Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Design of cyclopentadithiophene-based small organic molecules as hole selective layer for perovskite solar cells

Laura Calio[a], Samrana Kazim[a,b], Manuel Salado[a,b], Iwan Zimmermand [d], Mohammad Khaja Nazeeruddin [d], and Shahzada Ahmad[a,b,c]*

[a]Abengoa Research, Abengoa, C/ Energía Solar nº 1, Campus Palmas Altas-41014, Sevilla, Spain.

[b]Basque Center for Materials, Applications and Nanostructures, Bld. Martina Casiano, UPV/EHU Science Park, Barrio Sarriena s/n, 48940 Leioa, Spain Tel: +34 946128811

Email:shahzada.ahmad@bcmaterials.net

[c]IKERBASQUE, Basque Foundation for Science, Bilbao, 48013, Spain

[d]Group for Molecular Engineering of Functional Materials, Swiss Federal Institute of Technology Lausanne, EPFL Valais Wallis, CH-1951 Sion, Switzerland.

Corresponding Author

E-mail: shahzada.ahmad@bcmaterials.net, Tel: +34 946128811

Instrumentation Current density–voltage (*J–V*) curves were recorded with a Keithley 2400 source-measurement-unit under AM 1.5 G, 100 mW cm^2 illumination using a class AAA solar simulator (ORIEL, 94023 A, using 450 W xenon lamp as source). Light output power was calibrated using a NREL certified calibrated monocrystalline silicon solar cell. A black metal mask (0.16 cm^2) was used over the square solar cell active area (0.5 cm^2) to reduce the influence of scattered light. Photovoltaic parameters including J_{SC}, V_{OC}, fill factor (FF), and power conversion efficiency (PCE) were extracted from the photocurrent–voltage (*J–V*) curves of the solar cells (Active surface area: 0.16 cm^2, scan rate: 100 mV s^{-1}, pre-sweep delay: 10 s). The IPCE measurements were performed using a Newport 150 W Xenon lamp coupled to an Oriel Cornerstone 260 motorized 1/4 m monochromator as the light source, and a 2936-R power meter to measure the short circuit current. Absorption spectra were recorded for the perovskites by using an Agilent Cary 60 spectrophotometer. Cyclic voltammetry was done in a conventional three-electrode cell using an analyzer module (PGSTAT302N/FRA2, Autolab) over dichloromethane and deaerated sample solutions containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as supporting electrolyte at a scan rate of 50 mV/s. A glassy carbon working electrode, platinum (diam. 1.0 mm, 99.9 % trace metals basis, Sigma-Aldrich) wire counter and reference electrodes were used with ferrocene as an internal standard for all the measurements. Cross-sectional scanning probe electron images were performed by using a Hitachi S-4800 SEM.

Table S1. Current–voltage (*J–V*) characteristics of PSC-based devices with **CDTh 0**

Perovskite	**HTM**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
$(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$	**CDTh 0**	0.83	19.58	52.64	8.57
$MAPbI_3$		0.83	13.98	31.73	3.72

Table S2 Summary of the optical, electrochemical and thermal properties of **CDTh 0**

HTM	**λ_{max}(nm)**	**λ_{onset}(nm)**	**E_g (eV)**	**HOMO**	**LUMO**	**T_d(°C)**	**T_g (°C)**

				(eV)	(eV)		
CDTh 0	435	496	2.50	-5.39	-2.89	150	200

The electrochemical properties of the novel molecules were investigated using cyclic voltammetry (CV) experiments, (Figure S1b) measured in dichloromethane at room temperature [$c \sim 1 \cdot 10^{-3}$ M] with TBAPF [0.1 M] as supporting electrolyte. The highest occupied molecular orbital (HOMO) energy level was estimated from the equation $EHOMO = - 4.4 – (E_{ox} – E_{1/2}(Fc/Fc^{+}))$, where E_{ox} is the onset oxidation potential (vs. Fc/Fc^{+}). The lowest unoccupied molecular orbital (LUMO) levels were calculated from HOMO and E_g.

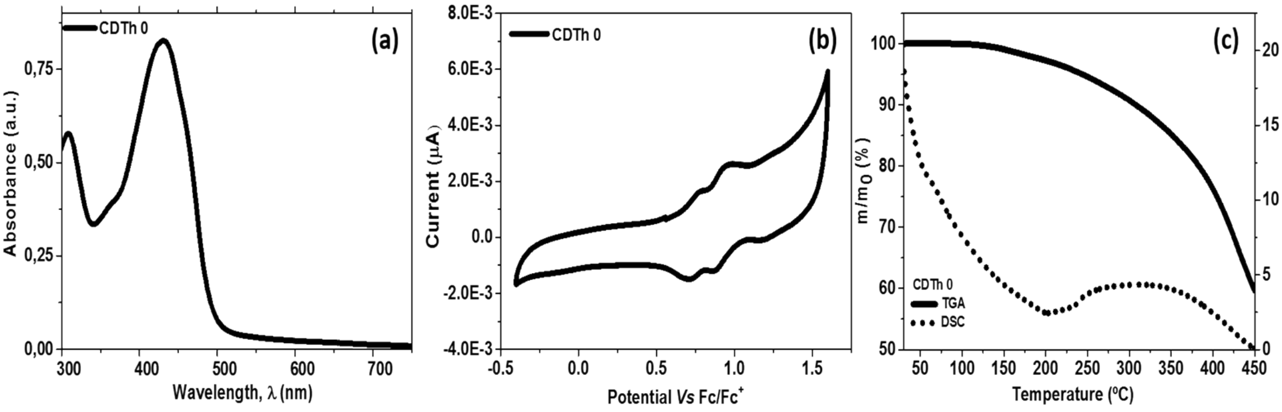


Figure S1(a) Normalized UV-vis absorption, (b) Cyclic voltammogram *Vs.* Fc/Fc^{+} in DCM at room temperature [$c \sim 1 \cdot 10^{-3}$ M] with TBAPF [0.1 M] as supporting electrolyte (c) Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves recorded for **CDTh 0**.

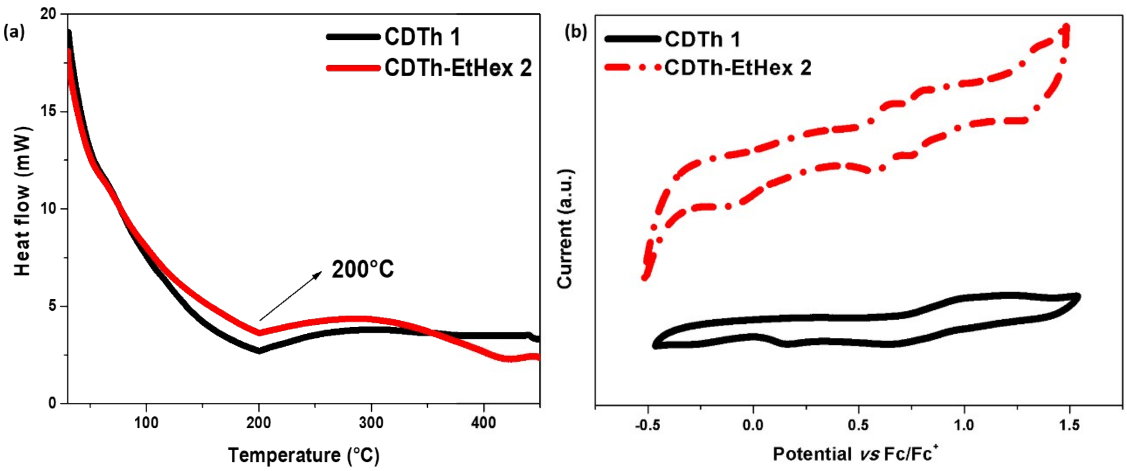


Figure S2 (a) Differential scanning calorimetry recorded for **CDTh 1** and **CDTh-EtHex 2** under N_2 atmosphere at a heating rate of 10°C/min. (b) Cyclic voltammogram of **CDTh 1** and **CDTh-EtHex 2** Vs. Fc/Fc^+ in DCM at room temperature [$c \sim 1 \cdot 10^{-3}$ M] with TBAPF [0.1 M] as supporting electrolyte.

Table S3 Statistical data for current–voltage (*J–V*) characteristics of $MAPbI_3$- and $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$-based devices with **CDTh 1** and **CDTh-EtHex 2** and Spiro-OMeTAD as HTM for comparison, calculated from 6 devices for each configuration.

Perovskite	**HTM**	**V_{OC} (V)**	**J_{SC} (mA/cm^2)**	**FF (%)**	**PCE (%)**
$(FAPbBr_3)_{0.85}(MAPbI_3)_{0.15}$	**CDTh 1**	0.99±0.03	20.90±0.78	66.38±1.46	13.77±0.75
$MAPbI_3$		1.03±0.02	21.10±0.52	68.05±2.25	14.78±0.37
$(FAPbBr_3)_{0.85}(MAPbI_3)_{0.15}$	**CDTh-EtHex 2**	0.97±0.03	20.40±0.53	66.59±3.74	13.20±0.58
$MAPbI_3$		1.03±0.03	20.68±0.69	70.73±3.69	15.15±0.42
$(FAPbBr_3)_{0.85}(MAPbI_3)_{0.15}$	**Spiro-OMeTAD**	1.04±0.02	21.38±0.13	71.22±3.83	15.77±0.47
$MAPbI_3$		1.02±0.03	21.24±0.36	71.53±4.09	15.48±0.47

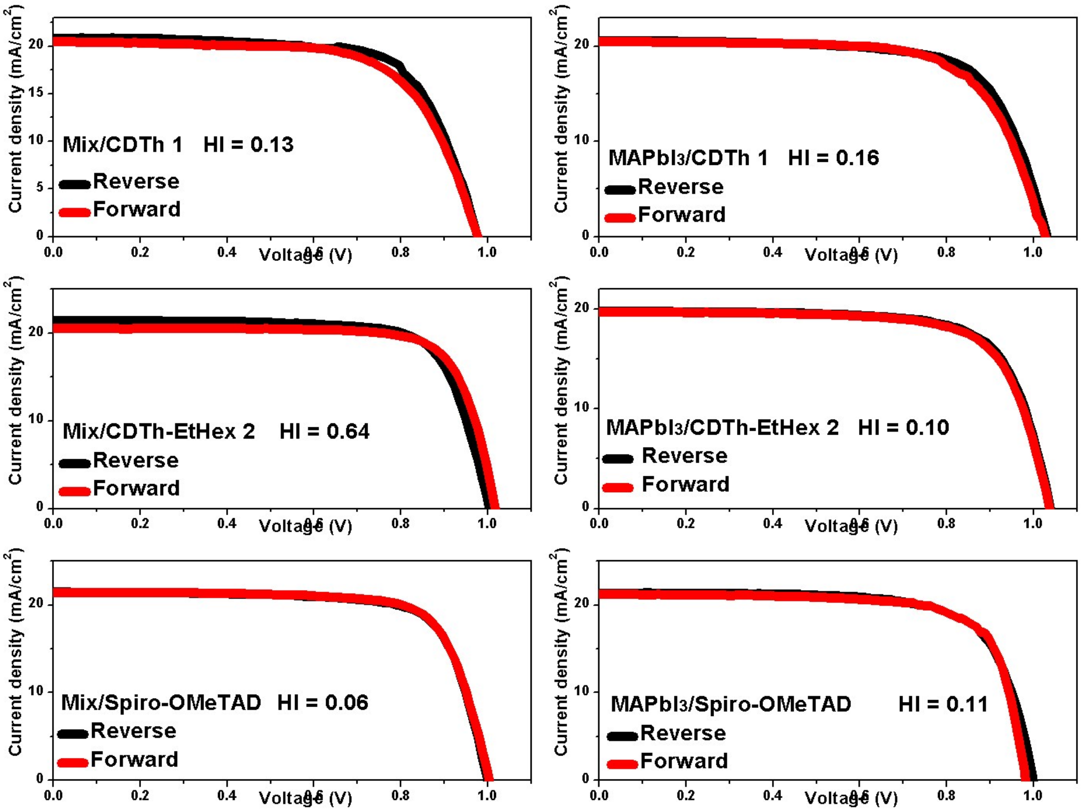


Figure S3 *J-V* curves recorded in forward (red lines) and reverse (black lines) bias for the devices, and the calculated HI for each configuration.

Table S4 Photovoltaic parameter for calculated from reverse and forward scan for each configuration.

Configuration		V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Mix/CDTh 1	Reverse	0.98	20.81	70.63	14.35
	Forward	0.98	20.59	69.03	13.94
MAPbI$_3$/CDTh 1	Reverse	1.026	20.51	68.49	14.49
	Forward	1.03	20.53	70.84	15.01
Mix/CDTh-EtHex 2	Reverse	1	20.51	66.86	13.77
	Forward	0.99	20.61	64.89	13.29
MAPbI$_3$/CDTh-EtHex 2	Reverse	1.02	19.55	77.69	15.51
	Forward	1.02	20.72	70.78	14.95
Mix/Spiro-OMeTAD	Reverse	1	20.41	75.54	16.30
	Forward	1	21.43	75.24	16.18
MAPbI$_3$/Spiro-OMeTAD	Reverse	0.98	21.16	78.08	16.19
	Forward	0.98	21.33	74.32	15.69

The hysteresis index (HI) have been calculated by the formula reported by Kim et al.[1], i.e.:

$$HI = \frac{J_{RS}(0.8\,V_{OC}) - J_{FS}(0.8\,V_{OC})}{J_{RS}(0.8\,V_{OC})}$$

where, J_{RS}(0.8Voc) and J_{FS} (0.8Voc) represent the photocurrent density at 80% of the open circuit voltage for the reverse and forward bias measurements, respectively.

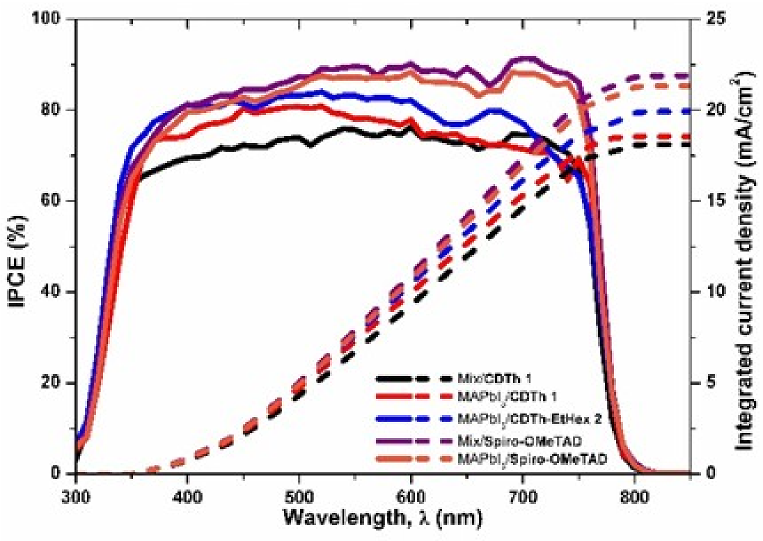


Figure S4 Incident photon-to-current conversion efficiency (IPCE) (solid lines) and integrated current density (dashed lines) reported for the different configuration of PSCs.

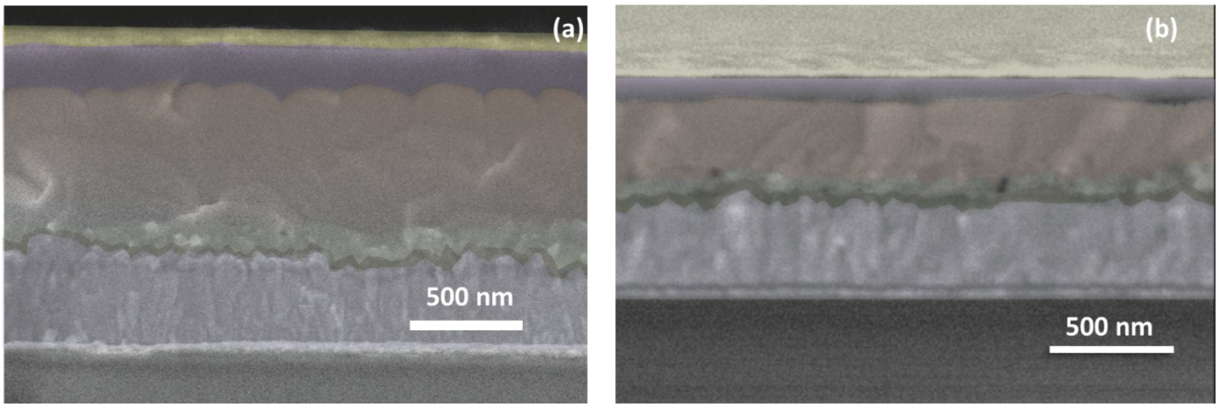


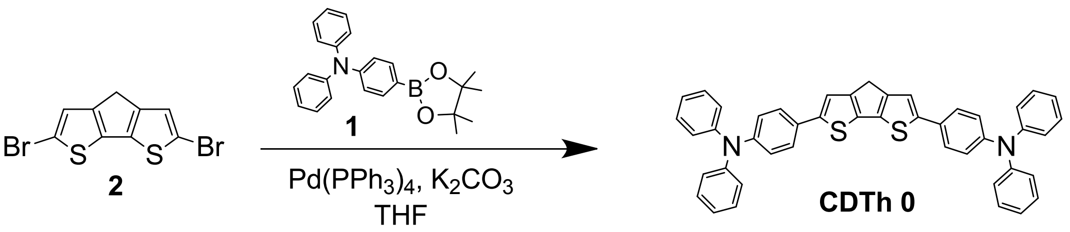
Figure S5 Cross-sectional SEM images of (a) mixed perovskite/Spiro-OMeTAD; (b) $MAPbI_3$/Spiro-OMeTAD.

---

[1] Kim, H. S. & Park, N.-G. Parameters Affecting I-V Hysteresis of CHNH3PbI3 Perovskite Solar Cells: Effects of Perovskite Crystal Size and Mesoporous TiO_2 Layer. *J. Phys. Chem. Lett.* **5,** 2927–2934 (2014).

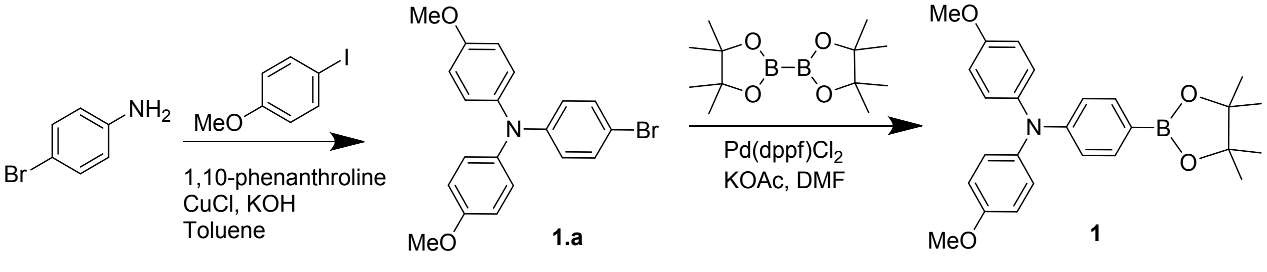
Synthesis of 4,4'-(4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl) bis (N,N-diphenylaniline)

CDTh 0:



compound 2 (80 mg, 0.24 mmol), compound 1 (4-(diphenylamino) phenylboronic acid pinacol ester) (0.15 g, 0.66 mmol), $Pd(PPh_3)_4$ (29 mg, 0.024 mmol) and K_2CO_3 (2M, 3 mL) were dissolved in THF (20 mL). The reaction mixture was stirred at reflux in the dark for 12 h, then was let to cool down and poured into water. The organic layer was dried over $MgSO_4$, concentrated and the residue mixture was purified by column chromatography on silica gel with CH_2Cl_2/hexane = 2:1 as eluent to obtain the product as bright orange solid (0.12 g, 75%) MW: 664.89 g/mol. ^{1}H RMN (400 MHz, CD_2Cl_2) δ = 7.47-6.88 (m, 28H, PhH); 7.36 (s, 2H, cyclopentaditiophene); 3.83 (s, 2H, cyclopentaditiophene);

Synthesis of intermediate 1:



1°step: synthesis of 4-Bromo-*N,N*-bis(4-methoxyphenyl)aniline (**1.a**)

4-bromoaniline (1.00 g, 5.81 mmol), 4-iodoanisole (3.40 g, 14.53 mmol), 1,10-phenanthroline (0.04 g, 0.22 mmol), CuCl (0.2 g, 0.21 mmol) and KOH (2.61 g, 46.51 mmol) were dissolved in 30 mL of toluene, and the mixture was stirred at 100°C for a day under N_2 atmosphere. Then the reaction mixture was cooled to room temperature and solvent was evaporated. The residue was diluted with CH_2Cl_2 (300 mL) and washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to afford the crude compound, which was purified by column chromatography (eluent: 20% CH_2Cl_2/Hexane) to obtain the pure compound 1.a as a white solid (2.03 g, 91%). ^{1}H NMR (300 MHz, DMSO-d6, ppm): δ 7.29 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 9.0 Hz,4H), 6.90 (d, J = 9.0 Hz, 4H), 6.67 (d, J = 9.0 Hz, 2H), 3.73 (s, 6H).

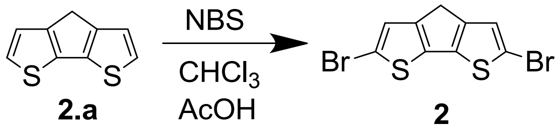
Reagent	**Amount**	**Price (€/g or €/mL)**	**Total price €**
4-bromoaniline	1.00 g	0.4	0.4
4-iodoanisole	3.40 g	1.2	4.08
1,10-phenanthroline	0.04 g	4.6	0.18
CuCl	0.2 g	1.12	0.22
KOH	2.61 g	0.056	0.15
Toluene	30 mL	0.021	0.63
Silica gel	100 g	0.037	3.7
dichloromethane	450 mL	0.023	1.04
Hexane	400 mL	0.01	4.00
Total cost	14.40 €		
Amount	2.03 g		
Cost for gram	7.09 €/g		

2°step: synthesis of 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (**1**)

4-Bromo-N,N-bis(4-methoxyphenyl)aniline (**1.a**) (1.00 g, 2.60 mmol), Bis(pinacolato)diboron (0.99 g, 3.90 mmol), Pd(dppf)Cl_2 (0.19 g, 0.26 mmol) and KOH (0.48 g, 7.80 mmol) were dissolved in 30 mL of DMF, and the mixture was stirred at 80°C for a day under N_2 atmosphere. Then the reaction mixture was cooled to room temperature, filtered through celite, diluted with CH_2Cl_2 (100 mL) and washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to afford the crude compound, which was purified by column chromatography (eluent: 60% CH_2Cl_2/Hexane) to obtain the pure compound 1.a as a white solid (0.97g, 86%). ^{1}H-NMR ($CDCl_3$): 7.57-7.54(m, 2H); 7.11-7.08 (m, 4H); 6.96-6.93 (m, 4H); 6.81-6.78 (m, 2H); 3.82 (s, 6H); 1.32 (s, 12H) ppm.

Reagent	**Amount**	**Price (€/g or €/mL)**	**Total price €**
1.a	1.00 g	7.09	7.09
Bis(pinacolato)diboron	0.99 g	6.50	6.44
Pd(dppf)Cl_2	0.19 g	15.44	2.93
KOH	0.48 g	0.056	0.03
DMF	30 mL	0.06	1.80
Silica gel	100 g	0.037	3.70
DCM	400 mL	0.023	9.20
Hexane	200 mL	0.01	2.00
Total cost	33.19 €		
Amount	0.97 g		
Cost for gram	34.22 €/g		

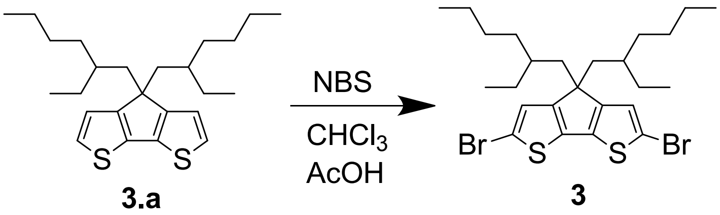
Synthesis of intermediate 2,6-dibromo-4H-cyclopenta[1,2-b:5,4-b']dithiophene (**2**):



4H-Cyclopenta[1,2-b:5,4-b']dithiophene (1.00 g, 5.61 mmol) was dissolved in 60 mL of a mixture of chloroform and acetic acid at 0°C, then N-bromosuccinimide (2.09 g, 11.22 mmol) was added slowly. The reaction mixture was stirred for 1 hour at 0°C and then let to cool down at room temperature and stirred for 1 hour more. Then 100 mL of DCM was added, and the reaction mixture was and washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to afford the crude compound, which was purified by column chromatography (eluent: Hexane) to obtain the pure compound 2 as a yellow solid (1.85 g, 98%). ^{1}H-NMR (CD_2Cl_2): 7.2 (s, 2H); 3.81 (s, 2H).

Reagent	**Amount**	**Price (€/g or €/mL)**	**Total price €**
2.a	1.00 g	98.6	98.6
NBS	2.09 g	0.11	0.23
$CHCl_3$	30 mL	0.021	0.63
AcOH	30 mL	0.051	1.53
Silica gel	100 g	0.037	3.7
DCM	100 mL	0.023	2.3
Hexane	400 mL	0.01	4.00
Total cost	110.99 €		
Amount	1.85 g		
Cost for gram	59.99 €/g		

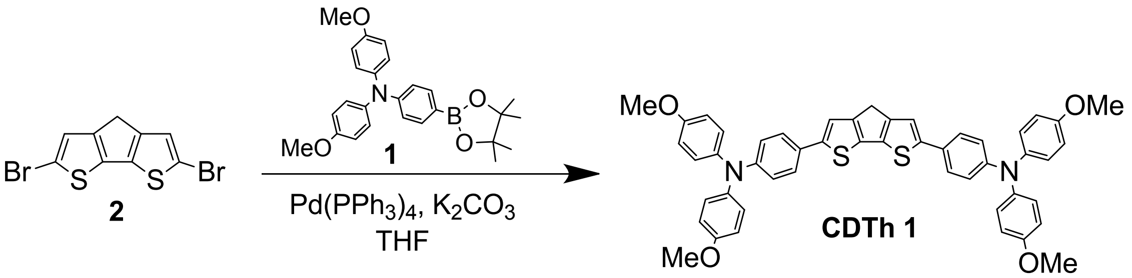
Synthesis of intermediate 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene (**3**):



4H-Cyclopenta[1,2-b:5,4-b']dithiophene (1.00 g, 2.48 mmol) was dissolved in 60 mL of a mixture of chloroform and acetic acid at 0°C, then N-bromosuccinimide (0.93 g, 11.22 mmol) was added slowly. The reaction mixture was stirred for 1 hour at 0°C and then let to cool down at room temperature and stirred for 1 hour more. Then 100 mL of DCM was added, and the reaction mixture was and washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated to afford the crude compound, which was purified by column chromatography (eluent: Hexane) to obtain the pure compound 2 as a green oil (1.11 g, 80%).^{1}H-NMR (CD_2Cl_2): 7.4 (s, 2H); 1.57-0.92 (m, 34H).

Reagent	**Amount**	**Price (€/g or €/mL)**	**Total price €**
3.a	1.00 g	104.00	104.00
NBS	0.93 g	0.11	0.10
$CHCl_3$	30 mL	0.021	0.63
AcOH	30 mL	0.051	1.53
Silica gel	100 g	0.037	3.7
DCM	100 mL	0.023	2.3
Hexane	400 mL	0.01	4.00
Total cost	116.26 €		
Amount	1.11 g		
Cost for gram	104.74 €/g		

Synthesis of 4,4'-(4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) **CDTh 1**:

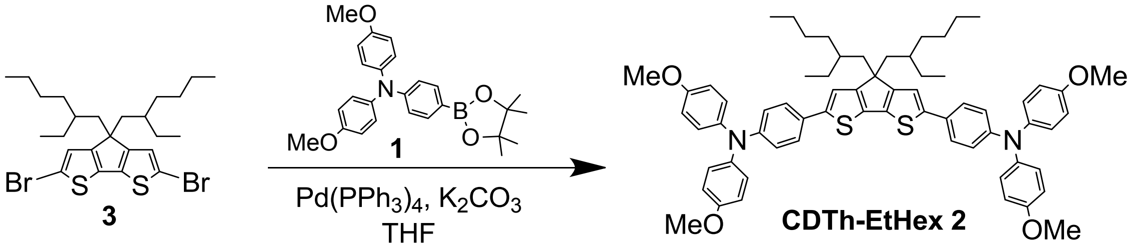


CDTh 1 was synthesized following the same procedure of CDTh 0, by using 2,6-dibromo-4H-cyclopenta[1,2-b:5,4-b']dithiophene, (150 mg; 0.28 mmol) and 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline as starting materials. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/hexane = 80:20 as eluent to obtain the product as a bright red solid (150 mg, Y = 80%). ^{1}H NMR (400MHz, CD_2Cl_2) δ = 7.47-7.35 (d, J = 8Hz; 4H, PhH); 7.36 (s, 4H, thiophene); 7.12-7.10 (d, 8H, PhH); 6.99-6.88 (m, 12H, PhH) 3.83 (s, 12H, OMe).

Reagent	Amount	Price (€/g or €/mL)	Total price €
2	0.1 g	59.99	5.99
1	0.29 g	34.22	9.92
$Pd(PPh_3)_4$	0.034 g	16.00	0.54
K_2CO_3	1.10 g	0.03	0.03
THF	20 mL	0.07	1.40
Silica gel	100 g	0.037	3.70
DCM	400 mL	0.023	9.20
Hexane	100 mL	0.01	1.00
Total cost	31.78 €		
Amount	0.19 g		

Cost for gram	167.26 €/g

Synthesis of 4,4'-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene-2,6-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) **CDTh-EtHex 2 :**



CDTh-EtHex 2 was synthesized by following the same procedure of CDTh 0, by using 2,6-dibromo-4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophene (80 mg; 0.143 mmol) and 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline as starting materials. The crude product was purified by column chromatography on silica gel with CH_2Cl_2/hexane = 80:20 as eluent to obtain the product as a bright red solid (105 mg, Y = 73%). ^{1}H-NMR (400MHz, CD_2Cl_2) δ = 7.48-7.47 (d, J = 4Hz; 4H, PhH); 7.42 (s, 2H, thiophene); 7.13-7.10 (d, 8H, PhH); 6.91-6.87 (m, 12H, PhH) 3.83 (s, 12H, OMe); 1.57-0.92 (m, 34H, ethylhexyl).

Reagent	Amount	Price (€/g or €/mL)	Total price €
3	0.15 g	104.74	15.71
1	0.26 g	34.22	8.89
$Pd(PPh_3)_4$	0.03 g	16.00	0.48
K_2CO_3	1.10 g	0.03	0.03
THF	20 mL	0.07	1.40
Silica gel	100 g	0.037	3.70
DCM	200 mL	0.023	4.60
Hexane	100 mL	0.01	1.00

Total cost	35.81 €
Amount	0.20 g
Cost for gram	179.05 €/g

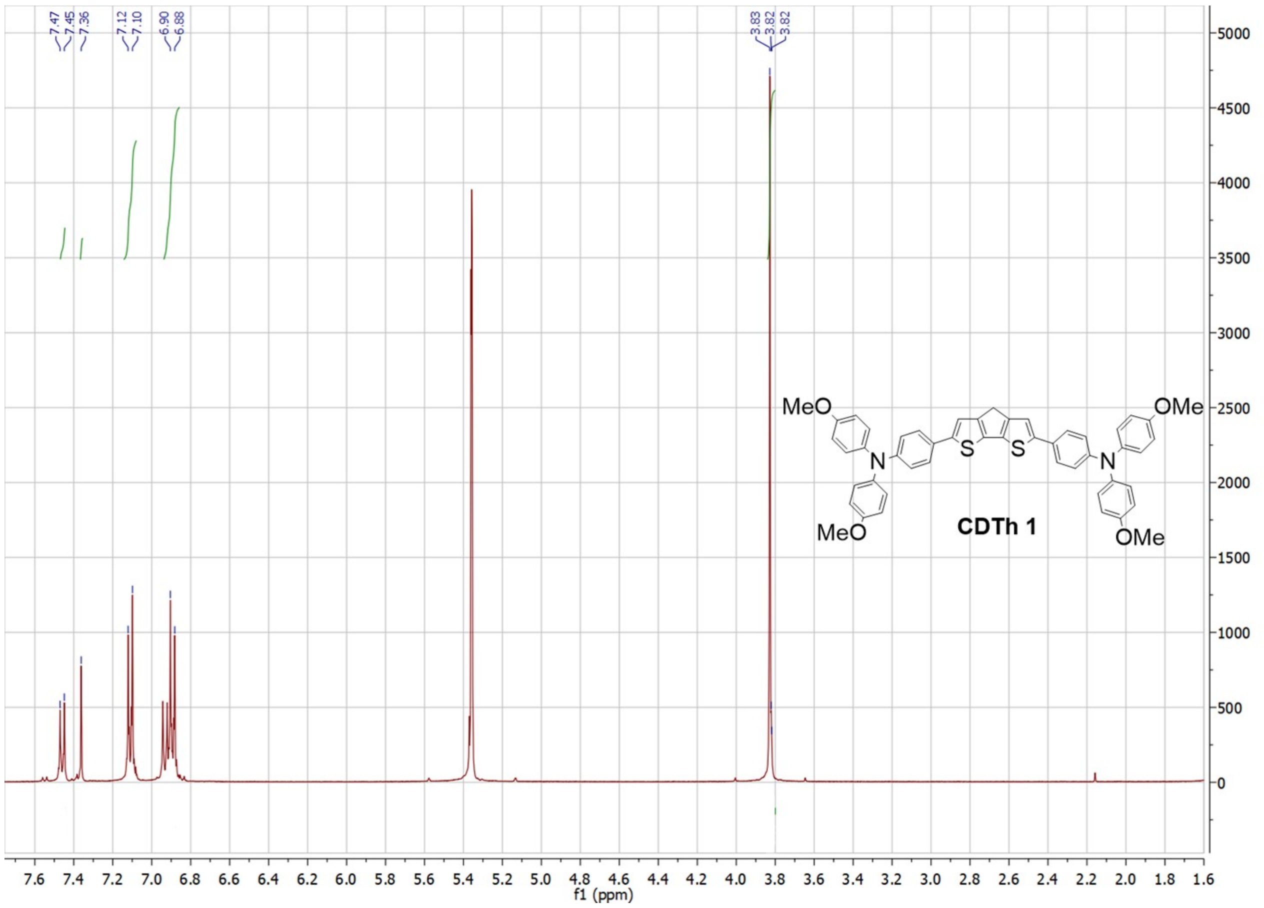


Figure S5 ^{1}H-NMR spectrum of CDTh-1 recorded in CD_2Cl_2.

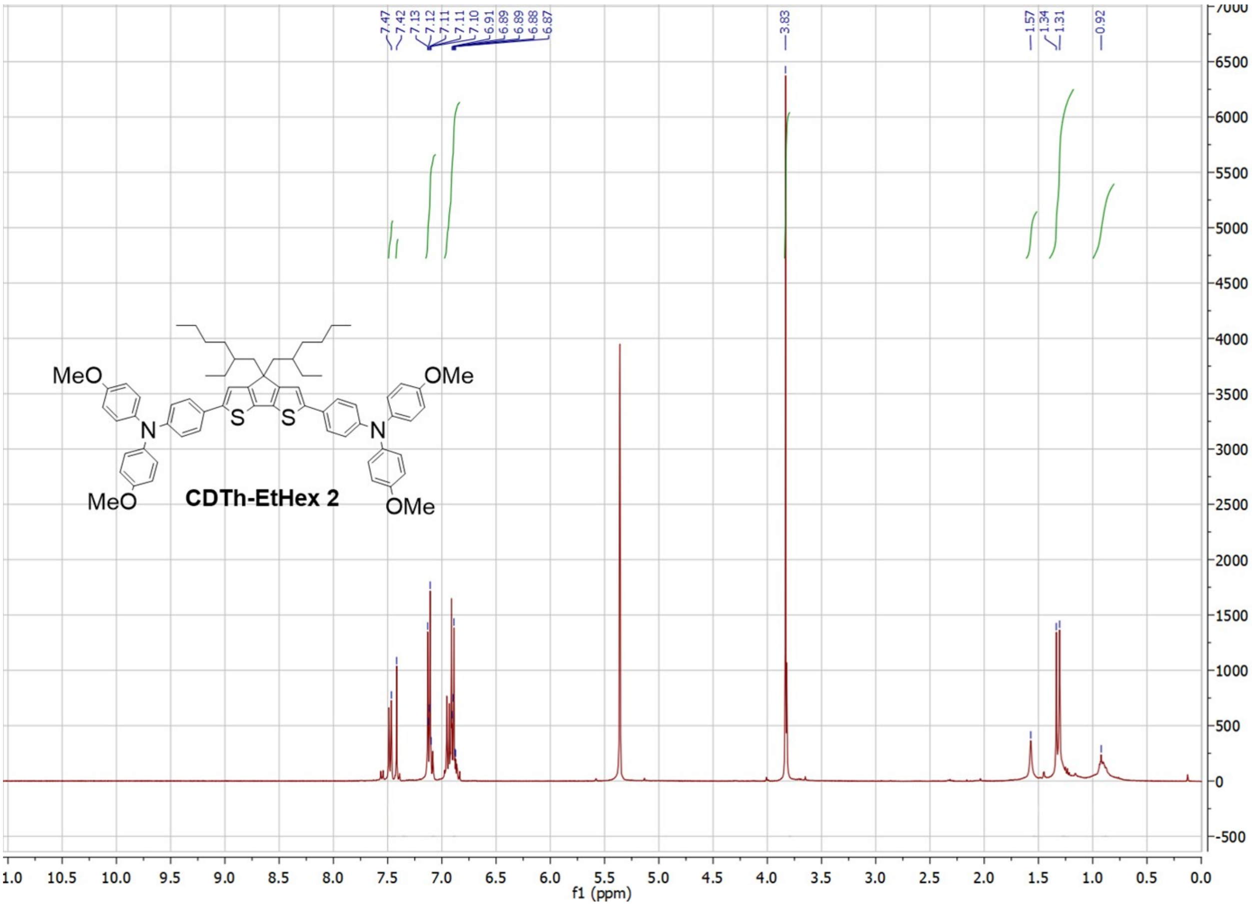


Figure S6. ^{1}H-NMR spectrum of CDTh-EtHex 2 recorded in CD_2Cl_2.