Supplementary Material (ESI) for Chemical Communications


# Supporting Information:
# Site-Selective Metal-Coordination-Based Patterning of Silane Monolayers

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## I. General

All chemicals were purchased from Aldrich or Acros and used as received unless otherwise indicated. Silica (100) wafers (test grade, 3 inches in diameter) were purchased from University Wafer, USA. Chromatography was carried out with silica gel 60 (mesh 230-400). $^{1}$H NMR spectra were recorded at 25°C on a Bruker AC 400 (400 MHz) spectrometer. $^{13}$C NMR spectra were obtained at 100.0 MHz on a Bruker AC 400 spectrometer. All chemical shifts are reported in parts per million (ppm) with reference to solvent residual peaks. Mass spectra were collected on an Agilent 1100 Series Capillary LCMSD Trap XCT Spectrometer. A Leica DM IRE 2 fluorescence microscope with CCD camera was used to capture the fluorescence images. All Fourier transform infrared reflection absorption (FT-IRRA) spectra were collected on a Nicolet Magna-IR 550 spectrometer. The instrument was equipped with a liquid nitrogen cooled mercury

cadmium telluride (MCT) detector. Photo-patterning was carried out with a Karl Suss MJB3 photomask aligner (SUSS MicroTec Inc., Germany). All AFM images were collected using a Dimension 3100 scanning probe microscope and non-conductive silicon nitride tips (Veeco, Model:NP Cantilever: T: 0.4~0.7μm). Contact angles were measured with a Nonius goniometer (Gaertner Scientific Corporation, Chicago, USA) under ambient conditions. Water (Millipore water) droplets were dispensed from a microburette. The reported values are the average of three measurements. Isothermal Titration Calorimetry (ITC) experiments were carried out on a Microcal VP-ITC isothermal calorimeter using degassed HPLC grade chloroform at 30 °C. Compound **4** was synthesized according to literature procedures.[2] For solubility reason, a n-hexane substituted SCS-$Pd^{II}$ pincer complex was used for all ITC experiments which was synthesized in analogy to compound **4**.

**II-1. Synthesis of 1.**

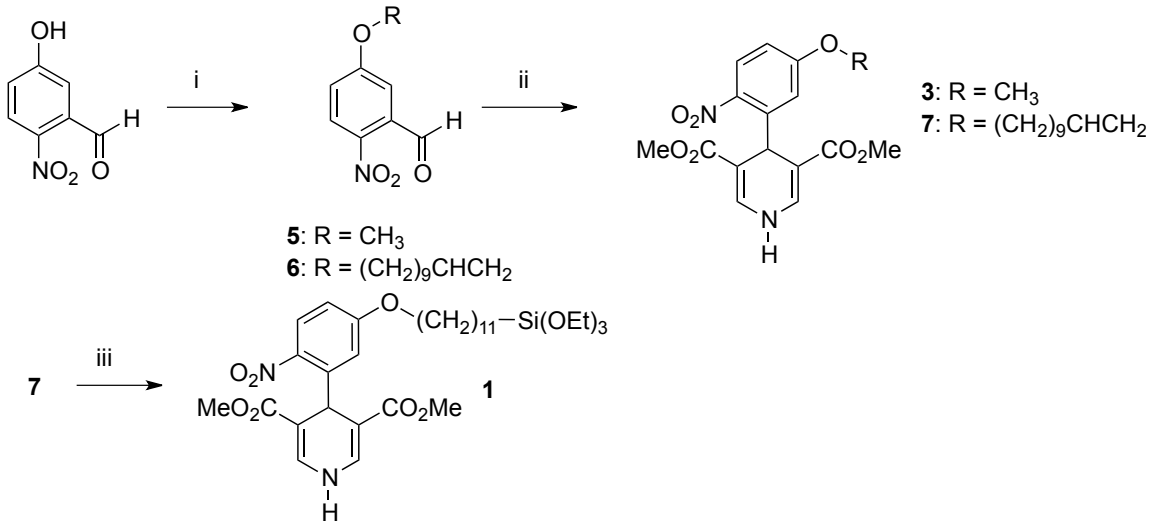


**Figure S1**. i) Alkyl halide, $K_2CO_3$, DMF, room temperature; ii) methyl propiolate, $NH_3.H_2O$, EtOH, MW, 120 $^0$C, 20 minutes; iii) $HSi(OEt)_3$, $PtO_2$, sealed tube, 2 hours; 85%.

**5-Methoxy-2-nitrobenzaldehyde (5)**. 5-Hydroxy-2-nitrobenzaldehyde (3 g, 18 mmol) was dissolved in N,N-dimethyl formamide (60 mL) followed by the addition of potassium carbonate (5 g, 36 mmol) and a catalytic amount of potassium iodide. While the reaction was stirred at room temperature, iodomethane (5.1 g, 36 mmol) was added dropwise to the mixture over a period of 30 minutes. The resulting mixture was stirred at room temperature overnight. The reaction mixture was then filtered, concentrated *in vacuo*, dissolved in ethyl acetate and sequentially washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated. Purification was accomplished by silica gel column chromatography using 10% ethyl acetate in hexanes as eluent to give **5** (3.1 g, 17 mmol) as yellow-green solid, yield 95%. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 10.49 (s, 1H), 8.16 (d, 1H, $J$ = 9.2Hz), 7.33 (d, 1H, $J$ = 2.8Hz), 7.15 (dd, 1H, $J_1$ = 9.2Hz, $J_2$ = 2.8Hz), 4.05 (s, 3H).

**5-(Dodec-11-enyloxy)-2-nitrobenzaldehyde (6)**. Compound **6** was prepared in analogy to **5**. 11-Bromoundec-1-ene was used. Purification was accomplished by silica gel column chromatography using 5% ethyl acetate in hexanes as eluent to give **6** as a yellow thick oil, yield 93%. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 10.42 (s, 1H), 8.25 (d, 1H, $J$ = 9.2Hz), 7.40 (d, 1H, $J$ = 2.8Hz), 7.23 (dd, 1H, $J_1$ = 9.2Hz, $J_2$ = 2.8Hz), 5.82 (m, 1H), 4.95 (m, 2H), 3.95 (t, 2H, $J$ = 6.4Hz), 2.05 (m, 2H), 1.75 (m, 2H), 1.31 (m, 12H).

**1,4-Dihydro-4-(5-methoxy-2-nitrophenyl)pyridine-3,5-dimethyl dicarboxylate (3)**. Aldehyde **5** (0.7 g, 2.1 mmol) and methyl propiolate (0.35 g, 4.2 mmol) were dissolved in 2 mL of ethanol in a pressure tube. To this solution, ammonium hydroxide (30% aqueous solution) (0.12 g, 2.1 mmol) was added. The sealed reaction vessel was then moved into a

microwave reactor and heated at 140 $^{o}$C for 20 minutes. The cooled content was transferred from the reaction vessel to a round bottom flask with ethanol as washing solvent and evaporated to the dryness under vacuum. Purification was accomplished by silica gel column chromatography using 30% ethyl acetate in hexanes as eluent to give **3** (0.65 g, 1.4 mmol) as a yellowish solid, yield 65%. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.85 (d, 2H, $J$ = 8.8Hz), 7.38 (d, 2H, $J$ = 5.2Hz), 6.97 (d, 1H, $J$ = 2.8Hz), 6.74 (dd, 1H, $J_1$ = 8.8Hz, $J_2$ = 2.8Hz), 6.29 (t, 1H, $J$ = 5.2Hz), 5.95 (s, 1H), 3.94 (s, 3H), 3.51 (s, 6H).

**1,4-Dihydro-4-(2-nitro-5-(undec-10-enyloxy)phenyl)pyridine-3,5-dimethyl dicarboxylate (7)**. Compound **7** was prepared in analogy to **3**. Aldehyde **6** was used. Purification was accomplished by silica gel column chromatography using 20% ethylacetate in hexanes as eluent to give **7** as a yellow oil, yield 55%. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.75 (d, 2H, $J$ = 9.0Hz), 7.32 (d, 2H, $J$ = 5.2Hz), 6.88 (d, 1H, $J$ = 2.8Hz), 6.63 (dd, 1H, $J_1$ = 9.0Hz, $J_2$ = 2.8Hz), 6.35 (t, 1H, $J$ = 5.2Hz), 5.89 (s, 1H), 5.75 (m, 1H), 4.90 (m, 2H), 3.75 (t, 2H, $J$ = 6.8Hz), 3.51 (s, 6H), 1.97 (m, 2H), 1.69 (m, 2H), 1.25 (bm, 12H); $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ 167.0, 162.7, 144.5, 141.8, 139.2, 134.5, 126.6, 118.0, 114.2, 111.5, 108.4, 68.5, 51.5, 33.8, 32.4, 29.5, 29.4, 29.3, 28.9, 25.9.

**4-(5-(11-(Triethoxysilyl)undecyloxy)-2-nitrophenyl)-1,4-dihydropyridine-3,5-dimethyl dicarboxylate (1)**. The hydrosilylation was carried out according to reported procedures.[1] Allyl dihydropyridine (1.6 g, 3.3 mmol) and triethoxy silane (0.54 g, 3.3 mmol) were stirred without solvent in a thick-wall tube under argon. To this mixture, platinum oxide (37 mg, 0.16 mmol) was added, and the tube was sealed and heated at 85

1. Sabourault, N.; Mignani, G.; Wagner ,A. and Mioskowski, C. *Org. Lett*., **2002**, *4*, 2117-2119.

°C overnight. After cooling to room temperature, the crude reaction mixture was transferred directly to the top of a short silica gel column for flash chromatography with 5% ethyl acetate in hexanes as eluent to afford **1** (2.15 g, 2.3 mmol) as a pale yellow oil in 71% yield. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.83 (d, 1H, $J$ = 9.2Hz), 7.38 (d, 2H, $J$ = 5.2Hz), 6.95 (d, 1H, $J$ = 2.8Hz), 6.63 (dd, 1H, $J_1$ = 9.2Hz, $J_2$ = 2.8Hz), 6.50 (t, 1H, $J$ = 5.2Hz), 5.97 (s, 1H), 3.94 (t, 2H, $J$ = 6.8Hz), 3.82 (q, 6H, $J$ = 7.2Hz), 3.60 (s, 6H), 1.76 (m, 2H), 1.2-1.5 (brm, 27H), 0.63 (m, 2H); $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ 167.0, 162.7, 144.5, 141.8, 134.4, 134.4, 126.6, 118.1, 111.4, 108.5, 68.5, 58.3, 51.2, 33.1, 32.3, 29.6, 29.6, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 25.9, 22.7, 18.3, 10.3; ESI MS m/z: 673.3 $[M+Na]^+$ Calcd. 673.3.

**II-2. Synthesis of dye conjugated SCS-Pd (II)-pincer.**

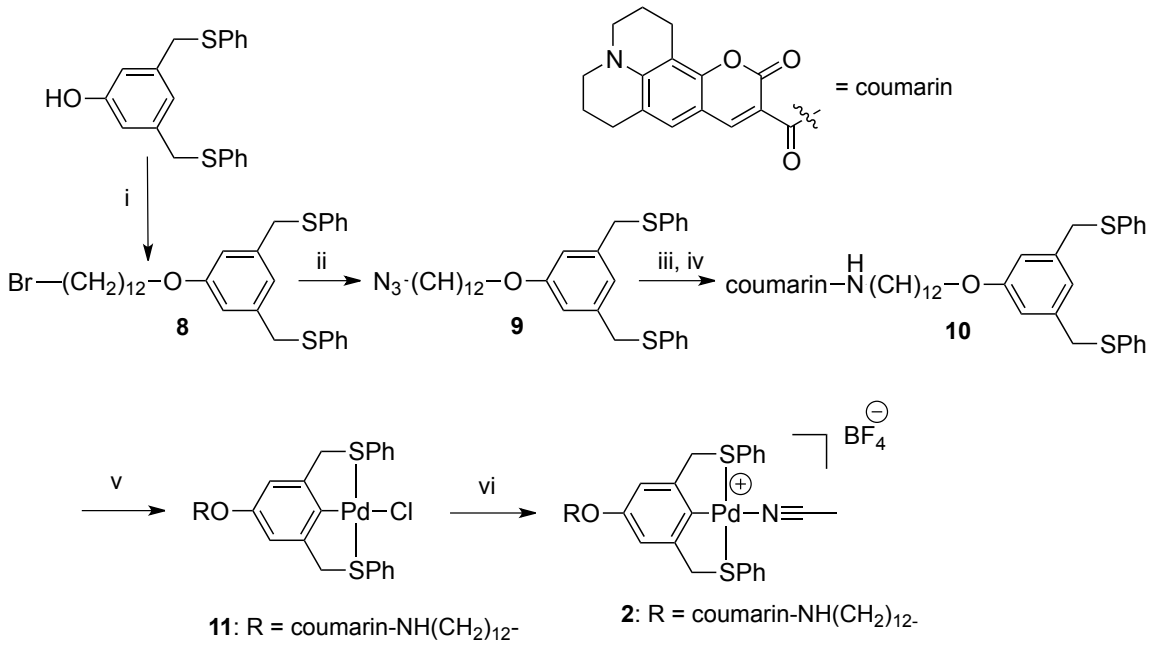


**Figure S2**. i) Alkyl halide, $K_2CO_3$, DMF, room temperature; ii) $NaN_3$, 80 $^0$C, 3 hours; iii) Pd/C, $H_2$, 1atm; iv) Coumarin 343, DCC, HOBt, DCM; v) a: $Pd[MeCN]_4(BF4)_2$ MeCN, rt 45 minutes b: $AgBF_4$, saturated brine, overnight; vi) MeCN, $AgBF_4$, water.

**1-Methoxy-3,5-bis((phenylthio)methyl)benzene (8)**. 1,12-dibromododecane (3.67 g, 11.2 mmol) was dissolved in N,N-dimethyl formamide (30 mL) followed by the addition of potassium carbonate (1.55 g, 11.2 mmol) and a catalytic amount of potassium iodide. While the mixture was stirred at room temperature, a N,N-dimethyl formamide solution (20 mL) of 3,5-bis(phenylthiomethyl)phenol (1.9 g, 5.6 mmol), which was prepared according to reported procedures,[2,3] was added dropwise over a period of 30 minutes. The resulting mixture was stirred at room temperature overnight. The reaction mixture was then filtered, concentrated *in vacuo*, dissolved in ethyl acetate and sequentially washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated. Purification was accomplished by silica gel column chromatography using 10% ethyl acetate in hexanes as eluent to give **8** (2.46 g, 4.2 mmol) as a light brown oil in 75% yield. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.18 (m, 8H), 7.15 (m, 2H), 6.73 (t, 1H, $J$ = 1.6Hz), 6.63 (d, 2H, $J$ = 1.6Hz), 3.95 (s, 4H), 3.77 (t, 2H, $J$ = 6.5Hz), 3.34 (t, 2H, $J$ = 7.1Hz), 1.78 (m, 2H), 1.64 (m, 2H), 1.34 (brm, 4H), 1.24 (brm, 12H).

**1-(3-(12-Azidododecyloxy)-5-((phenylthio)methyl)benzylthio)benzene (9)**. Bromide **8** (3 g, 5.1 mmol) was dissolved in N,N-dimethyl formamide (60 mL) followed by the addition of sodium azide (0.4 g, 6.1 mmol). The mixture was stirred at 80 $^0$C for three hours. The reaction mixture was then filtered, concentrated *in vacuo*, dissolved in ethyl acetate and sequentially washed with water and brine. The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated. Purification was accomplished by

2. Manen, H-J. V.; Nakashima ,K.; Shinkai, S.; Kooijman, H.; Spek, A. L.; Veggel, F., and Reinhoudt, D. N. *Eur. J. Inorg. Chem*. **2000**, 2533-2254.
3. Pollino, J. M.; Stubbs, L. P. and Weck, M. *Macromolecules* **2003**, *36*, 2230-2234.

silica gel column chromatography using 10% ethylacetate in hexanes as eluent to give **9** (2.4 g, 4.3 mmol) as a light brownish oil in 85% yield. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.21 (m, 8H), 7.10 (m, 2H), 6.74 (t, 1H, $J$ = 1.6Hz), 6.63 (d, 2H, $J$ = 1.6Hz), 4.09 (td, 2H, $J_1$ = 6.6Hz, $J_2$ = 1.2Hz), 3.95 (s, 4H), 3.77 (t, 2H, $J$ = 6.6Hz), 1.62 (m, 2H), 1.51 (m, 2H), 1.25 (m, 12H), 0.79 (m, 4H).

**Ligand 10**: Azide **9** (2 g, 3.6 mmol) was dissolved in 20 mL of methanol in a hydrogenation bottle. To this mixture, 0.8 g of palladium on carbon (Pd, 10%) was added under nitrogen. The hydrogenation reaction was carried out overnight at 1 atm hydrogen atmosphere at room temperature. The reaction mixture was filtered though Celite® and the filtrate was concentrated *in vacuo* to give the corresponding amine which was used in the next step without further purification. The amine (1.8 g, 3.6 mmol) and coumarin 343 (1.23g, 4.3 mmol) was dissolved in 10 mL of dry dichloromethane under nitrogen. The solution was then put into an ice-water bath, cooled to 0 $^0$C, and then N,N'-dicyclohexylcarbodiimide (1.11 g, 5.4 mmol) and 1- hydroxyl-benzotriazole (0.5 g, 3.6 mmol) were added in several portions. The resulting mixture was stirred at 0 $^0$C for 1 hour and allowed to warm to room temperature overnight. The reaction mixture was filtered, diluted with 150 mL of dichloromethane and sequentially washed with 1 M hydrochloric acid, saturated sodium bicarbonate aqueous solution, and brine. The organic layer was dried with anhydrous sodium sulfate, filtered, and evaporated. Purification was accomplished by silica gel column chromatography using 10% methanol in dichloromethane as eluent to give **10** (1.7 g, 2.2 mmol) as a yellowish oil with a two-step yield of 61%. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.83 (t, 1H, $J$ = 2.7Hz), 8.52 (s, 2H), 7.15 (m, 8H), 7.08 (m, 2H), 6.91 (s, 1H), 6.73 (s, 1H), 6.63 (d, 2H, $J$ = 1.2Hz), 3.95 (s, 4H),

3.76 (t, 2H, *J* = 6.4Hz), 3.29 (brm, 6H), 2.82 (t, 2H, *J* = 6.4Hz), 2.70(t, 2H, *J* = 6.4Hz), 1.85 (m, 4H), 1.71 (m, 2H), 1.55 (m, 2H), 1.29 (m, 16H).

**Chloro Complex of Pd pincer (11):** Ligand **10** (0.3g, 0.38mmol) was dissolved in $CH_2Cl_2$ (6 mL) and placed under an Argon atmosphere. $Pd[MeCN]_4(BF_4)_2$ (165mg, 0.38 mmol) in anhydrous MeCN (2 mL) was added in one portion at 25 °C. After stirring for 1hr, the 3:1 $MeCN/CH_2Cl_2$ mixture was poured into a sat. solution of NaCl (25 mL) and was stirred vigorously for 1 h. The Pd-Cl complex was then extracted from the brine using $CH_2Cl_2$. The combined organic layers were washed with water, dried with anhydrous sodium sulfate, and the solvent was removed under reduced pressure. Purification by silica gel column chromatography using 20% ethylacetate in hexanes as eluent to give compound **11** (0.31 g, 0.34 mmol) as a yellowish foam in 90% yield. $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.85 (t, 1H, *J* = 5.6Hz), 8.60 (s, 1H), 7.82(m, 4H), 7.35 (m, 6H), 6.70 (s, 1H), 6.57 (s, 2H), 4.55 (brs, 4H), 3.86 (t, 2H, *J* = 4.8Hz), 3.41 (m, 2H), 3.32 (m, 4H), 2.88 (t, 2H, *J* = 4.8Hz), 2.77 (t, 2H, *J* = 4.8Hz), 1.98 (m, 4H), 1.1-1.7 (m, 20H); $^{13}$C NMR (400 MHz, $CDCl_3$) $\delta$ 163.4, 163.1, 157.1, 152.6, 151.4, 150.1, 148.0, 148.0, 132.5, 131.4, 129.8, 129.6, 127.0, 119.6, 109.2, 108.8, 108.3, 105.7, 68.2, 51.7, 50.2, 49.8, 39.6, 29.7, 29.6, 29.5, 29.3, 29.3, 29.2, 27.5, 27.1, 26.0, 21.2, 20.2, 20.1; ESI-MS m/z: 893.2 $[M-Cl]^+$ Calcd. 893.2

**Acetonitrile complex of Pd pincer (2)**. Under nitrogen, ligand **11** (0.3 g, 0.32 mmol) was dissolved in 50mL of acetonitrile. Then $AgBF_4$ (77 mg, 0.4 mmol) and 1.5 mL water was added in one portion. The solution was stirred for four hours under a nitrogen atmosphere at room temperature. The reaction mixture was evaporated *in vacuo* to

dryness, dissolved in 60mL dichloromethane and filtered through Celite®. The filtrate was evaporated *in vacuo* to dryness to afford **2** (0.29 g, 0.29 mmol) as a yellowish foam in 90% yield. Compound **2** is unstable and was used immediately upon synthesis. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 8.85 (t, 1H, $J$ = 5.6Hz), 8.60 (s, 1H), 7.81(m, 4H), 7.49 (m, 6H), 6.70 (s, 1H), 6.59 (s, 2H), 4.57 (brs, 4H), 3.88 (t, 2H, $J$ = 4.8Hz), 3.41 (m, 2H), 3.32 (m, 4H), 2.88 (t, 2H, $J$ = 4.8Hz), 2.77 (t, 2H, $J$ = 4.8Hz), 2.06 (s, 3H), 1.98 (m, 4H), 1.1-1.7 (m, 20H).

**Aromatized Compound (3).** 200 mg of compound **3** was dissolved in 10 mL ethanol. The solution was exposed to a 290W longwave ultraviolet mercury lamp. After two hours, the color of the solution turns from yellow to light green. The aromatization was confirmed by $^{1}$H NMR (SI-Figure 3), which shows the disappearance of $H_b$ and $H_c$ and the upfield shift of $H_a$. The product was precipitated from solution as a dark-green crystal in 50% yield. $^{1}$H NMR ($CDCl_3$, 400 MHz) $\delta$ 9.35 (s, 2H), 7.22 (d, 1H, $J$ = 8.8Hz), 6.98 (dd, 1H, $J_1$ = 8.8Hz, $J_2$ = 2.4Hz), 6.74 (d, 1H, $J$ = 2.4Hz), 3.93 (s, 3H), 3.63 (s, 6H); $^{13}$C NMR (500 MHz, $CDCl_3$) $\delta$ 165.0, 165.0, 161.2, 153.9 149.3, 127.1, 113.7, 113.5, 56.1, 52.5; ESI-MS m/z: 331.1 $[M+H]^+$ Calcd. 331.1

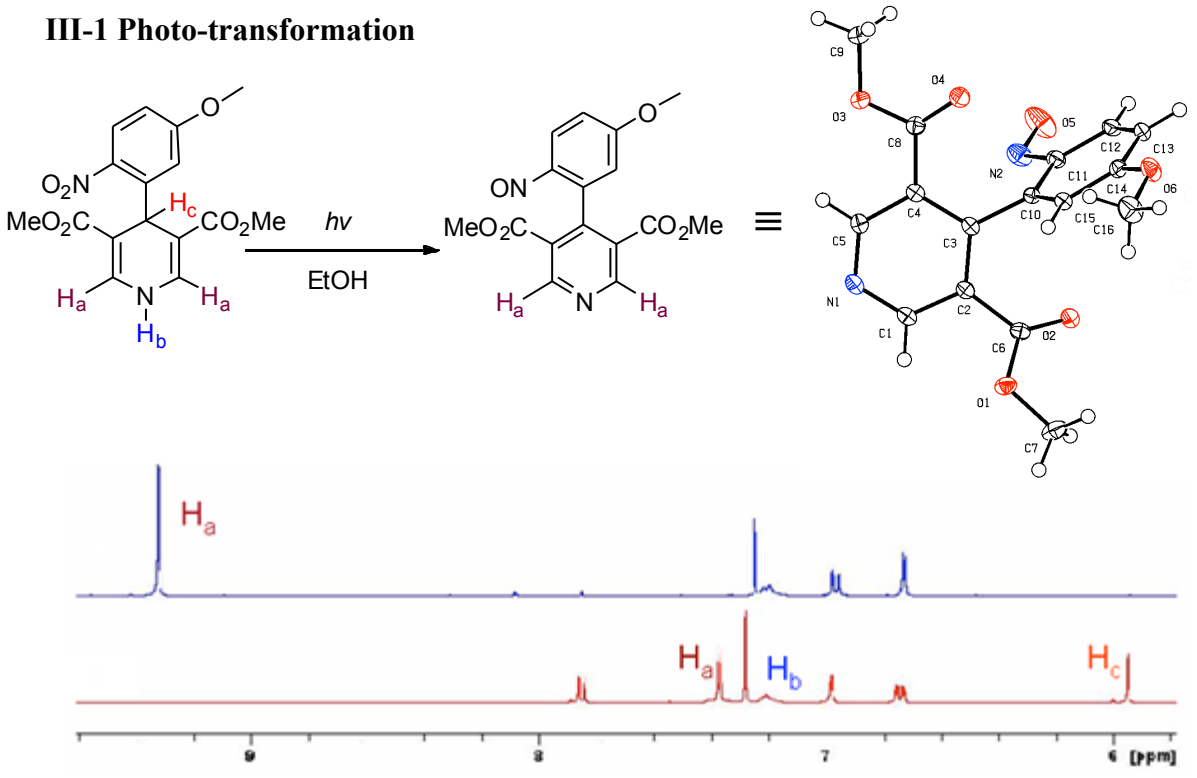


**Figure S3**. Single crystal structure of aromatized **3** and partial $^{1}$H NMR ($CDCl_3$, 400 MHz) spectra of **3** before (bottom) and after (top) UV exposure (356 nm, 2 hrs) in ethanol.

**III-2 Single Crystal Structure Determination Experiment**

A green block crystal of the aromatized compound **3** with the size of 0.20 × 0.25 × 0.42 $mm^3$ was selected for geometry and intensity data collection with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was controlled with an Oxford Cryosystems Series 700 plus instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data were collected using graphite-monochromated and 0.5 mm-MonoCap-collimated Mo-Kα radiation (λ = 0.71073 Å) with the ω scan method.[4] Data were processed with the INTEGRATE program of the APEX2 software[4] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for area detector. The structure was solved by the direct method and refined on F2 (SHELXTL).[5] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.93 or 0.96 Å) and included as riding with Uiso(H) = 1.2 or 1.5 Ueq(non-H). Crystal data, data collection parameters and refinement results are reported in the CIF file. Its molecular structure is shown in the Figure S4.

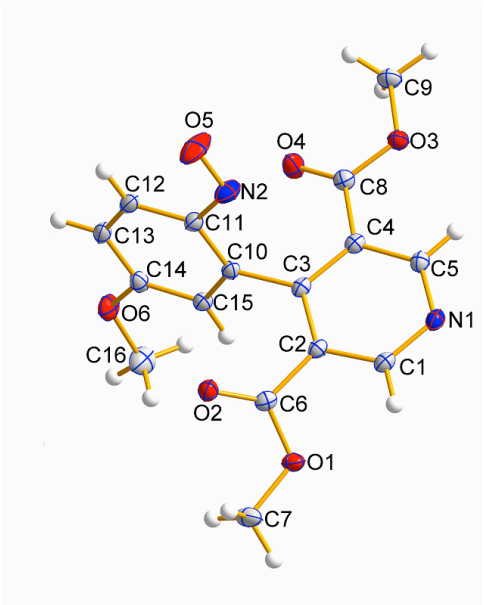


**Figure S4.** Single crystal X-ray structure of aromatized **3**

4 APEX2 (version 2009.11-0). Program for Bruker CCD X-ray Diffractometer Control, Bruker AXS Inc., Madison, WI, 2009.
5 G. M. Sheldrick, SHELXTL, version 6.14. Program for solution and refinement of crystal structures, Universität Göttingen, Germany, 2000.

### III-3 Ligand exchange of SCS-Pd(II)-pincer complex.

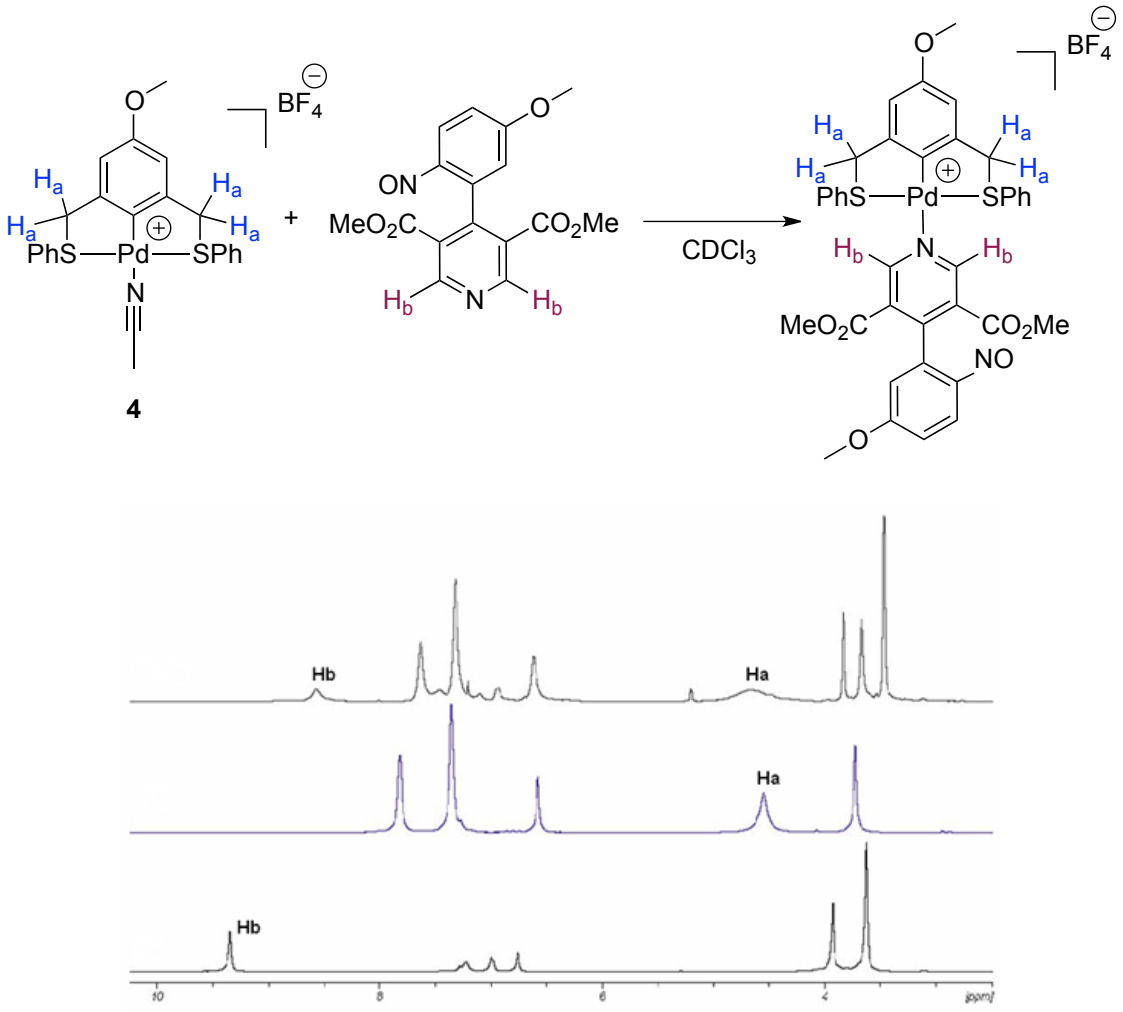


**Figure S5**. $^{1}$H NMR ($CDCl_3$, 400 MHz) spectra of the pincer complex formation between **4** and aromatized ligand **3** (1:1 molar ratio) in $CDCl_3$. Bottom spectrum: aromatized ligand **3**; middle spectrum: **4** and top spectrum: 1:1 mixture of **4** and aromatized **3**.

## IV. Silica wafer cleaning and surface silane monolayer formation.

### IV-1 Silica wafer cleaning

The polished Si(100) test grade wafers were pre-cleaned to remove organic contaminants and make the silica surface fully hydroxylated. Several cleaning processes were screened (see SI-Table 1) using advancing water contact angle as the criteria. It was found that sequential RCA and Piranha wash gave the best results in this study.

**Typical RCA cleaning procedure**: 160 mL of deionized water and 40 mL of $NH_4OH$ (27%) were added to a Pyrex crystallizing dish and heated to 75 °C. The dish was removed from the heat 40 mL of $H_2O_2$ (30%) was added. The silicon wafer was soaked in the solution for 15 minutes. Then, the wafer was removed, thoroughly rinsed with deionized water and dried with a stream of high purity nitrogen/argon.

**Typical Piranha cleaning procedure:** 100 mL of $H_2SO_4$ (96%) was added to a Pyrex crystallizing dish and heated to 120 °C. To this solution, 33 mL of $H_2O_2$ (30%) was carefully added. The silicon wafer was soaked in the solution for 25 minutes. Then, the wafer was removed from the solution, thoroughly rinsed with deionized water and dried under a stream of high purity nitrogen/argon.

### IV-2. Silanization –surface silane monolayer formation.

After drying in flowing argon, the wafers were immediately subjected to silanization. The clean and dried wafer was immersed in a dry toluene solution of the silane (10%, V/V) under an argon atmosphere and allowed to soak overnight at room temperature. Then, the wafer was removed from the solution and sequentially rinsed with toluene, chloroform, and then sonicated in chloroform for 3 minutes, rinsed again with chloroform and dried under a stream of argon.

| | After cleaning (contact angle) | Silane layer (contact angle) |
|---|---|---|
| Method A | $10^o$ | $45^o$ |
| Method B | $8^o$ | $47^o$ |
| Method C | $< 5^o$ | $85^o$ |
| Method D | $< 3^o$ | $65^o$ |

RCA wash: $H_2O$:$NH_4OH$ (27%) :$H_2O_2$(30%) = 4:1:1 at 80 $^0$C for 15 minutes. HCl wash: $H_2O$:HCl (aq. 36%): $H_2O_2$(30%) = 4:1:1 at 80 $^0$C for 25 minutes. Piranha wash: $H_2SO_4$ (96%):$H_2O_2$ = 3:1 at 120 $^0$C for 25 minutes. **Method A**: RCA then HCl wash; **Method B**: HCl then RCA wash; **Method C**: RCA then Piranha wash; **Method D**: Piranha then RCA wash.

**Table S1**. Screening for optimized pre-cleaning processes using advancing water contact angle changes as criteria.

## V. Images of patterned dye-SCS-Pd(II) pincer complex on silica surface.

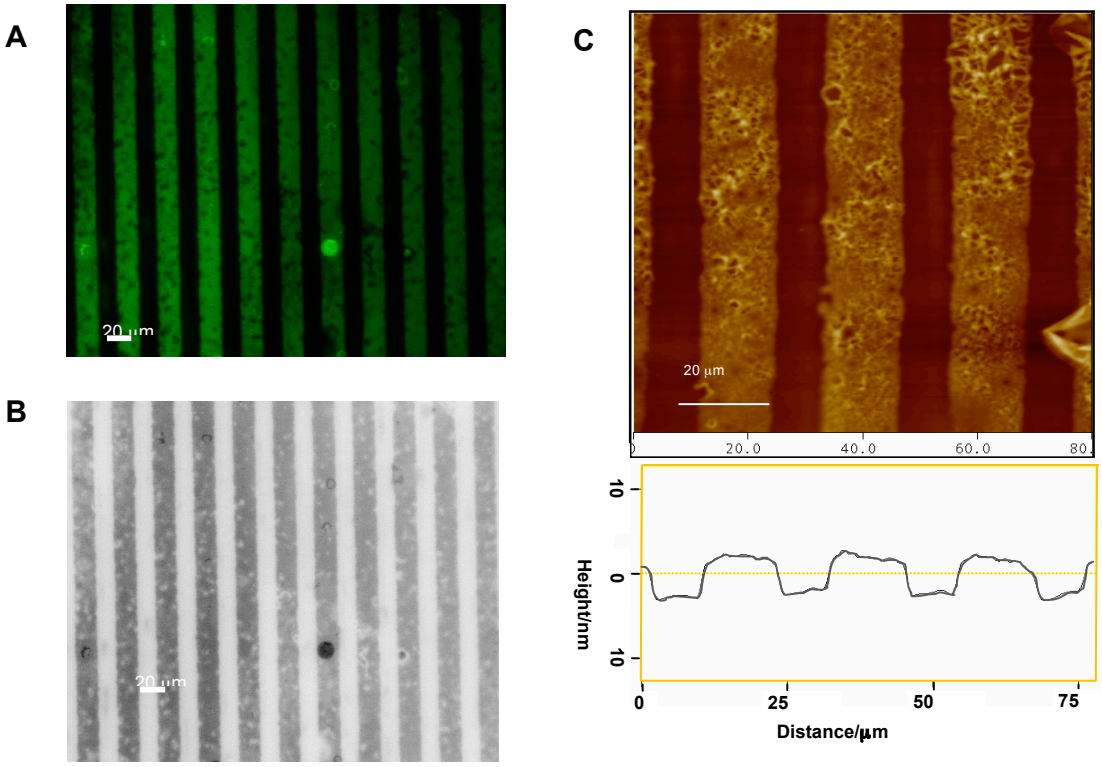


**Figure S5.** A) Microscopic image; B) Fluorescence microscopic image; C) Contact-mode AFM height image.