

Inhibition of the photochromic behaviour of a 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline ligand by coordination to Ag(I) ions

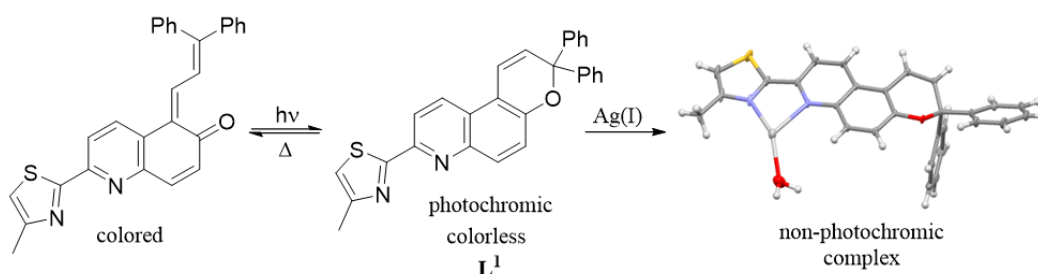
Ross J. L. Edgar,^a Paul I. P. Elliott,^a Rebecca V. Fennessy,^a Christopher D. Gabbutt,^a B. Mark Heron,^{*a} Simon J. A. Pope,^b Alessandro Sinopoli^a and Craig R. Rice^{*a}

^aDepartment of Chemical Sciences, School of Applied Science, University of Huddersfield, Queensgate, Huddersfield, HD1 3DH UK

^bSchool of Chemistry, Main Building, Cardiff University, Cardiff, CF10 3AT UK

Email: c.r.rice@hud.ac.uk; m.heron@hud.ac.uk

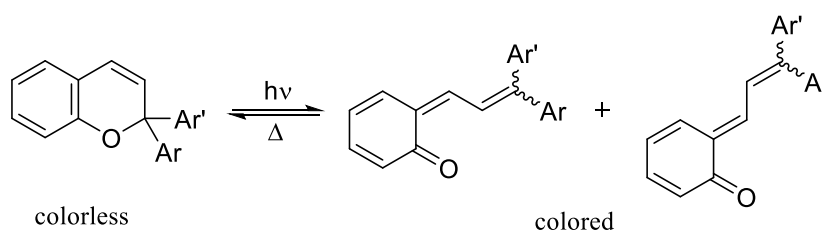
Abstract: The synthesis and characterisation of a photoresponsive 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline ligand which contains both quinoline and thiazole N-donor moieties is described. This ligand acts as a bidentate N-donor ligand and the solid-state structure of a Ag(I) complex is reported. Whereas the free ligand exhibits typical photochromic behaviour, coordination with Ag(I) results in complete inhibition of the photochromic response. However, excitation wavelength dependent emission spectra demonstrated an increase in fluorescence response of the new Ag(I) complex.



Keywords: photochromism, pyran, bidentate ligand, complex, fluorescence

Introduction

Pyrans are a class of heterocyclic compound which have been widely studied due to their thermally reversible isomerisation which occurs upon exposure to UV irradiation; this property has rendered benzo- and naphtho- fused pyrans of great interest in the ophthalmic sun lens industry as the structural reorganisation is accompanied by a distinct colour change (**Scheme 1**).¹



Scheme 1: Generic representation of the photoisomerisation of a benzopyran moiety

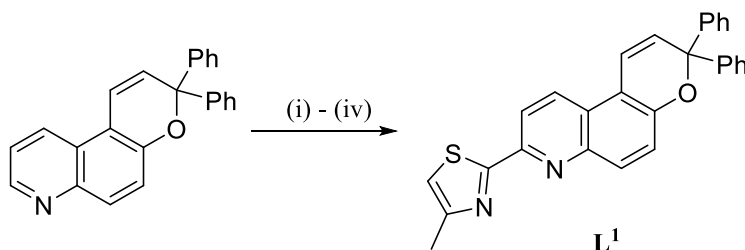
A large amount of both industrial and academic research has been applied to tuning and controlling the colour and longevity of the ring-opened form of the pyran through the addition of substituents to the aromatic systems about the pyran ring.²⁻⁸

Formation of metal coordination complexes from photochromes is attracting increasing attention.⁹⁻¹¹ Previous investigations in this area have included metal coordination of photochromic spirooxazines¹² in order to decrease thermal fading and increase photoresponsivity depending on the metal centre present and the quenching of the coloured form of pyridyl substituted dithienylethenes.¹³ Furthermore, dithienylethenes decorated with crown ether moieties have been employed to generate complex logic functions when coordinated with metal cations.¹⁴ More recently Ca²⁺ complexation of a derivative of a 3*H*-naphtho[2,1-*b*]pyran has been achieved¹⁵ in order to study Ca²⁺ extracellular signalling; this study employed the UV driven naphthopyran isomerisation to manipulate the coordination of the calcium ions, with the ring-opened form of the ligand being more receptive to coordination it was possible to engineer irradiation driven chelation of the calcium ions, followed by thermally driven release of the calcium ions.

In this work the synthesis and characterisation of compound **L**¹, a new 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline based ligand which contains two N-donor atoms, is reported together with the dramatic change in photochromic response of the subsequent Ag(I) coordination complex.

Results and Discussion

The starting 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline was successfully synthesised using the method described by Guglielmetti *et al.*,¹⁶ and subsequent transformation into ligand **L**¹ was accomplished in four efficient steps (**Scheme 2** and ESI) in a similar fashion to other thiazole-containing ligands.^{17,18}



Scheme 2. Formation of **L**¹ from 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline.

Reagents and conditions: (i) *m*-CPBA, DCM, RT (80 %); (ii) TMSCN, BzCl, DCM, reflux (93 %); (iii) H₂S, Et₃N, EtOH, RT (81 %); (iv) ClCH₂COCH₃, EtOH, reflux (73 %).

Reaction of **L**¹ with one equivalent of Ag(CF₃SO₃) in MeNO₂ resulted in a pale yellow solution. Silver ions were selected as the low coordination number of this metal would be a good match for the bidentate N-donor ligand (**L**¹). Upon slow diffusion of diisopropyl ether a pale yellow crystalline material was deposited from the initial pale yellow solution. Examination of the forgoing crystals by single crystal X-ray crystallography indicated the formation of a silver complex [**L**¹Ag]⁺ (CCDC1424260) in which the metal ion is coordinated by the quinoline and thiazole N-donor atoms as well as an adventitious water molecule, the

latter which may have arisen from either atmospheric moisture or the hygroscopic $\text{Ag}(\text{CF}_3\text{SO}_3)$ salt (**Fig. 1a**). The coordination sphere of the silver is supplemented by coordination of one of the π -bonds of the quinoline ring in a different complex resulting in a 4-coordinate metal centre and the formation of a dimer (**Fig. 1b**). The intra-ligand interaction is also accompanied by a hydrogen bond between the terminal methyl unit and the pyran oxygen atom. This coordination between silver ion and the π -bonds is a relatively new but well reported tool in supramolecular chemistry.¹⁹

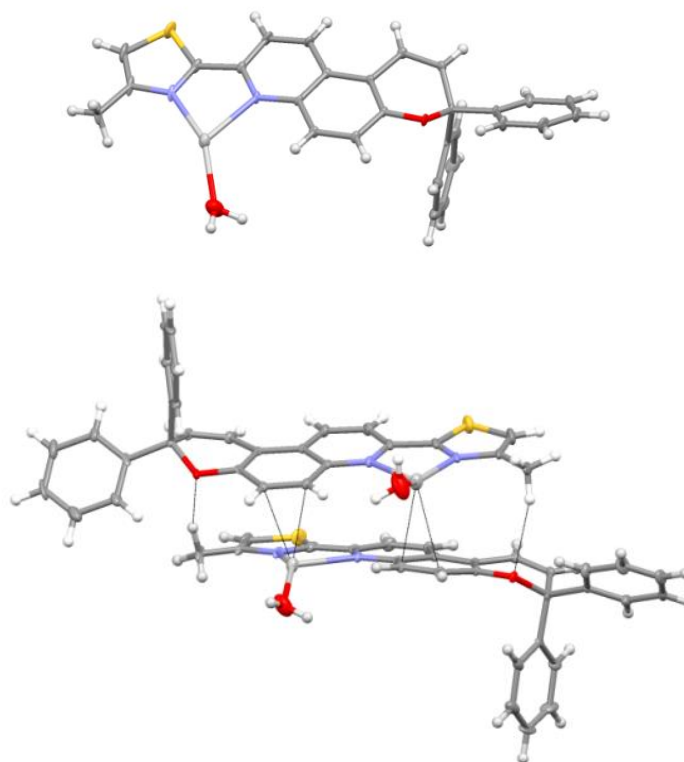


Fig. 1: X-ray crystal structure of $[\text{L}^1\text{Ag}(\text{H}_2\text{O})]$ complex; (a) the monomeric $\text{Ag}(\text{I})$ complex (top) and (b) the dimeric assembly (bottom).

Electrospray ionisation-mass spectrometry (EI-MS) of the silver complex gave ions at m/z 1229 and 973 which corresponds to $\{[(\text{L}^1)_2\text{Ag}_2](\text{CF}_3\text{SO}_3)\}^+$ and $[\text{L}^1_2\text{Ag}]^+$, respectively. However, although EI-MS agrees with X-ray data analysis *i.e.* that a dimer is formed, analysis by ^1H -NMR spectroscopy shows only ten signals corresponding to one ligand strand (**Fig. 2**). If the dinuclear assembly persists in solution a more complex ^1H NMR spectrum would result, and more specifically the *geminal* phenyl groups would be non-identical. Examination of the ^1H NMR spectrum shows both phenyl units in an identical environment and this is observed even at low temperatures ($-30\text{ }^\circ\text{C}$). These data support the theory that in solution the complex is a mononuclear species and the dimer is only observed in the solid and gas phase.

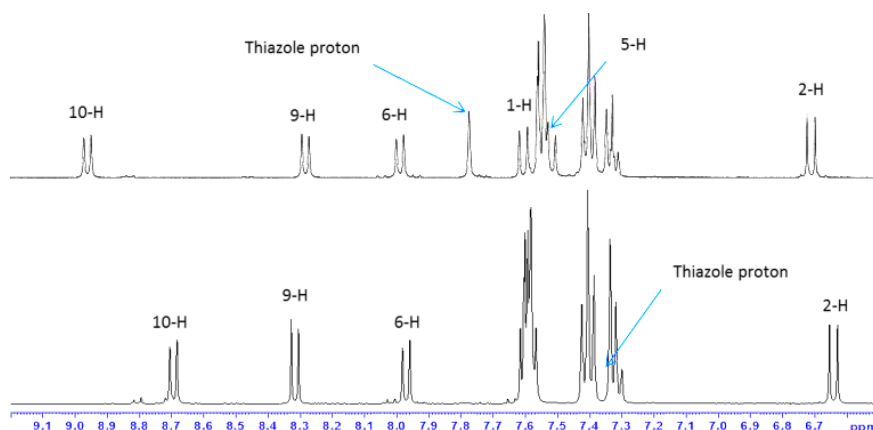


Fig.2: ^1H NMR spectra 6.5 – 9.2 ppm in $(\text{CD}_3)_2\text{CO}$ (L^1 lower, $[\text{L}^1\text{Ag}(\text{H}_2\text{O})]^+$ complex upper). Indicating shift of 10-H and the thiazole ring proton upon complexation formation.

The free ligand L^1 demonstrates typical photochromic behaviour in acetone solution (**Fig. 3**), with the irradiated species exhibiting an absorption maximum at around 450 nm ($t_{1/2} = 1823$ s) corresponding to the relatively slow fading, intense orange hue of the ring opened photomerocyanine valence tautomer.

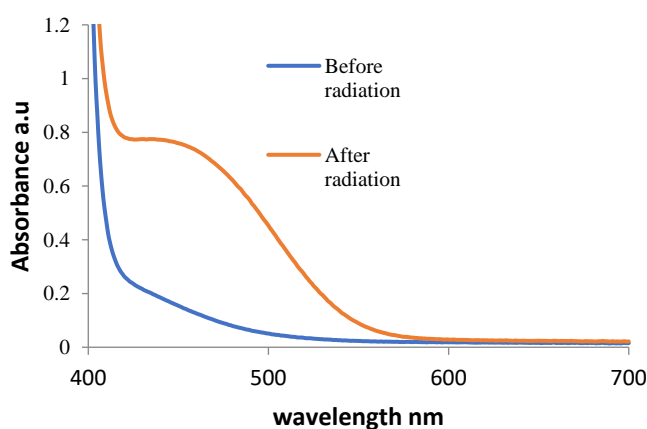


Fig.3: UV-Vis spectrum for free ligand L^1 (acetone) before and after UV radiation

Remarkably the Ag(I) complex exhibits no photochromic activity (**Fig. 4**), the electrocyclic ring-opening process has been inhibited completely with the spectra of the irradiated and unirradiated samples being identical in appearance (weak yellow hue). The generally accepted mechanism for photochromic behaviour is promotion of an electron to the singlet excited state followed by isomerisation to the coloured dienone species. Here it is apparent that upon coordination the isomerised, valence tautomer state is energetically inaccessible.

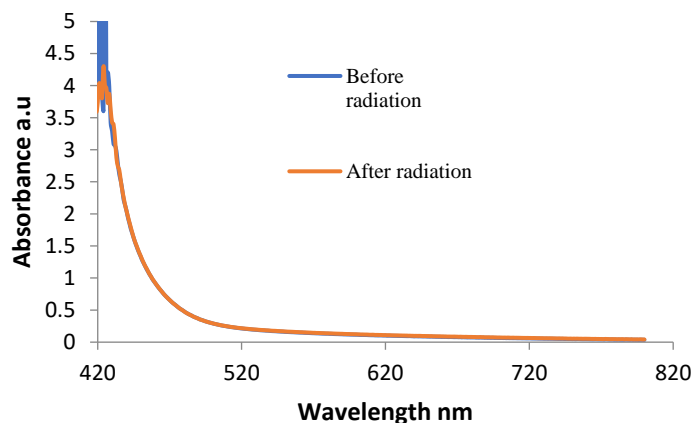


Fig.4: UV-Vis spectrum for L^1Ag complex before and after UV radiation (acetone as solvent)

The free ligand shows excitation wavelength dependent emission spectra (**Fig. 5**), with 405-445 nm excitation giving rise to the red-shifted emission albeit at a much weaker intensity. It is likely that the photoisomerised product can itself be excited using longer wavelength irradiation (correlating with the absorption spectra shown in ESI) with a corresponding new emission peak at *ca.* 530 nm. In contrast, there is an increased fluorescence intensity and bathochromic shift ($\lambda_{em} = 495$ nm) of the Ag(I) complex over the free ligand (**Fig.5**, inset). The corresponding excitation spectra show an increased intensity *ca.* 350-400 nm when compared to the two isomers of the free ligand (ESI, **Fig. S10**). The emission lifetime of the free ligand is *ca.* 0.4-0.5 ns ($\lambda_{ex} = 295$ nm) whilst the Ag(I) complex has a longer lifetime of 1.8 ns, which is consistent with a metal-perturbed fluorescence from the ligand. Molecular orbital analysis of $[L^1Ag]^+$ by DFT (ESI) showed that coordination of the silver ion to the ligand significantly influences the frontier orbitals distribution. In particular the LUMO of the $[L^1Ag(H_2O)]^+$ complex shows an interaction between the silver d_{xz} orbital and the chelating nitrogen orbitals, whereas the LUMO + 2 is dominated by the silver 5s orbital. It seems plausible that this change in the distribution of orbitals results in inhibition of the photoisomerism and a new red-shifted emission peak for the complex.

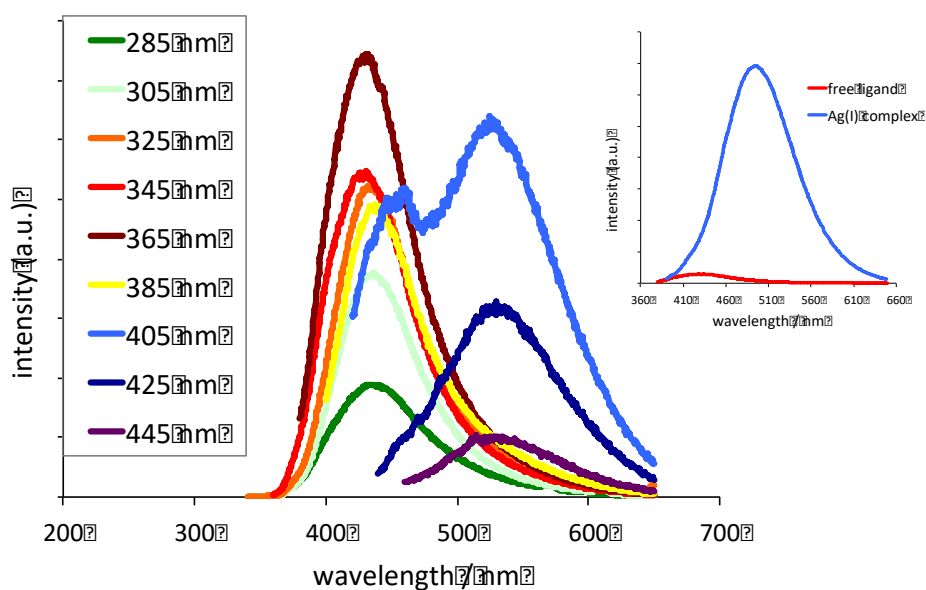


Fig.5: Excitation wavelength dependant emission spectra of the free ligand **L¹** in MeCN and (inset) comparison of relative emission intensities (both using $\lambda_{ex} = 285$ nm) with **[L¹Ag(H₂O)]⁺** complex (MeCN) See also Figure S

Conclusions

The synthesis, characterisation and photochromic behaviour of a novel 3,3-diphenyl-3*H*-pyrano[3,2-*f*]quinoline derived ligand and the solid-state structures of the Ag(I) complex is reported. Whilst the free ligand **L¹** undergoes photoisomerism in a similar fashion to other photochromic naphthopyran systems, metal coordination of the *N*-donor domains induces total inhibition of the photochromism and thus constitutes the first example of this phenomenon. Modulating the photophysical response, from photochromic behaviour to luminescent emission, of such a commercially important class of functional material may provide a new rational in the design of emissive sensor materials. Furthermore, as coordination of the benzopyran-containing ligand can have such a profound effect of the photochromic response, similar systems in which coordination could lead to modulation of the colour/response time, merit further investigation.

References and notes

Electronic supplementary information (ESI) available: Complete experimental procedures and characterization data for all new compounds, computed Cartesian coordinates, frontier molecular orbitals and vibronic spectra. Crystallographic data for **[L¹Ag(H₂O)]⁺** see CCDC 1424260 in CIF or other electronic format which are available upon request from the Cambridge Crystallographic Data Centre.

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The authors declare that there are no competing interests.