



Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

## **Supporting Information**

# **Chemical Communication between Metal Complex-based Monolayers**

Tarkeshwar Gupta and Milko E. van der Boom\*

*Department of Organic Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel*

\*Email: milko.vanderboom@weizmann.ac.il

## Experimental Section

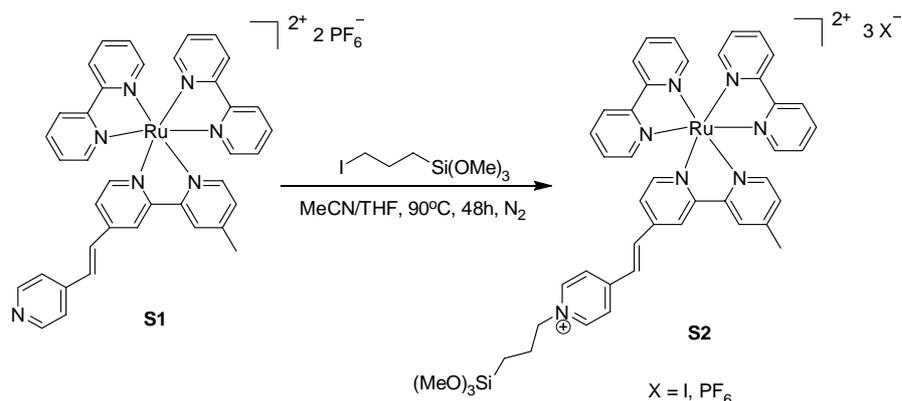
**Materials and Methods.** The known compound **S1** was prepared as previously described.<sup>[S1]</sup> Iodo-n-propyl-trimethoxysilane was purchased from Aldrich and used as received.  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  was purchased from BDH Chemicals Ltd. Anhydrous  $\text{FeCl}_3$  and  $\text{FeCl}_2$  were purchased from Merck and Aldrich, respectively. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa) or Mallinckrodt Baker (Phillipsburg, NJ). Pentane and toluene were dried and purified using an M. Braun (Garching, Germany) solvent purification system. Dichloromethane (DCM) was purified with  $\text{H}_2\text{SO}_4$  and distilled under  $\text{N}_2$  over  $\text{P}_2\text{O}_5$ . DCM was degassed and stored in a M. Braun glovebox with  $\text{O}_2$  and  $\text{H}_2\text{O}$  levels  $< 2$  ppm over activated 4 Å molecular sieves with exclusion of light. Single-crystal silicon (100) substrates were purchased from Wafernet (San Jose, CA), indium-tin-oxide (ITO) coated glass were purchased from Aldrich. Si(100) and ITO substrates were cleaned by sonication in hexane followed by acetone, then ethanol and dried under an  $\text{N}_2$  stream. Subsequently, they were cleaned for 20 min with UV and ozone in a UVOCS cleaning system (Montgomery, PA). Soda-lime glass (Chase Scientific Glass) was cleaned by immersion in a “piranha” solution (7:3 (v/v)  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ) for 1 h. *Caution: piranha solution is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection.* Subsequently, the substrates were rinsed with deionized (DI) water followed by the RCA cleaning protocol: 1:5:1 (v/v)  $\text{NH}_3 \cdot \text{H}_2\text{O}/\text{H}_2\text{O}/30\% \text{H}_2\text{O}_2$  at room temperature for 45 min. The substrates were washed with ample amount of DI water and were dried under an  $\text{N}_2$  stream. All substrates were then dried in an oven for 2 h at  $130^\circ\text{C}$ . The monolayer formation and characterization was carried out under an inert atmosphere using either standard Schlenk/cannula techniques or

a glovebox using previously reported procedures.<sup>[S2-5]</sup> All the glassware was silanized with octadecyltrichlorosilane or phenyltrichlorosilane and oven dried to reduce background noise due to the presence of traces of water.

UV/vis spectroscopy was carried out using a Cary 100 spectrophotometer. Atomic force microscopy (AFM) images were recorded using a Solver P47 (NT-MDT, Russia) 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. Spectroscopic ellipsometry was carried out using an M 2000V (J. A. Wollam Co. Inc.) instrument. Measurements were done at incident angles of 65°, 70° and 75° from 370 to 1000 nm, simulated using Wvase32 software over the entire range to fit the experimental parameters. Elemental analyses were done by H. Kolbe, Germany. A CHI-660A electrochemical analyzer was used to carry out electrochemical measurements using a previously reported set-up.<sup>[S3]</sup> All measurements were carried out at 298 K.

**Formation of Complex S2.** An excess of 3-iodo-n-propyl-1-trimethoxysilane (81 mg, 0.28 mmol) was added to a dry THF/acetonitrile (90:10 v/v) solution (20 mL) of complex **S1**<sup>[S5]</sup> (55 mg, 0.056 mmol) under N<sub>2</sub> in a pressure vessel. The reaction mixture was stirred and heated at 90°C for 48 h. Subsequently, the volume was reduced to ~2 mL. The addition of dry pentane (15 mL) at 25 °C to the reaction mixture resulted in the precipitation of the desired product. The solvent was decanted and the solid was washed with dry pentane (3 ×) and dried under vacuum to afford the analytically pure **S2** (60 mg, 85%). The analogous osmium complex was prepared according to a previously reported procedure.<sup>[S5]</sup> For **S2**: <sup>1</sup>H NMR (250 MHz, CD<sub>3</sub>CN): δ 8.79–7.17 (26H, m; ArH), 8.12 (1H, d; *J*=16.4 Hz), 7.56

(1H, d;  $J=16.4$  Hz), 4.45 (2H, t), 3.53 (9H, s), 2.59 (3H, s), 2.18 (2H, m), 0.65 (2H, t). ES MS:  $m/z$ : 1122 ( $M^+-PF_6^-$ ), 489 ( $M^{++}-2PF_6^-$ ), 285 ( $M^{+++}-2PF_6^-$ , I). UV/vis ( $CH_3CN$ ),  $\lambda$ , nm ( $\epsilon$ ,  $M^{-1}cm^{-1}$ ): 469 (21326), 335 (24731), 282 (90740), 239 (36439). El. Anal. For  $Ru_{44}C_{44}H_{46}F_{12}IN_7O_3P_2Si$ : Calc. (%): C, 41.71; H, 3.66. Found (%): C, 41.83; H, 3.69.

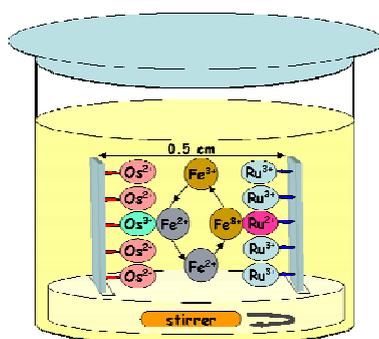


**Monolayer Formation.** Freshly cleaned glass, ITO coated glass and silicon substrate were loaded into a pressure vessel (Aceglass, Vineland NJ) in  $N_2$ -filled glovebox and immersed in dry acetonitrile/toluene (3:7 v/v) solutions (0.5 mM) of the osmium and ruthenium complexes and heated for 52 h at  $80^\circ\text{C}$  with the exclusion of light. The functionalized substrates were then rinsed with dichloromethane, acetonitrile in a glove box and sonicated for 6 min each in acetonitrile and isopropanol. The samples were then wiped with a task wipe then dried under a stream of  $N_2$ . The samples were cleaned with  $CO_2$  snow cleaning system and stored in the dark. The films were analyzed by AFM, ellipsometry and UV/vis spectroscopy as previously reported.<sup>[S2-5]</sup>

**Reversibility Tests: Alternating Treatment of the Ruthenium Monolayers (3, 4) with FeCl<sub>2</sub> and Ce(IV).** The Ru<sup>2+</sup>-based monolayers (4) on glass were chemically activated by immersion of the functionalized substrates for 3 min. in an acidified aqueous solution of Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O (1.0 mM, 0.01 M H<sub>2</sub>SO<sub>4</sub>) to generate the Ru<sup>3+</sup>-based monolayer (3). This monolayer (3) can be fully reduced with FeCl<sub>2</sub> (10 ppm in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN; 1 min) to yield again the Ru<sup>2+</sup>-based monolayer (4) as judged by UV/vis spectroscopy. More than 10 oxidation/reduction cycles were performed.

**Reaction of Monolayer 4 on Glass with FeCl<sub>2</sub>.** Monolayer 4 on glass (0.8 cm × 2.5 cm × 0.1 cm) immersed in a CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.02 ppm of FeCl<sub>2</sub> for 2.5 min, rinsed with dry CH<sub>2</sub>Cl<sub>2</sub> and carefully wiped with task paper in a glovebox before recording the optical (UV/vis) spectra. The reduction of this monolayer on glass was also monitored *ex-situ* by UV/vis spectrophotometry. Monolayer 3 can be reset as described above.

**Communication between Monolayers.** In a typical experiment, both the Os<sup>2+</sup>- and Ru<sup>3+</sup>-based monolayers (1, 3) on glass substrates were fixed in a Teflon holder equipped with a magnet to allow stirring as shown below. The distance between the two planes of the substrate surfaces is 0.5 cm. The set-up was immersed in a dry CH<sub>2</sub>Cl<sub>2</sub> solution containing 20 ppm of FeCl<sub>3</sub> and stirred for 3 min.



## References

- S1. D. Kim, E. Shin, E. J., *Bull. Kor. Chem. Soc.* **2003**, *24*, 1490-1494.
- S2. T. Gupta, M. E. van der Boom, *J. Am. Chem. Soc.* **2007**, *129*, 12296-12303.
- S3. T. Gupta, R. Cohen, G. Evmenenko, P. Dutta, M. E. van der Boom, *J. Phys. Chem. C* **2007**, *111*, 4655-4660.
- S4. T. Gupta, M. E. van der Boom, *J. Am. Chem. Soc.* **2006**, *128*, 8400-8401.
- S5. T. Gupta, M. Altman, A. D. Shukla, D. Freeman, G. Leitun, M. E. van der Boom, *Chem. Mater.* **2006**, *18*, 1379-1382.