

Supporting material:

1. *TiO₂-film electrodes*

The electrodes were prepared as follows: colloidal TiO₂¹ paste (NTera, Dublin) was coated on FTO glass modified electrodes (F-doped SnO₂, 15 Ω/cm², cleaned according to *Hillebrandt et al.*²) from LOF using the doctor-blade method to yield 3-5 μm thick mesoporous TiO₂ films. After firing at 450 °C the plates were cut into 20 mm x 10 mm pieces with an active TiO₂ surface of 1 cm².³

2. *Electrode surface modification*

E-1, E-2 and E-3: 2 mg of (1), (2) or (3) per ml were dissolved each in a solution of EtOH / H₂O (95:5 v/v). TiO₂ electrodes were exposed to these solutions for 1 h at r.t. The electrodes were then rinsed with the EtOH/H₂O.

E-6: TiO₂ electrodes were exposed to a solution of trimesic acid chloride (6), Fluka, (c = 20 mM) in toluene for 60 min at 60 °C, and then rinsed with toluene.

E-7: The TiO₂ electrodes were functionalized with the phosphonic acid (7) as described by *Felderhoff et al.*⁴.

E-6-(4-6)_n: **E-6** was exposed to a solution of the dicyano-cob(III)yrin-heptol (4) 2 mg/ml in MeCN for 1h at 60 °C and then treated with 6 (c = 20 mM) in toluene for 60 min at 60 °C (see Scheme 2) to yield **E-6-(4-6)₁**. This electrode was then treated with a solution of 4 (2mg/ml) in MeCN for 1h at 60 °C, followed by a treatment with 6 (c = 20 mM) in toluene for 60 min at 60 °C to yield **E-6-(4-6)₂**. The same reaction sequence was repeated again to yield **E-6-(4-6)₃**. Between each reaction step the electrode was rinsed with the pure solvent of the precedent step.

E-7-(5-8)_n: **E-7** was exposed to a solution of dicyano-cob(III)yrin-hexaiodide (5) (4 mg/ml in MeCN) for 6h at 60 °C (see Scheme 2), followed by a treatment of the

electrode in 50 mM bipyridine (**8**) for 6h at 60 °C in MeCN to yield **E-7-(5-8)₁** (at this time the reaction was stopped). The procedure was repeated once or twice to yield **E-7-(5-8)₂** and **E-7-(5-8)₃**, respectively. Between each reaction step the electrode was rinsed with the pure solvent of the precedent step.

2. Analytical Electrochemistry and Spectroelectrochemistry

Solvents: Propylene carbonate from *Merck* was freshly distilled, MeCN (synthesis grade) was used as purchased from *Fluka*. *Chemicals:* Trimesic acid chloride, TBAP, LiClO₄, C₂H₄Br₂ were purchased from *Fluka* and *trans*-1,2-dibromocyclohexane (DBCH) was from *Aldrich*. CVs were measured under Ar with the potentiostat PGSTAT 20 from AUTOLAB controlled by a PC running GPES version 4.2 (ECO Chemie 1995) under Windows. The reference electrode was Ag/AgCl/KCl (sat.), separated from the cell by a salt bridge (0.5 TBAP/PC), the counter electrode was a Pt-wire. The electrodes **E-1** (modified with aquo-cyano-cob(III)ester-c-acid perchlorate (monoacid)), **E-2** (modified with dicyano-cob(III)ester-c-EDTA-amide (triacide)), and **E-3** (modified with dicyano-cob(III)yrin-heptaacide (heptaacide)), i.e. all electrodes with coordinatively adsorbed B₁₂ monolayers lacking cross-linking, were studied in PC (0.5 M TBAP) by CV in presence of 0.1 % acetic acid (Tabel 1).

3. Controlled Potential Electrolysis.

A two-compartments cell was used with cathode and anode compartments connected by a medium-porosity glass frit. Prior to electrolysis, the working electrode compartment was purged with argon.

Reduction of 1,2-dibromoethane (DBEt) and dibromocyclohexane (DBCH) was performed using TiO₂-modified electrodes of with geometric areas of 0.5 to 1 cm² in a cell with a glass frit separated counter electrode compartment. The electrolysis

solution contained 232 μmol of DBEt and 73 (146) μmol of DBCH in 5 ml of solvent/electrolyte (0,5M TBAP/PC). Electrolysis was performed at -1.1 V vs. Ag/AgCl under stirred electrolyte conditions.

4. Determination of surface concentrations

All surface-confined vitamin B₁₂ derivatives were studied on rectangular OTE's of 0.5 to 1 cm² active surface. UV-vis spectra were measured with a *Hewlett-Packard* 8453 spectrophotometer. The blank spectrum was from a TiO₂-coated electrode in air. Surface concentrations were calculated from spectral changes using

$$A = \varepsilon \cdot \Gamma \cdot 1000$$

A = absorbance, ε = extinction coefficient (ε = 2512 at 525 nm, for non-cyanized and ε = 12880 at 613 nm for cyanized B₁₂-derivatives), and Γ = surface concentration.

Axial dicyano coordination at the Co(III)-center was established by incubation of the electrode for some seconds in a KCN-saturated ethanolic solution prior to the UV-vis absorption measurement.

Electrochemically, Γ was determined from the coulometric analysis of the cyclic voltammograms at 20 mV/s or 5 mV/s yielding Q and using

$$\Gamma = Q / E_a \cdot F$$

with E_a = electrode surfaces, F = Faraday constant.

References:

1. Cummins, D.; Boschloo, G.; Ryan, M.; Corr, D.; Rao, S. N.; Fitzmaurice, D., *J Phys Chem B* **2000**, 104, (48), 11449-11459.

2. Hillebrandt, H.; Wiegand, G.; Tanaka, M.; Sackmann, E., *Langmuir* **1999**, 15, (24), 8451-8459.
3. Campus, F.; Bonhote, P.; Gratzel, M.; Heinen, S.; Walder, L., *Sol Energ Mat Sol C* **1999**, 56, (3-4), 281-297.
4. Felderhoff, M.; Heinen, S.; Molisho, N.; Webersinn, S.; Walder, L., *Helv. Chim. Acta* **2000**, 83, (1), 181-192.