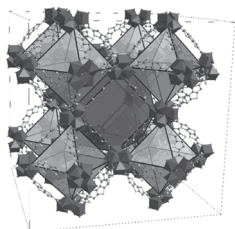


**MS26-P2 Mesoporous Zr(IV) and Hf(IV) Metal-Organic Frameworks with reo topology.** Volodymyr Bon,<sup>a</sup> Volodymyr Senkovskyy,<sup>b</sup> Irena Senkovska,<sup>a</sup> Stefan Kaskel<sup>a</sup>  
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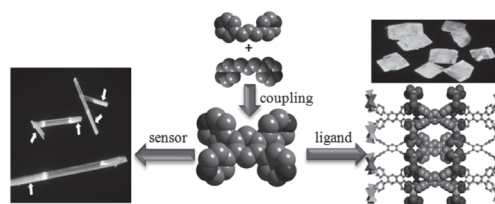
During last two decades, a rapid development of metal-organic frameworks (MOFs) chemistry was achieved exploring the widely applicable modular construction principles and the broad application potential [1]. Among thousands of MOFs, the Zr-based materials show ultimate thermal and especially chemical stability, and could be successfully applied in catalysis [3], hydrogen generation [4], and selective adsorption [5]. All previously reported Zr-based materials were based on 12 coordinated zirconium cluster  $Zr_6O_4(OH)_4(CO_2)_{12}$ , forming 12-connected framework with **fcu** topology limiting the availability of pore shape and size, and especially on pore windows size [5,6].

In this work, we pursued a strategy that focuses on reducing the ability of  $[Zr_6O_4(OH)_4]^{12+}$  cluster to coordinate multifunctional linker molecules. As a result, using modulator synthesis approach and bent dithienothiophene dicarboxylate as a linker, new porous crystalline materials, namely DUT-51(Zr) and DUT-51(Hf) (DUT – Dresden University of Technology), were synthesized. Crystal structures of both materials were determined by single crystal X-ray diffraction using synchrotron radiation [7]. Crystal structures involve 8-connected SBU (Secondary Building Unit), interconnected by linker molecules forming 8-connected uninodal framework that can be referred to **reo** topology. As a result of such combination of SBU and linker geometry, octahedral (15.6 Å in diameter) and cubo-octahedral pores (18.8 Å in diameter) are created. Resulted square and triangular pore windows have a diameters 9.0 and 4.2 Å correspondingly, allowing to adsorb relative large dyes molecules (Nile blue, Rhodamine 6G etc.) as well as fullerenes  $C_{60}$  and  $C_{70}$ . Both materials are highly porous showing specific surface area (multi-point BET model) of 2335  $m^2g^{-1}$  for DUT-51(Zr) and 1859  $m^2g^{-1}$  for DUT-51(Hf). They are stable against hydrolysis and can be stored at ambient conditions without loss of crystallinity and porosity.



**MS26-P3 From Stimuli-Responsive Organic Dye Crystals to Photoluminescent Three-Dimension Open-Framework**  
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Four photoluminescent crystals, TPB-n ( $n = 1-3$ ) and TPC $H_4H_2O$ , from carbon-carbon coupling of 4,4'-trimethylene-dipyridine (tmdp) have been synthesized in isolation in the absence of organic solvent and catalyst, a new breakthrough in *in situ* one-pot metal/ligand oxidative-dehydrogenation reactions. Their structures were characterized: TPB and TPC $H$  represent two tmdp dimers of two dissimilar oxidized forms, TPC $H$  was less oxidized but accompanied partial hydrolysis with molecular formula further confirmed by FAB-MASS analysis. They exhibit distinct photoluminescence (PL), and quantum efficiency was measured up to 42%. Heat-treatment products of TPB-2 and TPB-3 had been transformed into the anhydrous phase of TPB-1. And heat-induced luminescence change implies that the three TPB crystals with such distinctive luminescent properties are potential sensor materials. Importantly, from all three TPB crystals, the first tetrapyrrolyl-type ligands adaptable to metal phosphates have established to create an unparalleled cationic luminescent framework, NTHU-12. This study provides an inspiring new route beyond conventional C-C bond formation reactions and thus has generated inconceivable four tmdp dimers in isolation. The facile syntheses have facilitated ample production of a rare type of tetrapyrrolyl ligands, so as to stimulate the discovery of a unique tetradentate amine-mediated metal phosphate with a positively-charged hybrid topology unprecedented in nanoporous solids. The exceptional features of the four luminescent tmdp dimers and NTHU-12 embodied in synthesis, structure and optical property are reported.



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**Keywords: Coupling reaction; Luminescent sensor; Metal Phosphate**

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**Keywords: Zirconium; Hafnium; Mesoporous MOF**