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Novel conjugated copolymers with dithienyl and cyclopentadithienyl substituted dicyanoethene acceptor blocks

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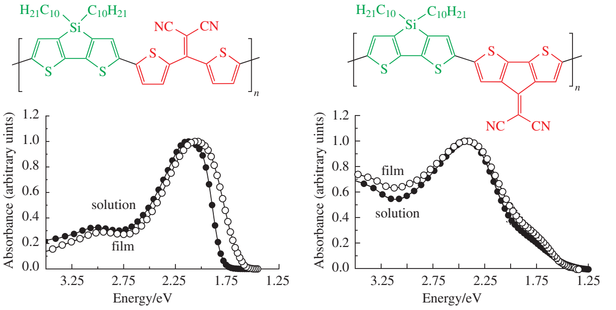
Novel bifunctional acceptor monomer, 2-[bis(5-bromothiophen-2-yl)methylidene]malononitrile, is obtained in three steps in a total yield of 79%. The Stille cross-coupling between this monomer and 2,6-ditin derivative of 4,4-didecyl-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene afforded donor–acceptor polymer whose properties were compared to the analogue containing a planar cyclopenta[2,1-*b*:3,4-*b*′]dithiophene acceptor block. The copolymers have low narrow optical band gaps and effectively absorb visible light, however the former possesses improved solubility and thermal stability as compared to the latter.



Organic π-conjugated compounds have attracted extensive attention in various fields of organic electronics and photonics. Conjugated compounds with D (donor) and A (acceptor) blocks, often linked to each other by a π-bridge, would form the simplest D–π–A structure.[1] Some of more complex π-conjugated compounds, for instance, low-molecular ones with the D–π–A and D–A–π–A structures, are used for Grätzel type photovoltaic cells.[3,4] On the other hand, compounds with the A–π–D–π–A structure can be used both as a donor[5–7] and acceptor component of bulk heterojunction organic solar cells.[8] Compounds with the A–π–D–π–A structure showed high luminescence efficiency.[9] More complex symmetric molecules with D–A–D–A–D[10] and D–A–D–π–D–A–D[11] and non-symmetric D1–A1–A2–π–D2[12] structures were used in photovoltaics. Various non-symmetric molecules of D1–D2–π–A1–A2 or D1–A1–π–D2–A2 structure type can serve as chromophores in nonlinear optical devices,[13] as fluorescent chemosensors[14–18] and as components of organic solar cell active layer.[19–22] Copolymers of alternating D–A class are actively used since they possess excellent film-forming properties and flexibility as compared to small D–A molecules.[23–26]

Low band gap polymers derived from bithiophene bridged by ketone, dicyanovinyl and other different acceptor functions were initially used as low bandgap semiconductors.[27–30] In this work, two new conjugated copolymers were obtained (Scheme 1). They have the same donor unit, 4,4-didecyl-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2,6-diyl moiety, but different acceptor units with dicyanovinyl groups, namely, [di(2-thienyl)methylidene]propanedinitrile **3** and (4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-ylidene)propanedinitrile **7**.

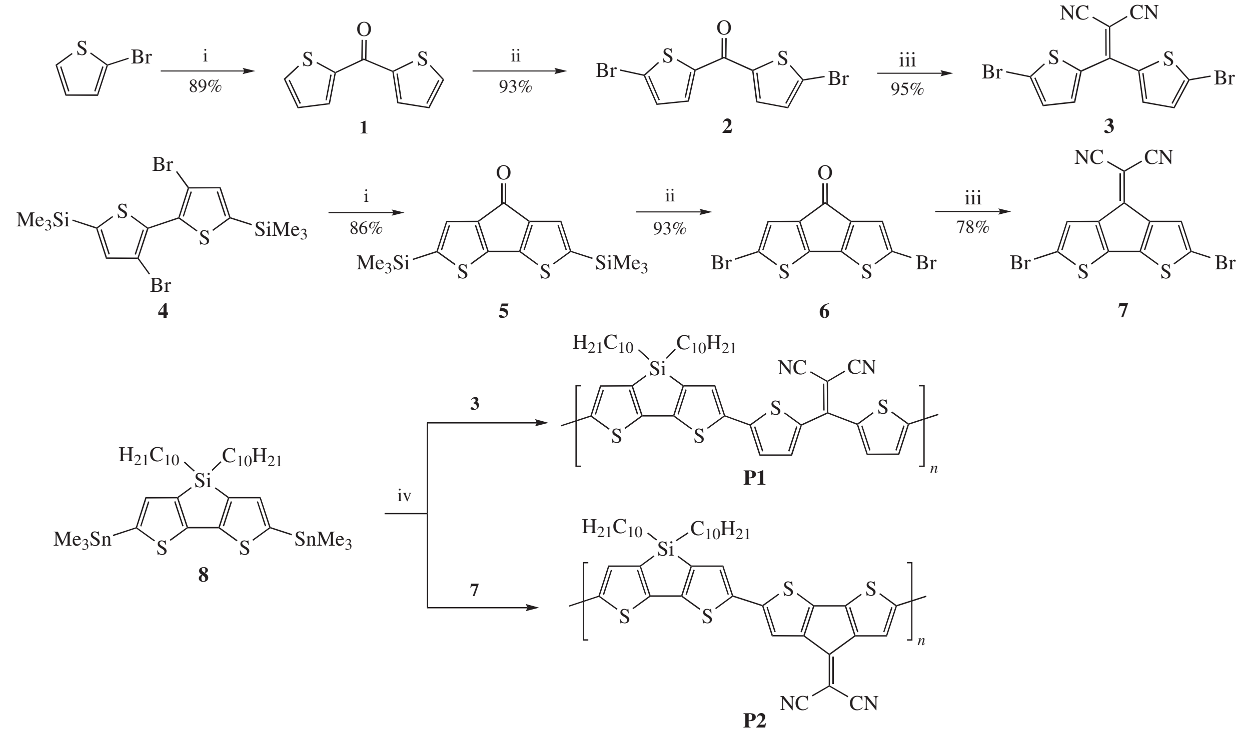
Symmetrical dithienyl ketone **1** was synthesized from 2-bromothiophene by its lithiation followed by treatment with *N*,*N*-dimethylcarbamoyl chloride. The subsequent bromination of compound **1** afforded dibromide **2** in 93% yield. The target monomer, 2-[bis(5-bromothiophen-2-yl)methylidene]malononitrile **3**, is new. Tuning the Knoevenagel conditions (solvent, temperature and reaction duration) provided the best (95%, GPC data) yield of dicyanoethene **3** upon stirring in pyridine at room temperature for 72 h (reflux in pyridine led to a partially hydrolyzed product with amide functionality).

The cyclopentadithiophene-based monomer **7** was synthesized from bithiophene derivative **4**. The Knoevenagel reaction between ketone **6** and malononitrile was carried out similarly to that for **3**. The full conversion of compound **6** into the target product was achieved after 3 h of stirring at room temperature. The yield of pure product was 78%, much higher as compared to the published synthesis.[31] The shorter reaction time in comparison to the synthesis of analogue **3** can apparently be explained by greater electophilicity of the keto group in compound **6**. The bifunctional donor monomer **8** was synthesized as described.[32] Using the monomers obtained, copolymers **P1** and **P2** were synthesized *via* the Stille cross-coupling reaction in a microwave reactor (GPC monitoring). The crude copolymers were purified from inorganic impurities and then from oligomeric products. Their number-average (M_n), weight-average (M_w) molecular weights and index of polydispersity (PDI) were measured by GPC using polystyrene standards (Table 1).

Table 1 Molecular weights, polydispersity properties and solubility of the copolymers obtained.

Copolymer	M_N	M_W	PDI	Solubility[a]/g dm^{-3}
P1	25500	42500	1.67	9
P2	17000	23300	1.37	7

[a] Solubility was measured in *o*-dichlorobenzene as it is a convenient solvent for fabrication of organic solar cells using the standard procedure.[17]



Scheme 1 *Reagents and conditions:* i, Bu^nLi, THF, –78 °C, then $Me_2NC(O)Cl$; ii, NBS, DMF; iii, $CH_2(CN)_2$, pyridine; iv, $Pd(PPh_3)_4$, toluene, reflux.

The average molecular weights and PDI of both copolymers are rather similar. The solubility of **P1** in *o*-dichlorobenzene was found to be 9 g dm^{-3}, which is a bit higher as compared to polymer **P2** having more rigid acceptor block.

The thermal stability of the copolymers was investigated by thermogravimetric analysis (TGA) under nitrogen and in air. The decomposition temperature calculated for 5% weight loss (T_d) in air was found to be 336 and 312 °C for polymers **P1** and **P2**, respectively [Figure 1(*a*)]. The course of the curves has the same profile in both cases and differs only above 500 °C. Under nitrogen, T_d were somewhat higher, 350 and 388 °C, respectively [Figure 1(*b*)] and the course of the curves differed significantly. One can see that the rate of destruction was much greater for **P2**. From the data obtained, one can conclude that copolymers based on cyclopentadithiophene blocks exhibit lower stability than their analogues both in air and in nitrogen atmosphere.

The electrochemical properties of the copolymers were examined by cyclic voltammetry. From the data obtained, the values of the HOMO and LUMO energies, as well as the E_g values were calculated (Table 2). It was also shown that the electrochemical band gap of copolymer **P2** (E_g^{EC} = 1.48 eV) is significantly narrower than that of **P1** (E_g^{EC} = 1.98 eV).

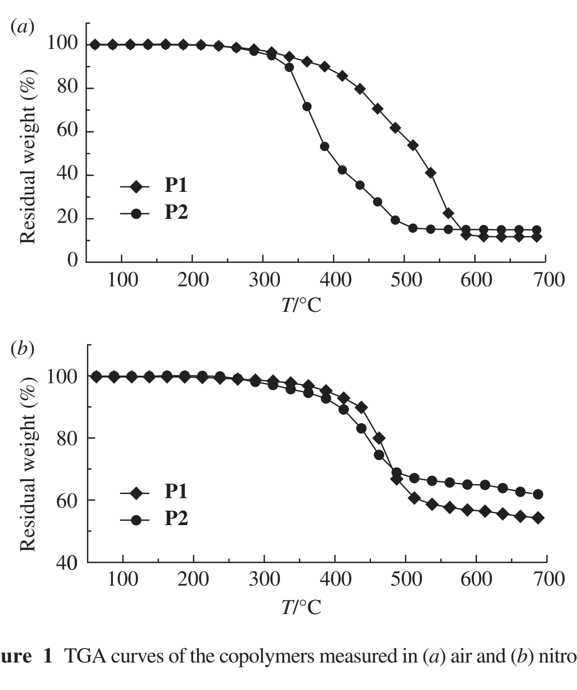


Figure 1 TGA curves of the copolymers measured in (*a*) air and (*b*) nitrogen.

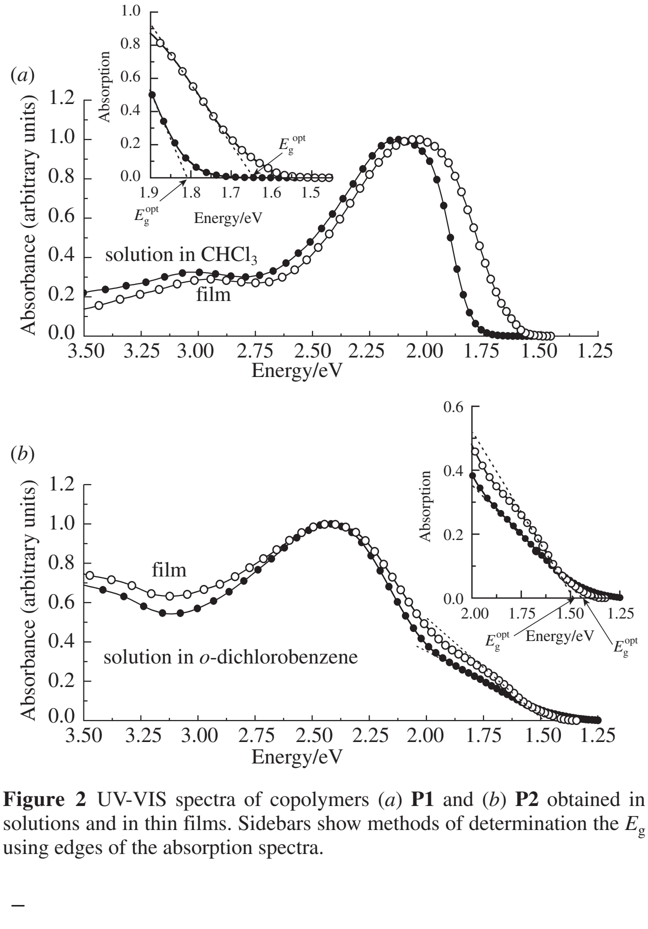


Figure 2 UV-VIS spectra of copolymers (*a*) **P1** and (*b*) **P2** obtained in solutions and in thin films. Sidebars show methods of determination the E_g using edges of the absorption spectra.

Table 2 UV-visible spectroscopy and cyclic voltammetry data of the copolymers.

Copolymer	Absorption in solution			Absorption in film			CV data				
	$\lambda_{\max}$/nm	λ_{onset}/nm	E_g^{opt}/eV	$\lambda_{\max}$/nm	λ_{onset}/nm	E_g^{opt}/eV	E_{ox}/V	HOMO/eV	E_{red}/V	LUMO/eV	E_g^{EC}/eV
P1	580	700	1.8	610	760	1.6	1.19	–5.59	–0.79	–3.61	2.0
P2	510	900	1.4	510	900	1.5	0.88	–5.28	–0.60	–3.80	1.5

The absorption spectra of both copolymers were measured in dilute solutions (10^{-5} M) in *o*-dichlorobenzene and in thin films obtained by depositing the copolymers on quartz substrates from solutions using spin coating (Figure 2). Based on the optical absorption data, the band gap (E_g^{opt}) was also estimated and the results are summarized in Table 2. The E_g^{opt} was determined from the intersection with the abscissa axis tangent to the long-wave shoulder of the absorption band (Figure 2, inset). The E_g^{opt} values found for **P2** in a solution and in film are close to each other (1.4 and 1.5 eV, respectively) and coincide well with E_g^{EC} (1.5 eV). For **P1**, the E_g^{EC} value (2.0 eV) is closer to the E_g^{opt} value obtained in solution (1.8 eV) but not in the film (1.6 eV).

In conclusion, the synthesis of two dicyanovinyl acceptor monomer blocks has been accomplished. New 2-[bis(5-bromothiophen-2-yl)methylidene]malononitrile **3** unit was prepared in three steps in a total yield of 79%. Both blocks are suitable for further polymerization with different donor units. Two new donor–acceptor alternating copolymers, **P1** and **P2**, were synthesized using the Stille cross-coupling reaction. The comparison of polymers properties demonstrates that **P1** with a novel acceptor block has higher molecular weight, better solubility and higher thermal stability. Thus, compound **3** looks more promising acceptor unit in terms of simplicity of its synthesis. Its copolymers seem to have good prospects to be used in organic photovoltaics.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.09.028.

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