

Supporting Information

The combination of a new organic D- π -A dye with different organic hole-transport materials for efficient solid-state dye-sensitized solar cells

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Experimental

1. Calculation details

Optimization and single point energy calculations are performed using the B3LYP¹/6-31G* basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09². The TDDFT excited state calculations were carried out in ethanol solution by the MPW1K³ functional.

The equation for calculating reorganization energy λ , is determined by the Nelson four-point method⁴⁻⁵:

$$\lambda = E_+^* - E_+ + E^* - E$$

where the E_+^* is the energy of the neutral molecule in the cation symmetry, and the E^* is the energy of the cationic molecule in the neutral symmetry; the E_+ and E are the optimized energies of the cationic and neutral molecules.

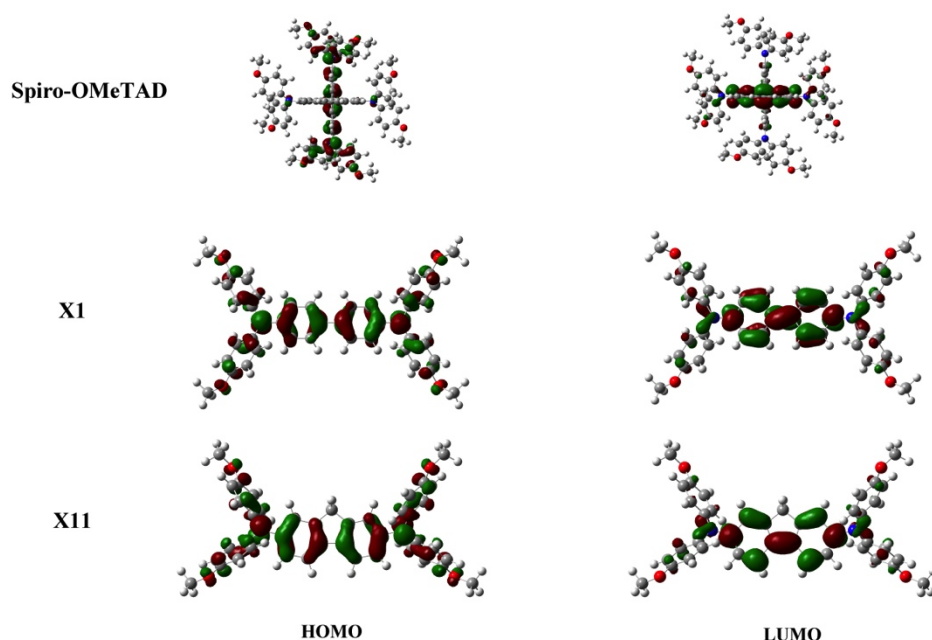


Figure S1. Frontier orbitals of different hole transport materials.

2. Electrochemistry measurement

For the characterization of the redox behaviour of the dye molecules and HTMs, a three-electrode electrochemical cell was used for the cyclic voltammetry experiments.. Whereas, the FTO/TiO₂/dye and FTO/TiO₂/HTMs layer were used as working electrode when monitoring the redox behaviour of the dye molecules and HTMs on the TiO₂ film, and the supporting electrolyte are 0.1M LiN(CF₃SO₂)₂ in acetonitrile and the ionic liquid 1-Methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide, respectively. In all cases, stainless steel was used as counter electrode with an area of 3 cm². The reference electrode was in all cases Ag/AgCl/2M LiCl in ethanol; a salt bridge electrolyte was interposed between working and reference electrode, containing 0.1 M LiN(CF₃SO₂)₂ in acetonitrile or ionic liquid depending on the

working electrode solvent. For experiments in above electrolyte, the reference electrode was calibrated with ferrocene in the same electrolyte; the literature value of 0.624 V_{SHE} was used for conversion of potential values⁶. All potentials are reported vs. SHE.

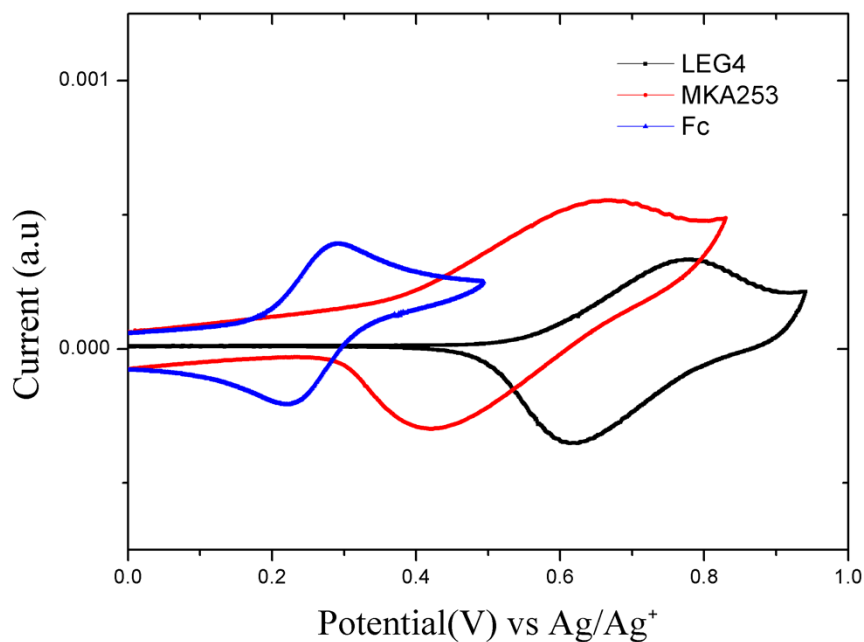


Figure S2. Cyclic voltammograms of LEG4 and MKA253 on TiO₂ film.

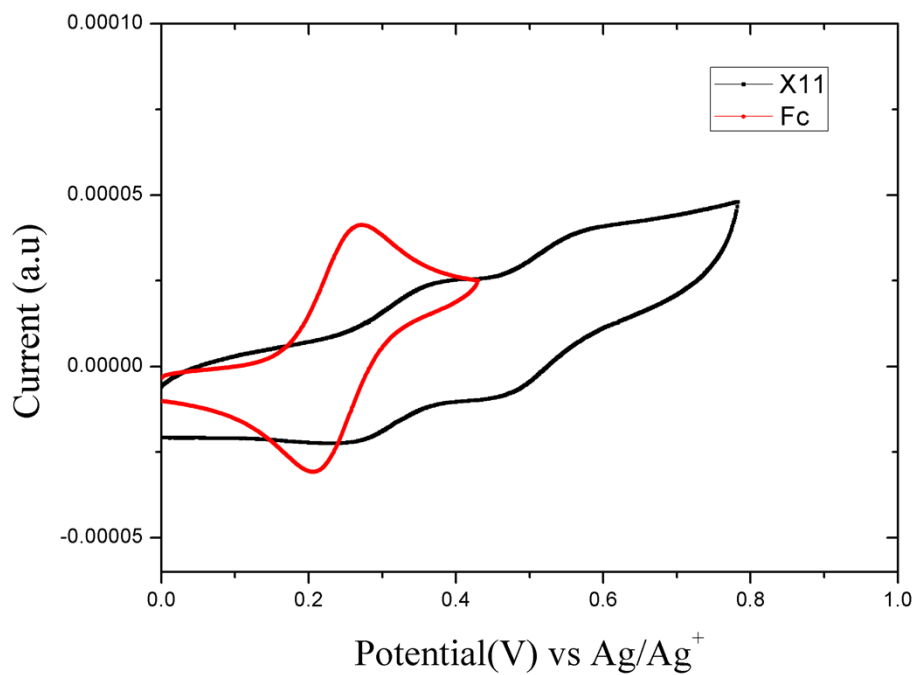
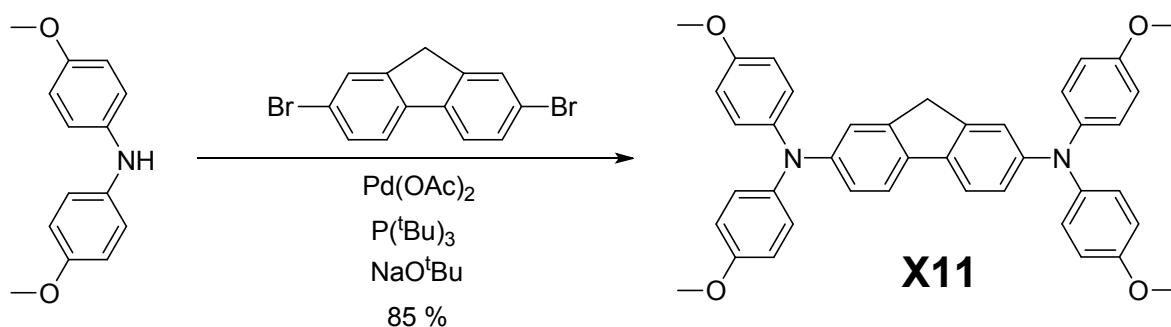
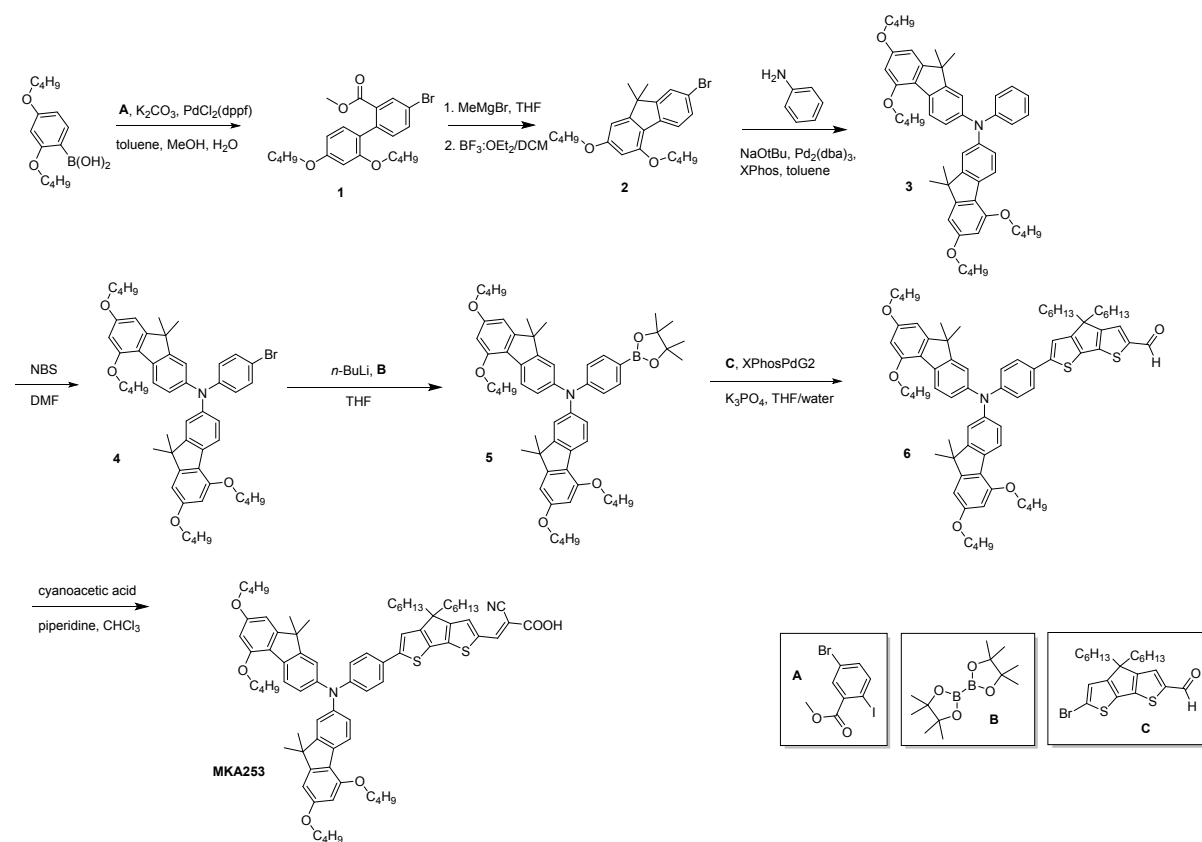
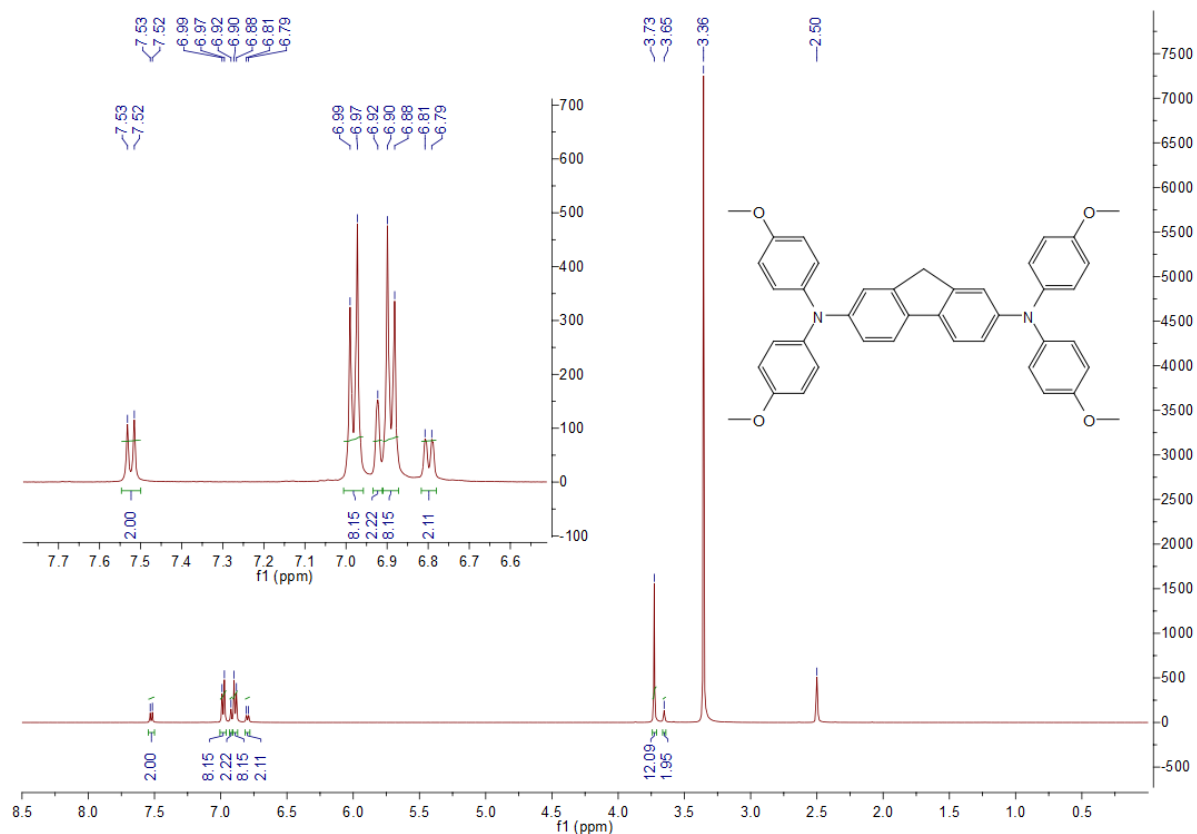


Figure S3. Cyclic voltammograms of X11 on TiO₂ film.

3. Synthesis



Synthesis of N₂,N₂,N₇,N₇-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (X11): A mixture of 4,4'-dibromo-1,1'-biphenyl (486 mg, 1.50 mmol), Pd(OAc)₂ (13.5 mg, 0.06 mmol), tri-tert-butyl phosphine (12.2 mg, 0.06 mmol), bis(4-methoxyphenyl)amine (688 mg, 3.00 mmol), and sodium tert-butoxide (360 mg, 3.75 mmol) was placed in a Schlenk flask. The flask was subjected to three vacuum/nitrogen refill cycles in order to remove water and oxygen. Anhydrous toluene (15 mL) was added, and the mixture was stirred overnight at 100 °C or until the reaction was complete by TLC analysis. After cooling, the reaction was quenched by water, and then followed by product extraction with ethyl acetate. The organic layer was dried over anhydrous Mg₂SO₄ and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 3:1) to give **X11** as pale yellow solid (578 mg, yield 95 %). ¹H NMR (*d*₆-DMSO, 500 MHz, 298 K), δ (ppm): 7.53 (d, 2 H, J = 2.5 Hz), 6.98 (d, 8 H, J = 5.0 Hz), 6.92 (s, 2 H), 6.89 (d, 8 H, J = 5.0 Hz), 6.80 (d, 2 H, J = 5.0 Hz), 3.73 (s, 12 H), 3.65 (s, 2 H). HR-MS (ESI) m/z: [M]⁺ calcd for 620.2675; found, 620.2736.



General Experimental : ¹H and ¹³C NMR spectra were recorded on Bruker 500 and 400 MHz instruments by using the residual signals $\delta = 7.26$ ppm and 77.0 ppm from CDCl₃, and $\delta = 2.05$, 29.84, and 206.26 ppm from acetone-*d*₆, as internal references for ¹H and ¹³C respectively. Chemicals used in the synthesis were purchased from Sigma-Aldrich unless otherwise specified. Tetrahydrofuran (THF) was dried by passing through a solvent column composed of activated alumina. *N*-Bromosuccinimide (NBS) was purified by recrystallization from water. Commercially available reactants were used without further purification unless otherwise noted. 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene was purchased from Chemtronica AB. 6-bromo-4,4-dihexyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-2-carbaldehyde (**C**) was prepared according to literature procedure⁷. Flash chromatography was performed using silica gel 60 Å (35–63 μm). All eluent ratios are given on v/v-basis.

The MKA253 sensitizer was synthesized in a similar manner to **JF419** but with some synthetic steps changed. Biphenyl **1** was synthesized using a Suzuki coupling with Pd(dppf)Cl₂ as catalyst and K₂CO₃ as base. The cyclization step is a two-step reaction starting with a Grignard reaction to yield the intermediate tertiary alcohol. This is followed by a Lewis acid promoted cyclization reaction to yield fluorine **2**. No purification is taken place between the two steps except a simple extraction. Triarylamine **3** is made by palladium catalyzed amination reaction. The earlier use of 4-chloroaniline yielded some dechlorinated product that was hard to separate from the desired compound. Therefore the step was divided into two, amination and subsequent bromination using NBS as brominating reagent. This increased the overall yield for triarylamine **4**. Treating **4** with *n*-BuLi and 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**B**) gave boronic ester **5** in good yield. A second Suzuki coupling with the linker **C** followed by a Knoevenagel condensation of aldehyde **6** yielded the final compound as a purple solid.

methyl 4-bromo-2',4'-dibutoxy-[1,1'-biphenyl]-2-carboxylate (1). (2,4-dibutoxyphenyl)boronic acid (3.14 g, 11.8 mmol), methyl 5-bromo-2-iodobenzoate (4.02 g, 11.8 mmol), K₂CO₃ and Pd(dppf)Cl₂ was dissolved in 50 ml degassed toluene/MeOH/water (60:40:1 v/v) in a flask with a water condenser attached. The solution was heated to 70 °C for 1h. After cooling to rt the solution was filtered through a silica plug and the solvent was evaporated. The product was purified by chromatography using petroleum ether/DCM (4:1→1:1) as eluent. The product was collected as a white solid (3.50 g, 69% yield). ¹H-NMR (500 MHz, CDCl₃): δ ppm 0.86 (3H, t, *J*=7.35 Hz), 0.99 (3H, t, *J*=7.38 Hz), 1.27 (2H, q, *J*=7.42 Hz), 1.55 (4H, m), 1.78 (2H, m), 3.66 (3H, s), 3.83 (2H, t, *J*=6.68 Hz), 3.99 (2H, t, *J*=6.43 Hz), 6.46 (1H, d, *J*=1.80 Hz), 6.53 (1H, dd, *J*=1.93, 8.28 Hz), 7.09 (1H, d, *J*=8.30 Hz), 7.16 (1H, d, *J*=8.20 Hz), 7.62 (1H, dd, *J*=1.83, 8.18 Hz), 7.98 (1H, d, *J*=1.85 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 13.70, 13.85, 19.01, 19.29, 30.88, 31.40, 51.85, 67.74, 68.09, 99.72, 104.95, 120.27, 122.38, 130.06, 132.29, 133.11, 133.17, 134.25, 138.02, 156.50, 160.26, 167.30

7-bromo-2,4-dibutoxy-9,9-dimethyl-9*H*-fluorene (2). **1** (4.05 g, 9.3 mmol) was dissolved in 150 ml dry THF. MeMgBr (3 M in diethylether, 74 mmol) was added slowly. The reaction was stirred overnight and then carefully quenched with water and neutralized with diluted HCl (aq). The mixture was extracted using water and diethyl ether. The organic phase was dried with MgSO₄ and evaporated. The crude product was redissolved in dry DCM and 4 ml BF₃·Et₂O was added drop wise. The reaction was stirred at rt overnight and then quenched with MeOH. The solution was

extracted with water/diethyl ether and the organic phase was evaporated. The crude product was run through a silica plug using petroleum ether/DCM (8:1 v/v). The solvent was evaporated and put into MeOH solution where it would precipitate into a fine white solid in the freezer (2.86 g, 73% over 2 steps). ¹H-NMR (500 MHz, *acetone-d6*) δ ppm 0.87 (3H, t, J=6.80 Hz), 0.98 (3H, t, J=7.40 Hz), 1.03 (3H, t, J=7.43 Hz), 1.29 (2H, m), 1.45 (6H, s), 1.52 (2H, m), 1.61 (2H, m), 1.77 (2H, m), 1.91 (2H, m), 4.07 (2H, t, J=6.43 Hz), 4.17 (2H, t, J=6.38 Hz), 6.53 (1H, d, J=1.55 Hz), 6.73 (1H, d, J=1.60 Hz), 7.43 (1H, dd, J=1.65, 8.10 Hz), 7.61 (1H, d, J=1.45 Hz), 7.86 (1H, d, J=8.10 Hz); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.15, 14.34, 19.96, 20.14, 23.33, 27.23, 32.18, 32.59, 48.20, 68.48, 68.60, 98.90, 101.12, 119.10, 119.35, 124.66, 126.14, 130.64, 138.88, 156.04, 156.99, 157.34, 162.18.

5,7-dibutoxy-N-(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-N-phenyl-9H-fluoren-2-amine (3). **2** (2.86 g, 6.84 mmol), NaO-*t*Bu (1.3 g, 13 mmol), Pd₂(dba)₃ and Xphos (79 mg, 0.165 mmol) was put in a flask with condenser. The flask was evacuated and 50 ml dry toluene and aniline (302 mg, 3.26 mmol) were added. The reaction mixture was heated to 90 °C overnight. The solution was run through a Si-plug using DCM/ petroleum ether (1:1 v/v) as eluent. The solvent was evaporated and the product was dissolved in hot EtOH. After cooling and storing in freezer over night the pure product was collected by filtration yielding 2.26 g (90% yield) as a white powder. ¹H-NMR (500 MHz, *acetone-d6*) δ ppm 0.99 (12H, m), 1.37 (12H, s), 1.52 (4H, m), 1.62 (4H, m), 1.77 (4H, m), 1.90 (4H, m), 4.06 (4H, t, J=6.45 Hz), 4.16 (4H, t, J=6.30 Hz), 6.52 (2H, d, J=1.65 Hz), 6.69 (2H, d, J=1.70 Hz), 6.99 (3H, m), 7.11 (2H, d, J=7.80 Hz), 7.21 (2H, d, J=1.85 Hz), 7.27 (2H, t, J=7.88 Hz), 7.86 (2H, d, J=8.20 Hz); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.14, 19.96, 20.18, 27.42, 32.25, 47.89, 68.33, 68.54, 98.74, 101.23, 119.12, 120.41, 122.81, 123.83, 123.86, 124.03, 130.00, 134.77, 146.58, 149.42, 154.96, 156.39, 157.32, 161.23.

N-(4-bromophenyl)-5,7-dibutoxy-N-(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-9H-fluoren-2-amine (4). **3** (3.22 g, 4.20 mmol) was dissolved in 100 ml DMF and the solution was cooled to 0 °C. NBS (747 mg, 4.20 mmol) was added and the reaction mixture was stirred at 0 °C for 1 h and then for 2 h at rt. Water was added to precipitate the product. The precipitate was filtered off and washed with MeOH. No further purifications were needed and **4** was collected as a white solid (2.79 g, 79% yield) ¹H-NMR (500 MHz, *acetone-d6*) δ ppm 1.00 (12H, m), 1.38 (12H, s), 1.52 (4H, m), 1.62 (4H, m), 1.77 (4H, m), 1.90 (4H, m), 4.06 (4H, t, J=6.43 Hz), 4.17 (4H, t, J=6.30 Hz), 6.52 (2H, d, J=1.55 Hz), 6.70 (2H, d, J=1.60 Hz), 7.01 (3H, m), 7.24 (2H, d, J=1.80 Hz), 7.39 (2H, d, J=8.85 Hz), 7.88 (2H, d, J=8.15 Hz); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.16, 19.98, 20.19, 27.40, 30.59, 32.26, 47.96, 68.37, 68.56, 98.77, 101.25, 119.59, 123.96, 124.32, 124.85, 132.83, 155.18, 156.51, 157.45, 161.40

5,7-dibutoxy-N-(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)-9,9-dimethyl-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-2-amine (5). **4** (2.80 g, 3.31 mmol) was dissolved in 60 ml dry THF and cooled to -78 °C. *n*-butyllithium (2.5 M in hexanes, 6.63 mmol) was added slowly and the reaction mixture was stirred at -78 °C for 1 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.54 g, 8.58 mmol) was added and the reaction was kept at -78 °C for 1 h and then at rt for 2 h. The reaction mixture was poured onto ice water and acidified by addition of

HCl (aq, 1M). The solution was extracted with water/diethyl ether. CH₃CN was added to the organic phase and the volatile organic solvents were evaporated making the product precipitating in the remaining CH₃CN. The product was collected by filtration giving a white solid (2.33 g, 79% yield) ¹H-NMR (500 MHz, *acetone-d6*) δ ppm 1.00 (12H, m), 1.32 (12H, s), 1.38 (12H, s), 1.52 (4H, m), 1.62 (4H, m), 1.77 (4H, m), 1.90 (4H, m), 4.06 (4H, t, J=6.43 Hz), 4.17 (4H, t, J=6.30 Hz), 6.53 (2H, d, J=1.60 Hz), 6.71 (2H, d, J=1.70 Hz), 7.04 (4H, m), 7.26 (2H, d, J=1.75 Hz), 7.61 (2H, d, J=8.45 Hz), 7.89 (2H, d, J=8.15 Hz); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.15, 19.97, 20.19, 25.21, 27.38, 32.24, 47.95, 68.34, 68.53, 84.16, 98.72, 101.20, 120.03, 120.25, 121.32, 123.91, 124.82, 135.55, 136.59, 145.85, 152.13, 155.09, 156.50, 157.46, 161.38.

6-(4-(bis(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene-2-carbaldehyde (6). **5** (2.33 g, 2.61 mmol), 4H-Cyclopenta[2,1-b:3,4-b']dithiophene (911 mg, 2.00 mmol), XPhos Pd G2 (47 mg, 0.06 mmol) was put in a round bottomed flask and evacuated to N₂ atmosphere. 25 ml degassed THF was added followed by the addition of K₃PO₄ (4 mmol, 0.5 M in water) using a syringe. The reaction mixture was stirred at rt for 10 min and then at 40 °C for 1.5 h. The reaction was extraction with water/EtOAc and the organic phase was evaporated. The crude product was redissolved in diethyl ether and EtOH was added to the solution. The ether was evaporated and the EtOH solution was left in freezer overnight to precipitate the product. The product was filtered off and washed with EtOH and dried with vacuum yielding **6** as a dark red solid (1.83 g, 80% yield). ¹H-NMR (400 MHz, *acetone-d6*) δ ppm 0.81 (6H, t, J=6.74 Hz), 1.01 (16H, m), 1.19 (12H, m), 1.41 (12H, s), 1.54 (4H, m), 1.63 (4H, m), 1.79 (4H, m), 1.92 (4H, m), 4.08 (4H, t, J=6.42 Hz), 4.19 (14H, t, J=6.26 Hz), 6.55 (2H, d, J=1.64 Hz), 6.73 (2H, d, J=1.68 Hz), 7.08 (2H, m), 7.14 (2H, d, J=8.68 Hz), 7.30 (2H, d, J=1.80 Hz), 7.54 (1H, s), 7.64 (2H, d, J=8.68 Hz), 7.92 (3H, m), 9.89 (1H, s); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.17, 14.26, 19.99, 20.20, 23.23, 25.23, 27.43, 32.26, 32.32, 38.39, 47.98, 55.13, 68.37, 68.57, 98.77, 101.25, 118.01, 119.73, 120.30, 123.21, 123.96, 124.52, 127.08, 128.35, 131.69, 134.24, 135.48, 144.35, 145.85, 147.81, 149.40, 150.26, 155.15, 156.52, 157.47, 158.48, 161.40, 164.67, 183.22. Some aliphatic protons are overlapping with the solvent peak at ppm 2.05

(E)-3-(6-(4-(bis(5,7-dibutoxy-9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (MKA253). **6** (1.83 g, 1.61 mmol), cyanoacetic acid (410 mg, 4.8 mmol) and piperidine (550 mg, 6.5 mmol) was dissolved in CHCl₃ (100 ml). The reaction mixture was refluxed overnight. The solvent was evaporated and the product was purified using chromatography. Two consecutive columns were performed where the first used DCM/EtOAc/TEA (6:1:1%) → DCM/MEOH (20:1). The second column used DCM/EtOC (2:1) → DCM/EtOAc/formic acid (1:1:1%). The collected fractions were extracted using acidic water (diluted HCl (aq)). The organic phase was evaporated and dried to give the product as a dark solid (1.38 g, 71% yield). ¹H-NMR (500 MHz, *acetone-d6*) δ ppm 0.79 (6H, t, J=6.80 Hz), 1.00 (16H, m), 1.17 (12H, m), 1.39 (12H, s), 1.52 (4H, m), 1.62 (4H, m), 1.78 (4H, m), 1.90 (4H, m), 4.06 (4H, t, J=6.43 Hz), 4.17 (4H, t, J=6.28 Hz), 6.54 (2H, s), 6.71 (2H, m), 7.07 (2H, m), 7.13 (2H, d, J=8.60 Hz), 7.29 (2H, d, J=1.50 Hz), 7.56 (1H, s), 7.65 (2H, d, J=8.65 Hz), 7.91 (3H, m), 8.42 (1H, s); ¹³C NMR (125 MHz, *acetone-d6*) δ 14.17, 14.27, 19.98, 20.20, 23.23, 25.23, 27.41, 32.25, 38.41, 47.98, 55.01, 68.35, 68.55, 98.74, 101.22,

117.74, 118.00, 119.80, 120.26, 123.04, 123.96, 124.60, 127.16, 128.12, 134.33, 135.55, 136.91, 145.75, 148.03, 149.57, 150.41, 151.64, 155.15, 156.51, 157.46, 158.73, 161.40, 164.54, 165.58.

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