

Supporting information

Increase in efficiency on using selenophene instead of thiophene in π -bridges for D- π -DPP- π -D organic solar cells

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1. Experimental Section.

1.1. General Remarks.

All solvents and reagents were purchased from Aldrich Chemicals. The solvents were used without previous purification. Anhydrous solvents were dried by purification system Pure-Sov 400. Chromatographic purifications were performed using silica gel 60 Merk 230-400 mesh ASTM. Gel Permeation Chromatography (GPC) column was performed using Bio-Beads® S-X1 Beads 200-400 Mesh as stationary phase. Analytical thin-layer chromatography was performed using ALUGRAM® SIL G/UV₂₅₄ silica gel 60. Nuclear magnetic resonance ¹H NMR and ¹³C NMR were performed using Bruker Innova 400 Hz. Chemical shifts (δ) values are denoted in ppm. Residual solvent peaks have been used as the internal standard (CHCl₃: δ = 7.27 ppm; THF: δ = 3.58 and 1.73 ppm). ¹³C NMR chemical shifts are reported relative to the solvent residual peaks (CDCl₃, δ = 77.00 ppm; THF: δ = 67.6 and 25.5 ppm). MALDI-TOF spectra were obtained in VOYAGER DETM STR spectrometry, using dithranol [1,8-dihydroxy-9(10H)-anthracenone] as matrix. Fourier transform infrared spectrophotometer (FT-IR) Thermo Nicolet AVATAR 370 was used with KBr pellet, in each case the most characteristic bands are indicated for each compound. Absorption spectra were performed on Shimadzu UV 3600 spectrophotometer. Solutions of different concentration were prepared in solvents with spectroscopy grade, with 0.3 absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. The thermal stability was evaluated by TGA on a Mettler Toledo TGA/DSC Start^e System under nitrogen, with a heating rate of 10 °C/min.

Electrochemical Measurements: Reduction (E_{red}) and oxidation potentials (E_{ox}) were measured by cyclic voltammetry with a potentiostat BAS CV50W in a conventional three-electrode cell equipped with a glassy carbon working electrode, a platinum wire counter electrode and a Ag/AgNO₃ reference electrode at scan rate of 100 mV/s. The E_{red} and E_{ox} were expressed vs. Fc/Fc⁺ used as external reference. In each case, the measurements were done in a deaerated solution containing 1 mM of the sample compound in 0.1 M of (*n*-Bu)₄NClO₄ in *o*-DCB:Acetonitrile (4:1) as an electrolyte solution.

Computational Details: Theoretical calculations were carried out within the density functional theory (DFT) framework by using the Gaussian 09, applying density functional theory at the B3LYP level. The basis set of 6-31G* was used in the calculations.

Device fabrication and characterization: The OSCs were fabricated with a conventional device architecture, i.e. ITO coated glass/PEDPOT:PSS/VC6 or VC7:PC₇₁BM /PFN/Al. Firstly, all of the ITO coated glass substrates were cleaned by successive sonication in detergent, deionized water, acetone and finally isopropanol (10 min in each step) and then dried in a vacuum oven for 1 hour. The PEDOT:PSS solution was spin-coated onto the clean ITO substrates at 2000 rpm followed by baking at 120 °C for 15 min in air. The active layer materials (VC6 or VC7:PC₇₁BM with different weight ratio) were dissolved in chloroform (CF) and then spin-coated onto the top of the PEDOT:PSS layer at 2500 rpm for 60 s under ambient atmosphere followed by heat treatment at 40 °C for 10 min to remove the residue of solvent. For the solvent vapour annealing the active layers were placed in a Petri-dish containing THF for 40 s and then removed. A methanol solution of PFN (1.5 mg/mL) was then spin-coated on top of the active layer at 3000 rpm for 30 s. The thickness of the active layers was 90 ± 5 nm. Finally, an Al top electrode was deposited onto the top of the PFN buffer layer by thermal evaporation at vacuum pressure of 2.0 × 10⁻⁵ Pa. The effective area of the devices was around 16 mm². OSCs based on binary BHJ active layers were also prepared for comparison. The current–voltage (*J–V*) characteristics of the BHJ organic solar cells were measured using a computer-controlled Keithley 2400 source meter in the dark and under a simulated AM 1.5 G illumination of 100 mW/cm². A Xenon light source coupled with an optical filter was used to provide the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured using IPCE system (Bentem make).

1.2. Synthetic Procedure.

The compound VC6 was synthesized according to the procedure described in the literature.¹

Synthesis of 2.² In a round bottom flask, under Ar atmosphere, NBS (178 mg, 0.71 mmol) was added to a solution of 2,5-bis(2-ethylhexyl)-3,6-di(selenophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione (200 mg, 0.32 mmol) in CHCl₃ (9 mL). The reaction was stirred in the dark overnight. Afterwards, it was quenched with water (15 mL) and extracted with

¹ V. Cuesta, M. Vartanian, P. de la Cruz, R. Singhal, G.D. Sharma, F. Langa. *J. Mater. Chem. A* **2017**, *5*, 1057.

² J. Hollinger, D. Gao, D.D. Seferos. *Isr. J. Chem.* **2014**, *54*, 817.

CHCl₃ (3x25 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed under vacuum. The obtained solid was purified by column chromatography with silica using as eluent a mixture of hexane:CHCl₃ (1:1) to obtain **2** as a dark solid (200 mg, 0.26 mmol, yield: 80%). ¹H NMR (400 MHz, CDCl₃) δ/ppm: 8.44 (d, *J* = 4.4 Hz, 2H), 7.42 (d, *J* = 4.4 Hz, 2H), 3.89 (t, *J* = 7.4 Hz, 4H), 1.84 (m, 2H), 1.30 (m, 20H), 0.88 (m, 12H); FT-IR (KBr) ν/cm⁻¹: 2954.5, 2923.7, 2861.98, 1666.28.

Synthesis of VC7. Under Ar atmosphere and anhydrous conditions a mixture of **3** (135 mg, 0.15 mmol), **2** (53 mg, 0.068 mmol), CuI (0.06 mg, 3.4x10⁻⁴ mmol) and Pd(PPh₃)₂Cl₂ (5.7 mg, 8.16x10⁻³ mmol), was kept under vacuum 1h. After the solid mixture was dissolved in toluene (20 mL) and freshly distilled triethylamine (4 mL) was added. The reaction was stirred overnight at 85° C and filtrated by Celite using toluene as eluent (100% toluene) and the solvent evaporated under reduced pressure. The obtained solid was purified by GPC using THF as eluent. The solid isolated was washed few times with MeOH and pentane to obtain **VC7** as a black solid (58 mg, 0.024 mmol, yield: 35%). ¹H NMR (400 MHz, THF-*d*₈) δ/ppm: 9.75 (d, *J* = 4.5 Hz, 4H), 9.28 (d, *J* = 4.5 Hz, 4H), 9.10 (d, *J* = 4.6 Hz, 4H), 9.08 (d, *J* = 4.6 Hz, 4H), 8.63 (s, 2H), 7.82 (d, *J* = 3.3 Hz, 4H), 7.81–7.77 (m, 2H), 7.74 (d, *J* = 3.1 Hz, 2H), 7.32 (d, *J* = 3.2 Hz, 4H), 7.16 (d, *J* = 2.8 Hz, 2H), 3.79 (s, 8H), 3.24 (t, *J* = 7.6 Hz, 8H), 3.07 (t, *J* = 7.6 Hz, 6H), 2.06 (m, 18H), 1.89 (m, 18H), 1.63–1.29 (m, 48H), 1.02 (m, 26H); ¹³C NMR (100 MHz, THF-*d*₈) δ/ppm: 165.2, 161.3, 160.4, 151.7, 150.9, 148.3, 146.3, 140.5, 138.8, 137.8, 133.4, 132.4, 130.1, 129.3, 128.5, 128.0, 126.4, 123.4, 115.3, 113.0, 112.2, 111.3, 101.1, 100.1, 91.3, 54.4, 54.2, 40.0, 37.6, 32.1, 31.7, 31.7, 30.2, 29.7, 29.0, 22.7, 22.6, 13.6, 13.5, 13.2; FT-IR (KBr) ν/cm⁻¹: 2923.7, 2854.27, 2159.99, 1612.28. MALDI-TOF MS (*m/z*): calculated for C₁₃₄H₁₄₄N₁₀O₂S₆Se₂Zn₂: 2404.67 [M⁺]; founded: 2404.43 [M⁺]; UV/vis (Toluene) λ/nm (log ε): 446 (5.4), 586 (4.7), 724 (4.8).

2. ^1H NMR, ^{13}C NMR, FT IR and MALDI-TOF MS spectra.

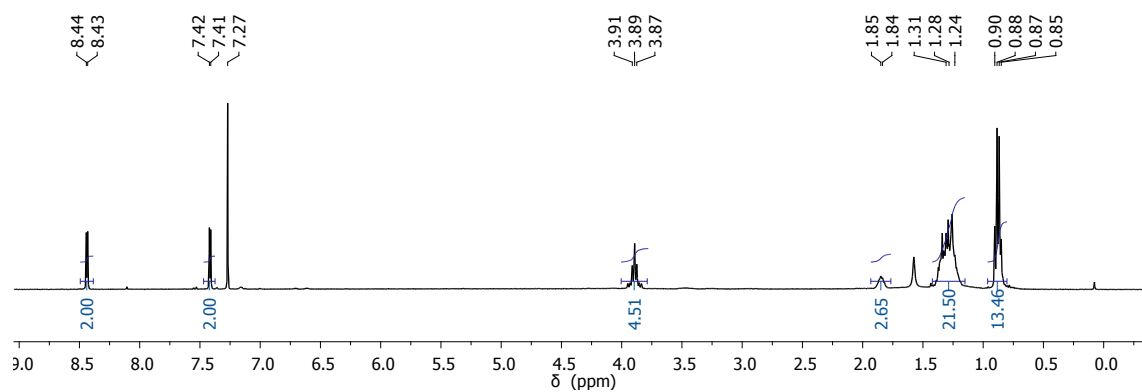


FIGURE S1. ^1H NMR spectrum of compound **2** (400 MHz, CDCl_3).

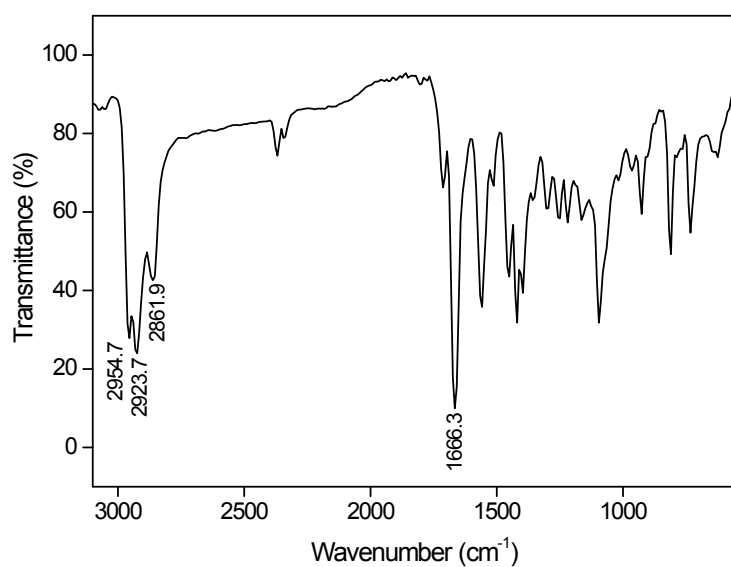


FIGURE S2. FT-IR spectrum of compound **2** (KBr).

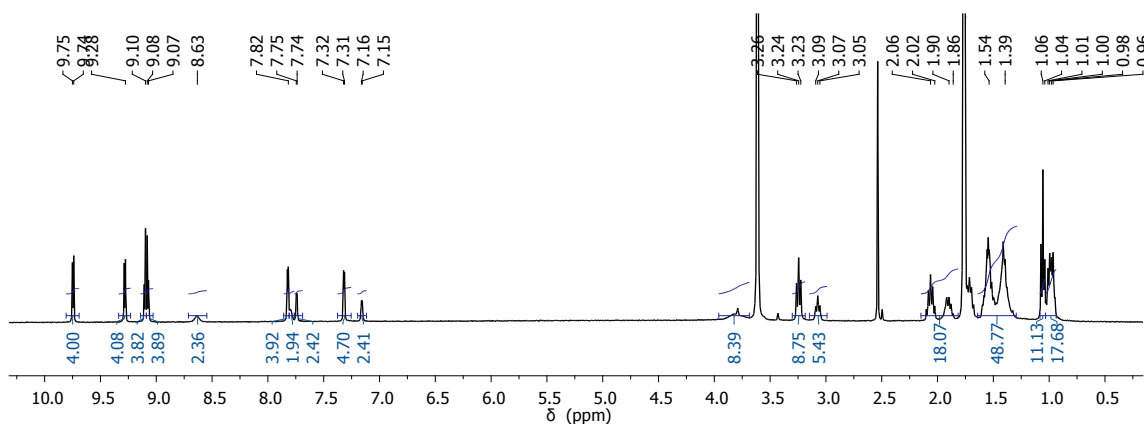


FIGURE S3. ^1H -NMR spectrum of VG7 (400 MHz, $\text{THF-}d_8$).

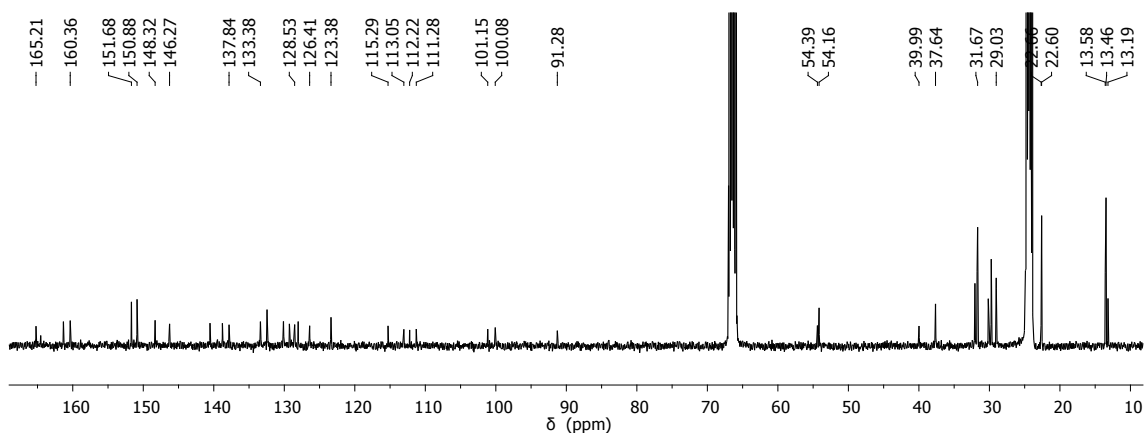


FIGURE S4. ^{13}C -NMR spectrum of VC7 (100 MHz, $\text{THF-}d_8$).

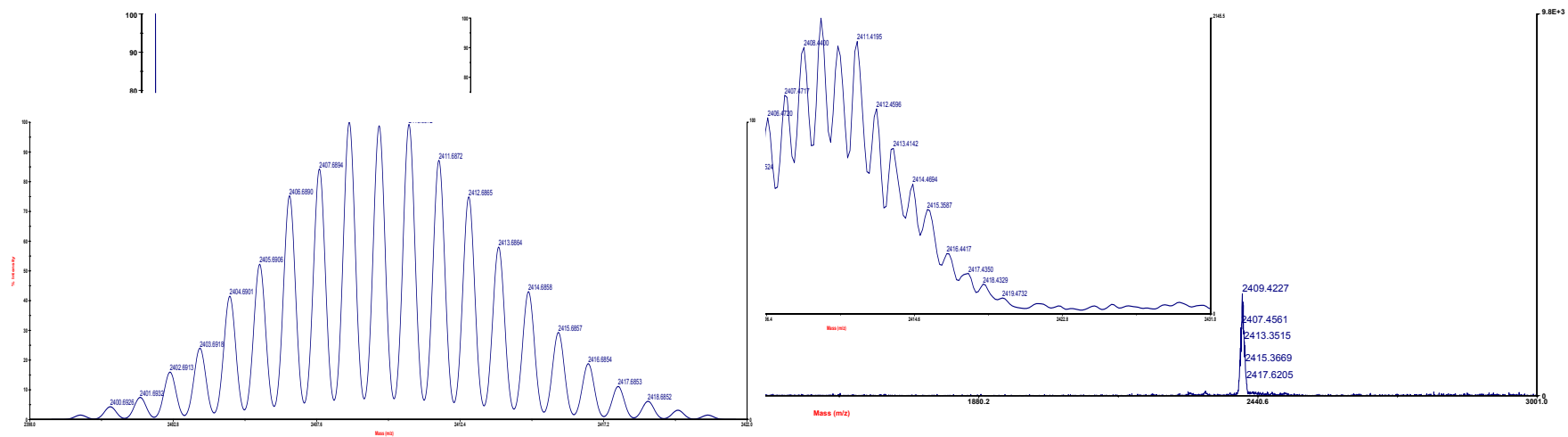


FIGURE S5. Up: Experimental MALDI-TOF MS spectrum of compound **VC7** (Matrix: Dithranol), down: theoretical isotopic distribution calculated for $C_{134}H_{144}N_{10}O_2S_6Se_2Zn_2$.

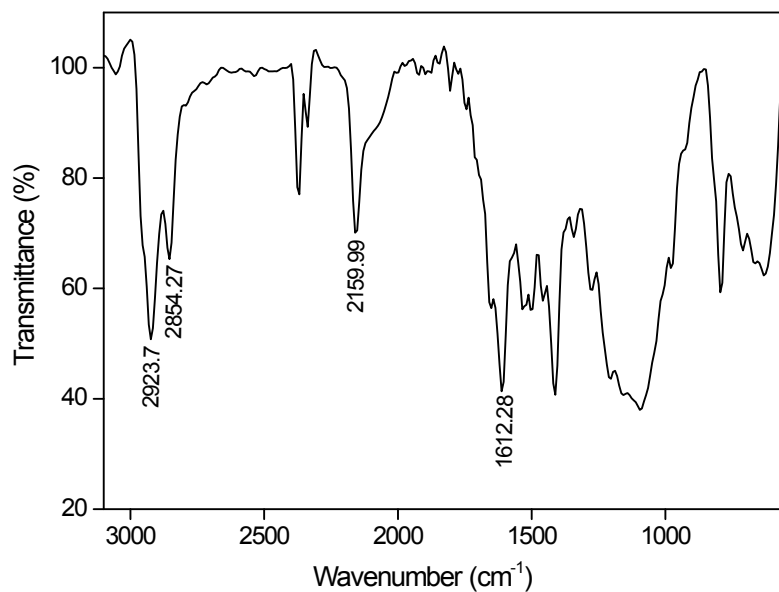


FIGURE S6. FT-IR spectrum of VC7 (KBr).

3. HPLC plot

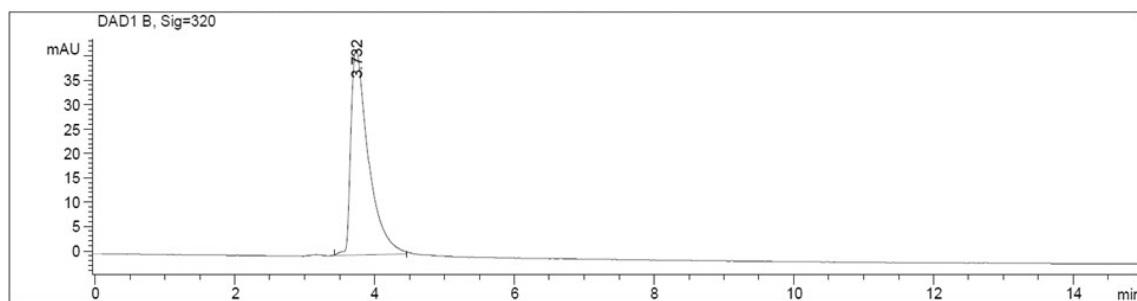


FIGURE S7. HPLC analysis of VC7 recorded using Agilent 1100 (column: Buckyprep (4.6ID x 250 mm)), with toluene as eluent (1 mL/min).

4. Thermogravimetric analysis.

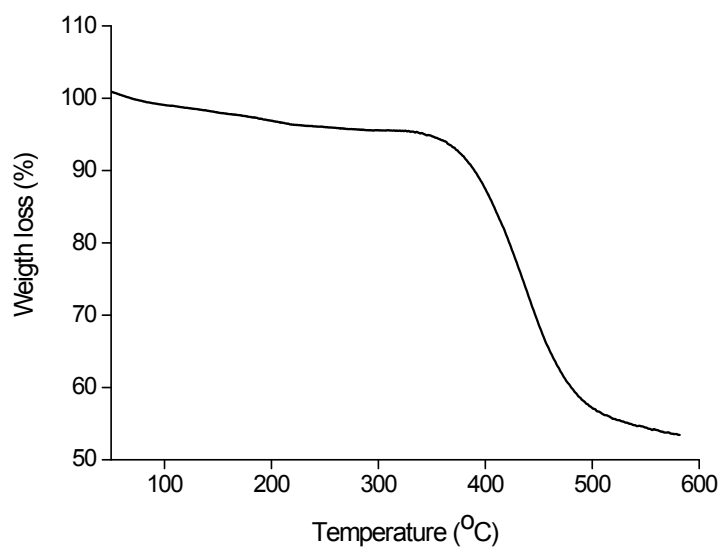


FIGURE S8. Thermogravimetric analysis of **VC7** under N₂ atmosphere.

5. Theoretical Calculations.

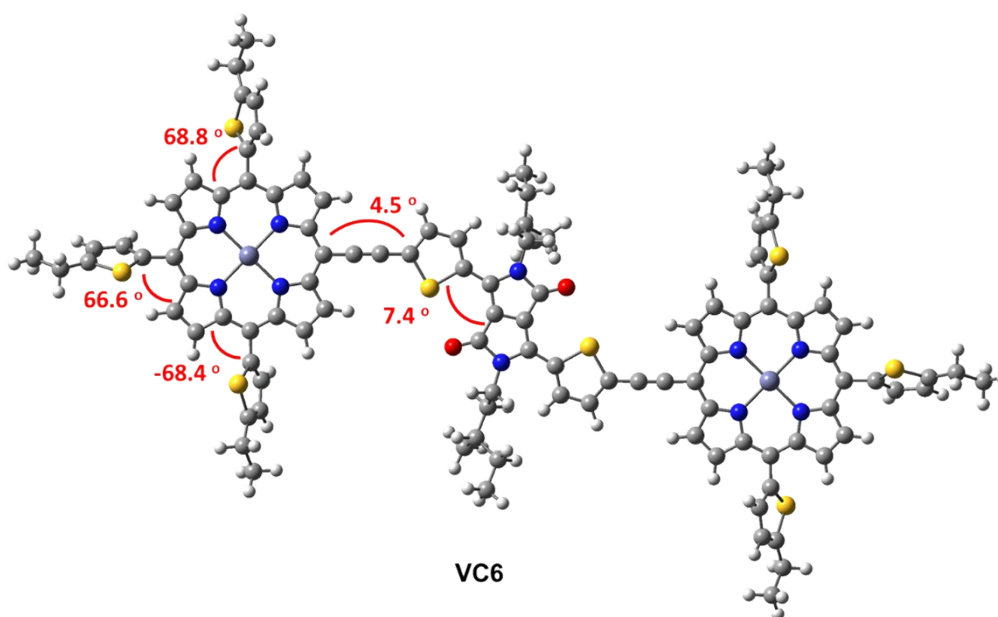
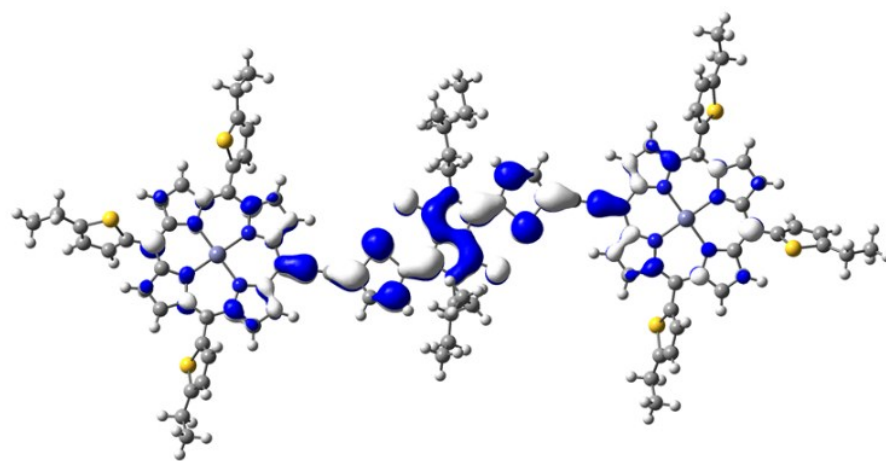
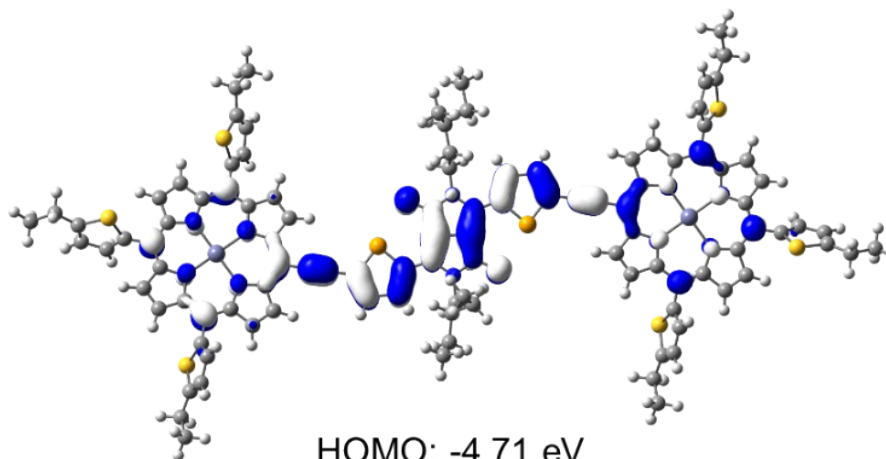


Figure S9. Molecular geometry and selected dihedral angles of compound **VC6**



LUMO: -2.96 eV

$\Delta E = 1.75 \text{ eV}$



HOMO: -4.71 eV

FIGURE S10. Theoretical electron densities and energy levels of molecular orbitals of VC7.

6. Electrochemical Studies.

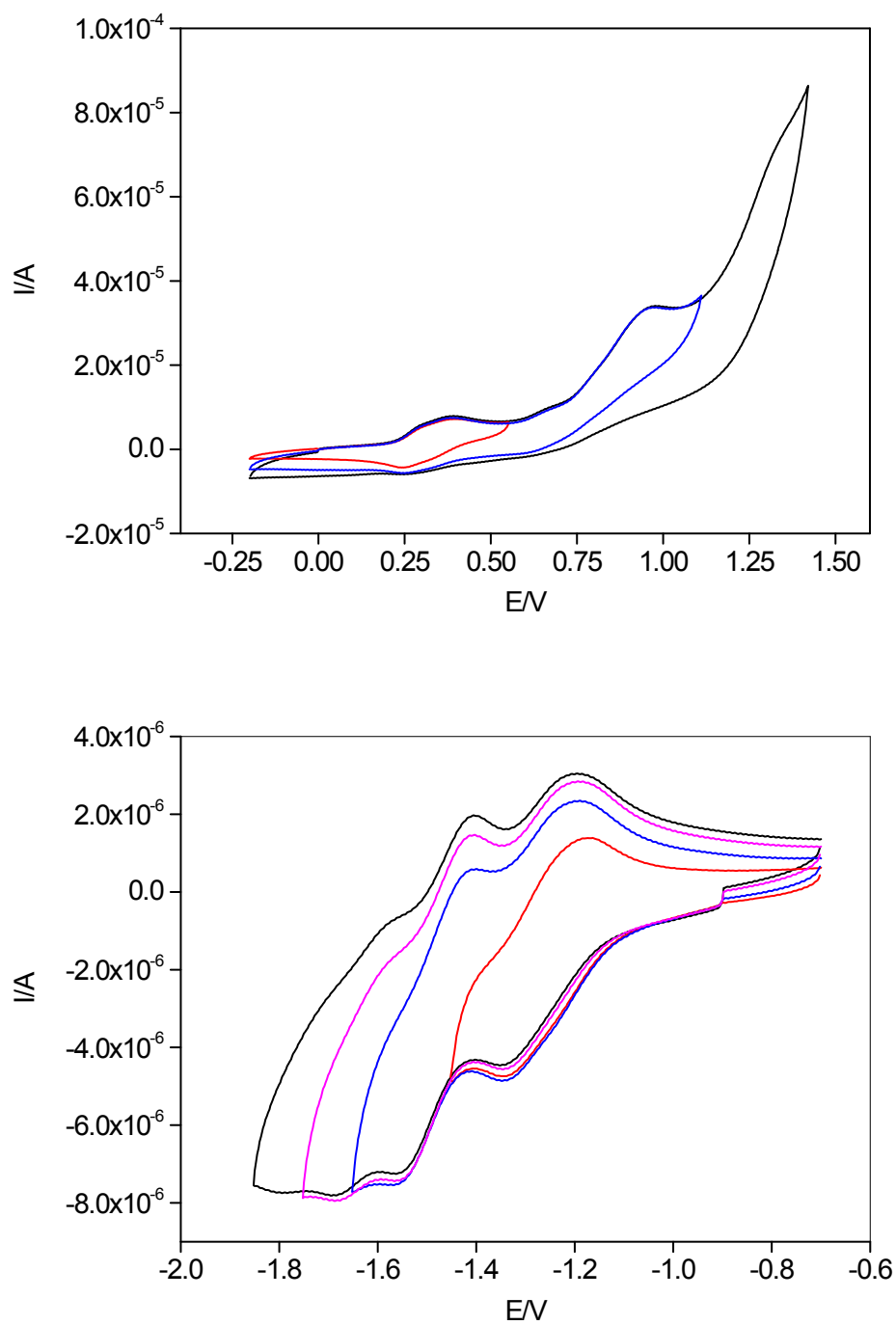


FIGURE S11. Cyclic voltammety plots of VC7: oxidation (up) and reduction (down).

7. Photovoltaic Studies

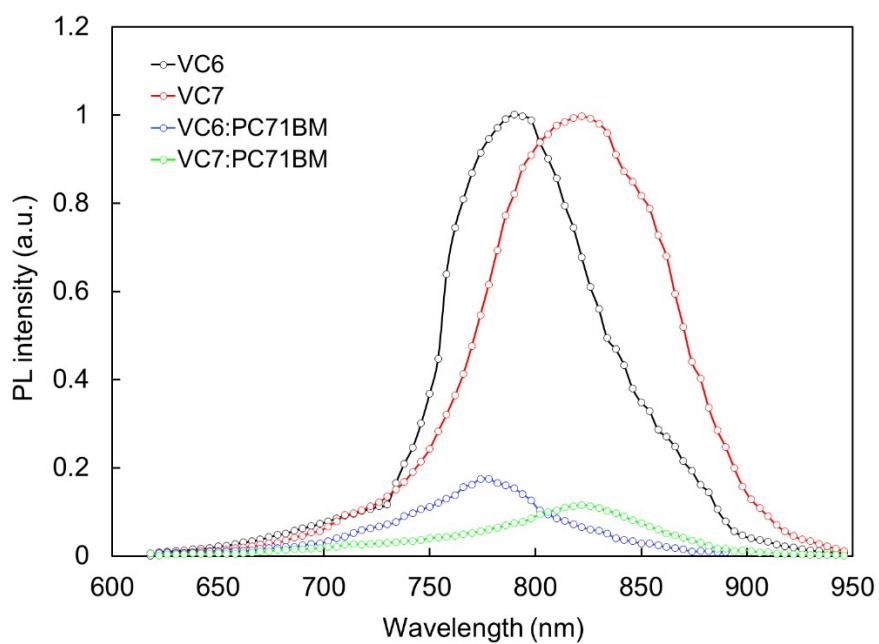


Figure S12. PL spectra of pristine VC6 and VC7 and their blends with PC₇₁BM excited at 450 nm.

Table S1. Photovoltaic parameters of OSCs based on different weight ratio of VC7 and PC₇₁BM.

Weight ratio	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
1:0.5	6.23	0.90	0.43	2.41
1:1	7.34	0.91	0.46	3.07
1:1.5	8.88	0.92	0.486	3.97
1:2	9.76	0.92	0.51	4.58
1:2.5	9.32	0.90	0.49	4.11