Supplementary Information for: Controlling Intermolecular Aurophilicity in Emissive Dinuclear Au(I) Materials and their Luminescent Response to Ammonia Vapour

Ryan J. Roberts, Debbie Le, and Daniel B. Leznoff*

Department of Chemistry, Simon Fraser University, 8888 University Drive,
Burnaby, British Columbia, V5A 1S6, Canada. E-mail: dleznoff@sfu.ca

1 Experimental

1.1 General Procedures

All reactions were carried out in air unless otherwise stated. $K_2(i\text{-mnt}) \cdot H_2O$[1], chloro(tetrahydrothiophene)gold(I), AuCl(tht),[2] and $[{}^{n}Bu_4N]_2[Au_2(i\text{-mnt})_2]$[3] were synthesized according to literature procedures. A stock solution of 3,5-dimethylpyrazolium chloride was prepared by the reaction of 3,5-dimethylpyrazole in water with HCl. All other reagents were obtained from commercial sources and used as received.

Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a Pike MIRacle attenuated total reflection (ATR) sampling accessory (Germanium crystal: 4000-700 cm^{-1}). Raman spectra were collected on a Renishaw inVia Raman Microscope equipped with a 200 mW 785 nm laser. Spectra were collected from 100 to 3200 cm^{-1} using a 1200 L mm^{-1} (633/780) grating.

Microanalyses (C, H, N, S) were performed by Paul Mulyk at Simon Fraser University on a Carlo Erba EA 1110 CHN elemental analyzer.

Solid-State UV-vis reflectance spectra were collected with an Ocean Optics SD2000 spectrophotometer equipped with a tungsten halogen and deuterium lamp.

Solid-state luminescence spectra were collected at 293 K or 77 K on a Photon Technology International (PTI) fluorometer using a xenon arc lamp and photomultiplier detector in conjunction with the PTI Cold Finger Dewar (CFD) Accessory. Polycrystaline samples were loaded into a standard NMR tube which was in turn loaded into the CFD. For 77 K spectra, liquid nitrogen was used as the cryogen. Ammonia exposure experiments were carried out via charging a pre-loaded NMR tube with ammonia from a the headspace of a bottle of 29% aqueous ammonia solution.

1.2 Synthesis

K_2[Au_2(*i*-mnt)$_2$]: Other multi-step preparations for this compound are also known in the literature.[3] To a 0 °C, 70 mL AuCl(tht) (770 mg, 2.4 mmol) suspension in acetone, a 2 mL K_2(*i*-mnt) $\cdot$ H_2O (625 mg, 2.65 mmol) aqueous solution was added dropwise. The cloudy white suspension gradually turned into a yellow solution upon addition, where it was allowed to stir at 0 °C for 15 min, during which a white precipitate (KCl) was formed. The KCl was filtered and the solution was evaporated. The thoroughly dried **K_2[Au_2(*i*-mnt)$_2$]** was redissolved in a minimal amount of acetone, filtered again to remove any remaining KCl and then the acetone was evaporated. Finally, the product was redissolved and hot-filtered in ethanol to remove any residual K_2(*i*-mnt) $\cdot$ H_2O and the solvent was rotary evaporated, affording **K_2[Au_2(*i*-mnt)$_2$]** as a red polycrystalline powder. Yield 620 mg (69 %).

Anal. Calcd. for $C_8Au_2K_2N_4S_4 \cdot (CH_3CH_2OH)_{1.25}$: C 15.04 %, H 0.94 %, N 6.92 %, S 15.80%. Found: C 15.59 %, H 1.02 %, N 6.90 %, S 15.40%.

IR (ATR, cm^{-1}): 3560 (w), 2197 ($\nu_{C\equiv N}$, s), 1595 (m), 1352 ($\nu_{C=C}$, s), 1241 (w), 956 (m), 872 (m)

[DMPzH]$_2$[Au_2(*i*-mnt)$_2$]: To a gently heated 20 mL aqueous solution of **K_2[Au_2(*i*-mnt)$_2$]** (150 mg, 0.2 mmol), 4.5 mL of a 0.1 mol L^{-1} (0.45 mmol) aqueous solution of 3,5-dimethylpyrazolium chloride ([DMPzH]Cl), was added in one portion. From the initially yellow solution a very fine orange precipitate immediately formed. The precipitate was stirred for 15 min at room temperature and was then centrifuged. The supernatant solution was discarded and the centrifugate was recrystallized from a 10 mL refluxing 10% solution of acetone in water which was allowed to cool slowly over 2 hours, forming fine orange needles of **[DMPzH]$_2$[Au_2(*i*-mnt)$_2$]**. Yield: 100 mg (58%). Anal. Calcd. for $C_{18}H_{18}Au_2N_8S_4$: C 24.89 %, H 2.09 %, N 12.90 %, S 14.77%. Found: C 24.90 %, H 2.03 %, N 12.91 %, S 15.01%.

IR (ATR, cm^{-1}): 3220 (m), 3133 (m), 3015 (m), 2845 (w), 2201 ($\nu_{C\equiv N}$, s) 2179, ($\nu_{C\equiv N}$, s), 1605 (m), 1318 ($\nu_{C=C}$, s), 1238 (w), 1160 (w), 974 (w), 864 (m), 823 (w), 730 (w). Raman (cm^{-1}): 2202 ($\nu_{C\equiv N}$, m), 2177 ($\nu_{C\equiv N}$, m), 1331 ($\nu_{C=C}$, m), 1235 (w), 1017 (w), 950 (w), 866 (m), 610 (m), 587 (m) 503 (vs), 401 (m), 250 (w), 235 (w), 188 (w), 157 (w), 118 (w).

[PipH]$_2$[Au_2(*i*-mnt)$_2$]: To a gently heated 20 mL aqueous solution of **K_2[Au_2(*i*-mnt)$_2$]** (150 mg, 0.2), piperidinium chloride ([PipH]Cl); (60 mg, 0.5 mmol) in 1 mL of water was added in one portion. From the initially yellow solution a very fine red precipitate immediately formed. The precipitate was stirred for 15 min at room temperature and was then centrifuged. The supernatant solution was discarded and the centrifugate was recrystallized from a refluxing 1:1 acetone/water solution which was allowed to cool slowly over 2 hours, forming fine red needles of **[PipH]$_2$[Au_2(*i*-**

mnt)$_2$]. Yield 145 mg (86%) Anal. Calcd. for $C_{18}H_{18}Au_2N_8S_4$: C 25.54 %, H 2.86 %, N 9.93 %, S 15.15%. Found: C 25.63 %, H 2.70 %, N 9.99 %, S 15.35%.

IR (ATR, cm^{-1}): 3080 (m), 2942 (w), 2199 ($\nu_{C\equiv N}$, s), 2190 ($\nu_{C\equiv N}$, s), 2175 ($\nu_{C\equiv N}$, s), 1598 (w), 1335 ($\nu_{C=C}$, s), 1295 (m), 1229 (m), 1161 (w), 952 (m), 912 (w), 858 (m), 843 (w). Raman (cm^{-1}): 2205 ($\nu_{C\equiv N}$, m), 2188 ($\nu_{C\equiv N}$, m), 2175 ($\nu_{C\equiv N}$, m), 1363 ($\nu_{C=C}$, m), 1226 (w), 949 (w), 862 (w), 800 (w), 613 (w), 493 (vs), 490 (m), 477 (m), 396 (m), 386 (w), 265 (w), 239 (w), 156 (w), 121 (w).

[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O): Exposing **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** to an atmosphere of ammonia from the headspace of a bottle of concentrated (29%) aqueous ammonia, the originally red powder turned to bright yellow **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)**. Alternatively, this material can be crystallized from a solution of concentrated aqueous ammonia, resulting in yellow needles. Due to the very rapid desolvation of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)** to its host material **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** elemental analysis and IR data could not be obtained.

Raman (cm^{-1}): 2205 ($\nu_{C\equiv N}$, m), 2189 ($\nu_{C\equiv N}$, m) 2175 ($\nu_{C\equiv N}$, w) 1365 ($\nu_{C=C}$, m), 1273 (w), 1226 (w), 1032 (w), 1018 (w), 940 (w), 862 (w), 800 (w), 613 (w), 496 (vs), 490 (m), 478 (m), 396 (m), 386 (w), 266 (w), 240 (w), 229 (w), 156 (w), 121 (w).

1.3 X-ray Crystallography

For **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]** and **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]** intensity data were collected at 150 K on a D8 goniostat equipped with a Bruker APEX II CCD detector at Beamline 11.3.1 at the Service for Crystallography at the Advanced Light Source (SCrALS) (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to λ = 0.77490 Å. Data collection frames were measured for a duration of 1 and 3 s respectively at 0.3° intervals of ω with a maximum 2θ value of $\approx 60°$. The data frames were collected using the program APEX II and processed using the program SAINT routine within APEX II. The data were corrected for absorption and beam corrections based on the multiscan technique as implemented in SADABS.[4]

Crystals of **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)**, which rapidly desolvate, were coated with Paratone and mounted onto a MiTeGen MicroMount. The data was collected at 150 K. Intensity data was collected on a Bruker APEX II diffractometer equipped with a Mo Kα (λ = 0.71073) source and an Oxford Cryosystems coldstream. Diffraction data was processed with the Bruker II software suite.

All structures were solved using intrinsic phasing[5] in APEX II[6] and subsequent refinements were performed in Shelxle.[7] Diagrams were prepared using ORTEP-3[8] and POV-RAY[9] with ellipsoids drawn at 50% probability unless otherwise stated. Crystallographic data is tabulated in Table S1.

Table S1: Selected bond lengths and angles of $[\mathrm{Au_2}(i\text{-mnt})_2]^{2-}$ salts.

	[DMPzH]	**[PipH]**	**[PipH]·$\mathbf{(NH_3)_2(H_2O)}$**
Au−Au$_{intra}$ (Å)	2.7998(8)	2.7792(6)	2.8260(5)
Au−Au$_{inter}$ (Å)	2.9840(9)	2.9115(6)	3.0305(5)
Au−S (Å)	2.287(2), 2.288(2)	2.2940(14)-2.3106(14)	2.288(2)-2.301(2)
C−S (Å)	1.705(7), 1.719(7)	1.722(5)-1.737(5)	1.731(7)-1.737(7)
C=C (Å)	1.401(11)	1.397(7), 1.402(7)	1.374(10), 1.389(11)
C≡N (Å)	1.146(10), 1.171(10)	1.143(7)-1.152(7)	1.139(10)-1.155(9)
S−Au−S (°)	172.71(7)	176.73(5)-177.14(5)	174.78(6)-175.27(7)
S−C−S (°)	128.4(5)	126.7(3), 126.8(3)	126.9(5), 127.3(4)

Table S2: Crystallographic data

	[DMPzH]$_2$-**[$\mathbf{Au_2}$($\boldsymbol{i}$-mnt)$_\mathbf{2}$]**	**[PipH]**$_2$-**[$\mathbf{Au_2}$($\boldsymbol{i}$-mnt)$_\mathbf{2}$]**	**[PipH]$_\mathbf{2}$[$\mathbf{Au_2}$($\boldsymbol{i}$-mnt)$_\mathbf{2}$] ·$\mathbf{(NH_3)_2(H_2O)}$**
Chemical formula	$C_{18}H_{18}Au_2N_8S_4$	$C_{18}H_{24}Au_2N_6S_4$	$C_{18}H_{32}Au_2N_8OS_4$
Formula weight (g·mol^{-1})	868.58	846.60	898.74
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
a (Å)	17.112(4)	9.6338(19)	10.5756(14)
b (Å)	12.896(4)	22.019(4)	23.180(3)
c (Å)	11.447(3)	11.351(2)	11.6908(16)
α (°)	90	90	90
β (°)	90.276(5)	91.513(3)	99.794(2)
γ (°)	90	90	90
V (Å^3)	2526.2(12)	2407.1(8)	2824.1(7)
Z	4	4	4
T (K)	150(2)	150(2)	150(2)
ρ_{calcd} (g·cm^{-3})	2.284	2.336	2.114
μ (mm^{-1})	14.813	15.538	10.700
R, R_w $[I_0 \geq 2\sigma\ (I_0)]$	0.0474, 0.1149	0.0294, 0.0798	0.0278, 0.0510
Goodness of fit	1.060	1.068	0.973
Reflections $[I_0 \geq 2\sigma\ (I_0)]$	2275	3858	4119

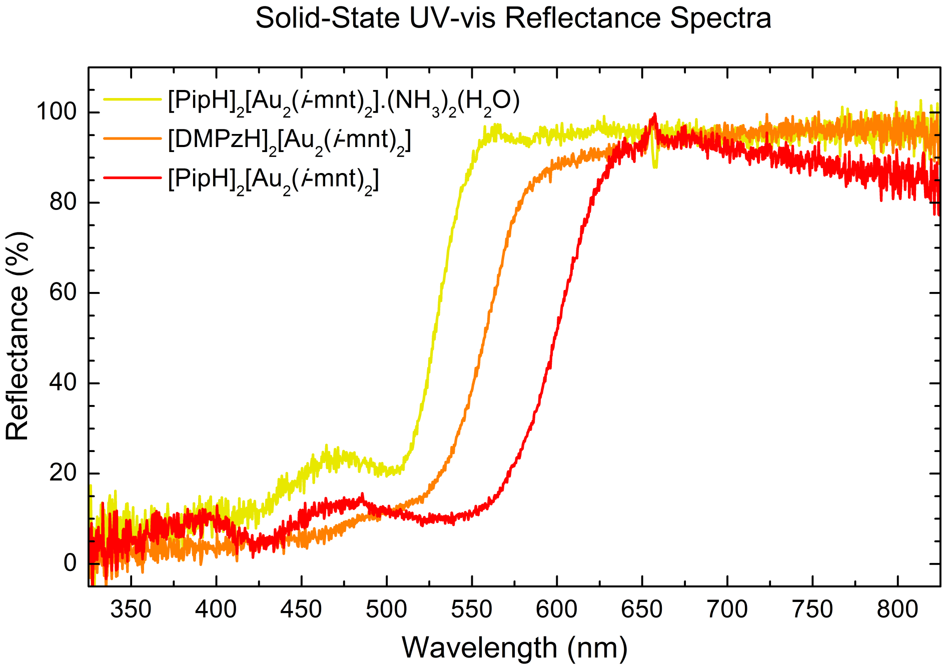

Figure S1: Solid state reflectance of the yellow **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]·(NH$_3$)$_2$(H$_2$O)**, orange **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]**, and red **[PipH]$_2$[Au$_2$(*i*-mnt)$_2$]**.

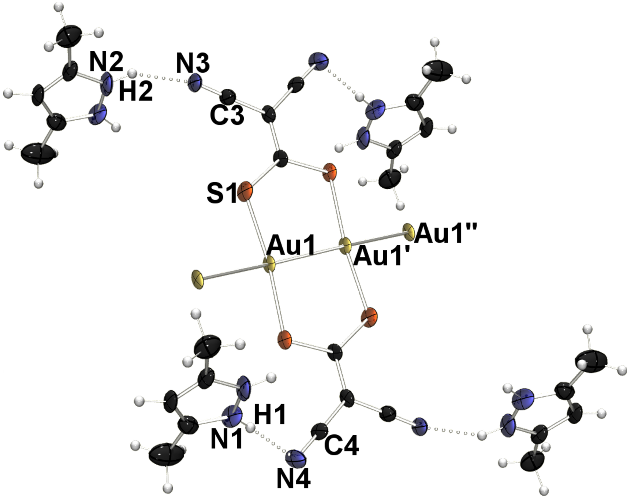

Figure S2: Crystal structure of **[DMPzH]$_2$[Au$_2$(*i*-mnt)$_2$]** illustrating the $[\mathrm{Au}_2(i\text{-mnt})_2]^{2-}$ anion (with neighboring gold atoms attached) and DMPzH cations hydrogen-bonding to *i*-mnt nitrile groups. Colour code; Au: gold, S: orange, C: black, N: blue, H: white.

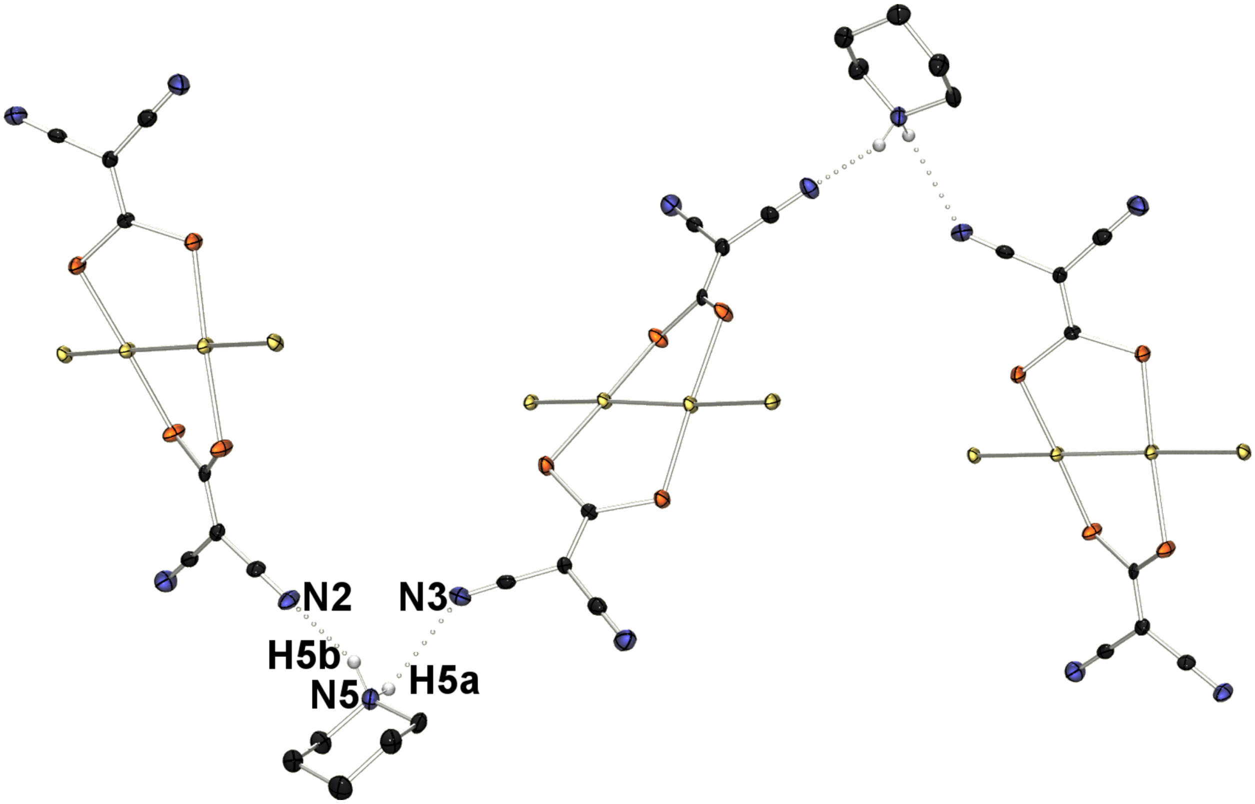

Figure S3: In $\mathbf{[PipH]_2[Au_2(\textit{i}\text{-}mnt)_2]}$ *Inter*chain hydrogen bonding interactions give rise to an overall 2-D network.

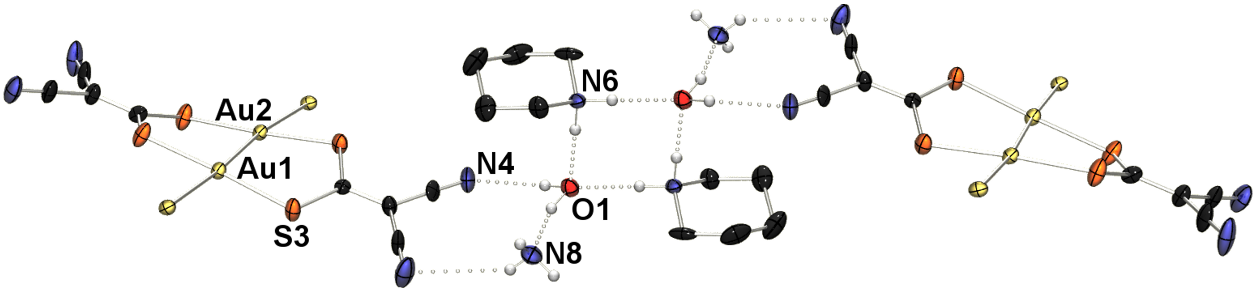

Figure S4: Crystal structure of $\mathbf{[PipH]_2[Au_2(\textit{i}\text{-}mnt)_2]\cdot(NH_3)_2(H_2O)}$ illustrating the complex hydrogen bonding network bridging chains of aurophilic $[\mathrm{Au_2}(i\text{-mnt})_2]^{2-}$.

References

[1] W. R. Hatchard, *J. Org. Chem.* **1964**, *29*, 660–665.

[2] R. Uson, A. Laguna, M. Laguna, D. A. Briggs, H. H. Murray, J. P. Fackler, Jr., *Inorg. Synth.* **2007**, 85–91.

[3] M. N. I. Khan, J. P. Fackler, Jr., C. King, J. C. Wang, S. Wang, *Inorg. Chem.* **1988**, *27*, 1672–1673.

[4] Bruker **2001**, SADABS, Bruker AXS Inc., Madison, WI, 53711, USA.

[5] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3–8.

[6] G. M. Sheldrick Bruker AXS Inc.: Madison, WI, 53711, USA.

[7] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.

[8] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[9] T. D. Fenn, D. Ringe, G. A. Petsko, *J. Appl. Crystallogr.* **2003**, *36*, 944–947.