# **Electronic Supplementary Information**

# Novel Calamitic Liquid Crystalline Organic Semiconductors Based on Electron-Deficient Dibenzo[c,h][2,6]naphthyridine: Synthesis, Mesophase, and Charge Transport Property by Time of Flight Technique

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ESI Figure1 Synthesis route for DBN derivatives



## Synthesis ( compounds i, j and h4)

## 2,8-dibromo-4b,5,6,10b,11,12-hexahydrodibenzo[c,h] [2,6]naphthyridine

## (compound i)

For compound i, the operation was same to the f1. The compound d(0.12g,0.28mmol) was added the suspension of LiAlH<sub>4</sub>(0.046g, 1.2mmol) in dioxane(10ml), the mixture was refluxed under argon protection for 3 hours. The post-processing was same to the i, yielding waxy silvery white solid, compound i (0.02g (0.051mmol), 18%)

 $\delta$ H(400MHz; CDCl3; Me4Si): 6.94-6.92(2H, d, Ph), 6.78-6.75(2H, q, Ph), 6.68(2H, s, Ph), 4.05(2H, br s, NH), 3.32-3.29(4H, m, NH*CH2*), 3.16-3.13(2H, m, NHCH2*CH*)

δC (100 MHz; CDCl3; Me4Si): 145.59(Ph), 131.27(Ph), 121.09(Ph), 120.12(Ph), 119.94(Ph), 116.72(Ph), 45.49(NH*CH2*), 34.10(NHCH2*CH*) HRMS (FAB-MS): [M]+ Calcd. For C16H14Br2N2 391.9524; Found: 391.9533 **2,8-dibromodibenzo[c,h][2,6]naphthyridine** 

## (compound j)

For compound j, the operation was same to the h1. The 10ml dry dioxane was added into the mixture of compound i (20mg, 0.05mmol) and DDQ(60mg, 0.26mmol) under argon protection and heated up to reflux for 3 hours. The post-processing was same to the h1, yielding bright white power, compound j (15mg (0.038mmol), 77%). This compound was poor solubility in common solvent and purity was rough. Thus, only <sup>1</sup>HNMR was done.

 $\delta$ H(400MHz; CDCl3; Me4Si): 10.46(2H, s, NCH) 9.14-9.12(2H, d, BrCCHCH), 8.5(2H, s, BrCCH), 8.08-8.06(2H, d, BrCCHCH).

#### 2-decyldibenzo[c,h][2,6]naphthyridine

#### (compound h4)

For compound h4, the compound j(10mg, 0.026mmol) and Bis(triphenylphosphine)palladium(II) dichloride (2mg, 0.0027mmol) were placed in the 25ml two-necked flask equipped with a reflux condenser, magnetic

bar and rubber stopper, then, replacing the air in flask with argon three times and injecting 5ml 0.1M decylmagnesium bromide in THF by injection syringe. Keep the mixture stir with 3 hours at reflux under the argon protection. After finishing the reaction, pouring the mixture into cold water and extracting the suspension by ethyl acetate. Then, removing the solvent by the rotary evaporator and obtained crude solid, further purification by the column chromatography and preparative thin film chromatography in order and the hexane:chloroform=1:2 as eluent, yielding h4 (3mg(0.008mmol)), ~25%). The h4 was on the below of h2 on the TLC. Both h4 and h2 showed blue with yellow fluorescent light under the 254nm light. The product was too few. Thus, only <sup>1</sup>HNMR was done.

δH(400MHz; CDCl3; Me4Si): 10.22(2H, s, NCH), 8.86-8.84(1H, d, Ph), 8.77-8.75(1H, d, Ph), 8.35-8.33(1H, d, Ph), 8.14(1H, s, Ph), 7.87-7.85(2H, m, Ph), 7.84-7.68(1H, d, Ph), 2.94-2.91(2H, t, PhCH2), 1.82-1.78(2H, m, PhCH2CH2), 1.27(14H, m, CH2CH2), 0.88(3H, m, CH2Me) HRMS (FAB-MS): [M+H]+ Calcd. For C26H31N2 371.2487; Found:371.2478 (base peak)



ESI Figure 2 Cyclic voltammetry curves of (a) background for 0.4M solution of Bu<sub>4</sub>NClO<sub>4</sub> in THF and (b) C10-DBN-C10 in the 0.4M solution of Bu<sub>4</sub>NClO<sub>4</sub> in THF.



ESI Figure 3 DSC curves of (a) C12-DBN-C12-DBN and C12-IQIQ-C12, (b) C10-DBN-C 10 and C10-IQIQ-C10 and (c)



ESI Figure 4 X-ray diffraction patterns of C12-DBN-C12 and C12-IQIQ-C12



ESI Figure 5 (a) X-ray pattern of C10-DBN-C10 in SmC phase with temperature dependence in wide angle on the silicon substrate; (b) X-ray pattern of C10-DBN-C10 in SmC phase with temperature dependence in small angle region of 2°-5°

ESI Table 1 Summar	ry of Full width at half	maximum in SmC of C10-D	DBN-C10 with tempe	erature dependence
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Temperature/°C	175°C	165°C	150°C	140°C
Δx	0.237	0.226	0.220	0.196
2θ (°)	3.00	2.99	2.99	2.97
D (size of domain)/ Å	80.84Å	79.19Å	81.35 Å	80.69 Å

ESI Table 2 Summary of X-ray diffraction peaks of C10-DBN-C10 and C12-DBN-C12 in Crystalline phase.

Sample Phase Spacing(Å)/2θ(degree) Miller index	(hkl)
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C10-DBN-C10	Crystalline at120 °C	25.91(3.41)	(001)
	a=9.47 Å, b=5.92 Å,	13.17(6.71)	(002)
	c=34 Å	8.82(10.03)	(003)
	<b>α=130.16°</b>	6.64(13.34)	(004)
	monoclinic	5.40(16.40)	(005)
		4.58(19.37)	(110)
		4.35(20.42)	(006)
		4.14(21.48)	(111)
		3.71(23.97)	(007)
		3.62(24.61)	(200)
		3.38(26.40)	(201)
		3.13(28.50)	(210)
		2.90(30.88)	(020)
C12-DBN-C12	Crystalline at120 °C	28.78(3.07)	(001)
	a=10.54 Å, b=5.43 Å,	14.73(6.00)	(002)
	c=41 Å	9.88(8.95)	(003)
	α=135.64°	5.26(16.87)	(006)
	monoclinic	4.46(19.92)	(007)
		4.37(20.31)	(110)
		4.07(21.86)	(111)
		3.68(24.16)	(200)
		3.44(25.90)	(201)
		2.98(29.96)	(210)
C12-IQIQ-C12	Crystalline at 130 °C	23.62(3.74)	(001)
	a=13.37 Å, b=5.57 Å,	12.13(7.29)	(002)
	c=38 Å	8.13(10.88)	(003)
	<b>α=141.56°</b>	6.31(14.04)	(004)
	monoclinic	4.91(18.07)	(005)
		4.62(19.19)	(110)
		4.26(20.85)	(111)
		4.16(21.38)	(200)
		3.69(24.11)	(201)
		3.39(26.26)	(210)
$a = \frac{2d_{200}}{2}$	$-h = -\frac{ad_{110}sin^{(m)}(\frac{\alpha\pi}{180})}{ad_{110}sin^{(m)}(\frac{\alpha\pi}{180})}$		
Equation:	$\int \int \frac{d\pi}{\sqrt{\left(a\sin\left(\frac{\alpha\pi}{180}\right)\right)^2 - d_{110}}}$	2	



ESI Figure 6 Transient photocurrents of C10-DBN-C10 in isotropic phase at 186 °C measured by time-of-flight technique. Inset is double logarithm plot.



The HPLC spectra for C10-DBN-C10

The HPLC for C10-DBN-C10: main peak 1 occupy 98.8% and another peak 2 occupy 1.2% with ODS as stationary phase and CH<sub>3</sub>CN mixed with THF as ratio of 3:1.

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR spectra



<sup>13</sup>C-NMR of the compound i



<sup>1</sup>H-NMR of the compound h4







<sup>1</sup>H-NMR of the compound e2



<sup>1</sup>H-NMR of the compound f1



<sup>13</sup>C-NMR of the compound f1



<sup>1</sup>H-NMR of the compound f2







<sup>1</sup>H-NMR of the compound h1



<sup>1</sup>H-NMR of the compound h2



<sup>13</sup>C-NMR of the compound h2