Supporting information

For

Cyclometallated Gold(III) Hydroxides as Versatile Synthons for Au-N, Au-C Complexes and Luminescent Compounds

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Preparation of complexes 2 - 16

General Considerations: Unless otherwise stated, all experiments were performed in air using bench solvents. In such exceptions, manipulations were performed using standard Schlenk techniques under dry nitrogen or a Saffron Scientific glovebox. Nitrogen was purified by passing through columns of supported P_2O_5, with moisture indicator, and activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. (^{tBu}Ph$_2$Py)AuCl[1] and tris(pentafluorophenyl)boron[2] was prepared using literature methods. AgOAc^F (Aldrich), AgOTf (Aldrich), $CsOH{\cdot}H_2O$ (Aldrich), phenylacetylene (Aldrich), pentafluorobenzene (Aldrich), 1,2,4,5- tetrafluorobenzene (Alfa Aesar) and the boronic acids (Aldrich) were commercially available and used as received.

^{1}H, ^{13}C{^{1}H} and ^{19}F NMR spectra were recorded using a Bruker DPX300 spectrometer. ^{1}H NMR spectra (300.13 MHz) were referenced to the residual protons of the deuterated solvent used. ^{13}C NMR spectra (75.47 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. ^{19}F (282.4 MHz) NMR spectra were referenced externally to $CFCl_3$ and internally to C_6F_6 (δ_F -164.9 ppm). Where applicable, resonances were assigned by using 2D COSY, HSQC and HMBC experiments. The numbering scheme for the assignments is given in Figure S1. Elemental analyses were performed by London Metropolitan University. UV-Vis spectra were collected on a Perkin Elmer Lambda 34 UV-Vis spectrometer. Photoluminescence measurements were recorded on a Perkin Elmer LS55 Fluorescence Spectrometer with a solids mount attachment where appropriate. Time resolved fluorescence data were collected on a TCSPC Fluorolog Horiba Jobin Yvon spectrofluorimeter using Horiba Jobin Yvon DataStation v2.4 software. A NanoLED of 370 nm was used as excitation source with a repetition rate of 1 MHz and a full width at half maximum of 1.2 ns. The collected data were analysed using a Horiba Jobin Yvon DAS6 v6.3 software.

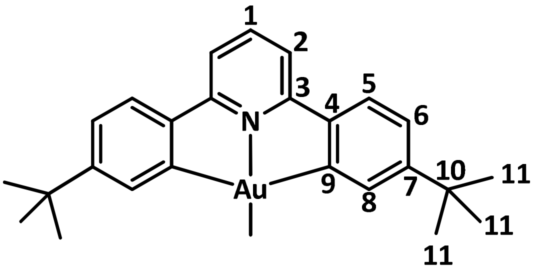

Fig. S1: Numbering scheme for ^{1}H and ^{13}C peak assignment

(^{tBu}Ph$_2$Py)AuOAc^F (2)

(^{tBu}Ph$_2$Py)AuCl (500 mg, 0.871 mmol) **1** and AgOAc^F (192.4 mg, 1.31 mmol) were charged in a flask and dichloromethane (100 mL) was added. The mixture was shielded from light and was stirred at room temperature for 2 h during which precipitation of AgCl was observed. The mixture was filtered, the volatile components were removed *in vacuo* and the resulting yellow powder was dissolved in toluene (50 mL) and stirred for 12 h in the presence of light to ensure that all the residual AgOAc^F is photolysed. Filtration and removal of the volatile components *in vacuo* yielded **2** as a bright yellow powder (499 mg, 88%). Single crystals suitable from X-ray diffraction were obtained by layering a concentrated dichloromethane solution of **2** with light petroleum.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.71 (t, 8.0 Hz, 1H, H1, pyridyl), 7.33 (d, 1.7 Hz, 2H, H8, phenyl), 7.30 – 7.11 (m, 6H, phenyl + pyridyl, overlapping), 1.33 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (*C*=O and *C*F$_3$ not observed) 169.93 (C9), 165.62 (C3), 155.99 (C7), 143.98 (C4), 143.78 (C1), 129.72 (C8), 125.13 (C5), 124.76 (C6), 116.34 (C2), 35.56 (C10), 31.17 (C11). ^{19}F NMR (282 MHz, CD_2Cl_2) δ -73.74 (s). Anal. Calcd for $C_{27}H_{27}AuF_3NO_2$ (found): C, 49.78 (49.85); H, 4.18 (4.21); N, 2.15 (2.02).

Attempted reaction of (^{tBu}Ph$_2$Py)AuCl with AgOTf

(^{tBu}Ph$_2$Py)AuCl (80 mg, 0.140 mmol) **1** and AgOTf (36 mg, 0.140 mmol) were charged in a flask and cooled to -78°C. Dichloromethane (20 mL) was added and the mixture was shielded from light and stirred for 2 h. The mixture was slowly warmed to room temperature during which precipitation of colloidal gold was observed. The mixture was filtered and the volatile components were removed *in vacuo* yielding a pale yellow powder which turned purple over a period of 15 minutes. ^{1}H NMR spectroscopy indicated a mixture of **1** and unidentified products.

(^{tBu}Ph$_2$Py)AuOMe (3)

Under a dry N_2 atmosphere, (^{tBu}Ph$_2$Py)AuOAc^F **2** (100 mg, 0.153 mmol) and dry KOMe (54 mg, 0.765 mmol) were charged in a Schlenk flask and dry MeOH (30 mL) was added. The mixture was stirred at room temperature for 12 h during which a black precipitate was observed. The solvent was removed under vacuum and the mixture was extracted with dry dichloromethane (30 mL). Removal of the solvent under vacuum yielded **3** as a yellow powder (48 mg, 55%)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.82 (d, 1.9 Hz, 2H, H8, phenyl), 7.79 (t, 7.9 Hz, 1H, H1 pyridyl), 7.52 (d, 8.1 Hz, 2H, H5, phenyl), 7.40 (d, 8.0 Hz, 2H, H2, pyridyl), 7.30 (dd, 8.2 Hz, 2.0 Hz, 2H, H6, phenyl), 4.14 (s, 3H, OC*H$_3$*), 1.38 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 170.84 (C9), 164.75 (C3), 155.14 (C7), 145.49 (C4), 142.49 (C1), 129.61 (C8), 124.90 (C5), 124.39 (C6), 116.35 (C2), 61.48 (O*C*H$_3$), 35.68 (C10), 31.34 (C11). Anal. Calcd. (found) for $C_{26}H_{30}AuNO$: C, 54.83 (54.77); H, 5.31 (5.25); N, 2.46 (2.53).

(^{tBu}Ph$_2$Py)AuOH (4)

Method 1:

(^{tBu}Ph$_2$Py)AuCl (500 mg, 0.871 mmol) **1** and $CsOH\cdot H_2O$ (731 mg, 4.33 mmol) were charged in a flask and a mixture of THF, toluene and water (100 mL, 1:1:1) was added. The mixture was stirred for 16 h at 60°C after which the organic layer was separated and washed with 2 x 100 mL water. The volatiles were then removed under vacuum resulting in a mixture of **3** and the analogous anhydride [(^{tBu}Ph$_2$Py)Au]$_2$(μ-O). Stirring the mixture in dichloromethane/water (60 mL, 1:1) for an additional 12 h followed by separation of the organic layer and removal of the volatiles yields **4** as a yellow powder (411 mg, 85%). Single crystals suitable for an X-ray diffraction study of **$4 \cdot H_2O$** were obtained by slow evaporation of a dichloromethane solution of **4**.

Method 2:

($^{tBu}Ph_2Py$)AuOAc^F **2** (100 mg, 0.153 mmol) and KOH (45 mg, 0.802 mmol) were charged in a flask and a mixture of toluene and water (30 mL, 1:1) was added. The mixture was stirred for 16 h at 60°C after which the organic layer was separated and washed with water (2 x 10 mL). The volatile components were then removed under vacuum resulting in a mixture of **4** and the analogous anhydride [($^{tBu}Ph_2Py$)Au]$_2$(μ-O). Stirring the mixture in dichloromethane/water (20 mL, 1:1) for an additional 12h followed by separation of the organic layer and removal of the volatile components yields **4** as a yellow powder (69 mg, 81%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.83 (t, 8.0 Hz, 1H, H1, pyridyl), 7.62 (d, 1.9 Hz, 2H, H8, phenyl), 7.54 (d, 8.2 Hz, 2H, H5, phenyl), 7.42 (d, 8.0 Hz, 2H, H2, pyridyl), 7.31 (dd, 8.2, 2.0 Hz, 2H, H6, phenyl), 1.37 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 169.30 (C9), 164.74 (C3), 155.10 (C7), 145.63 (C4), 142.43 (C1), 128.74 (C8), 125.18 (C5), 124.46 (C6), 116.48 (C2), 35.72 (C10), 31.33 (C11). Anal. Calcd. (found) for $C_{25}H_{28}AuNO$: C,54.06 (54.17); H, 5.08 (5.17); N, 2.52 (2.46).

[($^{tBu}Ph_2Py$)Au]$_2$(μ-O)

Under a dry N_2 atmosphere, ($^{tBu}Ph_2Py$)AuOAc^F **2** (50 mg, 0.076 mmol) and KOH (21 mg, 0.380 mmol) were charged in a Schlenk flask and dried and degassed toluene (20 mL) was added. The mixture was stirred for 16 h at 60°C and the resulting turbid solution was filtered. The toluene fraction was concentrated under vacuum to 5 mL, layered with light petroleum (5 mL) and cooled to -20°C for 16 h. The resulting yellow precipitate was isolated by filtration, dried *in vacuo* to give a yellow solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.32 (d, 2.0 Hz, 2H, H8, phenyl), 7.77 (t, 8.0 Hz, 1H, H1, pyridyl), 7.50 (d, 8.2 Hz, 2H, H5, phenyl), 7.41 (d, 8.0 Hz, 2H, H2, pyridyl), 7.20 (dd, 8.1, 2.1, 2H, H6, phenyl), 1.08 (s, 18H, H11, ^{t}Bu).

(^{tBu}Ph$_2$Py)AuC$_6$F$_5$ (5)

Method 1:

Under a dry N_2 atmosphere, (^{tBu}Ph$_2$Py)AuOMe **3** (47 mg, 0.082 mmol) was dissolved in dry toluene (20 mL) and C_6F_5H (18.5 µL, 28 mg, 0.164 mmol) added. The mixture was stirred at 110°C for 48 h after which the volatile components were removed under vacuum and the resulting solid was washed with light petroleum (5 mL). The solid was dried under vacuum giving **5** as a pale yellow powder (55 mg, 95%)

Method 2:

(^{tBu}Ph$_2$Py)AuOH **4** (30 mg, 0.054 mmol) was dissolved in toluene (20 mL) and C_6F_5H (12 µL, 18 mg, 0.108 mmol) was added. The mixture was stirred at 110°C for 48 h after which the volatile components were removed under vacuum and the resulting solid was washed with 10 mL light petroleum. The solid was dried under vacuum giving **5** as a pale yellow powder (36 mg, 95%)

Method 3:

Under a dry N_2 atmosphere, (^{tBu}Ph$_2$Py)AuOH **4** (40 mg, 0.072 mmol) and $B(C_6F_5)_3$ (37 mg, 0.072 mmol) were charged in a Schlenk flask and dry, degassed toluene (20 mL) added. The mixture was stirred for 12 h at room temperature after which the volatile components were removed *in vacuo*. The solid residue was dissolved in CH_2Cl_2 (10 mL) and passed through a silica plug. Removal of the solvent yielded **5** as a pale yellow powder (46 mg, 90%)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.83 (t, 8.2 Hz, 1H, H1, pyridyl), 7.53 (d, 8.1 Hz, 2H, H5, phenyl), 7.43 (d, 8.1 Hz, 2H, H2, pyridyl), 7.26 (dd, 8.1 Hz, 2.2 Hz, 2H, H6, phenyl), 7.15 (d, 2.0 Hz, 2H, H8, phenyl), 1.22 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 165.98 (C9), 164.52 (C3), 155.56 (C7), 147.22 (C4), 143.06 (C1), 133.09 (C8), 124.98 (C5), 124.28 (C6), 116.83 (C2), 35.37 (C10), 31.25 (C11). (C-F not observed) ^{19}F NMR (282 MHz, CD_2Cl_2) δ -118.18 – -120.91 (m, 2F), -159.76 (t, 19.7 Hz, 1F, p-F), -162.35 – -163.59 (m, 2F).

(${}^{tBu}Ph_2Py)AuC_6F_4H$ (6)

Under a dry N_2 atmosphere, (${}^{tBu}Ph_2Py$)AuOMe **3** (15 mg, 0.027 mmol) was charged in a J-Young NMR tube and dry toluene-*d_8* (0.6 mL) and 1,2,4,5 – tetrafluorobenzene (6.0 µL, 8.1 mg, 0.054 mmol) were added. The mixture was heated at 110°C and the reaction was monitored by ${}^{19}F$ NMR spectroscopy. Complete conversion was observed after 72 h. The volatile components were removed *in vacuo* and the mixture was redissolved in CD_2Cl_2.

${}^{1}H$ NMR (300 MHz, CD_2Cl_2) δ 7.88 (t, 8.0 Hz, 1H, H1, pyridyl), 7.56 (d, 8.3 Hz, 2H, H5, phenyl), 7.48 (d, 8.0 Hz, 2H, H2, pyridyl), 7.28 (dd, 8.2, 2.0 Hz, 2H, H6, phenyl), 7.20 (d, 1.8 Hz, 2H, H8, phenyl), 7.17 – 7.10 (m, 1H, C*H* from C_6F_4*H*) 1.23 (s, 18H, H11, ${}^{t}Bu$). ${}^{13}C$ NMR (75 MHz, CD_2Cl_2) δ (*ipso*-C of C_6F_4H not observed), 165.61 (C9), 164.12 (C3), 155.08 (C7), 146.86 (C4), 142.53 (C1), 132.80 (C8), 125.21 (C5), 123.82 (C6), 116.36 (C2), 34.92 (C10), 30.72 (C11). (C-F not observed) ${}^{19}F$ NMR (282 MHz, CD_2Cl_2) δ -121.93 (qt, 60.1, 30.0 Hz, 2F), -140.29 – -141.37 (m, 2F).

(${}^{tBu}Ph_2Py$)AuCCPh (7)

^{tBu}(Ph_2Py)AuOH **4** (97 mg, 0.175 mmol) was dissolved in toluene (20 mL) and phenylacetylene (40 µL, 18 mg, 0.350 mmol) was added. The mixture was stirred at 110°C for 12 h after which the volatile components were removed under vacuum and the resulting solid was washed with light petroleum (10 mL). The solid was dried under vacuum giving **7** as a yellow powder (100 mg, 90%). ${}^{1}H$ NMR spectroscopy matches the one reported by Yam et al.[1]

(${}^{tBu}Ph_2Py$)Au(3,5-dmpyr) (8)

(${}^{tBu}Ph_2Py$)AuOH **4** (40 mg, 0.072 mmol) and 3,5-dimethylpyrazole (7 mg, 0.072 mmol) were charged in a flask and toluene (30 mL) was added. The mixture was stirred at 110°C for 12 h after which the volatile components were removed under vacuum and the resulting solid was washed with light petroleum (5 mL). The solid was dried under vacuum giving **8** as a light yellow powder (44 mg, 95%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.84 (t, 8.0 Hz, 1H, H1, pyridyl), 7.47 (d, 8.1 Hz, 2H, H5, phenyl), 7.39 (d, 8.1 Hz, 2H, H2, pyridyl), 7.24 (dd, 8.0 Hz, 2.1 Hz, 2H, H6, phenyl), 7.19 (d, 2.0 Hz, 2H, H8, phenyl), 6.00 (s, 1H, pyrazolyl) 2.34 (s, 3H, Me), 2.26 (s, 3H, Me), 1.24 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 169.69 (C9), 165.60 (C3), 155.61 (C7), 149.87 (C4), 145.82 (*ipso*-C, pyrazolyl), 143.44 (C1), 143.10 (pyrazolyl), 131.94 (C8), 125.08 (C5), 124.47 (C6), 116.66 (C2), 103.60 (pyrazolyl), 35.50 (C10), 31.16 (C11), 14.42 (CH_3, pyrazolyl), 14.12 (CH_3, pyrazolyl).

(**^{tBu}Ph$_2$Py)Au(imidazolyl) (9)**

(^{tBu}Ph$_2$Py)AuOH **4** (40 mg, 0.072 mmol) and imidazole (5 mg, 0.072 mmol) were charged in a flask and toluene (30 mL) was added. The mixture was stirred at 110°C for 12 h after which the volatile components were removed under vacuum. The solid was dried giving **9** as a light yellow powder (40 mg, 92%)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.85 (t, 8.0 Hz, 1H, H1, pyridyl), 7.65 (br s, 1H, imidazolyl), 7.50 (d, 8.0 Hz, 2H, H5, phenyl), 7.40 (d, 8.0 Hz, 2H, H2, pyridyl), 7.33 (dd, 8.3, 1.9 Hz, 2H, H6, phenyl), 7.28 (d, 1.9 Hz, 2H, H8, phenyl), 7.20 (br s, 2H, imidazolyl), 1.28 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2) δ 168.91 (C9), 165.50 (C3), 156.01 (C7), 145.82 (C4), 143.48 (C1), 141.48 (ipso, imid), 130.89 (C8), 128.46 (imid), 125.48 (C5), 124.81 (C6), 124.04 (imid), 116.84 (C2), 35.72 (C10), 31.22 (C11). Anal. Calcd. (found) for $C_{28}H_{30}AuN_3$: C, 55.54 (55.56); H, 4.99 (4.93); N, 6.94 (7.05).

(**^{tBu}Ph$_2$Py)Au(benzotriazolyl) (10)**

(^{tBu}Ph$_2$Py)AuOH **4** (42 mg, 0.076 mmol) and benzotriazole (9 mg, 0.076 mmol) were charged in a flask and toluene (30 mL) was added. The mixture was stirred at 60°C for 12 h after which the volatile components were removed under vacuum. The solid was redissolved in a minimum amount of dichloromethane (2 mL), layered with light petroleum and left at -20°C overnight. **10** was isolated light yellow crystals consisting of a mixture of both 2H (**10a**) and 1H (**10b**) isomers in a 6:1 ratio (44 mg, 89%)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 – 8.16 (m, 1H), 8.02 – 7.84 (m, 3H), 7.72 – 7.59 (m, 1H), 7.50 – 7.38 (m, 2H), 7.39 – 7.24 (m, 7H), 7.17 (dd, 8.2, 1.9 Hz, 2H, H6, phenyl), 7.11 (d, 1.9 Hz, 2H, H8, phenyl), 1.38 (s, 3H, ^{t}Bu, **10b**), 1.12 (s, 18H, ^{t}Bu, **10a**). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.62 (C9 **10b**), 168.52 (C9 ipso **10a**), 165.52 (C3 ipso **10b**), 165.10 (C3 **10a**), 155.83 (C7 ipso **10a**), 155.74 (C7 ipso **10b**), 145.68 (benzotriazole *C*H), 145.14 (benzotriazole *C*H), 145.11 (C4 of **10a**), 145.04 (C4 of **10b**), 143.83 (C1, **10a**), 143.07 (C1, **10b**), 139.34 (*C*H benzotriazole), 131.94 (C8, **10a**), 130.91 (C8, **10b**), 125.22 (C6 or *C*H benzotriazole), 124.97 (C6 or *C*H benzotriazole), 124.82 (C5 or *C*H benzotriazole), 124.49 (C6 or *C*H benzotriazole), 124.26 (C6 or *C*H benzotriazole), 123.08(C6 or *C*H benzotriazole), 119.12 (C*H* benzotriazole), 116.62 (C2, **10a**), 116.32 (C2, **10b**), 114.37 (*C*H, benzotriazole), 113.68 (*C*H benzotriazole), 35.75(C10, **10b**), 35.40 (C10, **10a**), 31.37 (C11, **10b**), 31.04 (C11, **10a**). Anal. Calcd. (found) for $C_{31}H_{31}AuN_4$: C, 56.71 (56.77); H, 4.76 (4.70); N, 8.53 (8.45).

General protocol for the reactions of ($^{tBu}Ph_2Py$)AuOH with $ArB(OH)_2$

($^{tBu}Ph_2Py$)AuOH **4** (1 eq) and $ArB(OH)_2$ (1 eq) were charged in a flask and toluene (20 mL) was added. The mixture was stirred at 60°C for 12 h after which the volatile components were removed under vacuum. The resulting solid was washed with light petroleum (2 x 3 mL) and dried under vacuum, yielding the corresponding gold aryl. Additional purification can be achieved by passing a dichloromethane solution of the isolated gold aryl through a silica plug.

($^{tBu}Ph_2Py$)Au(*p*-F-C_6H_4) (11)

($^{tBu}Ph_2Py$)AuOH **4** (40 mg, 0.072 mmol) and $(C_6H_4F)B(OH)_2$ (10 mg, 0.072 mmol). **11** isolated as a yellow powder (42 mg, 92%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (t, 8.0 Hz, 1H, H1, pyridyl), 7.64 (dd, 8.5, 6.4 Hz, 2H, *m*-C_6H_4F), 7.56 (d, 8.2 Hz, 2H, H5, phenyl), 7.47 (d, 8.0 Hz, 2H, H2, pyridyl), 7.45 (d, 1.8 Hz, 2H, H8, phenyl), 7.23 (dd, 8.0 Hz, 2.1 Hz, 2H, H6, phenyl), 7.07 (t, 9.1 Hz, 2H, *o*-C_6H_4F), 1.26 (s, 18H, H11, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.24 (C9), 163.34 (C3), 154.57 (C 7), 166.81 (CF, J_{CF} = 259 Hz), 147.17 (C4), 141.52 (C1), 135.00 (d, J_{CF} = 6 Hz, Ph^F), 132.50 (C8), 129.07 (Ph^F), 124.81 (C5), 123.40 (C6), 115.86 (C2), 115.28 (d, J_{CF} = 20 Hz, Ph^F), 35.31 (C10), 31.14 (C11). ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.62 (m). Anal. Calcd. (found) for $C_{31}H_{31}AuFN$: C, 58.77 (58.64); H, 4.93 (4.84); N, 2.21 (2.23).

$^{tBu}(Ph_2Py)Au(p\text{-}^tBu\text{-}C_6H_4)$ (12):

$^{tBu}(Ph_2Py)AuOH$ **4** (40 mg, 0.072 mmol) and $(^tBu\text{-}C_6H_4)B(OH)_2$ (13 mg, 0.072 mmol). **12** isolated as a yellow powder (46 mg, 92%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (t, 7.9 Hz, 1H, H1, pyridyl), 7.65 (dd, 7.1 Hz, 5.5 Hz, 2H, *m*-$C_6H_4{}^tBu$), 7.59 (d, 1.8 Hz, 2H, H8, phenyl), 7.54 (d, 8.1 Hz, 2H, H5, phenyl), 7.49 – 7.35 (m, 4H, H2 pyridyl and H6 phenyl, overlapping), 7.25 (d, 2H, *o*-$C_6H_4{}^tBu$, overlapping with residual $CHCl_3$), 1.45 (s, 9H, $C_6H_4{}^tBu$), 1.31 (s, 18H, C11, $^{tBu}(Ph_2Py)$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.54 (C9), 163.11 (C3), 154.21 (C7), 147.17 (C4), 147.06 (^{tBu}Ph), 143.99 (^{tBu}Ph), 141.33 (C1), 133.88 (^{tBu}Ph), 132.68 (C8), 125.34 (C5 or ^{tBu}Ph), 124.68 (C5 or C6 or ^{tBu}Ph), 123.19 (C6 or ^{tBu}Ph), 115.73 (C2), 35.29 ($C_6H_4C(CH_3)_3$), 34.32 (C10), 31.52 ($C_6H_4C(CH_3)_3$), 31.14 (C11) .

$(^{tBu}Ph_2Py)Au$(5-acenaphthenyl) (13):

$(^{tBu}Ph_2Py)AuOH$ **4** (40 mg, 0.072 mmol) and (5-acenaphthenyl)$B(OH)_2$ (14 mg, 0.072 mmol). **13** isolated as a pale yellow powder (44 mg, 88%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.86 (t, 8.0 Hz, 1H, H1, pyridyl), 7.75 (d, 7.0 Hz, 1H, acenaphthenyl), 7.65 (d, 7.2 Hz, 1H, acenaphthenyl), 7.60 (d, 8.1 Hz, 2H, H5, phenyl), 7.53 (d, 8.0 Hz, 2H, H2, pyridyl), 7.31 (d, 7.0 Hz, 1H, acenaphthenyl), 7.27 – 7.21 (m, 3H, phenyl + acenaphthenyl, overlapping) 7.21 – 7.16 (m, 3H, phenyl + acenaphthenyl, overlapping), 3.44

(br s, 4H, CH_2 acenaphthenyl), 1.07 (s, 18H, H11, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 167.88 (C9), 163.18 (C3), 154.05 (C7), 147.46 (C4 or *C*H acenaphthenyl), 145.78 (C4 or *C*H acenaphthenyl), 143.90 (C4 or *C*H acenaphthenyl), 142.20 (C4 or *C*H acenaphthenyl), 141.67 (C4 or *C*H acenaphthenyl), 140.53 (*C*H acenaphthenyl), 134.43 (*C*H acenaphthenyl), 133.32 (C8), 132.04 (*C*H acenaphthenyl), 127.69 (*C*H acenaphthenyl), 125.70 (*C*H acenaphthenyl), 124.70 (C5), 123.07 (C6), 120.40 (*C*H acenaphthenyl) , 118.20 (*C*H acenaphthenyl), 116.02 (C2), 34.87 (C10), 30.67 (C11), 30.50 (*C*H_2 acenaphthenyl), 29.97 (*C*H_2 acenaphthenyl). Anal. Calcd. (found) for $C_{37}H_{36}AuN$: C, 64.25 (64.09); H, 5.25 (5.36); N, 2.03 (2.14).

($^{tBu}Ph_2Py$)Au(2-furanyl) (14):

($^{tBu}Ph_2Py$)AuOH **4** (40 mg, 0.072 mmol) and (2-furanyl)$B(OH)_2$ (8.7 mg, 0.072 mmol). The isolated powder was redissolved in dichloromethane and passed through a silica plug. The solvent was removed under vacuum, yielding **14** as a pale yellow powder (37 mg, 85%).

^1H NMR (300 MHz, CD_2Cl_2) δ 8.08 (d, 8.6 Hz, 1H, furanyl), 7.91 (d, 2.0 Hz, 2H, H8, phenyl), 7.84 (t, 8.0 Hz, 2H, H1, pyridyl), 7.68 (d, 7.5 Hz, 1H, furanyl), 7.47 (d, 8.2 Hz, 2H, H5, phenyl), 7.40 (d, 8.0 Hz, 2H, H2, pyridyl), 7.29 (dd, 8.2 Hz, 2.0 Hz, 2H, H6, phenyl), 1.37 (s, 18H, H11, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ (C-ipso and a CH furanyl resonance not observed) 170.29 (C9) 164.93 (C3), 155.52 (C7), 145.22 (C4), 142.91 (C1), 130.41 (C8), 126.51 (*C*H furanyl), 125.57 (*C*H furanyl), 124.90 (C5), 124.26 (C6), 116.41 (C2), 35.46 (C10), 30.92 (C11).

($^{tBu}Ph_2Py$)Au(2-thiophenyl) (15):

($^{tBu}Ph_2Py$)AuOH **4** (40 mg, 0.072 mmol) and (2-thienyl)$B(OH)_2$ (9.2 mg, 0.072 mmol). **15** isolated as a bright yellow powder (48 mg, 95%).

^1H NMR (300 MHz, CD_2Cl_2) δ 7.86 (t, 8.0 Hz, 1H, H1, pyridyl), 7.72 – 7.63 (m, 3H, H8 phenyl + C*H* thienyl, overlapping), 7.56 (d, 8.2 Hz, 2H, H5, phenyl), 7.48 (d, 8.0 Hz, 2H, H2, pyridyl), 7.35 – 7.26 (m, 3H, C6 phenyl +C*H* thienyl, overlapping), 7.23 (dd, 3.4Hz, 1.0 Hz, 1H, C*H* thienyl), , 1.31 (s, 18H, H11, ^{t}Bu). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2) δ 167.83 (C9), 164.02 (C3), 154.86 (C7), 147.52 (C4), 142.39 (C1), 140.18 (*ipso*-C, thienyl), 132.83 (C8), 129.17 (*C*H thienyl), 127.76 (*C*H thienyl), 126.31 (*C*H thienyl), 125.32 (C5), 123.88 (C6), 116.51 (C2), 35.59 (C10), 31.30 (C11). Anal. Calcd. (found) for $C_{29}H_{30}AuNS$: C, 56.04 (55.90); H, 4.86 (5.00); N, 2.25 (2.29).

($^{tBu}Ph_2Py$)Au(benzo[b]thiophenyl) (16):

($^{tBu}Ph_2Py$)AuOH **4** (92 mg, 0.166 mmol) and (2-benzo[b]thienyl)$B(OH)_2$ (29.5 mg, 0.166 mmol). The isolated powder was redissolved in dichloromethane and passed through a silica plug. The solvent was removed under vacuum, yielding **16** as a pale yellow powder (102 mg, 92%).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.93 (d, 8.0 Hz, 1H, benzo[b]thienyl), 7.86 (t, 8.1 Hz, 1H, H1, pyridyl), 7.85 (d, 8.1 Hz, 1H, benzo[b]thienyl), 7.65 (d, 2.0 Hz, 2H, H8, phenyl), 7.57 (d, 8.2 Hz, 2H, H5, phenyl), 7.49 (d, 8.0 Hz, 2H, H2, pyridyl), 7.40 (s, 1H, benzo[b]thienyl), 7.36 – 7.30 (m, 2H, benzo[b]thienyl), 7.27 (dd, 8.1 Hz, 2.1 Hz, 2H, H6, phenyl), 1.23 (s, 18H, ^{t}Bu). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.63 (C9), 163.88 (C3), 154.96 (C7), 147.09 (C4), 143.82 (*C*H benzothienyl), 143.03 (*C*H benzothienyl), 142.26 (C1 or *C*H benzothienyl), 142.08 (C1 or *C*H benzothienyl), 133.04 (C8), 125.31 (*C*H benzothienyl), 125.08 (C5), 123.67 (C6), 123.39 (*C*H benzothienyl), 122.18 (*C*H benzothienyl), 121.97 (*C*H benzothienyl), 121.94 (*C*H benzothienyl) , 116.10 (C2), 35.47 (C10), 31.31 (C11). Anal. Calcd. (found) for $C_{32}H_{32}AuNS$:C,59.01 (59.13); H, 4.80 (4.69); N, 2.09 (2.15).

Photoluminescence data

Fig. S2: UV/vis absorption spectra of (^{tBu}Ph$_2$Py)Au(Ar) complexes

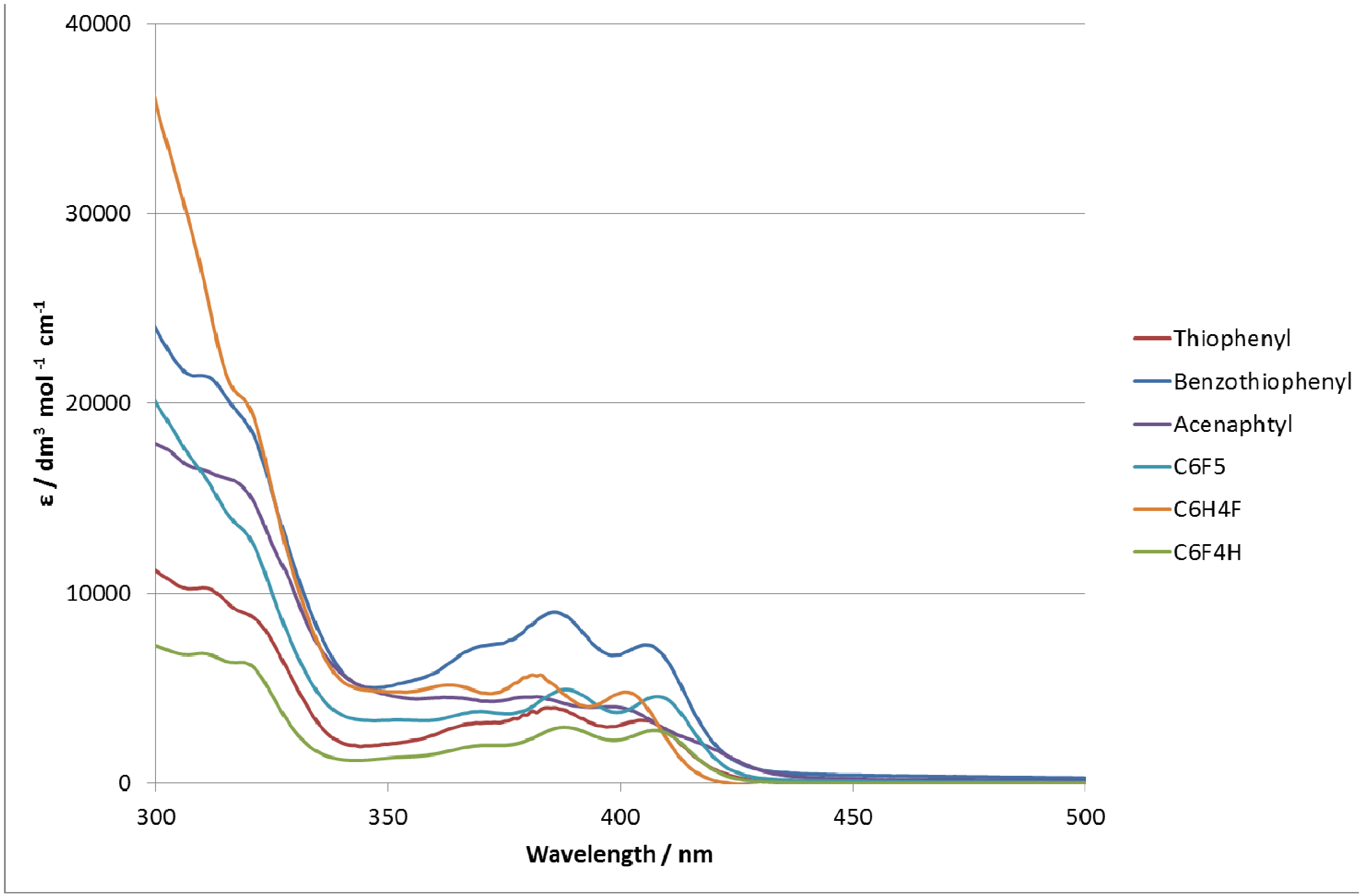

Fig S3: Normalised Emission spectra of (^{tBu}Ph$_2$Py)Au(Ar) complexes

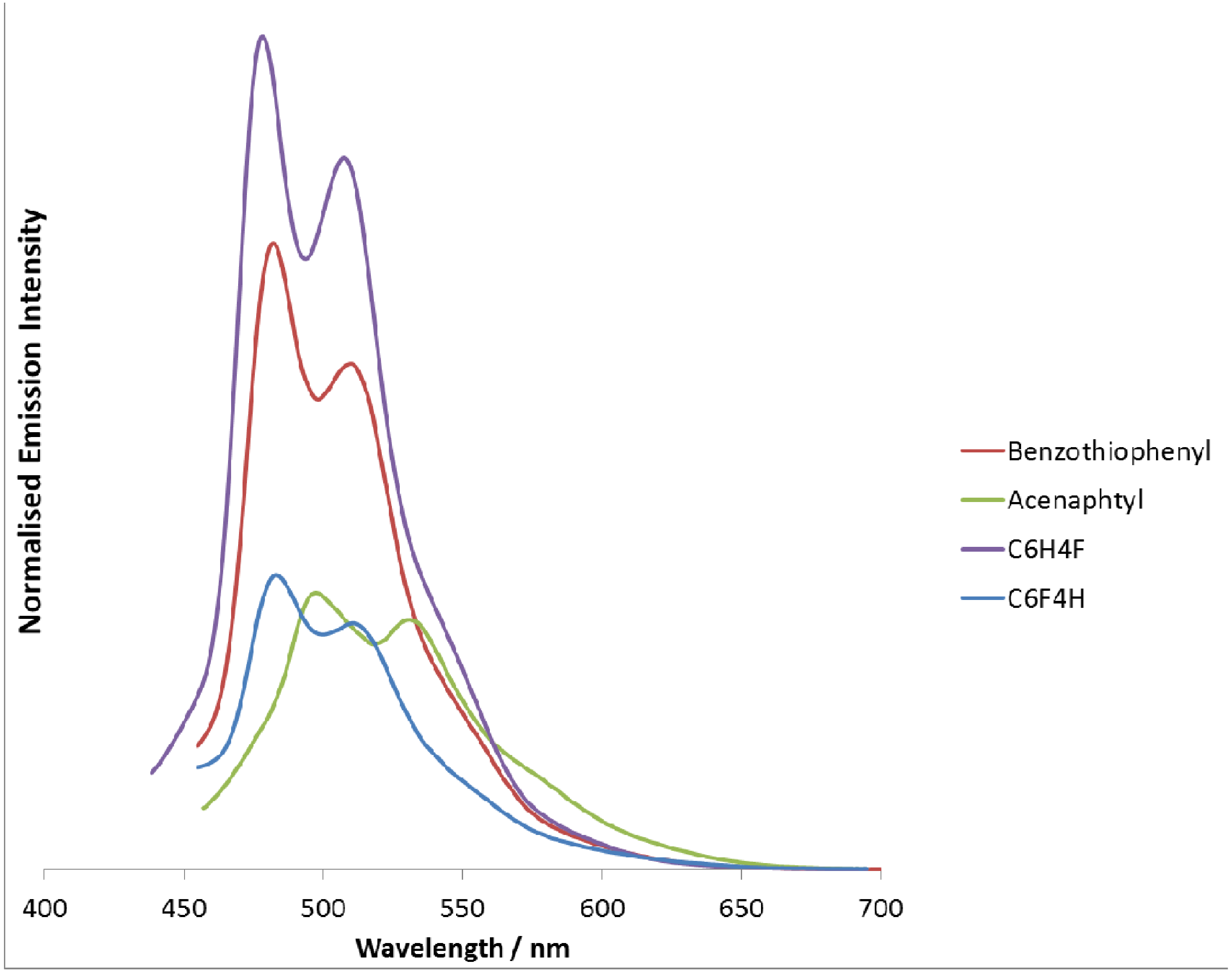

Fig. S4: PL of (CNC)AuR, R = thiophenyl (left), p-fluorophenyl (centre) and pentafluorophenyl (right).

Table S1. Emission lifetimes measured at room temperature in degasses CH_2Cl_2 solutions

Compound N°	Compound name	Lifetimes[*] ($\tau_{0/}$ns)
5	LAu(C_6F_5)	2, 7
6	LAu(C_6F_4H)	1, 13
11	LAu(p-F-C_6H_4)	2, 24
13	LAu(acenaphthenyl)	3, 11
15	LAu(2-thienyl)	3, 32
16	LAu(benzothienyl)	1, 18

[*] Double exponential decay

Crystallographic data for compound 4·H_2O

Crystallographic data for compound **4·H_2O** were collected at 140(2)K on an Oxford Diffraction Xcalibur03/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator. Data were processed using the CrystAlisPro-CCD and –RED[3] software. The structure was determined by direct methods in SHELXS program[4] and refined by full-matrix least squares methods on F^2 in SHELXL.[4] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions. No missed symmetry was reported by PLATON.[5] Refinement results are included in Table S2. Computer programs used in this analysis were run through WinGX.[6]

Table S2. Crystal data and structure refinement for **4·H_2O**

Identification code	rd-237	
Empirical formula	$C_{25} H_{30} Au N O_2$	
Formula weight	573.46	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.9668(4) Å	α = 90°.
	b = 11.3514(3) Å	β = 99.366(3)°.
	c = 12.9152(4) Å	δ = 90°.
Volume	2164.97(11) $Å^3$	
Z	4	
Density (calculated)	1.753 Mg/m^3	
Absorption coefficient	6.816 mm^{-1}	
F(000)	1120	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Crystal shape/colour	yellow prism	
θ range for data collection	3.46 to 27.48°.	
Index ranges	-18<=h<=18, -14<=k<=14, -16<=l<=16	

Reflections collected	33099
Independent reflections	4938 [R(int) = 0.0457]
Completeness to θ = 27.48°	99.2 %
Max. and min. transmission	0.5489 and 0.3426
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4938 / 0 / 263
Goodness-of-fit on F^2	1.160
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0547
R indices (all data)	R1 = 0.0277, wR2 = 0.0569
Largest diff. peak and hole	1.375 and -1.083 e.Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4·H_2O**. U(eq) is defined as one third of the trace of the orthogonalised U^{ij} tensor.

	x	y	z	U(eq)
O(2)	127(2)	10535(2)	1331(2)	35(1)
Au(1)	230(1)	6744(1)	965(1)	16(1)
O(1)	681(2)	8340(2)	616(2)	22(1)
C(10)	5(3)	3207(3)	1752(3)	24(1)
C(2)	-1547(2)	8226(3)	417(3)	20(1)
C(1)	-1126(2)	7179(3)	748(3)	19(1)
N(1)	-256(2)	5203(3)	1311(2)	18(1)
C(9)	-924(3)	3082(3)	1710(3)	26(1)
C(16)	2336(2)	6201(3)	1322(3)	21(1)
C(13)	2015(2)	3883(3)	1827(3)	22(1)
C(14)	2894(3)	4273(3)	1832(3)	25(1)
C(8)	-1514(3)	4018(3)	1482(3)	24(1)
C(17)	1449(2)	5846(3)	1313(3)	19(1)
C(11)	345(2)	4310(3)	1558(2)	18(1)

C(12)	1293(2)	4662(3)	1571(2)	20(1)
C(5)	-2584(2)	6348(3)	917(3)	24(1)
C(6)	-1653(2)	6216(3)	986(3)	20(1)
C(7)	-1166(2)	5117(3)	1276(2)	20(1)
C(21)	-2463(3)	10553(3)	582(3)	27(1)
C(18)	-2907(2)	9537(3)	-102(3)	25(1)
C(3)	-2488(2)	8368(3)	315(3)	21(1)
C(15)	3078(2)	5432(3)	1581(3)	22(1)
C(4)	-2994(2)	7416(3)	586(3)	24(1)
C(22)	4043(2)	5904(4)	1589(3)	28(1)
C(24A)	4230(3)	6889(4)	2416(4)	41(1)
C(19A)	-3929(3)	9588(4)	-98(3)	36(1)
C(20A)	-2739(3)	9696(4)	-1238(3)	35(1)
C(25A)	4132(3)	6384(4)	501(4)	40(1)
C(23A)	4761(3)	4944(4)	1879(4)	36(1)

Table S3. Bond lengths [Å] and angles [°] for **4·H_2O**.

Au(1)-N(1)	1.974(3)
Au(1)-O(1)	2.010(2)
Au(1)-C(1)	2.064(3)
Au(1)-C(17)	2.074(3)
C(10)-C(11)	1.389(5)
C(10)-C(9)	1.391(6)
C(2)-C(1)	1.380(5)
C(2)-C(3)	1.402(5)
C(1)-C(6)	1.410(5)
N(1)-C(7)	1.358(4)
N(1)-C(11)	1.358(4)
C(9)-C(8)	1.382(5)
C(16)-C(17)	1.385(5)
C(16)-C(15)	1.409(5)
C(13)-C(14)	1.387(5)
C(13)-C(12)	1.394(5)
C(14)-C(15)	1.393(5)
C(8)-C(7)	1.395(5)
C(17)-C(12)	1.414(5)
C(11)-C(12)	1.471(5)
C(5)-C(6)	1.390(5)
C(5)-C(4)	1.395(5)
C(6)-C(7)	1.462(5)
C(21)-C(18)	1.537(5)
C(18)-C(3)	1.528(5)
C(18)-C(19A)	1.532(5)
C(18)-C(20A)	1.539(5)
C(3)-C(4)	1.397(5)
C(15)-C(22)	1.539(5)

C(22)-C(25A)	1.533(6)
C(22)-C(23A)	1.533(5)
C(22)-C(24A)	1.540(6)
N(1)-Au(1)-O(1)	177.89(11)
N(1)-Au(1)-C(1)	81.49(13)
O(1)-Au(1)-C(1)	96.45(12)
N(1)-Au(1)-C(17)	81.92(13)
O(1)-Au(1)-C(17)	100.13(12)
C(1)-Au(1)-C(17)	163.38(14)
C(11)-C(10)-C(9)	118.6(3)
C(1)-C(2)-C(3)	121.9(3)
C(2)-C(1)-C(6)	119.5(3)
C(2)-C(1)-Au(1)	129.6(3)
C(6)-C(1)-Au(1)	110.9(3)
C(7)-N(1)-C(11)	125.2(3)
C(7)-N(1)-Au(1)	117.4(2)
C(11)-N(1)-Au(1)	117.4(2)
C(8)-C(9)-C(10)	122.0(3)
C(17)-C(16)-C(15)	122.6(3)
C(14)-C(13)-C(12)	119.9(3)
C(13)-C(14)-C(15)	121.5(3)
C(9)-C(8)-C(7)	118.9(3)
C(16)-C(17)-C(12)	118.0(3)
C(16)-C(17)-Au(1)	131.8(3)
C(12)-C(17)-Au(1)	110.2(2)
N(1)-C(11)-C(10)	117.8(3)
N(1)-C(11)-C(12)	113.7(3)
C(10)-C(11)-C(12)	128.5(3)
C(13)-C(12)-C(17)	120.4(3)
C(13)-C(12)-C(11)	122.7(3)

C(17)-C(12)-C(11)	116.8(3)
C(6)-C(5)-C(4)	120.0(3)
C(5)-C(6)-C(1)	119.5(3)
C(5)-C(6)-C(7)	124.1(3)
C(1)-C(6)-C(7)	116.4(3)
N(1)-C(7)-C(8)	117.5(3)
N(1)-C(7)-C(6)	113.8(3)
C(8)-C(7)-C(6)	128.7(3)
C(3)-C(18)-C(19A)	112.6(3)
C(3)-C(18)-C(21)	109.5(3)
C(19A)-C(18)-C(21)	108.0(3)
C(3)-C(18)-C(20A)	108.5(3)
C(19A)-C(18)-C(20A)	108.5(3)
C(21)-C(18)-C(20A)	109.7(3)
C(4)-C(3)-C(2)	117.8(3)
C(4)-C(3)-C(18)	123.4(3)
C(2)-C(3)-C(18)	118.8(3)
C(14)-C(15)-C(16)	117.6(3)
C(14)-C(15)-C(22)	123.2(3)
C(16)-C(15)-C(22)	119.2(3)
C(5)-C(4)-C(3)	121.3(3)
C(25A)-C(22)-C(23A)	108.3(3)
C(25A)-C(22)-C(15)	109.8(3)
C(23A)-C(22)-C(15)	112.0(3)
C(25A)-C(22)-C(24A)	110.1(4)
C(23A)-C(22)-C(24A)	107.8(3)
C(15)-C(22)-C(24A)	108.8(3)

Table S4. Anisotropic displacement parameters ($Å^2$x 10^3)for **$4·H_2O$**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	51(2)	27(2)	29(1)	-1(1)	8(1)	2(1)
Au(1)	17(1)	13(1)	17(1)	0(1)	3(1)	0(1)
O(1)	24(1)	16(1)	25(1)	6(1)	5(1)	3(1)
C(10)	33(2)	17(2)	19(2)	-1(1)	2(2)	-4(2)
C(2)	20(2)	20(2)	21(2)	1(1)	5(1)	-3(1)
C(1)	19(2)	22(2)	17(2)	-3(1)	4(1)	0(1)
N(1)	22(2)	15(1)	15(1)	-1(1)	2(1)	-3(1)
C(9)	39(2)	19(2)	20(2)	2(1)	3(2)	-10(2)
C(16)	23(2)	15(2)	24(2)	1(1)	5(1)	2(1)
C(13)	32(2)	16(2)	19(2)	0(1)	3(1)	4(2)
C(14)	29(2)	22(2)	24(2)	1(2)	1(2)	9(2)
C(8)	29(2)	23(2)	21(2)	-1(1)	3(1)	-8(2)
C(17)	25(2)	15(2)	17(2)	-1(1)	3(1)	3(1)
C(11)	25(2)	15(2)	14(2)	0(1)	1(1)	-1(1)
C(12)	28(2)	19(2)	14(2)	-1(1)	3(1)	2(1)
C(5)	22(2)	24(2)	26(2)	-1(2)	6(1)	-9(2)
C(6)	22(2)	21(2)	18(2)	-3(1)	4(1)	-5(1)
C(7)	25(2)	22(2)	14(2)	-1(1)	2(1)	-5(1)
C(21)	26(2)	23(2)	33(2)	3(2)	7(2)	4(2)
C(18)	20(2)	30(2)	27(2)	4(2)	4(1)	4(2)
C(3)	18(2)	26(2)	20(2)	-2(1)	4(1)	-1(1)
C(15)	23(2)	22(2)	21(2)	-1(1)	3(1)	3(1)
C(4)	16(2)	30(2)	27(2)	-2(2)	5(1)	-3(2)
C(22)	21(2)	26(2)	36(2)	2(2)	3(2)	4(2)
C(24A)	27(2)	32(2)	59(3)	-11(2)	-4(2)	-1(2)
C(19A)	20(2)	38(2)	48(2)	4(2)	3(2)	5(2)

C(20A)	33(2)	42(3)	28(2)	7(2)	4(2)	11(2)
C(25A)	23(2)	49(3)	50(3)	13(2)	11(2)	1(2)
C(23A)	26(2)	33(2)	50(3)	1(2)	4(2)	7(2)

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