Supplementary Material (ESI) for Chemical Communications

A pcu-Type Metal-Organic Framework with Spindle $[Zn_7(OH)_8]^{6+}$ Cluster as Secondary Building Units

Jian-Rong Li, Ying Tao, Qun Yu and Xian-He Bu*

Materials, methods and synthesis

All the reagents for synthesis were obtained commercially and purified by standard methods prior to use. Elemental analysis was performed on a Perkin-Elmer 240C analyzer. Melting point measurements were taken on an X-4 melting point meter. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets. Thermal analyses were performed in the temperature range of 20~600 ^{o}C on a Rigaku standard TG-DTA analyzer in N_2 with an increasing temperature rate of 10 °C/min^{-1}. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra was carried out by the single-crystal data and mercury (1.4.1) program.

9,10-Dibromoanthracene (DBA) was obtained in high yield from the bromination of anthracene according to the literature method.[1]

9,10-Dicyanoanthracene (DCA) was prepared by simulating a reported procedure:[2] to a 500 mL flask DBA (10.00 g, 0.03 mol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (2.91 g; 0.007 mol; 0.23 equiv), Na_2CO_3 (3.18 g; 0.03 mol; 1.0 equiv), $Pd(OAc)_2$ (0.2-0.4 mol %), and N,N-dimethylacetamide (DMAC, 200 mL) was added. The flask was evacuated and filled with argon (two times), and then heated and stirred in 140 °C for 48 h. After the reaction mixture cooled to room temperature, about 500 ml water was added to the mixture to isolate crude product as yellow solid. The crude product was dried, and then recrystallized (and decolorized) in toluene to obtain the pure product as yellow needle crystals. Yield: 40%; melting point: 337~339 ^{o}C; IR spectrum see Figure 2S. The structure of DCA has also been characterized by X-ray single crystal diffraction (see below).

$\{[Zn_7(OH)_8(DTA)_3]\cdot H_2O\}_n$ (1) was synthesized by the *in situ* solvothermal reaction of 9,10-dicyanoanthracene (DCA) with NaN_3 and $ZnCl_2$ in H_2O-EtOH, and it is insoluble in water and most of organic solvents, even in DMF and DMSO.

Caution! Although we have met no problems in handling Zn-azides and Zn-tetrazolate during this work, it should be treated with great caution owing to their potential explosive nature.

X-ray single crystal diffraction

Single-crystal X-ray diffraction measurements for complex **1** and DCA were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å) and unit cell dimensions were obtained with least-squares refinements. The program SAINT[3] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.[4] Zinc atoms in **1** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligand were added theoretically, riding on the concerned atoms and refined with fixed thermal factors, and those of OH groups were located in a difference map and were refined with an O–H distance restraint of 0.85(1) Å. Lattice water hydrogen atoms were not added in **1**.

Property characterizations

Optical diffuse reflectance spectrum of **1** was measured at room temperature with a PE Lambda 35 UV-vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as a standard (100% reflectance).

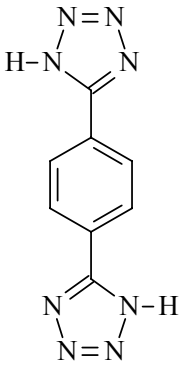
The transport properties of the sample pellet were measured by ac impedance spectroscopy over a frequency range from 20 Hz to 1 MHz using an HP 4284A LCR (inductance-capacitance-resistance) meter. Silver electrodes were painted onto the opposing sides of the pellet. The amplitude of the voltage was 1 V. The temperature ranges from –20 to 220 ^{o}C.

Solid state UV-vis spectra were recorded at room temperature on a computer-controlled Jasco V-550 Spectrometer (JASCO Corp.) in the wavelength range of 200~900 nm.

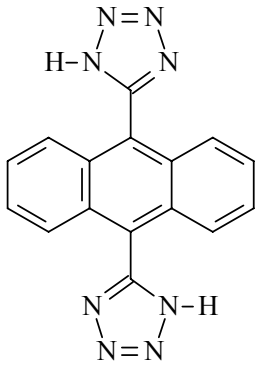
The solid-state fluorescence excitation and emission spectra were performed on a JY FluoroMax-3 spectrophotometer at room temperature with a wavelength increment of 1.0 nm and

integration time of 0.1 s. The luminescent lifetime was surveyed by a state-of-the-art intensified gated/modulated intensified charge coupled device (ICCD) camera system (ultrafast gate Picostar HR, Lavision Corp.) with the femtosecond (fs) laser system (Spectra-Physics Corp.), and the detected date was collected and recorded by a personal computer (PC).

Chart 1S



1,4-ditetrazolatebenzene (H_2DTB)



9,10-ditetrazolateanthracene (H_2DTA)

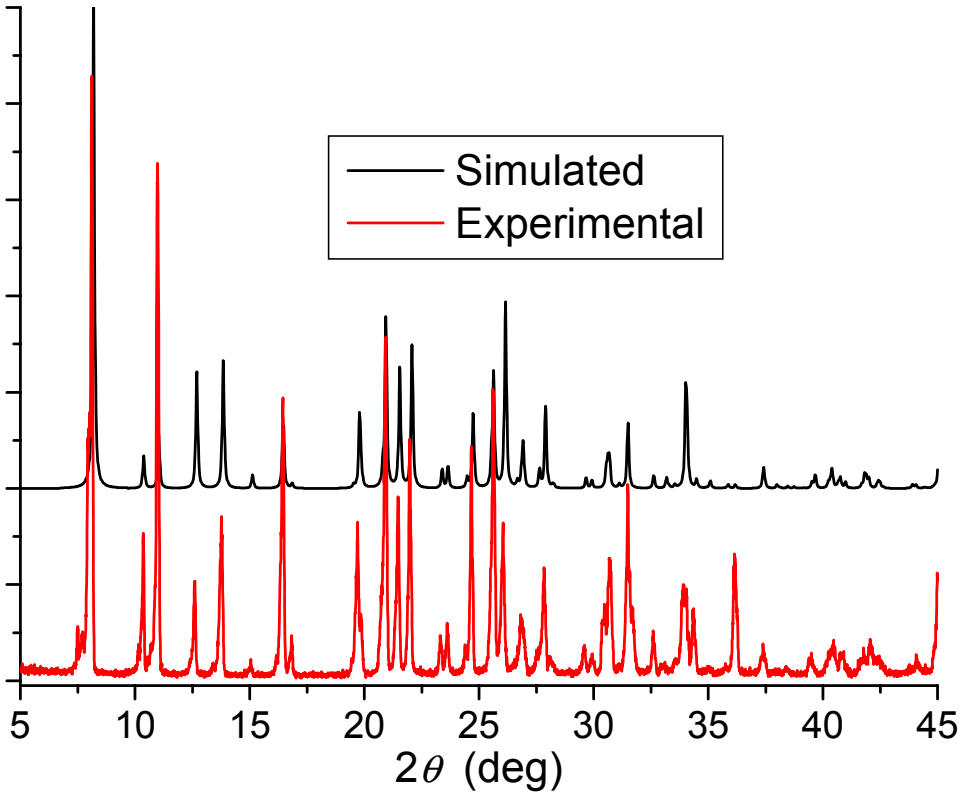
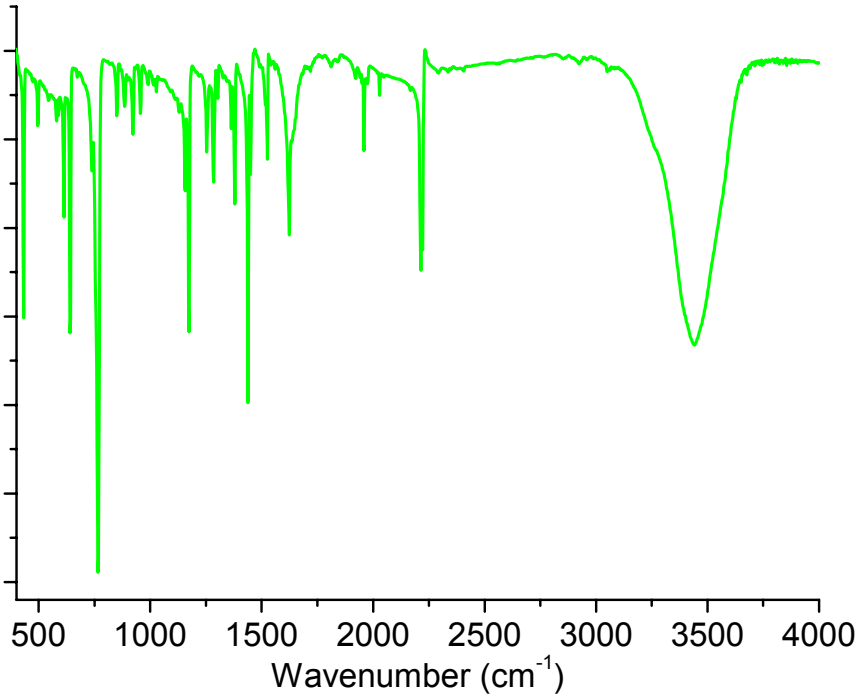


Figure 1S. XRPD patterns for **1**.



(a)

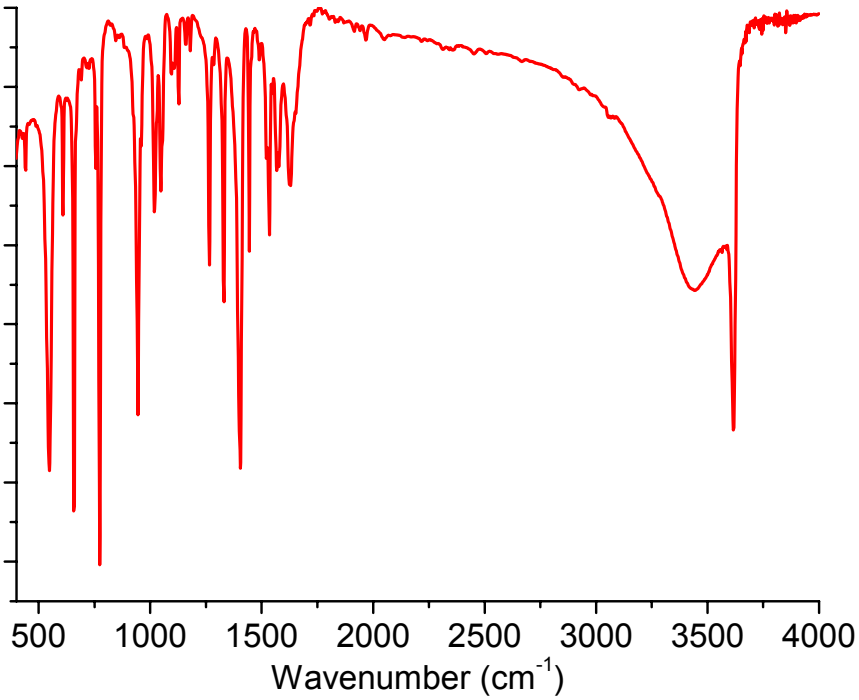


Figure 2S. IR spectra of DCA (a) and **1** (b).

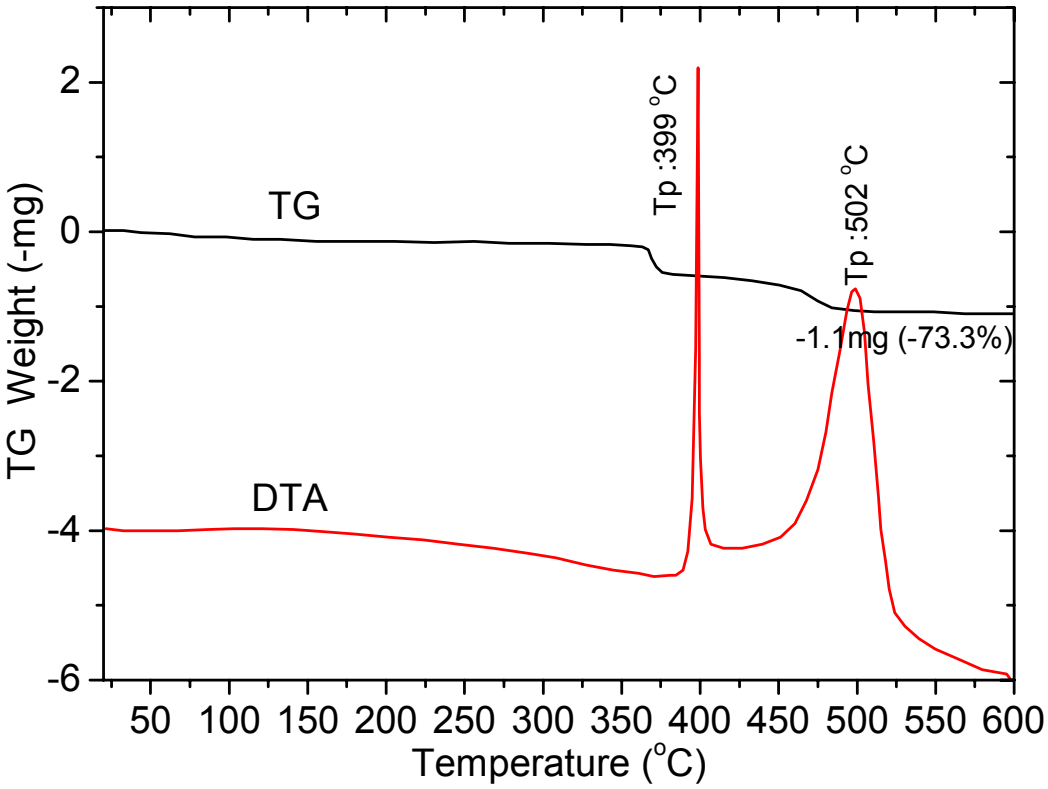


Figure 3S. The TG-DTA curve of **1**.

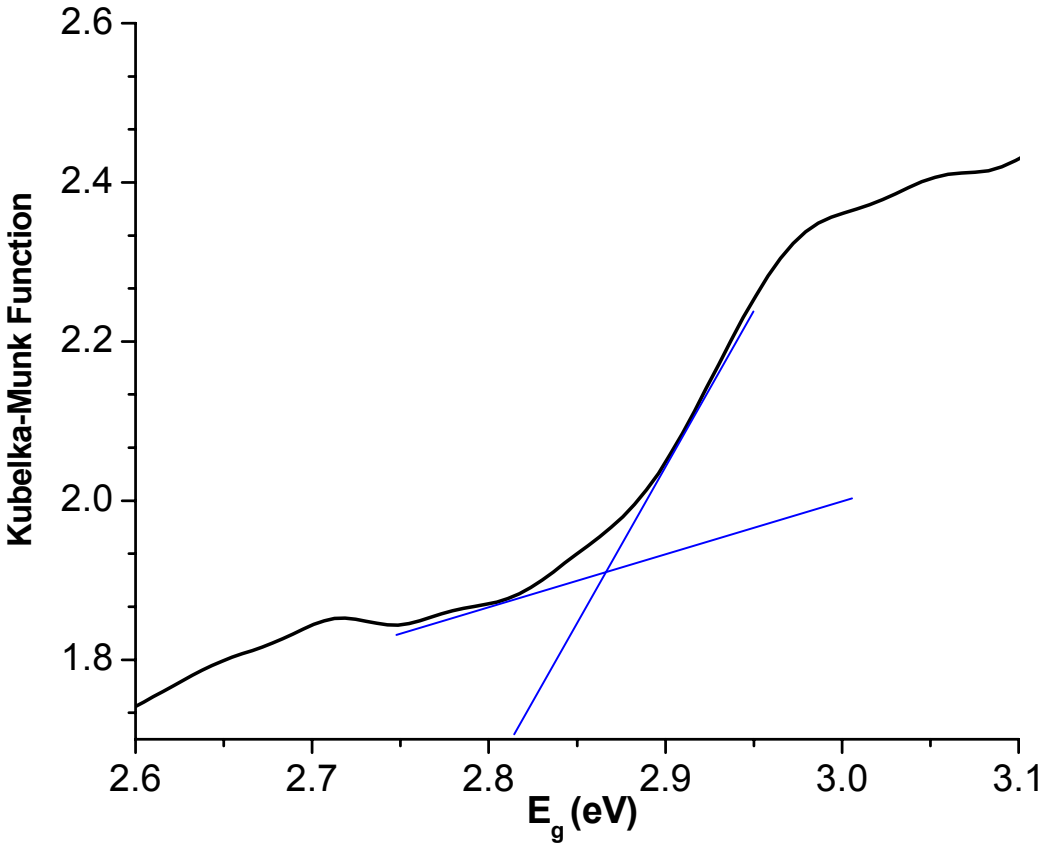


Figure 4S Diffuse reflectance spectrum of **1**.

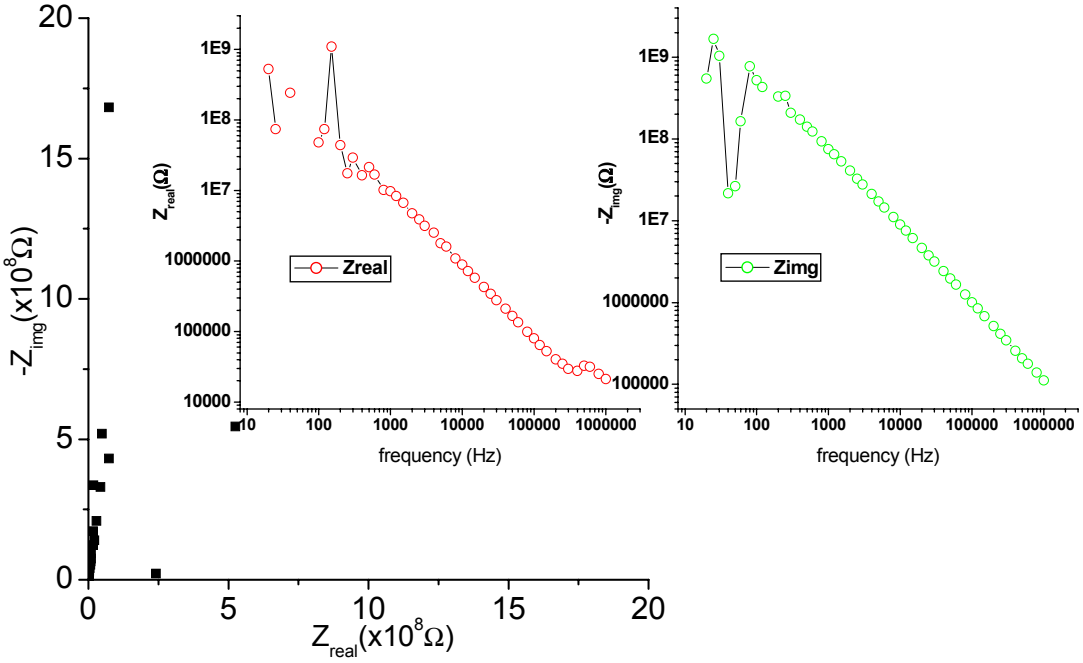


Figure 5S Impendence data recorded at 20 °C（We thank Prof. Guang-She Li, for the measurement of these data and the very helpful discussions）.

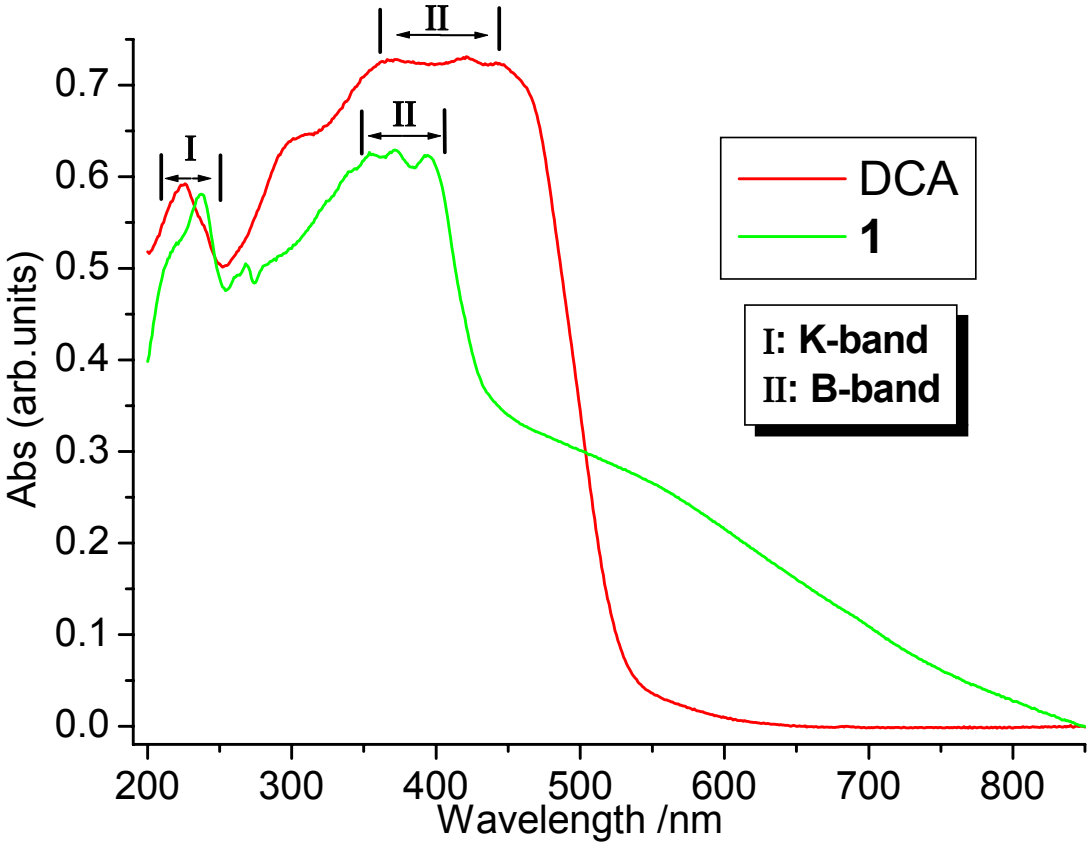


Figure 6S Solid state UV-vis absorption spectra at room temperature for DCA and **1**.

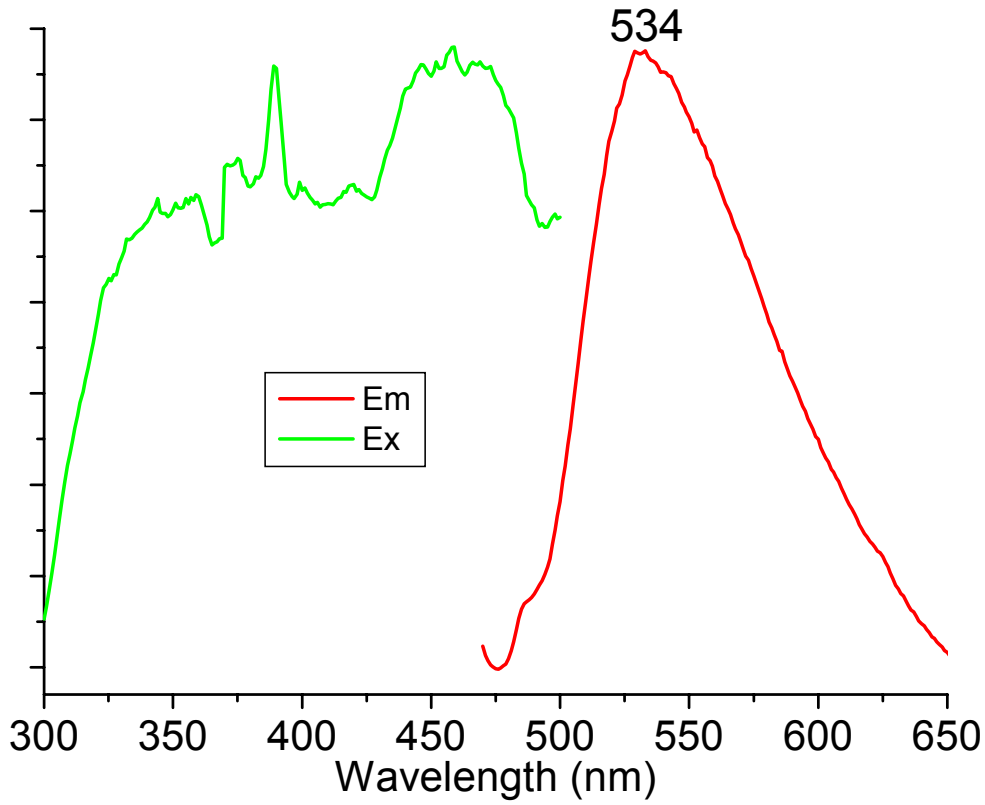


Figure 7S Solid-state photoluminescent spectra of DCA at room temperature.

Structure of DCA

The crystal data of DCA was provided as an additional file in cif format. As shown in Figure 8S, the molecule of DCA is centrosymmetric, with all atoms being coplanar. It is interesting that in the crystal, DCA molecules were aggregated to form a two-dimensional supramolecular network by C–H---N hydrogen-bond (red dotted line) and π---π (pink dotted line) interactions (Figure 9S).

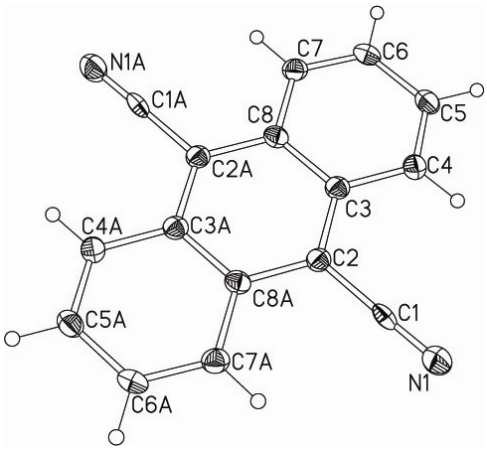


Figure 8S ORTEP view of DCA with 50% thermal ellipsoid probability.

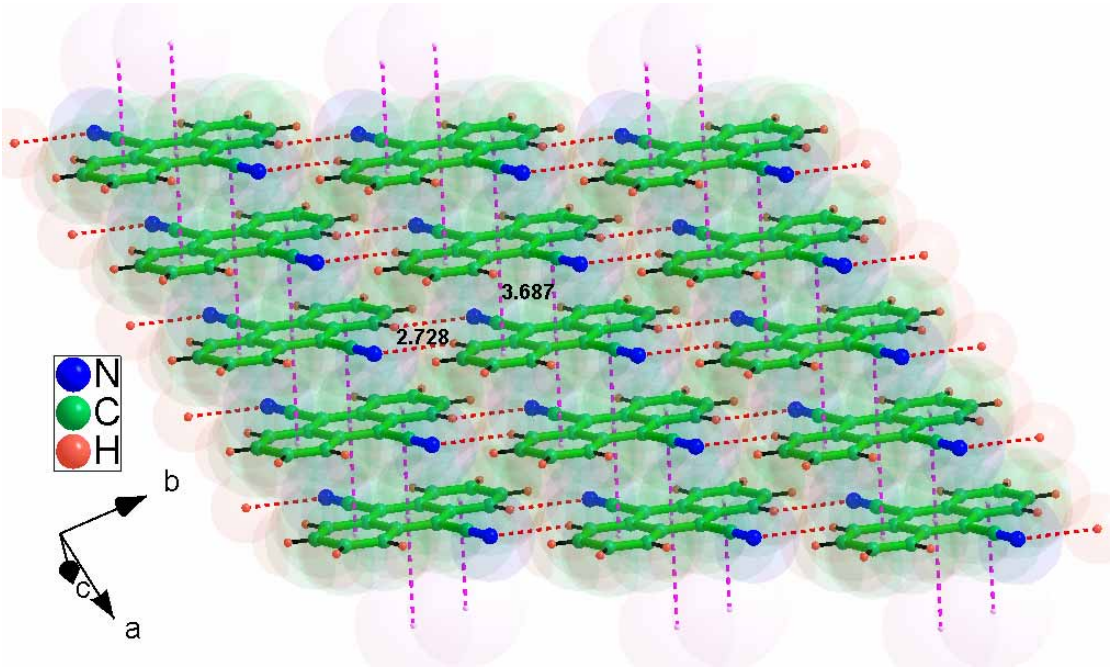


Figure 9S Two-dimensional supramolecular network formed by C–H---N hydrogen-bond (red dotted line) and π---π (pink dotted line) interactions.

References

1 S. Jones, J. C. C. Atherton, *Synth. Commun.*, 2001, **31**, 1799.

2 S. A. Weissman, D. Zewge, C. Chen, *J. Org. Chem.*, 2005, **70**, 1508.

3 G. M. Sheldrick, *SADABS: Program for Expirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1996.

4 G. M. Sheldrick, *SHELXTL Version 5.1. Program for Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.