Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2021

SUPPORTING INFORMATION

Imidazole substituted Zinc (II) Phthalocyanines for co-catalyst-free Photoelectrochemical and Photocatalytic Hydrogen Evolution: Influence of the Anchoring Group

A.Celil Yüzer,[a#] Eminegül Genc,[b#] Gülbin Kurtay,[c] Gizem Yanalak,[d] Emre Aslan,[d] Ersan Harputlu,[a] Kasim Ocakoglu,[a] Imren Hatay Patir [e*], Mine Ince [a*]

[a.] Department of Natural and Mathematical Sciences, Faculty of Engineering, Tarsus University, 33480, Mersin, Turkey

[b.] *Department of Nanotechnology and Advanced Materials, Selcuk University, 42250, Konya, Turkey.*

[c.] *Department of Chemistry, Ankara University, Faculty of Science, TR-06100, Ankara, Turkey.*

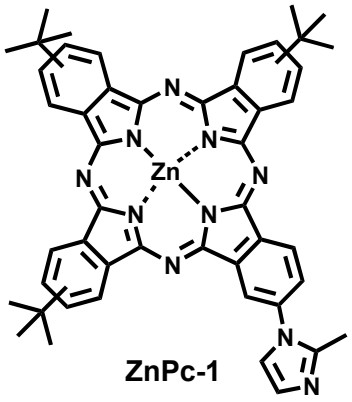
[d.] *Department of Biochemistry, Selcuk University, 42250, Konya, Turkey.*

[e.] *Department of Biotechnology, Selcuk University, 42250, Konya, Turkey.*

#These authors contributed equally to the work.

1. Synthesis and Characterization

All chemicals were purchased from Aldrich and used without further purification. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), and TLC was carried out on aluminum sheets percolated with silica gel 60 F254 (E. Merck). The IR spectra were performed with Jasco, FT-IR-6700 spectrophotometer. Mass spectrometry analysis was performed on an autoflex III MALDI TOF/TOF MS system (Bruker Daltonics, Bremen, Germany). UV-vis spectra and Fluoresans were recorded with an Agilent Technologies, Cary 100, and Cary Eclipse spectrophotometer respectively. Electrochemical measurements were performed on an IviumStat electrochemical analyzer with a three-electrode configuration at room temperature.



ZnPc-1

Zinc (II) (9(10),16(17),23(24)-tri-(tert-butyl)-2(3) (2-methyl-1Himidazol-1-yl)-phthalocyaninato-(2-)-N^{29}, N^{30}, N^{31}, N^{32} (*ZnPc-1*):

A mixture of 4-*tert*-butylphthalonitrile (500 mg, 2.71 mmol), 4-(2-methyl-1H-imidazol-1-yl)[1] phthalonitrile (190 mg, 0.90 mmol) and $Zn(OAc)_2$ (266 mg, 1.45 mmol) in DMAE (7-8 mL) was heated at reflux overnight under argon atmosphere. After cooling to room temperature, the solvent was evaporated in vacuum and the crude product was purified by column chromatography on silica gel (CH_2Cl_2/MeOH 200:1) to give ***ZnPc-1*** (35 mg, 0.042 mmol) a dark blue solid. Yield: 18%.

1H NMR (400 MHz, $CDCl_3$): δ (ppm)= 8.59 (s, 1H), 8.10 (s, 2H), 7.88 (s, 2H), 7.76 (s, 3H), 7.51 (d, *J*=8, 1H), 7.35 (s, 1H), 7.13-7.11 (m, 1H), 6.97 (s, 3H), 2.09-1.89 (m, 3H), 0.97-0.66 (bs, 27 H).

UV-vis (DMSO): λ_{max}, nm (log ε): 350 (4.89), 607 (4.52), 674 (5.27).

IR (ATR): ν, cm^{-1} = 2918, 2852, 1731, 1612, 1493, 1464, 1437, 1391, 1362, 1311, 1254, 1177, 1077, 970.

MS (MALDI-TOF) m/z: $C_{48}H_{32}N_{16}Zn$: 826.32; found 826.162 $[M]^+$.

Figure S1: ^{1}H NMR ($CDCl_3$) spectra of *ZnPc-1*.

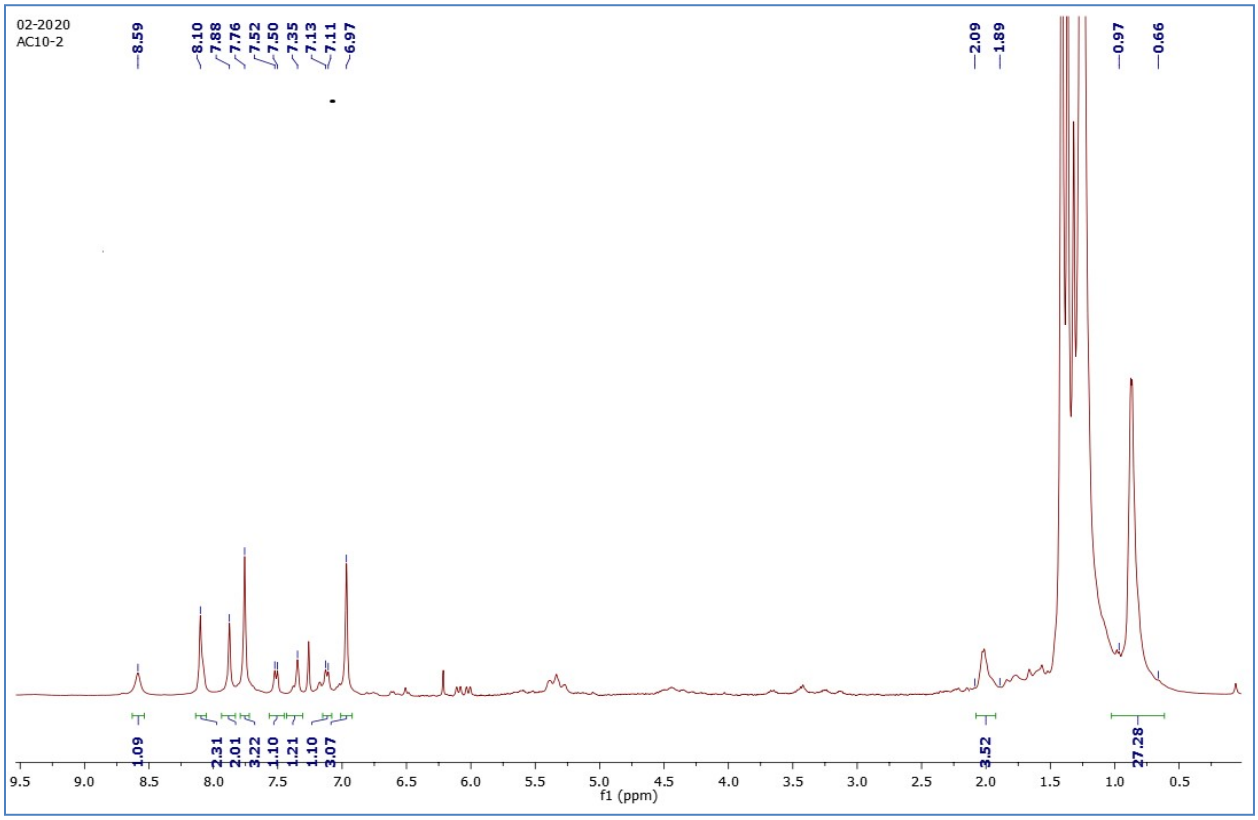
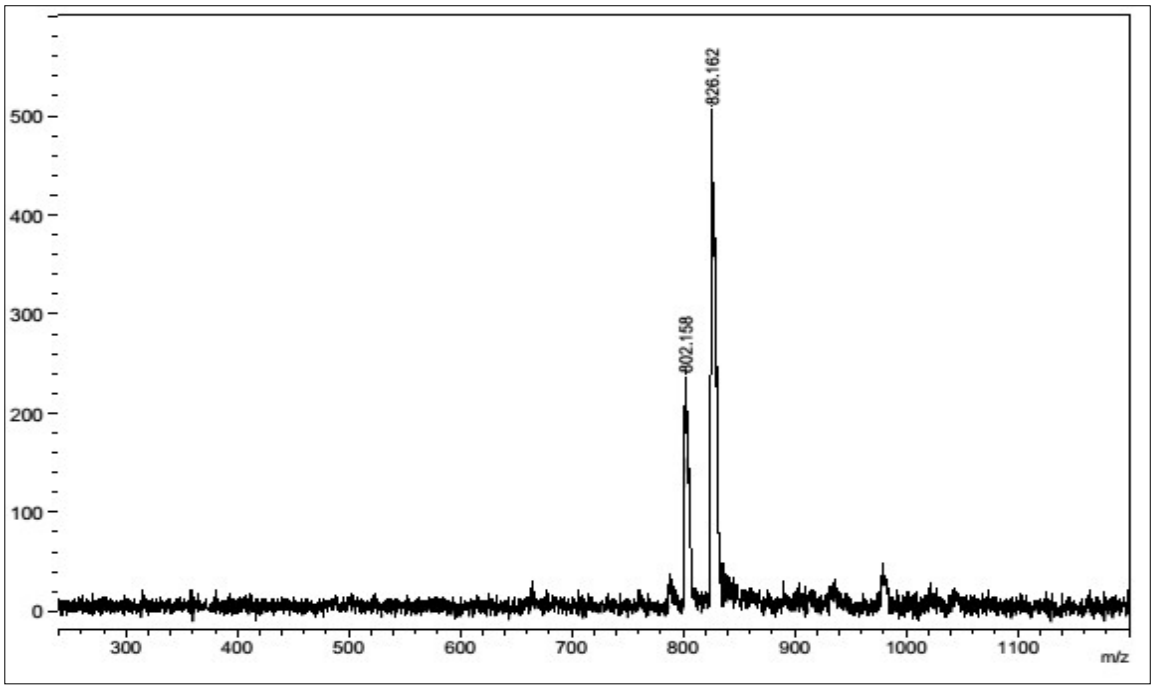
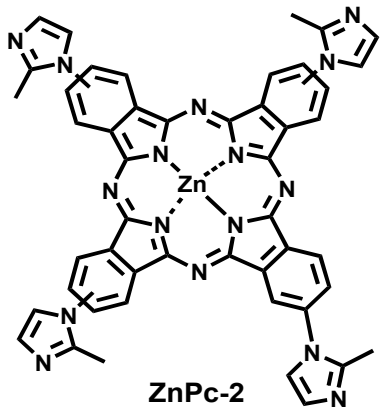


Figure S2: MALDI spectra of *ZnPc-1*.





Zinc (II) 2(3),9(10),16(17),23(24)-tetra-(2-methyl-1Himidazol-1-yl)-phthalocyaninato (2-)-N^{29}, N^{30}, N^{31}, N^{32} (*ZnPc-2*).

A solution of 4-(2-methyl-1H-imidazol-1-yl) phthalonitrile (1 g, 4.8 mmol) and $Zn(OAc)_2$ (297.3 mg, 1.51 mmol) in DMAE (10 mL) was heated at reflux overnight under argon atmosphere. After cooling to room temperature, the solvent was evaporated in vacuum and the crude mixture was washed with common organic solvents. In this way, ***ZnPc-2*** was obtained as a blue solid in 38% yield (410 mg, 0.456 mmol).

^{1}H NMR (CD_3OD/ with drop of TFA, 400 MHz): δ(ppm) = 9.41-9.19 (m, 6H), 9.07-8.99 (m, 2H), 8.51-8.35 (m, 8H), 8.04-7.92 (m, 4H), 2.98 (d, *J* = *4* Hz, 6H), 2.91 (d, *J* = *4* Hz, 6H).

IR (ATR): ν, cm^{-1}= 1610, 1490, 1407, 1335, 1298, 1170, 1137, 1085, 1052, 985, 900, 833.

UV-vis (DMSO): λ_{max}, nm (log ε): 344 (4.77), 608 (4.99), 674 (5.37).

MS (MALDI-TOF) m/z: $C_{48}H_{32}N_{16}Zn$: 898.265; found 899.028 $[M+H]^+$.

Figure S3: ^{1}H NMR (MeOD+TFA) spectra of *ZnPc-2*

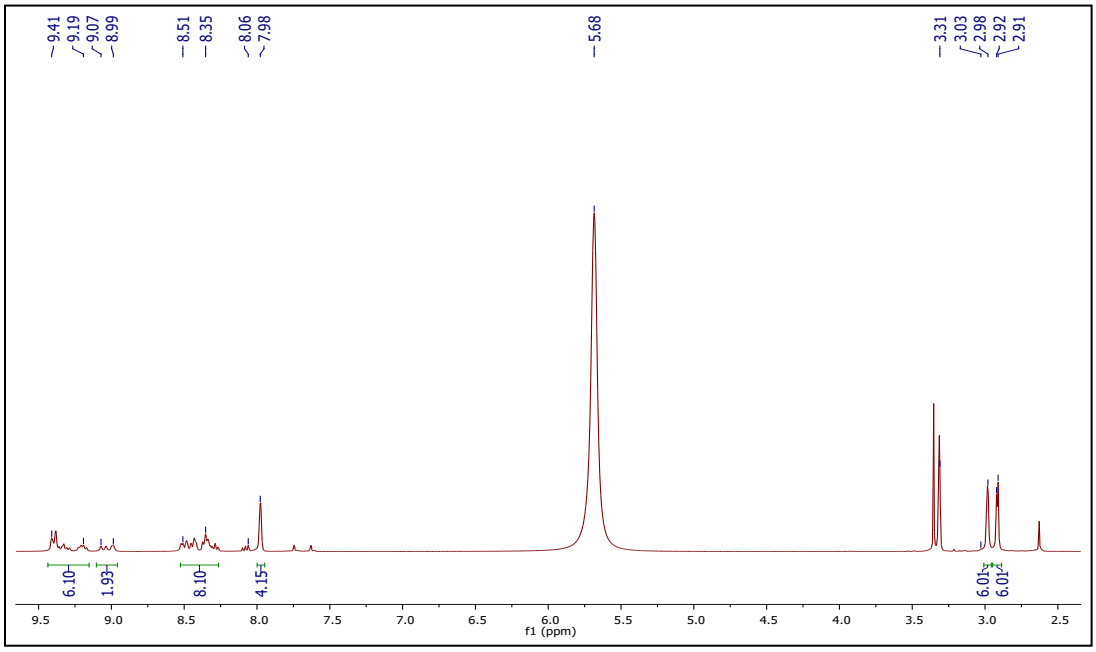


Figure S4: MALDI spectra of *ZnPc-2*.

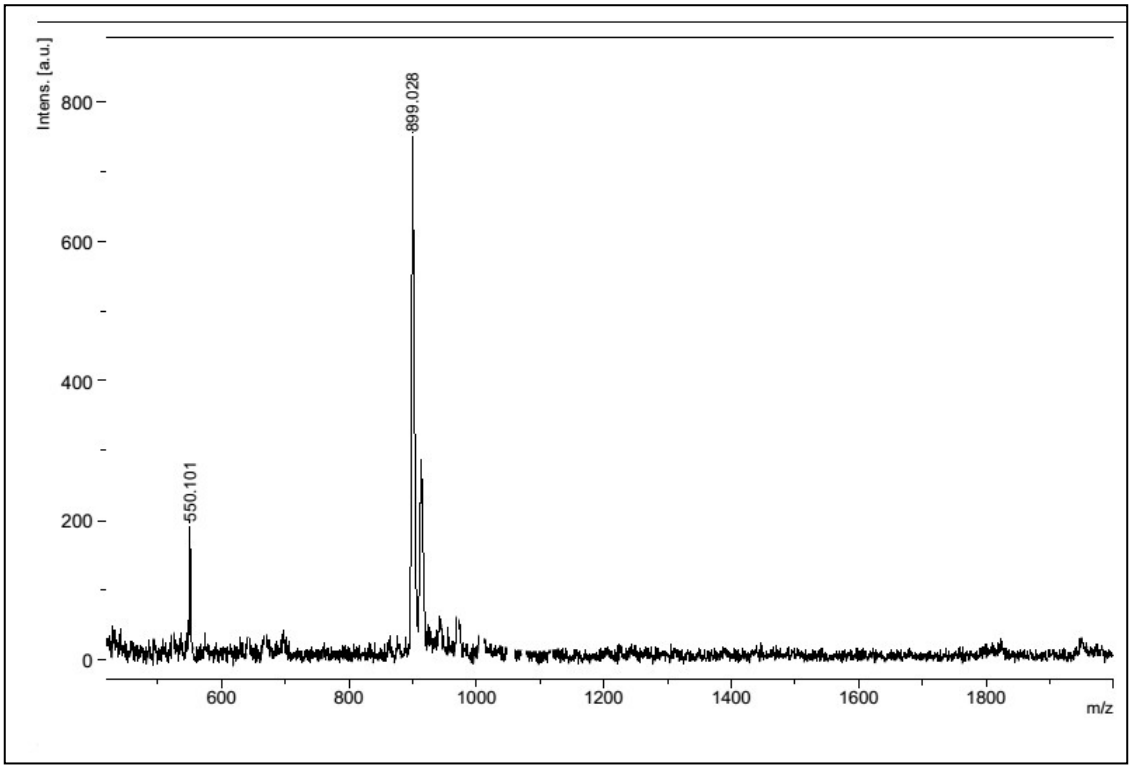
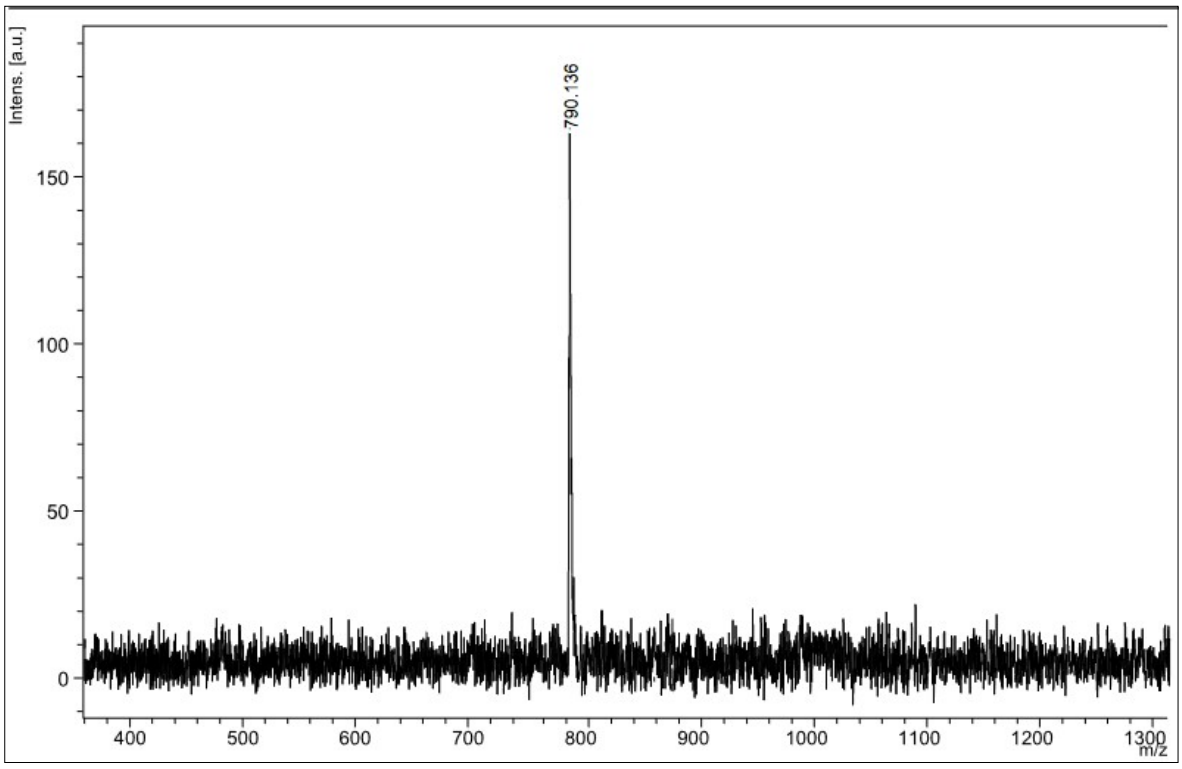


Figure S5: MALDI spectra of *ZnPc-3* (MS (MALDI-TOF) m/z: $C_{45}H_{40}N_8O_2Zn$:790.24; found 790.13 $[M]^{+)}$



Optical and Electrochemical Measurement

Optical characterization belonging to Pcs solutions and Pc derivatives sensitized TiO_2 were figured out via UV-*vis* absorption spectra (Shimadzu UV-1800 spectrophotometer). The electrochemical characterizations of Pcs were carried out by cyclic voltammetry methods (CH Instruments 760D electrochemical working station) and an Iviumstat electrochemical analyzer, which was employed in electrochemical measurements at room temperature. Herein, platinum (Pt) wire, $Ag/AgNO_3$ electrode, glassy carbon electrodes (GCE), and ferrocene were used as the counter electrode, reference electrode, working electrode, and internal standard. However, cyclic voltammograms were observed in the acetonitrile, which included 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as a supporting electrolyte. In addition, electrochemical energy levels of Pc derivatives were determined considering reduction and oxidation potentials.

Figure S6. FT-IR spectra of the ZnPc powders and the dyes adsorbed on TiO_2

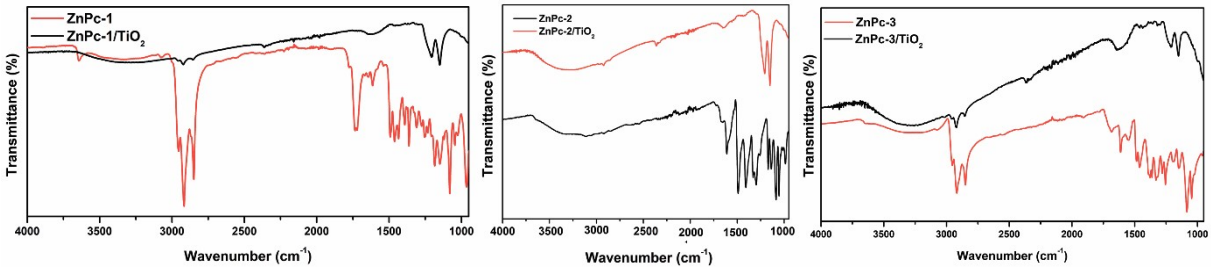


Figure S7: UV and Emission Spectra of *ZnPc-1-2-*3.

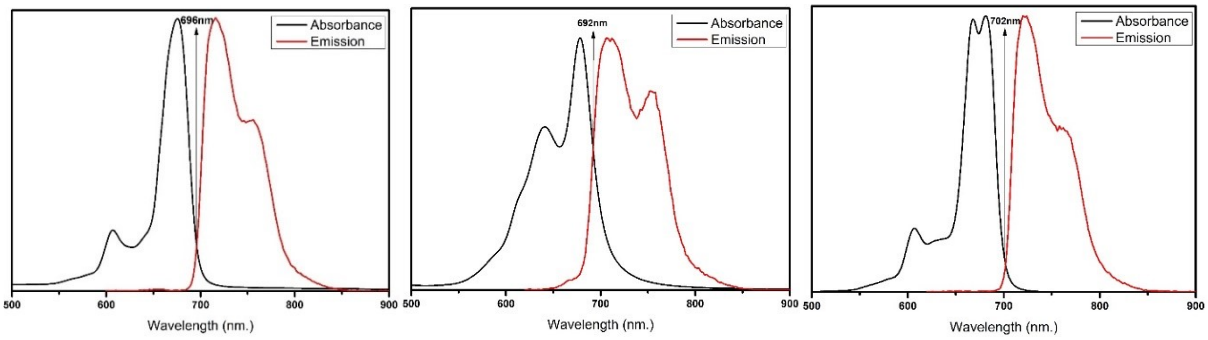


Figure S8. CV voltammograms of ZnPc1-2-3 with ferrocene

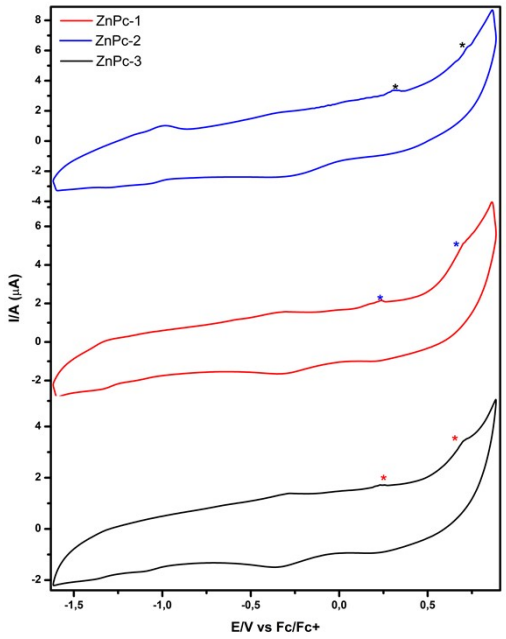


Table S1. Electrochemical[a] and optical[b] properties of the phthalocyanine samples.

ZnPc	λmax [nm]	$E_{0\text{-}0}$ [nm][b]	$E_{0\text{-}0}$ [eV]c	Eox [V][a] vs. Fc/Fc^+	HOMO [V] vs. NHE]	LUMO [V] vs. NHE]
1	674	696	1.78	0.38	1.02	-0.76
2	675	692	1.79	0.44	1.08	-0.71
3	681	702	1.76	0.35	0.99	-0.77

[a]Measured in DMF/TBAHFP (0.1 M), c=1×10^{-3} molL^{-1}, scan rate=100 mV s^{-1}, vs. Fc/Fc^+.[b]$E_{0\text{-}0}$ was calculated from the intersection between the absorption and emission spectra. [C]$E_{0\text{-}0}$=1240/ λonset, (E_{HOMO} = E_{ox} vs NHE), E_{LUMO}=E_{HOMO}-$E_{0\text{–}0}$.

2. Material Preparation

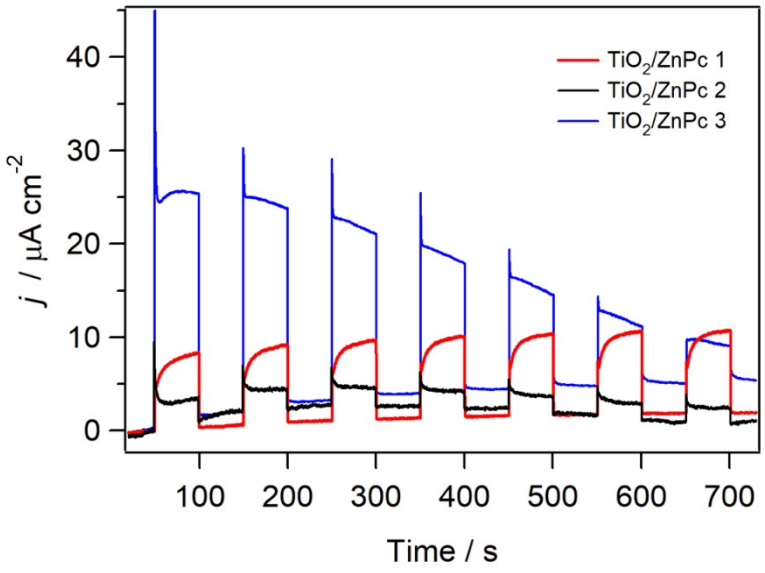
Pc sensitized TiO_2 was prepared according to the general procedure using 1.10^{-5} M Pc solution (in DMSO) and 100 mg TiO_2 [Degussa P25][2].

3. Photochemical HER Experiments

The PEC-HER studies were carried out by using chronoamperometry (CA) and linear sweep voltammetry (LSV) techniques with solar illumination system (Solar Light XPS-300™) by on/off sequence. A three-electrode cell configuration was arranged to detect electrochemical curves of ZnPcs in the aqueous TEOA/Na_2SO_4 electron donor at pH 7 to provide the same condition of PC studies. ZnPcs sensitized TiO_2 coated FTO electrode (ZnPc-1/TiO_2, ZnPc-2/TiO_2, and ZnPc-3/TiO_2), Ag/AgCl, and platinum (Pt) wire electrode was used as the working electrode, reference electrode, and counter

electrode, respectively, under N_2 flow. In addition, the electrochemical potentials were detected considering Ag/AgCl reference electrode (+0.211 V vs. NHE).

Figure S9. Transient photocurrent densities of ZnPc-1/TiO_2, ZnPc-2/TiO_2, or ZnPc-3/TiO_2 hybrid photoelectrodes in the presence of TEOA (5%) and Na_2SO_4 (0.1 M) solution at pH= 7.



The PC hydrogen evolution activities of ZnPc-1/TiO_2, ZnPc-2/TiO_2, and ZnPc-3/TiO_2 photocatalyst were observed in the deoxygenated aqueous TEOA sacrificial electron donor by using a quartz glass reaction flask (135 ml) with a single compartment at room conditions (25 ± 2°C). Before the light irradiation, all ingredients of the reaction mixture (20 ml oxygen-free TEOA at pH 7, 10 mg ZnPc-1/TiO_2, ZnPc-2/TiO_2, and ZnPc-3/TiO_2 powder photocatalysts) were carried into the anaerobic glove box media and prepared by adding into the cell. Afterward, the photo-reaction bottle was sealed with rubber septa under the same nitrogen atmosphere. The prepared HER mixture was taken out of the glove box and was suspended in sacrificial solution by sonication (15 min) towards efficient H_2 production. HER flask was placed in the view of the solar simulator to begin light reactions. The homogeneity of the experiment was continuously provided a magnetic stirrer under a 300 W xenon-lamp (Solar Light XPS300™ with cut-off filter $\lambda \geq 420$ nm). The evolved H_2 gas was observed during 20h with gas chromatography (Shimadzu GC2010Plus) by taking from the headspace of the reaction cell *via* a syringe.

4. TON, TOF and STH efficiency calculations

Turnover number (TON) and Solar-to-hydrogen (STH) efficiency were calculated according to the following equations[3],

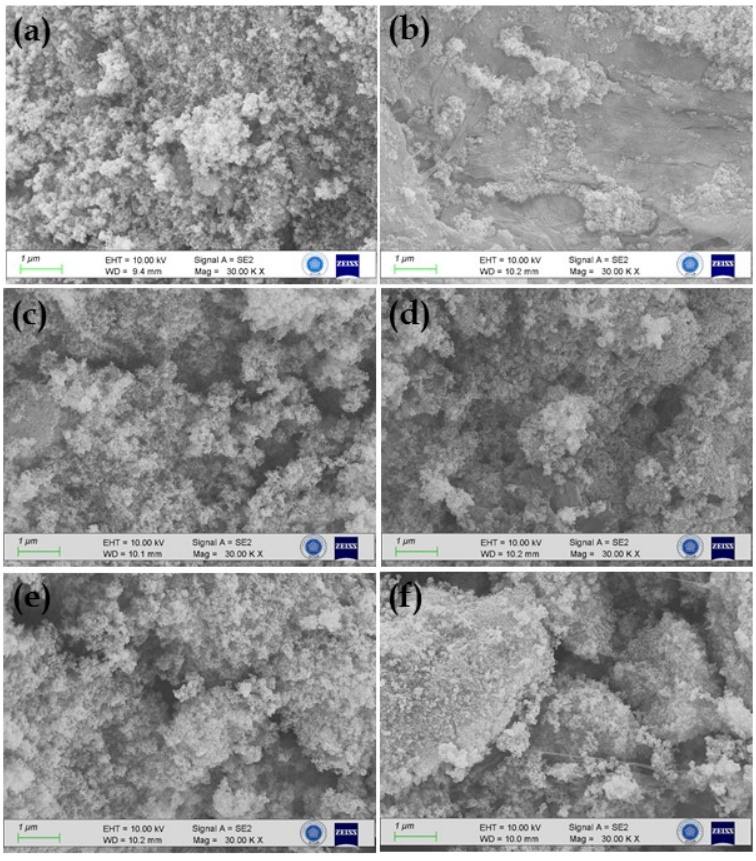
$$TON = \frac{2xNumber\ of\ evolved\ H_2\ molecules}{Number\ of\ dye\ molecules\ adsorbed}$$

Solar-to-hydrogen (STH) efficiency of photocatalysts calculated according to equation 1.

$$STH\% = \frac{R_{H_2} x \Delta G^{o}}{P x A} x100 \qquad (1)$$

Herein, R_{H_2}, ΔG^{o}, P, and A are pointed out as the amount of hydrogen (mmol s^{-1}), Gibbs free energy for generating one mole of hydrogen (J mol^{-1}), sunlight intensity (mW cm^{-2}) and irradiation area (cm^2), respectively. P is measured by Newport USB Virtual Power Meter (844-PE-USB) with irradiance sensor (818-RAD).

Figure S10. SEM images of ZnPcs/TiO_2 before (a,c,e) and after (b,d,f) photocatalytic reactions (ZnPc-1/TiO_2: a,b; ZnPc-2/TiO_2: c,d; ZnPc-3/TiO_2: e,f).



5. DFT and TD-DFT studies

The required electronic structure calculations of the investigated sensitizers and their corresponding TiO_2 clusters were all performed by Gaussian 09 (Revision D.01)[4]. To this purpose, the relevant starting geometries were prepared and the postprocessing processes were accomplished by using GaussView

(v5.0.8)[5] and Chemcraft (v1.8)[6] front-end visualization software. In order to detect the most adequate ground-state geometries, the potential isomers of the dyes including the tri-tertbutyl units in different positions were studied, and in the light of the experimentally detected chemical structures, the most stable and therefore acceptable geometries were detected, and the further calculations were made according to these findings. During the first step of the calculations, the structures were optimized with no symmetry restrictions by using density functional theory (DFT) with B3LYP hybrid functional at the relativistic effective core potential basis set of double zeta quality, LANL2DZ (Los Alamos National Laboratory 2 Double-Zeta)[7], which has been proven in the literature as ideal in order to predict the geometry of the macrocyclic metal complexes consisting of a cavity which is beneficial during the photocatalytic processes[8]. The outputs of this part were used to prepare surface projection and electrostatic potential (ESP) maps (**Figure S14-16** and **Figure S17-19**, respectively).

Following to the geometry optimization step, the required vibrational frequency calculations were also done in order to ensure the local minima. All these calculations were made in the solvent phase by using the theory of self-consistent reaction field (SCRF) using the polarizable conductor calculation model (CPCM) that was recognized as an accurate method for simulating the experimental findings[9,10]. In our case, the experimental UV-*vis* were obtained in DMSO, therefore in order to compare the findings from the computational studies with the experimental ones, the corresponding calculation of the reaction field was performed in the same solvent system. The C1 symmetry of the ZnPcs was confirmed from theoretical studies. The optimized geometries of the target systems are depicted in **Figure S11-S13** Further investigations were performed by using Multiwfn (v.3.8) software including the investigation of non-covalent interactions (NCIs)[11] and the executed data are subsequently visualized by using the VMD (visual molecular dynamics) molecular graphics viewer (v.1.9.3)[12]. The frontier orbital compositions, including the major and minor contribution of the specific orbitals, were detected by using AOMix (v.6.94b)[13].

In the following step, the global descriptors were predicted, including the highest occupied molecular orbital (ε_{HOMO}), lowest unoccupied molecular orbital (ε_{LUMO}), and consequently the bandgap ($\varepsilon_{gap=}$ ε_{LUMO-} ε_{HOMO}) energies and their contour plots were graphically presented (see Figure x). According to time-dependent DFT (TD-DFT) calculations, the first sixteen vertical excitations of the target ZnPcs and their TiO_2 clusters were studied. The defined optimized geometries of the compounds were used as input and the calculations were performed at the CPCM/TD-CAM-B3LYP/LANL2DZ level[14,15]. The maximum absorbance wavelength (max) and oscillator strength (f) values were predicted, and the partial contributions of various subunits to particular molecular orbitals, charting of the estimated UV–vis spectra, and transitions associated with this data were done using GaussSum (v3.0)[16].

As indicated before, the initial geometries of the ZnPcs and their TiO_2 clusters were first defined according to the experimental data obtained from spectral analysis, and different orientations of the tert-

butyl substituents were studied in order to assess the required cartesian coordinates to be used for the geometry optimization step.

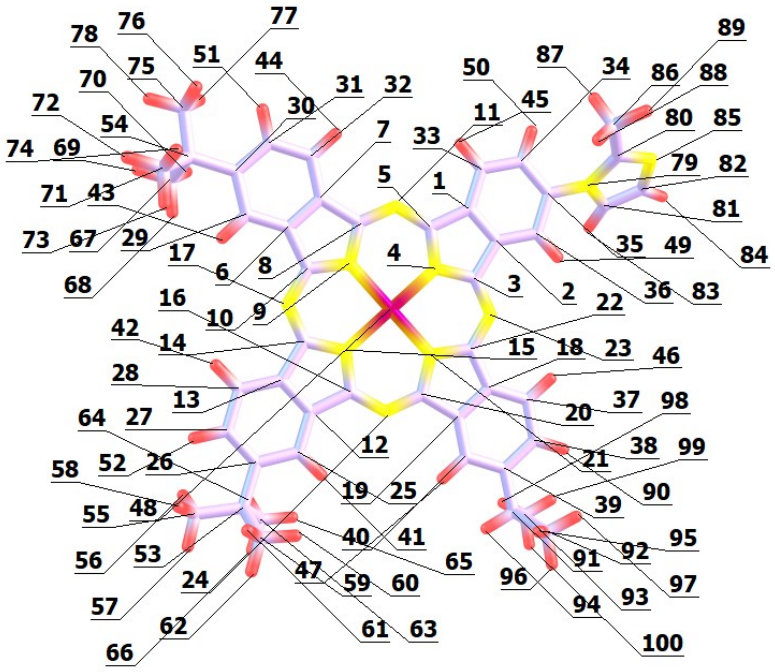
According to the obtained SCF energies, the most appropriate (lower in energy, higher in stability) isomers were defined for each macrosystem, and these input structures were executed for further computations. Compared to the traditional carboxylic acid anchoring group, the impact of the imidazole anchoring system is the joint point of both experimental and theoretical studies. In order to reveal this phenomenon, the initial geometries of the TiO_2 clusters of the investigated ZnPc sensitizers were also prepared, and depending on their consisting anchoring group number, the number of TiO_2 units was predicted (in the case of ZnPc-1 and ZnPc-3; only one TiO_2 unit was placed, whereas for ZnPc-2, the TiO_2 unit number was elevated to four).

According to geometry optimization and frequency calculations, the initial findings could be able to visualize comprising the most stable geometries (**Fig S11-S13**), surface projection (**Fig S14-S16**), and ESP (**Fig S17-S19**) maps. Surface projection and electrostatic potentials (ESP) are accepted as versatile tools to foresee the molecules' total charge distribution and electrostatic behavior (Kesavan et al., 2019). In the light of these studies, it could be clearly seen that the symmetry system for the whole macromolecules was found as C1. For each of the investigated systems, the planar configuration of the core zinc phthalocyanine system could directly facilitate the electron excitation from the dye to the semiconductor (in our case, TiO_2).

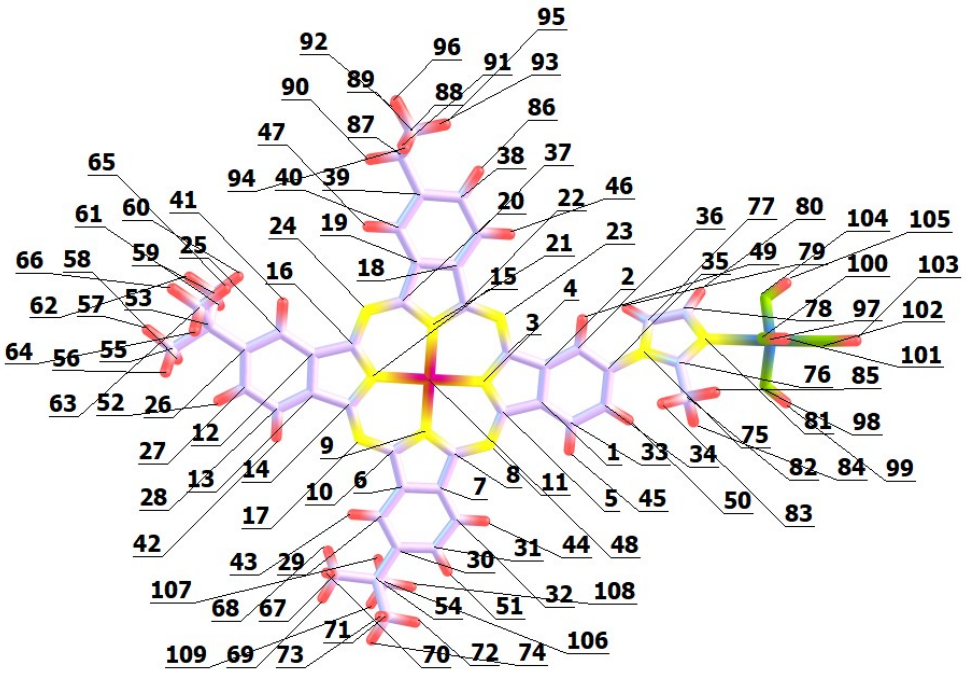
Especially when compared the ESP maps of ZnPc-1 and ZnPc-2, the dipole moment vectors of these systems could give a clue in the fundamental difference with these competitor molecules. ZnPc-2 system, due to symmetrical orientation of the four identical imidazole anchoring groups end up by the decrease of the total dipole moment of the system, whereas ZnPc-1 system has an elevated dipole moment vector, placed from the center of the zinc center to peripheral units, reveals the reactivity differences of these two photosensitizers. The same trend could be followed from the surface projection maps. The ZnPc-1 and ZnPc-3 were similar in the distribution of the Mulliken charges and, accordingly, their accumulation of the electrons on their scaffolds. In order to better understand these observations, the corresponding TiO_2 clusters should also be compared with pristine ZnPcs.

Accordingly, the major difference in charge distributions (see corresponding ESP maps) and dipole moment values could be detected in the case of ZnPc-1 (8.6313 D [ZnPc-1] to 6.5128 D [ZnPc-1@TiO_2]), which revealed the stronger interaction of the dye molecule with the TiO_2 counterpart.

Figure S11. Atomic numbering scheme of ZnPc-1 and ZnPc-1@TiO_2.

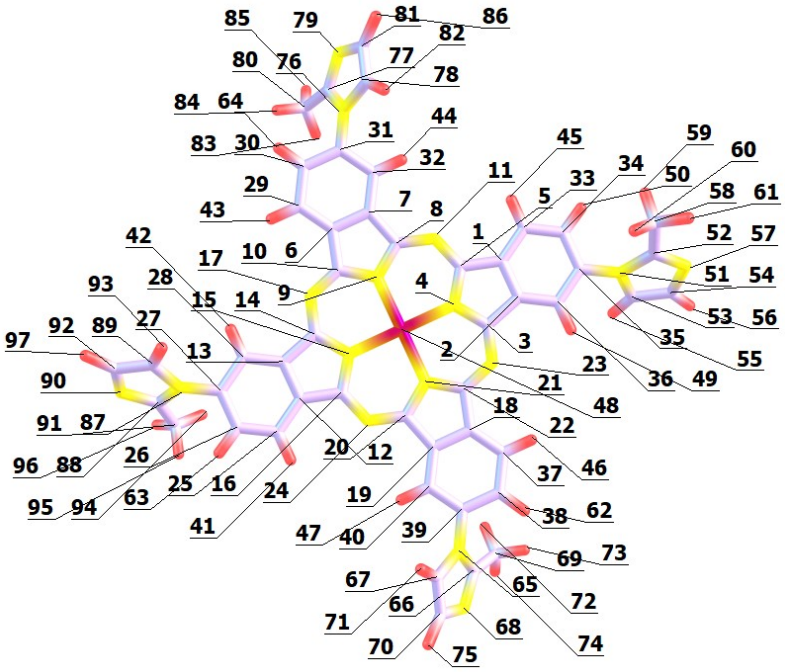


ZnPc-1

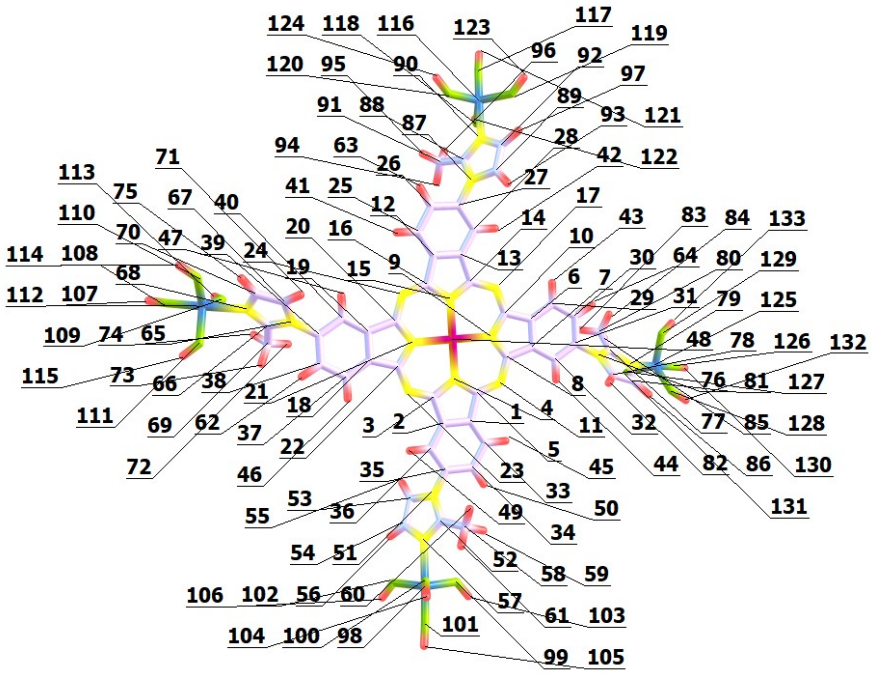


ZnPc-1@TiO_2

Figure S12. Atomic numbering scheme of ZnPc-2 and ZnPc-2@TiO_2.

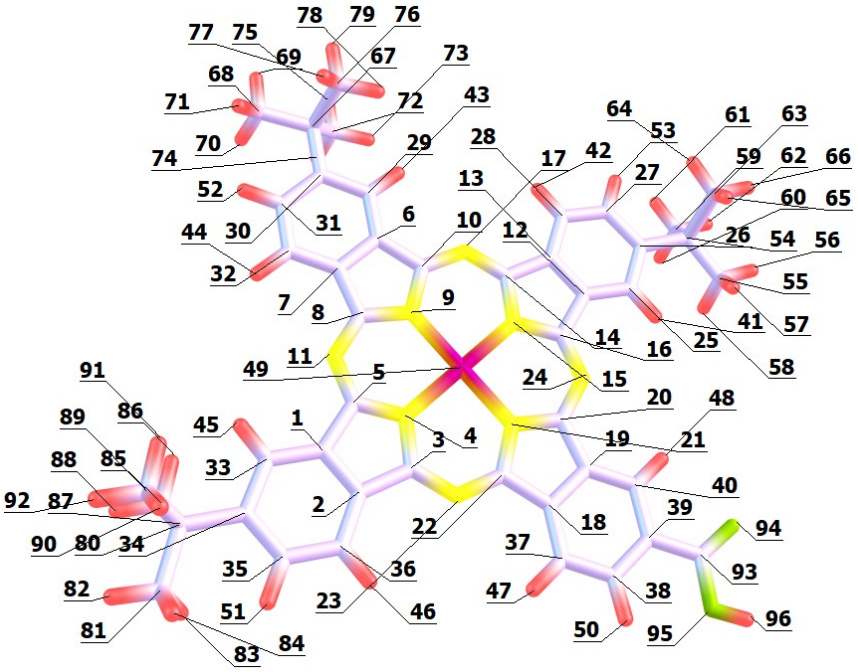


ZnPc-2

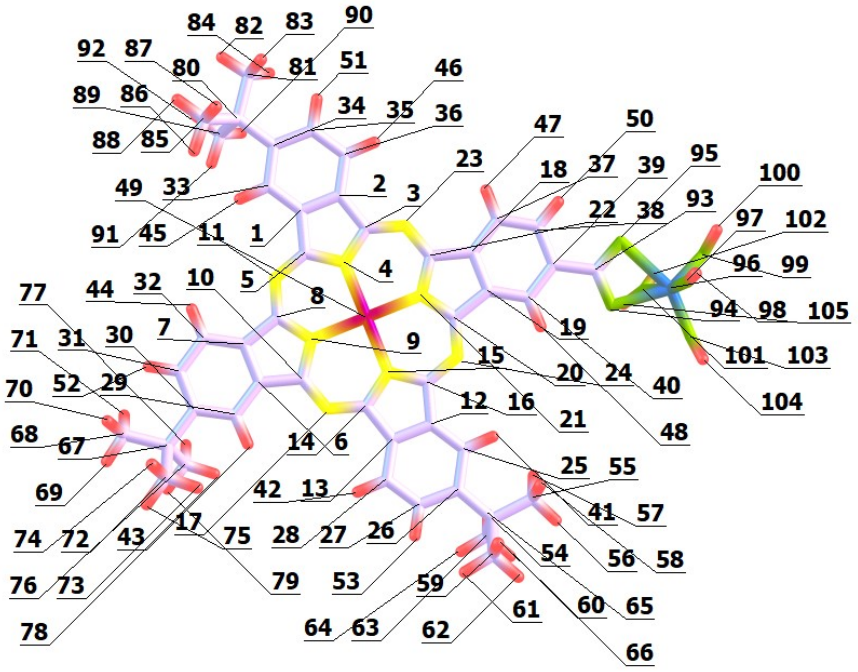


ZnPc-2@TiO_2

Figure S13. Atomic numbering scheme of ZnPc-3 and ZnPc-3@TiO_2.



ZnPc-3



ZnPc-3@TiO_2

Figure S14. Surface projection map of the investigated ZnPc-1 and ZnPc-1@TiO_2

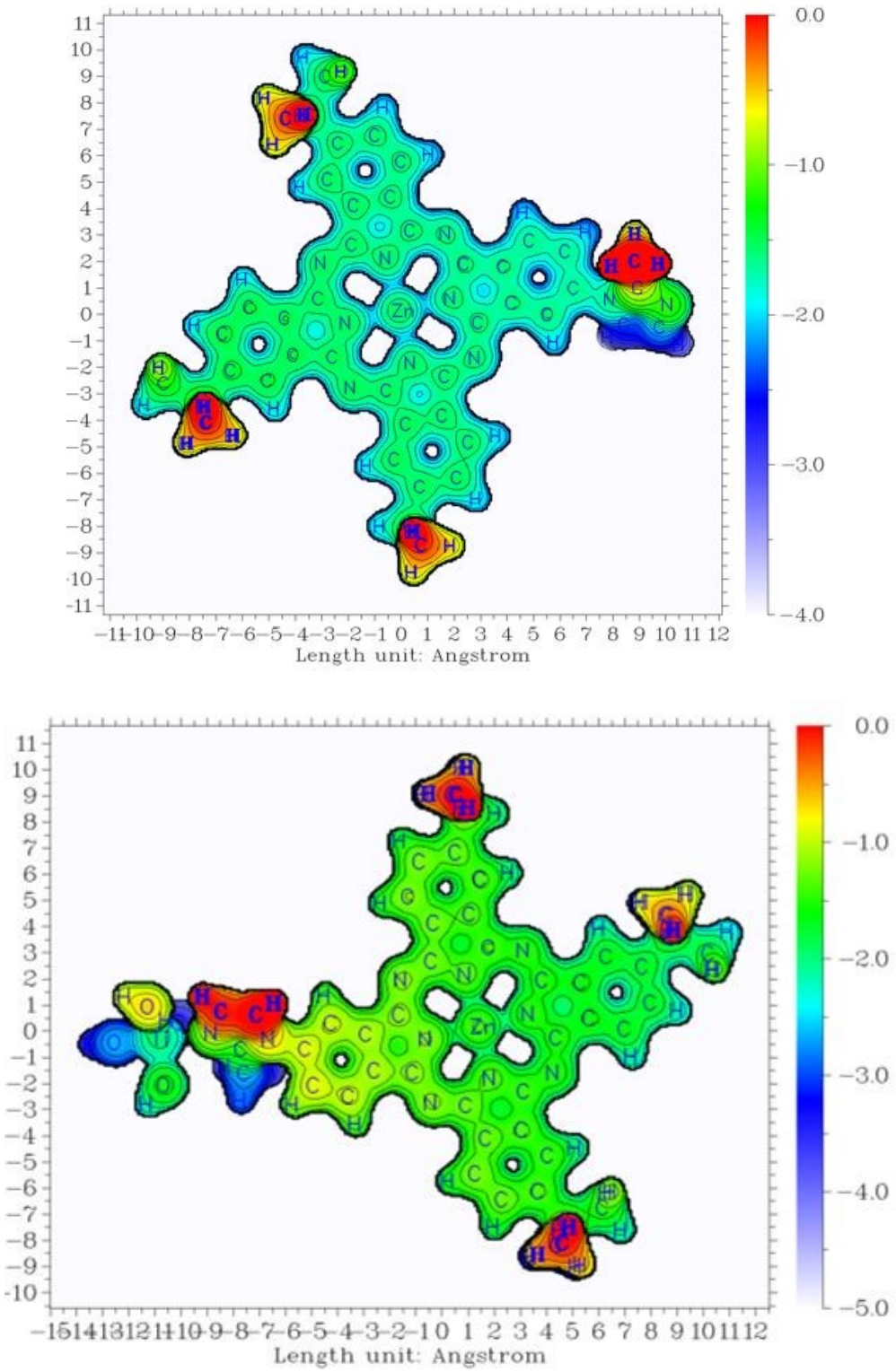


Figure S15. Surface projection map of the investigated ZnPc-2 and ZnPc-2@TiO_2

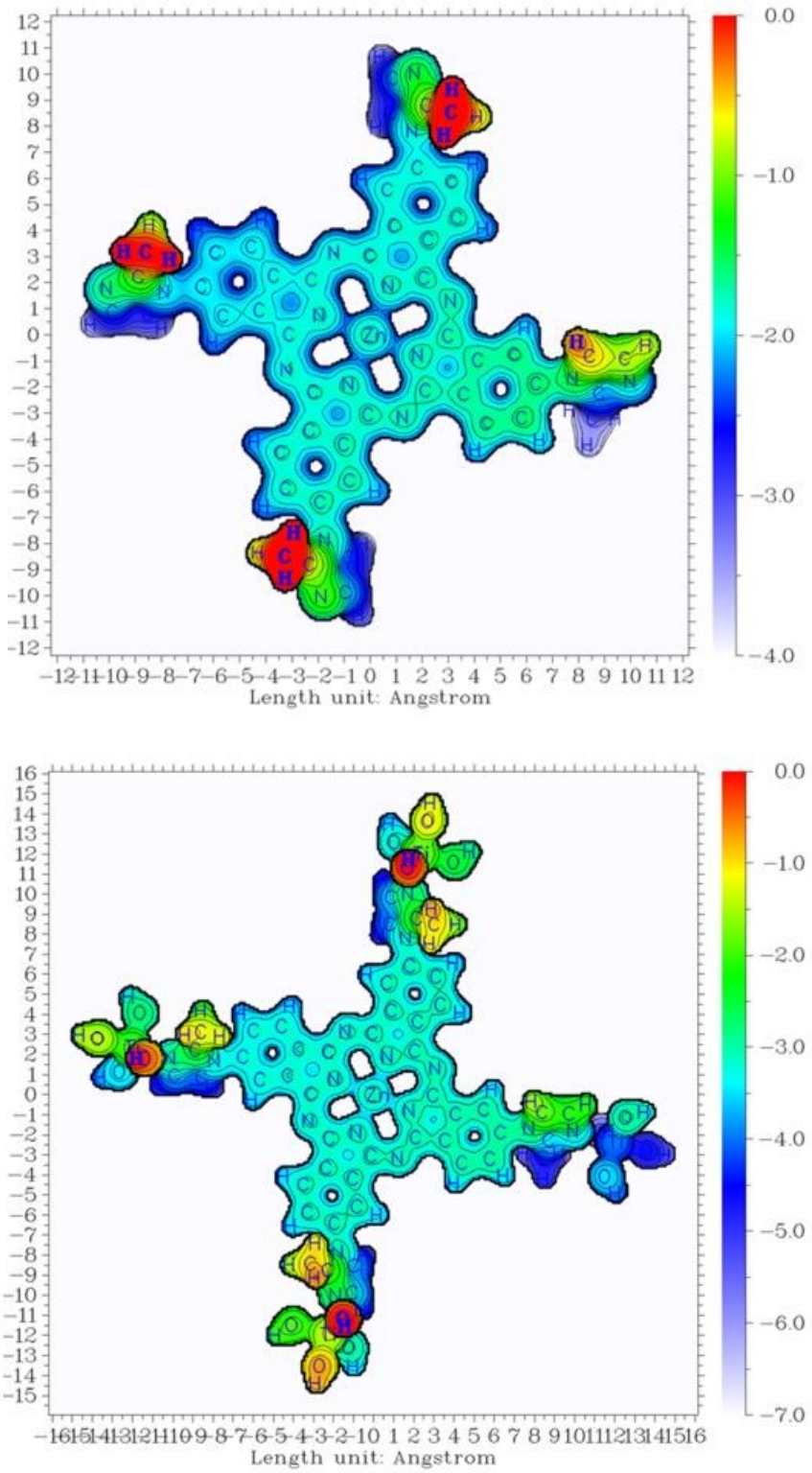


Figure S16. Surface projection map of the investigated ZnPc-3 and ZnPc-3@TiO_2

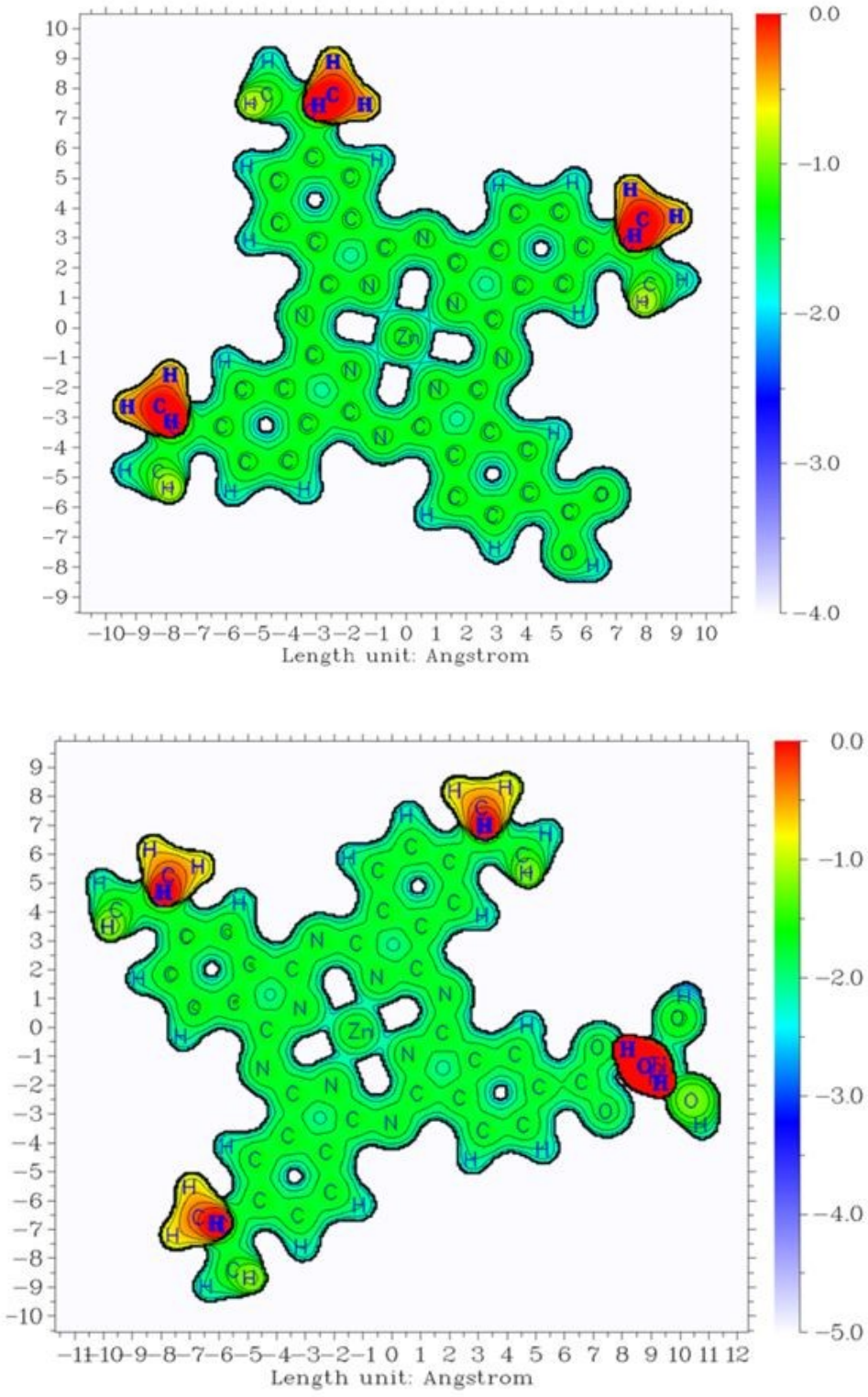


Fig S17. (*left*) Electrostatic potential (ESP) map representing charge density distributions of ZnPc-1 and ZnPc-1@TiO_2 [CPCM/B3LYP/LANL2DZ]. The counter surface is based on the Van der Waals surface with an isodensity of 0.001e/$Bohr^3$. (*right*)

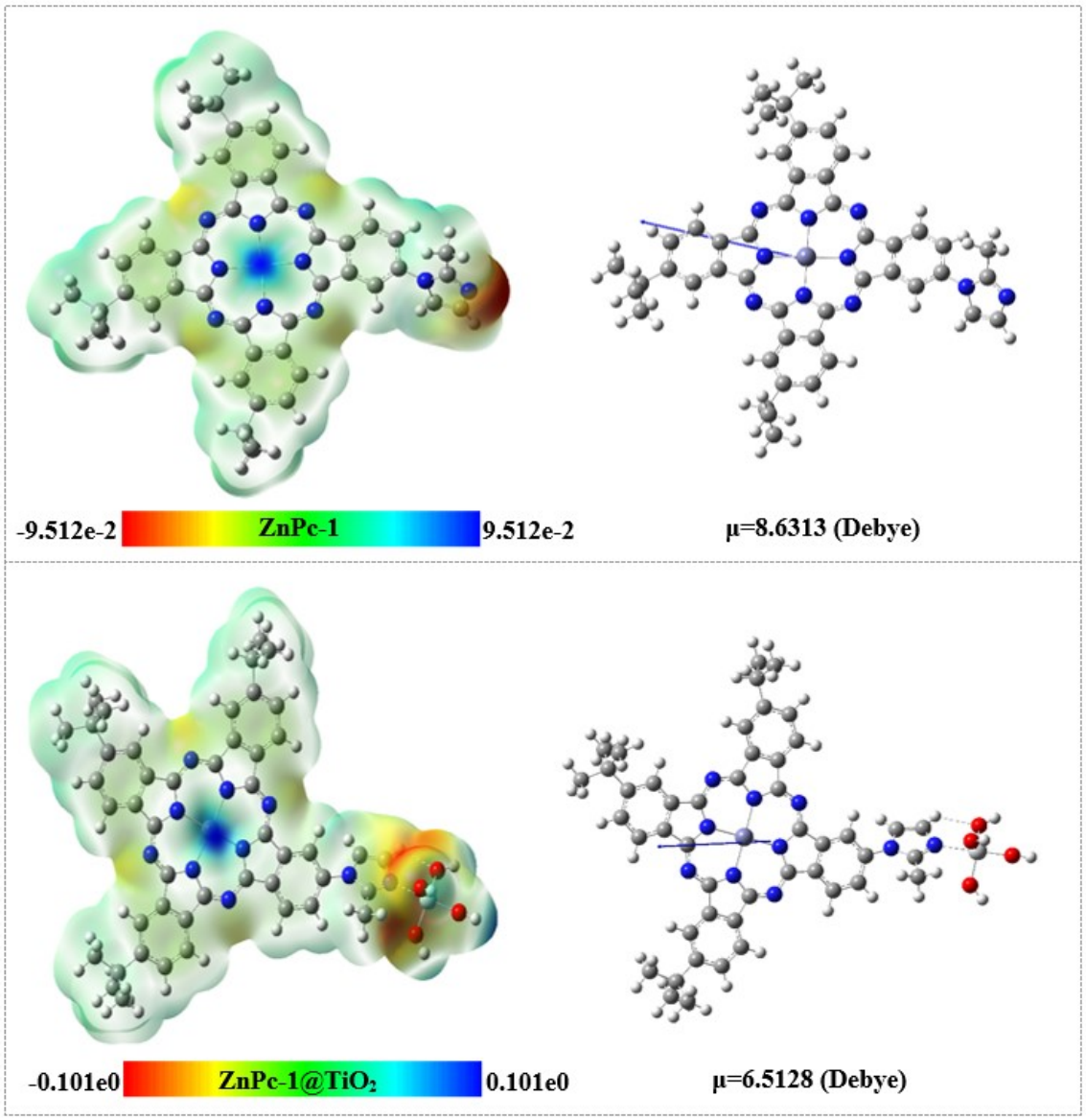


Fig S18. (*left*) Electrostatic potential (ESP) map representing charge density distributions of ZnPc-2 and ZnPc-2@TiO_2 [CPCM/B3LYP/LANL2DZ]. The counter surface is based on the Van der Waals surface with an isodensity of 0.001e/$Bohr^3$. (*right*)

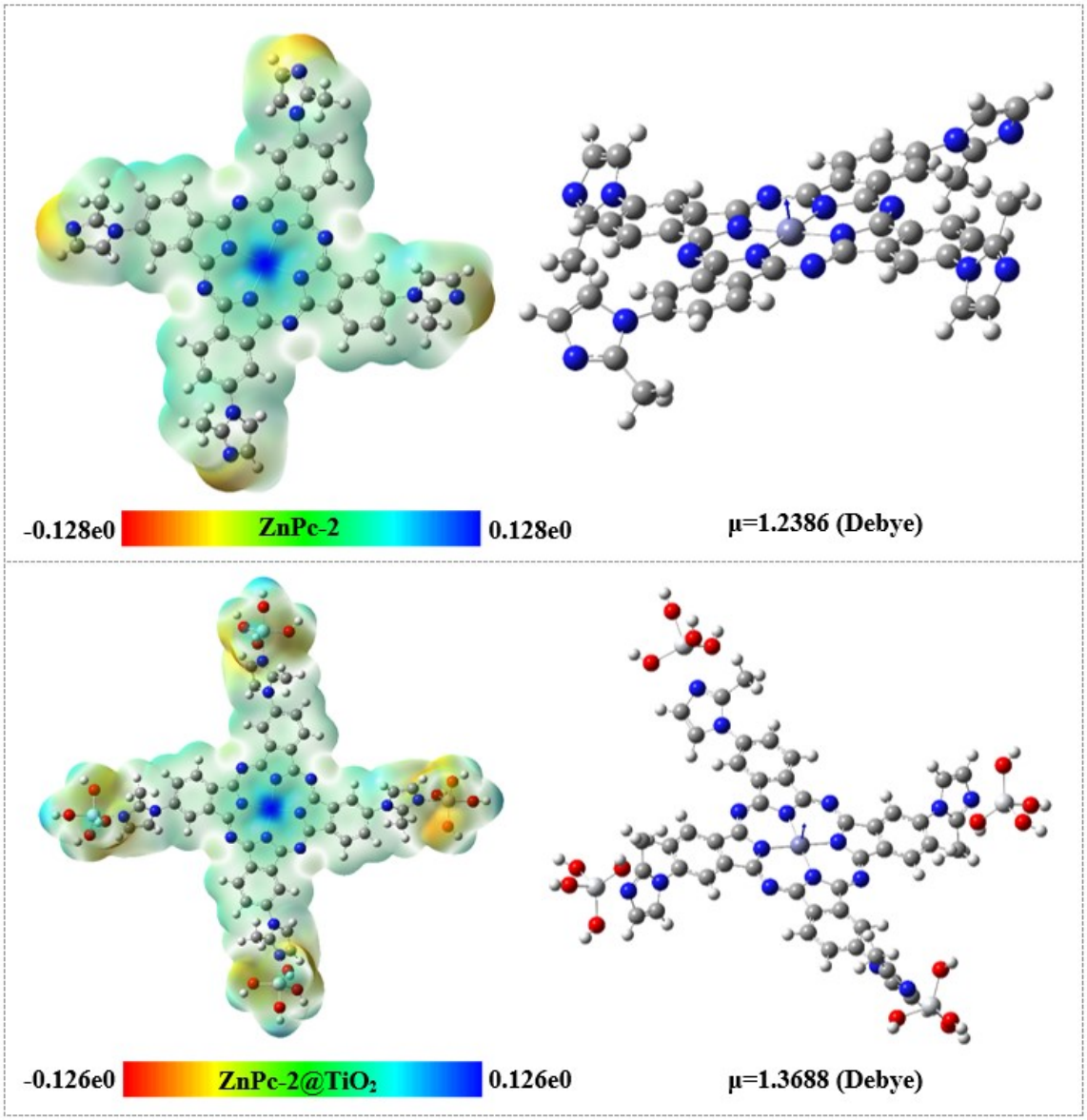
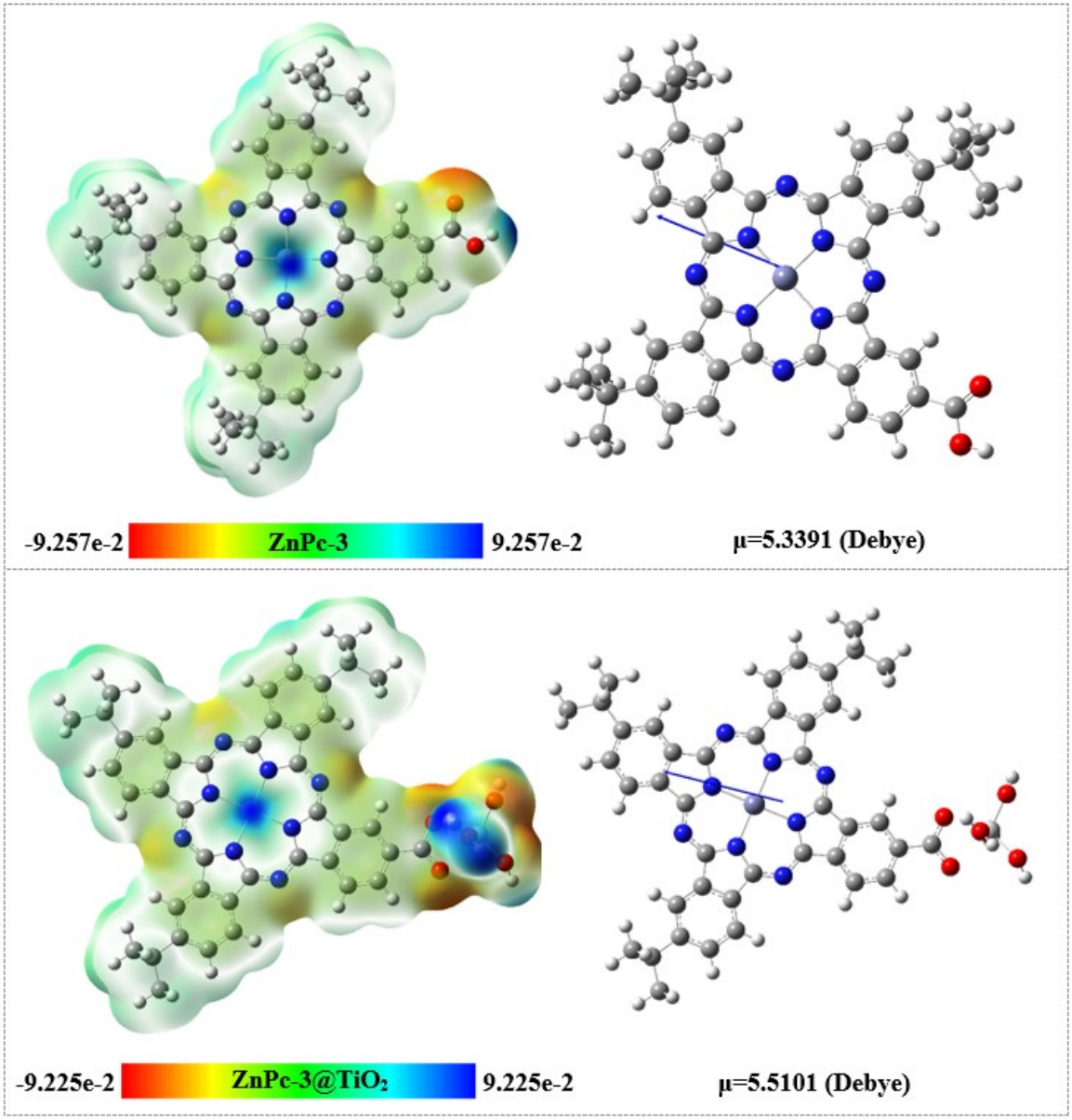


Fig S19. (*left*) Electrostatic potential (ESP) map representing charge density distributions of ZnPc-3 and ZnPc-3@TiO_2 [CPCM/B3LYP/LANL2DZ]. The counter surface is based on the Van der Waals surface with an isodensity of 0.001e/$Bohr^3$. (*right*)



According to DFT studies, the corresponding frontier orbital energies (HOMO, LUMO, and bandgap) were detected. These values are critical to reveal the interaction mechanism and foresee the kinetic stabilities of target photosensitizers. The corresponding HOMO and LUMO isodensity surface plots are provided in Fig x for ZnPcs, and their representative composition analysis, including the contour plots of ZnPcs-TiO_2 clusters, could be found in Table S2-S3. As it is known, these values are critical in order to reveal the interaction mechanism and to foresee the kinetic stabilities of target photosensitizers. It should be emphasized that the calculated orbital energy trend is in accordance with the experimental studies. In the case of ZnPcs-TiO_2 clusters, we could be able to observe the net difference in LUMO orbitals' distribution patterns. In these cases, the LUMO orbitals were found to be shifted to the TiO_2 cluster. ZnPc-2 demonstrated a highly organized and symmetrical pattern, howbeit for ZnPc-1 and ZnPc-3, the unidirectional orientation could explain their highest charge transfer characteristics.

Figure S20. Graphical representation of frontier orbital energy levels and bandgap (E_{gap}=E_{LUMO}-E_{HOMO}) values of ZnPc-1, ZnPc-2 and ZnPc-3 [CPCM/B3LYP/LANL2DZ] and their corresponding HOMO-LUMO contour plots (*the contour thresholds for corresponding molecular orbitals are taken as ±0.02 au).*

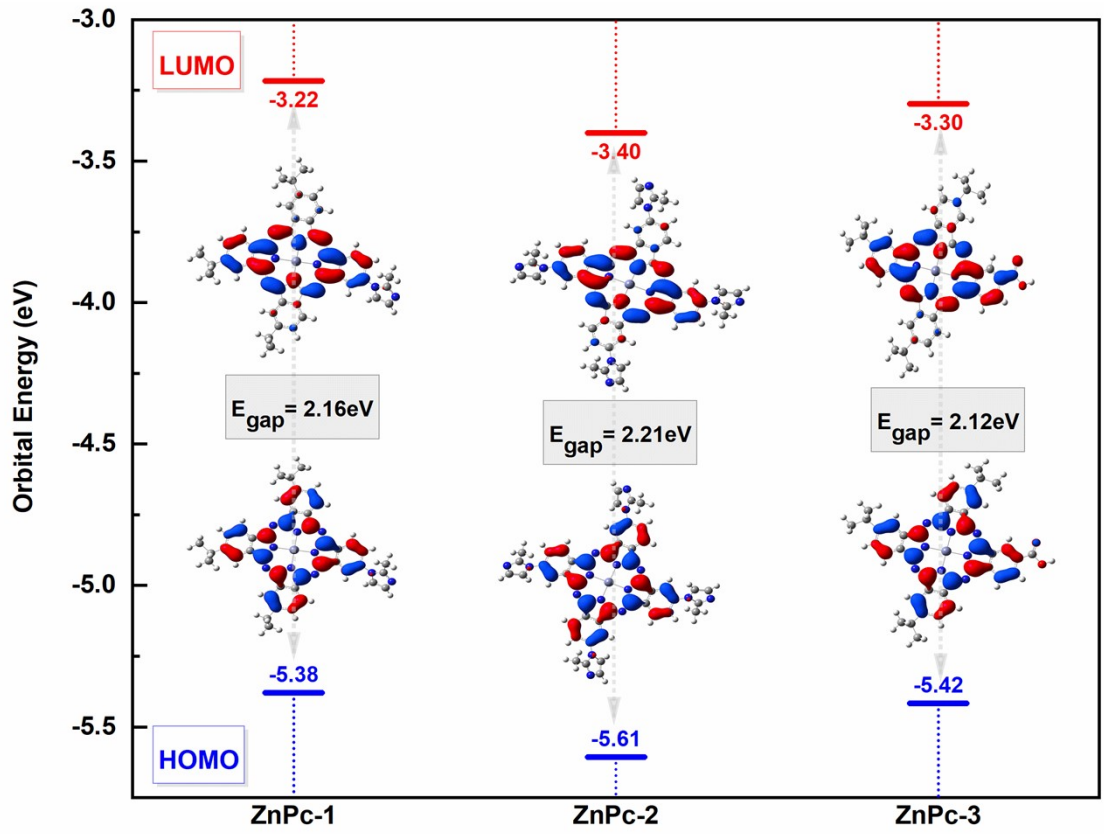


Table S2. HOMO and LUMO isodensity surface plots and their representative composition analysis of ZnPc-1, ZnPc-2 and ZnPc-3

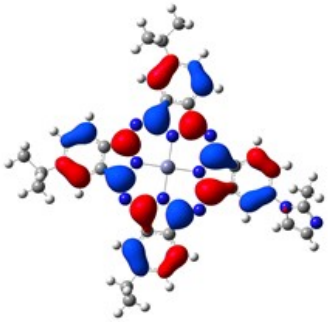
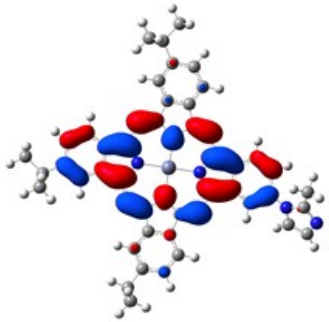
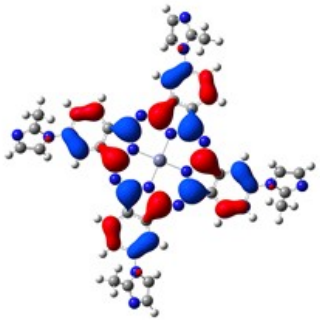
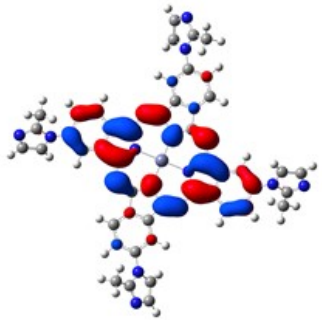
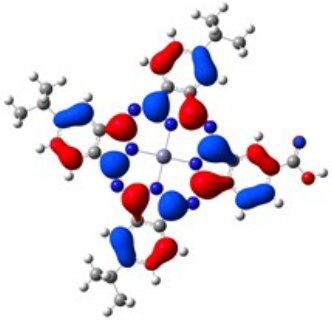
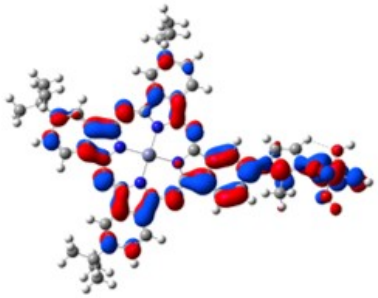
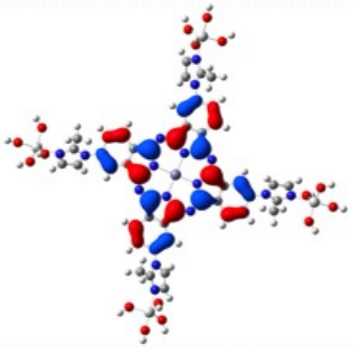
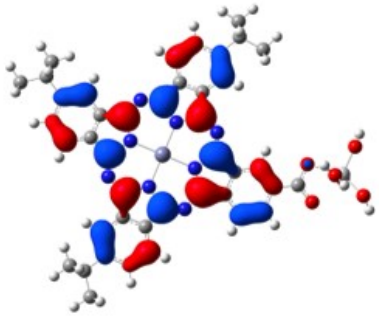
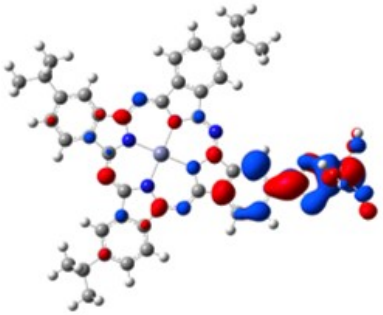
Entry	HOMO (the contour thresholds for molecular orbitals is ±0.02 au).	LUMO (the contour thresholds for molecular orbitals is ±0.02 au).	Composition of HOMO&LUMO MOs in terms of most important AOs (signs indicate the signs of the corresponding LCAO-MO coefficients)
ZnPc-1			**HOMO (Energy, eV: -5.379)** + 6.8% 4PZ(C3) - 6.7% 4PZ(C22) - 6.6% 4PZ(C5) + 6.4% 4PZ(C20) + 6.3% 4PZ(C8) - 6.2% 4PZ(C16) **LUMO (Energy, eV: -3.217)** + 7.4% 4PZ(C16) - 6.7% 4PZ(C5) - 6.2% 4PZ(C14) + 5.6% 4PZ(C3) - 4.7% 4PZ(N23) - 4.2% 4PZ(N9)
ZnPc-2			**HOMO (Energy, eV: -5.606)** + 6.5% 4PZ(C20) + 6.5% 4PZ(C3) + 6.5% 4PZ(C8) + 6.5% 4PZ(C14) - 6.4% 4PZ(C22) - 6.4% 4PZ(C16) **LUMO (Energy, eV: -3.401)** + 7.5% 4PZ(C5) - 7.5% 4PZ(C16) + 5.1% 4PZ(N23) - 5.1% 4PZ(N17) + 4.9% 4PZ(C14) - 4.9% 4PZ(C3)
ZnPc-3			**HOMO (Energy, eV: -5.417)** + 7.1% 4PZ(C22) - 7.0% 4PZ(C20) + 6.7% 4PZ(C16) - 6.5% 4PZ(C3) - 6.1% 4PZ(C14) + 6.0% 4PZ(C5) **LUMO (Energy, eV: -3.297)** + 7.8% 4PZ(C10) - 6.6% 4PZ(C22) - 5.5% 4PZ(N24) - 5.2% 4PZ(C8) + 4.4% 4PZ(N11) - 3.9% 4PZ(N4)

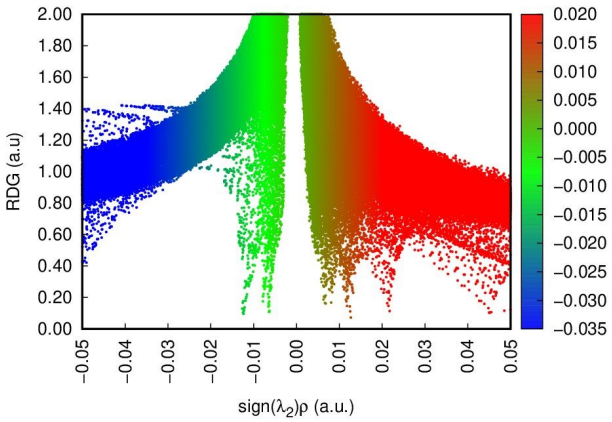
Table S3. HOMO and LUMO isodensity surface plots and their representative composition analysis of ZnPc-1@TiO_2, ZnPc-2@TiO_2 and ZnPc-3@TiO_2

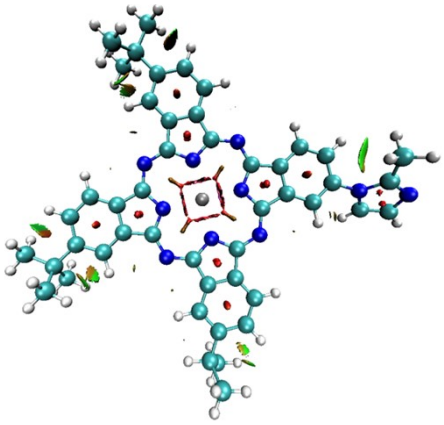
Entry	HOMO (the contour thresholds for molecular orbitals is ±0.02 au).	LUMO (the contour thresholds for molecular orbitals is ±0.02 au).	Composition of HOMO&LUMO MOs in terms of most important AOs (signs indicate the signs of the corresponding LCAO-MO coefficients)
ZnPc-1@TiO_2			**HOMO (Energy, eV: -5.405)** + 6.9% 4PZ(C3) - 6.8% 4PZ(C5) - 6.6% 4PZ(C22) + 6.5% 4PZ(C8) + 6.3% 4PZ(C20) - 6.1% 4PZ(C10) **LUMO (Energy, eV: -3.229)** + 11.5% 7D+1(Ti97) - 8.2% 7D0(Ti97) - 7.5% 7D-2(Ti97) + 3.7% 4PZ(C1) + 3.5% 4PZ(C35) + 2.7% 4PZ(N17)
ZnPc-2@TiO_2			**HOMO (Energy, eV: -5.664)** + 6.5% 4PZ(C8) + 6.5% 4PZ(C14) + 6.5% 4PZ(C20) + 6.5% 4PZ(C3) - 6.5% 4PZ(C10) - 6.5% 4PZ(C16) **LUMO (Energy, eV: -3.445)** + 3.1% 4PZ(C40) + 3.0% 7D+1(Ti116) + 2.9% 7D0(Ti107) - 2.9% 4PZ(C28) - 2.8% 7D+1(Ti98) - 2.7% 4PZ(C36)
ZnPc-3@TiO_2			**HOMO (Energy, eV: -5.403)** + 7.0% 4PZ(C22) - 6.9% 4PZ(C20) + 6.7% 4PZ(C16) - 6.5% 4PZ(C3) - 6.1% 4PZ(C14) + 6.0% 4PZ(C5) **LUMO (Energy, eV: -3.276)** 43.2% 7D+1(Ti96) + 8.2% 4PZ(C93) - 4.9% 4PZ(C40) + 4.6% 4PX(O97) - 2.8% 4PZ(O95) + 2.7% 4PZ(C18)

In the subsequent section of the theoretical studies, the non-covalent interaction (NCI) patterns were also investigated. The term non-covalent interaction (NCI) is useful in explaining a variety of interactions, including electrostatics, hydrogen bonding, Pauli repulsion, and dispersion. The related NCI analysis was carried out in this section of the research using a newly established computational theory called as the reduced density gradient (RDG) technique[17-20].The corresponding 2D and 3D NCI plots are provided in Fig S19-S20. According to corresponding calculations, the non-covalent interactions (NCI) in ZnPc-3@TiO_2 were found to be more abundant than ZnPc-1 and ZnPc-2's TiO_2 clusters due to the carboxylic acid anchoring group forming a stronger attraction with the TiO_2 subunit, and NCI of ZnPc-2 was detected to be augmented when compared to ZnPc-1 due to the impact of four imidazole units interacting with four TiO_2 subunits. This phenomenon has a potential lowering effect on the photocatalytic performance of ZnPc-2. In the shed of TD-DFT studies, similar to experimental observations, a slight blue shift could be detected for the ZnPc-1 and ZnPc-2 compared to ZnPc-3. As could be concluded from the acquired data, the HOMO to LUMO transitions was responsible for each first vertical transition (even in the case of TiO_2 clusters).

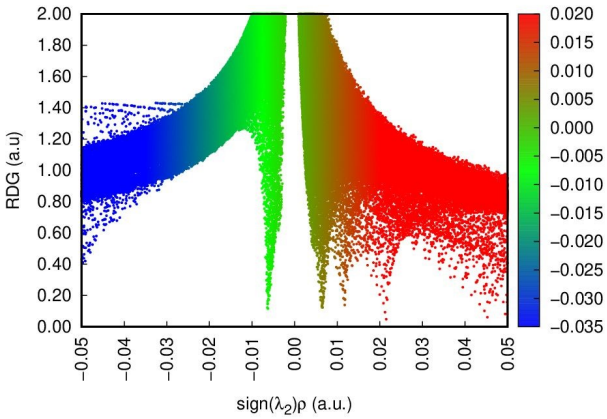
Figure S21. (*left*) Representative plots of the reduced density gradient *versus* the electron density multiplied by the sign of the second Hessian eigenvalue (RDG/*sign*($\lambda 2$)ρ), (*right)* non-covalent interaction plots of ZnPc-1, ZnPc-2 and ZnPc-3.

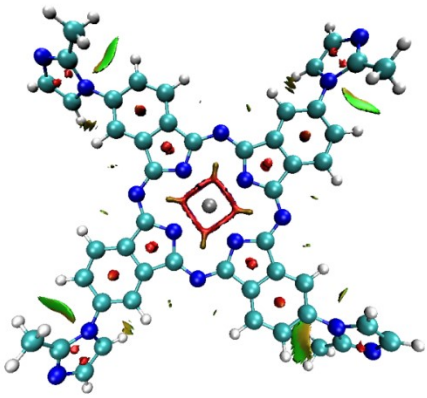
ZnPc-1



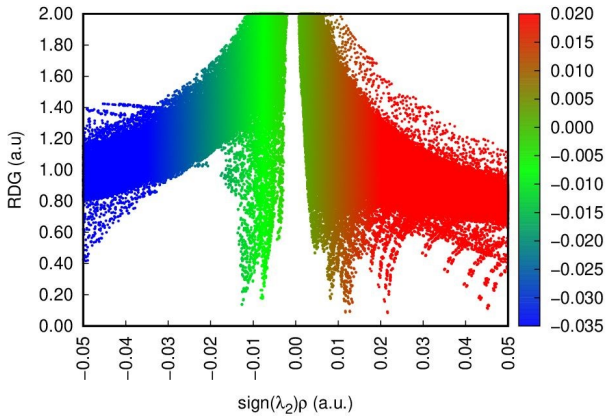


ZnPc-2





ZnPc-3



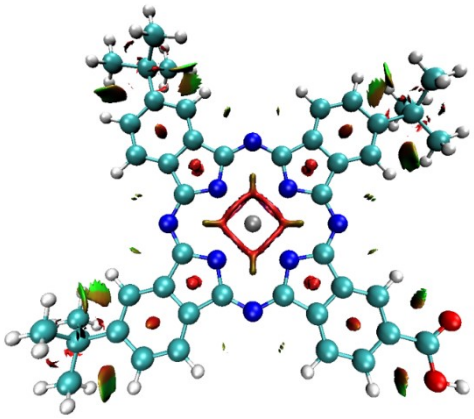
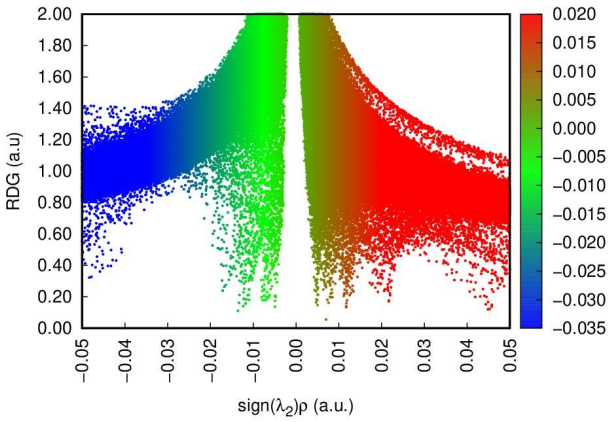
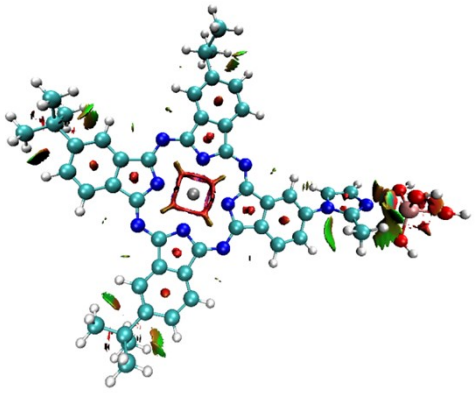


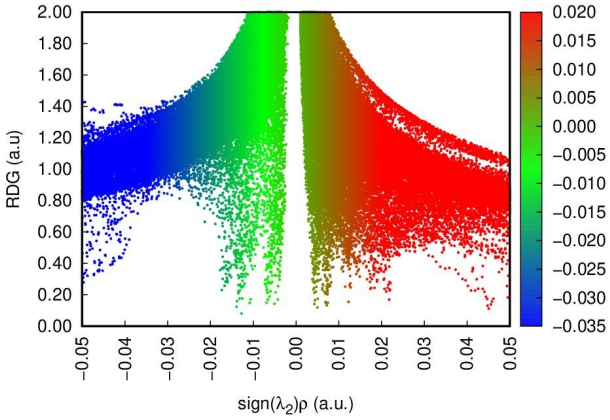
Figure S22. (*left*) Representative plots of the reduced density gradient *versus* the electron density multiplied by the sign of the second Hessian eigenvalue (RDG/*sign*(λ2)ρ), (*right)* non-covalent interaction plots of ZnPc-1@TiO_2, ZnPc-2@TiO_2 and ZnPc-3@TiO_2.

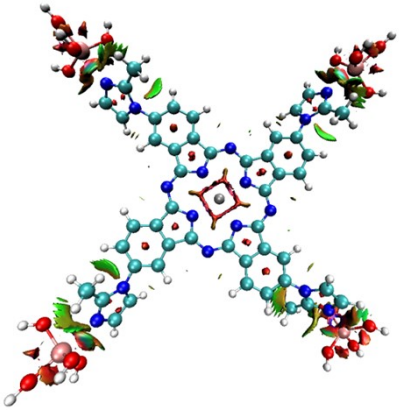
ZnPc-1@TiO_2



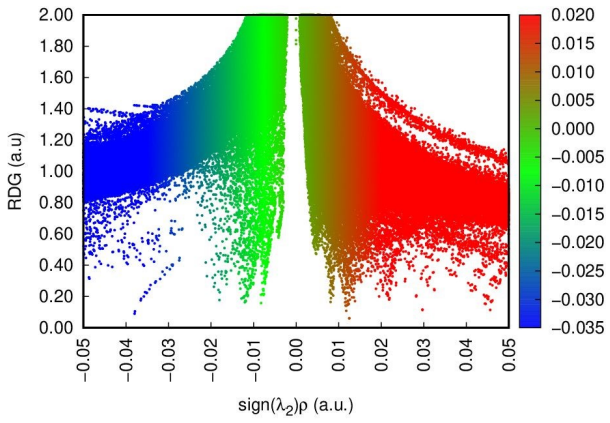


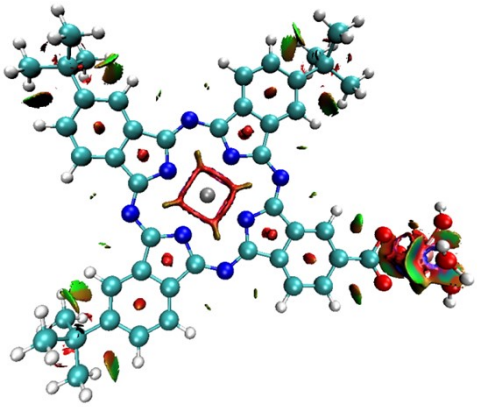
ZnPc-2@TiO_2





ZnPc-3@TiO_2





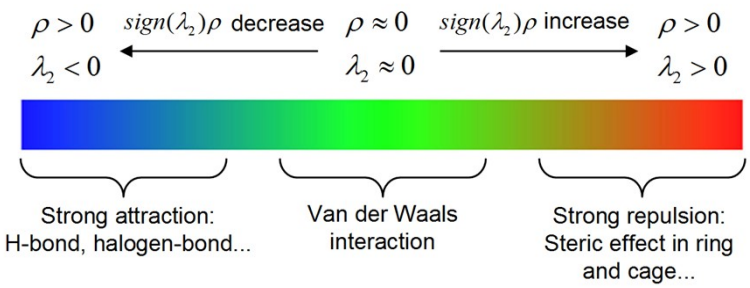


Table S4. Theoretical absorption wavelengths (λ, nm), oscillator strengths (*f*), and the orbitals involved in the transitions of ZnPc-1, ZnPc-2, ZnPc-3 and their TiO_2 clusters.

Entry	λ	*f*	Transitions (%)	
			major contributions	*minor contributions*
ZnPc-1	634	0.69	HOMO→LUMO (96%)	H-6→L+1 (3%)
	623	0.64	HOMO→L+1 (95%)	H-6→LUMO (3%)
ZnPc-2	625	0.71	HOMO→LUMO (95%)	H-9→L+1 (3%), H-8→L+1 (2%)
	624	0.71	HOMO→L+1 (95%)	H-9→LUMO (3%), H-8→LUMO (2%)
ZnPc-3	646	0.69	HOMO→LUMO (96%)	H-4→L+1 (3%)
	618	0.64	HOMO→L+1 (95%)	H-4→LUMO (4%)
ZnPc-1@TiO_2	631	0.70	HOMO→LUMO (96%)	H-5→L+1 (4%)
	621	0.64	HOMO→L+1 (95%)	H-5→LUMO (4%)
ZnPc-2@TiO_2	622	0.74	HOMO→LUMO (94%)	H-8→L+1 (4%), H-7→L+1 (2%)
	621	0.73	HOMO→L+1 (94%)	H-8→LUMO (4%), H-7→LUMO (2%)
ZnPc-3@TiO_2	646	0.72	HOMO→LUMO (96%)	H-4→L+1 (3%)
	619	0.65	HOMO→L+1 (95%)	H-4→LUMO (4%)

S1. Cartesian Coordinates of ZnPc-1

CPCM[DMSO]/B3LYP/LANL2DZ

C	-2.541889000	-1.502917000	0.337362000
C	-2.877490000	-0.118198000	0.339079000
C	-1.612931000	0.625216000	0.238677000
N	-0.574894000	-0.292147000	0.181958000
C	-1.078060000	-1.583410000	0.237587000
C	3.087822000	-3.768782000	-0.002152000
C	1.710406000	-4.103229000	0.092407000
C	0.963519000	-2.836564000	0.116569000
N	1.876353000	-1.790288000	0.034716000
C	3.163800000	-2.298244000	-0.033692000
N	-0.374415000	-2.732715000	0.206578000
C	5.348093000	1.876650000	-0.191904000
C	5.680257000	0.492767000	-0.196462000
C	4.412659000	-0.251422000	-0.131112000
N	3.370153000	0.664799000	-0.090929000
C	3.877269000	1.956491000	-0.123640000
N	4.310680000	-1.593228000	-0.109950000
C	-0.289485000	4.142497000	0.116930000
C	1.090486000	4.477090000	0.030406000
C	1.830661000	3.204861000	-0.017199000
N	0.918056000	2.163494000	0.036889000
C	-0.372344000	2.674666000	0.124516000
N	-1.514157000	1.968601000	0.211189000
N	3.173429000	3.102516000	-0.092955000
C	6.338694000	2.863422000	-0.240974000
C	7.703025000	2.479833000	-0.295907000
C	8.014793000	1.091713000	-0.300220000
C	7.021251000	0.093093000	-0.250965000
C	4.081873000	-4.758519000	-0.049410000
C	3.705739000	-6.118974000	-0.002149000
C	2.316506000	-6.435735000	0.095060000
C	1.316604000	-5.450187000	0.142869000
C	-3.542604000	-2.484624000	0.421583000
C	-4.880073000	-2.065705000	0.508235000
C	-5.206579000	-0.684505000	0.495685000
C	-4.211161000	0.306104000	0.413419000
C	-1.263302000	5.152720000	0.179551000
C	-0.834019000	6.491032000	0.154217000
C	0.545001000	6.841873000	0.070294000
C	1.512461000	5.815748000	0.008248000
H	6.051588000	3.910585000	-0.235173000
H	7.293368000	-0.958225000	-0.254580000
H	5.122454000	-4.465058000	-0.122588000
H	0.268738000	-5.725531000	0.216081000
H	-3.292422000	-3.540515000	0.430060000
H	-2.319124000	4.907193000	0.245445000
H	2.569503000	6.059951000	-0.055872000
Zn	1.394094000	0.186319000	-0.020489000
H	-4.470252000	1.359860000	0.396527000
H	-5.675103000	-2.799164000	0.599665000
H	2.012899000	-7.478281000	0.133691000
H	9.051807000	0.778282000	-0.341850000
C	8.798114000	3.570503000	-0.345387000
C	4.739226000	-7.267241000	-0.048518000
C	10.227907000	2.976918000	-0.401852000
H	10.379256000	2.360013000	-1.297014000
H	10.958225000	3.794918000	-0.434751000
H	10.452224000	2.366382000	0.482319000
C	8.692710000	4.463952000	0.926947000
H	7.713238000	4.951156000	1.002761000
H	8.848677000	3.869047000	1.836433000
H	9.458510000	5.250113000	0.895956000
C	8.588407000	4.454594000	-1.611223000
H	8.672452000	3.853679000	-2.526243000

H	7.604645000	4.939168000	-1.611716000
H	9.351651000	5.243109000	-1.647744000
C	6.192756000	-6.747490000	-0.176516000
H	6.478869000	-6.120131000	0.677644000
H	6.882667000	-7.599870000	-0.209008000
H	6.337757000	-6.166044000	-1.096311000
C	4.440731000	-8.183946000	-1.272490000
H	3.435876000	-8.619957000	-1.221214000
H	4.520021000	-7.620680000	-2.211565000
H	5.163374000	-9.009963000	-1.306496000
N	-6.585488000	-0.280887000	0.601989000
C	-7.644585000	-0.676286000	-0.204129000
C	-7.082144000	0.623747000	1.557819000
C	-8.431437000	0.742309000	1.310565000
H	-6.449215000	1.063166000	2.310894000
H	-9.184476000	1.323776000	1.814055000
N	-8.771020000	-0.063965000	0.215458000
C	-7.524764000	-1.602664000	-1.372736000
H	-6.535054000	-1.530046000	-1.834638000
H	-7.688266000	-2.646063000	-1.076572000
H	-8.285662000	-1.334658000	-2.109009000
H	-1.579024000	7.281526000	0.200467000
C	0.971846000	8.309935000	0.046134000
C	0.558453000	9.049056000	1.346069000
C	0.419994000	9.044687000	-1.204066000
H	0.977028000	8.556661000	2.233028000
H	0.922180000	10.084627000	1.324664000
H	-0.533504000	9.078953000	1.456859000
H	0.743141000	8.551090000	-2.129433000
H	-0.677593000	9.070337000	-1.197392000
H	0.780248000	10.081493000	-1.224076000
Ti	-10.840064000	-0.282446000	-0.616091000
O	-10.626599000	-2.060978000	-0.140428000
H	-11.264937000	-2.781760000	-0.307421000
O	-10.062696000	0.314402000	-2.193788000
H	-10.517552000	0.420412000	-3.052081000
O	-12.508345000	-0.436810000	-1.256455000
H	-13.421870000	-0.493170000	-1.570028000
O	-11.229376000	0.944206000	0.718197000
H	-12.103339000	1.327869000	0.923594000
C	4.634356000	-8.106557000	1.260249000
H	4.852377000	-7.487160000	2.140124000
H	3.634690000	-8.538921000	1.387819000
H	5.357778000	-8.932066000	1.234349000
C	2.509176180	8.344883720	-0.037499140
H	2.924098650	7.847180720	0.813988430
H	2.829114020	7.850230850	-0.930728290
H	2.842460420	9.361522160	-0.053866260

S2. Cartesian Coordinates of ZnPc-2

CPCM[DMSO]/B3LYP/LANL2DZ

C	3.652242000	-2.269654000	0.029644000
C	4.192281000	-0.952616000	0.035776000
C	3.049563000	-0.025317000	-0.007244000
N	1.883363000	-0.774349000	-0.032347000
C	2.188900000	-2.127127000	-0.010406000
C	-2.267347000	-3.652830000	-0.067466000
C	-0.950527000	-4.193305000	-0.044252000
C	-0.022934000	-3.049883000	-0.039521000
N	-0.771612000	-1.883372000	-0.058988000
C	-2.124354000	-2.189051000	-0.077291000
N	1.318462000	-3.153919000	-0.016591000
C	-3.649506000	2.267183000	-0.148188000
C	-4.189687000	0.950102000	-0.150903000
C	-3.046869000	0.022876000	-0.109210000
N	-1.880653000	0.771874000	-0.086115000
C	-2.186066000	2.124636000	-0.110499000
N	-3.150948000	-1.318728000	-0.101566000
C	2.270291000	3.650346000	-0.059263000
C	0.953542000	4.190526000	-0.089471000
C	0.025885000	3.047261000	-0.086057000
N	0.774490000	1.880842000	-0.059755000
C	2.127269000	2.186632000	-0.042430000
N	3.153756000	1.316254000	-0.015673000
N	-1.315582000	3.151342000	-0.108399000
C	-4.493292000	3.387654000	-0.187092000
C	-5.881151000	3.173449000	-0.236233000
C	-6.414185000	1.858359000	-0.228421000
C	-5.571651000	0.729608000	-0.184698000
C	-3.387958000	-4.497085000	-0.078910000
C	-3.174361000	-5.885797000	-0.069959000
C	-1.859819000	-6.418833000	-0.032387000
C	-0.730611000	-5.575544000	-0.020536000
C	4.496505000	-3.389840000	0.068517000
C	5.884145000	-3.175450000	0.120882000
C	6.417088000	-1.860121000	0.116513000
C	5.574106000	-0.731730000	0.073201000
C	3.390842000	4.494893000	-0.056936000
C	3.177511000	5.883268000	-0.091716000
C	1.862438000	6.415994000	-0.111144000
C	0.733269000	5.572816000	-0.109516000
H	-4.088953000	4.394608000	-0.195754000
H	-5.982608000	-0.274705000	-0.169650000
H	-4.394769000	-4.093336000	-0.107126000
H	0.273459000	-5.985564000	0.018037000
H	4.092524000	-4.396978000	0.074937000
H	4.397986000	4.091136000	-0.044539000
H	-0.271438000	5.983049000	-0.114503000
Zn	0.001326000	-0.001208000	-0.057746000
H	5.984145000	0.272981000	0.060636000
H	6.559174000	-4.022266000	0.188199000
N	7.838157000	-1.666028000	0.197300000
C	8.834708000	-2.240021000	-0.602155000
C	8.475622000	-0.804610000	1.106052000
C	9.827641000	-0.898005000	0.834980000
H	7.926041000	-0.250938000	1.849951000
H	10.646201000	-0.396227000	1.327990000
N	10.043139000	-1.785435000	-0.231049000
C	8.581424000	-3.186040000	-1.737558000
H	8.395176000	-4.210761000	-1.392319000
H	7.720256000	-2.876383000	-2.340492000
H	9.467773000	-3.205484000	-2.377560000
H	4.025657000	6.559192000	-0.125006000
H	-6.556371000	4.020354000	-0.302530000
H	-4.021560000	-6.562606000	-0.110514000
N	1.670789000	7.838397000	-0.168402000

C	2.225835000	8.817856000	0.664676000
C	0.832659000	8.495043000	-1.085087000
N	1.780819000	10.034197000	0.307781000
C	3.147544000	8.540407000	1.814288000
C	0.918154000	9.841067000	-0.782620000
H	0.296880000	7.961093000	-1.853033000
H	2.831036000	7.660569000	2.385807000
H	4.181531000	8.371414000	1.487816000
H	3.145505000	9.409116000	2.478392000
H	0.429231000	10.670069000	-1.271087000
N	-1.667997000	-7.842320000	-0.038559000
C	-2.258824000	-8.795165000	0.800652000
C	-0.793169000	-8.527389000	-0.898610000
N	-1.801705000	-10.022258000	0.500222000
C	-3.226496000	-8.482181000	1.902393000
C	-0.894613000	-9.863439000	-0.559253000
H	-0.224073000	-8.017904000	-1.659168000
H	-2.937269000	-7.580483000	2.453804000
H	-4.247231000	-8.331185000	1.528762000
H	-3.247356000	-9.326430000	2.597078000
H	-0.387031000	-10.707407000	-1.000827000
N	-7.835537000	1.664750000	-0.305199000
C	-8.829043000	2.239800000	0.496759000
C	-8.476185000	0.804489000	-1.212629000
N	-10.039178000	1.786363000	0.129314000
C	-8.571137000	3.188786000	1.628617000
C	-9.827474000	0.899061000	-0.937558000
H	-7.928808000	0.248926000	-1.956699000
H	-7.699196000	2.888432000	2.220518000
H	-8.399791000	4.215175000	1.280097000
H	-9.449461000	3.200199000	2.279853000
H	-10.647999000	0.398840000	-1.428894000

S3. Cartesian Coordinates of ZnPc-3

CPCM[DMSO]/B3LYP/LANL2DZ

C	-4.029572000	-2.018230000	0.000019000
C	-3.256396000	-3.213303000	0.000021000
C	-1.842666000	-2.807242000	0.000017000
N	-1.789539000	-1.415884000	0.000010000
C	-3.072644000	-0.897236000	0.000011000
C	-1.791030000	3.640354000	-0.000012000
C	-2.983768000	2.864370000	-0.000005000
C	-2.574078000	1.450636000	0.000000000
N	-1.186559000	1.398849000	-0.000004000
C	-0.666578000	2.685463000	-0.000011000
N	-3.422086000	0.406019000	0.000007000
C	3.868846000	1.403498000	-0.000014000
C	3.091287000	2.592590000	-0.000020000
C	1.679796000	2.181496000	-0.000014000
N	1.627138000	0.797112000	-0.000009000
C	2.917702000	0.278514000	-0.000007000
N	0.632582000	3.033183000	-0.000016000
C	1.622868000	-4.254620000	0.000014000
C	2.820721000	-3.478062000	0.000008000
C	2.411362000	-2.066439000	0.000004000
N	1.026893000	-2.018781000	0.000006000
C	0.504597000	-3.303974000	0.000013000
N	-0.798653000	-3.652799000	0.000018000
N	3.262631000	-1.020530000	-0.000002000
C	5.271695000	1.446072000	-0.000014000
C	5.925106000	2.698427000	-0.000020000
C	5.126050000	3.882288000	-0.000030000
C	3.722112000	3.847049000	-0.000030000
C	-1.831696000	5.038271000	-0.000016000
C	-3.086937000	5.699208000	-0.000017000
C	-4.267985000	4.906233000	-0.000006000
C	-4.232864000	3.496796000	-0.000002000
C	-5.428321000	-2.055093000	0.000023000
C	-6.092609000	-3.307663000	0.000032000
C	-5.302537000	-4.491334000	0.000027000
C	-3.893452000	-4.460655000	0.000023000
C	1.672477000	-5.659506000	0.000020000
C	2.931677000	-6.277962000	0.000019000
C	4.126867000	-5.503000000	0.000013000
C	4.077640000	-4.091630000	0.000008000
H	5.833594000	0.519423000	-0.000009000
H	3.142069000	4.765086000	-0.000036000
H	-0.902495000	5.599801000	-0.000019000
H	-5.152890000	2.919772000	0.000005000
H	-5.986913000	-1.124097000	0.000017000
H	-3.319580000	-5.382683000	0.000022000
H	0.761705000	-6.249508000	0.000025000
H	4.994609000	-3.511616000	0.000003000
Zn	-0.080891000	-0.308742000	-0.000001000
H	3.009662000	-7.359353000	0.000024000
H	-5.792404000	-5.458475000	0.000025000
H	-5.236586000	5.393112000	-0.000001000
H	5.616774000	4.851566000	-0.000039000
C	7.465032000	2.830492000	-0.000027000
C	8.175728000	1.454035000	-0.000072000
H	9.262384000	1.605564000	-0.000050000
H	7.922448000	0.863446000	0.890029000
H	7.922475000	0.863518000	-0.890227000
C	7.915992000	3.611327000	-1.270730000
H	7.624258000	3.074997000	-2.183198000
H	7.475955000	4.614953000	-1.310903000
H	9.008223000	3.722758000	-1.273031000
C	7.916015000	3.611255000	1.270714000
H	7.475996000	4.614886000	1.310943000
H	7.624280000	3.074882000	2.183156000
H	9.008248000	3.722667000	1.273012000
C	-3.131497000	7.245014000	-0.000014000
C	-4.578246000	7.799223000	0.000017000
H	-4.544720000	8.895735000	0.000023000
H	-5.137286000	7.483473000	-0.890278000
H	-5.137253000	7.483462000	0.890329000
C	-2.405928000	7.781545000	-1.270379000
H	-1.358265000	7.459960000	-1.308350000
H	-2.903705000	7.429094000	-2.183229000
H	-2.420648000	8.879453000	-1.274047000
C	-2.405877000	7.781539000	1.270325000
H	-2.903618000	7.429087000	2.183193000
H	-1.358213000	7.459950000	1.308253000
H	-2.420593000	8.879448000	1.273996000
C	-7.638709000	-3.348309000	0.000024000
C	-8.196659000	-4.793665000	0.000005000

H	-9.293099000	-4.757345000	-0.000021000
H	-7.882295000	-5.353517000	-0.890281000
H	-7.882339000	-5.353523000	0.890303000
C	-8.173614000	-2.621452000	-1.270240000
H	-7.849111000	-1.574679000	-1.308232000
H	-7.822511000	-3.120163000	-2.183115000
H	-9.271582000	-2.633170000	-1.273932000
C	-8.173629000	-2.621479000	1.270298000
H	-7.822537000	-3.120210000	2.183167000
H	-7.849128000	-1.574707000	1.308318000
H	-9.271598000	-2.633199000	1.273978000
C	5.460245000	-6.152905000	0.000012000
O	6.557081000	-5.552880000	0.000006000
O	5.395853000	-7.534811000	0.000017000
H	6.293983000	-7.937849000	0.000015000

S4. Cartesian Coordinates of ZnPc-1@TiO_2
CPCM[DMSO]/B3LYP/LANL2DZ

C	-2.541889000	-1.502917000	0.337362000
C	-2.877490000	-0.118198000	0.339079000
C	-1.612931000	0.625216000	0.238677000
N	-0.574894000	-0.292147000	0.181958000
C	-1.078060000	-1.583410000	0.237587000
C	3.087822000	-3.768782000	-0.002152000
C	1.710406000	-4.103229000	0.092407000
C	0.963519000	-2.836564000	0.116569000
N	1.876353000	-1.790288000	0.034716000
C	3.163800000	-2.298244000	-0.033692000
N	-0.374415000	-2.732715000	0.206578000
C	5.348093000	1.876650000	-0.191904000
C	5.680257000	0.492767000	-0.196462000
C	4.412659000	-0.251422000	-0.131112000
N	3.370153000	0.664799000	-0.090929000
C	3.877269000	1.956491000	-0.123640000
N	4.310680000	-1.593228000	-0.109950000
C	-0.289485000	4.142497000	0.116930000
C	1.090486000	4.477090000	0.030406000
C	1.830661000	3.204861000	-0.017199000
N	0.918056000	2.163494000	0.036889000
C	-0.372344000	2.674666000	0.124516000
N	-1.514157000	1.968601000	0.211189000
N	3.173429000	3.102516000	-0.092955000
C	6.338694000	2.863422000	-0.240974000
C	7.703025000	2.479833000	-0.295907000
C	8.014793000	1.091713000	-0.300220000
C	7.021251000	0.093093000	-0.250965000
C	4.081873000	-4.758519000	-0.049410000
C	3.705739000	-6.118974000	-0.002149000
C	2.316506000	-6.435735000	0.095060000
C	1.316604000	-5.450187000	0.142869000
C	-3.542604000	-2.484624000	0.421583000
C	-4.880073000	-2.065705000	0.508235000
C	-5.206579000	-0.684505000	0.495685000
C	-4.211161000	0.306104000	0.413419000
C	-1.263302000	5.152720000	0.179551000
C	-0.834019000	6.491032000	0.154217000
C	0.545001000	6.841873000	0.070294000
C	1.512461000	5.815748000	0.008248000
H	6.051588000	3.910585000	-0.235173000
H	7.293368000	-0.958225000	-0.254580000
H	5.122454000	-4.465058000	-0.122588000
H	0.268738000	-5.725531000	0.216081000
H	-3.292422000	-3.540515000	0.430060000
H	-2.319124000	4.907193000	0.245445000
H	2.569503000	6.059951000	-0.055872000
Zn	1.394094000	0.186319000	-0.020489000
H	-4.470252000	1.359860000	0.396527000
H	-5.675103000	-2.799164000	0.599665000
H	2.012899000	-7.478281000	0.133691000
H	9.051807000	0.778282000	-0.341850000
C	8.798114000	3.570503000	-0.345387000
C	4.739226000	-7.267241000	-0.048518000
C	10.227907000	2.976918000	-0.401852000
H	10.379256000	2.360013000	-1.297014000
H	10.958225000	3.794918000	-0.434751000
H	10.452224000	2.366382000	0.482319000
C	8.692710000	4.463952000	0.926947000
H	7.713238000	4.951156000	1.002761000
H	8.848677000	3.869047000	1.836433000
H	9.458510000	5.250113000	0.895956000
C	8.588407000	4.454594000	-1.611223000
H	8.672452000	3.853679000	-2.526243000
H	7.604645000	4.939168000	-1.611716000
H	9.351651000	5.243109000	-1.647744000
C	6.192756000	-6.747490000	-0.176516000
H	6.478869000	-6.120131000	0.677644000
H	6.882667000	-7.599870000	-0.209008000
H	6.337757000	-6.166044000	-1.096311000
C	4.440731000	-8.183946000	-1.272490000
H	3.435876000	-8.619957000	-1.221214000
H	4.520021000	-7.620680000	-2.211565000
H	5.163374000	-9.009963000	-1.306496000
N	-6.585488000	-0.280887000	0.601989000
C	-7.644585000	-0.676286000	-0.204129000
C	-7.082144000	0.623747000	1.557819000
C	-8.431437000	0.742309000	1.310565000
H	-6.449215000	1.063166000	2.310894000
H	-9.184476000	1.323776000	1.814055000
N	-8.771020000	-0.063965000	0.215458000
C	-7.524764000	-1.602664000	-1.372736000
H	-6.535054000	-1.530046000	-1.834638000
H	-7.688266000	-2.646063000	-1.076572000
H	-8.285662000	-1.334658000	-2.109009000
H	-1.579024000	7.281526000	0.200467000
C	0.971846000	8.309935000	0.046134000
C	0.558453000	9.049056000	1.346069000
C	0.419994000	9.044687000	-1.204066000
H	0.977028000	8.556661000	2.233028000
H	0.922180000	10.084627000	1.324664000
H	-0.533504000	9.078953000	1.456859000
H	0.743141000	8.551090000	-2.129433000
H	-0.677593000	9.070337000	-1.197392000
H	0.780248000	10.081493000	-1.224076000
Ti	-10.840064000	-0.282446000	-0.616091000
O	-10.626599000	-2.060978000	-0.140428000
H	-11.264937000	-2.781760000	-0.307421000

O	-10.062696000	0.314402000	-2.193788000
H	-10.517552000	0.420412000	-3.052081000
O	-12.508345000	-0.436810000	-1.256455000
H	-13.421870000	-0.493170000	-1.570028000
O	-11.229376000	0.944206000	0.718197000
H	-12.103339000	1.327869000	0.923594000
C	4.634356000	-8.106557000	1.260249000
H	4.852377000	-7.487160000	2.140124000
H	3.634690000	-8.538921000	1.387819000
H	5.357778000	-8.932066000	1.234349000
C	2.509176180	8.344883720	-0.037499140
H	2.924098650	7.847180720	0.813988430
H	2.829114020	7.850230850	-0.930728290
H	2.842460420	9.361522160	-0.053866260

S5. Cartesian Coordinates of ZnPc-2@TiO_2
CPCM[DMSO]/B3LYP/LANL2DZ

C	3.630357000	-2.276860000	-0.064518000
C	4.173297000	-0.960911000	-0.054197000
C	3.033132000	-0.030316000	-0.084779000
N	1.865484000	-0.776485000	-0.108338000
C	2.166658000	-2.129927000	-0.096728000
C	-2.294932000	-3.643455000	-0.147663000
C	-0.978840000	-4.186237000	-0.132132000
C	-0.048425000	-3.045708000	-0.127100000
N	-0.794584000	-1.877905000	-0.142401000
C	-2.147890000	-2.179296000	-0.156468000
N	1.292835000	-3.153725000	-0.107090000
C	-3.660500000	2.282426000	-0.206639000
C	-4.203576000	0.966489000	-0.212456000
C	-3.063457000	0.035895000	-0.181219000
N	-1.895679000	0.782094000	-0.161543000
C	-2.196788000	2.135452000	-0.176072000
N	-3.171595000	-1.305444000	-0.175779000
C	2.264565000	3.649006000	-0.113846000
C	0.948808000	4.191861000	-0.140157000
C	0.018259000	3.051291000	-0.145677000
N	0.764357000	1.883459000	-0.127366000
C	2.117613000	2.184921000	-0.107604000
N	3.141282000	1.311058000	-0.086650000
N	-1.322897000	3.159321000	-0.167522000
C	-4.501117000	3.405561000	-0.235697000
C	-5.889776000	3.195080000	-0.276626000
C	-6.422817000	1.880610000	-0.272070000
C	-5.586179000	0.748662000	-0.239827000
C	-3.418398000	-4.484297000	-0.151770000
C	-3.207766000	-5.873674000	-0.142917000
C	-1.893297000	-6.405440000	-0.116605000
C	-0.761109000	-5.569108000	-0.112894000
C	4.471054000	-3.399965000	-0.037109000
C	5.859624000	-3.189452000	0.006672000
C	6.392560000	-1.874930000	0.006475000
C	5.555816000	-0.742996000	-0.024088000
C	3.387466000	4.490391000	-0.104994000
C	3.177023000	5.879498000	-0.128076000
C	1.862490000	6.412145000	-0.143159000
C	0.730715000	5.574602000	-0.149531000
H	-4.094366000	4.411411000	-0.241060000
H	-5.999160000	-0.254820000	-0.228215000
H	-4.424139000	-4.077748000	-0.171963000
H	0.241746000	-5.982794000	-0.084411000
H	4.064424000	-4.405877000	-0.035060000
H	4.393544000	4.084307000	-0.094441000
H	-0.273131000	5.986811000	-0.152286000
Zn	-0.015095000	0.002798000	-0.135195000
H	5.968651000	0.260577000	-0.032378000
H	6.534935000	-4.037371000	0.059607000
N	7.817656000	-1.685049000	0.081887000
C	8.792228000	-2.238808000	-0.739026000
C	8.461660000	-0.865554000	1.027056000
C	9.808649000	-0.955194000	0.759655000
H	7.916047000	-0.335071000	1.789628000
H	10.648683000	-0.493934000	1.249626000
N	10.005130000	-1.805364000	-0.337826000
C	8.515406000	-3.136362000	-1.903567000
H	8.511159000	-4.192540000	-1.606882000
H	7.546570000	-2.907120000	-2.358627000
H	9.305153000	-2.992618000	-2.644312000
H	4.025508000	6.555685000	-0.152257000
H	-6.565127000	4.042899000	-0.330697000
H	-4.054733000	-6.551961000	-0.171376000
N	1.672811000	7.838360000	-0.193873000
C	2.209970000	8.796415000	0.657188000
C	0.867500000	8.500696000	-1.138567000
N	1.779572000	10.016560000	0.275270000
C	3.088951000	8.496211000	1.830037000
C	0.948602000	9.841735000	-0.840442000
H	0.351422000	7.970700000	-1.921774000
H	2.848098000	7.521267000	2.265752000
H	4.149431000	8.490569000	1.549068000
H	2.937801000	9.274600000	2.581145000
H	0.491873000	10.691050000	-1.318492000
N	-1.704770000	-7.833128000	-0.126221000
C	-2.221764000	-8.758625000	0.770894000
C	-0.921333000	-8.529259000	-1.064705000
N	-1.799878000	-9.991879000	0.424229000
C	-3.072487000	-8.413763000	1.952181000
C	-0.995213000	-9.859011000	-0.715834000
H	-0.422512000	-8.027055000	-1.876943000
H	-2.849271000	-7.407361000	2.319982000
H	-4.139987000	-8.460098000	1.704827000
H	-2.877229000	-9.138065000	2.746063000
H	-0.551119000	-10.725676000	-1.174449000
N	-7.848078000	1.690741000	-0.344701000
C	-8.821060000	2.245526000	0.477372000
C	-8.493876000	0.870258000	-1.287763000
N	-10.034759000	1.811747000	0.078912000
C	-8.541821000	3.144308000	1.640387000
C	-9.840366000	0.960328000	-1.017986000
H	-7.949696000	0.338810000	-2.050687000
H	-7.572649000	2.914551000	2.094498000
H	-8.536680000	4.200111000	1.342375000
H	-9.330772000	3.002339000	2.382308000
H	-10.681338000	0.498534000	-1.505831000
Ti	12.021589000	-2.374965000	-1.146363000
O	11.561493000	-4.070757000	-0.559875000

O	11.327014000	-1.795839000	-2.766863000
O	13.652992000	-2.793896000	-1.762280000
O	12.585922000	-1.132682000	0.109657000
H	12.092235000	-4.884405000	-0.664809000
H	11.786403000	-1.804958000	-3.629029000
H	14.552620000	-2.981667000	-2.064685000
H	13.506751000	-0.863933000	0.291439000
Ti	2.324532000	12.017882000	1.137863000
O	2.723896000	13.640294000	1.789486000
O	1.736976000	11.283002000	2.736719000
O	1.086912000	12.599512000	-0.115858000
O	4.031357000	11.581861000	0.564826000
H	2.902065000	14.536810000	2.106606000
H	1.731424000	11.721863000	3.609501000
H	0.816144000	13.523252000	-0.279232000
H	4.838184000	12.119032000	0.688339000
Ti	-12.049785000	2.381485000	0.891142000
O	-13.680419000	2.799535000	1.509761000
O	-11.351434000	1.804682000	2.510877000
O	-12.615999000	1.137922000	-0.362880000
O	-11.591792000	4.077079000	0.302680000
H	-14.579860000	2.986367000	1.813306000
H	-11.809164000	1.814159000	3.373922000
H	-13.537195000	0.868829000	-0.542307000
H	-12.122603000	4.890656000	0.407734000
Ti	-2.284671000	-11.937883000	1.427065000
O	-2.654981000	-13.516828000	2.193263000
O	-1.506069000	-11.149119000	2.915127000
O	-1.188852000	-12.602181000	0.086605000
O	-4.032610000	-11.485326000	1.012175000
H	-2.835830000	-14.388809000	2.571375000
H	-1.438033000	-11.543413000	3.806529000
H	-0.950787000	-13.537338000	-0.061915000
H	-4.833910000	-11.990198000	1.252518000

S6. Cartesian Coordinates of ZnPc-3@TiO_2 CPCM[DMSO]/B3LYP/LANL2DZ

C	-3.537846000	-3.759705000	-0.005924000
C	-2.227392000	-4.315492000	-0.012570000
C	-1.284976000	-3.185901000	-0.016058000
N	-2.021700000	-2.004453000	-0.011731000
C	-3.375066000	-2.295196000	-0.005751000
C	-4.859885000	2.179456000	0.008713000
C	-5.412638000	0.868168000	0.008847000
C	-4.280394000	-0.072414000	0.000871000
N	-3.102465000	0.662894000	-0.004250000
C	-3.393881000	2.019643000	0.000281000
N	-4.395823000	-1.413042000	-0.000205000
C	1.079027000	3.504895000	-0.017257000
C	-0.232490000	4.051427000	-0.010937000
C	-1.169197000	2.918996000	-0.008206000
N	-0.435337000	1.743798000	-0.012748000
C	0.923650000	2.039684000	-0.018206000
N	-2.513622000	3.036402000	-0.002021000
C	2.396732000	-2.438544000	-0.033208000
C	2.951615000	-1.123558000	-0.033308000
C	1.820227000	-0.185635000	-0.025206000
N	0.646957000	-0.923013000	-0.020306000
C	0.937015000	-2.279750000	-0.024828000
N	0.053988000	-3.299779000	-0.022384000
N	1.938137000	1.157685000	-0.023790000
C	2.215022000	4.329896000	-0.021468000
C	2.050219000	5.732924000	-0.019340000
C	0.723572000	6.262043000	-0.012907000
C	-0.417055000	5.443178000	-0.008704000
C	-5.677258000	3.314110000	0.016630000
C	-7.086965000	3.158341000	0.024755000
C	-7.621057000	1.839840000	0.024275000
C	-6.801800000	0.692220000	0.016505000
C	-4.675005000	-4.574740000	-0.000483000
C	-4.523089000	-5.984164000	-0.001658000
C	-3.205398000	-6.521560000	-0.008642000
C	-2.055823000	-5.705729000	-0.014075000
C	3.227253000	-3.573504000	-0.041203000
C	4.615792000	-3.375026000	-0.049338000
C	5.169213000	-2.063145000	-0.049306000
C	4.336951000	-0.923434000	-0.041079000
H	3.201111000	3.880587000	-0.026377000
H	-1.413353000	5.875026000	-0.003912000
H	-5.223589000	4.300295000	0.016922000
H	-7.240254000	-0.301307000	0.016717000
H	-5.659839000	-4.118122000	0.004876000
H	-1.063680000	-6.147348000	-0.019141000
H	2.805378000	-4.573395000	-0.041288000
H	4.769493000	0.071227000	-0.041366000
Zn	-1.228836000	-0.129690000	-0.012456000
H	5.294415000	-4.222314000	-0.055860000
H	-3.069039000	-7.597131000	-0.009697000
H	-8.696204000	1.700658000	0.030251000
H	0.583972000	7.339397000	-0.011226000
C	3.247256000	6.711031000	-0.023838000
C	4.610923000	5.976668000	-0.030212000
H	5.421828000	6.715763000	-0.033015000
H	4.739069000	5.345692000	0.858909000
H	4.731557000	5.347181000	-0.921435000
C	3.173402000	7.611482000	-1.293476000
H	3.232378000	7.005106000	-2.206781000
H	2.243609000	8.191617000	-1.329676000
H	4.012099000	8.319998000	-1.297498000
C	3.184429000	7.609800000	1.247574000
H	2.254979000	8.189855000	1.292659000
H	3.251395000	7.002200000	2.159518000
H	4.023088000	8.318380000	1.245263000
C	-7.987590000	4.415125000	0.034571000
C	-9.497390000	4.067719000	0.042562000
H	-10.081693000	4.996291000	0.049258000
H	-9.790909000	3.497055000	-0.848054000
H	-9.780126000	3.491016000	0.932779000
C	-7.692252000	5.269788000	-1.234468000
H	-6.643681000	5.588158000	-1.276904000
H	-7.912846000	4.702313000	-2.148050000
H	-8.317514000	6.172402000	-1.232226000
C	-7.676631000	5.260586000	1.306067000
H	-7.884072000	4.685761000	2.218131000
H	-6.628065000	5.580335000	1.336835000

H	-8.303338000	6.162086000	1.319046000
C	-5.781984000	-6.882131000	0.004944000
C	-5.437916000	-8.392757000	0.003782000
H	-6.367776000	-8.975054000	0.008994000
H	-4.869594000	-8.682562000	-0.889549000
H	-4.860098000	-8.681743000	0.891273000
C	-6.637879000	-6.577813000	-1.261113000
H	-6.954020000	-5.528307000	-1.296933000
H	-6.072057000	-6.794185000	-2.176742000
H	-7.541798000	-7.201229000	-1.261357000
C	-6.625126000	-6.576893000	1.279302000
H	-6.049684000	-6.791330000	2.189371000
H	-6.942044000	-5.527687000	1.316846000
H	-7.528289000	-7.201295000	1.289703000
C	6.641114000	-1.898751000	-0.057976000
O	7.186400000	-0.693194000	-0.053999000
O	7.466816000	-2.896692000	-0.072391000
Ti	9.207570000	-1.304283000	-0.114854000
O	9.249864000	-1.504050000	-1.871534000
H	9.211816000	-1.717850000	-2.815083000
O	10.447871000	-2.531085000	0.429735000
H	10.791007000	-3.362894000	0.054730000
O	8.799387000	-1.327552000	1.992860000
H	9.332097000	-1.922389000	2.552011000
O	9.965847000	0.328046000	0.066842000
H	10.215516000	1.065875000	-0.519337000
H	8.180278000	-0.767499000	2.494233000

References

1 X. Zhang, W. Guo, J. Phys. Chem. A 116 (2012) 7651−7657

2 E. Genc, A. C. Yüzer, G. Yanalak, E. Harputlu, E. Aslan, K. Ocakoglu, M. Ince and I. H. Patir, *Renew. Energy*, 2020, **162**,1340–1346.

3 N. Manfredi, M. Monai, T. Montini, F. Peri, F. De Angelis, P. Fornasiero and A. Abbotto, *ACS Energy Lett.*, 2018, **3**, 85–91. B) De Silva, N. L.; Jayasundera, A. C.; Folger, A.; Kasian, O.; Zhang, S.; Yan, C.-F.; Scheu, C.; Bandara, J., *Catalysis Science & Technology* **2018,** *8* (18), 4657-4664.

4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Had, and D. J. F. *et al.* (2013) 'Gaussian 09, Revision D.01', *Gaussian Inc., Wallingford*. doi: 10.1017/CBO9781107415324.004.

5 M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A.Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H.Nakatsuj, and J. A. P. (2009) 'GaussView 5', *Semichem Inc. , Shawnee Mission, KS*.

6 Zhurko, G. A. and Zhurko, D. A. (2019) 'ChemCraft-Graphical program for visualization of quantum chemistry computations', *version 1.8, build 562*.

7 Chiodo, S., Russo, N. and Sicilia, E. (2006) 'LANL2DZ basis sets recontracted in the framework of density functional theory', *Journal of Chemical Physics*. doi: 10.1063/1.2345197.

8 Bettanin, F. *et al.* (2017) 'Quantum-chemistry descriptors for photosensitizers based on macrocycles', in *Chemical Biology and Drug Design*. doi: 10.1111/cbdd.12791.

9 Asaduzzaman, A. M. and Schreckenbach, G. (2011) 'Computational studies of the interactions of I- and I3- with TiO2 clusters: Implications for dye-sensitized solar cells', Theoretical Chemistry Accounts. doi: 10.1007/s00214-011-0920-1.

10 Fahim, Z. M. E. *et al.* (2018) 'Ground state geometries, UV/vis absorption spectra and charge transfer properties of triphenylamine-thiophenes based dyes for DSSCs: A TD-DFT benchmark study', *Computational and Theoretical Chemistry*. doi: 10.1016/j.comptc.2018.01.002.

11 Lu, T. and Chen, F. (2012) 'Multiwfn: A multifunctional wavefunction analyzer', *Journal of Computational Chemistry*. doi: 10.1002/jcc.22885.

12 Humphrey, W., Dalke, A. and Schulten, K. (1996) 'VMD: Visual molecular dynamics', *Journal of Molecular Graphics*. doi: 10.1016/0263-7855(96)00018-5.

13 Gorelsky, S. I. (2019) 'AOMix: Program for Molecular Orbital Analysis'.

14 Jacquemin, D. et al. (2008) 'TD-DFT performance for the visible absorption spectra of organic dyes: Conventional versus long-range hybrids', Journal of Chemical Theory and Computation. doi: 10.1021/ct700187z.

15 Charaf-Eddin, A. *et al.* (2013) 'Choosing a functional for computing absorption and fluorescence band shapes with TD-DFT', *Journal of Chemical Theory and Computation*. doi: 10.1021/ct4000795.

16 O'boyle, N. M., Tenderholt, A. L. and Langner, K. M. (2008) 'cclib: A library for package-independent computational chemistry algorithms', *Journal of Computational Chemistry*, 29(5), pp. 839–845. doi: 10.1002/jcc.20823.

17 Saleh, G., Gatti, C. and Lo Presti, L. (2012) 'Non-covalent interaction via the reduced density gradient: Independent atom model vs experimental multipolar electron densities', *Computational and Theoretical Chemistry*. doi: 10.1016/j.comptc.2012.07.014.

18 Boto, R. A., Piquemal, J. P. and Contreras-García, J. (2017) 'Revealing strong interactions with the reduced density gradient: a benchmark for covalent, ionic and charge-shift bonds', *Theoretical Chemistry Accounts*. doi: 10.1007/s00214-017-2169-9.

19 Kesavan, R. *et al.* (2019) 'Simple diphenylamine based D-π-A type sensitizers/co-sensitizers for DSSCs: A comprehensive study on the impact of anchoring groups', *Physical Chemistry Chemical Physics*, 21(20), pp. 10603–10613. doi: 10.1039/c9cp01032g.

20 Neel, A. J. et al. (2017) 'Exploiting non-covalent π interactions for catalyst design', Nature. doi: 10.1038/nature21701.