Laboratory of UV-Emitting Materials and Technology, Ministry of Education, Northeast Normal University, Changchun 130024, China.

^{e.} State Key Laboratory of Supramolecular Structure and Materials, Institute of Theoretical Chemistry, College of Chemistry, Jilin University, Changchun 130021, China.

*Emails: langzl554@nenu.edu.cn; tanhq870@nenu.edu.cn

Computational details.

In aqueous solution, photocatalytic overall water splitting reaction consists of two half-reactions, namely, the two-electron (2*e*) hydrogen evolution reaction (HER) process and 4*e* oxygen evolution reaction (OER).

The 2e HER process can be decomposed into two 1e steps with each step consuming a proton and an electron:

$$^{*} + (\mathrm{H}^{+} + e^{-}) \rightarrow ^{*}\mathrm{H} \tag{1}$$

$$^{*}\mathrm{H} + (\mathrm{H}^{+} + e^{-}) \rightarrow ^{*} + \mathrm{H}_{2} \tag{2}$$

Meanwhile, 4*e* OER process can be decomposed into four 1*e* oxidation steps, corresponding to the deprotonation of water molecules, as follows:

$$* + H_2O \rightarrow *OH + (H^+ + e^-)$$
(3)

$$*OH \rightarrow *O + (H^+ + e^-) \tag{4}$$

$$*O + H_2O \to *OOH + (H^+ + e^-) \text{ or } *O + H_2O \to *O*OH + (H^+ + e^-)$$
(5)
$$*OOH \to * + O_2 + (H^+ + e^-) \text{ or } *O*OH \to *O*O + (H^+ + e^-)$$
(6)
$$*O*O \to * + O_2$$
(7)

Moreover, photocatalytic overall water splitting processes may be accompanied by 2e water oxidation reaction to generate H₂O₂. And the 2e water oxidation reaction toward H₂O₂ production can be described as:

$$* + H_2O \rightarrow *OH + (H^+ + e^-)$$
(8)

$$*OH + H_2O \rightarrow * + H_2O_2 + (H^+ + e^-)$$
 (9)

where * denotes the active site on photocatalyst, *(radical) denotes the corresponding radical adsorbed on the surface.

To compute the Gibbs free energy change (ΔG) of each elementary step, we employed the computational hydrogen electrode model that proposed by Nørskov *et al.*¹ Accordingly, the ΔG is defined by: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_U$. In this equation, ΔE is the reaction energy directly obtained from DFT calculations. ΔE_{ZPE} is the zero-point energy correction, T is the system temperature (298.15 K), and ΔS is the entropy change. The entropies of gas-phase molecules are looked up in the NIST database, and the post-processing of energy corrections (zero point energy and entropy) for adsorbed species are performed with the help of the VASPKIT code.² ΔG_{pH} is the free energy correction of pH, which can be calculated by $\Delta G_{pH} = 0.059 \times pH$. Under light irradiation, a light-drive potential will be imposed to promote HER and OER, thus the free energy change at an applied drive potential (ΔG_U) is expressed by $\Delta G = \Delta G_U - eU$. The U is the energy difference of VBM or CBM relative to hydrogen reduction potential (H⁺/H₂).

The geometry optimization and computed energy positions of HOMO and LUMO of benzene-derived molecular linkers are performed at the B3LYP/6-31g(d,p) level of theory as implemented in the Gaussian 16 program.³



Figure S1. The computed energy positions of HOMO and LUMO of benzene-derived molecular linkers.



Figure S2. The optimized structures of (a) CP-1, (b) CP-2, (c) CP-3, (d) CP-4, (e) CP-5, (f) CP-6, (g) CP-7 and (h) CP-8.



Figure S3. Illustration of polymerization process for 2D CPs.



Figure S4. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-1, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S5. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-2, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S6. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-3, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S7. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-4, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S8. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-5, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S9. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-6, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S10. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-7, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S11. Variations of temperature and energy against the time for the *ab initio* molecular dynamics simulations of CP-8, insert are top and side views of the snapshot of atomic configuration. The simulation is run under 300 K for 5 ps with a time step of 1 fs.



Figure S12. The computed electronic band structures relative to vacuum levels of (a) CP-1 and (b) CP-3.













Figure S13. The computed partial density of states (PDOS) on atomic orbitals and charge density of VBM and CBM for (a) CP-1, (b) CP-2, (c) CP-3, (d) CP-4, (e) CP-5, (f) CP-6, (g) CP-7 and (h) CP-8 with HSE06 method. Fermi level was set to zero.



Figure S14. (a) Schematics of the HER process on the optimal reaction site, and the possible OER processes *via* single-site or optimal dual-site reactions on benzene-derived molecular segment in CP-2, labeled as "s" or "d", respectively. The calculated Gibbs free energy diagrams of (b) HER and (c) OER. $U_e = 1.17$ V and $U_h = 1.23$ V are potentials provided by photogenerated electrons and holes for hydrogen reduction and water oxidation reactions at pH = 7, respectively.



Figure S15. (a) Schematics of the HER process on the optimal reaction site, and the possible OER processes *via* single-site or optimal dual-site reactions on benzene-derived molecular segment in CP-5, labeled as "s" or "d", respectively. The calculated Gibbs free energy diagrams of (b) HER and (c) OER. $U_e = 0.97$ V and $U_h = 1.55$ V are potentials provided by photogenerated electrons and holes for hydrogen reduction and water oxidation reactions at pH = 7, respectively.



Figure S16. (a) Schematics of the HER process on the optimal reaction site, and the possible OER processes *via* single-site or optimal dual-site reactions on benzene-derived molecular segment in CP-6, labeled as "s" or "d", respectively. The calculated Gibbs free energy diagrams of (b) HER and (c) OER. $U_e = 0.96$ V and $U_h = 1.55$ V are potentials provided by photogenerated electrons and holes for hydrogen reduction and water oxidation reactions at pH = 7, respectively.



Figure S17. (a) Schematics of the HER process on the optimal reaction site, and the possible OER processes *via* single-site or optimal dual-site reactions on benzene-derived molecular segment in CP-7, labeled as "s" or "d", respectively. The calculated Gibbs free energy diagrams of (b) HER and (c) OER. $U_e = 0.12$ V and $U_h = 2.53$ V are potentials provided by photogenerated electrons and holes for hydrogen reduction and water oxidation reactions at pH = 7, respectively.



Figure S18. (a) Schematics of the HER process on the optimal reaction site, and the possible OER processes *via* single-site or optimal dual-site reactions on benzene-derived molecular segment in CP-8, labeled as "s" or "d", respectively. The calculated Gibbs free energy diagrams of (b) HER and (c) OER. $U_e = 0.29$ V and $U_h = 2.16$ V are potentials provided by photogenerated electrons and holes for hydrogen reduction and water oxidation reactions at pH = 7, respectively.



Figure S19. (a) Schematic of the HER process on the optimal reaction site in CP-3. The calculated Gibbs free energy diagrams of (b) HER. $U_e = 1.68$ is the potential provided by photogenerated electrons for hydrogen reduction reaction at pH = 7.



Figure S20. The band alignments of Z-scheme heterostructures formed by (a) CP-2 and CP-7, (b) CP-2 and CP-8, (c) CP-3 and CP-7, (d) CP-3 and CP-8, respectively.

$CP_s = h(\hat{\lambda})$	VBM	CBM	Band gap			
015	Crs a = 0 (A)	(eV)	(eV)	(eV)	$O_e(V)$	$O_h(\mathbf{v})$
CP-1	16.38	-6.28	-3.13	3.15	0.90	2.25
CP-2	23.31	-5.26	-2.86	2.40	1.17	1.23
CP-3	23.10	-4.84	-2.35	2.49	1.68	0.81
CP-4	22.86	-5.61	-2.96	2.65	1.07	1.58
CP-5	23.68	-5.58	-3.06	2.52	0.97	1.55
CP-6	22.78	-5.58	-3.07	2.51	0.96	1.55
CP-7	22.58	-6.56	-3.91	2.65	0.12	2.53
CP-8	23.28	-6.19	-3.74	2.45	0.29	2.16

Table S1. The optimized lattice parameters, the VBM and CBM positions relative to vacuum level, the electronic band gap values, and U_e and U_h values of these 2D CPs using the HSE06 functional at pH = 7 (c = 15 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$).

Table S2. The computed average reaction energy (E_r , eV) per stoichiometric formula, cohesive energy per atom (E_{coh} , eV), and formation energy (E_f , eV) of 2D CPs.

CPs	Er	E_{coh}	Ef
CP-1	-1.96	-6.41	-2.30
CP-2	-3.59	-6.05	-2.17
CP-3	-3.25	-6.18	-2.05
CP-4	-2.90	-6.54	-2.41
CP-5	-3.53	-6.35	-2.24
CP-6	-2.87	-6.30	-1.86
CP-7	-2.42	-6.70	-2.22
CP-8	-3.15	-6.50	-2.03

CP-2	ΔG (1)	ΔG (2)
site 1	-	-
site 2	1.22	-0.39
site 3	2.53	-1.71
site 4	0.97	-0.15
site 5	1.74	-0.91
site 6	1.19	-0.36
site 7	1.33	-0.50

Table S3. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-2.

Note that "-" represents that the *H intermediate could not be adsorbed on the active site.

Table S4. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-4.

CP-4	ΔG (1)	ΔG (2)
site 1	2.00	-1.17
site 2	1.59	-0.76
site 3	2.67	-1.84
site 4	1.16	-0.34
site 5	2.01	-1.18
site 6	1.04	-0.22
site 7	1.40	-0.58

CP-5	ΔG (1)	ΔG (2)
site 1	2.64	-1.82
site 2	1.60	-0.77
site 3	2.54	-1.72
site 4	1.13	-0.30
site 5	2.00	-1.17
site 6	1.22	-0.39
site 7	1.41	-0.58

Table S5. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-5.

Table S6. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-6.

CP-6	ΔG (1)	ΔG (2)
site 1	2.51	-1.69
site 2	1.87	-1.04
site 3	2.44	-1.62
site 4	1.28	-0.46
site 5	2.11	-1.28
site 6	1.03	-0.20
site 7	1.40	-0.58

CP-7	ΔG (1)	ΔG (2)
site 1	1.66	-0.83
site 2	1.60	-0.77
site 3	2.49	-1.67
site 4	1.04	-0.22
site 5	1.88	-1.05
site 6	1.03	-0.20
site 7	1.36	-0.54

Table S7. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-7.

Table S8. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-8.

CP-8	ΔG (1)	ΔG (2)
site 1	2.40	-1.57
site 2	1.62	-0.79
site 3	2.43	-1.60
site 4	0.94	-0.11
site 5	1.85	-1.02
site 6	1.01	-0.18
site 7	1.35	-0.52

1					
CP-2	ΔG (3)	ΔG (4)	ΔG (5)	$\Delta G(6)$	ΔG (7)
single-site 1	-	-	-	-	
single-site 2	1.32	0.59	1.82	-0.46	
single-site 3	2.59	-0.69	1.83	-0.46	
single-site 4	1.14	-0.04	2.39	-0.22	
single-site 5	1.84	-0.74	3.14	-0.97	
single-site 6	1.10	0.21	2.24	-0.28	
single-site 7	1.41	0.36	2.05	-0.56	
dual-site 2	1.32	0.59	0.46	0.72	0.18
dual-site 3	2.59	-0.69	0.47	0.72	0.18
dual-site 4	1.14	-0.04	2.44	-0.61	0.34
dual-site 5	1.84	-0.74	2.44	-0.61	0.34

Table S9. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-2.

1					
CP-4	ΔG (3)	ΔG (4)	ΔG (5)	$\Delta G(6)$	ΔG (7)
single-site 1	-	-	-	-	
single-site 2	1.48	0.64	1.80	-0.66	
single-site 3	2.64	-0.51	1.80	-0.66	
single-site 4	1.36	0.02	2.42	-0.53	
single-site 5	1.84	-0.46	2.84	-0.95	
single-site 6	0.97	0.18	2.41	-0.29	
single-site 7	1.34	0.25	2.29	-0.62	
dual-site 2	1.48	0.64	0.83	0.27	0.05
dual-site 3	2.64	-0.51	0.83	0.27	0.05
dual-site 4	1.36	0.02	2.48	-0.64	0.05
dual-site 5	1.84	-0.46	2.48	-0.64	0.05

Table S10. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-4.

CP-5	ΔG (3)	ΔG (4)	$\Delta G(5)$	$\Delta G(6)$	ΔG (7)
single-site 1	2.15	-0.84	2.94	-0.98	
single-site 2	1.76	0.45	1.90	-0.85	
single-site 3	2.56	-0.35	1.90	-0.85	
single-site 4	1.34	0.21	2.16	-0.44	
single-site 5	2.08	-0.54	2.88	-1.16	
single-site 6	1.10	0.16	2.32	-0.32	
single-site 7	1.44	0.25	2.24	-0.66	
dual-site 2	1.76	0.45	0.69	0.46	-0.10
dual-site 3	2.56	-0.35	0.69	0.46	-0.10
dual-site 4	1.34	0.21	2.12	-0.29	-0.10
dual-site 5	2.08	-0.54	2.12	-0.29	-0.10

Table S11. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-5.

-					
CP-6	ΔG (3)	ΔG (4)	ΔG (5)	ΔG (6)	ΔG (7)
single-site 1	-	-	-	-	
single-site 2	1.85	0.34	1.99	-0.92	
single-site 3	2.33	-0.14	2.53	-1.46	
single-site 4	-	-	-	-	
single-site 5	1.95	-0.16	2.60	-1.12	
single-site 6	1.01	0.14	2.36	-0.24	
single-site 7	1.40	0.28	2.20	-0.62	
dual-site 2	1.85	0.34	1.44	0.45	-0.82
dual-site 3	2.33	-0.14	1.44	0.45	-0.82

Table S12. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-6.

1					
CP-7	ΔG (3)	ΔG (4)	ΔG (5)	ΔG (6)	ΔG (7)
single-site 1	-	-	-	-	
single-site 2	1.52	0.53	1.99	-0.77	
single-site 3	2.40	-0.35	1.99	-0.77	
single-site 4	2.86	-1.06	2.80	-1.32	
single-site 5	1.73	-0.47	2.98	-0.98	
single-site 6	1.00	0.38	2.19	-0.30	
single-site 7	1.39	0.53	2.01	-0.66	
dual-site 2	1.52	0.53	1.17	0.44	-0.40
dual-site 3	2.40	-0.35	1.17	0.44	-0.40

Table S13. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-7.

CP-8	$\Delta G(3)$	ΔG (4)	$\Delta G(5)$	$\Delta G(6)$	ΔG (7)
single-site 1	2.07	-0.48	2.66	-0.99	
single-site 2	1.77	0.38	2.07	-0.94	
single-site 3	2.34	-0.20	2.61	-1.49	
single-site 4	2.61	-1.11	2.72	-0.95	
single-site 5	1.90	0.09	2.36	-1.08	
single-site 6	1.02	0.35	2.18	-0.29	
single-site 7	1.40	0.49	2.02	-0.64	
dual-site 2	1.77	0.38	1.42	0.36	-0.66
dual-site 3	2.34	-0.20	1.42	0.36	-0.66

Table S14. The calculated Gibbs free energy changes (ΔG , eV) of 4*e* OER at pH = 7 on possible active sites in CP-8.

-		
CP-7	ΔG (8)	ΔG (9)
site 1	-	-
site 2	1.52	1.16
site 3	2.40	0.28
site 4	2.86	-0.18
site 5	1.73	0.94
site 6	1.00	1.68
site 7	1.39	1.28

Table S15. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* water oxidation reaction at pH = 7 on possible active sites in CP-7.

Note that "-" represents that the *OH intermediate could not be adsorbed on the active site.

Table S16. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* water oxidation reaction at pH = 7 on possible active sites in CP-8.

1		
CP-8	ΔG (8)	ΔG (9)
site 1	2.07	0.60
site 2	1.77	0.91
site 3	2.34	0.33
site 4	2.61	0.06
site 5	1.90	0.78
site 6	1.02	1.65
site 7	1.40	1.28

CP-3	ΔG (1)	ΔG (2)
site 1	2.73	-1.90
site 2	1.81	-0.98
site 3	2.61	-1.78
site 4	1.22	-0.39
site 5	2.20	-1.37
site 6	1.13	-0.30
site 7	1.44	-0.62

Table S17. The calculated Gibbs free energy changes (ΔG , eV) of 2*e* HER at pH = 7 on possible active sites in CP-3.

References

1 E. Skulason, G. S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jonsson and J. K. Nørskov, Density functional theory calculations for the hydrogen evolution reaction in an electrochemical double layer on the Pt(111) electrode, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3241-3250.

2 V. Wang, N. Xu, J. C. Liu, G. Tang and W. T. Geng, VASPKIT: A user-friendly interface facilitating high-throughput computing and analysis Using VASP Code, *Comput. Phys. Commun.*, 2021, **67**, 108033.

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, et al. Gaussian 16, Revision C.01, Gaussian, Inc., Wallingford CT, 2016.