

Multistate Switching of Scanning Tunnelling Microscopy Machined Polyoxovanadate–Dysprosium–Phthalocyanine Nanopatterns on Graphite

Marco Moors,^a Irina Werner,^a Jens Bauer,^a Jonas Lorenz,^a and Kirill Yu. Monakhov*^a

^a Leibniz Institute of Surface Engineering (IOM), Permoserstraße 15, 04318 Leipzig, Germany

Supporting Information

Synthesis.....	2
XPS measurements.....	3
SEM measurements.....	6
STM measurements.....	8
References.....	10

Synthesis of PcDy-POV12

100.0 mg (0.045 mmol, 1.0 equiv.) of $(n\text{Bu}_4\text{N})_4[\text{HV}_{12}\text{O}_{32}\text{Cl}]$ [S1] and 35.0 mg (0.045 mmol, 1.0 equiv.) of $\text{PcDyOAc}\cdot\text{MeOH}\cdot\text{H}_2\text{O}$ [S1] were dissolved in 5 mL of acetonitrile using an ultrasonic bath. The solution was allowed to stand for 5 days at room temperature without stirring. The solution was filtered off and the filtrate was dropped into 100 mL of diethyl ether. The resulting precipitate was centrifuged 5 min with 10000 rpm and washed with 20 mL of diethyl ether. The solid was redissolved in 5 mL of acetonitrile and precipitated in 60 mL of diethyl ether. The precipitate was centrifuged 5 min with 10000 rpm and washed two times with 20 mL of diethyl ether. The obtained green-blue solid was dried in air and stored in a desiccator. Yield: 115 mg (90%). Elemental analysis (%) calcd. for $\text{C}_{80}\text{H}_{125}\text{ClDyN}_{11}\text{O}_{32}\text{V}_{12}\cdot 3\text{Et}_2\text{O}\cdot 5\text{H}_2\text{O}$ ($M = 2874.62 \text{ g mol}^{-1}$): C 38.44, H 5.79, N 5.36. Found: C 38.76, H 5.81, N 5.15. FT-IR (KBr, cm^{-1}): $\tilde{\nu} = 2961$ (s), 2934 (s), 2873 (s), 2360 (w), 1945 (w), 1724 (w), 1635 (m), 1483 (s), 1460 (s), 1383 (s), 1329 (m), 1282 (w), 1159 (w), 1113 (w), 1079 (w), 1060 (w), 989 (vs), 884 (w), 828 (s), 760 (s), 743 (s), 733 (s), 679 (s), 628 (s), 428 (w). UV/Vis (MeCN, nm): $\lambda = 223, 238, 335, 607, 644, 673$. MS (MeCN, ESI): $m/z = [\text{M} + \text{H} + 2 n\text{Bu}_4\text{N}]^{2-} / [\text{M} + 2 n\text{Bu}_4\text{N}]^{2-}$ (5:2) 1159.875 (exp.), 1159.875 (theo.); $[\text{M} + \text{H} + n\text{Bu}_4\text{N}]^{2-}$, 1038.737 (exp.), 1138.757 (theo.); $[\text{M} + \text{H} + n\text{Bu}_4\text{N}]^{3-}$ 692.498 (exp.), 692.498 (theo.); $[\text{M} + \text{H}]^{3-}$ 611.738 (exp.), 611.740 (theo.); $[\text{M} = \text{V}_{12}\text{O}_{32}\text{ClDyPc}]$.

Synthesis of $(\text{PcDy})_2$ -POV12

75.0 mg (0.035 mmol, 1 equiv.) of $(n\text{Bu}_4\text{N})_4[\text{HV}_{12}\text{O}_{32}\text{Cl}]$ and 60.0 mg (0.077 mmol, 2.2 equiv.) of $\text{PcLnOAc}\cdot\text{MeOH}\cdot\text{H}_2\text{O}$ were dissolved in 5 mL of acetonitrile using an ultrasonic bath. The solution was allowed to stand for 2 days without stirring at 70°C . After cooling down to room temperature, the solution was filtered off and the filtrate was dropped into 100 mL of diethyl ether. The resulting precipitate was centrifuged 5 min with 10000 rpm and washed with 20 mL of diethyl ether. The solid was redissolved in 5 mL of acetonitrile and precipitated in 60 mL of diethyl ether. The precipitate was centrifuged 5 min with 10000 rpm and washed two times with 20 mL of diethyl ether. The obtained blue solid was dried in air and stored in a desiccator. Yield: 101 mg (82%). Elemental analysis (%) calcd. for $\text{C}_{96}\text{H}_{105}\text{ClDy}_2\text{N}_{18}\text{O}_{32}\text{V}_{12}\cdot 5\text{Et}_2\text{O}\cdot 8\text{H}_2\text{O}$ ($M = 3509.47 \text{ g mol}^{-1}$): C 39.70, H 4.91, N 7.18. Found: C 39.75, H 4.88, N 6.95. FT-IR (KBr, cm^{-1}): $\tilde{\nu} = 3059$ (w), 2961 (s), 2933 (s), 2873 (m), 2533 (w), 1957 (w), 1634 (m), 1483 (s), 1458 (s), 1384 (s), 1329 (s), 1282 (m), 1160 (w), 1113 (m), 1080 (m), 1060 (m), 995 (vs), 885 (w), 824 (m), 778 (m), 742 (s), 732 (s), 649 (m), 629 (m), 434 (w). UV/Vis (MeCN, nm): $\lambda = 222, 240, 336, 607, 642, 671$. MS (MeCN, ESI): $m/z = [\text{M} + 2 n\text{Bu}_4\text{N}]^{2-}$ 1496.927 (exp.), 1496.432 (theo.); $[\text{M} + \text{H} + n\text{Bu}_4\text{N}]^{2-} / [\text{M} + n\text{Bu}_4\text{N}]^{2-}$ (1:1) 1375.761 (exp.), 1375.790 (theo.); $[\text{M} + \text{H} + n\text{Bu}_4\text{N}]^{3-}$ 917.190 (exp.), 917.196 (theo.); $[\text{M} + \text{H}]^{3-}$ 836.428 (exp.), 836.100 (theo.); $[\text{M} = \text{V}_{12}\text{O}_{32}\text{Cl}(\text{DyPc})_2]$.

XPS measurements

The surface composition was explored by X-ray photoelectron spectroscopy (XPS, Kratos Ultra DLD). The measurements were performed at room temperature with a background pressure of 1×10^{-7} Pa. For excitation, monochromic Al K α radiation at 1486.6 eV was used. The X-ray source was operated at 150 W. Photoelectrons were released from the 300 $\mu\text{m} \times 700 \mu\text{m}$ analysis area and were analysed under normal detection angle configuration. The photoelectron yield was enhanced applying a magnetic immersion lens. To avoid sample charging a neutraliser supplied thermal electrons to the analysis area on sample 1 (powder sample). For sample 2 (thin film on HOPG) no charge neutralisation was necessary. A retarding lens system coupled by a hemispherical analyser with 40 eV pass energy was used for energy separation. The energy-filtered photoelectrons were amplified passing a microchannel plate and recorded by a delay line detector. The UNIFIT 2023 software was used for spectra analysis and composition calculation considering the specific transmission correction of the XPS machine. For curve fitting convolved Gaussian-Lorentzian peak profiles were simultaneously optimised with a Shirley background profile. The spectral calibration was performed by the Fermi level for sample 1 and by the graphite peak in the C 1s core-level spectrum at 284.5 eV for sample 2. The core-levels of V 2p and O 1s were fitted together to account for their overlapping. Because of the Coster-Kronig effect the linewidth of V 2p_{1/2} was about 2x the linewidth of V 2p_{3/2}. The peak area ratio V 2p_{1/2} / V 2p_{3/2} was kept at 1:2 and the V 2p_{1/2} - V 2p_{3/2} peak splitting at 7.33 eV. The V^(V) and V^(IV) oxidation state peaks were overlapping strongly. The best fit value for the V^(V) - V^(IV) peak separation was 0.95 eV, which is in good agreement with NIST values [S2].

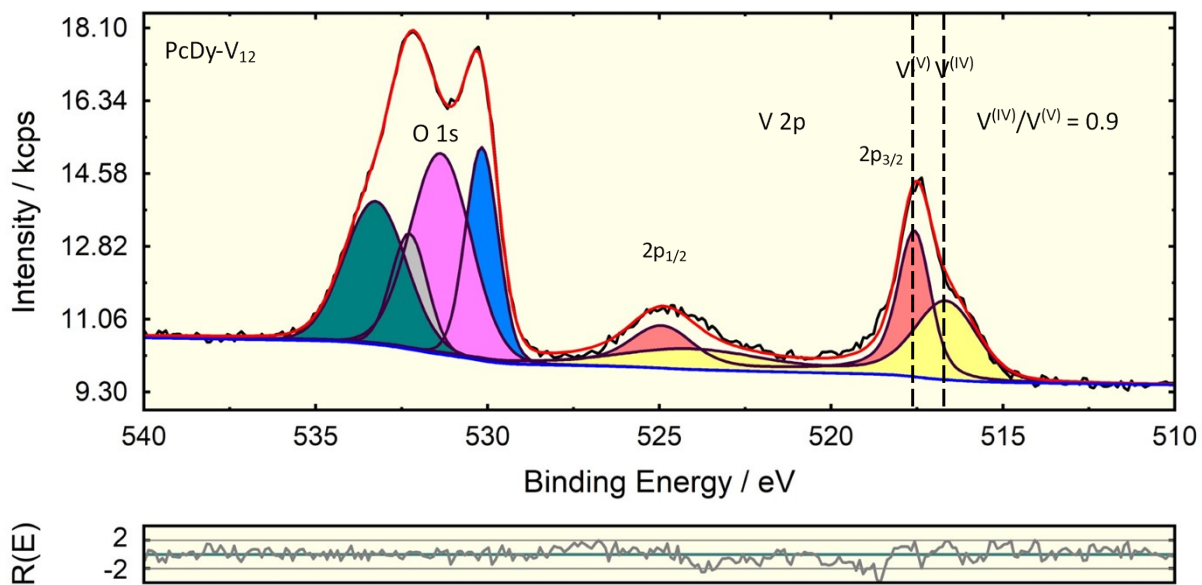


Figure S1. Vanadium XPS data of a PcDy-POV12 monolayer deposited from a 10^{-5} M acetonitrile solution on HOPG. The peak fitting yields a much higher V^(IV)/V^(V) ratio than observed on the bulk sample indicating an increased reduction state of the molecules in the 2D layer. The asymmetric peak shape indicates an electronically conducting material.

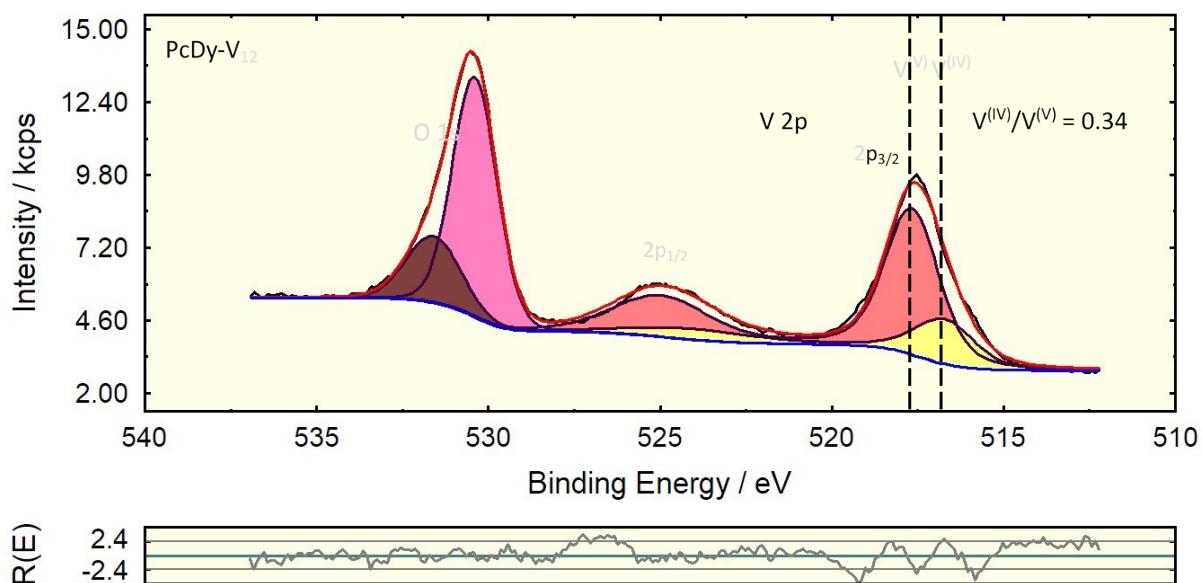


Figure S2. Vanadium XPS data of a PcDy-POV12 powder sample. The peak fitting yields a rather low $V^{(IV)}/V^{(V)}$ ratio of 1:3 indicating a clear excess of fully oxidised vanadium atoms in the bulk phase. The symmetric peak shape indicates an electronically isolating material.

SEM measurements

Scanning electron microscopy (SEM) was conducted using a Gemini Ultra 55 microscope (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). SEM imaging parameters were set as follows: an accelerating voltage of 10 kV, a beam aperture of 7.5 μm , and a working distance of 0.8 mm. Imaging was performed with Secondary electrons (SE) by use of an in-lens SE detector allowing topography contrast imaging without shadowing and a high image contrast.

For the sample preparation both drop-casting and dip-coating techniques were used. The results were rather similar, except that in the latter case the longer contact of the sample with the acetonitrile solution led to a full surface coverage already at lower solvent concentrations.

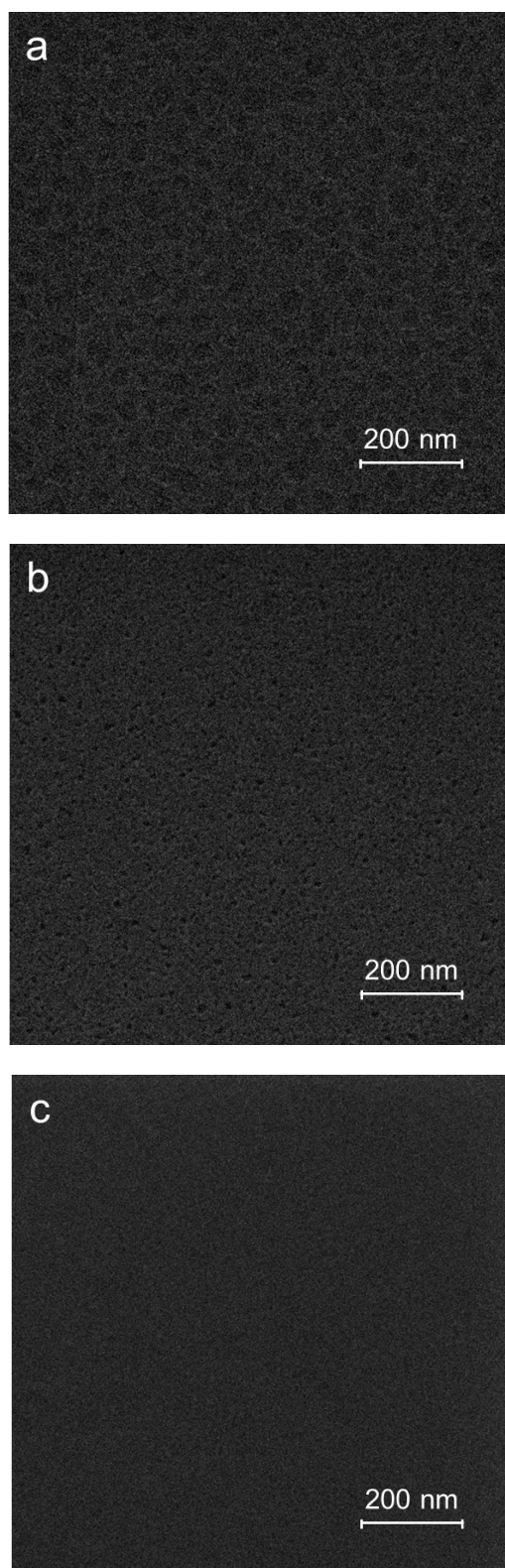


Figure S3. SEM images of PcDy-POV12 layers deposited on HOPG from differently concentrated acetonitrile solutions. (a) and (b) were prepared *via* drop-casting of a 1×10^{-5} mol L $^{-1}$ and 1×10^{-4} mol L $^{-1}$ concentration, respectively, and (c) *via* dip-coating the sample into a 1×10^{-5} mol L $^{-1}$ concentrated solution. The images exhibit a decreasing hole concentration in the molecular layer with increasing POV concentration and show similar structures to the STM images presented in Fig. 2a–2c.

STM measurements

After the preparation of the different SAM layers on freshly cleaved HOPG single crystal surfaces under ambient conditions the samples were directly transferred into vacuum to minimise contamination effects from the atmosphere. The STM measurements were performed under ultrahigh vacuum conditions at room temperature in a commercial VT-SPM system from Scienta Omicron. The system consists of a stainless steel vessel operating at a base pressure of 2×10^{-9} mbar. For the measurements performed in constant current mode and the tunnelling spectra commercial Pt tips from Bruker were used. The tips were cleaned by extensive voltage pulsing on a clean Au(111)/Mica substrate before every measurement cycle. As reference state, the depiction of sharp atomic steps on the reference sample was used. For data acquisition and processing the SPIP 6.7.5 software from Image Metrology was used. All STM images and spectra presented in the manuscript are shown without post filtering and smoothing.

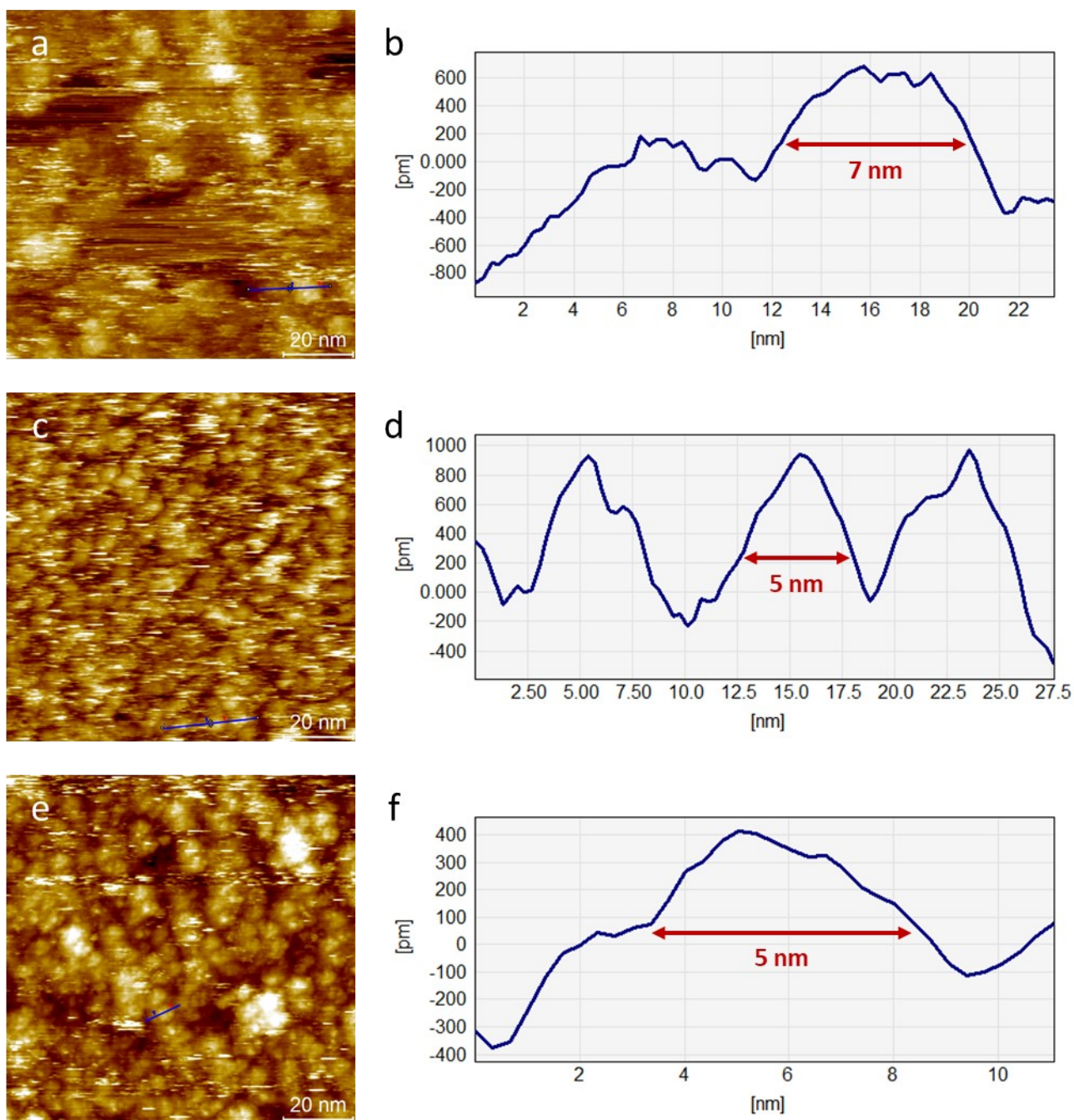


Figure S4. STM images ($U_B = 2$ V; $I_T = 10$ pA) and corresponding height profiles of PcDy-POV12 (a and b), (PcDy)₂-POV12 (c and d), and PcDyOAc (e and f), deposited on HOPG by dip-coating the sample into an acetonitrile solution. The latter two ones show a rather similar electronic diameter, while PcDy-POV12 exhibits a significantly increased electronic size.

References

- S1 I. Werner, J. Griebel, A. Masip-Sánchez, X. López, K. Załęski, P. Kozłowski, A. Kahnt, M. Boerner, Z. Warneke, J. Warneke and K.Y. Monakhov, *Inorg. Chem.*, 2023, **62**, 3761.
- S2 M.C. Biesinger, L.W.M. Lau, A.R. Gerson and R.S.C. Smart, *Appl. Surf. Sci.*, 2010, **257**, 887.