A rapidly-reversible absorptive and emissive vapochromic Pt(II) pincer-based chemical sensor


Selective, robust and cost-effective chemical sensors for detecting small volatile-organic compounds (VOCs) have widespread applications in industry, healthcare and environmental monitoring. Here we design a Pt(II) pincer-type material with selective absorptive and emissive responses to methanol and water. The yellow anhydrous form converts reversibly on a subsecond timescale to a red hydrate in the presence of parts-per-thousand levels of atmospheric water vapour. Exposure to methanol induces a similarly-rapid and reversible colour change to a blue methanol solvate. Stable smart coatings on glass demonstrate robust switching over $10^4$ cycles, and flexible microporous polymer membranes incorporating microcrystals of the complex show identical vapochromic behaviour. The rapid vapochromic response can be rationalised from the crystal structure, and in combination with quantum-chemical modelling, we provide a complete microscopic picture of the switching mechanism. We discuss how this multiscale design approach can be used to obtain new compounds with tailored VOC selectivity and spectral responses.
small-molecule chemical sensors have important technological applications ranging from industrial process monitoring, to medical diagnostics (e.g., the identification of disease biomarkers in exhaled breath), home security (e.g., explosives detection) and environmental surveying. An ideal sensing platform should show a robust, highly selective and unambiguous response. It should also be cheaply and easily deployed in a simple device architecture, without requiring a complex readout system.

Phosphorescent square-planar platinum complexes are an active area of research in this field, due to numerous systems showing solid-state vapochromic responses to small-molecule analytes. The solid-state photophysical properties of these materials arise from intermolecular metal-metal interactions. Minor changes to the local environment of the molecules in the solid state, e.g., due to external stimuli such as temperature, pressure or exposure to chemical vapour, can perturb these interactions and induce substantial changes in absorption and emission properties.

Results

Design and synthesis. The starting point for our design strategy is the planar skeleton of 1,3-di(2-pyridyl)benzene tridentate (N^N^N) Pt(II)-pincer complex (Fig. 1a, left), which has shown high quantum yields and greater promise for luminescent applications than similar N^N^C and C^N^C complexes (Fig. 1a, centre/right). The valence metal d orbitals in these square-planar Pt(II) complexes are high lying. The d_xz and d_yz orbitals have the correct symmetry to interact with π-type orbitals on the monodentate ligand, while the d_z^2 orbitals on adjacent molecules can interact in the typical molecular stacks adopted by these complexes in the solid state (Fig. 1b). The d_xz overlap produces high-energy crystal orbitals and makes the electronic structure sensitive to the crystal packing. Quantum-chemical calculations (see Methods section and Supplementary Note 1) show that by changing the monodentate ligand L the energy of the d_xz orbital can be raised towards the frontier in the molecular complex (Fig. 1c). Varying L for a given polypyridine therefore provides a means of fine-tuning the primary absorption and the vapochromic response due to changes in the Pt...Pt stacking. Subtle differences in the Pt...Pt stacking in response to structural perturbations effectively adjusts the energy of the crystal orbitals formed by the d_xz overlap, and hence the range of the energy gap between the highest-occupied and lowest-unoccupied crystal orbitals (HOCO/LUCO).

The (N^N^C^N) ligand type has an advantage over the related terpyridine ligands (N^N^N^N) in that with a monoanionic ligand, L, the Pt stacking in response to structural perturbations effectively adjusts the energy of the crystal orbitals formed by the d_xz overlap, and hence the range of the energy gap between the highest-occupied and lowest-unoccupied crystal orbitals (HOCO/LUCO).
highest-occupied molecular orbital (HOMO) can be manipulated, making interact in the stacked geometry typically adopted in the solid state (right). By adjusting the ancillary ligand, the energy of the ligand with K2[PtCl4], and complex prepared using an adapted procedure from the literature. The precursor chloride complex is obtained by reacting the pincer (2-pyridyl)benzoate and corresponding chloro-Pt complex chloro.

The synthesis of the target complex is reported in Fig. 2 and detailed in the Methods section. The pincer ligand methyl 3,5-di(2-pyridyl)benzoate and corresponding chloro-Pt complex chloro [methyl 3,5-di(2-pyridyl)benzoato]platinum were initially prepared using an adapted procedure from the literature. The synthesis of the ligand can be performed using a Stille coupling, but an alternative Sn-free route under milder conditions, based on a Negishi coupling, was found to afford a higher yield. The precursor chloride complex is obtained by reacting the pincer ligand with K2[PtCl4], and complex is formed by further heating or by placing the crystallites in the vacuum.

Exposing the films to liquid methanol or methanol vapour induces a similarly-rapid transition to a third, deep-blue Form-III, which is again rapidly and fully-reversible either by drying in air (yielding red Form-I) or under dry nitrogen (initially yielding Form-I, from residual water in the methanol, followed by rapid conversion to Form-II). Videos of the colour changes can be found in Supplementary Movies 1–3. The Form-I films showed no sensitivity to a range of other solvents, including ethanol, diethyl ether and acetone, apart from gradually turning yellow in some of the dry, water-miscible solvents due to the slow diffusion of water out of the crystals.

Notably, replacing the CN group in I with other anions such as OH− or NO2− did not lead to similar, fast vapochromic behaviour. We attribute the unique properties observed with the CN ligand to the electronic properties described above, and also to the overall planarity of the complex and the hydrogen-bond acceptor properties of CN−, which facilitate the interaction with water and methanol.

Colour switching between the three forms was quantified by solid state UV-visible absorption spectroscopy (Fig. 3b). All three spectra display strong, broad absorption bands in the visible region, and the transitions between the three forms are accompanied by significant wavelength shifts of the lowest-energy absorptions, in accordance with the observed colour changes. The absorption maximum of Form-II is blue-shifted to ~500 nm with respect to that of Form-I (560 nm), whereas Form-III has a red-shifted maximum at ~600 nm.

As in solution, all three solid forms are also emissive (Fig. 3a, c), with the order of emission wavelengths mirroring that of the absorption maxima. The peak emissions of the anhydrous Form-II and hydrated Form-I occur at ~670 nm and 720 nm, respectively, producing orange and red emissive colours, while the emission of the methanolic Form-III peaks around 770 nm. This infrared emission is notable given the comparative rarity of organometallic IR emitters.

To study the kinetics of the vapochromic switching, we exposed an initially anhydrous film, suspended under a nitrogen stream, to water vapour (Form-II → Form-I) and then to methanol (Form-I → Form-III) while monitoring the changes in the absorption profile using time-resolved UV-visible spectroscopy (Fig. 3d, e). From measurements made at 100 ms time resolution, both transitions were found to proceed on subsecond timescales, which is notably faster than other reported vapochromic Pt(II)-pincer systems. To the best of our knowledge, the only other system to exhibit such a rapid response is [Au(im (CH2Py)2)2(Cu(MeOH))2][PF6]3 (im = imidazole), an N-heterocyclic carbene complex that switches to green luminescence under UV excitation on replacement of the methanol by acetonitrile.

A similar preparation to the glass slides was carried out on carbon tape and studied by scanning-electron microscopy (SEM; Fig. 3f). This showed that the films consist of microcrystalline needles ~5 μm in length and 0.2–0.5 μm in diameter.

**Towards device applications.** The clear visual response of I to water, and the easy deployment as a coating on glass, are ideal for...
application as a humidity sensor. Using a LiCl salt test and
diffuse-reflectance spectroscopy (Supplementary Figs. 4–7), we
identified the Form-II ↔ Form-I transition (i.e. yellow-to-red) to
occur over a range of 4,500 to 6,000 p.p.m.V of water vapour. To
quantify the durability of the switching, a coated glass slide was
repeatedly passed through a dry nitrogen stream, inducing the
Form-I ↔ Form-II transition, at a rate of 0.6 Hz (Supplementary
Fig. 8 and Supplementary Movies 4 and 5). After continuous
cycling over a period of 6 h (>10^4 cycles), we observed no
obvious degradation in the speed or colour intensity of the
response. Similarly, drop-cast films stored under ambient condi-
tions retained their vapochromic behaviour for >6 months,
again with no significant degradation in the response.

We were also able to prepare flexible polymer membranes by
drop-casting solutions of 1 with the PIM-EA-TB polymer of
intrinsinc microporosity (PIM) onto a polyethylene terephthalate
(PET) support (Fig. 3g, h; see Methods section). The membranes
showed the same vapochromic response as the films on glass,
both when supported and free-standing (Fig. 3g, h, inset). Optical
micrographs of supported films indicated that the membranes
contain embedded micromaterials similar to those observed in
the glass coatings, but up to 10–20 μm in length (Supplementary
Fig. 9).

Structural origins of the fast optical switching. The three
crystalline forms of 1 were further studied by single-crystal X-ray
diffraction using synchrotron radiation (Fig. 4, Supplementary
Figs. 10–12 and Supplementary Table 1). A comparison of the
atomic-scale structures of the three forms explains the structural
origin of the optical switching and, crucially, provides a rational
explanation for the unusually rapid vapochromic response.

Red single-crystals of the hydrated Form-I were grown from
acetonitrile solution by slow evaporation in ambient air, while
blue single-crystals of the methanolic Form-III were obtained by
slow-cooling in methanol. In both cases, X-ray powder diffraction
patterns simulated from the single-crystal X-ray data were
consistent with those collected from the bulk powder samples (see
Supplementary Figs. 13–15).

Various needle-like yellow crystal forms were obtained by
crystallising 1 in a range of other solvents, of which slow
evaporation of a dilute acetone solution under dry nitrogen
produced crystals with a structure consistent with the bulk
powder sample of Form-II. Single-crystal-to-single-crystal
transformations from Form-I to Form-III could be effected slowly by
placing crystals of the hydrated form in a 5:1 mixture of
acetonitrile and methanol for 2 weeks. Exposure to pure methanol
resulted in rapid solvent uptake and fragmentation of the crystal.

Similarly, conversion of Form-III to Form-I, which occurred
rapidly when the Form-III crystals were exposed to ambient air,
resulted in crystal fragmentation.

Attempts to obtain yellow Form-II by single-crystal-to-single-
crystal transformation from the other forms likewise invariably
resulted in loss of crystallinity due to the stress induced by rapid
purging of the guest molecules. Given the stable switching
observed over many cycles in the films, we infer that the stress
induced by the transitions can be tolerated in smaller crystallites,
which thus retain the solvent selectivity and optical response.

The spectral properties of 1 are conveniently explained in
terms of the Pt...Pt intermolecular interactions in each of the
three crystal structures. All three forms crystallise in the
monoclinic space group P2_1/n, with 1D columnar stacks of
planar Pt-complex molecules extending parallel to the crystal-
lographic c-axis (Figs. 4 and 5).

The crystal structure of Form-I confirms the presence of
solvated water molecules, which create an extended hydrogen-
bonding network that bridges between the CN⁻ ligands on
neighbouring Pt-complexes. This effectively ties adjacent pincer
molecules into a relative orientation that brings the Pt-centres
close enough to interact, forming continuous molecular wires.
Stacked Pt atoms are separated by a Pt...Pt distance of 3.452(3)
Å, indicating a degree of metal-molecule interaction known to
facilitate triplet metal-metal-to-ligand charge-transfer (3MMLCT)
in related compounds. However, adjacent Pt-centres are not
directly overlapped. Instead, neighbouring pincer molecules
adopt a slight zig-zag arrangement (zPt–Pt–Pt 154.17(3)°),
whereby the Pt-centres are staggered with respect to one another
(z(CN)–Pt–Pt–(CN) 33.52(11)°).

X-ray analysis of Form-II confirms the expected un-solvated
structure, with no guest-mediated hydrogen-bonding network.
This allows for a slight planar shift between alternate complex
molecules, resulting in a more staggered arrangement of
Pt-centres along the stacking direction and an increased Pt...Pt
distance (zPt–Pt–Pt 142.48(2)°, Pt1–Pt1 3.663(1) Å).

The crystal structure of Form-III confirms the presence of
methanol solvent molecules, which again participate in
intermolecular hydrogen-bonding. In this case, each molecule forms
only one discrete interaction with a nearby CN⁻ ligand, leading to
further subtle changes in the Pt...Pt stacking. The metal-molecule
interactions benefit from the near-perfect overlap of the stacked
molecules (Fig. 4b), facilitating the shortest Pt...Pt distance across
all three forms of 3.388(1) Å and a near-linear chain of
interacting Pt-centres along the stacking direction (zPt–Pt–Pt
178.41(1)°).

These subtle variations in both the Pt...Pt stacking distance
and metal overlap would be expected to have a pronounced effect
on 3MLCT transitions in each of the three forms, providing a mechanism for the vapochromic response. This was qualified by first-principles electronic-structure calculations within the density-functional theory (DFT) formalism, which show that the HOCOs of all three forms are composed of antiphase chains of Pt $d_{z^2}$ orbitals (Fig. 4d). The effect of decreasing the Pt…Pt distance and aligning the orbitals is to enhance this antibonding interaction, destabilising the HOCO and decreasing the HOCO-LUCO energy gap. The LUCOs comprise extended in-phase interaction, destabilising the LUCO and decreasing the HOCO-LUCO gap (Supplementary Figs. 16 and 17). This provides an intuitive link between the structural changes and the observed colour shifts, and these conclusions were further verified by modelling the absorption spectra of the three structures (Supplementary Fig. 18).

Structural analysis of Form-I and Form-III also provides insight into the solvent-exchange mechanism, enabling rationalisation of the subsecond vapochromic response. The crystal structure of Form-I contains one solvent molecule per pincer complex, which was confirmed by thermogravimetric analysis (Supplementary Fig. 19). The water molecules occupy helical-shaped channels that extend along the $c$ direction, running parallel with the Pt…Pt pincer stacks (Fig. 4c). We confirmed that this corresponds to the long axis of the needle-like crystals in Fig. 2f by face-indexing a red Form-I crystal during our X-ray studies (Fig. 5 and Supplementary Fig. 20). These pores provide a clear route for water diffusion, and evidence for continuous diffusion was also observed in diffuse-reflectance measurements performed under controlled humidity (Supplementary Figs. 5–7). In Form-III, the methanol molecules reside in discrete solvent pockets that do not appear to form a continuous channel in the static crystal structure; however, natural lattice breathing motions would be expected to provide a viable route for methanol diffusion along the $c$-axis.

The channel structures explain how the solvent molecules can diffuse out of the structure rapidly during a transition to anhydrous Form-II. No significant void space is present in the Form-II crystal structure, indicating that the voids are filled by
the rotation of pincer molecules after solvent evacuation. This suggests that conversion to Form-II would proceed by attachment of solvent molecules at the crystal surface, followed by diffusion into the crystal and progressive conversion to the solvate. Evidence for this is visible in the humidity-controlled reflectance spectroscopy data (Supplementary Figs. 5–7). Under this mechanism, the solvent exchange is diffusion controlled, with the implication that smaller crystallites should reduce the switching time.

The significant structural rearrangements also explain why transitions between the anhydrous and solvate forms in large single crystals could not be achieved without loss of single crystallinity. The rapid solvent diffusion is also facilitated by the fact that the complexes are neutral, and by the absence of counterions in the crystals could not be achieved without loss of single crystallinity. The implication that smaller crystallites should reduce the switching time.

Both the extensive hydrogen-bonding between 1 and its solvent guests, and the steric demands of the surrounding crystal structure, help to rationalise the high selectivity of the vapochromic response. No change is induced in the presence of other sterically-undemanding solvent molecules that contain no hydrogen-bond donor groups (e.g., diethyl ether, acetone or dichloromethane), indicating that the formation of an energetically favourable host-guest hydrogen-bond array is a key driving force for the exclusive uptake of water and methanol. In addition, the size of the available channel space explains why no colour change is observed in 1 on exposure other, bulkier aprotic solvents, e.g., longer-chain alcohols, which might otherwise be expected to induce a vapochromic response. While methanol is small enough to diffuse through the channels, larger alcohols cannot permeate the structure without increasing the Pt...Pt separation beyond the range for significant Pt overlap. Evidence of this is provided in the observed formation of a yellow ethanol solvate of 1, which could only be obtained by slow evaporation from ethanol solution. The X-ray structure of the solvate (see Supplementary Figs. 21, 22 and Supplementary Table 4) confirms the disruption of the channel structure and shows that any significant Pt...Pt overlap is prevented by the steric demands of the ethanol guest.

The highest-occupied crystal orbitals (HOCO) of Form-I and III compared to Form-II of ~70–80 and 55–75 kJ mol$^{-1}$, respectively, which is consistent with the rapid conversion of Form-II to Form-I in air.

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Discussion
This study has highlighted the potential of Pt(II)-pincer systems as a platform for vapochromic VOC sensing. The visible response and chemical selectivity are both desirable properties, as is the robust switching over $>10^4$ cycles. The subsecond response time is unprecedented for this class of system and further broadens the range of potential applications.

The complex is readily deployed as a smart coating on glass or embedded in a flexible polymer membrane, retaining both visible colour changes and rapid response times. Both architectures comprise microporous needles of the complex, which facilitates the fast diffusion of guest molecules and allows the crystal integrity to be maintained through the stresses induced by the structural changes.

A combination of characterisation techniques has conclusively linked the vapochromic response to the perturbation of intermolecular Pt...Pt interactions in the solid state by the diffusion of guest molecules into and out of the solvent channels. The unusually fast vapochromic response can be explained in terms of the crystal packing arrangement, and indicates that the uptake and release of solvent molecules is diffusion-limited and facilitated by weak interactions with the host crystal structure.

The choice of ancillary ligand L is key to tuning the selectivity matrix least-squares on $E^2$ using SHELXL-2014[46]. A detailed description of the sample preparation and X-ray measurements, together with key crystallographic data, may be found in Supplementary Methods, Supplementary Figs. 10–22, and Supplementary Tables 1 and 4.

Crystallography. Single-crystal X-ray diffraction data were collected on a Rigaku Mercury 11.3.1 at the Advanced Light Source, Berkeley, CA, using a Bruker AXS D8 diffractometer equipped with an APEX II CCD detector. The temperature was controlled using an Oxford Cryosystems Cryostream Plus. Data collection and processing were carried out using the Bruker APEX II software. The structures were solved by dual-space methods using SHELXT-2014[47] and refined by full-matrix least-squares on $E^2$ using SHELXL-2014[46]. A detailed description of the sample preparation and X-ray measurements, together with key crystallographic data, may be found in Supplementary Methods, Supplementary Figs. 10–12 and 20–22, and Supplementary Tables 1 and 4.
Br and I were treated using the LANL2DZ effective-core pseudopotential50 and corresponding double-zeta basis set. Initial models of various Pt–pincer complexes were built using Avogadro1, optimised, and confirmed to be energetic minima by computing the vibrational frequencies. Natural population analyses (NPAs) were carried out on the optimised structures to obtain the energies of the d-orbitals27. Calculations were also carried out on species extracted from the X-ray structures to estimate gas-phase interaction energies. Solid-state calculations were carried out within the pseudopotential plane-wave DFT formalism implemented in the Vienna ab initio simulation package (VASP)53 and Quantum ESPRESSO (QE)54 codes. Initial coordinates were taken from the X-ray structures and optimised in VASP using the PBEsol functional55. Projector augmented-wave (PAW) pseudopotentials56 were used to model the ion cores, the electronic structures were extracted in a plane-wave basis with a 750 eV kinetic-energy cutoff, and the electronic Brillouin zones were sampled using a uniform f-centred k-point mesh with 1 × 1 × 3 subdivisions. Additional calculations were carried out on 1 × 1 × 3 supercell expansions of the optimised structures in QE using the same functional, and comparable PAW pseudopotentials and convergence criteria, to visualise the frontier wavefunctions. Calculations were also carried out on isolated molecules and complexes extracted from the crystal structures to obtain formation energies. The absorption spectra of the optimised crystal structures were modelled using the linear-optics routines in VASP53 with PBE0. A subset of the molecular and periodic calculations were performed with the DFT-D3 dispersion correction with the Becke-Johnson damping function58,59 applied to the respective base exchange-correlation functionals. More detailed information on the computational modelling performed in this study is given in Supplementary Note 1.

Data availability. The X-ray crystallographic coordinates for the structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers 954459, 954461, 1493352 and 1577640. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at http://www.ccdc.cam.ac.uk/data_request/cif. The data from the computational modelling, including optimised structures and simulated absorption spectra, are available online at https://doi.org/10.15125/BATH-00440. The computer code used to analyse the diffuse-reflection spectra is available in a public GitHub repository at https://github.com/JSkelton/MayaPy.

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