

# Synthetic Design of Porous Metal-Organic Frameworks

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Synthesis of technologically important materials such as crystalline porous solids is the key for emerging applications. Here, we seek to develop a versatile synthetic method (denoted as *urothermal* synthesis) based on the use of urea derivatives as solvents. One particular advantage of this method is that urea derivatives exhibit a range of bonding affinity for various metal sites, which is strong enough to allow them to bond competitively to metal sites during crystallization, and yet weak enough to be readily removed after synthesis to generate porosity and active metal sites. Such an integration of porosity and active metal sites can lead to applications of these materials as high capacity adsorbents for sequestration of carbon dioxides or as high-surface-area Lewis acid catalysts for petroleum-based chemical reactions. In one example, 1,3,5-benzenetricarboxylate (BTC) uses two of its three  $\text{-COO}$  groups to form a 3D framework with  $\text{In}^{3+}$  (top right) and within the channels, the third  $\text{-COO}$  groups from three BTC ligands work cooperatively to capture cobalt paddlewheel dimers with active metal sites occupied by urea-type solvent molecules (bottom right).

