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Light-harvesting capabilities of low band gap donor–acceptor polymers

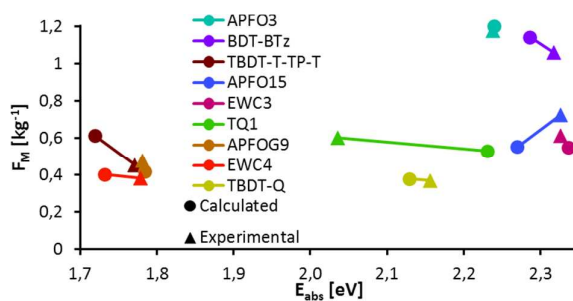
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The ability of three new and six existing donor-acceptor polymers to absorb strongly at low photon energies is studied experimentally and theoretically, and is related to their chemical structures.

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ABSTRACT

A series of nine donor–acceptor polymers, including three new and six polymers from previous work, have been investigated experimentally and theoretically. The investigation focuses on narrow band gaps and strong absorptions of the polymers, where experimentally determined first peak absorption energies range from 1.8 to 2.3 eV, and peak absorption coefficients vary between 19–67 L g⁻¹ cm⁻¹. An overall assessment of each polymer’s light-harvesting capability is made, and related to the chemical structure. Oligomer calculations using density functional theory are extrapolated to obtain size-converged polymer properties, and found to reproduce the experimental absorption trends well. Accurate theoretical predictions of absorption energies to within 0.06 eV of experiments, and absorption strength to within 12%, are obtained through the introduction of an empirical correction scheme. The computational and experimental results provide insight for the design of polymers with efficient absorption, concerning the intrinsic properties of the constituent units and the use of bulky side-groups.

INTRODUCTION

Organic photovoltaics (OPVs) are promising as energy producing devices.^{1,2,3} They typically consist of a conjugated polymer capable of absorbing visible light, mixed with a Buckminsterfullerene derivative. Since the polymer is the main light-absorbing component, the choice of polymer dictates the optical response of the cell. Poly(3-hexyl-thiophene-2,5-diyl) (P3HT) has been very commonly used since the late 20th century,⁴ but its limited spectral coverage has prompted extensive research to find donor-acceptor (D-A) copolymers with better light-harvesting capabilities.^{5,6,7,8} These D-A polymers consist of alternating electron-donating and -accepting moieties along the conjugated backbone, and by varying these building blocks, the absorption profile of the polymer can be tuned. Several experimental^{5,9,10,11} and computational^{12,13,14,15,16} studies have been published recently on D-A polymers yielding high-efficiency solar cells. The most important optical properties of D-A polymers are the absorption strength and optical band gap. Strong absorption and narrow optical band gaps of <2 eV both contribute to the number of photons absorbed and thus the external quantum efficiency (EQE),² and current (J) generated by the OPV device.

Optical and electronic properties of polymers typically depend on the conformation which is sensitive to the environment, as well as being hard to determine experimentally. In this study, polymers have been studied experimentally in solution, providing a good opportunity for deeper understanding of the intrinsic properties of individual polymer chains, and for detailed comparison with molecular quantum chemical calculations. Computational analysis provides a deeper understanding of the structure-property relationship in polymers, which can guide the development strategies for new polymer motifs. Quantitative calculations of optical properties furthermore have the potential to reduce the time-consuming effort of synthesizing a large number of D-A polymers, and subsequently making films and analyzing them experimentally.

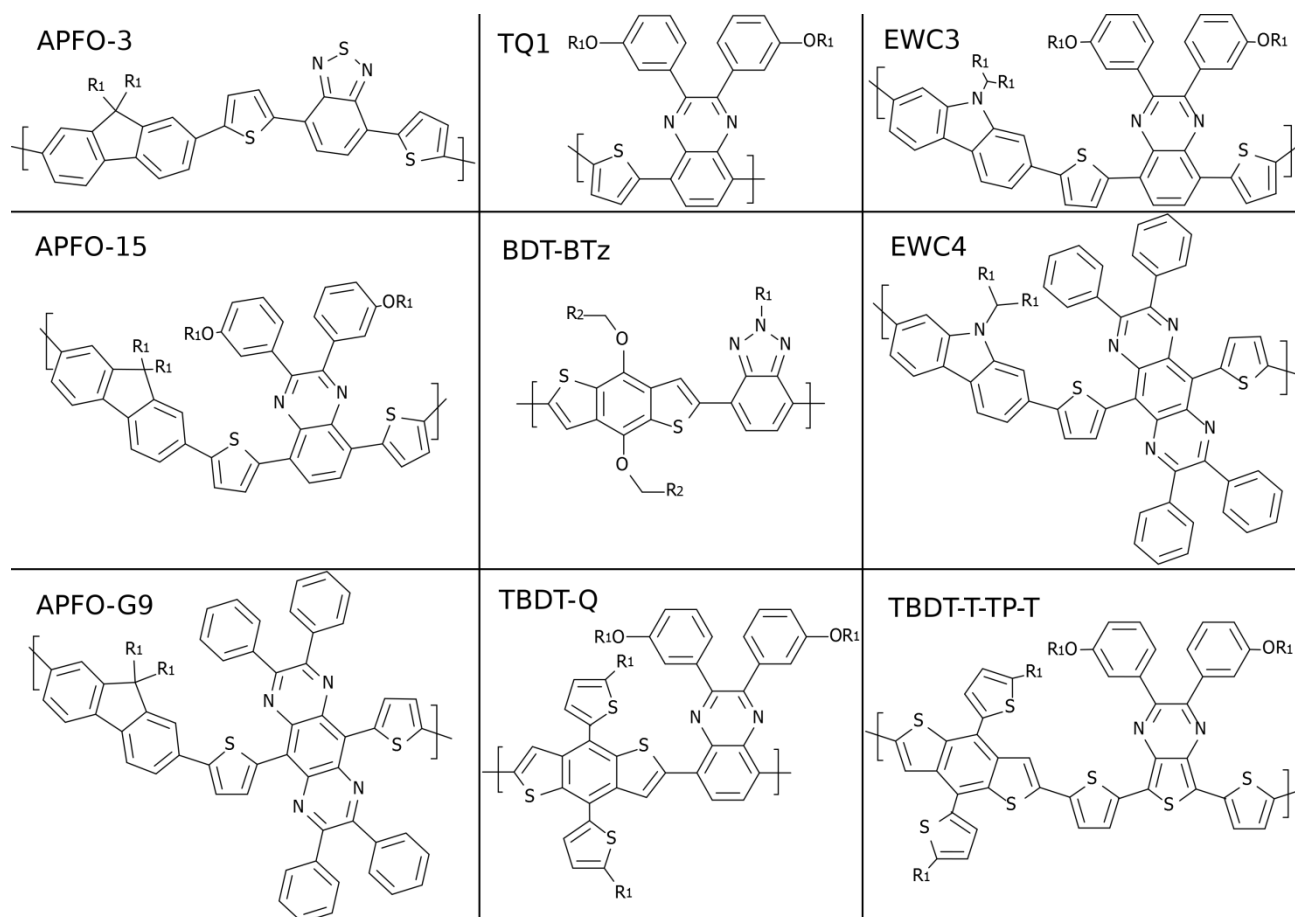
This aids the development of more efficient OPVs,^{17,5,18,19} even though complete accuracy of the computational methods remain a challenge. Single-molecule calculations constitute a stepping stone towards more elaborate calculations of polymer films and blends where intermolecular interactions play a more significant role.

Six previously reported D-A polymers with various donor and acceptor components and diverse optical traits are here investigated: APFO-3,²⁰ APFO-15,²¹ APFO-G9,²² EWC3,²³ and TQ1,²⁴ developed at Polymer Technology at Chalmers University, and BDT-BTz²⁵. Three new polymers were synthesized for the first time to further explore chemical components conferring narrow band gaps and/or strong absorption: TBDT-Q named for its thienylbenzodithiophene (TBDT) donor and quinoxaline (Q) acceptor, TBDT-T-TP-T with a thiophene–thienylbenzodithiophene–thiophene donor and thienopyrazine (TP) acceptor, and EWC4 with a thiophene–carbazole–thiophene donor and pyrazinoquinoxaline (PzQ) acceptor. TBDT-Q, BDT-BTz, and TQ1 consist of one donor and one acceptor ring-system per repeating unit, whereas the remaining six polymers have donors of type T–X–T where X = fluorene, carbazole, or thienylbenzodithiophene and T = thiophene. Overall, this set of selected polymers represents the diversity in structures and properties covered by D–A polymers applied in OPVs today. Five different donor and five acceptor units are used throughout the nine polymers, and their structures are outlined in Chart 1.

This article is centered on the assessment of light-harvesting capabilities across the series of nine polymers, with particular emphasis on narrow band gaps and strong absorption. Quantitative comparison between experimental measurements and calculated results was used to develop a highly accurate computational scheme for size-converged absorption energies and strengths, providing the means to efficiently predict experimental properties. In the results sections, structural features of the nine polymers are first presented, followed by electronic properties, and

a discussion regarding light-harvesting potential. The outcomes of measurements and calculations are finally discussed and compared in order to identify promising polymer design strategies.

Chart 1. Chemical structures of the nine investigated polymers. R_1 =1'-octyl, R_2 =3'-heptyl, R_3 =1'-hexyl.



METHODS

General

Unless otherwise stated all reactions were performed under nitrogen atmosphere and all chemicals were bought from Sigma-Aldrich or Acros and used as received. Anhydrous THF was dried over and distilled from sodium benzophenone ketyl under an atmosphere of dry nitrogen.

Optical characterization

Absorption spectra were measured using a Perkin Elmer 900 UV/VIS/NIR. Samples were prepared by dissolving ~1 mg polymer in 50 mL of ortho-dichlorobenzene (o-DCB), which was chosen for its good dissolving capacity, while its absorption in the UV region does not affect the results which focus on the red-most absorption peaks of the polymers. The polymer solutions were heated up to ensure complete dissolution of the polymer into the solvent and then allowed to cool down to room temperature before the spectra were recorded. The experimental absorption coefficients ϵ (in $\text{L g}^{-1} \text{cm}^{-1}$) were calculated from Beer-Lambert's law: $A = \epsilon cl$.

Electrochemical characterization

Square-wave voltammetric measurements were carried out using a 0.1-M solution of tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile as supporting electrolyte at a scan rate of 125 mV s^{-1} . A CH-Instruments 650 D electrochemical workstation using a three electrode setup was used, consisting of a Ag/Ag^+ reference electrode and platinum wires as working- and counter electrodes. The polymer was deposited onto the working electrode from chloroform solution. The electrolyte was bubbled with nitrogen gas prior to each experiment in order to remove oxygen from the system. During the scans the nitrogen inlet was raised above the electrolyte surface to not disturb the measurement. After each experiment a calibration scan using the ferrocene/ferrocenium (Fc/Fc^+) redox reaction was performed. The highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were approximated

from the third oxidation and reduction scan respectively, using the peak values and setting the oxidative potential of Fc/Fc^+ vs. the normal hydrogen electrode (NHE) to 0.630 V²⁶ and the NHE vs. vacuum to 4.5 V.²⁷

Size exclusion chromatography

Waters Alliance GPCV2000 with refractive index detector columns: Waters Styvigel HT GE $\times$ 1, Waters Styvigel HMW GE $\times$ 2. The operating temperature was 135 °C, the eluent used was 1,2,4-trichlorobenzene and the dissolution time was 2 h. The samples were filtered prior to analysis (0.45 μm) and the concentration was 0.5 mg mL⁻¹. The molecular masses were calculated using polystyrene standards for relative calibration.

Synthesis

See Supporting Information for the synthesis details of the polymers TBDT-Q, TBDT-T-TP-T, BDT-BTz, and EWC4.

Calculations

Density functional theory (DFT) relaxations at the PBE0²⁸/6-31G(d,p) level of theory were conducted on oligomers with 1, 2, 3, and 5 repeating units, except where the pentamer size was deemed too computationally demanding, and was replaced by a tetramer. TQ1 oligomers with 1–9 repeating units underwent relaxations at the same level. Long alkyl side-chains were truncated to shorter ones, depending on branching and chemical environment. Time dependent (TD)-DFT was then applied to each system in order to calculate the lowest energy vertical excitations that constitute the first absorption peak in the respective polymers. An extended TD-DFT scheme including excitations that cover the entire visible region was applied to the oligomer lengths that

give the best match to the respective experimental spectrum. PC₆₁BM underwent a PBE0/6-31G(d,p) calculation. BDT-BTz, TQ1, APFO-G9, TBDT-Q, and TBDT-T-TP-T were subject to TD-DFT calculations using an o-DCB polarizable continuum model (PCM) solvent. All DFT calculations were carried out with the Gaussian 09 package.²⁹

RESULTS

Structural properties

The average molecular weights of the polymers were determined by size exclusion chromatography (SEC). Table 1 shows that the polymers display considerable variation in weights and polydispersity indices. Optical traits generally depend somewhat on the number of repeating units until they converge for longer polymers. It is assumed that the weights in Table 1, corresponding in all cases to at least 7 repeating units, are sufficiently large for convergence.

Table 1. Structural properties. Molar mass averages, M_n and M_w , in kDa of the polymers measured by SEC. Weight fraction of the off-backbone side-groups in %. The average calculated dihedral angles between aryl rings along the backbone in optimized trimers, expressed as number of degrees out-of-plane.

	BDTBTz	TBDTTTPT	APFO3	APFO15	TBDTQ	EW3	TQ1	APFOG9	EW4
M_n /kDa	8.1	8.5	18	15	8.7	23	56	11	12
M_w /kDa	21	74	32	36	18	62	170	26	22
Sidegroup %	51	61	33	58	72	59	66	52	52
Out-of-plane/°	3.5	4.2	14.0	15.1	16.3	19.3	20.0	21.4	21.9

The polymers were modelled as oligomers for the computational investigation, due to size restrictions of the first-principle quantum chemical methods. Oligomers of 1–5 repeating units

were optimized computationally in order to determine the minimum energy conformation. Like most conjugated D–A polymers,⁶ the oligomers consist of stiff, planar ring-systems, connected by flexible single bonds along the backbones. Though a planar geometry is favored from an electronic conjugation perspective, the optimizations yield geometries with the ring-systems out of plane by 3–22° (see Table 1), due to steric hindrance. The non-planarity varies significantly between the polymers, with BDT-BTz and TBDT-T-TP-T having the smallest average angles corresponding to 3.5° and 4.2° out of plane respectively, which is due to the lack of H–H collisions between rings in these two polymers, (See the optimized monomers in Figure S1). APFO-G9, EWC4, and TQ1 have the largest calculated dihedral angles ~20° due to their bulky phenyl side-groups which for TQ1 imposes a helical minimum energy conformation.³⁰ Even larger dihedrals have been reported for TQ1 in the *trans*-conformation,³¹ but our calculations suggest the *cis*-form as the minimum-energy geometry.

The fact that the rigid ring-systems can rotate over the single bonds between them bestows conformational isomerism. Local structural energy minima occurs when the dihedral angle between neighboring units is either slightly larger or smaller than 0° or 180° respectively, generating four local minima per single bond. In the monomers, the number of such single bonds range between one in BDT-BTz to seven in APFO-G9, EWC4, and TBDT-T-TP-T, which for the latter means that under the approximation that the dihedral angles are individually independent, up to 28 locally optimized geometries must be compared to identify the global minimum for each polymer. However, the recurrence of certain structural elements reduces the number of conformations requiring exploration.

Long alkyl side-chains are included in the synthesized polymers for increased solubility.³¹ Since such effects are beyond the scope of this study, the chains are replaced by shorter alkanes in the calculations that focus on electronic properties. All polymers except APFO-3 and BDT-

BTz also contain off-backbone phenyl- and thiophene moieties. The weight fractions of side-groups are reported in Table 1.

Electronic structure

Electronic structure properties of the D-A polymers are crucial for the functioning of the solar cell. In particular, HOMO and LUMO frontier orbitals typically constitute the origin and target orbital of the first electronic excitation, respectively. The polymer HOMO is furthermore responsible for hole-transport to the anode, while the electron should be injected from the polymer LUMO to the fullerene after excitation. Calculated HOMOs and LUMOs are depicted in Figure 1. Generally, the HOMOs have good delocalization over the polymer backbones, favoring efficient hole-transport.¹⁶ The LUMOs are more determined by the acceptor unit, so *e.g.* APFO-15, EWC-3, TBDT-Q, and TQ1 consequently exhibit very similar appearance between since these all employ a Q acceptor. The LUMOs are also denser at the respective acceptor moieties, particularly apparent for the polymers with T–X–T donors where the acceptors are more spatially separated from each other. The frontier orbitals strongly affect the first electronic transition densities, also depicted in Figure 1. The tendency for LUMO to be localized on the acceptor unit induces a clear D–A effect for all polymers, with electrons moving from donor to acceptor upon excitation. This can be exploited to give more narrow band gaps by choosing acceptors with deeper LUMO level, such as PzQ in AFPO-G9 and EWC4. Furthermore, it is evident that electronic excitation generates larger electron density in the single bonds between ring-systems, giving them an increased double-bond character in the excited state, which in turn accounts for the trend among conjugated systems that the excited state is more planar than the ground state^{32,33,34,35,36,37}.

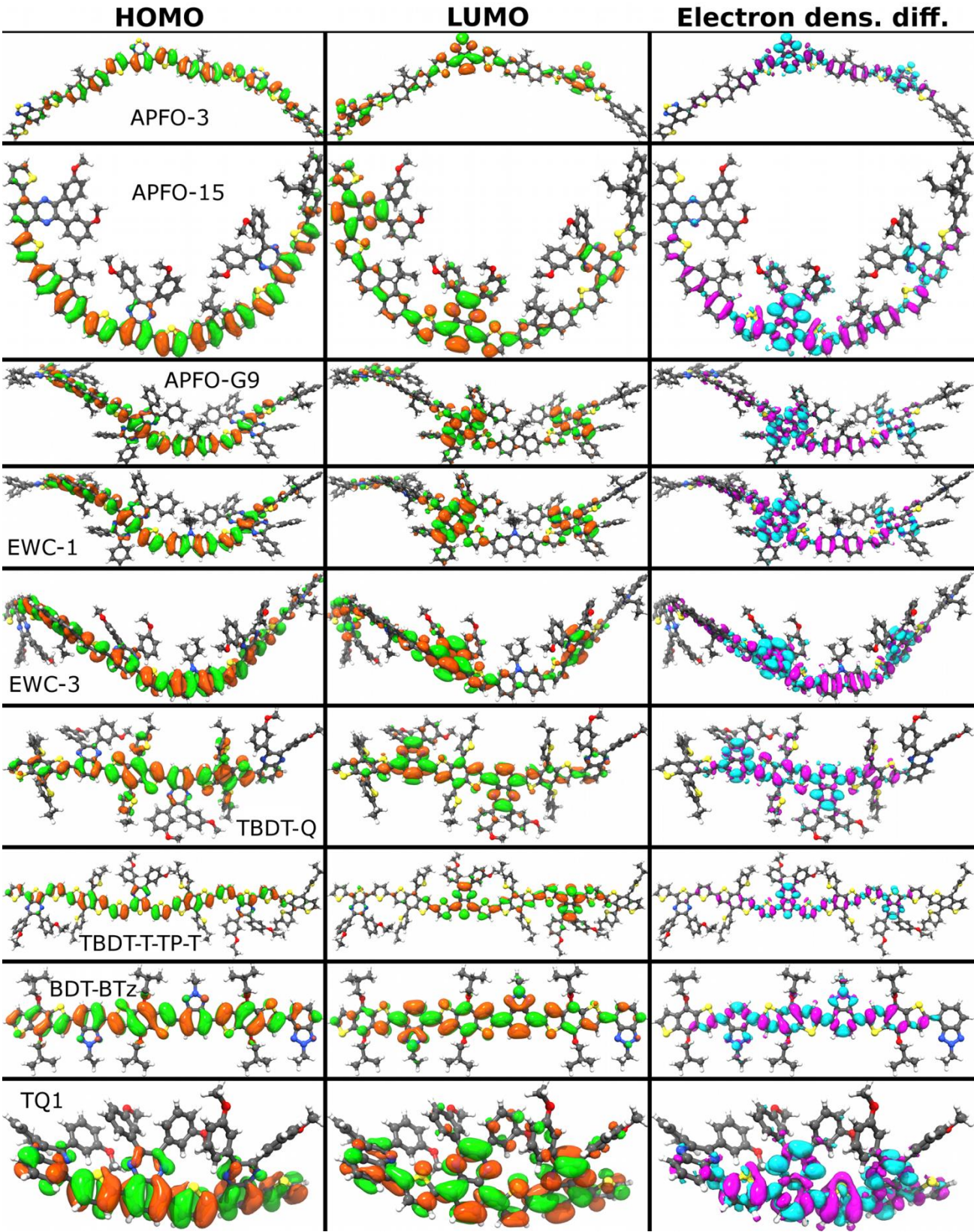


Figure 1. Frontier orbitals (isovalue=0.015), and excited state electron density difference (isovalue=0.0004) of optimized trimers, with electrons being transferred from purple to turquoise upon excitation. Calculated with TD-PBE0/6-31G(d,p). Note that a short repeating unit lead to a short trimer.

The polymer HOMO and LUMO energies are important since the difference between them is related to the optical energy of maximum absorption (E_{abs}). In addition, the LUMO(fullerene)–HOMO(polymer) energy difference determines the open circuit voltage of the cell, while the LUMO(polymer)–LUMO(fullerene) energy offset constitutes the electron injection driving force. Since our calculations are based on smaller oligomers, we employ an extrapolation technique to obtain size-converged frontier orbital energies, as follows. According to the tight binding approximation in theory of solids, a single orbital of a monomer splits into n orbitals upon oligomerization to a linear n -mer, with each orbital's energy given by the formula: ³⁸

$$E_k(n) = \alpha + 2\beta \cos\left(\frac{k\pi}{n+1}\right) \quad k = 1, 2, \dots, n \quad (1)$$

where α is the energy of the corresponding non-split orbital (that of a monomer, $n=1$). The parameters α and β are fitted to the calculated oligomer HOMO and LUMO energies, and the resulting function is plotted vs. the inverse oligomer length, $1/n$, in Figure 2.

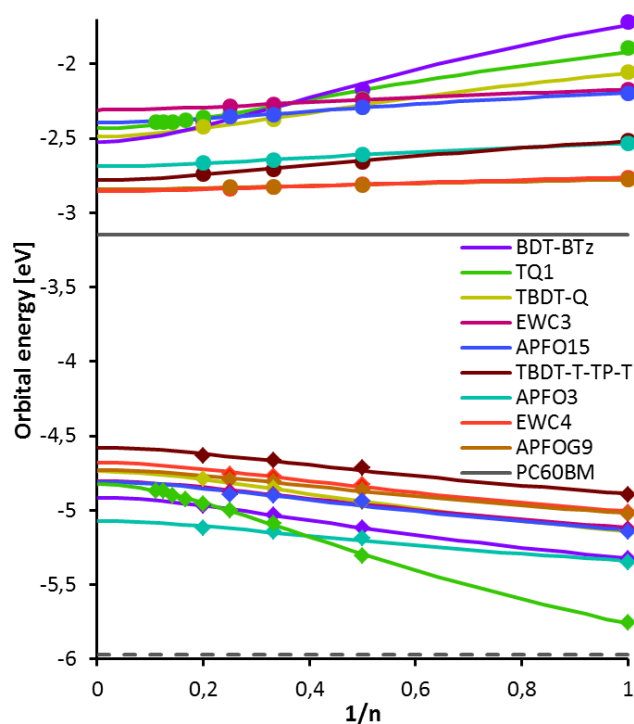


Figure 2. Calculated HOMO (diamonds) and LUMO (circles) energies as a function of inverse oligomer size, compared to the HOMO and LUMO energies of PC₆₁BM, solid and dotted lines, respectively. All energies calculated with PBE0/6-31G(d,p). Lines are fitted to the points according to the tight binding approximation of Equation 1.

The extrapolated frontier orbital energies in Figure 2 show spreads of ~0.5 eV for both HOMO and LUMO, owing to the diverse chemical composition of the polymers. The suggested^{39,40,41} minimum energy difference between polymer and fullerene LUMO 0.30–0.35 eV for efficient electron injection is fulfilled by all polymers herein. The HOMOs are more size-dependent than the LUMOs, which can be rationalized from the orbital pictures in the Figure 1, where HOMOs display continuous density along the entire backbone, whereas the LUMOs are more isolated on acceptor moieties, making their energies less size-sensitive. The steeper slopes for the smaller polymers in Figure 2 is explained by the fact that polymers with shorter repeat units require more

repeating units than a polymer with a long repeat unit to achieve the same extent of orbital delocalization. The polymers with only two ring-systems per unit: TQ1, BDT-BTz, and TBDT-Q show even more size-dependent LUMO energies, which is due to stronger delocalization of their LUMOs, as seen in Figure 1. Conversely, APFO-G9 and EWC4 exhibit negligible LUMO stabilization for increasing oligomer length, explained by the fact that their LUMOs are very isolated on their PzQ acceptors, and thus do not further delocalize upon polymerization.

The polymers with the same acceptor exhibit very similar extrapolated LUMO energy in Figure 2. APFO-G9 and EWC4 display the lowest LUMO energies, due to the strong electron-deficiency of their PzQ acceptor. The TBDT-T-TP-T LUMO energy is slightly higher, followed by APFO-3 with a benzothiadiazole (BTD) acceptor, and the benzotriazole (BTz) containing BDT-BTz. Q is the weakest of the acceptors employed, leading to the higher LUMO energies of EWC3, APFO15, TQ1, and TBDT-Q, which may limit their spectral coverage in the lower energy region. Similarly to the LUMO case, the order of the extrapolated HOMOs exhibits the same effect of dependence on acceptor unit, although less pronounced. APFO-3 displays the lowest HOMO energy which contributes to its high V_{oc} of 1.0 eV,⁴² whereas TBDT-T-TP-T has the highest HOMO, ~0.5 eV higher than APFO-3. For all polymers, the largest calculated oligomer size (4–5 repeating units) has a LUMO energy converged to within 0.02 eV of the extrapolated value, whereas the greater size-dependence of the HOMOs leads to largest oligomer energies up to 0.11 eV short of the polymeric extrapolated estimate.

The HOMO and LUMO levels were also investigated experimentally by square wave voltammetry (SWV), measurement plots can be found in Supporting Information. The polymer oxidation potential, *i.e.* extraction of electrons, is related to the HOMO of the material. Respectively, the reduction of the material corresponds to the reception of electrons, related to the LUMO.^{43,44,45} The ordering between polymers is retained in calculations except for TBDT-T-

TP-T and EWC3. The experimental SWV peaks in Table 2 are, however, of consistently lower energy than calculated HOMO and LUMO, which is generally the case for conjugated, organic systems.^{46,47,48,49,50} The difference is due to the fact that experimental orbital energies are not observables, but are derived from redox-potentials which can only be strictly compared to calculated redox energies. Comparing to calculated orbital energies is possible according to Koopman's theorem, though the disregard of orbital relaxation and solvent effects makes it highly approximate.⁵¹ Furthermore uncertainty arises in the comparison of wide experimental peaks to calculated point values. The discrepancy in HOMO energy between the two methods is similar for all polymers, amounting to 0.87–1.26 eV. The overestimations of calculated LUMOs show a greater variation: 0.35–1.11 eV, owing to their virtual nature,⁵² which is responsible for discrepancies in HOMO–LUMO gaps of -0.71–+1.16 eV between the two methods.

Table 2. Square wave voltammetry peak values vs. vacuum in eV (see Figure S2 for plots), and HOMO and LUMO as calculated with PBE0/6-31G(d,p). Sorted by experimental HOMO–LUMO gap.

	EWC4	APFOG9	BDTQ	TQ1	EWC3	BDTTTPT	APFO3	APFO15	BDTBTz
HOMO _{SWV}	-5,7	-5,7	-5,8	-5,7	-5,8	-5,8	-6,0	-6,1	-5,9
LUMO _{SWV}	-3,9	-4,0	-3,6	-3,3	-3,3	-3,3	-3,2	-3,2	-2,9
HOMO _{calc}	-4,7	-4,7	-4,7	-4,8	-4,8	-4,6	-5,1	-4,8	-4,9
LUMO _{calc}	-2,9	-2,8	-2,5	-2,4	-2,3	-2,8	-2,7	-2,4	-2,5
H-L gap _{SWV}	1,7	1,7	2,3	2,4	2,5	2,5	2,8	2,9	3,1
H-L gap _{calc}	1,8	1,9	2,3	2,4	2,5	1,8	2,4	2,4	2,4

Absorption spectra

Experimental polymer solution absorption spectra are shown in Figure 3, providing an overview of the light-harvesting capabilities of the polymers. There are obvious differences

between the measured absorption profiles of the investigated polymers, which are related to their chemical structure. Six of the polymers exhibit classical “double hump” absorption characteristics, while the three (T)BDT-containing polymers show more irregular spectra with additional peaks, making their absorption more panchromatic. Since the solar emission is weak at wavelengths shorter than ~400 nm, it is for all nine polymers the first, red-most, absorption peak that is most relevant for photovoltaic purposes.

The peak wavelengths ($\lambda_{\text{absmax}} = hc/E_{\text{abs}}$) of these first peaks range between 533 and 700 nm. The calculated HOMO–LUMO gaps agree better to calculated E_{abs} than to experimental HOMO–LUMO gaps, since the former do not involve orbital relaxation, unlike the latter which are approximated from redox-potentials. The novel polymers TBDT-T-TP-T and EWC4 have the smallest optical band gaps, with absorption onsets at ~900 nm, similar to APFO-G9, mainly attributed to the low LUMO afforded by their strong acceptors PzQ and TP. APFO-3, APFO-15, EWC3 and BDT-BTz all have absorption onsets at ~620 nm, which for APFO-3 is attributed to its low HOMO energy, and for the other three mainly due to high LUMO energies. They thus fail to capture significant part of the solar emission.

The maximum absorption coefficients ϵ_{max} , of the polymers appear related to the acceptor unit. APFO-3 with a BTD acceptor exhibit the greatest first peak absorption coefficient, 67 Lcm⁻¹g⁻¹, followed by BDT-BTz. The polymers with PzQ and TP acceptors absorb the weakest; leaving Q as an intermediate absorbing acceptor, except in TBDT-Q whose very low ϵ_{max} is partly explained by that it has the lowest M_w of all polymers, see Table 1.

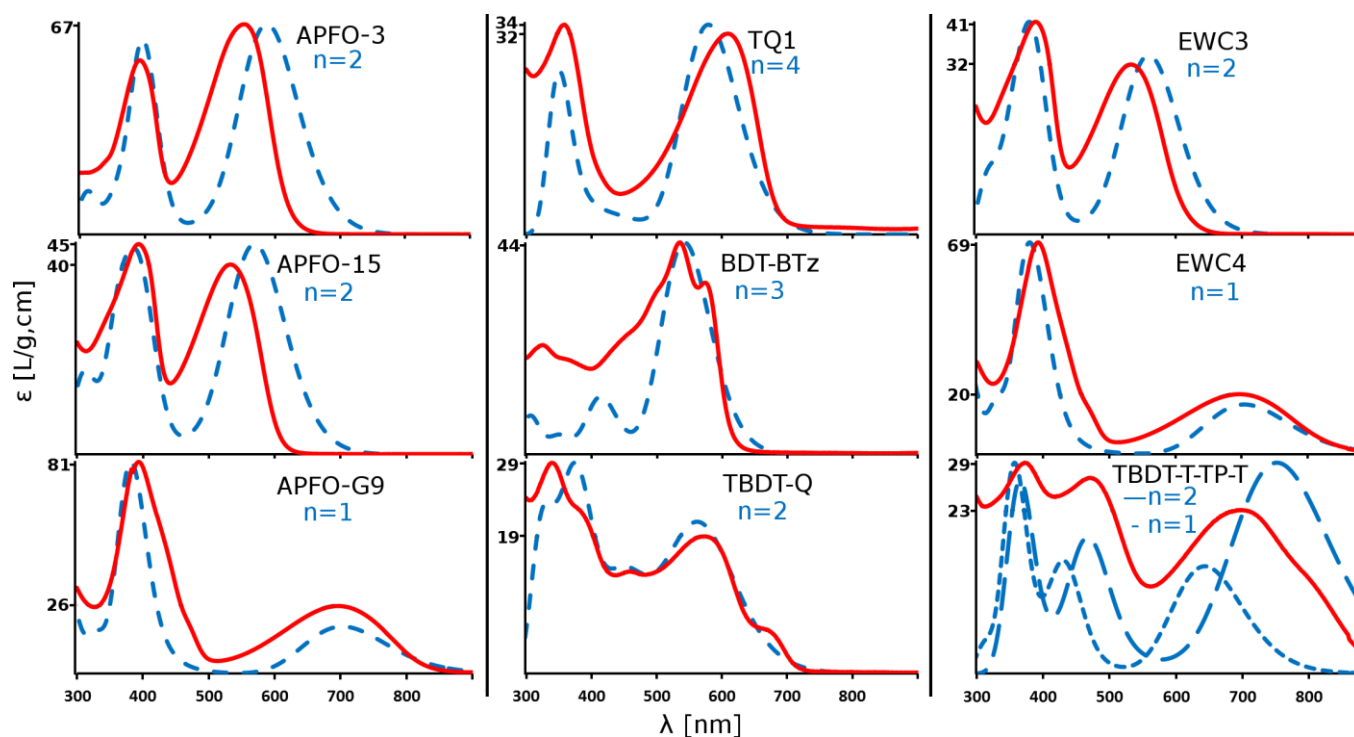


Figure 3. Experimental (red) and calculated (blue) absorption spectra of the investigated polymers. Experimental as recorded in o-DCB solvent. The experimental ϵ -values for the absorption maxima are marked on the y-axis, with secondary (lower) ϵ -values indicating the red-most peak maxima where this is not the most intense peak for that polymer. The calculated TD-DFT spectra were obtained by a 3000 cm^{-1} Gaussian broadening, and with absorption intensities normalized to match the most intense experimental peak. Numbers of repeating units (n) in the oligomer calculations were chosen to match experimental spectra. The TD-DFT calculations include only states $\geq 300\text{ nm}$ due to computational limitations.

Following a common,^{15,53,54,55,56} but non-predictive practice, the experimental polymer spectra in Figure 3 are compared to calculated spectra of oligomers whose sizes are chosen *a posteriori* to match the experimental absorption profiles. This provides good agreement between calculated and experimental spectra regarding the general shapes as well as relative peak heights, in

particular for the “double-hump” cases. For TBDT-T-TP-T, and to some extent also for APFO-3 and APFO-15, the experimental absorption is blueshifted compared to the calculated dimer but redshifted vs. the monomer, which demonstrates the precariousness of relating small and well defined oligomers to long and polydisperse experimental polymers. The Gaussian broadening of 3000 cm^{-1} that is arbitrarily chosen for calculated spectra, is in most cases slightly narrower than experimental peak widths, particularly for EWC4 and APFO-G9. Furthermore, this Gaussian function is symmetric, while the experimental broadening is inhomogeneous, extending further to the shorter wavelengths due to unresolved vibronic progression and uneven distributions of conformations. In the following sections we describe and apply a procedure which relies on extrapolations to size-converged properties, rather than an *ad hoc* choice of oligomer size as above. This permits accurate prediction of size-consistent absorption wavelengths and intensities which provides an in-depth understanding of the potential for efficient photon collection of these polymers based on their chemical structure and electronic properties.

Absorption energies

In recent years, low band gap polymers have been sought after, due to their ability to absorb a greater portion of the solar emission spectrum, yielding larger photo-currents.⁶ However, a low absorption threshold typically leads to a lower voltage output from the cell, and finding the ideal absorption energy becomes a complex optimization problem. A rough, qualitative estimation of the first transition energy of absorption (E_{abs}) in a copolymer can be made from the HOMO and LUMO of the donor and acceptor units, since the frontier orbitals of the copolymer are constructed from these units. For instance, polymers with the low-LUMO acceptor PzQ

exhibit low E_{abs} , both herein (APFO-G9 and EWC4) and elsewhere,⁵⁷ in contrast to *e.g.* the Q acceptor.

Any quantitative prediction of calculated E_{abs} however, requires a more elaborate quantum chemical treatment, *e.g.* with TD-DFT, which we employ to obtain calculated absorption energies (E_{abs}) and intensities for oligomers of 1–5 repeating units (excitations listed in Supporting Information). To obtain polymeric estimates from oligomer calculations, calculated E_{abs} are often extrapolated to the polymer limit by fitting them to a linear function vs. inverse number of repeating units ($1/n$),^{58,59,60,61} but more physically rigorous, non-linear approaches also exist.^{62,63,64} Since the optical band gap is strongly related to the HOMO–LUMO gap, we can rewrite Equation 1 in terms of $E_{\text{abs}}(n)$:

$$E_{\text{abs}}(n) \approx E_{\text{LUMO}} - E_{\text{HOMO}} = \alpha_{\text{LUMO}} - \alpha_{\text{HOMO}} - 2(\beta_{\text{LUMO}} + \beta_{\text{HOMO}}) \cos \frac{\pi}{n+1} \quad (2)$$

This function describes the size dependence of the HOMO–LUMO gap, and thus approximately that of E_{abs} . TD-DFT calculated $E_{\text{abs}}(n)$ were fitted to the right-hand side of Equation 2 using two fitting parameters: (α_{LUMO} – α_{HOMO}) and (β_{LUMO} + β_{HOMO}). The fits are good in all cases, as seen in Figure 4 where they are plotted vs. the inverse oligomer length, together with calculated oligomer absorption energies. TQ1, BDT-BTz, and TBBT-Q exhibit steeper slopes, as their shorter repeat unit necessitates more units for conjugation convergence, analogously to the orbital energy convergence in Figure 2. It is noticeable that polymers having common acceptors yield comparable results, *i.e.* APFO-G9 vs. EWC4 and APFO-15 vs. EWC3.

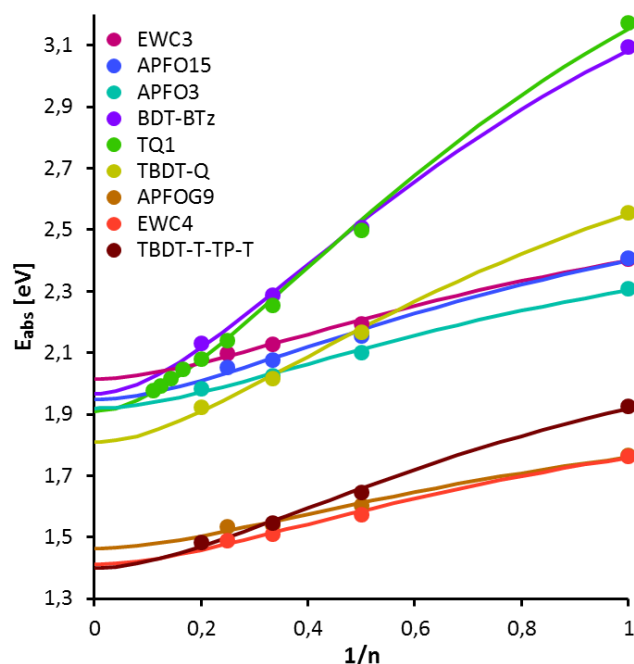


Figure 4. Calculated first peak absorption energy (E_{abs}) as function of inverse oligomer size. Lines are fitted according to the tight binding approximation of Equation 2. Color order from violet to red according to extrapolated E_{abs} .

Comparisons between experiment and calculations are complicated due to the difference in conditions, *e.g.* with respect to temperature, system size, solvents, *etc.*⁶² The extrapolated, calculated E_{abs} are compared to the experimental peak E_{abs} in Figure 5, where a systematic underestimation of the calculated values is apparent for all polymers. This is because the calculations are based on the minimum energy conformation of the oligomers, whereas under room-temperature conditions, a multitude of conformations is present. The optimized structures are usually more planar than the actual range of conformations. Planarity is associated with red-shifted absorption,^{65,66,67,68} so calculated absorption energies typically represent the lower limit of

experimental E_{abs} . Solvent effects and unresolved vibronic progression, present in experimental spectra but absent in calculations, further adds to the discrepancy.

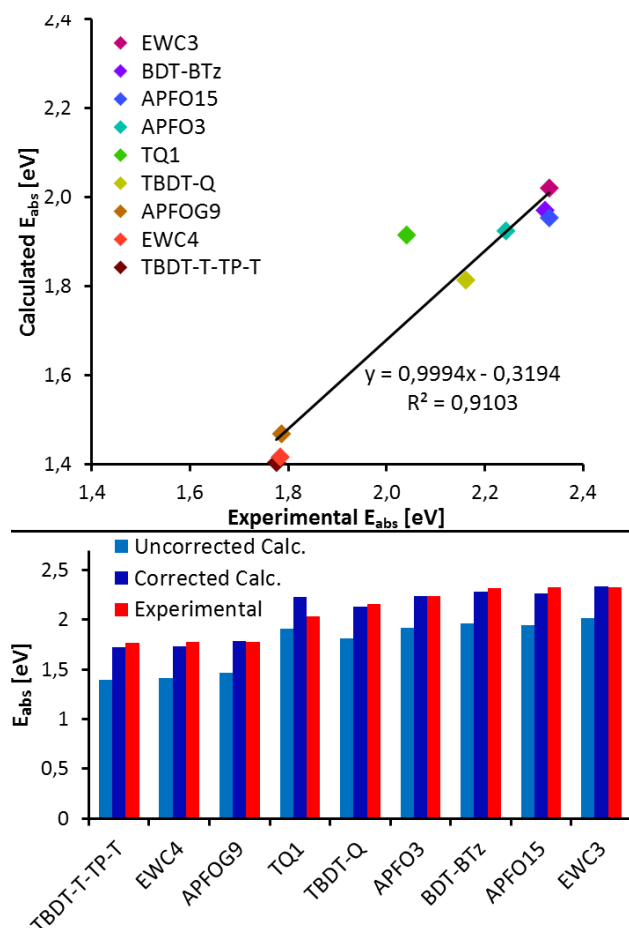


Figure 5. TOP: Calculated vs. experimental peak E_{abs} , with best linear fit. BOTTOM: Calculated E_{abs} with and without correction, as well as experimental. The calculated E_{abs} corresponds to the extrapolation to $1/n \rightarrow 0$ in Figure 4. The correction corresponds to a constant +0.32 eV amendment.

Despite the diverse nature of the studied polymers and their wide range of absorption energies, the underestimation of calculated E_{abs} is practically constant over the series, within a narrow

range of 0.31–0.38 eV, except for TQ1 for which it is limited to 0.13 eV since TQ1 is restricted to an experimental geometry closer to the optimized (calculated) structure due to its phenyl side-groups.³⁰ The calculated E_{abs} are plotted against experimental in the top panel of Figure 5, and the best linear fit exhibits a slope of virtually unity and an intercept of -0.32 eV. An empirical correction consisting of the addition of the 0.32 eV average underestimation to the calculated series is introduced to compensate for the highly systematic discrepancy. The uncorrected and corrected calculated E_{abs} are compared to the experimental numbers in the bottom panel of Figure 5. With the empirical correction, calculated E_{abs} match the experiments very well, exhibiting accuracy to within 0.06 eV, or 3% error to experiment for all polymers except TQ1. This is remarkable considering the large spread of experimental absorption energies of the series, ranging from 1.77 – 2.33 eV. Similar kinds of empirical corrections have commonly been applied to other types of calculated results, such as vibrational spectra,^{69–73,74} and NMR shifts,^{75–77,78,79} but also to electronic and optical properties.^{80–83,84}

Several computational shortcomings contribute to the total, uncorrected error. While implicit solvent effects have a minor influence on the E_{abs} , <0.05 eV (see Supporting Information, Table S3), explicit solvent and thermal/conformational effects contribute to the underestimation of calculated E_{abs} . Importantly, hybrid DFT functionals such as PBE0 used here, are known to overestimate the conjugation and planarity in conjugated polymers,^{64,85–87} leading to calculations predicting unrealistically flat geometries and red-shifted electronic transitions. Part of the calculated underestimation of E_{abs} can also be explained by experimental limitations: SEC measurements are known to overestimate the molar masses of D–A polymers. This stems from the fact that SEC uses the flexible polystyrene as a reference, whereas D–A polymers are generally more rigid. Further theoretical and experimental studies may elucidate the individual contributions from the respective sources of error.

Absorption strengths

While the absorption energy should not be too small or too large, a greater absorption strength is monotonically favorable for the OPV performance, since stronger absorption leads to larger currents, up to the limit of all photons absorbed. The electronic transport properties of an OPV are favored by a thin device, so to maximize absorption per device thickness, high absorption intensity per polymer volume is desired. This is equivalent to strong absorption per weight since most polymers have a density very close to 1 kg/dm³.

The first peak absorption intensities of the polymers herein were calculated for oligomers of 1–5 repeating units. The intensities as calculated with TD-DFT are expressed as oscillator strengths (f), an extensive property that increases linearly with oligomer length.⁸⁸ Calculated oscillator strengths divided by the oligomer molar mass yield a more relevant, intensive property: specific absorption strength (F_M). These are plotted *vs.* inverse number of repeating units in Figure 6. In agreement with theory and previous reports,^{62,89–93} a linear relation is evident for all polymers, allowing extrapolation to the polymer limit (see Supporting Information for details). Size-converged specific absorption strengths are thereby obtained, despite performing the calculations on smaller oligomers. It is noticeable that the polymers with lighter repeating unit BDT-BTz, APFO-3, and TQ1 are more size-dependent than the heavier ones, leading for APFO-3 and BDT-BTz to very strong calculated polymeric absorption, $\sim 2 \text{ kg}^{-1}$. TQ1 is the only polymer whose monomer does not follow the linear trend, a consequence of its unique ability to adopt a helical geometry in oligomers larger than the monomer.³⁰

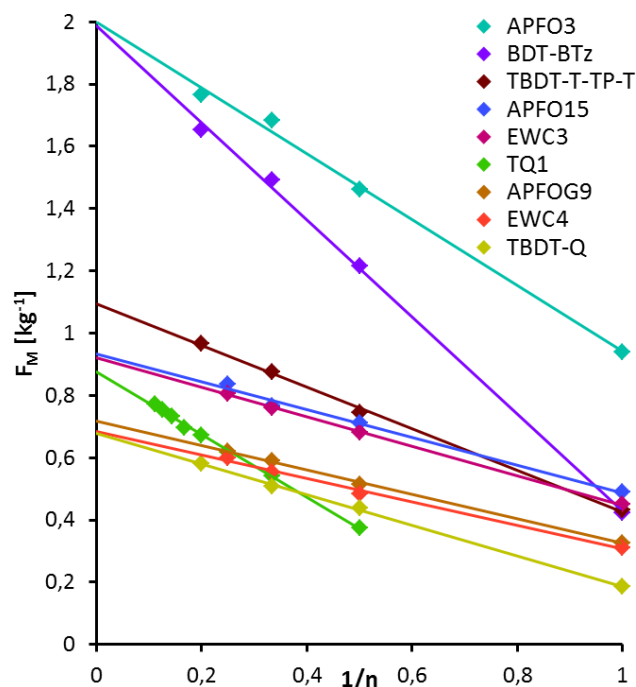


Figure 6. Calculated specific absorption strengths, F_M , vs. inverse oligomer order. Lines are best linear fits, extrapolated to $1/n=0$.

The specific absorption strength, F_M , is related to the absorption coefficients of the first peak through the relation:³⁸

$$F_M = \frac{4\ln(10)m_e c \varepsilon_0}{N_A e^2 M_w} \times \int \varepsilon(\nu) d\nu \quad (3)$$

where m_e and e are the electron mass and charge respectively, ε_0 is the vacuum permittivity, N_A is the Avogadro number, ν is the light frequency, M_w is the measured molecular weight average and the factor $\ln(10)$ enters since ε is the decadic (as opposed to natural), molar absorption coefficient. Accordingly, experimental F_M values are obtained by taking the integral over the first experimental absorption peak, as approximated through the trapezoidal rule to the local spectral minimum after the peak. The experimental F_M show a trend-wise agreement with $\varepsilon_{\max}$ since the peak widths are similar, see Figure3.

In Figure 7, the experimental F_M values are compared to the calculated ones, taken from the linear fit extrapolation in Figure 6. Analysis and quantification of the discrepancies provides possibility to assess and compensate for the errors, analogously to the E_{abs} case in the previous section. The best linear fit of calculated vs. experimental absorption strengths exhibits a negligible intercept, demonstrating that the overestimation is proportional to F_M , as seen in the top panel of Figure 7. The slope of 1.65 indicates a consistent error, meaning that dividing calculated F_M values by 1.65 constitutes an empirical correction that provides significantly more accurate theoretical estimates, as demonstrated in the bottom panel of Figure 7. The correction improves the mean absolute error from 0.40 to 0.07 kg^{-1} .

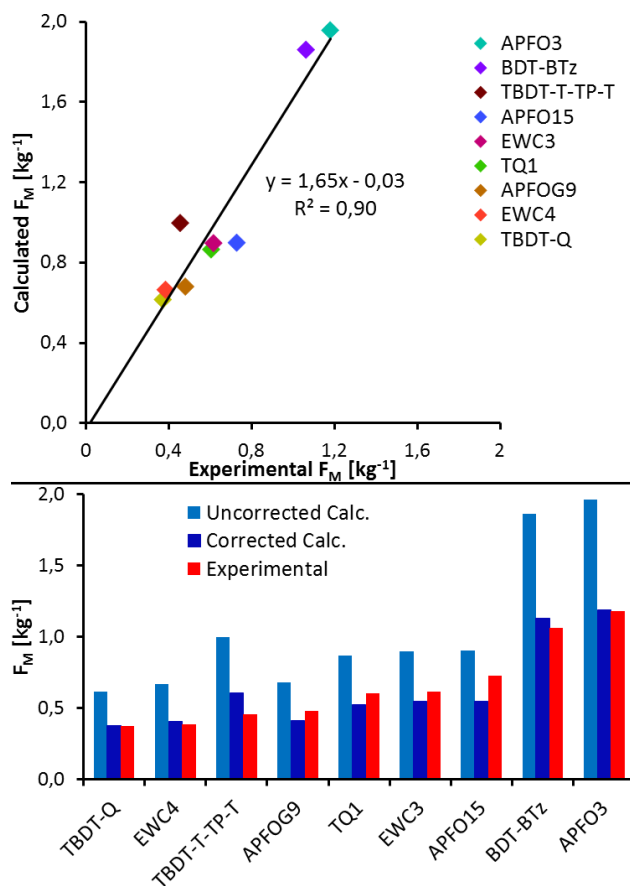


Figure 7. TOP: Calculated vs. experimental absorption strengths, F_M , for the investigated polymers, with best linear fit. BOTTOM: Comparison of uncorrected and corrected calculated absorption strengths to experimental absorption strengths, sorted by experimental values.

The uncorrected errors in oscillator strength are larger here than in many studies of smaller molecules.^{94,95,96,97} This can be explained in terms of the non-ideality of experimental conditions, where thermal effects and solvent interactions induce conformational twists, kinks, and coils in the polymer chains which reduce the conjugation¹⁶ and consequently the absorption intensity. The polarizability of the solvent affects the transition dipole moment in the polymers and thus the absorption strength. The F_M of five of the polymers was calculated using TD-DFT with an o-DCB polarizable continuum model solvent, showing in all cases stronger absorption than vacuum calculations (see Supporting Information, Figure S8). The effect of the solvent decreases with increasing oligomer size, leading to extrapolated F_M values 2–15% larger than the vacuum calculations. This is in decent agreement with other studies showing that continuum solvent models do not affect the absorption strength in polymers by more than ~10%.^{98,99,100} Overestimated masses from SEC are also responsible for part of the discrepancy between calculation and experiment. The findings suggest that the calculations represent the upper bound of experimental absorption strengths, in the limit of extended, non-kinked, non-coiled polymer chains. The comparison of absorption strengths between polymers is relatively uncommon, in particular in computational studies where the intensities in calculations are often normalized when related to experimental spectra,^{101,102,13,103,104,105,104,106,107}. Normalized absorption comparisons permit assessment of relative peak height and wavelength but not the intensity which is important for the performance of OPVs. Accurate quantum chemical predictions of

specific absorption strengths as demonstrated here are therefore important for modeling, aimed at rational design of new and better light-harvesting polymers.

BDT-BTz and APFO-3 are the strongest absorbers as seen in Figure 7, attributed to their respective BTz and BTD acceptors, and their very flat minimum-energy geometries, as seen in Table 1. APFO-3 furthermore has the lowest side-group weight fraction of the studied polymers. These side-groups give a negligible contribution to the first peak absorption and are thus “dead weight” with respect to the excitations, which is further corroborated by the lack of frontier orbital density on these groups in Figure 1. TBDT-Q, with the highest side-group weight ratio as listed in Table 1, consequently demonstrates the weakest specific absorption. Thus, stronger absorption is obtained by developing more streamlined polymers with a low side-group-to-backbone weight ratio, although some alkyl side-chains are required for solubility. While this study is limited to repeating units with a 1-to-1 D/A ratio, Beaujuge *et al.* have previously reported the effect of the D/A ratio on the absorption strength.¹⁰⁸ They also propose the disregard of the side-chain mass for a more fair comparison of the intrinsic specific absorption strength between polymers with different repeating units.

The absorption intensity assessment here only treats the first absorption peak, whereas consecutive peaks also may contribute to the photoelectric conversion efficiency in working OPVs. Secondary peaks may even be more important, *e.g.* APFO-G9 and EWC4 show much more intense peaks at ~400 nm, making those polymers suitable in tandem OPVs. It may therefore be interesting to extend the investigation of optical traits to the whole visible region in future studies.

Light-harvesting capability

The output power of an OPV is a product of the current I and the voltage V . The current depends on, among other things, the absorptivity, whereas the voltage is limited by the polymer's band gap and its HOMO energy relative to the fullerene LUMO. Scharber et al. have developed a method to anticipate the maximum energy-conversion efficiency of a polymer/PC₆₁BM solar cell as a function of the polymer LUMO and band gap.⁴¹ According to that study, the ideal polymer band gap is around 1.5 eV, assuming an ideal polymer LUMO energy 0.3 eV higher than the fullerene LUMO. APFO-G9 has a near-ideal LUMO 0.30 eV higher than the PC₆₁BM LUMO. Furthermore the E_{abs} of APFO-G9 lies very near the above mentioned optimum 1.5 eV, and would thus score very high in the model of Scharber's *et al.* However, that study does not take the absorption intensity into account explicitly, but rather approximates the EQE to 65% at all wavelengths above the band gap, and thus fails to predict the relatively bad performance of APFO-G9 due to its weak absorption.²² Assessing also the absorption strength allows for a more complete evaluation of the light-harvesting potential of a polymer in single-junction OPVs. If one moreover permits the use of other fullerene acceptors with different LUMO energies, the polymer LUMO becomes a less crucial parameter. This leaves F_M and E_{abs} as the most important intrinsic polymer light-harvesting properties for efficient OPVs, although charge transport and other attributes still affect the device performance. Experimental and calculated F_M and E_{abs} are compared in Figure 8 for all polymers included in the present investigation.

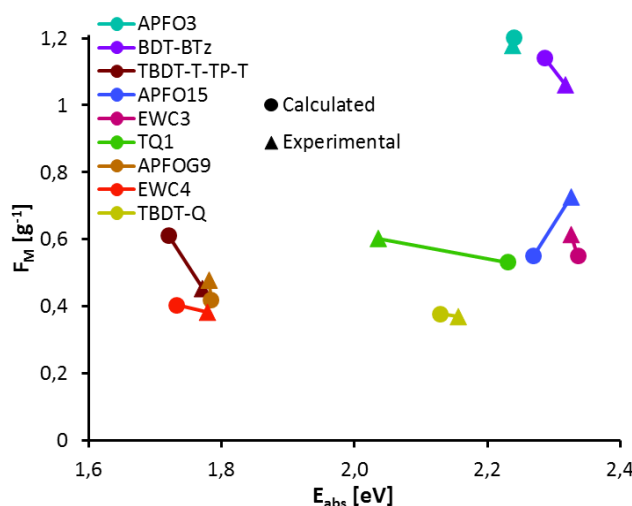


Figure 8. Light-harvesting capability plot for the investigated polymers showing the absorption strength, F_M , vs. E_{abs} . The plot includes a comparison of calculated values to experimental results. The calculated F_M and E_{abs} are taken from the extrapolated, corrected values shown in Figures 7 and 6 respectively.

The large variation in chemical structure of the polymer selection manifests itself as a considerably scattered distribution in Figure 8. This figure shows that the calculations provide a good assessment of the light-harvesting properties of the different polymers, as the discrepancy to experiments for all the individual polymers is significantly smaller than the overall spread of these traits across the polymer series. APFO-3 and BDT-BTz score best on absorption strength, attributed to the respective BTd and BTz acceptors, and for APFO-3 also to its low side-group weight ratio. However, the efficiency of these two polymers is limited by their higher absorption energy, and for BDT-BTz also by poorer LUMO alignment vs. PCBM.²⁵ Fluorination of BTz-containing polymers lowers the LUMO energy, and can give device efficiencies above 7%.¹⁰ The low-LUMO PzQ acceptor of EWC4 confers an in this respect near-ideal, lower E_{abs} of 1.73 eV, but it is second weakest absorber of the investigated polymers, also attributed to the PzQ

acceptor. The novel polymer TBDT-T-TP-T exhibits the lowest energy of absorption, but its high side-group ratio of 61% induces a relatively low F_M of 0.60 kg⁻¹. TBDT-Q is the only new polymer with an experimental E_{abs} in the central region of Figure 8, i.e. between 1.9 and 2.3 eV, but its limited F_M below 0.40 kg⁻¹ weakens its suitability for application in OPVs.

In summary this study highlights the current difficulty of finding D–A polymers that simultaneously display small optical band gap and strong absorption. To achieve such traits, one firstly needs to carefully choose appropriate acceptor units (and to some extent also donors). *E.g.* the BTQ acceptor grants strong and reasonably low-energy absorption, which why device efficiencies over 8% have been achieved using a this acceptor,¹⁰⁹ while the weak absorption of PzQ makes it unsuitable in conventional D–A polymer OPVs. Secondly, it is advised to avoid inclusion of too large side-groups that are “dead weight” with respect to the absorption strength. Thirdly, a sufficient degree of polymerization during synthesis, i.e. high enough polymer molecular weight is also beneficial for stronger and lower energy absorption.

CONCLUSIONS

Light-harvesting capabilities of a series of donor-acceptor type polymers have been investigated using a combination of experiments and calculations. The focus of the investigation concerns the ability to identify polymer candidates with promising optical characteristics at an early stage, specifically strong absorption at an adequately narrow band gap. The investigated set of polymers exhibits a significant span of experimentally determined first peak energies (E_{abs}) in solution from ca. 1.8 eV to ca. 2.3 eV, as well as having mass absorption intensities that vary by a factor of three.

Size-converged electronic and optical properties have here been obtained by means of oligomer calculations, extrapolated to the polymer limit. The calculated polymer absorption energies show

a trend-wise agreement with experiments, but are systematically underestimated. The clear, consistent trend between calculated and experimental E_{abs} enables the introduction of an empirical correction, which yields quantitative prediction of peak absorption energy to within an accuracy of 0.06 eV. The experimental and calculated absorption strengths per unit weight (F_M), vary by up to a factor of three across the polymer series, which is considerably more than E_{abs} . Nevertheless, the calculated specific absorption strengths (F_M) display an error to the experimental values limited to 12%, following the introduction of an empirical correction to the calculations. The quantitatively accurate calculations of absorption energies and intensities together provide good possibilities to predict intrinsic light-harvesting capabilities of D-A polymers. This offers a deeper understanding of the physical properties that govern the electronic and optical processes in the polymers, and also makes calculations an efficient tool to assess the suitability of the polymers in an OPV context.

Of the polymers in this study, APFO-3 scores best on absorption strength, concurring with its high performance in solar cells.^{20,42} This derives from its light repeating unit, with small side-group to backbone ratio, and the intrinsic properties of its BTD acceptor. Three of the investigated polymers: APFO-G9, EWC4, and TBDT-T-TP-T, show significantly lower optical band gaps of around 1.7 eV, owing mainly to the deep-LUMO acceptors PzQ and TP. The remaining six polymers all have band gaps above 2.0 eV. However, none of the here investigated polymers simultaneously display both suitably low E_{abs} and high F_M , suggesting that there is significant room for further improvements in the design of D-A polymers for efficient OPVs. One such opportunity is to focus on acceptor units with promising intrinsic electronic properties, and to pursue polymers with high backbone weight-ratio since side-groups do not contribute to light-absorption.

In a broader perspective, the ability to reliably predict light-harvesting capabilities of new polymers is an important part of the search for novel and improved solar cell materials that is largely driven by efficient screening of a wide range of materials. The here adopted predictive approach is already starting to yield promising results for the design of new polymers currently under development.

ASSOCIATED CONTENT

Supporting information. Images of optimized monomers; square wave voltammetry measurement plots; tabulated polymer E_{abs} and F_M ; details on size dependence of absorption strengths; synthesis procedure for the polymers TBDT-Q, TBDT-T-TP-T, BDT-BTz, and EWC4; calculated excitation data.

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Notes

The authors declare no competing financial interests.

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