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DICYANOVINYL END-CAPPED 9,10-BIS (PHENYLETHYNYL) ANTHRACENES FOR ORGANIC SOLAR CELLS

9,10-BIS (FENYLOETYNOŁO) ANTRACENY Z PERYFERYJNYMI GRUPAMI DICYJANOWINYLOWYMI DLA OGNIW SŁONECZNYCH

Abstract

A series of 9,10-bis(phenylethynyl)anthracene dicyanovinyl end-capped derivatives have been used in bulk heterojunction (BHJ) photovoltaic cells prepared by the solution process. The compounds were excessively decorated with moieties enhancing solubility to avoid spontaneous crystallisations in the blends. The topology of the dyes is of the acceptor-donor-acceptor (A-D-A) type. The quantum chemical calculations were done at the B3LYP/6-31G(d) level of theory and HOMO-LUMO levels were calculated. The solar cells' configuration was as follows: ITO/PEDOT:PSS/P3HT(P3OT)dyes/Al and parameters characterising them, open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF) and power conversion efficiency (PCE) are presented. Anthracene based A-D-A molecules showed photovoltaic activity with an average power conversion efficiencies (PCE) of 2.7%.

Keywords: anthracene, BPEA, solar cells, donor-acceptor systems, bulk-heterojunction cells

Streszczenie

Zsyntetyzowano grupę związków na podstawie 9,10-bis(fenyletynyl)antracenu z peryferyjnymi grupami elektron-akceptorowymi typu dicyjanowinyloenu. Związki zmodyfikowano grupami funkcyjnymi zwiększającymi ich rozpuszczalność i utrudniającymi krystalizację. Przygotowano komórki fotowoltaiczne o strukturze objętościowej metodą wirową. Obliczenia kwantowo-chemiczne przeprowadzono przy funkcjonale B3LYP na poziomie 6-31G(d) i wyliczono energię poziomów elektronowych HOMO-LUMO. Opisane ogniwa scharakteryzowano podając następujące parametry: sprawność urządzenia (PCE), współczynnik wypełnienia (FF), napięcie rozwarcia (Voc) i prąd zwarcia (Jsc). Skonstruowane urządzenie o konfiguracji: ITO/PEDOT:PSS/P3HT(P3OT)barwnik/Al osiągnęło sprawność 2.7%.

Słowa kluczowe: antracen, BPEA, ogniwa słoneczne, układy donorowo-akceptorowe, komórki objętościowe

1. Introduction

The beauty of the anthracene **1** (Fig. 1) molecule has been attracting the attention of the scientific community since many years. Its intrinsic reactivity at positions 9- and 10- gives the possibility to create a lot of compounds possessing many unique properties. The crystal of anthracene placed between two electrodes by Pope *at al.* as a source of light [1, 2] triggered extensive research, which gave rise to a huge number of publications concerning this molecule [3–9]. The high quantum yield and simple modification of the anthracene skeleton makes it an attractive object for different applications in many fields. Because of the electron-rich properties and the large π -conjugation system, anthracene can be substituted at the aforementioned positions with many different functionalised blocks in order to give a variety of compounds with interesting properties. For example, 9,10-bis(phenylethynyl) anthracene (BPEA) **2**, which exhibits an exceptionally high fluorescent quantum yield and excellent chemiluminescent performance, has been synthesised [10–15].

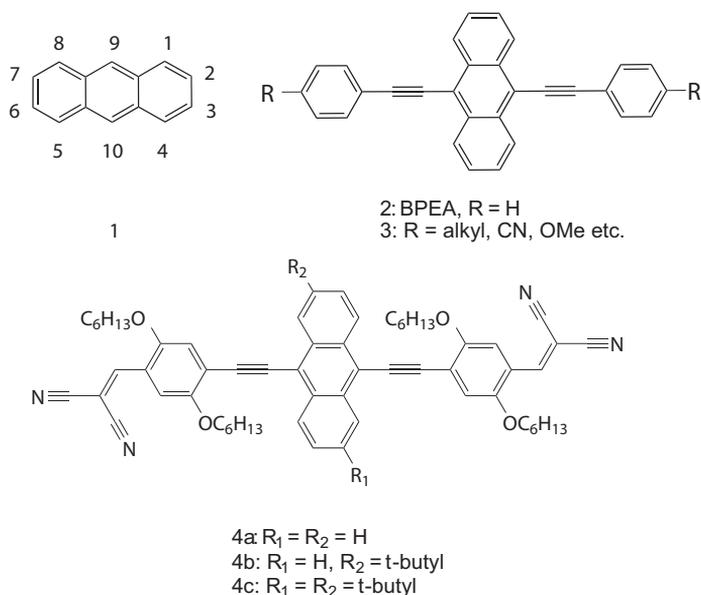


Fig. 1. Anthracene derivatives

Derivatives of BPEA **3** have been applied in the investigation of Langmuir Blodgett mono- and multilayer arrays [16–18], as well as good molecular probes, to study translational and rotational motions in diverse media, such as organic glasses and polymers [19–21]. Besides, they have been used for the synthesis of luminescent liquid crystals [22], sensors [23, 24], organic semiconductors [25, 26], useful fluorescent dyes for DNA labelling [27] and for the production of organic light-emitting diodes (OLEDs) [28, 29]. The combination of anthracene with strong acceptors to form an acceptor-donor-acceptor (A-D-A) system seems also to be an opportunity to enhance its optoelectronic properties and apply it in the dye-sensitised solar cells.

Up to now, the well-known A-D-A systems include different architectures of oligothiophenes, indolo[3,2-*b*]indoles, fluorenes and tetrathiafulvalenes end-capped with acceptors, as it was shown in a series of papers [30–33]. The potential of that type of molecules is connected with their ambipolar character, and due to the efficient transport of the charge carriers from the donor to the acceptor, which is reached by intramolecular charge transfer (ICT). Besides, acetylene-based materials were exploited extensively in organic photovoltaics (OPVs) [34], because of their electron-withdrawing character and a rigid, rod-like structure. Moreover, the availability of efficient synthetic protocols allows modifying the specific structural features: the π -conjugation length and the core functionalisation with proper chromophores. These can exert influence on the charge carrier mobility and photon/light harvesting, and leads to the improvement of short circuit current density and fill factor. Some time ago, we prepared strongly fluorescent BPEA dicyanovinyl (DCV) end-capped derivatives **4** as candidates for red light emitting devices, Fig. 1 [35]. However, substantial losses during the deposition process affected the good performance of the diodes. In the present study, we explore the compounds **4** as potential candidates for solar cells and the spin-coating is the method of choice to deposit them onto the ITO electrode, which helps to solve the stability problem of the chromophores. The preliminary study of photovoltaic performance revealed that anthracene-based A-D-A molecules exhibit photovoltaic activity with average power conversion efficiencies (PCE) of 2.7% (Table 2).

2. Experimental

2.1. Chemistry

The topology of the dyes in this study is as follows: the centre is an electron-rich anthracene core, decorated with two π -extended arms end-capped with electron accepting (EA) groups and four alkoxy groups to increase solubility. Their synthesis has been described in detail earlier [35, 36]; here is a short recollection of the synthetic path, Fig. 2:

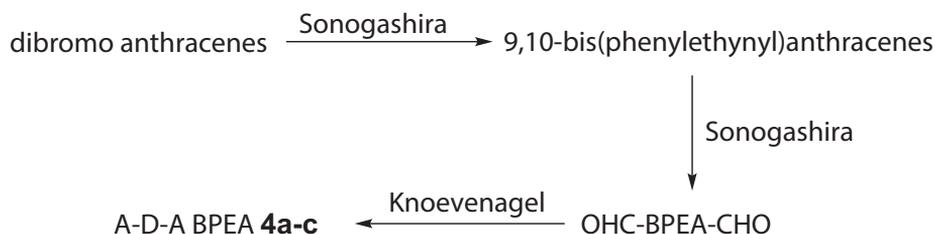


Fig. 2. Synthetic route to A-D-A BPEAs **4a-c**

The A-D-A BPEA **4a-c** were prepared in three consecutive steps from dibromoanthracenes to deliver BPEA dialdehydes followed by Knoevenagel condensation of the latter with malodinitrile.

2.2. Calculation procedures

Density Functional Theory (DFT) calculations of the fused A–D–A system were performed using Gaussian 03 at the B3LYP/6-31G(d) level of theory [37]. Full geometry optimisation confirmed that the lowest energy conformers of 4a-c are totally flat.

Table 1. Frontier orbital levels of arylethynylantracenes 4a-c

Molecule		Basis set	HOMO	LUMO	Bandgap, eV	Substituents
4a	F ^a	6-31G(2d,p)	-5.27	-3.21	2.06	R ₁ = R ₂ = H, Alk = C ₆ H ₁₃
4a	F	6-31G(d)	-5.29	-3.23	2.06	
4a	S ^b	6-31G(d)	-5.38	-3.33	2.05	R ₁ = R ₂ = H, Alk = CH ₃
4b	F	6-31G(d)	-5.31	-3.22	2.09	R ₁ = <i>t</i> -Bu, R ₂ = H, Alk = C ₆ H ₁₃
4b	S	6-31G(d)	-5.35	-3.30	2.05	R ₁ = CH ₃ , R ₂ = H, Alk = CH ₃
4c	S	6-31G(d)	-5.31	-3.27	2.04	R ₁ = R ₂ = CH ₃ , Alk = CH ₃

^a full structure, ^b simplified structure

The acetylene spacers are long enough to prevent a steric hindrance between alkoxy groups and the anthracene moiety that could disturb the planarity of the molecule. As hexyl and *t*-butyl groups do not influence the geometry of the backbone, they were replaced by methyl groups in order to simplify the calculations. In two cases (4a and 4b), hexyl and *t*-butyl moieties were included in optimised structures for comparison purposes. As it is possible to see from the data in Table 1, the structure simplification has been justified because

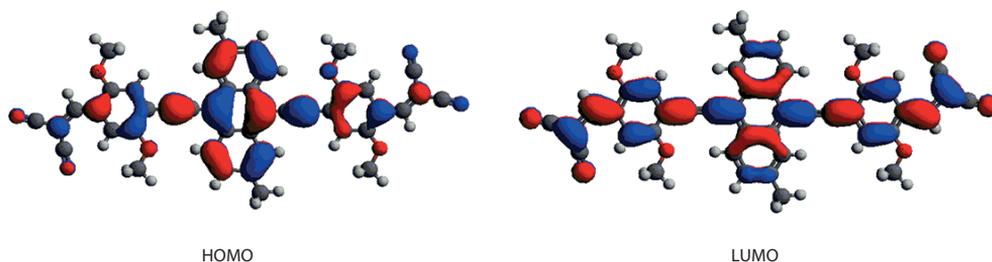


Fig. 3. Plots of the HOMO and LUMO density of the states of 4c calculated at the B3LYP/6-31G (d) level

of meaningless differences in energy level values. For all the discussed compounds, HOMO is essentially located on the anthracene core. The LUMO density of states is mainly delocalised along the longest axis of the BPEA backbone and within the DCV acceptor framework, Fig. 3.

It is easy to notice a slight dependence of both the HOMO and LUMO levels on the substitution of anthracene core with methyl groups. These slightly electron-donating substituents raise the HOMO and LUMO energy ($-5.38 < -5.35 < -5.31$; $-3.33 < -3.30 < -3.27$). Alkoxy groups also contribute to this substantially. Similar trends have been observed for the series of 9,10-disubstituted anthracenes **3** reported in the paper of Linker *et al.* [38]. The calculated energies for HOMO and LUMO are -5.31 eV and -3.27 eV in **4c**, respectively. The HOMO–LUMO gap in **4c** was estimated to be 2.04 eV. The band-gap estimated from the long wavelength absorption edge gives a similar value of 2.02 eV.

2.3. Absorption and fluorescence

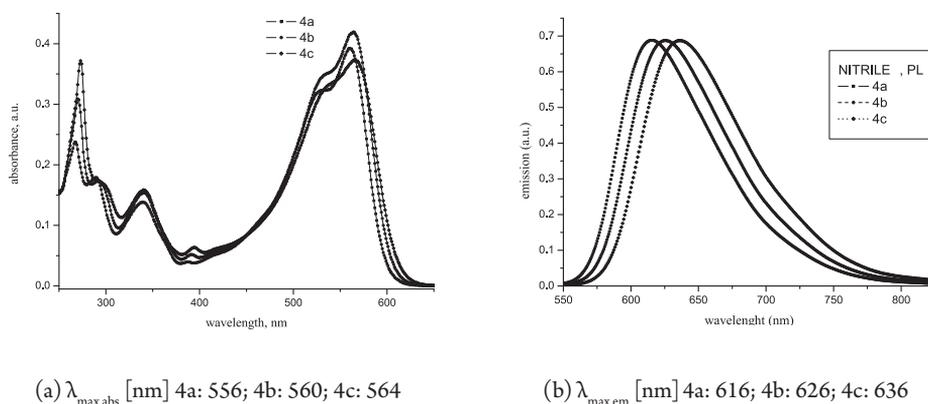


Fig. 4. Absorption (a) and emission (b) spectra of **4a**, **4b**, **4c** ($\lambda_{\text{ex}}=405$ nm)

The basic spectroscopic characterisation of BPEA dicyanovinyl (DCV) end-capped derivatives, i.e. their optical absorption and fluorescence spectra, can be derived from Fig. 4. The absorption spectrum exhibits two distinct bands in the CH_2Cl_2 solution, Fig. 4a. The absorption bands are similar to that of unsubstituted BPEA in the low energy region [15, 39]. The most prominent band associated with ICT transfer is centred around 560 nm. The band at the shorter wavelength region results from localised π – π^* transitions. The photoluminescence (PL) spectra of the compounds exhibiting featureless emission are also shown in Fig. 4b. They are slightly dependent on alkyl substitution and they are bathochromically shifted from 616 to 636 nm, respectively.

2.4. Device preparation

The current–voltage (I–V) characteristics of the devices were measured using the Keithley 2400 sourcemeter. The devices were illuminated with a light intensity of 1.3 mW/cm^2 . The thicknesses of layers were determined by spectroscopic ellipsometry. In the present work, the

Woollam Spectroscopic Ellipsometer (SE) with dedicated software has been used. The multilayer model was fitted to the following layer arrangements: glass / ITO / PEDOT: PSS / active layer / Al. This required the application of various models and sophisticated experimental procedures [40–43]. First of all, the parameters associated with the substrate, which is a glass coated with ITO, were set out using the Cauchy model. Then, the n and k parameters, as well as the thickness of the ITO (glass / ITO), were determined by means of the Drude model with the generic oscillator describing semiconducting properties. The latter-mentioned model was also employed to conduct separate measurements and to perform the calculations of n and k for: (a) poly-(styrenesulfonate) (PEDOT: PSS); (b) mixtures of poly(3-hexylthiophene-2,5-diyl (P3HT) and a synthesised compound; (c) 3-butylthiophene (P3OT) and a synthesised compound. They were all prepared on a glass substrate. The designated values of n and k for the above listed compounds were subsequently used to determine the parameters of the thin layers of PEDOT: PSS on an ITO substrate (glass / ITO / PEDOT: PSS). Finally, the layer of P3HT and a synthesised compound, as well as the layer of P3OT and a synthesised compound, were applied on this substrate (glass / ITO / PEDOT: PSS). The tests finished with ellipsometric measurements and the thickness of the active layer was determined using dielectric functions of bulk heterojunction (BHJ) by applying the effective medium approximation model (for the results, see Table 2).

2.5. Preparation of photovoltaic cells

Photovoltaic cells were fabricated on ITO-covered glass slides (15 mm x 15 mm), which were cleaned in an ultrasonic bath using organic solvents. Next, ITO was covered with a PEDOT:PSS thin film (thickness about 100 nm) by spin-coating at 6000 rpm for 30 s and left for 30 min in a vacuum heater at 120 °C. After 30 min, the mixture of BPEA derivatives 4 and thiophenes (dissolved in chloroform) was spun over (at 2000 rpm for 30 s) the PEDOT:PSS thin film in order to obtain the active layer (about 100 nm). Next, the devices were left for 30 min in a vacuum heater at 60 °C. After that, the samples were introduced into a high vacuum chamber (10^{-6} mbar) in order to deposit Al contacts (100 nm) by thermal evaporation. The active surface of the samples was 12 mm².

3. Results and discussion

The BPEA compounds (4a, 4b, 4c) were measured as components of the active layer in bulk heterojunction (BHJ) photovoltaic (PV) cells. Two kinds of solar cells were prepared and characterised based on active layers consisting of blends of P3HT or P3OT and BPEA (weight ratio 2:1, 1:1 or 1:2), Fig. 5a, where P3HT and P3OT play the role of a donor.

Consequently, the energy levels of the acceptors were chosen in such a way that caused the division of an exciton. When comparing HOMO and LUMO levels of our compounds and thiophenes, it is not possible to foresee unequivocally which pair of the compounds will have good photovoltaic properties. One has to also take into account problems caused by the

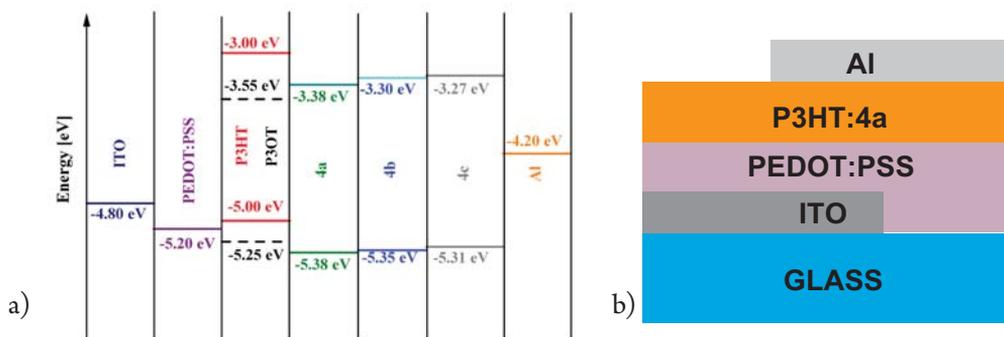


Fig. 5. a) Schematic diagram of HOMO/LUMO energy levels of donors: P3HT, P3OT and acceptors: 4a, 4b, 4c, b) a typical solar cell in this study

spatial arrangement of the chemical structures. The compounds mentioned were analysed in blends containing P3HT and P3OT.

The photovoltaic experiments were done for non-encapsulated devices. The fabricated BHJ PV cells consist of electrodes, Fig. 5b: aluminium acts as a cathode (collecting electrons) and ITO applied as the anode for the purpose of collecting holes, PEDOT:PSS used as a hole transporting material (HTM) and anode buffer layer and active layers. As donors in devices two poly(3-alkylthiophene)s were tested, that is, regioregular P3HT and P3OT. According to the estimated value of orbital energy levels (Table 1), it seems that both P3HT and P3OT could act as electron donors as compared to BPEA compounds (4a, 4b, 4c).

Table 2. Characteristics of devices in the configuration ITO/PEDOT:PSS/P3HT:4a/Al and ITO/PEDOT:PSS/P3OT:4a(4b,4c)/Al under light illumination (1.3 mW/cm²)

Active layer (weight ratio)	Thickness [nm]	U_{oc} [V]	J_{sc} [$\mu\text{A}/\text{cm}^2$]	FF	PCE [%]
4a:P3HT (1:1)	112	0.554	102	0.143	0.61
4a:P3HT (2:1)	98,4	0.651	76.7	0.060	0.417
4a:P3OT (1:2)	121	0.501	92.4	0.225	0.793
4a:P3OT (1:1)	106	0.406	112	0.190	0.659
4b:P3OT (1:2)	101	0.498	137	0.172	0.896
4b:P3OT (1:1)	119	0.680	58.1	0.105	0.315
4c:P3OT (1:2)	123	0.295	351	0.236	1.85
4c:P3OT (1:1)	99.1	0.321	415	0.274	2.77
4c:P3OT (2:1)	89.4	0.236	364	0.326	2.13

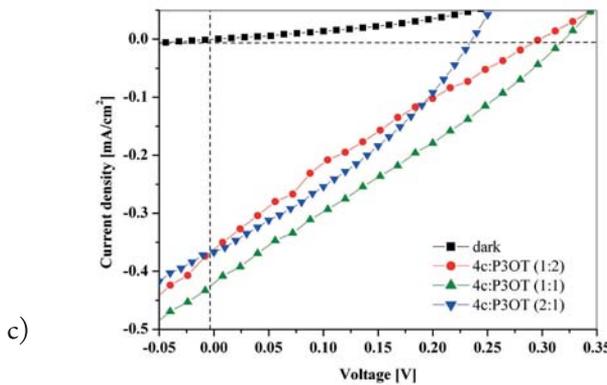
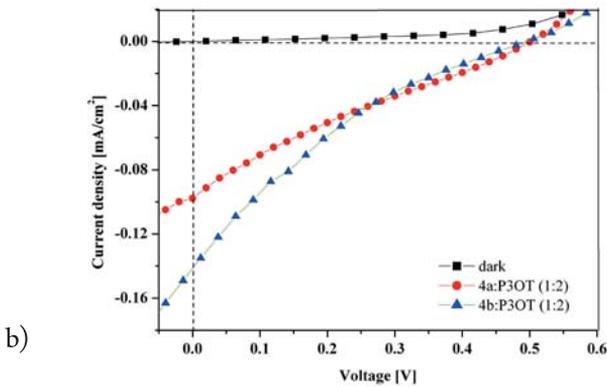
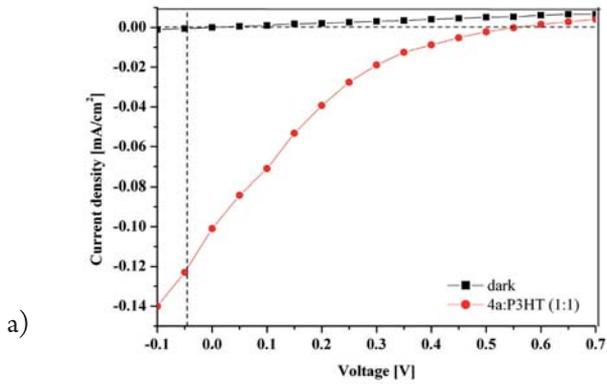


Fig. 6. Comparison of the dark and illuminated current density versus voltage characteristics for device a) ITO/PEDOT:PSS/P3HT:4a/Al, b) ITO/PEDOT:PSS/P3OT:4a(4b)/Al and c) ITO/PEDOT:PSS/P3OT:4c/Al

Table 2 shows that compound 4c is more compatible with P3OT in photovoltaic structures. Better results are shown by those that contain more polythiophene. This is connected with an easier conduction along the polymer chain. On the other hand, the blend of 4c with polythiophene (weight ratio 1:1) presents better photovoltaic parameters (Table 2) if combined with P3OT than with P3HT.

Considering the data presented in Table 2, one can conclude that the increase of compound 4a content in the active layer with P3HT from 1:1 to 2:1 results in a reduction in the value of the current density and the power conversion efficiency, but it causes a slight increase in the open circuit voltage.

Taking into account the effect of poly(3-alkylthiophene) on device performance, a higher value of both J_{sc} and open-circuit voltage was observed for P3OT given a higher value of PCE, except for 4b:P3OT (1:2). In the case of device with 4c, the higher J_{sc} and PCE showed the cell with P3OT. The best PCE of about 2.77 % was exhibited a device with 4c:P3OT (weight ratio 1:1). The value of PCE is significantly lower compared to BHJ PV cell based on P3HT and typical acceptor [6]-phenyl-C61 butyric acid methyl ester (PCBM) [44–47]. Comparing the results, it can be said that the higher PCE value was obtained for the device with the active layer consisting of 4c and P3OT in relation to cell containing 4a or 4b and P3OT. In the case of 4c, the PV parameters were strongly dependant on the weight ratios of components.

Figure 6 displays the representative dark and illuminated current density versus voltage (J - V) characteristic for a device based on 4a, 4b and 4c mixed with P3HT or P3OT. The photovoltaic parameters: open-circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) are gathered in Table 2.

4. Conclusions

The study revealed pronounced effects of the chemical structure on the optical properties of the investigated compounds. They absorbed light in the range from 250 to 600 nm. The maximum absorption band is centered around 570 nm and moves slightly bathochromically because of anthracene core substitution. The emission maxima move from 610 to 640 nm, respectively. The energy band gap is about 2 eV for all structures: 4a, 4b and 4c. The presented structures, based on photovoltaic tests, can be treated as n-type semiconductors with HOMO level between -5.31, -5.35 and -5.38 eV. Three compounds were studied for their photovoltaic effect. They were analysed in blends containing P3HT and P3OT. Better results are exhibited by those that contain more polythiophene. The best efficiency (2.77%) is seen in photovoltaic cell based on the 4c blended with P3OT (1:1 weight ratio). This can either be explained in terms of a better uptake of charge carriers by 4c, or it could also well be the mutual spatial arrangement of the molecules to support this point of view. It is known that anthracene based-oligomers possess greater structural symmetry, which may enhance supramolecular organisation in BHJ blends [48]. The comparison of HOMO-LUMO energy levels (see Fig. 5) clearly shows which of the produced photovoltaic cells will demonstrate the greatest efficiency. The electron donors are, of course, P3HT and P3OT thiophene polymers.

P3OT energy levels with a 4c compound provide the easiest possibility of separating charges as well as their transportation and delivery to the electrodes without losses associated with placing them in one molecule. When analysing the photovoltaic properties of 4c: P3OT for the weight ratios of 2:1, 1:1 and 1:2, one can see that the easiest conduction of holes in the device occurs for the weight ratio of 1:1. It, in turn, gives the highest efficiency of converting light to electric energy. In summary, 9,10-bis(phenylethynyl)anthracene, BPEA, extensively modified with electron donating and accepting groups, seems to be quite suitable as a material for optoelectronic applications.

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