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Acidochromism of C_2-symmetrical aza-analogues of 1,4-distyrylbenzene†,‡

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epoc ABSTRACT: A series of C_2-symmetrical aza-analogous 1,4-distyrylbenzenes were synthesised via two-fold PO-activated olefinations or Heck reactions. Pyridine, pyrimidine and quinoline were used as terminal rings, and the 2,5-positions of the central benzene ring were substituted with H, alkoxy, or alkylsulfonyl groups. These strongly fluorescent compounds are freely soluble in common solvents such as toluene or chloroform. Whereas the electronic spectra of the pyridine and pyrimidine chromophores were very similar to those of the parent compound 1,4-distyrylbenzene, the spectra of the former were altered considerably in the presence of trifluoroacetic acid. Depending on the concentration of the acid, protonation of the ground state and/or the excited state caused bathochromic shifts of the absorption and the emission spectra, accompanied by reductions in the fluorescence efficiencies. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: fluorescence; acidochromism; solvatochromism; heterocycles

INTRODUCTION

Over the last decade, organic molecules with extended conjugated systems have received considerable attention as a consequence of their semiconducting, luminescent and non-linear optical properties.[1–4] The main classes of compounds of interest are polyarylenes, poly(arylenevinylene)s and poly(aryleneethynylene)s. The prototype of the arylene subunit is a benzene ring, but a large variety of these materials contain aromatic heterocycles. Thiophene is the most important hetarene in electrically conducting polymers, but oxazoles, oxadiazoles and other azoles play a dominant role in organic luminescent materials such as scintillators or optical brighteners.[5] Donor groups have been widely used to tune the optical properties of the fluorophors, with dialkylamino groups being very efficient donors but diarylamino groups have proved to be superior in terms of photostability.[6]

Conjugated systems with higher electron affinity are obtained with *N*-heterocycles such as pyridine, quinoxaline, or 1,3,4-oxadiazole. Oligomers with well-defined conjugated systems are interesting as model compounds for the polymers and are also used as electronic[7] or scintillating[6] materials. Oligo(phenylenevinylene)s with terminal pyridines were investigated by Drefahl and co-workers.[8,9] As a result of exchanging phenyl for α- or γ-pyridyl, they observed small bathochromic shifts ($\Delta\lambda < 11$ nm) of the absorption maxima of corresponding oligomers. Similar results were obtained in the oligo(phenylene) series.[10] Oligo(phenylene)s with a terminal pyridine or benzimidazoles and their quarternary salts[10–12] have been investigated by Kauffman and co-workers for the development of new laser dyes and waveshifting fluorophors. In these series, as with the stilbenes, an increase in the length of the conjugated system shifted the absorption maximum towards a long-wavelength limit. Later Siegrist *et al.*,[13] in work on optical brigtheners, used the 'anil synthesis' for the preparation of intensively fluorescent stilbazole chromophores. During our work on conjugated π-systems with quadrupolar donor–acceptor–donor or acceptor–donor–acceptor substitution,[14–16] we became interested in oligomers containing electron-deficient heterocycles such as 1,3,4-oxadiazoles,[17,18] pyridine, or quinoline. In addition to the influence of solvent polarity on the fluorescence of the former compounds, pyridine and related azines offer a second mode of interaction with the surrounding medium. Protonation at the heterocyclic portions of the chromophore causes a significant electronic pertubation of the π-system, thus allowing modulation of the optical properties by changing the environment. This acidochromism of the absorption as well as of the emission could also be interesting in sensor technology.[19–21]

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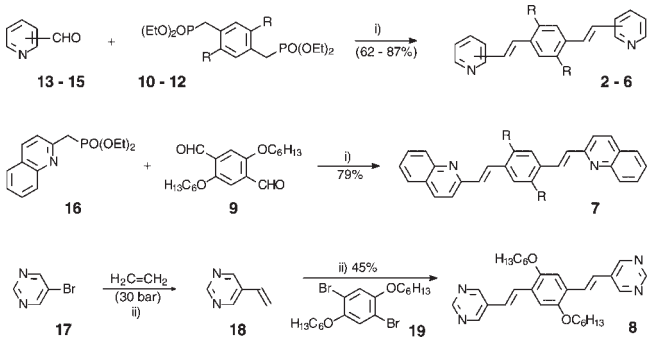

Scheme 1. Synthesis of Aza-OPVs: (i) THF, KOtBu, 0 °C, 30 min; (ii) DMF, NEt_3, $Pd(OAc)_2$, P(*o*-tol)$_3$, 110 °C

SYNTHESIS

A successful route for the synthesis of C_2-symmetrical distyrylbenzenes (DSB) such as **1–7** and higher homologues is the Horner olefination[22] of a central bifunctional component (dialdehyde **9** or bisphosphonates **10–12**) with two lateral monofunctional units **13–16**, depending on the availability of the starting materials. 2,5-Dioctyloxydistyrylbenzene[23] **1** and aza-DSBs **2–6** were prepared in good yields from benzaldehyde or pyridine carbaldehydes **13–15** and bisphosphonates[15,16] **10–12**, whereas **7** was obtained by the condensation of dialdehyde[24] **9** with quinolylmethyl phosphonate **16** (Scheme 1). A short route to the chromophore with terminal pyrimidines **8** is a sequence of two Heck reactions, first with bromopyrimidine **17** and ethene at 30 bar,[25] followed by the thus prepared aza-styrene[26] **18** with dibromobenzene **19**. DSBs **1–8** were purified by chromatography on silica gel with toluene–ethyl acetate and recrystallisation from dichloromethane–methanol. (All compounds were characterised by IR-, mass-, ^{1}H-, and ^{13}C-NMR-spectra and gave satisfactory elemental analyses.)

ELECTRONIC SPECTRA

The (aza-)distyrylbenzenes with side chains on the central ring are freely soluble in solvents such as toluene or dichloromethane, and the optical data are collected in Table 1. The chromophores are divided into two groups, donor-substituted DSBs **1**, **3–5**, **7** and **8** that give yellow, and those with acceptors (**6**) or H (**2**) that give colourless, but blue fluorescent solutions. [Electronic spectra were recorded at ambient temperature, using an MCS320/340 UV/Vis spectrometer (Zeiss) (c: $\approx 10^{-5}$ mol l^{-1}) for absorption and an LS 50B (PerkinElmer) for corrected fluorescence spectra (c: $\approx 10^{-7}$ mol l^{-1}), solvents: spectroscopic grade, not degassed.] Within these groups, the absorption and emission spectra are very similar in shape and wavelength. Exchanging H for electron withdrawing alkylsulfonyl groups on the central ring of aza-DSB **2** results in essentially identical absorption and emission spectra for **2** and **6**, the only visible effect being a red-shift of 8 nm in the emission of **6**, but even the vibrational structure is preserved. Contrary to acceptors, electron donating ether side chains in **5** considerably reduce the energies for excitation ($\lambda_{max} = 394$ nm, $\Delta\lambda = 44$ nm) and of the fluorescence ($\lambda^F{}_{max} = 459$ nm, $\Delta\lambda^F{}_{max} = 72$ nm). Although the electronegative nitrogen atoms at the ends and the central alkoxy groups of chromophore **5** induce some acceptor–donor–acceptor character in the π-system, the electronic transitions are only slightly reduced in energy compared with the isocyclic analogue **1** ($\lambda_{max} = 390$ nm; $\lambda^F{}_{max} = 441$ nm). Closely related to **5**, alkoxy-aza-DSBs **3**, **4** and **8** show very similar spectra ($\lambda_{max} = 394$–398 nm; $\lambda^F{}_{max} = 447$–454 nm), those of **7** are shifted about 20 nm to longer wavelengths, due to the extension of the conjugated system by two-fold benzo-annulation of **3**. The sequences of bathochromism are **1** < **8** < **4** < **5** < **3** < **7** in absorption and in the fluorescence **1** < **4** < **8** < **3** < **5** < **7**; hence this distinguishes aza-DSBs **3**, **5**, **7** with N in 'conjugated' α- or γ-positions from those of **4**, **8** with N in 'non-conjugated' β-positions.

In the absence of specific interactions, solvent polarity slightly influences the absorption spectra of C_2-symmetrical OPVs with a quadrupolar donor–acceptor substitution, but the dielectric constant of the solvent could have strong effects on the fluorescence. Stabilisation of the excited state by reorientation of solvent dipoles results in positive solvatochromism and often greatly reduced quantum yields.[15,16,18] As a result of the exchange of benzene rings in OPVs with pyridine,

Table 1. Substitution pattern and properties of DSBs **1–8**

DSB		R	Yield (%)	m.p. (°C)	Colour	λ_{max} (nm)	logε	$\lambda^F{}_{max}$ (nm)
1	phenyl[18]	OC_3H_7	67	177	yellow	390	4.59	441
2	γ-pyridyl[6]	H	87	262	off-white	352	4.57	390
3[a]	α-pyridyl	OC_8H_{17}	84	104	orange	396	4.45	454
4[a]	β-pyridyl	OC_8H_{17}	74	118	d.-orange	394	4.48	447
5	γ-pyridyl	OC_8H_{17}	62	133	yellow	396	4.44	459
6	γ-pyridyl	$SO_2R^{\#}$	78	205	white	353	4.51	398
7	2-chinolyl	OC_6H_{13}	79	179	d.-yellow	417	4.68	474
8	5-pyrimidyl	OC_6H_{13}	45	182	orange	393	4.49	453

[a] 2-(2-Ethylhexylsulfonyl)-5-(propylsulfonyl); optical data: in 1,4-dioxane.

Table 2. Optical data of aza-DSBs **2**–**7** in dioxane solution and increasing concentration of TFA

	Dioxane		10^{-3} M TFA in dioxane		10^{-2} M TFA in dioxane		10^{-1} M TFA in dioxane		1 M TFA in dioxane		50% H_2SO_4/ dioxane: 1/1	
DSB	λ_{max}	λ^F_{max} Φ_F	λ_{max}	λ^F_{max} Φ_F	λ_{max}	λ^F_{max} Φ_F	λ_{max}	λ^F_{max} Φ_F	λ_{max}	λ^F_{max} Φ_F	λ_{max}	λ^F_{max} Φ_F
2	352	(390)	353	(388)	352	(388)	(352)	427	354	443	(353)	484
		409		410	(363)	410	363		(363)		363	
		0.76		*0.65*		*0.97*		*0.52*		0.30		*0.28*
3	(333)	453	(333)	454	(341)	453	(364)	543	(364)	544	(364)	540
	396		397		407	(530)	443		450		449	
		0.65		*0.60*		*0.56*		*0.17*		*0.14*		*0.07*
4	(327)	447	(327)	447	(327)	469	(328)	484	(335)	484	(337)	—
	393		393		396		408		412		414	
		0.96		*0.90*		*0.48*		*0.04*		*0.05*		—
5	(327)	459	(328)	460	(343)	517	(352)	527	(353)	538	(364)	568
	396		401		422	(460)	433		447		452	
		0.77		*0.48*		*0.53*		*0.29*		*0.17*		*0.06*
6	353	398	352	398	353	(398)	353	430	354	431	358	433
		(417)		(417)		419						
		0.91		*0.78*		*0.52*		*0.23*		*0.09*		*0.04*
7	417	474	417	474	(398)	474	(394)	(472)	(394)	(472)	(394)	(472)
			(488)		488		497	593	499	593	503	594
		0.77		*0.78*		*0.27*		*0.07*		*0.02*		*0.01*

Wavelength (nm), values in parentheses: second maximum or shoulder, fluorescence quantum yields (italics) by comparison with quinine sulfate. (Fluorescence quantum yields were obtained by comparison with quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 0.577$) and corrected for the refractive index according to Ref. 28.)

Drefahl noticed only minor bathochromic shifts of the absorption spectra, even though pyridine is the prototype for a 'π-electron deficient' heterocycle.

An increasing solvent polarity[27] (e.g. dioxane/ $C_6H_5CH_3$/$CH_3COOC_2H_5$/CH_2Cl_2/C_2H_5OH) has only a slight effect on the electronic spectra of the aza-DSBs **2**–**8**, with **5** and **6** being the most sensitive chromophores [Dioxane: $\varepsilon = 2.209$, $E_T(30) = 36.0$; toluene: $\varepsilon = 2.379$, $E_T(30) = 33.9$; ethyl acetate: $E_T(30) = 38.1$; CH_2Cl_2: $\varepsilon = 8.93$, $E_T(30) = 40.7$; ethanol $\varepsilon = 24.55$, $E_T(30) = 51.9$]. In both compounds nitrogen occupies the terminal conjugated positions. For **5**, with donor-groups on the central ring, positive solvatochromism in absorption is shown (395 → 405 nm) and emission (459 → 470 nm), whereas acceptors (**6**) provoke hypsochromic shifts (absorbance: 354 → 350 nm; emission: 398 → 403 → 397 nm). It should be noted that the fluorescence efficiencies of **1**–**8** are virtually independent of the solvent. The low solvatochromism and the virtually solvent-independent fluorescence efficiencies are remarkable, as the emission of related fluorophors with quadrupolar[15,16,18] or dipolar[11] donor–acceptor substitution appears to be strongly dependent on the solvent.

Solvatochromism is the result of different dipole moments of a chromophore in the ground state and the excited states and their specific stabilisations by dipolar solvent molecules. Pyridine-containing chromophores exhibit a second mode of interaction with the solvent. Protonation at the basic sites causes a significant electronic pertubation of the π-system and strongly reduces the relative energies of the HOMO and, even more pronounced, of the LUMO resulting in a decreased band gap. Free base and protonated species are in an equilibrium, given by the concentrations and the specific equilibrium constant *K*. Excitation changes the energy, geometry and the wave functions of a chromophore; the excited species can be regarded as a different molecule with a specific equilibrium constant *K** for the protonation. Following the photophysical process, the thermodynamic acid–base equilibrium is re-established. All of these processes are combined in the Förster-cycle.[29]

As a general rule, excitation increases the acidity of phenols and protonated anilines considerably, whereas *N*-heterocyclic systems such as quinoline are much stronger bases[30] in their S_1- or T_1-states.

To study the influence of protonation on the electronic transitions of aza-analogous OPVs **2**–**7**, spectra were recorded from solutions of **2**–**7** in pure dioxane and dioxane with five concentrations of acid (10^{-3} M–5 M). A compilation of the data from excitation and fluorescence is given in Table 2.

As with polarity, the acidity of solutions provokes spectral changes, differentiating the chromophores into two groups **2**, **4**, **6** and **3**, **5**, **7**. Representative examples for both types are given in Fig. 1. The two isomeric chromophores **3** and **4** show entirely different spectral responses towards increasing concentrations of protons. Protonation of **3** generates a new species that absorbs at longer wavelengths. The [H^+]-concentration dependent equilibrium between the chromophore and its protonated

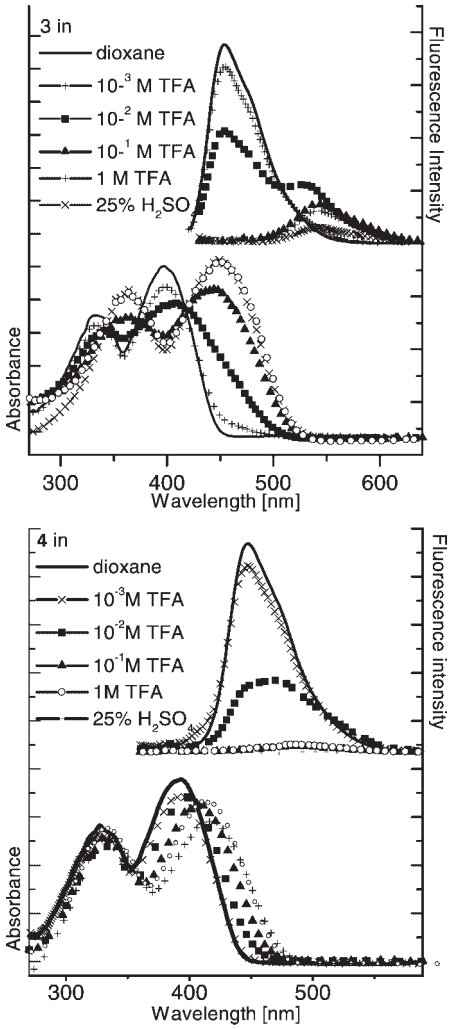

Figure 1. Electronic spectra of **3** and **4** dependence on acid concentration

form is characterised by three isosbestic points. Protonated excited **3** fluoresces at lower energy and with lower efficiency compared with its neutral form.

The interaction of protons with the isomeric aza-OPV **4** results in an entirely different set of absorption and emission spectra. With increasing TFA concentration, the absorption spectra are gradually shifted to the red: the maximum at 327 nm by about 10 nm and the long-wavelength maximum by about 20 nm and accompanied by hypochromism. The predominant effect of acid on the fluorescence of **4** is that of quenching. As this is more pronounced for the maximum (447 nm) than for the shoulder (480 nm), the result is an apparent bathochromism of the emission.

The spectroscopic behaviour of aza-OPVs **5** and **7** with donors on the central ring and γ-pyridyl- or α-quinolyl-moieties is comparable to **3**, with strongly red shifted electronic spectra of the protonated species. The energy required for the excitation of protonated **3**, **5** and **7** corresponds to the energy of the light emitted by the non-protonated chromophore. In the absence of donors on the central ring (**2**, **6**), the addition of acid provokes successive bathochromism of absorption and reduced fluorescence efficiency, a response similar to **4**. In the presence of 10^{-2} M trifluoroacetic acid, the absorption maximum of **4** is shifted about 3 nm to the red—this corresponds to 15% of the total shift from neutral solution to 25% sulfuric acid. The fluorescence from the same solution (10^{-2} M TFA), containing only minor amounts of protonated **4** in the ground state, is reduced to ≈50% of the efficiency and shifted about 22 nm to the red, 60% of the total acidochromism. Aza-DSB **5**, the γ-pyridyl isomer of **4**, is more basic in its ground state. The 10^{-2} M TFA gives rise to 50% of the total change of the absorption spectra, whereas the fluorescence of the neutral form is reduced to a ''notable'' shoulder on the fluorescence of protonated **5**. Starting with 10^{-2} M TFA the protonation of the third isomer **3** becomes visible. Here, a value of 40% of the entire spectral response of the excitation as well as of the fluorescence of the neutral form indicates fairly similar basicities of the ground and excited states. Replacing 2-pyridyl in **3** by 2-quinolyl gives **7** and increases the basicity. TFA in only 10^{-3} M solution protonates about 15% of **7**, reaching 90% in 10^{-2} M TFA. The fluorescence is less influenced, in 10^{-3} M TFA only the neutral form is visible and in 10^{-2} M TFA, even though 90% of **7** is protonated in the ground state, the residual fluorescence of neutral **7** amounts to 30% of the initial intensity. Contrary to the other aza-DSBs **2**–**6** and also to simple quinoline, the basicity of **7** decreases upon electronic excitation.

Whereas protonation reduced the fluorescence efficiencies of these aza-OPVs, Kauffman *et al.*[12] reported that oligo(phenylene)s with pyridine or benzimidazole end groups gave quaternary salts with excellent fluorescence quantum yields (Φ_F 0.8–1.0). Compared with the free base, quaternisation as well as protonation caused substantial bathochromic shifts in their UV spectra, presumably through the enhanced contribution of resonance forms in which the donor releases non-bonding electrons to the π-system. In the excited state, the negative charge can be stabilised by the electron-attracting quaternised heterocycle, resulting in highly efficient fluorescence. The intramolecular protonation in the excited states (ESIPT) of aza-oligo(phenylene)s has been used successfully for the design of fluorophors with large Stokes shifts, e.g. with benzimidazoles as H-bond acceptors,[12] but the fluorescence of chromophores containing the much stronger basic pyridine was quenched completely by the intramolecular proton transfer.[10] Such a (intermolecular) proton transfer pathway could be responsible for the quenching of the fluorescence of the aza-distyrylbenzenes.

Oligo(phenylenevinylene)s are less rigid than their oligo(phenylene) counterparts as the chromophore is assembled via a higher number of single bonds. In addition, the bond order of vinylene linkages can be

reduced in the excited state.[31] The fluorescence of OPVs with a pronounced acceptor–donor–acceptor structure has been reported to be influenced by the solvent. Increasing polarity resulted in bathochromism and decreasing fluorescence efficiencies due to stabilisation via intramolecular charge transfer in the excited state.[15] The UV-spectra of aza-DSBs **2–7** are only slightly shifted to lower energies compared with the isocyclic **1**, indicating minor effects of the π-electron-deficient heterocycles. On protonation, the electron-accepting ability of the heterocyclic units increases greatly, thus facilitating stabilisation of the excited state via charge transfer and nonradiative decay.

CONCLUSION

1,4-Bis(pyridylethenyl)benzenes with electron donating or withdrawing side chains on the central ring were prepared via Horner olefinations. Solvatochromism of the electronic transitions is small but protonation enhances the electron-attracting power of the azines and results in bathochromism of absorption and fluorescence and reduced quantum yields. As for other *N*-heterocyclic bases, the basicity of chromophores **2–6** that contain pyridine rings increases upon excitation, whereas the quinoline **7** is a stronger base in its ground state.

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