

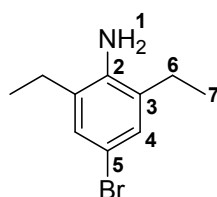
## ELECTRONIC SUPPLEMENTARY INFORMATION

### Selective formation of a two-dimensional coordination polymer based on a tridentate phospholane ligand and gold(I)

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#### 1) Experimental Details

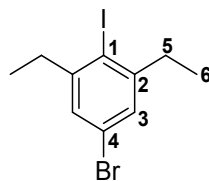
##### 4-Bromo-2,6-diethylaniline



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz):  $\delta$  = 7.03 (s, 2H, H<sup>4</sup>), 3.56 (s, 2H, H<sup>1</sup>), 2.41 (q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, H<sup>6</sup>), 1.19 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 6H, H<sup>7</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.16 MHz):  $\delta$  = 140.7 (s, C<sup>2</sup>), 129.6 (s, C<sup>3</sup>), 128.4 (s, C<sup>4</sup>), 110.1 (s, C<sup>5</sup>), 24.1 (s, C<sup>6</sup>), 12.7 ppm (s, C<sup>7</sup>).

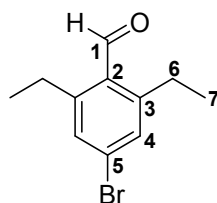
##### 5-Bromo-1,3-diethyl-2-iodobenzene



<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.13 MHz):  $\delta$  = 7.15 (s, 2H, H<sup>3</sup>), 2.73 (q, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, H<sup>5</sup>), 1.18 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 6H, H<sup>6</sup>).

<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.16 MHz):  $\delta$  = 148.8 (s, C<sup>2</sup>), 128.7 (s, C<sup>3</sup>), 122.6 (s, C<sup>4</sup>), 105.4 (s, C<sup>1</sup>), 35.3 (s, C<sup>5</sup>), 14.5 ppm (s, C<sup>6</sup>).

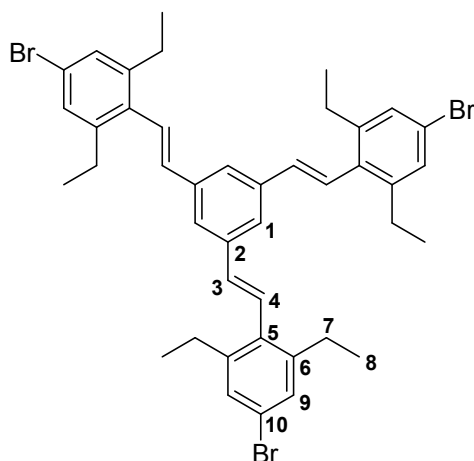
##### 4-Bromo-2,6-diethylbenzaldehyde



$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta$  = 10.52 (s, 1H, H<sup>1</sup>), 7.28 (s, 2H, H<sup>4</sup>), 2.93 (q,  $^3J_{\text{HH}}$  = 7.5 Hz, 4H, H<sup>6</sup>), 1.24 ppm (t,  $^3J_{\text{HH}}$  = 7.6 Hz, 6H, H<sup>7</sup>).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.16 MHz):  $\delta$  = 192.3 (s, C<sup>1</sup>), 149.1 (s, C<sup>3</sup>), 131.0 (s, C<sup>4</sup>), 130.3 (s, C<sup>2</sup>), 127.8 (s, C<sup>5</sup>), 26.4 (s, C<sup>6</sup>), 16.1 ppm (s, C<sup>7</sup>).

### 1,3,5-Tris[(*E*)-(4-bromo-2,6-diethyl)styryl]benzene (1a)



$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta$  = 7.53 (s, 3H, H<sup>1</sup>), 7.25 (s, 6H, H<sup>9</sup>), 7.16 (d,  $^3J_{\text{HH}}$  = 16.0 Hz, 3H, H<sup>4</sup>), 6.62 (d,  $^3J_{\text{HH}}$  = 16.0 Hz, 3H, H<sup>3</sup>), 2.70 (q,  $^3J_{\text{HH}}$  = 8.0 Hz, 12H, H<sup>7</sup>), 1.20 ppm (t,  $^3J_{\text{HH}}$  = 8.0 Hz, 18H, H<sup>8</sup>).

$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.16 MHz):  $\delta$  = 144.6 (s, C<sup>6</sup>), 138.1 (s, C<sup>2</sup>), 135.0 (s, C<sup>5</sup>), 133.9 (s, C<sup>3</sup>), 128.8 (s, C<sup>9</sup>), 126.5 (s, C<sup>4</sup>), 123.6 (s, C<sup>1</sup>), 121.2 (s, C<sup>10</sup>), 26.8 (s, C<sup>7</sup>), 15.9 ppm (s, C<sup>8</sup>).

### Single-crystal X-ray structure determination:

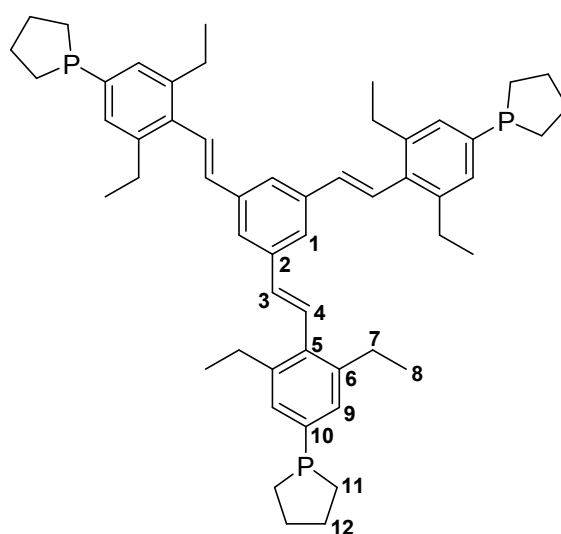
The data were collected on a Gemini diffractometer (Rigaku Inc.) using Mo-K $\alpha$  radiation ( $\lambda$  = 71.073 pm) and  $\omega$ -scan rotation. The structure solution was performed with SHELXS-2013<sup>[E]</sup> (direct method). Anisotropic refinement of all non-hydrogen atoms was performed with SHELXL-2018<sup>[C]</sup>. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. CCDC 1861124 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

**Table 1:** Crystallographic data of 1,3,5-tris[(*E*)-(4-bromo-2,6-diethyl)styryl]benzene

Empirical formula	$\text{C}_{42}\text{H}_{45}\text{Br}_3$	
Formula weight	789.51	
Temperature	130(2) K	
Wavelength	71.073 pm	
Crystal system	Monoclinic	
Space group	$C2/c$	
Unit cell dimensions	$a = 2861.00(8)$ pm	$\alpha = 90^\circ$

	$b = 1558.71(3) \text{ pm}$	$\beta = 96.537(2)^\circ$
	$c = 1621.90(3) \text{ pm}$	$\gamma = 90^\circ$
Volume	$7.1858(3) \text{ nm}^3$	
Z	8	
Density (calculated)	$1.460 \text{ Mg/m}^3$	
Absorption coefficient	$3.397 \text{ mm}^{-1}$	
F(000)	3216	
Crystal size	$0.5 \times 0.35 \times 0.07 \text{ mm}^3$	
Theta range for data collection	$2.516 \text{ to } 30.507^\circ$	
Index ranges	$-40 \leq h \leq 40, -22 \leq k \leq 21, -23 \leq l \leq 23$	
Reflections collected	64468	
Independent reflections	10973 [R(int) = 0.0705]	
Completeness to theta = $25.242^\circ$	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.49805	
Refinement method	Full-matrix least-squares on $F^2$	
Data / restraints / parameters	10973 / 0 / 586	
Goodness-of-fit on $F^2$	1.014	
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0447, wR2 = 0.1000$	
R indices (all data)	$R1 = 0.0928, wR2 = 0.1237$	
Largest diff. peak and hole	$1.521 \text{ and } -1.022 \text{ e} \cdot \text{\AA}^{-3}$	

### 1,3,5-Tris[(E)-(4-phospholano-2,6-diethyl)styryl]benzene (1)



$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400.13 MHz):  $\delta = 7.42$  (s, 3H,  $\text{H}^1$ ),  $7.15$  (d,  $^3J_{\text{HH}} = 16.8 \text{ Hz}$ , 3H,  $\text{H}^4$ ),  $7.05$  (d,  $^3J_{\text{HP}} = 6.8 \text{ Hz}$ , 6H,  $\text{H}^9$ ),  $6.56$  (d,  $^3J_{\text{HH}} = 16.8 \text{ Hz}$ , 3H,  $\text{H}^3$ ),  $2.66$  (q,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ , 12H,  $\text{H}^7$ ),  $1.97 - 1.68$  (m, 24H,  $\text{H}^{11} + \text{H}^{12}$ ),  $1.40$  ppm (t,  $^3J_{\text{HH}} = 7.5 \text{ Hz}$ , 18H,  $\text{H}^8$ ).

**$^{13}\text{C}\{^1\text{H}\}$  NMR** ( $\text{CDCl}_3$ , 100.16 MHz):  $\delta$  = 142.1 (d,  $^3J_{\text{CP}} = 5.2$  Hz,  $\text{C}^6$ ), 140.7 (d,  $^1J_{\text{CP}} = 21.9$  Hz,  $\text{C}^{10}$ ), 138.3 (s,  $\text{C}^2$ ), 135.2 (s,  $\text{C}^5$ ), 133.4 (s,  $\text{C}^3$ ), 128.1 (d,  $^2J_{\text{CP}} = 15.6$  Hz,  $\text{C}^9$ ), 127.0 (s,  $\text{C}^4$ ), 123.3 (s,  $\text{C}^1$ ), 27.9 (d,  $^2J_{\text{CP}} = 3.5$  Hz,  $\text{C}^{12}$ ), 27.1 – 27.0 (m,  $\text{C}^7+\text{C}^{11}$ ), 15.4 ppm (s,  $\text{C}^8$ ).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** ( $\text{CDCl}_3$ , 161.98 MHz):  $\delta$  = –16.8 ppm (s).

**Two-dimensional [M:L] 1:1 coordination polymer from [AuCl(tht)] and 1,3,5-tris[(E)-(4-phospholano-2,6-diethyl)styryl]benzene – Poly[ $\mu$ -1,3,5-tris[(E)-(4-phospholano-2,6-diethyl)styryl]-benzene- $\kappa^3\text{P},\text{P}',\text{P}''$ ]gold(I) chloride (2)**

**$^1\text{H}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 400.13 MHz):  $\delta$  = 7.53 (s, 3H,  $\text{H}^1$ ), 7.40 (d,  $^3J_{\text{HP}} = 13.2$  Hz, 6H,  $\text{H}^9$ ), 7.27 (d,  $^3J_{\text{HH}} = 16.7$  Hz, 3H,  $\text{H}^4$ ), 6.67 (d,  $^3J_{\text{HH}} = 16.6$  Hz, 3H,  $\text{H}^3$ ), 2.79 (q,  $^3J_{\text{HH}} = 7.5$  Hz, 12H,  $\text{H}^7$ ), 2.54 – 2.02 (m, 24H,  $\text{H}^{11}+\text{H}^{12}$ ), 1.22 ppm (t,  $^3J_{\text{HH}} = 7.5$  Hz, 18H,  $\text{H}^8$ ).

**$^{31}\text{P}\{^1\text{H}\}$  NMR** ( $\text{CD}_2\text{Cl}_2$ , 161.98 MHz):  $\delta$  = 26.5 ppm (s).

#### Single-crystal X-ray structure determination:

The data were collected on a Gemini diffractometer (Rigaku Inc.) using Mo- $\text{K}\alpha$  radiation ( $\lambda = 71.073$  pm) and  $\omega$ -scan rotation. Data reduction was performed with CrysAlis Pro<sup>[A]</sup> including the program SCALE3 ABSPACK for empirical absorption correction. The structure was solved by dual space methods (SHELXT-2014<sup>[B]</sup>) and the refinement of all non-hydrogen atoms was performed with SHELXL-2018<sup>[C]</sup>. All non-hydrogen atoms were refined with anisotropic thermal parameters. Some parts of the ligand are disordered. All hydrogen atoms were calculated on idealised positions. The crystal was obtained by diffusion of *n*-hexane into an *o*-difluorobenzene solution. With a regular structure determination, ten solvent molecules (2.5 for the asymmetric unit) could roughly be located with reduced accuracy as disordered species in 200 pm x 400 pm rectangular sized channels along (010). In this experiment, the electron density of all disordered solvents molecules had been removed with the SQUEEZE<sup>[D]</sup> routine implemented in PLATON. The squeezed electron density of 647 electrons for the unit cell may be related to approximately 11 poorly defined and diffuse oriented *o*-difluorobenzene molecules (11 x 58 = 638 electrons), i.e. 2.75 solvent molecules for the asymmetric unit. This is slightly more in comparison with the non-squeezed solution. A volume of 166 Å<sup>3</sup> for one *o*-difluorobenzene molecule (approximately 21 Å<sup>3</sup> for each non-hydrogen atom) is very close to the expected value for C and F atoms. The given formula was corrected for this solvent contribution. CCDC 1860064 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://summary.ccdc.cam.ac.uk/structure-summary-form> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

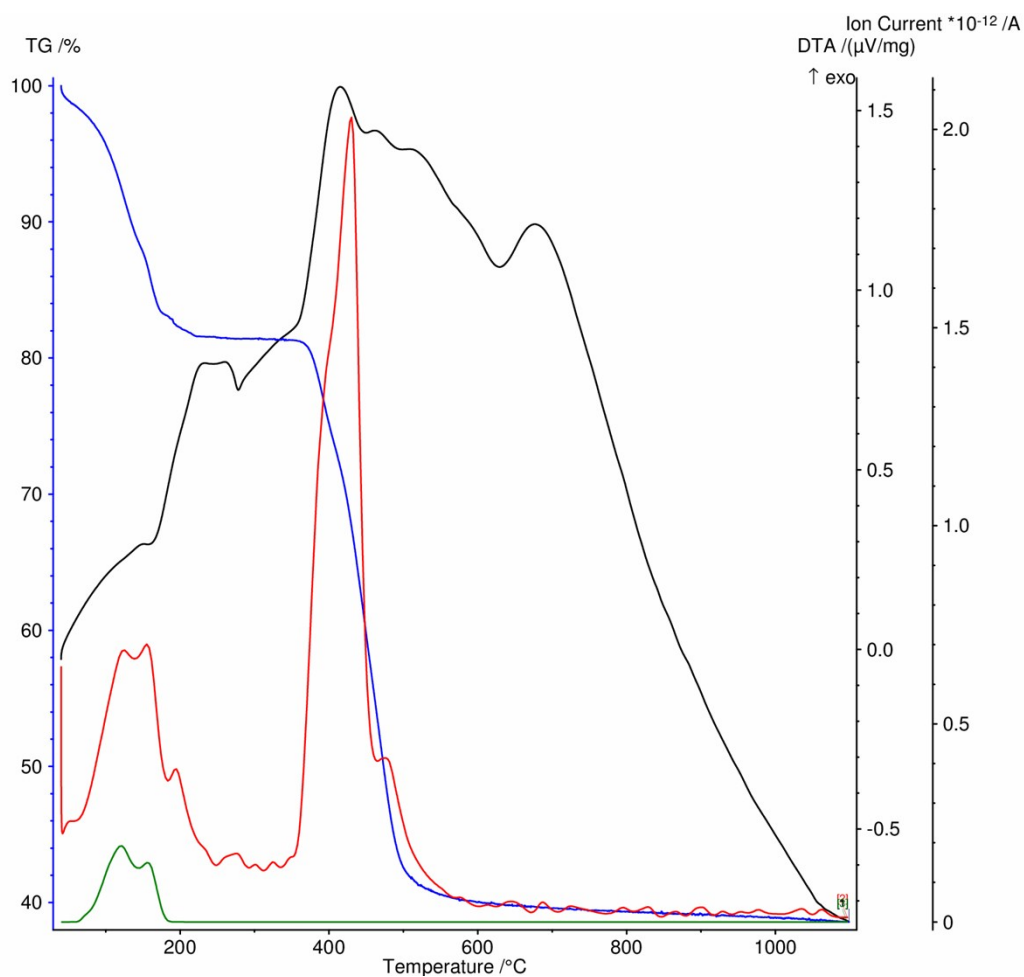
**Table 2:** Crystallographic data of 2

Empirical formula	$\text{C}_{54}\text{H}_{69}\text{AuClP}_3 \cdot 2.75 \text{C}_6\text{H}_4\text{F}_2$
Formula weight	1357.17
Temperature	130(2) K
Wavelength	71.073 pm

Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 1800.76(2)$ pm	$\alpha = 90^\circ$
	$b = 1336.91(2)$ pm	$\beta = 98.503(1)^\circ$
	$c = 2686.19(3)$ pm	$\gamma = 90^\circ$
Volume	$6.3958(1)$ nm <sup>3</sup>	
Z	4	
Density (calculated)	1.409 Mg/m <sup>3</sup>	
Absorption coefficient	2.474 mm <sup>-1</sup>	
F(000)	2774	
Crystal size	0.35 x 0.15 x 0.10 mm <sup>3</sup>	
Theta range for data collection	2.287 to 30.108°	
Index ranges	$-25 \leq h \leq 25, -18 \leq k \leq 8, -37 \leq l \leq 37$	
Reflections collected	94539	
Independent reflections	17655 [R(int) = 0.0563]	
Completeness to theta = 28.285°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.93302	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	17655 / 50 / 591	
Goodness-of-fit on F <sup>2</sup>	1.032	
Final R indices [I > 2σ(I)]	R1 = 0.0434, wR2 = 0.0982	
R indices (all data)	R1 = 0.0697, wR2 = 0.1075	
Largest diff. peak and hole	3.362 and -0.912 e·Å <sup>-3</sup>	

### TGA/DSC measurements

The TGA/DSC measurements were performed on a STA 449 F1 Jupiter from NETZSCH, using helium atmosphere and carrier gas. During TGA/DSC, mass fragments could be detected using a QMS 403 C Aeolos from NETZSCH. The samples were prepared in alumina crucibles and a heating rate of 10 K/min was applied.



**Fig. 1:** TG/DTA of **2** in the temperature range from 35 – 1000 °C with a temperature raise of 10 K/min. Blue – mass of the sample; green – mass flow of 114 g/mol; red – mass flow of 26 g/mol; black – heat of reaction.

#### References:

- [A] CrysAlis Pro: Data collection and data reduction software package, Rigaku Inc., Agilent (2014), *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.
- [B] SHELXT: Integrated space-group and crystal structure determination, G. M. Sheldrick, *Acta Cryst.*, **A71** (2015) 3–8.
- [C] SHELXL: G. M. Sheldrick, *Acta Cryst.*, **C71** (2015) 3–8.
- [D] PLATON SQUEEZE: A tool for the calculation of the disordered solvent contribution to the calculated structure factors, A. L. Spek, *Acta Cryst.*, **C71** (2015) 9–18.
- [E] SHELXS: G. M. Sheldrick, *Acta Cryst.*, **A64** (2008) 112–122.