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Synthesis and Characterization of New Low-Bandgap Diketopyrrolopyrrole-Based Copolymers

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ABSTRACT: Eleven new low bandgap diketopyrrolopyrrole-based copolymers have been prepared by Suzuki or Stille cross-coupling polycondensation reactions. Comonomers derived from thiophene, carbazoles, fluorene, dibenzosilole, and dithienylsilole have been investigated. The structural, thermal, optical, and electrochemical properties of all resulting copolymers have been characterized. These copolymers exhibit broad absorption extending into the near-infrared region with absorption maxima near 640−710 nm and optical band gaps ranging from 1.2 to 1.6 eV. HOMO energy levels of the copolymers vary between −5.6 and −5.2 eV whereas the LUMO energy levels are pinned between −3.9 and −3.8 eV. The combination of extending absorption into near-infrared region, optimal energy levels, and excellent mechanical and thermal properties makes this class of low bandgap copolymers very promising for photovoltaic applications.

1. Introduction

Low bandgap conjugated polymers are the subject of many recent studies because of their potential applications in polymer solar cells.[1] In bulk heterojunction (BHJ) devices, when blended with [6,6]-phenyl-C61 butyric acid methyl ester (PCBM), an ideal polymeric donor should exhibit a bandgap between 1.2 and 1.9 eV with a HOMO energy level between −5.8 and −5.2 eV and a LUMO energy level between −4.0 and −3.8 eV to ensure efficient charge separation while maximizing the open circuit voltage.[2]

Along these lines, some low bandgap diketopyrrolopyrrole (DPP) based copolymers have been recently synthesized by alternating electron-rich and electron-deficient units.[3,4] For instance, Winnewisser and co-workers[4] reported a new low-bandgap (ca.1.4 eV) polymer (BBTDPP1) containing thiophene (electron rich unit) and diketopyrrolopyrrole (DPP) (electron deficient) unit that exhibits excellent ambipolar charge transport properties (hole and electron mobilities up to 0.1 cm^2 V^{-1} s^{-1}). Janssen and co-workers[5] used a similar low-bandgap polymer (PBBTDPP2) for polymer solar cells. When the polymer is processed from a mixture of chloroform and ortho-dichlorobenzene (ODCB) and blended with [70]PCBM, the power conversion efficiency (PCE) goes up to 4.0%. Very recently, our research group reported a promising low bandgap DPP-based poly(2,7-carbazole) derivative (namely PCBTDPP and indicated as **P1** here), which shows high solubility together with a relatively high molecular weight.[6] Preliminary measurements have revealed a hole mobility of 0.02 cm^2 V^{-1} s^{-1} and a PCE of 1.6%.

Taking all of these results into account, we present the synthesis and detailed characterization of eleven new low bandgap copolymers derived from DPP units and different copolymerizing groups (carbazoles, fluorene, dibenzosilole, thiophene, and dithienosilole). Their thermal, optical, and electrochemical properties are also described.

2. Results and Discussion

2.1. Synthetic Strategies and Chemical Characterization. The synthesis of all comonomers and copolymers is outlined in Scheme 1. Comonomer **1** was synthesized according to a previously reported method.[6] A typical Stille coupling reaction in tetrahydrofuran (THF) between comonomer **1** and 2-(tributylstannyl)thiophene was performed to afford compound **2** with a high yield**;** this step was then followed by a dibromination reaction to provide comonomer **3**. Five different diboronic ester derivatives were prepared from the corresponding brominated derivatives and successive treatment with *n*-butyllithium and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane, respectively.[7] Two distannyl derivatives were synthesized from the corresponding dibrominated derivatives and followed by treatment of *n*-butyllithium and trimethyltin chloride. The method of direct lithiation of the nonbrominated precursors was not applied since the separation of mono- and bis-substituted stannanes is very difficult. The new copolymers were synthesized upon Suzuki or Stille cross-coupling polycondensation as shown in Scheme 1. Carbazole,[8a] fluorene,[8b] dibenzosilole,[8c] thiophene,[8d] and dithienosilole[8c,8e] moieties have been selected as electron rich units while the DPP group has been utilized as the electron deficient unit. We have decided to put some thiophene units next to the DPP moiety to minimize the steric hindrance and to lower the band gaps. For the versatile Suzuki polymerization,[9] we have tried different conditions to obtain high molecular weight polymers.[7a,10] Finally, we chose a mixture of THF/water (3:1) as the solvent, tetrakis(triphenylphosphine)palladium(0) as the catalyst, and K_2CO_3 as base to obtain the targeted copolymers.[11] Stille cross-coupling polymerizations were performed in the presence of tetrakis(triphenylphosphine)palladium(0) in toluene to obtain the desired copolymers.[12] Moreover, in order to increase the stability of the copolymers, end-capping reactions were carried out on all polymers. The polymers were purified by successive extractions with acetone, methanol, hexanes to remove catalyst and oligomers; then a chloroform fraction was collected, precipitated from methanol/water (10:1) and isolated. These fractions were further purified over Bio-Rad Bio-Beads S-X1, eluted with chloroform.

The polymerization yields and molecular weights of the copolymers are summarized in Table 1. The molecular weights of the copolymers were measured by size exclusion chromatography (SEC) against monodisperse polystyrene

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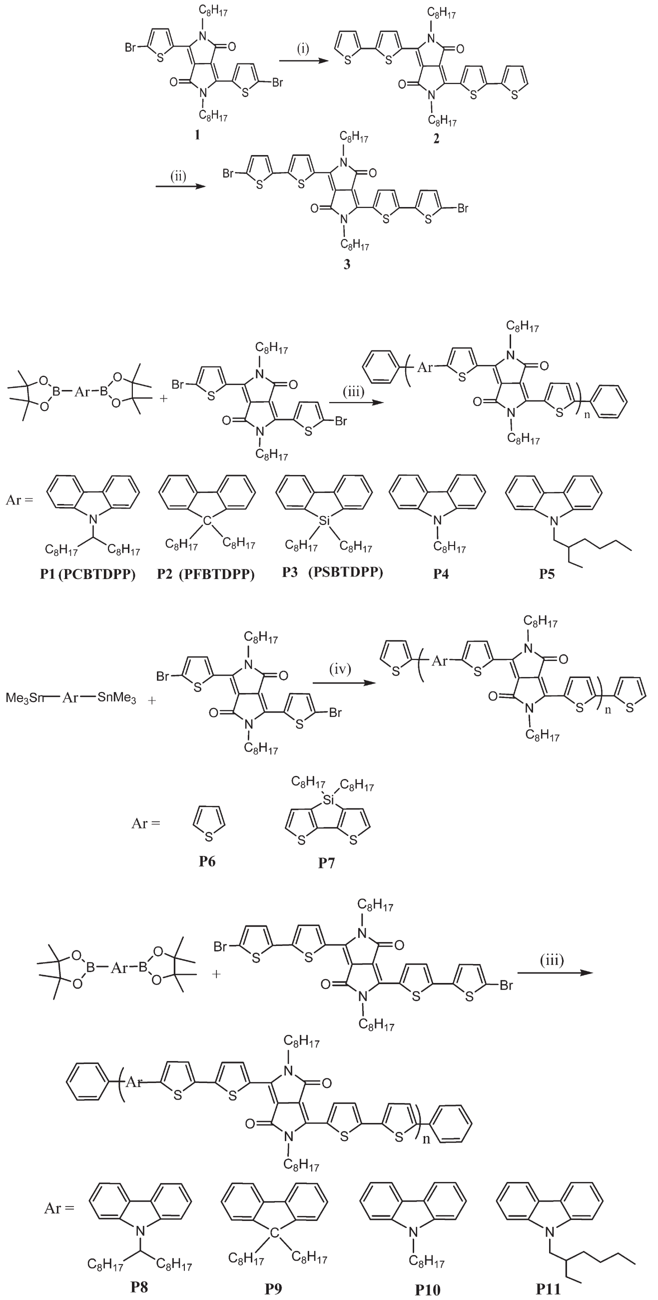
Scheme 1. Synthesis of Comonomers and Copolymers[a]



[a] Reagents and conditions: (i) 2-(tributylstannyl)thiophene, THF, $Pd(PPh_3)_2Cl_2$, reflux, overnight, 98% yield; (ii) 2.1 equiv of NBS, $CHCl_3$, dark, room temperature, 10 h, 92% yield; (iii)$Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80−85 °C for 72 h, then end-capped; (iv) $Pd(PPh_3)_4$, toluene, 110 °C for 24 h, then end-capped.

Table 1. Polymerization Yields, Molecular Weights,[a] **and Thermal Properties of the Copolymers**

polymer	yield (%)	M_n (kg/mol)	M_w/M_n	T_d[b] (°C)	T_g[c] (°C)
P1	94	47	4.3	430	122
P2	92	56	2.5	430	130
P3	88	41	6.8	441	
P4	10	4	1.3	425	134
P5	52	9	1.2	439	170
P6	36	3	1.1	411	179
P7	91	11	3.9	415	164
P8	64	8	1.3	420	191
P9	44	5	1.5	322	114
P10	63	5	1.8	382	72
P11	47	5	1.2	294	125

[a] Determined by SEC in $CHCl_3$ based on polystyrene standards. [b] Temperature at 5% weight loss under nitrogen. [c] Determined by DSC at a heating rate of 20 K/min under nitrogen.

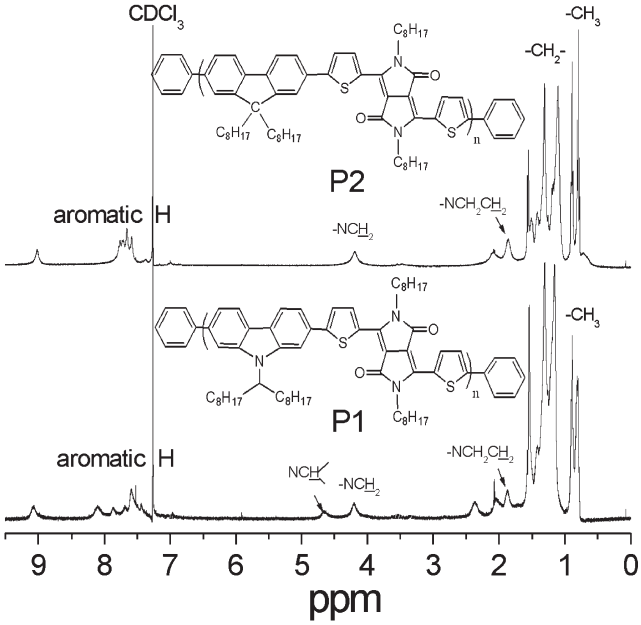


Figure 1. ^{1}H NMR spectra of the **P1** and **P2** in $CDCl_3$.

standards using chloroform as the eluent. Copolymers **P1**−**P3** and **P7** derived from comonomer **1** and copolymerizing units bearing one long and branched alkyl chain or two alkyl side chains suggests quite high molecular weights (M_n, 11−56 kDa; M_w, 44−280 kDa), probably due to a better solubility in common solvents. Indeed, free self-standing films can be easily obtained from solutions of copolymers **P1**, **P2**, and **P3.** Copolymers **P8**, **P9**, **P10**, and **P11** derived from comonomer **3** and copolymers **P4**, **P5**, and **P6** from comonomer **1** and copolymerizing groups bearing no or only one relatively short side chain exhibit low molecular weights due to a poor solubility in chloroform or THF. These properties can be partly related to the degree of substitution of each polymer; flexible long-branched substituent being necessary to obtain high molecular weight soluble DPP-based conjugated polymers. Nevertheless, all these copolymers can be processed by spin coating or by simple casting to get smooth films.

As examples, ^{1}H NMR spectra of **P1** and **P2** are reported in Figure 1. All spectra show peaks between 6.5 and 10 ppm for the aromatic protons; peaks between 0.7 and 4.70 ppm being attributed to the protons of the alkyl chains. Peaks related to the octyl substituted lactam groups of DPP appear between 0.7 and 2.5 ppm and the peaks of the methylene group adjacent to the lactam N atom of the DPP unit appears near 4.0−4.3 ppm. For carbazole-containing copolymers, peaks of the methylene or methine group adjacent to the carbazole N atom vary from 4.0 to 4.7 ppm according to the different carbazole structures. The number of aromatic and aliphatic protons estimated from integration of the peaks is consistent with the expected repeating unit of the copolymers.

2.2. Thermal Stability. The thermal stability of the polymers is also an important parameter for optoelectronic devices. The thermal properties of the copolymers were investigated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analyses and are also reported in Table 1. TGA analyses indicate that the copolymers

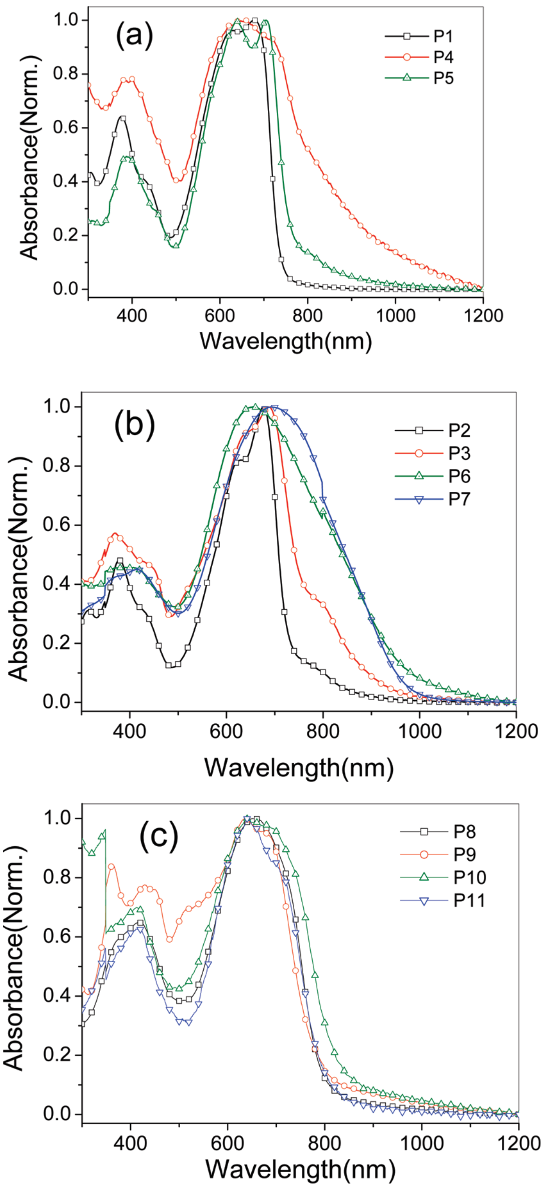


Figure 2. UV−vis−NIR absorption spectra of copolymer films: (a) **P1**, **P4**, and **P5**; (b) **P2**, **P3**, **P6**, and **P7**; (c) **P8**−**P11** spin-coated on a glass plate from chloroform solutions.

P1−**P8** and **P10** possess an excellent thermal stability (up to 380 °C) whereas copolymers **P9** and **P11** are thermally stable up to 290 °C. Moreover, most copolymers exhibit a glass transition temperature (T_g) between 100 and 200 °C except for copolymer **P10** which shows a T_g at 72 °C and copolymer **P3** which does not show any T_g. This is probably attributed to the stiff dibenzosilole moiety; similar phenomenon has been reported for other poly(2,7-dibenzosilole) derivatives.[7d]

2.3. Optical Properties. UV−vis−NIR absorption spectra could provide a good deal of information on the electronic structure of the conjugated polymers. The absorption spectra of the copolymers as thin films are shown in Figure 2 and the corresponding optical data of the copolymers are summarized in Table 2. All absorption spectra of these copolymers exhibit two peaks: one band in the wavelength range of ca. 300−480 nm and another band in the wavelength range of 480−1200 nm. The color of the copolymer solutions vary from blue, blue-green, and green depending upon the nature of the comonomer. The absorption maxima (λ_{max}) of the copolymers in chloroform solutions (see Supporting Information) are observed between 620 and 700 nm while those of thin films are located between 640 and 710 nm. Compared to the solution absorption, the UV−vis−NIR absorption of the copolymer films gets broaden and shows a red shift, indicating good intermolecular interactions in the solid state. The optical band gaps (E_g^{opt}), estimated from the absorption edge of the thin film absorption spectra, are between 1.2 and 1.6 eV. For copolymers derived from 2,7-carbazoles and comonomer **1**, the bandgaps (E_g^{opt}) are in the following order: **P4** (1.26 eV) < **P5** (1.44 eV) < **P1** (1.57 eV). **P4** containing 2,7-carbazole with linear alkyl chain has a lower bandgap which is likely due to a better packing of the polymer chains in the solid state and thus, to stronger interchain interactions. **P1** has a larger optical bandgap probably related to the presence of the bulky branched side chain, which partially hinders the molecular organization. However, this secondary alkyl chain explains the exceptional polymer solubility and film formability. Probably for similar reasons, the bandgaps (E_g^{opt}) of copolymers **P8**, **P10,** and **P11** derived from comonomer **3** and 2,7-carbazoles are in the following order: **P10** (1.39 eV) < **P11** (1.45 eV) < **P8** (1.48 eV). For **P1**, **P2**, **P3**, and **P7** derived from 9-heptadecanyl-2,7-carbazole, 9,9-dioctyl-2,7-fluorene, 9,9-dioctyl-2,7-dibenzosilole, 3,3-dioctyl-5,5-dithienosilole, and comonomer **1**, bandgaps (E_g^{opt}) vary in the following order: **P7** (1.24 eV) < **P3** (1.31 eV) < **P2** (1.42 eV) < **P1** (1.57 eV), which indicates that the properties of conjugated polymers are very sensitive to a slight change of the polymer structure. Among them, **P7** possesses the smallest bandgap due to the electron-rich dithienosilole unit which promotes an efficient intramolecular charge transfer and leads to an extensive delocalization within the polymer backbone. Finally, the electron rich thiophene ring contributes to the smallest optical bandgap (1.20 eV) as observed in **P6**.

2.4. Electrochemical Properties. Cyclic voltammetry (CV) is widely employed to estimate the HOMO and LUMO energy levels of conjugated polymers.[13,14] In this regard, the cyclic voltammograms of polymers are reported in Figure 3 and the related CV data (E_{on}^{ox} /E_{on}^{red}, HOMO and LUMO energy levels, E_g^{EC}) are summarized in Table 2. All copolymers exhibit quasi-reversible or reversible *p*-doping/dedoping (oxidation/rereduction) processes at positive potentials with onset potentials (E_{on}^{ox}) between 0.5 and 0.9 V vs SCE while *n*-doping/dedoping (reduction/reoxidation) processes at negative potential range are always irreversible with onset potentials (E_{on}^{red}) between −0.9 and −0.8 V vs SCE. Similar electrochemical curves were previously reported for other DPP-containing polymers.[3a,3b] The HOMO energy levels estimated from the E_{on}^{ox} range from −5.60 and −5.20 eV whereas the LUMO energy levels estimated from the E_{on}^{red} remain almost unchanged (−3.90 to −3.80 eV). These data indicate that the substitution of the electron rich unit and molecular packing have little effect on the polymer reductive potential but play some effect on the polymer oxidation potential. Interestingly, the energy levels estimated from these electrochemical measurements fit very well with the required electronic levels (E_{HOMO} level between −5.8 and −5.2 eV and E_{LUMO} level between −4.0 and −3.8 eV) for polymeric bulk heterojunction solar cells utilizing PCBM as the acceptor.[13b,15] For the similar copolymers **P1**−**P3** and **P7**, the onset oxidation potentials are in the following order: **P2** (0.82 V vs SCE) > **P1** ≈ **P3** (ca. 0.74 V) > **P7** (0.61 V) with the corresponding HOMO energy levels estimated from E_{on}^{ox} in the reverse order: **P2** (−5.52 eV) < **P1** ≈ **P3** (−5.44 eV) < **P7** (−5.31 eV). These results suggest that the incorporation of the more electron rich dithienosilole group into the backbone elevates the HOMO energy level and decreases the bandgap while the presence of the fluorene unit into the

Table 2. Optical and Electrochemical Properties of the Polymers

	UV−vis−NIR absorption spectra				cyclic voltammetry(vs SCE)		
		film[b]					
polymer	solution[a] λ_{max} (nm)	λ_{max} (nm)	λ_{onset} (nm)	E_g^{optc} (eV)	*p*-doping E_{on}^{ox}/HOMO[d] (V)/(eV)	*n*-doping E_{on}^{red}/LUMO[d] (V)/(eV)	E_g^{EC} (eV)
P1	642	679	792	1.57	0.74/−5.44	−0.78/−3.92	1.52
P2	656	676	875	1.42	0.82/−5.52	−0.85/−3.85	1.67
P3	623	688	944	1.31	0.73/−5.43	−0.80/−3.90	1.53
P4	630	652	984	1.26	0.54/−5.24	−0.83/−3.87	1.37
P5	643	705	859	1.44	0.61/−5.31	−0.86/−3.84	1.47
P6	692	656	1031	1.20	0.56/−5.26	−0.83/−3.87	1.39
P7	695	700	1001	1.24	0.61/−5.31	−0.90/−3.80	1.51
P8	631	660	836	1.48	0.56/−5.26	−0.9/−3.80	1.46
P9	629	639, 678 (sh)	866	1.43	0.70/−5.40	−0.90/−3.80	1.60
P10	649	648	889	1.39	0.54/−5.24	−0.89/−3.81	1.43
P11	641	648	852	1.45	0.58/−5.28	−0.86/−3.84	1.44

[a] Measured in chloroform solution. [b] Cast from chloroform solution. [c] Bandgap estimated from the onset wavelength of the optical absorption. [d] HOMO = $-e(E_{on}^{ox}+4.7)$ (eV); LUMO = $-e(E_{on}^{red}+4.7)$ (eV), assuming SCE to be −4.7 V.[13]

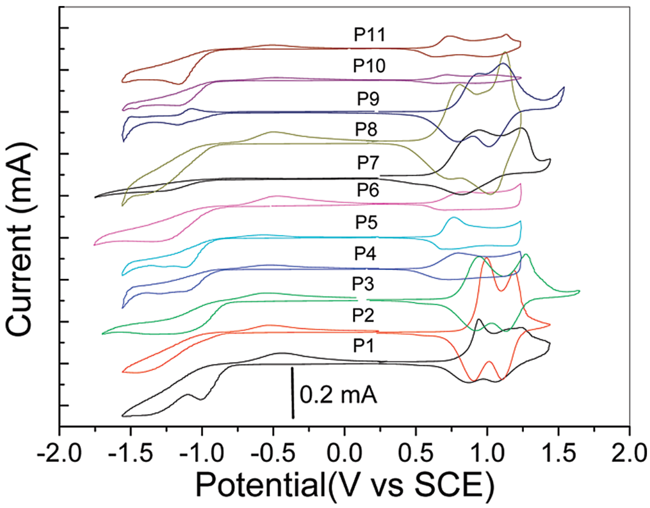


Figure 3. Cyclic voltammograms of polymer films on platinum wires in an acetonitrile solution of 0.1 mol/L [Bu_4N]BF_4 (Bu = butyl) with a sweep rate of 50 mV/s. SCE: standard calomel electrode.

backbone leads to the highest oxidation potential. All these polymers (**P1**−**P3** and **P7**) are air-stable (E_{on}^{ox}: 0.57 V vs SCE).[16] For polymers **P1**, **P4**, and **P5** derived from various 2,7-carbazole groups and comonomer **1**, the onset oxidation potentials vary in the following order: **P1** (0.74 V vs SCE) > P5 (0.61 V) > **P4** (0.54 V) which may be related to different molecular packing. As discussed in section 2.3, it seems that polymer **P4** has a better packing which leads to a more extensive delocalization of the electrons and to a smaller bandgap (E_g^{EC}: 1.37 eV) whereas polymer **P1** has a relatively low-lying HOMO energy level (−5.44 eV). The oxidation potentials of copolymers derived from comonomer **3** (except P10) are reduced to some extent compared to the corresponding copolymers derived from comonomer **1.** This is probably related to the presence of additional thiophene units along the conjugated backbone. Finally, it is worth noting that the electrochemical and optical bandgaps are in relatively good agreement (Table 2).

3. Conclusions

Eleven new low bandgap copolymers based on two electron-deficient DPP units and seven different electron-rich groups (thiophene, carbazoles, fluorene, dibenzosilole, and dithienylsilole) have been designed and synthesized by Pd-catalyzed Suzuki or Stille coupling reaction. These copolymers were characterized by size-exclusion chromatography, thermal analyses, UV−vis-NIR absorption spectroscopy, and cyclic voltammetry. The final polymers exhibit low to relatively high molecular weights depending upon the nature of the substitution pattern. Thermal analyses indicate that all copolymers have good thermal stabilities. The copolymers possess a wide range of bandgaps (ranging from 1.2 to 1.6 eV) through the variation of electron-rich moieties, DPP units, and side chains. All these results show that properties such as solubility, bandgap, and HOMO/LUMO energy levels can be fine-tuned by the nature of the different comonomers. In particular, the physical properties of copolymers **P1**−**P3** and **P7** (extended absorption, preferred energy levels, good film formability, etc.) make these new DPP-based copolymers particularly promising for photovoltaic applications. In this regard, different photovoltaic devices based on these new conjugated polymers are currently investigated and will be reported in due course.

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Supporting Information Available: Text giving the experimental details, syntheses of the monomers and polymers, instrumentation, and characterization procedures and figures showing the TGA curves and UV−vis−NIR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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