Crystal engineering, solid state spectroscopy and time-resolved diffraction†

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Highlight

The use of calixarene-based supramolecular solids in spectroscopy and time-resolved crystallography is discussed. A series of solids with, as guests, benzophenone, benzil, decamethylruthenocene and a binuclear Rh cationic complex have been synthesized and analyzed. The excited state lifetimes that have been measured show a pronounced dependence on the molecular environment.

1 Introduction

One of the prime attractions of the field of crystal engineering is the possibility to tailor-make solids with desirable physical or chemical properties. This is not limited to bulk properties but also includes the characteristics of the guest molecules embedded in the solids. The supramolecular frameworks that

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form the backbone of the engineered solids provide the opportunity to embed molecules in different environments and to achieve a solid-state dilution previously only attainable in amorphous glasses. Spectroscopists have routinely used dilution in amorphous matrices to isolate photoactive molecules from each other and to reduce exciton–exciton annihilation limiting lifetimes of excited species. In supramolecular solids these goals can be achieved without sacrificing three-dimensional periodicity. This means that molecular changes and the resulting distortions of the environment can be studied by diffraction methods, which have the ability to yield unambiguous evidence on molecular geometry.

Though time-resolved diffraction at atomic resolution is still in its infancy and being developed,[1,2] the search for suitable solids and the exploration of the spectroscopic properties of the incorporated guest molecules must proceed in parallel.

The advantages of dilution of the photoactive species with retention of crystallinity are manifold:

(1) the number of photons to be absorbed to achieve a certain conversion percentage is reduced, which relaxes the requirements for the intensity of the laser pulses and the concomitant danger of overheating (and possibly destroying) the sample crystal;

(2) the absorption of light in the crystal, *i.e.* the extinction coefficient, is reduced, and thus uniformity of illumination throughout the crystal is improved;

(3) for a given conversion percentage the distance between excited molecules is increased, and the likelihood of exciton–exciton annihilation reduced;

(4) by varying the nature of the framework, the dependence of the spectroscopic properties on the molecular environment can be studied.

On the other hand, much more complicated crystal structures must be analyzed. In this respect modern area detector data collection techniques become indispensable as do high speed computing methods, as is the case for all of modern crystal engineering, the development of which depends crucially on the capability for rapid structure determination of complex solids.

2 Time-resolved diffraction at atomic resolution

Considerable progress has been made in time-resolved crystallography of macromolecules with the polychromatic Laue method, which allows very rapid collection of vast amounts of data. For very short timescale experiments the use of polychromatic methods may be unavoidable. However, to attain atomic resolution, monochromatic methods offer the distinct advantage of higher resolution and better accuracy. We have developed a stroboscopic method in which a pulsed laser beam is synchronized with probing X-ray pulses, as shown schematically in Fig. 1. Immediately following the exciting laser pulse the crystal is probed by the X-ray beam for a time span smaller that the excited state lifetime, and not exposed to the X-ray beam until the excited state population is replenished by the next laser pulse. With a mechanical chopper, X-ray pulses of microsecond length can be easily obtained, thus achieving a time-resolution that is much shorter than the read-out time of the CCD detector which is counted in seconds.[1] To ensure heat dissipation and increase of spatial resolution, the sample is cooled in a liquid helium gas flow while its diffraction pattern and phosphorescence are being recorded. To maximize the sensitivity of the experiment, light-on and light-off frames of data are collected in immediate succession, so that the effect of experimental instabilities is minimized.

In a first experiment we have measured the contraction of the central Pt–Pt bond of the $[Pt_2(pop)_4]^{4-}$ ion [pop = pyrophosphate, $(H_2P_2O_5)^{2-}$] upon excitation to its lowest $^3A_{2u}(d\sigma^* \rightarrow p\sigma)$ excited state. At the temperature of the
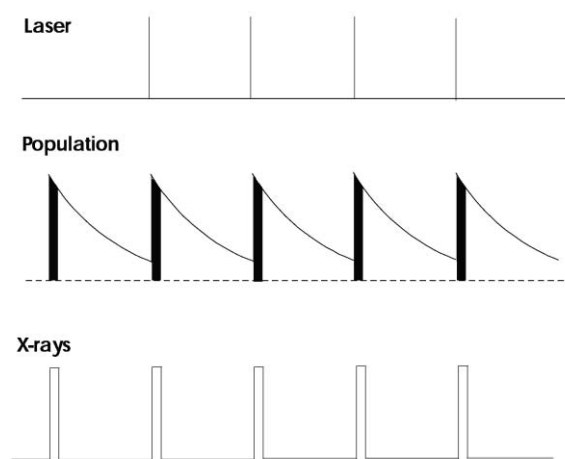

Fig. 1 Time structure of the stroboscopic experiment.

experiment the lifetime of the excited species is 50 μs. A frequency of 5100 Hz and an X-ray pulse length of 37 μs were used. The observed contraction of 0.28(9) Å was used to test quantum-mechanical DFT calculations of the excited state, and was found to be reproduced by some but not all of the theoretical methods tested.[3]

A major factor limiting the accuracy of the experiment is the small population of excited state molecules in the crystal, only 2% in the experiment described above. It is here that solid-state dilution has a crucial role to play by reducing the incident-photon to photoactive-molecule ratio. In the experiment described above the number of photons focused on the crystal and the number of photoactive molecules in the crystal are estimated at 2.3×10^{14} and 1.1×10^{14}, respectively, a 2:1 excess of photons. This is not adequate as not all photons should be absorbed in the crystal to ensure uniformity of illumination. The low excess of photons accounts to a large extent for the small conversion percentage achieved in the experiment. There are three solutions to this problem: (i) increasing the laser intensity with increased chance of destroying the crystal; (ii) reduction of crystal size, which requires more intense X-ray beams; or (iii) solid-state dilution by assembly of supramolecular solids.

3 Choice of suitable frameworks

3.1 General considerations

Though solid-state dilution has promising advantages for time-resolved diffraction studies, a number of conditions must be satisfied. First of all, the molecules composing the framework in the solids must be transparent to the exciting radiation and photochemically inert, which rules out most supramolecular solids containing metal atoms. Second, no phase transitions leading to disorder or deterioration of crystal quality must take place on cooling to the low temperatures required for the experiment. Finally, the guest molecules should show no or at most minor disorder, the reason we discontinued studies on cyclodextrin inclusion complexes,[4] in which guest molecules seemed invariably disordered.

MacGillivray *et al.* designed a family of solids in which the cavity of crown-shaped *C*-methylcalix[4]resorcinarene (CMCR) is extended through hydrogen bonding.[5,6] They showed that by using *exo*-bidentate 'pillar' molecules such as 4,4′-bipyridine (bipy), 1D polymeric 'wavelike' host structures can be formed between which guest molecules can be embedded. Guest molecules as large as ferrocene and its mono- and di-acetylated derivatives[7] and adamantanone and [2.2]paracyclophane[8] can be entrapped in the structure. In
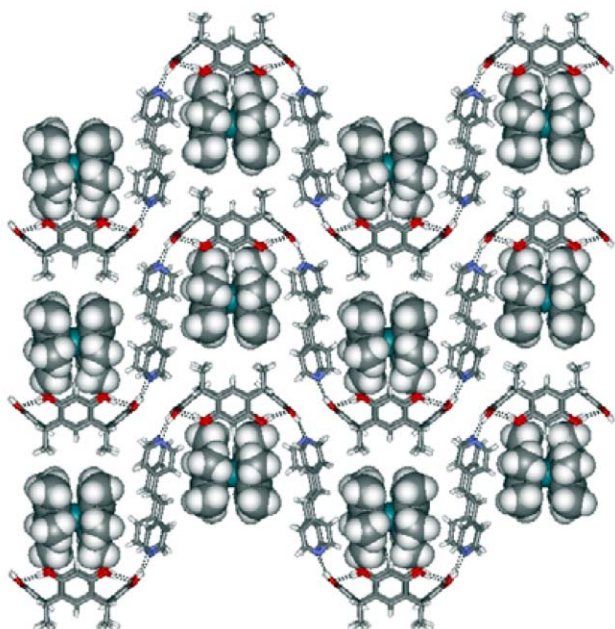
(a)

(b)

Fig. 2 Wavelike structure of [CMCR·2bpe]·DMR[10] [bpe = *trans*-1,2-bis(4-pyridyl)ethylene; DMR = decamethylruthenocene].
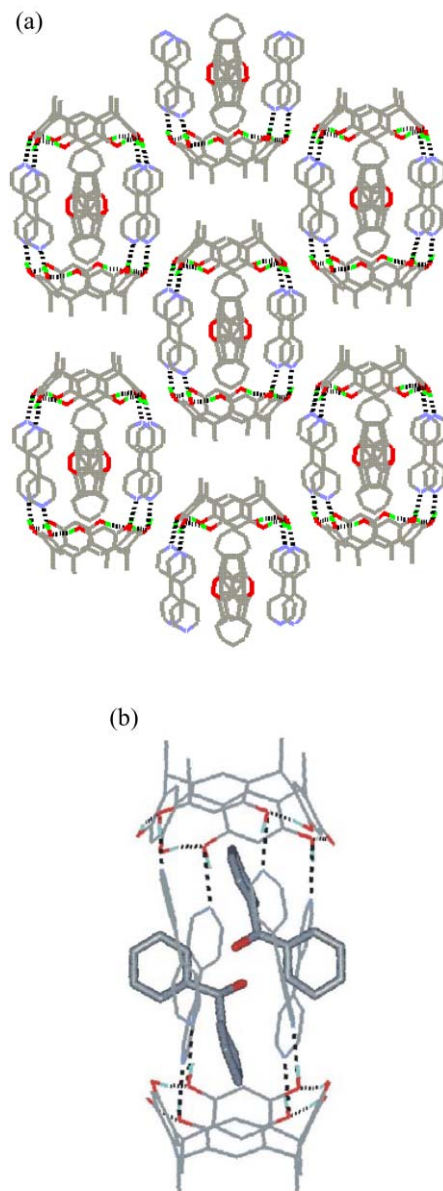
Fig. 3 Carcerand-like, face-centered structure of [CMCR·2bipy]·benzophenone. (a) The face-centered arrangement in the *ab* plane. (b) View of one capsule. The capsule has the crystallographic point-symmetry 222. The two benzophenone molecules included in the cavity each occupy two disordered positions related by one of the two-fold axes. Only one of the positions for each is shown.[11]

subsequent studies, cocrystallization of CMCR, bipy and nitrobenzene led to a 0D carcerand-like capsule, formed by two crown-conformation CMCR molecules linked by four bipys, in which nitrobenzene was encapsulated in a disordered arrangement.[9] Corresponding examples from our own work are shown in Figs. 2 and 3.

The variety of CMCR-based solids is greatly enhanced by the ability of CMCR to crystallize in different conformations. In addition to the wavelike and carcerand structures, in which CMCR occurs in the crown conformation, the boat (flattened cone) conformation gives rise to a series of 2D, brick-wall-like sheet structures (Fig. 4),[12–14] and a 3D network of non-intersecting, mutually perpendicular CMCR columns linked by pillar molecules (Fig. 5),[13] while 2D and 3D stepped-sheet structures are formed with CMCR in its chair conformation (Fig. 6).[13] As in other supramolecular framework solids, the variety is further extended by use of different pillar molecules. New solids are formed, for example, with *trans*-1,2-bis(4-pyridyl)ethylene,[15] and even longer and more complex linking molecules[16,17] may be exploited. This almost unlimited versatility of the CMCR-based solids is an attractive feature for their use in time-resolved diffraction studies. While the guest molecules frequently show disorder, this is by no means always the case, providing solids suitable for the intended use.

3.2 Examples of CMCR frameworks containing neutral organic and metallo-organic guests

3.2.1 Benzophenone as a guest molecule. *Photochemistry of benzophenone.* Benzophenone undergoes an $S_1(n,\pi^*) \leftarrow S_0$ transition upon photoexcitation and subsequently relaxes into a strongly phosphorescing excited triplet state with a lifetime of 3.0 µs in benzene solution at room temperature.[18]

From vibrational analysis of the spectrum it was concluded that in the $S_1(n,\pi^*)$ state the dihedral angle between the phenyl rings is smaller by *ca.* 13° than in the ground state,[19] a conclusion supported by earlier Extended Hückel and CNDO/2 calculations.[20] As may be expected for an n → π* transition, the spectra indicate a weakening of the C=O bond. The excited state of benzophenone is highly reactive, as indicated by the quenching of its phosphorescence in aqueous solutions containing cyclodextrins,[21] and photo-induced hydrogen

abstraction in protic solvents leading to dimerization and the formation of benzpinacols. But in a study by Barra and Agha,[22] no evidence for hydrogen abstraction was found in the diffuse reflectance laser-flash spectra of benzophenone embedded in a hexa-*tert*-butyl-37,38,39,40,41,42-hexaethoxy-calix[6]arene (HBHEC) host matrix, indicating that if hydrogen abstraction occurs, the resulting radicals decay rapidly by back hydrogen transfer in the tight environment. The benzophenone triplet decay followed a simple two-exponential function with room-temperature lifetimes reported as 460(10) ns and 42(6) µs, the latter noticeably longer than the lifetime of triplet benzophenone in benzene quoted above.

Benzophenone as guest in C-*methylcalix[4]resorcinarene-(CMCR) based host frameworks.* In our search for new supramolecular solids incorporating benzophenone we have synthesized three CMCR/bipy frameworks, with different architectures with stoichiometric composition [CMCR·3bipy·
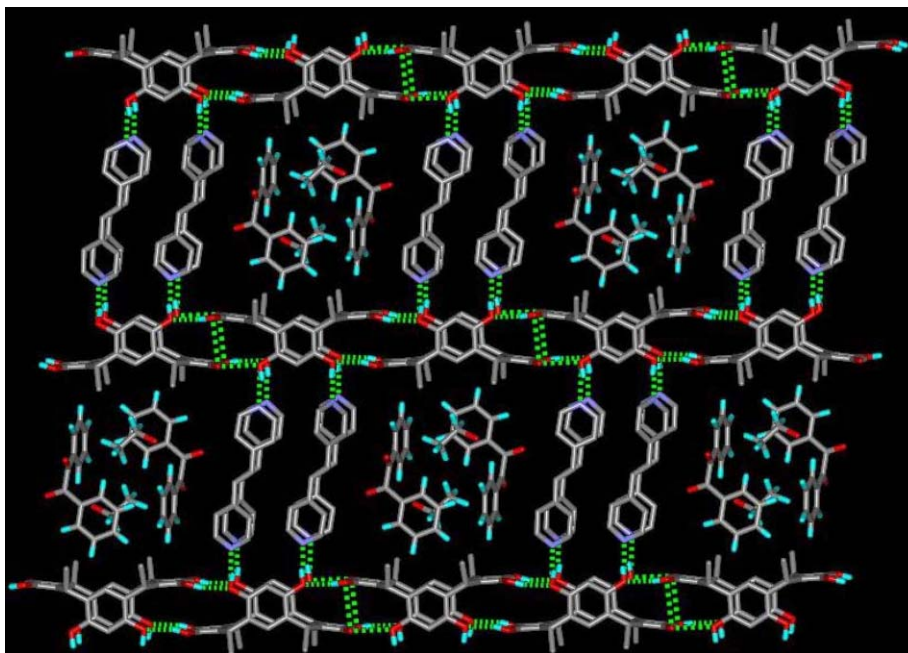
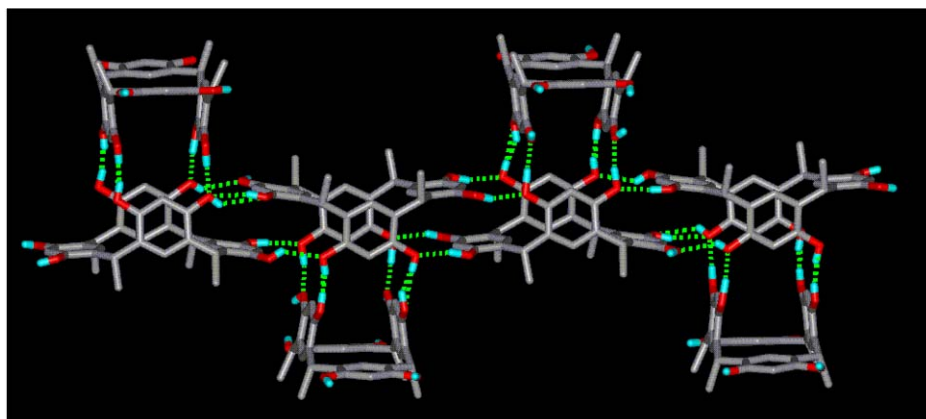**Fig. 4** Two-dimensional brick-wall structure of [CMCR·2bpe]·benzil·ethanol.

Fig. 5 Non-intersecting, perpendicular CMCR columns in [2CMCR·1.5bipy]·5H₂O.[13]

2H₂O]·benzophenone‡ (**1**), [CMCR·bipy]·benzophenone·H₂O (**2**) and [CMCR·2bipy]·benzophenone (**3**).[11] The solids were synthesized by hydrothermal synthesis with essentially identical procedures. Though **2** and **3** crystallized from the same reaction mixture, not only their stoichiometries but also their architectures differ widely. The flexible CMCR molecule has the chair, boat and crown conformations in **1**, **2** and **3**, respectively, leading to the corresponding stepped-sheet, brick-wall and carcerand-like frameworks. While in **1** the water molecules are an integral part of the framework structure, in **2** they are located in the guest cavities. The carcerand structure of **3** has the space group *Fddd*, with a structure reminiscent of that of simple, face-centered metals with the metal atoms replaced by the supramolecular capsules (Fig. 3).

Size of the cavities in different frameworks. Is there any relation between the volume occupied by the guest molecule and the molecular shape of a flexible guest molecule such as benzophenone? Cavity volumes were calculated as described by van der Sluis and Spek[23,24] with standard van der Waals radii. Results for the CMCR-based solids, together with those of other supramolecular phases containing benzophenone, are given in Table 1, together with the twist angles of the

benzophenone molecules. The corresponding cavity volume for the neat crystals has been calculated by reducing the space group to *P*1, and subsequently removing a single molecule.

Among the CMCR solids, the carcerand structure has the largest cavity volume, calculated as 621 Å³ for the two benzophenone molecules. The stepped-sheet structure of **1** contains a single, well-ordered benzophenone molecule in a cavity of 305 Å³, whereas in **2** the cavity volume is 568 Å³, which after correction for the volume of one included water molecule corresponds to 275 Å³ per benzophenone molecule. The volume occupied per benzophenone molecule in 3HBHEC·2benzophenone is larger (337 Å³), as are the atomic displacement parameters of the benzophenone molecule as determined in the structure analysis. There are large variations in twist angle around the C(=O)–C bond, but no apparent correlation with the size of the cavity, though its shape should obviously be important. Since all rotations are conrotatory, the variation among the interphenyl dihedral angles is much smaller. The energy differences between the different conformations, as calculated with the program Jaguar,[25] are quite small, in the range of 10–17 kJ mol⁻¹ above that calculated for the isolated molecule.

3.2.2 Benzil as a guest molecule. *Photochemistry of benzil.* The photochemistry of benzil in solution, in rigid glasses

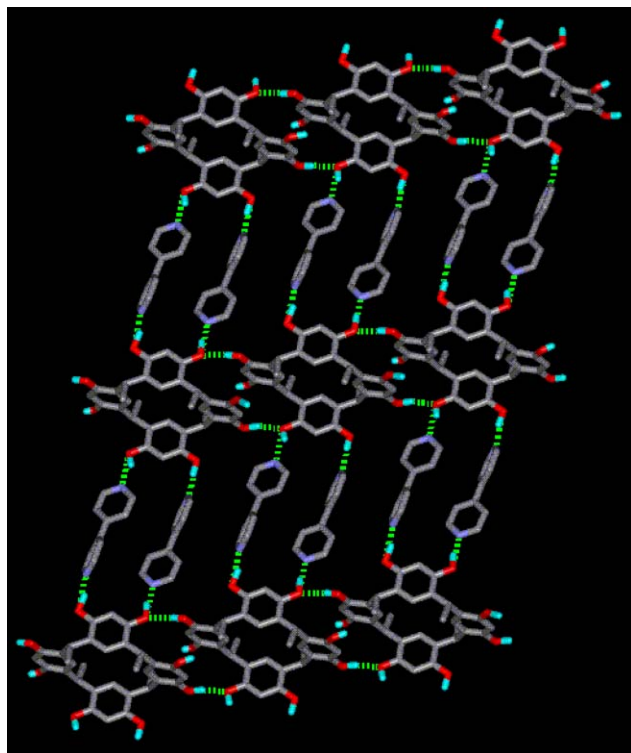‡Framework molecules are enclosed in square brackets.

Fig. 6 Stepped network structure of [CMCR·2bipy].[13]

and as a dopant in neat crystals has been the subject of many studies. The n → π* excited triplet state has a long lifetime of the order of milliseconds, even at room temperature.[26] Though it is generally accepted, based on the results of zero-field magnetic resonance,[27] time-resolved EPR and phosphorescence studies,[28,29] and microwave dipole measurements in a benzene solution,[30] that the T_1 triplet state of benzil assumes a *trans* or near-*trans* structure of the central (O=)C–C(=O) bond,

differences between the emission spectra of benzil appear nevertheless to be due to different molecular conformations of the triplet state. Roy *et al.* attributed a time-dependent change in the phosphorescence spectrum of benzil in semi-solid glasses to a structural relaxation from a skewed to a *trans*-planar conformation of the excited state.[31] According to the interpretation of the ENDOR data, an *x*-trapped triplet state with an emission peaking at 517 nm is due to a species with a twist angle of 157°,[32] while the *trans*-coplanar conformer (twist angle of 180°) emits with a peak at 570 nm.[29] Benzil as a dopant in dibenzyl crystals similarly gives rise to different emission spectra attributed to different unique molecular configurations.[33]

In general the geometry of the triplet state of benzil and its emission properties depend on the molecular environment, that cannot be precisely measured in either solution or rigid glasses, or when the molecule is introduced as a dopant in a crystalline lattice. This is not the case in supramolecular solids, in which structural changes of the guest, as well as the host framework, can be studied by time-resolved diffraction methods.

Benzil as guest in C-methylcalix[4]resorcinarene- (CMCR) based host frameworks. Using hydrothermal as well as conventional methods, we have synthesized four different supramolecular complexes with benzil as the guest molecule: [CMCR·bipy]·benzil (α) (**4**); [CMCR·bipy]·benzil (β) (**5**); [CMCR·2bpe]·benzil·ethanol (**6**); and [CMCR·2bpe]·benzil·2H$_2$O (**7**). The four structures have remarkable similarities. In all four CMCR adopts the boat conformation, and connects into one-dimensional infinite columns through intermolecular O–H···O hydrogen bonding. The bipy (**4** and **5**) or bpe (**6** or **7**) 'pillar' molecules link the columns into brick wall frameworks, with cavities containing in each case two benzil molecules. The number of pillar molecules connecting each pair of CMCRs is four in the bpe structures **6** and **7**, but only two for bipy in **4** and **5**, though four-bipy molecule brick-wall structures are known.[13]

Table 1 Molecular volume and twist and dihedral angles in a number of benzophenone-containing solids

Compound	Volume per benzophenone molecule/Å^3	Ph–C twist angles/°[a]	Ph–Ph dihedral angle/°
(a) Benzophenone in calixresorcinarene- and calixarene-based frameworks and neat benzophenone			
Benzophenone ($P2_1$)[b]	296	+30.8, +30.0	55.8
Benzophenone ($C2/c$)[b]	300	+29.3, +43.5	64.5
[CMCR·3bipy·2H$_2$O]·benzophenone (**1**)	305	+29.3, +16.7	42.0
[CMCR·bipy]·benzophenone·H$_2$O (**2**)	275	+37.8, +18.5	52.4
	284 (incl. one H$_2$O)		
[CMCR·2bipy]·benzophenone (**3**)[c]	310		
3HBHEC·2benzophenone[d]	337	+22.4, +38.8	52.1
Isolated benzophenone molecule (theory-optimized, B3LYP 6-311G**$^{++}$)		+28.9, +28.9	52.5
(b) Other benzophenone-containing solids			
Benzophenone/diphenylamine[e]	277	+29.6, +37.7	60.0
9,10-Bis(3,5-dihydroxy-1-phenyl) anthracene·bis(benzophenone)[f]	286	+16.1, +39.7	52.8
5,11,17,23-Tetra-*tert*-butyl-25,26,27-trihydroxy-28-trifluoromethylsulfonylcalix[4]arene benzophenone[g]	334	+29.7, +44.7	67.9
1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol·benzophenone[h]	307	+22.6, +38.1	55.3
Octakis(μ$_3$-hydroxo)-octadecacarbonylheptamanganese·benzophenone[i]	305 (molecule A)	+28.8, +35.5	57.5
	318 (molecule B)	+31.4, +31.4	57.7
	604 (A and B)		

[a]Twist angles are positive for clockwise rotation when viewed in the direction of the C(=O)–C bond. Equal signs imply conrotatory rotation. With the exception of **1**, all structures in Table 1 are centrosymmetric, so that clockwise and counterclockwise conrotatory twists occur in symmetry-related molecules. The twist angle is defined as the angle between the central CCOC plane and the plane of the phenyl ring. [b]Room temperature data. [c]Guest disordered. [d]HBHEC = hexa-*tert*-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene. [e]C. Brassy and J.-P. Mornon, *C. R. Acad. Sci., Ser. C*, 1972, **274**, 1728. [f]K. Endo, T. Sawaki, M. Kobayashi, H. Masuda and Y. Aoyama, *J. Am. Chem. Soc.*, 1995, **117**, 8341. [g]S. Chowdhury, J. N. Bridson and P. E. Georghiou, *J. Org. Chem.*, 2000, **65**, 3299. [h]D. R. Bond, L. Johnson, L. R. Nassimbene and F. Toda, *J. Solid State Chem.*, 1991, **92**, 68. [i]M. D. Clerk and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1991, 1607.

Table 2 Comparison of concentration, cavity size and torsional angle of benzil in neat crystals and host–guest compounds

Compounds	Concentration/ mol L^{-1}	Cavity size/Å^3 (two benzil)	Volume occupied by one benzil/Å^3	O=C–C=O torsion angle/°
[CMCR·bipy]·benzil (α) (**4**)	1.51	630	315	121.5
[CMCR·bipy]·benzil (β) (**5**)	1.51	654	338	108.0
			339	117.9
[CMCR·2bpe]·benzil·ethanol (**6**)	1.13	839	331	91.8
[CMCR·2bpe]·benzil·2H$_2$O (**7**)^a	1.06	1046	464	
Neat benzil crystal (HT phase, 100 K)^b	6.16	(618)	309	107.3
Neat benzil crystal (LT phase, 70 K)^c	6.20	(598)	299	103.1
				107.8
				113.8

^{a}Disordered guest molecule. ^{b}C. J. Brown and R. Sadanaga, *Acta Crystallogr.*, 1965, **18**, 158; E. J. Gabe, Y. Le Page, F. L. Lee and L. R. C. Barclay, *Acta Crystallogr., Sect. B*, 1981, **37**, 197; M. More, G. Odou and J. Lefebvre, *Acta Crystallogr., Sect. B*, 1987, **43**, 398. ^{c}M. More, G. Odou and J. Lefebvre, *Acta Crystallogr., Sect. B*, 1987, **43**, 398.

Size of the cavities in different frameworks. The considerably larger cavities formed with bpe (column 3 of Table 2) also contain other solvent molecules: two molecules of ethanol in the case of **6**, which was prepared by conventional methods, and four molecules of water in hydrothermally prepared **7**. The very large cavity size of **7** leads to a disorder of the guest molecules which interferes with the full structure solution. The volume occupied by one benzil molecule is listed in the fourth column of Table 2. In all supramolecular phases the benzil volume is larger than in the neat benzil crystals (last two rows of Table 2), and the range of torsional angles is increased. But as for benzophenone, there is no correlation between the O=C–C=O twist angle for the ground state molecule and the available volume, as the twist angles found in the supramolecular solids are both larger and smaller than those in the tighter neat phases. It is the shape of the cavity, rather than its total volume that affects the molecular conformation.

3.2.3 Decamethylruthenocene as a guest molecule. *Photochemistry of decamethylruthenocene.* The electronic absorption and emission spectra of ruthenocene have been measured in different media, including glasses, KBr pellets, and as single crystals. The first studies were carried out by Crosby *et al.*,[34] who analyzed the luminescence decay at 4.2–77 K. The observations were interpreted on the basis of a $^3E_1$ excited state generated by a d→d transition, and split by *ca.* 500 cm^{-1} through spin-orbit coupling into $A_2 + A_1 + E_1 + E_2$ components, in order of increasing energy. Franck–Condon analysis of the fine structure of the luminescence at 4.2 K indicated an expansion of the Ru-ring distance by 0.14 Å in the excited state, primarily along the principal symmetry axis. This conclusion is in quite good agreement with results of later studies. Hollingsworth *et al.*[35] measured the vibrational fine structure of the emission spectrum of crystalline ruthenocene at 10 K, and concluded that in addition to the major displacement along the metal–ring bond axis with a 0.12 Å increase along the Ru–Cp bond axis, distortions along ring tilting bending modes occur on excitation. Riesen *et al.*[36] measured the luminescence and excitation spectra of Ru(C$_5$H$_5$)$_2$, Ru(C$_5$D$_5$)$_2$ and Ru(C$_5$Me$_5$)$_2$, and found that deuteration increases the lifetime of the $^3E_1$ triplet state to 990 μs at 4.2 K, whereas for decamethylruthenocene the lifetime is 627 μs (4.2 K), compared with 127 μs for ruthenocene (1.5 K). The geometry and energies of the ground- and excited-state energies in the gas phase and in the crystal were calculated by Gilardoni *et al.*[37] using density functional theory. According to the calculation, the Ru–Cp distance increases by 0.145 Å upon excitation to the lowest excited state, a result in excellent agreement with the spectroscopic data. For the isolated molecule a strong Renner–Teller vibronic coupling leads to a structure that is strongly bent along the (Cp–Ru–Cp) bending coordinate, but a separate calculation indicates that in the crystal this distortion may be reduced considerably by lattice forces.

Crystallography of decamethylruthenocene in neat and supramolecular solids. At room temperature DMR crystallizes in the space group $P2_1/m$, with the DMR molecules disordered across a mirror plane.[38,39] The disorder disappears on cooling to 90 K with a lowering of the crystallographic symmetry from $P2_1/m$ to $P2_1/n$ and a doubling of the unit cell, but retention of the eclipsed configuration of the cyclopentadienyl rings.[12]

Crystals of [2CMCR·4bipy]·DMR (**8**) with DMR incorporated in a CMCR/bipy framework can be obtained readily by slow cooling of an ethanol solution of the components. The structure is isomorphous with that of the [CMCR·2bpe]· benzil·ethanol phase (**6**) (Fig. 4). In both, two CMCR molecules in different chains are linked by two pairs of pillar molecules to form a brick-wall framework, with, in the case of **8**, one DMR, two water and two ethanol solvent molecules rather than two benzil and two ethanol molecules located in each of the cavities. The DMR molecules and the solvent molecules each occupy one of two center-of-symmetry-related positions in a disordered arrangement of the DMR molecules.

When bipy in the reaction mixture is replaced by bpe, crystals of [CMCR·2bpe]·DMR (**9**) are obtained in which the DMR is fully ordered (Fig. 2),[10] with the wavelike, one-dimensional infinite polymer structure first identified by MacGillivray *et al.*[7]

Comparison of the DMR molecules in the three structures reveals only negligible differences in the molecular geometry: the Ru–Cp* distances are 1.805(0.016) and 1.792(0.007) Å in the [CMCR·2bipy]·DMR complex, compared with 1.800(3) and 1.800(3) Å in the neat DMR structure and 1.805(4) and 1.805(4) Å in [CMCR·2bpe]·DMR.

A third host/DMR–guest structure was obtained with HBHEC as host, in analogy with the HBHEC–benzophenone complex. Rather than being located in large cavities of the calix[6]arene, the DMR molecules in 3HBHEC·2DMR (**10**) are in channels between the host molecules, with some dichloromethane molecules at the edges of the channels.

3.3 Incorporating charged species in supramolecular frameworks

As many photochemical processes of interest involve charged species, both cationic and anionic, charged frameworks must be explored. In pioneering studies Atwood *et al.* developed the use of *p*-sulfonatocalix[4,5]arenes,[40] which can coordinate cations such as Ni(II) and Cu(II) aqua pyridinium complexes, and mono- and poly-nuclear Cr(III) and Rh(III) aqua ions through 'second-sphere coordination'.[41]

An alternative approach is provided by deprotonation of one or more of the hydroxy groups of the calixarene molecule.[42,43] We have prepared a 1:2 salt of Rh$_2$(dimen)$_4^{2+}$ (dimen = dimenthene) calix[4]arene-H in which the divalent cation is flanked by two monovalent calixarene anions with inter-ion contacts mainly existing of methyl–hydrogen aromatic ring interactions (Fig. 7).[44] Like [Pt$_2$(pop)$_4$]$^{4-}$, Rh$_2$(dimen)$_4^{2+}$ is
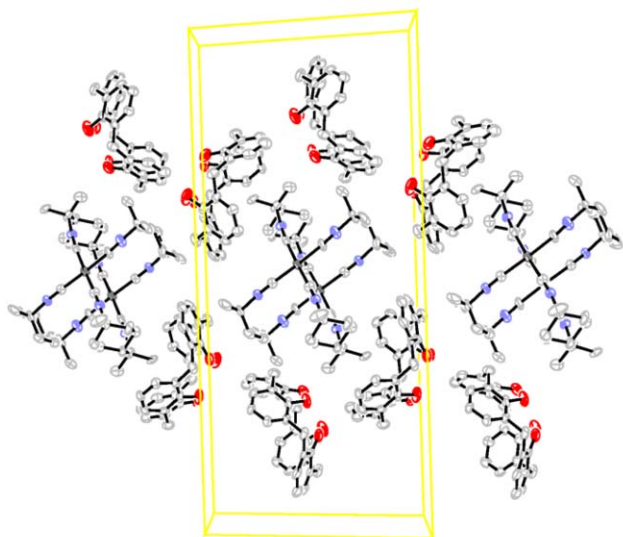
Fig. 7 Structure of the [Rh₂(dimen)₄](calix[4]arene-H)₂ salt.

Table 4 Energy differences between [CMCR·2bpe]·DMR^{exc} and [CMCR·2bpe]·DMR clusters before and after optimization of the environment with the MMFF94 force field

Energy difference excluding DMR molecule	ΔE/kJ mol^{-1}
Before optimization	345
Optimization without change in bond torsional and bending angles	70
Optimization with change of torsional and bending angles[a]	50

[a] Intramolecular bond lengths were allowed to vary, but did not change.

believed to undergo a pronounced shortening of the metal–metal distance upon excitation.

4 Solid state environment and spectroscopic properties

We find large variations in excited state lifetime in different solid state environments, a prime example being DMR in the fully ordered, small-cavity structure of [CMCR·2bpe]·DMR (Table 3), for which the triplet lifetime is 1.7 ms compared with 459 μs in the neat crystal, and only 191 μs in the large cavity matrix of 3HBHEC·2DMR. The solid-state dilution achieved by the supramolecular approach is considerable (Tables 2 and 3), with concentrations reduced by factors of 4–8 compared with the neat crystals, but still larger than found, for example, for CO in carboxymyoglobin (0.05 mol L^{-1}). However, the concentration achieved does not correlate with excited state lifetimes under the conditions of the phosphorescence experiments, in which conversion percentages to the excited states are estimated at 1% or less. For the three supramolecular solids containing DMR, the excited state lifetime decreases with the volume occupied by DMR, the looser the cavity, the shorter the lifetime, but the neat DMR structure does not follow this trend. It is also possible that phosphorescence is quenched when the solvent molecules are present in the cavity, as the longest lifetime is observed for the solvent-free solid [CMCR·2bpe]·DMR (**9**). We are currently measuring the emission spectra to identify possible differences between the photo-induced excited states of DMR in the three solids.

To explore to what extent the framework is distorted upon molecular excitation, we have performed a molecular mechanics calculation for a cluster of molecules mimicking the structure of [CMCR·2bpe]·DMR, with DMR at its center, with and without a 0.24 Å ring-to-ring expansion of the DMR

molecules. Several force fields were applied, but as differences between most were not pronounced, only results of the MMFF94[45] force field calculations are presented here. According to the calculation (Table 4), the excitation of the guest creates a strain in the surrounding lattice of more than 300 kJ mol^{-1}, which is reduced to *ca.* 50 kJ mol^{-1} by relaxation of the surrounding lattice. The MMFF94 force field predicts the distortion to include a stretching of the N···H–O hydrogen bonds connecting the CMCR and bpe molecules by amounts varying from 0.08–0.20 Å, and in the case of one proximal bpe molecule a change in the torsional angle around the bpe C–C bond of close to 12°. Upon return to the ground state, this rearrangement must be reversed, which conceivably creates a barrier accounting for the increase in lifetime of DMR in this tightly packed supramolecular solid.

5 Concluding remarks

Crystal engineering offers a largely unexplored opportunity to study the spectroscopic properties of molecules and geometry changes upon excitation in environments which can be engineered to have specific properties. As shown above, disorder of the guest molecules, while encountered, is not prevalent in the calixresorcinarene- and calixarene-based phases examined here, which are thus suitable systems for such studies.

The dependence of the physical properties of molecules on their surroundings is of importance in its own right, and is of relevance to molecular behavior in less-ordered and amorphous media, for which precise structural information can generally not be obtained. The study of photo-initiated processes at atomic resolution has broad applications, limited only by one's imagination, and includes understanding the mechanism of molecular devices and biological reactions.

Acknowledgements

Table 3 DMR-containing supramolecular solids

Compound	Volume per DMR/Å^3	Solvent molecules in cavity	Concentration/ mol L^{-1}	Phosphorescence lifetime (16 K)/μs
[CMCR·2bipy]·DMR (**8**)[a]	603	Ethanol, water	0.60	490
[CMCR·2bpe]·DMR (**9**)	582	None	1.13	1700
3HBHEC·2DMR (**10**)	589	Dichloromethane, water	0.49	191
DMR[10]	535	—	3.71	459

[a] Disordered guest molecule.

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