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# Synthesis and characterization of a new series of dibenzofulvene based organic dyes for DSSCs.

Agostina L. Capodilupo,<sup>a\*</sup> Luisa De Marco,<sup>b</sup> Giuseppina A. Corrente,<sup>a,b,c</sup> Roberto Giannuzzi,<sup>b</sup> Eduardo Fabiano,<sup>b,d</sup> Antonio Cardone,<sup>e</sup> Giuseppe Gigli<sup>a,f</sup> and Giuseppe Ciccarella.<sup>a,g\*</sup>

# Agostina Lina Capodilupo <sup>a\*</sup>

<sup>*a*</sup> CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce Italy. E-mail: <u>agostina.capodilupo@nanotec.cnr.it</u>

## Luisa De Marco<sup>b</sup>

<sup>b</sup> Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy. E-mail: <u>luisa.demarco@iit.it</u>

# Giuseppina Anna Corrente *a,b,c*

<sup>*a*</sup> CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce Italy.

<sup>b</sup> Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy.

<sup>c</sup> Dipartimento di Ingegneria dell'Innovazione, Università del Salento, via Monteroni, 73100, Lecce, Italy. E-mail: <u>giuseppinaanna.corrente@unisalento.it</u>

## Roberto Giannuzzi<sup>b</sup>

<sup>b</sup> Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy. E-mail: <u>roberto.giannuzzi@iit.it</u>

## Eduardo Fabiano<sup>b,d</sup>

<sup>b</sup> Center for Biomolecular Nanotechnologies (CBN) Fondazione Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, Arnesano, 73010, Italy.

<sup>d</sup> Istituto Nanoscienze–CNR, Euromediterranean Center for Nanomaterial Modelling and Technology (ECMT), Via per Arnesano, 73100 Lecce, Italy. E-mail: <u>eduardo.fabiano@nano.cnr.it</u>

## Antonio Cardone<sup>e</sup>

 <sup>e</sup> Istituto di Chimica dei Composti OrganoMetallici (ICCOM) – Consiglio Nazionale delle Ricerche CNR, via Orabona, 4 – 720125 Bari, Italy. E-mail: <u>cardone@ba.iccom.cnr.it</u>.

## Giuseppe Gigli <sup>*a*,*f*</sup>

<sup>*a*</sup> CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce Italy.

<sup>f</sup> Dipartimento di Matematica e Fisica "Ennio De Giorgi", Università del Salento, via Monteroni,
73100, Lecce, Italy. E-mail: <u>giuseppe.gigli@unisalento.it</u>

# Giuseppe Ciccarella<sup>*a,g\**</sup>

<sup>*a*</sup> CNR NANOTEC - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce Italy.

<sup>g</sup> Dipartimento di Scienze e Tecnologie Biologiche e Ambientali Universita' del Salento c/o Edificio "La Stecca" via Monteroni, 73100 Lecce, Italy. É-mail: <u>giuseppe.ciccarella@unisalento.it</u>

**Corresponding author at CNR NANOTEC** - Institute of Nanotechnology c/o Campus Ecotekne, University of Salento, Via Monteroni - 73100 Lecce, Italy. E-mail: agostina.capodilupo@nanotec.cnr.it.

Corresponding author at Dipartimento di Scienze e Tecnologie Biologiche e Ambientali, Università del Salento, Via Monteroni, 73100, Lecce, Italy. E-mail: <u>giuseppe.ciccarella@unisalento.it.</u>

## ABSTRACT

Three new 2D- $\pi$ -A dyes (**TK4**, **TK5** and **TK6**), composed of diarylamine donor groups, a dibenzofulvene-thiophene core as the  $\pi$ -bridge, and a cyanoacrylic acid anchoring group as the acceptor, have been successfully designed, synthesized, and characterized both experimentally and computationally. The performance in DSSC solar cells has been also studied. Octyloxy chains were introduced on the backbone of the dye, in order to increase donor capability, avoid aggregation side effects and increase physical insulation between electrolyte system and the TiO<sub>2</sub> layer. The dye containing the octyloxy chains on the donor group and two thiophene ring as an extension of  $\pi$ -bridge showed the best photovoltaic performance with a maximum of solar energy-to-electricity conversion yield of 7.8% under AM 1.5 irradiation (100 mW/cm<sup>2</sup>).

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# **KEYWORDS:**

Dibenzofulvene, Dyes, Dye-sensitized solar cells, energy conversion, Diarylamine.

## **1 INTRODUCTION**

Dye-sensitized solar cells (DSSCs) have attracted sustained attention over the past decades because of their potential in low-cost solar-to-electricity conversion.[1, 2] Sensitizers play a critical role in light harvesting and electron injection and thereby affect the power conversion efficiency (PCE) of the DSSCs.[3] Compared to expensive ruthenium complexes, metal-free organic dyes promise modest fabrication costs and grant flexibility in molecular tailoring.[4-6] Moreover, the metal free organic dyes have much stronger light-harvesting ability than metal complexes thanks to higher molar extinction coefficients. The common structure of solar dyes  $(D-\pi-A)$ [7-10] involves a donor (D) connected to an electron acceptor (A) by a  $\pi$ -bridge. This structure allows a fine-tuning of molecular absorption to attain panchromatic light-harvesting, taking advantage of the efficient intramolecular charge transfer (ICT) and the large control of electrochemical properties. Up to now, the cyanoacrylic acid unit, which is a strong electrondeficient anchoring group, is the most widely used acceptor moiety.[11, 12] On the other hand, diphenylamine (DPA),[13-18] carbazole,[19-22] electron-rich units such as and phenothiazine[23-25] are mostly adopted as donors. In addition to these, many different conjugated building blocks have been introduced as bridges between the donor and the acceptor. [26, 27] Despite its many advantages, the D- $\pi$ -A sensitizer structure also shows several limitations. In particular, it has a rod-like configuration, which may promote undesirable dye aggregation and charge recombination. [28] Indeed, a close  $\pi$ - $\pi$  aggregation can lead not only to self-quenching and to a reduction of electron injection into TiO<sub>2</sub> but also to the instability of the organic dyes due to the formation of excited triplet states and unstable radicals under light irradiation.[29] Several strategies have been adopted to overcome this problem. For example, the introduction of long chains into the dye[30] and the employment of starburst dyes with a bulky

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multi-donor arrangement.[27, 31, 32] The choice of a suitable donor group together with the optimization of its structure has, in fact, not only a positive effect on the absorption properties of the dye, but can also modify the charge recombination rate in the device, as a consequence of the redefinition of the energy levels, avoiding dye aggregation and enhancing the stability of the sensitizers.[33] With the above considerations in mind, we have designed and synthesized three new metal-free organic dyes with the starburst 2D- $\pi$ -A structure (Figure 1), labelled TK4, TK5 and TK6. This set, which extends our previous work on dibenzofulvene-containing dyes,[17] consists of dyes having para-alkoxy substituted diphenylamines as donor groups, the cyanoacrylic acid as the acceptor/anchoring group, and a dibenzofulvene core as the  $\pi$ -linker. Our strategy in the choice of the branched 2D-π-A structure of the dyes, was to pursue characteristics as high electron-donating ability, reduced dye-aggregation, and the charge recombination, with the aim to achieve enhanced photovoltaic performance. Theoretical calculations using time-dependent density functional theory (TD-DFT) have also been employed in order to optimize the geometry and to visualize location of the HOMOs and LUMOs. The dyes have been used as sensitizers in liquid DSSC fabrication, correlating the molecular structure with the device performance. As a result, a maximum efficiency of 7.8% has been recorded for the TK6 dye.



Figure 1. Structures of the sensitizers TK4-TK6

# **2 EXPERIMENTAL SECTION**

## 2.1 Materials and instrumentation.

The synthetic routes of **TK4-TK6** are detailed in Scheme 1. The solvents were freshly distilled prior to use, according to standard procedures. Commercial reagents were used as received. FT-IR spectra were measured on a Perkin-Elmer 1710 spectrophotometer using dry KBr pellets. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz spectrometer. LC-MS spectra were acquired with an Agilent 6300 Series Ion Trap interfaced to an Agilent 1200 HPLC, in the following general conditions: atmospheric pressure chemical ionization, positive ions, eluent

chloroform, flow rate 0.200 mL min1, drying gas flow 5.0 L min1, nebulizer pressure 60 psi, drying gas temperature 350 °C, vaporizer temperature 325 °C, mass range 100–2200 m/z. UV-Vis absorption spectra were recorded on a Varian-Cary 500 spectrophotometer. Elemental analyses were done by a Carlo Erba CHNS-O EA1108-Elemental Analyzer. Electrochemical characterization of dyes was carried out by cyclic voltammetry (CV) using a AutoLab potentiostat (Methrom). A typical three-electrode cell was assembled with a glassy carbon diskworking electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl non-aqueous reference electrode. Cyclic voltammograms were acquired at 0.1 V s 1 scan rate on 1mM dye solutions prepared in the electrolyte solution, which consisted of 0.1M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>). All the solutions were previously degassed with N<sub>2</sub> and kept under a N<sub>2</sub> atmosphere. Ferrocene was added as an internal reference for calibration of the potential scale versus  $Fc^+/Fc$  couple. Potentials referred to ferrocene were then converted to Normal Hydrogen Electrode (NHE) by addition of 0.63 V.

## 2.2 Computational details.

All calculations were carried out with the TURBOMOLE[34] program package using the COSMO solvation model.[35, 36] Ground-state calculations and geometry optimizations were performed using the BLOC functional.[37, 38] Time-dependent calculations were carried out with the BHLYP functional.[39] In all calculations a def2-TZVP basis set[40] was employed. To quantify the charge transfer character of each excited state two indicators were considered: the overlap indicator  $\Lambda$ ,[41] which is computed as the spatial overlap between the occupied and unoccupied orbitals involved in the excitation; the electron displacement indicator  $\Delta$ r,[42] which measures the distance between the ground-state and the excited-state charge distributions. We

recall that small values of  $\Lambda$  (i.e. a small overlap between the occupied and unoccupied orbitals) indicate a greater charge-transfer character (when  $\Lambda = 0$  an electron is completely transferred). In contrast, larger  $\Delta r$  values indicate a more pronounced charge-transfer character. To study the intermolecular interactions in the dimers of the new dyes calculations were performed using the APBE-D3 functional[43, 44] with a def2-TZVP basis set[45] and the resolution of identity approximation. [46-48]

# 2.3 Fabrication of DSSC devices and photovoltaic measurements.

Fluorine-doped tin oxide (FTO, 15  $\Omega$ /sq, provided by Solaronix S.A.) glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min, and then rinsed with water and ethanol. Double-layer electrodes (overall thickness 20 µm) were prepared as follows: two layers of commercial colloidal titania paste (Dyesol 18NR-T) were deposited onto the FTO glass using the doctor blade technique and gradually heated in air to obtain a ~15 µm transparent nanocrystalline film. The temperature gradient was programmed as follows: 170°C (40 min), 350°C (15 min) and 430°C (30 min). This procedure was repeated for the scattering layer (5 µm), prepared by a Solaronix D/SP colloidal paste. The double-layer electrode was sintered at 450°C for 30 min. The thickness of the sintered photo-anodes were measured using a profilometer (Veeco Dektak 150 Surface Profiler). The dye loading was performed by keeping the electrodes for 14 h and under the dark in 0.2 mM (CH<sub>3</sub>CN:CHCl<sub>3</sub> = 1:0.01 v/v) (dye **TK4**) or 0.2 mM THF solutions (dyes **TK5** and **TK6**), containing when needed, a known amount of chenodeoxycholic acid (CDCA). The counter-electrodes were prepared by sputtering a 50 nm Pt layer on a hole-drilled cleaned FTO plate. In a typical device construction procedure, the photo-anode and the counter-electrode were faced and assembled using a suitably cut 50 µm thick Surlyn® hot-melt

gasket for sealing. The redox electrolyte (0.1 M LiI, 0.03 M I<sub>2</sub>, 0.6 M 1-methyl-3propylimidazolium iodide, and 0.5 M tert-butylpyridine in dry acetonitrile) was injected into the vacuum spaces between the electrodes through pre-drilled holes on the back of the counter electrode. The holes were sealed using Surlyn® hot melt film and a cover glass. Photocurrentvoltage measurements were performed using a Keithley unit (Model 2400 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 1000 W xenon arc lamp) serving as a light source. The light intensity (or radiant power) was calibrated to 100 mW cm<sup>-2</sup> using as reference a Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured by the DC method, using a computer-controlled xenon arc lamp (Newport, 140 W, 67005) coupled with a monochromator (Newport Cornerstore 260 Oriel 74125). The light intensity was measured by a calibrated silicon UV-photodetector (Oriel 71675), and the short circuit currents of DSSCs were measured by using a dual channel optical power/energy meter, (Newport 2936-C). The surface concentrations (dye loading) of the dyes were assessed by spectrophotometric determination as follows: double layered photoanodes  $(15 + 5 \mu m, 1 \text{ cm}^2)$ were sensitized with the same solutions used for devices; then the dyes were completely desorbed from the TiO<sub>2</sub> surface by immersing the substrates in a 0.01 M tetrabutylammonium hydroxide in DMF solution. The evaluation of the dye concentration in the solvent, obtained by UV-Vis measurements, allowed an estimate of the amount of the adsorbed molecules, expressed in terms of moles of dye anchored per unit area of the photoelectrode to be calculated. Electrochemical impedance spectroscopy (EIS) was per-formed by an AUTOLAB PGSTAT 302N (Eco Chemie B.V.) in a frequency range between 100 kHz and 10 mHz. The impedance measurements were carried out at different voltage biases, under 1.0 sun illumination. The resulting impedance spectra were fitted by using ZView (Scribner Associates) software.

#### 2.4 Synthetic procedures

The synthetic routes of these dyes were shown in Scheme 1, and the detailed synthetic procedures are as follows.

2.4.1. 3,6-dibromo-9H-fluoren-9-one, 1. Was synthesized following the literature procedure.[49]

#### 2.4.2. 3,6-dibromo-9H-fluorene, 2.

To a suspension of aluminium chloride (1.177 g, 8.85 mmol) and borane-*tert*-butylamine (1.539 g, 17.7 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0°C, compound **1** (1 g, 2.95 mmol) was added in 15 min. The resulting mixture was allowed to warm at r. t, and stirred for 4 h before quenching with a 0.1 M hydrochloric acid aq. solution. The crude residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers were dried over anhydrous sodium sulfate. The solvent was evaporated under a reduced pressure, and the residue was purified by flash chromatography (silica gel), using 98/2 hexane/dichloromethane as the eluent. The pure product **2** was obtained as a white solid (80% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.66 (d, *J* = 1.67, 2H) 7.45 (dd, *J*<sub>1</sub> = 8.02, *J*<sub>2</sub> = 1.78, 2H) 7.41 (d, *J* = 8.02, 2H) 7.39 (s, 2H). <sup>13</sup>C (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  142.62, 142.20, 130.23, 126.54, 123.38, 121.01, 36.27. MS (APCI): calcd for C<sub>13</sub>H<sub>8</sub>Br<sub>2</sub>, 324.01; found: m/z = 325.01 [M+H]<sup>+</sup>.

2.4.3. 2-(5-((3,6-dibromo-9H-fluoren-9-ylidene)methyl)thiophen-2-yl)-5,5-dimethyl-1,3-dioxane, 3a.

A mixture of potassium *tert*-butoxide (0.08 g, 0.64 mmol), compound **2** (0.2 g, 0.64 mmol) and 5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene-2-carbaldehyde (**i**) (0.16 g, 0.7 mmol) in absolute ethanol (4 mL) was stirred in an ultrasonic bath for 30 min. The reaction mixture was cooled at rt

and the resulting precipitate was filtered and washed with absolute ethanol. The pure product **3a** was obtained as a yellow solid (84% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.036 (d, *J* = 8.36 Hz, 1H) 7.805 (dd, *J*<sub>1</sub> = 1.54 Hz, *J*<sub>2</sub> = 4.53 Hz, 1H) 7.675 (d, *J* = 1.09 Hz, 1H) 7.599 (d, *J* = 7.99 Hz, 1H) 7.552 (d, *J* = 9.88 Hz, 1H) 7.498 (dd, *J*<sub>1</sub> = 1.59 Hz, *J*<sub>2</sub> = 7.86 Hz, 1H) 7.456 (dd, *J*<sub>1</sub> = 1.79 Hz, *J*<sub>2</sub> = 8.21 Hz, 1H) 7.328 (m, 1H) 7.176 (d, *J* = 3.80 Hz, 1H) 5.687 (s, 1H) 3.805 (d, *J* = 11.28 Hz, 2H) 3.686 (d, *J* = 10.63 Hz, 2H) 1.314 (s, 3H) 0.832 (s, 3H) <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 139.2, 138.6, 138.3, 132.6, 130.2, 130.1, 129.6, 129.4, 125.5, 125.4, 124.0, 123.0, 122.9, 122.7, 122.1, 121.5, 120.3, 99.4, 97.9, 77.4, 30.1, 22.8, 21.7. MS (APCI): calcd for C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub>S, 531.05; found: m/z = 532.05 [M+H]<sup>+</sup>. FT-IR (KBr): v 2954, 2849, 1707, 1605, 1592, 1573, 1470, 1418, 1378, 1306, 1205, 1099, 1054, 1026, 989, 966, 922, 869, 821, 774 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub>S: C, 54.16; H, 3.79; S, 6.02. Found: C, 54.19; H, 3.75; S, 6.03.

# 2.4.4. 2-(5'-((3,6-dibromo-9H-fluoren-9-ylidene)methyl)-[2,2'-bithiophen]-5-yl)-5,5-dimethyl-1,3-dioxane, **3b**.

A mixture of potassium *tert*-butoxide (0.065 g, 0.58 mmol), compound **2** (0.186 g, 0.58 mmol) and 5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2'-bithiophene]-5-carbaldehyde (**3'**) (0.178 g, 0.58 mmol) in absolute ethanol (5 mL) was stirred in an ultrasonic bath for 30 min. The reaction mixture was cooled at r. t. and the resulting precipitate was filtered and washed with absolute ethanol. The pure product **3b** was obtained as an orange solid (77% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.197 (d, J = 8.40 Hz, 1H) 7.809 (dd,  $J_I$  = 1.75 Hz,  $J_2$  = 9.54 Hz, 2H) 7.585 (d, J = 8.23 Hz, 1H) 7.549 (s, 1H) 7.452 (dd,  $J_I$  = 1.74 Hz,  $J_2$  = 8.20 Hz, 1H) 7.388 (dd,  $J_I$  = 1.85 Hz,  $J_2$  = 8.37 Hz, 1H) 7.353 (d, J = 3.79 Hz, 1H) 7.196 (d, J = 3.79 Hz, 1H) 7.149 (d, J = 3.70 Hz, 1H) 7.079 (d, J = 3.54 Hz, 1H) 5.644 (s, 1H) 3.789 (d, J = 11.21 Hz, 2H) 3.667 (d, J = 10.91 Hz, 2H)

1.310 (s, 3H) 0.824 (s, 3H) <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  141.5, 141.2, 140.1, 139.0, 138.5, 137.3, 136.7, 134.6, 133.5, 132.5, 131.5, 130.2, 130.1, 125.8, 125.5, 124.1, 123.6, 123.1, 122.9, 122.6, 122.0, 121.3, 120.0, 97.9, 77.4, 30.0, 22.8, 21.6. MS (APCI): calcd for C<sub>28</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>2</sub>S<sub>2</sub>, 613.94; found: m/z = 614.97 [M+H]<sup>+</sup>. FT-IR (KBr): v 2952, 2851, 1609, 1589, 1469, 1420, 1376, 1366, 1322, 1307, 1212, 1185, 1087, 1067, 1015, 988, 965, 863, 816, 792 cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C, 54.74; H, 3.61; S, 10.44. Found: C, 54.71; H, 3.62; S, 10.46.

# 2.4.5. 9-((5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl)methylene)-N3,N3,N6,N6-tetrakis(4methoxyphenyl)-9H-fluorene-3,6-diamine, **4a**.

To a suspension of Pd(dba)<sub>2</sub> (0.008 g, 0.014 mmol) and PtBu<sub>3</sub> (0.16 mL, 0.16 mmol, 1M in toluene) in anhydrous toluene (5 mL), were added **3a** (0.2 g, 0.38 mmol), bis(4-methoxyphenyl)amine (0.19 g, 0.84 mmol) and sodium *tert*-butoxide (0.08 g, 0.84 mmol). The resulting mixture was reacted under a microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed under a reduced pressure, and the residue was purified by column chromatography (silica gel, 50/50 hexane/CH<sub>2</sub>Cl<sub>2</sub>) to give the pure product as a red solid (67% yield). <sup>1</sup>H-NMR (400 MHz, DMSO)  $\delta$  7.879 (d, *J* = 8.65 Hz, 1H) 7.691 (d, *J* = 8.46 Hz, 1H) 7.422 (s, 1H) 7.267 (d, *J* = 3.64 Hz, 1H) 7.114 (d, *J* = 3.78 Hz, 1H) 6.984 (m, 8H) 6.880 (m, 10H) 6.696 (dd, *J*<sub>1</sub> = 2.15 Hz, *J*<sub>2</sub> = 8.43 Hz, 1H) 6.563 (dd, *J*<sub>1</sub> = 2.28, *J*<sub>2</sub> = 8.61, 1H) 5.688 (s, 1H) 3.716 (s, 12H) 3.638 (d, 4H) 1.147 (s, 3H) 0.731 (s, 3H) <sup>13</sup>C-NMR (100 MHz, DMSO)  $\delta$  156.2, 155.8, 149.5, 149.1, 142.7, 141.8, 140.5, 139.3, 139.0, 134.7, 133.1, 129.2, 128.4, 127.0, 126.5, 126.1, 124.9, 121.8, 120.1, 118.4, 115.2, 115.18, 115.1. MS (APCI): calcd for C<sub>52</sub>H<sub>48</sub>N<sub>2</sub>O<sub>6</sub>S, 828.3; found: m/z = 829.4 [M+H]<sup>+</sup>. FT-IR (KBr): v 2956, 2833, 1687, 1596, 1505,

1484, 1451, 1361, 1329, 1276, 1246, 1177, 1105, 1032, 911, 827, 783, 677 cm<sup>-1</sup>. Anal. Calcd for C<sub>52</sub>H<sub>48</sub>N<sub>2</sub>O<sub>6</sub>S: C, 75.34; H, 5.84; S, 3.87. Found: C, 75.34; H, 5.86; S, 3.88.

# 2.4.6. 9-((5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2'-bithiophen]-5-yl)methylene)-N3,N3,N6,N6tetrakis(4-methoxyphenyl)-9H-fluorene-3,6-diamine, **4b**.

To a suspension of  $Pd(dba)_2$  (0.015 g, 0.024 mmol) and  $PtBu_3$  (0.096 mL, 0.096 mmol, 1M in toluene) in anhydrous toluene (5 mL), were added 3b (0.18 g, 0.3 mmol), bis(4methoxyphenyl)amine (0.18 g, 1.17 mmol) and sodium tert-butoxide (0.131 g, 1.17 mmol). The resulting mixture was reacted under a microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed under a reduced pressure, and the residue was purified by column chromatography, (silica gel, 50/50 hexane/CH<sub>2</sub>Cl<sub>2</sub>) to give the pure product 4b as a powder purple (70% yield) <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.109 (d, J = 8.58 Hz, 1H) 7.51 (d, J= 8.43 Hz, 1H) 7.259 (d, J = 3.93 Hz, 1H) 7.237 (s, 1H) 7.186 (s, 2H) 7.136 (d, J = 3.72 Hz, 1H) 7.066 (m, 10H) 6.845 (m, 9H) 6.754 (d, J = 8.61 Hz, 1H) 5.625 (s, 1H) 3.801 (s, 14H) 3.653 (d, J = 10.97 Hz, 2H) 1.315 (s, 3H) 0.820 (s, 3H)  $^{13}$ C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  155.7, 155.4, 149.2, 148.9, 142.1, 141.2, 140.7, 140.3, 139.5, 139.1, 138.0, 137.4, 135.3, 133.8, 129.9, 129.4, 126.2, 125.7, 125.6, 125.0, 123.9, 123.0, 12.2, 120.6, 119.7, 114.6, 114.5, 113.9, 113.0, 112.0, 98.0, 55.3, 55.29, 30.0, 22.8, 21.7. MS (APCI): calcd for  $C_{56}H_{50}N_2O_6S_2$ , 910.31; found: m/z = 911.4 [M+H]<sup>+</sup>. FT-IR (KBr): v 2948, 2830, 1600, 1502, 1452, 1377, 1322, 1272, 1238, 1178, 1095, 1034, 983, 825 cm<sup>-1</sup>. Anal. Calcd for C<sub>56</sub>H<sub>50</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 73.82; H, 5.53; S, 7.04. Found: C, 73.83; H, 5.55; S, 7.07.

# 2.4.7. 9-((5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2'-bithiophen]-5-yl)methylene)-N3,N3,N6,N6tetrakis(4-(octyloxy)phenyl)-9H-fluorene-3,6-diamine, **4c**.

To a suspension of Pd(dba)<sub>2</sub> (0.012 g, 0.02 mmol) and PtBu<sub>3</sub> (0.08 mL, 0.08 mmol, 1M in toluene) in anhydrous toluene (5 mL), were added 3b (0.128 g, 0.2 mmol), bis(4-(octyloxy)phenyl)amine (0.22 g, 0.5 mmol) and sodium tert-butoxide (0.058 g, 0.52 mmol). The resulting mixture was reacted under a microwave irradiation at a constant temperature of 110°C for 50 min. The solvent was removed under a reduced pressure, and the residue was purified by column chromatography (silica gel, 7/3 hexane/CH<sub>2</sub>Cl<sub>2</sub>) to give the pure product 4c as a red solid (60% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, J = 8.61 Hz, 1H) 7.50 (d, J = 8.40 Hz, 1H) 7.25 (d, J = 3.81, 1H) 7.22 (t, J = 4.31 Hz, 2H) 7.18 (s, 2H) 7.12 (d, J = 3.74 Hz, 1H) 7.08 (d, J = 3.69 Hz, 1H) 7.04-7.00 (m, 9H) 6.85 (d, J = 2.11 Hz, 1H) 6.81 (dd,  $J_1 = 8.98$ ,  $J_2 = 1.61$  Hz, 4H) 6.72 (dd,  $J_1 = 8.62$ ,  $J_2 = 2.33$  Hz, 1H) 5.62 (s, 1H) 3.92 (t,  $J_1 = 5.06$  Hz, 8H) 3.77 (d, J = 11.27Hz, 2H) 3.65 (d, J = 10.61 Hz, 2H) 1.81-1.73 (m, 8H) 1.35-1.26 (m, 40H) 0.93-0.88 (m, 15H) 0.81 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 155.2, 154.9, 141.0, 140.6, 139.2, 137.9, 137.4, 129.7, 129.3, 126.1, 125.6, 123.9, 122.9, 115.1, 115.0, 99.4, 98.4, 98.0, 68.1, 31.6, 30.0, 29.5, 29.2, 29.1, 25.9, 22.8, 22.5, 21.6, 13.9. MS (APCI): calcd for C<sub>84</sub>H<sub>106</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>, 1302.7; found: m/z = 1303.8 [M+H]<sup>+</sup>. FT-IR (KBr): v 2951, 2855, 1600, 1504, 1480, 1469, 1452, 1384, 1240, 1171, 1099, 1027, 825, 722 cm<sup>-1</sup>. Anal. Calcd for C<sub>84</sub>H<sub>106</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 77.38; H, 8.19; S, 4.92. Found: C, 77.37; H, 8.21; S, 4.90.

## 2.4.8. 5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene-2-carbaldehyde, 1'.

2,5-thiophene-dicarbaldehyde (2 g, 14.28 mmol), neopentylglycol (1.56 g, 15 mmol) and ptoluenesulfonic acid (0.142 g, 0.75 mmol) were dissolved in dry toluene (50 mL). The reaction mixture was refluxed for 5 h and then cooled to rt. The solvent was removed under a reduced pressure and the residue was dissolved in ethyl acetate and washed with brine. The organic layer was dried over anhydrous sodium sulfate and the solvent evaporated under a reduced pressure. The crude redidue was purified by flash chromatography on SiO<sub>2</sub>, using a mixture 9/1 hexane/ethyl acetate as the eluent. The pure product I was obtained as a white solid (85% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.90 (s, 1H) 7.67 (d, *J* = 3.84 Hz, 1H) 7.23 (d, *J* = 3.84 Hz, 1H) 5.64 (s, 1H) 3.78 (d, *J* = 11.30 Hz, 2H) 3.65 (d, *J* = 11.24 Hz, 2H) 1.27 (s, 3H) 0.82 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  183.0, 151.2, 143.3, 135.5, 125.7, 97.3, 77.3, 30.1, 22.7, 21.6. MS (APCI): calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>S, 226,07; found: m/z = 227.07 [M+H]<sup>+</sup>. FT-IR (KBr): v 2965, 2855, 2821, 1668, 1539, 1476, 1375, 1300, 1228, 1218, 1189, 1098, 1056, 1033, 1019, 988, 961, 813 cm<sup>-1</sup>. Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>S: C, 58.39; H, 6.24; S, 14.17. Found: C, 58.40; H, 6.22; S, 14.20.

## 2.4.9. 2-(5-bromothiophen-2-yl)-5,5-dimethyl-1,3-dioxane, 2'.

5-bromothiophene-2-carbaldehyde (5 g, 26 mmol), neopentylglycol (4.16 g, 40 mmol) and *p*toluenesulfonic acid (0.38 g, 2 mmol) were dissolved in dry toluene (100 mL). The reaction mixture was refluxed for 5 h and then cooled at r. t. The solvent was removed under a reduced pressure and the residue was dissolved in ethyl acetate and washed with brine. The organic layer was dried over anhydrous sodium sulfate and the solvent evaporated under a reduced pressure. The crude residue was purified by flash chromatography on SiO<sub>2</sub> using a mixture 9/1 hexane/ethyl acetate as the eluent. The pure product **2'** was obtained as a white solid (95% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.94 (d, *J* = 3.78 Hz, 1 H), 6.88 (dd, *J*<sub>1</sub> = 3.78 Hz, *J*<sub>2</sub> = 0.73 Hz, 1 H), 5.54 (s, 1 H), 3.75 (d, *J* = 11.30 Hz, 2 H) 3.62 (d, *J* = 11.30 Hz, 2H), 1.26 (s, 3H), 0.79 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  143.17, 129.17, 125.07, 113.22, 97.93, 77.12, 30.0, 22.71, 21.60. MS (APCI): calcd for  $C_{10}H_{13}BrO_2S$ , 277.98; found: m/z = 278.00 [M+H]<sup>+</sup>. FT-IR (KBr): v 2956, 2850, 1554, 1471, 1448, 1394, 1375, 1368, 1298, 1231, 1210, 1190, 1097, 1021, 986, 972, 930, 922, 796, 777 cm<sup>-1</sup>. Anal. Calcd for  $C_{10}H_{13}BrO_2S$ : C, 43.33; H, 4.73; S, 11.57. Found: C, 43.33; H, 4.72; S, 11.55.

2.4.10. 5'-(5,5-dimethyl-1,3-dioxan-2-yl)-[2,2'-bithiophene]-5-carbaldehyde, 5-3'. formylthiophen-2-ylboronic acid (1.24 g, 7.94 mmol), 2' (2,0 g, 7.22 mmol) Na<sub>2</sub>CO<sub>3</sub> (4.59 g, 43.32 mmol), toluene (35 mL), ethanol (8.75 mL) and water (8.75 mL) were purged with argon for 1.5-2 h. Pd(PPh<sub>3</sub>)<sub>4</sub> (0.083g, 0.072 mmol) was added and the reaction mixture was stirred at reflux for 20 h, Then, the reaction mixture was cooled at rt, poured into water and extracted with dichloromethane. The organic layer was washed with water, saturated aqueous NaHCO<sub>3</sub> solution and brine, then dried over anhydrous sodium sulfate. The solvent was evaporated under a reduced pressure and the crude residue was purified by column chromatography on silica gel (eluent: hexane/dichloromethane 60/40), to give the pure product **3'** (60% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.84 (s, 1H), 7.65 (d, J = 3.84 Hz, 1H), 7.23 (d, J = 3.84 Hz, 1H), 7.08 (d, J = 3.76 Hz, 1H), 7.01 (d, J = 3.72 Hz, 1H), 5.62 (s, 1H), 3.75 (d, J = 11.24 Hz, 2H) 3.66 (d, J = 11.24 Hz, 3H) 3.66 (d, J = 11.24 Hz, 11.23 Hz, 2H), 1.28 (s, 3H), 0.80 (s, 3H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 182.3, 146.9, 143.0, 141.6, 137.1, 135.9, 126.0, 125.4, 124.1, 123.0, 97.9, 97.6, 30.0, 22.8, 21.6. MS (APCI): calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>S, 308.05; found:  $m/z = 309.05 [M+H]^+$ . FT-IR (KBr): v 2947, 2861, 1650, 1474, 1455, 1433, 1378, 1309, 1298, 1224, 1214, 1199, 1159, 1096, 1042, 1027, 1014, 987, 965, 800, 776 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>S<sub>2</sub>: C, 58.42; H, 5.23; S, 20.79. Found: C, 58.44; H, 5.23; S, 20.78.

#### 2.4.11. bis(4-(octyloxy)phenyl)amine, 4'.

To a 50 mL round-bottomed flask were added, under a nitrogen atmosphere, anhydrous toluene 10 mL, 4-(octyloxy)aniline (1.8 g, 8.5 mmol) and 1-bromo-4-(octyloxy)benzene (2.13 g, 7.32 mmol). Then Pd<sub>2</sub>dba<sub>3</sub> (0.076 g, 0.073 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.081 g, 0.146 mmol) and sodium *tert*-butoxide (1.0 g, 10.46 mmol) were added. The reaction mixture was stirred at reflux for 4h, then cooled at rt and filtered through a short pad of celite. The solvent was removed at a reduced pressure and the crude product was purified by flash chromatography, using a mixture 8/2 hexane/dichloromethane as the eluent, to give the pure product **4'** (70% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  6.93 (m, 4H) 6.82 (m,4H), 5.27 (s, 1H) 3.94 (m, 4H) 1.77 (m, 4H), 1.45 (m, 4H) 1.33 (m, 16H), 0.87 (m, 6H) <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  129.2, 120.2, 114.3, 68.4, 31.6, 29.2, 29.1, 25.9, 22.5, 13.9. MS (APCI): calcd for C<sub>28</sub>H<sub>43</sub>NO<sub>2</sub>, 425.33; found: m/z = 426.33 [M+H]<sup>+</sup>.

# 2.4.12. 3-(5-((3,6-bis(bis(4-methoxyphenyl)amino)-9H-fluoren-9-ylidene)methyl)thiophen-2-yl)-2-cyanoacrylic acid, **TK4.**

A mixture of **4a** (0.083 g, 0.1 mmol), cyanoacetic acid (0.17 g, 2.0 mmol), acetic acid (20 mL) and ammonium acetate (0.095 g, 1.2 mmol) was heated at 120°C for 12 h. The resulting solution was poured into ice-cold water to produce a precipitate. Then, the precipitate was dissolved in dichloromethane and washed several times with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent removed by rotary evaporation. The crude product was purified by flash chromatography on SiO<sub>2</sub>, using a mixture 10/1 dichloromethane/methanol as the eluent. The pure product **TK4** was obtained as a purple solid (75% yield). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>8</sub>):  $\delta$  8.36 (s, 1H), 8.01 (d, *J* = 8.69 Hz, 1 H), 7.90 (d, *J* = 3.93 Hz, 1H) 7.73 (d, *J* 

= 8.52 Hz, 7.57, (d, J = 4.26 Hz, 1 H) 7.52 (s, 1H), 7.04-6.98 (m, 8H), 6.91-6.84 (m, 10H), 6.66 (dd,  $J_I = 5.47$ ,  $J_2 = 2.04$  Hz, 1H), 6.54 (dd,  $J_I = 8.62$ ,  $J_2 = 2.24$  Hz, 1H) 3.73 (s, 12H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>8</sub>)  $\delta$  156.43, 156.07, 150.07, 150.03, 149.71, 142.40, 140.25, 139.71, 139.34, 132.73, 127.54, 127.36, 126.82, 115.28, 115.21, 55.51. MS (APCI): calcd for C<sub>50</sub>H<sub>39</sub>N<sub>3</sub>O<sub>6</sub>S, 809.26; found: m/z = 810.26 [M+H]<sup>+</sup>. ]<sup>+</sup>. FT-IR (KBr): v 3428, 2927, 2830, 1600, 1568, 1506, 1450, 1346, 1323, 1272, 1240, 1179, 1126, 1104, 1033, 825, 715 cm<sup>-1</sup>. Anal. Calcd for C<sub>50</sub>H<sub>39</sub>N<sub>3</sub>O<sub>6</sub>S: C, 74.15; H, 4.85; N, 5.19; S, 3.96. Found: C, 74.14; H, 4.85; N, 5.18; S, 3.93.

# 2.4.13. 3-(5'-((3,6-bis(bis(4-methoxyphenyl)amino)-9H-fluoren-9-ylidene)methyl)-[2,2'bithiophen]-5-yl)-2-cyanoacrylic acid, **TK5**.

A mixture of **4b** (0.1 g, 0.126 mmol), cyanoacetic acid (0.214 g, 2.52 mmol), acetic acid (40 mL) and ammonium acetate (0.117 g, 1.81 mmol) was heated at 120°C for 12 h. The resulting solution was poured into ice-cold water to produce a precipitate. Then, the precipitate was dissolved in dichloromethane and washed several times with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent removed by rotary evaporation. The pure product **TK5** was obtained as a red solid (85% yield). <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>8</sub>)  $\delta$  8.15 (s, 1H) 8.10 (d, J = 8.64 Hz, 1H) 7.73 (d, J = 3.03 Hz, 1H), 7.70 (d, J = 8.55 Hz, 1H), 7.60 (d, J = 8.62 Hz, 1H), 7.53-7.50 (m, 2H), 7.47 (d, J =11.40, 1H), 7.37 (d, J = 3.83 Hz, 1H), 7.05-6.95 (m, 8H), 6.91-6.84 (m, 8H), 6.71-6.67 (m, 2H), 6.62 (dd,  $J_I$  = 8.65,  $J_2$  = 2.16 Hz, 1H), 6.42 (dd,  $J_I$  = 8.68,  $J_2$  = 2.21 Hz, 1H), 3.73 (s, 12 H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>8</sub>)  $\delta$  169.6, 156.3, 156.29, 156.2, 155.9, 149.7, 149.6, 149.5, 149.2, 142.0, 140.9, 140.5, 140.3, 140.0, 139.9, 139.0 138.5 136.5, 135.2, 134.8, 133.2, 132.1, 128.5, 128.1, 128.0, 127.9, 127.2, 127.19, 127.0, 126.6, 125.3, 115.3, 115.2, 55.5 MS (APCI): calcd for C<sub>54</sub>H<sub>41</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>, 891.24; found: m/z = 892.26 [M+H]<sup>+</sup>.

FT-IR (KBr): v 3434, 2929, 2832, 1602, 1504, 1454, 1368, 1324, 1275, 1239, 1180, 1106, 1035, 827 cm<sup>-1</sup>. Anal. Calcd for C<sub>54</sub>H<sub>41</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C, 72.71; H, 4.63; N, 4.71; S, 7.19. Found: C, 72.69; H, 4.65; N, 4.72; S, 7.18.

2.4.14. 3-(5'-((3,6-bis(bis(4-(octyloxy)phenyl)amino)-9H-fluoren-9-ylidene)methyl)-2,2'bithiophen-5-yl)-2-cyanoacrylic acid, **TK6**.

A mixture of **4c** (0.2 g, 0.15 mmol), cyanoacetic acid (0.214 g, 3.06 mmol), acetic acid (40 mL) and ammonium acetate (0.141 g, 1.84 mmol) was heated at 120°C for 12 h. The resulting solution was poured into ice-cold water to produce a precipitate. Then, the precipitate was dissolved in dichloromethane and washed several times with water. The organic layer was dried over anhydrous sodium sulfate, and the solvent removed by rotary evaporation. The pure product **TK6** was obtained as a red solid (70% yield). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (d, *J* = 6.26 Hz, 1H) 8.29 (d, *J* = 3.05 Hz, 1H) 7.98 (d, *J* = 8.70 Hz, 1H), 7.80 (d, *J* = 4.28 Hz, 1H), 7.71 (d, *J* = 4.28 Hz, 1H), 7.60 (d, *J* = 8.54 Hz, 1H), 7.52 (s, 1H), 7.50 (d, *J* = 8.34 Hz, 1H), 7.16 (s, 1H), 7.12 (m, 1H), 7.04-6.96 (m, 8H) 6.80 (m, 8H) 6.70 (dd, *J*<sub>1</sub> = 1.96 Hz, *J*<sub>2</sub> = 8.34 Hz, 1H) 6.54 (m, 1H) 3.92 (m, 8H) 1.77-1.30 (m, 48H) 0.89 (m, 12H). MS (APCI): calcd for C<sub>82</sub>H<sub>97</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>, 1283.68; found: m/z = 1284.70 [M+H]<sup>+</sup>. FT-IR (KBr): v 3434, 2923, 2853, 1602, 1504, 1486, 1470, 1455, 1386, 1238, 1168, 1108, 1028, 826, 721 cm<sup>-1</sup>. Anal. Calcd for C<sub>82</sub>H<sub>97</sub>N<sub>3</sub>O<sub>6</sub>S<sub>2</sub>: C, 76.66; H, 7.61; N, 3.27; S, 4.99. Found: C, 76.66; H, 7.60; N, 3.25; S, 4.98.

#### **3 RESULTS AND DISCUSSION**

3.1. Synthesis of organic dyes.

The synthesized organic dyes (TK) are shown in Figure 1, while the synthetic pathways are depicted in Scheme 1. Compound 2 was synthesized by a reduction with aluminum chloride and borane tert-butylamine complex[50] of compound 1. Compounds 3a and 3b were prepared by an ultrasound-assisted reaction of compound 2 with 5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophene-2carbaldehyde (1') and 5'-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithiophene-5-carbaldehyde (3'), respectively. The reactions were carried out in short times with good yields, and the products were readily purified. Compound 1' was obtained by reacting thiophene-2,5-dicarbaldehyde (commercial) with 2,2-dimethylpropane-1,3-diol. Compound 2' was obtained by treating 5bromothiophene-2-carbaldehyde with 2,2-dimethylpropane-1,3-diol, and then the resulting product was reacted with (5-formylthiophen-2-yl)boronic acid under typical Suzuki reaction conditions to prepare compound 3'. Compound 4a, 4b and 4c were obtained starting from 3a and 3b by a Buchwald-Hartwig cross coupling reaction (C-N amination) with 2.2 equivalents of diarylamine in the presence of  $Pd(dba)_2$  (dba = dibenzylideneacetone) and  $P(tBu)_{3,[51]}$  in a microwave reactor. Finally, TK4, TK5 and TK6 dyes were prepared via a Knoevenagel condensation, reacting cyanoacetic acid with compunds 4a, 4b and 4c, respectively, in the presence of ammonium acetate.



Scheme 1. Synthesis of organic dyes TK4, TK5 and TK6.

## 3.2. Photophysical properties.

UV-vis absorption spectra of dyes in CH<sub>2</sub>Cl<sub>2</sub> solution (ca.  $10^{-5}$  M) are shown in Figure 2, (the fluorescence spectra have been reported in the Supp. Info.) Absorption data are summarized in Table 1. As shown in Figure 2, all spectra show strong bands in the ranges 260 - 350 nm and 350 - 600 nm. The higher energy bands are attributed to local  $\pi - \pi^*$  transitions, while the lower energy bands are attributed to charge transfer (CT) transitions. **TK4** shows two maxima absorption peaked at 360 and 548 nm, with extinction coefficients  $\varepsilon = 13200$  and  $10100 \text{ M}^{-1}\text{ cm}^{-1}$ , respectively. The sensitizer **TK5** can be considered as obtained by incorporating two thiophene rings, instead of one, as spacer between the **DBF**-core and the acceptor unit in the basic structure of **TK4**. **TK5** shows two maxima absorption peaked at 413 nm ( $\varepsilon = 24800 \text{ M}^{-1}\text{ cm}^{-1}$ ) and 513 nm (17800 M<sup>-1</sup>cm<sup>-1</sup>), almost twice **TK4**. **TK6** can be considered as obtained by substituting the methoxy groups with longer octyloxy chains in the basic structure of **TK5**. **TK6** show two maxima absorption peaked at 420 nm ( $\varepsilon = 34500 \text{ M}^{-1}\text{ cm}^{-1}$ ) and 516 nm ( $\varepsilon = 25100 \text{ M}^{-1}\text{ cm}^{-1}$ ).



Figure 2. Absorption spectra of TK dyes in CH<sub>2</sub>Cl<sub>2</sub>.

#### 3.3. Electrochemical properties.

Cyclic voltammetry (CV) was carried out to investigate the possibility of electron injection from the excited state of the organic dyes to the conduction band (CB) of TiO<sub>2</sub>. The curves are collected in the Figure 3, and the corresponding data are depicted in Table 1.

From the onset of the first oxidation potential were calculated HOMO energies, while the LUMO energies were extimated from  $E_{HOMO} - E_{0-0}$ ,[52, 53] and are ultimately based on the absolute value for the normal hydrogen electrode (NHE), which was critically assessed in a fundamental review paper. [54] The optical band gap  $E_{0.0}$  was derived from the absorption edge. The LUMO values (-1.16, -1.22 and -1.15 V, for **TK4**, **TK5** and **TK6**, respectively) are sufficiently more negative than the conduction band edge of TiO<sub>2</sub> (-0.5 vs. NHE),[55] to forecast an efficient electron injection from excited dye into the TiO<sub>2</sub> electrode. Dye regeneration is essential to achieve a high stability and operational lifetime for the DSSCs. Efficient dye regeneration is possible if the ground-state redox potential of the dye is more positive than that of the electrolyte redox potential. The HOMO levels estimated (0.64, 0.68 and 0.73 V for **TK4**, **TK5** and **TK6**, respectively) are more positive than that of  $\Gamma/I_3^-$  redox couple (0.4 V *vs*. NHE),[1] which is necessary to ensure that the neutral dye is effectively regenerated after being oxidized.



Figure 3. Cycle voltammograms of dyes in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> supporting electrolyte.

Table 1. Absorption data, oxidation potentials, HOMO and LUMO levels, optical energy gaps.

Dye	$\lambda_{abs} (\epsilon \times 10^3 \text{M}^{-1} \text{cm}^{-1})^a$ (nm)	HOMO (V vs. NHE)	E <sub>0-0</sub> <sup>c</sup> (eV)	LUMO <sup>d</sup> (V vs. NHE)	
TK4	548 (10.1)	0,64	1.82	-1.18	
TK5	513 (17.8)	0.68	1.90	-1.22	
TK6	516 (25.1)	0.73	1.88	-1.15	

<sup>a</sup>Absorption maximum in dichloromethane (~10<sup>-5</sup> M) solution. <sup>b</sup> HOMO (*vs.* NHE) of the dyes by cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M of tetrabutylammonium hexafluorophosphate with a scan rate of 100 mVs<sup>-1</sup> and calibrated against ferrocene. <sup>c</sup> The bandgap, E<sub>0-0</sub> was determined from onset of absorption spectrum. <sup>d</sup> LUMO = HOMO - E<sub>0-0</sub>.

## 3.4. Theoretical approach.

To understand better the electronic and optical properties of the three new dyes, we performed a density functional theory (DFT) and time-dependent (TD) DFT investigations. The TD-DFT results, reported in Table 2, are in reasonably good agreement with the experimental spectra and allow the identification of several singlet excitations underlying the broad absorption bands observed experimentally (see Figure S15). All the dyes exhibit rather similar photophysical properties for the lowest-lying optically active excitations. Thus, we find that the lowest excitation lay in all cases at 2.12-2.5 eV, they are well described by a single particle transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), and they display a significant charge-transfer character ( $\Lambda$ =0.6 and  $\Delta$ r=5-6Å) (see Table 2). Iso-density plots of the HOMO and LUMO orbitals are reported in Figure 4. The highest excitations are found in an energy interval between S1 and about 3.5 eV. They show similar features as the S1 excited state, but generally an even larger charge-transfer character (as suggested by the values of the  $\Lambda$  and  $\Delta$ r indicators).

A comparison of the **TK4** and **TK5** results shows that the effect of the insertion of a thiophene unit into the spacer is to slightly increase the effective conjugation length. This effect is visible in the plots of the orbitals and can be also inferred by an inspection of the HOMO and LUMO energies of the two dyes as well as of the many-body ionization potentials (IP) and electron affinities (EA) reported in Table 3. Consequently, a little lowering of the S1 excitation energy is found.

Dye	Excitation	Energy	Single-particle	Λ	Δr (Å)
		( <b>eV</b> )	transition		$\boldsymbol{\varsigma}$
TK4	$S_1$	2.33	H→L (86%)	0.61	5.05
	$S_2$	2.40	H-1→L(82%)	0.39	6.19
	S <sub>3</sub>	3.35	H-2→L (88%)	0.70	3.22
TK5	$S_1$	2.17	H→L (84%)	0.58	6.66
	$S_2$	2.48	H-1→L (79%)	0.29	16.51
	S <sub>3</sub>	3.15	H-2→L (88%)	0.65	9.48
	$S_4$	3.31	H→L+1(86%)	0.67	9.25
TK6	$S_1$	2.56	H→L (83%)	0.61	6.54
	$S_2$	2.86	H-1→L (79%)	0.32	16.47
	S <sub>3</sub>	3.52	H-2→L (79%)	0.68	9.43
	$S_4$	3.70	H→L+1 (85%)	0.71	9.21

## Table 2 Excitation energies and absorption spectra

TD-DFT excitation energies (eV), oscillator strengths, main single-particle transitions, overlap indicator  $\Lambda$ , and electron displacement indicator  $\Delta r$ , for the lowest-lying singlet excitations of **TK4**, **TK5**, and **TK6**.

At the same time, the additional thiophene unit favors the charge separation in the excited states, as indicated by the values of  $\Delta r$ , having a potentially positive impact on the photovoltaic properties of the material, as already found in our previous work.[17] On the contrary, the inclusion of branched substituents on the phenyl rings, which marks the difference between **TK6** and **TK5**, is found to have a minor impact on the electronic properties of the dye, leaving frontier orbitals as well as IP and EA almost unchanged.



Figure 4. Isodensity plots of the most relevant frontier orbitals of the dyes.



**Table 3**. HOMO and LUMO energies, Ionization potential (IP) and electron affinity (EA) of the **TK4**, **TK5**, **TK6** dyes in eV calculated with DFT. Both quantities were obtained as energy differences between the neutral dye and the anion/cation.

	TK4	TK5	TK6	_
НОМО	-5.83	-5.69	-5.64	
IP	6.06	5.93	5.91	
LUMO	-2.31	-2.35	-2.33	$\mathcal{O}$
EA	1.98	2.02	2.00	_

Nevertheless, **TK6** shows quite larger excitation energies than **TK5**. This finding can be traced back to the fact that the branched substituents amplify somehow the effect of the electron-donor methoxy group. Finally, to study the aggregation properties of the dyes we investigated possible stable bound configurations of dimers of the different dyes. For **TK5** the simulations show that indeed a stable dimer geometry exists, being characterized by a cross-stacking arrangement of the two molecules (see Figure 5). The thiophene units of the two dyes are located on top of each other at a distance of about 3.5 Å, with a perpendicular orientation of the molecular backbone. In this geometry the side phenyl groups do not overlap each other but rather stack neatly, avoiding steric repulsion effects and the repulsive interaction of the carboxylic acid with the conjugate backbone of the molecule is also avoided. Thus, a binding energy of 30.8 kcal/mol is computed. We note that the present configuration allows for further stacking of additional **TK5** dyes (which was not investigated here, due to the excessive computational cost), suggesting that significant aggregation is possible for these dyes. On the other hand, we could not find any reasonably stable dimer for the other two dyes considered in this work. In particular, for these dyes the

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dimer configuration considered for **TK5** is not a possible option. In fact, in the case of **TK4**, the presence of only one thiophene unit would require, for good stacking to occur, that the **DBF** moieties and the corresponding side functionalization groups should come very close; for **TK6** the branched substituents prevent the correct spatial alignment of the molecules.



**Figure 5**. Optimized geometry of the **TK5** dimer as obtained from DFT calculations. The structures of the two dyes are reported either with ball-and-stick or lines representations.

## 3.5. Photovoltaic devices.

The photovoltaic properties of the novel sensitizers were tested in liquid DSSC cells. Their performances and detailed photovoltaic parameters (short-circuit photocurrent density,  $J_{SC}$ , open-circuit voltage,  $V_{OC}$ , fill factor, *FF*, and power conversion efficiency,  $\eta$ ) are reported in Table 4

and Figure 6. For the dyeing of the TiO<sub>2</sub> electrodes, several tests using different solvents and different amounts of chenodeoxycholic acid (CDCA) were carried out (details are reported in supporting info, Table S1). The best performances were achieved using THF as the solvent for **TK5** and **TK6** and  $CH_3CN:CHCl_3 = 1:0.01$  v/v for **TK4**. The appropriate amount of CDCA was found to be 15 mM for TK4 and TK5 sensitizers and 5 mM for TK6. The additive CDCA is known to diminish the undesirable formation of dye aggregates on the TiO<sub>2</sub> surface. The lower request of CDCA as anti-aggregating additive for the TK6 dye is in agreement with the expected role of the long alkyl chains ( $C_8H_{17}$ ), acting effectively as hindrance to the aggregation of the dye molecules. Starting from the basic molecular structure of TK4, the elongation of the  $\pi$ -bridge (introduction of a thienyl ring) in TK5, significantly enhances the device performance, passing from an efficiency of 5.9% for TK4, to an efficiency of 7.5% for TK5. The substantial increase being in accord with the increase of the molecular absorption capability. The additional structural variation introduced by the long  $C_8H_{17}$  alkyl chains in **TK6**, further enhances the photovoltaic performance, to reach a maximum efficiency of 7.8%, associated with a reduced needed of CDCA additive in the device. The enhancement of photovoltaic efficiencies follows the increase of the circuit current  $J_{sc}$ , from 13.29 mA/cm<sup>2</sup> for TK4 to 17.85 and 17.19 mA/cm<sup>2</sup> for TK5 and TK6, respectively. More statistics are reported in Table S2 and data of the reference device are reported in Table S3. This behavior is also confirmed by the IPCE spectra in Figure 7, which show that the TK4-based device presents the lower photoresponse, showing a maximum of ~55% at 450-550 nm compared to the plateau of ~70% and 75% in the same region obtained with TK5 and TK6-based devices, respectively, in good accordance with the absorption spectra. Comparing the photovoltaic performances of the TK4 and TK5 dyes with their methoxy-free

analogues **TK2** and **TK3** (previously published, ref. 17), we can observe as the improvement of the optical properties of the novel sensitizers positively affects the efficiency of the devices.

Actually, the introduction of methoxy group produced a red shift and an enlargement of absorption spectra of **TK4** and **TK5** dyes. As a consequence, we observed higher and extended IPCE curves and augmented photocurrent densities Jsc. In particular, **TK2** and **TK3**, at the best testing conditions, gave Jsc of 10.85 and 14.98 mA/cm<sup>2</sup>, respectively, while their novel analogues **TK4** and **TK5** gave Jsc of 13.29 and 17.85 mA/cm<sup>2</sup>, respectively, probably related to the enhanced light harvesting capability.

Table 4. Photovoltaic performance of TK dyes

Dye	ղ%	FF	Voc	Jsc	Dye Loading <sup>*</sup>
TK4	5.9	0.67	0.667	13.29	2.0
TK5	7.5	0.64	0.653	17.85	1.9
TK6	7.8	0.69	0.663	17.19	1.6
$[10^{-7} \text{ mol cm}^{-2}]$					



Figure 6. *J-V* curves of DSSCs based on the dyes TK4, TK5 and TK6.



Figure 7. IPCE spectra of DSSCs based on the dyes.

#### 3.6. Electrochemical Impedance Spectroscopy Studies

To further understand the relationship between the molecular structure and the photovoltaic performance, we studied the charge-transfer resistance at the TiO<sub>2</sub>/dye/electrolyte interface by electrochemical impedance spectroscopy (EIS), carried out at different voltage bias under 1 sun illumination. EIS spectra were analyzed through the well-known equivalent circuit proposed by Bisquert. [56] Figures 8a) and 8b) shows the capacitance and recombination resistance plotted versus potential drop at the sensitized electrode. V<sub>corr</sub> is obtained after correcting the applied potential (V<sub>app</sub>) for the drop of the total series resistance V<sub>series</sub> (contacts, counter electrode, electrolyte diffusion) collected from impedance spectroscopy data by  $V_{corr} = V_{app} - V_{series}$ .[57] The chemical capacitance,  $C\mu$ , represented in Figure 8a, provides quantitative information about the position of the conduction band.[58] Figure 8a shows that the chemical capacitance values are clearly shifted towards lower potentials for the **TK6** dye. Assuming that neither the distribution nor the total amount of trap states changed with dye, we may attribute the shift observed in Cµ to a displacement in the energy of the conduction band (CB).[59] The downward shift of the TiO<sub>2</sub> CB impacts on the photovoltaic performance of the solar cells, in particular by increasing Jsc values, thanks to a higher electron injection driving force (see LUMO level Table 1). An additional enhancement of the photovoltaic performance also comes from the decrease of Voc due to a reduction of the difference between the TiO<sub>2</sub> Fermi level and redox potential. However, all the dyes show comparable values of Voc (Table 4). The difference in chargetransfer resistance becomes more marked if the Rct of the three devices is plotted against the voltage drop in a common equivalent conduction band  $V_{ecb}[60]$  (Figure 8c). In this plot the effect of different TiO<sub>2</sub> CB between samples is removed. This allows an analysis of the recombination

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resistance on the base of an equal density of electrons n (*i.e.* the same distance between the electron Fermi level and the TiO<sub>2</sub> CB). Inspection of Figure 8c confirms that **TK6**-based devices show the highest R<sub>CT</sub> values, indicating a better suppression of charge recombination effects. This can be traced back to the presence of the long alkoxy chains on the donor groups.





**Figure 8.** Impedance results of the DSSCs based on **TK4**, **TK5**, **TK6** dyes. a) Measured capacitance vs corrected voltage b) Charge transfer resistance vs corrected voltage c) Charge transfer resistance represented at the equivalent CB position.

#### **4 CONCLUSIONS**

In conclusion, we have designed and synthesized three new organic dyes with a 2D- $\pi$ -A structure (**TK4**, **TK5** and **TK6**) and based on the dibenzofulvene  $\pi$ -bridge core, characterized by alkoxy-substituted diphenylamines as the donor groups and cyanoacetic acid as the acceptor/anchoring group. Starting from the molecular structure of **TK4**, which showed a promising efficiency of 5.9%, we introduced different structural variations in order to achieve an enhancement of photovoltaic performance and study the correlations between the molecular structure and the photovoltaic properties. The selected structural variations were the elongation of the  $\pi$ -bridge, by adding a thienyl ring, and the further substitution of methoxy group with longer octyloxy chains. The structural molecular variations evidenced positive effects on the photovoltaic performances of dyes, proved by efficiencies of 7.5% and 7.8% obtained with **TK5** and **TK6**, respectively. The electro-optical properties were then evaluated and correlated with the

photovoltaic properties and the molecular structure. The results evidenced the basic molecular conjugated backbone as suitable for photovoltaic application in DSSC devices, and the structural modification as a powerful tool to modulate and enhance their properties in the direction of the desired applications.

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# HIGHLIGHTS

- 1 New organic dyes based on the dibenzofulvene core have been synthesized.
- 2 Electrooptical, computational study and cell performances have been investigated.
- 3 DSSC cell efficiencies up to 7.5 and 7.8% have been achieved.