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Electronic Supplementary Information (ESI)

Dissolution behaviour and activation of selenium in phosphonium based ionic liquids

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Experimental section

Chemicals. Tetrabutylphosphonium chloride ($[P_{4\,4\,4\,4}]Cl$, >95%), trihexyltetradecylphosphonium chloride ($[P_{6\,6\,6\,14}]Cl$, >95%), trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide ($[P_{6\,6\,6\,14}][NTf_2]$, >98%), trihexyltetradecylphosphonium decanoate ($[P_{6\,6\,6\,14}]$[decanoate], >95%) were purchased from IO-LI-TEC, Germany. Selenium powder (99.99%) was purchased from ChemPur, Germany. Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$, 99%) and trioctylphosphine (TOP, 97%) were purchased from ABCR GmbH, Germany. The ionic liquids (ILs) are dried at 110 °C overnight before using. The other chemicals are used as received without further purification.

Materials characterization. Powder X-ray diffraction (XRD) patterns were typically recorded using a PANalytical X'Pert Pro diffractometer with Cu-$K_{\alpha1}$ radiation (λ=154.056 pm). The scanning electron microscopy (SEM) images were obtained at 3 kV using a Hitachi SU8020 field emission SEM Transmission electron microscopy (TEM) images were recorded at 200 kV with Titan Themis TEM equipped with both probe Cs corrector and image Cs corrector. NMR spectra were measured on a Bruker AVANCE III HD Nanobay (^{31}P (161.98 MHz) ^{19}F (376.50 MHz), ^{77}Se(95.38 MHz)) 400 MHz UltraSield or on a Bruker AVANCE III HDX, 500 MHz Ascend (^{31}P (202.45 MHz) ^{77}Se (95.38 MHz)). Chemical shifts were referenced to $\delta_{H3PO4(85\%)} = 0.00$ ppm (^{31}P) and $\delta_{(Me3Si)2Se} = -336.5$ ppm (^{77}Se). Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz.

Dissolution of Se in $[P_{6\,6\,6\,14}]Cl$. 2 mmol (157.92 mg) selenium powder was added to 5 g (9.63 mmol) $[P_{6\,6\,6\,14}]Cl$ and the reaction mixture was heated to 220 °C under Ar at a heating rate of 5 °C/min. After about 5 h of heating, the final reaction mixture was found to be clear light yellow. In addition, a dissolution reaction was also performed by heating stoichiometric amounts of selenium and $[P_{6\,6\,6\,14}]Cl$ mixture at 220 °C under Ar overnight. The supernatant was used for the following separation.

Separation of **2a**,**b** *via* flash chromatography: silica gel, 10 cm, 1 cm Ø, Et_2O.

^{31}P NMR ($CDCl_3$, 25 °C): $\delta(^{31}P) = 36.5$ ppm, $^1J_{PSe} = 680$ Hz; ^{77}Se NMR ($CDCl_3$, 25 °C): $\delta(^{77}Se) = -283.1$ ppm, -283.3 ppm.

Dissolution of Se in $[P_{6\,6\,6\,14}]$[decanoate]. 2 mmol (157.92 mg) selenium powder was added to 5 g (7.63 mmol) $[P_{6\,6\,6\,14}]$[decanoate] and the reaction mixture was heated to 220 °C under Ar at a heating rate of 5 °C/min. After about 10 min of heating, the final reaction mixture was found to be clear orange and to give an orange gel after cooling to room temperature. In addition, a dissolution reaction was also performed by heating stoichiometric amounts of selenium and $[P_{6\,6\,6\,14}]$[decanoate] mixture at 220 °C under Ar for 1 h. The selenium powder was completely dissolved and an orange gel was obtained after cooling down which was used for the following separation.

Separation of **2a**,**b** *via* flash chromatography: silica gel, 10 cm, 1 cm Ø, Et_2O.

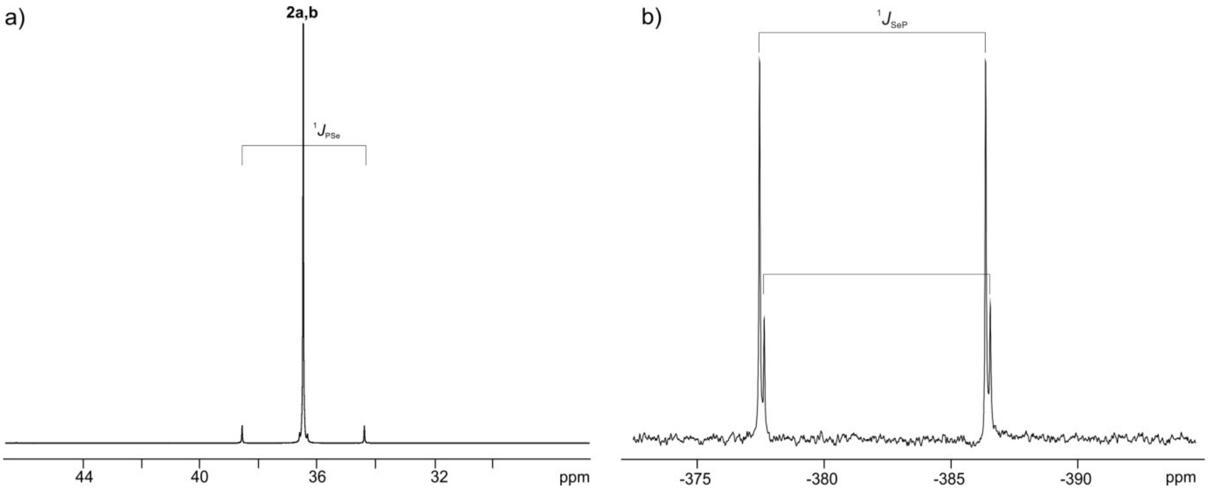

Fig. S1 a) ^{31}P NMR spectrum of **2a**,**b** ($CDCl_3$, 25 °C); b) ^{77}Se NMR spectrum of **2a**,**b** ($CDCl_3$, 25 °C).

Dissolution of Se in $[P_{4\,4\,4\,4}]$Cl. 2 mmol (157.92 mg) selenium powder was added to 5 g (16.96 mmol) $[P_{4\,4\,4\,4}]$Cl and the reaction mixture was heated to 220 °C under Ar at a heating rate of 5 °C/min. After about 4 h of heating, the final reaction mixture was found to be clear light yellow and to give a white solid after cooling to room temperature.

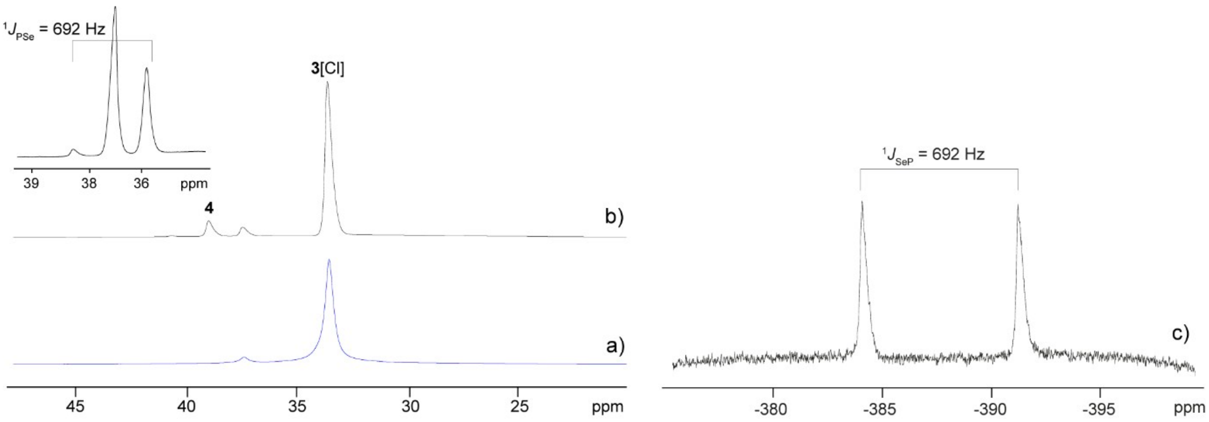

Fig. S2 a) ^{31}P NMR spectrum for $[P_{4\,4\,4\,4}]$Cl (**3**[Cl]) after drying (C_6D_6-capillary, 80 °C); b) ^{31}P NMR spectrum of the reaction solution of 2 mmol selenium in 5 g $[P_{4\,4\,4\,4}]$[Cl] at 220 °C for 4 h under Ar (C_6D_6-capillary, 80 °C); ^{77}Se NMR spectrum of the reaction solution of 2 mmol selenium in 5 g $[P_{4\,4\,4\,4}]$[Cl] at 220 °C for 4 h under Ar (C_6D_6-capillary, 80 °C).

Preparation of TOPSe solution (test reaction of Scheme 1). A mixture of stoichiometric amounts of selenium powder and TOP was stirred at room temperature under Ar overnight. A clear colourless solution was obtained and used for the NMR experiment.

Synthesis of nickel diselenides. 1 mmol (78.96 mg) selenium powder was added to 4 g [$P_{6\,6\,6\,14}$]Cl and heated up to 220 °C under Ar at a heating rate of 5 °C/min. When the selenium solution turned colourless, it was cooled down to 100 °C under constant stirring. 0.5 mmol (145.40 mg) $Ni(NO_3)_2 \cdot 6H_2O$ was added to 4 g [$P_{6\,6\,6\,14}$]Cl and stirred at 120 °C under Ar until a transparent solution formed. These two solutions were mixed and stirred at 100 °C for 5 min. The final mixture was transferred into a 25 mL Teflon-lined autoclave. Then the sealed autoclave was placed in the oven at 200 °C. After 24 h, the autoclave was removed from the furnace and cooled down. The precipitates were washed with water and ethanol several times and carefully collected by centrifugation. The final products were dried in vacuum at room temperature overnight. The synthesis of $NiSe_2$ was also performed using different amount of $Ni(NO_3)_2 \cdot 6H_2O$ and different temperatures with the same procedure as described above.

Synthesis of zinc selenides. 0.3 mmol (23.69 mg) selenium powder was added to 4 g [$P_{6\,6\,6\,14}$][decanoate] and heated up to 200 °C under Ar at a heating rate of 5 °C/min. When the selenium was dissolved completely, it was kept at 200 °C for another 30 min and then cooled down to 100 °C under constant stirring. 0.3 mmol (189.70 mg) zinc stearate was added to 4 g [$P_{6\,6\,6\,14}$][decanoate] and stirred at 130 °C under Ar until a transparent solution formed. These two solutions were mixed and stirred at 100 °C for 5 min. Then the mixture was heated to 250 °C at a heating rate of 5 °C/min and kept at 250 °C for 1 h to get a light yellow colloidal solution. After cooling down the reaction solution, the ZnSe nanocrystals were precipitated by adding 15 mL methanol into the colloidal solution, centrifuged, washed repeatedly, and dispersed in toluene for following characterizations.

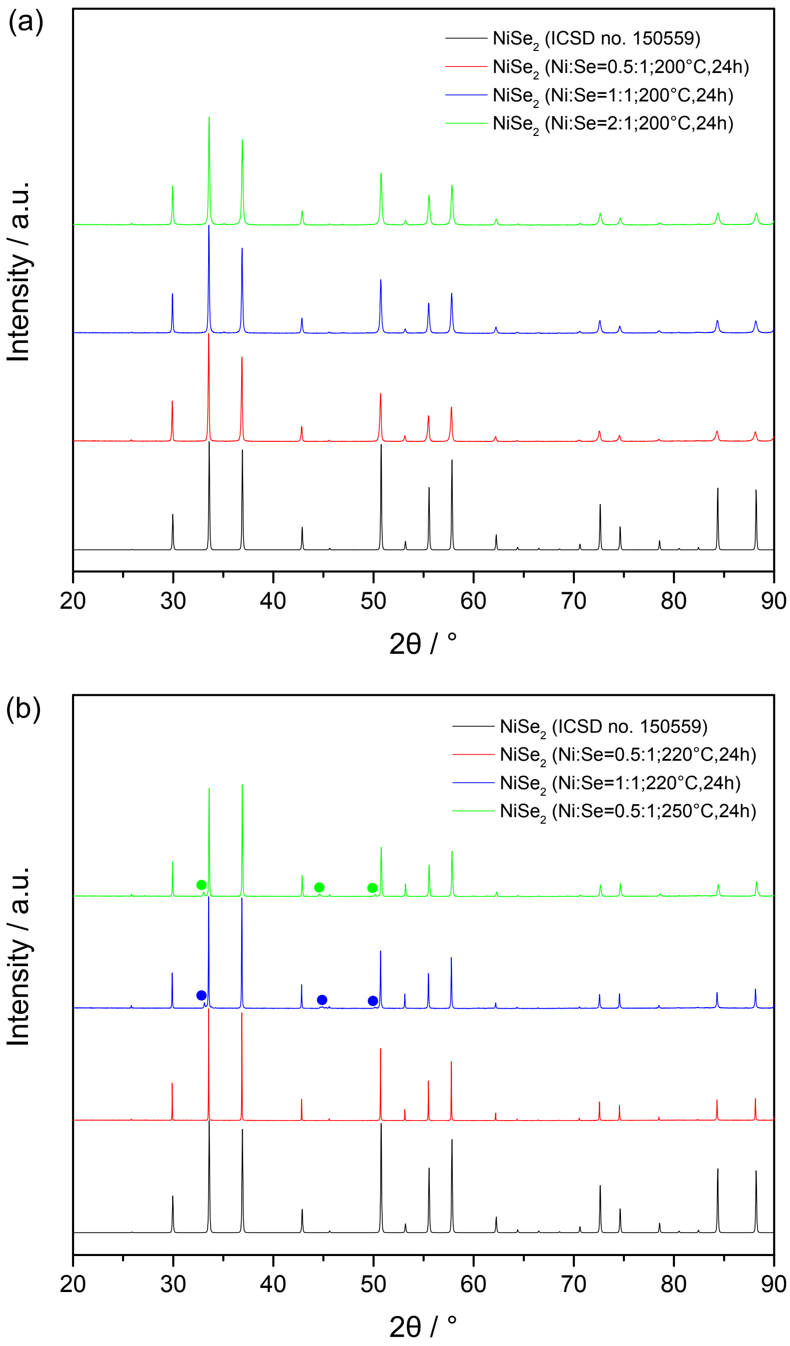

Fig. S3 X-ray diffraction (XRD) patterns of as-prepared NiSe$_2$ particles. (a) XRD patterns of NiSe$_2$ particles synthesized at 200 °C with different amount of Ni(NO$_3$)$_2$·6H$_2$O (indicated by coloured circles). (b) XRD patterns of NiSe$_2$ particles synthesized at 220 °C and 250 °C with different amount of Ni(NO$_3$)$_2$·6H$_2$O.

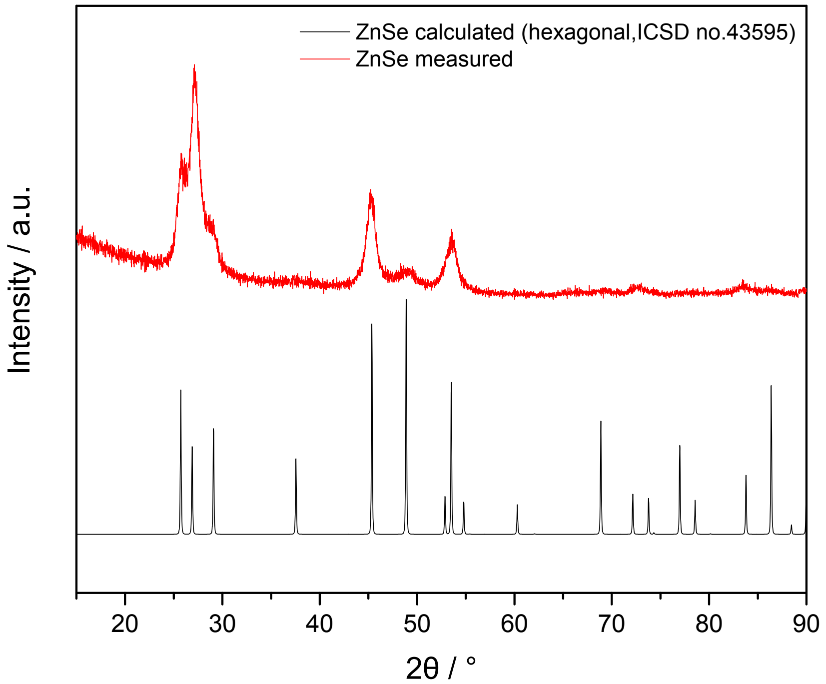

Fig. S4 XRD patterns of as-prepared ZnSe nanocrystals.