

Aminobenzodione-based polymers with low bandgaps and solvatochromic behavior[†]

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Pd-catalyzed amination polymerization of deep blue aminobenzodifuranone monomer 3-(4-bromo-phenyl)-7-(4-octylaminophenyl)-benzo[1,2-*b*:4,5-*b*']difuran-2,6-dione (**M1**) is described, as well as polymerization of symmetric dibromophenyl-benzodifuranone (**M2**), or the corresponding dibromophenylbenzodipyrrolidone (**M3**) with *N,N'*-dialkylated phenylenediamines (**M4a,b**). The resulting polymers **P1–3** exhibit low bandgaps (1.08–1.47 eV), broad UV/vis absorption bands (400–900 nm), and a large solvatochromic shift up to 3140 cm^{−1} from *n*-hexane to hexamethylphosphoramide. Multiple linear regression analyses of $\bar{\nu}_{\text{max}}$ of the solvent-dependent solvatochromic UV/vis absorption bands of **M1**, **P1** and **P2a** are presented, from which Kamlet–Taft and Catalán solvent parameters were determined. All monomers and polymers exhibit high extinction coefficients up to 8.6×10^4 L mol^{−1} cm^{−1} and high photostability, and might be suitable for electronic applications.

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Introduction

Molecular D–A (donor–acceptor) systems are of current interest owing to their potential applications in molecular electronic devices,¹ nonlinear optics,² and artificial photosynthetic systems.³ Among all kinds of electron acceptor moieties, benzodifuranone (BDF), benzodipyrrolidone (BDP) and their derivatives because of their quinonoid structure have received much attention recently as promising candidates for electron-deficient materials.^{4,5} BDF and BDP are high-performance pigments serving as important building blocks for near-infrared (NIR) absorption. They were first developed in the mid-1970s and commercialized as disperse dyes owing to their deep color and high photochemical stability.⁶ Depending on the substitution pattern, BDFs exhibit red to blue colors.⁷

Monomeric aminobenzodifuranone (ABDF) is a deep blue colored dye with interesting solvatochromic behavior,⁸ which has attracted our attention. The aminobenzodifuranone chromophore is a typical D–A system, in which aniline as an electron donor is combined with benzodifuranone as an acceptor unit. To our knowledge, only a few articles reported on derivatives of ABDF,⁸ while polymers based on ABDF are completely unknown.

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[†] Electronic supplementary information (ESI) available: Experimental details, the ¹H NMR spectrum of 4-(octyl amino)phenyl tartronic acid, UV/vis absorption spectra of **M2** and **M3** and polymers **P1**, **P2a** and **P3**, before and after irradiation in toluene, and solvatochromic data. See DOI: 10.1039/c3py01702h

Experimental section

Materials

Reagents. 4-Bromo-mandelic acid, alloxan monohydrate, hydroquinone, *N*-octylaniline, potassium hydroxide, ammonium persulphate, potassium persulfate, Pd₂(dba)₃, X-Phos, cesium carbonate, *t*-BuOK, *n*-octylamine, *n*-2-octyldecyldiamine, bromo-2-octyldecyldiamine and 1,4-cyclohexanedione were obtained from Aldrich and Fluka and used without further purification. Solvents were of analytical grade and used without further purification. **M2**,^{4a} **M3**^{5a} and **M4a,b**⁹ were prepared according to literature methods.

4-(Octyl-amino)phenyl tartronic acid. Alloxan monohydrate (1.6 g, 10 mmol) and *N*-octylaniline (2.05 g, 10 mmol) were dissolved in a mixture of 18 ml ethanol, 3 ml methanol and 5 ml water. While stirring, the clear yellowish solution was neutralized with acetic acid (1 ml, 17 mmol). Stirring was continued at 60 °C for 5 hours. After the reaction, the solvent was removed upon vacuum evaporation. The raw mixture was dissolved in a small amount of ethanol and precipitated in water. A fawn flaky substance was obtained after decantation and drying, with 54% (1.86 g) yield of 5-hydroxy-5-(4-octylaminophenyl)-barbituric acid. 1.86 g (5.4 mmol) of this intermediate were dissolved in an aqueous potassium hydroxide solution (3.1 g, 55 mmol, 1.4 M) and stirred between 40 and 45 °C for 5 hours. The solution was acidified with acetic acid and water was added. The product precipitated overnight. After filtration and drying, 0.78 g (yield 40%) of a light brown powder were obtained, which showed high purity by NMR analysis. ¹H NMR (300 MHz, d₆-DMSO) δ ppm: 7.03–7.06 (d, 2H), 6.55–6.58 (d, 2H), 6.27–6.28, (d, 1H), 5.83 (s, 1H), 2.98 (s, 2H), 1.50–1.52 (t, 2H), 1.26 (s, 10H), 0.86

(t, 3H). ^{13}C NMR (300 MHz, d_6 -DMSO) δ ppm: 172.9, 154.9, 149.9, 128.3, 118.9, 112.7, 82.8, 43.7, 29.4, 29.2, 27.1, 22.7, 14.1.

3-(4-Bromophenyl)-7-(4-octylaminophenyl)-benzo[1,2-b:4,5-b']difuran-2,6-dione (M1). 5-Hydroxy-2-oxo-3-(4-bromophenyl)-2,3-dihydrobenzo[1,2-b]furan (1.39 g, 4.6 mmol) and 4-(octyl-amino)phenyl tartronic acid mono potassium salt (2.48 g, 7.2 mmol) were stirred in acetic acid (20 ml). The mixture was heated to 110 °C and stirred for 5 h at this temperature. 1.05 g (4.6 mol) of ammonium persulphate was added in 8 portions at 80 °C. The mixture was stirred at 95 °C for 1 h. Subsequently, the mixture was cooled to room temperature and a small amount of water was added. The precipitate was filtered, washed with a small amount of acetic acid, and then with water. The crude product was refluxed in methanol giving a dark solid (1.05 g, yield: 42%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 7.83–7.96 (d, 2H), 7.65–7.72 (m, 4H), 6.99 (s, 1H), 6.82 (s, 1H), 6.69–6.72 (d, 2H), 4.37 (s, 1H), 3.22–3.27 (t, 2H), 1.64–1.72 (m, 2H), 1.32 (s, 10H), 0.89–0.95 (t, 3H). ^{13}C NMR could not be measured. UV/vis (DCM): 628 nm; ϵ (628)/L mol $^{-1}$ cm $^{-1}$: 65 241.

Polymer P1. In a Schlenk flask, **M1** (300 mg, 0.55 mmol), potassium phosphate (584 mg, 2.75 mmol), $\text{Pd}_2(\text{dba})_3$ (15.1 mg, 0.016 mmol) and X-Phos (50 mg, 0.11 mmol) are dissolved in dioxane (6 ml) under nitrogen. The mixture is heated to 100 °C and stirred for 40 hours under nitrogen. After cooling to room temperature, water is added in order to precipitate the product. The precipitate is filtered off and washed with methanol. After extraction with toluene, a black solid is obtained (95 mg, yield: 37%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 7.74–7.80 (m, 4H), 7.33–7.61 (m, 4H), 6.72 (s, 2H), 3.08–6.22 (s, 2H), 1.51–1.72 (s, 2H), 1.06–1.40 (m, 10H), 0.77–0.95 (t, 3H). Molecular weight (GPC, THF): M_w = 5.9 kDa, PD = 2.2. UV/vis (DCM): 645 nm, UV/Vis (thin film): 708 nm; ϵ (645)/L mol $^{-1}$ cm $^{-1}$: 30 600.

Polymer P2a. In a Schlenk flask, **M2** (214 mg, 0.43 mmol), *N,N*-bis(2-ethylhexyl)benzene-1,4-diamine dihydrochloride salt (**M4a**) (175 mg, 0.43 mmol), $\text{Pd}_2(\text{dba})_3$ (11.9 mg, 0.015 mmol) and X-Phos (39.2 mg, 0.082 mmol) are dissolved in a mixture of DMF-toluene (2 : 1) (6 ml) under nitrogen. Then, cesium carbonate (310 mg, 0.95 mmol) is added and the mixture is allowed to stir for 48 hours under nitrogen at 90 °C. After completion of the reaction, the dark blue solution is treated with DCM, washed three times with water and once with brine. Then the organic layer is dried over anhydrous magnesium sulfate, and the solvent is removed at reduced pressure. Subsequently the crude product is dissolved in a minimal amount of DCM and precipitated in methanol. The product is obtained as a dark solid (181.2 mg, yield: 63%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 7.71–7.78 (d, 4H), 6.88–7.06 (d, 2H), 6.90 (s, 4H), 6.71–6.78 (d, 2H), 6.63–6.69 (d, 2H), 3.55–3.65 (d, 2H), 3.03–3.09 (d, 2H), 1.70–1.86 (br, 2H), 1.22–1.49 (m, 16H), 1.06–1.40 (m, 10H), 0.88–0.99 (m, 12H). Molecular weight (GPC, THF): M_w = 5.7 kDa, PD = 1.5. UV/vis (DCM): 709 nm, UV/vis (thin film): 724 nm; ϵ (709)/L mol $^{-1}$ cm $^{-1}$: 16 721.

Polymer P2b. In a Schlenk flask, **M2** (137.6 mg, 0.28 mmol), *N,N*-bis(2-octyldodecyl)benzene-1,4-diamine dihydrochloride salt (**M4b**) (205 mg, 0.28 mmol), $\text{Pd}_2(\text{dba})_3$ (7.6 mg, 0.008

mmol) and X-Phos (25 mg, 0.053 mmol) are dissolved in a mixture of DMF-toluene (2 : 1) (3.2 ml) under nitrogen. Then, cesium carbonate (198 mg, 0.60 mmol) is added and the mixture is allowed to stir for 48 hours under nitrogen at 90 °C. After completion of the reaction, the dark solution is treated with DCM, washed three times with water and once with brine. Then the organic layer is dried over anhydrous magnesium sulfate and the solvent is removed at reduced pressure. Subsequently, the crude product is dissolved in a minimal amount of DCM and precipitated in methanol. The product is obtained as a dark blue solid (156.5 mg, yield: 54%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 7.70–7.76 (d, 4), 7.28 (s, 2H), 6.96–7.02 (d, 4H), 6.61–6.66 (d, 2H), 6.51–6.59 (d, 2H), 3.58 (s, 2H), 3.03 (s, 2H), 2.04 (s, 2H), 1.12–1.43 (br, 64H), 0.88–0.93 (br, 12H). Molecular weight (GPC, THF): M_w = 9.7 kDa, PD = 1.7. UV/vis (DCM): 725 nm, UV/vis (thin film): 741 nm; ϵ (725)/L mol $^{-1}$ cm $^{-1}$: 23 911.

Polymer P3. In a Schlenk flask, **M3** (100.0 mg, 0.095 mmol), **M4b** (38.4 mg, 0.095 mmol), $\text{Pd}_2(\text{dba})_3$ (2.6 mg, 0.029 mmol) and X-Phos (8.2 mg, 0.017 mmol) are dissolved in dry toluene (3 ml) under nitrogen. Then, *t*-BuOK (45 mg, 0.44 mmol) is added and the mixture is allowed to stir for 24 hours under nitrogen at 90 °C. After completion of the reaction, the dark blue solution is treated with DCM, washed three times with water and once with brine. Then the organic layer is dried over anhydrous magnesium sulfate and the solvent is removed at reduced pressure. After that, the crude product is dissolved in a minimal amount of DCM and precipitated in methanol. The product is obtained as a dark blue solid (65.7 mg, yield: 57%). 7.59–7.75 (br, 4H), 7.17 (s, 2H), 6.70–6.77 (d, 4H), 6.71–6.78 (d, 2H), 6.60–6.68 (d, 2H), 3.46–3.03 (br, 6H), 3.01–3.10 (br, 2H), 1.83 (s, 4H), 1.11–1.47 (br, 80H), 0.79–1.01 (br, 24H). Molecular weight (GPC, THF): M_w = 10.1 kDa, PD = 1.5. UV/vis (DCM): 623 nm, UV/vis (thin film): 638 nm; ϵ (623)/L mol $^{-1}$ cm $^{-1}$: 26 762.

Methods

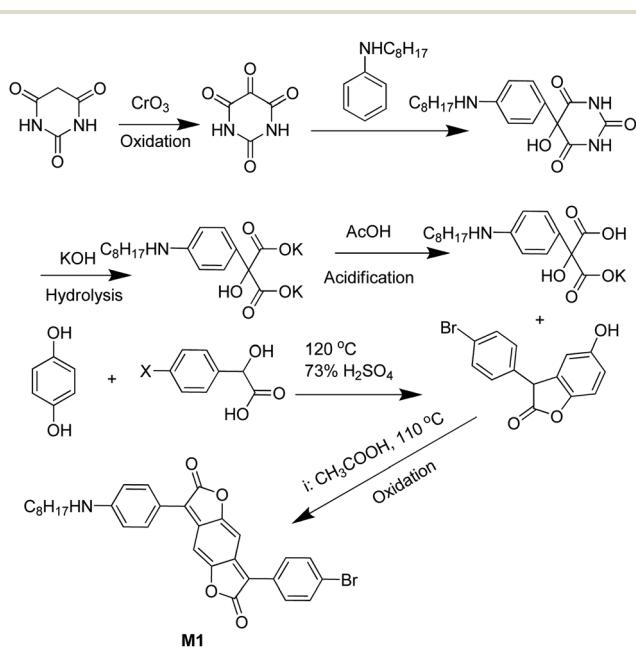
Instrumentation. UV/vis absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. Photoluminescence spectra were recorded using a Perkin-Elmer LS50B spectrometer. The photostability was recorded using a 200 W Hg lamp (Oriel Instruments 6283) at a distance of 20 cm at room temperature. ^1H NMR spectra were recorded using a Bruker DPX 300 spectrometer, which operates at 300 MHz. Molecular weights were determined by size exclusion chromatography (SEC) using a Water/Millipore UV detector 481 and a mixed gel column (Latek/Styragel 50/1000 nm pore size). All measurements were carried out in tetrahydrofuran at 45 °C. The column was calibrated using commercially available polystyrene standards. Cyclic voltammograms were recorded using a potentiostat PG 390 from Heka Company. The thin films of the polymers were cast on an ITO electrode and cycled in acetonitrile (saturated with nitrogen) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the electrolyte salt. Platinum was used as reference and counter electrodes. The voltage data were calculated for the ferrocene/ferrocenium redox couple. The scan rate was 100 mV s $^{-1}$ and the temperature was 20 °C.



Results and discussion

In this article, we report on the novel monomer **M1** and four aminobenzodione-based π -conjugated polymers. **M1** was prepared according to Scheme 1 which is very soluble in common organic solvents and suitable for Buchwald–Hartwig amination and Stille, Heck and Suzuki coupling because of the bromine and alkylamino end groups.

The polymers consist of amino groups as electron-donating units, and BDF or BDP as electron-accepting units causing low bandgaps, broad UV-vis absorption and high photostability. BDF/BDP-based monomers **M2** and **M3**, and the *N,N'*-dialkylaminobenzene monomer **M4** were prepared according to the literature.^{4a,5a,9} The polymers were synthesized by Buchwald–Hartwig amination using $\text{Pd}_2(\text{dba})_3$ as the catalyst and X-Phos as the ligand (Scheme 2).¹⁰



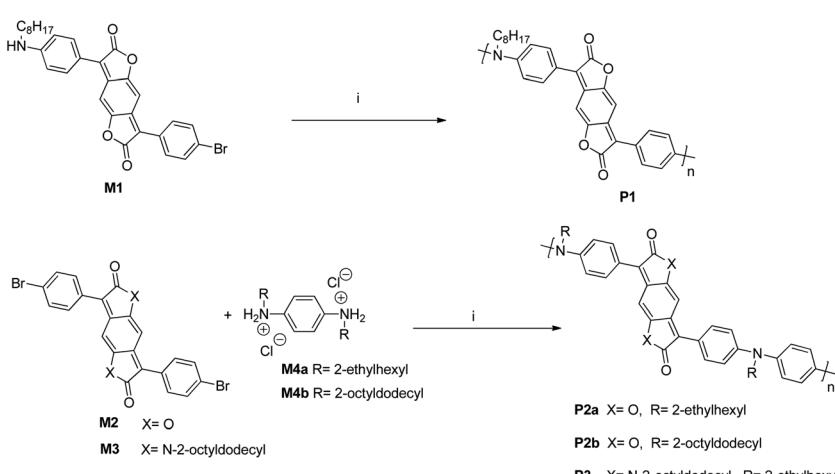
Scheme 1 Synthesis and structure of **M1**.

The polymers were characterized by ^1H NMR spectroscopy (Fig. 1) and gel permeation chromatography (GPC). The signals around 0.8–3.3 ppm originate from the alkyl groups, while the signals around 6.72–7.96 are typical for the protons of the core of BDF and the phenyl groups attached to the core. For **M1**, the chemical shifts at 4.37 ppm originate from the protons attached to the amino group while these signals disappear for the polymers due to polymerization. The number-average molecular weights were found to be 5.9 kDa (PDI: 2.2, **P1**), 5.7 kDa (PDI: 1.5, **P2a**), 9.7 kDa (PDI: 1.7, **P2b**) and 10.1 kDa (PDI: 1.5, **P3**), respectively.

Optical properties

In Fig. 2, the UV-vis spectrum of **M1** in dichloromethane solution is shown. **M1** exhibits a broad UV-vis absorption band with a maximum at 628 nm, the extinction coefficient of the maximum being $6.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The maximum of **M1** is 121 nm red-shifted compared with **M2** in dichloromethane since the alkylamino unit is a powerful donor, which shifts the UV-vis absorption to a longer wavelength. **M1** is readily soluble in common organic solvents such as toluene, *N,N*-dimethylformamide and so on, in contrast to **M2**, which is not very soluble in toluene or dichloromethane, and therefore not suitable for Suzuki coupling. This is firstly due to the presence of the amino group, which can form a highly polar resonance structure and interact with adjacent solvent molecules (see a suggested mechanism in S4†), and secondly the alkyl substituent of the amino group favors the solubility.

In Fig. 3, the UV-vis absorption spectra of the polymers in dichloromethane solution and as thin films are shown. All polymers are deep colored, the extinction coefficients of the strongest bands being $1.7\text{--}3.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The UV-vis absorption spectra of **P2a** and **P2b** in dichloromethane exhibit broad bands with maxima at 709 and 724 nm. The maximum of **P2b** is slightly red-shifted compared with **P2a**, since **P2b** has a higher molecular weight and a more strongly extended π -system. The UV-vis absorption spectrum of **P3** in dichloromethane exhibits a strong maximum at 623 nm. Compared with **P2a** and **P2b**, the maximum of **P1** is blue-



Scheme 2 Synthesis and structure of polymers **P1**–**3**. (i) $\text{Pd}_2(\text{dba})_3$, X-Phos, Cs_2CO_3 (*t*-BuOK for **P3**), DMF–toluene (2/1) (dioxane for **P1** and **P3**), N_2 .



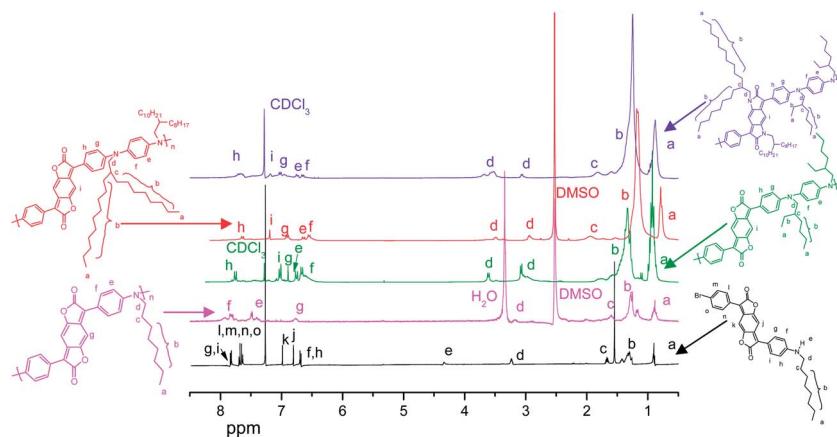
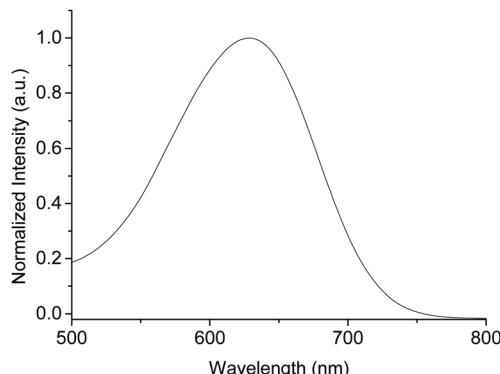
Fig. 1 ^1H NMR spectra of M1 and P1–P3.

Fig. 2 UV/vis absorption spectra of M1 in dichloromethane.

shifted (645 nm), giving rise to weaker D–A interactions between the alkylamino groups and the benzodifuranone core. In **P2a** and **P2b** enhanced intramolecular charge transfer (ICT) is due to the presence of the *N,N'*-dialkyl-1,4-phenylenediamine unit with a more powerful donor ability favoring the red shifted absorption. The red shift is stronger than those of the polymers containing the thiienyl-benzodione chromophore (88 nm for **P1**, 152 nm for **P2a**, 167 nm for **P2b** and 58 nm for **P3** in dichloromethane, respectively) since the alkylamino group is a more powerful electron donor than the thiienyl group.^{4a,5a} All polymers show a very broad

UV/vis absorption from 400 to 900 nm, which matches the solar photon most intense flux (that is in the 400–800 nm range)¹¹ in thin films with maxima between 638 and 725 nm (Fig. 2 and Table 1). All UV/vis absorption spectra of films are red shifted when compared to dichloromethane solution spectra. The strongest red-shift was found for **P1** with 63 nm. This indicates a gain of planar conformation and/or the presence of π – π interchain association in the solid state. The optical HOMO–LUMO energy gaps estimated from the onset of absorption for films are 1.19–1.47 eV.

Table 1 Optical, band gap and photostability data of the polymers

Polymers	λ_{max} [nm]		Extinct. coeff. ε (λ_{max}) [$\text{L mol}^{-1} \text{cm}^{-1}$]	$E_g^{\text{opt}}/E_g^{\text{cc}}$ [eV]	k^a [h^{-1}]
	In DCM	As thin films			
P1	645	708	30 600	1.19/1.19	0.11
P2a	709	724	16 721	1.31/1.23	0.26
P2b	725	741	23 911	1.20/1.08	0.33
P3	623	638	26 762	1.47/1.45	0.68

^a Photostability was determined upon irradiation with a 200 W Hg lamp. ^b Optical bandgap E_g^{opt} was measured at the onset of absorption of the polymer film ($E_g^{\text{opt}} = 1240/\lambda_{\text{abs, onset}}$ eV). ^c $E_g^{\text{cc}} = E_{\text{HOMO}} - E_{\text{LUMO}}$, $-E_{\text{LUMO}} = E_{\text{onset(red)}} + 4.8$ eV and $-E_{\text{HOMO}} = E_{\text{onset(ox)}} + 4.8$ eV, where $E_{\text{onset(red)}}$ and $E_{\text{onset(ox)}}$ are the onset potentials of the oxidation and reduction processes vs. ferrocene.

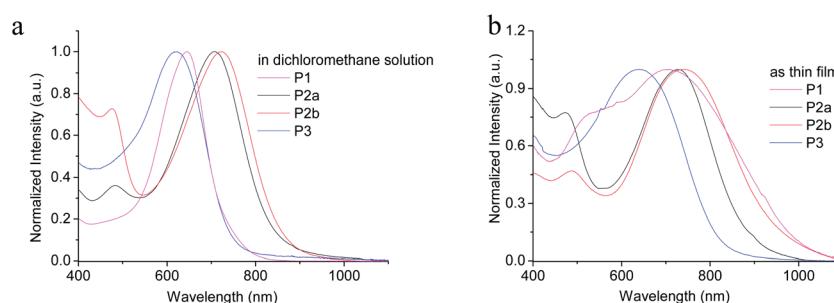


Fig. 3 UV/vis absorption spectra of polymers P1–3 in dichloromethane and as thin films.

Electrochemical properties

The electrochemical properties of the four polymers were investigated by cyclic voltammetry. The conditions of the measurement are described in the Experimental part. The HOMO and LUMO energy levels of the polymers were estimated from the onset of the oxidation and reduction curves, respectively (see Fig. 4). It can be seen that anodic oxidation of polymers sets in at low potentials of 0.32 V (**P1**), 0.17 V (**P2a**), 0.15 V (**P2b**) and 0.89 V (**P3**), respectively. Two to three anodic waves with maxima between 0.5 and 1.2 V occur, which can be ascribed to the formation of cation radicals and dications. The reductive cycles of all polymers exhibit two reversible cathodic waves, which originate from the reduction of the quinonoid to a benzoic structure. This can possibly be explained with a stabilizing negative charge of the oxygen atoms in the carbonyl groups of both the lactone groups in the benzodione units.

All polymers show low LUMO (-3.79 to -4.24 eV) and HOMO levels (-4.95 to -5.81 eV). Due to the low LUMO energy level of the polymers, good electron injection and ambient stabilities of OFET devices can be expected.^{5b} The polymers exhibit quite low HOMO–LUMO bandgaps (1.08 to 1.45 eV). In Table 1, optical and bandgap data of the polymers are compiled.

Photostability properties

The photostability was studied by exposing toluene solutions of the polymers to a 200 W Hg-lamp at a distance of 20 cm and measuring the decrease of the optical absorption *vs.* time. In Fig. 5a, UV/vis absorption spectra of **P2b** in toluene are shown before and after irradiation for different time

periods. Corresponding spectra of **M2**, **M3**, **P1**, **P2a** and **P3** are shown in Fig. S2 and S3.[†] The plots of $\ln(A_t/A_0)$ ($A_{t,0}$ = absorbance at time t and time $t = 0$) *vs.* time for irradiation of polymers lead to nearly straight lines. From the initial slope the rate constants (k) of the photoreaction were derived (Fig. 5 and Table 1). As can be seen from Fig. 5, **P2a** and **P2b** are more stable than **P1** since the *N,N'*-dialkyl-1,4-phenylenediamine unit exhibits a more powerful donor ability than the alkylamino unit. Probably the strong donor–acceptor character of these polymers prevents energy transfer from the amino groups to the BDF core and thus contributes to a higher photostability. Compared with **P2a**, **P3** is less stable, which can be ascribed to the fact that the monomer BDP chromophore is less stable than BDF in UV-light (see S2[†]). In general, polyiminobenzodiones are less stable than isoDPP-based conjugated polymers¹² or 1,10-naphthodifuranone-based polymers,^{4d,13} but more stable than benzodifuranone-based polymers^{4d} or DPP¹⁴ and DTPP-based polymers.¹⁵

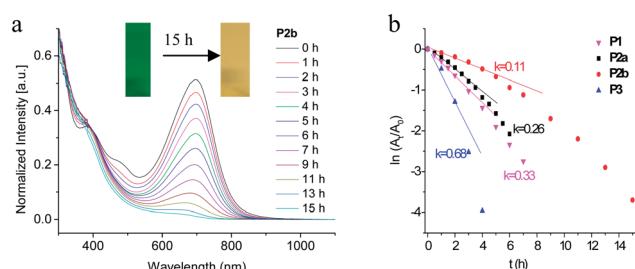


Fig. 5 UV/vis absorption spectra of **P2b** before and after irradiation in toluene with a 200 W Hg-lamp and $\ln(A_t/A_0)$ *vs.* time for determination of rate constants (k) for polymers.

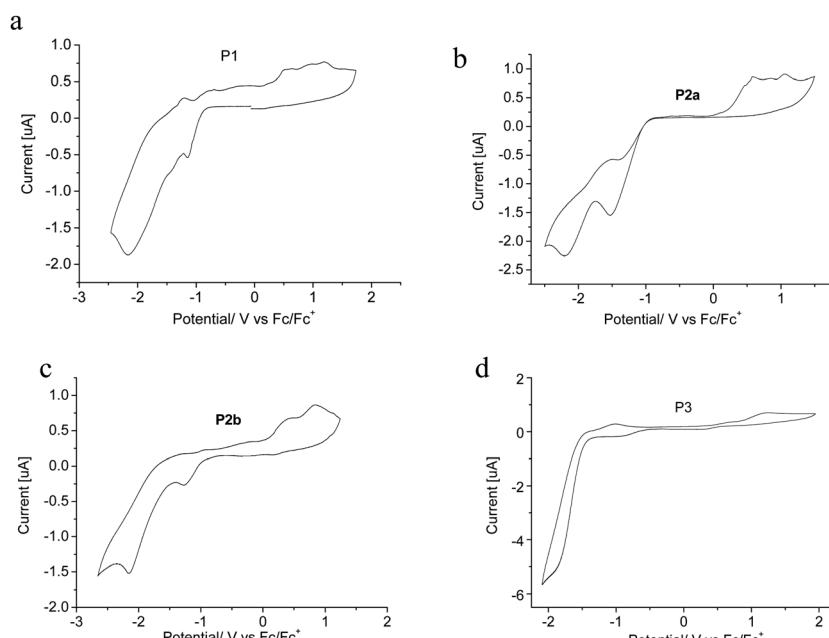


Fig. 4 Cyclic voltammograms of polymers as thin films deposited on the ITO surface. Solution: 0.1 M TBAPF₆/acetonitrile. Potential calculated versus ferrocene. Scan rate: 100 mV s⁻¹, $T = 20$ °C.



Table 2 Solvent-independent correlation coefficients a , b , d and e of the Catalán parameters SA, SB, SP and SdP, solute property of the reference system $\tilde{\nu}_{\max,0}$ cyclohexane, number of solvents (n), correlation coefficient (r), standard deviation (sd), and significance (f) of the calculated solvatochromism of the model compounds **M1**, **P1** and **P2a**

Compound	Catalán equation					Correlation data			
	$\tilde{\nu}_{\max,0}$	a	b	d	e	n	r	sd	f
M1	18.537	-0.582	-1.158	-2.726	-0.570	32	0.95	0.156	<0.0001
P1	20.284	-0.534	-1.191	-5.009	-1.246	33	0.93	0.284	<0.0001
P2a	16.629	0.137	-0.428	-2.452	-0.541	33	0.88	0.168	<0.0001

Solvatochromic properties

M1, **P1** and **P2a** were chosen to study the solvatochromic properties. Positive solvatochromic behavior can be attributed to a number of specific and non-specific solute–solvent interactions as summarized in the simplified Kamlet-Taft equation (eqn (1)),¹⁶ where s , a , and b are solvent independent coefficients, and π^* ,^{17a} α^{17b} and β^{17c} reflect the general solvent dipolarity/polarizability, its specific H-bond donating (HBD) ability, and its specific H-bond accepting (HBA) ability, respectively, which may or may not oppose one another in terms of solvatochromic contributions. $\tilde{\nu}_{\max,0}$ is the longest wavelength UV-vis absorption maximum of the compound measured in a particular solvent where $\pi^* = \alpha = \beta = 0$ (e.g. cyclohexane).^{8a}

$$\tilde{\nu}_{\max} = \tilde{\nu}_{\max,0} + a\alpha + b\beta + s\pi^* \quad (1)$$

Until now, empirical polarity scales have always described the polarizability and dipolarity of the solvent together in one parameter. The first and only successful attempt to separate polarizability and dipolarity was suggested by Catalán with the introduction of solvent acidity (SA),¹⁸ solvent basicity (SB),¹⁹ solvent polarizability (SP)²⁰ and solvent dipolarity (SdP)²¹ (eqn (2)).

$$\tilde{\nu}_{\max} = \tilde{\nu}_{\max,0} + a\text{SA} + b\text{SB} + d\text{SP} + e\text{SdP} \quad (2)$$

The three compounds show the shortest wavelength UV-vis absorption band in *n*-hexane, and exhibit the strongest bathochromic shift in DMSO (for **M1**, **P1** and **P2a**, Δ values ($\lambda_{\max,\text{pol}} - \lambda_{\max,\text{nonpol}}$) of 1700 cm^{-1} , 2400 cm^{-1} , and 1180 cm^{-1} , respectively). Both equations show good accuracy for **M1** with $r > 0.9$ (eqn (2) in Table 2 and eqn (1) in Table S2†). It is shown that especially the HBA ability of the solvents (β or SB) causes a strong bathochromic shift ($b < 0$). This can be easily explained by H-bonding between the NH-group in the main chain and HBA-solvents. The influence of the β -term of the solvents on the bathochromic shift of **M1** represents the interactions of HBA capacity solvents with the proton of the N-H group, which increases the +M-effect and therefore strengthening of the aromatic push-pull system occurs. HBD-solvents only exhibit a small effect typical for benzodifuranone-based dyes.^{8b-d} A weak bathochromic shift can be recognized due to the interaction with the carbonyl groups ($a < 0$). Polarizability and dipolarity cause a bathochromic shift (π^* , SP and SdP < 0), respectively. The solvatochromic range of **M1** is 1700 cm^{-1} from *n*-hexane to DMSO.

Hexamethylphosphoramide (HMPA) has not been included in the correlation, since it causes an unexpectedly high bathochromic shift of the UV-vis absorption maximum.

Since, in **P1**, the N-H function is substituted, the effect of HBA-ability (b) should be decreased, but this was not observed. The remaining influence of the HBA-ability of the solvent on the polymeric dye might be ascribed to an N-H end group, for example. Especially for short-chain polymers a visible influence of end groups is conceivable. The influences of H-bonding ($a + b$) are almost unchanged. The most dominant effect on the solvatochromic behavior is caused by interaction with solvents of different dipolarity/polarizability which is reflected in the large coefficient s in eqn (1) or coefficients d and e in eqn (2).^{8d} The dipolar structures of dyes with an enlarged π -system usually are stabilized within the molecule rather than by interaction with a solvent molecule. To our surprise, the effect of polarizability and dipolarity of **P1** increases significantly compared with **M1** (the rate SP/SdP remains unchanged). This could firstly be ascribed to the fact that **P1** exhibits poor solubility in some solvents, if the chain length gets larger. In those solvents only very short chains, probably dimers or trimers, are measured by UV-vis spectroscopy. Secondly, the presence of N-H end groups found by the unchanged high influence of SB, speaks for such short chains. The solvatochromic shift of **P1** from *n*-hexane to HMPA is 3140 cm^{-1} , and from *n*-hexane to DMSO is 2400 cm^{-1} , which are much larger than that of **M1**.

For **P2a**, the influence of HBA-solvents is smaller, since the N-H-functionality is not present anymore. The residual effect may point to an N-H-end group again. The influence of polarizability and dipolarity remains unchanged compared with **M1**. The solvatochromic shift is decreased compared with those of **M1** and **P1a**. From *n*-hexane to HMPA it is 1200 cm^{-1} , and from *n*-hexane to DMSO it is 1180 cm^{-1} .

Conclusions

In this article, the deep blue monomer **M1** and four π -conjugated polymers based on aminobenzodione are described. **M1** is very soluble in common organic solvents and suitable for Buchwald amination and Stille and Suzuki coupling because of the bromine and alkylamino substituent groups. The polymers exhibit quite low bandgaps (1.08–1.47 eV), high photostability and a large solvatochromic shift up to 3140 cm^{-1} . Furthermore, the polymers show broad UV-vis absorption bands in a range from 400 to 900 nm with high extinction coefficients of 1.7 to



3.1×10^4 L mol $^{-1}$ cm $^{-1}$. This matches well with the solar photon most intense flux. The broad absorption in the visible region of the spectra, combined with high color depth, high photostability and a low bandgap render aminobenzodione-based polymers interesting as building blocks for optoelectronic materials.

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References

- (a) T. Limori, T. Naito and N. Ohta, *J. Phys. Chem. C*, 2009, **113**, 4654–4661; (b) H. Kim, W. A. Goddard, S. S. Jang, W. R. Dichtel, J. R. Heath and J. F. Stoddart, *J. Phys. Chem. A*, 2009, **113**, 2136–2143.
- (a) S. R. Marder, B. Kippelen, A. K.-Y. Jen and N. Peyghambarian, *Nature*, 1997, **388**, 845–851; (b) C.-G. Liu, W. Guan, P. Song, L.-K. Yan and Z.-M. Su, *Inorg. Chem.*, 2009, **48**, 6548–6554.
- (a) *Photoinduced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1998; (b) H. Kurreck and M. Huber, *Angew. Chem.*, 1995, **107**, 927–947.
- (a) K. Zhang and B. Tieke, *Macromolecules*, 2011, **44**, 4596–4599; (b) P. A. Ulmann, H. Tanaka, Y. Matsuo, Z. Xiao, I. Soga and E. Nakamura, *Phys. Chem. Chem. Phys.*, 2011, **13**, 21045–21049; (c) K. Zhang, B. Tieke, J. C. Forgie, F. Vilela and P. J. Skabara, *Macromolecules*, 2012, **45**, 743–750; (d) H. Zhang and B. Tieke, *Polym. Chem.*, 2014, **5**, 646–652.
- (a) W. Cui, J. Yuen and F. Wudl, *Macromolecules*, 2011, **44**, 7869–7873; (b) P. Deng, L. Liu, S. Ren, H. Li and Q. Zhang, *Chem. Commun.*, 2012, **48**, 6960–6962; (c) W. Hong, C. Guo, Y. Li, Y. Zheng, C. Huang, S. Lu and A. Facchetti, *J. Mater. Chem.*, 2012, **22**, 22282–22289.
- (a) O. Annen, R. Egli, R. Hasler, B. Henzi, H. Jakob and P. Matzinger, *Rev. Prog. Color. Relat. Top.*, 1987, **17**, 72–85; (b) C. W. Greenhalgh, J. L. Carey and D. F. Newton, *Dyes Pigm.*, 1980, **1**, 103–120.
- (a) C. W. Greenhalgh, J. L. Carey and D. F. Newton, *J. Soc. Dyers Colour.*, 1994, **110**, 178–184; (b) S. J. Bentley and D. J. Milner, *Synth. Commun.*, 1996, **26**, 95–100; (c) Z. Cai, J. Gao, X. Li and B. Xiang, *Opt. Commun.*, 2007, **272**, 503–508; (d) G. Hallas and C. Yoon, *Dyes Pigm.*, 2001, **48**, 107–119.
- (a) A. A. Gorman, M. G. Huthings and P. D. Wood, *J. Am. Chem. Soc.*, 1996, **118**, 8497–8498; (b) S. Spange, S. Prause, E. Vilsmeier and W. R. Thiel, *J. Phys. Chem. B*, 2005, **109**, 7280–7289; (c) A. Oehlke, K. Hofmann and S. Spange, *New J. Chem.*, 2006, **30**, 533–536; (d) K. Hofmann, S. Brumm, C. Mende, K. Nagel, A. Seifert, I. Roth, D. Schaarschmidt, H. Lang and S. Spange, *New J. Chem.*, 2012, **36**, 1655.
- D. J. Zillman, G. C. Hincapie, M. R. Savari, F. G. Mizori and T. E. Cole, *Tetrahedron Lett.*, 2010, **51**, 3033–3036.
- D. S. Surry and S. L. Buchwald, *Chem. Sci.*, 2011, **2**, 27–50.
- P. K. Nayak, G. G. Belmonte, A. Kahn, J. Bisquert and D. Cahen, *Energy Environ. Sci.*, 2012, **5**, 6022–6039.
- H. Zhang, I. Welterlich, J.-M. Neudoerfl, B. Tieke, C. Yang, X. Chen and W. Yang, *Polym. Chem.*, 2013, **4**, 4682–4689.
- H. Zhang, J.-M. Neudoerfl and B. Tieke, *Macromolecules*, 2013, **46**, 5842–5849.
- T. Beyerlein and B. Tieke, *Macromol. Rapid Commun.*, 2000, **21**, 182–189.
- I. Welterlich and B. Tieke, *Polym. Chem.*, 2013, **4**, 3755–3764.
- (a) C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319–2385; (b) P. Mueller, *Pure Appl. Chem.*, 1993, **22**, 409–416.
- (a) M. J. Kamlet, T. N. Hall, J. N. Hall, J. Boykin and R. Taft, *J. Org. Chem.*, 1979, **44**, 2599–2604; (b) R. W. Taft and M. J. Kamlet, *J. Am. Chem. Soc.*, 1976, **98**, 2866–2894; (c) M. J. Kamlet and R. W. Taft, *J. Am. Chem. Soc.*, 1976, **98**, 377–383.
- (a) J. Catalán and C. Díaz, *Liebigs Ann.*, 1997, 1941–1949; (b) J. Catalán and C. Díaz, *Eur. J. Org. Chem.*, 1999, 885–891; (c) J. Catalán, V. López and P. Pérez, *Liebigs Ann.*, 1995, 793–795.
- (a) J. Catalán, C. Díaz, V. López, P. Pérez, J.-L. G. d. Paz and J. G. Rodríguez, *Liebigs Ann.*, 1996, 1785–1794; (b) J. Catalán, J. Palomar, C. Díaz and J.-L. G. d. Paz, *J. Phys. Chem. A*, 1997, **101**, 5183–5189.
- J. Catalán and H. Hopf, *Eur. J. Org. Chem.*, 2004, 4694–4702.
- J. Catalán, *J. Phys. Chem. B*, 2009, **113**, 5951–5960.

