Supporting Information

Versatile grafting chemistry for creation of stable molecular layers on oxides

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Calculations of surface coverage of the molecular layers on SiO_2 and TiO_2 by XPS

The overall number of the atoms of interest (X) per unit area of TiO_2, for example, can be calculated from the using:

$$N(X)=\frac{A(X)s(Ti)\rho(Ti,TiO_2)\sin(\theta)\exp\left(\frac{t}{\lambda(X,organic)\sin(\theta)}\right)}{A(Ti)s(X)\exp\left(\frac{t}{\lambda(Ti,organic)\sin(\theta)}\right)}$$

where N(X) is number of atoms per unit area, A(X)/A(Ti) is the ratio of integrated XPS peak areas, s(Ti)/s(X) is sensitivity factor ratio between titanium and atom of interest, $\rho(Ti, TiO_2)$ is number of Ti atoms per unit volume in SiO_2, $\lambda(Ti, TiO_2)$ is inelastic mean free path (IMFP) of Ti photoelectrons in TiO_2, t is thickness of the layer, λ(X, organic) and λ(Ti, organic) are IMFPs of X and Ti in organic films, respectively.[1] The angle θ is the take-off angle of photoelectrons with respect to the sample plane (θ = 45°). Neglecting the surface roughness[2] and using similar approximation of IMFPs of organic self-assembled monolayers from previous studies [λ(A°) =

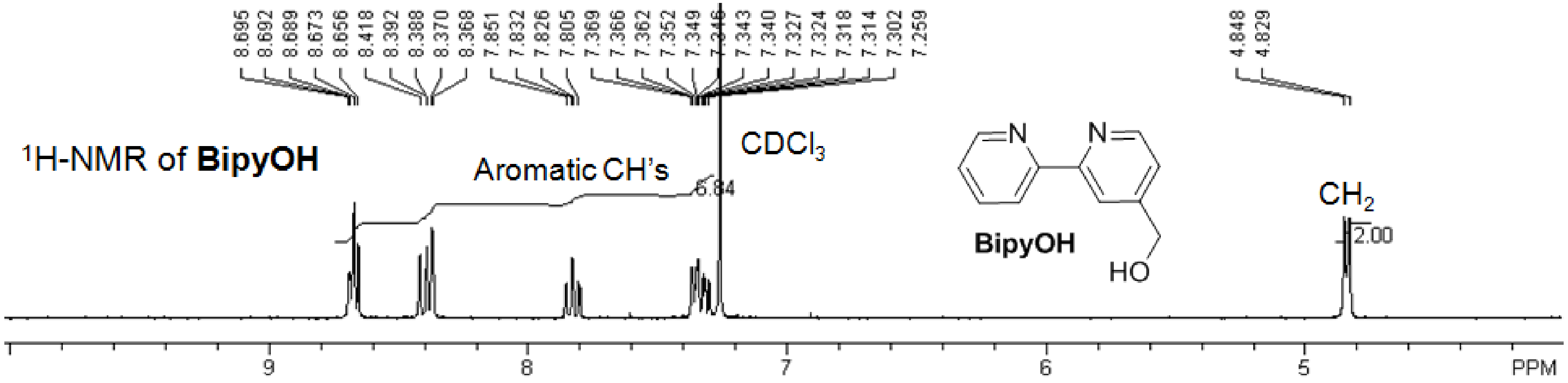
9.0 + 0.022*E(eV)] where E(eV) is the kinetic energy in electron volts,[3] λ(X, organic) ~ 2.8-3.5 nm and λ(Ti, TiO_2) ~ λ(Ti 2p, organic) = 3.3 nm. Since λ(X), organic) ~ λ(Ti 2s, organic) and t < λ for thin organic layer approximation, we conclude that

$$\frac{\exp(\frac{t}{\lambda(\mathrm{X,organic})\sin(\theta)})}{\exp(\frac{t}{\lambda(\mathrm{Ti,organic})\sin(\theta)})} \approx 1.$$

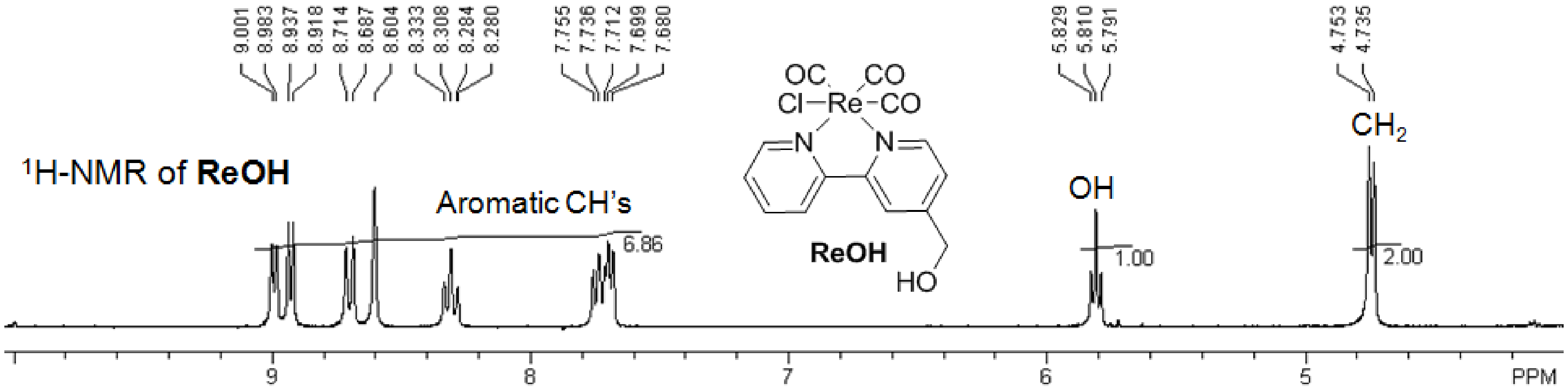
Using p(Ti, TiO_2) = $2.6*10^{22}$ atoms/cm^3, s(N 1s) = 0.477, s(Cl 2p) = 0.891, and s(Re 4f) = 3.961, the surface coverage of bipyridine and rhenium-bipyridine complex on TiO_2 was calculated. For the calculation of surface coverage of organic layers on SiO_2, ρ(Si, SiO_2) = 5.0 x 10^{22} atoms/cm^3 and s(Si 2s) = 0.399 were used.

Synthesis of ReOH

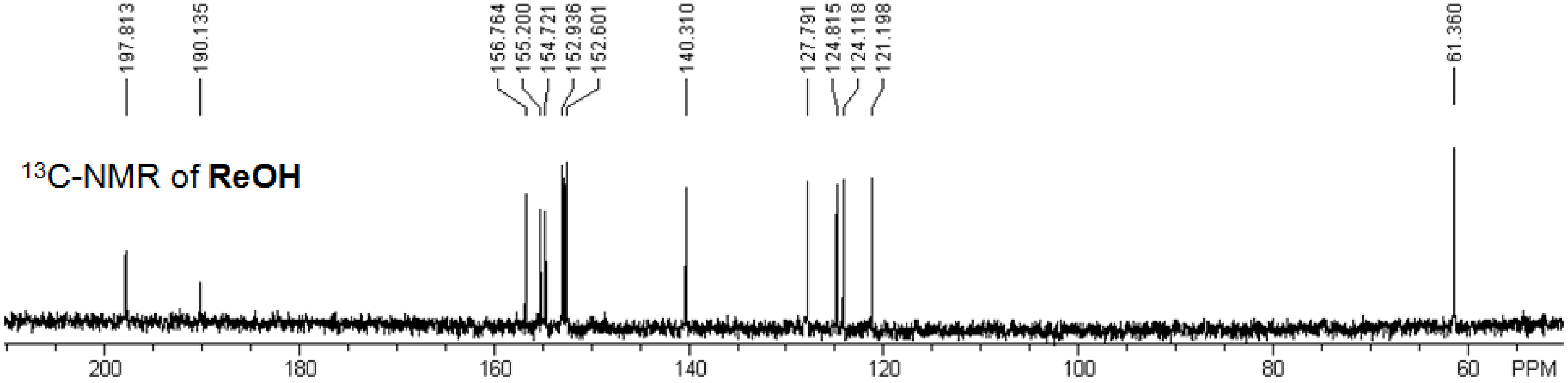
ReOH was synthesized using the literature procedure.[4] To a 50-mL round bottom flask, **BipyOH** (0.24 g, 1.3 mmol), $Re(CO)_5Cl$ (0.47 g, 1.3 mmol), and methanol (20 mL) were added. The reaction mixture was heated at 60 ˚C overnight. After cooling down to room temperature, the mixture was precipitated in hexane and then filtered and washed with cold hexane and cold methanol to yield the **ReOH** (0.48 g, 75%). ^{1}H NMR (300 MHz, DMSO-d_6, δ in ppm): 8.99 (d, J=5 Hz, 2H), 8.93 (d, J=9 Hz, 1H), 8.70 (d, J=8 Hz, 1H), 8.61 (s, 1H), 8.31 (dt, J=1, 8 Hz, 1H), 7.74 (dt, J=1, 8 Hz, 1H), 7.69 (d, J= 6 Hz, 1H), 5.81 (t, J=6 Hz, 1H, -OH), 4.74 (d, J=6 Hz, 2H, -CH_2-). ^{13}C NMR (75 MHz, DMSO-d_6, δ in ppm): 197.8, 190.1, 156.8, 155.2, 154.7, 152.9, 152.6, 140.3, 127.8, 124.8, 124.1, 121.2, 61.4.



^{1}H-NMR of **BipyOH**

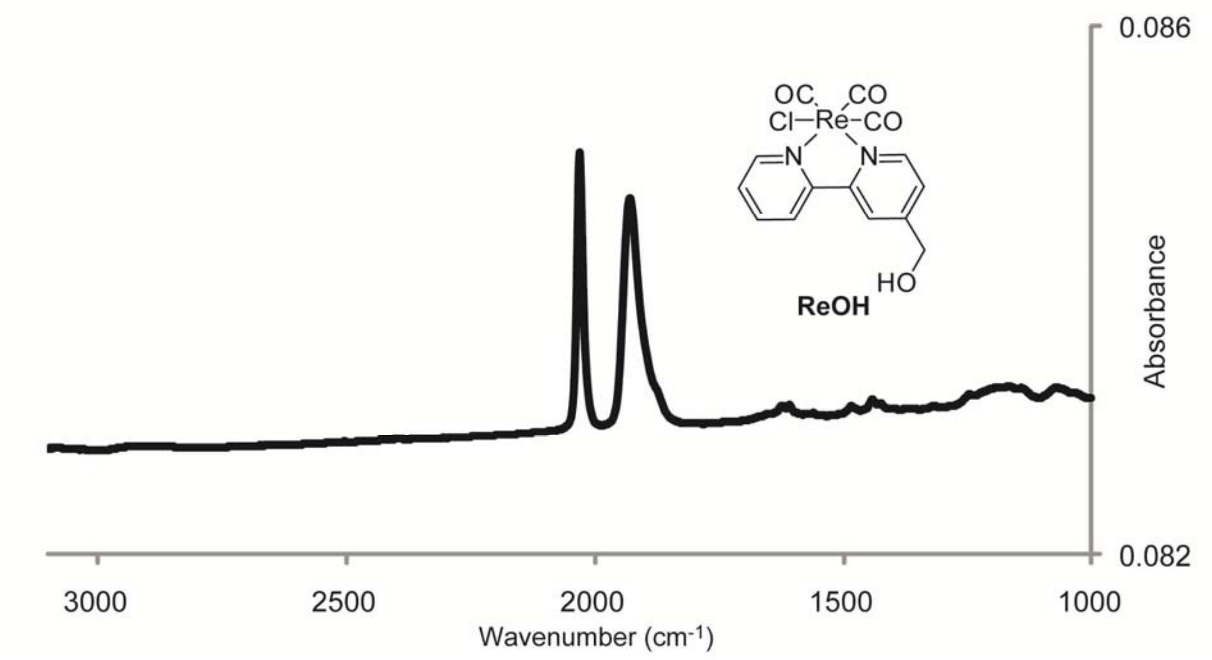


^{1}H-NMR of **ReOH**



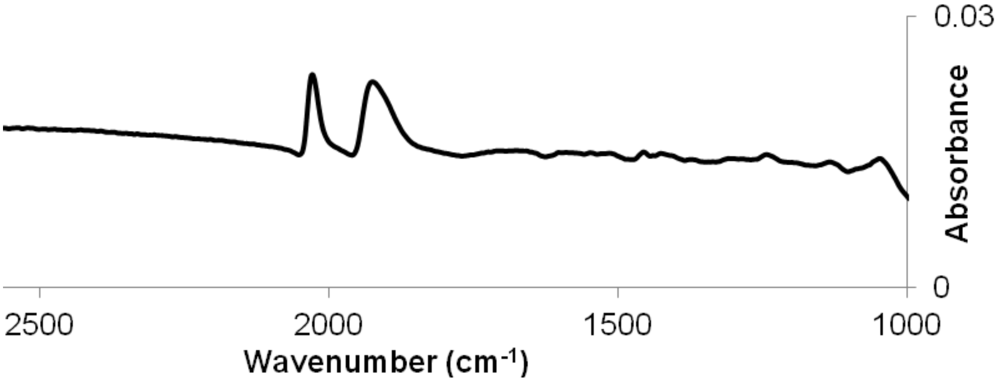
^{13}C-NMR of **ReOH**

IRRAS spectrum of spin-cast film of ReOH on SiO_2

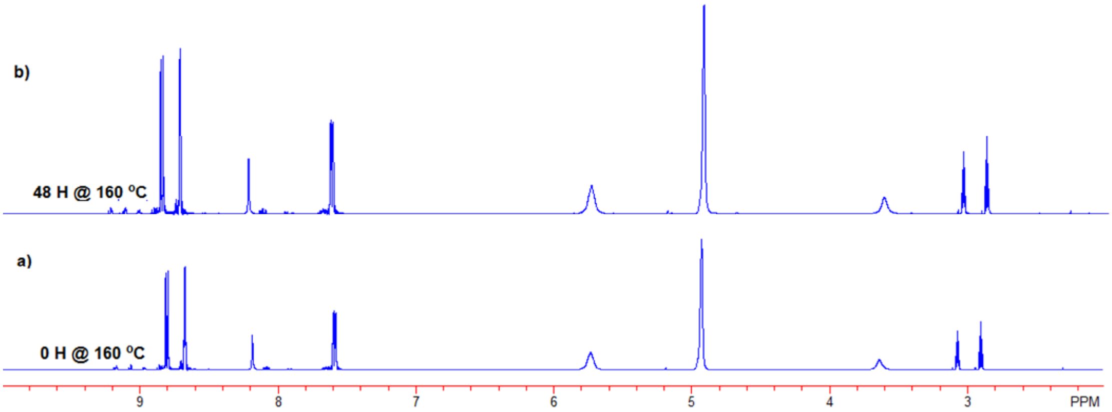


IRRAS spectrum of the grafted layer of rhenium-bipyridine complex (BipyOH-Re) on TiO_2

The IRRAS spectrum of grafted rhenium-bipyridine complex (**BipyOH-Re**) on TiO_2 is similar to that on SiO_2. Three C≡O stretching bands, one at 2024 cm^{-1} corresponding to the symmetric stretching mode of metal carbonyl groups and two overlapping asymmetric stretching bands at 1905 cm^{-1} were observed indicating the presence of rhenium-bipyridine complex on TiO_2 surface.



NMR spectra of Bipy(OH)$_2$: before and after heating at 160°C for 48 h showing no change in the spectrum. This rules out self-condensation or degradation upon thermal annealing on the substrate to form multilayers. Hence, the higher surface coverage of Bipy(OH)$_2$ is primararly due to bidentate anchoring to the substrate via ether bond formation.



Reference:

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(2) Franking, R. A.; Landis, E. C.; Hamers, R. J. *Langmuir* **2009**, *25*, 10676.

(3) Laibinis, P. E., C. D. Bain and G. M. Whitesides *J. Phys. Chem.* **1991**, *95*, 7017.

(4) Paoprasert, P.; Laaser, J. E.; Xiong, W.; Franking, R. A.; Hamers, R. J.; Zanni, M. T.; Schmidt, J. R.; Gopalan, P. *J. Phys. Chem. C* **2010**, *114*, 9898.