Visible-light-induced metathesis reaction between diselenide and ditelluride

Cheng Liu, Jiahao Xia, Shaobo Ji, Zhiyuan Fan and Huaping Xu*

Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Email address: xuhuaping@mail.tsinghua.edu.cn

Supporting Information

1. Experimental Procedures

1.1 Materials

Diphenyl diselenide ($(PhSe)_2$), dibenzyl diselenide ($(BenSe)_2$), diphenyl ditelluride ($(PhTe)_2$) and 8-bromooctanoic acid were purchased from TCI. Di-(1-hydroxylundecyl) diselenide ($(HOC11Se)_2$) was obtained from our own laboratory synthesized with the previously reported method.[S1] Selenium and tellurium powder was product from Aladdin Chemical Reagent Co. Ltd. Sodium borohydride was purchased from Alfa Aesar. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was purchased from Dojindo Molecular Technologies, Inc. Dimethyl sulfoxide-d6 (DMSO-d6) was product from Cambridge Isotope Laboratories, Inc. Chloroform-d1 was purchased from Meryer (Shanghai) Chemical Technology Co. Ltd. Methanol-d4, acetone-d6, and acetonitril-d3 were products from BASF. 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), 5-bromovaleric acid, 3-bromo-1-propanol, ultra-dry DMSO used for trapping radicals and DMSO-d6 used for kinetics study were purchased from J&K Chemical. The concentrated hydrochloric acid (HCl) and the other analytical-grade organic solvents used in this study were purchased from Beijing Chemical Reagent Company, Beijing, China.

1.2 Instruments and methods

The ^{1}H and ^{77}Se NMR spectra were conducted on BRUKER AVANCE Ⅲ HD 400 (400 M) spectrometer under ambient temperature (20 °C). The ^{125}Te and ^{1}H NMR spectra under variable-temperature (40 °C, 50 °C, 60 °C, 70 °C and 80 °C) were recorded on JEOL JNM-ECA 600 (600 M) spectrometer. EPR spectra were performed on JEOL JES-FA200 apparatus. For normal white light, white LED light with intensity of 118 Lux was used. For exchange reactions with wavelength above 600nm, the xenon lamp (PLS-SXE300/300UV) were used with light filters. High pressure mercury lamp (USH-500SC) with light filters which wavelength was above 420nm was used for the radical detection.

1.3 Synthetic procedures of $(HOOCC4Se)_2$

The synthesis route of di-(1-carboxylbutyl) diselenide ($(HOOCC4Se)_2$) was shown in Figure S2. First, Se powder (0.8848 g, 0.0112 mol) and sodium borohydride (0.4144 g, 0.0110 mol) were reacted with water (20 mL) at 50 °C for 30 minutes in the nitrogen atmosphere to prepare disodium diselenide. Then, tetrahydrofuran (THF) solution (40 mL) of 5-bromovaleric acid (2.0010 g, 0.0110 mol) was added and reacted at the same temperature overnight. After evaporating THF, the mixture was extracted by CH_2Cl_2 and washed with 1% HCl aqueous solution in total for three times. And the solvent was removed after drying by anhydrous sodium sulfate. Then the crude was re-dissolved in CH_2Cl_2 (10 mL) and recrystallized from cold petroleum ether (150 mL). After filtration, the pure yellow solid powder was finally obtained, the yield is 69.75%.

^{1}H-NMR (400 M, DMSO-d6). δ (ppm): 12.03 (2H, s, *COOH*), 2.91 (4H, t, $\mathit{CH_2}Se$), 2.23 (4H, t, $\mathit{CH_2}COOH$), 1.69 (4H, m, $\mathit{CH_2}CH_2Se$), 1.58 (4H, m, $\mathit{CH_2}CH_2COOH$).

1.4 Synthetic procedures of (HOOCC7Se)$_2$

The synthesis route of di-(1-carboxylheptyl) diselenide ((HOOCC7Se)$_2$) was similar with (HOOCC4Se)$_2$ as shown in Figure S2. First, disodium diselenide was obtained from degassed water (20 mL) through the reaction between Se powder (1.0615 g, 0.0134 mol) and sodium borohydride (0.4973 g, 0.0132 mol). Then the THF solution (40 mL) of 8-bromooctanoic acid (3.0120 g, 0.0134 mol) was added under nitrogen flow and reacted at 50 °C overnight. After the same procedures of post-treatment, the pure yellow solid powder was obtained and the yield was 83.60%. ^{1}H-NMR (400 M, DMSO-d6). δ (ppm): 11.94 (2H, s, *COOH*), 2.90 (4H, t, CH_2Se), 2.19 (4H, t, CH_2COOH), 1.67 (4H, m, CH_2CH_2Se), 1.48 (4H, m, CH_2CH_2COOH), 1.40-1.20 (12H SeCH$_2$CH$_2$$(CH_2)_3CH_2CH_2$COOH).

1.5 Synthetic procedures of (HOC3Te)$_2$

The synthesis route of di-(1-propanol) ditelluride ((HOC3Te)$_2$) was shown in Figure S2. First, disodium ditelluride was obtained from degassed water (35 mL) through the reaction between Te powder (2.4983 g, 0.0196 mol) and sodium borohydride (0.5698 g, 0.0151 mol) at 50 °C for one hour under the nitrogen atmosphere. Then the THF solution (25mL) of 3-bromo-1-propanol (2.0983 g, 0.0151 mol) was added and reacted overnight. After evaporating THF, the mixture was extracted by CH_2Cl_2. And the solvent was removed after drying by anhydrous sodium sulfate. Then the crude was purified by column chromatography using a CH_2Cl_2:EtOAc mixture of 1.5:1 as eluent. At last, the pure wine oil-like liquid was obtained, the yield is 37.10%.^{1}H-NMR (400 M, DMSO-d6). δ (ppm): 4.57 (2H, t, *OH*), 3.42 (4H, m, CH_2OH), 3.07 (4H, t, CH_2Te), 1.82 (4H, m, CH_2CH_2Te).

1.6 Metathesis between diselenide and ditelluride

Besides the (BenSe)$_2$, the other diselenide species such as di-(1-hydroxyundecyl) diselenide ((HOC11Se)$_2$), di-(1-carboxylbutyl) diselenide ((HOOCC4Se)$_2$) and di-(1-carboxylheptyl) diselenide ((HOOCC7Se)$_2$) could also exchange with (PhTe)$_2$. And besides the (PhTe)$_2$, the (BenSe)$_2$ could also exchange with (HOC3Te)$_2$. For the convenient real-time NMR detection, the exchange reaction was conducted in NMR tube directly with reactant ratio of 1:1. The NMR tube was irradiated with the white LED light while being immersed in a water bath for constant temperature. All the metathesis reactions induced by visible light were conducted with a concentration of 20 mM of each reactant in DMSO-d6 without catalyst. As all metathesis reactions were performed by means of the same method, the exchange procedure between (HOC11Se)$_2$ and (PhTe)$_2$ is emphasized as a representative. First, 0.012 mmol of (HOC11Se)$_2$ and 0.012 mmol of (PhTe)$_2$ were dissolved in 0.6 mL DMSO-d6 with a 4 mL vial. Then the vial was placed under the white LED light and exchanged in the nitrogen atmosphere for one hour. And water bath was used to keep the mixture cold.

2. Results and Discussion

2.1 The diselenides and ditellurides utilized for the formation of Se-Te DCB

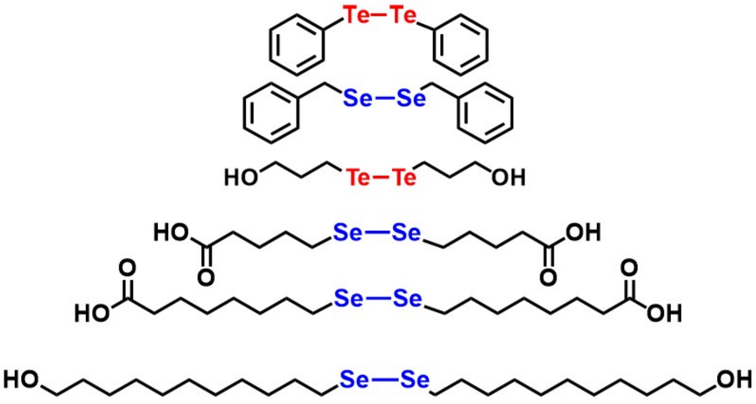

Fig. S1 The diselenides and ditellurides utilized for the formation of Se-Te bond.

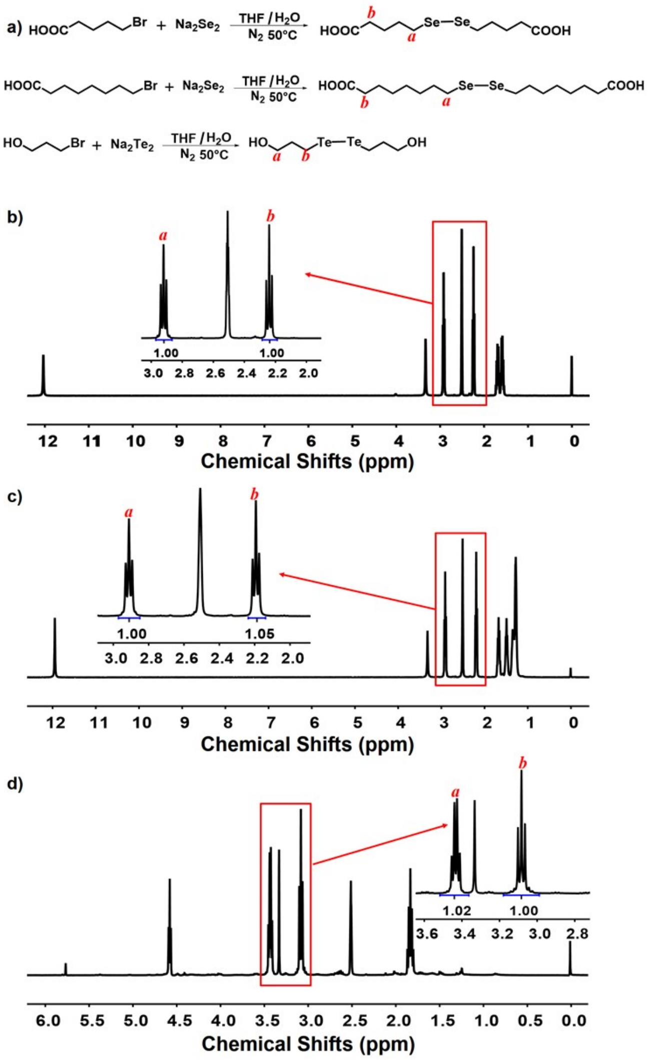

Fig. S2 The synthetic procedures and ^{1}H NMR spectra of $(HOOCC4Se)_2$, $(HOOCC7Se)_2$ and $(HOC3Te)_2$. a) The synthetic procedures of $(HOOCC4Se)_2$ and $(HOOCC7Se)_2$ and $(HOC3Te)_2$. b) ^{1}H NMR spectrum of $(HOOCC4Se)_2$. c) ^{1}H NMR spectrum of $(HOOCC7Se)_2$. d) ^{1}H NMR spectrum of $(HOC3Te)_2$.

2.2 The yields of products

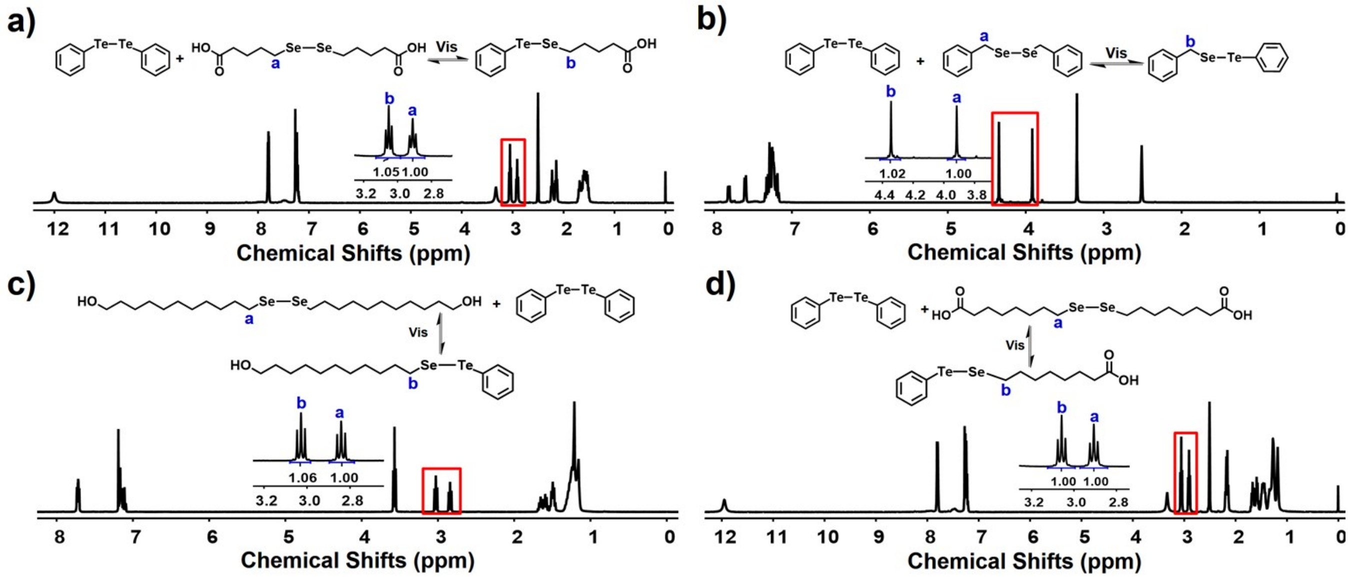

Fig. S3 The yields of metathesis reactions between diselenides (20 mM) and ditellurides (20 mM) under the irradiation of visible light. a) The yield of metathesis reaction between $(PhTe)_2$ and $(HOOCC4Se)_2$ in DMSO-d6. b) The yield of metathesis reaction between $(PhTe)_2$ and $(BenSe)_2$ in DMSO-d6. c) The yield of metathesis reaction between $(PhTe)_2$ and $(HOC11Se)_2$ in $CDCl_3$. d) The yield of metathesis reaction between $(PhTe)_2$ and $(HOOCC7Se)_2$ in DMSO-d6.

2.3 ^1H NMR spectra of the reactants and product

^1H NMR was conducted to prove that the exchange reaction occurred successfully. The metathesis reactions were conducted under irradiation from a white LED light with intensity of 118 Lux at room temperature (20 °C) with a concentration of 20 mM of both diselenides and ditellurides for 30 minutes. As shown in Figure S4, after the metathesis reaction between $(HOC11Se)_2$ and $(PhTe)_2$, the peak *a* for the CH_2Se protons in $(HOC11Se)_2$ at 2.89 ppm decreased in intensity, and a new peak *b* appeared at 3.05 ppm. Similarly, after the metathesis reaction between $(HOOCC4Se)_2$ and $(PhTe)_2$, the peak *a* corresponding to the α-methylene of the diselenide bond in $(HOOCC4Se)_2$ at 2.91 ppm decreased in intensity, and a new peak *b* appeared at 3.05 ppm. After the reaction between $(HOOCC7Se)_2$ and $(PhTe)_2$, the peak *a* belonging to the α-methylene of the diselenide bond in $(HOOCC7Se)_2$ at 2.90 ppm decreased in intensity, and a new peak *b* appeared at 3.05 ppm. And after the reaction between $(BenSe)_2$ and $(HOC3Te)_2$, the peak *c* corresponding to α-methylene of the diselenide bond in $(BenSe)_2$ at 3.90 ppm decreased in intensity, and a new peak *d* appeared at 4.18 ppm. The peak *a* corresponding to α-methylene of the ditelluride bond in $(HOC3Te)_2$ at 3.08 ppm decreased in intensity, and a new peak *b* appeared at 2.80 ppm.

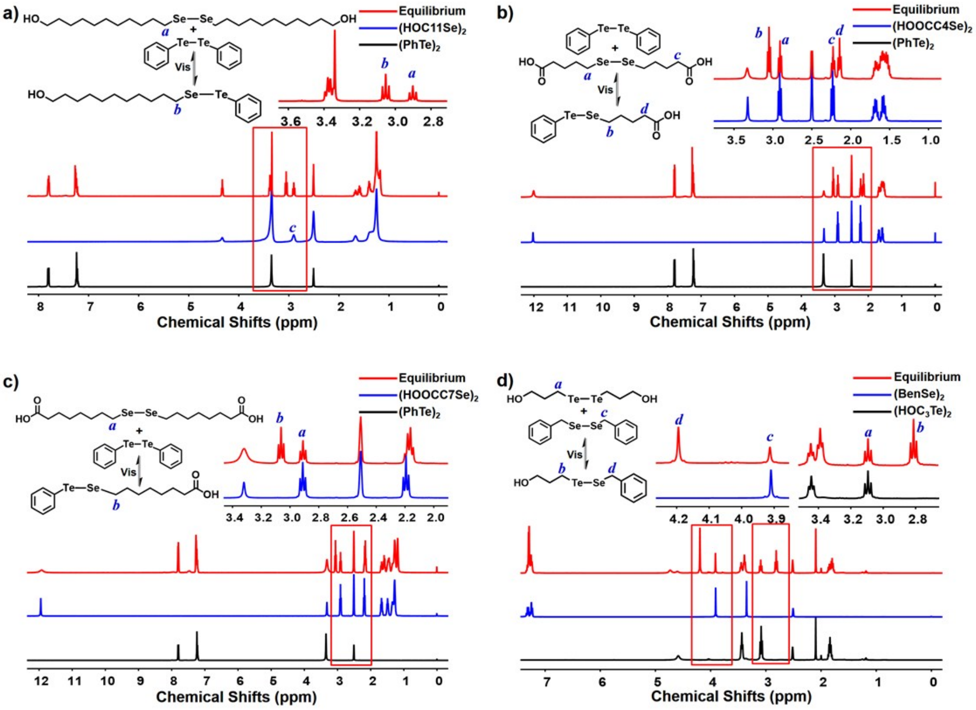

Fig. S4 ^{1}H NMR spectra of the metathesis reaction. a) ^{1}H NMR spectra of $(PhTe)_2$, $(HOC11Se)_2$ and the mixture in equilibrium. The cleavage effect of the peak *c* at 2.89 ppm is not obvious because of the low solubility of $(HOC11Se)_2$ in DMSO. b) ^{1}H NMR spectra of $(PhTe)_2$, $(HOOCC4Se)_2$ and the mixture in equilibrium. c) ^{1}H NMR spectra of $(PhTe)_2$, $(HOOCC7Se)_2$ and the mixture in equilibrium. d) ^{1}H NMR spectra of $(HOC3Te)_2$, $(BenSe)_2$ and the mixture in equilibrium. The peak in 2.08 ppm was the solvent acetone. The peaks in 1.99, 4.03 and 1.17 ppm were the solvent ethyl acetate.

2.4 ^{77}Se and ^{125}Te NMR spectra of the reactants and product

In addition to ^{1}H NMR, ^{77}Se and ^{125}Te NMR were also used to illustrate that such a metathesis reaction had occurred. The metathesis reaction was conducted with each reactant at a concentration of 40 mM for ^{77}Se NMR and 60 mM for ^{125}Te NMR. After the exchange reaction between $(HOC11Se)_2$ and $(PhTe)_2$, the peak *a* belonging to selenium in $(HOC11Se)_2$ at 290.76 ppm decreased in intensity, and a new peak *b* appeared at 127.12 ppm. The peak *a* belonging to tellurium in $(PhTe)_2$ at 403.73 ppm decreased in intensity, and a new peak *b* appeared at 688.90 ppm. After the reaction between $(HOOCC4Se)_2$ and $(PhTe)_2$, the peak *a* corresponding to selenium in $(HOOCC4Se)_2$ at 289.07 ppm decreased in intensity, and a new peak *b* appeared at 126.83 ppm. The peak *a* corresponding to tellurium in $(PhTe)_2$ at 404.11 ppm decreased in intensity, and a new peak *b* appeared at 691.68 ppm. After the exchange reaction between $(HOOCC7Se)_2$ and $(PhTe)_2$, The peak *a* for selenium in $(HOOCC7Se)_2$ at 289.69 ppm decreased in intensity, and a new peak *b* appeared at 126.81 ppm. The peak *a* for tellurium in $(PhTe)_2$ at 404.06 ppm decreased in intensity, and a new peak *b* appeared at 689.63 ppm. After the exchange reaction between $(BenSe)_2$ and $(HOC3Te)_2$, the peak *a* for selenium in $(BenSe)_2$ at 390.89 ppm decreased in intensity, and a new peak *b* appeared at 182.83 ppm. The peak *a* for tellurium in $(HOC3Te)_2$ at 113.16 ppm decreased in intensity, and a new peak *b* appeared at 566.52ppm. The ^{77}Se NMR spectra for the diselenides and the mixture at equilibrium are shown in Figure S5. The ^{125}Te NMR spectra for $(PhTe)_2$ and the mixture at equilibrium are shown in Figure S6.

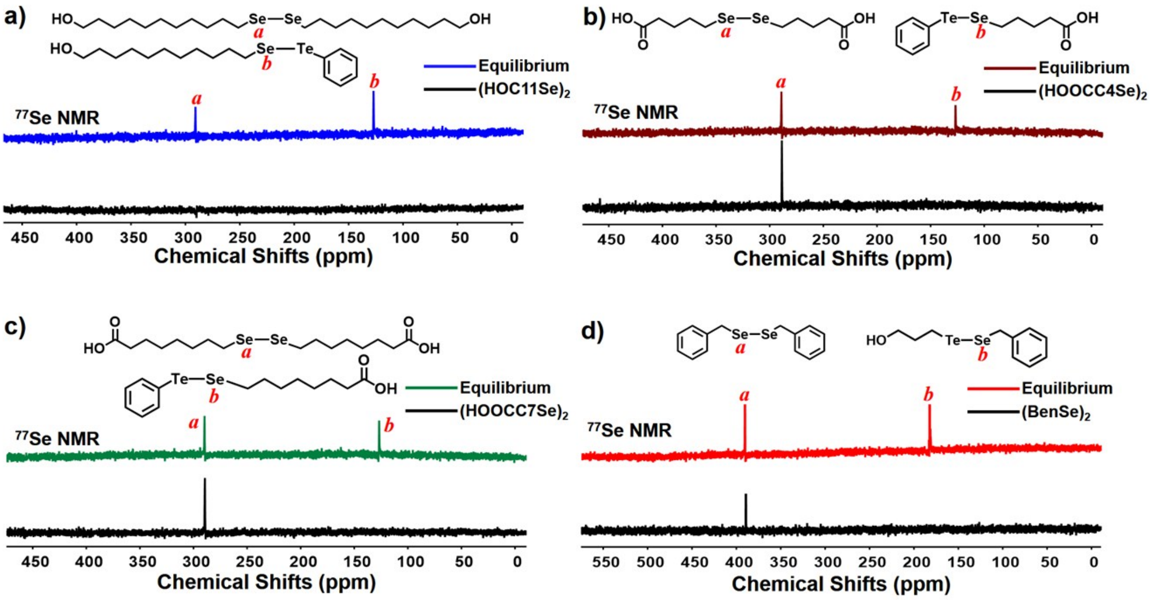

Fig. S5 ^{77}Se NMR spectra before and after the metathesis reaction. a) ^{77}Se NMR spectra of $(HOC11Se)_2$ and the mixture of $(HOC11Se)_2$ and $(PhTe)_2$ at equilibrium. Since $(HOC11Se)_2$ is not quite soluble in DMSO, there is no peak in the ^{77}Se NMR spectra of $(HOC11Se)_2$. b) ^{77}Se NMR spectra of $(HOOCC4Se)_2$ and the mixture of $(HOOCC4Se)_2$ and $(PhTe)_2$ at equilibrium. c) ^{77}Se NMR spectra of $(HOOCC7Se)_2$ and the mixture of $(HOOCC7Se)_2$ and $(PhTe)_2$ at equilibrium. d) ^{77}Se NMR spectra of $(BenSe)_2$ and the mixture of $(BenSe)_2$ and $(HOC3Te)_2$ at equilibrium.

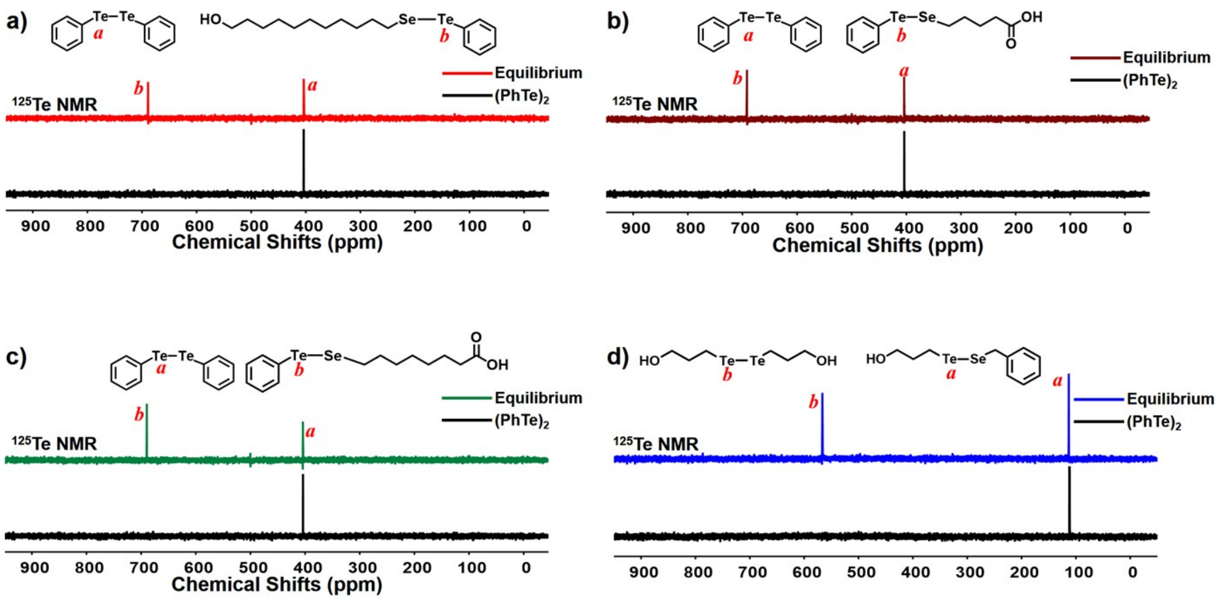

Fig. S6 ^{125}Te NMR spectra before and after the metathesis reaction. a) ^{125}Te NMR spectra of $(PhTe)_2$ and the mixture of $(HOC11Se)_2$ and $(PhTe)_2$ at equilibrium. b) ^{125}Te NMR spectra of $(PhTe)_2$ and the mixture of $(HOOCC4Se)_2$ and $(PhTe)_2$ at equilibrium. c) ^{125}Te NMR spectra of $(PhTe)_2$ and the mixture of $(HOOCC7Se)_2$ and $(PhTe)_2$ at equilibrium. d) ^{125}Te NMR spectra of $(HOC3Te)_2$ and the mixture of $(BenSe)_2$ and $(HOC3Te)_2$ at equilibrium.

2.5 Red-light-induced exchange reaction between $(HOC11Se)_2$ and $(PhTe)_2$

To demonstrate the sensitivity to light, the exchange reaction was conducted with a red-light filter at room temperature (20 °C) in DMSO with 5 mM $(HOC11Se)_2$ and 5 mM $(PhTe)_2$. The mixture was placed behind the filter, and the light from the xenon lamp (PLS-SXE300/300UV) was introduced through the window of the red-light filter. The light transmission of the filter is shown in Figure S7. Light at a wavelength above 600 nm was introduced, following which the reaction between $(HOC11Se)_2$ and $(PhTe)_2$ reached equilibrium within 80 minutes. The system induced by red light or white LED light contained the same molecule (Se-Se, Te-Te, Se-Te) when it reached equilibrium. And the equilibrium ratio of product (Se-Se, Te-Te, Se-Te) was about 1:1:2 for the reaction triggered by both red light and white LED light (Figure S8). The slower reaction rate could be attributed to the very small extinction coefficient for both diselenide and ditelluride at these wavelengths. However, this experiment demonstrated that irradiation with light at a wavelength above 600 nm is sufficient for the metathesis reaction to reach equilibrium.

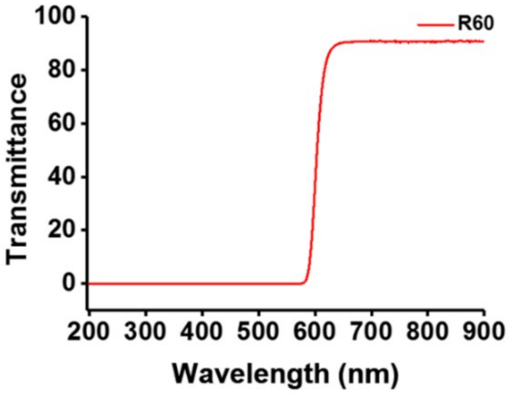

Fig. S7 The light transmission of red-light filter.

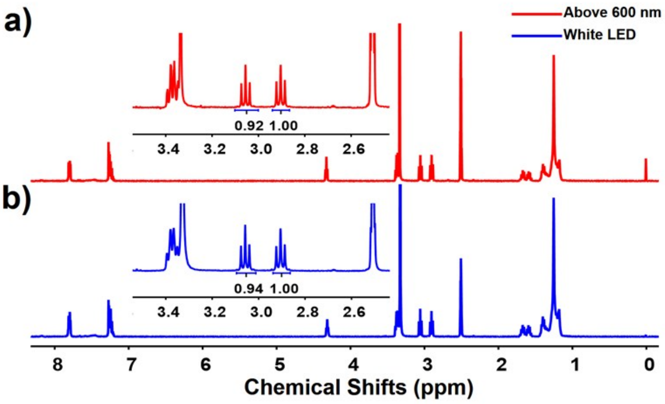

Fig. S8 a) Metathesis reaction between $(HOC11Se)_2$ (5 mM) and $(PhTe)_2$ (5 mM) was triggered by red light for 80 minutes. b) Metathesis reaction between $(HOC11Se)_2$ (5 mM) and $(PhTe)_2$ (5 mM) was triggered by white LED light for 30 minutes.

2.6 Indirect evidence for radical mechanism

The metathesis reaction induced by only heat without light irradiation was conducted with a concentration of 5 mM for both $(HOC11Se)_2$ and $(PhTe)_2$ in DMSO. Aluminum foil was wrapped to block out light. Three parallel experiments were performed at different temperatures (50 °C, 60 °C and 70 °C) for 30 minutes, and the results were recorded by ^1H NMR.

The exchange reactions with TEMPO were induced by light irradiation using white LED at room temperature (20 °C) with a concentration of 5 mM for both $(HOC11Se)_2$ (10 mM “selenol radical”) and $(PhTe)_2$ (10 mM “tellurol radical”) in DMSO. Three parallel experiments were conducted under conditions identical to those mentioned above except for the different concentrations of TEMPO (0 mM, 10 mM and 40 mM). The duration of the reaction was 40 minutes, and the results were recorded by ^1H NMR. The indirect evidence for radical mechanism is shown in Figure S9.

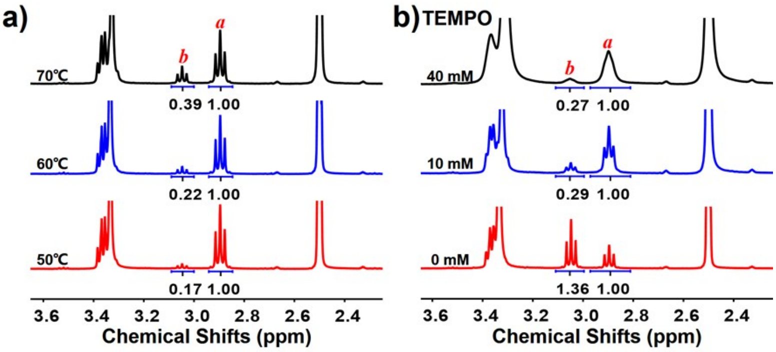

Fig. S9 a) The exchange reaction between $(HOC11Se)_2$ and $(PhTe)_2$ (5 mM each, in DMSO) conducted in darkness at different temperatures (50 °C, 60 °C and 70 °C). The reaction time was 30 minutes and the results were recorded by ^1H NMR. b) The metathesis reaction between $(HOC11Se)_2$ and $(PhTe)_2$ (5 mM each, in DMSO) was significantly suppressed by the addition of the radical scavenger TEMPO. The reaction time was 40 minutes and the results were recorded by ^1H NMR.

2.7 EPR experiments

All trapping experiments were performed at room temperature (20 °C) with a concentration of 5 mg/mL for each reactant in ultra-dry DMSO. The reactant solution was charged in a glass capillary, which was sealed before detection. The spectra were measured using a microwave power of 0.998 mW and a microwave frequency of 9066 MHz (for ditelluride) or 9051 MHz (for diselenide) with a sweep time of 1.0 minute and sweep width of ±5 mT. Since the methods used to acquire the radical signals for all the reactants were similar, the selenol radical trapping process for $(BenSe)_2$ is emphasized as a representative. First, a DMSO solution of $(BenSe)_2$ at a concentration of 5 mg/mL was prepared in the dark. Because the selenol and tellurol radicals are too active to be trapped, the spin trapping agent DMPO (50 mM) was added to the mixture in darkness to assist in capturing the radical signals. Then, the mixture of $(BenSe)_2$ and DMPO was assessed via EPR under conditions of both darkness and light irradiation. The result of EPR experiment is shown in Figure S10. The g value was calculated according to the following equation: g=hv/βH (Where h is Planck constant, v is the microwave frequency, β is the Bohr magneton and H is the magnetic field).

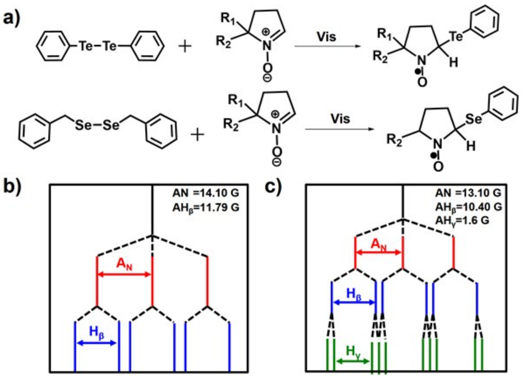

Fig. S10 a) Reactions between ditelluride or diselenide and DMPO. Cleavage effect of tellurol b) and selenol c) radical addition products of DMPO and relevant coupling-splitting constants.

No radical signal was observed under the condition of darkness. However, once the reactants were exposed to light from the high pressure mercury lamp (USH-500SC) with a wavelength above 420 nm, the radical signal appeared immediately. It is worth noting that $(PhTe)_2$ was more active than diselenide, and that a fluorescent lamp with an intensity of 26-28 Lux was sufficient for the generation of the tellurol radicals.

In addition to the $(BenSe)_2$ and $(PhTe)_2$, the radical signals for the other diselenides were also trapped as shown in Figure S11. The signal intensities changed along with different molecular structures, which demonstrated the variable radical stabilities. Although the intensities of the radical signals were different, the peak shapes for all the selenol radicals were similar.

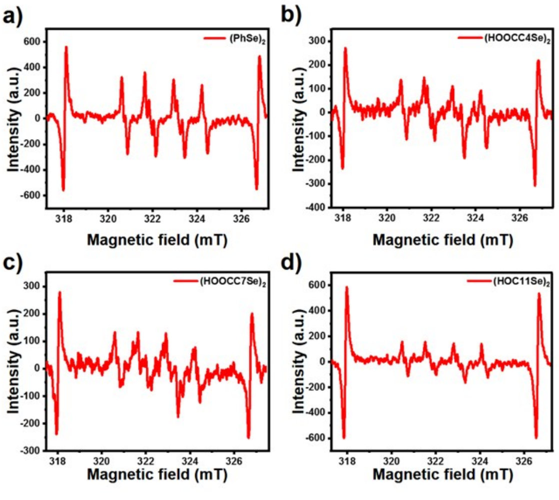

Fig. S11 Radical signals of the other diselenides trapped by the EPR. a) The radical signal of $(PhSe)_2$. The signal was strong because of the stabilization effect of phenyl group on free radicals. b) The radical signal of $(HOOCC4Se)_2$. c) The radical signal of $(HOOCC7Se)_2$. d) The radical signal of $(HOC11Se)_2$. The radical signal of

$(HOC11Se)_2$ is very weak, because the alkyl-selenol radical is more active than phenyl-selenol radical, and the solubility of $(HOC11Se)_2$ in DMSO is poor.

2.8 The other compatible solvents for exchange reaction

To illustrate that the metathesis reactions could be successfully realized in different solvents, the reactions were conducted using a white LED light at room temperature (20 °C) with a concentration of 10 mM for both $(HOC11Se)_2$ and $(PhTe)_2$. As shown in Figure S12, the metathesis reactions between $(HOC11Se)_2$ and $(PhTe)_2$ occurred successfully in chloroform (a low-polarity solvent), acetone (a low-polarity solvent), acetonitrile (a high-polarity solvent) and methanol (a high-polarity and protic solvent).

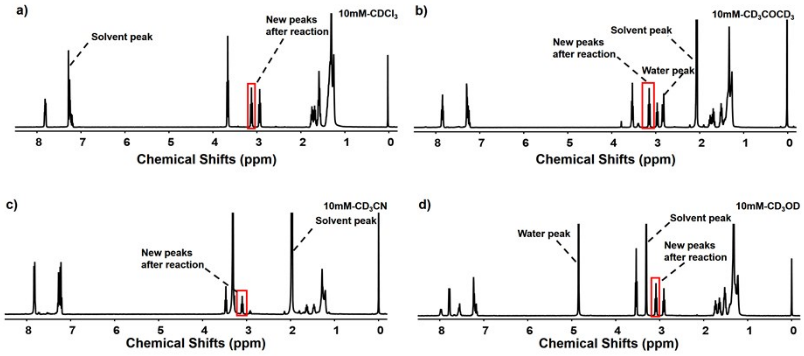

Fig. S12 Metathesis reactions between diselenides and ditellurides in different solvents. The peak of product appeared in all solvents after reaction under the condition of visible-light irradiation. a) $(HOC11Se)_2$ (10 mM) and $(PhTe)_2$ (10 mM) exchanged in chloroform (low polarity solvent) for 90 minutes. b) $(HOC11Se)_2$ (10 mM) and $(PhTe)_2$ (10 mM) exchanged in acetone for 3 hours. c) $(HOC11Se)_2$ (10 mM) and $(PhTe)_2$ (10 mM) exchanged in acetonitrile for 3 hours. And $(HOC11Se)_2$ is not quite soluble in acetonitrile. d) $(HOC11Se)_2$ (10 mM) and $(PhTe)_2$ (10 mM) exchanged in methanol (high polarity and protic solvent) for 10 minutes.

As shown in Figure S13, the metathesis reactions between $(BenSe)_2$ and $(PhTe)_2$ also occurred successfully in chloroform (a low-polarity solvent), acetone (a low-polarity solvent), acetonitrile (a high-polarity solvent) and methanol (a high-polarity and protic solvent).

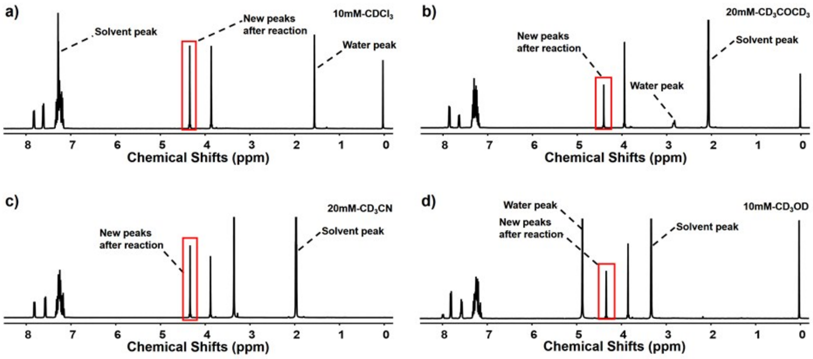

Fig. S13 Metathesis reactions between equivalent amounts of $(BenSe)_2$ and $(PhTe)_2$ in $CDCl_3$ (10 mM) a), CD_3COCD_3 (20 mM) b), CD_3CN (20 mM) c) and CD_3OD (10 mM) d). The peak of product appeared in all solvents after reaction under the condition of visible-light irradiation.

2.9 The exchange process of metathesis reactions

The exchange process in $CDCl_3$ between $(HOC11Se)_2$ and $(PhTe)_2$ (10 mM each) were recorded by ^1H NMR as shown in Figure S14.

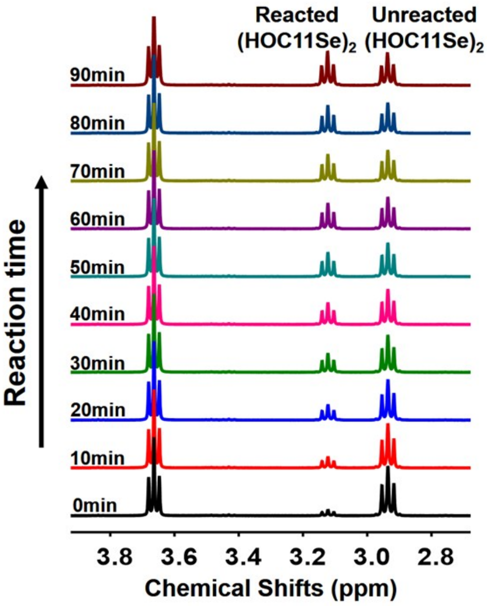

Fig. S14 Metathesis process between diselenides and ditellurides in $CDCl_3$. $(HOC11Se)_2$ (10 mM) exchanged with $(PhTe)_2$ (10 mM) in $CDCl_3$. The peak at 3.10 ppm increased continually until equilibrium.

The exchange process in $CDCl_3$ between $(BenSe)_2$ and $(PhTe)_2$ (10 mM each) were recorded by ^1H NMR as shown in Figure S15.

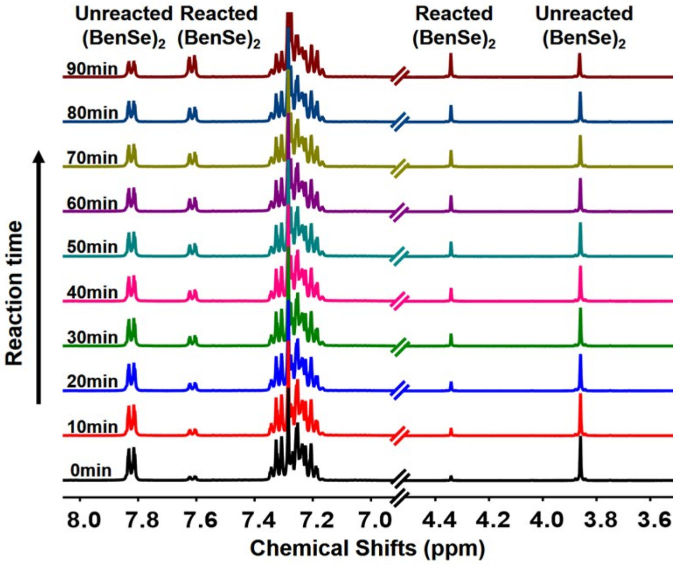

Fig. S15 Metathesis process between $(BenSe)_2$ (10 mM) and $(PhTe)_2$ (10 mM) in $CDCl_3$. The peak at 4.32 ppm and the peak at 7.60 ppm increased continually until equilibrium.

2.10 Oxygen tolerance of the dynamic exchange

The exchange reaction between $(PhTe)_2$ (20 mM) and $(BenSe)_2$ (20 mM) was conducted in air with no protective atmosphere and the ^{1}H NMR spectra was shown in Figure S16. The molar ratio between Se-Te and Se-Se reached 61.3 %, 103.9 % and 77.18 % after reacted for 15 min, 60 min and 90 min respectively. The content of Se-Te molecule increased first and then decreased, which might be attributed to the left shift of equilibrium caused by oxidation of ditelluride and reaction between oxygen and tellurol radicals.

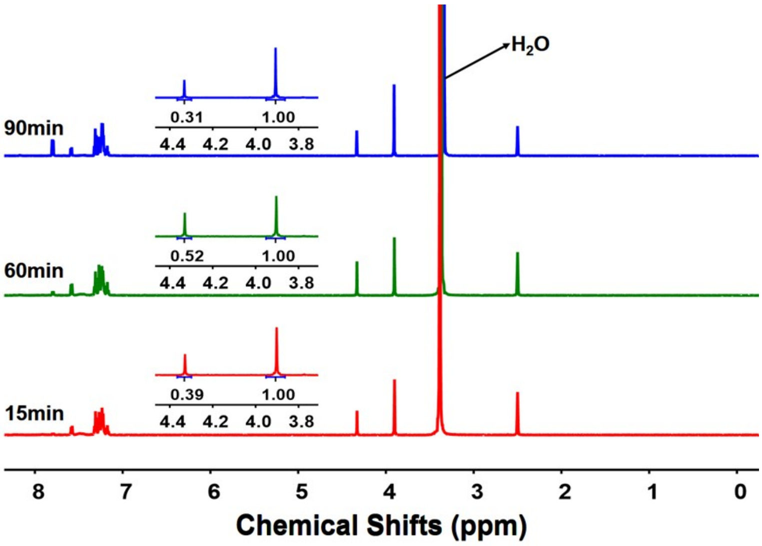

Fig. S16 Dynamic exchange in air without protective atmosphere.

2.11 Kinetics study

To confirm the reaction order, $(BenSe)_2$ and $(PhTe)_2$ were used as model molecules and were exchanged at a temperature of 40 °C in DMSO without light irradiation. First, the concentration of $(PhTe)_2$ was fixed at 10 mM, and a series of variable concentrations of $(BenSe)_2$ (5 mM, 10 mM, 20 mM, 30 mM and 40 mM) were prepared. Then, the initial reaction conversion between $(PhTe)_2$ and $(BenSe)_2$ (five parallel experiments at each concentration) was determined continuously by ^{1}H NMR until it reached 10 %. Thus, the initial reaction rate was obtained from the reaction time and conversion. The $[(BenSe)_2]$ and the initial reaction rate data were fitted to a straight line, which established a first-order kinetic. The dependence of the initial reaction rate on $[(PhTe)_2]$ was investigated by means of the same method. The initial reaction conversion between $(BenSe)_2$ (10 mM) and $(PhTe)_2$ (5 mM, 10 mM, 20 mM, 30 mM and 40 mM) was recorded by ^{1}H NMR. The results were also fitted to a straight line. Thus, the initial reaction rate also shown a first-order kinetic with respect to the $[(PhTe)_2]$.

To determine the apparent activation energy, $(BenSe)_2$ and $(PhTe)_2$ were utilized as model molecules and were exchanged at variable temperatures (from 40 °C to 80 °C, five parallel experiments per 10 °C) without light irradiation. First, a DMSO solution containing $(BenSe)_2$ (10 mM) and $(PhTe)_2$ (10 mM) was prepared. Then, the real-time reaction conversion at defined temperatures mentioned above was continuously determined by ^{1}H NMR until the conversion reached 10 %.

The reaction rate constant k at various temperatures could be obtained from the reaction time and the concentration of reactants according to the second-order kinetic equation (1). The Arrhenius equation (2) was finally utilized to calculate the apparent activation energy.

$$\frac{1}{a\text{-}x} = kt + C \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

$$lnk = \frac{-E_a}{RT} + C \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

References

S1. N. Ma, Y. Li, H. Xu, Z. Wang and X. Zhang, *J. Am. Chem. Soc.*, 2010, **132**, 442-443.