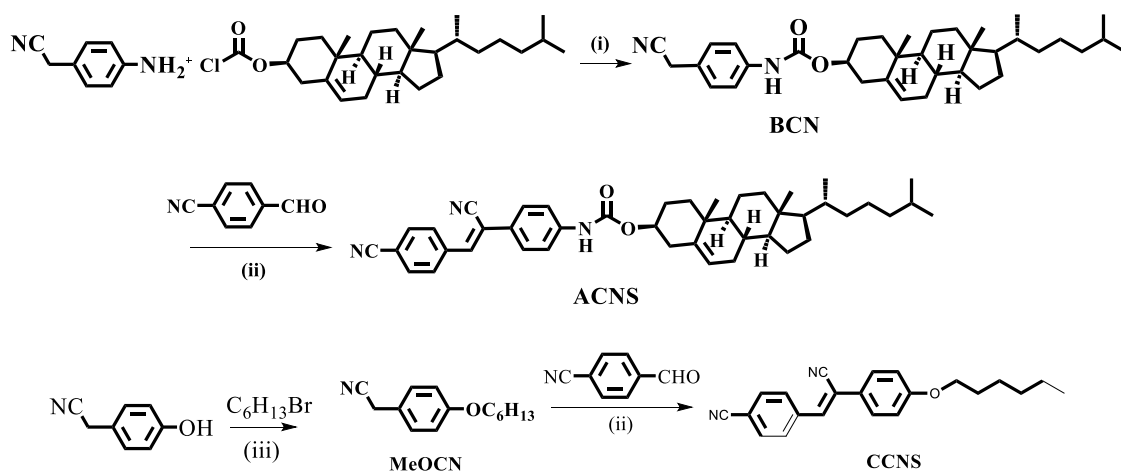


Experimental section

Materials: 2-(4-aminophenyl)acetonitrile, cholesteryl chloroformate and 4-formylbenzonitrile were purchased from commercial sources and used without further purification. All solvents and reagents (analytical grade) were used as received, unless otherwise claimed.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III 500-MHz instrument (Bruker, Switzerland) at 298K using chloroform-*d* (CDCl_3) as the solvent and tetramethylsilane as standard. The electrometer spray ionization (ESI) mass spectrum was recorded with a Thermo LCQ Fleet MS spectrometer. The UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer. The steady-state fluorescent measurements were recorded on a Jobin Yvon FluoroLog-3 luminescence spectrophotometer. Absolute fluorescence quantum yields were determined using a C11347-11 spectrometer (Hamamatsu, Japan). Time-resolved fluorescence spectra were recorded using a FLS920 time-corrected single photon counting system (Edinburgh, England). Powder X-ray diffraction (XRD) patterns were performed on X'Pert PRO, PANalytical, with Cu-K radiation operating at 40 kV and 40 mA. The FTIR spectra were recorded using a Nicolet 6700 Fourier-transform infrared spectrometer. Circular dichroism (CD) spectra were recorded on a Jasco J-815 spectrometer. Field-emission scanning electron microscopy (SEM) measurements were taken by using a Hitachi S-4800 scanning electron microscopy (Hitachi, Japan). Hydrostatic pressure experiments were carried out using a diamond anvil cell (DAC).



Scheme S1. Synthesis of ACNS and CCNS. (i) Ethylenediamine, dry THF, 0-20 °C, 12h; (ii) Sodium methoxide, anhydrous ethanol, r.t., 6h; (iii) K₂CO₃, KI, DMF, 80 °C, 12h.

Compound **MeOCN**: ¹H NMR (500 MHz, CDCl₃): (ppm) 7.23 (d, J = 8.65 Hz, 2H); 6.90 (d, J = 8.70 Hz, 2H); 3.96 (t, J = 6.60 Hz, 2H); 3.68 (s, 2H); 1.82-1.76 (m, 2H); 1.49-1.45 (m, 2H); 1.38-1.34 (m, 4H); 0.93 (t, J = 7.00 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃): 158.86, 128.95, 121.52, 118.17, 115.02, 68.07, 31.49, 29.10, 25.61, 22.69, 22.51, 13.93. MS m/z: [M⁺] calcd, 217.1; found, 217.1.

CCNS was synthesized with the procedure used for **ACNS**, but using compound **MeOCN** as the starting material. It was obtained as a white powder in an 82.0% yield. ¹H NMR (500 MHz, CDCl₃): 7.95 (d, J = 8.35 Hz, 2H); 7.75 (d, J = 8.45 Hz, 2H); 7.64 (d, J = 8.85 Hz, 2H); 7.42 (s, 1H); 6.98 (d, J = 8.90 Hz, 2H); 4.03 (t, J = 6.65 Hz, 2H); 1.84-1.80 (m, 2H); 1.51-1.48 (m, 2H); 1.39-1.35 (m, 4H); 0.93 (t, J = 7.05 Hz, 3H). ¹³C NMR (125 MHz, d-DMSO): (ppm) 160.04, 138.44, 138.21, 132.71, 131.16, 129.42, 127.57, 125.36, 118.48, 117.38, 115.12, 113.09, 111.85, 67.77, 54.87, 30.95, 28.51, 25.10, 22.03, 13.87. Mp. 101 °C, MS m/z: [M⁺] calcd, 330.2; found, 330.2.

Table S1. Crystal data and structure refinement for crystals ACNS.

Samples	ACNS (CCDC: 1863991)
Formula	C ₄₄ H ₅₅ N ₃ O ₂
<i>Mr</i>	657.91
Temperature (K)	298 K
Crystal system	Triclinic
Space group	P-1
Crystal size (mm)	
<i>a</i> (Å)	9.3185(4)
<i>b</i> (Å)	11.3873(4)
<i>c</i> (Å)	20.1187(7)
<i>α</i> (°)	86.468(3)
<i>β</i> (°)	80.778(3)
<i>γ</i> (°)	66.090(4)
<i>V</i> (Å ³)	1926.40(12)
<i>Z</i>	2
<i>D</i> _{calc} (mg/m ³)	1.134
Theta Range (°)	4.25-62.5
F (000)	712.0
<i>h</i> , <i>k</i> , <i>l</i> _{max}	10,13,23
N _{ref}	5819
T _{min} , T _{max}	0.857,0.901
Goodness-of-fit on F ²	1.043
<i>R</i> _{int}	453
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)]	0.0789(5529)
<i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.1927(5819)
<i>R</i> ₁ (all data)	0.08
<i>wR</i> ₂ (all data)	0.1890
S	1.043

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$$

Table S2. Optical Properties of **B**, **G** and **Y**-phase.

Samples	λ_{em} (nm)	PLQY (%)	τ_1 (ns)(%)	τ_2 (ns)(%)	τ_{av} (ns) ^a	k_r (ns ⁻¹) ^b	k_{nr} (ns ⁻¹) ^c
B-phase	456, 466	68.1	1.5(59.4)	3.7 (40.6)	2.4	0.284	0.133
G-phase	498	43.4	2.9(53.6)	13.4 (46.4)	7.7	0.056	0.073
Y-phase	539	55.0	6.8(15.9)	42.9 (84.1)	37.1	0.015	0.012

^aAverage lifetime τ_{av} was determined by using the relation $\tau_{av} = \sum_{i=1}^n A_i \times \tau_i$ ($n = 1 \sim 2$); Radiative^b and nonradiative^c rate constant were calculated according to the equations of $k_r = \text{PLQY} / \tau$ and $k_{nr} = (1 - \text{PLQY}) / \tau$, respectively.

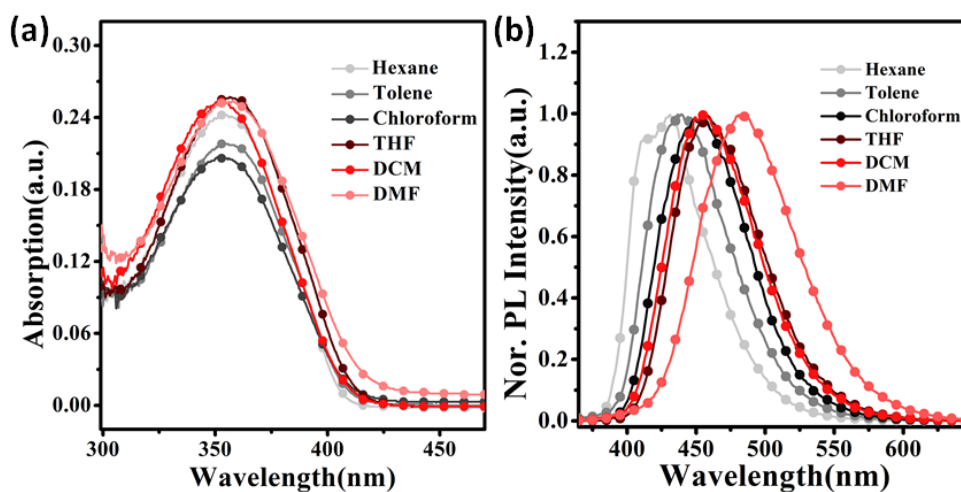


Figure S1 The UV absorption spectra and PL spectra of ACNS, measured in the different solvents with increasing polarity (the orientational polarizability of solvent, Δf , hexane: 0.0012; toluene: 0.014; chloroform: 0.149; tetrahydrofuran (THF): 0.210; Methylene chloride (DCM): 0.217; N,N-dimethylformamide (DMF): 0.276.

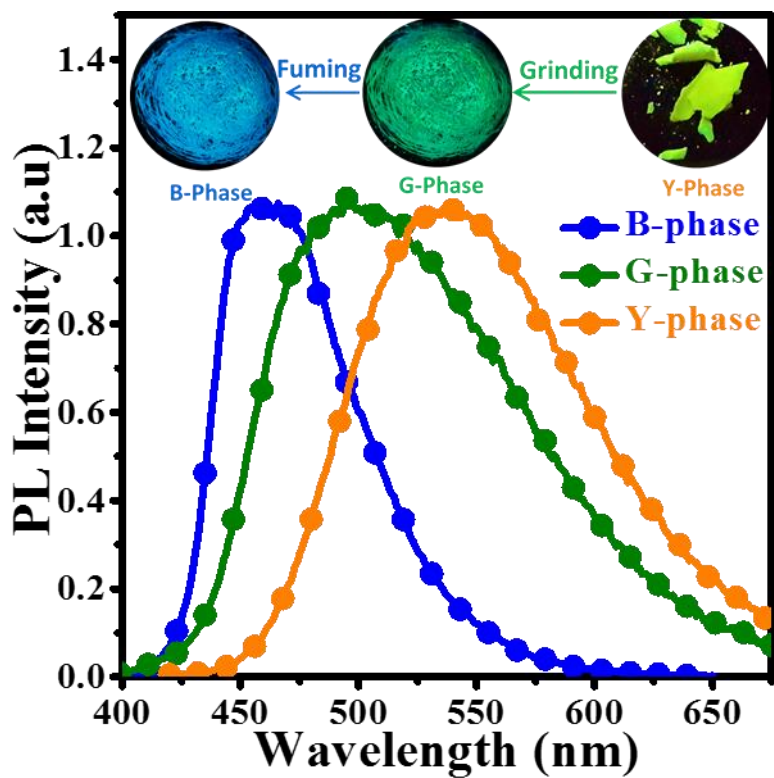


Figure S2 Normalized PL spectra of **B**, **G** and **Y-phase**, the inset images show the corresponding PL photographs under 365 nm UV light

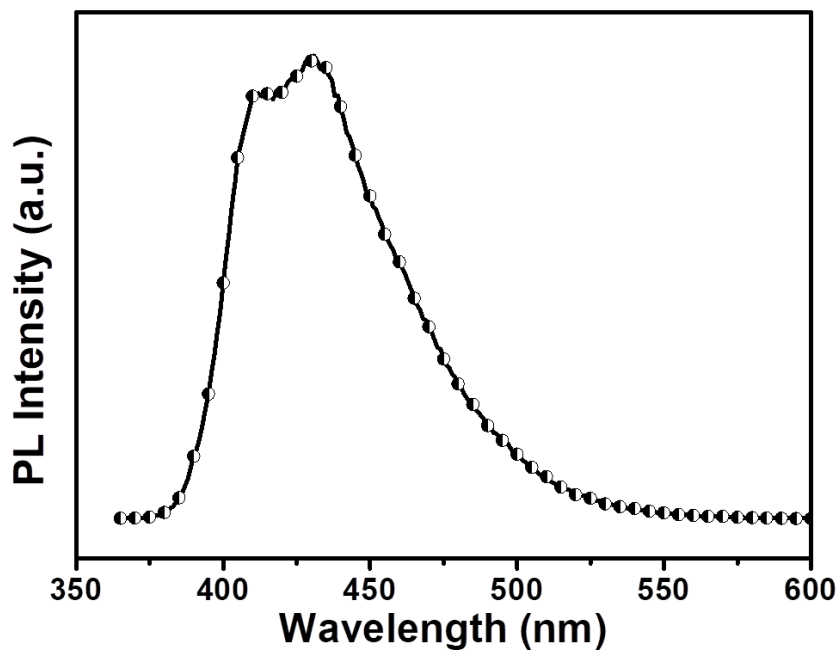


Figure S3. PL spectra of ACNS dissolved in dilute hexane solution.

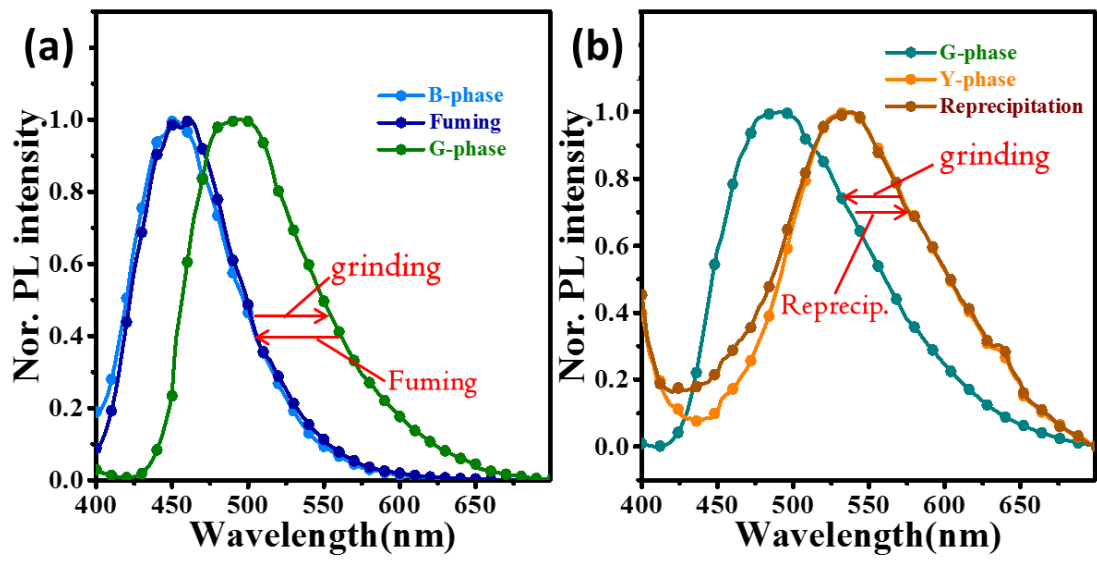


Figure S4 the reversible spectral change of ACNS under the different stimuli

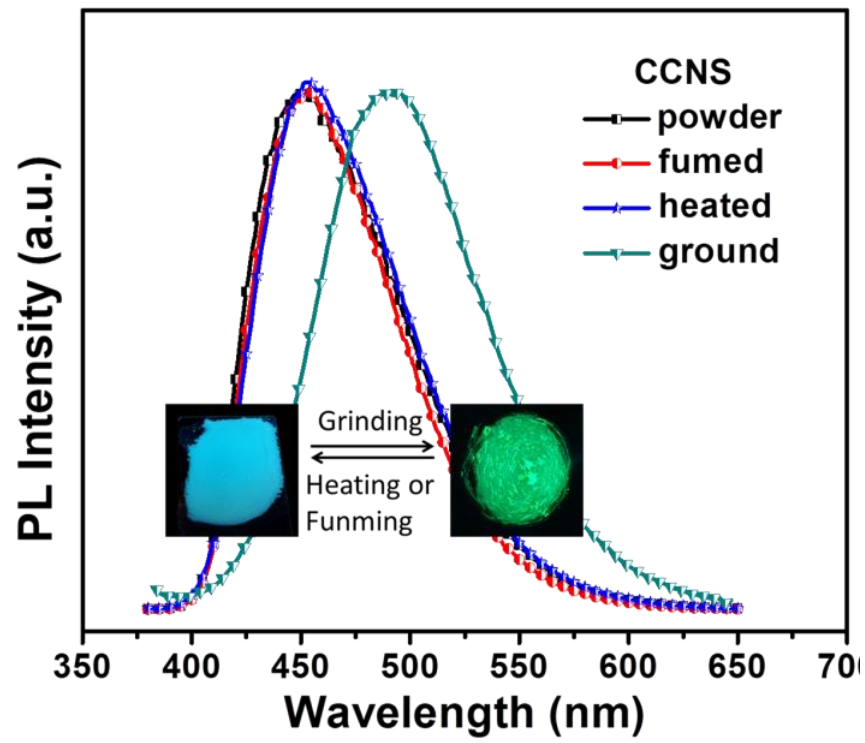


Figure S5 PL spectra and fluorescent images of CCNS in different solid state

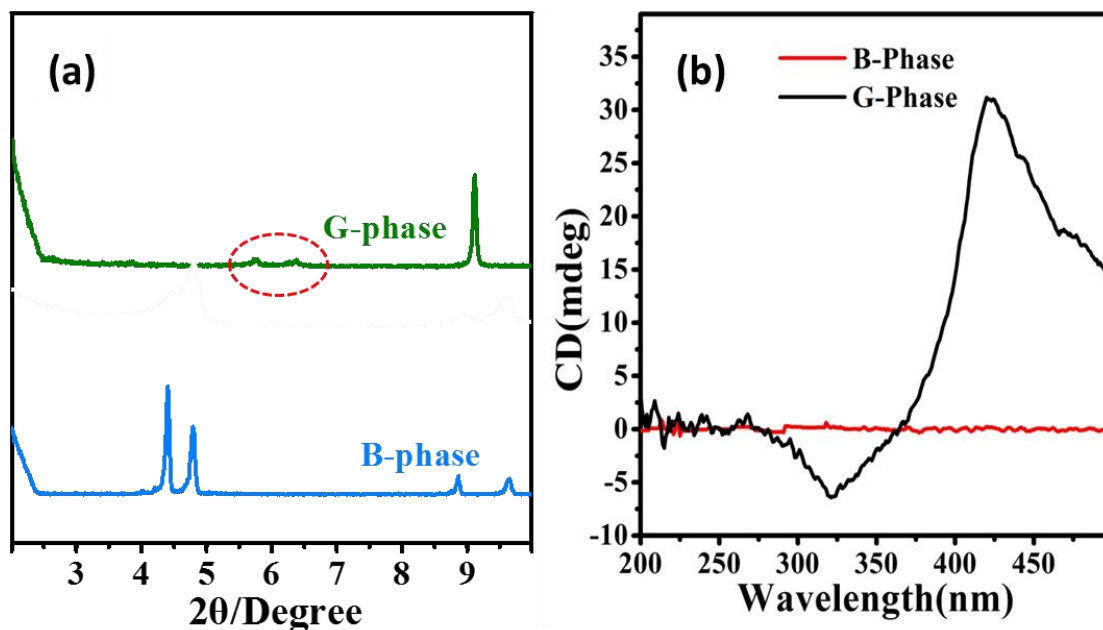


Figure S6 (a) XRD patterns of the **B** and **G** -phase at small angle region; (b) CD spectra of the B and G phases at longer wavelength region.

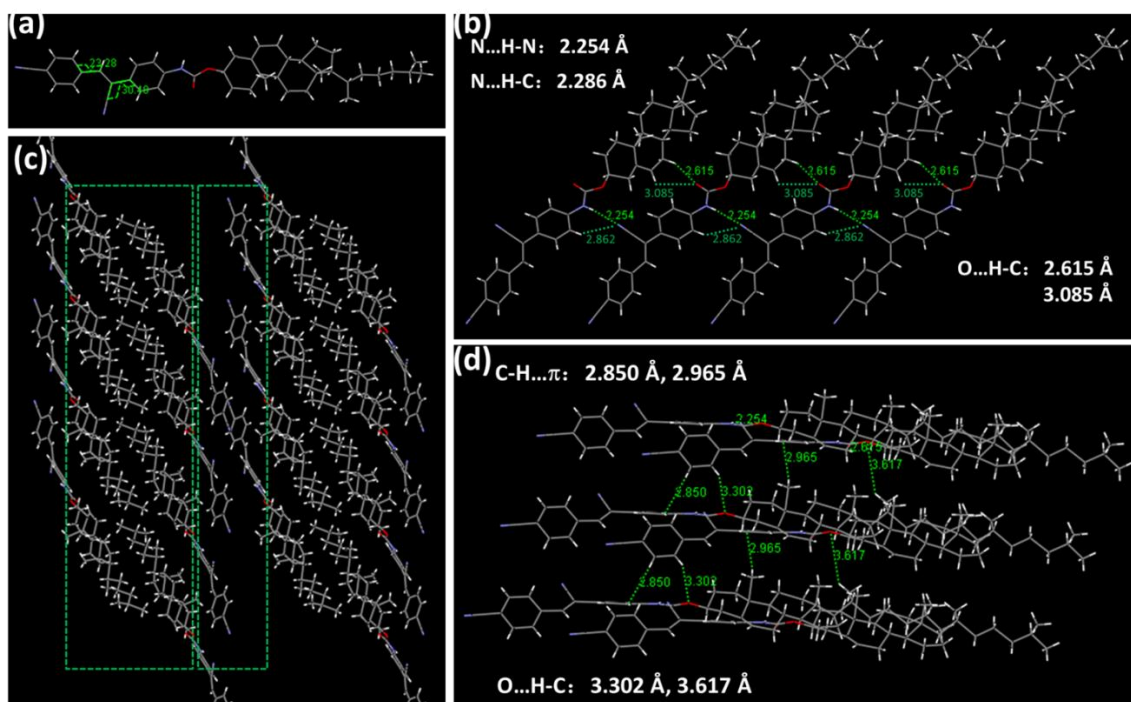


Figure S7 Single-crystal structure of **ACNS** (**B**-phase): (a) the dihedral angles in molecule; (b) lamellar packing structure and intermolecular hydrogen bonds viewed from the *c*-axis; (c) antiparallel packed columns viewed from the *a*-axis; (d) the arrangement and interactions between layers.

The molecule adopted a twisted conformation with a large dihedral angle of 53.8° between two phenyl planes, which was unfavorable to close π - π stacking (**Figure S6a**). The adjacent molecules were arranged side-by-side into a column (**Figure S6b**) and the columns were antiparallel packed with cholesteryl and CSB interdigitated with the same kind of unit respectively, producing a layer sheet (**Figure S6c**). The layers were further stacked on top of one another under the driving force of $C-H\cdots\pi$ (2.850 and 2.965 Å) and $O\cdots H-C$ (3.302 and 3.617 Å) (**Figure S6d**). Because of the loose triclinic structure, that is significantly large tilt angles between columns and layers, no effective π - π interaction was observed between conjugated CSB moieties in B-phase

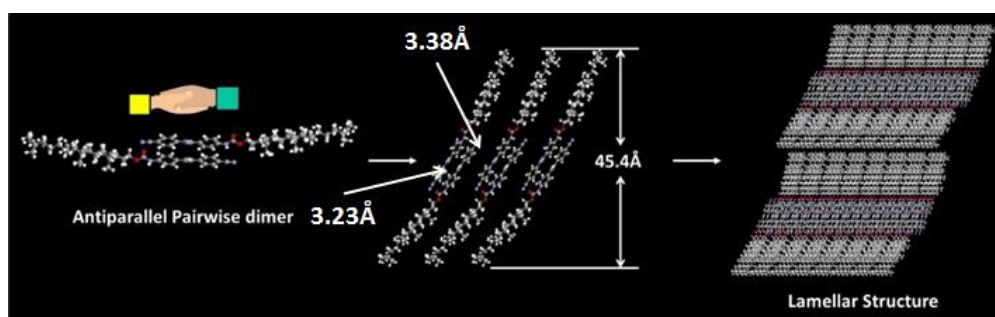


Figure S8 Proposed schematic representation of the molecular packing structure in the **Y-phase**.

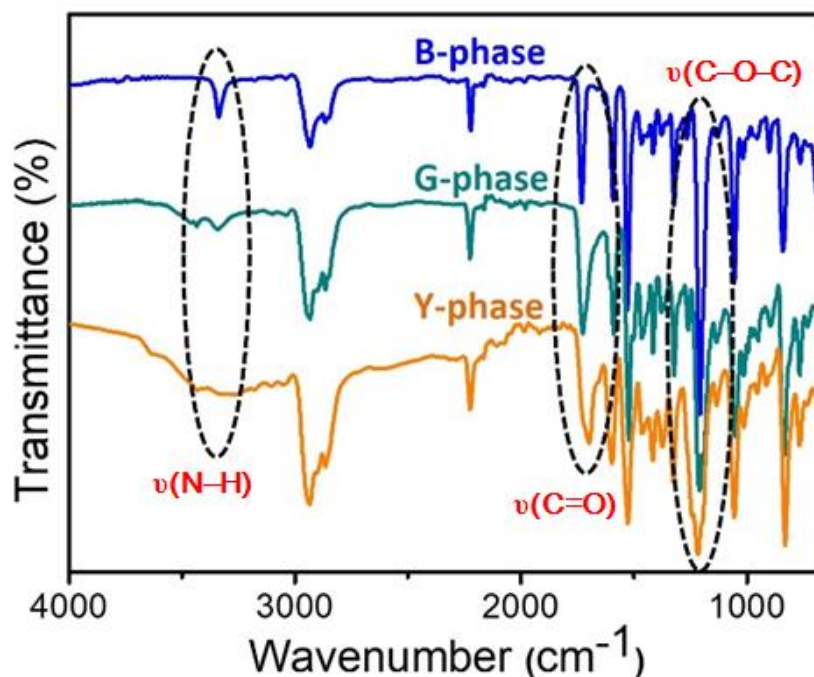


Figure S9 FT-IR patterns of **B**, **G** and **Y-phase** solids.

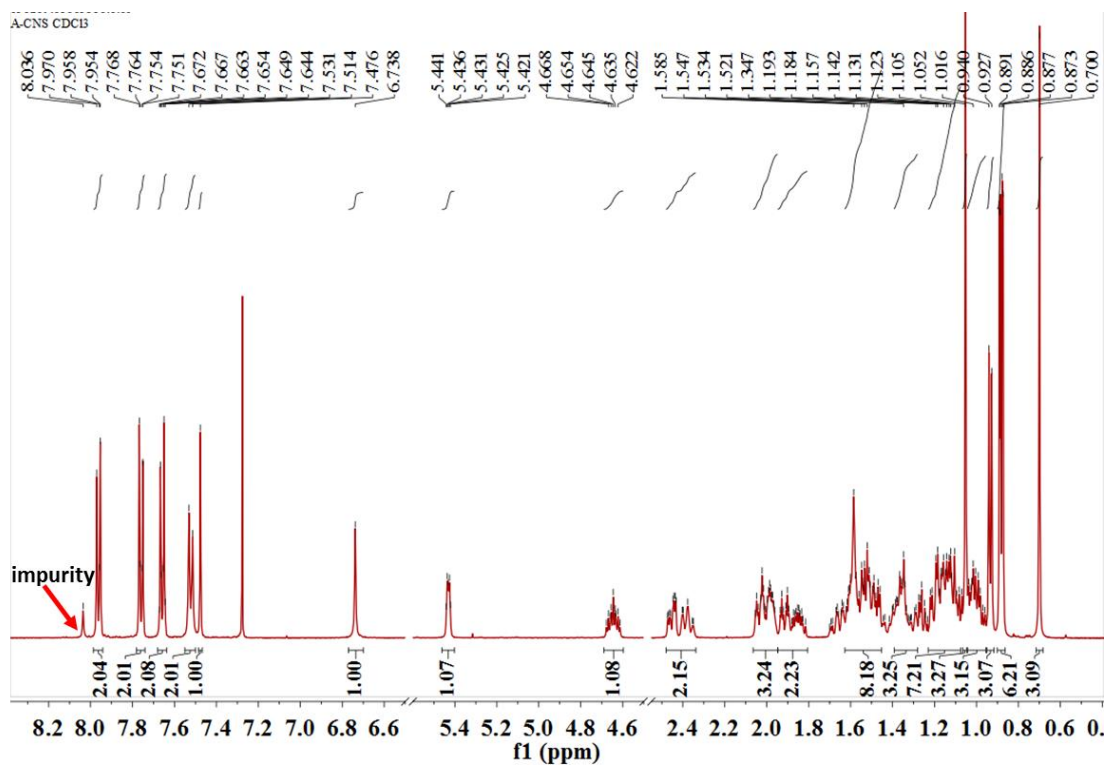


Figure S10 The ¹H NMR spectra of ACNS.

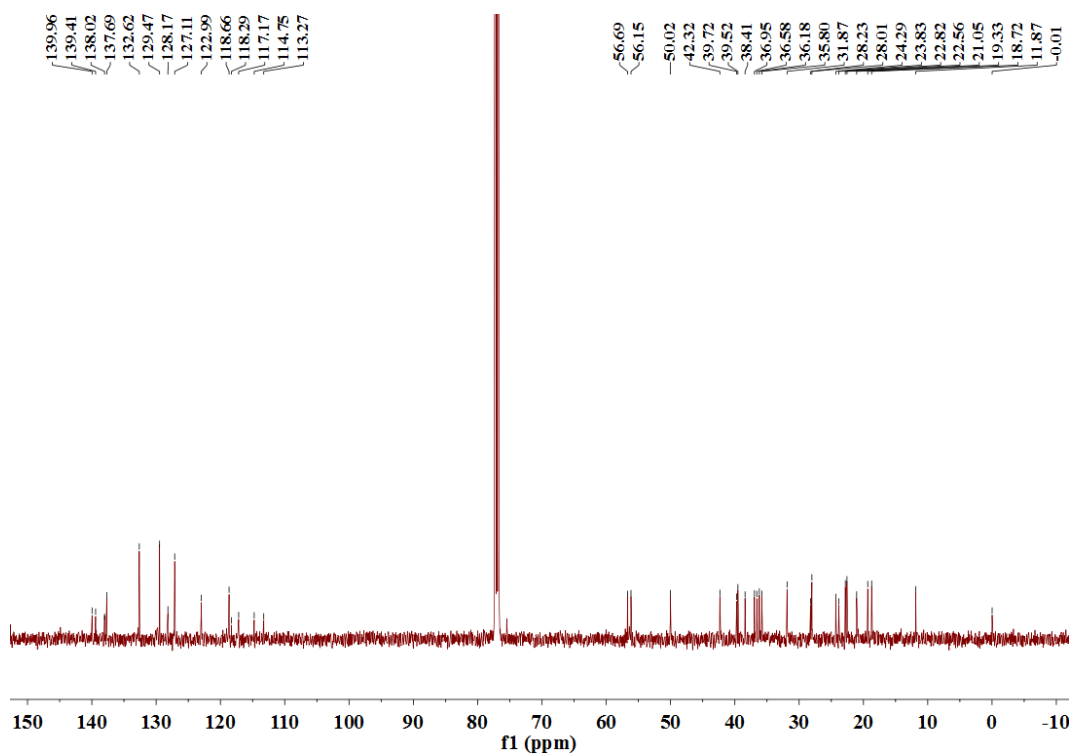


Figure S11 The ¹³C NMR spectra of ACNS.

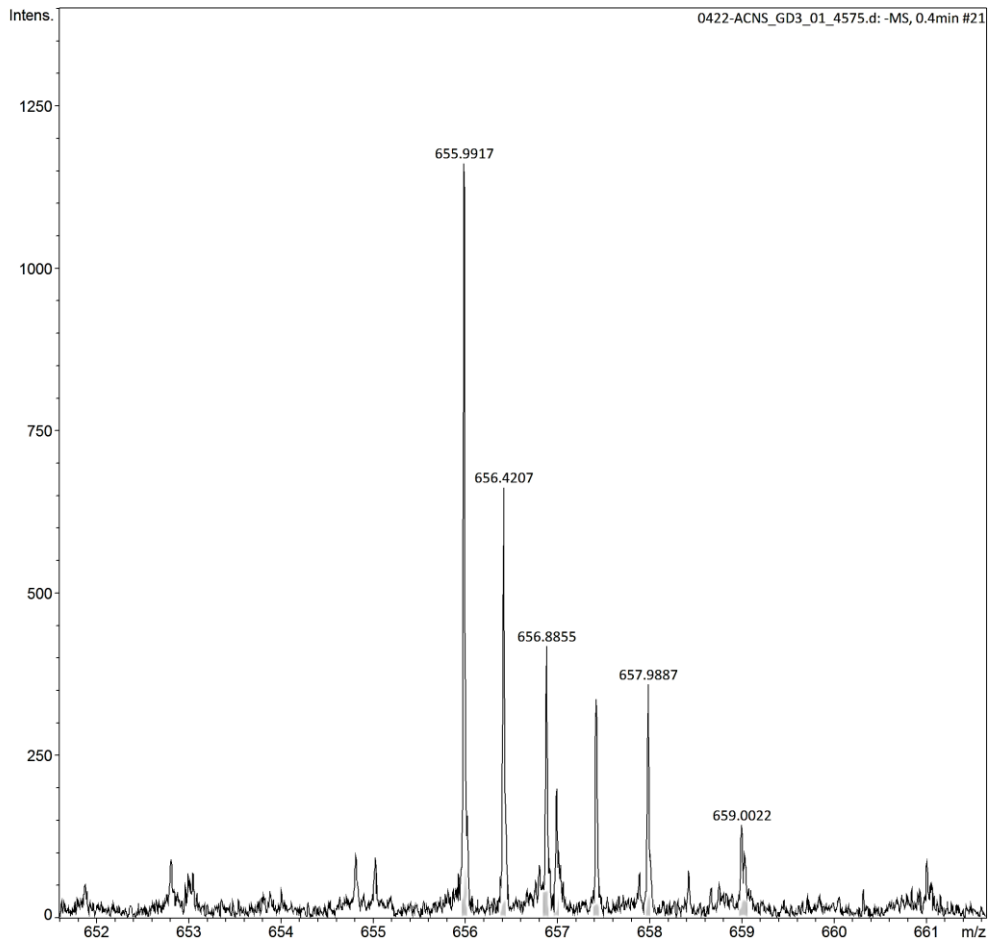


Figure S12 The HR-MS spectrum of the ACNS.