Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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

Dashu Chen, Hongzhu Xing,* Zhongmin Su and Chungang Wang*

Laboratory of Micro-Nano Functional Materials, College of Chemistry, Northeast Normal University, Changchun, 130024, China

E-mail: xinghz223@nenu.edu.cn; wangcg925@nenu.edu.cn

1. Materials and methods:

N,*N*-diethylforamide (DEF, 99%) was purchased from TCI. Other common reagents were of analytical grade and used as purchased without further purification.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D-MAX 2550 radiation (λ = 0.15417 nm) with 2θ ranging from 3° to 40°. Thermogravimetric analyses (TGA) were carried out with the Perkin-Elmer TGA-7 thermogravimetric analyzer at a heating rate of 10 ^{o}C min^{-1} from room temperature to 800 ^{o}C under atmosphere. The Fourier transform infrared (FT-IR) spectra were recorded based on KBr pellets in the range of 4000−400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Solid-state fluorescence spectrum was measured on FLSP920 Edinburgh Fluorescence Spectrometer at room temperature. The luminescence for all the as-prepared luminescent devices was measured using the Shimadzu RF5310PC spectrofluorometer. Current–voltage (*I*–*V*) curves of **NNU-27** were recorded with a Keithley 4200 SCS and a Cascade M150 probe station in a clean and shielded box at room temperature in air.

Single crystal X-ray diffraction: Single-crystal X-ray diffraction data collection of compound **NNU-27** was performed on a Bruker Smart Apex Ⅱ CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at room temperature. Absorption corrections were applied by using the multisacn program SADABS. The crystal structure was solved by direct methods and refind by full-matrix least-squares on F^2 with anisotropic displacement using SHELXTL.[1] The coordinated DEF molecule is disordered over two positions with each site occupancy of 50%. The reported structure is guest-free refined by PLATON/SQUEEZE program. For details of the data collection and refinement are supported, see Table S1. The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 995215. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement of **NNU-27**.

empirical formula	$C_{74}H_{54}O_{10}N_2Na_2Zn$
formula weight	1242.54
crystal system	Tetragonal
space group	$P4_2/nbc$
a / Å	30.871(3)
b / Å	30.871(3)
c / Å	10.6581(14)
α / °	90
V / Å^3	10157 (2)
Z	4
F(000)	2576
θ range collected	2.322 to 23.271
limiting indices	$-32 \leq h \leq 34$
	$-32 \leq k \leq 34$
	$-11 \leq l \leq 11$
Reflections collected / unique	42799 / 3651
data / restraints / parameters	3651 / 70 / 233
R(int)	0.1030
goodness-of-fit on F^2	0.998
Final R indices ([$I > 2\sigma(I)$])	$R_1 = 0.0581$, $wR_2 = 0.1666$
R indices (all data)	$R_1 = 0.1121$, $wR_2 = 0.2018$

Electrical conductivity measurements: The current density (*J*) and electric field strength (*E*) were used to measure the conductivity value of **NNU-27** according to Ohm's law,

$$\sigma = \frac{J}{E},\ J = \frac{I}{S},\ E = \frac{V}{L}$$

where σ is the conductivity, *J* is current density, *E* is electric field strength, *I* is current, *V* is voltage, *S* is sectional area of **NNU-27** and *L* is effective contacted length of **NNU-27**.

Synthesis of NNU-27: A mixture solution of $Zn(NO_3)_2 \cdot 6H_2O$ (13 mg), $NaNO_3$ (15 mg), H_2L (20 mg), DEF (10 ml) was consequently placed in a capped vial (20ml). The vial was then heated at 85 ^oC for 72 hours in an oven to afford orange needle-like crystals. Yield: ca. 60 % based on ligand. FT-IR (KBr pellets, cm^{-1}): 3446 (m), 3064 (w), 2340 (s), 1650 (m), 1596 (m), 1542 (m), 1382 (s), 1169 (m), 1014 (w), 856 (m), 768 (s), 695 (m), 638 (m).

Synthesis of Ligand: The synthesis of ligand was adapted from a literature procedure with minor revisions.[2] Typically, to a solution of ethyl 4-ethynylbenzoate (2.0 g, 11.49 mmol) in DMF (20 mL) was added 9,10-dibromoanthracene (1.74 g, 5.18 mmol), $Pd(Ph_3)_2Cl_2$ (90 mg, 0.13 mmol), CuI (45 mg, 0.24 mmol) and Et_3N (20 mL) under N_2. After being stirred at 80 ^oC for 48 h, the reaction was quenched with water, extracted with $CHCl_3$, washed with brine and dries over $MgSO_4$. Recrystallization from $CHCl_3$ gave the product as a red solid. To this product (0.708 g, 1.92 mmol) dissolved in THF/methanol/H_2O (1:1:1, 45 mL), KOH was added (1.74 g, 12.64 mmol) and the resulting solution was stirred under reflux for 24 h as monitored by TLC. The mixture was acidified with aq. HCl, and then the precipitate was filtered.

References:

1 G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64,** 112.

2 F. Yu, Y. M. Zhang, Y. H. Guo, A. H. Li, G. X. Yu and B. Li, *CrystEngComm*, 2013, **15,** 8273–8279.

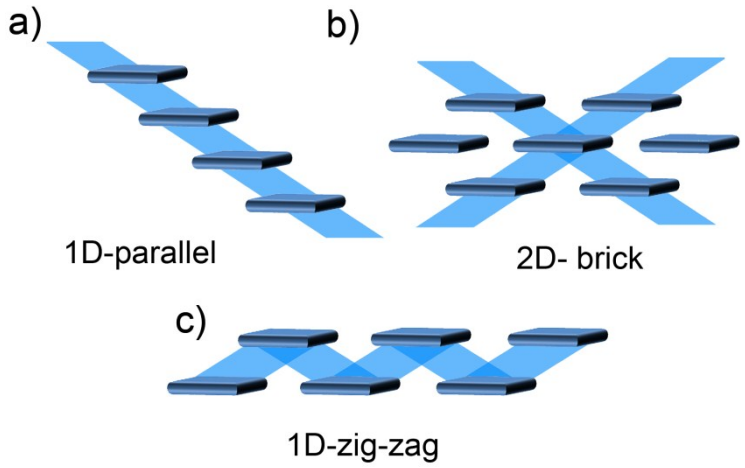

Fig. S1 The schematic diagrams of the spatial arrangement of anthracene derivatives. (a, b) in organic crystals. (c) in **NNU-27**.

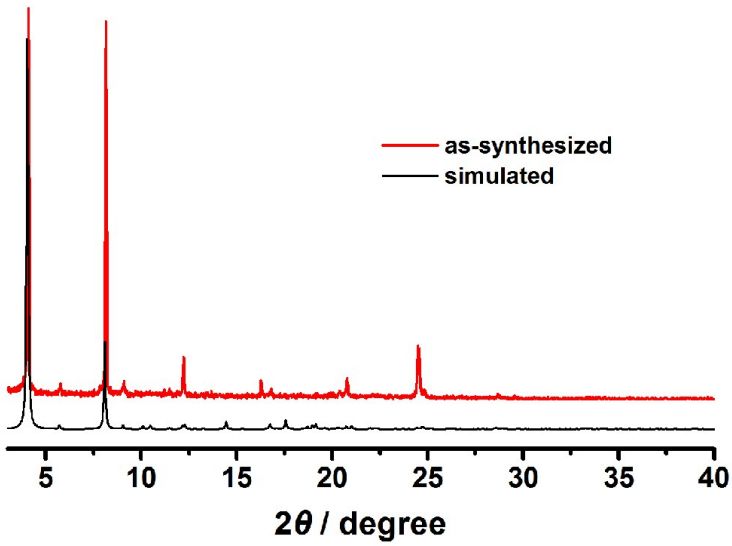

Fig. S2 The PXRD patterns of **NNU-27**.

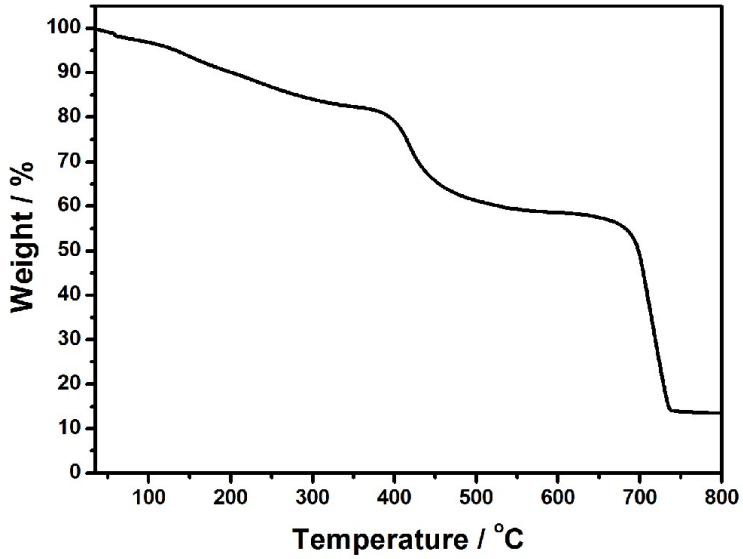

Fig. S3 The TG curve of **NNU-27**.

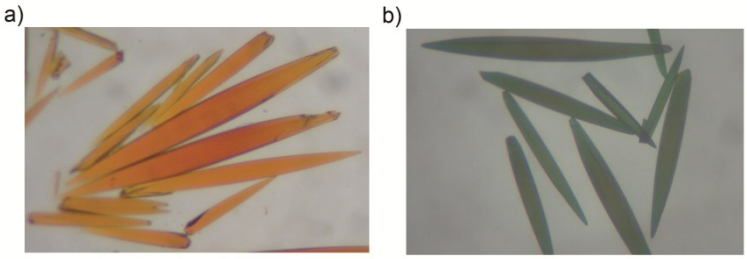

Fig. S4 Optical image of (a) as-synthesized **NNU-27** and (b) MB-loaded **NNU-27**.

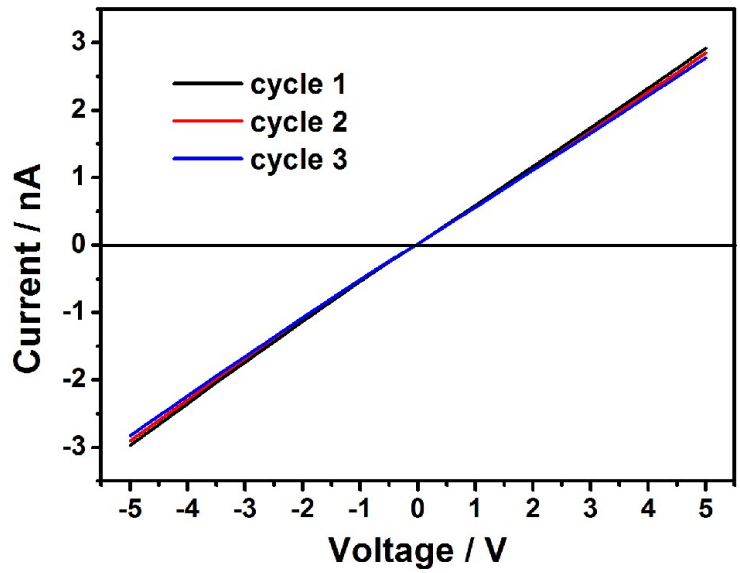

Fig. S5 The three cycles of sweeping voltage from -5 to 5 V for the same single

crystal.

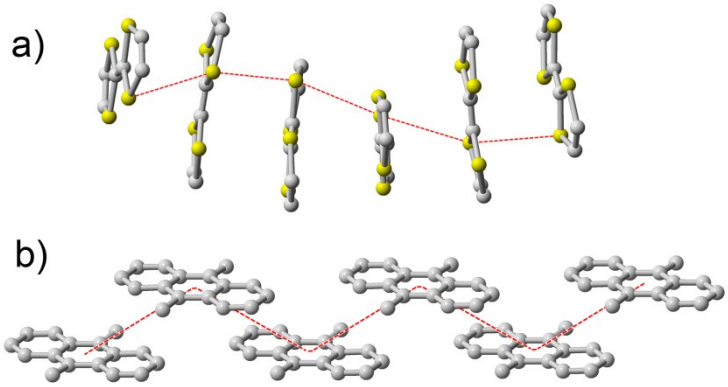

Fig. S6 (a) Helical TTF stack with a depiction of the shortest intermolecular S···S contacts in M_2(TTFTB) (dashed red line). (b) The long range π-conjugated zig-zag arrangement of ligand in **NNU-27** (dashed red line).

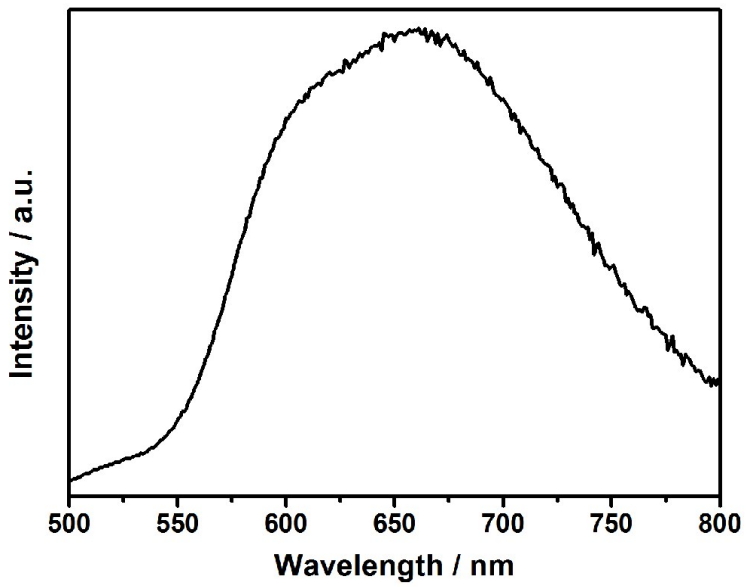

Fig. S7 The photoluminescence spectrum of **NNU-27** excited by 365 nm.