

Electronic supplementary information

Investigating the factors that influence sacrificial hydrogen evolution activity for three structurally-related molecular photocatalysts: thermodynamic driving force, excited-state dynamics, and surface interaction with cocatalysts

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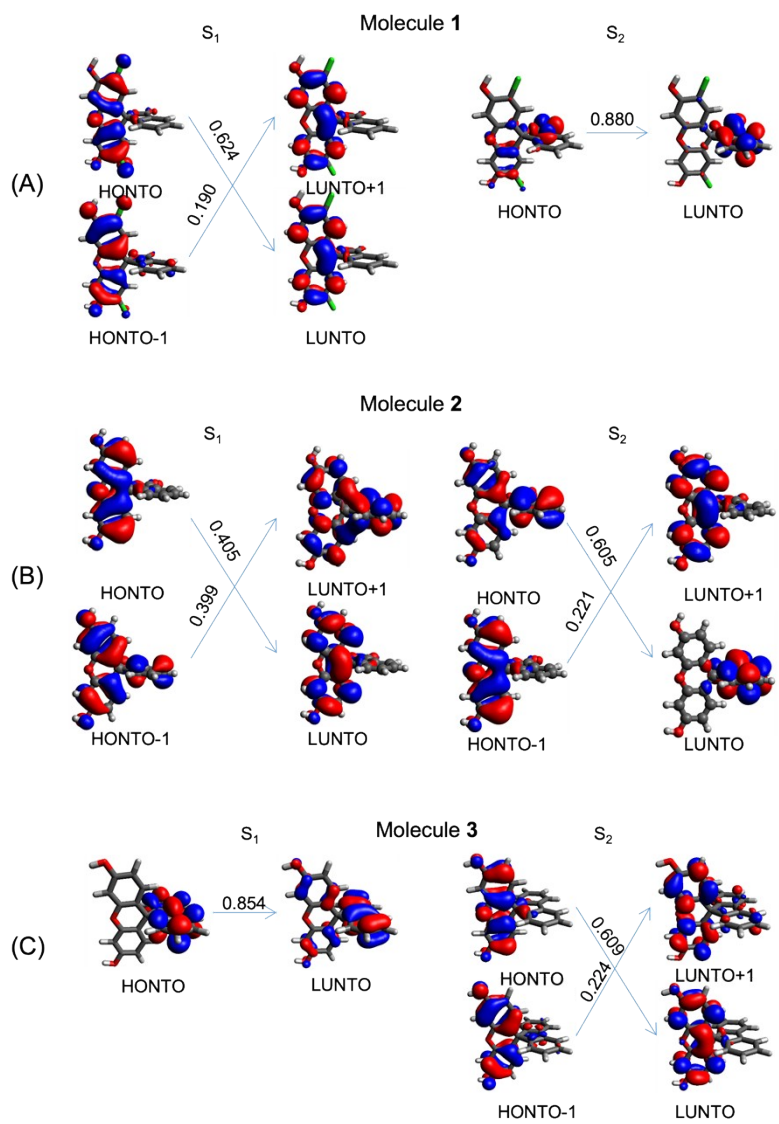


Figure S1. Natural transition orbitals (NTOs) for the dominant component transition of each of the first (S_1) and second (S_2) excited states for molecules **1** (A), **2** (B), and **3** (C), with the corresponding transition coefficients shown.

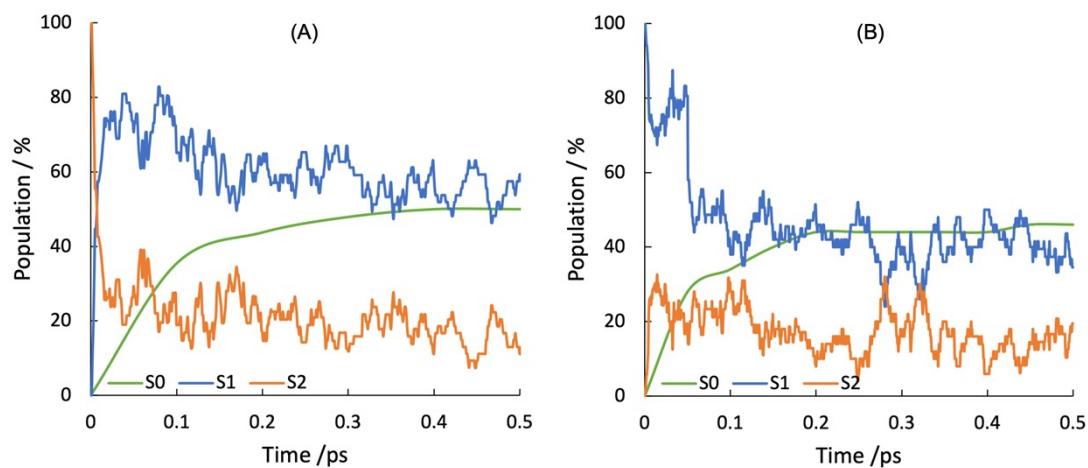


Figure S2. Dynamics of state-specific populations following photoexcitation for molecules **3**. Left: all initial states started on S2 (*i.e.*, Figure 3C of the main text). Right: all initial states started on S1, because of the much larger oscillator strength of S1 than that of S2.

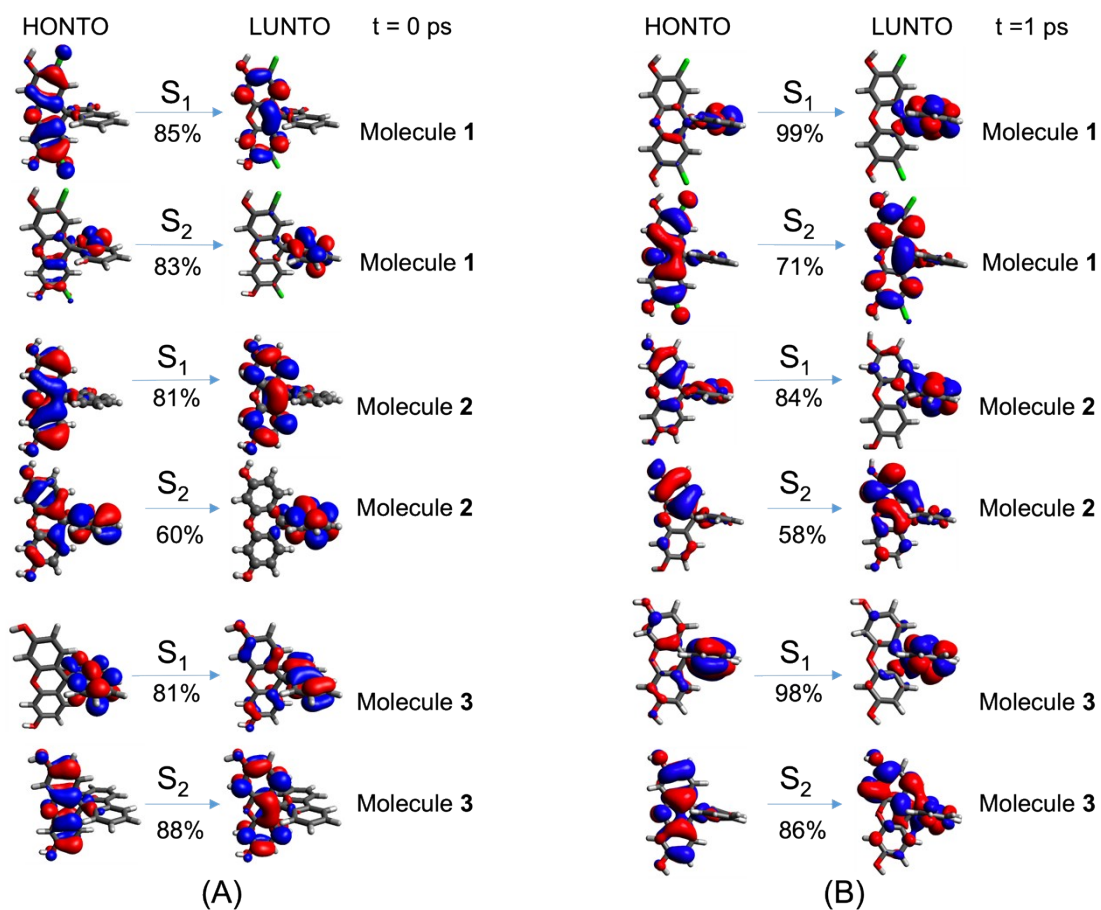


Figure S3. The frontier natural transition orbitals (NTOs; HO: highest occupied, LU: lowest unoccupied) of the first (S_1) and second (S_2) excited states of molecules 1 to 3 at $t = 0$ ps (A) and $t = 1$ ps (B); isosurface = 0.03 a.u.

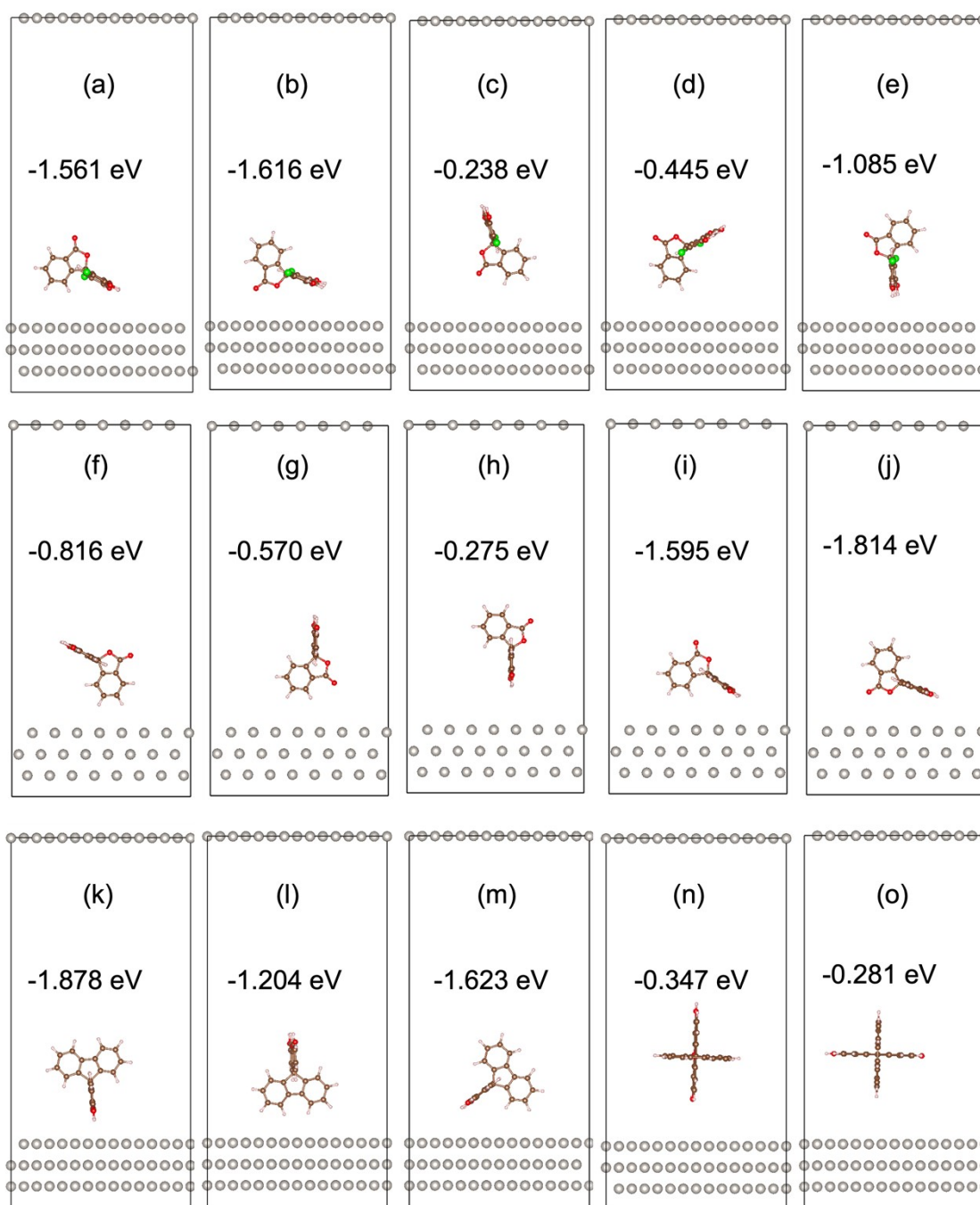


Figure S4. Different adsorption configurations of molecules **1** (a–e), **2** (f–j), and **3** (k–o) on the Pt(111) surface, together with binding energies.

Computational details

All DFT and TD-DFT calculations made use of the CAM-B3LYP density functional, together with the 6-31G* basis set. IP, EA, EA* and IP* are standard reduction potentials of half-reactions for free electrons/holes and excitons and were calculated adiabatically with molecular geometries fully optimized for the respective states. The effect of solvation by water was accounted for using the PCM/SMD solvation model.

S_r and E_C are descriptors from quantitative characterization of hole and electron distributions in real space, performed for the optimized S_1 state, using the Multiwfn software. S_r index quantifies the overlap between the hole distribution ($\rho^{\text{hole}}(\mathbf{r})$) and the electron distribution ($\rho^{\text{electron}}(\mathbf{r})$). S_r varies between 0 (no overlap) and 1 (complete overlap); the larger the value is, the greater the extent of overlap is. E_C is the Coulomb attraction energy between the electron and hole, given by

$$E_C = \iint \frac{\rho^{\text{hole}}(r_1)\rho^{\text{electron}}(r_2)}{|r_1 - r_2|} dr_1 dr_2$$

Table S1. Calculated values of S_r and E_C for molecules **1**, **2**, and **3**.

	S_r / a.u.	E_C / eV
Molecule 1	0.855	5.069
Molecule 2	0.739	3.404
Molecule 3	0.788	5.492

TD-DFT S1 and S2 results:

Molecule 1

Excited State 1: Singlet-A 4.9175 eV 252.13 nm f=0.0273 <S**2>=0.000

Excited State 2: Singlet-A 5.0955 eV 243.32 nm f=0.4042 <S**2>=0.000

Molecule 2

Excited State 1: Singlet-A 5.0291 eV 246.53 nm f=0.0096 <S**2>=0.000

Excited State 2: Singlet-A 5.0770 eV 244.21 nm f=0.1557 <S**2>=0.000

Molecule 3

Excited State 1: Singlet-A 4.6608 eV 266.01 nm f=0.6695 <S**2>=0.000

Excited State 2: Singlet-A 4.9917 eV 248.38 nm f=0.0036 <S**2>=0.000

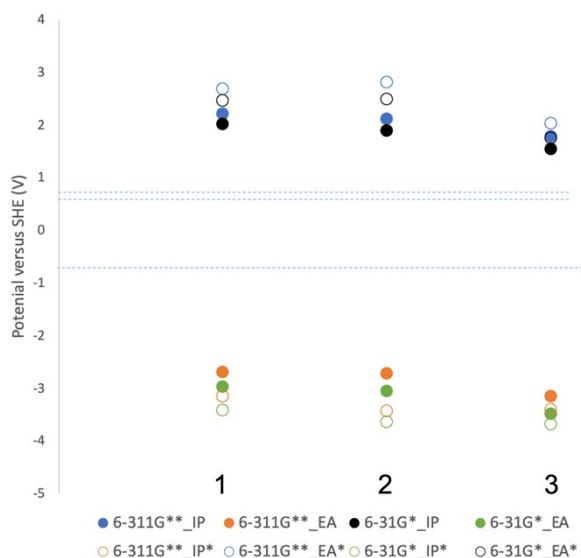


Figure S5. Comparison of basis sets for calculated IP, EA, IP*, and EA*.

Table S2. Comparison of basis sets for calculated values of S_r and E_C .

	6-31G*		6-311G**	
	S_r / a.u.	E_C / eV	S_r / a.u.	E_C / eV
Molecule 1	0.855	5.069	0.772	4.252
Molecule 2	0.739	3.404	0.808	4.038
Molecule 3	0.788	5.492	0.704	4.400

Periodic DFT calculations of adsorption configurations for molecules **1**, **2**, and **3** on the Pt(111) surface were carried out within the plane-wave pseudopotential formalism, using the Vienna *ab initio* Simulation Package (VASP) code. A kinetic-energy cutoff of 400 eV was used to define the plane-wave basis set, and the electronic Brillouin zone was sampled by Γ -centred Monkhorst–Pack grids using $1 \times 1 \times 1$ k -point for all the calculations. Geometry optimizations on atomic positions were performed employing the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional with the DFT-D3(BJ) dispersion correction. Tolerances of 10^{-6} eV and 0.02 eV \AA^{-1} were applied during the optimization of the Kohn–Sham wavefunctions and the geometry optimizations, respectively.

The binding energy of a single molecule **1/2/3** on the Pt(111) surface was calculated by

$$E_{\text{binding}} = E[\text{molecule@Pt(111)}] - E[\text{molecule}] - E[\text{Pt(111)}]$$

where $E[\text{molecule@Pt(111)}]$, $E[\text{molecule}]$, and $E[\text{Pt(111)}]$ are the total energies of the adsorption complex, isolated molecule, and empty Pt(111) surface, respectively. $E[\text{molecule}]$ was calculated by placing a single molecule **1**, **2** or **3** in a $19.22 \text{ \AA} \times 19.42 \text{ \AA} \times 40 \text{ \AA}$ box. Four layers of Pt was 6.9 \AA in thickness and placed on the ab plane of the simulation cell. The Pt(111) surface had an in-plane dimension of $a = 19.22 \text{ \AA}$, $b = 19.42 \text{ \AA}$ and was isolated on both sides by a vacuum layer of 33.1 \AA along the c direction.

Experimental details

Materials. Molecules **1** to **3** were purchased from commercial suppliers and used without further purification. Water for the hydrogen evolution experiments was purified using an ELGA LabWater system with a Purelab Option S filtration and ion exchange column ($\rho = 15 \text{ M}\Omega \text{ cm}$) without pH level adjustment.

Photocatalytic hydrogen evolution experiments. Agilent Technologies vials (10 mL) were charged with 5.0 ± 0.1 mg of small molecules and transferred to a Chemspeed Accelerator SWING robot for liquid transfer. Degassed jars with triethylamine, methanol, and a stock solution of H_2PtCl_6 were loaded into the automated liquid handling platform. The system was then closed and purged for 4 h with nitrogen. The automated liquid handling platform then dispensed the liquids as specified, which were degassed aqueous H_2PtCl_6 solution (1.7 mL, 3wt % Pt to small molecules), triethylamine (1.7 mL), and methanol (1.7 mL). The pH of the solution was around 11.5. The vials were then capped using the capper/crimper tool under inert conditions. Once capped, the samples were taken out, shaken briefly, and transferred to an ultrasonic bath to disperse the photocatalysts. An Oriel Solar Simulator 94123A with an output of 1.0 sun was then used to illuminate the vials on a Stuart roller bar SRT9 for the time specified (classification IEC 60904-9 2007 spectral match A, uniformity classification A, temporal stability A, 1600 W xenon light source, 12×12 in.2 output beam, air mass 1.5 G filter, 350–1000 nm). After photocatalysis, the gaseous products of the samples were measured on an Agilent gas connected to a headspace sampler (HS) and Shimadzu GC-HS. No hydrogen evolution was observed for mixtures of water/triethylamine/methanol or water/triethylamine/methanol/ H_2PtCl_6 under the identical conditions.

UV-Vis spectra of molecules **1** to **3**

There is significant difference in light absorption for the three molecules, as shown in Figure S6. As the spectrum of AM 1.5 lamp (used in HT screen) is from 350 to 1000 nm, molecule **3** sits on the edge of this spectrum. Hence, the photocatalytic hydrogen production of molecule **3** was also carried out by using Xenon lamp with a cut-off filter 295 nm (> 295 nm, light wavelength); after 3 hours, only 1 micromole of

hydrogen was observed. This indicates that the low activity of molecule **3** is not solely due to its poor light-harvesting ability in comparison to molecule **1** and **2**.

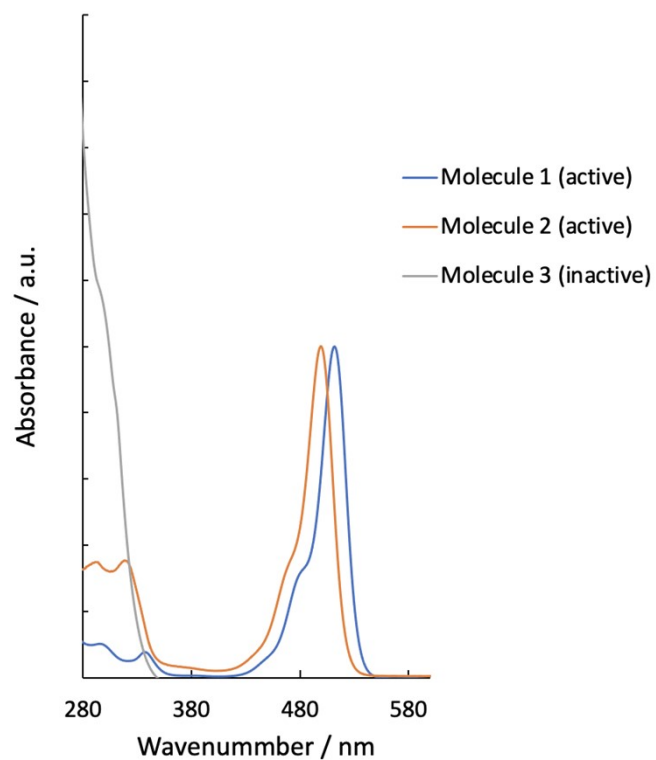


Figure S6. Experimental light absorption of molecules **1** (blue), **2** (orange), and **3** (grey).