

Pore modification of Metal-Organic Frameworks using Photochemical [2+2] Cycloaddition Reaction in the Solid-state

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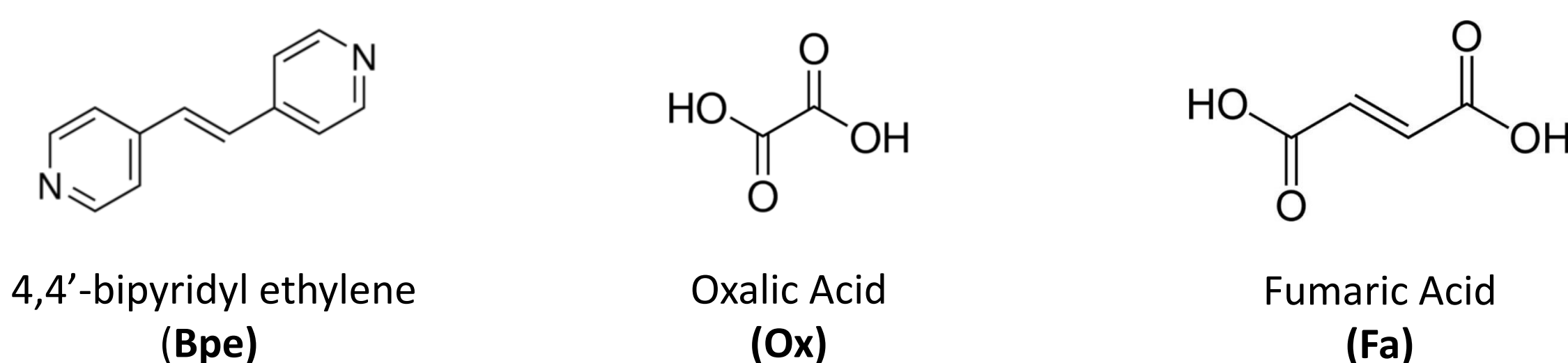
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Introduction

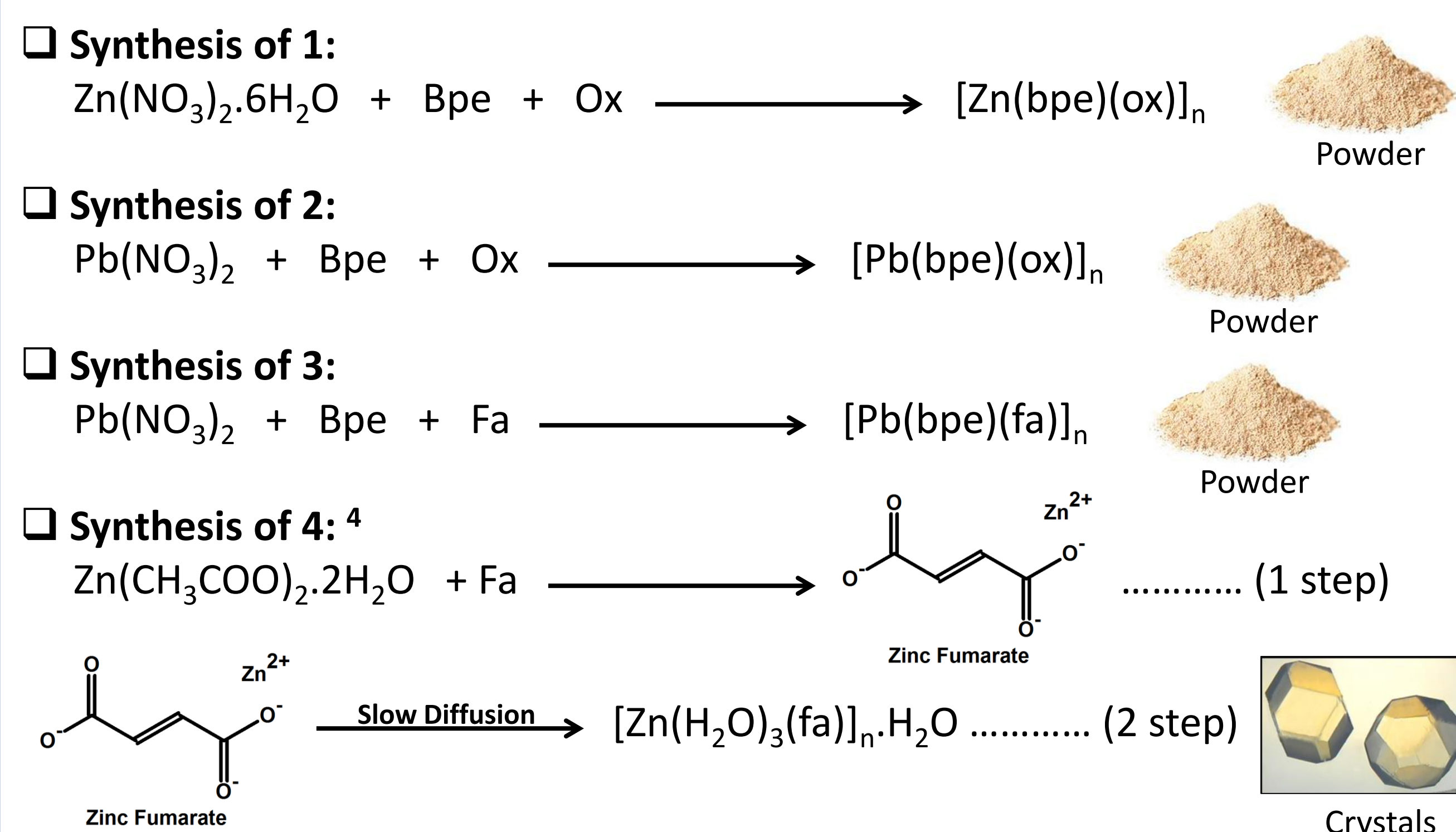
Although the criteria for solid-state photochemical [2+2] cycloaddition reactions have been well established, it is still a challenge to stack a pair of C=C bonds in the crystal lattice by design.¹⁻³ A number of weak interactions have been serendipitously discovered to align the double bonds in the crystal lattice congenial for the dimerization reactions. The strength and directionality of the hydrogen bonds have been elegantly exploited to align the double bonds in 4,4'-bipyridylethylene (**bpe**) and fumaric acid (**fa**) with considerable success. However, to the best of our knowledge, the pore modification of metal-organic frameworks (MOFs) using photodimerization reaction have been rarely reported. Here we report the design and synthesis of number of MOFs contains **bpe** and **fa** as spacer ligands to align the C=C olefinic bonds for photochemical dimerization reactions in MOFs. Four MOFs; [Zn(bpe)(ox)]_n (**1**), [Pb(bpe)(ox)]_n (**2**), [Pb(bpe)(fa)]_n (**3**) and [Zn(H₂O)₃(fa)]_n·H₂O (**4**), where (**ox**) is oxalic acid, have been synthesized. The photoreactivity of the above MOFs have been studied using ¹H-NMR spectroscopy. ¹H-NMR spectroscopy study indicates all the MOFs undergoes topochemical [2+2] photodimerization produces cyclobutane products quantitatively in the solid-state. However, the attempts still going on to produce crystals of some of the above MOFs to achieve photodimerization *via* single-crystal to single-crystal (SCSC) transformation. This strategy offers an excellent technique to the modification of functional pores of MOFs for various applications.

Experimental Data & Results

Ligands Structures:



Synthesis:



Crystal Structures:

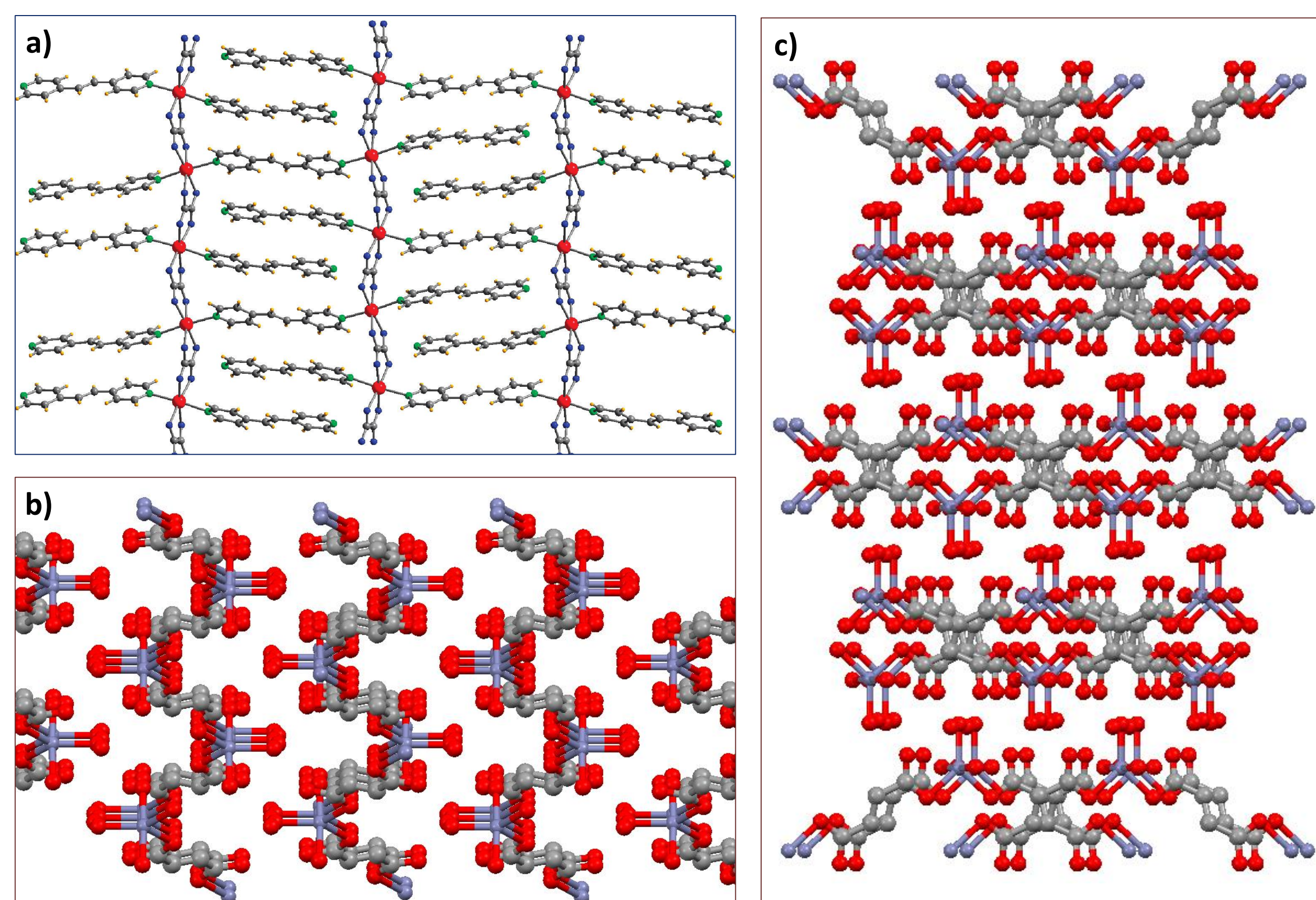
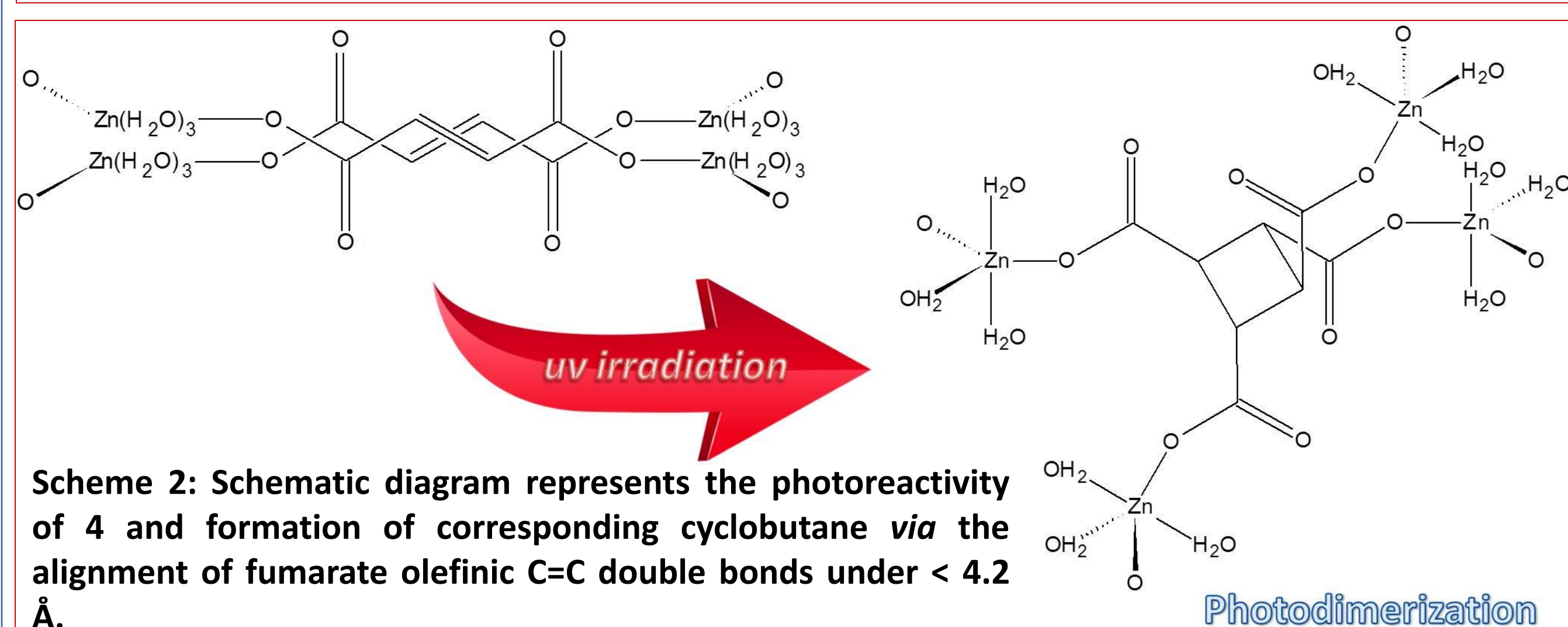
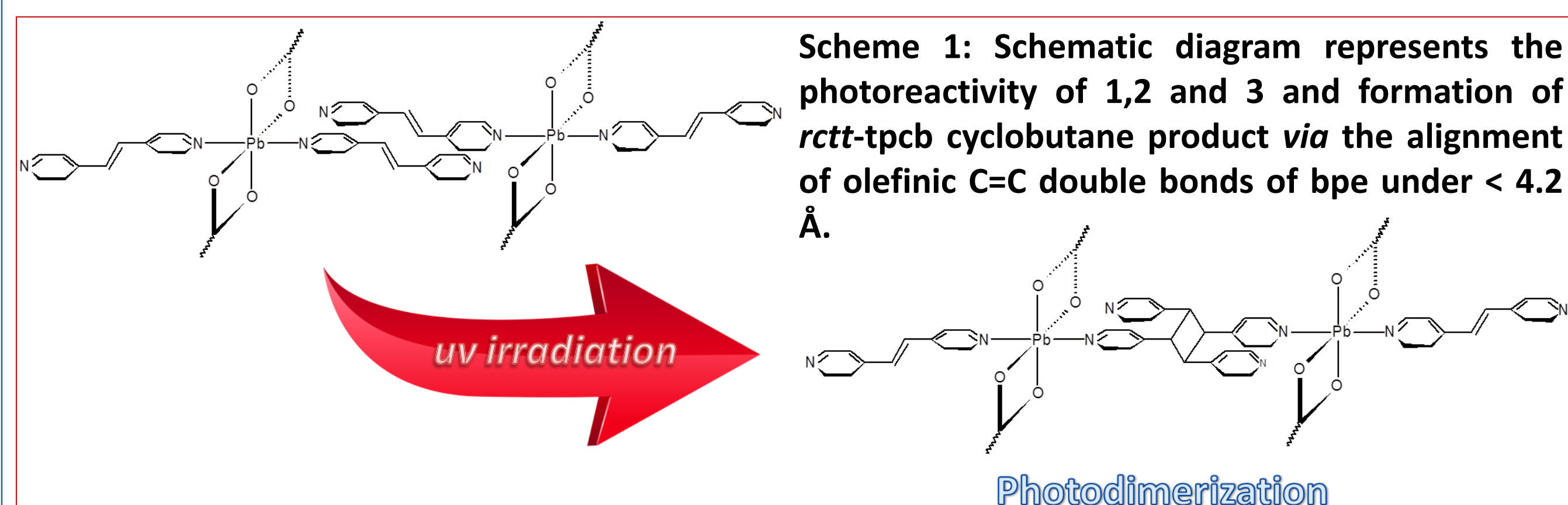


Fig. 1: (a) Expected layer of broken ladder-like structure of 1,2 and 3. (b) and (c) Crystal packing of compound 4 along *a* and *c* respectively.

Photodimerization in MOFs Structures:



¹H-NMR Data:

¹H-NMR Before UV irradiation:

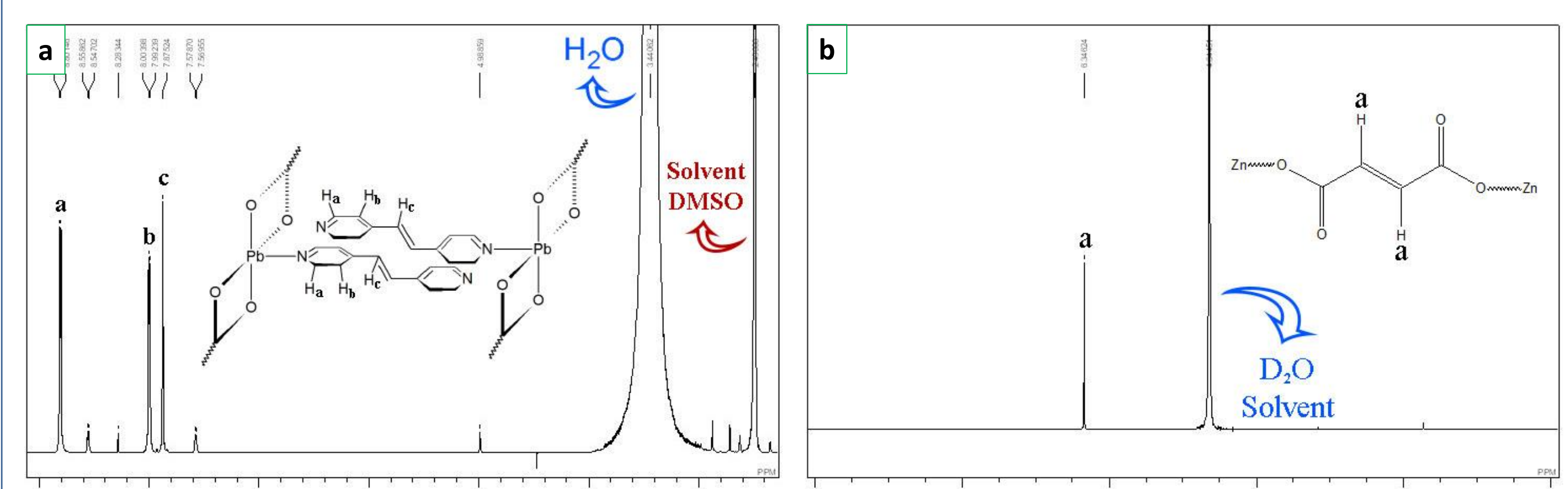


Fig. 3: a) ¹H-NMR spectra of compounds 2 (1 and 3 have similar spectra). b) ¹H-NMR spectra of compound 4.

¹H-NMR After UV irradiation:

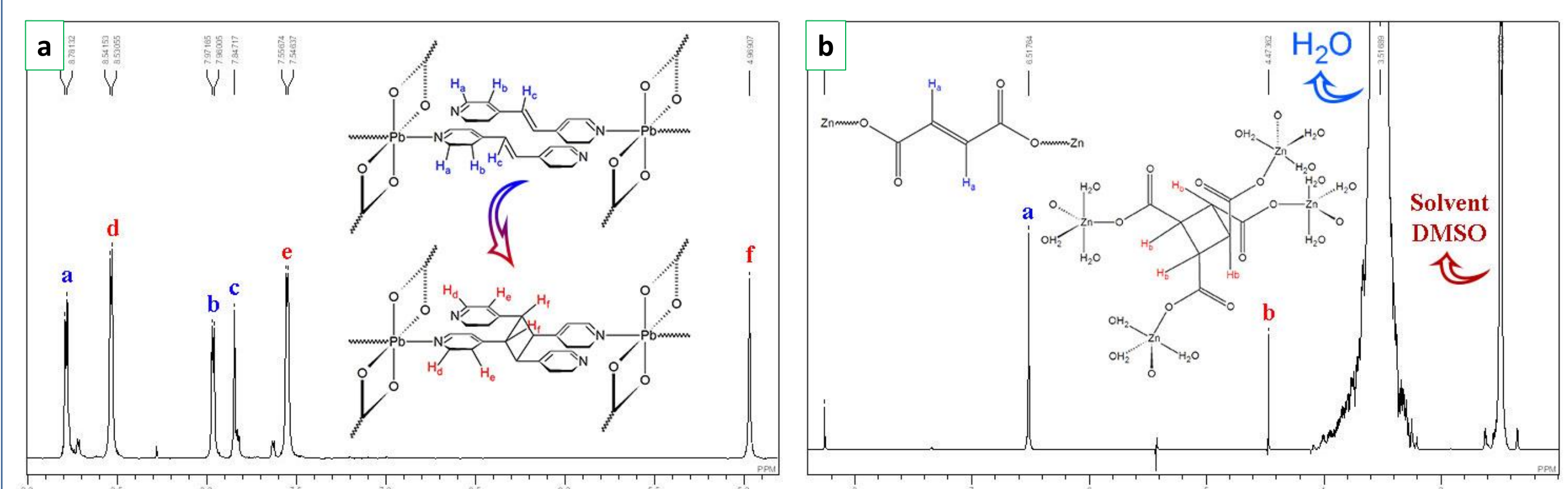


Fig. 4: a) ¹H-NMR spectra after 24 hours of UV irradiation of compounds 2, it has a conversion of 62% based on peaks area integration (1 and 3 have similar spectra). b) ¹H-NMR spectra after 24 hours of UV irradiation for compound 4.

Discussions

- The expected structure of **1-3** was predicted based on the synthesis of reported manganese (II) MOFs.⁵ A very similar reaction has been conducted to produce **1-3** compounds. ¹H-NMR spectrum support the assumption *via* the photoreactivity of **1-3**.
- ¹H-NMR spectrum of the irradiated product of **1-3** dissolved in DMSO-*d*₆ shows the disappearance of olefinic protons and appearance of cyclobutane protons, and the corresponding shifts in the bipyridyl protons (Fig.4a).
- ¹H-NMR spectrum of the irradiated product of **4** dissolved in DMSO-*d*₆ shows the disappearance of olefinic protons and appearance of cyclobutane protons (Fig.4b).

Conclusions

- The olefinic C=C bonds of **bpe** were successfully aligned in three MOFs using Zn(II) and Pb(II) as the metal and **ox** or **fa** are the organic templates.
- The olefinic C=C bonds of **fa** were successfully aligned in one MOFs using Zn(II) metal ion as the template.
- All the compounds undergo photochemical [2+2] cycloaddition reaction produces cyclobutanes quantitatively.
- Ongoing work is focused to grow single crystals of **1-3**, complete characterization of **1-4** and study the photoreactivity of **1-4** in details especially the photoreactivity *via* SCSC transformation.

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