Supporting Information

Stabilization of blue phase from hydrogen-bonded bent-shaped and T-shaped molecules featuring a branched terminal group

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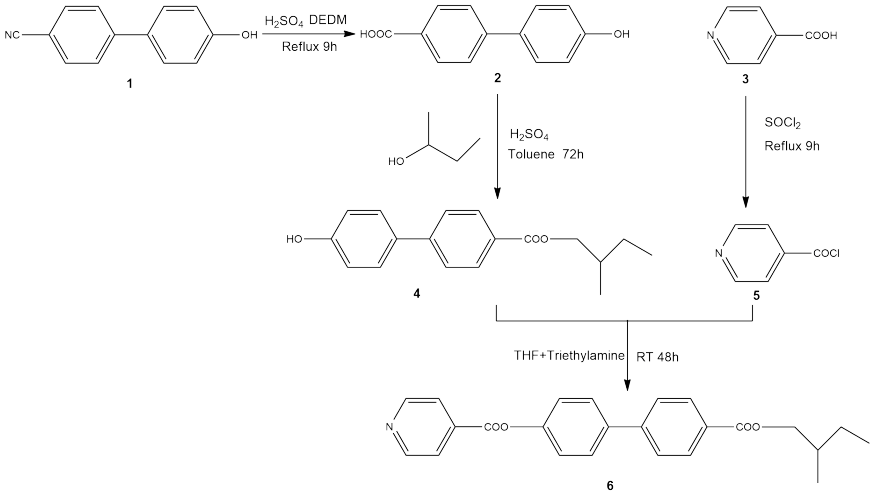
1. Synthesis of H-acceptor



< Scheme S1>

4'-hydroxy-[1,1'-biphenyl]-4-carboxylic acid **2**

4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (29.25g, 0.15mol) was added into 2-methoxyethyl ether (150ml) and the solution was stirred to 80 °C. Then 22.50g 75% H_2SO_4 (22.50g) was dropped into the solution slowly before the temperature was up to 120 °C. Then the mixture was stirred at 150 °C ~ 160 °C for 5h and up to 190 °C stirred for 2h. After the reaction, poured the mixture into cold water and filtered white precipitate, then recrystallization by ethanol and vacuum dried to obtain 2.

2-methylbutyl 4'-hydroxy-[1,1'-biphenyl]-4-carboxylate **4**

4'-hydroxy-[1,1'-biphenyl]-4-carboxylic acid (8.72g, 0.041mol) was add to a stirred solution of 2-methyl-1-butanol (13.68g, 0.155mol) in toluene (130ml). 98% H_2SO_4 (0.68ml) was dropped into the solution slowly and the stirred solution was watershed refluxed for 72h. Then the solution was filtered and the filter liquor was washed by 1% $NaHCO_3$ and water for 2 or 3 times. The organic layer was dried with magnesium

sulfate, the solvent was evaporated after filtering. The obtained crude product was recrystallized by toluene and hexane (1:1) to give 4.

Isonicotinoyl chloride **5**

Isonicotinic acid (4.92g, 0.04mol) was added into thionyl chloride (20ml) and refluxed for 9h, then evaporated the excess thionyl chloride to obtain isonicotinoyl chloride 5.

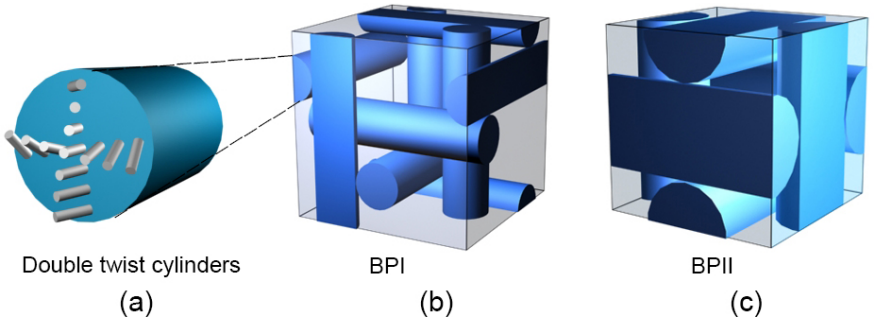
4'-((2-methylbutoxy)carbonyl)-[1,1'-biphenyl]-4-yl isonicotinate **6**

Triethylamine (10ml) was added into a stirred suspension of isonicotinoyl chloride (2.82g, 0.02mol) in THF (30ml) slowly. Over 0.5h a solution of 2-methyl-1-butyl 4'-hydroxy-4-biphenyl carboxylate (6.82g, 0.024mol) solved in THF (20ml) was added into the suspension slowly. The mixture was continuously stirred at room temperature for 48h, filtered and concentrated in vacuum. The obtained crude product was purified by column chromatography over silica gel with ethyl acetate/hexane (volume ratio 1/6) as the eluent. The product was recrystallized by ethanol and dried to get 6.

IR (FT-IR spectra were recorded on a Nicolet 5700 spectrometer at frequencies ranging from 400 to 4000 cm^{-1}) , δ/cm^{-1}: 2961, 2930, 2877, 1733, 1716, 1608, 1494, 1461, 1275, 1176, 1095, 859, 770, and 755.

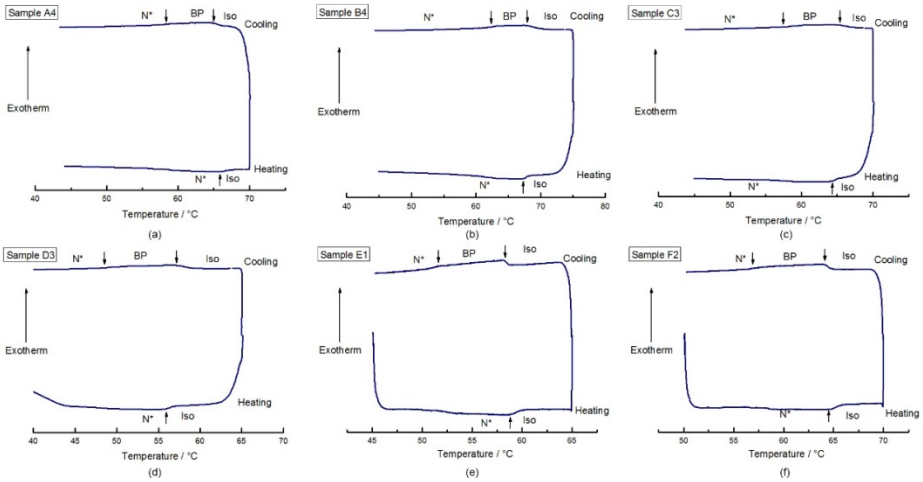
^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.92-8.15 (4H, 2d, J=5.6, 8.4 Hz, -Py<u>H</u>-), 8.09-7.71 (4H, 2d, J=5.92, 8.64 Hz, -ArAr<u>H</u>-), 7.70-7.35 (4H, 2d, J=8.44, 8.64 Hz, -OAr<u>H</u>-), 4.26-4.19 (2H, m, -C<u>H</u>$_2$O-), 1.92-1.91 [H, m, -C<u>H</u>(CH_3)-], 1.58-1.32 (2H, m, -C<u>H</u>$_2$$CH_3$), 1.07-1.00 [6H, m, -CH(C<u>H</u>$_3$)-CH_2C<u>H</u>$_3$]

2. Illustration of BPs

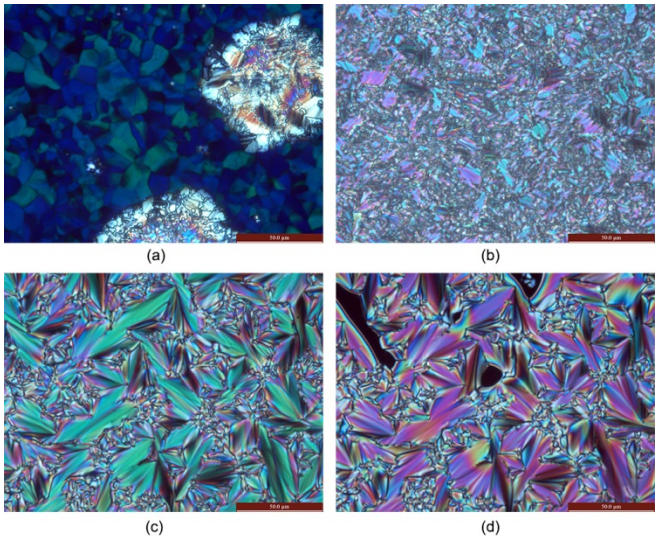


<Fig. S1>

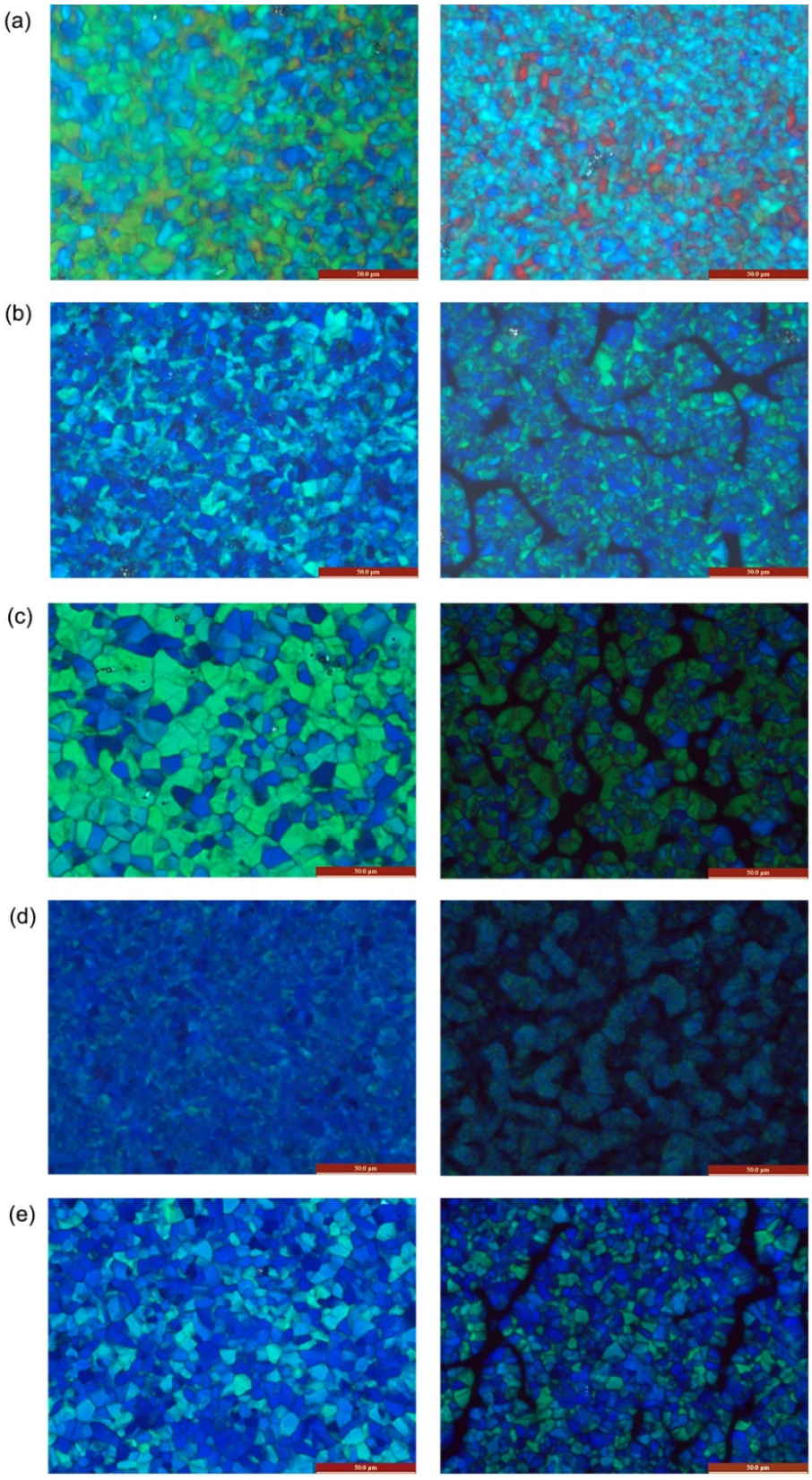
3. DSC curves and POM images



<Fig. S2>

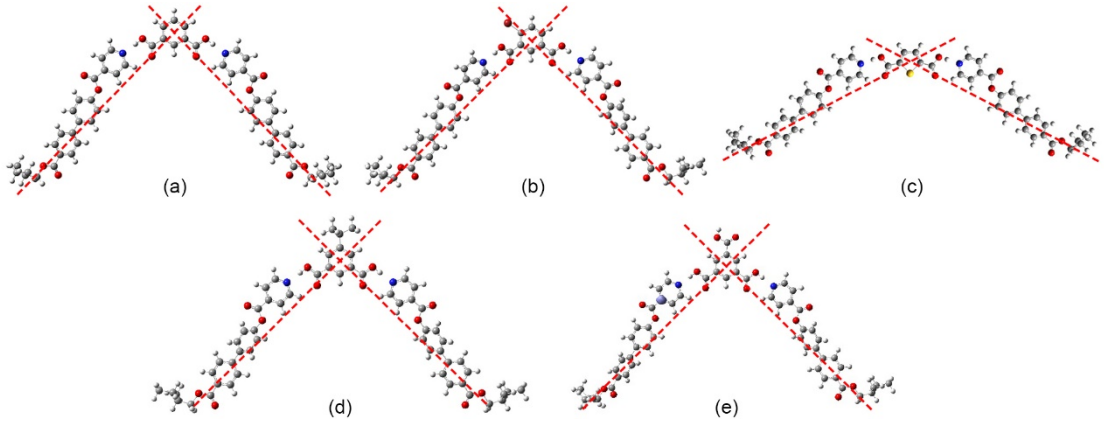


< Fig. S3>



< Fig. S4>

4. Molecular Simulation



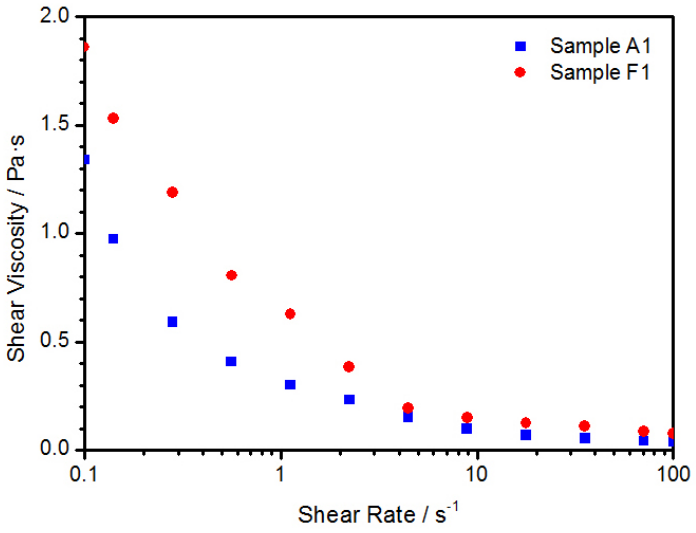
< Fig. S5>

HBAs	E_{HBA}[a] (au[b])	E_{Int}[b] (kJ/mol)
IPA-MBIN	-3177.62	94.65
BIPA-MBIN	-5748.72	97.43
TPBA-MBIN	-3497.47	149.80
TBOA -MBIN	-3334.88	93.10
BTOA-MBIN (1:2)	-3366.20	98.31
BTOA-MBIN (1:3)	-4650.31	143.06

[a] E_{HBA} represents the energy of H-bonded assembly. [b]1 au=2625.5kJ/mol.
[c] E_{Int} represents the interaction energy, $E_{Int}=| E_{H\text{-}bond} + E_{Def} |$.

<Table S1>

5. Viscosity Measurement



< Fig. S6>

Figure captions:

Scheme S1 Synthetic route of H-acceptor.

Table S1 The energy of HBAs and interaction energy about low energy structures calculated at B3LYP/6-31G(d).

Figure S1 Illustration of BP: (a) double twist cylinder of BPs, (b) the body-centered defect structure of Blue Phases I, (c) the simple cubic defect structure of Blue Phases II. BPIII is amorphous as foggy phase.

Figure S2 The DSC curves of different samples: (a) A4, (b) B4, (c) C3, (d) D3, (e) E1 and (f) F2.

Figure S3 POM images of sample D4 and D1 on cooling: a) BPI to N* of D4 at 39.7 °C, b) N* of D4 at 35.0 °C, c, d) No BP just N* appeared in sample D1 at 50.0 °C and 31.0 °C.

Figure S4 BPI of sample A2, B1, C3, E1 and F3: a) 59.0, 65.0 °C, b) 54.0, 60.0 °C, c) 57.0, 63.0 °C, d) 48.0, 54.0 °C, e) 50, 57 °C.

Figure S5 The measure of bend angles of bent-shaped HBAs: (a) IPA-MBIN, (b) BIPA-MBIN, (c) TPBA-MBIN, (d) TBOA-MBIN, (e) BTOA-MBIN (1:2). The bend angles were measured as the angles between the first, central, and final benzene rings' centers of the bent-core structures.

Figure S6 Variation of shear viscosity with shear rate for samples A1 and F1.