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Organic dyes end-capped with perfluorophenyl anchors: Synthesis, electrochemical properties and assessment of sensitization capacity of titania photoanodes

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Graphical Abstract



Two organic dye sensitizer families attached onto TiO_2 photoanodes via non-hydrolysable C-O-Ti bonds are "fighting" over DSSCs and PCEs. Superiority of EDOT-bearing dyes is demonstrated.

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1	Organic Dyes End-Capped with Perfluorophenyl Anchors:
2	Synthesis, Electrochemical Properties and Assessment of
3	Sensitization Capacity of Titania Photoanodes
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[1]

1 Abstract

2 In the present work, organic sensitizers are synthesized and attached on TiO₂ photoanodes via Ti-3 O-C bonds. All sensitizers, designed for this purpose are symmetrical and have two 4 perfluorophenyl end groups, which can lead to stable non-hydrolysable bonds on the TiO₂ 5 surface. Broad absorption in the UV-Vis region and low band gap energy levels have been 6 achieved through the alternation of carbazole- and benzothiadiazole- based units. All dyes and 7 their corresponding photoanodes, were characterized via various complementary techniques, including Cyclic Voltammetry measurements and sensitization capacity in Dye-sensitized solar 8 9 cell tests. 10 11

12 Keywords: organic dyes; perfluorophenyl anchors; benzothiadiazole-*alt*-carbazole; 3,413 ethylenedioxythiophene; DSSCs; Photoelectrochromic devices.

14

1 **1. Introduction**

Since their discovery, Dye-sensitized solar cells (DSSCs) have inaugurated a very interesting 2 3 field of research in the general frame of mesoscopic solar cells.[1,2] A great number of different 4 approaches have been employed for their study, but still, the full replacement of standard silicon-5 based photovoltaics, remains a tough task, even after decades of intensive research and significant 6 progress in the field. Nevertheless, DSSCs show significant advantages, such as low cost and environmentally friendly fabrication process, even if their efficiency is still much lower, 7 8 compared to inorganic solar cells.[3,4,5,6] This has led to increasing efforts for market 9 penetration of DSSCs, over the last years. A typical DSSC consists of two conducting substrates 10 that act as working and counter electrode, separated by an electrolyte that contains a redox couple. Dye molecules, which are anchored to a semiconductor (usually TiO₂ or ZnO) deposited 11 on the anode, absorb photons, leading to the excitation of electrons from a lower to a higher 12 energy state of the dye (sensitizer).[7,8] Thus, electrons from the excited state of the dye are 13 14 injected into the conduction band of the semiconductor. The dye should have suitable anchoring 15 groups to facilitate the formation of stable bonds with the semiconductor. The most commonly 16 used anchor is the carboxylic group, since it can form ester type bonds with the hydroxyl groups on the TiO₂ surface.[9,10] Other groups, such as sulfonic or phosphonic, have also been proven 17 18 functional,[11,12,13] but have a significant drawback compared to the carboxylic unit: their use is 19 limited in pure organic solvents, since they are not stable in aqueous environments. For this 20 reason, our group has developed an alternative anchoring methodology, which is based on the 21 perfluorophenyl unit. Through this route, the fluorine placed on the para- position can react under 22 mild alkaline conditions with the hydroxyl groups of the TiO₂ surface, forming stable, non-23 hydrolysable Ti-O-C bonds.[14,15]

The injected electrons are collected at the transparent conducting oxide (TCO), move through an external circuit towards the counter electrode and are exchanged with a redox couple in solution.

1 This electron transfer is facilitated in the presence of an appropriate electrocatalyst. The redox 2 shuttle finally compensates the holes left in the dye sensitizer and thus the cell functions in a cyclic manner. [16,17,18] Liquid electrolytes, based in the I^{-}/I_{3}^{-} couple, have proven to be the most 3 suitable, between several candidates, even though other couples such as Co^{3+}/Co^{2+} have showed 4 higher redox potential which leads to enhanced power conversion efficiencies, but still suffer 5 from slow mass transport and slow regeneration of Co²⁺ at the cathode.[19,20,21,22,23] On the 6 7 other hand, liquid electrolytes present important disadvantages, such as solvent evaporation and device short lifetime, which has led to the search for viscous variants, such as ionic liquids (ILs) 8 9 or polymer electrolytes (PEs).[24,25,26,27,28]

Regarding the DSSC operation, two major electrochemical limitations must be taken care of. At first, the lowest unoccupied molecular orbital (LUMO) of the sensitizer, has to be higher than the conduction band of the semiconductor, in order to encourage spontaneous electron injection. Secondly, the dye molecules may be regenerated, when their highest occupied molecular orbital (HOMO) is lower than the redox level of the electrolyte. It is clear, that the energy levels of the dye are very important, and the synthesis of the suitable dye is relevant with the oxide/electrolyte used.[29,30]

17 An additional important feature for the efficiency of dyes employed in DSSCs is the anchoring 18 moiety or moieties used for their connection with the TiO_2 NPs. Two (or more) anchoring groups 19 are mainly used in Ruthenium (or other metal) based sensitizers, [3,31] while for most organic 20 sensitizers the synthetic routes typically employed lead to only one anchoring group (D- π -A 21 structure).[32,33,34] However, some reports suggest that only one anchor may cause drawbacks 22 in the sensitizer's adsorption geometry on TiO₂ nanoparticles and the overall charge 23 injection. [35,36,37] In some polymeric dyes on the other hand, the α, ω -end modification of the polymeric chain enables the formation of sensitizers with two anchoring groups, a synthetic 24 25 strategy also used by us in a previous study.[15] More particularly, those polymeric entities based 26 on the combination of benzothiadiazole and N-alkyl-2,7-carbazole have attracted our attention

because of the high conjugation level, low bandgap and the good charge carrier transport and
mechanical properties they provide, which lead to high power conversion efficiencies in
OPVs.[38]

4 In the present work, we have synthesized novel small organic dyes of defined chemical structures and length based on thiophene derivatives, carbazole electron donating groups and benzothiazole 5 6 electron accepting groups. Two end-perfluorophenyl units have been incorporated as anchoring 7 groups for the subsequent sensitization of TiO₂ for DSSCs. The synthesis of the herein reported dyes was accomplished via two different synthetic paths. Furthermore, their optical and 8 9 electrochemical characterization is presented. Finally, initial DSSC tests of the four novel 10 chromophores have been performed, comparing the effect of the different structural motives of 11 the new chromophores and of the side solubilizing chains employed.

- 12
- 13

14 **2. Experimental Section**

15

16 **2.1 Materials**

17 4,7-Di-2-thienyl-2,1,3-benzothiadiazole (di-thien-BTZ),[39] 4,7-di-(5-bromothiophene-2-yl-18 2,1,3-benzothiadiazole (di-Br-di-thien-BTZ),[40] 2,7-dibromo-N-heptadecan-9-yl-carbazole (di-Br-HD-carbazole),[38] 2,7-dibromo-N-2-ethylhexyl-carbazole (di-Br-EH-carbazole),[41] 2,7-19 20 di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-N-2-ethylhexyl-carbazole (di-boronic ester-EHcarbazole),[38] 2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan)-N-heptadecan-9-yl-carbazole (di-21 22 boronic ester-HD-carbazole)[38] and the catalyst palladium (II)tetrakis triphenyl phosphine $[Pd(PPh_3)_4][42]$ were prepared according to literature. 23

All solvents and reagents were purchased from Sigma Aldrich, Alfa Aesar or Acros Organics
and were used without further purification unless otherwise stated. All reactions were carried out

1 under argon atmosphere. Tetrahydrofuran (THF) was dried and distilled just before use over 2 sodium wire in the presence of benzophenone. Commercial nanocrystalline titania Degussa P25 (specific surface area 50 m^2/g) was used in all cell constructions and Millipore water was used in 3 all experiments. SnO₂:F transparent conductive electrodes (FTO, Resistance 8 Ω /square) were 4 purchased from Pilkington. ITO transparent conductive electrodes (R_{sheet}<15 Ω/square) were 5 6 purchased from Aldrich. TiO₂ nanoparticles prior to their reactions with the perfluorophenyl 7 functionalized moieties were calcined at 400 °C for 3-4 hr to remove all hydrogen-bonded water 8 molecules.[43]

9

10 2.2 Characterization methods

¹H, and ¹⁹F NMR spectra were recorded on Bruker Advance DPX 400.13, and 376.5 MHz
 spectrometers, respectively, with CDCl₃ as solvent containing TMS as internal standard.

Thermogravimetric analysis (TGA) was carried out on 8 mg samples contained in alumina
crucibles in a Labsys TM TG apparatus of Setaram under nitrogen and at a heating rate of 10 °C
min⁻¹.

16 IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer and on an ALPHA-P
17 diamond ATR spectrometer of Bruker Optics GmbH.

18 UV-Vis spectra in solution were recorded using a Hitachi U-1800 spectrophotometer.
19 Photoluminescence (PL) spectra in solution were recorded using a Perkin–Elmer LS45
20 luminescence spectrometer, after excitation at the UV-Vis absorption maxima.

UV–Vis absorption spectra and diffuse reflectance spectra (DRS) of sensitized photoanodes
were recorded with a Shimadzu UV-2600 spectrophotometer equipped with integration sphere.

23 The electrochemical behaviour of the fabricated materials was investigated using cyclic

- voltammetry (CV thereafter). CV experiments were carried out in a three electrode cell.[44,45]
- 25 Two kinds of working electrodes have been used. An ITO/Glass with the synthesized sensitizers

1 to be measured drop-casted on the ITO conductive side and a dye- sensitized TiO₂/FTO/Glass. An 2 Ag/AgCl electrode served as reference and a platinum wire was used as the counter electrode. 3 Thin films of the fabricated materials were drop casted on ITO coated glass slides, (R_{sheet}<15 4 Ω /square), preheated at 80 °C for 20 min, from precursor solutions of chloroform. The resulting 5 films were further annealed at 80 °C for 15 min. Dye sensitized TiO₂/FTO/Glass was synthesized 6 as described below. An Autolab PGSTAT 302N electrochemical analyzer connected to a personal 7 computer running the NOVA 1.8 software was used for data collection and analysis. All 8 experiments were carried out at a scan rate of 0.1 V/s. Tetrabutylammonium hexafluorophoshate 9 $(TBAPF_6)$ 0.1 M in Acetonitrile (CH₃CN) was used as supporting electrolyte. Before carrying out 10 the measurements the cell was purged with pure argon for 20 min to remove diluted gasses. The reference electrode potential was calibrated against Ferrocene/Ferrocenium (Fc/Fc⁺) after each 11 12 voltammetry run.

The corresponding HOMO, LUMO energy levels and the energy gap (Eg) were calculated with
use of the redox potentials by the following empirical equations:[44]

15

$$E_{HOMO} = e \left(E_{ons}^{ox} - E_{1/2}^{Ferrocene} \right) - 5.2 \left[eV \right]$$
⁽¹⁾

$$E_{LUMO} = e \left(E_{ons}^{red} - E_{1/2}^{Ferrocene} \right) - 5.2 \left[eV \right]$$
⁽²⁾

$$E_g = e \left(E_{ons}^{ox} - E_{ons}^{red} \right) \tag{3}$$

16

Furthermore, the value of -5.2 eV in equations (1), (2) emerged from calibration of the Ag/AgCl
electrode versus a normal hydrogen electrode (NHE) and considering that the NHE redox
potential corresponds to -4.6 eV on the zero vacuum level scale.[46,47]

20

21

1 **2.3 Synthetic procedures**

2

3 2.3.1 Synthesis of the organic dye precursors

4

Synthesis of 4,7-di-2-(3,4-ethylenedioxythiophene)-2,1,3-benzothiadiazole (di-EDOT-BTZ) 5 6 4,7-Di-bromo-2,1,3-benzothiadiazole 7.00g (23.81 mmol, 1eq) were dissolved in 110 mL 7 dimethylacetamide (DMAc), followed by the addition of 10 eq of 3,4-ethylenedioxythiophene (EDOT). Afterwards, CH₃COOK (7.01 g, 71.43 mmol, 3 eq) and Pd(OAc)₂ (53.45 mg, 0.24 8 9 mmol, 0.01 eq) were added to the solution, which was stirred at 155 °C under Ar for 18 h. The 10 mixture was precipitated in 500 mL of a brine solution and extracted using ethyl acetate (EtOAc). 11 The organic layer was dried using MgSO₄, filtered and the solvent was removed under reduced 12 pressure. The resulted material was finally dried in a vacuum oven at 45 °C for 18 h. Yield 90%. ¹H NMR (CDCl₃, *δ* ppm): 4.30-4.33 (m, 2H), 4.39-4.42 (m, 2H), 6.57 (s, 2H), 8.39 (s, 2H) 13 14

Synthesis of 4,7-di-(5-bromo-3,4-ethylenedioxythiophene-2-yl)-2,1,3-benzothiadiazole (di-Br-diEDOT-BTZ)

Di-EDOT-BTZ 6.00g (14.41 mmol, 1 eq) were dissolved in 250 mL of dimethylformamide (DMF) and afterwards N-Bromosuccinimide (NBS, 5.77 g, 32.41 mmol, 2.25 eq) was added to that solution in 3 portions over 60 minutes. The solution was then stirred at RT for 18 h, followed by the addition of an aqueous Na₂SO₃ saturated solution. The desired product was taken after filtration and recrystallization using DMF/MeOH: 1/10 v/v. Yield 52%:

22 ¹H NMR (CDCl₃, δ ppm): 4.39-4.41 (m, 4H), 8.37 (s, 2H)

- 1 2.3.2 Synthesis of the small organic dye sensitizers
- 2

3 Synthesis of bis-{4,7-[2-pentafluorophenyl-7-thiophene-N-2-ethylhexyl-carbazole]} (dithien-EH

4 sensitizer)

(i) via Direct coupling: Di-thien-BTZ (70.00 mg, 0.235 mmol, 1 eq) and di-Br-EH-carbazole 5 6 (822.00 mg, 1.88 mmol, 8 eq) were dissolved in 10 mL of DMAc, in a round bottom flask 7 equipped with a stirring bar and a reflux condenser, under inert atmosphere, followed by the addition of CH₃COOK (78 mg, 0.7 mmol, 3 eq) and Pd(OAc)₂ (1.00 mg, 3.50 umol, 0.015 eq). 8 The mixture was refluxed for 24hr, cooled at RT and a solution of perfluorophenyl boronic acid 9 10 (104.60 mg, 0.49 mmol, 2.1 eq) in 0.6 mL of DMAc was then added for another 24hr under reflux. After cooling at RT, the mixture was poured into 50 mL of MeOH, stirred for 2hr, filtered 11 12 and consecutively washed with boiling petroleum ether, MeOH, H₂O and again with MeOH, before drying under vacuum at 45°C for 18 h. Yield 58%. 13

14 (ii) via Suzuki coupling: Di-Br-di-thien-BTZ (50.00 mg, 0.11 mmol, 1 eq) and di-boronic ester-EH-carbazole (462.00 mg, 0.09 mmol, 8 eq) were dissolved in 10 mL of degassed toluene, 15 in a round bottom flask equipped with a stir bar and a reflux condenser, under inert atmosphere, 16 17 followed by the addition of 0.4 mL Na₂CO₃ (aq. solution, 0.87 mmol, 8 eq) and 7.6 mg Pd(PPh₃)₄ 18 (6.00 umol, 0.06 eq). The mixture was refluxed for 48h, cooled at RT and 19 bromopentafluorobenzene (76 uL, 0.61 mmol, 5.6 eq) was then added and stirred for another 24 h 20 under reflux. The mixture was cooled at RT, filtered and extracted using CHCl₃ and H₂O. The organic layer was dried over MgSO₄, filtered and the solvent was removed in a rotary evaporator. 21 22 The final product thus obtained, was dried under vacuum at 45 °C for 18 h. Yield 82%.

¹H NMR (CDCl₃, δ ppm): 0.83-1.03 (two t, 12H), 1.04-1.5 (three broad, 16H), 2.12 (m, 2H),
4.20 (m, 4H), 7.35 (d, 2H), 7.51 (d, 4H), 7.69 (s, 4H), 7.94 (s, 2H), 8.08 (d, 4H), 8.21 (d, 2H). ¹⁹F
NMR (CDCl₃, δ ppm): -142.82 - -143.02 (two m, 4F), -156.09 - -156.24 (m, 2F), -162.16 - 162.52 (m, 4F).

1	1 Analogous conditions were used for the synthesis of	f the remaining sensitizers using both the
2	2 Direct coupling and the Suzuki coupling conditions	in each case (Table 1)
3	<i>bis-{4,7-[2-pentafluorophenyl-7-thiophene-N-</i>	- heptadecan-9-yl-carbazole]}
4	4 (<i>dithien-HD sensitizer</i>): Yield 30% via Direct	arylation, 65% via Suzuki coupling.
5	5 ¹ H NMR (CDCl ₃ , δ ppm):0.76-0.87 (t, 12H),	0.98 (m, 4H), 1.04-1.32 (broad, 44H), 1.97
6	6 (m, 4H), 2.34 (m, 4H), 4.70 (m, 2H), 7.53-7.	.60 (two broad, 2H), 7.66 (broad, 4H), 7.88
7	7 (broad, 2H), 7.96 (s, 2H), 8.02 (broad, 2H), 8.	.12 (m, 4H), 8.21 (d, 2H). ¹⁹ F NMR (CDCl ₃ ,
8	8 δ ppm): -142.86143.11 (two m, 4F), -156.	21156.29 (m, 2F), -162.39162.50 (m,
9	9 4F).	
10	• bis-{4,7-[2-pentafluorophenyl-7-(3,4-ethylene	edioxythiophene)-N-2-ethylhexyl-
11	11 <i>carbazole]} (diEDOT-EH sensitizer):</i> Yield	80% via Direct arylation, 70% via Suzuki
12	12 coupling. ¹ H NMR (CDCl ₃ , δ ppm): 0.86-0.9	94 (two t, 12H), 1.25-1.40 (m, 16H), 2.00-
13	13 2.02 (quint, 2H), 4.01-4.12 (m, 4H), 4.41-4.5	55 (two m, 8H), 7.32 (d, 2H), 7.51 (s, 2H),
14	14 7.74 (d, 2H), 7.93 (d, 2H), 7.95 (s, 2H), 8.04	4 (d, 2H), 8.45 (s, 2H). $^{19}\mathrm{F}$ NMR (CDCl ₃ , δ
15	15 ppm): -142.85 – -143.09 (two m, 4F), -156.2	2156.29 (m, 2F), -162.33162.59 (m,
16	16 4F).	
17	<i>bis-{4,7-[2-pentafluorophenyl-7-(3,4-ethylene</i>	edioxythiophene)-N-heptadecan-9-yl-
18	18 <i>carbazole]} (diEDOT-HD sensitizer):</i> Yield	67% via Direct arylation, 50% via Suzuki
19	19 coupling. ¹ H NMR (CDCl ₃ , δ ppm): 0.82 (t, 1	2H), 0.98 (m, 4H), 1.03-1.34 (b, 44H), 1.94
20	20 (m, 4H), 2.33 (m, 4H), 4.49 (d, 4H), 4.52 (d	d, 4H), 4.70 (quint, 2H), 7.67, (broad, 4H),
21	21 7.89 (s, 2H), 8.03 (s, 2H), 8.11-8.13 (dd, 4H	I), 8.5 (s, 2H). ¹⁹ F NMR (CDCl ₃ , δ ppm): -
22	22 142.87 – -143.10 (two m, 4F), -156.23 – -156	.30 (m, 2F), -162.37 – -162.45 (m, 4F).
23	23	

[10]

1 2.4 Dye Sensitization of TiO₂

2

3 2.4.1 Preparation of dye-sensitized powder TiO_2 NPs

The general method for sensitizing powder TiO₂ NPs or of photoanodes of deposited TiO₂
NPs on onto glass substrates, with organic molecules bearing perfluorophenyl units has been
described also previously.[14] In particular for the powder TiO₂ NPs these were thermally treated
prior to their sensitization at 400 °C for 3-4 h.

8 Briefly, 1eq (0.07 mmol) of sensitizer, 4 eq (0.28 mmol) of K_2CO_3 , and 50 mg of powder 9 TiO₂ NPs were dispersed in acetone and heated at reflux for 48 h. The as synthesized hybrids 10 were filtrated and thoroughly washed with acetone, THF and water to remove unreacted 11 molecules and salts, until a colourless filtrate was obtained. The dye-sensitized TiO₂ NPs were 12 dried in a vacuum oven overnight at 40 °C.

13

14 2.4.2 Preparation of sensitizer/TiO₂ physical blends

TiO₂ NPs in their powder form and the organic sensitizer were dispersed in 20 mL of acetone. The composition of each blend was calculated from the sensitization percentage obtained from TGA data of the dye-sensitized TiO₂ nanoparticles. The mixture was then sonicated for 30min, stirred at 60 °C for 48 h and finally purified, using conditions similar to the as described above for the dye-sensitized TiO₂ NPs.

20

21 2.4.3 Deposition of TiO_2 on FTO

Nanoparticulate titania films (np-TiO₂) were deposited on FTO electrodes. An FTO glass electrode was cut in the appropriate dimensions and was carefully cleaned first with soap and then by sonication in ethanol and acetone. A thin layer of compact titania was first sprayed over a FTO electrode using 0.2 mol L^{-1} diisopropoxytitanium bis(acetylacetonate) solution in ethanol and then it was heated at 500 °C for 1 h. On this thin bottom layer, a titania paste made of P25

nanoparticles was applied by screen printing. 90 mesh screen was used. The film was heated

again up to 500 °C for 20 min. Then, the film was treated with a 0.04 mol L⁻¹ aqueous solution of
TiCl₄ for 30 min at 70 °C, followed by heating up to 500 °C for 20 min. The geometrical area of
the film was 0.16 cm² (0.4 cm × 0.4 cm).

5

1

6 2.4.4 Preparation of dye-sensitized TiO₂ photoanodes

A TiO₂ photoanode was placed in a solution of sensitizer (0.07 mmol, 1 eq) and K₂CO₃ (0.28
mmol, 4 eq) in acetone and heated at reflux. After 48h the mixture was cooled at RT and the
photoanode was taken out, washed using subsequently acetone, THF, water and acetone, before
drying under vacuum overnight.

11

- 12
- 13

14 **3. Results and Discussion**

15

16 The main scope of this work was the design and synthesis of novel sensitizers for DSSCs with 17 enhanced absorption in the visible area of the solar spectrum, based on benzothiadiazole and 18 carbazole units connected in an alternating and regular manner as in the PCDTBT polymer electron donor case. Such low band gap organic semiconductors developed for organic 19 photovoltaics (OPVs) generally possess good charge transport characteristics and have shown 20 21 improved power conversion efficiencies (PCE). For such low band gap semiconductors several 22 monomers have been developed and combined in order to lead to the final polymer electron 23 donors.[48,49,50,51] Among these monomers, carbazoles are often preferred due to their chemical and environmental stability, along with good charge transport properties. Solubility 24 25 issues often encountered due to the rigidity of carbazoles are easily overcome using bulky side aliphatic chains.[52,53] Especially secondary alkyl chains attached on the nitrogen atom of
 carbazole have led to better solubility and efficiency of the polymer electron donors thereof in
 OPVs.[54]

Another important feature of the herein reported sensitizers is the incorporation of endperfluorophenyl functionalities. In general the perfluorophenyl unit has proven an excellent choice for the development of functionalized semiconductors as precursors of hybrid materials with carbon nanostructures (CNTs, fullerenes etc.)[55,56,57] or with inorganic nanoparticles (e.g. TiO₂ NPs),[14,15] as electron withdrawing groups for the energy levels modulation of the semiconductors,[58,59] or for the insertion of additional functionalities via nucleophilic aromatic substitution.[60]

11

12 3.1 Synthesis of the sensitizers

13 For the preparation of the desired small organic dyes bearing carbazole and benzothiadiazole units, the first step was the di-substitution of benzothiadiazole by either thienyl or 3,4-14 ethylenedioxythienyl rings. This was accomplished in a single step via Direct arylation 15 16 conditions, [61,62] as can be seen in Scheme 1. The Direct arylation proceeds using palladium 17 acetate [Pd(OAc)₂] as catalyst, potassium acetate (CH₃COOK) as base in dimethylacetamide (DMAc). Thus, the 4,7-di-2-thienyl-2,1,3-benzothiadiazole (di-thien-BTZ)[39] and the 4,7-di-2-18 19 (3,4-ethylenedioxythiophene)-2,1,3-benzothiadiazole (di-EDOT-BTZ) were prepared, respectively. The direct synthesis of these two central moieties of the final sensitizers, was 20 efficient and of high yields, namely 50% and 90% respectively. 21



2 Scheme 1. Synthesis of di-thien-BTZ and, di-EDOT-BTZ via Direct arylation, and of their
3 respective di-bromo derivatives.

1

In another step, was performed the synthesis of the two different 2,7-dibromo-N-alkylcarbazoles and in particular 2,7-dibromo-N-2-ethylhexyl-carbazole (**di-Br-EH-carbazole**) and 2,7-dibromo-N-heptadecan-9-yl-carbazole (**di-Br-HD-carbazole**). **Di-Br-EH-carbazole** was prepared in a one-step reaction between the commercially available 2,7-dibromo-9H-carbazole and 2-ethylhexyl bromide, using acetone as solvent.[41] On the other hand, **di-Br-HD-carbazole** was prepared in a sequence of four reactions,[38] since this synthetic route leads to the desirable product in high purity and better yield, in comparison to other reported procedures.[63,64]

After the successful synthesis of the di-Br-alkyl-carbazoles and of the central di-substituted-BTZ, the final step was the connection of the two different species and the insertion of the perfluorophenyl anchoring end-groups. For this scope, two coupling methods were employed, namely the Direct arylation[61] (**Scheme 2**) and the Suzuki coupling (**Scheme 3**).[65]

16 Through the Direct arylation route (**Scheme 2**) and with a monomers' ratio of 8/1 di-Br-alkyl-17 carbazoles to di-substituted-BTZ, the reactive intermediates with two end bromine groups were

- 1 prepared, which subsequently reacted with perfluorophenyl boronic acid giving the desired
- 2 sensitizers (**Table 1**).
- 3



5 Scheme 2. Synthesis of EH and HD decorated dithien- and diEDOT- sensitizers via Direct
6 arylation through a one-pot, two-step reaction.

In order to synthesize the desired sensitizers via Suzuki coupling (Scheme 3) the dibrominated benzothiadiazole derivatives were required, in particular the 4,7-di-(5bromothiophene-2-yl)-2,1,3-benzothiadiazole (di-Br-di-thien-BTZ)[40] and the 4,7-di-(5bromo-3,4-ethylenedioxythiophene-2-yl)-2,1,3-benzothiadiazole (di-Br-di-EDOT-BTZ) (Scheme 1). Moreover, the di-Br-alkyl-carbazoles were transformed to their respective boronic esters (Scheme S1).[38] Typical Suzuki coupling conditions using Pd(PPh₃)₄ as catalyst, aqueous Na₂CO₃ as base in toluene were employed.[65] The monomers' ratio was 8/1 di-boronic ester-

- 1 alkyl-carbazole to di-brominated-BTZ in order to provide the reactive intermediate with two end
- 2 boronic ester units that further on reacted with perfluorophenyl bromide in a second step.
- 3



Scheme 3. Synthesis of dithien-alkyl and diEDOT-alkyl sensitizers via Suzuki coupling through a
one-pot, two-step reaction.

4

8 Comparison of the two different synthetic strategies showed that the Suzuki coupling reaction 9 was more efficient for the preparation of the thienyl bearing sensitizers, namely the dithien-EH 10 and the dithien-HD, both in terms of purity and reactions' yields as can be seen in Table 1. On 11 the other hand, Direct arylation was more efficient, for the preparation of the EDOT-sensitizers, 12 namely the diEDOT-EH and diEDOT-HD. This fact is mostly attributed to the availability of all positions of the thienyl ring as reactive sites for the Direct arylation reaction in contrast to the 13 14 EDOT bearing molecules. The incorporation of the ethylenedioxythienyl group limits undesirable 15 byproducts produced during Direct arylation, since there is only one available hydrogenated

position that can react with the respective bromide. Thus, the Direct arylation route provided
 increased efficiencies for the preparation of the EDOT bearing sensitizers. On the other hand, the
 Suzuki coupling method is to be chosen for the preparation of the dithien-EH and the dithien HD sensitizers.

5 The chemical structures and the abbreviations of all synthesized sensitizers are shown in 6 Scheme 4. In all cases the NMR characterization of the precursors and of the final sensitizers 7 confirmed the materials proposed chemical structures. Additionally, ¹⁹F NMR spectroscopy gave 8 proof of the attachment of the end-perfluorophenyl units on the final sensitizers. Analytic data of 9 the ¹⁹F NMR examination of the prepared sensitizers are provided in the Experimental Section 10 while a representative spectrum is shown in **Figure S1** for the diEDOT-HD dye as prepared via 11 the Direct arylation procedure.



2 Scheme 4. Chemical structures of the four sensitizers

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4 3.2 Sensitization of powder TiO₂NPs

Based on our previous experience, the use of perfluorophenyl units as anchoring groups of polymer sensitizers provides an effective methodology for the sensitization of TiO_2 NPs and photoanodes for DSSCs.[14,15] Therefore, also in this work, the perfluorophenyl endfunctionalities of the small organic sensitizers described above, reacted under mild alkaline conditions, namely potassium carbonate as base in acetone, with the hydroxyl groups of TiO_2

NPs. Thus, non-hydrolysable bonds are formed "anchoring" the organic sensitizers onto the TiO₂
 surface (Scheme 5). The organic-inorganic hybrid materials created where thoroughly washed
 with acetone, THF, water and again acetone in order to remove any unreacted species and all
 inorganic salts.

The modification percentages of TiO_2 NPs with the four small organic dyes are given in 5 Table 1 as calculated from thermogravimetric analysis (TGA). Modification percentages up to 6 7 22% wt were recorded, but no particular trend was observed regarding the origin of the sensitizers, meaning via Direct arylation or Suzuki coupling, and their efficacy in TiO₂ modification. This 8 9 fact also points out to the successful introduction of the perfluorophenyl functionalities regardless 10 of the synthetic method employed. Moreover, and due to the smaller size of the herein employed sensitizers in comparison to previously reported polymeric analogues materials[14,15] higher 11 12 modification percentages were accomplished, 18-22% wt over the previous 10-13% wt percentages. Figure 1 shows the TGA analyses of the dithien-alkyl sensitizers and of the 13 respective dithien-alkyl/TiO₂ NP hybrids. The TGA analyses of the diEDOT-alkyl sensitizers and 14 of the diEDOT-alkyl/TiO₂ hybrids are provided in Figure S3 of the Sup. Info. section. The 15 16 organic molecular sensitizers degrade around 400° C, whereas pure TiO₂ NPs show negligible 17 weight loss up to 800°C. On the other hand, the hybrid materials in all cases show higher stability 18 compared to the organic sensitizers, both in terms of onset temperature of degradation and of 19 weight loss at 800°C, proving the successful binding of the sensitizer on the TiO₂ surface.

Further confirmation of the formation of the sensitized TiO_2 NPs was provided via ATR spectroscopy as shown in **Figure 2** for the dithien-alkyl materials. The ATR spectra of the diEDOT-alkyl sensitizers and of the respective hybrids with TiO_2 NPs are given in **Figure S2**. The absorption bands of pure TiO_2 NPs are located in-between 1750-1250cm⁻¹.[66] After the TiO₂ NPs sensitization, new peaks owing to the organic molecules are observed with more pronounced those at 1223cm⁻¹, 1155cm⁻¹, 2935cm⁻¹ and 2860cm⁻¹. More importantly, the absorption bands between 1300cm⁻¹ and 1100cm⁻¹, prove the formation of Ti-O-C bonds, in
combination with the presence of C-F streching vibrations.[67,68]

3 The optical properties of the organic sensitizers and of the hybrid organic-inorganic materials were examined by UV-Vis and PL spectroscopies. The absorption spectra of the organic 4 sensitizers dithien-alkyl and diEDOT-alkyl are given in the Sup. Info. section, Figures S4 and S5, 5 6 respectively, in comparison to the commercial polymeric semiconductors used as benchmark 7 materials in photovoltaic applications, namely the regioregular-poly(3-hexyl-thiophene) rr-P3HT poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-8 and the 9 benzothiadiazole)] PCDTBT. The main absorption bands of the dithien-alkyl molecules are found 10 at 360nm and 510nm, whereas for the diEDOT-alkyl at 390nm and 570nm. Compared to the polymeric electron donor rr-P3HT it is obvious that both the dithien-alkyl and the diEDOT-alkyl 11 12 sensitizers surpass its absorption to higher wavelengths. More importantly, the absorption spectra of the small organic sensitizers resemble that of the low-band gap PCDTBT. Especially, in the 13 14 case of the EDOT bearing sensitizers, diEDOT-EH and diEDOT-HD, their absorption is identical, if not better, than of the high molecular weight polymeric PCDTBT. These excellent absorption 15 16 characteristics of the herein presented small-organic semiconductors in the visible region of the 17 light spectrum, shows their potentiality as sensitizers in DSSCs.

18 The photoluminescence characterization of the organic and of the hybrid materials is in 19 Figures 3 and S6 for the dithien-alkyl and the diEDOT-alkyl materials, respectively. Moreover, 20 physical blends of TiO₂ and the sensitizers were prepared in order to distinguish differences of direct attachment of the sensitizers onto the TiO2 NPs surface versus simple mixtures of the two 21 22 components. The composition of each blend was based on the TiO₂ modification percentage as calculated from TGA analyses. As can be seen in Figures 3 and S6, the photoluminescence 23 24 behavior of the sensitized nanoparticles strongly differs from the pure organic sensitizers and the 25 physical blends, after excitation at the absorption maximum of sensitizers. In particular, both the 26 sensitizer and the physical blend show a broad emission bands around 600nm and 650nm for the

1 dithien-alkyl and the diEDOT-alkyl materials, respectively. On the other hand, the sensitized NPs 2 demonstrate photoluminescence quenching, which is attributed to the covalent attachment of the 3 sensitizers onto the TiO_2 surface. This direct attachment allows electronic interactions between 4 TiO_2 and the sensitizer in contrast to the physical blends. This behavior provides additional proof 5 of the success of the sensitization route employed herein.



- 7 Scheme 5. General synthetic strategy for the preparation of dithien-alkyl/TiO₂ and diEDOT-
- $8 \qquad alkyl/TiO_2\,hybrids.$
- 9

- 1 Table 1. Reaction yields of the synthesized sensitizers (Scheme 4) and modification percentages
- 2 of TiO₂ nanoparticles after their sensitization.

ala	Songitizon	Direct arylation	Suzuki coupling	TiO ₂ NPs
a/a	Sensitizer	Yield (%)	Yield (%)	modification (%)
1	dithien-EH	58	82	20.5
2	dithien-HD	30	65	22
3	diEDOT-EH	80	70	22
4	diEDOT-HD	67	50	18

4



5

6 Figure 1. TGA analyses of thienyl bearing sensitizers dithien-alkyl, of TiO₂ nanoparticles, and of

7 hybrid materials dithien-alkyl/TiO₂

8



2 Figure 2. ATR spectra of thienyl bearing sensitizers dithien-alkyl, of TiO₂ nanoparticles, and of



4



Figure 3. PL spectra of TiO₂ nanoparticles, dithien-alkyl sensitizers, hybrid materials dithienalkyl/TiO₂ and of the respective dithien-alkyl sensitizer/TiO₂ physical blends in CHCl₃ solutions,
after excitation at 510nm.

1 3.3 Sensitization of Photoanodes

2 For the preparation of the sensitized TiO₂ photoanode electrodes, the deposited 3 nanoparticulate titania films on FTO electrodes were immersed into acetone solutions of the 4 small-organic perfluorophenyl functionalized dyes in the presence of K₂CO₃. After 48 h at reflux, the sensitized photoanodes were removed from the reaction medium and washed thoroughly with 5 6 acetone, THF, water and finally acetone. Figure 4 shows representative examples of TiO₂ 7 sensitized photoanodes using the 4 types of small organic sensitizers presented in this study. 8 Uniformly colored photoanodes were obtained that preserved their color even after their extended 9 washing for the removal of un-attached organic species and of inorganic salts. Notably, the 10 diEDOT-alkyl sensitizers afforded more intense and darker colored photoanodes in consistency 11 with their deeper absorption in the red region of the visible spectrum. This phenomenon is also 12 evident in the diffuse reflectance absorption spectra (DRS) of the sensitized photoanodes as 13 shown in Figure 5.



Figure 4. Images of the photoanodes sensitized with a) dithien-EH, b) diEDOT-EH, c) dithienHD and d) diEDOT-HD sensitizer.





Figure 5. Reflection-absorbance spectra of np-TiO₂ on FTO photoanodes sensitized with: (a)
dithien-EH,(b) diEDOT-EH, (c) dithien-HD and (d) diEDOT-HD.

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6 3.4 Electrochemical characterization

7 Cyclic voltammetry was used for the estimation of HOMO and LUMO energy levels of the 8 investigated dyes. Knowledge of these values is important for the efficient design and operation 9 of a DSSC. In order to assess the repeatability of the method, the CV measurements for each 10 compound were repeated for different samples. Negligible deviations were recorded in some 11 cases in the HOMO, LUMO and E_g levels of up to 0.1eV, which can be considered as the 12 experimental error of the procedure.

Table 2 contains the cyclic voltammetry results of the investigated materials. HOMO, LUMO and Eg levels were calculated according to the empirical equations (1), (2) and (3) given in the Experimental Section. Reduction and oxidation onset potentials were deduced from reduction and oxidation peaks respectively, shown in Figure 6.

1	Table 2. Reduction and oxidation	onset potentials,	HOMO, LUI	MO energy levels	and E_g of the

2 sensitized np-TiO₂ on FTO and of films of the organic sensitizers deposited on ITO glass.

	$E_{ons}^{ox}(V)$	E _{ons} ^{red} (V)	E _o		
Sample				Homo (eV)	Lumo (eV)
_	vs Ag/AgCl	vs Ag/AgCl	(eV)		K
dithien-EH sensitizer on ITO	1.36	-0.79	2.2	-6.1	-3.9
dithien-EH/TiO ₂ /FTO	1.66	-0.46	2.1	-6.2	-4.1
					7
dithien-HD sensitizer on ITO	1.29	-1.00	2.3	-6.0	-3.7
				Y Y	
dithien-HD/TiO ₂ /FTO	1.56	-0.69	2.3	-6.2	-3.9
diEDOT-EH sensitizer on ITO	0.73	-1.17	1.9	-5.4	-3.5
diEDOT -EH/TiO ₂ /FTO	0.87	-0.95	1.8	-5.5	-3.7
diEDOT-HD sensitizer on ITO	0.94	-0.89	1.8	-5.6	-3.8
diEDOT-HD/TiO ₂ /FTO	0.83	-0.92	1.8	-5.5	-3.7

3





Figure 6. Cyclic voltammograms of (a) dithien-EH/ITO (b) dithien-EH/TiO₂/FTO (c) dithienHD/ITO (d) dithien-HD/TiO₂/FTO (e) diEDOT-EH/ITO (f) diEDOT-EH/TiO₂/FTO, inset cyclic
voltammogram of TiO₂/FTO (g) diEDOT-HD/ITO (h) diEDOT-HD/TiO₂/FTO, inset cyclic
voltammogram of TiO₂/FTO. Scan rate 0.1V/s.





2 Figure 7. Schematic energy levels diagram for the dye sensitized TiO₂/FTO/Glass samples.

4 <u>Effect of substrate.</u>

5 In order to investigate the influence of substrates on the electrochemical characteristics of the 6 compounds, two different materials were used: (i) "standard" ITO commonly used as substrate in 7 CV experiments of thin films and (ii) np-TiO₂/FTO as used in DSSCs simulating thus the 8 behavior of the compounds directly within the DSSC devices. In the latter case, the dyes were 9 anchored on the TiO₂ surface as in the preparation of the TiO₂ photoanodes.

10 At first the plain substrates were measured. ITO did not exhibit any significant features within 11 the range (-2.5V, +2.5V). On the other hand, TiO_2/FTO exhibited a reduction curve as shown in 12 the insets of **Figures 6f** and **6h**, which yielded the TiO_2 conduction band level at -4.3eV, as is 13 schematically shown in **Figure 7**. The optical band gap of TiO_2/FTO was also measured and it 14 was combined with the above electrochemical result to give the valence band level of -7.6eV.

15 As can be seen in **Table 2**, no significant changes were detected in the energy gap of the 16 compounds on different substrates. The small differences observed are within the experimental

error range (0,1eV). Regarding the HOMO and LUMO levels, all compounds exhibited slightly

more negative HOMO and LUMO levels on TiO_2/FTO (ranging from -0.1eV to -0.2eV), with the 3 exception of diEDOT-HD. However, these observed changes are not significant and thus, it can be safely concluded that the substrate effect is marginal. 4 In order to calculate the LUMO level of the diEDOT-EH and diEDOT-HD on TiO₂/FTO, the 5 6 second reduction peak of the voltammograms (at about -1.2V) was used, since the first peak (at 7 about -0.5V) was attributed to the reduction of TiO_2 . Indeed, from the insets of Figures 6f and 6h 8 it can be seen that the onset for the TiO_2 reduction appears at a similar potential. A possible 9 explanation could be that a part of the TiO_2 surface was not covered by the dye, thus producing a 10 weak reduction peak even for the sensitized TiO₂/FTO substrates. Notably, as observed in Figure 6, the Fc/Fc+ redox potentials are different for the two 11 12 substrates, namely higher for TiO₂/FTO case, while they also vary among the different compounds onto the same substrate. This is not an unexpected phenomenon since it is well 13

known that the position of the Fc/Fc+ redox potential depends on the working and reference 14 15 electrodes, the temperature and the electrolyte employed, etc.[69,70] It is therefore imperative to 16 measure the the Fc/Fc+ potentials in each experiment and not to assume typical values from the 17 literature.

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19 Comparison of the organic dyes

From a direct comparison of the energy levels of the herein examined small molecular 20 organic dyes it is evident that all are suitable for the sensitization of TiO₂ in DSSCs applications. 21 22 The energy gap (Eg) levels of the materials denote absorption maxima in the visible area of the 23 solar spectrum as detected also by the direct examination of the absorbance of the materials both 24 in solution and in the solid state (Figures S4, S5 and 5). Moreover, the diEDOT- bearing dyes presented lower Eg than the dithien- ones as expected due to the higher absorption maxima of the 25 26 materials. Furthermore, as schematically shown in Figure 7, the LUMO levels of all the organic dyes studied are higher than the conduction band of TiO₂ allowing thus, electron injection to the
 inorganic semiconductor from the organic dyes.

As regards the HOMO levels, the more negative values of the dithien- bearing dyes could prove advantageous, increasing the driving force for dye regeneration from iodide, used as electrolyte, since the I^{-}/I_{3}^{-} redox potential is approximately +0.4 V versus NHE, that corresponds to -5.0eV.[71]

A final noticeable fact, schematically shown also in Figure 7, is that the HD modification of
the carbazole moieties of the dithien-bearing dyes, increases the LUMO level by 0.2eV compared
to that of dithien-EH. However, no such alterations were observed when comparing the diEDOTHD and the diEDOT-EH dyes.

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12 3.5 Application in DSSCs and PECs proof of concept

The compounds developed herein were applied in DSSCs and photoelectrochromic (PEC) devices, in an effort to assess their potential for solar energy applications. The details of the fabrication and testing of these devices appear in the supplementary data.

16 In accordance with the favorable positions of the HOMO and LUMO levels of the dyes, all four dyes were found functional as sensitizers for DSSCs. Figure S7 shows the corresponding J-17 18 V curves while Table S1 lists the data extracted thereof. All dyes gave the same open-circuit 19 voltage within experimental error. The open circuit voltage is mainly defined by the difference between the electron injection level, i.e. the conduction band of TiO₂, and the redox potential of 20 21 the electrolyte. Differentiations may occur due to extreme modifications of the dye-22 semiconductor's interface. However, such modifications are obviously not expected in the present cases to derive from the present dyes. A larger variation was observed for the fill factor. 23 24 However, a striking difference was observed between the diEDOT-based dyes and the dithien-25 based dyes, with the former offering substantially higher short circuit currents, in part due to their 26 lower Eg values.

1 As a further demonstration of the fabricated dyes' applicability, the diEDOT-EH dye was 2 applied as sensitizer to "partly covered" photoelectrochromic devices (PECs). The devices are 3 essentially hybrids of DSSCs and electrochromics (ECs), aimed to become the next generation of 4 "smart" windows. The integration of DSSCs and ECs in one device is achieved by insertion of the 5 EC WO₃ film between the FTO glass and the TiO_2 film of the anode, and by modification of the 6 electrolyte in order to contain Li ions. Through this way, the photoelectrons injected into TiO_2 7 diffuse in WO₃ and attract Li⁺ from the electrolyte to form the Li_xWO₃ "tungsten bronze" that assumes an increasingly deep blue color with an increasing intercalation parameter (x in Li_xWO₃). 8 9 Electrons diffuse fast into WO_3 and it has been proven that covering a 15% to 20% of the total 10 device area with the opaque TiO_2 film is adequate for uniform coloration of the device.[72]

Transmittance spectra at different exposures of a typical device appear in Figure S8. It is 11 12 evident that the device is responsive, as the transmittance continuously decreases with prolonged exposure. The maximum achieved transmittance modulation at 550nm is 1.6:1 (e.g. from 61.8% 13 14 at the bleached state to 37.6% in the colored state) which is considered acceptable for practical 15 applications. The device could be bleached by short circuit in the dark. The coloration kinetics is 16 rather slow, as it takes 30 min for full coloration. This is due to the low efficiency of the incorporated DSSC (η=0.25%, J_{sc}=0.60mA/cm², V_{oc}=0.51V). Similar results were obtained for 17 the dithien-EH dye (Figure S9). Further improvements in the sensitization method could lead to 18 19 better performance of the PEC devices. However, the feasibility of the use of the diEDOT-EH dye in PECs was unambiguously demonstrated even by this initial attempt. 20

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1 4. Conclusions

In summary, four small organic dyes have been synthesized based on benzothiazole and carbazole untis connected by either thienyl or 3,4-ethylenedioxythiophene units, also differing on the side solubilizing alkyl chains located onto the carbazole moieties, either 2-ethylhexyl or heptadecan-9-yl ones. In all cases, perfluorophenyl anchors, introduced as end-capping units onto the dyes, were used for their attachment on TiO₂ NPs and photoanodes for DSSCs and photoelectrochromic devices.

8 The optoelectronic and electrochemical characterization of the dyes revealed that they are all 9 suitable for DSSC applications having energy gaps in the visible area, LUMO levels that permit 10 electron injection into the TiO₂ conduction band and HOMO levels that allow their regeneration by the I/I_3 couple. Comparison of the thienyl to the 3,4-ethylenedioxythiophene bearing dyes 11 revealed that the diEDOT compounds exhibit lower electrochemical energy gaps than the dithien 12 ones, indeed performing better in DSSCs, although the devices need further optimization to 13 14 unveil their full potentiality. In addition, comparison of the small molecular dyes was performed 15 in partly covered photoelectrochromic devices with promising results especially in the case of the 16 diEDOT carrying dyes.

17

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1 Appendix A. Supplementary data

2 Supplementary data related to this article such as DSSCs and PECs fabrication experimental

3 details, additional synthetic schemes and characterization data.

- 4
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Highlights

- Synthesis and characterization of carbazole-alt-benzothiadiazole molecular dyes
- Thienyl versus 3,4-ethylenedioxythiophene units
- Perfluorophenyl-anchors for TiO₂ photoanodes sensitization via stable C-O-Ti bonds
- DSSCs and PEC applications
- Exact chemical structure's impact on properties and devices performances

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