Supporting Information

N-Heterocyclic Carbene-Ended Polymers as Surface Ligands of Plasmonic Metal Nanoparticles

Srinivas Thanneeru,1 Kaitlynn M. Ayers,1 Murali Anuganti,1 Lei Zhang,1 Challa V. Kumar,1 Gaël Ung*1, Jie He*1,2
1Department of Chemistry, and 2Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States
Email: Gael.ung@uconn.edu (GU) and Jie.he@uconn.edu (JH)

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1. Synthesis of low molecular weight NHC-Cu(I) analogues

Synthesis of N-methyl-N'-benzylimidazolium bromide. N-methyl-N'-benzylimidazolium bromide was synthesized according to a reported procedure.\(^1\) \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K) \(\delta\) (ppm) = 10.6 (s, 1H, -NCH=N-), 7.49–7.27 (m, 7H, ArH, -CH\(_2\)), 5.6 (s, 2H, -CH\(_2\)-), 4.09 (s, 3H, -CH\(_3\)).

Synthesis of N-methyl-N'-benzylimidazolylidene-CuCl. N-methyl-N'-benzylimidazolylidene-CuCl was synthesized following the same general procedure as reported for the polymer. The complex was obtained as a pale green solid. \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K) \(\delta\) (ppm) = 7.38–7.15 (m, 5H, ArH), 6.81 (s, 1H, -CH\(_2\)-), 6.77 (s, 1H, -CH\(_2\)-), 5.22 (s, 2H, -CH\(_2\)-), 3.81 (s, 3H, -CH\(_3\)). MS (ESI+), Calcd [M+Na]\(^+\): 292.99; Found: 293.02.

\[\text{Scheme S1. Scheme showing the synthesis of imidazole-containing ATRP initiator.}\]

2. Synthesis of imidazole-containing ATRP initiator and polymers

2-(1-Imidazol-1-yl) ethanol (Im-EtOH) Im-EtOH was prepared by treating imidazole with ethylene carbonate as reported in literature (Scheme S1).\(^2\) Imidazole (5.18 g, 76 mmol) and ethylene carbonate (10.3 g, 118 mmol) were weighed into a 100 mL round bottom flask with a magnetic stirrer and dissolved in 20 mL of toluene. The solution was refluxed at 110 °C for 6 h. After cooling to room temperature, the solution was poured into a large amount of water. Two layers formed, the aqueous layer was collected and the toluene layer was discarded. Concentrated HCl was added to the solution to decrease the pH = 5. The mixture was washed three times with CHCl\(_3\) (30 mL) and potassium carbonate (40 g, 0.29 mol) was added to the solution. Finally, the product was extracted using CHCl\(_3\) (3×100 mL). The organic fractions were then combined and dried using anhydrous MgSO\(_4\). The solvent was removed in vacuo to yield Im-EtOH as orange oil. \(^1\)H NMR (400 MHz CDCl\(_3\), 298 K): \(\delta\) (ppm) = 7.34 (s, 1H, -NHC=CHN-), 6.91 (s, 1H, -CH\(_{imid}\)), 6.87 (s, 1H, -CH\(_{imid}\)), 4.01 (t, 2H, -CH\(_2\)-), 3.82 (s, 2H, -CH\(_2\)-), and 5.71 (s, br, 1H, -OH).

2-(1H-imidazol-1-yl)ethyl-2-bromo-2-methylpropanoate (Im-Et-Br) Preparation of this imidazole-containing ATRP initiator is similar to the procedure for the preparation of PEG-Br macroinitiator.\(^3\) Im-Et-OH (1.0 g, 8.9 mmol) and TEA (0.9 g, 8.9 mmol) were added to a 100 mL round bottom flask equipped with a magnetic stirrer and 30 mL of dry DCM. The solution was cooled to 0 °C and BMPB (2.05 g, 8.9 mmol) was added dropwise over 20 min. The reaction mixture was stirred for 4 h. After the reaction, the formed triethylammonium salt was removed by washing the solution with deionized water twice and then saturated aqueous NaHCO\(_3\) solution 4 times. The DCM solution was dried over anhydrous MgSO\(_4\) and the solvent was removed in vacuo to yield Im-Et-Br as a light yellow viscous liquid. \(^1\)H NMR (400 MHz CDCl\(_3\)
298 K): \( \delta \) (ppm) = 7.54 (s, 1H, \(-\text{NHC=CHN}\)), 7.08 (s, 1H, \(-\text{CH}_{\text{imid}}\)), 7.0 (s, 1H, \(-\text{CH}_{\text{imid}}\)), 4.42 (t, 2H, \(-\text{CH}_{2}\)), 4.26 (s, 2H, \(-\text{CH}_{2}\)), and 1.9 (s, 6H, \(-\text{CH}_{3}\)).

Scheme S2. Scheme showing the synthesis of PMMA\(_{85}\)-NHC-Cu(I).

**Synthesis of PMMA\(_{85}\)-Im.** Imidazolium-capped polymers were synthesized from imidazole capped polymers which used ATRP polymerization (Scheme S2). A typical procedure for the preparation of imidazole capped polymers is as follows. MMA (2.0 g, 20 mmol) and CuBr (48.1 mg, 334 \( \mu \)mol) were dissolved in 1 mL of anisole and purged with N\(_2\) for 5 min. PMDETA (57.7 mg, 334 \( \mu \)mol) was added to the solution and purged with N\(_2\) for another 10 min. Im-Et-Br (87 mg, 334 \( \mu \)mol) in 0.5 mL of anisole was added to the solution and purged with N\(_2\) for another 15 min. The solution was then placed in a pre-heated oil bath at 65 °C. After 45 min, the reaction mixture was exposed to air and DCM was added to quench the polymerization. The solution was passed through a neutral alumina column using DCM as the eluent to remove the copper catalyst. The obtained polymer solution was used without further purification to prepare imidazolium-end capped polymers. Next, 1 mL of iodomethane was added to the polymer solution which was then stirred for 8 h. Then, the polymer solution was concentrated using a rotary evaporator and precipitated three times in cold hexane. The yielded polymer has a \( M_n \) of 7.7 kg/mol and \( D \) of 1.18 measured by SEC. The average number of repeat units of the MMA was estimated to be 85 from \(^1\)H NMR measurement using end group analysis.

**Synthesis of PMEO\(_2\)MA\(_{125}\)-Im.** MEO\(_2\)MA (3.0 g, 15.9 mmol) and CuBr (28.6 mg, 199 \( \mu \)mol) were dissolved in 1 mL of anisole and purged with N\(_2\) for 5 min. PMDETA (34.5 mg, 199 \( \mu \)mol) was added to the solution and the solution was purged with N\(_2\) for another 10 min. Finally, Im-Et-Br (52.1 mg, 199 \( \mu \)mol) in 0.5 mL of anisole was added to the reaction mixture and purged with N\(_2\) for another 15 min. The mixture was then placed in a pre-heated oil bath at 35 °C for 1 h. After polymerization, DCM was added to the reaction solution to quench the polymerization. The polymer solution was passed through a neutral alumina column using DCM as the eluent to remove the copper catalyst. The obtained polymer solution was used without further purification to prepare imidazolium end capped polymer (Scheme S3). Next, 1 mL of iodomethane was added to the polymer solution and stirred for 8 h. Then, the polymer solution was concentrated using a rotary evaporator and precipitated three times in hexane solution. The yielded polymer has a \( M_n \) of 20.0 kg/mol and \( D \) of 1.09 measured by SEC. The average number of repeat units of the MMA was estimated to be 125 from \(^1\)H NMR measurement using end group analysis.

S3
Synthesis of PnBA\textsubscript{104-Im}. \(n\text{BA} (4.0\ g,\ 31.7\ \text{mmol})\) and CuBr (45.6 mg, 317 \(\mu\text{mol}\)) was dissolved in 1 mL of anisole and purged with N\(_2\) for 5 min. PMDETA (54.5 mg, 317 \(\mu\text{mol}\)) was added to the solution and purged with N\(_2\) for another 10 min. Finally, Im-Et-Br (83 mg, 317 \(\mu\text{mol}\)) in 0.5 mL of anisole was added to the reaction mixture and purged with N\(_2\) for another 15 min. The mixture was then placed in a pre-heated oil bath at 70 °C for 2 h. After polymerization, DCM was added to the reaction solution to quench the polymerization. The polymer solution was passed through a neutral alumina column using DCM as the eluent to remove the copper catalyst. The obtained polymer solution was used without further purification to prepare imidazolium end capped polymer. Next, 1 mL of iodomethane was added to the polymer solution and stirred for 8 h. Then, the polymer solution was concentrated using a rotary evaporator and precipitated three times in a cold water/ethanol (2/8 vol) mixture solution. The obtained polymer has a \(M_n\) of 19.9 kg/mol and \(\bar{D}\) of 1.14 measured by SEC. The average number of repeat units of the MMA was estimated to be 104 from \(^1\text{H}\) NMR measurement using end group analysis.

Synthesis of PMMA\textsubscript{85-NHC-Cu(I)}. Carbone-capped PMMA was prepared by treating imidazolium-ended PMMA with CuCl under basic conditions. PMMA\textsubscript{85-Im} (320 mg, 37.6 \(\mu\text{mol}\)), CuCl (10 mg, 101 \(\mu\text{mol}\)) and K\(_2\)CO\(_3\) (10 mg, 72.5 \(\mu\text{mol}\)) were dissolved in 25 mL of acetone. The resulting solution was refluxed at 80 °C overnight. The reaction solution was cooled to room temperature and passed through a medium glass frit with a plug of silica to remove the excess CuCl and K\(_2\)CO\(_3\). The obtained polymer solution was
concentrated using a rotary evaporator, precipitated in methanol, and dried under vacuum at 40 °C. The obtained polymer has a $M_n$ of 8.6 kg mol$^{-1}$ and $D$ of 1.16 as per SEC measurements.

**Synthesis of PMEO$_2$MA$_{125}$-NHC-Cu(I).** PMEO$_2$MA$_{125}$-Im (1.97 g, 82.1 μmol), CuCl (10 mg, 101 μmol) and K$_2$CO$_3$ (10 mg, 72.5 μmol) were dissolved in 70 mL of acetone and refluxed at 80 °C overnight. The reaction solution was cooled to room temperature and passed through a medium glass frit with a plug of silica to remove excess CuCl and K$_2$CO$_3$. The obtained polymer solution was concentrated using a rotary evaporator, precipitated in hexane, and dried under vacuum at 40 °C. The obtained polymer has a $M_n$ of 19.9 kg mol$^{-1}$ and $D$ of 1.16.

**Synthesis of PnBA$_{104}$-NHC-Cu(I).** PnBA$_{104}$-Im (520 mg, 37.5 μmol), CuCl (10 mg, 101 μmol) and K$_2$CO$_3$ (10 mg, 72.5 μmol) were dissolved in 30 mL of acetone. The resulting solution was refluxed at 80 °C overnight and then cooled to room temperature. The solution was then passed through a medium glass frit with a plug of silica to remove excess CuCl and K$_2$CO$_3$. The obtained polymer solution was concentrated using a rotary evaporator, precipitated in a cold water/ethanol (2/8 vol) mixture, and finally dried under vacuum at 40 °C. The obtained polymer has a $M_n$ of 21.0 kg mol$^{-1}$ and $D$ of 1.15.

**Table S1. Summary of molecular weights and dispersity of various polymers and their carbene polymers**

<table>
<thead>
<tr>
<th>Polymers $^a$</th>
<th>$M_n$ NMR (kg/mol) $^b$</th>
<th>$M_n$ SEC (kg/mol) $^c$</th>
<th>$D$ ($M_w/M_n$) $^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS$_{65}$-Br</td>
<td>6.9</td>
<td>11.9</td>
<td>1.13</td>
</tr>
<tr>
<td>PS$_{65}$-Im</td>
<td>7.0</td>
<td>11.5</td>
<td>1.18</td>
</tr>
<tr>
<td>PS$_{65}$-NHC-Cu(I)</td>
<td>7.0</td>
<td>11.8</td>
<td>1.13</td>
</tr>
<tr>
<td>PS$_{186}$-Br</td>
<td>19.4</td>
<td>18.1</td>
<td>1.12</td>
</tr>
<tr>
<td>PS$_{186}$-NHC-Cu(I)</td>
<td>19.5</td>
<td>18.0</td>
<td>1.11</td>
</tr>
<tr>
<td>PMMA$_{85}$-Im</td>
<td>8.9</td>
<td>7.7</td>
<td>1.18</td>
</tr>
<tr>
<td>PMMA$_{85}$-NHC-Cu(I)</td>
<td>8.8</td>
<td>8.6</td>
<td>1.16</td>
</tr>
<tr>
<td>PMEO$<em>2$MA$</em>{125}$-Im</td>
<td>23.9</td>
<td>20.0</td>
<td>1.09</td>
</tr>
<tr>
<td>PMEO$<em>2$MA$</em>{125}$-NHC-Cu(I)</td>
<td>23.8</td>
<td>19.9</td>
<td>1.16</td>
</tr>
<tr>
<td>PnBA$_{104}$-Im</td>
<td>13.5</td>
<td>19.9</td>
<td>1.14</td>
</tr>
<tr>
<td>PnBA$_{104}$-NHC-Cu(I)</td>
<td>13.4</td>
<td>21.0</td>
<td>1.15</td>
</tr>
</tbody>
</table>

$^a$The repeat unit numbers were calculated from $^1$H NMR; $^b$The number-average molecular weights were calculated from $^1$H NMR; $^c$The number-average molecular weights and dispersity index were determined by SEC using PS standards measured in THF.

3. Synthesis of $^{13}$C labelled N-methylimidazole and polymers

**Synthesis of $^{13}$C N-methylimidazole.** A 25 mL Schlenk tube fitted with a Teflon cap was submerged one-third in an ice bath. A micro-stirbar and 0.3 mL (3.32 mmol, 1.03 eq) of 35.3% w/w% methylamine solution were added. Next, 1.5 mL deionized water and 0.3 mL (4.38 mmol, 1.36 eq) of concentrated phosphoric acid was added. The pH was kept around 2. The ice bath was removed and 0.38 mL (3.32 mmol, 1.03 eq) 40% w/w% glyoxal solution was added to the solution followed by 100 mg (3.22 mmol, 1.00 eq) $^{13}$C labeled paraformaldehyde. The solution was warmed to room temperature and 3 mL of deionized water was added. Next, 3 mL of dioxane was added to solubilize the remaining solids. The solution was capped and heated to 70 °C and 0.71 mL (3.32 mmol, 1.03 equiv) of a 4.67 M ammonium chloride solution was added dropwise over 30 minutes. When the addition was finished, the reaction was capped and brought to 95 °C overnight while stirring vigorously. The next day, the solution was cooled to −5 °C using a salt ice bath and the cap of the Schlenk tube was removed. 18 mL of 1M NaOH was slowly added (ca. 0.5 mL at a time) while maintaining the temperature below 0 °C until the pH of the solution reached 12. The solution was brought to room temperature and filtered on a medium glass frit to remove the solid byproducts and the filtrate was
extracted 4 times with 10 mL of DCM. The DCM layers were collected, dried with sodium sulfate and the solvent was removed in vacuo yielding 69 mg (26%) of a yellow oil. 1H NMR (CDCl$_3$, 400 MHz) δ (ppm): 3.65 (d, $J = 3.36$ Hz, 3H), 6.84 (d, $J = 6.8$ Hz, 1H), 6.98 (d, $J = 10.4$ Hz, 1H), 7.38 (d, $J = 205.6$ Hz, 1H). 13C NMR (CDCl$_3$, 100.61 MHz) δ (ppm): 40.27, 129.63, 135.39, and 138.00.

Synthesis of $^{13}$C-labelled PS$_{65}$-$^{13}$C-Im and PS$_{65}$-$^{13}$CNHC-Cu(I). The synthetic procedures are the same as non-labeled polymer syntheses except $^{13}$C-N-methylimidazole is used.

4. Surface Plasmon Resonance (SPR) experiment and kinetic model for polymer binding

SPR experiment. In an experiment, degassed aqueous polymer solution was flowed into a SPR probe cell assembled with a gold sensor chip. The degassed solution was continuously flowed into the chamber for 30 min to allow for establishment of a stable baseline. Next, different concentrations of PMEO$_2$MA$_{125}$-NHC-Cu(I) or PMEO$_2$MA$_{174}$-SH solution (concentrations of the polymer solutions employed for SPR study were 31.25 nM, 62.5 nM, 125 nM, 250 nM, and 500 nM) were continuously introduced into the cell one at a time with a syringe pump at a flow rate of 25 µL/min. A fresh gold sensor chip was used for each experiment. All SPR traces were recorded at 20 °C on an SR7000DC dual channel flow SPR spectrometer from Reichert Analytical Instruments (NY, USA) with a semi-automatic injection setup with a maximum 100 µL PEEK injection loop and Harvard Apparatus flow pump.

Kinetic model. To elucidate the binding interaction of the NHC-Cu(I) and thiol-capped polymers with the Au surface, a simple association and dissociation model was adopted. Kinetic traces of real time SPR data of PMEO$_2$MA$_{125}$-NHC-Cu(I) or PMEO$_2$MA$_{174}$-SH with Au surface corresponding to association and dissociation phases were deconvoluted to yield the on and off rates. The nonlinear equations of the 1:1 equilibrium binding model (GraphPad prism software version 7.04) were used to fit the various concentration dependent data globally. The association phase was fitted using Eq 1 and the dissociation phase was fitted using Eq 2. This nonlinear regression analysis finds the minimum sum of squares solution giving the best values of the on-rate constant ($k_a$), off-rate constant ($k_d$), and maximum binding signal ($R_{max}$) where C = bulk concentration, $R_t$ = response time, $t$ = association and/or dissociation time. The on-rate ($k_a$), and off-rate ($k_d$) constants were used to calculate apparent binding constant ($K_a$) from Eq 3.

$$R_t = \frac{Ck_aR_{max}}{Ck_a + k_d}[1 - \exp(-(Ck_a + k_d)t)] \quad Eq \ (1)$$

$$R_t = R_{max}\exp(-k_dt) \quad Eq \ (2)$$

$$K_a = \frac{(k_a/k_d)} \quad Eq \ (3)$$

Table S2. Summary of the binding constant values measured using SPR spectroscopy

<table>
<thead>
<tr>
<th>Type of probe</th>
<th>$k_a$ (M$^{-1}$s$^{-1}$)</th>
<th>$k_d$ (s$^{-1}$)</th>
<th>$K_a$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMEO$<em>2$MA$</em>{174}$-SH</td>
<td>4.8 (±0.1) $\times$ 10$^4$</td>
<td>6.9 (±0.8) $\times$ 10$^{-5}$</td>
<td>7.1 $\times$ 10$^8$</td>
</tr>
<tr>
<td>PMEO$<em>2$MA$</em>{125}$-NHC-Cu(I)</td>
<td>3.3 (±0.1) $\times$ 10$^4$</td>
<td>4.5 (±0.2) $\times$ 10$^{-4}$</td>
<td>7.7 $\times$ 10$^7$</td>
</tr>
</tbody>
</table>

$k_a$ is the on-rate constant and $k_d$ is the off-rate constant. $K_a$ is the apparent binding constant.

5. Estimation of the grafting density

The number of polymer chains per nanoparticle is calculated from the following Equation 4:

$$Polymer \ chains/AuNP = \frac{V_{Au} \times N_A \times \rho_{Au}}{M_w(PS) \times \frac{\mu_{Au}}{mpoly}} \quad Eq \ (4)$$
In this equation, \( m_{Au} \) and \( m_{PS} \) are the mass of the pure gold nanoparticles and the mass of polymer ligands, respectively, both measured from TGA analysis. \( \rho_{Au} \) is the bulk density of gold \( (\rho_{Au} = 19.6 \text{ g/cm}^3) \) and \( V_{Au} \) is the volume of individual AuNPs calculated using the average diameter of 11.7 nm. \( M_n \) (PS) is the molecular weight of the PS ligands measured from \(^1\text{H} \) NMR. \( N_a \) is the Avogadro constant.

From the TGA thermograms as shown in Figure S3, 8 wt% was measured from PS\(_{65}\)-NHC attached to AuNPs and 80 wt% measured from pure gold after subtracting the solvent mass.

From the TEM image, the average diameter of PS\(_{65}\)-NHC grafted AuNPs was measured to be 11.7 nm. So, the volume of individual AuNPs is calculated to be:

\[
V_{Au} = \frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} (5.85 \times 10^{-9} m)^3 = 8.39 \times 10^{-25} m^3
\]

\[
\text{Polymer chains/AuNP} = \frac{8.39 \times 10^{-25} m^3 \times 6.023 \times 10^{23} \times 19.6 \times 10^6 g/m^3}{6900 g/mol \times \frac{80}{8}}
\]

\[
\text{Polymer chains/AuNP} = 144
\]

The grafting density is expressed in number of PS chains per nm\(^2\) and was calculated by dividing the number of PS polymer chains per AuNP by the surface area of AuNP:

\[
\text{Surface Area of AuNP} = 4 \pi r^2 = 4 \times \frac{22}{7} \times (5.85 \text{ nm})^2 = 430.2 \text{ nm}^2
\]

\[
\text{Grafting density} (\sigma) = \frac{144}{430.2} = 0.33 \text{ chains/nm}^2
\]

**Figure S1.** \(^1\text{H} \) NMR spectrum of PS\(_{65}\)-Br measured in CDCl\(_3\). (b) SEC elution curves of PS\(_{65}\)-Br (black), PS\(_{65}\)-Im (red) and PS\(_{65}\)-NHC-Cu(I) (blue) polymers measured in THF.
Figure S2. $^1$H NMR spectra of N-benzyl-N’-methylimidazolium bromide (black, bottom) and N-benzyl-N’-methylimidazol-2-ylidene-Cu(I)Cl (red, top) in CDCl$_3$.

Figure S3. Image showing control experiments for the transfer of citrate capped AuNPs using PS$_{65}$-Br, PS$_{65}$-Im, and PS$_{65}$-NHC-Cu(I) in toluene.
Figure S4. UV-vis spectra of PS$_{65}$-NHC-Au in DCM treated with 10 mM of dodecanethiol (DDT) at different times post addition. The AuNPs were stable at 24 h since no change in the SPR absorption wavelength was seen; while an obvious shift was observed after 48 h, indicating ligand exchange.

Figure S5. (a) Synthetic route of $^{13}$C-labelled PS$_{65}$-NHC-Au using $^{13}$CIm. (b) $^1$H NMR spectra of PS$_{65}$-$^{13}$Clm (black, bottom), PS$_{65}$-$^{13}$CNHC-Cu(I) (red, middle) and PS$_{65}$-$^{13}$CNHC-Au (blue, blue) in $d$-CHCl$_3$. The zoom-in image in (b) shows the $H-^{13}$Clm of PS$_{65}$-$^{13}$Clm. The doublet is due to the $^{13}$C-H coupling with $^1J = 260$ Hz.
Figure S6. TGA thermograms of free PS\textsubscript{65}-NHC-Cu(I) polymer and correspoding PS\textsubscript{65}-NHC modified AuNPs. The weight loss in the range of 200-300 °C is attributed to a trace amount of toluene. The weight loss between 350-450 °C is assigned to the decomposition of PS\textsubscript{65}-NHC-Cu(I).

Figure S7. (a) Synthetic route of PS\textsubscript{186}-NHC-Cu(I) using a post-polymerization functionalization reaction. (b) \textsuperscript{1}H NMR spectra of PS\textsubscript{186}-Im (black, bottom) and PS\textsubscript{186}-NHC-Cu(I) (red, top) in CDCl\textsubscript{3}. The peaks marked with * are residual solvent from DMF and acetone. (c) Images showing the dispersion of PS\textsubscript{186}-NHC modified AuNPs in various organic solvents. (d) UV-vis spectra showing the SPR absorption of AuNPs in various solvents.
Figure S8. (a) $^1$H NMR spectrum of Im-EtOH measured in CDCl$_3$. The peaks marked with * are residual solvent from diethyl ether and acetone. (b) $^1$H NMR spectrum of Im-Et-Br measured in CDCl$_3$.

Figure S9. SEC elution curves of PMMA$_{85}$-Im (black) and PMMA$_{85}$-NHC-Cu(I) (red) polymers measured in THF.
Figure S10. (a) Chemical reaction showing the synthesis of PMEO₂MA₁₂₅-NHC-Cu(I), (b) \(^1\)H NMR spectra of PMEO₂MA₁₂₅-Im (black, bottom) and PMEO₂MA₁₂₅-NHC-Cu(I) (red, top) polymers measured in CDCl₃. The peaks marked with * are residual solvent from DCM and acetone. (c) SEC elution curves of PMEO₂MA₁₂₅-Im (black, bottom) and PMEO₂MA₁₂₅-NHC-Cu(I) (red, top) polymers measured in THF.

Figure S11. SEC elution curves of PnBA₁₀₄-Im (black) and PnBA₁₀₄-NHC-Cu(I) (red) polymers measured in THF.
Figure S12. (a) Chemical reaction showing the synthesis of PnBA$_{104}$-NHC-Cu(I), and $^1$H NMR spectra of PnBA$_{104}$-Im (black, bottom) and PnBA$_{104}$-NHC-Cu(I) (red, top) measured in CDCl$_3$. The peak marked with * is residual solvent from acetone. (b) UV-vis spectra showing the SPR peaks of PnBA$_{104}$-NHC modified AuNPs dispersed in various solvents. (c) Image showing the solutions of PnBA$_{104}$-NHC modified AuNPs in various solvents.
Figure S13. $^1$H NMR spectra of PMEO$_2$MA$_{125}$-NHC-Cu(I) (black, bottom) and PMEO$_2$MA$_{125}$-NHC-Au (red, top) measured in CD$_2$Cl$_2$. The inset shows the chemical shift of protons corresponding to $i$, $h$ from the imidazole ring. The CD$_2$Cl$_2$ peak was suppressed during the acquisition of the PMEO$_2$MA$_{125}$-NHC-Au spectrum.

Similar results were observed for the PMEO$_2$MA$_{125}$-NHC-Cu(I) polymer and PMEO$_2$MA$_{125}$-NHC-Au as described in Figure S15. The protons $i+h$ from the imidazole ring of PMEO$_2$MA$_{125}$-NHC-Cu(I) have a chemical shift of 7.01 ppm. After transmetalation with AuNPs, $i+h$ protons were observed at 6.92 ppm. This decrease in the chemical shift implies that the PMEO$_2$MA$_{125}$-NHC-Cu(I) have transferred to AuNPs.
References