Supplementary Information

Electrodeposition and Electropolymerization of Polystyrenyl NHC Thin Films

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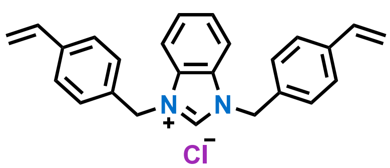
Synthetic Procedures

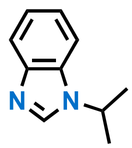
All reactions were performed under ambient conditions unless otherwise stated. Solvents were purchased from Sigma Aldrich, Alfa Aesar, or Fisher Scientific. All reagents were obtained from Sigma-Aldrich, Alfa Aesar, Oakwood Chemicals, or A2B Chemicals and used without further purification unless otherwise stated. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were acquired on a Bruker Avance III HD 400 MHz (^{1}H: 400.1 MHz, ^{13}C: 100.6 MHz) or 600 MHz (^{1}H: 599.5 MHz, ^{13}C: 150.8 MHz) spectrometer, and acquired spectra were calibrated internally using residual proteo-solvent signal relative to tetramethylsilane (δ = 0). FT-IR data were obtained on a Bruker Alpha II FT-IR spectrometer, and data are reported *via* signal strength in order of ranked intensity. Mass spectrometry data were recorded using a Bruker microToF II electrospray ionization spectrometer in positive mode.

1,3-Bis(4-vinylbenzyl)-1H-benzo[d]imidazol-3-ium Chloride (**1-Cl**):



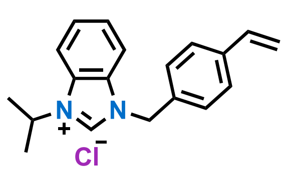
K_2CO_3 (3.51 g, 25.4 mmol) and 4-vinylbenzyl chloride (6.41 g, 42.0 mmol) were added to a solution of benzimidazole (2.00 g, 16.9 mmol) in MeCN (50 mL) in a pressure vessel, and the suspension was stirred at 90 °C for 18 h. Upon cooling to room temperature, the vibrant yellow oil was transferred to a round-bottom flask and the volatiles removed using a rotary evaporator. The yellow oil was triturated and sonicated in toluene (100 mL), resulting in the precipitation of a white solid. After collection *via* vacuum filtration and washing with diethyl ether (3 × 50 mL), the benzimidazolium chloride salt was isolated as a colourless powder. **Yield:** 3.19 g, 49%. **^{1}H NMR (600 MHz, methanol-*d$_4$*):** δ 7.88 (dd, *J* = 6.3, 3.2 Hz, 2H, aryl CH), 7.66 (dd, *J* = 6.3, 3.1 Hz, 2H, aryl CH), 7.58 – 7.48 (m, 4H, aryl CH – styrene), 7.45 (d, *J* = 8.0 Hz, 4H, aryl CH – styrene), 6.76 (dd, *J* = 17.6, 11.0 Hz, 2H, -HC=CH_2), 5.84 (dd, *J* = 17.6, 0.9 Hz, 2H, CH_2=CH-), 5.76 (s, 4H, -CH_2), 5.34 – 5.27 (m, 2H, CH_2=CH-) ppm.**^{13}C{^{1}H} NMR (151 MHz, methanol-*d$_4$*):** δ 140.11, 137.23, 133.82, 133.07, 129.66, 128.47, 128.16, 128.16, 115.53, 115.04, 51.78. **FT-IR (ATR, cm^{-1}):** 3336, 3033, 2970, 1607, 1557, 1514, 1460, 1433, 1409, 1372, 1338, 1210, 1188, 1119, 1016, 988, 931, 908, 856, 827, 754, 690 ppm. **ESI-MS:** calcd $[C_{25}H_{23}N_2]^+$ m/z = 351.1856, obs m/z = 351.186123.

1-Isopropyl-1H-benzo[d]imidazole (**BzPr**):



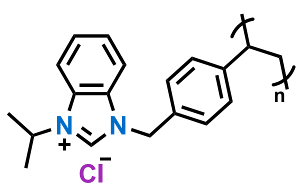
1-Isopropyl-1*H*-benzo[*d*]imidazole was synthesized according to a literature procedure and isolated as pale-yellow oil.[1] **Starting material:** Benzimidazole (1.00 g, 8.46 mmol). **Yield:** 1.17 g, 86.0%. Spectroscopic data are in agreement with literature values.[1]

1-Isopropyl-3-(4-vinylbenzyl)-1H-benzo[d]imidazol-3-ium Chloride (**2-Cl**):



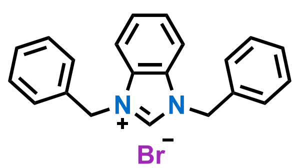
BzPr (1.00 g, 6.24 mmol) was dissolved in MeCN (50 mL) in a pressure vessel. 4-Vinylbenzyl chloride (1.43 g, 9.36 mmol) was added to the flask and the vibrant yellow solution was stirred at 90 °C for 18 h. Upon cooling to room temperature, the mixture was transferred to a round-bottom flask and the volatiles removed using a rotary evaporator. The yellow oil was triturated and sonicated in a mixture of acetone (5 mL) and diethyl ether (100 mL), resulting in the precipitation of a white solid. After collection *via* vacuum filtration and washing with diethyl ether (3 × 50 mL), the benzimidazolium chloride salt was isolated as a colourless powder. **Yield:** 1.60 g, 82%. **^{1}H NMR (400 MHz, methanol-*d$_4$*):** δ 9.83 (s, 1H, carbenic proton), 8.07 (dt, *J* = 8.4, 1.0 Hz, 1H, aryl CH), 7.88 – 7.83 (m, 1H, aryl CH), 7.69 (dddd, *J* = 22.0, 8.3, 7.3, 1.2 Hz, 2H, aryl CH), 7.55 – 7.37 (m, 4H, aryl CH – styrene),6.75 (dd, *J* = 17.6, 11.0 Hz, 1H, -HC=CH_2), 5.83 (dd, J = 17.6, 0.9 Hz, 1H, CH_2=CH-), 5.77 (s, 2H, -CH_2), 5.29 (dd, *J* = 11.0, 0.9 Hz, 1H, CH_2=CH-), 5.12 (p, *J* = 6.7 Hz, 1H, -CH(CH_3)$_2$), 1.78 (d, *J* = 6.7 Hz, 6H, -CH_3).**^{13}C{^{1}H} NMR (101 MHz, methanol-*d$_4$*):** δ 141.39, 139.94, 137.24, 134.13, 133.00, 132.67, 129.41, 128.37, 128.25, 128.07, 115.43, 115.06, 115.03, 52.84, 51.81, 22.18. **FT-IR (ATR, cm^{-1}, ranked intensity):** 3270, 2970, 2852, 1758, 1645, 1495, 1455, 1414, 1367, 1297, 1231, 1161, 1126, 1107, 950, 890,817, 728, 677. **ESI-MS:** calcd $[C_{19}H_{21}N_2]^+$ m/z = 277.170473, obs m/z = 277.1702.

Poly(1-isopropyl-3-(4-vinylbenzyl)-1H-benzo[d]imidazol-3-ium Chloride) (**3-Cl**):



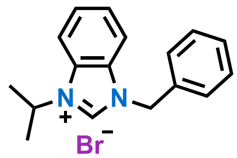
2-Cl (2.00 g, 6.39 mmol) and AIBN (0.052 g, 0.32 mmol) were dissolved in DMSO (10 mL) in a Schlenk flask, and the mixture was subjected to three freeze-pump-thaw cycles to remove dissolved gases. The flask was subsequently kept under a flow of N_2, and the reaction mixture was heated at 90 °C for 18 h. After cooling to room temperature, THF (225 mL) was added to the flask and resulted in the precipitation of a white solid. The precipitate was collected *via* vacuum filtration and washed with MeCN (3 × 50 mL) to remove remaining monomer. After drying on a Schlenk line, the product was isolated as a free-flowing, colourless powder. **Yield:** 1.09 g, 55%. **^{1}H NMR (600 MHz, methanol-*d$_4$*):** δ 10.32 (m, 1H, carbenic proton), 8.08 – 7.96 (m, 2H, aryl CH), 7.77 – 7.18 (m, 6H, aryl CH), 6.44 (d, 2H, -CH_2), 5.82 (br. s, 2H, -CH_2), 5.07 (br. s, 1H, -CH), 1.84 – 1.64 (m, 6H, -CH_3), 1.55 – 0.95 (m, 2H, polymeric CH_2).**^{13}C{^{1}H} NMR (151 MHz, methanol-*d$_4$*):** δ 141.80, 132.66, 129.64, 128.06, 115.13, 52.85, 51.94, 22.44. **FT-IR (ATR, cm^{-1}, ranked intensity):** 3340, 2980, 2920, 1608, 1556, 1513, 1478, 1422, 1373, 1315, 1266, 1214, 1135, 1095, 1018, 998, 850, 817,751, 658.

1,3-Bis(benzyl)-1H-benzo[d]imidazol-3-ium Bromide (**4-Br**):



K_2CO_3 (2.35 g, 17.0 mmol) and benzyl bromide (4.30 g, 25.1 mmol) were added to a solution of benzimidazole (1.00 g, 8.46 mmol) in MeCN (50 mL) in a pressure vessel, and the suspension was stirred at 90 °C for 18 h. Upon cooling to room temperature, the vibrant yellow oil was transferred to a round-bottom flask and the volatiles were removed using a rotary evaporator. The yellow oil was triturated and sonicated in toluene (100 mL), resulting in the precipitation of a white solid. After collection *via* vacuum filtration and washing with diethyl ether (3 × 50 mL) and acetone (3 × 50 mL), the benzimidazolium chloride salt was isolated as a colourless powder. **Yield:** 3.16 g, 98%. **^{1}H NMR (400 MHz, methanol-*d$_4$*):** δ 7.90 (dt, *J* = 6.7, 3.4 Hz, 2H, aryl CH), 7.67 (dt, *J* = 6.6, 3.3 Hz, 2H, aryl CH), 7.53 (qd, *J* = 4.5, 2.9, 2.4 Hz, 4H, aryl CH), 7.50 – 7.40 (m, 6H, aryl CH), 5.83 (s, 4H, -CH_2). **^{13}C{^{1}H} NMR (101 MHz, methanol-*d$_4$*):** δ 134.60, 133.00, 130.44, 130.29, 129.40, 128.38, 115.07, 52.06. **FT-IR (ATR, cm^{-1}, ranked intensity):** 3429, 3367, 3118, 3031, 2974, 2877, 1605, 1557, 1497, 1457, 1425, 1372, 1362, 1336, 1279, 1216, 1188, 1130, 1015, 944, 822, 755, 699. **ESI-MS:** calcd $[C_{21}H_{19}N_2]^+$ m/z = 299.154823, obs m/z = 299.1548.

1-Isopropyl-3-benzyl-1H-benzo[d]imidazol-3-ium Bromide (**5-Br**):



BzPr (2.02 g, 12.6 mmol) was dissolved in MeCN (50 mL) in a pressure vessel. Benzyl bromide (4.32 g, 25.3 mmol) was added to the flask and the vibrant yellow solution was stirred at 90 °C for 18 h. Upon cooling to room temperature, the mixture was transferred to a round-bottom flask and the volatiles were removed using a rotary evaporator. The yellow oil was triturated and sonicated in a mixture of acetone (5 mL) and diethyl ether (100 mL), resulting in the precipitation of a white solid. After collection *via* vacuum filtration and washing with diethyl ether (3 × 50 mL), the benzimidazolium chloride salt was isolated as a colourless powder. **Yield:** 2.49 g, 59.6%. **^{1}H NMR (400 MHz, methanol-*d_4*):** δ 8.09 (dd, *J* = 8.2, 1.1 Hz, 1H, aryl CH), 7.87 (dt, *J* = 8.2, 0.9 Hz, 1H, aryl CH), 7.70 (ddd, *J* = 24.3, 8.3, 7.3, 1.1 Hz, 2H, aryl CH), 7.56 – 7.51 (m, 2H, aryl CH), 7.48 – 7.38 (m, 3H, aryl CH), 5.83 (s, 2H, -CH_2), 5.16 (p, *J* = 6.7 Hz, 1H, -$CH(CH_3)_2$), 1.80 (d, *J* = 6.8 Hz, 6H, -CH_3) ppm.**^{13}C{^{1}H} NMR (101 MHz, methanol-*d_4*):** δ 141.13, 134.86, 132.92, 132.59, 130.35, 130.14, 129.20, 128.29, 128.19, 115.09, 115.07, 52.82, 52.06, 22.23 ppm. **FT-IR (ATR, cm^{-1}, ranked intensity):** 3425, 3384, 2976, 1628, 1557, 1490, 1478, 1458, 1427, 1374, 1335, 1324, 1267, 1225, 1181, 1138, 1097, 1080, 1027, 992, 823, 770, 699. **ESI-MS:** calcd $[C_{17}H_{19}N_2]^+$ m/z = 251.154823, obs m/z = 251.1533.

^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

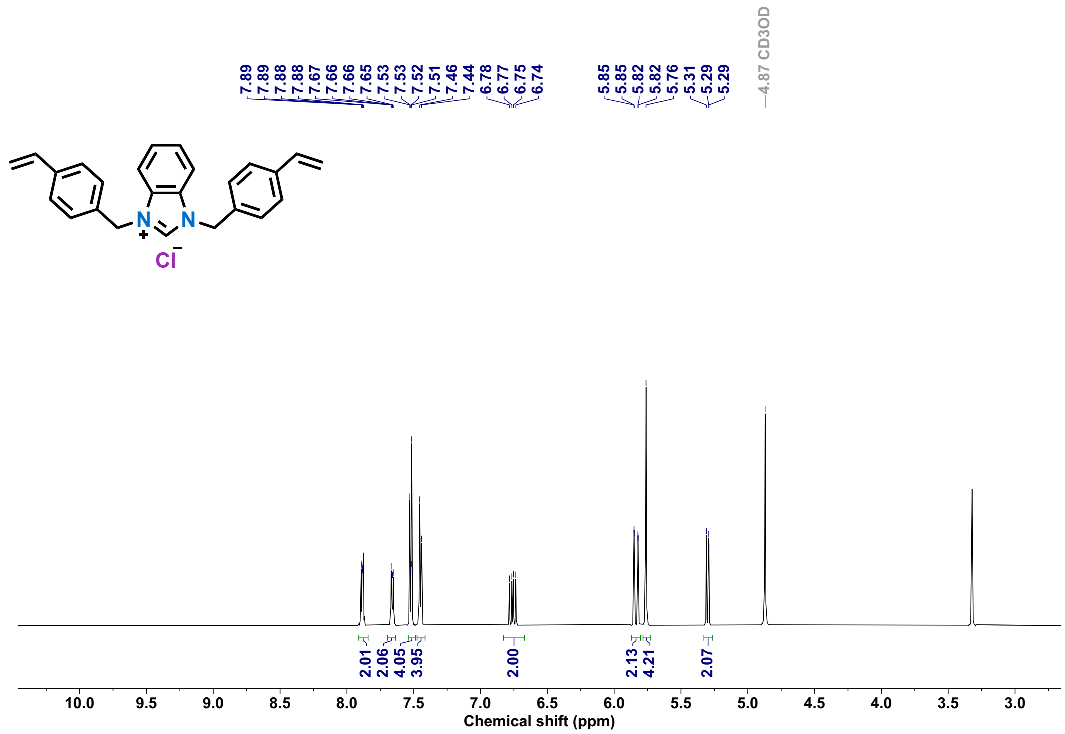


Figure S1. ^{1}H NMR spectrum of **1-Cl** in CD_3OD.

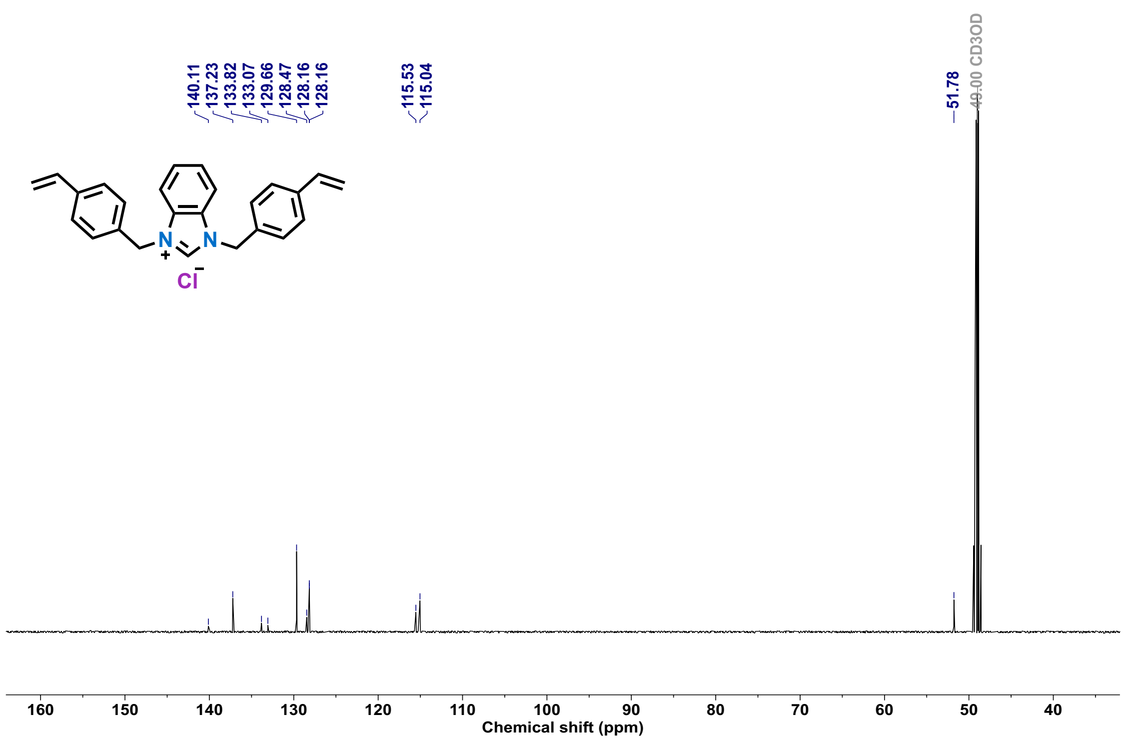


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1-Cl** in CD_3OD.

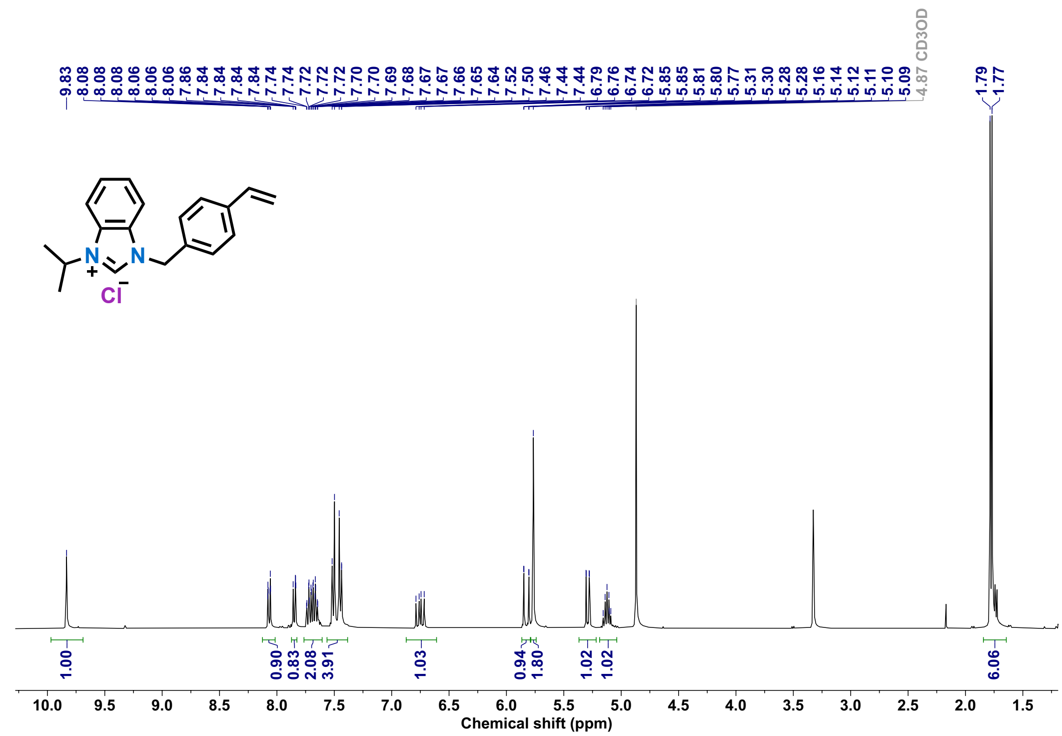


Figure S3. ^{1}H NMR spectrum of **2-Cl** in CD_3OD.

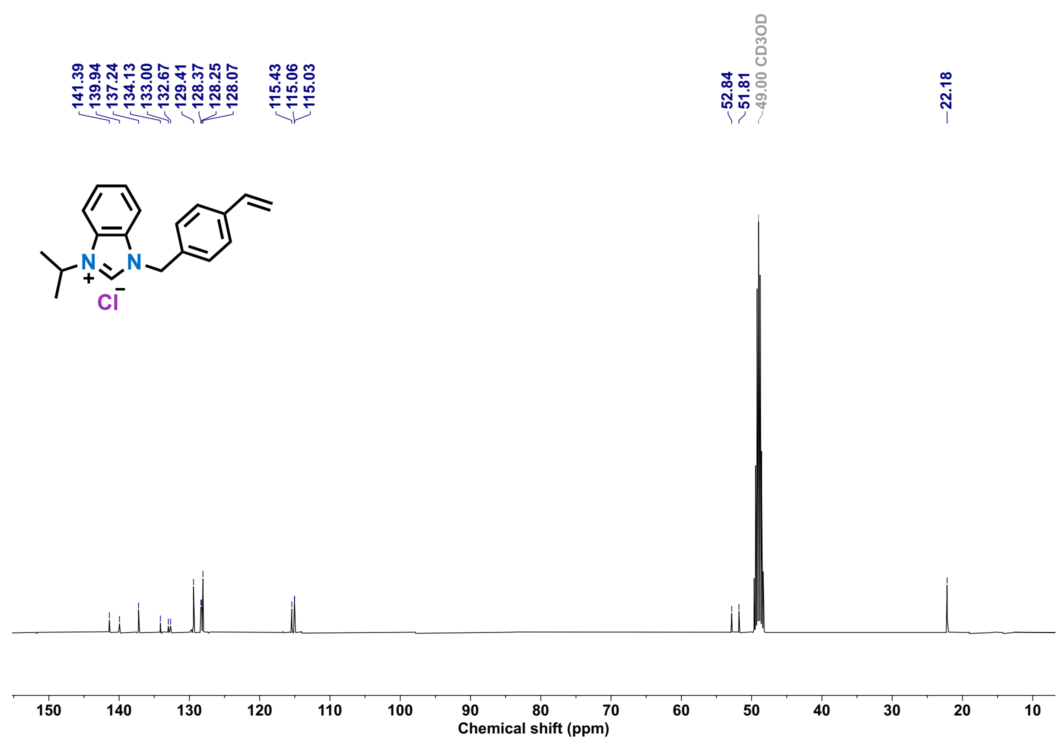


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Cl** in CD_3OD.

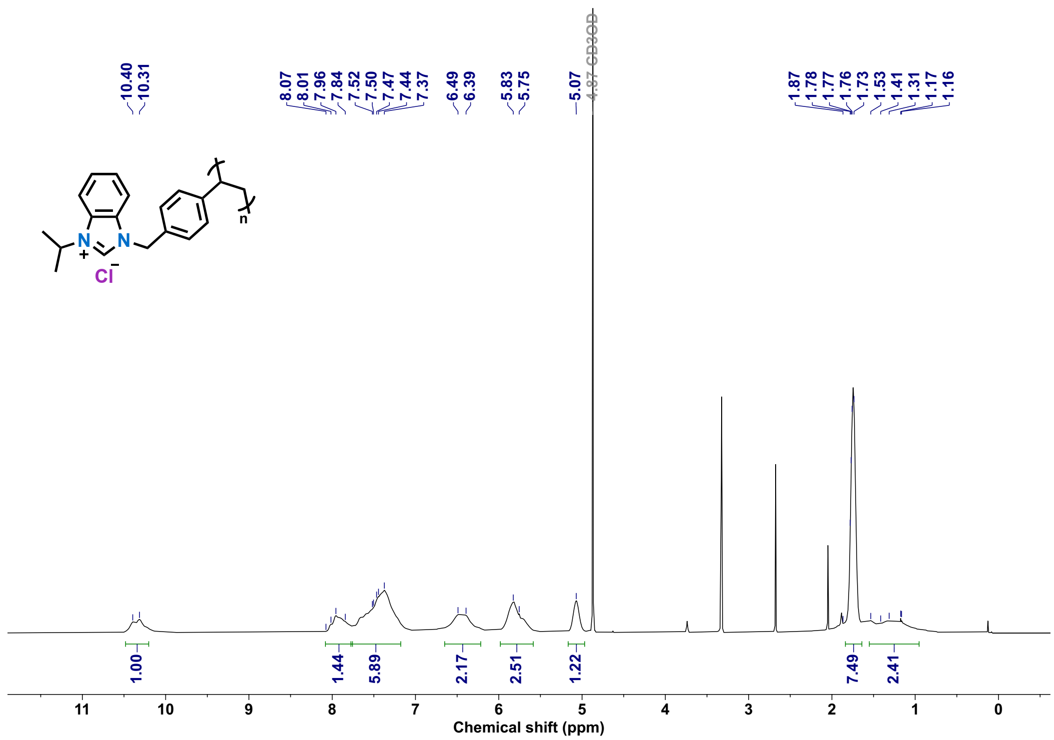


Figure S5. ^{1}H NMR spectrum of **3-Cl** in CD_3OD.

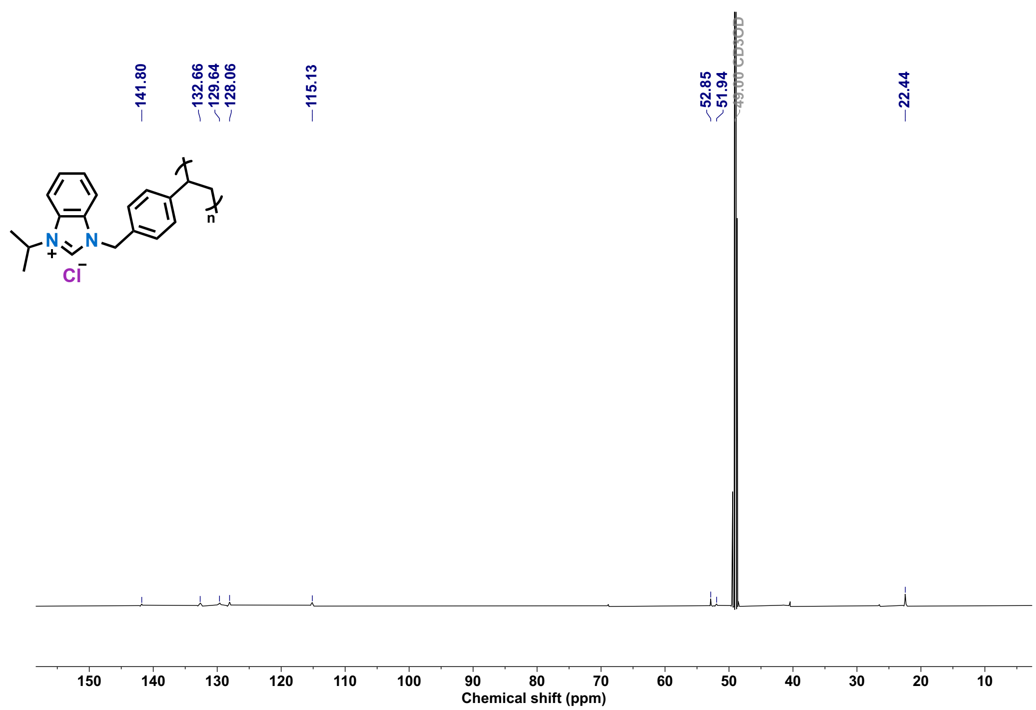


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **3-Cl** in CD_3OD.

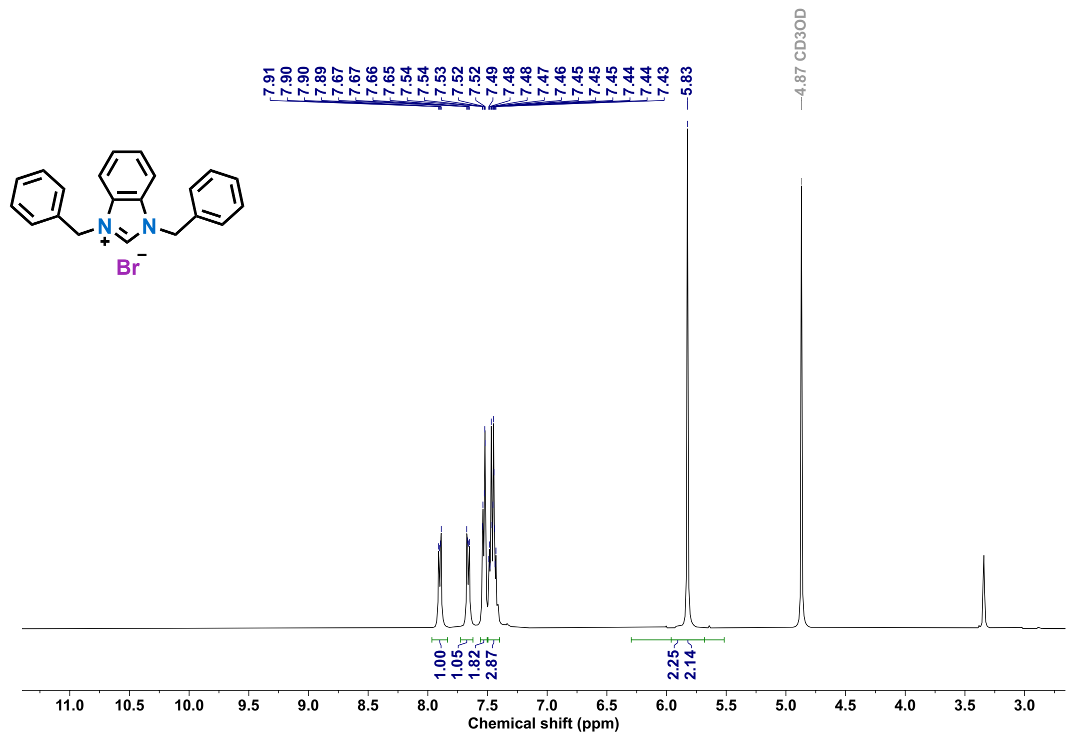


Figure S7. ^{1}H NMR spectrum of **4-Br** in CD_3OD.

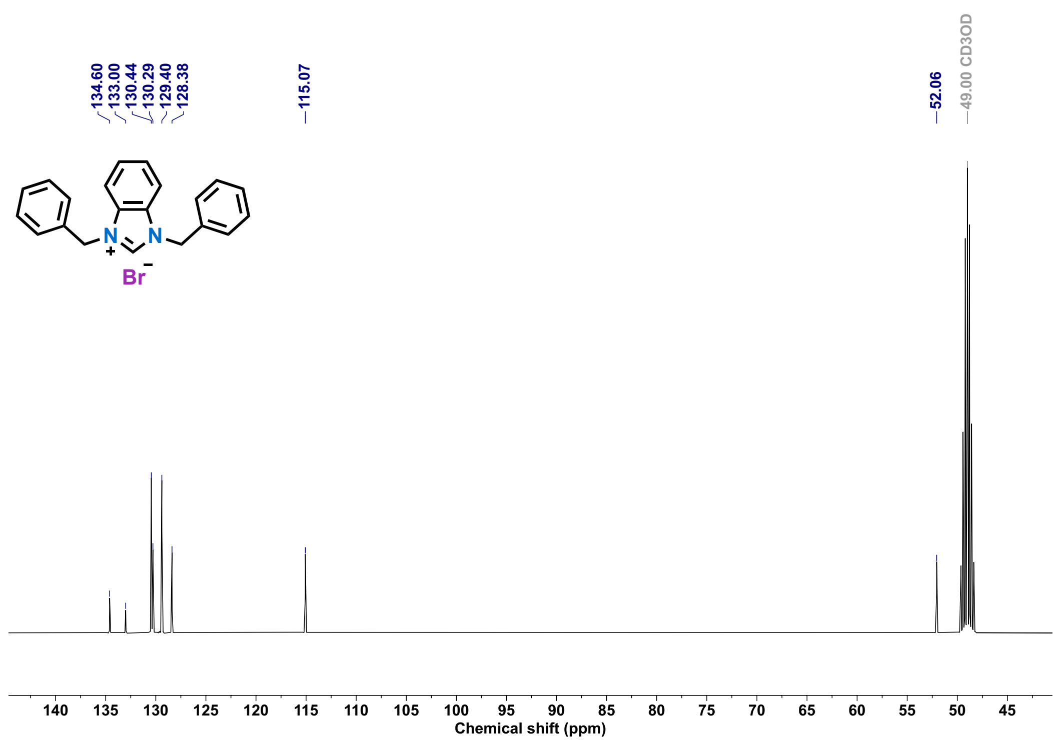


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **4-Br** in CD_3OD.

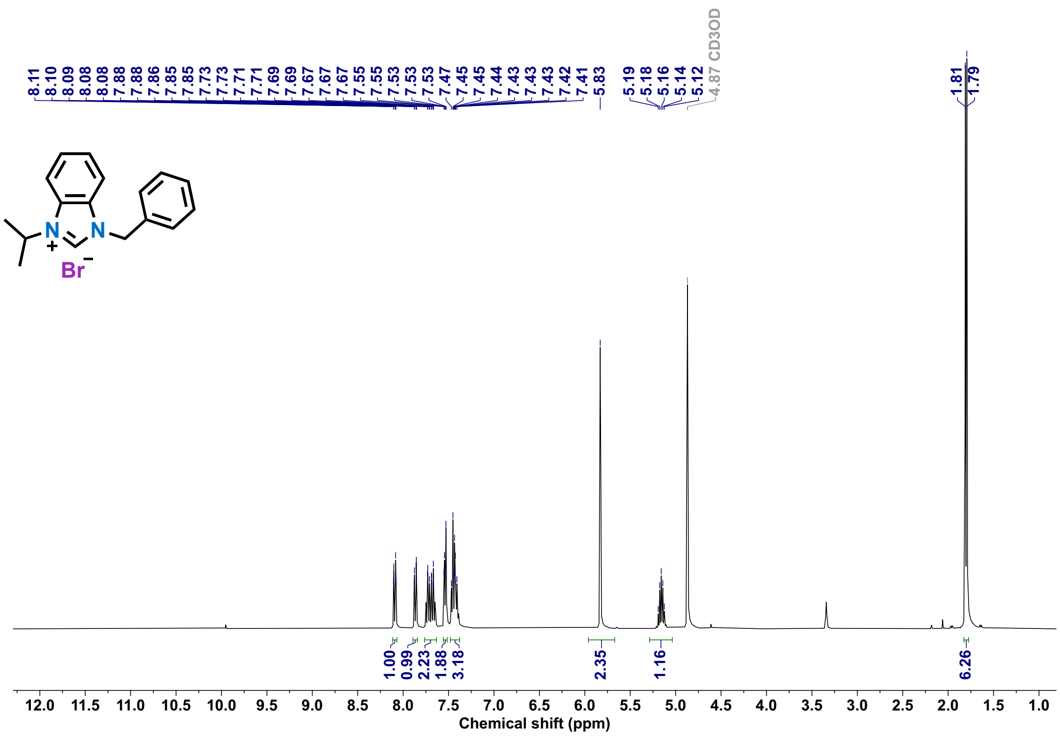


Figure S9. ^{1}H NMR spectrum of **5-Br** in CD_3OD.

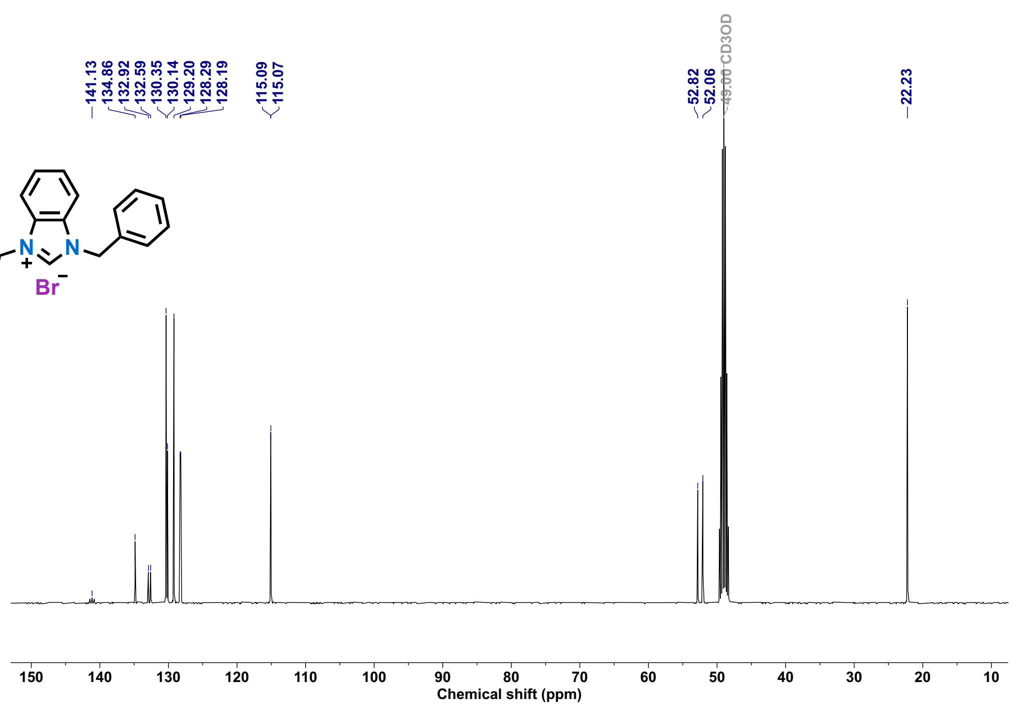


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **5-Br** in CD_3OD.

Molecular Weight Determination

The molecular weight (MW) of **3-Cl** was estimated using diffusion-order spectroscopy (DOSY) NMR using a Bruker Avance III HD 600 MHz spectrometer. Two calibration curves were obtained using monodisperse poly(ethylene glycol) (PEG) standards in methanol-d_4 and monodisperse polystyrene (PS) standards in chloroform-*d*. Four PEG standards with known molecular weights (3,930 g/mol, 6,430 g/mol, 12,140 g/mol, and 21,030 g/mol) were prepared at 10 mg/mL. Similarly, five PS standards (14,980 g/mol, 3,950 g/mol, 10,680 g/mol, 31,420 g/mol, and 70,950 g/mol) were prepared at the same concentration. All samples were analyzed by DOSY to obtain the logarithm of diffusion coefficient (log D), and the logarithm of molecular weight (log MW) was calculated for each standard. A log(D) vs. log(MW) plot was constructed and linearly fitted for PEG standards (Figure S1). Since PS standards were analyzed in chloroform-*d*, viscosity corrections were applied, thus a log(D) + log(η) vs. log(MW) plot was obtained, where η is the viscosity of chloroform-*d*. (Figure S2).[2] To determine the molecular weight of **3-Cl**, a 10 mg/mL solution in methanol-d_4 was prepared and analyzed using DOSY. The diffusion coefficient (D) was obtained, and the corresponding calibration equation was applied to estimate MW based on the PEG or PS calibration curves. The molecular weights obtained from the PEG and PS calibration curves were 28,350 g/mol and 39,250 g/mol, respectively.

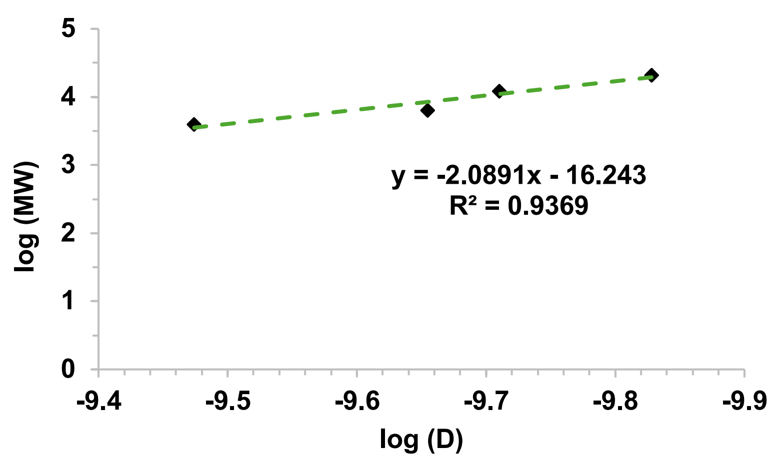


Figure S11. PEG calibration curve obtained by DOSY in CD_3OD.

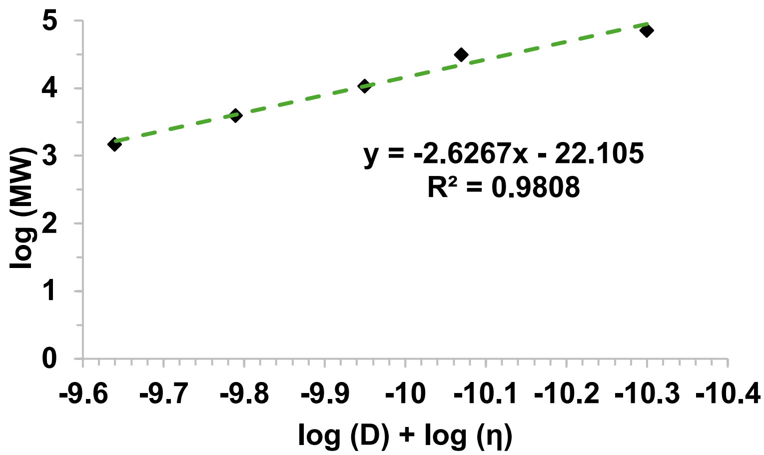


Figure S12. PS calibration curve obtained by DOSY in CD_3OD with viscosity corrections $\eta_{\text{chloroform-}d}$ = 0.563 mPa.s.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Samples were examined using an ION-TOF (GmbH) TOF-SIMS IV equipped with a Bi cluster liquid metal ion source. A pulsed 25 keV Bi_3^+ cluster primary ion beam was used to bombard the sample surface to generate secondary ions with a current of 1 μA. The positive (or negative) secondary ions were extracted from the sample surface, mass-separated, and detected via a reflectron-type time-of-flight analyzer. Reflector values for the positive and negative modes were +16 and −36 V, respectively. Sample charging was neutralized with a pulsed, low-energy electron flood. The ion mass spectra were collected in an area of 500 μm × 500 μm at 128 × 128 pixels with 20 scans. The high-resolution imaging spectra were collected with of 500 μm × 500 μm at 128 × 128 pixels with 100 scans, processed on the ION-TOF software and normalized to the total yield by a division normalization factor. The mass spectra were processed on ION-TOF software with a binning value of 256 and calibrated to H^+, C^+, and $C_2H_5^+$ mass signals.

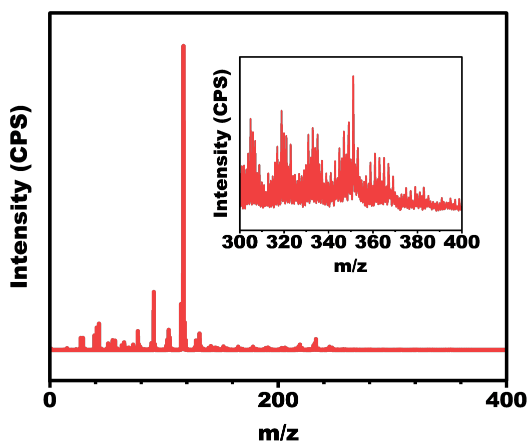


Figure S13. ToF-SIMS spectrum of **1-Au**.

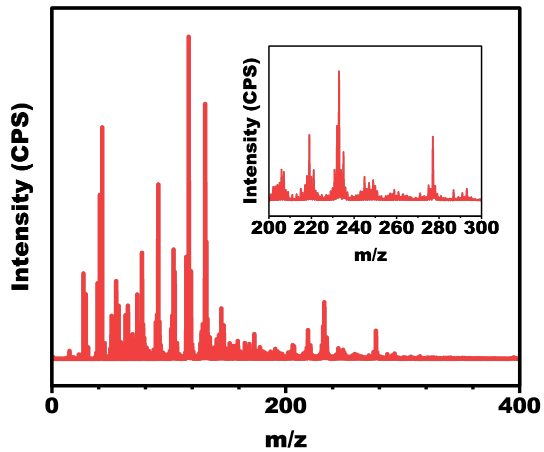


Figure S14. ToF-SIMS spectrum of **2-Au**.

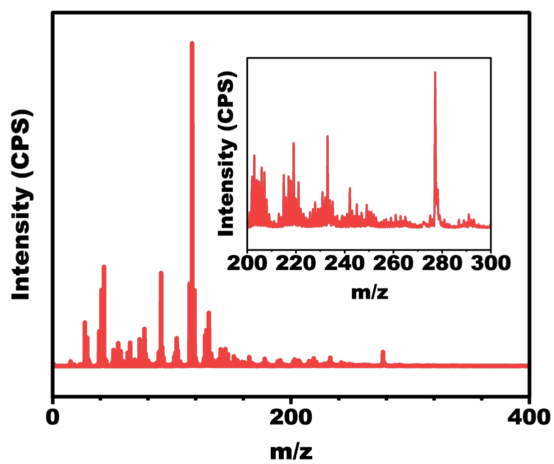


Figure S15. ToF-SIMS spectrum of **3-Au**.

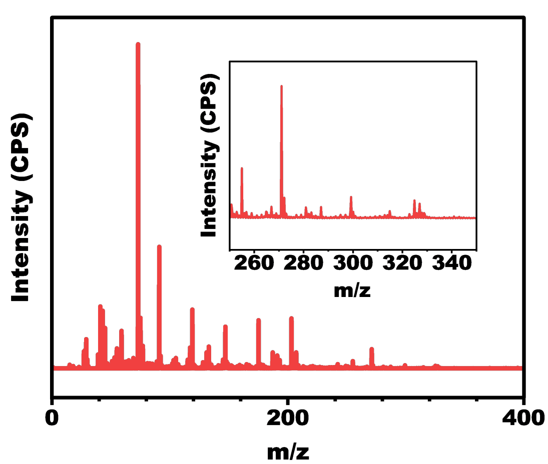


Figure S16. ToF-SIMS spectrum of **4-Au**.

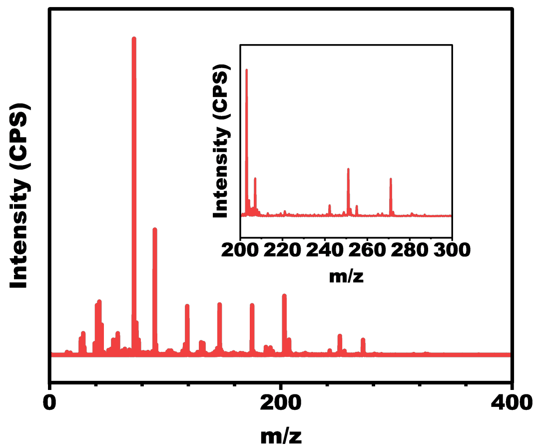


Figure S17. ToF-SIMS spectrum of **5-Au**.

X-ray Photoelectron Spectroscopy (XPS)

The XP spectra were acquired at Surface Science Western (SSW) with a Kratos AXIS Supra X-ray photoelectron spectrometer using a monochromatic aluminum Kα source (15 mA, 15 kV). Sample analysis is measured from a depth of 7–10 nm with detection limits ranging from 0.1 to 0.5 atomic percent. The instrument work function was calibrated to give a binding energy (BE) of 284.8 eV for C (1s) C–C/C–H peaks. The Kratos charge neutralizer system was used on all specimens. Both the survey scan and high-resolution analyses were collected at a takeoff angle of 90° with an analysis area of 300 μm × 700 μm and a pass energy 20 or 15 eV. CasaXPS (ver. 2.3.25) software was used for all deconvolution of spectra with N 1s linear background subtraction and all other high resolution with a Shirley background subtraction.

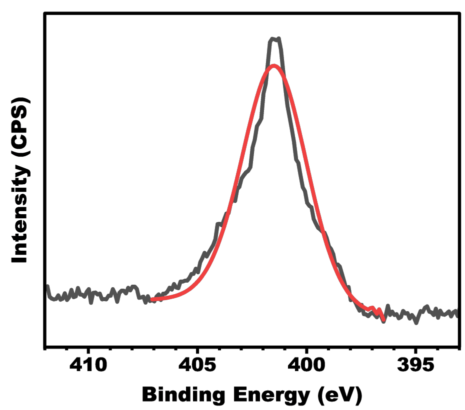


Figure S18. High-resolution N 1s XPS spectrum of bulk **1-Cl**.

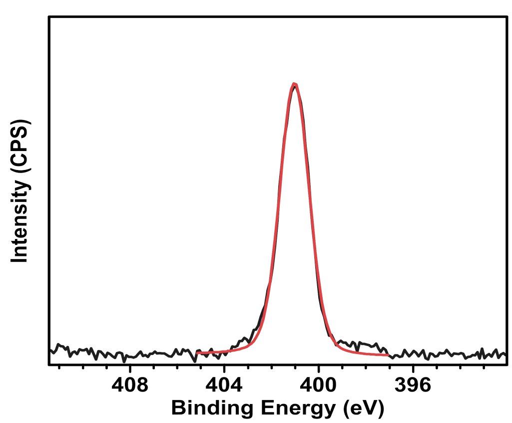


Figure S19. High-resolution N 1s XPS spectrum of bulk *n*Bu_4NPF_6.

Ellipsometry

Ellipsometric spectra (Ψ, Δ) were recorded on a Woollam M-2000 variable-angle spectroscopic ellipsometer equipped with an FLS-300 Xe ARC light source. Samples were rinsed with isopropanol and dried under N_2. Measurements were taken at 45° to 90° in 5° increments, averaging three scans under ambient conditions. Data fitting in CompleteEASE employed a Cauchy model for transparent films and a Tauc–Lorentz model for absorbing films, yielding film thicknesses and n/k values with MSE < 3.0.

Electrochemical Methods for Deposition and Polymerization

Au disc electrodes used in CV and EIS measurements were mechanically cleaned by immersion in piranha solution (3:1 H_2SO_4:H_2O_2) for 1 min, polishing with 0.3 μm (3 min) and 0.05 μm (3 min) alumina slurries, and sonication to remove remaining alumina (triple-distilled water, 10 min; HPLC-grade MeOH, 10 min; triple-distilled water, 10 min). The electrodes were then subjected to electrochemical cleaning in 0.5 M KOH (–0.04 V to –1.40 V; 0.5 V/s; 100 cycles) and 0.5 M H_2SO_4 (0.16 V to 1.55 V; 0.5 V/s; 100 cycles) and were immediately used for cyclic voltammetry analysis or deposition. Au wafers prepared to undergo XPS and ToF-SIMS analyses were cleaned pre-deposition by submersion in concentrated H_2SO_4 for 30 min and subsequently rinsed with DI water (3 × 1 mL) and HPLC-grade MeOH (3 × 1 mL).

Cyclic Voltammetry and Chronoamperometry

Cyclic voltammetry experiments were run at a scan rate of 100 mV s^{-1} in a degassed solution of $K_3Fe(CN)_6$ (5 mM), $K_4Fe(CN)_6$ (5 mM), $NaClO_4$ (1 M), and triple-distilled water. Cyclic voltammograms were measured prior to and post-deposition when using Au disc electrodes and were corrected for internal cell resistance using the BASi Epsilon software. Chronoamperometry experiments were used to achieve electrodeposition and began with a cleaned Au surface placed in a deposition solution containing a benzimidazolium halide salt (20 mM), $n$$Bu_4NPF_6$ (0.1 M), triple-distilled water (55 mM), and DMSO. A constant potential of –1.3 V was applied for 5 min under a flow of Ar, after which the NHC-functionalized surface was rinsed with DMSO (3 x 1 mL), triple-distilled water (3 x 1 mL), and HPLC-grade MeOH (3 x 1 mL).

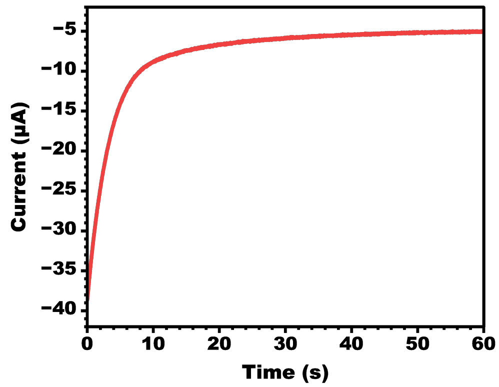


Figure S20. Chronoamperometry trace using a gold electrode during the electrodeposition of **1-Au** at 20 mM.

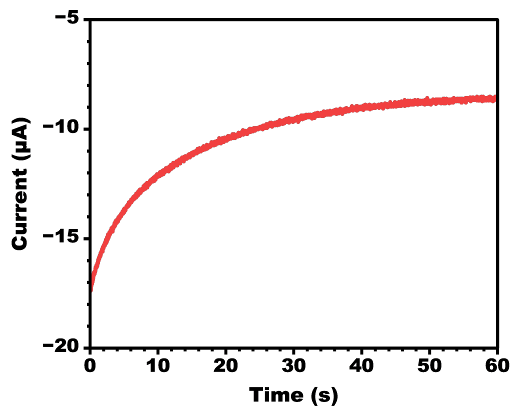


Figure S21. Chronoamperometry trace using a gold electrode during the electrodeposition of **2-Au** at 20 mM.

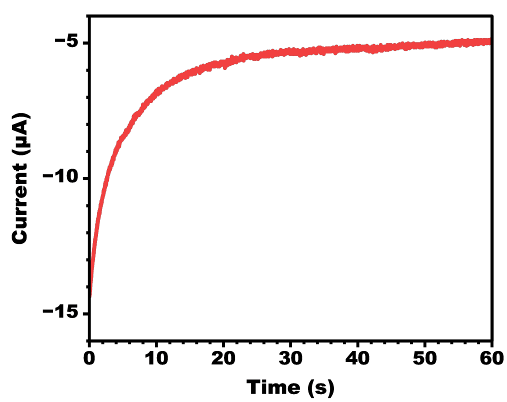


Figure S22. Chronoamperometry trace using a gold electrode during the electrodeposition of **3-Au** at 20 mM.

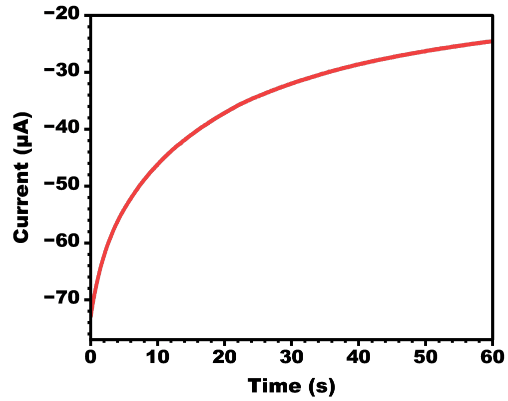


Figure S23. Chronoamperometry trace using a gold electrode during the electrodeposition of **4-Au** at 20 mM.

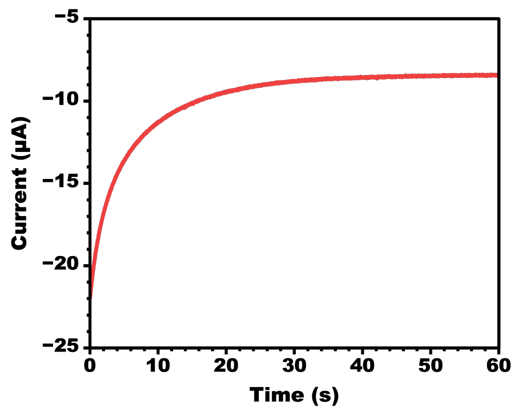


Figure S23. Chronoamperometry trace using a gold electrode during the electrodeposition of **5-Au** at 20 mM.

References

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