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Supporting Information

Interfacial Mass Transfer by Controlled Multilayer Disassembly

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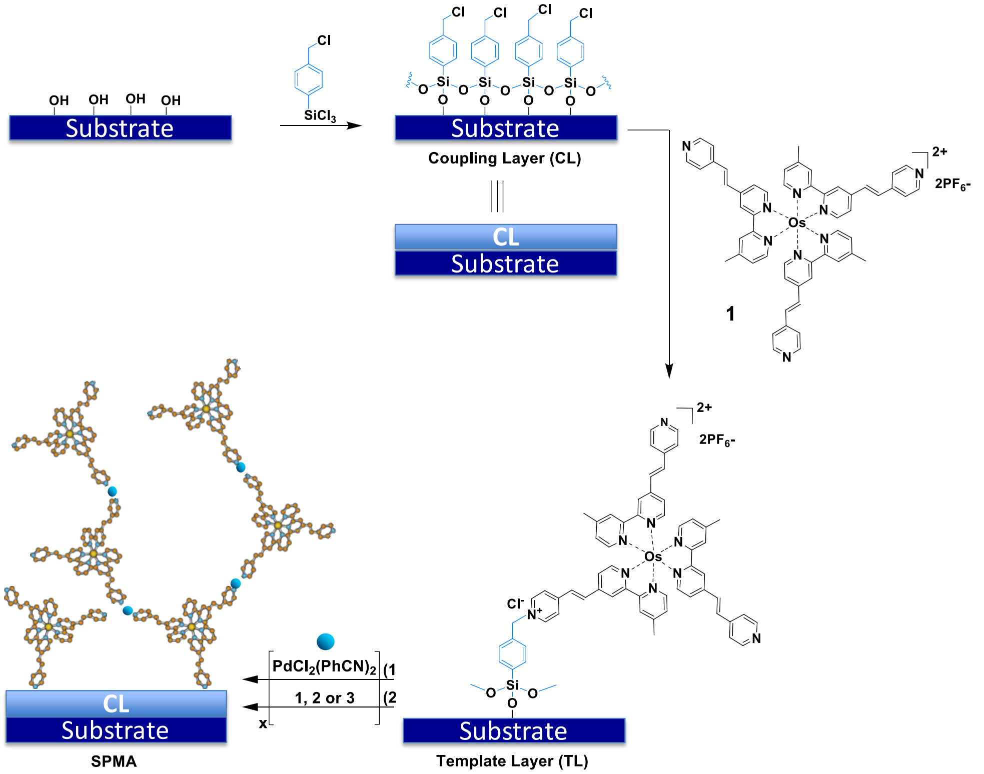
Materials and Methods. 4-Chloromethylphenyltrichlorosilane was purchased from Aldrich and used as received. Triethylphosphine was purchased from Fluka. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa), or Mallinckrodt Baker (Phillipsburg, NJ). Toluene was dried and purified 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 N_2 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) H_2SO_4/30% H_2O_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 (Radio Corporation of America) cleaning protocol: 1:5:1 (v/v) $NH_3 \cdot H_2O$/H_2O/30% H_2O_2 at room temperature for 45 min. The substrates were washed with ample amounts of DI water and were dried under an N_2 stream. All substrates were then dried in an oven for 2 h at 130^{O}C. Complexes **1**-**3**, coupling layer (CL) of 4-chloromethylphenyltrichlorosilane, the template layers (TLs) and the SPMAs were prepared according to previously reported procedures.[S2, S3] 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 $TBABF_4$ 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.[S4]

Preparation of complex 2. Complex **2** was obtained by using the same procedure to prepare complex **3**.[S3] *trans*-$(NH_4)_2OsCl_6$ (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%). ^{1}H NMR ($(CD_3)_2CO$, 300.13 MHz): δ (ppm) 8.6 (q, J = 9.0 Hz, 6H), 8.43 (d, J = 1.8 Hz, 1H), 8.40 (d, J = 1.8 Hz, 1H), 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 Hz, 4H), 3.79 (t, J= 6.9 Hz, J = 5.4 Hz, 6H), 3.14 (t, J = 6.9 Hz, J = 5.7 Hz, 6H). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$, 121.50 MHz): δ (ppm) -141.4 (sept, $J_{P–F}$ = 706.8 Hz, PF_6). ^{19}F{^{1}H}NMR (CD_3CN, 282.41 MHz): δ (ppm) -73.6 (d, $J_{P–F}$ = 706.8 Hz, PF_6). HRMS (ES$^+$) m/z: calcd. for $C_{57}H_{45}N_9OsPF_6$ $[M-PF_6]^+$ 1192.3055; found 1192.3042. UV/Vis (acetonitrile): λ_{max}, nm (ε, M-1 cm^{-1}) = 480 (38×10^3).

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_3 (0.1 M). The vessel was sealed and heated for 72 h at 90 °C under N_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:[S2,S3] Hydrophilic substrate surfaces are functionalized with a benzyl-chloride terminated coupling layer (**CL**) using siloxane chemistry, the **CL**s are reacted from solution at elevated temperatures with polypyridyl complex (**1**) affording template layers (**TL**s) consisting of covalently bound pyridinium salts of complex **1**that can bind metal salts, and the iterative exposure of these **TL**s to solutions of a polypyridyl complex (**1**-**3**) with multiple metal-binding sites and $PdCl_2(PhCN)_2$.

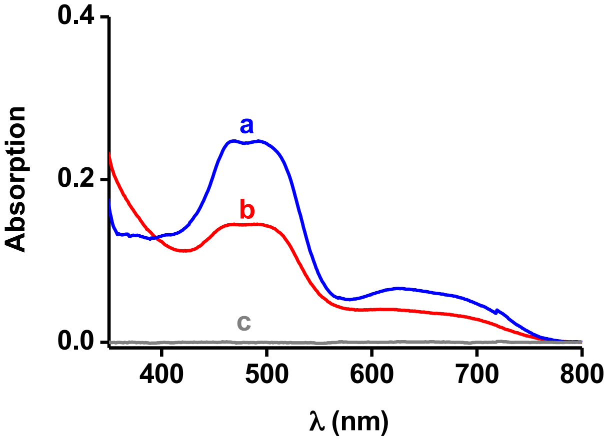


Figure S1. UV/vis absorption of (a) the solution phase after a mass transfer experiment with a **1**-based SPMA, and (b) a solution of complex **1** in acetonitrile/toluene (1:1, v/v). (c) baseline.

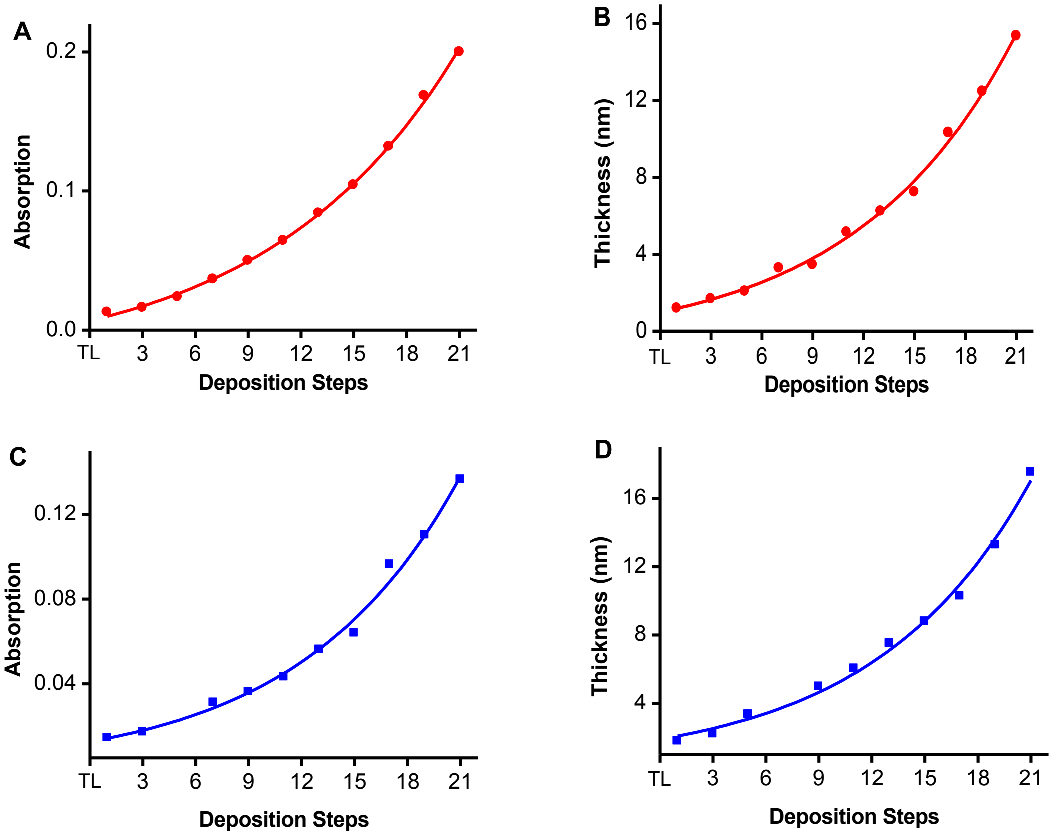


Figure S2. Characterization of **2**-based (red) and **3**-based (blue) SPMAs. (A and C) Exponential dependence of the intensities of the MLCT bands (λ = 500 nm) and (B and D) film thickness for compounds **2** and **3** vs the number of deposition steps, respectively. TL stands for the template layer.

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'.

Template layer	$E_{1/2}$ [V]	E_{ox} [V]	E_{Red} [V]	I_{pa} [A]	I_{pc} [A]	Γ_s [mol cm^{-2}]
I	0.90	0.92	0.89	1.45×10^{-5}	-1.12×10^{-5}	1.2×10^{-10}
II	0.91	0.94	0.89	1.48×10^{-5}	-1.31×10^{-5}	1.4×10^{-10}
III	0.89	0.91	0.87	1.54×10^{-5}	-1.28×10^{-5}	1.3×10^{-10}

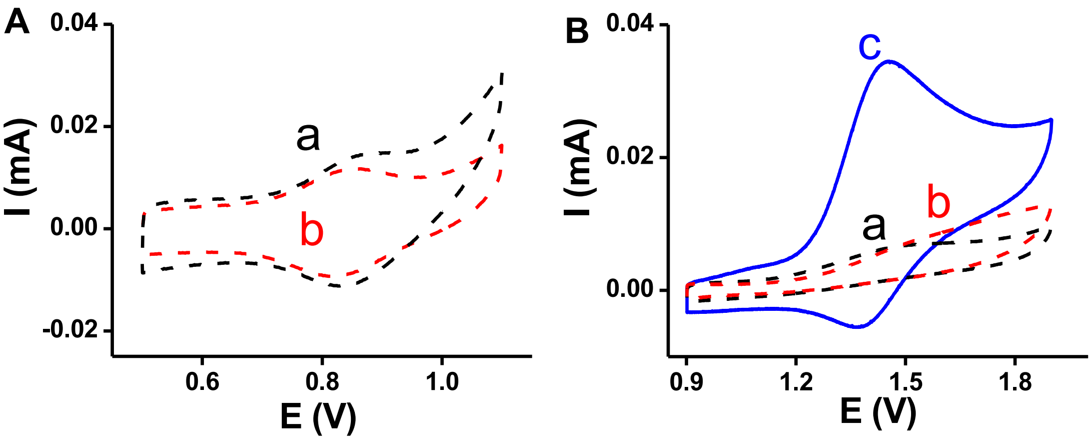


Figure S3. Representative cyclic voltammograms of the TLs on ITO-coated glass substrates. (a) TL formed by mass transfer upon disassembly of the osmium (**2**) and ruthenium (**3**)-based SPMAs with PEt$_3$, and (b) TL formed by reacting chlorobenzyl functionalized substrates with complex **2**, (c) 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 TBABF$_4$/CH$_3$CN.

References

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