Acidochromism of stilbenoid chromophores with a *p*-aminoaniline centre[†,‡]

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ABSTRACT: Oligo(phenylenevinylene)s (OPV) with a 2,5-diaminobenzene centre were prepared via twofold Horner olefinations of substituted terephthalaldehydes. Whereas variations of the environment only slightly alter the electronic excitation spectra, the fluorescence spectra appear to be highly responsive. Besides a positive solvatochromism, the emission is very sensitive towards protonation. Quenching or appearance of new emitting species depends on the substitution pattern and is controlled by the concentration of the acid. Very large Stokes shifts indicate extensive structural changes in the excited states. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: fluorescence; solvatochromism; acidochromism; halochromism; conjugated oligomers

INTRODUCTION

The substitution of conjugated polymers and oligomers with side chains of different types has been widely used to improve solubility and mechanical behaviour of these materials.[1,2] Another important aspect is the directed tuning of their electrical and optical properties for applications in optoelectronical devices. The combination of electron-pair-donating (EPD) and electron-pair-accepting (EPA) substituents can lead to materials for non-linear optical applications such as second harmonic generation or two-photon absorption.[3–5] In this context, amino groups, being efficient and typical donor groups, are often combined with strong acceptors like nitro, cyano, or sulfone groups. The donating ability of amines is inverted upon protonation or quaternisation, particularly the pyridinium ion is a common acceptor unit,[6,7] but ammonium ions have also received considerable attention.[8] The capability of amino groups to act as a donor or acceptor depending on environmental conditions can be used to change the optical properties of a chromophore directly attached to the basic site. Complexation with Lewis acids or protonation has been shown to cause significant changes of the UV/Vis-absorption and emission spectra of π-conjugated chromophores with the basic site on the terminal positions.[9–12] Herein, we report the synthesis of oligo(phenylenevinylene)s (OPVs) with a central phenylene-1,4-diamine unit and the impact of interaction with protons on their optical spectra.

SYNTHESIS

The condensation and *in situ* oxidation of primary amines with dimethyl cyclohexane-2,5-dionedicarboxylate **1** allows a rapid entry to 2,5-diaminoterephthalic esters **2,3**.[13] Further groups attached to the amine can be introduced via acylation or, in case of arenes, via Ullmann coupling[14] to yield **4–6**. LiAlH$_4$ reduces the esters and amides to give the 1,4-diaminobenzenedimethanols, which, in a twofold Swern oxidation, were converted to the intensively coloured terephthalaldehydes **7–9**. These dialdehydes were used as bifunctional units for Horner olefinations with 1-hexyloxybenzylphosphonate (**10**) and 1-hexyloxystilbenylmethylphosphonate (**11**). Recrystallisation gave pure **12–17** without detectable traces of *cis*-isomers[15] (Scheme 1).

ELECTRONIC SPECTRA

The solid distyrylbenzenes (DSBs) **12–14** are light yellow crystalline compounds which are good soluble in solvents like toluene or dichloromethane. Extension of the π-system to five phenyl rings (OPV-5) reduces the solubility and shifts the colour to orange. Only **17**, carrying two diphenylamino groups, forms yellow crystals. Solutions of these compounds in dichloromethane are yellow (**12–14**), yellowish-orange (**16**, **17**) or orange (**15**) and all are fluorescent.
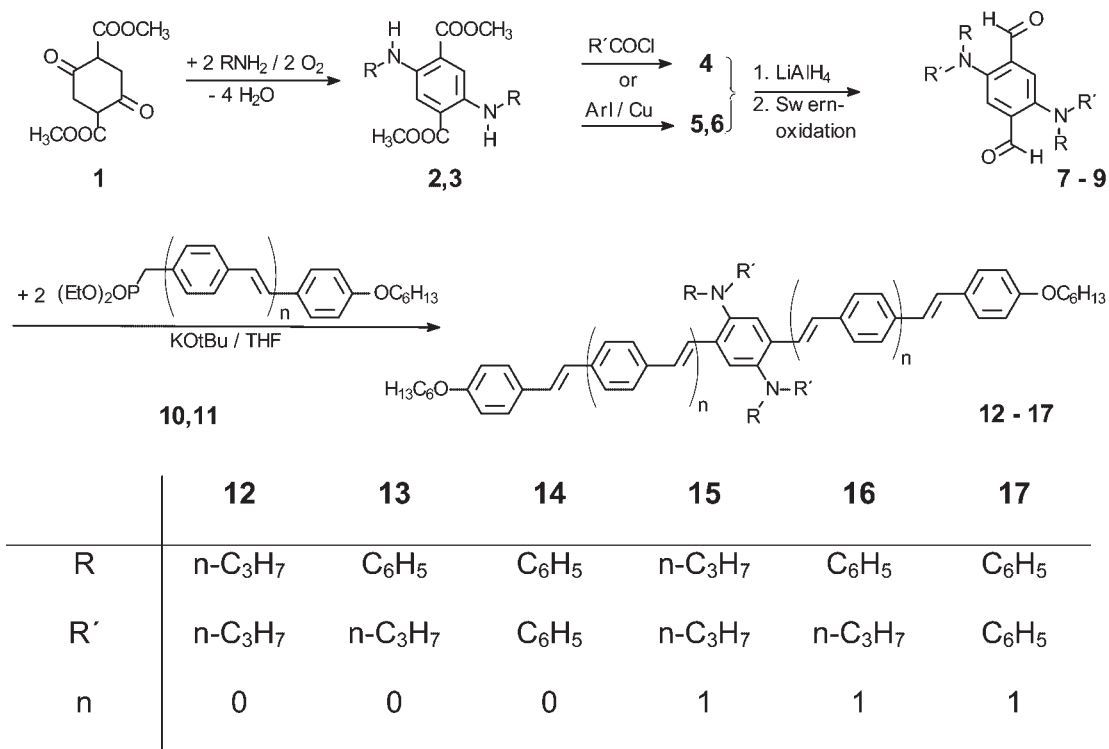
The UV/Vis-absorption spectra of these diamino-OPVs are dominated by a low energy band with a maximum

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Scheme 1. Synthesis of diamino-OPVs

	12	13	14	15	16	17
R	n-C_3H_7	C_6H_5	C_6H_5	n-C_3H_7	C_6H_5	C_6H_5
R′	n-C_3H_7	n-C_3H_7	C_6H_5	n-C_3H_7	n-C_3H_7	C_6H_5
n	0	0	0	1	1	1

around $\lambda = 360$ nm for the DSBs and $\lambda = 410$ nm for the OPV-5, respectively.[15] Both series show an additional shoulder on the red side of this band, which is further red-shifted in the sequence di(1-propyl)amino—phenyl(1-propyl)amino—diphenylamino. Compared with similar three- and five-ring OPVs carrying only alkoxy donors on the central and terminal positions (RO-OPVs),[16] the absorption maxima of **12–17** are strongly shifted to higher energies ($\Delta\lambda \approx 30$–40 nm). According to the molecule symmetry, solvatochromism of the absorption is negligible. The broad fluorescence spectra are separated from the excitation bands by huge Stokes shifts. These stabilisations of $\Delta\tilde{v} = 7700$–9700 cm^{-1} for the DSBs **12–14** and still more than $\Delta\tilde{v} = 6000$ cm^{-1} in the five-ring series (**15–17**) indicate large structural changes in the excited state. The related RO-OPVs and even acceptor-donor-acceptor substituted OPVs[17] show substantially smaller Stokes shifts which are in the range of $\Delta\tilde{v} = 2600$–3400 cm^{-1}. Since the fluorescence of all compounds is positive solvatochromic, an additional mechanism to stabilise the first excited state is probably an intramolecular charge transfer.[18] Bathochromic shifts of the emission extend to $\Delta\lambda \approx 30$ nm upon changes of the solvent from C_6H_{12} [$E_T(30) = 30.9$] to CH_2Cl_2 [$E_T(30) = 40.7$] or acetonitrile [$E_T(30) = 45.6$] but inverts in protic solvents to a negative solvatochromism ($\Delta\lambda \approx 10$ nm).[19] In addition to the bathochromic shifts, the efficiencies decrease by *ca.* 75% relative to the efficiencies in C_6H_{12}, but in the protic solvent ethanol not only the emission maxima are shifted to the blue, but also

the efficiencies recover the values found for solutions in toluene. Whereas the fluorescence of the DSBs **12–14** appears as a single, broadband centred around $\lambda_{max} = 510$ nm, the main emission of higher homologues is a broadband in the region of $\lambda_{max} = 540$ nm, but accompanied by a weak (**15**, **16**) or very weak (**17**), structured emission between $\lambda = 400$ and 450 nm. This high-energy emission of **15** is invisible in cyclohexane but becomes more prominent in dichloromethane or ethanol, those of **16**, **17** are nearly unbiased by solvent polarity (Table 1).

An addition of strong acids such as trifluoroacetic acid (TFA) to solutions of **12–17** in dichloromethane results in a protonation of the amino-OPVs, thus changing the strongly electron-donating amino groups to weak acceptors. Since (de)-protonation can occur in the ground as well as in the excited state, absorption and emission spectra can be altered independently.[20] Whereas phenylenevinylene chromophores are fairly stable towards light or acid, UV-irradiation of solutions with traces of acids initiated a fast and irreversible decomposition of these materials.[21] Chromophores with basic sites like **12–17** show a much higher photostability, even in very acidic solution. Protonation was studied by UV–Vis and fluorescence spectroscopy of the OPVs dissolved in dichloromethane containing 10^{-6}–1 molar concentrations of TFA. The impact of Brønsted acids on the UV/Vis-absorption spectra of **12–17** is mainly a reduction of the extinction coefficient and a loss of the low-energy shoulder. Contrary to the behaviour of the

Table 1. Solvatochromism of the diamino-OPVs **12–14**

	λ_{max}/nm DCM	$\Delta\tilde{\upsilon}$/cm^{-1} DCM	λ^{F}_{max}/nm CH	λ^{F}_{max}/nm Tol	λ^{F}_{max}/nm DCM	λ^{F}_{max}/nm AN	λ^{F}_{max}/nm EtOH
12	352 (398)	9683	505	526	534	534	526
13	365 (417)	8166	488	501	520	520	508
14	366 (422)	7789	484	497	510	511	499
15	394 (416)	6117	534	543	558	565	544
16	408 (445)	6427	534	540	553	549	542
17	399 (450)	6336	510	526	534	537	530

DCM, dichloromethane; CH, cyclohexane; Tol, toluene; AN, acetonitrile; EtOH, ethanol.

dipropylamino-OPVs (**12**, **15**), interaction of protons with propylphenylamino- (**13**, **16**) and diphenylamino-OPVs (**14**, **17**) results in the build-up of a new maximum around $\lambda_{max} = 340$ nm and, at very high concentrations of TFA (0.1–1 M), of a broad but weak long-wavelength band around $\lambda_{max} = 540$ nm (**13**, **14**) or 560 nm (**16**, **17**) (Table 2).

The emission spectra of these chromophores are strongly influenced by the presence of TFA. A gradual quenching of the emission of DSBs with phenylamino side groups (**13**, **14**) occurs upon the addition of acid. Compared to neutral solutions, the fluorescence intensity is reduced to *ca*. 60% in 10^{-3} M TFA and vanishes at higher TFA concentrations. Chromophore **12**, carrying the more basic (in the ground state) dipropylamino groups shows an entirely different behaviour. In the presence of traces of TFA (10^{-6} M) the long-wavelength band is retained but a prominent shoulder at $\lambda_{max} = 478$ nm arises-resulting in an increase of the fluorescence about 35%. This shoulder becomes the sole maximum (relative intensity equal to neutral solution) in slightly higher concentrations of TFA (10^{-5} M), the initial emission band turns to be now invisible. A further increase of the amount

of TFA results in a gradual decrease of this band to a residual intensity of *ca*. 8% in highly acidic solutions (0.1–1 M TFA). Figure 1 shows the titration curves of **12**, observed in the absorption and in the fluorescence at two different wavelengths each.

A related behaviour was found in the homologous series **15–17**. The emissions of **16**, **17** are nearly unaffected by TFA up to 10^{-3} M. At higher concentrations, the fluorescence of **17** is shifted to the red and becomes less efficient and is finally completely quenched (10^{-1} M) (Fig. 2).

A 10^{-2} M TFA solution is sufficient to quench the $\lambda = 530$ nm emission of **16** but does not alter the weak emission in the $\lambda = 430$ nm region. This band is reduced to *ca*. 50% in 10^{-1} M TFA and disappears only in acid as strong as 1 M TFA. The emission of dipropylamino-OPV **15** in dichloromethane has a broad maximum at $\lambda_{max} = 558$ nm with an efficiency of only 60% relative to the propylphenyl analogue **16**. The addition of traces of TFA (10^{-5} M) changes the fluorescence properties fundamentally. The long-wavelength maximum vanishes and a strong band centred at $\lambda_{max} = 480$ appears, the intensity increases by a factor of 6. Apart from a

Table 2. Acidochromism of the diamino-OPVs **12–14**

	DCM	10^{-6} M TFA	10^{-5} M TFA	10^{-4} M TFA	10^{-3} M TFA	10^{-2} M TFA	10^{-1} M TFA	1 M TFA
	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm	λ_{max}/nm
12	352 *398*	354	358	357	353	366	363	362
13	365 *417*			364	365	328	325 *528*	318 *523*
14	366 *422*			365	364	328	329 *534*	399 *523*
15	394 *416*	416	408	408	408	417	418	408
16	408 *445*			406	407	404	329 *558*	328 *552*
17	399 *450*			402	398	398	328 *559*	328 *555*
	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm	λ^{F}_{max}/nm
12	534 (1)	530 (1.34)	478 (0.99)	475 (0.68)	472 (0.35)	467 (0.16)	478 (0.08)	479 (0.08)
13	520 (1.25)			519 (1.15)	517 (0.79)	n.f.	n.f.	n.f.
14	510 (1.69)			511 (1.53)	510 (0.92)	498 (0.13)	n.f.	n.f.
15	558 (0.29)	492 (0.70)	488 (1.77)	483 (1.80)	480 (1.60)	486 (1.52)	531 (0.57)	533 (0.17)
16	537 (0.52)			538 (0.45)	534 (0.47)	433 (0.18)	438 (0.08)	n.f.
17	534 (0.75)			536 (0.80)	533 (0.91)	506 (0.46)	n.f.	n.f.

TFA: trifluoroacetic acid in dichloromethane, italics: second maximum, values in brackets: relative fluorescence intensities, normalized to solutions of equal optical density at = 345 nm and referenced to **12** in dichloromethane = 1.
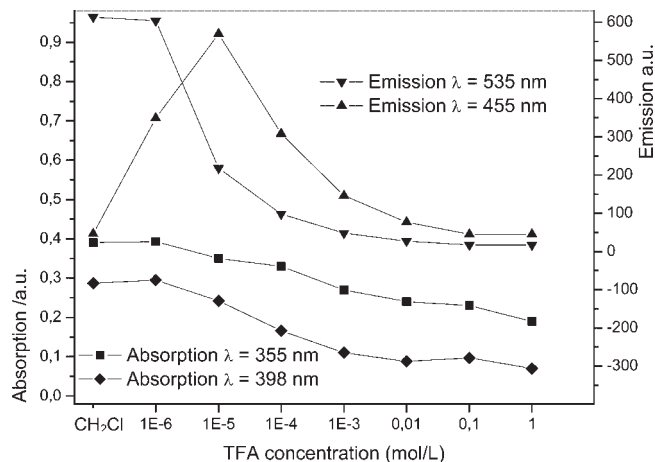
Figure 1. Titration curve of **12**

successive red shift of $\Delta\lambda = 8\,nm$ and variations of the relative intensity ($\pm 10\%$), this emission characterises solutions containing 10^{-5} to 10^{-3} M TFA. The same band still dominates the emission of **15** in 10^{-2} M TFA. Here, a shoulder emerges on the low-energy flank (530 nm) and develops to be the absolute maximum in TFA of 10^{-1}–1 M strength. **15** shows two distinct alterations of the fluorescence due to the presence of TFA. The transitions between the three different emitting species occur at 10^{-6} and 10^{-2} M TFA, spectra obtained from these solutions are superimposed spectra of **15** in dichloromethane and 10^{-5} M TFA, and 10^{-3} and 10^{-1} M TFA, respectively.

DISCUSSION

OPVs with a 2,5-diaminobenzene centre and terminal alkoxy groups can be regarded as quadrupolar chromophores with two weak and two strong donor groups. Like other quadrupolar substituted OPVs, solvatochromism of the UV/Vis-absorption spectra is very small, but the influence of a polar environment is visible as a positive solvatochromism of the fluorescence and reduced

fluorescence intensity. This holds for aprotic solvents, in ethanol the fluorescence spectra and intensities are similar to those from solutions in toluene. Enormous Stokes shifts separate the fluorescence maxima from the excitation maxima. Compared to the related RO-OPVs (**15**), the bathochromic shifts of the emission of **12**–**17** were expected since the amine is a powerful auxochrome. Contrary to the fluorescence, the absorption is shifted to higher energies compared to RO-OPVs. Though the amines are potent auxochromes, distortions of the π-system due to steric interaction of the substituents on the amines and the *ortho*-vinylene moieties predominate. Dihedral angles of 33–50° between the planes of the central benzene ring and the adjacent vinylene groups of **12**–**14** were calculated using AM1. The lone pair of the nitrogen is twisted out of the conjugation with the benzene ring by 44° (**12**) to 67° (**14**). Comprehensive changes of the geometry—and therefore of the conjugation within the OPV and of the OPV with the auxochromes—can occur in the excited state resulting in Stokes shifts of $\Delta\tilde{\upsilon} = 6000\text{–}9700\,cm^{-1}$.

The relative fluorescence intensities of the DSBs **12**–**14** are significantly higher than of the homologous OPV-5 **15**–**17**, a similar behaviour has been observed with RO-OPVs. Phenylamino-OPVs are stronger fluorescent (**14** > **13**; **17** > **16**) than those with propylamino groups (**12**, **15**), this may be attributed to the increasing energy gap between excited states and ground states and to the stiffness of the phenyl rings compared to propyl chains.

In general, the acidochromism of the excitation spectra is comparatively small, the main absorption is reduced in intensity and shifted to the blue, both resulting from the reduced auxochromic effect of the diaminophenylene when protonated. The appearance of a weak band at much longer wavelengths ($\lambda_{max} = 540\text{–}560\,nm$) upon protonation of **13**, **14** and **16**, **17** is unique for the *N*-phenyl-substituted chromophores and indicates a significant electronic interaction of the lateral aniline moieties and the phenylenevinylene strand. Indeed, AM1 calculations show a participation of the orbitals of the phenyl side
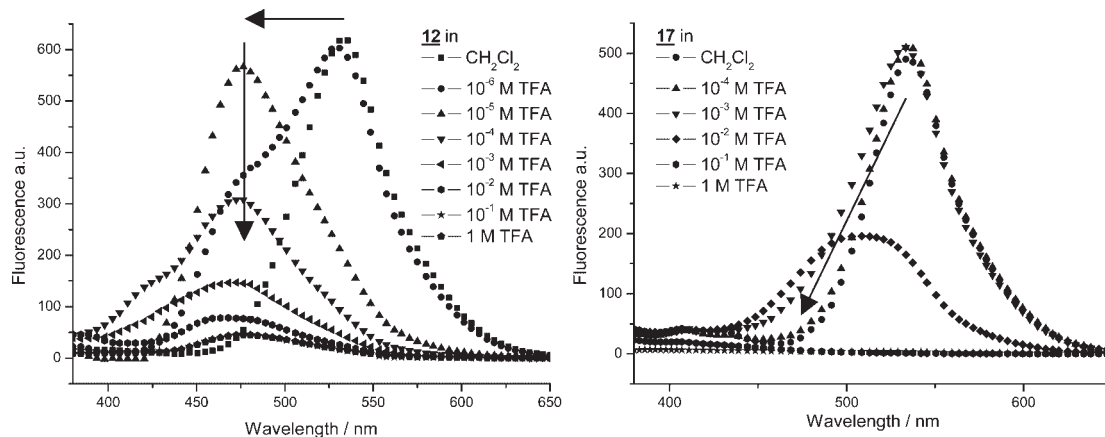

Figure 2. Emission spectra of **12** and **17** in dichloromethane containing TFA. Excitation at $\lambda = 345\,nm$

chains in the wave functions of HOMO, LUMO and energetically close orbitals of the neutral and protonated chromophores. Regarding the emission, a successive quenching of the fluorescence of **13**, **14**, **16** and **17** with increasing concentrations of acid results. Protonation is the most likely additional process and might be responsible for the quenching. Since the degree of fluorescence quenching is higher than the change of the absorption spectrum, it can be concluded, that the basicity of the excited diamino-OPVs is higher than the basicity of the ground-state molecules. This is in contrast with the observations that the basicity of aniline-type bases is reduced about several orders of magnitude upon excitation. The dipropylamino-OPVs **12** and **15** are the most interesting in this series. The fluorescence of **12** shows a new band at very low concentrations of TFA, already at 10^{-6} M this band appears as a strong shoulder and reaches maximum intensity at ca 10^{-5} M TFA. Further interaction with protons gives a successive quenching of this band.

The homologue **15** behaves similar. Here, the new blue-shifted emission band starts to evolve at 10^{-6} M TFA and gains a strong increase in intensity. This band dominates the spectrum over four orders of magnitude until at 10^{-2} M TFA a new band becomes visible and characterises higher concentrations of TFA. Two successive steps of protonation altering the electronic character of the central benzene ring are visible. The first proton changes the donor–donor substitution on this ring to a resonance-stabilised donor–acceptor. When the second amine is converted to ammonium, the whole π-system adopts a donor-acceptor-donor structure with the terminal 1-hexyloxy groups as donors.

CONCLUSION

The fluorescence of phenylenevinylene chromophores with a central *p*-aminoaniline moiety is much more sensitive towards changes of the environment than the UV/Vis-absorption spectra. Contrary to other aniline-type bases, the basicities of the excited states of these systems appear to be higher than of their ground states. Since concentrations as low as 10^{-6} M TFA change the emission behaviour of **12** and **15** significantly, these dyes are potent fluorescent sensors for changes in the local environments.

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