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We report the reversible chromism and luminescence of a cyclometallated platinum(II) complex that forms dimers, with close Pt···Pt interactions that can be modulated by solvent and temperature. The precise reversible control may be exploited in future stimuli-responsive chemosensing or optoelectronic devices.

Cyclometalated platinum(II) complexes¹ have drawn much attention due to their potential applications in optoelectronic devices,² chemosensing,^{3–5} photocatalysis^{6–8} and bioimaging.^{9,10} The square-planar geometries of these complexes enable assembly into extended aggregates^{11–20} driven by aromatic stacking, metal interactions, electrostatics and solvophobic effects.^{11,12,21,22} These aggregates often display interesting photophysical properties,^{23–25} attributed to ligand/metal charge transfer processes within the assemblies. Furthermore, the assembly structures may respond to concentration,^{26,27} solvent composition,^{12,22,28,29} organic vapours,^{3,4,14,30} redox state,¹² mechanical grinding,³⁰ temperature,^{31,32} counter ions^{33,34} and pH.^{32,35}

The extensive studies of supramolecular assemblies of platinum-based species have generally focussed on the formation of extended assemblies,^{11–17,21,22} which often form exquisite solid-state structures. Alternatively, bridging ligands have previously been employed to generate “butterfly complexes” where two platinum(II) centres are held in close proximity in an intermolecular fashion, allowing for precise control of metal–metal distance, and thus photophysical properties.^{35–38} It is desirable to combine features of responsive supramolecular systems with the precision of covalently linked systems to develop stimuli-responsive, precise, reversible control¹² over the assembly of cyclometalated platinum(II) complexes into discrete supramolecular structures,¹⁹ which may ultimately be exploited in photophysical applications.

Here we report the fully reversible dimerisation of a cyclometallated Pt(II) complex in solution and in the solid state (Fig. 1). We examine the solvatochromism in a range of polar and nonpolar solvents (Fig. 2 and 3), and probe the unusual behaviour in MeOH. Finally, we investigate reversible control over solvatochromism and thermochromism of the complex and identify the reversibly formed chromic species (Fig. 4).

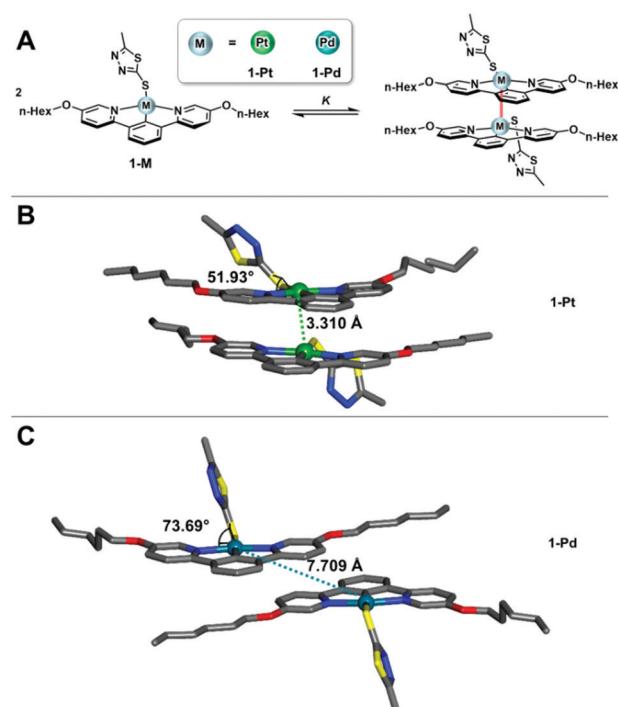


Fig. 1 (A) Structures and self-association of cyclometallated complexes **1**-Pt and **1**-Pd. (B) Dimer of **1**-Pt observed in the crystal structure showing the Pt centres in close proximity (CCDC deposition code: 1894950). (C) Dimer of **1**-Pd observed in the crystal structure showing an offset geometry (CCDC deposition code: 1894947). Crystal structures obtained by vapour diffusion of Et₂O into an acetone or CHCl₃ solution **1**-Pt and **1**-Pd originally reported in previous work.²¹

^a EaStCHEM School of Chemistry, University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, UK. E-mail: scott.cockroft@ed.ac.uk

^b Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, China

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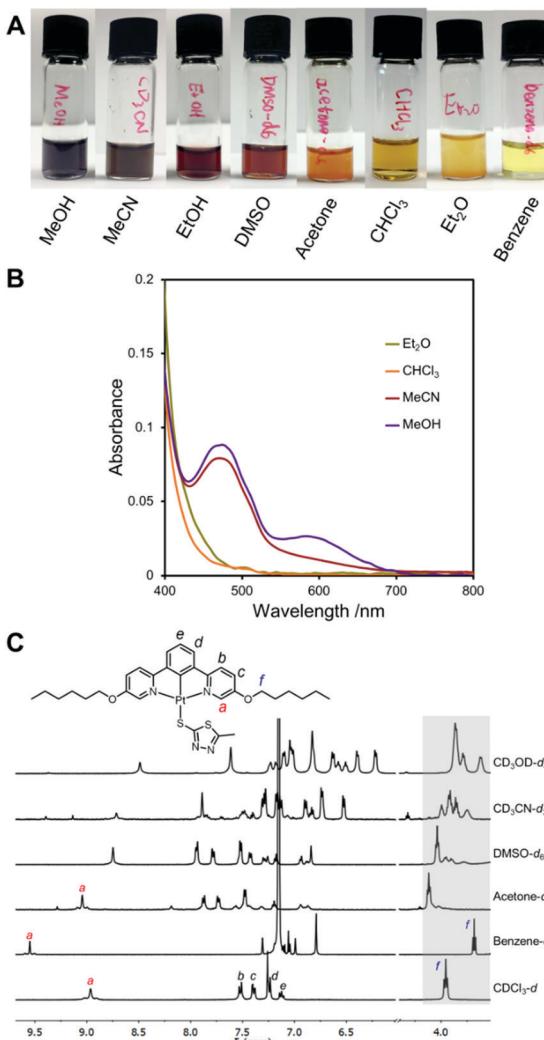


Fig. 2 (A) Photographs of freshly made solutions of complex **1-Pt** (approx. 2 mM) in different solvents under ambient light at room temperature. (B) UV-vis spectra of freshly made solutions of complex **1-Pt** (approx. 0.1 mM) in different solvents at room temperature. (C) ^1H NMR spectra (500 MHz, 298 K) of solutions of complex **1-Pt** (approx. 2 mM) in different solvents.

We previously designed and synthesised cyclometallated complexes **1-Pt** and **1-Pd** (Fig. 1A)²¹ to examine metallophilic interactions. The mercapto-thiadiazole (MTD) ligand on the metal orients orthogonally to the plane of the complex, preventing oligomerisation into extended chains, and thereby restricting self-association to dimer formation (Fig. 1A). We previously employed ^1H NMR spectroscopy to quantify the self-association of these complexes.²¹ The chemical shift changes in a series of dilution experiments in CDCl_3 fitted well to a 1:1 binding isotherm, indicating dimerisation with low binding constants ($K_a = 7.6 \pm 1.0 \text{ M}^{-1}$ for **1-Pt** and $3.9 \pm 1.5 \text{ M}^{-1}$ for **1-Pd**, three repeats).²¹

Crystal structures of complexes **1-Pt** and **1-Pd** confirmed the formation of dimers as expected,²¹ with the thiol group orientated orthogonally to the plane of the cyclometallated complex (CCDC deposition codes: 1894950, 1894947). However, only complex **1-Pt** showed close stacking of the metal centres in the solid state

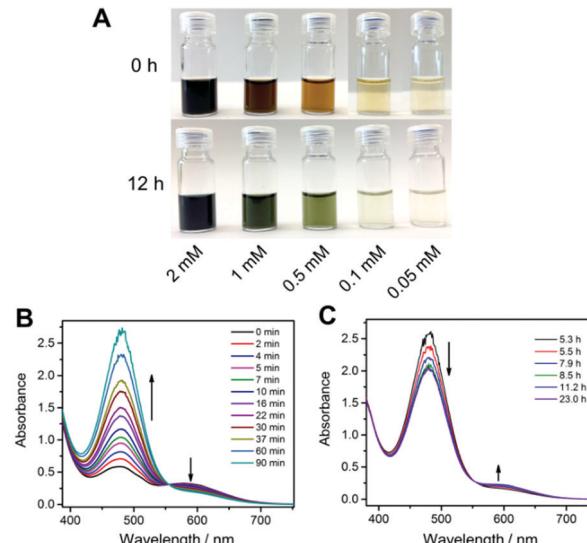


Fig. 3 (A) Photographs of complex **1-Pt** in MeOH under ambient light at room temperature immediately after preparation (top) and after 12 hours (bottom). UV-vis spectra of **1-Pt** (0.25 mM) showing the changing absorbance over time for (B) the first 90 min after adding solvent and (C) 5–24 hours after adding solvent.

(Fig. 1B), while **1-Pd** showed offset stacking (Fig. 1C), consistent with previous reports of Bosnich and co-workers.^{39,40} The solid sample of **1-Pt** exhibited strong photoluminescence under UV light (Fig. S2, ESI[†]). Such luminescence in similar complexes has previously been attributed to a mixed metal/ligand-to-ligand' charge-transfer (MMLL'CT) transition,^{27,41,42} arising from the proximity of the metal centres. This was further exemplified through solid-state emission spectra of **1-Pt**, which showed a strong emission from 600–675 nm (480 nm excitation) (Fig. S3, ESI[†]). Hence, we set out to explore whether the photophysical properties of complex **1-Pt** might be controlled *via* stimuli-induced changes in dimerisation.

The pendant alkyl chains of complex **1-Pt** ensured good solubility in a range of solvents. Solutions of complex **1-Pt** at approx. 2 mM showed strong solvatochromism in response to the polarity of the solvent (Fig. 2A), forming yellow solutions in apolar solvents and blue/purple solutions in polar solvents. We further investigated this phenomenon by examining the UV-vis absorption spectra of complex **1-Pt** (~0.1 mM) in a range of solvents (Fig. 2B). In apolar CHCl_3 and Et_2O , only absorption bands at wavelengths lower than 400 nm were observed, corresponding to intra-ligand absorption. However, in polar solvents such as MeCN and MeOH , an absorption band at around 475 nm appeared, characteristic of a $\pi_{\text{S/d}_{\text{Pt}}} \rightarrow \pi_{\text{L}}^*$ metal-to-ligand charge-transfer,⁴³ which is the transition from sulfur or platinum to the ligand L. An additional low-energy absorption band at 570 nm is observed in methanol, which is ascribed to metal–metal-to-ligand charge transfer. This suggests that close $\text{Pt} \cdots \text{Pt}$ interactions,^{43,44} which play a significant role in determining the photochemical properties of the complex, are well expressed in methanol. Similar trends were observed in the solution-phase emission spectra of **1-Pt** in a range of solvents (Section S3.7, ESI[†]).



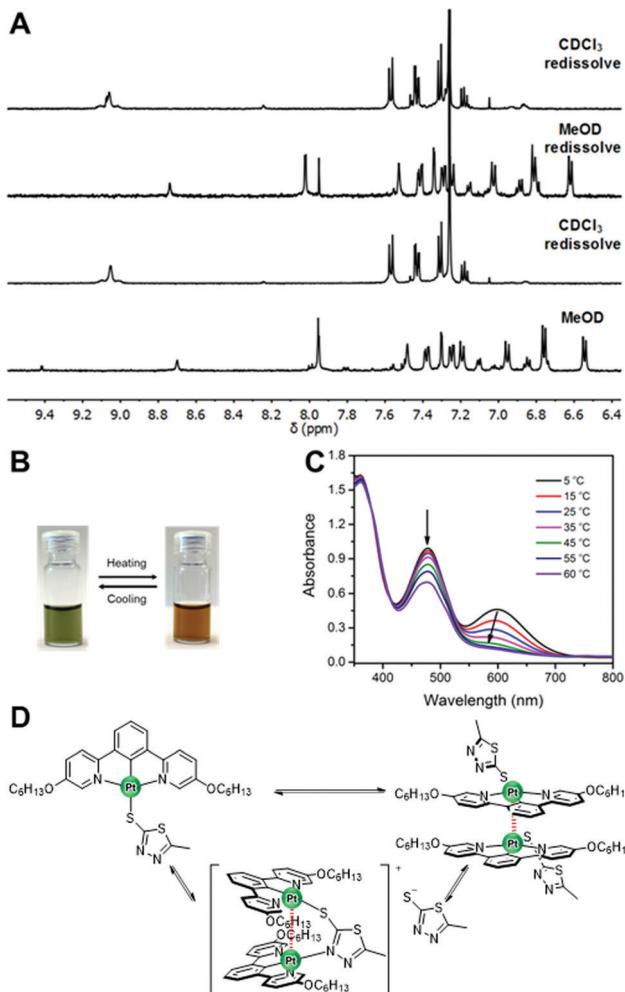


Fig. 4 (A) ^1H NMR spectra (500 MHz, 298 K) showing reversible solvent responsiveness of **1**-Pt upon redissolving and drying from methanol- d_4 and CDCl_3 . (B) Photographs of complex **1**-Pt in MeOH 24 hours after preparation under ambient light showing reversible thermochromism. (C) Temperature-dependant UV-vis spectra of complex **1**-Pt in MeOH (0.2 mM) 24 hours after preparation. (D) Reversible formation of $[\text{2-Pt}_2]^+$ occurs in MeOH solution (bottom).

The observed solvatochromism seems to relate to the ability of the complex to form dimers with the metal centres in close proximity. The dimerisation is more strongly driven in polar solvents (Fig. S4, ESI[†]), possibly due to increased aromatic stacking and solvophobic contributions.^{45,46} Dimerisation-associated solvatochromism is further supported by the non-linear increase in the absorption band at 570 nm with increasing concentration of **1**-Pt in MeOH (Fig. S6, ESI[†]), resulting in a colour change (Fig. 3A). However, NMR spectra of **1**-Pt in polar solvents showed additional peaks (Fig. 2C), indicating formation of other products, which may instead be responsible for the observed chromism (*vide infra*).

We further investigated the behaviour of **1**-Pt in polar solvents, focussing on MeOH. MeOH solutions of **1**-Pt changed from yellow/brown to green/blue over time (Fig. 3A). Time-dependant ^1H NMR spectroscopy in methanol- d_4 ($[\text{1-Pt}] = 0.5$ mM) showed gradual appearance of minor impurities (Fig. S7, ESI[†]). Time-dependent

UV-vis spectra of **1**-Pt in MeOH revealed two separate processes. Over the first 90 min, the absorption band at 475 nm increased and the band at 570 nm decreased (Fig. 3B and Fig. S10A, ESI[†]). After 5 hours, a reverse trend of decreasing absorbance at 475 nm and increasing absorbance at 570 nm was observed (Fig. 3C and Fig. S10B, ESI[†]). We ascribed this slower process to oxidative decomposition of **1**-Pt. Indeed, the growth of impurity peaks in the ^1H NMR (Fig. S7, ESI[†]), was suppressed under oxygen-free conditions (Fig. S8, ESI[†]).

The ^1H NMR spectrum of **1**-Pt in methanol- d_4 (Fig. S16, ESI[†]) shows the peaks split into three distinct environments compared to spectra in CDCl_3 . ^{195}Pt NMR spectroscopy (Fig. S17, ESI[†]) confirmed the presence of three distinct resonances in the expected region for Pt(II) complexes.⁴⁷ Resonances for the free ligand were not observed, indicating the Pt(II) remained associated with the planar aromatic ligand. The additional resonances might be attributed to decomposition, or to coordination of either a nucleophilic solvent to the platinum centre,⁴⁸ or the mercapto-thiadiazole (MTD) *via* a nitrogen to a second Pt centre.

Cycles of drying/re-dissolving **1**-Pt between methanol- d_4 and CDCl_3 showed that the formation of additional species in MeOH solution was reversible (Fig. 4A), with the original spectrum of **1**-Pt obtained in CDCl_3 after having been dissolved in methanol- d_4 . Intriguingly, electrospray ionisation mass spectrometry performed on both MeOH and CH_2Cl_2 solutions of **1**-Pt showed the same peak at 1383.4 m/z , corresponding to bridged cationic dimer $[\text{2-Pt}_2]^+$ (Fig. S33, ESI[†]).

To further examine the possible formation of this cationic dimer in MeOH solution, we undertook an independent synthesis of $[\text{2-Pt}_2]^+$ BF₄⁻ (Section S4.2, ESI[†]). Pleasingly, the chemical shifts of a freshly made MeOH solution of independently synthesised $[\text{2-Pt}_2]^+$ matched the spectra of **1**-Pt (Fig. S22, ESI[†]). This was also observed in other polar solvents (Fig. S23–S25, ESI[†]). Mass spectra of $[\text{2-Pt}_2]^+$ showed the same signal as spectra of **1**-Pt (Fig. S34 and S35, ESI[†]). Diffusion ordered NMR spectroscopy showed the same diffusion constants for solutions of **1**-Pt and $[\text{2-Pt}_2]^+$ in methanol (Fig. S26–S29, ESI[†]). Furthermore, a free mercapto-thiadiazole (MTD) was observed (Fig. S27, ESI[†]), likely acting as a loosely associated anion for $[\text{2-Pt}_2]^+$. Finally, ^1H – ^1H nuclear Overhauser effect spectroscopy showed exchange peaks between the methyl resonances of the three MTD peaks (Fig. S31 and S32, ESI[†]), indicating exchange between the MTD of **1**-Pt, $[\text{2-Pt}_2]^+$ and a free anion MTD⁻. Thus, we established that in MeOH solution, **1**-Pt exists reversibly in equilibrium with $[\text{2-Pt}_2]^+$ (Fig. 4D).

The observed stimuli-responsive chromism relates to the association of complexes in solution, either as non-covalent dimers, or more importantly, as the bridged cationic species $[\text{2-Pt}_2]^+$ in polar solvents (Fig. 4D). Since both modes of dimerisation are reversible, we reasoned that thermochromic responses might also occur if dimer stability varied with temperature. A solution of **1**-Pt in MeOH (0.2 mM) was stabilised overnight at room temperature. Subsequently, upon varying the temperature from 5 °C to 60 °C the colour of the solution changed from green to yellow/brown (Fig. 4B). UV-vis spectra

showed a decrease in the absorbance of peaks at 475 nm and 570 nm (Fig. 4C). A small blue shift (~ 20 nm) of the 570 nm was also observed. Due to the decrease of absorption bands and the blue shift, the green solution changed to a brown colour at higher temperature. Pleasingly, the thermochromism of a MeOH solution of the independently synthesised $[2\text{-Pt}_2]^+$ also matched that of **[1-Pt]** (Fig. S20, ESI \dagger). Analogous experiments on a CHCl_3 solution of **1-Pt** showed no change to the UV-vis absorption (Fig. S11, ESI \dagger).

In summary, we have prepared complex **1-Pt** and investigated its chromic properties. We confirmed the reversible formation of non-covalent dimers in both in the solid state and solution. Reversible formation of a bridged^{35–38} cationic $[2\text{-Pt}_2]^+$ dimer was confirmed in polar solvents. The extent of formation of $[2\text{-Pt}_2]^+$ is highly solvent dependent, and strongly affects the absorption spectra due to metal–metal-to-ligand charge transfer (at 570 nm absorbance), resulting in strong solvatochromic behaviour. Furthermore, reversible thermochromic behaviour was demonstrated in MeOH, where higher temperatures disrupted the close Pt···Pt contacts. The precise and reversible control of the chromic properties of complex **1-Pt** in response to a range of stimuli *via* the formation of both neutral and cationic dimers, rather than of higher-order supramolecular aggregates, may encourage the development of responsive optoelectronic devices.^{12,49} Such a strategy could be adopted more widely to expand the scope and utility of other supramolecular responsive materials.

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Conflicts of interest

There are no conflicts to declare.

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