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Citation for published version (APA):
Heintges, G. H. L., Bolduc, A., Meskers, S. C. J., & Janssen, R. A. J. (2020). Relation between the electronic properties of regioregular donor-acceptor terpolymers and their binary copolymers. Journal of Physical Chemistry C, 124(6), 3503-3516. https://doi.org/10.1021/acs.jpcc.9b11562

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DOI:
10.1021/acs.jpcc.9b11562

Document status and date:
Published: 13/02/2020

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
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Relation between the Electronic Properties of Regioregular Donor–Acceptor Terpolymers and Their Binary Copolymers

Gaëlle H. L. Heintges, Andréanne Bolduc, Stefan C. J. Meskers,* and René A. J. Janssen*

ABSTRACT: By analyzing the optical band gap and energy levels of seven different regioregular terpolymers in which two different electron-rich donor moieties are alternating with a common electron-deficient acceptor unit along the backbone, we establish a direct correlation with the properties of the corresponding binary copolymers in which one donor and one acceptor are combined. For this study, we use diketopyrrolopyrrole as the common acceptor and different π-conjugated aromatic oligomers as donors. We find that the optical band gap and frontier orbital energies of the terpolymers are the arithmetic average of those of the parent copolymers with remarkable accuracy. The same relationship is also found for the open-circuit voltage of the bulk heterojunction solar cells made with the ter- and copolymers in combination with [6,6]-phenyl-C71-butyric acid methyl ester. Comparison of these findings with data in the literature suggests that this is a universal rule that can be used as a tool when designing new π-conjugated polymers. The experimental results are supported by a semiempirical quantum chemical model that accurately describes the energy levels of the terpolymers after parametrization on the energy levels of the copolymers and also provides a theoretical explanation for the observed arithmetic relations.

1. INTRODUCTION

Control over the optical band gap \( (E_g) \) by adjusting the chemical structure is one of the critical virtues of π-conjugated polymers and is often employed to create novel materials with tailored properties to enhance charge transport, light emission, or photovoltaic energy conversion. Optical band gap control can be achieved by enlisting fused-ring systems and controlling the conjugation length via planarization of conjugated segments to enhance delocalization of electrons. A second important tool for optical band gap control is adjusting the balance between contributions of aromatic and quinoid resonance structures of fused π-conjugated rings in the main chain. The classical example of this approach is poly(isothianaphthene), first prepared by Wudl et al. In poly(isothianaphthene) a favorable quinoid structure reduces the bond length alternation and lowers the optical band gap to about 1 eV. Havinga and Tanaka advanced the donor–acceptor or “push–pull” concept, which became very popular for controlling the optical band gap and frontier energy levels of π-conjugated polymers. In this approach two conjugated units, one with electron-rich (donor) and one with electron-deficient (acceptor) properties, are combined in an alternating copolymer. By varying the strength of the donating and accepting properties, control over the optical band gap and energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) can be achieved. This gives access to an almost unlimited range of materials with different electronic characteristics. More recently, π-extended quinoids with strong withdrawing groups that include aromatic substructures in the resonance form have been used to create very small band gap polymers. Donor–acceptor polymers have been particularly useful for polymer solar cells. Structural variations that allow control of the optical band gap can maximize the open-circuit voltage \( (V_{oc}) \) and increase short-circuit current \( (J_{sc}) \). Recently, polymers with an extended π-system perpendicular to the backbone have been successfully introduced. These combined efforts have resulted in a surge of the power conversion efficiency (PCE) of polymer solar cells and enhanced the likelihood they will be employed as a lightweight, form-free, or flexible power source. Color control is especially important for building-integrated photovoltaic applications and essential to multijunction solar cells.

Lately, the terpolymer design motif has been established as a further tool to tune the HOMO and LUMO energy levels. This class of materials is an evolution of the donor–acceptor design motif, but in terpolymers three distinct π-conjugated units are used, allowing fine control of the electronic characteristics. Terpolymers can be obtained by incorporating two electron-rich and one electron-deficient unit or two electron-deficient and one electron-rich unit in the polymer backbone in a random or in a regular sequence.
with PCEs in organic solar cells above 9% have thus been achieved, and in some cases this design can be more efficient than making ternary blends out of the respective copolymers. Despite the increased synthetic effort required, regioregular terpolymers might offer more control over the electronic parameters of the material than regiorandom terpolymers. Intuitively, it can be expected that the electronic parameters of these materials occupy a middle ground between the two "parent" binary copolymers. However, a systematic design rule to predict these properties has not yet been firmly established. It is important not only to be able to predict the band gap but also to establish whether the optical absorption broadens, shifts, or a combination of both. Herein we systematically

**Scheme 1. Cross-Coupling Polymerization Reactions Towards (−D1−A−D2−A−)\textsubscript{n} DDP-Based Terpolymers**

![Chemical Structures](https://dx.doi.org/10.1021/acs.jpcc.9b11562)
investigate the optical band gap and redox potentials of regioregular \((-D_1-A-D_2-A^-)_{n}\) terpolymers and compare these to the corresponding parent \((-D_1-A^-)_{n}\) and \((-D_2-A^-)_{n}\) copolymers. For our study we use diketopyrrolopyrrole (DPP) as the common acceptor unit and vary the two donor moieties. DPP-based polymers have been extensively investigated in the past and show good performance in field-effect transistors and in single-junction and multi-junction polymer solar cells.\textsuperscript{34,35} A wide range of optical band gaps has been achieved by combining DPP with different electron donating moieties. Here, seven regioregular DPP-based terpolymers (Figure 1) and their corresponding copolymers are analyzed. In this way we can provide predictive rules for the electronic properties of regioregular terpolymers, thus establishing the regioregular terpolymer design motif as a reliable tool for the design of conjugated polymers. We augment the experimental results and conclusions with a basic semiempirical quantum chemical model that accurately predicts the frontier orbital energies of the terpolymers, after calibration on the copolymers.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Molecular Characterization. To investigate the electronic properties, a variety of DPP-based terpolymers and their copolymers were selected. PDPP(TPT-alt-2T),\textsuperscript{36} PDPP(TPT-alt-3T),\textsuperscript{37} PDPP(PyTPy-alt-2T), and PDPP(TDTPT-alt-TBTT)\textsuperscript{38} (Figure 1) were published before. To this data set three new terpolymers were added: PDPP(TPT-alt-4T), PDPP(TPT-alt-TT TT), and PDPP(TEDOTT-alt-3T) (Figure 1). Each of these polymers was synthesized by using an extended monomer \((A-D_1-A^-)\) strategy wherein a central electron-rich \((D_1)\) unit is flanked by two electron deficient \((A = DPP)\) units and reacted in a Stille or Suzuki condensation polymerization with the corresponding bisstannylated or bisboronic ester of the second donor moiety \((D_2)\) (Scheme 1).

The details of the synthesis of the new polymers can be found in the Supporting Information. For the preparation of PDPP(TPT-alt-4T) and PDPP(TPT-alt-TTTT), a T-DPP-T unit was first monobrominated before being coupled to a phenyl core to provide the extended precursor monomer (Scheme S1, Supporting Information). This precursor monomer could then be brominated in preparation for a Stille polymerization reaction with either 5,5′-bis(trimethylstannyl)-2,2′-bithiophene or bis(trimethylstannyl)thieno[3,2-b]-thiophene (Scheme 1). PDPP(TPT-alt-4T) carries 2-octyldodecyl side chains on the DPP units, in contrast to the other polymers that carry 2-hexyldecyl side chains. This longer side chain was chosen because the electron-rich quaterthiophene (4T) unit in PDPP(TPT-alt-4T) reduces the solubility compared to the other derivatives. This is also reflected in the corresponding copolymer, PDPP4T, where a 2-decyldodecyl chain has been employed to achieve sufficient solubility. For PDPP(TEDOTT-alt-3T), a monooiodination reaction was performed to offer the required asymmetry and allow coupling to a thiophene core (Scheme S2), after which the polymerization reaction could be performed by using 2,5-bis(trimethylstannyl)-3,4-ethylenedioxythiophene (Scheme 1). Except for PDPPTEDOTT,\textsuperscript{39} all \((-D_1-A^-)_{n}\) copolymers were synthesized before in our group.\textsuperscript{37–43} PDPPTEDOTT was synthesized by using a dibrominated thiophene-flanked DPP unit and 2,5-bis(trimethylstannyl)-3,4-ethylenedioxythiophene (Scheme S3). All co- and terpolymers showed high number-average \((M_n)\) and weight-average \((M_w)\) molecular weights when analyzed with gel permeation chromatography in o-dichlorobenzene \((o\text{-DCB})\) at 140 °C (Table 1). A high \(M_n\) is important for achieving a high efficiency when these polymers are used in bulk-heterojunction solar cells.\textsuperscript{34,45}

### Table 1. Molecular Weight Data for the Copolymers and Terpolymers

| polymer                        | \(M_n\) [kDa] | \(M_w\) [kDa] | \(D\)  |
|-------------------------------|---------------|---------------|--------|
| PDPPPTPT                      | 72            | 143           | 1.98   |
| PDPP(TPT-alt-2T)              | 135           | 540           | 3.99   |
| PDPP2T                        | 85            | 322           | 3.80   |
| PDPP(TPT-alt-3T)              | 42            | 154           | 3.68   |
| PDPP3T                        | 147           | 400           | 2.72   |
| PDPP(TPT-alt-4T)              | 138           | 254           | 1.84   |
| PDPP4T                        | 83            | 150           | 1.80   |
| PDPP(TPT-alt-TTTT)            | 94            | 273           | 2.90   |
| PDPP(TPT-alt-TT TT)           | above exclusion limit |
| PDPP(PyTPy-alt-3T)            | 81            | 192           | 2.37   |
| PDPPPyTPy                     | 67            | 176           | 2.60   |
| PDPP(TEDOTT-alt-3T)           | decomposes on column |
| PDPPTEDOTT                    | decomposes on column |
| PDPP(TDTPT)                   | interacts with column |
| PDPP(TDTPT-alt-TBTT)          | interacts with column |
| PDPP(TPT-alt-TBTT)            | 73            | 177           | 2.44   |

2.2. Optical Absorption and Redox Properties. UV–vis–NIR absorption spectra of thin, spin-coated films of the polymers were measured to establish the optical band gaps (Figure 2 and Table 2). Figure 2 clearly shows that the optical absorption bands of the terpolymers are positioned in between those of the corresponding copolymers. The only real exception to this is in the case of PDPP(TDTPT-alt-TBTT) (Figure 2g), but in this case the absorption spectra of the copolymers are very close to one another and the deviation from the average is not large. The optical band gap was determined from the onset of the absorption, which we defined as the crossing point of the tangent in the inflection point at the low-energy side of the absorption spectrum with the baseline.\textsuperscript{35} At the end of section 2.3, we motivate the use of this method. Figure 2h and Table 2 show that the optical band gaps of the terpolymers are almost always exactly the average of the band gaps of the corresponding copolymers. Only small deviations \((\Delta E)\) from the average are present, with a standard deviation of \(\sigma = 17\text{ meV}\).

There is an ongoing discussion on how to determine the energies levels of the HOMO \((E_H)\) and LUMO \((E_L)\) of conjugated polymers accurately.\textsuperscript{46–50} Recent work in our group has shown that square-wave voltammetry (SWV) on thin films of DPP polymers provides redox potentials that correlate very well with the open-circuit voltage of solar cells based on the same materials.\textsuperscript{35} In fact, in that sense SWV was superior to ultraviolet photoelectron spectroscopy (UPS).\textsuperscript{35} Hence, SWV was used to estimate the oxidation and reduction potentials of the polymers in thin films and the levels of the HOMO \((E_H)\) and LUMO \((E_L)\) the polymers (Figure 3, Tables 3 and 4). Similar to the optical band gap, the HOMO and LUMO energies of the terpolymers are very close to the average of the parent copolymers, with standard deviations of \(\sigma = 39\text{ meV}\) for \(E_H\) and \(\sigma = 38\text{ meV}\) for \(E_L\). These results indicate that the electronic energy levels of the terpolymers can be quite
accurately predicted simply by taking the average of the related copolymers.

2.3. Photovoltaic Properties. Having established that for the regioregular (D1−A−D2−A) terpolymers, \( E_g, E_H, \) and \( E_L \) are close to the averages of the corresponding energies of the (D1−A) and (D2−A) copolymers, it is also of interest to assess their performance in solar cells to understand the relation between the optical band gap, open-circuit voltage, and minimal photon energy loss, defined as \( E_{\text{loss}} = E_g - qV_{oc}. \)

Bulk-heterojunction solar cells were fabricated, combining the co- and terpolymers as electron donor with [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM) as electron acceptor. The device configuration was ITO/PEDOT:PSS/polymer: [70]PCBM/LiF/Al for all cells, except for the polymers containing pyridine (PDPPyTPy and PDPPP(PyTPy-alt-3T)), in which PEDOT:PSS was replaced with molybdenum oxide.

Figure 2. UV−vis−NIR absorption spectra of terpolymers and the corresponding parent copolymers in thin films: (a) PDPP(TPT-alt-2T), (b) PDPP(TPT-alt-3T), (c) PDPP(TPT-alt-4T), (d) PDPP(TPT-alt-TTTT), (e) PDPP(PyTPy-alt-3T), (f) PDPP(TEDOTT-alt-3T), and (g) PDPP(TDTPT-alt-TBTT). (h) \( E_g \) of the terpolymers vs the average of the \( E_g \)s of the corresponding copolymers. The solid line represents slope = 1.
Table 2. Optical Band Gaps of the Terpolymers and Their Respective Copolymers

| D1   | D2   | $E_g (D1-A) [eV]$ | $E_g (D2-A) [eV]$ | $E_g (D1-A-D2-A) [eV]$ | $\Delta_g^a [eV]$ |
|------|------|-------------------|-------------------|-------------------------|------------------|
| TPT  | 2T   | 1.53              | 1.20              | 1.37                    | -0.005           |
| TPT  | 3T   | 1.53              | 1.33              | 1.43                    | 0.000            |
| TPT  | 4T   | 1.53              | 1.46              | 1.50                    | -0.005           |
| TPT  | TTTT | 1.53              | 1.35              | 1.44                    | 0.000            |
| PyTPy| 3T   | 1.73              | 1.33              | 1.49                    | 0.040            |
| TEDOTT| 3T  | 1.17              | 1.33              | 1.25                    | 0.000            |
| TDTPPT| TBTT| 1.23              | 1.19              | 1.19                    | 0.020            |

$\Delta_g = \frac{E_g (D1-A) + E_g (D2-A)}{2} - E_g (D1-A-D2-A)$.

Table 3. HOMO Energies of the Terpolymers and Their Respective Copolymers

| D1   | D2   | $E_h (D1-A) [eV]$ | $E_h (D2-A) [eV]$ | $E_h (D1-A-D2-A) [eV]$ | $\Delta_h^a [eV]$ |
|------|------|-------------------|-------------------|-------------------------|------------------|
| TPT  | 2T   | -5.04             | -5.06             | -5.05                   | 0.000            |
| TPT  | 3T   | -5.04             | -4.93             | -4.97                   | -0.015           |
| TPT  | 4T   | -5.04             | -4.92             | -4.95                   | -0.030           |
| TPT  | TTTT | -5.04             | -4.96             | -4.94                   | -0.060           |
| PyTPy| 3T   | -5.41             | -4.93             | -5.16                   | -0.010           |
| TEDOTT| 3T  | -4.80             | -4.93             | -4.92                   | 0.055            |
| TDTPPT| TBTT| -4.62             | -4.91             | -4.71                   | -0.055           |

$\Delta_h = \frac{E_h (D1-A) + E_h (D2-A)}{2} - E_h (D1-A-D2-A)$.

Table 4. LUMO Energies of the Terpolymers and Their Respective Copolymers

| D1   | D2   | $E_F (D1-A) [eV]$ | $E_F (D2-A) [eV]$ | $E_F (D1-A-D2-A) [eV]$ | $\Delta_f^a [eV]$ |
|------|------|-------------------|-------------------|-------------------------|------------------|
| TPT  | 2T   | -3.05             | -3.35             | -3.22                   | 0.020            |
| TPT  | 3T   | -3.05             | -3.13             | -3.08                   | -0.010           |
| TPT  | 4T   | -3.05             | -3.05             | -3.01                   | -0.040           |
| TPT  | TTTT | -3.05             | -3.07             | -3.10                   | 0.040            |
| PyTPy| 3T   | -3.21             | -3.21             | -3.20                   | -0.010           |
| TEDOTT| 3T  | -3.18             | -3.13             | -3.18                   | 0.025            |
| TDTPPT| TBTT| -3.04             | -3.37             | -3.28                   | 0.075            |

$\Delta_f = \frac{E_F (D1-A) + E_F (D2-A)}{2} - E_F (D1-A-D2-A)$.

For depositing the layers, spin-coating from chloroform with o-DCB as cosolvent was used. For each active layer, the amount of o-DCB was optimized. Figure 4 shows the current density–voltage characteristics of the optimized solar cells in the dark and under simulated AM1.5G (100 mW/cm²) illumination. The $J_{sc}$ $V_{oc}$ fill factor (FF), PCE, and $E_{loss}$ of all cells are listed in Table S. In combination with [70]PCBM, the terpolymers exhibit PCEs up to 8%, comparable to and sometimes surpassing those of the respective copolymers.

Transmission electron microscopy was used to check that for the newly synthesized materials the bulk heterojunction morphology of the blend with [70]PCBM corresponds to the finely dispersed fibrillar morphology that is characteristic for high-performing solar cells based on DPP polymers (Figures S1–S4). The external quantum efficiencies (EQEs) of the photovoltaic devices based on the terpolymers and their parent copolymers (Figure S5) give further insight into the charge generation. As expected, the EQEs generally follow the thin-film absorption spectra, and at the wavelength of maximum EQE, the magnitude is comparable for the terpolymers and corresponding copolymers. A noticeable deviation, however, is seen for PDPP(TPT-alt-2T), which has an EQE that is significantly lower than that of PDPPPTPT but higher than that of PDPP2T, which is virtually 0% in the region of where the polymer absorbs light. The deviation is due to the fact that in the case of PDPP2T the of energy interfacial PDPP2T/PCBM charge transfer state ($E_{CT}$) is comparable to the optical band gap of PDPP2T, $E_g$, such that photoinduced charge generation is slow or even inhibited. $E_{CT}$ can be estimated from the empirical relation $E_{CT} \approx qV_{oc} + 0.6$ eV. Using $V_{oc} = 0.68$ V for PDPP2T/PCBM solar cells (Table S), we find $E_{CT} \approx 1.28$ eV, which is higher than the optical band gap of PDPP2T ($E_g = 1.20$ eV, Table 2). As a consequence and in accordance with the EQE spectrum (Figure S5a), excitation of PDPP2T does not contribute to the photocurrent. Because $E_{loss} = E_g - qV_{oc} \approx E_g - E_{CT} + 0.6$ eV, the requirement that $E_g \geq E_{CT}$ for electron transfer to occur is equivalent to $E_{loss} \geq 0.6$ eV. Indeed, electron transfer is slowed when the minimal photon energy loss $E_{loss}$ becomes less than 0.6 eV. For PDPP2T, $E_{loss}$ is only 0.52 eV and below this empirical threshold. For solar cells based on PDPP(TPT-alt-2T) and PDPPPTPT, $E_{loss}$ increases to 0.63 and 0.73 eV, respectively. For PDPP(TPT-alt-2T) $E_{loss}$ is very close to the 0.60 eV threshold, and it is therefore likely that this is the cause for the moderate EQE of the solar cells with PDPP(TPT-alt-2T). The same effect can be seen for PDPPPTBT:[70]PCBM solar cells, where the minimal photon energy loss is insufficient (0.53 eV), causing the very low EQE in the spectral region where the

Figure 3. HOMO (a) and LUMO (b) energies of the terpolymers vs the average of the HOMO and LUMO energies of corresponding copolymers. The solid lines represent slope = 1.
polymer absorbs (Figure S5g), whereas the cell based on PDPP(TDTPT-alt-TBTT) with $E_{\text{loss}} = 0.67$ eV shows a reasonably high EQE.

The $V_{\text{oc}}$ of organic solar cells is related to the energy difference between the HOMO of the donor and LUMO of the acceptor. As the HOMO energies of the terpolymers are the average of those of the respective copolymers, the same can be expected for the $V_{\text{oc}}$. Figure 5a confirms this is indeed the case, with a standard deviation of $\sigma = 30$ mV of the $V_{\text{oc}}$ of the terpolymer from the average $V_{\text{oc}}$ of the copolymers. With 30 mV, the standard deviation in $V_{\text{oc}}$ is on the same order of magnitude as the standard deviation for $E_{\text{H}}$. This correspondence is noteworthy because, unlike the optical band gap or the redox potentials, the $V_{\text{oc}}$ is influenced by other factors than the HOMO energy of the polymer alone.54 With clear correlations for $E_{\text{g}}$ and $V_{\text{oc}}$, it is expected that also $E_{\text{loss}}$ is correlated. As can be seen in Figure 5b and Table S, most polymers are in good agreement with this expectation, with the notable exception of Figure 4.

Figure 4. Current density–voltage ($j$–$V$) characteristics of solar cell devices made with the terpolymers and the corresponding parent copolymers in combination with [70]PCBM: (a) PDPP(TPT-alt-2T), (b) PDPP(TPT-alt-3T), (c) PDPP(TPT-alt-4T), (d) PDPP(TPT-alt-TTTT), (e) PDPP(PyTPy-alt-3T), (f) PDPP(TEDOTT-alt-3T), and (g) PDPP(TDTPT-alt-TBTT).
PDPP(PyTPy-alt-3T) which shows a $E_{\text{loss}}$ of 0.61 eV, lower than that of either of the parent copolymers (0.66 and 0.73 eV). The standard deviation for $E_{\text{loss}}$ is 41 meV.

These results clearly indicate that the electronic characteristics of the terpolymers and their solar cells with [70]PCBM coincide with the average of the characteristics their respective copolymers. The standard deviation from the expected values of $V_{\text{oc}}$ and $E_{\text{loss}}$ over all seven terpolymers is small. Even for $J_{\text{sc}}$, Figure 4 shows that the photocurrent of the terpolymer solar cells is often close to the average of the two copolymer solar cells. With respect to $E_{\text{loss}}$, we note that its value depends on how $E_g$ is determined. For $E_g$ we use the crossing point of the tangent in the inflection point at the low-energy side of the absorption spectrum with the baseline.35 In a recent study two methods using the EQE spectrum were described.55 In the Supporting Information (Figure S6 and Table S1) we show that, apart from a small (∼0.04 eV) and virtually constant

Table 5. Photovoltaic Characteristics of the Optimized Solar Cells

| polymer                  | $J_{\text{sc}}$ [mA/cm$^2$] | $V_{\text{oc}}$ [V] | FF  | PCE [%] | $E_{\text{loss}}$ [eV] | ref |
|--------------------------|-----------------------------|---------------------|-----|---------|------------------------|----|
| PDPPTTPT                 | 14.0                        | 0.80                | 0.67| 7.4     | 0.73                   | 37 |
| PDPP(TPP-alt-2T)         | 6.44                        | 0.74                | 0.67| 3.2     | 0.63                   | 36 |
| PDPP2T                   | 2.03                        | 0.68                | 0.50| 0.7     | 0.52                   | this work |
| PDPP(TPP-alt-3T)         | 15.9                        | 0.75                | 0.67| 8.0     | 0.68                   | 37 |
| PDPP3T                   | 15.4                        | 0.67                | 0.69| 7.1     | 0.66                   | 37 |
| PDPP(TPP-alt-4T)         | 14.4                        | 0.71                | 0.69| 7.0     | 0.80                   | this work |
| PDPP4T                   | 15.3                        | 0.64                | 0.69| 6.8     | 0.82                   | 43 |
| PDPP(TPP-alt-5T)         | 14.2                        | 0.74                | 0.66| 6.9     | 0.70                   | this work |
| PDPPTTTT                  | 14.8                        | 0.66                | 0.70| 6.9     | 0.69                   | 43 |
| PDPP(PyTPy-alt-3T)$^b$   | 11.9                        | 0.88                | 0.63| 6.6     | 0.61                   | 38 |
| PDPPPPyTPy$^b$           | 7.00                        | 0.99                | 0.60| 4.1     | 0.73                   | 42 |
| PDPP(TEDOTT-alt-3T)      | 14.1                        | 0.47                | 0.53| 3.5     | 0.78                   | this work |
| PDPPTEDOTT               | 16.1                        | 0.36                | 0.49| 2.8     | 0.81                   | this work |
| PDPPTTDTPT               | 16.6                        | 0.43                | 0.54| 3.9     | 0.80                   | 38 |
| PDPP(TDTPT-alt-TBTT)     | 12.2                        | 0.52                | 0.58| 3.7     | 0.67                   | 38 |
| PDPPTTBTT                | 2.8                         | 0.66                | 0.66| 1.2     | 0.53                   | 38 |

$^a$ $J_{\text{sc}}$ was determined by integrating the EQE spectrum with the AM1.5G spectrum. $^b$MoO$_3$ was used as hole transport layer instead of PEDOT:PSS. $^c$The synthesis of the polymer was described in ref 40.

Figure 5. $V_{\text{oc}}$ (a) and $E_{\text{loss}}$ (b) the terpolymer vs the average of the $V_{\text{oc}}$ and $E_{\text{loss}}$ energies of the corresponding copolymers. The solid lines represent slope = 1.

Figure 6. (a) $E_g$ of the terpolymers vs the average of the $E_g$s of the corresponding copolymers. (b) $V_{\text{oc}}$ of the terpolymers vs the average of the $V_{\text{oc}}$s of corresponding copolymers. The literature data are collected from refs 56–84, and details can be found in the Supporting Information. The solid lines represent slope = 1.
offset, the band gaps for the polymers are the same according to the three methods.

2.4. Extending to Other Terpolymers. To further substantiate the claim that the electronic characteristics of the terpolymers lie exactly in between those of the respective copolymers, a literature survey was carried out.56 The band gaps of several terpolymers and their associated copolymers are summarized in Table S2. In some cases, the terpolymers were published without direct comparison to their copolymers, necessitating the use of other publications to extract the required data. Another issue was the presence of low-energy bands of several terpolymers and their associated copolymers, a literature survey was carried out.56 The band gaps for the polymers are the same according to the three methods.

Nevertheless, as can be seen in Figure 6b, the deviation from the expected value of the \( V_{oc} \) remains in most cases under 100 mV, with a standard deviation of 50 mV for 22 terpolymers.

These results confirm that in first approximation the electronic characteristics of the terpolymers are the arithmetic average of the corresponding values respective copolymers. Especially in the case of the optical band gap this is very clear: 12 out of the 21 materials reported in the literature have an optical band gap that is close to exactly the average of that of the copolymers with a deviation of less than 0.02 eV, and only 4 materials have a deviation larger than 0.05 eV. Interestingly, the polymers with the largest deviations from the average all have a lower band gap than expected, which could be consistent with homocoupling defects. In the case of the solar cell characteristics, which are as indicated above subject to many other parameters, the spread in the data is larger, making the conclusion less clear. The deviations from the expected values remain however within 100 mV.

2.5. Semiempirical Quantum Chemical Model. In this section we describe a simple semiempirical quantum chemical model for the electronic states of the terpolymers using the properties of the copolymers as input. As we will demonstrate, the model accurately predicts the experimentally determined band gap and frontier orbital energy levels of the \((D1−A−D2−A)_n\) terpolymers after parametrization on the \((D−A)_n\) copolymers without any additional parameters and also provides a rationale why the optical band gap and frontier orbital energies of the terpolymers are the arithmetic mean of their constituent copolymers \((D1−A)_n\) and \((D2−A)_n\).

We model the individual monomeric conjugated donor and acceptor units each as effectively consisting of two "atoms" (i.e., D−D and A−A) and thus provide them with HOMO and LUMO levels that are parametrized via an effective Coulomb interaction with the \( V_{oc} \) remaining in most cases under 100 mV.

Figure 7. (a) Schematic representation of the model used to describe the \( \pi \) electrons in the copolymer. The acceptor and donor monomeric units are modeled as conjugated moieties, each with their own Coulomb (\( \alpha \)) and resonance (\( \beta \)) integrals. To calculate the HOMO and LUMO energies of the infinite polymer, it suffices to calculate the HOMO and LUMO energies of the cyclized repeat unit for which the Hamilton matrix \( \hat{H}_{\text{cop}} \) is shown. (b) Same for the terpolymer, showing the Hamiltonian \( \hat{H}_{\text{terp}} \). Adjustable parameters are in red and blue fonts, and parameters taken constant are in black font. The green dashed line indicates the mirror symmetry (\( \sigma_n \)) in the cyclized repeat units.

The solar cell characteristics of the terpolymers are summarized in Table S3. Solar cells have not been reported for every material of interest. In some cases, a clear Ohmic current contribution could be seen in the current−voltage characteristics, thus potentially influencing the \( V_{oc} \). Nevertheles, as can be seen in Figure 6b, the deviation from the expected value of the \( V_{oc} \) remains in most cases under 100 mV,
energy $\alpha_D$ for each donor unit and an effective resonance energy $\beta_D$ for the interaction between two donor units. Likewise, we assign an $\alpha_A$ to each acceptor unit and $\beta_A$ to their interaction. This is schematically shown in Figure 7a. To find the HOMO and LUMO energies of the copolymers, we use a Hückel approximation in which the adjacent donor and acceptor units interact with each other via a resonance integral $\beta$. The $\pi$-conjugated polymers under study have a direct band gap and the orbital energies for HOMO and LUMO can be found at the wave vector $k = 0$. To calculate the HOMO and LUMO energies, the infinite Hamilton matrix for the perfect polymer ($n = \infty$) can then be reduced to a smaller matrix, $\tilde{H}_\text{cop}$, for the cyclized repeat unit (Figure 7a). As can be seen in Figure 7a, this cyclized repeat unit has a mirror plane ($\sigma_v$) symmetry. The HOMO and LUMO energies are among the eigenvalues of $\tilde{H}_\text{cop}$. These can be solved analytically (see the Supporting Information) because of the $\sigma_v$ mirror plane, which confers $C_1$ point group symmetry to the cyclized repeat unit of the copolymers.

We then used the experimental data for the copolymers as a “training set” to find the optimal $\alpha_D$ and $\beta$ as fit parameters, while keeping $\alpha_A = 0.01$ eV, $\beta_A = -1.9$ eV, and $\beta_D = -2.0$ eV constant. The value for $\alpha_A$ is just an arbitrary offset. The values for $\beta_D$ and $\beta_A$ are chosen such that optical band gaps of the individual donor ($2\beta_D$) and acceptor ($2\beta_A$) units are large as expected for donor–acceptor copolymer. For all copolymers we take the difference in HOMO and LUMO energies ($E_{\text{gap}} = E_L - E_H$) and the average energy of HOMO and LUMO ($E_{\text{mid}} = (E_L + E_H)/2$) as experimental input parameters and determine $\alpha_D$ and $\beta$ via a search of the least squares between experimental data and the gap and $E_{\text{mid}}$ as calculated from the relevant eigenvalues of $\tilde{H}_\text{cop}$. Given the fact that the fitting procedure involves two adjustable parameters ($\alpha_D$ and $\beta$) and two experimental data points ($E_{\text{gap}}$ and $E_{\text{mid}}$) per copolymer, the sum of the minimized square error between fit and data tends to zero. The fitted values are listed in Table S4. Unsurprisingly, for electron-rich (donor) units, $\alpha_D$ is generally higher than $\alpha_A$. As expected, the Coulomb energies $\alpha_D$ correlate strongly with $E_{\text{mid}}$ but bear little relation to the experimental gap. Conversely, the fitted resonance integrals $\beta$ reflect the experimental gap but do not tally with the average orbital energy.

The fitted effective Coulomb and resonance energies $\alpha_D$ and $\beta$ determined for the copolymers were then used to predict the orbital energies of the terpolymers. Similar to the copolymers, the HOMO and LUMO energies of the terpolymers can be extracted by solving the Hamiltonian, $\tilde{H}_\text{terp}$, for the cyclized repeat unit as shown in Figure 7b. Also, the cyclized repeat unit of the terpolymer has $C_1$ point group symmetry. The parameters $\alpha_D$, $\beta_D$, and $\beta_D$ are assigned the same constant values as for the copolymers. The predicted $E_{\text{gap}}$ and $E_{\text{mid}}$ of the terpolymers are plotted in Figure 8a,b versus the corresponding experimental quantities. As can be seen in Figure 8a,b, the semiempirical Hückel model predicts the energy gap ($E_{\text{gap}}$) and midpoint ($E_{\text{mid}}$) for the terpolymers with an accuracy of roughly a few hundredths of an electronvolt. Standard deviations for $E_{\text{gap}}$ ($\sigma = 8$ meV) and $E_{\text{mid}}$ ($\sigma = 22$ meV) are within the accuracy of the error on the experiments. As shown
in Figure 8c,d, the Hückel model confirms the correspondence between the HOMO–LUMO gap of the terpolymer and the average gap of the two corresponding copolymers shown in Figure 6a. For the terpolymer with the smallest gap (1.18 eV) a deviation from the average gap for the corresponding copolymers is noticeable. This suggests that the correlation between the electronic properties of the terpolymer and the corresponding copolymers may hold only in a limited energy range. Apart from the deviations noted, the overall correspondence is very satisfactory and demonstrates that the HOMO and LUMO energy levels of donor−acceptor terpolymers can be predicted with sufficient accuracy after parametrization on the copolymers.

Finally, we provide a theoretical justification for the experimentally and computationally observed correlation between the HOMO and LUMO energy levels of the terpolymers and those averaged over the two corresponding copolymers. In Figure 9a, we compare the cyclized repeat unit of a terpolymer (1) with that of an averaged cyclized repeat unit (2). For 2, the two donor units are taken to be identical with Hückel parameters \( \alpha = (\alpha_{D1} + \alpha_{D2})/2 \) and \( \beta = (\beta_{1} + \beta_{2})/2 \) that equal the arithmetic means of those of the two donor units in the terpolymer. As shown in Figure 9a, the averaged cyclized repeat unit 2 has more symmetry elements than 1, and its point group symmetry corresponds to \( C_{2v} \). The \( \pi \)-orbital energies in the Hückel approximation of 2 found by solving \( \hat{H}_{\text{terp,avg}} \) are shown schematically in Figure 9b. We can compare the energy levels of 2 to those of a reduced cyclized repeat unit 3 for an average copolymer with donor unit described by \( \hat{H}_{\text{cop,avg}} \) (Figure 9c). The repeat unit 3 is only half the size of 2, and hence it has four instead of eight solutions. Because of symmetry, the energies of the levels with \( A_{1} \) and \( A_{2} \) symmetry of 2 in the \( C_{2v} \) point group are exactly the same as the energies with \( A' \) and \( A'' \) symmetry of 3 in the \( C_{1v} \) point group. The eigenvalues of the Hamiltonian of 3, \( \hat{H}_{\text{cop,avg}} \) can be solved analytically as we showed for the copolymers (see the Supporting Information). By use of elementary algebra, it can be shown that the orbital energies of the average...
copolymers 3 are within first-order approximation equal to the averaged orbital energies of the two copolymers (see the Supporting Information). The lowest order correction term is proportional to the product of $\delta \alpha$ and $\delta \beta$, defined as $\delta \alpha = (\alpha_{12} - \alpha_{13})/2$ and $\delta \beta = (\beta_{12} - \beta_{13})/2$. We conclude that the HOMO and LUMO levels of the average terpolymer will be approximately equal to the averaged HOMO and LUMO levels of the two corresponding copolymers.

Lastly, we need to relate the energy levels of the cyclized repeat unit 2 of the average terpolymer to those of the cyclized repeat unit 1 of the full terpolymer. Here we can formulate a perturbation Hamiltonian $V_{\text{terp}}$ in terms of parameters $\delta \alpha$ and $\delta \beta$ and use it to approximate the energy levels and states of 1 in terms of those of 2 (Figure 10a). The full Hamiltonian $H_{\text{terp}}$ is then the sum of $H_{\text{terp,avg}}$ for the averaged cyclized repeat unit 2 and the perturbation term $V_{\text{terp}}$. We use group theory to investigate the effect of $V_{\text{terp}}$ on the HOMO and LUMO of the averaged cyclized repeat unit. In the $C_2$ point group $H_{\text{terp,avg}}$ of 2 is fully symmetric for all symmetry operations (Figure 9a) and thus transforms as the irreducible representation $A_1$. Figure 9a also shows that $H_{\text{terp}}$ for 1 is not fully symmetric in $C_2$, because it has the 2-fold rotation ($C_2$) and the second mirror plane ($\sigma_v$) operations and has $\sigma_v$ as the only symmetry element. Within $C_{2v}$, $H_{\text{terp}}$ therefore transforms as the irreducible representation $B_1$. Then, because $H_{\text{terp}} = H_{\text{terp,avg}} + V_{\text{terp}}$, $V_{\text{terp}}$ must also transform as $B_1$. This is also shown in Figure 10b where it can be seen that the only symmetry element of $V_{\text{terp}}$ is the $\sigma_v$ mirror plane. In perturbation theory, the first-order corrections to the HOMO and LUMO energies are given by the integrals $(\psi_{\text{HOMO}}|V_{\text{terp}}|\psi_{\text{HOMO}})$ and $(\psi_{\text{LUMO}}|V_{\text{terp}}|\psi_{\text{LUMO}})$, respectively. Because $\Gamma((\psi_{\text{HOMO}}|V_{\text{terp}}|\psi_{\text{HOMO}})) = A_1 \times B_1 \times A_1 = B_1$ and $\Gamma((\psi_{\text{LUMO}}|V_{\text{terp}}|\psi_{\text{LUMO}})) = A_1 \times B_1 \times A_1 = B_1$, these integrals do not have $A_1$ symmetry and are thus equal to zero. Hence, in first-order perturbation theory $V_{\text{terp}}$ does not change the HOMO and LUMO levels of 2.

This demonstrates that in the semiempirical model used the HOMO and LUMO energy levels of the terpolymer are in first-order approximation equal to the average energy levels of the corresponding copolymers, as found experimentally, which affords a theoretical basis for the experimental results.

3. CONCLUSION

The electronic structure of seven regioregular $(-D_1-\text{A}-D_2-\text{A}^-)_n$ terpolymers in which the common acceptor unit is a DPP moiety, of which three not previously published, have been studied and compared to their related terpolymers, e.g., $(-D_1-\text{A}^-)_n$ terpolymers. It was found that the optical band gap of the terpolymers is close to the average of the optical band gaps of their copolymers, with only minor deviations. This is a useful design rule and allows to precisely control the optical band gap of new conjugated polymers. Likewise, the HOMO and LUMO energies of the terpolymers are the average of their related copolymers, indicating that the electronic properties of terpolymers could be predicted on the basis of their related copolymers. In bulk heterojunction solar cells made of these terpolymers as donor with [70]PCBM as acceptor, the $V_{\text{oc}}$ and $E_{\text{loss}}$ were also found to be the average of the $V_{\text{oc}}$ and $E_{\text{loss}}$ of cells made with the corresponding copolymers. This is unexpected, as these parameters are closely related to the HOMO energy and optical band gap of the materials.

A comparison of these findings with data in the literature confirmed the notion that the optical band gap is almost always the average of the band gaps of the copolymers, with only three polymers showing a substantial deviation from this rule. On average, this was also the case in terms of the $V_{\text{oc}}$, although the deviation from the expected value was larger for more materials. This could be due to the fact that $V_{\text{oc}}$ is not exclusively influenced by the HOMO of the polymer but by many other factors.

A semiempirical quantum chemical model in which the donor and acceptor unit are parametrized with effective Coulomb and resonance energies gives an accurate estimate of the frontier orbital energy levels of the terpolymers after parametrization on the copolymer and provides a theoretical justification that in a first-order approximation the optical band gap of the terpolymers is close to the arithmetic mean of the optical band gaps of their copolymers.

In conclusion, this study gives an experimentally and theoretically verified predictive rule for the band gap and $V_{\text{oc}}$ of regioregular terpolymers, namely, that these characteristics will be the average of those of their related copolymers. This can be a useful tool in the design of new conjugated polymers. We envision that the semiempirical model can be used to predict the energies of other more complex chain motifs than those of $(-D_1-\text{A}-D_2-\text{A}^-)_n$ terpolymers, e.g., chains containing more than three different units or chains in which the ratio of $D_1$ to $D_1$ differs from 1:1.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b11562.

Experimental methods, description of synthesis and characterization of new polymers, TEM images of polymer–fullerene blends, EQE spectra, comparison of different methods to determine the optical band gap, details of the literature analysis, analytical expressions for the orbital energies of copolymers, analysis of the average orbital energies (PDF)

## AUTHOR INFORMATION

### Corresponding Authors

**Stefan C. J. Meskers** — Molecular Materials and Nanosystems & Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; orcid.org/0000-0001-9236-591X;
Email: s.c.j.meskers@tue.nl

**Rene A. J. Janssen** — Molecular Materials and Nanosystems & Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; Dutch Institute for Fundamental Energy Research, 5612 AJ Eindhoven, The Netherlands; orcid.org/0000-0002-1920-5124;
Email: r.a.j.janssen@tue.nl

### Authors

**Gaël H. L. Heintges** — Molecular Materials and Nanosystems & Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands; Institute for Materials Research (IMOMEC), Design & Synthesis of Organic Semiconductors (DSOS), Hasselt University, 3590 Diepenbeek, Belgium

**Andrècanne Bolduc** — Molecular Materials and Nanosystems & Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands
Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.9b11562

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
We thank Prof. Weiwei Li, Dr. Koen Hendriks, and Pieter Leenaers for their contributions in terms of materials and data to the work. Pieter Leenaers is further acknowledged for the GPC analysis. Dr. Mengmeng Li and Dr. Alice Furlan are thanked for the TEM analysis. G.H.L.H. acknowledges the Agency for Innovation by Science and Technology in Flanders (IWT). A.B. acknowledges Fonds de recherche du Québec - Nature et technologies (Grant 173542). The work was further supported by the European Research Council under the European Union’s Seventh Framework Programme (FP/2007-2013) ERC Grant Agreement No. 339031, the Ministry of Education, Culture and Science (Gravity program 024.001.035), and the NWO Spinoza prize awarded to R.A.J.J. by The Netherlands Organization for Scientific Research (NWO).

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