Pyridyl substitution at 2,6-positions of anthracene toward crystal polymorphs with distinct optical characteristics

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Experimental section

Materials and Chemicals: 2,6-Di(pyridin-4-yl)anthracene was synthesized by a Suzuki coupling reaction.[1] Acetonitrile (CH_3CN, HPLC) were purchased from Beijing Chemical Co., China. Deionized water (18.2 MΩ·cm^{-1}) was made by using a Milli-Q (Millipore) water purification system.

Preparation of two phases of crystals: Two phases of crystals were prepared by solution drop-casting. In a typical experiment, DPYA was dissolved in acetonitrile solution. The DPYA solution was then directly dropped onto the substrate (quartz, glass or SiO_2/Si wafer), and two phases of crystals were observed after the solvent evaporated completely.

Single crystal X-ray Diffraction measurements: Large crystals of DPYA (β phase) suitable for single crystal data ananlysis, were grown from the cooled solutions in CH_3CN, which were firstly heated at reflux and then cooled to room temperature. The crystal analysis was performed on Rigaku Saturn724 CCD at 173 K using MoK$_α$ with diffraction radiation (40 kV, 30 mA)

wavelength of 0.71073Å and graphite as monochromator. The crystal structure was solved and refined using Olex2-1.0 with anisotropic displacement parameters for non-H atoms. H atoms were experimentally located through the difference-Fourier electron density maps in all crystal structures. A check of the final crystallographic information file (CIF) with PLATON (Spek, 2009) did not show any missed symmetry. Crystallographic parameters are summarized in Figure S1, CIF files are also deposited with the (CCDC No. 2166838).

DFT calculation: The total energies of for the two phases are calculated by the density functional theory (DFT) adopting the PBE functional[2] with the dispersion energy correction given by the DFT-D3 method with Becke-Jonson damping[3].

Powder X-ray diffraction (PXRD) measurement: PXRD measurement was performed on an Empyrean X-ray diffractometer (PANalytic, Netherlands), flat-bed sample holder, where in crystals were grown on slide, next for the few experiments the powder samples are dispersed on glass slide uniformly and then diffraction was carried out with Cu Kα radiation.with Cu Kα radiation.

DSC measurement: Differential scanning calorimetry (DSC) was performed on a TA Discovery DSC 250 calorimeter. Under N2 gas, samples were examined at a scanning rate of 10 °C/min by applying heating cycle.

Optical Characterization:

Solid UV–vis absorption measurement: The steady absorption spectra of crystals were performed on a Cary 5000 UV-VIS-NIR (Varian, USA) instrument and also an UV-2600 spectrometer (Shimadzu, Japan) using an integrating sphere

Solid PL measurement: Photoluminescence (PL) spectra were recorded on a Horiba FluoroMax-4-NIR spectrofluorometer, the excitation wavelength was 375 nm for single crystals. The average PLQY ($\Phi_{PL)}$ was measured absolutely according to the five samples by using an integrating sphere on an Edinburgh FLS980 spectrometer. The PL lifetime were detected with a streak camera (C5680, Hamamatsu Photonics), dispersed by a polychromator (250is, Chromex), with a spectral resolution of 1 nm and a time resolution of 10 ps.

Confocal laser scanning microscopy: (CLSM) images were recorded on a quartz substrate using an Olympus Research inverted system microscope (FV1000-IX81, Tokyo, Japan) equipped with a charge-coupled device (CCD, Olympus DP71, Tokyo, Japan) camera. The excitation source was a xenon lamp equipped with a band-pass filter (330−380 nm).

Optical Waveguide: The μ-PL spectra were collected on a home-made optical microscopy system (Supplementary Figure 6). The grown crystals on a quartz coverslip were excited with a UV laser (λ = 375 nm, semiconductor laser). PL spectra were coupled into an optical fiber and

collected using a liquid nitrogen-cooled CCD (SPEC-10-400B/LbN, Roper Scientific) attached to a polychromatic (Spectropro-550i, Acton). The excitation laser was filtered with a band pass filter (330–380 nm), then focused to excite the crystals with an objective (50×0.9 NA).
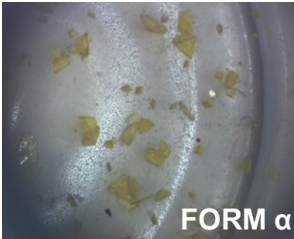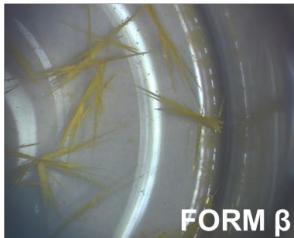

	FORM α	FORM β
a (Å)	12.582(10)	3.7587(8)
b (Å)	5.997(5)	11.009(2)
c (Å)	10.882(9)	19.568(4)
β (°)	103.308	90.97(3)
V (Å³)	799.044	809.599
Space group	$P2_1/c$	$P2_1/c$
CCDC No.	1439496	2166838

Figure S1. Two phases of bulk single crystals grown in acetonitrile solution along with the crystallographic parameters.

Table S1. Crystal structure parameters of the Form β.

Parameters	Form β
Empirical Formula	$C_{24}H_{16}N_2$
Formula weight	332.39
Crystal system	Monoclinic
Space group	$P2_1/n$
T (K)	173
a (Å)	3.7587(8)
b (Å)	11.009(2)
c (Å)	19.568(4)
α (°)	90
β (°)	90.97
γ (°)	90
V (Å³)	809.6(3)
D_{calcd} (gcm^{-3})	1.363

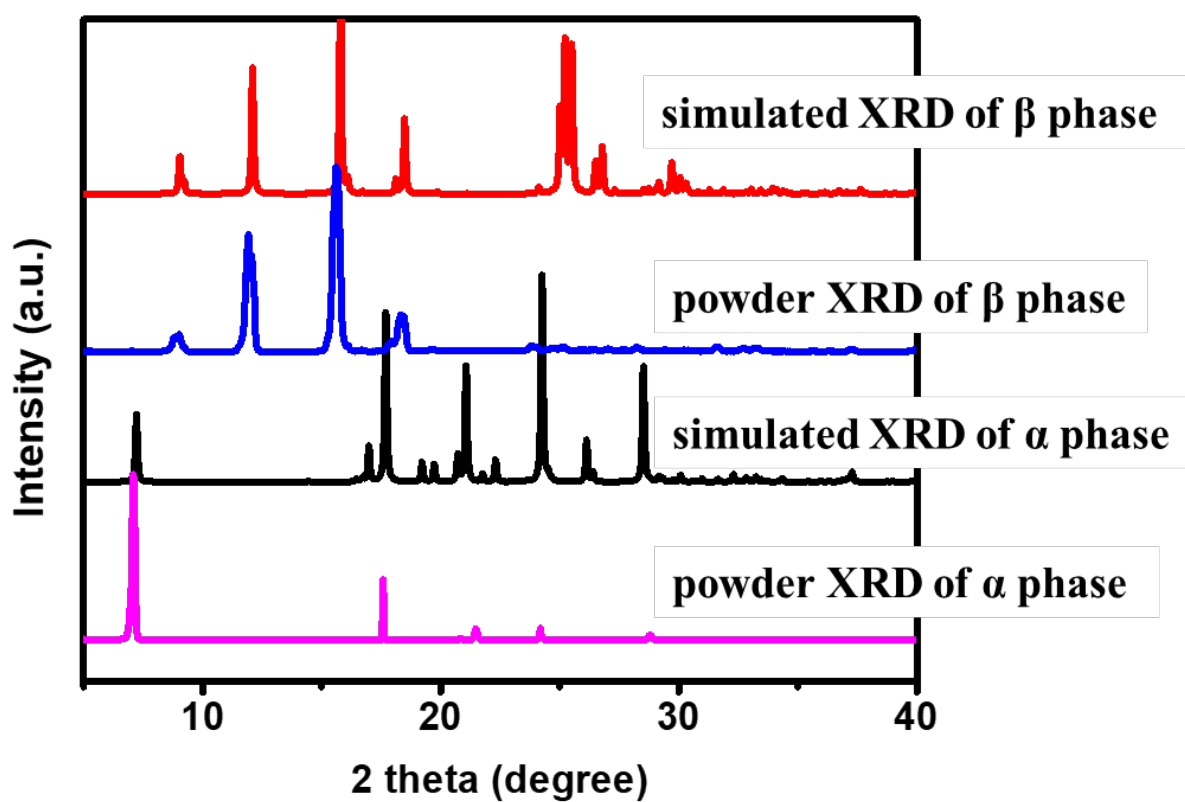|	
Z	2
$R_1[I > 2\sigma(I)]$	0.0507
wR_2 (all)	0.1310
Goodness–of–fit	1.110
No. of reflections used	1796
Total number of reflections	1836
X–Ray Diffract meter	Rigaku

Figure S2. XRD patterns of the two phases of crystals on the quartz substrate compared with the simulated XRD pattern.
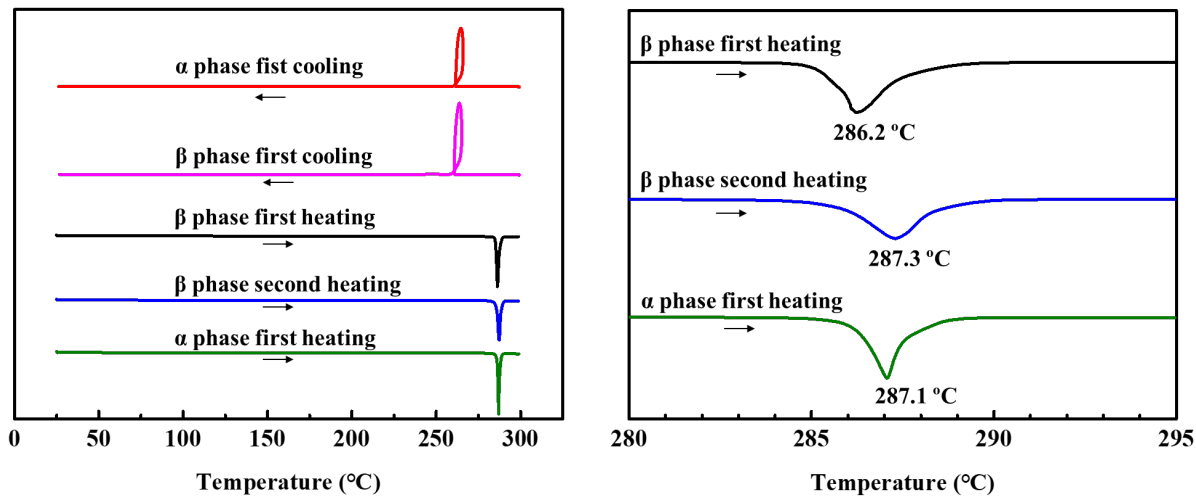
Figure S3. DSC curves of two phases of DPYA. There is a small difference of melting point for the α phase and β phase as shown in the right figure.
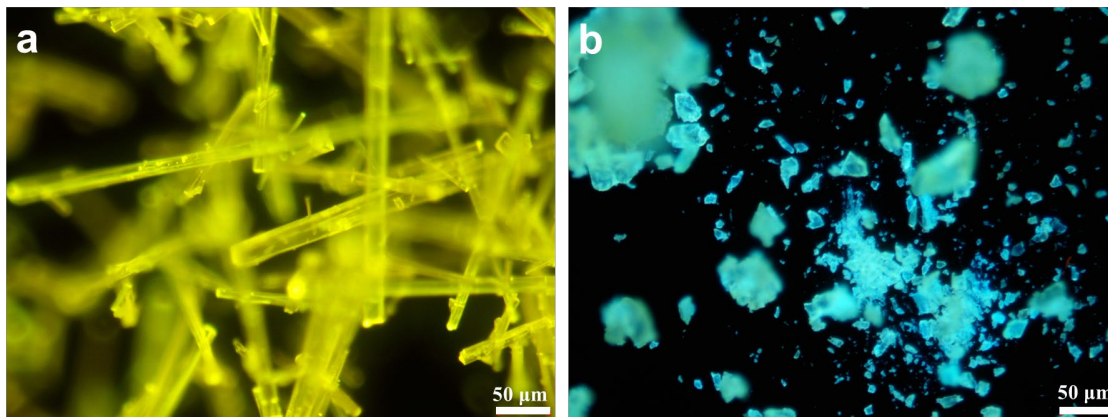

Figure S4. CLSM images of β phase crystals before (a) and after (b) DSC measurement
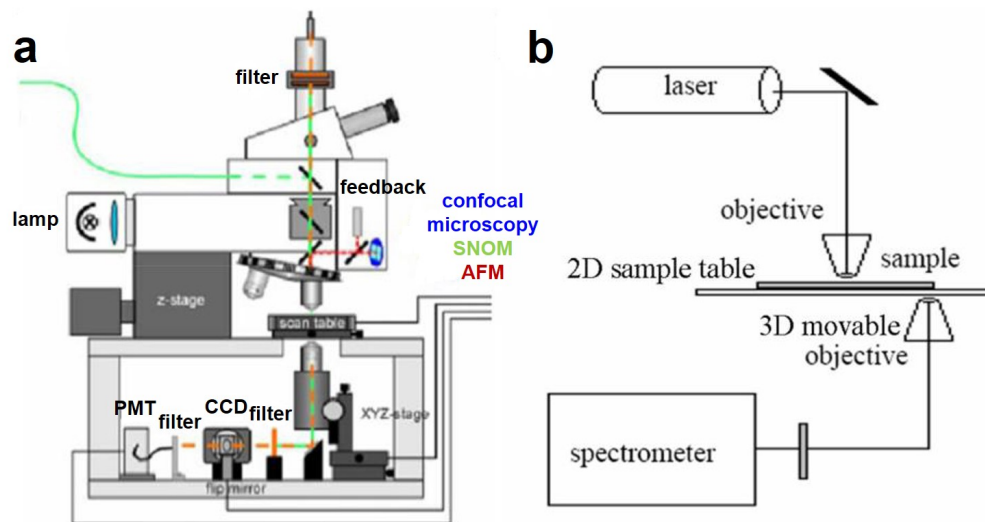
Figure S5. Schematic illustration of home-build confocal μ-luminescence system. (a) The near-field scanning optical microscopy. (b) The transmittance optical path for the waveguide measurements.

Reference

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