

Synthesis of 5, 6, 11, 12-tetrahydroindolo[3,2-b]carbazole-based dicarboxylate acid for MOFs fabrication *via in-situ* oxidative dehydrogenation

Guoliang Liu^{†,a,*} and Chunqing Ji^{†,b}

^a *State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic Innovation Center for Advanced Material (SICAM), College of Chemical Engineering, Nanjing Tech University, Nanjing 211816, China*

^b *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, China*

[†] *These authors contributed equally to this work.*

*Corresponding author. E-mail: glliu@njtech.edu.cn.

Abstract

The indolocarbazole derivatives has been shown great potentials as one of the key important compounds in the field of organic electronics owing to their attractive structural and electrical properties. However, studies that directly and systematically introduce indolocarbazole unit into MOFs are still lacking. Herein, we reported the synthesis of 6,12-di(hetero)aryl substituted 5,6,11,12-tetrahydroindolo[3,2-b]carbazole synthetic motifs in a facile way. The potential of these synthetic motifs as building block for porous materials fabrication is unveiled through the preparation of **Zn-MOF-ICZ** and **UiO-68-ICZ** by using 5,6,11,12-tetrahydroindolo[3,2-b]carbazole terminated with dicarboxylate acid. The resultant **Zn-MOF-ICZ** and **UiO-68-ICZ** feature 5,11-dihydroindolo[3,2-b]carbazole unit as a result of in-situ oxidative dehydrogenation, which was confirmed by ¹H NMR and single crystal X-ray diffraction study. The successful construction of these MOFs indicated the powerful of 6,12-di(hetero)aryl substituted 5,6,11,12-tetrahydroindolo[3,2-b]carbazole unit for porous materials synthesis and this provides a broad platforms for potential applications investigation considering their fine optical properties.

Keywords: 5,6,11,12-tetrahydroindolo[3,2-b]carbazole, 5,11-dihydroindolo[3,2-b]carbazole, in-situ oxidative dehydrogenation, Metal-organic frameworks, Synthetic motifs

Porous materials, such as metal-organic frameworks (MOFs), metal-organic cages (MOCs) and covalent organic frameworks (COFs), have gained increasing attention owing to their structural diversity and potential applications, including gas storage and separation, heterogeneous catalysis, performance promote filler in mixed matrix membranes for desalination or gas separation, and biomedical imaging[1-3]. It is well known that selection of proper synthetic motifs are key to tune the structures and properties of porous materials[4-6]. To date, many mature synthetic motifs, such as the ones based on aromatic, porphyrin, salen, imide functionalized aromatic, clathrochelate[7-8] and corrol units, as building blocks have been used for porous material design and synthesis[4]. For example, one of the most studied synthetic motifs is based on the porphyrin unit[9]. The carboxylate acid or pyridyl functionalized porphyrins can be used for MOFs and MOCs synthesis and while the porphyrin was decorated with boronic acid, aldehyde or amino can be used for COFs synthesis. Besides, the diversity of the resultant porous materials can be further tuned by introducing different numbers of functional groups into the porphyrin unit. To further push the development of the novel porous materials with functional-oriented applications, there is a need to design and synthesis new functional unit based synthetic motifs with general functional group compatibility.

Indolocarbazole derivatives (ICZs) are alkaloids exhibiting attractive biological properties[10]. The strict and co-planar structural features give ICZs high HOMO levels and remarkable hole-transporting properties. Consequently, ICZs with excellent optical properties has been introduced as key electron-rich π -conjugated backbones in optoelectronic materials for applications such as electrophotographic materials, light-emitting diodes, photorefractive

materials, and photovoltaic devices[11-12]. Among these compounds, 5,11-dihydroindolo[3,2-b]carbazole (DH-ICZ) have shown attractive structural and electrical properties (high charge carrier mobility) combined with excellent stability under atmospheric changes that makes them good components for use in organic electronics[12-13]. It is highly desired to incorporate DH-ICZs into porous materials as novel properties would be expected by taking advantages of merits of porous materials[4, 14-15]. However, studies that directly and systematically introduce this unit into porous materials are still lacking.

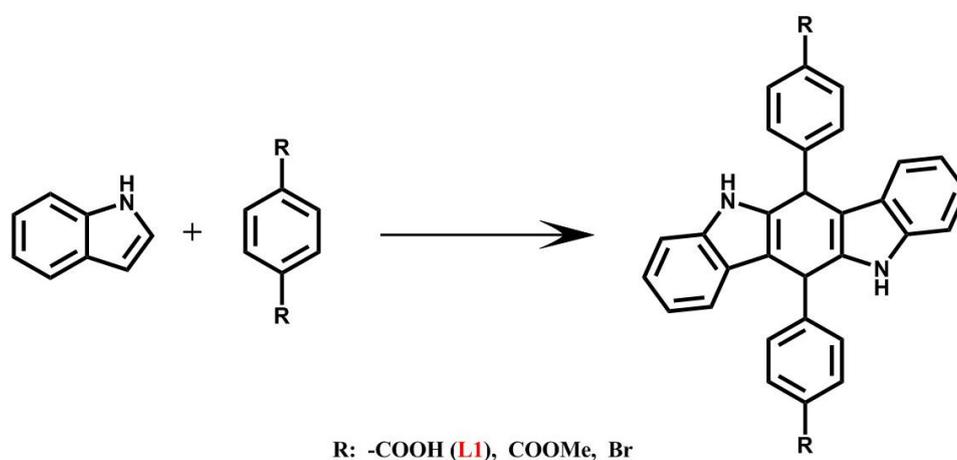


Fig. 1. Scheme for the synthesis of 6,12-di(hetero)aryl substituted TH-ICZ derivatives.

Herein, we reported the design and synthesis 6,12-di(hetero)aryl substituted 5,6,11,12-tetrahyroindolo[3,2-b]carbazole (TH-ICZ) in a facile way. The TH-ICZ unit shown excellent functional groups tolerance and can be terminated with carboxylate acid and bromo. The one decorated with bromo also can be further transformed to extended carboxylate acid *via* Suzuki coupling and then hydrolysis reaction. As a demonstration of concept, TH-ICZ terminated with dicarboxylate acids (**L1**) were used for **Zn-MOF-ICZ** and **UiO-68-ICZ** synthesis. Interestingly, the resultant **Zn-MOF-ICZ** and **UiO-68-ICZ** feature DH-ICZ unit as a result of in-situ oxidative dehydrogenation. The porosity of stable **UiO-68-ICZ** was analyzed by small gas adsorption study.

The 6,12-bis(4-carboxyphenyl) substituted TH-ICZ (**L1**) can be facially synthesis according to the reported procedures[16] with slight modification (Fig. 1). The product can be easily purified and the composition was checked by ^1H NMR (Fig. 2b). The diagnostic protons assigned to the NH were observed at about 10.66 ppm and the feature signal for H-6, 12 was identified around 5.66 ppm. These feature signals are similar to the reported TH-ICZ compounds[17]. Single crystal X-ray diffraction study indicated the ligand feature ladder-type geometry (Fig. 2b and Table S1) [18]. This reaction type show generality and different functional group, such as methoxycarbonyl and bromo functional groups also can be easily incorporated by selectively choosing the corresponding aromatic aldehyde derivatives (Fig. 1). The composition of these compounds was also checked by ^1H NMR after recrystallization. The feature peaks for NH and H-6,12 were also observed with slightly shift compared to **L1** (Figs. S1 and S2). The facile introduction of different terminated functional groups, such as methoxycarbonyl and bromo provides a platform for further reaction. 6,12-bis(methoxycarbonyl) substituted TH-ICZ can be transformed into **L1** *via* hydrolysis (Fig. 2b). Considering the reactivity of bromo moiety in 6,12-bis(4-bromobenzene) substituted TH-ICZ, we tried to synthesis extended dicarboxylate acid terminated ligand.[14] Specifically, the extended ligand (**L2**) were synthesized *via* Suzuki coupling reaction by reacting 6,12-bis(4-bromobenzene) substituted TH-ICZ with 4-methoxycarbonylphenyl boronic acid in the presence of Pd(0) catalyst and then hydrolysis of the resultant ester (Fig. S3). The composition of **L2** was also checked by ^1H NMR with feature peaks for NH were observed at about 10.47 ppm and H-6,12 were identified around 5.46 ppm (Fig. S4). The successfully synthesis of **L2** *via* Suzuki coupling and then hydrolysis reaction indicated that the stability of TH-ICZ motif

and this result indicated many 6,12-di(hetero)aryl substituted TH-ICZ synthetic motifs decorated with specific functional groups can be synthesized considering the fact that the bromo intermediates have been commonly used for synthetic motifs synthesis[19]. The successful synthesis **L1** and **L2** indicated that the versatility of this synthetic motifs.

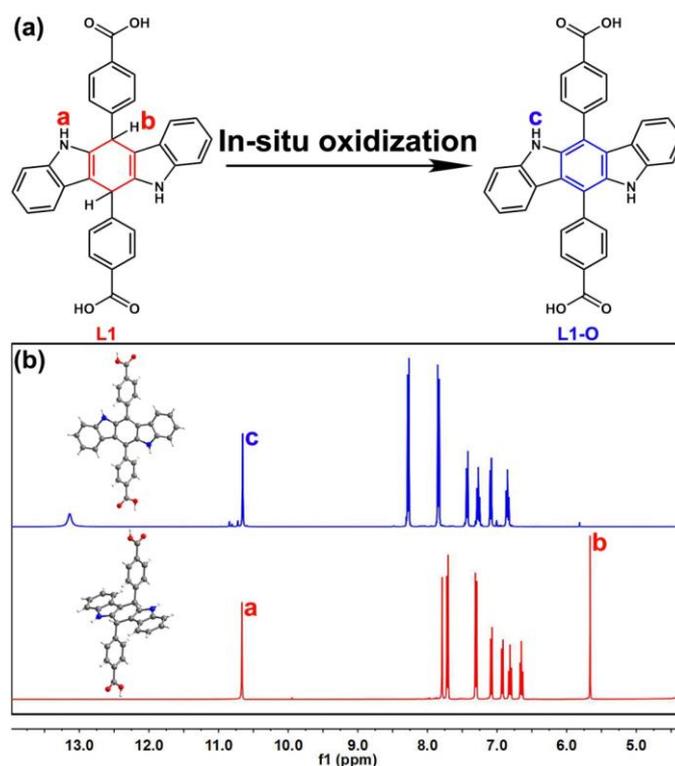


Fig. 2. (a) In-situ oxidation of **L1** to **L1-O** during the solvothermal reaction for MOFs synthesis. (b) ¹H NMR analysis of as-synthesized **L1** and **L1-O** (digested from **Zn-MOF-ICZ**), the insert images are the crystal structures of **L1** and **L1-O**.

To demonstrate the potential of 6,12-di(hetero)aryl substituted TH-ICZ synthetic motifs for porous materials synthesis, we tried to use **L1** as an example to explore the synthesis of zinc MOF and zirconium MOF with the expectation of fabrication of novel structures owing to ladder-type geometry of **L1** ligand[20].

Solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and **L1** in N, N-dimethylformamide (DMF) afford dark red single crystal of **Zn-MOF-ICZ** (Fig. S5). Single crystal X-ray diffraction study

indicated that it crystallizes in the $Fm\bar{3}m$ space group with a unit cell parameter of $a=42.9 \text{ \AA}$ and volume of 79195 \AA^3 at 100 K (Fig. 3a and Table S2). These parameters are well matched with the simulated one obtained from non-interpenetrated IRMOF-16 single crystal structure[21]. The obtained **Zn-MOF-ICZ** with non-interpenetrating structure probably owing to the steric hindrance imparted by bulky group of **L1**. **Zn-MOF-ICZ** is isostructural to IRMOF-16, which is different to the proposed one from ladder-type **L1** (Fig. S6). To get a deep understanding of this phenomenon, the as-synthesized **Zn-MOF-ICZ** was digested by CsF in DMSO- D_6 and D_2O and analysed by 1H NMR. 1H NMR result indicated that **L1** has in-situ oxidized into large π -conjugated fully aromatic 6,12-bis(4-carboxyphenyl) substituted DH-ICZ (**L1-O**) with the disappearance of feature peak for H-6,12 of **L1** (Fig. 2). The in-situ oxidization was driven by the fact for the formation of more thermodynamic stable π -conjugated fully aromatic compound[22-23]. Similar to IRMOF-16, the core of the cluster consists of a central μ_4 -oxygen atom bonded to four tetrahedral Zn^{2+} cations forming a Zn_4O secondary building units (SBUs). Each SBU was connected by six carboxylate acid from **L1-O** to form the 3D extended non-interpenetrated frameworks (Fig. 3a). The phase purity of the sample was confirmed by powder X-ray diffraction (PXRD) study. The peaks of the as-synthesized sample are identical to the calculated peaks derived from the single crystal structure of IRMOF-16 (Fig. S7). In order to assess the gas adsorption properties of the **Zn-MOF-ICZ**, we carried out the N_2 physisorption experiment. **Zn-MOF-ICZ** after activation shown less N_2 uptake at 77 K, and less CO_2 and CH_4 uptake at 273 K (Figs. S8 and S9) and this indicated that the framework has collapsed upon activation which is similar to IRMOF-16.

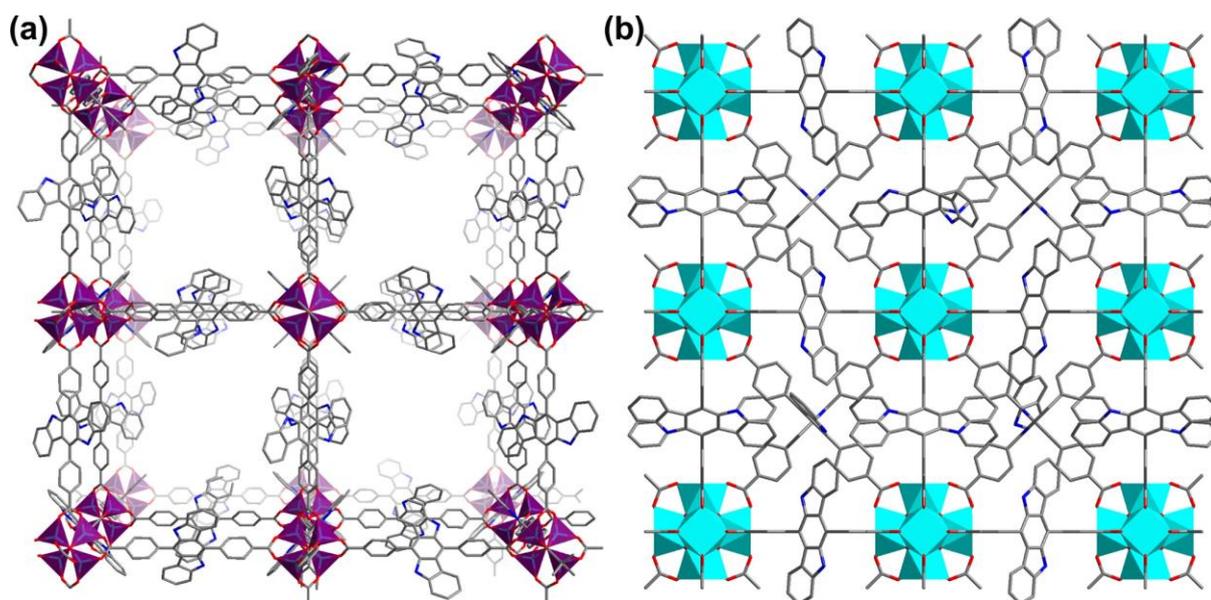


Fig. 3. Simulated crystal structure for **Zn-MOF-ICZ** and **UiO-68-ICZ** based on IRMOF-16 and UiO-68. The statistical indolo[3,2-b]carbazole units were simplified for clarity.

In order to assess the versatility of **L1** in the synthesis of other types of MOF, we turned to Zr-MOFs. In 2018, Lillerud and co-workers reported the synthesis of a new inorganic SBU, namely $Zr_6O_4(OH)_4(CO_2)_{12}$ for the synthesis of Zr-MOFs[24]. Since then, a series of Zr-MOFs were synthesized as a platform for different kinds of potential application studied owing to their high thermal and chemical stability[20, 25-28]. Solvothermal reaction of zirconium tetrachloride ($ZrCl_4$) and **L1** in DMF modulated with trifluoroacetic acid result in the crystals of **UiO-68-ICZ** with yellow colour and octahedron morphology, feature morphology for UiO-66 series Zr-MOFs (Figs. S10 and S11). Single crystal X-ray diffraction study indicated that it crystallizes in the $Fm\bar{3}m$ space group with a unit cell parameter of $a=32.7 \text{ \AA}$ and volume of 34978 \AA^3 at 100 K (Fig. 3b and Table S2). These parameters are matched with the reported UiO-68[24]. This indicated that the obtained **UiO-68-ICZ** is isostructural to UiO-68, which is also different to the proposed one from ladder-type **L1** (Fig S6). 1H NMR result also indicated that **L1** has also in-situ oxidized into large π -conjugated

fully aromatic 6,12-bis(4-carboxyphenyl) substituted DH-ICZ (**L1-O**) with the disappearance of feature peak for H-6,12 of **L1** (Fig. 2). During the synthesis condition exploration for **UiO-68-ICZ**, we successfully obtained some block crystals of **L1-O** (Fig. S12) and SCXRD analysis indicated the formation of large π -conjugated moiety (Fig. 2b and Table S1) [18].

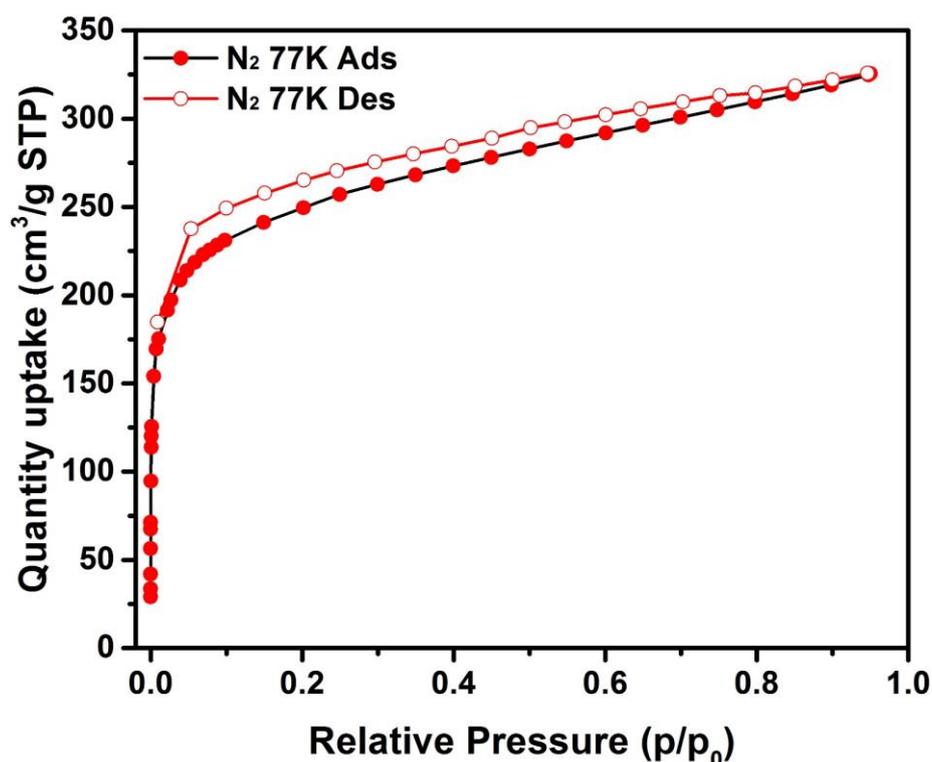


Fig. 4. N₂ sorption property of **UiO-68-ICZ** at 77 K.

The phase purity of **UiO-68-ICZ** was confirmed by PXRD analysis, which shown similar diffraction patterns to calculated patterns derived from **UiO-68** crystal structure (Fig. S13). **UiO-68-ICZ** showed high stability after activation compared to **Zn-MOF-ICZ**. The surface area and porosity parameters of **UiO-68-ICZ** was analysed by standard N₂ adsorption at 77 K. **UiO-68-ICZ** displayed a type I isotherm with a steep nitrogen uptake at a low relative pressure indicating their microporosity nature (Fig. 4). The pore size distribution (PSD) calculated by density functional theory (DFT) from the N₂ sorption curve indicates that the pores of **UiO-68-ICZ** are predominantly distributed at 8.9 and 13.0 Å assignable to the tetrahedral and

octahedral pores (Fig. S14), which are consistent with the crystallographic data when the van der Waals contact is taken into account. This PSD value is comparable to the UiO-68 series of Zr-MOFs with bulky ligand[29]. The calculated BET surface area is about 929 m²/g, which is comparable to UiO-68 series of Zr-MOFs with bulky ligands[30-32] but lower than some UiO-68 series of MOFs. The lower performance may be attributed to low crystallinity as defects are formed owing to bulky ligands were used, which was confirmed by PSD data with mesopore appearing around 3.25 nm (Fig. S14). Besides, the incomplete activation owing to the bulky groups may also contribute to low BET surface area. **UiO-68-ICZ** showed moderated CO₂, CH₄ and water vapour adsorption uptake (Figs. S15 and S16) which are matched with its BET surface area.

In summary, we have reported the facile synthesis of 6,12-di(hetero)aryl substituted TH-ICZ synthetic motifs, which shown excellent functional groups tolerance. As a proof of concept, TH-ICZ synthetic motif terminated with carboxylate acid was successfully used for **Zn-MOF-ICZ** and **UiO-68-ICZ** synthesis *via in-situ* oxidative dehydrogenation and this indicated the potential of this synthetic motif for enrichment of the family of MOFs. However, the implications of our work are wider. It is expected that TH-ICZ based ligands with different functional groups can be obtained in a related fashion by using other aldehydes derivatives. Therefore, we predict that TH-ICZ based synthetic motifs will play an important role in porous materials design and this will provide a platform for diversity function exploration considering the abundance optical properties imparted by the ICZ unit.

Declaration of Competing Interests

The authors declare no competing financial interest.

Acknowledgments

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