Supplementary Information
Mixed Cu(I)/Au(I) Coordination Polymers as Reversible Turn-On Vapoluminescent Sensors for Volatile Thioethers

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Experimental

General Procedures

Caution! Although $KAu(CN)_2$ is significantly less toxic than other cyanometallates, typical precautions regarding handling of hazardous materials should still be followed. All reactions were performed in air. $CuAu(CN)_2$,[1] $Cu_{2/3}Au_{1/3}CN$,[1] and $[Cu_{1/2}Au_{1/2}CN]_2(DMS)$[2] were synthesized using literature procedures. All other reagents were obtained from commercial sources and used as received.

Infrared spectra were collected on a Thermo Nicolet Nexus 670 FT-IR spectrometer equipped with a Pike MIRacle attenuated total reflection (ATR) sampling accessory. Raman spectra were collected using a Renishaw inVia Raman microscope equipped with a 514 nm laser.

Synthetic Procedures

$[Cu_{2/3}Au_{1/3}CN]_2(DMS)$

$[Cu_{2/3}Au_{1/3}CN]_2(DMS)$ powder was obtained by stirring $Cu_{2/3}Au_{1/3}CN$ in a solution of DMS (10% by volume) in MeCN. IR (cm^{-1}): 2907 (w), 2168 (s, ν_{CN}), 2139 (m, ν_{CN}), 1421 (m), 1033 (m), 980 (m). Raman (cm^{-1}): 2176 (s, ν_{CN}), 2147 (w, ν_{CN}), 2127 (m, ν_{CN}), 727 (w), 676 (w). The same product can also be obtained by vapour absorption of DMS by $Cu_{2/3}Au_{1/3}CN$. $[Cu_{2/3}Au_{1/3}CN]_2$-(DMS) decomposes to $Cu_{2/3}Au_{1/3}CN$ when removed from an atmosphere of DMS, precluding elemental analysis.

$[Cu_{2/3}Au_{1/3}CN]_2(DES)$

$[Cu_{2/3}Au_{1/3}CN]_2(DES)$ powder was obtained by stirring $Cu_{2/3}Au_{1/3}CN$ in a solution of DES (10% by volume) in MeCN. IR (cm^{-1}): 2991 (w), 2976 (w), 2930 (w), 2164 (s, ν_{CN}), 2147 (w, ν_{CN}), 2131 (s, ν_{CN}), 1450 (w), 1441 (w), 1372 (m), 1286 (w), 1259 (m), 982 (w), 787 (m). Raman (cm^{-1}): 2173 (s, ν_{CN}), 2144 (m, ν_{CN}), 2127 (m, ν_{CN}), 669 (w), 509 (w), 345 (w), 329 (w, sh), 156 (w). The same product can be obtained by vapour absorption of DES by $Cu_{2/3}Au_{1/3}CN$. $[Cu_{2/3}Au_{1/3}CN]_2(DES)$ decomposes to $Cu_{2/3}Au_{1/3}CN$ when removed from an atmosphere of DES, precluding elemental analysis.

Emission and excitation spectroscopy

Excitation and emission spectra were measured at room temperature on a Horiba Jobin Yvon Fluorolog-3 fluorimeter equipped with a Xe arc lamp and a TBX single-photon counter. Samples of $[Cu_{2/3}Au_{1/3}CN]_2(DMS)$ and $[Cu_{2/3}Au_{1/3}CN]_2(DES)$ were stirred in 10% DMS in MeCN and 10% DES in MeCN respectively. These suspensions were placed into NMR tubes for spectroscopic analysis. Samples reached approximately 3 cm in the NMR tube after the suspension had settled. Excess solvent was removed and the NMR tubes were sealed while the samples were still wet. Excitation spectra were corrected for lamp response.

All luminescent responses of the samples to analyte were measured using an Ocean Optics Flame Spectrometer and excited using a DH-2000 light source equipped with a deuterium lamp passed through a Thorlabs 275–375 nm bandpass optical filter. Samples were prepared by dropcasting a $Cu_{2/3}Au_{1/3}CN$ suspension in MeCN on a glass slide. Time-resolved responses were measured by flowing air through the desired analyte to the sample in a vented cuvette (Figure S4). Limit

of detection measurements were performed using a sealed chamber with a quartz window and a septum for injecting small quantities of DMS or DES with a gas-tight syringe.

X-ray crystallography

All crystallographic data (powder and single-crystal) were collected on a Bruker SMART Apex II Duo diffractometer equipped with a $Mo_{K\alpha}$ (λ=0.7109 Å) TRIUMPH monochromated source and a $Cu_{K\alpha}$ Incoatec microsource. All samples were mounted on MiTeGen sample holders using Paratone oil, and data were collected at 150 K, using an Oxford Cryosystems cold stream. Data were collected for single crystals using a combination of φ and ω scans; data for powder samples were collected using six 360°φ scans encompassing a total 2ϑ range of 5–83°. Diagrams were generated using ORTEP-3[3] and POV-ray.[4]

All single-crystal diffraction data were processed and initial solutions found with the Bruker Apex II software suite. Subsequent refinements were performed with ShelXle.[5] Hydrogen atoms were placed geometrically and refined using a riding model. Additional crystallographic information can be found in Table S1. CCDC 1537965 contains the supplementary crystallographic data for this paper. This data is provided free of charge by The Cambridge Crystallographic Data Centre.

All PXRD patterns were indexed and Pawley[6] refinements were performed in the 2ϑ range 8–65° using Topas Academic.
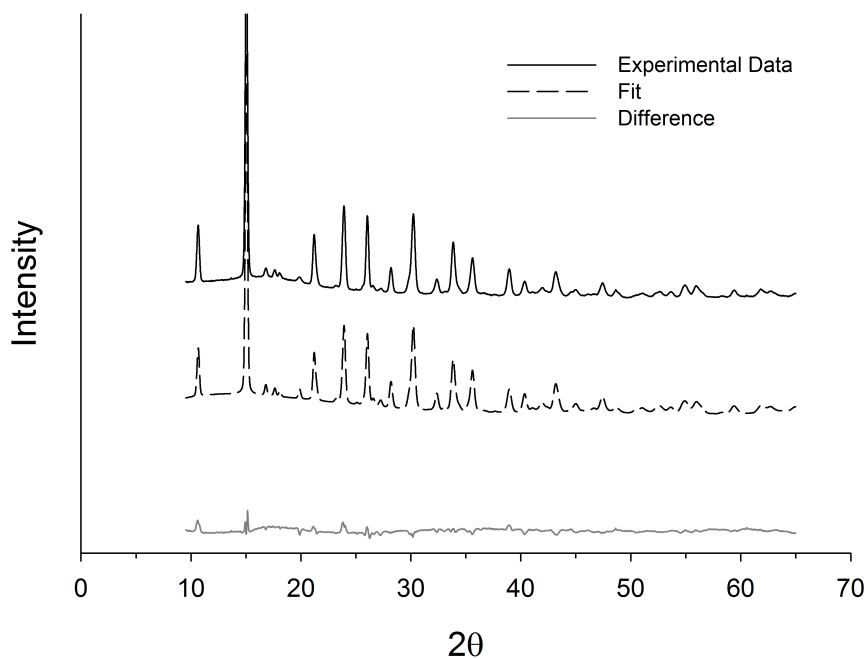

Figure S1: The PXRD pattern of $[Cu_{2/3}Au_{1/3}CN]_2$(DES) fitted by refining against the structure of $[Cu_{1/2}Au_{1/2}CN]_2$(DES). The difference between the experimental data and the fit is also shown.

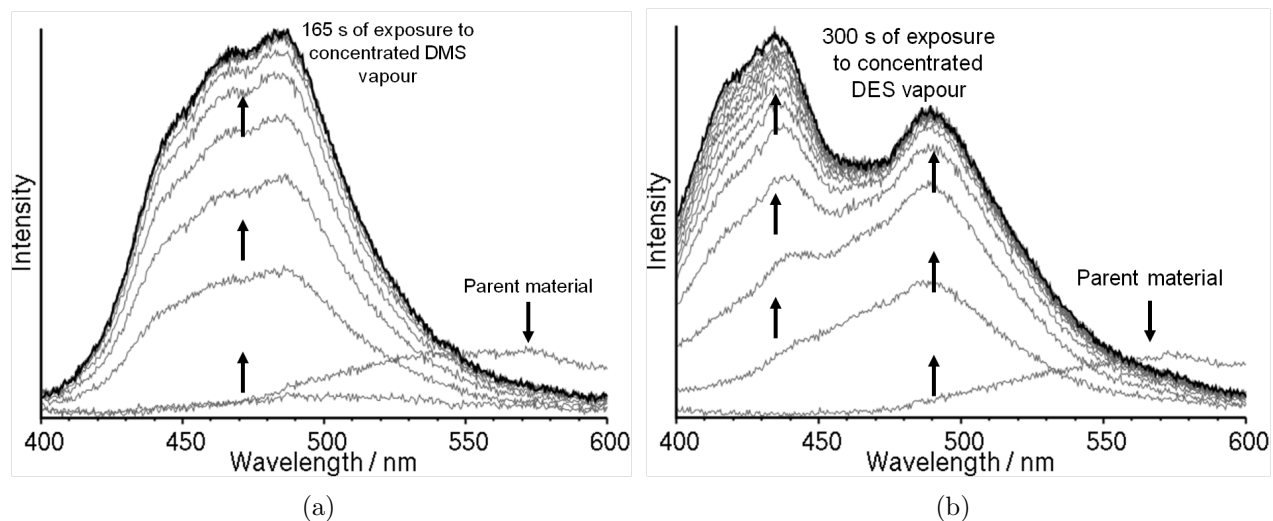(a)   (b)

Figure S2: The change in the emission spectrum of $Cu_{2/3}Au_{1/3}CN$ over time as a sample is exposed to (a) concentrated DMS vapours and (b) concentrated DES vapours. In (a) each curve represents a 15 second interval. In (b) each curve represents a 20 second interval. Arrows indicate whether peaks are increasing or decreasing in intensity as the experiment proceeds.
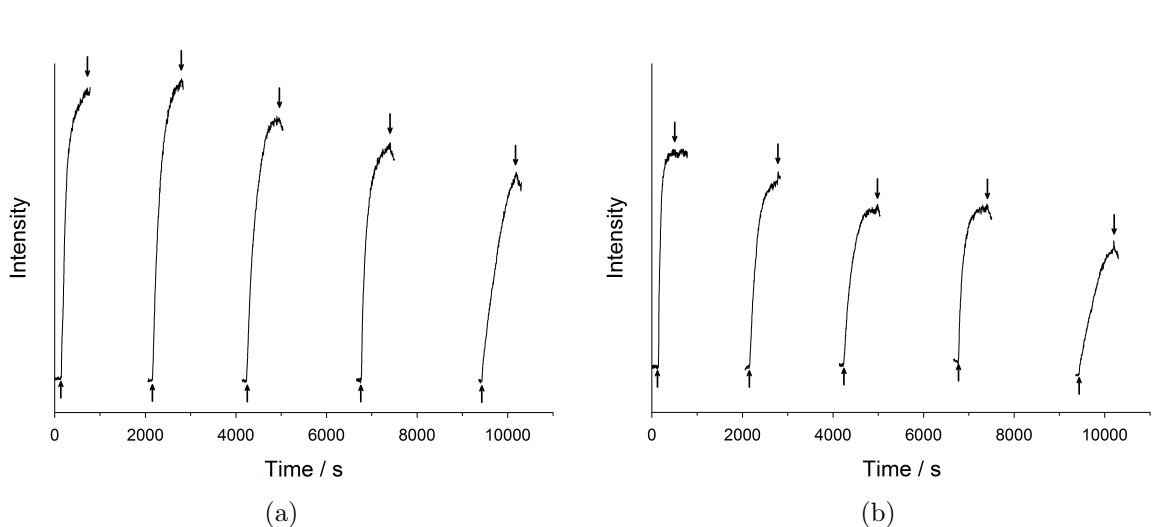

(a)   (b)

Figure S3: Monitoring the emission intensity of $Cu_{2/3}Au_{1/3}CN$ at (a) 435 nm and (b) 490 nm while cycling concentrated DES vapour exposure. The sample was placed in an oven at 120 °C for 15 minutes between curves.
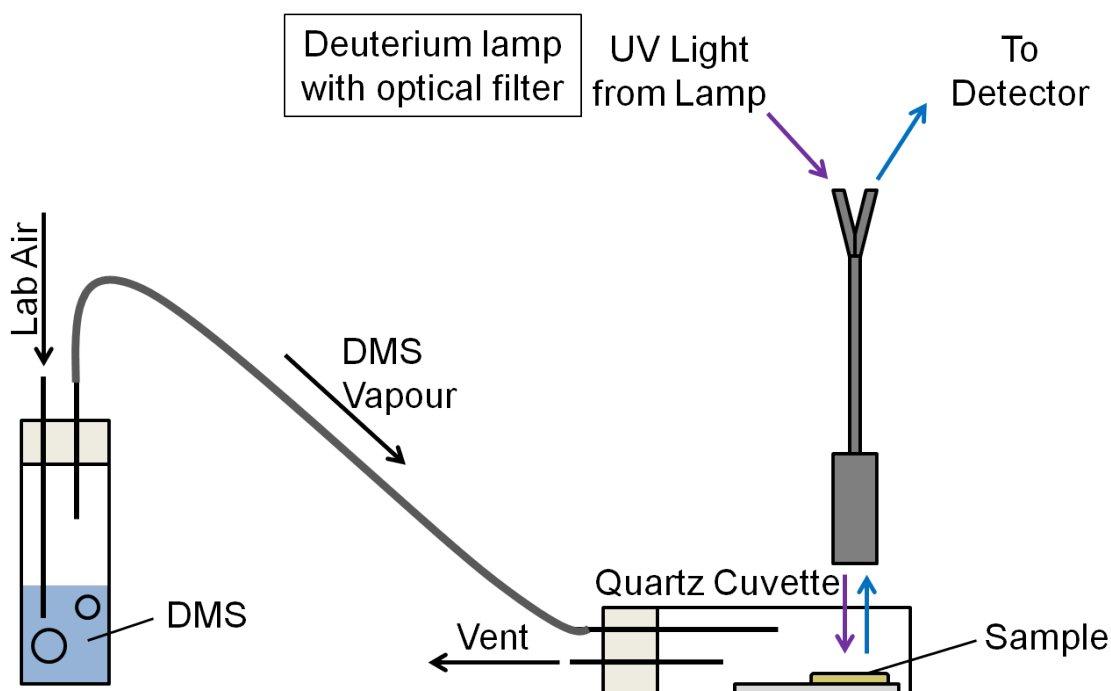
Figure S4: Diagram of apparatus used to perform vapour exposure cycling experiments.

Table S1: Crystallographic data for $[Cu_{1/2}Au_{1/2}CN]_2(DMS)$.

Compound reference	$[Cu_{2/3}Au_{1/3}CN]_2(DMS)$
Chemical formula	$C_4H_6AuCuN_2S$
FW (g·mol^{-1})	374.67
Crystal system	Orthorhombic
Space group	Pbca
a (Å)	15.764(2)
b (Å)	6.7092(10)
c (Å)	16.818(2)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1778.7(4)
Z	8
T (K)	150(2)
μ (mm^{-1})	19.025
Reflns. all	45396
Reflns. unique	2754
R_{int}	0.0694
R1 $[I_0 \geq 2\sigma\ (I_0)]$	0.0226
wR(F2)	0.0460
R1 (all data)	0.0411
wR(F2) (all data)	0.0405
Goodness of fit	1.052

References

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