Cost-Effective Dyes Based on Low-Cost Donors and Pd-Free Synthesis for Dye-Sensitized Solar Cells

Artit Jarusarunchai, Arivazhagan Valluvar Oli, Aruna Ivaturi, and Neil Robertson*

The structural design of photosensitizers for dye-sensitized solar cells (DSSCs) usually involves modification of the donor and π-spacer moieties using expensive Pd cross-coupling reactions. Herein, the concept of more sustainable and cost-effective dyes to realize large-scale production is presented. Two dyes, coded BzC and PTZC, with low-cost donors, phenyl and phenothiazine, respectively, and 4H-cyclopenta [2,1-b:3,4-b']dithiophene π-spacer, are synthesized by Pd-free reactions, including Horner–Wadsworth–Emmons, with high overall yield (68% for BzC and 55% for PTZC). The best photovoltaic performances exhibit 3.00% and 5.92% together with a relatively low ideality factor of 1.03 and 1.12 for BzC and PTZC, respectively, indicating efficient retardation of electron recombination from surface trap states. Finally, the synthesis costs for BzC and PTZC are estimated to be about 7.5–9 times lower than that of LEG-4 (as a commercial reference dye). The cost performances of BzC and PTZC are estimated to be around 5 times better than that of LEG-4.

1. Introduction

Renewable solar energy has attracted much attention and is an essential alternative energy supply to address the increasing energy demand and environmental concerns. In this aspect, photovoltaic (PV) technology is a good candidate for utilization of solar energy. One of the promising emerging PV technologies is dye-sensitized solar cells (DSSCs), where dye molecules, so-called photosensitizers, are used as the light absorber. In this regard, dyes can be considered among the most important components in DSSCs. The very first dyes used for high-performance DSSCs were based on Ru–polypyridyl complexes. However, they usually show relatively low extinction coefficient and involve difficult synthesis and purification steps. Thus, a new group of dyes called metal-free organic dyes subsequently emerged for DSSC applications. The organic dyes provide high extinction coefficient and flexibility in design and tuning of their electronic properties. The structures of organic dyes are usually based on the state-of-the-art donor–π-acceptor (D–π–A) design. Unlike Ru–polypyridyl complexes whose excitation process is based on metal-to-ligand charge transfer (MLCT), the relevant electronic transition upon photoexcitation in the organic dyes is intramolecular charge transfer (ICT). The electron density moves from the donor part to the acceptor part, leading to efficient charge separation.

A great deal of research in DSSCs has focused on the dye design and modification to tune the dye properties. In general, the structures of organic dyes usually contain a large extended conjugated system from the donor and π-spacer units to give broad and intense spectral absorption in visible light. The molecular design for the organic dyes normally relies on linking conjugated units via C–C or C–N bond formation. The reactions involved inevitably are Pd cross-coupling reactions, such as the Suzuki–Miyaura, Stille, and Buchwald–Hartwig reactions. These reactions involve the use of Pd-based catalysts including a specific coupling partner, for example, organoborons for the Suzuki–Miyaura reaction and organostannanes for the Stille reaction. Notwithstanding their versatility, the Pd catalysts are normally expensive as Pd is a rare metal and they need additional ligands added to perform the catalysis. The high cost of the catalysts can increase the total cost of dye synthesis, making the dyes more expensive. Moreover, some starting materials, such as organostannanes, cause toxicity concerns and possible tin contamination in the products. The organostannanes have been acknowledged to cause toxicity to a range of neurological and liver systems. Therefore, more sustainable alternative reactions must be sought to address the toxicity concerns and lower the cost of dye production. One of the promising alternative reactions is the Wittig or Horner–Wadsworth–Emmons (HWE) reaction.

As mentioned earlier, the organic dye architecture is based on D–π–A design and the modification of the dye structure is normally carried out by changing the donor and π-linker to tune the properties. One of the most commonly used materials for the donor part in the organic dyes is the derivatized triarylamine unit due to its electron donor capability. To further improve the donor moiety, many modifications on the triarylamine-based donor are usually carried out, such as the addition of alkyl chains or further extending the conjugation lengths.

A. Jarusarunchai, N. Robertson
School of Chemistry
University of Edinburgh
Edinburgh EH9 3FJ, UK
E-mail: neil.robertson@ed.ac.uk
A. Valluvar Oli, A. Ivaturi
Smart Materials Research and Device Technology (SMaRDT) Group
Department of Pure and Applied Chemistry
University of Strathclyde
Glasgow G1 1XL, UK

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/solr.202200375.

© 2022 The Authors. Solar RRL published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/solr.202200375
These modifications, however, increase the costs associated with the already high synthesis cost of the organic dyes.

Phenothiazine (PTZ) has also been used in DSSCs due to its electron donor capability, low cost, and butterfly conformation which prevent molecular aggregation.[18,19] Buene et al. studied the effect of various auxiliary donors connected to PTZ-donor and thiophene as π-spacer to achieve D–π–D–π–A structure.[20] The power conversion efficiency (PCE) of auxiliary donor-incorporated dyes was enhanced by moderate 4–11% relative improvement. This highlights that the auxiliary donor may not be necessary for PTZ-based dyes. Moreover, PTZ-based dyes with various π-spacers, such as thiophene,[19–21] furan,[19] 3,4-ethylenedioxy thiophene (EDOT),[19,22] phenyl,[23] and 4H-cyclopenta[2,1-b:3,4-b’]dithiophene (CPDT),[24] for DSSCs have been investigated. Out of these π-spacers, CPDT possesses large conjugation and ease of structural modification, such as introduction of long alkyl chains, and large conjugation. To demonstrate the low synthesis cost, estimation was made not only for the synthesis costs but also for the cost performance per cm² per %PCE of these two dyes in comparison with highly efficient commercial dye LEG-4.

2. Results and Discussion

2.1. Synthesis

BzC was synthesized according to Scheme 1. CPDT was first alkylated with hexyl chains to give compound 1 which subsequently underwent the Vilsmeier–Haack reaction to yield compound 2. To achieve a conjugated structure suitable for a dye, CPDT unit was joint to the phenyl ring by a double bond using the HWE reaction. Benzyl bromide was changed to compound 3 by the Michaelis–Arbuzov reaction using triethyl phosphite (P(OEt)₃). After that, compound 3 and compound 2 underwent the HWE reaction to give compound 4. The Vilsmeier–Haack reaction was performed again with compound 4 to synthesize compound 5 which was subsequently transformed into BzC by the Knoevenagel condensation with cyanoacetic acid catalyzed by piperidine, yielding a pink solid BzC with the overall yield of 68.5%.

Scheme 2 shows the synthesis procedure of PTZC which started with the N-alkylation of PTZ with hexyl bromide giving compound 6. The Vilsmeier–Haack reaction was used to formylate compound 6 to give compound 7. The formyl group in

In this work, we designed and synthesized two new dyes, BzC and PTZC (Figure 1), which do not involve Pd cross-coupling reaction. The reaction used to connect the donor and π-spacer was based on the Horner-Wadsworth-Emmons (HWE) reaction. Moreover, low-cost PTZ and phenyl moieties were used as the donor to further lower the synthesis cost. PTZ also possesses electron-donor ability[18] in which we expect it can substitute the triarylamine-based moiety leading to lower synthesis cost. The use of phenyl ring as the donor in BzC is for a control dye structure so as to compare the effect of the donor group within this dye design. For π-spacer, commonly used CPDT was chosen due to its facile modifications, such as introduction of long alkyl chains, and large conjugation. To demonstrate the low synthesis cost, estimation was made not only for the synthesis costs but also for the cost performance per cm² per %PCE of these two dyes in comparison with highly efficient commercial dye LEG-4.
compound 7 was reduced by NaBH4 to yield compound 8. We first tried the Wittig reaction to connect alkylated PTZ with compound 2 via double bond, as shown in Scheme S1, Supporting Information. This method has been used to connect PTZ and the \( \pi \)-spacer with a double bond in previous literature\(^{21-23,25,26}\) for DSSC applications. However, it leads to a mixture of (E)- and (Z)-isomers in which the (E)-isomer is the major product (around 80%) as seen from \(^1\)H NMR spectrum of compound 10 in Figure S1, Supporting Information. To convert the (Z)-isomer into (E)-isomer, isomerization of the mixture of isomers with a catalytic amount of iodine is often carried out. However, this treatment leads to more synthetic steps and gives relatively low yield\(^{23,25}\). The isomerization reaction can be avoided using the HWE reaction instead of the Wittig reaction. To perform the HWE reaction, a conversion of compound 8 to 9 was necessary which can be done by the Michaelis–Arbuzov reaction via PTZ–CH\(_2\)Br. The attempts to convert compound 8 to PTZ–CH\(_2\)Br as shown in Scheme S2, Supporting Information, by either reacting with PBr\(_3\) or the Appel reaction (with CBr\(_4\) and triphenylphosphine) were unsuccessful. This may be due to the instability of the intermediate or PTZ–CH\(_2\)Br. To solve the problem of the unsuccessful attempts to prepare PTZ–CH\(_2\)Br, a direct conversion\(^{27}\) from compound 8 to compound 9 using ZnI\(_2\) and P(OEt)\(_3\) was successfully performed, as shown in Scheme 2. After obtaining compound 9, it underwent the HWE reaction with compound 2 to yield compound 10, as shown in Scheme 2. The Vilsmeier–Haack reaction was performed on compound 10 giving compound 11. The final dye PTZC was synthesized by the Knoevenagel condensation reaction of compound 11 with cyanoacetic acid and piperidine as the catalyst, giving rise to a purple solid of PTZC with the overall yield of 55.6%. To the best of our knowledge, compound 9 in Scheme 2 is novel and can be prepared easily by the direct conversion from its alcohol counterpart. This can open up a new way to synthesize bulky PTZ-bearing phosphate reagents which may be widely used for the HWE reaction, avoiding the formation of isomers.

### 2.2. Photophysical and Electrochemical Properties

The UV–vis absorption and normalized emission spectra of BzC and PTZC in DCM are presented in Figure 2A. Their corresponding results are shown in Table 1. BzC and PTZC exhibit a prominent peak in the visible region. BzC shows the maximum absorption (\(\lambda_{\text{max}}\)) and extinction coefficient of 523 nm and 58 500 M\(^{-1}\)cm\(^{-1}\), respectively, while PTZC exhibits \(\lambda_{\text{max}}\) at 547 nm, which has a bathochromic shift of 838 cm\(^{-1}\) compared with BzC, with extinction coefficient of 63 000 M\(^{-1}\)cm\(^{-1}\). These prominent peaks (\(\lambda_{\text{max}}\)) are ascribed to an ICT process. The bathochromic shift of PTZC reflects the larger conjugation of the PTZ unit compared with the phenyl ring, leading to a smaller optical gap. It is worth mentioning that their extinction coefficient values are astonishingly high with such simple dye structures. The high extinction coefficients may be due to the fact that their structure is highly conjugated due to the double bond as well as the CPDT unit which facilitates ICT process. For the photoluminescent results of BzC and PTZC in DCM (Figure 2A, S2, Supporting Information and Table 1), BzC shows the emission peak maximum (O) at 589 nm with Stokes shift of 2142 cm\(^{-1}\), whereas PTZC is observed at 624 nm with Stokes shift of 2256 cm\(^{-1}\). Moreover, the emission peak of PTZC exhibits a small shoulder around 650 nm, which is not seen for BzC. The larger Stokes shift and small shoulder of PTZC may imply that PTZC experiences different processes of structural reorganization during the electronic transition\(^{28}\). As shown in Figure 2A, the intersection point of the absorption and emission spectra can be used to estimate the optical gaps (\(E_{\text{o-o}}\)) of BzC and PTZC, which are 2.23 and 2.10 eV for BzC and PTZC, respectively.
The spectral response of BzC and PTZC adsorbed on the 4-μm-transparent TiO₂ film was determined by UV–vis absorption and the results are depicted in Figure 2B. When compared with the corresponding absorption spectra in DCM (Figure 2A), their spectral profiles on film become broader due to H-aggregates. The broader spectral profile can benefit the light-harvesting efficiency. As shown in Figure 2B, the absorption from around 350 to 450 nm from both dyes improves significantly when compared with the corresponding absorption in DCM.

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) were used to characterize the electrochemical properties of BzC and PTZC. Their CVs in positive potential range (Figure S3, Supporting Information) reveal that both BzC and PTZC show both forward and return waves, representing their chemical and electrochemical reversibility upon oxidation reaction. It is worth mentioning that although BzC shows incomplete chemical reversibility at slow scan rate (Figure S3, Supporting Information), this improves with increasing scan rate, confirming the chemical stability of BzC in the context of a DSSC photosensitizer, given that dye regeneration is usually in a microsecond timescale.

According to Figure 3A and Table 1, SWVs of BzC and PTZC show that the oxidation process of BzC occurs at 0.57 V against Fe/Fc⁺ or 1.20 V against normal hydrogen electrode (NHE), which is more positive than the first oxidation potential of PTZC (0.22 V against Fe/Fc⁺ or 0.85 V against NHE). Moreover, PTZC shows two oxidation processes within the potential range (−1.70 to 1.35 V). The difference in oxidation potential between BzC and PTZC can be explained in terms of the difference in the donor group. The less-positive oxidation potential of PTZC is attributed to more extended conjugation of the PTZ unit than phenyl ring in BzC. In contrast to oxidation processes, the reduction processes of BzC and PTZC occur at similar potential (around −2.0 V against Fe/Fc⁺ or −1.4 V against NHE, Figure 3A and Table 1, respectively). The similar reduction potentials imply that the reduction process is attributed to cyanoacrylic acid.

The evaluation of the optical and electrochemical properties is crucial as they provide information about the driving force for dye regeneration, charge injection, and light-harvesting capability. Figure 3B illustrates a visual diagram of energy-level alignment of TiO₂/dye/electrolyte (I⁻/I⁻). It is clearly seen that the oxidation potentials of BzC and PTZC are well below the redox potential of I⁻/I⁻ (0.35 V vs NHE), which indicates favorable driving force for dye regeneration. When compared with the conduction band edge energy level (E_CB) of TiO₂, the excited oxidation potential (E_OX) values of the dye molecules are higher than E_CB of TiO₂ (−0.5 V vs NHE), confirming sufficient driving force for electron injection to the conduction band of TiO₂.

### Table 1. Photophysical and electrochemical properties of BzC and PTZC.

| Dye  | λ_{max} [nm] | r | λ_{em} [nm] | ε_{max} [M⁻¹ cm⁻¹] | E_{OX}^{2.76} versus NHE [V] | E_{RED}^{2.75} versus NHE [V] | E_{HOMO} [eV] | E_{LUMO} [eV] | E_{FU} [eV] |
|------|-------------|---|-------------|---------------------|-----------------------------|-----------------------------|---------------|---------------|-------------|
| BzC  | 523, 59 000 | 589 | 2.23 | 1.20 | −1.42 | −5.37 | −2.75 | −1.03 |
| PTZC | 547, 63 000 | 624 | 2.10 | 0.85 | −1.41 | −5.02 | −2.76 | −1.25 |

*The optical gap (E_{OX}) was determined by the intersection point of normalized absorbance and emission in DCM. **Potentials were measured in DCM with 0.3 M TBAPF₆ as a supporting electrolyte versus Fc/Fc⁺ and were converted to be against NHE by addition of 0.63 V. The HOMO and LUMO energies were estimated by: E_{HOMO/LUMO} = −4.8 – E_{OX}^{2.76} vs Fc/Fc⁻.**

---

**Figure 2.** A) UV–vis spectra and normalized emission spectra of BzC and PTZC in DCM and B) UV–vis absorption spectra of BzC and PTZC on transparent TiO₂.
of PTZC is reduced upon more conjugation present in the structure. To time-dependent DFT (TDDFT) calculations at CAM-B3LYP[32] PTZC energies are unaffected. As a result, the HOMO mental values (electrochemical results), whereas the LUMO more extended conjugation of PTZ corresponds to the experi-

sitions are summarized in Table 2. According to Figure S4, Supporting Information, and the corresponding tran-

The experimental and calculated absorption spectra are shown in Figure 3. A) Square-wave voltammograms of BzC and PTZC in DCM and B) energy alignment of BzC and PTZC in comparison with TiO2 and 1–/I3 redox couple.

To shed light on the spectroscopic properties of BzC and PTZC, the optimized geometry of BzC and PTZC was subjected to time-dependent DFT (TDDFT) calculations at CAM-B3LYP[32] level of theory with 6-31G(d) basis set in DCM solvation model. The experimental and calculated absorption spectra are shown in Figure S4, Supporting Information, and the corresponding transitions are summarized in Table 2. According to Figure S4, Supporting Information, the calculated spectra exhibit λmax at 491 and 517 nm for BzC and PTZC, respectively, which are slightly underestimated, compared with experimental results. However, the trend of phenyl and PTZ units on absorption and extinction coefficient is in line with the experimental values, where PTZC exhibits bathochromic shift and higher extinction coefficient with respect to BzC. Table 2 also highlights the dif-

ference in the molecular orbital (MO) contributions to electronic transition at calculated λmax of BzC and PTZC as well as oscillator strength (f). For BzC, the major %MO contribution to the transition at 491 nm (523 nm from experiment) originates from HOMO to LUMO, accounting for 93%. On the contrary, the major MO contributions to the transition at 517 nm (547 nm from experiment) for PTZC are attributed to a mixture of HOMO to LUMO and HOMO-1 to LUMO in which the former has a larger contribution of 74%. The oscillator strength is related to the probability of the transition from ground state to excited state[33] and is proportional to extinction coefficient.[14] As shown in Table 2, the oscillator strength of PTZC is larger than that of BzC, which indicates that the probability of the transition in PTZC is higher, and that contributes to higher extinction coefficient.

2.4. Photovoltaic Performance

Solar cells based on BzC and PTZC were fabricated with double-

layer TiO2 (4 µm transparent layer and 4 µm scattering layer) and 1–/I3 electrolyte. The photovoltaic performances were measured under AM 1.5G simulated solar light (100 mW cm–2). The corresponding results are shown in Table 3, and their champion current–voltage (J–V) curves are shown in Figure 5A. The devi-

ces with LEG-4 were also fabricated for cost analysis discussion only and the results are tabulated in Table 3. From the results of BzC and PTZC, the best device with BzC exhibited short-circuit current density (Jsc), open-circuit voltage (Voc), and fill factor (FF) of 7.88 mA cm–2, 0.52 V, and 0.73, respectively, giving PCE of 3.00%, whereas the best device with PTZC achieved Jsc, Voc, and FF of 12.92 mA cm–2, 0.61 V, and 0.75, respectively, leading to PCE of 5.92%. It is clearly seen that the higher PCE obtained from PTZC is due to higher Jsc and Voc.

To gain more insight into the photovoltaic performances, the incident photon-to-electron conversion efficiency (IPCE) measurements were carried out (Figure 5B). IPCE can be expressed in terms of light harvesting efficiency (LHE), injection efficiency (φinj), charge collection efficiency (ηcol), and dye regeneration efficiency (φreg), as shown in Equation (1)[37]

\[
\text{IPCE} = \text{LHE}(\lambda) \times \phi_{\text{inj}} \times \phi_{\text{reg}} \times \eta_{\text{col}}
\]

(1)

As mentioned earlier, Eox of BzC and PTZC are more positive than the redox potential of 1–/I3, which can ensure sufficient driving force for dye regeneration. When compared with the CB level of TiO2, their Eox are more negative, and the difference between Eox and CB is greater than 0.2 V, which indicates that fast electron injection rate is possible.[35] Moreover, the Eox of PTZC is more negative than that of BzC, reflecting larger driving force for electron injection. In terms of LHE, it can be expressed in relation with absorbance of the film (Aλ) as shown in Equation (2):[146]

\[
\text{LHE}(\lambda) = 1 - 10^{-A\lambda}
\]

(2)
As shown in Figure 5B, PTZC exhibits broad IPCE spectrum ranging from 400 to 600 nm with the maximum IPCE around 75%. The onset of the IPCE of PTZC appears around 700 nm, which is consistent with the absorption spectrum. On the other hand, BzC shows much narrower IPCE spectrum with the maximum around 70% at 450 nm. This difference in IPCE profile between BzC and PTZC originates from their absorption properties in which PTZC exhibits higher extinction coefficient and broader absorption spectrum on transparent TiO2 (Figure 2B). Apart from the absorption profiles, the amount of adsorbed dye on the TiO2 surface also determines the LHE. The analysis of dye uptake by dye desorption reveals that the dye loading of PTZC is higher than that of BzC (Table 3). The combination between higher extinction coefficient, broader absorption spectrum, and greater amount of adsorbed dye from PTZC leads to superior LHE. In terms of $\eta_{col}$, it can be determined by Equation (3).[7]

![Calculated frontier molecular orbitals in DCM solvation model with experimental energy levels (Table 1) of BzC and PTZC.](image)

**Table 2.** Calculated lowest electronic transition of BzC and PTZC with corresponding molecular orbital (MO) contribution and oscillator strength ($f$).

| Dye  | $\lambda_{\text{max}}$ [nm] | %MO contribution | $f$ |
|------|----------------|------------------|-----|
| BzC  | 491            | HOMO to LUMO (93%) | 1.74 |
| PTZC | 517            | HOMO to LUMO (74%)    | 2.62 |
|      |                | HOMO-1 to LUMO (18%)  |     |

As shown in Figure 5B, PTZC exhibits broad IPCE spectrum ranging from 400 to 600 nm with the maximum IPCE around 75%. The onset of the IPCE of PTZC appears around 700 nm, which is consistent with the absorption spectrum. On the other hand, BzC shows much narrower IPCE spectrum with the maximum around 70% at 450 nm. This difference in IPCE profile between BzC and PTZC originates from their absorption properties in which PTZC exhibits higher extinction coefficient and broader absorption spectrum on transparent TiO2 (Figure 2B). Apart from the absorption profiles, the amount of adsorbed dye on the TiO2 surface also determines the LHE. The analysis of dye uptake by dye desorption reveals that the dye loading of PTZC is higher than that of BzC (Table 3). The combination between higher extinction coefficient, broader absorption spectrum, and greater amount of adsorbed dye from PTZC leads to superior LHE. In terms of $\eta_{col}$, it can be determined by Equation (3). [7]

**Table 3.** Photovoltaic parameters of the champion solar cells based on BzC and PTZC with $l^-/l_2^-$ electrolyte under illumination with AM 1.5 G (100 mW cm$^{-2}$); with the average results calculated from six individual cells mentioned in brackets.

| Dye  | $J_{sc}$ [mA cm$^{-2}$] | $V_{oc}$ [V] | FF | PCE [%] | Dye loading [mol cm$^{-2}$] |
|------|-------------------------|--------------|----|--------|----------------------------|
| BzC  | 7.88 (6.19 ± 0.98)      | 0.52 (0.48 ± 0.02) | 0.73 (0.72 ± 0.02) | 3.00 (2.16 ± 0.46) | 1.78 × 10$^{-7}$ |
| PTZC | 12.92 (12.70 ± 0.29)    | 0.61 (0.60 ± 0.01)  | 0.75 (0.74 ± 0.01) | 5.92 (5.66 ± 0.15) | 2.11 × 10$^{-7}$ |
| LEG-4 | 15.41 (15.50 ± 0.26)   | 0.68 (0.67 ± 0.002) | 0.71 (0.68 ± 0.05) | 7.41 (7.10 ± 0.004) | 1.22 × 10$^{-7}$ |

*LEG-4 results given in brackets are averaged from three individual cells*
\[ \eta_{\text{col}} = \frac{1}{1 + \tau_t \tau_{\text{rec}}} \] (3)

where \( R_t \) and \( R_{\text{rec}} \) are transport and recombination resistances, which can be obtained from electrochemical impedance spectroscopy (EIS) measurement. More details on the determination of these parameters can be found in the EIS section. The results show that BzC exhibits \( \eta_{\text{col}} \) around 95% which is higher than that of PTZC (around 88%). Nonetheless, the effect of higher \( \eta_{\text{col}} \) of BzC on IPCE is less pronounced than the better LHE of PTZC.

As a result, the overall parameters determining IPCE of PTZC are superior to those of BzC.

2.5. EIS Measurement

EIS is a powerful technique that can be used to analyze the processes governing the performance of DSSCs, especially \( V_{\text{oc}} \). The EIS measurements were performed in the frequency range from 1 MHz to 0.1 Hz under white LED illumination at various forward biases. The results were fit using a transmission line model\(^{[37]}\) and the equivalent circuit is depicted in Figure S5, Supporting Information. In general, the EIS spectra (Figure 6) show a typical DSSC feature with two semicircles where the first semicircle at high-frequency range represents Pt/electrolyte...

---

**Figure 5.** A) \( J-V \) curves for BzC and PTZC obtained for the best devices under illumination of AM 1.5G (100 mW cm\(^{-2}\)) and B) IPCE spectra of BzC and PTZC based solar cells with integrated current density.

**Figure 6.** A) Nyquist plots of BzC- and PTZC-based solar cells measured under white LED illumination and forward bias of \(-0.42 \text{ V}\) and B) enlarged Nyquist plots at the same forward bias.
interface and the second semicircle at intermediate-frequency range represents TiO2/dye/electrolyte interface.[38] As shown in Figure 6B, the EIS spectrum of BzC also shows a minor feature of the third semicircle at low-frequency range which represents electrolyte diffusion. [38] However, due to an unclear semicircle, parameters related to electrolyte diffusion are omitted in the equivalent circuit. To represent the EIS spectra close to their respective $V_{oc}$, Figure S6, Supporting Information, shows the Nyquist plots at $-0.48$ V for BzC and at $-0.56$ V for PTZC.

As shown in $J$–$V$ curve results, the difference in the dye structure also plays a role in $V_{oc}$ determination in the full device. $V_{oc}$ of the device is determined by the difference between quasi-Fermi level of TiO2 ($E_{qn}$) and the redox potential of electrolyte ($E_{F,\text{redox}}$) as depicted in Figure 7 and described by Equation (4)[39]

$$V_{oc} = \frac{E_{qn} - E_{F,\text{redox}}}{q}$$

where $q$ is elementary charge. As the two devices were made with the same electrolyte ($I_{1}/I_{2}$), $E_{F,\text{redox}}$ is considered unchanged. Therefore, the difference in $V_{oc}$ between the two devices stems from the variation of $E_{qn}$. This alteration of $E_{qn}$ can be expressed by Equation (5).[39]

$$E_{qn} = E_{CB} + k_{B}T \ln \left( \frac{n_{c}}{N_{c}} \right)$$

where $E_{CB}$ is the conduction band edge of TiO2, $k_{B}$ is Boltzmann constant, $T$ is temperature, $n_{c}$ is the free carrier density, and $N_{c}$ is the density of states in CB of TiO2 taken as $7 \times 10^{20}$ cm$^{-3}$.[40] Equation (5) implies that raising $E_{CB}$ leads to an increase in $E_{qn}$, hence, higher $V_{oc}$.

The parameters mentioned above are influenced by the dye properties. For example, some dyes can cause a large upward shift in $E_{CB}$ which might lead to higher $V_{oc}$. Moreover, changing dye may influence the trap states[41] which, subsequently, impacts the performance of the devices. EIS measurement allows us to analyze these variables affected by dye through fitted EIS parameters, such as transport resistance ($R_{t}$), chemical capacitance ($C_{\mu}$), and recombination resistance ($R_{rec}$). The following discussion will focus on each fitted parameter associated with the variable affected by dye properties.

The transport resistance ($R_{t}$) is one of the useful parameters extracted from EIS fitting with the equivalence circuit shown in Figure S5, Supporting Information. It provides information about $E_{CB}$ and its relationship with voltage can be displayed in Equation (6)[42]

$$R_{t} = R_{t0} \exp \left[ -\frac{qV}{k_{B}T} \right]$$

where $R_{t0}$ is the transport resistance at zero bias, $q$ is elementary charge, $k_{B}$ is Boltzmann constant, $T$ is temperature, and $V$ is the applied voltage.

Figure 7. Graphical illustration of the photogenerated voltage of sensitized TiO2 film under illumination.

Figure 8. A) Transport resistance ($R_{t}$) as a function of applied bias where dotted lines show the fitting according to Equation (6) and B) chemical capacitance ($C_{\mu}$) as a function of applied bias where dotted lines show the fitting according to Equation (7). The parameters used for fitting are obtained from EIS measurement with transmission line model at various applied forward bias.
where $A$ denotes film area, $L$ is the film thickness (8 μm), $p$ is porosity taken as 0.6, $\mu_0$ is electron mobility of TiO$_2$ taken as 4 cm$^2$ V$^{-1}$ s$^{-1}$.[140] Fitting $R_t$ as a function of voltage (Figure 8A) shows an exponential decrease in $R_t$ with increasing voltage. Figure 8A indicates that PTZC shows a positive shift in voltage around 100 mV with respect to BzC. Assuming that $A$, $L$, $\mu_0$, and $N_s$ are identical across the devices,[37,42] this positive shift implies the upward displacement of $E_{CB}$ in the case of PTZC. To give quantitative estimation of $E_{CB}$ of BzC and PTZC, which is explained in terms of $E_{CB} - E_{F,redox}$ (see Figure 7 for clarity), the intercepts from ln($R_t$) versus $V$ plot (Figure 8A and Equation (6)) were used, and the results are shown in Table 4. The trend in $R_t$ is consistent with the results from the $J$–$V$ curve measurement in which PTZC shows higher $V_{oc}$ than BzC.

The chemical capacitance ($C_{\mu}$) at the TiO$_2$/dye/electrolyte interface is also a useful parameter which can also give information about $E_{CB}$, a trap distribution parameter denoted as $\alpha$ (the exponential shape of TiO$_2$ in Figure 7) and the number of trap states denoted as $N_t$. Equation (7)[44] expresses the exponential relationship between $C_{\mu}$ and voltage together with the dependency of $C_{\mu}$ on parameters listed above.

$$C_{\mu} = L(1-p) \alpha \frac{q^2 N_s}{k_B T} \exp \left[ \frac{\alpha (E_{F,redox} - E_{CB})}{k_B T} \right] \exp \left[ \frac{\alpha q V}{k_B T} \right]$$

As seen from the equivalent circuit in Figure S5, Supporting Information, constant phase element (CPE) was used for fitting instead of capacitor. CPE was converted to the equivalent capacitance, hereafter $C_{\mu}$, using Equation (8).[38]

$$C_{\mu} = \frac{(R Q)^{\beta}}{R}$$

where $R$ is the resistor parallel to the corresponding CPE, $Q$ is the CPE prefactor, and $\omega$ is the CPE index. The linear fitting to Equation (7) allows $\alpha$ to be extracted, giving 0.42 and 0.36 for BzC and PTZC, respectively. Figure 8B exhibits that BzC has lower $C_{\mu}$ than PTZC at the same voltage. From Equation (7), it suggests that the lower $C_{\mu}$ in BzC may originate from lower $N_t$ at the same voltage with similar $\alpha$. To show the trend in $C_{\mu}$ quantitatively from BzC and PTZC, $N_t$ was estimated by Equation (7) together with the corresponding $E_{CB} - E_{F,redox}$ (from $R_t$ results in Table 4) and $\alpha$ (from linear fitting to Equation (7)) through the intercepts of ln($C_{\mu}$) versus $V$ (Figure 8B). The results of estimated $N_t$ are tabulated in Table 4. It is clearly seen that PTZC device possesses ~9 times larger $N_t$ than BzC. As suggested in Equation (7) that $C_{\mu}$ is proportional to $N_t$, the consequence of lower $N_t$ results in lower $C_{\mu}$ in BzC at the same voltage. Thus, from the results of $C_{\mu}$ and $R_t$, they suggest that BzC and PTZC modify the trap states differently, and PTZC shows more upward displacement in $E_{CB}$.

EIS results also allow the recombination resistance ($R_{rec}$) at the TiO$_2$/dye/electrolyte interface to be determined. The dependency of $R_{rec}$ on voltage can be expressed in Equation (9)[44]

$$R_{rec} = \frac{\sqrt{\pi \lambda k_B T}}{q^2 \lambda \alpha \sqrt{k_B T} N_s} \exp \left[ \alpha \frac{E_{CB} - E_{F,redox}}{k_B T} \right] \exp \left[ \frac{-\lambda q V}{4 k_B T} \right]$$

$$R_{rec} = R_0 \exp \left[ -\frac{q V}{\lambda k_B T} \right]$$

where $\lambda$ is reorganization energy of acceptor species in the electrolyte, $c_{ac}$ is the concentration of acceptor species in the electrolyte, $k$, denotes the rate constant for recombination kinetics, $N_s$ is the total number of surface states contributing to interfacial

---

**Table 4.** Parameters from fitted $R_{rec}$, $C_{\mu}$, and $R_{rec}$ results, from fitting Equation (6), (7), and (9), respectively.

| Dye  | $\alpha$ | $E_{CB} - E_{F,redox}$ [eV] | $N_t$ [cm$^{-2}$] | $m$ |
|------|---------|-----------------------------|-----------------|----|
| BzC  | 0.42    | 0.76                        | $7.33 \times 10^{18}$ | 1.03 |
| PTZC | 0.36    | 0.90                        | $6.69 \times 10^{19}$ | 1.12 |

---

**Figure 9.** A) Recombination resistance ($R_{rec}$) as a function of voltage where dotted lines show the fitting according to Equation (9) and B) electron lifetime ($\tau_{el}$) as a function of electron density ($n$).
recombination, and \( m \) denotes ideality factor explaining the coefficient determining nonlinear charge transfer. Fitting \( R_{\text{rec}} \) against voltage exhibits an exponential decrease in \( R_{\text{rec}} \) with increasing voltage, as shown in Figure 9A. The results show that PTZC exhibits larger \( R_{\text{rec}} \) than BzC, which implies more efficient charge recombination retardation from PTZC. Furthermore, this fitting enables \( m \) to be determined and the results are shown in Table 4. Normally, the value of \( m \) for DSSCs is larger than 1 due to nonlinear charge transfer through surface trap states.\(^{[40]}\) Therefore, the relatively low values of \( m \) (close to 1) from BzC and PTZC may suggest efficient suppression of electron recombination from surface trap states with higher degree of the suppression from BzC. Recently, Zhang et al. reported a low value of \( m \) (1.08) obtained by dye MS5.\(^{[45]}\) As shown in Table 4, PTZC shows \( m \) value of 1.12 which is close to the above value reported. Moreover, BzC achieved even lower \( m \) (1.03), which is the lowest value reported.

To gain further insight into recombination kinetics between BzC and PTZC, electron lifetime \( (\tau_n) \) was calculated by Equation (10).\(^{[46]}\)

\[
\tau_n = C_p R_{\text{rec}} \quad (10)
\]

As highlighted by Barnes et al., charge concentration can be used to decouple the contribution of voltage to differences in electron recombination observed between devices.\(^{[41]}\) Therefore, total electron density \( (n) \) should be used as a basis to compare the electron recombination instead of voltage. The total electron density \( (n) \) can be determined by Equation (11).\(^{[41]}\)

\[
n = \frac{C_p q g T}{\varepsilon_0 L \alpha} \quad (11)
\]

Figure 9B illustrates \( \tau_n \) as a function of \( n \) in which both dyes show exponential decrease in \( \tau_n \) with increasing \( n \). It is clearly seen that PTZC has much longer electron lifetime than BzC at the same electron density. This indicates that the recombination kinetics of electron with acceptor species in electrolyte is much slower for PTZC than BzC. Thus, the longer electron lifetime for PTZC enables higher \( V_{\text{oc}} \) which is consistent with \( J-V \) curve results (Table 3).

Overall, the EIS results reveal the different influence of each dye to the energetics and kinetics of the device. Changing from BzC to PTZC gives rise to both an upward shift in \( E_{\text{CB}} \), and also slower electron recombination kinetics under the same total electron density, which prolongs electron lifetime. These points together explain the higher \( V_{\text{oc}} \) for the device sensitized with PTZC than that sensitized with BzC. Moreover, analysis of \( R_{\text{rec}} \) results reveal that both dyes effectively suppress interfacial charge recombination from surface states as seen by relatively low \( m \) values.

To rationalize these effects in terms of dye properties, the effect of dye structure on \( E_{\text{CB}} \) is discussed below. The energetics of TiO\(_2\) can be explained in terms of dipole moment of dyes and dye coverage, as suggested in Equation (12).\(^{[47]}\)

\[
\Delta E_{\text{CB}} = -\frac{q \mu_{\text{normal}}}{\varepsilon_0 \varepsilon} \gamma \quad (12)
\]

where \( \Delta E_{\text{CB}} \) is the shift in TiO\(_2\) CB, \( \gamma \) is the dye surface concentration, \( \mu_{\text{normal}} \) is the dipole moment component of individual molecule perpendicular to TiO\(_2\) surface, and \( \varepsilon_0 \) and \( \varepsilon \) are the dielectric constant of the monolayer and the permittivity of the vacuum, respectively. Equation (12) suggests that higher dye surface concentration and larger \( \mu_{\text{normal}} \) cause the negative shift (upward shift) in \( E_{\text{CB}} \). The total dipole moment (\( \mu_{\text{total}} \)) is used to compare the effect of dipole moment on \( E_{\text{CB}} \) shift by assuming that the orientation of the dye is perpendicular to TiO\(_2\) surface. From DFT calculations results, the dipole moments of BzC and PTZC are 11.08 and 12.07 D, respectively (Figure 10). Although \( \mu_{\text{total}} \) of BzC and PTZC are similar, the angle of \( \mu_{\text{total}} \) with respect to \( \mu_{\text{normal}} \) for BzC is larger than that of PTZC. It suggests that \( \mu_{\text{total}} \) of PTZC induces more upward shift in \( E_{\text{CB}} \) compared with BzC, as the direction of \( \mu_{\text{total}} \) of PTZC is more perpendicular to TiO\(_2\) surface or closer to \( \mu_{\text{normal}} \). Moreover, the dye uptake results (Table 3) show that PTZC exhibits higher dye-loading amount than BzC, implying better dye coverage (relating to \( \gamma \)) from PTZC. Thus, the combined results between the dipole moment and dye coverage indicate the trend in more upward shift in \( E_{\text{CB}} \) from PTZC. Apart from the shift in \( E_{\text{CB}} \), PTZC structure is composed of PTZ unit featuring the hexyl chain. It is well known that the long alkyl chain can retard electron recombination with acceptor species in the electrolyte.\(^{[48,50]}\) This may also contribute to slower recombination kinetics for PTZC.

2.6. Synthesis Cost Analysis

Most reported DSSC dyes were synthesized using versatile Pd cross-coupling reactions. In such studies, the amount of Pd catalyst may not be optimized and the typical %loading range may fall around 5–10%. This may be more than the reaction needs, leading to higher synthesis costs. Although efforts to optimize the %loading of Pd catalysts could make some contribution to lower costs, using alternative Pd-free reactions circumvents the issue entirely. Hence, in our case, we have used the HWE reaction to connect the donor and π-spacer. To demonstrate the concept of alternative reactions for Pd cross-coupling reactions and low-cost donor moiety, the synthesis costs of BzC and PTZC are calculated. This estimation is only based on the preparation cost in which the work-up and purification costs are not included as they depend on the
scale of the synthesis and the purification techniques may be substituted by other appropriate techniques for the larger-scale synthesis. The estimated cost analysis was carried out following Maciejczyk et al.\(^{(11)}\), which is based on 1 gram of product. The synthesis yield at each step was taken into account in the cost estimation (Scheme 1 and 2). Table S1 and S2, Supporting Information, depict the estimated synthesis cost for the CPDT unit from two-step reactions. The overall cost for the CPDT unit for the next steps is $37.43 \, \text{g}^{-1}$. The synthesis of BzC comprises four steps and the corresponding cost analysis for each step is shown in Table S3–S6, Supporting Information. The total estimated synthesis cost for BzC is $50.06 \, \text{g}^{-1}$. In the case of PTZC, there are 7 steps involved in the synthesis and the corresponding cost analysis for each step is depicted in Table S7–S13, Supporting Information. The total estimated synthesis cost for PTZC is $61.94 \, \text{g}^{-1}$. From the estimation, one can see that the large share of the synthesis cost is the CPDT unit, accounting for \(\approx 63\%\) of the total synthesis cost.

To prove the concept of the cost-effective synthesis, LEG-4, one of the efficient commercial dyes, was chosen to compare with BzC and PTZC (see the synthetic method and structure in Scheme S1, Supporting Information). Unless stated otherwise, the synthesis methods and yields were taken from Gabrielsson et al.\(^{(11)}\) and only material costs are considered so as to allow the direct comparison with BzC and PTZC. Table S14–S22, Supporting Information, show 10 steps of LEG-4 synthesis, including relevant intermediates, and the estimated synthesis cost of LEG-4. The total synthesis cost of LEG-4 is estimated to be $467.63 \, \text{g}^{-1}$. It is clearly seen that approximately 65\% ($310) of the total synthesis cost falls in the synthesis of the donor part as it involves an expensive boronic acid derivative. Moreover, the prices of the Pd catalysts for the Suzuki–Miyaura cross-coupling used to synthesize LEG-4 are more than or equal to the total synthesis price of BzC and PTZC, respectively.

When compared with BzC and PTZC, the total synthesis cost of LEG-4 is around 7.5–9 times higher than those for BzC and PTZC. This indicates the possibility of alternative Pd-free reactions for dye synthesis. For example, in our case, we show that the HWE reaction to link the donor with \(\pi\)-spacer is endowed with the potential for cost-effective synthesis which may be able to replace Pd cross-coupling reaction. It is also worth highlighting the use of hazardous pyrophoric reagents, such as \(n\)-BuLi, when considering large-scale synthesis. Although the synthesis of CPDT may need \(n\)-BuLi as one of the reagents, we have avoided the use of pyrophoric reagents in subsequent steps (Scheme 2), and this can also serve as a guide toward more sustainable dye design and synthesis in the future.

Finally, for a complete picture of the cost analysis, the photovoltaic performance needs to be taken into account to determine the cost performance. Note that the associated cost of glass, TiO\(_2\), Pt, and electrolyte is not taken into account. The DSSC devices with LEG-4 were also fabricated with \(1^-1/1^-1\) electrolyte to reference the cost performance. The photovoltaic results show that the best device (from three individual cells) with LEG-4 attained PCE of 7.41\% (Table 3), which compares favorably well with literature.\(^{(30)}\) The cost performance calculation was determined by cost per unit area per \%PCE following Tanaka et al.\(^{(53)}\) The calculated results are shown in Table 5. Although the synthesis cost of BzC is lower than that of PTZC, the cost performance of PTZC is only 3.12\% higher than that of BzC when considering the photovoltaic performance. This is due to higher photovoltaic performance obtained from PTZC and comparable synthesis cost of PTZC with BzC. When compared with LEG-4, it is clearly seen that the cost performance of BzC and PTZC are around 5 times cheaper than that of LEG-4. This is due to the much lower synthesis cost and broadly comparable PCE (5.92\% for PTZC and 7.41\% for LEG-4). The cost performances of PTZC could be even lower if meticulous device optimizations were carried out.

### Table 5. The estimated cost performance of BzC, PTZC, and LEG-4.

| Dye   | Cost \([\$ \, \text{g}^{-1}]\) | Quantity \([\text{mol} \, \text{cm}^{-2}]\) | Cost \([\$ \, \text{cm}^{-2}]\) | Cost performance \([\% \, \text{cm}^{-2}] / \% \text{PCE}\) |
|-------|-------------------------------|-------------------------------|-------------------------------|-----------------------------------|
| BzC   | 50.06 | \(1.78 \times 10^{-7}\) | 0.0048 | 0.160 |
| PTZC  | 61.94 | \(2.11 \times 10^{-7}\) | 0.0098 | 0.165 |
| LEG-4 | 467.63 | \(1.22 \times 10^{-7}\) | 0.0640 | 0.867 |

*The values were estimated from dye desorption (Table 3).*

3. Conclusion

Two new dyes (BzC and PTZC) based on low-cost donor moiety and simple structures were successfully synthesized with Pd-free reactions. The aims of Pd-free reactions are not only to reduce the synthesis cost but also to highlight environmental concerns, especially when the Stille coupling is used in the synthesis. For optical properties, both dyes exhibit high extinction coefficient with PTZC showing slightly higher extinction coefficient compared with BzC. Due to large conjugation in PTZC, it shows the first oxidation potential of about 0.35 V less than that of BzC. The study on photovoltaic performance reveals that PTZC shows better efficiency with around 6\% obtained from the best device. The higher \(J_{sc}\) for PTZC is attributed to better light harvesting efficiency and more dye loading on the TiO\(_2\) film. The EIS measurements reveal that BzC and PTZC exhibit relatively low ideality factor \((m)\) with the values of 1.03 and 1.12, respectively, indicating efficient suppression of electron recombination from surface trap states. The device with PTZC shows slower recombination kinetics and upward shift of TiO\(_2\) conduction band, leading to higher \(V_{oc}\) than BzC. We also demonstrated the cost analysis for the synthesis of BzC and PTZC, which are estimated to be around $50 \, \text{g}^{-1}$ and $60 \, \text{g}^{-1}$, respectively. When compared to LEG-4 used as the reference dye, the synthesis costs of BzC and PTZC are around 7.5–9 times lower. Moreover, the overall yields of BzC and PTZC are very high (around 55–70\%) which can be scalable. The comparison of the BzC and PTZC cost performances with LEG-4 reveals that they are around 20\% of the cost of LEG-4 per \%PCE. Indeed, the efficiency does matter but we also believe that when it comes to practical use, that is, large-scale production, the associated price should be taken into account.

4. Experimental Section

**Dye Synthesis:** All reagents were purchased from Sigma-Aldrich (Merck), Alfa-Aesar, Fisher Scientific, Acros Organics, and Fluorochem unless stated otherwise and were used without further purification. CPDT was purchased from Shanghai Qinghang Chemical Co. Ltd.,
China, and was used as received. The synthetic methodology of BzC and PTZC is described as follows.

Synthesis of 4,4-Diethyl-4-H-Cyclopenta-[2,1-b:3,4-b’]-dithiophene [1]: CPDT (1.50 g, 8.42 mmol), 1-bromohexane (3.6 mL, 25.7 mmol), and KI (0.14 g, 0.84 mmol) were dissolved in 60 mL of DMSO and bubbled with N₂ for 10 min. Ground KOH (1.92 g, 34.2 mmol) was added into the mixture, and the resulting mixture was stirred overnight at room temperature in the dark. After adding distilled water, the mixture was extracted with hexane. The organic phase was collected, dried over anhy. Na₂SO₄, filtered, and evaporated to remove hexane. The residue was purified by column chromatography on SiO₂ gel column eluted with hexane to obtain light yellow oil (2.67 g, 91.6%). ¹H NMR (500 MHz, Chloroform-d) δ 7.17 (d, J = 4.8 Hz, 2H), 6.65 (d, J = 4.9 Hz, 2H), 1.87–1.83 (m, 4H), 1.21 (dddd, J = 9.6, 7.5, 3.7 Hz, 4H), 1.15 (dddd, J = 7.6, 4.6, 2.7 Hz, 8H), 0.97 (ddt, J = 10.1, 7.9, 5.0 Hz, 4H), 0.84 (t, J = 7.1 Hz, 6H). ¹³C NMR (126 MHz, Chloroform-d) δ 158.15, 136.45, 124.41, 121.65, 53.26, 37.76, 31.62, 29.70, 24.49, 22.60, 14.03.

Synthesis of 4,4-Diethyl-4-H-Cyclopenta-[2,1-b:3,4-b’]-dithiophene-2-carbaldehyde [2]: Compound (0.26 g, 0.75 mmol) was dissolved in 5 mL anhy. 1,2-dichloroethane, and the solution was cooled down to 0 °C and stirred at 50 °C for about 1.5 to 2 h. After that, the mixture was added saturated aqueous solution of NaOAc resulting in a separation into two phases. The mixture was stirred at 50 °C for about 2 min before adding 0.42 mL (4.24 mmol) of piperidine. The resulting mixture was diluted at 75 °C for 6 h (TLC monitor). After that, the mixture was diluted with DCM and extracted with 1 M HCl and the mixture was refiltered, and evaporated to remove HCI. The crude product was diluted with dry column vacuum chromatography (DCV) technique with gradient elution (hexane to DCM with 10% increment of DCM, pure DCM for 10 fractions, and DCM to 20% MeOH with 2% increment of MeOH). The pure product was diluted with DCM, extracted with 1 M HCI, dried over MgSO₄, filtered, and evaporated to obtain pink solid (0.26 g, 90.2%). ¹H NMR (500 MHz, Chloroform-d) δ 8.34 (s, 1H), 7.63 (s, 1H), 7.54–7.48 (m, 2H), 7.38 (t, J = 7.7 Hz, 2H), 7.31–7.26 (m, 2H), 7.05 (d, J = 16.4 Hz, 2H), 1.91 (dp, J = 10.0, 6.8 Hz, 4H), 1.22–1.13 (m, 12H), 0.96 (p, J = 7.4 Hz, 4H), 0.82 (t, J = 7.0 Hz, 6H). ¹³C NMR (126 MHz, Methylenedichloride-d) δ 182.77, 162.60, 158.28, 149.87, 143.30, 135.72, 129.73, 121.99, 53.92, 37.79, 31.70, 29.85, 29.73, 24.68, 22.71, 14.14.

Synthesis of Diethyl Benzylic Phosphonate [3]: Benzyl bromide (1.00 g, 8.55 mmol) and triethylphosphite (5 mL, 29.2 mmol) were added to a reaction flask. The mixture was refluxed at 135 °C for 6 h. The excess triethylphosphite was removed by distillation under vacuum to obtain pale yellow liquid (1.34 g, quant.). ¹H NMR (400 MHz, Chloroform-d) δ 7.35–7.27 (m, 3H), 4.03 (dd, J = 8.2, 7.1, 3.2 Hz, 4H), 3.18 (d, J = 21.6 Hz, 2H), 1.26 (t, J = 7.1 Hz, 9H). ¹³C NMR (100 MHz, DMSO-d) δ 182.77, 162.58, 158.97, 150.92, 149.79, 148.07, 136.58, 136.33, 134.56, 129.22, 128.82, 121.18, 126.48, 120.05, 120.87, 116.80, 54.15, 37.64, 31.51, 29.54, 24.51, 22.55, 13.75. MS (EI): [M + H]⁺ Calcld for C₃₂H₂₇NO₂P: 544.2338; found: 544.2334. Anal. Calcd for C₃₂H₂₇NO₂P: 544.2339; found: 544.2338. Anal. Calcd for C₃₂H₂₇NO₂P: 544.2339; found: C₃₂H₂₇NO₂P: 52.89%; H: 6.86%; N: 2.58%; found: C: 72.53%; H: 7.12%; N, 2.13%

Synthesis of 10-Hexyl-10-Phenanthroline (6): Phenoanthroine (PTZ) (3.00 g, 15.05 mmol), 1-bromohexane (3.2 mL, 22.87 mmol), and KI (0.18 mmol) were dissolved in 50 mL of DMSO and bubbled with N₂ for 10 min. Ground KOH (2.60 g, 46.13 mmol) was added into the mixture, and the resulting mixture was stirred overnight at room temperature in the dark. After adding distilled water, the mixture was extracted with ether. The organic phase was collected, dried over anhy. MgSO₄, filtered, and evaporated to remove ether. The residue was purified by column chromatography on SiO₂ gel eluted with 2% EtOAc in hexane to obtain pale yellow oil (4.05 g, 95.0%). ¹H NMR (500 MHz, Methylenedichloride-d) δ 7.15 (ddd, J = 8.2, 7.4, 1.6 Hz, 2H), 7.11 (dd, J = 7.6, 1.5 Hz, 2H), 6.91 (dd, J = 7.5, 1.2 Hz, 2H), 6.90–6.87 (m, 2H), 3.82–3.82 (m, 2H), 1.82–1.74 (m, 2H), 1.47–1.39 (m, 2H), 1.30 (h, J = 3.6 Hz, 4H), 0.89–0.86 (m, 3H). ¹³C NMR (126 MHz, Methylenedichloride-d) δ 145.96, 127.79, 127.77, 128.82, 125.34, 116.03, 47.93, 30.12, 27.44, 27.16, 21.38, 14.32.

Synthesis of 10-Hexyl-10-Phenanthroline-3-carbaldehyde (7): Compound 6 (0.46 g, 1.62 mmol) was diluted in 10 mL of anhy. 1,2-dichloroethane in a reaction flask equipped with a condenser and the solution was cooled down to 0 °C. In another container, 0.45 mL (4.83 mmol) of POCl₃ was added dropwise to a cooled solution of anhy. DCM (0.63 mL, 8.14 mmol) in 5 mL of anhy. 1,2-dichloroethane. The mixture of POCl₃ and DMF was added to the solution of compound 6 (dropwise while being stirred at 0 °C). After that, the mixture was refluxed at 90 °C for 4 h. The resulting mixture was added saturated aqueous solution of NaOAc and stirred at 50 °C for 1 h. Then, the mixture was extracted with EtOAc, dried over MgSO₄, filtered, and evaporated to remove EtOAc. The crude product was purified by column chromatography on SiO₂ and eluted with 15%
EtOAc.85%hexane to obtain yellow solid (0.40 g, 80.0%).$^1$H NMR (500 MHz, Methylene Chloride-\(d_2\)) $\delta$ 9.78 (s, 1H), 7.63 (dd, $J$ = 8.4, 2.0 Hz, 1H), 7.56 (d, $J$ = 2.0 Hz, 1H), 7.18 (dd, $J$ = 8.1, 7.3, 1.6 Hz, 1H), 7.11 (dd, $J$ = 7.6, 1.6 Hz, 1H), 6.99–6.90 (m, 3H), 3.92–3.88 (m, 2H), 1.83–1.77 (m, 2H), 1.48–1.41 (m, 2H), 1.33–1.29 (m, 4H), 0.90 – 0.85 (m, 3H).$^{13}$C NMR (126 MHz, Methylene Chloride-$d_2$) $\delta$ 190.19, 151.13, 143.98, 131.58, 130.48, 132.82, 127.98, 127.79, 125.33, 124.12, 123.87, 116.48, 115.31, 60.64, 48.40, 31.79, 27.09, 26.86, 22.99, 21.19, 14.19, 14.13.

Synthesis of (10-Hexyl-10-H-Phenothiazin-3-yl)methyl-Phosphonate (9): In an oven-dried flask equipped with a condenser, ZnI$_2$ (0.32 g, 1.00 mmol) was added, followed by evaporation and refluxed with N$_2$ for three times. The solid ZnI$_2$ was suspended in 5 mL anh. THF before adding 0.22 mL (1.28 mmol) of triethylphosphite. In another container, compound 8 (0.20 g, 0.65 mmol) was dissolved in 10 mL of anh. THF. After that, the solution of compound 8 was added in the above mixture of ZnI$_2$ and triethylphosphite, followed by reflux at 75 °C for 16 h. The mixture was diluted with ether and extracted with 2 mL NaOH. The ether phase was collected, dried over MgSO$_4$, and evaporated. The crude product was distilled under vacuum to remove excess triethylphosphite to obtain light yellow oil (0.25 g, 90.0%).$^{1}$H NMR (500 MHz, Methylene Chloride-$d_2$) $\delta$ 7.15 (dd, $J$ = 7.6, 2.7, 2.1 Hz, 7H), 7.12–7.09 (m, 1H), 7.06 (dq, $J$ = 7.3, 2.4 Hz, 1H), 7.03 (t, $J$ = 2.6 Hz, 1H), 6.92–6.80 (m, 2H), 6.83–6.80 (m, 1H), 4.04–3.96 (m, 4H), 3.82 (t, $J$ = 5.3 Hz, 2H), 3.63–3.52 (m, 2H), 1.31–1.40 (m, 4H), 0.97 (dd, $J$ = 7.5, 3.5 Hz, 4H), 1.25 (td, $J$ = 7.2, 3.4 Hz, 6H).$^{13}$C NMR (126 MHz, Methylene Chloride-$d_2$) $\delta$ 145.69, 144.51, 128.86, 126.85, 126.73, 126.25, 124.22, 124.79, 122.61, 115.76, 115.68, 62.48, 47.78, 33.39, 32.29, 31.87, 30.10, 27.17, 26.98, 16.63, 14.15.$^{31}$P NMR (202 MHz, Methylene Chloride-$d_2$) $\delta$ 25.97. MS (ESI): [M + H]+ Calcd for C$_{23}$H$_{29}$N$_5$O$_5$P: 434.1913; found: 434.1920.

Synthesis of (E)-3-(2-(4-Diethyl-4-H-Cyclopenta[2,1-b:3,4-b]dithiophen-2-yl)vinyl)-10-Hexyl-10H-Phenothiazine (10): Compound 9 (0.58 g, 1.34 mmol) and compound 2 (0.42 g, 1.12 mmol) was dissolved in 10 mL of anh. THF and the solution was cooled down to 0 °C. In another container, KOtBu (0.31 g, 2.75 mmol) was dissolved in 10 mL of anh. THF. The KOtBu solution was added to the cooled mixture dropwise, stirred at 0 °C, and gradually warmed up to 25°C before being left to stir overnight under N$_2$. After this, the water was added to the mixture before it was extracted with DCM and dried over MgSO$_4$, filtered, and evaporated to remove DCM. The crude product was purified by column chromatography SiO$_2$ with 20%DCM:80%hexane elution to obtain yellow wax (0.70 g, 95.6%).$^{1}$H NMR (500 MHz, Methylene Chloride-$d_2$) $\delta$ 7.77 (t, $J$ = 2–1 Hz, 7H), 7.23 (d, $J$ = 4.8 Hz, 1H), 7.20 (d, $J$ = 8.1, 7.3, 1.6 Hz, 1H), 7.17–7.12 (m, 2H), 6.99 (d, $J$ = 4.8 Hz, 1H), 6.87–6.93 (m, 2H), 6.92 (dd, $J$ = 8.1, 1.2 Hz, 1H), 6.88 (d, $J$ = 9.0 Hz, 1H), 6.81 (d, $J$ = 16.0 Hz, 1H), 3.91–3.87 (m, 2H), 1.92–1.80 (m, 6H), 1.48 (t, $J$ = 7.7 Hz, 2H), 1.38–1.33 (m, 12H), 1.29–1.13 (m, 12H), 1.06–0.94 (m, 4H), 0.94–0.90 (m, 3H), 0.83 (t, $J$ = 7.0 Hz, 6H).$^{13}$C NMR (126 MHz, Methylene Chloride-$d_2$) $\delta$ 159.00, 158.88, 145.34, 144.82, 143.69, 136.96, 135.84, 132.13, 127.67, 125.86, 125.46, 125.35, 125.16, 124.69, 124.51, 122.75, 122.13, 121.58, 121.07, 115.83, 47.91, 38.16, 32.05, 31.88, 30.10, 27.23, 26.98, 24.91, 23.02, 14.18. MS (ESI): [M]$^+$ Calcd for C$_{23}$H$_{29}$N$_5$O$_5$P: 653.3178; found: 653.3165.
carried out by O. McCullough at London Metropolitan University using a Carlo Erba CE1108 Elemental Analyzer.

Optical Characterization: UV–vis absorption spectra were recorded on Jasco V-670 UV/vis/NIR spectrophotometer controlled by the SpectraManager software. All solutions were prepared in DCM. All extinction coefficients were determined by the Beer-Lambert plot with various concentrations in the range of 10−3–50μM of corresponding dye. The dye desorption was carried out by diluting 1 M of tetrabutylammonium hydroxide (TBAOH) in methanol to 5 mM TBAOH with DCM. The sensitised films were soaked in 5 mM TBAOH for 30 min before making up the volume with DCM. The absorption spectra were measured in a similar manner to UV–vis absorption characterization.

Electrochemical Characterization: All voltammetry measurements were performed in anhydrous DCM with 0.3 M TBAPF6 as supporting electrolyte in a three-electrode system at room temperature. Each solution was purged with N2 prior to measurement. The working electrode was a Pt disk while the counter electrode and reference electrode were a Pt rod and Ag/AgCl in 2 M LiCl in ethanol, respectively. All measurements were carried out using μAUTOLAB Type III potentiostat driven by the electrochemical software GPES. The scan rates used in CV were 25, 50, 100, 200, and 400 mV s−1. SWV were conducted at a step potential of 2.1 mV, amplitude of 250 mV, and frequency of 25 Hz, which gave a scan rate of 52.5 mV s−1. All measurements were referenced to Ferrocene/ Fericinium (Fc/Fc+) as an internal standard.

Theoretical Calculations: The molecular dye structures were built in Avogadro[54] and the drawn molecule was adjusted using basic optimization in Avogadro. The drawn molecules were optimized by using Gaussian 09[55] at B3LYP[56] level of theory with 6-31G(d) basis set under vacuum. After that, the optimized structures were subject to re-optimization in DCM (PCM solvation model).[54] The TDDFT calculations used the optimized structures in solution model and were conducted by using Gaussian 09 at CAM-B3LYP[56] level of theory with 6-31G(d) basis set and in DCM (PCM solvation model). The 50 states of singlet electronic transitions obtained from TDDFT calculations were processed with the Gaussian software package.[57] For the dyes’ dipole moment, the DFT optimized dyes in DCM solvent model were subjected to GaussView 6[58] for visualization.

Solar Cell Fabrication: Fluorine-doped tin oxide (FTO)-coated glass (Merck, 71 Ω/sq) was cleaned using 2% Hellmanex solution with sonication in deionized water for 30 min, followed by sonication in ethanol for 30 min. The cleaned glass was treated with UV-Ozone treatment for 20 min. After that, the cleaned and treated glass was pretreated with 40 mM aqueous solution TiCl4 at 70 °C for 30 min, which was subsequently rinsed with deionized water and ethanol, respectively. The TiCl4-treated glass was sintered at 500 °C for 30 min. Upon cooling down, the sintered glass was screen printed with commercial transparent TiO2 paste (Ti-Nanooxide TJP/SP, Solaronix), followed by drying at 120 °C for 10 min. The scattering TiO2 paste (Ti-Nanoxide TJP/SP, Solaronix) was screen printed on printed glass, followed by drying at 120 °C for 10 min. The films were annealed at 500 °C for 15 min using programmable hotplate. The resulting TiO2 film thickness was 8 μm with the area of 0.28 cm². The sintered films were allowed to cool down and were treated with 40 mM aqueous solution TiCl4 at 70 °C for 30 min, rinsed with deionized water and ethanol, and were sintered again at 500 °C for 30 min. When the temperature dropped to about 90 °C, the films were soaked in 0.5 mM dye bath containing 2.5 mM CDCA for BzC and PTZC and containing 5 mM CDCA for LEG-4 in tert-butyl alcohol:acetonitrile 1:1 v/v for 20 h. The sensitized working electrodes were removed from dye bath and washed with acetonitrile to remove unadsorbed dye molecules. The counter electrodes were predrilled on FTO glass, washed by sonication in 0.1 M HCl in ethanol for 15 min, and followed by sonication in ethanol for 15 min and deionized water for 15 min, respectively. The cleaned predrilled glass was doctor bladed with Platsol (Solaronix) and sintered at 450 °C for 15 min. The DSSCs were assembled using hot-melt sealing film (Solaronix). The composition of electrolyte was 0.1 M LiI, 0.05 M I2, 0.6 M DMPBi, and 0.5 M 4-tert-butyl pyridine (4-TBP) in acetonitrile. The electrolyte was injected into the assembled cells using Vac’n’Fill Syringe (Solaronix). The hole was covered by cover glass with hot-melt sealing film (Solaronix).

Solar Cell Characterization: The photocurrent–voltage (J–V) measurements were carried out on an Autolab potentiostat (Metrohm), driven by electrochemical software GPES, with class AAA SLB300A solar simulator (Scientech) as the light source at University of Edinburgh. The light intensity was calibrated to AM 1.5G (100 mW cm−2) using a silicon reference cell. A black metal mask with a circular aperture of 0.0707 cm² was applied when measuring J–V curves. The EIS spectra of fl−/fl− electrolyte-based devices setup was similar to the J–V measurements, except for using white LED as the light source and Frequency Response Analyser (FRA) software. The EIS spectra were recorded in the frequency range between 1 MHz and 0.1 Hz at various forward biases set to the corresponding voltage produced by white LED illumination. The obtained spectra were fit with a transmission line model[53] using Zview (Scribner Associates) software. IPCE measurements were conducted at University of Strathclyde. The IPCE of the solar cells were measured with a photospectrometer setup (Bentham PVE300) by illuminating the solar cell with modulated monochromatic light (Xenon and quartz halogen lamps) through 1.85 mm slit. The intensities of the lamps were calibrated with a silicon photodiode. The photospectrometer was operated in DC mode and the spectral resolution was set to 5 nm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
A.J. would like to thank the Royal Government of Thailand through the Development and Promotion of Science and Technology Talents Project (DPST) for scholarship. A.I. would like to thank UK Research and Innovation (UKRI), Engineering and Physical Sciences Research Council (EPSRC) for the fellowship grant (EP/P011500/1) and the EPSRC ECR Capital Equipment grant (EPS0179171) and ScotChem for funding IPCE setup.

Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
cost-effective dyes, CPDT, dye-sensitized solar cells, high extinction coefficients, phenothiazine

Received: April 29, 2022
Revised: June 14, 2022
Published online: July 1, 2022

[1] B. O’Regan, M. Grätzel, Nature 1991, 353, 737.
[2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Mueller, P. Liska, N. Vlachopoulos, M. Graetzel, J. Am. Chem. Soc. 1993, 115, 6382.
[3] M. K. Nazeeruddin, P. Pechy, T. Renouard, S. M. Zakeeruddin, R. Humphry-Baker, P. Cointe, P. Liska, L. Cevey, E. Costa,
