Electrical conductivity and electroluminescence of a new anthracene-based metal-organic framework with π-conjugated zigzag chains

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Electrical conductivity and electroluminescence of a new anthracene-based metal-organic framework with π-conjugated zigzag chains†

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A new three-dimensional microporous MOF has been constructed by using a highly conjugated anthracene-based ligand. The rarely occurred long-range π-stacking of ligand in the form of zigzag chain has been found in the MOF structure, which provids not only a new charge transport pathway with high electrical conductivity of 1.3 (±0.5) × 10^{-3} S cm^{-1} but also the electroluminescence property with emission centred at 575 nm.

Metal-organic frameworks (MOFs), also known as coordination polymers, are microporous crystalline materials constructed by organic ligands and inorganic nodes.[1] They are featured by tunable structures and multiple functionalities owing to the high flexibility of coordination interaction.[2] The development of MOFs as prospective functional materials responding to various external stimuli, such as light, pressure, magnetic and electric fields, has attracted much more attentions[3-6], where MOFs have shown great potential for bio-imaging[7], explosives detection[8] and sensors of pressure[4]. While the functionalities of MOFs under external electric field are still less studied as that the alternative connection of inorganic and organic components in the structures inherently block the long-range charge transport, leading to their in general insulating nature. Very recently, a few conductive coordination polymers have been reported, sharing more lights for the synthesis of new MOFs with higher electrical conductivity, and their further applications under electric field.[9-16] As enlightened by organic molecular conductors, the constitution of π-conjugated pathway in MOFs structures seems the most feasible method to achieve the electrical conductivity; however the target arrangement of aromatic ligands in the MOFs structures is a great challenge due to the complexity of self-assembled system and much efforts need to be devoted in this emerging area.

Aromatic anthracene and its derivatives are among the most widely studied conductive organic molecules due to their planar moiety, which is potentially beneficial for desired long-range face-to-face arrangement via π-π interactions in the consequent organic crystals.[17] Meanwhile anthracene and its derivatives have also been demonstrated to be excellent organic electroluminescent materials.[18] Ever since the electroluminescence of anthracene crystal was first studied, a large number of anthracene derivatives with interesting electroluminescence (EL) properties have been prepared for their potential application in organic light-emitting diodes (OLEDs).[19-23] Studies have revealed that the EL property of these molecules depends not only on the structure of the molecules, but also on their spatial arrangements. In fact, it has been demonstrated in the MOFs structures that abundant π-π interactions between ligands are usually observed when anthracene-based ligand was used.[24] In this content, it is highly expected that the conductivity of MOFs constructing from anthracene-based ligand would be achieved by the formation of π-conjugated pathway in the structure. In this manuscript we report a new three-dimensional MOF (denoted as **NNU-27**) by using carboxylate ligand derived from anthracene, in which the charge transport pathway of long-range π-conjugation of ligand in a zig-zag fashion is observed. As expected, **NNU-27** is electric field active with a high conductivity of 1.3 (±0.5) × 10^{-3} S cm^{-1}. Furthermore the electroluminescence of **NNU-27** was studied upon single-crystal samples, where it shows orange red emission centered at 575 nm.

The alkynyl-elongated dicarboxylate ligand of anthracene derivative (H_2L, 4,4'-(anthracene-9,10-diylbis(ethyne-2,1-diyl))dibenzoic acid) was synthesized via typical coupling reaction according to the reported procedure.[24] Then a mixture of $Zn(NO_3)_2{\cdot}6H_2O$, $NaNO_3$ and H_2L in N,N-diethylformamide (DEF) was placed in a capped glass vial at 85 ^{o}C for 72 hours to afford the needle-like crystals of **NNU-27**. The yield is ca. 60 % based on ligand.

Single crystal X-ray diffraction revealed that **NNU-27**, $[ZnNa_2(L)_2(DEF)_2]{\cdot}DEF$, crystallizes in the tetragonal space group $P4_2/nbc$. The three-dimensional framework of **NNU-27** is constructed from anthracene-based ligand and metal ions (Fig.

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1). The Zn^{2+} ion in the structure is coordinated by four carboxylic oxygen atoms forming tetrahedral geometry, while the Na^{+} ion is coordinated by four carboxylic oxygen atoms and two oxygen atoms from DEF molecules generating distorted octahedral geometry. The carboxylate groups link the Na^{+} and Zn^{2+} ions together to form infinite bimetal chain with Na^{+}/Zn^{2+} molar ratio of 2:1 (Fig. 1c). Interestingly, as shown in Fig. 1b, the ditopic anthracene-based aromatic ligands between neibouring metallic chains interact with each other via π–π interactions in a zig-zag fashion along the crystallographic *c*-axis. The face to face distances of adjacent ligands are about 3.420 Å. These zigzag chains of ligand constitute a double-wall carbon-nanotube mimicked channels along the *c*-axis with pore diameters of 16×16 Å. It is notable that the long-range π-conjugated zig-zag arrangement of ligand is rarely observed in MOFs and such spatial arrangement is different from those typically occured in organic crystals of anthracene derivatives (Fig. S1, ESI†).

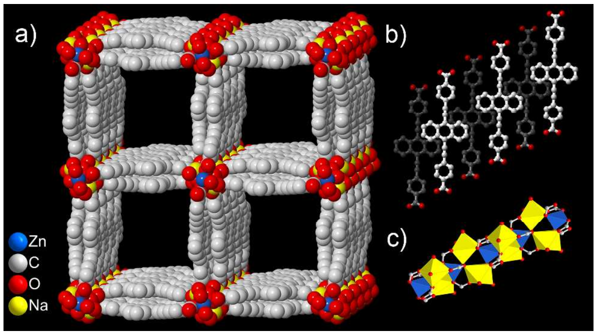

Fig. 1 (a) Framework structure of **NNU-27** along *c*-axis. (b) View of the stacking of ligand in the structure. (c) The infinite bimetal Zn^{2+}/Na^{+} chain.

The powder X-ray diffraction patterns of the as-synthesized bulk **NNU-27** are in accordance with the simulated patterns based on the single-crystal X-ray data (Fig. S2, ESI†), indicating the formation of pure phase. The TG curve of **NNU-27** exhibited a weight loss of 22.12% below 400 °C (Anal. Calcd.: 22.58%), which is attributed to the removal of all DEF molecules. The subsequent weight loss from 400 to 740 °C corresponds to the decomposition of ligand. (Found: 65.02%, Anal. Calcd.: 65.57%) (Fig. S3, ESI†). The solvent accessible volume of **NNU-27**, calculated by PLATON/SOLV,[25] is as high as 39.5% after being activated. However it shows no gas absorption after activation by solvent exchange process, due to the loss of its pristine structure by removal of coordinated guset molecules during activating process. Hence the porosity of **NNU-27** was ascertained by dye uptake measurements instead of gas uptake (Fig. S4, ESI†). **NNU-27** exhibited 40 wt% encapsulation of methylene blue (MB) molecules at room temperature.

The one dimensional long-range arrangement of π–π interactions between ligands in **NNU-27** provides a conjugated pathway for the potential space charge transport. Owing to its large size over hundred microns along crystallographic *c*-axis and the needle-like morphology of **NNU-27**, electrical conductivity measurement on single crystal sample is feasible.

The electrical conductivity was then measured by two-probe method where a single crystal was immobilized between two blocks of conducting silver resins to form the desired ohmic contact (Fig. 2a and 2b). Tens of different crystals of **NNU-27** were tested and all the current-voltage (*I-V*) measurements were performed in ambient condition by sweeping the voltage from -5 V to 5 V. Three representative *I-V* curves among these samples are shown in Fig. 2c. Typically the *I-V* measurements showed a well-fitted linear dependence at ambient temperature, illustrating the charge transport in the crystals of **NNU-27**. The electric current intensity is in the level of nanoampere during the measurement. The conductivity was then elucidated by measuring the effective contact of the device (ca. 600 × 140 × 140 μm). The average electric conductivity of **NNU-27**, obtained from tens of single crystals, is about 1.3 (±0.5) × 10^{-3} S cm^{-1} according to Ohm's law (ESI†). Moreover, the sample is stable as that the *I-V* curves are almost identical when the applied voltage was switched on-off for several times (Fig. S5, ESI†).

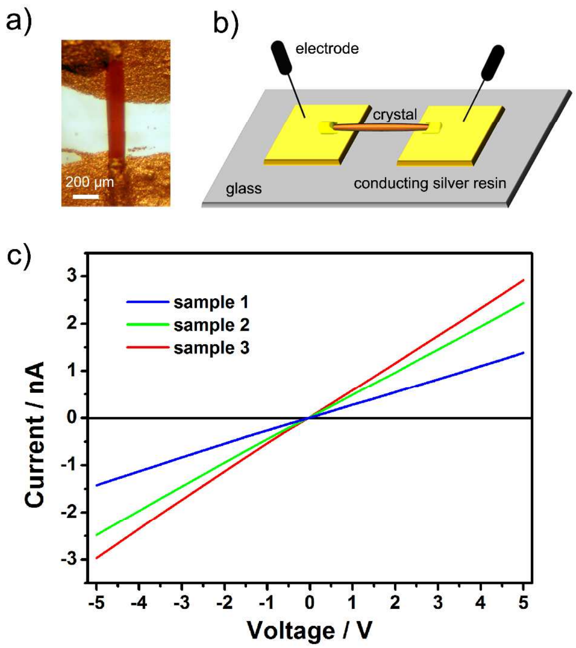

Fig. 2 (a) The optical image of **NNU-27** (contacts made with conducting silver resins). (b) The schematic diagram of electric conductivity measurement. (c) The *I-V* curves of the single crystals of **NNU-27** measured in the dark.

It is notable that **NNU-27** shows the best conductivity among the reported three dimensional MOFs. Recently, Dincă *et al.* have reported series of three-dimensional conductive MOFs including M_2(DEBDC) (M=Fe, Mn and E = S, O) and M_2(TTFTB) (M= Mn, Co, Zn, and Cd; H_4TTFTB = tetrathiafulvalene tetrabenzoate).[26,27] For coordination polymers of M_2(DEBDC), their structures are featured by infinite M-O/S chains which account for their charge transport with the best performance at about 3.9 × 10^{-6} S cm^{-1}. In contrast, the M_2(TTFTB) compounds are featured by the long-range π-stacking in the structures to achieve the conductivity via space charge transport, and M_2(TTFTB) compounds show higher electrical conductivity than M_2(DEBDC) with a maximum of 2.86 (±0.53) × 10^{-4} S cm^{-1}. These studies suggest the π-stacking pathway seems more advanced than M-O bonds by two orders of magnitude to achieve charge transport. The same as M_2(TTFTB), the conductivity of **NNU-27** is primarily through space charge transport; however **NNU-27** exhibits even higher conductivity of five times than M_2(TTFTB). The high conductivity of **NNU-27** is attributed to the new fashion of long-range π-conjugation in the structure, which is different from that in M_2(TTFTB). Both M_2(TTFTB) and **NNU-27** possess long-range π-conjugation arrangement along the crystallographic *c*-axis, where the plane of ligand in M_2(TTFTB) is perpendicular to the *c*-axis, but the plane of the ligand in **NNU-27** is parallel to the *c*-axis. Hence the space charge transport in M_2(TTFTB) is in a "spiral staircase" fashion, while the conductive pathway in **NNU-27** is a zigzag chain (Fig. S6, ESI†). As a result the charge transport pathway in **NNU-27** is more conjugated than in M_2(TTFTB), in which it is well known that the extension of π-conjugation between aromatic molecules has been proven key factor to enhance the charge mobility.

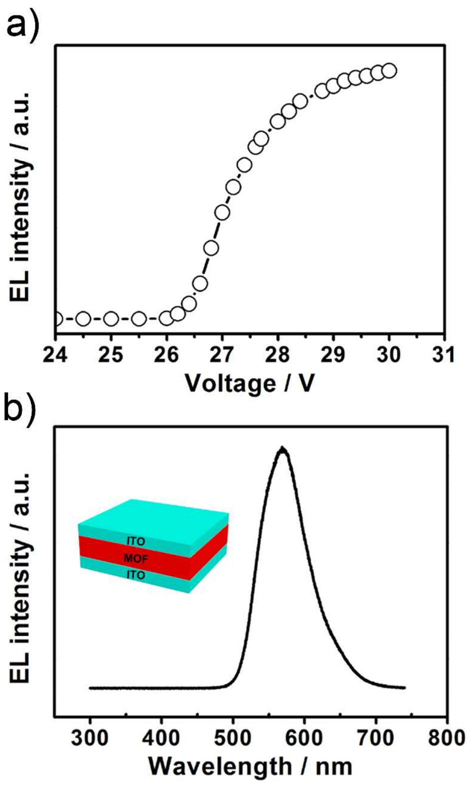

Fig. 3 (a) The EL intensity vs. voltage. (b) The EL spectrum of **NNU-27** (the inset is a schematic of the crystal-based EL device).

The same as single crystal of anthracene, the long-range π–conjugated molecules not only provide a pathway for charge transport but also introduce the potential electroluminescence property. The EL property of **NNU-27** was then studied by single crystal sample at ambient condition. The measurements were carried out using devices with structure of ITO (indium tin oxide) / **NNU-27** / ITO. Commercially available ITO substrates with nominal sheet resistance of ca. 100 Ohm were used in the tests. Before device fabrication, the ITO substrates were ultrasonically cleaned by deionized water, ethanol and acetone for 30 min. Tens of **NNU-27** crystals of almost identical sizes were placed between ITO substrates to fabricate the electroluminescent device. The devices were connected with external electrical field by silver wires, and they were protected by additional tandem resistance (1000 Ohm). The working voltage of the luminescent device was counted by voltmeter and the electroluminescence was measured by spectrofluorometer.

As shown in Fig. 3, the electroluminescence of **NNU-27** was first observed when the fabricated crystal-based device was applied with a voltage of ca. 27 V. Different from its fluorescence at about 660 nm (Fig. S7, ESI†), **NNU-27** exhibits an orange red emission centred at 575 nm. The dependence of the luminescence intensities on the applied voltages were measured simultaneously under ambient condition. The intensity of EL emission increased when the applied voltage was enhanced, behaving like typical OLEDs. More than twelve electroluminescent devices were fabricated and tested, where these devices behaved similarly, with the turn-on voltages varied from 24 V to 30 V. The turn-on voltage of EL for **NNU-27** is much higher than those of OLEDs (usually 3-8 V),[28,29] this is due to the very large thickness of the device (larger than 100 μm caused by single crystal sample). The electroluminescence of **NNU-27** should result from the electric-field induced electromers relying on the unique spatial arrangement of anthracene-based ligand in the structure.

In summary, a new three-dimensional microporous MOF **NNU-27** has been constructed solvothermally by using the anthracene-based carboxylate ligand. It is interesting that a new charge transport pathway of long-range π-conjugation of ligand in a zig-zag fashion is observed in the structure. As expected, **NNU-27** is electric field active showing a high conductivity of 1.3 (±0.5) × 10^{-3} S cm^{-1}. Furthermore the EL property of the as-prepared MOF material was studied by fabrication of single crystal based electroluminescent devices. **NNU-27** exhibits an orange red emission centred at 575 nm with turn-on voltage of about 27(±3) V. The study illustrates that, by incorporation of functional groups into ligands followed by the self-asssembly of MOFs structures, the orientation and the interaction between these functionalized ligands can be regulated spatially in long-range order through crystal engineering, hence the electrical conductivity and electroluminescence of MOF materials can be achieved.

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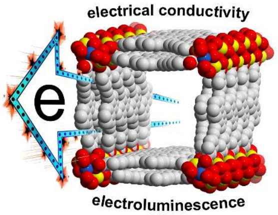

A new metal-organic framework with π-conjugated zigzag chains of anthracene-based ligand exhibits electrical conductivity and electroluminescence.