Rational Synthesis of Molecular Gyroids and their Structure-Derived Solid-State Properties

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A.H. Shoen discovered the gyroid, an infinitely-connected triply-periodic minimal surface that separates 3D space into a pair of enantiomorphic channels called single gyroids [1]. These gyroidal structures are ubiquitous in nature, appearing in various materials of different sizes. In fact, the gyroidal structure can be formed by atoms and bonds, corresponding to space discretization in geometry, as well as molecules and intermolecular interactions, and metal ions and ligands.

We have been working on the rational construction of gyroidal structures using polyhedral π -conjugated

molecules that consist of three π planes with normal vectors forming C_3 symmetry. It was found that the electrochemical crystallization of NDI (naphthalene diimide)- Δ resulted in single crystals of (TBA)_{1.5}[(-)-NDI- Δ] (TBA = tetrabutylammonium), where (-)-NDI- Δ forms a chiral single gyroid lattice due to its triangular molecular structure and intermolecular π - π overlap between the NDI moieties [3] (Fig. 1). The line graph consideration revealed that this lattice is identical to the hyper-kagome lattice of *S*=1/2 Mott dimers, exhibiting 3D spin frustration. Indeed, low-temperature magnetic and heat capacity measurements indicated the presence of a spin-liquid ground state [4,5].



Fig. 1. Molecular gyroid, formed by (-)-NDI- Δ .

Among microscopic gyroidal materials, the coordination gyroids, which consist of magnetic metal centers and ligands, have been explored for more than 20 years [2]. The gyroidal oxalate complexes are

the most investigated family due to their extensive magnetic properties. Recently, we examined the circularly polarized luminescence (CPL) for $[Ru(bpy)_3]I_2$ (1) and $[Ru(bpy)_3][M_2(ox)_3]$ (M=Zn (2) and Mn (3)). Whereas Compound 1 is a simple salt of $[Ru(bpy)_3]^{2+}$, 2 and 3 are the MOFs in which the chiral $[Ru(bpy)_3]^{2+}$ ions are encapsulated in a homochiral gyroidal skeleton of $[M_2(ox)_3]^{2-}$. Whereas the solution of 1 exhibited a weak CPL with a luminescence dissymmetry factor of $|g_{lum}|\sim 10^{-4}$, the CPL was significantly enhanced in the solid-state $1\sim 3$ with $|g_{lum}|=2x10^{-2}$ for 1, $4x10^{-2}$ for 2, and $1x10^{-1}$ for 3. The enhanced CPL in 3 was attributable to an energy transfer between the homochiral guest and host in 3 [6] (Fig. 2).



Fig. 2. Enhanced CPL in gyroidal oxalate complexes.

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