# Molecular Strategies to Modulate the Electrochemical Properties of P-Type Si(111) Surfaces Covalently Functionalized with Ferrocene and Naphthalene Diimide

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#### 1. General Aspects, Materials and Instrumentation

Air sensitive materials were handled inside a Braun Labmaster DP glove box. Standard Schlenk techniques were used to carry out reactions that are air-sensitive. Unless otherwise mentioned, all the chemicals were used as received from commercial sources. For instance, tetrabutylammonium fluoride, i.e., TBAF, in the form of 1 M solution in THF (Sigma-Aldrich), ferrocenecarboxylic acid (Chem-Impex), 4-ethynylbenzyl alcohol (Santa Cruz Biotechnology), N-ethyl-N'-(3-dimethylaminopropyl)carbodiimide hydrochloride, i.e., EDCI *N*,*N*,*N*',*N*'-tetramethyl-*O*-(1*H*-benzotriazol-1-yl)uronium (Chem-Impex), hexafluorophosphate, i.e., HBTU (TCI Chemicals), 4-(dimethylamino)pyridine (Chem-Impex), tetramethylfluoroformamidinium hexafluorophosphate, i.e., TFFH (TCI Chemicals), 1,7-octadiyne (TCI Chemicals), 2-azidoethanol (Toronto Research Chemicals), anhyd CuSO<sub>4</sub> (Acros Organics), sodium L-ascorbate (TCI Chemicals), etc. were used as received without any further purification whatsoever. Conc. H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub> were purchased from VWR. Hydrofluoric acid (48 wt% in H<sub>2</sub>O, >99.99% trace metals basis) was obtained from Sigma-Aldrich. All of the organic solvents (HPLC grade) employed for synthesis and purification via column chromatography were purchased from VWR; they were, namely, n-hexane, ethyl acetate, toluene, tetrahydrofuran (THF), dichloromethane (DCM), N,N-dimethylformamide (DMF), acetonitrile (MeCN), methanol (MeOH), ethanol (EtOH), water, etc. Anhyd THF was prepared by distillation over Na/benzophenone under Ar. Toluene, DCM, DMF, MeCN and N,N-diisopropylethylamine, i.e., Hünig's base (Sigma-Aldrich) were dehydrated by distillation over anhyd calcium hydride (Strem Chemicals) under Ar and stored over activated molecular sieves in Schlenk round bottom flasks prior to using. Column chromatography was carried out on the bench top using silica gel (VWR, 70-90 µm). Solution-state photolysis reactions were carried out using a Rayonet photochemical reactor (Model: RMR-600; Southern New England Ultraviolet Company) fitted with 8 (each of 35 W) UV lamps ( $\lambda =$ 254 nm). IR spectra were obtained on a Perkin Elmer Frontier FTIR instrument. NMR spectra were recorded on an Advance Bruker 400 MHz spectrometer using CDCl<sub>3</sub> as the solvent (Cambridge Isotope Laboratories, Inc.) and referenced in ppm with respect to TMS using the residual CDCl<sub>3</sub> signal as the internal reference. Mass spectra were recorded on a MicroQ-TOF ESI mass spectrometer. Room temperature (rt) refers to 25 °C. The synthesis of 1,2diazidoethane<sup>1</sup> and bis(2-(N,N-dimethylamino)ethyl)-substituted NDI (4)<sup>2</sup> was accomplished according to the literature-reported procedures.

#### 2. Synthetic Procedures and Characterization Data

#### Synthesis of ((4-Ethynylbenzyl)oxy)triisopropylsilane (1)

This compound was synthesized according to the literature-reported procedure in three steps as described below.<sup>3</sup>



**Step 1: Synthesis of ((4-Iodobenzyl)oxy)triisopropylsilane (B).**<sup>3</sup> The synthesis of **B** was accomplished by silylation of 4-iodobenzyl alcohol (A) with triisopropylsilyl chloride (TIPSCI) in the presence of imidazole.

In a typical procedure, a mixture of A (5.0 g, 21.36 mmol) and imidazole (1.745 g, 25.63 mmol) in dry DCM (200 mL) was stirred under Ar gas atmosphere at 0 °C. To this stirred reaction mixture, TIPSCl (4.94 g, 5.5 mL, 25.63 mmol) was added dropwise to give a milky white suspension. The contents were then stirred at rt for 12 h and subsequently quenched with water. The organic layer was extracted with DCM ( $3 \times 60$  mL), dried over anhyd Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure to obtain crude product as a colorless oil. Crude purification using silica gel column chromatography (short-pad filtration column, 10% DCM in hexane as the mobile phase) afforded the pure product as a colorless oil in 84% yield (7.0 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.08-1.14 (m, 21 H), 4.80 (s, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.67 (d, 2H, *J* = 8.0 Hz).

**Step 2: Synthesis of Triisopropyl((4-((trimethylsilyl)ethynyl)benzyl)oxy)silane (C).**<sup>3</sup> This compound was accessed by the Sonogashira cross coupling of **B** with trimethylsilylacetylene under Pd(II)-catalyzed condition. A representative synthetic procedure is described below.

To a mixture of **B** (0.79 g, 2.02 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.142 g, 0.202 mmol) and CuI (0.038 g, 0.202 mmol) contained in a Schlenk tube (100 mL), dry and deoxygenated THF (20 mL) and NEt<sub>3</sub> (20 mL) was added via cannulation under Ar gas atmosphere. To this stirred reaction mixture, trimethylsilylacetylene (0.396 g, 0.56 mL, 4.04 mmol) was added dropwise at rt and stirred at rt under Ar for 12 h, exhibiting a color change of orange-yellow to red and eventually to brownish-black. The reaction mixture was filtered through a short pad of celite and the black precipitate was washed with ethyl acetate (10 mL). The combined, filtered organic layer was evaporated under reduced pressure to obtain a crude material which, upon subjection to silica gel column chromatography (5% DCM in hexane as the mobile phase), yielded the pure product as a colorless oil in 83% yield (0.605 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  0.26 (s, 9H), 1.08-1.22 (m, 21 H), 4.83 (s, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H). ESI-MS<sup>+</sup> m/z Calcd for C<sub>21</sub>H<sub>36</sub>OSi<sub>2</sub>Na 383.2202 [M+Na]<sup>+</sup>, found 383.2201.

**Step 3: Synthesis of ((4-Ethynylbenzyl)oxy)triisopropylsilane (1).**<sup>3</sup> Synthesis of 1 was accomplished by deprotection of the trimethylsilyl moiety in **B** under mild basic condition.

In a typical procedure, to a solution of **B** (0.35 g, 0.97 mmol) in a solvent mixture (30 mL) of THF/MeOH (1:9, v/v), solid K<sub>2</sub>CO<sub>3</sub> (6.7 g, 48.52 mmol) was added and the reaction mixture was stirred at rt for 12 h, before solvent evaporation under reduced pressure. The dried contents were extracted with 100 mL of water with DCM (3 × 15 mL), dried over anhyd Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure to give the crude product as a colorless oil. The oil was purified by silica gel column chromatography (short-pad filtration column, hexane as the mobile phase), giving the pure product as a colorless oil (0.272 g, 97%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.16-1.27 (m, 21 H), 3.07 (s, 1H), 4.89 (s, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H). ESI-MS<sup>+</sup> m/z Calcd for C<sub>18</sub>H<sub>28</sub>OSiNa 311.1807 [M+Na]<sup>+</sup>, found 311.1813.

#### Synthesis of 4-Ethynylbenzyl Ferrocene Carboxylate (2)

This ester was synthesized by the esterification of ferrocene carboxylic acid (Fc-CO<sub>2</sub>H) with 4-ethynylbenzyl alcohol (EBA) in the presence of *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) as the esterifying agent and 4-(dimethylamino)pyridine (DMAP) as the base, according to the route shown below.



In a typical procedure, a mixture of Fc-CO<sub>2</sub>H (0.870 g, 3.78 mmol), EDCI (1.451 g, 7.57 mmol) and DMAP (2.31 g, 18.90 mmol) in dry THF (40 mL) was stirred at rt under Ar gas atmosphere for 1 h. Subsequently, a solution of EBA (0.5 g, 3.78 mmol) in dry THF (15 mL) was added dropwise and the resulting mixture was stirred at rt under Ar for 1 d and gave a white precipitate. The precipitate was removed after filtration and washing with THF and the resulting filtrate was dried to give an orange residue which was dissolved in DCM (30 mL). Subsequently, this DCM solution was washed with water and the organic layer was extracted with DCM ( $3 \times 15$  mL). The combined organic layer was dried over anhyd Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated under reduced pressure to obtain a crude orange solid. The latter was purified by silica gel column chromatography (8% ethyl acetate in hexane as the mobile phase) to give rise to the pure product as a crystalline orange-yellow solid in quantitative yield (1.25 g, 96%). IR (neat solid) cm<sup>-1</sup> 3268, 1695, 1461, 1270, 1128; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.08 (s, 1H), 4.12 (s, 5H), 4.40 (s, 2H), 4.83 (s, 2H), 5.25 (s, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 8.0 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  65.22, 69.68, 70.15, 71.40, 77.60, 83.26, 121.91,128.04, 132.26, 137.31, 171.39; ESI-MS<sup>+</sup> m/z Calcd for  $C_{20}H_{16}O_2FeNa 367.0397 [M+Na]^+$ , found 367.0382.

#### Synthesis of 2-Azidoethyl Ferrocene Carboxylate (3)

This ester was synthesized by the esterification of ferrocene carboxylic acid (Fc-CO<sub>2</sub>H) with 2-azidoethanol (Az-EtOH) in the presence of *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) as the esterifying agent and 4-(dimethylamino)pyridine (DMAP) as the base, according to the route shown below.



The synthetic procedure was carried out in the same manner as that of **2**. In a typical procedure, the following reaction scale was employed for the synthesis of **3**: Fc-CO<sub>2</sub>H (1.0 g, 4.35 mmol), EDCI (1.67 g, 8.70 mmol), DMAP (2.66 g, 21.75 mmol), Az-EtOH (0.379 g, 0.33 mL, 4.35 mmol) and dry THF (50 mL). Usual work up, as mentioned above, followed by purification of the crude material using silica gel column chromatography (8% ethyl acetate in hexane as the mobile phase) led to the pure product as crystalline orange-yellow solid in nearly quantitative yield (1.22 g, 94%). IR (neat solid) cm<sup>-1</sup> 2100, 1704, 1456, 1260, 1132; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.54 (t, *J* = 4.0 Hz, 2H), 4.23 (s, 5H), 4.40 (t, *J* = 4.0 Hz, 2H), 4.42 (s, 2H), 4.84 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  50.08, 62.99, 69.83, 70.25, 71.56, 171.48; ESI-MS<sup>+</sup> m/z Calcd for C<sub>13</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub>Fe 299.0357 [M]<sup>+</sup>, found 299.0378.

#### Synthesis of Alkyne-Substituted NDI (5)

The alkyne-substituted NDI **5** was synthesized by mono-quaternization of the bis(2-(N,N-dimethylamino)ethyl)-substituted NDI **4** with propargyl chloride according to the route shown below. NDI **4** was prepared by a literature-reported procedure.<sup>2</sup>



In a typical experiment, **4** (3.0 g, 7.35 mmol) was dissolved in 90 mL of anhydrous CHCl<sub>3</sub> under Ar gas atmosphere. To this solution, propargyl chloride (0.48 mL, 6.61 mmol) was added and the reaction mixture was stirred at 50 °C overnight under Ar. Subsequently, the reaction mixture was cooled to rt and the resulting precipitate was filtered and washed with DCM. This crude product was purified by dissolving in DMF and re-precipitating using diethyl ether. The precipitate was then filtered and dried under vacuum to give rise to pure **5** as a dark yellow solid in 26% yield (0.84 g). IR (neat solid) cm<sup>-1</sup> 3230, 1700, 1658, 1583, 1455, 1332, 1250, 1160, 1048; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  0.86 (s, 6H), 1.23 (t, *J* = 6.6 Hz, 2H), 1.78-1.80 (m, 2H), 1.88 (s, 6H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.83 (t, *J* = 6.6 Hz, 2H), 3.01 (s, 1H), 3.16 (t, *J* = 7.0 Hz, 2H), 7.19-7.28 (m, 4H); <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>OD)  $\delta$  35.37, 39.21, 45.93, 51.71, 55.93, 57.79, 61.82, 71.86, 72.30, 83.76, 127.52, 128.03, 128.44, 131.80, 132.18, 164.36, 164.43; ESI-MS<sup>+</sup> m/z Calcd for C<sub>25</sub>H<sub>27</sub>N<sub>4</sub>O<sub>4</sub> 447.2032 [M]<sup>+</sup>, found 447.2064.

#### 3. Tapping Mode AFM Images and Surface Roughness Data

The tapping mode AFM images were recorded for all functionalized Si surfaces using a Digital Instruments Dimension 3100 microscope (located at the Dr. John T. Macdonald Foundation BioNIUM Institute in the University of Miami). The microscope was operated with 'Nanoscope 6' controller. The AFM images were collected under air at rt using tapping mode silicon tips (n-type, tip radius < 10 nm, f = 43-81 kHz, k = 0.6-3.7 N/m) obtained from AppNano (FORTA-10). Typical scan rate was 0.8 Hz. The data were analyzed using Gwyddion software (version 2.51).



**Figure S1.** Tapping mode AFM image of the **Si-BnE** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



**Figure S2.** Tapping mode AFM image of the **Si-BnA** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



Figure S3. Tapping mode AFM image of the Si-Fc@2 surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



**Figure S4.** Tapping mode AFM image of the **Si-Oct** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



**Figure S5.** Tapping mode AFM image of the **Si-Fc@4** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



**Figure S6.** Tapping mode AFM image of the **Si-Az** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.



**Figure S7.** Tapping mode AFM image of the **Si-NDI@5** surface. The area on the AFM image marked with the blue square was probed to analyze the cross-section profile of the surface which is shown at the bottom. The  $R_q(RMS)$  calculated for the cross-section profile is also shown in the profile; the standard deviation for the  $R_q(RMS)$  data is based on at least 3 independent measurements.

## 4. XPS Characterization Data

XPS data was collected on a Kratos Axis Ultra DLD system with a monochromatic Al K $\alpha$  source and a base pressure of ca. 6 \*10<sup>-9</sup> torr. Survey and high resolutions scans were obtained at pass energies of 80 and 20 eV, respectively. A charge neutralizer was used for charge compensation, and all data was corrected to the C 1s peak at 284.6 eV.

#### 4.1. Representative High Resolution XPS Spectra



**Figure S8.** High resolution XPS spectra (blue), deconvoluted spectra (red), and sum (dashed green) of the pre-functionalized Si surface **Si-BnA**. (A) C 1s area. The high-energy peak centered at 288.6 eV is assigned to C=O bonds formed by the oxidation of benzylic alcohol. The contributions at 286.0 eV and 284.6 eV are ascribed to C-O and C-C bonds, respectively. (B) O 1s area. (C) Si 2p area that underscores the formation of SiO<sub>x</sub> as evidenced by the peak centered at 102.5 eV.



**Figure S9.** High resolution XPS spectra (blue), deconvoluted spectra (red), and sum (dashed green) of the Fc-functionalized surface **Si-Fc@2**: (A) C 1s area; the high-energy peak centered at 288.5 eV is assigned to C=O bonds, the contributions at 286.24 eV, and 284.6 eV are ascribed to C-O, and C-C bond, respectively. (B) O 1s area. (C) Si 2p area of **Si-Fc@2** that underscores the formation of SiO<sub>x</sub> as evidenced by the peak centered at 102.5 eV. (D) Fe 2p area of **Si-Fc@2** that shows two spin-orbit split components 1/2 and 3/2 centered at 725.8 eV and 711.7 eV, respectively.



**Figure S10.** High resolution XPS spectra (blue), deconvoluted spectra (red), and sum (dashed green) of the Fc-functionalized surface **Si-Fc@3**: (A) C 1s area; the high-energy peak centered at 288.6 eV is assigned to C=O bonds, the contributions at 286. 4 eV, and 284.7 eV are ascribed to C-O, and C-C bond, respectively. (B) N 1s area. The deconvolution into two Gaussian functions centered at 401.9 eV and 400.1 eV confirms the presence of two chemically distinct nitrogen atoms. (B) O 1s area. (C) Si 2p area of **Si-Fc@3** that underscores modest formation of SiO<sub>x</sub> as evidenced by the peak centered at 102.5 eV. (D) Fe 2p area of **Si-Fc@3** that shows two spin-orbit split components 1/2 and 3/2 centered at 720.1 eV and 707.7 eV, respectively.

#### 4.2. Qualitative Elemental Analysis

Exploiting the high-resolution XPS spectra shown in Section 4.1 and applying a relative sensitivity factor (RSF), the ratio of Fe and <u>C</u>=O was estimated for **Si-Fc@1-4**. The atomic concentration of <u>C</u>=O was calculated using the area of the deconvoluted spectra centered at 288.6 eV and the total atomic concentration of C 1s can be found in the table below summarizing the atomic concentration (corrected with relative sensitivity factor RSF) for relevant atoms. For example, using the deconvolution curves shown in Figure 2B, one can estimate the area of the <u>C</u>=O (288.6 eV, area = 811), C-O (286.4 eV, area = 869), and C-C (284.6 eV, area = 3371) curves. The area of the carbon double bond oxygen peak is 16.05% of the total C 1s peak area, resulting in an atomic concentration of C=O of 4.6% in the table below. Comparing the atomic concentration of C=O with that of Fe provides a means to estimate the ratio of Fe:<u>C</u>=O. This procedure has been applied to surfaces **Si-Fc@1-4**.

## Analysis for Si-Fc@1:

State : Angle N	Name : 16_	1						
Peak	Туре	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	Comp	288.678	1.543	5222.4	0.278	12.011	28.62	17.39
0 1s	Reg	532.131	1.616	17707.0	0.780	15.999	31.94	25.85
Si 2p	Reg	99.031	0.963	7939.8	0.328	28.086	38.92	55.30
Fe 2p	Reg	711.431	2.524	1150.2	2.957	55.846	0.52	1.46

Considering that the atomic concentration of C=O is 4.6%, an estimated ratio of 1:9 for Fe:<u>C</u>=O characterizes **Si-Fc@1**. It is fair to assume that the overestimation of C=O may stem from adsorption of carbon-derived contaminants on the surface such as  $CO_2$ .

## Analysis for Si-Fc@2:

Peak	Туре	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	Comp	288.501	1.537	4540.6	0.278	12.011	26.66	15.91
0 1s	Reg	532.238	1.593	16287.4	0.780	15.999	31.47	25.02
Si 2p	Reg	99.138	0.932	7889.9	0.328	28.086	41.42	57.82
Fe 2p	Reg	711.438	1.510	941.3	2.957	55.846	0.45	1.26

Considering that the atomic concentration of C=O is 4.8%, an estimated ratio of 1:11 for Fe:<u>C</u>=O characterizes **Si-Fc@2**. It is fair to assume that the overestimation of C=O may stem from adsorption of carbon-derived contaminants on the surface such as  $CO_2$ .

## Analysis for Si-Fc@3:

Peak	Туре	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C ls	Comp	288.431	1.776	3749.2	0.278	12.011	26.56	15.52
O ls Si 2p Fe 2p	Reg Reg Reg	532.032 99.032 711.132	1.669 0.958 1.074	11951.2 7135.6 630.7	0.780 0.328 2.957	15.999 28.086 55.846	27.86 45.21 0.37	21.69 61.79 0.99

Considering that the atomic concentration of C=O is 3.1%, an estimated ratio of 1:8 for Fe:<u>C</u>=O characterizes **Si-Fc@3**. It is fair to assume that the overestimation of C=O may stem from adsorption of carbon-derived contaminants on the surface such as  $CO_2$ ..

#### Analysis for Si-Fc@4:

Peak	Туре	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc %
C 1s	Comp	288.496	1.622	5764.5	0.278	12.011	31.96	19.65
0 1s	Reg	532.057	1.793	15039.8	0.780	15.999	27.44	22.48
N 1s	Reg	399.957	0.867	455.5	0.477	14.007	1.42	1.02
Si 2p	Reg	98.957	0.984	7827.9	0.328	28.086	38.82	55.81
Fe 2p	Reg	711.057	2.577	798.5	2.957	55.846	0.36	1.04

Considering that the atomic concentration of C=O is 4.2%, an estimated ratio of 1:12 for Fe:<u>C</u>=O characterizes **Si-Fc@4**. It is fair to assume that the overestimation of C=O may stem from adsorption of CO<sub>2</sub> on the surface. In contrast, it is interesting to compare the atomic concentration ratio N:Fe. As can be seen from the table above, a ratio of 1:3.99 Fe:N can be calculated and matches the theoretical 1:3 ratio expected for **Si-Fc@4**.

## Analysis for Si-NDI@5:

State : Angle Name	: ARII	N-69						
Peak	Туре	Position BE (eV)	FWHM (eV)	Raw Area (cps eV)	RSF	Atomic Mass	Atomic Conc %	Mass Conc (
N 1s C 1s Cl 2p Si 2p	Reg Reg Reg Reg	400.327 284.627 195.327 98.727	2.399 2.163 0.000 0.935	1716.3 7251.9 0.0 4921.7	0.477 0.278 0.891 0.328	14.007 12.011 35.460 28.086	7.65 57.47 0.00 34.88	6.03 38.85 0.00 55.12



4.3. Representative XPS Survey (Full) Spectra

Figure S11. XPS survey spectrum (full) recorded for Si-BnE.



Figure S12. XPS survey spectrum (full) recorded for Si-BnA.



Figure S13. XPS survey spectrum (full) recorded for Si-Fc@1.



Figure S14. XPS survey spectrum (full) recorded for Si-Fc@2.



Figure S15. XPS survey spectrum (full) recorded for Si-Fc@3.



Figure S16. XPS survey spectrum (full) recorded for Si-Fc@4.



Figure S17. XPS survey spectrum (full) recorded for Si-Az.



Figure S18. XPS survey spectrum (full) recorded for Si-NDI@5.

# 5. Electrochemical Characterization of Functionalized Si Surfaces: Various Cyclic Voltammograms and Related Plots

Cyclic voltammetry (CV) measurements were carried out on a PARSTAT 3000A potentiostat/galvanostat/EIS analyzer (Ametek Scientific Instruments) using a self-designed and customized three-electrode Teflon cell under Ar. The ferrocene- and NDI-functionalized Si(111) surfaces were used as the working electrodes. In a typical setup, the unpolished rear side of the Si substrate was mechanically scratched (removal of native oxide layer) to expose the atomic Si surface and an Ohmic contact was immediately made with a copper conductive tape (Electron Microscopy Sciences; electrical resistance = 0.032 ohm/cm) by applying a drop (~ 0.3 mL) of gallium-indium eutectic (Sigma-Aldrich). The top functionalized surface of the Si substrate was then pressed against an opening at the Teflon cell bottom via the usage of a customized O-ring seal; the inner diameter of the latter was 0.8 cm. Given that only the surface under the O-ring was subjected to electrochemical measurements, the effective electro-active surface area ( $A_{ESA}$ ) was calculated to be 0.5026 cm<sup>2</sup>. The counter electrode was a Pt wire and the reference electrode was Ag/AgCl (3 M NaCl). A solution (0.1 M) of tetra-nbutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>, Sigma-Aldrich) in dry and degassed MeCN was used as the supporting electrolyte. About 15 mL of this electrolyte solution (dried further on activated molecular sieves) was transferred to the Teflon cell by passing through a Whatman syringe filter (PTFE, pore size =  $0.2 \mu m$ , GE Healthcare Life Sciences) and subsequently purged with Ar bubbling for 10 min prior to the experiment. All measurements were carried out at rt. All the reported potentials are referenced to Ag/AgCl electrode.



**Figure S19.** Representative cyclic voltammograms of **Si-Fc@1** at different scan rates (v). All the voltammetric experiments were carried out under argon gas atmosphere at 25 °C in dry acetonitrile using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the **Si-Fc** surface as working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and Pt as the counter electrode. The  $\Delta E_p$  is shown in the blue box in each case. Notice the increase in  $\Delta E_p$  with increasing scan rate.



**Figure S20.** A plot that shows a regular increase in  $\Delta E_p$  with increasing scan rate in the case of **Si-Fc@1**. The ideal boundary (considering one-electron redox system) of  $\Delta E_p = 60$  mV is shown with a green line/shadow.



**Figure S21.** Representative cyclic voltammogram of **Si-Fc@2** at the scan rate of 0.1 V/s. The voltammetric experiment was carried out under argon gas atmosphere at 25 °C in dry acetonitrile using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the **Si-Fc** surface as working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and Pt as the counter electrode.



**Figure S22.** Representative cyclic voltammograms of **Si-Fc@3** at different scan rates (v). All the voltammetric experiments were carried out under argon gas atmosphere at 25 °C in dry acetonitrile using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the **Si-Fc** surface as working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and Pt as the counter electrode. The  $\Delta E_p$  is shown in the blue box in each case. Notice the increase in  $\Delta E_p$  with increasing scan rate.



**Figure S23.** Representative cyclic voltammograms of **Si-Fc@4** at different scan rates (v). All the voltammetric experiments were carried out under argon gas atmosphere at 25 °C in dry acetonitrile using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the **Si-Fc** surface as working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and Pt as the counter electrode. The ratio of anodic and cathodic currents and the  $\Delta E_p$  are shown within the blue box in each case. Notice the increase in  $\Delta E_p$  with increasing scan rate.



Figure S24. A plot showing increase in  $\Delta E_p$  with increasing scan rate in the case of Si-Fc@4.

## 6. Calculation of Surface Coverage of Immobilized Ferrocene in Si-Fc@1-4

The calculation of the total surface coverage of immobilized ferrocene on the Si-Fc@1-4 surfaces was performed by following several steps as discussed below.

- 1. To begin, cyclic voltammograms were recorded at a low scan rate to make sure that  $\Delta E_p \le 60 \text{ mV}.$
- 2. From the entire voltammogram, the capacitive current-corrected anodic cycle (i.e., oxidation wave) was selected.
- 3. The actual mathematical area ' $A_1$ ' (unit = AV) under the anodic peak was calculated from the integration using 'Origin 8' software.
- 4. The amount of charge passed 'Q' (unit = A.s or Coulomb) was calculated from the formula:

Q (Coulomb) = 
$$A_1(AV)$$
 / scan rate (V/s)

5. Surface coverage ' $\Gamma$ ' (unit = mol/cm<sup>2</sup>) was calculated from the following equation:<sup>4</sup>  $\Gamma = Q / nFA_{ESA}$ 

where, 'n' is the number of electrons exchanged, 'F' is the Faraday constant (F = 96485.3329 Coulomb/mol) and ' $A_{ESA}$ ' is the electro-active surface area (also known as geometric surface area), i.e., inner area of the O-ring which is exposed to the surface.

For the present investigation: n = 1 and  $A_{ESA} = 0.5026$  cm<sup>2</sup>.

Shown below are the details of the calculation for each of the surfaces.





Figure S25. Calculation of area under the anodic peak for Si-Fc@1 (scan rate = 0.1 V/s).

From above calculation,  $A_1 = 0.2361 \times 10^{-7} \text{ AV}$ 

Therefore,  $Q = A_1 / \text{scan rate}$ 

$$= 0.2361 \times 10^{-7} \text{ AV} / 0.1 \text{ V/s}$$
$$= 0.2361 \times 10^{-6} \text{ As}$$
$$= 0.2361 \times 10^{-6} \text{ Coulomb}$$

Hence, surface coverage (mol/cm<sup>2</sup>) can be determined as:

$$\Gamma = Q / nFA_{ESA}$$
  
= (0.2361 × 10<sup>-6</sup> Coulomb) / {(96485.3329 Coulomb/mol) × (0.5026 cm<sup>2</sup>)}  
= 4.87 × 10<sup>-12</sup> mol/cm<sup>2</sup>

Surface coverage (molecules/cm<sup>2</sup>) can also be expressed as following:

$$\Gamma = 4.87 \times 10^{-12} \text{ mol/cm}^2$$
  
= 4.87 × 10<sup>-12</sup> x 6.023 x 10<sup>23</sup> molecules/cm<sup>2</sup>  
= 29.33 × 10<sup>11</sup> molecules/cm<sup>2</sup>

Thus, the area on the Si(111) surface which contains one organo-iron unit should be:

$$A_{s} = \{1 / (29.33 \times 10^{11})\} \text{ cm}^{2}$$
$$= \{10^{14} / (29.33 \times 10^{11})\} \text{ nm}^{2}$$
$$= 34.09 \text{ nm}^{2}$$

The ratio of Si atoms and organo-iron units on the surface considering the atomic density of  $Si(111)^5$  to be 7.8 x  $10^{14}$  atoms/cm<sup>2</sup> should be:

$$R_{Si/Fe} = (7.8 \times 10^{14}) / (29.33 \times 10^{11})$$
$$= 265.9$$

This means that a single organo-iron unit is present per 266 atoms of Si on the surface.





Selected only anodic cycle

Figure S26. Calculation of area under the anodic peak for Si-Fc@2 (scan rate = 0.1 V/s).

From above calculation,  $A_1 = 0.359 \times 10^{-7} \text{ AV}$ 

Therefore,  $Q = A_1 / \text{scan rate}$ 

$$= 0.359 \times 10^{-7} \text{ AV} / 0.1 \text{ V/s}$$
$$= 0.359 \times 10^{-6} \text{ As}$$
$$= 0.359 \times 10^{-6} \text{ Coulomb}$$

Hence, surface coverage (mol/cm<sup>2</sup>) can be determined as:

$$\Gamma = Q / nFA_{ESA}$$
  
= (0.359 × 10<sup>-6</sup> Coulomb) / {(96485.3329 Coulomb/mol) × (0.5026 cm<sup>2</sup>)}  
= 7.4 × 10<sup>-12</sup> mol/cm<sup>2</sup>

Surface coverage (molecules/cm<sup>2</sup>) can also be expressed as following:

$$\Gamma = 7.4 \times 10^{-12} \text{ mol/cm}^2$$
  
= 7.4 × 10<sup>-12</sup> × 6.023 × 10<sup>23</sup> molecules/cm<sup>2</sup>  
= 44.57 × 10<sup>11</sup> molecules/cm<sup>2</sup>

Thus, the area on the Si(111) surface which contains one organo-iron unit should be:

$$A_{s} = \{1 / (44.57 \times 10^{11})\} \text{ cm}^{2}$$
$$= \{10^{14} / (44.57 \times 10^{11})\} \text{ nm}^{2}$$
$$= 22.44 \text{ nm}^{2}$$

The ratio of Si atoms and organo-iron units on the surface considering the atomic density of  $Si(111)^5$  to be 7.8 x  $10^{14}$  atoms/cm<sup>2</sup> should be:

$$R_{Si/Fe} = (7.8 \times 10^{14}) / (44.57 \times 10^{11})$$
$$= 175$$

This means that a single organo-iron unit is present per 175 atoms of Si on the surface.



<u>Case 3:</u> Si-Fc@3 (Scan rate = 0.1 V/s and  $\Delta E_p = 23$  mV)

Figure S27. Calculation of area under the anodic peak for Si-Fc@3 (scan rate = 0.1 V/s).

From above calculation,  $A_1 = 0.6066 \times 10^{-6} \text{ AV}$ 

Therefore,  $Q = A_1 / \text{scan rate}$ 

$$= 0.6066 \times 10^{-6} \text{ AV} / 0.1 \text{ V/s}$$
$$= 0.6066 \times 10^{-5} \text{ As}$$
$$= 0.6066 \times 10^{-5} \text{ Coulomb}$$

Hence, surface coverage (mol/cm<sup>2</sup>) can be determined as:

$$\Gamma = Q / nFA_{ESA}$$
  
= (0.6066 × 10<sup>-5</sup> Coulomb) / {(96485.3329 Coulomb/mol) × (0.5026 cm<sup>2</sup>)}  
= 1.25 × 10<sup>-10</sup> mol/cm<sup>2</sup>

Surface coverage (molecules/cm<sup>2</sup>) can also be expressed as following:

$$\Gamma = 1.25 \times 10^{-10} \text{ mol/cm}^2$$
  
= 1.25 × 10<sup>-10</sup> × 6.023 × 10<sup>23</sup> molecules/cm<sup>2</sup>  
= 7.53 × 10<sup>13</sup> molecules/cm<sup>2</sup>

Thus, the area on the Si(111) surface which contains one organo-iron unit should be:

$$A_{s} = \{1 / (7.53 \times 10^{13})\} \text{ cm}^{2}$$
$$= \{10^{14} / (7.53 \times 10^{13})\} \text{ nm}^{2}$$
$$= 1.33 \text{ nm}^{2}$$

The ratio of Si atoms and organo-iron units on the surface considering the atomic density of  $Si(111)^5$  to be 7.8 x  $10^{14}$  atoms/cm<sup>2</sup> should be:

$$R_{Si/Fe} = (7.8 \times 10^{14}) / (7.53 \times 10^{13})$$
$$= 10.36$$

This means that  $\sim 1$  organo-iron unit is present per 10.4 atoms of Si on the surface.





Selected only anodic cycle

Figure S28. Calculation of area under the anodic peak for Si-Fc@4 (scan rate = 0.05 V/s).

From above calculation,  $A_1 = 2.418 \times 10^{-6} \text{ AV}$ 

Therefore,  $Q = A_1 / \text{scan rate}$ 

$$= 2.418 \times 10^{-6} \text{ AV} / 0.05 \text{ V/s}$$
$$= 48.36 \times 10^{-6} \text{ As}$$
$$= 48.36 \times 10^{-6} \text{ Coulomb} = 4.836 \times 10^{-5} \text{ Coulomb}$$

Hence, surface coverage (mol/cm<sup>2</sup>) can be determined as:

$$\Gamma = Q / nFA_{ESA}$$
  
= (4.836 × 10<sup>-5</sup> Coulomb) / {(96485.3329 Coulomb/mol) × (0.5026 cm<sup>2</sup>)}  
= 9.972 × 10<sup>-10</sup> mol/cm<sup>2</sup>

Surface coverage (molecules/cm<sup>2</sup>) can also be expressed as following:

$$\Gamma = 9.972 \times 10^{-10} \text{ mol/cm}^2$$
  
= 9.972 × 10<sup>-10</sup> x 6.023 x 10<sup>23</sup> molecules/cm<sup>2</sup>  
= 60.06 × 10<sup>13</sup> molecules/cm<sup>2</sup>

Thus, the area on the Si(111) surface which contains one organo-iron unit should be:

$$A_{s} = \{1 / (60.06 \times 10^{13})\} \text{ cm}^{2}$$
$$= \{10^{14} / (60.06 \times 10^{13})\} \text{ nm}^{2}$$
$$= 0.166 \text{ nm}^{2}$$

The ratio of Si atoms and organo-iron units on the surface considering the atomic density of  $Si(111)^5$  to be 7.8 x  $10^{14}$  atoms/cm<sup>2</sup> should be:

$$R_{Si/Fe} = (7.8 \times 10^{14}) / (60.06 \times 10^{13})$$
$$= 1.3$$

This means that  $\sim 1$  organo-iron unit is present per 1.3 atoms of Si on the surface.

#### 7. Determination of the Rate of Electrochemical Oxidation of Organo-Iron

The rates of electrochemical oxidation ( $k_s$  in s<sup>-1</sup>) of the organo-iron units in the ferrocenefunctionalized Si(111) surfaces (namely, **Si-Fc@3** and **Si-Fc@4**, as the two representative cases) were determined using the Laviron's formalism.<sup>6</sup> The latter correlates the changes in peak current ( $i_p$ ) and over-potential ( $E_p - E^0_{1/2}$ ) with increasing scan rate (v). Therefore, when the anodic peak current ( $i_{pa}$ ) and the anodic over-potential ( $E_{pa} - E^0_{1/2}$ ) are linearly correlated, the Laviron's equation for electrochemical oxidation can be represented as:

$$i_{pa} = nFA_{ESA}k_s \Gamma \exp\left[\frac{\alpha nF\left(E_{pa} - E_{1/2}^{0}\right)}{RT}\right]$$

The symbols in the equation refer to the following:

n: number of electrons exchanged (n = 1 for ferrocene/ferricenium redox system)

F: Faraday constant = 96485.33 Coulomb/mol

 $A_{ESA}$ : Electro-active surface area ( $A_{ESA} = 0.5026$  cm<sup>2</sup> in this case, as mentioned earlier)

- $\Gamma$ : Surface coverage of organo-iron (mol/cm<sup>2</sup>)
- $\alpha$ : Transfer coefficient ( $\alpha = 0.5$  for a reversible redox system)
- $k_{\rm s}$ : Standard rate constant for electrochemical oxidation (s<sup>-1</sup>)
- $E^{0}_{1/2}$ :  $E_{1/2}$  at very low scan rate
- $E_{pa}$ : Anodic peak potential at different scan rate

Using n = 1 and  $\alpha = 0.5$ , the equation can be represented as:

$$i_{pa} = FA_{ESA}k_s \Gamma \exp\left[\frac{F\left(E_{pa} - E_{1/2}^{0}\right)}{2RT}\right]$$

Therefore, the logarithm expression of the above equation translates to:

$$lni_{pa} = ln(FA_{ESA}k_s \Gamma) + \frac{F}{2RT}(E_{pa} - E_{1/2}^0)$$

Thus a linear plot of  $(\ln i_{pa})$  and  $(E_{pa} - E^{0}_{1/2})$  should give rise to the intercept of  $(\ln(FA_{ESA}k_s\Gamma))$ . Since the values of F,  $A_{ESA}$  and  $\Gamma$  (for a system) are already known, one can evaluate  $k_s$ ' from the intercept. Shown below are the associated data for determination of the rates  $(k_s)$  of electrochemical oxidation of ferrocene units in **Si-Fc@3** and **Si-Fc@4**.



**Figure S29.** Linear plot of  $(\ln i_{pa})$  and  $(E_{pa} - E_{1/2}^{0})$  in the case of **Si-Fc@3**. Please note that the intercept of the line is -12.60.



**Figure S30.** Linear plot of  $(\ln i_{pa})$  and  $(E_{pa} - E_{1/2}^{0})$  in the case of **Si-Fc@4**. Please note that the intercept of the line is -12.83.

Table S1. Determination of the Rates of Electrochemical Oxidation  $(k_s)$  of Organo-Iron Units in Si-Fc@3 and Si-Fc@4.

System	$\ln(FA_{ESA}k_{s}\Gamma)$	$\Gamma$ (mol/cm <sup>2</sup> )	$k_{\rm s}$ (s <sup>-1</sup> )
Si-Fc@3	-12.60	$1.25 \times 10^{-10}$	0.56
Si-Fc@4	-12.83	$9.97 \times 10^{-10}$	0.052

8. Electrochemical Properties of Si-NDI@5 and Calculation of Surface Coverage of Immobilized NDI



**Figure S31.** (A) and (B): Representative cyclic voltammograms of **Si-NDI@5** at a scan rate of 25 mV/s (A) and 100 mV/s (B). The CVs were recorded under argon gas atmosphere at 25 °C in dry acetonitrile using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the **Si-NDI@5** surface as working electrode, Ag/AgCl (3 M NaCl) as the reference electrode and Pt as the counter electrode. (C): The CV profiles in (A) and (B) have been shown together in one plot for easy comparison of the electrochemical signatures of **Si-NDI@5** at two different scan rates. (D): Expanded region of the CVs in (C) in the range of 0 to -1.5 V for a clear observation of the redox processes associated with the NDI chromophores in **Si-NDI@5**.



#### Calculation of Surface Coverage of Immobilized NDI in Si-NDI@5

Figure S32. Calculation of area under the anodic oxidation wave for reduced NDI in Si-NDI@5 (scan rate = 0.025 V/s).

From above calculation,  $A_1 = 1.40977 \text{ E-6 AV}$ 

Therefore,  $Q = A_1 / \text{scan rate}$ 

= 
$$1.40977 \times 10^{-6} \text{ AV} / 0.025 \text{ V/s}$$
  
=  $56.39 \times 10^{-6} \text{ As}$   
=  $56.39 \times 10^{-6} \text{ Coulomb}$ 

Hence, surface coverage (mol/cm<sup>2</sup>) can be determined as (considering n = 2):

$$\Gamma = Q / nFA_{ESA}$$
  
= (56.39 x 10<sup>-6</sup> Coulomb) / {2 x (96485.3329 Coulomb/mol) x (0.5026 cm<sup>2</sup>)}  
= 5.81 x 10<sup>-10</sup> mol/cm<sup>2</sup>

Surface coverage (molecules/cm<sup>2</sup>) can also be expressed as following:

$$\Gamma = 5.81 \text{ x } 10^{-10} \text{ mol/cm}^2$$
  
= 5.81 x 10<sup>-10</sup> x 6.023 x 10<sup>23</sup> molecules/cm<sup>2</sup>  
= 34.99 x 10<sup>13</sup> molecules/cm<sup>2</sup>

Thus, the area on the Si(111) surface which contains one NDI unit should be:

$$A_{s} = \{1 / (34.99 \text{ x } 10^{13})\} \text{ cm}^{2}$$
$$= \{10^{14} / (34.99 \text{ x } 10^{13})\} \text{ nm}^{2}$$
$$= 0.29 \text{ nm}^{2}$$

The ratio of Si atoms and NDI units on the surface considering the atomic density of Si $(111)^5$  to be 7.8 x 10<sup>14</sup> atoms/cm<sup>2</sup> should be:

$$R_{Si/NDI} = (7.8 \times 10^{14}) / (34.99 \times 10^{13})$$
$$= 2.2$$

This means that ~1 NDI unit is present per 2.2 atoms of Si on the surface.

## 9. IR, NMR and ESI-Mass Spectra



**Figure S33.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **B**. Please note that the solvent residual peak is referenced to 7.26 ppm.



**Figure S34.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **C**. Please note that the solvent residual peak is referenced to 7.26 ppm.



Figure S35. ESI-TOF mass (HRMS) spectrum of C.



**Figure S36.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **1**. Please note that the solvent residual peak is referenced to 7.26 ppm.

Analysis Na Sample Na Comment	ESI-TOF Mass Spectrum Report D:\Data\UMiami\1003ArMu01_LOW_MEOH_CHCL3_wFA_POS.d ARIN-5 MEOH_CHCL3 (50:50 0.1% FA)	Acquisition Date Instrument Method	10/3/2018 12:07:04 PM micrOTOF-Q II tune_low_Bruker_Calibration.m
Intens. x10 <sup>5</sup>	311.1813 [M+NA] +		+MS, 0.2-0.4min #(11-24)
1.5-			
1.0-			
0.5-			
0.0	139.0730 204.1031 102.1276 102.1276 200 400 600	800	

Figure S37. ESI-TOF mass (HRMS) spectrum of 1.



Figure S38. IR (neat solid) spectrum of 2.



**Figure S39.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **2**. Please note that the solvent residual peak is referenced to 7.26 ppm.



**Figure S40.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of **2**. Please note that the triplet at 77.0 ppm is associated with CDCl<sub>3</sub>.



Figure S41. ESI-TOF mass (HRMS) spectrum of 2.



Figure S42. IR (neat solid) spectrum of 3.



**Figure S43.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of **3**. Please note that the solvent residual peak is referenced to 7.26 ppm.



**Figure S44.** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of **3**. Please note that the triplet at 77.0 ppm is associated with CDCl<sub>3</sub>.



Figure S45. ESI-TOF mass (HRMS) spectrum of 3.



Figure S46. IR (neat solid) spectrum of 5.



**Figure S47.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) spectrum of **5**. Please note that the solvent residual peak is referenced to 3.31 ppm.



**Figure S48.** <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>OD) spectrum of **5**. Please note that the septet at 49.15 ppm is associated with CD<sub>3</sub>OD.



Figure S49. ESI-TOF mass (HRMS) spectrum of 5.

А	Ampere
AFM	Atomic force microscopy
anhyd	Anhydrous
Ar	Argon
A <sub>ESA</sub>	Electro-active surface area
°C	Degree Celsius
ca.	Circa (from Latin, which means roughly/approximately)
Calcd	Calculated
cf.	Confer (from Latin, which means compare)
cm	Centimeter
Conc.	Concentrated
CV	Cyclic voltammetry/voltammogram
δ	Delta
d	Doublet/Day
$\Delta E_{\rm p}$	Difference of peak potentials of the anodic and cathodic waves
DCM	Dichloromethane
DMAP	4-(Dimethylamino)pyridine
DMF	<i>N</i> , <i>N</i> -Dimethylformamide
eV	Electron volt
Epa	Anodic peak potential
Epc	Cathodic peak potential
$E_{1/2}$	Average of the anodic and cathodic peak potentials
EBA	4-Ethynylbenzyl alcohol
EDCI	<i>N</i> -Ethyl- <i>N</i> '-(3-dimethylaminopropyl)carbodiimide
	hydrochloride
Eq.	Equation
ESI-MS	Electrospray ionization mass spectrometry
EtOH	Ethanol
F	Faraday constant
Fc	Ferrocene
FTIR	Fourier-transform infrared
FWHM	Full width at half maximum
g	Gram
Г	Gamma (refers to surface coverage)
h	Hour
HBTU	<i>N</i> , <i>N</i> , <i>N</i> ', <i>N</i> '-Tetramethyl- <i>O</i> -(1 <i>H</i> -benzotriazol-1-yl)uronium
	hexafluorophosphate
hv	Photoirradiation
НОМО	Highest occupied molecular orbital
HPLC	High performance liquid chromatography
HRMS	High resolution mass spectrometry
Hz	Hertz
i <sub>pa</sub>	Anodic peak current
<i>i</i> <sub>pc</sub>	Cathodic peak current
IR	Infrared

## 10. Key Abbreviations/Acronyms/Symbols Used

Κ	Kelvin
ks	Standard rate constant for electrochemical oxidation
λ	Wavelength
m	Multiplet
М	Molar
μ	Micro
μm	Micrometer
MeCN	Acetonitrile
MeOH	Methanol
MHz	Megahertz
min	Minute(s)
mL	Milliliter
mM	Millimolar
mmol	Millimol
mol	Mole(s)
mV	Millivolt
n	Number of electrons exchanged during the redox process
v	Scan rate
NDI	Naphthalene diimide
nm	Nanometer
NMR	Nuclear magnetic resonance
ppm	Parts per million
PTFE	Polytetrafluoroethylene
Q	Total amount of charge passed (in coulomb)
R	Ideal gas constant
$R^2$	Coefficient of linear regression/fitting
$R_q$ (RMS)	Root-mean-square roughness
rt	Room temperature
S	Singlet/Second
t	Triplet
Т	Temperature in K
TBAF	Tetrabutylammonium fluoride
TFFH	Tetramethylfluoroformamidinium hexafluorophosphate
THF	Tetrahydrofuran
TIPS	Triisopropylsilyl
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TOF	Time-of-flight
UV	Ultraviolet
V	Volt
W	Watt
XPS	X-ray photoelectron spectroscopy

## 11. References

- 1. Betzler, F. M.; Klapötke, T. M.; Sproll, S. М., Synthesis of polymer Glycidyl-5-(carboxyethyl-1H-tetrazole) and 1, 2-Bis (5-carboxyethyl-1H-tetrazolyl) ethane as Polymeric Precursor. Eur. J. Org. Chem. 2013, 509-514.
- Matsunaga, Y.; Goto, K.; Kubono, K.; Sako, K.; Shinmyozu, T., Photoinduced color change and photomechanical effect of naphthalene diimides bearing alkylamine moieties in the solid state. *Chem. Eur. J.* 2014, *20*, 7309–7316.
- Nguyen, N.-H.; Apriletti, J. W.; Baxter, J. D.; Scanlan, T. S., Hammett analysis of selective thyroid hormone receptor modulators reveals structural and electronic requirements for hormone antagonists. *J. Am. Chem. Soc.* 2005, *127*, 4599-4608.
- Leroux, Y. R.; Fei, H.; Noël, J.-M.; Roux, C.; Hapiot, P., Efficient covalent modification of a carbon surface: use of a silyl protecting group to form an active monolayer. *J. Am. Chem. Soc.* 2010, *132*, 14039-14041.
- Gauthier, N.; Argouarch, G.; Paul, F.; Humphrey, M. G.; Toupet, L.; Ababou-Girard, S.; Sabbah, H.; Hapiot, P.; Fabre, B., Silicon surface-bound redox-active conjugated wires derived from mono- and dinuclear iron (II) and ruthenium (II) oligo (phenyleneethynylene) complexes. *Adv. Mater.* 2008, 20, 1952-1956.
- 6. Laviron, E., General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. *J. Electroanal. Chem.* **1979**, *101*, 19-28.