

Supplementary Information for

First tellurium-containing phthalocyanine analogues: Strong effect of tellurium on spectral, redox and conductivity properties of porphyrazines with annulated chalcogenodiazole ring(s)

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1. Synthesis of 1,2,5-Telluradiazole-3,4-dicarbonitrile (1).

Solution of TeCl₄ (2.5 g, 9.25 mmol) in dry pyridine (70 ml) was dropped to solution of diaminomaleodinitrile (1 g, 9.25 mmol) in the same solvent (50 ml) under intense stirring at room temperature. After 10 min an excess of tributylamine (20 ml, 85 mmol) was added, the mixture was stirred for further 15 min and the product was crystallized upon staying overnight in refrigerator at ~ -20°C. After filtration and drying in vacuum desiccator till constant weight the product was obtained as long yellow needles of pyridine solvate (2.7 g, 93.6%). Calculated for C₄N₄Te×C₅H₅N, %: C, 34.78; H, 1.62; N, 22.54. Found, %: C. 33.89; H, 1.61; N. 22.09. IR (KBr), ν, cm⁻¹: 2228m, 1511s, 1387w, 1263s, 1105s, 700s, 578s. NMR (DMSO-d₆): ¹H (δ_{TMS}, ppm) 8.57 (2H), 7.79 (1H), 7.39(2H) (py); ¹³C (δ_{TMS}, ppm) 149.5 (py), 141.3 (C⁰), 123,9 (py), 119,4 (CN); ¹²⁵Te (δ_{TeMe2}, ppm) 2409.5.

2. Cyclic voltammetry of [TTeDPAMg] and its S- and Se-analogues ([TSDPAMg], TSeDPAMg).

Electrochemical measurements were fulfilled in a 3-electrode electrochemical glass cell with Pt wire counter electrode and Ag|AgCl reference electrode and a carbon-paste working electrode modified with the studied Mg^{II} complex in an aqueous 0.1 M KOH solution under Ar atmosphere (99,99%). A thin layer of the paste containing a mixture of the complex, fluoroplast (FP-4D) and carbon powder (TY-14-7-24-80) in 1:2:7 ratio was placed on the bottom edge of carbon-graphite rod with walls isolated by a fluoroplast shell. Cyclic *I,E*-curves were measured using potentiostat PI-50-1 in the range 0.2 ÷ -1.5 V with the potential sweep rate from 10 to 100 mV/s. The accuracy of potential measurements is ±0,005 V.

Table. Redox potentials for carbon paste electrodes with Mg-porphyrazines. Scan rate 20 mV/s.

Compound	Process I			Process II		
	E _{kat} , V	E _{an} , V	E _{red/ox} , V	E _{kat} , V	E _{an} , V	E _{red/ox} , V
MgTSDPA	-0,64	-0,21	-0,425	-1,22	-0,78	-1,00
MgTSeDPA	-0,50	-0,26	-0,38	-1,25	-1,00	-1,125
MgTTeDPA	-0,45	-0,00	-0,225	-1,20	-0,84	-1,02

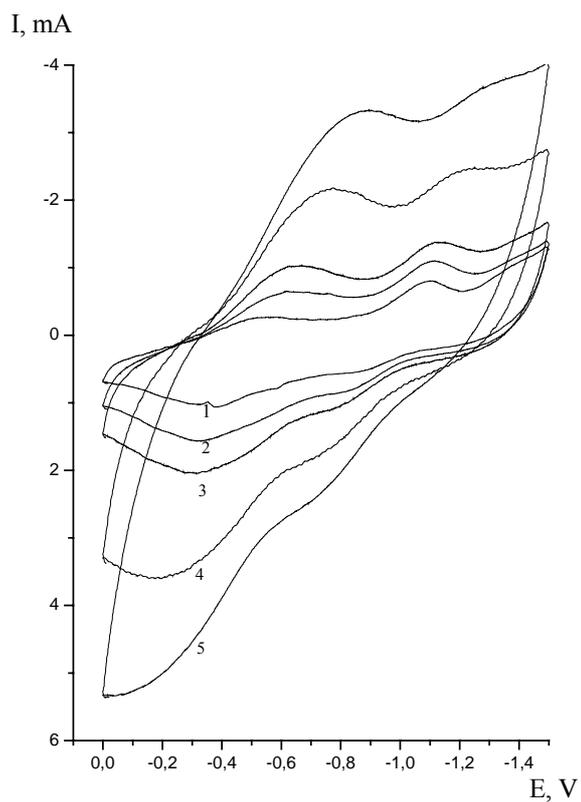


Figure 2.1. CVA-curves for electrodes with для электродов с [TSDPAMg] in Ar; 0,1 M KOH. Sweep rates, mV/s: 1-5; 2-10; 3-20; 4-50; 5-100.

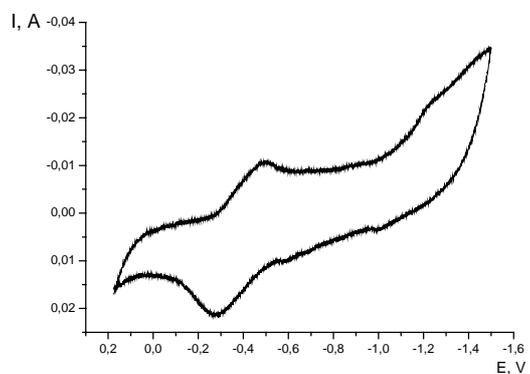


Figure 2.2. CVA-curve for electrodes with [TSeDPAMg] in Ar; 0,1 M KOH. Sweep rates 20 mV/s.

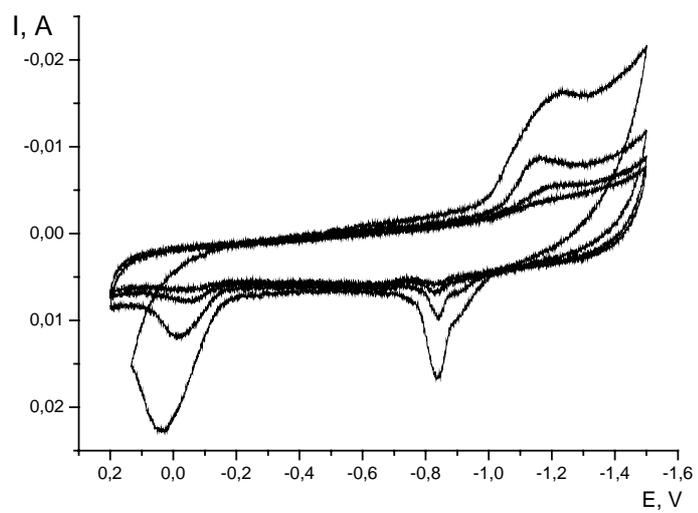


Figure 2.3. CVA-curves for electrode with [TTeDPAMg] in Ar; 0,1 M KOH. Sweep rate 20 mV/s (4 cycles).

3. Study of conductivity of thin films of [TTeDPAMg]

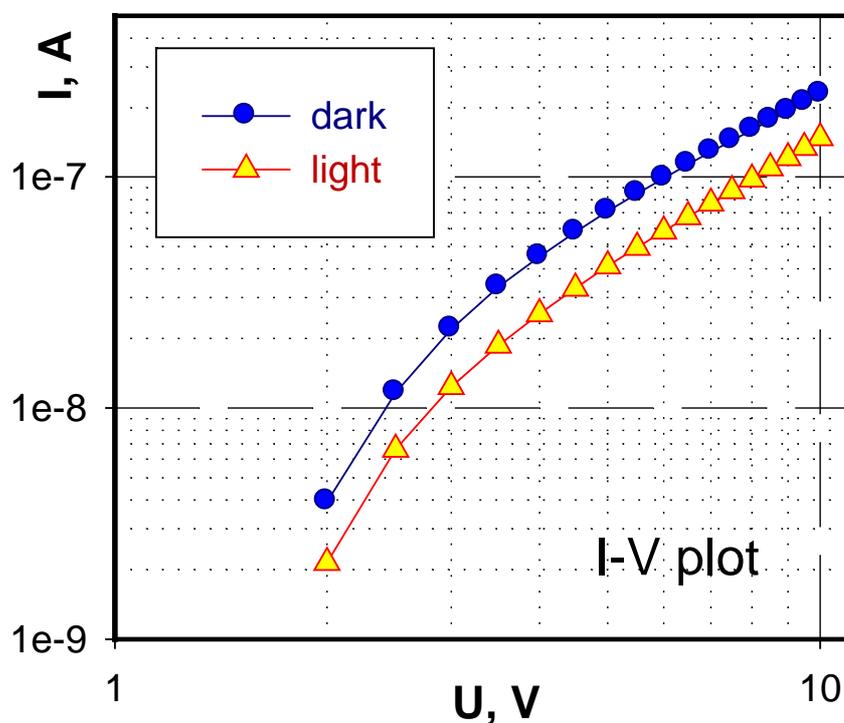


Figure 3.1. Steady state I-V plots in full logarithmic scale for [TeTDPAMg] film in the dark and when exposed to the white light. The measurements were done in air, at room temperature, using a Keithley 4200-SCS instrument in a two-probe arrangement in the range of -10...+10 V. Samples were placed into shielded steel cuvette with quartz window, through which they were illuminated using a 40W tungsten lamp providing the incident light intensity of 17-20 mW/cm² at the film surface.

4. ^1H NMR spectrum of the low-symmetry porphyrazine (4)

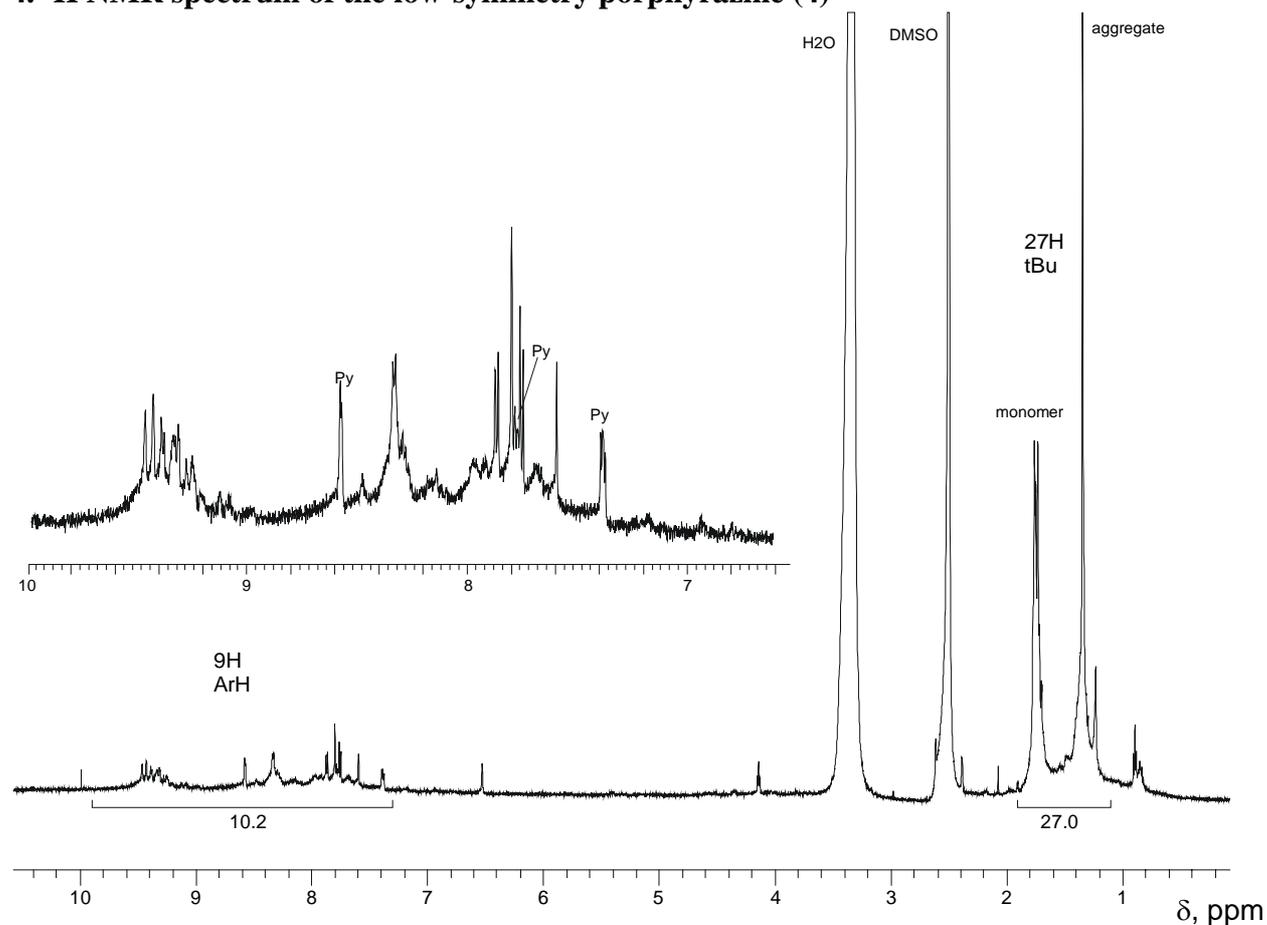


Figure 4.1. ^1H NMR spectrum of **4** in DMSO-d_6 . Complex spectrum in the aromatic region indicates a mixture of randomers (see Chart 4.1). Aggregated form gives additional broad lines in the aromatic region and signal of the *tert*-butyl group at 1.34 ppm.

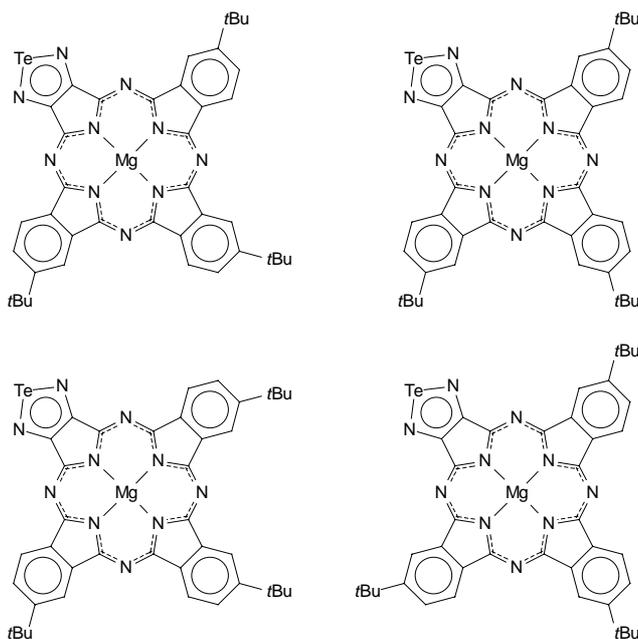


Chart 4.1. Randomers of **4**.