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Quantitative cascade energy transfer in semiconductor thin films

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Abstract

In this contribution we report the photophysical study of three organic blend systems comprising [60]PCBM along with different combinations of five extended semiconducting arylacetylenes, i.e. p-[(2-([m,p-didodecyloxyphenyl]ethynyl)-7-fluorenyl)ethynyl]benzotrile, 4,7-bis(5-([m,p-bis(hexyloxy)phenyl]ethynyl)thien-2-yl)-2,1,3-benzothiadiazole, 9,10-bis-[(m,m-bis([m,m-bis(hexyloxy)phenyl]ethynyl)phenyl)ethynyl]-anthracene, pseudo-p-[(10-([m,p-bis(hexyloxy)phenyl]ethynyl)-9-anthryl[2.2]paracyclophane, and oligo{2,5-bis(hexyloxy)[1,4-phenylene ethynylene]-alt-[9,10-anthraceneethynylene]}, and one semiconducting arylvinylene, i.e. 9,10-bis-{(E)-[m,p-bis(hexyloxy)phenyl]vinyl}-anthracene, that evidenced an efficient quantitative energy transfer from the hypsochromic to the bathochromic species (the potential efficient charge-donor components), useful to extend the collection of sunlight. An interesting emission enhancement in thin film has been observed only for the arylvinylene derivative.

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1. INTRODUCTION

Organic semiconductors have received much attention in the last decades for their use as active layers in organic photovoltaic (OPV) cells because they offer the prospect of large area coverage, (semi)transparency, compatibility with lightweight flexible substrates, and low manufacturing cost using solution-processing methods.¹⁻⁴

In this regard, soluble small molecule semiconductors have great potential, including facile chemical modification and purification, monodispersity, large charge carrier mobilities, and reproducible, batch-to-batch device performance. A record power conversion efficiency (PCE) of ~9% has been recently achieved by Bazan, Heeger and coworkers for small molecule bulk heterojunction (SM BHJ) solar cells.⁵

Recently, we reported the synthesis and photophysical properties of a series of semiconducting arylacetylenes, that are promising for implementation in photovoltaic devices, because of their easy tunable absorption, redox, and film-forming properties.⁶⁻¹⁰ They resulted photostable under prolonged irradiation showing absorption spectra in the visible region and high fluorescence quantum yields.^{7,8} Further, in the case of a so-called *push-pull* architecture, it was found that for systems peripherally functionalized with alkoxy chains (i.e. electron-donating species) and cyano- or nitro-groups at the extremities, the presence of excited states with charge-transfer character causes a useful red shift of the absorption spectra and interesting NLO properties.^{8,11}

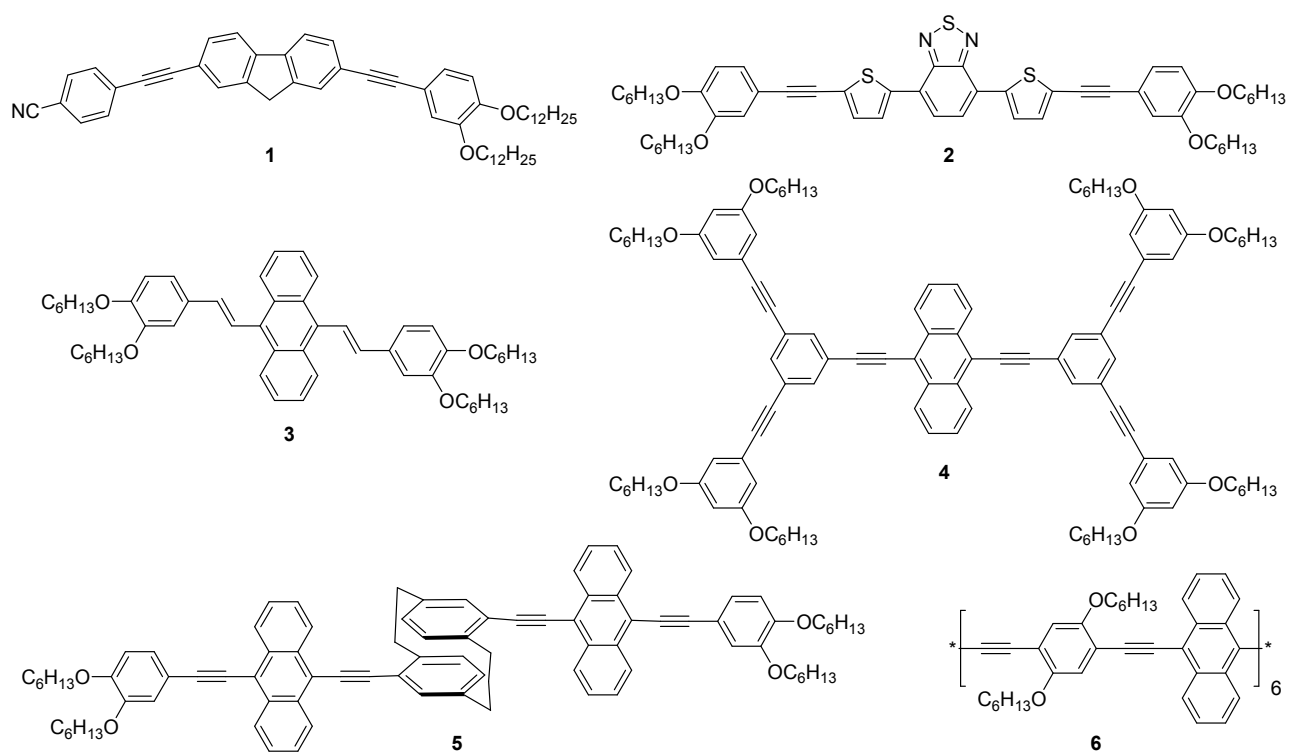
Bulk heterojunction (BHJ) photovoltaic devices using various among these arylacetylenes as donor materials and phenyl-C₆₁butyric acid methyl ester ([60]PCBM) as electron acceptor have been also fabricated, and power conversion efficiencies up to ~3% have been reported.^{6,9,10}

In parallel, a promising new approach to enhance the power conversion efficiency of photovoltaic devices involves preparing of ternary blend solar cells consisting of two donors (polymers or small molecules) and a fullerene acceptor or one donor and two acceptors, having

complementary absorption spectra with the aim to cover a wider wavelength range of the solar radiation spectrum.¹²⁻¹⁶

Thus, in the present paper the photophysics of the previously studied compounds **1-3** (Scheme 1) has been further investigated. Moreover, the work is devoted to the spectral and photophysical properties of the arylacetylene derivatives **4-6** (Scheme 1), as well as of three organic blend systems potentially useful in photovoltaic devices, comprising [60]PCBM and different combinations of semiconductors **1-6** both in solution and in thin film.

Additionally, the efficient quenching of fluorescence by [60]PCBM acceptor is demonstrated.



Scheme 1. Chemical structure of the investigated compounds **1-6**

2. EXPERIMENTAL

p-[(2-([*m,p*- didodecyloxyphenyl]ethynyl)-7-fluorenyl)ethynyl]benzotrile **1**, 4,7-bis(5-([*m,p*-bis(hexyloxy)phenyl]ethynyl}thien-2-yl)-2,1,3-benzothiadiazole **2**, 9,10-bis-{(E)-[*m,p*-bis(hexyloxy)phenyl]vinyl}-anthracene **3**, 9,10-bis- [(*m,m*-bis {[*m,m*-bis-(hexyloxy)phenyl]ethynyl}phenyl)ethynyl]-anthracene **4**, *pseudo-p*- [(10-([*m,p*-bis-(hexyloxy)phenyl]ethynyl}-9-anthryl[2.2]paracyclophane **5**, and oligo{2,5-bis(hexyloxy)[1,4-phenylene ethynylene]-*alt*-[9,10-anthraceneethynylene]} **6**, were synthesized following previously reported procedures.⁶⁻¹⁰ [60]PCBM (99.5%) was purchased from Solenne BV, and used without further purification. Spectrophotometric grade chloroform was purchased from Sigma-Aldrich.

Thin-films were prepared by spin coating (Chemat Scientific, KW-4A series Spin Coater) a 8 mg/mL chloroform solution of **1-6**, as well as of Mixture 1 (*Mix1*, **2/4** 1:1 wt/wt ratio), Mixture 2 (*Mix2*, **1/5/6** 1.5:1:1.5 wt/wt ratio) and Mixture 3 (*Mix3* **2/3** 1:1 wt/wt ratio) on glass substrates. The films used to test the fluorescence quenching by [60]PCBM were prepared by spin coating a blend solution of [60]PCBM and pristine compounds 1-6 or *Mix1-3* (50 weight% [60]PCBM at 8 mg/mL). Before thin-film preparation, the glass substrates were cleaned by ultrasonic treatment with water + detergent, deionized water, ethanol and acetone, sequentially. To prevent any degradation, the films were covered with a glass slide by using an epoxy resin.

A Perkin-Elmer Lambda 800 spectrophotometer was used for the absorption measurements. The fluorescence spectra were recorded by a Spex Fluorolog-2 F112AI spectrofluorimeter. Dilute solutions (absorbance less than 0.1 at excitation wavelength, λ_{exc}) were used for fluorimetric measurements. Tetracene in air equilibrated cyclohexane was used as fluorimetric standard ($\phi_F = 0.17^{17}$). Fluorescence lifetimes were measured with the single photon counting method (time

resolution $\cong 0.5$ ns) by an Edinburgh Instrument 199S spectrofluorimeter, equipped 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.

All the photophysical measurements were carried out at room temperature in spectroscopic-grade air-equilibrated chloroform. The fluorescence quantum yields and lifetimes are averages of at least three independent experiments with a mean deviation of ca. 10%.

3. RESULTS AND DISCUSSION

3.1. Spectral and photophysical behavior of compounds 1-6.

The absorption and emission properties of the investigated compounds in CHCl_3 are reported on Table 1 and their spectra in CHCl_3 solution and thin film are shown in Fig. 1. Compounds **1-3** have been already studied in non-polar solvents;^{7,8} in the present paper their spectral and photophysical behavior is reported in CHCl_3 in order to have information in the same experimental conditions used for studying compounds **4-6** and because the thin films have been prepared by spin-coating of highly concentrated CHCl_3 solutions.

Table 1. Spectral and photophysical properties of the investigated compounds in CHCl_3 .

| Compound | 1 | 2 | 3 | 4 | 5 | 6 |
|--|----------|--------------------|--------------------|----------|----------|----------|
| λ_{abs}^{max} (nm) ^a | 364 | <u>358</u> , 502 | 317, <u>419</u> | 472 | 481 | 492 |
| ϵ^{max} ($\text{M}^{-1}\text{cm}^{-1}$) | 79200 | 50300 ^b | 23600 ^b | 49000 | 100000 | 72100 |
| λ_F^{max} (nm) | 435 | 648 | 670 | 481 | 500 | 545 |
| ϕ_F | 0.81 | 0.59 | 0.02 | 0.75 | 0.72 | 0.24 |
| τ_F (ns) | 1.1 | 5.0 | < 0.5 | 2.7 | 2.3 | 1.3 |
| k_F (10^8 s^{-1}) | 7.4 | 1.2 | > 0.4 | 2.8 | 3.1 | 1.8 |

^a the main maxima are underlined; ^b from ref. 7.

The new compounds (small molecules **4** and **5** and the donor oligomer **6**) show an interesting absorption spectrum with an intense main band centered at 470-490 nm.

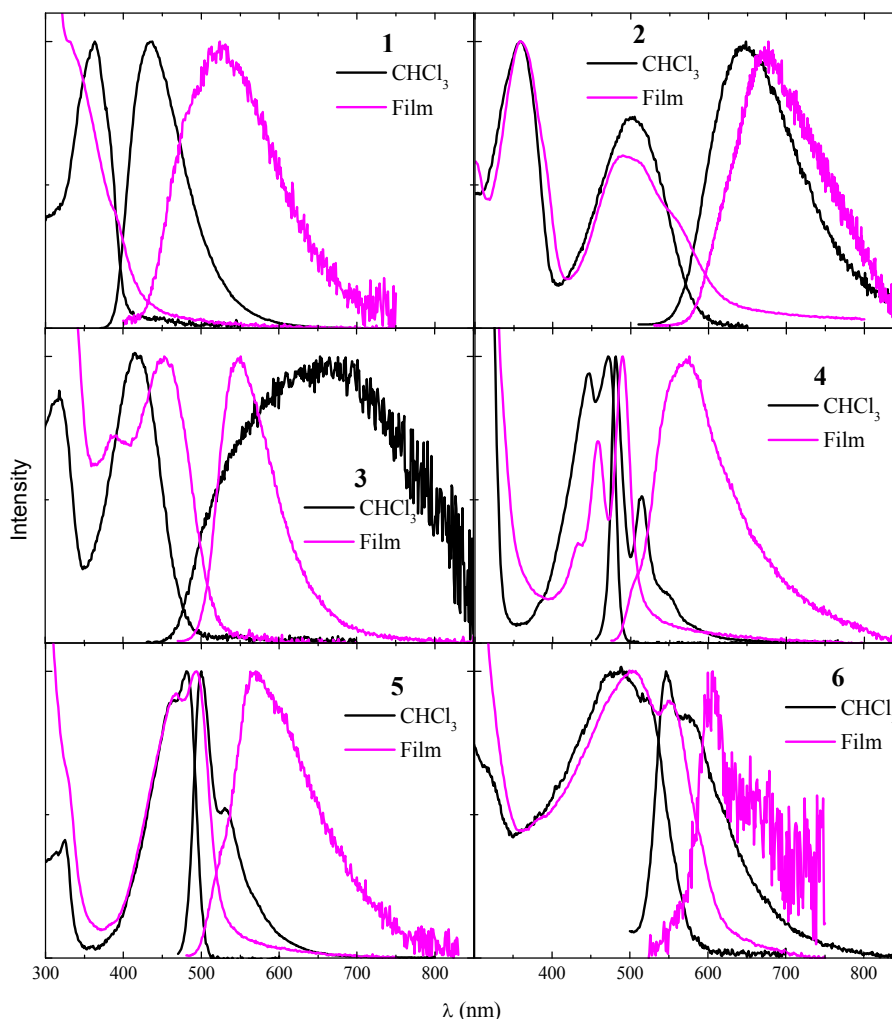


Figure 1. Normalized absorption and emission spectra of **1-6** in CHCl_3 and thin film.

All compounds show high fluorescence quantum yield (ϕ_F), with the exception of **6** and mainly of **3**. For the latter a strong reduction of ϕ_F (one order of magnitude) in CHCl_3 with respect to the value reported in aerated cyclohexane (0.26),⁷ was observed. Usually the decrease of the emissive pathway in polar solvents is accompanied in arylvinylene derivative by an increase of photoisomerization, the solvent polarity favoring the opening of reactive pathways to the

deactivation of the excited states because of experienced lower energy barriers for the rotation around the double bonds.¹⁸ However, in this case the reactivity of **3** remains very low also in the more polar CHCl₃ (the disappearance yield was estimated $< 10^{-3}$) pointing to the increase of non-radiative and non-reactive deactivation channels in this solvent.

The fluorescence lifetimes (τ_F) are of the order of few ns with the exception of **1** that show a $\tau_F \cong 1$ ns, accompanied by a high k_F , as previously found,¹¹ and of **3** whose lifetime resulted under the resolution time of our apparatus (see Table 1).

Generally the thin films absorption spectra of the investigated compounds are broader than those in solution (Figure 1); in particular compounds **2** and **6** have in thin film the absorption spectrum extending to 700 nm. The emission spectra lose the structure (when present) and show lower intensity, particularly in the case of the oligomer **6** whose emission is nearly completely depressed in thin film. The diminished intensity can be related to intermolecular radiationless deactivation favored by aggregation.

An opposite behavior was found in the case of **3** where, on going from CHCl₃ solution to film, the absorption is sensibly shifted towards the red and the broad emission band of low intensity, centered at 615 nm, becomes a sharp intense band centered at 550 nm. This fact caused a strong reduction of the Stokes shift, calculated as the difference between the absorption and emission maxima, that falls down from 7660 cm⁻¹ in CHCl₃ to 3890 cm⁻¹ in thin film. For compound **3** had been previously reported⁷ that the presence of double bonds gives flexibility to the molecule and the broad absorption and emission spectra (full width at half maximum, FWHM $\cong 4200$ cm⁻¹) and the large Stokes shift in cyclohexane solutions were explained by the presence of sets of non-planar structures caused by geometric distortions around the single bonds between the anthryl group and the ethenic carbons, as previously reported for *trans*-9-styrylanthracene¹⁹ and

for analogous flexible compounds.²⁰ Probably the aggregation in the thin film forces the molecules in more planar geometries thus reducing the set of different distorted conformations, the emission from more rigid structures becoming an efficient deactivation pathway, as usually observed when flexible molecules are trapped in rigid matrices at low temperature. To confirm this explanation the emission spectrum of **3** was recorded in EPA at 293 and 77 K. The spectrum looks like a broad bell of low intensity at room temperature that becomes a sharp narrower band at 77K, where a transparent glassy matrix is formed, shifting towards the blue and strongly increasing its intensity (see Fig. 2). The ratio between the area under the emission spectrum in EPA at room temperature and that at 77 K \cong 30.

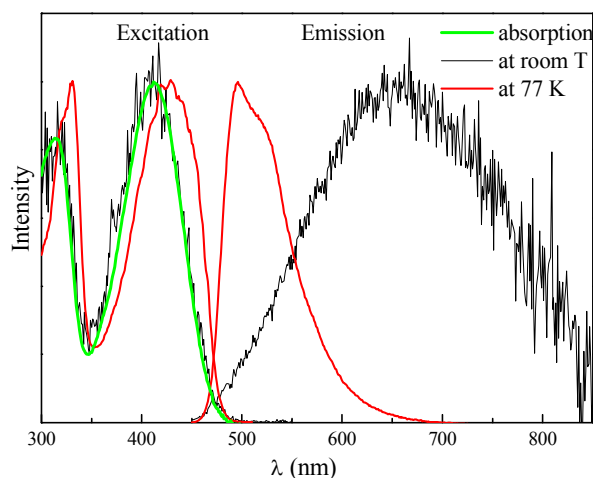


Figure 2. Fluorescence excitation and emission spectra of **3** in EPA at room temperature and 77 K. The absorption at room temperature is also shown.

As a matter of fact, the emission spectrum of **3** in CHCl_3 is broader ($\text{FWHM} \cong 6900 \text{ cm}^{-1}$) than that in cyclohexane and broader than its absorption in CHCl_3 ($\text{FWHM} \cong 4300 \text{ cm}^{-1}$). This further enlargement of the fluorescence spectrum is not due to impurities in the sample evidenced in solvents where ϕ_F of **3** is very low. In fact, the excitation spectra, recorded at

different λ_{em} , roughly overlap the absorption and the emission does not significantly change by exciting at the tail of the absorption, as shown in Fig. 3. The aforementioned further enlargement could hide a charge-transfer character of the emitting state or the presence of an emission from an upper excited state or the presence of different conformers in dynamic equilibrium in fluid solution. Further investigation in different solvents, with the help of fast and ultrafast techniques and refined quantum-mechanical calculations, is needed to have more information on the nature of the observed phenomenon.

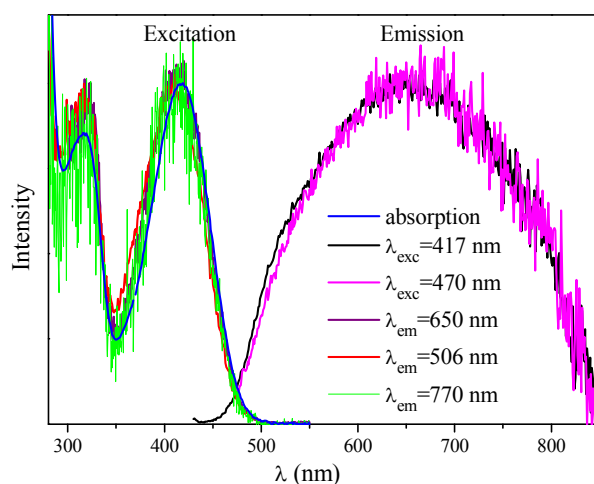


Figure 3. Wavelength effect on the emission and excitation spectra of **3** in CHCl₃. The absorption spectrum is reported for comparison.

In any case, this peculiar behavior of compound **3** is very interesting. In fact, light emissions of the organic dyes are generally quenched when the luminophores are fabricated into solid thin films, as we have observed for the other investigated compounds, and this fact greatly limits their use for practical applications, such as organic light-emitting diodes, chemosensors/biosensors etc. Usually the fluorescence quenching in highly concentrated solutions or in aggregated systems is due to intermolecular interactions. Probably the distorted

geometry of compound **3** conformations prevent a good package in H aggregates avoiding π - π stacking interactions and the efficient emission quenching. The prevalence of J (end-to-end arrangement) aggregates is in agreement with the shape of the absorption spectrum of **3** recorded in film that show a new band shifted in the red with respect to the main transition observed in CHCl_3 (see Fig. 1). According to the exciton theory, H- and J-aggregates are expected to show larger and smaller transition energy, respectively, with respect to the main transition of the unaggregated (or "unstacked") molecules in solution.²¹ The presence of J aggregates, characterized by red shifted absorption spectra, provides a greater harvesting of sun light.

The organic compounds with excellent emission properties at aggregate state or solid state (as found for **3**) attract more and more attention.^{22,23}

3.2 Photobehaviour of Mix1-3 in CHCl_3

The absorption spectra of the three mixtures in CHCl_3 and in thin film are shown in Fig. 4.

In solution both the absorption and emission spectra of the three mixtures can be considered as the sum of the spectra of the separated species (see also Fig.1). Moreover, the emission spectrum shape depended strongly on λ_{exc} , based on the weight of the absorption of each mixture component at that λ_{exc} (see Fig. 5). As a matter of fact, the emission spectrum of *Mix 3* changes only a little in the 450-570 nm onset, owing to the very low ϕ_{F} of **3** in CHCl_3 if compared with that of **2**, while ϕ_{F} was reduced by four times by exciting at the absorption maximum of **3** ($\lambda_{\text{exc}}=419$ nm, see below and Table 4).

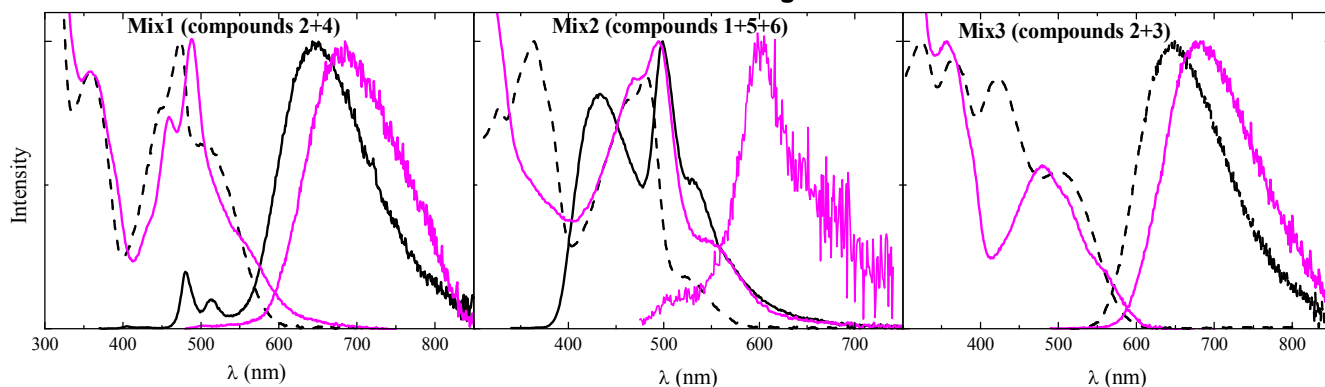


Figure 4. Normalized absorption and emission spectra of *Mix1-Mix3* in CHCl_3 solutions (black) and thin films (magenta).

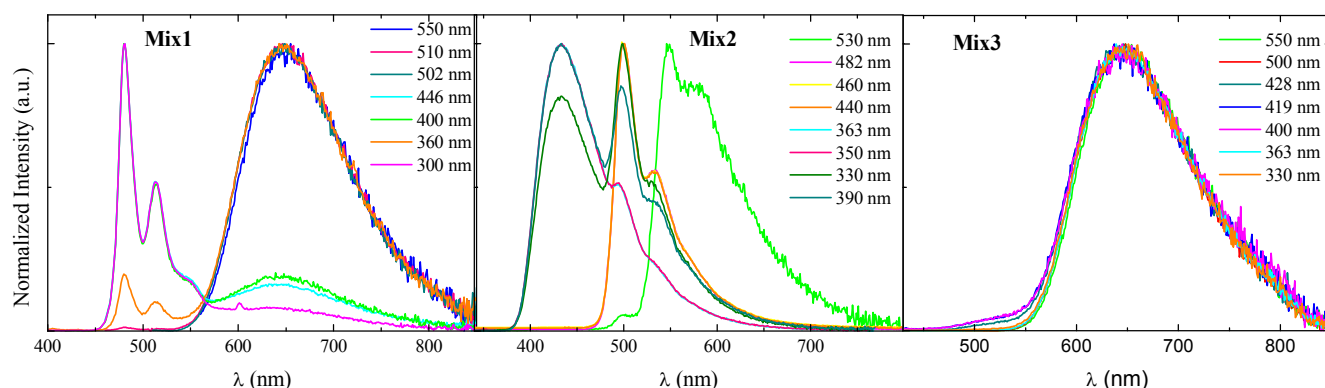


Figure 5. Effect of λ_{exc} on the emission spectra of the three mixtures in CHCl_3 .

The fluorescence quantum yield (ϕ_F) as a function of λ_{exc} resulted in good agreement (within the experimental error) with that calculated as the sum of the contributions of the different components. The obtained results are shown in Tables 2-4 for *Mix1-3*, respectively. The ϕ_F values, calculated by eq. 1,

$$\phi_{F,\text{mix}}^{\text{calc}}(\lambda_{\text{exc}}) = \sum_i \phi_{F,i} \times \frac{A_i(\lambda_{\text{exc}})}{A_{\text{tot}}(\lambda_{\text{exc}})} \quad (1)$$

are reported in the last column of Tables 2-4 and have to be compared with the experimental ϕ_F values ($\phi_{F,mix}^{exp}$, second last columns). The absorbance of the mixture components at different λ_{exc} (A_1 - A_6 in Tables 2-4) are calculated on the basis of their absorption coefficient.

The fluorescence decays were generally found to be polyexponential. As a matter of fact, a good biexponential decay with the same lifetimes ($\tau_F = 2.7$ and 4.5 ns) as those found for the separated compounds (see Table 1), was observed only in the case of *Mix 1*, by exciting with a led source ($\lambda_{exc} = 460$ nm) and analyzing the emission at $\lambda_{em} = 580$ nm, where both components are able to emit. In the other cases, the τ_F values of the mixtures components resulted too similar to be separated. Decays well fitted by mono-exponential functions were found with values longer or shorter according to the weight of the longer-lived component at that λ_{em} .

Moreover, all the emissive components were efficiently quenched by [60]PCBM with a diffusional rate ($k_Q \cong 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

All these findings point to an independent photobehaviour of the different compounds in the mixtures.

Table 2. Experimental and calculated ϕ_F as a function of λ_{exc} for *Mix1* in CHCl_3 .

| λ/nm | $\epsilon_2 (\text{M}^{-1} \text{cm}^{-1})$ | $\epsilon_4 (\text{M}^{-1} \text{cm}^{-1})$ | A_{tot} | A_2 | A_4 | $\phi_{F,mix}^{exp}$ | $\phi_{F,mix}^{calc}$ |
|---------------------|---|---|-----------|--------|---------|----------------------|-----------------------|
| 550 | 18910 | 10 | 0.0267 | 0.0266 | 0.00001 | 0.56 | 0.59 |
| 510 | 36640 | 40 | 0.0517 | 0.0514 | 0.00003 | 0.60 | 0.59 |
| 502 | 37150 | 200 | 0.0526 | 0.0522 | 0.0002 | 0.61 | 0.59 |
| 446 | 17060 | 47030 | 0.0619 | 0.0243 | 0.0377 | 0.66 | 0.69 |
| 400 | 7120 | 13510 | 0.0194 | 0.0094 | 0.0100 | 0.69 | 0.67 |
| 360 | 50150 | 5680 | 0.0729 | 0.0683 | 0.0044 | 0.63 | 0.60 |
| 300 | 21060 | 96290 | 0.1252 | 0.0352 | 0.0905 | 0.79 | 0.71 |

Table 3. Experimental and calculated ϕ_F as a function of λ_{exc} for *Mix2* in $CHCl_3$.

| λ/nm | $\epsilon_1 (M^{-1}cm^{-1})$ | $\epsilon_5 (M^{-1}cm^{-1})$ | $\epsilon_6 (M^{-1}cm^{-1})$ | A_{tot} | A_1 | A_5 | A_6 | $\phi_{F,mix}^{exp}$ | $\phi_{F,mix}^{calc}$ |
|--------------|------------------------------|------------------------------|------------------------------|-----------|--------|---------|--------|----------------------|-----------------------|
| 560 | 220 | 270 | 23160 | 0.0042 | 0.0001 | 0.00008 | 0.0040 | 0.35 | 0.27 |
| 530 | 260 | 570 | 63970 | 0.0157 | 0.0002 | 0.0002 | 0.0151 | 0.33 | 0.25 |
| 482 | 320 | 100190 | 70940 | 0.0838 | 0.0004 | 0.0580 | 0.0243 | 0.65 | 0.57 |
| 460 | 340 | 89020 | 65160 | 0.0749 | 0.0004 | 0.0513 | 0.0222 | 0.61 | 0.57 |
| 440 | 390 | 64074 | 54190 | 0.0562 | 0.0005 | 0.0367 | 0.0184 | 0.59 | 0.55 |
| 390 | 33780 | 11667 | 33810 | 0.0490 | 0.0335 | 0.0056 | 0.0096 | 0.68 | 0.68 |
| 363 | 79200 | 5770 | 28650 | 0.0955 | 0.0832 | 0.0029 | 0.0086 | 0.82 | 0.75 |
| 350 | 69730 | 5970 | 26890 | 0.0851 | 0.0733 | 0.0030 | 0.0081 | 0.77 | 0.75 |
| 330 | 38020 | 34570 | 36280 | 0.0722 | 0.0418 | 0.0183 | 0.0114 | 0.79 | 0.69 |

Table 4. Experimental and calculated ϕ_F as a function of λ_{exc} for *Mix3* in $CHCl_3$.

| λ/nm | $\epsilon_2 (M^{-1}cm^{-1})$ | $\epsilon_3 (M^{-1}cm^{-1})$ | A_{tot} | A_2 | A_3 | $\phi_{F,mix}^{exp}$ | $\phi_{F,mix}^{calc}$ |
|--------------|------------------------------|------------------------------|-----------|--------|---------|----------------------|-----------------------|
| 550 | 18910 | 10 | 0.0271 | 0.0271 | 0.00002 | 0.63 | 0.59 |
| 500 | 37090 | 180 | 0.0522 | 0.0519 | 0.0003 | 0.70 | 0.59 |
| 428 | 10240 | 22270 | 0.0515 | 0.0146 | 0.0369 | 0.20 | 0.18 |
| 419 | 7900 | 23610 | 0.0511 | 0.0114 | 0.0397 | 0.16 | 0.15 |
| 400 | 7120 | 20240 | 0.0437 | 0.0102 | 0.0335 | 0.15 | 0.15 |
| 363 | 49370 | 6890 | 0.0809 | 0.0696 | 0.0113 | 0.49 | 0.51 |
| 330 | 34100 | 15010 | 0.0725 | 0.0480 | 0.0245 | 0.36 | 0.40 |

3.3 Photobehaviour of thin films of the *Mix1-3* blends

The same blends have been analyzed in thin films. Their absorption and emission spectra are shown in Fig. 6 together with those of the films obtained for the separated compounds for comparison purposes. *Mix 1* and *Mix 2* showed an absorption extending to 700 nm.

As observed for the mixtures in $CHCl_3$, the absorption spectra of the mixtures films are the sum of those of the separated compounds, pointing to the absence of interaction among them in the ground state. However, the emission behavior of the mixtures films is quite different: their emission spectrum looks like that of the bathochromic species (see Fig. 4) and no effect of λ_{exc}

on the emission spectrum shape, to evidence the different contributions of the emissive components at various λ_{exc} , was found, particularly evident for *Mix1* (see Fig. 7). Moreover, the excitation spectra monitored at the wavelength of the emission maximum ($\lambda_{\text{em}}^{\text{max}}=690, 605$ and 680 nm for *Mix1-3*, respectively) overlapped the absorption ones (Fig. 7) and the ratio between the integrated emission spectrum (Area) obtained by exciting at a specific λ_{exc} and the mixture absorbance (A_{tot}) at the same λ_{exc} , resulted not to vary appreciably at different λ_{exc} , regardless of which is the mainly absorbing species (see Table 5).

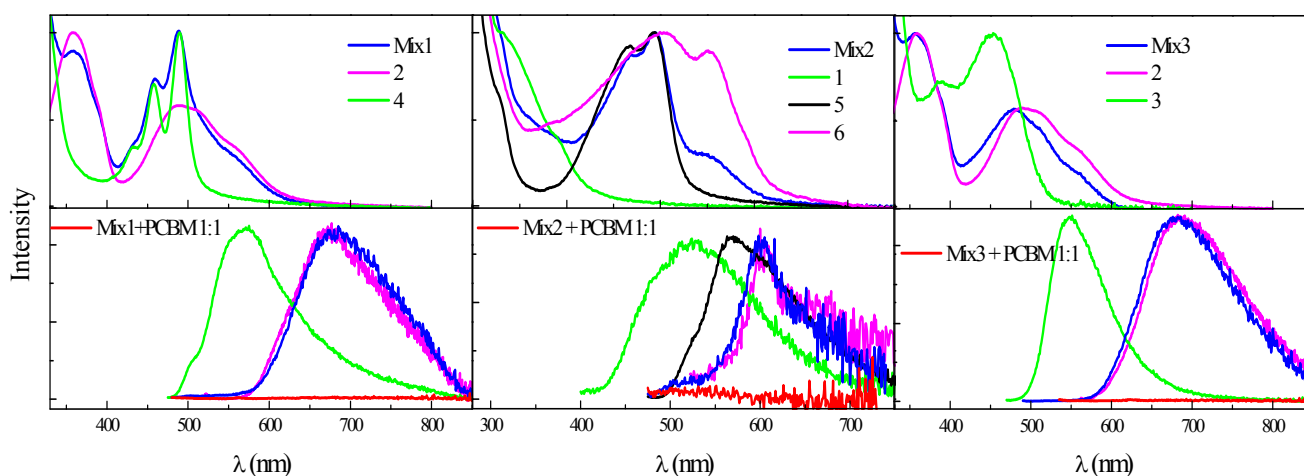


Figure 6. Normalized absorption (top panels) and fluorescence (bottom panels) spectra of thin films of *Mix1-3* compared with those of thin films of the separated components.

These interesting findings are in agreement with an energy transfer from the excited state of the hypsochromic species (**4** for *Mix1*, **1** and **5** for *Mix2* and **3** for *Mix3*) to that of the bathochromic one (**2** for *Mix1* and *Mix3* and **6** for *Mix2*), that is the main responsible for the fluorescence.

Fig. 6 shows a very good match among the emission spectra of the hypsochromic species and the absorption of the bathochromic one that suggests a very efficient non radiative energy

transfer induced by dipole-dipole interaction of the donor-acceptor pair through an electric-dipole field (Förster mechanism) should occur.

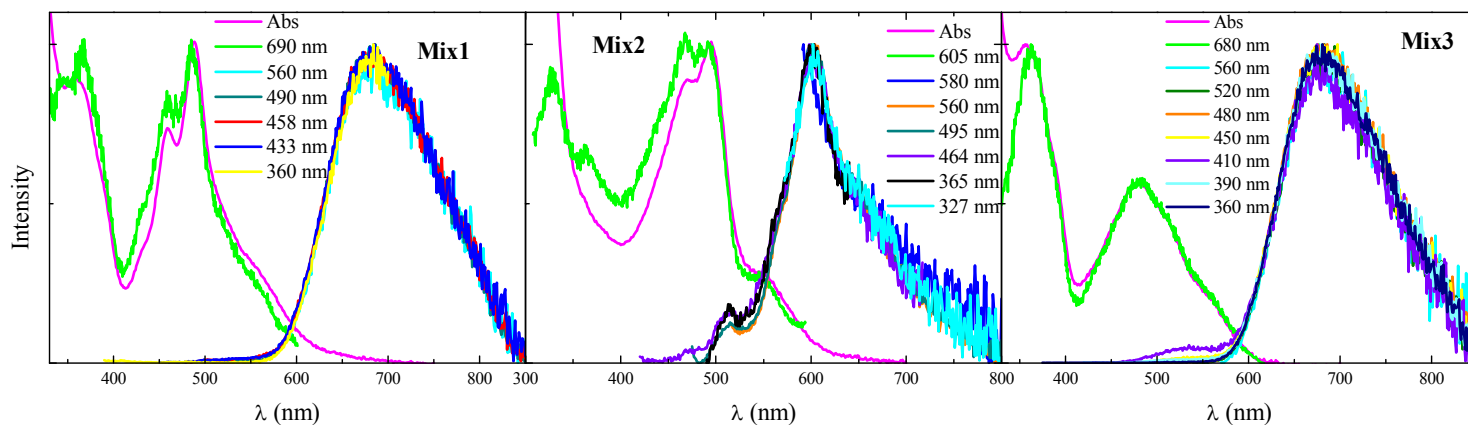


Figure 7. Normalized emission spectra as a function of λ_{exc} for thin films of *Mix1-3*. The excitation (at $\lambda_{\text{em}}^{\text{max}}$) and absorption spectra are also shown.

Table 5. Effect of λ_{exc} on the ratio between the integrated emission spectrum (Area) and the mixture absorbance (A_{tot}).

| <i>Mix1</i> | | | | <i>Mix2</i> | | | | <i>Mix3</i> | | | |
|--------------------------------|------------------|------------------------------|--|--------------------------------|------------------|------------------------------|--|--------------------------------|------------------|------------------------------|--|
| λ_{exc} (nm) | A_{tot} | Area ($\times 10^{-8}$) | Area/ A_{tot} ($\times 10^{-9}$) | λ_{exc} (nm) | A_{tot} | Area ($\times 10^{-7}$) | Area/ A_{tot} ($\times 10^{-8}$) | λ_{exc} (nm) | A_{tot} | Area ($\times 10^{-8}$) | Area/ A_{tot} ($\times 10^{-9}$) |
| 600 | 0.023 | 0.25 | 1.10 | 580 | 0.023 | 0.97 | 4.28 | 560 | 0.033 | 1.51 | 4.61 |
| 560 | 0.062 | 1.06 | 1.72 | 560 | 0.037 | 1.66 | 4.55 | 520 | 0.063 | 2.95 | 4.70 |
| 490 | 0.216 | 4.29 | 1.98 | 495 | 0.145 | 6.58 | 4.54 | 480 | 0.090 | 4.45 | 4.92 |
| 458 | 0.159 | 3.80 | 2.40 | 464 | 0.124 | 6.77 | 5.48 | 450 | 0.069 | 3.25 | 4.72 |
| 433 | 0.079 | 2.34 | 2.96 | 365 | 0.070 | 4.30 | 6.12 | 410 | 0.040 | 1.66 | 4.15 |
| 360 | 0.193 | 4.16 | 2.15 | 327 | 0.154 | 5.62 | 3.64 | 360 | 0.159 | 7.19 | 4.52 |

The proper emission of the mixture components that absorb at shorter wavelengths has a very low intensity, particularly for *Mix 1* (see Fig.7) and was evidenced, in the latter case, only monitoring the excitation spectrum of the mixture at λ_{em} corresponding to $\lambda_{\text{em}}^{\text{max}}$ observed for thin

films of the pure hypsochromic components. This fact points to a very efficient, practically quantitative, energy transfer to the bathochromic species, favored in thin films, where the different components become closer in the aggregates and a Förster mechanism can be favored.

It has to be stressed that the overlapping of the mixture excitation spectra and their absorption and the constancy of the $A_{\text{exc}}/A_{\text{tot}}$ ratio (Table 5) on varying λ_{exc} , not only suggest the presence of an efficient energy transfer from the absorbers to the emitting species, but exclude other possible mechanism, such as charge transfer, for the fluorescence quenching of the hypsochromic species. In fact, all the absorbed quanta produce the excited state of the fluorophores.

Similar behaviors have been previously found.^{15,24,25}

The red lines in Fig. 6 show that the emission falls down practically to zero in the mixture films in the presence of [60]PCBM owing to an efficient quenching by the charge acceptor also in the solid state.

4. CONCLUSIONS

The photobehaviour of three blend systems comprising [60]PCBM and different combinations of five extended arylacetylenes and one arylvinylene, evidenced different behaviour in CHCl_3 solution and in the solid state as thin films. In CHCl_3 solutions the spectral and photophysical properties of the mixtures can be considered as the sum of those of the separated components. On the contrary, the photobehaviour of the thin films of the mixtures showed an independent behaviour in the ground state but pointed to an efficient quantitative energy transfer among the singlet excited states of the mixture components that practically led to observe emission only

from the low-lying S_1 state of the bathochromic species. Its fluorescence was then efficiently quenched by the charge-acceptor [60]PCBM.

This mechanism can be of interest to enhance the sun light harvesting. Particularly noteworthy is the peculiar behaviour of the arylvinylene derivative **3** that showed a broad and weak fluorescence band in CHCl_3 and a sharp intense emission in thin films. This behavior, opposite to that (more common) found for the studied arylacetylenes semiconductors, makes this compound interesting for application in optoelectronics.

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Energy transfer mechanism, interesting to enhance the sun light harvesting, was found to be operative in donor arylacetylenes' blend thin films, leading to observe emission only from the bathochromic species, efficiently quenched by charge transfer to [60]PCBM.

