# Electronic Supporting Information for

## Reversible oxidation of a water-soluble tellurophene

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### **Experimental**

**General Considerations:** All reagents were used as received unless otherwise noted. Tellurium, 4-iodophenol, tetra(ethylene glycol) monomethyl ether, tetra(ethylene glycol), caesium carbonate bis(trimethylsilyl)butadiyne, palladium tetrakis(triphenylphosphine) (Pd(PPh<sub>3</sub>)<sub>4</sub>), tetrabutylammonium fluoride and bromine, were purchased from Sigma-Aldrich. Acetone, HCl, MgSO<sub>4</sub>, dichloromethane, hexanes, DMSO, KOH and sodium thiosulfate were purchased from Fisher Scientific. Fluorene, CuI, sodium borohydride and iodobenzene were purchased from Alfa Aesar. Silica gel was purchased from Silicycle.

Absorption spectra were recorded using a Varian Cary 5000 spectrometer. Emission spectra were recorded on a Photon Technologies Inc (model) fluorometer with a photodiode detector and xenon arc light source. NMR spectra were recorded on a Varian Mercury 300 spectrometer (300 MHz), Varian Mercury 400 spectrometer (400 MHz), or Agilent DD2 500 MHz spectrometer as noted. Masses were determined on a Waters GCT Premier ToF mass spectrometer (ESI or DART). Electrochemistry was performed with a BASi Epsilon potentiostat.

**Cyclic Voltammetry:** In a 5 mL aqueous solution of 0.1 M LiCl, 5 mg of compound **1** or **2** were dissolved. The working electrode was a 2 mm Pt-disk, the counter electrode was a Pt wire electrode, and the reference electrode was Ag/AgCl. The scan rate was 100 mV/s.

**Peroxide Tests:** The presence of peroxide was tested using QUANTOFIX peroxide test strips. The concentration of peroxide was quantified using a Peirce quantitative peroxide assay kit.

**Synthesis**: Iodoocta(ethylene glycol) monomethyl ether<sup>1</sup> and benzene iodobenzene dichloride<sup>2</sup> were synthesized as previously described. The known compounds were characterized by  ${}^{1}\text{H}^{-1}$  NMR and TOF MS and were in agreement with literature.

**4-iodophenoxy (octa(ethylene glycol) monomethyl ether).** 4-iodophenol (0.44 g, 2.02 mmol) and caesium carbonate (6.58 g, 20.2 mmol) were heated to reflux in dry acetone for 1 h. Iodoocta(ethylene glycol) monomethyl ether (2 g, 4.04 mmol) was added dropwise over 10 minutes to the refluxing mixture and subsequently stirred for 5 h. The acetone was removed under reduced pressure. The resulting mixture was dissolved in dichloromethane and washed 3x with 0.1 M HCl and 1x with brine. The organic layer was dried with MgSO<sub>4</sub>. The solvent was removed and the product was purified by column chromatography with an ethyl acetate:hexanes

(9:1) eluent to afford 1.13 g (1.98 mmol, 98 % yield) of the desired product. HRMS- DART-ESI+: calc C<sub>23</sub>H<sub>40</sub>IO<sub>9</sub>: 587.17170, measured: 589.17098. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (d, J = 8.90 Hz, 2H), 6.70 (d, J = 8.90 Hz, 2H), 4.09 (t, J = 4.84 Hz, 2H), 3.83 (t, J = 4.84 Hz, 2H), 3.68-3.63 (m, 26 H), 3.55 (t, J = 4.48 Hz, 2H), 3.38 (s, 3H).

1,4-bis(phenoxy(octa(ethylene glycol)monomethyl ether)butadiyne. А solution of 4-iodophenoxy (octa(ethylene glycol) monomethyl ether) (1.13 g, 1.98 mmol) in 25 mL of toluene was dried over 3 Å molecular sieves overnight. 1,4-bis(trimethylsilyl)buta-1,3-diyne (0.10 g, 0.914 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.106 g, 0.091 mmol), and CuI (0.035 g, 0.18 mmol) were added to a dry 500 mL solvent bomb and placed under a nitrogen atmosphere. Toluene (200 mL) was added and the mixture was cooled to 0 °C. Tetrabutylammonium fluoride (1 M solution in THF, 2.10 mL, 2.10 mmol) was quickly added and the bomb was sealed. The mixture was allowed to warm to room temperature and stirred overnight. The mixture was extracted into dichloromethane and washed 2x with water and once with brine. The organic layer was dried with MgSO<sub>4</sub> and purified by column chromatography with ethyl acetate:acetone 85:15 eluent to give 0.65 g (0.674 mmol 73.9 %) of the desired product. HRMS- DART-ESI+: calc C<sub>50</sub>H<sub>79</sub>O<sub>18</sub>: 967.5260, measured: 967.5246. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.44 (d, J = 8.80 Hz, 4H), 6.68 (d, J = 8.80 Hz, 4H), 4.14 (t, J = 4.84 Hz, 4H), 3.86 (t, J = 4.89 Hz, 4H), 3.73-3.71 (m, 4H), 3.68-3.67 (m, 4H), 3.66-3.63 (m, 44 H), 3.55-3.53 (m, 4H), 3.38 (s, 6H). <sup>13</sup>C NMR (125 MHz, ppm, CDCl<sub>3</sub>) 159.4, 134.0, 114.7, 113.9, 81.1, 72.9, 71.9, 70.7, 70.5, 70.4, 70.3, 69.5, 67.5, 59.1, 59.0, 53.8, 30.8, 24.2, 19.8, 13.7, 8.64.

**2,5-bis(phenoxy(octa(ethylene glycol)monomethyl ether) tellurophene**. A degassed mixture of tellurium metal powder (0.107 g, 0.842 mmol) and sodium borohydride (0.131 g, 3.37 mmol) in ethanol (95 %) was heated to reflux for 4 h until the metal was consumed and the solution was light purple in color. The solution was cooled to room temperature. A degassed solution of 1,4-bis(phenoxy(octa(ethylene glycol)monomethyl ether)butadiyne in ethanol (0.27 g, 0.28 mmol) was slowly added and allowed to stir at room temperature overnight. Air was blown over the mixture with rapid stirring for 1h and black precipitate was observed. The mixture was filtered through celite to give a yellowish brown solution. The solvent was removed under reduced pressure. Dichloromethane was added and the mixture was washed 3x with water and 1x with brine. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced

pressure. A small amount of dichloromethane was added to the brown waxy product. This solution was added drop-wise to cold hexanes to afford the purified product as a yellow wax after centrifugation, as determined by NMR (0.169 g, 0.154 mmol, 55%). HRMS- DART-ESI+: calc C<sub>50</sub>H<sub>81</sub>O<sub>18</sub>Te: 1099.4479, measured: 1099.4522. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 ( $J_{Te} = 5.0, 2H$ ), 7.38 (d, J = 8.58 Hz, 4H), 6.88 (d, J = 8.58, 4H), 4.14 (t, J = 5.1 Hz, 4H), 3.86 (t, J = 5.0, 2H), 3.75-3.62 (m, 52H), 3.54 (t, J = 4.3 Hz, 4H), 3.37 (s, 6H) <sup>13</sup>C NMR (125 MHz, ppm, CDCl<sub>3</sub>): 158.4, 146.6, 132.7, 128.4, 127.7, 114.9, 71.9, 70.6, 70.5, 70.5, 69.6, 67.5, 59.0.



**Figure S1**. Absorption spectra (in water) of **1** ( $1.9 \times 10^{-5}$  M) (purple), and after reaction with H<sub>2</sub>O<sub>2</sub> (yellow), 1 eq Br<sub>2</sub> (red), and Cl<sub>2</sub> (green). \*added as iodobenzene dichloride.



**Figure S2**. Initial rate (change in absorption per minute at 435 nm) of  $5.0 \times 10^{-5}$  M **1** at varying H<sub>2</sub>O<sub>2</sub> concentrations.



**Figure S3**. Integrated rate law (natural log of absorption at 435 nm) of  $5.0 \times 10^{-5}$  M **1** in water with  $6.2 \times 10^{-3}$  M H<sub>2</sub>O<sub>2</sub> as a function of time.



**Figure S4**. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>) of **1** treated with  $H_2O_2$  for 48 h at rt. Red line 0.75 eq  $H_2O_2$ , green line 1 eq  $H_2O_2$ . Note the solvent satellites and spinning side bands are indicated by \*, apparent due to the low concentration of analyte.



**Figure S5**. <sup>1</sup>H NMR (500 MHz; CDCl<sub>3</sub>) of **1** treated with excess  $H_2O_2$  for 12 h at rt (red line), and after 12 h of irradiation with 447 nm LED (green line).



Figure S6. Absorption spectra of 1 after 24 h of irradiation with 447.5 nm LED under  $O_2$  and  $N_2$  atmosphere in water.



**Figure S7**. Absorption of a of  $2.7 \times 10^{-5}$  M solution of **1** irradiated with 447.5 nm LED overnight in pure water or a phosphate buffer solution as indicated.



Figure S8. Cyclic voltammograms of 1 in 0.5 M phosphate buffer at the pH indicated.



**Figure S9.** Excitation and emission spectra of **1** oxidized with excess of  $H_2O_2$  (purple), also shown is **1** oxidized with 1.1 eq  $H_2O_2$  (blue), and **1** untreated (red). In all cases the excitation energy is 334 nm.



Figure S10. Mass spectrum of compound 1 (DART ionization, positive ion mode).



Figure S11. Mass spectrum of compound 2 (DART ionization, positive ion mode).

#### References

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- (2) Zhang, C.; Zhao, X. Synthesis **2007**, *4*, 551-557.