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Dicyclopenta[cd,jk]pyrene Based Acceptors in Conjugated Polymers

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A series of reduced band gap donor-acceptor copolymers that contain electron accepting 1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene were prepared. The hydrocarbon acceptor relies on its cyclopenta-fused polycyclic aromatic hydrocarbon (CP-PAH) character to access a relatively reduced lowest unoccupied molecular orbital. The donor unit was varied between thiophene, bithiophene, and 1,4-diethynyl-2,5-bis((2-octyldodecyl)oxy)-benzene producing polymers with band gaps between 1.69 – 1.74 eV. The synthetic methodology as well as the optoelectronic properties of the donor-acceptor copolymers, including thin-film absorption and cyclic voltammetry, are presented.

Introduction

Electron deficient monomers used to create donor-acceptor copolymers[1] traditionally rely on inductively withdrawing (e.g., fluorinated)[2,3] or pi-electron withdrawing groups with heteroatoms (e.g., imides)[4–6] to achieve reduced lowest unoccupied molecular orbitals (LUMOs). When these monomers are combined with a suitable donor monomer, orbital mixing between the donor and acceptor units can then lead to materials with reduced band gaps that can have beneficial attributes for electronic devices such as organic photovoltaics.[7–9] The use of purely hydrocarbon monomers (e.g., only carbon and hydrogen) are typically limited in role to electron rich (albeit relatively weak) donor monomers. The use of simple hydrocarbon building blocks as electron accepting units are much rarer.[10–12] Because traditional alternant polycyclic aromatic hydrocarbons (PAHs) have no inherent dipoles, significantly large PAHs[13,14] or unique molecular frameworks that manipulate aromatic/antiaromatic properties[15–19] of a molecule must be utilized to gain access to noteworthy physical properties such as reduced LUMOs. We have recent interest in using functionalizable cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) as electron accepting units.[12,20–23] The unique reduction chemistry of CP-PAHs lie in their ability to form 4n+2 cyclopentadienyl anions that are formally aromatic in their reduced state. This chemistry allows the effective lowering of LUMO energy levels and therefore provides utility for donor-acceptor copolymers or in accessing n-type semiconductors.[24–28] In this contribution, we show that 4,9-dibromo-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta-[cd,jk]pyrene can be readily synthesized and is a capable acceptor monomer in the synthesis of donor-acceptor copolymers and give reduced band gap materials (**1**-**3**) when copolymerized with thiophene, bithiophene, and 2,5-dioctyloxyphenylene-1,4-ethynylene (Figure 1).

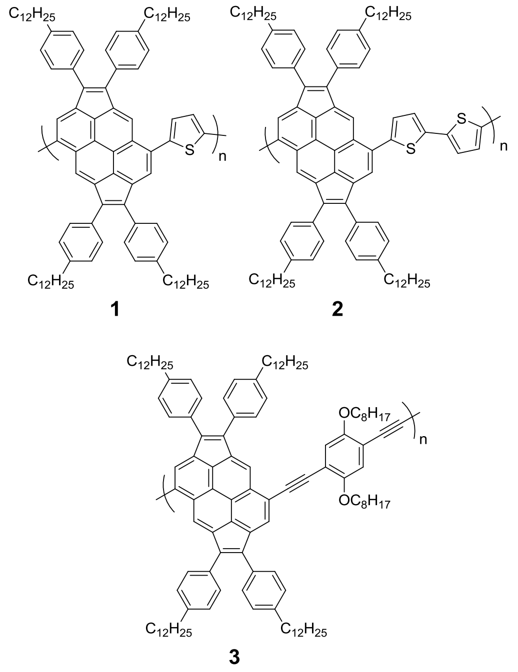

Figure 1. Donor-acceptor copolymers with 1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene based acceptors.

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Scheme 1. Synthesis of 4,9-dibromo-1,2,6,7-tetraaryldicyclopenta[cd,jk]pyrene and polymers **1**-**3**.

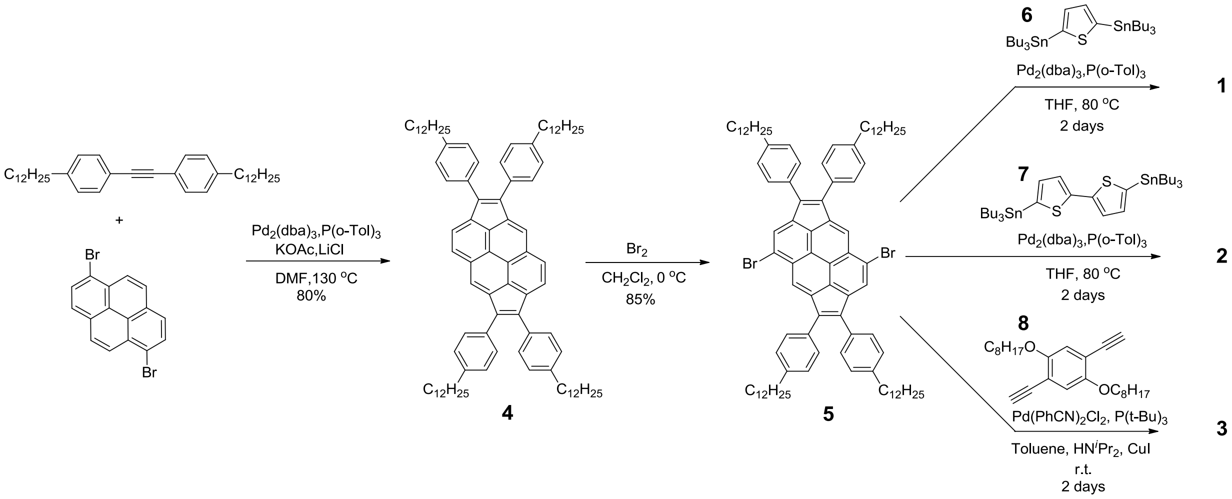

Table 1. Summary of molecular weight and optoelectronic properties of polymers **1**-**3**.[a]

Polymer	M_n[b]	*Đ*	$E_{ox,onset}$ (V)[a]	$E_{red,onset}$ (V)[a]	HOMO (eV)	LUMO (eV)	E_{gap}^{ec} (eV)	λ_{onset} (nm)	E_{gap}^{opt} (eV)
1	20,833	2.6	0.54	-1.39	-5.34	-3.41	1.93	711	1.74
2	69,981	2.5	0.51	-1.39	-5.31	-3.41	1.90	715	1.73
3	20,715	2.6	0.72	-1.23	-5.48	-3.57	1.91	732	1.69

[a]Potentials are measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 4). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential and were used to calculate the HOMO and LUMO[c] via ferrocene reference in vacuum (4.8 eV). [b]Determined by GPC in THF with polystyrene standards. *Đ* = dispersity.

Results and Discussion

We have employed our recently optimized[23] palladium-catalysed cyclopentannulation[29–33] conditions to combine 1,6-dibromopyrene and 1,2-bis(4-dodecylphenyl)ethyne to give 1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene **4** in high yield (Scheme 1). The presumed mechanism[31] for the cyclopentannulation transformation proceeds through oxidative addition of the palladium species to the aryl bromide bond followed by association with the alkyne via an eta-2 coordination. Full insertion of the palladium into the alkyne forms a stable alkenyl palladium intermediate that can perform a second palladium insertion into the pyrene core. Base promoted elimination of the palladium species lead to aromatization giving the final CP-PAH. This precursor can be transformed into the desired monomer via the known regioselective functionalization chemistry of pyrene.[34] Bromination with molecular bromine afforded 4,9-dibromo-1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta[cd,jk]pyrene **5** in good yields upon following appropriate workup conditions. We utilized the Nuclear Overhauser Effect (NOE) to provide support for the assigned bromination regiochemistry (Supporting Information). We found that direct TLC analysis of the reaction mixture, or running a silica-gel column directly led to complete decomposition of the compound with the byproducts not immediately obvious. We believe the compound reacts with the silanol functionality via an HBr catalyzed transformation. Therefore, workup to obtain **5** involved evaporation of all the reaction solvent followed by trituration with hot methanol to give a dark red solid. Interestingly, after appropriate workup, the molecule is stable to chromatography on silica gel. The bromination selectivity is also noteworthy owing to the lack of bromine addition across the isolated double bond of the five-member ring as one would expect for simple alkenes. This result supports the hypothesis the fused pi-bond of the five-membered ring is more aromatic like and participates in significant conjugation with the inner aromatic core.

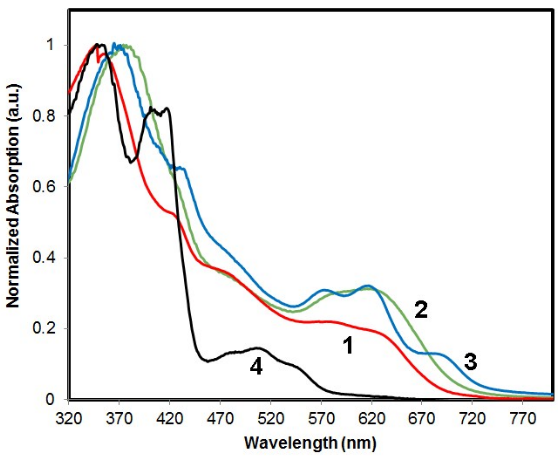

Figure 2. Solution absorption of **1**-**4** in chloroform.

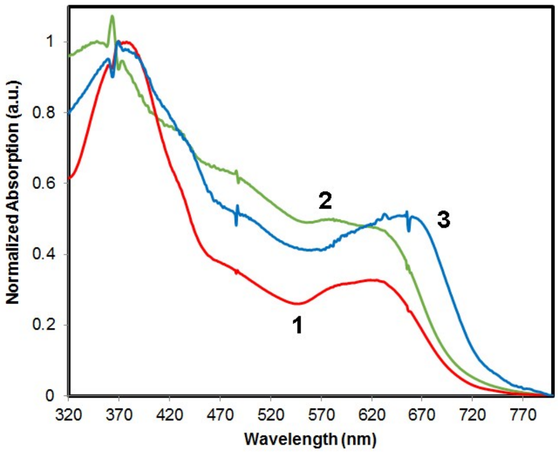

Figure 3. Thin film absorption of **1**-**3**. Optical band gaps (Table 1) taken from the onset of absorption.

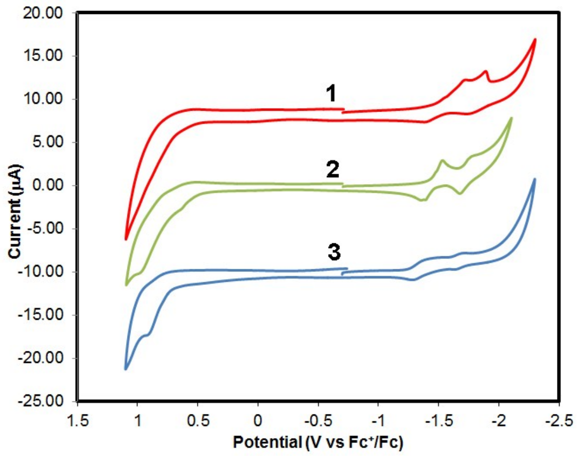

Figure 4. Cyclic voltammetry of **1**-**3** (top to bottom) in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile with platinum working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV/sec. Ferrocene added as internal standard and referenced to 0 V in following scan (not shown).

With the CP-PAH monomer **5** in hand, we performed polymerizations with 2,5-bis(tributylstannyl)thiophene (**6**), 5,5'-bis(tributylstannyl)-2,2'-bithiophene (**7**), and 1,4-diethynyl-2,5-bis((2-octyldodecyl)oxy)-benzene (**8**) under palladium catalysis conditions. For the Stille-type cross-couplings with tributylstannanes **6** and **7**, the polymerizations were carried out for 2 days with the catalyst system of $Pd_2(dba)_3$ and $P(o\text{-Tol})_3$ in THF. After purification by precipitation and washings, polymers **1** and **2** were obtained as dark green solids in 82 and 84 % yield, respectively. For the Sonogashira cross-coupling with **8**, the polymerization was carried out for 2 days with the catalyst system of $Pd(PhCN)_2Cl_2$, $P(t\text{-Bu})_3$ and CuI in toluene with diisopropylamine as a base. The resulting polymer was similarly obtained via precipitations to give a dark green solid in 72% yield. All polymers reached moderate molecular weights of between 20-70 kDa (Table 1) and were soluble in common organic solvents such as THF, toluene, and chloroform.

Solution based absorption spectra of polymers **1**-**3** and CP-PAH acceptor **4** are shown in Figure 2. A definitive bathochromic shift is found upon polymer incorporation with **4** having a longest wavelength absorption (λ_{onset}) of ~570 nm while the polymeric materials absorb out to ~700 nm. Thin film absorption and cyclic voltammograms were obtained to probe the solid-state optoelectronic properties of **1**-**3** with films being prepared by drop-casting dichloromethane solutions on a glass slide or a platinum electrode, respectively. The thin film absorption spectra of **1**-**3** (Figure 3) show they all broadly absorb visible light between 320-720 nm with slight differences in relative intensity. The λ_{onset} of the thiophene containing polymers (Table 1) bathochromically shift going from the monothiophene polymer **1** (711 nm) to the bithiophene polymer **2** (715 nm). A further bathochromic shift is found when switching to the bis((2-octyldodecyl)oxy)-benzene monomer in **3** (732 nm). These absorption onsets represent reduced-band gap polymeric materials with energies in the range 1.69-1.74 eV. [35–37]

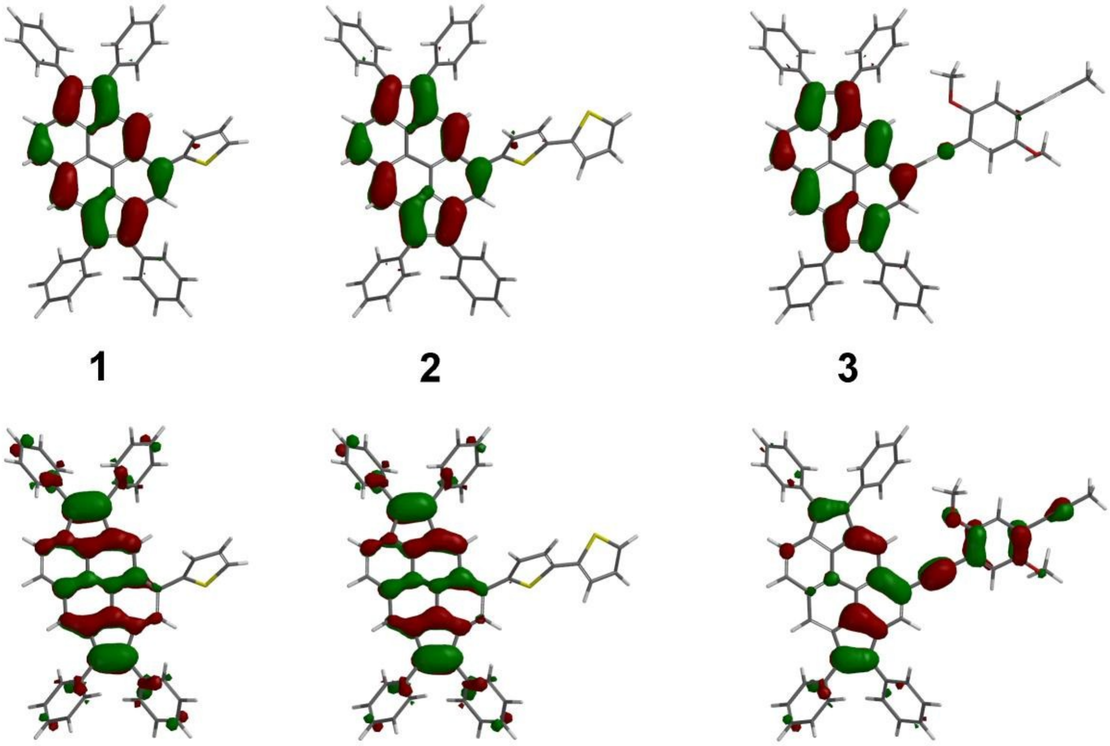

Figure 5. The B3LYP/6-311g DFT calculated HOMO (bottom) and LUMO (top) contours of **1**-**3** fragments.

The redox chemistry was interrogated via cyclic voltammetry to calculate the highest occupied molecular level (HOMO) and LUMO energies of the materials (Figure 4). Each polymer gave an irreversible anodic process and two cathodic processes that were reversible or pseudo-reversible. As expected, the HOMO was destabilized when going from monothiophene **1** (-5.34 eV) to bithiophene **2** (-5.31 eV) with the LUMO level staying equivalent at -3.41 eV. Surprisingly, the HOMO of **3** was lower in energy (-5.48 eV) than the thiophene derivatives even with the electron rich alkoxy substituents. Furthermore, the LUMO of **3** was also reduced to -3.57 eV. Because the HOMO and LUMO were both stabilized in a similar magnitude, the resulting optical band gap was not strongly modulated in relation to the thiophene polymers. This behavior is seemingly not consistent with traditional donor-acceptor theory where stronger donors lead to elevated HOMO levels and stronger acceptors lead to lowered LUMO levels. The significant difference of molecular structure between the thiophene polymers and bis((2-octyldodecyl)oxy)-benzene polymer may affect the overall redistribution of frontier molecular orbitals upon mixing in the polymer state. The DFT generated HOMO and LUMO energy levels were calculated and used to show the distribution of electrons at the frontier orbitals. As shown in Figure 5, the LUMO contours of each polymer are essentially identical with the electron density localized on the CP-PAH core. This is expected as the CP-PAH character of this unit is known to develop the reduced cyclopentadienyl character. The HOMO contours of **1** and **2** are similar with the majority of the electron density resides on the CP-PAH core. Only in **3** is the HOMO more distributed onto the presumed donor unit. The difference between the frontier orbitals of these polymers may play a significant role in the difference in energies found in the CV data. More electron rich monomers may further the separation of the HOMO and LUMO overlap.

Conclusions

In conclusion, we have demonstrated that donor-acceptor copolymers with 1,2,6,7-tetra(4-dodecylphenyl)dicyclopenta-[cd,jk]pyrene accepting units can be prepared and are reduced band gap materials. The synthetic strategy to access the all hydrocarbon acceptor monomer unit is short and can be accomplished in high yields. The defining feature of the polymer system is the unique CP-PAH character of the acceptor unit that provides access to reduced LUMO levels, a feature that is traditionally only accessed with monomer units that have heteroatom inclusion. This strategy utilizes the unique play of aromaticity / antiaromaticity to form unique polymeric materials and is a subject we continue to pursue.

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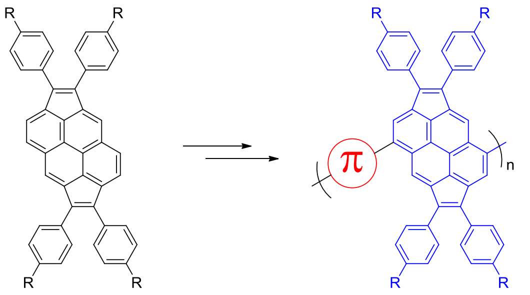

All Hydrocarbon Acceptor

Donor-Acceptor Copolymers