1. Diamond Samples:
Two types of diamond samples were used. Electrochemical grade (“EC”) boron-doped diamond samples were purchased from Element VI Corporation. These samples are free-standing diamond substrates grown by chemical vapor deposition and boron-doped during growth; under the conditions of growth some non-diamond carbon is formed in the bulk, leaving the samples dark in appearance. All experiments in the main manuscript were performed using this type of diamond. A limited number of experiments (below) were also performed using boron-doped diamond thin films (BDDTF) (1.53 um thick) grown on highly doped p-type silicon substrates at the U.S. Naval Research Laboratory. Boron concentrations are estimated at ~ $10^{21}$ cm$^{-3}$ based upon the growth conditions used. We refer to these types of samples as “EC” diamond and “BDDTF”, respectively.

Fig. S1 shows a Raman spectrum of the EC grade diamond sample using 532 nm incident light. The sharp 1332 cm$^{-1}$ peak of diamond can be observed, along with additional broad peaks due to non-diamond (graphitic or amorphous) phases. Raman spectroscopy is highly sensitive to trace amounts of non-diamond carbon impurities, which gives rise to intense features at 1000-1600 cm$^{-1}$. The Raman cross-sections for graphitic and amorphous carbons are much stronger than those of diamond because they are resonantly enhanced by the $\pi-\pi^*$ electronic transitions of sp$^2$-hybridized carbon. The spectrum shown in Fig. S1 is similar to spectra reported previously from synthetic diamond produced by chemical vapor deposition methods. The hydrogen-termination process used in our studies (below) is also known to selectively remove graphite contamination, so that the amount of graphite at the surface of the diamond is expected to be significantly smaller than that in the bulk.

2. Surface functionalization of diamond:

Azide termination of diamond:
Diamond samples were hydrogen terminated prior to use by hydrogen plasma treatment in a manner similar to that developed by Thoms and co-workers. The diamond samples were exposed to a radio-frequency hydrogen plasma (~20 Watts) of pure hydrogen (20 Torr), while heating to ~800°C, for a period of approximately 30 minutes. XPS data (not shown) have established that this leaves the diamond samples terminated with C-H bonds. The resulting “hydrogen-terminated” diamond samples were removed from the vacuum system and covered with a layer of argon-purged 10-undecen-1-ol (Sigma Aldrich), covered with a fused silica
window, and illuminated with UV light (254 nm, ~10 mW/cm²) in a sealed cell under an argon atmosphere. The EC-grade bulk diamond and the BDDTF diamond graft at different rates; reaction times of 10-15 hours (EC grade) and ~ 4 hours (BDDTF) were used to achieve similar coverages of the 11-undecene-1-ol on the surfaces. After reaction the samples were sonicated in isopropanol and dried under N₂. To convert the alcohol-terminated surface into the mesylate, samples were placed in a solution containing 10 mL methylene chloride, 1 mL triethylamine, and 1 mL methane sulfonyl chloride. The samples were reacted for 1 h in an ice bath. After reaction, the samples were sonicated in methylene chloride and dried under N₂. Replacement of the mesylate intermediate with azide was accomplished by treating the samples overnight in a saturated solution of sodium azide in dry DMSO at 80°C.

“Click” Functionalization of Azide-Terminated Diamond Surfaces

The azide-modified diamond samples were immersed in a solution of 100 µM alkyne-complex with 0.8 mM Cu(II)(tris-(benzyltriazolyl-methyl)amine)SO₄ (TBTA) and 15 mM sodium ascorbate in a 3:1 (v:v) DMSO:H₂O mixture for 5 hours. The samples were sonicated in MeOH, CHCl₃, and isopropanol (IPA) for 30 seconds each and stored in isopropanol until further use.

3. Electrochemical Characterization methods:

Cyclic voltammetry measurements were performed using a three-electrode cell. The diamond samples were used as the working electrode with an exposed area of 0.275 cm² and a platinum wire was used as the counter-electrode. For measurements performed in aqueous electrolytes a Ag/AgCl reference electrode was used. For measurements performed in nonaqueous electrolytes a Ag/Ag⁺ reference electrode (0.01 M AgClO₄ in supporting electrolyte) was used. The Ag/Ag⁺ reference electrode was calibrated against a Ag/AgCl reference by direct potentiometric measurement; data reported in the main paper were corrected to compensate for this difference. The cell was capped to prevent evaporation over long periods of scanning. We also calibrated both reference electrodes against the ferrocene/ferrocinium couple by measuring E⁰ of this redox couple in each solvent. The resulting values of E⁰ were: 0.14 V vs. Ag/AgCl in 1M LiClO₄/H₂O, 0.052 V vs. Ag/Ag⁺ in 1M LiClO₄/Acetonitrile, and 0.035 V vs. Ag/Ag⁺ in 1M LiClO₄/propylene carbonate.

4. Spectroscopic Characterization methods:

4a. X-ray photoelectron spectroscopy (XPS) XPS data were obtained using a modified Physical Electronics system equipped with an aluminum Kα source, a quartz-crystal X-ray monochromator, and a 16-channel detector array. Surface coverage of ruthenium was determined using two methods, with equivalent results. In the first method, the Ru and C signals from the same sample are used. The Ru covered can then be estimated from the ratio of the Ru(3d₃/2) to C(1s) peaks according to:

\[
Ru(\text{atoms/cm}^2) = \frac{A_{\text{Ru}(3d_5/2)}}{A_{\text{C}(1s)}} \cdot \frac{S_{\text{C}(1s)}}{S_{\text{Ru}(3d_5/2)}} \cdot \rho_{\text{C,diamond}} \cdot IMFP_{\text{C,diamond}} \cdot \cos(45°)
\]

where \(A\) is the XPS peak area, \(S\) is the atomic sensitivity factor, \(\rho\) is the number density of carbon atoms in diamond, and \(IMFP\) is the inelastic mean free path of C(1s) photoelectrons in diamond (~2 nm). Since the Ru(3d₃/2) peak overlaps with the C(1s) peak, coverage was
estimated using only the Ru(3d$_{5/2}$) peak whose sensitivity factor was calculated to be 2.2 based on the 3:2 peak area ratio of the spin-orbit split pair.\textsuperscript{4,6} The $\cos(45^\circ)$ term compensates for the fact that electrons were collected at an angle of $45^\circ$ with respect to the surface normal. Since the Ru atoms are at the topmost surface, the Ru(3d) photoelectrons do not experience scattering; however, the underlying C(1s) photoelectrons do, and the factor of $\cos(45^\circ)$ is need to correctly calculate the effective number of C(1s) photoelectrons detected. Using a single sample minimizes errors arising from sample alignment, but makes the assumption that the C(1s) signals from the initial molecular layer and from the underlying diamond can be treated as being equivalent.

We also calculated the Ru coverage using a second approach using the Ru(3d) signal from a functionalized sample, but using the C(1s) signal from non-functionalized, H-terminated diamond. This approach requires careful placement of the samples to minimize any changes in C(1s) intensity due to changes in sample alignment with respect to the X-ray source and the input lens of the hemispherical analyzer. Both methods of calculation yielded the same coverage.

4b. \textit{Fourier-transform Infrared (FTIR) Spectroscopy}: FTIR spectra were collected using a Bruker Vertex 70 instrument in a single-bounce external-reflection geometry using p-polarized light at a 50° angle of incidence, with a liquid nitrogen-cooled HgCdTe detector. Clean, hydrogen-terminated samples were used for the background.

5. \textbf{XPS and FTIR Characterization of surface functionalization}:

5a. \textit{FTIR characterization of azide formation on diamond}:
One challenge in functionalization of the surfaces is making the azide-terminated surface. To demonstrate that the initial photochemical grafting to produce a hydroxyl-terminated surface is important to the overall functionalization scheme, we collected infrared spectra of samples after that azidization step, and a comparable sample that was treated in the same manner except that the initial photochemical grafting step was eliminated.

Figure S2 shows infrared spectra of two samples at intermediate stages of functionalization. One sample was functionalized with 10-undecen-1-ol as the first step, then mesylated and finally converted to the azide. The second sample was not functionalized by 10-undecene-1-ol but was otherwise treated in the same manner as the first. Only the first sample shows the 2090 cm$^{-1}$ vibrational mode that is characteristic of the azide group. The results demonstrate that formation of surface –OH groups is important to achieving azide functionalization of the diamond surface and that azide groups do not otherwise bind to the diamond surfaces.
5b. **XPS Characterization of “click” reaction:**

XPS spectra were obtained of the azide-modified diamond before and after the Cu-I-catalyzed azide-alkyne cycloaddition (CuAAC) (“click”) reaction. Fig. S3 shows spectra of the C(1s) and Ru(3d\textsubscript{5/2}) region (Fig. S3a), an enlarged view of the Ru(3d\textsubscript{5/2}) region (Fig. S3b), and the N(1s) region (Fig. S3c).

After the click reaction with the Ru(tpy)\textsubscript{2} complex, the C(1s) spectrum shows one main peak from the bulk diamond with a smaller shoulder at higher binding energy that arises from the molecular layer grafted to the surface. After exposure to the Ru(tpy)\textsubscript{2} complex under conditions optimized for the click reaction, a new peak is observed at lower binding energy, near 279-280 eV that arises from the photoemission from the 3d\textsubscript{5/2} level of the Ru atoms in the Ru(tpy)\textsubscript{2} complex. The corresponding Ru(3d\textsubscript{3/2}) spin-orbit component should occur ~ 4 eV higher in binding energy than the 3d\textsubscript{5/2} component, placing the 3d\textsubscript{3/2} component directly under the main C(1s) peak. Further confirmation that the CuAAC reaction was successful comes from the N(1s) spectra. Fig. S3c shows that the azide-modified diamond has three broad N(1s) features that correspond to the three N(1s) nitrogen atoms within the azide group, in agreement with the FTIR data presented above; the azide group is sensitive to electron damage and difficult to detect reliably by XPS. However, after the CuAAC reaction the N(1s) signal increases substantially in intensity, as expected from the N atoms within the terpyridine ligands.

Quantitative measurements of the Ru(3d\textsubscript{3/2}) and C(1s) peaks were made on several different samples to establish an average number density of grafted Ru(tpy)\textsubscript{2} molecules. Analysis of the Ru(3d\textsubscript{5/2}) peaks yields a typical surface coverage of $(6 \pm 1) \times 10^{13}$ molecules/cm\textsuperscript{2}. This value is in agreement with the electrochemical current measurements.
5c. Infrared characterization of CuAAC (“click”) reaction:
FTIR spectra were obtained of the diamond sample before and after the cycloaddition reaction. The azide group gives rise to a reasonably sharp feature near 2090 cm\(^{-1}\). Although the signal is weak (only \(\sim 10^{-4}\) absorbance units), it can be detected. After reaction, this peak is reduced in intensity by 70%, suggesting that \(\sim 70\%\) of the surface azide groups react during the cycloaddition step.

5d. Control samples for CuAAC reaction
Two control experiments were run in which the exposure to sodium azide was eliminated, with all other steps carried out normally. This study effectively compares the reactivity of the azide-
terminated diamond compared to that of the alcohol-terminated diamond when both are subjected to the CuAAC reaction conditions.

The XPS data below show that without the azide step, there is no evidence for Ru on the surface (left) and also no evidence for nitrogen. Since the Ru(tpy)$_2$ complex has 6 nitrogen atoms per molecule, the absence of any detectable nitrogen shows that the Ru(tpy)$_2$ complex does not have any detectable physisorption or other non-covalent bonding to the surface.

This result is further corroborated by electrochemical measurements examining the cyclic voltammograms of a sample in which the azide step was eliminated but all other steps carried out as normal. The resulting CV (Fig. S6 below) shows no evidence for a redox peak; the small separation between forward and reverse sweeps is due to the interfacial capacitance.
6. Cycling stability in acetonitrile: Cyclic voltammograms were obtained on Ru(tpy)$_2$-modified diamond surfaces in 1 M LiClO$_4$ in acetonitrile. Fig. S7 shows the changes that occur over 1 million cycles. The corresponding peak areas are presented as Figure 1c of the main paper. While the redox peak potential undergoes a shift during the experiment, the total area under the redox peaks remains nearly unchanged over the 1 million cycles. It is not known whether the shift arises from a change in the redox-active layers or whether it arises from changes in the semiconductor band-bending. Changes in band-bending might arise from partial oxidation of the diamond surface or other changes in the surface electronic structure.

7. Effect of cycling 1 million times on chemical composition:
We obtained XPS spectra of an electrochemical-grade diamond functionalized with the Ru(tpy)$_2$ complex before and after cycling for $10^6$ times in 1 M LiClO$_4$/acetonitrile, yielding the result shown in Fig. S8. Analysis of the Ru 3d$_{5/2}$ peaks yields a surface coverage of $(6 \pm 1) \times 10^{13}$ molecules/cm$^2$ before cycling and $(6.5 \pm 1) \times 10^{13}$ molecules/cm$^2$ after cycling. Thus, within the experimental error no significant changes are observed in the total N(1s) or O(1s) signals.

Figure S7. Cyclic voltammograms of Ru(tpy)$_2$ tethered to EC diamond in 1 M LiClO$_4$ in acetonitrile. CVs are shown after 1 cycle; 100,000 cycles; and 1,000,000 cycles. Analysis of the peak areas is shown in the main paper as Figure 1c.

Figure S8. XPS spectra of EC diamond sample before and after 1 million cyclic voltammograms in 1 M LiClO$_4$ in acetonitrile.
Similar experiments were performed in 1M LiClO$_4$/propylene carbonate, yielding the results shown in Fig. S9.

![XPS spectra of EC diamond sample before and after 1 million cyclic voltammograms in 1 M LiClO$_4$ in propylene carbonate.](image)

Figure S9. XPS spectra of EC diamond sample before and after 1 million cyclic voltammograms in 1 M LiClO$_4$ in propylene carbonate.

**8) Effect of cycling in aqueous solutions on electrochemical response and chemical composition:**
The electrochemical response of a Ru(tpy)$_2$-modified electrochemical grade diamond was measured for $10^6$ cycles in 1 M LiClO$_4$ in water. Fig. S10 shows the electrochemical response. The sample exhibits excellent stability for at least $5 \times 10^5$ cycles, but undergoes some slow degradation at more extended times.

![Cathodic peak area during $10^6$ cyclic voltammograms of Ru(tpy)$_2$-modified EC diamond.](image)

Figure S10: Cathodic peak area during $10^6$ cyclic voltammograms of Ru(tpy)$_2$-modified EC diamond.
XPS data were obtained before and after cycling to identify any chemical changes that occurred in the sample. XPS spectra before and after show that the loss in electrochemical activity is accompanied by reduction in the amount of Ru on the surface. There is also a small shift toward lower binding energy for both the Ru(3d$_{5/2}$) and N(1s) features after cycling. These observations demonstrate that there is partial loss of the ligands after extended cycling in water. Because the N(1s) peak arises from unreacted azide groups, the triazole linkage, and the (tpy) groups of the ligand, the signal-to-noise ratio of the experiment is not sufficient to determine whether there is loss of the initial functionalization layer or loss of only the Ru(tpy) moieties.

9. Electrochemical stability on boron-doped diamond thin film:
To establish that the outstanding stability of the electrochemical grade diamond is not unique to this specific type of diamond, we also performed a more limited number of experiments using boron-doped diamond thin films grown by chemical vapor deposition at the U.S. Naval Research Laboratory. These samples were functionalized as described above. Fig. S12 shows cyclic voltammograms of the tethered Ru(tpy)$_2$ complex on boron-doped diamond thin films, measured in 1 M LiClO$_4$ in acetonitrile. The samples once again show excellent stability.
Figure S12: Left: Cyclic voltammograms of Ru(tpy)$_2$ tethered to boron doped diamond electrodes obtained in 1 M LiClO$_4$ in acetonitrile. Right: The anodic peak area as a function of the number of CV cycles for the same sample.

References for Supporting Information: