Supporting Information

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One-Pot Synthesis of Heterocycle-Fused 1,3-Diselenole-2-selones as the Key Precursors of Tetraselenafulvalene-Type Electron Donors

α,ω-Bis(chalcogenocyanato)alkanes: α,ω-Bis(chalcogenocyanato)alkanes were conventionally prepared by treating the corresponding alkylene dibromides with sodium thiocyanate or potasium selenocyanate in acetone according to the literatures; bis(thiocyanato)methane: Lermontoff, J. *Chem. Ber*. **1874**, *7*, 1282–1284; 1,2-bis(thiocyanato)ethane: Glutz, A. *Justus Liebigs Ann. Chem.* **1870**, *153*, 313; 1,3-bis(thiocyanato)propane: Hagelberg, L. *Chem. Ber*. **1890**, *23*, 1083–1092; bis(selenocyanato)methane and 1,2-bis(selenocyanato)ethane: Proskauer, B. *Chem Ber*. **1874**, *7*, 1279–1282; 1,3-bis(selenocyanato)propane: Morgan, G. T.; Burstall, G. T. *J. Chem. Soc*. **1930**, 1496–1502.

4,5-(Methylenedithio)-1,3-diselenole-2-selone (2a): 71% yield; red plates from carbon disulfide; mp 149–150 ºC dec; ^{1}H-NMR ($CDCl_3$) δ 4.98 (s, 2H, CH_2); IR (KBr) ν 909 cm^{-1} (C=Se); MS *m/z* 352 (M^+) with an isotropic pattern of three selenium atoms. Anal. Calcd for $C_4H_2S_2Se_3$: C, 13.69; H, 0.57. Found: C, 13.69; H, 0.57.

4,5-(Propylenedithio)-1,3-diselenole-2-selone (2c): 64% yield; red needles from chlorobenzene; mp 156–157 ºC; ^{1}H-NMR ($CDCl_3$) δ 2.47 (quin, *J* = 5.5 Hz, 2H, CH_2) and 2.80 (t, *J* = 5.5 Hz, 4H, CH_2); IR (KBr) ν 903 cm^{-1} (C=Se); MS *m/z* 380 (M^+) with an isotropic pattern of three selenium atoms. Anal. Calcd for $C_6H_6S_2Se_3$: C, 19.01; H, 1.60. Found: C, 19.15; H, 1.57.

4,5-(Methylenediseleno)-1,3-diselenole-2-selone (2d): 66% yield; red plates from carbon disulfide; mp 174–175 ºC; ^{1}H-NMR ($CDCl_3$) δ 5.00 (s, 2H, CH_2); IR (KBr) ν 895 cm^{-1} (C=Se); MS *m/z* 446 (M^+) with an isotropic pattern of five selenium atoms. Anal. Calcd for $C_4H_2Se_5$: C, 10.80; H, 0.45. Found: C, 11.03; H, 0.41.

4,5-(Ethylenediseleno)-1,3-diselenole-2-selone (2e): 74% yield; red prisms from chlorobenzene; mp 132–133 ºC dec (lit.,[3a] 123–125 ºC dec); ^{1}H-NMR ($CDCl_3$) δ 3.45 (s, 4H, CH_2); IR (KBr) ν 899 cm^{-1} (C=Se); MS *m/z* 460 (M^+) with an isotropic pattern of five selenium atoms. Anal. Calcd for $C_5H_4Se_5$: C, 13.09; H, 0.88. Found: C, 13.27; H, 0.90.

4,5-(Propylenediseleno)-1,3-diselenole-2-selone (2f): 61% yield; red plates from chlorobenzene; mp 163–164 ºC; ^{1}H-NMR ($CDCl_3$) δ 2.79 (quin, *J* = 5.5 Hz, 2H, CH_2) and 2.92 (t, *J* = 5.5 Hz, 4H, CH_2); IR (KBr) ν 901 cm^{-1} (C=Se); MS *m/z* 474 (M^+) with an isotropic pattern of five selenium atoms. Anal. Calcd for $C_6H_6Se_5$: C, 15.24; H, 1.28. Found: C, 15.25; H, 1.27.

4,5-Bis(methylthio)-1,3-diselenole-2-selone (3): 58% yield; red needles from chloroform-hexane; mp 101–102 ºC; ^{1}H-NMR ($CDCl_3$) δ 2.53 (s, 6H, CH_3); IR (KBr) ν 901 cm^{-1} (C=Se); MS *m/z* 368 (M^+) with an isotropic pattern of three selenium atoms. Anal. Calcd for $C_5H_6S_2Se_3$: C, 16.36; H, 1.65. Found: C, 16.35; H, 1.57.