Electronic Supplementary Information

Anion-Induced Palladium Nanoparticle Formation During the On-Surface Growth of Molecular Assemblies

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Materials and Methods. Reagents and chemicals were purchased from Sigma-Aldrich, Acros Organics, Next Chimica, and Apollo. Solvents were reagent grade (AR) and purchased from either Bio-Lab (Jerusalem), Frutarom (Haifa), or Merck. Toluene was dried using a M. Braun solvent purification system and degassed before being introduced into a M. Braun glovebox (H₂O and O₂ levels <2 ppm). Anhydrous CH₃CN (99.8%) was purchased from Aldrich. (E)-4-Methyl-4’-styryl-2,2’-bipyridine (L₁; Fig. S1),¹ complex 1•PF₆ (Scheme 1, Fig. S1),² 1,3,5-tri-[4-vinylpyridine]-benzene,³ PdCl₂(PhCN)₂,⁴ Ru(bpy)₃(PF₆)₂ and Ru(bpy)₃(BPh₄)₂ were prepared according to known procedures.⁵ All glassware and Teflon holders used for SPMA formation were cleaned by immersion in a piranha solution (7:3 v/v H₂SO₄ / 30% H₂O₂) for 10 min and washed with DI water. Caution: piranha is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection. Single-crystal silicon (100) substrates, purchased from Wafernet (San Jose, CA) and ITO, purchased from Delta Technologies (Stillwater, MN) were cleaned by sonication in n-hexane, acetone, and ethanol, for 8 min in each solvent, and dried under a stream of N₂. Subsequently, the slides were cleaned with UV and ozone in a UVOCS cleaning system (Montgomery, PA), washed with iso-propanol, dried under a stream of N₂, and heated for 2 h at 130 °C in an oven. Quartz slides (Chemglass, Vineland, NJ) were rinsed several times with DI water and cleaned by
immersion in a piranha solution for 1 h. The substrates were then rinsed with DI water, followed by the RCA cleaning protocol: 1:5:1 (v/v) NH₄OH/H₂O/30% H₂O₂ solution at room temperature for 1 h. The substrates were subsequently thoroughly washed with DI water and with iso-propanol, dried under a stream of N₂ and heated at 130 °C for 2 h in an oven. ¹H, ¹¹B{¹H}, ¹³C{¹H}, ¹⁹F{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer or on a Bruker Avance 300 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) are in Hz. The ¹H and ¹³C{¹H} NMR chemical shifts are reported relative to TMS or to residual solvent peaks. ¹¹B{¹H} NMR were measured in acetone and referenced to external BF₃·O(CH₂CH₃)₂. Mass spectrometry (MS) analyses were performed on a SYNAPT high-definition-Q-TOF mass spectrometer. UV/Vis spectra were recorded using a Varian Cary 100 spectrophotometer (in double beam transmission mode). The spectra were recorded in the range of 200-800 nm. Baseline measurements were recorded using bare quartz slides. Atomic Force Microscopy (AFM) was recorded using a Solver P47 (NT-MDT, Russia) operating in semicontact scanning mode. The ~100 μm silicon cantilevers were used with a resonant frequency of 70-90 kHz. The roughness values, Rrms, were obtained from 500 nm × 500 nm images. Several areas with different scanning sizes were taken on silicon (100) (from 5 μm to 500 nm). Film thicknesses were estimated using a J. A. Woollam (Lincoln, NB) model M-2000V variable angle spectroscopic ellipsometer with VASE32 software. Measurements were performed on silicon (100) for each 5 degrees at a range of 60°-80° over wavelengths of 399-1000 nm. Parameters A, B, and C were 1.45, 0.01, and 0.00, respectively, with MSE < 10 for a Cauchy model. The SiO₂ layer was calibrated to be 17 Å. The error was always < 0.05 Å. X-ray data were collected at the 12-BM-B beamline at the Advanced Photon Source (APS) in the Argonne National Laboratory (Argonne, IL), using a Huber four-circle diffractometer in the specular reflection mode (i.e., the incident angle is equal to the exit angle θ). X-rays of energy E = 10 keV (λ = 1.24 Å) were used for these measurements. The beam size was 0.40 mm vertically and 0.60 mm horizontally. The samples were placed under helium during measurements to reduce background scattering and radiation damage. Details of the data acquisition and analysis are given elsewhere.⁵⁵-⁷ X-ray photoelectron spectroscopy (XPS) measurements were carried out on silicon (100) substrates (0.8 cm × 2.0 cm) with a Kratos AXIS ULTRA system.
using a monochromatic Al Kα X-ray source (\( h\nu = 1486.6 \text{ eV} \)) at 75 W and detection pass energies ranging between 20 and 80 eV. Electrochemical experiments were carried out using a CHI660A electrochemical workstation; ITO-single and double-side-coated glass substrates (7 mm × 50 mm × 0.7 mm) served as a working electrode, Ag/Ag⁺ was used as a reference electrode, and a Pt wire was used as a counter electrode. "Bu₄NPF₆ (0.1 M) in dry ACN was used as a supporting electrolyte and ferrocene as the internal standard under ambient conditions. High-resolution scanning electron microscope (HRSEM) secondary electron (SE) imaging was carried out with a LEO-Supra 55 VP HRSEM.

**Preparation of complex 1•BPh₄.** RuCl₃·xH₂O (81 mg; 0.39 mmol) and ligand L1 (320 mg; 1.17 mmol) were refluxed in ethylene glycol (35 mL) for 5 h under argon (Fig. 1). Subsequently, the mixture was cooled and complex 1•BPh₄ was precipitated by the addition of a saturated aqueous solution of NaBPh₄ (~1.0 g in 200 mL water, ~3.0 mmol) and filtered-off. The residue was washed with an excess of water (100 mL) and diethyl-ether (300 mL), and dried under vacuum. This procedure yielded 365 mg (60 %) of complex 1•BPh₄ as a dark red powder. ¹H NMR \([(CD₃)₂CO, 400.36 MHz]\): \( \delta \) (ppm) 8.95 (d, 3H ), 8.69 (s, 3H ) 8.59 (m, 6H), 7.94 (d, \( J = 5.8 \text{ Hz} \), 1H), 7.85 (d, \( J = 6.1 \text{ Hz} \), 1H), 7.78 (d, \( J = 5.7 \text{ Hz} \), 2H), 7.67 (d, 3H), 7.55 (d, 3H), 7.49 (d, \( J = 4.8 \text{ Hz} \), 9H), 7.42 (m, 3H), 7.29 (m, 24H, Ar-H), 7.18 (m, 3H), 7.10 (t, \( J = 7.2 \text{ Hz} \), 3H), 6.83 (t, \( J = 7.3 \text{ Hz} \), 8H, BPh₄), 6.69 (t, \( J = 7.3 \text{ Hz} \), 4H, BPh₄) 2.50 (s, 9H). ¹³C{¹H} NMR \[((CD₃)₂CO, 100.67 MHz]\): \( \delta \) (ppm) 166.71 (BPh₄), 166.22 (BPh₄), 165.73 (BPh₄), 165.24 (BPh₄), 159.50, 159.37, 158.51, 158.34, 137.94 (q, \( J = 1.4 \text{ Hz} \), 136.37, 135.66, 130.66, 130.46, 128.73, 127.07 (q, \( J = 2.8 \text{ Hz} \), 126.83, 126.77, 123.28, 123.16, 22.31 (CH₃). ¹¹B{¹H} NMR \[((CD₃)₂CO, 128.45 MHz]\): \( \delta \) (ppm) -5.85 (BPh₄). UV/Vis (\( \epsilon \)) (CH₃CN) \( \lambda_{\text{max}} = 311 \text{ nm} \), 80.51 (\( \epsilon \), cm⁻¹ mM⁻¹), \( \lambda = 477 \text{ nm} \), 28.87 (\( \epsilon \), cm⁻¹ mM⁻¹). HRMS (ES⁺) \( m/z \): calcd. for C₇₈H₆₅N₉RuB [M-TPB]+ 1240.4530: found 1240.4526. Spectra are shown in Fig. S10-S14.
Fig. S1 Preparation of complexes 1•PF$_6$ and 1•BPh$_4$. a) RuCl$_3$·xH$_2$O, ethylene glycol, 5 h, Ar; b) NH$_4$PF$_6$, H$_2$O; c) NaBPh$_4$, H$_2$O.

Formation of Self-Propagating Molecular Assemblies (SPMAs) with complexes 1•PF$_6$ and 1•BPh$_4$. A Teflon holder containing substrates functionalized with a template layer (TL)$^{88}$ (Fig. S2) was immersed for 15 minutes in a 1.0 mM solution of PdCl$_2$(PhCN)$_2$ in THF (120 mL). The samples were then sonicated twice in THF and once in acetone for 3 min each. Subsequently, the samples were immersed in a 0.2 mM solution of complexes 1•PF$_6$ or 1•BPh$_4$ (Fig. S1) in THF/DMF (120 mL: 7:3, v/v) for 15 min at room temperature. The samples were then sonicated twice in THF and once in acetone for 3 min each. This deposition procedure was repeated 12 times. The slides were stored under ambient conditions with the exclusion of light.

Fig. S2 Schematic representation of the functionalization of quartz, silicon(100), and ITO with a template layer (TL) available for coordination to palladium.$^{88}$
**Fig. S3** UV/Vis absorption data of self-propagating molecular assemblies (SPMAs) of 1-PF$_6$.
The bottom spectra (black lines) correspond to the template layer (TL, Fig. S2).

**Fig. S4** Representative UV/Vis absorption data (A) of the MLCT band ($\lambda = 500$ nm) and (B) assembly thickness versus the number of complex deposition steps for 1-PF$_6$ (●), 1-BF$_4$ (■), and alternating deposition of 1-BF$_4$ and 1-PF$_6$ (▲). $R^2 \geq 0.99$ for all fits. TL refers to the template layer (Fig. S2).
**Fig. S5** Representative synchrotron X-ray reflectivity (XRR) data of a self-propagating molecular assemblies (SPMAs) formed from $1\cdot PF_6$ (2.2 nm) on a silicon substrate in which $R$ is the reflectivity normalized to the Fresnel reflectivity $R_c$. The red trace is a fit to the experimental data.

**Reaction of Ru(bpy)$_3$(PF$_6$)$_2$ or Ru(bpy)$_3$(BPh$_4$)$_2$ with PdCl$_2$(PhCN)$_2$.** A 1.0 mM solution of PdCl$_2$(PhCN)$_2$ in THF (2 mL) and a 0.2 mM solution of Ru(bpy)$_3$(PF$_6$)$_2$ or Ru(bpy)$_3$(BPh$_4$)$_2$ in THF/DMF (2 mL: 7:3, v/v) were mixed. No visible change was observed in the reaction mixture containing PdCl$_2$(PhCN)$_2$ and Ru(bpy)$_3$(PF$_6$)$_2$; however, a black precipitate appeared within seconds upon reacting PdCl$_2$(PhCN)$_2$ with Ru(bpy)$_3$(BPh$_4$)$_2$ (Fig. S6). MS analysis revealed the formation of [Ru(bpy)$_3$]Cl$^+$ (605.07). $^{11}$B$^{1}$H NMR showed a peak at $\delta$ 45 ppm (BPh$_3$). Spectra are shown in Fig. S15-S16.

**Fig. S6** Photographs showing the reaction of PdCl$_2$(PhCN)$_2$ (1.0 mM in THF) with a 0.2 mM solution of Ru(bpy)$_3$(PF$_6$)$_2$ (left) or Ru(bpy)$_3$(BPh$_4$)$_2$ (right) in THF/DMF (7:3 v/v). (A) Solutions before the addition of the Pd salt. (B) Reaction mixtures immediately after the addition of solutions of PdCl$_2$(PhCN)$_2$. (C) The reaction mixtures after 5 min. A black precipitate is formed after the reaction between PdCl$_2$(PhCN)$_2$ and Ru(bpy)$_3$(BPh$_4$)$_2$. Similar observations were made using NaBPh$_4$. 
Fig. S7 Representative cyclic voltammograms (CVs) of self-propagating molecular assemblies (SPMAs) formed from 1•PF₆ (7 nm, dotted line; 12 nm, solid line) recorded on single-sided ITO-coated glass at a scan rate of 100 mVs⁻¹. The experiments were carried out at rt under ambient atmosphere in 0.1 M "Bu₄NPF₆/CH₃CN. Single-sided ITO-coated glass, Pt wire and Ag/Ag⁺ were used as working, counter, and reference electrodes, respectively.

**Molecule- and electron-transfer through the SPMAs.** In a 1.3 mM CH₃CN solution of 2,6-dimethoxy-1,4-benzoquinone or 3,3’,5,5’-tetra-tertbutylidiphenyloquinone were immersed in a consecutive manner: (i) a bare single-sided ITO-coated glass-electrode, (ii) SPMAs (7 nm thick) formed from 1•BPh₄ or 1•PF₆. Subsequently, the CV experiments were carried out at room temperature in the presence of 0.1 M "Bu₄NPF₆ under argon. The functionalized double-sided ITO-coated glass, Pt wire, and Ag/Ag⁺ were used as working, counter, and reference electrodes, respectively.

Fig. S8 Representative cyclic voltammograms (CVs) of 3,3’,5,5’-tetra-tertbutylidiphenyloquinone (1.3 mM, CH₃CN) for a double-sided ITO electrode (blue dashed line), and the same electrodes coated with SPMAs formed from 1•BPh₄ (7 nm, black line) and from 1•PF₆ (7 nm; red line). The experiments were carried out under argon at rt in 0.1 M "Bu₄NPF₆/CH₃CN with a scan rate of 100 mVs⁻¹. Double-sided ITO-coated glass, Pt wire and Ag/Ag⁺ were used as working, counter, and reference electrodes, respectively.
**Fig. S9.** UV/Vis absorption of the MLCT band ($\lambda = 500$ nm) vs. SPMA thickness of $1\cdot\text{PF}_6$ (●) and $1\cdot\text{BF}_4$ (■). $R^2 \geq 0.998$ for both fits.

**Fig. S10.** $^1$H NMR of complex $1\cdot\text{BPh}_4$ in acetone-$d_6$. *diethyl ether, **acetone and ***H$_2$O.
Fig. S11. $^{13}\text{C}^{1\text{H}}$ NMR of complex 1·BPh$_4$ in acetone-$d_6$. *acetone.

Fig. S12. $^{11}\text{B}^{1\text{H}}$ NMR of complex 1·BPh$_4$ in acetone-$d_6$.

Fig. S13. UV/Vis spectra of complex 1·BPh$_4$ in acetonitrile.
**Fig. S14.** Left: HRMS (ES+) m/z of complex 1-BPh₄. Right: calculated spectrum for C₇₈H₆₅N₉RuB [M-BPh₄]⁺.

**Fig. S15.** Top: 

\[ ^{11}B\{ ^{1}H\} \text{ NMR spectrum of Ru(bpy)}_{3}(\text{BPh}_{4})_{2} \text{ in acetone-}d_{6}. \] 

Bottom: 

\[ ^{11}B\{ ^{1}H\} \text{ NMR spectrum of the product solution of the reaction between Ru(bpy)}_{3}(\text{BPh}_{4})_{2} \text{ and PdCl}_{2}(\text{PhCN})_{2}. \]
Fig. S16. (A) MS (ES+) m/z of the product solution of the reaction between Ru(bpy)$_3$(BPh$_4$)$_2$ and PdCl$_2$(PhCN)$_2$. (B) Calculated spectrum for C$_{30}$H$_{24}$N$_6$RuCl [M-Cl]$^+$.

References