We describe some of most representative examples of metallosupramolecular architectures and dynamic hybrid materials recently published by our group in which supramolecular functional devices are constitutionally self-sorted by crystallization or by sol-gel polymerization. The self-selection is based on constitutional interactions resulting in the dynamic amplification of self-optimized architectures. The dynamic constitutional materials reported here therefore illustrate the convergence of the combinatorial self-sorting of dynamic combinatorial libraries (DCLs) with the specific self-optimized functions, extending the application of constitutional dynamic chemistry from materials science to functional constitutional devices.