Enhanced bi-stability in a ruthenium alkynyl spiropyran complex†

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The inclusion of a ligated ruthenium moiety to ethynyl spiropyran, 5′-ethynyl-1′,3′,3′-trimethyl-6-nitrospiroadamantane-2′,2′-indoline, has been shown to increase the lifetime of the ring-opened merocyanine form of the metal alkynyl complex arises from the capacity for greater delocalisation of charge consequent of the presence of the ruthenium moiety. The complex may provide a different switching mechanism to the 5,5′-dithienylperfluorocyclopentene electrode decoupling seen previously.

Molecular switches can be broadly defined as molecular species that undergo reversible changes between two or more distinct structures in response to some thermal, chemical, electronic or, most commonly, photochemical stimulus. In addition to the intrinsic interest in such bi- (or multi-) stable compounds, these elementary molecular machines and photoclicks attract considerable attention arising from their potential applications in sensing, molecular-scale data storage and processing, and for optical or electronic signal modulation.1-4 Each of these potential application areas has different requirements in terms of the nature of the triggering stimulus and the lifetime of the ‘switched’ state. Surprisingly, despite the essentially limitless chemical space, the number of structural motifs that have been established as robust molecular switching elements is relatively sparse; prominent examples of the molecular architectures that are able to undergo structural isomerisation between two or more distinct states, and have been investigated as potential molecular switches, include azobenzenes,5-7 stilbenes,8-10 spiropyans,5,11-13 diarylenes,14-16 and fulgides.5,17-19

Although the great majority of photochemically controlled molecular switches explored to date have been based on organic structures, the incorporation of photochromic entities into metal complexes can provide a number of advantages, allowing the combination of magnetic, electrochemical, and optical properties of the metal complexes with the photochromic reaction,20-23 providing access to a broader diversity of molecular architectures and permitting an element of control over the switching characteristics.24 For example, diarylthene moieties, specifically 5,5′-dithiethylfluorocyclopentene (DTE), which represents perhaps the archetypal molecular switch, has been incorporated into metal alkynyl complexes.23,27-34 In one example, the metal was able to mediate the switching of cubic nonlinear optical properties of the molecule utilising electro-, halo- and photochromic phenomena specific to the organo-metallic complex.27 In another organometallic DTE example, the metal also serves to decouple the molecule from the electrodes thereby allowing the photoreversion reaction to the closed form of the DTE to proceed efficiently.29

Whilst DTE is perhaps the best known of the photochromic molecular switches, the synthetic accessibility of the spiropyran motif, and its photochromic nature, make it an attractive basis for alternative molecular switch design and development. Like other light-actuated switches it has advantages and disadvantages; chief amongst the latter are photo-degradation, which can be ameliorated by covalent immobilisation,35 and the relatively fast rate of thermal reversion from the photo-activated open (conducting, merocyanine) state to the closed (resistive, spiropyran) form (e.g., Scheme 1).36 The factors influencing the thermal and photoinitiated opening and closing of spiropyrans have been extensively explored.37,38

We are exploring the incorporation of the spiropyran motif into metal complexes via an alkynyl linkage utilising the ligand 5′-ethynyl-1′,3′,3′-trimethyl-6-nitrospiroadamantane-2′,2′-indoline (1, Scheme 1), with a view to optimising the photoswitching properties, and this communication describes our initial efforts in this area.

Ethynyl-substituted spiropyrans have been previously prepared from condensation of 5-ethynylsalicyaldehyde with

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Fischer's base\textsuperscript{40} or from the corresponding formyl spiropyran via a Wittig reaction with (bromomethyl)triphenylphosphine bromide and subsequent HBr elimination.\textsuperscript{41} Ligand 1 was prepared\textsuperscript{41} for the current work by an improved procedure involving condensation of the appropriately substituted trimethylsilylthiyl indolium salt with 5-nitrosalicylaldehyde, in the presence of piperidine, in excellent yield (ESI†). Subsequent de-protection gave the required terminal alkyne.

The metal complex was prepared using established methodology,\textsuperscript{42–44} thus reaction of 1-SP with \([\text{Ru(dppe)}_2\text{Cl}](\text{OTF})\) gave the ruthenium alkynyl complex, \([\text{Ru}[\text{C}==\text{C}(1',3',3'+\text{trimethyl-6-nitrospiropyrromone-2,2'-indoline})]_{2}\text{Cl}](\text{dppe})_2\) (2-SP, Scheme 1) in good yield, after deprotonation of the intermediate vinylidine species. Complex 2-SP was characterised spectroscopically, with the presence of the triple bond inferred from the absorption at 127.0 ppm, showing coupling to the two equivalent phosphorus atoms, with the signal for the \(\beta\)-carbon at 116.3 ppm. The phosphorus nuclei gave a peak at 69.4 ppm in the \(^{31}\text{P}\) NMR spectrum.

Spiropyrans can exist in two observable isomeric states, a closed nearly, colourless spiropyran (SP) (e.g. 2-SP, Scheme 1) and an open, coloured merocyanine (MC) (e.g. 2-MC). In nitro-substituted spiropyrans the open, MC state is accessed photo-chemically with UV wavelengths via the triplet manifold, a pathway associated with the presence of the nitro group.\textsuperscript{38} The MC form reverts thermally to the closed SP state, or can be turned to DFT calculations. The geometries of complexes 1-SP and 2-SP and the corresponding ligand 1-SP and 1-MC precursors were optimized at the B3LYP/3-21G\* level of theory, using a CPCM dichloromethane solvent model. Whilst the basis set employed is relatively small, previous benchmarking calculations on this class of compound have demonstrated that it provides accurate electronic descriptions with pragmatic computational expense.\textsuperscript{45} Selected bond lengths and angles are summarized in Table S1, ESI† atomic contributions to key molecular orbitals are given in Table S2 and Mulliken charges are listed in Table S3.\textsuperscript{†}

The geometry of the \textit{trans}-\text{RuCl(dppe)}\textsubscript{2} fragment changes little in response to the switch of the spiropylic ligand geometry to the merocyanine form. There are, of course, greater changes evinced in the SP/MC ligand backbones, which are largely reflected in the valence bond descriptions given in Scheme 1. Whilst there are few bond lengths worthy of comment in the ring-closed/SP form, consideration of the bond lengths along the \(\text{N}-\text{C}_9\text{–C}_{11}\text{–C}_{13}\) chain in the ring-open/MC form, together with the planarity of the extended ligand suggests extensive delocalization, which is subtly enhanced by the presence of the organometallic fragment. Such ideas are supported by the distribution of the frontier orbitals, with HOMO and LUMO of the spiropylic compounds 1-SP and 2-SP (Fig. 1) being rather spatially separated and localized on the phenylethynyl portion of the molecule and the LUMOs on the nitrobenzene moiety (Table S2,\textsuperscript{†} Fig. 1), whilst those the MC forms are rather more delocalized over the extended molecular backbone. In addition, a more positive net Mulliken charge at Ru is predicted in the ring-open, MC form compared to the ring-closed, SP form (\(+0.779\) vs. \(+0.664\)), consistent with a degree of extended donor–acceptor character in the MC.
complex. The donor effect of the metal fragment also serves to
decrease the net positive charge at C(9) in the MC form of the metal complex when compared with that of the free alkyne (+0.369 vs. +0.507). There is also a small net decrease in the charge at the O-atom involved in forming the C=O spiro centre in the open (MC) form of the metal complex (−0.520) vs. the open (MC) form of the free alkyne (−0.566). The decreased rates of ring-closing in the metal complex when compared with the organic ligand is consistent with the modulation of the charge density arising from charge transfer from the metal to the alkylnyl ligand and substituents, further suggesting the ring-closing reaction takes place under charge control.

We have demonstrated that appending a ruthenium alkylnyl unit to a spiropyran core prolongs the lifetime of the merocyanine form of the molecule more than twenty-fold. The metal enhances the extent of charge delocalisation through donation of electron density into the organic ligand. Chiefly the metal acts to decrease the charge/electron density localisation on the spirocyclic ring-forming atoms in the open form of the complex, thus slowing the electrostatically driven ring-closing reaction. Theoretical calculations suggest that the metal provides a different switching mechanism to the 5,5′-dithienylperfluorocyclopentene electrode decoupling seen previously and presages the opportunity of the electrochemical address of the bi-stability of the molecule.

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Notes and references