

Supporting Information

Sb₂S₃ Solar Cells with Cost-effective and Dopant-free Fluorene-based Enamine as Hole Transport Material

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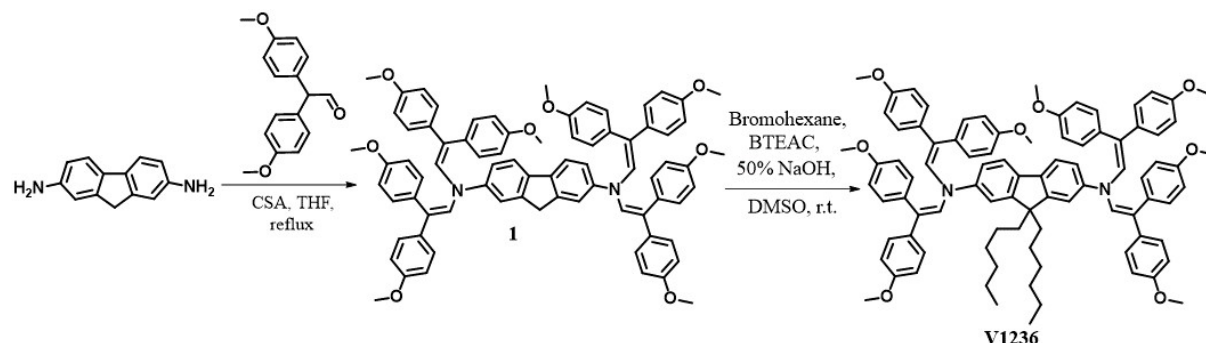
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Detailed Synthesis procedure of V1236

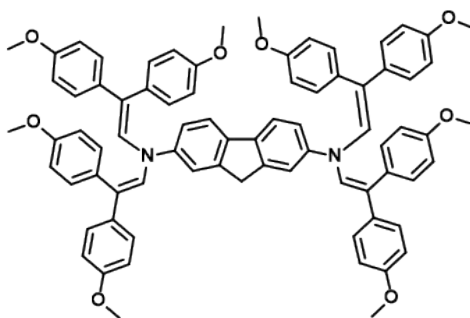
Chemicals required for the synthesis were purchased from Sigma-Aldrich and TCI Europe and used as received without additional purification. Spectral data of intermediate compounds is in agreement with the values reported in the literature. ¹H NMR and ¹³C NMR spectra were collected at 400 and 101 MHz, 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/. MS were recorded on Thermo Fisher Q Exactive HF Hybrid Quadrupole Orbitrap Mass Spectrometer using matrix assisted laser desorption/ionization (MALDI) technique.

Materials

Fluorene-based enamine **V1236** was prepared according to the procedure described in the Ref. [1].



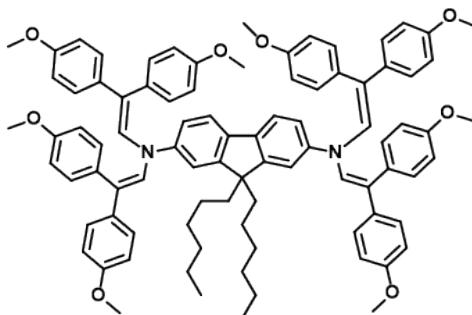
Synthesis route to fluorene-based enamine **V1236**



*N*²,*N*²,*N*⁷,*N*⁷-tetrakis[2,2-bis(4-methoxyphenyl)vinyl]-9*H*-fluorene-2,7-diamine (intermediate compound **1**)

2,7-diaminofluorene (0.3 g, 1.5 mmol) was dissolved in toluene (9 mL + volume of the Dean-Stark trap), (+/-) camphor-10-sulphonic acid (0.36 g, 1.5 mmol) was added and the mixture was heated at reflux for 20 minutes. Afterwards, 2,2-bis(4-methoxyphenyl) acetaldehyde (2.4 g, 9.2 mmol) was added and reflux continued using a Dean-Stark trap for 2 hours. After cooling to room temperature, reaction mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄, filtered and solvent evaporated. The crude product was crystallized from ethanol (30 mL). The obtained crystals were filtered off and washed with hot ethanol for three times. The product was recrystallized from acetone/ethanol 1:1 gave as light yellow-green crystals (1.42 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.20 (m, 2H), 7.19 – 6.94 (m, 10H), 6.84 (d, *J* = 8.4 Hz, 8H), 6.67 (d, *J* = 8.4 Hz, 8H), 6.49 (d, *J* = 8.4

Hz, 8H), 5.82 (s, 4H), 4.04 – 3.57 (m, 26H). ^{13}C NMR (101 Mhz, CDCl_3) δ 159.01, 158.71, 144.37, 132.82, 130.66, 130.18, 128.85, 114.43, 113.92, 113.63, 113.05, 55.46, 55.26, 37.05 ppm. Analytically calculated for $\text{C}_{77}\text{H}_{68}\text{N}_2\text{O}_8$: C, 80.46; H, 5.96; N, 2.44; found: C, 80.14; H, 5.82; N, 2.48. $\text{C}_{77}\text{H}_{68}\text{N}_2\text{O}_8$ [M^+] exact mass = 1148.50, MS (ESI) = 1149.90.



***N*²,*N*²,*N*⁷,*N*⁷-tetrakis[2,2-bis(4-methoxyphenyl)viny]-9,9-dihexyl-9*H*-fluorene-2,7-diamine (V1236)**

Compound **1** (0.5 g, 0.4 mmol) in dimethylsulfoxide (20 mL) was dissolved and purged with argon for 30 minutes. Afterwards, benzyltriethylammonium chloride (0.01 g, 0.04 mmol) and 50% NaOH (0.15 mL) solution were added. The color of the reaction should turn black and then was slowly dropped bromohexane (0.16 g, 1.0 mmol) under argon atmosphere and was stirred at room temperature for 26 hours. The reaction mixture was filtered off and washed repeatedly with water three times. The crude product was purified by column chromatography using 4:21 v/v tetrahydrofurane/*n*-hexane as an eluent to collect **V1236** as a yellow solid (0.36 g, 63%). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, J = 8.0 Hz, 2H), 7.12 – 6.93 (m, 12H), 6.85 (d, J = 8.4 Hz, 8H), 6.65 (d, J = 8.4 Hz, 8H), 6.50 (d, J = 8.8 Hz, 8H), 5.81 (s, 4H), 3.81 (d, J = 38.0 Hz, 24H), 1.97 – 1.82 (m, 4H), 1.21 – 1.01 (m, 12H), 0.85 – 0.66 (m, 10H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 158.99, 158.69, 152.04, 134.48, 132.95, 130.64, 128.90, 119.25, 115.91, 113.92, 113.02, 111.31, 55.38, 55.26, 40.11, 31.39, 29.38, 23.62, 22.48, 14.12 ppm. Analytically calculated for $\text{C}_{89}\text{H}_{92}\text{N}_2\text{O}_8$: C, 81.12; H, 7.04; N, 2.13; found: C, 81.24; H, 7.11; N, 2.10. $\text{C}_{89}\text{H}_{92}\text{N}_2\text{O}_8$ [M^+] exact mass = 1316.69, MS (ESI) = 1318.15.

Table S1. Materials, quantities and cost for the synthesis of V1236

Chemical	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of chemical (€/kg)	Cost of chemical (€/g product)	Total cost (€/g)
4-Bromoanisole	3.98			25.2	0.10	
Formic acid	20			3.87	0.08	
Sulfuric acid	4			2.63	0.01	
Methyl methoxyacetate	0.739			304	0.22	
Magnesium	0.518			104	0.05	
Diethyl ether				6.92	1.38	
Ethyl acetate				2.85	0.43	
2,2-bis(4-methoxyphenyl) acetaldehyde	29.237	200	150			2.28
2,2-bis(4-methoxyphenyl) acetaldehyde	1.426			2300	3.28	
2,7-Diaminofluorene	0.182			31480	5.73	
10-Camphorsulfonic acid	0.218			260	0.06	
Toluene				2.46	0.02	
Ethyl acetate		9	200	2.85	0.57	
Na ₂ SO ₄			50	6.08	0.30	
Ethanol			80	6.08	0.49	
<i>N</i> ² , <i>N</i> ² , <i>N</i> ⁷ , <i>N</i> ⁷ -tetrakis[2,2-bis(4-methoxyphenyl)vinyl]-9 <i>H</i> -fluorene-2,7-diamine (V1275)	1.826	9	330			10.45
<i>N</i> ² , <i>N</i> ² , <i>N</i> ⁷ , <i>N</i> ⁷ -tetrakis[2,2-bis(4-methoxyphenyl)vinyl]-9 <i>H</i> -fluorene-2,7-diamine (V1275)	1.39			10450	14.53	
Benzyltriethylammonium chloride	0.028			159.8	0.00	
1-Bromohexane	0.439			128	0.06	
Sodium hydroxide	0.214			38.08	0.01	
Dimethyl sulfoxide			10	47.27	1.94	
THF		41	50	8.88	0.09	
Ethanol				6.08	0.30	
<i>N</i> ² , <i>N</i> ² , <i>N</i> ⁷ , <i>N</i> ⁷ -tetrakis[2,2-bis(4-methoxyphenyl)vinyl]-9,9-dihexyl-9 <i>H</i> -fluorene-2,7-diamine (V1236)	2.071	41	60			16.93

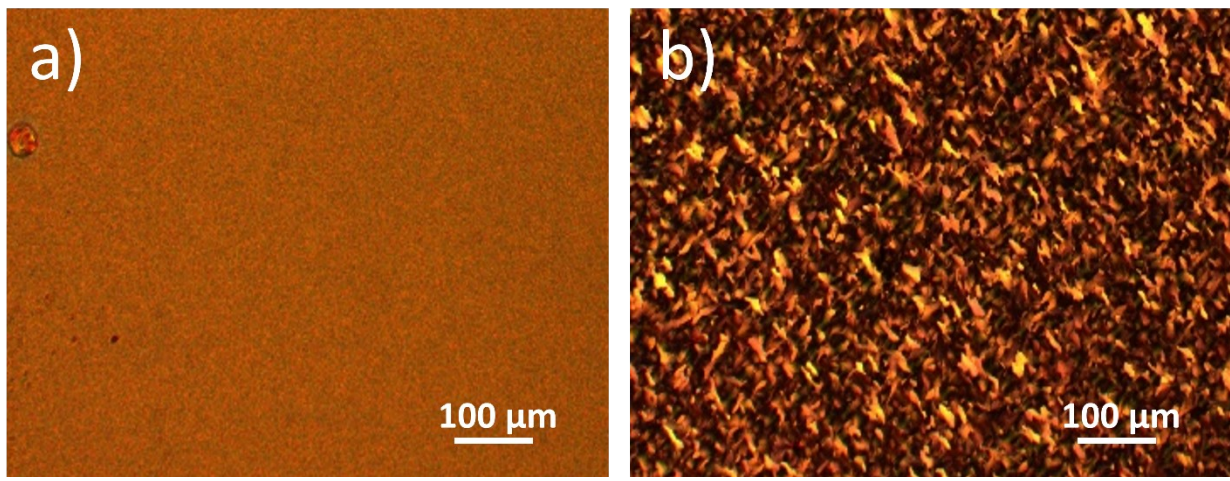
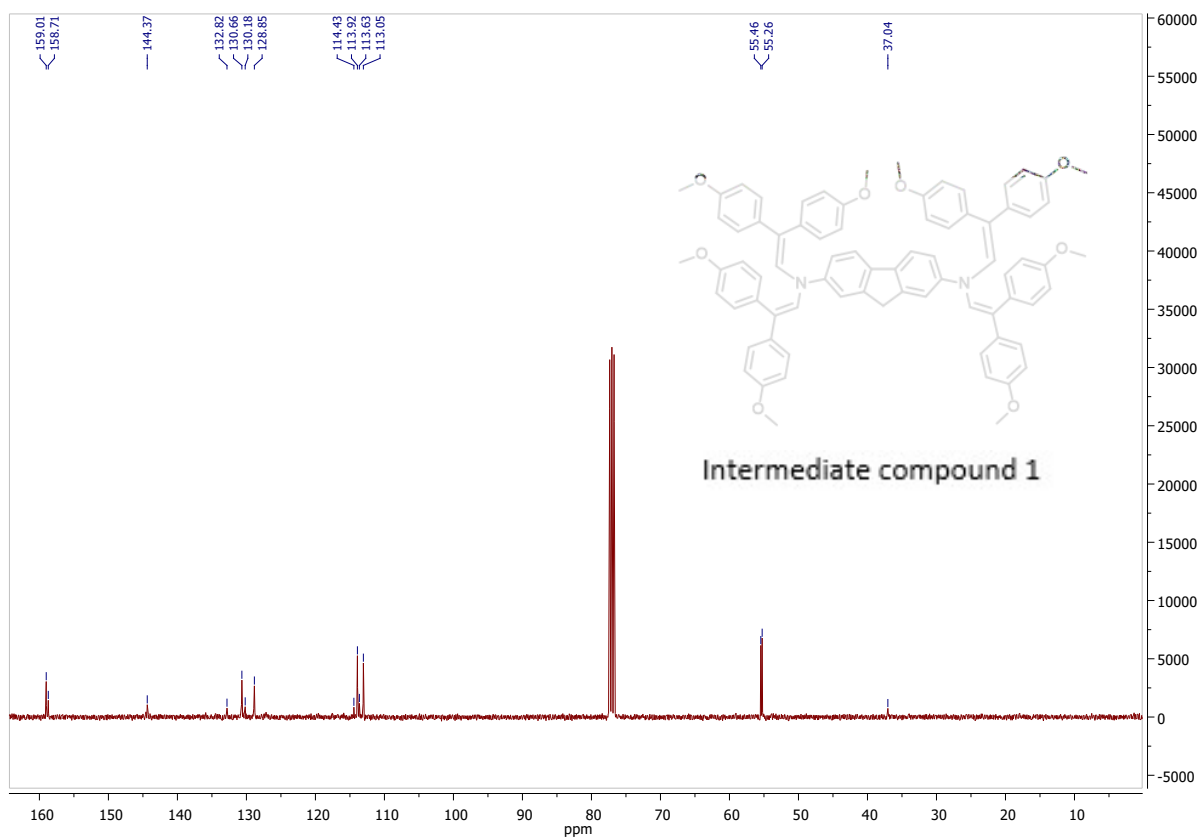
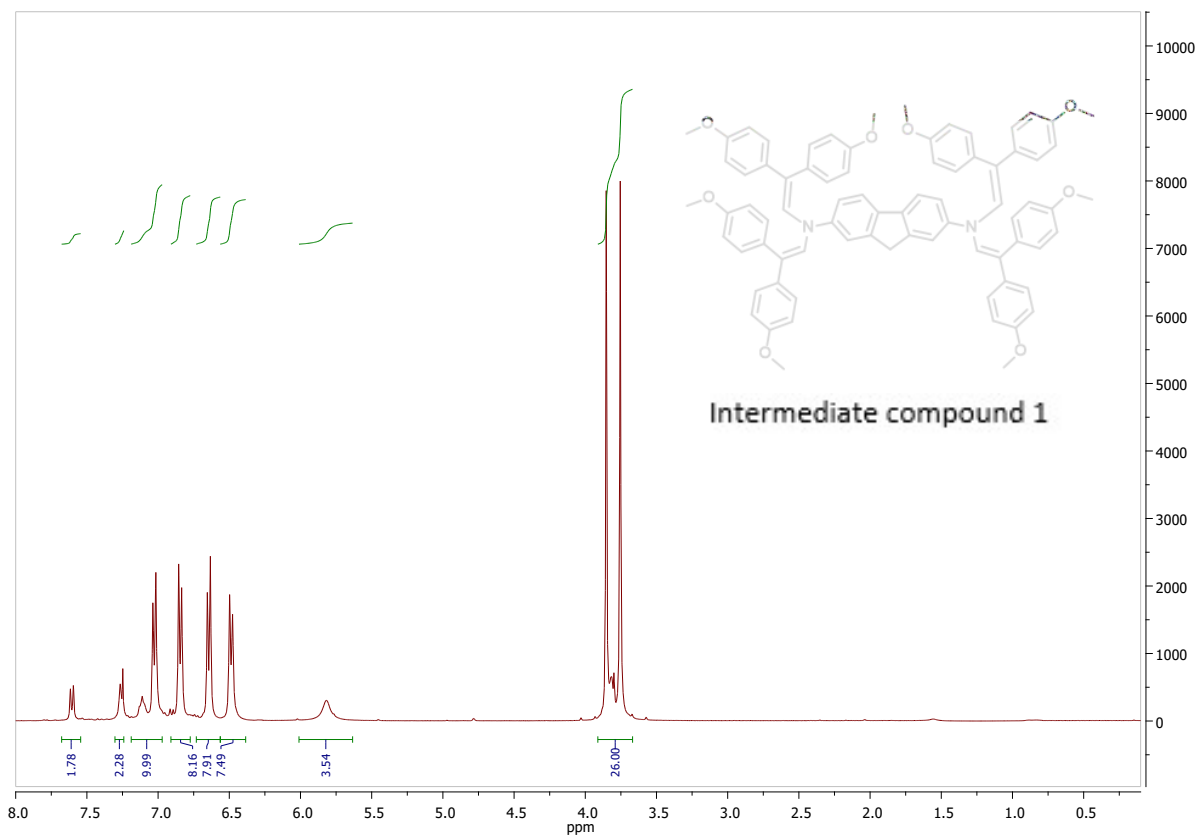


Figure S1: Optical microscopic images of as deposited and annealed Sb_2S_3 films.
Substrate: glass/FTO/ TiO_2 .



Figure S2: Sb_2S_3 films undergo a change in color from light brown in as deposited state to dark brown post annealing. Substrate: glass/FTO/ TiO_2 .



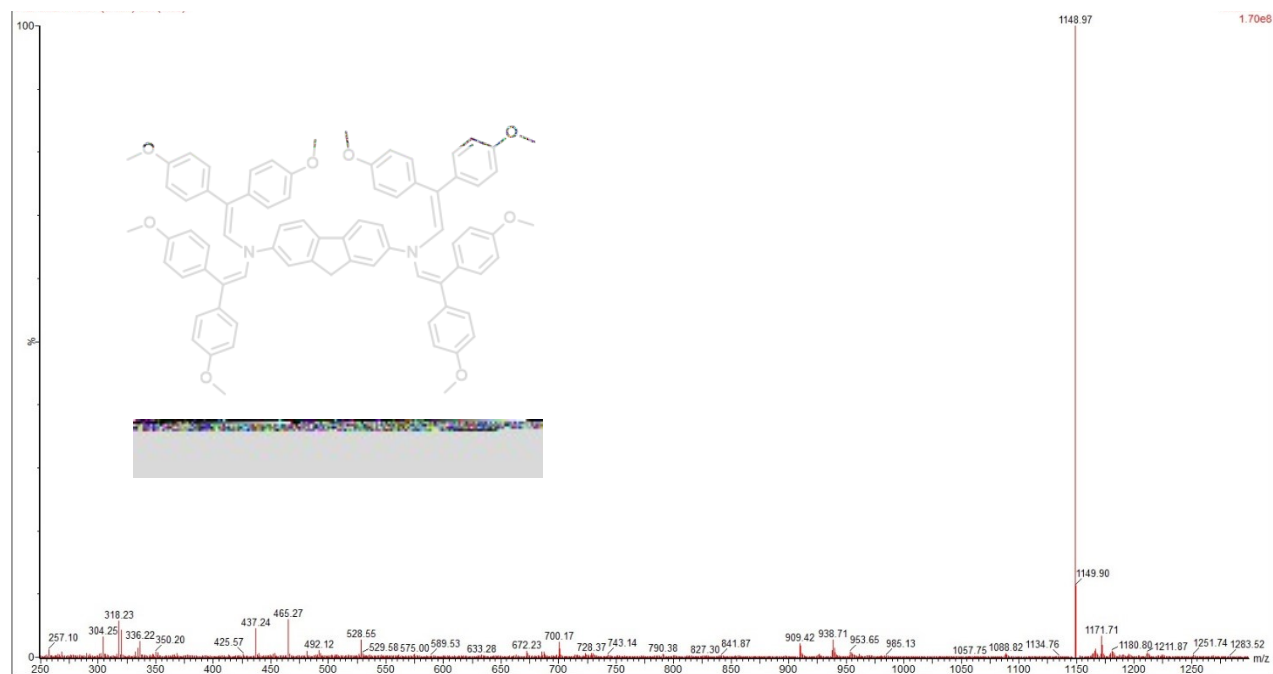
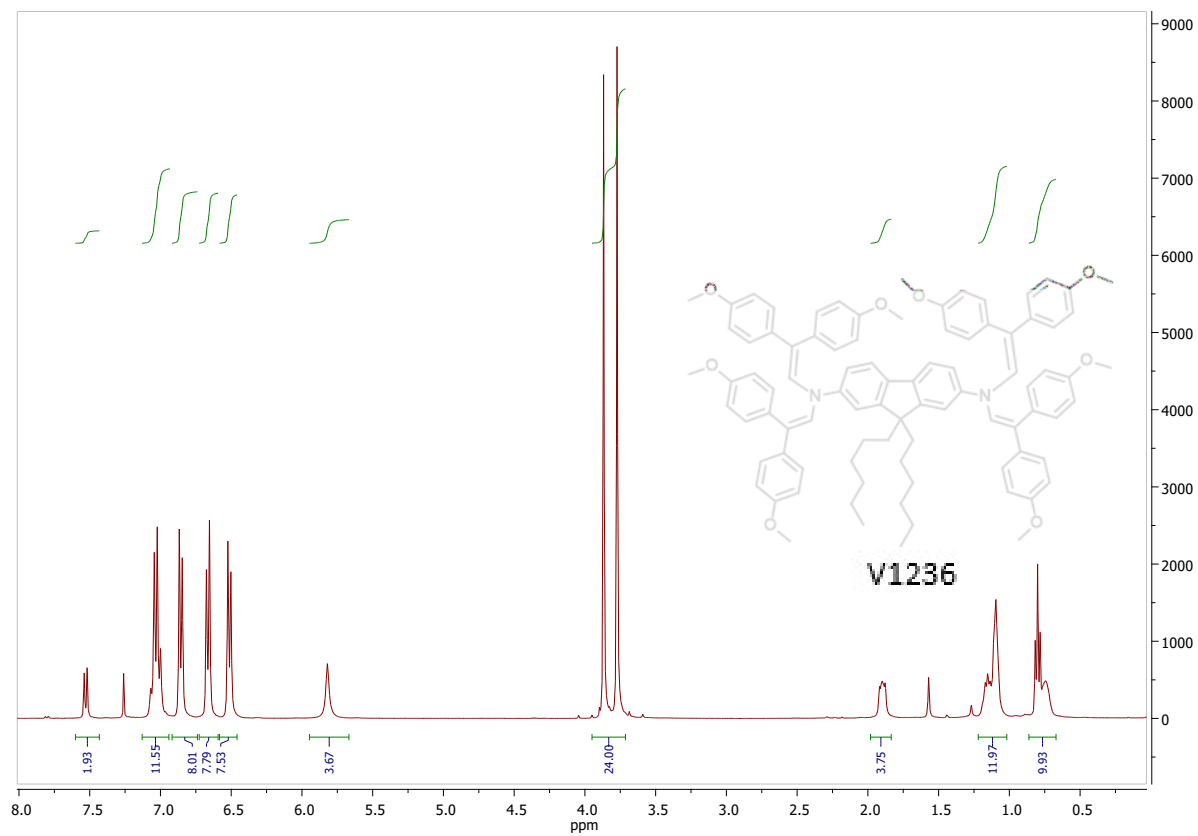


Figure S3: ^1H , ^{13}C NMRS and Mass spectra of intermediate compound **1**



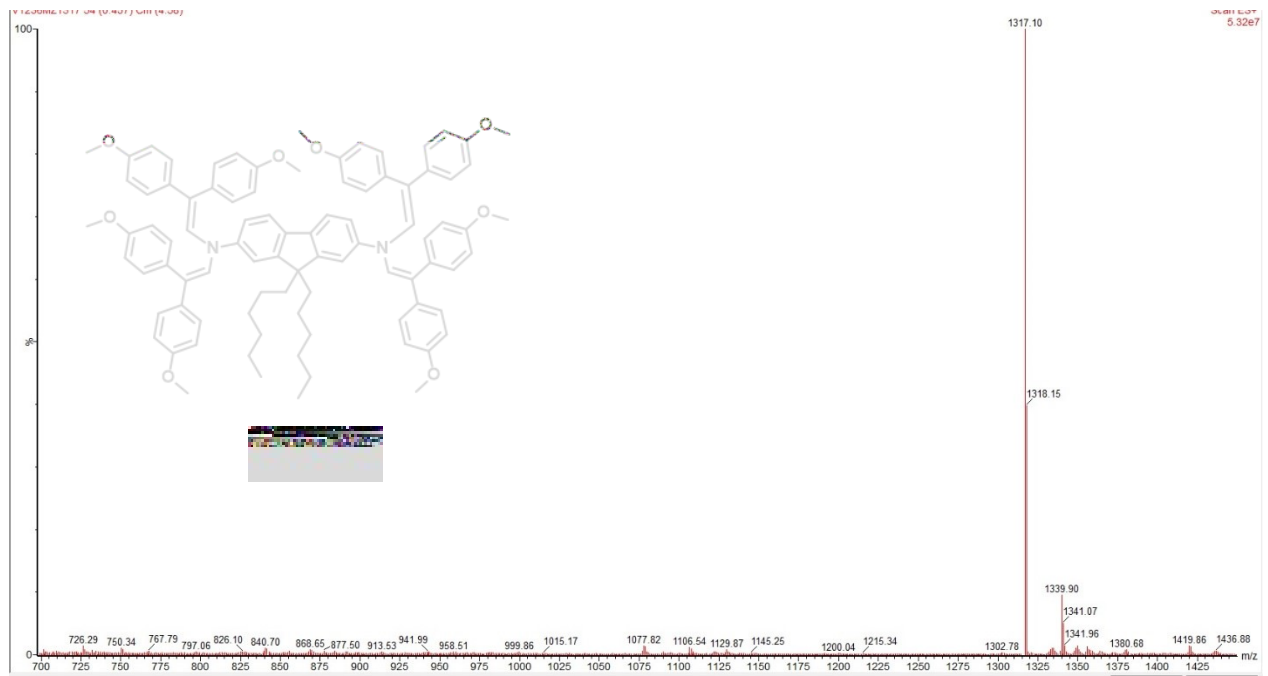
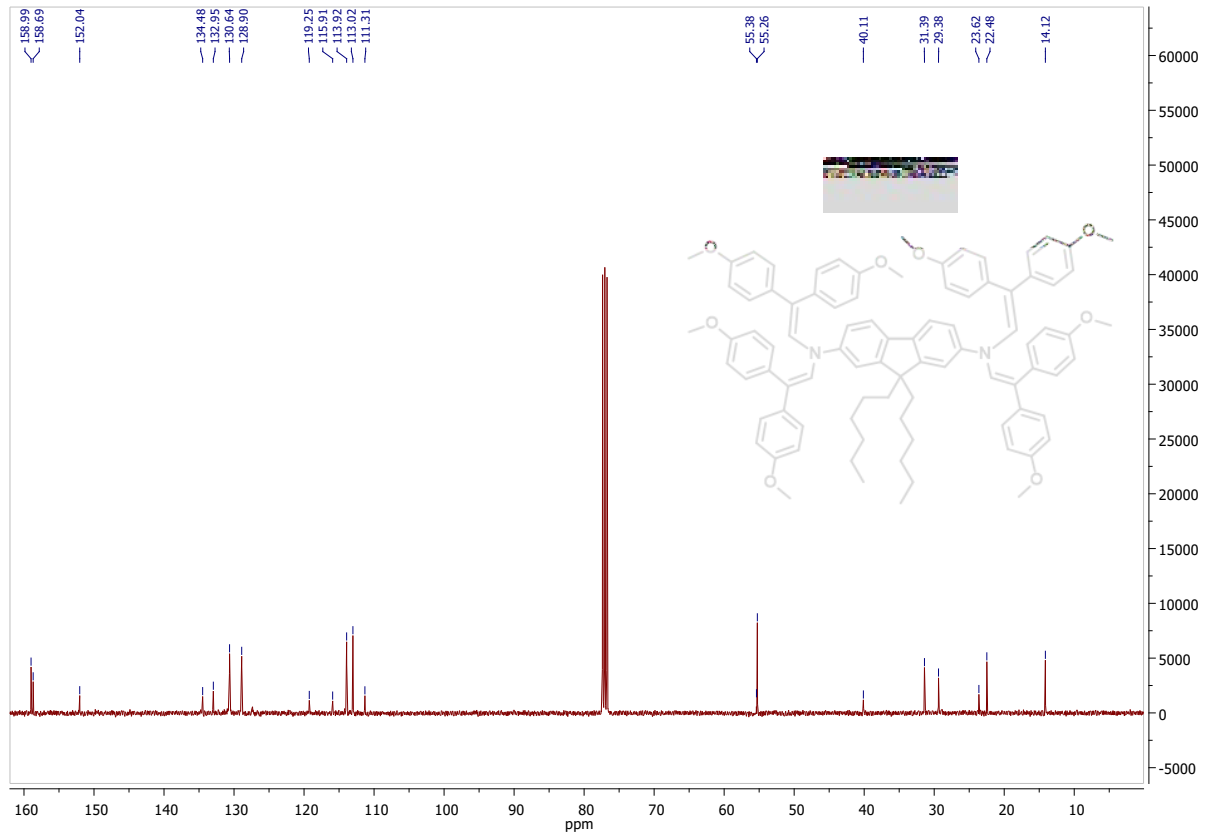


Figure S4: ¹H, ¹³C NMRs and Mass spectra of **V1236**

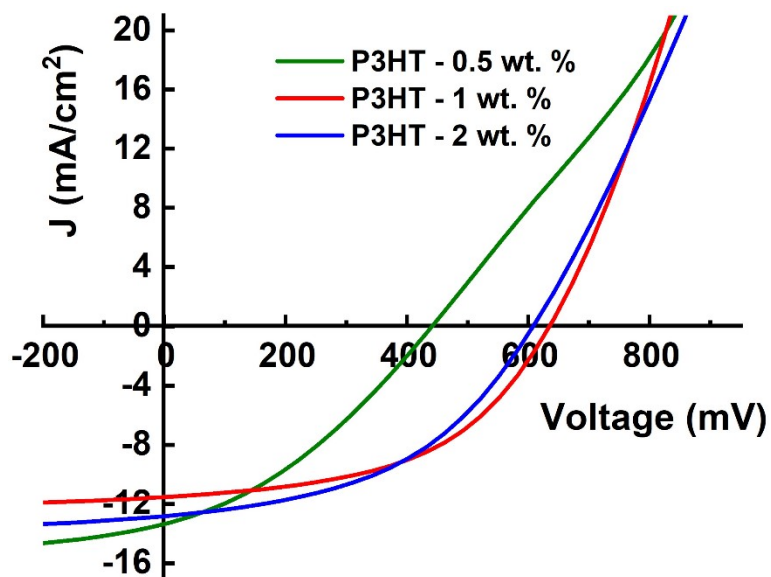


Figure S5: J-V curves of the champion Sb_2S_3 solar cells with different concentrations of P3HT as HTM (0.5, 1 and 2 wt. %). Structure: glass/FTO/ TiO_2 / Sb_2S_3 /P3HT/Au.

Table S2. Device parameters of Sb_2S_3 solar cells with 0.5, 1 and 2 wt. % of P3HT

Device with P3HT concentration (wt. %)	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
0.5	441	13.2	35	2.0
1	634	11.5	50	3.7
2	608	12.8	46	3.6

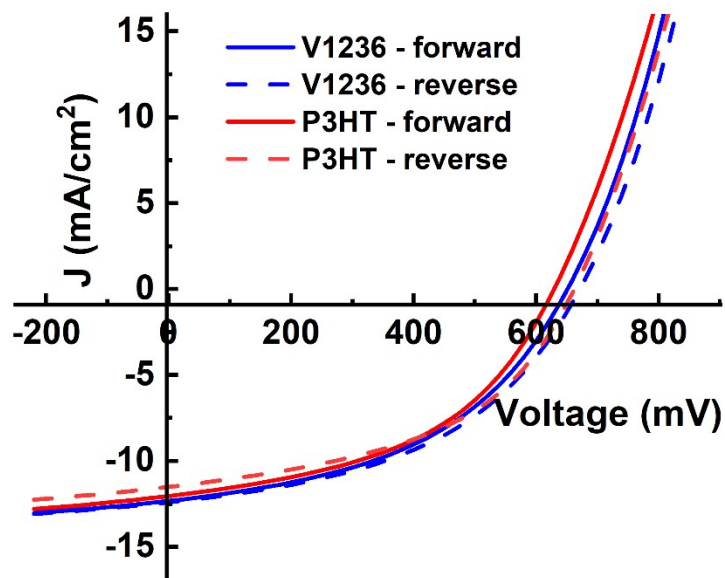


Figure S6: Forward and reverse J-V characteristics of solar cells with V1236 and P3HT. The hysteresis index is < 0.05 for both the cases.

$$\text{Hysteresis index (HI)} = (\text{PCE reverse}) - (\text{PCE forward}) / (\text{PCE reverse})$$

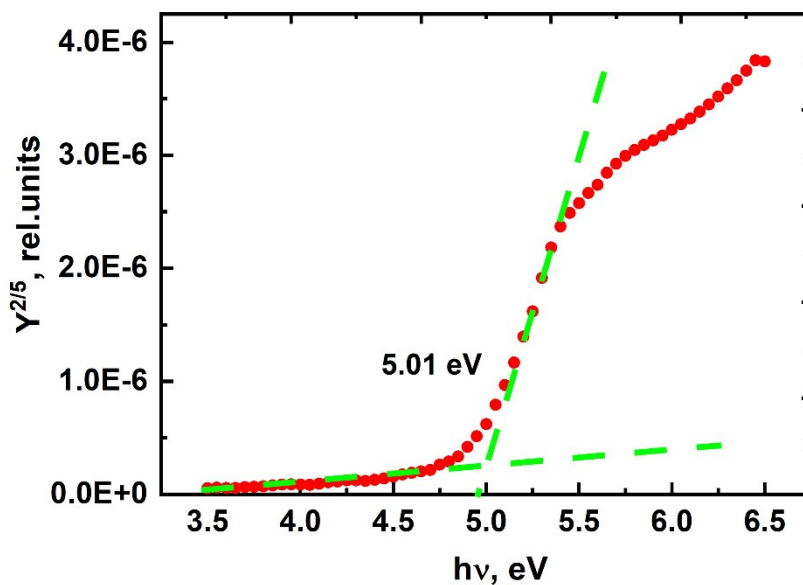


Figure S7: Ionization energy (HOMO) of V1236 determined using the photoelectron emission spectroscopy method. ^[3,4]

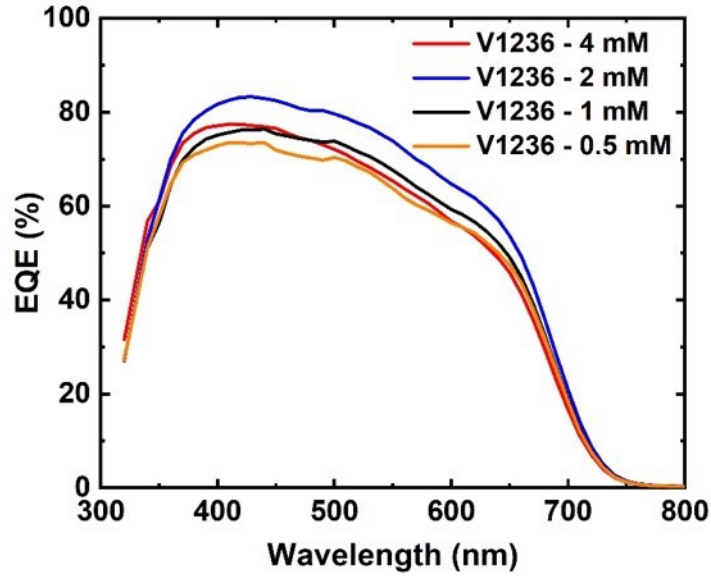


Figure S8: EQE of Sb_2S_3 solar cells with different concentrations of V1236 (4 mM, 2 mM, 1 mM and 0.5 mM). Structure: glass/FTO/ TiO_2 / Sb_2S_3 /HTM/Au.

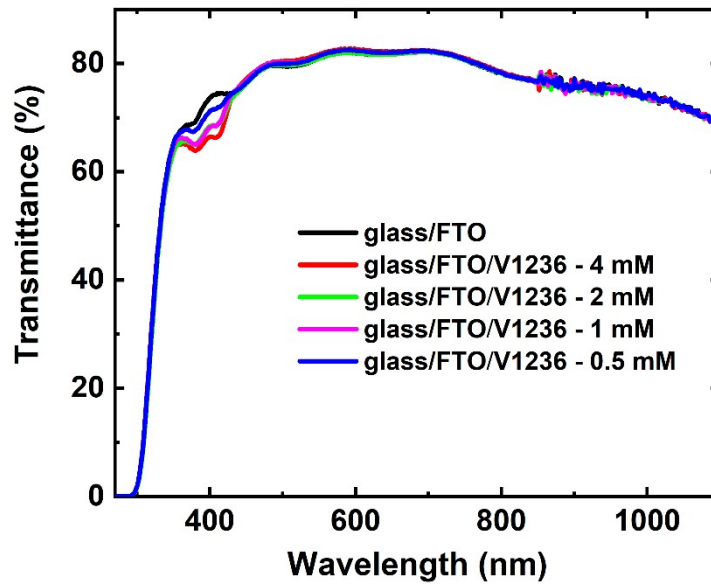


Figure S9: Total transmission of glass/FTO and different concentrations of V1236 (4 mM, 2 mM, 1 mM and 0.5 mM).

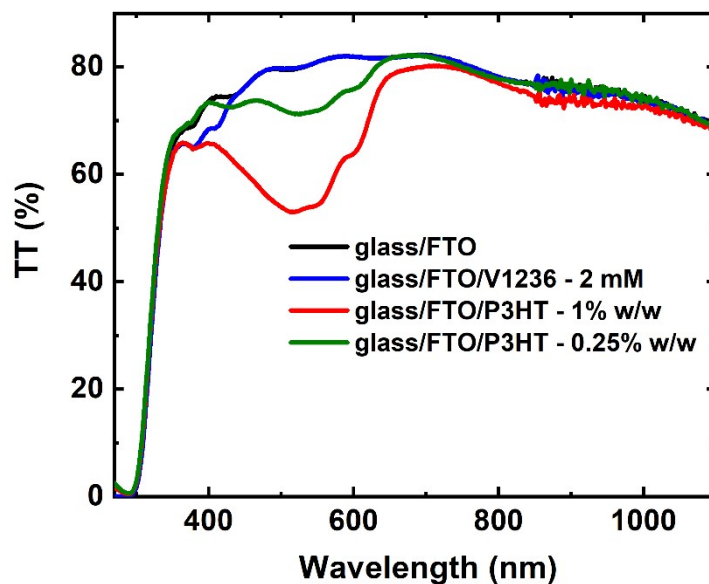


Figure S10: Total transmission of FTO, V1236 - 2mM, P3HT (1% w/w) and P3HT (0.25% w/w) layers on glass/FTO substrates.

Table S3. Hole mobility of V1236 and P3HT

V1236 ^[1]	P3HT ^[2]
$10^{-4} - 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$	$10^{-3} - 10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

References

- [1] Daskeviciute, S. *et al.* Fluorene-based enamines as low-cost and dopant-free hole transporting materials for high performance and stable perovskite solar cells. *Journal of Materials Chemistry A* **9**, 301–309 (2021).
- [2] <https://www.sigmaaldrich.com/LT/en/product/aldrich/445703>, accessed 04-2022.
- [3] R. Grzibovskis, A. Vembris, K. Pudzs, Relation between molecule ionization energy, film thickness and morphology of two indandione derivatives thin films, *J. Phys. Chem. Solids*. **95** (2016) 12–18. doi:10.1016/j.jpcs.2016.03.010
- [4] K. Kanai, M. Honda, H. Ishii, Y. Ouchi, K. Seki, Interface electronic structure between organic semiconductor film and electrode metal probed by photoelectron yield spectroscopy, *Org. Electron*. **13** (2012) 309–319. doi:10.1016/j.orgel.2011.11.024