

thus bypassing the wavelength dependence of the Laue intensities. A monochromatic reference structure is then used to recover the 'light-on' intensities. Using polychromatic radiation time-resolution becomes limited only by the larger of the width of the synchrotron and laser pulses. In addition to allowing studies of much shorter-lived excited states, this should make it possible to monitor the initial steps of chemical reactions in solids. The suitability for this purpose of a number of solid-state reactions have been explored by steady state methods [1-3]. We find that trans-cis, cis-trans isomerizations and [2+2] cycloadditions in solids are highly stereospecific and activation-energy-controlled, so that their rate can be manipulated by adjustment of the temperature. A number of examples will be presented. Research supported by the US Department of Energy.

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Keywords: time-resolved diffraction, solid-state reaction, excited state geometry

MS.17.2

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Reactive crystalline molecular assemblies

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Effects of long-range molecular packing on solid-state structure are a nemesis of the crystal engineer. One way to circumvent effects of long-range packing so as to control the properties of organic solids is to centralize molecules within zero-dimensional (0D), or discrete, structures. A discrete assembly of molecules possesses a structure that is largely independent of crystal packing. This means that properties introduced by the components of a discrete system can, in principle, be modified in the wake of unpredictable effects of packing. In this presentation, we will describe an approach to engineer the formation of discrete molecular assemblies in the solid state. The components of the 0D structures undergo reactions in the solid state. The reactions of the components are accompanied by a number of movements (e.g. tilting, flipping) that, in some cases, proceed via single-crystal processes.

Keywords: crystal engineering, hydrogen bonds, reactivity

MS.17.3

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Vapor-induced transformation followed by luminescence switching for a dinuclear platinum(II) complex

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Vapochromism is one of the recent interesting topics for luminescent metal complexes. We have found that the crystalline sample of a

dinuclear platinum(II) complex, syn-[Pt₂(pyt)₂(bpy)₂](PF₆)₂ (pyt = pyridine-2-thiolate ion, bpy = 2,2'-bipyridine) exhibits a remarkable change in its luminescence by sensing organic vapors [1]. The light-red form with red luminescence converts to the "dark" dark-red form on exposure to acetonitrile and ethanol vapors, while the reverse change occurs in the presence of chloroform vapor. We have elucidated that the dynamic transformation of the molecular arrangement as the mechanism of the vapochromism. For the dark-red form including vapor molecules, the dinuclear complex units are arranged in a head-to-head manner with a short Pt...Pt distance. However, the arrangement is shifted drastically by the release of vapor molecules to form a ππ stack of bipyridine ligands for the light-red form. Thus it is concluded that the luminescence switching occurs by the change in the electronic Pt...Pt interaction between the dinuclear complexes.

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Keywords: platinum coordination compounds, luminescence, transformation

MS.17.4

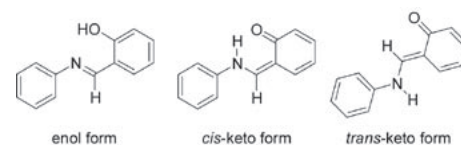
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Photochromism and thermochromism of crystalline salicylideneanilines

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Salicylideneaniline (SA) is one of the most well known families of photochromic and thermochromic compounds. The reversible color changes of the compounds take place in crystals and have been a subject of substantial interest. For the past 10 years we have studied the photo- and thermochromism of SAs in the solid state using X-ray diffraction analysis and variable-temperature diffuse reflectance spectroscopy. We have succeeded in providing a new framework of understanding the chromic phenomenon of crystalline SAs: The photochromism is due to the transformation between the enol and *trans*-keto forms. The thermochromism is mainly due to the temperature-induced change of fluorescence.



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Keywords: photochromism, tautomerism, fluorescence