Supporting Information

Directional photoinduced electron transfer in paraquat silicate thin films containing entrapped ruthenium(II)-tris(bathophenanthrolinedisulfonate)

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Materials.

Tetrabutylammonium chloride (TBACl), tetrabutylammonium perchlorate (TBAClO₄), 4,4' bipyridine, (3-iodopropyl)trimethoxysilane and dry acetonitrile were purchased from Aldrich and used as received. ITO was purchased from Delta Technology Limited. Tetrasodium *tris*(bathophenanthrolinedisulfonate) ruthenium(II) (**RuBPS**) was synthesized from literature methods (1).

Electrochemical methods.

CV measurements were performed using a three electrode configuration with a Model 440 electrochemical workstation (CH Instruments, Austin, TX). An ITO working electrode, Pt counter electrode, and a Ag/AgCl reference electrode (Cypress) were used in a one compartment Teflon cell. For plotting the cyclic voltammograms, the IUPAC convention was used where positive potentials are plotted in the positive x direction, and anodic currents are positive.

The ITO electrodes were irradiated using an Oriel Model 66001 UV-visible High Intensity 150 W Xe Lamp Assembly mounted to the optical table. The lamp assembly was positioned such that the light output was directed vertically onto the Teflon cell from a position ~90 cm above the ITO electrode. The lamp was operated at 145 W using an Oriel Model 68805 Universal Power Supply equipped with Model 68850 Photofeedback Controller, which was maintained at a level of 3.72 ± 0.01 during lamp operation to provide maximum light output with minimal intensity variation during the experiments. An Oriel Model 76995 Electronic Shutter was used to control exposure of the ITO electrode to the light. The light was filtered using an 430 nm long pass filter or by an Oriel #77250 monochromator. Lamp output profiles were acquired with a calibrated International Light IL-1700 radiometer. Incident photon-to-current efficiencies (IPCE) were calculated from Eq. (1).

$$IPCE(\lambda) = (1240 \text{ eV nm})I_{ph}/(\lambda P_0)$$
(1)

In this equation, I_{ph} is the incident photocurrent density in mA/cm², λ the wavelength of incident radiation in nm, and P₀ is photon flux in mW/cm².

Kelvin probe force microscopy (KFM)

The KFM measurements were carried out with JEOL JSPM-5200 scanning probe microscope. Conductive cantilevers were prepared by evaporation of 4 nm Cr adhesion layer and 300 nm Au layer on Si cantilevers (Budget Sensors BS-300). Prior to the evaporation the cantilevers were treated with oxygen plasma for 1 min to remove organic residue.

Topographic and potential images (each containing 512×512 pixels) were recorded simultaneously using the frequency modulation mode. The cantilever was grounded, while DC and AC (1 kHz, amplitude=1V) potentials were applied to the substrate. During the scan a feedback mechanism adjusted the DC potential until the modulation of the cantilever frequency monitored at 1 kHz using the lock-in technique was nulled. The negative of the adjusted DC substrate potential recorded as a function of the cantilever position over the sample constituted the surface potential image. The cantilever scan rate was set to 4.8 msec/pixel. The photo-induced changes in the sample were recorded by alternately turning on and off laser radiation incident on the sample and simultaneously measuring topographic and potential images. The laser radiation (532 nm, 1 mW) was collimated into a parallel beam with a cross-section 1 mm in diameter. The surface potential image recorded from the **RuBPS/PQS** sample shows that when the laser radiation was turned on, the surface potential became more positive than in the absence of the radiation. This behavior indicates that the **RuBPS/PQS** film was charging positive in response to the illumination with the laser light. Upon turning the laser radiation off, the surface potential returned to its initial value indicating the film returning to its initial neutral state.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was performed using a Potentiostat (Model 760 D) purchased from CH Instruments (Austin, TX). Three electrodes were used. The ITOsupported films were connected to the working electrode and immersed in low concentration electrolyte (1 mM sodium toluenesulfonate in water). An Ag/AgCl electrode was used as the reference, and a platinum wire was used as the counter electrode. Impedance spectroscopy measurements were made in the frequency range 10^5 Hz- 10^{-2} Hz with a 10 mV oscillation amplitude, at 0 V DC potential. The Nyquist plot for the **POS** and **RuBPS/POS** films is given in Figure S2, and a proposed equivalent circuit is given in Figure S3. In the Nyquist plot, both films exhibit significant resistive and capacitive reactances, which combine to form the arcs shown. The absolute value of the total impedance is larger in the RuBPS/PQS film than in the PQS film. In the left plot, the low-frequency region appears in the right-most portion of each arc, and a final (lowest) frequency of 2.55×10^{-3} Hz was used. In the right plot, which is an expansion of the high-frequency regime, the frequency at which -Z" is at a minimum is 9.67 x 10^3 for both films. The films were modeled with the equivalent circuit shown in Figure S3, and the results of the fit are given in the Nyquist plot (orange line, RuBPS/PQS fit; red line, PQS fit) and in the Table, Figure S3.

The equivalent circuit contains an initial resistor that accounts for electrolyte resistance (R_{elyte}) , followed sequentially by three parallel segments. The first segment contains a constant phase element (Q) that may represent roughness in the film surface, which is in contact with bulk

electrolyte. The impedance of the constant phase element (CPE) can be defined by the expression $Z_{CPE} = 1/Q(j\omega)^n$, where Q is a constant and n is an exponent having values between zero and one. The parameter n can be derived from a plot of log(-Z") vs. log(frequency), since it is equal to the absolute value of the slope (2). These plots were constructed for the PQS and **RuBPS/PQS** films, and n values of 0.72 and 0.76 were obtained, respectively. This is an indication that both films have a relatively high surface heterogeneity that may be on an atomic scale. The CPE is in parallel with an interfacial charge-transfer resistance R_{int1}. For both films, this resistance is relatively low, in the Ω to k Ω range. The second two parallel segments are Randles-type circuits. Modified Randles circuits have been used to model electrostatic layer-bylayer films (3), and films based on viologen, (paraquat) that are similar to PQS (4). The first circuit segment is taken to represent the bulk region of the film, away from any interfaces. The PQS film is found to have a capacitance of $\sim 10 \,\mu\text{F}$, whereas that of the **RuBPS/PQS** film is ~ 5 nF. The bulk resistance R_{bulk} of both films is quite low, in the range 10-100 Ω . The films are evidently able to act as very effective conduits of charge, but are not able to store charge effectively. The Warburg impedance W represents the resistance that is encountered by longrange diffusion processes (2, 5). Of considerable interest is the difference between the Warburg impedance of the bulk layer (W_{bulk}) in the PQS film, and that of the RuBPS/PQS film. That of the former is \sim 4.5-fold larger than the latter, suggesting that the bulk PQS film is considerably denser than the bulk **RuBPS/POS** film. This is consistent with both the 2:1 and the 3:1 PQS:RuBPS ion-pairing models proposed in the main text, which have a heterogeneity requiring a relatively low packing efficiency. The third circuit segment is taken to represent the interface between the bulk film and the ITO support. In both materials, this interface has a capacitance of ~1 to 2 μ F, and a very high charge transfer resistance (R_{int2}) of ~1-2 M Ω . The high concentrations of OH^- ions generated in the aqueous solution there by the potentials near -1.0 Vused in film synthesis may have led to a localized film with a molecular structure that retards charge transport. They may also have altered the structure of the ITO film surface itself, causing an increase in its resistance. At this interface, the Warburg impedance (W_{int2}) of the PQS film is nearly equal to that of its bulk region, but that of the RuBPS/PQS film is ~30-fold larger than that of its bulk region. The high concentration of OH⁻ ions may have led to reactions with

RuBPS that yielded a localized dense film having a high charge transfer resistance as well as a low porosity.

Supporting Figures



Figure S1. Cyclic voltammograms showing the growth of a PQ silane film on ITO with the concentration of **PQS** and **RuBPS** at 500 μ M in water with no additional electrolyte. Scan rate = 100 mV/s.



Figure S2. Nyquist plots of the films on ITO support. Left, entire frequency range from 9.67 x 10^4 Hz to 2.55 x 10^{-3} Hz; right, high frequency range only.



	R _{elyte} (Ω)	Q (S·sec ⁿ)	R_{int1} (Ω)	C _{bulk} (F)	$\frac{R_{bulk}}{(\Omega)}$	W_{bulk} (Ω)	C _{int2} (F)	R_{int2} (Ω)	$\frac{W_{int2}}{(\Omega)}$	error
PQS	2115	6.32×10^{-5} n = 0.72	2954	1.35 x10 ⁻⁵	21	6.71x10 ⁴	2.09x10 ⁻⁵	1.48x10 ⁶	4.81x10 ⁴	0.034
PQS- RuBPS	743	1.91×10^{-4} n = 0.76	164	4.97x10 ⁻⁹	255	1.55x10 ⁴	9.79x10 ⁻⁶	2.36x10 ⁶	4.67x10 ⁵	0.035

Figure S3. Equivalent circuit for the PQS and RuBPS/PQS films.



Figure S4. Photocurrent (\uparrow light on and \downarrow light off) of thin films on ITO measured comparing different electrolytes, film coverage and composition. A. The dash-dot-dot line = electrode 1 measured in acetonitrile with 100 mM TBACl; dashed line = electrode 2 measured in acetonitrile with 100 mM TBACl; dotted line = electrode 2 measured in acetonitrile with 100 mM TBACl; dotted line = electrode 2 measured in acetonitrile with 100 mM TBACl; solid line = electrode 2 measured in a 100mM potassium phosphate buffer at pH 7. B Electrode 2 (dashed) and electrode 3 (solid) measured in a 100mM potassium phosphate buffer at pH 7. The measurements were made at an applied potential of -0.1 V vs. Ag/AgCl with 100 mM TEOA in the electrolyte. The excitation source was a 150 W Xe lamp filtered with a 430 nm long pass filter.



Figure S5. **A**. Topography and **B**. surface potential images of the **PQS** on gold recorded with KFM. All images are $2.65 \times 2.65 \ \mu m^2$.



Figure S6. Average of three traces for the change in substrate potential as a function of time for laser light on (Rise) and off (Decay) fit to single exponential functions. For the rise, $y = A(1-\exp(-kt)) + B$ with A = 305 mV, B = 40.6 mV and k = 0.0321 s⁻¹. For the Decay, $y = A(\exp(-kt)) + B$ with A = 219 mV, B = 84.2 mV and k = 0.0316 s⁻¹.

References

1. Zanarini, S.; Della Ciana, L.; Marcaccio, M.; Marzocchi, E.; 1386 Paolucci, F.; Prodi, L. J. *Phys. Chem. B* 2008, **112**, 10188–10193.

2. Orazem, M. E., Tribollet, B. *Electrochemical Impedance Spectroscopy*, John Wiley and Sons, New Jersey, 2008.

3. Vyas, R. N., Li, K. Y., Wang, B., J. Phys. Chem. B, 2010, 114, 15818-15824.

4. Vergaz, R., Barrios, D., Sanchez-Pena, J. M., Pozo-Gonzalo, C., Salsamendi, M., Pomposo, *J., Displays* 2008, **29**, 401-407.

5. Macdonald, J. R. *Impedance Spectroscopy, Emphasizing Solid Materials and Systems*, John Wiley and Sons, New York, 1987.