Angewandte
International Edition Chemie

DOI: 10.1002/anie.201206145

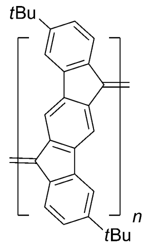
Polycyclic Aromatic Hydrocarbons

Electron Acceptors Based on an All-Carbon Donor–Acceptor Copolymer**

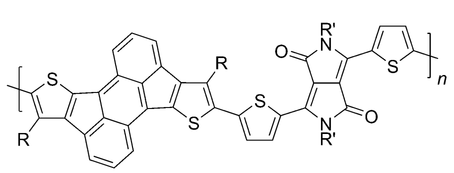
*Jessica L. Jellison, Che-Hsiung Lee, Xinju Zhu, Jordan D. Wood, and Kyle N. Plunkett**

Donor–acceptor-conjugated polymers[1] have been successfully employed to improve organic field effect transistors (OFETs) and organic photovoltaic devices (OPVs).[2a–d] These polymers provide access to low-band-gap materials by increasing the energy level of the highest occupied molecular orbital (HOMO) through electron-donor units while decreasing the energy level of the lowest unoccupied molecular orbital (LUMO) with electron-acceptor units. The reduced band gap leads to beneficial properties such as longer wavelength absorption to match the solar spectrum as well as the opportunity to create n-type or ambipolar semiconductor materials. Over the past decade, several impressive acceptor comonomers, such as benzothiadiazole,[3a,b] fluorinated aromatics,[4a,b] imide and bisimide aromatics,[5a–c] as well as novel ring systems[6] have been copolymerized into conjugated polymers. In general, these electron-accepting monomers require the utility of heteroatoms that are incorporated in pendant π-acceptor functionalities (cyano, imide, etc.) or inductively withdrawing substituents (fluorine) to stabilize the LUMO. We have recently become interested in creating new materials that utilize alternative modes of LUMO stabilization including stabilization through aromatic cyclopentadienyl anions.[7]

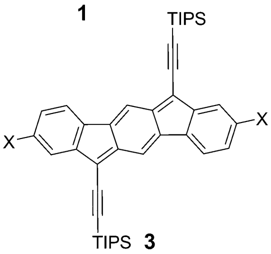
Nonalternant cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) have been extensively studied in the past several decades owing to their structural similarities to fullerenes, interesting optical properties, and remarkable ability to accept electrons.[8a,b] Although these properties would lend themselves favorably to conducting polymers, they have rarely been utilized. Notable exceptions include the low-band-gap poly(indenofluorenes)[9a,b] **1** and newer polymers based on emeraldicene[10a,b] (**2**). Two major drawbacks can be cited for the overall absence of other CP-PAH systems. First, these materials were typically difficult to prepare in large quantities owing to their inefficient (flash-vacuum-pyrolysis methodology)[11] or sometimes time-consuming (Suzuki–Heck methodology)[12] syntheses. Second, they were often difficult to selectively functionalize after formation of the five-membered rings. Recent synthetic advances have led to new scalable and functionalizable small-molecule CP-PAH systems including indenofluorenes **3** (TIPS = triisopropylsilyl),[13a-c] dibenzopentalenes **4**,[14a,b] and cyclopenta[*hi*]aceanthrylene units **5**[15a–d] that show promising electronic and photophysical properties.



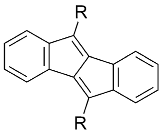
1



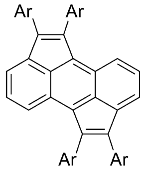
2



3



4



5

In an effort to create new functionalizable CP-PAHs, our group has recently extended the cyclopentenelation methodology of Garcia-Garibay[15a,b] to create gram quantities of 2,7-dibromocyclopenta[*hi*]aceanthrylene (**8**).[7] The synthesis can be accomplished in two steps from the commercially available 9,10-dibromoanthracene (**6**) (Scheme 1). The methodology takes advantage of a unique ring-closure mechanism that is accessible by eliminating CuI from a typical Sonogashira-like cross-coupling with trimethylsilylacetylene. The resulting 2,7-bis(trimethylsilyl)cyclopenta[*hi*]aceanthrylene (**7**) can then be subjected to bromination under mild conditions with *N*-bromosuccinimide (NBS) in THF to give the dibrominated monomer **8** as a green/black solid.

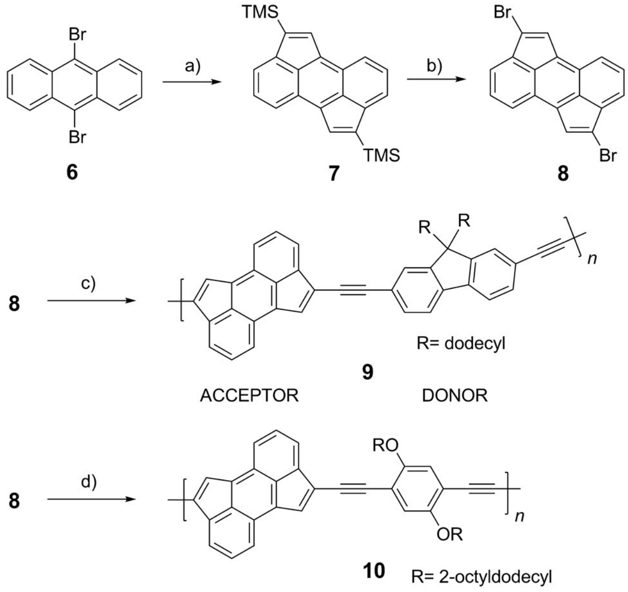
We have found that **8** can be subjected to Sonogashira cross-couplings to create discrete small molecules with relatively small band gaps.[7] With these promising results, we were intrigued by the possibility of utilizing the cyclopenta[*hi*]aceanthrylene unit as an acceptor in donor–acceptor copolymers. We purposely chose a fluorene donor unit that is also composed solely of carbon, and ironically, is also a CP-PAH. However, the five-membered ring in this monomer serves only as a scaffold to help planarize the two benzene rings and does not lend electron-accepting behavior to the polymer. We carried out the Sonogashira cross-coupling polymerization of 9,9-didodecyl-2,7-diethynylfluorene with **8**

---

[*] J. L. Jellison, C.-H. Lee, X. Zhu, J. D. Wood, Prof. K. N. Plunkett
Department of Chemistry and Biochemistry
Southern Illinois University
Carbondale, IL (USA)
E-mail: kplunkett@chem.siu.edu
Homepage: http://www.kyleplunkett.com

[**] This work was supported by startup funds and a seed grant provided by Southern Illinois University.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206145.



Scheme 1. Synthetic pathway to polymers **9** and **10**. Conditions: a) trimethylsilyl(TMS)-acetylene, $[Pd(PPh_3)_2Cl_2]$, PPh_3, NEt_3, benzene, pressure tube at 110°C, 16 h (62%); b) NBS, THF, 0°C, 3 h (66%); c) 9,9-didodecyl-2,7-diethynylfluorene, $[Pd(PhCN)_2Cl_2]$, $PtBu_3$, iPrNH, CuI, toluene, RT, 1–6 h; d) 1,4-diethynyl-2,5-bis((2-octyldodecyl)oxy)benzene, $[Pd(PhCN)_2Cl_2]$, $PtBu_3$, iPrNH, CuI, toluene, RT, 1–6 h.

at room temperature with a catalyst system consisting of $[Pd(PhCN)_2Cl_2]$, $PtBu_3$, and CuI in a toluene/diisopropylamine solvent mixture.[16] Reaction times as low as 1 h provided polymers with reasonable molecular weights (M_n = 19750, PDI = 2.0) and good thermal stability (T_d = 421 °C) after purification by repeated precipitation. Longer reaction times led to modest increases in the molecular weight, larger polydispersities (6 h, M_n = 20980, PDI = 2.75), and less soluble materials. The resulting polymers are dark green and soluble in THF as well as chlorinated solvents to create emerald green solutions (see the Supporting Information).

In the UV/Vis spectrum of the resulting polymer **9** (Figure 1) the low-energy absorption is dramatically red-shifted and much greater in intensity than the analogous absorption of **7**. Such an absorption shift suggests a highly delocalized π-conjugated polymer backbone. The spectrum demonstrates the classical dual-band absorption found in many other donor–acceptor copolymers.[17] The simultaneous absorption of red ($\lambda < 500$ nm) and blue ($\lambda > 600$ nm) light leads to the saturated green color analogous to other green polymeric electrochromic materials.[18a,b] The optical band gap ($E_{gap,opt}$) is estimated to be 1.49 eV. When a film was created, the absorption was further red-shifted ($E_{gap,opt} = 1.42$ eV), which suggests even further planarization and aggregation in the solid state. Similar to small-molecule analogues of CP-PAHs,[7,15b,19] **9** demonstrated no fluorescence in solution. We were therefore unable to perform solvatochromic fluorescence studies to confirm the presence of charge-separated states.[20a,b] Furthermore, absorption spectra of **9** in various solvents and concentrations were all identical. Cyclic voltammetry (Figure 2) was utilized to determine the HOMO (−5.27 eV) and LUMO (−3.69 eV) energy levels in THF (see the Supporting Information). The characteristic two-electron reduction (Scheme 2) of the cyclopenta[*hi*]aceanthrylene, which is assigned to the formation of two stabilized, $(4n+2)$ electron benzocyclopentadienyl anions, was present in both monomer **7** and polymer **9**, albeit shifted to lower potentials for the polymer.

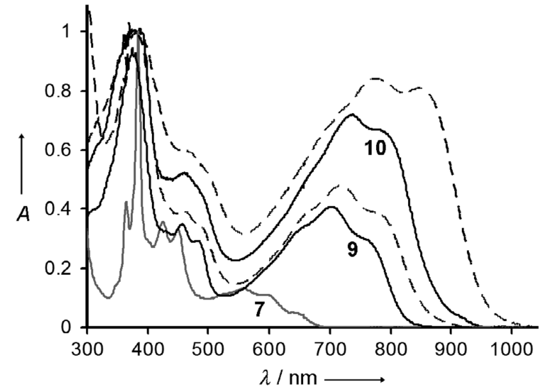


Figure 1. Absorbance of **7** in THF (gray), **9** in THF (middle) and in film (dashed line), and **10** in THF (top) and in film (dashed line).

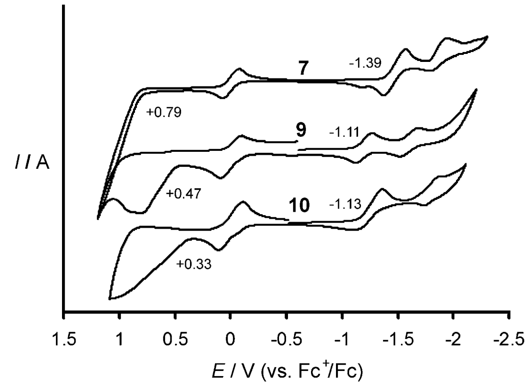
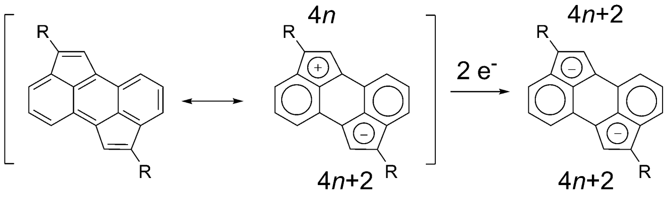


Figure 2. Cyclic voltammograms of **7** (top), **9** (middle), and **10** (bottom) in THF with 0.1 M tetrabutylammonium hexafluorophosphate. Values listed are the onset values of oxidation (left) or reduction (right). Scan rate = 50 mV s^{-1}. Ferrocene added as internal standard and referenced to 0 V.



Scheme 2. Benzocyclopentadienyl anion stabilization.

The copolymer **9** possesses an impressively small band gap for an all-carbon system, although it is similar in energy to the that of the all-carbon poly(indenofluorenes) homopolymers previously described.[9a] To demonstrate the benefit of the donor–acceptor copolymer system, we employed a stronger donor unit to modulate the energy gap. Although it is not entirely composed of carbon, we chose the well-known bis(alkoxy)benzene donor due to its synthetic accessibility and because it is known to be a stronger donor than fluorene. Utilizing similar polymerization conditions as described above, **8** was copolymerized with 1,4-diethynyl-2,5-bis((2-octyldodecyl)oxy)benzene to create the donor–acceptor copolymer **10** (Scheme 1). The molecular weight and polydispersity increased, similar to **9**, when the reaction time was extended from 1 h ($M_n = 25\,260$, PDI = 2.47) to 6 h ($M_n = 25\,057$, PDI = 3.26). The stability ($T_d = 365\,°C$) and solubility of **10** is poorer than **9**, and are a result of the more symmetrical alkoxy monomer. As expected for a copolymer with a stronger donor unit, a bathochromic shift of the absorption in solution ($E_{gap,opt} = 1.38$ eV) and in the film ($E_{gap,opt} = 1.27$ eV) was observed (Figure 1). Furthermore, the intensity of the low-energy absorption increased compared to **9**, which has been found in other donor–acceptor copolymer systems when stronger donor units are utilized. Overall, the copolymer absorbs intensely over the entire UV and visible region of the spectrum. In the cyclic voltammogram of **10,** reduction onset is similar to that of **9** (-1.13 V vs. -1.11 V, respectively) while the oxidation signal of **10** is considerably lowered compared to that of **5** ($+0.33$ V vs. $+0.47$ V) (Figure 2). The electrochemistry clearly demonstrates the selective destabilization of the HOMO energy level with the increased donor strength of the bis(alkoxy)benzene unit.

Finally, to demonstrate the electron-accepting behavior of **9**, we performed solution-phase fluorescence quenching of the prototypical donor poly(3-hexylthiophene) (P3HT, 10 $\mu g\,mL^{-1}$) with varying concentrations of **9** (1–10 $\mu g\,mL^{-1}$, Figure 3). The LUMO energy level of **9** (-3.69 eV) is comparable in energy to those of PCBM-C_{61} (-3.7 eV) and perylene bisimide (-3.83 eV), which are well-known electron acceptors. A dramatic decrease in the fluorescence of P3HT with increasing concentrations of **9** can be observed. Stern–Volmer analysis of the quenching provided a K_{SV} value of 134 $mL\,mg^{-1}$ ($K_{SV} = 1.1 \times 10^5\,M^{-1}$ based on repeat unit), which demonstrates the efficient electron-accepting behavior of the described CP-PAH polymers.

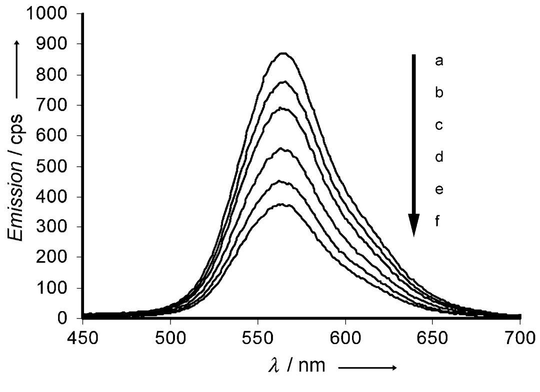


Figure 3. Emission spectrum of P3HT (10 $\mu g\,mL^{-1}$) in THF with varying concentrations of the electron acceptor **9**. Concentrations of **9** (from top to bottom): a) 0, b) 1.0 $\mu g\,mL^{-1}$, c) 2.5 $\mu g\,mL^{-1}$, d) 5.0 $\mu g\,mL^{-1}$, e) 7.5 $\mu g\,mL^{-1}$, f) 10.0 $\mu g\,mL^{-1}$. Corrected for inner filter effect.

In conclusion, we have demonstrated the utility of an externally fused CP-PAH as a unique electron-accepting unit in donor–acceptor copolymers. The electron-accepting behavior is directly attributed to the stabilization of the reduced ($4n+2$) aromatic benzocyclopentadienyl anions rather than traditional stabilization modes such as inductively withdrawing groups or π-accepting heteroatoms. The resulting polymers display low band gaps (< 1.5 eV) and are efficient electron acceptors that may be of utility as n-type materials in OPVs and organic field-effect transistors.

Received: July 31, 2012

Keywords: copolymerization · donor–acceptor systems · polycyclic aromatic hydrocarbons

---

[1] E. E. Havinga, W. ten Hoeve, H. Wynberg, *Synth. Met.* **1993**, *55*, 299–306.

[2] a) B. C. Thompson, J. M. J. Fréchet, *Angew. Chem.* **2008**, *120*, 62–82; *Angew. Chem. Int. Ed.* **2008**, *47*, 58–77; b) M. Zhang, H. N. Tsao, W. Pisula, C. Yang, A. K. Mishra, K. Müllen, *J. Am. Chem. Soc.* **2007**, *129*, 3472–3473; c) C. Li, M. Liu, N. G. Pschirer, M. Baumgarten, K. Müllen, *Chem. Rev.* **2010**, *110*, 6817–6855; d) A. Facchetti, *Chem. Mater.* **2011**, *23*, 733–758.

[3] a) C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. van Hal, R. A. J. Janssen, *Adv. Funct. Mater.* **2002**, *12*, 709–712; b) J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, G. C. Bazan, *Nat. Mater.* **2007**, *6*, 497–500.

[4] a) A. Facchetti, M. Mushrush, M.-H. Yoon, G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 13859–13874; b) Y. Wang, M. D. Watson, *Macromolecules* **2008**, *41*, 8643–8647.

[5] a) X. Guo, F. S. Kim, S. A. Jenekhe, M. D. Watson, *J. Am. Chem. Soc.* **2009**, *131*, 7206–7207; b) F. S. Kim, X. Guo, M. D. Watson, S. A. Jenekhe, *Adv. Mater.* **2010**, *22*, 478–482; c) H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature* **2009**, *457*, 679–686.

[6] L. Gao, W. Senevirathna, G. Sauvé, *Org. Lett.* **2011**, *13*, 5354–5357.

[7] J. D. Wood, J. L. Jellison, A. D. Finke, L. Wang, K. N. Plunkett, *J. Am. Chem. Soc.* **2012**, *134*, 15783–15789.

[8] a) B. D. Steinberg, E. A. Jackson, A. S. Filatov, A. Wakamiya, M. A. Petrukhina, L. T. Scott, *J. Am. Chem. Soc.* **2009**, *131*, 10537–10545; b) A. Ayalon, A. Sygula, P.-C. Cheng, M. Rabinovitz, P. W. Rabideau, L. T. Scott, *Science* **1994**, *265*, 1065–1067.

[9] a) H. Reisch, U. Wiesler, U. Scherf, N. Tuytuylkov, *Macromolecules* **1996**, *29*, 8204–8210; b) E. J. Meijer, D. M. De Leeuw, S. Setayesh, E. V. Veenendaal, B.-H. Huisman, P. W. M. Blom, J. C. Hummelen, U. Scherf, T. M. Klapwijk, *Nat. Mater.* **2003**, *2*, 678–682.

[10] a) A. R. Mohebbi, J. Yuen, J. Fan, C. Munoz, M. F. Wang, R. S. Shirazi, J. Seifter, F. Wudl, *Adv. Mater.* **2011**, *23*, 4644–4648; b) A. R. Mohebbi, F. Wudl, *Chem. Eur. J.* **2011**, *17*, 2642–2646.

[11] L. T. Scott, M. S. Bratcher, S. Hagen, *J. Am. Chem. Soc.* **1996**, *118*, 8743–8744.

[12] H. A. Wegner, L. T. Scott, A. de Meijere, *J. Org. Chem.* **2003**, *68*, 883–887.

[13] a) D. T. Chase, B. D. Rose, S. P. McClintock, L. N. Zakharov, M. M. Haley, *Angew. Chem.* **2011**, *123*, 1159–1162; *Angew.*

Chem. Int. Ed. **2011**, *50*, 1127–1130; b) D. T. Chase, A. G. Fix, B. D. Rose, C. D. Weber, S. Nobusue, C. E. Stockwell, L. N. Zakharov, M. C. Lonergan, M. M. Haley, *Angew. Chem.* **2011**, *123*, 11299–11302; *Angew. Chem. Int. Ed.* **2011**, *50*, 11103–11106; c) F. G. Brunetti, A. Varotto, N. A. Batara, F. Wudl, *Chem. Eur. J.* **2011**, *17*, 8604–8608.

[14] a) T. Kawase, A. Konishi, Y. Hirao, K. Matsumoto, H. Kurata, T. Kubo, *Chem. Eur. J.* **2009**, *15*, 2653–2661; b) M. Saito, M. Nakamura, T. Tajima, *Chem. Eur. J.* **2008**, *14*, 6062–6068.

[15] a) H. Dang, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2001**, *123*, 355–356; b) H. Dang, M. Levitus, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* **2002**, *124*, 136–143; c) C. L. Eversloh, Y. Avlasevich, C. Li, K. Müllen, *Chem. Eur. J.* **2011**, *17*, 12756–12762; d) H. Xia, D. Liu, X. Xu, Q. Miao, *Chem. Commun.* **2012**, DOI: 10.1039/C2CC34992B.

[16] T. Okamoto, Z. Bao, *J. Am. Chem. Soc.* **2007**, *129*, 10308–10309.

[17] P. M. Beaujuge, C. M. Amb, J. R. Reynolds, *Acc. Chem. Res.* **2010**, *43*, 1396–1407.

[18] a) G. Sonmez, C. K. F. Shen, Y. Rubin, F. Wudl, *Angew. Chem.* **2004**, *116*, 1524–1528; *Angew. Chem. Int. Ed.* **2004**, *43*, 1498–1502; b) G. Sonmez, H. B. Sonmez, C. K. F. Shen, R. W. Jost, Y. Rubin, F. Wudl, *Macromolecules* **2005**, *38*, 669–675.

[19] B. F. Plummer, M. J. Hopkinson, J. H. Zoeller, *J. Am. Chem. Soc.* **1979**, *101*, 6779–6781.

[20] a) S. A. Jenekhe, L. Lu, M. M. Alam, *Macromolecules* **2001**, *34*, 7315–7324; b) G. L. Gibson, T. M. McCormick, D. S. Seferos, *J. Am. Chem. Soc.* **2012**, *134*, 539–547.