Supporting information

Submitted to New Journal of Chemistry

3 Figures.
1 Section.
**Figure S1.** The experimental apparatus for Se reduction by CO/H$_2$O in the ILs

**Figure S2.** The standard curve of polyselenide concentration vs. absorption

\[ y = 397.61x - 19.98 \]
\[ R^2 = 0.99 \]
Section S1. The formation of Se$_{2}^{2-}$ and Se$_{4}^{2-}$

The UV–Vis transmittance spectroscopy was carried out during the 105 min of this reaction to verify the product of the solution (Figure S3). All spectra in Fig S3 were compared with those of standard substances (Na$_2$Se$_2$ and Na$_2$Se$_4$).

As shown in the graph, standard Se$_{2}^{2-}$ had an obvious characteristic absorption peak at 428 nm and. As seen, within the 60 min, the absorbance at 428 generally increased, possibly attributed to the formation of some Se$_{2}^{2-}$. Meanwhile, a shoulder peak at 565 nm is observed with the reaction progressed (>60 min), indicating the formation of trace Se$_{4}^{2-}$. With further reaction, the absorbance at 428 nm was blue shift to 409 nm when reaction time was increased from 60 to 105 min. The peak at 409 nm can be identified as the Se$_{4}^{2-}$. This phenomenon indicated that the formed Se$_{2}^{2-}$ in this system seems unstable. Once Se$_{2}^{2-}$ is formed, it will transform to Se$_{4}^{2-}$ via disproportionation.

Figure S3. UV-vis spectra of reaction solution at different reacting times