Static and time-resolved photocrystallographic studies in supramolecular solids

Philip Coppens[*], Shao-Liang Zheng and Milan Gembicky

Chemistry Department, University at Buffalo, State University of New York, Buffalo, NY 14221, USA

Abstract. The supramolecular solid state is a medium *par excellence* for photochemical studies of molecules in a well-defined environment. If the photoactive molecule is embedded within a strong photochemically-inert framework, reactions can proceed without breakdown of the crystal lattice. A number of examples of *trans-cis* and *cis-trans* reactions are presented. A variable temperature study of Zn-coordinated tiglic acid shows that the reaction is energy-controlled with a small activation energy of $\sim$2 kJ/mol, dependent on the size of the cavity in which the molecule is located. Time-resolved studies of the instantaneous dimer-formation of an organic and an inorganic species are presented. The $Cu(I)(NH_3)_2$ cation forms a dimeric species with a contracted $Cu(I)-Cu(I)$ distance through promotion of an electron from an antibonding to a weakly bonding orbital, whereas xanthone forms an excimer with decrease interplanar spacing. The concept of the photodifference map is defined and used thoughout the article.

Introduction

Although the term photocrystallography was only coined in the late nineties (Coppens, 1997), the study of chemical processes in solids has a long and illustrious history. It was especially G. M. J. Schmidt at the Weizmann Institute of Science who realized almost 60 years ago that the then rapidly increasing power of X-ray crystallography should be used to learn more about chemical reactions in molecular crystals. The *topochemical postulate*, first proposed by Kohlshutter in 1918 (Kohlshutter, 1918), and systematically developed by Schmidt and coworkers with new insight on molecular packing from X-ray diffraction, states that chemical reactions in crystals proceed with a minimum amount of atomic motion (Cohen & Schmidt, 1964, Cohen *et al.*, 1964, Schmidt, 1964). Though exceptions have been found, it is clearly possible in many cases to predict the reaction that will occur from the crystal structure of the reactants.

Beyond the study of the topological requirements for reactions to occur and the nature of the reaction products, it is of great interest to know how a reaction proceeds, *i.e.* what are the intermediate states, even if short-lived, what is the rate of the reaction in the crystal, and how does the rate depend on temperature and on the size and nature of the reaction cavity. For such studies it is especially important that the crystal lattice retains its integrity during the course of the reaction, *i.e.* that a topotactic, single-crystal-to-single-crystal reaction occurs. Though the [2 + 2] cycloadditions that were studied in the early work invariably led to crystal breakdown when conversion percentages exceeded a few percent, it was discovered by Enkelmann and coworkers (Enkelmann *et al.*, 1994), and confirmed in subsequent work (Abdelmoty *et al.*, 2005), that irradiation in the tail of the absorption band can lead to preservation of crystal integrity during the reaction.

In this paper we will discuss an alternative approach that uses the versatility of co-crystals and especially supramolecular solids to achieve topotacticity and allows variation of the molecular environment.

Visualizing externally induced changes in crystals

In any study of chemical changes in crystals it is important to visualize the induced modifications of the molecular structure and orientation. When the crystalline lattice is preserved as in single-crystal-to-single-crystal (SCSC) reactions this can be achieved by applying the methods of charge density analysis. The electron density in the crystal both before and after the induced process has taken place can be obtained by conventional Fourier techniques. Initially phases of the reflections after reaction may be assumed as identical to those before reaction, an assumption of better validity in the case of centrosymmetric structures. For photo-induced processes a photodifference map is obtained as

$$\Delta\varrho(\boldsymbol{r}) = \varrho_{\text{exposed}}(\boldsymbol{r}) - \varrho_{\text{initial}}(\boldsymbol{r}) = \frac{1}{V}$$
$$\times \sum \left[F_{\text{exposed}}(\boldsymbol{H}) \exp i\phi_{\text{exposed}} - F_{\text{initial}}(\boldsymbol{H}) \exp i\phi_{\text{initial}} \right]$$
$$\times \exp - 2\pi \boldsymbol{H} \cdot \boldsymbol{r} \tag{1}$$

---

* Correspondence author (e-mail: coppens@buffalo.edu)

in which $\varrho(\mathbf{r})$ represents the electron density at the point $\mathbf{r}$, F the amplitude of a reflection and Φ its phase, and $\mathbf{H}$ the corresponding reciprocal space vector. Subsequent least-squares refinement will be based on the photo-induced peaks identified in the difference maps. If the phases Φ of the reflections change significantly in the subsequent refinement of the exposed structure, (1) must be recalculated with the new phases and the process iterated until convergence. This is usually not a problem for centrosymmetric crystals but must be considered in the acentric case. Equation (1) must be modified if the volume V of the unit cell changes appreciably on exposure, which is generally not the case for solids in which the photoactive molecules are embedded in a strong host framework. Examples of photodifference maps are given in Figs. 2 and 7 for a photo-induced chemical reaction and a photo-excitation respectively.

Supramolecular solids

Solid-state dilution and photo-physical properties

Supramolecular solids are an unusually suitable medium for the study of photo-chemical processes in solids. Unlike rigid glasses used in conventional spectroscopy for this purpose, they allow molecular dilution of the photo-active components with retention of three-dimensional periodicity. As structural stability is provided by the inert components, they are much less subject to crystal breakdown than neat crystals. They are also very versatile, in the sense that a photo-active molecule can be embedded in a great many different matrices. In ten different supramolecular solids with benzophenone (BZP) (Ma *et al.*, 2001; Ma & Coppens, 2004) and seven with benzil (BZ) (Ma & Coppens, 2003; Ma *et al.*, 2004; Zheng & Coppens, 2005c) as guests, the guest concentration was reduced from typically 6 mol/L in the neat crystals to 1–1.5 mol/L and in one case to 0.6 mol/L. However, although the neat crystals of both BZ and BZP tend to be highly luminescent, none of these supramolecular phases is a strong light emitter. This is attributed to efficient energy transfer from the excited state to the molecular environment. In general such quenching can also be due to electron transfer, in which case a color change is often observed. Energy transfer is related to the relative spacing of the energy levels of the host-framework and the guest molecules, and can be minimized by raising the Excited State-Ground State energy gap of the framework molecules (Zheng & Coppens, 2005b). This is experimentally confirmed by a subsequent study of eight different three-dimensional anionic frameworks incorporating the $[\text{Cu(dmp)}_2]^+$ photosensitizer cation (Zheng *et al.*, 2006). A large variation in the emission lifetime of the cation in the series correlates with the relative energy-level spacings of the guest- and host-framework components as obtained from theory, culminating in a value for the 1,3,5-cyclohexanetricarboxylic acid inclusion compound that exceeds that of the $[\text{Cu(dmp)}_2]^+$ cation in its conventional salts. Clearly, the photophysical properties of the guest molecules can be manipulated by variation of the molecular environment, a conclusion of prime interest for the design of highly luminescent solids.

Co-crystals and framework solids

We will distinguish here between co-crystals and framework solids (Herbstein, 2005). In the former, for a crystal with components A and B, A−B interactions are dominant, whereas in the latter A−A interactions give rise to a framework with cavities in which the B molecules can be located. In the latter A−B interactions play a less dominant role, although the nature of the framework may be determined by the templating effect of the B species (Herbstein, 2005). In co-crystals with a major ditopic component, with two adjacent functional groups, templating can serve to bring two reactant molecules in close proximity in a geometry suitable for a bimolecular reaction to occur (Toda & Bishop, 2004). Examples are provided by MacGillivray and coworkers, with templating achieved by diols like resorcinol and metal coordination (Georgiev & MacGillivray, 2007). Toda *et al.* have used diols such as 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol and derivatives as templates for enantioselective [2 + 2] dimerization of coumarin, thiocoumarin and cyclohex-2-enone (Tanaka *et al.*, 2000; Toda, 2001). Using the same diol, Kaftory and coworkers achieved highly stereospecific [2 + 2] and [4 + 4] additions in the solid state (Zouev *et al.*, 2006), including a case in which contraction of the lattice during the reaction leads to the absorption of water molecules (Lavy & Kaftory, 2007). Other examples include the [2 + 2] cyclodimerizations of 4,4′-bis-pyridylethylene and analogues (Chu *et al.*, 2005; Friscic *et al.*, 2004; Friscic & MacGillivray, 2005; MacGillivray *et al.*, 2005; Papaefstathiou *et al.*, 2004) and larger homologues, some leading to the formation of unique ladder compounds (Gao *et al.*, 2003).

Isomerization reactions in supra-molecular frameworks

Tiglic acid in two structural arrangements

The $E \rightarrow Z$ photoisomerization of tiglic acid in CECR · HTA · 2 MeOH · 1.5 H$_2$O (**1**) (HTA = tiglic acid, CECR = *C*-ethylcalix[4]resorcinarene) is an example of a SCSC isomerization reaction in a supramolecular framework (Fig. 1).
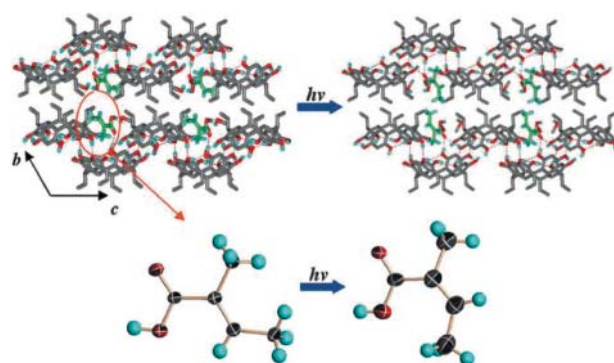

Fig. 1. Three-dimensional supramolecular architecture of CECR · HTA · 2 MeOH · 1.5 H$_2$O viewed along the *a*-axis direction (top) and and perspective views showing 50% probability displacement ellipsoids of the *E* molecule before exposure and the *Z* molecules after 3 h exposure (bottom) (Zheng, Messerschmidt *et al.*, 2007a).
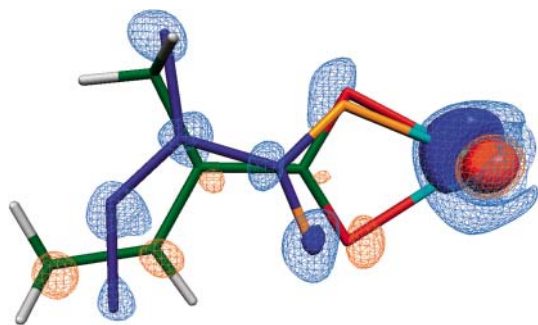
Fig. 2. Photodifference map of tiglic acid in the small cavity in CECR · [Zn(TA)₂(H₂O)₂] · 4 H₂O after 2 hours exposure. Note the displacement of the Zn atom and its changing coordination. Blue: 2.0, light blue: 1.0, orange: −1.0, red: −2.0 eÅ⁻³ (Zheng *et al.*, 2007d).

It proceeds with preservation of the crystal lattice, indicating the 'scaffolding effect' of the molecular framework, which holds the crystal together notwithstanding the change in shape of the embedded guest molecules. In the reaction a photostationary state is reached at a concentration of ca. 30% of the *Z* isomers. Analysis of the isomeric composition from diffraction data after 1, 3, 6 and 12 hour exposure shows the reaction to closely follow first order kinetics, as may be expected, with the $Z \rightarrow E$ back-reaction proceeding with a larger rate constant than the $E \rightarrow Z$ forward isomerization (Zheng *et al.*, 2007a).

More insight into the isomerization of tiglic acid is provided by the study of the Zn-coordinated tiglic acid anion (TA) in CECR · [Zn(TA)₂(H₂O)₂] · 4 H₂O (**2**) (Zheng *et al.* 2007d). It is noteworthy that in both structures the [2 + 2] cycloaddition is suppressed as the molecules are isolated in (**1**), and arranged non-parallel in (**2**). In the precursor crystal the Zn is five-coordinate. The two coordinated TA are located in cavities of very different size, the smaller and the larger cavity having volumes of 92.6 and 153.8 Å³ respectively, offering the opportunity to examine the environment-dependence of the reaction rates. The 2-hr-exposure photodifference map for the molecule in the small cavity is shown in Fig. 2. A reduction in the coordination of the Zn atom (from 5 to 4-fold) on exposure is evident, as are shifts of both the tiglate ligand and the Zn atom. It is noteworthy that the volume of the small cavity increases from 92.6 to 111.7 Å³ as a result of the *E* to *Z* isomerization, whereas the volume increase of the large cavity is limited to 4 Å³, indicating the presence of steric restrictions in the former case. In a first quantitative study of a solid-state reaction in a supramolecular crystal the reaction rate was determined at a series of temperatures at four different time points after its initiation. The results are presented in Fig. 3. As is clear from the curves, the reaction is indeed faster in the larger cavity, and its rate is limited by the occurrence of an activation barrier. The first order rate constants for both the forward and the backward reaction can be derived from the conversion percentages combined with the composition of the photostationary state. Arrhenius plots of the temperature dependence of the rates indeed show the activation energy to be larger for the reaction in the small cavity than for the large cavity, the two values being 2.3(3) and 1.8(1) kJ/mol for the forward reaction in the two cases respectively, and 2.1(2) and
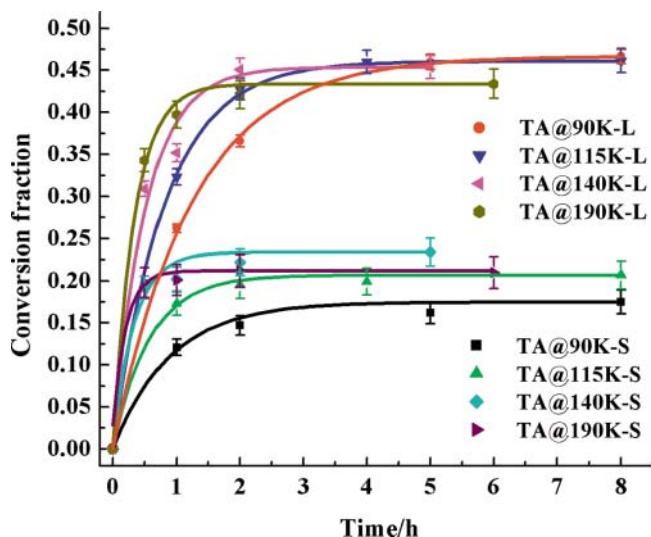

Fig. 3. Conversion fractions of Zn-coordinated TA molecules in the small (S) and large (L) cavities in CECR · [Zn(TA)₂(H₂O)₂] · 4 H₂O as a function of irradiation time at different temperatures (Permission requested Copyright 2007 Wiley-VCH) (Zheng *et al.*, 2007c).

1.9(1) kJ/mole for the *Z* to *E* isomerizations in the same cavities. Though the differences in activation energy are relatively small, they have a significant effect on the temperature dependence of the reaction rates, as is evident from Fig. 3. The nature of the activation barrier is envisioned in Fig. 4 (adopted from Lewis, Lewis *et al.*, 1994) as due to an intermediate state on the path between the Frank-Condon excited state structure and the conical intersection of the potential surfaces (Martinez, 2006). The activation energies are considerable lower than values obtained by Lewis *et al.* for isomerization with a singlet intermediate state. Activation energies of ∼35 kJ/mol as measured by Lewis *et al.* for the *E* to *Z* isomerization of phenylpropene in hexane solution would not allow the reaction to preceed perceptibly at the low temperatures at which the diffraction experiments have been conducted. This suggests that a triplet pathway, for which activation
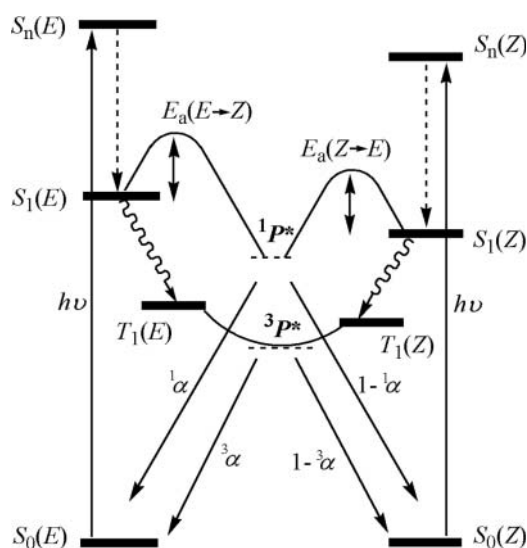

Fig. 4. Schematic energy level diagram for $E \rightarrow Z$ and $Z \rightarrow E$ isomerizations (modified from and reproduced with permission from J. Am. Chem. Soc. **116** (1994) 10477−10485. Copyright 1994 American Chemical Society).

energies are much lower, is involved at reduced temperatures in the supramolecular solid. A contribution to the activation energy from the interaction with the walls of the reaction cavity seems likely.

3-chloroacrylic acid: approaching the photostationary state from two directions

A third study on 3-chloroacrylic acid (HClA) embedded in CECR · HClA · 2 MeOH · 1.5 H$_2$O, similarly shows an SCSC reaction (Zheng *et al.*, 2007b). It is of particular interest since in this case the reaction can be approached from both sides, as both the *E* and the *Z* inclusion solids can be synthesized. The reactions are again first order, but, interestingly, both the *Z* to *E* and the *E* to *Z* reactions are faster in the *Z* inclusion complex, in which a 50% stationary state is reached, whereas in the photostationary state of the *E*-complex the *E* structure is favored (Fig. 5).

The ability to monitor chemical reactions of molecules confined within an inert periodic framework is of particular importance for the field of ultrafast time-resolved diffraction as it indicates that elucidation of the mechanism of chemical reactions with pump-probe techniques may be within our reach.

Excited state diffraction with supramolecular solids

Though the X-ray diffraction produces a time (and space) averaged image of the diffracting crystal, the advent of high brilliance pulsed sources, such as synchrotrons, and area detectors has made it possible to greatly reduce the time over which the image is averaged. Many reactions of interest can be sharply triggered by photon-exposure, accordingly laser-pump/X-ray probe techniques have been developed, and applied with spectacular success in macromolecular crystallography (Anderson *et al.*, 2004; Aranda *et al.*, 2006; Bourgeois *et al.*, 2006; Schotte *et al.*, 2003). For smaller complexes higher spatial resolution can be achieved (Coppens *et al.*, 2005; Guerin *et al.*, 2004).
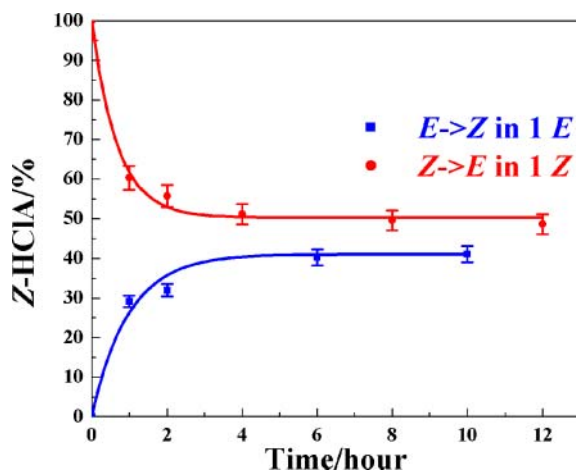
Supramolecular solids are a relatively unexplored terrain in this respect, but they have the advantage of molecular dilution, of the ability to study the excitation in different environments and of providing an inert framework that can act as a scaffold and maintain the integrity of the crystal during the photo-induced process. In some cases otherwise unstable species can be encapsulated in the cavities of the framework and be subjected to identification and analysis (Zheng & Coppens, 2005a; Zheng *et al.*, 2005; Zheng *et al.*, 2007c). Negative factors which must be avoided are that crystal quality is frequently insufficient and that energy or electron transfer to the 'inert' components can drastically shorten the lifetime of the excited state and even lead to full quenching of the emission, as described above for several cases. Selection of strongly hydrogen-bonded frameworks composed of maximally saturated components can alleviate such problems. We have completed two such studies which are described in the following.

The [Cu(NH$_3$)$_2$]$_2^{2+}$ dimer in a strongly hydrogen-bonded framework

As shown by Carvajal *et al.* (2004) the dimeric species [Cu(NH$_3$)$_2$]$_2^{2+}$ does not show a local energy minimum as a function of Cu(I)−Cu(I) distance, and thus is not a stable species. Nevertheless, it can be isolated within an anionic framework of H$_2$THPE$^-$ molecules (H$_2$THPE$^-$ = the monoanion of tris (hydroxyphenyl)ethane) to give a solid of composition [Cu(NH$_3$)$_2$]$_2$[H$_2$THPE]$_2$ · 3.25 H$_2$O (Fig. 6) (Zheng *et al.*, 2005d). The dimeric species is stabilized by the hydrogen bonding to the host lattice, creating a 'cage effect' by which the unstable species is captured by the electrostatic bonding. Its triplet excited-state has a lifetime of 52 µs at 17 K. The time-resolved experiment was conducted with the monochromatic technique using a 16.5 µs shutter opening and 355 nm laser light pulses at the rapid repetition rate of 15 000 Hz, produced by a Nd-vanadate laser. The photodifference map, shown in Fig. 7, indicates depletion at the Cu-position and a peak of 7 eÅ^3 displaced

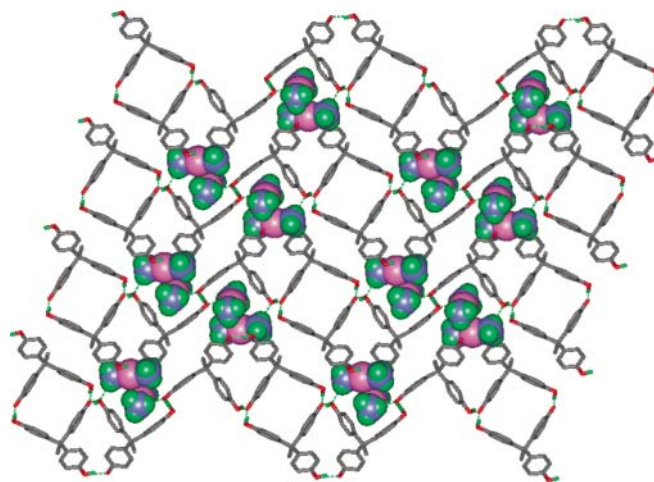**Fig. 5.** Percentage of Z-chloroacrylic acid in the CECR host-guest complex as a function of irradiation time (Reproduced with permission from Chem. Comm. (2007b) 2735–2737. Copyright 2007 Royal Society of Chemistry).

Fig. 6. Three-dimensional supramolecular architecture of [Cu(NH$_3$)$_2$]$_2$ · [H$_2$THPE]$_2$ · 3.25 H$_2$O viewed along the a axis. The water molecules are located in the square-shaped channels. (Reproduced with permission from CrystEngComm **8** (2006) 735–741. Copyright 2006 Royal Society of Chemistry).
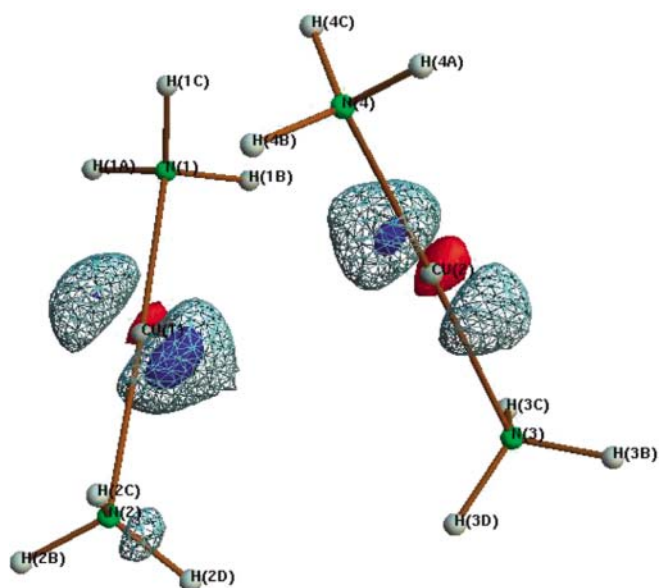
Fig. 7. Time-resolved photodifference map for the $[Cu(NH_3)_2]_2^{2+}$ ion in $[Cu(NH_3)_2]_2[H_2THPE]_2 \cdot 3.25 \ H_2O$. Blue: 7 e/Å^{-3}, Gray: 2 e/Å^{-3}, Red: -3 eÅ^{-3}

Fig. 9. Three-dimensional supramolecular architecture of HECR · 2 xanthone · 6 MeOH, containing dimeric xanthone, viewed along the *c* axis. Methanol molecules are omitted for clarity. (Reproduced with permission from CrystEngComm **8** (2006) 735–741. Copyright 2006 Royal Society of Chemistry).

from the ground-state Cu position in a direction approximately, but not exactly towards the neighboring Cu atom. This corresponds to a shortening of the Cu(I)–Cu(I) bond and an accompanying rotation of $\sim 7°$ of the cation on excitation, a result confirmed by the subsequent least-squares refinement. The refinement is performed with the program Laser5, which minimizes the differences between the observed and calculated fractional changes in the intensities on illumination. The Cu–Cu distance shortens from 3.025(1) to 2.72(1) Å on excitation, compared with 2.60 Å according to theory. As in other binuclear complexes studied by us (Coppens *et al.*, 2004; Coppens *et al.*, 2005; Novozhilova *et al.*, 2003), the shortening is due to the promotion of an anti-bonding electron from a full shell, to a weakly bonding orbital, in this case $4p_\sigma$, as illustrated in the HOMO and LUMO diagrams in Fig. 8.

A xanthone excimer embedded in a supramolecular framework

Excimer formation of aromatic molecules has received considerable attention in the past decades (see for example East & Lim, 2000; Lim, 1987), but experimental information on the structure of the excited dimers, in which intermolecular
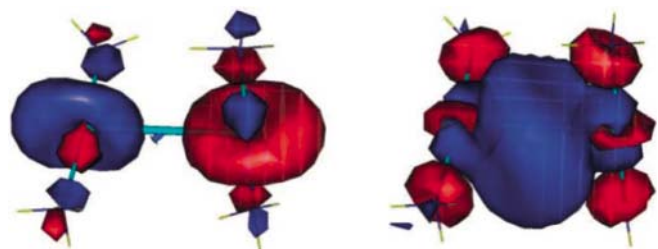
bonding is enhanced, has not been available. To explore the potential of time-resolved diffraction we have synthesized a supramolecular solid in which two molecules of xanthone form a dimer in a host lattice of HECR · 2 xanthone · 6 MeOH (HECR = hexaethylresorcin[6]arene) (Fig. 9). The molecular dilution is pronounced, the xanthone concentration being 1.752 mol/L, compared with 7.106 mol/L in neat xanthone crystals.

Like benzil and benzophenone, xanthone has a long-lived excited triplet state. At all but the very lowest temperatures xanthone emits from the $T_2(n, \pi^*)$ excited state (Connors & Christian, 1982; Vala *et al.*, 1981). The 17 K lifetimes for a xanthone monomer in CECR · xanthone · MeOH and the dimer in HECR · 2 xanthone · 6 MeOH are 0.22 and 5.56 μs, respectively, compared with 887 μs for neat xanthone crystals, indicating significant luminescence quenching in both solids, but less for the dimer. The luminescence maximum of xanthone in the monomer supramolecular solid occurs at ca. 420 nm, while the emission maximum of the xanthone dimer occurs at 460 nm, in agreement with the red-shifts commonly found in the luminescence spectra of excimers in solution, and supported by our calculations of the energy level spacings. The stroboscopic time-resolved experiments on

Fig. 8. Antibonding HOMO (left) and bonding LUMO (right) of the $[Cu(NH_3)_2]^{2+}$ ion. Surfaces at $+0.04$ and -0.04 a. u. (Reproduced with permission from CrystEngComm **8** (2006) 735–741. Copyright 2006 Royal Society of Chemistry).
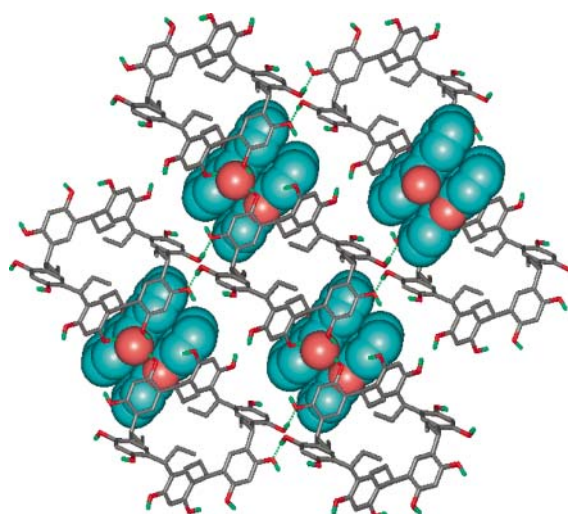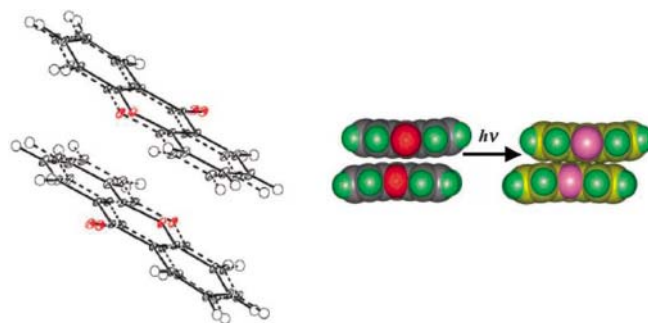

Fig. 10. Instantaneous contraction of the xanthone dimer on excitation (left: full lines, ground state; dotted lines excimer) (Reproduced with permission from CrystEngComm **8** (2006) 735–741. Copyright 2006 Royal Society of Chemistry).

were performed with a 10 kHz, 355 nm laser/X-ray pulse repeat frequency. Photodifference maps show a contraction of the interplanar distance, quantified as 0.26(3) Å (from 3.41 to 3.15 Å) by the least-squares refinement. The contraction is accompanied by a lateral relative shift of the molecular planes by 0.24 Å (Fig. 10). The excimer thus has the conrotated structure discussed by East and Lim for the naphtalene dimers (East & Lim, 2000). This is not surprising as configurations such as the disrotated and T-shaped comformations require much larger rearrangements which would be inhibited in the confined space in the crystal. The experiment is supported by a theoretical calculation (MP2/6–31G**) which gives the interplanar distance in the optimized geometry of the triplet dimer as $\sim$3.144 Å.

The relative excited state populations achieved in two successive experiments are 8% and 13%, the second obtained with increased power in the laser beam. This is larger than 3–6% excited-state populations achieved in the experiments with neat crystals, a result attributed to the improved ratio between incident photons and photoactive molecules in the supramolecular crystals and to the increased light penetration in a more dilute system.

Concluding remarks

The supramolecular solid state introduces a new medium for photocrystallographic experiments, that has only cursorily been exploited so far. This is of particular interest, as the variety of multicomponent systems that can be synthesized is practically unlimited. Only the tip of the iceberg has been touched. Much further progress may be expected in photocrystallography in supramolecular crystals, a field that combines synthesis, crystallography, spectroscopy with other chemical and physical disciplines.

References

Abdelmoty, I.; Buchholz, V.; Di, L.; Guo, C.; Kowitz, K.; Enkelmann, V.; Wegner, G.; Foxman, B. M.: Polymorphism of Cinnamic and α-Truxillic Acids: New Additions to an Old Story. Cryst. Growth Des. **5** (2005) 2210–2217.

Anderson, S.; Srajer, V.; Pahl, R.; Rajagopal, S.; Schotte, F.; Anfinrud, P.; Wulff, M.; Moffat, K.: Chromophore Conformation and the Evolution of Tertiary Structural Changes in Photoactive Yellow Protein Structure. **12** (2004) 1039–1045.

Aranda, R. I. V.; Levin, E. J.; Schotte, F.; Anfinrud, P. A.; Phillips, G. N., Jr.: Time-dependent atomic coordinates for the dissociation of carbon monoxide from myoglobin. Acta Crystallogr. D**62** (2006) 776–783.

Bourgeois, D.; Vallone, B.; Arcovito, A.; Sciara, G.; Schotte, F.; Anfinrud, P. A.; Brunori, M.: Extended subnanosecond structural dynamics of myoglobin revealed by Laue crystallography. Proc. Natl. Acad. Sci. **103** (2006) 4924–4929.

Carvajal, M. A.; Alvarez, S.; Novoa, J. J.: The nature of intermolecular CuI . . . CuI interactions: A combined theoretical and structural database analysis. Chem. Eur. J. **10** (2004) 2117–2132.

Chu, Q.; Swenson, D. C.; MacGillivray, L. R.: A Single-Crystal-to-Single-Crystal Transformation Mediated by Argentophilic Forces Converts a Finite Metal Complex into an Infinite Coordination Network. Angew. Chem. Int. Ed. **44** (2005) 3569–3572.

Cohen, M. D.; Schmidt, G. M. J.: Topochemistry. I. A survey J. Chem. Soc. (1964) 1996–2000.

Cohen, M. D.; Schmidt, G. M. J.; Sonntag, F. I.: Topochemistry. II. The photochemistry of trans-cinnamic acids. J. Chem. Soc. (1964) 2000–2013.

Connors, R. E.; Christian, W. R.: Origin of the unusual triplet-state properties of xanthones. J. Phys. Chem. **86** (1982) 1524–1528.

Coppens, P.: Time-resolved diffraction in chemistry and materials science: The developing field of photocrystallography. Synchrotron Radiation News **10** (1997) 26–30.

Coppens, P.; Gerlits, O.; Vorontsov, I. I.; Kovalevsky, A. Y.; Chen, Y.-S.; Graber, T.; Novozhilova, I. V.: A very large Rh–Rh bond shortening on excitation of the [Rh$_2$(1,8-diisocyano-p-menthane)$_4$]$^{2+}$ ion by time-resolved synchrotron X-ray diffraction. Chem. Comm. (2004) 2144–2145.

Coppens, P.; Vorontsov, I. I.; Graber, T.; Gembicky, M.; Kovalevsky, A. Y.: The structure of short-lived excited states of molecular complexes by time-resolved X-ray diffraction. Acta Cryst. A**61** (2005) 162–172.

Coppens, P.; Zheng, S.-L.; Gembicky, M.; Messerschmidt, M.; Dominiak, P. M.: Supramolecular solids and time-resolved diffraction CrystEngComm **8** (2006) 735–741.

East, A. L. L.; Lim, E. C.: Naphthalene dimer: Electronic states, excimers, and triplet decay. J. Chem. Phys. **113** (2000) 8981–8994.

Enkelmann, V.; Wegner, G.; Novak, K.; Wagener, K. B.: Crystal-to-crystal photodimerizations. Mol. Cryst. Liq. Cryst. A**240** (1994) 121–126.

Friscic, T.; Drab, D. M.; MacGillivray, L. R.: A Test for Homology: Photoactive Crystalline Assemblies Involving Linear Templates Based on a Homologous Series of Phloroglucinols. Org. Lett. **6** (2004) 4647–4650.

Friscic, T.; MacGillivray, L. R.: Single-crystal-to-single-crystal [2 + 2] photodimerizations: From discovery to design. Z. Kristallogr. **220** (2005) 351–363.

Gao, X.; Friscic, T.; MacGillivray, L. R.: Supramolecular construction of molecular ladders in the solid state. Angew. Chem. Int. Ed. **43** (2003) 232–236.

Guerin, L.; Collet, E.; Lemee-Cailleau, M.-H.; Cointe, M. B.-L.; Cailleau, H.; Plech, A.; Wulff, M.; Koshihara, S.-Y.; Luty, T.: Probing photoinduced phase transition in a charge-transfer molecular crystal by 100 picosecond X-ray diffraction. Chem. Phys. **299** (2004) 163–170.

Herbstein, F. H.: Crystalline Molecular Complexes and Compounds, Vol 1. (2005). Oxford University Press, Oxford, UK.

Kohlshutter, H. W.: Zur Kenntnis des Graphitischen Kohlenstoffs und der Graphitsäure. Anorg. Allg. Chem. **105** (1919) 121–144.

Lavy, T.; Kaftory, M.: Channels formation through photodimerization of guest molecules within solid inclusion compounds. CrystEngComm **9** (2007) 123–127.

Lewis, F. D.; Bassani, D. M.; Caldwell, R. A.; Unett, D. J.: Singlet State Cis, Trans Photoisomerization and Intersystem Crossing of 1-Arylpropenes. J. Am. Chem. Soc. **116** (1994) 10477–10485.

Lim, E. C.: Molecular Triplet Excimers. Acc. Chem. Res. **20** (1987) 8–17.

Ma, B.-Q.; Coppens, P.: Multiple conformation of benzil in resorcinarene-based supramolecular host matrices. J. Org. Chem. **68** (2003) 9467–9472.

Ma, B.-Q.; Ferreira, L. F. V.; Coppens, P.: Structure and photoluminescence of a benzil nanocolumn in a C-methylcalix[4]resorcinarene-based framework. Org. Lett. **6** (2004) 1087–1090.

Ma, B.-Q.; Zhang, Y.; Coppens, P.: Multiple structures in supramolecular solids: benzophenone embedded in three different methylcalix[4]resorcinarene/bipyridine frameworks. Crystal Growth and Design **1** (2001) 271–275.

Ma, B.; Coppens, P.: Variable conformation of benzophenone in a series of resorcinarene-based supramolecular frameworks. Crystal Growth & Design **4** (2004) 1377–1385.

MacGillivray, L. R.; Papaefstathiou, G. S. M.; Friscic, T.; Varshney, D. B.; Hamilton, T. D.: Template-controlled synthesis in the solid-stat.e Top. Curr. Chem. **248** (2005) 201–221.

Martinez, T. J.: Insights for Light-Driven Molecular Devices from Ab Initio Multiple Spawning Excited-State Dynamics of Organic and Biological Chromophores. Acc. Chem. Res. **39** (2006) 119–126.

Novozhilova, I.; Volkov, A. V.; Coppens, P.: Theoretical analysis of the triplet excited state of the $[Pt_2(H_2P_2O_5)_4]^{4-}$ ion and comparison with time-resolved X-ray and spectroscopic results. J. Am. Chem. Soc. **125** (2003) 1079–1087.

Papaefstathiou, G. S.; Zhong, Z.; Geng, L.; MacGillivray, L. R.: Co-ordination-Driven Self-Assembly Directs a Single-Crystal-to-Single-Crystal Transformation that Exhibits Photocontrolled Fluorescence. J. Am. Chem. Soc. **126** (2004) 9158–9159.

Schmidt, G. M. J.: Topochemistry. III. The crystal chemistry of some trans-cinnamic acids. J. Chem. Soc. (1964) 2014–2021.

Schotte, F.; Lim, M.; Jackson, T. A.; Smirnov, A. V.; Soman, J.; Olson, J. S.; Phillips, G. N. Jr.; Wulff, M.; Anfinrud, P. A.: Watching a Protein as it Functions with 150-ps Time-Resolved X-ray Crystallography. Science **300** (2003) 1944–1947.

Tanaka, K.; Mochizuki, E.; Yasui, N.; Kai, Y.; Miyahara, I.; Hirotsuc, K.; Toda, F.: Single-Crystal-to-Single-Crystal Enantioselective [212] Photodimerization of Coumarin, Thiocoumarin and Cyclohex-2-enone in the Inclusion Complexes with Chiral Host Compounds. Tetrahedron **56** (2000) 6853–6865.

Toda, F.: Crystalline Inclusion Complexes as Media of Molecular Recognitions and Selective Reactions. Aust. J. Chem. **54** (2001) 573–582.

Toda, F.; Bishop, R. (Eds.): Separations and Reactions in Organic Supramolecular Chemistry. West Sussex, England: John Wiley & Sons, (2004).

Vala, M.; Hurst, J.; Trabjerg, I.: Temperature dependence of the dual phosphorescence from xanthone in n-hexane matrixes. Mol. Phys. **43** (1981) 1219–1234.

Zheng, S.-L.; Coppens, P.: Syntheses, structures, photoluminescence and theoretical studies of xanthone in crystalline resorcinarene-based inclusion complexes Chem. Eur. J. **11** (2005a) 3583–3590.

Zheng, S.-L.; Coppens, P.: Luminescence quenching and energy transfer in supramolecular solids. Crystal Growth & Design **5** (2005b) 2050–2059.

Zheng, S.-L.; Coppens, P.: Emission quenching of photoactive molecules embedded in supramolecular solids: Synthesis, structure and photoluminescence studies of benzil in a CMCR-based inclusion complex with a saturated linker molecule. CrystEngComm **7** (2005c) 289–293.

Zheng, S.-L.; Gembicky, M.; Messerschmidt, M.; Dominiak, P. M.; Coppens, P.: The effect of the environment on molecular properties: synthesis, structure, and photoluminescence of Cu(I) Bis(2,9-dimethyl-1,10-phenanthroline) nano-clusters in eight different supramolecular frameworks. Inorg. Chem. **45** (2006) 9281–9289.

Zheng, S.-L.; Messerschmidt, M.; Coppens, P.: An unstable ligand-unsupported copper(i) dimer stabilized in a supramolecular framework. Angew. Chem. Int. Ed. **44** (2005) 4614–4617.

Zheng, S.-L.; Messerschmidt, M.; Coppens, P.: Single-crystal-to-single-crystal E to Z isomerization of tiglic acid in a supramolecular framework. Acta Cryst. B**63** (2007a) 644–649.

Zheng, S.-L.; Messerschmidt, M.; Coppens, P.: Single-crystal-to-single-crystal $E \rightarrow Z$ and $Z \rightarrow E$ isomerizations of 3-chloro-acrylic acid within the nanocavities of a supramolecular framework. Chem. Comm. (2007b) 2735–2737.

Zheng, S.-L.; Volkov, A.; Nygren, C. L.; Coppens, P.: The nature of the Ag(I)Ag(I) interaction in different $Ag(NH_3)_2$ dimers embedded in supramolecular solids. Chem. Eur. J. **13** (2007c) 8583–8590.

Zouev, I.; Lavy, T.; Kaftory, M.: Solid-State Photodimerization of Guest Molecules in Inclusion Compounds. Eur. J. Org. Chem. (2006) 4164–4169.