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# Enhanced Performance of NiO-Based Dye-Sensitized Solar Cells Using a Covalent Porphyrin-$C_{60}$ Dyad

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This study presents the synthesis and the characterization of a new covalent zinc porphyrin-fullerene (ZnP-$C_{60}$) dyad, featuring a π-conjugated bridge to link the donor (ZnP) and the acceptor ($C_{60}$). This system, along with a couple more reference compounds, namely **ZnP-3DoH-COOH** and **$C_{60}$*tr*ZnPCOOH**, is tested as photosensitizers in *p*-type dye-sensitized solar cells (*p*-DSSCs). Photophysical studies, including absorption and emission spectroscopy, reveal strong electronic communication between the porphyrin core and the fullerene unit, corroborated by theoretical calculations demonstrating efficient electron transfer from the donor to the acceptor. Electrochemical measurements, supported by theoretical insights, confirm that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital(LUMO) energy levels of the **$C_{60}$-3PV-ZnP-2DoH-COOH** dyad are well aligned for effective integration into NiO-based DSSCs. Notably, photovoltaic performance measurements show that solar cells sensitized with the covalent dyad exhibit significantly enhanced efficiencies compared with those using the reference compounds and other "ZnP-Acceptor" dyads. These findings highlight the potential of covalent ZnPor-$C_{60}$ assemblies in advancing the design of high-performance *p*-type DSSCs.

## 1. Introduction

One of the most pressing challenges faced by modern society is meeting the ever-growing global energy demand in a sustainable manner. To address this, several environmentally friendly strategies have been developed, with dye-sensitized solar cells (DSSCs) emerging as a particularly promising solution.[1] While theoretical models suggest that tandem DSSCs could achieve power conversion efficiencies (PCEs) as high as 43%,[2] the experimentally reported PCEs remain significantly below this threshold, underscoring the need for further advancements in this field.[3] This weak performance is attributed to the fast charge recombination (CR) that takes place in *p*-DSSCs.[4] Therefore, the development of better performing *p*-DSSCs is essential.

Over the last decades, several classes of organic and inorganic derivatives have been used as sensitizers in *p*-type DSSCs, such as diketopyrrolopyrroles, squaraine dyes, triphenylamines, perylene imides, metal (Ru, Ir, Rh, etc.) complexes, and porphyrinoids.[5] Among the various classes of compounds investigated, porphyrin derivatives stand out due to their remarkable light-harvesting ability and their versatility for functionalization with a wide range of electron-donating and electron-withdrawing groups.[6] These unique properties have enabled porphyrins to serve as effective photosensitizers and/or catalysts toward hydrogen production,[7] in artificial photosynthetic schemes[8] and in photovoltaic devices.[9] While porphyrin-based dyes have demonstrated outstanding performance in n-type DSSCs (record PCE),[10] their application in *p*-type DSSCs remains limited, with reported systems exhibiting relatively low overall conversion efficiencies.[11] This can be ascribed to the ultra-fast CR, which can be delayed by attachment of an electron acceptor to the sensitizer.[3,12] Few examples of such porphyrin based push-pull systems have already been reported incorporating various electron acceptors, such as PDI and fullerenes ($C_{60}$).[13] Quite recently we reported the first covalently linked ZnPor-$C_{60}$ dyads that were tested in *p*-DSSCs and proved that the distance between the macrocycle and the electron withdrawing unit plays a pivotal role in the photovoltaic performance.[13c]

The *p*-DSSCs sensitized by these three dyads displayed higher photovoltaic performances compared to the reference dye owing to the electron shift from the porphyrin ring to the $C_{60}$. The

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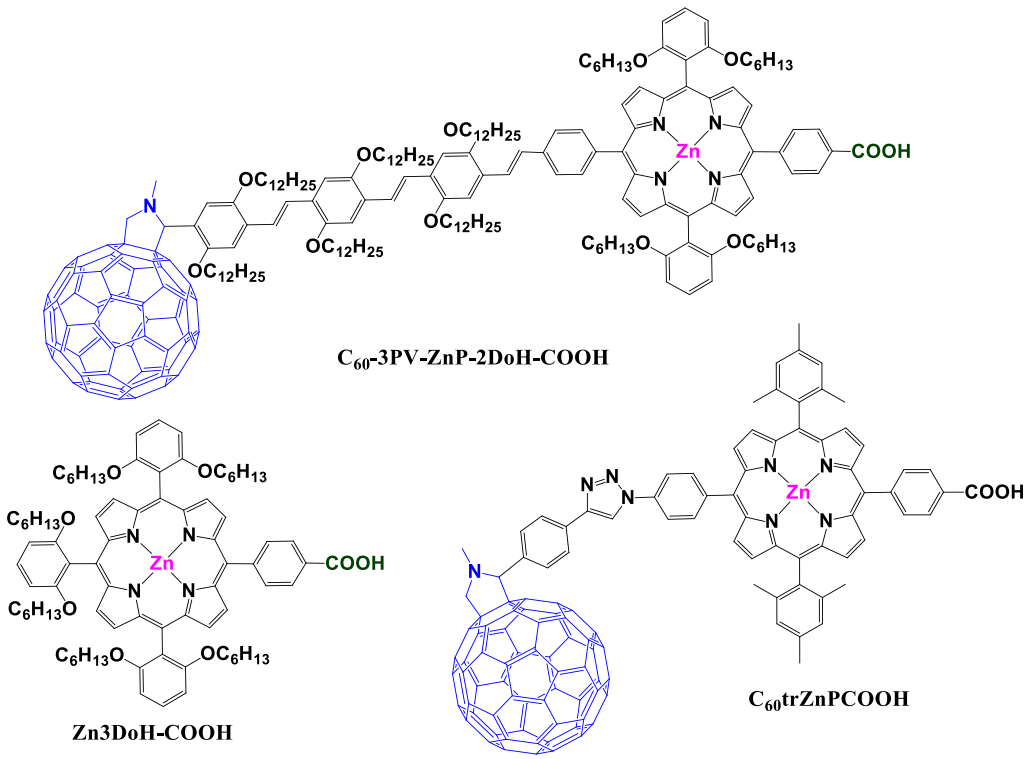
photophysical measurements also revealed an enhanced overall lifetime of the reduced system due to the presence of the electron acceptor moiety. This study highlighted the importance of incorporating donor–acceptor systems in NiO-based DSSCs. Moreover, the highest efficiencies were obtained for dyads **$C_{60}$*tr*ZnPCOOH** and **$C_{60}$*tr*ZnP*tr*COOH**, proving that the triazole spacer improves the electronic communication and their performance. Based on these findings, several modified porphyrin-fullerene dyes should be explored, in which the distance between the porphyrin macrocycle and the electron acceptor gets elongated by inserting spacers with varied lengths known to decrease the CR.[14]

Encouraged by these findings, we prepared a new ZnPor-$C_{60}$ dyad (**$C_{60}$-3PV-ZnP-2DoH-COOH**, **Scheme 1**), where the distance between the macrocycle ring and the fullerene unit was elongated by inserting a conjugated oligo(*p*-phenylenevinylene) (oPPV) bridge. In this system, the porphyrin bears a benzoic acid anchoring group for the successful attachment onto NiO and the $C_{60}$ unit is placed at a distance of ≈30 Å from the ZnPor moiety.[15] Furthermore, **$C_{60}$-3PV-ZnP-2DoH-COOH** bears two alkoxy-substituted phenyls at its periphery, in order to prevent the formation of aggregates on the semiconductor surface. This newly prepared dyad has been tested as a photosensitizer in NiO-based *p*-DSSCs and was compared to the performance of some reference porphyrin-based dyes, namely **ZnP-3DoH-COOH**,[16] **$C_{60}$*tr*ZnPCOOH**[13c] (Scheme 1), and **ZnP-$CO_2$H-eNDI**.[13a] The first being a Zn-metallated porphyrin while the other two are ZnPor-based donor–acceptor dyads, with either a $C_{60}$ or a naphthalene diimide (NDI) electron acceptor unit, respectively. Both reference dyads presented shorter distance between the electron donating and accepting units compared to the newly reported system.

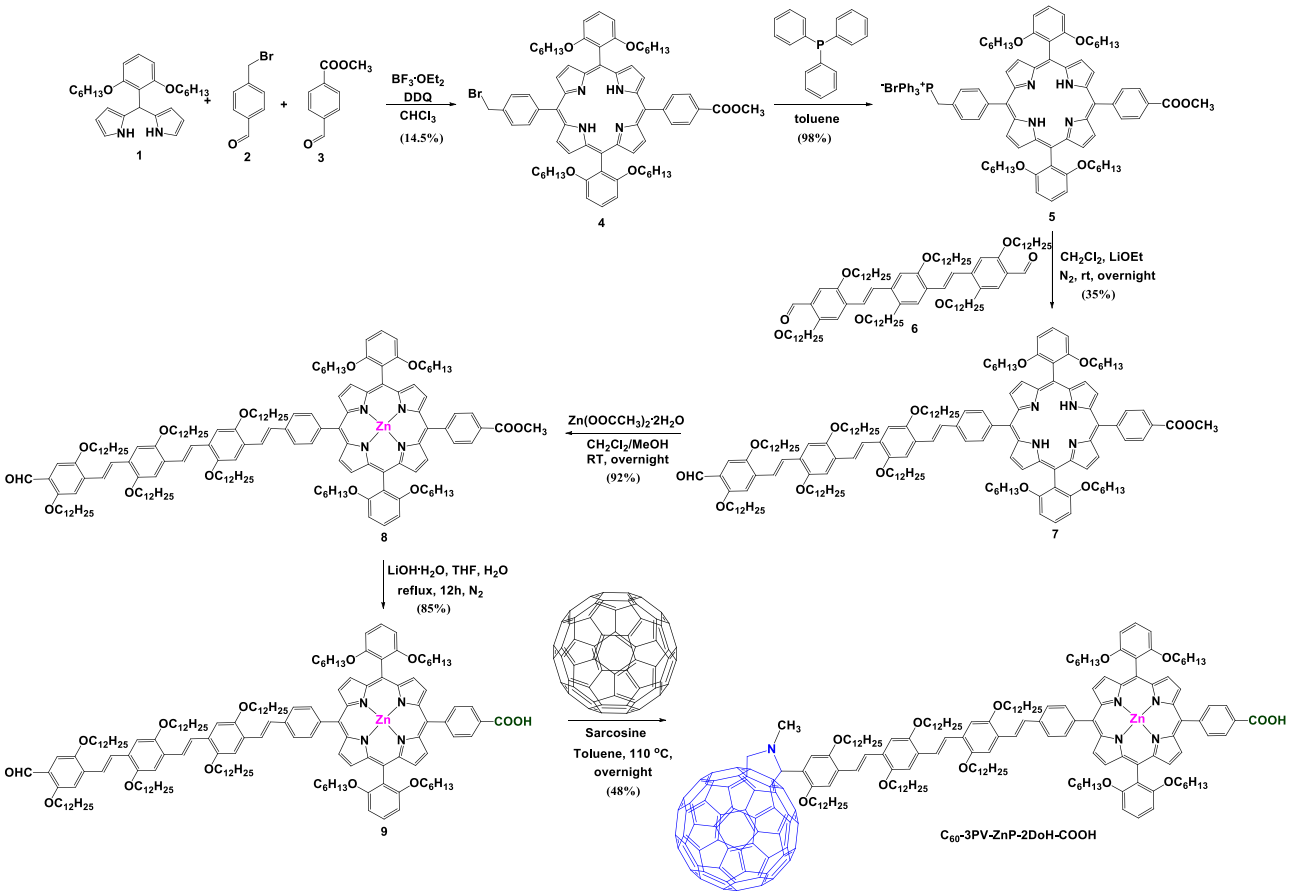
## 2. Results and Discussion

The synthetic route for the preparation of **$C_{60}$-3PV-ZnP-2DoH-COOH** is outlined in **Scheme 2** and contains six steps.

It starts with the condensation of dipyrrylmethane **1**,[17] with the two aldehydes **2**[18] and **3** to form porphyrin **4**. In the following step, porphyrin **4** was transformed into the corrresponding phosphonium ylide **5**. Then, a Wittig reaction was performed between derivatives **5** and bis-aldehyde **6** producing intermediate **7**. The (oPPV)-dialdehyde compound **6** has been prepared following previously reported procedures.[15] The E configuration of the newly formed double bond of aldehyde-porphyrin **7** was confirmed by its $^1$H NMR spectrum (Figures S12–S13, Supporting Information), since a coupling constant of 16.5 Hz was determined for the corresponding AB system of the vinylic protons. Subsequently, derivative **7** underwent a metallation reaction forming zinc-porphyrin **8**. Then the methylester group was transformed into the desired carboxylic acid anchoring group through a basic hydrolysis reaction to afford compound **9**. Finally, the latter was covalently linked with $C_{60}$ *via* a Prato reaction to obtain the desired product (**$C_{60}$-3PV-ZnP-2DoH-COOH**). The $^1$H NMR spectrum (Figures S35 and S37, Supporting Information) displays fulleropyrrolidine signals around 5 ppm, while the characteristic carbon peak of the carboxylic acid unit can be observed in the $^{13}$C NMR spectrum (Figure S39–S40, Supporting Information) at 171.4 ppm. The structures of all intermediate products, as well as that of the final functionalized $C_{60}$ derivative, were confirmed through $^1$H and $^{13}$C NMR spectroscopy (Figures S1–S44, Supporting Information) and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight (MALDI-TOF) mass spectrometry (Figures S45–S48,




**Scheme 1.** Structure of the dyads described in this work along with the reference **Zn3DoH-COOH**.




**Scheme 2.** The synthetic route followed for the preparation of **$C_{60}$-3PV-ZnP-2DoH-COOH**.

Supporting Information). The synthesis of all three reference compounds, such as **ZnP-3DoH-COOH**, **$C_{60}$*tr*ZnPCOOH**, and **ZnP-$CO_2$H-eNDI**, has already been described in previously published procedures.[13a,13c,16] These two moieties were used as reference photosensitizers in this work to evaluate the performance of our newly reported donor–bridge–acceptor (D-B-A) dyad.

Absorption and fluorescence spectroscopy and electrochemical studies were used in order to determine the applicability of the chromophore-$C_{60}$ conjugate reported herein in *p*-DSSCs. All the recorded optical data are summarized in Table S1, Supporting Information. The absorption spectrum of **$C_{60}$-3PV-ZnP-2DoH-COOH** in $CH_2Cl_2$ (**Figure 1**a) displays typical porphyrin absorption features at 424, 550, and 591 nm, as well as a shoulder at ≈466 nm, which is ascribed to the $\pi$–$\pi$* transition of the oPPV bridge. Further comparison of **$C_{60}$-3PV-ZnP-2DoH-COOH**'s spectrum with those recorded for its constituents revealed that, in the ground state, the ZnPor and $C_{60}$ entities interact only slightly when covalently connected.

To elucidate the potential electron transfer process occurring within the dyad, fluorescence spectroscopy experiments were conducted. For that reason the emission spectrum of **$C_{60}$-3PV-ZnP-2DoH-COOH** in $CH_2Cl_2$ was compared to the one recorded for derivative **9** (Figure 1b). The latter exhibited a characteristic ZnP emission spectrum that contains two intense peaks located at 603 and 649 nm. It is apparently clear that in the case of the dyad, the porphyrin based emission is significantly quenched, indicating a decay channel, *via* electron or energy transfer that originates from the first singlet excited state of the porphyrin towards $C_{60}$.

Both cyclic and square wave voltammetry were used for the determination of the electrochemical properties of **$C_{60}$-3PV-ZnP-2DoH-COOH** (Figure S49, Supporting Information), and the data are listed in Table S2, Supporting Information. The measurements were carried out in $CH_2Cl_2$ exhibiting four reversible oxidation processes around 0.76, 0.88, 1.05, and 1.20 V and three reversible reduction waves at −0.70, −1.09 and −1.59 V *versus* SCE. On one hand, the first oxidation process is attributed to the OPV bridge, while the second corresponds to the zinc porphyrin unit (see density functional theory (DFT) calculations above). On the other hand, the first and second reductions are assigned to the fullerene moiety. Based on the redox potentials of ZnP and $C_{60}$ in the dyad **$C_{60}$-3PV-ZnP-2DoH-COOH** and its photophysical properties, the calculated driving force for photoinduced electron transfer is −0.52 eV, indicating a highly probable quenching of ZnP* through electron transfer to $C_{60}$. This conclusion is supported by fast photoinduced electron transfer according to a superexchange mechanism mediated by OPV bridge of similar systems reported by Guldi and co-workers.[19] Although singlet-to-singlet energy transfer from ZnP* to $C_{60}$ is thermodynamically feasible ($\Delta G = -0.33$ eV),[20] it is less favorable and thus less likely to occur. This conclusion is also supported by the absence of a fluorescence band of $C_{60}$* around 700 nm in the emission spectrum,

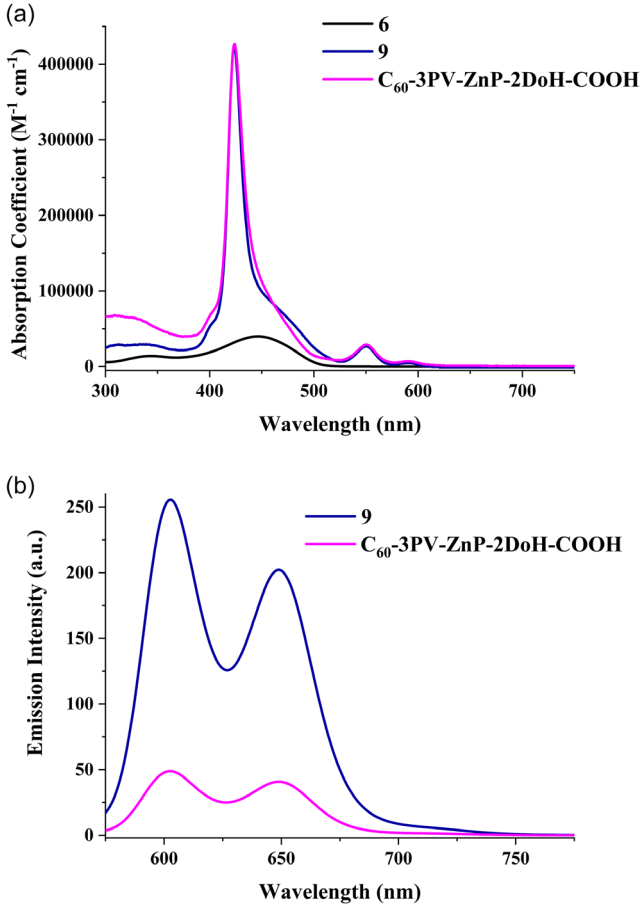



**Figure 1.** a) Absorption spectra of **$C_{60}$-3PV-ZnP-2DoH-COOH** (magenta) and compounds **6** (black) and **9** (blue) in $CH_2Cl_2$. b) Emission spectra of isoabsorbing $CH_2Cl_2$ solutions of compound **9** (blue) and **$C_{60}$-3PV-ZnP-2DoH-COOH** (magenta) upon excitation at 550 nm.

suggesting a low energy transfer efficiency. Notably, the intramolecular charge separation in the dyad is a favorable feature for application in *p*-DSSCs, as the hole localized on ZnP is well-positioned for injection into the valence band of NiO and that CR is probably very slow as reported on parent systems by Guldi and co-workers.[19]

The suitability of **$C_{60}$-3PV-ZnP-2DoH-COOH** for *p*-DSSCs was verified by examining its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (Table S3, Supporting Information) along with those of the NiO valence band, and the $I^{3-}/I^{-}$ redox potential. In **Table 1**, the reduction potentials of the dyad as well as the Gibbs free energies of the hole injection ($\Delta G^{o}_{inj}$) and regeneration ($\Delta G^{o}_{reg}$) reactions are listed. Importantly, it is further supporting that **$C_{60}$-3PV-ZnP-2DoH-COOH** is a suitable sensitizer for *p*-DSSCs, since negative values were calculated for the driving forces of both the injection and regeneration reaction with the redox couple.[21] DFT calculations were performed in order to gain insight on the molecular geometry as well as the potential electron transfer process that takes place in this covalently linked dyad (**Figure 2** and Figure S50 and Table S4, Supporting Information). In order to accelerate convergence, the structure of **$C_{60}$-3PV-ZnP-2DoH-COOH** was simplified by replacing the long dodecyloxy chains of the bridge with methoxy groups. This simplification of the dyad`s structure was applied due to the rather large total number of atoms and, as it has been reported before, it should not influence the HOMO and LUMO energy levels.[22] The resulted electronic distributions in the frontier orbitals further indicate that this ZnP-$C_{60}$ hybrid can act as a push–pull dye, since the electronic density in the highest occupied molecular orbitals is mainly spread over the porphyrin core and over the oPPV-bridge. Moreover, the LUMO, LUMO + 1 and LUMO + 2 orbitals of **$C_{60}$-3PV-ZnP-2DoH-COOH** are predominantly located at the $C_{60}$ moiety, thus revealing that upon photoirradiation an electron shift takes place from the ZnP unit to the $C_{60}$ acceptor. Finally, Table S5, Supporting Information summarizes the HOMO and LUMO energies, the HOMO-LUMO gap (HL) and the calculated dipole moment for **$C_{60}$-3PV-ZnP-2DoH-COOH**. The HL theoretical gap was calculated in $CH_2Cl_2$ solution and is in agreement with the HL electrochemical gap observed from the electrochemistry experiments.

The **$C_{60}$-3PV-ZnP-2DoH-COOH** dyad along with the reference compound (**ZnP-3DoH-COOH**) were examined as sensitizers in NiO-based *p*-DSSCs and compared with the previously reported dyads: **ZnP-$CO_2$H-eNDI**[13a] and **$C_{60}$*tr*ZnPCOOH**[13c] (the *J*/*V* curves of the DSSCs are illustrated in Figure S51, Supporting Information).The metrics of the solar cells, which contained the $I_3^{-}/I^{-}$ electrolyte are summarized in **Table 2**. First, all the dyads exhibit higher short photocurrent density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) than the reference compound **Zn3DoH-COOH**. This is most likely the direct consequence of retarded CR (hole in NiO and electron on the dye), which improves the charge collection efficiency. Interestingly, the dyads containing the fullerene electron acceptor perform better than that with NDI. This is certainly ascribed to the lower reorganization energy of fullerene that diminishes the back CR.[20b,23] Then, the dyad **$C_{60}$-3PV-ZnP-2DoH-COOH** delivers a higher $J_{sc}$ than **$C_{60}$*tr*ZnPCOOH**, which is also certainly due to the extra absorbance of the OPV bridge located after the Soret absorption band of ZnP (Figure 1a) and lower CR reaction due to the longer distance with the hole in NiO.

**Table 1.** Redox potentials recorded by cyclic voltammetry *vs.* SCE as well as the Gibbs free energies of the hole injection ($\Delta G^{o}_{inj}$) and regeneration reactions ($\Delta G^{o}_{reg}$).

| Compound | $E_{1/2}$ (ZnP/ZnP$^{-}$) [V] | $E_{1/2}$ ($C_{60}/C_{60}^{-}$) [V] | $E_{1/2}$ (ZnP*/ZnP$^{-}$)[a] [V] | $\Delta G^{o}_{inj}$[b] [eV] | $\Delta G^{o}_{reg}$[c] with $I_3^{-}$ [eV] |
|---|---|---|---|---|---|
| **$C_{60}$-3PV-ZnP-2DoH-COOH** | −1.59 | −0.70 | 0.51 | −0.21 | −0.36 |

[a]Calculated according to the equation $E_{1/2}(ZnP^*/ZnP^-) = E_{1/2}(ZnP/ZnP^-) + E_{00}$, where $E_{00} = 2.1$ eV. [b]Calculated according to the equation $\Delta G^{o}_{inj} = E_{VB}(NiO) - E_{1/2}(ZnP^*/ZnP^-)$, where $E_{VB}(NiO) = 0.30$ V *vs.* SCE. [c]Calculated according to the equation $\Delta G^{o}_{reg} = E_{1/2}(S/S^-) - E(I^{3-}/I^{2-})$, where $E(I^{3-}/I^{2-}) = -0.32$ V *vs.* SCE.

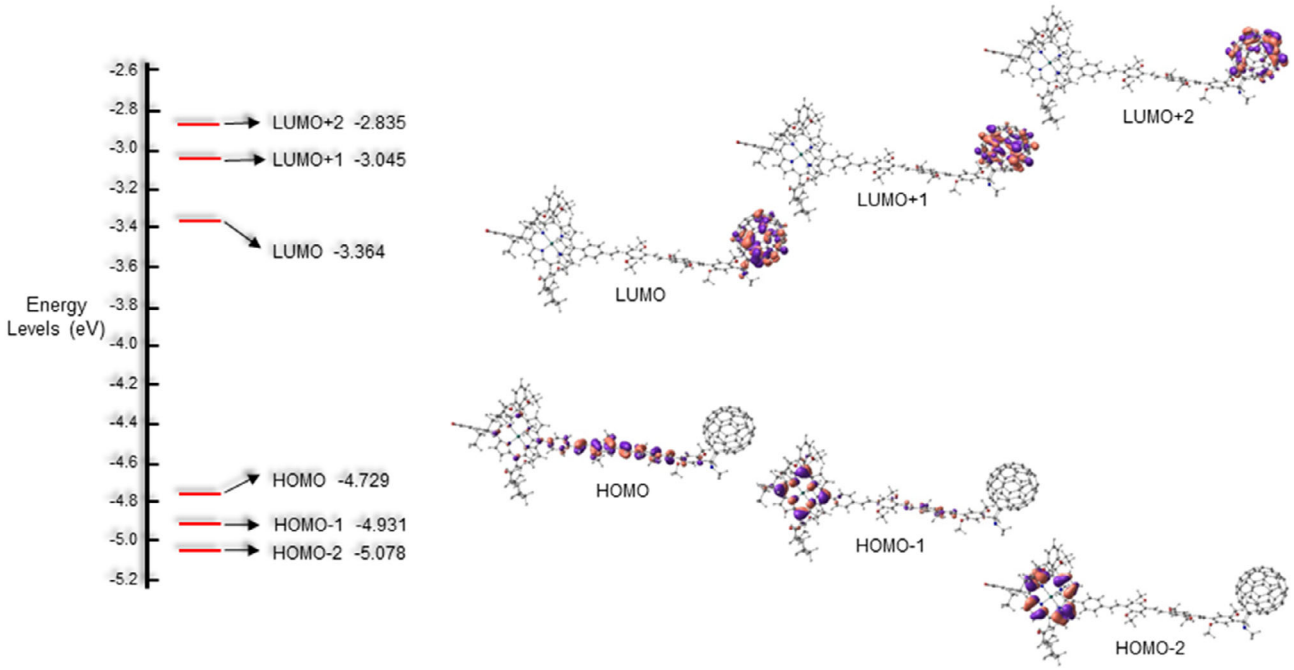



**Figure 2.** Frontier molecular orbitals of **$C_{60}$-3PV-ZnP-2DoH-COOH** with the corresponding energy levels.

**Table 2.** Photovoltaic characteristics of the solar cells made with $C_{60}$-3PV-ZnP-2DoH-COOH and the reference systems Zn3DoH-COOH, $C_{60}$*tr*ZnPCOOH[13c] and ZnP-$CO_2$H-eNDI,[13a] containing the $I_3^-/I^-$ electrolyte.

| Compound | $J_{sc}$ [mA/[cm]$^2$] | $V_{oc}$ [V] | *ff* [%] | PCE [%] |
|---|---|---|---|---|
| **$C_{60}$-3PV-ZnP-2DoH-COOH** | 2.17 ± 0.1 | 117 ± 5 | 34 ± 1 | 0.085 ± 0.004 |
| **Zn3DoH-COOH** | 0.59 ± 0.09 | 75 ± 3 | 37 ± 1 | 0.016 ± 0.003 |
| **$C_{60}$*tr*ZnPCOOH** | 1.86 | 109 | 37 | 0.076 |
| **ZnP-$CO_2$H-eNDI** | 1.38 | 127 | 32 | 0.056 |

## 3. Conclusion

To sum up, a new D-B-A covalent ZnPor-$C_{60}$ dyad has been prepared as a dye for NiO-based DSSCs. Both photophysical and electrochemical studies revealed that it is a suitable candidate for such application. Also, two other porphyrin-based sensitizers were examined for comparison reasons. The theoretical investigation of the dyad system showed that an electron shift from the porphyrin core to the fullerene takes place upon photoexcitation. Our initial thought regarding this project was that the efficiency of the conjugated dyad would be better than that obtained for the **$C_{60}$*tr*ZnPCOOH** reference one, due to the elongation between the $e^-$ donating and accepting units and absorbance brought by the insertion of a oPPV bridge. Furthermore, regarding the **ZnP-3DoH-COOH** porphyrin reference dye, which lacks the $C_{60}$ electron acceptor, we also expected a poorer performance. Indeed, the highest values for all the photovoltaic parameters were obtained for the *p*-DSSC sensitized by the covalent dyad **$C_{60}$-3PV-ZnP-2DoH-COOH**. What is more, if we compare the conjugated dyad's performance with the efficiencies of other conjugated systems,[11a,13a] we observe that **$C_{60}$-3PV-ZnP-2DoH-COOH** is one of the best reported porphyrin-based photosensitizers in *p*-type solar cells.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

**Keywords:** donor–bridge–acceptor dyad · fullerene (C60) · NiO-based p-dye-sensitized solar cells · photosensitizer · porphyrin

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