Donor-Acceptor Copolymers from Cyclopentannulation Polymerizations with Dicyclopenta[cd,jk]pyrene and Dicyclopenta[cd,lm]perylene Acceptors

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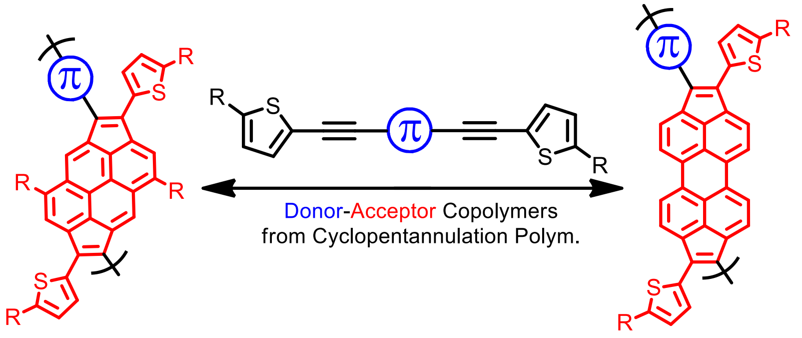


Abstract:

A series of donor-acceptor copolymers with dicyclopenta[*cd,jk*]pyrene and dicyclopenta[*cd,lm*]perylene acceptor units was prepared via palladium catalyzed cyclopenta-annulation reactions. The acceptor units were paired with diethynyl containing donor groups based on benzo[1,2-*b*:4,5-*b*']dithiophene, thieno[3,2-b]thiophene, and 4-octyl-4H-dithieno[3,2-b:2',3'-d]pyrrole to create six polymer variants. The cyclopentannulation polymerization resulted in copolymers with molecular weights (Mn) of 6-14 kDa and broad light absorption in the visible region with band gaps of 1.38-1.85 eV. The synthetic methodology, as well as optoelectronic properties, including thin-film absorption and cyclic voltammetry, of the donor-acceptor copolymers are presented.

Introduction:

Donor- acceptor copolymers have been widely utilized for organic electronic applications due to their unique advantages including broad light absorption, tunable energy levels and charge transfer capabilities.[1–3] A variety of acceptor functionalities have been developed with most relying on motifs incorporating either pi-electron withdrawing groups, such as imides or other heteroatom containing species.[4–8] Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) are alternative acceptor motifs that contain only carbon.[9,10] These systems have low-lying lowest unoccupied molecular orbitals (LUMOs) owing to their ability to form 4n+2 cyclopentadienyl anions in their reduced state.[11–13] In our previous work, we showed that conjugated donor-acceptor copolymers could be prepared by a palladium-catalyzed annulation polymerization.[14] Here the growth of the polymer arises from the formation of a new ring instead of a new aryl-aryl sigma bond, as traditionally realized in metal-catalyzed cross-coupling polymerizations.[15] This strategy is reminiscent of C-H activation polymerization chemistry that is an atom economical process. The annulation polymerization approach has only more recently been utilized to grow polymeric materials.[16–23] Our preliminary work involved only the cyclopenta[*h,i*]aceanthrylene acceptor unit. To develop a larger library of donor-acceptor copolymers, we have designed and synthesized a series of new donor-acceptor copolymers with new acceptor units based on dicyclopenta[*cd,jk*]pyrenes and dicyclopenta[*cd,lm*]perylenes. These acceptor units were paired with three donor groups based on benzodithiophene, thieno[3,2-b]thiophene, and dithieno[3,2b:2′,3′-d]pyrrole to afford a series of six new donor-acceptor copolymers **1**-**6** (Figure 1).

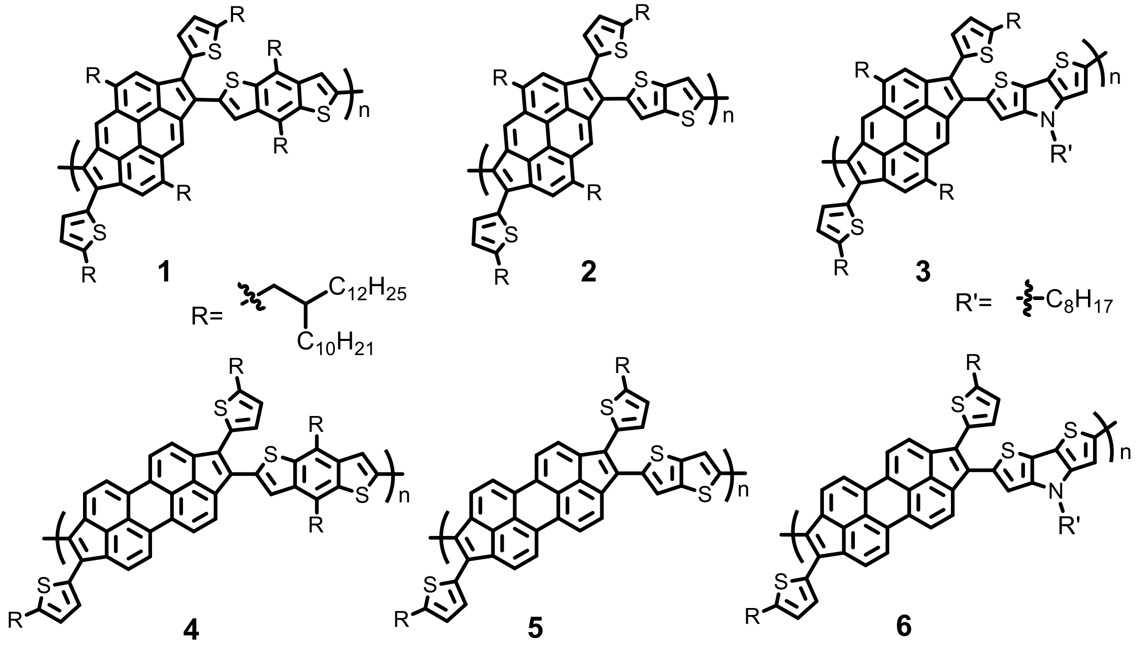


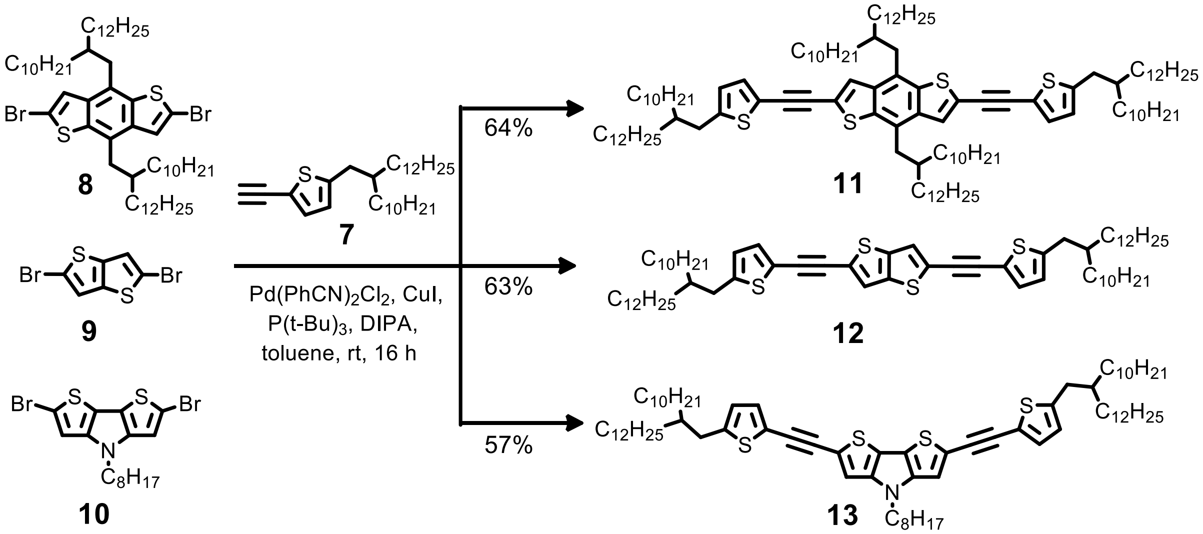
Figure 1. Donor-acceptor polymers with dicyclopenta[*cd,lm*]perylene and dicyclopenta[*cd,jk*]pyrene based acceptors.

The palladium-catalyzed annulation chemistry employed here is an efficient ring forming reaction that we have utilized to create both small molecule and polymeric materials. While molecular systems with 1,6-dibromoanthracene as the aromatic precursor has been developed the most,[13,24–27] we and others have also investigated small molecule systems based on higher acenes, anthradithiophene, and pyrene.[28–31] In this work, we have extended the cyclopentannulation polymerization chemistry to include monomers based on 1,6-dibromopyrene and 3,9-dibromoperylene. These monomers open new possibilities to further tune frontier orbital energies of CP-PAH based copolymers over a broad range and give access to unique carbon rich materials.[32] An initial version of this work was deposited in ChemRxiv on May 21, 2020.[ref]

Results and Discussion

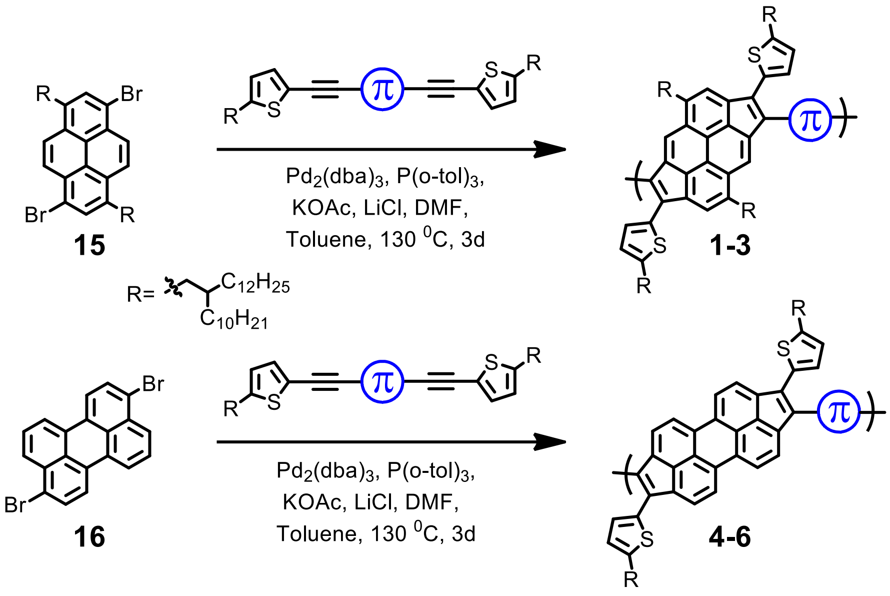
The difunctional monomer requirement for the donor portion of the annulation polymerization necessitates two ethynylene groups (Scheme 1). To access these monomers, we employed the Sonogashira cross-coupling reactions of 2-(2-decyltetradecyl)-5-ethynylthiophene **7** with 2,6-dibromo-4,8-bis(2-decyldodecyl)benzo[1,2-b:4,5-b']dithiophene **8**, 2,5-dibromothieno[3,2-b]thiophene **9**, and 2,6-dibromo-4-octyl-4H-dithieno[3,2-b:2',3'-d]pyrrole **10** (Scheme 1). The cross-coupling conditions utilized a catalyst system of $Pd(PhCN)_2Cl_2$, $P(t\text{-}Bu)_3$, diisopropylamine, and CuI in toluene. The bis-ethynylene containing monomers **11**, **12** and **13** were prepared in 57-64% yield.

Scheme 1. Synthesis of donor groups using Sonogashira cross-coupling reactions.



Our preliminary investigations into copolymers prepared from the polymerization with 1,6-dibromopyrene resulted in materials that were too insoluble for characterization. To help solubilize the resulting co-polymers, branched solubilizing chains were incorporated onto the pyrene scaffold through a Kumada cross-coupling reaction of 1,6-dibromopyrene followed by bromination (Supporting Information). The series of donor-acceptor copolymers **1-6** were synthesized by combining either dibromide **15** or **16** with bis-ethynylenes **11**-**13** using a catalyst system of $Pd_2(dba)_3$, $P(o\text{-}Tol)_3$, KOAc, and LiCl in a solvent system of DMF and toluene at 130 ^{o}C (Scheme 2). The molecular weights (M_n) of donor-acceptor copolymers, as determined by gel permeation chromatography, range between ~6-14 kDa (Table 1) and were similar to the molecular weights obtained previously for the cyclopenta[*hi*]aceanthrylene based

Scheme 2. General synthesis route of D-A polymers based on pyrene and perylene cores.



materials.[14] The resulting polymers were reasonably soluble in common solvents such as chloroform, toluene, and THF.

The optical and electronic properties of the series of polymers were investigated by UV-Vis spectroscopy and cyclic voltammetry. Thin film absorption spectra, using diffuse reflectance spectroscopy, of the polymers are shown in Figure 2. The absorption profiles were modulated with the varying strength of the donor unit. The optical band gaps of the pyrene-based materials, as determined by the onset of absorption, decreased with increasing donor strength with values of 1.85 eV, 1.58 eV, and 1.46 eV for **1**, **2**, and **3**, respectively. Likewise, a similar trend was found for the perylene-based polymers with values of 1.52 eV, 1.51 eV, and 1.38 eV for **4**, **5**, and **6**, respectively. Overall, the series of perylene based polymers gave lower band gap materials.

Cyclic voltammetry (CV) of the polymeric materials was performed in dichloromethane. Using the onset of the reduction waves, the lowest unoccupied molecular orbitals (LUMOs) were found to be between -3.2 eV and -3.4 eV for the pyrene-based copolymers (**1**-**3**) and -3.5 eV to -3.6 eV for the perylene based copolymers (**4**-**6**). The highest occupied molecular orbitals (HOMOs) were also more stabilized in the perylene based materials with energies of -5.11 eV to -5.14 eV for **4**-**6** compared to -5.03 to -5.07 eV for **1**-**3**. While the total energies the molecular orbitals in general were decreased in the dicyclopenta[*cd*,*lm*]perylene cases, the observed smaller optical gaps can be related

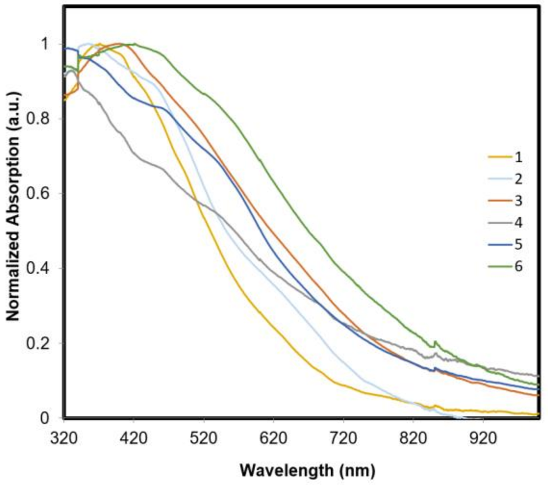


Figure 2. Solid thin film absorption spectra of D–A type polymers **1** to **6**.

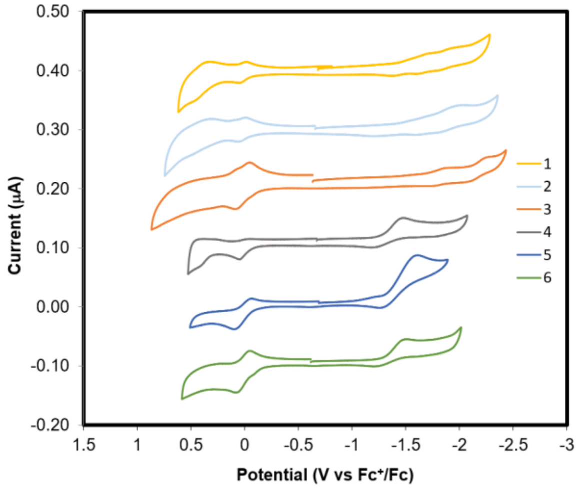


Figure 3. Cyclic voltammetry of **1**-**6** in 0.1 M tetrabutylammonium hexafluorophosphate in dichloromethane with glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 100 mV/sec. Ferrocene added as internal standard and referenced to 0 V.

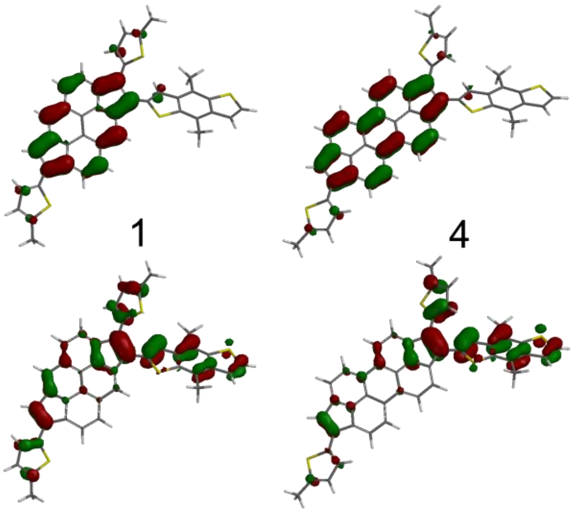


Figure 4. DFT calculated HOMO (bottom) and LUMO (top) contours of polymers **1** and **4**.

back directly related to their better electron accepting properties (e.g., far lower LUMO). Representative DFT calculated structures of the polymer repeat units are shown in Figure 4. In both polymer systems the HOMO contours are located predominantly on the donor aromatic segment, with a smaller probability on the CP-PAH portion of the polymer. Likewise, the LUMO contours of all polymers are specifically isolated on the CP-PAH portion of the polymer repeat unit. These results show that the optical properties of these series of copolymers can be modulated with varying donor and acceptor strength.

Table 1. Summary of molecular weight and optoelectronic properties of polymers **1-6**

Polymer	M_n	PDI	$E_{ox/onset}$ (V)	$E_{red/onset}$ (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	λ_{onset} (nm)	Optical gap (eV)
1	6,023	1.20	0.27	-1.45	-5.07	-3.35	1.72	670	1.85
2	13,424	1.97	0.23	-1.42	-5.03	-3.38	1.65	785	1.58
3	9,319	1.67	0.26	-1.63	-5.06	-3.17	1.89	848	1.46
4	12,193	2.10	0.32	-1.22	-5.12	-3.58	1.54	812	1.52
5	13,965	1.83	0.31	-1.31	-5.11	-3.49	1.62	817	1.51
6	12,729	2.10	0.34	-1.30	-5.14	-3.50	1.64	899	1.38

Conclusions

We have synthesized a series of donor-acceptor copolymers based on dicyclopenta[*cd*,*jk*]pyrenes and dicyclopenta[*cd*,*lm*]perylenes accepting units. The materials were prepared using an efficient palladium catalyzed cyclopentannulation polymerization that gave reasonably high molecular weights. The optical gaps of the polymers for each series of polymers was guided by the donor unit's strength, with the dicyclopenta[*cd*,*lm*]perylene based materials giving lower optical gaps in general owing to their better electron accepting behavior. These results show that the cyclopentannulation polymerization chemistry can be utilized as an alternative synthetic route to new complex carbon-based materials.

Acknowledgments

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