Electronic Supplementary Information

Conjugated Ligand-based Tribochromic Luminescence

Angela M. Kuchison, Michael O. Wolf* and Brian O. Patrick

*Department of Chemistry, University of British Columbia, Vancouver British Columbia, V6T 1Z1. *E-mail: mwolf@chem.ubc.ca*

Experimental Details

General. 3,3"-Dibromo-2,2':5',2"-terthiophene (Br_2T_3) and AuCl(tht) were synthesized according to literature procedures.[1, 2] ^1H and $^{31}P\{^1H\}$ NMR spectroscopy experiments were carried out on a Bruker AV-300 spectrometer. The ^1H NMR spectra were referenced to residual solvent and the $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Solution absorption spectra were recorded on a Cary 5000 UV/vis/near-IR spectrometer and the emission spectra were recorded on a Cary Eclipse spectrometer. Powder absorption spectra of $(AuCl)_2P_2T_3$ were obtained using an Ocean Optics SD2000 fiber optics spectrometer with a DH-2000 mikropack UV-Vis-NIR light source. For these measurements, the $(AuCl)_2P_2T_3$ was diluted with MgO (~1 mg of $(AuCl)_2P_2T_3$ in 50 mg of MgO). Fluorescence lifetime measurements were carried out using a Horiba Jobin Yvon TBX Picosecond Photon Detection Module (Nanoled 370 nm) for P_2T_3 and a Princeton Instruments Spectra Pro 2300i Imaging Triple Grating Monochromator/Spectrograph with a Hamamatsu Dynamic Range Streak Camera (excitation source: EKSPLA Nd:YAG laser, λ = 355 nm) for $(AuCl)_2P_2T_3$. Raman spectra were carried out using a Renishaw System 1000 confocal microscope with a 785 nm diode laser source and charge-coupled device (CCD) detector. Spectra were collected

for 30 s from 350-1800 cm^{-1} using 1% laser power. Powder XRD (PXRD) data were recorded on a Bruker D8 Advance diffractometer with graphite monochromated Cu Kα radiation. The $(AuCl)_2P_2T_3$ powder used for the PXRD was crushed after the measurement on a zero background silicon wafer and a diffractogram was then obtained.

Solid State Emission Spectroscopy

Samples of $(AuCl)_2P_2T_3 \cdot CH_2Cl_2$ for emission measurements were recrystallized four times from $CHCl_3/CH_2Cl_2$/hexanes. To prepare thin films of $(AuCl)_2P_2T_3$ for emission measurements, the solid was dissolved in minimal $CHCl_3$ and the solution drop-cast onto a quartz slide and dried at room temperature. The emission spectrum of $(AuCl)_2P_2T_3$ was obtained by preparing a slurry of $(AuCl)_2P_2T_3$ in hexanes which was drop-cast onto a quartz slide and dried at room temperature. The ground $(AuCl)_2P_2T_3$ sample was prepared by pressing a second quartz slide on top of the slide of microcrystalline $(AuCl)_2P_2T_3$ and then twisting the two slides while pressing them against each other.

X-Ray Crystallographic Analysis of $(AuCl)_2P_2T_3$

A pale yellow plate-shaped crystal of $(AuCl)_2P_2T_3$, having dimensions 0.30 × 0.20 × 0.015 mm^3, was placed on the tip of a mitegen micromount with paratone® oil. The sample was then cooled to 113(2) K using an Oxford Cryostream controller. Data was collected in the range $3° \leq 2\theta \leq 63°$ on a Bruker SMART diffractometer equipped with an APEX II CCD detector and a graphite monochromated Mo Kα sealed X-ray tube operating at 1.5 kW (50 kV, 30 mA). The data were corrected by integration for the effects of absorption with a transmission range 0.490 – 0.746. Final unit-cell dimensions were determined on the basis of 9991 well-centred reflections with range $4° \leq 2\theta \leq 63°$.

The programs used for the absorption correction, and data reduction were from the Bruker APEX II Crystal Structure System. The structure was solved with Sir92 and refined using CRYSTALS.[3] Diagrams were made using ORTEP-3,[4] and POV-RAY.[5] Complex scattering factors for neutral atoms were used in the calculation of structure factors.[6]

The structure appeared to exhibit some disorder due to rotation about two of the C-P bond. Due to the low (5%) disorder only the gold atoms were found, but are not included in our model. One of the dichloromethane units and a thiophene unit were also found to be disordered and were treated accordingly. Selected bond lengths and angles for one of the two molecules of $(AuCl)_2P_2T_3$ can be found in Table S3.

X-Ray Crystallographic Analysis of P_2T_3

An orange plate crystal of $C_{36}H_{26}P_2S_3$ having approximate dimensions of 0.03 × 0.18 × 0.25 mm was mounted on a glass fiber. Data were collected at a temperature of -100.0 ± 0.1°C to a maximum 2θ value of 56.1°, on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. Data were collected in a series of φ and ω scans in 0.50° oscillations with 20.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Of the 24614 reflections that were collected, 7094 were unique (R_{int} = 0.050); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT[7] software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 3.84 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (SADABS[8]), with minimum and maximum transmission coefficients of 0.884 and 0.989, respectively. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods[9]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement (Least Squares function minimized: $\Sigma w(F_o^2-F_c^2)^2$) on F^2 was based on 7094 reflections and 370 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.095$

$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2)/ \Sigma w(Fo^2)^2]^{1/2} = 0.108$

The standard deviation of an observation of unit weight (Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$; where: N_o = number of observations, N_v = number of variables) was 1.00. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.51 and –0.32 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[10] Anomalous dispersion effects were included in Fcalc;[11] the values for Δf' and Δf'' were those of Creagh and McAuley[12]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[13]. All refinements were performed using the SHELXTL[14] crystallographic software package of Bruker-AXS. Diagrams were made using ORTEP-3,[4] and POV-RAY.[5]

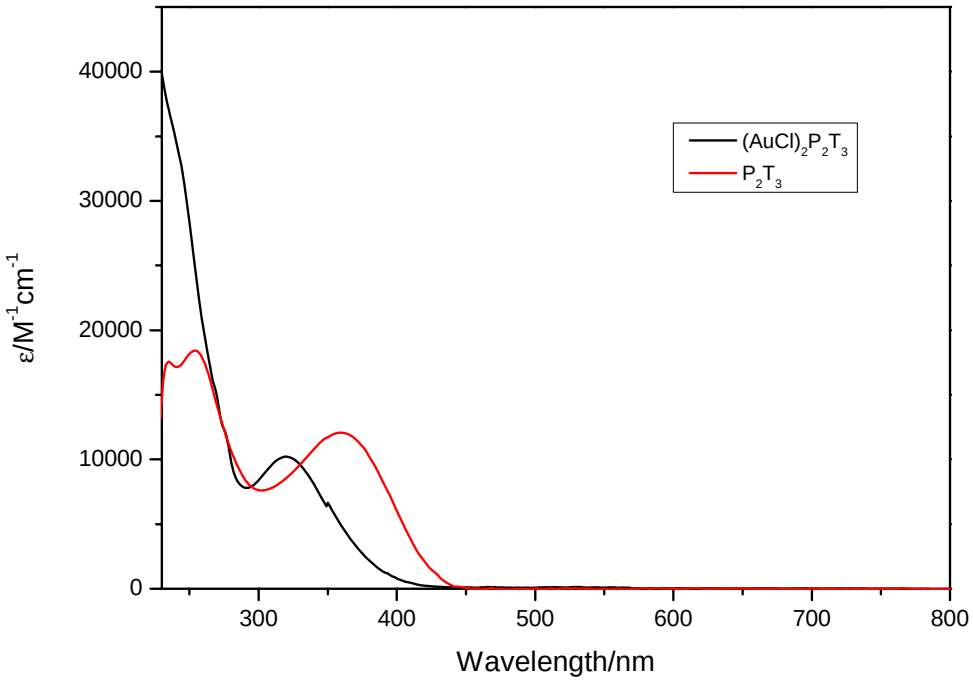

Figure S1. Absorption spectra of $(AuCl)_2P_2T_3$ and P_2T_3 in CH_2Cl_2.

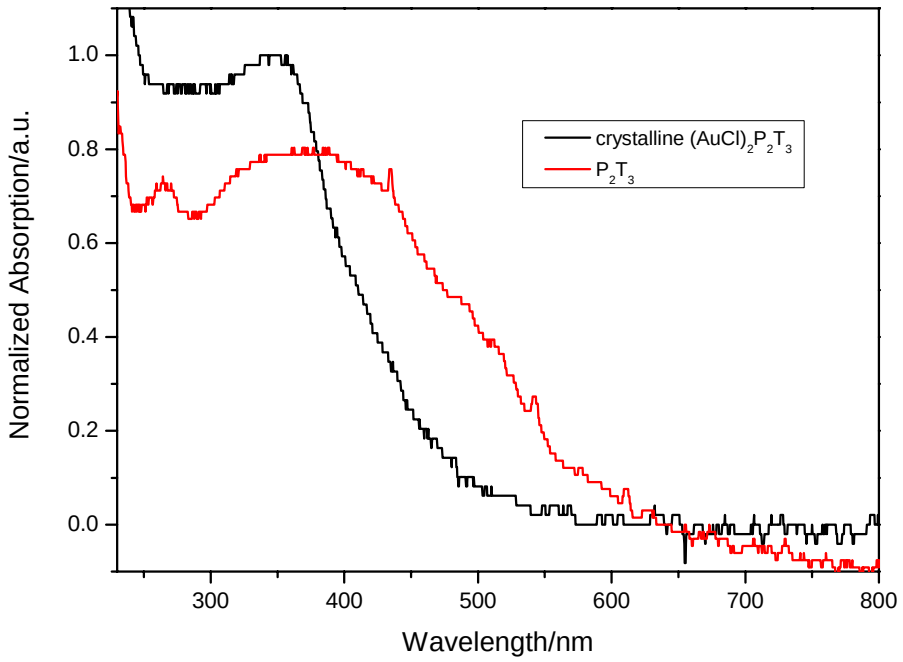

Figure S2. Solid state absorption spectra of $(AuCl)_2P_2T_3$ and P_2T_3.

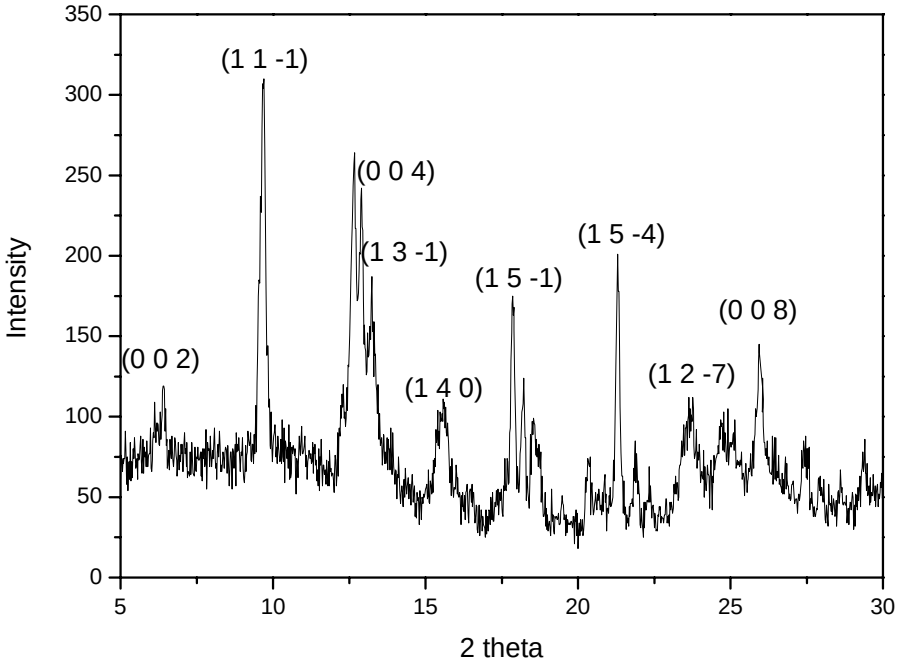

Figure S3. Powder XRD of microcrystalline $(AuCl)_2P_2T_3$.

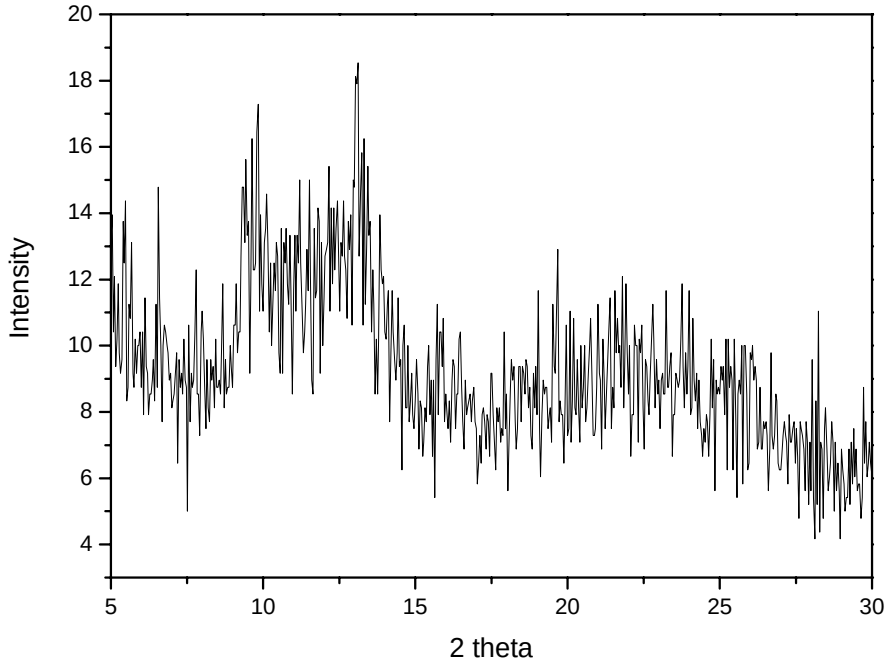

Figure S4. Powder XRD of ground $(AuCl)_2P_2T_3$.

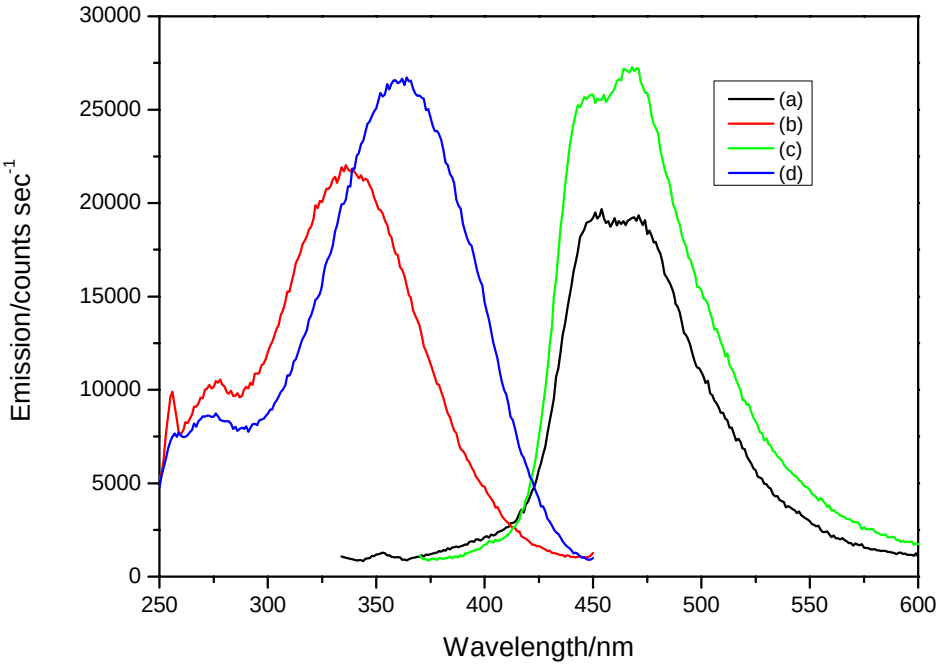

Figure S5. Emission and excitation spectra of $(AuCl)_2P_2T_3$ and P_2T_3 in CH_2Cl_2 (a) emission scan of $(AuCl)_2P_2T_3$, λ_{ex} = 320 nm; (b) excitation scan of $(AuCl)_2P_2T_3$, λ_{em} = 460 nm; (c) emission scan of P_2T_3, λ_{ex} = 360 nm; (d), excitation scan of P_2T_3, λ_{em} = 460 nm.

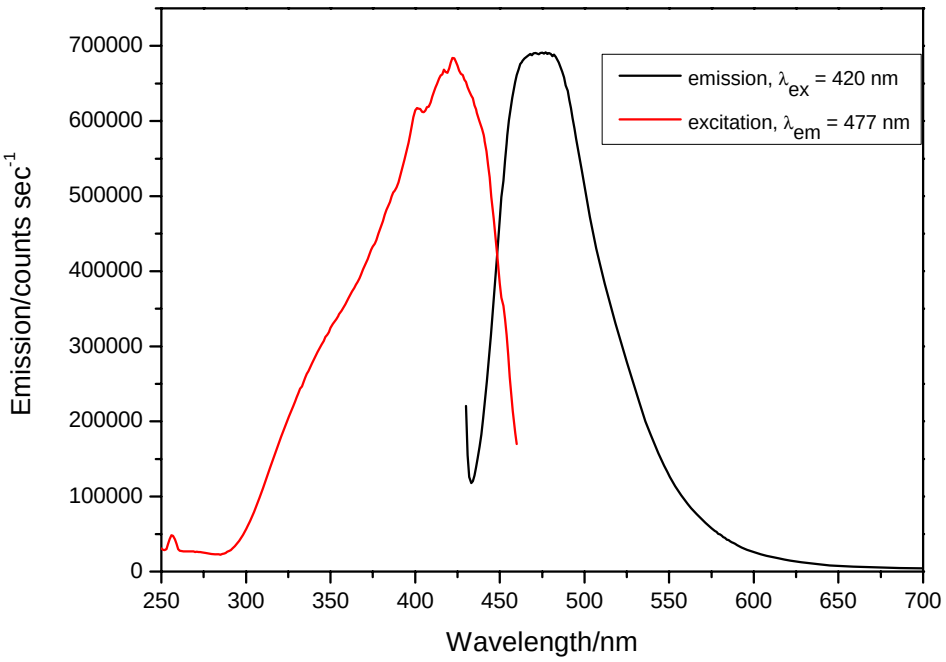

Figure S6. Excitation and emission spectra of solid, ground $(AuCl)_2P_2T_3$.

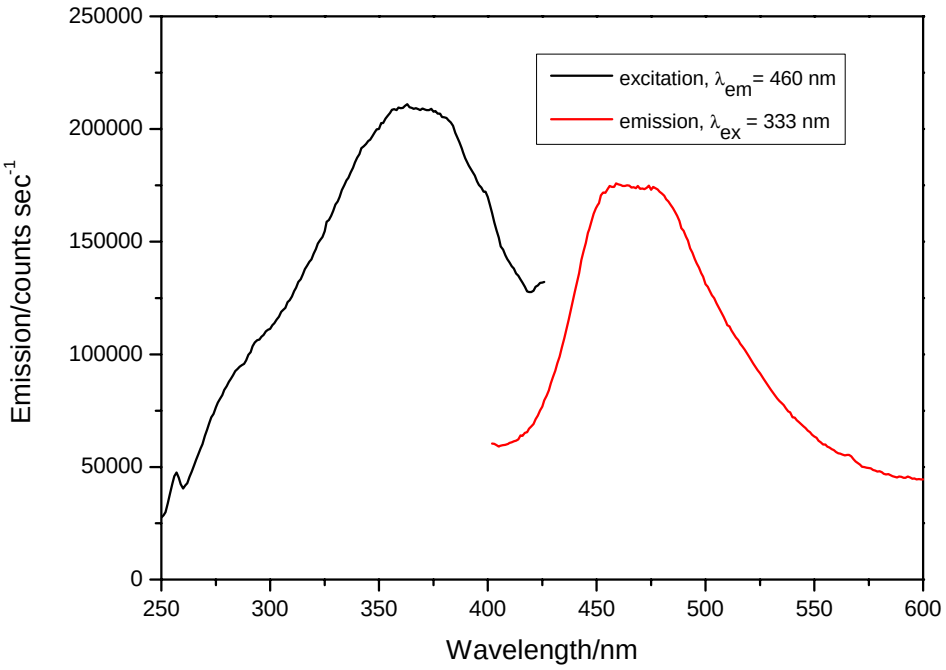

Figure S7. Excitation and emission spectra of $(AuCl)_2P_2T_3$ (dropcast film).

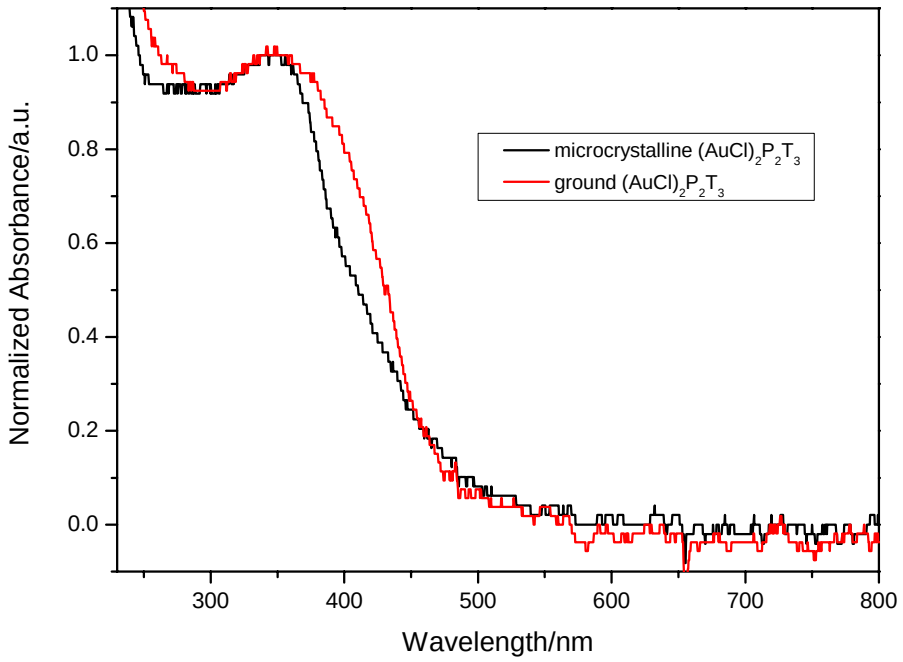

Figure S8. Absorption spectra of $(AuCl)_2P_2T_3$.

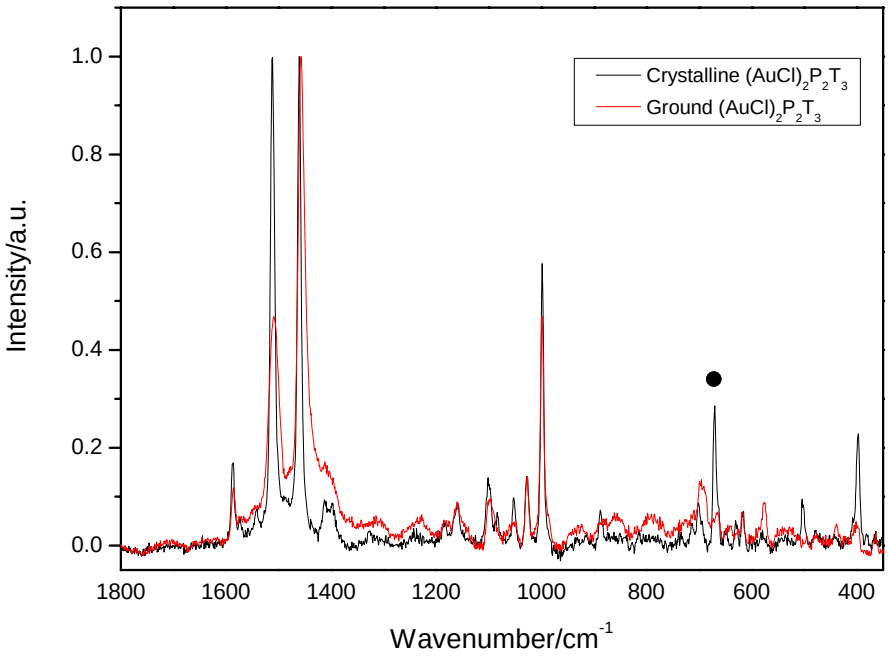

Figure S9. Baseline corrected Raman spectra of crystals of $(AuCl)_2P_2T_3$ and ground crystals of $(AuCl)_2P_2T_3$.

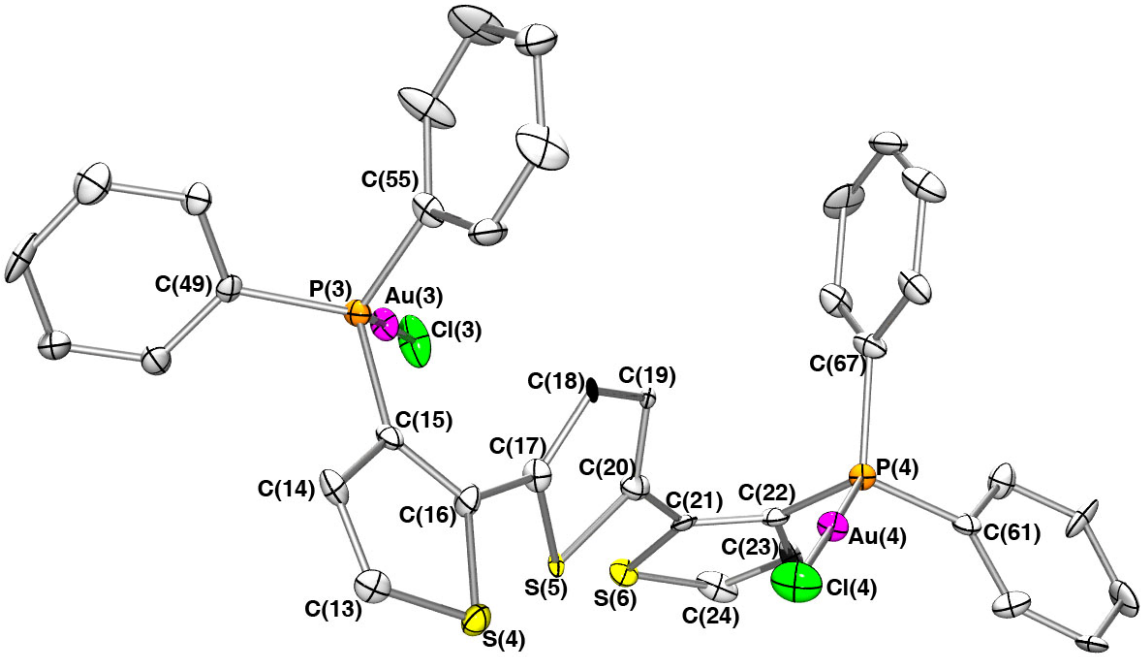

Figure S10. Solid-state molecular structure of the second $(AuCl)_2P_2T_3$ molecule in the unit cell (molecule B). Hydrogen atoms and occluded solvent are omitted for clarity and thermal ellipsoids are drawn at 50% probability.

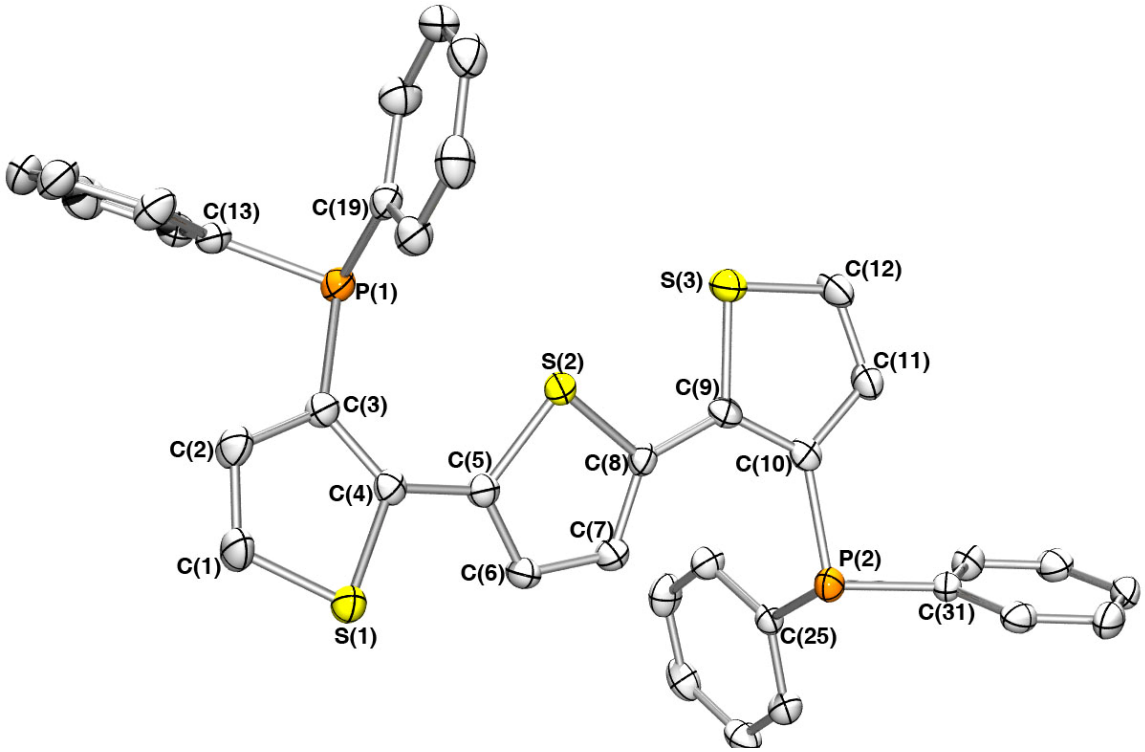

Figure S11. Solid-state molecular structure of P_2T_3. Hydrogen atoms are omitted for clarity and thermal ellipsoids are drawn at 50% probability.

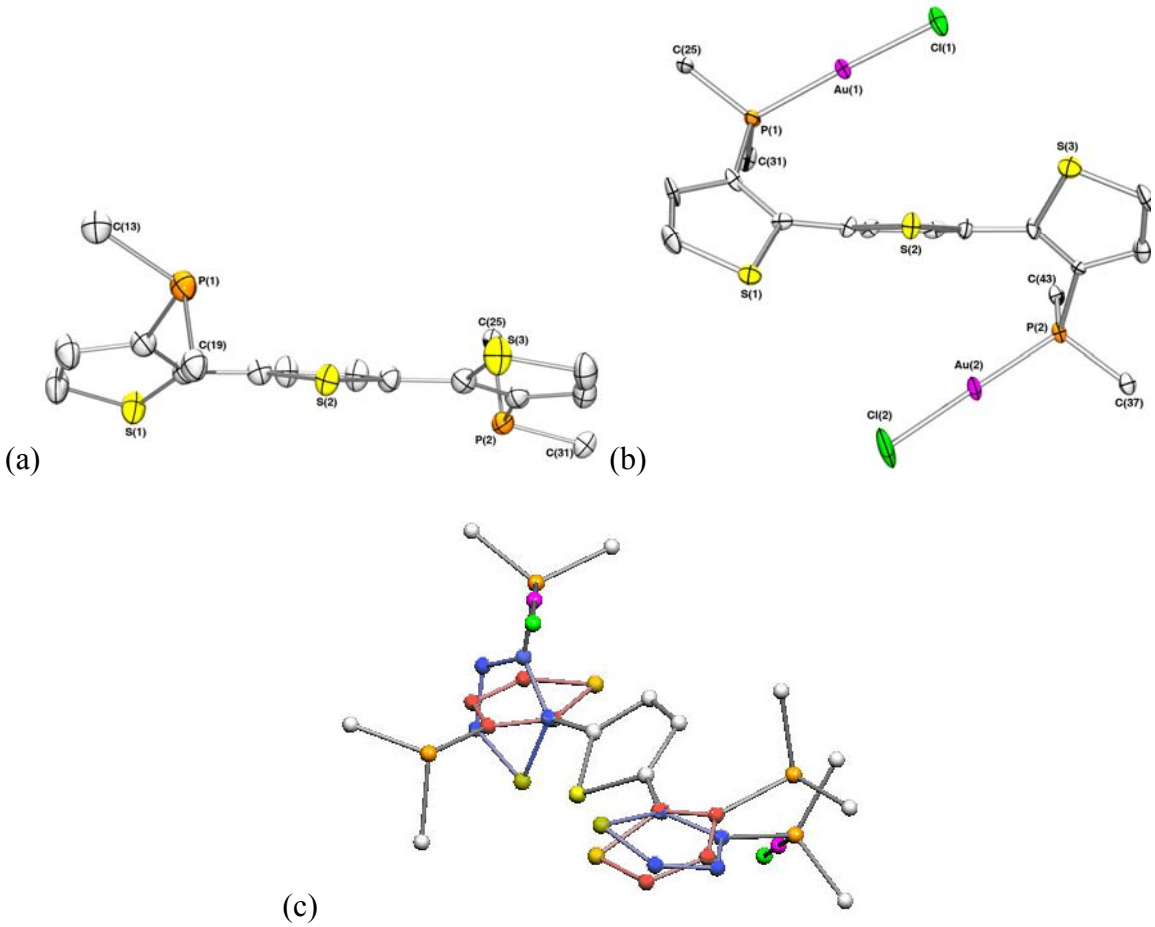

Figure S12. Solid-state molecular structures of (a) P_2T_3, (b) Molecule A of $(AuCl)_2P_2T_3$ showing the interannular torsion angle differences. Hydrogen atoms, occluded, and phenyl rings are omitted for clarity and thermal ellipsoids are drawn at 50% probability. (c) superimposed image of the atomic coordinates of P_2T_3 (with terminal thiophenes highlighted in red) and $(AuCl)_2P_2T_3$ (with terminal thiophenes highlighted in blue) generated from their solid-state molecular structures with phenyl rings and hydrogen atoms omitted for clarity.

Table S1. Assignments of Raman bands for crystalline $(AuCl)_2P_2T_3$ and ground $(AuCl)_2P_2T_3$.

Crystalline $(AuCl)_2P_2T_3$		**Ground $(AuCl)_2P_2T_3$**	
Band (cm^{-1})	Assignment	Band (cm^{-1})	Assignment
1586 (w)	ν(C=C) (ph)*	1586 (w)	ν(C=C) (ph)*
1512 (s)	ν_{asym}(C=C) (th)**	1509 (s)	ν_{asym}(C=C) (th)**
1460 (s)	ν_{sym}(C=C) (th)**	1457 (s)	ν_{sym}(C=C) (th)**
1400 (br, w)	ν(C-C) (th)**	1400 (br, vw)	ν(C-C) (th)**
1158(w),	δ(C-H)** and ν(P-C)*	1157(w),	δ(C-H)** and ν(P-C)*
1101(w),		1100(w),	
1053(w),		1056(w),	
1028(w)		1028 (w)	
998 (s)	ν(C-S)** and/or ring	998 (s)	ν(C-S)** and/or ring
	breathing (ν(C=C) (ph))*		breathing (ν(C=C) (ph))*
702 (w)	Ph vib*	695 (w)	Ph vib*
671 (m)	Ring bending (th)***	668 (vw)	Ring bending (th)***
504 (w)	Ring deformation*	616 (w)	Ring vibrations*
		577 (w)	Ring vibrations*

*Assignments based on reference.[15]

**Assignments based on reference.[16]

***Assignments based on reference.[17]

ph = phenyl, th = thienyl

Table S2. Selected Crystallographic Data for $(AuCl)_2P_2T_3{\cdot}CH_2Cl_2$ and P_2T_3.

	$(AuCl)_2P_2T_3{\cdot}CH_2Cl_2$	P_2T_3
formula	$C_{37}\ H_{28}\ Au_2\ Cl_4\ P_2\ S_3$	$C_{36}H_{26}P_2S_3$
habit	plate	plate
dimensions/mm	0.015 × 0.20 × 0.30	0.03 × 0.18 × 0.25
temperature/K	113(2)	173(2)
cryst syst	monoclinic	triclinic
space group	P 2_1/c (#14)	P –1 (#2)
a/Å	9.6976(2)	9.3829(7)
b/ Å	28.8439(6)	11.5838(9)
c/Å	27.6767(6)	14.4954(12)
α/deg	90	89.673(4)
β/deg	97.3710(10)	72.855(4)
γ/deg	90	80.512(4)
V/ Å^3	7677.7(3)	1483.4(2)
Z	8	2
ρ_{calc}/g cm^{-1}	2.018	1.381
μ (Mo Kα)/mm^{-1}	8.187	0.384
R[a] (I > 2.0σ(I))	0.0715	0.0462
R_w[a] (I > 2.0σ(I))	0.0669	0.0920
goodness of fit	1.15	1.00

[a]Function minimized $\Sigma w(|F_o| - |F_c|)^2$ $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$.

Table S3. Selected bond lengths and angles of $(AuCl)_2P_2T_3 \cdot CH_2Cl_2$.

$(AuCl)_2P_2T_3$ (A)		**$(AuCl)_2P_2T_3$ (B)**	
Bond Lengths (Å)			
Au(1)-Cl(1)	2.288(3)	Au(3)-Cl(3)	2.289(3)
Au(2)-Cl(2)	2.283(3)	Au(4)-Cl(4)	2.287(3)
Au(1)-P(1)	2.232(3)	Au(3)-P(3)	2.220(3)
Au(2)-P(2)	2.223(3)	Au(4)-P(4)	2.229(3)
P(1)-C(3)	1.791(11)	P(3)-C(15)	1.800(11)
P(1)-C(25)	1.807(12)	P(3)-C(49)	1.801(11)
P(1)-C(31)	1.812(12)	P(3)-C(55)	1.814(11)
P(2)-C(10)	1.804(10)	P(4)-C(22)	1.795(12)
P(2)-C(37)	1.815(12)	P(4)-C(61)	1.797(12)
P(2)-C(43)	1.811(11)	P(4)-C(67)	1.808(11)
S(1)-C(1)	1.723(14)	S(6)-C(21)	1.719(11)
S(1)-C(4)	1.736(11)	S(6)-C(24)	1.703(15)
C(1)-C(2)	1.335(17)	C(21)-C(22)	1.378(15)
C(2)-C(3)	1.426(15)	C(22)-C(23)	1.443(16)
C(3)-C(4)	1.414(16)	C(23)-C(24)	1.367(17)
C(4)-C(5)	1.440(15)	C(20)-C(21)	1.494(12)
Angles (deg)			
Cl(1)-Au(1)-P(1)	177.14(11)	Cl(3)-Au(3)-P(3)	177.22(13)
Cl(2)-Au(2)-P(2)	178.47(17)	Cl(4)-Au(4)-P(4)	178.85(12)

Au(1)-P(1)-C(3)	112.1(3)	Au(4)-P(4)-C(22)	111.3(4)
Au(1)-P(1)-C(25)	115.6(4)	Au(4)-P(4)-C(61)	114.9(4)
C(3)-P(1)-C(25)	101.9(5)	C(22)-P(4)-C(61)	104.4(5)
Au(1)-P(1)-C(31)	114.5(4)	Au(4)-P(4)-C(67)	114.1(4)
C(3)-P(1)-C(31)	106.6(5)	C(22)-P(4)-C(67)	106.2(5)
C(25)-P(1)-C(31)	105.0(5)	C(61)-P(4)-C(67)	105.0(5)
C(1)-S(1)-C(4)	92.4(6)	C(21)-S(6)-C(24)	91.5(6)
S(1)-C(1)-C(2)	111.2(9)	C(23)-C(24)-S(6)	112.5(9)
C(1)-C(2)-C(3)	115.6(11)	C(22)-C(23)-C(24)	112.7(11)
C(2)-C(3)-C(4)	110.3(10)	C(21)-C(22)-C(23)	110.4(10)
C(3)-C(4)-S(1)	110.5(8)	S(6)-C(21)-C(22)	112.8(8)
C(2)-C(3)-P(1)	127.7(9)	P(4)-C(22)-C(23)	125.5(9)
P(1)-C(3)-C(4)	121.7(8)	P(4)-C(22)-C(21)	123.7(8)
Torsion Angles (deg)			
S(1)-C(4)-C(5)-S(2)	51(1)	S(4)-C(16)-C(17)- S(5)	51(1)
S(2)-C(8)-C(9)-S(3)	-49(1)	S(5)-C(20)-C(21)-S(6)	50.3(9)

Table S5. Selected bond lengths and angles of P_2T_3.

Bond Lengths (Å)			
C(3)-P(1)	1.830(2)	C(19)-P(1)	1.834(2)
C(13)-P(1)	1.845(2)	C(10)-P(2)	1.826(3)
C(25)-P(2)	1.842(2)	C(31)-P(2)	1.833(2)
C(1)-C(2)	1.343(4)	C(1)-S(1)	1.707(3)
C(2)-C(3)	1.429(3)	C(3)-C(4)	1.376(3)
C(4)-C(5)	1.453(3)		
Angles (deg)			
C(3)-P(1)-C(19)	103.19(11)	C(3)-P(1)-C(13)	101.58(11)
C(19)-P(1)-C(13)	100.07(11)	C(2)-C(1)-S(1)	112.0(2)
C(1)-C(2)-C(3)	114.2(2)	C(4)-C(3)-C(2)	110.7(2)
C(4)-C(3)-P(1)	123.02(18)	C(2)-C(3)-P(1)	125.90(19)
C(3)-C(4)-S(1)	111.58(18)		
Torsion Angles (deg)			
S(1)-C(4)-C(5)-S(2)	-149.65(15)	S(2)-C(8)-C(9)-S(3)	-17.7(3)

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