Responsive and flexible metal-organic frameworks represent a very promising class of porous solids, exhibiting huge potential for a variety of applications. The combination of zeolite-like regularity together with high specificity puts these compounds in a very unique position. Even though flexible MOFs are reported frequently in the current literature, a synthetic method to trigger and to control the responsive properties of such hybrid materials was not known so far. In this work an elaborated study on the impact of additional flexible substituents, such as alkoxy chains, which are connected to the organic backbone of the MOF, on the responsiveness of the functionalised materials is reported for the first time.

In order to allow a systematic investigation, a modular route for the synthesis of diverse functionalised 1,4-benzenedicarboxylate linkers has been developed. The prepared functionalised bdc derivatives feature a wide variety of flexible substituents, ranging from simple alkoxy groups to ethers, sulphides and hydroxides, as well as alkenyl and alkynyl groups with tuneable chain lengths, and provide the foundation for an elaborated study on the responsiveness of functionalised MOFs. According to the principle of reticular synthesis these novel linkers were used to target for isoreticular, but functionalised derivatives of well known prototypic bdc-based zinc-carboxylate MOF. Notice, that the linkers prepared within this work may find usage in the synthesis of numerous other bdc-based MOFs in the future, which allows analogous in-depth investigations on related MOF systems.

The data on IRMOFs and pillarated layer-based DMOFs obtained here, show that a remarkable responsive behaviour can be initiated in both MOF classes. The phenomenon of very specific host-guest interaction together with a structural adaptivity of the host dependent on the guest molecules, relates these unique materials to biomolecules (e.g. enzymes), which can execute a specific function in response to decisive stimuli. Reversible crystalline-to-amorphous transformations (IRMOFs) or reversible crystalline-to-crystalline transformations (DMOFs) in dependence on adsorbed guest molecules are triggered in these formerly non-responsive or just weakly responsive MOFs by implementation of particular functionalised linkers. The structural response is highly dependent on the employed substituted linker (functionality
and chain length of the substituents) and on the nature of the adsorbed guests. Therefore, a systematic tuning of host-guest chemistry, responsiveness and selective sorption properties of these materials is possible.

The underlying mechanisms and interactions, which are responsible for the framework dynamics are very different for the IRMOF and DMOF materials. For the IRMOFs structural responsiveness is only observed if the substituents connected to the linker feature polar head groups (e.i., methoxy groups). The reason for the reversible crystalline-to-amorphous transition of such IRMOFs is a weak interaction between the Lewis-basic donor groups of the flexible substituents, and the inorganic $[\text{Zn}_4\text{O}]^{6+}$ building unit of the framework. If polar guest molecules are present the methoxy-terminated substituents are ‘solvated’ and the framework exhibits a crystalline structure. Upon removal of the polar guests the methoxy groups are likely to coordinate to the weakly Lewis-acidic Zn-centres of the inorganic building brick. Driven by this additional coordination, random distortions and displacements emerge, which lead to a loss in long-range translational order and thus to an X-ray amorphous material.

The functionalised DMOFs feature a drastic breathing behaviour in response to the adsorption of molecules. Upon guest removal the original open-pored phase transfers to a contracted narrow-pored phase, which possesses a drastically reduced cell volume. This breathing effect can be ascribed to attractive intermolecular interactions between the flexible substituents or between the substituents and the framework backbone. An interaction of the substituents with the metal centres of these pillared layer-based DMOFs can be excluded, because the metal centres are coordinatively saturated. Despite these obvious differences for both framework classes, the chain length, bulkiness and chemical nature of the substituent (non-polar versus polar), as well as the substitution pattern of the bdc linker have a drastic influence on the general presence and the magnitude of the structural response in the functionalised MOFs.

The bistable nature of the functionalised DMOFs results in stepped gas sorption isotherms possessing large hysteresis loops, which are characteristic for such kind of breathing MOFs. Interestingly, many of these DMOFs adsorb selectively CO$_2$, whereas N$_2$ and CH$_4$ is hardly adsorbed. Non-polar gases can not penetrate into the porous coordination network due to the contracted narrow pores, which are blocked by the functional substituents. Owing to its strong quadruple moment CO$_2$ can attractively interact with the substituents and infiltrate into the porous structures, whereby the frameworks breathe and transfer from the narrow-pored to the open-pored form. Remarkably, if the substituents at the linker feature a particular chain
length, these breathing-like phase transitions can not only be triggered by adsorption of molecules, but also by applying heat. Such kind of thermo-responsiveness, induced by the thermal motion of the pendant substituents connected to the linkers, is a very unusual property, suggesting potential for a variety of application, for example in heat storage or transfer, which are usually not associated to porous materials.

The results obtained in this thesis show further, that functionalisation of the linker can not only have a major impact on the responsive properties of related isoreticular frameworks, but also on the conformations and rotational barriers of the linker itself. The direct proximity of the additional substituents to the carboxylate groups results in a tilting of the carboxylates from the plane of the central phenyl ring. As a consequence, both carboxylate groups of a substituted bdc-type linker must not imperatively be coplanar, but can be twisted against each other. This fact dramatically influences the structural variability of the substituted linkers, and permits the formation of novel unexpected framework topologies, which are not accessible with non-functionalised linkers.

It was found that the topology of \( [\text{Zn}_2 \text{L}_2(\text{bipy})]_n \) networks is highly dependent on the used substituted linkers. Only the substituents connected to the bdc linker determine the structure of the obtained networks, which represent either trivial pillared square-grid frameworks or novel honeycomb-like frameworks. For the formation of the honeycomb-like structure an increased conformational freedom of the carboxylate groups of the linkers is mandatory. Packing effects and interactions between adjacent substituents, as well as the metrics of the coligand bipy play a significant role as well.

The one-dimensional channels of the honeycomb-like MOFs are lined with the flexible substituents of the linkers. The flexible functionalities act as molecular gates for gas molecules and allow highly selective adsorption of CO\(_2\) compared to N\(_2\) and CH\(_4\). Importantly, the nature of the substituent significantly influences the gas sorption affinity of the materials. Polar alkyl ether substituents significantly increase the affinity of the networks towards CO\(_2\) in comparison to isostructural networks featuring non-polar alkyl chains.

In each study reported in this work, the substitution pattern of the phenyl ring of the bdc-type linker, as well as the chain length and chemical nature of the flexible substituents have far reaching consequences, either on the structure, the sorption selectivity or the responsive behaviour of the MOFs. Strikingly, even slight changes in the molecular structure of the functionalised linkers can yield drastically different frameworks with very different properties. This fact shows, that it is possible to fine-tune sorption selectivity and responsiveness by design of the linker molecule.
Stimulated by these results, a transfer of the derived methodology to other prototypic MOF structures will give more information on the general applicability of the developed procedure. The presented methodology should also be extended to the preparation of multifunctional MOFs via the simultaneous utilisation of several differently functionalised linkers in varying ratios side-by-side in MOF synthesis. Such multivariate (MTV) MOFs\textsuperscript{[209]} feature a drastically extended parameter space, which can provide valuable, non-linear combinations of the individual properties.