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Spray Drying for Making Covalent Chemistry II: Synthesis of Covalent−Organic Framework Superstructures and related Composites †

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Here we report a method that combines the spray-drying technique with a dynamic covalent chemistry process to synthesize zero-dimensional, spherical and microscale superstructures made from the assembly of imine-based COF nanocrystals. This methodology also enables the integration of other functional materials into these superstructures forming COF-based composites.

Covalent Organic Frameworks (COFs) are an emerging class of crystalline porous materials, where two-dimensional (2D) or three-dimensional (3D) architectures are formed from organic building blocks linked by dynamic covalent bonds (*e.g*. imine, boroxine, β-keto-enamine and azine).[1-3] These materials are characterized by their high porosity, high thermal stability and low mass density, which confer them potential for myriad applications, such as gas sorption and storage,[4-7] catalysis,[8-10] sensors[11-13] and optoelectronics.[14, 15] Seeking to exploit these possibilities, researchers have developed several fabrication methods for COFs, including not only the traditional solvothermal synthesis but also microwave,[16] microfluidic,[17] mechanochemical,[18] ionothermal,[19] and continuous-flow synthesis.[20, 21]

While many efforts have been devoted to the synthesis of new COFs and to their production methods, there is a growing interest in structuring these COFs at the micro/macroscopic scale forming more complex, high-order super- or mesostructures from the assembly of COF nanoparticles. As their Metal-Organic Framework (MOF) counterparts,[22, 23] these type of structures made from COF nanocrystals are especially attractive due to the possibility of (i) controlling the shaping and sizing of COFs at the micro/macroscale, two parameters that are very important to control for many applications; (ii) enhancing the initial performance *via* design of their morphology; and (iii) combining COFs with other materials to create functional composites, which can further expand the scope for applications.[24-27]

To date, there are a few studies based on the creation of COF superstructures. For example, Banerjee *et al*. synthesized a highly crystalline and porous COF in the form of hollow spheres that were used for immobilizing the enzyme trypsin.[28] In a more recent study, core-shell microspheres containing Fe_3O_4 nanoclusters were synthesized using a template assisted route. The resulting hybrid microspheres showed photothermal conversion ability after exposing them to near infrared light.[25]

Despite these advances, synthesis of higher-order COF superstructures is still challenging mainly due to the harsh conditions usually needed to synthesize highly crystalline COF nanoparticles. In these sense, we have recently reported that the spray drying method can be used to synthesize MOFs in the form of spherical hollow or compact superstructures made from the assembly of MOF nanoparticles.[29-32] Additionally, we have recently reported that spray drying is also an effective methodology to perform Schiff-base condensation reactions, either between discrete organic molecules or on the pore surfaces of MOFs.[33] Herein, we combine both achievements and extend the applicability of spray drying to synthesize imine-based COF nanocrystals while structuring them into spherical hollow superstructures. This strategy consists in a two-step process. In a first step, the spray drying allows the formation and shaping of amorphous imine-based polymer spheres. Then, in a second step, these spheres are subjected to a dynamic covalent chemistry to crystallize them under similar conditions to those reported by Dichtel *et al*.[34] Remarkably, after the crystallization step, the resulting superstructures preserve the initial size and morphology of the amorphous spheres. Further,

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