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Design of Dye-Sensitized Solar triphenodioxazine using TiO₂ as a semiconductor

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Abstract: *The present work deals with the synthesis of multichromophores which strongly absorb the solar spectrum to functionalize the nanoparticle oxide semiconductor used in the hybrid cells. At first, we developed a material that forms a chromophore triphenodioxazine. We obtained some triphenodioxazines with high yields up to 70 percent. On the other hand, we have carried out many tests such as UV-Visible, Cyclic voltammetry for our molecules to check their electronic and optical properties. The results confirmed that these chromophores meet the criteria for use in photovoltaic cells. Finally, we have successfully realized photovoltaic cells with triphenodioxazine. The findings were very interesting since the photovoltaic conversion efficiencies ranged from 4.30% to 6.30%. The new synthesis strategy of these chromophores opens a way for the development of organic materials used for photovoltaics.*

Key words: photovoltaic conversion; hybrid materials; chromophore; Triphenodioxazine; solar cells.

Introduction:

Photovoltaic cells are a major issue for sustainable development. The challenge is to replace conventional silicon cells by low cost technologies that can be extended over large areas. Among the new concepts, the hybrid approach to photo-sensitized oxide plays an important role but knows some limitations due in particular to the use of rare metals.

The family of solar cells decompose into three categories such as: the inorganic cells (if, GaAs, CIS and CdTe), the organic cells (conjugated polymers) and the hybrid cells. The hybrid cells consist mainly of inexpensive hybrid materials (metal-oxide, dye and electrolyte) and are easy to implement. The hybrid cell is composed of an electrode of metal-oxide sensitized by a dye or chromophore, immersed in an electrolyte and a counter electrode. The chromophore must fulfill certain essential characteristics to fit its use in the solar cell:

The absorption spectrum of the photo-generated must cover a large part of the spectrum of solar emission (400 to 800 nm). The photo-sensitizer must have groups of attaching to the oxide (e.g. -COOH, -H₂PO₃, -SO₃H) .

The level of potential energy of the excited state of the photo-sensitizer must be lower than the low potential of the band conduction of the titanium oxide (approximately -0.5 V vs NHE). Similarly, in order to be able to regenerate the dye, the reduction potential of the chromophore oxide should be higher than the potential for oxidation of I⁻ (approximately 0.5 V vs NHE).

The aggregates of chromophores to the surface of the oxide are often to avoid. In fact, the stacking of the structures p-conjugated modifies the electronic properties of the chromophore alone and can thus move the energy levels outside the criteria 3 and 4. In addition, the formation of aggregate often speeds up the process of deexcitation. Therefore, either the structures of chromophores include groupings of bulky; either a co-adsorbent is added during the grafting. The photo-sensitizer must-be photo-stable, stable to the oxide state and thermally stable

In this work, we have developed a material that forms a chromophore triphenodioxazine characterized by very interesting properties and used successfully to perform the hybrid solar cell [1-3].

Experimental

Preparation

The triphenodioxazine or the TPDO (Figure 1) fulfilled the criteria of energy levels 3 and 4 as well as those of stability. In addition, its absorption maxima of 500 nm and high intensity allow the addition of substituting to even reduce the gap highest occupied (HOMO) and the lowest vacancy (LUMO).

However, in order to meet the other criteria, the derivatives of the original triphenodioxazine are designed and synthesized. Thus, after a study by molecular modeling, the following structures have been successfully proposed (Figure 2) [3-5].

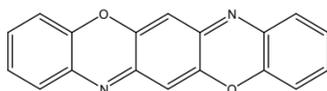
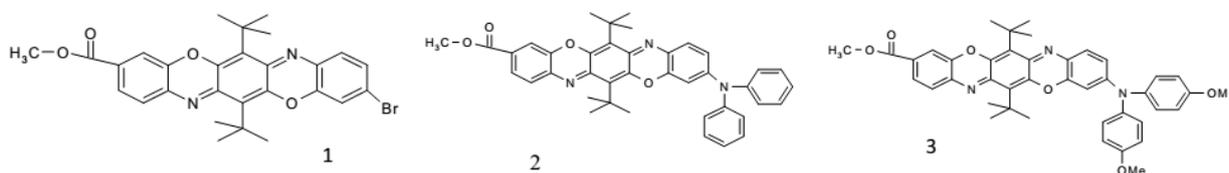


Fig.1: The structure of the TPDO

Fig. 2 shows the obtained molecules. The results are in agreement with several reported studies.



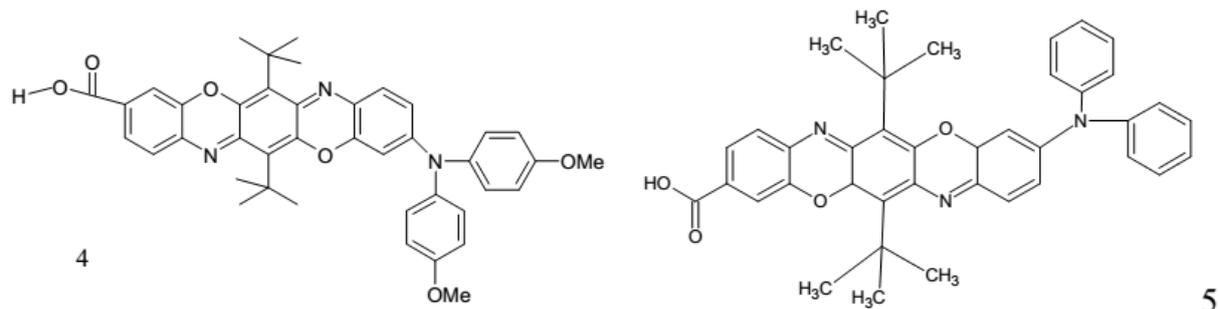


Fig.2: The developed triphenodioxazines

Several procedures for the drafting of the TPDO have been undertaken in the laboratory before we finally managed to acquire this chromophore by a series of chemical reactions (addition, condensation, catalytic conversion, etc).

Optical and electrochemical characterization

Spectroscopy UV-Visible

The UV-Visible absorption spectra have been accomplished on a device UV-1650 pc in a solution of chloroform and dichloromethane. The positions of the absorption bands are expressed in Nm The extinction molar coefficient " ϵ " is $l.cm^{-1}$.

Cyclic Voltammetry

The studies of cyclic voltammetry were made with a potentiostat-galvanostat auto lab. The compound to be analyzed is dissolved in the dichloromethane containing the tetra-n-butyl ammonium-hexafluorophosphate 0.1 M as electrolyte media. The cell electrolyte used has three electrodes: the torque ferrocene/ferrocenium ion is used as reference electrode. The sweep speed is 0.1 V/s [6].

Preparation of films and photovoltaic cells

The films

Thin films of the molecule have been achieved by spin-coating and by dye sublimation on media in quartz of approximately 1 cm^2 via the filing of $70\ \mu\text{l}$ of a solution of 8.3 mg of the TPDO in $700\ \mu\text{l}$ of chlorobenzene. The solution is distributed to the surface of the media with a rotation speed of 1000 rev/min.^[7]

The cells

The nanoparticle TiO_2 is deposited on the plates of conductive glasses according to the technique of doctor Blade. Then we dive the plates in an aqueous solution of TiCl_4 . These plates underwent treatment (heating to 200°C , washing with ethanol, with ultrasound, with the UV, etc). Once the plates are treated, they will be immersed in the chromophores (0.3M with CH_2Cl_2) overnight.

Results and discussion:

Synthesis of the chromophore

We have synthesized the TPDO (Figure 2 and Figure 3) with the grouping of ester yields arriving at 70 %. We have also prepared other TPDO by substituting the ester group with a nitro group. The latter contains bulky tertio-butyl groups in the center of the molecule in order to avoid the aggregation of dyes and to improve the solubility. A carboxylic acid group was added to one side of the molecule in order to

ensure the grafting of the chromophore on the oxide and finally several amine donor groupings are introduced to the other end of the molecule in order to modulate the optical and electronic properties.

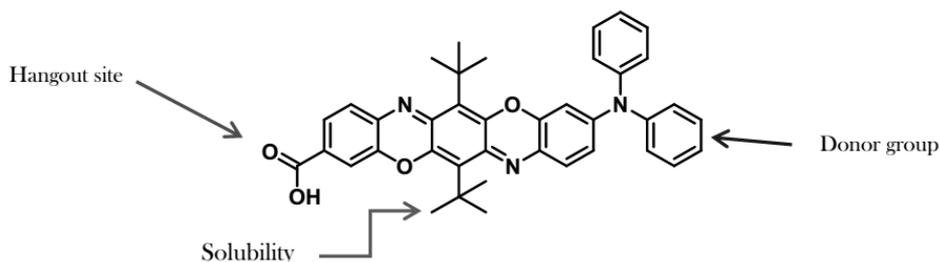


Fig. 3: The chromophore TPDO

Optical properties

The difference in energy levels of the highest occupied (HOMO) and the lowest vacancy (LUMO) of molecules 1,2,3,4 and 5 has been evaluated by UV-visible absorption spectroscopy. Table 1 displays the values of the wavelengths of the absorption maximum of these different chromophores.

Table 1: experimental values of optical measurements and electrochemical

Molecule	λ_{onset} (nm)	E_{OX} (V vs Fc/Fc ⁺)	E_{RED} (V vs Fc/Fc ⁺)	$E_{\text{OX}}-E_{\text{red}}$ (ev)
Ester-TPD-Br(1)	542 (2.28 eV)	0.75	-1.46	2.21
Ester-TPD-(ph) ₂ 2	625(1.98 eV)	0.52	-1.54	2.06
Ester-TPD-(ph-MeO) ₂ 3	657(1.88 eV)	0.33	-1.55	
HOOC-TPD-(ph-MeO) ₂ 4	662 (1.87 eV)	0.18	-1.69	
		$E_{\text{OX}} (I^-/I_3^-) = -0,2 \text{ V}$	$E_{\text{red}}(\text{TiO}_2) = -1,2 \text{ V}$	

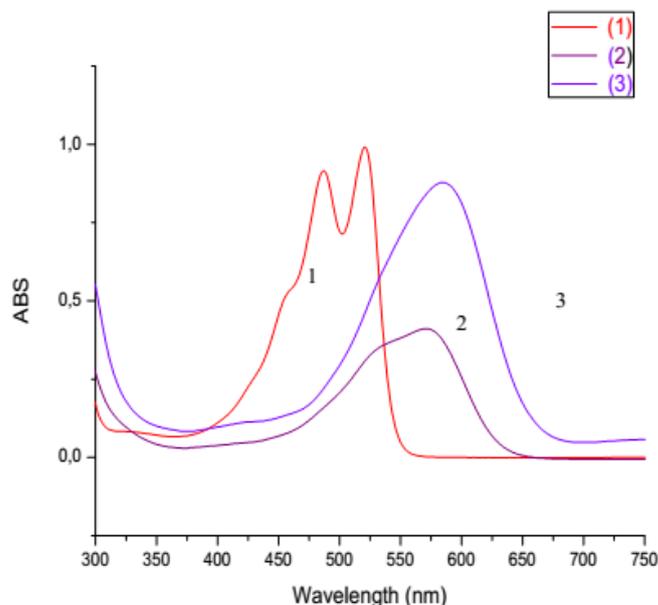


Fig. 4: Absorption spectra of TPDO

The absorption spectra of these molecules (Figure 4) indicate that the addition of brominated substituents or amines on the triphenodioxazine bis-alkylated allows reducing the gap HOMO-LUMO. Indeed, as can be seen in the spectra, we observed a displacement of λ_{max} , towards red corresponding to bathochrome effect absorption maxima. The strengthening with the MeO (3) increased the wave length and the extinction coefficient (ϵ).

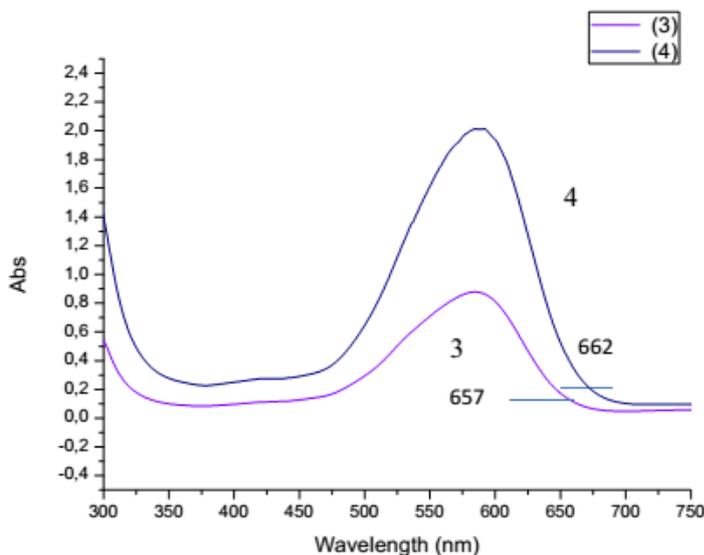


Fig. 5: Spectra of absorbance for TPDO 3 and 4

By comparing the curves of the TPDO 3 and 4 (Figure 5), we see a slight shift of wavelength; therefore the acid function has a neglected effect on the spectrum.

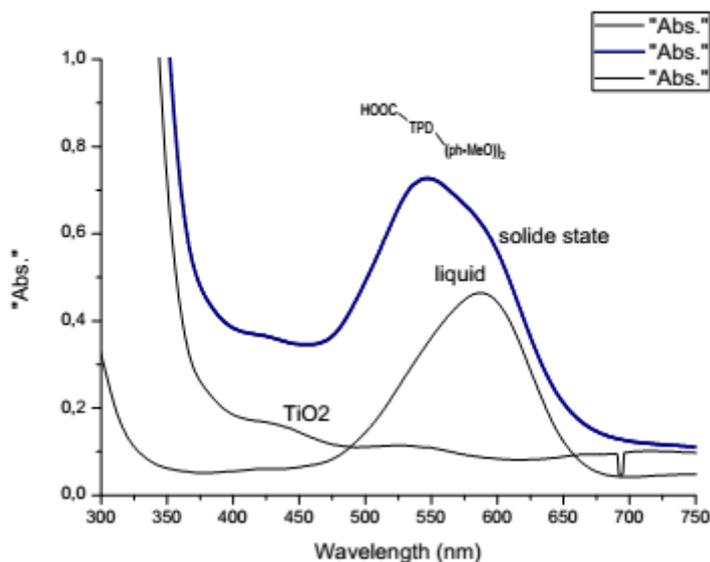


Fig. 6: Spectrum of the chromophore grafted on the TiO₂ in the solid state

Electrochemical proprieties

The cyclic voltamperometry has enabled us to measure the potential of reduction and oxidation of different molecules (see Table 1).

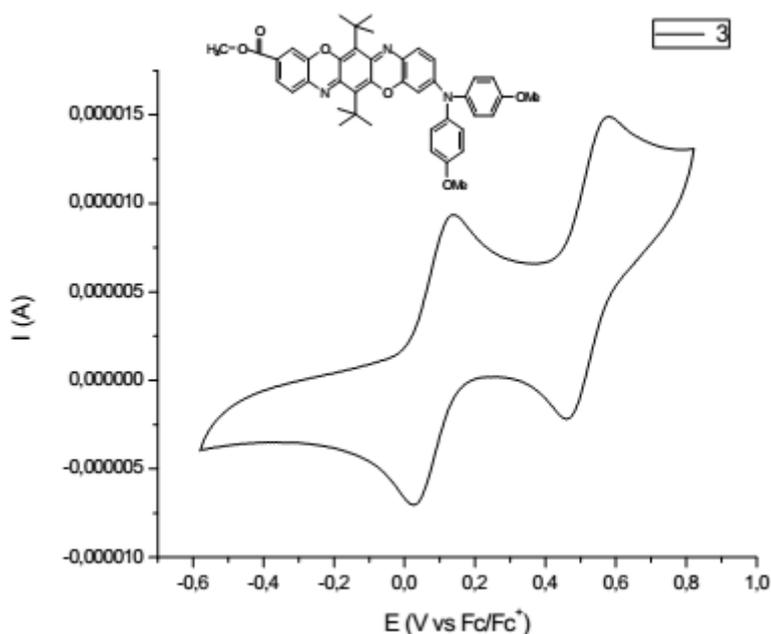


Fig. 7: Electrochemical curve

Fig. 7 shows the variation of the electric current as a function of electrochemical potential. By examining the curve, we find 2 waves of reversible oxidation indicating that the cation form is stable during the redox, therefore the TPDO 1,2,3 and 4 are adapted to the electronic device .

Design of the photovoltaic cells

We used the TPDO in photovoltaic cells which serves as an electrode. The assembly with a counter electrode is performed with the help of an electrolyte; the cell is carried out as shown in Figure 8.

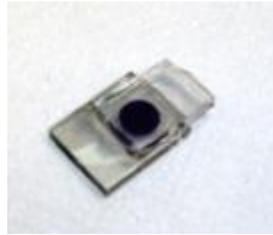


Fig. 8: A solar cell realized in the laboratory

To make photovoltaic measures, we have exposed to light a surface of 0.16 cm² from the cell to the light by using a simulator of sunshine. We have obtained the following waves: (figure 9).

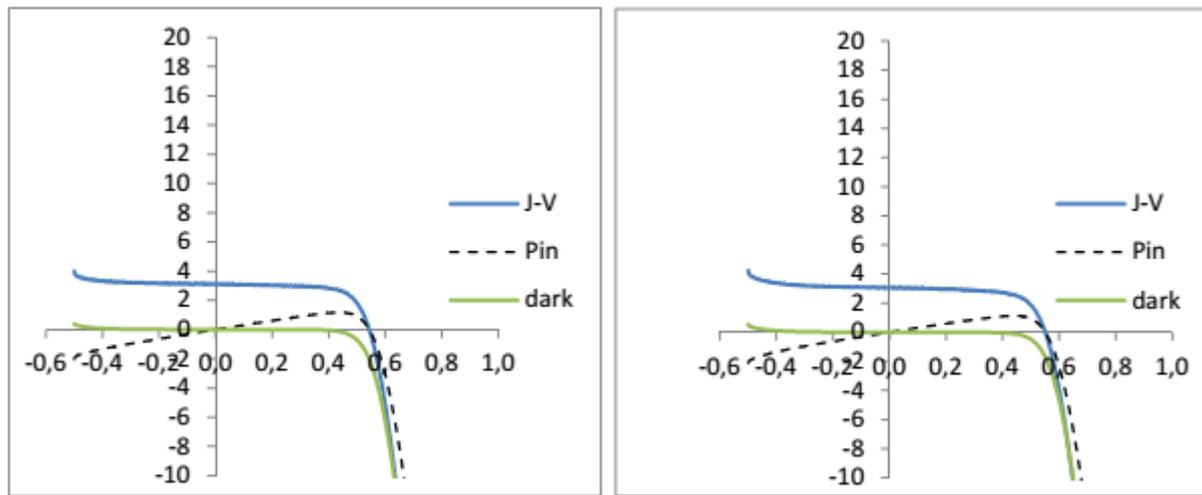


Fig. 9: Photovoltaic measures

The Fig. 9 shows the variation of the current as a function of voltage. The test of the cell shows that there are light absorption by the chromophore and there a photovoltaic conversion.

Conclusion:

In the present work we have obtained new triphenodioxazines with a high yield reaching 70% with an original synthesis strategy. These chromophores possess very interesting optical and electronic properties in the field of photovoltaics. The TPDO derivatives covered a large part of the solar spectrum with strong molar extension coefficients while preserving the high photostability. Moreover this chromophore possesses high solubility owing to presence of two tertibutyl substituents. On the other hand, a carboxyl acid group has been added on one side of the molecule so as to ensure the grafting of the chromophore on the oxide (TiO₂).

Regarding the optical and electronic properties of chromophores, we obtained wavelengths ranging from 625 nm to 662 nm and a potential difference ranging from 2.06 V to 2.21V. The results revealed interesting properties for the photovoltaic field which led to build a solar cell based on molecules 1,2,3,4 and 5 with a yield of 6.30%.

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