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Solvent-dependent fluorescence of donor-substituted (*E*)-1,2-bis(stilbenyl-1,3,4-oxadiazolyl)ethenes†

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ABSTRACT: The Huisgen reaction of aryltetrazoles and fumaryl chloride leads to symmetrically aryl-substituted 1,2-bis(1,3,4-oxadiazolyl)ethenes. Molecules with extended conjugated systems are accessible using stilbenyltetrazoles or higher homologues. The substitution with solubility-permitting alkoxy side-chains results in molecules of C_{2h} symmetry, consisting of a central electron-accepting segment and two terminal electron density-releasing units. The solvatochromism of the absorption spectra is negligible, while in the emission spectra a strong positive solvatochromism connected with a dramatic decrease of the quantum yield is observed, indicating intramolecular charge transfer. The influences of different alkoxy substitution patterns on the luminescence properties are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: fluorescence; solvatochromism; heterocycles

INTRODUCTION

Since the late 1980s, organic molecules with extended conjugated systems such as poly(phenylenevinylene)s or polythiophenes have received considerable attention thanks to their semiconducting, luminescent and non-linear optical properties.[1–4] Oligomers with well-defined conjugated systems are interesting as model compounds for the polymers and are also used as electronic materials.[5] The low electron affinity of (alkoxylated) oligo- and poly(phenylenevinylene)s is disadvantageous for using these materials in light-emitting diodes owing to high barriers for electron injection from aluminium cathodes reducing the efficiencies of these devices.[6,7] Additional layers of conjugated materials with a high electron affinity, based on heterocycles such as 1,3,4-oxadiazole,[8,9] 1,3,5-triazine,[10,11] or quinoxaline,[12,13] were used to improve the electron injection process. Alternatively, the electron affinity of the luminescent materials can be enhanced by substitution with electron-accepting nitriles[14,15] or sulfonyl groups.[16,17] Here we report our work on soluble oligo(phenylenevinylene)s with additional 1,3,4-oxadiazoles in the main chain. Two stilbenes are connected to the centre of these compounds, a heterocyclic analogue of stilbene. Flexible alkoxy side-chains on the lateral rings improve the solubility tremendously. However, this substitution pattern leads to π-systems with a pronounced donor–acceptor–donor structure.

SYNTHESIS

The synthesis of aryl-substituted (*E*)-1,2-bis(1,3,4-oxadiazolyl)ethenes from 5-aryltetrazoles and fumaryl chloride via acylation of the heterocycles and thermal ring transformation (Huisgen reaction) has recently been reported.[18] Stilbenyltetrazoles **4a–e** with solubilizing side-chains were prepared by PO-activated olefinations of alkoxy-substituted benzaldehydes **1a–e** with *p*-cyanobenzyl phosphonate **2** and subsequent addition of azide to yield the tetrazoles **4a–e**. (Scheme 1) Using LiN_3 in methylglycol or DMF, excellent yields (91–97%) of tetrazoles were obtained from simple benzonitriles and cyanostilbene **3a**, whereas the additions of azide to alkoxylated cyanostilbenes **3b–e** were slow and accompanied by partial cleavage of the alkyl ethers. Tetrazoles **4b–e** with up to three alkoxy groups on the stilbene were isolated in moderate to good yields when the addition of azide was performed in toluene and in the presence of triethylammonium ions. The title molecules **6a–e** (Table 1) were assembled by acylation of the tetrazoles **4a–e** with fumaryl chloride in anisole containing stoichiometric amounts of pyridine and subsequent thermolysis of the tetrazolide (80–120 °C). The amine reduces the temperature for the thermal ring transformation, but it also induces a decomposition of fumaryl chloride **5**.

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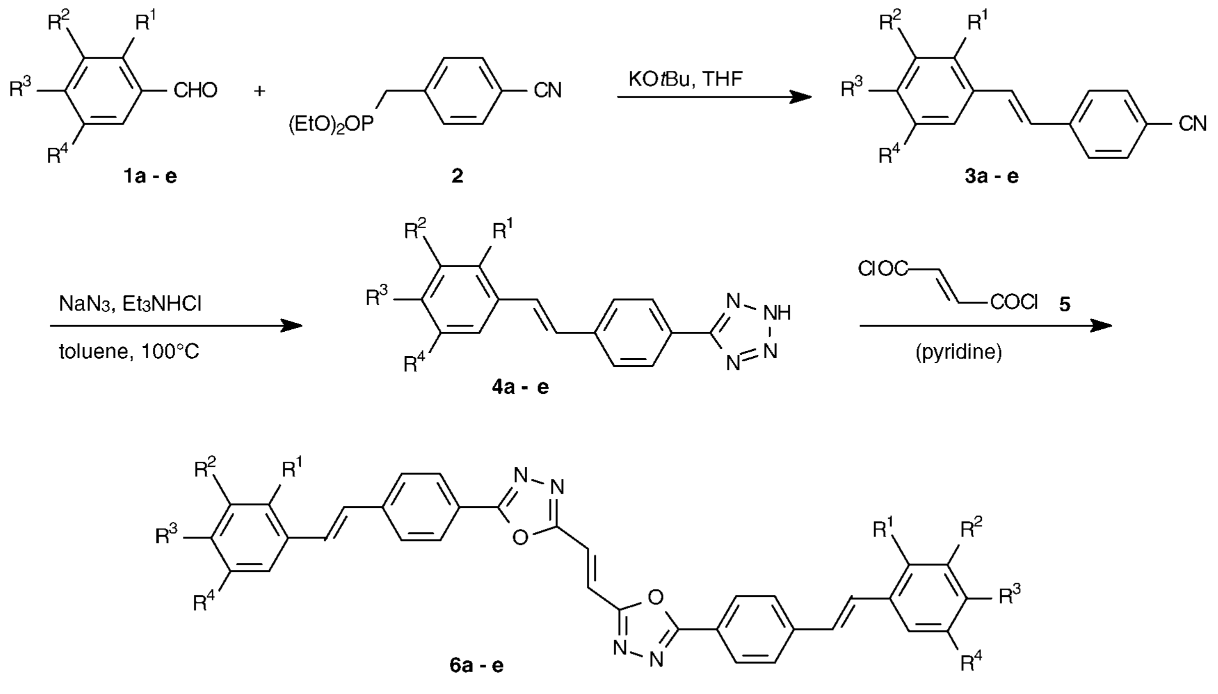

Scheme 1

Preferentially, Huisgen reactions with **5** were performed in the absence of a base using 1,2-dichlorobenzene as a solvent (**6b, d** and **e**). All compounds were characterized by IR, mass and ^{1}H and ^{13}C NMR spectra and gave satisfactory elemental analyses.

ELECTRONIC SPECTRA

(*E*)-1,2-Bis(stilbenyl-1,3,4-oxadiazolyl)ethene **6a**, representing the basic chromophore of the title compounds, is an almost colourless but nearly insoluble material which emits blue–green light upon UV irradiation. Substitution on the terminal rings with flexible alkoxy side-chains results in highly soluble, yellow–orange solids, but causes a gradual (**6b**) to complete loss of fluorescence for crystalline materials **6c–e**. Compared with solutions of the reference molecule **6a**, both the absorption and fluorescence spectra of **6b–e** are shifted to lower energies, owing to the auxochromic effect of the alkoxy groups. The absorption spectra of **6b–e** are nearly unbiased by the solvent. Compared with solutions in cyclohexane, only small hypsochromic shifts ($\Delta\lambda_{max} = 2$–9 nm) were recorded with ethanol as a solvent [electronic spectra were recorded at ambient temperature, using a MCS320/340 UV/Vis spectrometer (Zeiss) ($c \approx 10^{-5}$ mol l^{-1}) for absorption and an LS 50B spectrometer (Perkin-Elmer) for fluorescence spectra ($c \approx 10^{-5}$–10^{-8} mol l^{-1})]. Solutions of **6a–e** in cyclohexane [$\varepsilon = 2.023$, $E_T(30) = 30.9$][19] show an intense fluorescence band with a well resolved vibrational structure. This structure is blurred in solvents with a slightly higher dielectric constant, such as 1,4-dioxane [$\varepsilon = 2.209$, $E_T(30) = 36.0$] or toluene [$\varepsilon = 2.379$, $E_T(30) = 33.9$]. The loss of structure is accompanied by bathochromic shifts and reduced fluorescence intensities of the alkoxylated compounds **6b–e**, whereas the fluorescence intensity of the basic chromophore **6a** is increased. In dichloromethane, a moderately polar solvent [$\varepsilon = 8.93$, $E_T(30) = 40.7$], the fluorescence intensities of the alkoxylated title compounds **6b–e** are strongly reduced.

Table 1. Substitution pattern of (*E*)-1,2-bis(stilbenyl-1,3,4-oxadiazolyl)ethenes **6a–e**

Compound	R^1	R^2	R^3	R^4	Yield (%)	M.p. (°C)
6a			CH_3		92	368
6b	OC_8H_{17}			$C(CH_3)_3$	87	170
6c[a]	OC_8H_{17}		CH_3	OC_8H_{17}	68	165
6d[a]		OC_8H_{17}	OCH_3		86	225
6e		OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	77	189

[a] OC_8H_{17} = 2-ethylhexyloxy.

Table 2. Solvent-dependent absorption and emission spectra of **6a–e**[a]

Compound	λ_{max} (CH)	λ_{max} (DCM) (logε)	λ_{max} (EtOH)	$\lambda_{f,max}$ (CH)	Φ_F	$\lambda_{f,max}$ (Dio)	$\lambda_{f,max}$ (Tol)	$\lambda_{f,max}$ (DCM)	$I_{f,\ rel}$ ($A_{f,\ rel}$)	$\lambda_{f,max}$ (EtOH)
6a		376 ($CHCl_3$)		412 (683) 436 (601)	0.77	442 (948)	422 (948) 442 (825)	473 (619)	1.1 (0.7)	443 (45)
6b	388	387 (4.87)	384	422 (962) 447 (792)	0.88	449 (771)	456 (714)	511 (213)	4.5 (2.4)	490 (2)
6c	400	398 (4.80)	398	440 (560) 467 (414)	0.54	478 (456)	457 (522)	455 (4)	135 (78)	484 (5)
6d	392	399 (4.92)	387	428.5 (207) 454.5 (167)	0.44	473.5 (185)	454.5 (151)	531 (0.4)	460 (250)	517 (1)
6e	389	387 (4.94)	380	429.5 (688) 452.5 (638)	0.43	475 (619)	435.5 (319) 466 (438)	455 (0.5)	1280 (599)	453 (0.4)

[a] CH = cyclohexane; DCM = dichloromethane; EtOH = ethanol (96%); Dio = 1,4-dioxane; tol = Toluene; λ_{max} = absorption maximum (nm); $\lambda_{f,max}$ = emission maxima (nm) and intensities (a.u.); $I_{f,\ rel}$ = ratio of fluorescence intensities at $\lambda_{f,max}$ of solutions of a compounds in cyclohexane and in CH_2Cl_2; $A_{f,\ rel}$ = relative intensities of the fluorescence bands in these solvents.

Depending on the number and position of the peripheral auxochromic groups, the intensities at $\lambda_{f,max}$ are reduced to values of 20% (**6b**) to less than 1‰ (**6e**) compared with solutions of these compounds in cyclohexane. Considering the broadening of the fluorescence band, the residual fluorescence is in the range of 40% (**6b**) to 2‰ (**6e**). In contrast to the alkoxylated compounds, the fluorescence band of the basic chromophore **6a** in CH_2Cl_2 is about 50% over that recorded from solutions in cyclohexane [$A_{f\ (CH)}/A_{f\ (DCM)} = 0.7$] In ethanol [$\varepsilon = 24.55$, $E_T(30) = 51.9$], the fluorescence of all 1,2-bis(1,3,4-oxadiazolyl)ethenes is barely detectable; even the emission of **6a** is reduced to about 7%. Details of the spectra are given in Table 2.

The fluorescence quantum yields were calculated from fluorescence intensities of solutions of **6a–e** in cyclohexane and compared with the intensity of quinine sulphate ($\Phi_f = 0.577$) in aqueous 0.1 M H_2SO_4 and corrected for the refractive indices.[20] Intense fluorescence is observed with solutions of the basic chromophore **6a** ($\Phi_f \approx 0.8$), substitution of **6a** with two alkoxy groups results in a further increase in the fluorescence quantum yield (**6b**: $\Phi_f \approx 0.9$), whereas the introduction of additional auxochromes substantially reduces the fluorescence (**6c–e**: $\Phi_f \approx 0.4$–0.5).

In addition, the introduction of several peripheral alkoxy groups limits the photostability. The absorption and fluorescence of those compounds showing the highest response on solvent polarity and the lowest fluorescence quantum yields, **6d** and **e**, slowly decrease upon continued exposure to UV radiation (366 nm, cyclohexane).

DISCUSSION

Conjugated systems composed of an electron-deficient heterocyclic analogue of stilbene and two lateral stilbene units were investigated. The alkoxylated (*E*)-1,2-bis-(stilbenyl-1,3,4-oxadiazolyl)ethenes are molecules with a distinct donor–acceptor–donor structure. The influence of the dielectric constant of the solvent on the ground state of these molecules is only small, but the pronounced solvatochromism of the fluorescence indicates severe interaction of the excited state with the solvent molecules. These shifts of the emission to lower energies can

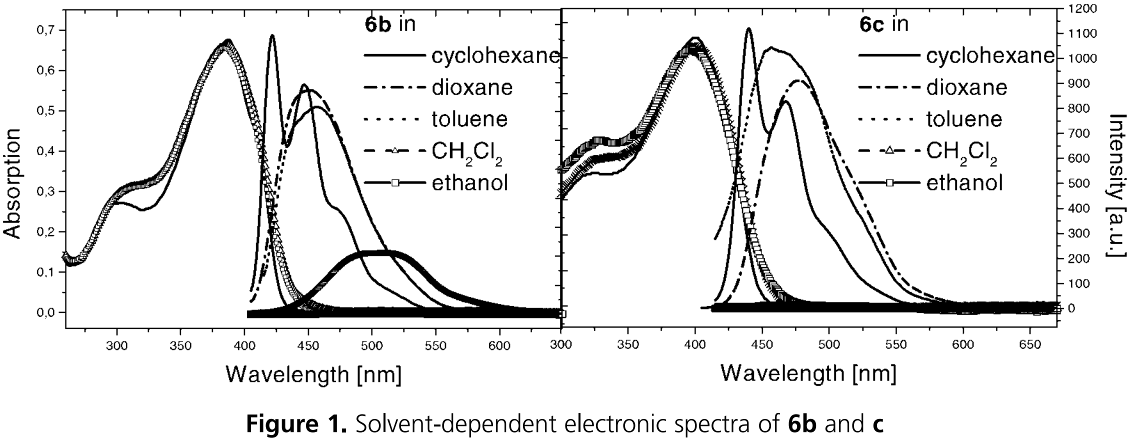

Figure 1. Solvent-dependent electronic spectra of **6b** and **c**

be attributed to a stabilization of a charge-transfer state by reorientation of the solvent molecules.[19] As the structure of the fluorescence bands of **6a–e** changes completely with solvent polarity, no meaningful correlation of $\Delta\lambda_{f,max}$ and a solvent parameter can be obtained.[21] In addition to the influence on the energy of the emitted light, solvent polarity has a strong impact on the fluorescence quantum yield. The intense light emission from solutions in non-polar solvents (cyclohexane, dioxane) is reduced to negligible values in the polar and protic ethanol. Using cyclohexane and the moderately polar dichloromethane as reference solvents, the ratios of the fluorescence intensities [$I_{f\ (CH)}/I_{f\ (DCM)}$; $A_{f\ (CH)}/A_{f\ (DCM)}$] discriminate **6a–e** according to the extent of the increasing donor–acceptor–donor structure of these compounds. Whereas Φ_f of the basic chromophore **6a** remains nearly constant in these solvents, progressive introduction of donor groups gradually reduces the individual quantum yield. The fluorescence intensity of **6e** in CH_2Cl_2 is reduced to about 1‰ of its intensity from solutions in cyclohexane. This behaviour is closely related to the positive solvatochromism and reduction of fluorescence intensities found for cyano-substituted oligo(phenylenevinylene)s with a pronounced acceptor–donor–acceptor structure. In this series, a minimum fluorescence intensity of 5% was preserved even in acetonitrile.[15]

The substitution of a fluorescent π-system with auxochromes is known to increase the fluorescence,[22] and this also holds for the first set of alkoxy groups comparing **6a** ($\Phi_f = 0.8$) with **6b** ($\Phi_f = 0.9$). However, additional ether groups reduce the fluorescence quantum yield to about half the value (**6c–e**: $\Phi_f = 0.4$–0.5). The impact of polarity on Φ_f parallels the fluorescence behaviour of these compounds in different solvents: an enlarged donor–acceptor–donor character (**6b–e**) and an increased solvent polarity favour a charge transfer in the excited state. An enhanced radiationless decay results from this stabilization.

CONCLUSION

1,2-Bis(1,3,4-oxadiazolyl)ethenes with extended conjugated systems were prepared via Huisgen reaction of stilbenyltetrazoles. Chromophores with a pronounced donor–acceptor–donor structure are obtained upon substitution with solubilizing alkoxy side-chains. This favours a charge transfer in the excited state, resulting in solvatochromism of the emission and a marked decline in the fluorescence quantum yield in polar solvents.

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