Supplementary Material (ESI) for Dalton Transactions

Supporting Information

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

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Experimental

[Au(C_{16}-bim)Cl]. White solid, yield 89%. ^{1}H NMR (ppm, $CDCl_3$) : δ 0.88 (t, ^3J = 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, ^3J = 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, ^3J = 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) : δ 0.82 (t, ^3J = 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, ^3J = 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, ^3J = 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 $C_{23}H_{38}N_2AuCl$: C, 48.05; H, 6.66; N, 4.87. Found: C, 47.99; H, 6.61; N, 4.99%.

[Au(C_{18}-im)Cl]. White solid, yield 90%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.88 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.25-1.31 (m, 30, CH_2, ionic and neutral

overlapped), 1.82 (m, 2H, CH_2, ionic and neutral overlapped), 4.01 (t, ^3J = 7 Hz, 2H, CH_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, ^3J = 7 Hz, 2H, CH_2, ionic form), 7.26 (s, 1H, CH, ionic form), 7.27 (s, 1H, CH, ionic form),8.42 (s, 1H, CH, ionic form).
^{1}H NMR (ppm, d_6-DMSO) : δ 0.83 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.10-1.21 (m, 30, CH_2, ionic and neutral overlapped), 1.74 (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). 4.11 (t, ^3J = 7 Hz, 2H, CH_2, ionic form), 7.34 (s, 1H, CH, ionic form), 7.78 (s, 1H, CH, ionic form), 8.53 (s, 1H, CH, ionic form). ^{13}C NMR (ppm, $CDCl_3$): δ 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 $C_{21}H_{40}N_2AuCl$: C, 45.61; H, 7.29; N, 5.07. Found: C, 45.57; H, 7.13; N, 4.80%.

[Au(C_{16}-im)Cl]. White solid, yield 86%. ^{1}H NMR (ppm, $CDCl_3$) : δ 0.88 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.19-1.31 (m, 26, CH_2, ionic and neutral overlapped), 1.85 (m, 2H, CH_2, ionic and neutral overlapped), 4.00 (t, ^3J = 7 Hz, 2H, CH_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, ^3J = 7 Hz, 2H, CH_2, ionic form), 6.9 (s, 1H, CH, ionic form), 7.09 (s, 1H, CH, ionic form), 8.05 (s, 1H, CH, ionic form).
^{1}H NMR (ppm, d_6-DMSO) : δ 0.83 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.21 (m, 26, CH_2, ionic and neutral overlapped), 1.76 (m, 2H, CH_2, ionic and neutral overlapped), 4.0 (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), 7.33 (s, 1H, CH, ionic form), 7.68 (s, 1H, CH, ionic form), 8.53 (s, 1H, CH, ionic form). Anal. Calcd. for $C_{19}H_{36}N_2AuCl$: C, 43.47; H, 6.91; N, 5.34. Found: C, 43.30; H, 6.57; N, 5.09%.

[Au(C_{14}-im)Cl]. White solid, yield 88%. ^{1}H NMR (ppm, $CDCl_3$) : δ 0.88 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.19-1.31 (m, 22, CH_2, ionic and neutral overlapped), 1.84 (m, 2H, CH_2, ionic and neutral overlapped), 4.08 (t, ^3J = 7 Hz, 2H, CH_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, ^3J = 7 Hz, 2H, CH_2, ionic form), 6.9 (s, 1H, CH, ionic form), 7.60 (s, 1H, CH, ionic form), 8.40 (s, 1H, CH, ionic form).
^{1}H NMR (ppm, d_6-DMSO) : δ 0.83 (t, ^3J = 7 Hz, 3H, CH_3, ionic and neutral overlapped), 1.21 (m, 22, CH_2, ionic and neutral overlapped), 1.76 (m, 2H, CH_2, ionic and neutral overlapped), 4.06 (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 $C_{17}H_{32}N_2AuCl$: C, 41.09; H, 6.49; N, 5.64. Found: C, 41.30; H, 6.52; N, 5.64%.

[Au(C_{12}-im)Cl]. White solid, yield 86%. ^{1}H NMR (ppm, $CDCl_3$) : δ 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) : δ 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 $C_{15}H_{28}N_2AuCl$: C, 38.43; H, 6.02; N, 5.98. Found: C, 388.50; H, 6.05; N, 5.97%.

[Au(C_{16}-im)$_2$][NO_3] · 2 H_2O. White solid, yield 85%. ^{1}H NMR (ppm, $CDCl_3$): δ 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 $C_{38}H_{76}N_5O_5Au$: 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_2O. White solid, yield 79%. ^{1}H NMR (ppm, $CDCl_3$): δ 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 $C_{34}H_{68}N_5O_5Au$: 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_2O. White solid, yield 75%. ^{1}H NMR (ppm, $CDCl_3$): δ 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 $C_{30}H_{60}N_5O_5Au$: 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_2O. White solid, yield 71%. ^{1}H NMR (ppm, $CDCl_3$): δ 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 $C_{26}H_{52}N_5O_5Au$: C, 43.88; H, 7.36; N, 9.84. Found: C, 43.78; H, 7.35; N, 9.81%.

$[Au(C_{18}\text{-bim})_2][NO_3]$. 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 $C_{50}H_{84}N_5O_3Au$: 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(C_{16}-bim)Cl], Ⅱ = [Au(C_{12}-im)$_2$][$AuCl_2$], Ⅲ = [Au(C_1-im)$_2$][$AuCl_2$], Ⅳ = [Au(C_{14}-im)$_2$][NO_3]·2H_2O.

	Ⅰ	Ⅱ	Ⅲ	Ⅳ
Formula	$C_{23}H_{38}N_2ClAu$	$C_{30}H_{56}N_4Cl_2Au_2$	$C_8H_{12}N_4Au_2Cl_2$	$C_{34}H_{68}N_5O_5Au$
Fw	574.97	937.64	629.05	823.90
Crystal syst	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	C2/c	P-1	P-1
a, Å	6.9675(4)	38.885(12)	9.1626(2)	8.2729(11)
b, Å	8.3571(5)	8.920(3)	9.3947(2)	9.1630(12)
c, Å	21.1920(13)	10.471(3)	9.5693(2)	25.254(3)
α/°	82.377(1)	90	71.388(1)	92.838(2)
β/°	85.304(1)	92.140(6)	87.392(1)	92.054(2)
γ/°	77.721(1)	90	61.453(1)	101.360(2)
Volume/Å^3	1193.25(12)	3629.5(18)	681.97(3)	1872.5(4)
Z, Density (calc.)/Mg m^{-3}	2, 1.600	8, 1.716	2, 3.063	2, 1.461
T, K	295(2)	295(2)	295(2)	100(2)
μ, mm^{-1}	6.286	8.245	21.859	3.973
F(000)	572	1824	560	852
Crystal size/mm	0.90 x 0.10 x 0.10	0.20 x 0.02 x 0.05	0.20 x 0.10 x 0.10	0.40 x 0.30 x 0.20
θ_{min}, θ_{max}, deg	0.97-28.28	1.05-26.54	2.26-28.36	0.81-28.38
Reflections collected	14155	10798	10516	22107
Independent reflections(R_{int})	5879 (0.0820)	3758(0.1012)	3416(0.0767)	9258(0.0573)
Data/restraints/ parameters	5879/0/244	3758/0/174	3416/0/148	9258/0/406
Goodness-of-fit on F^2	1.010	0.848	0.948	1.068
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0307	*R*1 = 0.0460	*R*1 = 0.0317	*R*1 = 0.0470
	*wR*2 = 0.0712	*wR*2 = 0.0871	*wR*2 = 0.0803	*wR*2 = 0.1231
R indices (all data)	*R*1 = 0.0352	*R*1 = 0.1291	*R*1 = 0.0398	*R*1 = 0.0529
	*wR*2 = 0.0858	*wR*2 = 0.1272	*wR*2 = 0.0950	*wR*2 = 0.1293

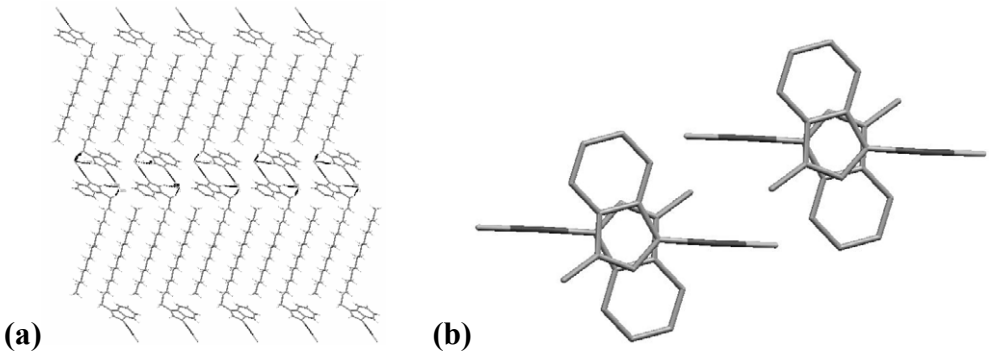

Figure S1. [Au(C_{16}-bim)Cl], (a) H-bonding interactions between the cation and anions. (b) imidazole-imidazole ring π-π interaction between neighboring neutral compounds.

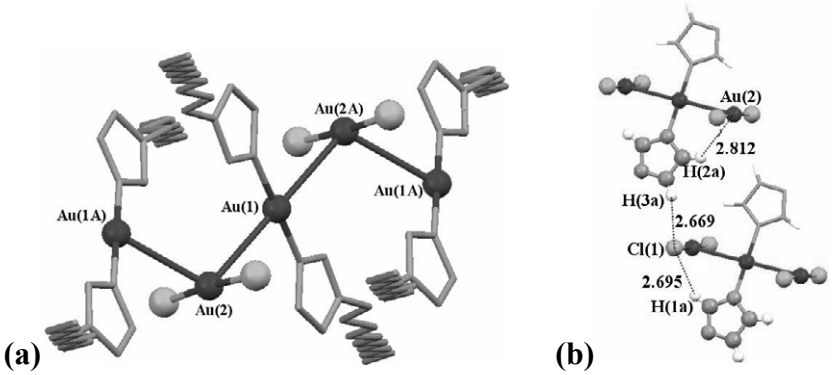

Figure S2. [Au(C_{12}-im)$_2$][$AuCl_2$], (a) the zigzag Au(I)-Au(I) interactions. (b) The C-H…Cl H-Bonding interactions between the cation and anions.

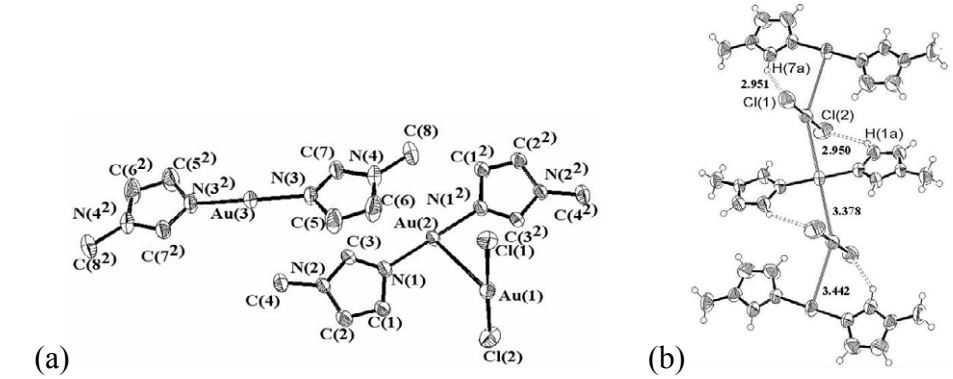

Figure S3. (a) ORTEP drawing of [Au(C_1-im)$_2$][$AuCl_2$] (30 % thermal ellipsoids) with partial atomic numbering, hydrogens being omitted for claeity; selected distances [Å] and [°]: Au(1)-Cl(2) 2.262(3), Au(1)-Cl(1) 2.271(2), Au(1)-Au(2) 3.3778(3), Au(2)-N(1) 2.001(6), Au(3)-N(3) 2.007(6), Cl(2)-Au(1)-Cl(1) 177.88(8), Cl(2)-Au(1)-Au(2) 86.33(6), Cl(1)-Au(1)-Au(2) 95.23(6), N(1^i)-Au(2)-N(1) 180.0, N(1)-Au(2)-Au(1^i) 87.93(17), N(1^i)-Au(2)-Au(1^i) 92.07(17), N(3)-Au(3)-N(3^{ii}) 180.0(4). (b) the crystal packing of [Au(CH_3-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.

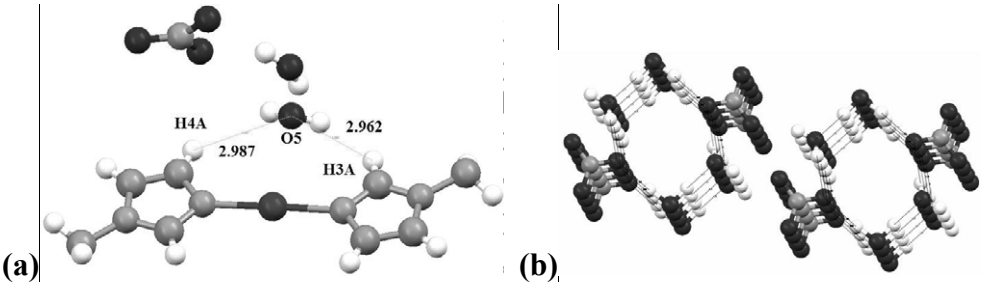

Figure S4. $[Au(C_{14}\text{-im})_2][NO_3]\cdot 2H_2O$ showing (a) the H-bonding interactions from imidazole, nitrate and water, (b) the hexagon channel formed from nitrate anions and water molecules.

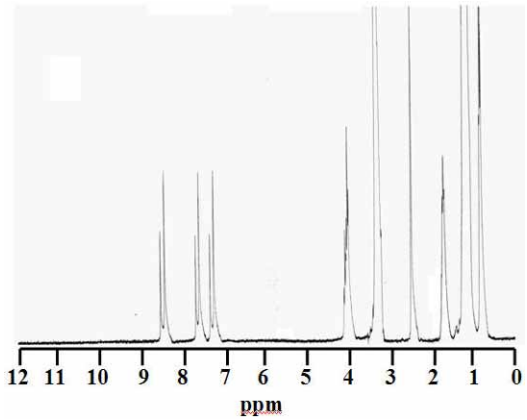

Figure S5. ^{1}H-NMR spectrum of $[Au(C_{16}\text{-im})Cl]$ in d_6-DMSO.

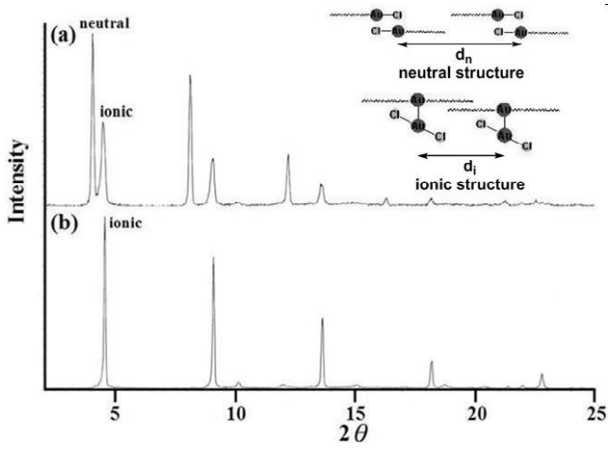

Figure S6. XRD diffractograms of $[Au(C_{12}\text{-im})_2][AuCl_2]$. (a) powder sample obtained by adding hexane to the $CHCl_3$ solution, (b) single crystals (ionic compound).

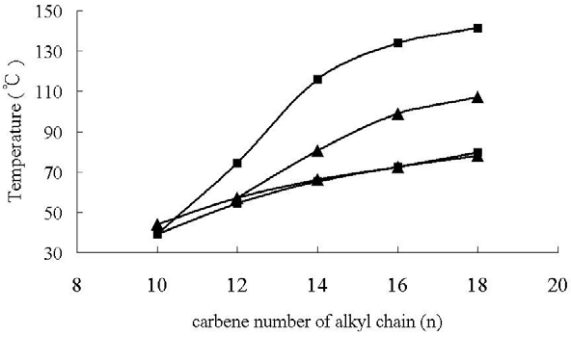

Figure S7. phase transition temperatures of $[Ag(C_n\text{-im})][NO_3]$ V. S. $[Au(C_n\text{-im})][NO_3]$: (▲) : $[Ag(C_n\text{-im})][NO_3]$, (■) : $[Au(C_n\text{-im})][NO_3]$.

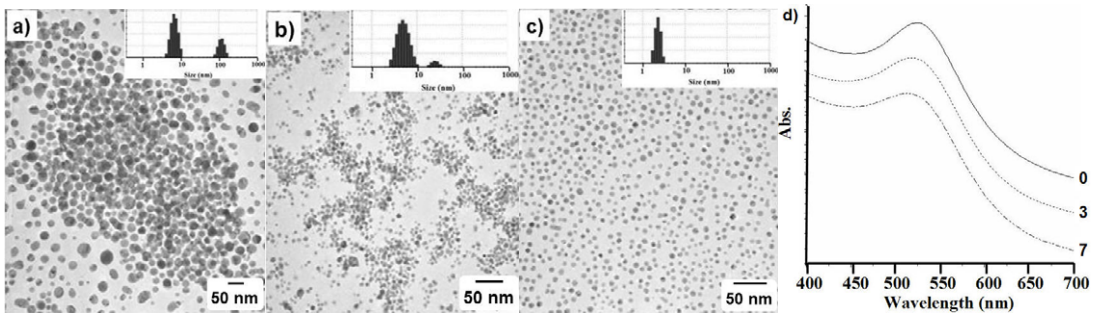

Figure S8. TEM images and size distributions (in inset) of Au NPs from $[C_{18}\text{-bim}]/[Au(C_{18}\text{-bim})_2][NO_3]$ with molar ratios of (a) 0, (b) 3, and (c) 7; (d) the corresponding UV-visible absorption spectra for Au NPs obtained at different molar ratios (from top to bottom).

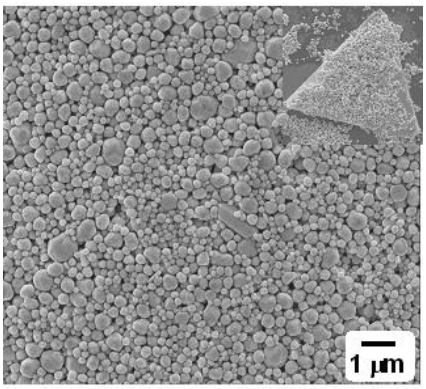

Figure S9. SEM image of gold nanomaterials from thermolysis of $[Au(C_{18}\text{-im})_2][AuCl_2]$ at 200 ^oC for 1 h.

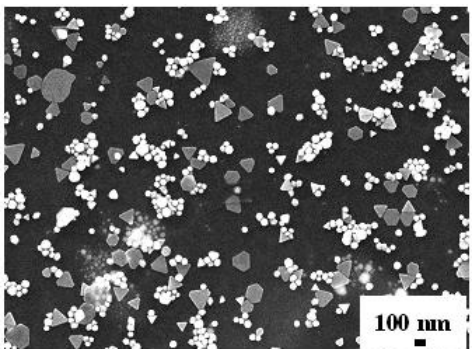

Figure S10. SEM image of triangular, hexagonal and spherical gold nanomaterials from thermolysis of $[Au(C_{18}\text{-bim})_2][NO_3]$ at 200 ^oC.

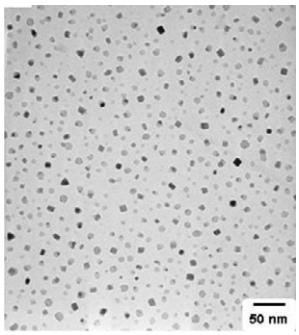

Figure S11. TEM images of gold nanomaterials from thermolysis of $[Au(C_{18}\text{-im})_2][NO_3]$ at 100 ^oC (mesophase) for 1 h.

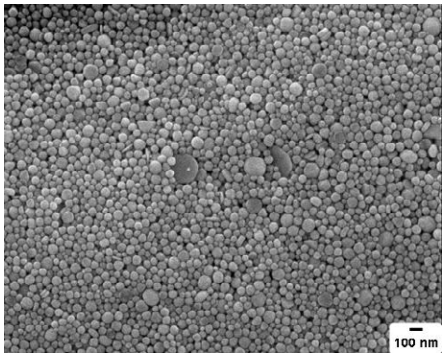

Figure S12. SEM image of gold nanomaterials from thermolysis of $[Au(C_{18}\text{-im})_2][NO_3]$ at 200 ^oC (isotropic phase) for 1 h.