Synthesis and photobehaviour of donor-π-acceptor conjugated arylacetylenes

Rebecca Flamini, Ivan Tomasi, Assunta Marrocchi*, Benedetta Carlotti, Anna Spalletti**

Dipartimento di Chimica and Centro di Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università degli Studi di Perugia, Via Elce di Sotto, 8, 06123 Perugia, Italy

ABSTRACT

Two series of soluble and thermally stable asymmetric arylacetylene derivatives bearing a fluorene (Fl-Xs) or an anthracene (An-Xs) core unit and end-substituted with different electronically active groups ($X = NO_2$, CN, CHO and OR) were synthesized and characterized. The spectral and photophysical behaviour of these compounds was studied in two solvents of different polarity to evaluate them as candidates for the role of active materials in optoelectronic devices. The presence of intramolecular charge transfer states, strongly stabilized in the polar solvent, was found mainly in the nitro-anthryl and fluorenyl-derivatives. A complete picture of the excited states nature and their deactivation channels was also achieved by semiempirical quantum-mechanical calculations.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

During the last decades the interest in push–pull (D-π-A) systems, comprising an electron-releasing donor unit (D), a π-conjugated bridge, and an electron-withdrawing acceptor unit (A) has increased dramatically due to potential applications in several fields such as telecomunication, organic electronics, optical data storage and optical information. Moreover, these materials have been used extensively for non-linear optic (NLO) applications. Because efficient intramolecular charge transfer may occur from the donor unit to the acceptor unit upon excitation, such chromophores are strong light-absorbing dyes possessing a broad absorption window extending to the near-IR region. More importantly, the band-gap of D-π-A chromophores can be simply controlled by adjusting the electron donating strength of the donor and the electron withdrawing strength of the acceptor units in the dye. As a result, D-π-A chromophores have been used as effective photoactive materials in energy conversion devices [1–4].

In this context, linear conjugated organic molecules peripherally functionalized with electron donating and electron accepting species at the extremities are good candidates for the role of active materials in optoelectronic devices [5–10].

Here we report the synthesis, the spectral characterization and the photobehaviour of two series of soluble and thermally stable asymmetric arylacetylene derivatives comprising a fluorene or anthracene core unit and end-substituted with different electronically active groups (Scheme 1).

Conjugated (poly)arylacetylenes have emerged as a promising class of semiconducting materials [11–13]. Among their important properties are their rigid shape-persistent structures, which are highly controllable due to precise and efficient synthetic approaches, their interesting photophysics, and structural diversity.

Note that the fluorene-based compounds **1** have been designed keeping in mind that π-conjugated fluorene-based semiconductors exhibit a great ability in displaying high-levels of photo- and electroluminescence as well as useful electronic charge transport properties [14,15]. Recently, a promising photovoltaic performance has been achieved through incorporation of such compounds in bulk heterojunction solar cells [16–18]. Additionally, we report here anthracene-containing arylacetylene derivatives **2** and **3**. It is known that anthracene structure may enable large carrier mobilities, greater solubility, and improved stability as compared to pentacene [19,20], which has become a benchmark in the organic opto-electronic field. Moreover, it is a good chromophore. For these reasons we synthesized new arylacetylenes **2** as analogues of compounds **1** in which an anthracene unit replaces the fluorene core. The nitro-derivative **3** was also resynthesized [21] for comparison purposes.

The comparison of the **1–3** spectral and photophysical behaviour allowed to gain insights into the correlation between molecular structure and excited state electronic properties. The effects of the presence of different electronically active peripheral substituents on the photobehaviour of these systems have been also discussed and related to the presence of intramolecular charge transfer (ICT) states strongly stabilized by polar solvents.

* Corresponding author. Tel.: +39 075 5855547; fax: +39 075 5855560.
** Corresponding author. Tel.: +39 075 5855575; fax: +39 075 5855598.
E-mail addresses: assunta@unipg.it (A. Marrocchi), faby@unipg.it (A. Spalletti).
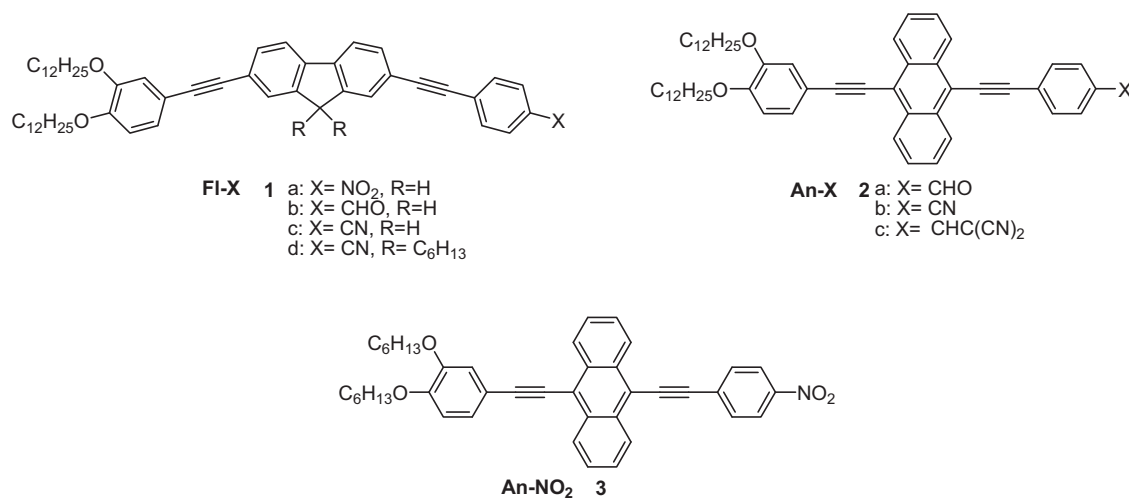
Scheme 1. Investigated compounds.

Furthermore, we performed semiempirical quantomechanical calculations to estimate the dependence of the spectral properties, heats of formation, and dipole moments of the ground and excited states on the structure of the corresponding arylacetylene derivatives. Finally, this study can be helpful to drive the synthesis towards innovative functionalized materials with progressively higher performance in optoelectronic devices.

2. Experimental

2.1. Synthesis

All reagents were purchased from Sigma–Aldrich Co. and used without further purification unless otherwise noted. Anhydrous THF was distilled from Na/benzophenone, and toluene was distilled from LiAlH$_4$. Petroleum ether was used as the 40–60° boiling fraction. Chromatography was performed on Riedel de Haën silica gel (230–400 mesh ASTM). Melting points were determined on a Büchi melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Associates VXR-400 multinuclear spectrometer (internal SiMe$_4$). Elemental analyses were performed on a Fisons EA 1108 instrument. Mass spectrometry was performed with a Thermo Finnegan model LCQ Advantage mass spectrometer.

*Synthesis of 2-{[m,p-didodecyloxyphenyl]ethynyl}-7-[(p-nitrophenyl)ethynyl]-fluorene (**1a**).* Dry toluene (6 ml), bromoderivative **6a** (0.42 g, 1.1 mmol), CuI (0.04 g, 0.02 mmol), Pd(PPh$_3$)$_4$ (0.02 g, 0.02 mmol) and diisopropylamine (3 ml) were placed in a flask and degassed with argon at 0 °C. m,p-(Dodecyloxy)-4-ethynylbenzene (0.47 g, 1 mmol) was then added and the mixture was kept at 75 °C overnight. Next, the solvent was evaporated to dryness, and the crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 4:1). Yield: 62% (yellow crystals); m.p.: 135–136 °C (toluene); ^{1}H NMR (CDCl$_3$) δ: 8.19 (d, J = 9 Hz, 2H), 7.76–7.50 (m, 8H), 7.09–7.02 (m, 2H), 6.80 (d, J = 8.2 Hz, 1H), 3.95 (m, 6H), 1.77 (m, 4H), 1.51–1.22 (m, 36H), 0.82 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 149.7, 148.7, 146.8, 143.6, 142.3, 140.5, 132.2, 131.0, 130.6, 130.4, 128.4, 128.0, 124.9, 123.7, 122.5, 120.2, 120.2, 116.5, 115.2, 113.1, 95.6, 90.4, 88.3, 87.9, 69.2, 69.1, 36.5, 31.9, 29.7, 29.6, 29.4, 29.4, 29.2, 26.0, 22.7, 14.1. An. Calcd. for C$_{53}$H$_{65}$NO$_4$: C, 81.60; H, 8.40; N, 1.80. Found: C, 82.90; H, 8.39; N, 1.78%. MS (high resolution, EI) *m/z*: M+ Calcd: 780.088, Found: 780. 089.

*Synthesis of p-[(2-{[m,p-didodecyloxyphenyl]ethynyl}-7-fluorenyl)ethynyl]benzaldehyde (**1b**).* This compound was prepared by coupling of **6b** with m,p-(dodecyloxy)-4-ethynylbenzene (1:1.1 molar ratio), following the above procedure. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 1.5:1). Yield: 71% (yellow crystals); m.p.: 124–126 °C (ethyl acetate); ^{1}H NMR (CDCl$_3$) δ: 9.99 (s, 1H), 7.86–7.50 (m, 10H), 7.06 (m, 2H), 6.80 (d, J = 8.3 Hz, 1H), 3.95 (m, 6H), 1.77 (m, 4H), 1.49–1.22 (m, 36H), 0.82 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 149.8, 143.6, 142.0, 132.0, 130.9, 130.6, 129.6, 128.4, 128.0, 125.0, 120.8, 120.2, 120.1, 116.6, 115.3, 113.3, 69.3, 69.2, 36.6, 31.9, 29.6, 29.4, 29.4, 29.2, 26.0, 22.7, 14.1. An. Calcd. for C$_{54}$H$_{66}$O$_3$: C, 84.99; H, 8.72. Found: C, 83.90; H, 8.71%. MS (high resolution, EI) *m/z*: M+ Calcd: 763.100, Found: 763.092.

*Synthesis of p-[(2-{[m,p-didodecyloxyphenyl]ethynyl}-7-fluorenyl)ethynyl]benzonitrile (**1c**).* This compound was prepared by coupling of **6c** with m,p-(dodecyloxy)-4-ethynylbenzene (1:1.1 molar ratio), following the above procedure. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 2.5:1). Yield: 37% (yellow crystals); m.p.: 124–125 °C (toluene); ^{1}H NMR (CDCl$_3$) δ: 7.68 (m, 4H), 7.58 (m, 6H), 7.05 (m, 2H), 6.80 (d, J = 8.3 Hz, 1H), 3.96 (m, 4H), 3.88 (s, 2H), 1.78 (m, 4H), 1.51 (s, 2H), 1.42 (m, 4H), 1,21 (m, 30H), 0.82 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 143.6, 140.6, 132.0, 132.0, 130.9, 130.5, 128.3, 128.0, 124.9, 122.5, 120.4, 120.2, 120.1, 116.7, 115.3, 113.3, 69.2, 69.1, 36.5, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 22.6, 14.1. An. Calcd. for C$_{54}$H$_{65}$NO$_2$: C, 85.33; H, 8.62; N, 1.84. Found: C, 86.90; H, 8.63; N, 1.80%. MS (high resolution, EI) *m/z*: M+ Calcd: 760.099, Found: 760.100.

*Synthesis of p-[(2-{[m,p-didodecyloxyphenyl]ethynyl}-9,9-dihexyl-7-fluorenyl)ethynyl]benzonitrile (**1d**).* This compound was prepared by coupling of **6a** with m,p-(dodecyloxy)-4-ethynylbenzene (1:1.1 molar ratio), following the above procedure. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 4:1). Yield: 84% (white crystals); m.p.: 69–70 °C (hexane); ^{1}H NMR (CDCl$_3$) δ: 7.60 (m, 6H), 7.47 (m, 4H), 7.08 (dd, J = 1.95, 1.92 Hz,1H), 7.02 (s, 1H), 6.79 (d, J = 8.3 Hz), 3.97 (m, 4H), 1.92 (m, 4H), 1.78 (m, 4H), 1.50 (s, 2H), 1.42 (m, 5H), 1.21 (m, 33H), 1.04 (m, 12H), 0.83 (m, 6H), 0.71 (m, 6H), 0.55 (m, 4H); ^{13}C NMR (CDCl$_3$) δ: 151.2, 151.1, 149.8, 148.7, 141.6, 140.0, 132.0, 132.0, 131.0, 130.6, 128.4, 126.0, 125.8, 124.9, 122.6, 120.6, 120.0, 120.0, 118.5, 116.6, 115.2, 113.2, 111.3, 95.0, 90.2, 88.6, 88.0, 69.2, 69.1, 55.2, 40.4, 31.9, 31.5, 29.7, 29.6, 29.4, 29.3, 29.2, 26.0, 23.7, 22.6, 22.6, 14.1, 14.0. An. Calcd. for C$_{66}$H$_{89}$NO$_2$: C, 85.38; H, 9.66; N, 1.51. Found: C, 86.52; H, 9.67;

N, 1.37%. MS (high resolution, EI) *m/z*: M+ Calcd: 928.418, Found: 928.419.

*Synthesis of p-[(10-{[m,p-didodecyloxyphenyl]ethynyl}-9-anthryl)ethynyl]benzaldehyde (**2a**).* This compound was prepared by coupling of **8a** with m,p-(dodecyloxy)-4-ethynylbenzene (1:1.1 molar ratio), following the procedure described for **1a**. Reaction temperature: 50 °C. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 3:1). Yield: 90% (orange crystals); m.p.: 118–119 °C (ethyl acetate); ^{1}H NMR (CDCl$_3$) δ: 10.00 (s, 1H), 8.59–8.66 (m, 4H), 7.60 (m, 4H), 7.30–7.35 (m, 2H), 6.88 (d, 2H, *J* = 8.4 Hz), 4.03 (m, 4H), 1.83 (m, 4H), 1.47 (m, 7H), 1.22 (s, 29 H), 0.83 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 191.2, 150.3, 148.9, 132.3, 132.0, 131.8, 129.7, 129.6, 127.4, 127.1, 126.9, 126.7, 125.3, 113.3, 103.6, 90.7, 69.4, 69.1, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1. An. Calcd. for C$_{55}$H$_{66}$O$_3$: C, 85.23; H, 8.58. Found: C, 85.90; H, 8.55%. MS (high resolution, EI) *m/z*: M+ Calcd: 775.111, Found: 775.112.

*Synthesis of p-[(10-{[m,p-didodecyloxyphenyl]ethynyl}-9-anthryl)ethynyl]benzonitrile (**2b**).* This compound was prepared by coupling **8b** with m,p-(dodecyloxy)-4-ethynylbenzene (1:1.1 molar ratio), following the above procedure. Reaction temperature: 50 °C. The crude product was purified by column chromatography (silica gel, petroleum ether/dichloromethane 4:1). Yield: 70% (red crystals); m.p.: 144–145 °C (ethyl acetate); ^{1}H NMR (CDCl$_3$) δ: 8.65 (m, 2H), 8.57 (m, 2H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.61 (m, 4H), 7.30 (m, 1H), 7.20 (m, 1H), 6.88 (m, 1H), 4.32 (m, 4H), 1.82 (m, 4H), 1.46 (m, 4H), 1.22 (m, 32 H), 0.82 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 150.4, 148.9, 132.3, 132.2, 132.0, 131.8, 128.3, 127.5, 127.2, 126.8, 126.7, 125.4, 120.3, 118.5, 116.8, 116.4, 115.2, 113.3, 111.6, 103.7, 100.16, 91.0, 84.8, 69.5, 69.2, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. An. Calcd. for C$_{55}$H$_{65}$NO$_2$: C, 81.88; H, 8.27; N, 1.77. Found: C, 82.29; H, 8.28; N, 1.75%. MS (high resolution, EI) *m/z*: M+ Calcd: 772.110, Found: 772.110.

*Synthesis of {p-[(10-{[m,p-didodecyloxyphenyl]ethynyl}-9-anthryl)ethynyl]benzylidene}malono nitrile (**2c**).* A 50 ml-flask was charged with aldehyde **2a** (0.10 g, 0.13 mmol), malononitrile (0.026 g, 0.39 mmol), ethanol (16 ml) and dry THF (4 ml). The reaction mixture was kept under nitrogen and magnetically stirred at 45 °C for 72 h. The solvent was then removed in vacuo. The residue was purified by column chromatography (silica gel, petroleum ether/dichloromethane 2:1) to obtain compound **2c** (50% yield) as a red solid; m.p.: 142–143 °C (ethyl acetate); ^{1}H NMR (CDCl$_3$) δ: 8,65 (m, 2H), 8.56 (m, 2H), 7.93 (d, 2H, *J* = 8.0 Hz), 7.82 (d, 2H, *J* = 8.0 Hz), 7.72 (s, 1H), 7.58–7.65 (m, 4H), 7.30 (dd, 1H, *J* = 8.0, 2.0 Hz), 6.88 (m, 1 H), 4.03 (m, 4H), 1.81 (m, 4H), 1.45 (m, 6H), 1.21 (m, 30H), 0.82 (m, 6H); ^{13}C NMR (CDCl$_3$) δ: 158.2, 150.4, 148.9, 132.4, 132.3, 131.8, 130.7, 130.3, 127.5, 127.3, 126.7, 125.4, 120.7, 116.7, 116.3, 115.2, 113.7, 113.3, 112.6, 104.0, 101.1, 92.5, 84.8, 69.5, 69.1, 31.9, 29.6, 29.4, 29.3, 29.2, 29.1, 26.0, 22.6, 14.0. An. Calcd. for C$_{58}$H$_{66}$N$_2$O$_2$: C, 84.63; H, 8.08; N, 3.40. Found: C, 85.10; H, 8.05; N, 3.27%. MS (high resolution, EI) *m/z*: M+ Calcd: 823.157, Found: 823.150.

For details on the preparation of intermediate compounds **6a–d** and **8a** and **b** see Supporting Information.

2.2. Thermal stability

Solutions of compounds were prepared in deuterated chloroform and toluene and then transferred into NMR tubes. NMR tubes were sealed and submersed in water baths maintained at 50 °C (chloroform) and at 80 °C (toluene). At predetermined times NMR tubes were removed and their contents analyzed by ^{1}H NMR spectroscopy. No changes were observed in the spectra as to the reference ones, for which NMR tubes were kept at room temperature.

2.3. Spectral and photophysical experiments

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The experimental oscillator strength was derived by $f = (4.39 \times 10^{-9}/n) \int \varepsilon(\bar{v}) \, d\bar{v}$ [22a], neglecting the refraction index. The fluorescence spectra were measured in dilute solutions (absorbance <0.1 at the excitation wavelength, λ_{exc}) by a Spex Fluorolog-2 F112AI spectrofluorimeter. The emission quantum yields were determined at λ_{exc} corresponding to the maximum of the first absorption band (λ_{max}) using tetracene and 9,10-diphenylanthracene in cyclohexane as fluorimetric standards (ϕ_F = 0.17 [22b] and ϕ_F = 0.73 [23], respectively, in aerated solvent).

The fluorescence lifetimes (τ_F) were measured by a spectrofluorometer based on the single photon counting technique, equipped for anthracene derivatives with a LED source centered at 461 nm using an interference filter centered at 460 nm in the excitation line and a cut-off in emission at 500 nm. For fluorene derivatives a pulsed lamp filled with H$_2$ at 330 nm and a LED source centered at 370 nm (using an interference filter centered at 370 nm in the excitation line and a cut-off in emission at 396 nm) were used. The resolution time of the experimental set-up is 0.2 and 0.5 ns when the filled lamp and LED are used as a source, respectively.

All the photophysical measurements were carried out at room temperature in spectroscopic grade cyclohexane (CH) and acetonitrile (AcN) or N–N dimethylformamide (DMF), from Sigma–Aldrich. When required, the solutions were de-aerated by purging with pure nitrogen. The parameters reported in the tables are averages of at least three independent measurements with mean deviation of ca. 10%.

2.4. Theoretical calculations

The theoretical calculations were performed by using the Hyper-Chem computational package (version 7.52): the heats of formation and dipole moments were obtained for geometries optimized by the PM3 method. The electronic spectra (transition energies, λ, and oscillator strengths, *f*) were calculated by ZINDO/S at the PM3 ground state optimized geometries. Calculations of the configuration interaction included 169 (13 × 13) single excited configurations. The dipole moment of the first singlet excited state was estimated by ZINDO/S with the function "next lowest". A Conformational Search analysis was performed in the case of two compounds (see Section 3.3 and Scheme 8 and Table 2 in the Supplementary Data) changing the torsional dihedral angle between the X group and the adjacent phenyl ring using PM3 as geometry optimization method.

3. Results and discussion

3.1. Synthesis

Schemes 2 and 3 detail the synthetic routes to the new compounds **1a–d** and **2a–c**, while compound **3** was synthesized as previously described [21]. The synthesis of compound **1** (Scheme 2) begins with the selective coupling between 2-bromo-7-iodofluorenes **4** and the alkynes **5** in toluene/diisopropylamine. The resulting bromo-derivatives **6** (71–85%) are then subjected to additional coupling with m,p-bis(dodecyloxy)-4-ethynyl benzene to provide target compound **1** in good yield (37–84%). Pd(PPh$_3$)$_4$/CuI catalyzed Sonogashira coupling of 9-bromo,10-iodo-anthracene (**7**) with terminal alkynes **5a** and **b** led to bromoarylethynyl anthracenes **8** in high yield (84–90%, Scheme 3). These compounds were then subjected to coupling with m,p-bis(dodecyloxy)-4-ethynyl benzene to afford the diarylethynyl anthracenes **2a** and
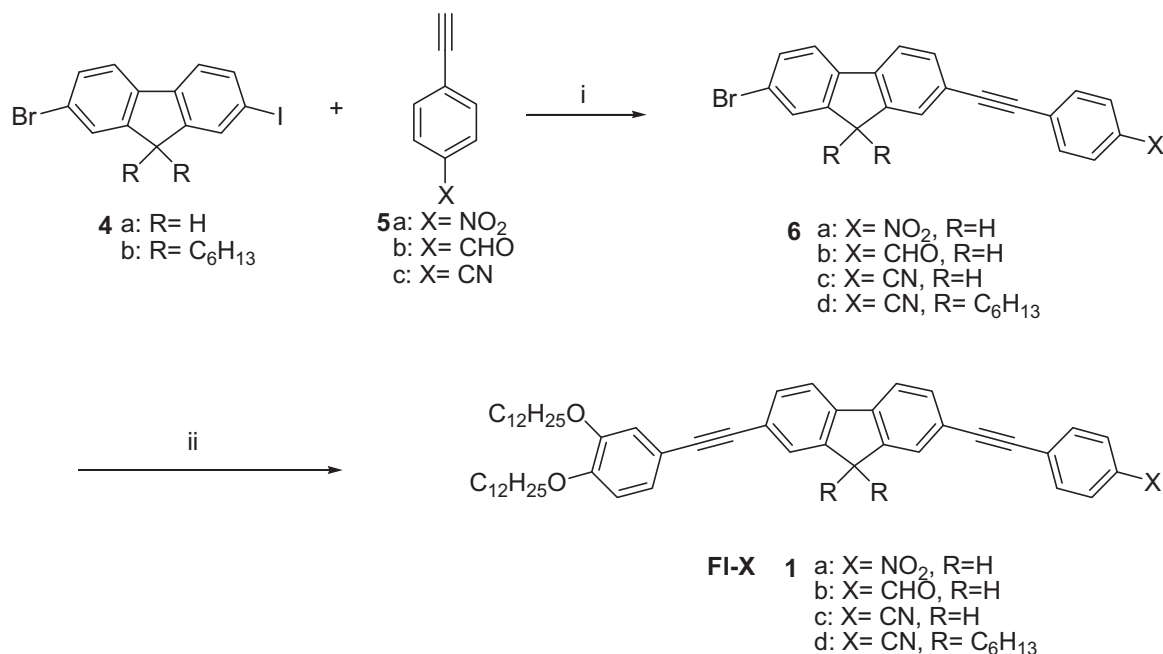
Scheme 2. Synthesis of fluorene-based compounds **1**. (i) Pd(PPh₃)₄/CuI, diisopropylamine, PhMe, 50 °C, 71–85% and (ii) m,p-bis(dodecyloxy)-4-ethynyl benzene, Pd(PPh₃)₄/CuI, diisopropylamine, PhMe, 75 °C, 37–84%.

b (75–99% yield). The synthesis of target compound **2c** was accomplished by Knoevenagel condensation between aldehyde **2a** and malononitrile, and subsequent dehydration reaction.

3.2. Spectral properties

In Figs. 1 and 2 the absorption and emission spectra of the fluorene and anthracene derivatives, respectively, are reported in two solvents of different polarity, namely CH and DMF (or AcN). The absorption of all compounds shows a main bell-shaped band, not influenced by the solvent polarity, centered around 370 nm in the case of the fluorene derivatives. The replacement of the fluorene central ring with an anthracene unit leads to an absorption spectrum that is a little structured and extended till 550 nm. In this case the polar solvent produces a different intensity of the vibronic peaks in the absorption spectra.

The fluorescence spectra are structured in CH showing a very similar shape with a vibrational progression around
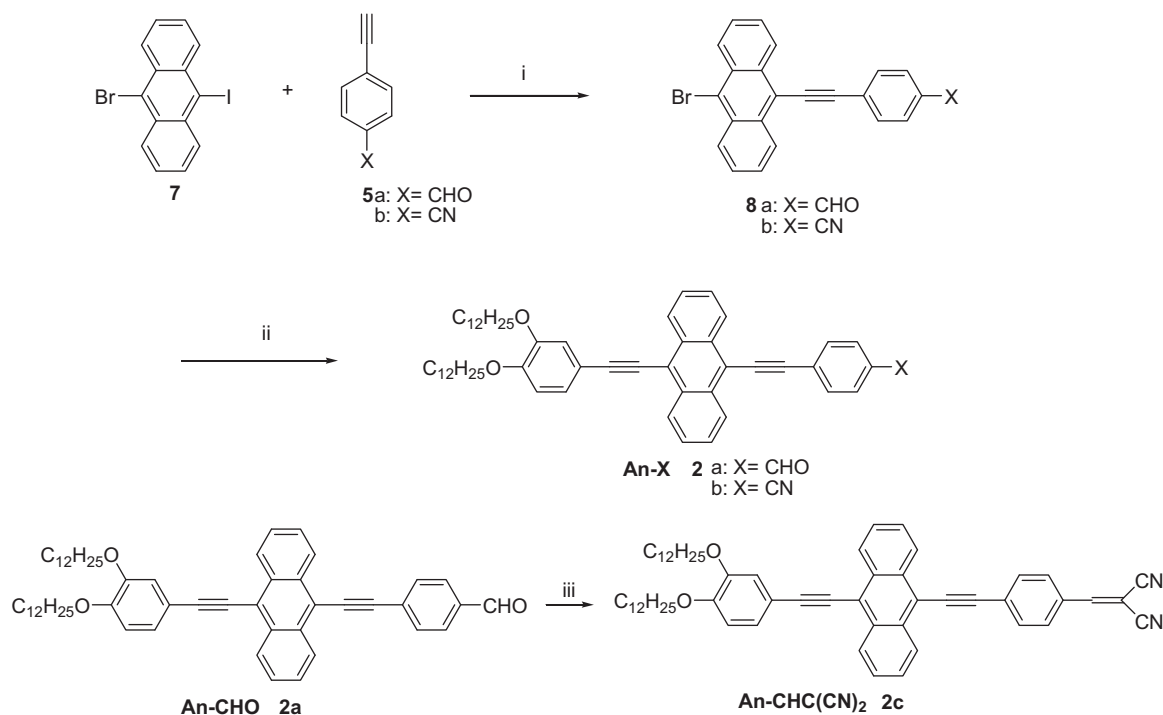
Scheme 3. Synthesis of anthracene-based compounds **2**. (i) Pd(PPh₃)₄/CuI, diisopropylamine, PhMe, 50 °C, 84–90%; (ii) m,p-bis(dodecyloxy)-4-ethynyl benzene, Pd(PPh₃)₄/CuI, diisopropylamine, PhMe, 50 °C, 75–99%; (iii) malononitrile, ethanol/THF, 45 °C, 44%.

Table 1
Spectral properties of fluorene derivatives (Fl-Xs) in two solvents.[a]

X	Solvent	λ_{abs}^{max} (nm)	λ_F^{max} (nm)	$\Delta\tilde{v}_{S,max}$ (cm^{-1})
NO$_2$	CH	337[sh], 370	<u>418</u>, 440	3100
	DMF	344[sh], 370		
CHO	CH	364, 384[sh]	<u>397</u>, 420	2280
	DMF	364	520	8240
CN	CH	364, 380[sh]	<u>392</u>, 415	1960
	DMF	363, 378[sh]	500	7550
CN(R)	CH	369, 386[sh]	<u>396</u>, 419	1850
	DMF	366, 379[sh]	493	7040

[a] The underlined wavelengths refer to the maxima; sh means shoulder.

1300–1400 cm^{-1}, for all the investigated compounds. They are very sensitive to the solvent polarity, becoming red shifted (particularly in the case of the NO$_2$-anthryl- and fluorene-derivatives) bell shaped bands. The observed fluorosolvatochromism causes a large increase of the Stokes shift ($\Delta\tilde{v}_{S,max}$, calculated by $1/\lambda_{abs}^{max} - 1/\lambda_F^{max}$ and reported in Table 1) on going from CH to DMF, as reported for analogous push–pull systems [24,25]. The only exception to this behaviour is the compound with the dicyanoethenyl group where the Stokes shift slightly decreases in the polar solvent (Table 2). As a matter of fact, the so called "anomalous Stokes shift", calculated as the difference between the 0,0 transition in absorption and emission in the two solvents ($\Delta\tilde{v}_{S,00} = 730$ cm^{-1} and 1270 cm^{-1} in CH and DMF, respectively) showed the correct trend: in fact it doubled on going from a non polar to a polar solvent.

The broad absorption band of An-CH=C(CN)$_2$ in CH becomes narrower and little structured with a blue shifted maximum in the polar solvent, the fluorescence spectrum loosing the structure and shifting towards high energies. The broad absorption in non polar solvent could be due to a superimposition of spectra belonging to slightly different structures of these flexible molecules (see Section 3.3 and Refs. [26,27]) the polar solvent selecting only the most polar ones. On the other hand, the structured emission of this compound points to a relaxed emitting species.

3.3. Quantum-mechanical calculations

Most of these molecules are expected to exist as a mixture of different conformers [28,29] (due to rotation around the quasi-single bonds between the triple bonds and the aromatic rings) where the position of the lateral aliphatic chains is changed (see the conformations of Fl-CN in Scheme 4, as an example). The results obtained by theoretical calculations on the different rotamers of the investigated compounds are collected in Table 3. Generally, the conformers resulted equally abundant but with very similar dipole moments and UV–vis spectra, pointing to experimentally indistinguishable species. This fact was in agreement with no wavelength effect on the emission spectrum, the overlapping of the excitation

with the absorption spectrum and the mono-exponential decay found for all the investigated compounds (see Section 3.4 and Figs. S1–S3 of the Supplementary Data where typical excitation spectra are compared with the absorption ones).
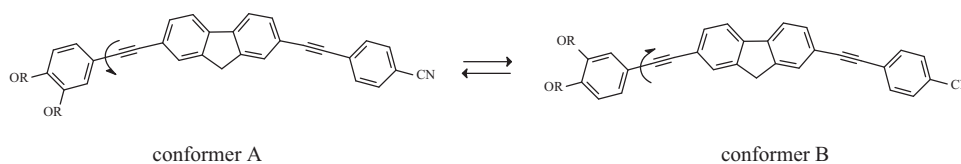
The calculated dipole moment of the ground state (μ) was found sizable for these push–pull systems (the biggest one being that of the nitro-derivatives and the smallest that of An-CHO) and that of the first excited singlet state (μ^* in Table 3) even higher, in agreement with the positive solvatochromism observed for the studied compounds and discussed in Section 3.2. μ^* is roughly twice as high as μ for the anthracene-derivatives, but it is even higher, till to three times of μ, in the case of the Fl-Xs. This fact is in agreement with the large fluorosolvatochromism (high $\Delta\tilde{v}_{S,max}$), particularly evident for all the fluorene-derivatives and only in the nitro-anthracene compound which bears the strongest electron acceptor substituent. The different behaviour of the fluorene and anthracene derivatives is illustrated in Fig. 3 where the molecular orbitals mostly involved in the first electronic transition for the nitro-derivatives are shown (MO for the other compounds are reported in Schemes S1–S7 and Table S1 of the Supplementary Data). The fluorene unit favours transitions with high charge transfer character (particularly in Fl-NO$_2$, Fig. 3 and Schemes S1–S4) while, in the presence of an anthracene unit, the HOMO → LUMO + 1 configuration, that contributes to the first transition with a high coefficient (0.43 in Table S1 of Supplementary Data), reduces the charge transfer character of S$_1$. Moreover the first transition seems to be strongly localized in the anthracene in the case of the other antracene-derivatives (see Schemes S5–S7) in agreement with similar Stokes shifts observed in non-polar and polar solvents (Table 2) suggesting a scarce contribution of ICT to the excited state composition of these compounds.

The calculated spectral properties showed that S$_1$ is reached by an allowed transition (π,π^* nature with partial charge transfer character) for all the investigated compounds with a particularly high oscillator strength in the case of the fluorene-derivatives and resulted in good agreement with the experimental absorption spectra and with the k_F values (see below, Section 3.4).

Table 2
Spectral properties of anthracene derivatives (An-Xs) in two solvents.[a]

X	Solvent	λ_{abs}^{max} (nm)	λ_F^{max} (nm)	$\Delta\tilde{v}_{S,max}$ (cm^{-1})
NO$_2$	CH	467, 490[sh]	<u>510</u>, 546	1800
	AcN	464, <u>484</u>	780	7840
CHO	CH	439[sh], 460, 480[sh]	<u>497</u>, 530	1620
	DMF	463, <u>486</u>	550	2390
CH=C(CN)$_2$	CH	490, 526[sh]	<u>547</u>, 590	2130
	DMF	459, <u>479</u>	510[sh], 530	2010
CN	CH	436[sh], 458, 477[sh]	<u>495</u>, 528	1630
	DMF	460, <u>483</u>	537	2080

[a] The underlined wavelengths refer to the maxima; sh means shoulder.

Scheme 4. Conformations of Fl-CN.

Table 3
Calculated spectral properties (transition wavelength, λ, and oscillator strength, f)[a], heats of formation (ΔH_f^0) and dipole moment of the ground (μ) and excited singlet (μ^*) states for the conformers of anthracene and fluorene derivatives. The transition wavelength and oscillator strength as derived by integrating the first band of the experimental spectrum in CHCl$_3$, λ_{exp} and f_{exp}, respectively, are also reported for comparison.

Compound	Conformer	μ (D)	μ^* (D)	ΔH_f^0 (kcal/mol)	λ (nm)	f		λ_{exp}	f_{exp}
Fl-NO$_2$	A	8.21	25.54	−1.436	371	1.74	S_1		
					321	0.71	S_2		
Fl-NO$_2$	B	7.30	24.03	−1.448	371	1.75	S_1	378	1.54
					321	0.71	S_2		
Fl-CHO[b]	A	4.18	11.41	26.683	342	2.60	S_1		
					259	0.26	S_9		
Fl-CHO[b]	B	4.79	11.32	26.657	343	2.56	S_1	367	1.98
					258	0.25	S_9		
					218	0.66	S_{15}		
Fl-CN	A	3.77	9.55	42.608	345	2.45	S_1	364	1.97
					257	0.30	S_9		
Fl-CN	B	4.28	9.93	42.674	345	2.44	S_1		
					257	0.30	S_9		
Fl-CN(R)	A	3.51	9.33	−18.990	344	2.40	S_1	368	1.36
					257	0.33	S_9		
Fl-CN(R)	B	4.50	10.48	−18.969	345	2.40	S_1		
					257	0.33	S_9		
An-NO$_2$		7.81	14.43	79.680	447	1.45	S_1	471	0.72
					286	0.38	S_{10}		
					264	0.60	S_{13}		
					262	1.17	S_{14}		
An-CHO	A	3.79	6.91	−10.437	429	1.40	S_1		
					290	0.22	S_9		
					262	1.76	S_{13}		
An-CHO	B	2.95	6.04	−10.498	429	1.40	S_1	465	0.70
					289	0.23	S_9		
					262	1.76	S_{13}		
An-CH=C(CN)$_2$	A	5.64	10.26	108.531	432	1.61	S_1		
					285	0.50	S_9		
					262	1.76	S_{13}		
An-CH=C(CN)$_2$	B	6.22	11.22	112.988	433	1.64	S_1		
					286	0.54	S_9		
					262	1.76	S_{13}		
An-CN		5.76	8.99	58.611	429	1.40	S_1	462	0.61
					291	0.27	S_8		
					262	1.80	S_{12}		

[a] The reported values refer to transitions with $f > 0.2$ and $\lambda > 250$ nm.
[b] For this compound the configuration interaction included 100 (10 × 10) single excited configurations.

A Conformational Search performed by the PM3 method, changing the torsion dihedral angle φ between the X group and the adjacent phenyl ring (see Scheme S8 in the Supplementary Data) confirmed that, in the case of An-CH=C(CN)$_2$, a set of different conformations having very similar ground state energies but slightly different transition wavelengths is expected to contribute to the broadening of the absorption spectrum. The results obtained for a prototype of An-CH=C(CN)$_2$ (where the long side chains are replaced by two methoxy groups for calculation time problems, the spectral and physical properties of the system being not affected by the different length of the side chains) are reported in Table S2 of the Supporting Data together with those found for a prototype of An-NO$_2$ for comparison. The different conformations show different dihedral angles φ and also different dipole moments of the ground state (μ). This fact could be responsible of the narrower absorption band observed in DMF, the polar solvent strongly stabilizing the molecules with higher μ thus selecting a smaller set of similar energy geometries.

3.4. Photobehaviour

The emission of the fluorene derivatives (Table 4) is characterized by short lifetimes (below 1 ns) that fall under the detection limit of our apparatus in the case of Fl-NO$_2$ and Fl-CHO. The

Table 4
Photophysical parameters of fluorene derivatives (Fl-Xs) in two solvents.

X	Solvent	ϕ_F	τ_F (ns)	k_F (10^8 s^{-1})
NO$_2$	CH	3×10^{-4}	<0.5	
	DMF	$<1 \times 10^{-4}$		
CHO	CH	0.37	0.2	19
	DMF	0.002	<0.5	
CN	CH	1.0	0.8	13
	DMF	0.17	0.7	2.4
CN(R)	CH	1.0	0.8	13
	DMF	0.22	0.8	2.8

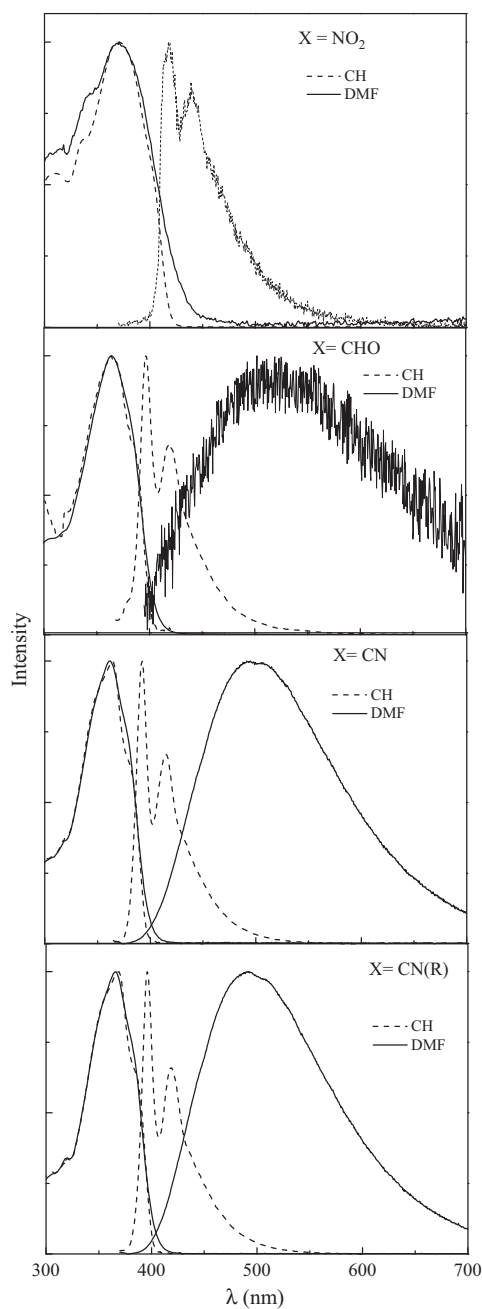**Fig. 1.** Normalized absorption and emission spectra of Fl-Xs in two solvents.

Fig. 2. Normalized absorption and emission spectra of An-Xs in two solvents.

fluorescence quantum yield goes from unity for the cyano-derivatives to the undetectable value of Fl-NO$_2$ in DMF. The k_F values resulted high ($\cong 10^9$ s^{-1}) in CH, in agreement with a full allowed transition, as suggested by theoretical calculations (Section 3.3), and decreased by almost an order of magnitude ($\cong 2 \times 10^8$ s^{-1}) in DMF pointing to a different nature of the emitting state in polar solvents. This fact well agrees with the spectral results showing the presence of an ICT state, strongly stabilized by the polar solvent, that becomes the emitting state.

The low ϕ_F value found for Fl-CHO, and particularly for Fl-NO$_2$, is expected [24,30,31] and probably due to an increased ISC rate constant for the presence of $^3n,\pi^*$ states located near the S$_1$ of π,π^* character. In fact, preliminary results obtained by ns flash photolysis showed the presence, in these two systems, of a triplet state efficiently populated by direct excitation [32]. No sign of
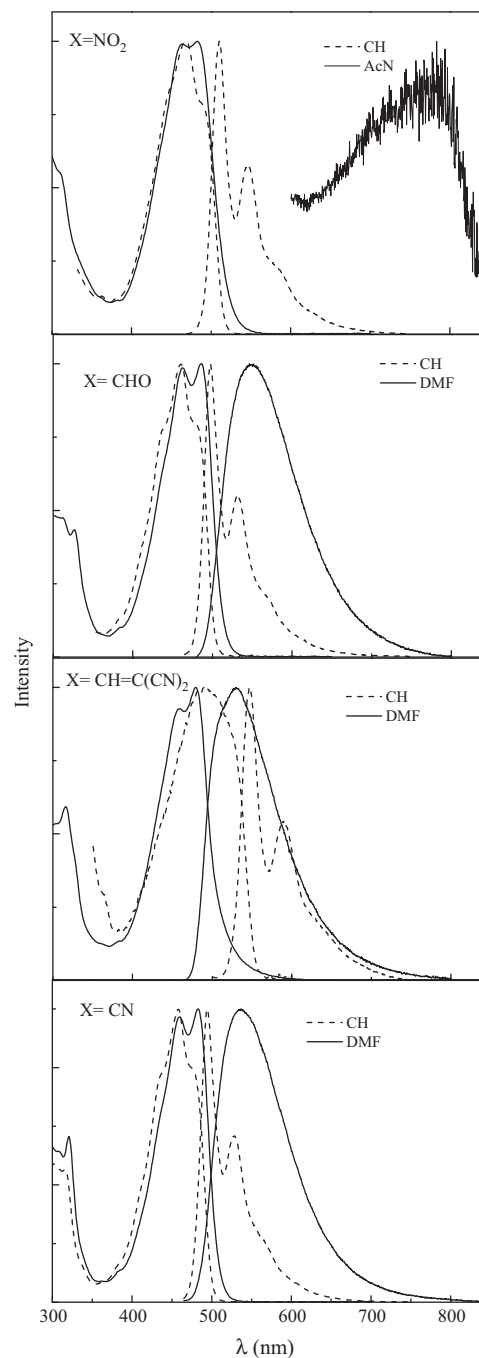
photo-oxidation or photo-degradation of the compounds was observed during the experiments even under prolonged irradiation.

The reduction of fluorescence and the huge red shift of the emission spectra in DMF (see Section 3.2) could indicate the internal conversion (IC) to the ground state as the main process deactivating S$_1$ of these fluorene derivatives in polar solvents, as observed in analogous compounds [33].

When the central fluorene ring is replaced by an anthracene unit, the photobehaviour becomes quite different (Table 5). In fact, the radiative decay is the largely prevalent deactivation channel of S$_1$ even in a polar solvent. The only exception is An-NO$_2$ in AcN (see Table 5) where ϕ_F collapsed to a very low value.

The fluorescence lifetime is around 3 ns for all the anthryl-derivatives in the two solvents (CH and DMF) giving a k_F value of
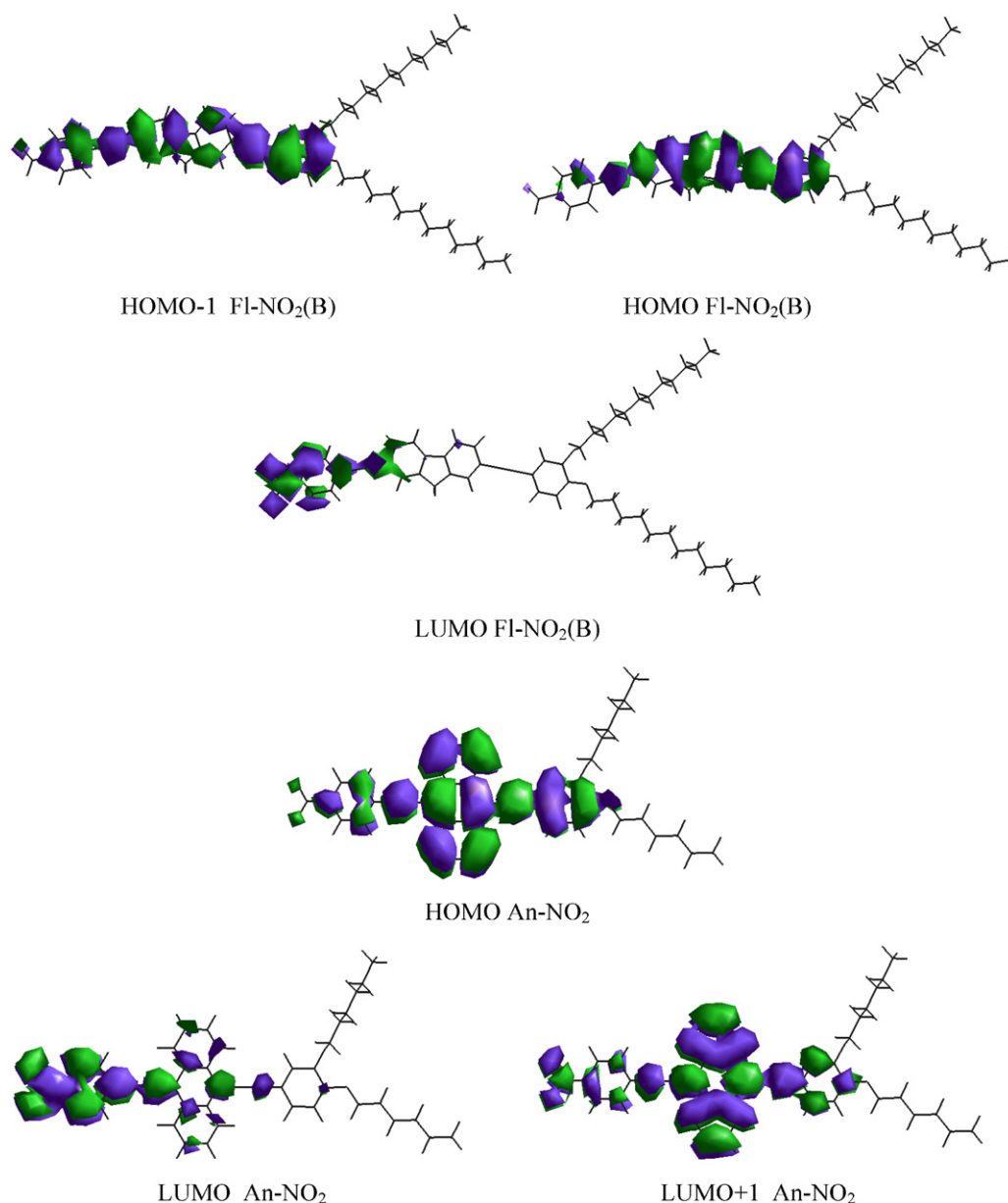
Fig. 3. Molecular orbitals mainly involved in the first electronic transition of the nitro-derivatives of the investigated compounds, as derived by ZINDO/S method using PM3 ground state optimized geometries.

$\sim 3 \times 10^8\,\mathrm{s}^{-1}$, lower than that of fluorene analogues, in agreement with the oscillator strength calculated by ZINDO/S and derived by the experimental absorption spectra (f and f_{exp}, respectively, see Table 3). In An-Xs, k_F does not change on going from CH to DMF (or AcN), indicating that the fluorescence originates from the same state in both solvents.

Table 5
Photophysical properties of anthracene derivatives (An-Xs) in two solvents.

X	Solvent	ϕ_F	τ_F (ns)	k_F ($10^8\,\mathrm{s}^{-1}$)
NO₂	CH	0.98	2.8	3.5
	AcN	3×10^{-4}		
CHO	CH	0.90	2.7	3.3
	DMF	0.80	2.7	3.0
CH=C(CN)₂	CH	0.94	2.5	3.8
	DMF	0.58	2.8	2.1
CN	CH	0.84	3.0	2.8
	DMF	0.77	2.9	2.7

The photophysical and spectral behaviour suggests that ICT is not helped by the introduction of anthracene as a central ring, the noticeable exception being An-NO₂ due to the presence of the strongest electron acceptor group.

As a matter of fact, a non-negligible reduction of ϕ_F was observed in the case of An-CH=C(CN)₂ on going from CH to DMF. This fact would indicate the presence of a partial ICT character of the excited singlet state in this system bearing two electron-drawing CN groups, as suggested by the calculated MO involved in the first transition (see Table S1 and Scheme S6 of the Supplementary Data).

4. Conclusions

The present study showed a peculiar photobehaviour of these push–pull systems depending on the nature of the electron acceptor group in the side benzene and/or on the different central ring (namely anthracene or fluorene) as summarized in the following items:

- The presence of the anthracene unit in the central moiety of the structures leads to an absorption spectrum placed at longer wavelenghts (more than 100 nm) that makes these anthryl derivatives very interesting for solar energy storage.
- The fluorene unit favours transitions with high charge transfer character while the absorption seems to be strongly localized in the anthracene derivatives, as evidenced by the spectral behaviour in non-polar and polar solvents and the strong reduction of the fluorescence in favour to IC in the polar solvent in the case of Fl-Xs only. The calculated MO for the two series of compounds nicely confirmed the presence of ICT states and localized transitions in the case of fluorene- and anthracene-derivatives, respectively.
- The ICT character of the excited states of the investigated compounds decreased in the order $NO_2 > CHO > CN$ in agreement with the electronic affinity (EA) of the side group (EA = +2.1, +0.42 and +0.25 eV for nitro-benzene, benzaldehyde and benzonitrile, respectively [34,35]).

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.08.011.

References

[1] L.-Y. Lin, C.-H. Tsai, K.-T. Wong, T.-W. Huang, C.-C. Wu, S.-H. Chou, F. Lin, S.H. Chen, A.-I. Tsai, J. Mater. Chem. 21 (2011) 5950.
[2] J. Peet, L. Wen, P. Byrne, S. Rodman, K. Forberich, Y. Shao, N. Drolet, R. Gaudiana, G. Dennler, D. Waller, Appl. Phys. Lett. 98 (2011) 043301.
[3] K.N. Gherab, R. Gatri, J.-L. Fillaut, L. Jerome, B. Sahraoui, J. Niziol, Nonlinear optics, Quantum Opt. 38 (2008) 281.
[4] E.M. Maya, E.M. Garcia-Frutos, P. Vazquez, T. Torres, G. Martin, G. Roio, F. Agullo-Lopez, R.H. Gonzalez-Ionte, V.R. Ferro, J.M. Garcia de la Vega, J. Phys. Chem. A 107 (2003) 2110.
[5] M. Kivala, F. Diederich, Acc. Chem. Res. 42 (2009) 235.
[6] A.S. Anderson, L. Kerndrup, A. Madsen, K. Kilsa, M.B. Nielsen, P.R. La Porta, I. Biaggio, J. Org. Chem. 74 (2008) 375.
[7] X.B. Sun, Y.Q. Liu, X.J. Xu, C.H. Yang, G. Yu, S.Y. Chen, Z.H. Zhao, W.F. Qiu, Y.F. Li, D.B. Zhu, J. Phys. Chem. B 109 (2005) 10786.
[8] B.J. Coe, J.A. Harris, B.S. Brunschig, J. Garin, J. Orduna, S.J. Coles, M.B. Hursthouse, J. Am. Chem. Soc. 126 (2004) 10418.
[9] R.R. Tykwinski, M. Schreiber, R.P. Carlon, F. Diederich, M. Gramlich, V. Gramlich, Helv. Chim. Acta 79 (1996) 2249.
[10] C. Dehu, F. Meyers, J.L. Bredas, J. Am. Chem. Soc. 115 (1993) 6198.
[11] U.H.F. Bunz, Chem. Rev. 100 (2000) 1605.
[12] J. Liu, J.W.Y. Lam, B.Z. Tang, Chem. Rev. 109 (2009) 5799.
[13] F. Silvestri, A. Marrocchi, Int. J. Mol. Sci. 11 (2010) 1471.
[14] M. Grell, D.D.C. Bradley, M. Inbasekaran, E.P. Woo, Adv. Mater. 9 (1997) 798.
[15] H. Sirringhaus, R.J. Wilson, R.H. Friend, M. Inbasekaran, W. Wu, E.P. Woo, M. Grell, D.D.C. Bradley, Appl. Phys. Lett. 77 (2000) 406.
[16] J.J.M. Halls, A.C. Arias, J.D. MacKenzie, W. Wu, M. Inbasekaran, E.P. Woo, R.H. Friend, Adv. Mater. 12 (2000) 498.
[17] R. Pacios, D.D.C. Bradley, J. Nelson, C.J. Brabec, Synth. Met. 137 (2003) 1469.
[18] M. Svensson, F. Zhang, S.C. Veenstra, W.J.H. Verhees, J.C. Hummelen, J.M. Kroon, O. Inganäs, M.R. Andersson, Adv. Mater. 15 (2003) 988.
[19] J.E. Anthony, Chem. Rev. 106 (2006) 5028.
[20] H. Meng, F. Sun, A.B. Goldfinger, G.D. Jaycox, Z. Li, J. Marshall, G.S. Blackman, J. Am. Chem. Soc. 127 (2005), 2406.
[21] A. Marrocchi, A. Spalletti, S. Ciorba, M. Seri, F. Elisei, A. Taticchi, J. Photochem. Photobiol. A 211 (2010) 162.
[22] (a) J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970, p. 51, Eq. (3.49);
(b) J.B. Birks, Photophysics of Aromatic Molecules, Wiley-Interscience, London, 1970, p. 123.
[23] G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi, F. Momicchioli, J. Phys. Chem. 91 (1987) 4733.
[24] I. Baraldi, E. Benassi, S. Ciorba, M. Šindler-Kulyk, I. Škorić, A. Spalletti, Chem. Phys. 361 (2009) 61.
[25] S. Ciorba, B. Carlotti, I. Škorić, M. Šindler-Kulyk, A. Spalletti, J. Photochem. Photobiol. A 219 (2011) 1.
[26] K. Ogawa, H. Suzuki, M. Futakami, J. Chem. Soc. Perkin Trans. 2 (1988) 39.
[27] L. Angeloni, E. Castellucci, G. Bartocci, U. Mazzucato, A. Spalletti, G. Marconi, Gazz. Chim. Ital. 126 (1996) 609.
[28] U. Mazzucato, F. Momicchioli, Chem. Rev. 91 (1991) 1679.
[29] G. Bartocci, A. Spalletti, U. Mazzucato, in: J. Waluk (Ed.), Conformational Analysis of Molecules in Excited States, Wiley-VCH, New York, 2000 (Chapter 5 and references therein).
[30] H. Görner, J. Photochem. 126 (1999) 15.
[31] S. Ciorba, G. Galiazzo, U. Mazzucato, A. Spalletti, J. Phys. Chem. A 114 (2010) 10761.
[32] B. Carlotti, R. Flamini, A. Spalletti, A. Marrocchi, F. Elisei, Chem. Eur. J., submitted.
[33] B. Carlotti, M. Šindler-Kulyk, A. Spalletti, F. Elisei, Phys. Chem. Chem. Phys. 13 (2011) 4519.
[34] M. Montalti, A. Credi, L. Prodi, M.T. Gandolfi, Handbook of Photochemistry, CRC Press Taylor & Francis Group, Boca Raton, 2006, p. 502.
[35] W.E. Wentworth, E. Chen, J. Phys. Chem. 71 (1967) 1929.