Journal Name

COMMUNICATION

A coloring tool for spiropyrans: Solid-state organometallic complexation versus salification

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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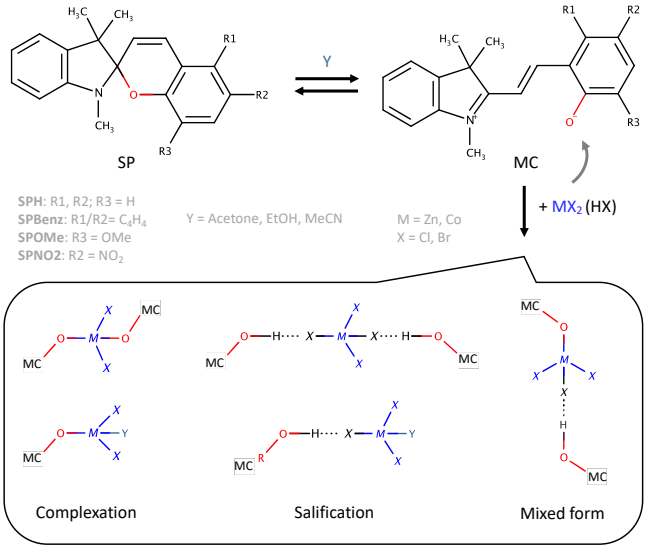
In this communication we examine the nature of the spiropyran metal interaction in the solid-state and highlight the various linking possibilities. The ability to form a complex, salt or mixed form requires different synthetic pathways. Changing the solid state form has a strong impact on the absorption properties, resulting in a tool allowing to color spiropyrans in the solid-state covering a large scale spectrum from red to green.

Photochromic compounds such as spiropyrans (SP) are able to transform in solution upon UV irradiation into the zwitter-ionic open merocyanine form (MC)[1]. The structural change associated with the transition to the open form, has a strong impact on the delocalization of the π-electron system throughout the molecule, which impacts the UV-*vis* absorption properties and hence the color of the compounds[2]. The charge separation in the zwitter-ionic form results in a higher electron density on the phenolate oxygen atom increasing the attraction to metal cations.[3] This resulted in a high interest in these compounds as solution based metal sensors[4] and switchable catalysts.[5] To our surprise, the spiropyran metal interaction at the solid-state has been mainly left unexplored with only a narrow number of publications[6]. As illustrated here, these interactions offer a multitude of linking possibilities, which allow fine-tuning the absorption properties at the solid-state and thus opening possibilities for solid-state color-based applications. Prior to exploring and developing such applications, one first requires a fundamental understanding of the solid-state interactions at a molecular level. Furthermore, robust pathways to the different accessible phases should be available if bulk properties such as color are ~~developed~~ considered for development of~~in~~ future applications. In this work we introduce a classification of the different spiropyran metal solid-state forms, identify synthetic pathways that allow synthesis of a single solid phase at g scale and highlight the impact of the solid-state form on the UV-*vis* absorption properties.



Scheme 1: The ring opening isomerisation of the spiropyran to the open merocyanine form in solution and its stabilisation by a bivalent metal salt resulting in different coordination possibilities as single crystal structure analysis has proven.

To explore the variety of accessible solid forms we employed three metal salts, i.e. $ZnCl_2$, $ZnBr_2$ and $CoCl_2$, and coupled these to four spiropyran compounds, 1,3,3-trimethylindolinobenzo-pyrylospiran (**SPH/MCH**), 1,3,3-trimethylindolino-β-naphtho-pyrylospiran (**SPBenz/MCBenz**), 1,3,3-trimethylindolino-8'-methoxybenzopyrylospiran (**SPOMe/MCOMe**) and 1,3,3-tri-methylindolino-6'-nitrobenzopyrylospiran (**SPNO2/MCNO2**) for which we identified 19 novel phases (Chart S1). Careful analysis of their structure allowed establishing a classification scheme as shown in Scheme 1, with either a phenolate oxygen M–O_{MC} complexation, a protonation characterized by an M–

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† Electronic Supplementary Information (ESI) available: For ESI and crystallographic data in CIF or other electronic formats see DOI: 10.1039/x0xx00000x

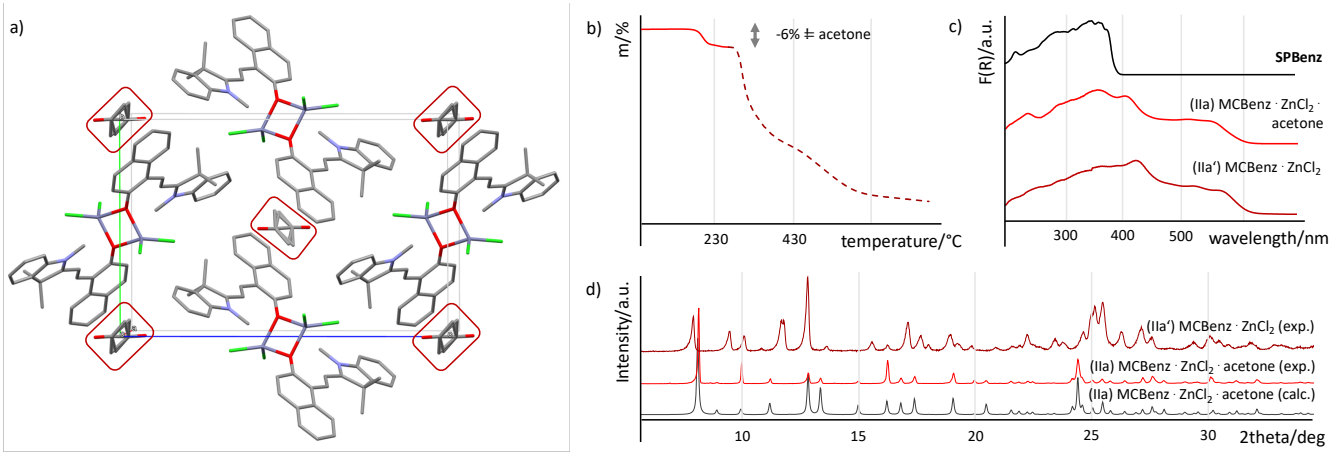

Figure 1: Overview for **SPBenz** complexed to $ZnCl_2$: a) A partial packing diagram of (IIa) showing the **SPBenz** molecule coordinated to the zinc metal with one disordered acetone molecule per asymmetric unit, b) TGA analysis showing the loss of acetone at ~147°C, c) the diffuse reflectance spectra for the closed form of **SPBenz**, the red material of (IIa) with and without acetone in the crystal packing and d) the simulated powder x-ray patterns of (IIa) compared to the obtained bulk material by reflux and the resulting product after the evaporation of acetone.

X…H–O_{MC} hydrogen bond, or a mixed form containing both types of bonding. The formation of these different solid forms can be understood considering the ability of the merocyanine to form highly preferable charge assisted hydrogen bonds by protonation of the oxygen atom,[7] which results in an interaction competing with a direct metal—oxygen bonding. As the protonation of the oxygen atom is pH dependent, the outcome of the solid form will ~~be~~ depend~~ing~~ on the reaction conditions (nature of the metal salts, pH, solvent, …).[8]

When using $ZnCl_2$ and $ZnBr_2$ most reaction conditions led to the formation of complexes for all spiropyrans investigated. As expected, the replacement of chloride by bromide in the starting material entails an isomorphous product. **MCH** and **MCBenz** form 1:1 dimers, which consequently results in a tetrahedral arrangement of the zinc center with two chlorines and two merocyanine ligands. Complexes of **MCH** with $ZnCl_2$/Br_2, (Ia) and (Ib) (Figure S1), are orange colored with absorption bands up to 580 nm in the case of chlorine and 600 nm for bromine (Figure S10a), whereas the parent spiropyran compound (**SPH**; white) shows absorption up to 350 nm. For the combination of **MCH** and $ZnCl_2$ the salt showing an Zn–Cl···H– O_{MCH} bond was also obtained as a single crystal ((Ic); Figure S2), but no conditions are identified so far leading to bulk material. The complexes **MCBenz**, (IIa) and (IIb), were found as acetone solvates with one disordered acetone molecule per asymmetric unit (Figure 1a and S3). Thermogravimetric analysis (TGA) shows a very strong stabilization of acetone at the solid-state with its loss only occurring at 147°C (Figure 1b and S11). Both the solvate and the resulting ansolvate (IIa' and IIb') (Figure 1d and S11), show additional absorption bands up to 560/575 nm (Cl/Br) compared to the parent **SPBenz** molecule (400 nm) (Figure 1c and S10b). Desolvation leads to a slight red-shift as illustrated by a deeper red coloration. We observed, the reversible solvation-desolvation process by inserting/removing the powder in/from an acetone atmosphere, switching reversibly between a light and dark-red colored solid phase. This process can therefore be used to alter the coloration of the solid form.

MCOMe and MCNO2 were also found to complex $ZnCl_2$ and $ZnBr_2$. The former is shown to form ethanol and water (IIIb) solvates with $ZnCl_2$/Br_2 ((IIIa)/IIIb); Figure S4) resulting in deep red colored products (Figure S10c). The chelating methoxy group gives additional stabilization of the metal center. This interaction pattern was already observed before for similar derivatives in solution and is here confirmed in the solid-state[9]. Stoichiometrically diverse 1:1 and 2:1 complexes of

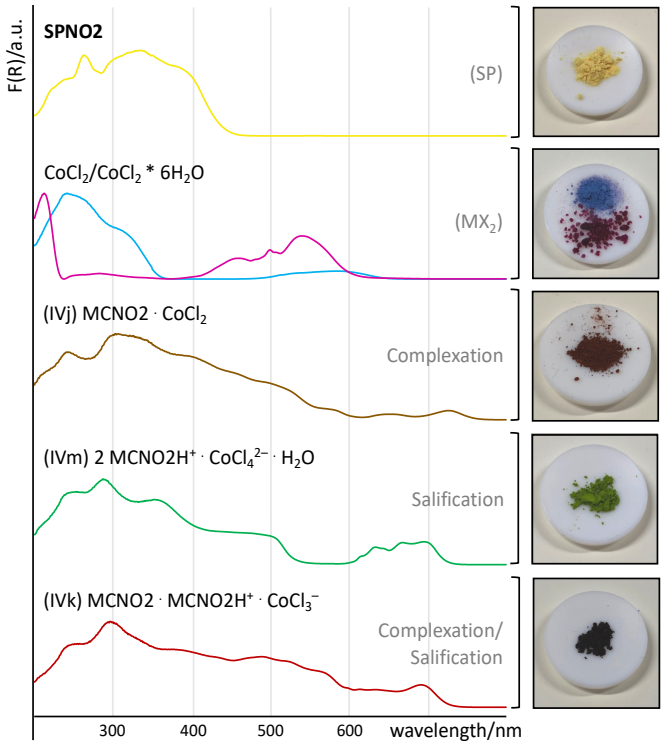

Figure 2: Diffuse reflectance spectroscopy of the parent SP compound (**SPNO2**), the metal salt $CoCl_2$ and their different linking possibilities in the solid-state resulting in different coloration; due to complexation, salification and the combined form (top down).

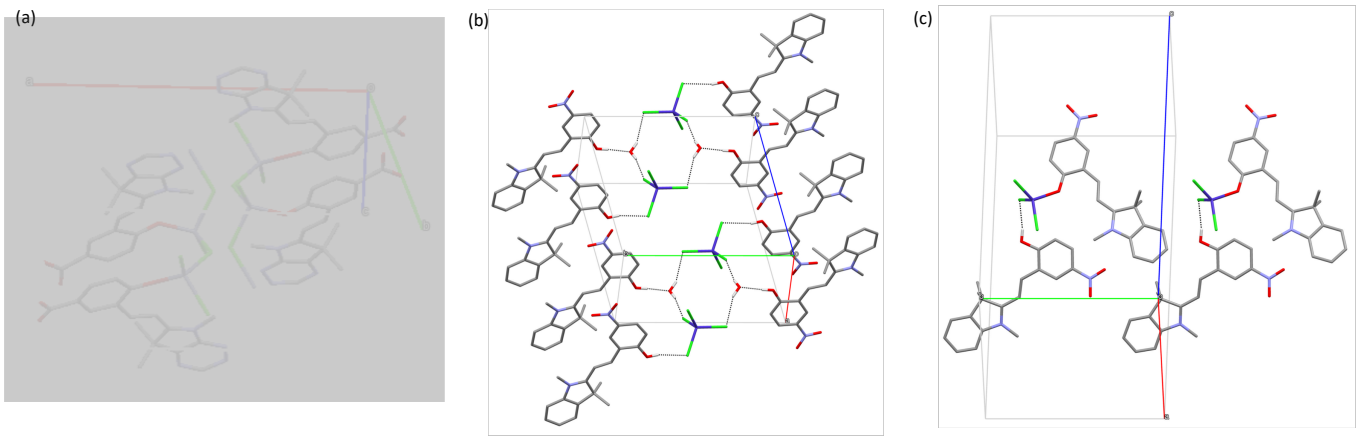

Figure 3: Partial packing diagrams demonstrating the different linking possibilities of **SPNO2** with $CoCl_2$: (a) the 1:1 complex; structure solution from powder (IVj), (b) the hydrated salt (IVm) and (c) the mixed form (IVk). Hydrogen bonds are indicated as dashed lines.

MCNO2 with $ZnCl_2/Br_2$ are found, showing either one or two **MCNO2**s linked to the metal (structures (IVa), (IVb), (IVf) and (IVg); Figure S5)[10]. The zinc center has a tetrahedral arrangement with either three chlorines/ bromines and one merocyanine using one chloride as a bridging module (for 1:1) or two chlorines/ bromines and two spiropyrans as ligands (2:1). All of these show a red coloration with strong absorption bands up to 600 nm (Figure S10d) compared to the yellow parent compound (absorption up to 450 nm). **MCNO2** $ZnCl_2$ hydrates ((IVd) and (IVe) Figure S6) and $ZnBr_2$ acetonitrile solvates (IVh; Figure S7) are also identified, as well as combined salt-complexes with $ZnCl_2/Br_2$ (structures (IVc)/(IVi); Figure S8), but once again conditions could not be identified to obtain this form as a bulk material.

Switching to cobalt, the full diversity of solid-state forms could be identified and reaction conditions obtained to reach bulk material. All three cases are illustrated for **MCNO2** (Figure 3) showing the Co—O_{MCNO2} bond for the complex, the Co—Cl···H–O_{MCNO2} bond for the salt and both for the mixed salt-complex. The formation of bulk material of the different solid forms of a given spiropyran/metal combination can be controlled by tuning reaction conditions. Complexes are typically obtained by refluxing in acetone for 20 min up to 6 hours until precipitation occurs. The salt form (IVm) is also obtained from acetone but by slurrying a 1:1 mixture of the parent compounds at approx. 30°C for 24h. Considering the fact that identical starting conditions are used for both experiments, the provided energy in form of heat is believed to enhance the complex formation. A 2:1 (**MCNO2**:$CoCl_2$) slurrying in acetone yielded the combined salt-complex form (IVk), pointing the importance equally towards the ratio of the starting materials for the orientation of the reaction towards a selected form.

Interconversion between the different forms could also be achieved at the solid state. Submitting the complex (IVj) or the mixed form (IVk) to a HCl atmosphere for 1-2 days led to transformation of the salified form (IVm) as shown by XRPD. The type of solid form/connectivity has a very strong impact on the UV *vis* absorption thus leading to impressive color changes between the different forms. This is shown in the case of **SPNO2/MCNO2** with $CoCl_2$ in Figure 2. The parent compounds show a yellow (**SPNO2**) and blue/purple coloration ($CoCl_2$/ $CoCl_2$*$6H_2O$). A combination of these leads to a red-brown, green and dark red coloration for the complexation, salification and mixed forms respectively. UV-*vis* analysis confirms the visible color change with absorption bands at 750 nm for the complex (IVj), 710 nm for the salt (IVm) and 690 nm for the mixed form (IVk). Protonation of the spiropyran and inserting a chlorine atom between metal salt leads to a lower bathochromic shift compared to the complexation with the metal center directly bond to the chromophoric compound. This color change is also obvious when performing the solid-state transformation of the complex and mixed form to the salt under a HCl atmosphere.

In summary, we presented the first systematic solid-state study between ~~applied~~ spiropyrans and metal salts. Analyzing the structural variations, we are able to identify three different solid state forms for these compounds, classifying them either as complexes, salts or mixed form, according to the type of bonding to the metal. We furthermore highlighted how fine-tuning the reaction conditions can lead to a controlled synthesis of either of these forms. By showing the important impact of the type of form on the UV-*vis* absorption, we identified a reliable coloring tool for spiropyran compounds by controlling the type of interaction between the metal and the spiropyran. The described results open opportunities for the use of these compounds in color-based applications.

This work was published thanks to funding of “Actions de Recherche Concertées (ARC) de la direction générale de L’Enseignement non obligatoire et de la Recherche scientifique – Direction de la Recherche scientifique – Communauté française de Belgique”.

Conflicts of interest

There are no conflicts to declare.

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