Supporting Information

Interfacial Mass Transfer by Controlled Multilayer Disassembly

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Materials and Methods. 4-Chloromethylphenyltrichlorosilane was purchased from Aldrich and used as received. Triethylphosphine was purchased from Fluka. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa), or Mallinckrodt Baker (Phillipsburg, NJ). Toluene was dried and purified using an M. Braun solvent purification system. ITO-coated glass slides (7 mm × 50 mm × 0.7 mm) were obtained from Delta Technologies and Single-crystal silicon(100) substrates, purchased from Wafernet (San Jose, CA) were cleaned by sonication in hexane followed by acetone, then ethanol and dried under an N₂ stream. Subsequently, they were cleaned for 20 min with UV and ozone in a UVOCs cleaning system (Montgomery, PA). Soda-limeglass (Chase Scientific Glass) was cleaned by immersion in a “piranha” solution (7:3 (v/v) H₂SO₄/30% H₂O₂) 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 (Radio Corporation of America) cleaning protocol: 1:5:1 (v/v) NH₃·H₂O/H₂O/30% H₂O₂ at room temperature for 45 min. The substrates were washed with ample amounts of DI water and were dried under an N₂ stream. All substrates were then dried in an oven for 2 h at 130°C. Complexes 1-3, coupling layer (CL) of 4-chloromethylphenyltrichlorosilane, the template layers (TLs) and the SPMAs were prepared according to previously reported procedures. The SPMAs are prepared upon the TL of compound 1. One deposition step is defined as the deposition of one type of metal complex (1, 2 or 3) or the palladium salt. UV/vis spectroscopy was carried out using a Cary 100 spectrophotometer. Cyclic voltammetry was performed using a potentiostat (CHI660A) connected to a personal computer. All measurements were performed in a three-electrode cell configuration consisting of an ITO-modified substrate (working electrode), a Pt wire (counter electrode), and Ag/AgCl (a reference electrode). The experiments were performed at room temperature using 0.1 M solutions of TBABF₄ in dry acetonitrile. Angle-resolved X-ray photoelectron spectra (AR-XPS) were made at different takeoff angles with a PHI 5600 Multi Technique System (base pressure of the main chamber 2×10⁻¹⁰ Torr). Resolution, corrections for satellite contributions,
procedures to account for steady-state charging effects, and background removal have been described elsewhere. Experimental uncertainty in binding energies lies within ± 0.4 eV.\textsuperscript{54}

**Preparation of complex 2.** Complex 2 was obtained by using the same procedure to prepare complex 3.\textsuperscript{53} \textit{trans-(NH}_4\textsubscript{2}OsCl\textsubscript{6}} (120 mg, 0.27 mmol) and 4-(2-(pyridin-4-yl)ethyl)-1,10-phenanthroline (239 mg, 0.84 mmol) were used. Yield: 130 mg (35%). \textsuperscript{1}H NMR ((CD\textsubscript{3})\textsubscript{2}CO, 300.13 MHz): \(\delta\) (ppm) 8.6 (q, \(J = 9.0 \text{ Hz}, 6\text{H})\), 8.43 (d, \(J = 1.8 \text{ Hz}, 1\text{H})\), 8.40 (d, \(J = 1.8 \text{ Hz}, 1\text{H})\), 8.36 (m, 3H), 8.3-8.2 (m, 3H), 8.17-8.05 (m, 3H), 7.71 (m, 4H), 7.55 (m, 3H), 7.17 (t, \(J = 5.7 \text{ Hz}, 4\text{H})\), 3.79 (t, \(J = 6.9 \text{ Hz}, J = 5.4 \text{ Hz}, 6\text{H})\), 3.14 (t, \(J = 6.9 \text{ Hz}, J = 5.7 \text{ Hz}, 6\text{H})\). \textsuperscript{31}P\textsuperscript{1}H NMR ((CD\textsubscript{3})\textsubscript{2}CO, 121.50 MHz): \(\delta\) (ppm) -141.4 (sept, \(J_{PF} = 706.8 \text{ Hz}, PF\textsubscript{6}\)). \textsuperscript{19}F\textsuperscript{1}H)NMR (CD\textsubscript{3}CN, 282.41 MHz): \(\delta\) (ppm) -73.6 (d, \(J_{PF} = 706.8 \text{ Hz}, PF\textsubscript{6}\)). HRMS (ES\textsuperscript{+}) m/z: calcd. for \(C\textsubscript{57}H\textsubscript{45}N\textsubscript{9}OsPF\textsubscript{6}\) [M-PF\textsubscript{6}]\textsuperscript{+} 1192.3055; found 1192.3042. UV/Vis (acetonitrile): \(\lambda_{max}\) nm (\(\varepsilon\), M\textsuperscript{-1} cm\textsuperscript{-1}) = 480 (38 \times 10\textsuperscript{3}).

**Mass Transfer Experiments.** In a typical experiment, two glass substrates coated with a SPMA (16 nm-thick assemblies) were placed in a Teflon holder. Subsequently, two or four ITO-coated glass slides functionalized with a coupling layer (CL) of 4-chloromethylphenyltrichlorosilane were placed in the sample holder as well. The distance between the planes of the substrate surfaces is 0.25 to 2 cm. The set-up was transferred into a glass pressure vessel and immersed in a dry acetonitrile/toluene (1:1, v/v) solution containing PEt\textsubscript{3} (0.1 M). The vessel was sealed and heated for 72 h at 90 °C under N\textsubscript{2}. The system was allowed to attain room temperature and the slides were thoroughly washed with acetonitrile, acetone, and ethanol.
Scheme S1. Formation of the SPMAs: Hydrophilic substrate surfaces are functionalized with a benzyl-chloride terminated coupling layer (CL) using siloxane chemistry, the CLs are reacted from solution at elevated temperatures with polypyridyl complex (1) affording template layers (TLs) consisting of covalently bound pyridinium salts of complex 1 that can bind metal salts, and the iterative exposure of these TLs to solutions of a polypyridyl complex (1-3) with multiple metal-binding sites and PdCl$_2$(PhCN)$_2$. 
Figure S1. UV/vis absorption of (a) the solution phase after a mass transfer experiment with a 1-based SPMA, and (b) a solution of complex 1 in acetonitrile/toluene (1:1, v/v). (c) baseline.
**Figure S2.** Characterization of 2-based (red) and 3-based (blue) SPMAs. (A and C) Exponential dependence of the intensities of the MLCT bands ($\lambda = 500$ nm) and (B and D) film thickness for compounds 2 and 3 vs the number of deposition steps, respectively. TL stands for the template layer.

**Table S1.** The cyclic voltammetry data of the template layers: I TL used for the built-up of a 1-based SPMA, II TL after disassembly of the 1-based SPMA with PEt$_3$, and III replicated TL$'$.  

<table>
<thead>
<tr>
<th>Template layer</th>
<th>$E_{1/2}$ [V]</th>
<th>$E_{ox}$ [V]</th>
<th>$E_{Red}$ [V]</th>
<th>$I_{pa}$ [A]</th>
<th>$I_{pc}$ [A]</th>
<th>$\Gamma_s$ [mol cm$^{-2}$]</th>
</tr>
</thead>
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<tr>
<td>I</td>
<td>0.90</td>
<td>0.92</td>
<td>0.89</td>
<td>$1.45 \times 10^{-5}$</td>
<td>-1.12 $\times 10^{-5}$</td>
<td>$1.2 \times 10^{-10}$</td>
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<tr>
<td>II</td>
<td>0.91</td>
<td>0.94</td>
<td>0.89</td>
<td>$1.48 \times 10^{-5}$</td>
<td>-1.31 $\times 10^{-5}$</td>
<td>$1.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>III</td>
<td>0.89</td>
<td>0.91</td>
<td>0.87</td>
<td>$1.54 \times 10^{-5}$</td>
<td>-1.28 $\times 10^{-5}$</td>
<td>$1.3 \times 10^{-10}$</td>
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Figure S3. Representative cyclic voltammograms of the TLs on ITO-coated glass substrates. (a) TL formed by mass transfer upon disassembly of the osmium (2) and ruthenium (3)-based SPMAs with PEt₃, and (b) TL formed by reacting chlorobenzyl functionalized substrates with complex 2, (c) TL formed by reacting chlorobenzyl functionalized substrates with complex 3. All experiments were carried out at a scan rate of 100 mVs⁻¹ at room temperature in 0.1 M TBABF₄/CH₃CN.

References


