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Synthesis, spectral properties and photobehaviour of push–pull distyrylbenzene nitro-derivatives

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ABSTRACT

Six novel asymmetric 2,5-distyryl-furan, 2,5-distyryl-thiophene and 2,6-distyrylpyridine derivatives, bearing an electron acceptor (*p*-nitro) group at one side and an electron donor (*p*-methoxy or *p*-dimethylamino) group at the other side, have been prepared. The experimental absorption properties have been measured and compared with the computed parameters. Theoretical and experimental results indicate that one conformational isomer (the compressed one) is largely prevalent in all compounds. The measured radiative and reactive relaxation properties of these donor/acceptor disubstituted compounds were also compared with those of the unsubstituted analogues previously investigated. The presence of the donor/acceptor groups leads to a significant increase of the charge transfer character of both the ground and the excited states and to strong red shifts of the absorption spectra, an effect that can be useful for potential applications in material science. The fluorescence/photoisomerization competition of the furan and thiophene derivatives was found to be rather similar to that of the unsubstituted analogues whereas significant changes were found for the pyridine derivatives where a drastic decrease of fluorescence, a sizable increase of photoisomerization and a predominance of radiationless deactivation to the ground state becomes operative.

1. Introduction

We reported recently the synthesis and photophysical study of conjugated systems bearing electron-donor/acceptor groups at the extreme ends, connected by a spacer [1–7]. The design and study of these push–pull (D-π-A) systems have attracted our attention because of their potential application as fluorescent probes, as dye laser systems and in optoelectronics [8,9], especially for their hyperpolarizability properties which make them candidates as components of non linear optical (NLO) materials [10–13].

A positive fluorosolvatochromism was observed for these compounds caused by an increase of the dipole moment under photoexcitation. The occurrence of intramolecular charge transfer (ICT) from the locally excited (LE) singlet state to a singlet CT state, characterized by an increased charge separation was reported. The singlet CT state was found to be strongly stabilized in polar solvents becoming in this condition the lowest (often poor) fluorescent state.

Of particular interest was the study of 2-(*p*-nitrostyryl),5-styrylfuran and 2-(*p*-methylstyryl),3-(*p*-nitrostyryl)benzofuran [1,2,4,5], where the nitro group and the central π-excessive furan ring are responsible for the introduction of electronic states with a strong CT character. Moreover, in the first molecule a peculiar, very interesting, dependence of the intersystem crossing kinetic constant (k_{ISC}) on the dielectric constant (ε) of the solvent was evidenced [14]. The k_{ISC} value was found very high in non-polar solvents and sensitive to very small differences of dielectric constant in the range of the low polarity solvents, reaching a lower and constant value in more polar solvents.

On the line of these results our effort was directed to design asymmetric distyrylbenzene analogues with heteroaromatic central rings and strong push/pull groups at the ends with the aim to induce a more efficient ICT.

This paper deals with the synthesis and photobehaviour of the EE isomers of 2,5-distyryl-furan, 2,5-distyryl-thiophene and 2,6-distyrylpyridine derivatives with a strong electron-acceptor (nitro) group and an electron-donor substituent (dimethyl-amino or methoxy) of different strength at the opposite side. The comparison of the spectral properties and photobehaviour of the new synthesized compounds with those of the unsubstituted analogues previously studied [15–18] was particularly useful and led the role of the central ring and the side push/pull groups to be highlighted.

2. Experimental

2.1. Synthesis

The compounds investigated are shown in Scheme 1.

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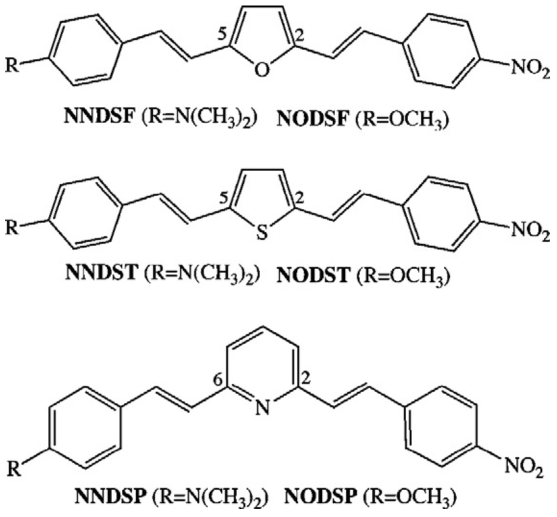


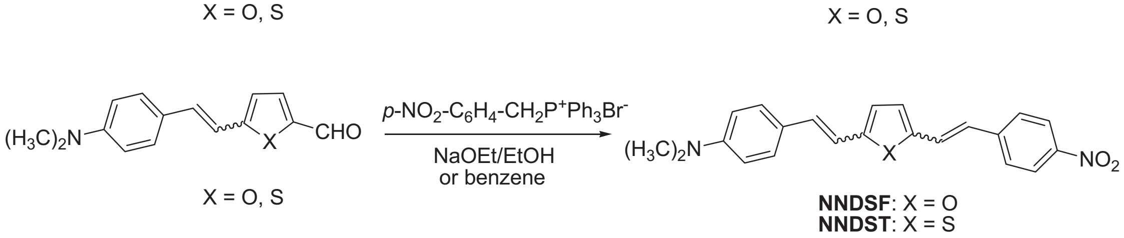
Scheme 1. Molecular structures of *EE*-2-(*p*-nitrostyryl)-5-(*p*-*N*,*N*-dimethylaminostyryl)furan (**NNDSF**), *EE*-2-(*p*-nitrostyryl)-5-(*p*-methoxystyryl)furan (**NODSF**), *EE*-2-(*p*-nitrostyryl)-5-(*p*-*N*,*N*-dimethylaminostyryl)thiophene (**NNDST**), *EE*-2-(*p*-nitrostyryl)-5-(*p*-methoxystyryl)thiophene (**NODST**), *EE*-2-(*p*-nitrostyryl)-5-(*p*-*N*,*N*-dimethylaminostyryl)pyridine (**NNDSP**), *EE*-2-(*p*-nitrostyryl)-5-(*p*-methoxystyryl)pyridine (**NODSP**).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-600 Spectrometer at 300 and 600 MHz and 75 or 150 MHz, respectively. All NMR spectra were measured in $CDCl_3$ using tetramethylsilane as reference. High-resolution mass spectra (HRMS) were obtained on a matrix-assisted laser desorption/ionization time-of-flight MALDI-TOF/TOF mass spectrometer (4800 Plus MALDI-TOF/TOF analyzer, Applied Biosystems Inc., Foster City, CA, USA) equipped with Nd:YAG laser operating at 355 nm with firing rate 200 Hz in the positive ion reflector mode. 1600 shots per spectrum were taken with mass range 100–1000 Da, focus mass 500 Da and delay time 100 ns. Nicotinamide and azithromycin were used for external mass calibration in positive ion mode. Each spectrum was internally calibrated, providing measured mass accuracy within 5 ppm of theoretical mass. The GC–MS analyses were performed on a Varian CP-3800 Gas Chromatograph-Varian Saturn 2200 equipped with FactorFour Capillary Column VF-5ms, 30 m × 0.25 mm ID; GC operating conditions for all experiments: column temperature programmed from 110 °C to 300 °C (6 min isothermal) at a rate of 33 °C min^{-1}; carrier gas: helium; flow rate: 1 mL min^{-1}; injector temperature: 300 °C; volume injected: 5 μL. Melting points were obtained using an Original Kofler Mikroheitztisch apparatus (Reichert, Wien) and are uncorrected. Silica gel (Merck 0.063–0.2 mm) was used for chromatographic purifications. Solvents were purified by distillation. Boiling range of petroleum ether, used for chromatographic separation, was 40–70 °C. *p*-Dimethylaminobenzaldehyde, 6-methyl-2-pyridinecarboxaldehyde, furan-2-carboxaldehyde and thiophene-2-carboxaldehyde were obtained from a commercial source. 2-Furyl- and 2-thienyl-triphenylphosphonium bromide and *p*-methoxybenzyl- and *p*-nitrobenzyl-triphenylphosphonium bromides were synthesized from the corresponding bromides and triphenylphosphine in benzene solution.

Preparation of **NNDSF** and **NNDST**. To a stirred solution of 2-furyl- or 2-thienyl-triphenylphosphonium bromide (3 mmol) and *p*-dimethylaminobenzaldehyde (3 mmol), in absolute ethanol (50 mL) a solution of sodium ethoxide (69 mg, 3 mmol Na in 10 mL ethanol) was added dropwise (Scheme 2). Stirring was continued under a stream of nitrogen for 3 h at RT. After removal of the solvent, the residue was worked up with water and toluene. The toluene extracts were dried and concentrated. The pure *cis*- and *trans*-*p*-dimethylamino-2-styrylfuran/thiophene were obtained in the first fractions by column chromatography on silica gel using petroleum ether/diethyl ether mixture as eluent and subjected to formylation. Vilsmeier formylation was carried out from *p*-dimethylamino-2-styrylfuran/thiophene (1.8 mmol) dissolved in dry dimethylformamide (1.4 mL). After adjusting the temperature at ~10 °C, phosphorus oxychloride (2 mmol) was added and the reaction mixture was allowed gradually to warm up to room temperature and stirred for 24 h. The reaction mixture was decomposed by the continuous addition (with cooling) of 10% NaOH solution and the product was extracted with diethyl ether. The ether extracts were washed with water and then dried with $MgSO_4$. After removal of the solvent, the crude reaction product of formyl derivatives, as mixture of *cis*- and *trans*-isomers, was used in the next reaction step. To a stirred solution of formyl derivatives (0.4 mmol) and *p*-nitrobenzyl-triphenylphosphonium bromide (0.4 mmol) in absolute ethanol or benzene (40 mL), respectively, sodium ethoxide (9.0 mg, 0.4 mmol Na dissolved in 5 mL ethanol and evaporated to obtain powder NaOEt for benzene solution) was added (Scheme 2). Stirring was continued under a stream of nitrogen for 3 h at RT. After removal of the solvent, the residue was worked up with water and toluene and dried with $MgSO_4$. The crude reaction product was purified and the mixtures of four isomers of **NNDSF** and **NNDST** were obtained by column chromatography on silica gel using petroleum ether/diethyl ether mixture as eluent. The geometrical isomers thus obtained were separated and purified by HPLC.

Yield for the mixture of four isomers of **NNDSF**: 50%.

E,*E*-**NNDSF**: R_f 0.86 (petroleum ether/diethyl ether 1:0.25); red solid; m.p. 195 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ_H 8.20 (d, J = 8.8 Hz, 2H, Har), 7.58 (d, J = 8.8 Hz, 2H, Har), 7.40 (d, J = 8.7 Hz, 2H, Har), 7.12 (d, J = 16.0 Hz, 1H, Het), 7.10 (d, J = 16.0 Hz, 1H, Het), 7.00 (d, J = 16.0 Hz, 1H, Het), 6.71 (d, J = 8.7 Hz, 1H, Har), 6.70 (d, J = 16.0 Hz, 1H, Het), 6.51 (d, J = 3.5 Hz, 1H, Hf), 6.33 (d, J = 3.5 Hz, 1H, Hf), 3.00 (s, 6H, CH_3); ^{13}C NMR (150 MHz, $CDCl_3$) δ_C 155.4 (s), 151.2 (s), 150.4 (s), 146.3 (s), 144.0 (s), 129.2 (s), 127.7 (2d), 127.5 (d), 126.4 (2d), 125.0 (d), 124.2 (2d), 123.4 (d), 120.2 (d), 114.3 (d), 112.4 (d), 111.7 (d),



Scheme 2. Preparation of **NNDSF** and **NNDST**.

109.6 (d), 40.3 (q); HRMS (TOF ES$^+$) m/z calculated for $C_{22}H_{20}N_2O_3$ 360.1468; found 360.1470.

Yield for the mixture of four isomers of **NNDST**: 35%.

E,E-**NNDST**: R_f 0.62 (petroleum ether/diethyl ether 1:0.18); brown solid; m.p. 240 °C; ^{1}H NMR (CDCl$_3$, 600 MHz) δ_H 8.22 (d, 8.8 Hz, 2H, Har), 7.58 (d, J = 8.8 Hz, 2H, Har), 7.40 (d, J = 8.7 Hz, 2H, Har), 7.36 (d, J = 16.0 Hz, 1H, Het), 7.06 (d, J = 3.6 Hz, 1H, Het), 7.03 (d, J = 16.0 Hz, 1H, Het), 6.93 (d, J = 3.6 Hz, 1H, Ht), 6.92 (d, J = 15.8 Hz, 1H, Het), 6.74 (d, J = 8.7 Hz, 2H, Har), 3.03 (s, 6H, CH$_3$); ^{13}C NMR (150 MHz, CDCl$_3$) δ_C 154.2 (s), 151.2 (s), 145.9 (s), 139.2 (s), 136.5 (s), 129.7 (d), 129.0 (d), 127.2 (2d), 126.0 (d), 125.9 (2d), 125.0 (d), 124.3 (d), 123.7 (2d), 116.7 (d), 111.9 (2d), 39.8 (q), one singlet is not seen; HRMS (TOF ES$^+$) m/z calculated for $C_{22}H_{20}N_2O_2S$ 376.1240; found 376.1247.

Preparation of **NNDSP**. To a stirred solution of *p*-nitrobenzyl-triphenylphosphonium bromide (4 mmol) and 6-methyl-2-pyridinecarboxaldehyde (4 mmol) in absolute ethanol (40 mL) a solution of sodium ethoxide (92 mg, 4 mmol in 10 mL abs ethanol) was added dropwise and stirred for 3 h at RT (Scheme 3). After removal of solvent an extraction with toluene was carried out. The extract was dried and concentrated. The crude reaction product was purified and the mixture of *cis*- and *trans*-isomers of styrylpyridine derivative was obtained by column chromatography on silica gel using petroleum ether/diethyl ether mixture as eluent. A solution of styrylpyridine derivative (1.1 mmol), *N*-bromosuccinimide (1.8 mmol) and azobisisobutyronitrile (AIBN) (30 mg) in CCl$_4$ (9 mL) was stirred at RT and then irradiated with a halogen lamp under reflux for 12 h. The reaction mixture was filtered to remove succinimide and evaporated. The residue was dissolved in benzene and triphenylphosphine (PPh$_3$) in benzene was added. After stirring over night at RT the precipitate was filtered off and used in next step after drying. To a stirred solution of obtained phosphonium salt (0.45 mmol) and *p*-dimethylaminobenzaldehyde (0.45 mmol) in benzene sodium ethoxide was added (10.3 mg, 0.45 mmol Na dissolved in 5 mL ethanol and evaporated to obtain powder NaOEt for benzene solution) (Scheme 3). Stirring was continued for 4 h at RT. After removal of the solvent, the residue was worked up with water and toluene and dried with MgSO$_4$. The crude reaction product was chromatographed and the mixtures of isomers of **NNDSP** were obtained on silica gel column using petroleum ether/diethyl ether mixture as eluent. The geometrical isomers thus obtained were separated and purified by HPLC.

Yield for the mixture of four isomers of **NNDSP**: 15%.

E,E-**NNDSP**: R_f 0.08 (petroleum ether/diethyl ether 1:1); brown solid; ^{1}H NMR (CDCl$_3$, 300 MHz) δ_H 8.27 (d, J = 8.7 Hz, 2H, Har), 7.84 (d, J = 16.0 Hz, 1H, Het), 7.81 (d, J = 16.3 Hz, 1H, Het), 7.79–7.75 (m, 3H), 7.67 (d, J = 16.0 Hz, 1H, Het), 7.54 (d, J = 8.6 Hz, 2H, Har), 7.39 (d, J = 7.8 Hz, 2H, Hp), 7.38 (d, J = 16.0 Hz, 1H, Het), 6.75 (d, J = 8.7 Hz, 2H, Har), 3.04 (s, 3H, CH$_3$); HRMS (TOF ES$^+$) m/z calculated for $C_{23}H_{21}N_3O_2$ 371.1634; found 371.1637.

Preparation of **NODSF** and **NODST**. The mixtures of four isomers of **NODSF** and **NODST** were obtained after the third reaction step (Scheme 4) by column chromatography on silica gel using petroleum ether/diethyl ether mixture as eluent. The geometrical isomers thus obtained were separated and purified by HPLC. The complete procedure for the preparation of **NODSF** and **NODST** can be found in Supporting material.

Yield for the mixture of four isomers of **NODSF**: 40%.

E,E-**NODSF**: R_f 0.52 (petroleum ether/diethyl ether 1:0.43); red solid; m.p. 169 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ_H 8.20 (d, J = 8.8 Hz, 2H, Har), 7.59 (d, J = 8.8 Hz, 2H, Har), 7.45 (d, J = 8.7 Hz, 2H, Har), 7.13 (d, J = 16.3 Hz, 1H, Het), 7.12 (d, J = 16.2 Hz, 1H, Het), 7.00 (d, J = 16.3 Hz, 1H, Het), 6.91 (d, J = 8.7 Hz, 2H, Har), 6.76 (d, J = 16.2 Hz, 1H, Het), 6.51 (d, J = 3.5 Hz, 1H, Hf), 6.38 (d, J = 3.5 Hz, 1H, Hf), 3.84 (s, 3H, OCH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ_C 159.7 (s), 154.6 (s), 151.6 (s), 146.4 (s), 143.8 (s), 129.5 (s), 128.3 (s), 128.3 (d), 127.8 (2d), 126.5 (2d), 124.2 (2d), 124.0 (d), 120.1 (d), 114.3 (2d), 114.1 (d), 113.9 (d), 110.7 (d), 55.4 (q); HRMS (TOF ES$^+$) m/z calculated for $C_{21}H_{17}NO_4$ 347.1163; found 347.1158.

Yield for the mixture of four isomers of **NNDST**: 30%.

E,E-**NODST**: R_f 0.27 (petroleum ether/diethyl ether 1:0.25); orange solid; m.p. 203 °C; ^{1}H NMR (CDCl$_3$, 600 MHz) δ_H 8.20 (d, J = 8.80 Hz, 2H, Har), 7.56 (d, J = 8.8 Hz, 2H, Har), 7.42 (d, J = 8.4 Hz, 2H, Har), 7.33 (dd, J = 16.0 Hz, 1H, Het), 7.06 (dd, J = 16.0 Hz, 1H, Het), 7.05 (d, J = 3.8 Hz, 1H, Ht), 6.95 (d, J = 3.8 Hz, 1H, Ht), 6.91 (d, J = 15.7 Hz, 1H, Het), 6.90 (d, J = 8.7 Hz, 2H, Har), 6.89 (d, J = 15.7 Hz, 1H, Het), 3.84 (s, 3H, CH$_3$); ^{13}C NMR (150 MHz, CDCl$_3$) δ_C 159.7 (s), 146.6 (s), 144.4 (s), 143.6 (s), 139.9 (s), 129.4 (s), 129.3 (2d), 127.8 (2d), 126.5 (2d), 126.4 (d), 126.3 (d), 125.3 (d), 124.2 (2d), 119.5 (d), 114.3 (2d), 55.4 (q); HRMS (TOF ES$^+$) m/z calculated for $C_{21}H_{17}NO_3S$ 363.0934; found 363.0930.

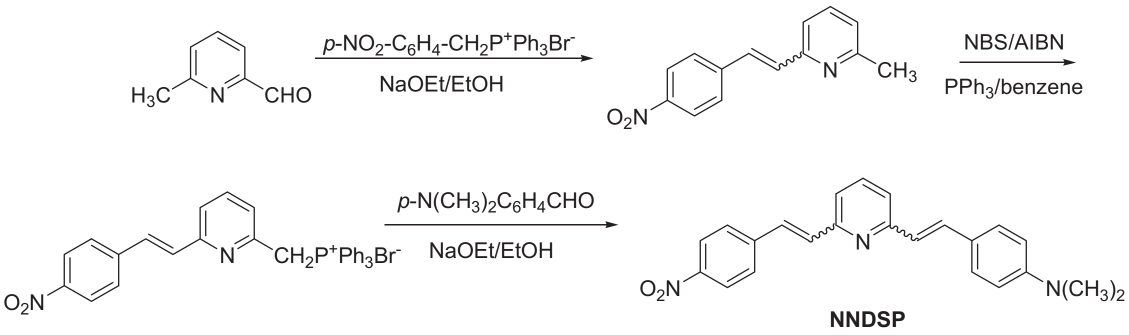
Preparation of **NODSP**. A solution of sodium ethoxide was added dropwise (92 mg, 4 mmol Na in 10 mL ethanol) to a stirred solution of 6-methyl-2-pyridinecarboxaldehyde (4 mmol) and *p*-methoxybenzyl–triphenylphosphonium bromide (4 mmol) in absolute ethanol (50 mL) (Scheme 5). Stirring was continued under the stream of nitrogen for 1 day at RT. After removal of the solvent, water was added to the residue, extracted with benzene and the benzene extract dried with MgSO$_4$. The product was purified by column chromatography on silica gel using petroleum ether/diethyl ether mixture as eluent. A suspension of the obtained mixture of *cis* and *trans* isomers of styrylpyridine derivative (3.3 mmol) in acetic anhydride (3 mL) and *p*-nitrobenzaldehyde (3.3 mmol) was heated at 160 °C for 10 h (Scheme 5). The solution is then concentrated to a small volume at reduced pressure giving a crystalline solid. After filtration of solid reaction mixture the product **NODSP** was purified by column chromatography on silica gel using diethyl ether as eluent. The geometrical isomers thus obtained were separated and purified by HPLC.

Yield for the mixture of four isomers of **NODSP**: 50%.

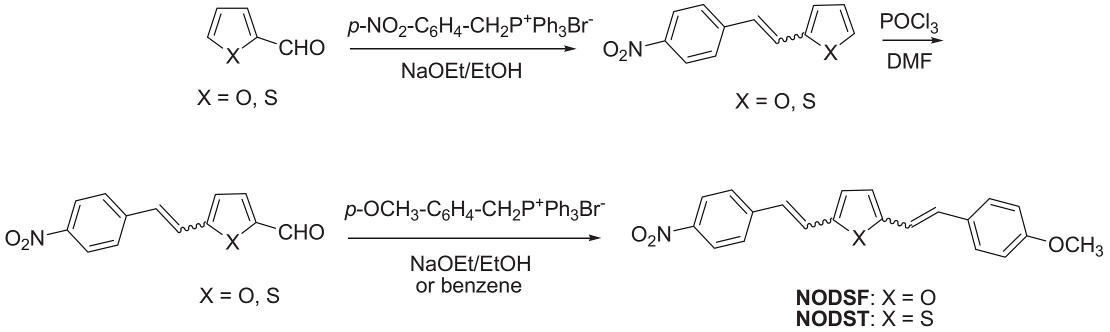
E,E-**NODSP**: R_f 0.10 (petroleum ether/diethyl ether 1:0.25); yellow solid; m.p. 171 °C; ^{1}H NMR (CDCl$_3$, 300 MHz) δ_H 8.25 (d, J = 8.8 Hz, 2H, Har), 7.78 (d, J = 16.1 Hz, 1H, Het), 7.73 (d, J = 8.8 Hz, 2H, Har), 7.68 (d, J = 16.1 Hz, 1H, Het), 7.67 (t, J = 7.7 Hz, 1H, Hp), 7.56 (d, J = 8.8 Hz, 2H, Har), 7.32 (d, J = 16.1 Hz, 1H, Het), 7.30 (dd, J = 7.7; 0.7 Hz, 1H, Hp), 7.26 (dd, J = 7.7; 0.7 Hz, 1H, Hp), 7.09 (d, J = 16.1 Hz, 1H, Het), 6.93 (d, J = 8.8 Hz, 2H, Har), 3.85 (s, 3H, OCH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$) δ_C 160.0 (s), 156.1 (s), 154.0 (s), 147.2 (s), 143.4 (s), 137.1 (d), 132.9 (d), 132.6 (d), 130.2 (d), 129.4 (s), 128.5 (2d), 127.5 (2d), 125.8 (d), 124.1 (2d), 121.2 (d), 121.0 (d), 114.2 (2d), 55.4 (q); HRMS (TOF ES$^+$) m/z calculated for $C_{22}H_{18}N_2O_3$ 359.1389; found 359.1386.

2.2. Spectral, photophysical and photochemical measurements

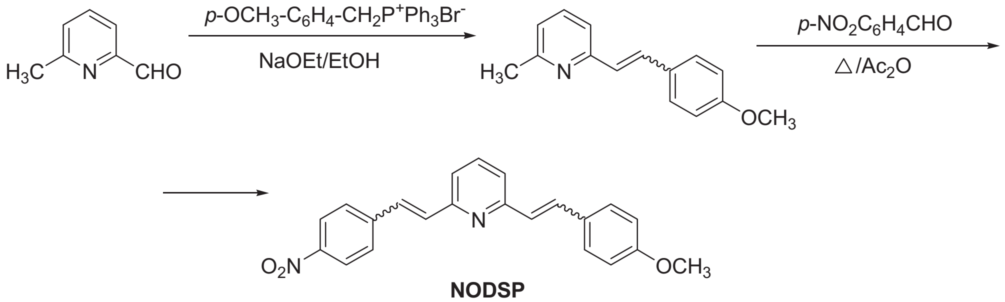
Absorption spectra were recorded on a Perkin-Elmer Lambda 800 and a Cary 4E Varian spectrophotometers. The experimental oscillator strength was derived by $f = (4.39 \times 10^{-9} \int \varepsilon(\bar{\nu})\, d\bar{\nu})/n$ [19], considering the refraction index $n \cong 1$. Fluorescence emission spectra were measured with a Fluorolog-2 (Spex, F112AI) fluorimeter. Dilute solutions (absorbance smaller than 0.1 at the excitation wavelength, λ_{exc}) were used for fluorimetric steady-state measurements. Fluorescence quantum yields (ϕ_F, experimental error of ca. 10%, from three independent experiments) were determined by use of tetracene in cyclohexane (CH) (ϕ_F = 0.17 in air-equilibrated solvent) [20] and 9,10-diphenylanthracene in CH (ϕ_F = 0.90 in



Scheme 3. Preparation of **NNDSP**.



Scheme 4. Preparation of **NODST**.



Scheme 5. Preparation of **NODSP**.

de-aerated solvent) [21] as fluorimetric standards. Fluorescence lifetimes were measured by an Edimburgh Instrument 199S spectrofluorimeter, using the single photon counting method with a LED source centred at 461 nm, coupled with an interference filter centred at 460 nm in the excitation line and a cut-off in emission at 500 nm (time resolution of the experimental set-up ca. 0.5 ns).

For photochemical measurements, a 500 W mercury lamp coupled with an interferential filter at λ_{exc} = 436 nm was used for **NODSF** and **NODST**; a xenon lamp coupled with appropriate interferential filters was used for **NNDSF, NNDST**, **NODSP** and **NNDSP**. Potassium ferrioxalate in 0.1 N sulphuric acid was used as actinometer. The photoreaction (solute concentration $\sim 10^{-4}$ M) was monitored by HPLC using a Waters apparatus equipped with a Prontosil 200-3-C30 (4.6 mm × 250 mm; 3 μm) column at 40 °C and an UV detector. Water/acetonitrile mixtures (10%/90% or 20%/80%) were used as eluents during the first minutes of the separation procedure replaced then by 100% acetonitrile. The monitoring wavelength was at the isosbestic point between the EE isomer and the photoproduct absorption, otherwise corrections for different absorption coefficients were introduced. The conversion percentage was held at below 8% to avoid the competition from the back photoreaction. The photoreaction quantum yields (ϕ_{ISO}) are averages of at least two independent experiments with mean deviations of 15%. A larger uncertainty should be ascribed to the value of **NNDSP** where the sample available allowed only one measurement.

All the measurements were performed in deaerated solutions by bubbling with nitrogen.

2.3. Computational details

Quantum-mechanical calculations were carried out using the HyperChem computational package (version 7.5). Total energies and dipole moments were obtained for geometries optimized by HF ab initio (3-21-G level) method. The computed transition energies and oscillator strengths were obtained by ZINDO/S at the optimized geometries, the configuration interaction including 64 (8 × 8) single excited configurations. The value of the excited state dipole moment (μ^*) was estimated by the "next lowest" function in the ZINDO/S method.

Table 1
Spectral properties (absorption maxima wavelength, λ_{abs}, and coefficient, ε^{max}, fluorescence maxima wavelength, λ_F, emission vibronic progression, $\Delta\bar{\nu}_F$ and Stokes shift, $\Delta\bar{\nu}_S$) of the investigated compounds in CH (those of the unsubstituted analogues are reported for comparison).[a]

Compound	λ_{abs} (nm)	ε^{max} (M^{-1} cm^{-1})	λ_F (nm)	$\Delta\bar{\nu}_F$ (cm^{-1})	$\Delta\bar{\nu}_S$ (cm^{-1})
NNDSF	$\underline{465}$, 505^{sh}	35,550	536, $\underline{577}$, 620^{sh}	1330	4170
NNDST	$\underline{460}$, 505^{sh}	33,750	536, $\underline{576}$, 620^{sh}	1300	4380
NNDSP	336^{sh}, $\underline{362}$		472, $\underline{500}$	1190	7620
NODSF	420^{sh}, $\underline{441}$, 470^{sh}	29,750	486, $\underline{519}$, 555	1310	3410
NODST	416^{sh}, $\underline{436}$, 463^{sh}	27,920	486, $\underline{518}$, 557	1270	3630
NODSP	$\underline{323}$, 365	41,940, 23,350	–	–	–
2,5-DSF[b]	363^{sh}, $\underline{382}$, 400^{sh}	44,400	416, $\underline{442}$, 470	1400	3550
2,5-DST[c]	374^{sh}, $\underline{392}$, 415^{sh}	41,000	435, $\underline{461}$, 489^{sh}	1300	3820
2,6-DSP[d]	$\underline{291.5}$, 306^{sh}	44,000	367^{sh}, $\underline{379}$, 400^{sh}	1390	6290

[a] The underlined values and ε^{max} refer to the main maxima.
[b] From Ref. [17].
[c] From Ref. [15].
[d] From Ref. [18].

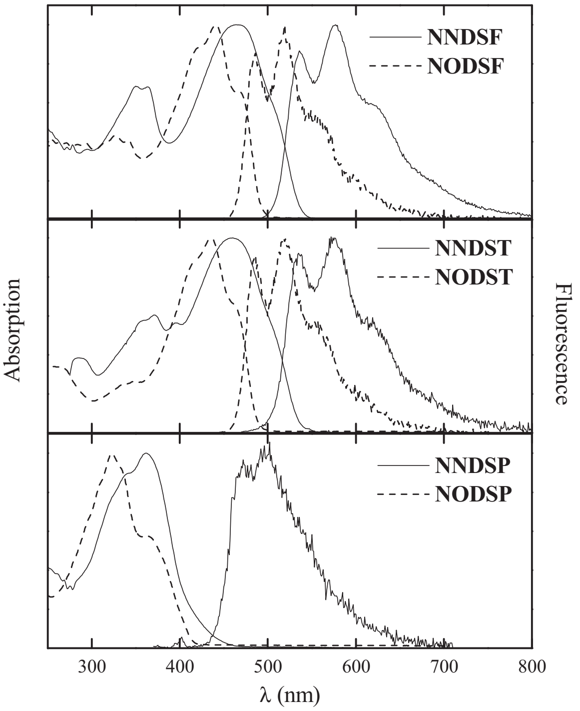


Fig. 1. Normalized absorption and emission spectra of the investigated compounds in CH.

3. Results and discussion

3.1. Spectral properties

The absorption and emission spectra of the investigated compounds in CH are shown in Fig. 1 and the main spectral properties are collected in Table 1 with those of the unsubstituted analogues (2,5-distyrylfuran, **2,5-DSF**, 2,5-distyrylthiophene, **2,5-DST**, and 2,6-distyrylpyridine, **2,6-DSP**) for comparison purposes.

The absorption and emission spectra of the compounds having the furan and thiophene as a central ring, are shifted to the red with respect to the pyridine-derivatives, in agreement with their highly conjugated structures. As previously reported for analogous compounds, the presence of poorly aromatic furan or thiophene is responsible for the spectral behaviour very similar to that of α,ω-diphenyloctatetraenes [17,22] and for the appearance of a second absorption band at higher energy, in the 300–400 nm range. In the case of the unsubstituted analogues, the latter band was assigned to the *cis* peak predicted by calculations as peculiar of the compressed rotamer [22].

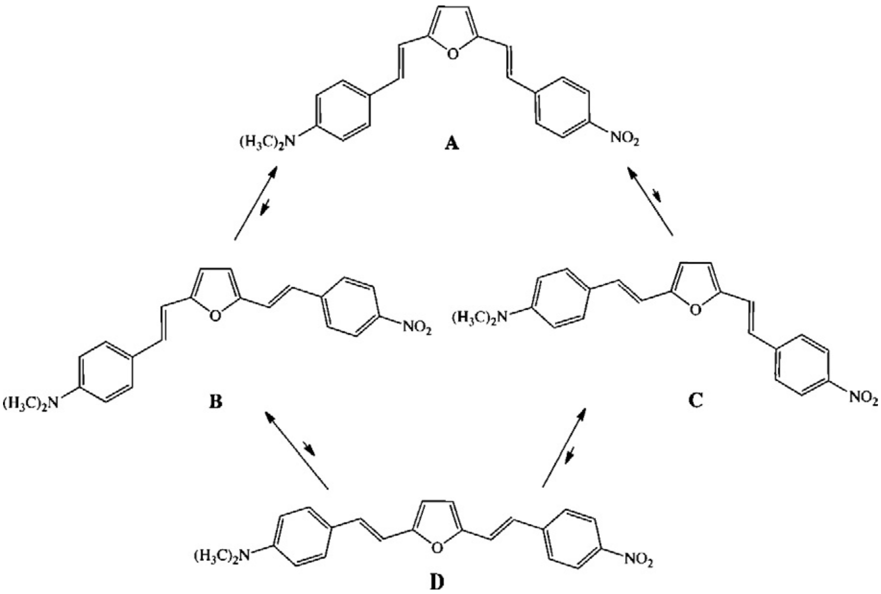
The dimethylamino group causes a further red shift of the spectra if compared with the analogous methoxy-derivatives, the first absorption band becoming a bell-shaped curve (see Fig. 1). In **NODSP**, the double absorption band, characteristic of systems with ethenic bridges in the ortho position with respect to the nitrogen heteroatom of pyridine [18,23], is particularly evident.

The emission spectra of furan and thiophene-derivatives are well structured with a vibrational progression around 1300 cm^{-1}, characteristic of ethene derivatives. The **NNDSP** is poorly fluorescent, while its methoxy analogue does not emit at all. Comparison of the spectral properties of these push–pull systems bearing electron donor/acceptor groups with the unsubstituted (Table 1) and monosubstituted [4] analogues shows a significant red shift, reasonably assignable to the CT character of the first transitions (see below).

In principle, these flexible molecules could exist at room temperature as an equilibrium mixture of different conformers [24,25], originating by rotation around the quasi-single bonds between the central ring and the ethenic bridges (see the conformational equilibrium of *EE*-**NNDSF** in Scheme 6, as an example). Table 2 reports the dipole moments of the ground and excited states, the total energy and the spectral properties computed for the compounds investigated. The calculations were carried out for all the four rotamers of **NNDSF**, as an example, and for the pyridyl-derivatives, where a conformational equilibrium was expected on the basis of the comparison with the unsubstituted analogue [18]. In the other cases, only the results for elongated and compressed species are reported.

In the furan and thiophene analogues, quantum-mechanics calculations predicted a conformational equilibrium completely shifted towards the compressed most stable conformer (see Table 2 and Scheme 6), as in the case of the unsubstituted **2,5-DSF** and **2,5-DST**. This finding is in agreement with the absence of a wavelength effect on the excitation and emission spectra and with the observed mono-exponential decay (see below, Table 3).

Also for the pyridine-derivatives the compressed species was found to be the most stable conformer, the other rotamers not contributing to the spectral and photophysical properties owing to their total energy (E_{tot} in Table 2) higher (>2 kcal/mol) than that of the compressed one. This behaviour is contrary to what was reported for the unsubstituted **2,6-DSP**, where at least two conformers were predicted to exist in equilibrium at room temperature and the photophysical and photochemical study allowed the properties of two different species to be separated [18]. Unluckily, the very scarce emission yield of these pyridine derivatives did not allow the usual excitation wavelength effect on the conformational



Scheme 6. Conformational equilibrium of *EE*-**NNDSF**.

equilibria [24,25] to be investigated. This behaviour, contrary to that of **2,6-DSP**, suggests that the push–pull substituents stabilize preferentially the more rigid and planar compressed rotamer.

It has to be noted that interactions between the heteroatom of the central ring and the ethenic hydrogens can play a role in the conformational equilibrium of these systems, at least in the pyridine-derivatives [18,26]. The NMR spectrum carried out in deuterated chloroform containing a small water percentage shows four doublets at δ = 7.78, 7.68, 7.32 and 7.09 ppm with coupling constants typical of ethenic hydrogens in a *trans* configuration (J = 16.1 Hz), assigned to H_1, H_3, H_2 and H_4, respectively (see Scheme 7). In deuterated benzene the resonance of H_1 and H_3 occurs at lower frequencies (δ = 7.99 and 7.76 ppm, respectively), while the signal of H_2 and H_4 shifts to higher frequencies (δ = 7.2 and 7.0 ppm, respectively), as expected because of the shielding effect of the benzene ring. The shift to lower frequencies observed for H_1 and H_3 (0.21 and 0.08 ppm, respectively) in the non-protic solvent, even if smaller than that found for the unsubstituted analogue (0.42

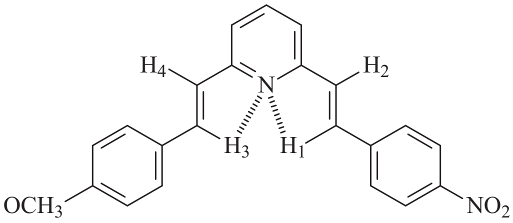
Table 2
Calculated spectral properties (transition wavelength, λ, and oscillator strength, f), total energy (E_{tot}) and dipole moment of the ground (μ) and excited (μ^*) states for the rotamers of the investigated compounds. The experimental absorption maximum (λ_{exp}) and oscillator strength (f_{exp}) are reported for comparison.

Compound	Conformer	μ (D)	μ^* (D)	E_{tot} (kcal/mol)	λ (nm)	f		λ_{exp} (nm)	f_{exp}
NNDSF	Elongated(D)	10.1	24.89	−735,098.750					
	Semicomp(C)	9.86	24.37	−735,101.313					
	Semicomp(B)	9.23	23.96	−735,101.125					
	Compressed(A)	9.01	22.96	−735,103.813	441	0.94	S_1	467	0.70
					352	0.45	S_2	364,351	0.51
					289	0.61	S_6		
NODSF	Elongated	9.24	22.58	−723,117.688					
	Compressed	6.26	18.9	−723,122.750	432	1.00	S_1	441	0.61
					345	0.37	S_2	327	0.22
					282	0.53	S_6		
NNDST	Elongated	10.61	24.91	−936,601.688					
	Compressed	10.14	23.73	−936,605.563	428	1.32	S_1	460	0.90
					347	0.46	S_2	372	0.42
					283	0.35	S_6		
NODST	Elongated	9.04	21.77	−924,620.689					
	Compressed	7.24	19.15	−924,624.563	429	0.96	S_1	435	0.57
					339	0.44	S_2	344	0.18
					285	0.48	S_6	270,245	
NNDSP	Elongated	8.56	23.87	−746,362.500					
	Semicomp(C)	9.31	25.16	−746,368.438					
	Semicomp(B)	8.44	25.35	−746,368.189					
	Compressed	8.41	21.53	−746,370.813	374	0.83	S_1	362	
					323	0.49	S_2	340	
					313	0.33	S_4		
					286	0.59	S_7	240	
NODSP	Elongated	9.55	24.0	−734,384.688					
	Semicomp(C)	9.57	24.08	−734,387.500					
	Semicomp(B)	5.89	19.85	−734,387.438					
	Compressed	6.03	20.11	−734,389.938	372	0.86	S_1	363	0.28
					319	0.35	S_2	323	1.23
					276	0.77	S_7	220	0.38
					259	0.25	S_8		

Table 3
Fluorescence properties and *trans* → *cis* photoisomerization quantum yields (ϕ_{ISO}) of the investigated compounds in CH. The parameters for the unsubstituted analogues are reported for comparison.

Compound	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})	ϕ_{ISO}
NNDSF	0.80	2.6	3.1	0.0025
NNDST	0.74	1.8	4.2	0.0074
NNDSP	0.085	<0.5	>1.7	(~0.20)[a]
NODSF	0.77	2.2	3.5	0.028
NODST	0.30	0.87	3.5	0.20
NODSP	–	–	–	0.26 (EZ), 0.072 (ZE)
2,5-DSF[b]	0.68	2.9	2.3	0.0003
2,5-DST[c]	0.30	0.85	3.5	0.03
2,6-DSP[d]	0.72/0.24	3.5/1.5	2.1/1.6	0.075/0.14

[a] The value in parentheses accounts for its larger uncertainty (see Section 2).
[b] In toluene, from Ref. [17].
[c] In toluene, from Ref. [15].
[d] In MCH/3MP, from Ref. [18] (the two fluorescence and photoisomerization parameters refer to the two main conformers).



Scheme 7. H-type bonds between the ethenic hydrogens and the central nitrogen atom in the compressed rotamer of **NODSP**.

for **2,6-DSP** on going from methanol to benzene [18]) indicates that stabilizing intramolecular N···H interactions in the latter solvent favour the compressed rotamer whereas in more protic solvent such stabilization is broken by intermolecular interactions with the medium.

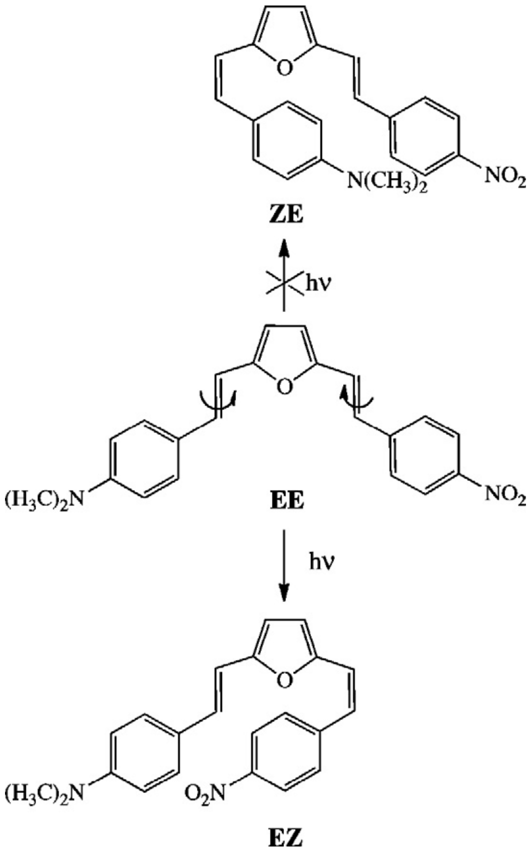
The computed dipole moments, already high for the ground state, increase strongly under excitation indicating a further significant increase of the CT character. This was also confirmed by the computed charge distribution of the main configurations involved in the $S_0 \rightarrow S_1$ transition of the all-*trans* isomers (the case of **NODSF** is shown in Fig. 2 as an example, while the others can be found in Supplementary Data) that shows a net shift of the charge density towards the double bond adjacent to the *p*-nitrophenyl moiety under excitation (see also next section).

3.2. Photobehaviour

The fluorescence quantum yields (ϕ_F) and lifetimes (τ_F) together with the emission kinetic constant (k_F) and the geometrical photoisomerization quantum yield (ϕ_{ISO}) in CH are collected in Table 3.

High fluorescence quantum yields were found in the case of dimethylamino-substituted furan and thiophene derivatives while they selectively photoisomerize towards the EZ isomer (see Scheme 8) with very low yields. The fluorescence rate constants of the order of 10^8 s^{-1} point to an allowed transition for the $S_1 \rightarrow S_0$ emission.

The replacement of the dimethylamino by the methoxy group in the compounds with 5-membered central groups causes an increase of reactivity of roughly one order of magnitude that leads to a significant value for $\phi_{EE \rightarrow EZ}$ and an important decrease of ϕ_F and τ_F in the case of **NODST**. The coupling between emission and photoreaction could suggest a singlet diabatic mechanism for the photoreaction that involves $S_1 \rightarrow S_0$ internal conversion (IC) at the perpendicular configuration (P, at about 90°) and relaxation to the ground-state isomers, $^1E^* \rightarrow {}^1P^* \rightarrow {}^1P \rightarrow \alpha {}^1Z + (1-\alpha){}^1E$, where the partitioning factor α towards Z and E, is assumed to be ~0.5 in most cases [27]. However, a contribution of ISC followed by rotation in the triplet state cannot be ruled out at this stage.



Scheme 8. Geometrical isomers formed by irradiation of *EE*-**NNDSF**.

The selective rotation of the double bond adjacent to the nitrophenyl group is hypothesized on the basis of the calculated spectra of the EZ and ZE geometric isomers and confirmed by NMR measurements [28]. In Fig. 3 the calculated spectra (vertical bars) for the EE, EZ and ZE isomers of **NODSF**, as an example, are compared with the experimental spectra of the reagent (EE) and the photoproduct detected by HPLC. This comparison led to the assignment of the main photoproduct to the EZ structure.

The preferential photoisomerization of the double bond adjacent to the nitrophenyl group is in agreement with the localization of the excitation energy in this moiety of the molecule as shown in Fig. 2 for **NODSF**, by the calculated highest occupied and lowest unoccupied molecular orbitals.

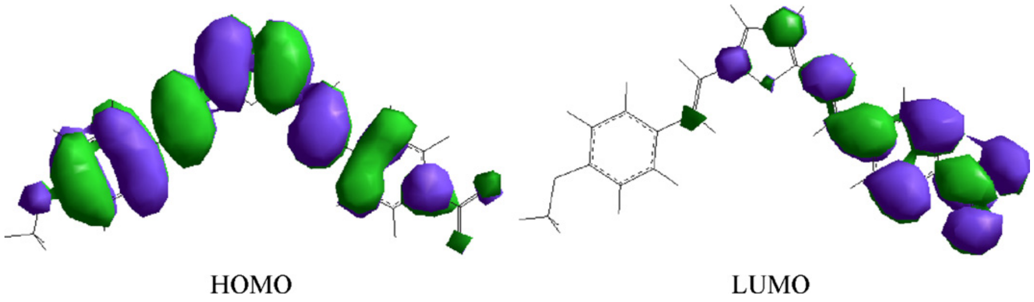


Fig. 2. Molecular orbitals of **NODSF** as derived by ZINDO/S method. The HOMO-LUMO configuration contributes to the main electronic transition with the highest coefficient (−0.566225).

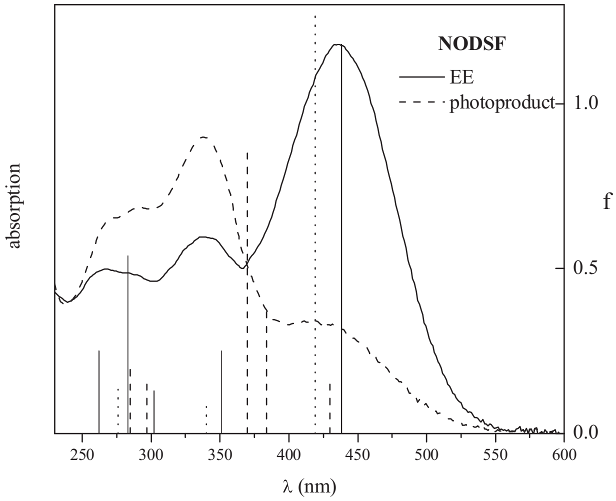


Fig. 3. Absorption spectrum of *EE*-**NODSF** and its photoproduct as derived by HPLC diode-array instrument. The vertical bars refer to the calculated transitions for the most stable rotamer of EE (full line), EZ (dashed) and ZE (dotted) isomers.

In the case of **NODSP**, internal rotation of the double bond adjacent to the methoxy-phenyl group, that leads to the ZE isomer, was also observed, but with a lower yield (Table 3).

The excited state relaxation yields of the compounds with a central furan group do not show important changes with respect to the unsubstituted [17] and mono(nitro)-substituted [4] analogues previously investigated (high emission and quite low isomerization yields). The sizable decrease of fluorescence and increase of reactivity of the thiophene compared to the furan derivatives, previously reported and probably due to ISC induced by the sulphur heteroatom [15], was here maintained for the methoxy-substituted **NODST** only, whereas the dimethylamino-substituted **NNDST** displays a behaviour similar to the furan analogue.

The compounds with the central pyridine ring, despite the scarce amount of the sample of **NNDSP** available, that limited the measurements, showed the strongest changes in the relaxation properties. In fact, while the unsubstituted compound, **2,6-DSP**, where two rotamers are present in solution, shows prevalent emissive and modest reactive decays [18], the largely prevalent rotamer of the di-substituted compounds here investigated shows a strong decrease of fluorescence accompanied by a significant increase of photoreactivity.

4. Conclusive remarks

The push–pull systems synthesized and studied here can be considered very interesting for applications in photonics due to their peculiar spectral properties and photobehaviour.

The computed formation enthalpies indicate that only the most stable compressed A rotamer is present in solution at room temperature, even if these systems can exist, in principle, as a dynamic equilibrium of different conformers.

The introduction of strong electron donor/acceptor groups in conjugative (para) position of the side phenyl rings, leads to a strong red shift of the absorption and emission spectra, mainly in the case of dimethylamino-derivatives, indicating an increased CT character of the excited singlet states, making these systems of potential interest as active materials in organic solar cells.

The different nature of the first excited singlet state of these compounds (also underlined by the large values of their computed dipole moments) with respect to the unsubstituted analogues, does not affect the emissive properties in the case of thiophene and furan derivatives, where ϕ_F remains high, at least in a non polar solvent.

On the other hand, in the pyridine-derivatives, the absorption spectral shape does not change too much if compared with that of **2,6-DSP** but the photobehaviour is quite different with a drastic reduction of fluorescence and an increase of the non-radiative deactivation pathways.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jphotochem.2012.06.009.

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