

Electronic Supplementary Information

Novel Quadrilateral-pore 2D-COFs as Visible-Light Driven Catalysts Evaluated by the Descriptor of Integrated p_z -orbital population

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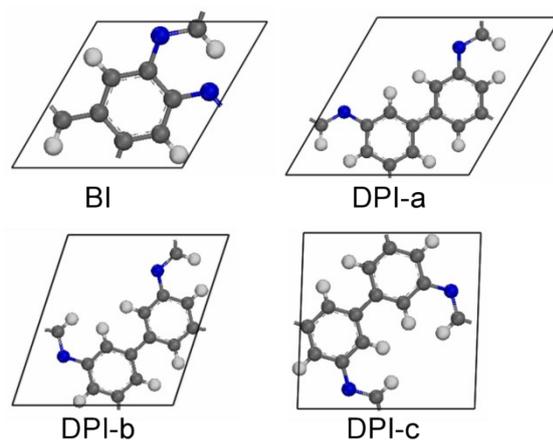


Figure S1. The periodical structures of the BI, DPI-a, DPI-b and DPI-c.

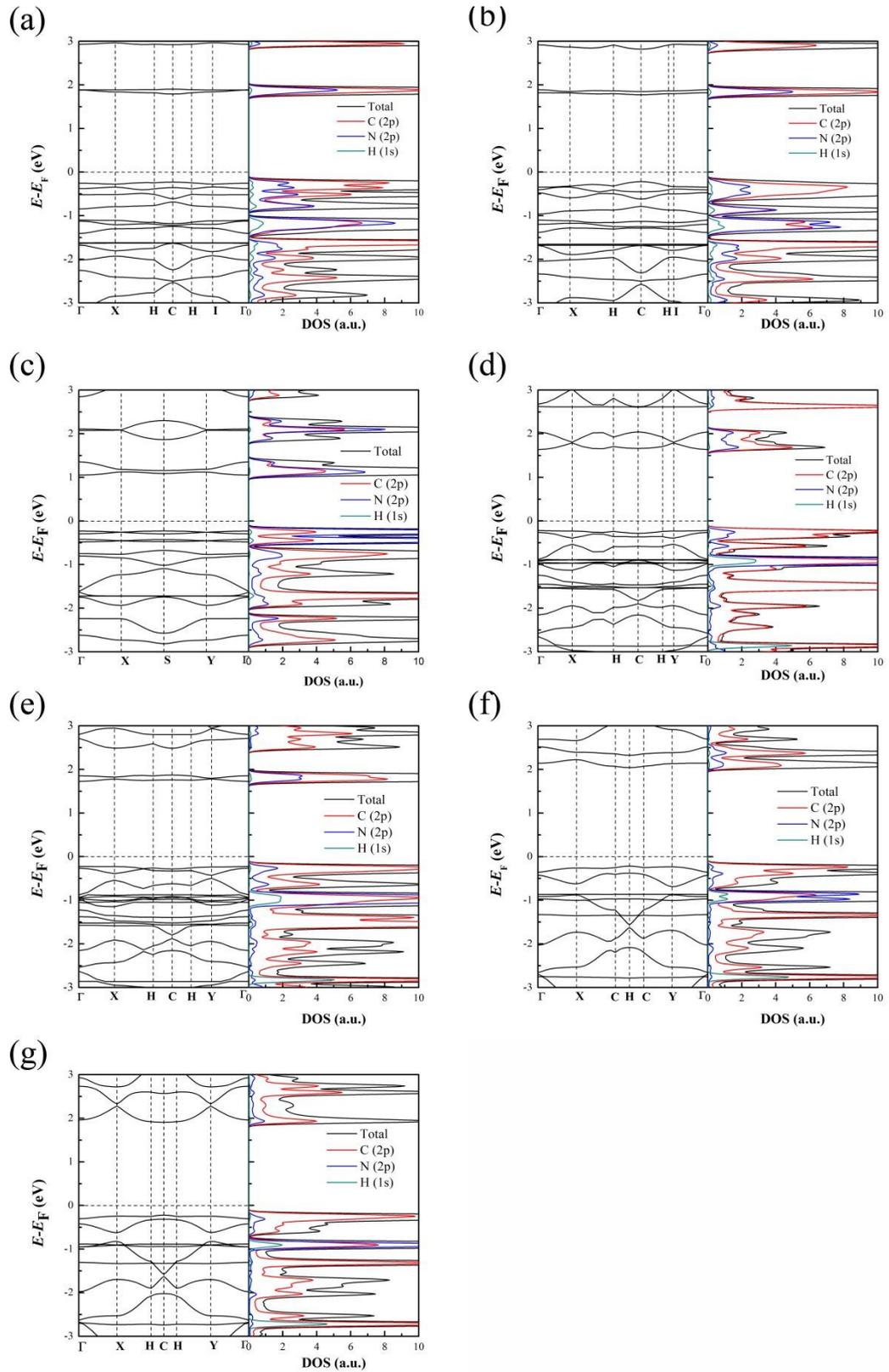


Figure S2. Band structures and density of states (DOS) of the (a) DPBI-b, (b) DPBI-c, (c) DPBA (d) TPBI-b, (e) TPBI-c, (f) TPI-a and (g) TPI-b, respectively. Fermi level was set to zero.

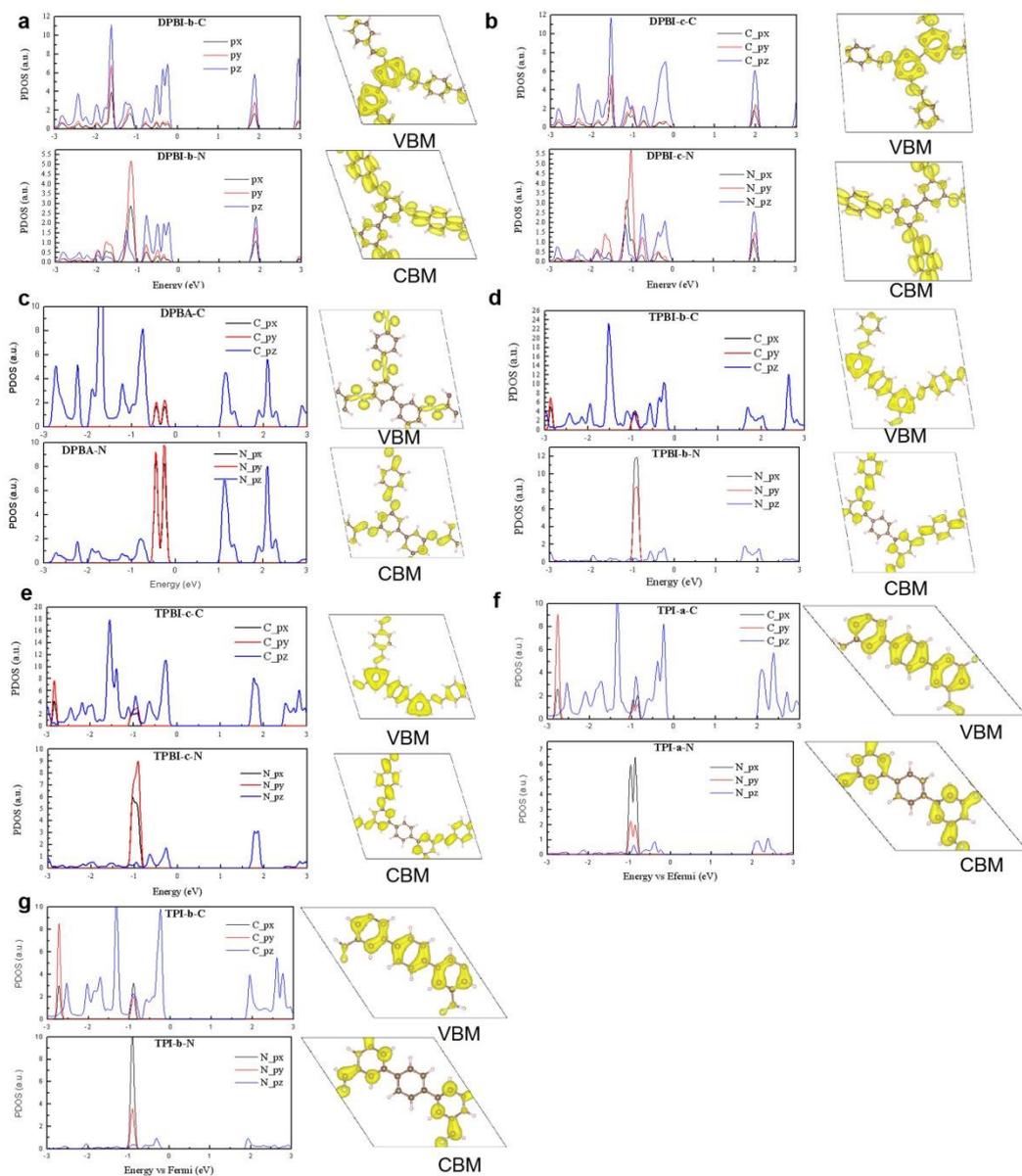


Figure S3. Projected density of states (PDOS) on atomic orbitals and charge densities of the VBM and CBM for the (a) DPBI-b, (b) DPBI-c, (c) DPBA (d) TPBI-b, (e) TPBI-c, (f) TPI-a and (g) TPI-b, respectively. Fermi level was set to zero.

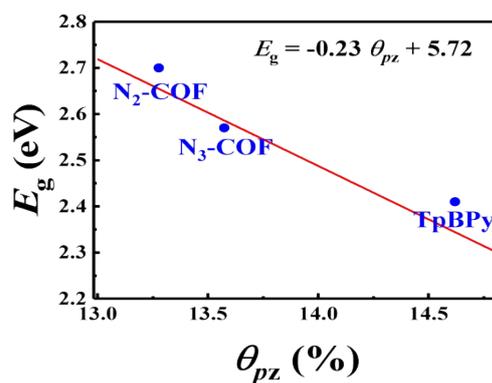


Figure S4. Predicted and corresponding experimental band gaps versus the descriptor θ_{pz} . The line represents the corrected linear relationship between the band gaps and the θ_{pz} .

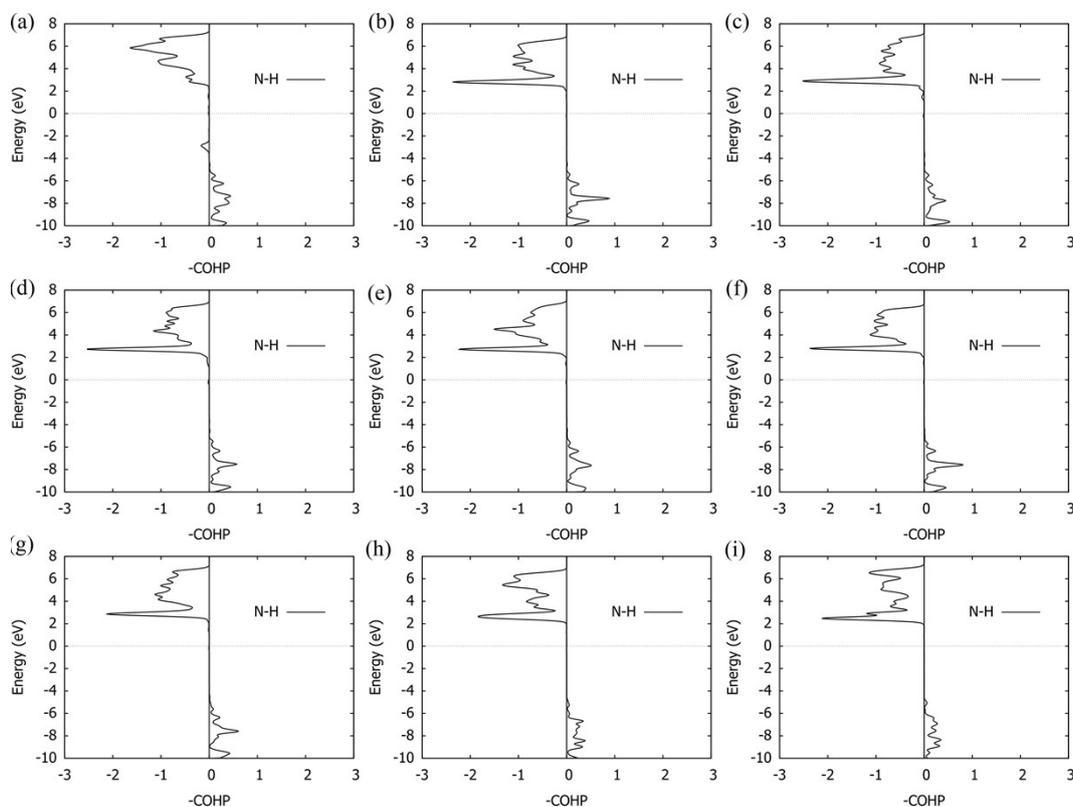


Figure S5. COHP bonding analysis of the N-H interaction on the N active sites of the (a) BBI, (b) DPBI-a, (c) DPBI-b, (d) DPBI-c, (e) TPBI-a, (f) TPBI-b, (g) TPBI-c, (h) TPI-a and (i) TPI-b. The Fermi levels were set to zero energy. The bonding interaction occurs at COHP larger than zero, whereas the anti-bonding interaction occurs at COHP smaller than zero.

Table S1 The integrated pz-orbital population (θ_{pz} , %), experimental band gaps (E_g , eV) and free energy changes of H adsorption (ΔG_{H^*} , eV) for the 6 photocatalytic 2D-COFs.

	N ₂ -COF ^{a)}	N ₃ -COF ^{a)}	Tp-BPy ^{b)}
θ_{pz}	13.27	13.57	14.62
E_g	2.70 ^{a)}	2.57 ^{a)}	2.41 ^{b)}
$\Delta G_{H^*}(U_e > 0)$	-3.30	-2.93	-3.05

a) Cited from Ref. [32]. The values in parenthesis are reported in experiment. b) Cited from Ref. [53]. The value in parenthesis is reported in experiment.

Reference

[32] V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld and B. V. Lostch, *Nat. Comm.*, 2015, **6**, 8508.

[53] Z. Mi, T. Zhou, W. Weng, J. Unruangsri, K. Hu, W. Yang, C. Wang, K. A.-I. Zhang and J. Guo, *Angew. Chem. Int. Ed.*, 2021, **60**, 9642-9649.