Supramolecular solids and time-resolved diffraction

Philip Coppens,* Shao-Liang Zheng, Milan Gembicky, Marc Messerschmidt and Paulina M. Dominiak

DOI: 10.1039/b610286g

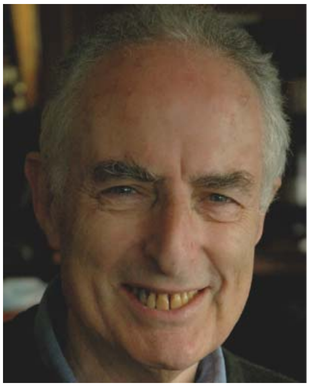
Supramolecular solids are an ideal medium for time-resolved diffraction studies at atomic resolution as they allow dilution of the active species, and the study of a species in different states of aggregation and different environments, but attention must be paid to excited-state quenching due to energy transfer. Crystallinity must be preserved up to reasonable product concentrations if chemical reactions are to be monitored at the atomic level.

1. Introduction

The development of the supramolecular solids state is providing access to a very large range of novel phases which are not only pleasing because of the beautiful molecular architectures they represent, but also they present new horizons in solid state chemistry and in the use of the molecular solid state for practical applications. While hundreds of thousands of crystal structures of neat crystals and their polymorphs and pseudopolymorphs have been determined, the advance to solids with two, three and more components, made possible by the dramatic growth in power of crystallographic methods, corresponds to an exponential increase in the number of accessible solids. As the principles of crystal structure engineering are becoming better understood, the challenge is to

Milan Gembicky

Milan Gembicky studied chemistry at Slovak Technical University in Bratislava, receiving his MS in 1998 and his PhD in Inorganic Chemistry in 2001. After a short industrial experience, he joined Professor Coppens lab as Postdoctoral Fellow in 2002. He has been involved in synthetic, and spectroscopic work as well as in development of instrumentation for time-resolved X-ray diffraction.



Philip Coppens

Philip Coppens received his Ph.D. from the University of Amsterdam and has since been employed at the Weizmann Institute of Science, Brookhaven National Laboratory and the State University of New York at Buffalo, where he is currently Distinguished Professor of Chemistry. He is a Corresponding Member of the Royal Dutch Academy of Sciences and a Doctor Honoris Causa of the University of Nancy, France. He served as President of the International Union of Crystallography from 1993–1996. Among his awards are the Gregori Aminoff Prize of the Royal Swedish Academy of Sciences, the Martin Buerger Award of the American Crystallographic Association and the 2006 Ewald Prize of the International Union of Crystallography. His research interests include X-ray charge density analysis, photocrystallography, the study of light-induced metastable and transient species in crystals, the latter by time-resolved X-ray diffraction, and the interpretation of experimental results by theoretical methods.

Shao-Liang Zheng

Shao-Liang Zheng was born in 1974 in Guangdong, China. He earned his Ph.D. degree under the supervision of Xiao-Ming Chen at Sun Yat-Sen University in 2003, where he worked on d^{10} metal coordination complexes and polymers, then joined Philp Coppens's group at the State University of New York at Buffalo as a Postdoctoral Associate. His current interest is in time-resolved photocrystallographic studies of host–guest crystals.

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000, USA. E-mail: coppens@buffalo.edu

exploit the new phases in the broadest sense possible.[1] This includes gas storage applications,[2,3] chiral separation,[4] optical and photophysical properties, and chemical reactions in dilute but fully 3-D periodic systems. Application of molecular solids in the study of bimolecular reactions was initiated in the 1960's by Schmidt and coworkers.[5]

We will distinguish between co-crystals, in which the molecular components fulfil structurally equivalent roles, and host–guest solids in which the structural integrity is essentially provided by a framework of host molecules, with the guests being embedded in cavities within the host framework. In the latter class we include 3-D framework crystals in which the guests are embedded between layers of host molecules, as occurs, for example, in some CMCR†-based solids. This highlight will focus on host–guest systems formed by a selection of organic node and linker molecules, and their application in the study of the influence of the crystal matrix on physical properties of the guest and in time-resolved X-ray diffraction studies of chemical processes in solids.

2. Time-resolved diffraction

Though the X-ray scattering process is a very fast process that occurs on a time-scale of $\sim 10^{-18}$ s, data collection is much slower, therefore the resulting image corresponds to a time (and space) average over the diffracting crystal. But with the increasing intensity and brightness of the now available sources, diffraction patterns can be measured on ever shorter time scales, so that the averaging is over a shorter and shorter time interval. This fundamental advance has opened up the field of time-resolved (TR) diffraction, thereby extending the field into an area of great importance in the natural sciences, including rapid dynamical processes in chemistry and biology.

An important distinction in TR diffraction is between reversible processes with a rapid relaxation back to the initial state such as molecular excitation, and irreversible processes like photo-initiated chemical reactions which proceed to a final stage once triggered. The former can be initiated repeatedly at very high repeat rates and examined stroboscopically, while the latter require a series of snapshots along the reaction path. Since detectors are currently not fast enough to allow very short time intervals between measurements, the study of irreversible processes requires a large number of samples or, if possible, one large sample that can be moved rapidly to allow exposure of different areas of the same crystal. Though in recent studies several reactions have been monitored as the reaction proceeds in the crystal,[6–8] in only a few cases has the study of reaction mechanism on a time-scale of picoseconds been attempted.[9] The latter class is clearly much more demanding experimentally and has not been achieved as yet for chemical reactions in solids at atomic resolution.

For μs-timescale reversible processes stroboscopic monochromatic techniques have been employed.[10] However for shorter time-scales and irreversible processes it is necessary to make a more efficient use of the synchrotron photons by utilizing a wider energy bandpass, and using polychromatic Laue methods which allow simultaneous recording of many reflections.[11–13]

3. Supramolecular solids for time-resolved diffraction

3.1 General considerations

Our time-resolved studies on neat crystals have been summarized elsewhere.[10] The last one of this series, on the long-lifetime luminescent state of $\{[3,5\text{-}(CF_3)_2\text{pyrazolate}]Cu\}_3$,[14] is unique among the compounds studied as it concerns an inter- rather than an intramolecular excitation. On excitation a weak instantaneous Cu^I–Cu^I bond is formed between adjacent molecules in a stack. It is noteworthy that the bond is not between the two molecules with the shortest ground-state spacing, but rather between two molecules with a somewhat

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† Abbreviations used in this article: ACA = apocholic acid; BIMB = 1,4′-bis(imidazol-1-yl-methyl)benzene; BPE = *trans*-1,4-bis(pyridyl)ethylene; BPMH = bis-(1-pyridin-4-yl-methylidene)-hydrazine; BPEH = bis-(1-pyridin-4-yl-ethylidene)-hydrazine; BPY = 4,4′-bipyridine; BZ = benzil; BZP = benzophenone; CHTA = 1,3,5-cyclohexane-tricarboxylic acid; CMCR = *C*-methylcalix[4]resorcinarene; CECR = *C*-ethylcalix[4]resorcinarene; DCA = deoxycholic acid; DPP = 1,3-di-(4-piperidyl)propane; HECR = hexaethylresorcin[6]arene; dmp = bis(2,9-dimethyl-1,10-phenanthroline); THPB = 1,1,4,4-tetrakis(4-hydroxyphenyl)buta-1,4-diene; THPE = tris(4-hydroxyphenyl)ethane; THPM = tris(4-hydroxyphenyl)methane; THPiPB = α,α,α′-tris(4-hydroxyphenyl)-1-ethyl-4-isopropylbenzene.

Marc Messerschmidt

Marc Messerschmidt received a Diploma in Chemistry in 2001 from the Free University of Berlin. He continued to work there on high resolution X-ray diffration experiments and received a Dr. rer. nat. in 2004 from this university. Since 2004 he is a Postdoctoral Research Associate at the State University of New York at Buffalo where his research is focussed on excited states diffraction.

Paulina M. Dominiak

Paulina M. Dominiak graduated in biology (2000) and chemistry (2001) at Warsaw University (Poland). After visiting NASA Space Flight Center in Huntsville (2002) she received her Ph.D. in chemistry (2005) from the Warsaw University. Her thesis was on weak interactions in small molecules and protein crystals. In 2005 she joined Prof. P. Coppens laboratory at the State University of New York at Buffalo and is involved in the time-resolved X-ray diffraction studies and development of a method to reconstruct the charge density in protein crystals from a databank of transferable aspherical atoms.

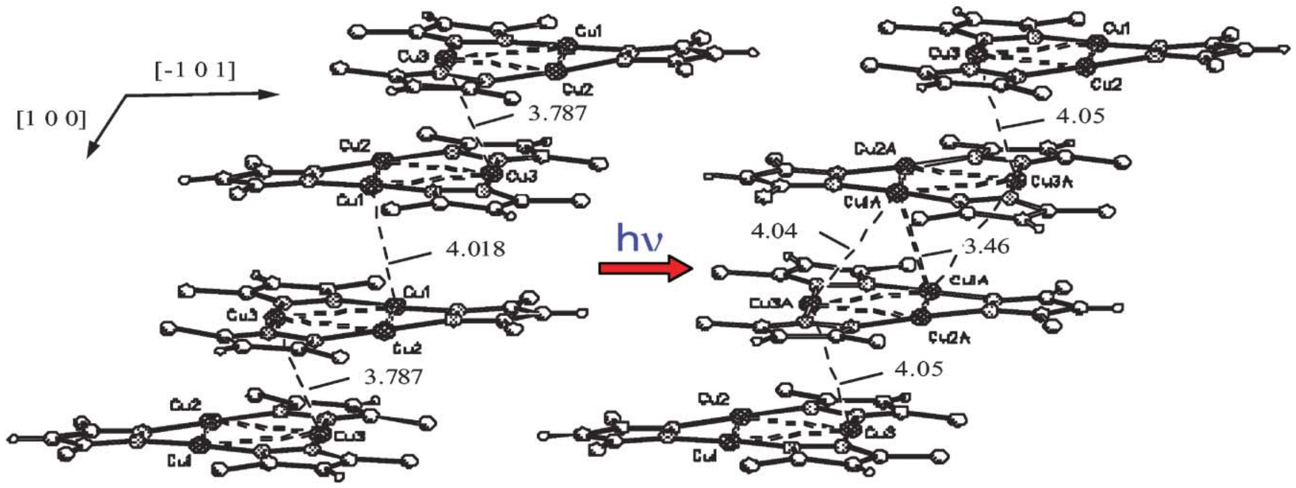

Fig. 1 Left: a column of the ground state $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ trimers before exposure. Right: excimer formation within the same column. Fluorine atoms are omitted for clarity. Figure reprinted with permission from: I. I. Vorontsov, A. Yu. Kovalevsky, Y.-S. Chen, T. Graber, M. Gembicky, I. V. Novozhilova, M. A. Omary and P. Coppens, *Phys. Rev. Lett.*, 2005, **94**, 193003/1–193003/4. Copyright (2005) by the American Physical Society.

larger spacing, as illustrated in Fig. 1. The molecular packing plays a decisive role in such processes, which are no longer characteristic for a single molecule.

What about molecules in supramolecular solids? Supramolecular solids are a largely untested medium for spectroscopic and photocrystallographic research. Yet, like widely applied rigid glasses they offer the prospect of molecular dilution but without the loss of 3-D periodicity and molecular orientation. The molecular dilution isolates identical molecules from each other and thus reduces exciton–exciton annihilation but, perhaps more importantly, reduces the number of photons required to achieve a certain conversion percentage of the active molecules in the crystal, and thereby reduces the heat load imposed on the crystal by the intense exciting light source. In sixteen supramolecular solids with benzophenone (BZP)[15] or benzil (BZ)[16] guests, the guest concentration is reduced from ~ 6 mol L^{-1} in the neat crystals of BZP and BZ to typically 1–1.5 mol L^{-1} and, in one case, the capsule-containing structure of CECR·2BPE·0.5BZP·0.5 ethanol, to 0.6 mol L^{-1}.[15] This reduction by a factor of 10 may be a record (though molecular concentrations are usually not reported in supramolecular structure publications), but almost certainly is not the limit that can be achieved.

As illustrated below, in contrast to solution studies, in supramolecular solids the state of aggregation of the guests can be unambiguously identified, so that monomers, dimers, and larger aggregations of guest molecules can be investigated. In addition, because of restrictions imposed by the environment, one molecule may occur in very different conformations in different solids, as illustrated for benzil in Fig. 2.

However, there are conditions that must be fulfilled: (a) good quality crystals must be available; (b) excited-state lifetime should not be drastically curtailed if excited state structure determination is to be accomplished; and (c) reasonably homogeneous illumination throughout the crystal requires that the framework components must not absorb the exciting light. An additional requirement is crucial if photo-induced chemical reactions are to be monitored on timescales of picoseconds or less. To apply diffraction methods, the crystalline lattice has to be preserved at least up to a significant conversion percentage. Results reported in the past decades indicate that *topotactic* reactions are very rare in neat or co-crystals of photo-reacting species.[17] These are reactions in which molecular migration is minimal and the basic crystal structure is preserved. Many of the reported solid-state reactions involve large molecular motions, which lead to crystal breakdown when conversion percentages exceed 5–10%.[17,18] Such reactions are usually not single-crystal-to-single-crystal reactions, even though the external shape of the crystals may be perfectly retained.[19] In protein crystallography in which reactive centers are typically embedded in a protein envelope and much solvent is present, the danger

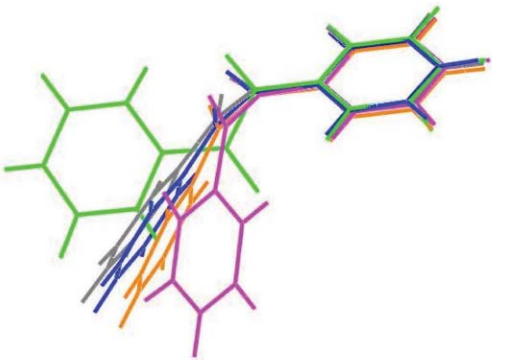

Fig. 2 Diagram of the conformation of benzil in a number of different supramolecualr solids. Reprinted with permission from: B.-Q. Ma, Y. Zhang and P. Coppens, *J. Org. Chem.*, 2003, **68**, 9467–9472. Copyright (2003) American Chemical Society.

of crystal breakdown initiated by the light-induced process is much less severe or absent, as illustrated by time-resolved and freeze-trapping studies of, for example, the dissociation and recombination of CO in myoglobin,[20] and the photoreaction of photoactive yellow protein.[21] The last case and that of bacteriorhodopsin,[22] are examples of reactions initiated by *trans–cis* and *cis–trans* isomerizations, respectively. But lack of atomic resolution in the protein environment prevents analysis of the detailed reaction mechanism at the initial stage of the process. Crystal engineering promises to provide a well-organized periodic environment in which such reactions can proceed with retention of the integrity of the inert host framework, thus opening the way for 'snapshots' at atomic resolution. Crystals will have to be engineered to provide sufficient space for the molecular rearrangement. An example has been reported by Lavy *et al.* who showed that the ring closure of 4-(oxyphenylacetyl)morpholine within a co-crystal proceeds as a homogeneous single-crystal-to-single crystal reaction.[23]

3.2 Intermolecular energy transfer in closely-packed molecular solids

Excitation of a guest molecule in a supramolecular host is likely to lead to energy transfer and therefore to shortening of the lifetime of the excited state, often to the extent that the emission is fully quenched. The T(n,π*) excited triplet states of benzophenone is a case in point. Benzophenone shows long-lifetime phosphorescence in rigid glasses and in neat crystals. However, the luminescence is fully quenched in ten different supramolecular phases prepared with the node molecules CMCR, CECR and linker such as BPY, BPE, BPMH, BPEH and BIBM.[15,24] The related benzil molecule shows a similar absence of its phosphorescence in six supramolecular complexes with the same type of framework components. The control of excited state quenching by energy transfer is of crucial importance in solid state TR diffraction studies.

Because of the close packing of molecules and the resulting intermolecular interactions, the short-range mechanism of luminescence quenching is of enhanced importance in crystalline solids. At distances above ∼5–10 Å the Coulombic Förster mechanism[25] plays the major role in excitation energy transfer.[26,27] It is the dominant mode of deactivation of excited singlet states at long distances, but is not a factor in the deactivation of triplet states, as triplet–triplet energy transitions (*i.e.* $^3D^* + {}^1A \rightarrow {}^1D + {}^3A^*$) (D = donor, A = acceptor) are forbidden.[28] At shorter distances (<∼10 Å) exciton energy transfer (EET) is historically described by the Dexter exchange mechanism,[29] in which triplet–triplet energy transfer is allowed.[28] A more recent treatment shows that resonance interactions through intermediate charge-transfer (CT) ionic states are also of prime importance.[26,30] The derivations by Harcourt *et al.*[30] show EET at shorter distances to also include intermediate-range Coulombic terms for transfer between singlet states. The triplet–triplet energy transfer plays a prominent role in phosphorescence quenching.

Within first-order perturbation theory the thermally-averaged transfer rate constant is given by Fermi's Golden Rule, which contains a weighted sum over terms $\delta(\Delta E_{\mathrm{D(ES\text{-}GS)}} - \Delta E_{\mathrm{A(ES\text{-}GS)}})$ over the vibrationally populated energy levels, where δ is the Kronecker delta function. Thus matching of the energy level spacings of D and A is required for EET. This provides a convenient criterion for optimizing the lifetime of luminescent supramolecular crystals. However, the often applied practice of judging the likelihood of EET by the overlap of the absorption and emission spectra is misleading as optically dark states are not considered in such an analysis.[27,31] The crucial role of the relative host–guest energy-level spacings is confirmed by comparison of theoretical level spacings with luminescence lifetimes for 22 different supramolecular solids based on CMCR, CECR, HECR, DCA and ACA, and illustrated in Fig. 3.[31] For the resorcinarene based solids use of non-conjugated linker such as BIMB, leads to a phase with a benzil–guest luminescence lifetime of 580 ns at 77 K,[32] much shorter than the 145 μs lifetime reported for neat benzil crystal at room temperature, but long compared with the <100 ns benzil lifetimes when conjugated linkers such as BPY and BPE are used.[16,33,31] A striking example of the effect of the relative energy level spacings is provided by 8 different host–guest complexes embedding the photosensitizer-dye cation $[\mathrm{Cu(dmp)_2}]^+$, as illustrated in Fig. 4. As shown in the figure

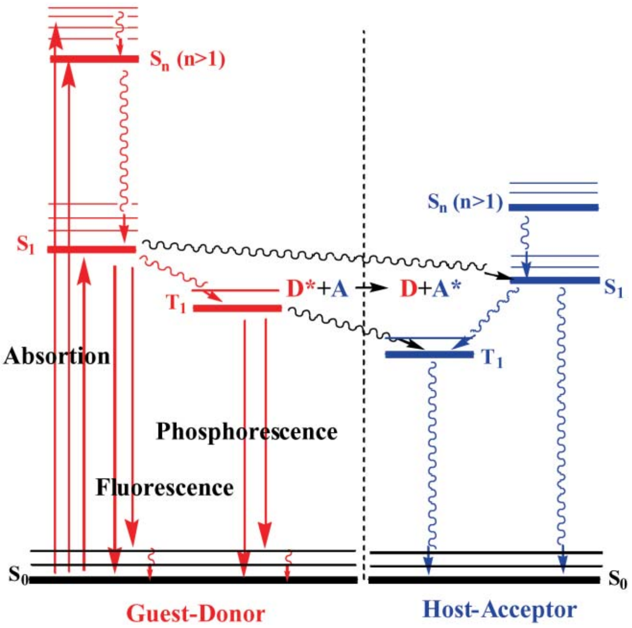

Fig. 3 The role of energy level spacings in the guest(red)-to-host(blue) singlet and triplet energy transfer mechanisms in crystalline supramolecular solids. Straight arrows: radiative processes. Wavy arrows: non-radiative processes. Reprinted with permission from: S.-L. Zheng and P.Coppens, *Cryst. Growth Des.*, 2005, **5**, 2050–2059. Copyright (2005) American Chemical Society.

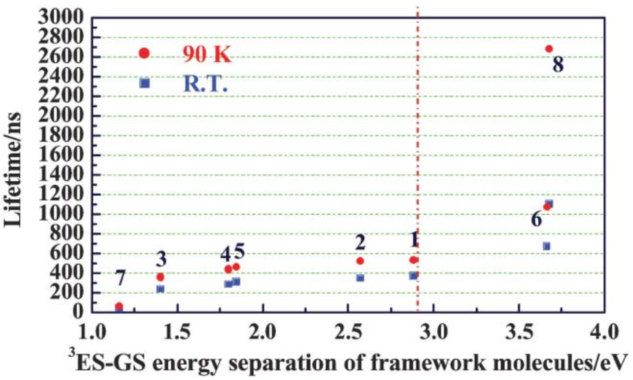

Fig. 4 Triplet excited state lifetimes of $Cu(dmp)_2^+$ in 8 different supramolecular solids *vs.* the theoretical ^{3}ES-GS energy gaps of the framework components. The vertical line represents the ^{3}ES-GS energy gap (2.78 eV) of $[Cu(dmp)_2]^+$. The numbers refer to the following solids: $[Cu(dmp)_2][(CECR)^-\text{-}2H_2O]$-benzene (**1**), $[Cu(dmp)_2][(CMCR)^-\text{-}2H_2O]$-benzene (**2**), $[Cu(dmp)_2][(THPM)^-]$ (**3**), $[Cu(dmp)_2][(THPE)^-]$ (**4**), $[Cu(dmp)_2][(THPiPB)^-]$ (**5**), $[Cu(dmp)_2][(2THPE)^-]\text{-}2H_2O$ (**6**), $[Cu(dmp)_2][(THPB)^-]$ (**7**), $[Cu(dmp)_2][(CHTA)^-]$-EtOH (**8**).

use of the fully saturated cyclohexane tricarboxylic acid CHTA leads to a very significant increase in luminescent lifetime. Significantly shorter lifetimes are observed when the ES-GS energy spacing of the host is smaller than the 2.78 eV calculated for the guest molecule. Though the guest molecules are distorted differently in different supramolecular crystals, there is no correlation between the distortion and either cavity size or luminescence lifetime.

4. The first examples of supramolecular time-resolved diffraction

We will discuss the first two examples of diffraction studies of molecular excited states in supramolecular crystals. In both cases the experiments have been performed with monochromatic synchrotron X-rays. Additional studies with polychromatic radiation are planned to complement what is presented here.

The dimeric species $[Cu(NH_3)_2]_2^{2+}$ was isolated in a host framework composed of $THPE^-$,[34] leading to a solid with the composition $[Cu(NH_3)_2]_2[THPE]_2\cdot 3.25H_2O$ (Fig. 5), in which no photoactive molecules other than the Cu^I dimer are present. Interestingly, IMPT (intermolecular perturbation theory),[35] MP2 and DFT calculations, performed with the X-ray geometry of the $[Cu(NH_3)_2]_2^{2+}$ dimer, indicate that because of electrostatic repulsions, the Cu^I dimer in the geometry found in the supramolecular crystals is less stable by 250–300 kJ mol^{-1} than the isolated monomers. Variation of the $Cu^I\cdots Cu^I$ distance shows no local minimum at the observed configuration, suggesting that such a dimer is unlikely to occur in dilute solution. This is in agreement with an earlier analysis by Carvajal *et al.*[36] Nevertheless, the dimer can be stabilized in the supramolecular environment.

Emission measurements show an intense photoluminescence at 17 K with emission at 495 nm, and a lifetime of ~4.2 μs, typical for a triplet excited state. Time-resolved diffraction data on a specimen embedded in a cold helium gas flow were collected with the stroboscopic technique[10] at beamline 15-ID at the Advanced Photon Source using 0.49384 Å radiation and 532 nm laser-excitation with a pulse repeat frequency of 12 kHz. The results indicate a contraction of the Cu–Cu distance from the ground state value of 3.0248(5) to 2.72(1) Å (Fig. 6), corresponding to an increased metal–metal bonding interaction, as well as a rotation of 11.8° of the Cu–Cu vector. Theoretical optimization of the excited triplet state gives a reduced $Cu^I\cdots Cu^I$ distance of 2.61 Å, in quite reasonable agreement with the experimental shortening. The contraction is due to promotion of a non-bonding electron from the full 3d-shell with

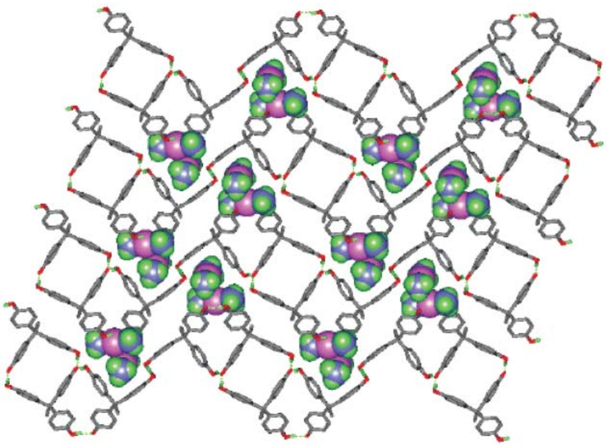

Fig. 5 Molecular packing in crystals of $[Cu(NH_3)_2]_2[THPE]_2\cdot 3.25H_2O$ The square-shaped channels are filled with disordered water molecules. Reprinted with permission from: S.-L. Zheng, M. Messerschmidt and P. Coppens, *Angew. Chem.*, 2005, **117**, 4690–4693. Copyright (2005) by John Wiley and Sons, Inc.

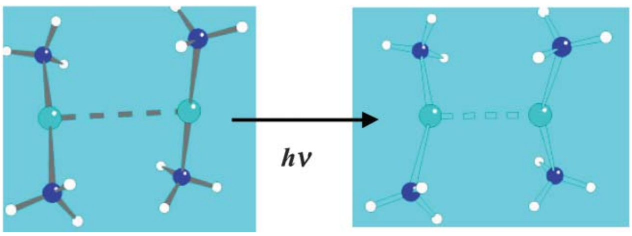

Fig. 6 Contraction of the Cu–Cu distance in the $[Cu(NH_3)_2]_2^{2+}$ ion (from 3.02 to 2.72 Å) on excitation.

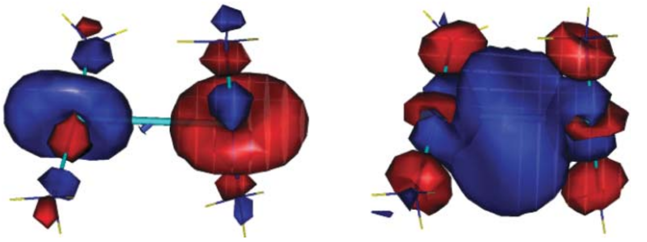

Fig. 7 Antibonding HOMO (left) and bonding LUMO (right) of the $[Cu(NH_3)_2]_2^{2+}$ ion.

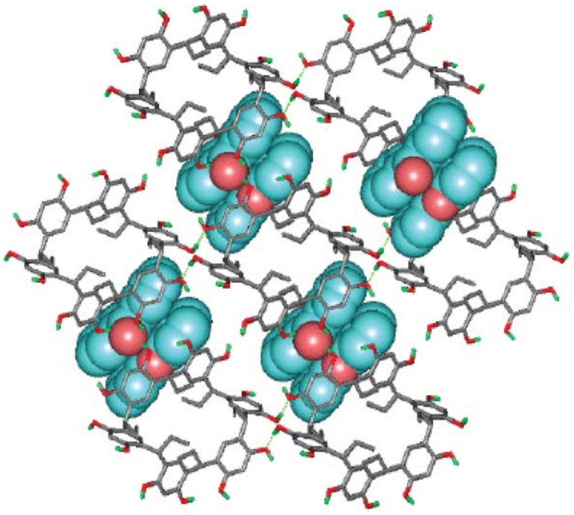

Fig. 8 The structure of HECR-2xanthone-6MeOH. Reprinted with permission from: S.-L. Zheng and P.Coppens, *Chem. Eur.–J.*, 2005, **11**, 3583–3590. Copyright (2005) by John Wiley and Sons, Inc.

an anti-bonding HOMO, to a weakly bonding LUMO σ_{4p} orbital on the metal atoms (Fig. 7), similar to the distance contraction observed in our earlier diffraction studies of neat crystals of $(TEA)_3H[Pt_2(H_2P_2O_5)_4]$ (TEA = tetraethylammonium),[37] $[Rh_2$(1,8-diisocyano-*p*-menthane)$_4](PF_6)_2$[38] and {[3,5- $(CF_3)_2$pyrazolate]Cu}$_3$.[14]

The second example presented here is a fully organic solid. Like benzil[16,32,39] and benzophenone,[40] xanthone has a long-lived excited triplet state.[41–43] The xanthone molecule occurs as a monomer in CECR–xanthone–MeOH and as a dimer in HECR–2xanthone–6MeOH (Fig. 8).[44] The molecular dilution is pronounced, the xanthone concentration being 1.642 and 1.752 mol L^{-1} for the two solid,s respectively, compared with 7.106 mol L^{-1} in neat xanthone crystals.

At all but the very lowest temperatures xanthone emits from the $T_2(n, \pi^*)$ excited state.[45] Although we find the lifetime of neat xanthone crystals at 17 K to be 887 μs, the corresponding numbers at the same temperature for the monomer and dimer supramolecular crystals are only 0.22 and 5.56 μs, respectively, indicating significant luminescence quenching. 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 HECR-2xanthone·6MeOH were performed at the 15-ID beamline at the Advanced Photon Source at a 10 kHz laser/X-ray pulse repeat frequency. As in the Cu^{I} complex, the results indicate a contraction corresponding to excimer formation. The interplanar distance in the dimer is reduced by 0.26(3) Å (from 3.39 to 3.14 Å), as expected from the stronger bonding in an excimer, and is accompanied by a lateral relative shift of the molecular planes of ∼0.24 Å (Fig. 9).[46] The excited state populations are found to be 0.08 and 0.13 in two successive experiments, the second 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 tentatively attributed to the improved photon/photoactive molecule ratio in the supramolecular crystals. Though the contraction and the magnitude of the lateral shift agree well in two separate experiments, the direction of the lateral shift is not exactly the same, a result that calls for further experiments, which are to be conducted with a pink beam using the Laue technique.

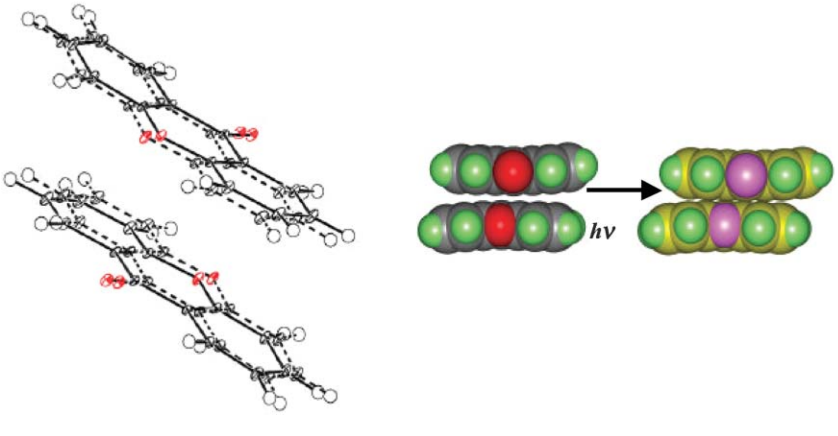

Fig. 9 Contraction of the xanthone dimer on excimer formation. Left: dotted lines, excited state, oxygen atoms in red. Right: CPK model.

5. Concluding remarks

The experiments on $[Cu(NH_3)_2]_2$-$[THPE]_2 \cdot 3.25H_2O$ and HECR-2xanthone-6MeOH are the first in which information on the geometry of excimers has been revealed by experimental methods, and the first in which supramolecular crystals have been used in time-resolved diffraction experiments. In the experiments performed so far the geometry changes determined are limited to gross features such as the metal–metal distances and interplanar spacings. These limitations should be removed in further experiments employing broader X-ray bandpass techniques. At this time the frontiers of the field are wide open and new insight into a wide range of dynamic processes is within reach.

Acknowledgements

The authors would like to thank the US Department of Energy for support of the time-resolved experiments at APS through grant DE-FG02-02ER15372. Support of this work by the Petroleum Research Fund of the American Chemical Society (PRF32638AC3) and the National Science Foundation (CHE0236317) is gratefully acknowledged.

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