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The iron complex of dimethyl chlorin e_6–thioctic acid conjugate and its monolayers on the water and gold surfaces

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General

Commercially available reagents were used without additional purification. TLC analyses were carried out on Merck TLC silica gel 60 F254. Column chromatography was performed by using Macherey–Nagel Kieselgel 60 (70–230 mesh). NMR spectra were obtained with Agilent DD2 400 spectrometer, with the residual solvent peak as an internal reference. Mass-spectra were recorded on a BrukerMicroflex LT spectrometer(MALDI-TOF).

Langmuir films and monolayers

Experiments were provided using Nima LB Deposition Trough112D (KSV Nima, Sweden) system applying water (resistivity > 18 MS, Simplicity, Millipore Inc.) with pH 5.5 as a subphase at 20 ± 1◦C. Wilhelmy plate method was used for registration of the surface pressure–area (π–A) isotherms at 20 ± 1◦C. The time of solvent evaporation and compression speed were chosen to provide as low hysteresis of the films as possible. Compression of the film was provided in continuous mode at the rate of 60 cm^2/min by two symmetric frames. Spreading solutions was prepared by dissolving the appropriate amount of conjugates in chloroform-methanol mixture (v/v=1:2) (concentration 1.0 mg/mL). Then 20 μL of the solution was spread on the aqueous subphase with a chromatographic microsyringe in several stages; solvent evaporation and equilibration of the amphiphile on the interface took 30–40 min.

Nitric oxide preparation

NO solutions were prepared by the addition of 2 M H_2SO_4 to solid $NaNO_2$ in a Kipps apparatus. The NO gas passed through four NaOH (20%) traps (to remove NO_2), and then through a solid CO_2 trap. The gas was collected in a phosphate buffer solution that had under-

gone four vacuum/N_2 deoxygenation cycles. The NO concentration in the solution varied from 1.2 to 2 mM.

*NMR spectra of compound **1***

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 9.56 (s, 1H), 8.82 (s, 1H), 8.00 (dd, *J* 17.8, 11.5 Hz, 1H), 7.37 (s, 1H), 7.06 (s, 1H), 6.28 (d, *J* 17.9 Hz, 2H), 6.08 (d, *J* 12.5 Hz, 2H), 5.45 (d, *J* 19.3 Hz, 1H), 5.22 (d, *J* 18.8 Hz, 1H), 4.85 (s, 1H), 4.49 (q, *J* 7.1 Hz, 1H), 4.39 (d, *J* 9.1 Hz, 1H), 3.79–3.73 (m, 2H), 3.69 (s, 3H), 3.66–3.62 (m, 3H), 3.45 (s, 3H), 3.34 (s, 3H), 3.21 (s, 3H), 3.10–3.05 (m, 1H), 2.90 (ddd, *J* 16.1, 12.6, 4.6 Hz, 3H), 2.70–2.62 (m, 1H), 2.57 (dd, *J* 15.2, 7.8 Hz, 1H), 2.25 (dd, *J* 16.1, 8.5 Hz, 2H), 2.04–1.98 (m, 1H), 1.84–1.77 (m, 1H), 1.71 (t, *J* 7.6 Hz, 6H), 1.57–1.40 (m, 4H), 1.21 (dd, *J* 14.6, 8.6 Hz, 2H), 1.11 (dd, *J* 14.6, 7.4 Hz, 2H), 0.95–0.78 (m, 2H).

^{13}CNMR (101 MHz, $CDCl_3$): δ 173.86, 173.61, 173.58, 170.16, 169.16, 167.05, 154.28, 149.11, 144.99, 139.02, 136.34, 134.99, 134.90, 134.75, 130.44, 129.78, 129.36, 128.15, 121.96, 102.52, 101.51, 98.88, 93.89, 56.24, 53.21, 52.33, 51.80, 49.29, 40.03, 40.01, 38.34, 35.55, 34.40, 34.39, 31.19, 29.82, 28.62, 25.05, 25.03, 23.27, 19.79, 17.93, 12.27, 11.90, 11.40.

Atomic Force Microscopy (AFM) Imaging and AFM Measurements

The formation of the monolayer films of **3** on the gold surface was investigated using atomic-force microscopy method with the microscope Solver P47 (NT-MDT). The scanning was performed in the semi-contact mode.

UV−Vis Analysis

UV−Vis spectra of transferred films on quartz substrate were recorded by using the UV−vis spectrometer “Shimadzu UV-1800” in the wavelength range 200−800 nm (standard quartz).

Contact Angle Measurements

The contact angles were measured by Digidrop goniometer (GBX, France) equipped with a video camera system at 20 ± 1 °C. The advancing contact angles of the probe liquids were measured after setting 1 μL droplets on the surface. The readings were taken on the left and right sides of the droplet profile for all probe liquids. In each series and for each liquid, the contact angles were measured for four droplets at least. Generally, the reproducibility of the contact angle measurements was less than one degree.

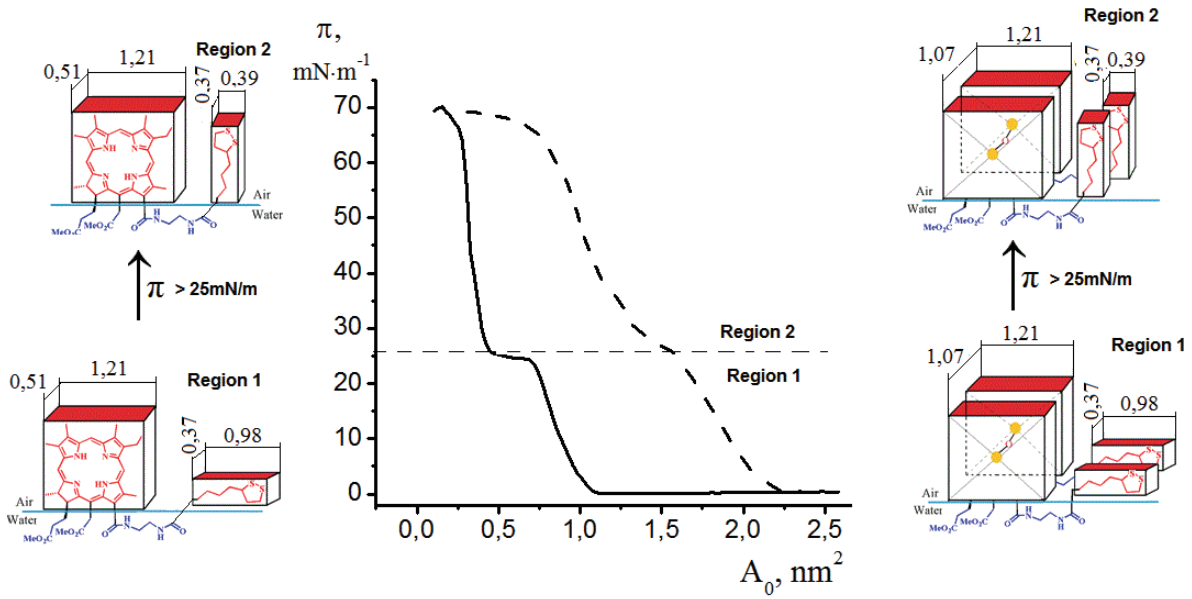

Figure S1 π-A isotherms of conjugates **1** (solid line) and **2** (broken line) on the water subphase and schematic illustration of the orientation of **1** (left side) and **2** (right side) at "air-water" interface. Note: calculated sizes of molecules are given in nanometers (nm).

Table S1 Properties of conjugates **1** and **2** monolayers.

Parameters	Conjugate	Conjugate
Region 1		
A_0, nm^2/molecule	1,02±0,02	2,02±0,02
A_0, nm^2/molecule	0,98	2,02
C_s^{-1}, mN/m	95±16	106±20
Region 2		
A_0, nm^2/molecule	0,44±0,03	1,64±0,02
A_0, nm^2/molecule	0,76	1,58
C_s^{-1}, mN/m	295±16	176±17

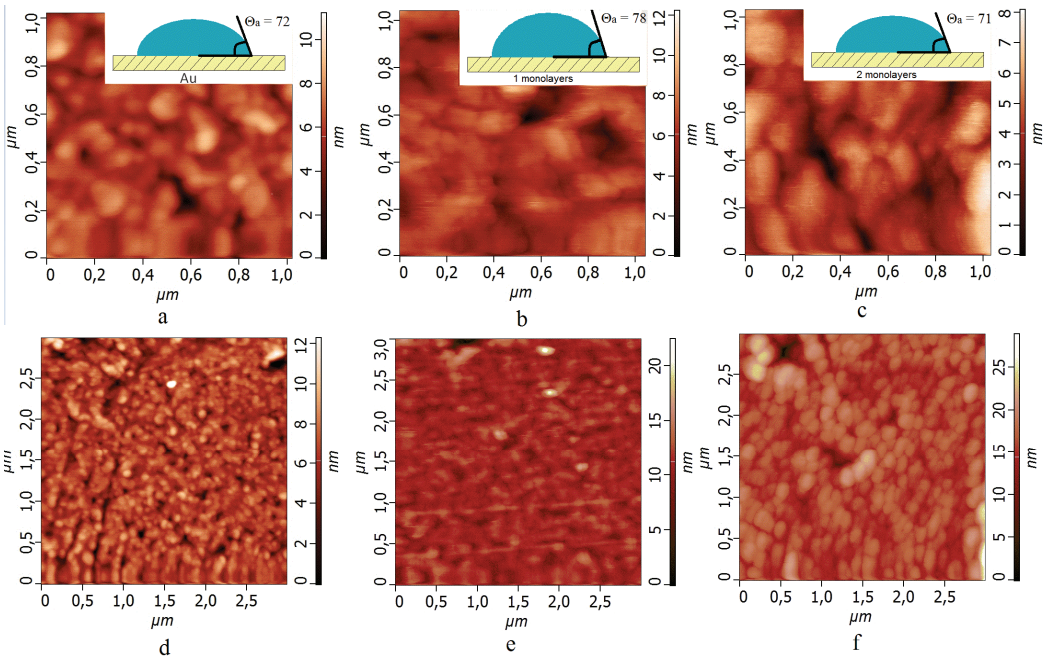

Figure S2 AFM vizualization of goldsupport: gold surface (**a**,**d**) 1 monolayer ofcompound **2**(**b**,**e**); 2 monolayers of compound**2** (**c**,**f**).

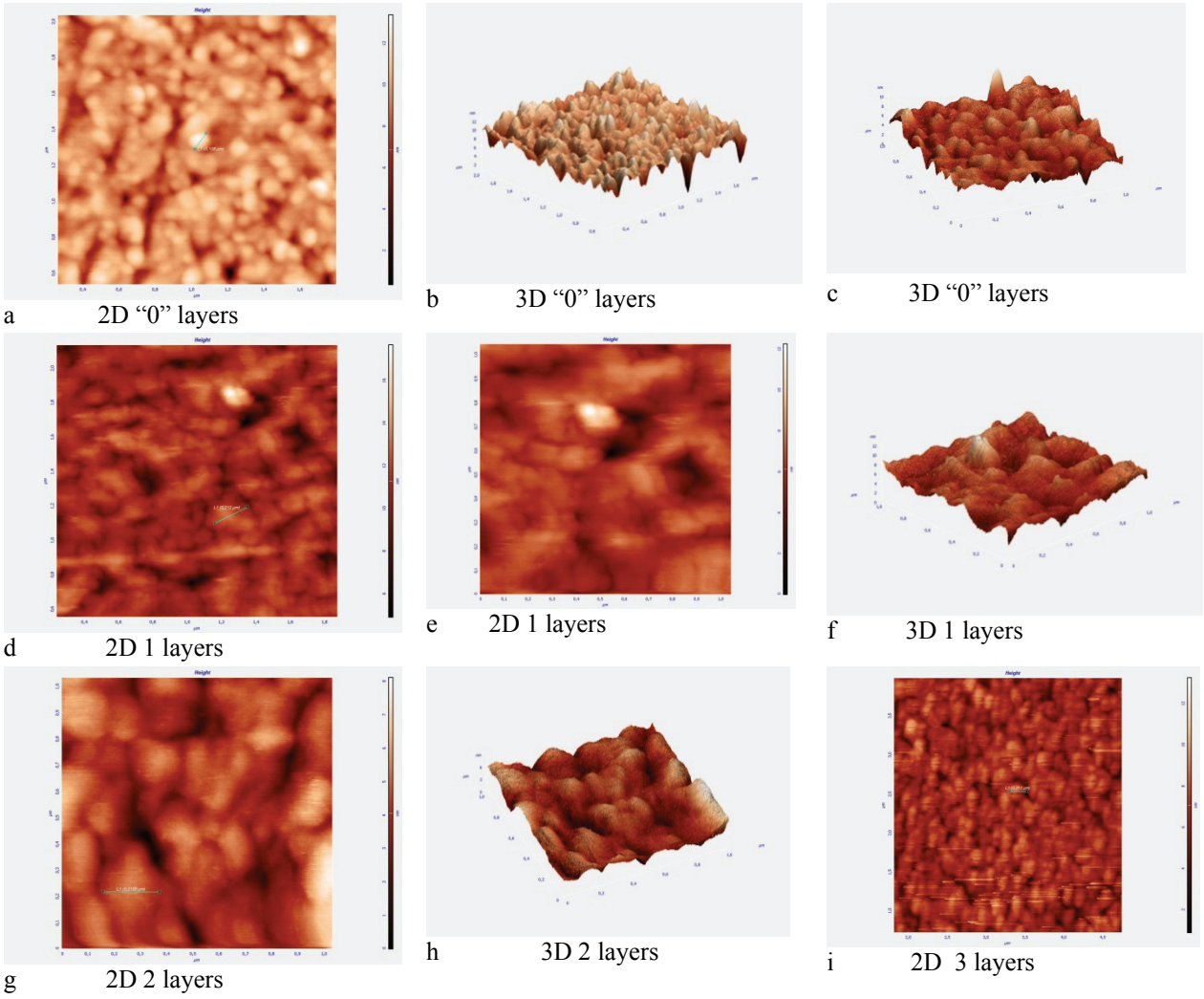

Figure S3 AFM vizualization of solid substrate: gold surface 2D (**a**) and gold surface 3D (**b,c**); 1 monolayer of **2** on gold 2D (**d**, **e**) and 3D (**f**); 2 monolayers of **2** on gold 2D (**g**) and 3D (**h**); 3 monolayers of **2** on gold 2D (**i**).

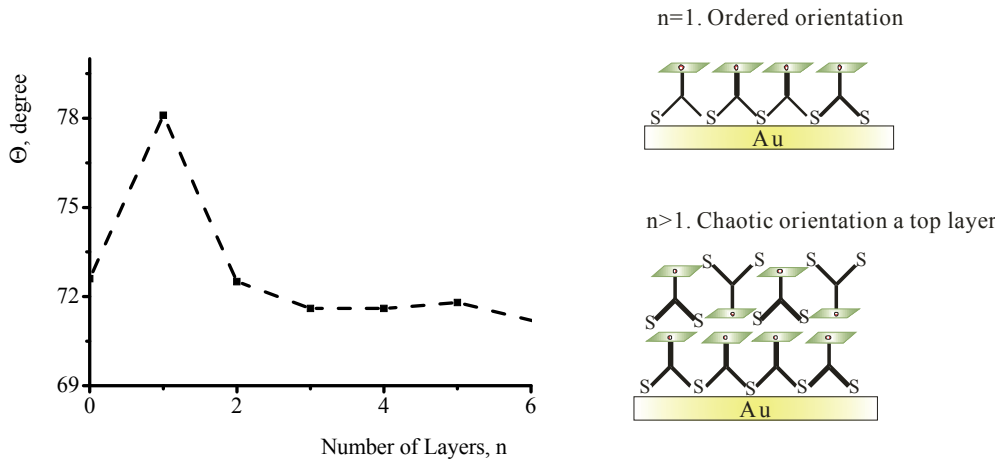

Figure S4 The dependence of contact anglee on the number *n* of conjugate **2** monolayers transferred onto gold substrate.

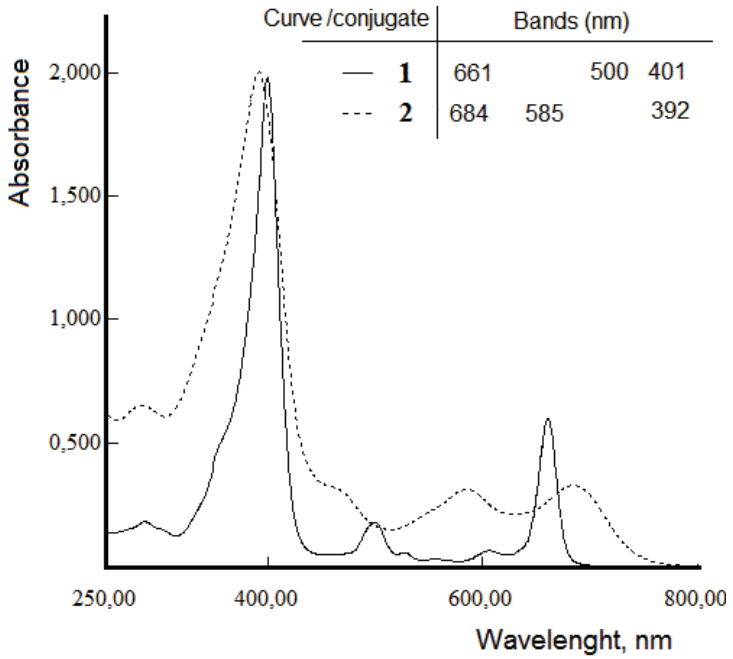

Figure S5 UV-Vis spectra of conjugates **1** ($4{,}4 \cdot 10^{-5}$ M)and **2** ($1{,}4 \cdot 10^{-5}$ M) in $CHCl_3$: CH_3OH (v/v 1:2) solution.