Supporting Information

Effects of Heteroatom Substitution in Conjugated Heterocyclic Compounds on Photovoltaic Performance: From Sulfur to Tellurium

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Materials and Methods

All reactions were carried out in oven-dried glassware under an argon atmosphere. Anhydrous solvents were obtained either from solvent purification systems (Vacuum Atmosphere Company) or from commercial sources. Every solution addition or transfer was performed with argon-flushed syringes. Chromatographic purifications were performed on an Isolera One system (Biotage) using normal phase silica columns. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker UltraShield 400 MHz / 54 mm at room temperature and referenced to either TMS (0.00 ppm for ^{1}H NMR), methylene chloride (5.32 ppm for ^{1}H NMR), or chloroform (77.23 ppm for ^{13}C NMR) peaks. UV-vis absorption spectra were obtained on a PerkinElmer Lamda 25 UV-vis spectrophotometer. Mass spectra were recorded on a Thermo TSQ Quantum Access Triple Quadrupole Mass Spectrometer (Thermo-Fisher) and a Voyager-DE *STR* MALDI-TOF (Applied Biosystems) in reflector mode. Masses for base peaks are reported unless otherwise noted. Cyclic voltammetry was performed using a Princeton Applied Research potentiostat/galvanostat PARSTAT 2273. Thin films of MoO_x and Al were evaporated using a Kurt J. Lesker PVD-75 evaporator. All starting materials were purchased from commercial sources and used without further purification. 2-Tributylstannylbenzo[*b*]selenophene (**7**) was prepared according to literature procedures[1],[2] as confirmed by ^{1}H NMR spectroscopy.

Synthetic Procedures

(2-Benzotellurophenyl)diphenylmethanol (8)

To a stirred solution of benzo[*b*]tellurophene[1] (0.35 g, 1.5 mmol) in anhydrous THF was added dropwise *sec*-butyllithium (1.1 mL, 1.5 mmol, 1.4 M in cyclohexane) at 0 °C and the resulting orange colored solution was allowed to react for 1 h at the same temperature under Ar atmosphere. After benzophenone (0.25 g, 1.4 mmol) was added in one portion, the green reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated NH_4Cl (aq.) and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with water, followed by saturated NaCl (aq.), and dried over anhydrous Na_2SO_4. After concentration in vacuo, the crude mixture was purified by column chromatography to give the product as a white solid (0.40 g, 64%).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.88 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.47-7.45 (m, 4H), 7.35-7.29 (m, 8H), 7.08 (t, *J* = 7.2 Hz, 1H), 3.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.4, 148.7, 146.1, 134.3, 133.4, 132.0, 128.4, 128.1, 127.9, 127.6, 125.4, 124.5, 83.5; HRMS (ESI-MS, negative ion mode) *m/z*: $[M-H]^-$ calcd. for $C_{21}H_{16}OTe$-H, 413.01918; found, 413.01956.

DPP2T(BTh)$_2$ (**2**): To a deaerated solution of DPP2TBr$_2$ (0.313 g, 0.39 mmol) in toluene (50 mL) was added Pd(PPh_3)$_4$ (0.023 g, 0.020 mmol) followed by 2-tributylstannylbenzothiophene (0.50 g, 1.18 mmol). The reaction mixture was stirred at 110 °C overnight under Ar atmosphere, cooled to room temperature, filtered through Celite and washed with chloroform. After the solution was concentrated in vacuo, the crude product was purified by column chromatography using hexane and chloroform (hexane:chloroform = 100:0 to 33:67 as a gradient) as eluent. The product was dissolved in a minimal amount of chloroform, precipitated into methanol, and then collected by filtration to give **DPP2T(BTh)**$_2$ as a brown solid (0.28 g, 79%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.93 (d, *J* = 4.4 Hz, 2H), 7.85 - 7.79 (m, 4H), 7.59 (s, 2H), 7.48 (d, *J* = 4.0 Hz, 2H), 7.41 - 7.35 (m, 4H), 4.07 (d, *J* = 7.6 Hz, 4H), 1.98 (m, 2H), 1.36 - 1.25 (m, 32H), 0.90 - 0.82 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 142.8, 140.4, 139.9, 139.7, 136.8, 136.1, 129.4, 126.2, 125.5, 125.2, 124.1, 122.4, 121.6, 108.9, 46.6, 38.2, 32.1, 31.6, 31.3, 30.0, 28.8, 26.6, 23.3, 22.9, 14.3; MALDI-TOF (m/z) $[M+H]^+$ calcd. for $C_{54}H_{64}N_2O_2S_4$+H, 901.3923; found, 901.4188.

DPP2T(BSe)$_2$ (**3**): This compound was prepared in the same manner as **DPP2T(BTh)**$_2$ with DPP2TBr$_2$ (0.36 g, 0.45 mmol), Pd(PPh_3)$_4$ (0.026 g, 0.022 mmol) and 2-tributylstannylbenzoselenophene (0.64g, 1.34 mmol) to give **DPP2T(BSe)**$_2$ as a brown solid (0.38 g, 85%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.92 (d, *J* = 4.0 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.74 (s, 2H), 7.41 - 7.39 (m, 2H), 7.38 (d, *J* = 4.0 Hz, 2H), 7.32 - 7.28 (m, 2H), 4.06 (d, *J* = 7.6 Hz, 4H), 1.97 (m, 2H), 1.36 - 1.25 (m, 32H), 0.90 - 0.82 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 144.8, 142.8, 141.4, 139.7, 138.0, 136.7, 129.5, 126.9, 125.9, 125.7, 125.6, 125.5, 125.2, 109.0, 46.5, 38.2, 32.1, 31.6, 31.3, 30.0,

28.8, 26.6, 23.3, 22.9, 14.3; MALDI-TOF (m/z) $[M+H]^+$ calcd. for $C_{54}H_{64}N_2O_2S_2Se_2$+H, 997.2825; found, 997.2921.

DPP2T(BTe)$_2$ (**4**): To a deaerated solution of DPP2TBr$_2$ (0.36 g, 0.45 mmol) and (2-benzotellurophenyl)diphenylmethanol (0.56 g, 1.4 mmol) in *o*-xylene (50 mL) was added Pd(OAc)$_2$ (0.010 g, 0.044 mmol), PCy$_3$(0.025 g, 0.089 mmol) and Cs_2CO_3 (0.886 g, 2.72 mmol). The reaction mixture was stirred at 140 °C overnight under an Ar atmosphere, cooled to room temperature, filtered through Celite and washed with chloroform. After the solution was concentrated in vacuo, the crude mixture was purified by column chromatography using hexane and chloroform (hexane:chloroform = 100:0 to 33:67 as a gradient) as eluent. The product was dissolved in a minimal amount of chloroform, precipitated into methanol, and then collected by filtration to give **DPP2T(BTe)**$_2$ as a brown solid (0.21 g, 42%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.90 (d, *J* = 4.0 Hz, 2H), 8.01 (s, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.42 - 7.38 (m, 2H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.19 - 7.15 (m, 2H), 4.06 (d, *J* = 7.6 Hz, 4H), 1.98 (m, 2H), 1.36 - 1.25 (m, 32H), 0.90 - 0.82 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): 161.8, 149.0, 148.4, 139.6, 136.7, 133.8, 132.8, 132.2, 130.5, 129.4, 128.3, 127.7, 126.2, 125.6, 109.0, 46.5, 38.2, 32.1, 31.6, 31.3, 30.0, 28.9, 26.6, 23.4, 22.9, 14.4, 14.3; MALDI-TOF (m/z) $[M]^+$ calcd. for $C_{54}H_{64}N_2O_2S_2Te_2$,1092.2504; found, 1092.3246.

^{1}H NMR Spectra

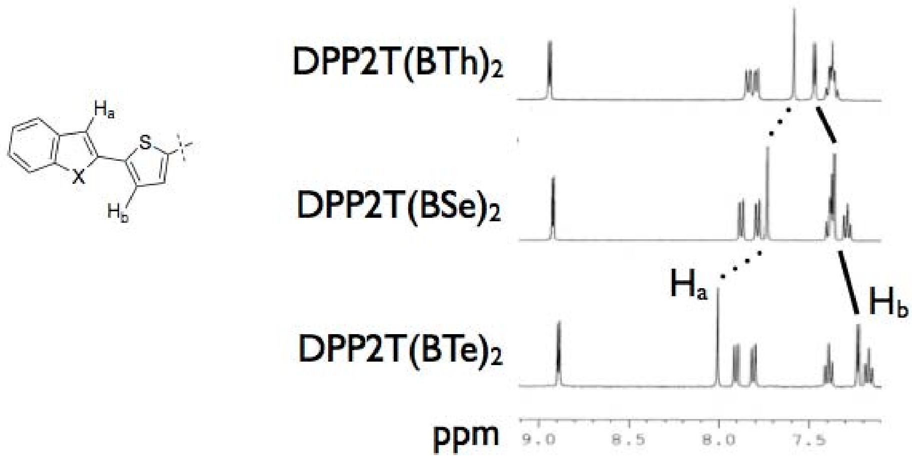


Figure S1. ^{1}H NMR spectra (400 MHz in CD_2Cl_2) of 2, 3, and 4 in aromatic region

UV-Vis Absorption Spectra

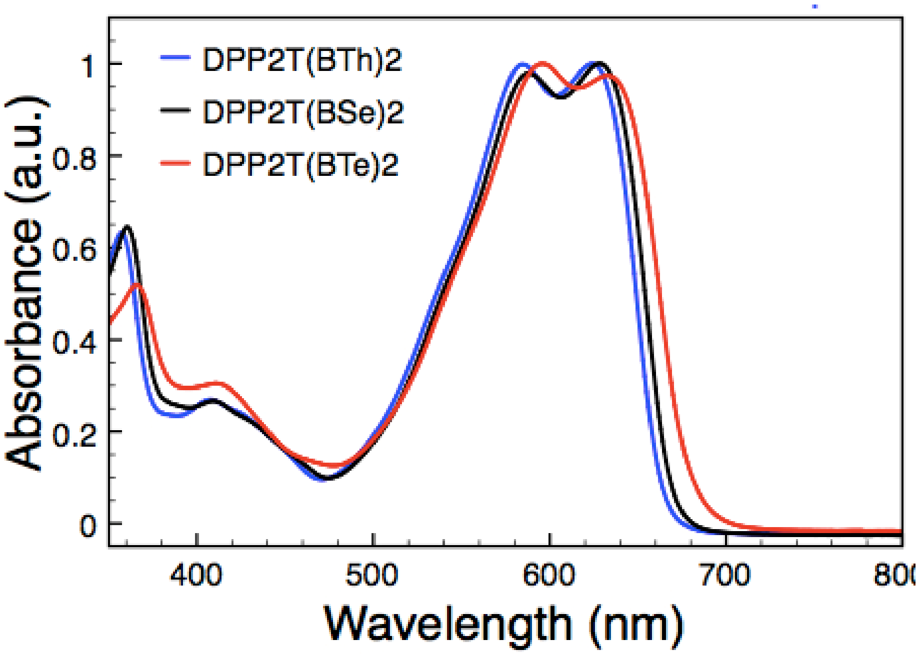


Figure S2. Optical absorption spectra in chloroform.

Table S1. Absorption maxima and optical bandgaps

Compound	In solution			In film		
	$\lambda_{1,\ max}$ (nm)	$\lambda_{2,max}$ (nm)	Bandgap (eV) [a)]	$\lambda_{1,\ max}$ (nm)	$\lambda_{2,max}$ (nm)	Bandgap (eV) [a)]
DPP2T(BTh)$_2$	584	624	1.87	611	673	1.74
DPP2T(BSe)$_2$	588	629	1.85	618	683	1.71
DPP2T(BTe)$_2$	596	633	1.82	618	694	1.66

[a)] Estimated from onsets of absorption.

Cyclic Voltammetry

Cyclic voltammetry was performed using a standard three electrode apparatus based on a Pt working electrode, a silver wire pseudo-reference electrode (calibrated vs Fc/Fc$^+$), and a Pt wire counter electrode. Films of compounds **2**, **3**, and **4** were drop cast from chloroform onto a Pt disk electrode (2 mm in diameter) and were measured in acetonitrile containing 0.1 M tetra(*n*-butylammonium) hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte at a scan rate of 50 mV/s (Figure S3). HOMO and LUMO energy levels were calculated from onsets of oxidation and reduction as below, respectively (Table S2).[3]

$$\text{HOMO} = -[E_{ox} + 5.1]\ \text{eV}$$

$$\text{LUMO} = -[E_{red} + 5.1]\ \text{eV}$$

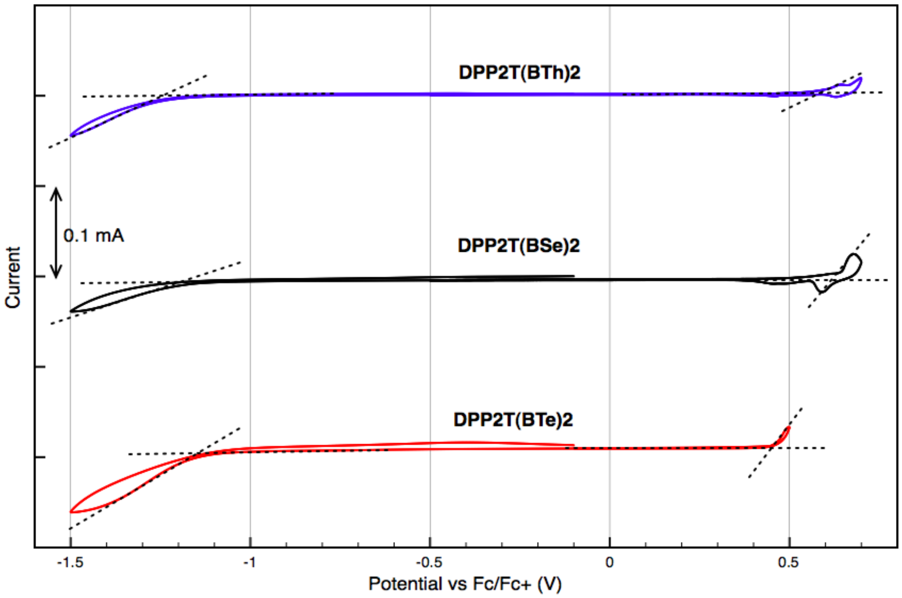


Figure S3. Cyclic voltammograms for **2**, **3**, and **4**.

Table S2. Electrochemical Data

Compound	$E_{ox,\ onset}$ (V)	$E_{red,\ onset}$ (V)	HOMO (eV)	LUMO (eV)	Bandgap (eV)
DPP2T(BTh)$_2$	0.58	-1.25	-5.68	-3.85	1.83
DPP2T(BSe)$_2$	0.61	-1.19	-5.71	-3.91	1.80
DPP2T(BTe)$_2$	0.45	-1.15	-5.55	-3.95	1.60

Mobility Measurements

Hole mobilities of compounds were measured by analyzing *I*-*V* characteristics of hole-only ohmic devices under the space-charge-limited current (SCLC) model in which *I*-*V* relation is expressed as: $I / A = 9/8\ \varepsilon_o \varepsilon_r \mu V^2 d^{-3}$, with device area *A*, vacuum permittivity ε_o, relative dielectric constant of compound ε_r (~3), hole mobility *m*, and active layer thickness *d*. Specifically, the mobility was obtained from the slope of linear region of $I^{1/2}$-*V* plot as shown in (Figure S4)[4],[5] and *d* measured by scanning electron microscopy (Figure S5). The ohmic device consisted of ITO (135 nm)/MoO$_x$ (20 nm)/compound **2**, **3**, or **4** (60 nm)/MoO$_x$ (20 nm)/Au (100 nm) (Figure S5), and the measured mobility values are summarized in Table S3.

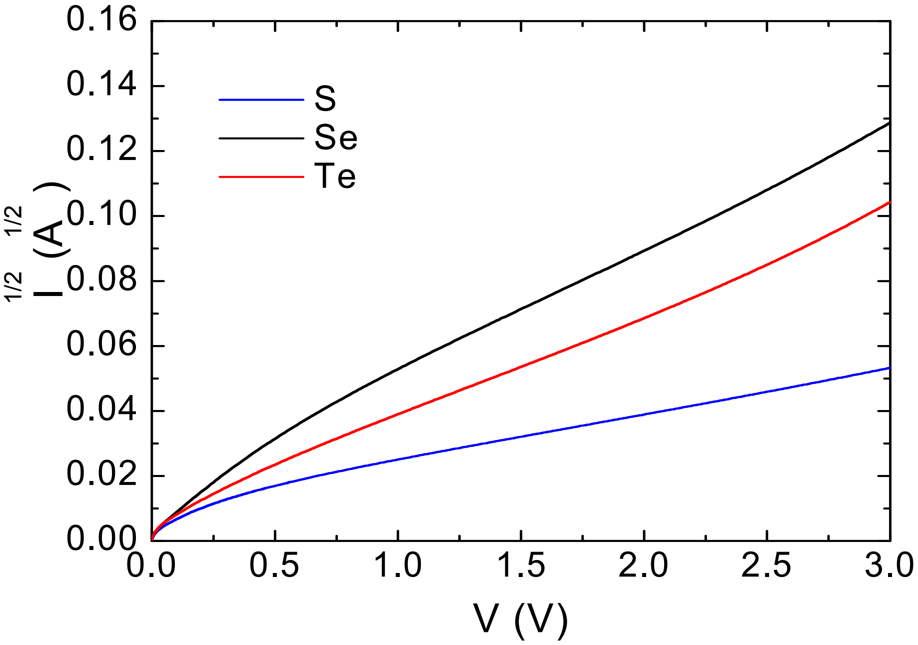


Figure S4. *I*-*V* characteristics of hole-only ohmic devices consisting of ITO/MoO$_x$/compound /MoO$_x$/Au. Blue, black, and red lines refer to compounds DPP2T(BTh)$_2$ (**2**), DPP2T(BSe)$_2$ (**3**), and DPP2T(BTe)$_2$ (**4**), respectively. The linear regions in ~1-3 V bias range in the plots follow SCLC model while the non-linear regions in low bias range (< ~1 V) originates from ohmic current contribution from dark carriers.

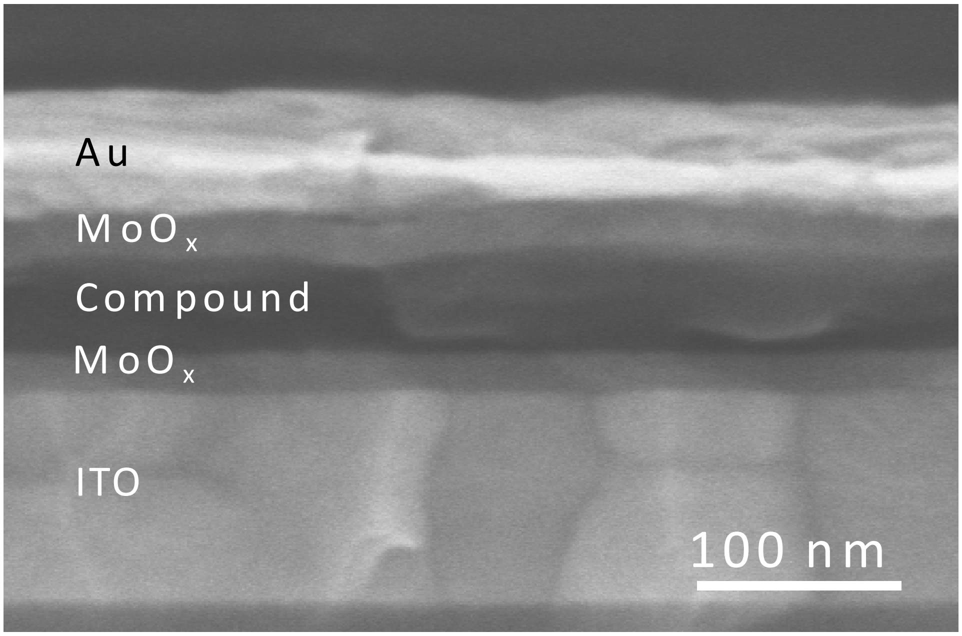


Figure S5. Representative scanning electron micrograph of the cross-section of hole-only ohmic device. The particular device shown here had compound **2** as an active layer.

Table S3. Summary of measured SCLC mobility values of each compound [a)]

Compound	**DPP2T(BTh)$_2$** (**2**)	**DPP2T(BSe)$_2$** (**3**)	**DPP2T(BTe)$_2$** (**4**)
Mean	7.4×10^{-6} cm^{2}V^{-1}s^{-1}	5.2×10^{-5} cm^{2}V^{-1}s^{-1}	3.1×10^{-5} cm^{2}V^{-1}s^{-1}
Max.	1.0×10^{-5} cm^{2}V^{-1}s^{-1}	6.8×10^{-5} cm^{2}V^{-1}s^{-1}	3.6×10^{-5} cm^{2}V^{-1}s^{-1}
Min.	5.1×10^{-6} cm^{2}V^{-1}s^{-1}	3.9×10^{-5} cm^{2}V^{-1}s^{-1}	2.7×10^{-5} cm^{2}V^{-1}s^{-1}

[a)] For each compound, three devices were measured. Variation in measured mobilities mainly arises from the variation in active layer thickness, which was measured by cross-sectional scanning electron microscopy (Figure S3).

Fabrication and Measurement of Solar Cell Devices

Solar cells were fabricated and measured in air. ITO-coated glass substrates were cleaned using UV-ozone for 5 min, and a thin-layer of MoO_x film (~9 nm) was evaporated ($P < 5x10^{-6}$ Torr) on top of ITO. A blend solution of donor **2**, **3**, or **4** and $PC_{61}BM$ in chloroform was prepared in an Ar-filled glove box [Total concentration (with a weight ratio of donor : $PC_{61}BM$); $DPP2T(BTh)_2$: 20.0 mg/mL (1.5 : 1), $DPP2T(BSe)_2$: 25.5 mg/mL (2 : 1), $DPP2T(BTe)_2$: 14.4 mg/mL (2 : 1)]. The blend solution was spin-cast in air on top of a MoO_x layer pre-cleaned with UV-ozone for 5 min. For $DPP2T(BTh)_2$, the solution was heated gently on hot plate (50 ^{o}C) before spin-coating. Then, Al cathode (~100 nm) was deposited through a shadow mask (1.25 mm in diameter) by thermal evaporation ($P < 10^{-6}$ Torr). Finally, devices were thermally annealed in a vacuum oven after silver was pasted onto the ITO electrode [Annealing temperatures and times: $DPP2T(BTh)_2$: 130 ^{o}C for 10 min, $DPP2T(BSe)_2$: 120 ^{o}C for 10 min, $DPP2T(BTe)_2$: 90 ^{o}C for 30 min]. *J-V* characteristics were measured using a custom modified probe station and an Agilent 4156C precision semiconductor parameter analyzer under a solar simulator (150 W) equipped with an Air Mass 1.5 Global (AM 1.5G) filter. The light intensity was calibrated for 100 mW cm^{-2} (1 SUN) by a KG5 color filtered Si reference solar cell (Newport) and cross-checked by a spectrometer calibrated for an absolute spectral irradiance measurement. IPCE was measured by a UV-enhanced Si photodiode (Newport) using a 300 W xenon arc lamp and a monochromator with the light power for each wavelength.

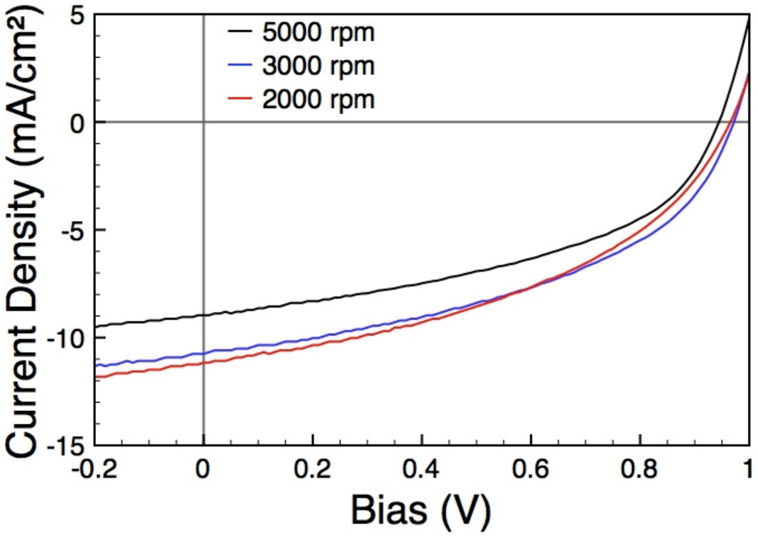


Figure S6. Selected *J-V* curves of compound **3** for device optimization.

Table S4. Solar cell device parameters of compound 3 [a)]

Spin speed (rpm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	
				Max	Avg [b)]
5000	0.935	8.96	0.465	3.89	3.82
3000	0.965	10.76	0.456	4.74	4.63
2500	0.955	11.08	0.439	4.65	4.59
2000	0.955	11.16	0.436	4.65	4.38
1500	0.955	11.41	0.411	4.48	3.74

[a)]From Figure S4; [b)]Averaged over 4 devices.

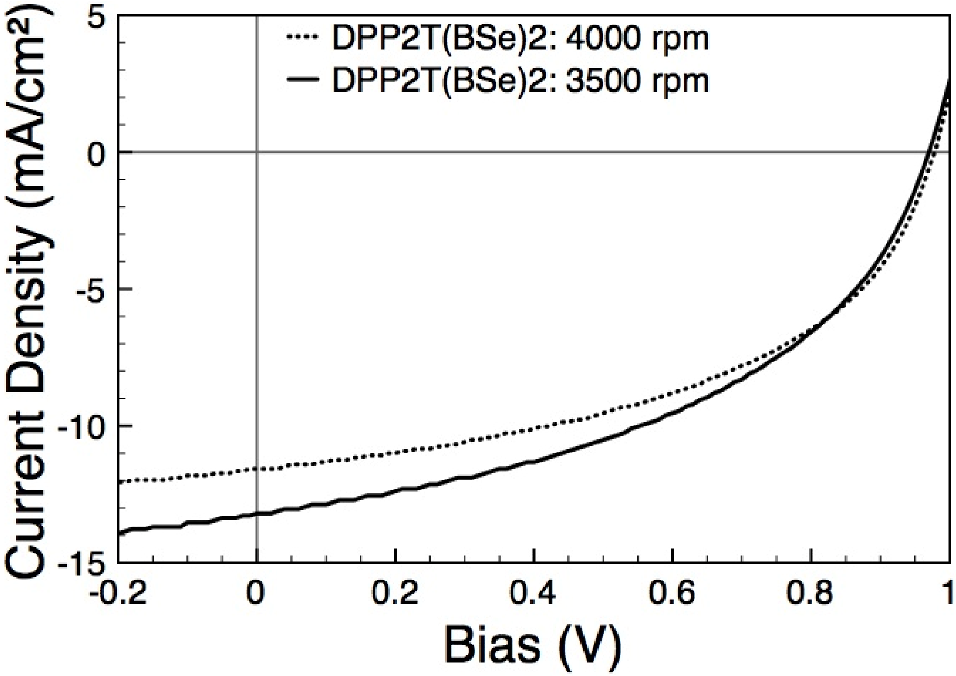
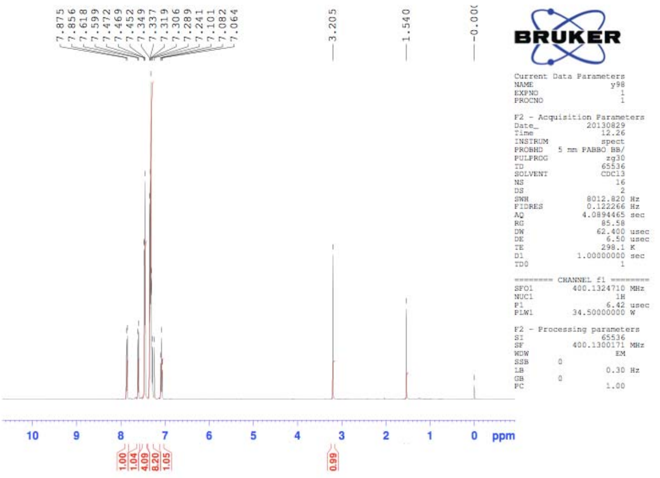


Figure S7. *J-V* curves of solar cell devices of compound 3 for optimization process.

Table S5. Solar cell device parameter of compound 3 during final optimization process [a)]

Spin speed (rpm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)	
				Max	Avg [b)]
4000	0.975	11.57	0.485	5.48	5.10
3500	0.975	13.20	0.454	5.84	5.09

[a)]From Figure S5; [b)]Averaged over 25 devices.



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RG                   85.58
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TE                   298.1 K
D1              1.00000000 sec
TD0                      1

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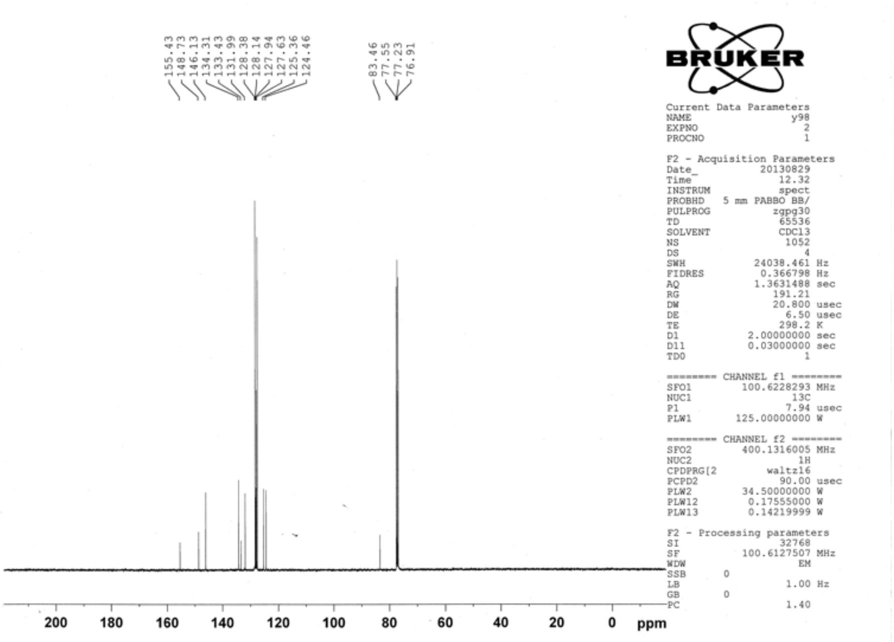
Figure S8. ^{1}H NMR spectra of (2-benzotellurophenyl)diphenylmethanol (**8**).



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RG                  191.21
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TE                   298.2 K
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TD0                      1

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F2 - Processing parameters
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Figure S9. ^{13}C NMR spectra of (2-benzotellurophenyl)diphenylmethanol (**8**).

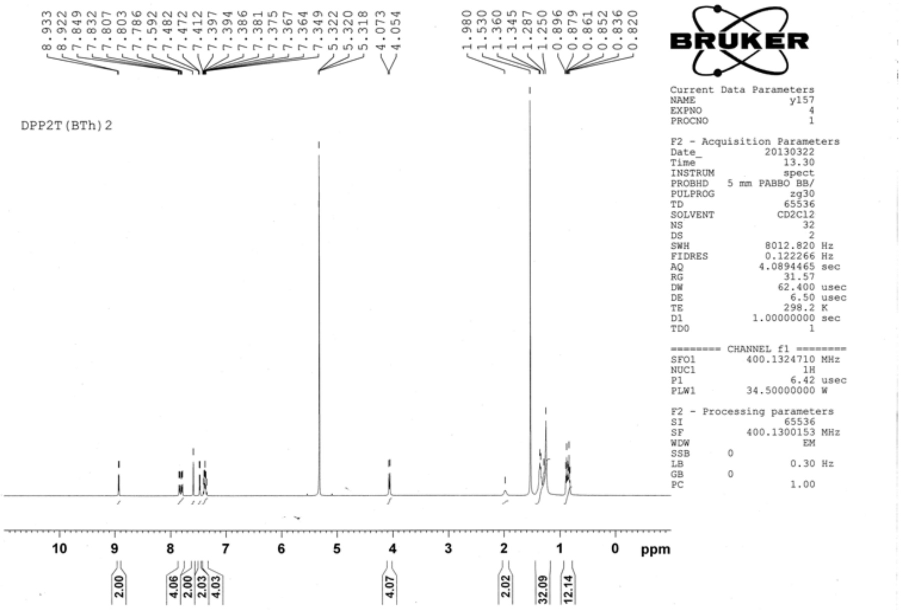


Figure S10. ^{1}H NMR spectra of DPP2T(BTh)$_2$ (**2**).

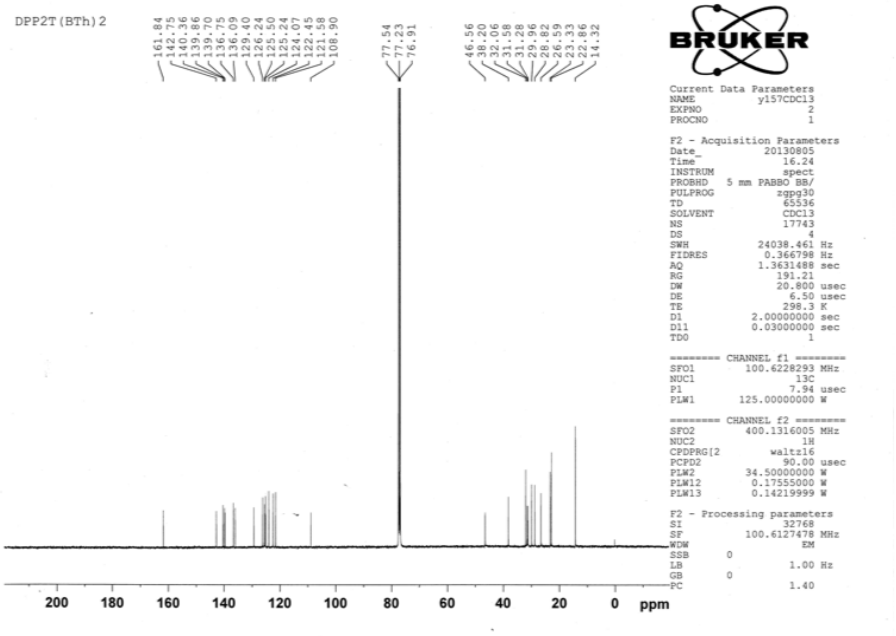


Figure S11. ^{13}C NMR spectra of DPP2T(BTh)$_2$ (**2**).

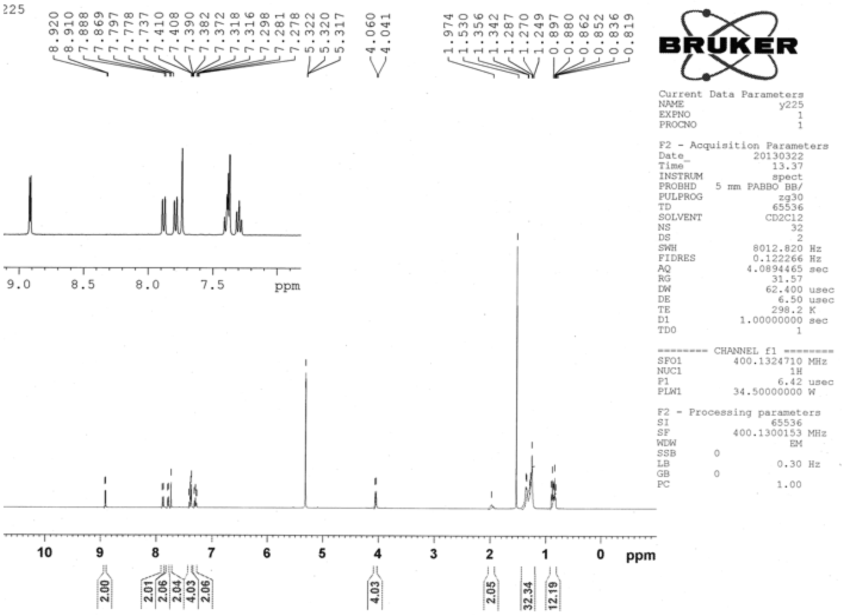


Figure S12. ^{1}H NMR spectra of DPP2T(BSe)$_2$ (**3**).

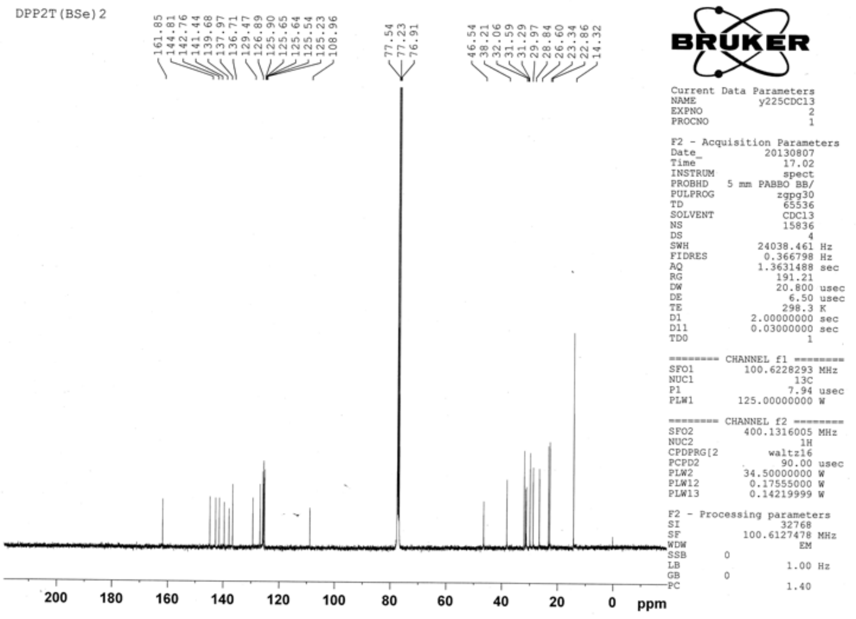
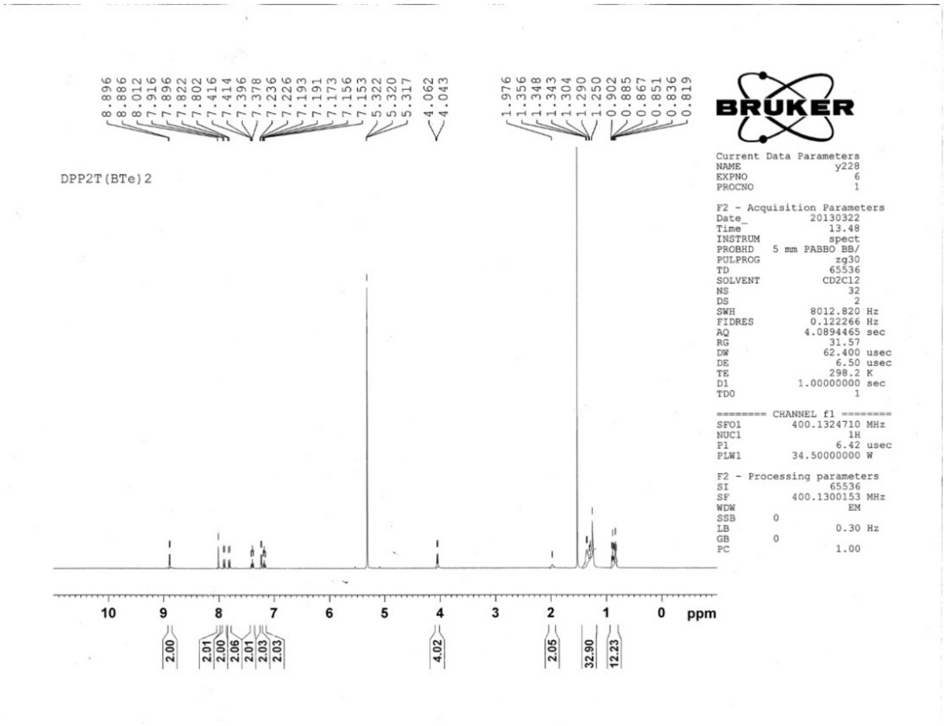


Figure S13. ^{13}C NMR spectra of DPP2T(BSe)$_2$ (**3**).



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FIDRES            0.122266 Hz
AQ               4.0894465 sec
RG                   31.57
DW                  62.400 usec
DE                    6.50 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                      1

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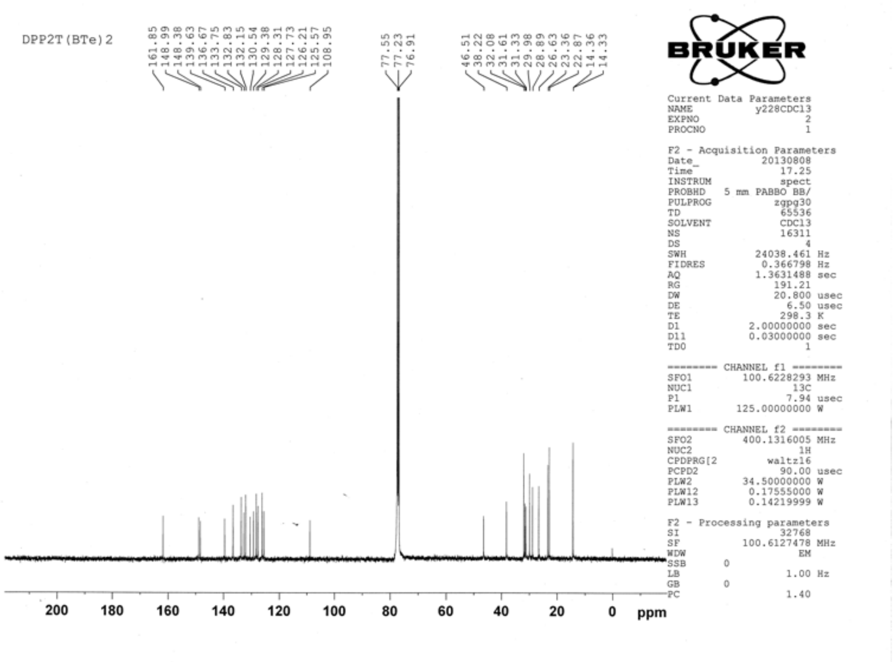
Figure S14. ^{1}H NMR spectra of DPP2T(BTe)$_2$ (**4**).



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FIDRES            0.366798 Hz
AQ               1.3631488 sec
RG                  191.21
DW                  20.800 usec
DE                    6.50 usec
TE                   298.3 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                   13C
P1                    7.94 usec
PLW1          125.00000000 W

======== CHANNEL f2 ========
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NUC2                    1H
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PCPD2                90.00 usec
PLW2           34.50000000 W
PLW12           0.17555000 W
PLW13           0.14219999 W

F2 - Processing parameters
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LB                    1.00 Hz
GB       0
PC                    1.40
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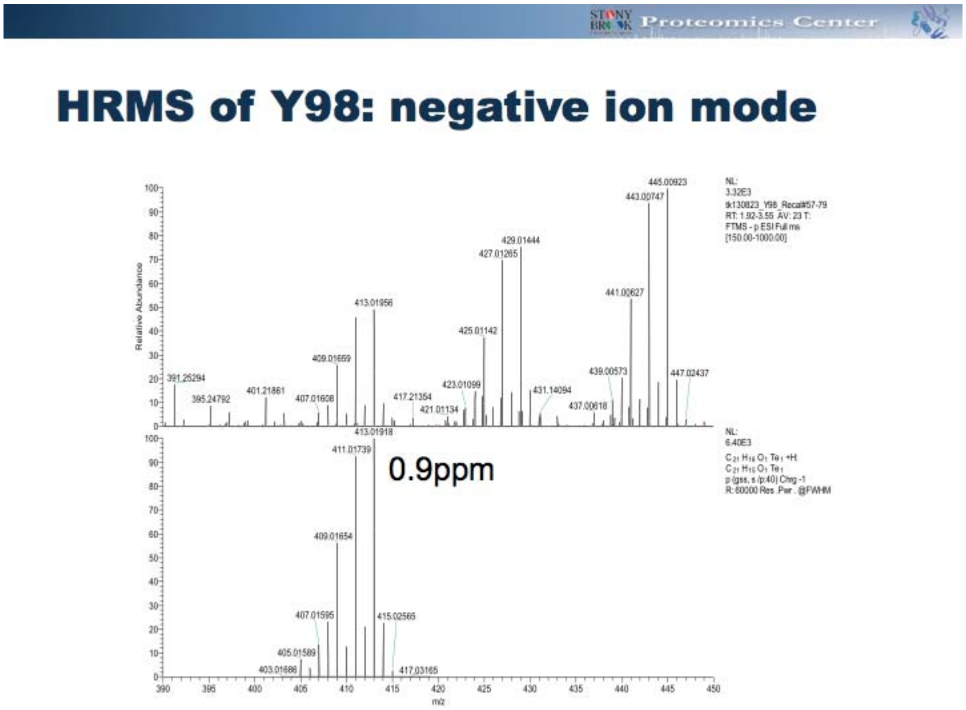
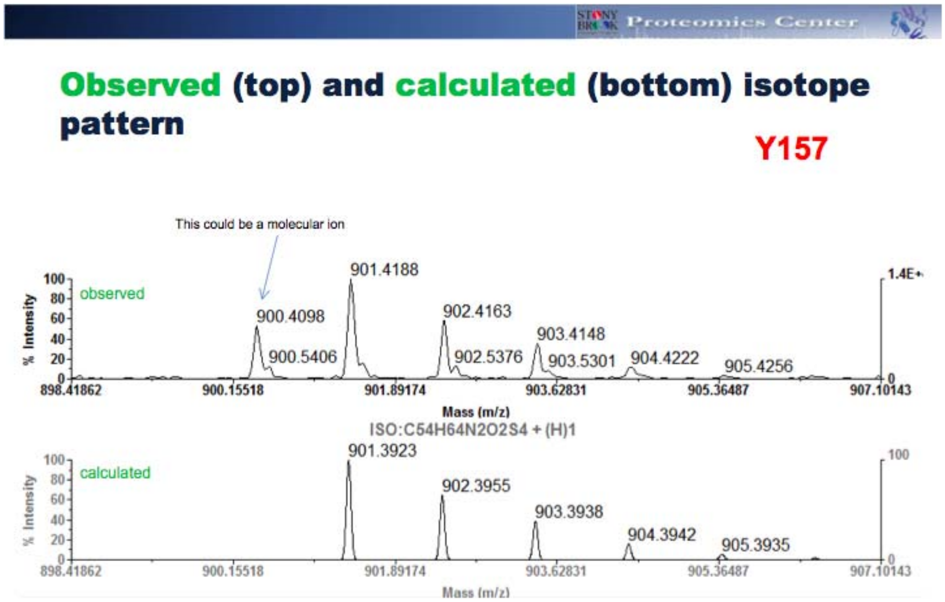
Figure S15. ^{13}C NMR spectra of DPP2T(BTe)$_2$ (**4**).



HRMS of Y98: negative ion mode

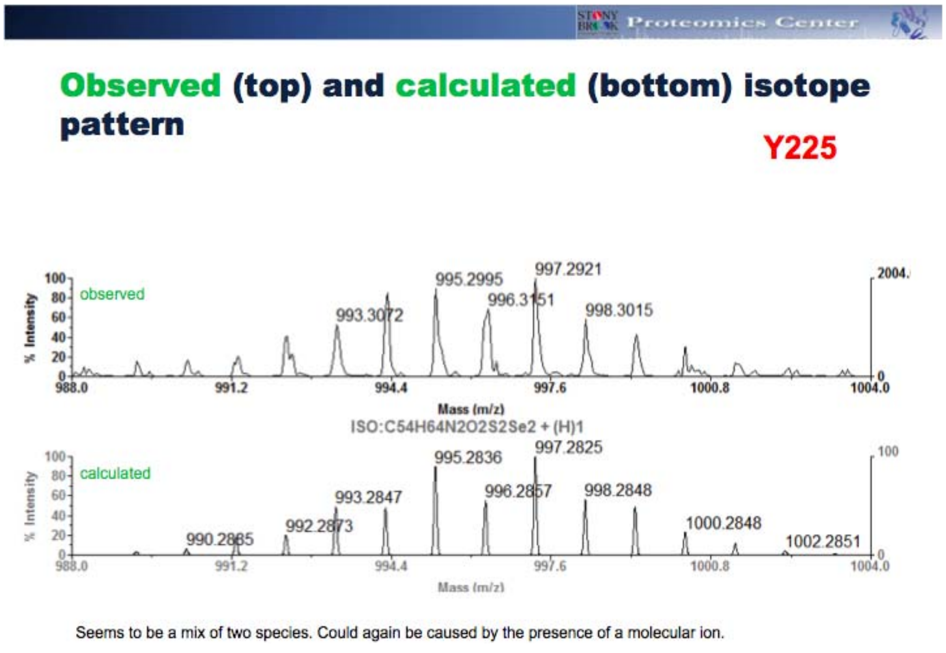
Figure S16. HRMS of (2-benzotellurophenyl)diphenylmethanol (**8**).



Observed (top) and calculated (bottom) isotope pattern

Y157

Figure S17. MALDI-TOF MS of DPP2T(BTh)$_2$ (**2**).

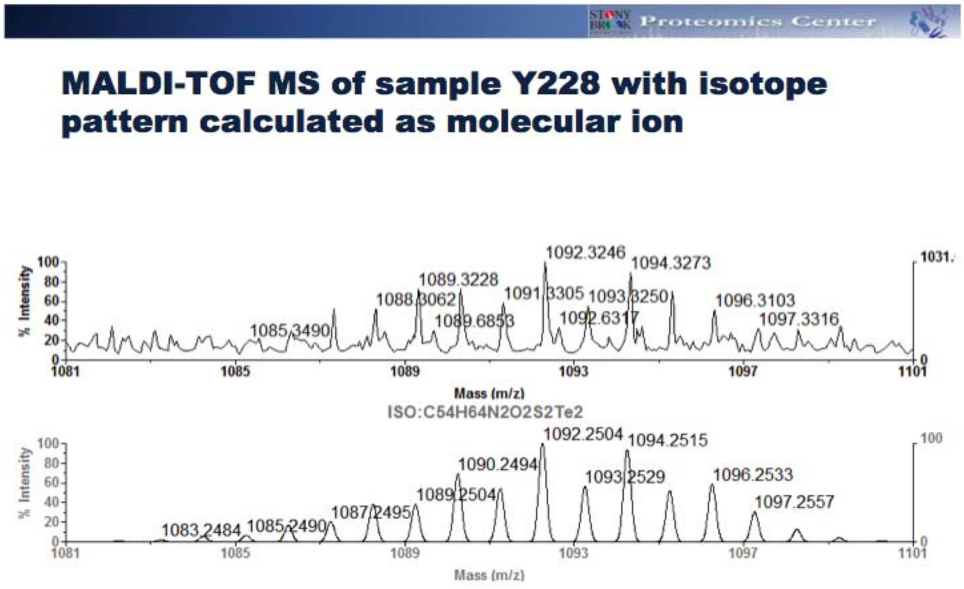


Observed (top) and **calculated** (bottom) isotope pattern

Y225

Seems to be a mix of two species. Could again be caused by the presence of a molecular ion.

Figure S18. MALDI-TOF MS of DPP2T(BSe)$_2$ (**3**).



MALDI-TOF MS of sample Y228 with isotope pattern calculated as molecular ion

Figure S19. MALDI-TOF MS of DPP2T(BTe)$_2$ (**4**). Observed (top) and calculated (bottom) isotope pattern.

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