

Electronic Supplementary Material (ESI) for DALTON TRANSACTIONS.

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## **A Photoluminescent Au(I)/Ag(I)/PNN coordination complex for Relatively Rapid and Reversible Alcohol Sensing**

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## Experimental Procedures

### Materials and methods

The synthesis of dppmaphen followed a procedure in the literature.<sup>[S1]</sup> All chemicals were obtained from commercial sources and were used as received without further purification unless otherwise noted. NMR spectra were measured on a Varian UNITY plus-600 MHz NMR instrument at room temperature, with chemical shifts referenced to the solvent signal of DMSO-*d*<sub>6</sub>. Elemental analyses (C, H and N) were performed on a Carlo-Erba CHNO-S microanalyzer. Powder X-ray diffraction (PXRD) measurements were acquired on a PANalytical X'Pert PRO MPD system (PW3040/60) with Cu-*K*<sub>α</sub> radiation. IR spectra were obtained on a VERTEX 70 FT-IR spectrometer (4000–500 cm<sup>-1</sup>) with ATR probe. TGA were obtained on a TA SDT-600 analyzer (N<sub>2</sub> stream, heating rate of 10 °C·min<sup>-1</sup>). Emission spectra were obtained on a Hitachi F2500 spectrofluorometer. Transient photoluminescence and quantum yield measurements were performed on a FLS980 (Edinburgh Instruments, U.K.) spectrometer.

### Synthesis of compound 1

A mixture of dppmaphen (15.7 mg, 0.04 mmol) and AuCN ( 8.91 mg, 0.04 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and MeOH (2 mL) was stirred for 3 h at room temperature to afford a light yellow solution. AgPF<sub>6</sub> (5.05 mg, 0.02 mmol) was then added and stirred for 3h to obtain the yellow turbid solution. The mixture was then centrifuged and the supernatant slowly diffused with hexane/Et<sub>2</sub>O (1:1), which afforded light yellow blocks of 1·2MeOH after 2 days. The MeOH solvate could be removed *in vacuo* (or blown dry in a stream of N<sub>2</sub> for 3h.) to afford 1. Yield: 26.02 mg (88% based on AuCN). Anal. Calcd. For C<sub>52</sub>H<sub>40</sub>AgAu<sub>2</sub>F<sub>6</sub>N<sub>8</sub>P<sub>3</sub>: C, 42.04; H, 2.71; N, 7.54, Found: C, 42.38%; H, 2.70%; N, 7.36%. IR (ATR): 3413(m), 3050 (w), 2139(m), 1630(m), 1593(w), 1570(w), 1540(s), 1512(m), 1483(w), 1470(m), 1436(s), 1409(w), 1386(w), 1362(s), 1256(m), 1156(m), 1104(m), 1042(w), 1026(w), 998(w), 944(w), 845(vs), 742(m), 719(w), 692(s), 633(w), 557(s), 508(m)cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, DMSO-*d*<sub>6</sub>): δ 8.95 (*d*, 1H), 8.53 (*d*, *J* = 7.9 Hz, 1H), 8.27 (*s*, 1H), 8.21 (*d*, *J* = 8.8 Hz, 1H), 7.85 (*d*, *J* = 8.6 Hz, 2H), 7.77–7.73 (*m*, 4H), 7.57 (*s*, 3H), 7.37 (*d*, *J* = 8.8 Hz, 3H), 7.08 (*s*, 1H), 6.58 (*s*, 1H), 5.55 (*s*, 1H), 5.11 (*s*, 1H). <sup>13</sup>C NMR(151 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 157.08, 150.45, 150.09, 141.53, 140.43, 139.38, 138.89, 134.66, 132.00, 129.87, 128.29, 124.32, 123.94, 122.90, 117.92. <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 33.06 (*s*), -146.41 (hept).

### Preparations of 1·2EtOH

1·2EtOH was isolated as single crystals using a similar procedure to that used for 1·2MeOH, except using EtOH instead of MeOH as solvent.

### Single-crystal X-ray structure determinations

Single-crystal X-ray diffraction (SCXRD) data for all crystals were obtained on a Bruker Smart CCD diffractometer with graphite monochromated Mo *K*<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Single crystals were coated with Paratone oil on a Cryoloop pin and enveloped in an Oxford Cryosystems cryostream at 120 K during data collection. Data were processed with the Bruker APEX2 software package<sup>[S2]</sup> using SAINT v8.34A<sup>[S3]</sup> and corrected for absorption by multi-scan (no correction was made for extinction or decay)<sup>[S4]</sup> The structures of 1·2MeOH and 1·2EtOH were solved by direct methods and refined on F<sup>2</sup> by full-matrix least-squares using the SHELXTL-2016 program package.<sup>[S5]</sup> In 1·2EtOH, the solvated EtOH molecules were disordered over two sites with occupancies of 0.70/0.30, while the PF<sub>6</sub><sup>-</sup> anion was disordered over three sites with occupancies of 0.50/0.30/0.20 by rotating over a F-P-F axis. All other non-hydrogen atoms except for those of the disordered EtOH molecule were refined anisotropically. H atoms of the –OH groups were located from the difference Fourier maps with their coordinates refined freely and thermal parameters constrained to  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . All other hydrogen atoms were added theoretically. Selected crystallographic data and refinement parameters are listed in Table S1.

CCDC 2056644 and 2056645 contain the supplementary crystallographic data for **1**·2MeOH and **1**·2EtOH, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

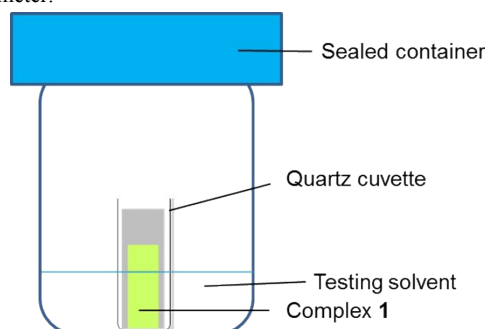
**Table S1.** Selected crystallographic data and refinement parameters for **1**·2MeOH and **1**·2EtOH

Compound	<b>1</b> ·2MeOH	<b>1</b> ·2EtOH
Formula	C <sub>54</sub> H <sub>48</sub> AgAu <sub>2</sub> F <sub>6</sub> N <sub>8</sub> O <sub>2</sub> P <sub>3</sub>	C <sub>56</sub> H <sub>52</sub> AgAu <sub>2</sub> F <sub>6</sub> N <sub>8</sub> O <sub>2</sub> P <sub>3</sub>
Fw	1549.71	1577.77
Crystal system	monoclinic	monoclinic
space group	<i>P2/c</i>	<i>P2/c</i>
<i>a</i> /Å	13.393(4)	13.4700(7)
<i>b</i> /Å	11.321(4)	11.4324(6)
<i>c</i> /Å	19.152(5)	19.0084(11)
<i>α</i> /deg	90	90
<i>β</i> /deg	110.223(9)	109.0308(15)
<i>γ</i> /deg	90	90
<i>V</i> /Å <sup>3</sup>	2724.7(14)	2767.2(3)
<i>Z</i>	2	2
<i>P</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.889	1.894
<i>μ</i> (mm <sup>-1</sup> )	5.885	5.796
<i>F</i> (000)	1496	1528
<i>R</i> <sub>1</sub> <sup>a</sup>	0.0305	0.0243
w <i>R</i> <sup>b</sup>	0.0846	0.0634
GOF <sup>c</sup>	1.073	1.058

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$ . <sup>c</sup>GOF =  $\{\sum w((F_o^2 - F_c^2)^2) / (n - p)\}^{1/2}$ , where *n* = number of reflection and *p* = total number of parameters refined.

### Measurement of PL On/Off effect of **1** toward different solvent vapors.

Powdered samples of **1** were coated onto a quartz slide (1 × 1.5 cm<sup>2</sup>) and placed in a quartz cuvette, which was then left in a sealed container (100 mL) containing ~5 mL of solvent (Fig. S1) for 0.5 h. The cuvette was then sealed and transferred to the spectrofluorometer.



**Fig. S1** Experimental setup for the measurement of the PL On/Off effect of **1** toward different solvent vapors.

### PL On/Off switching experiments

Powdered samples of **1** were coated onto a quartz slide ( $1 \times 1.5$  cm), sealed in a quartz cell fitted with gas inlet and outlet, and placed in a spectrofluorometer. The excitation light (372 nm) was adjusted to irradiate the surface of the slide (Fig. S2).  $N_2$  were bubbled through thermostatically controlled MeOH or  $H_2O$  to achieve saturated MeOH/ $N_2$  and  $H_2O/N_2$  streams using peristaltic pumps.

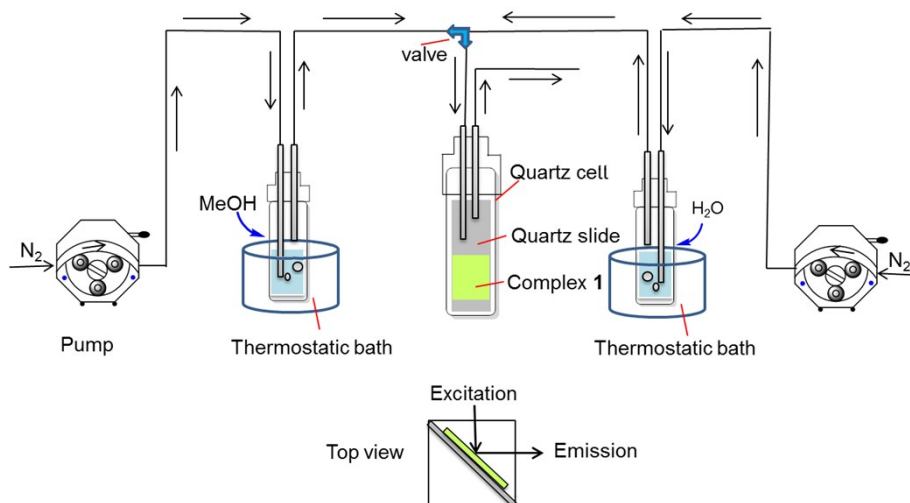


Fig. S2 Equipment for PL On/Off switching experiments.

### Characterization of compound **1**

Compound **1** was insoluble in water, but readily soluble in acetone and DMSO. The elemental analysis of the solvent-free **1** was consistent with its molecular formula. PXRD pattern correlated well with the simulated spectrum generated from the SCXRD data of **1**·2MeOH, indicating its structure remained intrinsic and did not collapse on loss of MeOH. The IR spectrum of **1** showed absorptions at 1630, 1540 and 1436  $cm^{-1}$  attributable to the skeleton vibrations of -Ph, at 2139  $cm^{-1}$  attributable to  $CN^-$  and at 845  $cm^{-1}$  attributable to  $PF_6^-$ . TGA analyses in a  $N_2$  atmosphere showed decomposition between 220~400 °C with weight loss of about 43% (Calcd 42%) which is consistent with the elimination of the  $-NH-CH_2-PPh_2$  unit together with  $PF_6^-$  and  $CN^-$ . The  $^1H$  NMR spectrum (Figure S1) in  $DMSO-d_6$  contained signals for the  $-CH_2-$  group (5.11, 5.55 ppm),  $-NH-$  (6.58 ppm),  $-Ph$  and phen groups (8.95-7.08 ppm). Two signals for  $-PPh_2$  (33.06 ppm) and  $PF_6^-$  (-146.41 ppm) were also identified in the  $^{31}P\{^1H\}$  NMR spectrum.



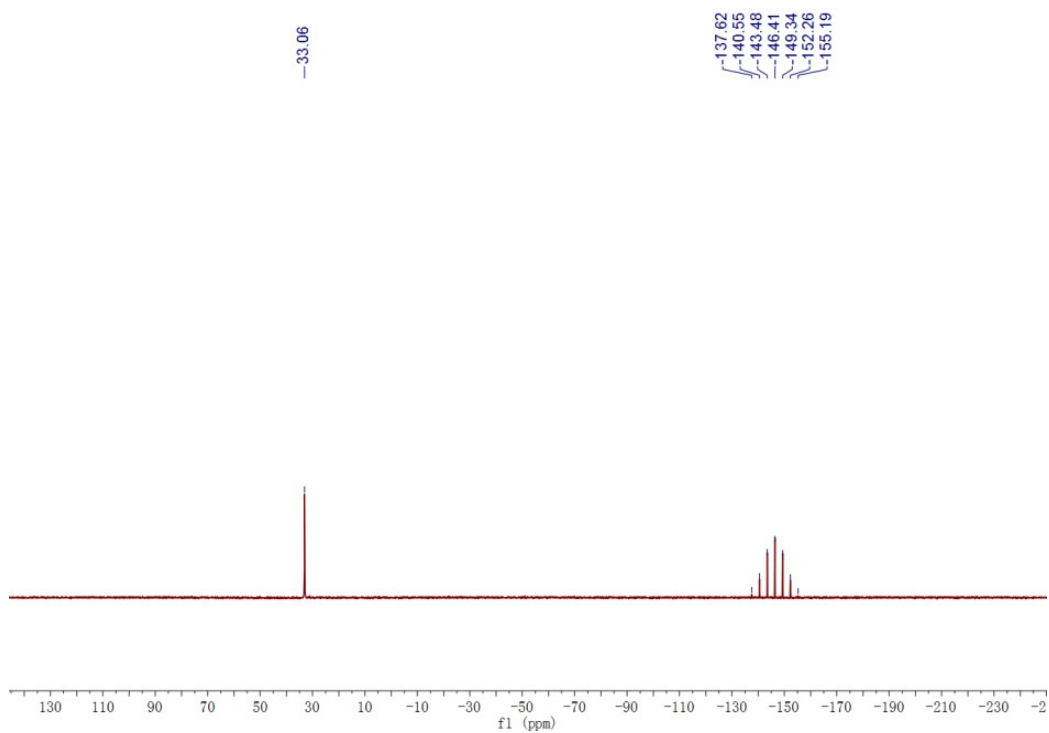


Fig. S5  $^{31}\text{P}$  NMR spectrum of **1**

Table S2. Hydrogen-bonding geometries in **1**·2MeOH and **1**·2EtOH (Å, °)

Compound	D-H···A	D-H	H···A	D···A	D-H···A
<b>1</b> ·2MeOH	N3-H3N···O1	0.83	2.02	2.845(5)	174.0
	O1-H1A···N4 <sup>i</sup>	0.84	2.00	2.780(6)	157.4
<b>1</b> ·2EtOH	N3-H3N···O1	0.88	2.10	2.886(5)	147.7
	O1-H1A···N4 <sup>i</sup>	0.83	2.09	2.861(6)	155.1

Symmetry code: <sup>i</sup> 1-x,-y,1-z.

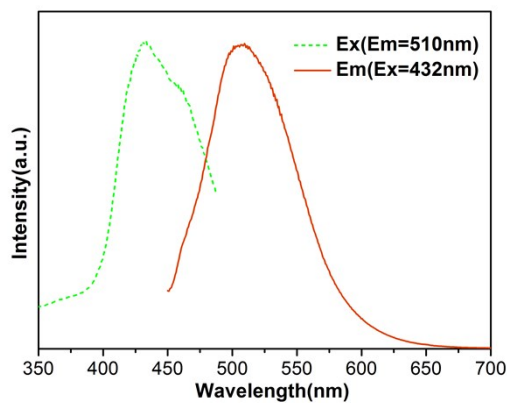
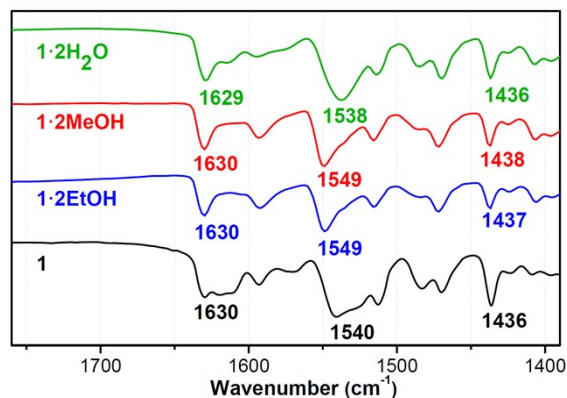
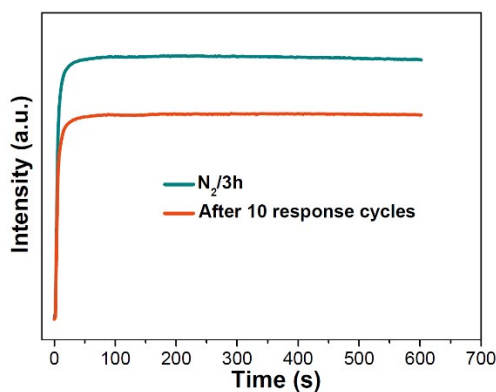


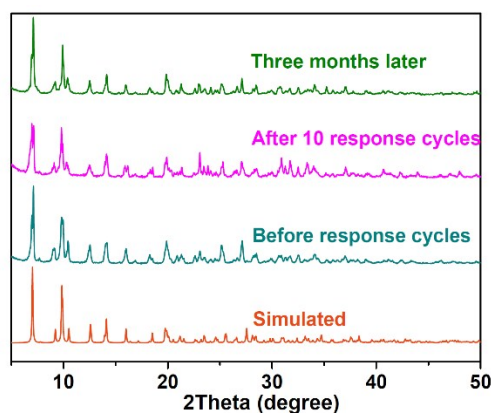
Fig. S6 Excitation (green, Em = 510nm) and emission (red, Ex = 432 nm) spectra of ligand dppmaphen in solid state.



**Fig. S7** Comparison of the IR spectra of **1**, **1·2MeOH**, **1·2EtOH** and **1·2H<sub>2</sub>O** in the region 1400–1700 cm<sup>-1</sup> showing the shifting of the vibration absorptions of the –PPh<sub>2</sub> groups.



**Fig. S8** Time-dependent emission spectra of **1** in a MeOH/N<sub>2</sub> stream after 10 response cycles (orange line) and further treatment in dry N<sub>2</sub> for 3h (green line).



**Fig. S9** PXRD patterns of **1**: simulated from SCXRD data of **1·2MeOH**, before response cycles, after 10 response cycles and three months later.

## References

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