

## Electronic Supplementary Information

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

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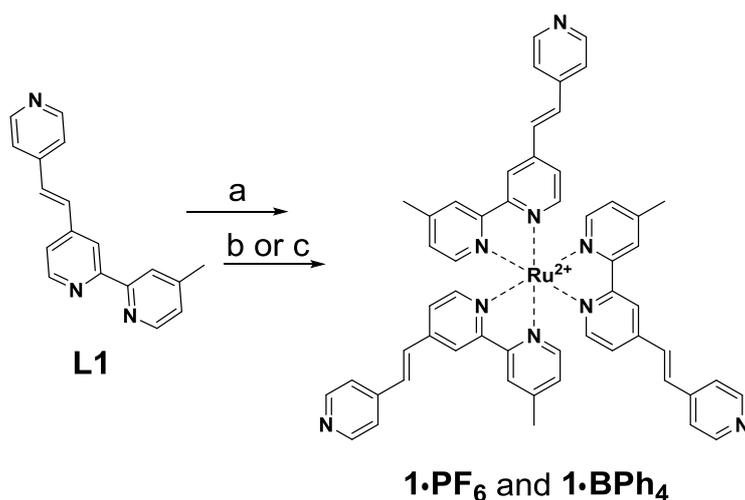
**Materials and Methods.** Reagents and chemicals were purchased from Sigma-Aldrich, Acros Organics, Next Chimica, and Apollo. Solvents were reagent grade (AR) and purchased from either Bio-Lab (Jerusalem), Frutarom (Haifa), or Merck. Toluene was dried using a M. Braun solvent purification system and degassed before being introduced into a M. Braun glovebox (H<sub>2</sub>O and O<sub>2</sub> levels <2 ppm). Anhydrous CH<sub>3</sub>CN (99.8%) was purchased from Aldrich. (*E*)-4-Methyl-4'-styryl-2,2'-bipyridine (**L1**; Fig. S1),<sup>S1</sup> complex **1**•PF<sub>6</sub> (Scheme 1, Fig. S1),<sup>S2</sup> 1,3,5-tri-[4-vinylpyridine]-benzene,<sup>S3</sup> PdCl<sub>2</sub>(PhCN)<sub>2</sub>,<sup>S4</sup> Ru(bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> and Ru(bpy)<sub>3</sub>(BPh<sub>4</sub>)<sub>2</sub> were prepared according to known procedures.<sup>S2</sup> All glassware and Teflon holders used for SPMA formation were cleaned by immersion in a piranha solution (7:3 v/v H<sub>2</sub>SO<sub>4</sub> / 30% H<sub>2</sub>O<sub>2</sub>) 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 N<sub>2</sub>. 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 N<sub>2</sub>, 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)  $\text{NH}_4\text{OH}/\text{H}_2\text{O}/30\% \text{H}_2\text{O}_2$  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  $\text{N}_2$  and heated at 130 °C for 2 h in an oven.  $^1\text{H}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{19}\text{F}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer or on a Bruker Avance 300 NMR spectrometer. All chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) are in Hz. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts are reported relative to TMS or to residual solvent peaks.  $^{11}\text{B}\{^1\text{H}\}$  NMR were measured in acetone and referenced to external  $\text{BF}_3 \cdot \text{O}(\text{CH}_2\text{CH}_3)_2$ .

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  $\sim 100 \mu\text{m}$  silicon cantilevers were used with a resonant frequency of 70-90 kHz. The roughness values,  $R_{\text{rms}}$ , were obtained from  $500 \text{ nm} \times 500 \text{ nm}$  images. Several areas with different scanning sizes were taken on silicon (100) (from  $5 \mu\text{m}$  to  $500 \text{ nm}$ ). 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  $60^\circ$ - $80^\circ$  over wavelengths of 399-1000 nm. Parameters A, B, and C were 1.45, 0.01, and 0.00, respectively, with  $\text{MSE} < 10$  for a Cauchy model. The  $\text{SiO}_2$  layer was calibrated to be  $17 \text{ \AA}$ . The error was always  $< 0.05 \text{ \AA}$ . 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  $\theta$ ). X-rays of energy  $E = 10 \text{ keV}$  ( $\lambda = 1.24 \text{ \AA}$ ) were used for these measurements. The beam size was  $0.40 \text{ mm}$  vertically and  $0.60 \text{ mm}$  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.<sup>55-7</sup> X-ray photoelectron spectroscopy (XPS) measurements were carried out on silicon (100) substrates ( $0.8 \text{ cm} \times 2.0 \text{ cm}$ ) with a Kratos AXIS ULTRA system

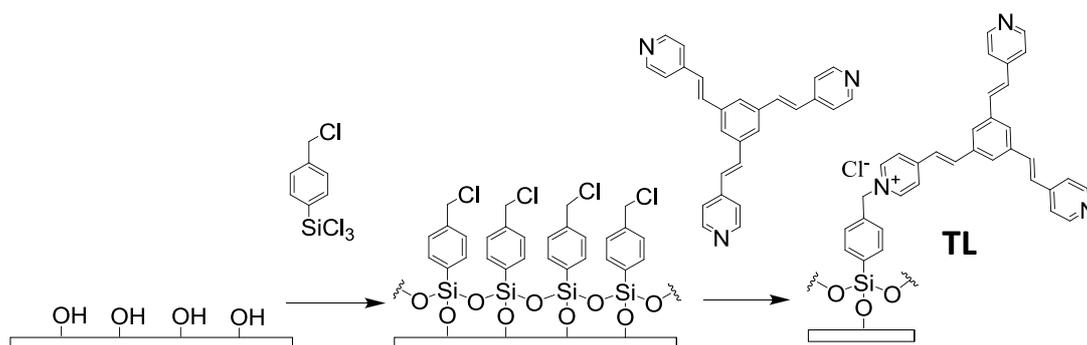
using a monochromatic Al K $\alpha$  X-ray source ( $h\nu = 1486.6$  eV) at 75 W and detection pass energies ranging between 20 and 80 eV. Electrochemical experiments were carried out using a CHI660A electrochemical workstation; ITO-single and double-side-coated glass substrates (7 mm  $\times$  50 mm  $\times$  0.7 mm) served as a working electrode, Ag/Ag<sup>+</sup> was used as a reference electrode, and a Pt wire was used as a counter electrode. <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> (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•BPh<sub>4</sub>.** RuCl<sub>3</sub>· $x$ H<sub>2</sub>O (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•BPh<sub>4</sub>** was precipitated by the addition of a saturated aqueous solution of NaBPh<sub>4</sub> (~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•BPh<sub>4</sub>** as a dark red powder. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>CO, 400.36 MHz]:  $\delta$  (ppm) 8.95 (d, 3H ), 8.69 (s, 3H ) 8.59 (m, 6H), 7.94 (d,  $J = 5.8$  Hz, 1H), 7.85 (d,  $J = 6.1$  Hz, 1H), 7.78 (d,  $J = 5.7$  Hz, 2H), 7.67 (d, 3H), 7.55 (d, 3H), 7.49 (d,  $J = 4.8$  Hz, 9H), 7.42 (m, 3H), 7.29 (m, 24H, Ar-H), 7.18 (m, 3H), 7.10 (t,  $J = 7.2$  Hz, 3H), 6.83 (t,  $J = 7.3$  Hz, 8H, BPh<sub>4</sub>), 6.69 (t,  $J = 7.3$  Hz, 4H, BPh<sub>4</sub>) 2.50 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 100.67 MHz):  $\delta$  (ppm) 166.71 (BPh<sub>4</sub>), 166.22 (BPh<sub>4</sub>), 165.73 (BPh<sub>4</sub>), 165.24 (BPh<sub>4</sub>), 159.50, 159.37, 158.51, 158.34, 137.94 (q,  $J = 1.4$  Hz), 136.37, 135.66, 130.66, 130.46, 128.73, 127.07 (q,  $J = 2.8$  Hz), 126.83, 126.77, 123.28, 123.16, 22.31 (CH<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>CO, 128.45 MHz]:  $\delta$  (ppm) -5.85 (BPh<sub>4</sub>). UV/Vis ( $\epsilon$ ) (CH<sub>3</sub>CN)  $\lambda_{\max} = 311$  nm, 80.51 ( $\epsilon$ , cm<sup>-1</sup> mM<sup>-1</sup>),  $\lambda = 477$  nm, 28.87 ( $\epsilon$ , cm<sup>-1</sup> mM<sup>-1</sup>). HRMS (ES<sup>+</sup>)  $m/z$ : calcd. for C<sub>78</sub>H<sub>65</sub>N<sub>9</sub>RuB [M-TPB]<sup>+</sup> 1240.4530: found 1240.4526. Spectra are shown in Fig. S10-S14.

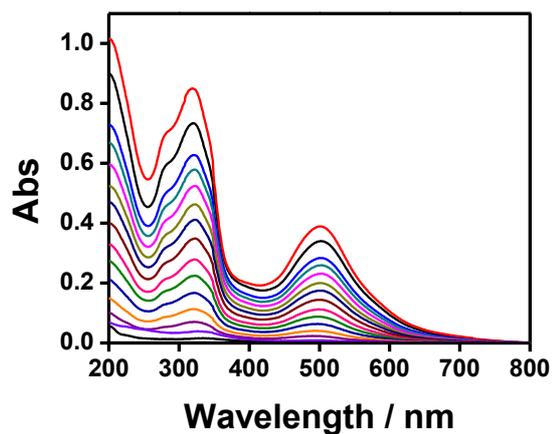


**Fig. S1** Preparation of complexes **1·PF<sub>6</sub>** and **1·BPh<sub>4</sub>**. a) RuCl<sub>3</sub>·xH<sub>2</sub>O, ethylene glycol, 5 h, Ar; b) NH<sub>4</sub>PF<sub>6</sub>, H<sub>2</sub>O; c) NaBPh<sub>4</sub>, H<sub>2</sub>O.

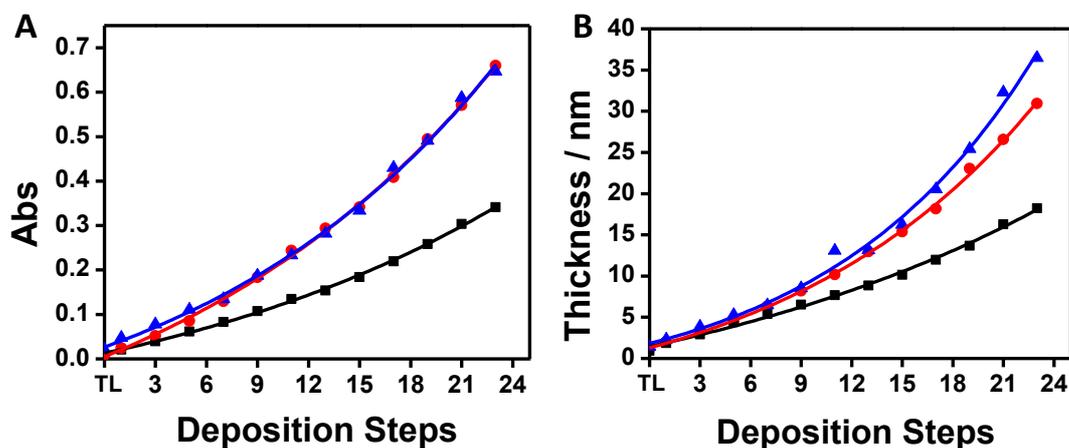
**Formation of Self-Propagating Molecular Assemblies (SPMAs) with complexes **1·PF<sub>6</sub>** and **1·BPh<sub>4</sub>**.** A Teflon holder containing substrates functionalized with a template layer (TL)<sup>S8</sup> (Fig. S2) was immersed for 15 minutes in a 1.0 mM solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> 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<sub>6</sub>** or **1·BPh<sub>4</sub>** (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.



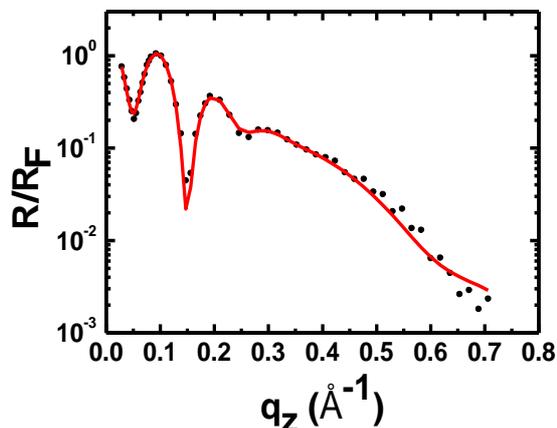
**Fig. S2** Schematic representation of the functionalization of quartz, silicon(100), and ITO with a template layer (TL) available for coordination to palladium.<sup>S8</sup>



**Fig. S3** UV/Vis absorption data of self-propagating molecular assemblies (SPMAs) of  $1\cdot\text{PF}_6$ . The bottom spectra (black lines) correspond to the template layer (TL, Fig. S2).

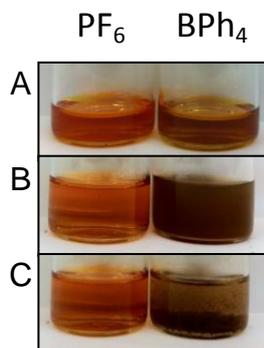


**Fig. S4** Representative UV/Vis absorption data (A) of the MLCT band ( $\lambda = 500$  nm) and (B) assembly thickness versus the number of complex deposition steps for  $1\cdot\text{PF}_6$  ( $\bullet$ ),  $1\cdot\text{BF}_4$  ( $\blacksquare$ ), and alternating deposition of  $1\cdot\text{BF}_4$  and  $1\cdot\text{PF}_6$  ( $\blacktriangle$ ).  $R^2 \geq 0.99$  for all fits. TL refers to the template layer (Fig. S2).

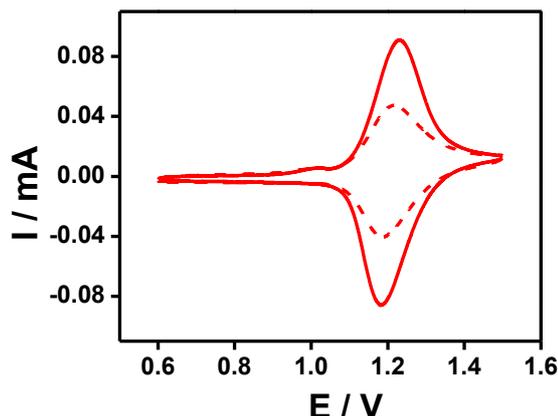


**Fig. S5** Representative synchrotron X-ray reflectivity (XRR) data of a self-propagating molecular assemblies (SPMAs) formed from  $1 \cdot \text{PF}_6$  (2.2 nm) on a silicon substrate in which  $R$  is the reflectivity normalized to the Fresnel reflectivity  $R_F$ . The red trace is a fit to the experimental data.

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

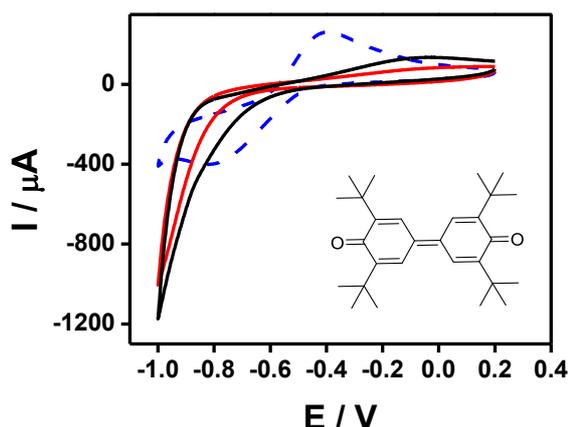


**Fig. S6** Photographs showing the reaction of  $\text{PdCl}_2(\text{PhCN})_2$  (1.0 mM in THF) with a 0.2 mM solution of  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  (left) or  $\text{Ru}(\text{bpy})_3(\text{BPh}_4)_2$  (right) in THF/DMF (7:3 v/v). (A) Solutions before the addition of the Pd salt. (B) Reaction mixtures immediately after the addition of solutions of  $\text{PdCl}_2(\text{PhCN})_2$ . (C) The reaction mixtures after 5 min. A black precipitate is formed after the reaction between  $\text{PdCl}_2(\text{PhCN})_2$  and  $\text{Ru}(\text{bpy})_3(\text{BPh}_4)_2$ . Similar observations were made using  $\text{NaBPh}_4$ .

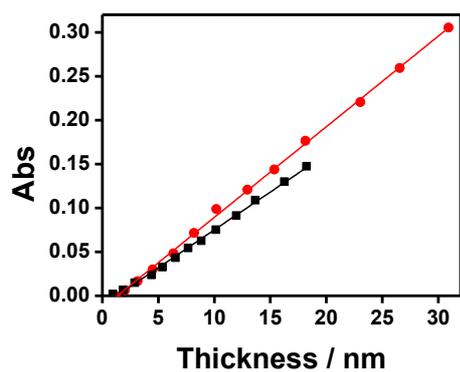


**Fig. S7** Representative cyclic voltammograms (CVs) of self-propagating molecular assemblies (SPMAs) formed from **1•PF<sub>6</sub>** (7 nm, dotted line; 12 nm, solid line) recorded on single-sided ITO-coated glass at a scan rate of 100 mVs<sup>-1</sup>. The experiments were carried out at rt under ambient atmosphere in 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN. Single-sided ITO-coated glass, Pt wire and Ag/Ag<sup>+</sup> were used as working, counter, and reference electrodes, respectively.

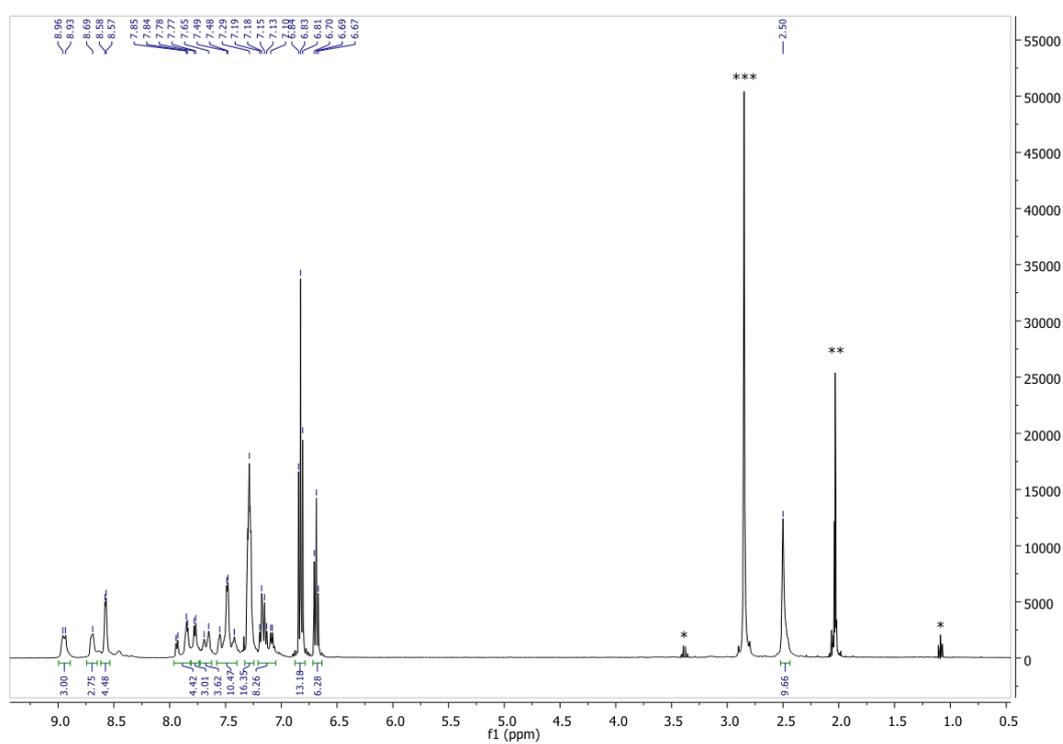
**Molecule- and electron-transfer through the SPMAs.** In a 1.3 mM CH<sub>3</sub>CN solution of 2,6-dimethoxy-1,4-benzoquinone or 3,3',5,5'-tetra-tertbutyldiphenylphenoquinone were immersed in a consecutive manner: (i) a bare single-sided ITO-coated glass-electrode, (ii) SPMAs (7 nm thick) formed from **1•BPh<sub>4</sub>** or **1•PF<sub>6</sub>**. Subsequently, the CV experiments were carried out at room temperature in the presence of 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> under argon. The functionalized double-sided ITO-coated glass, Pt wire, and Ag/Ag<sup>+</sup> were used as working, counter, and reference electrodes, respectively.



**Fig. S8** Representative cyclic voltammograms (CVs) of 3,3',5,5'-tetra-tertbutyldiphenylphenoquinone (1.3 mM, CH<sub>3</sub>CN) for a double-sided ITO electrode (blue dashed line), and the same electrodes coated with SPMAs formed from **1•BPh<sub>4</sub>** (7 nm, black line) and from **1•PF<sub>6</sub>** (7 nm; red line). The experiments were carried out under argon at rt in 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>3</sub>CN with a scan rate of 100 mVs<sup>-1</sup>. Double-sided ITO-coated glass, Pt wire and Ag/Ag<sup>+</sup> 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•PF<sub>6</sub>** (●) and **1•BF<sub>4</sub>** (■).  $R^2 \geq 0.998$  for both fits.



**Fig. S10.** <sup>1</sup>H NMR of complex **1•BPh<sub>4</sub>** in acetone-*d*<sub>6</sub>. \*diethyl ether, \*\*acetone and \*\*\*H<sub>2</sub>O.

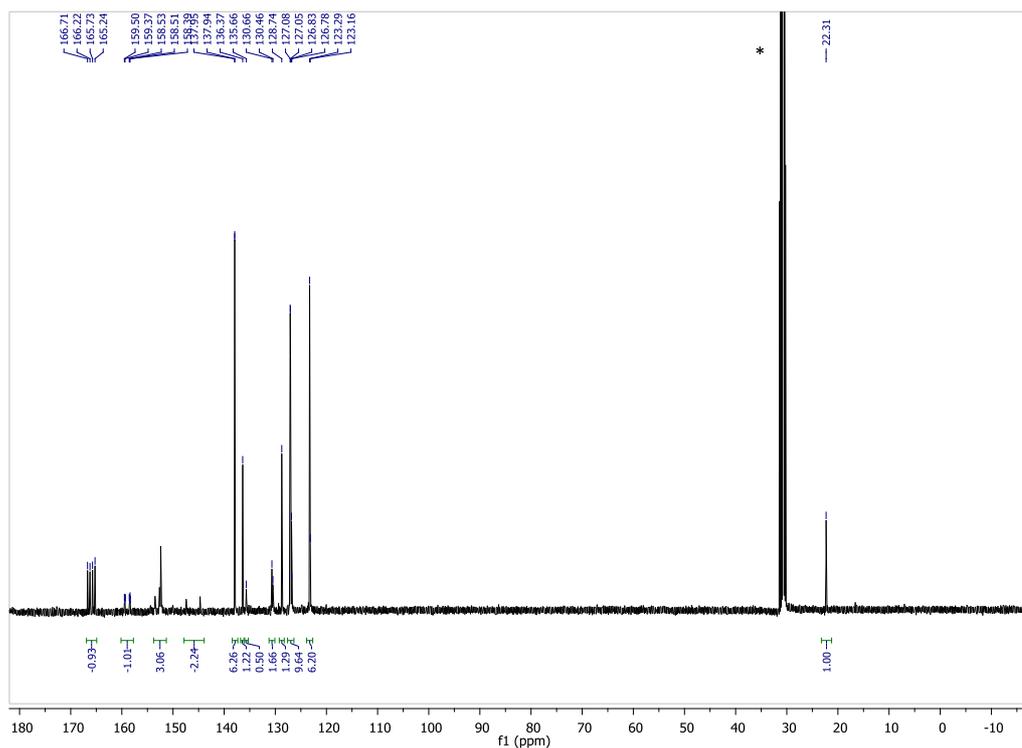


Fig. S11.  $^{13}\text{C}\{^1\text{H}\}$  NMR of complex  $1\cdot\text{BPh}_4$  in acetone- $d_6$ . \*acetone.

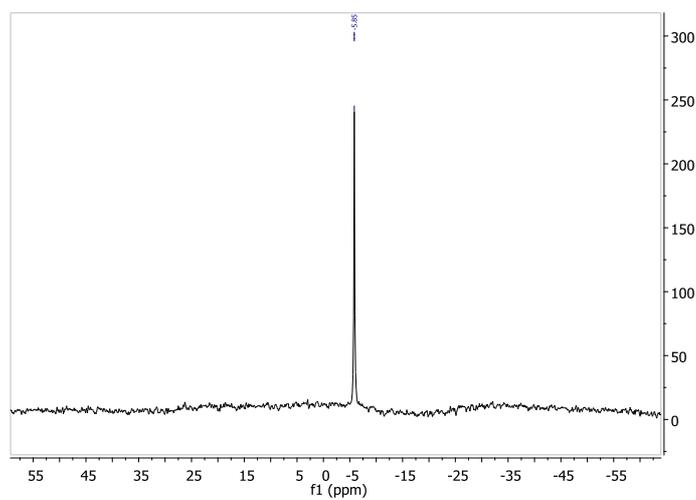


Fig. S12.  $^{11}\text{B}\{^1\text{H}\}$  NMR of complex  $1\cdot\text{BPh}_4$  in acetone- $d_6$ .

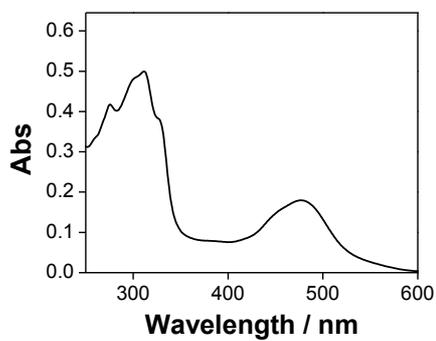
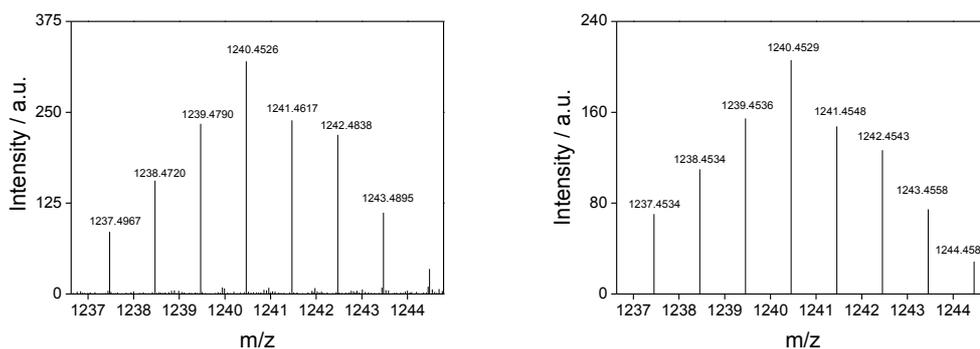
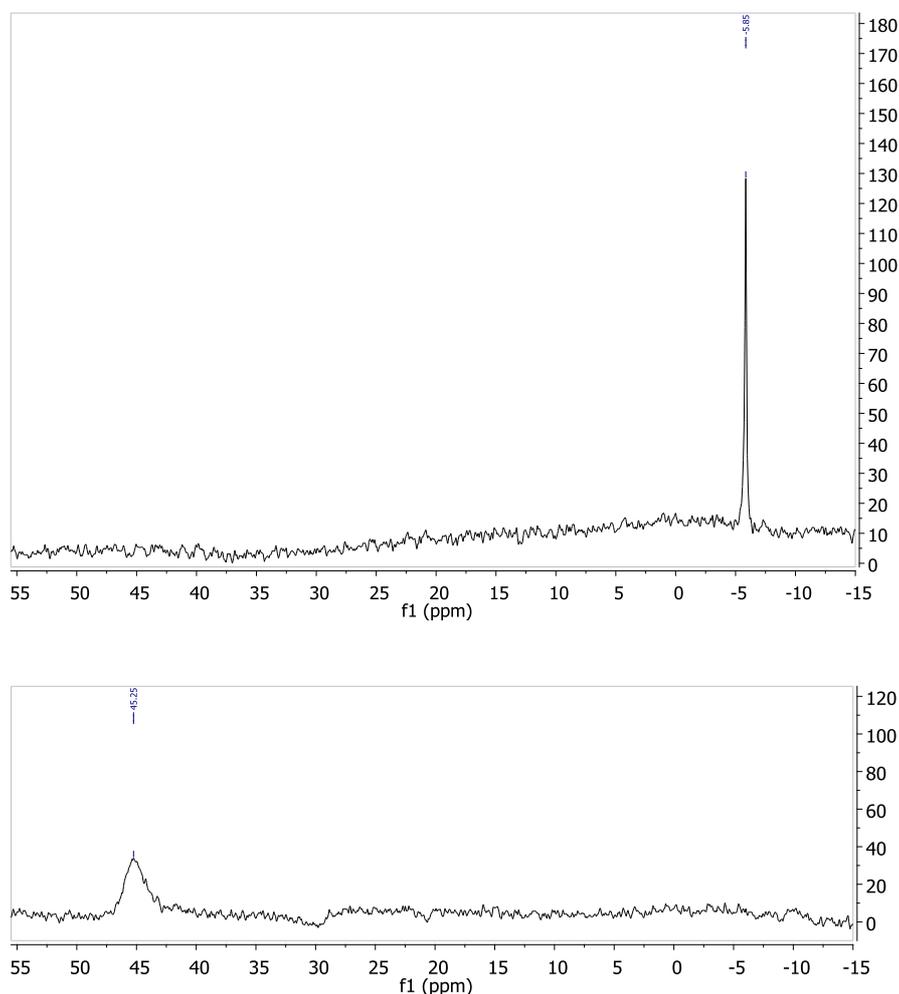


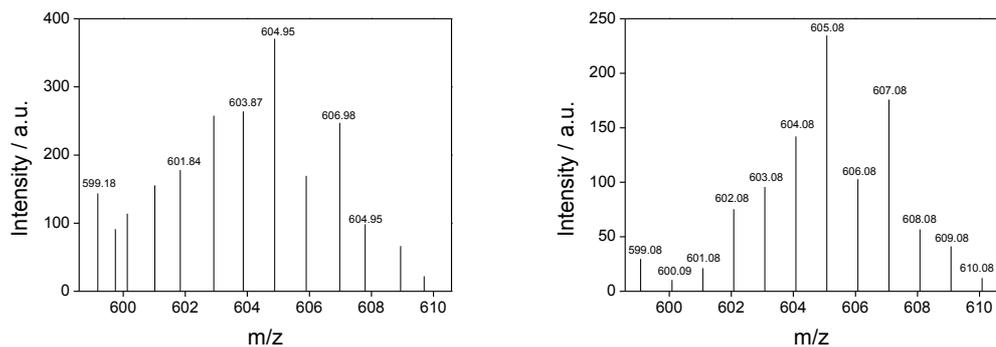
Fig. S13. UV/Vis spectra of complex  $1\cdot\text{BPh}_4$  in acetonitrile.



**Fig. S14.** Left: HRMS (ES+)  $m/z$  of complex **1**·**BPh<sub>4</sub>**. Right: calculated spectrum for  $C_{78}H_{65}N_9RuB [M-BPh_4]^+$ .



**Fig. S15.** Top:  $^{11}B\{^1H\}$  NMR spectrum of  $Ru(bpy)_3(BPh_4)_2$  in acetone- $d_6$ . Bottom:  $^{11}B\{^1H\}$  NMR spectrum of the product solution of the reaction between  $Ru(bpy)_3(BPh_4)_2$  and  $PdCl_2(PhCN)_2$ .



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

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