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Synthesis, characterization and photo physical-theoretical analysis of D- π -A compounds. 2. Chain length effect through even-odd effect on the photophysical properties

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Abstract

In the continuous search for new compounds for solar devices, the family of dipolar D- π -A molecules, which have a donor (D) and an acceptor (A) charge joined by a conjugate bridge, have been the focus of attention in the recent years due their different properties. As we have shown before, there is a connection between the geometry of molecules based on tertiary asymmetric amines and their quantum yield. In the current work, four new compounds based on the same backbone molecule ((*E*)-2-cyano-3-(5-((*E*)-2-(9,9-diethyl-7-(phenylamino)-9*H*-fluoren-2-yl)vinyl)thiophen-2-yl)acrylic acid),but with different substituent, were synthesized. It is shown that the chain-size of the substituent group modifies the quantum yield. The news substituents introduced are a propyl (M8-3), butyl (M8-4), pentyl (M8-5) or hexyl (M8-6) group. In general, it was possible to see that the new substituents were able to increase their performances. Furthermore, an odd-even substituent effect, between propyl/pentyl and butyl/hexyl, was found and the theoretical geometrical data was able to follow the trend. However, theoretically, this substituent effect was inverted in the case of M8-3 and M8-4, which may be due to the disappearance in the emission patterns of an excited state close to 450 nm (at λ_2), as it was shown in the experimental data. The most suitable behaviour belongs to [(*E*)-2-cyano-3-(5-((*E*)-2-(9,9-diethyl-7-(phenyl(propyl)amino)-9*H*-fluoren-2-yl)vinyl)thiophen-2-yl)acrylic acid] (M8-3). M8-3 has the highest

quantum yields on average in all studied solvents; even higher than the last reported compounds with methyl (M8-1) and ethyl (M8-2) groups. Theoretically, the most likely explanation is that the dihedral angle formed between the carbonyl acceptor and nitrogen electron donor (Aryl-CO), should be as small as the molecule M8-3. This isolated compound has an average quantum yield including all solvents of 58.1% (average value), showing that a long group is not necessary to improve the performance.

Keywords: Dye, quantum efficiency, dihedral angle, chain length effect, odd-even substituent effect.

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1. Introduction

Due to their promising optical properties for use in optoelectronic devices, D- π -A compounds, which have a donor (D) and an acceptor (A) joined by a conjugate bridge, are attracting increasing scientist interest. Dyes based on this backbone, *((E)*-2-cyano-3-(5-((*E*)-2-(9,9-diethyl-7-(phenylamino)-9*H*-fluoren-2-yl)vinyl)thiophen-2-yl)acrylic acid) (fig.1), were used with some success in organic solar cells [1]. This type of compounds has a donor moiety, an electron rich component, generally a triarylamine, oligothiophene or some heterocycles moiety. On the other hand, acceptors have two functions, firstly to attract the electron density after light absorption and to deliver it to the anchor material and second to chemically bond over this material (adsorption). Classical structures are fractions of cyanoacetic acid [2], fluorene, aniline and thiophenes fractions have commonly been used because of their photoelectrochemical properties [3-7]. Previously we reported the synthesis and characterization of four D- π -A -type dyes, in two series: alkyl- and alloy-substituted, M8-n and M8-On (Figure 1, R = Me (n=1) or Et (n=2)) [2]. The alkyl substituted series exhibited good photophysical properties. We showed that these D- π -A compounds have a connection between their geometry and quantum yield values. Therefore, in the present work we have synthesized four new molecules, which keep the structure and only increase

the substituent chain-size. Actually, in our previous work, the molecules showed an excellent performance, only in specifics solvents, such as 1, 4 dioxane. The quantum yield (in average) does not reach high values or the behaviour is not continuous on the studied solvents due the short substituent. In this work; the aim is to improve this behaviour, introducing new longer substituent which could be able to increase the performance in different solvents, even in polar solvents usually useful in solar cell manufacturing for instance. These new organic compounds were tested, in terms of photophysical properties, to obtain information about their behaviour [9-13]. Synthesis and characterization via UVvis. spectroscopy, elemental analysis, NMR, FT-IR, mass and fluorescence spectroscopy of four new dyes: M8-3, M8-4, M8-5 and M8-6 (Fig. 1a), were performed (Table 1). The study, both photophysical and theoretical, was conducted using eight solvents, sorted in ascending order relative to their polarity index: dichloromethane (DCM), tetrahydrofuran (THF), ethyl acetate (ETA), such as 1,4-dioxane (DIO), acetone (ACT), acetonitrile (ACN), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). In DCM and ACN, studies were qualitative since the dyes are not completely soluble therein. We show there is a relationship between the substituent length and the quantum yield. There is a difference between the molecules with methyl, propyl and pentyl substituents and ethyl, butyl and hexyl substituents. Theoretically, it is possible to follow each different experimental trend. This effect has been named ODD-EVEN effect, because it only occurs between the different substituents, the even ones (M8-2, 4 and 6) and the odd ones (M8-1, 3, 5) (Fig. 1).

2. Materials and methods

In general, the conditions are the same as reported in our previous work [2]. All solvents used in both syntheses and subsequent analyses were high purity anhydrous, and purchased from Aldrich. Synthesis methods are shown in "dyes synthesis" section (SI-2. Section 2). FT-IR spectra were recorded on a Bruker, VECTOR 22 model spectrophotometer (Spectra available on the SI-3. Section 3). NMR spectra were recorded on a Bruker 400 MHz Spectrometer (Spectra available on the SI-3. Section 3.). Subsequently, measurements of solutions of each dye, concentrations between 0.5 and 3 mmol L ¹, were used for quantum yield determinations. UV-Vis spectra were recorded on an Agilent spectrophotometer and fluorescence on a HORIBA Scientific Fluoromax-4spectrofluorometer. The samples have been prepared with KBr (for solid ones), and KBr liquid film (for oils), the resolution used

is 16 cm⁻¹ with 32 scans and a range of measurement of 600-4500 cm⁻¹. For mass spectrometry, a Triple Quad, 4500 AB SCIEX-mass spectrometer was employed. Theoretical calculations were performed with the Gaussian 09 program, utilizing the density functional theory (DFT), specifically, the B3LYP method and 6-31 g(d) basis set for optimizations. As for photo-physical, calculations were performed using time dependent methods, TD-DFT, to obtain three of the most important dyes intensities [1, 2].

3. Results and discussion

3.1 Dye synthesis

The synthetic route to obtain these products is signalled in the scheme 1. The synthesis of these new products is similar to that reported in our previous work [2], although in this case, to generate compounds with longer substituent chains, the amine (reactant) in the of Buckwald-Hartwig reaction is changed by *N*-propylaniline, *N*-butylaniline, *N*-pentylaniline and *N*-hexylaniline, respectively. As already mentioned, details of synthetic methodology and classical characterization are given at supplementary material (SI-2).IR and NMR spectra are also showed (SI-3).

3.2. Photophysical properties

3.2.1. UV-Vis spectrophotometry

Similar to the previously described M8-n series [2], two notable bands are shown in the UV-Vis region. It can be seen that there is an hypsochromic effect of the absorption maxima of the n- π^* transition. (Table 2) [14].In solvents wherein the compounds were soluble, the molar extinction coefficient (ϵ_0) (Table 2) was determined and were similar to those of the previously studied compounds, they have values in the 10⁴ M⁻¹ cm⁻¹ range.

3.2.2 Fluorescence Spectroscopy

In the emission or fluorescence spectra of the synthesized dyes, from 1 to 4 different bands can be observed, depending on the solvent and the excitation wavelength. In this case, the fluorescence patterns are obtained by excitation at two different wavelengths (λ_1 and λ_2). λ_1 , is the maximum absorption wavelength (table 2). λ_2 , is a wavelength selected to measure quantum yield values. In general, no clear trend between these maxima exists, even when it is compared with the increasing polarity of the used solvent.

In all spectra, each molecule, shows different patterns, where 1 to 4 bands can be found. In table 3, it a summary of the maxima and intensities are shown. The different bands are related to different excited states, in particular, each one was labelled (ordered from lowest energy to highest energy), S₁, S₂, S₃ and S₄, which have a value (in average) of 640, 600, 500 and 450 nm, all this according to the reference [2]. The intensities are labelled from 1 to 3 or 4, where 1 is the highest and 3 or 4 the lowest. When these molecules are excited at two different wavelengths, different patterns are obtained. When they are excited at λ_1 (Figs. 2 [a, b] and SI1.1, SI1.2, SI1.3 [a, b]), different bands are seen. Nevertheless, when they are excited at different wavelength (Figs. 2 [c, d] and SI1.1, SI1.2, SI1.3 [c, d]), a solvent-dependent change of the previous pattern occurs. As summary, in the tables 3 and SI1.1, SI1.2, SI1.3, are the different values of each emission maximum. It is possible to see that only M8-5 has an S₄ state at λ_{max} . Moreover, the appearance of S₁ and S₂ is common for all molecules. In the other hand, at another wavelength (λ_2), the quenching of S₁ and S₂ signals is common. The Föster resonance energy transfer (FRET) effect is still appearing in these compounds, therefore this effect is definitively associated with the molecular architecture D- π -A [1].In addition, the quenching of the first two excited states (at λ_2 excitation wavelength) can be attributed to the fact that the excited states (S₁ and S_2), do not generate stable excited complexes in the employed solvent [15-16].

3.2.3 Excited states polarity estimation, absorption and emission graphic analysis using Lippert equation and Lippert–Mataga plots

To estimate the difference of dipole moment change of the compounds, the Lippert equation is used (S_0) . Therefore, by plotting the Stokes shift (Table SI1.4) absolute value of all solvents *vs.* the dipolar factor of the same solvent (Lippert-Mataga plot), the difference in dipole moment for each dye is obtained from the respective slope [17-19].

A plot of the Stokes shift (in frequency units (cm⁻¹)) *vs.* dipolar solvent factor (S_o, Eq. 1), allows inferring a high value slope (fig. 3[a, b, c, d]), indicating the dye presents a greater difference between its ground state and excited states, which is ascribed to nitrogen nonbonding electron pair donation. For the estimation of the polarity of the excited state, Onsager radius (a), is estimated as the ninth of the distance between the carbon corresponding to carbonyl and nitrogen [2], currently 17.87 Å. The difference of the dipole moment in this case corresponds to the difference between the ground state and the excited state dipole moment. Having in mind the kind of transition occurring in these molecules, the ground state is more polar than the excited state [20]. Ground state values are estimated by performing theoretical calculations using the Gaussian 09 program and optimizing the chemical structures [2].

As it has been seen in our previous work [2], the points in the graphs tend to diverge. Nevertheless, this is not an isolated fact and other compounds show this behaviour [21]. In summary, the aim is to compare, then this plot has been made to obtain some information related with substituents and only qualitative information could be obtained. Comparing dipole moment difference of dyes (Table 4), M8-6 exhibits the largest difference as compared to the other dyes (among the molecules of this work). If it is included two molecules from our last work (M8-1 and M8-2), it is possible to realize that the difference decrease until M8-6. Therefore, the length of the *N*-alkyl chain has an inversely proportional relation with the difference between these two states (ground and excited). In terms of state polarity, ground and excited state increase progressively their polarity with the substituent chain length (not the case of M8-6).

3.2.4 Quantum yield (Φ_F)

For the determination of quantum yields, a comparative method reported by Williams et al. [22, 23], using zinc phthalocyanine (ZnPc) as standard in a 1% pyridine solution in toluene (Eq. 1) was utilized. For solvents where solubility is not total, such as DCM and ACN, the above method is used but as an equation with unknowns not as an equation derived from a plot (Eq. 2).

$$\Phi_{\rm X} = \Phi_{\rm ST} \left(\frac{{\rm Grad}_{\rm X}}{{\rm Grad}_{\rm ST}} \right) \left(\frac{\eta_{\rm X}^2}{\eta_{\rm ST}^2} \right)$$
(1)

Equation 2 is used to determine quantum yields by Williams. Φ_X refers to the quantum yield of the sample and Φ_{ST} is the quantum yield of the reference standard, in this case 0.30 (30.0 %). Grad_x is the slope of integrated emission intensity *vs.* absorbance plot, for the sample and Grad_{ST} the slope for the standard. η_X and η_{ST} , correspond to the refractive index of sample and standard solvent, respectively.

$$\Phi_{\rm S} = \frac{\rm Abs_{\rm R}}{\rm Abs_{\rm S}} \times \frac{\rm Area_{\rm S}}{\rm Area_{\rm R}} \times \frac{n_{\rm S}}{n_{\rm R}} \times \Phi_{\rm R}$$
(2)

Equation 3, is used to determine quantum yields in solvents where the dye is not fully soluble. In this case, Φ_S refers to the quantum yield of the sample and Φ_R is the quantum yield of the standard. S and R Area stand for sample and standard integrated emission intensity, respectively. Abs_R and Abs_S, correspond to sample and standard absorbance, η_S and η_R , stand for sample and standard solvent refractive index, respectively.

As for the values of quantum yields (Table 5), they showed no linear relation with solvent polarity, but some trends are possible to be found taking into account the main factors affecting fluorescence: chemical structure, structural rigidity, temperature, solvent, pH and concentration effect [24]. For measurements, temperature (room), structural rigidity, pH (not applicable) and low concentrations (absorbance lower than 0.1 units) are kept constant. The chemical structure varies and the modifications are mentioned in the introductory section. Different solvents were tried in order to observe their responses. The comparison of compounds demonstrated that the quantum yield is not proportional to neither substituent length nor to the polarity of the solvent (Table 5). It was observed that, in general, in each studied solvent the molecules bear a relationship to viscosity. The solvents showed a linear relationship between quantum yield and viscosity (fig. 4), attaining a maximum for DIO and slightly decreasing for DMSO, the solvent with the highest viscosity (higher viscosities negatively affect the quantum yield).

A general comparison of quantum yields between the previously reported M8-1,2 [2] and the new M8-3, 4, 5, 6 molecules, shows that this yields tend to increase (on average) in the new series of compounds

In consequence, increasing the alkyl group size favours quantum yield.

The quantum yield results show values higher in non-polar solvent than polar solvent. An explanation for this is that longer chains improve solubility, contact between molecules and chemical environment, also the geometry in such a way that the excited states decay only in fluorescence [25-27] improving yield. On average, M8-3 exhibits the largest quantum yield of the dye series, evidencing that it is unnecessary to have such long chains in the molecular structure, as M8-6 with hexyl group, to increase yields. Another important difference, on average (Table 6), is observed among compounds M8-1, 3, 5 and M8-2, 4, 6. In all cases, the odd compounds have a higher yield than its next neighbour even compounds (1>2, 3>4 and 5>6). In particular, it is possible to see (table 6), that M8-3 tends to have the same quantum yield value (with a difference of 5.1 units) between polar and non-polar solvents; being higher in non-polar solvent. Nevertheless, in the case of M8-4 this trend changes, this value being higher in polar solvents (difference of 3.1 units).

3.3 Theoretical approach to molecular properties, dihedral angles and their relationship to quantum yield.

Another way to find an answer to quantum yield values is to compare dihedral angles [2]. In this case, the angle formed between the carbonyl acceptor and amine donor is compared, as an approximation between these two groups, due the π -bridge linearity (fig. 5). In addition, theoretically the structure shows this linearity among the different moieties involved in the π -bridge. This approximation is because both, HOMO and LUMO orbitals situate around these functional groups (fig. 6 [a, b] for M8-3). In this comparison, two possible angles exist, Aryl-CO, which refers to that formed between the nitrogen-ring and carbonyl group, the second, Alkyl-CO, to the one formed between aliphatic chainnitrogen and carbonyl group. In table SI1.5, it is showed the values taken for both dihedral angles in non-polar solvents for all the compounds into this family. M8-1 has the highest value. Separately, it is difficult to find tendencies; nevertheless, it is possible to see the value change in M8-6. This could have a relation with the break in the dipolar moment difference tendencies (table 4). A summary of values is showed in the table SI 1.6. In general, values do not seem to change, whatever the different solvents.

On average, it was found Aryl-CO values are smaller in polar than in non-polar solvents and Alkyl-CO values are bigger in polar than in non-polar solvents (table 7). This means, the geometrical factor has an important effect or influence in quantum yield and all depends on the type of solvent. In this case, to explain the experimental changes, it favours Alkyl-CO lower values and Aryl-CO higher values. As quantum yield values, here a difference was found between even and odd chain length substituents. However, the tendencies are diverse. For Aryl-CO values, M8-1 is bigger than M8-2, which is correct. M8-3 is smaller than M8-4, which does not follow the tendency. M8-5 is higher than M8-6, which is correct. M0-4, which does not follow the trend. M8-5 is smaller than M8-6, which is correct. As summary, only M8-3 and M8-4 do not follow the trend, for the rest, it is true. It is this fact together with the disappearance of the state close to 450 nm (S₄), at the moment to measure quantum yields (at λ_2); which could explain the different behaviour of M8-3 and 4 in the studied solvent.

3.3.1 Theoretical photophysics, comparison of assignments

In order to corroborate the assignments of the patterns of fluorescence spectra, theoretical calculations were conducted using the Gaussian 09 program, employing the density function theory (DFT), specifically the B3LYP method and the 6-31g (d) basis set for optimizations. In the photophysics case, it is calculated using time-dependent methods, TD-DFT, in order to obtain three of the most important intensities of the molecules [2].Most transitions occur between frontier orbitals and other nearby orbitals. The HOMO (H), the orbital previous to HOMO (H-1) and the anterior to this (H-2) appear in this case. As for LUMO (L), the next to LUMO (L+1) and the next to this (L+2) also appear (fig. SI1.6 [a, b, c, d]). The orbitals, both HOMO and LUMO, for both families are seen in fig. SI1. 5(a, b). In general, the Stokes shifts are explained by the Franck-Condon principle, and at the same time explain that at two different excitation wavelengths (λ_1 and λ_2), where the former has less energy than the second, some or all of the excited states are shown [28]. In table SI1.7, the different values of each peak are shown (experimental). In addition, the theoretical values are also shown (table SI1.8). As it was reported [2], the state S₂ is not possible to estimate in M8-5 and 6. In M8-3 and 4, it does not exist with that value. Nevertheless, the first state, S₁, it is accurately predicted, for M8-3, 4 and 5, with an error of 3.1% and for M8-6, with an error of 3.6%.

4. Conclusions

Four new dyes, aimed at determining whether lengthening the chains of the previously synthesized molecules, M8-1 and 2, could improve their quantum yields, were synthesized. The yields of the total synthesis of M8-3, 4, 5 and 6 were 8.6, 8.3, 7.5 and 8.1%, respectively. In general, a trend to maintain the previous general hypsochromic behaviour was observed. For the value of the difference between the ground and the excited state, it decreases from M8-1 until M8-6. M8-3 has the highest quantum yield on average, 58.1%. Searching for an explanation for quantum yields, it was concluded that the dihedral angle Alkyl-CO should be small and the angle Aryl-CO should be large, to favour better yields. In general, an odd substituent improves yields, making M8-1 > M8-2, M8-3 > M8-4 and M8-5 > M8-6. Nevertheless, M8-3 and M8-4 do not follow the dihedral angle trend (inverse relation), and this seems to have some relation with both do not show the excited state at 450 nm, which appears in all other members of the series. Finally, all this data points to these compounds as possible candidates for solar cells. As consequence, future additional measurements will be made.

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Figure index

Figure 1. Structural formula of the synthesized dyes and the previous reported ones. In red, it is signalled the non-changing backbone.

Figure 2. M8-3 emission spectra in the surveyed solvents, excited at λ_1 : (a) and (b), and at λ_2 : (c) and (d).

Figure 3. Dyes Lippert-Mataga plots: (a) M8-3. (b) M8-4. (c) M8-5. (d) M8-6.

Figure 4. Viscosity vs average quantum yield.

Figure 5. Approximate structures for the determination of dihedral angles of: a) M8-3 and M8-4. b) M8-5 and M8-6.

Figure 6. Surfaces for the frontier orbitals of M8-3: (a) HOMO, (b) LUMO.

Scheme index

Scheme 1.Sinthetic route to the M8 compounds i) KOH, KI, CH₃CH₂Br, DMSO; ii) n-BuLi, DMF, THF, -78°C; iii) NaBH₄, MeOH, THF; iv) PHPh₃Br, CHCl₃, reflux; v) thiophen-2-carbaldehyde, *t*-BuOK, reflux, toluene. vi) secondary amine, PdCl₂, (*t*-bu)₃PHBF₄, *t*-BuOK, toluene; vii) n-BuLi, DMF, THF, -78°C; viii) cyanoacetic acid, ammonium acetate, acetic acid, 120 °C.

Table index

Table 1. Nomenclature employed for the synthesized dyes.

Table 2. Dyes maximum absorption wavelength (λ_{max}) in different solvents.

Table 3. M8-3 λ_{em} excited at λ_1 and λ_2 . The numbers indicated are related to intensity.

Table 4. Dipole moment from Lippert plots.

 Table 5. Dyes quantum yield in different solvents.

Table 6. Average quantum yield in polar and non-polar solvents.

Table 7. Angles grouped according non polar and polar solvents.

Table 1.Nomenclature employed for the synthesized dyes.

Dye IUPAC Name	Code Name
(E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(phenyl(propyl)amino)-9H-fluoren-	M8-3
2-yl)vinyl)thiophen-2-yl)acrylic acid (E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(phenyl(butyl)amino)-9H-fluoren- 2-yl)vinyl)thiophen 2-yl)acrylic acid	M8-4
(E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(pentyl(phenyl)amino)-9H-fluoren-	M8-5
2-y1)viny1)thiophen-2-y1)acrylic acid (E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(hexyl(phenyl)amino)-9H-fluoren- 2-y1)viny1)thiophen-2-y1)acrylic acid	M8-6

Dye	Parameter	DCM	THF	ETA	DIO	ACT	ACN	DMF	DMSO
M8-3									
	λ_{max}	480	462	444	460	458	428	412	430
	ε _o .10 ⁴	1.4	1.5	1.8	1.4	1.2	1.3	1.6	2.3
	λ_{em}	600	572	552	617	575	531	593	514
M8-4								2	
	λ_{\max}	486	466	460	474	464	434	424	433
	ε _ο .10 ⁴	2.9	3.7	3.9	3.1	2.9	2.8	3.7	3.6
	λ_{em}	595	622	590	621	576	518	605	520
M8-5			-						
	λ_{\max}	470	456	460	464	464	430	418	430
	ε _ο .10 ⁴	3.9	4.4	3.5	3.8	7.0	3.2	4.1	5.1
	λ_{em}	584	597	580	618	574	496	504	517
M8-6									
	λ_{max}	479	464	462	466	465	427	426	430
	ε _ο .10 ⁴	4.0	4.2	3.9	4.5	3.8	3.4	3.9	3.1
	λ _{em}	594	651	654	620	574	554	605	627
Polarity Index		3.1	4.0	4.4	4.8	5.1	5.8	6.4	7.2

CEP (E)

Table 2. Dyes maximum absorption wavelength (λ_{max}) in different solvents.

Solvent	Excitation at λ₁ (nm)		λ _{em} (nm)		Excitation at λ ₂ (nm)		λ _{em} (nm)
	State	e	6	e	Stato	6	6	c
DCM	480	638(2)	<u> </u>	3	<u>395</u>	<u> </u>	<u> </u>	490(1)
THF	462	640(2)	572(1)		382.3	(-)	R	4723(1)
ETA DIO	444 460	638(2) 637(2)	552(1) 617(1)	473(3)	376.7 381 6	637(3)	611(2)	471(1) 466(1)
ACT	458	639(2)	575(1)		386	001(0)	011(2)	492(1)
ACN	428	639(3)	604(2)	531(1)	380	637(3)	588(2)	531(1)
DMF DMSO	412 430	638(3) 638(3)	593(1) 607(2)	525(2) 514(1)	381.4 369.5	639(3)	579(2)	506(1) 511(1)

Table 3: M8-3 λ_{em} obtained from	n excitations at the	wavelengths λ_1 and λ_2 .
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Dye	Slope	Dipole moment difference (D)	Ground state dipole moment (D)	Excited state dipole moment (D)	R ²
M8-1 [14]	24162.04	3.69	11.47	7.778	
M8-2 [14]	21356.95	3.47	14.24	10.767	
M8-3	18757.27	3.25	14.28	11.030	0.791
M8-4	18374.84	3.22	14.33	11.114	0.787
M8-5	16095.54	3.01	14.32	11.312	0.738
M8-6	22573.83	3.57	14.34	10.768	0.829

Table 4. Dipole moment from Lippert plots.

CER ANA

Solvent	DCM	THF	ETA	DIO	ACT	ACN	DMF	DMSO
Polarity	3.1	4.0	4.4	4.8	5.1	5.8	6.4	7.2
index								
Viscosity	0.40	0.51	0.41	1.15	0.31	0.37	0.77	2.13
				Dye				
M8-1[14]	20.5	32.7	61.4	98.8	10.9	8.2	56.1	17.6
M8-2[14]	18.4	47.1	34.2	62.5	26.3	25.5	60.2	31.7
M8-3	62.4	35.5	58.4	86.2	48.6	22.9	89.4	61.1
M8-4	7.2	69.4	18.5	58.6	39.7	0.9	77.7	47.5
M8-5	0.5	40.5	80.1	96.9	22.3	2.5	65.1	62.2
M8-6	4.7	45.8	44.3	81.3	25.1	10.5	63.8	32.2
Average	19.0	45.2	49.5	80.7	28.8	11.8	68.7	42.1

 Table 5. Dyes quantum yield in different solvents.

Table 6. Average quantum yield in polar and non-polar solvents.

_	Average ne solvents	on-polar	Average p	olar solvents	General average	
Dye / Angle	Ar-CO	AI-CO	Ar-CO	AI-CO	Ar-CO	AI-CO
M8-1	45.5	122.7	44.1	124.8	44.8	123.7
M8-2	21.3	170.0	19.7	171.5	20.5	170.8
M8-3	19.3	171.7	18.4	172.5	18.9	172.2
M8-4	21.5	169.6	21.2	170.0	21.4	169.8
M8-5	22.1	169.2	22.1	169.0	22.1	169.1
M8-6	20.3	172.3	20.2	172.4	20.2	172.4

 Table 7. Angles grouped according non-polar and polar solvents.



R = Me [2], Et [2], Pr (M8-3), Bu (M8-3), Pen (M8-3), Hex (M8-3).



Figure 1.



Figure 2a.



Figure 2b.





Figure 2d



Figure 3a











Figure 5.







Scheme 1.Sinthetic route to the M8 compounds i) KOH, KI, CH₃CH₂Br, DMSO; ii) n-BuLi, DMF, THF, -78°C; iii) NaBH₄, MeOH, THF; iv) PHPh₃Br, CHCl₃, reflux; v) thiophen-2carbaldehyde, *t*-BuOK, reflux, toluene. vi) secondary amine, PdCl₂, (*t*-bu)₃PHBF₄, *t*-BuOK, toluene; vii) n-BuLi, DMF, THF, -78°C; viii) cyanoacetic acid, ammonium acetate, acetic acid, 120 °C.

Highlights

- 1. A- π -D systems performance improved due the substituent extension
- 2. Propyl substituent is able to have close values on both, polar and non-polar solvents.
- 3. For the butyl substituent the polar solvent quantum yield value is greater than that measured in the non-polar solvent.
- 4. Experimental and theoretical data (through dihedral angles) reveals an oddeven effect on this new series.