TARSUS UNIVERSITY

Photocatalytic Hydrogen Production by Phthalocyanine based Photocatalyst

Mine Ince

TARSUS UNIVERSITY

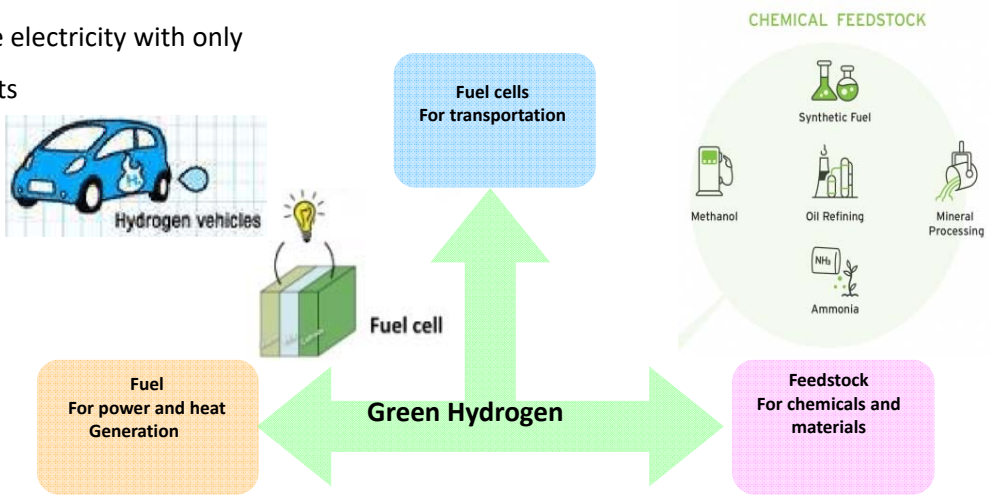
Outline

- **Introduction to Hydrogen Energy**
- **Photocatalytic H_2 Evolution from Water**
- **Phthalocyanine-based Photocatalytic H_2 Production**
- **SubPhthalocyanines as Photosensitizers**
- **Summary&Conclusion**

Hydrogen as an Energy Carrier

Hydrogen is an energy carrier, not an energy source!!!

- One of the most abundant element on earth
- Exhibits 3–4 fold higher mass energy density
- Hydrogen fuel cells generate electricity with only water and heat as byproducts



Chem. Soc. Rev., 2022, [10.1039/D2CS00183G](10.1039/D2CS00183G)

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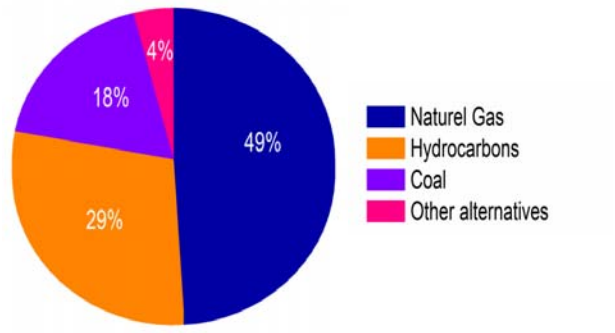


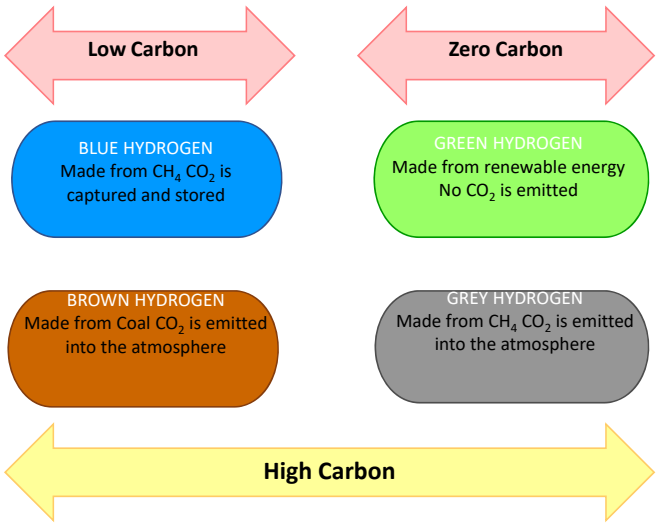
Steam reforming reaction

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

Shift reaction

$CO + H_2O \leftrightarrow CO_2 + H_2$

Hydrogen color codes

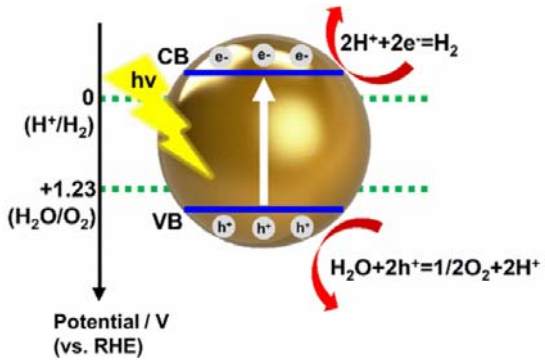


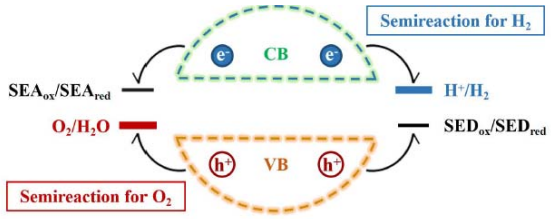
Chem. Soc. Rev., 2022, [10.1039/D2CS00183G](10.1039/D2CS00183G)

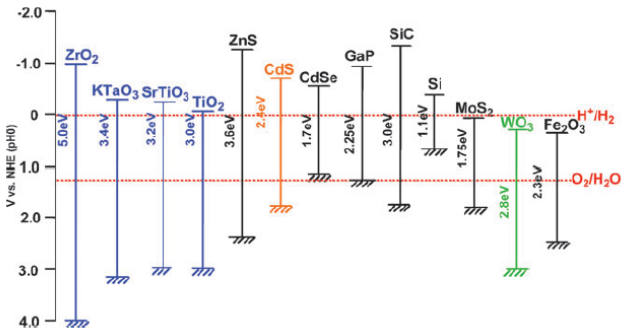
Solar Hydrogen Production

Photocatalytic Water Splitting (Artificial Photosynthesis)

- Simple and clean reaction
- Only a photocatalyst, sunlight and water are required
- The reaction occurs under mild conditions

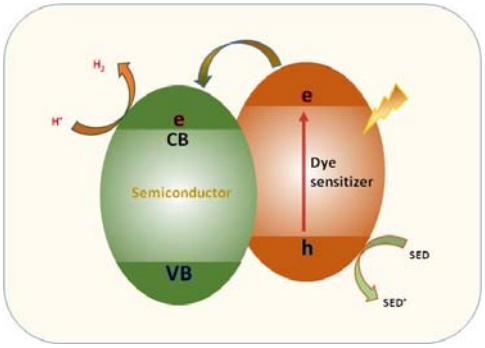


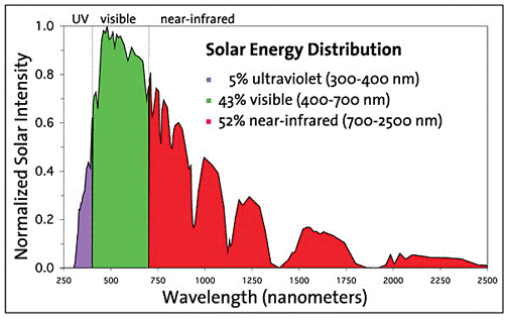


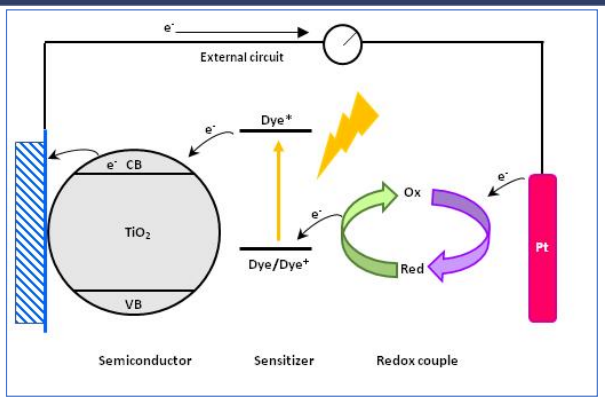


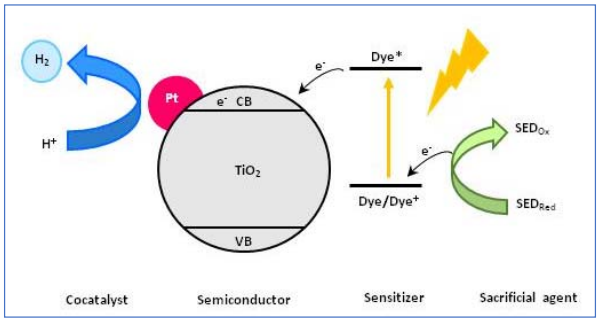
Chem. Soc. Rev., 2022, [10.1039/D2CS00183G](10.1039/D2CS00183G)

Dye-Sensitized Photocatalyst for Visible-light-driven H_2 Evolution



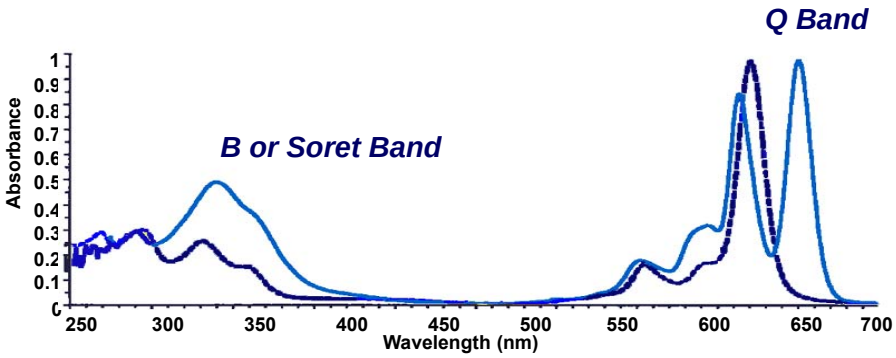


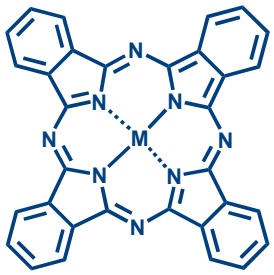


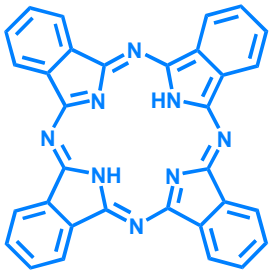


Chem. Soc. Rev., 2022, [10.1039/D2CS00183G](10.1039/D2CS00183G)

Phthalocyanines



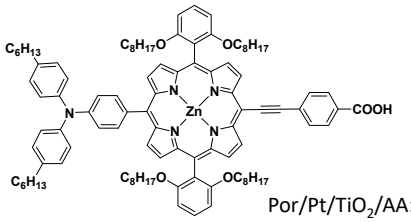




- Intense absorption around 700 nm
- High extinction coefficients
- Unusual physical properties (semiconducting, optical...)
- Thermal, chemical and optical stability
- Structural versatility
- Can act both as electron-donors/acceptors

The Chemical Record, 2008, *8, 75.*

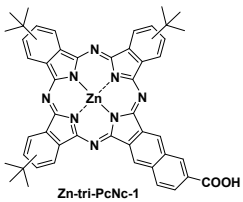
Porfinoids Based Sensitizers for Photocatalytic H_2 evolution



YD2-o-C8

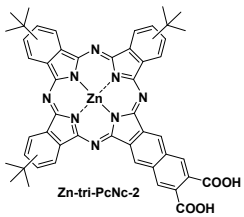
Por/Pt/TiO_2/AA: **272 mmol/$g^{-1}h^{-1}$**
TON 12 000 over 120 h.

ChemSusChem, 2018, *11, 2517.*



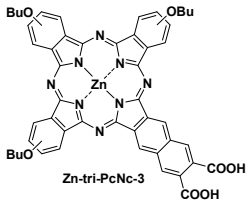
Zn-tri-PcNc-1

203 µmol/h^{-1}



Zn-tri-PcNc-2

263 µmol/h^{-1}

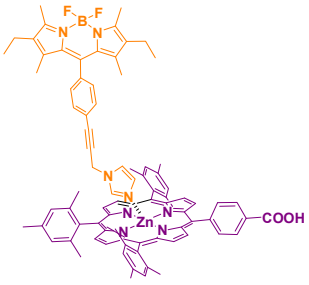


Zn-tri-PcNc-3

101 µmol/h^{-1}

ZnPc/Pt/ g-C_3N_4/AA

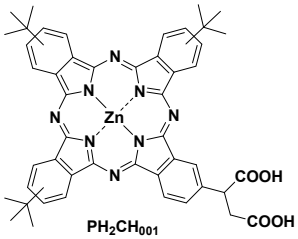
Catalysis Science and Technology, 2014, *4, 3251.*



BDP(Im)-Por

Por/Pt/TiO_2/AA: **225 mmol/$g^{-1}h^{-1}$**

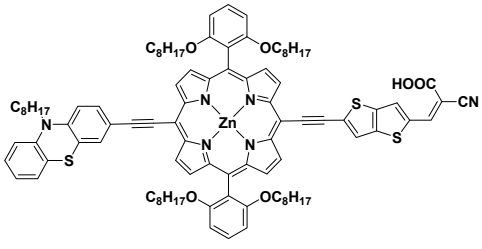
ACS Applied Energy Materials, 2021, *4, 10042.*



PH_2CH_{001}

Pc/Pt/TiO_2/TEOA: **7396 µmol/$g^{-1}h^{-1}$**

J. Photochem. Photobiol. A, 2020, *392.*

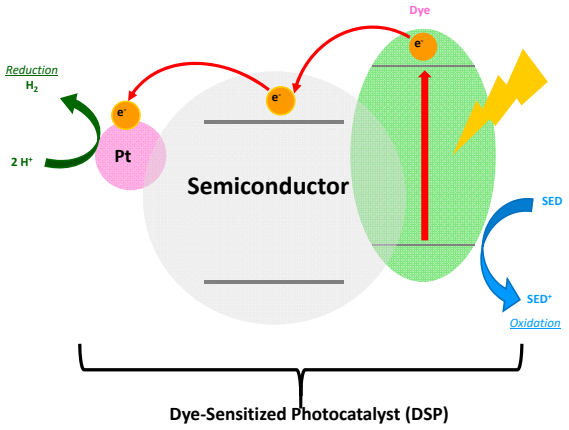


ZnPcPt/ TiO_2 (HPT)/TEOA: **2260 µmol**

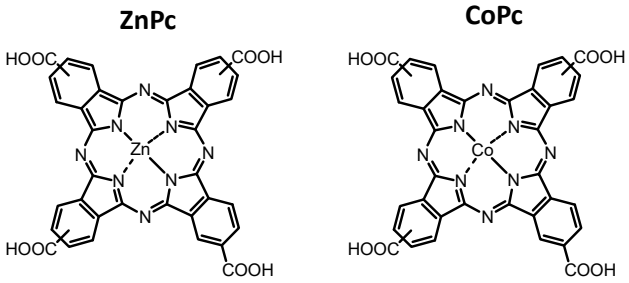
J. Phys. Chem. C, 2018, *122, 495.*

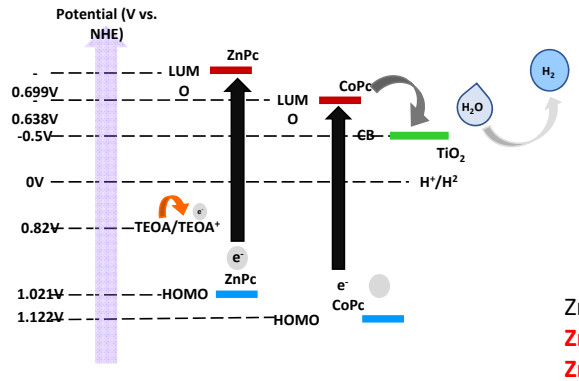
Motivation

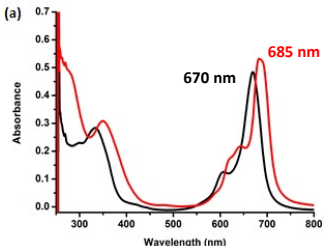
- Pc sensitized photocatalytic H_2 production has been studied over the years. However, the design of new Pcs for photocatalytic H_2 production still needs some improvements.
- With this motivation, our research has focused on preparation of novel Pc derivatives as sensitizers in dye-sensitized photocatalytic H_2 generation. Within our molecule design, we aim for better charge transfer properties and improved optoelectronic properties.

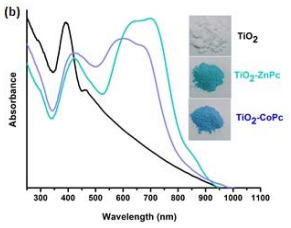


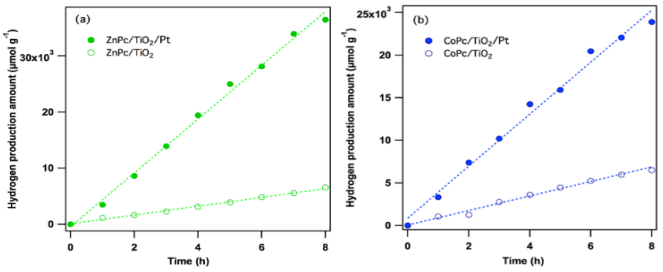
Pc Based Photosensitizers for Photocatalytic H_2 Production









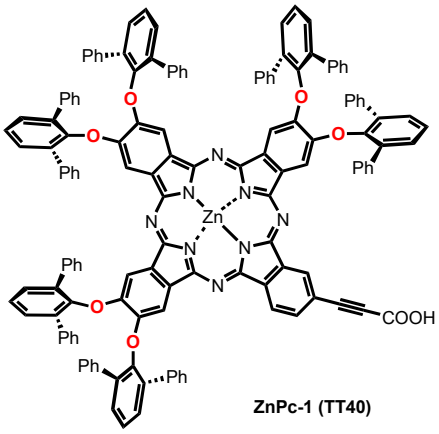


ZnPc/TiO_2 and CoPc/TiO_2; 1.15 and 1.05 mmol/gh
ZnPc/TiO_2/Pt and **CoPc/TiO_2/Pt** ; **3.45** and **3.33** mmol/gh
ZnPc/TiO_2/Pt and **CoPc/TiO_2/Pt** : **36.46 mmol/g** and **23.91** mmol/g

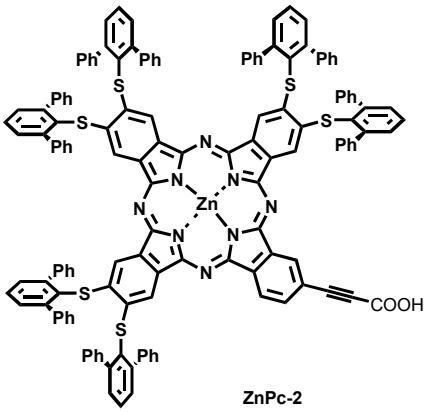
Renewable Energy 162 (2020) 1340e1346

Non-aggregated Push-pull Zn(II)Phthalocyanines

- Investigating the effect of sulfur atoms
- Comparing the photocatalytic activity of both sensitizers



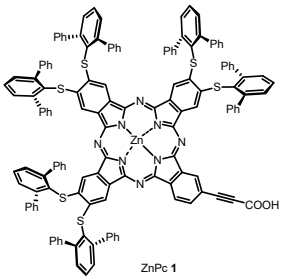
ZnPc-1 (TT40)



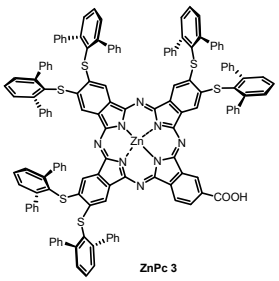
ZnPc-2

Non-aggregated Push-pull Zn(II)Phthalocyanines

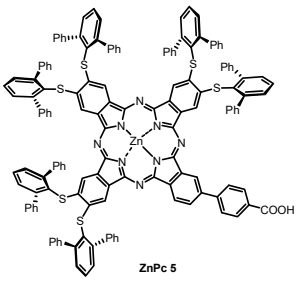
- To shift absorption into NIR region
- Maintaining the minimization of aggregation
- Investigating the effect of the sulfur atom
- Size of peripheral substituents



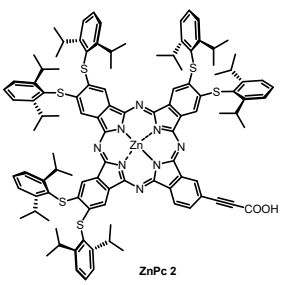
ZnPc 1



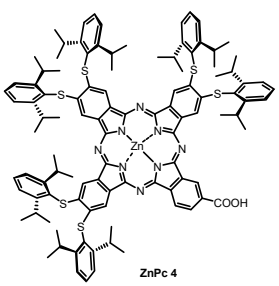
ZnPc 3



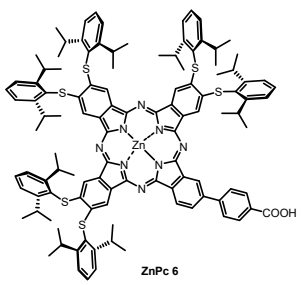
ZnPc 5



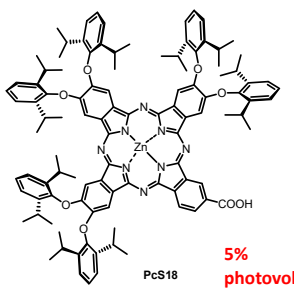
ZnPc 2



ZnPc 4



ZnPc 6



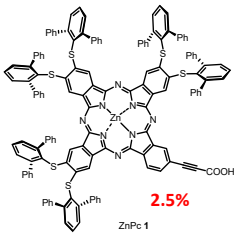
PcS18

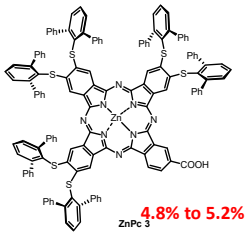
5% photovoltaic conversion effeicnecy

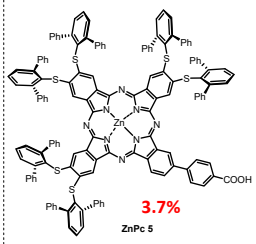
Published by Prof. Kimura

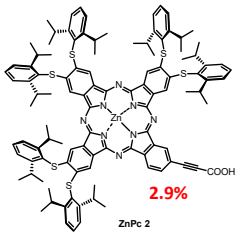
Sustainable Energy Fuels, 2021, *5, 584.*

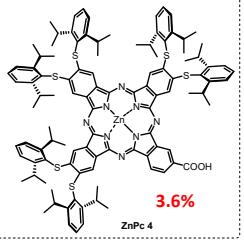
Bulky Electron-donating Thioether Substituted Pc Based DSSCs

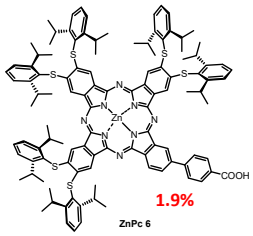


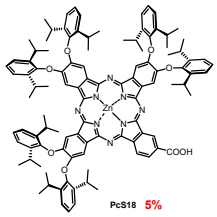








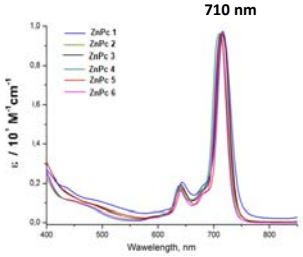




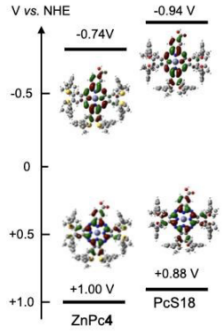
ZnPc 4

PcS18

Low LUMO energy level!!!
Low adsorption density!!!

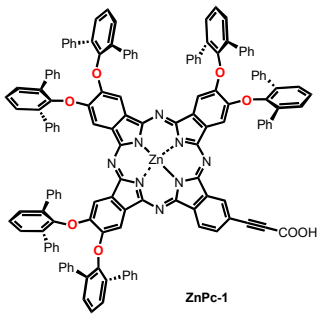


Sustainable Energy Fuels, 2021,5, 584-589

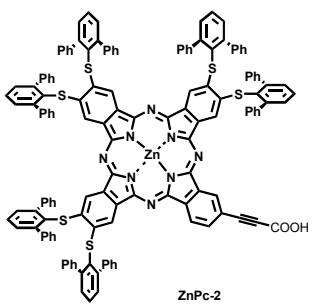


Dyes	Adsorption density[a] / x10^4/mol cm^{-3}	Thickness[b] /mm	Time[c]/h	V_{oc}/ mV	J_{sc} /mA cm^{-1}	*FF*	PCE / %
1	10.4	7.2+4	24	530	6.2	0.75	2.5
2	11.2	7.2+4	48	550	7.0	0.75	2.9
3	9.9	7.2+4	24	590	10.8	0.76	4.8
		12+5.7	48	586	12.4	0.71	5.2
4	8.8	7.2+4	24	550	9.0	0.73	3.6
5	9	7.2+4	24	580	8.8	0.73	3.7
6	8.7	7.2+4	24	560	4.6	0.75	1.9
PcS18	13.6	7.2+4	24	621	11.4	0.70	5.0

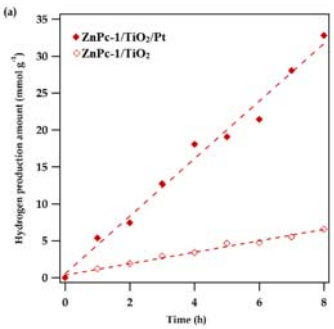
Bulky electron-donating thioether substituted Pcs based DSSCs

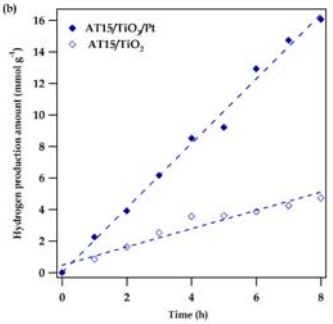


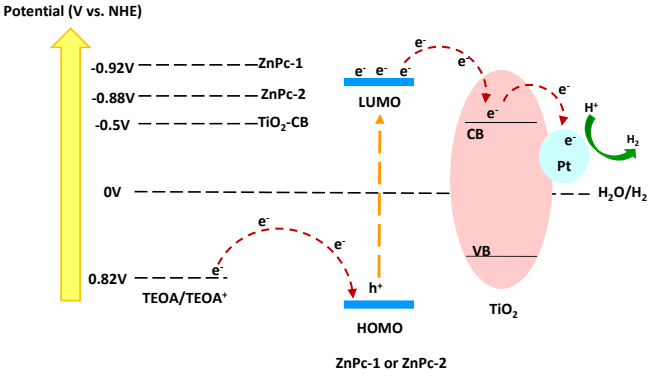
ZnPc-1



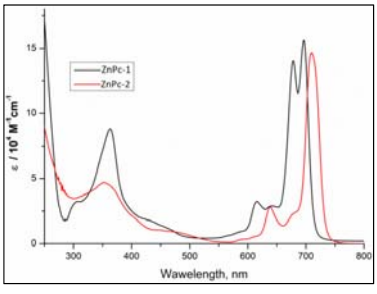
ZnPc-2







ZnPc-1 or ZnPc-2

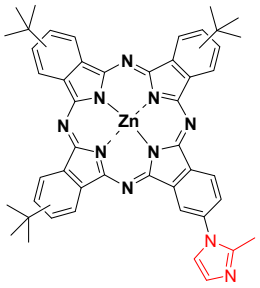


ZnPc 1/ TiO_2: 1.221 mmol/gh
ZnPc 2/ TiO_2 /Pt: 0.864 mmol/gh

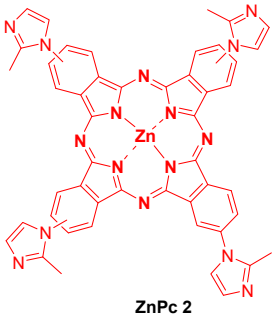
ZnPc 1/TiO_2/Pt: 5.4 mmol/gh
ZnPc 2/TiO_2/Pt: 2.3 mmol/gh

ACS Appl. Energy Mater. 2021, *4, 9, 10222.*

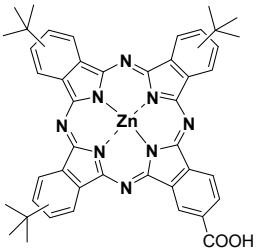
Imidazole Substituted ZnPcs for Photocatalytic H_2 Evolution



ZnPc 1



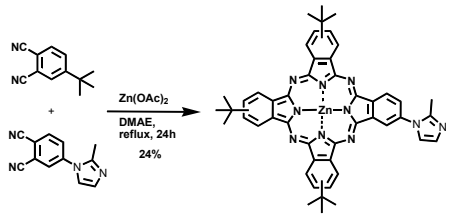
ZnPc 2

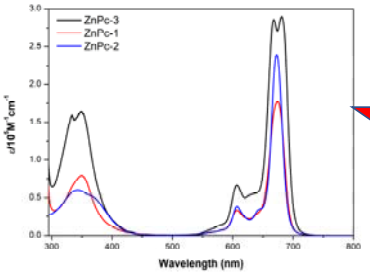


ZnPc 3 (TT1)

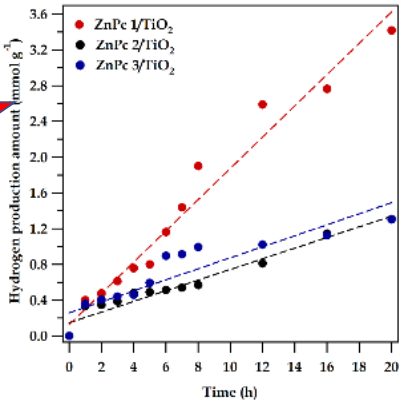
Chemical Communications, 2021, *57*, 9196 - 9199

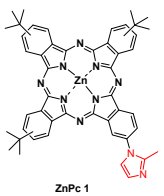
Imidazole Substituted ZnPcs for Photocatalytic H_2 Evolution



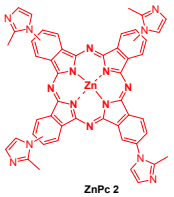


Co-catalyst free

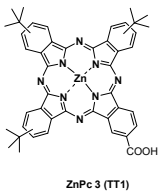




ZnPc 1



ZnPc 2



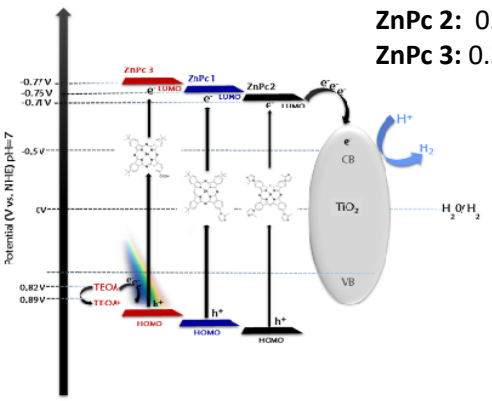
ZnPc 3 (TT1)

H_2 production rate

ZnPc 1: 0.4 mmolg^{-1}h^{-1}

ZnPc 2: 0.33 mmolg^{-1}h^{-1}

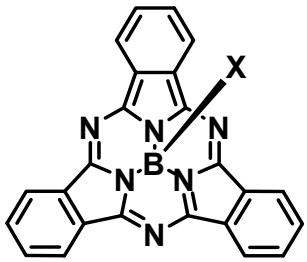
ZnPc 3: 0.35 mmolg^{-1}h^{-1}

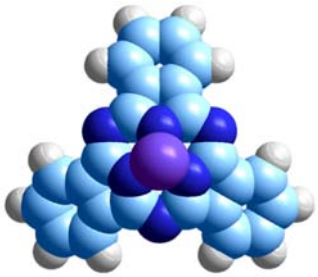


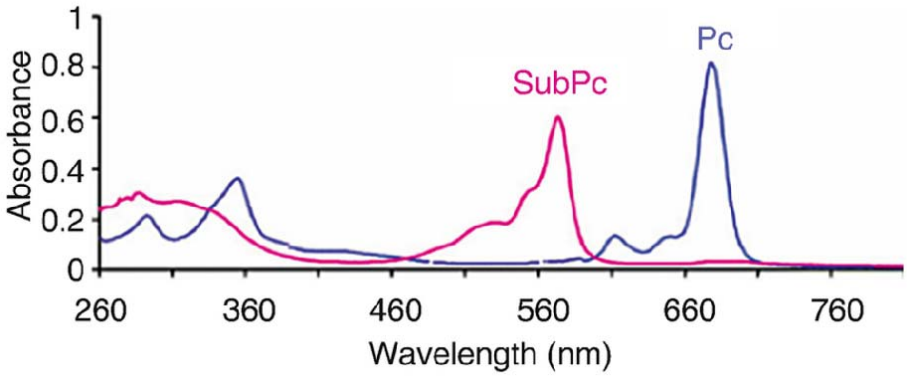
ZnPc	H_2 amount (mmol g^{-1} at 20h)	Dye loading (µmol g^{-1})	TON (mmol(H_2)/ mmol(adsorbed dye)$^{-1}$at 20 h	TOF (mmol (H_2) mmol(dye)$^{-1}$s^{-1}	STH (%)
1	3.4187	0.46	14863	0.2	1.03
2	1.3078	0.76	3441	0.05	0.86
3	1.3042	0.83	3142	0.04	0.91

Chemical Communications, 2021, 57, 9196 - 9199

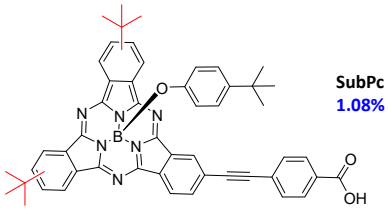
SubPhthalocyanines



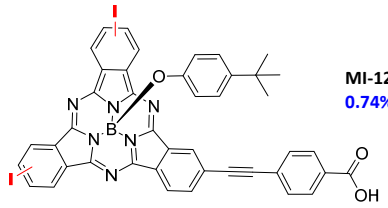




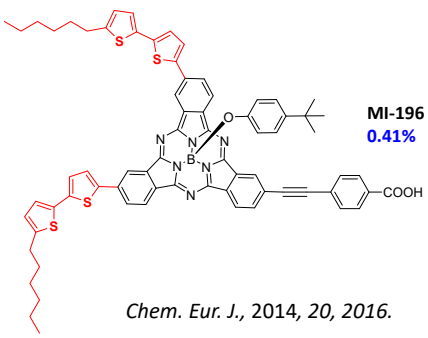
Subphthalocyanines For DSSCs



SubPc 2
1.08% (with AY3)



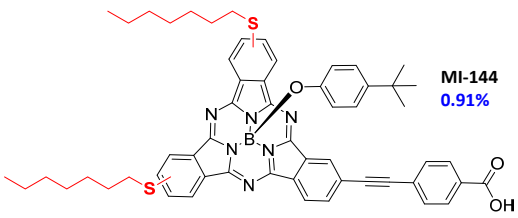
MI-124
0.74%



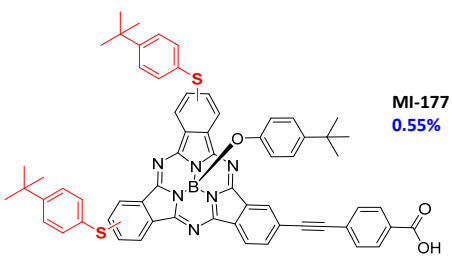
MI-196
0.41%

Chem. Eur. J., 2014, *20, 2016.*

Low-lying LUMO levels

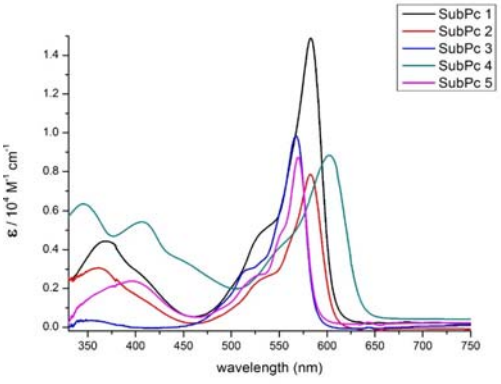


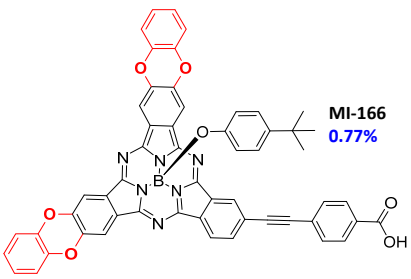
MI-144
0.91%



MI-177
0.55%

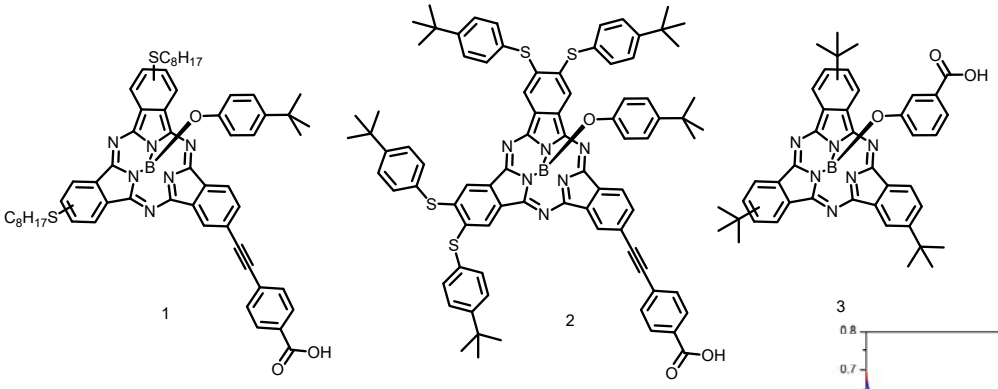
Chem. Asian J., 2016, *11, 1, 223.*

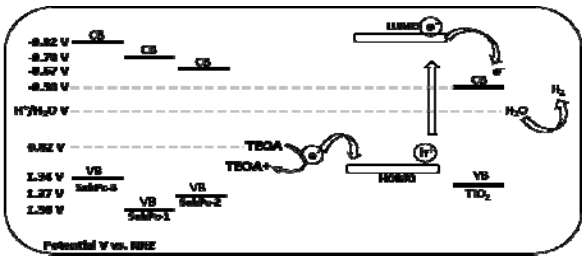


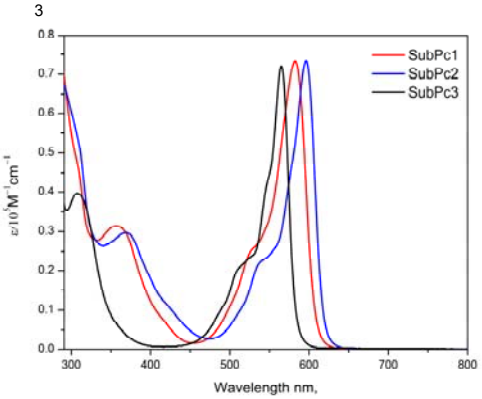


MI-166
0.77%

SubPc-sensitized TiO_2 Photocatalyst

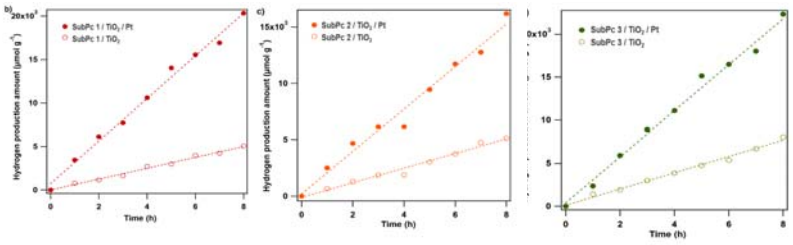




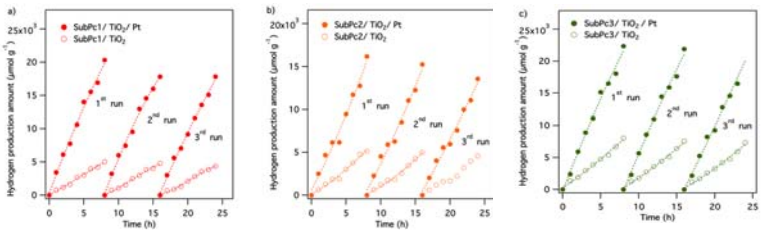


Dalton Trans., 2020, *49, 12550.*

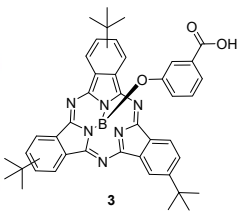
SubPc-sensitized TiO_2 Photocatalyst



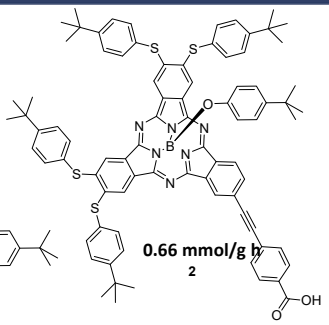
Stability of the SubPc sensitized –TiO2 catalyst for H_2 production



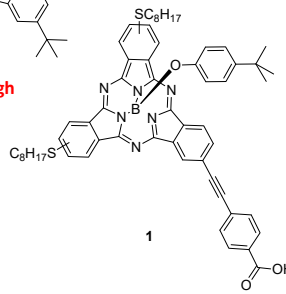
Dalton Trans., 2020,**49**, 12550-12554



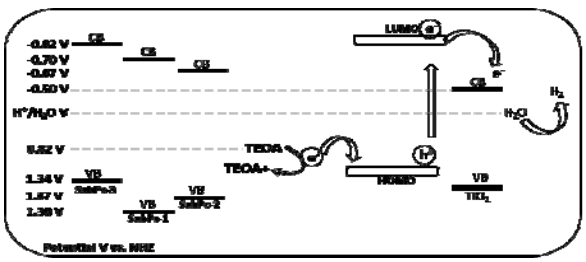
1.39 mmol/gh



0.66 mmol/g h



SubPc-1/TiO_2: 0.77 mmol/g h



Summary and Conclusion

- **Non-aggregated bulky phenoxy substituted ZnPc 1/TiO_2/Pt: 5.4 mmol/gh**
- **Thioether groups** can be used to **broaden the absorption spectrum without facilitating recombination.**
- **SubPc derivatives were used for the first time as a sensitizer for photocatalytic H_2 generation**. The promising results (**SubPc-3/TiO_2/Pt: 2.37mmol /gh)** shows their potential as a sensitizer in dye-sensitized photocatalytic hydrogen evolution.
- Despite all the encouraging results, improving Pc-sensitised photocatalysts' efficiency and long-term stability **remains a great challenge** for their practical applications.
- Further works (charge-transfer analysis between dye/semiconductor/co-catalyst/electron donor, stability tests etc.) should be carried out to investigate the relationship between molecular structure and photocatalytic performance.

Thank You For Your Attention

In the field of catalytic chemistry, a key evaluation criterion for the performance of catalyst is the turnover number (TON). The TON is defined as the number of the substrate molecules that react divided by the number of active sites before the catalyst loses its activity completely. The calculation of TON can be described by Equation 8.

$$\mathrm{TON} = \frac{\text{mol of produced } H_2}{\text{mol of loaded dye}}$$

$$\mathrm{TON} = \frac{2 \times \text{mol of produced } H_2}{\text{mol of loaded dye}}$$

In most reported cases of H_2 evolution by DSPs, the number of active sites is usually considered to be the number of dye molecules, while the number of the substrate molecules that react can be taken to be the number of produced H_2 molecules (also considered to be the number of electrons involved to produce H_2, which is twice the number of H_2 molecules), then the practical expression is simplified as Equation 9 or 10.