# **Deposition Condition Impacts Charge Tunneling and**

# **Thermoelectric Properties of N-Heterocyclic Carbene Monolayers**

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# 1. Experimental Details

#### 1.1 Materials

Benzimidazole (98%), potassium carbonate ( $\geq$ 98%), 2-bromopropane (99%), and potassium hexafluorophosphate ( $\geq$ 99%) were purchased from Sigma-Aldrich. All reagents were used as supplied unless otherwise specified. All organic solvents were purchased from Daejung while water was purified using an Aqua MAX-Basic System (deionized water, electrical resistivity of which is ~18.2 M $\Omega$ ·cm). Gold thin films (300 nm) were deposited onto silicon wafer (100 mm in diameter; 1–10 ohm-cm, 525 ± 50 microns thick) by e-beam evaporator (ULVAC).

# 1.2. Synthesis of NHC-Br



The compound NHC-**Br** was synthesized following the previously reported procedure.<sup>1</sup> A mixture of benzimidazole (2.00 g, 16.93 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.57 g, 18.62 mmol) was suspended in CH<sub>3</sub>CN (20 mL) and stirred at ambient temperature for 1 h. To the suspension was added isopropyl bromide (4.77 mL, 50.78 mmol). The reaction mixture was stirred under reflux conditions for 24 h followed by a second addition of isopropyl bromide (4.77 mL, 50.78 mmol). Stirring under reflux continued for an additional 72 h. After removing the volatiles in vacuo, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added to the residue and the resulting suspension was filtered over Celite. The remaining solid was washed with CH<sub>2</sub>Cl<sub>2</sub> (5 × 50 mL), and the solvent of the filtrate was removed in vacuo to give a spongy solid, which upon washing with ethyl acetate afforded the product as a white powder (3.84 g, 13.54 mmol, 80%). The analytical data for this compound was in excellent agreement with the reported data.<sup>1</sup>

### 1.3. Synthesis of NHC-PF<sub>6</sub>



The compound NHC-**PF**<sub>6</sub> was synthesized following the previously reported procedure.<sup>2</sup> To the solution of NHC-**Br** (0.50 g, 1.77 mmol) in acetone (5 mL) was added the solution of KPF<sub>6</sub> (0.65 g, 3.53 mmol) in acetone and white precipitate came out instantly. The reaction mixture was stirred for 1 hour at room temperature and then filtered over Celite, after which the solvent of the filtrate was removed under vacuum. CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to partially dissolve the residues. Filtration again over Celite followed by removal of the solvent from the filtrate afforded NHC-**PF**<sub>6</sub> as a white powder (0.58 g, 1.68 mmol, 95%). The analytical data for this compound was in excellent agreement with the reported data.<sup>2</sup>

#### **1.4. SAM Preparation**

We prepared N-heterocyclic carbene (NHC) self-assembled monolayers (SAMs) using benzo[*d*]imidazole with PF<sub>6</sub><sup>-</sup> counterion in three different deposition conditions, ambient incubation (AI) incubation, base-induced deprotonation (BD), and electrochemical-induced deprotonation (ED), which have been reported previously.<sup>3-6</sup> Briefly, for the AI condition, freshly prepared template-stripped gold (Au<sup>TS</sup>) chip (1 cm × 1 cm) was incubated in an ethanolic solution containing 3 mM NHC precursor in ambient conditions for 12 hrs. For the BD condition, potassium tert-butoxide (KO*t*-Bu; 6 mM) was added to the same solution used in the AI condition, and the resulting mixture was left for 2 hrs. Then, freshly prepared Au<sup>TS</sup> chip was placed in the solution and incubated in N<sub>2</sub>-filled glovebox for 12 hrs. For the ED condition, we constructed a conventional three-electrode cell consisting of Ag/AgCl as a reference electrode, a Pt wire as a counter electrode, and an NHC-coated Au<sup>TS</sup> chip as the working electrode. The solution was prepared with 0.1 M tetrabutylammonium tetrafluoroborate and 5 mM NHC precursor in a mixture of water and acetonitrile  $(1:10^3 \text{ in volume ratio})$ . A voltage of -1 V was applied to the cell for 2 mins. The rinsing process was the same for the three deposition conditions. The NHC-coated Au<sup>TS</sup> chips were thoroughly rinsed by pure ethanol, following 1 min flow of N<sub>2</sub>.

#### 2. Electrical Measurements

#### 2.1 Preparation of EGaIn Conical Tip

To create a conical tip of EGaIn, we followed the method described in literature.<sup>7</sup> Firstly, a 10  $\mu$ L gas-tight syringe was filled with EGaIn (≥99.99%, Aldrich). Next, a drop of EGaIn was pushed to the tip of the syringe needle, and the hanging drop was brought into contact with a surface that would allow the EGaIn to stick (e.g., an oxidized Ag surface). Finally, using a micromanipulator, the needle was gently pulled away from the drop, resulting in a conical tip. We formed a new conical tip of EGaIn for each junction, to avoid any complexities that may arise from contamination of the EGaIn surface by volatile organics in the air. If visible whiskers formed during tip fabrication, we discarded the tip and formed a new one.

### 2.2 Electrical Measurements and Data Analysis

Junction formation and measurements were done following the method reported in the literature.<sup>8</sup> All junction formation and measurements in this work were carried out in ambient conditions. Briefly, a SAM was gently brought into contact first with a gold metal electrode. Then using a micromanipulator, a conical tip of EGaIn was gently brought into contact with the surface of SAM. The SAM-bound bottom electrode was grounded, and the EGaIn top electrode was biased. We measured the diameter of the contact area at high magnification and assumed a circular contact to calculate the area from the measured diameter. From this, we calculated the current densities (J, A/cm<sup>2</sup>). To confirm the contact and the presence of SAM, we ran a single J-V scan and then 20 more scans if there was an indication of contact and

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tunneling. Each trace was based on the following voltage sweep sequence:  $0V \rightarrow +1.0 V \rightarrow 0$   $V \rightarrow -1.0 V \rightarrow 0 V$ . Therefore, one trace corresponds to two scans. The yield (%) of working junctions was calculated based on the total number of working junctions versus those that shorted. Shorts were excluded prior to analysis as they do not provide information about the SAM and can bias current density distributions toward high values. Values corresponding to shorts were discarded when performing operations on the raw distribution of log-current density (log|J|). Shorts were defined as values of current that reached the compliance limit of our electrometer (±0.105 A).

### 2.3 Determination of the Tunneling Conductivity and Power Factor

Electrical conductivity was determined following the method reported in the literature.<sup>9</sup> Electrical conductivity,  $\sigma$ , is the inverse of resistivity ( $\rho$ ):

$$\sigma = \frac{1}{\rho} \; (\mu \text{S/cm}) \tag{Eq. S1.}$$

Conductivity uses the unit of microsiemens per centimeter ( $\mu$ S/cm). Typically, the resistivity at a particular point is the ratio of the electric field to the density of the current:

$$\rho = \frac{E}{J} \text{ (cm/\mu S)}$$
(Eq. S2)

where  $\rho$  (µS/cm) is the resistivity of the conductor material, J (A/cm<sup>2</sup>) is the current density, and E (GV/m) is the electric field. The E is defined as follows:

$$E = \frac{v}{d} \text{ (GV/m)}$$
(Eq. S3)

where V is the applied voltage between the gold as a bottom electrode and the EGaIn as a top electrode, and d is the distance between the two electrodes. We assumed that d is the length of rigid NHC molecule (0.85 nm) since our NHC molecule with iso-propyl side group is known to has upright configuration.<sup>3</sup> Finally, power factor (PF) was calculated as following equation:

$$PF = \sigma \times S^2 (\mu Wm^{-1}K^{-2})$$
 (Eq. S4)

# 3. Thermoelectric Measurements

#### **3.1 Junction Formation and Thermoelectric Measurements**

We placed a SAM on a hot chuck and covered the rest of the area with glass to block or minimize heat transfer to the EGaIn tip. The SAM was gently brought into contact with a tungsten ground electrode. To measure the temperature of the bottom electrode, we placed a thermocouple onto the electrode. Once we monitored the temperature of the substrate with the thermocouple, we found that the heat transfer from the hot chuck to the gold-coated SAM was sufficient to carry out the desired experiments. To create a temperature difference, we varied the temperature of the hot chuck from 290 to 310 K. At each temperature, we allowed a few seconds for the temperature measured at the bottom-electrode thermocouple to stabilize. Then, using a micromanipulator, we gently brought an EGaIn conical tip into contact with the surface of the SAM, and measured the output voltage.

# **3.2 Thermopower Analysis of Junctions**

To derive the Seebeck coefficient (S,  $\mu$ V/K) value of SAMs, histograms of thermovoltage ( $\Delta V$ ,  $\mu$ V) at different temperature differentials ( $\Delta T = 4$ , 8, and 12 K) were obtained using the EGaIn based junction technique. From the histograms, Gaussian-based mean and standard deviation of  $\Delta V$  were extracted. The number of junctions and data traces were 30 and 2250, respectively (3-5 different samples were used) for each molecule. The *S* value of SAM ( $S_{SAM}$ ) was derived following the previously reported method.<sup>10</sup>

# 4. Characterization

#### 4.1 Nuclear Magnetic Resonance (NMR)

<sup>1</sup>H NMR spectra were recorded on a Bruker FT-NMR Advance-500 using CDCl<sub>3</sub> as solvent and residual solvents as an internal standard. Chemical shifts are expressed in parts per million (ppm) related to internal TMS and coupling constant (*J*) are in Hertz.

# 4.2 X-ray Photoelectron Spectroscopy (XPS) Measurements

The XPS measurements were carried out on a Thermofisher (Nexsa) with a monochromated Al K $\alpha$  (1486.6 eV) source. The measurements were done at room temperature in a vacuum of  $6.7 \times 10^{-8}$  Pa. The binding energies were calibrated by setting Au 4f<sub>7/2</sub> of bulk metals to values 84.0 eV.<sup>11</sup> The Au 4f, C 1s and N 1s XPS spectra of the NHC SAMs were examined to obtain information regarding the chemical structure and composition of the NHC SAMs. Each peak positions and shapes of the core level photoelectron spectra were analyzed with a XPS Peak Fit program, in which a Shirley-type background correction was utilized.

The thickness of our NHC SAM was determined by the following equation:<sup>12, 13</sup>

$$Au_d = Au_{d=0}(e^{-d/\lambda_{Au}sin\theta})$$

where Au<sub>d</sub> and Au<sub>d=0</sub> are the intensities of the Au(4f<sub>7/2</sub>) peak for SAM-bound and bare gold substrates, respectively; *d* is the thickness of SAM;  $\lambda_{Au}$  is the inelastic mean free path of the Au4f<sub>7/2</sub> photoelectron (42 Å); and  $\theta$  is the angle between the analyzer and the sample. XPS analysis indicated that the thickness of our NHC SAMs ranged from 1.16 nm to 1.24 nm, which is comparable to the literature value (~1.1 nm).<sup>14</sup> Considering that the NHC molecules with *i*-Pr side groups exhibit consistent tilt angles irrespective of surface coverage,<sup>3</sup> we can infer that the decay of the Au 4f peak intensity in the sample primarily depends on surface coverage in our study.

# 4.3 Electrochemical Impedance Spectroscopy (EIS) Measurements

Electrochemical impedance spectroscopy (EIS) measurements were obtained in a conventional three electrode electrochemical cell using a potentiostat (MULTI AUTOLAB M204, Metrohm Autolab B. V.). The counter and reference electrodes were a platinum mesh and a Ag/AgCl electrode (3 M NaCl), respectively. By using a custom-built equipment, the measurement area (0.15 cm2) of SAM was kept identical across all samples. The impedance spectra at an applied potential of 0 V (vs Ag/AgCl) in K5/2HPO4 (30 mM, pH 7.7-8.7). The effect of ReSEM on SAM permeability was investigated over a frequency range from 1Hz to

10 kHz by applying a sinusoidal signal of  $\pm$ 10 mV against open circuit voltage. Each measurement comprised one frequency scan, and two measurements were taken per sample at intervals of 20 min. The impedance spectra were analyzed by fitting appropriate equivalent circuit models to the measured data (NOVA 2.0).

# 4.4 Kelvin Probe Force Microscopy (KPFM) Measurements

For KPFM measurement (in ambient conditions, Bruker AFM Multimode model), the Pt/Ir coated conductive probes (SCM-PIT-V2, Bruker) were calibrated by using the highly oriented pyrolytic graphite (HOPG) substrate, resulting in the work function of the probes. KPFM measurements were operated in the lift mode with a constant distance of 80 nm from the surface with a scan rate of 0.5 Hz.

# 5. DFT Calculations

We calculated the work function of SAM-coated Au(111) surface depending on the coverage ( $\alpha$ ) of NHC SAM using the SIESTA package.<sup>15</sup> The fully packed ( $\alpha$ =1) structure of the NHC SAM was adopted from a literature and top views of the structures employed for the calculations are shown in **Figure S7**.<sup>3</sup> The Au(111) slab contains four layers and more than 20 Å vacuum was inserted between the bottom Au layer and the top of the NHC molecule. We employed double-zeta plus polarization besis sets and Troullier–Martins norm-conserving pseudopotentials with the Kleinman–Bylander nonlocal projector.<sup>16, 17</sup> The exchange-correlation functional was approximated by the PBE flavor of the generalized gradient approximation. The slab dipole correction scheme was employed to obtain the work functions of both sides of the slab. The molecular structures were optimized until the maximum atomic force becomes smaller than 0.04 eV/ Å, while the Au atoms except for adatoms below NHC were fixed at the experimental positions. The structural stability was confirmed from the absence of the negative frequency vibrational modes in the frozen-phonon calculations. The K-points were sampled by the 1×2×1 mesh except for the  $\alpha$ =0.125

system, where only the gamma point was sampled. **Figure S8** indicates that work function decreases when the surface coverage increases, supporting the enhancement of the Seebeck coefficient observed in the densely packed SAMs.

For modeling molecular junctions with hetero-electrodes, the lattice mismatch between two electrodes often forces us to artificially compress or expand either of the electrode metals during DFT calculations. However, Al and Au have the same fcc cryastal structure with similar lattice constants, 4.05 Å and 4.08 Å for Al and Au, respectively, resulting in the deviation less than 1%. Therefore, we can just replace Au atoms in the top electrode with Al atoms keeping the atomic positions to compute the Au-NHC SAM-Al junction. The transport calculations were performed using the nonquilibrium Green's function method implemented in the SMEAGOL code. Because the 2 nm long surface cell is a bit too large for transport calculations, we reduced the cell size as shown in **Figure S7**.<sup>18-20</sup>

# **Supplementary Figures**



Figure S1. 500 MHz <sup>1</sup>H NMR spectrum of NHC-Br in CDCl<sub>3</sub>.



Figure S2. 500 MHz <sup>1</sup>H NMR spectrum of NHC-PF<sub>6</sub> in CDCl<sub>3</sub>.



**Figure S3.** (a) XPS survey spectrum and (b) high resolution C 1s spectra for SAMs formed with NHC-PF<sub>6</sub><sup>-</sup> precursor in the AI condition.



Figure S4. (a) XPS survey spectrum and (b) high resolution C 1s spectra for SAMs formed

with NHC-PF $_6$ <sup>-</sup> precursor in the BD condition.



**Figure S5.** (a) XPS survey spectrum and (b) high resolution C 1s spectra for SAMs formed with NHC-PF<sub>6</sub><sup>-</sup> precursor in the ED condition.



Figure S6. (a) Cyclic voltammograms and (b) %EAS data for the NHC SAMs.



Figure S7. Top views of the structures employed for DFT calculations.



**Figure S8.** Computationally calculated coverage-dependent work function changes of NHC SAM/Au(111).



Figure S9. (a) Log J-V traces and (b) histogram of  $\log |J(+1.0 \text{ V})|$  of the

Au<sup>TS</sup>/NHC//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions formed with NHC-PF<sub>6</sub>- precursor in the AI condition.



**Figure S10.** (a) Log*J-V* traces and (b) histogram of  $\log |J(+1.0 \text{ V})|$  of the

Au<sup>TS</sup>/NHC//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions formed with NHC-PF<sub>6</sub>- precursor in the BD condition.



**Figure S11.** (a) Log*J*-*V* traces and (b) histogram of  $\log |J(+1.0 \text{ V})|$  of the

 $Au^{TS}/NHC//Ga_2O_3/EGaIn$  junctions formed with NHC-PF<sub>6</sub>- precursor in the ED condition.



Figure S12. Schematic description of the junction structure for measuring (a) current density (*J*), electrical conductivity ( $\sigma$ ) and (b) Seebeck coefficient (*S*).



**Figure S13.** Transmission functions of Au-NHC-Au and Au-NHC-Al junctions. The coverage of the NHC-SAM is 0.50.



**Figure S14.** Plots of transition voltage ( $V_t$ ) at +V and -V obtained by transition voltage spectroscopy (TVS) analysis.



**Figure S15.** Plots of transition voltage ( $V_t$ ) for the Au<sup>TS</sup>/NHC//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions formed with NHC-PF<sub>6</sub>- precursor in the (a) AI, (b) BD, and (c) ED conditions.



**Figure S16.** (a) Transmission function, T(E), and (b) simulated *S* based on the transmission function and Mott formula for the Au<sup>TS</sup>/NHC//Ga<sub>2</sub>O<sub>3</sub>/EGaIn junctions formed with NHC-PF<sub>6</sub><sup>-</sup> precursor in the AI, BD, and ED conditions. The inset shows the magnified plot near the Fermi level.

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