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3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiathiophene) (EDTT) as terminal blocks for oligothiophene dyes for DSSCs

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Abstract: Thiophene pentamers with a cyanoacrylic acid anchoring group at one end and 3,4-ethylenedioxythiophene (EDOT) or 3,4-ethylenedithiathiophene (EDTT) units at the other end have been synthesized. Preliminary evaluation in DSSCs with a iodide/triiodide liquid electrolyte shows that in spite of the very close electronic properties of the two dyes, replacing EDOT by EDTT leads to a noticeable improvement of conversion efficiency under simulated solar light.

Introduction

Dye-sensitized solar cells (DSSCs) based on titanium dioxide have been a focus of sustained interest for more than two decades.[1-3] For many years ruthenium complexes have represented the major class of sensitizers for DSSCs. While these dyes have permitted to reach conversion efficiencies of ~12%,[4] problems of cost, purification and environmental impact have triggered the development of purely organic dyes.[5-7] Most of these metal-free sensitizers are built according to a **D-π-A** model in which a bulky electron-donor block such as *e.g.* triarylamine or carbazole is connected to an electron-acceptor unit (**A**) through a π-conjugating spacer. In many cases **A** is a cyanoacrylic acid group which acts at the same time as electron-withdrawing unit and anchoring group on the TiO_2 surface.[5-7] During the past decade many **D-π-A** dyes have been synthesized and *PCE* exceeding 10.0% have been reported.[8] The optimization of the structure of the dyes has led to analyze various structural factors such as the size of the donor group,[9] the nature of the π-conjugating spacer, the introduction of auxiliary acceptor group,[5-7] or the hydrophilic/lipophilic balance of the dye.[10] As for organic electronics in general, the development of active materials of simple structure

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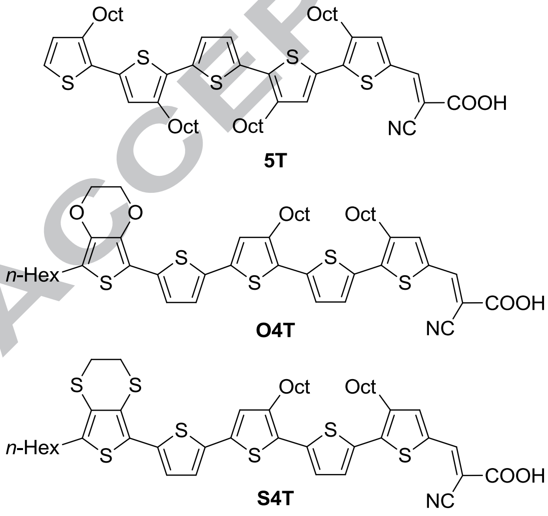
by efficient, clean and scalable synthesis represents a major issue for the a possible industrial future.[11-14]

In this context, chromophores based on linearly π-conjugated oligothiophenes have been described by several groups.[15-19] Thus, we have shown that octyl-substituted thiophene tetramer, pentamer and heptamer with a cyanoacrylic acid end-group can reach *PCE* approaching that obtained with the reference ruthenium dye N719 under the same conditions.[16,17]

In our continuing interest for structure-properties relationships in oligothiophene sensitizers[16,17,19,20] we have undertaken a systematic analysis of the effects of insertion of 3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiathiophene (EDTT) on the electronic properties of the dyes and on the performances of the resulting DSSCs.[20] In this context, we report here preliminary results on two quinquethiophene-chromophores in which the terminal thiophene ring of a reference dye **5T**[17] has been replaced by (EDOT) (**O4T**) and (EDTT) (**S4T**), (Scheme 1). In both cases an hexyl chain was attached at the terminal ring in order to prevent possible reaction of the highly reactive free α-position of the cation radical of these two systems. As in the case of "classical" **D-π-A** dyes, the redox gradient resulting from the introduction of a terminal donor unit is expected to contribute to localize the positive charge of the oxidized state on the terminal thiophene ring and thus to limit intramolecular recombination while facilitating hole-transfer to the redox shuttle of the electrolyte.



Scheme 1. Chemical structure of the target chromophores.

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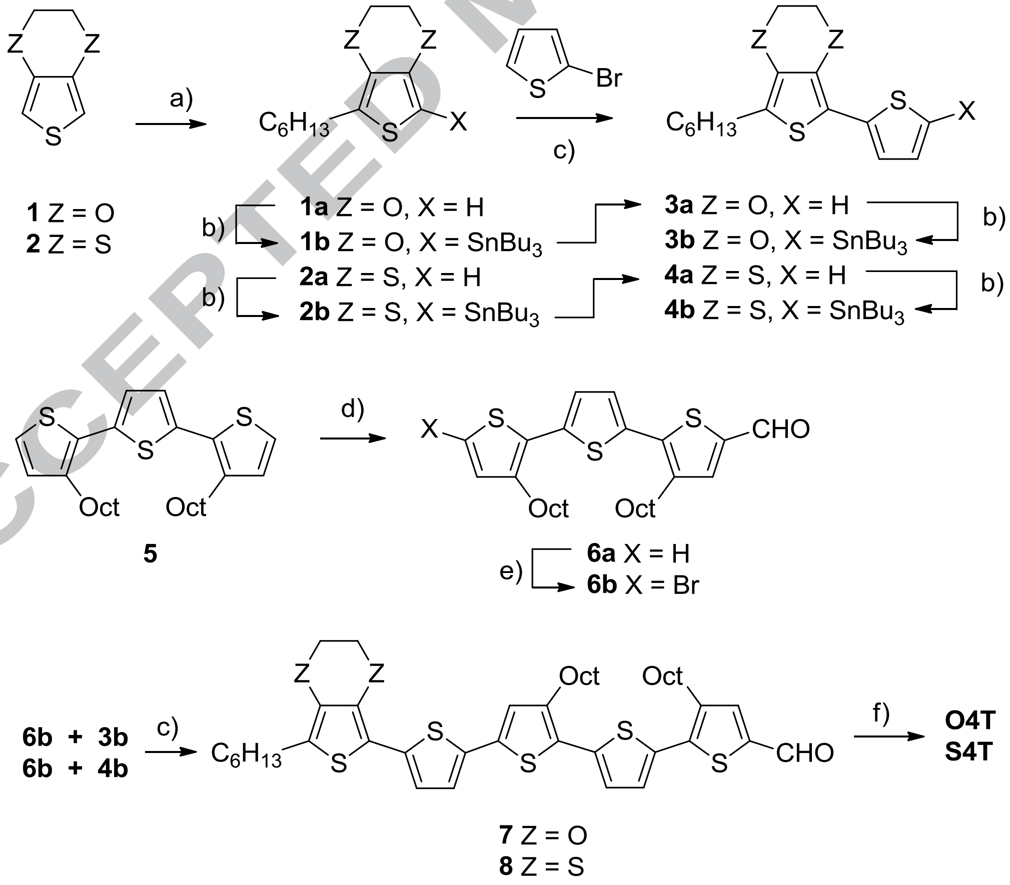
Results and discussion

The synthesis of **O4T** and **S4T** is depicted in Scheme 2. EDTT (**2**),[21] 2-tributylstannyl-5-hexyl-3,4-ethylenedioxythiophene (**1b**),[22] 3,3’’-dioctyl-2,2’:5’,2’’-terthiophene (**5**)[17] were prepared according to the already reported procedures. Treatment of EDTT (**2**) with butyllithium and bromohexane in THF gave the corresponding 2-hexyl derivatives **2a** in 35 % yield. Compound **2a** was converted into the corresponding Stille reagents **2b** by reaction with butyllithium and tributyltinchloride. Stille coupling of **1b** and **2b** with 2-bromothiophene afforded the bithienyls **3a** and **4a** which were then again converted into the corresponding stannylated derivatives **3b** and **4b**. Vilsmeier-Hack formylation of 4,4”-dioctylterthienyl **5** gave aldehyde **6a** in 89 % yield. Bromination of **6a** by NBS afforded the bromoaldehyde **6b** in 89% yield. Coupling of **6b** with the Stille reagents **3b** and **4b** in the presence of a palladium catalyst gave aldehydes **7** and **8** in 72 and 50 % yield respectively. Finally a Knoevenagel condensation of aldehydes **7** and **8** with cyanoacrylic acid afforded the target compounds **O4T** and **S4T** in 70 and 75 % yields respectively.



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Scheme 2. Synthesis of **O4T** and **S4T**. a) *n*-BuLi, bromohexane, THF, -78°C; b) *n*-BuLi, THF, -78°C, Bu_3SnCl; c) $Pd(PPh_3)_4$, toluene reflux 12 h; d) $POCl_3$/DMF, dichloroethane, 0°C; e) NBS,$CHCl_3$/AcOH ; f) cyanoacetic acid, $AcONH_4$/AcOH, reflux 12h.

Fig. 1 shows the UV-Vis absorption spectra of **O4T** and **S4T** in dichloromethane (DCM). The spectrum of **O4T** exhibits a first transition with a maximum at 414 nm ($\lambda_{max}1$) assigned to a $\pi-\pi^*$ transition followed by a more intense band with $\lambda_{max}2$ at 497 nm corresponding to an internal charge transfer. Replacement of the terminal 2-hexyl-EDOT by 2-hexyl-EDTT leads to a further small red shift of $\lambda_{max}1$ to 418 nm but to a 12 nm hypsochromic shift of $\lambda_{max}2$ with a decrease of the relative intensity of the ICT transition. As we have shown in many examples, the introduction of EDOT in a conjugated oligothiophene chain leads to a planarization and rigidification of the systems through intramolecular non covalent sulfur-oxygen interactions.[22-25] These self-rigidification effects are illustrated by the emergence of a vibrational fine structure in the absorption spectrum as observed in Fig. 1 for **O4T**.

Although these results indicate that **O4T** has a smaller HOMO-LUMO gap than **S4T**, it is well known that EDTT is a stronger donor than EDOT with an oxidation potential 0.18 V lower than that of EDOT (1.32 *vs* 1.50 V).[21] This apparent discrepancy could be due to the generation of a dihedral angle between the plane of the conjugated system and the EDTT end-group due to steric interactions between EDTT and the adjacent thiophene.[26]

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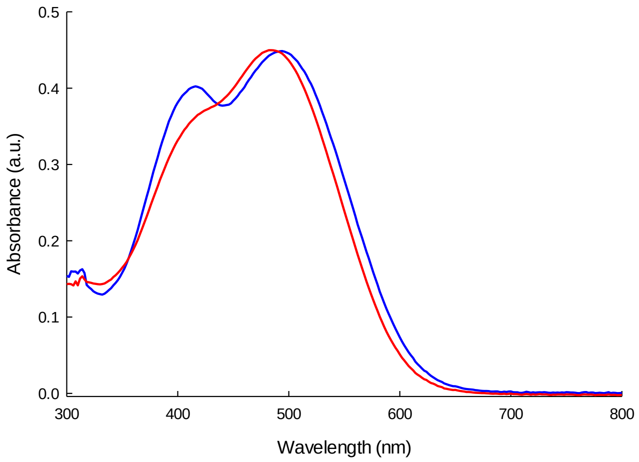

Fig. 1. UV-Vis absorption in spectra in DCM. Blue: **O4T**, red: **S4T**.

Cyclic voltammetry was performed in DCM in the presence of tetrabutylammonium hexafluorophosphate as the electrolyte. The CV of **OT4** presents two successive reversible oxidation processes corresponding to the formation of the cation radical and di-cation with

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anodic peak potentials $E_{pa}1$ and $E_{pa}2$ at 0.71 and 1.03 V (Fig.2). Replacement of EDOT by EDTT leads to a positive shift of $E_{pa}1$ to 0.78V, which is consistent with the shorter effective conjugation length indicated by UV-Vis absorption results. Comparison of the data in Table 1 to those of quinquethiophene **5T** shows that the EDOT and EDTT end-groups lead to a negative shift of $E_{pa}1$ corresponding to an increase of the HOMO level by 0.19 and 0.12 eV respectively.

The energy level of the HOMO and LUMO have been calculated by B3LYP/6-31G(d,p) in CH_2Cl_2 solvent and the obtained results are in satisfying agreement with experimental results with in particular a decrease of the HOMO level when replacing EDOT by EDTT (Table 1 and Fig. 3).

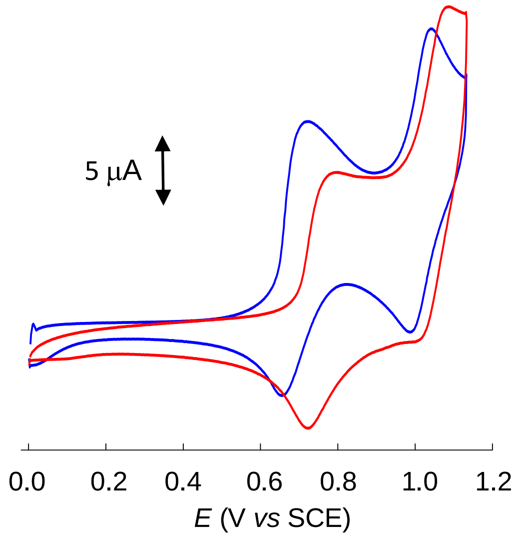

Fig.2. Cyclic voltammograms recorded in in 0.10 M Bu_4NPF_6/DCM, scan rate 100 mV s^{-1}, Pt electrodes. Blue **O4T,** Red: **S4T**.

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

Dye	$\lambda_{max}1$, $\lambda_{max}2$, (nm)	logε ($M^{-1}cm^{-1}$)	$E_{pa}1$ (V)	ΔE^{b} (eV)	E_{pr} (V)	$E_{HOMO}{}^{c}$ (eV)	$E_{LUMO}{}^{d}$ (eV)	$E_{HOMO}{}^{e}$ (eV)	$E_{LUMO}{}^{e}$ (eV)
5T[a]	372, 479	4.54	0.90	2.59	-1.06	-5.86	-3.41	-4.97	-2.86
OT4	414, 497	4.56	0.71	2.49	-1.08	-5.67	-3.18	-4.87	-2.84
ST4	418, 485	4.54	0.78	2.56	-1.10	-5.74	-3.18	-4.95	-2.85

[a] from ref. 17; [b] based on $\lambda_{max.}$ [c] using E^{0}_{ox} with an offset of 4.99 eV for SCE *vs* the vacuum level. [d] determined by E_{HOMO}-ΔE. [e] calculated by B3LYP/6-31G(d,p) in CH_2Cl_2 solvent.

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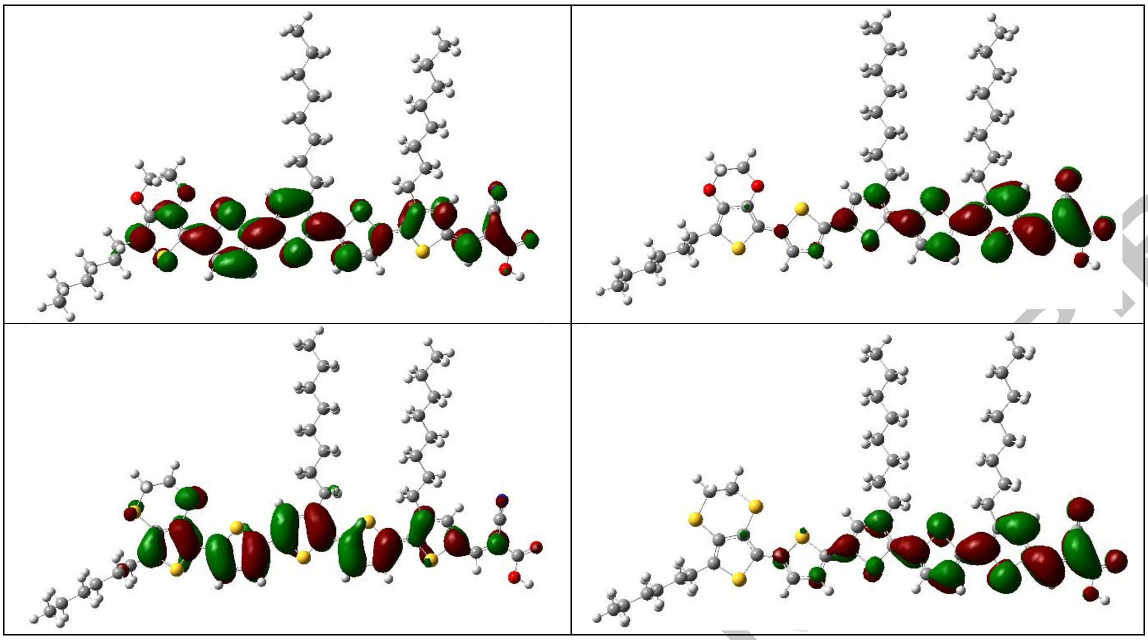

Fig. 3. HOMO (Left) and LUMO (right) distribution of the dyes calculated by B3LYP/6-31G(d,p) in CH_2Cl_2 solvent. Top : **O4T**, bottom: **S4T**.

O4T and **S4T** have been evaluated as sensitizers in DSSC with a liquid electrolytes according to already reported procedures.[17] The absorption spectra of **O4T** and **S4T** adsorbed on mesoporous TiO_2 under the conditions used for cells fabrication are shown in Fig. 4. The small differences observed in the absorption maxima and band intensities agree well with the optical data of the two dyes.

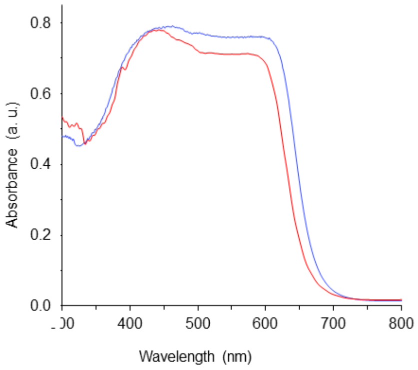

Fig. 4. UV-Vis absorption spectra of **O4T** (blue) and **S4T** (red) adsorbed on mesoporous TiO_2 .

Fig. 5 shows the current density *vs* voltage curves of the cells under AM 1.5 simulated solar illumination with a power light intensity of 100 mW cm^{-2}. The cells based on **O4T** deliver a short-circuit current-density (J_{sc}) of 10.7 mA cm^{-2} and an open-circuit voltage (V_{oc}) of 0.63 V which combined with a fill factor (*FF*) of 0.75 leads to a *PCE* of 5.06 %.

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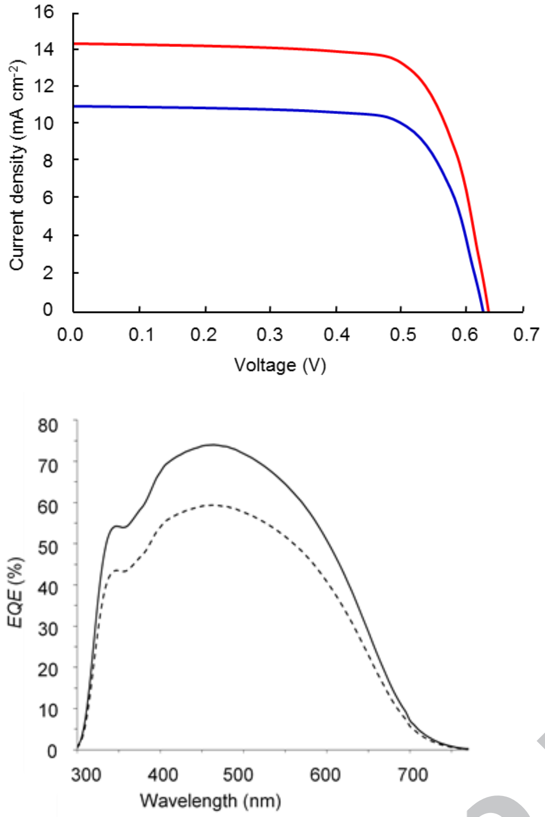

Fig. 5. Top: Current-density *vs* voltage curves for DSSCs based on **O4T** (blue) and **S4T** (red) under AM 1.5 simulation solar illumination with a power light intensity of 100 mW cm^{-2}. Bottom: external quantum efficiency of DSSCs based on **O4T** (dashed line) and **S4T** (solid line).

These values are lower than those obtained with the octyl-substituted pentathiophene **(5T)** (12.6 mA cm^{-2} and 6.30 %).[17] However direct comparison is difficult and care should be observed when comparing **O4T** and **S4T** with **5** as the different placement of the octyl chains and the absence of end-capping hexyl chain in **5T** can strongly affect the efficiency of the dyes.[17] On the other hand, comparison of the *J/V* curves for **O4T** and **S4T** shows that replacement of EDOT by EDTT leads to an increase of J_{sc} from 10.7 to 14.4 mA cm^{-2} with a slight increase of V_{oc} to 0.64 V leading to a *PCE* of 6.73 %. The external quantum efficiency spectra in Fig. 5 agree well with the results obtained under simulated solar illumination and show a broad maximum of ~ 60% in the 440-480 nm region for **O4T** raising to 75 % for **S4T**. These results clearly show that **S4T** leads to significantly higher efficiency than **O4T**. While a definitive explanation of this effect requires further work, this result can be tentatively attributed to a reduced charge-recombination due the synergistic effects of the stronger electron donor properties of EDTT and of the dihedral twist angle between EDTT and the rest of the conjugated chain. These combined effect could contribute to localize the

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positive charge of the oxidized dye at the end of the chain thus limiting charge recombination while favoring hole transfer to the redox shuttle of the electrolyte.

Table 2. Photovoltaic characteristics of the DSSC based on **O4T** and **S4T** under simulation solar illumination (average values of three cells with deviation of less than 5%).

Compd	J_{sc} mA cm^{-2}	V_{oc} (V)	*FF*	*PCE (%)*
OT4	10.7	0.63	0.75	5.06
ST4	14.4	0.64	0.73	6.73

Conclusion

Optical, electrochemical and theoretical results show that in spite of a stronger intrinsic donor properties, the EDTT end-group leads to a shorter effective conjugation than EDOT due possibly to steric hindrance to planarity. Nevertheless, replacement of EDOT by EDTT leads to significant increase of conversion efficiency of the corresponding DSSCs. Although a detailed understanding of the origin of this phenomenon clearly requires further work, these first results can already have interesting implications for the structural optimization of metal-free sensitizers for DSSCs. On the other hand, they also underline the need of further investigations of structure-properties relationships in this class of compounds. Work in this direction is now underway and will be reported in future publications.

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Experimental Part

General

NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75 MHz). Chemical shifts are given in ppm relative to TMS. UV-Vis spectra were recorded with a Perkin Elmer Lambda 19 or 950 spectrometer. Melting points are uncorrected. Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol as matrix.

Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.10 M as supporting electrolyte) was purchased from Acros and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and saturated calomel reference electrode (SCE) with a Biologic SP-150 potentiostat with positive feedback compensation.

Synthesis

EDTT (**2**),[26] 2-tributylstannyl-5-hexyl-3,4-ethylenedioxythiophene (**1b**)[22] and 3,3’’-dioctyl-2,2’:5’,2’’-terthiophene (**5**)[17] were prepared according to the already reported procedures.

6a. $POCl_3$ (0.5 mL, 5.3 mmol) and 3mL of dry DMF are added to a solution of dioctylterthienyl **5** (1.67 g, 3.53 mmol) in 1,2-dichloroethane (50 mL) at 0 °C under Ar. After 24 h stirring at 70 °C the solution is cooled to room temp, diluted with DCM and stirred with a solution of $NaCOOCH_3$ for 2 h. The organic layer is then washed with water and brine and dried over $MgSO_4$. After solvent removal the residue is chromatographed on silica gel 1:1 (eluent DCM/petroleum ether (1:1) to afford the desired compound (1.57 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$: 9.83 (s, 1H), 7.59 (s, 1H), 7.27 (dd, 2H), 7.10 (d, 1H), 6.96 (d, 1H), 2.85-2.75 (m, 4H), 1.17 -1.54 (m, 4H), 1.14-1.26 (m, 20H), 0.88-0.85 (m, 6H).

6b. NBS (0.61 g, 3.44 mmol) is added in small portions to a solution of aldehyde **6b** (1.57 g, 3.13 mmol) in 100 mL of 1:1 chloroform/acetic acid at 0 °C. After 3 h stirring at room temp the mixture is poured into water and extracted with DCM. The organic layer is washed with water, aqueous sodium bicarbonate, brine and again with water, and dried over Na_2SO_4. After solvent removal chromatography on silica gel with 1:1 DCM/petroleum ether as eluent gives (1.6 g, 89%) of a slightly yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$: 9.83 (s, 1H), 7.59 (s, 1H), 7.23 (d, 1H), 7.05 (d, 1H), 6.91 (s, 1H), 2.81 (t, 2H), 2.71 (t, 2H), 1.73 - 1.56 (m, 4H), 1.14-1.26 (m, 20H), 0.89-0.85 (m, 6H).

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3a. A mixture of 2-bromothiophene (0.75 g, 4.5 mmol), Stille reagent **1b** (2.91 g, 5.63 mmol) and Pd(PPh$_3$)$_4$ (0.26 g, 5mol %) in 50 mL of anhydrous toluene is refluxed for 12 h. After concentration, the residue is taken in DCM and the organic phase is washed twice with an aqueous solution of NaHCO$_3$ then with water. After drying over MgSO4 and solvent removal, the residue is chromatographed on silica gel eluting with 1:3 DCM/petroleum ether (1: 3) to give (0.78 g, 60 %) of yellowish oil . ^{1}H NMR (300 MHz, CDCl$_3$): 7.16 (dd, 1H), 7.14 (dd, 1H), 7.00 (dd, 1H), 4.32-4.29 (m, 2H), 4.24-4.20 (m, 2H), 2.63 (t, 2H), 1.65-1.55 (m, 2H), 1.39-1.27 (m, 6), 0.92-0.86 (m, 3H). ^{13}C NMR (75 MHz, CDCl$_3$): 137.4, 137.2, 135.1, 126.9, 122.9, 121.9, 116.1, 107.8, 65.0, 64.5, 31.5, 30.3, 28.7, 25.6, 22.5, 14.1.

2a. *n*-BuLi (1.6 M in hexane, 9.65 mmol, 6.03 mL) is added dropwise at -78 °C to a solution of EDTT (1.6 g, 9.19 mmol) in dry THF under Ar atmosphere. The mixture is stirred for 1 h at -78°C and 1-bromohexane (12 mmol, 1.72 ml) is added dropwise. After 30 min stirring the mixture is allowed to warm slowly to room temperature and stirred for 12 h. After dilution with diethyl ether, the organic phase is washed successively with a saturated NH$_4$Cl and water. After drying over MgSO$_4$ and evaporation of the solvent, the residue is **c**hromatographed on silica gel eluting with 1:2 DCM petroleum ether to afford (0.8 g, 35%) of a colorless oil. ^{1}H NMR (300 MHz, CDCl$_3$): 6.78 (s, 1H), 3.19 (s, 4H), 2.68 (t, 2H), 1.64-1.59 (m, 2H), 1.33-1.29 (m, 6), 0.86 (t, 3H) ^{13}C NMR (75 MHz, CDCl$_3$): 137.1, 124.8, 120.6, 114.6, 31.5, 30.2, 28.8, 28.2, 27.8, 27.7, 22.5, 14.0**.** MS MALDI: 258.1**.** HRMS: calculated 258.0571; found 258.0574.

2b. *n*-BuLi (2.5 M in hexane, 3.11 mmol, 1.24 mL) is added dropwise at -20 °C to a solution of **2a** (0.73 g, 2.82 mmol) in dry THF under Ar atmosphere. The mixture is stirred for 1 h at -78°C. Tributyltin chloride (0.97 ml, 3.38 mmol) is added dropwise at the same temperature. The mixture is stirred at -20°C for 30 min and then allowed to warm slowly to room temperature. After dilution with diethyl ether, a saturated solution of NaF is added and the mixture is stirred for 1 h. The precipitate is filtered off using celite and the filtrate is washed with a saturated solution of NaHCO$_3$ and water. After drying over MgSO$_4$, the solvent is evaporated and the product is used in the next step without further purification. ^{1}H NMR (300 MHz, CDCl$_3$): 3.19-3.16 (m, 4H), 2.70 (t, 2H), 1.64-1.50 (m, 8H), 1.39-1.26 (m, 12), 1.17-1.12 (m, 6H), 0.94-0.86 (m, 12H).

4a. A mixture of 2-bromohiophene (0.46 g, 2.81 mmol), Stille reagent **2b** (1.54 g, 2.81 mmol) and Pd(PPh$_3$)$_4$ (0.32 g, 10 mol %) in 50 mL of anhydrous toluene is refluxed for 12 h. After concentration, the residue is taken in DCM and the organic phase is washed twice with an aqueous solution of NaHCO$_3$ then with water. After drying over MgSO$_4$ and solvent

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removal, the residue is chromatographed on silica gel eluting with 1:3 DCM petroleum ether to afford 0.43 g, (46 %)of a yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): 7.28 (d, 1H), 7.23 (d, 1H), 7.06 (dd, 1H), 3.27-3.19 (m, 4H), 2.70 (t, 2H), 1.69-1.59 (m, 2H), 1.41-1.28 (m, 6), 0.92-0.85 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 135.9, 135.4, 127.3, 125.3, 124.9, 122.1, 121.9, 31.5, 30.2, 28.8, 28.4, 28.2, 27.6, 22.5, 14.0. MS MALDI: 340.1. HRMS: calculated 340.0448; found 340.0445.

(4b) *n*-BuLi (2.5 M in hexane, 1.51 mmol, 0.6 mL) is added dropwise at -78 °C to a solution containing of **3a** (0.43 g, 1.26 mmol) in dry THF. The mixture is stirred for 1 h at at -78 °C. Tributyltin chloride (0.43 ml, 1.51 mmol) is then added dropwise at -40°C. The mixture is stirred at -40°C for 30 min and allowed to warm slowly to room temp. After dilution with diethyl ether, a saturated solution of NaF is added and the mixture is stirred for 1 h. The precipitate is filtered off using celite and the filtrate is washed with a saturated solution of $NaHCO_3$ then with water. After drying over $MgSO_4$, the solvent is evaporated and the product is used in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): 7.35 (d, 2H), 7.10 (d, 2H), 3.24-3.22 (m, 4H), 2.72 (t, 2H), 1.64-1.51 (m, 8H), 1.41-1.25 (m, 12), 1.37-1.08 (m, 6H), 0.93-0.86 (m, 12H)

7. A mixture of aldehyde **6b** (0.74 g, 1.34 mmol), Stille reagent **3b** (0.66 g, 1.12 mmol) and $Pd(PPh_3)_4$ (77 mg, 5%) in 50 mL of anhydrous toluene is refluxed for 12 h. After concentration, the residue is taken in DCM and the organic phase is washed twice with an aqueous solution of $NaHCO_3$ then with water. After drying over $MgSO_4$ and solvent removal, the residue is chromatographed on silica gel eluting with DCM to afford a red-orange solid (0.65 g, 72 %). M.p.: 110-115 °C.

8. Prepared using the procedure already described for **7** from aldehyde **6b** (0.21 g, 0.38 mmol), Stille reagent **24** (0.3 g, 0.47 mmol) and $Pd(PPh_3)_4$ (44 mg, 10%) in 50 mL of anhydrous toluene to afford a red-orange oil (150 mg, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$): 9.83 (s, 1H), 7.59 (s, 1H), 7.26 (d, 1H), 7.15 (d, 1H), 7.12 (d, 1H), 7.11 (d, 1H), 7.03 (s, 1H), 3.31-3.27 (m, 2H), 3.25-4.21 (m, 2H), 2.85-2.69 (m, 6H), 1.71-1.63 (m, 6H), 1.39-1.28 (m, 26), 0.89-0.85 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): 182.4, 141.1, 141.0, 140.2, 140.1, 139.0, 138.1, 136.1, 135.9, 135.5, 134.7, 134.3, 128.7, 127.8, 126.5, 125.9, 125.7, 125.3, 123.9, 122.4, 122.3, 31.8, 31.5, 30.4, 30.2, 29.6, 29.4, 29.3, 29.2, 28.8, 28.5, 28.2, 27.5, 22.6, 22.5, 14.0. MS MALDI: 838.3. HRMS: calculated 838.2533; found 838.2510 (2.6 ppm)

OT4. Aldehyde **7** (0.2 g, 0.25 mmol) is mixed with cyanoacetic acid (43 mg, 0.50 mmol), ammonium acetate (99 mg, 1.24 mmol) in glacial acetic acid (30 mL) and the solution is refluxed for 12 h. After slowly cooling to room temp, a dark precipitate is formed, filtered

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and washed with a diluted solution of sodium hydroxide and then with water to afford a black solid (150 mg, 70%). M.p.: 240-245 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 8.20 (s, 1H), 7.60 (s, 1H), 7.30 (d, 1H), 7.10 (d, 1H), 7.04 (d, 1H), 7.01 (d, 1H), 6.97 (s, 1H), 4.34-4.32 (m, 2H), 4.24-4.21 (m, 2H), 2.84-2.73 (m, 4H), 2.64 (t, 2H), 1.72-1.58 (m, 6H), 1.45-1.36 (m, 26), 0.91-0.83 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$ not every carbon is visible): 141.8, 141.2, 140.5, 139.2, 137.9, 137.6, 137.5, 136.2, 134.6, 134.0, 133.6, 132.4, 128.4, 128.1, 126.0, 125.8, 123.9, 122.3, 116.8, 107.8, 65.1, 64.4, 31.9, 31.8, 31.5, 30.3, 30.1, 29.7, 29.6, 29.5, 29.4, 29.2, 28.8, 25.7, 22.6, 22.5, 14.1 MS MALDI: 873.1 HRMS: calcd 873.30476; found 873.30721.

ST4. Prepared using the procedure already described for **OT4** from aldehyde **8** (0.1 g, 0.12 mmol), cyanoacetic acid (20 mg, 0.24 mmol), ammonium acetate (47 mg, 0.6 mmol) in 30 mL of glacial acetic acid (30 mL) to afford a black solid (75 mg, 75%). M.p.116-118°C**.** ^{1}H NMR (300 MHz, THF-d8): 8.28 (s, 1H), 7.74 (s, 1H), 7.38 (d, 1H), 7.22 (d, 1H), 7.17 (m, 3H), 3.26-3.28 (m, 2H), 3.24-3.22 (m, 2H), 2.90-2.82 (m, 4H), 2.72 (t, 2H), 2.02-2.04 (m, 6H), 1.26-1.29 (m, 26), 0.82-0.88 (m, 9H)**.** ^{13}C NMR (75 MHz, THF-d8): 204.3, 164.0, 145.7, 141.9, 141.5, 140.9, 138.7, 136.4, 136.3, 135.7, 134.9, 134.3, 132.3, 132.2, 129.4, 129.1, 129.0, 128.9, 127.3, 126.9, 126.2, 125.6, 124.6, 123.7, 123.6, 116.4, 100.2, 32.6, 32.3, 31.1, 30.9, 30.4, 30.3, 30.2, 30.1, 29.8, 29.5, 28.9, 28.6, 27.8, 25.6, 23.4, 23.2, 14.2**.** MS MALDI: 905.3**.** HRMS: calcd 905.2591; found 905.2590.

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Highlights

- Synthesis of metal-free sensitizers for dye-sensitized solar cells
- Analysis of the effect of the structure of the terminal thiophenic ring
- Replacement of EDOT by EDTT leads to a noticeable improvement of conversion efficiency

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Graphical Abstract

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3,4-ethylenedioxythiophene (EDOT) and 3,4-ethylenedithiathiophene) (EDTT) as terminal blocks for oligothiophene dyes for DSSCs

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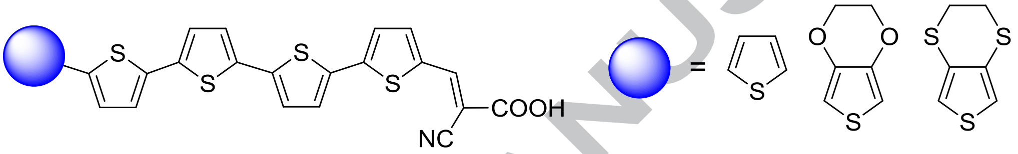
Dora Demeter, Fabio Melchiorre, Paolo Biagini,* Siriporn Jungsuttiwong, Riccardo Po and Jean Roncali*



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