

Electronic Supporting Information for
Molecular-Structure Control of Electron Transfer Dynamics of Push-Pull Porphyrins as
Sensitizer for NiO Based Dye Sensitized Solar Cells

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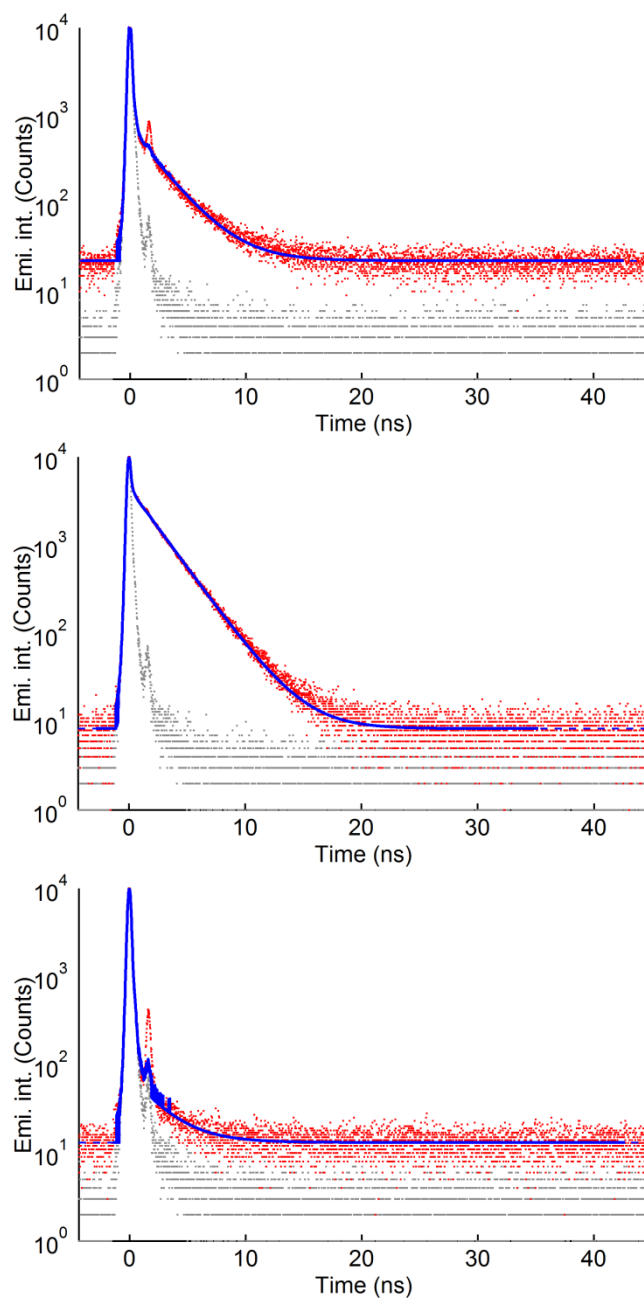


Figure S1. TCSPC results of porphyrin dyes in EtOH, up is **ZnP_{ref}** (2.8 ns), middle is **ZnP-TPA-NO₂** (2.4 ns), bottom is **ZnP-NDI** (13 ps), excitation at 405 nm.

Table S1. TCSPC results of porphyrin dyes in ethanol.

Sample	lifetime
ZnP_{ref}	$\tau = 2.35$ ns
ZnP-TPA-NO₂	$\tau = 2.78$ ns
ZnP-NDI	$\tau = 15$ ps

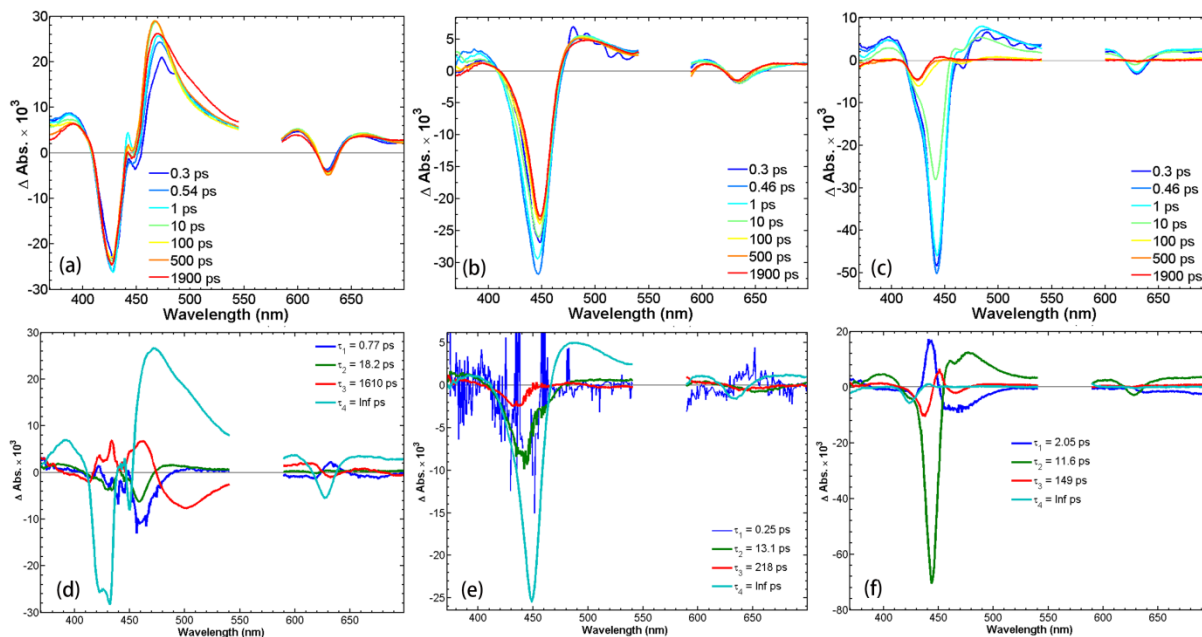


Figure S2. Femtosecond transient absorption spectra of porphyrin dyes in ethanol (up), and the decay associated spectra from global analysis (down). Left row is **ZnP_{ref}**, middle is **ZnP-TPA-NO₂**, and right row is **ZnP-NDI**, excitation at 560 nm.

Global analysis of the time evolution of the transient spectra in Figure S2 (top panels) was performed using a sum of four exponential functions and resulted in time constants of 0.77 ps, 18.2 ps, 1610 ps and $\gg 2$ ns. The corresponding decay associated spectra (DAS) are shown in the bottom panels of Figure S2, which demonstrate that the fast 0.77 ps and 18.2 ps components can be assigned to vibrational and solvent relaxation. This is seen from the red-shift of the negative band at 625 nm as the time delay increases from 1 ps to tens of ps. The negative band at 625 nm is a combination of two negative signals due to the ground-state depopulation and the S_1 stimulated emission that undergoes a small dynamic Stokes shift (cf. the 0-0 fluorescence band, Table 1). Most of the transient absorption changes are, however, described by the 1600 ps component, which is due to $S_1 - T_1$ intersystem crossing. With a 2 ns optical delay line, and the similarity in spectra for the two states, this lifetime value is uncertain and should be identical to the 2350 ps that was more accurately determined by TCSPC.

ZnP-TPA-NO₂ shows similar TA spectra features as **ZnP_{ref}**, and with very small signal changes up to 2 ns. Therefore the S_1 lifetime is taken from the TCSPC measurements as 2780 ps. The resulting T_1 lifetime is about 4.6 μ s.

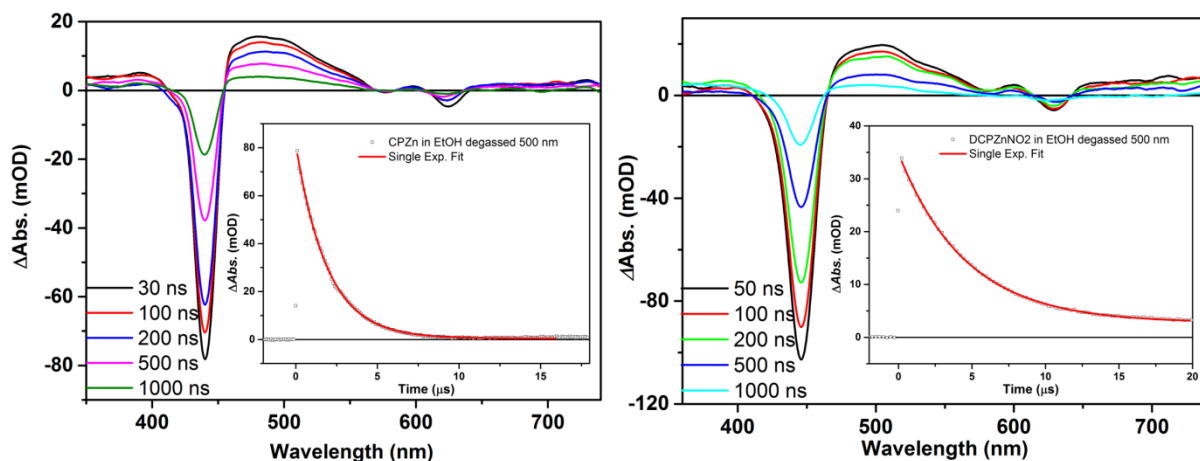


Figure S3. Transient absorption spectra and kinetic traces of the triplet state of ZnP_{ref} (left) and ZnP-TPA-NO_2 (right) in ethanol, excitation at 450 nm.

Table S2. Triplet excited state lifetime of porphyrin dyes in degassed ethanol.

Sample	Probe	$\tau(\mu\text{s})$
ZnP_{ref}	500 nm	1.92
ZnP-TPA-NO_2	500 nm	4.57
ZnP-NDI	480 nm	0.38

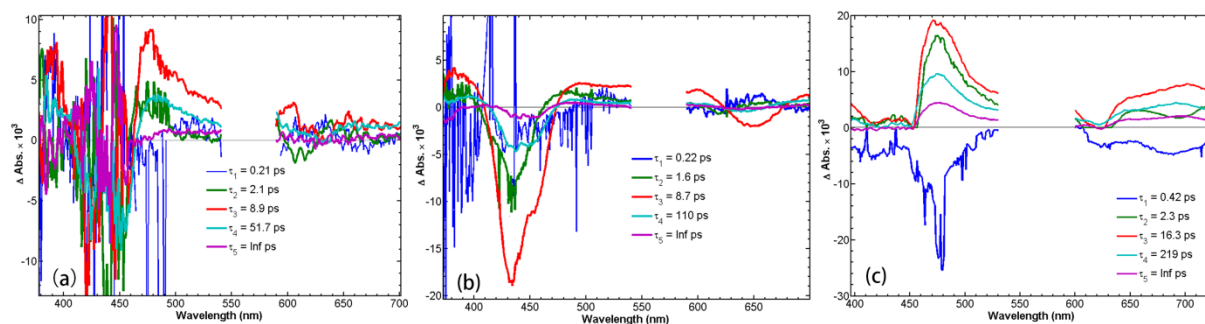


Figure S4. Decay associated TA spectra of porphyrin dyes on NiO from global analysis, a) $\text{NiO/ZnP}_{\text{ref}}$, b) NiO/ZnP-TPA-NO_2 and c) NiO/ZnP-NDI . The Soret band region is noisy because of low transmission of the probe light in the experiment.

Table S3. Charge recombination fitting results of porphyrin dyes on NiO.

Sample	Probe and condition	$\tau(\mu\text{s})$
$\text{NiO/ZnP}_{\text{ref}}$	470 nm with LiClO_4	1.73
NiO/ZnP-TPA-NO_2	490 nm with LiClO_4	2.45
NiO/ZnP-NDI	475 nm with LiClO_4	2.33

Synthesis and characterization of the porphyrin dyes

Zinc porphyrin **2**

In a round bottom flask were introduced bromo porphyrin **1** (251 mg, 0.17 mmol, 1 eq.), copper iodide (3mg, 0.017 mmol, 0.1eq.), Pd(PPh₃)₄ (20 mg, 0.0017 mmol, 0.1eq.), triisopropylsilylacetylene (0.4 mL, 1.72 mmol, 10 eq.) in THF (10 mL) under argon atmosphere. The degassed mixture of THF/Et₃N (3:1) (8 mL) was then injected in the flask. The resulting solution was stirred overnight at reflux. After cooling to room temperature, the solvents were evaporated under reduced pressure and the crude reaction mixture was directly purified by chromatography on silica gel (eluent: CH₂Cl₂/MeOH: 99/1). The desired zinc porphyrin **2** was obtained as a solid in 78% yield (210 mg). ¹H NMR (400 MHz, CDCl₃, 25°C), δ (ppm): 9.77 (d, J=4.62Hz, 2H), 8.98 (d, J=4.63Hz, 2H), 8.88 (d, J=4.68Hz, 2H), 8.78 (d, J=4.63Hz, 2H), 8.48 (d, J=8.10Hz, 2H), 8.33 (d, J=8.18Hz, 2H), 7.71 (t, J=8.35Hz, 2H), 7.02 (d, J=8.47Hz, 4H), 3.86 (t, J=6.40Hz, 8H), 1.49 (s, 18H), 0.89-1.32 (m, 46H), 0.85 (t, J=7.21Hz, 12H), 0.37-0.72 (m, 38H). ¹³C NMR (100 MHz, CDCl₃, 25°C), δ (ppm): 171.74, 160.02, 152.54, 151.01, 150.82, 150.60, 149.22, 148.72, 134.53, 132.22, 131.34, 131.16, 130.84, 129.79, 128.23, 128.16, 121.23, 119.50, 114.63, 110.16, 105.32, 99.19, 96.26, 68.70, 31.84, 29.45, 29.29, 29.22, 29.19, 29.02, 28.67, 28.61, 25.21, 22.64, 19.15, 14.07, 12.01. HRMS (MALDI-TOF) m/z: [M]⁺ calculated for C₉₈H₁₄₀N₄O₆SiZn, 1560.9828; found, [M]⁺ 1560.9779. Δ= 3.1 ppm.

ZnP_{ref}

In a round bottom flask, the porphyrin **2** (55 mg, 0.035 mmol, 1 eq.) was solubilized in THF (10 mL) and degassed under argon, then a solution of TBAF (1 M) in THF (0.14 mL, 4 eq.)

was injected *via* a septum. The resulting solution was stirred for 2 hours at room temperature. The solvent was evaporated and the crude was directly engaged in the following reaction without further purification. In a Schlenk tube containing the porphyrin, was introduced under argon atmosphere phenyliodide (72 mg, 0.35 mmol, 10 eq.), triphenylarsine (32 mg, 0.11 mmol, 3 eq.), and Pd(dba)₂ (6 mg, 0.011 mmol, 0.3 eq.). The degassed mixture THF/Et₃N (3:1) (8 mL) was then injected. The resulting solution was stirred for 3 hours at 50°C. After cooling to room temperature, solvents were evaporated under reduced pressure and the crude was directly purified by chromatography on silica gel (eluent: CH₂Cl₂/MeOH: 96/4). The desired compound **ZnP_{ref}** was obtained as a green solid in 99% yield (52 mg). ¹H NMR (300 MHz, CDCl₃, 25°C), δ (ppm): 9.75 (d, J=4.59Hz, 2H), 8.94 (d, J=4.61Hz, 2H), 8.82 (d, J=4.61Hz, 2H), 8.73 (d, J=4.64Hz, 2H), 8.46 (d, J=8.06Hz, 2H), 8.29 (d, J=8.06Hz, 2H), 8.01 (m, 2H), 7.69 (t, J=8.21Hz, 2H), 7.54 (m, 2H), 7.46 (m, 1H), 7.00 (d, J=8.41Hz, 4H), 3.84 (m, 8H), 0.84-1.30 (m, 46H), 0.81 (t, J=7.18Hz, 12H), 0.34-0.71 (m, 34H). ¹³C NMR (75 MHz, CDCl₃, 25°C), δ (ppm): 162.94, 159.96, 151.96, 150.95, 150.45, 148.89, 134.45, 132.11, 131.54, 131.32, 130.56, 129.78, 128.58, 128.09, 124.81, 121.15, 114.58, 106.79, 105.26, 95.19, 93.20, 68.63, 31.84, 29.45, 29.33, 29.23, 29.06, 28.69, 28.58, 25.20, 22.64, 14.09. HRMS (MALDI-TOF) m/z: [M]⁺ calculated for C₉₅H₁₂₄N₄O₆Zn, 1480.8807; found, [M]⁺ 1480.8863. Δ= 3.8 ppm.

Zinc porphyrin 5

To a sealed tube containing, the iodo porphyrin **3** (64 mg, 42 μmol, 1 eq.), the boronic ester **4** (100 mg, 175 μmol, 4 eq), Ba(OH)₂.H₂O (2 eq.) was added a mixture of THF and H₂O (6.5 mL) (3/1 v/v). The solution mixture was degassed by three freeze-pump-thaw cycles and Pd(PPh₃)₄ (5% mol.) was added, the tube was sealed and the reaction was heated at 80° C overnight. After being cooled down to room temperature, the crude mixture was filtrated on celite and the

solvents were evaporated. The crude reaction mixture was first purified by column chromatography on silica gel (eluent: CH₂Cl₂/petroleum ether: 4/6 to 6/4 (v/v) followed by a preparative TLC (eluent: CH₂Cl₂/petroleum ether: 5/5) to give the desired zinc porphyrin **5** (72 mg, 39 μmol, 95 %) as a green solid. ¹H NMR (400 MHz, CDCl₃) δ_H = 9.61 (d, *J* = 4.7 Hz, 2H), 8.84 (d, *J* = 4.7 Hz, 2H), 8.76 (s, 4H), 8.14 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 4H), 7.69 (t, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 4H), 6.99 (d, *J* = 8.5 Hz, 4H), 3.82 (t, *J* = 6.5 Hz, 8H), 1.64 (s, 18H), 1.46 (s, 18H), 1.3 - 0.3 (m, 95H), -2.26 (s, 2H). ¹³C (101 MHz, CDCl₃) δ_C = 165.56, 160.22, 151.06, 150.98, 145.86, 139.28, 135.87, 132.70, 131.19, 130.15, 126.66, 126.38, 123.92, 123.09, 120.62, 119.51, 113.91, 109.62, 105.39, 98.32, 96.98, 80.91, 68.91, 31.95, 29.55, 29.41, 29.33, 29.29, 29.12, 28.82, 28.76, 28.44, 25.49, 25.42, 22.75, 19.26, 19.19, 14.20, 12.11. HRMS MALDI-TOF: *m/z* calculated for 1823.2657 [M⁺], found 1823.2689 [M⁺], Δ = 1.8 ppm.

Zinc porphyrin **6**

The porphyrin **5** was dissolved in THF (6.5 mL) and a solution of TBAF (1 M in THF) was added (3 eq.) and the mixture was stirred at room temperature for 2 hours. Water was added, and the organic phase was extracted with CH₂Cl₂, washed with water and dried over Na₂SO₄. The free-base porphyrin was dissolved in a mixture of CH₂Cl₂/MeOH (1/1) and an excess of Zn(OAc)₂·2 H₂O (10 eq.) was added. The solution was then heated to reflux for 4 hours. After cooling down to RT, CH₂Cl₂ and water were added. The organic phase was washed with water, dried over Na₂SO₄. Evaporation of the solvent gave the desired zinc porphyrin that was directly used in the Sonogashira coupling reaction without further purification. To a sealed tube containing the above terminal alkyne zinc porphyrin (72 mg, 39 μmol, 1 eq.) and 1-iodo-4-nitrobenzene (48 mg, 193 μmol, 5 eq.), THF (6 mL) and Et₃N (0.5 mL) were added under argon.

The solution was degassed with three freeze-pump-thaw cycles, AsPh₃ (2 eq.) and Pd₂(dba)₃.CHCl₃ (5% mol.) were added. The tube was sealed and the reaction was heated at 80 °C overnight. After being cooled down to room temperature, water was added, the organic phase was collected and washed with water and finally dried over Na₂SO₄. After evaporating the solvents, purification by column chromatography (eluent: CH₂Cl₂/petroleum ether: 4/6 (v/v)) followed by precipitation in CH₂Cl₂/MeOH mixture gave the pure desired zinc porphyrin **6** (48 mg, 26 μmol, 67%). ¹H NMR (400 MHz, CDCl₃) δ_H = 9.55 (d, *J* = 4.6 Hz, 2H), 8.92 (d, *J* = 4.6 Hz, 2H), 8.79 (AB system, *J* = 4.5 Hz, 4H), 8.07 (d, *J* = 8.7 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 4H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.66 (t, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 9 Hz, 2H), 7.30 (d, *J* = 8.7 Hz, 4H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 4H), 3.88 (t, *J* = 6.4 Hz, 8H), 1.63 (s, 18H), 1.29 (m, 24H), 1.00 (m, 16H), 0.76 (m, 20H), 0.7-0.4 (m, 32H). ¹³C (101 MHz, CDCl₃) δ_C = 165.57, 160.16, 152.27, 151.45, 151.08, 150.56, 149.62, 145.78, 139.72, 135.79, 132.66, 131.96, 131.40, 131.19, 130.32, 130.11, 126.63, 123.89, 123.52, 123.07, 121.52, 121.08, 115.39, 105.42, 99.77, 80.92, 77.48, 77.36, 77.16, 76.84, 68.86, 31.92, 29.86, 29.52, 29.42, 29.31, 29.29, 29.18, 28.83, 28.79, 28.45, 25.41, 22.73, 14.17. HRMS MALDI-TOF: *m/z* calculated for 1849.0543 [M⁺], found 1849.0559 [M⁺], Δ = 0.9 ppm.

ZnP-TPA-NO₂:

Porphyrin **6** (48 mg, 26 μmol.) was dissolved in THF (6.5 mM) and a 1M methanol solution of sodium hydroxide (100 eq) was then added and the mixture was heated at reflux overnight. Water was added and the organic phase was extracted with CH₂Cl₂, washed with aqueous HCl solution (1 M) and finally dried over Na₂SO₄. Evaporation of the solvent gave the desired product **ZnP-TPA-NO₂** (42 mg, 24 μmol., 92 %). ¹H NMR (500 MHz, CDCl₃+C₅ND₅) δ_H = 9.36 (d, *J* = 4.5 Hz, 2H), 8.59 (d, *J* = 4.5 Hz, 2H), 8.52 (d, *J* = 4.5 Hz, 2H), 8.46 (d, *J* = 4.5 Hz,

2H), 7.87 (d, $J = 9.0$ Hz, 4H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 9.0$ Hz, 2H), 7.06 (d, $J = 9$ Hz, 4H), 6.99 (m, 2H), 6.69 (d, $J = 8.0$ Hz, 4H), 3.51 (m, 8H), 1.00-0.04 (m, 92H). ^1H NMR spectra. HRMS MALDI-TOF: m/z calculated for 1736.9291 [M^+], found 1736.9231 [M^+], $\Delta = 3.4$ ppm.

Representation of the frontier MOs

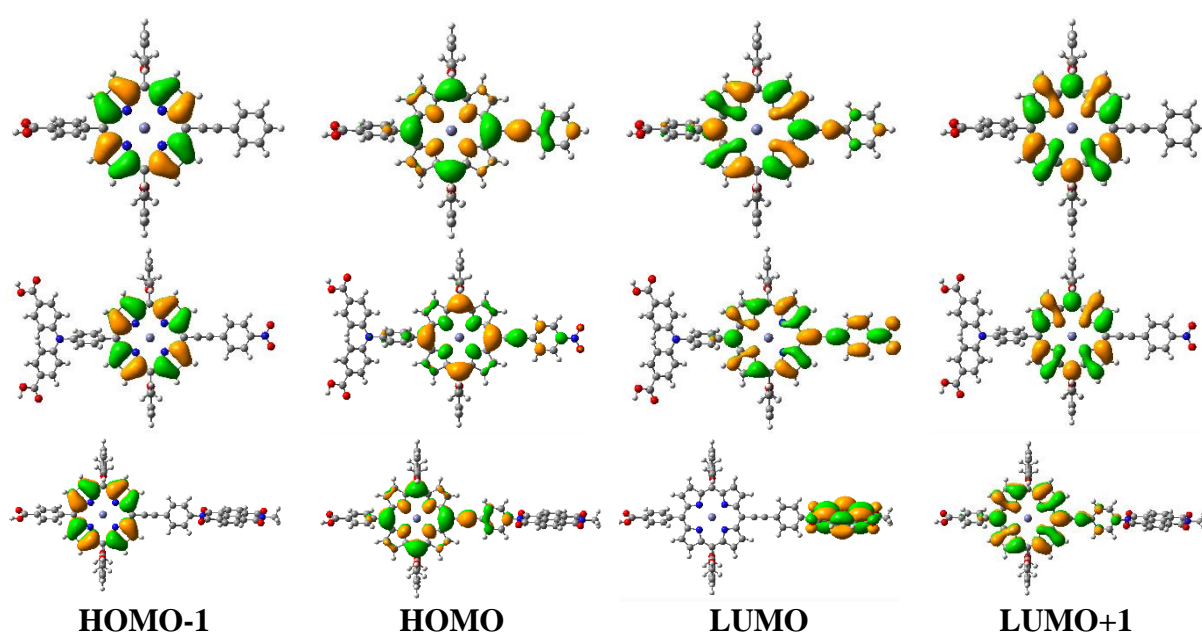


Figure S5. Representation of the four frontier MOs determined for the three dyes. From top to bottom: **ZnP_{ref}**, **ZnP-TPA-NO₂** and **ZnP-NDI**.