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PAPER

A precursor strategy for the synthesis of low band-gap polymers: an efficient route to a series of near-infrared electrochromic polymers[†]

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A precursor strategy for the synthesis and screening of a series of conjugated donor-acceptor polymers is demonstrated by successful preparation of low band-gap polymers (**P2-P5**) containing triphenylamine as an electron donor and several heterocycles as acceptors, such as [1,2,5]thiadiazolo [3,4-g]quinoxaline, [1,2,5]thiadiazolo[3,4-*i*]dibenzo[*a*,*c*]phenazine, benzo[1,2-*c*:4,5-*c'*]bis([1,2,5] thiadiazole), and selenadiazole[3,4-*f*]benzo[*c*][1,2,5]thiadiazole, that are transformed from a single reactive polymer (**P1**). Polymers **P2-P5** have the band gap of 1.71–1.29 eV and show the absorption and emission in the near infrared (NIR) spectral region. All the polymers are also NIR electrochromic. In particular, polymer **P3** is electrochemically switchable between leaf-like green coloring and nearinfrared absorbing states with an efficiency of 479 cm² C⁻¹ at 1310 nm or 232 cm² C⁻¹ at 1550 nm, making it potentially useful for electrically switchable day-to-night camouflage applications.

Introduction

The low band-gap conjugated polymers with absorption in the near-infrared (NIR) region are potentially useful in NIR optoelectronic applications, such as NIR light-emitting diodes,¹⁻⁴ NIR photovoltaics,^{2,5-17} NIR optical attenuators,^{18,19} biomedicals,²⁰ and camouflage in warfare.²¹ The band gaps of conjugated polymers mainly correlate to alternation of the single and double bond length, conjugation length, coplanarity, substituent effect and intermolecular interactions.²²⁻²⁵ Lowering the band gap will result in a spectral shift to the long wavelength or even into the NIR region. One of the common strategies is to introduce the electron donor (D) and acceptor (A) groups into the conjugated polymer backbone, resulting in hybridization of the electronic levels of donor and acceptor units due to a resonance structure with the reduced alternation in the bond length between single and double bonds.23 Therefore, the strong D-A charge transfer is required to lower the band gap level and realize the NIR absorption.²⁶⁻³⁴ One of the widely used acceptors is based on benzobisthiadiazole or the related selenium-containing and quinoxaline analogs, due to their strong electron-withdrawing ability and the low LUMO level.

We have previously investigated a series of the $D-\pi-A-\pi-D$ type of NIR chromophores containing the strongly

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† Electronic supplementary information (ESI) available: Thermoproperties, optical spectra and CV measurements of these polymers. See DOI: 10.1039/c1jm10629e electron-withdrawing benzo[1,2-c:4,5-c']bis([1,2,5]thiadiazole) (BBTD) or its selenium analogues,^{35–38} whose quinoidal character contributes to the low band-gap nature of these chromophores.³⁹ As the band gap level is readily changed by introducing the different donors and acceptors, it can then be expected that the corresponding conjugated polymers containing the BBTD and other structurally related acceptors with a gradual change in the electron-withdrawing ability or the LUMO level are likely to absorb at different wavelengths and show various colors.

To obtain the corresponding polymers derived from each of the acceptors that are structurally related to BBTD, one would need to tediously synthesize and purify each of the acceptor monomers and carry out a large number of polymerizations. For making high molecular weight conjugated aromatic polymers, such as polyfluorenes, the Suzuki cross-coupling reaction is more favorable and widely used than other cross-coupling reactions. However, the strong acceptors such as BBTD are rather labile to alkaline bases and some nucleophiles (e.g., fluoride and hydroxide anions),⁴⁰ making it very difficult, if not impossible, to polymerize the BBTD-based monomers by the Suzuki crosscoupling reaction. Although the Stille cross-coupling reaction could be applied for polymerization, the required trialkylstannyl monomers are toxic and often difficult to purify. Therefore, in order to utilize the Suzuki reaction in polymer synthesis and have a quick access to a series of low band gap polymers based on BBTD and its analogs for systematic studies on the structureproperty relationship and screening certain properties, an alternative synthetic strategy is needed.

On the basis of the synthetic viability for BBTD and its analogs, we propose to use a precursor strategy for making a series of structurally related conjugated polymers from a single reactive polymer. In principle, a polymer that contains the

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5,6-diaminobenzothiadiazole unit can be converted to many other polymers by performing specific reactions involving this reactive moiety with various reagents. It is known that *o*-di-aminobenzene and its derivatives can be converted to a number of heterocyclic compounds such as benzothiadiazole, benzosele-nadiazole, phenazine and quinoxaline in high yields.^{38,41,42} Accordingly, a polymer containing 5,6-diaminobenzothiadiazole can be used as a precursor to a series of polymers containing the electron-deficient heterocyclic units (Scheme 1).

Herein we demonstrate the feasibility of a precursor approach to a series of low band-gap conjugated polymers (**P2–P5**) by facile transformation of a single polymer (**P1**) containing a reactive 5,6-diaminobenzothiadiazole unit. These D–A type polymers have different band gaps due to a structural variation only at the acceptor part and are all electrochromic and NIR absorbing. Interestingly, polymer **P3** is leaf-like green and can be switched electrochemically to become NIR absorbing at the telecommunication wavelengths (*e.g.*, at 1310 and 1550 nm).

Experimental section

Materials

All chemicals and reagents were used as received from commercial sources without purification. Solvents for chemical synthesis were purified by distillation. Chemical reactions were carried out under an argon atmosphere. 4,7-Bis[4-(*N*-phenyl-*N*-(4-methylphenyl) amino)phenyl]-5,6-diamino-2,1,3-benzothiadiazole (1)⁴ and 9,9-dioctyl-2,7-bis(trimethyleneboronate)fluorene (3)⁴³ were prepared according to literature methods.

Methods

¹H NMR spectra were recorded using a Bruker Avance 300 NMR spectrometer. The number- and weight-average molecular weights of the polymers were determined by gel-permeation chromatography (GPC) with a Waters 410 instrument and polystyrene as standard and THF as eluent. Thermogravimetric analysis (TGA) was carried out in nitrogen on a Hi-Res TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C min⁻¹. Absorption and fluorescence spectra were recorded with a Shimadzu UV-3600 spectrophotometer and a PTI fluorescence system or a Lambda 900 Perkin-Elmer spectrophotometer, respectively. FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Cyclic voltammetry was performed using a BAS 100B/W electrochemical workstation. Spectroelectrochemistry was performed in dry acetonitrile containing Et₄NClO₄ (0.1 M) at room temperature under argon, using an



Scheme 1 Transformation of 5,6-diaminobenzothiadiazole moiety in a precursor polymer to various heterocyclic-containing polymers.

indium tin oxide (ITO)-coated glass slides as the working electrode, a platinum wire as the counter electrode and a silver wire as the reference electrode.

4,7-Bis[4-(*N*-(4-bromophenyl)-*N*-(4-methylphenyl)amino)phenyl]-5,6-diamino-2,1,3-benzothiadiazole (2)

To a solution of 4,7-bis[4-(*N*-phenyl-*N*-(4-methylphenyl)amino) phenyl]-5,6-diamino-2,1,3-benzothiadiazole (1) (0.61 g, 0.9 mmol) in freshly distilled dichloromethane (45 mL) was added tetrabutylammonium tribromide (0.96 g, 2.0 mmol). The mixture was stirred at room temperature for 3 h. The precipitates were filtered and washed with dichloromethane. The solid was dried under vacuum to give the product as orange solid (0.55 g, 73%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.44 (d, 4H, J = 8.3 Hz), 7.35 (d, 4H, J = 8.7 Hz), 7.20 (d, 4H, J = 8.5 Hz), 7.13 (d, 4H, J = 8.6 Hz), 7.09 (d, 4H, J = 9.1 Hz), 7.05 (d, 4H, J = 8.7 Hz), 2.34 (s, 6H).

Polymer P1

To a mixture of 9,9-dioctyl-2,7-bis(trimethyleneboronate)fluorene (3) (0.2792 g, 0.5 mmol) and 4,7-bis[4-(N-(4-bromophenyl)-N-(4methylphenyl)amino)-phenyl]-5,6-diamino-2,1,3-benzothiadiazole (2) (0.4193 g, 0.5 mmol) were added Aliquat 336 (0.12 g), $Pd(PPh_3)_4$ (7.9 mg, 0.007 mmol), degassed toluene (7 mL) and aqueous potassium carbonate (2 M, 3 mL), under a dry argon atmosphere. The mixture was heated to 95 °C and stirred in the dark for 48 h. After cooling, the mixture was poured into methanol. The precipitate was collected by filtration and then dissolved in dichloromethane. The solution was washed with water, dried over anhydrous Mg₂SO₄, and then concentrated to an appropriate volume. The fiber-like brown polymer (0.5 g, 94%) was obtained by pouring the concentrated solution into methanol. ¹H NMR $(300 \text{ MHz}, \text{CDCl}_3) \delta$ (ppm): 7.74 (d, 2H, J = 7.9 Hz), 7.61–7.55 (m, 8H), 7.47 (d, 4H, J = 8.7 Hz), 7.29–7.25 (m, 8H), 7.20–7.13 (m, 8H), 2.36 (s, 6H), 2.00 (br, 4H), 1.20–1.00 (m, 20H), 0.80–0.75 (m, 10H).

Polymer P2

To a suspension of polymer **P1** (107 mg, 0.1 mmol) in acetic acid (20 mL) was added 1,4-dioxane-2,3-diol (53 mg, 0.44 mmol) in argon. The mixture was heated to 60 °C overnight. Ethanol was then added to precipitate the polymer. After washing with ethanol and drying at 80 °C under vacuum blue polymer **P2** was obtained (109 mg, 99%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.87 (s, 2H), 7.81 (d, 4H, J = 8.7 Hz), 7.74 (d, 2H, J = 7.7 Hz), 7.63–7.56 (m, 8H), 7.35–7.18 (m, 16H), 2.37 (s, 6H), 2.09 (b, 4H), 1.05 (m, 20H), 0.90–0.70 (m, 10H).

Polymer P3

Following the procedure for the preparation of polymer **P2**, by changing 1,4-dioxane-2,3-diol to phenanthrene-5,6-dione, polymer **P3** was obtained as a dark green solid. Yield: 89%. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.03 (br, 2H), 8.42 (br, 2H), 8.07 (br, 4H), 7.75–7.16 (m, 30H), 2.39–2.35 (m, 6H), 2.03 (br, 4H), 1.06 (br, 20H), 0.76 (br, 10H).

Polymer P4³⁵

To a solution of polymer **P1** (106.9 mg, 0.1 mmol) in dry pyridine (10 mL) were added *N*-sulfinylaniline (0.5 mL, 4 mmol) and chlorotrimethylsilane (0.5 mL, 3.6 mmol) in argon atmosphere. The mixture was stirred at 80 °C overnight. An excess of chlorotrimethylsilane was then distilled off. The solution was concentrated to 5 mL and poured to methanol. The fiber-like dark blue polymer **P4** (98 mg, 89%) was collected by filtration, washed with ethanol and dried at 80 °C under vacuum. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.20 (d, 4H, *J* = 8.5 Hz), 7.75 (d, 2H, *J* = 7.4 Hz), 7.63–7.56 (m, 8H), 7.34–7.16 (m, 16H), 2.37 (s, 6H), 2.06 (br, 4H), 1.06 (br, 20H), 0.80–0.75 (m, 10H).

Polymer P5

To the solution of polymer **P1** (106.9 mg, 0.1 mmol) in THF (45 mL) was added SeO₂ (118 mg, 1.1 mmol) in argon. The mixture was refluxed for 4 h. The solution was then concentrated to 10 mL and poured to methanol. The fiber-like dark grey polymer **P5** (0.1 g, 87%) was collected by filtration, washed with ethanol and dried at 80 °C under vacuum. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.13 (d, 4H, J = 8.7 Hz), 7.79–7.65 (m, 2H), 7.65–7.40 (m, 8H), 7.36–7.18 (m, 16H), 2.38 (s, 6H), 2.07 (br, 4H), 1.30–1.00 (m, 20H), 0.82–0.76 (m, 10H).

Results and discussion

Design and synthesis

Linking a donor and an acceptor through a π -spacer is a common method of construction of low band gap compounds and polymers.^{23,36} In particular, the D– π –A– π –D structure promotes an effective interaction between donor and acceptor units, which can result in a significant decrease in the energy gap. In this work, we chose triphenylamine (TPA) as an electron donor, along with the four different acceptors, namely [1,2,5] thiadiazolo[3,4-g]quinoxaline (TQ), [1,2,5]thiadiazolo[3,4-*i*] dibenzo[*a*,*c*]phenazine (TDP), benzo[1,2-*c*:4,5-*c'*]bis([1,2,5]thiadiazole) (BBTD), and selenadiazole[3,4-*f*]benzo[*c*][1,2,5]thiadiazole (SBTD), to construct the D– π –A– π –D repeat unit in the main chain of conjugated polymers (Fig. 1). The 9,9-dioctylfluorene moiety is introduced to extend the π -conjugation and impart the solubility to the target polymers.

A precursor strategy is applied to the synthesis of target polymers in order to overcome the problem associated with the instability of the strong acceptors under the Suzuki reaction conditions. We reasoned that 5,6-diaminobenzothiadiazole should be a suitable functional group to be present in a monomer and also in a precursor polymer, since its benzothiadiazole moiety is fairly stable under the basic conditions and its o-diaminobenzene moiety can be readily converted into various electron acceptors (e.g., quinoxaline and benzothiadiazole).44 Accordingly, monomer 2 was designed and synthesized from the known compound 1 by bromination with tetrabutylammonium tribromide. Polymerization of monomers 2 and 3 by the Suzuki cross-coupling reaction afforded the precursor polymer P1. Using a specific reagent as indicated for each polymer, the cyclization reaction of the phenylenediamine moiety in P1 proceeded smoothly to yield P2 (1,4-dioxane-2,3-diol), P3 (phenanthrene-5,6-dione), P4 (N-thionylaniline) and P5 (selenium dioxide) in high yield (>87%) (Scheme 2).

Structural characterization

The chemical structures of polymers **P1–P5** were characterized by the ¹H NMR and IR spectroscopic methods. A peak at 4.18 ppm in the ¹H NMR spectrum (Fig. 2a) of **P1** is assigned to the amine hydrogen, which is an indicator for transformation of the amino groups. In Fig. 2b–e, the peaks at 8.88, 9.04, 8.42, 8.08, 8.20 and 8.13 ppm are assigned to the H^a–H^f, respectively, since these chemical shifts coincide well with those of compounds with similar structures (δ 8.85, ³⁸ 9.05, ³⁸ 8.44, ³⁸ 8.07, ³⁸ 8.18⁴ and 8.02⁴ ppm). Because of the presence of the strong electron-withdrawing BBTD and SBTD, the chemical shift of the adjacent hydrogens H^e and H^f in **P4** and **P5** shifted to a lower field. The IR spectrum of polymer **P1** exhibits the v_{asym} (HNH) and v_{sym} (HNH) at 3442 and 3357 cm⁻¹, respectively. As expected, these two bands are absent in the IR spectra of polymers **P2–P5** (Fig. 3).

The molecular weights were determined by GPC using THF as eluent and polystyrene as standard. The precursor **P1** had a number-average molecular weight (M_n) of 56 000 g mol⁻¹ and a polydispersity index (PDI) of 3.2 (Table 1). In comparison, polymers **P2–P4** appear to have relatively lower molecular weights (16 000, 18 000 and 28 000 g mol⁻¹, respectively), which is mainly due to the exclusion of less soluble but higher molecular weight fractions in THF.

Copolymers **P1–P5** exhibited good thermal stability (Table 1 and Fig. S1†), as assessed by thermogravimetric analysis (TGA), and had the onset temperatures for 5% weight loss in nitrogen over 300 °C. A small weight loss occurred at *ca.* 100 °C, presumably due to the presence of a small amount of solvent in polymer samples.

Optical property

The absorption and emission spectra of polymers **P1–P5** in chlorobenzene and film are shown in Fig. 4 and S2† and the data are summarized in Table 2. Without a strong acceptor, the precursor **P1** absorbs in the short wavelength region with a maximum (λ_{max}) at 440 nm and emits at 559 nm in chlorobenzene. Because of the introduction of strong electron acceptors





Scheme 2 Synthetic routes to polymers P1–P5. *Reagents and conditions*: (i) Bu_4NBr_3 , CH_2Cl_2 , 25 °C, 3 h; (ii) $Pd(PPh_3)_4$, K_2CO_3 (aq, 2 M), toluene, Aliquat 336, 95 °C, 48 h; (iii) 1,4-dioxane-2,3-diol, AcOH, 60 °C, overnight; (iv) phenanthrene-5,6-dione, AcOH, 60 °C, overnight; (v) PhNSO, TMSCl, pyridine, 80 °C, overnight; (vi) SeO₂, THF, reflux, 4 h.



Fig. 2 ¹H NMR spectra (300 MHz, CDCl₃) of polymers P1–P5.

by cyclization of the 1,2-diaminophenylene moiety in **P1**, the absorption and emission peaks of polymers **P2–P5** are red shifted dramatically. The electronic absorption spectra of these four polymers display two discrete bands (Fig. 4a): the bands in the short wavelength region plus the shoulders ranging from 300–450 nm ascribed to the π – π * and n– π * transitions of the conjugated aromatic segments, and those in the long wavelength region are due to the intramolecular charge transfer (ICT) transitions



Fig. 3 FT-IR spectra of polymers P1–P5.

Table 1 Molecular weights and thermal properties of polymers P1-P5

Polymer	$M_{\rm n}{}^{a}$ (×10 ³)	$M_{\rm w}^{\ a}$ (×10 ³)	PDI ^a	$T_{\rm d}/^{\circ}{\rm C}^b$	
P1	56	179	32	423	
P2	16	32	2.0	438	
P3	18	34	1.9	430	
P4	28	75	2.7	419	
P5	NA	NA	NA	341	

^{*a*} Determined by gel permeation chromatography using THF as eluent and polystyrene as standard. ^{*b*} Temperature at which 5% weight loss is observed using TGA under N₂ at a heating rate of 10 °C min⁻¹.

between the donors and the acceptors. The maximum absorption wavelength (λ_{max}^{abs}) varies in the order of P1 < P2 < P3 < P4 < P5. The λ_{max}^{abs} of P3 is red-shifted about 90 nm relative to P2, due to the extension of the conjugation length in the TDP core. Replacement of sulfur atom by selenium atom led to a further



Fig. 4 (a) Normalized absorption and (b) fluorescence emission spectra of polymers **P1–P5** in chlorobenzene.

red-shift (P5 vs. P4), due to the polar effect of selenium atom.⁴² The colors of polymers P1-P5 vary according to their absorption characteristics, depending on the acceptor core structure in the repeat units, and are typically orange, blue, green, grey and dark goldenrod (Fig. S3[†]). It is worth noting that P3 absorbs at 380 and 720 nm, with a valley at 503 nm and has a color of a green leaf (Fig. S4[†]). Unlike the absorption spectra, the emission spectra just show one peak in the visible or near infrared spectral region in solution. The emission wavelengths of P1-P5 vary in the same trend as for the absorption. It is interesting to note that polymers P2-P5 exhibit a large Stokes shift (Table 2), which further confirms the presence of a strong ICT in these polymers. In comparison with the absorption spectra in solution, the absorption maxima of the polymer films are red-shifted by 7-87 nm, indicating the presence of intermolecular interaction. Moreover, the fluorescence spectra of the polymer films display several peaks, which may be attributed to the vibronic bands and

intermolecular charge transfer bands. The longest emission wavelength reaches 1280 nm, falling in the telecommunication window. Unlike many NIR dyes, the films of polymers **P2–P5** emit strongly in the NIR spectral region (Fig. S2†), making them potentially useful in light emitting diodes (LEDs).

Electrochemical property

The electrochemical properties of polymers P1-P5 (except for P2 due to its low solubility) are investigated by cyclic voltammetry (CV) and the data are summarized in Table 2. The chlorobenzene solution of each polymer with a concentration of 10 mg mL⁻¹ was used to spin coat thin films on ITO-coated glass slides. Once the solvent was fully evaporated, CV was performed in a 0.1 M Et₄NClO₄ electrolyte in acetonitrile with Pt wire counter electrode and Ag/Ag⁺ reference electrode. The cyclic voltammograms of P1 and P3-P5 are shown in Fig. S5[†]. The less soluble P2 could not be cast in a film for CV experiment. Two quasireversible waves are observed for all the polymers in the oxidation region, which are attributed to the oxidation of TPA segments, and the two electrons are removed successively from the two nitrogen atoms. The oxidation potential of ferrocene/ ferrocenium (Fc/Fc⁺) was measured to be 0.44 V to the Ag/Ag⁺ electrode under the same conditions and the redox potential of Fc/Fc⁺ has an absolute energy level of -4.8 eV to vacuum.^{45,46} Thus the HOMO levels of polymers are calculated according to the following equation:

$$E_{\rm HOMO} = -e(E_{\rm ox} + 4.36) \,(\rm eV) \tag{1}$$

where E_{ox} is the onset oxidation potential of the sample vs. Ag/Ag⁺. Due to the strong electron-donating TPA and amino groups, the precursor polymer **P1** exhibits a low onset oxidation potential (E_{onset}^{ox}) at 0.31 V and the HOMO level of -4.67 eV, which coincide well with those of polymers containing TPA and NMe₂ groups.⁴⁷ Due to the presence of the D- π -A- π -D structure in **P3-P5**, their onset oxidation potentials increase and HOMO levels decrease about 0.3 eV. Accordingly, the band-gap levels of **P2-P5** are in the range of 1.3-1.7 eV.

Electrochromic property

Polymers **P1–P5** are all electrochromic, changing from orange, blue, green, grey and dark goldenrod in the neutral state to grey or sienna in the oxidized state (Fig. 5). In the oxidized state or radical cation form, all the polymers absorb intensely in the NIR region, with a maximum peak around 1200 nm. For **P1**, its color

Table 2 Optical and electrochemical data of P1-P5

Polymer	$\lambda_{\max}^{abs}/nm^a$ (solution)	λ_{\max}^{PL}/nm^a (solution)	Stokes shifts ^{<i>a</i>} /cm ⁻¹	λ_{\max}^{abs}/nm (film)	λ_{\max}^{PL}/nm (film)	$E_{\rm g}$ optical/ eV ^b	$E_{\text{onset}}^{\text{ox}}$ /V	HOMO/ eV	LUMO/ eV ^c
P1 P2	371, 440 (sh) ^d 608	559 834	9065 4457	369, 527 (sh) ^d 626	NA 750,822	2.67 1.71	0.31 NA	-4.67 NA	-2.00 NA
P3 P4 P5	697 714 814	945 1017 1072	3765 4173 2957	727 744 821	962, 1026, 1158 1028, 1156, 1265 1098, 1171, 1279	1.50 1.44 1.29	0.63 0.52 0.51	$-4.99 \\ -4.88 \\ -4.87$	$-3.28 \\ -3.38 \\ -3.58$

^{*a*} Measured in chlorobenzene, excitation wavelengths are at their maximum absorption wavelengths. ^{*b*} Optical band gap, estimated from the onset wavelength of optical absorption spectra. ^{*c*} Calculated from the HOMO level and optical band-gap. ^{*d*} Shoulder peak.



Fig. 5 UV/Vis/NIR absorption spectra of polymer **P1** and **P3–P5** thin films on ITO-coated glass substrate (in CH_3CN with 0.1 M Et_4NClO_4 as the supporting electrolyte) in its neutral (dashed line) and oxidized states (solid line).

changes from orange to slate gray in the oxidized state. Similar to other conjugated electrochromic polymers, various hues, tints, shades or tones of these polymer films could be obtained by applying different oxidation potentials.⁴⁸ Moreover, if two or three colors are mixed, the resulting color will lie on a straight line connecting two points on the chromaticity diagram and the mixed color position can be changed along the line by tuning the ratio of the amounts of the two mixed colors.⁴⁹ Interestingly, the colors of **P1–P3** are close to secondary and primary subtractive colors (orange, blue and green) and thus many different colors could be obtained from the mixture of **P1–P3**.

The green polymer P3 was subjected to more extensive investigation for its visible and NIR electrochromism. The film of P3 was made from its chlorobenzene solution by spin-coating and the film thickness was about 80 nm. When the applied voltage increases from 0.0 V to 1.0 V, the π - π * absorption band at 380 nm decreases gradually (Fig. 6) and at the same time, a new broad band appears in the NIR region at about 1160 nm, due to the formation of radical cations (polarons) in the main chain (Fig. S6†). Meanwhile, the color of film P3 changed from green to grayish brown. When the potential was increased to a more positive value of 1.3 V, corresponding to the second-step oxidation, the absorption band at 1160 nm disappeared and a new band appeared at about 630 nm (Fig. S7†), indicating the formation of bipolarons at a higher level of p-doping.

The rate of change in transmittance upon oxidation/neutral states provides a direct evaluation of the switching ability of a material. The transmittance of the film of polymer **P3** coated on



Fig. 6 Absorption spectra of a P3 film on ITO glass slide in 0.1 M Et_4NCIO_4 from 0.0 V to 1.0 V.

ITO glass was monitored at the telecommunication wavelengths of 1310 nm and 1550 nm respectively, while the potential was switched between 0.0 V and 1.0 V (vs. Ag wire) using square wave potentiometry. The changes in percent transmittance ($\Delta T\%$) between the neutral (at 0.0 V) and oxidized states (at 1.0 V) were found to be 36% at 1310 nm and 30% at 1550 nm wavelengths, respectively (Fig. 7). The response time from the neutral to oxidized state or *vice versa* was found to be 2.0 s for 95% of full optical recovery. The optical contrast kept nearly constant after hundreds of cycles switch, indicating good stability and robustness of **P3**.



Fig. 7 Current consumption (a) and optical transmittance changes of **P3** at 1310 nm (b) and at 1550 nm (c) over time with stepping potentials between +1.0 V and 0.0 V vs. Ag wire.

Coloration efficiency (CE, η) is an important term to evaluate the power efficiency of the electrochromic devices and is defined as:⁵⁰

$$\eta = \Delta \text{OD}(\lambda)/Q_{\rm d} \tag{2}$$

where ΔOD is the change in optical density at a given wavelength and Q_d is the charge passed during the redox switch. The optical density (ΔOD) is determined by:

$$\Delta OD = \log \left[\frac{1}{T_{b}}(\lambda) / \frac{1}{T_{c}}(\lambda) \right]$$
(3)

where $T_{\rm b}$ and $T_{\rm c}$ are the transmittance of the materials in the bleached (neutral) and colored (oxidized) states. Accordingly, the CE of **P3** was calculated to be 479 cm² C⁻¹ at 1310 nm and 232 cm² C⁻¹ at 1550 nm, respectively (Table 3). Furthermore, optical attenuation (*A*) can be calculated from:

$$A = 10 \times \Delta \text{OD}/L = 10 \times \log \left(\% T_{\rm b}(\lambda) / \% T_{\rm c}(\lambda)\right)/L$$
(4)

Table 3 Electrochromic properties of P3

Wavelength/ nm	Contrast $(\Delta T\%)^a$	Attenuation ^b / dB µm ⁻¹	$\frac{\text{CE}^{c}/\text{cm}^{2}}{\text{C}^{-1}}$	Response time/s ^d
1310	36	44	479	2.0
1550	30	21	232	2.0

^{*a*} Difference in transmittance between the fully oxidized and neutral states. ^{*b*} Optical attenuation per film thickness in μ m. ^{*c*} Color efficiency at a given wavelength. ^{*d*} Response time to reach 95% of maximum attenuation range during oxidation.

where *L* is the thickness (μ m) of the electrochromic active layer. Accordingly, the optical attenuation of **P3** is calculated to be 44 dB μ m⁻¹ at 1310 nm and 21 dB μ m⁻¹ at 1550 nm, which is comparable to those of PEDOT film.⁵¹

Conclusions

We have demonstrated a feasibility of the precursor strategy for a quick access to a series of low band-gap D–A polymers containing different strong acceptor units. By varying the electron acceptor strength, the band-gap levels of polymers **P2–P5** change from 1.71 eV to 1.29 eV and therefore exhibit different colors as orange, blue, green, grey and dark goldenrod. After being electrochemically oxidized to radical cations, the color changed to grey or sienna and all the polymers had strong NIR absorption in the oxidized state. Polymer **P3** is potentially a switchable camouflage material for use in day and at night.

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References

- M. Chen, E. Perzon, M. R. Andersson, S. Marcinkevicius, S. K. M. Jönsson, M. Fahlman and M. Berggren, *Appl. Phys. Lett.*, 2004, 84, 3570.
- 2 C. J. Brabec, C. Winder, N. S. Sariciftci, J. C. Hummelen, A. Dhanabalan, P. A. van Hal and R. A. J. Janssen, *Adv. Funct. Mater.*, 2002, **12**, 709.
- 3 M. R. Andersson, M. Berggren, O. Inganaes, G. Gustafsson, J. C. Gustafsson-Carlberg, D. Selse, T. Hjertberg and O. Wennerstroem, *Macromolecules*, 1995, 28, 7525.
- 4 G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, Z. Y. Wang and D. Ma, Adv. Mater., 2009, 21, 111.
- 5 F. Zhang, W. Mammo, L. M. Andersson, S. Admassie, M. R. Andersson and O. Inganäs, *Adv. Mater.*, 2006, 18, 2169.
- 6 D. Mühlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, **18**, 2884.
- 7 E. Bundgaard and F. C. Krebs, Sol. Energy Mater. Sol. Cells, 2007, 91, 954.
- 8 C.-Y. Yu, C.-P. Chen, S.-H. Chan, G.-W. Hwang and C. Ting, *Chem. Mater.*, 2009, 21, 3262.
- 9 W. Yue, Y. Zhao, S. Shao, H. Tian, Z. Xie, Y. Geng and F. Wang, J. Mater. Chem., 2009, 19, 2199.
- 10 G. Zhang, Y. Fu, Q. Zhang and Z. Xie, Polymer, 2010, 51, 2313.
- 11 M. M. Wienk, M. Turbiez, J. Gilot and R. A. J. Janssen, Adv. Mater., 2008, 20, 2556.
- 12 G.-Y. Chen, C.-M. Chiang, D. Kekuda, S.-C. Lan, C.-W. Chu and K.-H. Wei, J. Polym. Sci., Part A: Polym. Chem., 2010, 48, 1669.
- 13 E. Zhou, S. Yamakawa, K. Tajima, C. Yang and K. Hashimoto, *Chem. Mater.*, 2009, 21, 4055.

- 14 M. Koppe, H.-J. Egelhaaf, G. Dennler, M. C. Scharber, C. J. Brabec, P. Schilinsky and C. N. Hoth, *Adv. Funct. Mater.*, 2010, **20**, 338.
- 15 E. Zhou, Q. Wei, S. Yamakawa, Y. Zhang, K. Tajima, C. Yang and K. Hashimoto, *Macromolecules*, 2010, 43, 821.
- 16 A. P. Zoombelt, M. Fonrodona, M. G. R. Turbiez, M. M. Wienk and R. A. J. Janssen, J. Mater. Chem., 2009, 19, 5336.
- 17 F. Zhang, J. Bijleveld, E. Perzon, K. Tvingstedt, S. Barrau, O. Inganäs and M. R. Andersson, J. Mater. Chem., 2008, 18, 5468.
- 18 W. Qiao, J. Zheng, Y. Wang, Y. Zheng, N. Song, X. Wan and Z. Y. Wang, Org. Lett., 2008, 10, 641.
- 19 A. M. McDonagh, S. R. Bayly, D. J. Riley, M. D. Ward, J. A. McCleverty, M. A. Cowin, C. N. Morgan, R. Varrazza, R. V. Penty and I. H. White, *Chem. Mater.*, 2000, **12**, 2523.
- 20 S. Xun, G. LeClair, J. Zhang, X. Chen, J. P. Gao and Z. Y. Wang, Org. Lett., 2006, 8, 1697.
- 21 G. Sonmez, P. Schottland, K. Zong and J. R. Reynolds, J. Mater. Chem., 2001, 11, 289.
- 22 R. E. Peierls, *Quantum Theory of Solids*, Oxford University Press, London, 1956.
- 23 H. A. M. van Mullekom, J. A. J. M. Vekemans, E. E. Havinga and E. W. Meijer, *Mater. Sci. Eng.*, *R*, 2001, **32**, 1.
- 24 J. Roncali, Chem. Rev., 1997, 97, 173.
- 25 C. Winder and N. S. Sariciftci, J. Mater. Chem., 2004, 14, 1077.
- 26 O. Atwani, C. Baristiran, A. Erden and G. Sonmez, Synth. Met., 2008, 158, 83.
- 27 G. Sonmez, H. B. Sonmez, C. K. F. Shen, R. W. Jost, Y. Rubin and F. Wudl, *Macromolecules*, 2005, 38, 669.
- 28 A. A. Argun, P.-H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid and J. R. Reynolds, *Chem. Mater.*, 2004, 16, 4401.
- 29 A. Cihaner and F. Algı, Adv. Funct. Mater., 2008, 18, 3583.
- 30 D. Baran, A. Balan, S. Celebi, B. Meana Esteban, H. Neugebauer, N. S. Sariciftci and L. Toppare, *Chem. Mater.*, 2010, 22, 2978.
- 31 M. Içli, M. Pamuk, F. Algi, A. M. Önal and A. Cihaner, *Chem. Mater.*, 2010, **22**, 4034.

- 32 A. Balan, D. Baran and L. Toppare, J. Mater. Chem., 2010, 20, 9861.
- 33 M. I. Özkut, S. Atak, A. M. Ônal and A. Cihaner, *J. Mater. Chem.*, 2011, **21**, 5268.
- 34 S. Günes, D. Baran, G. Günbas, A. Durmus, A. Fuchsbauer, N. S. Saricifici and L. Toppare, *Polym. Chem.*, 2010, 1, 1245.
- 35 G. Qian and Z. Y. Wang, Can. J. Chem., 2010, 88, 192.
- 36 G. Qian and Z. Y. Wang, *Chem.-Asian J.*, 2010, **5**, 1006.
- 37 G. Qian, B. Dai, M. Luo, D. Yu, J. Zhan, Z. Zhang, D. Ma and Z. Y. Wang, *Chem. Mater.*, 2008, **20**, 6208.
- 38 G. Qian, Z. Zhong, M. Luo, D. Yu, Z. Zhang, D. Ma and Z. Y. Wang, J. Phys. Chem. C, 2009, 113, 1589.
- 39 M. Karikomi, C. Kitamura, S. Tanaka and Y. Yamashita, J. Am. Chem. Soc., 1995, 117, 6791.
- 40 G. Qian, X. Li and Z. Y. Wang, J. Mater. Chem., 2009, 19, 522.
- 41 S. Braverman and M. Cherkinsky, *Tetrahedron Lett.*, 1997, **38**, 487.
- 42 Y. Yamashita, K. Ono, M. Tomura and S. Tanaka, *Tetrahedron*, 1997, **53**, 10169.
- 43 W.-L. Yu, J. Pei, Y. Cao, W. Huang and A. J. Heeger, Chem. Commun., 1999, 1837.
- 44 I. Yamaguchi, B.-J. Choi, T.-a. Koizumi, K. Kubota and T. Yamamoto, *Macromolecules*, 2007, 40, 438.
- 45 Y. Li, Y. Cao, J. Gao, D. Wang, G. Yu and A. J. Heeger, Synth. Met., 1999, 99, 243.
- 46 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, Adv. Mater., 1995, 7, 551.
- 47 S.-H. Hsiao, G.-S. Liou, Y.-C. Kung and H.-J. Yen, *Macromolecules*, 2008, 41, 2800.
- 48 G. Sonmez, H. B. Sonmez, C. K. F. Shen and F. Wudl, Adv. Mater., 2004, 16, 1905.
- 49 R. D. Overheim and D. L. Wagner, *Light and Color*, Wiley, New York, 1982.
- 50 B. D. Reeves, C. R. G. Grenier, A. A. Argun, A. Cirpan, T. D. McCarley and J. R. Reynolds, *Macromolecules*, 2004, 37, 7559.
- 51 J. D. Zhang, H. A. Yu, X. G. Wu and Z. Y. Wang, *Opt. Mater.*, 2004, 27, 265.