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Observation of photochromic γ-cyclodextrin host–guest inclusion complexes

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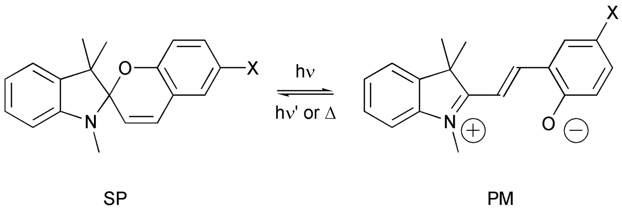
Substituted photochromic spiropyrans were included in γ-CD inclusion complexes and the photochromic behavior was monitored optically.

Photochromic molecules can switch reversibly between two forms by excitation with the appropriate wavelength of light.[1] If the switching process can be controlled, photochromic compounds can potentially be used as active components for molecular electronics,[2] nanoscale machines[3] or sensors.[4] One class of organic photochromics that has been studied are spiropyrans.[5] Upon UV absorption the spiropyran (SP) converts to the photomerocyanine (PM) form. The photomerocyanine form can either be photochemically or thermally switched back to the spiropyran. The thermal decay rate of the PM to the SP form is dependent upon the nature of the substituents on the pyran ring and the medium of the photochromic compound. The nitro substituted SP structure (X = NO_2 in Scheme 1) has been studied extensively due to the longer lifetime of the PM and the relatively greater fatigue resistance compared to other substituents. In contrast, the halogen substituted spiropyrans (**1** and **2**) have received little attention due to the fact that in solution at room temperature there is no permanent color, since the half-life of the PM is generally too short.[6]

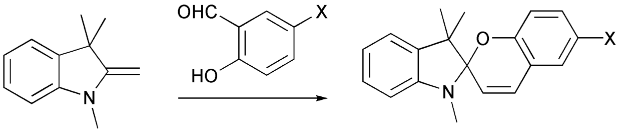
In order to study the effect of substituents upon the photochromic properties of a series of spiropyrans this study attempted to include the spiropyran into a host matrix. Presumably the host matrix will offer stability to the photogenerated PM to increase the lifetime and to hinder photodegradation pathways. Previously spiropyrans have been included in polymer matrices,[7] self-assembled monolayers,[8] sol–gels,[9] clays[10] and zeolites[11] in order to improve the thermal half-life of the photogenerated PM. In this study we wanted to test the effect of an organized organic crystalline environment upon the properties of these organic photochromic compounds.

The host matrix studied was γ-cyclodextrin (γ-CD).[12] With a suitably sized guest, CD's are known to form host–guest crystals in which the guest resides within the cavity of the CD ring. The size of the inner diameter of the CD complexes is controlled by the number of D-glucose units in the ring (α-CD has 6, β-CD 7 and γ-CD 8). Since the width of a typical spiropyran is ~6–7 Å, the γ-CD was chosen because the smallest inner diameter (~7.5 Å) was wide enough to include the photochromic guest.

Photochromic guest complexation inside the CD ring has been observed previously in solid state studies. Arima *et al.* studied the powders of γ-CD–nitro spiropyran inclusion complex and observed photochromism of the spiropyran presumably due to the sufficient free volume of the cavity to allow the interconversion to occur.[13] Photodimerizations have also been observed within the cyclodextrin cavity with coumarins[14] and diaryl ethenes.[15]



Scheme 1 Spiropyran–photomerocyanine interconversion.



1 X = Br
2 X = I
3 X = CHO

Scheme 2 Synthesis of spiropyran compounds

In this study we are interested in studying the effect of a crystalline CD host environment on photochromic SPs with different substituents (**1**–**3**). The spiropyrans were prepared by reacting the appropriate halogen substituted salicylaldehyde with 1,3,3-trimethylindolenine. Crystals were grown by slow evaporation of a 1:2 mixture of γ-CD and photochromic compound in a DMF–H_2O–ethanol solution.[16]

Once crystals were obtained the host–guest complex was demonstrated by powder X-ray diffraction patterns. As seen in Fig. 1 the host–guest complexes of compounds **2**–**4** have a different powder pattern than either the pure host or guest compounds. The powder diffraction is nearly identical for **1**–**3** regardless of the substituent which is typical for γ-CD inclusion complexes.[17] The inclusion ratio was determined to be 2:1 host:guest by the ratio of the corresponding peaks in the ^1H NMR of dissolved crystals.

Upon photolysis with 500 W Hg arc lamp with a 365 nm line filter the host–guest crystals of **1**–**3** turned deeply colored. The

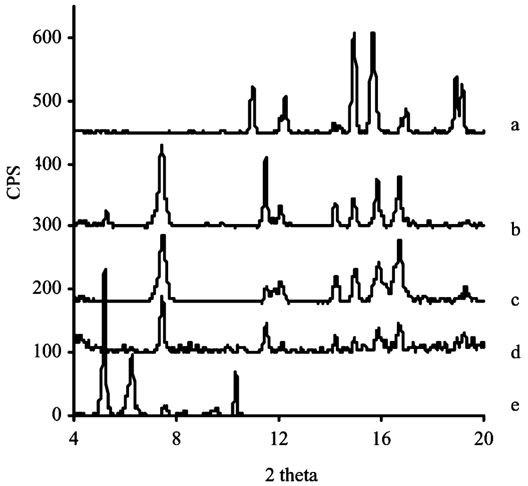


Fig. 1 Powder XRD data spectra obtained on a Scintag XRD 2000 diffractometer with a graphite monochromated Cu-Kα radiation: (a) pure **3**, (b) γ-CD–**3** host–guest crystal, (c) γ-CD–**1** host–guest crystal, (d) γ-CD–**2** host–guest crystal, (e) pure γ-CD.

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λ_{max} of the photogenerated peaks were 604, 583 and 555 nm for compound **1**–**3** in γ-CD, respectively. After allowing the PM to decay in the host cavity to the spiropyran the PM could be regenerated by subsequent photolysis.

As seen in Fig. 2 this color change for the photolyzed host–guest crystals was dramatic. Single crystals of pure **1**–**3**, however, showed no change in color upon photolysis, presumably due to the steric constraints of the crystalline lattice on the molecular reorganization required for this transformation. The decay kinetics for the three host–guest crystals were fitted to a first order exponential as seen in Fig. 3 and the half-lives are listed in Table 1.[18] As can be seen the inclusion complex offers stability for the PM form as evidenced by the observation of photochromism for the halogen substituted SP (**1** and **2**) which was not observed in solution and also the increased lifetime of the aldehyde substituted SP (**3**) by an order of magnitude in the nonpolar γ-CD cavity compared to the polar methanol solution.

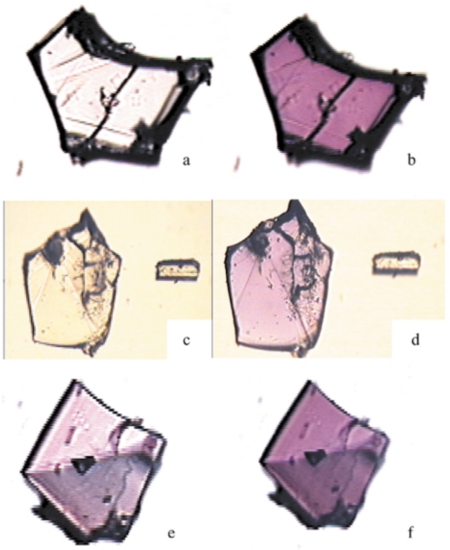

Fig. 2 Optical pictures of photochromic host–guest complexes: (a) host–guest complex γ-CD–**1**, before photolysis, crystal size is 0.10 × 0.05 mm, (b) γ-CD–**1** after 365 nm photolysis, (c) γ-CD–**2** before photolysis, crystal size is 0.10 × 0.20 mm, smaller crystal to right is pure **2**, (d) both γ-CD–**2** and pure **2** crystals after 365 nm photolysis, (e) γ-CD–**3** before photolysis, crystal size is 0.20 × 0.20 mm, (f) γ-CD–**3** after photolysis.

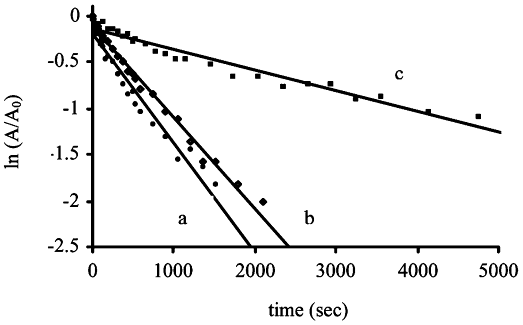

Fig. 3 Plot of ln (A/A_0) *versus* time absorbance decay of photochromic peak for the host–guest complexes: (a) γ-CD–**1**, (b) γ-CD–**2**, (c) γ-CD–**3**.

Table 1 Decay data for photochromic complexes

Compound	λ_{max} (nm) host–guest	$t_{1/2}$ (s) host–guest	λ_{max} (nm) methanol	$t_{1/2}$ (s) methanol
1	604	320 ± 20	*	*
2	583	530 ± 20	*	*
3	555	1500 ±130	530	186 ± 2

In conclusion, photochromic host–guest crystals were obtained with differently substituted SPs in a γ-CD complex. The photogenerated PM form was longer lived in the inclusion complex compared to polar solvents. In the case of the bromo- and iodo- substituted spiropyrans inclusion within the host–guest complex allowed observation of photochromism which was not observed in solution.

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18 Half-life values were obtained by absorbance measurement of λ_{max} over time by mounting crystals on a glass slide and photolyzing with a 500 W Hg arc lamp with a 365 nm line filter inside an HP 8453 UV–Vis instrument.