Electronic Supplementary Information

Polymorphism-dependent and Piezochromic Luminescence Based on Molecular Packing of a Conjugated Molecule

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Contents

1. Materials and Methods

All starting materials were obtained from commercial supplies and used as received. ^{1}H NMR spectrum was recorded on Varian or Bruker instruments, using $CDCl_3$ as solvent. Chemical shifts are reported in ppm with $CDCl_3$ as reference (7.26 ppm). Uv-vis and fluorescent measurements were carried out on Hitachi U-3010 and F-4500, respectively. XRD diagrams were tested on a D8 ADVANCE and DAVINCI-DESIGN (Bruker). The data of the fluorescence quantum yield of liquid and solid were obtained from a Hamamatsu Absolute PL Quantum Yield Spectrometer C11347 (λ_{ex} = 365 nm). The concentration of the solution (compound in methanol) was 10^{-5} mol/L, and the original solid was ground into powder and then be heated at 108ºC. The high-pressure experiments were performed on hydraulic machine (WE-300 made in Jinan China). The DSC diagram was tested on a DSC Q2000, the temperature was from 25ºC up to 120ºC and then back to 25ºC (5 ºC/min). Single crystals suitable for X-ray measurements were obtained by slow evaporation method, and single-crystal X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer with graphite monochromated Mo Ka radiation (λ=0.71073 Å) at 298 K. The solvents are mixture of ethyl acetate and petroleum, or cyclohexane, or methanol. And the CCDC numbers of the C1, C2, C3, C4 are 993934, 993933, 993932, 993935, respectively.

2. Synthesis

2.1 General procedure for synthesis of imidazole derivatives

A mixture of benzil (1.0 g, 4.76 mmol), aromatic carbaldehyde (4.76 mmol), ammonium acetate (1.84 g, 23.8 mmol) and acetic acid (15 mL) was heated to reflux overnight under N_2. After the completion of the reaction, the mixture was poured into ice-cold water to give a yellow amorphous solid as crude product, which was subjected to column chromatography to provide pure product.

2,4,5-Triphenyl-1*H*-imidazole (TPI), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, J = 10.8 Hz, 1H), 8.2 (d, J = 6.0 Hz, 1H), 7.74 (m, 3H), 7.34 (m, 9H), 7.05 (t, J = 8.0 Hz, 1H).

2-(Naphthalen-1-yl)-4,5-diphenyl-1*H*-imidazole (NDPI), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (br, 1H), 8.84 (d, J = 8.0 Hz, 1H), 7.91 (m, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.57 (m, 7H), 7.36 (m, 6H).

2-(Anthracen-9-yl)-4,5-diphenyl-1*H*-imidazole (ADPI), ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (br, 1H), 8.55 (s, 1H), 8.03 (m, 4H), 7.60-7.77 (m, 4H), 7.36-7.50 (m, 10H).

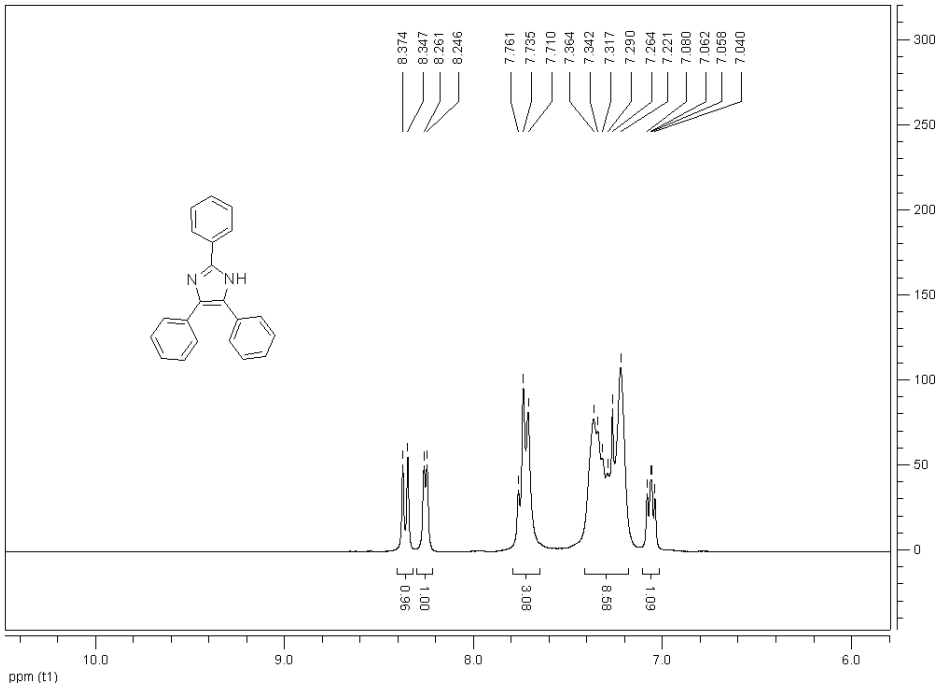

Fig. S1 ^{1}H NMR spectrum of **TPI** in $CDCl_3$ (400 MHz)

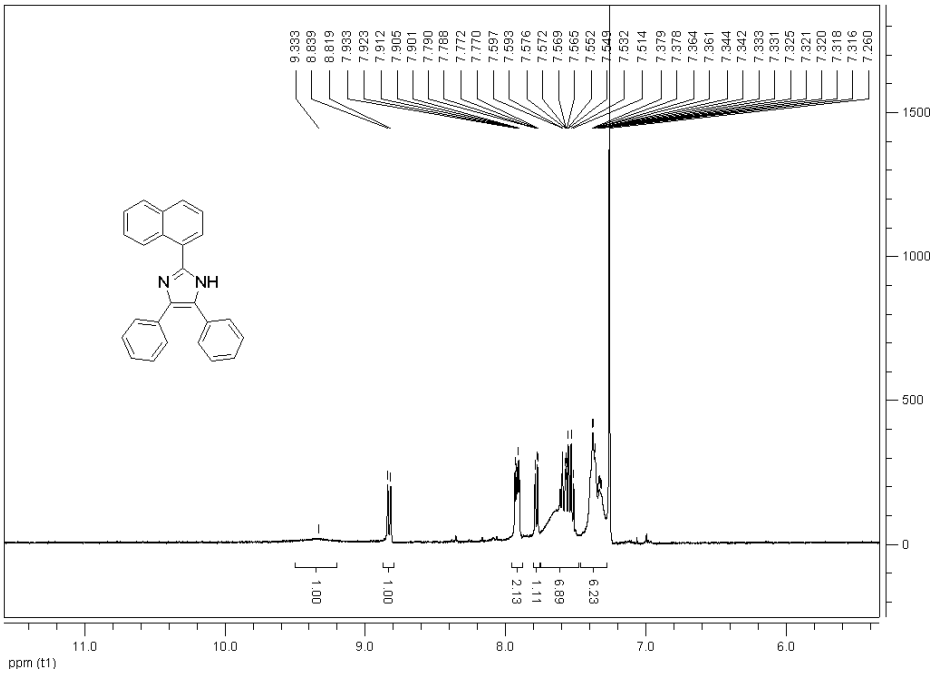

Fig. S2 ^{1}H NMR spectrum of **NDPI** in $CDCl_3$ (400 MHz)

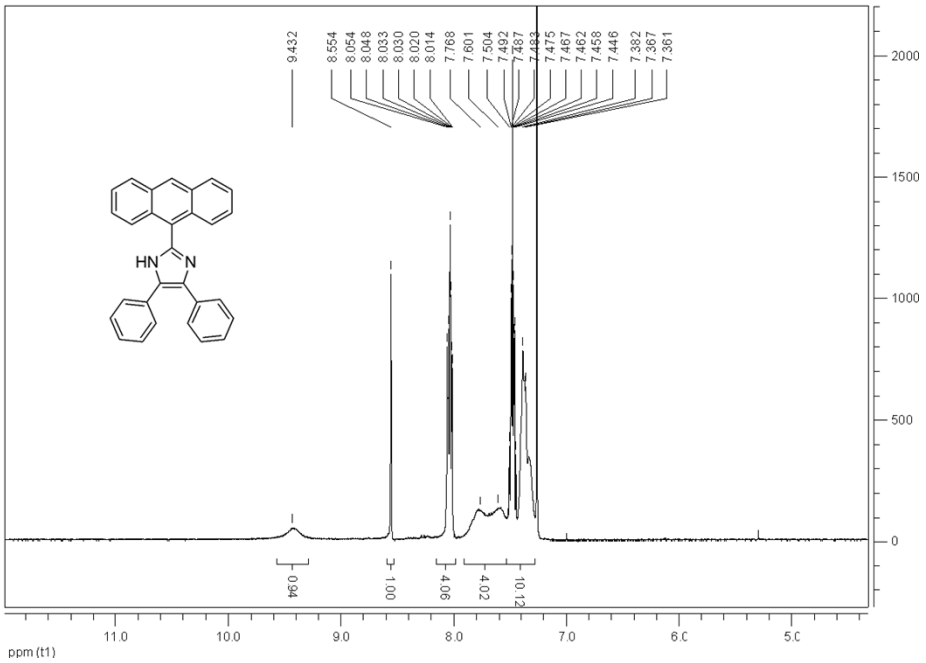

Fig. S3 ^{1}H NMR spectrum of **ADPI** in $CDCl_3$ (400 MHz)

2.2 Synthesis of 2-(Anthracen-10-yl)-1-methyl-4,5-diphenyl-imidazole (AMDPI)

ADPI (0.5 g, 1.26 mmol) and K_2CO_3 (0.36 g, 2.53 mmol) were mixed in dry DMF (10 mL), followed by addition of iodomethane (0.09 mL, 1.39 mmol) at room temperature. The mixture was kept stirring at room temperature for 10 h. After washing with ice water, the aqueous phase was extracted with ethyl acetate three times. The combined organic phases were washed with water, dried over Na_2SO_4, and evaporated in vacuo. The crude residue was subjected to a silica gel column to afford target product as yellow solid (0.37g) with 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 8.61 (s, 1H), 8.10 (m, 2H), 7.77 (m, 2H), 7.69 (d, J = 7.2 Hz, 2H), 7.53 (m, 9H), 7.24 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 3.09 (s, 3H).

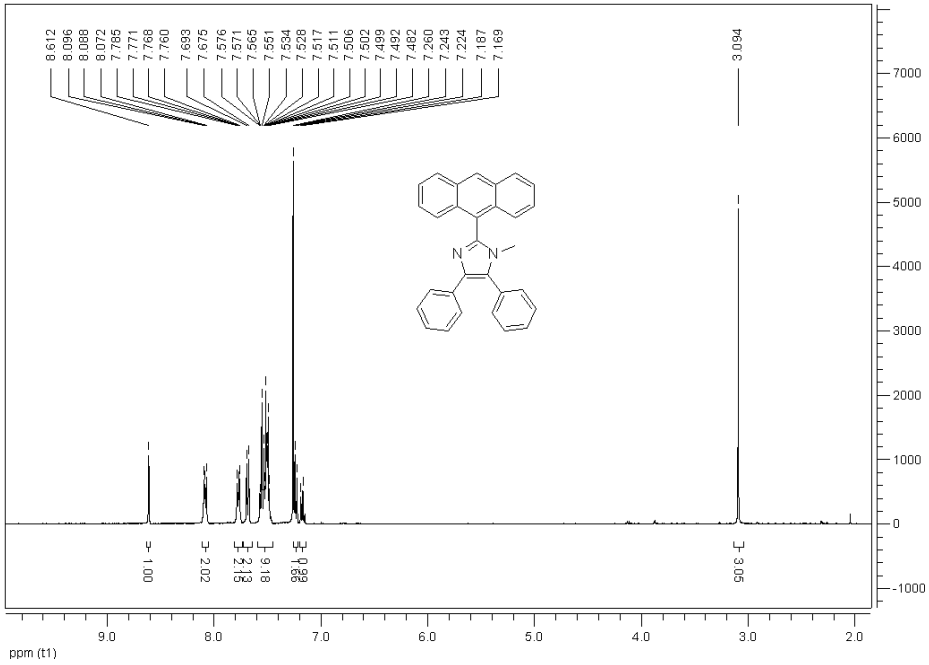

Fig. S4 ^{1}H NMR spectrum of **AMDPI** in $CDCl_3$ (400 MHz)

3. Photophysical Spectra in solutions

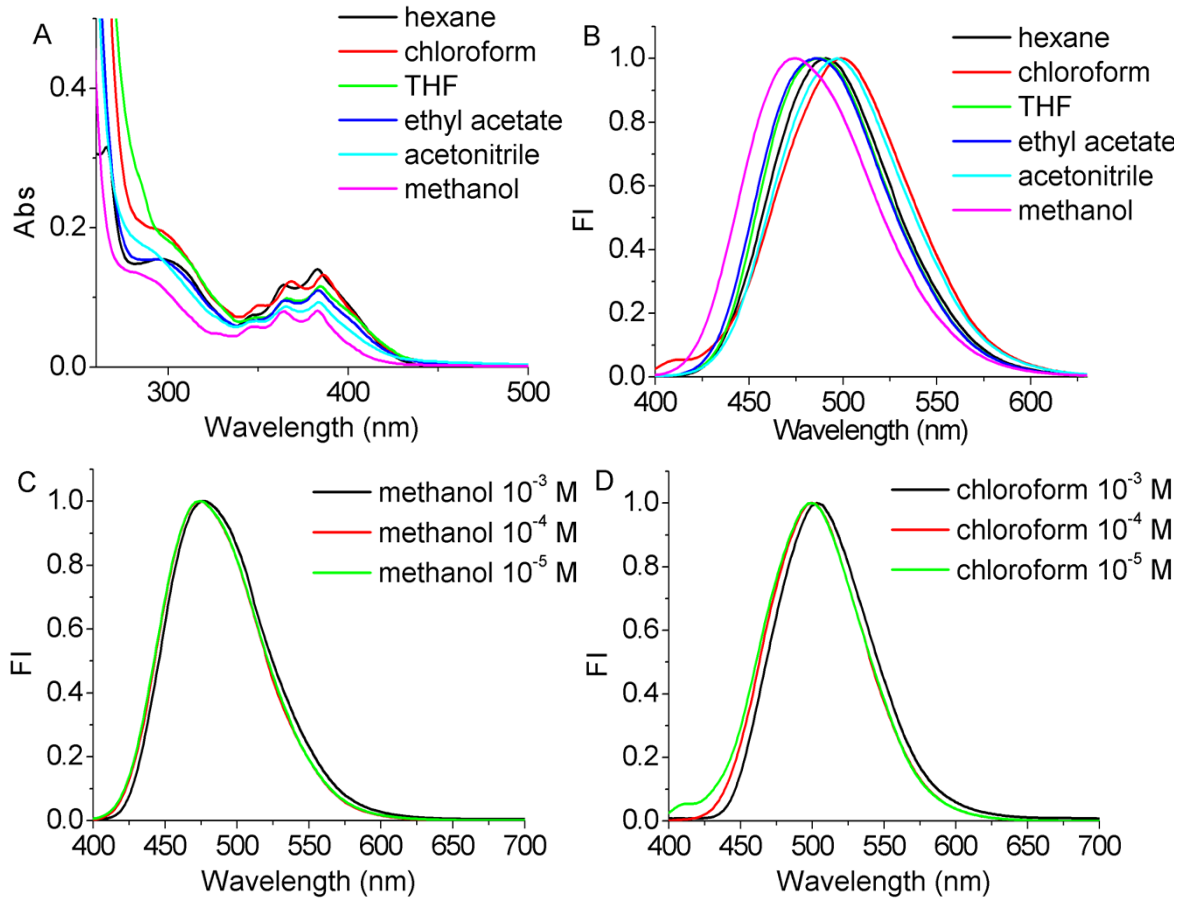

Fig. S5 (A) Absorption; (B) fluorescent spectra of **ADPI** in different organic solvents; (C) concentration-dependent fluorescent spectra in methanol; (D) concentration-dependent fluorescent spectra in chloroform.

4. Single crystal analysis

Fig. S6 Fluorescent images of **ADPI** crystals

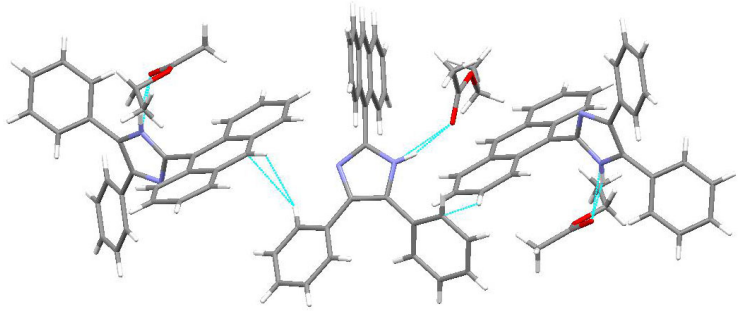

Fig. S7 Stacking of **ADPI** molecules in **C2** (comprising ethyl acetate)

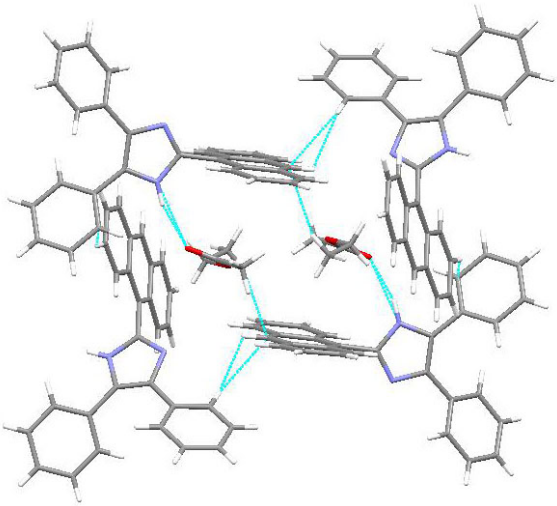

Fig. S8 Stacking of **ADPI** molecules in **C4** (comprising ethyl acetate)

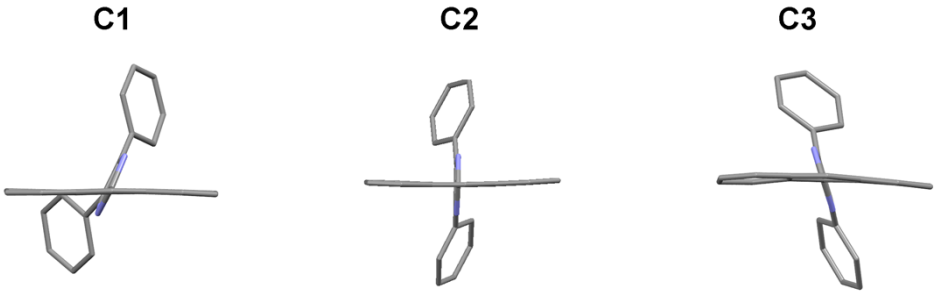

Fig. S9 Planarity of anthracene in three different single crystals

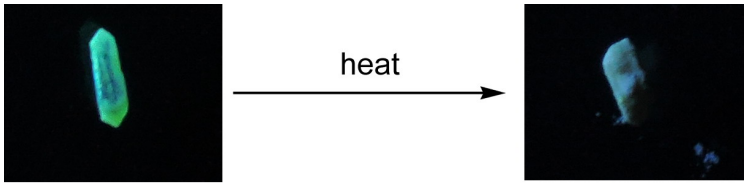

Fig. S10 Fluorescent images of **C1** upon heating

5. Fluorescent changes of powder during piezochromism

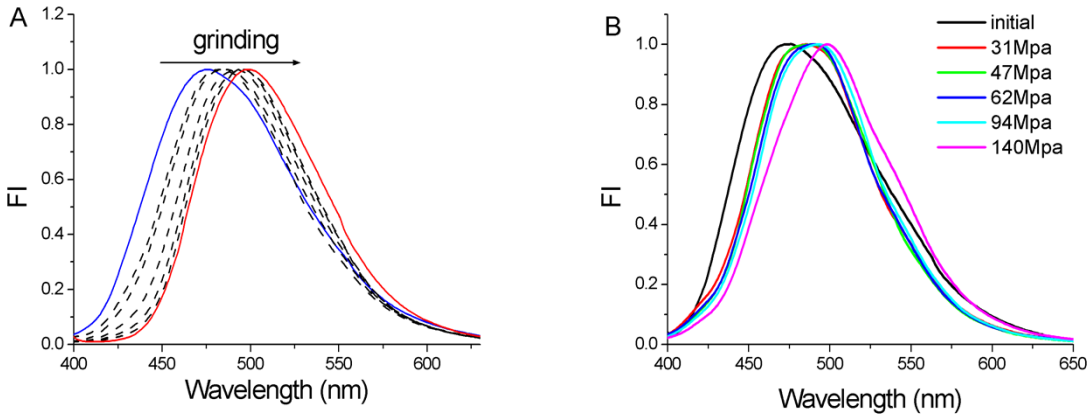

Fig. S11 Fluorescent changes of **ADPI** during grinding (A) and pressing under different pressure (B)

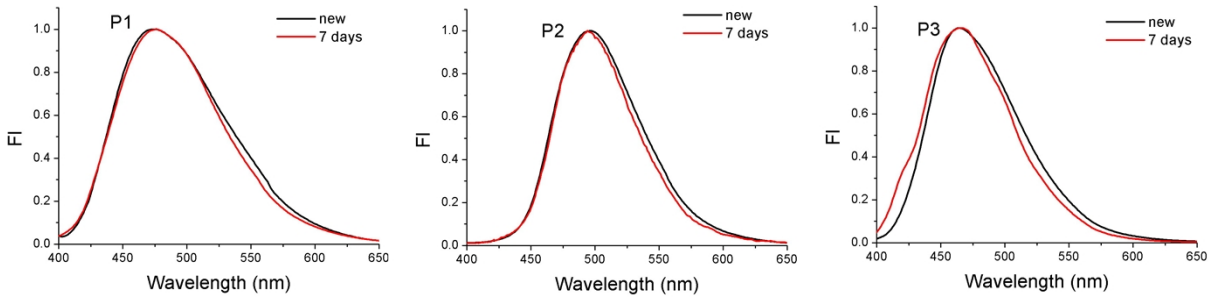

Fig. S12 Stability of **P1**, **P2** and **P3** samples. (Comparison of the new prepared samples with the samples laid aside for one week)

6. XRD analysis

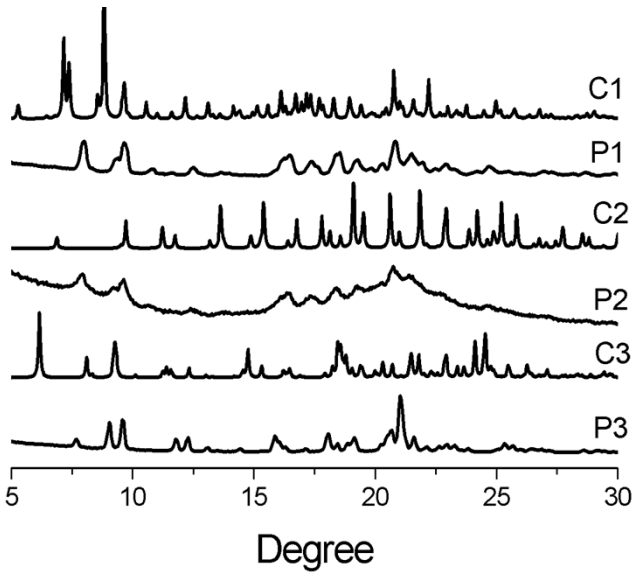

Fig. S13 Comparison of XRD patterns in powder states and in crystals states

7. DSC curves

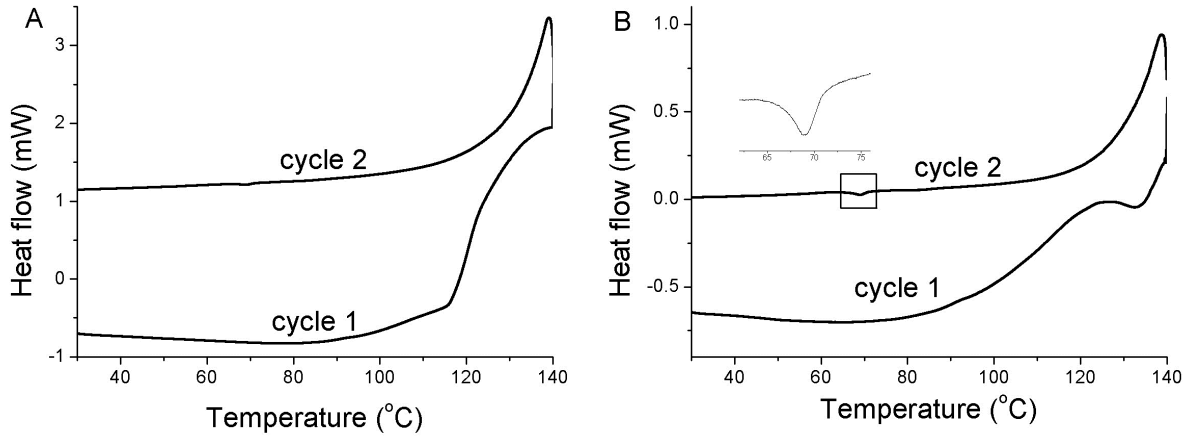

Fig. S14 DSC curves of initial powder (A) and ground sample (B)

8. Fluorescence changes of NDPI and AMDPI upon grinding

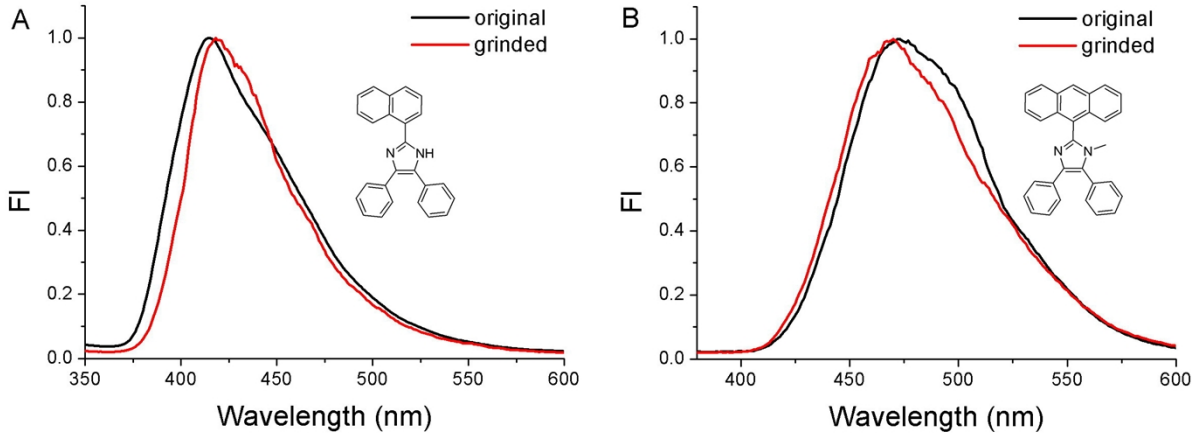

Fig. S15 Fluorescent spectra of **NDPI** (A) and **AMDPI** (B) before and after grinding. (Note: The fluorescence of **TPI** in solid state is negligible)

9. Crystal data and structure refinements of the crystals

	C1	C2	C3	C4
Empirical formula	C87 H62 N6 O	C26.40 H22.40 N1.60 O1.60	C60 H48 N4 O2	C33 H28 N2 O2
Formula weight	1207.43	387.66	857.02	484.57
Temperature, K	296(2)	293(2)	273(2)	293(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
space group	P 21/n	P bca	P 21/n	P bca
a, Å	19.548(9)	12.859(5)	11.0962(17)	12.852(5)
b, Å	18.292(8)	15.737(6)	21.800(3)	15.692(5)
c, Å	21.819(10)	25.688(10)	19.774(3)	25.641(8)
alpha, deg	90	90	90	90
beta, deg	108.996(5)	90	105.379(3)	90
gamma,deg	90	90	90	90
volume, $Å^3$	7377(6)	5198(3)	4612.0(12)	5171(3)
Z	4	10	4	8
Mg/m^3	1.087	1.238	1.234	1.245
Reflections collected	77220	52231	51289	52261
Unique Reflections	16918	5952	15183	5941
R(int)	0.1763	0.0883	0.0784	0.1095
GOF	1.625	1.101	1.022	1.130
R1[I>2sigma(I)]	0.1879	0.0768	0.0721	0.0763
wR2[I>2sigma(I)]	0.3855	0.1763	0.1811	0.1726
R1 (all data)	0.3205	0.1182	0.1376	0.1022
wR2(all data)	0.4361	0.2019	0.2139	0.1886