ASSEMBLY AND CO-ASSEMBLY OF COVALENT ORGANIC FRAMEWORK PARTICLES INTO ORDERED SUPERSTRUCTURES

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Assembly and co-assembly of colloidal particles offer a versatile strategy for creating ordered superstructures whose properties arise from the nature and spatial organization of their constituent building blocks [1]. Here, covalent organic frameworks (COFs) are shown to serve as colloidal building blocks that may assemble into unary ordered superstructures and co-assemble into binary ordered superstructures (**Figure 1**).

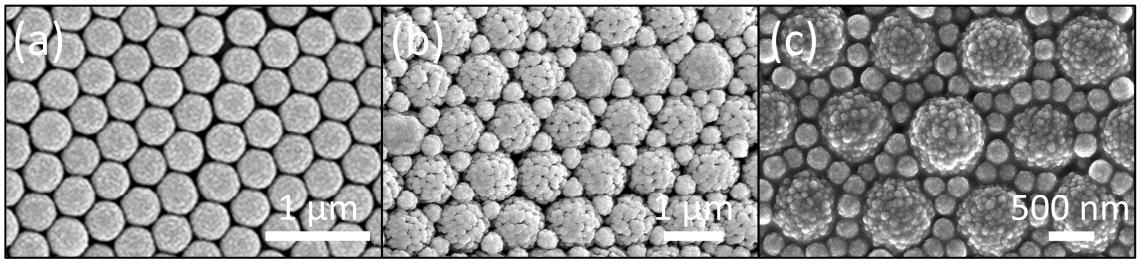

Figure 1. FE-SEM images of superstructures formed from (a) spherical TAPB-BTCA-COF particles (416 ± 7 nm); (b) co-assembly of spherical TAPV-DVA-COF particles with diameters of 946 ± 26 nm and 302 ± 6 nm; and (c) co-assembly of spherical TAPB-DVA-COF particles (946 ± 26 nm) and spherical TAPB-BTCA-COF particles (242 ± 7 nm).

Monodisperse spherical COF particles are demonstrated to assemble into crack-minimized, long-range ordered colloidal photonic crystals (PhCs) with an underlying face-centered cubic (*fcc*) arrangement [2]. Monodisperse spherical COF particles are further shown to co-assembly into binary ordered superstructures [3]. By tuning the particle size ratio, 2D COF-COF binary ordered superstructures with different stoichiometries (LS_2 and LS_6) are obtained, highlighting the entropic origin of the assembly process. The first example of co-assembly between COF and metal-organic framework (MOF) particles is also demonstrated.

These results expand the design space of porous materials by enabling the construction of complex superstructures from COF building blocks with diverse sizes, shapes, porosities, and chemical compositions. The structural diversity, modularity, and tunable physicochemical properties of COFs establish their assembly and co-assembly as a general platform for the preparation of colloidal ordered superstructures with emergent and potentially unprecedented functionalities.

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[1] Javier Fonseca, Li Jiao, Anna Broto-Ribas, Gurvinder Singh, and Angang Dong. Co-Assembly of Nanometer- and Submicrometer-Sized Colloidal Particles into Multi-Component Ordered Superstructures. *Soft Matter*, 2025, 21, 5583-5654

[2] Javier Fonseca, Lingxin Meng, Pedro Moronta, Inhar Imaz, Cefe López, and Daniel Maspoch. Assembly of Covalent Organic Frameworks into Colloidal Photonic Crystals. *J. Am. Chem. Soc.* 2023, 145, 37, 20163-20168

[3] Javier Fonseca, Tingchuan Zhou, Bingyang Lu, Jinlong Yang, and Xu Deng. Co-Assembly of Covalent Organic Framework Particles into Binary Ordered Superstructures. *J. Am. Chem. Soc.* 2025, 147, 32, 28617–28623