Electronic Supplementary Material (ESI) for New Journal of Chemistry.

# Supplementary Information

# A new sterically hindered asymmetric zinc phthalocyanine as an efficient sensitizer for dye-sensitized solar cells

Kevser Harmandar[a], Kevin Granados-Tavera[b], Merve Gezgin[c], Mehmet Nebioğlu[c,d], İlkay Şişman*[c,d], Gloria Cárdenas-Jirón*[b], Devrim Atilla*[a], Ayşe Gül Gürek[a]

[a]*Department of Chemistry, Gebze Technical University, Kocaeli, Turkey*

[b]*Laboratory of Theoretical Chemistry, Faculty of Chemistry and Biology, University of Santiago de Chile (USACH), Santiago, Chile*

[c]*Department of Chemistry, Sakarya University, Sakarya, Turkey*

[d]*Biomedical, Magnetic and Semiconductor Materials Research Center (BIMAS-RC), Sakarya University, Sakarya, Turkey*

*Corresponding authors

*Prof. Dr. Devrim Atilla (datilla@gtu.edu.tr)

*Prof. Dr. Gloria Cárdenas-Jirón (gloria.cardenas@usach.cl)

*Prof. Dr. İlkay Şişman (isisman@sakarya.edu.tr

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## 1. Materials

Fluorine-doped $SnO_2$ conducting glass (FTO, sheet resistance 15 Ω/sq), $TiO_2$ paste (Ti-nanoxide T/SP), platinum paste (Platisol T/SP), sealing film (Surlyn, Meltonix 1170–25), redox electrolyte (Iodolyte HI-30) containing 30 mM iodide/tri-iodide in acetonitrile and additives of ionic liquid and 2-cyano-3-(4-(7-(5-(4- (diphenylamino)phenyl)-4-octylthiophen-2-yl)benzo[c][1,2,5] thiadiazol-4-yl)phenyl) acrylic acid (RK1) were purchased from Solaronix. Chenodeoxycholic acid (CDCA), tetrabutylammonium tetrafluoroborate ($TBABF_4$), tetrahydrofuran (THF), ethanol, dimethylsulfoxide (DMSO), ferrocene/ferrocenium ($Fc/Fc^+$) were also purchased from Sigma-Aldrich. The solvents were purified using standard procedures.

## 2. Instruments

Elemental analyses were obtained using a Thermo Finnigan Flash 1112 Instrument. Mass analyses were recorded on a Bruker MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight mass, Rheinstetten, Germany) spectrometer using dihydroxybenzoic acid (DHB) as matrix material. HRMS was recorded on a Micromass Q-Tof 359 Micro (3000 V) apparatus or a Q Exactive Quadrupole-Orbitrap Mass Spectrometer. $^1H$ and $^{13}C$ NMR spectra were recorded in THF-$d_8$ on a Varian INOVA 500 MHz spectrometer. IR spectra were recorded between 4000 and 500 $cm^{-1}$ using a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection (ATR) accessory featuring a zinc selenide (ZnSe) crystal. The absorption spectra of the dyes and the sensitized films were measured using Shimadzu UV 2600 spectrophotometer. Cyclic voltammetry experiments for the dyes were performed by using a potentiostat/galvanostat (PARSTAT 2273, Princeton Applied Research) with a three-electrode cell with a glassy carbon as working electrode, Pt disk as reference electrode, Pt wire as counter electrode at a scan rate of 0.050 V $s^{-1}$. The electrolyte solution contains 2 mM dye and 0.1 M $TBABF_4$ in DMSO, and the $Fc/Fc^+$ redox couple was used as an external standard. The half-wave potential ($E_{1/2}$) of the $Fc/Fc^+$ was found to be 0.34 V versus the reference electrode. The potentials versus the normal hydrogen electrode (NHE) were calibrated by addition of 0.63 V to the potentials versus Fc/Fc+. Therefore, the $E_{ox}$ potentials, which are related to the HOMO levels, measured versus the reference electrode were converted to NHE by addition of 0.29 V.

## 3. Characterization

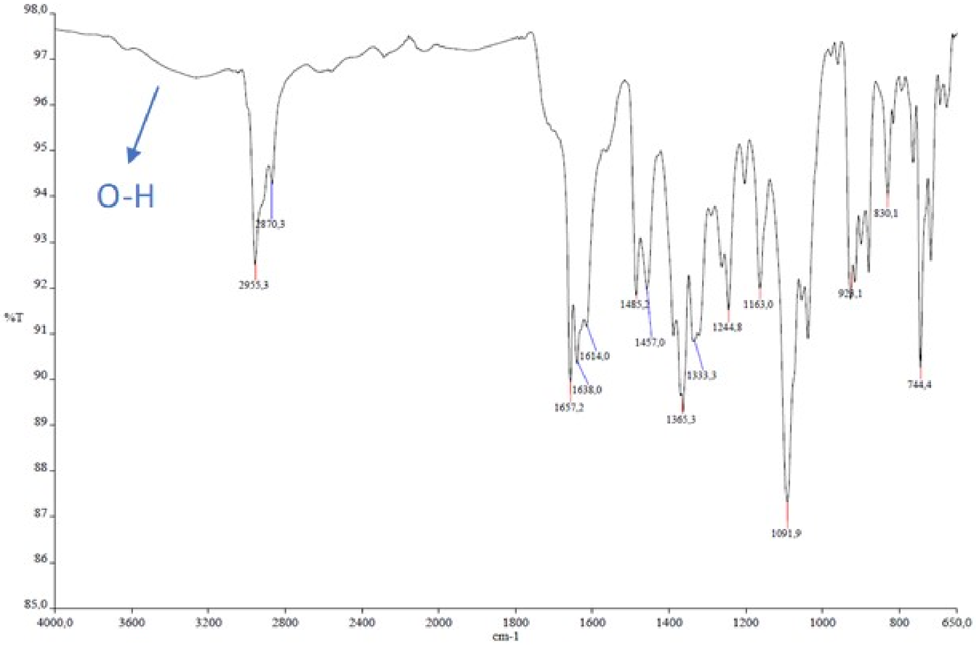


**Figure S1.** FT-IR spectrum of compound **KH1**.

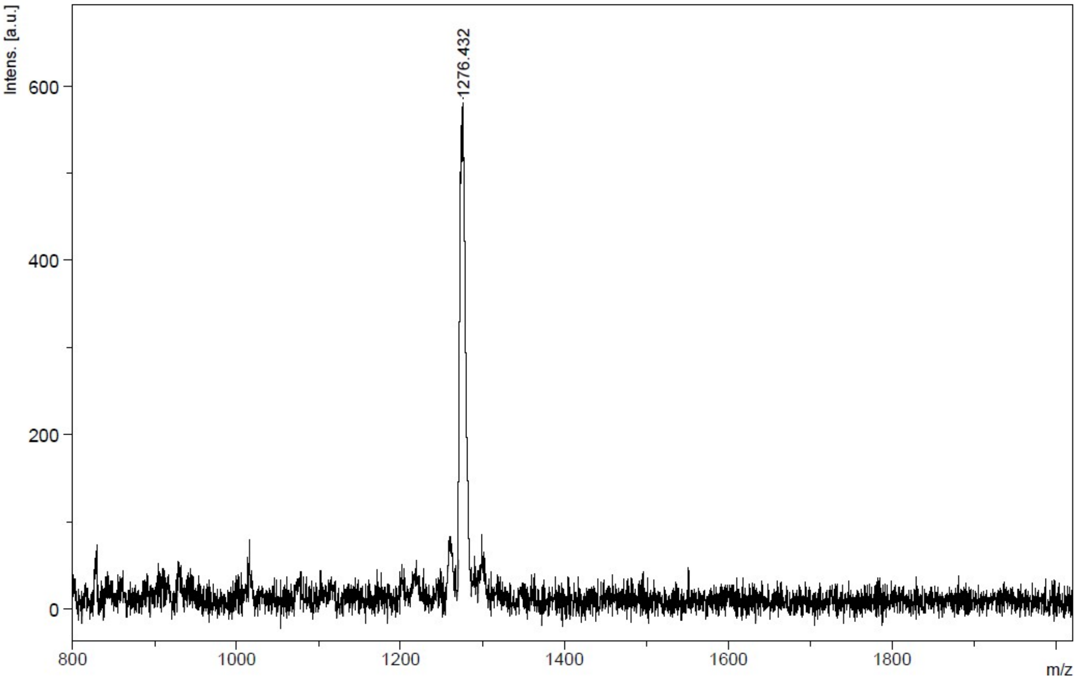
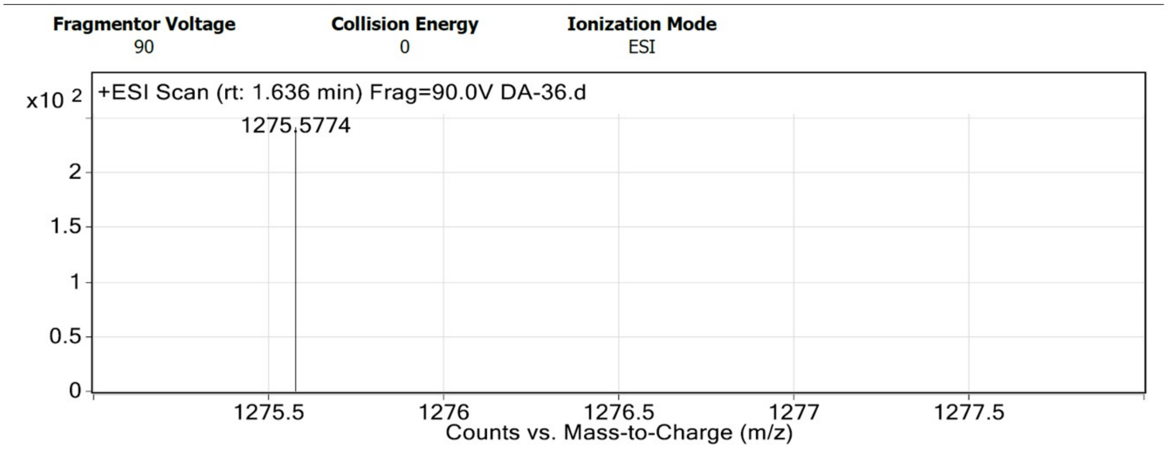


**Figure S2.** Mass spectrum of compound **KH1** (matrix: DHB)



| Fragmentor Voltage | Collision Energy | Ionization Mode |
|---|---|---|
| 90 | 0 | ESI |

+ESI Scan (rt: 1.636 min) Frag=90.0V DA-36.d

**Figure S3.** HRMS Mass spectrum of compound **KH1.**

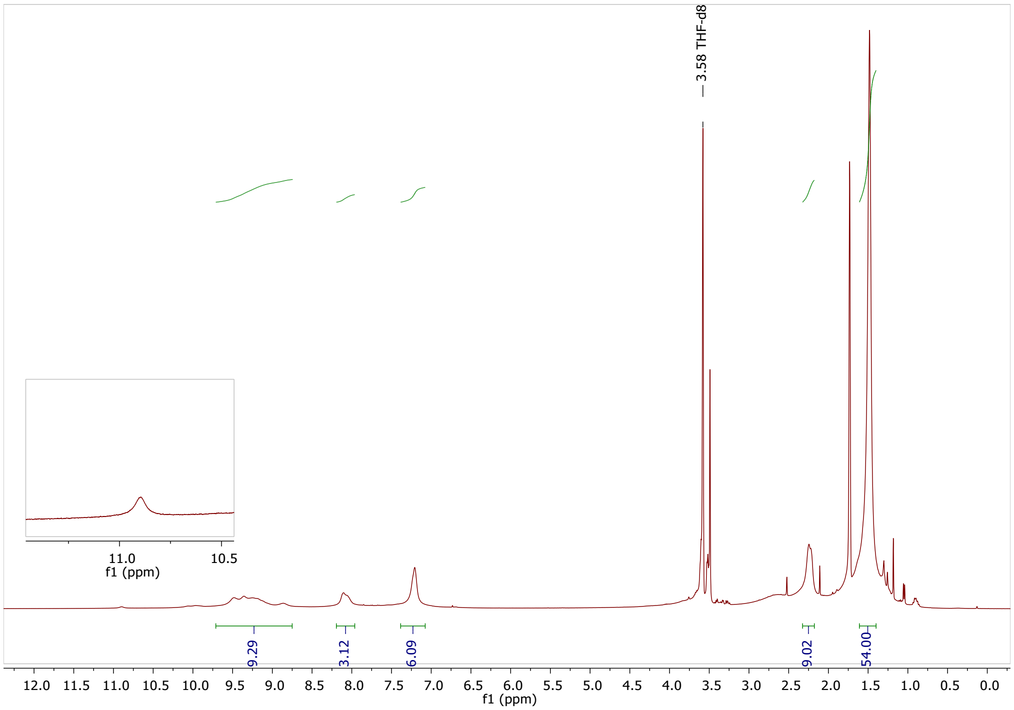


**Figure S4.** $^1$H NMR spectrum of compound **KH1** (600 MHz, THF-$d_8$).

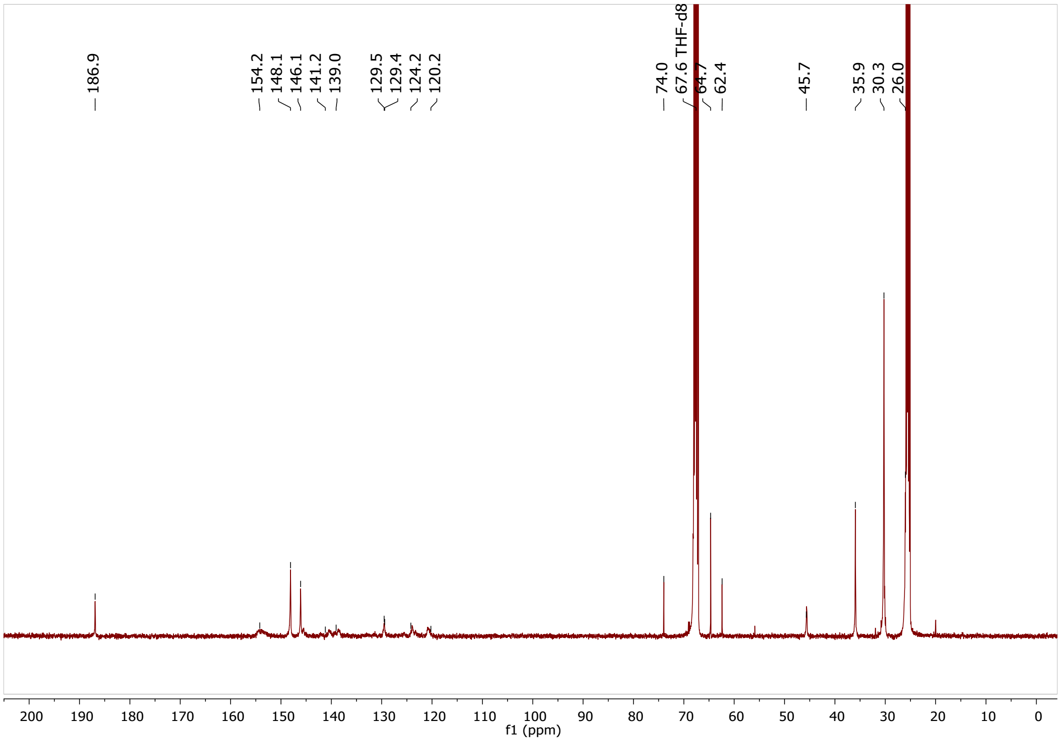


**Figure S5.** $^{13}$C NMR spectrum of compound **KH1** (125 MHz, THF-$d_8$).

## 4. Preparation and characterization of DSSCs

For DSSCs fabrication, two transparent $TiO_2$ pastes were deposited using Doctor Blade's method on the conductive side of FTO substrate. In order to prepare the dye-sensitized $TiO_2$ films (photoanodes), the coated FTO substrates were immersed into 0.3 mM **KH1** solution in THF for 3 h. 0.1 or 0.3 mM chenodeoxycholic acid (CDCA) as a coadsorbent was also introduced into the dye solution. For comparison, the $TiO_2$ film was also immersed in a solution made of 0.3 mM **RK1** in THF for 6 h. In addition, to cosensitize the two dyes, the electrode was first immersed in **KH1** (0.3 mM) solution for 3 hours in the dark and then washed with ethanol. Secondly, it was immersed in **RK1** (0.3 mM) solution for 6 hours in the dark and then washed with ethanol. The Pt counter electrodes were prepared on the FTO substrates by casting platinum paste solution. Both the photoanode and counter electrode were sealed with Surlyn film. The redox electrolyte was injected between the electrodes through a drilled hole at the counter electrode. The current density-voltage ($J$–$V$) charecteristics were investigated by using the potentiostat/galvanostat under AM 1.5 global one sun illumination (100 mW $cm^{-2}$) from a solar simulator (96000, Newport). During the measurements, a black mask of an area of 0.280 $cm^2$ was covered on the cells. The incident photon-to-current conversion efficiency (IPCE) of the DSSCs were carried out a monochromator (74004, Oriel) from the region from 350 to 800 nm. The electrochemical impedance spectroscopy (EIS) of the solar cells were recorded with the potentiostat/galvanostat, under dark conditions, at a forward bias 0.62 V in the frequency range 0.1 Hz−$10^5$ Hz.

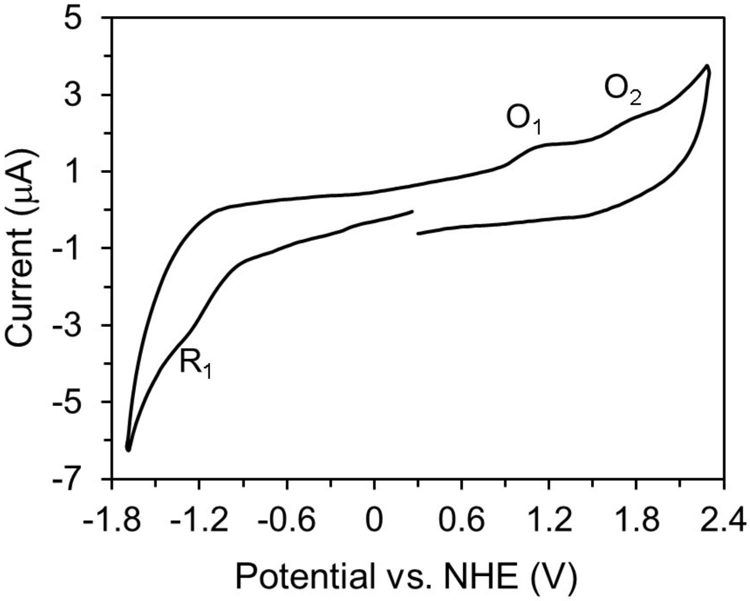
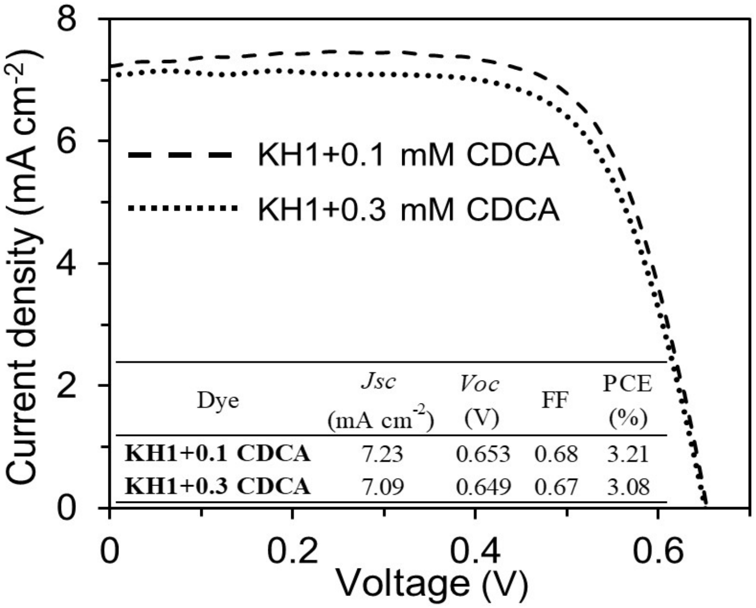


**Figure S6.** Cyclic voltammogram of KH1 dye in DMSO containing 0.1 M $TBABF_4$ at a scan rate of 50 mV $s^{-1}$.



| Dye | *Jsc* (mA cm$^{-2}$) | *Voc* (V) | FF | PCE (%) |
|---|---|---|---|---|
| **KH1+0.1 CDCA** | 7.23 | 0.653 | 0.68 | 3.21 |
| **KH1+0.3 CDCA** | 7.09 | 0.649 | 0.67 | 3.08 |

**Figure S7.** *J-V* curves of DSSCs based on **KH1** dye with different CDCA concentrations.

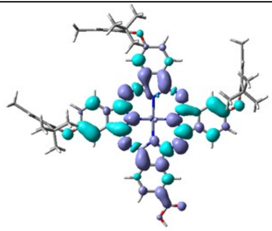
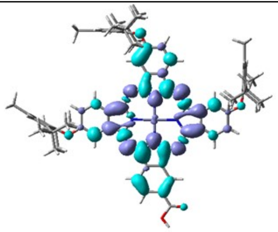
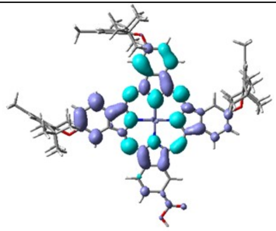
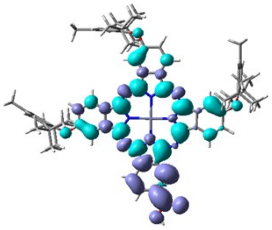
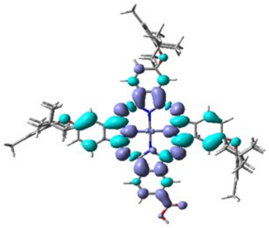
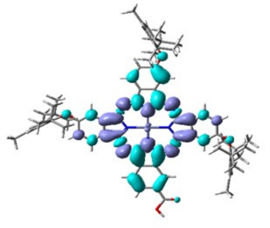
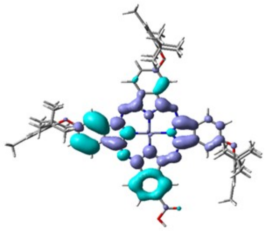
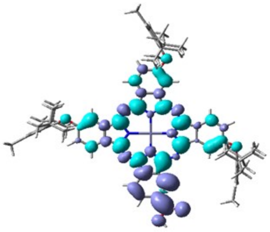
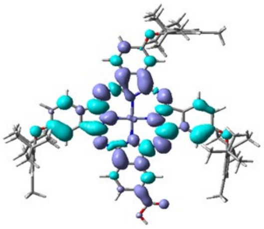
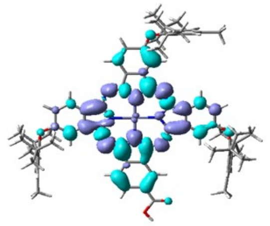
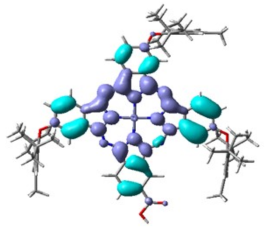
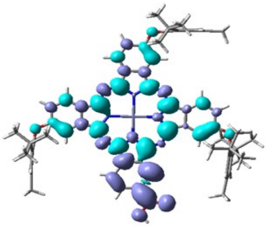
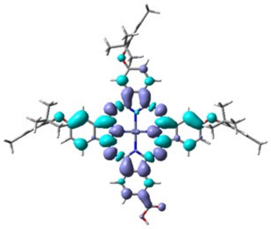
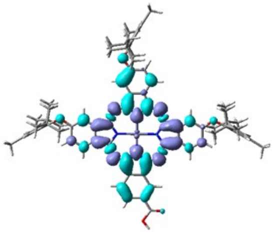
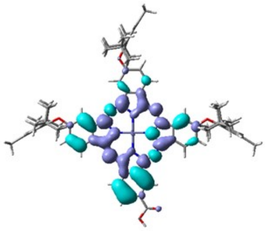
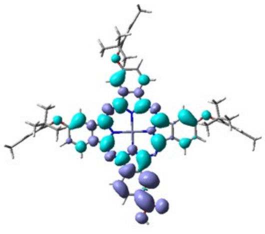
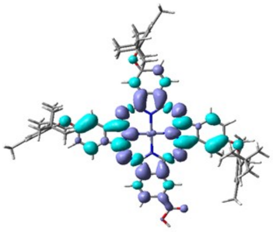
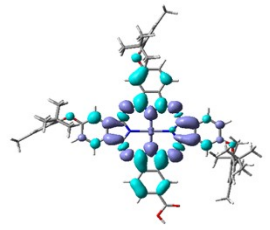
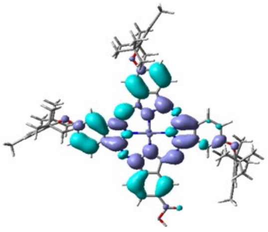
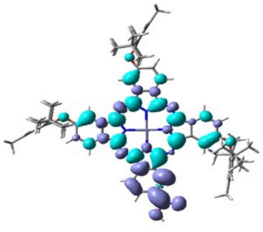
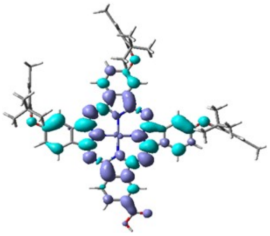
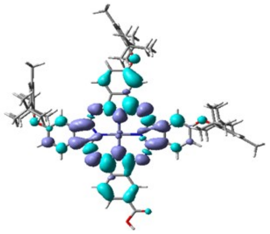
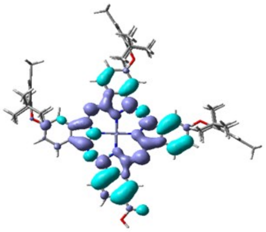
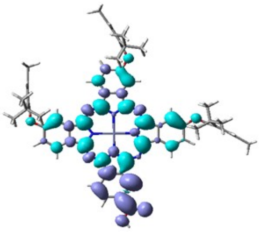
**Table S1.** Photovoltaic parameters of the co-sensitized systems.

| Dye | Immersion time (h) | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) |
|---|---|---|---|---|---|
| **RK1+KH1**[a] | 6h+1h | 11.55 | 0.727 | 0.69 | 5.79 |
| **RK1+KH1**[a] | 6h+2h | 11.59 | 0.729 | 0.69 | 5.83 |
| **RK1+KH1**[a] | 6h+3h | 11.64 | 0.730 | 0.70 | 5.95 |
| **RK1+KH1**[a] | 6h+4h | 11.58 | 0.728 | 0.70 | 5.90 |
| **KH1+RK1**[b] | 3h+3h | 11.06 | 0.712 | 0.70 | 5.51 |
| **KH1+RK1**[b] | 3h+4h | 11.84 | 0.731 | 0.72 | 6.23 |
| **KH1+RK1**[b] | 3h+5h | 12.01 | 0.738 | 0.72 | 6.38 |
| **KH1+RK1**[b] | 3h+6h | 12.20 | 0.749 | 0.73 | 6.67 |
| **KH1+RK1**[b] | 3h+7h | 11.97 | 0.733 | 0.72 | 6.32 |

[a] $TiO_2$ film first immersed in **RK1** solution and then in **KH1** solution for the established times.

[b] $TiO_2$ film first immersed in **KH1** solution and then in **RK1** solution for the established times.

## 5. Theoretical Calculations

| Isomer | Q | Q | B | H → L+2 |
|---|---|---|---|---|
| **a** |  |  |  |  |
| **b** |  |  |  |  |
| **c** |  |  |  |  |
| **e** |  |  |  |  |
| **f** |  |  |  |  |
| **g** |  |  |  |  |

**h**

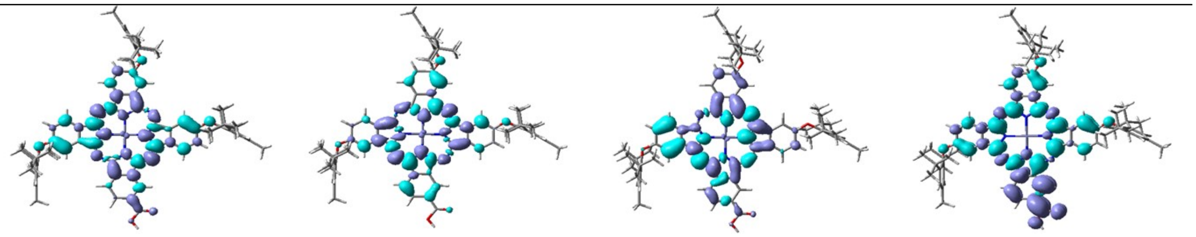
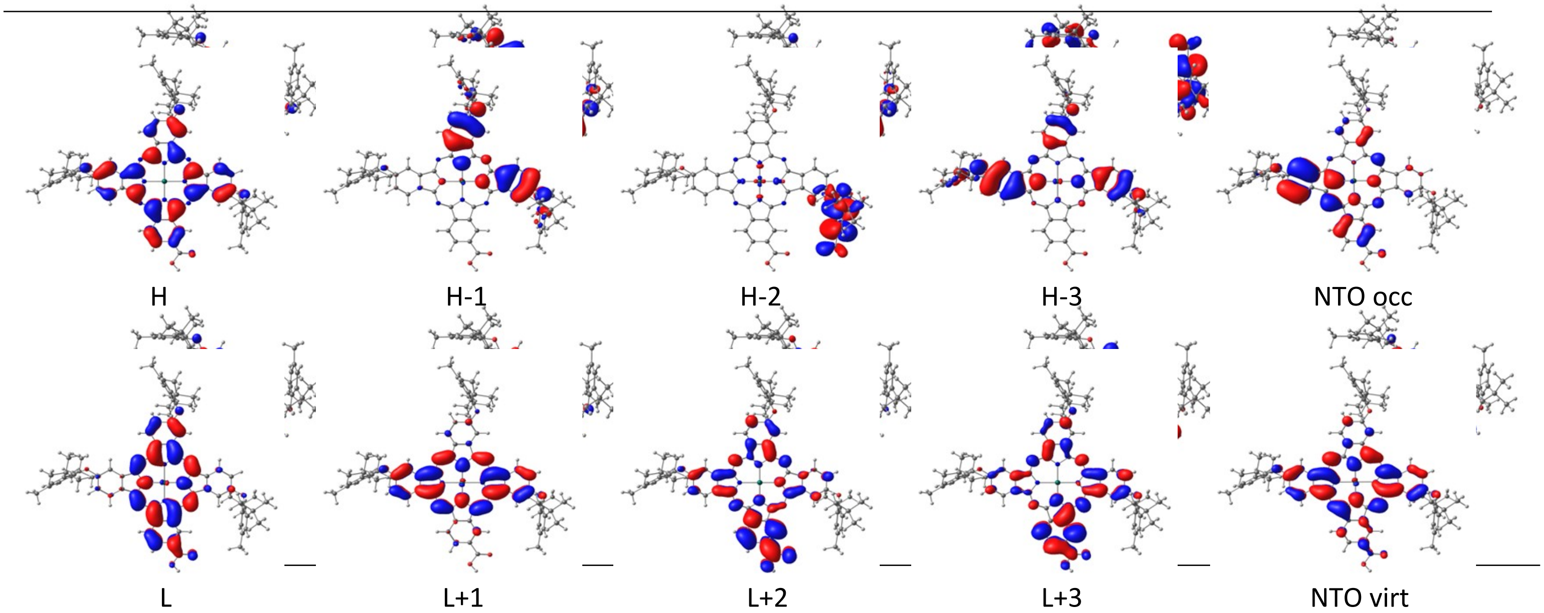


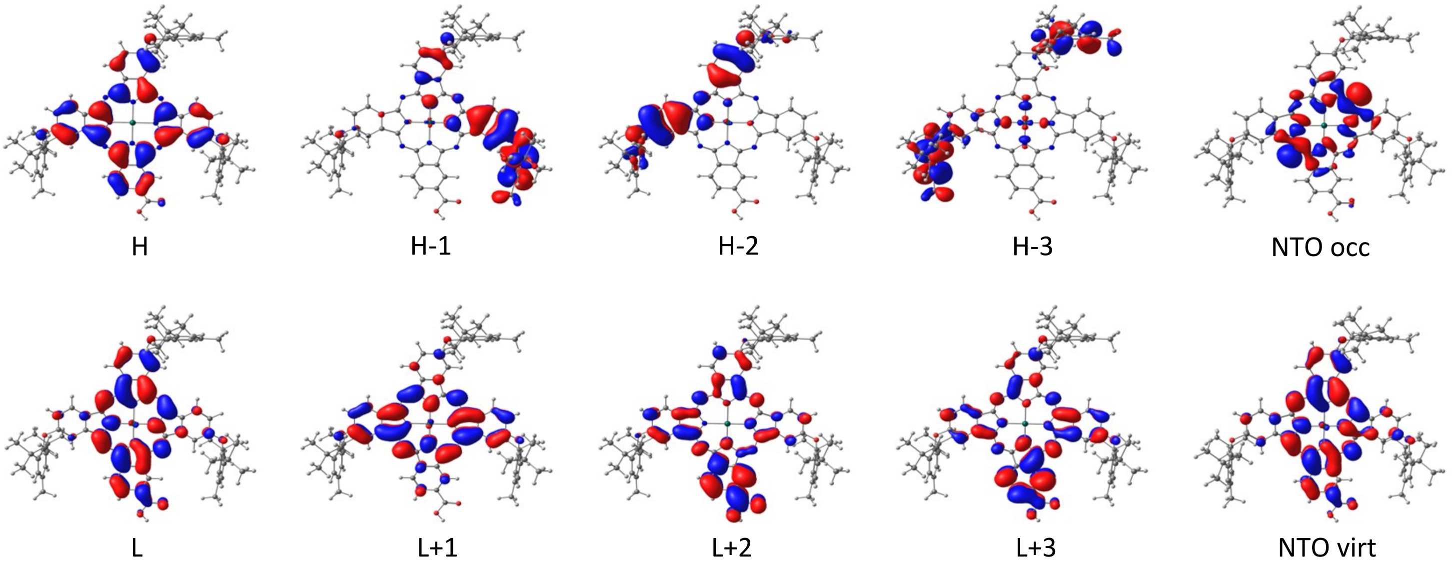
**Figure S8.** The charge density difference (CDD) between the singlet excited state (Q, Q, B and H → L+2) and the ground state of **a, b, c, e, f, g** and **h** isomers obtained at the TPSSh/def2-SVP level of theory in the solution phase (THF). Blue is the electron and green is the hole.

**Isomer a**

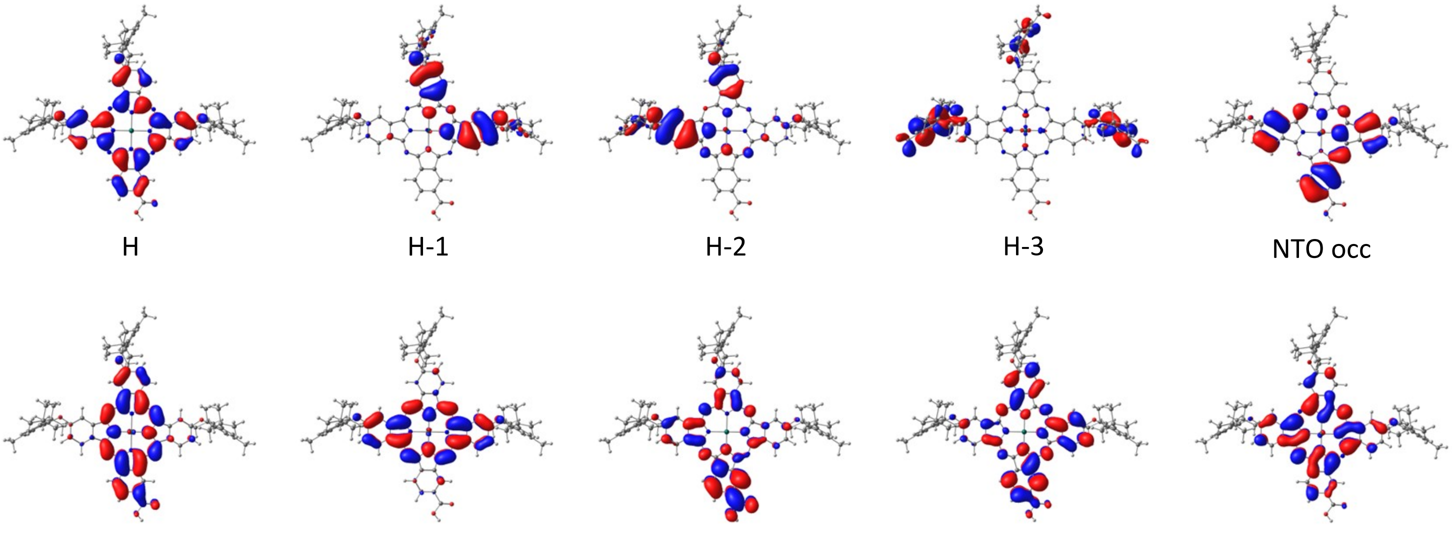
**Isomer b**



**Isomer c**

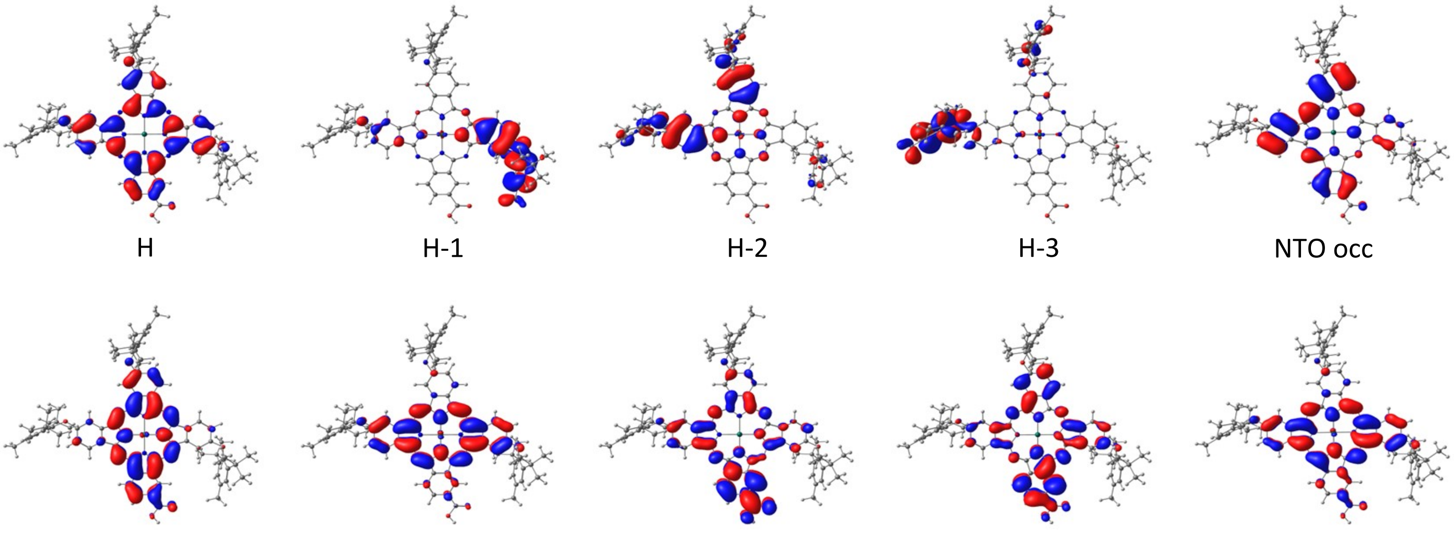


**Isomer e**


H H-1 H-2 H-3 NTO occ

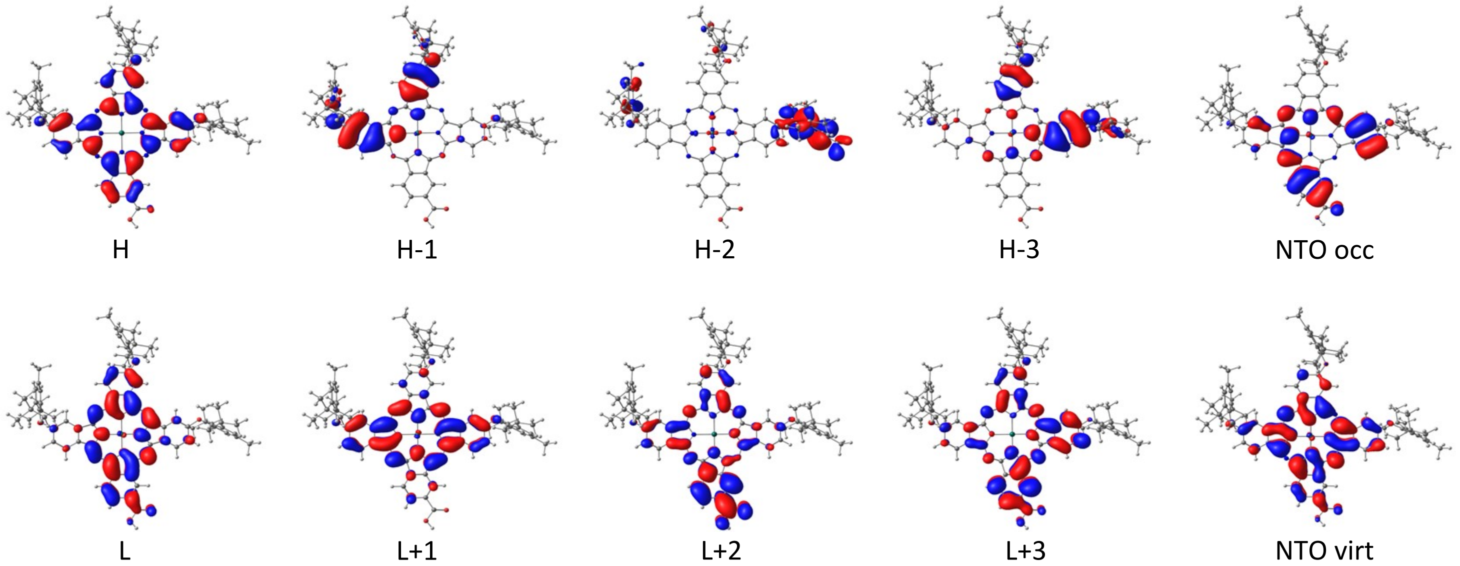
L L+1 L+2 L+3 NTO virt

**Isomer f**


H H-1 H-2 H-3 NTO occ

L L+1 L+2 L+3 NTO virt

**Isomer g**



**Isomer h**

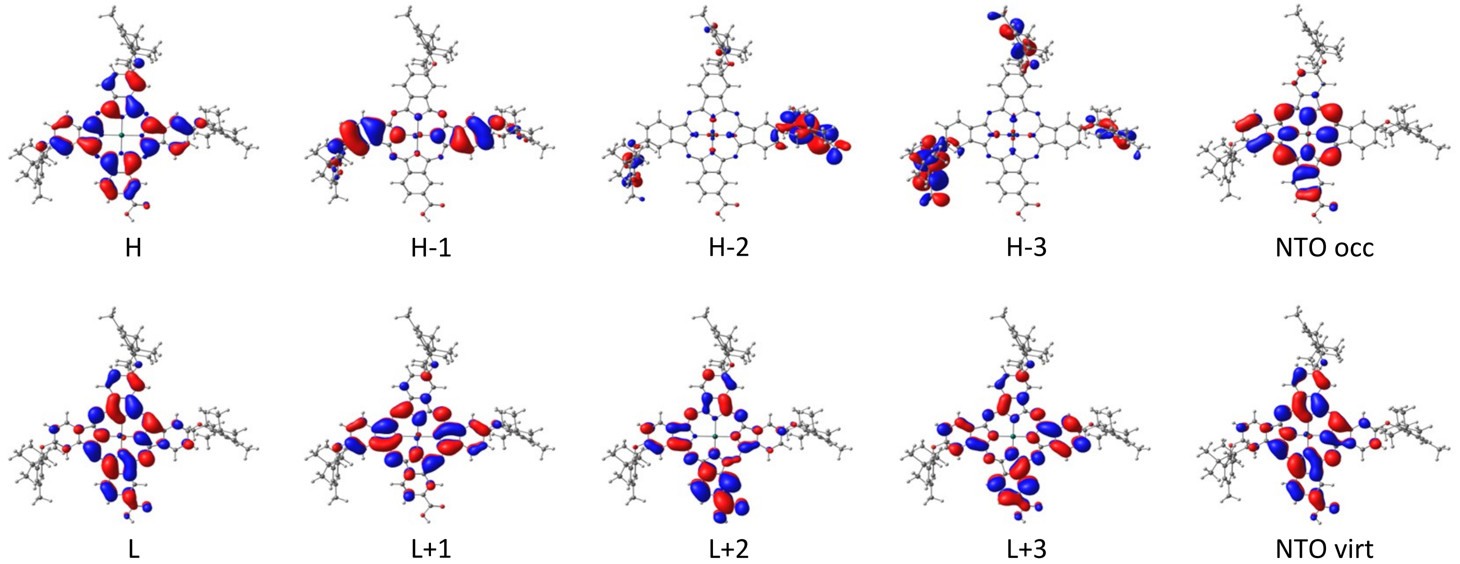
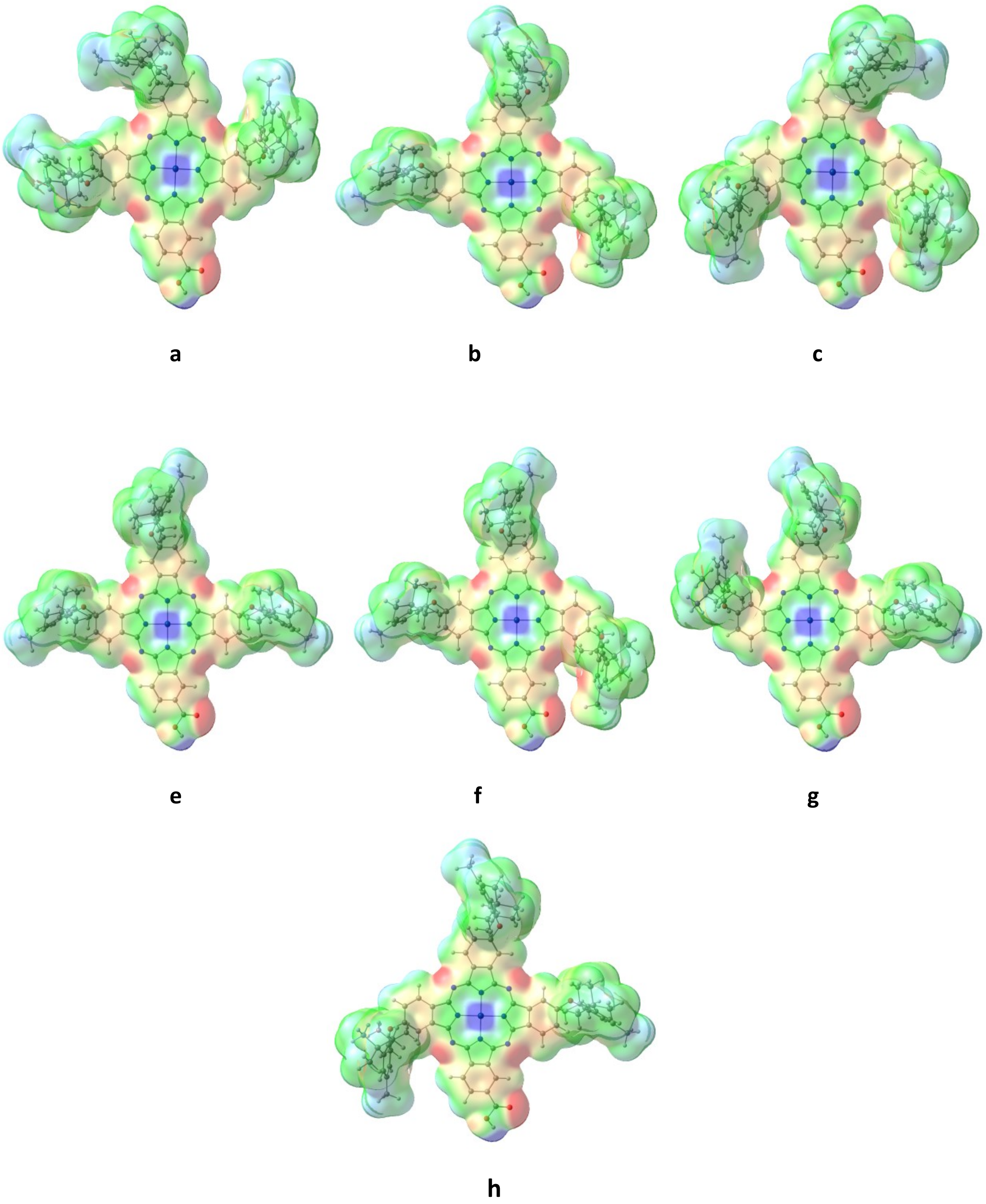


**Figure S9.** Surfaces of the main molecular orbitals that participate in the electronic absorption bands of **a, b, c, e, f, g** and **h** isomers obtained at the TPSSh/def2-SVP level of theory in the solution phase (THF).



a
b
c
e
f
g
h

**Figure S10.** Molecular electrostatic potential mapped onto the 0.001 a.u. electron density surface for **a, b, c, e, f, g** and **h** isomers in the solution phase (THF). Color coding, blue -0.032 a.u. to red 0.032 a.u.

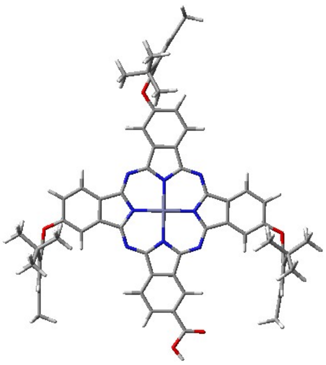
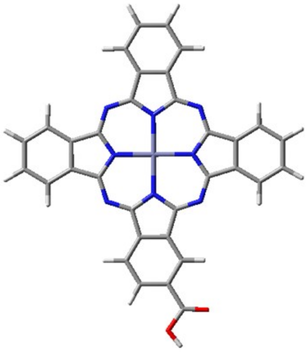
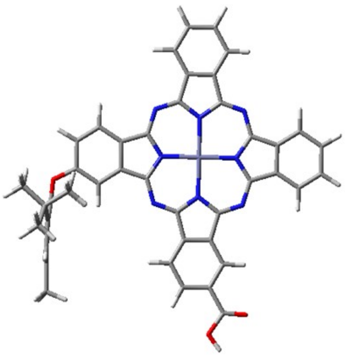
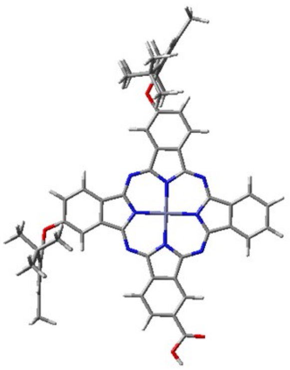
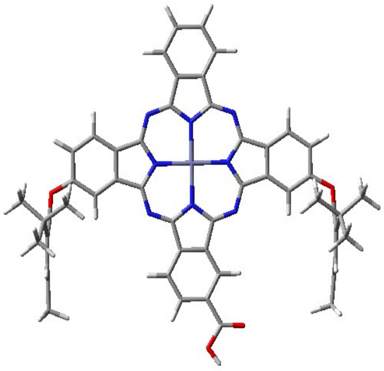
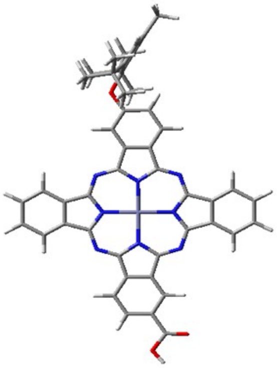
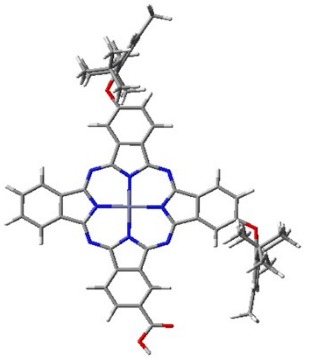
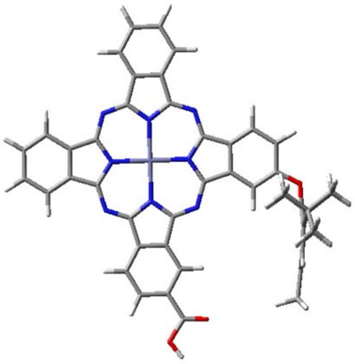
| **Molecule** | **Isomer d** | **ZnPc** | **ZnPc_2** |
|---|---|---|---|
| |  |  |  |
| $E_{tot}$/a.u. | -5612.447008 | -3633.658806 | -4293.255019 |
| | **ZnPc_23** | **ZnPc_24** | **ZnPc_3** |
| |  |  |  |
| $E_{tot}$/a.u. | -4952.850597 | -4952.851543 | -4293.254313 |
| | **ZnPc_34** | **ZnPc_4** | |
| |  |  | |
| $E_{tot}$/a.u. | -4952.850840 | -4293.255310 | |

**Figure S11.** Optimized molecular structures of isomer **d** with y without substituents calculated at the B3LYP/def2-SVP level of theory in the gas phase.

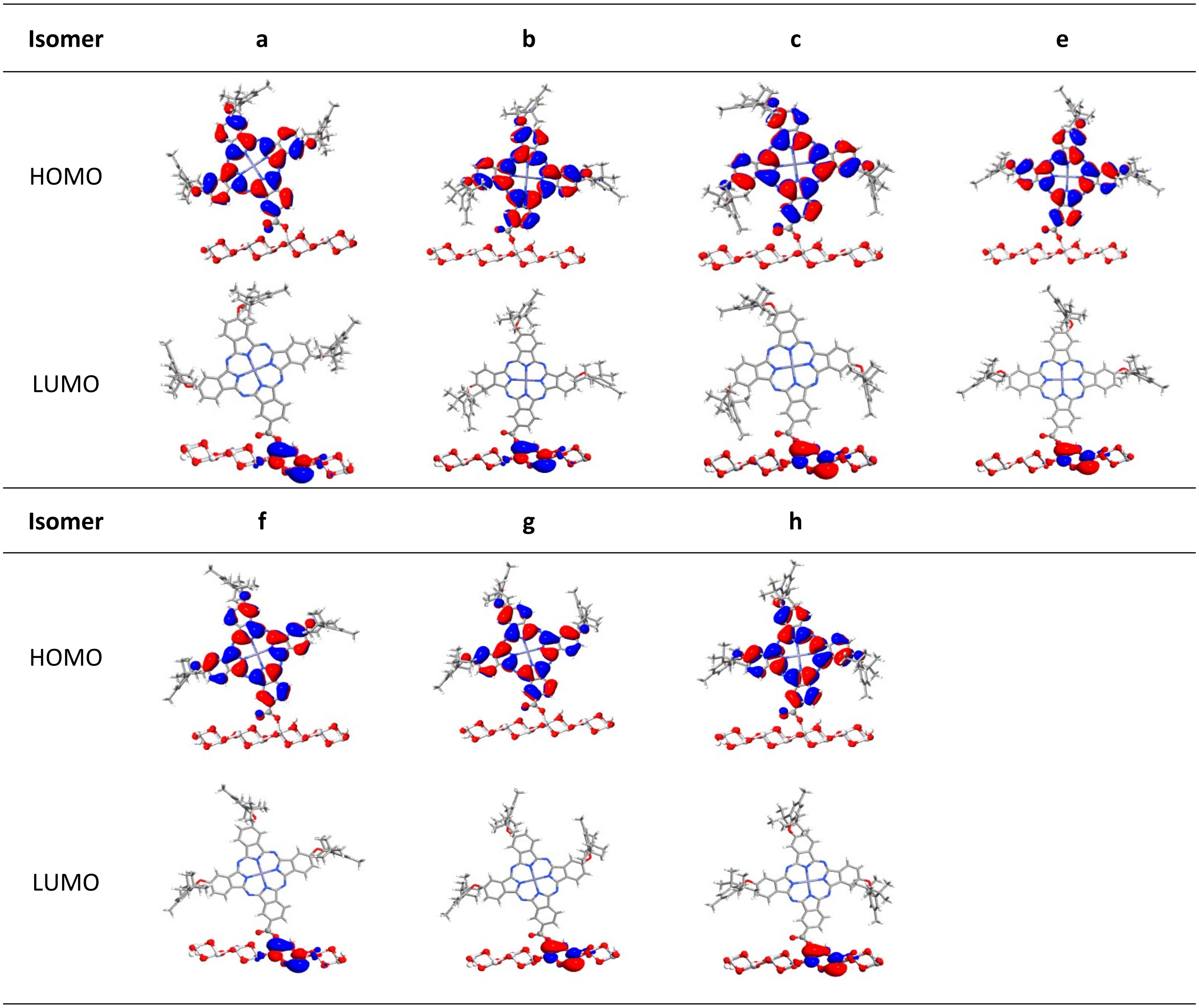


**Figure S12.** Optimized molecular structure and the HOMO and LUMO molecular orbitals for **a, b, c, e, f, g** and **h -TiO$_2$** complexes.