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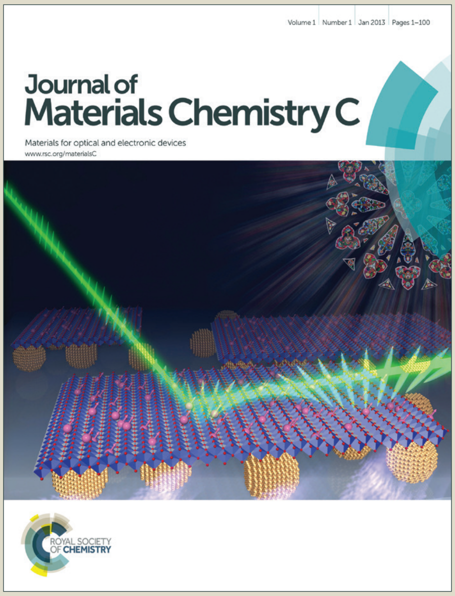

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Linearly π-conjugated oligothiophenes as simple metal-free sensitizers for dye-sensitized solar cells

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Abstract

Four linear oligothiophenes containing 4, 5 and 7 thiophene rings substituted by a variable number of octyl chains attached at a beta-position of some of the thiophene rings and possessing a terminal cyanoacrylic acid anchoring group have been synthesized. Results of UV-Vis absorption spectroscopy and cyclic voltammetry show that as expected the extension of the π-conjugated system leads to a decrease of the optical gap with an increase of the HOMO level. The four compounds have been evaluated as sensitizers in Dye-sensitized solar cells (DSSCs) using a iodide/triiodide liquid electrolyte and the results are discussed in terms of structure-properties relationships with regard to the extension of the conjugated system and the number and position of the octyl side chains using N719 as reference system. A power conversion efficiency of ~7.30% corresponding to 90% of the value given by N719 under identical conditions has been obtained with one of the heptamers.

1. Introduction

Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 have received a considerable attention in the last two decades.[1-9] Recently power conversion efficiencies (*PCE*) in the range of 12.0 % have been reported,[4,5] while prototypes and pre-commercial applications have been discussed.[6] Although, ruthenium(II) complexes have represented the archetype of sensitizers for almost two decades,[1-3] recent years have witnessed the strong emergence of research on metal-free organic dyes. Interest in these compounds is motivated by simpler syntheses and purifications, lower cost and a greater flexibility for the structural control of the energy levels and light-harvesting properties.[7-9] Furthermore, metal-free chromophores can present high molar absorption coefficients thus allowing their use in thinner light-absorbing layers. During the past decade, a huge number of metal-free sensitizers have been synthesized and evaluated in DSSCs cells and *PCE* exceeding 10.0% have been reported.[9] On the other hand, some examples of cells combining metal-free chromophores and quantum dots have been published.[11,12]

Most of metal-free sensitizers possess a **D-π-A** structure where "**D**" represents an electron-donating moiety such as a diarylamine or carbazole, "**π**" a π-conjugating spacer and "**A**" an electron-accepting moiety. In many cases **A** is a cyanoacrylic acid group to serve at the same time as electron-withdrawing unit and anchoring group on the TiO_2 surface.[7-10]

Whereas many push-pull sensitizers based on this model have been synthesized, examples of sensitizers with a simple **π-A** structure namely devoid of terminal donor group remain scarce.[12-19] Thiophene oligomers (nTs) have been frequently used a π-conjugating spacers in D-π-A sensitizers, [7-9] but there are very few examples of sensitizers based on pure nTs. Thus, a *PCE* of 3.36% was obtained with a quinquethiophene derivative with two carboxylic groups.[12] DSSCs based on simple oligothiophenes with terminal carboxylic or cyanoacrylic acid anchoring groups have been described,[13,14] while efficiencies of ~5.0% have been obtained with sensitizers based on oligothiophenes with a terminal dithienothiophene unit.[15] A *PCE* of 6.52 % was reported for a cell based on spiro-system based on quaterthiophene with two anchoring groups.[16] Very recently, a sensitizer based on a pentamer of 3-hexylthiophene was described and a *PCE* of 4.40 % was reported for a solid-state DSSC.[18] This latter result prompted us to publish the results of the work carried out independently in our laboratories on oligothiophene sensitizers.[19]

In this work, a series of oligothiophene chromophores involving four (**4T**), five (**5T**) and seven (**7T**) thiophene rings with terminal cyanoacrylic group have been synthesized. All oligomers contains octyl side chains in variable number and positions in order to provide appropriate solubility to the chromophore and contributing to prevent inter-chain aggregation. Two different thiophene heptamers have been synthesized that contain either two internal octyl chain on the terthienyl (3T) block (**7Ti**) or three octyl chain in a regio-regular arrangement (**7Tr**) (Figure 1).

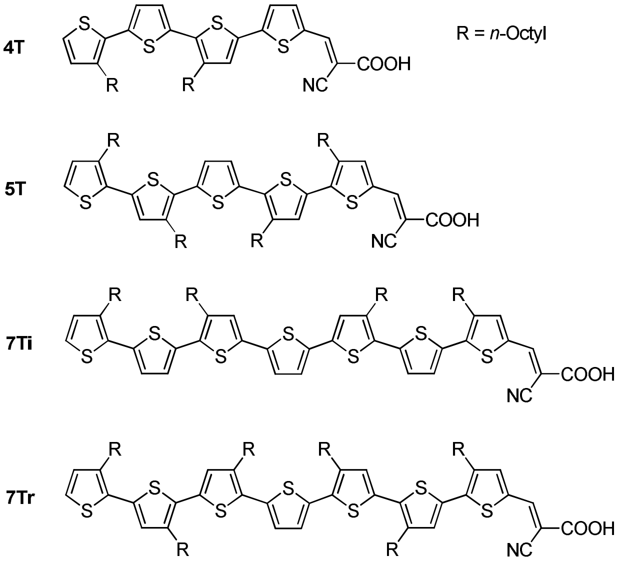


Figure 1. Chemical structures of the oligothiophene sensitizers

We describe the synthesis of the chromophores and the analysis of their electronic properties by cyclic voltammetry, UV-Vis spectroscopy and theoretical calculations. These new chromophores have been evaluated as sensitizers in DSSCs with iodide/triiodide-based conventional liquid electrolyte formulations. The results are discussed in terms of structure-properties relationships with regard to the effects of the length of the π-conjugated system and number and position of the octyl side-chains.

2. Results and Discussion

Synthesis

3,4’’-dioctyl terthienyl (**1a**), 3,3’,4’’’,4’’’’-tetraoctyl-quinquethienyl (**4a**) and 3,3’,3’’4’’’’,4’’’’’-hexaoctyl-septithienyl (**5a**) have been synthesized according to already reported procedures.[20] Bromination of terthienyl **1a** with NBS gave the mono-bromo compound **1b** in 63 % yield. Lithiation of **1a** with *n*-butyllithium and reaction with tributylstannyl chloride gave the Stille reagent **1c** in quantitative yield. A Stille coupling reaction between **1c** and 2-bromo-5-formyl thiophene (**2**) give the formyl-quaterthiophene **3** in 92%

yield. Carboxaldehydes **4b** and **5b** were synthesized in 33 % and 30 % yields by Vilsmeier–Hack formylation of quinque- and septi-thienyl **4a** and **5a** respectively.[20,21]

2,5-distannyl-thiophene **6** was synthesized in quantitative yield from 2,5 dibromo-thiophene *via* a classical double lithiation/stannylation. This reagent was then engaged in a double Stille coupling reaction to give septithienyl **7a** in 47 % yield. Vilsmeier-Hack formylation of **7a** gave the carboxaldehyde **7b** in 34 % yield. The target compounds were finally obtained by Knoevenagel condensation of carboxyaldehydes **3**, **4b**, **5b** and **7b** with cyanoacetic acid in the presence of ammonium acetate to give the corresponding cyanoacids **4T**, **5T**, **7Tr** and **7Ti** in 53, 59, 57 and 66 % yield respectively (See SI).

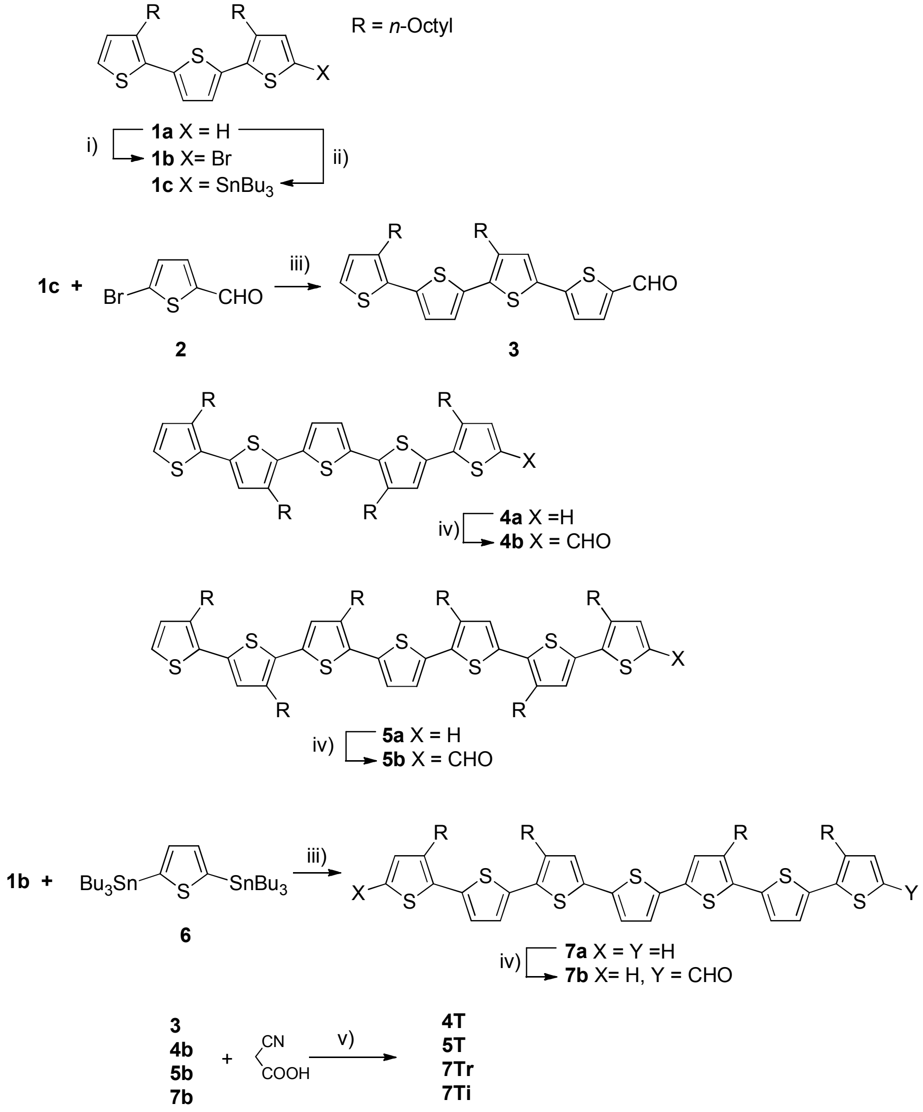


Figure 2. Synthesis of the target compounds. i) NBS, $CHCl_3$/acetic acid (1:1); ii) *n*-BuLi, Bu_3SnCl, THF; iii) $Pd(PPh_3)_4$, toluene; iv) DMF, $POCl_3$, 1,2-dichloroethane; v) $NCCH_2CO_2H$, ammonium acetate, glacial acetic acid.

Cyclic voltammetry

Figure 3 shows the oxidative cyclic voltammograms (CV) of the sensitizers in CH_2Cl_2 in the presence of tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The CV of **4T** shows a first quasi-reversible oxidation wave with an anodic peak potential (E_{pa}) at 1.04 V corresponding to the formation of the cation-radical (Table 1).

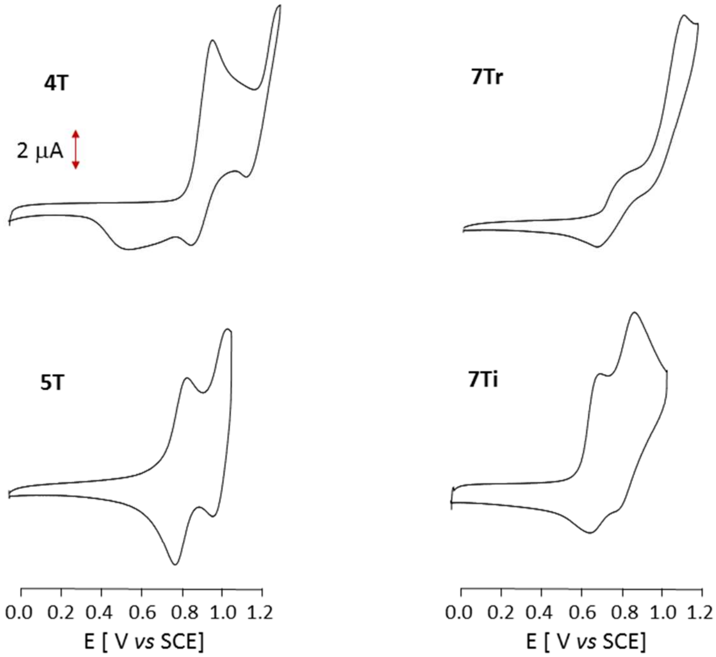


Figure 3. Cyclic voltammograms corresponding to the oxidation of oligothiophene sensitizers in 0.10 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, scan rate 100mV s^{-1}.

The occurrence of a broad cathodic wave on the reverse scan is indicative of a follow-up chemical reaction of the cation-radical presumably associated to the formation of the dimer of 4T by coupling at the free α-position.[22] In contrast, the CV of the longer oligomers shows two successive reversible oxidation waves indicative of stable cation-radical and di-cation.

As expected, the extension of the oligothiophene chain produces a negative shift of E_{pa} from 1.04 V for **4T** to 0.75 V for **7Tr**. In the negative potential region, the CV of all compounds presents an irreversible reduction wave with a cathodic peak potential (E_{pc}) varying from -0.91 V for dye **7Ti** to -1.06 V for dye **5T**.

Table 1. Data of UV-Vis spectroscopy (in CH_2Cl_2) and cyclic voltammetry (in 0.10 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV s^{-1}, Pt electrodes, ref. SCE) for the target compounds.

Dye	λ_{max} (nm)	λ_{maxICT} (nm)	ΔE^{a} (eV)	ε_{max} ($M^{-1}cm^{-1}$)	E_{pa} (V)	E_{pc} (V)	E_{HOMO} (eV)^{b}	E_{LUMO} (eV)^{c}
4T	350	480	2.58	36000	1.04	-1.01	-5.78	-3.20
5T	372	479	2.59	35000	0.90	-1.06	-5.59	-3.00
7Tr	400$^{[s]}$	457	2.71	32000	0.75	-0.95	-5.54	-2.83
7Ti	430$^{[s]}$	473	2.62	35000	0.81	-0.91	-5.55	-2.93

[a:] based on the long wavelength absorption onset
[b] using E^{0}_{ox} with an offset of -4.99 eV for SCE *vs* the vacuum level.
[c] determined by E_{HOMO}-ΔE .
[s] Shoulder

UV-Vis absorption spectroscopy

Figure 4 shows the UV-Vis absorption spectra of the target compounds in methylene chloride solution. The spectrum of the shortest dyes **4T** and **5T** presents a first absorption band with a maximum (λ_{max}) in the range 350-400 nm which shifts bathochromically with the extension of the conjugated system from 350 for **4T** to *ca* 430 nm for **7Ti.** These λ_{max} values are in good agreement with the absorption maxima reported for oligomers of 3-octylthiophene.[23] This first band is followed by a second more intense band attributed to an internal charge transfer (ICT). The λ_{max} of this second band which is observed at *ca* 480 nm for **4T** and **5T** presents an hypsochromic shift to 457 and 473 nm for **7Tr** and **7Ti**. For these two septithiophenes the two transitions merge into a single broad band as confirmed by the large increase of *FWHM* (full width at half maximum) of the absorption band from ~ 0.60 eV for **4T** to ~ 1.10 eV for **7Tr** and **7Ti**. These results show that whereas the λ_{max} of the first transition shifts bathochromically with chain extension, the maximum of the ICT and hence the optical HOMO-LUMO gap (ΔE) converge towards a limit (Table 1). This phenomenon suggests that, beyond a certain chain length, the lengthening of the conjugated chain does not produce any further increase the electron donor strength of the oligothiophene chain.

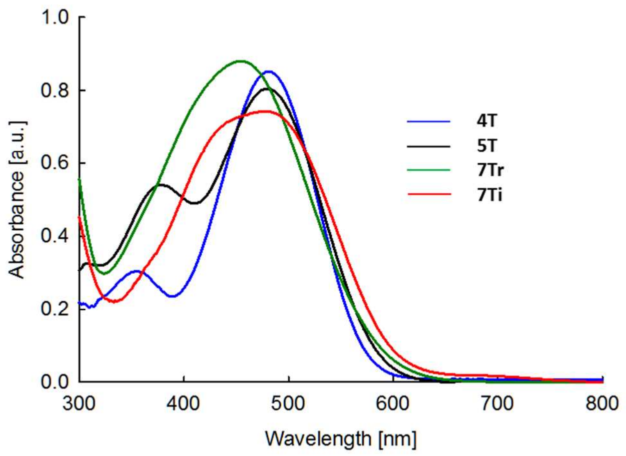


Figure 4. UV-Vis absorption spectra of the oligothiophene sensitizers ~2×10^{-5} M in methylene chloride solutions.

It is well known that the effective conjugation length (or energy gap) of all π-conjugated oligomers converges towards a limit for a chain length determined by structural factors such as bond length alternation, aromatic resonance energy and planarity.[24,25] In this context, the above results suggest that in the specific case of the **π-A** oligomers discussed here, the maximum chain length effective for ICT is limited to 4-5 thiophene units due the rotational disorder inherent to oligothiophenes. Nevertheless, the fact that **7Ti** absorbs at a longer wavelength than **7Tr** remains intriguing.

In order to gain further insight on this question the structure of different conformations of **7Ti** and **7Tr** have been investigated using DFT/B3LYP/6-31G(d,p) level of theory. Based on the above discussed limit of the effective chain length for ICT only a chain length of four thiophene rings has been considered for calculations and the absorption spectra of these systems have studied by TD-CAM-B3LYP/6-31G(d,p) level in CH_2Cl_2 as the solvent (see Fig. S5 and S6). Table 2, lists the calculated absorption maxima of the terminal **4T** fragment of **7Tr** and **7Ti**. The results show that for both dyes the *anti-anti-anti* conformation (*a-a-a*) leads to the longest λ_{max} and hence smallest optical gap whereas the *anti-syn-syn* (*a-s-s*) conformation leads to the most blue shifted λ_{max}. However, comparison of the two series of data shows that for each conformation the **7Tr** fragment absorbs at a shorter wavelength. Furthermore, the difference between the shortest and longest λ_{max} is of 37 nm for **7Ti** and increases to 51 nm for **7Tr**. If one considers that the conformation of oligothiophene molecules in solution is a statistical average of different rotational conformers these results suggest that in any case **7Ti** should absorb at a longer wavelengths.

Table 2. Calculated absorption maxima for various conformations of the end 4T fragment of **7Tr** and **7Ti.**

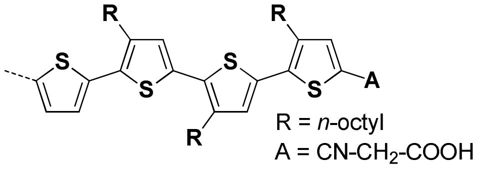
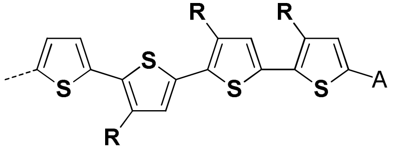
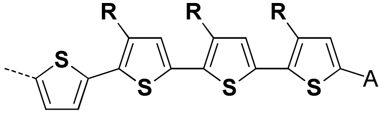
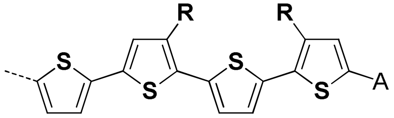
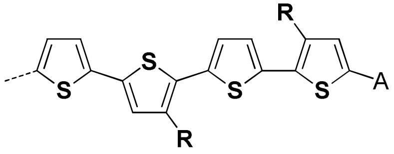
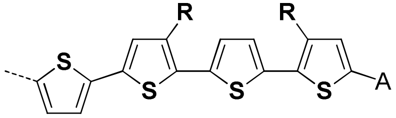
Dye		**Conformation**	**λ_{max} (nm)**
7Tr	***a-a-a***	 R = *n*-octyl A = CN-CH_2-COOH	486
	a-a-s		451
	a-s-s		435
7Ti	***a-a-a***		492
	a-a-s		477
	a-s-s		455

Figure 5 shows the UV-Vis absorption spectra of of the four dyes adsorbed on nanoporous titanium dioxide films. These spectra agree well with the solution spectra of Fig. 4 and confirm that under these conditions **7Ti** still absorbs at longer wavelengths than **7Tr**.

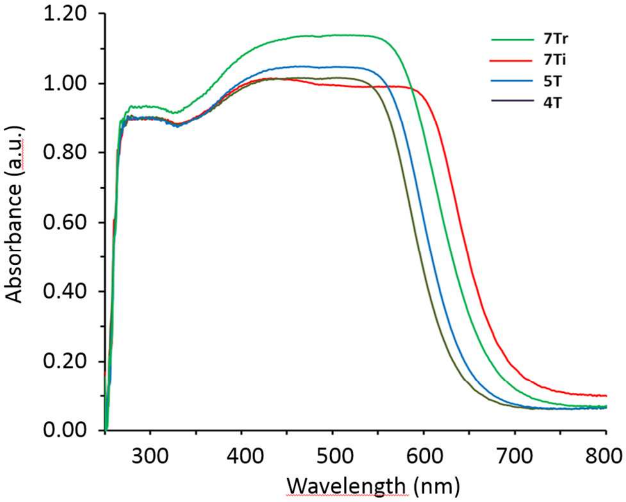


Figure 5. UV-Vis absorption spectra of the sensitizers adsorbed on TiO_2 films of *ca* 8 µm thickness .

Photovoltaic properties

The performances of the four molecules as sensitizers have been investigated in DSSCs with liquid electrolyte (see SI). Devices based on the well-known highly efficient ruthenium dye N719 were fabricated under the same conditions for comparison. Figure 6 shows the current density *vs* voltage curves of the various devices under AM 1.5 simulated solar illumination with a power light intensity of 100 mW cm^{-2} through a mask of *ca* 10 mm^2 aperture. Under these experimental conditions, the benchmark sensitizer N719 gives a short-circuit current density (J_{sc} of 15.2 mA cm^{-2}, an open-circuit voltage (V_{oc}) of 0.745 V and a fill-factor (*FF*) of 0.72 leading to a power conversion efficiency (*PCE*) of 8.10% (Table 2). The results obtained with the four oligothiophene dyes show that the extension of the π-conjugated system from four to seven thiophenes leads to an marked increase of J_{sc} from 9.40 to 14.40 mA cm^{-2} together with a *ca* 200 mV increase of V_{oc} values leading to *PCE* values comprised between 3.80 to 7.30 %.

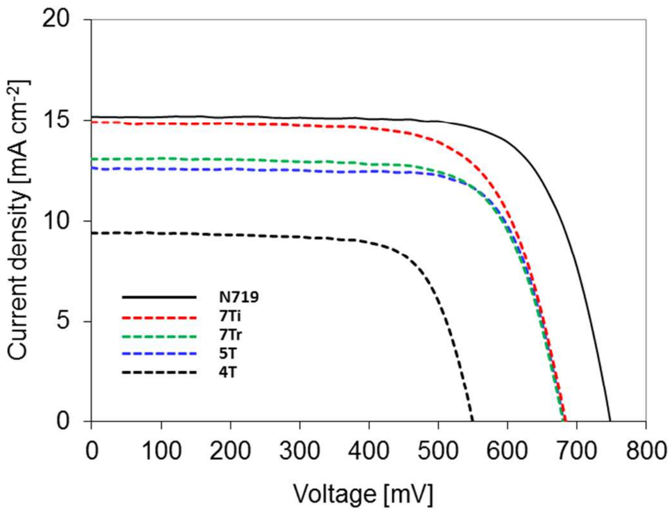


Figure 6. Current-density *vs* voltage for DSSCs based on oligothiophene sensitizers and N719 under AM 1.5 simulated solar illumination.

The values of the fill factors are high 70-75% and independent of the structure of the sensitizer. The data in Table 3 show that the lengthening of the conjugated chain leads to an increase of V_{oc}. This result might be related to a decrease of charge recombination due to a better delocalization of the positive charge for the longer oligomers. Figure 7 shows the external quantum efficiency (*EQE*) spectra of the various DSSCs. As expected the curves show that the extension of the conjugation length of the sensitizer produces a progressive bathochromic of the onset of photo-current from ~ 650 nm for **4T** to ~715 nm for **7Ti** and 725 nm for the reference dye **N719**. The spectra reveal also a gradual increase of the photo-response which presents a broad plateau of ~70 % between 400 and 650 nm for **7Ti.**

Table 3. Photovoltaic characteristics of the DSSC based on the oligothiophene sensitizers and N719 under sAM 1.5 simulated solar illumination. Data in bolt are the best results obtained for each dye.

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	*PCE* (%)
4T	**9.40**	550	0.73	**3.80**
	8.80	553	0.72	3.60
5T	**12.6**	681	0.74	**6.40**
	12.8	654	0.75	6.30
7Tr	**14.3**	687	0.69	**6.70**
	13.7	665	0.72	6.50
7Ti	**14.4**	708	0.71	**7.30**
	14.4	692	0.69	6.90
N719	**15.2**	745	0.72	**8.10**
	15.0	727	0.73	8.00

The integration of the *EQE* response with respect to the solar irradiation spectrum leads to J_{sc} values corresponding to 85-90% of the values measured under white light illumination.

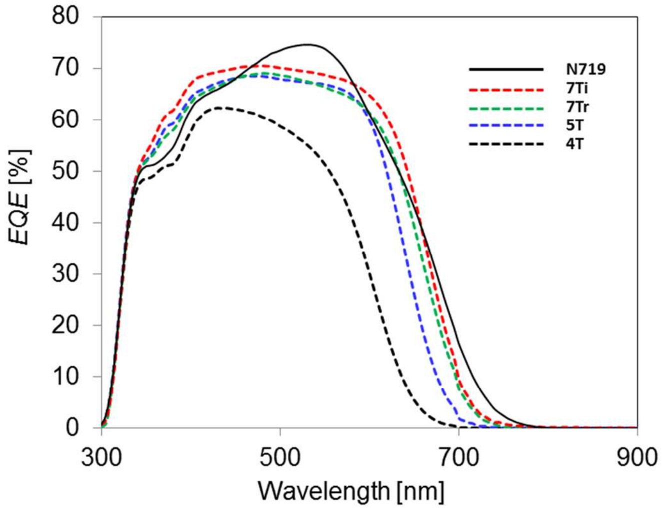


Figure 7. External quantum efficiencies of the DSSCs based on oligothiophene sensitizers under monochromatic irradiation.

Comparison of the above results with the literature data on other oligothiophene sensitizers reported so far,[13,19] shows that the new chromophores can lead to significantly higher *PCE* with values reaching up to 90% of the efficiency of N719 in the case of **7Ti**. The increase of efficiency with chain length observed between **4T** and **7T** can be rationalized on the basis of the extension of the effective conjugation and reduced optical gap leading to better light-harvesting properties. On the other hand, the higher *PCE* values found for the cells based on **7Ti** compared to **7Tr** are consistent with UV-Vis absorption and theoretical results.

As a representative example, preliminary evaluation of the stability of the cells based on **7Tr** in conditions similar to ISOS-1 protocol developed for organic solar cell has been carried out.[26] To this end the cells have been aged at room temperature under indoor light and tested at regular time intervals. Figure 8 shows the variation of *PCE* and J_{sc} during a period of two months. A first decrease of *PCE* of about 20% due to a corresponding decrease of J_{sc} is observed after 400 h. However, no significant variation was observed in the following 800 h. This result demonstrates the excellent stability of this π-A compound, even when combined with a conventional iodide-triiodide based electrolyte.

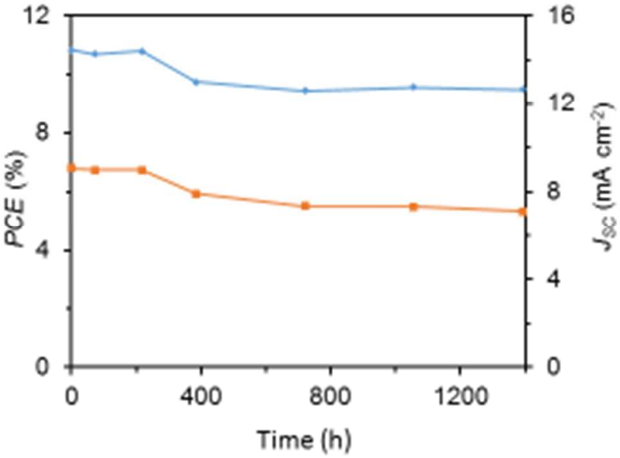


Figure 8. Variation of the power conversion efficiency (red) and short-circuit current density (blue) for a DSSC cell based on **7Tr** upon indoor storage in ambient conditions

Conclusion

A series of chromophores based on oligothiophenes substituted by octyl chains with a terminal cyanoacrylic acid anchoring group been synthesized. Optical and electrochemical results show that as expected, the extension of the π-conjugated system leads to a decrease of the optical gap with an increase of the HOMO level. These compounds have been evaluated under simulated solar illumination as sensitizers in DSSCs with a diiode/iodide liquid electrolyte chains using N719 as reference system. Although a general trend indicating an increase of efficiency with the length of the conjugated system is observed, the results obtained with the two heptamers reveal interesting differences that suggest that the number and position of the alkyl side chains play a major role in the control of both the conformation of the molecule and intermolecular interactions. These results suggest that in addition to light-harvesting properties, the design of sensitizers with a simple linearly π-conjugated structure should also take into account the structural control of intermolecular interactions in order to minimize charge-recombination and deactivation of the excited state through non-radiative intermolecular processes. Further work in this direction is now underway in our laboratories and will be reported in future publications.

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TOC

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