

Supporting Information

Single-Molecule Imaging of Platinum Ligand Exchange Reaction Reveals Reactivity Distribution

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I. General Information

Unless otherwise noted, all reagents and solvents were used as received from their respective suppliers. Reactions were monitored by thin-layer chromatography on pre-coated glass-backed plates (Merck F₂₅₀) and components were visualized using UV light or by treatment with I₂ adsorbed onto silica gel. Flash chromatography was performed on Dynamic Absorbents 43-60 micron silica gel. *N,N'*-Bis[(3-triethoxysilyl)propyl]thiourea was either synthesized (vide infra) or purified from technical grade material provided by Gelest, Inc (Morrisville, PA).

¹H NMR and ¹³C NMR spectra were acquired on either Bruker DRX-500 or DRX-400 spectrometers or a DRX-500 spectrometer equipped with a cryogenic probe. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual protiated solvent peaks as reported in the literatureⁱ with the exception of nitromethane-*d*₃, which was calibrated to 4.33 ppm for ¹H NMR and 62.7 ppm for ¹³C NMR. ¹³C NMR spectra acquired in D₂O are uncalibrated. Spectra are reported with the following abbreviations: app, apparent; br, broad; m, multiplet; q, quartet; s, singlet; t, triplet; td, triplet of doublets. High-resolution mass spectrometry (HRMS) was performed at the facility operated by the University of California, Irvine, Department of Chemistry. Ultra-pure water with >18 M Ω resistance and total organic content of <5 ppb was obtained from a Milli-Q Gradient A-10 water purifier (Millipore, Billerica, MA) using a Q-Gard 2 purification pack and a Quantum EX Ultrapure Organex cartridge. Fluorescence spectra were measured on an F-4500 fluorescence spectrofluorometer maintained at a facility operated by the University of California, Irvine, Department of Chemistry. All solvents used for single molecule studies were spectrophotometric grade.

II. Coverslip Preparation

Glass coverslips (25 × 25 mm, No. 1.5, VWR Scientific) with a thickness of 0.17 mm were cleaned by sonication in 20 mL of a 0.6% (v:v) solution of Hellmanex Detergent (Fisher Scientific) in MilliQ water for 60 min and then rinsed sequentially with MilliQ water and spectrophotometric grade EtOH six times each. The rinsed coverslips were dried with compressed air, then placed on aluminum foil and further dried in an oven at 115 °C for 10 to 20 min. Coverslips were either stored covered for functionalization the following day or functionalized immediately after drying.

The coverslips were functionalized by soaking the cleaned coverslips in solutions of the appropriate silanization reagents in Coplin staining jars (Bel-Art) for 1 h. For thiourea functionalization, the solution consisted of 0.5 g of *N,N'*-Bis[(3-triethoxysilyl)propyl]thiourea in 20 mL of spectrophotometric grade CHCl₃. After soaking, coverslips were rinsed sequentially with MilliQ water and spectrophotometric EtOH six times each and heated on aluminum foil in an oven at 115 °C for 30 min to cure and dry. For each experiment, a control set of coverslips was soaked in spectrophotometric grade CHCl₃ and carried through all subsequent steps except in the absence of the functionalization reagent to provide unfunctionalized glass surfaces.

III. Construction of Reaction Cells

Hollow glass cylinders approximately 50 × 13 mm were cut from glass test tubes (13 × 100 mm, VWR Scientific) after scoring with a file or dremel. The tubes were rinsed

thoroughly with MilliQ water and spectrophotometric grade ethanol and dried in an oven at 115 °C for 20 to 30 min.

To assemble the reaction cells, the cleaned and dried hollow cylinders were attached to the freshly functionalized coverslips by applying nail polish to the outside base of the tubes. All completed cells (Figure S1) were covered and stored for use the following day.



Figure S1. Reaction cell.

IV. Microscopy and Image Acquisition

A schematic of the microscopy set up is shown in Figure S2 below. Imaging was done on an IX71/IX51 inverted microscope (Olympus Corporation, San Diego, CA) configured for fluorescence microscopy. Laser light was generated by an Innova model 70C Kr/Ar ion laser (Coherent Inc., Santa Clara, CA) with the power set to 23 A (1.01-1.10 W). The laser light was split into its constituent lines by an acousto-optic tunable filter in a laser launch, (Prairie Technologies, Middleton, WI) with the 488 nm line being used for excitation of samples. The laser light was coupled to the microscope by way of a fiber-optic cable which focused the laser light on the back focal plane of the microscope objective. The objective used for magnification was an oil-immersion PlanApo N (Olympus Corporation, Japan) with a 1.45 numerical aperture. The laser light was reflected off a dichroic mirror (FF506-Di02-25X36, Semrock, Rochester, NY). Emitted light was passed by the dichroic mirror through a bandpass emission filter (FF01-525/30-

25, Semrock, Rochester, NY) that passed light between 510 and 540 nm. The field iris on the fiber light illuminator was constricted so that a circular area 132 μm in diameter was illuminated on the sample. All images were acquired in total internal reflectionⁱⁱ (TIR) mode. The microscope hardware and laser shutter were controlled using the SlideBook software package version 4.2.0.8 (Intelligent Imaging Innovations, Denver, CO). The focus was maintained constant throughout the experiment by keeping the sample stage the same distance from the objective using a continuous reflective-interface feedback focus system (CRIFF, Applied Scientific Instruments, Inc., Eugene, OR) with a z-axis controller (MFC-2000, Applied Scientific Instruments, Inc.) and a nanopositioner (Mad City Labs, Madison WI). The 780 nm laser light used by the CRIFF was reflected by a dichroic mirror between the filter turret and the objective of the microscope that reflected the CRIFF laser but passed the 510 to 540 nm fluorescence light emitted by the sample.

Images were acquired using a C9100-13 electron multiplier CCD camera (Hamatsu Photonics, Bridgewater, NJ). The CCD chip was a back-thinned electron multiplication type with an effective 512×512 array of pixels and a 16-bit analog-to-digital converter (65536 available intensity levels). The cell size was 16 μm , which with a 60 \times objective meant that each pixel in the acquired images represented an actual area of 267×267 nm. The CCD gain was set to 1 (minimum value) and the intensification to 141 (out of 250). The SlideBook software was configured to acquire continuous images with 300 ms per frame.

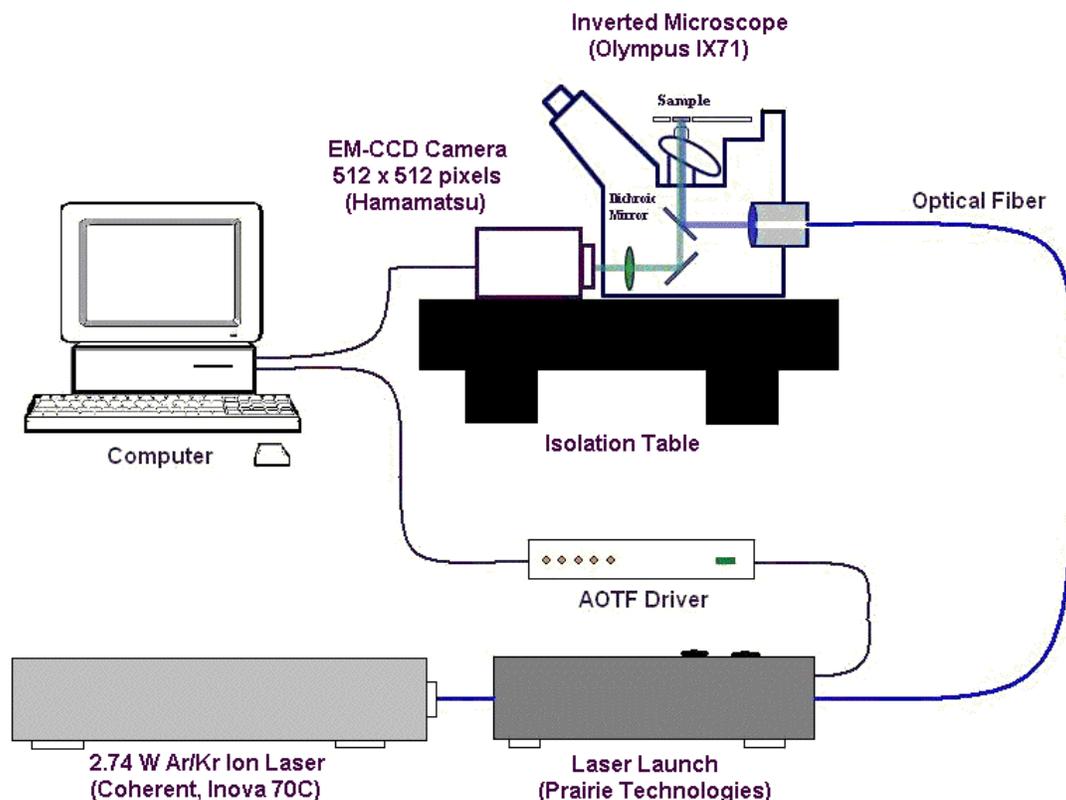


Figure S2. Schematic of microscopy setup.

V. Fluorophore Solution Preparation

The stock solutions of **1** and **3** were prepared on the same day as the experiment. A 10^{-3} M stock solution of **3** was prepared by dissolving the solid compound in spectrophotometric grade acetone. Final solutions of appropriate concentrations of **3** were obtained by serial dilution of the initial stock solutions into MilliQ water, affording a final solution of a 2000:1 ratio H₂O/acetone. For **1**, a 10^{-4} M stock solution was prepared by dissolving **17** in MilliQ water. Final solutions of appropriate concentrations were obtained by serial dilution of the initial stock solutions into MilliQ H₂O/acetone such that the resulting solution used for experiment was also a 2000:1 ratio of H₂O/acetone. For

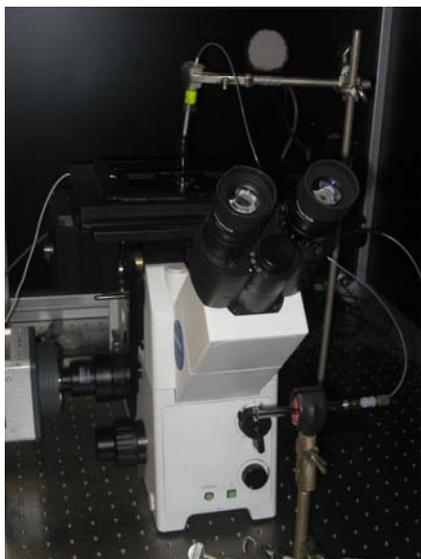
both complexes, final solutions were always prepared fresh by serial dilution of the stock solution immediately (<3 min) before each data acquisition. The last dilution was done directly into the reaction cell.

VI. Experimental Acquisition of Images

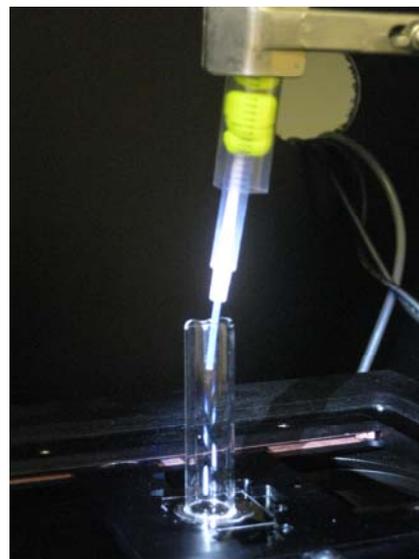
A reaction cell was filled with 2.0 mL H₂O and was placed on the objective on top of a drop of immersion oil ($n = 1.516$, Olympus) and illuminated with the laser light. After satisfactory focus was achieved on the reaction sample, the autofocus CRIFP was locked. Data acquisition was begun and 90 s of the solvent-only sample was acquired to serve as the background measurement. A 200 μ L aliquot of solution of **1**, **3**, or blank solvent was then injected into the reaction cell using a gastight syringe and PTFE tube to afford a final concentration of 5×10^{-10} M for **1** and **3** in the reaction cell, and images were acquired for another 90 s. The injection time was defined as $t = 0$.

The injection apparatus is shown in Figure S3. The tubing used was 0.020" ID PTFE tubing with an experimentally predetermined internal volume of 200 μ L. To ensure the reproducible delivery of 200 μ L, each injection began with a careful priming of the 500 μ L gas-tight syringe and coupled 0.020" ID PTFE tubing by aspirating and dispensing repeatedly to ensure the absence of air bubbles. To confirm the syringe was accurately calibrated to dispense 200 μ L of solution, this aspirate/dispense priming procedure was performed and 200 μ L of water was delivered into a tared glass beaker on a microbalance.

a.



b.



c.



Figure S3. Injection setup. **a.** Overall view of microscope, reaction cell, and injection apparatus. **b.** Close up view of injection apparatus and reaction cell. **c.** Close up of gastight syringe with tubing (tubing leads to reaction cell).

VII. Image Processing and Data Analysis

The time-lapse images were initially recorded by the SlideBook software as Shockwave Flash Objects and were converted by the same software to TIFF files. Images were viewed in ImageJ (NIH, <http://rsbweb.nih.gov/ij/>).

Single-molecule activity from the images was quantified with a home-written MATLAB program. Curve fitting was performed with Origin (Origin Lab). A general description follows. The average of the noise was used to set a baseline (Figure S3A). A single-molecule binding event was identified as a signal that was a certain value above the baseline (threshold one). Any pixel exhibiting a signal intensity above the threshold for three or more frames was treated as a pixel that had the signal from a single molecule. Often, the signal from one molecule was distributed over more than one pixel. According to on/off trajectory similarity and spatial adjacency, all single molecule pixels belonging to the same molecule were identified. The center-pixel coordinates were kept and the rest were eliminated. Once the center-pixel coordinates were identified, the single molecule's trajectory through time was analyzed for on/off events. Specifically, a threshold was applied and the start of the time that the signal was above the threshold for three consecutive frames was defined as the "on" time. Use of a slightly lower threshold in this step than in the previous step (threshold two vs. threshold one, Figure S4A) was found to provide the most accurate results. Figure S4B provides an example of the outcome. The "on" time was used to identify the number of new molecules binding to the surface per time (Figure S4A). The duration of the signal and its "on" time were used to count the total number of observed molecules per time (Figure S4B).

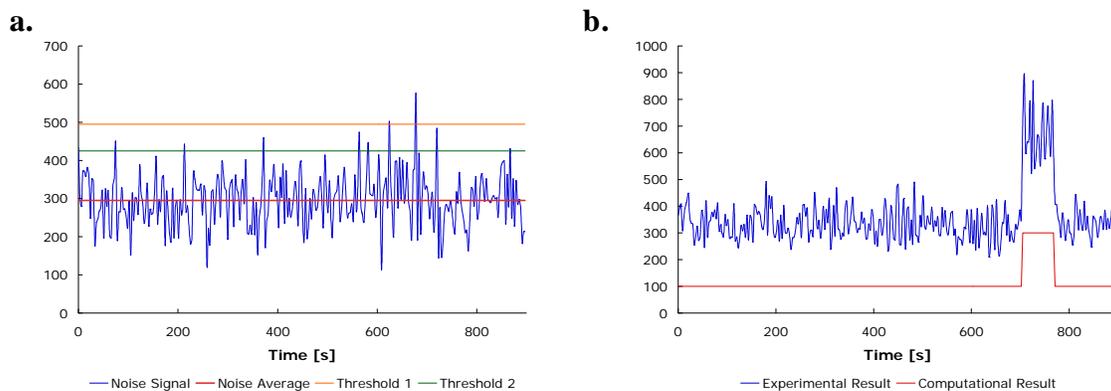


Figure S4. **a.** Noise sample showing how the baseline and threshold were determined. **b.** A typical single-molecule signal and its computer-extracted result.

VIII. Example Time Traces

Due to the anticipated multidisciplinary readership of our paper, we have included time traces of representative individual single molecules (Figures S5-S7) in order to demonstrate how the quantized termination of fluorescent signal serves as the well-established characterization fingerprint of individual single molecules.^{vii}

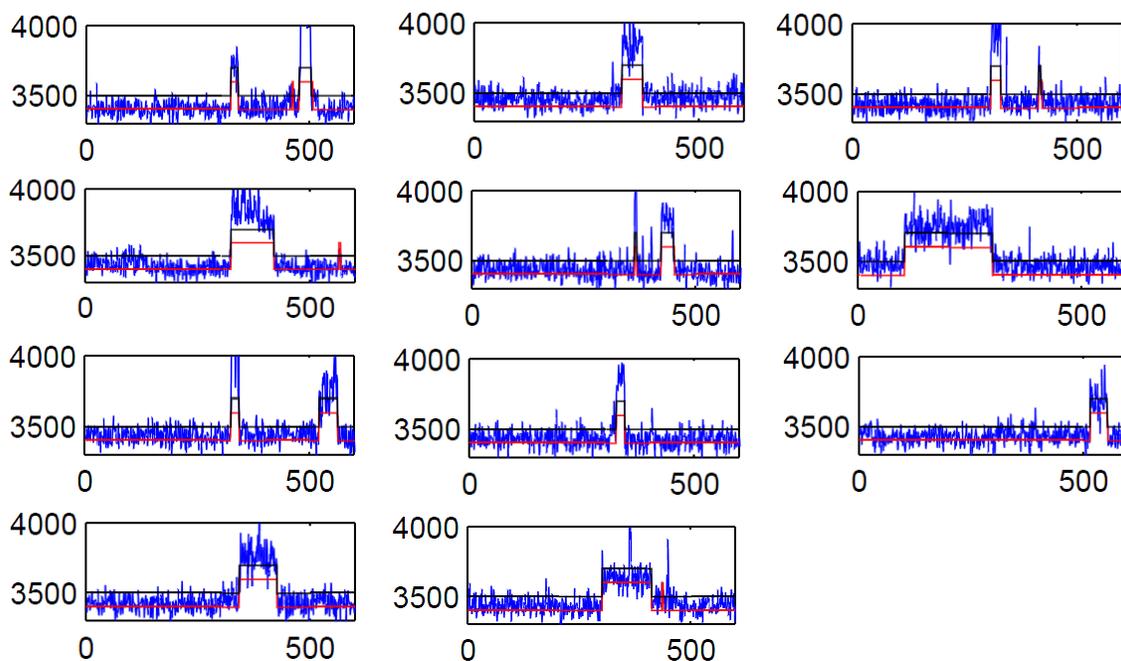


Figure S5. Example time traces for **1** on thiourea surface, showing the quantized behavior that is a well-established fingerprint of single molecules. The y-axis corresponds to the intensity of the signal and the X axis corresponds to frame number. The duration of each frame is 300 ms.

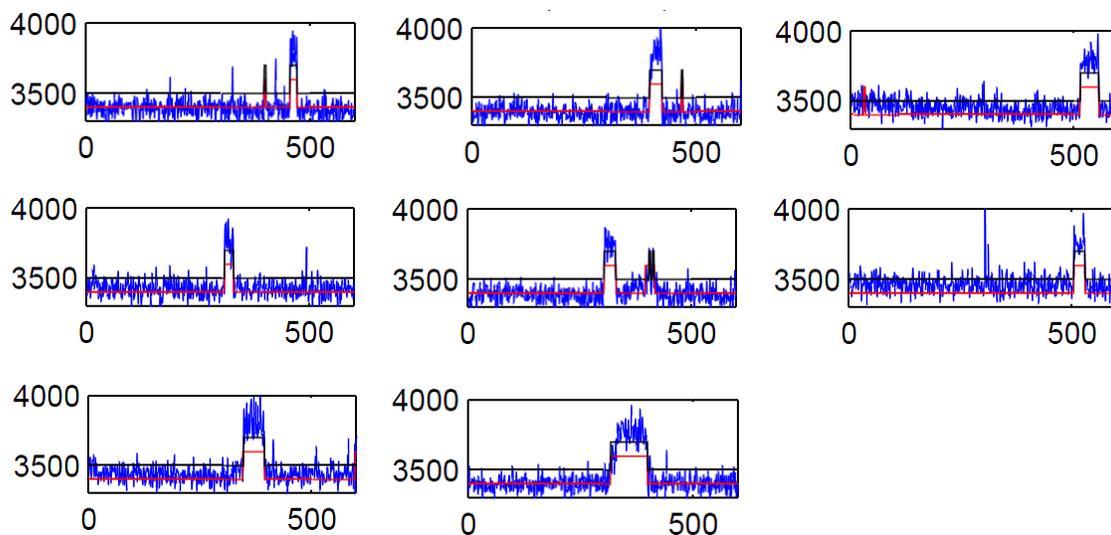


Figure S6. Example time traces for **1** on glass surface, showing the quantized behavior that is the well-established fingerprint of single molecules. The y-axis corresponds to the intensity of the signal and the X axis corresponds to frame number. The duration of each frame is 300 ms.

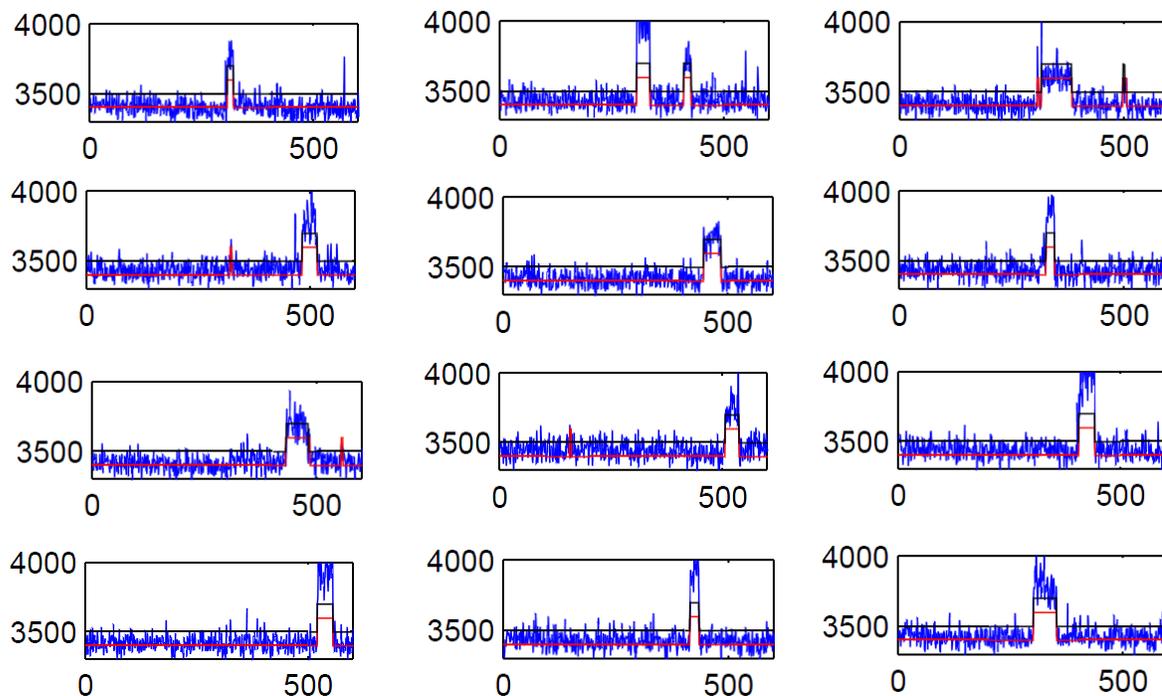


Figure S7. Example time traces for **3** on thiourea surface, showing the quantized behavior that is the well-established fingerprint of single molecules. The y-axis corresponds to the intensity of the signal and the X axis corresponds to frame number. The duration of each frame is 300 ms.

IX. Atomic Force Microscopy (AFM) Imaging and Analysis

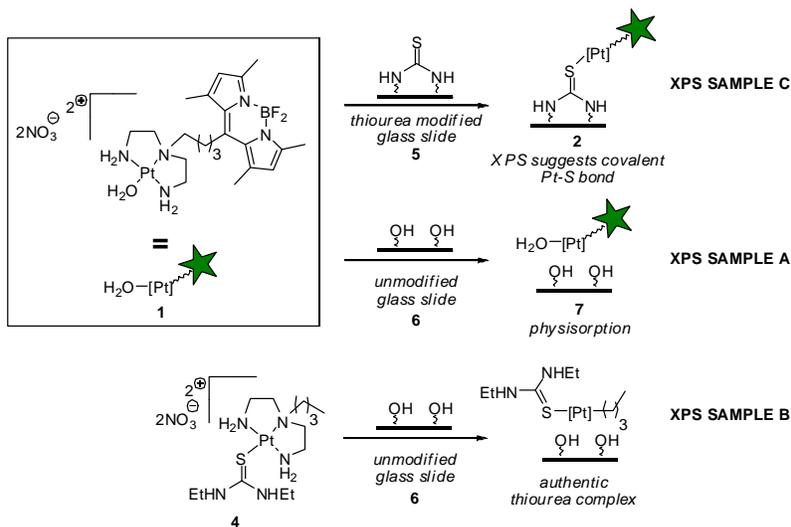
Topographic images were acquired on an Asylum Research MFP-3D™ Stand Alone atomic force microscope (MFP-3D-SA, Asylum Research, Santa Barbara, California) at ambient pressure and temperature. Images were acquired in the repulsive regime of AC mode using highly-doped silicon tips (Budget Sensors) with a 3 N m^{-1} force constant. Topographs were obtained as 256×256 pixels and were flattened line-by-line and analyzed using image processing software supplied by Asylum Research.

X. Surface Characterization: Estimation of Density of Coverage

Surface coverage of the glass coverslip by the silanizing reagent was estimated as one site/20 Å² (i.e., approximately one monolayer), based on prior XPS and fluorescence studies from our laboratory.ⁱⁱⁱ

XI. X-ray Photoelectron Spectroscopy

Scheme S1.



XPS spectra were acquired with an ESCALAB MKII photoelectron spectrometer. The instrument is an ultrahigh vacuum system equipped with a Al/Mg twin anode X-ray source and a 150 mm hemispherical electron energy analyzer. Spectra were taken by using the Al K α radiation (1286.6 eV) and the base pressure in the chamber was 1×10^{-9} torr throughout the experiment. The constant analyzer energy mode was used during the experiment and the pass energy for high resolution scans was 20 eV. All binding energies were calibrated by using C (1s) = 284.5 eV.

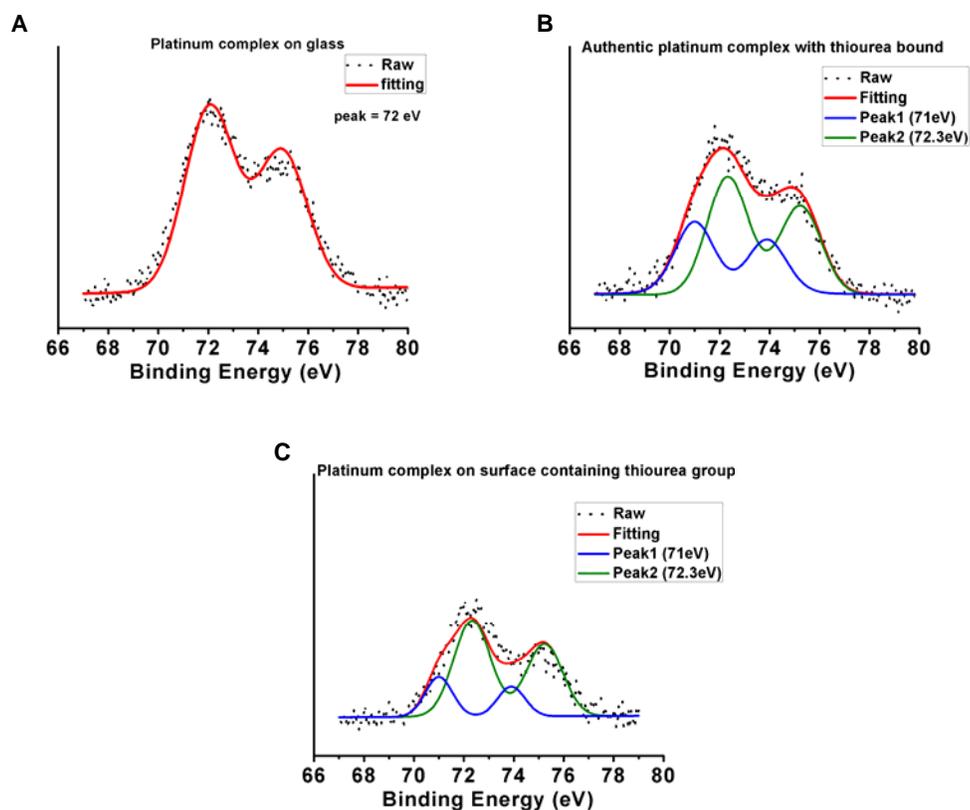


Figure S8. Comparison of XPS data. **A.** Platinum complex **1** on unmodified glass surface (**6**). **B.** Authentic platinum-thiourea complex **4** on unmodified glass surface **6**. **C.** Platinum complex **1** on thiourea surface (**2**).

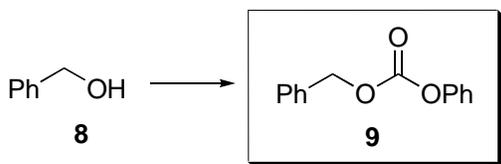
A sample of potential thiourea complex **2** with sufficient coverage for XPS analysis was prepared by dipping thiourea-modified glass slide **5** into an aqueous solution of complex **1** at 10^{-4} M, followed by rinsing with miliQ water and EtOH (Scheme S1). A sample of authentic thiourea complex **4** was prepared by dipping the unmodified glass slide **6** into an aqueous solution of complex **4** at 10^{-4} M, followed by rinsing with miliQ water and EtOH. XPS analysis of the platinum center revealed that authentic thiourea complex **4** and potential thiourea complex **2** shared similar characteristics (Figure S8). Specifically, two doublets provided the best fit for the XPS data of both **2** and **4**, and in both complexes these peak maxima were at 71.0 and 72.3 eV. This indicated a similarity

in the platinum binding environments in **2** and **4**, consistent with the presence of a covalent platinum-thiourea bond in both samples.

For comparison, a sample of physisorbed complex **7**, which did not contain a platinum-thiourea covalent bond, was prepared by dipping the unmodified glass slide **6** into an aqueous solution of complex **1** at 10^{-4} M, followed by rinsing with miliQ water and EtOH. This sample exhibited only one doublet by XPS, with a peak maximum of 72.0 eV (Figure S8).

XII. Synthetic Procedures

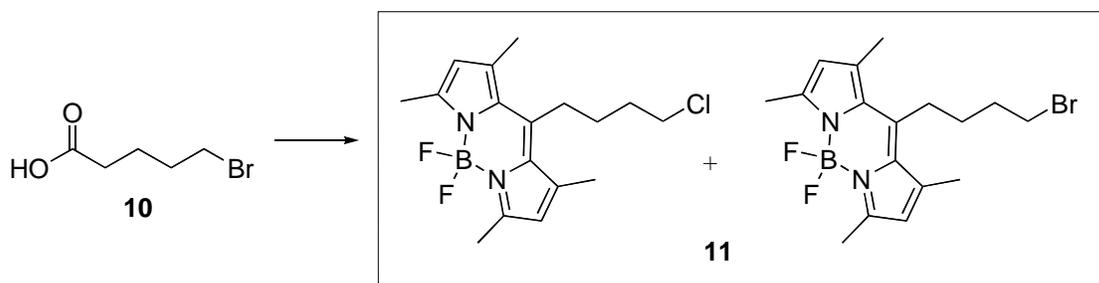
Benzyl phenyl carbonate (**8**)



A 100-mL round-bottom flask was charged with CH_2Cl_2 (50 mL), benzyl alcohol (6.60 mL, 63.8 mmol), pyridine (6.20 mL, 76.7 mmol), and a stir bar. The flask was fitted with a rubber septum equipped with a vent needle. Phenyl chloroformate (8.00 mL, 63.8 mmol) was added dropwise to the stirring mixture over ca. 15 min. The mixture increased in temperature during the addition and by the end of the addition a white solid had precipitated which eventually became pink. Additional CH_2Cl_2 (20 mL) was added and the pink slurry was stirred at room temperature for 2.5 h. Water (20 mL) was added to the stirring mixture and all solids dissolved. The biphasic mixture was transferred to a separatory funnel and washed with H_2SO_4 (2 M, 2×50 mL) and the combined aqueous layers were back-extracted with CH_2Cl_2 (20 mL). The combined organic layers were

dried over magnesium sulfate and concentrated in vacuo to afford 14.6 g (63.8 mmol, quantitative) of a pale yellow oil that was spectroscopically identical to the literature compound.^{iv} The product was taken on without further purification.

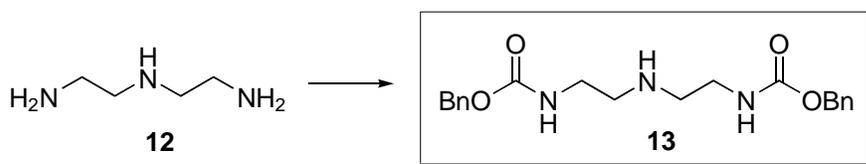
BODIPY(CH₂)₄Cl and BODIPY(CH₂)₄Br (11)



An oven-dried 100-mL round-bottom flask was charged with 5-bromovaleric acid (1.37 g, 7.54 mmol) and a stirbar, and then placed under a nitrogen atmosphere. Dry CH₂Cl₂ (40 mL) and dry DMF (0.040 mL, 0.052 mmol) were added to dissolve the solid. Thionyl chloride (0.66 mL, 9.1 mmol) was added via syringe causing a slow evolution of gas. After the evolution of gas subsided, the solution was stirred at room temperature for 1 h. The solution was concentrated in vacuo to yield a colorless oil and then put on a high vacuum line for 1 h to remove excess thionyl chloride. The acid chloride was redissolved in dry CH₂Cl₂ (10 mL) and added dropwise over a period of 5 min to a solution of 2,4-dimethylpyrrole (1.94 mL, 18.9 mmol) and phosphorus oxychloride (0.775 mL, 8.31 mmol) in dry CH₂Cl₂ (40 mL) under N₂. The mixture was stirred at reflux for 5 h, cooled to room temperature, and concentrated in vacuo. Hexanes (80 mL) were added and the mixture was stored at -35 °C overnight. The hexanes were decanted and the residue was placed under high vacuum for 1 h, then dissolved in dry toluene (55 mL) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (1.69 mL, 11.3 mmol). The solution was stirred for 1

h at 80 °C. Boron trifluoride dimethyl etherate (1.06 mL, 10.1 mmol) was added via syringe and the mixture was stirred at 80 °C for 1 h. The red solution was cooled to room temperature and washed with brine (3 × 50 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to yield a dark red solid. The solid was purified by flash chromatography (CH₂Cl₂:hexanes (1:1), R_f = 0.3) to yield 1.01 g (2.95 mmol, 39%) of the product as a dark red solid (10:1 mixture of chloride to bromide). ¹H NMR (500 MHz, CDCl₃) δ: 6.06 (s, 2H), 3.59 (t, *J* = 6 Hz 2H), 3.00-2.07 (m, 2H), 2.52 (s, 2H), 2.43 (s, 6H), 2.00-1.94 (m, 2H), 1.84-1.77 (m, 2H).

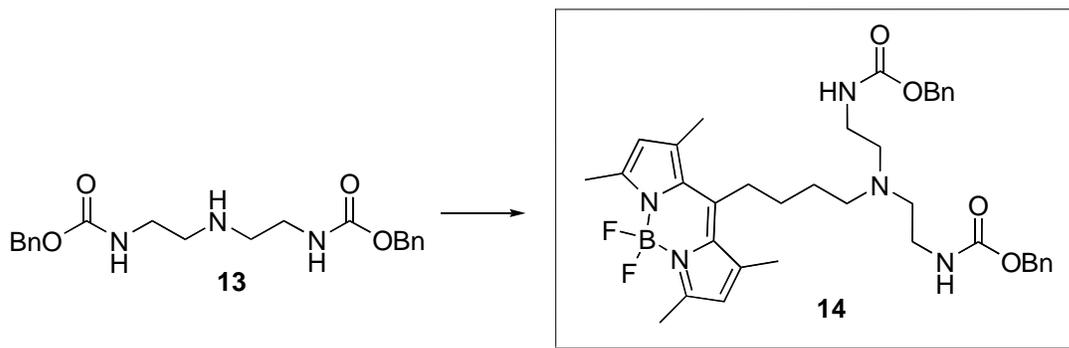
[2-(2-Benzyloxycarbonylaminoethyl)ethyl]carbamic Acid Benzyl Ester (13)



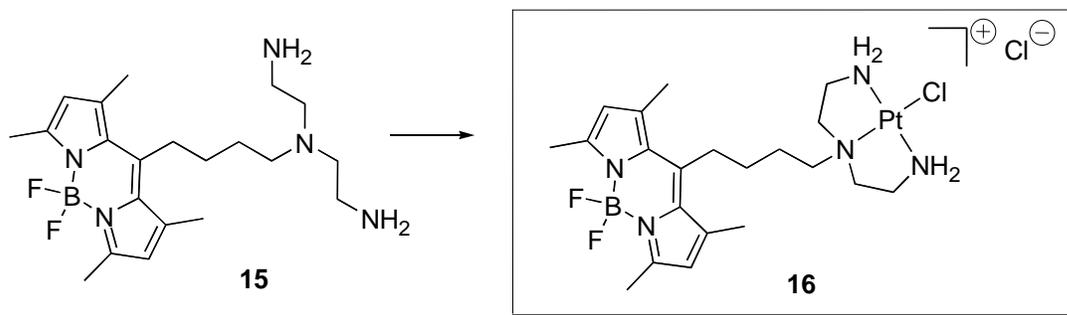
To a 250-mL round-bottom flask charged with CH₂Cl₂ (50 mL), diethylenetriamine (3.13 mL, 29.0 mmol), and a stir bar was added **9** (14.6 g, 63.8 mmol) in portions. The faint yellow solution was stirred at room temperature overnight, then concentrated in vacuo. The resulting oil was dissolved in EtOH (ca. 25 mL). Concentrated HCl (ca. 2.9 mL) was added dropwise. The resulting precipitate was isolated by vacuum filtration and washed with EtOH. The resulting solid was dried by placing it on a high vacuum line at 40 °C for 1 h. The hydrochloride salt was free-based with 1.5 equiv of aqueous sodium hydroxide and extracted with CH₂Cl₂. The resulting oil was purified by flash chromatography (CH₂Cl₂:MeOH:TEA (90:5:5), R_f = 0.5) to afford 4.45 g (12.0 mmol,

41%) of an oil that became an amorphous white solid upon standing and was spectroscopically identical to the literature compound.^{iv}

BODIPY(CH₂)₄(dien)Cbz (**14**)

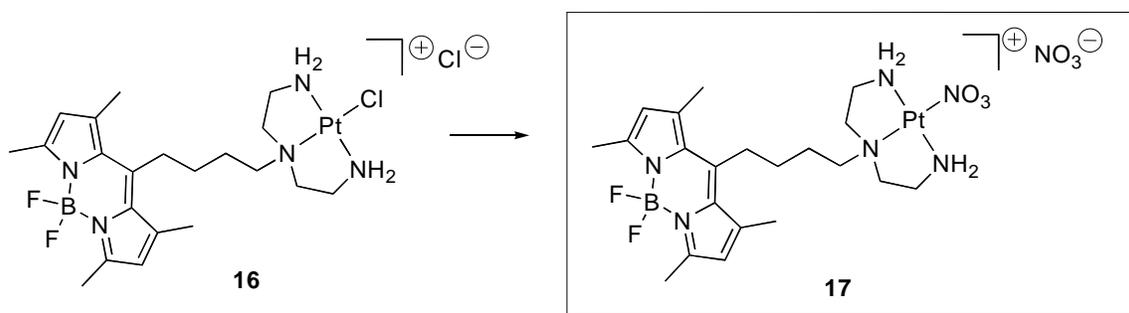


A 50-mL round-bottom flask was charged with **13** (1.10 g, 2.96 mmol), **11** (1.01 g, 2.95 mmol), sodium iodide (1.78 g, 11.9 mmol), potassium carbonate (0.820 g, 5.93 mmol) and a stirbar. The contents of the flask were suspended in acetone (12 mL) and stirred at reflux for 4 d. During this time, the system was sealed with grease and stoppers. The solution was cooled to room temperature and concentrated in vacuo to afford a red solid. Dichloromethane was added and the insoluble parts were removed by filtration. The filtrate was concentrated in vacuo to afford the crude product as a red oil. The product was purified by flash chromatography (1.5% MeOH in CH_2Cl_2 (5% MeOH in CH_2Cl_2 used for TLC development, $R_f = 0.4$)) to yield a thick oil which was stored under hexanes (30 mL) at $-35\text{ }^\circ\text{C}$ overnight. The product solidified and the hexanes were decanted. The product was placed under high vacuum to remove solvent residues, affording 1.44 g (2.14 mmol, 72%) of a red-orange solid. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ : 7.37-7.26 (m, 10H), 6.00 (s, 2H), 5.16 (br s, 2H), 5.04 (s, 4H), 3.26-3.14 (m, 4H), 2.94-2.87 (m, 2H), 2.58-2.52 (m, 4H), 2.52-2.44 (m, 2H), 2.50 (s, 6H), 2.37 (s, 6H), 1.57 (app br s, 4H). ^{13}C



A 100-mL round-bottom flask was charged with dichlorobis(dimethylsulfoxide)-platinum(II)^v (0.787 g, 1.86 mmol), **15** (0.830 g, 2.05 mmol), MeOH (60 mL) and a stirbar. The mixture was stirred at reflux for 1 h. The flask was cooled to room temperature and the solution was concentrated in vacuo to a volume of ca. 5 mL at which point a solid precipitated. Dichloromethane (2-3 mL) was added to the flask to redissolve the solid to afford clear red solution. Benzene was gradually added to the solution to induce precipitation. The resulting solid was isolated by filtration through a fine frit to afford 0.470 g of a red-orange solid, which was carried on without further purification.

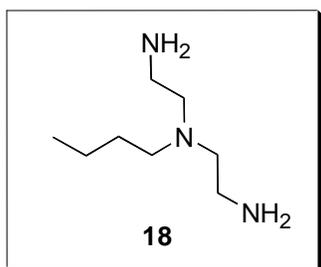
(BODIPY)(CH₂)₄(dien)nitratoplatinum nitrate (17)



A 100-mL round-bottom flask was charged with **16** (0.100 g, 0.149 mmol), silver nitrate (53.5 mg, 0.315 mmol), MeOH (25 mL), and a stirbar. The solution was stirred at reflux for 1 h, cooled to room temperature, and filtered through celite to afford a clear orange-red solution. The solution was concentrated in vacuo to a volume of ca. 2-3 mL at which

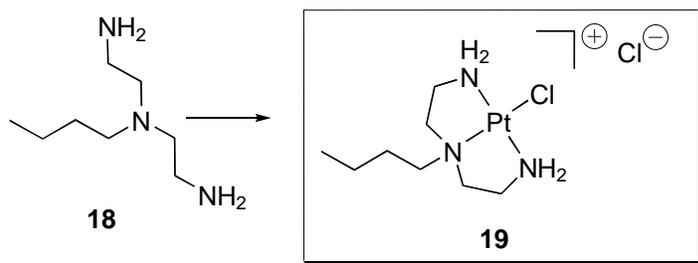
point a solid precipitated. Dichloromethane (2-3 mL) was added to the flask to redissolve the solid, affording a clear red solution. Benzene was graduatedly added to the solution to induce precipitation. The resulting solid was isolated by filtration through a fine glass frit to afford 31 mg (0.043 mmol, 29%) of a red-orange solid. ^1H NMR (500 MHz, CD_3NO_2) δ : 6.20 (s, 2H), 4.94 (br s, 2H), 4.52 (br s, 2H), 3.67-3.61 (m, 2H), 3.59-3.49 (m, 2H), 3.48-3.39 (m, 2H), 3.38-3.30 (m, 2H), 3.20-3.12 (m, 4H), 2.49 (s, 6H), 2.46 (s, 6H), 2.02-1.94 (m, 2H), 1.82-1.74 (m, 2H). ^{13}C NMR (126 MHz, CD_3NO_2 , determined from long-range C–H coupling in an HMBC spectrum due to limited solubility of compound; 12 out of 13 resonances identified in this manner) δ : 155.6, 147.6, 142.9, 132.6, 123.1, 63.0, 56.1, 48.9, 29.6, 28.9, 16.7, 14.6. HRMS (ESI): m/z calculated $[\text{M}]^+$ 662.2410, found 662.2419.

Butyldien (18)



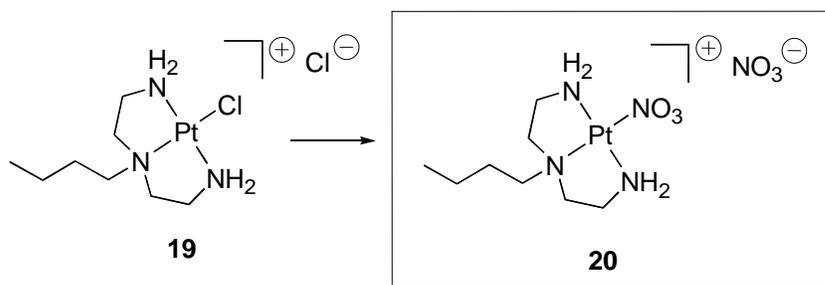
Butyldien was synthesized according to literature methods.^{vi} ^1H NMR (500 MHz, CDCl_3) δ : 2.70 (t, $J = 6$ Hz, 4H), 2.45 (t, $J = 6$ Hz, 4H), 2.39 (t, $J = 8$ Hz, 2H), 1.46 (br s, 4H), 1.93 (quintet, $J = 7$ Hz, 2H), 1.27 (sextet, $J = 8$ Hz, 2H), 0.88 (t, $J = 7$ Hz, 3H). B.P. = 70 °C (0.1 mmHg).

(Butyldien)chloroplatinum chloride (19)



A 100-mL round-bottom flask was charged with **18** (248 mg, 1.59 mmol), dichlorobis(dimethylsulfoxide)platinum(II)^v (619 mg, 1.47 mmol), MeOH (60 mL) and a stirbar. The mixture was stirred at reflux for 1 h, and then concentrated in vacuo to a volume of ca. 10 mL. Diethyl ether (30 mL) was added and the suspension was stirred at 0 °C for 10 min. The product was isolated by filtration to afford 0.600 g (1.41 mmol, 89 %) of a gray solid. ¹H NMR (500 MHz, D₂O) δ: 5.38 (br s, 2H), 4.97 (br s, 2H), 3.47-3.34 (overlapping m, 4H), 3.28 (td, *J* = 14, 5 Hz, 2H), 3.18-3.02 (m, 4H), 1.59 (quintet, *J* = 8 Hz, 2H), 1.35 (sextet, *J* = 8 Hz, 2H), 0.93 (t, *J* = 8 Hz, 3H). ¹³C NMR (126 MHz, D₂O) δ: 61.2, 54.6, 48.2, 23.7, 19.5, 13.0.

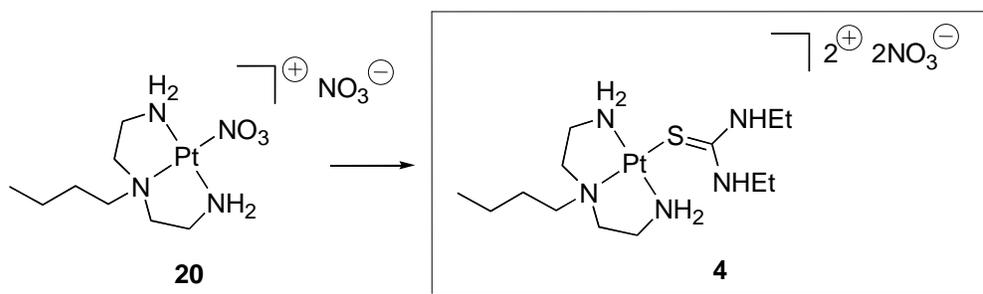
(Butyldien)nitratoplatinum nitrate (20)



A 250-mL round-bottom flask was charged with **21** (0.300 g, 0.705 mmol), silver nitrate (0.240 g, 1.41 mmol), MeOH (100 mL) and a stirbar. The solution was stirred at reflux for 1 h, cooled to room temperature, filtered through celite to afford a clear solution, and

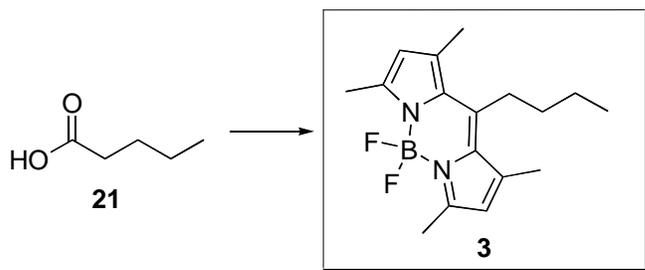
concentrated in vacuo to a volume of ca. 10 mL. Benzene (40 mL) was added and a fine solid precipitated. The product was isolated by filtration through a fine glass frit and air-dried to afford 0.180 g (0.376 mmol, 53 %) of a gray solid. ^1H NMR (500 MHz, D_2O) δ : 5.67 (br s, 2H), 5.26 (br s, 2H), 3.45-3.30 (m, 4H), 3.28-3.20 (m, 2H), 3.18-3.08 (m, 2H), 3.02 (d, $J = 10$ Hz, 2H), 1.61-1.52 (m, 2H), 1.34 (sextet, $J = 8$ Hz, 2H), 0.92 (t, $J = 8$ Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ : 61.8, 55.1, 47.1, 23.5, 19.4, 12.9.

(Butyldien)(*N,N'*-diethylthiourea)platinum dinitrate (4)



A 50-mL round-bottom flask was charged with **20** (0.120 g, 0.250 mmol), *N,N'*-diethylthiourea (33 mg, 0.25 mmol), MeOH (20 mL), and a stirbar. The solution was stirred at room temperature for 1 h and concentrated in vacuo to afford a volume of ca. 3 mL. Diethyl ether (30 mL) was added to form a thick oil layered with a clear solution. The clear solution was decanted. The thick oil was dried under high vacuum to afford 95 mg (0.16 mmol, 62%) of a gray solid. ^1H NMR (500 MHz, D_2O) δ : 3.60 (br s, 2H), 3.51-3.40 (m, 4H), 3.34-3.19 (m, 6H), 3.13 (dd, $J = 13, 4$ Hz, 2H), 1.63 (quintet, $J = 8$ Hz, 2H), 2.72 (sextet, $J = 8$ Hz, 2H), 1.21 (t, $J = 8$ Hz, 6H), 0.94 (t, $J = 8$ Hz, 3H). ^{13}C NMR (126 MHz, D_2O) δ : 59.6, 53.2, 48.6, 40.7 (br), 38.2 (br), 23.7, 19.6, 13.9, 13.0 (br), 12.7 (br).

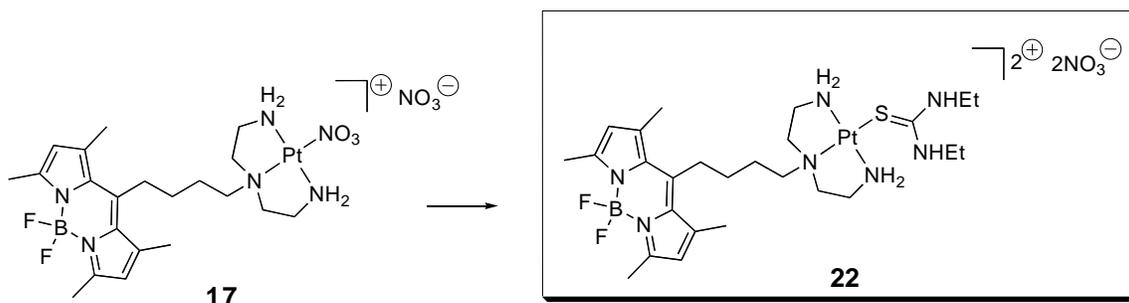
n-Butyl-BODIPY (3)



A 100-mL oven-dried flask was charged with CH₂Cl₂ (20 mL), 2,4-dimethylpyrrole (1.0 mL, 9.4 mmol), phosphorus oxychloride (0.39 mL, 4.2 mmol), and a stir bar, and placed under nitrogen. Valeryl chloride (0.45 mL, 3.8 mmol) in CH₂Cl₂ (10 mL) was added dropwise over 5 min under nitrogen. The solution was stirred at reflux under nitrogen for 5 h, cooled to room temperature, and concentrated in vacuo. Hexanes (80 mL) were added and the mixture was stored at -36 °C overnight, producing a residue. The hexanes were decanted and the remaining residue was placed under high vacuum for 1 h, then dissolved in dry toluene (30 mL) and treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (0.85 mL, 5.6 mmol) under nitrogen. The solution was stirred for 1 h at 80 °C. Boron trifluoride dimethyl etherate (0.50 mL, 5.4 mmol) was added by syringe and the stirring was continued at 80 °C for 1 h. The resulting red solution was cooled to room temperature and washed with water (3 × 30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to yield a dark red solid. The solid was purified by flash chromatography (CH₂Cl₂:hexanes (1:1) R_f = 0.4) to yield 0.38 g (1.5 mmol, 40%) of a dark red solid. ¹H NMR (500 MHz, CDCl₃) δ: 6.05 (s, 2H), 2.96-2.90 (m, 2H), 2.51 (s, 6H), 2.41 (s, 6H), 1.66-1.58 (m, 2H), 1.52 (sextet, *J* = 8 Hz, 2H), 0.99 (t, *J* = 8 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ: 153.8, 146.9, 140.4, 131.6, 121.7, 33.9,

28.2, 23.6, 16.5, 14.6 (t, $J_{C-F} = 3$ Hz), 13.9. HRMS (ESI): m/z calculated $[M+Na]^+$ 327.1823, found 327.1819.

[BODIPY(CH₂)₄](dien)(*N,N'*-diethylthiourea)platinum dinitrate (22)

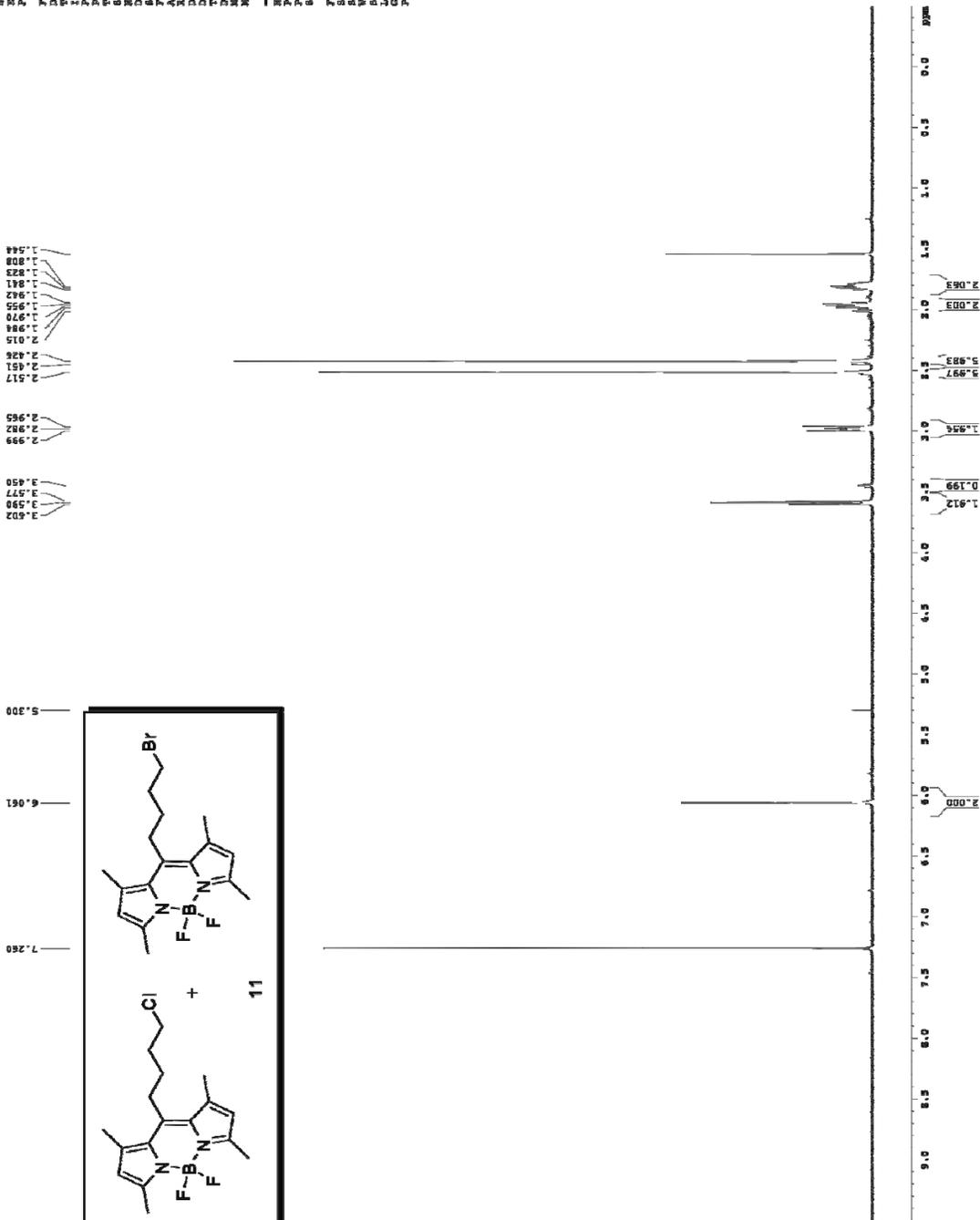


To a solution of **19** (0.0025 g, 0.0032 mmol) in CD₃NO₂ (2.25 mL) was added 0.065 mL of a 0.051 M solution of *N,N'*-diethylthiourea in CD₃NO₂. The solution went from slightly cloudy fluorescent green to clear fluorescent green. Yield was determined to be quantitative by comparison of the ¹H NMR spectrum of the solution with the spectrum of **4**.

XIII. NMR Spectra

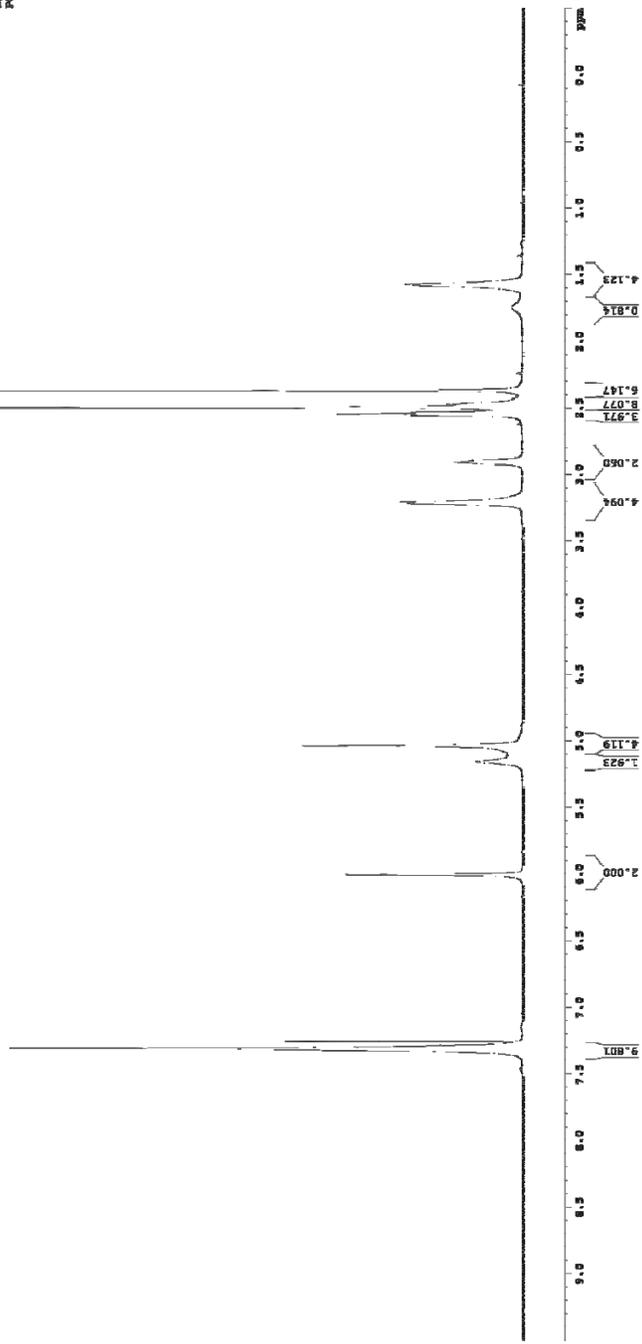
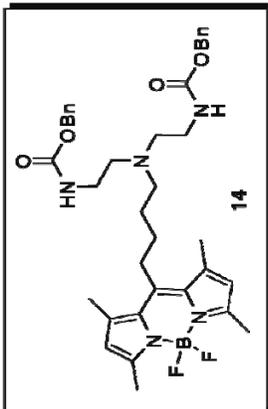
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AQ         62.400 uS
DE         6.00 uS
TE         300.2 K
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MAGNET     spect
PCPROG    MZSPP
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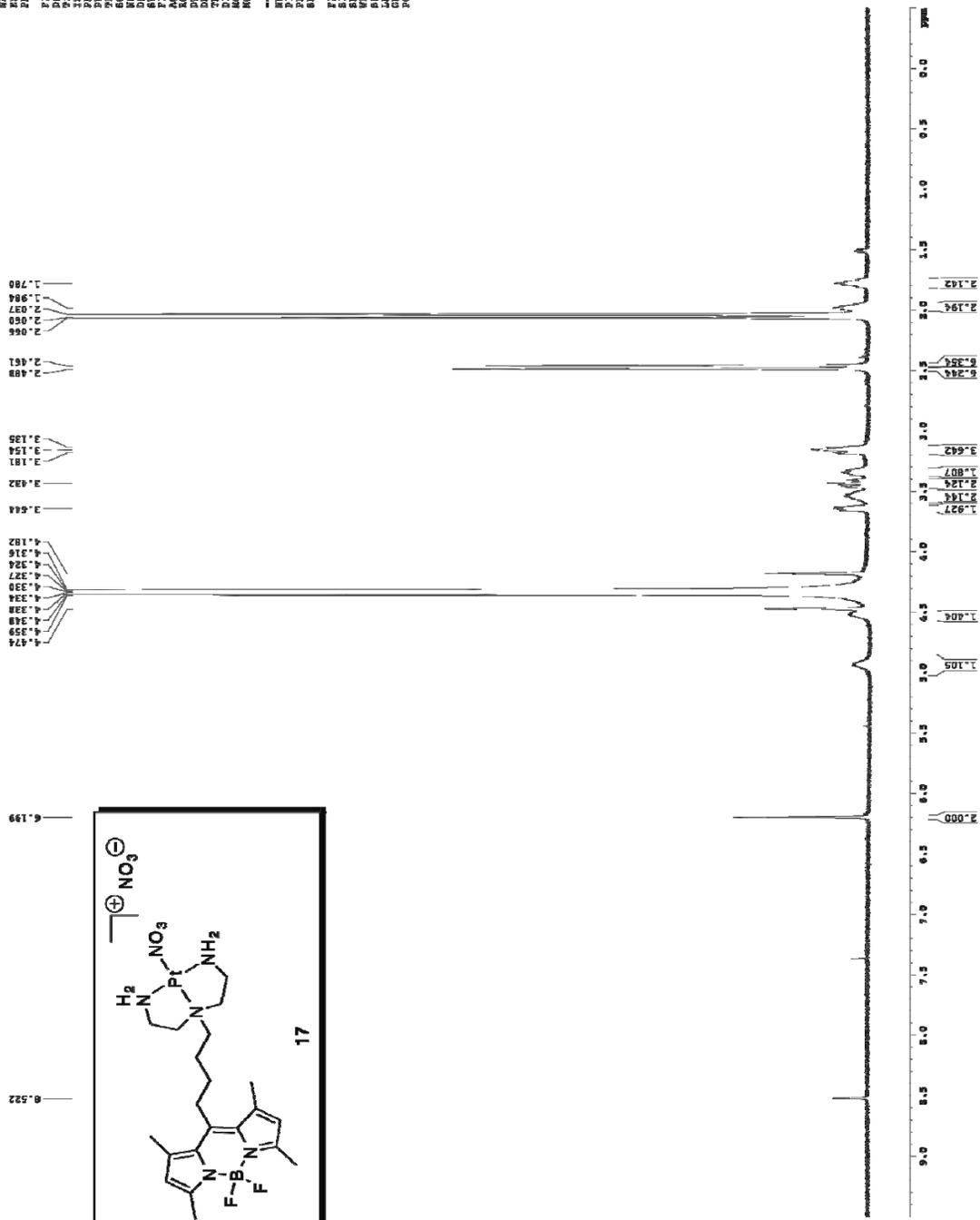


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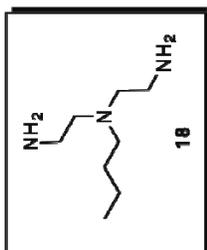


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 MCNCR: 0.01500000 sec
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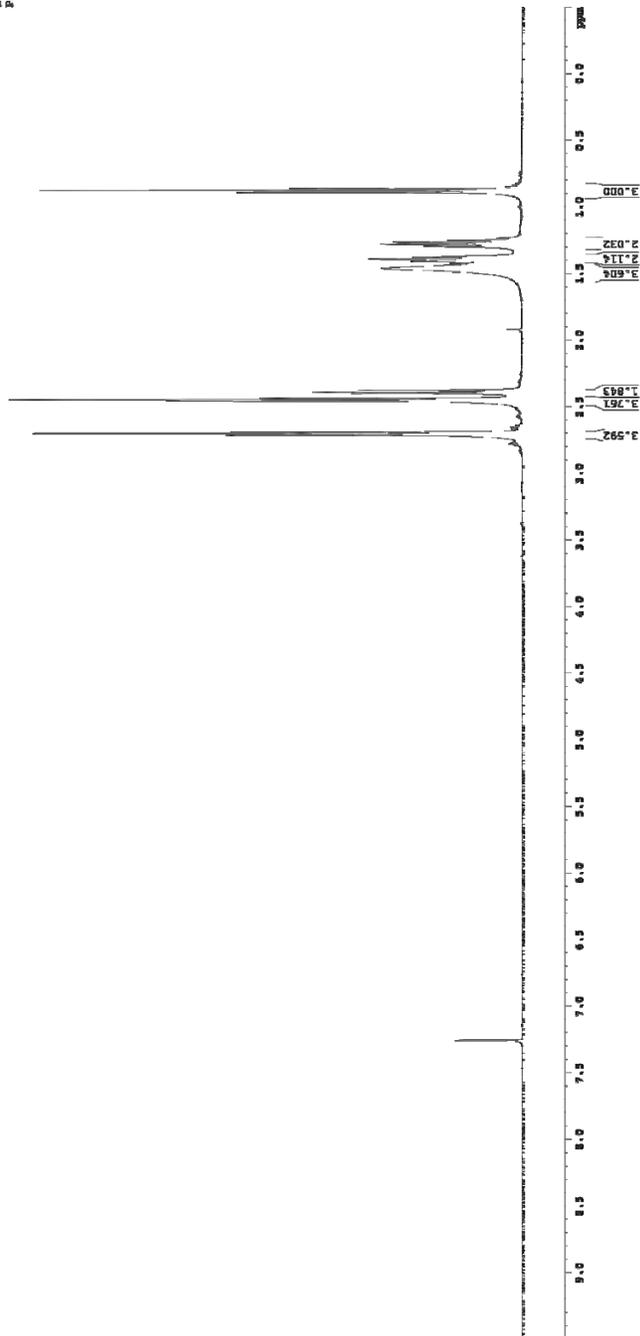


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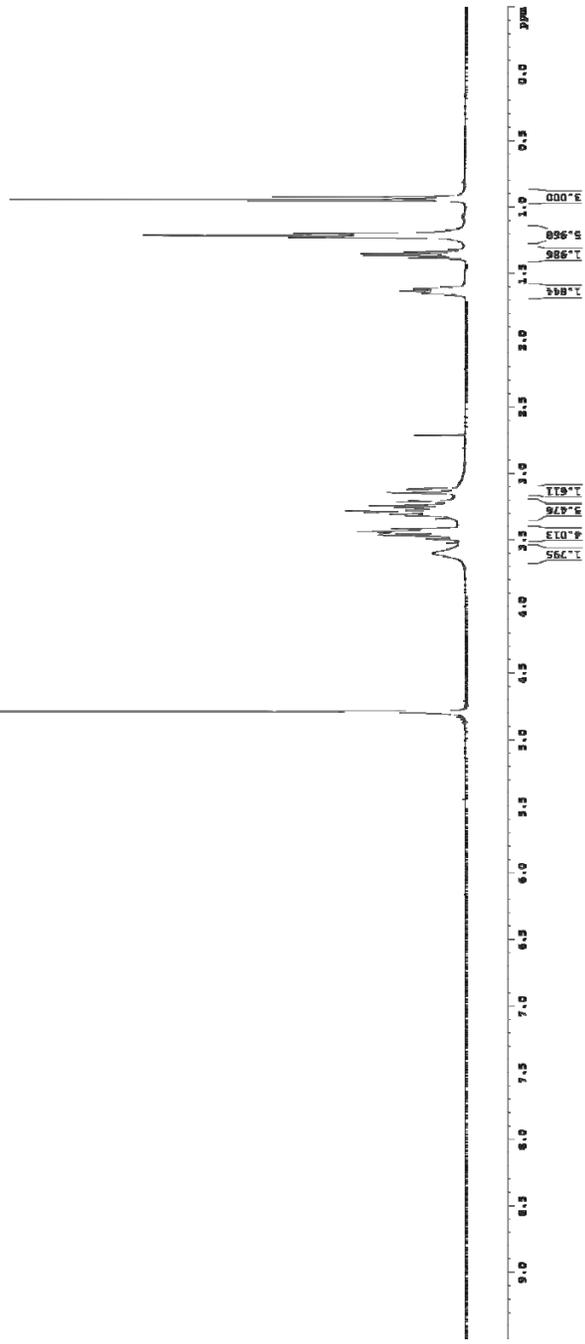
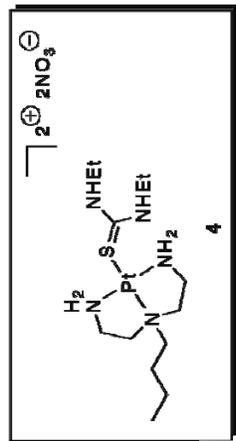


7.260



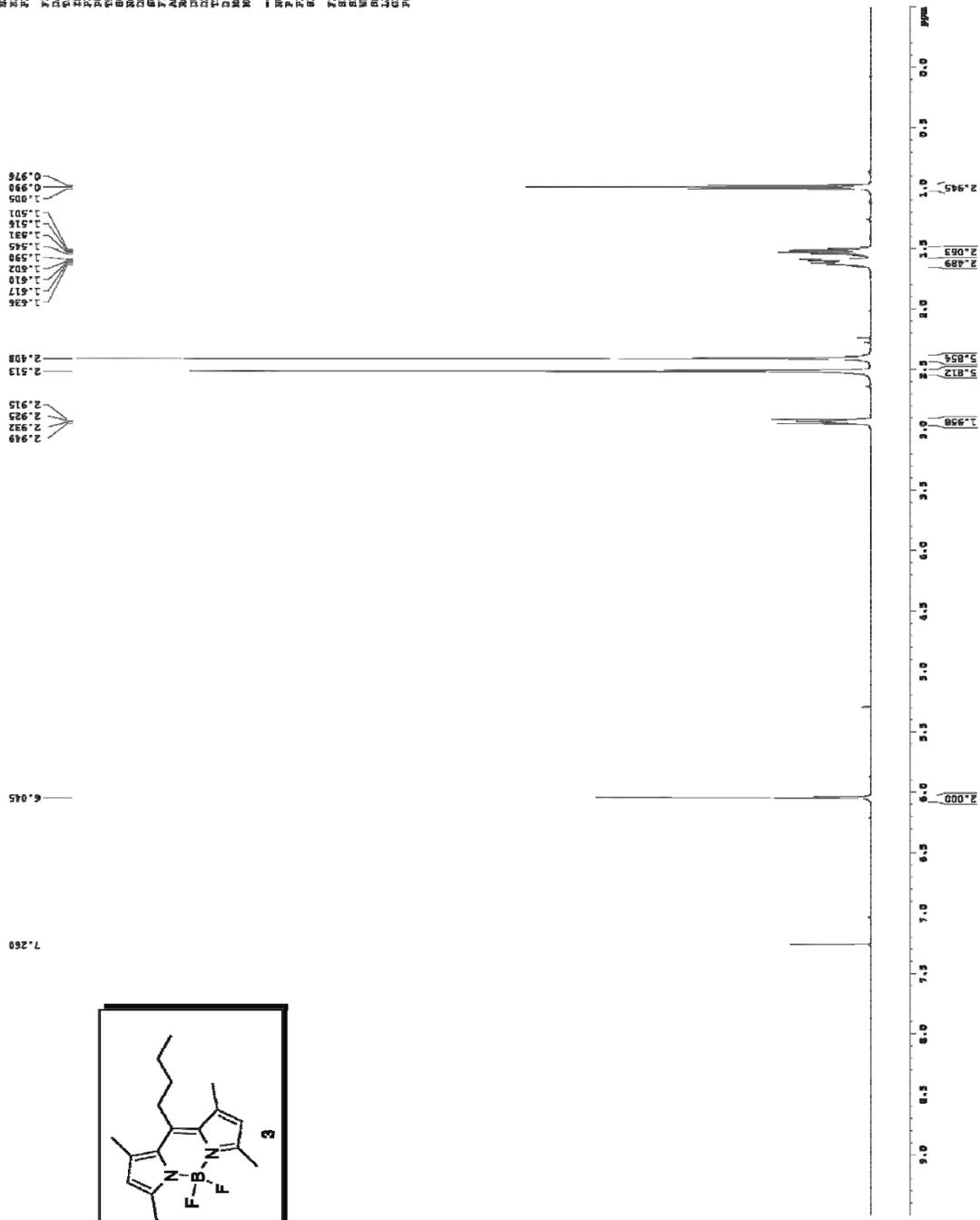
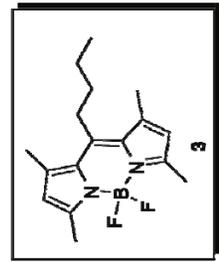
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Current Data Parameters
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1.005
0.976



XIV. Author Contributions

N. M. E. collected and analyzed data, and created figures. Y. W. collected data, developed Matlab analysis, and synthesized and purified fluorophore-tagged compounds. N. M. E. and Y. W. contributed equally to the study. J. Y. B. synthesized and purified compounds and aided the design of the study and data collection. T. P. C. and D. A. L. O. designed and constructed the reaction apparatus. M. H. C. acquired XPS data. J. C. H. and M. H. C. analyzed XPS data. J. C. H. supervised the XPS portion of the research. T. M. M. acquired AFM data. V. A. M. wrote a program for the radial pair correlation function. S. A. B. conceived of the study, supervised the research (except for XPS), and wrote the manuscript. All authors discussed the results and commented on the manuscript.

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