

Supporting Information

Catalytic oxidation of Ascorbic Acid via copper-polypyridyl complex immobilized on glass

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Materials and methods: 2-Acetyl pyridine, 4-pyridine carboxaldehyde, 1-10, phenanthroline, 3-iodo-n-propyltrimethoxysilane and sodium perchlorate were purchased from Sigma-Aldrich and were used as received. Copper acetate monohydrate was purchased from s. d. fine chemicals (India). Methanol and ethanol were purchased from Merck and was distilled over activated magnesium turnings and iodine before use. 30% aq. Ammonia, H₂O₂, dry n-pentane, toluene, dichloromethane and acetonitrile (All AR grade) were purchased from s. d. fine chemicals (India). Schott Nexterion uncoated glass slides B were purchased from Schott India Pvt. Ltd. and Single-crystal silicon [100] substrates were purchased from Georg Albert PVD- Beschichtungen (Silz, Germany). Hydrothermal bombs (25mL & 50mL) were purchased from Prakash Scientific Works (India). *Water used for the experiment was double distilled, deionized and degassed using liquid N₂.*

Glass slides were cleaned by immersing them in *piranha* solution (7:3 (v/v)), Conc.H₂SO₄: 30% H₂O₂) for 1h and subsequent washing with ample amount of de-ionized (DI) water. (*Caution: Piranha is an extremely strong and dangerous oxidising agent and all protective measures must be adopted to prevent any harm.*) Then the slides were kept in RCA solution (1:5:1 (v/v), aq. NH₃:H₂O:H₂O₂) for 1h followed by rinsing with ample amount of de-ionized water, dried with N₂ stream and kept in oven for 2h at 110 °C. Silicon wafers were cleaned by sonication for 15 minutes each in n-hexane, acetone and isopropanol followed by drying under N₂ stream before placing in oven at 110 °C for 2h. The monolayer formation was carried out under an inert atmosphere using standard Schlenk/cannulatechniques.

Physical measurements: All ¹H NMR spectra were recorded on Jeol JNMECX 400P spectrometer. Infrared spectra were recorded on Perkin-Elmer FT-IR spectrometer. Elemental analyses were performed on a GMBH VarioEL elemental analyzer. All the above data collection was performed at Central Instrumentation Facility (CIF), University of Delhi. Electronic absorption spectra were recorded using JASCO UV-Vis-NIR spectrophotometer (660D). Mass spectra were recorded on THERMO Finnigan LCQ Advantage max ion trap mass spectrometer (MSAIF, CDRI, Lucknow, India).

Preparation of 4'-pyridyl-2,2':6',2''-terpyridine (Pytpy): The 4'-pyridyl-2,2':6',2''-terpyridine was synthesized following reported procedure^{S1} and purity was checked by ¹HNMR and Mass spectrometry. ¹HNMR (400 MHz, CDCl₃); δ/ppm: 8.76 (s, 2H), 8.78 (d, 2H), 8.68 (d, 2H), 7.8(d, 2H), 7.89 (t, 2H), 8.75 (d, 2H), 7.39 (t, 2H). ESI-MS: *m/z*: 310 (M⁺).

Preparation of 1^{S2}: Synthesis given in main text. Yield: 0.28g (60%). UV-Vis: λ_{max}/nm (ε/M⁻¹ cm⁻¹): 220 (12139), 270 (12917), 336 (4676), 347 (5891), 626 (63). FT-IR (KBr disk) (cm⁻¹): 421, 1090, 1553, 1585, 1609, 1618. (ESI-MS): *m/z* =246 (M²⁺).

Characterization of the monolayers: The monolayers were characterized by a combination of aqueous contact angle measurements, semicontact atomic force microscopy (AFM), optical (UV/vis) transmission spectroscopy, spectroscopic ellipsometry, X-ray photoelectron spectroscopy and Near Edge X-ray Absorption Fine Structure.

The XPS measurements were performed using a Mg K α X-ray source and a hemispherical analyzer. The spectra acquisition was carried out in normal emission geometry with an energy resolution of ~ 0.9 eV. The X-ray source was operated at a power of 260 W and positioned ~ 1.5 cm away from the samples. The binding energy (BE) scale of the XPS spectra was referenced to the Si 2p doublet (appearing as a single peak) at 99.15 eV^{S3}. The spectra were fitted by symmetric Voigt functions and Shirley-type background. The peak fits were carried out self-consistently, i.e., the similar peak parameters were used for identical spectral regions. The intensity ratios of the Cu 2p and N 1s signals, corrected for the atomic sensitivity factors, are close to the values expected from the molecular composition, which underlines the intact adsorption of the molecules. In contrast, the C 1s/Cu 2p and C 1s/N 1s ratios are little higher than expected suggesting that there is a residual contamination on the surface, parallel to the molecular adsorption.

Static contact angles of water were measured on a Rame-Hart goniometer. Atomic force microscopy (AFM) images were recorded using a Solver P47 (NTMDT) operated in the semicontact mode. OTESP-type Si SPM probes were used with a resonance

frequency of tip ~ 250 kHz and a tip radius of ~ 10 nm. Roughness data were extracted from $500 \text{ nm} \times 500 \text{ nm}$ images.

Spectroscopic ellipsometry measurements were carried out using an M 2000V (J. A. Wollam Co. Inc.) spectroscopic ellipsometer over a range of 370 to 1000 nm. Measurements were done at incident angles of 60° , 70° and 80° . The data were simulated using Wvase32 software over the entire range to fit the experimental parameters. A Cauchy model was used to fit the data for the organic layer, assuming model parameters of $A=1.45$, $B=0.01 \text{ nm}^2$, $C=0$ and $\exp=0$. The native oxide layer was estimated to be 20 \AA , for the purpose of the calculation, based on ellipsometry measurements of freshly cleaned Si(100) pieces.

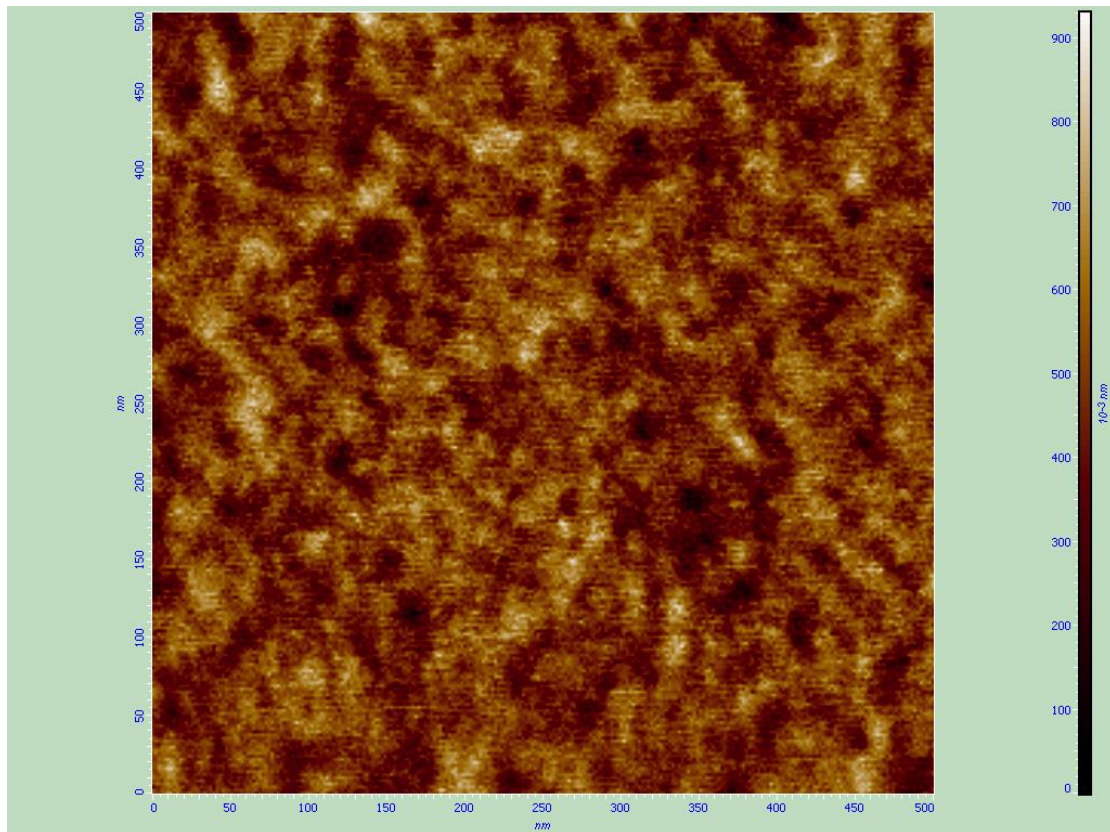


Figure S1: Representative AFM image of the 1-based monolayer on Si(100) recorded on a Solver P47 (NT-MDT) operated in semi-contact mode using a Si OTESP-type SPM probe with a resonance frequency of tip ~ 250 kHz. Scan area $500 \times 500 \text{ nm}$, resolution 300×300 pts. Scan speed ~ 0.5 Hz.

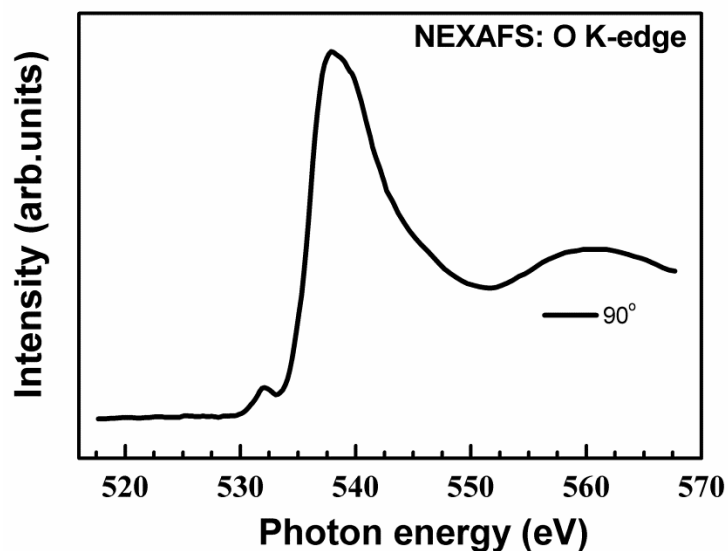


Figure S2: Representative NEXAFS O K-edge spectrum of **1**- based monolayer on Si (100) surface at an incident angle of 90°.

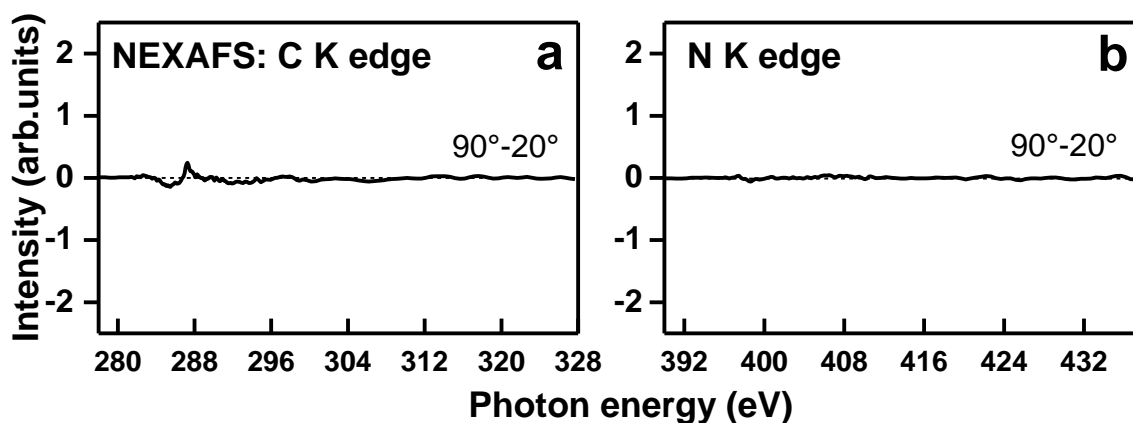


Figure S3: Representation of the difference of the two NEXAFS spectra acquired at 90° and 20° at the C K-edge and N K-edge show linear behavior. Influence of orientation effects could possibly, thus, be excluded.

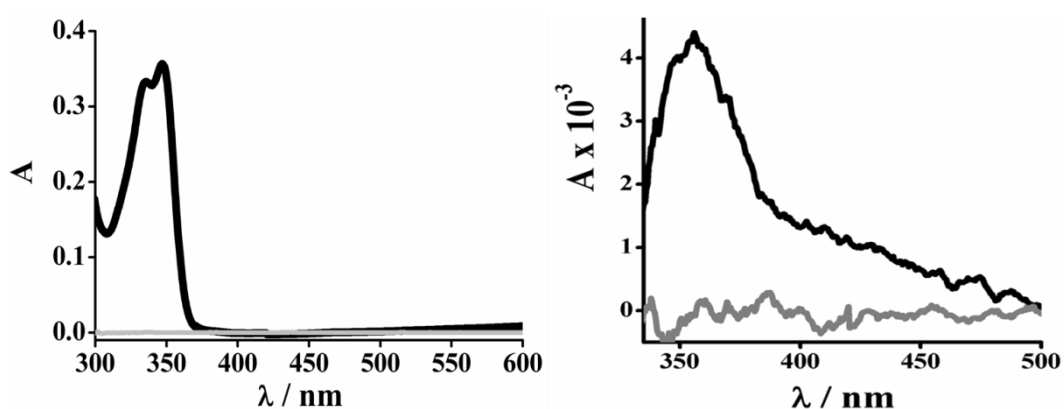


Figure S4: Representative UV-Vis spectra for **1** in methanol (Left, black line) and for **1**-based monolayer on glass (Right, black line). Respective baselines corresponding either to methanol or to glass without monolayer are shown as well (grey lines).

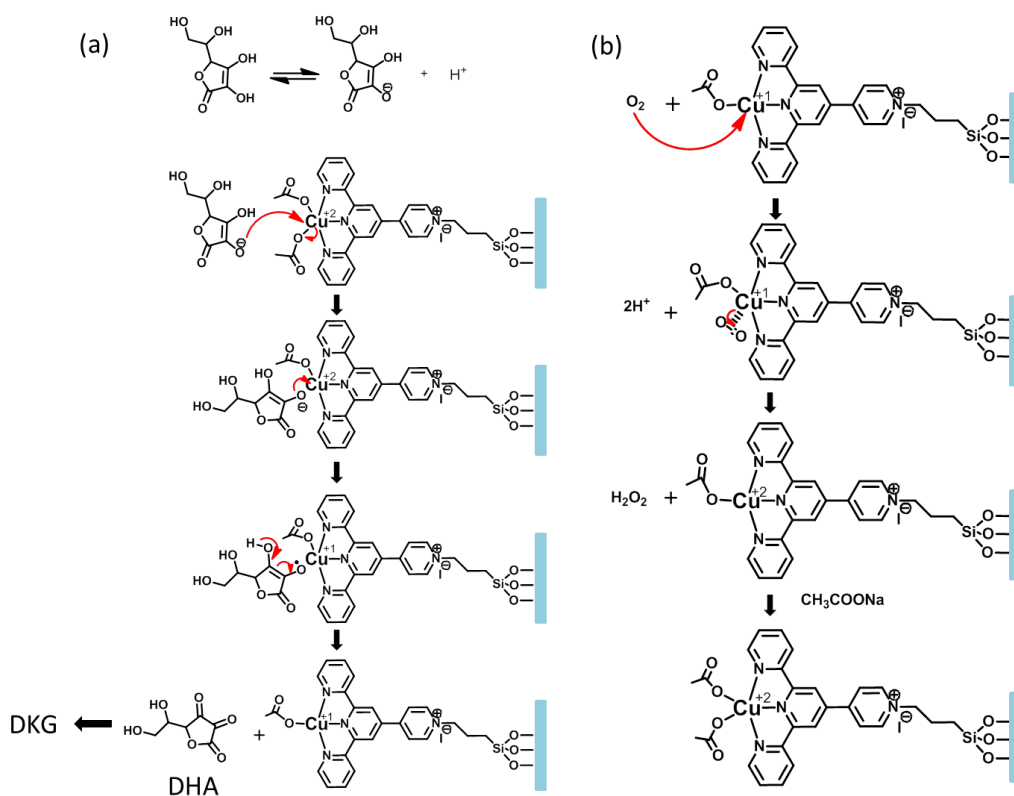


Figure S5. Proposed mechanism for electron-transfer-based AA oxidation (a) and subsequent regeneration (b) of the **1**-based monolayer catalyst.

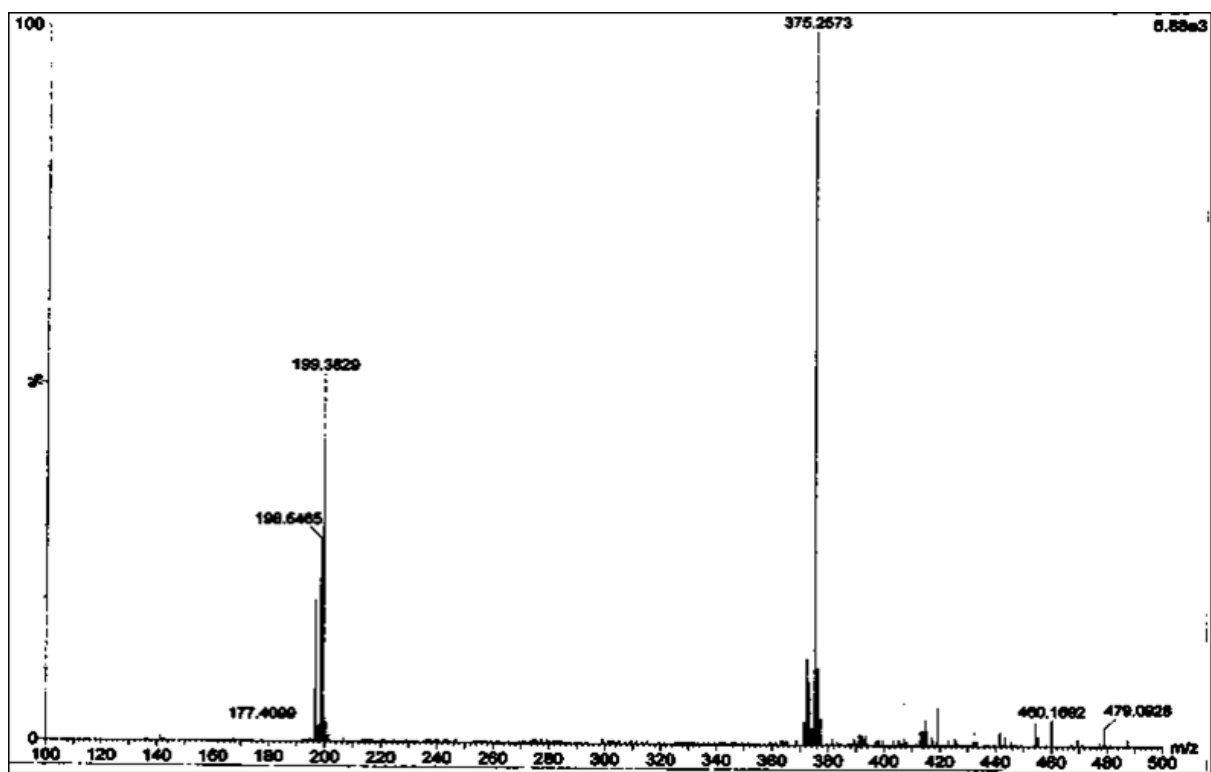


Figure S6: ESI-MS of AA in DI, N₂ purged water.

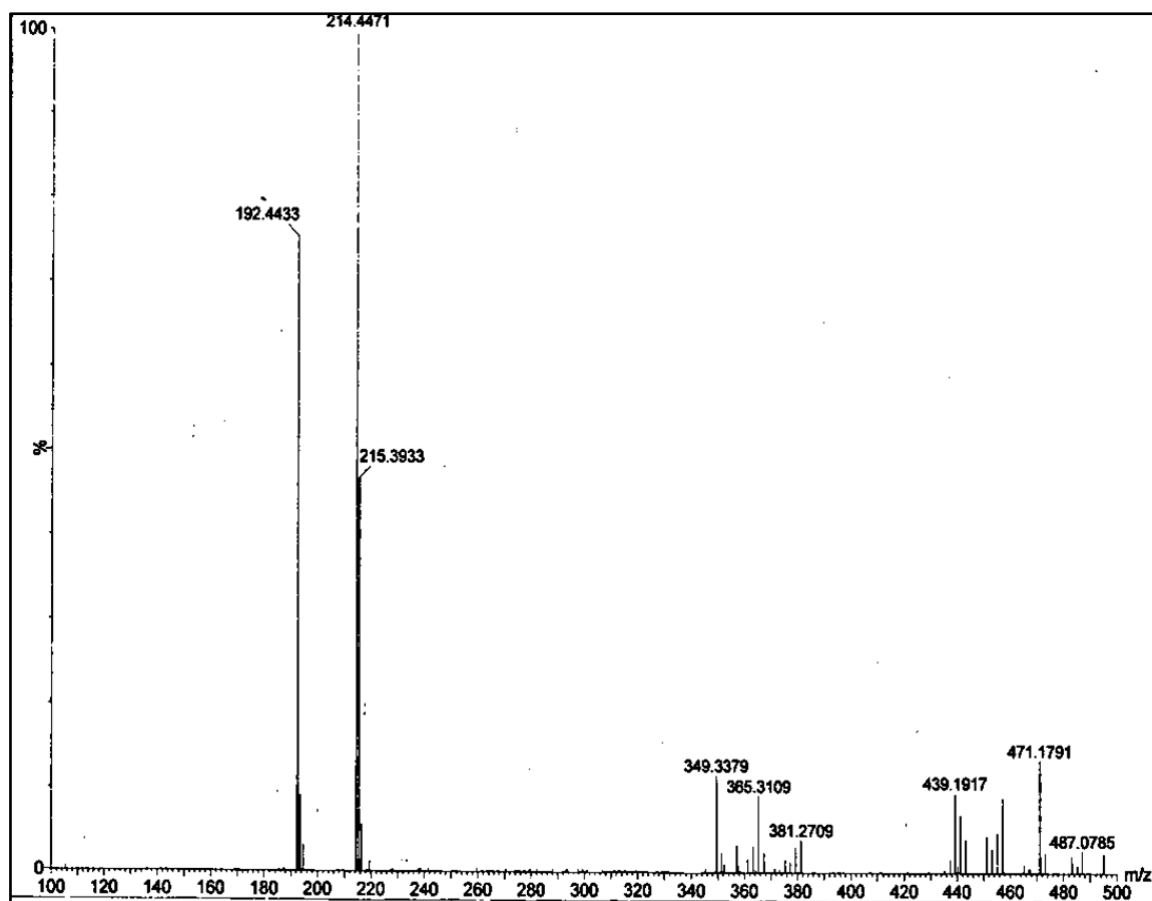


Figure S7: ESI-MS (+ve mode) of AA oxidation products.

References:

S1: A. Winter, A. M. J. van den Berg, R. Hoogenboom, G. Kickelbick, U. S. Schubert, *Synthesis* **2006**, *17*, 2873-2878.

S2: W. -J. Shi, L. Hou, D. Li, Y. -G. Yin, *Inorgan. Chim. Acta* **2007**, *360*, 588-598.

S3: J. F. Moulder, W. E. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*; J. Chastian, Ed.; Perkin-Elmer Corp.: Eden Prairie, MN, **1992**.