

Electronic Supplementary Information

**Rational modifications on champion porphyrin dye SM315 by using different
electron-withdrawing moieties toward high performance dye-sensitized solar cells**

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Computational details for optimization of dye-(TiO₂)₃₈ system using Siesta

The optimization of dye/(TiO₂)₃₈ systems were performed by means of SIESTA package, employing norm-conserving pseudopotentials (Troullier–Martins nonlocal form) and localized atomic orbitals as basis set.¹⁻³ The dye-(TiO₂)₃₈ structure was considered fully relaxed when the magnitude of forces on the atoms was smaller than 0.04 eV/Å. Standard DFT using the general gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)⁴ and double- ζ plus polarization (DZP) basis set with an equivalent real-space mesh cutoff 250 Ry were used to optimize the geometries of the studied systems in this work.

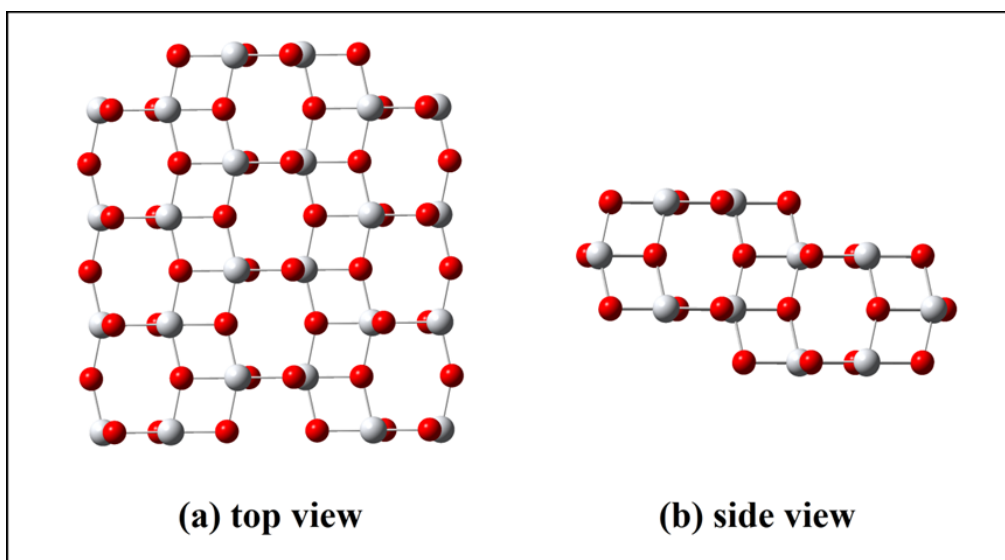
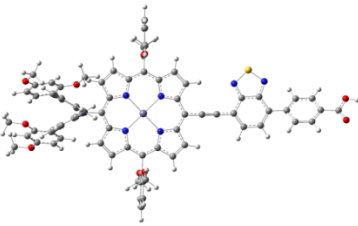
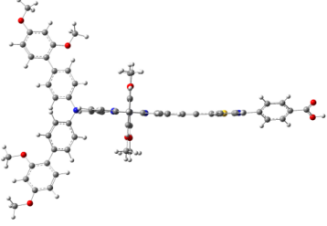
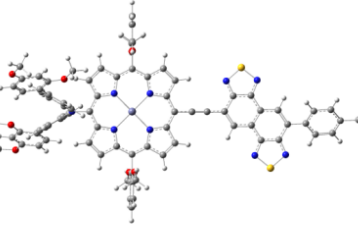
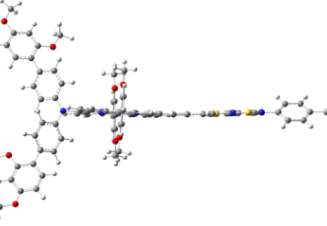
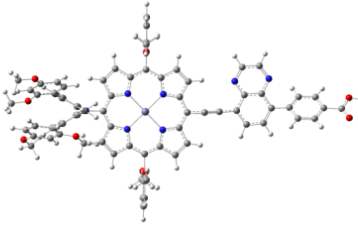
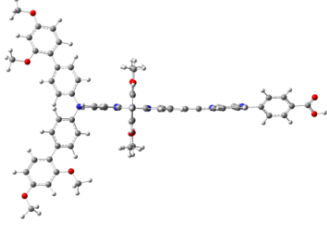
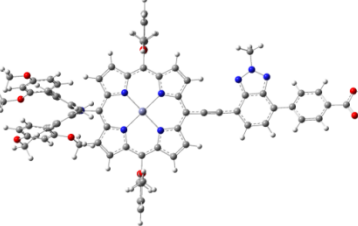
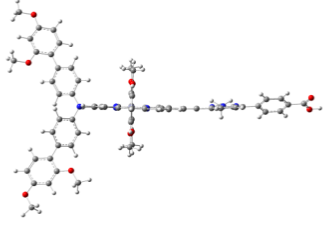
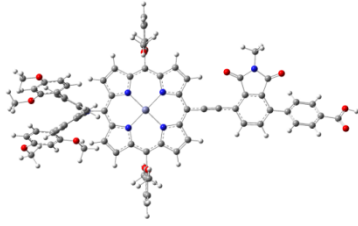
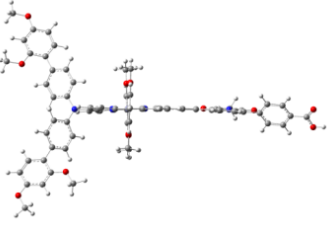
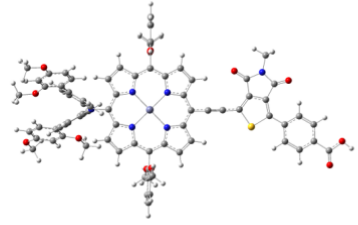
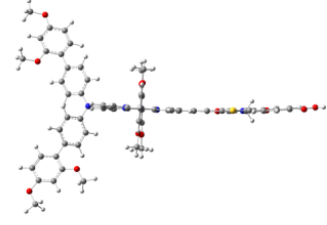
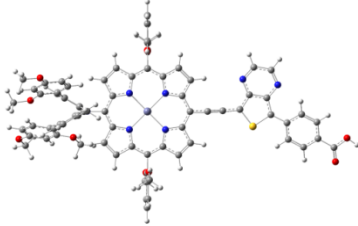
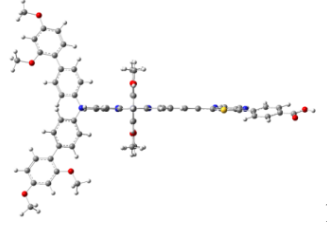


Fig. S1. Initial structure of $(\text{TiO}_2)_{38}$ cluster in side and top view.

Dye	Front view	Side view
SM315		 37.23°
1		 37.75°
2		 45.67°
3		 30.97°
4		 46.95°
5		 4.35°
6		 18.60°

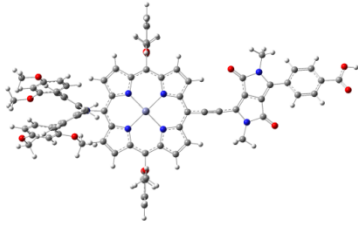
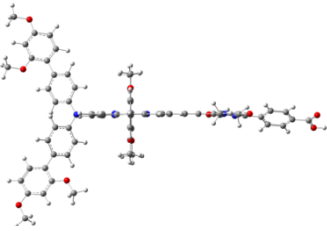
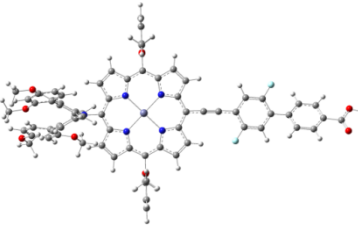
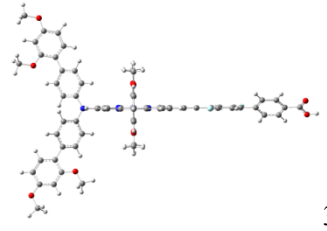
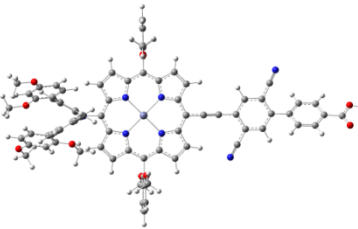
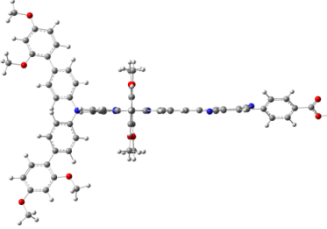
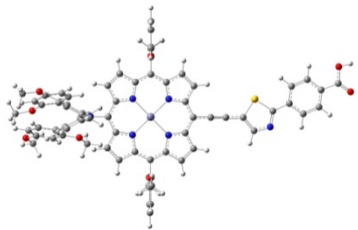
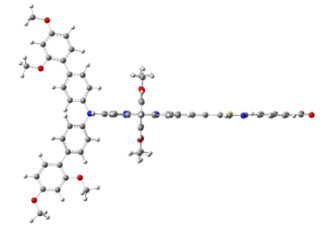
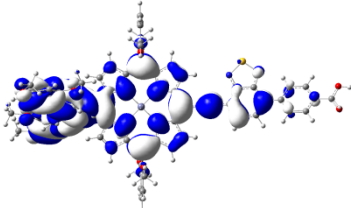
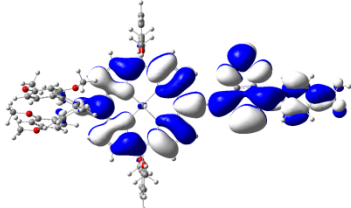
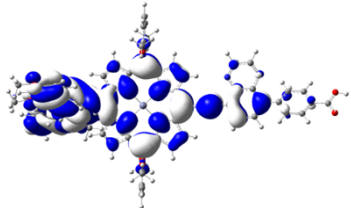
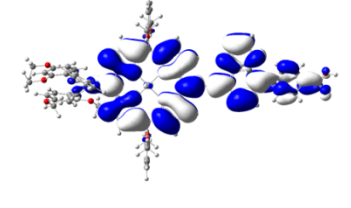
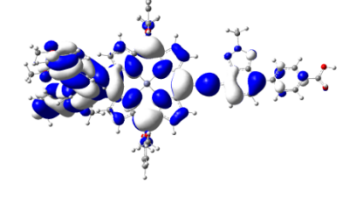
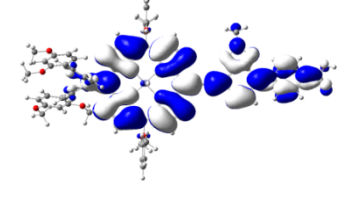
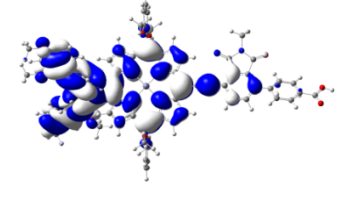
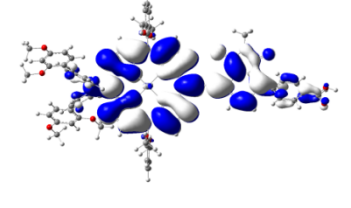
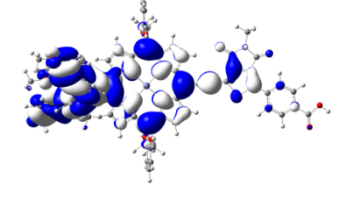
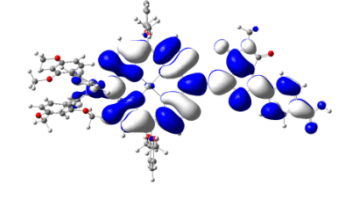
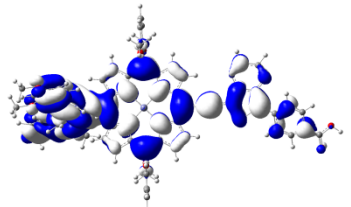
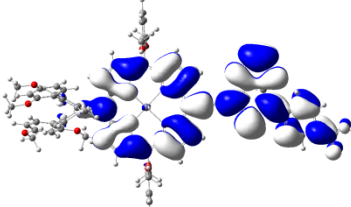
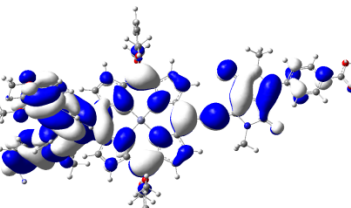
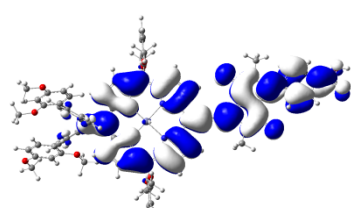
7		 <p style="text-align: right;">26.96°</p>
8		 <p style="text-align: right;">39.06°</p>
9		 <p style="text-align: right;">46.15°</p>
10		 <p style="text-align: right;">0.70°</p>

Fig. S2 The optimized geometries of reference dye **SM315** and designed dyes at PCM-M06/6-31G*(LANL2DZ for Zn atom) level in THF solvent as well as the dihedral angle between the EWG and the acceptor part (benzoic acid).

Dye	HOMO	LUMO
SM315		
2		
3		
4		
5		
6		
7		

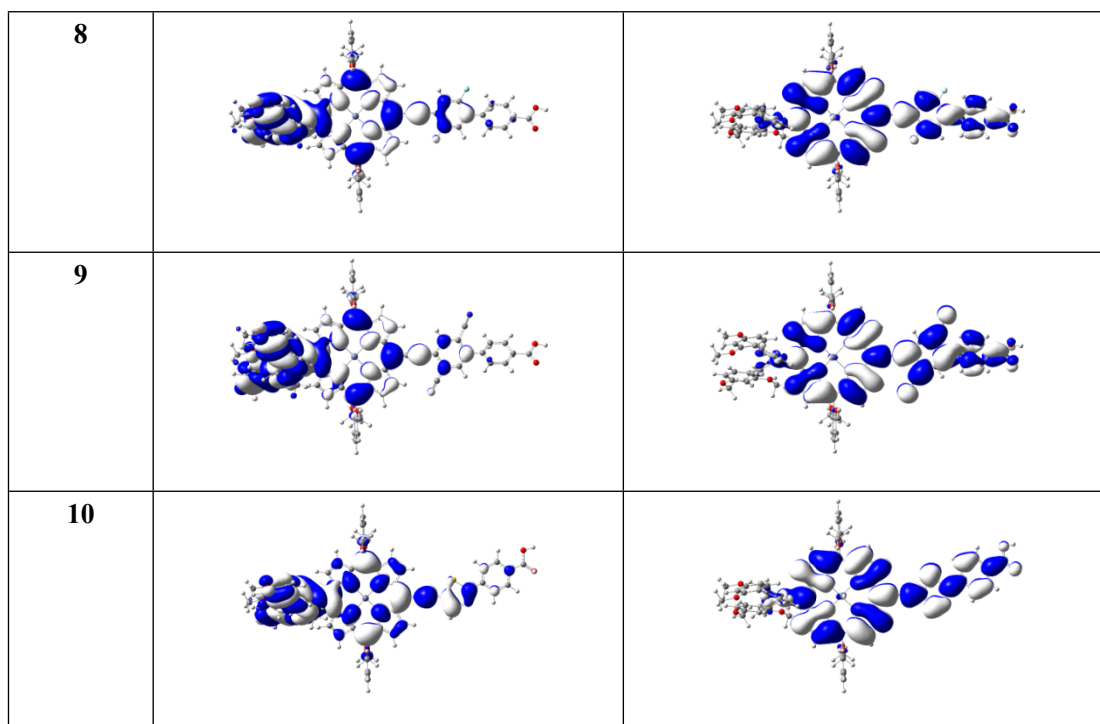


Fig. S3 Illustration of the frontier molecular orbitals of designed dyes at PCM-M06/6-311G** level in THF solvent with iso-surface of 0.01 au.

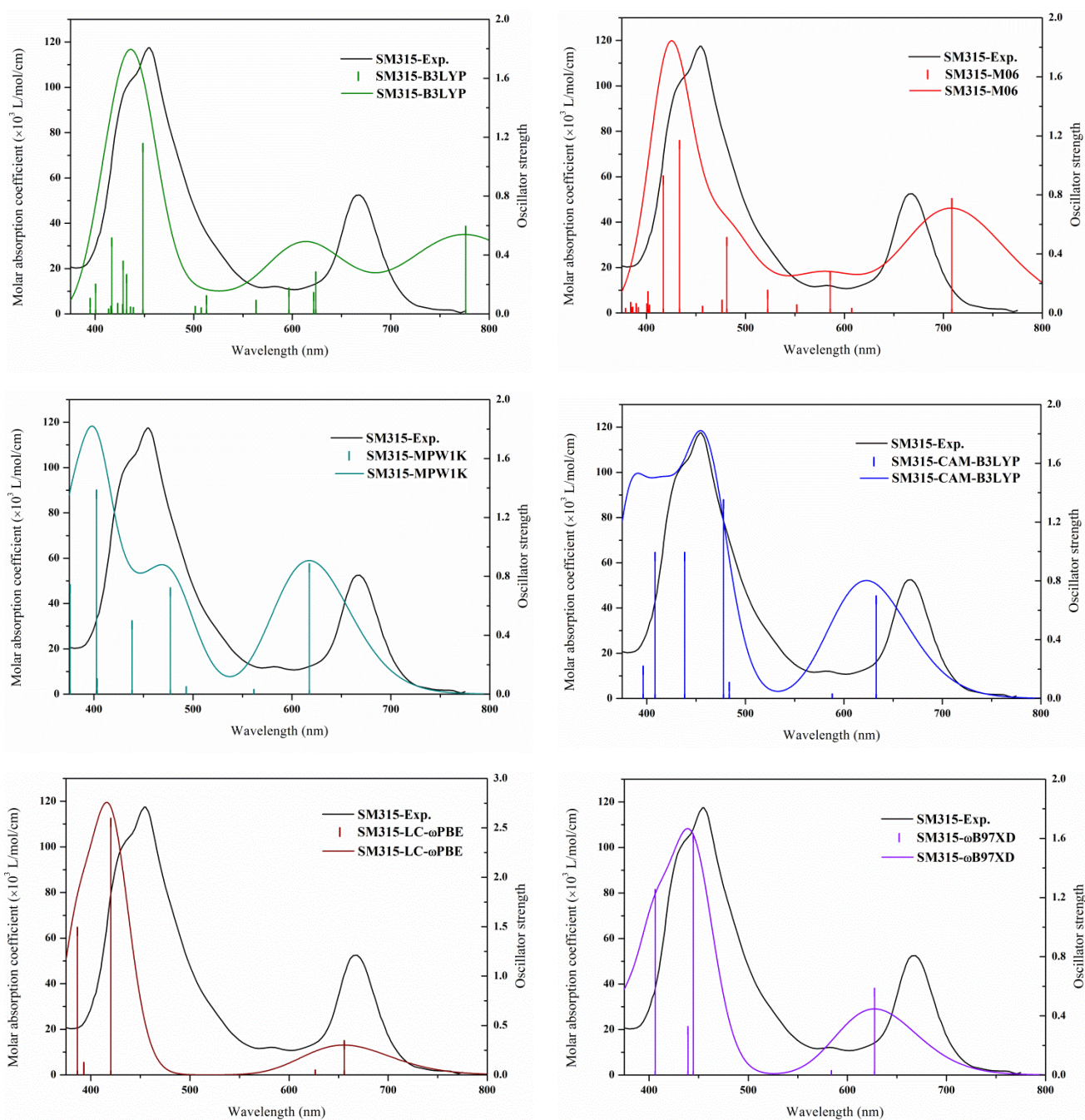


Fig. S4 The experimental spectrum (in THF) of **SM315** (taken from ref.5), and the theoretical electronic transitions as well as the simulated spectra under PCM-TD-Functional/6-31+G* level. (The theoretical spectra were simulated with Multiwfn program,^{6, 7} using Gaussian functions with full width at half maximum (FWHM) of 0.3 eV)

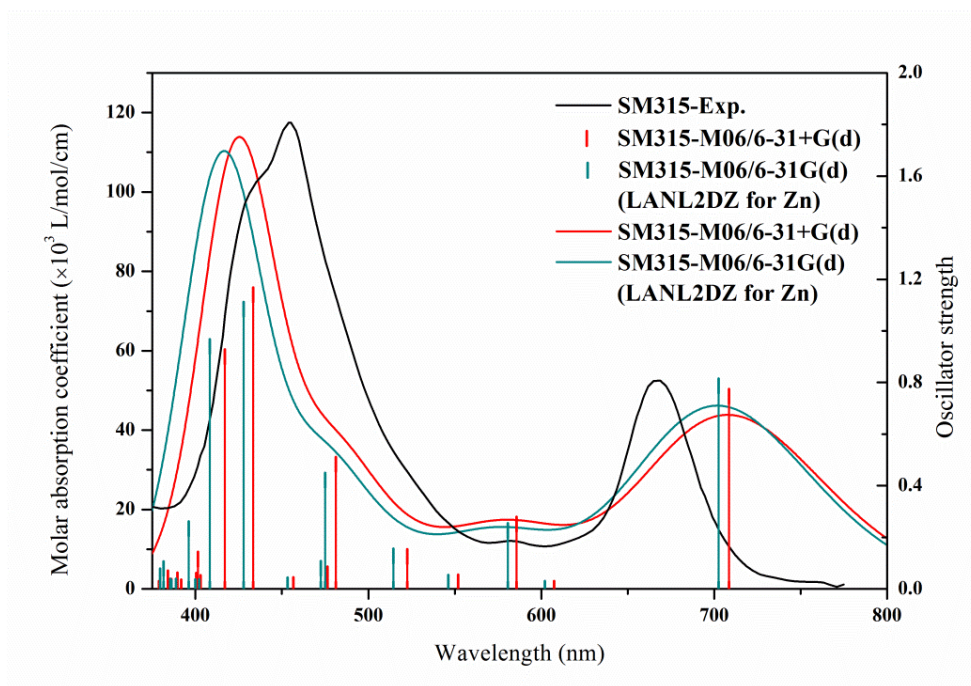


Fig. S5 The experimental spectrum (in THF) of **SM315** (taken from ref. 5), and the theoretical electronic transitions as well as the simulated spectra under PCM-TD-M06/Basis Set level.

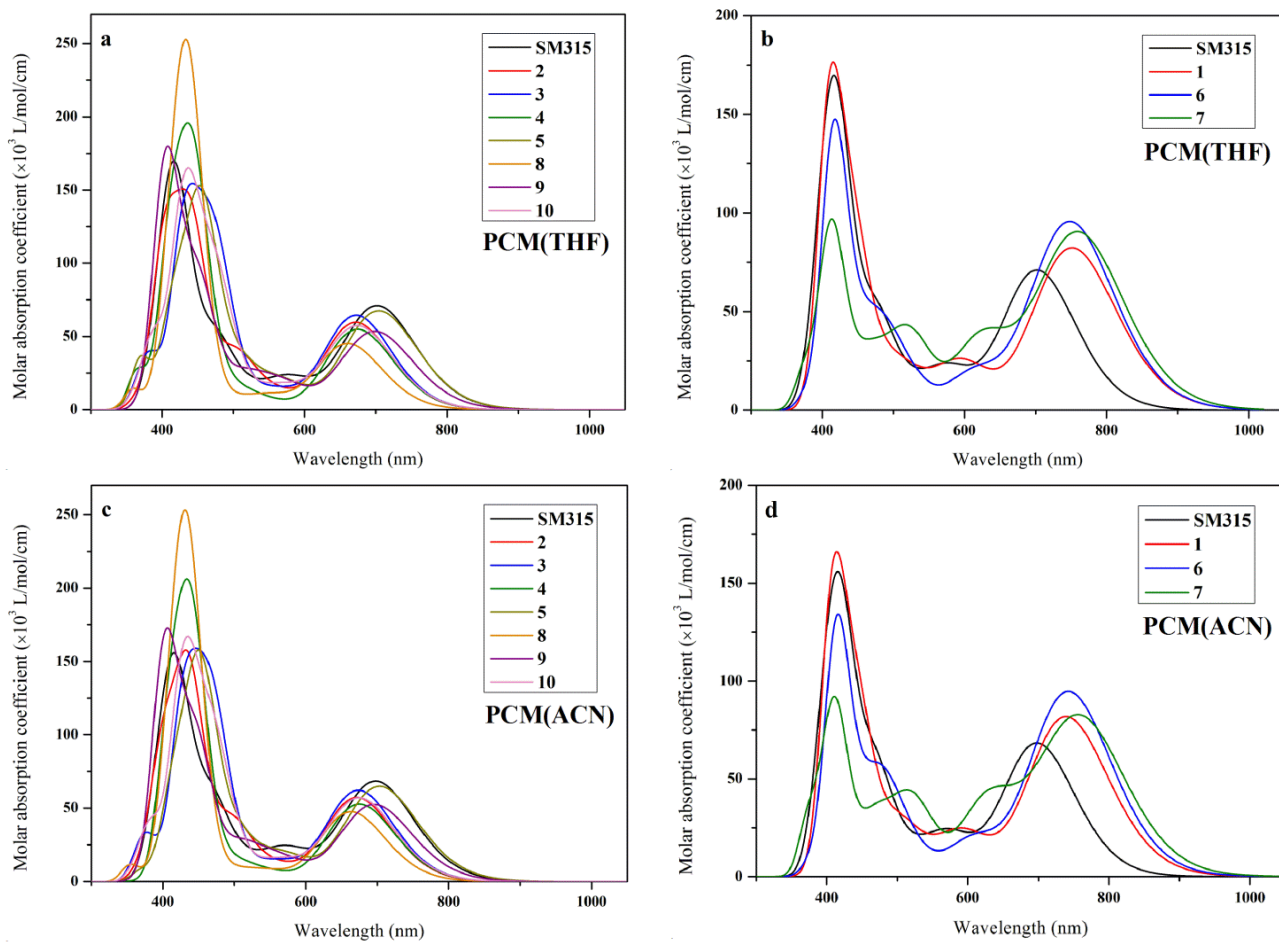


Fig. S6 Simulated absorption spectra of porphyrin dyes under study at PCM-TD- M06/6-31G*(LANL2DZ for Zn atom) level.

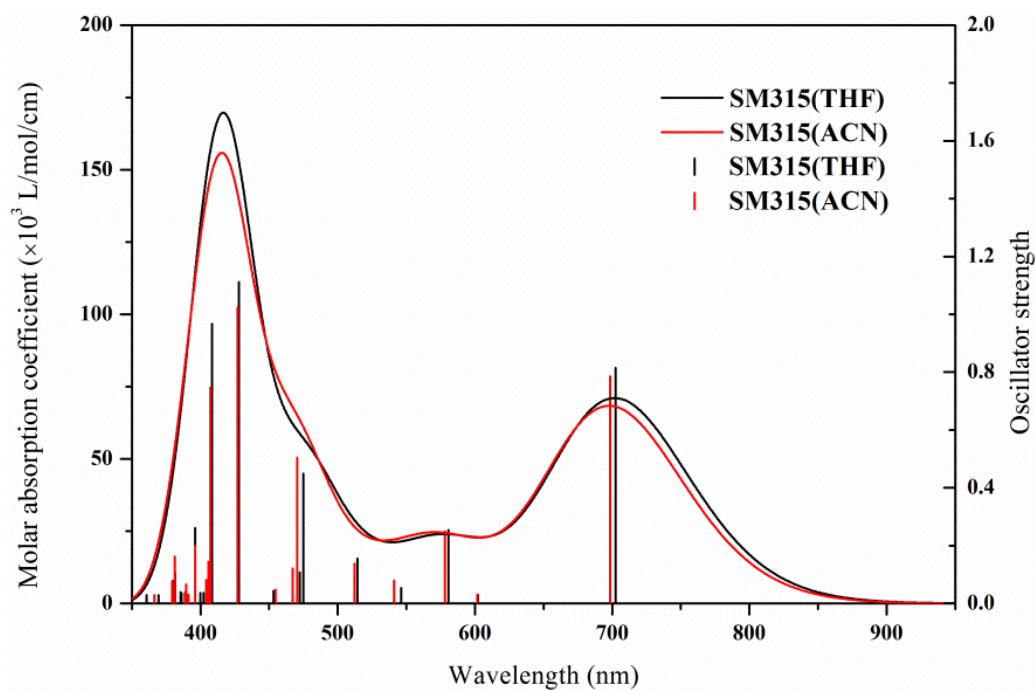


Fig. S7 The theoretical electronic transitions as well as the simulated spectra under PCM-TD-M06/6-31G*(LANL2DZ for Zn atom) of SM315.

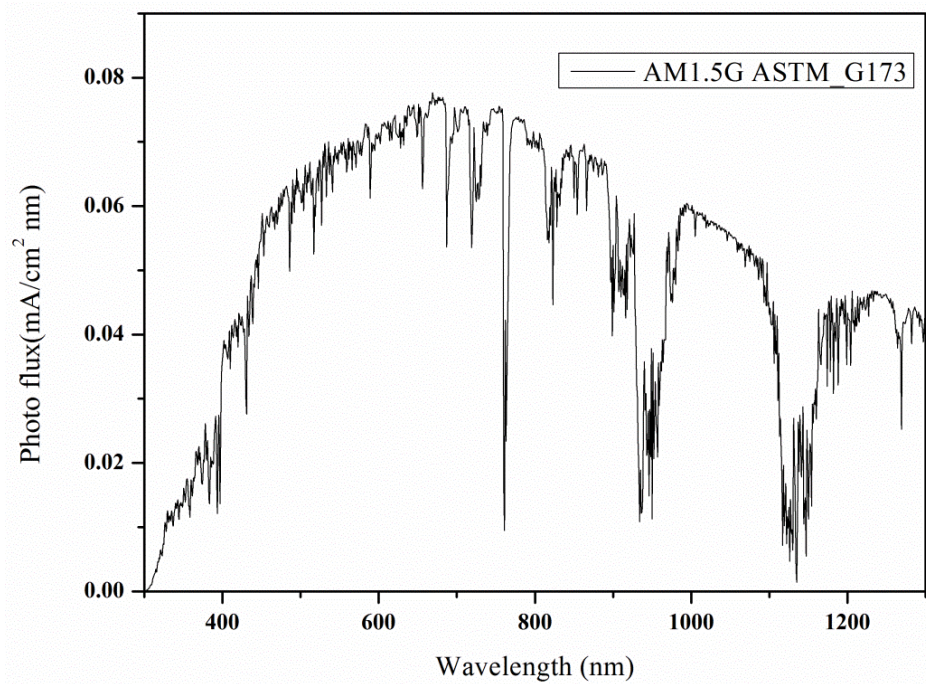


Fig. S8 The standard solar photo flux spectrum for AM1.5 irradiation

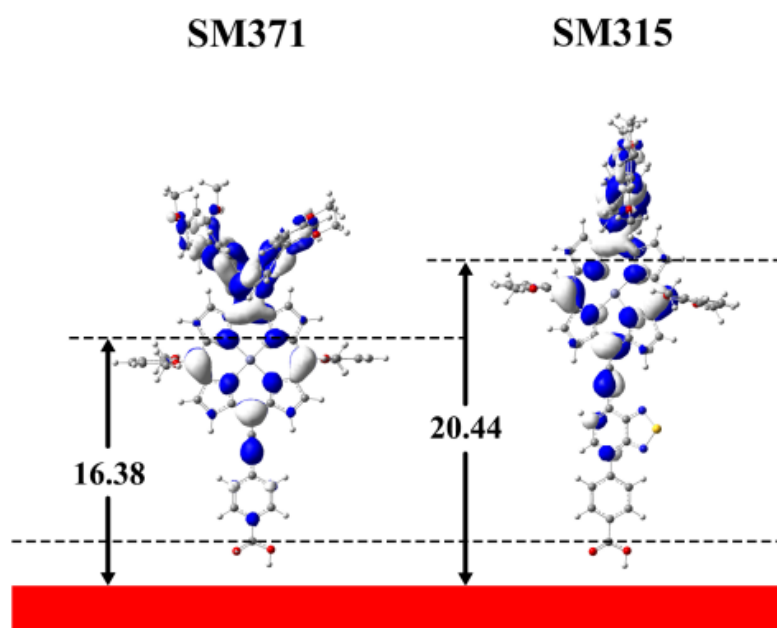


Fig. S9 Illustration of distance (\AA) between the dye cation hole and the semiconductor surface.

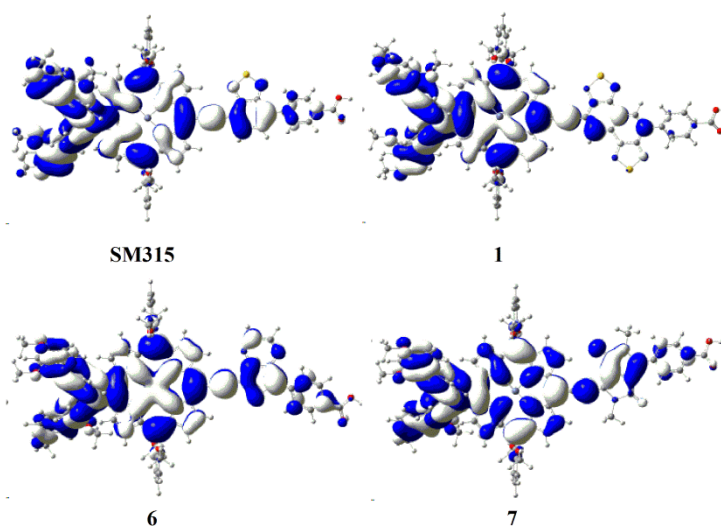


Fig. S10 The distributions of cation hole for SM315, 1, 6 and 7 at PCM-M06/6-31G*(LANL2DZ for Zn atom) level in THF solvent with iso-surface of 0.01 au.

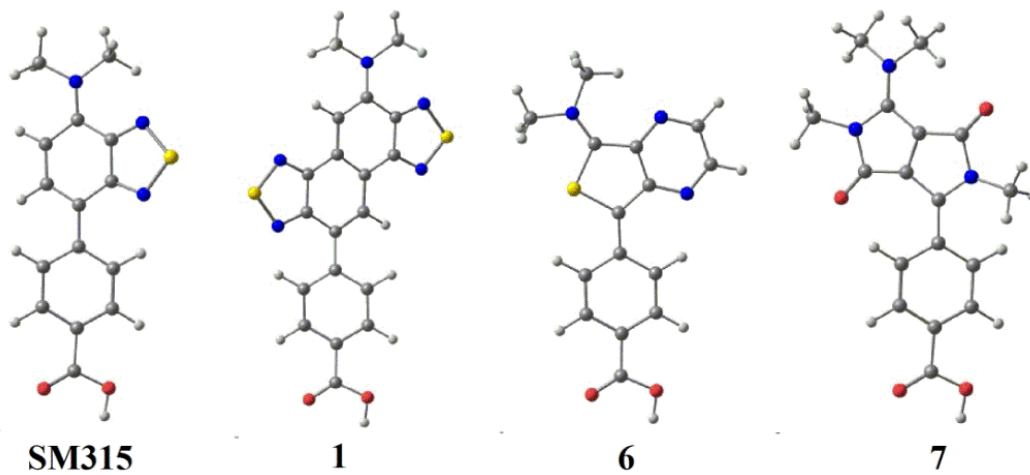


Fig. S11. Molecular structures of simplified sensitizers.

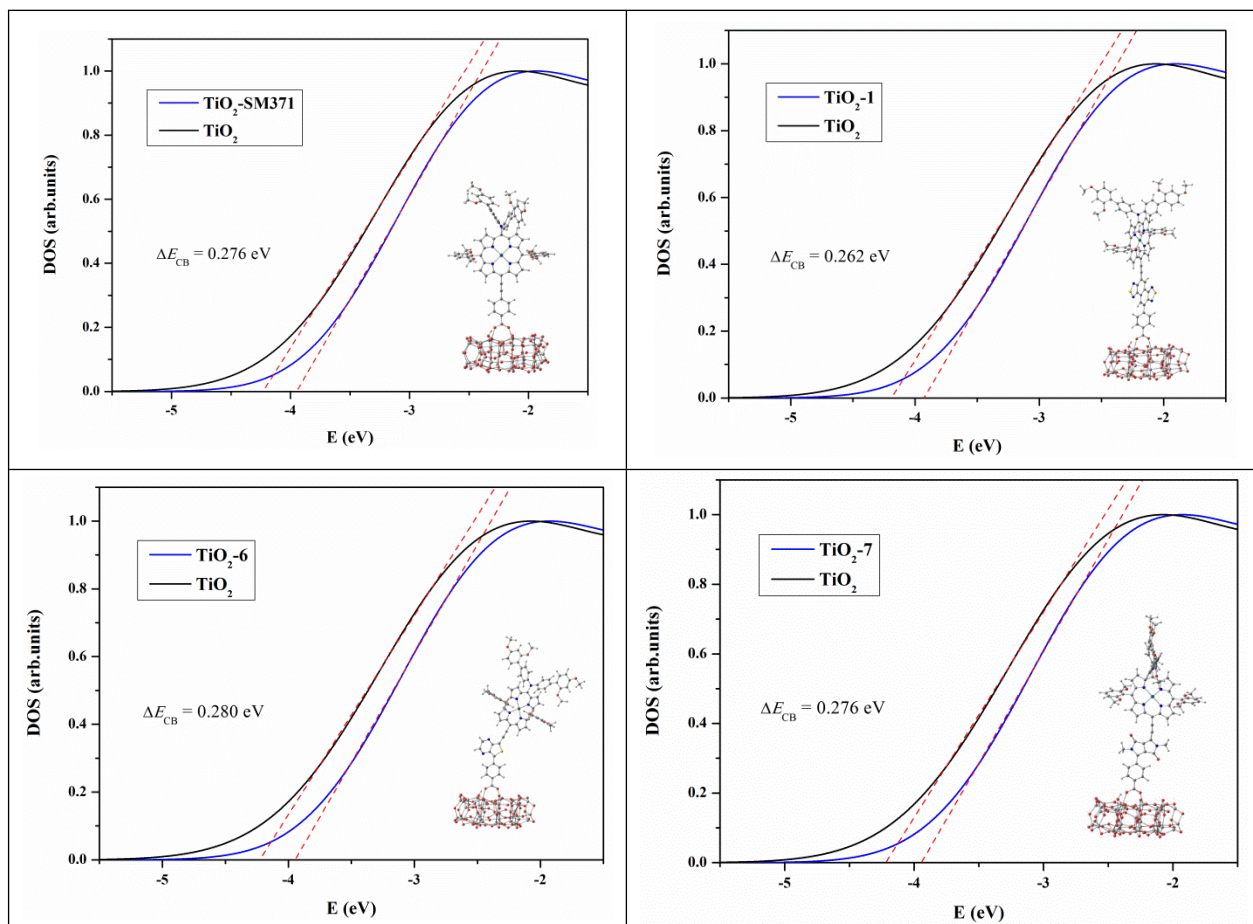


Fig. S12. Total and Partial Density of States (DOS) for porphyrin dyes adsorbed on $(\text{TiO}_2)_{38}$ cluster. (black solid line) $(\text{TiO}_2)_{38}$ cluster DOS, (blue solid line) PDOS, $(\text{TiO}_2)_{38}$ cluster contribution to the total DOS. The red dash lines intercepts with the energy axis correspond to the calculated CB edges. And Charge displacement curve for dye- $(\text{TiO}_2)_{38}$ systems in acetonitrile solution under PCM-B3LYP/SVP level in ACN solvent.

Table S1

Computed absorption wavelength (λ_{abs} , nm/ E_x , eV), oscillator strength (f), transition nature and configuration as well as the available experimental data for the experimental reported dye **SM315** at TD-PCM-M06/Basis Set level in THF solvent (ϵ represents molar absorption coefficient; H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

SM315	Exp.	PCM-TD-M06/6-31G* (LANL2DZ for Zn atom)		PCM-TD-M06/6-31+G*	
		$\lambda_{\text{abs}}/E_x/f$ ($10^3 \text{ M}^{-1}\text{cm}^{-1}$)	Transition nature and configuration	$\lambda_{\text{abs}}/E_x/f$	Transition nature and configuration
A1	668/1.86/53	702/1.77/ 0.7867	S ₀ -S ₁ H→L (87%)	708/1.75/0.7462	S ₀ -S ₁ H→L (87%)
A2	581/2.13/12	580/2.14/ 0.2263	S ₀ -S ₃ H-1→L(83%)	585/2.12/0.2502	S ₀ -S ₃ H-1→L(82%)
A3	454/2.73/117	428/2.90/ 1.0835	S ₀ -S ₉ H-1→L+1(30%) H- 2→L+2(26%) H-7→L (21%)	433/2.86/1.1396	S ₀ -S ₉ H-1→L+1(33%) H-2→L+2(30%) H-7→L (17%)
A4	440/2.82/105	408/3.04/ 0.9396	S ₀ -S ₁₀ H-2→L+1(49%) H- 1→L+2(34%)	416/2.98/0.9004	S ₀ -S ₁₀ H-2→L+1(49%) H-1→L+2(35%)

Table S2

Computed wavelength (λ , nm), excitation energy (E_x , eV), oscillator strength (f) and major transition configurations of porphyrin sensitizers at TD-PCM-M06 /6-31G* level in THF solvent

<p style="text-align: right;">2</p>	<p>S_0-S_1 672 nm 1.85 eV $f = 0.6619$ $H \rightarrow L$ (89%) S_0-S_3 559 nm 2.22 eV $f = 0.1205$ $H-1 \rightarrow L$ (81%) S_0-S_7 442 nm 2.80 eV $f = 0.8767$ $H-2 \rightarrow L+1$ (22%) $H \rightarrow L+2$ (19%) S_0-S_{10} 400 nm 3.10 eV $f = 0.7593$ $H-2 \rightarrow L+2$ (64%) $H-1 \rightarrow L+1$ (21%)</p>
<p style="text-align: right;">3</p>	<p>S_0-S_1 673 nm 1.84 eV $f = 0.7146$ $H \rightarrow L$ (90%) S_0-S_3 561 nm 2.21 eV $f = 0.1459$ $H-1 \rightarrow L$ (83%) S_0-S_5 473 nm 2.62 eV $f = 1.2022$ $H-2 \rightarrow L+1$ (31%) $H \rightarrow L+2$ (48%) S_0-S_7 433 nm 2.86 eV $f = 0.7997$ $H \rightarrow L+2$ (43%) $H-2 \rightarrow L+1$ (27%)</p>
<p style="text-align: right;">4</p>	<p>S_0-S_1 674 nm 1.84 eV $f = 0.6105$ $H \rightarrow L$ (91%) S_0-S_3 550 nm 2.25 eV $f = 0.0618$ $H-1 \rightarrow L$ (77%) S_0-S_6 446 nm 2.78 eV $f = 1.6075$ $H-2 \rightarrow L+2$ (42%) $H \rightarrow L+3$ (25%) S_0-S_{10} 414 nm 2.99 eV $f = 0.7050$ $H-2 \rightarrow L+1$ (28%) $H-1 \rightarrow L+2$ (41%)</p>

<p style="text-align: right;">5</p>	<p>S_0-S_1 704 nm 1.76 eV $f = 0.7494$ $H \rightarrow L$ (92%) S_0-S_3 571 nm 2.17 eV $f = 0.2008$ $H-1 \rightarrow L$ (83%) S_0-S_7 458 nm 2.71 eV $f = 1.3668$ $H-2 \rightarrow L+2$ (43%) $H \rightarrow L+3$ (19%) S_0-S_{11} 414 nm 2.99 eV $f = 0.4049$ $H-2 \rightarrow L+1$ (53%)</p>
<p style="text-align: right;">8</p>	<p>S_0-S_1 661 nm 1.88 eV $f = 0.5003$ $H \rightarrow L$ (91%) S_0-S_3 558 nm 2.22 eV $f = 0.0991$ $H-1 \rightarrow L$ (79%) S_0-S_5 440 nm 2.82 eV $f = 2.1229$ $H-2 \rightarrow L+1$ (51%) $H \rightarrow L+2$ (18%) S_0-S_7 417 nm 2.97 eV $f = 0.9657$ $H-2 \rightarrow L$ (32%) $H-1 \rightarrow L+1$ (46%)</p>
<p style="text-align: right;">9</p>	<p>S_0-S_1 700 nm 1.77 eV $f = 0.5938$ $H \rightarrow L$ (89%) S_0-S_3 570 nm 2.18 eV $f = 0.1904$ $H-1 \rightarrow L$ (80%) S_0-S_7 454 nm 2.73 eV $f = 0.7464$ $H-2 \rightarrow L+1$ (23%) $H-1 \rightarrow L+2$ (31%) S_0-S_9 416 nm 2.98 eV $f = 0.9670$ $H-2 \rightarrow L+1$ (23%) $H-1 \rightarrow L+2$ (28%) $H \rightarrow L+3$ (29%)</p>
<p style="text-align: right;">10</p>	<p>S_0-S_1 675 nm 1.84 eV $f = 0.6347$ $H \rightarrow L$ (90%) S_0-S_3 567 nm 2.19 eV $f = 0.1741$ $H-1 \rightarrow L$ (83%) S_0-S_5 475 nm 2.61 eV $f = 0.9364$ $H-2 \rightarrow L+1$ (24%) $H \rightarrow L+2$ (55%) S_0-S_7 434 nm 2.85 eV $f = 1.0141$ $H \rightarrow L+2$ (38%) $H-2 \rightarrow L+1$ (32%)</p>

Table S3

Computed absorption wavelength (λ_{abs} , nm/ E_x , eV), oscillator strength (f), transition nature and configuration for **SM315** at TD-PCM-M06/6-31G* (LANL2DZ for Zn atom) in THF or ACN solvent (H=HOMO,L=LUMO,L+1=LUMO+1,etc.)

SM315	THF		ACN	
	$\lambda_{\text{abs}}/E_x/f$	Transition nature and configuration	$\lambda_{\text{abs}}/E_x/f$	Transition nature and configuration
A1	702/1.77/ 0.7867	S ₀ -S ₁ H→L (87%)	698/1.78/0.7570	S ₀ -S ₁ H→L (88%)
A2	580/2.14/ 0.2263	S ₀ -S ₃ H-1→L(83%)	578 /2.15/0.2215	S ₀ -S ₃ H-1→L(83%)
A3	428/2.90/ 1.0835	S ₀ -S ₉ H-1→L+1(30%) H- 2→L+2(26%) H-7→L (21%)	427/2.91/0.9950	S ₀ -S ₉ H-1→L+1(29%) H- 2→L+2(23%) H-7→L (20%)
A4	408/3.04/ 0.9396	S ₀ -S ₁₀ H-2→L+1(49%) H- 1→L+2(34%)	407/3.05/0.7177	S ₀ -S ₁₀ H-2→L+1(40%) H- 1→L+2(24%)
HOMO	-5.02 eV		-5.09 eV	
LUMO	-2.73 eV		-2.79 eV	

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