



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)-9H-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)-9H-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.

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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)-9H-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 photo-electrochemical properties [3–8]. 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 (Fig. 1, R = Me (n = 1) or Et (n = 2)) [2]. The alkyl substituted series exhibited good

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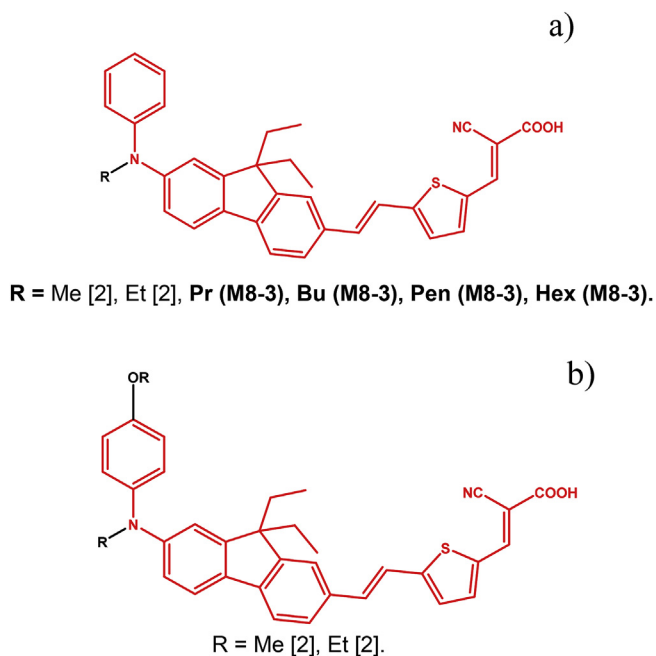


Fig. 1. Structural formula of the synthesized dyes and the previous reported ones. In red, it is signalled the non-changing backbone. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 specific 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* UV–vis. 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-4 spectrofluorometer. 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 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 a 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.

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-2-yl)vinyl)thiophen-2-yl)acrylic acid	M8-3
(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-2-yl)vinyl)thiophen-2-yl)acrylic acid	M8-5
(E)-2-cyano-3-(5-((E)-2-(9,9-diethyl-7-(hexyl(phenyl)amino)-9H-fluoren-2-yl)vinyl)thiophen-2-yl)acrylic acid	M8-6

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