Ultrafast pump-probe methods offer the capability of deciphering a plethora of excited-state dynamics in molecular and solid-phase materials. Among such methods, structurally sensitive probing methods based on hard X-rays and high-energy electrons have undergone tremendous developments in recent years. In this presentation I will introduce the power and challenges of ultrafast electron microscopy for the study of light-induced switching of molecular spin crossover materials. In addition, I will also present our recent UV-broadband spectroscopy results on the ultrafast photoswitching of strongly-cooperative Fe-triazole nanoparticles as a function of particle size.