

Spectral Engineering in π -Conjugated Polymers with Intramolecular Donor–Acceptor Interactions

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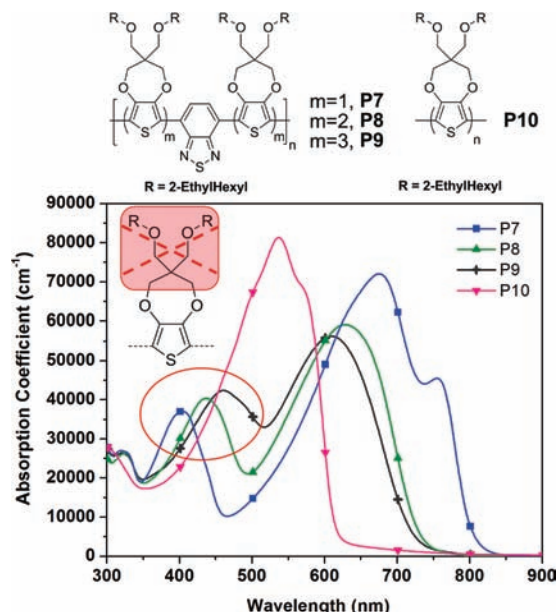
CONCEPTUS

With the development of light-harvesting organic materials for solar cell applications and molecular systems with fine-tuned colors for nonemissive electrochromic devices (e.g., smart windows, e-papers), a number of technical challenges remain to be overcome. Over the years, the concept of “spectral engineering” (tailoring the complex interplay between molecular physics and the various optical phenomena occurring across the electromagnetic spectrum) has become increasingly relevant in the field of π -conjugated organic polymers. Within the spectral engineering toolbox, the “donor–acceptor” approach uses alternating electron-rich and electron-deficient moieties along a π -conjugated backbone. This approach has proved especially valuable in the synthesis of dual-band and broadly absorbing chromophores with useful photovoltaic and electrochromic properties.

In this Account, we highlight and provide insight into a present controversy surrounding the origin of the dual band of absorption sometimes encountered in semiconducting polymers structured using the “donor–acceptor” approach. Based on empirical evidence, we provide some schematic representations to describe the possible mechanisms governing the evolution of the two-band spectral absorption observed on varying the relative composition of electron-rich and electron-deficient substituents along the π -conjugated backbone.

In parallel, we draw attention to the choice of the method employed to estimate and compare the absorption coefficients of polymer chromophores exhibiting distinct repeat unit lengths, and containing various extents of solubilizing side-chains along their backbone. Finally, we discuss the common assumption that “donor–acceptor” systems should have systematically lower absorption coefficients than their “all-donor” counterparts.

The proposed models point toward important theoretical parameters which could be further explored at the macromolecular level to help researchers take full advantage of the complex interactions taking place in π -conjugated polymers with intramolecular “donor–acceptor” characteristics.



Introduction

While the concept of “band gap engineering” has so far prevailed in identifying useful design prin-

ciples for π -conjugated polymers finding application in light-harvesting devices,¹ the requirement for full spectral (color) control in materials appli-

cable in both emissive and nonemissive display technologies is now motivating an expansion of this classical approach. Extending beyond tuning the energy levels and the charge transport properties of semiconductors, the notion of “spectral engineering” relates the simple energy gap of a material to its more complex electromagnetic absorption or emission spectrum. In particular, when considering the optical absorption of a macromolecular system with extended π -conjugation, a certain number of interesting optical phenomena are frequently encountered including vibronic transitions, H- and J-type aggregation features, long-wavelength absorption bands frequently attributed to low-energy charge-transfer transitions, and so on. Importantly, the true color state of an organic chromophore is not governed by its band gap but is provided by the combination of the various optical transitions (both in energy/wavelength and intensity) present across its full spectrum. This is especially true in “donor–acceptor” molecular structures where multiple absorption bands of various breadths and relative intensities are frequently observed.

First introduced in the early 1990's by Havinga et al. in macromolecular π -conjugated systems,^{2,3} the “donor–acceptor” approach alternating electron-rich and electron-deficient moieties along the same backbone has recently been found to offer synthetic access to dual-band and broadly absorbing polymer chromophores with photovoltaic and/or electrochromic properties. While several possible rationales have been explored in the past to justify the presence of a second absorption band in the optical spectrum of those systems, the origins of the dual-band of absorption in “donor–acceptor” π -conjugated polymers remains a source of debate.

In this Account, we provide important empirical considerations with respect to the evolution of the two-band spectral absorption as a function of the concentration of electron-rich and electron-deficient substituents incorporated along the polymer main-chain. Further, we draw attention to the possible mechanisms responsible for the spectral changes observed. We also discuss important parameters influencing the absorption coefficient values estimated for π -conjugated polymers in general, such as the presence of nonaromatic and/or solubilizing side groups appended to the backbone. Since those aspects are not commonly addressed in the literature, we further suggest how coefficients with physical significance can be obtained when comparing polymer chromophores with distinct repeat units.

Dual-Band-Absorbing Polymers via the “Donor–Acceptor” Approach

Initiated by work from various groups on the design and synthesis of neutral state green polymer electrochromes,^{4–7} our idea of implementing a palette of colors available in π -conjugated polymers (potentially complementary as to create a full set of color combinations) could certainly drive the perspectives of electrochromic polymers in display applications.⁸ Electrochromic polymers have long been thought to possess intrinsic color limitations related to the constraint for a low oxidation potential (i.e., a high-lying HOMO) aimed at allowing the material to undergo rapid and reversible redox switching. With relatively high-lying HOMOs narrowing their energy gap to values in the 1.6–1.8 eV range (i.e., extending their spectral absorption to longer wavelengths), dioxithienyl-based electrochromes, for example, have been shown to exhibit neutral state colors ranging from red, to purple, and to blue.⁹ Other useful colors have occasionally been obtained via the synthesis of anodically coloring electrochromes, such as the dioxypyrrroles, for instance.¹⁰

In our attempt to generate the color green, and scanning the literature, we found that dual-band optical features are in general observed for conjugated polymers alternating electron-rich and electron-deficient heterocycles. In most reported cases, the shorter-wavelength optical transition is found in the UV which yields polymer chromophores with color states ranging from purple to blue, depending on the onset of absorption of the longer-wavelength optical transition.^{11,12}

Following this simple observation, we envisaged that a two-band absorption spectrum could be shifted toward the longer wavelengths by simply increasing the electron-rich character of the polymer backbone (while keeping the same electron-deficient moiety). To this end, we proposed the synthetic design shown in Figure 1a, incorporating the high-lying HOMO 3,4-propylenedioxythiophene (ProDOT) along with unsubstituted thiophenes or 3,4-ethylenedioxythiophenes, and aimed at fully transferring the dual-band spectrum into the visible region. As illustrated in Figure 1b, the corresponding polymers containing 2,1,3-benzothiadiazole (BTD) as the electron-deficient building core were found to exhibit a transmission window in the 500–550 nm region as expected for a chromophore green in color. The first set of spray-processable green-to-transmissive switching polymer electrochromes was subsequently demonstrated with excellent long-term switching stabilities (as monitored over 10 000 cycles).⁷

With the idea that π -conjugated semiconducting polymers could be solution-processed into power-generating displays of

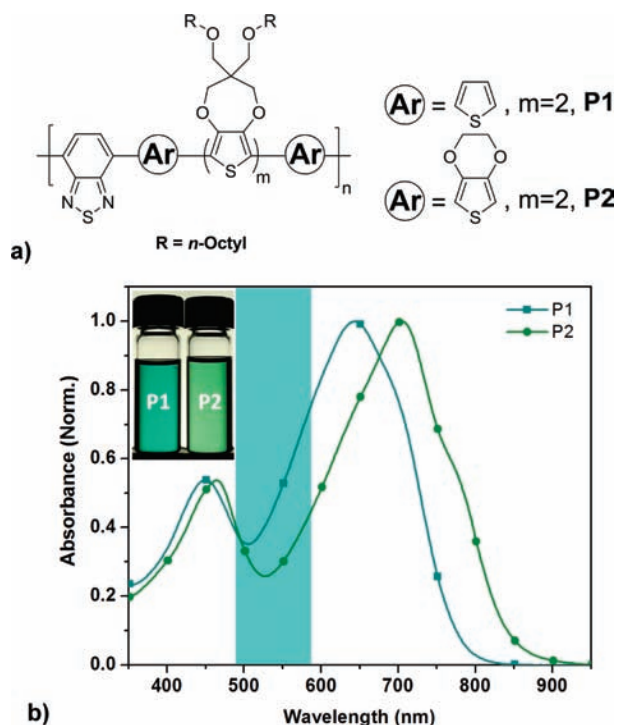


FIGURE 1. (a) Molecular structures for the DA copolymer **P1** and **P2**. (b) Superimposed UV–visible solution absorption spectra of **P1** and **P2** in toluene (the spectra are normalized at the longer-wavelength absorption maximum of the polymers). (Figure adapted with permission from ref 7. Copyright 2008 Wiley-VCH.)

varied color motifs, the molecular structure of dual-band absorbing green polymers was further adjusted to address the requirements for organic photovoltaic applications, including charge transport.^{13–15} Solar cell devices incorporating the resulting 3,4-dioxythienyl- and BTD-based copolymers have so far revealed power conversion efficiencies exceeding 3% under AM 1.5 illumination.¹⁵

In subsequent work from our group,¹⁶ reducing the composition of electron-deficient heterocycles incorporated along the conjugated backbone (i.e., increasing the length of the electron-rich oligothiophylene blocks) was shown to induce a simultaneous bathochromic shift of the short-wavelength absorption band and hypsochromic shift of the long-wavelength counterpart, with both peaks tending toward the λ_{max} of the all-donor control homopolymer. This phenomenon resulted in the merging of the two optical transitions, with the relative intensity of the low and high energy peaks evolving toward balancing each other.

In an effort to reach a better understanding of the subtle spectral variations being induced by changing the ratio of electron-rich to electron-poor heterocycles, two polymer series were synthesized with various contents of 3,4-dioxythiophene and BTD in the main-chain (see Figure 2a and b, **P3–P6** and **P7–P10**).¹⁶ At this point, it is worth noting that, in spite of the

discrepancies sometimes found throughout the literature, conjugated polymers should not be considered as small-molecule chromophores, as they do not possess a well-defined molecular weight which could be used in the determination of molar absorption coefficients (in $\text{L mol}^{-1} \text{cm}^{-1}$). In most instances, the reported molar absorption coefficients are estimated considering the molecular weight of the polymer repeat unit as the mass of the “chromophore”. However, it is well-accepted that the effective conjugation length in polymer chromophores is normally not limited to a single repeat unit, and the electronic delocalization of the π -system extends beyond a few heterocycles.¹⁷ In addition, conjugated polymers often possess repeat units with various numbers of heterocycles (i.e., of various masses), and the same calculations would certainly lead to results without physical significance. An assumedly more elegant alternative would consist in reporting “attenuation coefficients” (formerly “extinction coefficients”), that is, values directly measured from the polymer thin films and accounting for scattering and luminescence.¹⁸ Nevertheless, in any study involving subtle changes in the molecular structure of a homologous series of polymers, the spectral changes induced are expected to be relatively subtle as well. As such, it is likely that the experimental error inherent to the film-thickness measurements (film inhomogeneity in particular)¹⁹ will be sufficient to compromise the relevance of the results here as well. Following these considerations, polymers **P3–P10** are herein investigated in terms of their mass absorption coefficients (in $\text{L g}^{-1} \text{cm}^{-1}$) in toluene, which were subsequently converted to “thin-film” absorption coefficient values (in cm^{-1}) by assuming a density of 1 g cm^{-3} for all polymers (e.g., poly(3-octylthiophene) $\sim 1.05 \text{ g cm}^{-3}$).²⁰ Figure 2 illustrates the corresponding spectral changes among **P3–P6** (Figure 2c) and **P7–P10** (Figure 2d), respectively.

Following this approach, the absorption coefficients estimated for the polymers across the UV–visible region, and represented in Figure 2c and d, indicate a depletion of the longer-wavelength absorption band with decreasing extent in electron-accepting heterocycles along the polymer main-chain. This depletion appears especially sudden from **P3** to **P4** as well as from **P7** to **P8**, which points toward a stronger donor–acceptor effect as the electron-deficient units remain in sufficiently close spatial proximity (i.e., as the all-donor spacers remain sufficiently short). In parallel, the shorter-wavelength absorption bands shift toward longer wavelengths (i.e., toward the optical spectrum of the all-donor control polymer) with a relatively constant intensity according to the optical data presented in Figure 2c and d. The relative leveling off of the short-wavelength optical transition is somewhat unex-

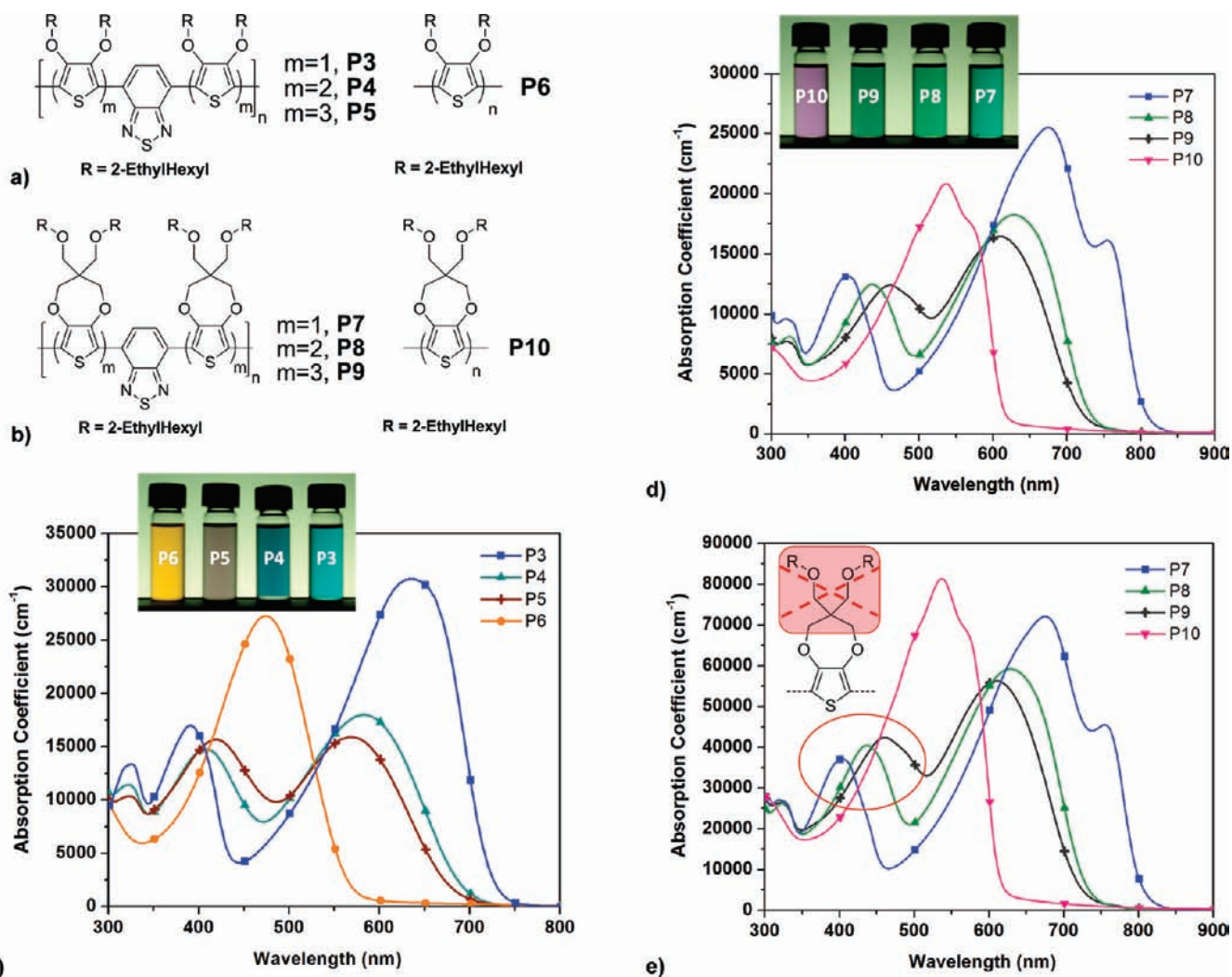


FIGURE 2. Molecular structures for the DA-polymer series (a) **P3–P5** (along with that for the control polymer **P6**) and (b) **P7–P9** (along with that for the control polymer **P10**). Absorption coefficients as a function of wavelength among the DA-polymer series (c) **P3–P5** (along with those for the control polymer **P6**) and (d) **P7–P9** (along with those for the control polymer **P10**). The absorption coefficients (in cm⁻¹) are derived from the mass absorption coefficients (in L g⁻¹ cm⁻¹) measured in toluene solution by assuming a density of 1 g cm⁻³ for all polymers. The insets show the various colors obtained across the polymer series (solutions in toluene) as a function of the number of electron-donating and -accepting units composing the polymer repeat unit. (e) Absorption coefficients for the DA-polymer series **P7–P9** (along with those for the control polymer **P10**) are represented considering hypothetical unsubstituted backbones (i.e., by subtracting the mass associated to the side-chains as illustrated on inset).

pected, although it is likely that this transition develops as rapidly as the long-wavelength transition depletes on further reducing the concentration of electron-accepting heterocycle along the polymer main-chain. The distinct optical feature observed in the 750–800 nm range in the case of **P7** is attributed to an intermolecular interaction, as both solvent and temperature were found to alter its intensity. It is worth noting that the absorption coefficients of all the DA systems characterized remain particularly high (in the 10 000–30 000 cm⁻¹ range) in agreement with the extended electronic delocalization expected for π -conjugated polymers.

Finally, it is essential to keep in mind that these optical results were obtained from mass absorption coefficients

estimated from a given mass of material subsequently dissolved in a given volume of solvent. At the same time, all polymers do not possess the same concentration of solubilizing group, and as a result the various weighted quantities of polymers do not contain the same quantity of chromophore (conjugated segment ideally unsubstituted). For instance, a given mass of **P3** should contain a larger extent of chromophores than the same mass of **P5**, since one heterocycle out of three is unsubstituted in the case of **P3**, whereas only one heterocycle out of seven is unsubstituted in the case of **P5**. This important fact could be a contributing factor in the leveling off observed for the short-wavelength optical transition of **P4** and **P5** relative to **P3**,

and of **P8** and **P9** relative to **P7**. Although the approximations made in this contribution so far appear reasonable (Figure 2c and d), the variations induced by side-chain length and density along the backbone highlight the need for a more accurate approach to determining polymer absorption coefficients based on the concentration of actual chromophores in the main-chain (i.e., factoring out the side-chain dependence).

To exemplify the large contribution of the nonaromatic and/or solubilizing side groups in the absorption coefficient values estimated for π -conjugated polymers in general, the mass of actual chromophore contained in the repeat unit of each polymer composing the series **P7–P10** (i.e., the mass of covalently bound aromatic building units excluding their pendant-substituents here) was first assessed and then used to calculate the weight ratio with each substituted repeat unit. Those ratios yielding the fraction of the repeat unit truly contributing to the polymer optical spectrum were utilized to better represent the relative intensity of absorption across the polymer series. The “corrected” absorption coefficients are shown as a function of wavelength in Figure 2e. In this configuration, the shorter-wavelength absorption bands (circled red) shift toward

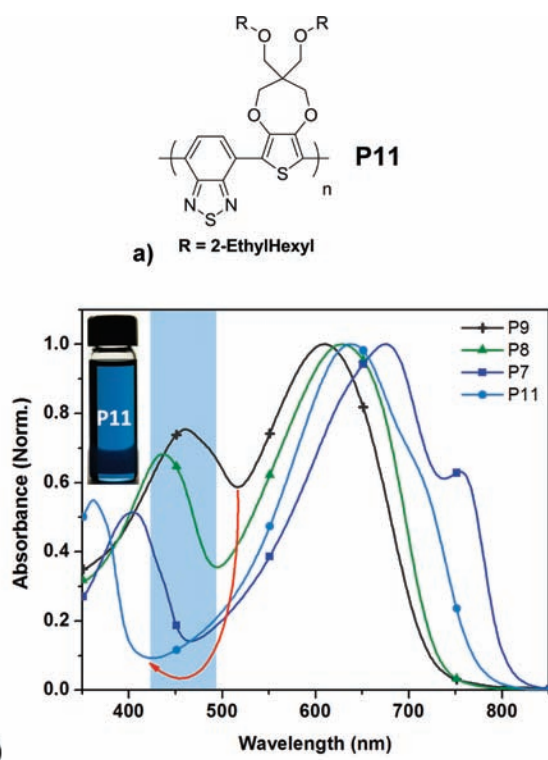


FIGURE 3. (a) Repeat unit structure for the strictly alternating DA copolymer **P11**. (b) Superimposed UV–visible solution absorption spectra of **P7–P9** and **P11** in toluene (the spectra are normalized at the longer-wavelength absorption maxima of the polymers). (Figure adapted with permission from ref 21. Copyright 2009 Wiley-VCH.)

longer wavelengths as previously observed, but now also develop in intensity (as opposed to leveling off as in Figure 2d) with increasing number of electron-rich units incorporated in the repeat unit. In addition, the depletion of the longer-wavelength absorption band observed on going from **P7** to **P8** is not as large as that described in Figure 2d where no account for the solubilizing side-chains is made. Importantly, the coefficients estimated for the hypothetical “nonsubstituted” polymers appear much larger (in the 30 000–80 000 cm^{-1} range) than those of their substituted counterparts illustrated in Figure 2d. Overall, this approach considering the mass of actual chromophore contained in a given amount of π -conjugated polymer dissolved in solution (and exemplified in Figure 2e) appears especially suitable in the representation and comparison of optical spectra among polymer systems with distinct repeat units.

In an extension of the “donor–acceptor” approach, the strictly alternating ProDOT-BTD copolymer **P11** was synthesized to demonstrate how the spectrum can be tailored to open a broad window of transmission in the high-energy region of the visible, thereby producing neutral state saturated blue electrochromes.²¹ As illustrated in Figure 3, the extent of electron-rich building units along the polymer backbone was reduced to a point where the short-wavelength absorption band of the polymer is fully transferred into the UV to maximize the blue transmission, while the long-wavelength optical transition extends from the green region, up to the near-IR.

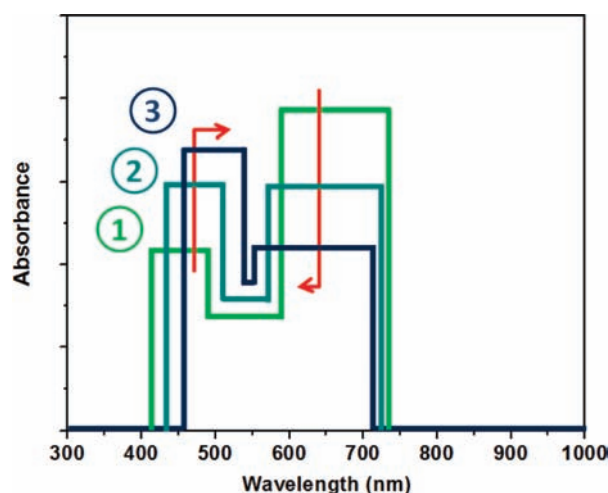


FIGURE 4. Schematic representation of the evolution of the dual-band spectral absorption across a series of DA conjugated polymers with varying concentration of electron-rich and electron-deficient substituents along the backbone (with well-defined repeat units). The increase in electron-rich character of the main-chain induces the optical changes occurring on going from spectrum 1 to 3.

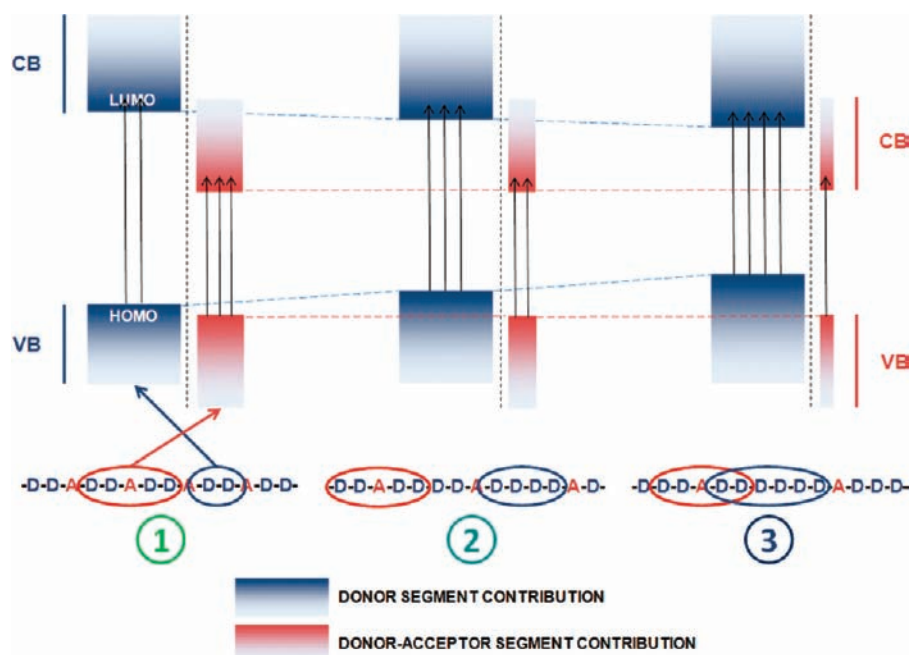


FIGURE 5. DA conjugated polymers are seen with “distinct chromophores along the backbone”.

On the Origin of the Dual Band of Absorption

Following the empirical considerations developed throughout the previous section of this Account, a certain number of assumptions can be made regarding the origin of the dual-band spectral absorption seen in π -conjugated polymers with moderately strong intramolecular “donor–acceptor” interactions. In this respect, Figure 4 consists of a schematic representation of the logical evolution of the dual-band absorption among a series of DA conjugated polymers with varying concentration of electron-rich and electron-deficient units along the backbone (yet with well-defined repeat units, in analogy with the polymer series previously discussed). In this most plausible configuration (see absorption coefficient values estimated for hypothetical unsubstituted backbones in Figure 2e), the increase in electron-rich character of the main-chain induces the optical changes occurring on going from spectrum 1 to 3. Those optical changes include a depletion of the longer-wavelength absorption band with decreasing number of electron-deficient heterocycles (right arrow), along with an increase of intensity and a significant bathochromic shift for the shorter-wavelength absorption band (left arrow). With the relative intensity and position on the spectrum varying for the two transitions observed, the width of the transmission window separating the bands changes, and a fine color tuning occurs in the neutral state of the resulting polymer electrochrom. A selected number of conceptual representations of

the possible mechanisms governing the optical pattern observed are presented within the next subsections.

Donor–Acceptor Polymers Seen with “Distinct Chromophores along the Conjugated Backbone”. In a first assumption, a model considering the described conjugated polymers as involving “two distinct chromophores” can be proposed. The corresponding model is shown as Figure 5. In this simplistic approximation, the optical changes schematically described in Figure 4 can be seen as the result of the coexistence of an electron-rich chromophore (whose set of energy bands is represented in blue), involving an increasing number of heterocycles (i.e., whose energy gap narrows gradually, hence red-shifting the corresponding optical transition in the spectrum), with a second chromophore (whose set of energy bands is represented in red) resulting from the donor–acceptor interaction induced by the presence of an electron-deficient heterocycle. In this configuration, the spectral absorption relative to the chromophore arising from the DA interaction should remain relatively constant in terms of its position on the spectrum (onset of absorption, absorption maximum) as each flanked accepting unit should only be able to interact with a limited number of neighboring donors. Its intensity should deplete as the DA chromophores are dispersed along the main-chain (i.e., as the all-donor spacers become longer, in turn increasing the electron-rich character of the polymer). The diminution of DA chromophores is schematically represented by the narrowing of the width of their

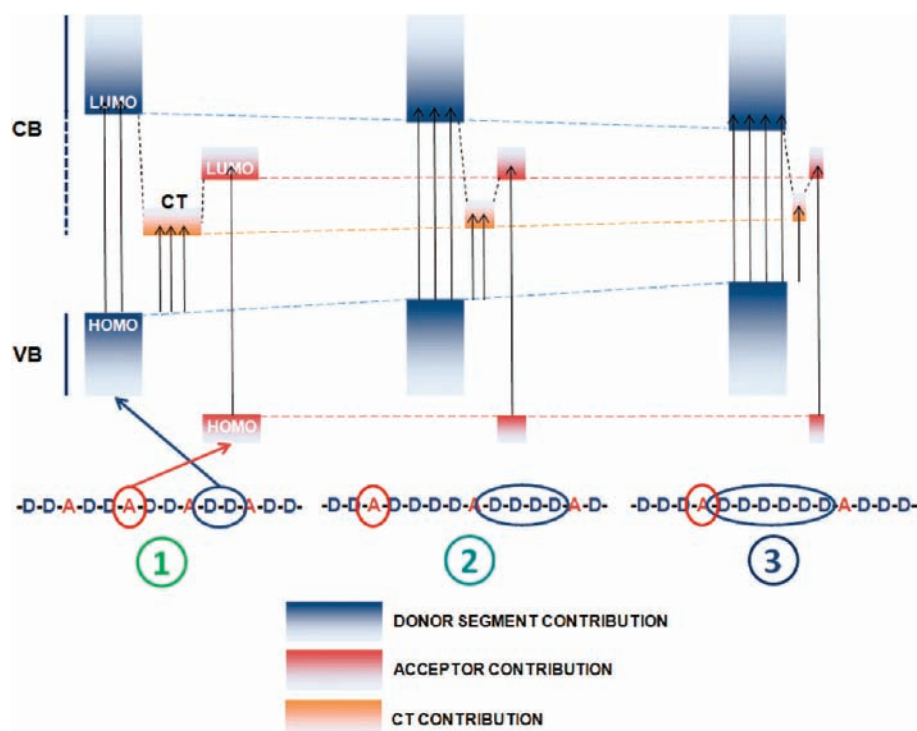


FIGURE 6. Electron-accepting units are seen as “isolated dopants” which induce the formation of low-lying charge separated energy states (CTs) with the neighboring electron-donating units.

corresponding energy band diagram (on going from case 1 to 3). A diminution of the number of optical transitions occurring between the valence and conduction bands should correlate to the diminution of DA chromophores. In parallel, an increase in the number of optical transitions occurring between the valence and the conduction bands of the growing electron-rich segments can reasonably be expected (see case 3).

As a close alternative to the model shown in Figure 5, the configuration described in Figure 6 proposes to see the electron-accepting heterocycles as “isolated dopants” which can interact with the neighboring electron-donating heterocycles to induce the formation of low-lying charge-transfer energy states (CT). This consideration implies an effective formation of intramolecular charge-transfer states stabilizing the donor–acceptor complexes covalently bound along the polymer backbone. In this case, the long-wavelength absorption band can be seen as the result of low-energy transitions occurring from the ground state of the polymer (S_0) to the CT (represented in orange in Figure 6). As the concentration in “dopants” decreases along the backbone, the concentration of accessible CTs decreases as well to the point where most transitions are localized on the donor segments. The diminution of “dopants” in the main-chain is schematically represented by the narrowing of the width of their energy correlation diagram (on going from case 1 to 3). In parallel, an increase in

the number of optical transitions occurring between the valence and the conduction bands of the growing electron-rich segments (whose energy gap narrows gradually, hence red-shifting the corresponding optical transition in the spectrum) can reasonably be expected here as well. Additionally, it is worth noting that, in this configuration, even higher-energy optical transitions from energy states localized on the “dopants” could possibly arise in the UV.

Such a model based on the assumption of low-energy charge transfer transitions is routinely implied throughout the literature. For instance, on the basis of some specific examples, it has been suggested that the two-band optical absorption can be associated with a π – π^* transition localized on either the donor or the acceptor (high-energy transition yielding a first chromophore), along with a transition arising from the *intramolecular* charge transfer inherent to the DA system (low-energy transition affording the second chromophore) and identified as a spin-allowed transition from the ground state of the system (S_0) to a charge-separated state (CT).^{22,23}

Importantly, this interpretation assumes that the internal electron-accepting moiety is sufficiently strong to induce the formation of an actual charge-separated state (either partially or fully separated in character), which further implies that a true charge-transfer process is at work within the polymer main-chain, and that a relatively strong degree

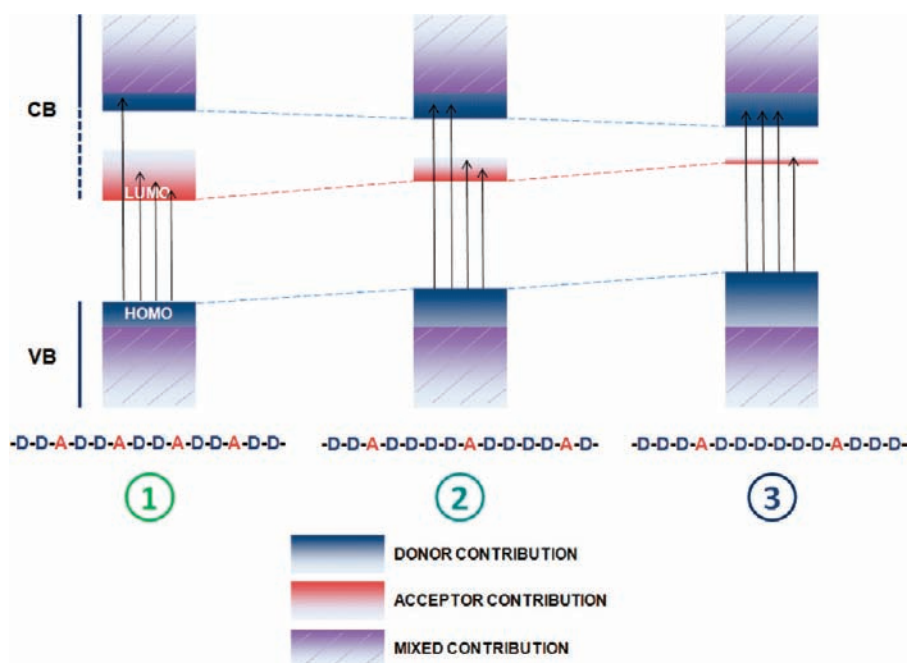


FIGURE 7. DA conjugated polymers are seen as “following frontier molecular orbital theory principles”.

of charge localization occurs along the backbone. In general, and depending on the context, it appears that a disambiguation of the concept of “intramolecular charge-transfer” itself may be necessary to indicate whether the transfer of an actual electron is involved, or if partial transfer of charge density qualifies as “intramolecular charge transfer”.

With the idea of probing the relevance of a model relying on charge-transfer characteristics, the transition densities (indicating regions of the molecule associated with a given transition) and the charge-difference densities (visualizing changes in electron density upon excitation) have been modeled in DA polymers possessing distinct electron-accepting strengths.²⁴ The corresponding study indicated that the lower-energy optical transitions of the polymers considered were significantly localized onto the acceptor and its adjacent heterocycles, suggesting a relatively strong charge-transfer character. On the other hand, the higher-energy optical transitions were more delocalized along the backbones, suggesting more valence character.

Donor–Acceptor Conjugated Polymers Seen as “Following Frontier Molecular Orbital Theory Principles”. An alternative to the approach described above relies on basic “frontier molecular orbital theory” principles. In this instance, the DA π -conjugated polymer is seen as an extended array of π orbitals delocalizing electrons along the backbone. These orbitals are hybridized to produce a unique energy band diagram for the DA macromolecular system. The corresponding model is shown as Figure 7. In this case, the presence of two bands of absorption in the optical spectrum of the polymer is

tentatively explained by the introduction of a discrete energy band (represented in red) in the “band gap” of the semiconducting material, easily accessed from the valence band (represented in blue and purple) and which can act as a “conduction band” for the system. Here, the existence of low-lying unoccupied and localized energy levels within the “band gap” of the conjugated system in its ground-state would stem from the incorporation of electron-deficient heterocycles having low LUMOs with limited orbital mixing with those of the electron-rich moieties. In turn, the concentration of accessible energy states is expected to increase with increasing number of accepting moieties incorporated along the main-chain (on going from case 3 to 1). The low-energy transitions to the discrete energy band can subsequently be envisaged to produce a long-wavelength absorption band, whereas high-energy transitions arising from the top of the valence band (dominated by the donors, and represented in blue) to the electron-rich segments’ first unoccupied energy levels (also represented in blue) can be seen to produce a blue-shifted absorption band in the visible spectrum. In this configuration, the optical absorption associated with the low-energy transitions could undergo a progressive hypsochromic shift in the visible spectrum, and depletion in terms of its intensity, with diminishing number of electron-deficient heterocycles along the main-chain (i.e., as the all-donor spacers become longer, the extent of hybridization between accepting units is reduced, and the concentration of “midgap” energy levels accessible decreases). The diminution of accessible energy levels within the discrete energy band is schematically represented by the

narrowing of its size in the energy correlation diagram of the DA macromolecular system (on going from case 1 to 3), to which a diminution of the number of related optical transitions is expected to correlate. In parallel, an increase in the number of optical transitions occurring between the valence band and the first unoccupied energy levels governed by the growing electron-rich segments can reasonably be expected (with the energy gap between the valence band and those unoccupied energy levels narrowing gradually, hence red-shifting the corresponding optical transition in the spectrum).

This view has been explored by Salzner and co-workers, for example, throughout theoretical work aimed at addressing the relevance of the “donor–acceptor” approach for designing organic metals.^{25–27} It has frequently been considered as a reasonable approach throughout the literature looking to provide an origin for the relatively unconventional dual-band optical spectra.^{4,6,7}

Extending the Concept to the Synthesis of Broadly Absorbing Chromophores

By “Filling” the Dual-Band Polymer Absorption with a Complementary Spectrum. Given the present fast-growing interest for e-paper technologies and information displays,²⁸ extending the absorption spectrum of a polymer electrochrome homogeneously across the visible region to produce a chromophore essentially black in its neutral state appears to be the next logical step in the design of electrochromics addressing the requirements for the cost-effective manufacturing of large-area flexible device applications. In an attempt to overcome the lack of coverage in the red and blue-green regions of the visible in the case of **P5** and in the blue and green regions in the case of **P9** (see Figure 2), it was anticipated that, by oxidatively copolymerizing, for instance, the monomers constitutive of **P7** and **P10** (**P10** being the all-donor control polymer) in a random fashion but in an appropriate feed ratio, the molecular structure of the resulting hybrid could be sufficiently disordered to provide a broad and relatively homogeneous spectral absorption over the visible region. This hypothetical situation is exemplified by the blue dotted spectrum presented in Figure 8 (and further detailed in the corresponding caption). In practice, an optimal feed ratio was found to be 1 equiv of the donor–acceptor monomer block of **P7** to 4 equiv of the donor monomer unit of **P10**, which corresponded to the same monomer composition as that of the well-defined analogue **P9** in terms of electron-rich to electron-poor substituents incorporated. The repeat unit structure of the resulting copolymer hybrid **P12** and its spectroelectrochemical profile under progressive application of an

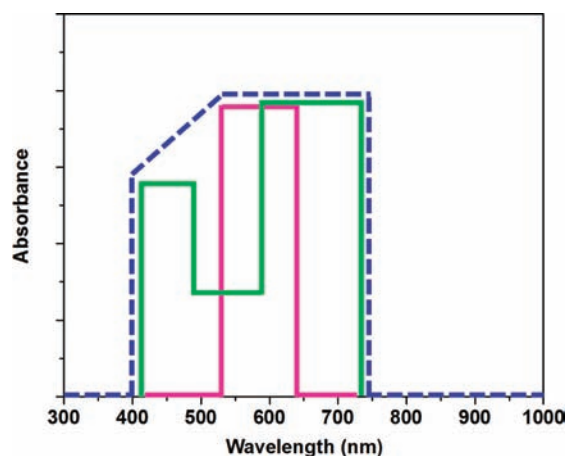


FIGURE 8. Schematic representation of the optical spectrum of a dual-band absorbing polymer reflecting the color blue-green (green curve, e.g., **P7**), superimposed to that of a polymer possessing a unique (and complementary) π – π^* transition (pink curve, e.g., **P10**). Copolymerization of their constitutive monomers could result in a polymer hybrid possessing segments of various compositions, in turn producing the hypothetical optical spectrum shown as the blue curve. The extensive absorption from 400 to 700 nm is characteristic of an inklike black chromophore with minimal blue transmission.

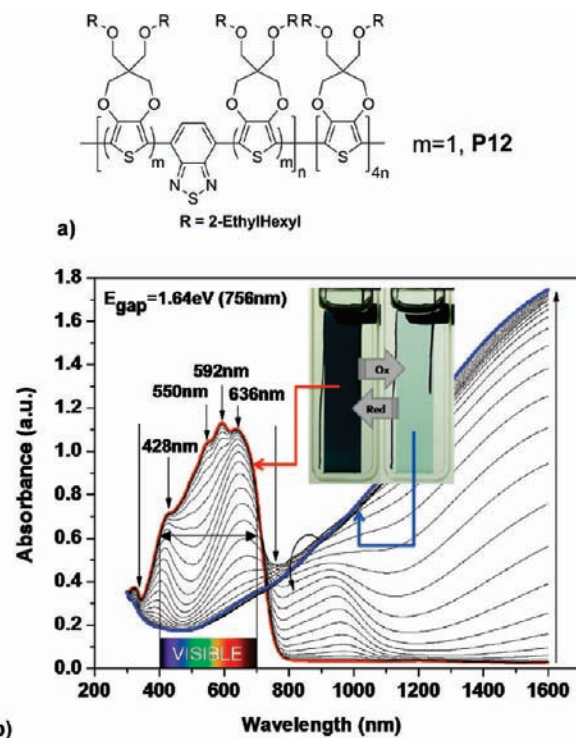


FIGURE 9. (a) Repeat unit structure for the DA copolymer hybrid **P12**. (b) Spectroelectrochemistry of **P12** in 0.1 M LiBF₄/polycarbonate supporting electrolyte. The film was spray-cast onto ITO-coated glass from solution (4 mg mL⁻¹) in toluene. The applied potential was increased in 25 mV steps from +0.04 to +0.74 V (against Fc/Fc⁺). (Figure adapted with permission from ref 16. Copyright 2008 Nature Publishing Group.)

external bias oxidizing the electrochrome (a highly transmissive state is attained) are shown in Figure 9.

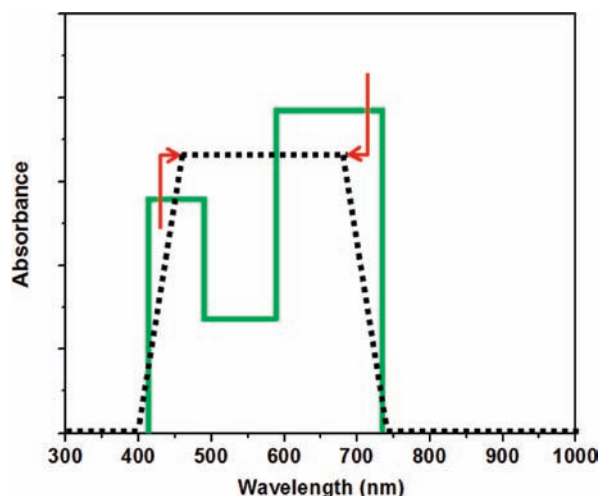


FIGURE 10. Schematic representation of the hypothetical coalescence of a dual-band optical spectrum as desired in achieving broadly absorbing chromophores essentially black in color (dotted black curve). Could low- and high-energy transitions be controlled in terms of their intensity and extent of mutual overlap so as to balance and extend the optical pattern of the subsequent chromophore over the visible region?

By Coalescence of the Two Bands of Absorption. In the ideal case, the optical spectrum of a π -conjugated semiconducting polymer addressing the requirements for light-harvesting applications extends across the entire visible spectrum and into the near-IR, while maintaining large absorption coefficients. This spectral coverage should be possible for a chromophore combining low band gap and a widespread continuum of accessible energy states forming the conduction band.

Based on the empirical results obtained when varying the relative extent of electron-rich and electron-deficient heterocycles along a “donor–acceptor” backbone, and summarized in Figure 2, it can be argued that the coalescence of a dual-band optical absorption into a relatively balanced spectrum spanning the visible could occur by employing a particularly electron-donating moiety (in the case where the higher-energy transition is indeed strongly dominated by the donors). This hypothetical situation is exemplified by the black dotted spectrum presented in Figure 10. In analogy with the optical changes illustrated in Figure 4, the two bands of absorption evolve toward balancing their relative intensities on increasing the number of electron-rich units incorporated in the main-chain (according to red arrows), while their more rapid merging closes the blue-green window of transmission previously emphasized. Under this same assumption, bridged bithienyl building blocks such as the high-lying HOMO unit dithieno[3,2-*b*:2',3'-*d*]silole (DTS, shown in Figure 11a) were envisioned to replace the 3,4-dioxythienyl moieties incorpo-

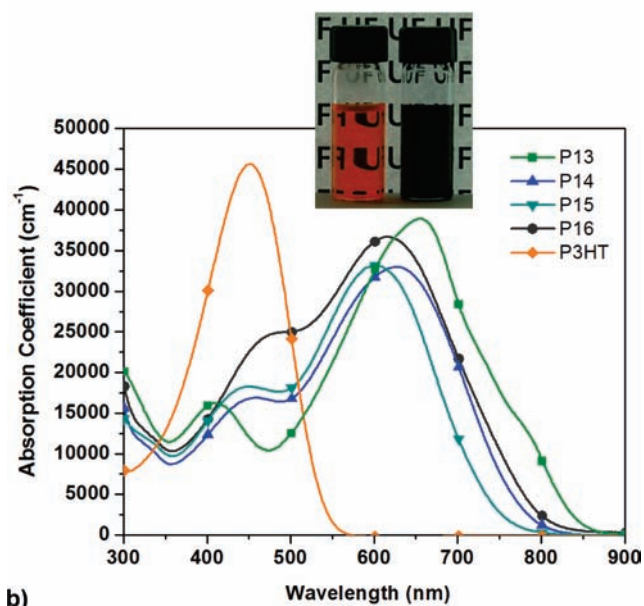
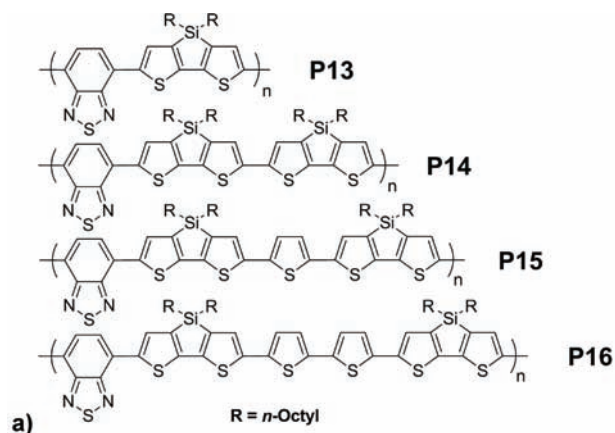


FIGURE 11. (a) Molecular structures for the DA-copolymer series **P13–P16**. (b) Absorption coefficients as a function of wavelength among the DA-copolymer series **P13–P16** (along with those for **P3HT**). The absorption coefficients (in cm^{-1}) are derived from the mass absorption coefficients (in $\text{L g}^{-1} \text{cm}^{-1}$) measured in toluene solution by assuming a density of 1 g cm^{-3} for all polymers. The inset shows a solution of P3HT (left) and **P16** (right) in toluene (both 0.3 mg mL^{-1}).

rated in the polymer backbones described so far in this Account, as a candidate for light-harvesting applications where charge transport also is a critical parameter.

As illustrated in Figure 11, π -conjugated polymers composed of the bridged electron-rich DTS in conjunction with the electron-deficient BT (DTS and unsubstituted thiophenes), exhibit especially broad absorption spectra in the visible.²⁹ In this case, the dual-band of absorption arising from the “donor–acceptor” characteristics of the conjugated main-chain merges rapidly into a more continuous spectrum across the polymer series (on going from **P13** where

the dual-band is evident to **P16** where the dual-band is coalesced). The shorter-wavelength optical transition undergoes the most notable shift in the visible region, hence supporting the large contribution from the most electron-rich heterocycles. Here, it is worth noting that the longer-wavelength absorption band dominated by the “donor–acceptor” interaction itself remains relatively intense across the polymer series, which can be attributed to the difference in concentration of solubilizing side-chains for the various analogues (**P16** presenting the largest concentration of chromophores at a given mass of material subsequently dissolved in a given volume of organic solvent), as previously argued in this Account.

In comparison to poly(3-hexylthiophene) (P3HT, orange curve in Figure 11 b), this homologous series of DTS-BTD copolymers absorbs more effectively where the solar photon flux is maximum (in the 600–800 nm range), while retaining similarly large absorption coefficients at their longer-wavelength absorption maximum and exhibiting a spectral breadth of absorption extending over the visible spectrum. Overall, as can be seen in the inset to Figure 11, **P16** absorbs across the whole visible spectrum, hence its black hue in solution, while P3HT absorbs selectively in the blue region and does not harvest light at longer wavelength. Along those lines, the 2-ethylhexyl-derivatized counterpart of **P13** was recently shown to exhibit state-of-the-art power conversion efficiencies in the 4.7–5.3% range in bulk heterojunctions (BHJs) with PC₇₀BM.^{1,30} Inspection of the BHJ devices made with **P13** revealed particularly broad external quantum efficiency patterns extending from 400 to 800 nm with values ranging from 40 to 60% in the same region. In parallel, beyond the breadth of their spectral absorption, it is expected that the variations in microstructural order and charge transport properties observed on going from **P13** to **P16** impact the photovoltaic performance throughout the polymer series.²⁹

Concluding Remarks

In summary, the concept of “spectral engineering”, broadly defined as looking to tailor the complex interplay lying between molecular physics and the various optical phenomena occurring across the electromagnetic spectrum of π -conjugated polymers, applies beyond simple band gap control principles. With perspectives in the optimization of the light-harvesting properties of photovoltaic polymers, as well as in the fine-tuning of colors in nonemissive electrochromes for display applications, deciphering the correlations between structural modifications and the spectral changes induced in “donor–acceptor” systems with extended π -conjugation remains a *sine qua non* of new material design.

The schematic representations proposed to depict the possible mechanisms at the origin of the spectral changes observed in two-band absorbing conjugated polymers with varying concentrations of electron-rich and electron-deficient units along the main-chain suggest further empirical and theoretical developments aimed at elucidating the controversy. Taking full advantage of the complex interactions existing in semiconducting “donor–acceptor” polymers intentionally designed to address the challenges of optoelectronic device applications may require a more comprehensive understanding of this approach at both molecular and macromolecular levels.

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Pierre M. Beaujuge received his Ph.D. in August 2009 working with Prof. John R. Reynolds at University of Florida, Gainesville. His doctoral research was directed toward developing novel π -conjugated semiconducting polymers with tunable optical and charge transport properties for optoelectronic applications. Pierre is now a Postdoctoral Associate at University of California, Berkeley, working with Prof. Jean M. J. Fréchet.

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John R. Reynolds is a V.T. and Louise Jackson Professor of Chemistry at the University of Florida with expertise in polymer chemistry and serves as an Associate Director for the Center for Macromolecular Science and Engineering. His research interests have involved electrically conducting and electroactive conjugated polymers for over 30 years with work focused on the development of new polymers by manipulating their fundamental organic structure to control their optoelectronic and redox properties.

FOOTNOTES

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