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In the rationalization process of the complex structures called coordination networks / Metal-Organic Frameworks (MOF) it is very helpful the "topological approach" that consists in the simplification by rational principles of the complex structures to schematized reference nets. A higher level of complexity comes from the interpenetration and entanglement of different periodic motifs whose rationalization and classification we have illustrated in the last years. We think that the understanding of the topology and the entanglement phenomena in this kind of materials could be a powerful tool to disclose the relationships between structure and function. We will address the most recent results and leave some open questions. See: "TOPOLOGICAL CRYSTAL CHEMISTRY: Polycatenation weaves a 3D web" D. M. Proserpio, Nature Chemistry (2010), 2(6), 435-436. "Underlying nets in three-periodic coordination polymers: topology, taxonomy and prediction from a computer-aided analysis of the Cambridge Structural Database" E. V. Alexandrov, V. A. Blatov, A. V. Kochetkov and D. M. Proserpio, CrystEngComm, 2011, 13, 3947-3958 (Received December 27, 2011)