abstract
The large-scale anthropogenic emission of carbon dioxide into the atmosphere leads to many unintended consequences, from rising sea levels to ocean acidification. While a clean energy infrastructure is growing, mid-term strategies that are compatible with the current infrastructure should be developed. Carbon capture and storage in fossil-fuel power plants is one way to avoid our current gigaton-scale emission of carbon dioxide into the atmosphere. However, for this to be possible, separation techniques are necessary to remove the nitrogen from air before combustion or from the flue gas after combustion. Metal-organic frameworks (MOFs) are a relatively new class of porous material that show great promise for adsorptive separation processes. Here, potential mechanisms of O2/N2 separation and CO2/N2 separation are explored.

First, a logical categorization of potential adsorptive separation mechanisms in MOFs is outlined by comparing existing data with previously studied materials. Size-selective adsorptive separation is investigated for both gas systems using molecular simulations. A correlation between size-selective equilibrium adsorptive separation capabilities and pore diameter is established even in materials with complex pore distributions. A method of generating mobile extra-framework cations which drastically increase adsorptive selectivity toward nitrogen over oxygen via electrostatic interactions is explored through experiments and simulations. Finally, deposition of redox-active ferrocene molecules into systematically generated defects is shown to be an effective method of increasing selectivity towards oxygen.