

The Eternal Quest for Practical Low Bandgap Polymers

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Abstract The bandgap (E_g) of conjugated materials effects a variety of critical properties such that efforts to control the bandgap have become a basic tenet in the design of conjugated polymers. One goal of such efforts is to minimize the E_g with the goal of producing technologically useful low bandgap ($E_g < 1.5$ eV) polymers. This perspective will introduce the two primary approaches to low E_g polymers (*i.e.*, quinoidal systems and donor-acceptor frameworks) and discuss important new directions for both design principles.

Keywords low bandgap, narrow bandgap, quinoidal, donor-acceptor, ambipolar units

Since initial reports by F. F. Runge dating back to the early 1800s,^[1] conjugated organic polymers have grown to receive considerable fundamental and technological interest due to their combination of the electronic and optical properties of classical inorganic semiconductors, with many of the desirable properties of organic plastics. This eventually gave rise to the current field of organic electronics, with various technological applications such as sensors, electrochromic devices, organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and organic field effect transistors (OFETs).^[2–8]

A critical parameter of conjugated materials is the bandgap (E_g), which is defined as the energetic separation between the valence and conduction bands of the bulk, solid-state material.^[2–8] As the bandgap corresponds to energy between the HOMO and LUMO of the material in the solid state, it determines such material properties as the onset of absorbance or the energy of any potential emission. For conjugated polymers, the majority of reported materials exhibit E_g values of 1.5–3.0 eV (Figure 1), and thus absorb and emit light primarily in the visible regime.

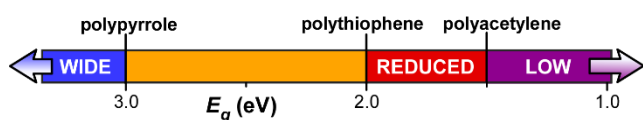


Figure 1 Range and classifications of polymer bandgaps.

Of course, lowering the polymer E_g allows more effective absorption in the red and near infrared (NIR) wavelengths, a critical ability for OPVs and NIR photodetectors. Furthermore, a smaller E_g allows greater thermal population of the conduction band, leading to more intrinsic charge carriers and enhanced conductivity.^[2,3,6,7] Reducing the E_g also typically involves destabilization of the HOMO energy, resulting in lower potentials of oxidation and stabilization of the p-doped (*i.e.*, oxidized) state.^[2,3] As such, there has been significant motivation for minimizing the E_g with the goal of producing technologically useful low bandgap ($E_g < 1.5$ eV) polymers.

It should be noted that the terms *small*, *narrow*, and *low bandgap* are used sloppily in the literature to refer to a range

of E_g values. The original definition given by Pomerantz in 1998 was limited to values below 1.5 eV to differentiate them from the commonly studied parent polymers (Figure 1).^[3,6] Of course, as many polymers of interest for OPVs exhibit E_g values below that of polythiophene (2.0 eV), some also refer to those as low E_g materials. To reduce the confusion introduced by such multiple definitions, we have continued to support the original cutoff of < 1.5 eV, while advocating the term *reduced bandgap* for materials between 1.5–2.0 eV (Figure 1).^[3,6]

Methods for Minimizing Bandgap

While the E_g is known to be dictated by a number of factors,^[2,3,6] there are really only two primary design methods for the successful production of low E_g polymers (Figure 2). The older of these dates back to 1984, with efforts by Wudl and coworkers to enhance the quinoidal nature of the polymer

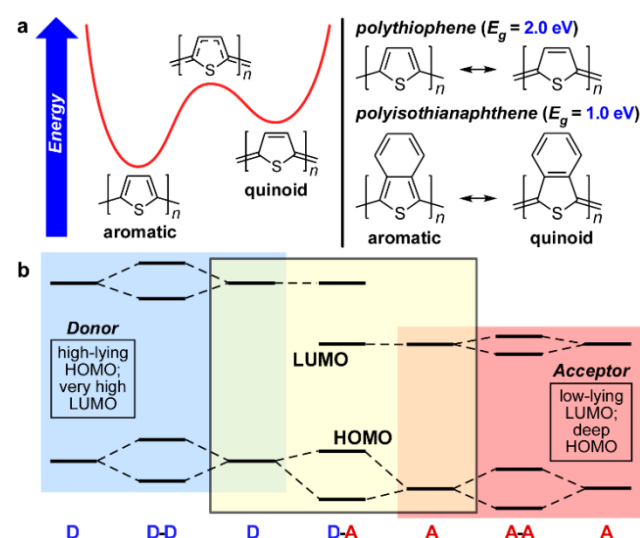


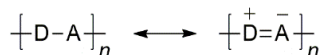
Figure 2 Minimizing polymer bandgap: (a) enhancing the quinoidal character of the polymer ground state; (b) frontier orbital hybridization in donor-acceptor (D-A) units.

backbone.^[2,3] As shown in Figure 2a, polyaromatics such as polythiophene have non-degenerate resonance structures, with the more stable aromatic form representing the ground-state. Theoretical studies, however, have shown the quinoidal form to have a much lower E_g , with the polymer E_g decreasing with increasing quinoidal contribution to the ground state.^[3,4,6-8]

It was found that the quinoidal nature of the polymer could be enhanced by fusing rings of greater aromaticity to thiophene. Here, the higher resonance energy of the added ring favors the resonance form in which it remains aromatic. As a consequence, this enhances the quinoidal nature of the thiophene ring, contributing more quinoidal character to the resulting polymeric backbone.^[3,4] The successful application of this approach in polyisothianaphthene (PITN) resulted in an E_g of 1.0 eV, after which a number of other such fused-ring, low bandgap materials were developed.^[3,4,7,8]

A second approach was then introduced by Havinga and coworkers in 1992, which utilized donor-acceptor (D-A) frameworks to reduce the polymer E_g .^[3,4,6,9] These D-A frameworks are based on a regular alternation of electron-rich (donor) and electron-poor (acceptor) groups in a conjugated backbone. As illustrated in Figure 2b, the lower E_g of such materials is rationalized via hybridization of the frontier orbitals of the donor and acceptor units, which results in a hybrid D-A unit with HOMO levels characteristic of the donor and LUMO levels characteristic of the acceptor.^[3-7,9] As a result, the HOMO-LUMO energy of the D-A unit is smaller than either of the respective homodimers and further hybridization upon chain extension would continue this trend to give a reduced E_g in the extended D-A framework.^[3,9] It should be pointed out, however, that while pictorial representations typically show hybridization with equivalent mixing of the HOMO and LUMO,^[4-7] this is usually not the case. In reality, the HOMO levels of the donor and acceptor are usually much more energetically similar than the corresponding LUMO levels, resulting in reduced mixing between LUMO levels.^[10] This is particularly true in the cases of strong acceptors, where LUMO levels are too energetically and spatially separated to see any substantial mixing in the initial D-A unit, although some additional mixing can sometimes be seen with extension of the polymer backbone.^[9,10]

A common alternate explanation for the lower E_g in D-A systems has been in terms of reduced bond length alternation or enhanced quinoidal content.^[3,6] This stems from the view that if the donor and acceptor units are strong enough, it should be possible to evoke a new resonance form exhibiting double bond character between the donor and acceptor units:



The contribution of this new resonance form would then lead to enhanced quinoidal content or reduced bond length alternation and thus a decreased E_g .^[3,6] It should be noted, however, that no real experimental evidence has been reported to support this belief and a recent crystal structure of a strong donor-acceptor dimer revealed no shortening of the bond between the donor and acceptor units.^[10] Still, such D-A frameworks have become the prevalent design criteria for low E_g polymers.

Of course, the successful production of polymers that effectively combine a low E_g , suitable solubility, and good film formation properties can still be a challenge. Most low E_g materials incorporate various fused-ring units, the rigid nature of which tends to reduce polymer solubility. While solubility limitations can be overcome, it may require bulky, branched sidechains that can limit interchain coupling, thus working

against further E_g reduction. Even if the desired combination of properties can be achieved, really low E_g values are often achieved by destabilizing the HOMO, frequently making orbital energies incompatible with typical device configurations.^[9]

New Directions in Enhancing Quinoidal Nature

Fused-ring monomers such as isothianaphthene that were the basis for early efforts to enhance the quinoidal nature of conjugated polymers are sometimes referred to as *proquinoidal* units,^[8] as these are aromatic units without any quinoidal content in the monomeric form, but can then induce quinoidal character in the resulting polymers. For homopolymers such as PITN and poly(thieno[3,4-*b*]pyrazine), experimental evidence has supported at least partial quinoidal character.^[2]

As the ability to control multiple material properties can be quite challenging when limited to homopolymers, modern efforts tend to focus on copolymeric products in order to allow greater structural diversity and additional possibilities for the tuning of material properties.^[9] As a result, proquinoidal units have been incorporated into a wide range of copolymeric materials to successfully generate low E_g polymers.^[2,4,6-8] However, as the bulk of these materials can also be viewed as D-A polymers,^[4] it is unclear how much quinoidal content is contributing to the lower E_g values and claims of quinoidal character have only been supported by computational studies.

A more recent approach has been to move beyond proquinoidal units to units that adopt a true quinoidal constitution in the ground state.^[7,8] Such units can thus be introduced into copolymeric materials via the direct polymerization of stabilized quinoidal monomers.^[8] The most commonly applied of such stabilized quinoidal building blocks are various pyrrole-based monomers, examples of which are given in Figure 3.^[7,8]

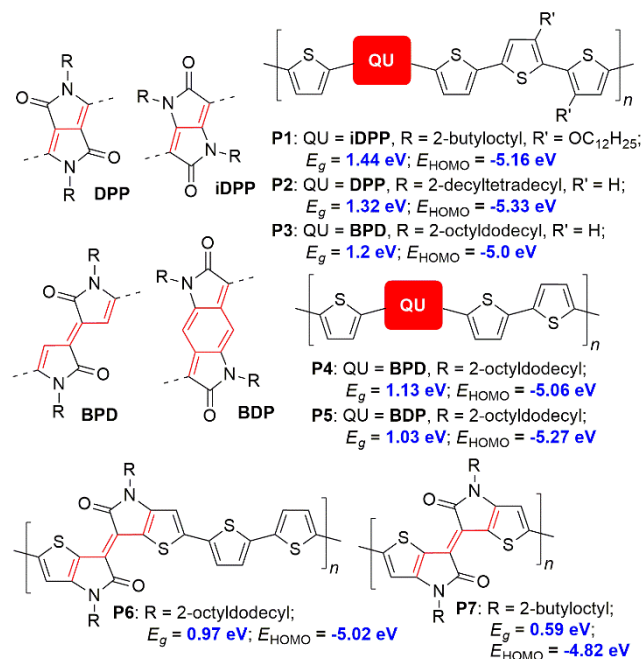


Figure 3 Polymers of pyrrole-based quinoidal units.

These pyrrole-based quinoid structures combine quinoid content with electron deficiency due to the two lactam rings, which should contribute to both lower E_g materials and stabilized frontier energy levels. Furthermore, solubilizing

groups can be easily added at the N-positions to improve solubility and provide solution processability.^[7] As shown in Figure 3, all of the included examples fall below the 1.5 eV cutoff for low E_g materials, with E_g values that correlate to the quinoid content of the polymer backbone. This can easily be seen by comparing **P2** to **P3**, in which the inclusion of one less thiophene in the repeat unit results in a lowering of the E_g from 1.2 to 1.13 eV. In a similar manner, the larger quinoid units **BPD** and **BDP** result in smaller E_g values than **DPP** or **IDPP**. More importantly, the copolymeric nature of these materials allows further tuning via the use of other monomers in place of oligothiophenes, resulting in even lower E_g values. Analogous thiophene and furan-based quinoid units have also been reported and many of these materials exhibit good charge mobilities.^[7]

Another successful quinoid building block is the stable thiophene-capped *p*-azaquinodimethane (**p-AQM**) unit introduced by Liu and coworkers in 2017.^[7,8,11,12] While not quite as successful at lowering the E_g as the pyrrole-based quinoid units, this structurally simple monomer can be efficiently synthesized in two simple steps and provides solubility via the two alkoxy sidechains. Examples of polymers based on **p-AQM** are given in Figure 4.

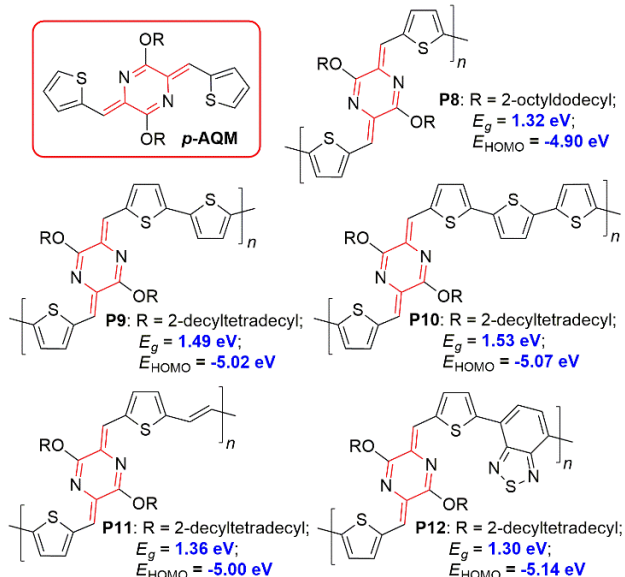


Figure 4 Polymers of *p*-azaquinodimethane (**p-AQM**) units.

As with the previous pyrrole-based systems, the E_g values correlate to the quinoid content of the polymer backbone. Comparing **P8**–**P10**, the E_g values systematically increase with increasing thiophene content, with the value of **P10** exceeding the 1.5 eV cutoff such that it is correctly a reduced E_g polymer. Again, due to their copolymeric nature, other monomers can be incorporated in place of the simple oligothiophenes, as evidenced by **P11** and **P12**.^[11,12] Such approaches thus allow further lowering of the E_g of the resulting polymers. Finally, simple synthetic modification also allowed the production of analogues with cationic triphenylphosphonium groups in place of the alkoxy sidechains, resulting in low E_g polyelectrolytes with reasonable stability and water solubility.^[8]

Advances in Donor-Acceptor Materials

As stated above, the D-A approach has become the prevalent design model for the production of low E_g materials and is far more commonly applied than efforts to enhance

quinoidal nature. With that said, it should be pointed out that many D-A frameworks utilize electron-deficient proquinoidal units as the acceptor, which has led to claims that the lower E_g values in these materials are actually due to a geometrical mismatch between quinoidal and aromatic units, resulting in reduced bond length alternation.^[7,8] Furthermore, while a great many D-A materials have been reported in the literature, the bulk of these are technically not low E_g materials and more correctly fall within the scope of reduced E_g systems.^[4,5] This is often due to efforts to keep the polymer HOMO levels deep enough for effective application to OPVs, which then limits the extent that the E_g can be minimized.^[4]

Perhaps one of the most impactful recent advances in D-A systems has been the recognition that the basic assumption that all monomeric units act exclusively as donors, acceptors, or neutral 'spacers' (often viewed as not affecting the E_g) is drastically oversimplified, if not outright incorrect. This new insight resulted from the determination that a commonly used acceptor, thieno[3,4-*b*]pyrazine (**TP**, Figure 5), also exhibits the properties of a very strong donor, essentially equivalent to the donor 3,4-ethylenedioxythiophene (**EDOT**).^[9,10,13-15]

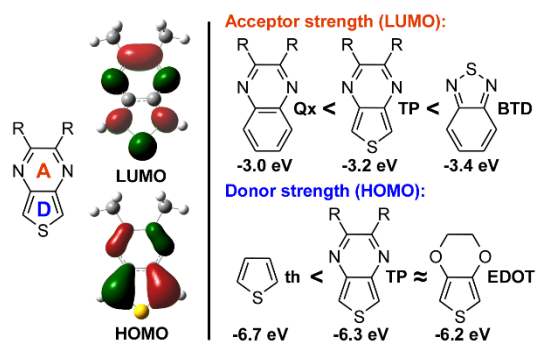


Figure 5 Ambipolar nature of thieno[3,4-*b*]pyrazine (**TP**).

As outlined in Figure 5, the electron-deficient pyrazine ring does make **TP** a significantly strong acceptor, with its acceptor strength falling between the common acceptors quinoxaline (**Qx**) and 2,1,3-benzothiadiazole (**BTD**). At the same time, however, the **TP** HOMO is found to be highly localized on the thiophene ring, with the HOMO significantly destabilized in comparison to the simple donor thiophene and roughly equivalent to the strong donor **EDOT**. As **TP** thus acts simultaneously as both an acceptor and donor, such units have been designated *ambipolar units*.^[9,10,13-15]

This new-found understanding can now be used to explain unexpected trends in **TP**-based polymers (Figure 6), where the pairing of **TP** with various donors results in larger E_g values (i.e., **P13** vs. **P14**–**P15**), rather than the decreases typical of D-A frameworks. While some have viewed this as a result of reduced proquinoidal content,^[7] this would not explain the observed differences in **P14** and **P15**. In reality, most donors applied are weaker than the **TP** unit, which results in stabilization of the hybrid D-A HOMO, rather than the destabilization shown in Figure 2b. The deeper HOMO thus gives a larger E_g , as can be seen by comparing both the E_g and HOMO energies of **P13** and **P14**. It is only the application of very strong donors, as in **P15**,^[9] that the donor abilities are matched to retain the high HOMO and low E_g values of **P13**.

The strong donor ability of **TP** also allows the unconventional pairing of **TP** with acceptors to give low E_g materials (**P16**–**P18**).^[14,15] Here, the acceptor unit stabilizes the polymer HOMO levels, while hybridization of the low-lying LUMOs of both units results in a quite deep polymer LUMO and E_g

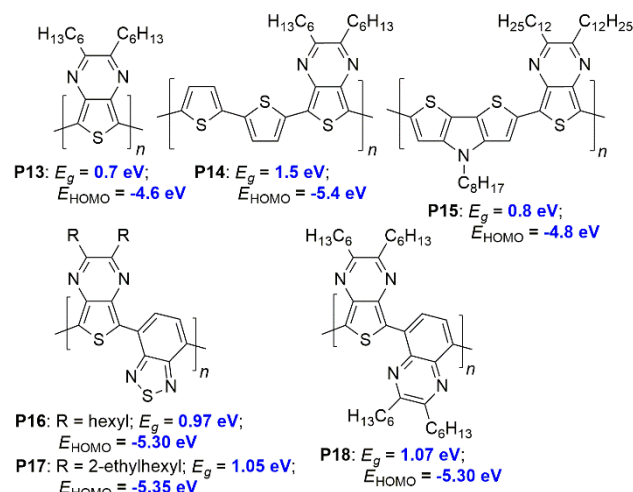


Figure 6 Thieno[3,4-*b*]pyrazine-based polymers.

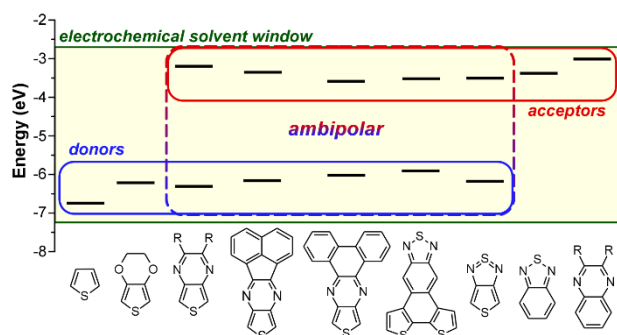


Figure 7 Currently known ambipolar units.

values of 0.97–1.07 eV. The combination of the deep LUMO and low E_g then opens the possibility of using such materials as NIR-absorbing, non-fullerene acceptors in OPVs. Lastly, since the ambipolar nature of **TP** was initially reported, additional units have been found to exhibit similar properties (Figure 7), which could lead to further extension of this new approach.

Conclusions

The production of practical low E_g ($< 1.5 \text{ eV}$) polymers with stabilized HOMO energies that can be applied to various technological devices is still an ongoing pursuit. While the design of such low E_g polymers is generally viewed to involve one of two separate approaches, the low E_g nature of many conjugated polymers may be actually due to complementary effects of both enhanced quinoidal nature and beneficial D-A interactions. Still, advances in both the application of stabilized quinoidal monomers and D-A frameworks have allowed various new low E_g copolymers that can be tuned via the choice of the two monomeric species involved, as well as via solubilizing sidechains and functional groups. At the same time, however, it is clear that additional targeted studies are needed to elucidate the underlying factors (*i.e.*, quinoidal contributions vs. donor-acceptor effects) that most contribute to the reduction in the corresponding E_g values. Finally, the number of materials with E_g values below 1.0 eV is still limited and thus additional advances to further minimize the bandgap of practical, useful polymers are still needed.

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Author Contributions

Following are the details of the contributions made by each of the authors for the manuscript: S. C. R. organized and wrote the initial manuscript, with the remaining authors collecting relevant literature and contributing to manuscript editing and revision.

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Conflict of Interest

The authors declare no conflict of interest.

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References

- [1] Rasmussen, S. C. Conjugated and Conducting Organic Polymers: The First 150 years. *ChemPlusChem* **2020**, *85*, 1412–1429.
- [2] Rasmussen, S. C.; Pomerantz, M. Low Bandgap Conducting Polymers. In *Conjugated Polymers: Theory, Synthesis, Properties, and Characterization*, Eds.: Skotheim, T. A.; Reynolds, J. R., Handbook of Conducting Polymers, 3rd Ed., CRC Press, Boca Raton, FL, **2007**, pp. 421–462.
- [3] Rasmussen, S. C. Low-Bandgap Polymers. In *Encyclopedia of Polymeric Nanomaterials*, Eds.: Muellen, K.; Kobayashi, S., Springer, Heidelberg, **2015**, pp. 1155–1166.
- [4] Dou, L.; Liu, Y.; Hong, Z.; Li, G.; Yang, Y. Low-Bandgap Near-IR Conjugated Polymers/Molecules for Organic Electronics. *Chem. Rev.* **2015**, *115*, 12633–12665.
- [5] Holliday, S.; Li, Y.; Luscombe, C. K. Recent advances in high performance donor-acceptor polymers for organic photovoltaics. *Prog. Polym. Sci.* **2017**, *70*, 34–51.
- [6] Scharber, M. C.; Sariciftci, N. S. Low Band Gap Conjugated Semiconducting Polymers. *Adv. Mater. Technol.* **2021**, 2000857.
- [7] Mikie, T.; Osaka, I. Small-bandgap quinoid-based π -conjugated polymers. *J. Mater. Chem. C* **2020**, *8*, 14262–14288.
- [8] Ji, X.; Fang, L. Quinoidal conjugated polymers with open-shell character. *Polym. Chem.* **2021**, *12*, 1347–1361.
- [9] Evenson, S. J.; Mulholland, M. E.; Anderson, T. E.; Rasmussen, S. C. Minimizing Polymer Band gap via Donor-Acceptor Frameworks: Poly(dithieno[3,2-*b*:2',3'-*d'*]pyrrole-*alt*-thieno[3,4-*b*]pyrazine)s as Illustrative Examples of Challenges and Misconceptions. *Asian J. Org. Chem.* **2020**, *9*, 1333–1339.
- [10] Anderson, T. E.; Culver, E. W.; Badia-Domínguez, I.; Wilcox, W. D.; Buysse, C. E.; Delgado, M. C. R.; Rasmussen, S. C. Probing the Nature of Donor-Acceptor Effects in Conjugated Materials: A Joint Experimental and Computational Study of Model Conjugated Oligomers. *Phys. Chem. Chem. Phys.* **2021**, *23*, 26534–26546.
- [11] Liu, X.; He, B.; Garzón-Ruiz, A.; Navarro, A.; Chen, T. L.; Kolaczowski, M. A.; Feng, S. F.; Zhang, L.; Anderson, C. A.

- Chen, J.; Liu, Y. Unraveling the Main Chain and Side Chain Effects on Thin Film Morphology and Charge Transport in Quinoidal Conjugated Polymers. *Adv. Funct. Mater.* **2018**, *28*, 1801874.
- [12] Liu, C.; Xuncheng Liu, X.; Zheng, G.; Gong, X.; Yang, C.; Liu, H.; Zhang, L.; Anderson, C. L.; He, B.; Xie, L.; Zheng, R.; Liang, H.; Zhou, Q.; Zhang, Z.; Chen, J.; Liu, Y. An unprecedented quinoid-donor-acceptor strategy to boost the carrier mobilities of semiconducting polymers for organic field-effect transistors. *J. Mater. Chem. A* **2021**, *9*, 23497–23505.
- [13] Wen, L.; Heth, C. L.; Rasmussen, S. C. Thieno[3,4-*b*]pyrazine-based Oligothiophenes: Simple Models of Donor-Acceptor Polymeric Materials. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7231–7240.
- [14] Culver, E. W.; Anderson, T. E.; Navarrete, J. T. L.; Delgado, M. C. R.; Rasmussen, S. C. Poly(thieno[3,4-*b*]pyrazine-*alt*-2,1,3-benzothiadiazole)s: A new design paradigm in low band gap polymers. *ACS Macro Lett.* **2018**, *7*, 1215–1219.
- [15] Anderson, T. E.; Culver, E. W.; Almyahi, F.; Dastoor, P. C.; Rasmussen, S. C. Poly(2,3-dihexylthieno[3,4-*b*]pyrazine-*alt*-2,3-dihexylquinoxaline): Processible, Low Bandgap, Ambipolar-Acceptor Frameworks via Direct Arylation Polymerization. *Synlett* **2018**, *29*, 2542–2546.

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