

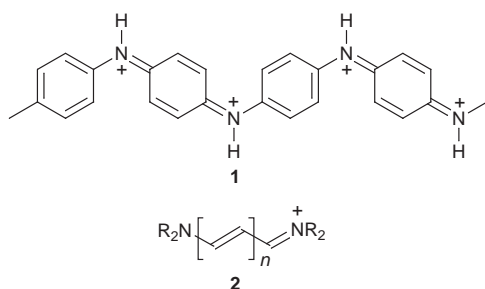
Polymeric malondialdehyde dianils—a novel type of electrically conducting polymers

Rudolf Gompper,* Thomas J. J. Müller* and Kurt Polborn

Institut für Organische Chemie der Universität München, Karlstr. 23, D-80333 München, Germany

The reaction of vinamidinium salts with *para*-substituted aromatic diamines gives rise to polymeric 2-aryl malonaldehyde dianils in good yields. Polymeric cyanines can be obtained from tetramethoxypropane and a pentamethine cyanine, respectively, and *para*-substituted aromatic diamines. The degree of polymerisation P_n ($n = 10\text{--}40$) was estimated by measuring the intrinsic viscosity η . The polymers show high electrical powder conductivities ($\sigma = 0.03\text{--}50 \text{ S cm}^{-1}$) after doping with iodine or FeCl_3 .

The electrical conductivity of polymers¹ such as polyacetylene,² polyaniline³ **1**, poly-*p*-phenylene⁴ and polythiophene⁵ is based on a conjugated π -electron system.⁶ In their native or undoped state, however, these polymers exhibit only a low electrical conductivity which is due to a rather large energy band gap caused by Peierls distortion.⁷ Only by doping—oxidatively or reductively—can they be converted into ‘organic metals’.⁸

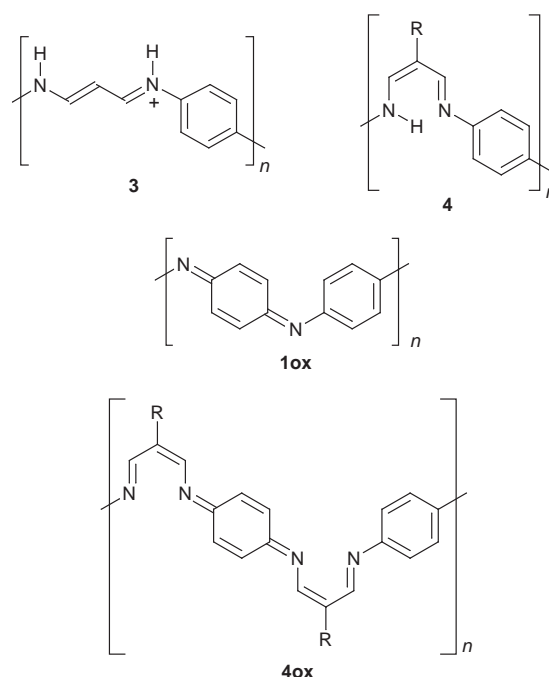


Cyanine dyes **2** have relatively small HOMO–LUMO gaps,⁹ double-bond delocalization⁹ and they are easily polarizable.^{9,10} Thus, since cyanine dyes fulfill essential requirements for ‘synthetic metals’¹⁰ we set out to synthesize arylene-bridged polymeric vinamidinium salts **3** and vinamidines **4**.¹¹ These compounds combine the structural features of polyaniline **1**, polyarylenes, polyarylenevinyls and cyanine dyes **2**. The fully oxidized form **4ox** of **4** is an azabutadienediyl homologue of deprotonated **1**. In particular, polyvinamidines **4** with functional groups *R* in position 2 could be of interest as model compounds for molecular electronic devices.¹²

Results and Discussion

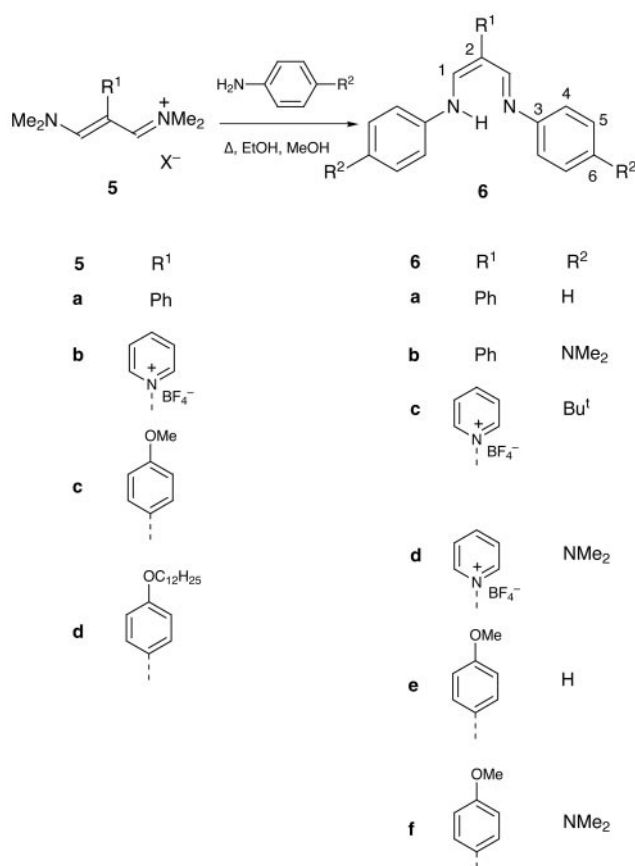
Synthesis and structural aspects of 2-arylmalonaldehyde dianils

Although malonaldehyde dianil **6**, $R^1, R^2 = \text{H}$,¹³ and its metal complexes¹⁴ have been known for a long time, 2-arylmalonaldehyde dianils have not been investigated that much (cf. NMR properties of highly substituted vinamidines and their nickel chelates¹⁵). We have now synthesized a range of malonaldehyde dianils **6** as models for polymers **4** by reacting 2-arylvinamidinium salts **5**¹⁶ with primary aromatic amines (Scheme 1). The electronic spectra of **6a** and **6e** show longest wavelength absorption maxima at 398 and 408 nm, respectively, which are red-shifted compared with λ_{max} of **6**, $R^1, R^2 = \text{H}$, at 360 nm.¹⁷ This is consistent with PMO theory¹⁸ predicting a red shift of the $\pi\text{--}\pi^*$ transition by donor substituents at an even-numbered position in a cyanine system. An acceptor substituent is



expected to cause the opposite effect. Unexpectedly, the pyridinio group in **6c** does not exert a distinct hypsochromic shift. This can be rationalized on the basis of the *cis*–*trans* isomerism¹⁷ of vinamidines. In less polar solvents and in the solid state the *cis*, *cis* structure (‘horseshoe-form’) is thermodynamically favoured.¹⁷ The contribution of the all-*trans* structure (‘W-form’) increases with increasing polarity of solvents (e.g. DMSO).¹⁷ The equilibrium between horseshoe- and W-forms of **6** is responsible for the broad absorption bands in the electronic spectra. Apparently, the cationic pyridinio group of **6c** stabilizes the all-*trans* structure of the vinamidine system presumably by an enhanced aggregation of DMSO molecules. In addition, in all-*trans* structures of vinamidines, aryl substituents in position 2 are orthogonally arranged and have therefore no mesomeric effect on the $\pi\text{--}\pi^*$ transition of cyanines.¹⁹

In the spectra of **6b** ($\lambda_{\text{max}} = 450 \text{ nm}$ [in DMSO]), **6d** ($\lambda_{\text{max}} = 403 \text{ nm}$) and **6f** ($\lambda_{\text{max}} = 452 \text{ nm}$) the longest wavelength absorption maxima are shifted bathochromically compared with λ_{max} of **6a** due to the extended π -electron system ($R^2 = \text{H}$ vs. $R^2 = \text{NMe}_2$).



Scheme 1

Crystal structure of 6e

Compound **6e** is a model for a segment of the polymers **7**. Therefore, a crystal structure analysis of **6a** would help to understand the properties of **7**.

The unit cell of a crystal of **6e** consists of eight molecules. There are two independent types of molecules (molecules 1 and 2), both exhibiting a horseshoe-shaped trimethine imine system (Fig. 1). These two molecules are different in some aspects. The differences in the dihedral angles as well as in the

NH bond lengths are caused by nonstoichiometric amounts of methanol molecules included in the crystal. These molecules bring about a stronger perturbation of the NH...N bond in molecule 1 than in molecule 2. The bond lengths in the trimethine imine systems are affected as well. The terminal phenyl rings are only slightly twisted out of the plane of the trimethine system (Fig. 2) so that a maximum overlap of the *p*-orbitals can be expected in the solid state. The *p*-methoxyphenyl substituent is twisted by 44.16° (molecule 1) and 46.72° (molecule 2) with respect to the cyanine system (Fig. 2). The horseshoe shape is characteristic for solid state structures of vinamidines bearing aryl substituents in position 2 (*cf.* the dianil of acetylacetone²⁰).

Synthesis of polymeric arylene-bridged cyanines and vinamidines

Dark red polymeric vinamidines **7** are readily obtained when vinamidinium salts **5** are refluxed with equimolar amounts of *p*-phenylenediamine (→**7a,d-f**), benzidine (→**7b**) or 4,4'-diaminostilbene (→**7c,g**) in ethanol, diglyme or methanol in the presence of catalytic amounts of acetic acid. A model of the structure of polymers **7a-e** is displayed in Scheme 2.

The comparison of the IR data of **6** and **7** reveals that these compounds have similar structural features (horseshoe-shape of the trimethine imine moieties).

All polymers are air and water stable. Solutions of those polymers that are soluble in chloroform were used to form thin films on glass plates.

The degree of polymerisation and the chain length of **7** can be estimated by determining the average molecular weight by measuring the intrinsic viscosity η (Table 1) of the soluble polymers (**7a-c**) in trichloromethane (polystyrene standard).²²

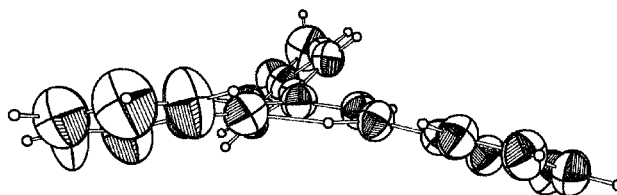


Fig. 2 ORTEP plot of molecule 2 of **6e**, view down the C(2A)–C(10A) bond.

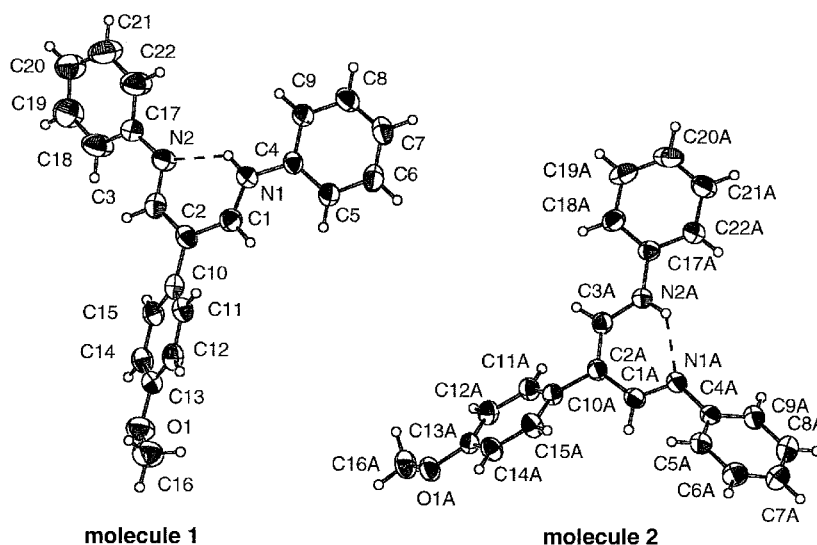
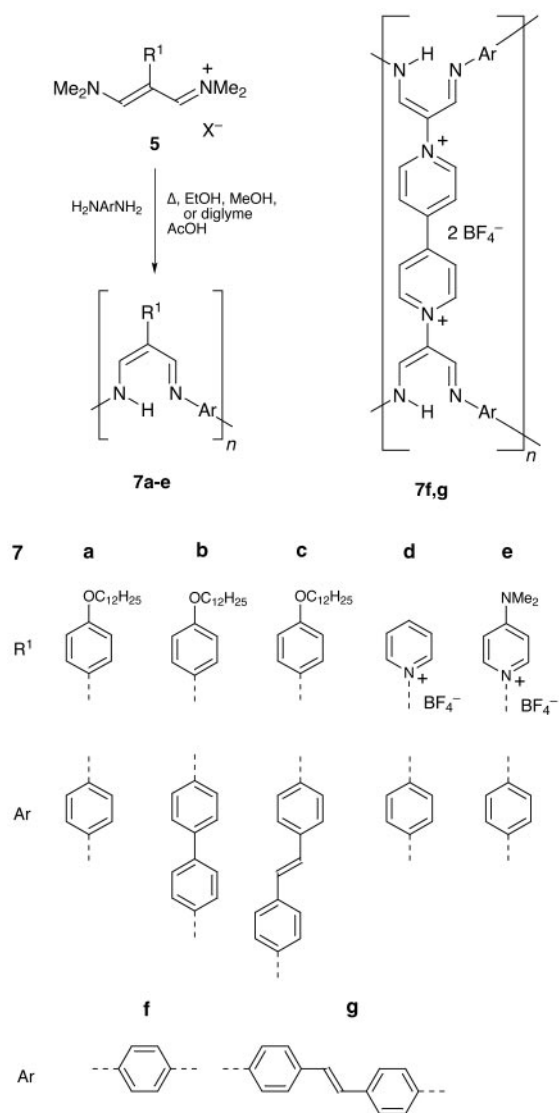
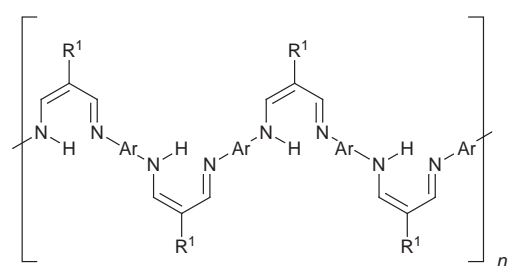


Fig. 1 Structure of **6e** in the crystal (ORTEP plots of two independent molecules).²¹ Selected bond lengths (pm) and bond angles (°): Molecule 1: N1–C1 135.3(4), C1–C2 137.2(5), C2–C3 142.1(5), C3–N2 129.1(4), C2–C10 148.7(5), N1–C4 139.9(4), N2–C17 141.2(5), N1–H 90.4, N2–H 206.6; N1–C1–C2 124.4(3), C1–C2–C3 122.1(3), C2–C3–N2 125.5(3), N1–H–N2 129.64. Molecule 2: N1A–C1A 132.5(5), C1A–C2A 138.1(6), C2A–C3A 142.9(5), C3A–N2A 130.3(5), C2A–C10A 146.7(5), N1A–C4A 139.7(5), N2A–C17A 140.7(4), N1A–H(A) 168.8, N2A–H(A) 109.5; N1A–C1A–C2A 125.9(4), C1A–C2A–C3A 119.5(3), C2A–C3A–N2A 126.0(4), N1A–H(A)–N2A 150.31.



Scheme 2



Model of the structures of polymeric vinamidines **7a-e**

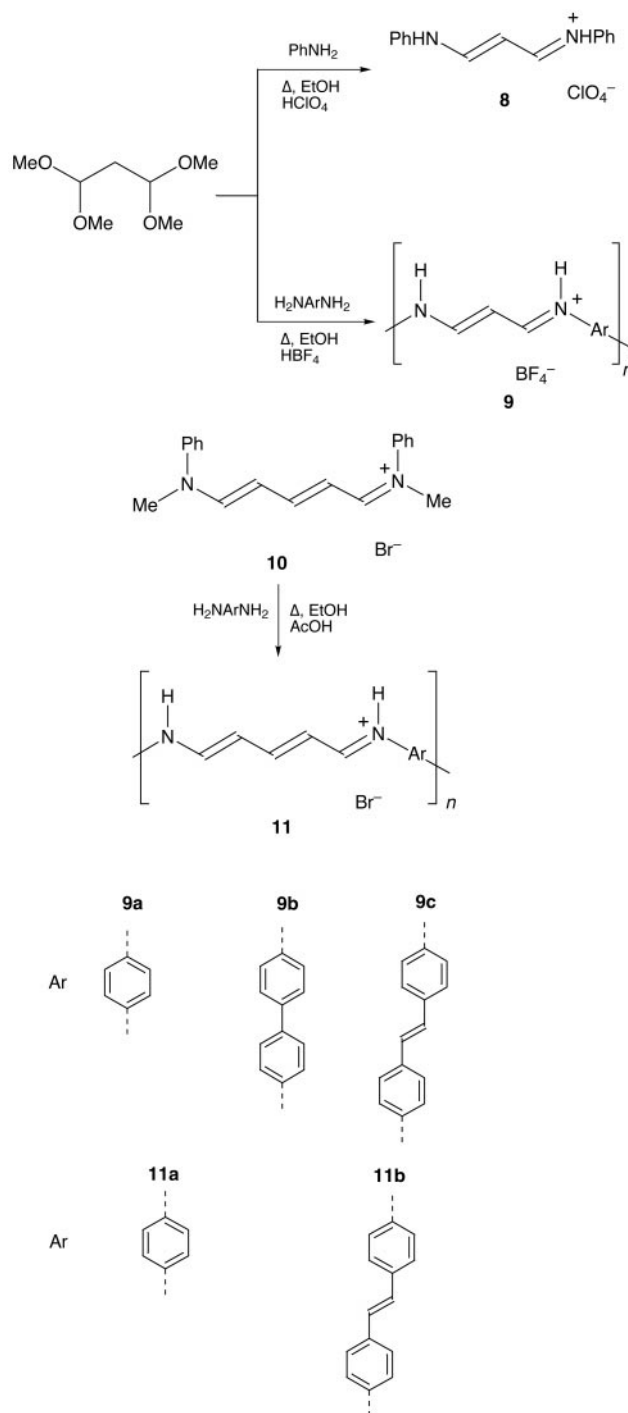
Table 1 ²² Intrinsic viscosities η , molecular weight M_n of the polymer, molecular weight M_m of the repeating unit and degree P_n of polymerisation of **7a-c**

	$\eta/\text{dl g}^{-1}$	$M_n/\text{g mol}^{-1}$	$M_m/\text{g mol}^{-1}$	P_n
7a	0.8	17000	404.6	42
7b	0.4	8000	480.7	17
7c	0.6	15000	506.7	30

The average degree P_n of polymerisation is defined by $P_n = M_n/M_m$, where M_n is the molecular weight as determined by the intrinsic viscosity η and M_m is the molar weight of the repeating unit of the polymer. The high values of η (0.4–0.8

dl g^{-1}) reveal that the polymeric vinamidines **7** have a high degree P_n of polymerisation.

N^1,N^2 -Diarylvinamidinium salts such as **8** can be obtained by reacting tetramethoxypropane with primary and secondary aromatic amines in the presence of perchloric acid (Scheme 3).²³ By performing this reaction with *para*-substituted aromatic diamines in the presence of tetrafluoroboric acid, polymeric arylene-bridged cyanines **9** can be prepared. In the same way, the condensation of the pentamethinium salt **10**²⁴ with *para*-substituted aromatic diamines yields the polymers **11**.



Scheme 3

The degrees of polymerisation P_n of **9** ($n=8, 11$) (Table 2) are lower than those of **7a-c** ($n=42, 17, 30$) (Table 1). Obviously, the condensation leading to **9** is terminated by precipitation of the polycationic polymeric cyanines. The polymers **9** and **11** have similar spectroscopic properties to those

Table 2 ²² Intrinsic viscosities η , molecular weight M_n of the polymer, molecular weight M_m of the repeating unit and degree P_n of polymerisation of **9a,c**

	$\eta/\text{dl g}^{-1}$	$M_n/\text{g mol}^{-1}$	$M_m/\text{g mol}^{-1}$	P_n
9a	0.1	2500	232.0	11
9c	0.1	2500	334.1	8

of **8**. Compared with **8**, a bathochromic shift of the longest wavelength absorption maxima in the electronic spectra of **9** (**9a**: $\lambda_{\text{max}} = 499 \text{ nm}$, **9b**: $\lambda_{\text{max}} = 461 \text{ nm}$, **9c**: $\lambda_{\text{max}} = 492 \text{ nm}$) and **11** (**11a**: $\lambda_{\text{max}} = 595 \text{ nm}$, **11a**: $\lambda_{\text{max}} = 541 \text{ nm}$) is observed indicating rather strong intramolecular electronic interaction between the cyanine systems in the polymer chains.

In order to obtain polymers of the type **4ox**, **7c** was treated with sodium chromate in trifluoroacetic acid²⁵ or with tetrafluoroboric acid in ether in the presence of air (Scheme 4). The products **12a** and **12b** were identical according to their IR (KBr) and UV–VIS (DMSO) spectra (**12a**: $\lambda_{\text{max}} = 470 \text{ nm}$, $\tilde{\nu}_{\text{C=N}} = 1614 \text{ cm}^{-1}$; **12b**: $\lambda_{\text{max}} (\log \epsilon) = 470 \text{ nm} (4.509)$, $\tilde{\nu}_{\text{C=N}} = 1614 \text{ cm}^{-1}$).

The ESR spectrum of **12a** reveals that there is a significant contribution of unpaired spins (Fig. 3). The ESR spectrum (Fig. 4) of a sample of **7c** doped with iodine²⁶ is very similar to that of **12a** showing that unpaired spins are generated upon doping. Apparently, the electronic structures of **12a** and **7c(ox)** are closely related.

Electrical conductivities²²

The electrical powder conductivities^{22,26} (Table 3) of pellets of native and doped²⁶ (with iodine or ferric chloride) **7**, **9**, **11** and **12**, measured at room temperature and ambient pressure, are remarkably high even in the native state. While the conductivities of undoped **7** are close to those of semiconductors, those of the polymeric salts **7f**, **7g**, **9**, **11** and **12** are distinctly higher. The conductivities of the undoped bipyridinediio-bridged polymeric vinamidines **7f** and **7g** are similar to the conductivity of the polymeric viologen derivative **13** ($10^{-3} \text{ S cm}^{-1}$).²⁷

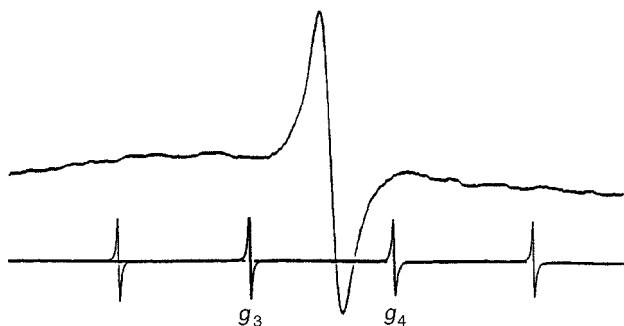


Fig. 3 ESR spectrum of **12a**: $g = 2.0048$ (sweep: 400 G, standard signal [MnO]): $g_3 = 2.0336$ and $g_4 = 1.9809$)

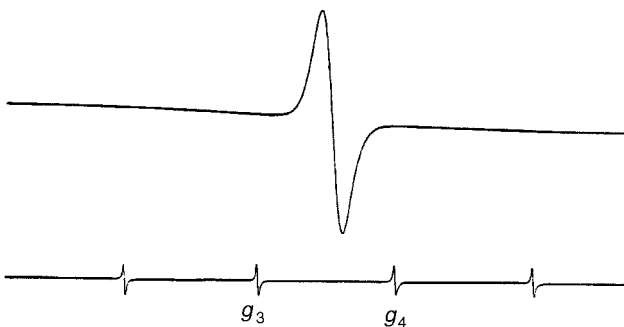
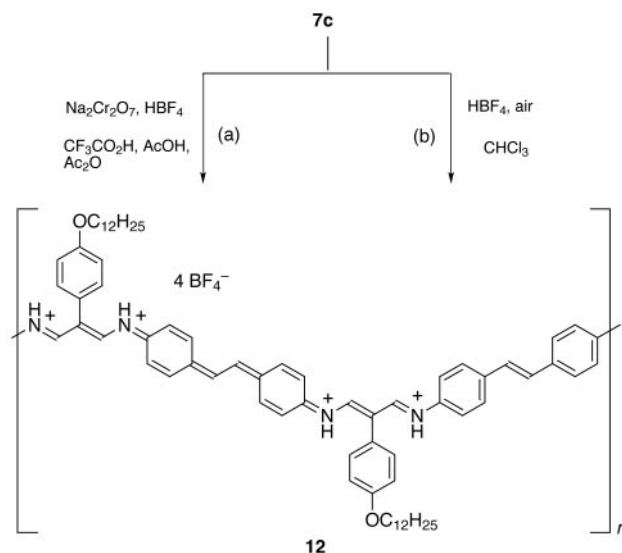


Fig. 4 ESR spectrum of **7c** doped with iodine: $g = 2.0048$ (sweep: 400 G; standard signal [MnO]: $g_3 = 2.0336$ and $g_4 = 1.9808$)

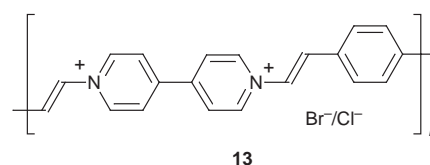


Scheme 4

Table 3 Powder conductivities σ of undoped and doped polymeric vinamidines **7** and cyanines **9**, **11** and **12**

	$\sigma/\text{S cm}^{-1}$			$\sigma/\text{S cm}^{-1}$	
	undoped	doped		undoped	doped
7a	10^{-5}	0.8	9a	3×10^{-2}	—
7b	10^{-4}	17	9b	2.5×10^{-2}	10
7c	10^{-4}	30	9c	0.1	—
7d	5×10^{-3}	0.35	11a	0.15	35
7e	4×10^{-3}	0.2	11b	4.5×10^{-2}	20
7f	2.5×10^{-3}	0.4	12a	6×10^{-2}	35
7g	4.8×10^{-2}	50	12b	2×10^{-2}	30

Apparently, in **7f,g** a charge transfer from the vinamidine moieties to the bipyridinediio moieties takes place which amounts to a self-p-doping of the polymer.



The resonance stabilization of positive charges in the polymeric cyanines **9**, **11** and **12** seems to suppress the Peierls distortion⁷ locally. According to Dähne²⁸ the electrical conductivity of cyanines is caused by the aggregation of cations and anions in one- and two-dimensional rods. The electrical conductivities of polymers **7**, **9**, **11** and **12** increase upon doping by two to six orders of magnitude ($0.03\text{--}50 \text{ S cm}^{-1}$). The observed values are in the same order of magnitude as those of polyaniline (5 S cm^{-1}).³

Conclusion

Polymeric cyanines and vinamidines are a novel type of electrically conducting polymers, are readily accessible and feature high electrical conductivities after doping. They combine the electronic properties of cyanines and vinamidines with those of polyarylenevinylenes and polyaniline.

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie. T. J. J. M. thanks the Freistaat Bayern for a Promotionsstipendium. We thank the BASF AG for the

donation of chemicals and particularly Dr H. Naarmann (BASF AG, Ludwigshafen) for measuring inherent viscosities and electrical conductivities.

Experimental

The ^1H NMR spectra were recorded on Bruker WP 80 (80 MHz), Varian VXR 400 S (400 MHz) and JEOL EX-400 (400 MHz) spectrometers. The ^{13}C NMR spectra were recorded on Varian VXR 400 S (100 MHz) and JEOL EX-400 (100 MHz) spectrometers. All NMR spectra were recorded with tetramethylsilane (TMS) as internal standard. Intrinsic viscosities were determined in chloroform (with polystyrene as internal standard) with the Mark–Houwink–Sakurada parameters $k = 0.21 \times 10^5 \text{ dl g}^{-1}$ and $a = 0.94$. The ESR spectra were recorded on a Varian E-Line (9.28 GHz) spectrometer with MnO as internal standard. The IR spectra were recorded on Perkin-Elmer 125 and Bruker IFS 145 spectrometers and the UV–VIS spectra on Zeiss DMR 10 and Perkin-Elmer Lambda 3 spectrometers. The pellets for measuring the electrical conductivities were prepared at 300 bar pressure.²¹ The crystal structure analysis was performed on a ENRAF-NONIUS CAD4 single crystal diffractometer. The melting points are not corrected. Solvents were dried by standard methods, products *in vacuo* (10^{-2} torr) at 60–80 °C. Ether refers to diethyl ether.

All chemicals were commercially available or prepared by literature procedures. Carcinogenic chemicals such as benzidine should be handled with special care and only in a fume hood.

p-(Dodecyloxy)phenylacetic acid

p-Hydroxyphenylacetic acid (9.13 g, 60.0 mmol), dodecyl bromide (16.45 g, 66.0 mmol) and potassium hydroxide (6.73 g, 120 mmol) in ethanol (50 ml) were refluxed for 20 h. After cooling, potassium hydroxide (3.37 g, 60.0 mmol) was added, the mixture refluxed for 2 h and after cooling acidified with 2 M HCl. After adding water (100 ml), the precipitate was suction filtered and extracted with diethyl ether. The ether phase was dried with anhydrous magnesium sulfate. The solvent was removed *in vacuo* at 25 °C. Yield, 15.82 g (82%); colourless flakes; mp 78–79 °C. ^1H NMR (80 MHz, CDCl_3): $\delta = 0.86\text{--}1.80$ (m, br, 23 H, alkyl-H), 3.48 (s, 2 H, aryl- $\text{CH}_2\text{-CO}_2\text{H}$), 3.85 (t, 2 H, aryl- $\text{OCH}_2\text{-alkyl}$), 6.47–7.07 (AA'BB', J 9.6 Hz, 4 H, phenylene-H), 10.24 (s, br, 1 H, CO_2H). Calc. for $\text{C}_{20}\text{H}_{32}\text{O}_3$ (320.5): C, 74.96; H, 10.06%. Found: C, 75.52; H, 10.25%.

3-Dimethylamino-2-[*p*-(dodecyloxy)phenyl]-*N,N*-dimethylprop-2-eniminium perchlorate 5d

p-(Dodecyloxy)phenylacetic acid (3.54 g, 11.0 mmol) was added in small portions at 0 °C to Vilsmeier's reagent prepared from dimethylformamide (4.25 ml, 55.0 mmol) and phosphoryl chloride (3 ml, 33.0 mmol). The mixture was heated to 80–90 °C for 13 h. After cooling, the mixture was poured into ice–water (50 ml) and sodium perchlorate (1.50 g, 12.2 mmol) was added under stirring. The precipitate was collected by suction filtration and washed with water and ether. Yield, 4.02 g (75%); colourless powder; mp 101–102 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 2922, 2854, 1610, 1585, 1521, 1418, 1400, 1289, 1248, 1109, 1092, 815, 785, 624$; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) = 319 (4.614); ^1H NMR (80 MHz, CDCl_3): $\delta = 0.88\text{--}1.85$ (s, 23 H, alkyl-H), 2.50 (s, 6 H, NCH_3), 3.29 (s, 6 H, NCH_3), 3.92 (t, 2 H, aryl- $\text{OCH}_2\text{-alkyl}$), 6.83–7.10 (AA'BB', J 8.0 Hz, 4 H, phenylene-H), 7.73 (s, 2 H, NCHC). Calc. for $\text{C}_{25}\text{H}_{43}\text{ClN}_2\text{O}_5$ (487.1): C, 61.65; H, 8.90; N, 5.75%. Found: C, 61.58; H, 8.83; N, 5.67%.

2-Phenyl-3-anilino-*N*-phenylprop-2-enimine 6a

A suspension of **5a**²⁹ (0.60 g, 1.98 mmol) and aniline (0.39 g, 4.28 mmol) in MeOH (10 ml) was refluxed for 3.5 h. After

cooling and adding water (10 ml) a lemon-colored solid precipitated. The precipitate was collected by suction filtration, washed with water, and recrystallized (EtOH). Yield, 0.30 g (50%); lemon-colored platelets; mp 126–128 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 1640, 1594, 1544, 1294, 757, 695$. UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) = 292 (4.260), 398 (4.241); ^1H NMR (400 MHz, CDCl_3): $\delta = 7.08\text{--}7.39$ (m, 15 H, phenyl-H), 8.06 (s, 2 H, NCHC); ^{13}C NMR (CDCl_3): $\delta = 109.58$ (s, C-2), 118.37 (d, C-4), 123.81 (d, C-6), 125.56, 126.05, 128.75, 129.42 (d, C-5), 140.22, 146.47 (s, C-3), 149.22 (d, C-1). Found C, 84.34; H, 5.92; N, 9.38%. Calc. for: $\text{C}_{21}\text{H}_{18}\text{N}_2$ (298.4) C 84.53 H 6.08 N 9.39%.

3-(*p*-Dimethylaminophenylamino)-2-phenyl-*N*-(*p*-dimethylaminophenyl)prop-2-enimine 6b

A suspension of **5a**²⁹ (0.45 g, 1.49 mmol) and *N,N*-dimethyl-*p*-phenylenediamine (0.27 g, 2.96 mmol) in MeOH (20 ml) was refluxed for 1 h. After cooling and adding water (20 ml) an orange solid precipitated. The aqueous solution and the precipitate were extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate. The solvent was removed *in vacuo* at 25 °C and the residue recrystallized (MeOH). Yield, 0.13 g (23%), orange needles; mp 91–92 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 1637, 1608, 1544, 1512, 1294, 1219, 1165, 816, 761, 700$; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) = 245 (4.220), 317 (4.370), 450 (4.430); ^1H NMR (80 MHz, CDCl_3): $\delta = 2.91$ (s, 12 H, NCH_3), 6.64–7.35 (m, 13 H, phenyl-H, phenylene-H), 7.95 (s, 2 H, NCHC). Calc. for $\text{C}_{25}\text{H}_{28}\text{N}_4$ (384.5): C, 78.09; H, 7.34; N, 14.57%. Found C, 78.36; H, 7.11; N, 14.03%.

2-(1-Pyridinio)-3-(*p*-*tert*-butylphenylamino)-*N*-(*p*-*tert*-butylphenyl)prop-2-enimine tetrafluoroborate 6c

A suspension of **5b**³⁰ (0.76 g, 2.00 mmol) and *p*-*tert*-butylaniline (0.60 g, 4.07 mmol) in MeOH (10 ml) was refluxed for 3.5 h. After cooling, the solvent was removed partially *in vacuo* at 50 °C. The precipitate was collected by suction filtration, washed with diethyl ether, and recrystallized (MeOH). Yield, 0.71 g (71%), yellow quadratic plates; mp 241–242 °C (decomp.). IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 1658, 1587, 1521, 1471, 1364, 1310, 1267, 1084, 836$; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) = 250 (4.190), 297 (3.978), 357 (4.540); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.33$ (s, 18 H, $(\text{CH}_3)_3\text{C}$), 6.94–7.41 (m, 8 H, phenylene-H), 7.90 (s, 1 H, NCHC), 8.15–9.19 (m, 5 H, pyridinio-H). Calc. for $\text{C}_{28}\text{H}_{34}\text{BF}_4\text{N}_3$ (499.9): C, 67.34; H, 6.86; N, 8.41%. Found: C, 67.21; H, 6.87; N, 8.36%.

2-(1-Pyridinio)-3-(*p*-dimethylaminophenylamino)-*N*-(*p*-dimethylaminophenyl)prop-2-enimine tetrafluoroborate 6d

A suspension of **5b**³⁰ (1.52 g, 4.01 mmol) and *N,N*-dimethyl-*p*-phenylenediamine (1.10 g, 8.08 mmol) in MeOH (10 ml) was refluxed for 6 h. After cooling, the solvent was removed *in vacuo* at 50 °C, the residue was stirred with hot EtOH, immediately collected by suction filtration, and recrystallized (acetonitrile–ether). Yield, 0.70 g (38%), dark red crystals; mp 192 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1} = 1656, 1522, 1084, 946, 821$; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ ($\log \epsilon$) = 263 (4.299), 336 (4.220), 403 (4.520); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 2.81$ (s, 12 H, NCH_3), 6.65–7.25 (m, 8 H, phenylene-H), 8.14–9.13 (m, 7 H, NCHC, pyridinio-H); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 40.93$ (q, NCH_3), 113.03 (d, C-5), 119.88 (d, C-4), 122.47 (s, C-2), 128.73, 134.56 (s, C-3), 145.78 (d, C-1), 146.47, 148.34 (s, C-6), 148.39. Calc. for $\text{C}_{24}\text{H}_{28}\text{BF}_4\text{N}_5$ (473.3): C, 60.90; H, 5.96; N, 14.80%. Found: C, 60.73; H, 6.12; N, 14.84%.

2-(*p*-Methoxyphenyl)-3-phenylamino-*N*-phenylprop-2-enimine 6e

A suspension of **5c**³⁰ (0.66 g, 1.98 mmol), aniline (0.39 g, 4.19 mmol), and triethylamine (0.62 ml, 4.28 mmol) in EtOH

(10 ml) was refluxed for 12 h. After cooling, water (20 ml) was added and the mixture was extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate, the solvent was removed *in vacuo* at 25 °C, and the residue was recrystallized (MeOH). Yield, 0.14 g (21%), yellow needles; mp 102–103 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1641, 1598, 1545, 1502, 1292, 1242, 832, 761, 752, 690; UV–VIS (CHCl₃): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 251 (4.248), 398 (4.494), 445 (sh, 4.303); (HCO₂H): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 384 nm (5.084); ¹H NMR (400 MHz, CDCl₃): δ = 3.83 (s, 3 H, OCH₃), 6.92–7.37 (m, AA'BB', *J* 8.7 Hz, 14 H, phenyl-H, phenylene-H), 8.01 (s, br, 2 H, NCHC); ¹³C NMR (100 MHz, CDCl₃): δ = 55.41 (q, OCH₃), 109.46 (s, C-2), 114.38, 118.33 (d, C-4), 127.85 (d, C-6), 129.45 (d, C-5), 129.80, 133.11, 146.37 (s, C-3), 149.00 (d, C-1), 158.41. Calc. for C₂₂H₂₀N₂O·25 CH₃OH_{0.25} (336.4): C, 79.44; H, 6.29; N, 8.33%. Found: C, 79.35; H, 6.17; N 8.34%.

3-(*p*-Dimethylaminophenylamino)-2-(*p*-methoxyphenyl)-*N*-(*p*-dimethylaminophenyl)prop-2-enimine 6f

A suspension of **5c**³⁰ (0.66 g, 1.98 mmol), *N,N*-dimethyl-*p*-phenylenediamine (0.54 g, 3.96 mmol), and triethylamine (0.78 ml, 5.38 mmol) in EtOH (10 ml) was refluxed for 12 h. After cooling, water (20 ml) was added and the mixture was extracted with dichloromethane. The organic phase was dried over anhydrous sodium sulfate and the solvent was removed *in vacuo* at 25 °C. The residue was dissolved in diethyl ether, the solution filtered over silica gel, dried with anhydrous magnesium sulfate and the solvent was evaporated at room temperature. Yield, 0.12 g (14%), yellow brownish powder; mp 147–148 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1636, 1608, 1542, 1512, 1293, 847; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 307 (4.396), 452 (4.436); (HCO₂H): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 385 (4.763), 499 (3.123); ¹H NMR (400 MHz, CDCl₃): δ = 2.93 (s, 12 H, NCH₃), 3.83 (s, 3 H, OCH₃), 6.76–7.09 (AA'BB', *J* 9.0 Hz, 8 H, phenylene-H), 6.91–7.29 (AA'BB', *J* 8.4 Hz, 4 H, phenylene-H), 7.93 (s, 2 H, NCHC); ¹³C NMR (100 MHz, CDCl₃): δ = 41.15 (q, NCH₃), 55.41 (q, OCH₃), 108.10 (s, C-2), 113.92 (d, C-5), 114.15, 119.34 (d, C-4), 127.22, 133.76, 137.27 (s, C-3), 147.39 (d, C-1), 147.75 (s, C-6), 157.64. Calc. for C₂₆H₃₀N₄O (414.6): C, 75.33; H, 7.29; N, 13.52%. Found: C, 74.83; H, 7.26; N, 13.27%.

Poly[3-amino-2-(*p*-dodecyloxyphenyl)prop-2-eniminyl(*p*-phenylene)] 7a

The solution of **5d** (2.85 g, 6.01 mmol), *p*-phenylenediamine (0.66 g, 6.11 mmol), and five drops of AcOH in EtOH (15 ml) was refluxed for 15 h. After cooling, the precipitate was collected by suction filtration and washed with EtOH, then with a 1:1 mixture of EtOH and triethylamine, and finally with EtOH. After triturating with ether, the residue was collected by filtration. Yield, 1.11 g (45%), dark red powder with a greenish lustre; mp 199–200 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2924, 2853, 1637, 1606, 1538, 1508, 1279, 1243, 1027, 827; UV–VIS (CHCl₃): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 283 (4.210), 484 (4.210); (CF₃CO₂H): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 465 (4.459). Calc. for (C₂₇H₃₆N₂O·0.5 H₂O)_{*n*} [(413.6)_{*n*}]: C, 78.41; H, 9.02; N, 6.77%. Found: C, 78.65; H, 8.89; N, 7.12%.

Poly[3-amino-2-(*p*-dodecyloxyphenyl)prop-2-eniminyl(*p*-phenylphenylene)] 7b

Triethylamine (0.30 ml, 2.07 mmol) and **5d** (0.95 g, 2.00 mmol) were added successively to a suspension of benzidine dihydrochloride (0.52 g, 2.02 mmol) in EtOH (10 ml). The mixture was refluxed for 18 h. After cooling, the precipitate was suction filtered and washed with EtOH, then with a 1:1 mixture of EtOH and triethylamine, and finally with EtOH. The residue was dissolved in chloroform and the solution was filtered. The solvent was removed *in vacuo* at 50 °C, the residue was triturated with ether and collected by filtration. Yield, 0.67 g (69%), red

powder with a greenish lustre; mp 165–166 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2922, 2851, 1639, 1608, 1536, 1513, 1283, 1241, 1210, 1175, 816; UV–VIS (CHCl₃): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 278 (4.241), 448 (4.620); (CF₃CO₂H): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 261 (4.352), 441 (4.731). Calc. for (C₃₃H₄₀N₂O·0.25 H₂O)_{*n*} [(485.2)_{*n*}]: C, 81.69; H, 8.41; N 5.77%. Found: C, 81.68; H, 8.31; N, 5.56%.

Poly[3-amino-2-(*p*-dodecyloxyphenyl)prop-2-eniminyl(*p*-phenylenevinylphenylene)] 7c

As described for **7a** with **5d** (0.95 g, 2.00 mmol) and 4,4'-diaminostilbene (0.42 g, 2.00 mmol). Yield, 0.62 g (60%), brown-red powder with a greenish lustre; mp 156–157 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2922, 2851, 1639, 1606, 1538, 1511, 1286, 1243, 1177, 1027, 827; UV–VIS (CHCl₃): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 310 (4.260), 473 (4.620); (CF₃CO₂H): $\lambda_{\text{max}}/\text{nm}$ = 296, 458. Calc. for (C₃₅H₄₂N₂O·0.5 H₂O)_{*n*} [(515.7)_{*n*}]: C, 81.52; H, 8.40; N, 5.43%. Found: C, 81.66; H, 8.18; N 5.71%.

Poly[3-amino-2-(1-pyridinio)prop-2-eniminyl(*p*-phenylene)tetrafluoroborate] 7d

The suspension of **5b**³⁰ (0.76 g, 2.01 mmol) and *p*-phenylenediamine (0.22 g, 2.04 mmol) in a mixture of diglyme (18 ml) and AcOH (2 ml) was heated to 120 °C for 3.5 h. After cooling, the precipitate was suction filtered and washed with MeOH and ether. Yield, 0.56 g (91%), dark red powder; mp 296 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1646, 1516, 1301, 1084, 827, 774, 681, 520; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 256 (4.111), 453 (4.369). Calc. for (C₁₄H₁₂BF₄N₃·0.4 H₂O)_{*n*} [(316.3)_{*n*}]: C, 53.17; H, 4.08; N, 13.29%. Found: C, 53.36; H, 4.38; N, 13.10%.

Poly[3-amino-2-(4-dimethylamino-1-pyridinio)prop-2-eniminyl(*p*-phenylene)tetrafluoroborate] 7e

The suspension of **5e**³¹ (0.84 g, 1.99 mmol) and *p*-phenylenediamine (0.22 g, 2.04 mmol) in MeOH (20 ml) and AcOH (five drops) was refluxed for 1 h. After cooling, the precipitate was suction filtered (Schlenck funnel) and washed with acetic acid, MeOH and ether. Yield, 0.54 g (71%), dark red powder; mp 280 °C (decomp.). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1647, 1608, 1575, 1516, 1403, 1289, 1190, 1123, 1084, 825, 522; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 292 (4.361), 440 (4.439). Calc. for (C₁₆H₁₇BF₄N₄·1.5 H₂O)_{*n*} [(379.2)_{*n*}]: C, 50.68; H, 5.32; N, 14.78%. Found: C, 50.80; H, 5.07; N 15.73%.

Poly{2,2'-(4,4'-bipyridine-1,1'-diylum)di[3-aminoprop-2-eniminyl(*p*-phenylene)] bis(tetrafluoroborate)} 7f

The suspension of **5f**³¹ (0.38 g, 0.50 mmol) and *p*-phenylenediamine (0.12 g, 1.11 mmol) in MeOH (20 ml) and AcOH (five drops) was refluxed for 9 h. After cooling, the precipitate was suction filtered (Schlenck funnel) and washed with AcOH, MeOH, a 1:1 mixture of MeOH and triethylamine, MeOH, and ether. Yield, 0.28 g (100%), black powder; mp > 350 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1637, 1608, 1514, 1299, 1084, 833, 523. Calc. for (C₂₈H₂₂B₂F₈N₆·C₆H₈N₂·CH₃OH)_{*n*} [(756.3)_{*n*}]: C, 55.58; H, 4.53; N, 14.82%. Found: C, 56.11; H, 4.67; N, 14.60%.

Poly{2,2'-(4,4'-bipyridine-1,1'-diylum)di[3-aminoprop-2-eniminyl(*p*-phenylvinylphenylene)] bis(tetrafluoroborate)} 7g

As described for **10f** with **8f**³¹ (0.38 g, 0.50 mmol) and 4,4'-diaminostilbene (0.22 g, 1.05 mmol). Yield, 0.35 g (77%), black powder; mp > 350 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1636, 1603, 1576, 1300, 1084, 1063, 964, 835, 522. Calc. for (C₄₄H₃₄B₂F₈N₆·0.5 CH₃OH)_{*n*} [(836.4)_{*n*}]: C, 63.90; H, 4.34; N, 10.05%. Found: C, 64.15; H, 4.72; N, 12.00%.

Poly[*p*-phenylene-3-aminoprop-2-eniminium tetrafluoroborate] 9a

1,1,3,3-Tetramethoxypropane (1.64 g, 9.99 mmol) and then 50% aqueous tetrafluoroboric acid (1 ml) were added under stirring to a solution of *p*-phenylenediamine (1.08 g, 10.0 mmol) in EtOH (10 ml). After 20 min, the mixture was refluxed for 9 h. After cooling, the precipitate was suction filtered and stirred at room temperature with a mixture of 50% aqueous tetrafluoroboric acid (10 ml) and EtOH (10 ml) for 1 h. The precipitate was suction filtered and washed with EtOH and ether. Yield, 1.04 g (46%), brown-red powder; mp 331–332 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 3003, 1615, 1585, 1505, 1324, 1275, 1192, 1084, 835, 668, 532; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 317 (3.808), 499 (4.486). Calc. for $(\text{C}_9\text{H}_9\text{BF}_4\text{N}_2 \cdot 0.5 \text{H}_2\text{O})_n$ [(241.1) $_n$]: C, 44.85; H, 4.18; N, 11.62%. Found: C, 44.22; H, 4.30; N, 12.07%.

Poly[4,4'-biphenylene-3-aminoprop-2-eniminium tetrafluoroborate] 9b

1,1,3,3-Tetramethoxypropane (0.66 g, 4.02 mmol), triethylamine (0.5 ml), and 50% aqueous tetrafluoroboric acid (1 ml) were added successively under stirring to a suspension of benzidine hydrochloride (1.03 g, 4.01 mmol) in EtOH (10 ml). After 20 min the mixture was refluxed for 5 h. After cooling, the precipitate was suction filtered and stirred at room temperature with a mixture of 50% aqueous tetrafluoroboric acid (10 ml) and EtOH (10 ml) for 1 h. The precipitate was suction filtered and washed with EtOH and ether. Yield, 1.01 g (87%), red powder; mp > 250 °C (decomp.). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1624, 1604, 1576, 1492, 1336, 1192, 1084, 820; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 461, (4.571). Calc. for $(\text{C}_{15}\text{H}_{13}\text{BF}_4\text{N}_2 \cdot \text{H}_2\text{O})_n$ [(326.1) $_n$]: C, 55.25; H, 4.64; N, 8.59%. Found: C, 50.84; H, 4.22; N 8.32%.

Poly[3-iminioprop-2-eniminiumyl(*p*-phenylenevinylphenylene-iminium) tetrafluoroborate] 9c

1,1,3,3-Tetramethoxypropane (0.66 g, 4.02 mmol) and 50% aqueous tetrafluoroboric acid (1 ml) were added under stirring to a suspension of 4,4'-diaminostilbene (0.84 g, 3.99 mmol) in EtOH (10 ml). After 20 min the mixture was refluxed for 9 h. After cooling the precipitate was suction filtered and washed with EtOH and ether. Yield, 1.25 g (89%), dark red powder; mp 288–289 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1623, 1600, 1576, 1506, 1330, 1194, 1084, 1021, 830; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 492 (4.760), 509 (sh, 4.750). Calc. for $(\text{C}_{17}\text{H}_{15}\text{BF}_4\text{N}_2 \cdot \text{H}_2\text{O})_n$ [(352.1) $_n$]: C, 57.99; H, 4.87; N, 7.96%. Found: C, 58.25; H, 4.95; N 8.36%.

Poly[*p*-phenylene-5-aminopenta-2,4-dieniminium bromide] 11a)

AcOH (10 drops) was added to a suspension of **10**²⁴ (0.36 g, 1.01 mmol) and *p*-phenylenediamine (0.11 g, 1.02 mmol) in EtOH (10 ml) and the mixture was refluxed for 30 h. After cooling, the precipitate was suction filtered and washed with EtOH and ether. Yield, 0.16 g (64%), black powder; mp 183–185 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1616, 1549, 1501, 1311, 1150, 833; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 595 (4.388). Calc. for $(\text{C}_{11}\text{H}_{11}\text{BrN}_2)_n$ [(251.1) $_n$]: C, 52.61; H, 4.42; N, 11.16%. Found: C, 53.15; H, 5.04; N, 11.34%.

Poly[*p*-phenylenevinylphenylene-5-aminopenta-2,4-dieniminium bromide] 11b

As described for **11a** with **10**²⁴ (0.36 g, 1.01 mmol) and 4,4'-diaminostilbene (0.21 g, 1.00 mmol). Yield, 0.32 g (88%), black powder with a greenish lustre; mp 263–264 °C. IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 1618, 1541, 1505, 1312, 1161, 836; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 350 (4.060), 541 (4.247). Calc. for

$(\text{C}_{19}\text{H}_{17}\text{BrN}_2 \cdot 0.5 \text{H}_2\text{O})_n$ [(362.3) $_n$]: C, 62.99; H, 5.07; N, 7.73%. Found: C, 62.95; H, 5.46; N, 8.53%.

Oxidation of 7c with sodium dichromate (→ 12a)

Sodium dichromate (0.18 g, 0.68 mmol) was added under stirring at 0 °C to a mixture of AcOH (10 ml), Ac₂O (10 ml), and 50% ethereal tetrafluoroboric acid (3 ml) prepared under external ice cooling. The mixture was filtered and a solution of **10c** (0.26 g, 0.51 mmol) in trifluoroacetic acid (30 ml) was added dropwise. The mixture was stirred overnight at room temperature. The precipitate was suction filtered and washed with AcOH and ether. Yield, 0.19 g (56%), red powder with a greenish lustre; mp 230 °C (decomp.). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2922, 2851, 1614, 1596, 1561, 1516, 1464, 1318, 1299, 1253, 1193, 1179, 1084, 833, 720, 533; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ = 330, 470; ESR (solid state, MnO): $g = 2.0034$. Calc. for $(\text{C}_{35}\text{H}_{43}\text{B}_2\text{F}_8\text{N}_2\text{O})_n$ [(681.4) $_n$]: C, 61.70; H, 6.36; N, 4.11%. Found: C, 61.58; H, 6.52; N, 4.29%.

Oxidation of 7c with air and HBF₄ (→ 12b)

50% Ethereal tetrafluoroboric acid (10 ml) was added dropwise to a solution of **10c** (0.10 g, 0.20 mmol) in chloroform (20 ml). The mixture was stirred for 20 h in an open vessel at room temperature and then ether (200 ml) was added. The precipitate was suction filtered and washed with ether. Yield, 0.09 g (76%), dark red powder with a greenish lustre; mp 240 °C (decomp.). IR (KBr): $\tilde{\nu}/\text{cm}^{-1}$ = 2923, 2853, 1614, 1596, 1559, 1516, 1465, 1318, 1299, 1253, 1193, 1179, 1084, 833, 725, 533; UV–VIS (DMSO): $\lambda_{\text{max}}/\text{nm}$ (log ϵ) = 325 (4.228), 469 (4.509). Calc. for $(\text{C}_{35}\text{H}_{43}\text{B}_2\text{F}_8\text{N}_2\text{O})_n$ [(681.4) $_n$]: C, 61.70; H, 6.36; N, 4.11%. Found: C, 61.66; H, 6.69; N, 4.60%.

Doping of 7c with iodine²⁶ [→ 7c(ox); general procedure for 7, 9, 11, 12]

Compound **7c** (0.51 g, 1 mmol) was stirred with a saturated solution of iodine in tetrachloromethane for 30 min in the dark. The solvent was removed *in vacuo* at 25 °C. Yield, 0.52 g, black powder; ESR (solid state, MnO): $g = 2.0034$.

Doping of 7c with FeCl₃²⁶ (general procedure for 7, 9, 11, 12)

Compound **7c** (0.51 g, 1 mmol) was stirred with a 10% solution of ferric chloride in nitromethane at room temperature for 30 min. The precipitate was suction filtered and the residue was dried *in vacuo* at 25 °C. Yield, 0.49 g, black powder; ESR (solid state, MnO): $g = 2.014$ (br, Fe³⁺), 4.120 (Fe²⁺).

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Paper 8/01654B; Received 27th February, 1998