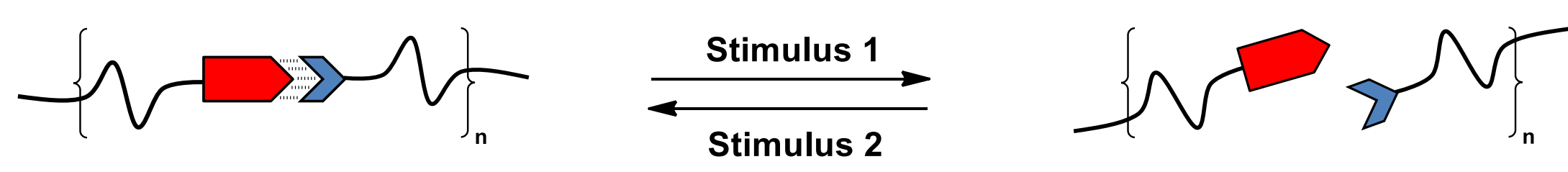


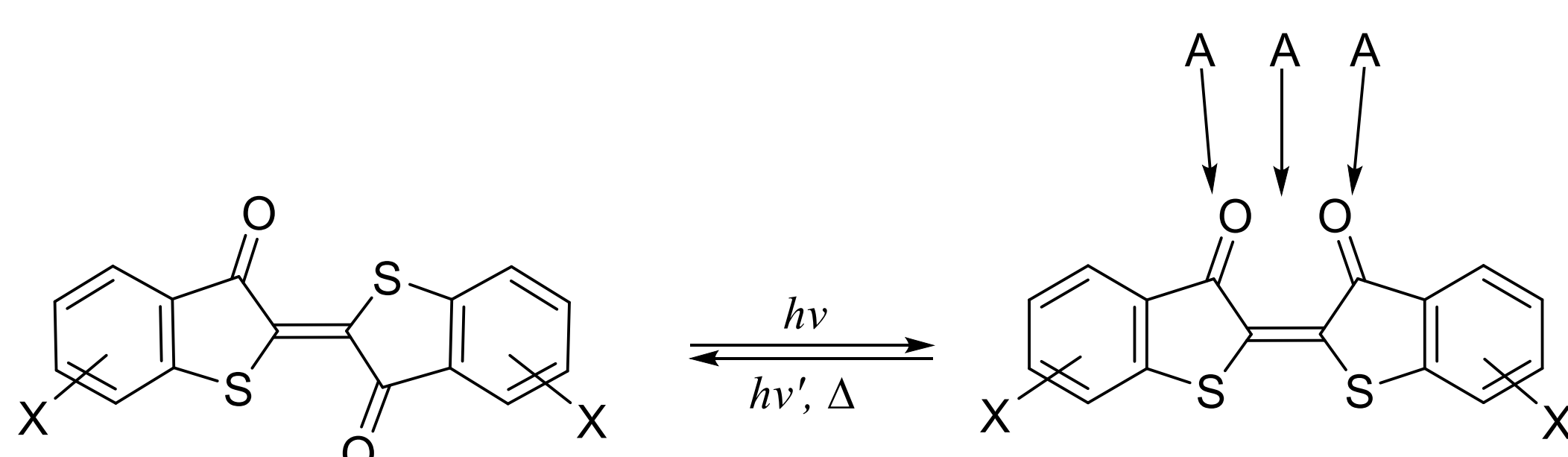
## Introduction

Photochromism is the reversible transformation of a chemical material to another form by the absorption of electromagnetic radiation (light), where the two metastable forms have distinct absorption spectra and other properties. Photochromism in materials allows for the switching of their function based on irradiation with light. Our research is exploring hydrogen bonded complexes containing a (hemi)thioindigo moiety which might be incorporated into a “smart polymer” and controlled using visible light as an external stimulus (Figure 1).



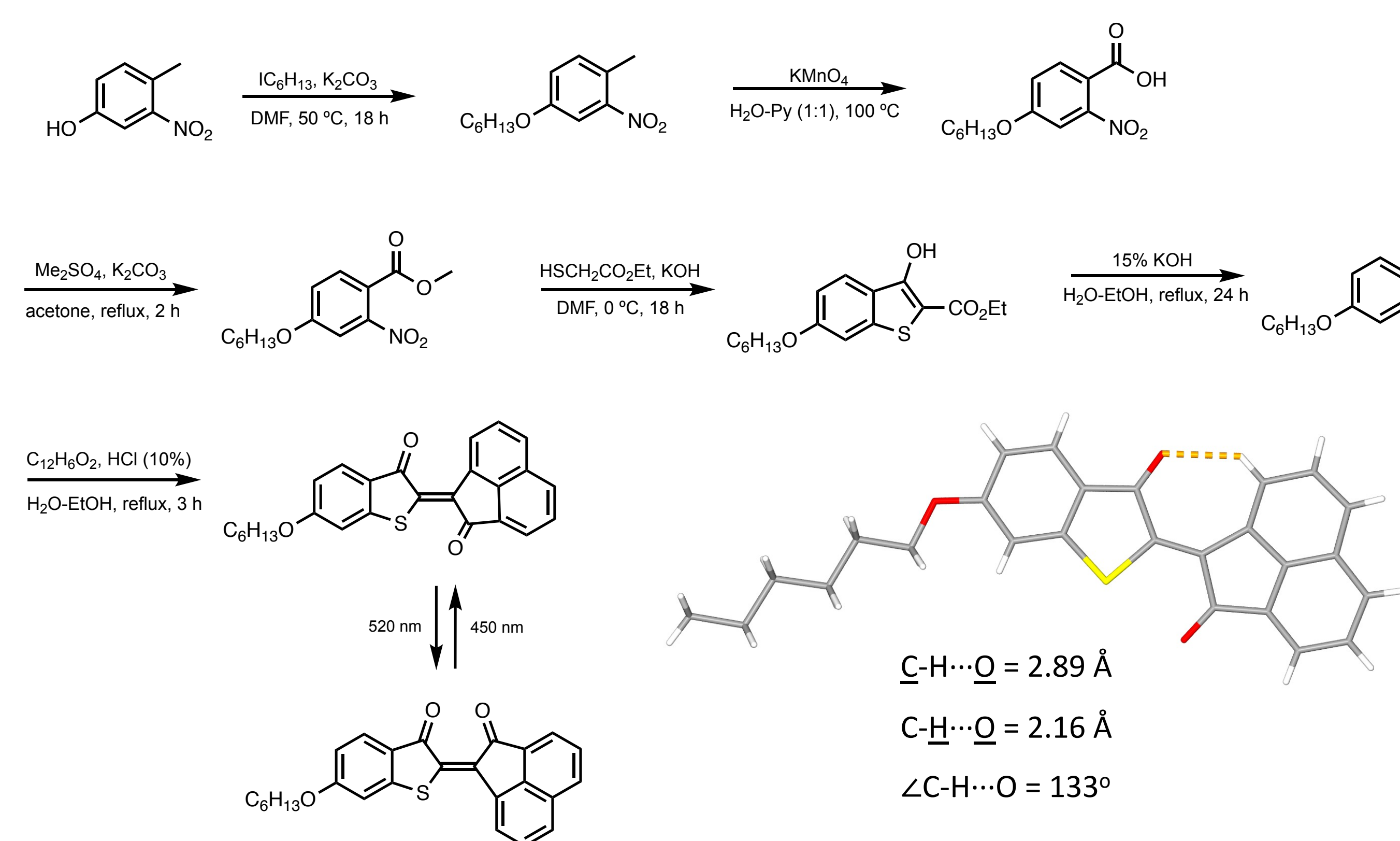
**Figure 1:** The reversible interactions of a supramolecular polymer when exposed to external stimuli

Light provides a non-invasive technique to alter the arrangement (reversible *trans* to *cis* isomerization) of the hemithioindigo-containing component, in turn rearranging the non-covalent hydrogen bonding array and making the potential interactions much stronger. Scheme 1 illustrates this basic concept and functionality of these compounds.



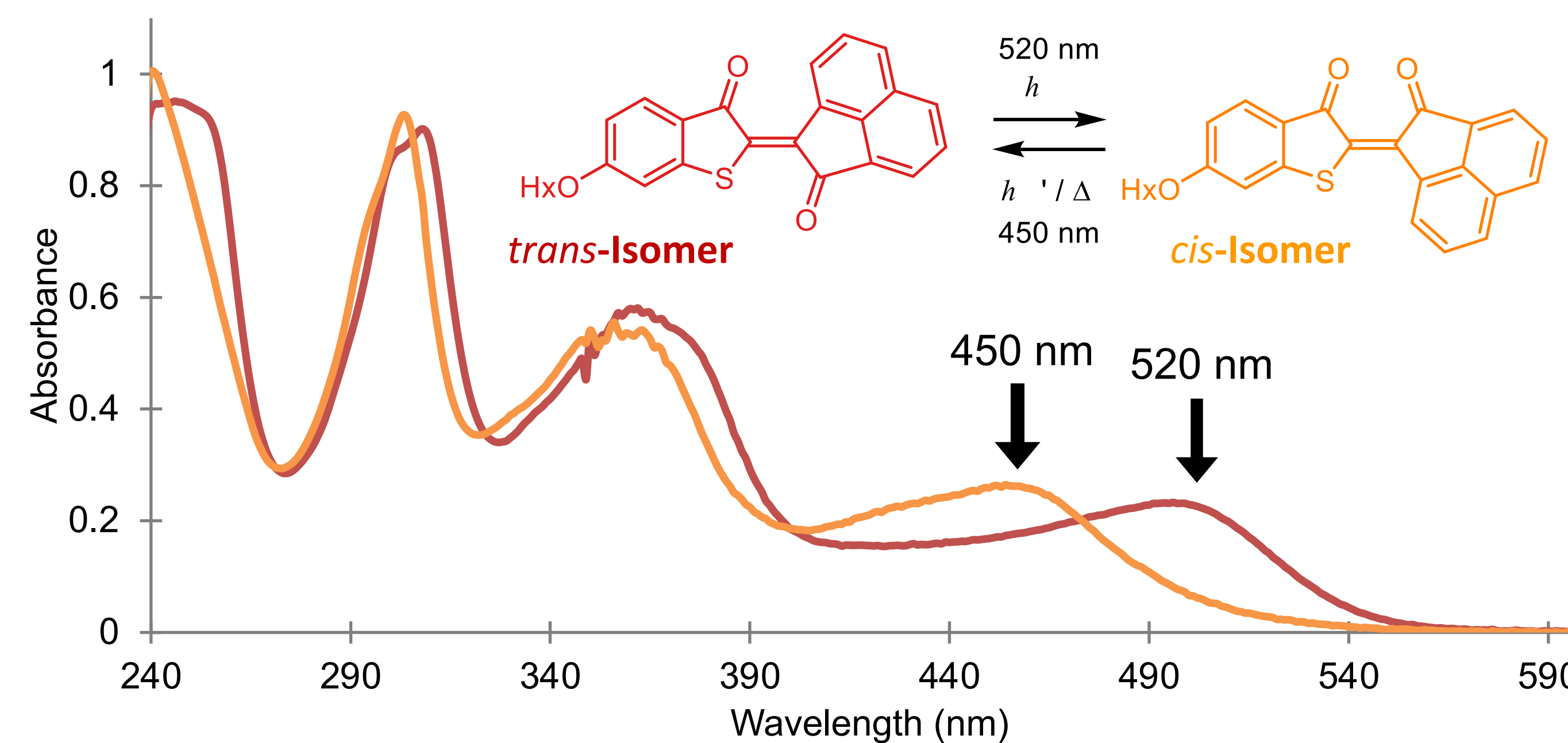
**Scheme 1:** Photoisomerization of a thioindigo-based hydrogen bond array. (A = hydrogen bond acceptor site in the array)

## Synthesis of Hemithioindigo Hydrogen Bond Arrays



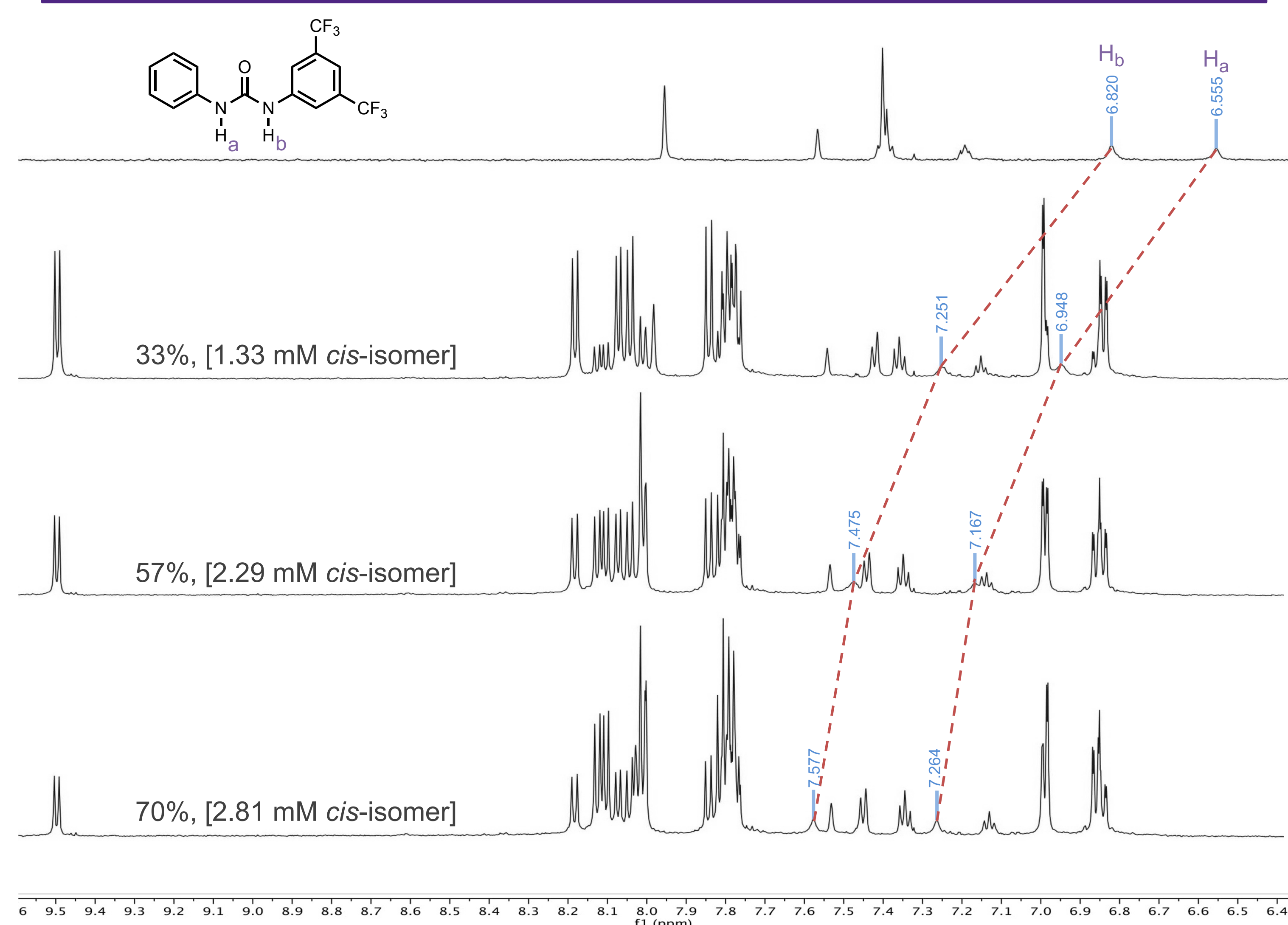
**Figure 2:** Synthesis and X-ray structure of photoswitchable hydrogen bond acceptor array.

## UV-vis Spectra of Hemithioindigo Isomers

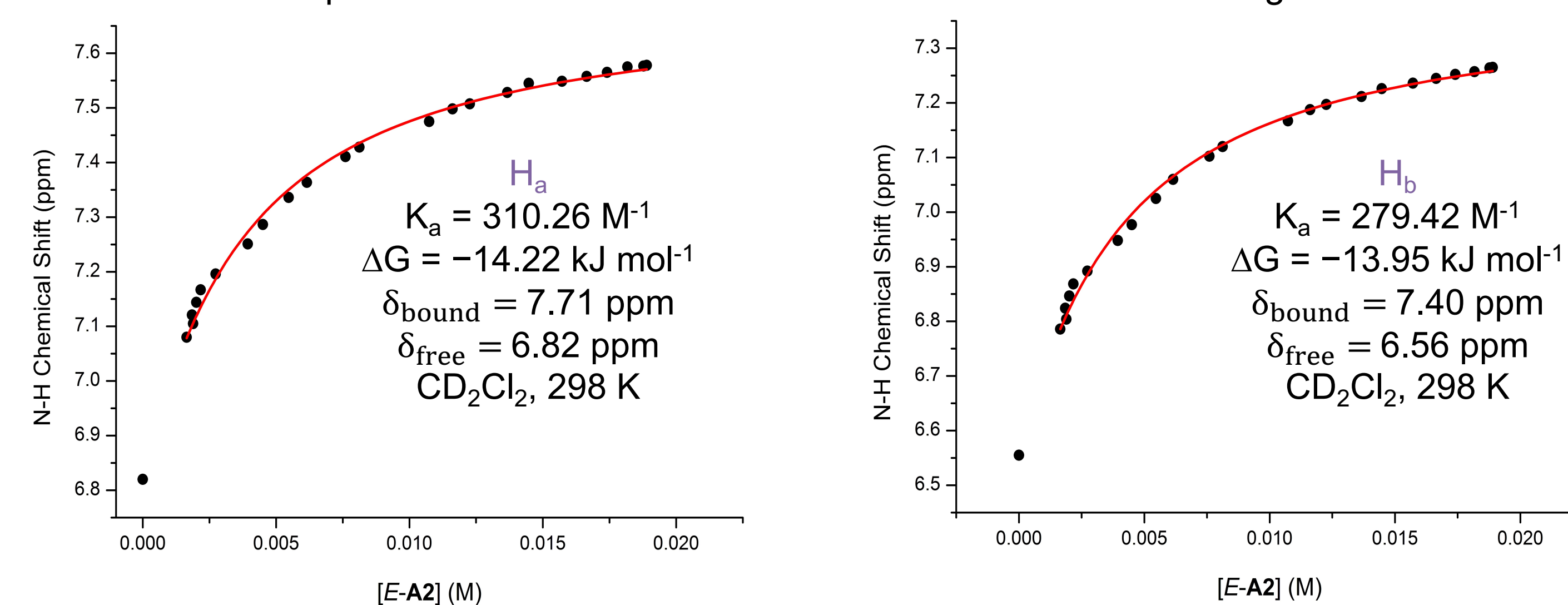


**Figure 3:** UV-vis spectra of *cis* and *trans* isomers of the photoswitchable hemithioindigo hydrogen bond acceptor array.

## Binding is Exclusively to the *Cis*-Isomer by <sup>1</sup>H NMR

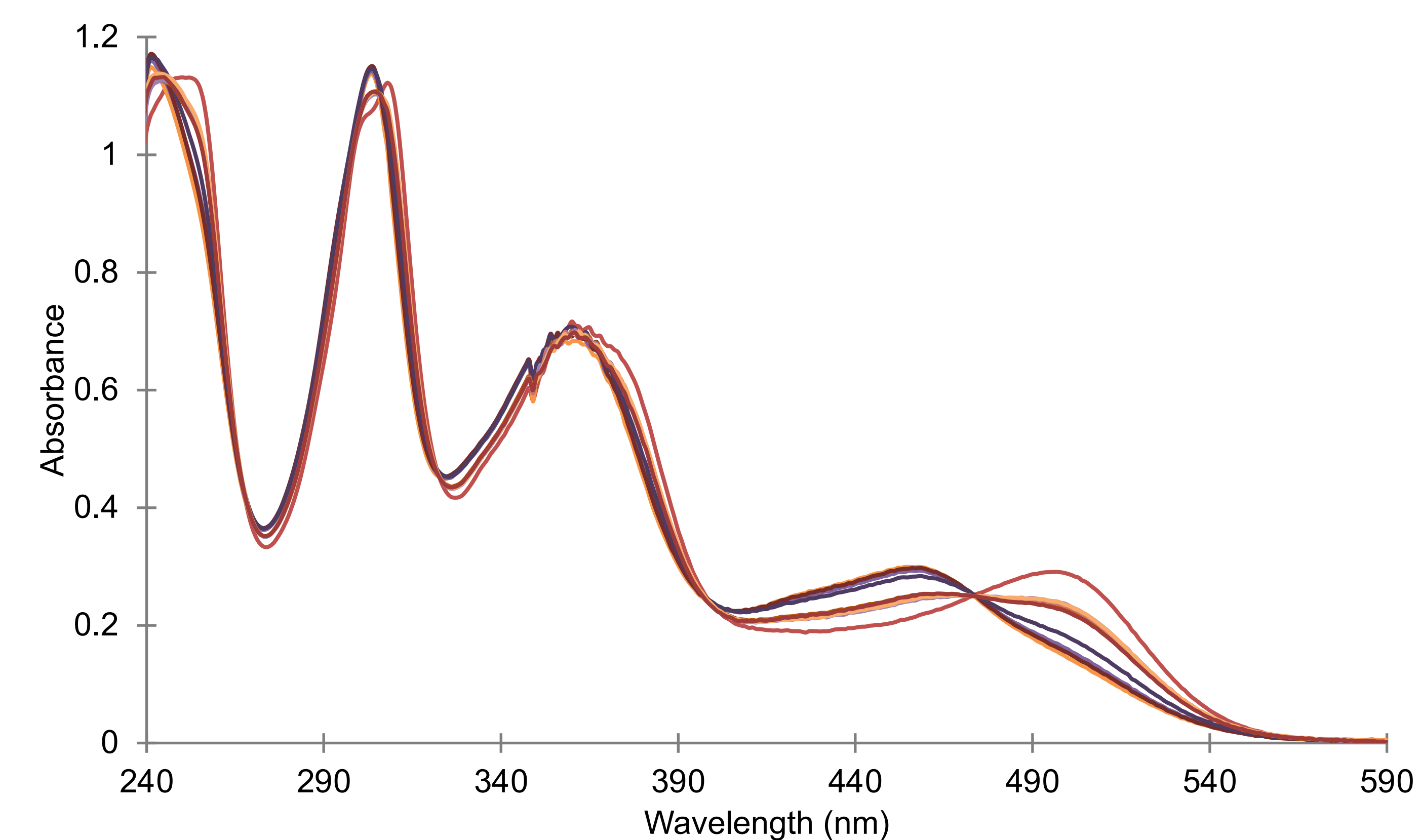


**Figure 4:** <sup>1</sup>H NMR of donor binding solely to the *cis*-isomer as the hemithioindigo photoisomerizes from *trans* to *cis* form under 520nm led light.



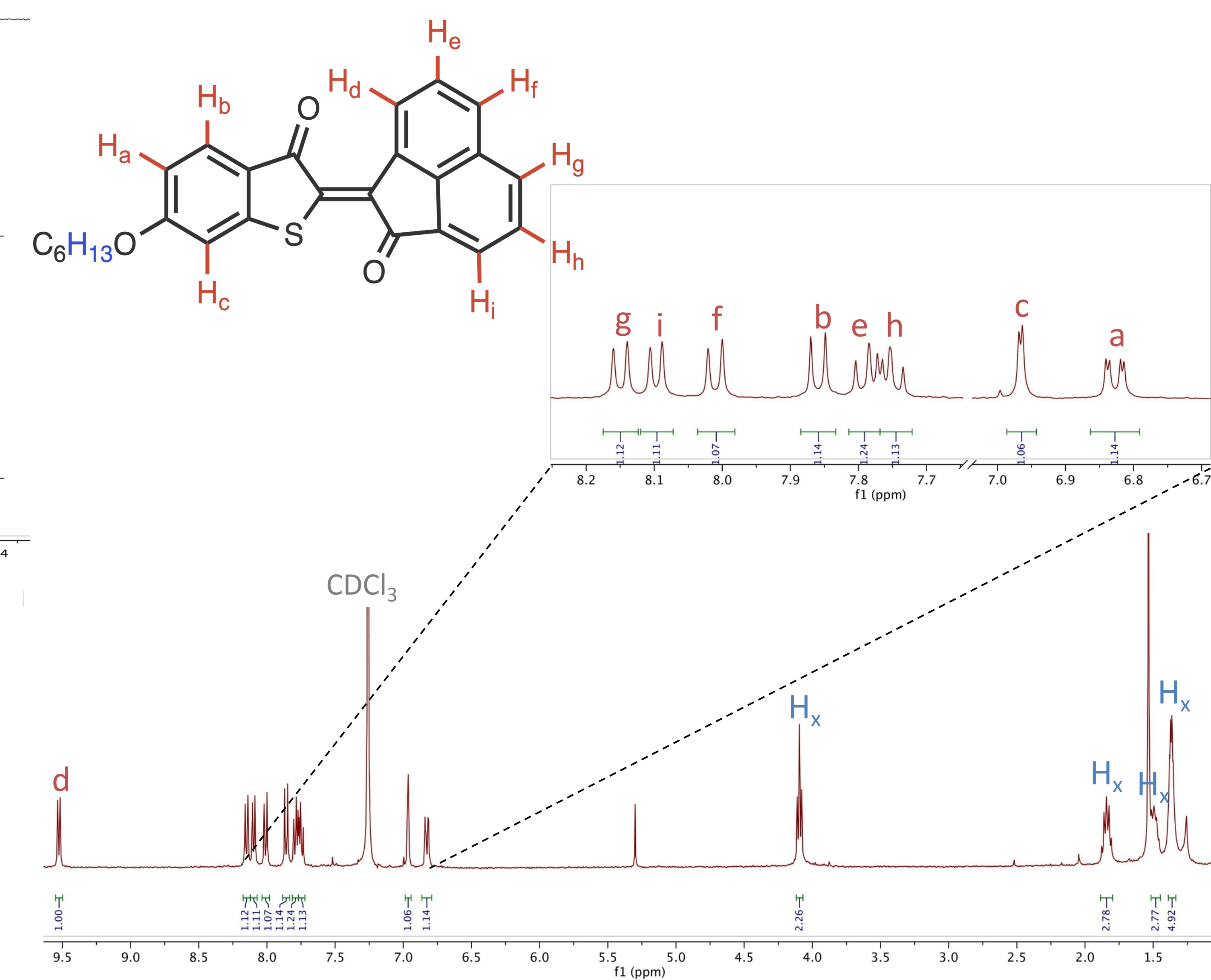
**Figure 5:** <sup>1</sup>H NMR Titration data, calculated binding isotherm and thermodynamic parameters.

## Photostationary States in Chloroform



**Figure 6:** UV-vis spectra of the photostationary states of the hemithioindigo in  $\text{CHCl}_3$  after being irradiated at set wavelengths.

## <sup>1</sup>H NMR of the *Trans*-Isomer



**Figure 7:** <sup>1</sup>H NMR spectrum of the *trans*-hemithioindigo hydrogen bond array (298 K,  $\text{CDCl}_3$ ).