Conjugated ligand-based tribochromic luminescence†

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A Au(I) complex containing a terthienyl diphosphine ligand is non-emissive in the crystalline form, but exhibits intense ligand-based emission upon grinding attributed to increased planarization in the terthienyl ligand.

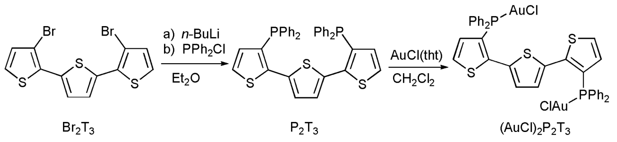
Materials that show changes in photoluminescence with applied pressure are of interest due to their potential application in data recording, forensics (*i.e.* fingerprinting) and stress–strain sensors. This phenomenon, known either as tribochromic[1,2] or mechanochromic[3] luminescence, is typically a result of either alterations in intermolecular interactions resulting in phase transformations,[3,4] chemical reactions which result in changes in the solid-state structure,[1] or solid-state defects.[5] Most examples of pressure dependent luminescence are attributed to metal–metal interactions, particularly in Au(I) and Pt(II) complexes.[6] In an effort to identify new structural motifs designed to elicit a luminescence response with applied pressure, we became interested in the possibility of pressure-induced conjugation changes in conjugated ligands attached to metals. A few organic molecules such as sterically congested dicyanomethylene derivatives[7] are known to undergo changes in conformation under mild applied pressure (scratching of a solid sample) resulting in tribochromic behaviour. The π–π* absorption bands of poly(3-alkylthiophenes) red-shift at high applied pressure due to more extended conjugation resulting from packing of the alkyl substituents under pressure.[8,9]

In order to evoke tribochromic luminescence under mild pressure, conjugated molecules must undergo structural transformations resulting in a change in conjugation when ground or pressed. Many conjugated oligomers pack preferentially as planar structures in the solid state,[10] for example, oligothiophenes tend to adopt planar conformations in the solid state despite a low energy barrier for rotation between thiophene rings[11] and the reduction in steric stress that arises when adjacent rings are twisted out of plane relative to one another. Judiciously chosen substituents on the oligomer are needed to allow for more than one stable solid structure to exist at near ambient pressures. One strategy is to incorporate conjugated groups as ligands on metal complexes. This introduces a powerful structural organization element (the metal) which may be used to influence ligand conjugation.[12,13] Au(I) complexes are a particularly good choice as these metal centers have been shown to primarily affect structure, while having only minimal electronic effects, with other conjugated ligands.[12] Here we report the first example of a metal complex which exhibits conjugated ligand-based tribochromic luminescence.

The diphosphine 3,3″-bis(diphenylphosphino)-2,2:5′,2″-terthiophene (P_2T_3) was selected as a suitable conjugated ligand. Conjugated phosphines[13–16] have been previously used as ligands, including in gold(I) complexes.[12,17] P_2T_3 was synthesized *via* lithiation of Br_2T_3,[18] followed by reaction with Ph_2PCl (Scheme 1). After warming to room temperature, addition of water immediately precipitated P_2T_3 as a yellow solid. Reaction of AuCl(tht) (tht = tetrahydrothiophene) with P_2T_3 resulted in the formation of $(AuCl)_2P_2T_3$ which was isolated as an off-white solid.‡

Crystals of $(AuCl)_2P_2T_3$ were grown from a CH_2Cl_2–hexanes solution. The solid-state structure contains two, crystallographically unique, molecules of $(AuCl)_2P_2T_3$. The solid-state molecular structure of one of the two molecules is shown in Fig. 1. The Au centers are linearly coordinated, and the Au–P and Au–Cl bond lengths are similar to those in $ClAuPPh_3$[19] and other related Au complexes.[12,17] The central thiophene is twisted significantly out of plane with the adjacent, terminal thiophene rings. The bond lengths and angles in the second $(AuCl)_2P_2T_3$ molecule in the structure are very similar. No intermolecular or intramolecular gold–gold interactions are present in the solid state.

Crystalline $(AuCl)_2P_2T_3$ has an absorption band with λ_{max} = 350 nm (see ESI†), attributed to a terthienyl ligand-based π–π* transition. This is blue-shifted relative to the absorption of yellow P_2T_3 in the solid state (λ_{max} = 400 nm). The higher energy of the π–π* absorption in $(AuCl)_2P_2T_3$ is consistent with the reduced coplanarity between thiophene rings in the structure of $(AuCl)_2P_2T_3$ (interannular torsion angles ~45–50°) compared with those in the single crystal X-ray structure of P_2T_3 (interannular torsion angles ~17–30°, see ESI†). When a solid sample of $(AuCl)_2P_2T_3$ (dropcast on a quartz slide from a hexanes slurry) is photoexcited with a 365 nm hand-held UV-lamp, no emission is observed by eye. When a second quartz slide was pressed by hand onto the sample and twisted several times to grind the $(AuCl)_2P_2T_3$, the sample began to emit blue light under 365 nm excitation. This emission remains when the pressure is released from the slide. The solid-state



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data, absorption and emission spectra, PXRD, Raman spectra and selected crystallographic data. CCDC 742148 and 749960. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b915089g

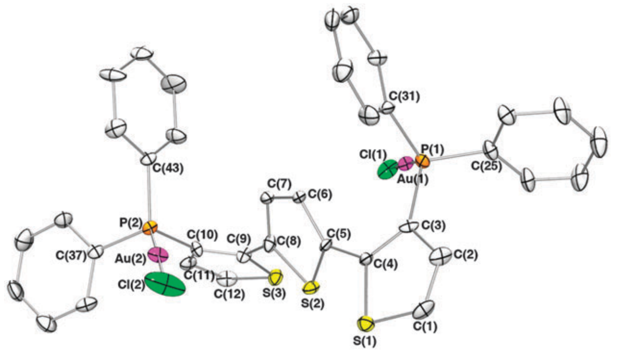

Fig. 1 Solid-state molecular structure of one of the two $(AuCl)_2P_2T_3$ molecules. Hydrogen atoms and occluded solvent are omitted for clarity and thermal ellipsoids are drawn at 50% probability.

emission spectra of the sample before and after grinding are shown in Fig. 2. The ground sample shows a strong emission band with a maximum at 475 nm.

The powder X-ray diffractogram (PXRD) of the microcrystalline material deposited on the quartz slide matches the diffractogram calculated from the single crystal structure confirming that the structure of $(AuCl)_2P_2T_3$ prior to grinding is the same as in the single crystal structure. When the sample is ground, the sharp reflections disappear in the PXRD and are replaced with a broad reflection with a maximum at $2\theta = 20^\circ$. An additional broad reflection is observed at 13°, with underlying sharp reflections at 9° and 13° which are coincident with the peaks observed for as-prepared $(AuCl)_2P_2T_3$. These sharper reflections may be due to remaining unground $(AuCl)_2P_2T_3$. Overall, the PXRD results indicate that grinding reduces the crystallinity of the sample.

To elucidate the origin of the tribochromic luminescence, absorption and emission data of $(AuCl)_2P_2T_3$ and P_2T_3 were compared. In CH_2Cl_2 solution, both $(AuCl)_2P_2T_3$ and P_2T_3 emit with $\lambda_{max} = 465$ nm (see ESI†), however the excitation spectra differ with $\lambda_{max} = 336$ nm for $(AuCl)_2P_2T_3$ and $\lambda_{max} = 362$ nm for P_2T_3. Both excitation spectra match the respective absorption spectra of the two compounds. Time-resolved emission decays for both P_2T_3 and $(AuCl)_2P_2T_3$ are multiexponential with lifetimes of ~250 ps (~51%) for P_2T_3 and ~90 ps (~90–95%) for $(AuCl)_2P_2T_3$. The similarity of the emission spectra and lifetimes, and their insensitivity to the presence of oxygen, support the conclusion that the emissive excited state in solution is a terthiophene-localized π–π^* singlet state for both $(AuCl)_2P_2T_3$ and P_2T_3. The sterically hindered gold centers in $(AuCl)_2P_2T_3$ prevent aurophilic interactions, which have previously led to emission from low-lying Au–Au excited states,[20,21] and mechanochromic luminescence.[1,3] Thin films of $(AuCl)_2P_2T_3$ dropcast from $CHCl_3$ solution also emit strongly at 465 nm, suggesting that the conformation of the molecules in these films is similar to the solution structure.

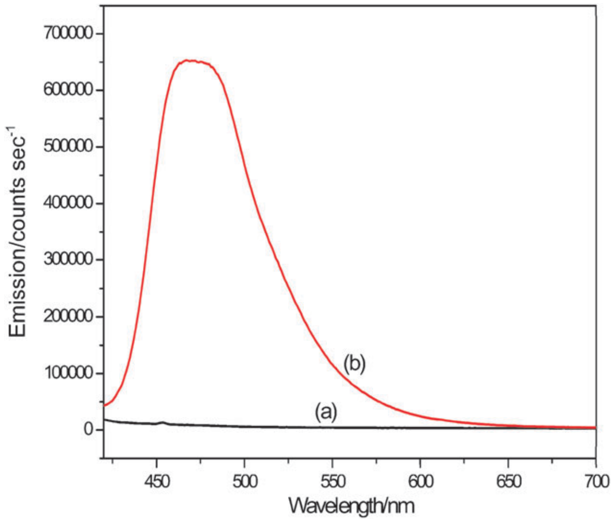

Fig. 2 Emission spectra of solid $(AuCl)_2P_2T_3$ (a) as prepared and (b) after grinding. $\lambda_{ex} = 400$ nm.

The solid-state emission of $(AuCl)_2P_2T_3$ ($\lambda_{max} = 475$ nm) after grinding is very similar to the emission in solution ($\lambda_{max} = 465$ nm), suggesting that emission arises from the same state in both cases. The emission of solid P_2T_3 is also influenced by grinding. A new emission band with $\lambda_{max} = 490$ nm appears when a sample of P_2T_3 is ground, in addition to the original broad emission band at 560 nm, however this new emission feature is temporary and disappears when the sample rests overnight. Ground $(AuCl)_2P_2T_3$ shows no decrease or change in luminescence after one week.

Grinding of the $(AuCl)_2P_2T_3$ sample results in a small (~10 nm) red-shift in the solid-state absorption spectrum (see ESI†). This red-shift is consistent with an increase in the interannular conjugation in the terthienyl group in the ground sample relative to what is observed in the crystal structure. This is similar to the red-shift in absorption observed for poly(3-dodecylthiophene) under pressure which has been postulated to result from the uncoiling and flattening of the polythiophene backbone.[9] It is likely that weak inter- or intramolecular interactions result in the observed large interannular torsion angle in the microcrystalline $(AuCl)_2P_2T_3$ sample, but these are disrupted upon grinding, bringing the thiophene rings into greater conjugation.

Both crystalline and ground $(AuCl)_2P_2T_3$ have Raman spectra characteristic of oligo- and polythiophenes with strong bands at 1510, 1459, and 998 cm^{-1} assigned to the asymmetric ν(C=C), symmetric ν(C=C), and ν(C–S) stretches, respectively (see ESI†).[22] Between 400 and 800 cm^{-1} the spectra of the crystalline and ground samples show significant differences. Notably, the crystalline $(AuCl)_2P_2T_3$ sample has a band at 670 cm^{-1} which is absent in the spectrum of the ground material. Analysis of the Raman spectra of 2,2′:5′,2″-terthiophene in solution and the solid state has shown that ring bending vibrations between 650 and 700 cm^{-1} are dependent on the interannular torsion angles.[23] Solid terthiophene, where the rings are coplanar, has a peak at 691 cm^{-1}, while in solution the presence of non-coplanar conformers gives rise to four peaks in this region. The Raman spectrum of $ClAu(PPh_3)$[24] also has phenyl vibrations in this region, less intense bands in the spectra of as-prepared and ground $(AuCl)_2P_2T_3$ are assigned to these vibrations. The enhanced intensity of the Raman band at 670 cm^{-1} in crystalline $(AuCl)_2P_2T_3$ is therefore attributed to a Raman mode in the less planar terthienyl group which, upon application of pressure, weakens in intensity as the terthiophene group becomes more planar. The other intensity differences in the Raman spectra are also attributed to conformational changes upon grinding. These Raman spectral differences provide additional support for the conclusion that grinding results in increased coplanarity of the terthienyl group. This structural change apparently results in deactivation of a non-radiative decay pathway present in the crystalline solid, causing the observed increase in luminescence.

In summary, we report tribochromic luminescence resulting from planarization of a conjugated terthienyl group attached to Au(I) centers. This is the first example of conjugated ligand-based emission tribochromism in a metal complex. Further explorations of this new type of tribochromic luminescence are underway.

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Notes and references

‡ *Synthesis of P_2T_3.* An ether solution (50 mL) of Br_2T_3 (1.00 g, 2.46 mmol) was cooled to −78 °C and 1.6 M *n*-BuLi (3.84 mL, 6.15 mmol) in hexanes was added dropwise. The reaction was slowly warmed to −30 °C and $PClPh_2$ (1.15 mL, 6.40 mmol) was added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched by addition of water (50 mL). P_2T_3 immediately precipitated as a bright yellow solid, and was collected by vacuum filtration. Yield = 1.01 g (67%). Crystals suitable for single crystal X-ray diffraction were grown from a $CDCl_3$–hexanes–acetone solution. ^1H NMR (300 MHz, $CDCl_3$): δ 6.59 (d, 2H, J = 5 Hz), 7.06 (s, 2H), 7.16 (d, 2H, J = 5 Hz), 7.33 (m, 20H). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ −24.50 (s). EI-MS m/z 616 (100%, $[M]^+$). Anal. calcd for $C_{36}H_{26}P_2S_3$: C, 70.11; H, 4.25%. Found: C, 69.58; H, 4.30%. *Synthesis of $(AuCl)_2P_2T_3\cdot CH_2Cl_2$.* A solution (10 mL) of P_2T_3 (125 mg, 0.203 mmol) in CH_2Cl_2 was added to a stirring CH_2Cl_2 solution (20 mL) of AuCl(tht) (130 mg, 0.405 mmol). After one hour, the CH_2Cl_2 was removed *in vacuo*, leaving a yellow residue. The residue was dissolved in a minimal amount of CH_2Cl_2 and an equal amount of hexanes was added. The mixture was left undisturbed overnight, and $(AuCl)_2P_2T_3$ was collected as a white crystalline solid by vacuum filtration. Yield = 97 mg (44%). Crystals suitable for X-ray diffraction were grown from CH_2Cl_2–hexanes solution. ^1H NMR (300 MHz, $CDCl_3$): δ 6.61 (m, 2H), 6.81 (s, 2H), 7.38 (d, 2H, J = 6.6 Hz), 7.48 (m, 20H). $^{31}P\{^1H\}$ (121 MHz, $CDCl_3$): δ 15.08 (s). TOF-MS m/z 1045 ($[M - Cl]^+$). Anal. calcd for $C_{36}H_{26}Au_2Cl_2P_2S_3\cdot CH_2Cl_2$: C, 38.10; H, 2.42%. Found: C, 38.05; H, 2.49%. *Crystal data* for $(AuCl)_2P_2T_3\cdot CH_2Cl_2$: $C_{37}H_{28}Au_2Cl_4P_2S_3$, M = 1166.51, monoclinic, space group $P2_1/c$ (#14), Z = 8, a = 9.6976(2), b = 28.8439(6), c = 27.6767(6) Å, α = 90°, β = 97.3710(10)°, γ = 90°, V = 7677.7(3) Å^3, T = 113(2) K, 55 083 reflections measured, 24 495 unique (R_{int} = 0.0619) final R_1 ($I > 2.0\ \sigma(I)$) = 0.0715, wR_2 ($I > 2.0\ \sigma(I)$) = 0.0669. CCDC 742148. *Crystal data* for P_2T_3: $C_{36}H_{26}P_2S_3$, M = 616.69, triclinic space group $P\bar{1}$ (#2), Z = 2, a = 9.3829(7), b = 11.5838(9), c = 14.4954(12) Å, α = 89.673(4)°, β = 72.855(4)°, γ = 80.512(4)°, V = 1483.4(2) Å^3, T = 173(2) K, 24 4601 reflections measured, 7094 unique (R_{int} = 0.050) final R_1 ($I > 2.0\ \sigma(I)$) = 0.0462, wR_2 ($I > 2.0\ \sigma(I)$) = 0.0920. CCDC 749960.

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