Supporting Information

Au(I)-benzimidazole/imidazole Complexes. Liquid Crystals and Nanomaterials

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Experimental

[\textbf{Au(C16-bim)Cl}]. White solid, yield 89%. $^1$H NMR (ppm, CDCl$_3$) : $\delta$ 0.88 (t, $^3$$J$ = 7 Hz, 3H, CH$_3$, ionic and neutral overlapped), 1.25-1.34 (m, 26H, CH$_2$, ionic and neutral overlapped), 1.95 (m, 2H, CH$_2$, ionic and neutral overlapped), 4.28 (t, $^3$$J$ = 7 Hz, 2H, CH$_2$, neutral form), 7.45-7.54 (m, 1H, CH, neutral form), 7.89-7.92 (m, 1H, CH, neutral form), 8.21 (s, 1H, CH, neutral form), 4.56 (t, $^3$$J$ = 7 Hz, 2H, CH$_2$, ionic form), 7.58-7.69 (m, 1H, CH, ionic form), 7.96-7.99 (m, 1H, CH, ionic form), 9.21 (s, 1H, CH, ionic form). $^1$H NMR (ppm, d$_6$-DMSO) : $\delta$ 0.82 (t, $^3$$J$ = 7 Hz, 3H, CH$_3$, ionic and neutral overlapped), 1.18-1.20 (m, 26H, CH$_2$, ionic and neutral overlapped), 1.83 (m, 2H, CH$_2$, ionic and neutral overlapped), 4.35 (t, $^3$$J$ = 7 Hz, 2H, CH$_2$, neutral form), 7.46 (m, 1H, CH, neutral form), 7.77-7.95 (m, 1H, CH, neutral form), 9.1 (s, 1H, CH, neutral form), 4.45 (t, $^3$$J$ = 7 Hz, 2H, CH$_2$, ionic form), 7.54 (m, 1H, CH, ionic form), 7.95-8.00 (m, 1H, CH, ionic form), 9.26 (s, 1H, CH, ionic form). Anal. Calcd. for C$_{23}$H$_{38}$N$_2$AuCl: C, 48.05; H, 6.66; N, 4.87. Found: C, 47.99; H, 6.61; N, 4.99%.

[\textbf{Au(C18-im)Cl}]. White solid, yield 90%. $^1$H NMR (ppm, CDCl$_3$) : $\delta$ 0.88 (t, $^3$$J$ = 7 Hz, 3H, CH$_3$, ionic and neutral overlapped), 1.25-1.31 (m, 30, CH$_2$, ionic and neutral overlapped).
overlapped), 1.82 (m, 2H, CH\textsubscript{2}, ionic and neutral overlapped), 4.01 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, neutral form), 7.08 (s, 1H, CH, neutral form), 7.09 (s, 1H, CH, neutral form), 7.76 (s, 1H, CH, neutral form). 4.33 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, ionic form), 7.26 (s, 1H, CH, ionic form), 7.27 (s, 1H, CH, ionic form)).

\[ \text{1H NMR (ppm, d\textsubscript{6}-DMSO)} : \delta \ 0.83 (t, \(\textit{J} = 7\) Hz, 3H, CH\textsubscript{3}, ionic and neutral overlapped), 1.10-1.21 (m, 30, CH\textsubscript{2}, ionic and neutral overlapped), 1.74 (m, 2H, CH\textsubscript{2}, ionic and neutral overlapped), 4.03 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, neutral form), 7.25 (s, 1H, CH, neutral form), 7.60 (s, 1H, CH, neutral form), 8.43 (s, 1H, CH, neutral form). 4.11 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, ionic form), 7.34 (s, 1H, CH, ionic form), 7.78 (s, 1H, CH, ionic form), 8.53 (s, 1H, CH, ionic form). \]

\[ \text{13C NMR (ppm, CDCl\textsubscript{3}) :} \delta \ 14.05, 22.65, 26.34, 28.90, 29.31, 29.43, 29.53, 29.65, 30.43, 31.89, 48.74, 119.88, 129.93, 138.32. \]

Anal. Calcd. for C\textsubscript{21}H\textsubscript{40}N\textsubscript{2}AuCl: C, 45.61; H, 7.29; N, 5.07. Found: C, 45.57; H, 7.13; N, 4.80%.

[\textbf{Au(C\textsubscript{16-im})Cl}]. White solid, yield 86%.

\[ \text{1H NMR (ppm, d\textsubscript{6}-DMSO)} : \delta \ 0.83 (t, \(\textit{J} = 7\) Hz, 3H, CH\textsubscript{3}, ionic and neutral overlapped), 1.21 (m, 22, CH\textsubscript{2}, ionic and neutral overlapped), 1.84 (m, 2H, CH\textsubscript{2}, ionic and neutral overlapped), 4.08 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, neutral form), 7.06 (s, 1H, CH, neutral form), 7.07 (s, 1H, CH, neutral form), 7.80 (s, 1H, CH, neutral form). 4.20 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, ionic form), 6.90 (s, 1H, CH, ionic form), 7.60 (s, 1H, CH, ionic form), 8.40 (s, 1H, CH, ionic form). \]

Anal. Calcd. for C\textsubscript{19}H\textsubscript{36}N\textsubscript{2}AuCl: C, 43.47; H, 6.91; N, 5.34. Found: C, 43.30; H, 6.57; N, 5.09%.

[\textbf{Au(C\textsubscript{14-im})Cl}]. White solid, yield 88%.

\[ \text{1H NMR (ppm, CDCl\textsubscript{3}) :} \delta \ 0.83 (t, \(\textit{J} = 7\) Hz, 3H, CH\textsubscript{3}, ionic and neutral overlapped), 1.19-1.31 (m, 26, CH\textsubscript{2}, ionic and neutral overlapped), 1.85 (m, 2H, CH\textsubscript{2}, ionic and neutral overlapped), 4.00 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, neutral form), 7.08 (s, 1H, CH, neutral form), 7.10 (s, 1H, CH, neutral form), 7.72 (s, 1H, CH, neutral form). 3.97 (t, \(\textit{J} = 7\) Hz, 2H, CH\textsubscript{2}, ionic form), 6.90 (s, 1H, CH, ionic form), 7.60 (s, 1H, CH, ionic form), 8.40 (s, 1H, CH, ionic form). \]

Anal. Calcd. for C\textsubscript{19}H\textsubscript{36}N\textsubscript{2}AuCl: C, 43.47; H, 6.91; N, 5.34. Found: C, 43.30; H, 6.57; N, 5.09%.
[Au(C_{12}-im)Cl]. White solid, yield 86%. $^1$H NMR (ppm, CDCl$_3$): $\delta$ 0.88 (t, $^3J = 7$ Hz, 3H, CH$_3$, ionic and neutral overlapped), 1.16-1.2 (m, 18, CH$_2$, ionic and neutral overlapped), 1.80 (m, 2H, CH$_2$, ionic and neutral overlapped), 4.00 (t, $^3J = 7$ Hz, 2H, CH$_2$, neutral form), 7.05 (s, 1H, CH, neutral form), 7.24 (s, 1H, CH, neutral form), 7.78 (s, 1H, CH, neutral form). 4.25 (t, $^3J = 7$ Hz, 2H, CH$_2$, ionic form), 7.07 (s, 1H, CH, ionic form), 7.29 (s, 1H, CH, ionic form), 8.5 (s, 1H, CH, ionic form).

$^1$H NMR (ppm, d$_6$-DMSO): $\delta$ 0.84 (t, $^3J = 7$ Hz, 3H, CH$_3$, ionic and neutral overlapped), 1.22 (m, 18, CH$_2$, ionic and neutral overlapped), 1.75 (m, 2H, CH$_2$, ionic and neutral overlapped), 4.03 (t, $^3J = 7$ Hz, 2H, CH$_2$, neutral form), 7.25 (s, 1H, CH, neutral form), 7.60 (s, 1H, CH, neutral form), 8.43 (s, 1H, CH, neutral form). 4.09 (t, $^3J = 7$ Hz, 2H, CH$_2$, ionic form), 7.34 (s, 1H, CH, ionic form), 7.68 (s, 1H, CH, ionic form), 8.53 (s, 1H, CH, ionic form). Anal. Calcd. for C$_{15}$H$_{28}$N$_2$AuCl: C, 38.43; H, 6.02; N, 5.98. Found: C, 38.88; H, 6.05; N, 5.97%.

[ Au(C$_{16}$-im)$_2$][NO$_3$] · 2 H$_2$O. White solid, yield 85%. $^1$H NMR (ppm, CDCl$_3$): $\delta$ 0.88 (t, $^3J = 7$ Hz, 6H, CH$_3$), 1.19-1.31 (m, 52H, CH$_2$), 1.83 (m, 4H, CH$_2$), 4.08 (t, $^3J = 7$ Hz, 4H, CH$_2$), 7.09 (s, 2H, CH), 7.10 (s, 2H, CH), 8.58 (s, 2H, CH). FAB/Mass: m/z 781.3, (M$^+$). Anal. Calcd. for C$_{36}$H$_{76}$N$_5$O$_5$Au: C, 51.86; H, 8.70; N, 7.96. Found: C, 51.87; H, 8.77; N, 7.97%.

[ Au(C$_{14}$-im)$_2$][NO$_3$] · 2 H$_2$O. White solid, yield 79%. $^1$H NMR (ppm, CDCl$_3$): $\delta$ 0.88 (t, $^3J = 7$ Hz, 6H, CH$_3$), 1.21-1.31 (m, 44H, CH$_2$), 1.83 (m, 4H, CH$_2$), 4.08 (t, $^3J = 7$ Hz, 4H, CH$_2$), 7.07 (s, 2H, CH), 7.09 (s, 2H, CH), 8.59 (s, 2H, CH). FAB/Mass: m/z 725.4, (M$^+$). Anal. Calcd. for C$_{34}$H$_{68}$N$_5$O$_5$Au: C, 49.57; H, 8.32; N, 8.50. Found: C, 49.41; H, 8.31; N, 8.49%.

[ Au(C$_{12}$-im)$_2$][NO$_3$] · 2 H$_2$O. White solid, yield 75%. $^1$H NMR (ppm, CDCl$_3$): $\delta$ 0.88 (t, $^3J = 7$ Hz, 6H, CH$_3$), 1.21-1.31 (m, 36H, CH$_2$), 1.84 (m, 4H, CH$_2$), 4.08 (t, $^3J = 7$ Hz, 4H, CH$_2$), 7.07 (s, 2H, CH), 7.09 (s, 2H, CH), 8.59 (s, 2H, CH). FAB/Mass: m/z 669.3, (M$^+$). Anal. Calcd. for C$_{30}$H$_{60}$N$_5$O$_5$Au: C, 46.93; H, 7.88; N, 9.12. Found: C, 47.06; H, 7.95; N, 9.22%.

[ Au(C$_{10}$-im)$_2$][NO$_3$] · 2 H$_2$O. White solid, yield 71%. $^1$H NMR (ppm, CDCl$_3$): $\delta$ 0.88 (t, $^3J = 7$ Hz, 6H, CH$_3$), 1.19-1.31 (m, 28H, CH$_2$), 1.84 (m, 4H, CH$_2$), 4.08 (t, $^3J = 7$ Hz, 4H, CH$_2$), 7.07 (s, 2H, CH), 7.09 (s, 2H, CH), 8.58 (s, 2H, CH). FAB/Mass: m/z...
613.2, (M)$^+$. Anal. Calcd. for C$_{26}$H$_{52}$N$_5$O$_5$Au: C, 43.88; H, 7.36; N, 9.84. Found: C, 43.78; H, 7.35; N, 9.81%.

$[\text{Au(C}_{18}\text{-bim)}_2][\text{NO}_3]$]. White solid, yield 88%. $^1$H NMR (ppm, CDCl$_3$): δ 0.86 (t, $^3J = 7$ Hz, 3H, CH$_3$), 1.18-1.33 (m, 30H, CH$_2$), 1.87 (m, 2H, CH$_2$), 4.12 (t, $^3J = 7$ Hz, 2H, CH$_2$), 7.31 (m, 1H, CH), 7.36 (m, 1H, CH), 9.45 (m, 1H, CH). $^{13}$C NMR (ppm, CDCl$_3$): 14.1, 22.7, 26.5, 26.7, 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 46.3, 110.7, 118.3, 124.0, 124.5, 131.5, 139.3, 147.0. Anal. Calcd. for C$_{50}$H$_{84}$N$_5$O$_3$Au: C, 60.04; H, 8.46; N, 7.00 Found: C, 59.74; H, 8.36; N, 6.92%.
Table S1. Summary of crystallographic data for I = [Au(C16-bim)Cl], II = [Au(C12-im)2][AuCl2], III = [Au(C1-im)2][AuCl2], IV = [Au(C14-im)2][NO3] · 2H2O.

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<th>II</th>
<th>III</th>
<th>IV</th>
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<td>C8H12N4Au2Cl2</td>
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<td>681.97(3)</td>
<td>1872.5(4)</td>
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<td>2, 3.063</td>
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<td>3758(0.1012)</td>
<td>3416(0.0767)</td>
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<td>R1 = 0.0460</td>
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Figure S1. [Au(C₁₆-bim)Cl], (a) H-bonding interactions between the cation and anions. (b) imidazole-imidazole ring π-π interaction between neighboring neutral compounds.

Figure S2. [Au(C₁₂-im)₂][AuCl₂], (a) the zigzag Au(I)-Au(I) interactions. (b) The C-H…Cl H-Bonding interactions between the cation and anions.

Figure S3. (a) ORTEP drawing of [Au(C₁-im)₂][AuCl₂] (30 % thermal ellipsoids) with partial atomic numbering, hydrogens being omitted for clarity; selected distances [Å] and [°]: Au(1)-Cl(2) 2.262(3), Au(1)-Cl(1) 2.271(2), Au(1)-Au(2) 3.3778(3), Au(2)-N(1) 2.001(6), Au(3)-N(3) 2.007(6), Cl(2)-Au(1)-Cl(1) 177.88(8), Cl(2)-Au(1)-Au(2) 86.33(6), Cl(1)-Au(1)-Au(2) 95.23(6), N(1')-Au(2)-N(1) 180.0, N(1)-Au(2)-Au(1') 87.93(17), N(1')-Au(2)-Au(1) 92.07(17), N(3)-Au(3)-N(3') 180.0(4). (b) the crystal packing of [Au(CH₃-im)Cl]. view along the a-axis, and C-H…Cl H-Bonding interactions between
the cation and anions. Symmetry operations used to generate equivalent atoms: (i) \(-x+1, -y, -z-1\); (ii) \(-x+2, -y, -z\).

Figure S4. \([\text{Au(C}_{14-}\text{im})_2][\text{NO}_3]\) \(\cdot\) \(2\text{H}_2\text{O}\) showing (a) the H-bonding interactions from imidazole, nitrate and water, (b) the hexagon channel formed from nitrate anions and water molecules.

Figure S5. \(^1\text{H}-\text{NMR}\) spectrum of \([\text{Au(C}_{16-}\text{im})\text{Cl}]\) in \(d_6\)-DMSO.

Figure S6. XRD diffractograms of \([\text{Au(C}_{12-}\text{im})_2][\text{AuCl}_2]\). (a) powder sample obtained by adding hexane to the \(\text{CHCl}_3\) solution, (b) single crystals (ionic compound).
Figure S7. phase transition temperatures of [Ag(Cn-im)][NO3] V. S. [Au(Cn-im)][NO3]:
(▲): [Ag(Cn-im)][NO3], (■): [Au(Cn-im)][NO3].

Figure S8. TEM images and size distributions (in inset) of Au NPs from
[C18-bim]/[Au(C18-bim)2][NO3] with molar ratios of (a) 0, (b) 3, and (c) 7; (d) the
corresponding UV-visible absorption spectra for Au NPs obtained at different molar ratios
(from top to bottom).

Figure S9. SEM image of gold nanomaterials from thermolysis of [Au(C18-im)2][AuCl2]
at 200 °C for 1 h.
**Figure S10.** SEM image of triangular, hexagonal and spherical gold nanomaterials from thermolysis of [Au(C_{18-bim})_2][NO_3] at 200 °C.

**Figure S11.** TEM images of gold nanomaterials from thermolysis of [Au(C_{18-im})_2][NO_3] at 100 °C (mesophase) for 1 h.

**Figure S12.** SEM image of gold nanomaterials from thermolysis of [Au(C_{18-im})_2][NO_3] at 200 °C (isotropic phase) for 1 h.