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### Novel DPP derivatives functionalized with auxiliary electron-acceptor groups and characterized by narrow bandgap and ambipolar charge transport properties

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#### ABSTRACT

Four novel diketopyrrolopyrrole (DPP) derivatives have been synthesized and characterized: the dyes are based on a DPP electron acceptor core symmetrically functionalized with donor bi-furyl moieties and end capped with four different auxiliary electron-acceptor groups. Because of the alternation along the molecular backbone of electron acceptor and donor groups, all the dyes are characterized by optical absorption maxima approaching or exceeding 700 nm. In the solid state, this optical behavior determines for all the dyes a very low optical bandgap ranging from 1.57 eV to 1.29 eV, while electrochemical characterization shows a clear dependence of the LUMO energies on the strength of the auxiliary electron-acceptor groups. All the dyes are characterized by stable LUMO energies suitable for their application as n-type semiconductors. Organic field-effect transistors based on the reported compounds display actually n-type behavior and, in three cases, a very interesting and balanced ambipolar charge transport behavior was moreover observed.

### 1. Introduction

Nitrogen containing heterocycles have received in the last years a great deal of interest as promising building blocks for the realization of functional materials for advanced applications in electronics or optoelectronics [1–6]. Among these, diketopyrrolo-pyrrole (DPP) derivatives represent one of the most investigated class of materials: in a pristine, non-alkylated form, DPP derivatives have been widely used as high-performance pigments that, because of their intense colour, excellent stability and low solubility, have found several industrial applications in paints, varnishes, and high-quality printing [7,8]. By means of N-alkylation, DPP derivatives can be easily transformed in very soluble dyes that in recent years, have been applied as active materials in different field of organic electronics [9-15]. In particular, by combination with electron rich units, the electron deficient nature of DPP fragment has been exploited for the realization of alternated donor-acceptor molecular structures (polymers [16-19] or small molecules [20] [-] [25]) with an increased solar photon harvesting ability and promising photovoltaic properties. In addition, DPP fused unit is highly planar and enables efficient intermolecular  $\pi$ - $\pi$  interactions which, in turn, positively affects the charge carrier mobility in Organic Filed-Effect Transistors (OFETs); in this application too, the synthetic versatility of this unit allows the combination with different molecular blocks (electron rich or poor, both in polymers and small molecules) providing a fine tuning of frontier molecular orbitals (HOMO and LUMO) energies and thus optimizing hole and electron mobility in, respectively, p-type [26–29] and n-type materials [30,31]. Several examples of ambipolar DPP derivatives are also reported [32–34].

While most of the DPP containing organic semiconductors reported in the literature are based on polymeric materials, in the last years the number of papers reporting DPP small molecules for optoelectronic applications is continuously growing [9,15]. Indeed, the molecular systems exhibit some advantages, since they don't suffer from the batch-to-batch variation of performance as a consequence of their well-defined molecular structures; moreover, a proper molecular engineering design could finely tune electronic properties and structural

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packing as well. Finally, an intrinsic higher mobility is expected because of an increased structural order.

In this context, we report here four novel DPP based molecules, whose chemical structure is reported in Scheme 1.

The molecules share a common molecular fragment constituted by a DDP electron acceptor core (A), symmetrically linked to two electron donor bifuran moieties (D). This common molecular motif is end functionalized, on both sides, with auxiliary electron acceptor groups (A'). A similar approach has been followed in other recent works based on thienyl-substituted DPP derivatives, with promising results [35-37]: in those reported cases auxiliary acceptors as cyano acetic acid derivatives, dicyanovinyl and rhodamine groups were used and a maximum electron mobility in the order of  $10^{-2}$  cm<sup>2</sup>/V s was measured. In the present work, the novel dyes are end capped with four different electron acceptor groups of different strength, specifically a dicyanovinyl group (DCV), a thiobarbituric acid (TB), an indandione (ID) and a dicyanovinyl functionalized indandione (IDM). The end capping of conjugated donor fragment with strong electron acceptor (in particular, indandione derivatives) have been widely used in the last years as terminal groups in non-fullerene acceptors for bulk heterojunction solar cells [38]. The prepared dyes are moreover characterized by the presence of furan rings rather than thiophenes in the molecular backbone. While thiophenes rings are typically inserted in small molecules (or polymers) investigated in the field of organic electronics, their close analogues furan rings have been studied so far in a much lower extent; in the last years, anyway, furans containing small molecules for organic electronics have been experienced a growing interest [39,40], first of all because furan can be obtained from renewable resources and, in addition, for the proved biodegradability of many furan derivatives [41,42]. Moreover, as compared to thiophene analogues, furan-based derivatives are known to be characterized by a higher solubility while being more tightly packed [43]. Finally, replacement of a sulphur atom with oxygen lowers the oxidation potential and make HOMO levels more accessible [43]: in the framework of the molecular structures we are here proposing this could be beneficial to achieve ambipolar charge transport properties by favoring hole transport in systems where electron transport properties are fueled by the several electron acceptor moieties present.

The strength of several terminal electron acceptor groups on the dye's properties is investigated as well: the four novel dyes differ in fact for the nature of the auxiliary acceptor groups, whose strength increases in the order: DCV < TB < ID < IDM. The resulting A'-D-A-D-A' structure is characterized by an alternation of electron poor and electron rich units along the molecular backbone and this is one of the molecular



Scheme 1. Chemical structures of the synthesized dyes.

engineering principle to achieve low-band gap dyes; this class of materials is highly demanded in the field of OPVs, because their absorption spectrum better overlaps the solar emission spectrum and thus a higher solar photon harvesting is achieved [44]; this class of materials is extremely appealing in OFETs technology as well, because of their potential ambipolar charge transport [44,45]. The synthesized dyes were characterized in terms of structural, optical and thermal properties. An electrochemical characterization provided moreover a better insight on the relative energies of frontier molecular orbitals of the dyes. The compounds were finally processed as thin films and used as active layers in OFET to investigate their charge transport properties.

### 2. Experimental section

#### 2.1. Synthesis

All reagents were purchased by Sigma Aldrich or Alfa Aesar and used without any further purification, unless otherwise specified. All air- or moisture-sensitive reactions were carried out under nitrogen atmosphere.

# 2.1.1. Synthesis of 3,6-di(furan-2-yl)pyrrolo[3,4-c]pyrrole-1,4 (2H,5H)-dione (1)

4.81 g (209 mmol) of Na metal and a catalytic amount of FeCl<sub>3</sub> were placed in 100 ml of anhydrous t-amyl alcohol. The system was taken at 90 °C under nitrogen atmosphere until to complete oxidation of sodium (around 1 h). Then, 15 g of 2-cyanofuran (161 mmol) were added and the temperature was increased to 120 °C. After 1 h, 9.24 g (63 mmol) of dimethyl succinate were added dropwise. The temperature was further increased to 130 °C and the reaction continued for 3 h, during which solution colour turned to dark red. The system was then cooled down to 80 °C and quenched with a solution of 60 mL of methanol and 20 mL of acetic acid. After cooling down the mixture to room temperature the product was collected by suction filtration and washed with 300 ml of a hot methanol/water solution (2/1 v/v). The washed product was again recovered by suction filtration. Yield: 56%.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ: 6.83 (s, 2H); 7.67 (m,2H); 8.05 (m, 2H); 11.18 (s,2H).

# 2.1.2. Synthesis of 3,6-di(furan-2-yl)-2,5-di(2-ethylhexyl)pyrrolo[3,4-c] pyrrole-1,4(2H,5H)-dione (2)

4.31 g (16 mmol) of 1 and 6.85 g (49.6 mmol) of  $K_2CO_3$  were put in 50 mL of anhydrous DMF and the system was taken under nitrogen atmosphere. The about 30 mg of dibenzo-18-crown-6-ether were added, and the temperature was increased up to 100 °C. After 1 h, 7.4 g (38.4 mmol) of 2-bromoethylhexan were added dropwise. The system was finally increased to 130 °C and reacted overnight at this temperature for 18 h. The mixture is then cooled down to room temperature and the temperature was further decreased by using means of an ice-salt bath. The solid was collected by filtration and washed in 200 mL of HCl(aq) 0.5 M in order to remove the excess potassium carbonate. The remaining solid was recovered by filtration, solved in chloroform and re-filtered to remove the unreacted insoluble compound 1. After removal of chloroform by means of a rotary evaporator, 3.02 g of crystalline product was recovered. M.p. 153 °C. Yield: 38%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 0.91 (m, 12H); 1.32 (m,16H); 1.75 (m, 2H); 4.04 (d, 4H, J = 6.7 Hz); 6.70 (dd,4H, J1 = 3.6 Hz, J2 = 1.6 Hz); 7.62 (d,2H, J = 1.6 Hz); 8.34 (d, 2H, J = 3.6 Hz).

## 2.1.3. Synthesis of 3,6-bis(5-bromofuran-2-yl)-2,5-di(2-ethylhexyl)pyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione (3)

2.2 g (4.47 mmol) of **2** were dissolved in a mixture of 50 ml of chloroform and conditioned in an ice bath. The solution was put under nitrogen atmosphere and in the darkness in order to protect it from light. Then, 1.91 g (10.7 mmol) of *N*-bromosuccinimide (NBS) were added portion wise. The reaction was left under stirring and inert atmosphere

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overnight. The day after, the solvent was removed by using a rotary evaporator. The obtained product was, finally, purified by chromatography column with silica gel as stationary phase and  $\rm CH_2Cl_2$  as eluent. M.p. 167 °C. Yield: 51%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.86-0.93$  (m. 12H); 1.27-1.37 (m,16H); 1.56 (s broad,2H); 1.72 (m, 2H); 3.98 (d, 4H, J = 6.7 Hz); 6.62 (d,2H, J = 3.6 Hz); 8.03 (d, 2H, J = 3.6 Hz).

### 2.1.4. Synthesis of 5',5'''-(2,5-di(2-ethylhexyl)-3,6-dioxo-2,3,5,6tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(([2,2'-bifuran]-5carbaldehyde)) (4)

750 mg (1.15 mmol) of 3 were dissolved in 20 mL of anhydrous THF. The system was degassed and 965 mg (6.9 mmol) of 5-formylfuranylboronic acid and 4.5 ml of 2 M Na<sub>2</sub>CO<sub>3</sub> solution (9 mmol) were added. Then, after a further degassing, 245 mg of Pd[P(Ph)<sub>3</sub>]<sub>4</sub> (0.212 mmol) were added and the mixture reacted for 18 h under reflux. In few hours the mixture colour turned from purple to blue. The system was then cooled down to room temperature and the solvent is evaporated in vacuo. The residue was collected and extracted with 50 mL of chloroform and 80 mL of water. The organic phase is dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated again by rotary evaporator. The product in the round-bottom flask is dissolved in 15 ml of CH<sub>2</sub>Cl<sub>2</sub> and diluted with 30 mL of methanol. By setting rotary evaporator bath at room temperature and reducing the pressure, dichloromethane (solvent) was distilled off causing at the same time a decrease of the temperature in the round bottom flask: a sort of solvent/non-solvent recrystallization of the product at low temperature occurred in this way. The obtained solid was finally recovered by suction filtration. M.p. 208 °C. Yield: 60%.

<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 0.87$  (t, 6H, J = 7.2 Hz); 0.93 (t, 6H, J = 7.4 Hz) 1.26–1.41 (m,16H); 1.86 (m, 2H); 4.09 (d, 4H, J = 7.6 Hz); 6.92 (d,2H, J = 3.6 Hz); 7.17 (d,2H, J = 3.8 Hz); 7.38 (d,2H, J = 3.8 Hz); 8.46 (d, 2H, J = 3.8 Hz); 9.68 (s, 2H).

<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz): 10.2; 13.8; 23.1; 28.4; 29.7; 30.1; 39.6; 46.4; 108.2; 109.7; 112.6; 122.0; 132.5; 134.5145.4; 146.8; 149.4; 152.5; 160.7; 176.9.

# 2.1.5. Synthesis of 2,2'-((5',5'''-(2,5-di(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis(([2,2'-bifuran]-5,5'-diyl))bis (methanylylidene))dimalononitrile (DCV)

In a round-bottom flask 100 mg (0.147 mmol) of 4 were dissolved in a solution consisting of 3 mL of absolute anhydrous ethanol and 12 mL of anhydrous dichloroethane. Afterwards, 39 mg (0.588 mmol) of malononitrile and 39 mg (0.441 mmol) of  $\beta$ -alanine were added. The mixture reacted under nitrogen atmosphere and refluxed overnight and solution colour turned from blue to green. Then the system was allowed to cool down to room temperature and the formed solid was recovered by filtration. The crude product was dissolved in chloroform (5 mL), filtered and the collected solution treated by rotary evaporator in order to remove the solvent. Afterwards, the solid was dissolved in the minimum amount of dichloromethane, poured into boiling heptane dropwise and filtered from hot heptane. Finally, the product was dissolved in the minimum amount of dichloromethane and poured in boiling ethanol: the formed precipitate was recovered by vacuum filtration from hot ethanol. M.p. 292 °C. Yield: 72%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 0.85$  (t, 6H, J = 6.5 Hz); 0.91 (t, 6H, J = 7.5 Hz), 1.25–1.41 (m, 16H); 1.82 (m, 2H); 4.12 (d, 4H, J = 7.5 Hz); 6.99 (d, 2H, J = 3.5 Hz); 7.24 (d, 2H, J = 4.0 Hz); 7.41 (broad, 2H); 7.46 (s, 2H); 8.47 (d, 2H, J = 4.0 Hz).

 $^{13}$ C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): d = 11.0; 14.0; 23.0; 23.5; 28.3; 30.1; 39.5; 46.4; 76.4; 108.5; 108.9; 111.4; 113.1; 114.2; 114.7; 122.6; 132.5; 145.8; 146.0; 148.0; 150.5; 160.6.

FTIR (KBr, cm<sup>-1</sup>): 3032, 2958, 2873, 2221, 1665, 1570, 1529, 1434, 1386, 1286, 1095, 1029.

Anal. Calcd. for  $C_{46}H_{44}N_6O_6{:}$  C 71.12, H 5.71, N 10.82; found: C 71.29, H 5.57, N 10.71.

ESI-MS: Calcd. for MH<sup>+</sup>: 777.34; Found: 777.24.

2.1.6. Synthesis of 5,5'-((5',5'''-(2,5-di(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bifuran]-5,5'-diyl))bis (methanylylidene))bis(1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione) (TB)

**TB** was synthetized according to the same procedure adopted for **DCV**, with the only exception that *N*,*N*-diethyl-thiobarbituric acid, was used instead of malononitrile. M.p. 279 °C. Yield: 73%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 0.84$  (t, 6H, J = 7.3 Hz); 0.94 (t, 6H, J = 7.3 Hz); 1.24–1.43 (m, 28 H); 1.86 (m, 2H); 4.12 (d, 4H, J = 7.6 Hz); 4.57 (q, 4H, J = 7.1 Hz); 7.03 (d, 2H, J = 4.0 Hz); 7.19 (d, 2H, J = 4.0 Hz); 8.36 (s, 2H); 8.54 (d, 2H, J = 4.0 Hz); 8.85 (d, 2H, J = 4.0 Hz).

 $^{13}$ C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta = 10.5; 12.4; 14.0; 23.5; 28.4; 29.7; 30.1; 39.6; 43.4; 44.1; 46.7; 108.9; 112.4; 113.1; 114.4; 123.0; 130.6; 132.1; 139.1; 146.0; 146.7; 151.4; 152.2; 160.4; 160.7; 178.4.$ 

FTIR (KBr, cm<sup>-1</sup>): 2961, 2933, 2871, 1671, 1551, 1381, 1284, 1216, 1107, 1030.

Anal. Calcd. for  $C_{56}H_{64}N_6O_{10}S_2\!\!:$  C 64.35, H 6.17, N 8.04; found: C 64.55, H 6.32, N 7.94.

ESI-MS: Calcd. for MH+: 1045.42; Found: 1045.34.

2.1.7. Synthesis of 2,2'-((5',5'''-(2,5-di(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bifuran]-5',5-diyl))bis (methanylylidene))bis(1H-indene-1,3-(2H)-dione) (ID)

ID was synthetized according to the same procedure adopted for DCV, with the only exception that 1,3-indandione was used instead of malononitrile. M.p. 328  $^\circ$ C. Yield: 84%.

<sup>1</sup>H NMR (CDCl3, 500 MHz): δ = 0.84 (t, 6H, J = 7.2 Hz); 0.93 (t, 6H, J = 7.2 Hz); 1.24–1.42 (m, 16H); 1.88 (m, 2H); 4.14 (d, 4H, J = 7.6 Hz); 7.01 (d, 2H, J = 3.9 Hz); 7.16 (d, 2H, J = 4.0 Hz); 7.77 (s, 2H); 7.78 (m, 2H); 7.96 (m, 2H); 8.52 (d, 2H, J = 4.0 Hz); 8.69 (d, 2H, J = 4.0 Hz).

 $^{13}\text{C}$  NMR (1,1–2,2-C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 400 MHz):  $\delta$  = 10.1; 13.6; 22.7; 23.0; 27.8; 29.6; 39.0; 46.2; 107.9; 112.0; 112.8; 122.3; 122.4; 124.7; 126.6; 131.7134.5; 134.7; 138.0; 139.6; 141.6; 144.8; 146.4; 149.4; 151.4; 154.4; 160.1; 189.0.

FTIR (KBr, cm<sup>-1</sup>): 2956, 2928, 2855, 1681, 1577, 1508, 1456, 1349, 1282, 1221, 1099, 1023.

Anal. Calcd. for  $C_{58}H_{52}N_2O_{10}$ : C 74.34, H 5.59, N 2.99; found: C 74.67, H 5.75, N 2.90.

ESI-MS: Calcd. for MH<sup>+</sup>: 937.37; Found: 937.33.

2.1.8. Synthesis of 2,2'-((2Z,2'Z)-((5',5'''-(2,5-dioctyl-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)bis([2,2'-bifuran]-5',5-diyl))bis (methanylylidene))bis(3-oxo-2,3-dihydro-1H-indene-2,1-diylidene)) dimalononitrile (IDM)

**IDM** was synthetized according to the same procedure adopted for **DCV**, with the only exception that, 1,1-dicyanomethylene-3-indanone was used instead of malononitrile. M.p. no detectable. Yield: 86%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 0.86 (t, 6H, *J* = 7.5 Hz); 0.93 (t, 6H, *J* = 7.5 Hz); 1.26–1.43 (m, 16H); 1.84 (m, 2H); 4.10 (d, 4H, *J* = 8.0 Hz); 7.03 (d, 2H, *J* = 4.0 Hz); 7.23 (d, 2H, *J* = 3.5 Hz); 7.73 (m, 2H); 7.90 (m, 2H); 8.45 (s, 2H); 8.56 (d, 2H, *J* = 4.0 Hz); 8.85 (d, 2H, *J* = 4.0 Hz).

 $^{13}$ C NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta=10.5;\,14.0;\,23.1;\,23.5;\,28.5;\,29.7;\,30.2;\,39.6;\,46.8;\,70.8;\,109.4;\,113.4;\,114.0;\,114.3;\,114.5;\,123.1;\,123.9;\,124.6;\,125.2;\,127.8;\,129.7;\,132.2;\,134.6;\,135.2;\,137.0;\,139.6;\,146.0;\,146.7;\,151.0;\,151.7;\,187.1.$ 

FTIR (KBr,cm<sup>-1</sup>): 2959, 2928, 2857, 2221, 1708, 1669, 1561, 1540, 1501, 1371, 1343, 1292, 1239, 1127, 1091, 1023.

Anal. Calcd. for  $C_{64}H_{52}N_6O_8{:}$  C 74.40, H 5.07, N 8.13; found: C 74.58, H 5.13, N 8.03.

ESI-MS: Calcd. for MH<sup>+</sup>: 1033.39; Found: 1033.34.

### 2.2. Chemical-physical characterization

The compounds identity was confirmed by NMR analysis performed on Bruker 400 MHz and 500 MHz Varian spectrometers. ESI (Electro Spray Ionization) experiments were conducted with a Thermo Finnigan

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Advantage Max Ion trap spectrometer in positive ion acquiring mode: samples are dissolved in chloroform and slightly acidified with formic acid to improve the MH<sup>+</sup> detectability. Sheath gas flow rate was set at 25 (arbitrary unit), auxiliary gas flow rate at 5 (arbitrary unit), spray voltage at 3.25 (KV), capillary temperature at 270 °C, capillary voltage at 7 (V), and tube lens offset at 60.00 (V). Nitrogen was used as sheath and auxiliary gases. Thermogravimetric analysis (TGA) was carried by TA4000 Perkin- Elmer instrument at a heating rate of 20 °C/min under air in the temperature range 30-900 °C. The reported decomposition temperature refers to 5% weight loss. Differential scanning calorimetry (DSC) analysis was performed on a PerkinElmer Pyris 1 instrument under a nitrogen flow at a heating rate of 10 °C/min. Absorption spectra were recorded on Jasco V-530 UV-vis spectrophotometer at room temperature with a scanning rate of 200 nm/min. FTIR spectra were recorded dispersing the dye in KBr pellets and using a Jasco F-430 spectrophotometer. Thin films of the dyes have been prepared by spincoating a chloroform solution of the dyes on glass substrates for optical characterization by means of a Laurell WS-650Mz-23NPP spin processor. Electrochemical characterization was performed by means of cyclic voltammetry (CV) using was recorded with a BioLogic sp150. The samples were drop-casted onto a Pt working electrode from dichloromethane solution in a three-electrode set-up, being a Pt wire the counter-electrode and Ag/AgCl the reference electrode. Electrolyte consisted in a tetrabutylammoiun hexafluorophosphate 0.1 M solution in anhydrous acetonitrile. CV were conducted at 100 mV/s. The found potential values were referred to Fc/Fc + acting as internal standard. Before each measurement, the electrolyte was degassed with Argon to avoid the presence of oxygen.

#### 2.3. Transistor fabrication and electrical characterization

For the transistor fabrication, DPP dyes films were prepared by spin coating starting from a 5 mg/ml chloroform/tetrachloroethane 99/1 v/v solution (filtered through a 0.2 µm syringe filter), at 1500 rpm for 1 min; the obtained films were dried in a vacuum oven, at 80 °C, for 1 h. Typical thickness values were comprised in the range between 50 and 150 nm. The organic dyes were spin-coated specifically on standard multilayer structures consisting of a 500- $\mu$ m thick highly-doped silicon (Si<sup>++</sup>) acting as a gate electrode, a 200-nm thick SiO2 dielectric barrier and 150-nm thick pre-patterned source/drain gold electrodes with interdigitated layout. The considered electrode geometry allows the definition of semiconducting active channels characterized by a ratio between width (W) and length (L) of about 550. For our experimental set-up, this feature provides a reliable estimation of the field-effect mobility values down to  $10^{-6}$  cm<sup>2</sup>/V·s, making possible the accurate electrical characterization of films achieved by evaporated small molecules [46], solution-processed polymers [47] and even semi-insulating bio-oriented compounds [48]. Before the film deposition, all multilayer Si<sup>++</sup>/SiO<sub>2</sub>/Au substrates were functionalized by applying HMDS (hexamethyldisilazane) self-assembling monolayers using a process lasting 7 days (see Refs. [48] for more detail). In this way, the final water-contact angle ( $\theta_c$ ) of the SiO<sub>2</sub> surface was increased up to about 110° (starting from an initial  $\theta_C \sim 60^\circ$  ). It is well known, indeed, that the enhancement of the hydrophobic degree of SiO<sub>2</sub> surface allows strongly reducing the occurrence of charge trapping mechanisms related to the presence of water molecules absorbed at the dielectric/semiconductor interface. The deposited films surfaces were investigated by atomic force microscopy (AFM) in non-contact mode, in order to prevent surface damages, using a Park system XE100 microscope. The electrical measurements were carried out mounting the samples in a Janis cryogenic probe station, connected to a Keithely 2612A dual-channel source-meter in order to apply contemporarily the  $V_{GS}$  and  $V_{DS}$  voltages and to record, in parallel, the related  $I_{\text{DS}}$  and  $I_{\text{GS}}$  currents. Field-effect measurements were systematically carried out in vacuum, with a base pressure  $P_r\,{\sim}10^{-5}$  mbar. The values of the field-effect mobility  $(\mu_{sat})$  and of the threshold voltage (V<sub>th</sub>) were extracted in the saturation regime (V<sub>DS</sub> = + or - 50 V) through

the related MOSFET equation used to fit linearly the square root of the measured current by:

$$\sqrt{I_{ds}} = \sqrt{\frac{W}{2L}} C_{OX} \mu_{sat}^{*} (V_{GS} - V_{th})$$
<sup>(1)</sup>

where  $C_{ox}$  is the oxide capacitance per unit area ( $C_{ox} = 17.25 \text{ nF/cm}^2$ ).

### 3. Results and discussion

### 3.1. Synthesis and chemical-physical properties

The novel DPP dyes were synthesized through a multistep synthetic procedure that is graphically sketched in Scheme 2.

DPP unit was obtained by the base catalyzed reaction between 2-cyanoforan and dimethyl succinate at 130 °C under inert atmosphere. DPP core was then *N*-functionalized by reacting **1** with 1-bromo-2-ethylhexane in dimethylformamide (DMF) and in presence of K<sub>2</sub>CO<sub>3</sub> as base, with 38% yield. Afterwards, bromuration in darkness with *N*-bromosuccinimide (NBS) allowed to get the dibromo derivative **3**. Once dibromo difuran DPP was obtained, it was combined with 5-formyl-2-furanboronic acid by Pd(0) catalyzed Suzuki coupling, affording a symmetrical formyl terminated precursor. This common diformyl precursor was finally functionalized with four different acceptor groups to afford the reported DPP dyes: the last synthetic step consisted in a Knoevenagel condensation of **4** with compound containing acid methylene group, specifically malononitrile (**DCV** dye), *N*,*N*-diethyl thiobarbituric acid (**TB**), indandione (**ID**) and 1,1-dicyanomethylene-3-indanone (**IDM**).  $\beta$ -alanine was used as catalytic base in this condensation reaction.

NMR analysis provided an indication of the relative strength of the auxiliary terminal acceptor groups of the four dyes, as shown in Fig. 1. In particular, the resonance value of the proton of the methine group is influenced by the adjacent electron acceptor moiety: values of 7.46, 8.36, 7.77 and 8.45 were found for, respectively, **DCV**, **TB**, **ID** and **IDM**; this trend suggests that the electron acceptor strength is in the order **DCV** < **ID** < **TB** < **IDM**.

Thermal properties of the dyes were investigated by means of DSC and TGA analysis and are summarized in Table 1. All the dyes but **IDM** showed, during DSC scan, a melting point at 292, 279 and 328 °C (see Fig. S1). The thermal stability of the dyes was assessed by TGA analysis: all the dyes featured a fair good thermal stability in air with decomposition temperature ranging from 337 °C (**TB**) to 375 °C (**DCV**). TGA scan is reported in Fig. S2.

Optical characterization was performed on the reported dyes both in solution and as thin films; dyes optical properties are summarized in Table 2, while their optical absorption spectra in chloroform solution are reported in Fig. 2.

All the dyes absorb at very high wavelengths because of the alternation of electron donor and electron acceptor groups along the molecular backbone. The wavelength of the absorption maxima of the dyes is clearly influenced by the terminal electron acceptor groups functionalizing the common molecular fragment: in particular, as the strength of the electron acceptor end group increases, the dye's absorption moves to higher wavelengths. We thus observed  $\lambda_{max}$  values of 683, 705, 724 and 768 nm, respectively, for DCV, ID, TB and IDM. This trend is consistent with the previously discussed NMR analysis. As shown in previous papers [50,51], functionalizing a specific molecular fragment with electron acceptor groups of different strength have a relevant effect on tuning optical absorption properties of the molecular systems, occurring mainly through the stabilization of LUMO energies of the dyes. All the dyes present a second optical feature at higher energy ranging from 444 nm (DCV) to 488 nm (IDM) that eventually contributes to the final colour of the solutions, being green for all the dyes but IDM, which affords midnight blue colored solutions. The optical absorption of IDM is particularly interesting being widely spread in all visible range and hence appealing for light harvesting application.

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Scheme 2. Synthetic procedure followed for the preparation of the dyes; i) Na (1.3 eq.), FeCl<sub>3</sub>, dimethylsuccinate (0.8 eq.) in t-amyl alcohol, 130 °C, 3 h, in N<sub>2</sub>; ii) Na<sub>2</sub>CO<sub>3</sub>, 1.2 eq. of 1-bromo-2-ethylhexane, DMF, 130 °C, N2, 20 h; iii) 1.2 eq. of *N*-bromosuccinimide, chloroform, in the dark, N<sub>2</sub>, RT, 16 h; iv) 3 eq. of 5-formyl-2-furanylboronic acid, Pd[P(PH<sub>3</sub>)]<sub>4</sub>, dry THF, N<sub>2</sub>, reflux, 20 h; v) 2 eq. of acceptor, dichloroethane-ethanol 4:1,  $\beta$ -alanine, reflux, 20 h, N<sub>2</sub>.



**Fig. 1.** <sup>1</sup>H NMR spectra of the dyes in CDCl<sub>3</sub>; the peak corresponding to the methine resonance is starred to highlight its dependence from the strength of the terminal acceptor groups.

Table 1	
Thermal properties of DPP dy	yes.

Dye	$T_m (^{\circ}C)^a$	$T_d (^{\circ}C)^b$
DCV	292	375
ТВ	279	337
ID	328	374
IDM	-	363

 $^{\rm (a)}$  Melting temperature determined by DSC analysis at 10  $^\circ \rm C/min$  under nitrogen atmosphere.

 $^{\rm (b)}$  Decomposition temperature determined as the temperature corresponding to the 5% weight loss of the samples in TGA measurement performed at 20 °C/min in air.

Optical	properties	of the	dyes in	chloroform	solution	and as	thin	films.
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Dyes	$\lambda_{MAX}(nm)$	$\varepsilon(\text{cm}^{-1} \cdot \text{M}^{-1})$	$\lambda_{MAX}^{FILM}(nm)^{a}$	Eg(eV) <sup>b</sup>
DCV	683	$7.27\cdot 10^4$	759	1.57
TB	724	$9.84 \cdot 10^4$	779	1.45
ID	705	$8.15\cdot 10^4$	782	1.41
IDM	768	$8.28\cdot 10^4$	861	1.29

 $^{(a)}$  UV–vis analysis on film obtained by  $CHCl_3$  solution by spin coating and annealed at 85  $^\circ C$  in vacuum for 1 h.

<sup>(b)</sup> Optical Bandgap extrapolated by Tauc plot [49].



Fig. 2. Normalized absorption spectra of the synthesized dyes in chloroform solution.

Quantitatively, all compounds show a fair high molar extinction coefficient ranging from 73000 (**DCV**) to 98000 cm<sup>-1</sup> M<sup>-1</sup> (**TB**) as shown in Table 2.

reported in Fig. 3. It is possible to observe that, in solid state, optical absorption became broader and red shifted as compared to solution optical spectra.

Optical characterization was also performed on thin films of the dyes spin coated from chloroform solution and the optical spectra are The absorption of the dye's films extends significantly in the NIR part of the spectrum. The optical bandgap of the dyes has been graphically



Fig. 3. Normalized absorption spectra of the synthesized dyes as thin films spin coated from chloroform solution.

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evaluated by applying Tauc relationship [49]. All the dyes are characterized by a very low bandgap with values arriving to the extremely interesting value of 1.29 eV for **IDM**.

The dyes were electrochemically characterized by means of cyclic voltammetry. CV experiments were performed on the dyes drop casted as thin films on platinum working electrode, as described in the Experimental Section. CV graphs are reported in Fig. 4.

The analysis of these graphs provides important electrochemical parameters which, in turn, allow the estimation of HOMO and LUMO energies of the dyes: HOMO and LUMO energies can be related, respectively, to oxidation and reduction potentials of the dyes, if these are measured relative to ferrocene/ferrocenium ( $Fc^+/Fc$ ) potential, by applying the following equations:

$$E_{HOMO} = -(E_{ox vs Fc^+/Fc} + 5.1)(eV)$$

 $E_{LUMO} = - \left( E_{red vs Fc^+/Fc} + 5.1 \right) (eV)$ 

where  $Fc^+/Fc$  redox potential is assumed 5.1 eV below vacuum level [52].

HOMO and LUMO energies along with oxidation and reduction potentials of the dyes are reported in Table 3.

Two oxidation processes are evident for all the dyes and being these processes semi-reversible it has been possible to calculate the relative oxidation potentials as the halfwave potential of the anodic and cathodic peaks (E  $\frac{1}{2}$ ). The single reduction event was not reversible for all the four

### Table 3

Electrochemical potentials vs  $\mathrm{FC}^+/\mathrm{FC}$  and estimated HOMO and LUMO energies vs vacuum.

Dyes	$E_{ox1}(V)^a$	E <sub>ox2</sub> (V) <sup>a</sup>	E <sub>red</sub> (V) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>c</sup>	E <sup>CV</sup> (eV)
DCV	0.53	0.74	-1.00	-5.63	-4.08	1.55
ТВ	0.45	0.61	-0.96	-5.55	-4.14	1.41
ID	0.41	0.59	-0.97	-5.51	-4.13	1.38
IDM	0.48	0.70	-0.78	-5.58	-4.28	1.30

<sup>a)</sup> Calculated as the half wave potential of the anodic and cathodic peaks.

<sup>b)</sup> Calculated as the onset of the reduction potential.

<sup>c)</sup> Calculated according to ref. 52.

dyes so that the reduction potentials were calculated by considering the  $E_{onset}^{red}$ . While electrochemically determined HOMO energies do not present a clear trend, LUMO energies are consistent with the strength of the electron acceptor terminal group: in fact, the more and the less stabilized LUMO are presented by, respectively, **IDM** and **DCV**, the two dyes bearing the stronger and the weaker electron acceptor terminal groups. **TB** and **ID** showed similar and intermediate LUMO energies. The electrochemical bandgap is in a quite good accord with the observed optical bandgap.



Fig. 4. CV graphs of the synthesized dyes drop casted as thin film on a Pt working electrode.

### 3.2. Electrical characterization of dye based OFETs

The synthesized dyes have been spin coated as active layers of OFET (see the experimental section from more details about the fabrication process) in order to assess their electrical properties by estimating the corresponding field-effect response parameters. Different batch of the synthesized molecules were characterized, all giving comparable results; in this report we will discuss in particular the transistors affording the best performance. The results of the electrical characterization of these transistors are reported in Table 4. The OFET characterization was specifically pursued by recording in vacuum both transfer (IDS vs VGS at fixed  $V_{DS}$ ) and output (I<sub>DS</sub> vs  $V_{DS}$  at fixed  $V_{GS}$ ) curves. Fig. 5, in particular, reports a set of transfer curves acquired in the saturation regime for both hole (negative  $V_{GS}$  and  $V_{DS} = -$  50 V) and electron (positive  $V_{GS}$ and  $V_{DS} = +50$  V) accumulation regions. As expected from the low lying LUMO [53], all the dyes presented a significant electron mobility. As shown, field-effect transistors based on the TB, ID and IDM molecules exhibited a clear ambipolar behavior and the IDS current could be enhanced by both positive and negative V<sub>GS</sub> voltages. On the contrary, the DCV device displayed a pure n-type response and no hole accumulation phenomenon was observed.

Table 4 summarizes the mobility and the threshold voltage values extracted from the transfer curves recorded in the saturation regime. From this, it is immediately clear that **TB** is the dye providing the best charge transport properties, with mobility values, for both electrons and holes, largest by far. ID and IDM molecules, on the other hand, behave rather similarly, with the former showing, however, significantly higher (by about a factor 2x) electron mobility values. As aforementioned, for DCV no hole accumulation effect could be detected. This compound was characterized by the worst performances in terms of low mobility values and high threshold voltages also as far as the n-type response is concerned. In particular, for  $\ensuremath{\text{DCV}}$  , the mean  $V_{th}$  value was very close to 40 V. Only IDM showed similar values of V<sub>th</sub>, which, on the contrary, was found to be significantly reduced for the other two molecules. For all the analyzed compounds, specific field-effect tests carried out in air suggested a considerable reduction of the mobility values by a factor exceeding, typically, one order of magnitude. As expected, mobility degradation was more severe for electrons.

Fig. 6 reports the output curves recorded for a **TB** transistor considering both hole (negative  $V_{GS}$  and  $V_{DS}$ ) and electron (positive  $V_{GS}$  and  $V_{DS}$ ) accumulation regimes. Similar sets of curves acquired for the other compounds are included in the Supplementary Information File (see Fig. S15–17). The ambipolar nature of **TB** is confirmed by the observation that, in the p-type response (i.e. output curves on the left), at low  $V_{GS}$  and high  $V_{DS}$  (both considered in absolute value), the  $I_{DS}$  behavior is basically ruled by the injection of electrons from the drain electrode (i.e. in these conditions,  $V_{GD}$  is largely positive and electrons can be accumulated in the semiconducting region near the drain

#### Table 4

Electron and hole mobility ( $\mu)$  and threshold voltage ( $V_{th})$  values estimated by Eq. (1) for the transistors based on the reported dyes.

Dyes	µe <sup>av</sup> * (cm²/ V·s)	μ <sub>e</sub> <sup>MAX</sup> (cm <sup>2</sup> /V·s)	V <sub>th</sub> / n- type (V)	$\mu_h^{av_*}(cm^2/V_{\cdot s})$	µhAX (cm²/ V·s)	V <sub>th</sub> /p- type (V)
TB DCV	$\begin{array}{l}(1.7\pm\\ 0.4)^*10^{-2}\\(1.0\pm\\ 0.2)^*10^{-3}\end{array}$	$2.2*10^{-2}$ $1.2*10^{-3}$	$15 \pm 3 \\ 39.5 \\ \pm 1.7$	$(1.6 \pm 0.4)*10^{-3}$ No Field effect	2.1*10 <sup>-3</sup> No Field effect	−22 ± 1.5 No Field
ID IDM	$(3.7 \pm 0.8)*10^{-3}$ $(1.9 \pm 0.2)*10^{-3}$	4.8*10 <sup>-3</sup> 2.05*10 <sup>-3</sup>	$25 \pm 3 \\ 36 \pm 1.4$	$(5.2 \pm 0.6)*10^{-4}$ $(7.4 \pm 1.0)*10^{-4}$	6.1*10 <sup>-4</sup> 8.1*10 <sup>-4</sup>	$\begin{array}{c} \text{effect} \\ -16 \pm \\ 2 \\ -16.5 \\ \pm 5 \end{array}$

<sup>\*</sup> Mean values were achieved by considering at least four transistors for any molecule. Error bars represent the standard deviation values.

### electrode).

The curves in Fig. 6 reveal also that, in the low (i.e  $V_{\rm DS}$  <5 V) region, the transistor response is far from being perfectly linear, as predicted by the MOSFET model. This feature is commonly observed for n-type bottom-contact organic field-effect transistors based on both evaporated [54] and solution-processed active layers [55]. This undesired effect is related to the so-called contact resistance phenomenon whose physical reasons can be ascribed both to the deteriorated film morphology close the electrodes and/or to the mismatch between the gold Fermi level and the energy levels (i.e. LUMO or HOMO) of the frontier orbitals involved in the charge transport phenomenon.

In parallel with the electrical characterization, semiconducting film surfaces were investigated by atomic force microscopy (AFM). In Fig. S3, representative morphologies are reported for all the analyzed compounds. All the film surfaces result compact and slightly wrinkled with the presence of sparse precipitates. Surfaces of the samples DCV in Fig. S18(a) and ID in Fig. S18(b) seem rather similar, being very flat and characterized by the presence of small holes of about 100 nm for DCV and 200 nm in the case of ID. Moving on to the other two samples, the surface morphologies became more structured and small grains and clusters can be more easily identified. In the case of TB samples (Fig. S18 (d)), in particular, the microstructure is composed of uniformly distributed grains with a few hundreds of nm size. In the Table S1, the roughness ( $\sigma$ ) and the correlation length ( $\xi$ ) of the images are reposted for completeness. Typically, the correlation length is an underestimation of the average size of the grains. As a whole, TB sample seems to be morphologically the best with a low roughness and a relative high correlation length. These features should explain the superior electrical performances of this compound as compared to the other dyes.

### 4. Conclusions

In this paper, we reported on the synthesis of four novel organic dyes, characterized by a common molecular fragment based on a DPP electron acceptor core symmetrically functionalized with two electron donor bifuran moieties and differing only for the terminal units constituted by auxiliary electron acceptor groups of different strength. The dyes were characterized by a fair good thermal stability in air, with decomposition temperature higher than 337 °C. The optical properties of the synthesized dyes were, moreover, analyzed both in solution and as thin film. All the dyes showed a very high molar extinction coefficients approaching  $10^5 \text{ cm}^{-1} \text{ M}^{-1}$  and a clear dependence of the absorption maximum wavelengths from the strength of the auxiliary electron acceptor groups. As expected, the alternation of electron donor and electron acceptor groups along the molecular backbone determines an optical absorption significantly extending in the NIR zone of the spectrum; this feature is particularly enhanced in the optical absorption of thin films which is broader as compared to that of dyes in solution. Thin films of the dyes are characterized by very low optical bandgaps, ranging from 1.57 eV (DCV dye) to the very striking value of 1.29 eV for IDM. Electrochemical characterization performed by Cyclic Voltammetry on drop casted dye films provided some information about HOMO and LUMO energies of the reported molecules. As far as LUMO energies are concerned it was found that the LUMO stability becomes higher with increasing the strength of the auxiliary electron acceptor groups. All the dyes show sufficiently low LUMO energies to act as n-type semiconductors. Films spin-coated from chloroform/tetrachloroethane solutions of the synthesized dyes were then used as active layers in OFETs in order to assess the nature and the quality of their charge transport properties. As expected, all the dyes show electron-transporting properties. Moreover, three of them exhibit also a quite balanced holetransporting capability resulting thus in ambipolar properties: ambipolar behavior can emerge also because of the extremely low bandgap of these materials. **TB** is the dye with the best charge transport properties, with maximum electron and hole mobility of, respectively,  $2.2 \cdot 10^{-2}$  and  $2.1 \cdot 10^{-3}$  cm<sup>2</sup>/V·s. In conclusion, this work demonstrates the possibility,



Fig. 5. Transfer curves recorded in saturation regime for the four different DPP dye-based transistors. The p-type (negative  $V_{GS}$ ,  $V_{DS} = -50$  V) and n-type (positive  $V_{GS}$ ,  $V_{DS} = 50$  V) responses are reported on the left and on the right, respectively.



Fig. 6. Output curves recorded for a TB based transistor under negative (on the left) or positive (on the right) V<sub>GS</sub> and V<sub>DS</sub> voltages.

in relatively easy way, of engineering the molecular structures of DPP derivatives to tune optical properties and electrical performances by properly modifying electron acceptor end groups in a common molecular motif. The good electrical properties along with a significantly narrow bandgap suggest these dyes as interesting candidate in the field of organic photovoltaics and this aspect will be addressed in upcoming works.

### CRediT authorship contribution statement

Sandra Fusco: Investigation, Data curation, Writing - original draft. Mario Barra: Investigation, Writing - review & editing. Matteo Bonomo: Investigation. Antonio Cassinese: Conceptualization, Resources. Roberto Centore: Conceptualization, Supervision. Fabio Chiarella: Investigation. Francesco Senneca: Investigation. Antonio Carella: Conceptualization, Supervision, Writing - review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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