Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Synthesis of decyl selenocyanate (RSeCN)

A mixture of KSeCN and 1-bromodecane in the mole ratio of 1:1 was dissolved in dimethyl formamide (DMF) and allowed to stir for 16 h at 60^{o} C. After the completion of the reaction, the resulting mixture was hydrolyzed and the compound was extracted into dichloromethane (DCM). The desired product was obtained after evaporating the organic layer. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8 (t, 3H), 1.2 (m, 12 H), 1.37 (q, 2H), 1.8 (q, 2H), 3 (t, 2H); ^{13}C NMR ($CDCl_3$) δ 102.1 (CN), 23.1, 29.3, 29.5, 29.7, 29.8, 29.9, 30.1, 31.3, 31.8, 32.3; ^{77}Se NMR ($CDCl_3$) 206.8.

Synthesis of didecyldiselenide (DDDSe)

The above synthesized selenocyanate (3 mmol) was dissolved in warm ethanol and to which $NaBH_4$ (3 mmol) was added in proportions. The resulting mixture was stirred for 2 h at room temperature and later the mixture was hydrolyzed. The compound was extracted into DCM and the organic layer was washed with water. The crude product obtained after solvent evaporation was subjected to silica gel column chromatography. The desired product was eluted with pure hexane. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, 6H), 1.3 (m, 24 H), 1.38 (q, 4H), 1.72 (q, 4H), 2.91 (t, 4H); ^{13}C NMR ($CDCl_3$) δ 23.1, 29.6, 29.8, 30.0, 30.7, 31.4, 32.3; ^{77}Se NMR ($CDCl_3$) 305.5.

$$\mathbf{KSeCN} + \mathbf{C_{10}H_{21}Br} \xrightarrow[\text{16 h, 60° C}]{\text{DMF}} \mathbf{C_{10}H_{21}SeCN} + \mathbf{KBr}$$

$$\mathbf{C_{10}H_{21}SeCN} \xrightarrow[\text{2 h, RT}]{NaBH_4\text{, EtOH}} \mathbf{C_{20}H_{42}Se_2}$$

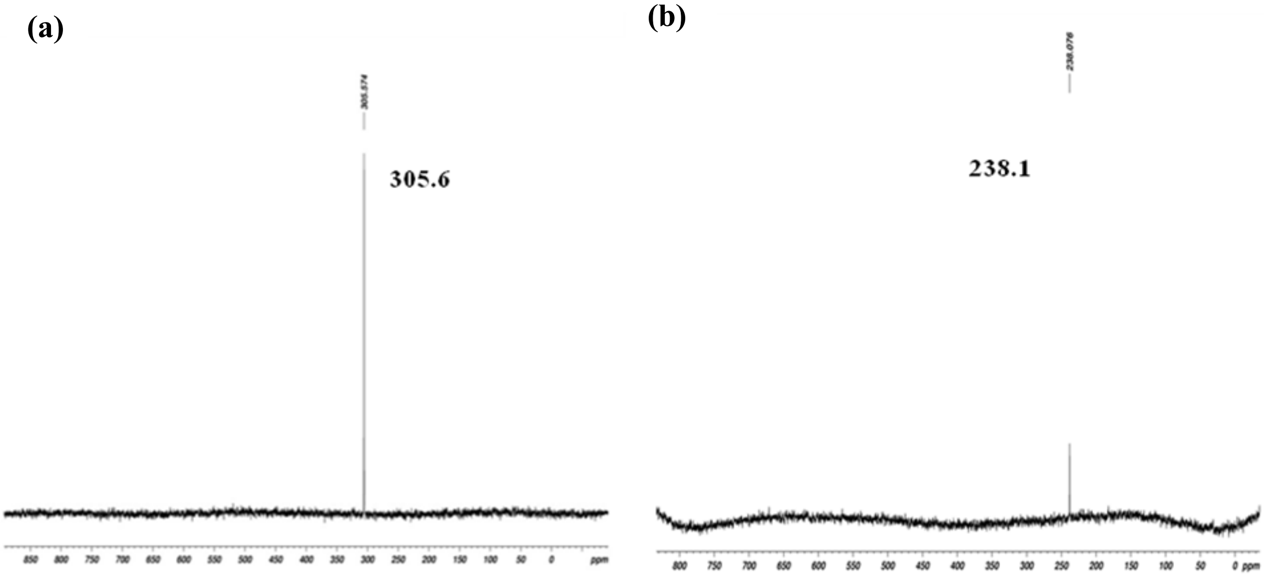

Figure S1. ^{77}Se NMR spectra for (a) pure RSeSeR and (b) $Pd(SeR)_2$ prepared using molar ratio of 1:1 of the precursors (A11 complex).

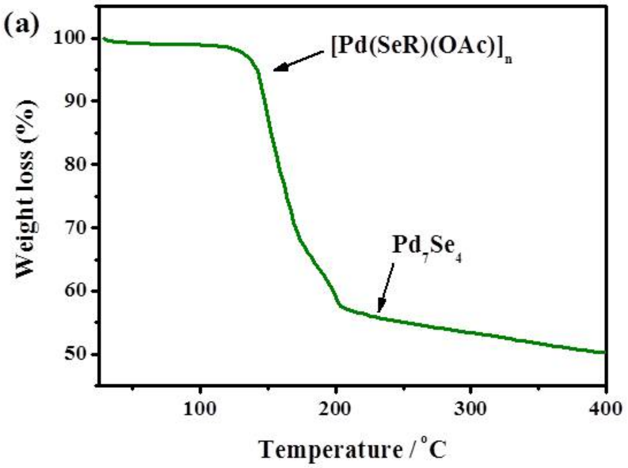

Figure S2. Thermo gravimetric (TG) curve of complex A41 carried out in presence of argon flow with a rate of 10°C / min.

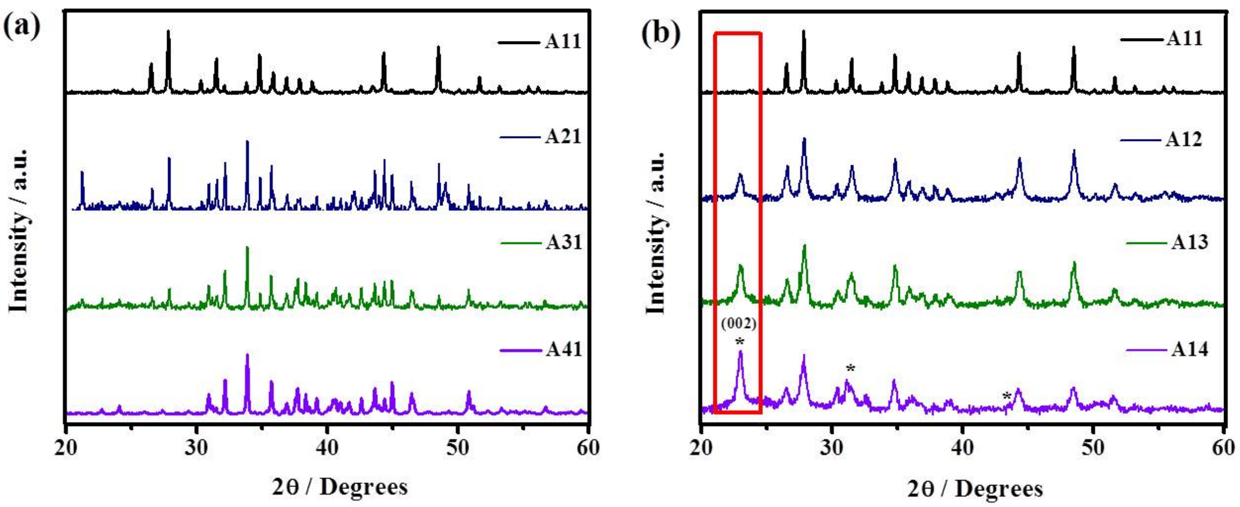

Figure S3. (a) & (b) XRD patterns of different phases formed on thermal decomposition of complexes A by varying the mole ratio of RSeSeR (A) and Pd(OAc)$_2$.

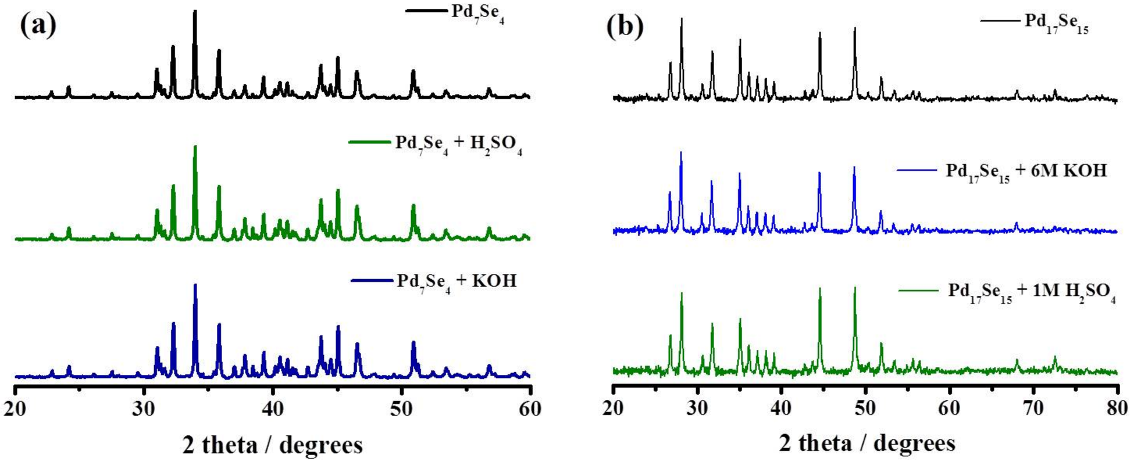

Figure S4. XRD patterns of the films after exposure to different environments of 6 M KOH and 1M H_2SO_4 for 24 h. (a) Pd_7Se_4 and (b) $Pd_{17}Se_{15}$ phases.

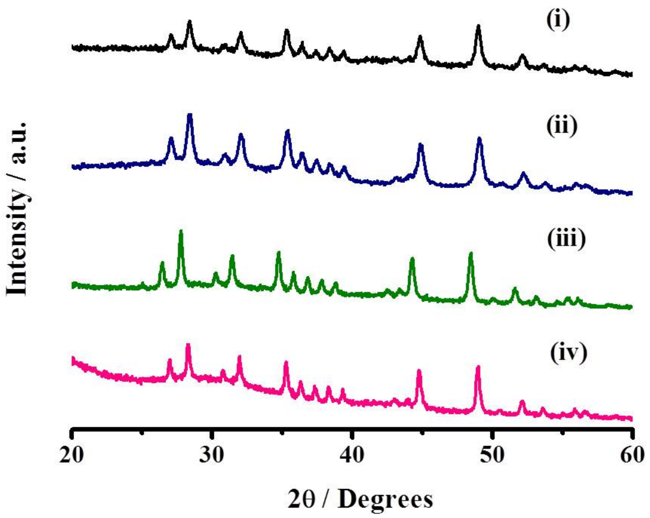

Figure S5. XRD patterns of phases formed on thermal decomposition of complex A11 at different temperatures (i) 200; (ii) 250; (iii) 300, and (iv) 400°C for 1h in presence of N_2.

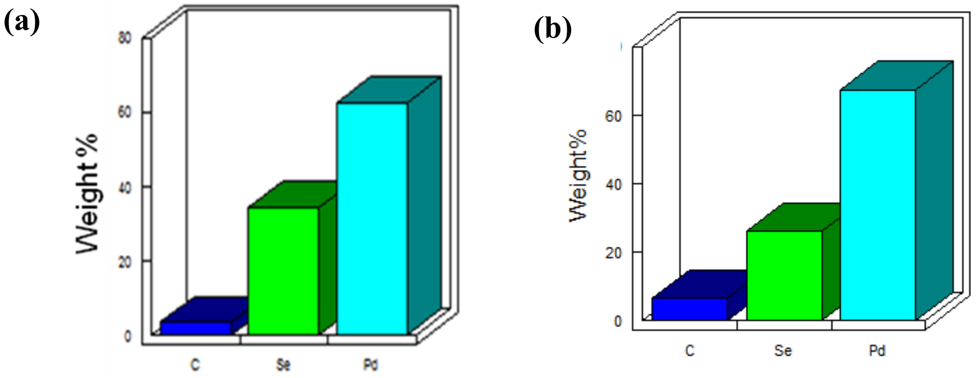

Figure S6. Weight percentages of Pd and Se in (a) $Pd_{17}Se_{15}$ and (b) Pd_7Se_4 obtained from the elemental analysis from SEM. Carbon is observed to a small extent along with the Pd and Se, which is due to the remnants of alkyl groups after thermal decomposition of the complexes.

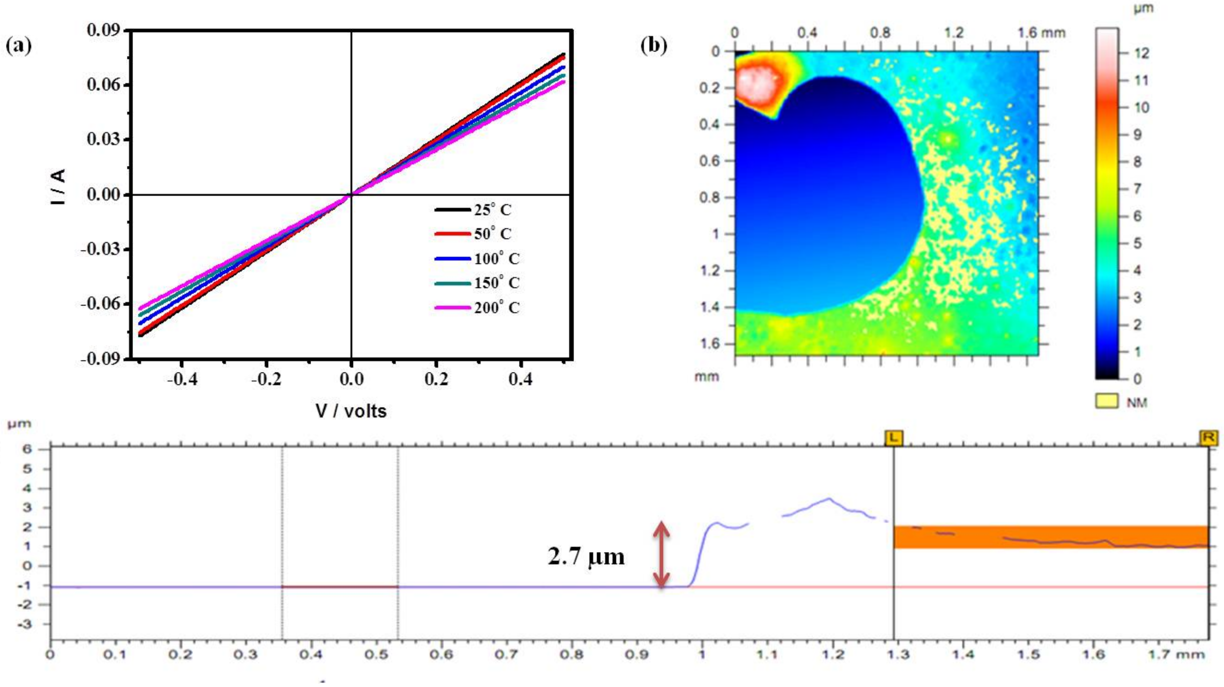

Figure S7. (a) Resistivity of $Pd_{17}Se_{15}$ film as a function of temperature (b) Stylus profilometric measurements on the $Pd_{17}Se_{15}$ film used for the resistivity measurements and (c) Line profile image on figure (b).

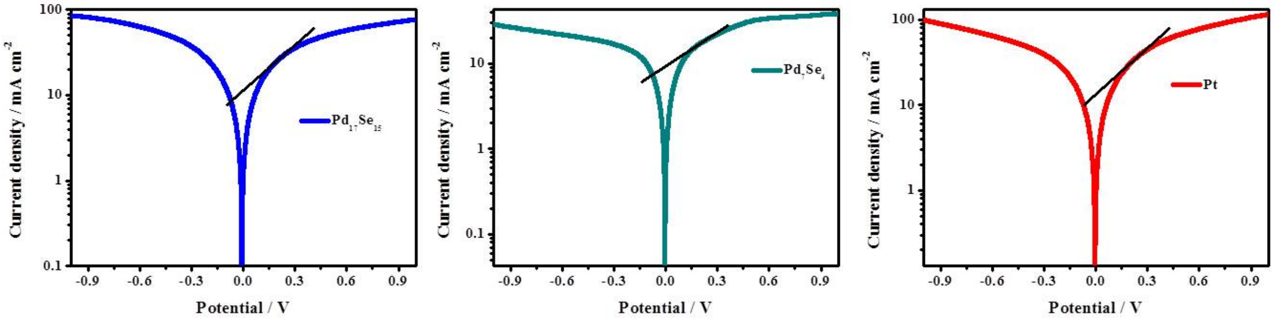

Figure S8. Tafel polarization curves for all the three electrode materials with symmetric cell configuration.

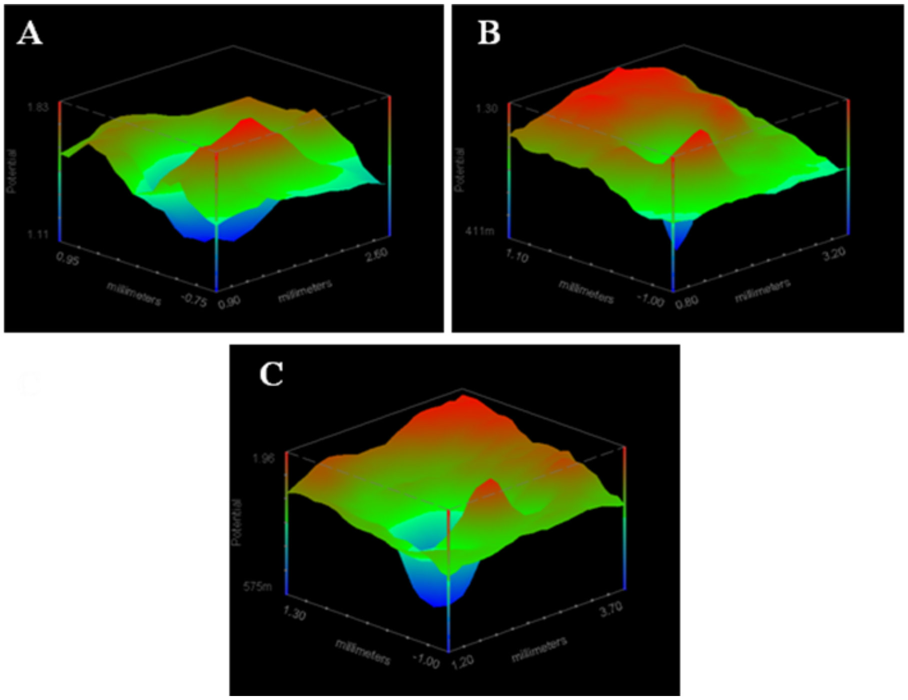

Figure S9. 3-D contour scanning Kelvin probe (SKP) images for work function measurements (a) $Pd_{17}Se_{15}$, (b) Pd_7Se_4 and (c) Pd (prepared from thermal decomposition of $Pd(OAc)_2$).