SUPPORTING INFORMATION

Mechanochemical synthesis of mononuclear gold(I) halide complexes of diphosphine

ligands with tunble luminescent properties

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21. Synthesis and characterisation

Complex	Amount of diphos	CH ₂ Cl ₂		Due last solution	$V_{11}^{(0)}$
	ligand (mg/mmol)	(µL)	$\eta \ (\mu L/mg)$	Product color	Y 1eld (%) ^a
1	289 / 0.50	110	0.25	white	94 (87) ¹⁻²
2	289 / 0.50	115	0.25	yellowish	90 (87) ³
3	275.5 / 0.50	105	0.25	white	98 (98) [*]

 Table S1. Reaction conditions for mechanochemical synthesis of mononuclear 1–3 complexes.

^aYields given in parenthesis refer to the synthesis of complexes 1–3 in solution (reaction times (min): 60, 30 and 120, respectively); *this work

Complex 1: white powder (380.5 mg, 94% yield); ³¹P NMR (202 MHz, CD₂Cl₂) δ (ppm): 25.6; ¹H NMR (500 MHz, CD₂Cl₂) δ (ppm): 7.61 (dd, J = 7.8, 1.3 Hz, 2H), 7.47 (dd, J = 12.8, 6.3 Hz, 8H), 7.38 (t, J = 7.4 Hz, 4H), 7.29 (t, J = 7.4 Hz, 8H), 7.14 (t, J = 7.7 Hz, 2H), 6.65 (dtd, J = 7.7, 4.6, 1.2 Hz, 2H), 1.65 (s, 6H, 2 x CH₃); HRMS-ESI: Calculated for [Au(XantPhos)]⁺ {[C₃₉H₃₂O₁P₂Au₁]⁺}: 775.1588; found: 775.1584.

Complex **2**: yellowish powder (406 mg, 90% yield); ³¹P NMR (202 MHz, CD_2Cl_2) δ (ppm): 26.2; ¹H NMR (500 MHz, CD_2Cl_2) δ (ppm): 7.60 (dd, J = 7.8, 1.3 Hz, 2H), 7.46 (dd, J = 12.6, 6.3 Hz, 8H), 7.36 (t, J = 7.4 Hz, 4H), 7.29 (t, J = 7.4 Hz, 8H), 7.14 (t, J = 7.7 Hz, 2H), 6.66 (dtd, J = 7.7, 4.7, 1.3 Hz, 2H), 1.66 (s, 6H, 2 x CH₃); HRMS-ESI: Calculated for [Au(XantPhos)]⁺ {[C₃₉H₃₂O₁P₂Au₁]⁺}: 775.1588; found: 775.1562.

Complex **3**: white powder (384.5 mg, 98% yield); the poor solubility of **3** in common organic solvents such as dichloromethane, ethanol, *n*-hexane hampered its characterisation by NMR spectroscopy in solution. Its low solubility is similar to that of Au(*N*-XantPhos)I complex;³ HRMS-ESI: Calculated for $[Au(N-XantPhos)]^+ \{ [C_{36}H_{27}O_1P_2N_1Au_1]^+ \}$: 748.1228; found: 748.1221.

Complexes 1 and 2 were soluble in dichloromethane, which enabled their recrystallisation by layering n-heptane or diethyl ether onto the solution. In the case of complex 3, no comparisons can be made, as complex 3 is practically insoluble, precipitating out from dichloromethane, used as the reaction solvent, during its solution-based preparation or in the work-up during LAG mechanochemical synthesis.

Complexes 1 and 2 were also synthesized according to the published solution-based procedures.^{1–3} The as-obtained white solids were recrystallized from dichloromethane/n-heptane.

Procedure for the synthesis of gold(I) diphosphine complex 3 in solution

A 100 mg (0.34 mmol) portion of (Me₂S)AuCl was dissolved in 15 mL of dichloromethane. While stirring, 187 mg (0.34 mmol) of *N*-xantphos was added and a clear solution was obtained. After 1-2 minutes of stirring, a white solid started to precipitate. The stirring was continued for 120 minutes to complete the reaction. The as-obtained white precipitate was filtered off and washed with dichloromethane. Yield: 261 mg (98 %). HRMS-ESI: Calculated for $[Au(N-XantPhos)]^+$ { $[C_{36}H_{27}O_1P_2N_1Au_1]^+$ }: 748.1228; found: 748.1222.



Formula	Calculated mass	Error (mDa)	Error (ppm)	DBE
C39H32OP2Au	775.1588	-0.5858	-0.4541	25.5
C78H65O2P4Au2	775.6627	-8.1333	-5.2428	49.5

Figure S1. HR-MS spectrum of crude product 1. Calculated for $[Au(XantPhos)]^+ \{[C_{39}H_{32}O_1P_2Au_1]^+\}:$ 775.1588; found: 775.1584.



Figure S2. HR-MS spectrum of 1 after recrystallization. Calculated for $[Au(XantPhos)]^+$ { $[C_{39}H_{32}O_1P_2Au_1]^+$ }: 775.1588; found: 775.1579.



Formula	Calculated mass	Error (mDa)	Error (ppm)	DBE
C39H32OP2Au	775.1588	-2.6541	-3.424	25.5
C78H65O2P4Au2	775.6627	-9.3333	-6.0163	49.5



Figure S3. HR-MS spectrum of crude product 2. Calculated for $[Au(XantPhos)]^+ \{[C_{39}H_{32}O_1P_2Au_1]^+\}:$ 775.1588; found: 775.1562 and $[Au(XantPhos)I + H]^+ \{(C_{39}H_{33}O_1P_2I_1Au_1)^+\}:$ 903.0717; found: 903.0688.



Formula	Calculated mass	Error (mDa)	Error (ppm)	DBE
C39H32OP2Au	775.1588	-3.7541	-4.843	25.5
C78H65O2P4Au2	775.6627	-10.1333	-6.532	49.5





Formula	Calculated mass	Error (mDa)	Error (ppm)	DBE
C36H27NOP2Au	748.1228	-0.7029	-0.9396	25.5
C72H55N2O2P4Au2	748.6267	-7.0309	-4.6959	49.5





Formula	Calculated mass	Error (mDa)	Error (ppm)	DBE
C36H27NOP2Au	748.1228	-0.6029	-0.8059	25.5
C72H55N2O2P4Au2	748.6267	-7.0309	-4.6959	49.5





Figure S7. ¹H NMR spectra of compound 1 in CD₂Cl₂.



Figure S8. ³¹P NMR spectra of compound 1 in CD₂Cl₂.

In accordance with an earlier ³¹P NMR study,¹⁻² 1 was detected as the major product with small amounts of Au₂(xantphos)Cl₂ and [Au(xantphos)₂]Cl resulted from its partial disproportionation in CH₂Cl₂.



Figure S10. ³¹P NMR spectra of compound 2 in CD₂Cl₂.



Figure S11. PXRD patterns of mechanochemically prepared compounds 1–3, as well as, of 3 obtained by conventional solution-based synthesis.



Figure S12. Comparison of the PXRD patterns of complexes 1 (i) and 2 (ii) prepared by mechanochemistry *versus* solution-based method.



Figure S13. TGA/MS analysis of 1. The TGA analysis showed a weight loss of 2.52% corresponding to 0.25 dichloromethane molecule per formula unit of 1.



Figure S14. TGA/MS analysis of 2. The TGA analysis showed a weight loss of 8.07% corresponding to 0.94 dichloromethane molecule fused in the crystalline phase of 2.



Figure S15. TGA/MS analysis of 3. The TGA analysis showed a weight loss of 0.90% corresponding to 0.085 dichloromethane molecule per formula unit of 3.



Figure S16. Normalized solid-state excitation (solid lines) and emission (dotted lines) spectra of mechanochemically prepared 1 and 2.

Single Crystal X-ray Diffraction

Crystal data, data collection and refinement details for 2B and 2G are listed in Table S2.

Single crystals of **2B** and **2G** were mounted in Paratone-N oil within a conventional cryo-loop, and intensity data were collected on a Rigaku R-AXIS RAPID image plate diffractometer (λ (Mo-K α radiation) = 0.71070 Å), fitted with an X-stream low temperature attachment. Several scans in the φ and ω direction were made to increase the number of redundant reflections, which were averaged over the refinement cycles. The structures were solved by direct method (*SIR*2014)⁴ and refined by full-matrix least-squares (*SHELXL*-2016).⁵ All calculations were carried out using the *WinGX* package of crystallographic programs.⁶ In **2B**, the phenyl ring (C1B–C6B) was found to be disordered and the occupancies ratio were refined to be 0.505(13):0.495(13). The dichloromethane molecule was also disordered and it was modelled with a site occupancy factor of 0.437(5). The disordered methyl hydrogen atoms were positioned geometrically and then they were constrained. The molecular and crystal structures were visualized and analyzed by using the program *Mercury*.⁷

Compound	2B	2G
Formula	C ₃₉ H ₃₂ AuIO ₁ P ₂ , 0.874(CH ₂ Cl ₂)	$C_{39}H_{32}AuIO_1P_2$, (CH ₂ Cl ₂)
Formula weight	976.82	987.38
Crystal size [mm]	$0.30 \times 0.50 \times 0.60$	$0.52 \times 0.55 \times 0.70$
Colour	colourless	colourless
Crystal system	monoclinic	monoclinic
Space group	$P 2_1/m$	$P 2_1/n$
Temp. (K)	103	103
<i>a</i> [Å]	8.6584(2)	9.1868(3)
<i>b</i> [Å]	18.3753(4)	21.0096(6)
<i>c</i> [Å]	12.2711(3)	18.6435(6)
α [°]	90	90
eta[°]	109.481(2)	95.516(1)
γ [°]	90	90
V [Å3]	1840.57(8)	3581.7(2)
Z	2	4
$d_{\rm calc}$ [Mg/m ³]	1.762	1.831
$\mu[\mathrm{mm}^{-1}]$	5.080	5.240
No. of collected reflns.	124016	148538
No. of unique refln./ R_{int}	4895/0.098	8186/ 0.070
No. of obsd. reflns. $I > 2\sigma(I)$	4816	7990
No. of parameters	285	426
GOOF	1.06	1.21
R1 (obsd. data)	0.0328	0.0331
wR2 (all data)	0.0837	0.0808
Largest diff. peak/ hole (e Å ⁻³)	2.70/-0.94	1.82/-0.83

Table S2. Crystal data, data collection and refinement details for 2B and 2G, respectively.



Figure S17. PXRD diffractograms showing the simulated patterns of 2B and 2G forms and the experimental patterns of mechanochemically prepared crude product 2 and recrystallized product 2.

Complex	$\lambda_{max}(nm)^a$	$ au_1 \ (\mu s)^b$	$ au_2 \ (\mu s)^b$	$\tau_3 \ (\mu s)^b$
2B	489	$8.36 \pm 0.05 \; (93\%)$	2.17 ± 0.05 (7%)	_
2G	502	$10.81 \pm 0.04 \ (100\%)$	_	_
2Y	588	$7.66 \pm 0.04 \; (72\%)$	$1.70 \pm 0.04 \; (26\%)$	$0.16 \pm 0.04 \; (2\%)$
2B _Y	487	$8.04 \pm 0.04 \ (93\%)$	1.31 ± 0.04 (7%)	_
$2G_Y$	501.5	$11.77\pm 0.04\;(92\%)$	3.07 ± 0.04 (8%)	_
$2B_t$	480, 600 shoulder	$5.70 \pm 0.04 \ (90\%)$	$1.49 \pm 0.04 \ (10\%)$	-

 Table S3. Solid-state photophysical data of crystalline and amorphous phases of 2.

^a $\lambda_{em} = 355$ nm; ^b weak excitation at 355 nm, detection at 460 nm, except for **2B**_t which is at 470 nm.



Figure S18. Yellow-emitting amorphous 2Y phase under 365 nm UV light illumination obtained upon mechanical grinding in a mortar with a pestle of a) 2B and b) 2G polymorphs.



Figure S19. PXRD diffractograms of ground 2Y, $2B_Y$ (obtained from 2Y after exposure to EtOH EtOH vapor), $2G_Y$ (obtained from 2Y after exposure to CH_2Cl_2 vapor) and $2B_t$ (obtained upon thermal treatment of 2B).



Figure S20. The sample chamber and temperature sensor of Linkam DSC600 stage with removed lid and the aluminium crucible with 2B.

Movie S1. Reversible thermochromic luminescence of **2B**. The crucible containing 5 mg of **2B** was placed into the sample chamber (Figure S20) heated to 300 °C. The system was illuminated with 365 nm UV light. A yellow luminescence turned on immediately, which rapidly changed back to blue, when the crucible was taken out from the sample chamber and left to cool. The movie taken under 365 nm UV light illumination shows this reversible switching between blue and yellow emission during multiple heating and cooling cycles.

1 st heating					
Dm/T _{max}	Q/T _{max}		MS/T _{max}		
wt% (°C)	J/g (°C)		m/z (°C)		
-0.40 (259.9)		49 (259.1)	36 (80–300)	44 (130–325)	
0	-39.4 (305.9)				
		2 nd heating			
-0.02 (120-310)					
0	1.67 (184.1)				
0	23.63 (205.3)				
0	2.75 (224.7)				
0	-4.67 (285)				
0	-6.41 (293.8)				
0	-11.01 (305)				

Table S4. Simultaneous thermal analysis (STA) of 2B.

The details of the simultaneous thermal analysis (STA) of **2B** are summarized in Table S3. The graph of STA at the first heating of **2B** is shown in Figure S21. The TG curve shows a gradual decrease in the weight of the sample (-0.40%) in the temperature range 25–350 °C, which was associated with the gradual release of minimal amount of gaseous CO₂ (surface absorbed) and

HCl (resulted from the cleavage of CH₂Cl₂ solvate molecules). The sharp DTG (differential thermal gravimetry) peak is related to the release of dichloromethane (m/z = 49) solvate. The high cleavage temperature (259.1 °C) indicates relatively strong binding of the dichloromethane molecules in the crystal lattice of 2B. It should be noted that the structure of 2B remained unaltered as no thermal effect was observed upon its desolvation. The DSC curve showed that complex **2B** melted at 305.9 °C (Q = -39.3 J/g) and this solid-to-liquid phase transformation begins at 289.6 °C and ends at 315.6 °C. The heat of fusion of the 2B complex is 16.43 kJ/mol. Figure S18 showed that no phase transformation occurred upon cooling back to room temperature. The graph of the STA at the second heating of the 2B shown in Figure S24 is fundamentally different from Figure S21. The DSC curve displayed three exothermic peaks in the temperature range 175–235 °C and three endothermic peaks in the range 270–320 °C, however the TG curve does not reveal any weight change. Exothermic peaks with temperature maximum of 184.1, 205.3 and 224.7 °C confirm the transformation of amorphous phase into three structurally different phases. The three endothermic peaks corresponding to the melting points of these three phases confirm the change in the phase composition during the second heating.



Figure S21. The graph of the STA at the first heating of 2B.



Figure S22. The overall program of the STA of 2B.



Figure S23. The graph of the STA: the first cooling of 2B.



Figure S24. The graph of the STA at the second heating of 2B.



Figure S25. The graph of the STA: decomposition of 2B upon heating above 350 °C.



Figure S26. The luminescence intensity decay of $2B_t$. The laser excitation was made at 355 nm, while the emission wavelengths are shown on the inset.

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