

Supplementary Data

Dopant-free Fluorene Based Dimers linked with Thiophene Units as Prospective Hole Transport Materials for Sb₂S₃ Solar Cells

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General

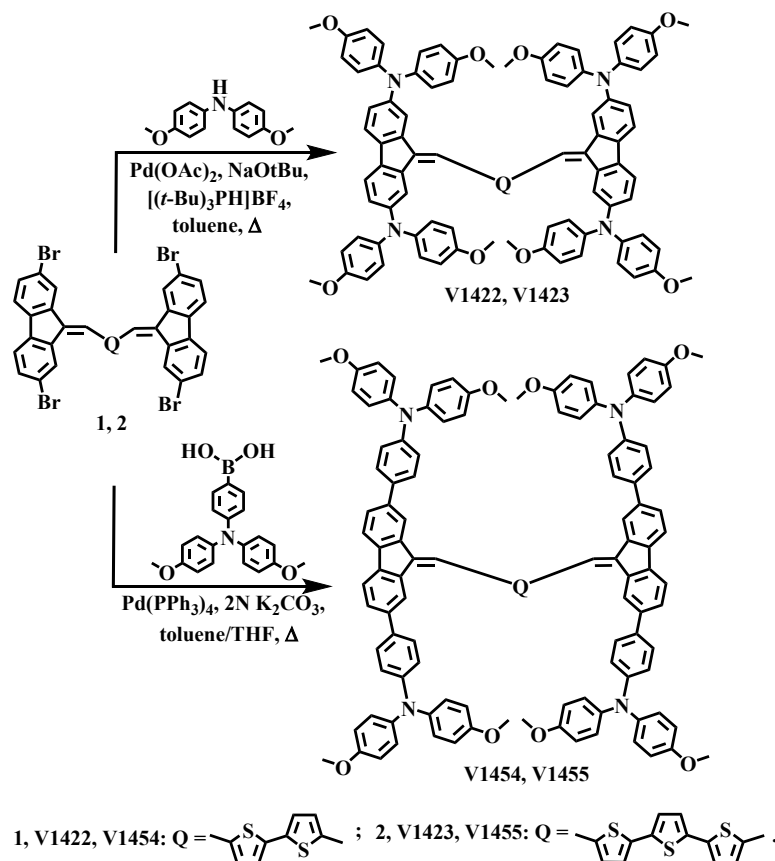
Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. ¹H NMR and ¹³C NMR spectra were collected at 400 and 101 MHz, respectively on a Bruker Avance III spectrometer. The chemical shifts, expressed in ppm, were relative to tetramethylsilane (TMS). All the experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and developed with UV light. Silica gel (grade 9385, 230–400 mesh, 60 Å, Aldrich) was used for column chromatography. Elemental analysis was performed with an Exeter Analytical CE-440 elemental analyzer, Model 440 C/H/N.

Thermogravimetric analysis (TGA) was performed on a Q50 thermogravimetric analyser (TA Instruments) at a scan rate of 10 °C min⁻¹ under nitrogen atmosphere. The values are given for a weight-loss of 5% (*T*_{d5}). Differential scanning calorimetry (DSC) was performed on a TA Instruments Q2000 differential scanning calorimeter under nitrogen atmosphere. Heating and cooling rate is 10 °C min⁻¹.

UV–vis spectral analysis of the sample in solution (THF, 10⁻⁴ mol L⁻¹) was performed on a Perkin Elmer Lambda 35 UV/VIS spectrophotometer. The layer thickness of the solution is *d* = 1 mm. Diffraction grating crack width is 2 nm. Spectral recording speed is 2 nm s⁻¹. The wavelength λ is given in nm.

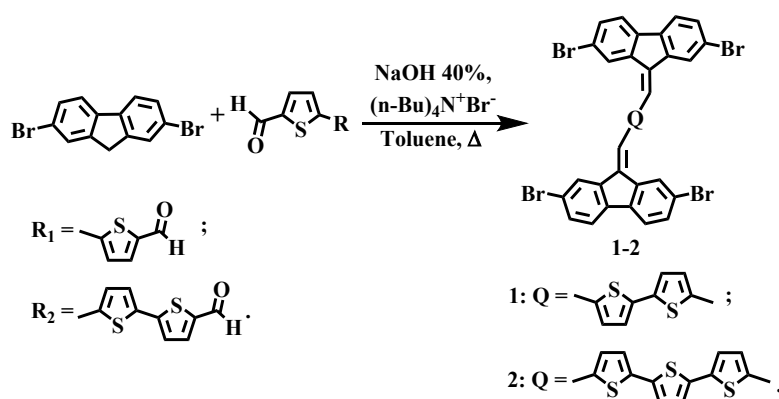
V1422 and V1423 containing diphenylamine chromophores were obtained through palladium cross-coupling reactions connecting the central dithiophene or trithiophene-based fluorenylidene-

terminated unit with 4,4'-dimethoxydiphenylamine (**Scheme 1**). New p-type photoconductors - V1454 and V1455 with triphenylamine side fragments were obtained under Suzuki coupling reaction conditions (**Scheme 1**). The starting compounds **1** and **2** were synthesized by a condensation reaction of 2,7-dibromofluorene with corresponding thiophene dicarbaldehyde catalyzed by a base.



Scheme 1. Synthesis route to the HTMs **V1422**, **V1423**, **V1454**, and **V1455**.

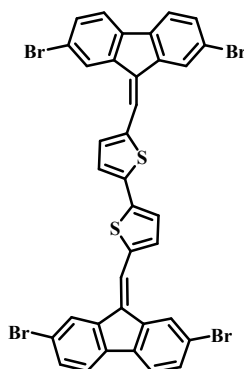
Detailed synthetic procedures



Scheme S1. Synthesis of the intermediates **1**, **2**.

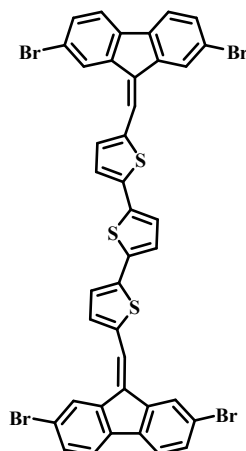
Detailed synthetic procedures

5,5'-Bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]-2,2'-bithiophene (1)



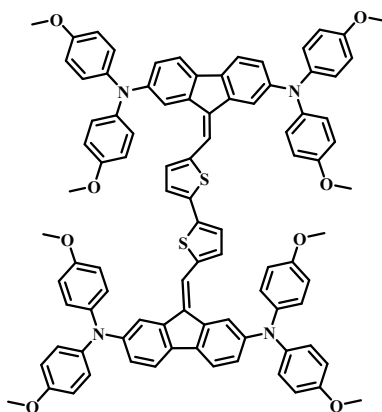
A mixture of [2,2'-bithiophene]-5,5'-dicarbaldehyde (0.5 g, 2 mmol), 2,7-dibromofluorene (1.62 g, 5 mmol), and toluene (10 mL) was stirred for 10 minutes. Afterwards, NaOH solution (10 mL, 40% W/W) and tetrabutylammonium bromide (0.25 g, 0.76 mmol) were added and the reaction mixture was heated at reflux for 4 hours (TLC control, acetone/*n*-hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were washed with water, ethanol and ethyl acetate to obtain terracotta crystals ($M_p = 326\text{--}327\text{ }^\circ\text{C}$). Yield 1.1 g (66%). In the next step crude crystals were used without any further purification.

5,5''-Bis[(2,7-dibromo-9H-fluoren-9-ylidene)methyl]-2,2':5,2''-terthiophene (2)



A mixture of [2,2':5,2''-terthiophene]-5,5''-dicarbaldehyde (0.5 g, 1.6 mmol), 2,7-dibromofluorene (1.3 g, 4 mmol), and toluene (9 mL) was stirred for 10 minutes. Afterwards, NaOH solution (9 mL, 40% W/W) and tetrabutylammonium bromide (0.2 g, 0.06 mmol) were added and the reaction mixture was heated at reflux for 4 hours (TLC control, acetone/*n*-hexane 1:1.5). After cooling to room temperature, the reaction mixture was filtered off and crude crystals were washed with water, ethanol and ethyl acetate to obtain dark red crystals. Yield 1 g (69%). In the next step crude crystals were used without any further purification.

9,9'-[(2,2'-Bithiophene)-5,5'-diylbis(methanylylidene)]bis[*N*²,*N*²,*N*⁷,*N*⁷-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine] (V1422)



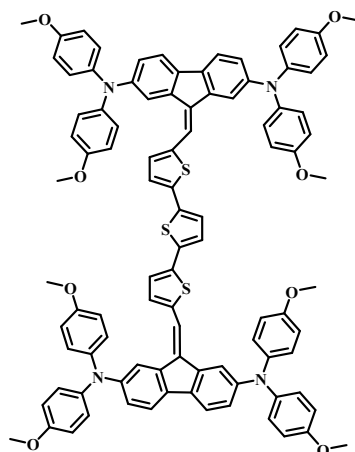
A mixture of 5,5'-bis((2,7-dibromo-9*H*-fluoren-9-ylidene)methyl)-2,2'-bithiophene (**1**) (0.45 g, 0.5 mmol), bis(4-methoxyphenyl)amine (0.69 g, 3 mmol), and anhydrous toluene (6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.007 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.017 g, 0.06 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 7:18, v:v). The crude product was recrystallized from toluene to obtain brown crystals. Yield 0.5 g (70%). M_p = 273–274 °C.

¹H NMR (400 MHz, CDCl₃) δ: 7.85 (s, 2H), 7.57 – 6.52 (m, 48H), 3.79 (s, 12H), 3.70 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 138.6, 138.3, 136.9, 135.1, 132.8, 132.2, 131.2, 130.7, 130.3, 129.7, 129.1, 128.3, 125.8, 124.3, 124.0, 123.8, 123.5, 119.6, 119.4, 118.6, 118.4, 118.3, 115.3, 114.9, 114.6, 114.4, 114.2, 114.0, 55.52, 55.5.

Anal. Calcd. For: C₉₂H₇₄N₄O₈S₂: C 77.40; H 5.22; N 3.92; O 8.96; S 4.49; found: C 77.35; H 5.26; N 3.89.

9,9'-[(2,2':5',2''-Terthiophene)-5,5'-diylbis(methanylylidene)]bis[*N*²,*N*²,*N*⁷,*N*⁷-tetrakis(4-methoxyphenyl)-9*H*-fluorene-2,7-diamine] (V1423)



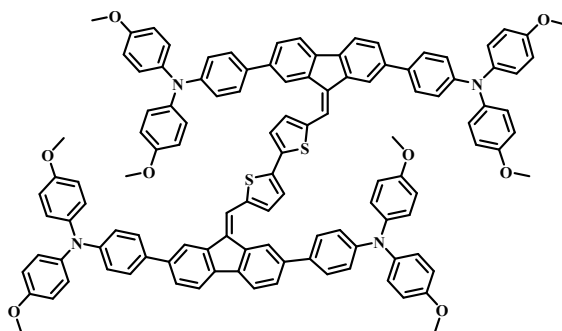
A mixture of 5,5''-bis((2,7-dibromo-9*H*-fluorene-9-ylidene)methyl)-2,2':5,2''-terthiophene (**2**) (0.45 g, 0.5 mmol), bis(4-methoxyphenyl)amine (0.69 g, 3 mmol), and anhydrous toluene (6 mL) was purged with Ar for 30 minutes. Afterwards, palladium (II) acetate (0.007 g, 0.03 mmol) and tri-*tert*-butylphosphonium tetrafluoroborate (0.017 g, 0.06 mmol) was added and the reaction mixture was stirred for 10 minutes under argon. Then, sodium *tert*-butoxide (0.29 g, 3 mmol) was added and the mixture was heated at reflux for 5 hours (TLC control, acetone/*n*-hexane 1:4). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 9:16, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a red powder was filtered off, washed with ethanol, and dried. Yield 0.48 g (64%).

¹H NMR (400 MHz, CDCl₃) δ: 7.83 (s, 2H), 7.59 – 6.32 (m, 50H), 3.79 (s, 12H), 3.75 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 151.1, 141.0, 140.8, 138.6, 138.1, 137.0, 136.2, 135.6, 134.9, 131.0, 125.0, 123.9, 119.2, 118.4, 118.3, 118.2, 114.8, 114.7, 114.6, 114.2, 113.8, 103.6, 77.4, 77.0, 76.7, 55.5, 55.48.

Anal. Calcd. For: C₉₆H₇₆N₄O₈S₃: C 76.37; H 5.07; N 3.71; O 8.48; S 6.37; found: C 76.29; H 5.09; N 3.75.

4,4',4'',4'''-((([2,2'-bithiophene]-5,5'-diylbis(methanylylidene))bis(9*H*-fluorene-2,7-diyl-9-ylidene))tetrakis(*N,N*-bis(4-methoxyphenyl)aniline) (V1454)



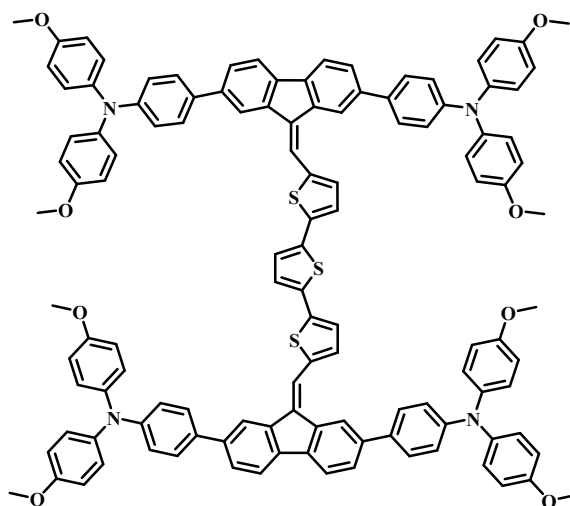
A mixture of 5,5'-bis((2,7-dibromo-9*H*-fluoren-9-ylidene)methyl)-2,2'-bithiophene (**1**) (0.5 g, 0.6 mmol), 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.6 g, 6 mmol), and anhydrous toluene/THF (16.6 mL/33.4 mL) was purged with Ar for 20 minutes. Afterwards, tetrakis(triphenylphosphine)palladium (0.8 g, 0.7 mmol) and 2M K₂CO₃ solution (20 mL) was added, and the reaction mixture was heated at 90 °C for 24 hours (TLC control, THF/*n*-hexane 1:1). After cooling to room temperature, the reaction mixture was filtered through celite and extracted with ethyl acetate. Organic layer was dried over Na₂SO₄, filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 11:14, v:v). The crude product was recrystallized from toluene to obtain wine red crystals. Yield 0.5 g (48%). M_p = 295–296 °C.

¹H NMR (400 MHz, CDCl₃) δ: 8.50 (s, 2H), 7.80 (s, 2H), 7.62 (t, *J* = 9.0 Hz, 4H), 7.55 – 7.41 (m, 10H), 7.40 – 7.28 (m, 6H), 7.19 – 6.76 (m, 34H), 6.69 (d, *J* = 8.2 Hz, 8H), 3.78 (s, 12H), 3.61 (s, 12H).

¹³C NMR (101 MHz, CDCl₃) δ: 155.9, 141.0, 140.7, 140.6, 139.6, 139.4, 139.2, 139.0, 138.9, 137.3, 136.9, 136.2, 131.4, 127.5, 127.3, 126.6, 124.5, 122.7, 120.9, 120.4, 120.0, 119.8, 118.4, 118.2, 114.7, 114.6, 55.5, 55.4.

Anal. Calcd. For: C₁₁₆H₉₀N₄O₈S₂: C 80.44; H 5.24; N 3.23; O 7.39; S 3.70; found: C 80.40; H 5.26; N 3.24.

4,4',4'',4'''-([2,2':5',2''-terthiophene]-5,5''-diylbis(methanylylidene))bis(9*H*-fluorene-2,7-diyl-9-ylidene))tetrakis(*N*, *N*-bis(4-methoxyphenyl)aniline) (V1455)



A mixture of 5,5''-bis((2,7-dibromo-9*H*-fluoren-9-ylidene)methyl)-2,2':5',2''-terthiophene (**2**) (0.5 g, 0.5 mmol), 4-methoxy-*N*-(4-methoxyphenyl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (2.2 g, 5 mmol), and anhydrous toluene/THF (16.6 mL/33.4 mL) was purged with Ar for 20 minutes. Afterwards, tetrakis(triphenylphosphine)palladium (0.7 g, 0.6 mmol) and 2M K₂CO₃ solution (20 mL) was added, and the reaction mixture was heated at 90 °C for 24 hours (TLC control, THF/*n*-hexane 11:14). After cooling to room temperature, the reaction mixture was filtered through

celite and extracted with ethyl acetate. Organic layer was dried over Na_2SO_4 , filtered and the solvent was removed by vacuum rotary evaporation. The product was purified by column chromatography (eluent: THF/*n*-hexane 11:14, v:v). 20% solution of the final product in THF was poured with intensive stirring into a 15-fold excess of ethanol. The precipitate as a dark red powder was filtered off, washed with ethanol, and dried. Yield 0.4 g (42%).

^1H NMR (400 MHz, CDCl_3) δ : 8.57 (s, 2H), 7.79 (s, 2H), 7.63 (dd, $J = 13.4, 13.5$ Hz, 4H), 7.54 – 7.37 (m, 14H), 7.35 (d, $J = 3.7$ Hz, 2H), 7.12 – 6.91 (m, 28H), 6.83 (d, $J = 8.5$ Hz, 8H), 6.76 (d, $J = 8.5$ Hz, 8H), 3.78 (s, 12H), 3.69 (s, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ : 156.0, 148.1, 140.9, 140.7, 139.6, 139.5, 139.2, 139.0, 138.5, 137.2, 136.9, 136.4, 135.7, 133.4, 133.0, 131.6, 127.5, 127.3, 126.9, 126.8, 126.6, 125.0, 124.1, 122.6, 120.9, 120.8, 120.0, 119.8, 118.5, 118.2, 114.7, 55.5, 55.45.

Anal. Calcd. For: $\text{C}_{120}\text{H}_{92}\text{N}_4\text{O}_8\text{S}_3$: C 79.44; H 5.11; N 3.09; O 7.05; S 5.30; found: C 79.40; H 5.16; N 3.06.

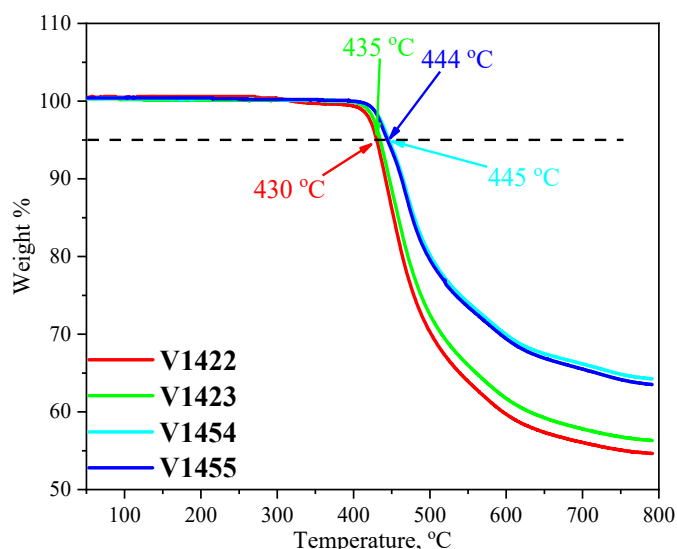
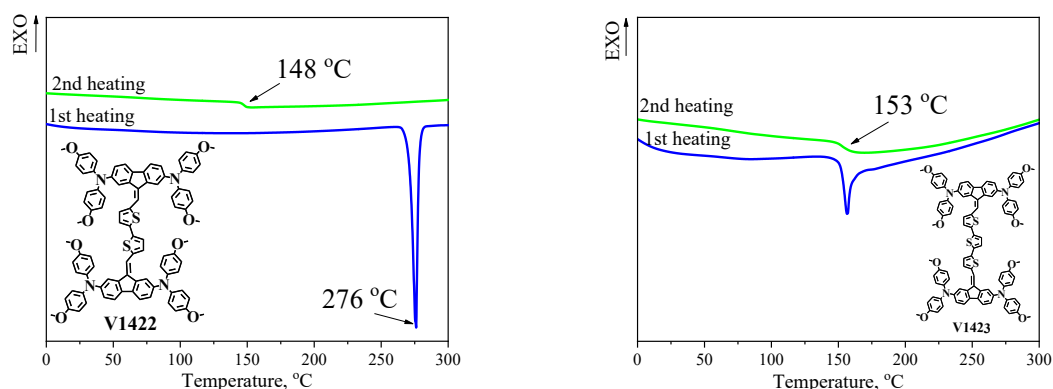


Figure S1. TGA heating curves of the HTMs (heating rate of $10\text{ }^\circ\text{C min}^{-1}$, N_2 atmosphere).



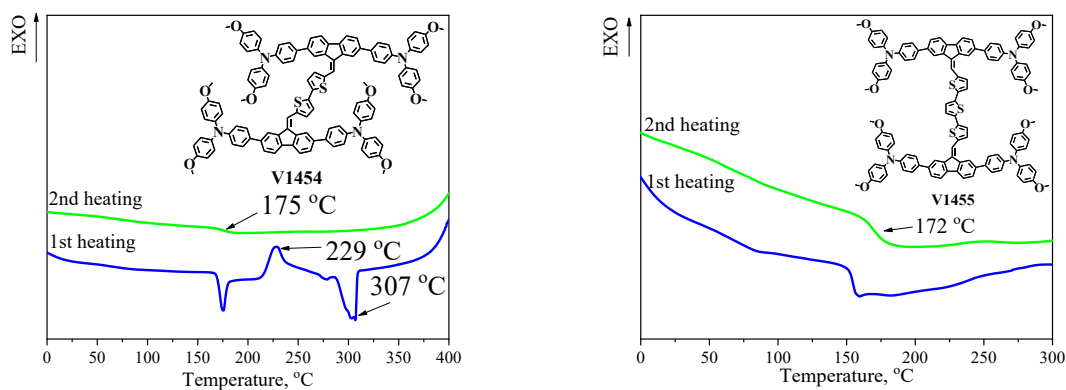


Figure S2. The first and second heating DSC curves of **V1422**, **V1423**, **V1454** and **V1455** HTMs.

The ultraviolet–visible (UV–vis) absorption spectra of the new HTMs were measured in a tetrahydrofuran (THF) solution (Fig. S3). The spectra of all compounds have two main absorption peaks at around 300 and 375 nm, which represent the π – π^* transitions of the side chromophores. As can be seen, the spectra of these molecules have an extra peak in the 425–550 nm range, which most likely corresponds to the π – π^* transitions with some charge transfer character, due to the electron-rich nature of thiophenes π systems. Comparison of the spectra of molecules featuring diphenylamine units in their side fragments (**V1422** and **V1423**) and molecules containing triphenylamine units (**V1454** and **V1455**) has revealed that the latter possess higher absorption. It can be assumed that this is due to the presence of an additional phenyl fragment in these compounds.

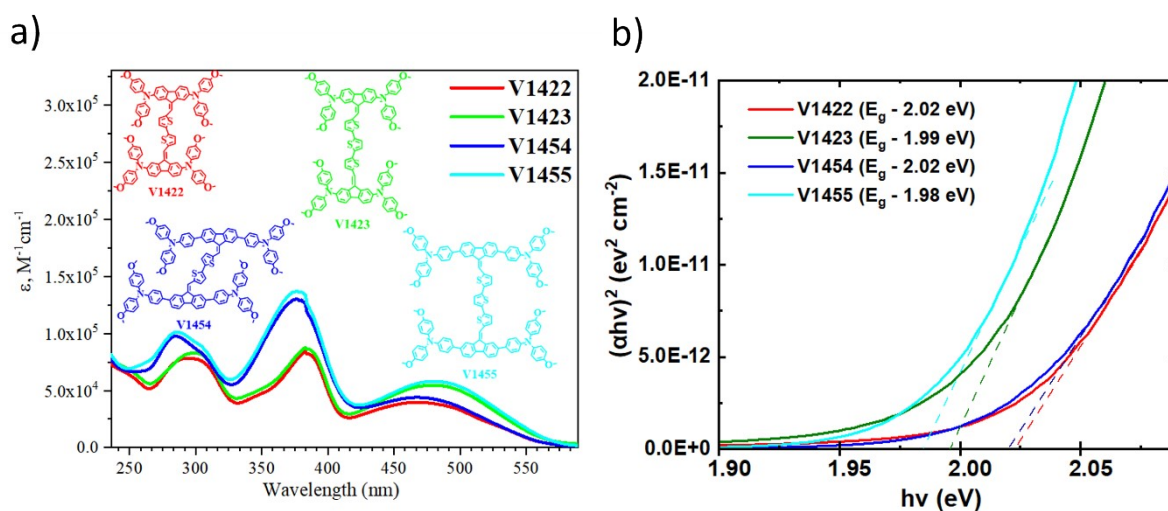


Figure S3. a) UV–vis absorption spectra of HTMs in THF solutions (10^{-4} M), and b) band gap (E_g) values calculated from the absorption spectra using Tauc plots for the HTMs in THF solution.

To evaluate the energy levels of the synthesized materials in the solid state, the ionization potential (I_p) was measured by photoelectron spectroscopy in air (PESA), where the

measurement error was evaluated to be 0.03 eV. All tested materials have a relatively high HOMO energy level at ~ 5.0 eV. Data analysis has revealed that the side fragments rather than the central core have the major influence on I_p . The same I_p values for **V1422** and **V1423** (4.94 eV) and almost similar ones for **V1454** and **V1455** (5.05 eV and 5.08 eV) can be explained by the unfavourable arrangement of thiophene fragments in the central unit of the photoconductors. This correlates well with the data of UV-Vis spectra (see Fig. S3), which undoubtedly show that the increase of the conjugated system is very slight with the increasing number of thiophene moieties in the molecule, and, therefore, the highest occupied molecular orbital (HOMO) levels can be very similar.

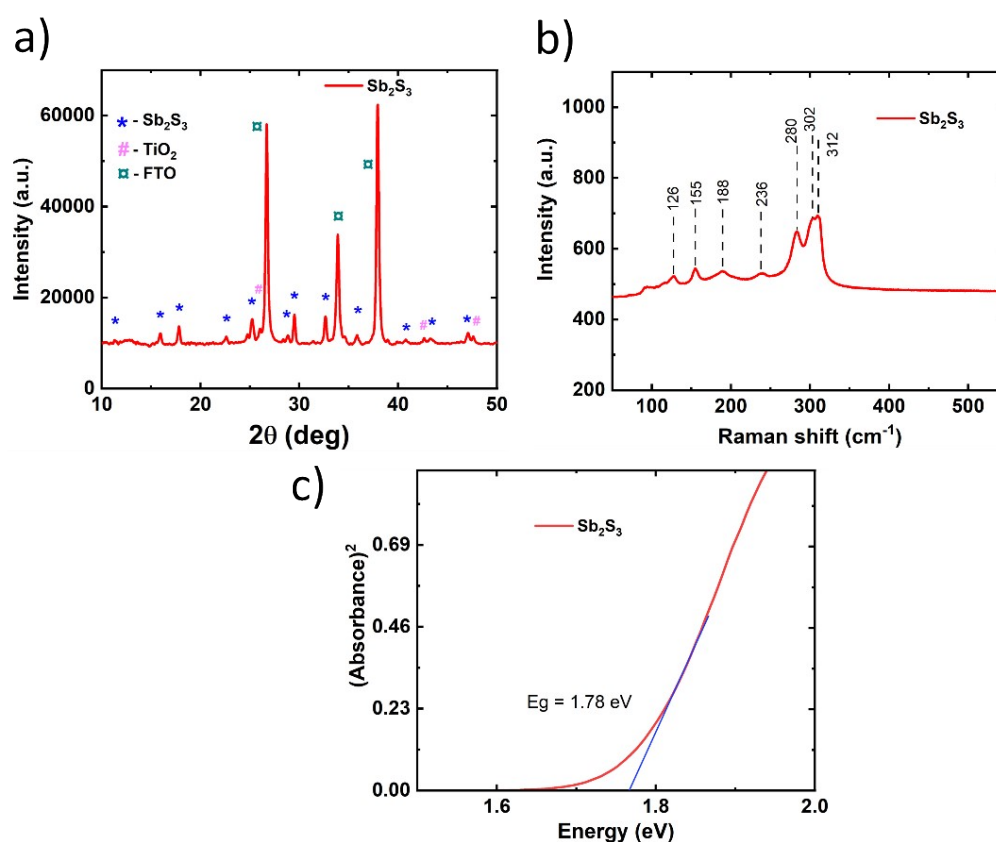


Figure S4: a) XRD pattern of glass/FTO/ TiO_2 / Sb_2S_3 stack, b) Raman spectrum of glass/FTO/ TiO_2 / Sb_2S_3 stack, and c) Tauc's plot of the Sb_2S_3 absorber film calculated from absorption curve obtained from UV-Vis measurement (Stack: glass/FTO/ TiO_2 / Sb_2S_3).

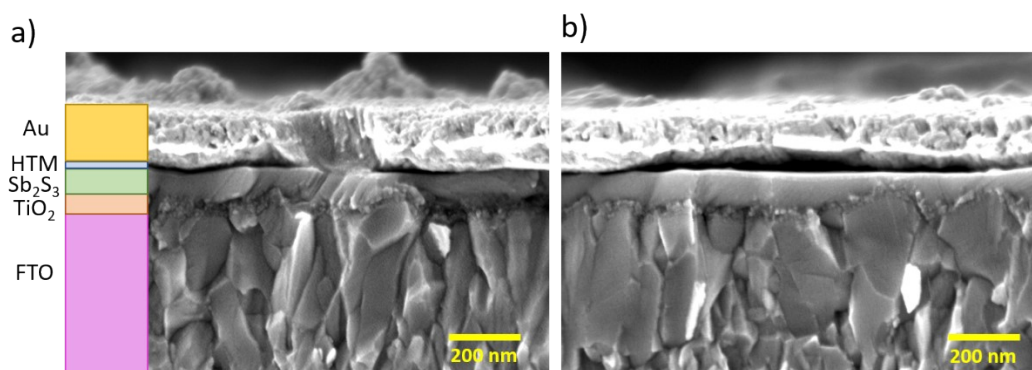


Figure S5. SEM cross-sectional images of glass/FTO/TiO₂/Sb₂S₃/HTM/Au superstrate configuration solar cells with a) V1423 – 2 mM and b) V1454 – 2 mM as HTMs. Layer thickness of absorber Sb₂S₃ absorber layer and HTMs (V1423, V1454) thickness is around 80 nm and 20 nm, respectively.

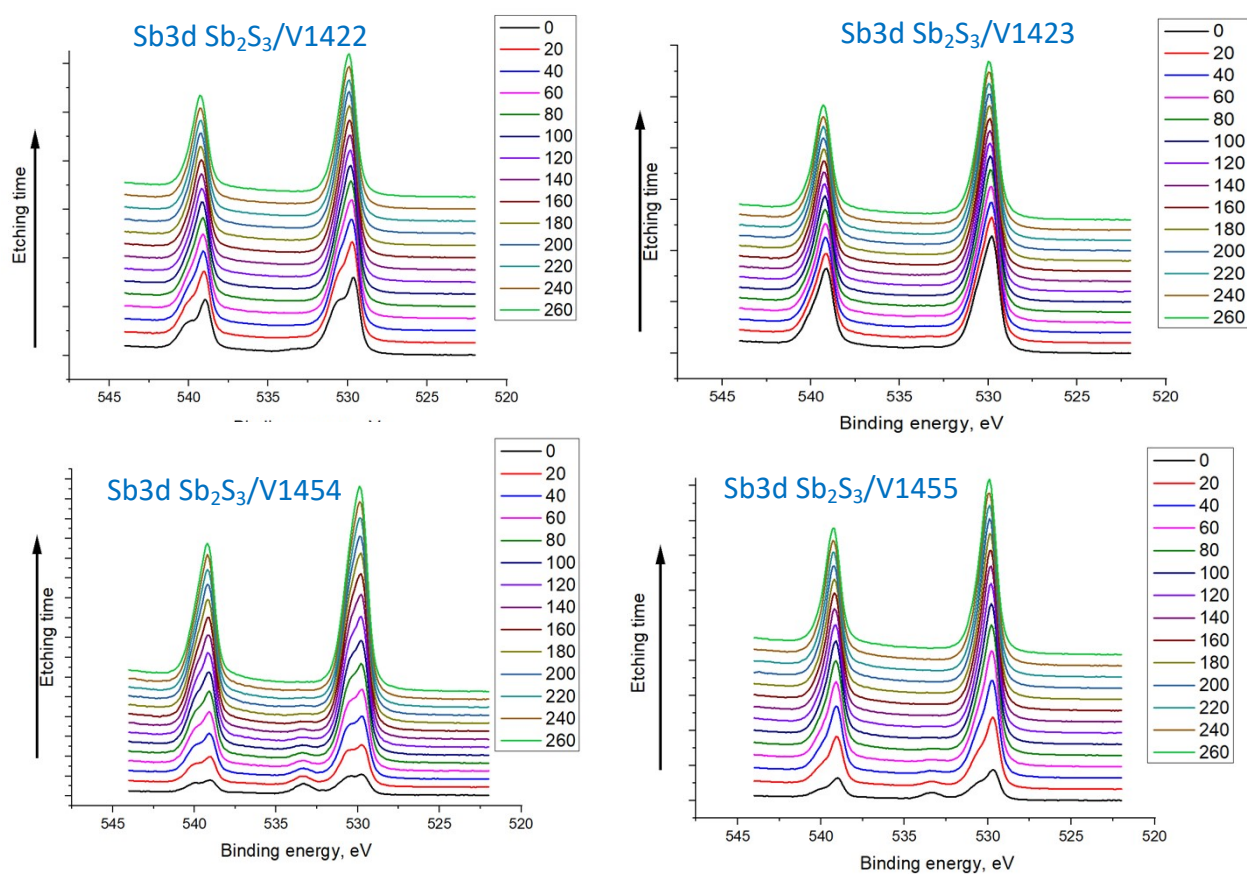


Figure S6: The XPS spectra of Sb₂S₃/HTM (V1422, V1423, V1454 and V1455) samples in Sb 3d region.

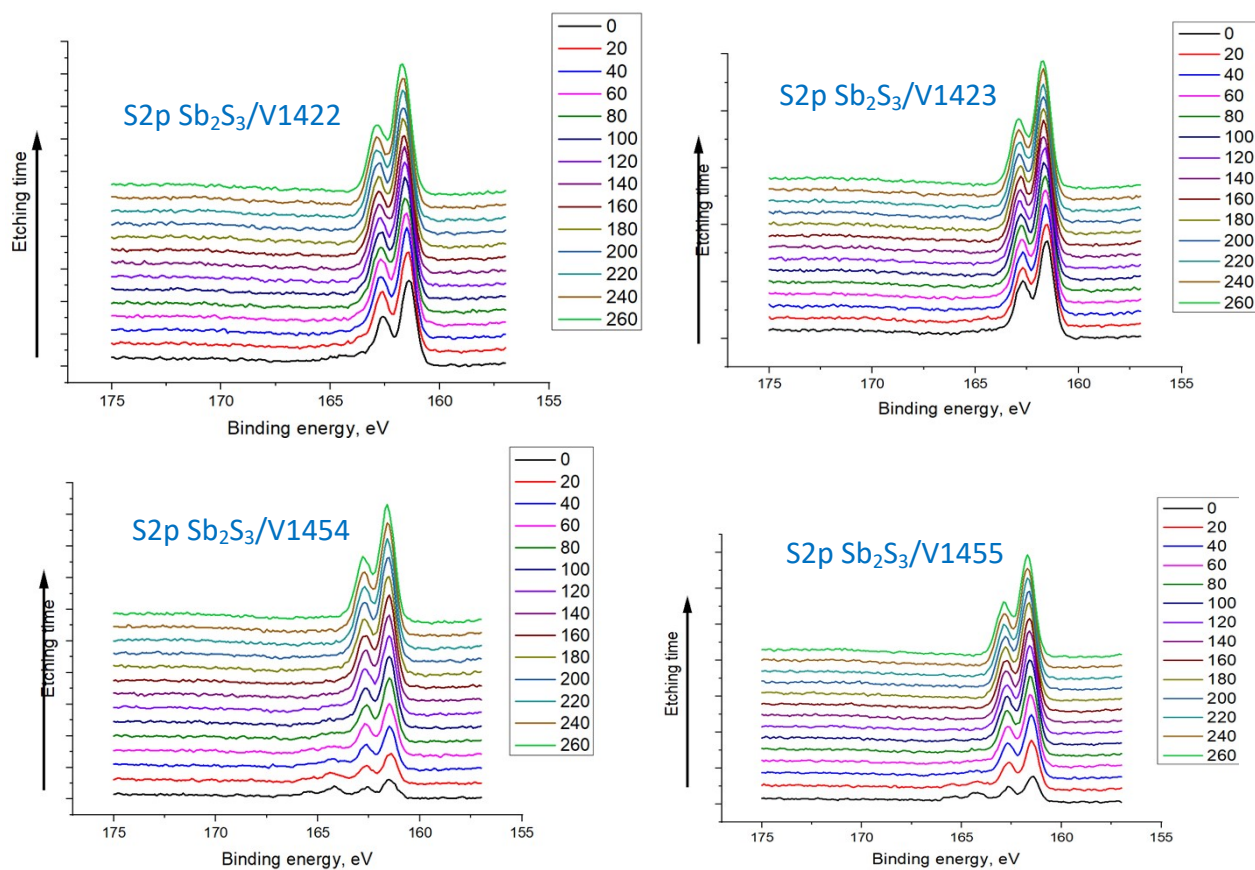


Figure S7: The XPS spectra of $\text{Sb}_2\text{S}_3/\text{HTM}$ (V1422, V1423, V1454 and V1455) samples in S 2p region.

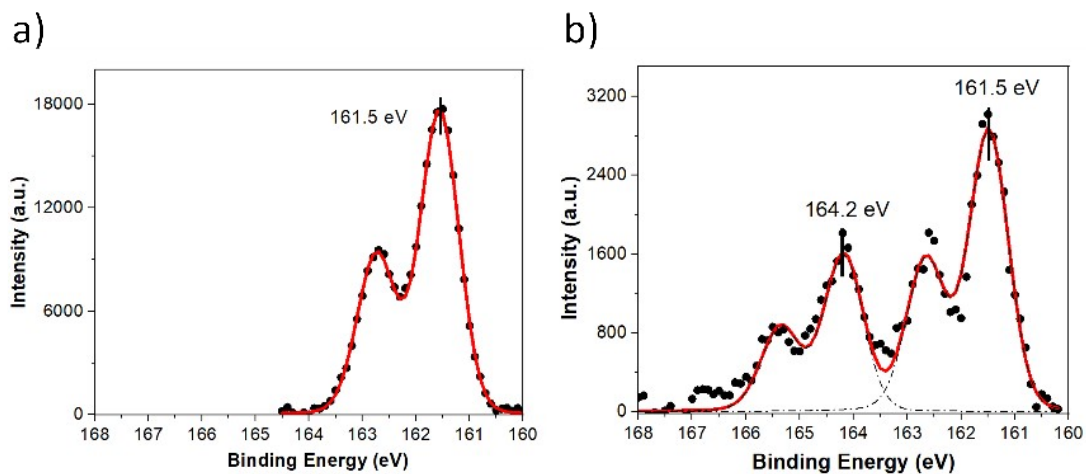


Figure S8: Deconvoluted XPS curves of samples a) S2p – $\text{Sb}_2\text{S}_3/\text{V1423}$, and b) S2p – $\text{Sb}_2\text{S}_3/\text{V1454}$

Table S1: Solar cell parameters of champion Sb_2S_3 solar cells with different concentrations (4 mM, 2 mM, 1 mM and 0.6 mM) of studied HTMs – V1422, V1423, V1454 and V1455.

HTM	HTM conc. (mM)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	R_s (Ohm*cm ²)
V1422	4	619	4.5	40	1.8	4.6
	2	656	9.7	43	3.9	1.7
	1	605	4.9	42	1.9	1.5
	0.6	530	4.7	41	1.6	1.1
V1423	4	606	4.8	40	1.8	4.1
	2	673	12.1	56	4.5	1.3
	1	565	8.8	35	2.6	1.0
	0.6	557	4.0	30	0.8	0.7
V1454	4	448	3.1	34	0.5	5.7
	2	439	5.7	35	0.8	2.7
	1	422	5.2	34	0.7	2.3
	0.6	418	2.8	31	0.4	2.2
V1455	4	429	3.3	35	0.5	5.2
	2	437	6.1	33	0.7	4.9
	1	406	3.7	36	0.5	2.1
	0.6	401	1.7	29	0.2	2.0

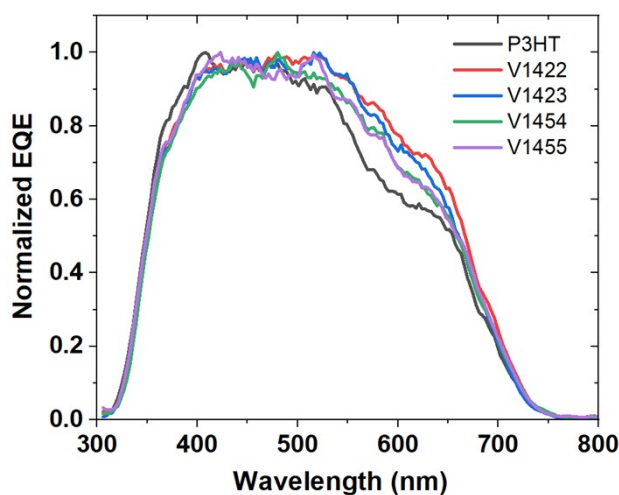


Figure S9. Normalized External quantum efficiency (EQE) curves of the champion solar cells with different HTMs (P3HT, V1422, V1423, V1454 and V1455).

The overall transparency of HTM layers are determined by depositing them on glass substrate and measuring the total transmittance (see Fig. S8a). P3HT layer exhibits parasitic absorption in range 450-650 nm. Next, the device stacks without top metal contact are analysed and the solar weighted average visible transmittance (AVT) (400-800 nm) of devices are shown in Fig. S8b and S8c, respectively. Devices with V-series HTMs are 15-22% more transparent than device with P3HT.

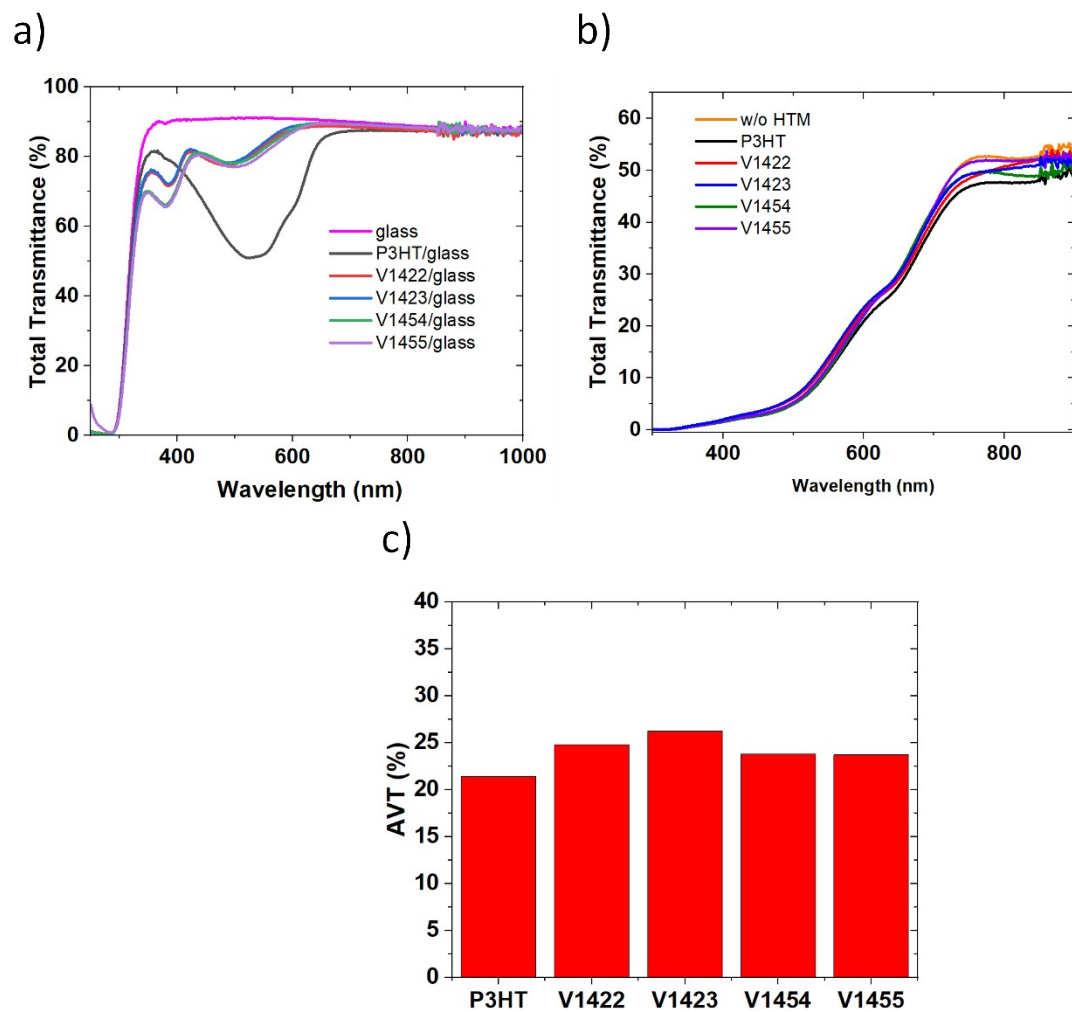


Figure S10: Transmittance curves of a) glass/HTMs, b) glass/FTO/Sb₂S₃/HTMs and c) Average visible transmittance (AVT) values of glass/FTO/Sb₂S₃/HTMs calculated in the 400-800 nm range.