Supporting Material
Fabrication of Photomagnetic Carbon Surfaces via Redox Assembly

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In this work, $Ru(bpy)_2(phendione)^{2+}$ was synthesized by reacting $Ru(bpy)_2Cl_2.2H_2O$ with phendione in a molar ratio of 1:1.2 under a reflux in CH_3OH/H_2O (volume ratio 1:1). The product was purified via recrystallization in ether prior to its application in surface modification. The X-ray structure is shown in Figure S1.

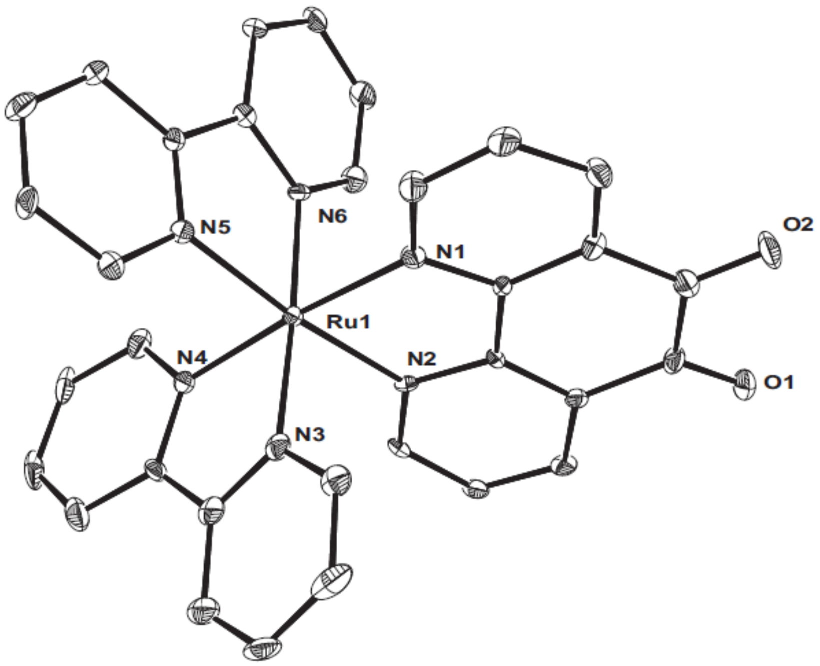


FIGURE S1: The X-ray crystal structure of $Ru(bpy)_2(phen\text{-}dione)^{2+}$.

For EIS analysis, data simulations were carried out based on a simplified Randles circuit (Figure S2) with the software provided by Autolab.

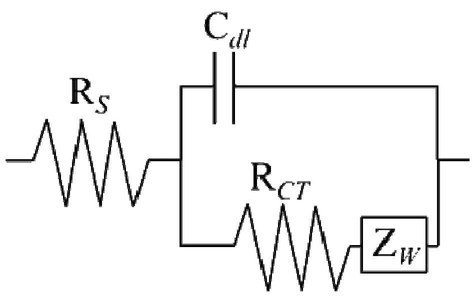


FIGURE S2: A simplified Randles ciruit used for EIS data fitting.

When APBA was diazotized in acidic $NaNO_2$ solutions and subsequently reduced by HOPG electrodes, STM showed that nanoscale films were formed and deposited on the electrodes. $Ru(bpy)_2(phendione)^{2+}$ could thus be adhered to the electrodes after the phendione ligand was reduced to the corresponding alcohol. The ratio of thickness of the APBA layer to the $Ru(bpy)_2(phendione)^{2+}$ film was roughly 1:2. Surface scratch experiments, Figure S3, confirmed the STM results. The thickness of the APBA film was 0.25 nm, and 0.38 nm, for the ruthenium layer.

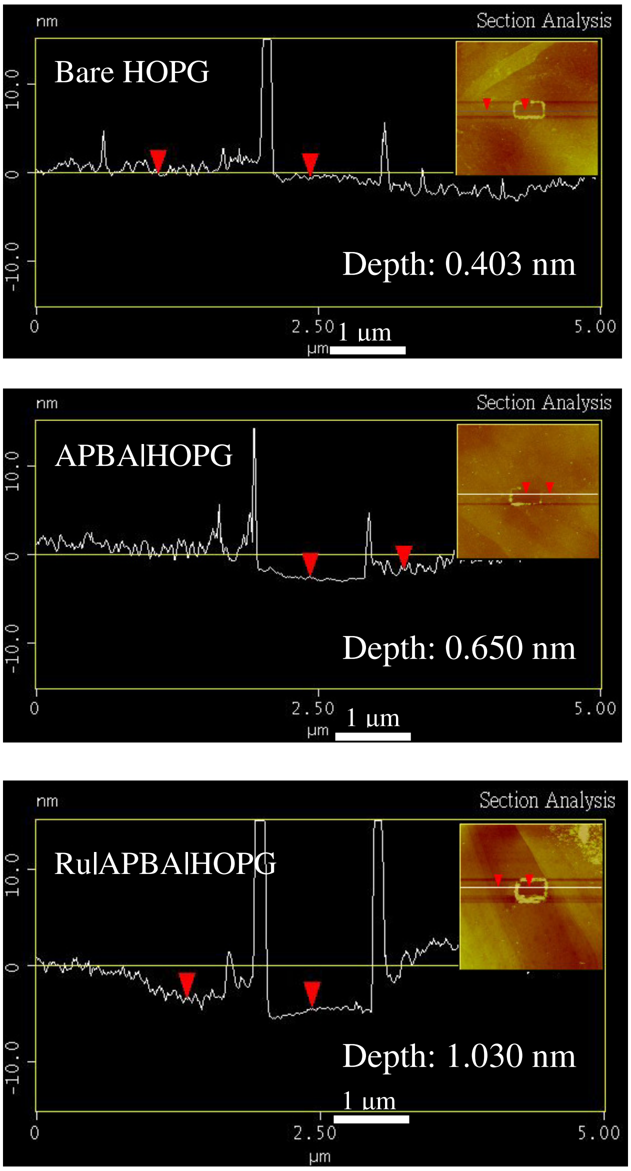


FIGURE S3: Surface scratching for bare HOPG, APBA|HOPG, and Ru|APBA|HOPG. Scan size: 5 µm × 5 µm; scratch size: 1 µm × 0.5 µm.

Phendione can form boronate ester with APBA after being reduced to phendiol. This reactivity was identified by in situ STM, in which the surface roughness (*r*) of the APBA-modified electrode increased significantly when the electrode potential (*E*) became more negative than 0 V vs. SCE. In contrast, trivial *r* was observed if APBA was excluded from the electrodes, as shown in Figure S4. The contrast indicates that APBA is an effective adhesive for $Ru(bpy)_2(phendiol)^{2+}$ to carbon substrates.

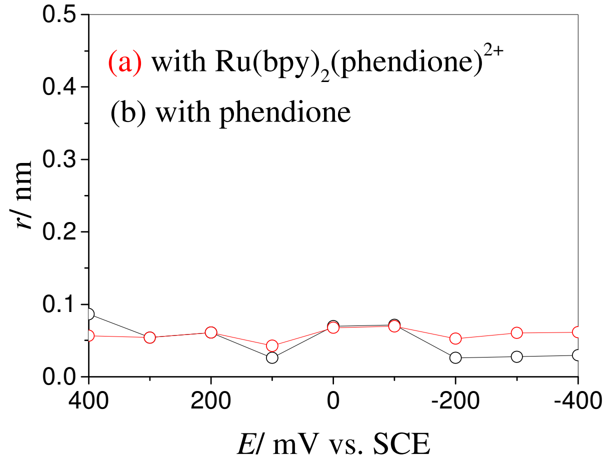
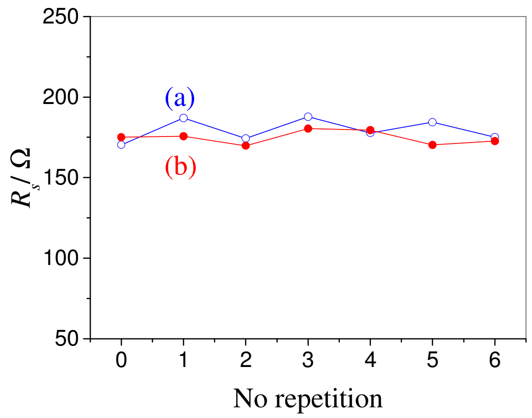


FIGURE S4: Correlations between the *r* of bare HOPG electrodes and *E* in the presence of 1 mM of $Ru(bpy)_2(phendione)^{2+}$ (a) or phendione (b).

EIS measurements for the R_{CT} of $Fe(CN)_6^{3-/4-}$ at the HOPG electrodes showed that the solution resistance (R_s), the double-layer capacitance (C_{dl}), and the Warburg impedance (Z_W) also changed systematically with the increase in the number of repetition of the electrodes being treated with APBA and the ruthenium complex, but in a minor way. The results are shown in Figure S5 for comparison.



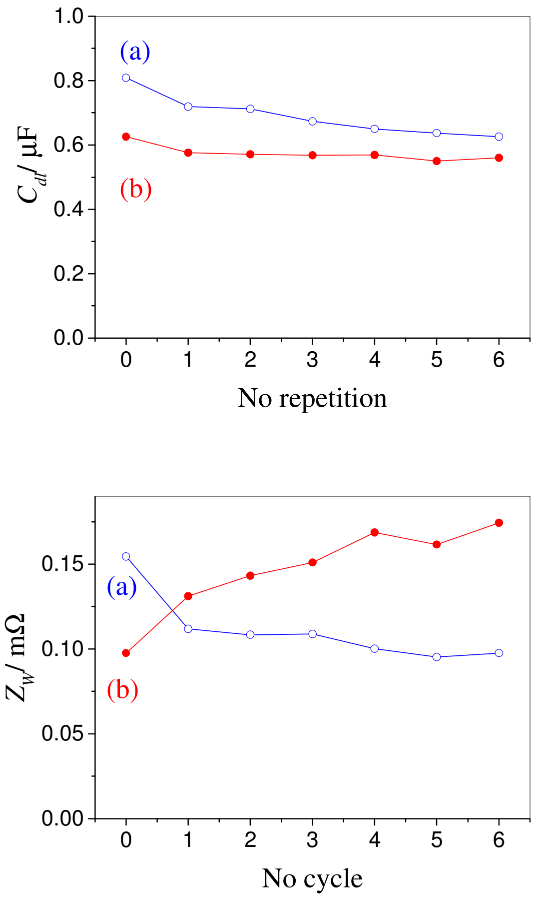


FIGURE S5: Correlations of R_s, C_{dl}, and Z_W with the number of repetitions (No.) of the HOPG electrode being treated with 1 mM APBA (a) and further with 1 mM of $Ru(bpy)_2(phendione)^{2+}$ (b).