

## Atomic-level Description of Cutting-Edge Energy Materials for a Sustainable Society

### Collaborative Research Center on Energy Materials

In order to attain clean and economical energy systems, the Center creates and studies advanced energy materials with superior functional properties that have important roles in energy generation and consumption. Through joint efforts in both science and engineering, high-performance energy materials that efficiently convert and transport energy are investigated.

At our Center, research and development focus on the atomic-level control of the multiple structure–property relationships of advanced energy materials, as well as on the design of devices that lead to effective carrier conversion, high-speed energy transport, and increasing renewable energy production. This can be achieved by integrated control of spin, electron, ion, hole, and phonon-like carriers.

One of the Center's research activities is directed towards the development of materials that can be used in sustainable gas storage/separation technologies. This requires precise control of the structure on an atomic level and accurate analysis of the interactions that occur during the adsorption process.

In the Material Processing and Social Implementation Division, we estimate the important properties of various nanoporous materials using highly accurate computational methods in order to accelerate the experimental realization of novel storage media. In the search for novel functional adsorbents, metal–organic framework (MOF) materials with unprecedented regular nano-sized spaces have been studied.

Recently, a new soft porous coordination polymer,  $\text{Cu}^{2+}$ (5-azidoisophthalate), with adaptable pores that selectively adsorb CO from a CO/N<sub>2</sub> gas mixture was discovered. The key feature of this structure is the presence of two channels having different pore sizes, with the size of the small one increasing owing to the interaction of CO molecules with the  $\text{Cu}^{2+}$  sites, as shown in Fig. 1a. This allows one to control the next step of the separation process. In agreement with the experimental data, the calculation results showed a remarkable distinction in adsorption properties of the CO-coordinated MOF towards CO and N<sub>2</sub> separation. The electron distribution of the CO adsorption process indicated favorable attraction between the guest molecule and the small channel of the host structure. In the case of N<sub>2</sub>, the electron distribution showed repulsion between nitrogen molecules and the host framework. Thus, high selectivity is achieved by the synergetic effect of the local interaction between CO and accessible  $\text{Cu}^{2+}$  metal sites and a

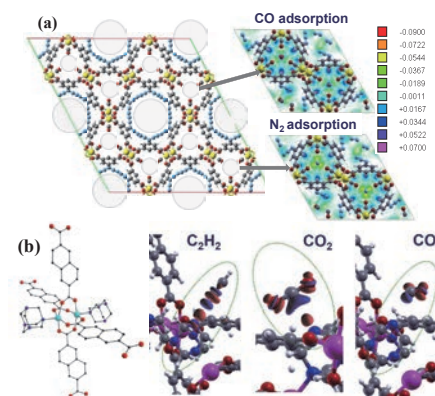


Fig. 1 (a)  $\text{Cu}^{2+}$ (5-azidoisophthalate) structure and electron density contours of CO and N<sub>2</sub> adsorbed inside small channels. (b) Fragment of  $\text{Zn}_4(\text{dmf})(\text{ndc})_4(\text{ur})_2$  with urotropine ligand and charge density isosurfaces for the  $\text{C}_2\text{H}_2$ ,  $\text{CO}_2$ , and CO interactions.

global transformation of the framework [1].

The adsorption properties of the porous  $\text{Zn}_4(\text{dmf})(\text{ndc})_4(\text{ur})_2$  structure were also investigated (see Fig. 1b). This material is a rare example of a microporous compound with open basic sites decorating the inner surface of the MOF host. It was found that the inclusion of the urotropine ligand into the MOF framework enhanced the adsorption of acetylene and carbon dioxide. Thus, only in the case of the  $\text{C}_2\text{H}_2$  molecule, the most favorable attraction with the host is through the formation of a C–H $\cdots$ N hydrogen bond between the H atoms of acetylene and the N atoms of urotropine [2]. The use of urotropine as a co-bridging ligand in metal–carboxylate MOFs may therefore result in a variety of other porous materials with notable basic functionality derived from non-coordinated N-centers.

#### References

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Rodion Belosludov (Corresponding Author, Collaborative Research Center on Energy Materials)

E-mail: rodion@imr.tohoku.ac.jp

Shin-ichi Orimo (Head of Collaborative Research Center on Energy Materials)

E-mail: orimo@imr.tohoku.ac.jp

URL: <http://www.e-imr.imr.tohoku.ac.jp/>