Luminescent Gold(III) Thiolates: Supramolecular Interactions
Trigger and Control Switchable Photoemissions from Bimolecular
Excited States

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1. Synthesis and Characterization

When required, manipulations were performed using standard Schlenk techniques under dry nitrogen or in a MBraun glove box. Nitrogen was dried by passing through columns of supported P₂O₅, with moisture indicator, and activated 4 Å molecular sieves. Anhydrous solvents were freshly distilled from appropriate drying agents. (C^Npz^C)AuCl and (C^Npy^C)AuCl were synthesised using literature methods.¹¹H and ¹³C{¹H} spectra were measured on a Bruker Avance DPX-300 spectrometer using CD₂Cl₂ as solvent and signals were referenced to the residual protons of the deuterated solvent. IR spectra were recorded using a Perkin Elmer Spectrum 65 FT-IR spectrometer with a diamond ATR attachment. Elemental analyses were carried out at London Metropolitan University with a Perkin-Elmer 2400 CHNS/O microanalyzer.

Synthesis of (C^Npz^C)AuSPh (1)

**Method 1:** (C^Npz^C)AuCl (0.050 g, 0.087 mmol), K₂CO₃ (0.024 g, 0.174 mmol) and thiophenol (0.013 mL, 0.087 mmol) were stirred in acetone (5 mL) at room temperature for 3 h. The solvent was evaporated and the orange solid obtained was dissolved in dichloromethane. The solution was filtered over celite and evaporated to dryness to give the pure product as a yellow powder (0.054 g, 99% yield). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a solution in dichloromethane/isopropanol (9:1). Both red and yellow crystals were obtained under the same conditions. Anal. Calcd for C₃₀H₃₁N₂AuS (648.2): C, 55.55; H, 4.82; N, 4.32. Found: C, 55.47; H, 4.81; N, 4.38. ¹H NMR (CD₂Cl₂, 300.13 MHz, 298 K): δ 8.85 (s, 2 H, H²), 7.65 (m, 4 H, H⁵ + H¹¹), 7.39 (d, ⁴J_HH = 1.9 Hz, 2 H, H⁸), 7.29 (dd, ³J_HH = 8.2 Hz, ⁴J_HH = 1.9 Hz, 2 H, H⁶), 7.21 (m, 3 H, H¹² + H¹³), 1.17 (s, 18 H, tBu). ¹³C{¹H} NMR (CD₂Cl₂, 75.48 MHz, 298 K): δ 169.2 (s, C⁹), 156.2 (s, C⁵⁷), 156.1 (s, C⁵⁷), 145.0 (s, C⁷), 138.8 (s, C⁶), 137.6 (s, C⁰), 135.0 (s, C⁵¹), 131.5 (s, C⁸), 128.9 (s, C¹₂), 126.7 (s, C¹³), 125.7 (s, C⁵¹¹), 124.4 (s, C⁶), 35.6 (s, C(CH₃)₃), 31.1 (s, CH₃).
Figure S1. $^1$H and $^{13}$C($^1$H) NMR spectra of compound 1.
**Synthesis of (C^Npz^C)AuSC_{6}H_{4}tBu-4 (2)**

**Method 2:** Under a nitrogen atmosphere, a flask was charged with (C^Npz^C)AuCl (56.0 mg, 0.097 mmol), K_{2}CO_{3} (26.9 mg, 0.191 mmol) and degassed acetone (5 mL). 4-tert-butybenzenethiol (15 µL, 0.097 mmol) was added and the mixture was stirred at room temperature for 3 hours. The acetone was removed *in vacuo* and the resulting solid was extracted into dichloromethane (5 mL). The suspension was filtered through celite and washed with dichloromethane (5 mL). The solvent was removed. The solid residue was washed with cold hexane to give 2 as a yellow solid (56.7 mg, 0.081 mmol, 83%).

Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a dichloromethane and isopropanol (4:1) solution. Anal. Calcd for C_{34}H_{39}AuN_{2}S (704.73): C, 57.95; H, 5.58; N, 3.98. Found: C, 57.80; H, 5.65; N, 4.12. \(^1\)H NMR (CD_{2}Cl_{2}, 300.13 MHz, 298 K): δ 8.83 (s, 2 H, H^2), 7.64 (d, \(^3\)J_{H-H} = 8.2 Hz, 2 H, H^3), 7.56 (d, \(^3\)J_{H-H} = 8.4 Hz, 2 H, H^11), 7.43 (d, \(^4\)J_{H-H} = 1.9 Hz, 2 H, H^8), 7.26 (m, 4 H, H^6 + H^12), 1.29 (s, 9 H, \(\text{tBu(SPh-4-tBu)}\)), 1.17 (s, 18 H, \(\text{tBu(C^Npz^C)}\)). \(^{13}\)C{\(^1\)H} NMR (CD_{2}Cl_{2}, 75.48 MHz, 298 K): δ 169.1 (s, C^9), 156.1 (s, C^{3/7}), 156.0 (s, C^{3/7}), 149.7 (s, C^{13}), 145.1 (s, C^4), 138.8 (s, C^5), 134.7 (s, C^{11}), 133.8 (s, C^{10}), 131.4 (s, C^8), 126.1 (s, C^{612}), 125.7 (s, C^6), 124.4 (s, C^{612}), 35.7 (s, C(CH_{3})_{3}(C^Npz^C)), 34.7 (s, C(CH_{3})_{3}(SPh-4-tBu)), 31.4 (s, CH_{3}(SPh-4-tBu)), 31.2 (s, CH_{3}(C^Npz^C)).
Figure S2. $^1$H and $^{13}$C($^1$H) NMR spectra of compound 2.
Synthesis of (C^Npz^C)AuSC_2H_4N-2 (3)

**Method 1:** (C^Npz^C)AuCl (50.0 mg, 0.087 mmol) and K_2CO_3 (24.0 mg, 0.174 mmol) were dissolved in acetone (5 mL). Then, 1-mercaptopyridine (9.8 mg, 0.087 mmol) was added and the mixture was stirred at room temperature for 3 h. The acetone was removed *in vacuo* and the resulting solid was extracted into dichloromethane (5 mL). The suspension was filtered through celite and washed with dichloromethane (5 mL). The solvent was removed to give a yellow solid. This was washed with cold hexane to give 3 as a yellow powder (41.0 mg, 0.063 mmol, 72%). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a dichloromethane and isopropanol (4:1) solution.

Anal. Calcd. for C_{29}H_{30}AuN_3S (649.61): C, 53.62; H, 4.66; N, 6.49. Found: C, 53.53; H, 4.77; N, 6.54. ¹H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.83 (s, 2 H, H^2), 8.25 (bd, ¹J_{H-H} = 4.9 Hz, 1 H, H^14), 7.64 (m, 3 H, H^5 + H^11), 7.57 (d, ²J_{H-H} = 1.9 Hz, 2 H, H^8), 7.40 (m, 1 H, H^12), 7.29 (dd, ³J_{H-H} = 8.2 Hz, ⁴J_{H-H} = 1.9 Hz, 2 H, H^6), 6.96 (m, 1 H, H^13), 1.19 (s, 18 H, tBu). ¹³C{¹H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 170.1 (s, C^9), 162.4 (s, C^10), 156.7 (s, C^37), 156.4 (s, C^37), 149.5 (s, C^14), 144.8 (s, C^4), 138.8 (s, C^3), 135.8 (s, C^12), 132.6 (s, C^8), 127.8 (s, C^5), 125.8 (s, C^6), 124.5 (s, C^6), 119.9 (s, C^13), 35.7 (s, C(CH_3)3), 31.1 (s, CH_3).
Figure S3. $^1$H and $^{13}$C($^1$H) NMR spectra of compound 3.
Synthesis of \((\text{C}^\text{N^pz}^\text{C})\text{AuSNp-1} \) (4)

The synthesis of 4 used method 2. \((\text{C}^\text{N^pz}^\text{C})\text{AuCl} \) (62.3 mg, 0.108 mmol), K\(_2\)CO\(_3\) (30.0 mg, 0.216 mmol) and 1-naphthalenethiol (15 µL, 0.108 mmol) gave 4 as an orange solid (60.0 mg, 0.086 mmol, 80%). Anal. Calcd. For C\(_{34}\)H\(_{33}\)AuN\(_2\)S (698.68): C, 58.45; H, 4.76; N, 4.01. Found: C, 58.45; H, 4.67; N, 4.00. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300.13 MHz, 298 K): \(\delta\) 8.44 (s + d, 3 H, H\(_2\)^{17/19}), 7.86 (m, 1 H, H\(_{15}\)), 7.82 (d, \(J_{H-H} = 8.4\) Hz, 1 H, H\(^{17/19}\)), 7.63 (d, \(J_{H-H} = 8.1\) Hz, 2 H, H\(^5\)), 7.49 (m, 2 H, H\(^{13}\) + H\(^{14}\)), 7.40 (dd, \(J_{H-H} = 8.0\) Hz, 1 H, H\(^{18}\)), 7.24 (dd, \(J_{H-H} = 8.1\) Hz, \(J_{H-H} = 1.8\) Hz, 2 H, H\(^6\)), 7.18 (d, \(J_{H-H} = 1.8\) Hz, 2 H, H\(^8\)), 1.02 (s, 18 H, \(\text{tBu}\)). \(^{13}\)C\(^{\{1\}H}\) NMR (CD\(_2\)Cl\(_2\), 75.48 MHz, 298 K): \(\delta\) 168.5 (s, C\(^9\)), 156.0 (s, C\(^3\) + C\(^7\)), 145.2 (s, C\(^4\)), 138.8 (s, C\(^2\)), 136.4 (s, C\(^{10/11/16}\)), 135.6 (s, C\(^{17/19}\)), 134.7 (s, C\(^{10/11/16}\)), 134.6 (s, C\(^{10/11/16}\)), 130.7 (s, C\(^8\)), 128.9 (s, C\(^{15}\)), 128.8 (s, C\(^{17/19}\)), 127.6 (s, C\(^{12}\)), 126.7 (s, C\(^{13/14}\)), 126.4 (s, C\(^{13/14}\)), 126.1 (s, C\(^{18}\)), 125.8 (s, C\(^5\)), 124.3 (s, C\(^6\)), 35.5 (s, C(CH\(_3\))\(_3\)), 30.9 (s, CH\(_3\)).
Figure S4. $^1$H and $^{13}$C{$^1$H} NMR spectra of compound 4.
Synthesis of (C^Npz^C)AuSNp_2 (5)

Using method 1. (C^Npz^C)AuCl (50.0 mg, 0.087 mmol), K_2CO_3 (24.0 mg, 0.174 mmol) and 2-naphthalenethiol (14.0 mg, 0.087 mmol) gave 5 as an orange solid (51.2 mg, 0.073 mmol, 84%). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a dichloromethane and isopropanol (4:1) solution (yellow polymorph) and slow evaporation of a dichloromethane solution (red polymorph). Anal. Calcd. for C_{34}H_{33}AuN_2S (698.68): C, 58.45; H, 4.76; N, 4.01. Found: C, 58.34; H, 4.62; N, 4.12. 

^1H NMR (CDCl_3, 300.13 MHz, 298 K): δ 8.83 (s, 2 H, H^9), 8.22 (s, 1 H, H^11), 7.79 (d, J_{H-H} = 6.7 Hz, 1 H, H^16), 7.72 (d, J_{H-H} = 6.7 Hz, 1 H, H^13), 7.67 (m, 2 H, H^18 + H^19), 7.62 (d, J_{H-H} = 8.2 Hz, 2 H, H^11), 7.44 (m, 2 H, H^14 + H^15), 7.29 (d, J_{H-H} = 1.9 Hz, 2 H, H^5), 7.24 (dd, J_{H-H} = 8.2 Hz, 2 H, H^6), 1.00 (s, 18 H, tBu). 

^13C{^1H} NMR (CDCl_3, 75.48 MHz, 298 K): δ 169.0 (s, C^9), 156.2 (s, C^1 + C^7), 145.1 (s, C^8), 138.8 (s, C^2), 134.8 (s, C^{10/12/17}), 134.3 (s, C^{10/12/17}), 133.7 (s, C^{18/19}), 133.3 (s, C^11), 132.7 (s, C^{10/12/17}), 131.3 (s, C^8), 128.1 (s, C^{18/19}), 127.9 (s, C^{16}), 127.5 (s, C^{13}), 126.7 (s, C^{14/15}), 126.0 (s, C^{14/15}), 125.8 (s, C^5), 124.4 (s, C^6), 35.5 (s, C(CH_3)_3), 30.8 (s, CH_3).
Figure S5. $^1$H and $^{13}$C-$^1$H NMR spectra of compound 5.
Synthesis of \((C^Npz^C)\)AuQuinoline (6)

Using method 1. \((C^Npz^C)\)AuCl (50.0 mg, 0.087 mmol), \(K_2CO_3\) (24.0 mg, 0.174 mmol) and 2-quinolinethiol (14.0 mg, 0.087 mmol) gave 6 as an orange solid (42.0 mg, 0.060 mmol, 69%). Anal. Calcd. For \(C_{33}H_{32}AuN_3S\) (699.67): C, 56.65; H, 4.61; N, 6.01. Found: C, 56.58; H, 4.55; N, 6.09. \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300.13 MHz, 298 K): \(\delta\) 8.86 (s, 2 H, H\(^2\)), 7.90-7.50 (bm, 4 H, H\(^{13/16/18/19}\)), 7.64 (d, \(^3\)J\(_{H-H}\) = 8.1 Hz, 2 H, H\(^5\)), 7.52 (bs, 2 H, H\(^6\)), 7.45-7.35 (bm, 2 H, H\(^{14}\)+H\(^{15}\)), 7.26 (dd, \(^3\)J\(_{H-H}\) = 8.1 Hz, \(^4\)J\(_{H-H}\) = 1.6 Hz, 2 H, H\(^6\)), 1.04 (s, 18 H, tBu). \(^1\)H NMR (CD\(_2\)Cl\(_2\), 300.13 MHz, 223 K): \(\delta\) 8.83 (s, 2 H, H\(^2\)), 7.82 (d, \(^3\)J\(_{H-H}\) = 8.6 Hz, 1 H, H\(^{13/16/18/19}\)), 7.78 (d, \(^3\)J\(_{H-H}\) = 8.6 Hz, 1 H, H\(^{13/16/18/19}\)), 7.70 (d, \(^3\)J\(_{H-H}\) = 7.4 Hz, 1 H, H\(^{13/16/18/19}\)), 7.60 (m, \(^3\)J\(_{H-H}\) = 8.3 Hz, 4 H, H\(^5\)+H\(^{14}\)+H\(^{15}\)), 7.41 (d, \(^3\)J\(_{H-H}\) = 8.0 Hz, 1 H, H\(^{13/16/18/19}\)), 7.37 (d, \(^4\)J\(_{H-H}\) = 1.4 Hz, 2 H, H\(^6\)), 7.21 (dd, \(^3\)J\(_{H-H}\) = 8.2 Hz, \(^4\)J\(_{H-H}\) = 1.4 Hz, 2 H, H\(^6\)), 0.95 (s, 18 H, tBu). \(^13\)C\({^1}\)H NMR (CD\(_2\)Cl\(_2\), 75.48 MHz, 298 K): \(\delta\) 170.1 (s, C\(^0\)), 156.8 (s, C\(^{27}\)), 156.4 (s, C\(^{37}\)), 144.7 (s, C\(^4\)), 138.9 (s, C\(^2\)), 132.6 (s, C\(^8\)), 127.7 (s, C\(^{quinoline}\)), 127.1 (s, C\(^{quinoline}\)), 125.9 (s, C\(^5\)), 124.4 (s, C\(^6\)), 35.6 (s, C(CH\(_3\))\(_3\)), 30.9 (s, CH\(_3\)).
Figure S6. $^1$H NMR spectrum of 6 at 298 K (top) and 223 K (middle). Bottom: $^{13}$C($^1$H) NMR spectrum.
Synthesis of (C^Npz^C)AuS-4-methylcoumarin (7)

Slight variation of method 1: (C^Npz^C)AuCl (50.0 mg, 0.087 mmol), K_2CO_3 (24.0 mg, 0.174 mmol) and 7-mercapto-4-methylcoumarin (16.7 mg, 0.087 mmol) were allowed to react for 18 h. The product was isolated as a yellow solid (22.3 mg, 35%). method 3: To a flask charged with (C^Npz^C)AuCl (40.0 mg, 0.070 mmol) and potassium t-butoxide (9.4 mg, 0.084 mmol) under N_2 was added dry toluene (5 mL), this was left to stir for 3 hours. Then 7-mercapto-4-methylcoumarin (13.4 mg, 0.070 mmol) was added and reaction stirred for further 3 hours. Solvent removed under vacuum, solid suspended in dichloromethane and passed through celite plug. The solution was evaporated to dryness to give 7 as a yellow solid (43 mg, 0.059 mmol, 84%). Anal. Calcd. For C_{34}H_{33}AuN_2O_2S (704.73): C, 55.89; H, 4.55; N, 3.83. Found: C, 56.02; H, 4.48; N, 3.91. ^1H NMR (CD_2Cl_2, 300.13 MHz, 298 K): δ 8.84 (s, 2 H, H^2), 7.65 (d, ^3J_{H-H} = 8.2 Hz, 2 H, H^5), 7.58 (d, ^4J_{H-H} = 1.7 Hz, 1 H, H^11), 7.55 (dd, ^3J_{H-H} = 8.3 Hz, ^4J_{H-H} = 1.9 Hz, 1 H, H^19), 7.42 (d, ^4J_{H-H} = 1.9 Hz, 2 H, H^8), 7.40 (d, ^3J_{H-H} = 8.3 Hz, 1 H, H^16), 7.34 (dd, ^3J_{H-H} = 8.2 Hz, ^4J_{H-H} = 1.9 Hz, 2 H, H^6), 6.14 (bq, ^4J_{H-H} = 1.2 Hz, 1 H, H^15), 2.36 (bd, ^4J_{H-H} = 1.2 Hz, 3 H, H^20), 1.13 (s, 18 H, ^3Bu). ^13C{^1H} NMR (CD_2Cl_2, 75.48 MHz, 298 K): δ 169.5 (s, C^9), 160.8 (s, C^{10/12/14/17}), 156.4 (s, C^{3/7}), 156.3 (s, C^{0/7}), 153.4 (s, C^{10/12/14/17}), 152.6 (s, C^{10/12/14/17}), 144.9 (s, C^4 + C^{10/12/14/17}), 138.9 (s, C^2), 131.9 (s, C^6), 130.3 (s, C^{10}), 125.9 (s, C^5), 124.6 (s, C^6), 124.3 (s, C^{18}), 121.8 (s, C^{1}), 118.1 (s, C^{16}), 113.9 (s, C^{15}), 35.7 (s, C(CH_3)_3), 30.9 (s, CH_3), 18.7 (s, C^20).
Figure S7. $^1$H and $^{13}$C($^1$H) NMR spectra of compound 7.
Synthesis of (C^Npz^C)AuSAd (8)

Under an atmosphere of nitrogen, a flask was charged with (C^Npz^C)AuCl (55.0 mg, 0.097 mmol), K$_2$CO$_3$ (26.9 mg, 0.191 mmol) and 1-adamantanethiol (16 mg, 0.097 mmol). Degassed acetone (5 mL) was added and the mixture was stirred at room temperature for 24 hours (the reaction was incomplete after 6 h, so an excess 1-adamantanethiol was added and the reaction was left overnight). The acetone was removed in vacuo and the resulting solid extracted into dichloromethane (5 mL). The suspension was filtered through celite and washed with dichloromethane (5 mL). Solvent was removed to give a red solid which was further purified by flash column chromatography (1:1 dichloromethane and petroleum ether) (22.0 mg, 0.031 mmol, 36%). Using Method 3: (C^Npz^C)AuCl (40.0 mg, 0.070 mmol), potassium t-butoxide (9.4 mg, 0.084 mmol) and 1-adamantanethiol (11.7 mg, 0.070 mmol) gave a red solid (36.1 mg, 0.051 mmol, 73%). Anal. Calcd. for C$_{34}$H$_{41}$AuN$_2$S (706.74): C, 57.78; H, 5.85; N, 3.96. Found: C, 57.52; H, 5.90; N, 4.12. $^1$H NMR (CD$_2$Cl$_2$, 300.13 MHz, 298 K): δ 8.83 (s, 2 H, H$_2$), 8.44 (d, $^4$J$_{H-H}$ = 1.9 Hz, 2 H, H$_6$), 7.63 (d, $^3$J$_{H-H}$ = 8.2 Hz, 2 H, H$_5$), 7.31 (dd, $^3$J$_{H-H}$ = 8.2 Hz, $^4$J$_{H-H}$ = 1.9 Hz, 2 H, H$_8$), 2.13 (bd, $^3$J$_{H-H}$ = 2.3 Hz, 6 H, H$_{11}$), 1.92 (brs, 3 H, H$_{12}$), 1.61 (brs, 6 H, H$_{13}$), 1.39 (s, 18 H, t-Bu). $^{13}$C{($^1$H) NMR (CD$_2$Cl$_2$, 75.48 MHz, 298 K): 172.8 (s, C$_9$), 156.7 (s, C$_{17}$), 156.1 (s, C$_{17}$), 145.0 (s, C$_4$), 138.7 (s, C$_5$), 134.5 (s, C$_8$), 125.5 (s, C$_5$), 124.1 (s, C$_6$), 50.1 (s, C$_{11}$), 49.1 (s, C$_{10}$), 36.6 (s, C$_{13}$), 36.0 (s, C(CH$_3$)$_3$), 31.3 (s, CH$_3$), 31.2 (s, C$_{12}$).
Figure S8. $^1$H and $^{13}$C($^1$H) NMR spectra of compound 8.
Synthesis of (C^N^P^A^C)AuSNp-2 (9)

Method 1: (C^N^P^A^C)AuCl (50.0 mg, 0.087 mmol), K_2CO_3 (24.0 mg, 0.174 mmol) and 2-naphthalenethiol (14.0 mg, 0.087 mmol) were reacted for 18 h to give the product as a pale yellow solid, it was purified by recrystallisation by slow evaporation of a dichloromethane isopropanol solution to give a pure product (40.7 mg, 0.058 mmol, 67%). Single crystals suitable for X-ray diffraction were obtained from slow evaporation of a dichloromethane/isopropanol (4:1) mixture. Anal. Calcd. For C_{35}H_{34}AuNS (697.69): C, 60.25%; H, 4.91%; N, 2.01%. Found: C, 60.07%; H, 4.97%; N, 2.16%.

^1H NMR (CDCl_2, 300.13 MHz, 298 K): 8.20 (s, 1 H, H_{11}), 7.88 (t, ^3J_{H-H} = 8.0 Hz, 1 H, H_{1}), 7.75 (d, ^3J_{H-H} = 7.4 Hz, 1 H, H_{16}), 7.70 (d, ^3J_{H-H} = 7.0 Hz, 1 H, H_{13}), 7.64 (m, 2 H, H_{18} + H_{19}), 7.55 (d, ^3J_{H-H} = 8.1 Hz, 2 H, H_{2}), 7.51 (d, ^3J_{H-H} = 8.0 Hz, 2 H, H_{3}), 7.43 (m, 2 H, H_{14} + H_{15}), 7.38 (d, ^4J_{H-H} = 2.0 Hz, 2 H, H_{5}), 7.21 (dd, ^3J_{H-H} = 8.1 Hz, ^4J_{H-H} = 2.0 Hz, 2 H, H_{6}), 1.00 (s, 18 H, t-Bu).

^13C(^1H) NMR (CDCl_2, 75.48 MHz, 298 K): δ 168.0 (s, C_{9}), 163.6 (s, C_{3}), 154.9 (s, C_{7}), 147.3 (s, C_{4}), 142.4 (s, C_{1}), 135.9 (s, C_{10/12/17}), 134.3 (s, C_{10/12/17}), 133.6 (s, C_{18/19}), 132.6 (s, C_{11}), 132.4 (s, C_{10/12/17}), 131.1 (s, C_{8}), 127.9 (s, C_{18/19} + C_{16}), 127.3 (s, C_{13}), 126.6 (s, C_{14/15}), 125.7 (s, C_{14/15}), 125.3 (s, C_{5}), 124.1 (s, C_{6}), 116.7 (s, C_{5}), 35.3 (s, C(CH_{3})_{3}), 30.9 (s, CH_{3}).
Figure S9. $^1$H and $^{13}$C{$^1$H} NMR spectra of compound 9.
2. X-ray crystallography

Crystals of each sample were mounted on a MiTeGen MicroMesh and fixed in the cold nitrogen stream on a diffractometer. Diffraction intensities were recorded at low temperature on an Oxford Diffraction Xcalibur-3/Sapphire3-CCD diffractometer, equipped with Mo-Kα radiation and graphite monochromator or Rigaku HG Saturn724+ (2×2 bin mode). Data were processed using the CrystAlisPro-CCD and –RED software or CrystalClear-SM Expert 3.1 b27, been the absorption correction done at this stage.\textsuperscript{S2}

The structures of all samples were determined by the direct methods routines with SHELXS or SHELXT programs and refined by full-matrix least-squares methods on F\textsuperscript{2} in SHELXL.\textsuperscript{S3} Non-hydrogen atoms were generally refined with anisotropic thermal parameters. Hydrogen atoms were included in idealised positions. No missed symmetry was reported by PLATON.\textsuperscript{S4} Refinement results are included in Table S1. Computer programs used in this analysis were run through WinGX.\textsuperscript{S5} Scattering factors for neutral atoms were taken from reference \textsuperscript{S6}. 
Table S1. Selected crystal data and structure refinement details for

|                  | (C^Npz^C)AuSPh (1) | (C^Npz^C)AuSC\textsubscript{6}H\textsubscript{4}Bu-4 (2) | (C^Npz^C)AuSC\textsubscript{6}H\textsubscript{4}N-2 (3) |
|------------------|---------------------|--------------------------------------------------------|-------------------------------------------------------|
| CCDC number      | 1495509             | 1495510                                                | 1495511                                               |
| Empirical formula| C\textsubscript{30}H\textsubscript{31}AuN\textsubscript{2}S    | C\textsubscript{30}H\textsubscript{31}AuN\textsubscript{2}S | C\textsubscript{30}H\textsubscript{31}AuN\textsubscript{2}S |
| Crystal dimensions (mm), colour | 0.065x0.14x0.35, red | 0.35x0.09x0.08, pale yellow | 0.048x0.033x0.019, yellow |
| F\textsubscript{w}  | 648.59              | 648.59                                                 | 700.66                                                |
| T (K)             | 140(2)              | 140(2)                                                 | 100(2)                                                |
| Crystal system, space group | triclinic; P\textsubscript{-1} | monoclinic; P 2\textsubscript{1}/m | Monoclinic; P2\textsubscript{1}/c |
| a(Å)              | 12.2846(2)          | 12.5213(8)                                             | 14.4504(6)                                           |
| b(Å)              | 14.7009(3)          | 6.9443(2)                                              | 16.8527(4)                                           |
| c(Å)              | 15.3192(2)          | 15.8652(6)                                             | 13.2971(4)                                           |
| \(\alpha\)(deg)  | 98.283(2)           | 90                                                     | 90                                                   |
| \(\beta\)(deg)   | 109.863(2)          | 110.495(5)                                             | 114.412(4)                                           |
| \(\gamma\)(deg)  | 93.835(2)           | 90                                                     | 90                                                   |
| Volume (Å\textsuperscript{3}) | 2554.81(8)          | 1292.19(11)                                            | 2948.71(19)                                          |
| Z                 | 4                   | 2                                                      | 4                                                    |
| \(D\textsubscript{calc}\) (Mg/m\textsuperscript{3}) | 1.686               | 1.677                                                  | 1.578                                                |
| absorption coefficient (mm\textsuperscript{-1}) | 5.861               | 5.794                                                  | 5.085                                                |
| F(000)            | 1280                | 640                                                    | 1392                                                 |
| \(\theta\) range for data collection (º) | 3.143 to 29.999     | 3.238 to 27.496                                         | 2.129 to 27.482                                       |
| data // restraints // params | 14889 // 0 // 613   | 3213 // 0 // 193                                        | 6719 // 0 // 352                                      |
| goodness-of-fit on \(F\textsuperscript{2}\)\textsuperscript{[a]} | 1.044               | 1.153                                                  | 1.031                                                |
| final R indexes [I>2\(\sigma\)(I)]\textsuperscript{[a]} | R1 = 0.0304, wR2 = 0.0651 | R1 = 0.0372, wR2 = 0.0798 | R1 = 0.0276, wR2 = 0.0531 |
| R indexes (all data)\textsuperscript{[a]} | R1 = 0.0484, wR2 = 0.0701 | R1 = 0.0456, wR2 = 0.0819 | R1 = 0.0379, wR2 = 0.0563 |
| largest diff peak and hole (e.Å\textsuperscript{-3}) | 1.661 and -1.297   | 2.630 and -0.993                                       | 0.746 and -1.277                                      |

\textsuperscript{[a]} R1 = \(\sum(\mid F_o \mid - \mid F_c \mid )/\sum\mid F_o \mid \); wR2 = \(\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2\)\textsuperscript{1/2}; goodness of fit = \(\sum[w(F_o^2 - F_c^2)^2]/(N\text{obs} - N\text{param})\)\textsuperscript{1/2}; \(w = [\sigma^2(F_o) + (g_1 P)^2 + g_2 P]\); P = \(\max(F_o^2;0 + 2F_c^2)/3\).
Table S1 (Cont). Selected crystal data and structure refinement details for

|                          | Red polymorph | Yellow polymorph | (C^N^P^A^C)AuSnp-2 (5) | (C^N^P^A^C)AuScoum (7) | (C^N^C)AuSnp-2 · CH₂Cl₂ (9 · CH₂Cl₂) |
|--------------------------|---------------|-----------------|------------------------|------------------------|----------------------------------------|
| CCDC number              | 1495513       | 1495514         | 1495515                | 1495516                |                                        |
| Empirical formula        | C₃₅H₃₃AuN₂S  | C₃₅H₃₃AuN₂S    | C₃₅H₃₃AuN₂O₂S         | C₃₅H₃₅AuCl₂NS         |                                        |
| Crystal dimensions (mm), colour | 0.074×0.032×0.012, red | 0.235×0.049 × 0.014, yellow | 0.2×0.2×0.014, orange | 0.15×0.02×0.02, yellow |                                        |
| F_w                      | 698.65        | 698.65          | 730.65                 | 782.58                 |                                        |
| T (K)                    | 100(2)        | 140(2)          | 140(2)                 | 100(2)                 |                                        |
| Crystal system, space group | monoclinic; P 2₁/n | monoclinic; P 2₁/n | monoclinic; P 2₁/n | triclinic; P-1 |                                        |
| a(Å)                     | 15.2707(4)    | 6.36960(10)     | 9.9308(2)              | 9.7612(4)              |                                        |
| b(Å)                     | 6.3728(2)     | 17.2085(3)      | 17.6575(4)             | 11.4058(8)             |                                        |
| c(Å)                     | 29.0818(8)    | 25.1788(5)      | 16.8512(4)             | 16.1645(11)            |                                        |
| α(deg)                   | 90            | 90              | 90                     | 89.924(5)              |                                        |
| β(deg)                   | 101.425(3)    | 91.386(2)       | 103.620(2)             | 74.521(4)              |                                        |
| γ(deg)                   | 90            | 90              | 90                     | 65.656(4)              |                                        |
| Volume (Å³)              | 2774.08(14)   | 2759.07(8)      | 2871.81(11)            | 1568.0(2)              |                                        |
| Z                        | 4             | 4               | 4                      | 2                      |                                        |
| D_caled (Mg/m³)          | 1.673         | 1.682           | 1.69                   | 1.658                  |                                        |
| Absorption coefficient (mm⁻¹) | 5.405      | 5.434           | 5.23                   | 4.955                  |                                        |
| F(000)                   | 1384          | 1384            | 1448                   | 776                    |                                        |
| θ range for data collection (°) | 2.3 to 29.572 | 2.502 to 27.482 | 3.127 to 29.801        | 2.635 to 27.538        |                                        |
| Data // restraints // params | 7378 // 0 // 349 | 6269 // 0 // 343 | 7041 // 0 // 368       | 7141 // 0 // 376       |                                        |
| Final R indexes [I>2σ(I)][a] | R1 = 0.0527, wR2 = 0.1045 | R1 = 0.0237, wR2 = 0.0504 | R1 = 0.0241, wR2 = 0.0405 | R1 = 0.0453, wR2 = 0.1147 |                                        |
| R indexes (all data)[a]  | R1 = 0.0635, wR2 = 0.1103 | R1 = 0.0282, wR2 = 0.052 | R1 = 0.0375, wR2 = 0.0429 | R1 = 0.0488, wR2 = 0.1179 |                                        |
| Largest diff peak and hole (eÅ⁻³) | 3.026 and -4.187 | 1.344 and -0.716 | 1.02 and -0.727        | 3.213 and -2.257        |                                        |

[a] R1 = Σ(|F_o| - |F_c|)/Σ|F_o|; wR2 = [Σw(F_o² - F_c²)²/ΣwF_o²]¹/²; goodness of fit = [Σ[w(F_o² - F_c²)²]/N_{obs} - N_{param})]¹/²; w = [σ²(F_o) + (g₁P)^2 + g₂P]⁻¹; P = [max(F_o²,0 + 2F_c²)/3].
**Figure S10:** Structure of (C^N^pz^C)AuSC₆H₄Bu-4 (2). Au1-S1 2.2781(9), Au1-N1 2.017(2), Au1-C6 2.090(4), Au1-C16 2.090(4), N1-Au1-S1 171.62(8), C6-Au1-N1 80.4(1), C16-Au1-N1 80.5(1), C6-Au1-S1 107.9(1), C16-Au1-S1 91.2(2), Au1-S1-C25 112.7, torsion Au1-S1-C25-C26 77.2(3).

**Figure S11:** Structure of (C^N^pz^C)AuSC₆H₄N-2 (3). Au1-S1 2.289(1), Au1-N1 2.009(4), Au1-C6 2.104(4), Au1-C16 2.090(4), N1-Au1-S1 174.0(1), C6-Au1-N1 80.2(2), C16-Au1-N1 80.7(2), C6-Au1-S1 104.9(1), C16-Au1-S1 94.1(1), Au1-S1-C25 109.4(1), torsion Au1-S1-C25-N3 49.8(4).
Figure S12: Structure of (C^N^p^z^C)AuSCoum(7). Au1-S1 2.2785(9), Au1-N1 2.009(2), Au1-C6 2.097(3), Au1-C16 2.084(3), N1-Au1-S1 173.88(7), C6-Au1-N1 80.2(1), C16-Au1-N1 80.7(1), C6-Au1-S1 105.87(8), C16-Au1-S1 93.19(8), Au1-S1-C25 111.1(1), torsion Au1-S1-C25-N3 35.2(3).

Figure S13: Structure of (C^N^C)AuSNp-2·CH_2Cl_2 (9·CH_2Cl_2). Au1-S1 2.282(2), Au1-N1 2.019(5), Au1-C7 2.078(5), Au1-C17 2.070(5), N1-Au1-S1 170.7(1), C7-Au1-N1 80.4(2), C17-Au1-N1 80.7(2), C7-Au1-S1 108.7(1), C17-Au1-S1 90.3(2), Au1-S1-C26 112.0(2), torsion Au1-S1-C26-C35 72.5(5).
Figure S14. Crystal packing and intermolecular distances of (C^Npz^C)AuSPh (1red) (side and top views). (a), (b): Stacking of Au(1)···Au(1) molecules. (c), (d): Stacking of Au(2)···Au(2) molecules.

Figure S15. Crystal packing and intermolecular distances of the yellow polymorph of (C^Npz^C)AuSPh (1yellow) (a: side and b: top view).
Figure S16. Crystal packing and intermolecular distances of (C^Npz^C)AuSC₆H₄Bu-4 (2) (a: side and b:top view).

Figure S17. Crystal packing and intermolecular distances of (C^Npz^C)AuSC₅H₄N-2 (3) (a: side and b:top view).

Figure S18. Crystal packing and intermolecular distances of (C^Npz^C)AuSNp-2 (5:red) (a: side and b:top view).
Figure S19. Crystal packing and intermolecular distances of (C^NpzC)AuSNp-2 (5yellow) (a: side and b: top view).

Figure S20. Crystal packing and intermolecular distances of (C^NpzC)AuSCoum (7) (a: side and b: top view).
Figure S21. Crystal packing and intermolecular distances of (C^N^C)AuSNp-2 · CH₂Cl₂ (9 · CH₂Cl₂) (a: side and b: top view).
3. Aggregation of (C^N^Pz^C)AuX complexes in solution

3.1 Diffusion NMR measurements

$^1$H PGSE NMR measurements were performed by using a double stimulated echo sequence with longitudinal eddy current delay on a Bruker DRX 300 spectrometer equipped with a smartprobe and Z-gradient coil, at 297K without spinning. In the typical PGSE experiment, the dependence of the resonance intensity ($I$) on a constant waiting time and on a varied gradient strength $G$ is described by the following equation:

$$\ln \frac{I}{I_0} = \left( \frac{2}{3} \right) D_t \left( \frac{G^2}{\Delta} \right)$$

where $I$ is the intensity of the observed spin echo, $I_0$ the intensity of the spin echo in the absence of gradient, $D_t$ the self-diffusion coefficient, $\Delta$ the delay between the midpoints of the gradients, $\delta$ the length of the gradient pulse, and $\gamma$ the magnetogyracic ratio. The shape of the gradients was rectangular, their length $\delta$ was 4–5 ms, and their strength $G$ was varied during the experiments. All spectra were acquired for 64K points and a spectral width of 6200 Hz and processed with a line broadening of 1.0.

The semi-logarithmic plots of $\ln(I/I_0)$ versus $G^2$ were fitted by using a standard linear regression algorithm. Different values of $G$ and number of transients were used for different samples.

The self-diffusion coefficient $D_t$, which is directly proportional to the slope of the regression line obtained by plotting $\ln(I/I_0)$ versus $G^2$, was estimated by evaluating the proportionality constant for a sample of HDO (5%) in D$_2$O (known diffusion coefficients in the range 274–318 K)$^{57}$ under the exact same conditions as the sample of interest. The solvent was taken as internal standard. The actual concentration of the samples was measured by relative integration to an external standard. The relationship between $D_t$ and hydrodynamic dimensions is expressed by the modified Stokes-Einstein equation:

$$D_t = \frac{kT}{f c \sqrt[3]{a b d}}$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the solution viscosity, $c$ is the “size factor”, which depends on the solute-solvent radius ratio and $f$ is the “shape factor”, which takes into account the deviation from sphericity of the diffusing molecule. $a$, $b$ and $d$ are the semi-axes of the ellipsoid that better approximates the shape of the diffusing molecule.$^{88}$

Structural parameter values ($P = f c \sqrt[3]{a b d} = kT / D_t$) were derived from the measured $D_t$ values at different concentration in CD$_2$Cl$_2$ and the data are collected in Table S3.1 and Figure S22.

Assuming a monomer/dimer equilibrium, the observed $P$ values can be treated as the average between the parameters of both monomer ($P_M$) and dimer ($P_D$), according to the following relationship:

$$P_i = P_M x_M + P_D x_D$$
where $x_M$ and $x_D$ are the molar fractions of monomer and dimer at a given concentration. $P_M$ and $P_D$ parameters are depending on the dimensions of monomer ($a_M$, $b_M$, $d_M$), dimer ($a_D$, $b_D$, $d_D$) and solvent ($r_{sol}$, approximated at the van der Waals radius of CD$_2$Cl$_2$). $P_M$ parameters can be derived from X-ray structures of monomers, by approximating their shape to ellipsoids. $P_D$ parameters have been calculated by using packing data derived by X-ray diffraction (see below).

Table S3.1. Diffusion coefficient ($D$), structural parameters ($P$) and estimated percentage of dimers ($\%_D$) for (C$^\text{N}_2$Pz$^\text{C}$)AuCl, (C$^\text{N}_2$Pz$^\text{C}$)AuSPh and (C$^\text{N}_2$Pz$^\text{C}$)AuSNp-2 as a function of concentration in CD$_2$Cl$_2$ at 297 K.

| $c$ (mM) | $10^{10}D$ (m$^2$ s$^{-1}$) | $P$ (Å) | mol-% dimer |
|----------|----------------------------|---------|-------------|
| (C$^\text{N}_2$Pz$^\text{C}$)AuCl $P_M=27.9$ Å; $P_D=39.6$ Å |
| 0.8      | 11.0                       | 27.8    | <1          |
| 4.3      | 11.0                       | 27.8    | <1          |
| 11.8     | 10.9                       | 28.0    | 1.5         |
| 23.9     | 10.6                       | 28.8    | 13          |
| (C$^\text{N}_2$Pz$^\text{C}$)AuSPh $P_M=29.3$ Å; $P_D=39.8$ Å |
| 2.9      | 10.4                       | 29.5    | 2           |
| 8.8      | 10.2                       | 29.9    | 5           |
| 17.5     | 10.1                       | 30.3    | 9           |
| 22.3     | 10.1                       | 30.4    | 10          |
| 23.5     | 10.0                       | 30.5    | 11          |
| 53.8     | 9.8                        | 31.3    | 19          |
| 55.5     | 9.7                        | 31.5    | 21          |
| (C$^\text{N}_2$Pz$^\text{C}$)AuSNp-2 $P_M=30.4$ Å; $P_D=44.0$ Å |
| 0.6      | 10.0                       | 30.7    | 2           |
| 1.3      | 9.8                        | 31.1    | 5           |
| 1.9      | 9.8                        | 31.2    | 6           |
| 4.1      | 9.7                        | 31.5    | 8           |
| 19.3     | 9.5                        | 32.3    | 14          |
| 42.6     | 9.3                        | 32.8    | 18          |
| 72.5     | 9.0                        | 34.0    | 26          |
Figure S22. Trend of $P$ values versus concentration for (C$^{N}$Pz$^{+}$C)AuCl, (C$^{N}$Pz$^{+}$C)AuSPh and (C$^{N}$Pz$^{+}$C)AuSNp$^{-2}$ (CD$_2$Cl$_2$, 297 K).

3.2 NMR chemical shift

Figure S23. Evolution of the aromatic region of the $^1$H NMR spectrum of (C$^{N}$Pz$^{+}$C)AuSNp-2 as a function of the concentration in CD$_2$Cl$_2$. 
Figure S24. Trend of $\Delta\delta$(ppm) for (C$^{N^2z}$C)AuCl, (C$^{N^2z}$C)AuSPh and (C$^{N^2z}$C)AuSNp-2 (CD$_2$Cl$_2$, 297 K).

The amount of dimers was quantified by using standard equations for monomer-dimer equilibrium:  

$$i = m \cdot f_M + d \cdot f_D = \frac{[A]}{[A]_0} + \frac{2[A_i]}{[A]_0}$$

$$i = m + (d - m) \left(1 + 8K[A]_0\right)^{1/2} \frac{1}{2K[A]_0} + 1$$

where $f_m$ and $f_d$ are the molar fractions of monomers and dimers, $\delta_m$ and $\delta_d$ are the limit chemical shift values of monomer and dimer, respectively, $K$ is the association constant. After fitting chemical shift versus concentration trends, the molar fractions of dimers were obtained as:

$$f_D = -1 + \frac{2[A_i]}{[A]_0 + \sqrt{1 + 8K[A]_0} \frac{1}{4K}}$$

Data are reported in Table S3.2.
Table S3.2. Molar fraction of dimers derived by fitting chemical shift vs. concentration trends for \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuCl},\) \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuSPh}\) and \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuSNp-2}\) (CD$_2$Cl$_2$, 297 K).

| C (mM) | \(f_D\) (%) |
|--------|--------------|
| \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuCl}\ K=3.6 \text{ M}^{-1}\) | \(0.8\) | <1 |
|        | \(4.3\)     | 3  |
|        | \(11.8\)    | 7  |
|        | \(23.9\)    | 13 |
| \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuSPh}\ K=1.0 \text{ M}^{-1}\) | \(2.9\) | <1 |
|        | \(8.8\)     | 2  |
|        | \(17.5\)    | 3  |
|        | \(22.3\)    | 4  |
|        | \(23.5\)    | 4  |
|        | \(53.8\)    | 9  |
|        | \(55.5\)    | 9  |
| \((\text{C}^\text{N}\text{Pz}\text{C})\text{AuSNp-2}\ K=1.8 \text{ M}^{-1}\) | \(0.6\) | <1 |
|        | \(1.3\)     | <1 |
|        | \(1.9\)     | <1 |
|        | \(4.1\)     | 1  |
|        | \(19.3\)    | 6  |
|        | \(42.6\)    | 12 |
|        | \(72.5\)    | 18 |
4. Photophysical Properties

UV–visible absorption spectra were recorded using a Perkin-Elmer Lambda 35 UV/vis spectrometer. Excitation and emission spectra were measured using a (TCSPC) FluoroLog Horiba Jobin Yvon spectrofluorometer or an Acton Research Corporation, Spectrapro 2500i 0.500m imaging triple grating monochromator/spectrograph. Lifetime measurements were conducted with a Datastation HUB-B with a nanoLED controller and software DAS6. The nanoLEDs employed for lifetime measurements were of 370 nm with pulse lengths of 0.8–1.4 ns. Quantum yields in the solid state were measured upon excitation at 370-400 nm using an F-3018 integrating sphere mounted on a Fluorolog 3-11 Tau-3 spectrofluorimeter. In solution, relative quantum yields were determined with reference to [Ru(bpy)$_3$]$_{2+}$ in H$_2$O ($\phi_{stn} = 2.8\%$) in accordance with ref. S10.

Polymeric sample preparation: PMMA, PS and PVK were purchased from commercial sources. Thin films were prepared by spin/drop cast from a solution of the corresponding complex and the amount of polymer that correspond to reach the concentration in each case. Films were then placed under vacuum for 10 minutes to remove residual solvent.

Cryogenic time resolved photoluminescence (ICCD and TCSPC)

ICCD: An electrically gated intensified CCD (ICCD) camera (Andor iStar DH740 CCI-010) with a calibrated grating spectrometer (Andor SR303i) were used for the time resolved PL spectra. 400nm laser light pulsed at 1 KHz was used to pump the sample. This was produced from the second harmonic generation of a 800nm femtosecond laser using a BBO crystal. The fundamental output had a 80 fs pulse width and 1.5 eV pulse energy from a Ti:Sapphire laser system (Spectra Physics Solstice). Time resolution of the emission was achieved by changing the delay of the gate relative to the 1 KHz pulsed pump laser. The minimum gating width was ~2.5 ns. A 495 nm long pass filter was used to remove any scattered light from the pump laser. This setup was used for the green emitting film.

Time correlated single photon counting: A pulsed 407 nm laser was used to photo-excite the samples, with pulse width <200 ps and a rep rate of 2.5MHz. The detector was a Si based single photon avalanche photodiode. The instrument response function was ~200 ps also. A 495 nm long pass filter was used as in the ICCD. This setup was used for the red emitting film.

Cryogenics: samples were cooled with liquid Helium in a flow cryostat with a temperature controller.
| Complex                        | Absorbance [nm] (10^3 ε/M^-1 cm^-1)                                                                 |
|-------------------------------|---------------------------------------------------------------------------------------------------|
| (C^N^pz^C)AuPh 1              | 320 (9.1), 344 (6.2), 365 (4.3), 421 (4.3), 441 (4.3), 470 (1.4), long tail up to 530.          |
| (C^N^pz^C)AuSCH_{3}Bu-4 2     | 321 (10.0), 348 (6.0), 421 (4.1), 440 (5.0), 471 (1.7), long tail up to 530.                   |
| (C^N^pz^C)AuSCH_{3}N-2 3      | 321 (11.5), 349 (8.9), 425 (5.1), 443 (5.0), 470 (1.1), tail up to 500.                        |
| (C^N^pz^C)AuSNp-1 4           | 320 (10.3) broad shoulder, 419 (3.4), 439 (3.4), 470 (0.8), long tail up to 530.              |
| (C^N^pz^C)AuSNp-2 5           | 323 (15.9), 348 (11.0), 420 (7.3), 440 (7.3), 469 (2.1), long tail up to 530.                 |
| (C^N^pz^C)AuSQuin-2 6         | 322 (13.6), 351 (11.9), 424 (5.9), 445 (5.2), 470 (1.8), tail up to 515.                     |
| (C^N^pz^C)AuSCoum 7           | 324 (23.2), 373 (17.3), 423 (7.8), 442 (7.5), 471 (2.3), long tail up to 530.                 |
| (C^N^pz^C)AuSAld 8            | 322 (7.2), 348 (4.4), 395 (2.4), 423 (2.9), 445 (3.1), 469 (0.8), tail up to 530.            |
| (C^N^pz^C)AuSNp-2 9           | 319 (13.8), 368 (8.0), 384 (7.6), 405 (6.1), 470 (0.3).                                      |
Table S4.2 PL properties of the complexes in the solid state.

| Complex                   | $\lambda_{em}$ / nm ($\lambda_{ex}$ / nm)          | 298 K                        | 77 K                          |
|---------------------------|----------------------------------------------------|-------------------------------|-------------------------------|
| (C^N^p^z^A^C)AuSPh 1      | 574 (350-500)                                      |                               | 558$_{\text{max}}$, 593$_{\text{sh}}$ (360-500) |
| (C^N^p^z^A^C)AuSC$_6$H$_4$Bu-4 2 | 600 (350-500)                                      |                               | 548$_{\text{max}}$, 593$_{\text{sh}}$ (350-500) |
| (C^N^p^z^A^C)AuSC$_6$H$_2$N-2 3 | 492 (300-450) [a]                                 |                               | 534$_{\text{max}}$, 579$_{\text{sh}}$ (300-480, 360$_{\text{max}}$, 430$_{\text{sh}}$, 460$_{\text{sh}}$) |
| (C^N^p^z^A^C)AuSNp-1 4    | 618 (360br-510$_{\text{max}}$)                    |                               | 547$_{\text{sh}}$, 630 (350-460, 518) |
| (C^N^p^z^A^C)AuSNp-2 5    | 650 (350-600, 370$_{\text{max}}$, 480$_{\text{sh}}$) |                               | 650 (360-550)                 |
| (C^N^p^z^A^C)AuSQuin-2 6  | [b]                                                |                               | 519$_{\text{sh}}$, 532$_{\text{max}}$, 553$_{\text{sh}}$ (350-470) |
| (C^N^p^z^A^C)AuSCoum 7    | [b]                                                |                               | 540, 577, 621 (360-550)       |
| (C^N^p^z^A^C)AuSAd 8      | 633 (370-470)                                      |                               | 630 (360, 470, 500-570br)     |
| (C^N^p^z^A^C)AuSNp-2 9    | [b]                                                |                               | 514$_{\text{max}}$, 544$_{\text{sh}}$ (400-450) |

[a] Weak emission [b] Non-emissive.
Table S4.3 PL properties of complexes 1-8 in 10% PMMA matrix at 298 K

| Complex                        | λ_{em} / nm (λ_{ex} / nm) | τ / ns [a] | Φ / % (λ_{ex} / nm) [b] |
|-------------------------------|---------------------------|------------|-------------------------|
| (C^Npz^C)AuSPh 1              | 530sh, 616_{max} (320-390); 616 (500) | 355.2±4.4(95%), 44.5±2.0(5%) | < 1                     |
| (C^Npz^C)AuSC,H_{Bu}-4 2      | 622 (340-580, 370sh, 510_{max}) | 345.6±3.9(96%), 38.2±3.9(5%) | 3.4 (510)               |
| (C^Npz^C)AuSC,H_{N-2} 3       | 540_{max}, 573sh, 614sh (320-350, 400, 420) [c] | 342.2±5.7(96%), 25.0±2.1(5%) | < 1                     |
| (C^Npz^C)AuSNp-1 4            | 516sh, 615_{max} (350-580, 515_{max}) | 368.8±3.0(95%), 47.7±1.2(5%) | 1.8 (515)               |
| (C^Npz^C)AuSNp-2 5            | 611 (320-560, 380sh, 470_{max}) | 366.9±6.9(94%), 51.8±2.5(6%) | 3.7 (480)               |
| (C^Npz^C)AuSQuin-2 6          | 508 (340-450, 390_{max}) | 369.5±4.8(95%), 46.4±1.7(5%) | 4.7 (390)               |
| (C^Npz^C)AuSCoum 7            | 595 (330-450) | 376.0±1.2(94%), 56.7±4.8(6%) | < 1                     |
| (C^Npz^C)AuSAd 8              | 642 (350-600, 320sh, 470sh, 550_{max}) | 374.3±5.7(95%), 46.1±2.3(5%) | < 1                     |
| (C^Npz^C)AuSNp-2 9            | ~480 [b]                  |            |                         |

[a] Measured at λ_{em}^{max}. [b] Determined by absolute methods using an integrating sphere. [c] Weak emission.
### Table S4.4A Steady State properties of complex (C^Npz^C)AuSNp\textsuperscript{-2} at 298 K in different polymeric matrix

| Matrix         | \( \lambda_{em} \) / nm (\( \lambda_{ex} \) / nm) | \( \tau_{av} \) / ns \[a\] | \( \phi \) / % (\( \lambda_{ex} \) / nm) \[b\] |
|----------------|---------------------------------|----------------|---------------------------------|
| 1% in PMMA     | 600 (350-540, 375\textsubscript{max}, 450\textsubscript{sh}, 490\textsubscript{sh}) weak | 82.2          | < 1                             |
| 5% in PMMA     | 611 (320-560, 380\textsubscript{sh}, 470\textsubscript{max}) | 186           | 1.9 (480)                       |
| 10% in PMMA    | 619 (350-575, 380\textsubscript{sh}, 500\textsubscript{max}) | 204           | 3.7 (480)                       |
| 20% in PMMA    | 628 (350-580, 505\textsubscript{max}) | 194           | 4.1 (480)                       |
| 30% in PMMA    | 630 (350-590, 380\textsubscript{sh}, 505\textsubscript{max}) | 204           | 5.0 (480)                       |
| 40% in PMMA    | 644 (350-600, 540\textsubscript{max}) | 198           | 6.6 (480)                       |
| 50% in PMMA    | 649 (350-650, 520\textsubscript{max}) | 267           | 11.2 (480)                      |
| 10% in PS      | 626 (350-580, 380\textsubscript{sh}, 515\textsubscript{max}) | 223           | 4.4 (480)                       |
| 10% in PVK     | 632 (350-580, 380\textsubscript{sh}, 505\textsubscript{max}) | 226           | 3.3 (480)                       |

[a] Measured at \( \lambda_{max}^{em} \). Fit to tri-exponential decay functions in all cases. Only the average lifetime is given and used for calculate the radiative and non-radiative constants. [b] Determined by absolute methods using an integrating sphere.

### Table S4.4B Steady State properties of complex (C^Npz^C)AuSQuin\textsuperscript{-2} at 298 K in different polymeric matrix

| Matrix | \( \lambda_{em} \) / nm (\( \lambda_{ex} \) / nm) | \( \tau_{av} \) / ns \[a\] | \( \phi \) / % (\( \lambda_{ex} \) / nm) \[b\] |
|--------|---------------------------------|----------------|---------------------------------|
| 10% in PMMA | 508 (340-450, 390\textsubscript{max}) | 28           | 4.7 (390)                       |
| 30% in PMMA | 508 (340-450, 390\textsubscript{max}) | 30           | 1.2 (390)                       |
| 50% in PMMA | 517\textsubscript{br} (350-450) | 94           | < 1 (390)                       |

[a] Measured at \( \lambda_{max}^{em} \). Fit to tri-exponential decay functions in all cases. Only the average lifetime is given and used for calculate the radiative and non-radiative constants. [b] Determined by absolute methods using an integrating sphere.
| Cmplx | T / K | λ_{em} / nm (λ_{ex} / nm) | τ [μs] | Φ / % (λ_{ex} / nm) |
|-------|-------|--------------------------|--------|---------------------|
| 1     | 298   | 540 sh, 600_{max} (370-480) (10^{-2} M) | 28.7±1.1 μs [600] |
|       | 77    | 539 sh, 555 sh, 616_{max} (320-480) (10^{-2} M) // 616 nm (340-500) (10^{-2} M) | 106.8±2.6 μs [540], 30.2±1.9 μs [616] |
| 2     | 298   | 680 (350-500, 360_{max}, 430 sh) (10^{-4} M) | 17.1±0.1 ns [680] | 1.94×10^{-4} (436) |
|       | 77    | 516_{max}, 546 sh (320-350, 400, 420) (10^{-4} M) | 11.0±0.1(40), 156.4±5.8(60) ns [516] |
| 3     | 298   | 540_{max}, 580 sh (350-600, 370_{max}, 480 sh) (10^{-4} M) | 84.3±1.5 μs (10^{-4} M) [540] |
| 4     | 298   | 685 (400-600, 530_{max}) (10^{-4} M) | 8.7±0.1 ns [689] | 5.58×10^{-3} (436) |
|       | 77    | 516 sh, 529_{max}, 565 sh (320-420) (10^{-5} M) // 516 sh, 529 sh, 599_{max} (320-550) (10^{-4} M) // 529 sh, 617 (320-550) (10^{-2} M) | 43.8±1.0 μs (10^{-2} M) [617] |
| 5     | 298   | 680 (300-480) (10^{-2} M) // 683 (300-600, 540_{max}) (10^{-2} M) | 17.3±0.1 ns [680] | 2.62×10^{-3} (436)[e] |
|       | 77    | 605 (360-460) (10^{-4} M) // 614 (540_{max}) (10^{-2} M) | 35.3±0.4 μs [614] |
| 6     | 298   | 508 (340-420) (10^{-2} M) | 10.6±0.2(14), 211.2±6.4(86) ns [508] |
|       | 77    | 544_{max}, 579 sh (300-470) (10^{-4} M) | 118.4±3.7 μs [540] |
| 7     | 298   | 621 (350-570, 370 sh, 520_{max}) (10^{-2} M) | 2.34×10^{-3} (436) |
|       | 77    | 587_{max} (320-470, 514_{max}) (10^{-2} M) // 541_{max}, 574 sh (320-420) (10^{-4} M) | 63.8±1.0 μs [541] |
| 8     | 298   | 670 (350-470) (10^{-4} M) // 665 (360-600, 500_{max}) (10^{-2} M) | 16.2±0.07 ns [670] | 1.45×10^{-2} (436) |
|       | 77    | 540 sh, 609 (320-480, 365, 430, 450) (10^{-4} M) // 629 (320-570, 370, 460) (10^{-2} M) | 12.6±0.2 μs [629] |
| 9     | 298   | 517_{max}, 552 sh (300-460, 370_{max}, 410 sh, 440 sh) (10^{-4} M) | 50.2±0.1 μs [517] |

[a] Relative to standard. b) Non-emissive. c) Same at 10^{-3} M. d) Very weak at 10^{-5} M. e) 2.30×10^{-3} (372), 2.47×10^{-3} (419), 2.62×10^{-3} (436), 9.59×10^{-3} (472), 1.70×10^{-2} (495).
Table S4.6 Steady State emission of (C^Npz^C)AuSC$_2$H$_4$Bu-4 2 in different solvents.

| Solvent     | Conc.   | 298 K                                      | 77 K                          |
|-------------|---------|-------------------------------------------|-------------------------------|
| CH$_2$Cl$_2$| $10^{-4}$ M | 680 (350-500, 360$_{max}$, 430sh)         | 515, 535sh, 605 (320-550, 365$_{max}$, 440sh) |
|             | $10^{-2}$ M | 680 (350-600, 540$_{max}$)                | 622 (500)                     |
| THFMe-2     | $10^{-4}$ M | weak                                      | 520, 591$_{max}$ (380-470)    |
|             | $10^{-2}$ M | 660 (360-450, 540)                       | 522, 542sh, 584 (380-470)     |

Table S4.7 Steady State emission of (C^Npz^C)AuSNp-2 5 in different solvents.

| Solvent     | Conc.   | 298 K                                      | 77 K                          |
|-------------|---------|-------------------------------------------|-------------------------------|
| CH$_2$Cl$_2$| $10^{-4}$ M | 680 (300-480)                             | 605 (360-460)                 |
|             | $10^{-2}$ M | 683 (300-600, 540$_{max}$)                | 614 (540$_{max}$)             |
| THFMe-2     | $10^{-4}$ M | 663 (300-500, 365$_{max}$, 440sh)         | 520, 591$_{max}$ (360-450)    |
|             | $10^{-2}$ M | 664 (350-600, 540$_{max}$)                | 520, 585$_{max}$ (360-460)    |
| Toluene     | $10^{-4}$ M | 642 (300-500, 370$_{max}$, 430sh)         | 604 (350-450)                 |
|             | $10^{-2}$ M | 642 (350-600, 540$_{max}$)                | 600 (540$_{max}$)             |

Figure S25. Microscope images of crystals of 5. Main picture: crystals under white light, showing both yellow and red polymorphs. Inset: the same sample under UV light.
Figure S26. UV-Vis spectra of (C^Npz^C)AuSNp-2 (5) in CH₂Cl₂ at different concentrations.

Figure S27. Normalized Emission spectra of complex (C^Npz^C)AuSC₆H₄Bu-4 2 in the solid state.

Figure S28. Normalized Emission spectra of complex (C^Npz^C)AuSNp-2 5red in the solid state.
Figure S29. Emission spectra of complex (C^Npz^C)AuSQuin 6 in the solid state.

Figure S30. Emission spectra of complex (C^Npz^C)AuSCoum 7 in the solid state.

Figure S31. Normalized Emission spectra in CH₂Cl₂ (10⁻⁴ M) at 77 K of complexes (C^Npz^C)AuSR (R = C₆H₅Bu-4 2, C₅H₅N-2 3, Quin 6) and (C^Npz^C)AuSnp-2 9.
**Figure S32.** Normalized Emission spectra of complex \((C^Npz^C)AuSNp-2\) 5 in \(CH_2Cl_2\) at different concentrations.

**Figure S33:** Emission (solid lines) and excitation (doted lines) spectra of complex \((C^Npz^C)AuSCoum\) 7 in \(CH_2Cl_2\) at different concentrations.

**Figure S34.** Normalized Emission spectra of complex \((C^Npz^C)AuSAd\) 8 in \(CH_2Cl_2\) at different concentrations.
**Figure S35.** Emission spectra of complex \((C^NpzC)AuNp-2 \textbf{5red} (50 \text{ wt.-\%})\) in a PMMA drop-cast film, showing superimposable spectra for the prompt and delayed (200-250 ns) emissions.

**Figure S36.** Normalized emission profile (left) and integrated emission intensity at 630 nm (right) of complex \((C^NpzC)AuNp-2 \textbf{5red} (50 \text{ wt.-\%})\) in a drop-cast PMMA film at different temperatures, both in the range 0-300 ns.
**Figure S37.** Emission profile (left) of complex (C^NpzA)AuSNp-2 5 in solution (10%) and temporal decay of the emission intensity at different wavelengths (right). In all cases, a lifetime of around 28 ns is found. The solution tested was 1mg/ml in Chlorobenzene prepared in an argon environment in a cleaned 1mm path length quartz cuvette.

| Temperature / K | τ(ns)       | Standard Error (ns) |
|-----------------|-------------|---------------------|
| 4               | 18000 (18 µs) | 3500                |
| 50              | 14000 (14 µs) | 2000                |
| 100             | 10000 (10 µs) | 1000                |
| 150             | 4400 (4.4 µs) | 200                 |
| 200             | 1800 (1.8 µs) | 40                  |
| 250             | 720         | 10                  |
| 300             | 328         | 7                   |
5. Theoretical Calculations

All structures were optimised using density functional theory, within the approximation of the PBE0 exchange and correlation functional\textsuperscript{511} as implemented within the ORCA quantum chemistry program.\textsuperscript{512}

A def2-SVP basis set\textsuperscript{513} was used throughout. To account for the weak π−π interactions, the calculations were supplemented with Grimme’s D3 dispersion correction with the Becke–Johnson damping scheme.\textsuperscript{514}

The absorption spectrum of complex 5 was calculated using pertubrative spin orbit coupling TDDFT (pSOC-TDDFT)\textsuperscript{515} calculated using the ZORA Hamiltonian\textsuperscript{516} as implemented within ADF.\textsuperscript{517}

The PBE0 exchange and correlation functional was used, and a DZP basis set for all atoms, except gold, for which a TZP basis was used. All emission energies were calculated using both uDFT and pSOC-TDDFT within ADF.

| Table S5.1 Experimental vs. optimized geometries for (C^Npz^C)AuSPh. |
|-------------------------------|-----------------|-----------------|-----------------|
| Bond lengths / Å              | Experimental    | Ground state    | Excited state   |
| N-Au                          | 2.006           | 2.03            | 2.05            |
| C-Au                          | 2.086           | 2.10            | 2.12            |
| Au-C                          | 2.091           | 2.11            | 2.13            |
| Au-S                          | 2.273           | 2.32            | 2.31            |

| N-Au-S-C torsion angle / °   | Experimental    | Ground state    | Excited state   |
|-------------------------------|-----------------|-----------------|-----------------|
| 50.14                         | 48.15           | 17.28           |
**Table S5.2** Experimental vs. optimized geometries for (C^N^pz-C)AuSNp-2

| Bond lengths / Å | Experimental | Ground state | Excited state |
|------------------|--------------|--------------|---------------|
| N-Au             | 2.014        | 2.03         | 2.08          |
| C-Au             | 2.086        | 2.10         | 2.13          |
| Au-C             | 2.095        | 2.12         | 2.13          |
| Au-S             | 2.284        | 2.31         | 2.33          |

| N-Au-S-C torsion angle / º | Experimental | Ground state | Excited state |
|----------------------------|--------------|--------------|---------------|
|                            | 56.5         | 58.28        | 16.30         |

| π···π distance / Å | Experimental | Computed |
|-------------------|--------------|----------|
| **5red**          | 3.235        | 3.26     |
| **5yellow**       | 3.45         | 3.482    |

**Figure S38.** Optimised Structures of the monomer, the pz-pz overlap dimer and the pz-S overlap dimer.
Figure S39. Experimental (black line) vs. Calculated (red line) UV-Vis spectra for 5.

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