

Structure and Photoluminescence of a Benzil Nanocolumn in a C-Methylcalix[4]resorcinarene-Based Framework

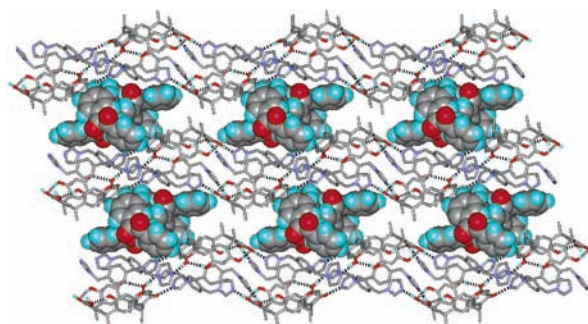
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ABSTRACT



A new framework based on C-methylcalix[4]resorcinarene and the flexible nonconjugated spacer 1,4-bis(imidazol-1-yl-methyl)benzene encloses a large one-dimensional channel, containing benzil nanocolumns. Unlike in a previously reported series of benzil-containing supramolecular solids with conjugated linker molecules, benzil luminescence is observed, but the lifetime of 580 ns at 77 K is considerably shorter than the 145 μ s reported for neat benzil at room temperature.

Solid-state dilution of photoactive species plays an important role in time-resolved diffraction studies of excited-state structure.^{1,2} Molecular dilution without sacrificing the three-dimensional crystalline periodicity achieved in supramolecular solids has the advantage over amorphous mixtures that precise information on the molecular geometry can be obtained by conventional diffraction methods, while time-resolved diffraction experiments can be greatly facilitated.³

The benzil molecule can be incorporated in a great variety of supramolecular solids, thus opening the possibility of probing the effect of the host environment on photochemical behavior. Its excited triplet state has a millisecond lifetime at low temperature in rigid glasses. Spectroscopic studies in the crystalline state and in organic glasses indicate that the excited-state geometry and lifetime are affected by the constraining environment.⁴ Because the torsion angle around the central carbon–carbon bond is variable, benzil has a flexible conformation, though its conformational freedom is restricted when the molecule is enclathrated within the limited cavity space of a host matrix. Thus, the luminescence of benzil appears to be strongly dependent on the host environment as investigated in *p*-tert-butylcalix[n]arene

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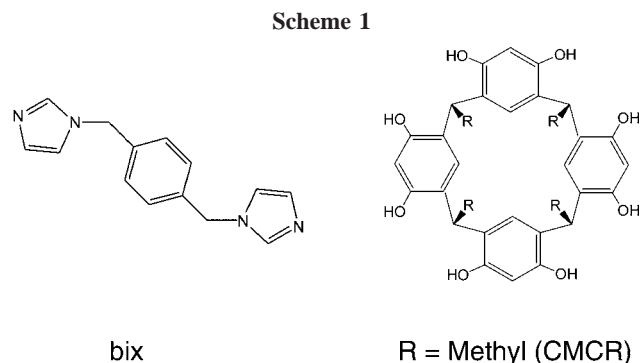
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($n = 4, 6, 8$) and silicalite matrixes.⁵ However, no crystals suitable for X-ray structure determination have been obtained for these materials. In many cases, when crystal structures are available, as for benzil in cholic acid channels⁶ and in β -cyclodextrin,⁷ the benzil molecules are highly disordered. In contrast, fully ordered structures are often found in the resorcinarene-based solids, allowing detailed analysis of guest geometry.⁸

C-Methylcalix[4]resorcinarene (CMCR) is a versatile building block that can form supramolecular frameworks capable of accommodating molecules of photochemical interest.⁹ In part because of the flexible conformation of CMCR, it has been possible to generate a remarkable variety of different frameworks with rigid pyridyl-based spacers such as 4,4'-bipyridine and 4,4'-bis-(pyridyl)ethylene. They include the zero-dimensional capsule, one-dimensional wave-like, two-dimensional brick-wall, and three-dimensional stepped networks.^{9–11} Notably, most resorcinarene-based frameworks have been constructed with the rigid pyridyl-based linker molecules. Though flexible pyridyl spacers such as 4,4'-bis-(pyridyl)ethane and 4,4'-bis-(pyridyl)propane have also been employed to assemble CMCR-based networks,¹² the resulting frameworks were found not to include large molecules such as benzil.

No luminescence was observed in a reported series of benzil/CMCR inclusion compounds with conjugated linkers.⁸ Our modified strategy is to use a nonconjugated spacer with limited flexibility, which allows flexing of the resorcinarene node yet retains the rigidity required to produce a large cavity. We here describe the first CMCR framework based on a bis-imidazol-based linker molecule. By use of the 1,4-bis(imidazol-1-yl-methyl)benzene (bix) spacer (Scheme 1),



prepared as described in the literature,¹³ a new solid CMCR·2bix·2benzil **1** was obtained that incorporates nanosized benzil columns, and its spectroscopic properties were investigated.

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Good quality crystals of **1** were obtained by slow room-temperature evaporation of an ethanol solution of CMCR/bix/benzil with a 1/2/2 ratio of the components.¹⁴ No other types of crystals were obtained. Low temperature (90 K) X-ray diffraction analysis shows that **1** consists of a one-dimensional hydrogen bonded network.¹⁵ The CMCR molecules adopt a bowl conformation with four intramolecular hydrogen bonds along the upper rim of CMCR [$O1 \cdots O8 = 2.758(2)$ Å, $O1-H1 \cdots O8 = 166(2)^\circ$; $O2 \cdots O3 = 2.811(2)$ Å, $O2-H2 \cdots O3 = 169(2)^\circ$; $O5 \cdots O4 = 2.785(2)$ Å, $O5-H5 \cdots O4 = 163(2)^\circ$; $O6 \cdots O7 = 2.880(2)$ Å, $O6-H6 \cdots O7 = 172(2)^\circ$]. Adjacent CMCRs are connected by two bix linkers through O–H \cdots N hydrogen bonds [$O3 \cdots N3 = 2.655(2)$ Å, $O3-H3 \cdots N3 = 171(2)^\circ$; $O4 \cdots N7 = 2.643(2)$ Å, $O4-H4 \cdots N7 = 174(2)^\circ$; $O7 \cdots N5a = 2.602(2)$ Å, $O7-H7 \cdots N5a = 169(2)^\circ$; $O8 \cdots N1a = 2.617(2)$ Å, $O8-H8 \cdots N1a = 165(2)^\circ$; $a = x - 1, y, z + 1$] into a one-dimensional buckled polymer chain along the [010] direction (Figure 1),

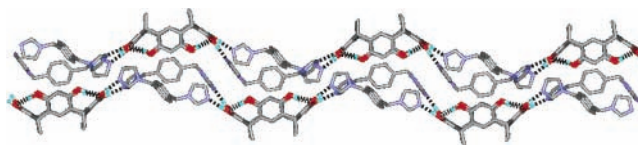


Figure 1. Double-buckled chainlike polymer formed by CMCR and bix.

in which the CMCR molecules are all oriented in the same direction. It is distinct from the commonly observed wavelike polymer formed by CMCR and rigid pyridyl spacers,^{9b,16} in which the CMCRs are directed in up-and-down fashion, but shows similarity with the rodlike polymer CMCR·2bipy·4-bromobiphenyl.¹⁷

The two bix spacers bridging the CMCR nodes display trans and gauche conformations. Two adjacent chains are

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(14) CMCR (0.05 mmol, 27.2 mg), 1,4-bis(imidazol-1-yl-methyl)benzene (0.1 mmol, 20.8 mg), and benzil (0.1 mmol, 21 mg) were mixed in 5 mL of ethanol solution and heated until the solution became clear. The solution was filtered and allowed to stand. Orange prismatic crystals of **1** were obtained from the filtrate at room temperature after 1 week.

shifted by half a period relative to each other such that the central phenyl ring of the gauche conformational bix is located within the bowl cavity of the CMCR in an adjacent chain, generating a double buckled polymer (Figure 1). The central phenyl plane of the gauche bix spacer is approximately parallel to the principal rotation axis of CMCR and interacts with the CMCR by way of C–H··· π contacts.

Neighboring double-buckled polymer assemblies pack in the (011) plane. CMCR molecules in adjacent bichains are arranged such that the lower rims face each other with only a small offset to give rise to a layer motif with a large guest-accessible void. This “out-of-phase” arrangement leads to voids that accommodate four benzil guests, two-by-two related by an inversion center (Figure 2).

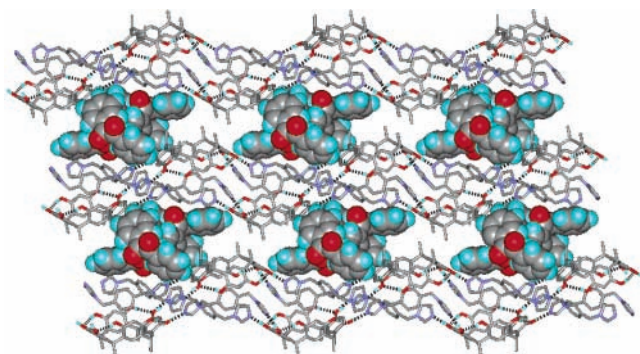


Figure 2. Layer motif formed by double-buckled chainlike polymers, leaving a large cavity including four benzil molecules.

To our knowledge, this is the largest two-dimensional void observed in any CMCR framework at the present time. One of the advantages of the buckled-chainlike frameworks is that the cavity size can be tuned during the assembly process through a mutual shift of the polymer along the parallel and perpendicular directions in the layer plane. Though the wavelike polymer here occurs in an out-of-phase arrangement, the wavelike polymers known so far all show the in-phase motif, making the cavities relatively small, while the out-of-phase arrangement observed in **1** gives rise to a large cavity. The four benzil molecules within each layer are held together by intermolecular interactions, including strong π – π stacking, with interplanar and center to center distances of

(15) Crystal data. Compound **1**: $C_{88}H_{80}N_8O_{12}$; $M_r = 1441.60$, triclinic, space group $P1$, $a = 14.9262(15)$, $b = 15.3584(10)$, $c = 17.1309(13)$ Å, $\alpha = 111.443(4)^\circ$, $\beta = 95.318(3)^\circ$, $\gamma = 90.261(3)^\circ$, $U = 3636.4(5)$ Å³, $Z = 2$, $D_c = 1.317$ Mg/m³, crystal size $0.26 \times 0.18 \times 0.10$ mm³, μ (Mo K α) = 0.088 mm^{–1}, $F(000) = 1520$, GOF = 0.917. Among 48 602 reflections, 20 192 reflections are unique ($R_{int} = 0.0612$). The final R_1 and wR_2 are 0.0465 and 0.0936, respectively, for 1294 parameters and 11 599 reflections [$I > 2\sigma(I)$]. Data were collected on a Bruker SMART 1000 CCD with Mo K α radiation ($\lambda = 0.71073$ Å) at 90(1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on F^2 using the SHELXL 97 program.

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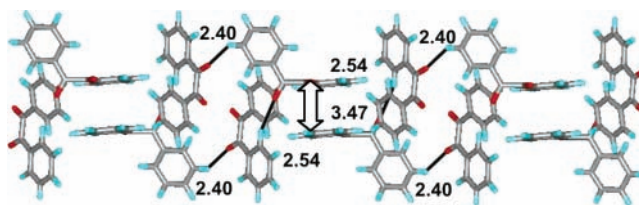


Figure 3. One-dimensional nanosized benzil column. Intermolecular interactions are indicated.

3.47 and 3.56 Å, respectively (Figure 3), and C–H···O interactions between carbonyl groups and phenyl rings. The tetramers in successive layers are linked into infinite rods along the [100] direction by way of C–H···O interactions (Figure 3). The channels in which the rods are located have a volume corresponding to 35% of the crystal space (Figure 4a). The nanosized rods have a rectangular cross-section with

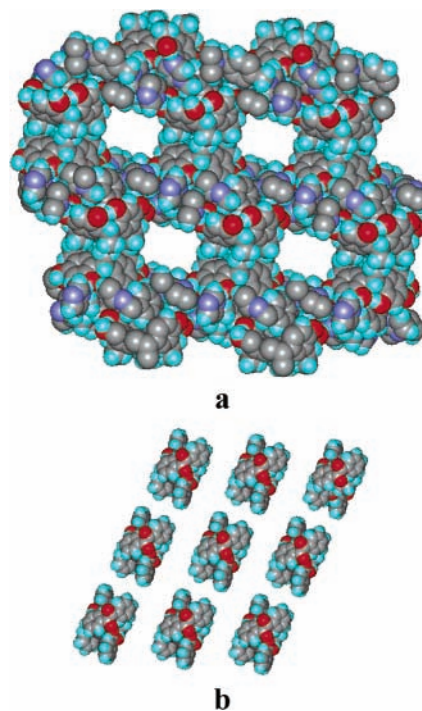


Figure 4. (a) Packing diagram of **1**, showing one-dimensional rectangular channels along the a direction. (b) Nanosized benzil columns viewed along the channel direction.

a dimension of 11.2 Å \times 9.7 Å and are well separated by the host framework (Figure 4b). Nanosized benzil columns have not been observed before, though benzil monomers and dimers have frequently been found in supramolecular frameworks.⁸

The two independent benzil molecules in **1** are fully ordered, the O=C–C=O torsion angles being 97.3 and 105.2° . These values fall in the range reported for neat benzil crystals and benzil inclusion compounds⁸ but significantly differ from one another.

The time-resolved phosphorescence spectrum of **1**, measured at 77 K,¹⁸ is shown in Figure 5.

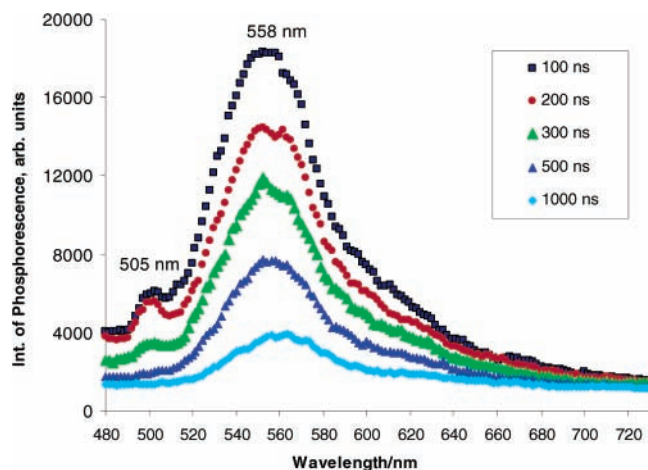


Figure 5. Low-temperature (77 K) time-resolved phosphorescence emission spectra from an air-equilibrated sample of **1**.

It displays both a weak and a strong emission, peaked at 505 and 558 nm, and assigned to delayed fluorescence and phosphorescence, respectively. In comparison with pure benzil microcrystals emitting at 524 nm, a significant red shift occurs in **1**, as observed for benzil absorbed within host materials such as calixarenes and cyclodextrins.^{4h,5} This red shift differs from that found in calix[6]arene and calix[8]arene hosts,⁵ indicating the pronounced influence of the host

(18) Luminescence measurements at room temperature gave exceedingly weak signals. The instrument for luminescence measurement has been described in ref 5.

environment on the photobehavior of the guests. Benzil in **1** was found to luminesce with a lifetime of 580 ns (Figure 5), which is much shorter than that of neat benzil, which has a lifetime of 145 μ s at room temperature,⁵ but nevertheless a behavior different from that of benzil inclusion compounds with conjugated linkers⁸ in which the luminescence appears fully quenched. It is well-known that hosts such as calixarene and cyclodextrin can prevent oxygen quenching of the emission that occurs in solutions, thereby enhancing the lifetime of benzil. The emission quenching of benzil in the imidazole-linker-supported CMCR framework, evidenced by the comparison with neat benzil, suggests the presence of an alternative deactivation pathway, which may be due to the energy transfer from the guest to host framework. A further investigation of the quenching mechanism is under way.

In summary, a novel framework based on the CMCR and a flexible imidazole-based linker has been constructed. It contains large channels, capable of including nanosized benzil columns. The great variety of aggregation of benzil observed in supramolecular crystals is a nanoscale equivalent of crystal polymorphism that merits further attention in the study of molecular packing modes.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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