

Chemically Stable Carbazole-Based Imine Covalent Organic Frameworks with Acidochromic Response for Humidity Control Applications

Leisan Gilmanova, Volodymyr Bon,* Leonid Shupletsov, Darius Pohl, Marcus Rauche, Eike Brunner, and Stefan Kaskel*



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ABSTRACT: Isoreticular chemically stable two-dimensional imine covalent organic frameworks (COFs), further denoted as DUT-175 and DUT-176, are obtained in a reaction of 4,4'-bis(9*H*-carbazol-9-yl)biphenyl tetraaldehyde with phenyldiamine and benzidine. The crystal structures, solved and refined from the powder X-ray diffraction data and confirmed by high-resolution transmission electron microscopy, indicate AA-stacked layer structures. Both structures feature distorted hexagonal channel pores, assuring remarkable porosity ($S_{\text{BET}} = 1071 \text{ m}^2 \text{ g}^{-1}$ for DUT-175 and $S_{\text{BET}} = 1062 \text{ m}^2 \text{ g}^{-1}$ for DUT-176), as confirmed by adsorption of gases and vapors. The complex conjugated π system of the COFs involves electron-rich carbazole building units, which in combination with the imine groups allow reversible pH-dependent protonation of the frameworks, accompanied by charge transfer and shift of the absorption bands in the UV–vis spectrum. The sigmoidal shape of the water vapor adsorption and desorption isotherms with a steep adsorption step at $p/p_0 = 0.4\text{--}0.6$ in combination with excellent stability over dozens of adsorption and desorption cycles ranks these COFs among the best materials for indoor humidity control applications.

According to the U.S. Environmental Protection Agency, the ideal indoor relative air humidity ranges from 40 to 60%. Deviations from this range often cause severe diseases such as asthma or encourage the growth of fungus, mold, and dust mites. This problem is in particular urgent in Southeast Asia, where the relative humidity seldom falls below 60%, or at the another extreme, the Middle East Region with dry air. Beyond humidity, more severe problems originate from emissions of nitric and sulfur oxide in industrial regions.¹ This encourages the development of sustainable and energy-efficient air purification systems and sensors that are able to maintain the indoor relative humidity within the recommended range and can identify low concentrations of industrial pollutants in air. The working principle of air dehumidifiers that are available on the market relies on highly energy-consuming evaporator/condenser technologies. As an alternative to this technology, adsorptive heat pumps have been intensively discussed in recent years.² In particular, porous crystalline framework materials are prospects for such applications because of their modular building principle and nearly unlimited functionalization capabilities.^{3–9} In terms of water adsorption, unique features of a few frameworks are their sigmoidal isotherms and high capacity.^{10–14} Depending on the pore size and polarity of the inner surface, materials start to adsorb water at a predefined relative humidity level and therefore could be suitable for either air drying, adsorption heat pumps, or indoor humidity control. Additional functionalization of the inner surface may result in extra functions such as conductivity, fluorescence, optical, and redox properties that can be used for the sensing of the target guest molecules.^{15–17}

Covalent organic frameworks (COFs) are a relatively young class of metal-free porous crystalline solids with low density and high thermal and chemical stability that are built through a modular principle exclusively using organic building blocks.^{18–23} A wide variety of linking chemistries have been used for reticulating molecular building blocks into extended organic frameworks.^{24,25} Two-dimensional (2D) and three-dimensional COFs were successfully used in gas storage and separation,^{26,27} catalysis,^{28,29} energy conversion and storage, etc.^{30–32} Since the first report,³³ imine-linked COFs have gained a lot of attention and have been used extensively in various fields.³⁴ Schiff base chemistry allows the creation of highly crystalline ordered frameworks, the thermal and chemical stability of which ascertained their value in environmental applications.^{35–38} Recently COFs have become attractive for sensory applications,³⁹ including humidity,^{40,41} pH,⁴² gas,^{43,44} and vapor^{45,46} sensing.⁴⁷ The mechanisms and the essence of these sensory processes are strongly dependent on the chemistry and topology of the 2D COFs.

The rigorous selection of suitable building blocks (linkers and linkages) allows the creation of materials with desired properties. Nitrogen-rich building blocks provide a framework with donor–acceptor charge transfer units, providing an

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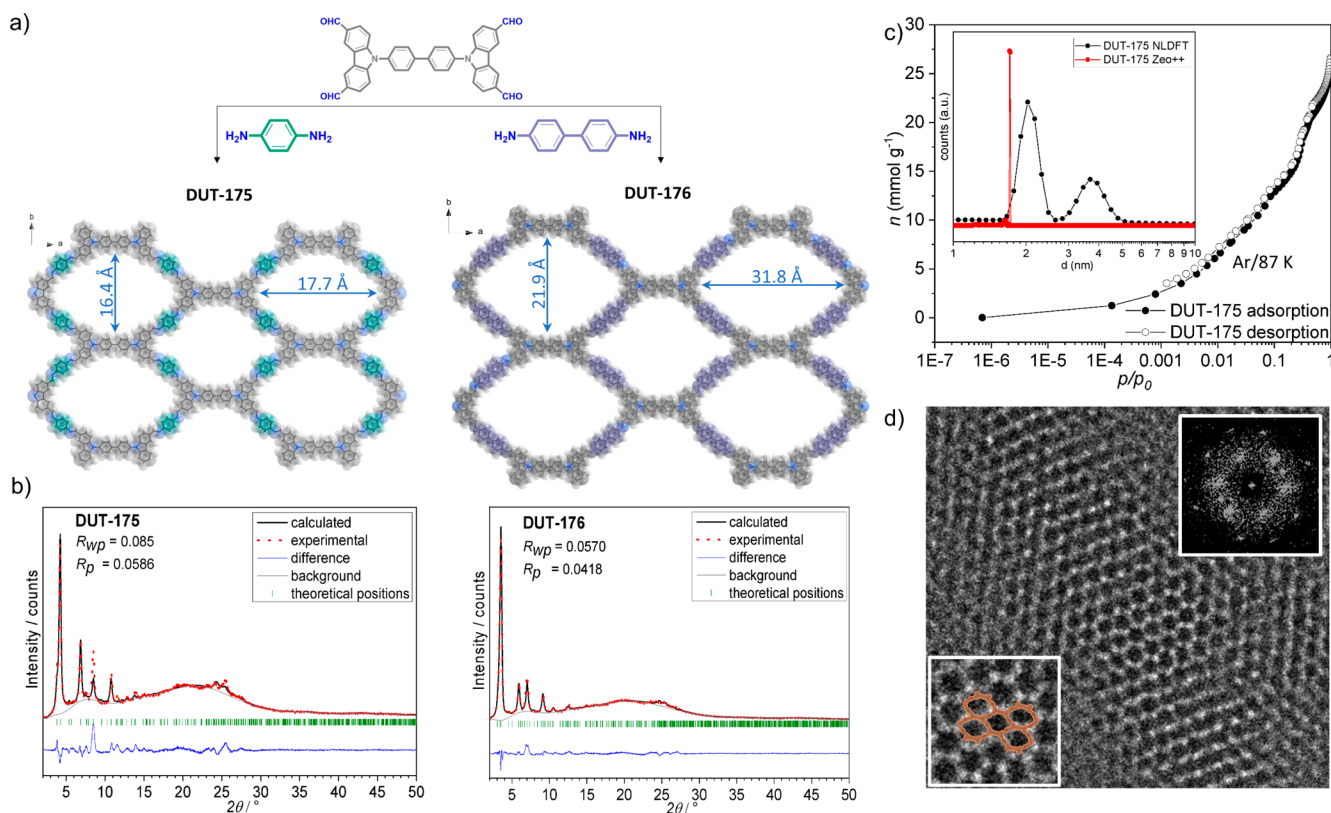


Figure 1. (a) Design and crystal structures of the isoreticular 2D imine COFs DUT-175 and DUT-176. (b) Rietveld refinement plots. (c) Argon physisorption at 87 K on DUT-175. The inset shows NLDFT (black curve) and geometrical (red curve) pore size distributions. (d) HR-TEM image of DUT-176 (inset: FT-image).

opportunity to detect changes in the structure spectroscopically or even with the naked eye.^{48,49} Carbazole units are famous for outstanding optoelectronic properties^{50,51} and hence are excellent candidates for the design of materials with optical sensing functionality.

Herein we report two new chemically stable 2D imine-linked COFs, DUT-175 and DUT-176 (DUT stands for Dresden University of Technology), that are based on a biphenylbiphenyl-carbazole linker and show a high capacity for water and a sigmoidal adsorption isotherm with a steep adsorption step in the range $p/p_0 = 0.4$ – 0.6 coupled with pronounced acidochromic functionality.

The new bicarbazolebiphenyl formyl linker was synthesized using DMF as the formylation agent (Scheme S1). Condensation with phenyldiamine and benzidine yields two isostructural COFs DUT-175 and DUT-176 respectively (all of the synthetic conditions are described in detail in the Supporting Information). The atomic-level constitution of both COFs was confirmed by solid-state ¹³C CP/MAS NMR spectroscopy (Figure S10).

Superposition of the aldehyde and COF spectra revealed the elimination of all carbonyl signals at ca. 190 ppm and the appearance of two new signals at ca. 148.7 and 157.8 ppm corresponding to N–C_{Ar} and C=N bonds formed in the COF. The IR spectra of the obtained polymers confirmed the disappearance of the NH₂ group from the diamine at 3269 cm⁻¹ and the C–H bond of the formyl group at 2782 cm⁻¹. The vanishing of the C=O band at 1679 cm⁻¹ and the appearance of a new C=N band at 1610 cm⁻¹ indicate the formation of the corresponding imine bonds (Figure S11). Powder X-ray diffraction analysis showed high crystallinity of

the synthesized COFs (Figure 1b). Both crystal structures were solved by applying semiempirical computation-assistant techniques using Materials Studio 5.0 software. Three different isomeric structures were simulated, and the models were subsequently refined against the experimental data. The best fit was obtained for the model crystallized in space group *Pmmm* (No. 47) (Figure 1a), indicating AA layer stacking. Rietveld refinement of both structures additionally confirmed the accuracy of the structural model (Figure 1b). Further details on the structure solution and refinement are provided in the Supporting Information. The excellent crystallinity of the synthesized COFs allowed the collection of high-resolution transmission electron microscopy (HR-TEM) images, which showed elongated stripelike crystallites (Figure S8) and distorted hexagonal channel pores while viewing in the *ab* plane direction (Figure 1d). Additionally, the crystallite size was evaluated by scanning electron microscopy (SEM), which indicated that the agglomerates consisted of nanosized plate-like crystals (Figure S9). The crystal structures of DUT-175 and DUT-176 contain guest-accessible void spaces of 59.5% and 64.6% of the unit cell, indicating the potential porosity of both systems, which was also corroborated by calculations of the geometrical porosity (Figure S5). To confirm the calculations experimentally, N₂ adsorption measurements at 77 K were recorded (Figure S7) after Soxhlet extraction and subsequent activation using supercritical CO₂. The steep nitrogen uptake in the low-pressure range confirms the expected microporous nature of the polymers. The experimental pore size distributions were calculated from low-pressure 87 K Ar adsorption measurements (Figures 1c and S6) and correspond to pore sizes of 1.9 and 2.2 nm for DUT-

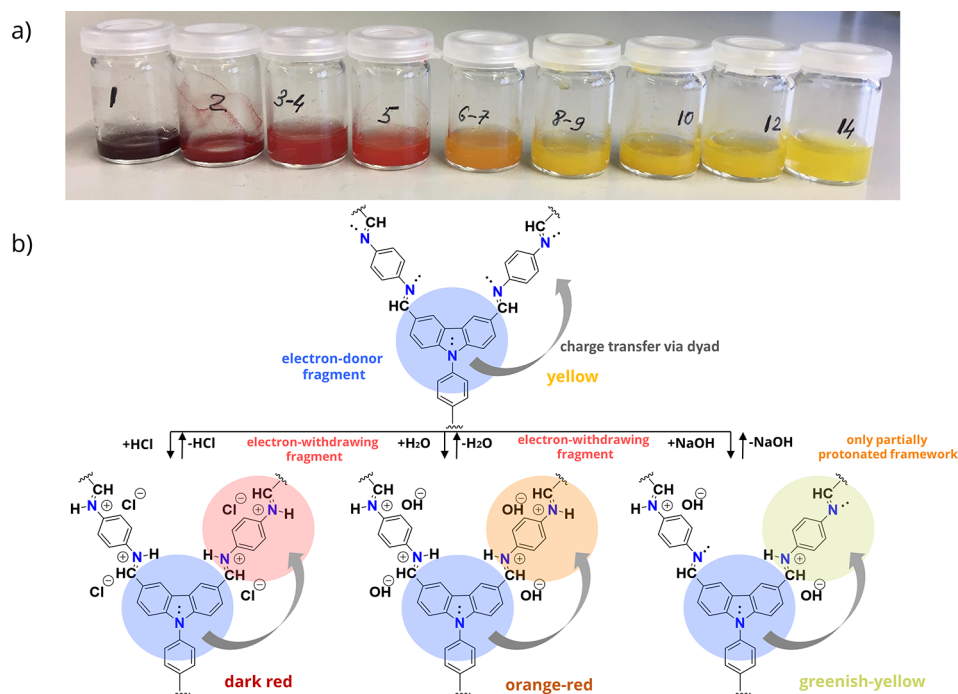


Figure 2. (a) DUT-175 color change in water solutions with different pH (from 1 to 14). (b) Mechanism of the protonation processes in the framework.

175 and DUT-176, respectively, which are in good agreement with the structural model considering the limited optimization of the commercial density functional theory (DFT) kernels.

Designing porous crystalline materials that are resistant to harsh conditions such as humidity and a broad range of pH is a key challenge and crucial for advancing applications.^{36,52,53} Our stability investigations covering a wide pH range revealed that the new COFs are remarkably stable and remain crystalline and porous after 7 days in boiling water as well as in acid (1 M AcOH) and base (1 M NaOH) solutions (Figures S12 and S13). A pronounced color change was observed during the treatment of DUT-175 with aqueous solutions at various pH (Figure 2a). The activated yellow-colored COF powder immediately turns dark red after exposure to acid, orange after exposure to water, and pale-yellow after a few minutes of soaking in a base (Figure 2a). This interesting feature of optical response toward pH changes was quantified using solid-state UV–vis spectroscopy (Figure S14). In all cases a bathochromic red shift was observed under the influence of changes in the environment. This kind of color transformation is apparently due to the protonation of nitrogen atoms of imine bonds (Figure 2b). The mechanism of color change as a response to moisture, acidity, and organic vapors in COFs is typically related to protonation of nitrogen in the framework.^{46,49,54} The interaction of H⁺ originating from moisture, acid solution, acidic gas, etc. with the framework can range from extremely strong to weak, resulting in a more or less fully protonated structure. The degree of protonation also depends on the abundance and nature of accessible nitrogen sites in the framework and on intramolecular electronic transitions in a structure, and thus, it can undergo intense or barely noticeable changes. The sensing mechanism of DUT-175 was proven by ¹³C solid-state NMR spectroscopy, which showed the absence or lower intensity of the C=N bond at 160 ppm for protonated samples and slight shifts of the C_{Ar}–N bond at 149 ppm and the C–C_{Ar} bond at 138 ppm (Figure

S15). The absence of the aldehyde group signal provides evidence about preservation of the integrity of the framework. Imine bond protonation was also proven by FT-IR spectroscopy, which showed the appearance of new bands at 1046 and 2973 cm⁻¹ due to the slight changes in atomic structure (Figure S16).

While the new solids show no color changes in common organic solvents of varying composition and polarity, DUT-175 shows pronounced color changes that can be easily visually detected for a wide range of pH levels, changing gradually from very deep wine (pH 1) to varying red (pH 2–5) and then to orange (pH 6–7). Slightly altering yellow colors are observed from pH 8 to pH 11 and significantly distinct yellow-greenish suspensions for increasingly basic media at pH 12 and pH 14. In comparison with previously reported COFs,^{42,55} DUT-175 can be used to probe the full range of pH with the naked eye in the liquid phase without degradation over numerous cycles.

The remarkable behavior toward aquatic solutions and stability of DUT-175 encouraged us to investigate in-depth the water adsorption performance. Vapor physisorption at 298 K revealed a characteristic S-shaped adsorption isotherm with colossal water uptake reaching 0.72 g g⁻¹ at saturation (Figure 3a). The isotherm is typical for intermediate hydrophobic materials, with a first steep adsorption step at $p/p_0 = 0.4$ as desired, following by the second less-steep step at $p/p_0 = 0.5$ – 0.8 . The desorption branch shows a hysteresis of variable width (Figures 3a and S20) and may be related to the framework flexibility, which is currently under investigation. Water vapor adsorption on DUT-176 starts at higher pressure ($p/p_0 = 0.5$), indicating a more hydrophobic inner surface of the framework. The typical S-shaped isotherm is similar, but it does not include the second step and reaches only 0.48 g g⁻¹ capacity in saturation.

The high water adsorption capacity and sensing abilities of DUT-175 inspired us to study its humidity control potential. An in situ UV–vis measurement illustrated the optical

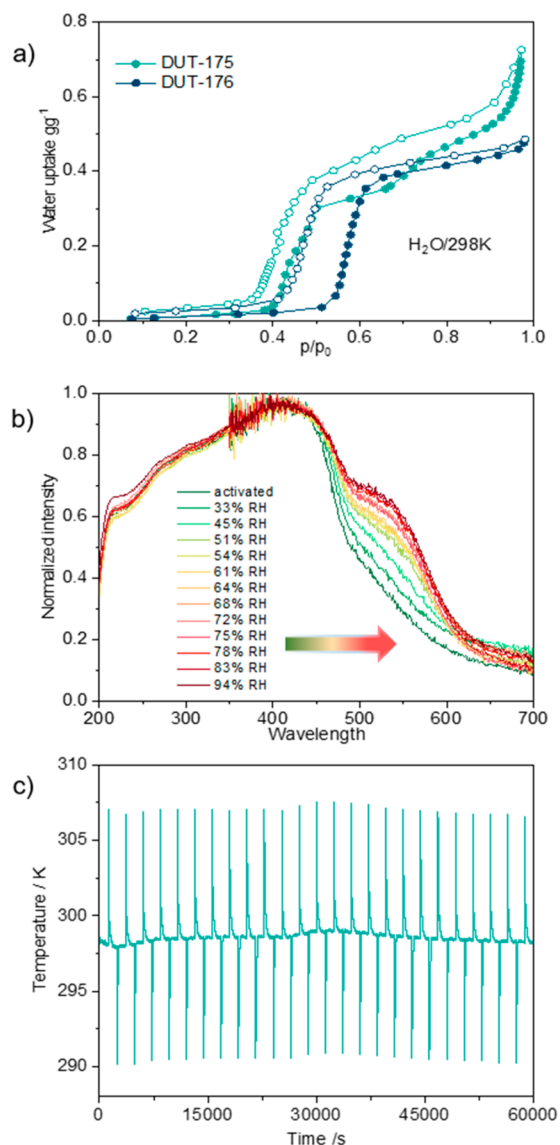


Figure 3. (a) Water adsorption isotherms of DUT-175 and DUT-176 at 298 K. (b) In situ UV-vis absorption spectra of DUT-175. (c) Temperature profile measured upon multiple water vapor adsorption/desorption cycles on DUT-175.

response of the activated COF material after the relative humidity (RH) was gradually increased from 0 to 94% in a dynamic flow. A characteristic absorbance shift toward longer wavelengths was observed for each 3–5% step change in RH (Figure 3b). This process is reversible, as proven by flushing the sample with dry N₂. The reverse shift in absorbance appeared already after 2 min of drying, and nearly complete recovery of the material was observed after 10 min (Figure S17). To verify the high working capacity of DUT-175 over cycling, water adsorption/desorption experiments were intensified via the Infrisorp accelerated testing technology.⁵⁶ The temperature profile, measured over 25 cycles of water sorption (Figures 3c and S18) well reflects both adsorption steps in the isotherm (Figure S24) and primarily elucidates the adsorption/desorption kinetics of water vapor. The adsorption curve reaches the baseline in 650 s after exposure of the COF to humid nitrogen gas (140 cm³ min⁻¹, 90% RH). Desorption of water terminated after 350 s in dry nitrogen flow. These values did not change over 25 cycles, indicating the stable

performance of the solid. Hence, DUT-175 combines the optical humidity sensor functionality with high cycling stability and capacity in water vapor adsorption.

In summary, we designed two novel 2D imine COFs, DUT-175 and DUT-176, based on the 9*H*-carbazole tetratopic aldehyde and linear aromatic diamines. Both structures show AA stacking of layers and form one-dimensional channels with diameters of 17–22 Å and high pore accessibility, as demonstrated by gas and vapor adsorption experiments. Reversible protonation of the imine nitrogen leads to electronic structure changes in the conjugated π system of the frameworks, leading to a characteristic colorimetric pH response over a wide pH range without COF decomposition. The S-shaped water isotherms with a steep adsorption step at $p/p_0 = 0.4$ – 0.6 renders these frameworks promising for indoor humidity regulation devices. The ability to easily detect the state of loading in operation is a promising feature for novel functional materials combining high molecular storage abilities with optical response functions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c07148>.

Synthesis and characterization details of DUT-175 and DUT-176, powder X-ray diffraction analysis data, computational modeling, ¹³C MAS NMR and FT-IR spectra, stability tests, and humidity sensing (PDF)

AIF data (ZIP)

Animations showing color changes (ZIP)

Accession Codes

CCDC 2094063 and 2094064 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Volodymyr Bon – Chair of Inorganic Chemistry I, Technische Universität Dresden, 01069 Dresden, Germany;

orcid.org/0000-0002-9851-5031;

Email: volodymyr.bon@tu-dresden.de

Stefan Kaskel – Chair of Inorganic Chemistry I, Technische Universität Dresden, 01069 Dresden, Germany;

orcid.org/0000-0003-4572-0303; Email: stefan.kaskel@tu-dresden.de

Authors

Leisan Gilmanova – Chair of Inorganic Chemistry I, Technische Universität Dresden, 01069 Dresden, Germany

Leonid Shupletsov – Chair of Inorganic Chemistry I, Technische Universität Dresden, 01069 Dresden, Germany

Darius Pohl – Dresden Center of Nanoanalysis, cfaed, Technische Universität Dresden, 01069 Dresden, Germany

Marcus Rauche – Chair of Bioanalytical Chemistry, Technische Universität Dresden, 01069 Dresden, Germany

Eike Brunner – Chair of Bioanalytical Chemistry, Technische Universität Dresden, 01069 Dresden, Germany;

orcid.org/0000-0003-3511-9899

Complete contact information is available at:

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Notes

The authors declare no competing financial interest.

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