Supporting Information

Electrochemical Characterization and Catalytic Application of Gold-Supported Ferrocene-Containing Diblock Copolymer Thin Films in Ethanol Solution

Govinda Ghimire,[†] Herman Coceancigh,[†] Yi Yi,[§] and Takashi Ito[†,*]

[†] Department of Chemistry, Kansas State University, 213 CBC Building, Manhattan, Kansas 66506-0401, USA

[§] Department of Chemistry, Indiana University, 800 E Kirkwood Ave, Bloomington, IN 47405 USA.

* To whom correspondence should be addressed.

Email: ito@ksu.edu

This Supporting Information provides a schematic illustration of an electrochemical cell employed in this study (**Figure S1**), AFM phase images (1 x 1 μm^2) of a thin film of PS_{154}-*b*-$PAEFc_{12}$ (f_{PAEFc} = 0.17; 38 nm thick) before and after electrochemical measurements in the MeCN and EtOH solutions (**Figure S2**), AFM phase images (1 x 1 μm^2) of a thin film of PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 38 nm thick) before and after immersion in the MeCN and EtOH solutions (**Figure S3**), plots of logi_p vs log$v$ obtained at the films that gave the voltammograms shown in **Figure 3** (**Figure S4**), ^{1}H-NMR spectra of the reaction mixtures of MVK and E2OC upon no potential application to electrodes coated with activated thin films of (a) PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 64 nm thick) and (b) PS_{154}-*b*-$PAEFc_{12}$ (f_{PAEFc} = 0.17; 65 nm thick) at Day 0 and Day 3 (**Figure S5**), ^{1}H-NMR spectra shown in **Figure 5** with the integrations of the peak areas for **5d** and **5** protons (**Figure S6**), reaction yields for PS_{154}-*b*-$PAEFc_{26}$ and PS_{154}-*b*-$PAEFc_{12}$ estimated from the **5d** and **5** proton signals in ^{1}H-NMR spectra (**Figure S7**), and ^{1}H-NMR spectra of the reaction mixtures of MVK and E2OC upon potential application of +0.31 V (Day 1), -0.20 V (Day 2) and +0.31 V (Day 3) to an electrode coated with a thin film of PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 38 nm thick) and the reaction yields as a function of reaction time (**Figure S8**).

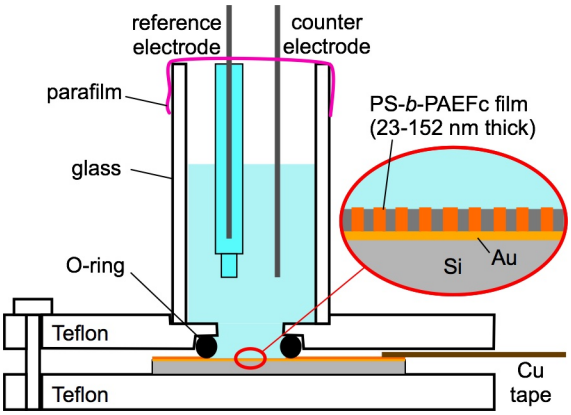

Figure S1. Schematic illustration of an electrochemical cell employed in this study. For the catalysis experiments, the upper opening of the glass tube was sealed by parafilm.

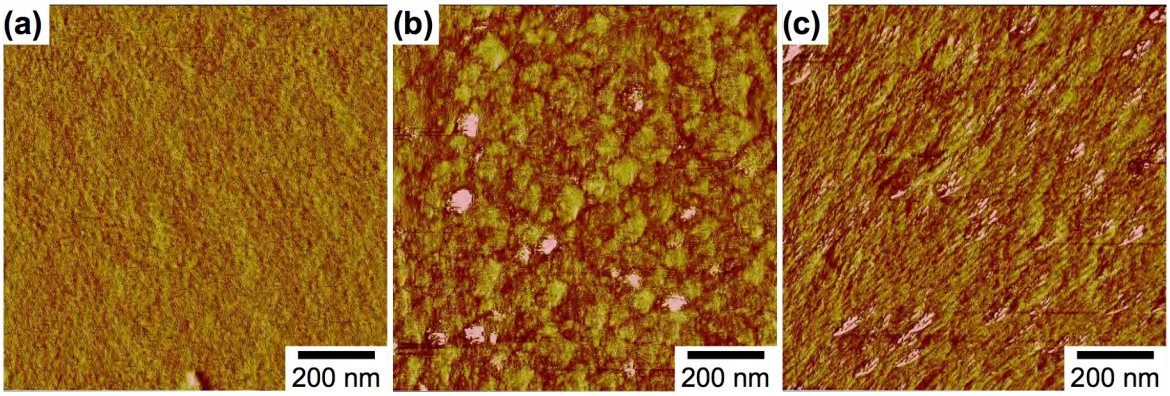

Figure S2. AFM phase images (1 x 1 μm^2) of a thin film of PS_{154}-*b*-$PAEFc_{12}$ (f_{PAEFc} = 0.17; 38 nm in ellipsometric thickness). (a) Pristine, (b) after electrochemical experiments in 0.1 M $TBAPF_6$/MeCN, and (c) after electrochemical experiments in 0.1 M $NaPF_6$/EtOH.

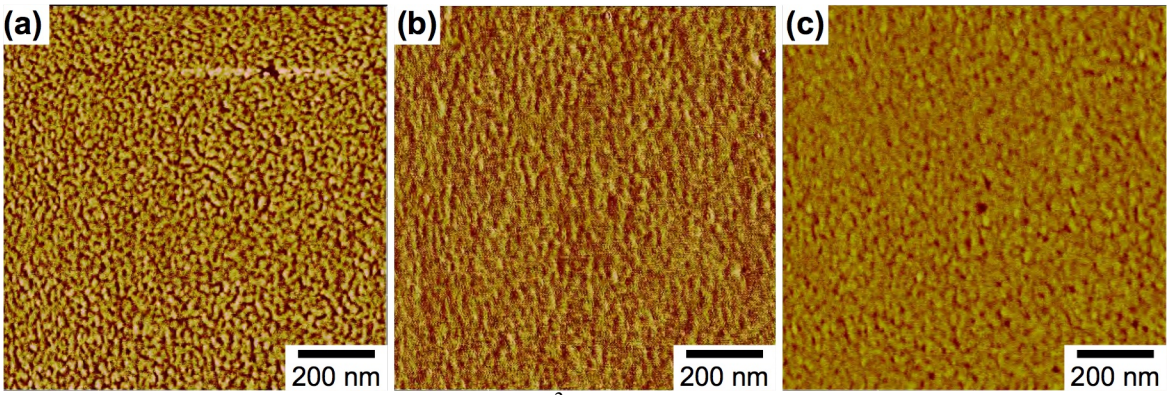

Figure S3. AFM phase images (1 x 1 μm^2) of a thin film of PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 38 nm in ellipsometric thickness). (a) Pristine, (b) after immersion in 0.1 M $TBAPF_6$/MeCN, and (c) after subsequent immersion in 0.1 M $NaPF_6$/EtOH with no potential application.

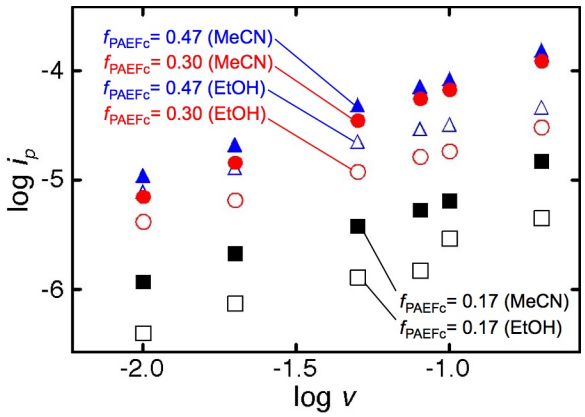

Figure S4. Plots of logi_p vs log$v$ (i_p: anodic peak current; v = 0.01 ~ 0.2 V/s, where voltammograms of surface-confined species were observed in 0.1 M TBAPF$_6$/MeCN) obtained at the samples that gave the voltammograms shown in **Figure 3**. The slopes are 0.88 (in MeCN; filled blue triangles) and 0.58 (in EtOH; open blue triangles) for PS$_{154}$-*b*-PAEFc$_{51}$ (f_{PAEFc} = 0.47), 0.96 (in MeCN; filled red circles) and 0.66 (in EtOH; open red circles) for PS$_{154}$-*b*-PAEFc$_{26}$ (f_{PAEFc} = 0.30), and 0.79 (in MeCN; filled black squares) and 0.78 (in EtOH; open black squares) for PS$_{154}$-*b*-PAEFc$_{12}$ (f_{PAEFc} = 0.17).

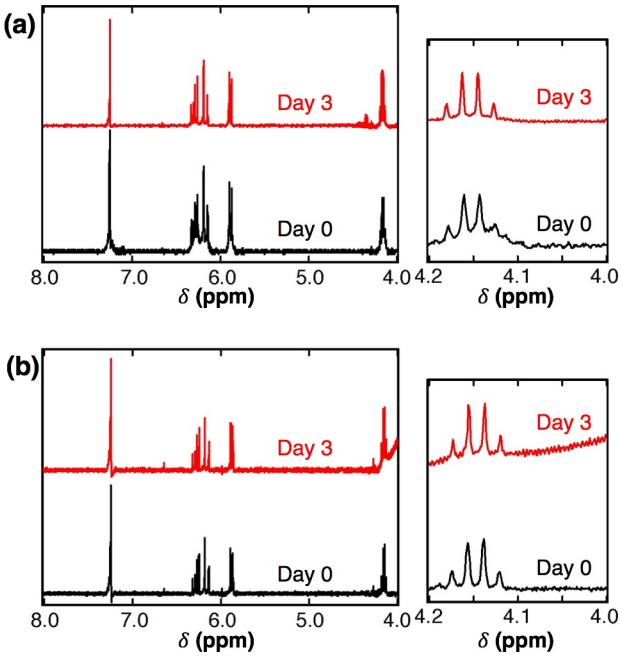

Figure S5. ^{1}H-NMR spectra (4.0–8.0 ppm) of the reaction mixtures of MVK and E2OC upon no potential application to electrodes coated with activated thin films of (a) PS$_{154}$-*b*-PAEFc$_{26}$ (f_{PAEFc} = 0.30; 64 nm thick) and (b) PS$_{154}$-*b*-PAEFc$_{12}$ (f_{PAEFc} = 0.17; 65 nm thick) at Day 0 and Day 3. The solutions consisted of (a) 1.1 M MVK and 0.36 M E2OC in 0.1 M NaPF$_6$/EtOH and (b) 1.0 M MVK and 0.35 M E2OC in 0.1 M NaPF$_6$/EtOH. The magnified spectra at 4.0–4.2 ppm are also shown (right).

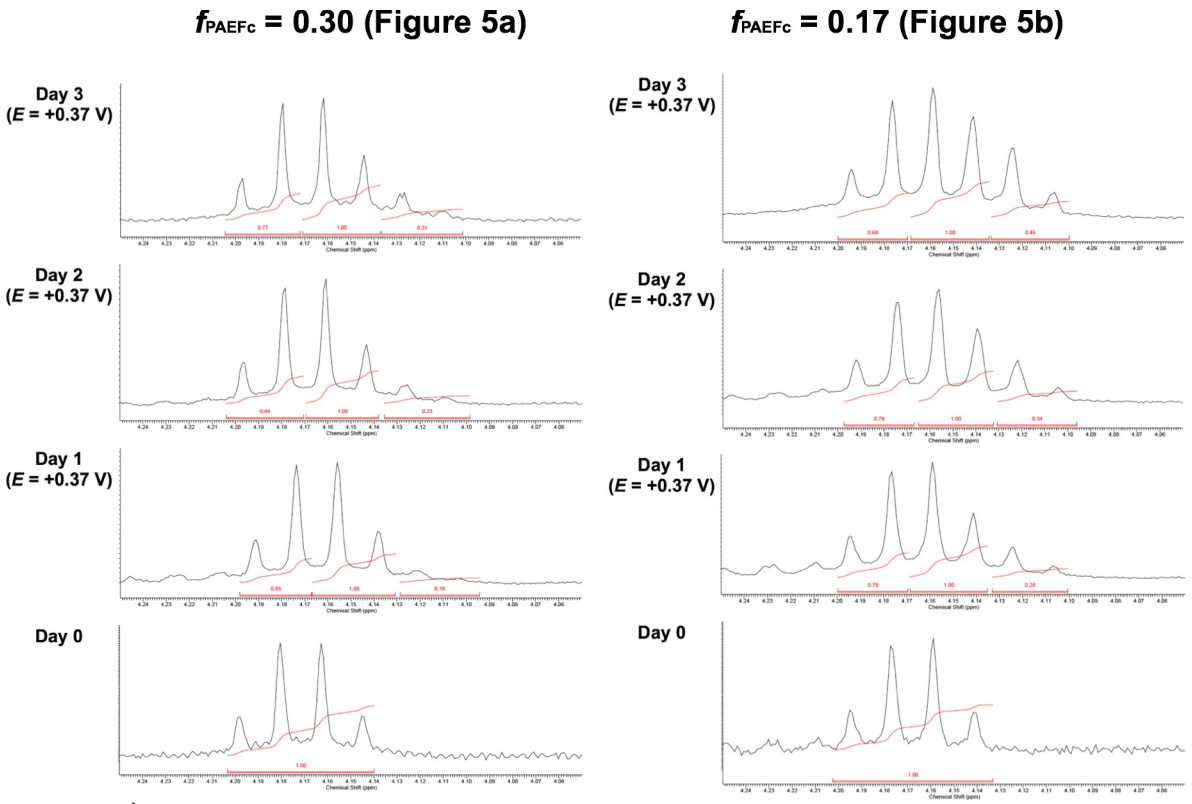

Figure S6. ^{1}H-NMR spectra (4.05–4.25 ppm) shown in **Figure 5** with the integrations of the peak areas for **5d** and **5** protons.

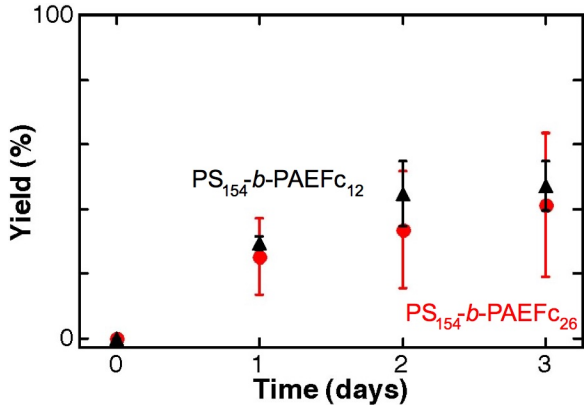

Figure S7. Reaction yields (average ± standard deviation; measured from three different samples for each PS-*b*-PAEFc) for MVK and E2OC measured at PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 54-64 nm thick; red circles) and PS_{154}-*b*-$PAEFc_{12}$ (f_{PAEFc} = 0.17; 65-80 nm thick; black triangles) as a function of reaction time. The reaction mixtures consisted of 1.0~1.1 M MVK and 0.35~0.36 M E2OC in 0.1 M $NaPF_6$/EtOH. A potential of +0.37 V vs Ag/Ag^+ was applied during the reaction. ^{1}H-NMR spectra including the integrations of the peak areas for **5d** and **5** protons, corresponding to those in **Figure 5ab**, are given in **Figure S6**.

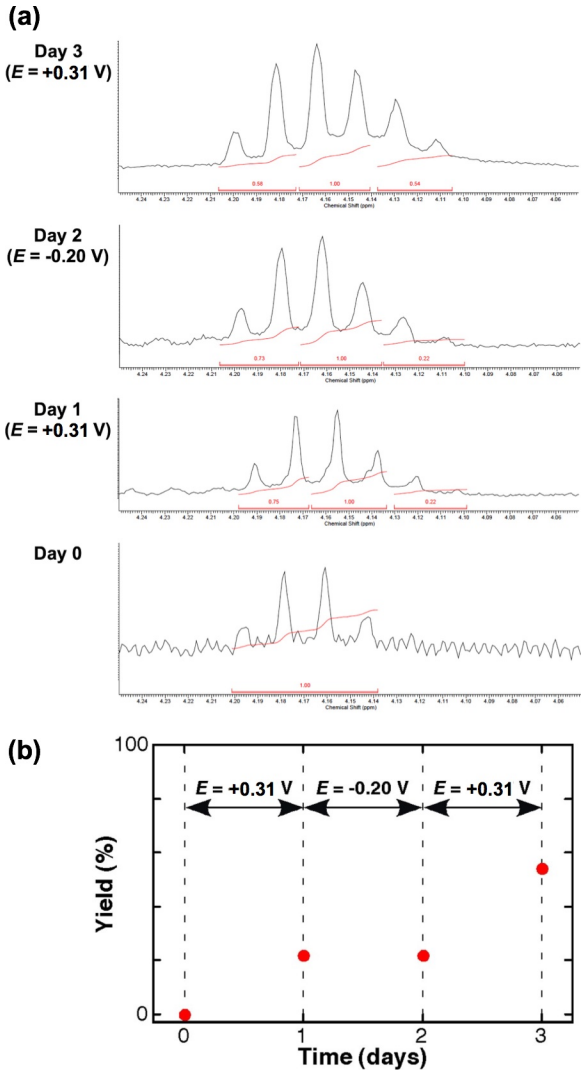

Figure S8. (a) ^{1}H-NMR spectra of the reaction mixtures of MVK and E2OC before and after potential application of +0.31 V (Day 1), -0.20 V (Day 2) and +0.31 V (Day 3) to a gold electrode coated with an activated thin film of PS_{154}-*b*-$PAEFc_{26}$ (f_{PAEFc} = 0.30; 38 nm thick). (b) The reaction yield as a function of reaction time obtained from the ^{1}H-NMR spectra shown in (a).