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Porous Organic Molecular Frameworks with Extrinsic Porosity: A Platform for Carbon Storage and Separation

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The assembly of porous organic molecular frameworks (POMFs), which typically evidence common feasibility and compatibility, purification, and regeneration at practical conditions, remains a strategic challenge in modern materials science and is crucial for their favorable applications in biological, medical, and environmental realms. However, instructive knowledge of well-organized POMF assembly by supramolecular interactions is, in general, ambiguous to date. Nevertheless, a significant advance in controlled POMF assembly has been recently achieved. This Minireview highlights these approaches, with a particular focus on the design of molecular constituents and assembly strategies. We also look beyond the field of solid-state POMF materials into the assembly and recognition in solution, thus covering recent advances in POMFs based on material design and applications in carbon storage and separation.

1. Introduction

There is ever-increasing concern over the sustainability and security of energy supplies, coupled to the problems of environmental pollution and global warming associated with the combustion of fossil fuels, which currently produce excess emissions of CO_2, SO_x, NO_x, and heavy metals. CO_2 is also a major contributor to climate change and ocean acidification.[1] Implementation of carbon capture and sequestration technologies has been proposed as a means of enabling the continued use of fossil fuels in the short term, while renewable energy sources gradually replace the existing infrastructure.[2] Thus, the safe and efficient capture of CO_2 and other toxic gases and substrates are key issues in the development of new energy portals and for the reduction in greenhouse gas emissions. Likewise storage, separation, and purification of carbon values underpin much of modern industry and technology. There are, therefore, significant impetuses to develop novel separation methods and materials.

Porous materials, such as porous carbon, zeolites, and porous framework materials, are prominent absorbents for molecular storage and separation, as well for advanced technology in energy and environmental science. Porous organic molecular frameworks (POMFs), in particular, have been advanced as new chemistry materials thanks to their low framework density resulting from the use of light elements (typically H, C, N, O, B), low toxicity, as well as their controlled assembly taking advantage of the crystal engineering concepts.[3–7] POMFs presenting permanent porosity secure inherent design flexibility since the choice of organic constituents can be varied and designed to incorporate multifunctional components. Such materials can be divided roughly into intrinsic and extrinsic POMFs. Intrinsic porosity is defined as porosity that is inherent in the molecular constituents, such as shape-persistent voids, clefts, or cavities. And extrinsic porosity is only realized by means of molecular construction and/or packing. POMFs can be modulated according to design and synthesis, and are exemplified by organic zeolites based on dipeptides,[8,9] porous networks constructed from molecular tectonics,[10] organic nanoporous magnets derived from polychlortriphenylmethyl radicals,[11] open frameworks assembled from multiple carboxylic acids and organic amines,[12] and organic cages.[13]

However, prediction on the packing of even the simplest molecular assembly is a daunting challenge because of the fact that intermolecular forces for upholding the molecules are poorly interpreted, especially for organic materials.[14–16] Most hydrogen bonds are primarily electrostatic in nature and

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flexible in strength according to different electron donors and acceptors. At the same time, notwithstanding their weak bonding, hydrogen bonds have been approved as directional and predictive intermolecular cohesive forces in molecular packing.[17–19] Hydrogen bonds, as main driving forces in assembly of organic molecules featuring O- and N-donor functional groups, or a mixture of the two, are particularly promising and viable.[20–25] Notably, O- and N-donor interplay has been confirmed to be a type of stable and robust driving force for the exploitation of new solid materials and the well-defined hydrogen bonds furnished in the molecular materials have been found crucial for the generation of porous supramolecular aggregates.[26–29]

2. General Concept

This Minireview focuses on a class of porous organic molecular frameworks (POMFs) with extrinsic porosity,[30–32] and represents the recent advances in the field of porous framework materials. POMFs with extrinsic porosity are defined by the porous space generated between the organic constituents. Thus, POMFs with intrinsic porosity which appears within the organic constituents, such as porous solids of calixarenes,[33,34] cyclodextrins,[35,36] and cucurbiturils,[37,38] as well as porous organic cage compounds,[13] will not be discussed. We also look beyond the field of solid-state POMF materials into the assembly and recognition in solution, since this wider perspective has not yet been reviewed.

The assembly of POMF materials with extrinsic pores depends greatly on the design of molecular constituents having various sizes, shapes, and functionalities, which decide the structure and property of the pore channels. Meanwhile, predictable and robust POMF architectures require design principles which guide assembly of the molecular constituents.[39] Hydrogen bonding, π–π, and halogen bonding interactions are dominant supramolecular forces by which self-assembly is guided to create predictably ordered networks in spite of the soft and flexible nature of these interactions. Moreover, POMF materials can be highly crystalline, which is an advantage not only for structural determination, but also for investigation of structure–property relationships. However, upon guest removal many POMF materials undergo phase changes to give close-packed structures, lose porosity, and/or undergo structure collapse resulting from the relatively weak supramolecular interactions which underpin framework structures.[40,41] Of particular interest, POMF materials based on primary hydrogen bonds[32,33] can be exceptionally robust and guest-independent, and are superior for applications in storage and separation.

3. Single-Component Porous Organic Molecular Frameworks

The assembly and adsorption properties of POMFs were firstly recognized through the crystallization of the organic molecule tris(phenylenedioxy)cyclophosphazene [TPP (**M1**), Scheme 1] by Sozzani and co-workers.[30,42,43] The organic molecular solid has shown permanent nanoporosity, although assembled exclusively by weak interactions, which enables the selective adsorption of CO_2 and CH_4 over N_2, O_2, and H_2. This aspect is an important proof-of-concept result since it confirms that stable, porous POMFs can not only be prepared, isolated, and studied, but can also be used for guest uptake, with discrimination and selectivity. The successful investigation of porous TPP molecular materials, to some extent, triggered a worldwide study of stable POMF materials assembled through hydrogen-bonding interactions. A phenomenal POMF material has recently been documented by Mastalerz and Oppel,[44] by using an optimized molecule triptycenetrisbenzimidazolone [TTBI (**M2**), Scheme 1] based on the criteria put forth by McKeown and co-workers.[45] The construction of **M2** forms a permanent porous crystal with a very high specific surface area (Langmuir model) of 3020 $m^2\cdot g^{-1}$ (Figure 1). This value is the highest reported surface area of any porous material consisting of discrete molecules. Furthermore, this material adsorbs a relatively high amount of H_2 (2.2 wt%; 77 K and 1 bar), and selectively adsorbs CO_2 (15.9 wt%; 273 K and 1 bar) over CH_4. Schröder et al. reported a POMF material based upon long-range interactions and it was derived from a functionalized dihydropyridyl species, 9,10-bis(4-((3,5-dicyano-2,6-dipyridyl)dihydropyridyl)phenyl)anthracene (**M3**; Scheme 1).[31] The assembly of the relatively bulky organic molecule incorporating multifunctional groups by hydrogen-bonding and π–π stacking interactions has generated an open framework material (**SOF-1**), which is stable up to 500 °C. The activated sample **SOF-1a** shows impressive adsorption selectivity with the order $C_2H_2 > CO_2 > CH_4 > N_2$, at low pressures (Figure 2).

Another thermally stable POMF material, **HOF-8**, based on functionalized multipyridyl constituents, has been assem-

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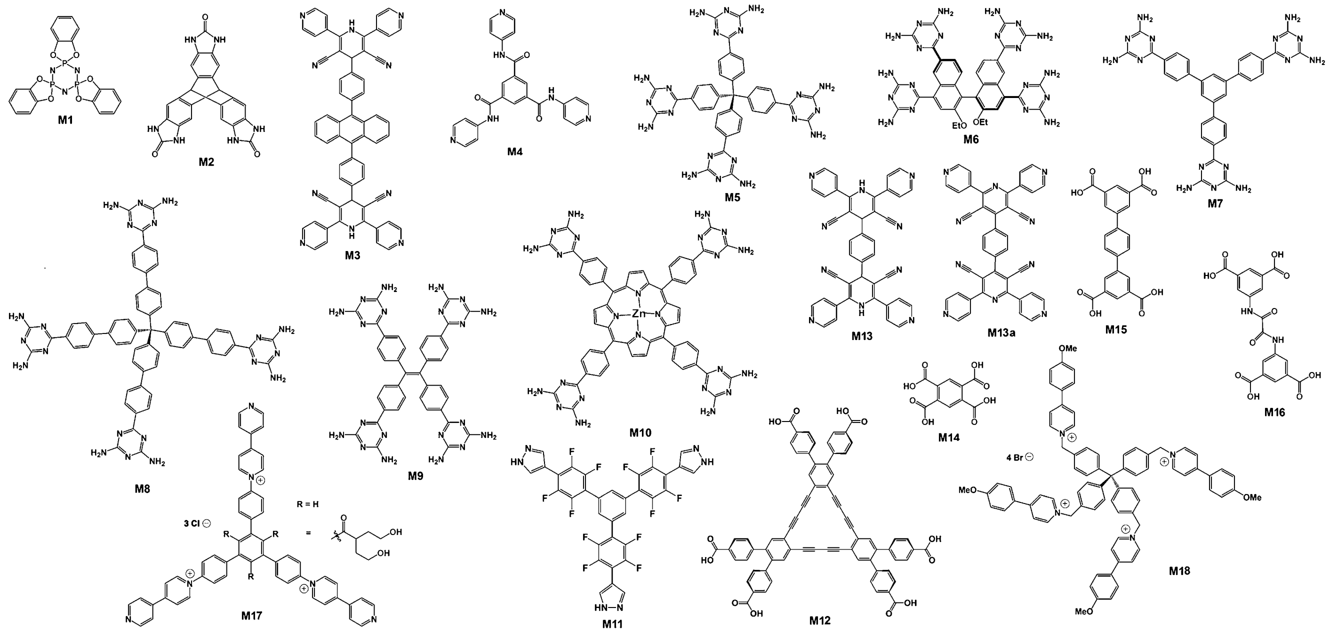

Scheme 1. The molecular constituents used for the porous organic molecular frameworks.

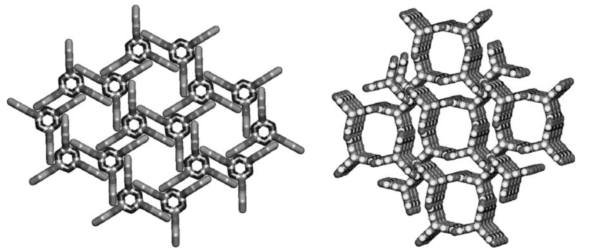

Figure 1. The 3D packing patterns of **M1** (left) and **M2** (right), showing their structural porosity. Color code: C, medium gray; N, dark grey, H, light grey.

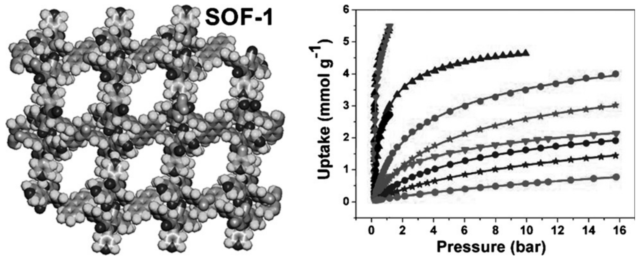

Figure 2. The 3D supramolecular structure of **SOF-1** (left) and gas adsorption isotherms of the activated sample **SOF-1a** (right; adapted from Ref. [31], copyright ACS). C_2H_2 (black), CO_2 (medium grey), CH_4 (dark grey), and N_2 (light grey) at 195 K (triangles), 270 (or 273) K (circles) and 298 K (stars).

bled from triangular N^1,N^3,N^5-tris(pyridin-4-yl)benzene-1,3,5-tricarboxamide (**M4**),[46] and presents mutual and interdigitated hydrogen-bonding interactions between the pyridyl and amide groups presented in **M4**. A two-dimensional (2D) honeycomb layered structure is thus formed, and these layers pack into a three-dimensional (3D) supramolecular framework structure through π–π interactions. **HOF-8** exhibits excellent stability against water and common organic solvents. More interestingly, the desolvated **HOF-8a** demonstrates permanent porosity with highly selective adsorption of CO_2 over N_2/H_2 (Figure 3), as well as adsorption of C_6H_6 over other hydrocarbons (i.e., *n*-hexane, cyclohexane, toluene, or pxylene) at ambient temperature. Of special note, the adsorption of CO_2 for **HOF-8a** at 298 K and 1 atm (57.3 cm^3-(STP)·g^{-1}) is higher than that of any other crystalline porous organic materials reported in the literature.[34,47,48]

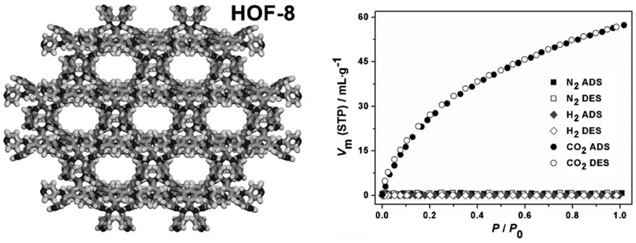

Figure 3. The 3D supramolecular structure of **HOF-8** (left) and gas adsorption isotherms of activated sample **HOF-8d** at 298 K (right; adapted from Ref. [31], copyright ACS). CO_2 (dark grey), H_2 (medium grey), and N_2 (black).

Chen et al. demonstrated the permanent porosity and adsorption ability of the POMF material **HOF-1** (Figure 4),[32] which was introduced earlier by Wuest and co-workers (**M5**).[49] **HOF-1** shows extraordinarily high and selective adsorption of ethylene over ethane at ambient temperature. Structural studies indicate that one of the amine groups of the 2,4-diaminotriazine moiety is involved in primary hydrogen bonding to construct the framework host, while the other amine group is exposed on the pore surfaces for potential interactions with guest molecules. By incorporating the same functional group on various central backbones (**M6**–**M10**),

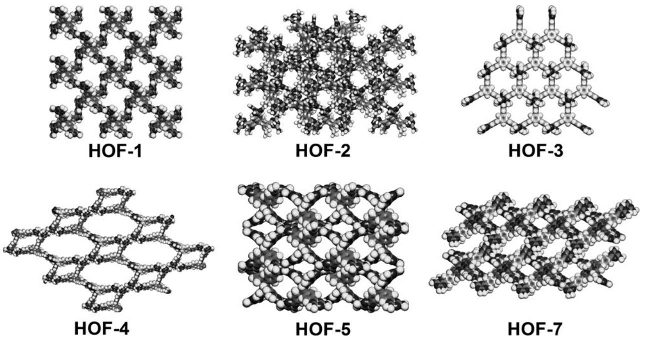

Figure 4. The structures of a series of HOF materials.

a series of molecular constituents have been designed to build POMFs (**HOF-2–HOF5** and **HOF-7**; Figure 4),[50–54] thus indicating that 2,4-diaminotriazine groups are viable for various POMF assembly thanks to the formation of mutual hydrogen-bonding interactions. These POMF materials have shown extensive selective adsorption of CO_2, CH_4, and small hydrocarbons. It is particularly worth mentioning that a homochiral POMF material, **HOF-2**, with permanent porosity and highly enantioselective separation of chiral secondary alcohols, of which separation for 1-phenylethanol was achieved with *ee* values of up to 92 %, has been constructed based on organic constituents incorporating central BINOL fragments.[50]

It has been demonstrated that functional groups, notably pyridyl and 2,4-diaminotriazine, are reliable in assembly. Pore size and function of these materials can be tuned by means of the design of organic constituents which lead to the porous materials having selective adsorption properties for CO_2 and small hydrocarbons. However, the coexistence of multiple hydrogen-bond donating and hydrogen-bond accepting groups, in some cases (i.e., **SOF-1** and **HOF-8**), brings indeterminacy to the hydrogen-bonding recognition, and increases the difficulty for POMF assembly. Moreover, molecular constituents with other types of functionality, for example organosulfates[39,55,56] and organophosphates,[57] which have shown great promise in hydrogen-bonding-directed assembly, are rarely used in the creation of POMF materials.

Miljaniæ and co-workers have achieved a fluorinated POMF material with a trispyrazole derivative (**M11**),[58] which affords an unusual and highly robust combination of hydrogen-bonding and ð···ð interactions. This material is thermally and hydrolytically stable and shows significant adsorption ability for hydrocarbons, CFCs, and fluorocarbons (ca. 75 wt %). Another exquisite example of a C_3-symmetric ð-conjugated macrocycle (phenylene triangle; **M12**) which assembles into a crystalline porous material gives a POMF with pore volume of about 58 %.[59] The structure of the POMF material includes three kinds of pores having different sizes and shapes. The activated POMF material absorbs CO_2 up to 96 $cm^3 \cdot g^{-1}$ at 195 K and 1 atm.

4. Multicomponent Porous Organic Molecular Frameworks

The development of single-component POMFs has been somewhat restricted by the design of appropriate molecular constituents and sometimes involves harsh reaction conditions, multistep syntheses, and the use of relatively expensive catalysts. However, if specific intermolecular interactions can be optimized and balanced, two-component and multicomponent POMF materials are achievable by molecular recognition between the functional organic constituents.[60–62] Schröder and co-workers have adopted a binary design strategy in which two different organic components, one possessing a hydrogen-bond donor and one possessing aa hydrogen-bond acceptor, which assemble to form a stable POMF. By means of this design strategy, new and interesting binary POMF materials have been effectively programmed.

The 1,4-bis-(4-(3,5-dicyano-2,6-dipyridyl)dihydropyridyl)benzene (**M13**) has been proven to form various porous networks with tertracarboxylic derivatives (**M14-16**) using the binary design strategy.[63] The resultant POMF materials (**SOF-5–SOF-7**), of which **SOF-6** and **SOF-7** are isostructural, display controlled structures and functions in terms of pore size and functionality. Within these materials, complementary N···H–O hydrogen bonds between pyridyl and carboxylic groups are dominant supramolecular forces. Of note, **SOF-7** exhibits excellent thermal stability, and solvent and moisture durability, as well as permanent porosity. The activated **SOF-7 a** shows a high CO_2 adsorption capacity (7.07 $mmol\,g^{-1}$ at 20 bar and 273 K; Figure 5) and selectivity over N_2, H_2, and CH_4, compared with other POMF materials assembled solely through hydrogen bonds. It has been confirmed that the decorated functional groups, amide and cyano, act as favorable binding sites for CO_2 molecules, thereby enhancing CO_2/CH_4 selectivity.

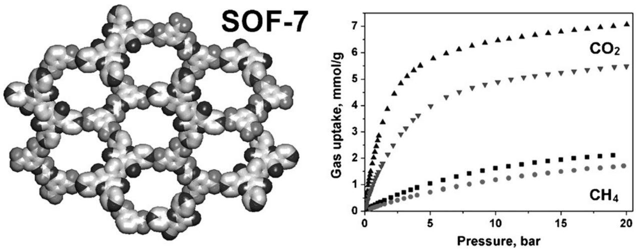

Figure 5. The 3D supramolecular structure of **SOF-7** (left) and gas adsorption isotherms of the activated sample **SOF-7 a** (right) up to 20 bar. CO_2 and CH_4 at 273 K (medium grey) and 298 K (dark grey).

Inspired by the success of the binary assembly method, reticular POMFs with various pore functionality can be engineered by means of the modulation of central backbones of organic constituents,[64] and further demonstrates the feasibility of binary design strategy by uncovering the structure–function relationship in related systems. It opens up new possibilities for the exploration of extended systems, as well as tertiary and higher component porous assemblies.

Furthermore, other types of viable and directional supramolecular forces, for example, halogen bonding, which can be somewhat stronger than hydrogen bonding, are also promising candidates for POMF assembly.[62,65] It is a rational and viable pathway to synthesize binary POMF materials using two different organic modules with complementary hydrogen-bond donating/accepting functional groups. This design strategy may open up new possibilities and push the boundaries in the synthesis of porous organic molecular frameworks.

5. Solution-Phase Porous Organic Molecular Frameworks

Cucurbit[*n*]uril[66,67] (CB[*n*]; $n = 5$–10) molecules represents a class of macrocyclic cavitands featuring a barrel-like shape and two carbonyl fringed portals (Figure 6). Because of the intrinsic molecular cavity of CB[*n*], gas uptake within CB[6] and CB[7], has been demonstrated by the group of Kim[37] and Atwood[38] et al. However, one conceptual class of solution-phase extrinsic porous organic molecular frameworks (POMFs) has recently been achieved by means of sacrificing the intrinsic porosity of CB[*n*], thus taking advantage of the inclusion property of their molecular cavity. In such a way, 2D nanoporous layers have been assembled through triangular organic molecules with long pendant groups, as illustrated in Figure 6.

Despite a number of solid-state POMFs having been reported, the assembly of highly soluble periodic POMFs in solution phase is still a great challenge. The assembly of a single-layer 2D honeycomb POMF in water has been achieved using CB[8] and 4,4′-bipyridin-1-ium (BP) derivatives (**M17**).[68] Molecular aggregation in water was monitored by 2D ^{1}H NMR diffusion ordered spectroscopy (DOSY) and electrospray ionization mass spectrometry (ESI-MS), and the microstructural information for the single-layer POMFs was revealed by solution-phase small-angle X-ray scattering (SAXS) and atomic force microscopic (AFM) studies. It has been concluded that 2D single-layer POMFs, which are facilitated by the homodimerization between CB[8] and BP-containing aromatic guests,[69] can be generated in water through a robust self-assembling strategy. The formation of solution-based POMFs offers unprecedented accessibility of 2D soft nanostructures.[70]

Further, a unique 3D POMF built by tetrahedral **M18** and CB[8], which cannot only exist in solution, but also can be maintained in the solid state.[71] Solidification of the POMF material has been accompanied with microcrystallization, and the microcrystals are soluable in water at elevated temperature and pressure, and therefore reflects the reversible feature of POMF assembly process. Moreover, the 3D POMF possesses high porosity with a void volume of about 77% (calculated based on model), and can attract a variety of anionic organic molecules, including dyes, drugs, peptides, nucleic acids etc., by electrostatic interactions in both solution and the solid state. Inclusion capacity of the 3D POMF has been performed based on systematic investigation of guest-induced fluorescence quenching, which further confirms the effective guest uptake of the material. Such guest inclusion and release properties at the heterogeneous solid–liquid phases make the 3D POMF material an attractive candidate for material applications, such as membranes, sensors and controlled delivery.

6. Summary and Outlook

We illustrate here a number of approaches which are now achievable to control the assembly of porous organic molecular frameworks (POMFs), in both the solid state and solution phase. Effective strategies, including single-component and complementary binary assembly of POMF materials, have been outlined. The directional and predictive intermolecular hydrogen bonds can be somewhat intricate, and to be fully understood much more in-depth research is required. In contrast, utilization of more exotic supramolecular interactions, such as halogen bonding, ð···ð interactions, and hydrophobicity, in POMF assembly will, as ever, provide new insights and inspiration for new systems. Most importantly, many long-standing prospects of applications in the arenas of industry, environment, biologicals, and medicine

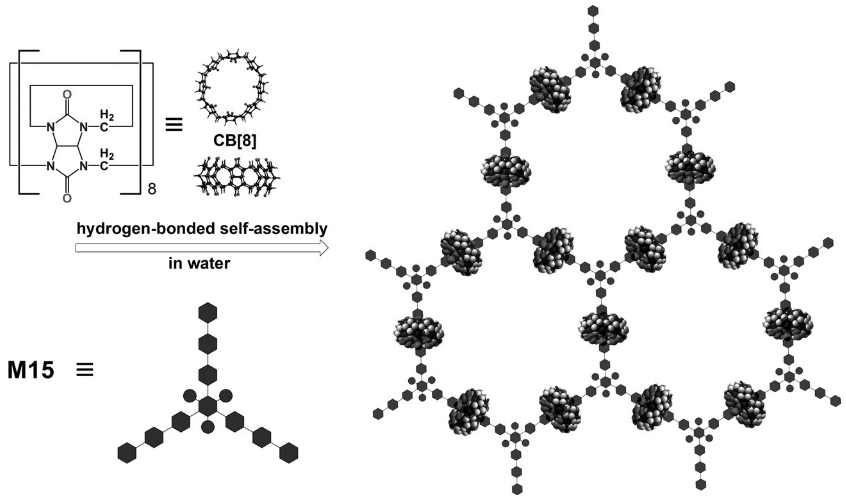

Figure 6. Supramolecular self-assembly of **M15** and CB[8] into honeycomb layers in water.

will develop into real-life technologies as synthetic porous chemistry materials become prevalent.

Acknowledgements

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