Microporous Materials

A 3D Hybrid Network Containing Large Spherical Cavities Formed through a Combination of Metal Coordination and Hydrogen Bonding**

*Reyes García-Zarracino and Herbert Höpfl**

Dedicated to Professor Heinrich Nöth on the occasion of his 75th birthday

Assembling organic, organometallic, and/or inorganic building blocks to supramolecular structures through metal–ligand binding,[1] hydrogen bonds,[2] or π–π interactions[3] has become a powerful tool for the generation of large cagelike molecules or microporous substances with nanoscale cavities. Although important progress has been made in the construction of such assemblies by applying any one of these intermolecular interactions individually, a lot of research dealing with combinations of two or all three of them can still be carried out, thus allowing the construction of an almost infinite number of new supramolecular entities.[4]

Here, we report how a three-dimensional (3D) hybrid network containing large spherical cavities can be formed by the two-step self-assembly of 2,5-pyridinedicarboxylate and di-*n*-butyltin(IV) in a mixture of water and ethanol by using a combination of metal coordination and hydrogen-bonding interactions. We also describe the inclusion of hydrophobic molecules in this microporous material.

The preparation of the trinuclear macrocyclic complex $[\{(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{D})\}_3]$ (**2**; 2,5-pdc = 2,5-pyridinedicarboxylate; D = Lewis base, see below), which is similar to the synthesis of the recently reported, structurally related trimer $[\{(n\mathrm{Bu})_2\mathrm{Sn}(1,3\text{-bdc})\}_3]$ (**1**; 1,3-bdc = 1,3-benzenedicarboxylate), was carried out by the equimolar combination of di-*n*-

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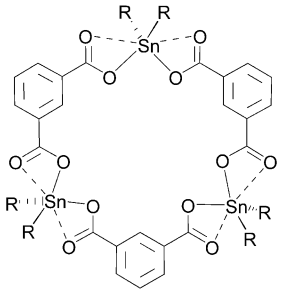
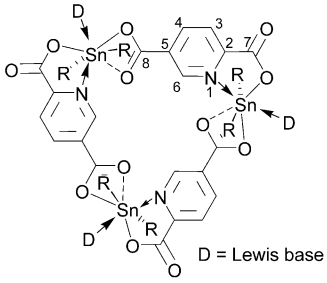


1 R = *n*Bu



2 R = *n*Bu

butyltin(IV) oxide and 2,5-pyridinedicarboxylic acid in a 5:1 solvent mixture of toluene and ethanol (72% yield).[5]

The formation of a 1:1 complex has been proved by integration of the ^{1}H NMR spectrum in CD_3OD. In contrast to **1**, complex **2** exhibits a five-membered NCCOSn chelate ring, with a N→Sn coordinative bond, whose presence in the complex can be shown by a downfield shift of the signal for the carbon atom in the *para* position relative to the pyridine nitrogen atom.[6] According to the ^{119}Sn NMR spectrum recorded in CD_3OD, the coordination number of the tin atom is seven ($\delta = -412$ ppm),[7] however, the signal is broadened, which indicates that the solvent molecules are interacting with the tin atom in a rapid-exchange equilibrium. That the structure is indeed cyclic in solution is evidenced by the FAB$^+$ mass spectrum, in which peaks of relatively high intensity at m/z 1194.22 and 1136.15 corresponding to the molecular ion of trinuclear $[\{(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})\}_3]$ (**2**) and the corresponding ion formed through the loss of a *n*Bu group have been detected.

Crystallographic studies of crystals obtained from solutions in DMSO and MeOH showed that this structure is maintained in the solid state and that the heptacoordination of the tin atoms can be achieved either by coordination of solvent molecules like DMSO to the tin atoms, thus giving a crystal lattice with discrete molecules of the composition $[\{(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})(\text{DMSO})\}_3]$, or by intermolecular C=O→Sn coordination between neighboring molecules, giving a 2D polymeric coordination network of the composition $[\{[(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})]_3\}_n]$.[8]

Interestingly, recrystallization of the latter compound in the presence of ethanol and water leads to a change in the molecular and/or supramolecular structure, since the solid-state IR spectrum changes significantly in the region corresponding to the vibrations of the carboxylate groups. While the spectrum of $[\{[(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})]_3\}_n]$ reveals strong absorptions at $\tilde{\nu} = 1642$, 1604, 1404, and 1361 cm^{-1}, which correspond to the symmetric and antisymmetric carboxylate stretches,[5] the spectrum of the new compound shows bands at 1687, 1609, 1398, and 1333 cm^{-1}. New absorptions at $\tilde{\nu} =$ 2665 and 2552 cm^{-1} indicate the presence of hydrogen bonding within the structure, most probably involving water molecules coordinated to the tin atoms. In further experiments we discovered that a compound with the same characteristics can be prepared more readily from di-*n*-butyltin(IV) dichloride and the potassium salt of the ligand in a mixture of ethanol and water (see Experimental Section). Apparently, between zero and three ethanol molecules per trinuclear complex can be included in the solid state, as revealed by solution-state ^{1}H NMR spectra recorded on several occasions for different series of crystals. It seems that the number of ethanol molecules in the crystal lattice depends on the ethanol/water ratio used in the crystallization process, which indicates that the ethanol molecules are most probably located at interstitial sites in the crystal structure; these sites may be only partially filled and/or filled by additional water molecules instead of ethanol. The fact that all crystals obtained were cube-shaped and had the same unit cell (about 20 crystals have been examined), confirms this supposition. These observations and the detailed X-ray crystallographic study performed on one of the monocrystals showed their composition to be $[\{[(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})(\text{H}_2\text{O})]_3 \cdot 3\,\text{H}_2\text{O} \cdot y\,\text{EtOH}\}_n]$ (**3**, $0 < y < 3$); a crystal where $y = 3$ is discussed herein.

The crystal structure of $[\{[(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})(\text{H}_2\text{O})]_3 \cdot 3\,\text{H}_2\text{O} \cdot 3\,\text{EtOH}\}_n]$ consists of a chiral, highly symmetrical 3D hybrid network containing trinuclear complex molecules, in which each tin atom is strongly coordinated by one water molecule, $d(\text{Sn-O}) = 2.287(4)$ Å.[5] The macrocycles are arranged in such a way that large spherical cavities are formed, whose centers are located at the 0,0,0 and $^1/_2,^1/_2,^1/_2$ positions in the cubic unit cell (space group $I23$).[9a] The unit cell of the title compound contains a capsule with nanometer dimensions (diameter ≈3.5 nm) being formed through hydrogen-bonding interactions between eight of the cyclotrimeric molecules (Figure 1).

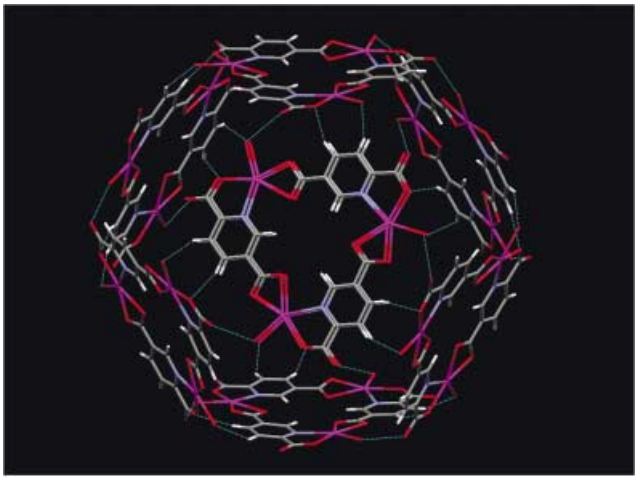


Figure 1. The unit cell of $[\{[(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})(\text{H}_2\text{O})]_3 \cdot 3\,\text{H}_2\text{O} \cdot 3\,\text{EtOH}\}_n]$ viewed along the [111] direction showing one of the capsules present in the crystal lattice (*n*Bu groups and uncoordinated solvent molecules have been omitted for clarity.

Each capsule consists of 24 $n\text{Bu}_2\text{Sn}$ units and 24 ligand molecules giving a total of 48 starting components, which are held together by covalent coordination bonds to form $[\{(n\text{Bu})_2\text{Sn}(2,5\text{-pdc})(\text{H}_2\text{O})\}_3]$ and a total of 36 hydrogen bonds of three different types to form the sphere: C–H···O interactions between one of the exocyclic aromatic CH groups and the oxygen atoms of the Sn–OH_2 water molecules

(2.58 Å, 3.38 Å, 142°), C-H···O interactions between the second exocyclic aromatic CH group and the oxygen atoms of the chelate ring (2.45 Å, 3.33 Å, 154°), and O–H···O hydrogen bonds between the Sn–OH_2 water molecules and the uncoordinated carbonyl oxygen atoms (2.80 Å). Each trinuclear complex is involved in a total of 18 hydrogen bonds in the crystal lattice (Figure 2), which combine to form the 3D

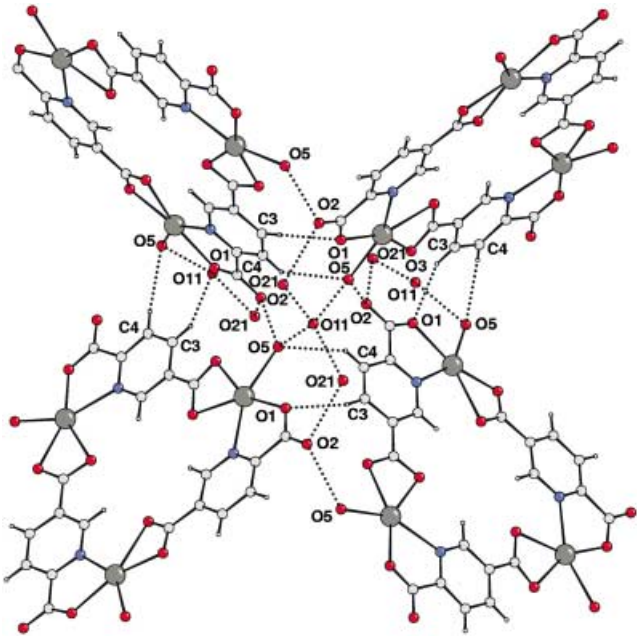


Figure 2. The intermolcular hydrogen-bonding interactions between $[\{(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})\}_3]$ and uncoordinated solvent molecules present in the crystal lattice of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3\cdot 3\,\mathrm{H_2O}\cdot 3\,\mathrm{EtOH}\}_n]$. Oxygen atoms O11 correspond to uncoordinated water molecules and O21 to uncoordinated ethanol molecules. The hydrogen-bonding pattern shown is identical to the one found for the other two tin atoms in each complex molecule. The aliphatic groups of the tin complexes and ethanol molecules have been omitted for clarity.

network, and additionally in six further O–H···O hydrogen bonds to three ethanol and three water molecules (2.71–2.79 Å), which strengthen the union between the capsules in the 3D hybrid structure.

The capsules in the crystal lattice exhibit a body-centered-cubic packing motif in the solid state. However, the spherical supramolecular arrangements found in this crystal lattice can not be identified as isolated capsules, unlike for fullerenes. In this case, they are found as species that share faces with neighboring units, rather like the arrangement in a honeycomb. The eight trinuclear molecules of each capsule occupy the hexagonal faces of a truncated octahedron,[1f,10] in which the centers of two opposite faces are separated by a distance of 21.5 Å. Thus, the overall crystal structure can be described as a 3D network built up from the 3D union of truncated octahedra sharing all of their eight hexagonal faces with neighboring polyhedra.

Due to the 3D arrangement described above, half of the 48 butyl groups of one capsule are orientated into its interior, while the other half contributes to the filling of another eight neighboring capsules. Although in each capsule 24 butyl groups are oriented into the interior of the cavity, there still remain very large voids in the center, which have a volume of 1850 $Å^3$.[11] It should be mentioned that this is the only type of void present in the crystal structure and that their combined volume forms 24% of the crystal lattice volume; this space can be used to include guest molecules (see below). In the absence of guest molecules (other than solvents of crystallization), only smears of electron density could be detected within the cavities, which in this case therefore are most probably occupied by water molecules. Assuming a volume of 30 $Å^3$ for a single water molecule in the liquid phase, a maximum of 61 water molecules may be present per void.[12]

If the hydrogen-bonded, noncoordinated water and ethanol molecules present in the crystal lattice of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3\cdot 3\,\mathrm{H_2O}\cdot 3\,\mathrm{EtOH}\}_n]$ are omitted, channels of two different sizes can be identified along the [100], [010], [001], and [111] directions of the crystal lattice, whose bottlenecks correspond to the access windows into the interior of the capsules. Along the [100], [010], and [001] directions, the narrowest diameters of the channels are 6.3 Å, while along the [111] direction the diameter is 1.7 Å and corresponds to the diameter of the cavity localized in the center of the macrocyclic $[\{(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})\}_3]$ (**2**) rings (Figure 3).

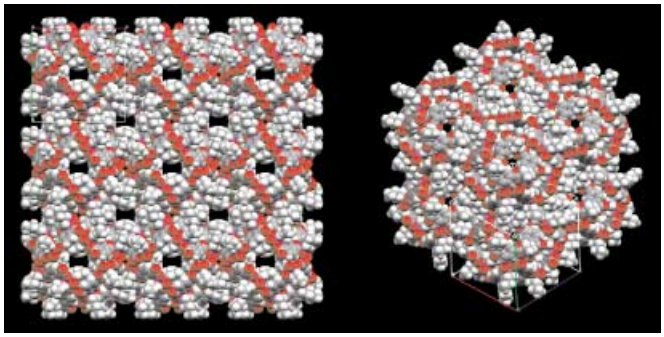


Figure 3. Channels along the [100], [010], [001], and [111] direction of the crystal lattice of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3\cdot 3\,\mathrm{H_2O}\cdot 3\,\mathrm{EtOH}\}_n]$ are observed when uncoordinated solvent molecules are omitted.

To evaluate the capacity of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3\cdot 3\,\mathrm{H_2O}\cdot y\,\mathrm{EtOH}\}_n]$ to act as a host for guest molecules, two different kinds of experiments have been carried out. First, a thermogravimetric analysis has been carried out to study the evacuation of the solvent molecules present at the intersitial sites. A continuous loss of weight starting at 30 °C is observed, which approaches 16.5% at 275 °C, after which decomposition occurs. However, during thermal treatment under vacuum the crystal lattice collapses at relatively low temperatures (< 100 °C). X-ray crystallography proves that the crystalline 3D hybrid network was transformed into an amorphous material. To evaluate the porosity of this material, crystals of the title compound were thermally treated for a period of 1.5 h (180 °C at 10 Torr) and then exposed to vapors of ethanol and THF. In both cases only a small quantity of guest molecules were included, however, in the presence of gaseous methylamine combined with THF (2 M solution in THF), a total of four molecules of

$MeNH_2$ and one molecule of THF were included for every molecule of **2**, as shown by an integration of the ^1H NMR spectrum in CD_3OD. Therefore, assuming a volume of 48 Å^3 for $MeNH_2$ and of 135 Å^3 for THF, a total of 327 Å^3 of free space per complex molecule is available. For comparison, the analogous space in the title compound is $1850/4 = 460$ Å^3. Studies in order to detail the function of the methylamine in the cavity formation are under way.

Cocrystallization experiments were also used to evaluate the host-binding capacity of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3 \cdot 3\,\mathrm{H_2O}\cdot y\,\mathrm{EtOH}\}_n]$; diphenylmethane, triphenylmethane, sodium tetraphenylborate, and triptycene have been added to a solution of the starting materials in ethanol/water to form the tin complex. Since the 24 butyl groups oriented to the interior of the spherical cavities generate a hydrophobic environment, hydrophobic guests were initially studied. In all four cases a crystalline material was obtained, whose unit cell dimensions were identical to the ones found for $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3 \cdot 3\,\mathrm{H_2O}\cdot 3\,\mathrm{EtOH}\}_n]$. In all cases, electron density was located in the interior of the cavities, which indicates the presence of the guest molecules, however, due to disorder of the guests within the cavities, a well-refined solution of the structure could only be obtained in the case of the triphenylmethane inclusion complex.[9b] That in all four cases inclusion occurred was shown by integration of the ^1H NMR spectra of samples dissolved in CD_3OD. The guest molecules were included with different stoichiometries. In the case of diphenylmethane, an average of 2.5 molecules were included per capsule, such that 695 Å^3 of the available 1850 Å^3 were occupied; the remaining space is most probably filled by water molecules. In the other cases, 1.5 molecules of triphenylmethane (600 Å^3), one molecule of sodium tetraphenylborate (486 Å^3), and three molecules of triptycene (1260 Å^3) were found to be present in each void. Figures 4 and 5 give two views of the host–guest complex with triphenylmethane: Figure 4 shows one capsule occupied by two of the guest molecules, while Figure 5 provides a cross-sectional view of a capsule showing one guest molecule. In this case only water molecules (no ethanol molecules) have been found in the hydrogen-bonded network, which confirms the observation that the amount of ethanol molecules can indeed be zero. Although the void should be large enough for the inclusion of C_{60}, all attempts to prepare this inclusion complex have been unsuccessful so far, one of the problems being the insolubility of C_{60} in a mixture of ethanol and water.

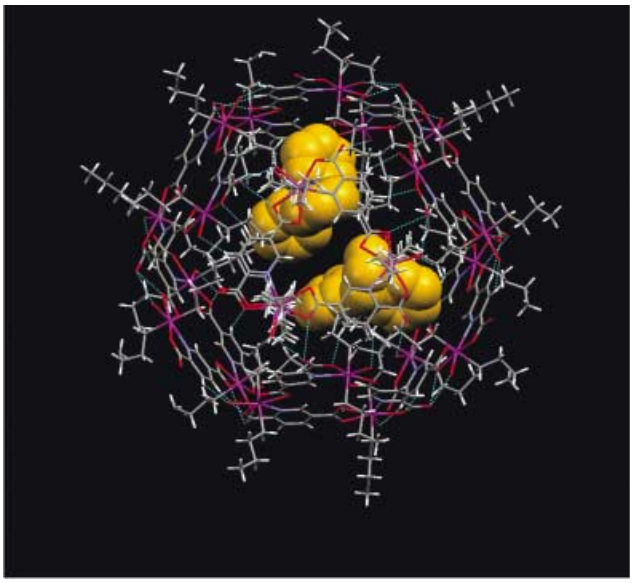


Figure 4. Inclusion of 2 equivalents of triphenylmethane in one of the capsules present in $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3 \cdot 3\,\mathrm{H_2O}\cdot 3\,\mathrm{EtOH}\}_n]$. Uncoordinated solvent molecules have been omitted for clarity.

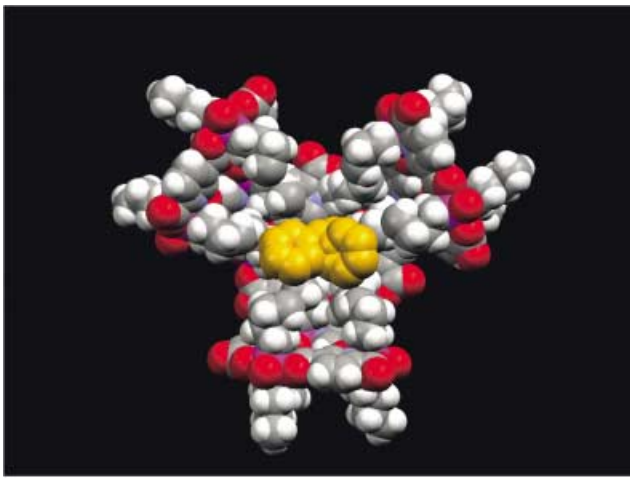


Figure 5. A cross-sectional view of the capsule shown in Figure 4 with one guest molecule.

In conclusion, we have shown that interesting supramolecular structures with large internal spherical cavities can be obtained from simple starting materials by assembling them in two steps; first by metal coordinative bonding, and then by combining these "intermediates" through hydrogen-bonding interactions. The spherical cavities in the supramolecular structure of $[\{[(n\mathrm{Bu})_2\mathrm{Sn}(2,5\text{-pdc})(\mathrm{H_2O})]_3 \cdot 3\,\mathrm{H_2O}\cdot y\,\mathrm{EtOH}\}_n]$, whose size may be modulated varying the size of the organic substituents in the diorganotin groups, could be exploited further for the selective trapping of various guest molecules, the stabilization of labile reactive species, selective transport through channel systems, and for conducting chemical reactions by using the cavities as reaction vessels.

Experimental Section

2: A solution of 2,5-pyridinedicarboxylic acid (0.167 g, 1.00 mmol) and di-*n*-butyltin(IV) oxide (0.250 g, 1.00 mmol) was refluxed for 8 h using a Dean–Stark apparatus. After filtration of the light-yellow solid, the product was extracted with ethanol. The microcrystalline powder obtained after evaporation of the solvent is soluble in methanol, DMSO, and pyridine. Yield: 72%; m.p. 290°C (decomp).

3: A solution of di-*n*-butyltin(IV) dichloride (0.092 g, 0.30 mmol) in EtOH (2 mL) was added to a solution (6 mL) of 2,5-pyridinedicarboxylic acid (0.050 g, 0.30 mmol) and potassium hydroxide (0.034 g, 0.60 mmol) in EtOH/H_2O (3:1). After a few hours (though sometimes a few days) cubic, colorless crystals of **3** were formed. Crystals can be grown faster, if additional water is added to the reaction mixture after a few hours. According to the proportion of ethanol present in the reaction mixture, the quantity of ethanol

present in the crystal lattice varies as shown by integration of ^{1}H NMR spectra of samples dissolved in CD_3OD. Yield: 77%; m.p. 290°C (dec.).

Cocrystallization reactions to form the inclusion compounds were carried out by adding an excess of the guest (triphenylmethane, diphenylmethane, triptycene, or sodium tetraphenylborate) dissolved in an EtOH solution.

X-ray diffraction studies were carried out on a BRUKER-AXS APEX diffractometer with a CCD area detector ($\lambda Mo_{K\alpha} = 0.71073$ Å, monochromator: graphite). Frames were collected at $T = 100$ K via ω-rotation ($\Delta/\omega = 0.3°$) at 10 s per frame.[13] The measured intensities were reduced to F^2 and corrected for absorption with SADABS.[14] Structure solution, refinement, and data output were carried out with the SHELXTL-NT program package.[15] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions using a riding model. Figures were created by the CRYSTALS[16] and MERCURY[17] software packages. Hydrogen-bonding interactions and voids in the crystal lattice were calculated by PLATON.[11]

CCDC-219315 and -219316 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[8] These results will be published in detail elsewhere.

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