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Synthesis and electrochemical study of 4,4′,5-tris(methylthio)-5′-{2-[4,6-di(thiophen-2-yl)-1,3,5-triazin-2-yloxy]ethylthio}tetrathiafulvalene

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The ^{1}H NMR spectra were recorded on a Varian Mercury plus 300 spectrometer (operating frequency - 300 MHz, GMDS as internal standard). Progress of reactions and the purity of the obtained substances were monitored by TLC (Silufol, Kavalier). Mixture separation and the target products purification were performed by column chromatography (Silica gel 60, 0.060-0.2 mm, Lancaster). The mass-spectra (EI, 70 eV) were recorded on an Agilent 6890N - 5975B GC-MS system.

2,4-Dichloro-6-(2-thiophen-2-yl)-1,3,5-triazine **2a** and *2-chloro-4,6-di(thiophen-2-yl)-1,3,5-triazine* **2b**. (Thiophen-2-yl)magnesium bromide solution in THF (Mg, 2.9 g, 0.12 mol; 2-bromothiophene, 16.4 g, 0.1 mol; THF, 150 ml) was added dropwise to the precooled (0−10 ^{0}C) solution of 2,4,6-trichloro-1,3,5-triazine (9.22 g, 0.05 mol) in THF (150 ml). The reaction mixture thus obtained was refluxed for 10 h, then the solvent was removed, the residue was acidified with 12% HCl solution, extracted with CH_2Cl_2 and dried with Na_2SO_4. The solvent was evaporated off to give a greenish residue which was purified by column chromatography (Silica gel, hexane−CH_2Cl_2, 2:1). Solutions of **2a** and **2b** in CH_2Cl_2 glow bright turquoise under UV-exposure. **2a**: light-yellow needles. 21% yield, mp 145−146 ^{o}C. ^{1}H NMR ($CDCl_3$), δ: 7.23 (t, 2H, 2CH, thiophene, *J* 4.2 Hz); 7.78 (d, 2H, 2CH, thiophene, *J* 4.8 Hz); 8.27 (d, 2H, 2CH, thiophene, *J* 4.2 Hz). MS, m/z (%): 234.9 (13) [M^++2H], 232.9 (69) [M^+] $C_7H_3Cl_2N_3S$, 231.9 (10) [M^+-H], 230.9 (100), 135 (61), 109 (26.7), 86 (24.5). **2b**: light-yellow plates, 59% yield, mp 159−160 ^{o}C. ^{1}H NMR ($CDCl_3$), δ: 7.22 (t, 2H, 2CH, thiophene, *J* 4.2 Hz); 7.69 (d, 2H, 2CH, thiophene, *J* 4.8 Hz); 8.26 (d, 2H, 2CH, thiophene, *J* 4.2 Hz). MS, m/z (%): 281.9 (42.9) [M^++2H], 279.9 (15) [M^+] $C_{11}H_6ClN_3S_2$, 278.9 (100) [M^+-H], 135 (23), 110 (10.4), 109 (96).

2-Chloroethoxy-4,6-di(thiophen-2-yl)-1,3,5-triazine **4** and *2-chloro-4-(2-chloroethoxy)-6-(thiophen-2-yl)-1,3,5-triazine* **3**. Suspension of **2b** (**2a**) (29 mmol), 2-chloroethanol (2.76 g, 34 mmol) and K_2CO_3 (8 g, 57 mmol) in acetone (150 ml) was heated under reflux and under TLC

control for 24 h. The following filtration and the solvent evaporation gave a heavy thick oil which was separated further by column chromatography (Silica gel, hexane–CH_2Cl_2, 1:1). Solutions of **4** and **3** in CH_2Cl_2 glow bright turquoise under UV-exposure. **4**: light-yellow needles, mp 124–127 ^{0}C, 10% yield. ^{1}H NMR ($CDCl_3$), δ: 3.91 (t, 2H, CH_2Cl, J 6.0 Hz), 4.78 (t, 2H, OCH_2, J 6.0 Hz), 7.19 (t, 2H, thiophene, J 4.2 Hz), 7.62 (d.d , 2H thiophene, J_1 4.5, J_2 0.9 Hz), 8.22 (d.d , 2H, thiophene, J_1 3.6, J_2 1.2 Hz). MS, m/z (%): 326 (9) [M^++2H], 325 (44) [M^++H], 324 (36) [M^+] $C_{13}H_{10}ClN_3OS_2$, 323 (100) [M^+-H], 322 (10), 289 (11), 288 (53), 287 (16), 283 (13.5), 281 (33), 262 (10), 261 (30) [2-hydroxy-4,6-di(2-thienyl)-1,3,5-triazine]$^+$, 260 (37), 228 (20), 219 (32), 178 (11.5), 172 (19), 165 (16), 136 (25), 135 (23), 123 (11), 110 (100), 109 (47), 97 (10), 83 (10.5), 63 (17.5), 58 (14), 56 (18), 45 (18), 39 (20), 27 (18). **3**: light-yellow crystals, mp 96–97 ^{o}C, yield 85%. ^{1}H NMR ($CDCl_3$), δ: 3.87 (t, 2H, CH_2Cl, J 6.3 Hz), 4.74 (t, 2H, OCH_2, J 6.3 Hz), 7.19 (t, 1H, thiophen, J 4.35 Hz), 7.68 (d.d, 1H, thiophene, J_1 5.1, J_2 1.5 Hz), 8.20 (d.d, H, thiophene, J_1 3.5, J_2 1.2 Hz). MS, m/z (%): 276.9 (20) [M^+] $C_9H_7Cl_2N_3S_2OS$, 274.9 (29.15) [M^+-2H], 242(24), 240 (63), 243 (24), 216 (10), 215 (28), 214 (59), 213 (71) [6-chloro-2-hydroxy-4-(2-thienyl)-1,3,5-triazine]$^+$, 212 (95), 178 (64), 173 (10), 171 (28), 135 (42), 110 (100), 109 (23), 87 (19), 69 (12), 64 (11), 44.9 (10), 39 (12), 27 (17).

4,4',5-Tris(methylthio)-5'-{2-[4,6-di(thiophen-2-yl)-1,3,5-triazin-2-yloxy]ethylthio}tetrathia-fulvalene **1**. Triazine **4** (0.26 g, 82 mmol) was added in one portion to a prepared *in situ* solution of cesium thiolate [$CsOH{\cdot}H_2O$, 0.14 g 0.82 mmol, 2 ml of dry MeOH; 4-(2-cyanoethylthio)-4′,5,5′-tris(methylthio)TTF, 0.53 g, 0.2 mmol, 10 ml of dry DMF]. The reaction mixture thus obtained was stirred for 2–3 h at 35–40 ^{o}C up to disappearing of crimson color inherent to the intermediate thiolate. The slow evaporation at an ambient temperature gave well-formed ruby colored crystals of TTF **1** which were washed with plenty of hexane, mp 135–136 ^{o}C, yield 43%. ^{1}H NMR ($CDCl_3$), δ: 2.38 (s, 3H, SCH_3), 2.42 (s, 6H, SCH_3), 3.25 (t, 2H, SCH_2, J 7.5 Hz), 4.73 (t, 2H, OCH_2, J 6.9 Hz), 7.18 (t, 2H, thiophene, J 4.2 Hz), 7.61 (d.d, 2H, thiophene, J_1 5.1 J_2 3.9 Hz), 8.20 (d.d, 2H, thiophene, J_1 3.9, J_2 2.4 Hz).