

## Metal-Organic Frameworks as “Solid Solvents” for Spiropyrans?

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Spiropyrans are an intensively studied class of photochromic molecules, as their switching results in significant changes in structure, absorption properties and dipole moments.<sup>[1]</sup> Due to the necessary sterical degree of freedom, switching of spiropyrans requires either a dissolved state or incorporation into matrices (polymer films or porous hosts), that spatially separate the single molecules from each other. For this purpose, metal-organic frameworks (MOFs) appear to be ideal host materials. MOFs consist of inorganic metal nodes or metal-oxo-clusters, which are connected by organic linker molecules forming a 3D framework with accessible voids.<sup>[2]</sup> These voids enable spatial separation of guest molecules. Depending on the nature of the linker molecule, various forms of host-guest interactions are envisioned for photoswitches embedded in different MOF host materials.

For our experiments 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (SP-1) was selected as the photoactive guest molecule and MOF-5 (**1**)<sup>[3]</sup>, MIL-68(Ga) (**2**)<sup>[4]</sup>, MIL-68(In) (**3**)<sup>[4]</sup> and MIL-53(Al) (**4**)<sup>[5]</sup> were chosen as host materials. Synthesis of the spiropyran@MOF-systems was carried out via a gas phase reaction to exclude any solvent molecule from all further considerations. The resulting systems were analyzed by XRPD (to confirm the successful embedding) and XPS (to determine the composition of the spiropyran@MOF-systems). Investigations of the switching behavior were carried out by means of UV/Vis and IR spectroscopy.

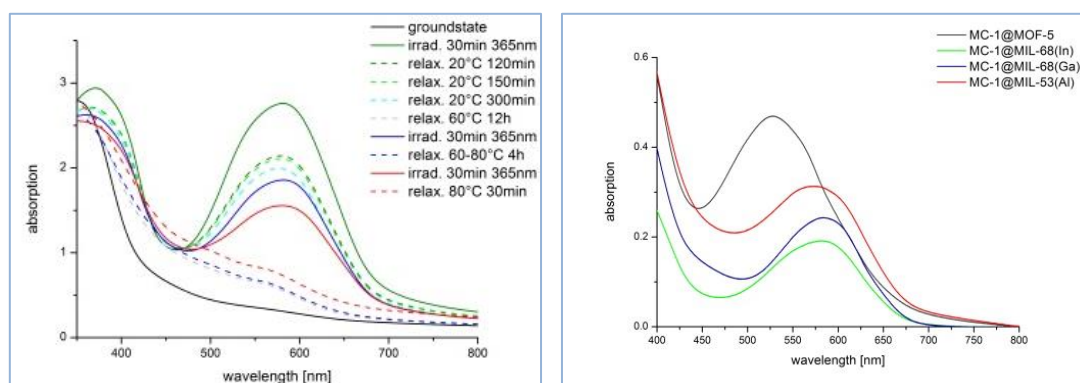


Figure 1. Left: UV/Vis spectra of SP-1@MIL-68(Ga) after irradiation with UV light ( $\lambda = 365$  nm) and heat supply; right: UV/Vis spectra of different spiropyran@MOF-systems after irradiation with UV light ( $\lambda = 365$  nm).

For all systems we found a switching of SP-1 inside the MOF matrices to its merocyanine form (MC-1) (see figure 1, left).<sup>[6]</sup> Furthermore, depending on the used host, different absorption maxima of the resulting MC-1 were observed (see figure 1, right). The surrounding chemical environment given by the MOF's pore seems to influence the absorption properties of the embedded dye. As this resembles the solvatochromic behavior of spiropyrans in solution, MOFs can be understood as "solid solvents" for these molecules. This new aspect of porous materials to act as a solvent for dye molecules offers new opportunities in fundamental research: by understanding the underlying host-guest interactions on the switching behaviour of the embedded dye its optical properties can be tuned by modifying the MOF's pores in size and shape.

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