

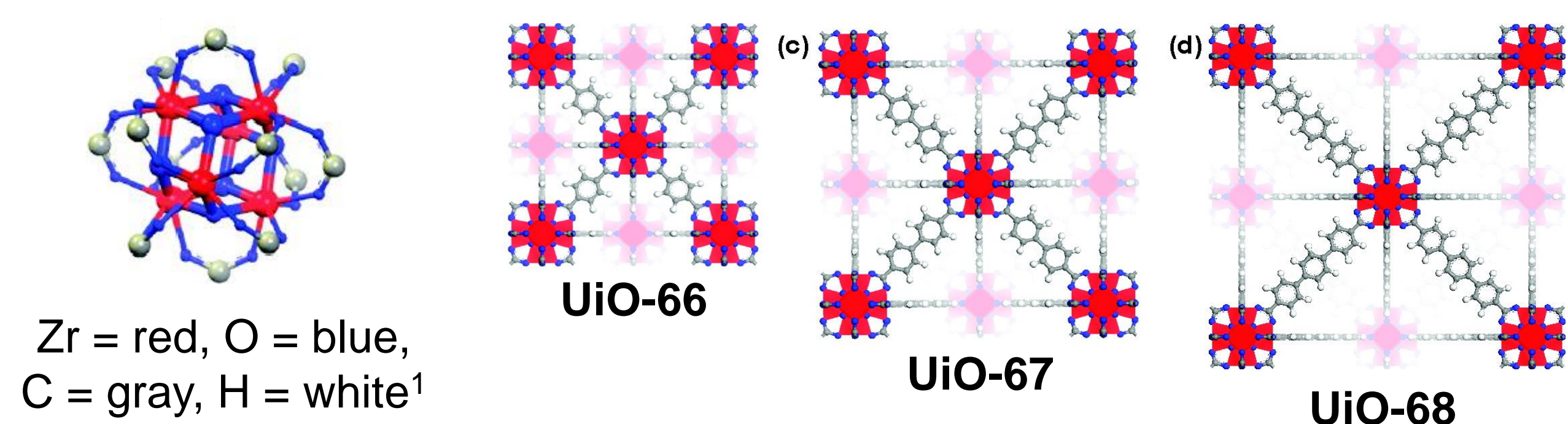
Incorporation of Donor-Acceptor Stenhouse Adducts into UiO Metal-Organic Frameworks

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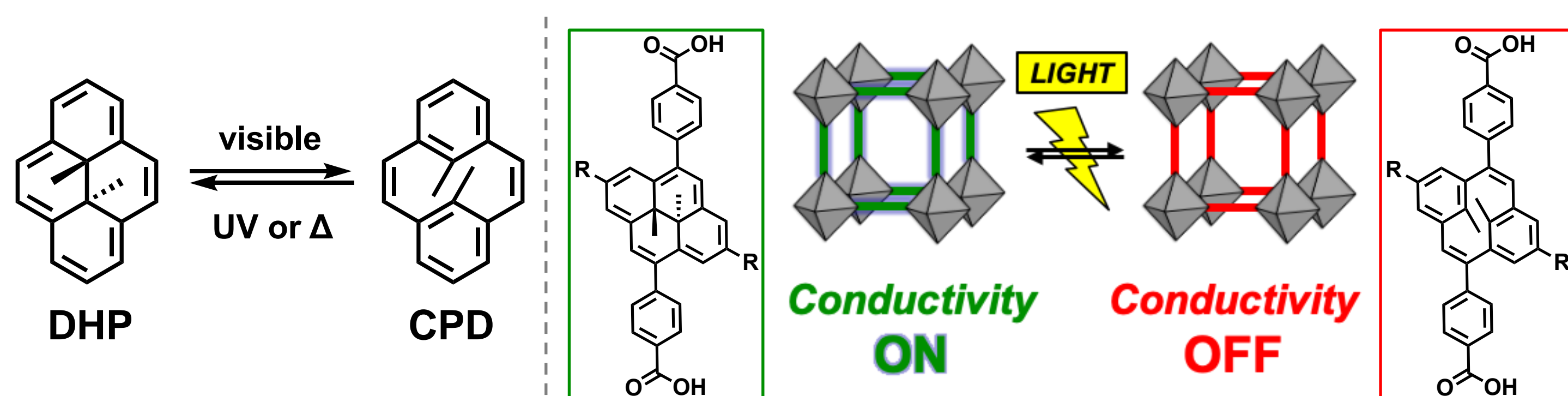
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Introduction

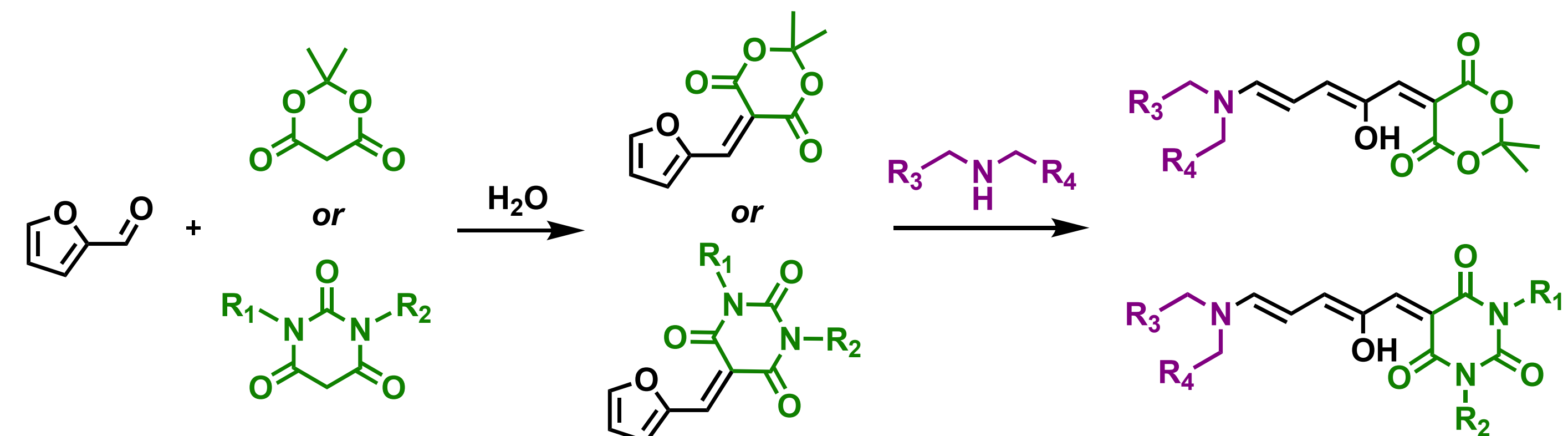
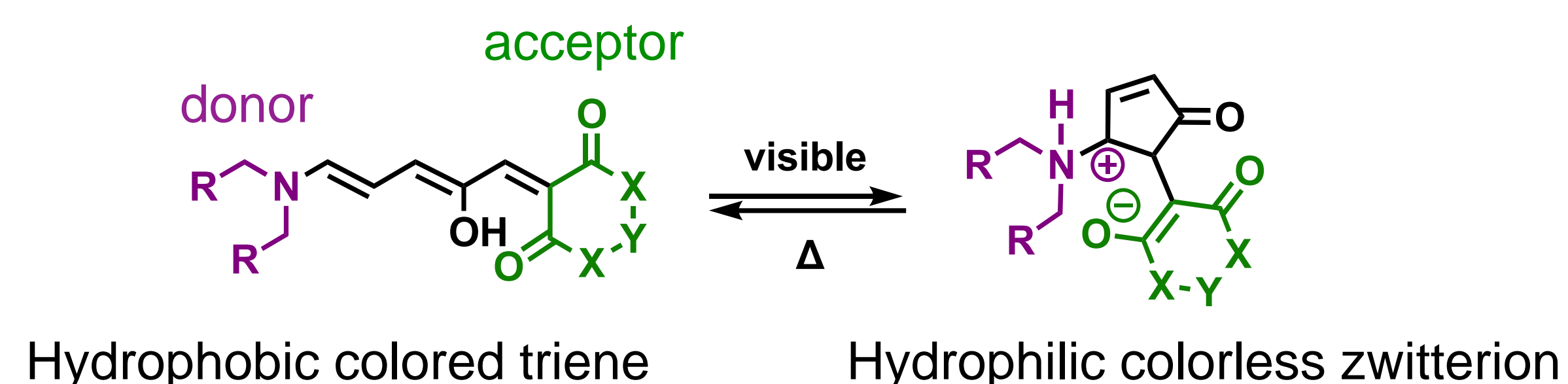
Metal-organic frameworks (MOFs) are permanently porous crystalline coordination materials composed of metal centers or clusters connected to organic linkers with the ability to extend in multiple dimensions. MOFs are modular due to the variety of metals and linkers that can be used, creating an array of structures with different properties. Zirconium-based UiO MOFs are robust and stable to a variety of solvents and high temperatures, which has allowed for the introduction of many functional groups on the organic linker directly or by post-synthetic modification.^{1,2}



Installing photochromic molecules inside MOFs can create triggerable photoresponsive materials. In the Waldie group, we are studying the Dimethyldihydropyrene (DHP) photochrome and incorporating it as the organic linker backbone in conductive MOFs in order to gain optical control over electrical conductivity. Under visible light irradiation, DHP isomerizes to the CPD form and reverts to DHP under UV or heat.

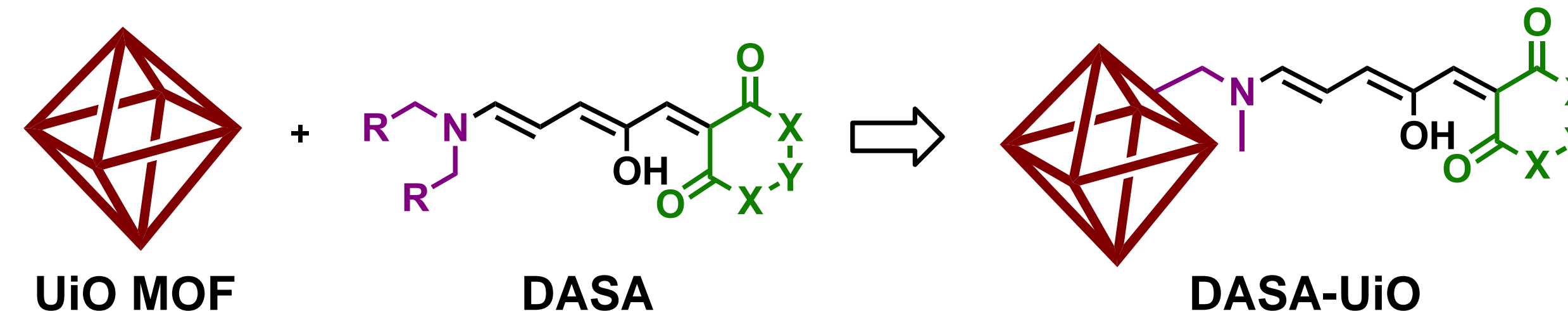


Donor-Acceptor Stenhouse Adducts (DASAs) are modular organic photochromes that when irradiated with visible light convert from a colored, hydrophobic triene to a colorless, hydrophilic zwitterion.³ While the structural change of this photoisomerization is too large for DASAs to be used as the linker backbone in a MOF, we envision that DASAs could be installed such that they hang into the MOF pore. This should result in a dramatic change in pore size and polarity upon light exposure.



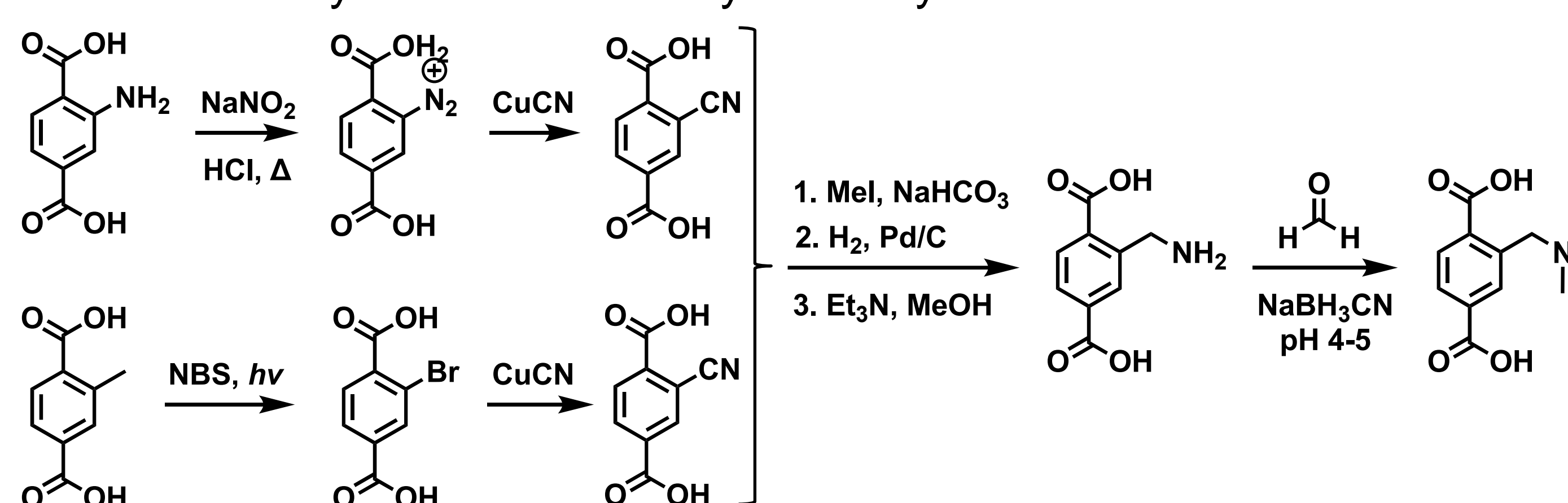
Proposal Objectives

DASAs have been incorporated into polymers for drug delivery and sensing applications through the amine donor group. Inspired by the stability of UiO MOFs and the ability of DASAs to confer new optical properties to materials, we propose to design a series of DASA-UiO MOFs and study their photochromic properties.

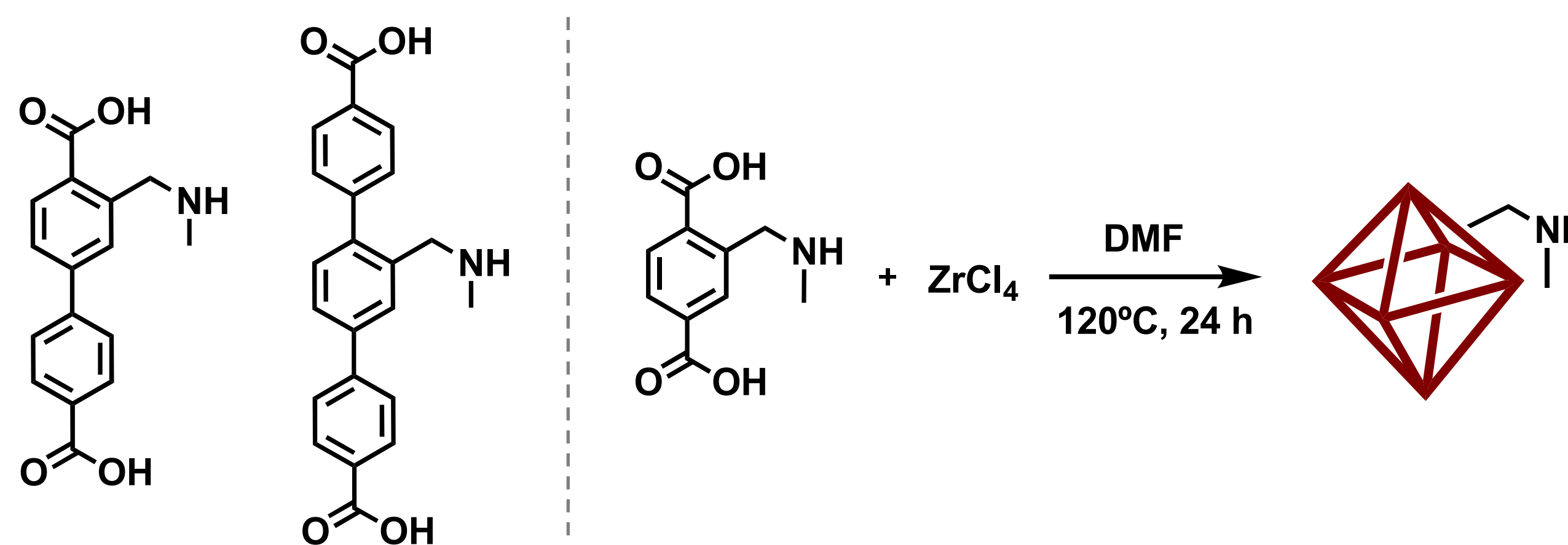


Proposed Synthesis

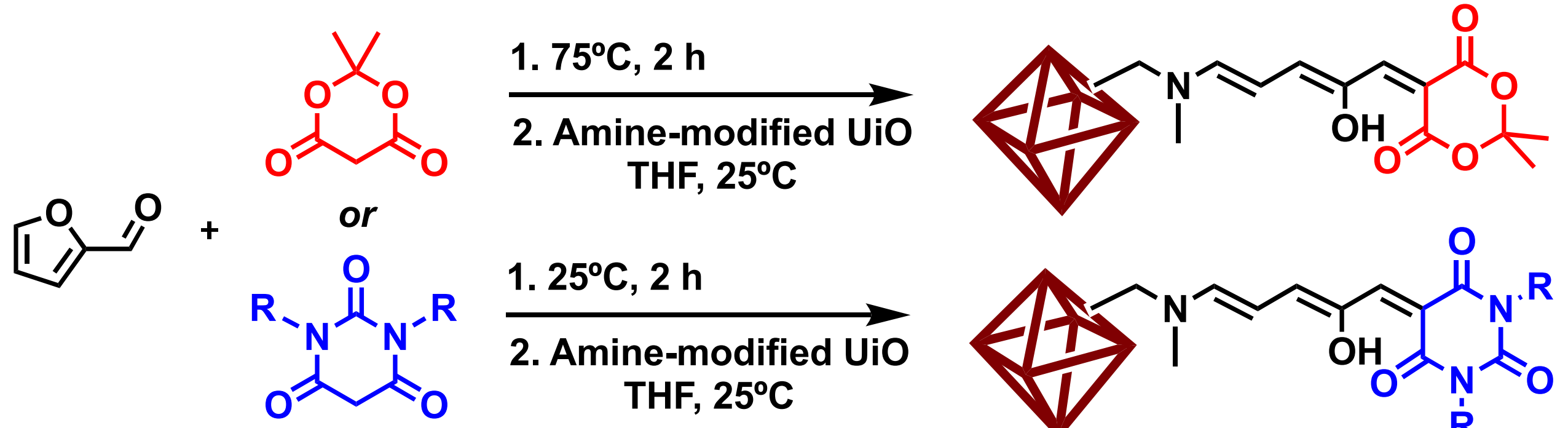
The first aim is to design a modified dicarboxylic acid molecule that can function as the linker for UiO MOFs and the donor for DASAs. We propose to install an -NH₂ group on the central benzene ring, starting from the methyl- or amine-substituted starting material. A final reductive amination will yield the secondary *N*-methyl amine.



Other linkers with extended structures will also be synthesized in a similar fashion to prepare analogues of UiO-67 and 68, which have larger pore sizes than UiO-66. The *N*-methyl amine linkers will be incorporated into UiO MOFs by the reaction with ZrCl₄ in DMF.^{1,2}



Post-synthetic modification of the amine-UiO MOFs will then be performed to prepare the DASA groups using the amine as the donor.³



Proposed Characterization

Characterization by UV/Vis and ¹H NMR spectroscopy will be performed to confirm the DASA photoisomerization still occurs in the MOF network. When the DASA molecules photoisomerize to the zwitterionic form, it is expected that the MOF pore volume will increase significantly, which will be identified by N₂ adsorption isotherms. The change in polarity of the pore surface upon isomerization may lead to increased and/or preferential uptake of certain gases or polar molecules, which will be screened by these methods.

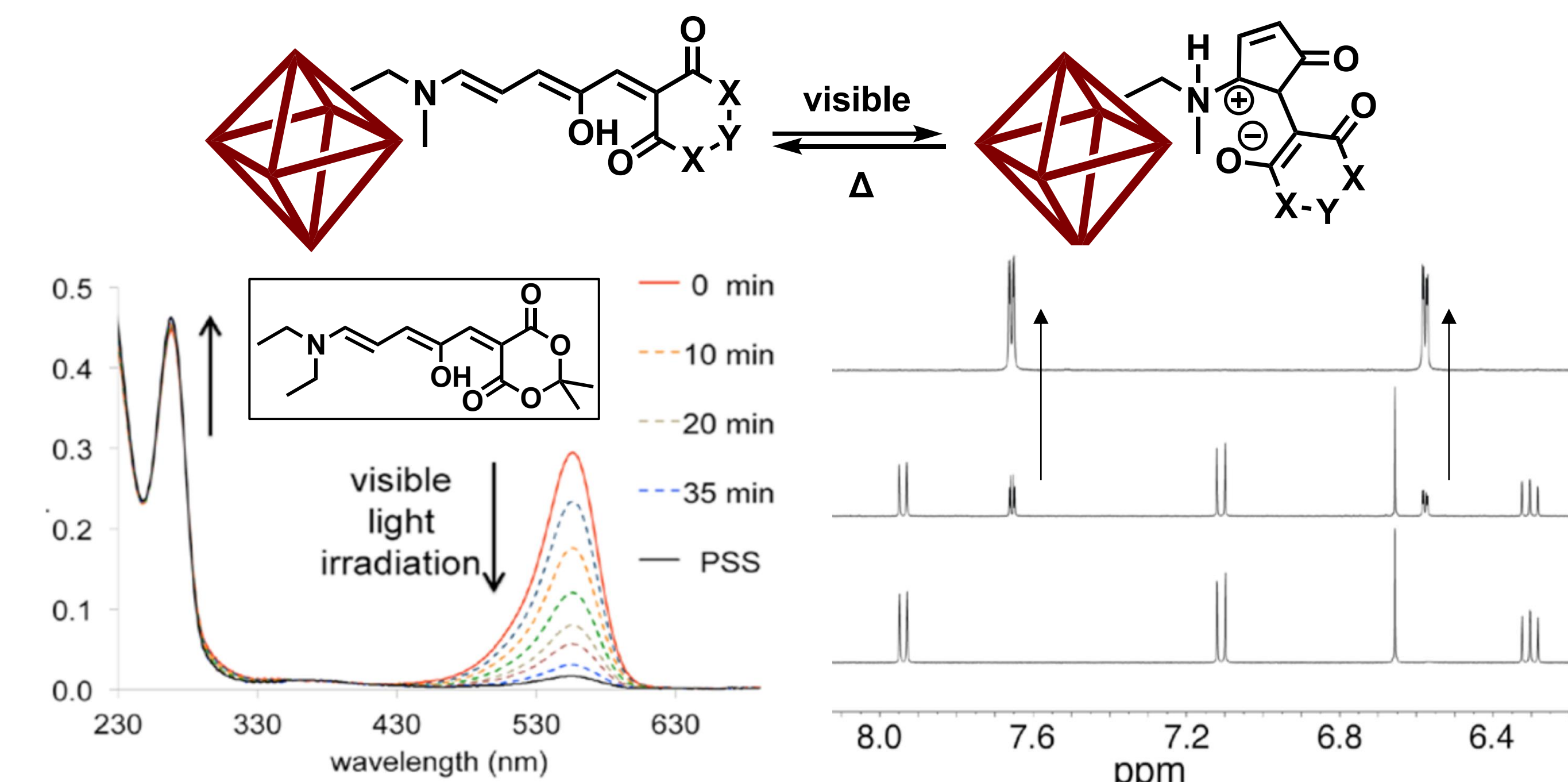


Figure 1. UV/Vis (left) and ¹H NMR (right) spectra of DASA photoisomerization in methanol converting from the extended to closed form.³

Conclusions

The incorporation of DASAs into UiO MOFs is proposed to create a new class of photoresponsive materials. A synthesis route was designed to install an *N*-methyl amine group onto the organic linkers used in UiO MOFs that will function as the donor group in the DASA adduct. These materials may have application where a change in MOF pore properties triggered by an external stimulus is useful, such as drug delivery or gas storage activated by visible light irradiation.

References

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