Assembly, charge-transfer and solar cell performance with porphyrin-C$_{60}$ on NiO for p-type dye-sensitized solar cells

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Abstract

A series of zinc tetraphenyl porphyrin photosensitizers furnished with three different anchoring groups, benzoic acid, phenylphosphonate and coumarin-3-carboxylic acid were prepared using ‘click’ methodology. All three gave modest performances in liquid junction devices with I$_3^\text{−}$/I$^-$ as the electrolyte. The distinct spectroscopic properties of the porphyrins allowed a detailed investigation of the adsorption behaviour and kinetics for charge transfer at the NiO|porphyrin interface. The adsorption behaviour was modelled using the Langmuir isotherm model and the phosphonate anchoring group was found to have the highest affinity for NiO (6.65 x 10$^4$ M$^{-1}$) and the fastest rate of adsorption (2.46 x 10$^7$ cm$^2$ mol$^{-1}$ min$^{-1}$). The photocurrent of the p-DSCs increased with increasing dye loading and corresponding light harvesting efficiency of the electrodes. Coordinating the zinc to a pyridyl-functionalised fullerene (C$_{60}$PPy) extended the charge-separated state lifetime from ca. 200 ps to 4 ns and a positive improvement in the absorbed photon to current conversion efficiency (APCE) was observed. Finally, we confirmed the viability of electron transfer from the appended C$_{60}$PPy to PCBM, a typical electron transporting layer in organic photovoltaics. This has implications for assembling efficient solid-state tandem solar cells in the future.

Keywords
Nickel oxide, photocathodes, artificial photosynthesis, dye-sensitized solar cells, tandem cells, transient absorption spectroscopy

1. Introduction

A significant part of the scientific community focus on developing new approaches to meet the demand of global energy thirst, which avoid damaging the environment. Hydrocarbons will continue to play the major role in the energy portfolio for the coming decades, but the rising cost, diminishing availability and concerns over CO₂ emissions adds increasing pressure to develop sustainable and secure alternatives. Solar energy utilization has been the subject of intense research, development, and deployment efforts that have accelerated during the past decade.[1] Chemistry has played a fundamental role in the design of materials and molecular systems for solar energy conversion into electricity. One example which has attracted attention is the dye-sensitized solar cell (DSC), which offers a versatile, printable alternative to conventional crystalline silicon technology.[2] The efficiencies reached by the state-of-the-art DSC devices under full-sunlight conditions are only half of that reached by silicon.[3,4] Although, much higher efficiencies are possible under ambient light.[5]

State-of-the-art DSCs contain a single photoactive electrode (i.e. photoanodes or n-type DSCs). The efficiency can potentially be improved by constructing tandem cells in which a second sensitized photocathode is incorporated in place of the platinised counter electrode found in n-DSCs.[6,7] In a tandem cell, the light transmitted by the photoanode can be converted by the photocathode, increasing the theoretical efficiency to around 45%.[8] Despite an increasing amount of work devoted to developing p-type DSCs, an efficiency which matches the state of the art n-type devices has not been reported yet.[9] In p-DSCs, light absorption by the dye is followed by rapid electron transfer from the valence band of the semiconductor, typically NiO, to the dye, followed by electron transfer from the dye to the redox mediator (typically I₃⁻/I⁻). For an efficient p-DSC, the dye must be strongly adsorbed onto the semiconductor surface, to promote an efficient charge transfer. Therefore, the dye should possess an anchoring group which can react with surface hydroxyl groups on the metal oxide to form covalent bonds. For n-type devices, the most commonly
studied anchoring units are carboxylic and cyanoacetic acids, but a wide range of others including phosphonates, sulfonates and catechol have been used.[2,10] Conversely, for p-type devices, the range of anchors which have been studied is much smaller, with carboxylic acids predominantly utilized.[11–13] Furthermore, the dyes employed for p-DSCs which have performed the most efficiently were synthesised through linear synthetic routes.[9,14,15] Following this approach, it is difficult to tune individual components (such as the anchor, donor and acceptor groups) without following separate linear routes for each new dye. This is particularly true for the anchoring group, which is generally synthesised either via oxidation of a carbonyl introduced using the Vilsmeier formylation[16–18] or the hydrolysis of tert-butyl benzoate.[9] A more modular approach would be desirable, where the chromophore and anchoring group could be synthesised separately and then assembled, using the minimum number of reactions possible.

The aim of this work is to use click chemistry[19–22] to introduce a range of anchoring groups, employing a porphyrin as the chromophore. Porphyrins are often derivatised using ‘click’ reactions,[23] are typically robust to anchor group hydrolysis [24] and provide a distinct spectroscopic handle for anchoring studies. On the other hand, previous work with porphyrins as sensitizers (Figure 1) has given modest results (For ZnP, J_{SC} = 0.19 mA cm^{-2}, V_{OC} = 98 mV, FF = 35, \eta = 0.006\%; for ZnTCPP, J_{SC} = 0.5 mA cm^{-2}, V_{OC} = 120 mV, FF = 40 \%, \eta = 0.02 \%).[25,26] It has been postulated that the limiting factor was fast electron-hole recombination at the interface between the dye and the NiO and by appending an NDI electron acceptor to ZnP the p-DSC performance was improved (ZNP-NDI J_{SC} = 1.38 mA cm^{-2}, V_{OC} = 127 mV, FF = 32 \%, \eta = 0.012 \%).[27] The hypothesis that the increased performance arose from a longer-lived charge separated state when NDI was present was supported by transient absorption spectroscopy, which showed that recombination between NiO and the excited dye occurred on a 50-100 ps time scale for NiO/ZnP_{ref}, whereas for NiO/ZNP-NDI most of the excited species decayed on a < 2 ns time scale. The longer lifetime for ZNP-NDI permits more efficient regeneration of the dye by the redox electrolyte which manifested in a higher J_{SC}. The higher V_{OC} for ZNP-NDI can also be explained by reduced recombination, as fewer electrons in the NiO valence band will increase the difference between the NiO Fermi-level and the redox potential of the electrolyte.
Likewise, Tian also tested a supramolecular system with ZnTCPP coordinated to N-methyl-2-(4'-pyridyl)-3,4-fulleropyrrolidine (C_{60}PPy). This was inspired by previous reports of supramolecular interactions between porphyrins and C_{60} derivatives, which showed a fast porphyrin to C_{60} charge transfer process and a long lifetime for the reduced fullerene. NiO films sensitised using ZnTCPP/C_{60}PPy performed more efficiently than the porphyrin alone (J_{SC} = 1.5 mA cm^{-2}, V_{OC} = 158 mV, FF = 38 %, η = 0.09 %). The authors attributed this increased performance to a suppression of recombination between the reduced dye and NiO. However, time-resolved experiments were not reported to confirm an increase in charge-separated state lifetime.

Figure 1. Chemical structure of porphyrins synthesised and tested in p-DSCs previously; ZnP_{ref} and ZNP-NDI reported by Odobel et al.[30]; ZnTCPP and C_{60}PPy reported by Tian et al.[26]

In this study, three porphyrins (Figure 2) were functionalised with a carboxylic acid, a phosphonate and a coumarin-based anchoring system. The effect of the anchoring
group on dye adsorption and p-DSC performances has been studied. The carboxylic acid was chosen as this is the most widely used anchor for p-DSCs. The phosphonate has been used as a direct comparison, as it is widely used for TiO$_2$ and is reported to be much more stable toward desorption than its carboxylate counterparts.[31] Finally, the coumarin anchor was chosen as a multidentate binding mode between the carboxylic acid and the ketone, which should improve the anchoring stability. Charge transfer from NiO to coumarin based dyes has been previously reported and occurs on the fs timescale.[32,33] Therefore, this anchoring group should facilitate efficient photoinduced charge transfer from NiO to the porphyrin. A C$_{60}$ acceptor was coordinated through the Zn following the approach by Tian et al.[26] The dynamics of charge-separation have been investigated using transient absorption spectroscopy to evaluate the effect of the electron acceptor on the charge-separated state lifetime and the results compared with the performance of the corresponding p-type DSCs.
2. Results and Discussion

2.1 Synthesis and characterisation of the porphyrins

1-3 were prepared via a copper-catalysed azide-alkyne cycloaddition reaction (details available in the supporting information). The alkyne fragment chosen was 5-ethynyl-10,15,20-tri-p-tolyl-porphyrin and the anchors were functionalised with the azide group. The porphyrin was coordinated with zinc to stop copper insertion occurring during the click reaction and the tolyl groups were used to help reduce porphyrin
stacking. This was intended to improve solubility and suppress aggregation when the dye was adsorbed onto NiO. The alkyne group was synthesised as a direct meso-substituent using TMS-propynal, rather than using TMS-ethynyl-benzaldehyde, which is more commonly used.[34–36] This was intended to improve electronic coupling between the porphyrin core and the anchor, as meso-phenyl rings in tetra-aryl porphyrins are non-planar.[37]

The identity of the products was confirmed by $^1$H NMR spectroscopy and the spectra were in general agreement with typical tetraphenyl porphyrin derivatives. However, for 1, the triazole was shifted upfield in comparison with 2 and 3 and appeared as two 1H doublets (with J = 1.5 Hz) at 6.97 and 6.49 ppm. This is not consistent with a mixture of regioisomers, due to the 1:1 integral ratio and absence (or broadening) of any other aromatic peaks. The weak splitting of these peaks suggests a $^4$J$_{HH}$ coupling, possibly indicative of a protonated triazole, which could arise due to a zwitterionic interaction (Figure S6 in the ESM). The chemical shift of these peaks (6.97 and 6.49 ppm) are similar to a porphyrin appended to an unfunctionalised meso-triazole group (6.57 ppm) reported by the group of Osuka.[38] This zwitterionic interaction could also explain why the $^1$H NMR spectrum of 1 (when M = Zn) is clearly defined, whereas for 2 and 3 the peaks were considerably broadened compared to the free-base derivatives (Figure S7). This broadening has been observed for triazole-functionalised porphyrins due to self-assembly of the triazole subunits with zinc.[39] The dynamic exchange between the monomeric and self-assembled species occurs on a shorter timescale with respect to the NMR measurement,[40] leading to peak averaging, which causes the broadened signals. If the triazole is protonated (as is possibly the case with 1), then the loss of one nitrogen lone-pair and a decrease in the electron density of the ring will hinder this self-assembly. This self-assembly of 2 and 3 was not observed when coordinating solvents (THF or MeCN) were employed which will compete with the triazole for coordination to the zinc porphyrin.

2.2 Optical studies

The UV-visible absorption and emission spectra of 1-3 are reported in Figure S8-11 and corresponding parameters are summarised in Table S2. The absorption spectra of 1-3 are typical of metalloporphyrins, with three major bands in the visible region.[41–43] The Soret bands of 1 and 2 were very similar, with a small decrease in intensity
and a slight broadening for 2. Otherwise, 3 presented a larger decrease in the peak intensity and an increased broadening compared to 1 and 2.

The steady state emission spectra of 1-3 show two bands at 606-610 nm and 657-659 nm, whereas for 1 and 2 the emission spectra were mostly independent from the excitation wavelength, however for 3 the emission from the second band was more intense when excited at 550 nm (relative intensity 1.0 vs. 0.95). Quantum yields were not determined, but for samples measured under the same instrumental settings with identical absorptions at the excitation wavelength, the relative intensities of the band at ca. 610 nm follows the trend 1 (1.0) > 2 (0.64) > 3 (0.59). Compared to the absorption spectra, the most emissive porphyrin was 1, which had the narrowest absorption band, while the least emissive porphyrin was 3, which had the broadest band. The uncorrected excitation spectra were recorded for both emission bands as shown in Figure S12-14. A good agreement of the absorption and excitation spectra was obtained for both the Soret and Q-bands, indicating that the emissive species for both bands was the same. Zero-zero energy of the molecules, which is used to estimate the electrochemical driving force for the electron transfer process in DSC, was calculated by taking the intercept of the normalised absorption and emission spectra. For porphyrins that do not have a clear overlap of the absorption and emission spectra, different methods have been used to calculate $E_{0 \cdot 0}$. Here it has been calculated using either the median wavelength values between corresponding absorption/emission bands (method A) or from the intercept of Lorentzian fits of the absorption/emission bands (method B). The values obtained from both methods were similar and the average excited state energies were mostly independent on the nature of theanchoring group (Table S3).

### 2.3 Electrochemistry

The redox potentials of 1-3 were determined using cyclic voltammetry and DPV and are summarised in Table S4 and cyclic voltammograms of the oxidation and reduction processes for 1-3 are provided respectively in Figure S18-S20. Concerning porphyrin 1, two quasi-reversible oxidation peaks were observed, with the peak separation dependent on scan rate. Upon increasing the oxidative scan window a third irreversible process was revealed, with a peak current five times higher than the first two processes. For porphyrin 2 the same pattern was observed, however quasi-reversible
oxidation peaks presented a smaller separation (ca. 100 mV). Similarly, upon increasing the oxidative scan window a third process was revealed, but the peak current of this wave was roughly equal to the first two processes. As for 1, only one reductive process (Figure S19) was observed, which was quasi-reversible, as a return wave was present at higher scan rates. At a scan rate of 100 mV s⁻¹ a shoulder peak was seen on the reductive wave, but this was not resolved at slower or faster scan rates. Cyclic voltammograms of the oxidation process for 3 show two quasi-reversible processes and upon increasing the potential window an irreversible oxidation process was observed, with a peak current roughly twice the size of the first two processes. The reduction process could not be resolved using cyclic voltammetry, as a broad reduction was recorded that overlapped with the solvent window.

DPV was used to resolve the peak potentials of the oxidation (Figure S21) and reduction (Figure S22) processes of 1-3. In each case there were three well resolved oxidation processes and a fourth that is generally broader and less well-defined. There was little variation in the first oxidation potential; all three porphyrins were oxidised between +0.29 and +0.32 V vs. Fc, with 3 the easiest to oxidise (+0.29 V vs. Fc) and 2 the hardest (+0.32 V vs. Fc). The reduction processes occur within a potential range of -1.74 to -1.87 V vs. Fc, with 2 reduced at lower potentials (-1.74 V vs. Fc) and 3 requiring the highest potential (-1.87 V vs. Fc).

These redox potentials can be used to estimate the driving force for electron transfer from the valence band of NiO to the photoexcited dye and regeneration of the reduced dye by the redox mediator, which are summarised in Table S5 and represented schematically in Figure S23. ΔG_{reg} is reasonably large in all cases, with the highest driving force of -1.05 eV for 3 and the lowest of -0.92 eV for 1. This suggests that regeneration will not be a limiting factor to device performances. The estimated value of ΔG_{inj} was highest for 2 (-0.33 eV) and lowest for 3 (-0.20 eV), as the HOMO was higher in potential. It is worth noting that these driving forces are similar to a porphyrin studied by Odobel and co-workers (ZnP_{ref} ΔG_{inj} = -0.30 eV and ΔG_{reg} = -1.09 eV).[25]

Liu et al.[45] proposed that ca. -0.8 eV driving force is needed for a high quantum yield for hole injection. Consequently, the low ΔG_{inj} for 1-3 (and those of Odobel et al.) could contribute to the low performances typically obtained from porphyrin sensitised p-DSCs.[25]
2.4 Computational Studies

Theoretical energy levels and the corresponding molecular orbital distributions were calculated using the hybrid B3LYP exchange functional and a 6-311G(d,p) basis set. Solvation was treated using the PCM. Initially, the ground state geometries were optimised (in THF) then frequency calculations were performed to check if this was a true energy minimum. TDDFT calculations were then used to determine the vertical excitation energies.

The orbital distributions for HOMO-1 through to LUMO+2, alongside the calculated energy levels, are shown in Figure S25 - Figure S26 and the energies are summarised in Table S6. In each case, there were four orbitals localised on the porphyrin core; the HOMO-1 to LUMO+1 for 1 and 2 and the HOMO-1/HOMO and LUMO+1/+2 for 3. The calculated energies of these orbitals were within 0.05 eV. The electron density of the HOMO was located on the porphyrin core and the four meso-substituents (with electron density on the triazole, but not on the anchor) for all three porphyrins. For the unoccupied porphyrin orbitals, the lower energy orbital was localised on the core and the meso-substituents in the x-axis, while the higher energy orbital was distributed across the core and y-axis substituents. The major difference between the three porphyrins was the unoccupied orbital associated with the anchor. For 1 and 2, this was the LUMO+2 which was higher in energy for the phosphonate than the carboxylic acid, but for 3 this orbital was lower in energy and was the LUMO. For 1 and 2 this orbital had electron density on the triazole, thus the anchor and porphyrin are coupled. However, for 3, there was no electron density on the triazole in the LUMO, therefore the anchor and porphyrin are seemingly decoupled.

TDDFT was used to compare the experimentally obtained absorption spectra and the calculated electronic transitions. The calculated energies are summarised in Table S7 and these transitions, overlaid with the experimental UV-visible absorption spectra, are shown in Figure S27-29. There was a reasonable agreement between the calculated and experimental absorption spectra, with lower intensity transitions calculated at lower energy (corresponding to the Q-bands) and higher intensity transitions at higher energy (the Soret band). In each case, the calculated Q-band
transitions were predominantly from HOMO to LUMO (or LUMO+1, the lowest porphyrin orbital, for 3) and HOMO to LUMO+1 (+2 for 3) transitions. The Soret band transitions were primarily due to excitations to the higher energy porphyrin orbitals. This agrees with the theory that the Soret band is from $S_0$-$S_2$ transitions and the Q-bands from $S_0$-$S_1$. For 1 and 3, the orbital localised on the anchoring group was not involved with any of the excitations, but for 2, there was a small charge-transfer contribution to the Soret band from porphyrin to anchor transition.

2.5 Dye Adsorption Studies

To investigate how the chemical structure of the different anchoring groups affects the dyes affinity to NiO, dye loading studies were performed (Figure 3). NiO films were prepared employing the same procedure used for solar cell tests (provided in the supplementary material). The concentration dependence on dye loading was investigated by measuring the equilibrium surface concentration from a range of initial dye bath concentrations (20 – 300 µM). Surface concentration at full monolayer coverage ($\Gamma_{\text{max}}$) and binding constants (K), as determined using the Langmuir adsorption isotherm model, are summarised in Table 1.

![Figure 3 (a). Equilibrium surface concentration of three-layer (1.5 µm thick) NiO films as a function of dye bath concentration (films immersed for 18 hours in a THF solution of the dye). The surface concentration was determined using the absorbance of the Soret band (ca. 420 nm) at lower dye bath concentrations and the highest energy Q-band (ca. 550 nm) at higher concentrations.](image)
Figure 3 (b). Surface concentration of a three-layer (1.5 µm thick) NiO film as a function of time (film immersed in a 300 µM THF solution of the dye) for 2. The surface concentration was determined using the absorbance of the Soret band (ca. 420 nm) at lower surface concentrations and the highest energy Q-band (ca. 550 nm) at higher concentrations.

Figure 3 (c). Surface concentration of a three-layer (1.5 µm thick) NiO films as a function of time (film immersed in a 300 µM THF solution of the dye) for 3. The surface concentration was determined using the absorbance of the Soret band (ca. 420 nm)
at lower surface concentrations and the highest energy Q-band (ca. 550 nm) at higher concentrations.

Figure 3 (d). UV-visible absorption spectra of 1-3 adsorbed onto NiO (18 hours adsorption from a 300 µM THF dye bath).

Table 1. Binding constants ($K_L$) and surface concentration at full monolayer coverage ($\Gamma_{\text{max}}$) as determined using the Langmuir adsorption isotherm model (Non-linear fitting, equation 7). Data is reported as an average value with standard errors in parenthesis.

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<th>1</th>
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<th>3</th>
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<tr>
<td>$K_L$ ($M^{-1}$)</td>
<td>$\text{—}$</td>
<td>$6.65 \times 10^4$</td>
<td>$2.81 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5.35 x $10^3$)</td>
<td>(8.04 x $10^3$)</td>
</tr>
<tr>
<td>$\Gamma_{\text{max}}$ (mol cm$^{-2}$)</td>
<td>$8.41 \times 10^{-10}$</td>
<td>$1.07 \times 10^{-8}$</td>
<td>$1.30 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>(7.65 x $10^{-12}$)</td>
<td>(2.16 x $10^{-10}$)</td>
<td>(4.47 x $10^{-10}$)</td>
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</table>

$^a$ Could not be fit to the Langmuir model. $^b$ $\Gamma_{\text{max}}$ reported as the surface concentration from adsorption with a dye bath concentration of 300 µM.

For 2 and 3, the dye loading depended on the concentration of the dye bath, with the absorption of the film (and corresponding surface concentration) increasing as the dye bath concentration increased (Figure 3a). The surface concentration reached a plateau between 75 and 150 µM. Giovannetti et al.[48] observed changes in the shape of the Q-bands at higher dye bath concentrations, for the adsorption of a porphyrin onto TiO$_2$, indicating aggregation is occurring. Here, there was no change to the shape of the absorption spectra upon increasing dye bath concentration. This suggests there
was little interaction between the adsorbed dye molecules and that only a monolayer had formed. The dye loading was higher for 3 (1.30 x 10^{-8} mol cm^{-2}) than 2 (1.07 x 10^{-8} mol cm^{-2}), possibly due to the larger footprint of the phosphonate with respect to the coumarin. There was a much lower dye loading for 1 than 2 or 3, which was surprising as there were only small steric differences between the three dyes (with 1 being the smallest). As carboxylic acids are so prevalent in the literature, it is intriguing that 1 had the lowest dye loading. It is possible that there were alternative anchoring modes competing with the acid for 1, which were not present for 2 and 3. For 2 and 3, the equilibrium data could be analysed using isotherm models, but for 1, the film absorbances were comparatively much lower at each dye bath concentration studied (Figure 3). The low dye uptake and high error associated with the measurements performed at lower dye bath concentrations made accurate analysis of the data impossible. All further thermodynamic/kinetic analysis of the adsorption process has been carried out for just 2 and 3. The fitting is described in detail in the supporting information. The data were found to be most accurately modelled using the Langmuir isotherm. Langmuir adsorption isotherm is one of the simplest models for the adsorption of molecules on a solid surface. It has been routinely used to describe dye adsorption onto semiconductor surfaces[49–51] and is based on four assumptions:

1. Only a monolayer of adsorbent forms on the solid surface.
2. All adsorption sites are uniform and equally accessible.
3. There is no interaction between adsorbed molecules.
4. All adsorption occurs through the same mechanism.
The binding constants, as determined from the various methods (see supporting material, Table S9)), were in the range of 6.03 - 6.81 x 10^4 M\(^{-1}\) and 2.61 – 3.02 x 10^4 M\(^{-1}\) for 2 and 3 respectively, with the values agreeing within error. This indicates that the phosphonate anchoring group has a higher affinity for NiO than the coumarin anchor. The binding constant for 2 is larger than for the phosphonate-anchored ruthenium trisbipyridine complex studied by Odobel et al.[11] (K = 1.7 x 10^4 M\(^{-1}\)). In the same report, a larger binding constant of 1.8 x 10^5 M\(^{-1}\) was calculated for a ruthenium complex anchored using carboxylic acid groups. Wu et al. studied the adsorption behaviour of the benchmark dye P1 onto NiO and reported a binding constant of 3.54 (± 0.16) x 10^5 M\(^{-1}\).[51] As the two reported binding constants for dyes containing carboxylic anchoring groups are on the order of 10^5 M\(^{-1}\), it is surprising that the binding of 1 was so poor. It is possible that 1 was instead bound through the triazole instead of the acid. This could explain the lower dye loading compared to 2 and 3, because anchoring through the triazole could cause the porphyrin to lie flat onto the NiO surface, reducing the amount of dye that would be able to adsorb. The surface area occupied by each dye molecule on NiO (details provided in the Supporting Material) was estimated to be 1.81 and 1.34 nm\(^2\) for 2 and 3, respectively, which corresponds to 11 and 13 dye molecules per NiO crystal, respectively.

Studying the kinetics of adsorption provides additional insight into the adsorption process. NiO films were immersed in a 300 µM solution of the dye (the same concentration used for the solar cell studies) and the surface concentration was determined at regular intervals from the film absorbance (using Equation 1 in the Supplementary Material). The evolution of surface concentration over time is provided in Figure 3b,c and the kinetic parameters for dye uptake, fit to various kinetic models, are summarised in Table S10. For the adsorption of both 2 and 3 onto NiO, there was an initial fast uptake of dye followed by a slower uptake, until a plateau is reached. For the uptake of 2 on NiO, the surface concentration reached 75% of the final saturated value in the first 10 minutes. A saturated surface concentration was then reached after 40 minutes. The uptake of 3 on NiO was much slower, with the surface concentration reaching 50% of the final value over 20 minutes in the initial fast uptake process. A saturated surface concentration was then reached after 280 minutes, which was seven times slower than for 2. The adsorption kinetics for the uptake of 2 and 3 onto NiO...
have been modelled using pseudo-first and second-order rate equations (Figure S36 - Figure S39 and Table S10).

A pseudo-first-order model has been previously used to model the uptake of N719[52] onto TiO₂ and the uptake of P1 onto NiO.[53] However, in this case, the pseudo-first-order model did not accurately describe the kinetic data (Figure S36 and Figure S37). If the reaction does have a first order dependence on a reactant, then a plot of ln ((qₑ - q)/qₑ) vs. time should be linear. Two linear relationships can be seen here; an initial part with a larger gradient at shorter times (t < 10 min), then another at longer times with a lower gradient. The linear regressions were lower here than for the second-order model (R² = 0.904 - 0.926 vs 0.998 - 0.999).

The pseudo-second-order model has been used to describe the uptake of a catechol-thiophene sensitisers onto TiO₂.[54] This was successfully used to model the adsorption of 2 and 3 onto NiO (Figure S36 and Figure S37), as plots of t/qₑ vs. time were linear, with high R² values. Pseudo-second-order rate constants of 2.46 x 10⁷ and 2.97 x 10⁶ cm² mol⁻¹ min⁻¹ were calculated for 2 and 3 respectively. This indicates that the phosphonate anchor has both a higher affinity for NiO (as determined by the Langmuir adsorption studies) and that the adsorption of the phosphonate occurred with a higher rate. It has been suggested that a second-order kinetic process for dye adsorption indicates the rate-limiting step is a chemisorption process, where an adsorbate-adsorbent electron exchange takes place.[54]

2.6 Device Performances

Devices were constructed from 1-3 by soaking the 1.5 µm thick NiO films for 18 hours in a solution of the dye in THF (0.3 mM). The electrolyte used was 1 M LiI and 0.1 M I₂ in MeCN. The performances of the champion cells and representative standard deviations are summarised in Table 2 and compared to previously reported values for ZnP ref as a benchmark.[25]

Table 2. Photovoltaic performance of p-DSCs constructed using 1-3. Standard deviations as determined for 5 devices constructed from the same batch of cells for Jsc, Voc, FF and η are provided in parenthesis.
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<tr>
<th></th>
<th>$J_{SC}$ / mA cm$^{-2}$</th>
<th>$V_{OC}$ / mV</th>
<th>FF</th>
<th>$\eta$ / %</th>
<th>IPCE / % ($\lambda$ / nm)</th>
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<tr>
<td>1</td>
<td>0.28 (0.05)</td>
<td>57 (3)</td>
<td>0.35</td>
<td>0.006 (9 x 10$^{-4}$)</td>
<td>5.4 (430), 1.0 (570), 0.6 (610)</td>
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<tr>
<td>2</td>
<td>0.45 (0.02)</td>
<td>74 (3)</td>
<td>0.35</td>
<td>0.012 (6.8 x 10$^{-4}$)</td>
<td>8.2 (430), 2.9 (570), 1.8 (610)</td>
</tr>
<tr>
<td>3</td>
<td>0.51 (0.04)</td>
<td>76 (6)</td>
<td>0.37</td>
<td>0.014 (8.1 x 10$^{-4}$)</td>
<td>9.8 (430), 3.5 (570), 2.2 (610)</td>
</tr>
<tr>
<td>ZnP$_{ref}$</td>
<td>0.19</td>
<td>98</td>
<td>0.35</td>
<td>0.006</td>
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$J_{SC}$ is the short-circuit current density at the $V = 0$ intercept, $V_{OC}$ is the open-circuit voltage at the $J = 0$ intercept, FF is the device fill factor, $\eta$ is the power conversion efficiency; IPCE is the monochromatic incident photon-to-current conversion efficiency.

The J-V curves for the champion devices were measured under illumination (Figure 4 (a)) and in the dark (Figure 4 (b)). Only modest performances were achieved for any of the dyes, with the highest $V_{OC}$ and $J_{SC}$ (76 mV and 0.51 mA cm$^{-2}$ respectively) obtained for 3. While the performances of 1-3 were relatively low, these results are similar to previously reported p-DSCs that use porphyrins which do not contain a secondary electron acceptor, such as ZnP and ZnTCPP.

[25,26] The trend in both $V_{OC}$ and $J_{SC}$ followed the order of 3 > 2 > 1, which was almost the same trend followed for dye loading and thus film absorbance. The trend in $J_{SC}$ is consistent with the differences in optical density, as the films with a higher absorbance will have an increased LHE and therefore produce a higher $J_{SC}$. Examination of the J-V curves measured in the dark (Figure 4 (b)) shows that the dark current was higher for 1 than 2 or 3, which were almost identical. This also helps to explain the trend in $J_{SC}$, as net currents are equal to the photocurrent produced under illumination minus the dark current. The dark currents are due to recombination between the redox electrolyte and NiO. As the dark currents have an inverse relationship with dye loading, it is likely that the reduced surface coverage of 1 did not protect the NiO surface from recombination to the same extent as 2 or 3. The higher dark current for 1 leads to a lower $V_{OC}$, as increased recombination causes the Fermi-level of NiO to be less positive (thereby reducing the energy gap between $E_F$-NiO and the redox potential of the electrolyte).
The IPCE spectra of the highest-performing devices are shown in Figure 4 (c). The IPCE at 430 nm, which corresponds to the porphyrin Soret band, is indicative of contributions to the photocurrent from dye excitation. This contribution is lowest for 1 and almost masked by the IPCE from the photolysis of triiodide. For 2 and 3, the IPCE at 430 nm is higher (8.2 and 9.8% respectively) and contribution from the Q-bands can also be observed.

Figure 4 (a). J-V curves of p-DSCs constructed using 1-3 measured under illumination (AM 1.5, 100 mW cm⁻²).

Figure 4 (b). J-V curves of p-DSCs constructed using 1-3 measured in the dark.
Figure 4 (c). IPCE spectra of p-DSCs constructed using NiO films sensitised with 1-3.

Figure 4 (d). Charge lifetime as a function of extracted charge density for p-DSCs constructed using 1-3.

The devices were also analysed using small amplitude square wave modulated photovoltage (Figure S40) and charge extraction (Figure S41) experiments.[55] From the charge extraction measurement (Figure S41), the $V_{OC}$ at the same extracted charge density follows the trend $1 > 2 > 3$. This indicates a positive shift in the valence band position. Additionally, it appears that the charge lifetime of 1 is higher (Figure
S40). These two factors would be expected to reduce the dark current and increase $J_{SC}$. However, care must be taken in comparing devices with different charge densities, as the amount of injected charge will effect $E_{F,NiO}$.

Combining these measurements gives the charge lifetime as a function of extracted charge density (Figure 4 (d)), which corrects for any shifts in the valence band. For each dye, the charge lifetimes were longer at lower charge densities, as there was a lower concentration of holes in the NiO valence band to recombine with the electrolyte. Charge lifetimes (at the same charge density) follows the trend of $3 > 2 > 1$, suggesting that the suppression of recombination, as dye coverage increases, leads to a higher $J_{SC}$.

The supramolecular system, reported in Figure 2, was employed to try to improve the performances of 3 (Figure 2). Porphyrin-fullerene dyad systems have been thoroughly investigated elsewhere and electron transfer from the chromophore to the acceptor is typically highly efficient.[56–58] $C_{60}PPy$ was synthesised following a literature procedure via the Prato reaction:[59] 4-pyridinecarboxaldehyde and N-methylglycine were reacted with $C_{60}$ in refluxing toluene to form the pyrrolidinofullerene. This was coordinated to the porphyrin through a sequential adsorption process, where the porphyrin was first adsorbed onto NiO and then the dyed film was immersed in a toluene solution of $C_{60}PPy$ overnight. $C_{60}PPy$ cannot be directly observed using UV-visible absorption spectroscopy, as the major absorption band is in the UV-region ($\lambda_{max} = 310$ nm) which overlaps with the absorption from FTO/NiO, while a less intense absorption ($\lambda_{max} = 431$ nm) overlaps with the porphyrin Soret band. However, a red-shift of the porphyrin Soret and Q-bands has been previously reported as evidence for the formation of supramolecular interactions between a porphyrin and $C_{60}$ (Figure S15).[60] The photovoltaic performances of p-DSCs sensitised using 3 with and without the presence of $C_{60}PPy$ are summarised in Table 3.

Table 3. Photovoltaic performance of p-DSCs constructed using 3 with and without cheno/$C_{60}PPy$. Standard deviations as determined for 5 devices constructed from the same batch of cells for $J_{SC}$, $V_{OC}$, FF and $\eta$ are provided in parenthesis.

<table>
<thead>
<tr>
<th></th>
<th>$J_{SC}$ / mA cm$^{-2}$</th>
<th>$V_{OC}$ / mV</th>
<th>FF</th>
<th>$\eta$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.51 (0.04)</td>
<td>76 (6)</td>
<td>0.37 (0.006)</td>
<td>0.014 (8.1 x 10$^{-4}$)</td>
</tr>
<tr>
<td>3/$C_{60}PPy$</td>
<td>0.42 (0.08)</td>
<td>46 (0.5)</td>
<td>0.32 (0.007)</td>
<td>0.006 (1.2 x 10$^{-3}$)</td>
</tr>
</tbody>
</table>
J_{SC} is the short-circuit current density at the $V = 0$ intercept, $V_{OC}$ is the open-circuit voltage at the $J = 0$ intercept, $FF$ is the device fill factor, $\eta$ is the power conversion efficiency.

The J-V curves measured under illumination are shown in Figure 5. While Tian and co-workers observed improved performances for the supramolecular porphyrin-\(\text{C}_{60}\)PPy system,[26] in this case, 3 performed worse when the fullerene was coordinated. There was a 0.09 mA cm\(^{-2}\) decrease in $J_{SC}$ and a 30 mV decrease in $V_{OC}$, combined with a reduced fill factor for the optimum device. This produced an efficiency that was less than half the value of 3-sensitised NiO alone. The J-V measurements performed in the dark (Figure 5 (b)) show a large increase in the dark current when \(\text{C}_{60}\)PPy is present. This suggests that the reduced $V_{OC}$ is due to an increase in recombination, possibly as \(\text{C}_{60}\)PPy has introduced an additional recombination pathway. As pyridine rings can anchor to semiconductor surfaces,[61,62] it is possible that \(\text{C}_{60}\)PPy is both coordinated to the porphyrin and anchored to free binding sites on NiO. If this is the case, then the fullerenes anchored to the surface could intercept electrons from the reduced porphyrin and recombine with NiO, instead of being regenerated by the redox electrolyte, which could explain the decreased $J_{SC}$.

![Figure 5 (a). J-V curves of p-DSCs constructed using 3 with and without cheno/\(\text{C}_{60}\)PPy measured under illumination (AM 1.5, 100 mW cm\(^{-2}\)).](image-url)
Figure 5 (b). J-V curves of p-DSCs constructed using 3 with and without cheno/C_{60}PPy measured in the dark.

Figure 5 (c). IPCE spectra of p-DSCs constructed using NiO films sensitised with 3 (THF, 0.3 mM, 18 hours) with and without the sequential adsorption of cheno (ethanol, 0.3 mM, 16 hours) and then C_{60}PPy (toluene, 0.3 mM, 16 hours).
Figure 5 (d). Charge lifetime as a function of extracted charge density for p-DSCs constructed using 3 and 3/cheno/C$_{60}$PPy.

The porphyrins developed in this work have only one anchoring group, but ZnTCPP contains four carboxylic acids capable of binding to NiO. Tian et al. provided evidence, in the form of XPS and FTIR measurements, to indicate that the majority of ZnTCPP adsorbs to NiO ‘lying down’ in a flat orientation.[26] This would effectively cover the NiO surface with porphyrin rings, blocking C$_{60}$PPy from binding directly to the surface. As the porphyrin is only anchored through one group for 3, it could possibly ‘stand up’ and point away from the surface, thereby leaving binding sites accessible to C$_{60}$PPy. To try and replicate this concept of surface coverage, the 3-sensitised NiO films were dyed overnight in an ethanolic solution of chenodeoxycholic acid (cheno, Figure S16) prior to coordination with C$_{60}$PPy. Cheno is routinely added to dye baths as a co-adsorbent to prevent dye aggregation as its carboxylic acid group allows efficient adsorption onto NiO. The smaller size of cheno compared to 3 could allow it to bind to sites that the larger porphyrin could not reach. The NiO films were sensitised in a sequential process; first with the porphyrin, then cheno and finally C$_{60}$PPy. The UV-visible absorption spectra of a NiO film after immersion in each solution is provided in Figure S17. There was a large reduction in the porphyrin film absorptivity after immersion in the cheno dye bath, indicating that cheno displaced some of the porphyrin molecules. A red-shift of the Soret band was again seen after immersion in the solution of C$_{60}$PPy, which indicated the successful coordination of the fullerene to
the porphyrin. The photovoltaic properties of p-DSCs constructed using 3-sensitised NiO with and without treatment with cheno/C₆₀PPy are summarised in Table 3.

The J-V curves measured under illumination are shown in Figure 5 (a). Despite the reduction in film absorptivity after treatment with cheno (and corresponding reduction in LHE), devices made using the cheno/C₆₀PPy treated films slightly outperformed the untreated films. There was an increase in both J_sc and V_oc which, despite a reduced FF, gave a slightly higher efficiency. The J-V measurements performed in the dark (Figure 5 (b)) show a reduced dark current for 3/cheno/C₆₀PPy. This suggests that the high dark current (and reduced J_sc and V_oc) for 3/C₆₀PPy was due to C₆₀PPy anchored onto the NiO surface facilitating recombination. The reduced dark current for 3/cheno/C₆₀PPy indicates that cheno effectively blocks the redox electrolyte from recombining with the NiO surface.

The IPCE spectra of the highest performing devices for 3 and 3/cheno/C₆₀PPy are shown in Figure 5 (c). In general, the IPCE profile was lower for 3/cheno/C₆₀PPy than 3, except for at the maximum absorption of the Soret band. This is to be expected, as the IPCE of a device is dependent on its light harvesting efficiencies (LHE) and the film absorption was reduced after treatment with cheno. The IPCE is the product of the LHE, the injection efficiency and the charge collection efficiency. For 3/cheno/C₆₀PPy the LHE was lower and the injection efficiency was assumed to be similar for both systems, as the dye is the same for both. Therefore, the charge collection efficiency must be higher for the supramolecular system. The charge collection efficiency is dependent on the probability of the holes in NiO reaching the conducting substrate, rather than recombining with the electrolyte or the reduced dye. It is possible that both factors have been improved in this system, as cheno is expected to reduce the electrolyte/NiO recombination and C₆₀PPy is expected to reduce the dye/NiO recombination.

Comparing the shape of the IPCE for both systems, the Soret band is more clearly pronounced for 3/cheno/C₆₀PPy than 3 alone. For 3/cheno/C₆₀PPy the IPCE between 330-400 nm, which is caused by the photolysis of triiodide,[63] is reduced. This was likely due to cheno blocking the electrolyte from reaching the NiO surface, thereby hindering electron transfer from NiO to the diiodide radical. Therefore, for 3/cheno/C₆₀PPy the porphyrin provided a larger contribution to the photocurrent than
in devices made using only 3. As the LHE was lower for 3/cheno/C_{60}PPy, but the IPCE are similar, the absorbed photon to current conversion efficiency (APCE) would be higher. Indeed, the APCE at 440 nm = 10 % for 3 and 12 % for 3/cheno/C_{60}PPy.

Charge extraction measurements (Figure S42) show a higher extracted charge at the same photovoltage for the system without cheno/C_{60}PPy, suggesting reduced recombination. This contradicts the dark current measurements (Figure 5 (b)), where the current is lower for cheno/C_{60}PPy, suggesting a reduction in recombination. However, the dark current measurement is a combination of any shifts in $E_{\mathrm{VB,NiO}}$ and $E_{\mathrm{F,NiO}}$ and any reduction in recombination. Charge lifetime measurements (Figure S43) show that the lifetimes were mostly similar for both systems, which would suggest that recombination rates were similar. On the other hand, it is difficult to compare systems with different dye loadings, as different amounts of charge injection from NiO will affect the charge density within the NiO valence band. Therefore, it is necessary to compare the charge lifetimes as a function of charge density (Figure 5 (d)). Charge lifetimes were shorter for 3/cheno/C_{60}PPy than 3 at the same charge density, which suggests there was more recombination for 3/cheno/C_{60}PPy. As for 3/C_{60}PPy, it is possible that the presence of C_{60}PPy introduced a new recombination pathway that was not fully blocked by using cheno.

In conclusion, while using C_{60}PPy alone caused a reduction in p-DSC performances, the combination of cheno/C_{60}PPy produced a small improvement, despite a reduction in film absorption. From the IPCE measurements (Figure 5 (c)), this improvement appears to be due to a higher APCE compensating for the reduced LHE. Further improvements can be imagined by optimising the porphyrin:cheno ratio, to block the surface sites not occupied by porphyrin molecules without displacing the dye. This would lead to a higher LHE, which coupled with the higher charge collection efficiency would improve the device IPCE/$J_{SC}$, leading to a higher power conversion efficiency.

2.7 Kinetics

The charge transfer dynamics of dyes 1, 2, and 3 were investigated by femtosecond time-resolved transient absorption spectroscopy in order to evaluate the charge separation at the dye|NiO interface. Details concerning the apparatus employed to
carry out measurements are reported in the supplementary material. Firstly, the excited states of 1, 2, and 3 in THF solution were recorded, then the experiments were repeated with the porphyrins adsorbed on NiO (NiO|1, NiO|2, and NiO|3) to explore the formation and decay of the NiO+|dye− charge-separated state. The transient absorption spectra of 1, 2, 3 in solution are reported in Figure 6 and Figure S44 and the transient absorption spectra of porphyrins on NiO are presented in Figure 7 and Figure S45. Global analysis was carried out using the OPTIMUS software and corresponding spectra are reported on supporting information (Figure S46-Figure S51).[64]

The spectral shape of 1, 2, 3 excited states at 550 nm are generally similar. The bleach centred at ca. 420 nm corresponds to the loss of the ground state, while the large positive absorption between 440–500 nm was attributed to the formation of the singlet excited state, which evolves over ca. 2 ns to be replaced by the triplet excited state (Figure 6). The minimum number of time components required to fit the decays of the porphyrin transient absorption using global analysis of the solution data was three (for 1) or four (for 2 and 3). Short components (within 200 ps) are consistent with vibrational and solvent relaxation and the major component was of the order of 1000 ps which is consistent with S1 – T1 intersystem crossing.[25] The last component in the time scale of microseconds is associated to the decay of the porphyrin triplet state, and the lifetime was resolved by fitting the transient at around 460 nm (see Figure 6 insets, Table S11) with a monoexponential function. All porphyrins presented a triplet lifetime around 1 μs (see Table S11), with 3 presenting the longest lifetime. The lifetimes obtained by fitting single-point traces at 460 nm were in excellent agreement with the kinetic constants obtained by global analysis.
Figure 6 a) Femtosecond transient absorption spectra of 1 in THF solution after excitation at 550 nm, the inset kinetic trace is probed at 461 nm.
Figure 6 b) Femtosecond transient absorption spectra of 2 in THF solution after excitation at 550 nm, the inset kinetic trace is probed at 474 nm.

Figure 6 c) Femtosecond transient absorption spectra of 3 in THF solution after excitation at 550 nm, the inset kinetic trace probed at 475 nm.

The spectral features between 430–500 nm in the transient spectra for NiO|1, NiO|2, and NiO|3 (Figure 7) were similar to those of the dyes in solution and formed within the time resolution of the instrument. All spectra contain a bleaching of the ground state, along with formation of the excited state. For NiO|1 and NiO|2 the weak negative signal at around 650 nm is consistent with stimulated emission. The excited states of NiO|1, NiO|2, and NiO|3 decayed three orders of magnitude faster than the dyes in solution, which suggests that, in all cases, the excited state is rapidly quenched by electron transfer from the NiO to the dye followed by formation of charge separated state. To exclude that the rapid excited state quenching is due to dye aggregation, experiments were performed with samples in which chenodeoxycholic acid (cheno), that is known to break aggregates, was used as co-adsorbent.[65] As the decay of the transient absorption was slightly faster in the presence of this additive (Figure S55), we can exclude aggregation. Consistent with this, a broad, weak absorption was observed for 1 at wavelengths longer than 600 nm, which is characteristic of holes
introduced in NiO. Furthermore, for NiO\textsuperscript{2} a weak feature at 660 nm, which can be attributed to the porphyrin radical anion, was present after about 10 ps. Changes associated with charge transfer from NiO to 3 were more significant. The broad stimulated emission band (centred around 560-600 nm) was quenched, and, at the same time, a weak absorption similar to that detected for NiO\textsuperscript{2} was identified around 660 nm, which is also consistent with the porphyrin radical anion.

Global analysis of the time evolution of the TA spectra measured upon 550 nm excitation was performed, using three (for NiO\textsuperscript{1}) and five (NiO\textsuperscript{2} and NiO\textsuperscript{3}) exponential functions to determine the numbers of time constants required to represent the data. As previously reported by Odobel et al., these time constants should not be interpreted as unique processes, but they represent an approximate description of the multi-exponential kinetics.\cite{25} The decay associate spectra (DAS) contain shorter components ($\tau_1 = 15$ ps for NiO\textsuperscript{1}, $\tau_1 = 0.75$ ps and $\tau_2 = 3$ ps for NiO\textsuperscript{2}, $\tau_1 = 0.8$ ps and $\tau_2 = 4$ ps for NiO\textsuperscript{3}) which were similar to decay of the S1 excited state in solution (Fig S49-51a). Likewise, the species associated spectra (SAS; Figure S50-51b) of NiO\textsuperscript{2} and NiO\textsuperscript{3} show that the bleach/stimulated emission at ca. 650 nm for $\tau_2$ components shift to ca. 640 nm for $\tau_3$ components, which suggests that the initial three components ($\tau_1$-$\tau_3$) for NiO\textsuperscript{2} and NiO\textsuperscript{3} and the first component ($\tau_1$) for NiO\textsuperscript{1} mainly reflect hole injection.\cite{24} The ca. 200 ps time constants ($\tau_2 = 190$ ps for NiO\textsuperscript{1}, $\tau_3 = 200$ ps for NiO\textsuperscript{2} and $\tau_3 = 210$ ps for NiO\textsuperscript{3}) were associated with the rapid charge-recombination at the NiO\textsuperscript{+}|porphyrin\textsuperscript{–} interface. Very little signal survived on a time scale >1 ns. Time constants obtained by fitting of decay traces around 460 nm were in excellent agreement with the time constant assigned to the rapid recombination step from global analysis (see inset Figure 7, Table S12) and in both cases the transient lifetimes were longer for 3. In summary, the results from global analysis of the data (DAS and SAS) allows us to conclude that hole injection into NiO occurred following excitation of porphyrins with time constants around 1–40 ps and this was followed by rapid charge recombination, mainly on the 200 ps time scale, with consequent recovery of 70% of the signal.
Figure 7a): Femtosecond transient absorption spectra of 1 on NiO after excitation at 550 nm, the inset kinetic trace is probed at 458 nm.
Figure 7b): Femtosecond transient absorption spectra of 2 on NiO after excitation at 550 nm, the inset kinetic trace is probed at 463 nm.

Figure 7c): Femtosecond transient absorption spectra of 3 on NiO after excitation at 550 nm, the inset kinetic trace is probed at 461 nm.

The kinetics of the supramolecular system (NiO|cheno|3-C₆₀PPy), where the C₆₀ acceptor was employed to improve the solar cell performance of 3 (Figure 2), were also analysed, and the associate spectra are reported in Figure S52. It is worth mentioning that we obtained generally longer-lived signals for NiO|cheno|3-C₆₀PPy with respect to NiO|3 (Figure 8). Global analysis of the 600-700 nm wavelength region was carried out by fitting kinetic traces with four time constants (Figure S53). The results were similar to those for NiO|3, with short components (T₁, T₂) that are consistent with vibrational relaxation and simultaneous decay of the stimulated emission (around 660 nm). The T₃ = 320 ps and T₄ = 4300 ps components did not contain a stimulated emission feature and the presence of a more prominent band around 670 nm is consistent with a combination of the 3 radical anion and the C₆₀PPy radical anion. T₃ is on the order of hundreds of picoseconds and is consistent with
charge-recombination. This component was also resolved by fitting the decay of NiO|cheno|3-C60PPy at 660 nm with a monoexponential function, unless otherwise states. Results are reported in Figure S54 and Table S13, in which the time constant associated with NiO|cheno|3-C60PPy was higher with respect to NiO|3.

Figure 8: Femtosecond transient absorption spectra of NiO|3 and NiO|cheno|3-C60PPy after excitation at 550 nm at two different delays.

The positive effect of the C60 acceptor on the charge-separated state lifetime prompted us to explore the possibility of applying this approach in solid state p-type DSCs. In previous work, it has been shown that poor electron transfer from the dye to PCBM limited the photocurrent and engineering the dye|PCBM interface is key to increase the device performance.[66,67] In this work, a layer of phenyl-C61-butyric acid methyl ester (PCBM) was applied by spin coating on top of NiO|cheno|3-C60PPy, in order to investigate the effect of this electrode structure (NiO|cheno|3-C60PPy|PCBM) on the charge separated state lifetime. The results were investigated by employing global analysis, fitting kinetic traces with four time constants. Results for NiO|cheno|3-C60PPy|PCBM are reported in Figure S56 and are quite similar to those obtained for NiO|cheno|3-C60PPy with short components (T1, T2) that can be associated to vibrational relaxation and simultaneous decay of the stimulated emission. In the presence of PCBM, the components T3= 700 ps and T4 = ∞ ps did not contain a stimulated emission feature. At the same time, the SAS for NiO|cheno|3-C60PPy|PCBM reveal that the porphyrin fine structure was lost in the T2 = 50 ps component and the signal centred at around 640 nm was broader with respect to the
equivalent component observed for NiO|cheno|3-C_{60}PPy. The lifetime constant attributed to rapid recombination (\(T_3\)), was longer in the presence of PCBM than the corresponding lifetime observed with NiO|cheno|3-C_{60}PPy. Furthermore, a long-lived component (\(T_4\)) was present in the spectra for NiO|cheno|3-C_{60}PPy|PCBM, which survived beyond the duration of the experiment. This suggests that PCBM intercepts the electrons from the dye/C_{60} conjugate and so recombination with holes in the NiO valence band is slower.

3. Conclusions

We have described a simple ‘click’ chemistry approach to functionalise dyes with different anchoring groups and systematically studied their adsorption behaviour on mesoporous NiO and their performance in p-type dye-sensitized solar cells. We observed a limitation of the triazole linker, which appeared to form a zwitterion in the benzoic acid derivative, 1. This affected the dye loading. The adsorption behaviour agreed with the Langmuir isotherm model, which indicates that a monolayer of dye binds to the surface. The adsorption kinetics were fitted to a pseudo-second order rate model and adsorption occurred more rapidly for the anchor that had a higher affinity for NiO (2). IPCE measurements confirmed that excitation of the porphyrin was contributing toward the photocurrent for each device and the characteristics of the p-DSCs incorporating 1-3 were comparable or higher to other porphyrins tested in the literature, which do not contain a secondary electron acceptor. p-DSC performances followed the trend of 3 > 2 > 1, which has been partially attributed to higher dye loading increasing the LHE, thereby increasing the J_{SC}. p-DSCs made using NiO|3-C_{60}PPy had a lower PCE than the dyes alone, possibly due to the fullerene anchoring directly to NiO and introducing an alternative charge-recombination pathway. Cheno was used as a co-adsorbent to block the free surface sites prior to the coordination of C_{60}PPy, to try and block this anchoring. The addition of cheno reduced the concentration of the porphyrins on the NiO surface, however, devices made using NiO|cheno|3-C_{60}PPy slightly outperformed NiO|3 alone, leading to an improved APCE.
The distinct spectroscopic properties of the porphyrins and C₆₀ radical permitted us to monitor the charge-separation and recombination processes in the photocathodes. The rate of electron transfer from the NiO to the photoexcited porphyrins occurred rapidly (τ = 1–40 ps) and was followed by rapid charge recombination, (≈ 70% of the signal decayed with τ < 200 ps), which is consistent with our previous work on organic dyes adsorbed on NiO. The structure of the anchoring group or the presence of cheno did not appear to greatly affect the dynamics. The coordination of the electron acceptor, C₆₀, to the porphyrin extended the charge-separated state lifetime, however. Furthermore, adding an electron transport layer (PCBM) to the film provided a pathway to intercept the charge and extend charge-separation on > µs timescales. This has implications for solid state tandem DSSCs and the information provided by these experiments will enable us to engineer optimised dyes which bind strongly to the NiO surface and drive electron transfer from the metal oxide towards a solid-state electron transport layer in tandem solar cells.

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Electronic Supplementary Material (ESM) available: [experimental section: synthesis and characterisation, methods electrochemical and photoelectrochemical characterisation, DFT, adsorption isotherms, TA and TRIR spectra].
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