

# A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

## **Accepted Article**

- Title: Non-Interpenetrated Single-Crystal Covalent Organic Frameworks
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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202007230

Link to VoR: https://doi.org/10.1002/anie.202007230

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## Non-Interpenetrated Single-Crystal Covalent Organic Frameworks

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Abstract: Growth of covalent organic frameworks (COFs) as single crystals is extremely challenging. Inaccessibility of open-structured single-crystal COFs prevents the exploration of structure-oriented applications. Herein we report for the first time a non-interpenetrated single-crystal COF, LZU-306, which possesses the open structure constructed exclusively via covalent assembly. With a high void volume of 80%, LZU-306 was applied to investigate the intrinsic dynamics of reticulated tetraphenylethylene (TPE) as the individual aggregation-induced-emission moiety. Solid-state <sup>2</sup>H NMR investigation has determined that the rotation of benzene rings in TPE, being the freest among the reported cases, is as fast as 1.0 ×  $10^4$  Hz at 203 K to  $1.5 \times 10^7$  Hz at 293 K. This research not only explores a new paradigm for single-crystal growth of open frameworks, but also provides a unique matrix-isolation platform to reticulate functional moieties into a well-defined and isolated state.

#### Introduction

Covalent assembly of organic molecules into extended single crystals is a long-standing challenge.<sup>[1-4]</sup> The bottleneck lies in the contradiction between the critical demand for errorchecking in crystallization and the intrinsic lack of reversibility in covalent bonding. This severe limitation in three-dimensional (3D) assembly has not been broken through until very recently. Wuest succeeded in linking tetranitroso monomers via weak azodioxy bonds into nonporous single-crystal polymers.[4a] We developed a modulation strategy to construct, for the first time, single-crystal covalent organic frameworks (scCOFs) with porosity.[4b] Nevertheless, densely-packed permanent interpenetrated networks are exclusively formed<sup>[4]</sup> with the ubiquitous existence of non-covalent interactions (such as  $\pi$ - $\pi$ stacking) between the adjacent nets. This interpenetration will hinder the structure-oriented applications, especially when the availability of abundant void spaces<sup>[5]</sup> becomes the key factor. Therefore, further advance to grow non-interpenetrated scCOFs as open frameworks is in urgent need.

Herein, we report the first non-interpenetrated scCOF, named LZU-306, which is covalently assembled<sup>[6]</sup> from a tetraphenylethylene (TPE)<sup>[7,8]</sup> based quadrilateral linker, and an

(a) Synthesis of single-crystal LZU-306 (200 nm ~ 50 μm)



(b) Non-interpenetrated pts topology



Figure 1. (a) Covalent assembly of TPE-NH2 and ADA-CHO into single-crystal LZU-306 via the modulation strategy; (b) Non-interpenetrated pts topology; (c) Crystal structure of LZU-306. TPE moieties: blue; ADA moieties: gray; hydrogen atoms were omitted for clarity.

adamantane (ADA)<sup>[6f,9]</sup> based tetrahedral node (Figure 1). Applying the modulation strategy developed by us,[4b] we were able to grow LZU-306 as tunable-sized single crystals. Structural analysis concluded that it possesses a non-interpenetrated open framework with a pts[6g] topology. Unlike previously reported scCOFs,[4b] LZU-306 is structurally featured in the entire connection via covalent bonding, in which the TPE moieties have been spatially and evenly separated by the rigid ADA spacers. Accordingly, it provides a matrix-isolation platform to investigate the intrinsic dynamics of individual TPE moiety and the ultrafast rotation of phenyl rings has been verified by solid-

state <sup>2</sup>H NMR spectroscopy. We expect that this research will pave the way for the covalent growth of open-structured single crystals, based on which many new applications may become feasible.

#### **Results and Discussion**

With aniline as the modulator,<sup>[4b]</sup> we previously succeeded in synthesizing dia- and lon-topological 3D scCOFs. However, the use of methane-based tetrahedral monomers has inevitably resulted in the formation of densely-packed interpenetrated scCOFs. We therefore selected bulkier ADA-based nodes together with a propeller-like TPE linker so as to grow scCOFs with new topology and less interpenetration. Adamantane-1,3,5,7-tetracarbaldehyde (denoted as ADA-CHO) was eventually employed because it has much better solubility than its amine analogue. Indeed, the modulation strategy is well applicable to grow pts-topological LZU-306 as tunable-sized scCOFs from ADA-CHO and tetrakis(4-aminophenyl)ethylene (denoted as TPE-NH<sub>2</sub>) (Figure 1a). The synthetic details have been described in the Supporting Information. Optical microscopy and scanning electron microscopy (SEM) images revealed that all the samples possessed uniform octahedral morphology (Figure 2). For example, under the synthetic condition without aniline [120 °C, 5 days, in 1,4-dioxane/6M HOAc (10/1)], 200 nm-sized crystals were obtained (Figure 2a). While by adding aniline (50 equiv.) [30 °C, 25 days in 1,4dioxane/15M HOAc (7.5/1)], yellow-colored single crystals could be harvested with the size of 50  $\mu$ m (Figures 2e and 2f).



**Figure 2.** (a to e): SEM images of single-crystal LZU-306 with the average sizes of ~200 nm, 1  $\mu$ m, 5  $\mu$ m, 20  $\mu$ m, and 50  $\mu$ m, obtained in the presence of aniline with the amount of 0, 10.0, 12.5, 40.0, and 50.0 equiv., respectively. (f) The optical microscopy image of 50  $\mu$ m-sized LZU-306.

Structural analysis disclosed that LZU-306 possesses a noninterpenetrated **pts** structure, as shown in Figure 1. SXRD measurement with synchrotron light sources on a 50  $\mu$ m-sized solvent-exchanged sample (Figure 3a) indicates an original tetragonal unit cell with a = b = 15.32 Å, c = 24.89 Å. Rotation electron diffraction (RED) on a 500 nm-sized activated sample (Figure 3b) gives a similar unit cell with a = b = 15.72 Å, c =24.05 Å. Based on the diffraction data, a non-interpenetrated **pts** framework could be established in the tetragonal symmetry. By combining the powder X-ray diffraction (PXRD) data, the structure was rationally converted into a *C*-centered monoclinic lattice with a slight incline of  $\beta$  (Figure S15-S18). Le Bail fitting of PXRD data (Figure S16) further confirmed the structure of the activated sample with the unit cell of *a* = 23.45 Å, *b* = 20.75 Å, *c* = 23.85 Å,  $\alpha = \gamma = 90^{\circ}$ , and  $\beta = 91.56^{\circ}$  in the *C*2 space group. As shown in Figure 3c, the calculated PXRD pattern of the non-interpenetrated structure agrees well with the experimental pattern of the activated LZU-306.







**Figure 3.** (a) Reciprocal planes of SXRD data from a 50  $\mu$ m-sized solventexchanged single crystal. (b) Reconstructed 3D RED data of a 500 nm-sized activated single crystal. (c) Experimental (red) and calculated (black) PXRD patterns of the activated LZU-306. The positions of Bragg reflections under the patterns are shown in blue.

Further characterization confirmed the highly-ordered and non-interpenetrated structure. Solid-state <sup>13</sup>C cross-polarization magic-angle spinning (CP/MAS) NMR measurement gave sharp peaks with the full width at half maximum (FWHM) narrow to 125 Hz: the carbon atoms can be resolved with the resolution down to 1 ppm (Figure 4a). The absence of characteristic signals of the terminal -CHO groups (at ca. 205 ppm in the <sup>13</sup>C CP/MAS NMR spectrum in Figure S3 and at ca. 1717 cm<sup>-1</sup> in the FT-IR spectrum in Figure S5) indicates the completeness of covalent linking in LZU-306. Nitrogen adsorption-desorption isotherms showed a reversible type-I isotherm (Figure 4b); the Brunauer-Emmett-Teller (BET) and Langmuir surface areas were determined as large as 2059 and 2402 m<sup>2</sup> g<sup>-1</sup>, respectively (Figures S6 and S7). The average pore width of ~10.9 Å with a narrow pore-size-distribution (Figure 4b inset) matches well with the theoretical value of 11.0 Å. <sup>129</sup>Xe atoms adsorbed in LZU-306 showed only one signal ( $\delta$  = 121 ppm) with a narrow FWHM of 671 Hz in the <sup>129</sup>Xe NMR spectrum (Figure 4c), further verifying the formation of uniform pores. In addition, the thermogravimetric analysis (TGA) demonstrated that LZU-306 is stable up to 530 °C under nitrogen atmosphere (Figure S12).

As shown in Figure 1c, the fragments in LZU-306 are loosely packed into a highly open framework that possesses a large void volume of  $80\%^{[10]}$  and a low density of 0.33 g cm<sup>-3</sup>. Note that, more densely packed structures with 2- or 3-fold interpenetration would lead to a lower void volume of 56% or 30%, and, a higher density of 0.66 or 1.00 g cm<sup>-3</sup>, respectively.<sup>[10]</sup> In reported *sc*COFs, the dense packing in the interpenetrated **dia** or **Ion** topology renders the  $\pi \dots \pi$  distance

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between the adjacent nets into the range of 4.6 to 5.1 Å (Table S2).<sup>[4b]</sup> On the contrary, the shortest intermolecular  $\pi \cdots \pi$  distance in LZU-306 reaches 10.6 Å. As expected, the use of rigid and bulky ADA spacer did render loosely-packed **pts** structures.<sup>[9]</sup>

#### (a) <sup>13</sup>C CP/MAS NMR spectrum



**Figure 4.** Characterization of single-crystal LZU-306. (a) <sup>13</sup>C CP/MAS NMR spectrum. Assignments of <sup>13</sup>C chemical shifts were indicated in the chemical structure. The peak region between 36 to 44 ppm has been magnified in the inset. Asterisks denote the spinning sidebands. (b) N<sub>2</sub> adsorption (filled symbols) and desorption (empty symbols) isotherms. Inset: pore-size distribution. (c) <sup>129</sup>Xe NMR spectrum of adsorbed xenon atoms in LZU-306.

Accurate isolation of molecules into an individual state, especially in a single-crystal state, helps to study the singlesuch dynamics, molecule behavior, as magnetism, luminescence, or single-site catalysis.[11] For example, in order to reveal the mechanism of intramolecular rotation in AIE systems,<sup>[12]</sup> elimination of intermolecular interactions by efficient isolation of AIE moieties is crucial.[13] In this context, the archetypal AIE moiety, TPE,[7] has been precisely reticulated and remotely separated from each other in LZU-306. This new model allowed us to further investigate the intrinsic dynamics of AIE moieties without the disturbance of intermolecular interactions (Figure 5).

To quantitatively evaluate the rotational dynamics of TPE, we performed variable-temperature solid-state <sup>2</sup>H NMR experiments<sup>[14]</sup> on a selectively deuterated LZU-306 sample (denoted as *d*-LZU-306 in which the hydrogen atoms of TPE moieties were deuterium-substituted; the synthetic detail and structural characterization have been shown in Supporting Information). In the spectra recorded at temperatures from 203 to 293 K (Figure 5b), the line shapes showed progressive variation from a typical Pake pattern (Q = 129 kHz) to a small-splitting pattern (Q/4 = 31 kHz). The line shapes indicate that the fast flipping of phenyl rings occurs even at 293 K. The spectra were further simulated to derive the rotational frequency (*k*) of benzene-rings around the *C*2 symmetry axis (Figure 5c). The results indicate that the rotation frequency of benzene rings in

LZU-306 ( $k = 1.5 \times 10^7$  Hz at 293 K, Figure 5b) is three orders of magnitude faster than that of TPE-containing MOF ( $k = 1.0 \times 10^4$ at 300 K).<sup>[89]</sup> Moreover, as shown in Figures S28 and S29, Arrhenius plot and density functional based tight binding plus (DFTB+) method have derived the experimental activation energy of 40 kJ mol<sup>-1</sup> with the pre-exponential factor<sup>[15]</sup> of  $k_0 =$ 2.5 × 10<sup>14</sup> Hz and the theoretical activation barrier of 32 kJ mol<sup>-1</sup>, respectively. Comparison of these values with those for TPEcontaining materials<sup>[8g-i]</sup> concluded that the benzene rings in LZU-306 experienced the freest rotation. Therefore, in difference from the dispersion states in solution or the aggregation states in solid, a new dispersion state of TPE molecules in single crystals has been provided herein, based on which the intramolecular rotation of  $\pi$ -flipping could be explicitly analyzed.



**Figure 5.** (a) Covalent isolation of TPE moiety in the framework of LZU-306. (b) Experimental (black) and simulated (blue) quadrupolar spin-echo solidstate <sup>2</sup>H NMR spectra of activated *d*-LZU-306 recorded at 203 to 293 K. (c)  $\pi$ flipping around the *C*2 symmetry axis of benzene rings in *d*<sub>16</sub>-TPE moiety.

#### Conclusion

In conclusion, we have accomplished the preparation of the first single-crystal organic framework that is exclusively connected via covalent bonding. Constructed with the rigid and bulky adamantane-based node by using the aniline-based modulation strategy, the **pts**-topological LZU-306 possesses a highly-open structure with the void volume of 80%. This unique structure provides a matrix-isolation platform to further study the single-molecule behavior in the absence of non-covalent interactions. As an example, the intrinsic rotation dynamics of the TPE moiety has been assessed via variable-temperature solid-state <sup>2</sup>H NMR spectroscopy. This approach thus explores a new protocol to covalently assemble organic molecules into extended single crystals for structure-property-relationship investigations.

#### Acknowledgements

We acknowledge the financial support from the National Natural Science Foundation of China (Nos. 21632004, 21871009,

21621061, and 21527803) and the 111 Project (No. 111-2-17). We thank the staff of beamlines BL17B/BL17U at Shanghai Synchrotron Radiation Facility for assisting with the SXRD data collection.

**Keywords:** 3D COF • single-crystal • non-interpenetrated • matrix-isolation • solid-state NMR

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A 3D single-crystal COF with a non-interpenetrated structure was constructed for the first time. The highly open framework provides a unique matrix-isolation platform to investigate the intrinsic dynamics of individual AIE moiety.