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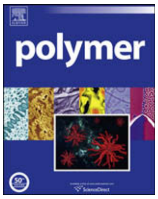

Purple red and luminescent polyiminoarylenes containing the 1,4-diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) chromophore

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ABSTRACT

New DPP-containing polyiminoarylenes were prepared from 1,4-diketo-2,5-dihexyl-3,6-di(4′-bromophenyl)pyrrolo[3,4-*c*]pyrrole and various arylamine derivatives using palladium-catalyzed amination reactions. The arylamine comonomers were aniline (ANI), *t*-butylaniline (TBA), 2-aminoanthracene (AAN), 1-aminopyrene (APY) and *N*,*N*′-diphenyl-*p*-phenylenediamine (PDA). Purple red polymers with good solubility in common organic solvents and molecular weights between 4.4 and 35.8 kDa were obtained. Polymer solutions were readily fluorescent with quantum yields between 19 and 62%, while solution-cast films only showed a weak fluorescence. All polymers exhibit low band gaps of approximately 1.9 eV. Cyclovoltammetric studies indicate quasireversible oxidation for polymers with TBA, APY and PDA as comonomer units, and quasireversible reduction for the polymer with AAN comonomer unit. Polymers with APY and PDA comonomer units are electrochromic and can be switched between red in the neutral and greenish grey in the oxidized state.

1. Introduction

1,4-Diketo-3,6-diphenylpyrrolo[3,4-*c*]pyrrole (DPP) and a number of substituted derivatives represent a class of red pigments with excellent photostability and high quantum yield of photoluminescence [1,2]. Because of their optical properties, DPP-based compounds have recently become attractive for the development of new materials with potential use in electronic devices. In this context, we [3–7] and others [8–10] have demonstrated that DPP-based compounds can also be used as monomers and comonomers in the preparation of novel π-conjugated polymers with low band gap and intense orange to red photo- [3–7,9,10] and electroluminescence [4,7,9,10]. DPP-based polymers [3–10] and oligomers [11] have previously been prepared by Pd-catalyzed coupling reactions such as Suzuki- [3–5,7,9–11], Stille- [6,8] and Heck coupling [6], Ni-mediated Yamamoto coupling [5], and by electrochemical polymerization [12].

In a continuation of these studies, we now synthesized DPP-based polymers from dialkylated dibromo-DPP and aniline derivatives using Pd-catalyzed amination reactions previously reported by the groups of Hartwig [13], Buchwald [14], Kanbara et al. [15] and others [16,17]. Following this method new DPP-containing polyiminoarylenes of general structures I and II (see Scheme 1) could be prepared. These polymers are interesting because it can be expected that the presence of electron-rich triarylamine units in the conjugated backbone causes a red-shift of the polymer absorption and fluorescence. A similar effect was already reported from dialkylamino-substituted low-molecular-weight DPP-derivatives [2]. Furthermore, it was expected that the nitrogen atoms in the backbone lower the oxidation potential of the polymers.

Purpose of the present article is to report the synthesis of new DPP-based polyiminoarylenes and to describe their characteristic photophysical and electrochemical properties. Studies were mainly carried out using spectroscopic methods (UV and fluorescence spectroscopy, IR and ^{1}H NMR-spectroscopy) and cyclic voltammetry.

2. Experimental section

2.1. Materials

2.1.1. Reagents

The monomers 4-(*t*-butyl)aniline, 4-nitroaniline, 2-aminoanthrancene, 1-aminopyrene and *N*,*N*′-diphenyl-*p*-phenylenediamine were obtained from Acros Organics and Fluka and used without further purification. 1,4-Diketo-3,6-bis(4-bromophenyl)-pyrrolo[3,4-*c*]pyrrole was kindly supplied by Ciba Specialty Chemicals, Basle (Switzerland) and converted into the 2,5-dihexylated monomer following a procedure described in the literature [3]. 1-Bromohexane, tris(dibenzylideneacetone)dipalladium(0), tri-*t*-butylphosphine, sodium *t*-butylate and potassium phosphate

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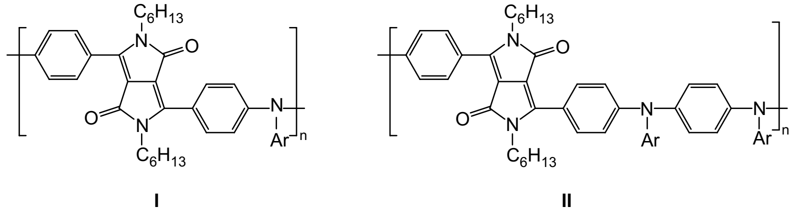


Scheme 1. General structures of DPP-containing polyiminoarylenes.

were obtained from Aldrich, Acros Organics and Fluka and used without further purification. Solvents were of analytical grade and used without further purification. Chromatographic purification of the dihexylated DPP monomer was carried out using Acros silica gel 60 (0.060–0.200 mm).

2.2. Instrumentation

^{1}H NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz. UV/vis absorption spectra were recorded on a Perkin–Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded on a Perkin–Elmer LS50B spectrometer. Molecular weights were determined using size exclusion chromatography (SEC). A Waters/Millipore UV detector 481 and an SEC column combination (Latek/styragel 50/1000 nm pore size) were used. All measurements were carried out in tetrahydrofuran at 45 °C. The columns were calibrated vs. commercially available polystyrene standards. Cyclic voltammograms were recorded using a potentiostat PG390 from Heka Company. A thin film of the polymer was cast on an ITO electrode or a glassy carbon electrode (from CH Instruments, Austin, TX) and cycled in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as electrolyte salt. Counter and reference electrodes were platinum. The voltage data are calculated for the standard calomel electrode (SCE). Scan rate: 25 mV s^{-1}. T: 20 °C. Onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammogram.

2.3. Synthesis of the polymers

2.3.1. P-DPP-ANI

In a 30 mL Schlenk tube 0.2 g (0.33 mmol) dibromo-DPP together with 0.03 g (0.33 mmol) aniline were dissolved in 7 mL degassed toluene. The solution was stirred under nitrogen at 50 °C followed by the addition of the premixed catalyst solution prepared from 9 mg (3 mol %) $Pd_2(dba)_3$ and 12 mg (16 mol%) tri-*t*-butylphosphine in 1 mL toluene. The temperature was gently raised to 90 °C while 0.094 g (3 mmol) sodium *t*-butoxide were added stepwise over a period of $2\frac{1}{2}$ h. After complete addition of the base, the reaction mixture was stirred under nitrogen at 90 °C for further 12 h and was then allowed to cool. The reaction was quenched upon addition of 20 mL water. After stirring for half an hour, the mixture was diluted with an appropriate amount of dichloromethane. The organic phase was then separated, washed with water and dried over magnesium sulphate. After concentration in vacuo, the residue was poured into hexane to induce precipitation of the polymer, which was filtered off and thoroughly washed with acetone. After drying under ambient conditions a purple powder was obtained. Yield: 72%. For molecular weight and optical data see Table 1.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.81 (d, 2H, arom. DPP), 7.41 (d, 2H, arom. DPP), 7.20 (d, 2H, arom. aniline), 7.11 (d, 2H, arom. aniline), 6.99 (m, 1H, arom. aniline), 3.79 (m, 2H, α-CH_2), 0.8–1.8 (m, 22H, alkyl chain DPP). UV (toluene) 522 nm, $\varepsilon = 8.6 \times 10^3$ cm^2 monomol^{-1}.

2.3.2. P-DPP-TBA

In a 30 mL Schlenk tube 0.3625 g (0.6 mmol) dibromo-DPP together with 0.881 g (0.6 mmol) 4-*t*-butylaniline were dissolved in 5 mL degassed toluene. The solution was stirred under nitrogen at 50 °C, followed by the addition of the premixed catalyst solution prepared from 12 mg (2.2 mol %) $Pd_2(dba)_3$ and 16 mg (13.2 mol%) tri-*t*-butylphosphine in 1 mL toluene. The temperature was gently raised to 90 °C while 0.125 g (1.32 mmol) sodium *t*-butoxide were added stepwise over a period of $2\frac{1}{2}$ h. After complete addition of the base, the reaction mixture was stirred under nitrogen at 90 °C for further 12 h and was then allowed to cool. The reaction was quenched upon addition of 20 mL water. After stirring for half an hour, the mixture was diluted with an appropriate amount of dichloromethane. The organic phase was then separated, washed with water and dried over magnesium sulphate. After concentration in vacuo, the residue was poured into hexane to induce precipitation of the polymer, which was filtered off and thoroughly washed with acetone. After drying under ambient conditions a purple powder was obtained. Yield: 79%. For molecular weight and optical data see Table 1.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.80 (d, 2H, arom. DPP), 7.41 (d, 2H, arom. DPP), 7.24 (d, 2H, arom. aniline), 7.14 (d, 2H, arom. aniline), 3.79 (m, 2H, α-CH_2), 1.36 (9H, *t*-butyl), 0.8–1.8 (m, 22H, alkyl chain DPP). UV (toluene) 552 nm, $\varepsilon = 1.48 \times 10^4$ cm^2 monomol^{-1}.

2.3.3. P-DPP-AAN

In a 30 mL Schlenk tube 0.2 g (0.33 mmol) dibromo-DPP together with 0.03 g (0.33 mmol) 2-aminoanthracene were dissolved in 7 mL degassed toluene. The solution was stirred under nitrogen at 50 °C, followed by the addition of the premixed

Table 1
Molecular weights and photophysical properties of DPP-based polyiminoarylenes.

	M_w	Polydispersity	λ_{max} (nm), solution/film	λ_{em} (nm), solution/film	Stokes-shift	ϕ_{fl} (%)
P-DPP-ANI	8800	1.7	522/534	619/624	97/90	52
P-DPP-TBA	35,800	2.4	552/558	633/650	81/92	19
P-DPP-AAN	10,200	1.4	543/552	631/654	88/102	38
P-DPP-APY	4300	1.3	527/564	607/–	80/–	62
P-DPP-PDA	14,000	1.9	539/544	608/–	69/–	48

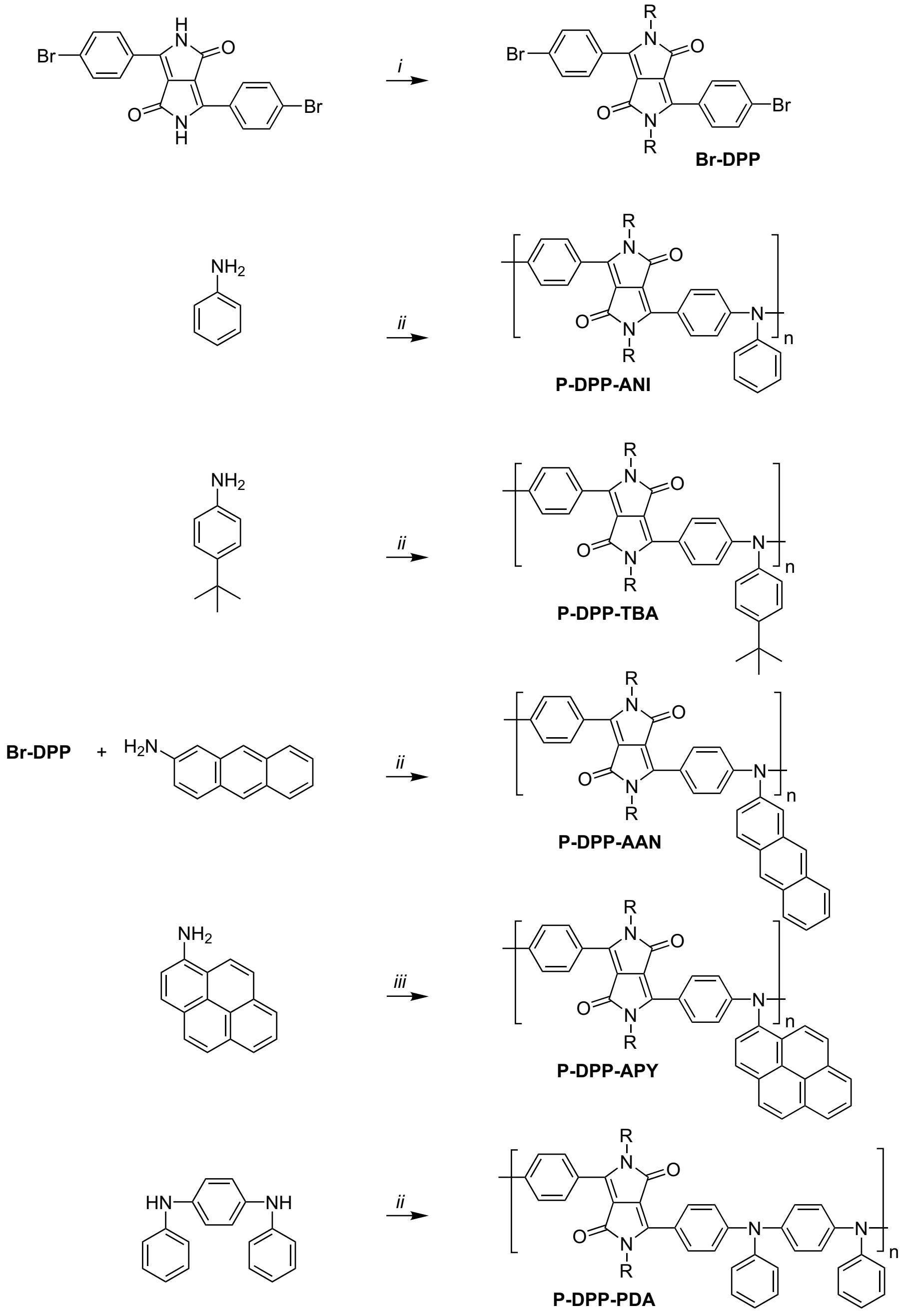
UV and photoluminescence were measured in toluene. The excitation wavelength for photoluminescence spectra is 350 nm. Quantum yields of the polymers were measured in toluene solution with an excitation wavelength of 400 nm, the values were calculated by comparing with Rhodamine 6G in ethanol ($\phi_{fl} = 0.95$).

catalyst solution prepared from 9 mg (3 mol %) $Pd_2(dba)_3$ and 12 mg (16 mol%) tri-*t*-butylphosphine in 1 mL toluene. The temperature was gently raised to 90 °C while 0.094 g (1 mmol) sodium *t*-butoxide were added stepwise over a period of $2\frac{1}{2}$ h. After complete addition of the base, the reaction mixture was stirred under nitrogen at 90 °C for further 12 h and was then allowed to cool. The reaction was quenched upon addition of 20 mL water. After stirring for half an hour, the mixture was diluted with an appropriate amount of dichloromethane. The organic phase was then separated, washed with water and dried over magnesium sulphate. After concentration in vacuo, the residue was poured into hexane to induce precipitation of the polymer, which was filtered off and thoroughly washed with acetone. After drying under ambient conditions a purple powder was obtained. Yield: 85%. For molecular weight and optical data see Table 1.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.42 (s, 1H, anthracene), 8.27 (s, 1H, anthracene), 8.01 (m, 3H, anthracene), 7.85 (d, 2H, arom. DPP), 7.80 (s, 2H, anthracene), 7.46 (m, 2H, anthracene), 7.33 (d, 2H, arom. DPP), 3.81 (m, 2H, α-CH_2), 0.8–1.8 (m, 22H, alkyl chain DPP). UV (toluene) 543 nm, $\varepsilon = 1.63 \times 10^4$ cm^2 $monomol^{-1}$.

2.3.4. P-DPP-APY

In a 30 mL Schlenk tube 0.122 g (0.20 mmol) dihexylated dibromo-DPP, 0.043 g (0.2 mmol) 1-aminopyrene and 0.17 g (0.80 mmol) potassium phosphate were dissolved in 8 mL dry and



Scheme 2. Synthetic route to monomers and polymers ($R = -n\text{-}C_6H_{13}$). Reagents and conditions: (i) 1-bromohexane, KO^{t}Bu, NMP. (ii) $Pd_2(dba)_3$, P(^{t}Bu)$_3$, NaO^{t}Bu, toluene, reflux. (iii) $Pd_2(dba)_3$, P(^{t}Bu)$_3$, K_3PO_4, toluene, reflux.

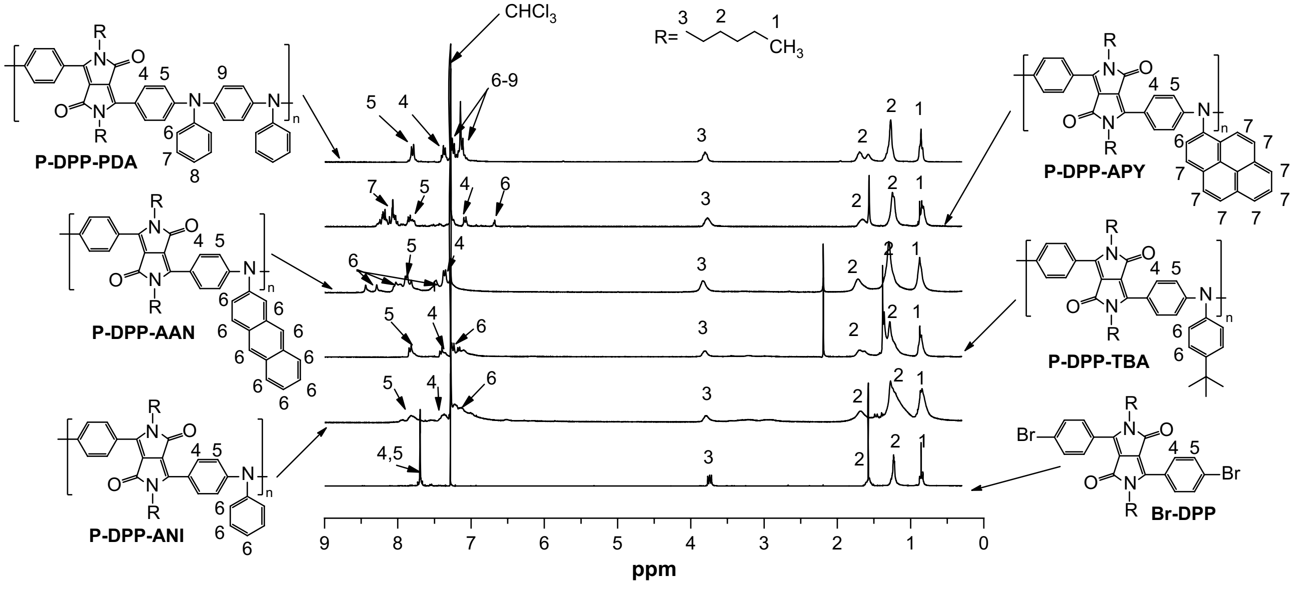


Fig. 1. 300 MHz ^{1}H NMR spectra of monomer **Br-DPP** and polymers **P-DPP-ANI**, **P-DPP-TBA**, **P-DPP-AAN**, **P-DPP-APY** and **P-DPP-PDA**.

degassed toluene. The solution was stirred under nitrogen at 20 °C, followed by the addition of the premixed catalyst solution prepared from 6 mg (2 mol%) Pd$_2$(dba)$_3$ and 2.7 mg tri-*t*-butylphosphine in 1 mL toluene. The temperature was heated to 100 °C and stirred under nitrogen for 24 h. After cooling, 50 mL of toluene were added and the mixture was washed with brine and water. The organic phase was filtered through Celite to remove residual palladium and then dried over magnesium sulphate. After concentration in vacuo, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The precipitate was filtered off and dried under vacuum for 24 h. A purple red powder was obtained. Yield: 81%. For molecular weight and optical data see Table 1.

^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 7.9–8.3 (m, 8H, arom. pyrene), 7.8 (d, 2H, arom. DPP), 7.3 (d, 2H, arom. DPP), 7.08 (d, 1H, arom. pyrene), 3.7 (t, 2H, α-CH$_2$), 0.7–1.8 (m, 22H, alkyl chain DPP). ^{13}C NMR (75 MHz, CDCl$_3$, ppm): δ 165.1 (2× C=O), 145.1 (2× C–N, DPP phenylene), 142.6 (2× C, DPP core), 139.4 (C–N, pyrene), 132.9 (2× C, DPP phenylene), 131.4 (C, pyrene), 129 (2× C, DPP core), 127–120 (several C and CH, pyrene and DPP phenylene), 45.4 (N–CH$_2$), 31.5

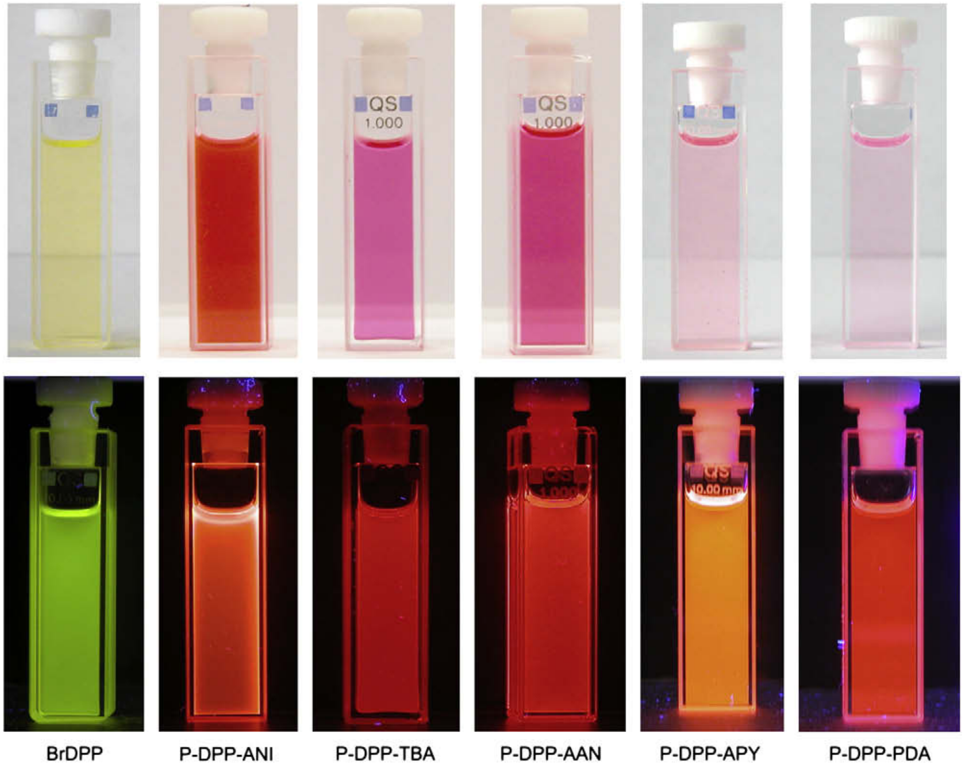

BrDPP P-DPP-ANI P-DPP-TBA P-DPP-AAN P-DPP-APY P-DPP-PDA

Fig. 2. Photographic images of the absorption and fluorescence colours of various monomer and polymer solutions described in this study (solvent: toluene).

(CH_2), 31.1 (CH_2), 26.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3). UV (toluene) 527 nm, $\varepsilon = 5.03 \times 10^4$ cm^2 monomol^{-1}.

2.3.5. P-DPP-PDA

In a 30 mL Schlenk tube 0.122 g (0.20 mmol) dihexylated dibromo-DPP, 0.052 g (0.2 mmol) *N,N′*-diphenyl-*p*-phenylenediamine and 0.041 g (0.60 mmol) sodium *t*-butylate were dissolved in 8 mL dry and degassed toluene. The solution was stirred under nitrogen at 20 °C, followed by the addition of the premixed catalyst solution prepared from 6 mg (2 mol%) $Pd_2(dba)_3$ and 2.7 mg tri-*t*-butylphosphine in 1 mL toluene. The temperature was heated to 100 °C and stirred under nitrogen for 24 h. After cooling, 50 mL of toluene were added and the mixture was washed with brine and water. The organic phase was filtered through Celite to remove residual palladium and then dried over magnesium sulphate. After concentration in vacuo, the residue was redissolved in a minimum amount of chloroform and precipitated in acetone. The precipitate was filtered off and dried under vacuum for 24 h. A purple red powder was obtained. Yield: 80%. For molecular weight and optical data see Table 1.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ, 7.80 (d, 2H, arom. DPP), 7.37 (d, 2H, arom. DPP), 7.15–7.25 (14H, arom. PDA), 3.81 (t, 2H, α-CH_2), 0.7–1.8 (m, 22H, alkyl chain DPP). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 165.1 (2× C=O), 145.9 (2× C–N), 145.1 (2× C–N, DPP phenylene), 142.6 (2× C, DPP core), 140.3 (2× C–N), 135.1 (2× CH, amine-phenylene), 134.9 (2× CH, amine-phenylene), 132.9 (2× C, DPP phenylene), 129 (2× C, DPP core), 127–120 (CH, amine-phenylene and DPP phenylene), 45.4 (N–CH_2), 31.5 (CH_2), 31.1 (CH_2),

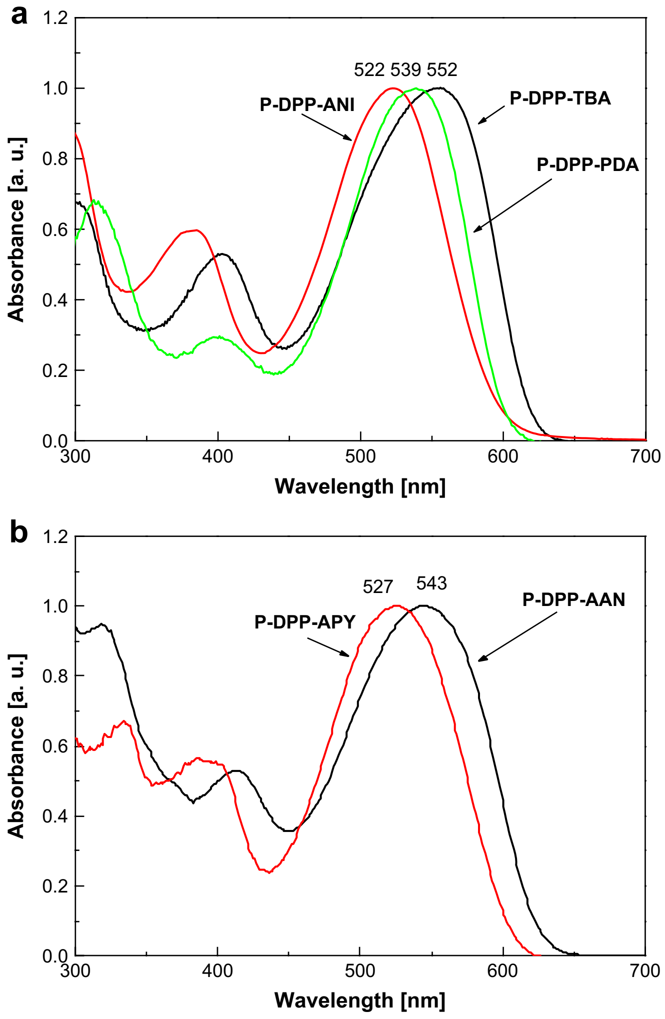


Fig. 3. UV/vis absorption spectra of DPP-polyiminoarylenes **P-DPP-ANI**, **P-DPP-TBA** and **P-DPP-PDA** (a), and **P-DPP-APY** and **P-DPP-AAN** (b) in toluene solution.

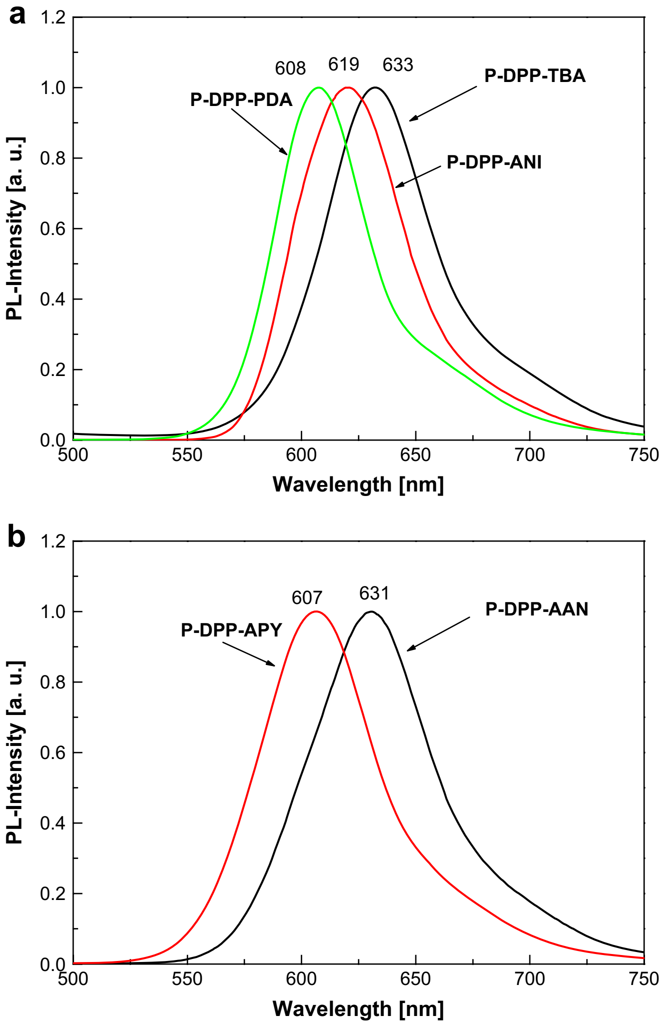


Fig. 4. Fluorescence spectra of DPP-polyiminoarylenes **P-DPP-ANI**, **P-DPP-TBA** and **P-DPP-PDA** (a), and **P-DPP-APY** and **P-DPP-AAN** (b) in toluene solution. Excitation at 350 nm.

Table 2
Band gap data of DPP-based polyiminoarylenes.

Polymer	Absorption λ_{onset} (nm) on film	Opt./electrochem. band gap (eV)	Oxidation onset (V) {HOMO (eV)}	Reduction onset (V) {LUMO (eV)}
P-DPP-ANI	630	1.98/1.91	0.84 {−5.24}	−1.07 {−3.33}
P-DPP-TBA	650	1.91/1.91	1.01 {−5.41}	−0.90 {−3.50}
P-DPP-AAN	650	1.91/2.13	1.01 {−5.41}	−1.12 {−3.28}
P-DPP-APY	647	1.92/1.84	0.84 {−5.24}	−1.00 {−3.40}
P-DPP-PDA	627	1.98/1.76	0.66 {−5.06}	−1.10 {−3.30}

Band gap (E_{opt}) measured at the onset of electronic absorption of the polymer film ($E_{opt} = 1240/\lambda_{onset}$ eV). HOMO–LUMO gap according to the equation: $-E_{LUMO} = E_{onset(red)} + 4.4$ eV and $-E_{HOMO} = E_{onset(ox)} + 4.4$ eV, where $E_{onset(ox)}$ and $E_{onset(red)}$ are the onset potentials for the oxidation and reduction processes of polymer thin films vs. SCE.

26.8 (CH_2), 22.7 (CH_2), 14.1 (CH_3). UV (toluene) 539 nm, $\varepsilon = 2.27 \times 10^4$ cm^2 monomol^{-1}.

3. Results and discussion

The complete monomer synthesis starts from 4-bromobenzonitrile and dialkyl succinate, which are converted in a single step reaction into dibrominated DPP according to known procedures [18]. The dibrominated DPP is rendered soluble upon N-alkylation of the lactam units using *n*-hexylbromide in alkaline solution, and the readily soluble dihexyl-dibromo-DPP (**Br-DPP**) is obtained in good yield [3]. For the subsequent polymerization it is very important to prepare the monomer in a highly purified state, which can be facilitated by column chromatography (see experimental part) and recrystallization.

Polymerization was carried out in toluene using tris(dibenzylideneacetone)dipalladium(0) and tri-*t*-butylphosphine as catalyst. The conditions are described in detail in the experimental part. Since the DPP monomer is not very stable under strongly basic conditions, sodium *t*-butoxide could be used in the coupling reaction only if the polymerization proceeded rapidly and was complete within a few hours. Fortunately this was the case for most of the aniline-type monomers used in our study. The only exception was 1-aminopyrene containing the amino group in the sterically unfavorable 1-position. In this case, the reaction was much slower and therefore potassium phosphate was used as the base. The

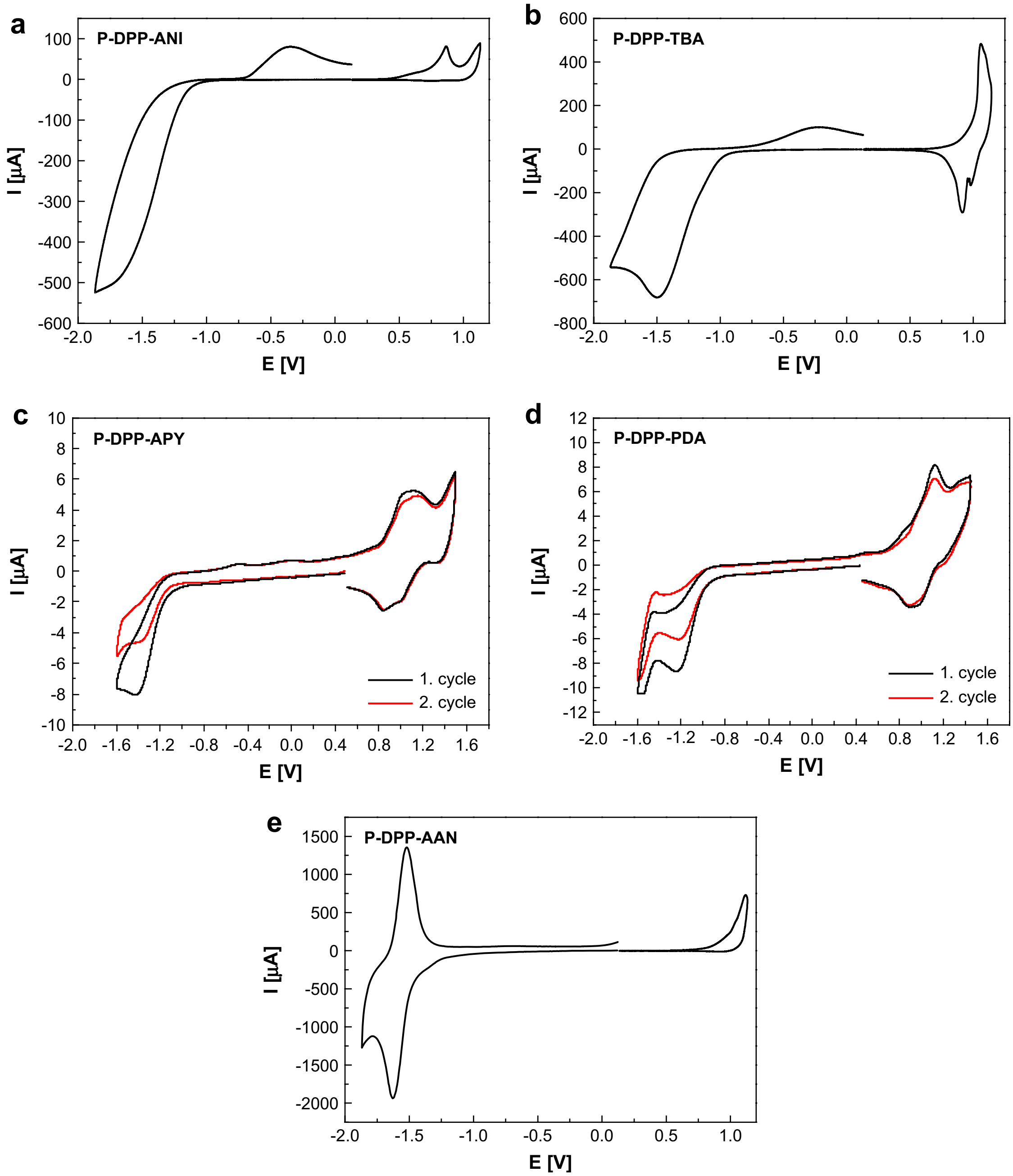


Fig. 5. Cyclic voltammograms of polymers **P-DPP-ANI** (a), **P-DPP-TBA** (b), **P-DPP-APY** (c), **P-DPP-PDA** (d) and **P-DPP-AAN** (e). Scan rate: 25 mV s^{-1}, $T = 20$ °C. Electrolyte solution: 0.1 M $TBAPF_6$ in acetonitrile.

disadvantage of using potassium phosphate was a comparatively low molecular weight of the polymer of only 4300 Da. For the other polymers, the molecular weights were between 8800 and 35,800 Da. The highest molecular weight was obtained for **P-DPP-TBA** containing *t*-butylaniline as comonomer probably because of its improved solubility. The synthetic routes to monomers and polymers are summarized in Scheme 2.

The proton NMR spectra of the DPP monomer and the various polymers are shown in Fig. 1. All spectra show signals of the DPP phenylene protons at about 7.6 ppm, and signals of the *n*-hexyl-substituted lactam groups of DPP in the region from 0.7 to 1.8 ppm. The signal of the methylene groups adjacent to the lactam nitrogen of DPP appears at about 3.8 ppm. For the aniline-containing polymer **P-DPP-ANI**, the signals of the N-phenyl substituent groups appear at 7.20, 7.11 and 6.99 ppm. Regarding **P-DPP-TBA**, the signals of the N-phenyl substituent groups occur at 7.24 and 7.14 ppm, and the signal of the *t*-butyl group at 1.36 ppm. The signals of the anthracene group of **P-DPP-AAN** appear at 8.42, 8.27, 8.01, 7.80 and 7.46 ppm, and the signals of the pyrene group of **P-DPP-APY** are located at 8.3–7.9 and 7.08 ppm. **P-DPP-PDA** exhibits signals of the *N*,*N*′-diphenyl phenylenediamine unit at 7.25 and 7.15 ppm.

3.1. *UV/vis absorption*

The polymers are easily soluble in chloroform, toluene and tetrahydrofuran. Bright red purple solutions are obtained with absorption maxima around 540 nm (see Table 1). Photographs of the polymer solutions are shown in Fig. 2, the UV/vis absorption spectra of the polymers in toluene are shown in Fig. 3. Compared with the absorption maximum of the dihexyl-dibromo-DPP monomer at 476 nm, the absorption maxima of the polymers are red shifted by about 50–70 nm. The bathochromic shift is caused by the introduction of the electron-donating diarylamino groups in the backbone adjacent to the diphenyl-DPP chromophore. Introduction of dimethylamino groups in the para-positions of diphenyl-DPP is known to shift the DPP absorption from yellow–red (λ_{max}: 504 nm) to violet–blue (λ_{max}: 554 nm) [2]. In addition, electron delocalisation along the polymer backbone may also contribute to the bathochromic shift.

3.2. *Fluorescence*

The polymer solutions exhibit a bright red fluorescence (Fig. 2). The fluorescence spectra in Fig. 4 indicate fluorescence maxima between 607 and 631 nm, the Stokes-shift being between 62 and 97 nm. The smallest Stokes-shift was found for **P-DPP-TBA**, the largest for **P-DPP-ANI**. Fluorescence quantum yields ϕ_{fl} are moderate, the highest values of 52 and 62% were found for **P-DPP-ANI** and **P-DPP-APY**, the excitation wavelength being 400 nm. The high ϕ_{fl} value of **P-DPP-APY** might originate from energy transfer from the highly fluorescent pyrene unit to the polymer backbone. The other polymers exhibit ϕ_{fl} values between 19 and 48% (see Table 1).

Surprisingly the solid films of the polymers only showed a poor luminescence. It is unlikely, that the poor solid state luminescence is due to catalyst residues, because (a) the polymer solutions were highly fluorescing and (b) the polymer was highly purified by several dissolution and reprecipitation steps. Probably strong donor–acceptor interactions between the electron-rich nitrogen atoms and the DPP chromophores in different polymer chains lead to a quenching of the fluorescence in the solid state. These interactions are lacking in solution because of the expanded coil-structure of the rod-like polymer chains.

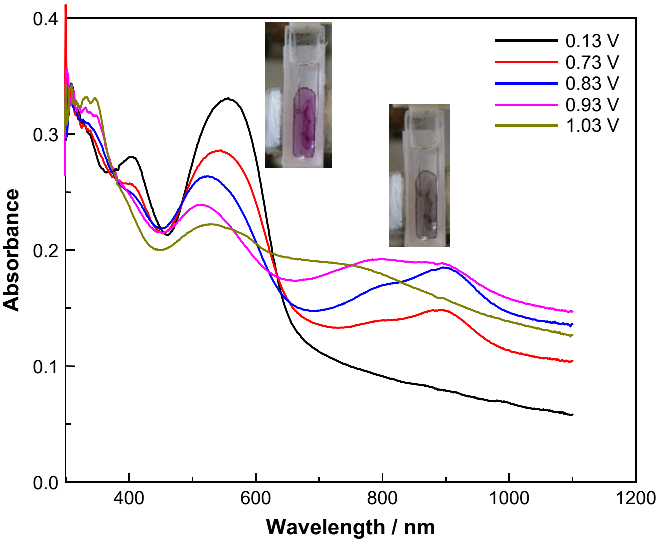
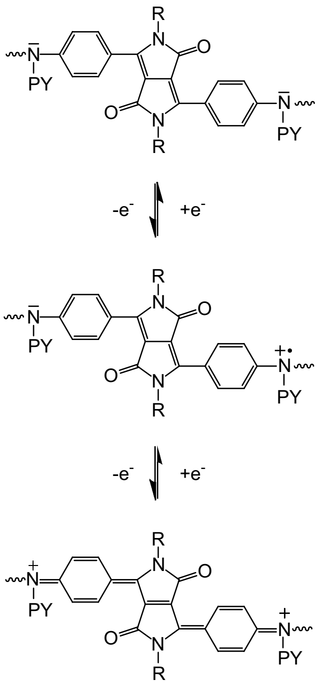


Fig. 6. Spectroelectrochemical analysis of **P-DPP-APY** film cast on an ITO anode. Solvent: 0.1 M TBAPF$_6$/acetonitrile; $T = 20\,°C$, Potential vs. SCE. The colours of the neutral and oxidized film are shown in insets.

3.3. *Electrochemical properties*

The electrochemical properties of the polymers were studied using cyclic voltammetry (CV). CV-data are compiled in Table 2, the corresponding CV diagrams are shown in Fig. 5. **P-DPP-TBA**, **P-DPP-APY** and **P-DPP-PDA** exhibit quasireversible oxidation behaviour, whereas the oxidation of **P-DPP-ANI** and **P-DPP-AAN** is irreversible. For **P-DPP-APY** and **P-DPP-PDA**, the first and second oxidative cycles are nearly identical, as shown in Fig. 5c and d. Reductive cycles are irreversible except for **P-DPP-AAN**. For this polymer, reversibility originates from the reversible reduction of the anthracene unit already known from other studies [19]. The



Scheme 3. Reversible electrochemical oxidation and reduction of DPP-based polyiminoarylenes.

oxidative onset potentials $E_{onset(ox)}$ of poly-DPP-iminoarylenes are significantly lower than those of the poly-DPP-arylenes prepared upon Suzuki coupling [7]. This is caused by the presence of the electron-rich N-atoms in the main chain, which can be easily oxidized. As shown in Table 2, the band gap values from the optical and the electrochemical measurements match well. The band gaps of the poly-DPP-iminoarylenes are between the values for poly-DPP-thienylenes prepared upon Stille coupling [6] and those of the poly-DPP-arylenes synthesized via Suzuki coupling [7]. Compared with the previously reported DPP-containing polymers, **P-DPP-PDA** has the lowest onset oxidation potential of 0.66 V.

3.4. Electrochromism

The low oxidation potentials and the quasireversible oxidation behaviour of some of the polymers are excellent prerequisites for the use of the polymers as active layer in electrochromic devices. For the study of electrochromic properties **P-DPP-APY** was cast from chloroform solution onto ITO (indium tin oxide)-coated glass anodes. Then the films were anodically cycled in pure acetonitrile containing 0.1 M TBAPF$_6$ as electrolyte. The counter and reference electrodes were platinum. At different potentials, UV/vis absorption spectra of the films were monitored (Fig. 6). If the potential was increased, the π–π^* transition of the neutral polymer film at 564 nm diminished, and a new band with maximum at 900 nm with long wavelength tail into the infrared appeared. It can be ascribed to nitrogen oxidation and formation of polarons in the conjugated backbone (Scheme 3). The occurrence of the new absorption band matches well with the first anodic wave at about 0.9 V. As soon as the potential exceeds 1 V, a new and very broad absorption occurs, the sample turning greenish and becoming more transparent. The change in the absorption is in accordance with the second anodic wave at 1.05 V. The second oxidation can be ascribed to the formation of bipolarons along the backbone with formation of a quinoid structure as suggested in Scheme 3. Up to 0.93 V the polymer film is stable and can be switched between purple and greenish grey many times, whereas at higher potentials the polymer film becomes soluble and detaches from the electrode. The behaviour of films of **P-DPP-PDA** is very similar to **P-DPP-APY**.

4. Summary and conclusions

Using established Pd-catalyzed coupling reactions it was possible to prepare new DPP-containing polyiminoarylenes with high molecular weight in good yield. The polymers are readily soluble in common organic solvents exhibiting bright red colours and strong red fluorescence in solution. The fluorescence quantum yields of polymer solutions are moderate, a maximum quantum yield of 62% was found for **P-DPP-APY**. However, solid state fluorescence was poor. This is probably due to donor–acceptor interactions between electron-rich nitrogen atoms and electron-deficient DPP units in adjacent polymer chains, which effectively quench the luminescence. The nitrogen atoms in the backbone lower the band gap of the polymer to approximately 1.9 eV. The band gaps are lower than for the conjugated DPP-arene copolymers prepared upon Suzuki coupling [7], but higher than for the DPP-thienylene copolymers made upon Stille coupling [6]. The polymers exhibit low oxidation potentials and, with the exception of **P-DPP-ANI** and **P-DPP-AAN**, quasireversible oxidation behaviour. **P-DPP-AAN** can also be reversibly reduced due to presence of the anthracene unit.

Some of the polymers show pronounced colour changes upon oxidation or reduction, i.e., they exhibit electrochromic properties. **P-DPP-APY** can be switched between purple in the neutral state and greenish grey in the oxidized state. Unfortunately the oxidized polymer tends to partially detach from the electrode affecting the reversibility of the electrochromism. This problem may be solved by introducing cross-linkable substituent groups in the polymer which enable to immobilize the polymer upon network formation [20].

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