

## Supplementary Information

### **Unexpected synthesis, delayed emission and solid-state acidochromism of novel 2,7-naphthyridine derivatives obtained from 2-(3,5-diaryl-4*H*-pyran-4-ylidene)malononitrile**

Yitian Jiang,<sup>a</sup> Miaochang Liu,<sup>a,b</sup> Mengzhu Wang,<sup>a</sup> Yunxiang Lei,<sup>\*a</sup> Qiuping Ding,<sup>\*b</sup> Huayue Wu and Xiaobo Huang<sup>\*a</sup>

<sup>a</sup> College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

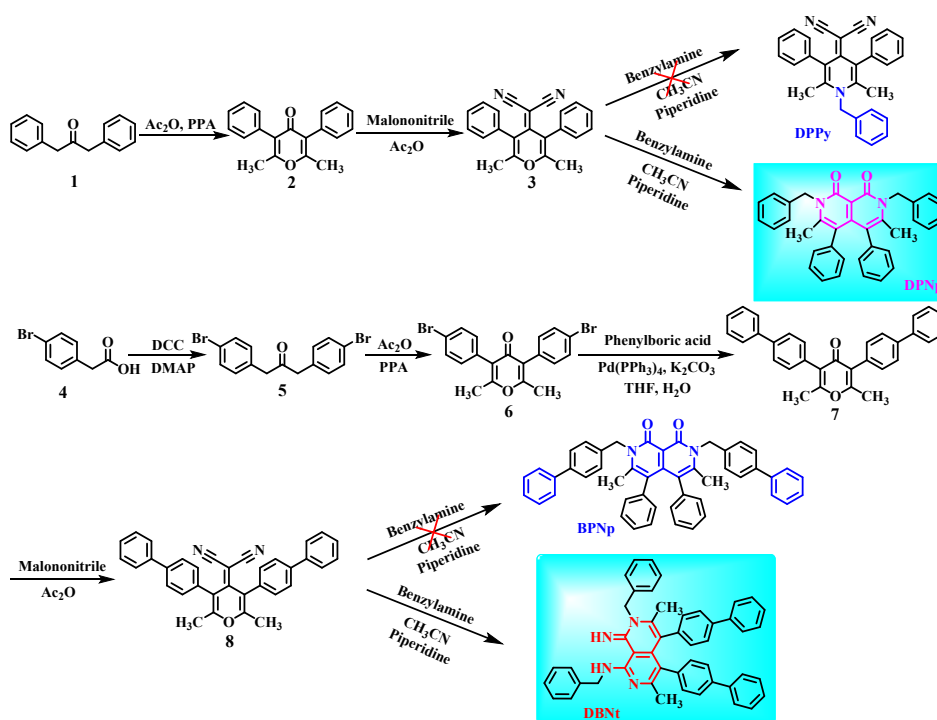
E-mail: yunxianglei@wzu.edu.cn (Y. Lei), xiaobhuang@wzu.edu.cn (X. Huang)

<sup>b</sup> Key Laboratory of Functional Small Organic Molecules, Ministry of Education, Jiangxi Normal University, 99

Ziyang Road, Nanchang 330022, P. R. China

E-mail: dqpjxnu@gmail.com (Q. Ding)

## Contents:



Scheme S1 Synthetic routes to DPNp and DBNt.

## 1. Experimental

### Measurements and materials

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were tested on a Bruker DRX 500 NMR spectrometer. High-resolution electrospray ionization mass (HRMS-ESI) spectra were performed with a Hitachi Nano Frontier LD spectrometer. Fluorescence spectra were obtained using a Cary Eclipse fluorescence spectrophotometer. The absolute fluorescence quantum yields and fluorescence lifetime decays were performed using Jobin Yvon Horiba FluoroMax-4 fluorometer. UV-vis absorption spectra were conducted on a UV-3600 Shimadzu spectrophotometer. Fluorescence microscopic images were obtained using a Leica DMI3000B inverted optical microscope. Delayed emission spectra were conducted on a FLS920 lifetime and steady state spectrometer. Single-crystal X-ray data were collected with graphite-monochromated MoK $\alpha$  radiation on a Bruker-Nonius Smart Apex CCD diffractometer. 1,3-Diphenylpropan-2-one (1), 2-(4-bromophenyl)acetic acid (4), acetic anhydride, polyphosphoric acid (PPA), malononitrile, dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMPA), benzylamine, piperidine, phenylboric acid, and Pd(PPh<sub>3</sub>)<sub>4</sub> were commercially available and used directly. 2-(2,6-Dimethyl-3,5-diphenyl-4H-pyran-4-ylidene)malononitrile (3)<sup>[1]</sup> and 3,5-di([1,1'-biphenyl]-4-yl)-2,6-dimethyl-4H-pyran-4-one (7)<sup>[2]</sup> were obtained according to the previous reports.

### Synthesis of 2-(3,5-di([1,1'-biphenyl]-4-yl)-2,6-dimethyl-4H-pyran-4-ylidene)malononitrile (8)

Compound 7 (0.428 g, 1.0 mmol) and acetic anhydride (10 mL) were added to 50 mL eggplant shaped bottle. After the compound 7 was fully dissolved under stirring conditions, malononitrile (0.08 g, 1.2

mmol) was added to the bottle and the reaction mixture was stirred at 140°C for 8 h. The mixture was cooled to room temperature and then poured into 100 mL water. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The organic solvent was removed under reduced pressure and the residue was passed through a silica gel column chromatography (petroleum ether: ethyl acetate = 10:1) to give a light red solid (0.248 g, 52% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.72 (d, *J* = 8.0 Hz, 4H), 7.67 (d, *J* = 7.5 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 4H), 7.38-7.34 (m, 6H), 2.14 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 159.1, 153.7, 142.5, 140.3, 132.4, 131.3, 128.7, 127.8, 127.6, 127.2, 120.5, 115.1, 63.4, 19.0 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calculated for C<sub>34</sub>H<sub>25</sub>N<sub>2</sub>O, 477.1961; found, 477.1950.

**Synthesis of 2,7-Dibenzyl-3,6-dimethyl-4,5-diphenyl-2,7-naphthyridine-1,8(2*H*,7*H*)-dione (DPNp).**

Compound **3** (0.324 g, 1 mmol), benzylamine (4 mL), and acetonitrile (15 mL) were added to a Schlenk tube. The reaction mixture was stirred at 80°C for 12 h under a N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature and then poured into 20 mL ethanol. A large number of precipitates were precipitated out of the mixture. After vacuum filtration, the crude product was washed using ethanol and petroleum ether in turn, and dried to give a yellow solid (0.47 g, 90% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.48 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 2H), 7.33-7.29 (m, 3H), 7.24-7.20 (m, 3H), 6.91-6.86 (m, 6H), 6.59 (t, *J* = 6.5 Hz, 4H), 5.04 (s, 2H), 4.88 (s, 2H), 2.00 (s, 3H), 1.80 (s, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 157.5, 156.5, 143.0, 141.0, 140.5, 140.1, 135.0, 131.6, 131.4, 129.2, 128.7, 128.6, 128.3, 127.9, 127.7, 127.4, 127.3, 126.5, 125.6, 125.4, 125.0, 119.3, 116.2, 103.9, 50.3, 45.3, 24.4, 18.3 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calculated for C<sub>36</sub>H<sub>31</sub>N<sub>2</sub>O<sub>2</sub>, 523.2380; found, 523.2383.

**Synthesis of 4,5-Di([1,1'-biphenyl]-4-yl)-*N*,7-dibenzyl-8-imino-3,6-dimethyl-7,8-dihydro-2,7-naphthyridin-1-amine (DBNt).**

Compound **8** (0.476 g, 1 mmol), benzylamine (4 mL), and acetonitrile (15 mL) were added to a Schlenk tube. The reaction mixture was stirred at 80°C for 12 h under a N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature and then poured into 20 mL ethanol. A large number of precipitates were precipitated out of the mixture. After vacuum filtration, the crude product was washed using ethanol and petroleum ether in turn, and dried to give a light green solid (0.323 g, 48% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 11.69 (br, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.40-7.32 (m, 15H), 7.25-7.23 (m, 3H), 7.11-7.09 (m, 4H), 6.70-6.68 (m, 4H), 5.06 (s, 2H), 4.89 (s, 2H), 2.07 (s, 3H), 1.89 (s, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 157.5, 156.6, 143.3, 141.1, 140.8, 140.5, 140.2, 139.2, 138.4, 137.9, 135.0, 132.1, 131.9, 130.9, 129.2, 128.8, 128.6, 128.5, 128.3, 127.9, 127.7, 126.9, 126.8, 126.6, 126.1, 125.9, 125.4, 118.7, 115.7, 103.9, 50.4, 45.4, 29.7, 18.5 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calculated for C<sub>48</sub>H<sub>41</sub>N<sub>4</sub>, 673.3326; found, 673.3306.

## References

- [1] F. Xiao, M. Wang, Y. Lei, Y. Xie, M. Liu, Y. Zhou, W. Gao, X. Huang, H. Wu, *Chem. Asian J.* **2020**, *15*, 3437–3443.
- [2] F. Xiao, X. Liu, K. Lin, Y. Zhou, W. Gao, Y. Lei, M. Liu, X. Huang, H. Wu, *J. Phys. Chem. C* **2021**, *125*, 16792–16802.

## 2. Figures and tables

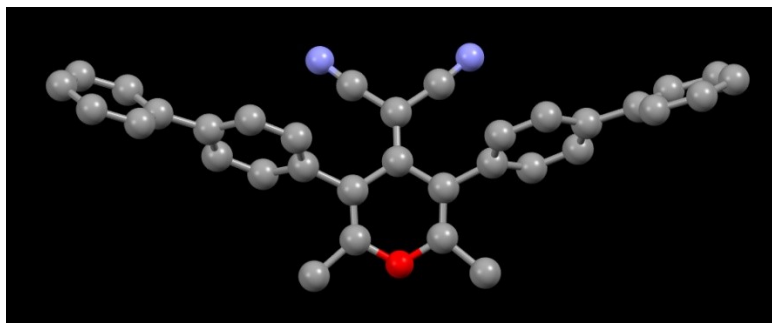
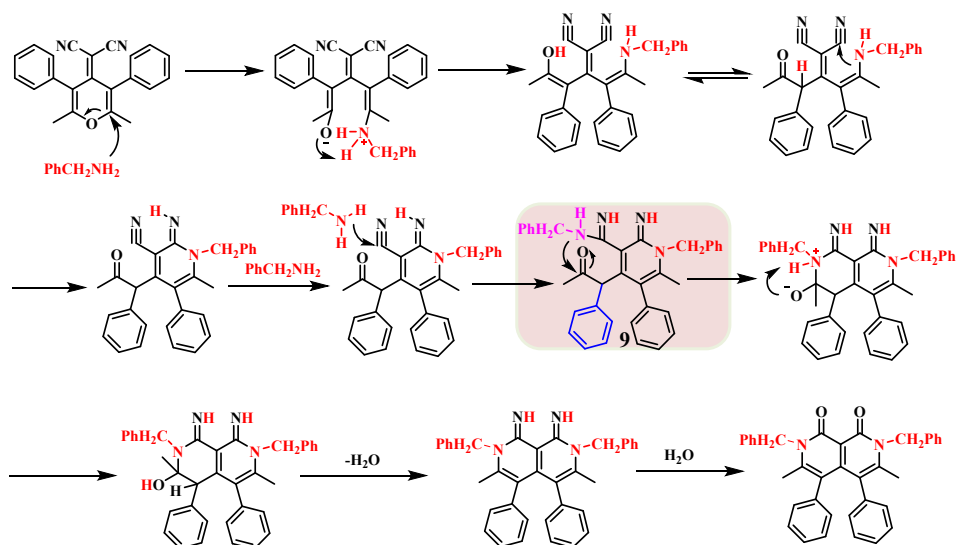
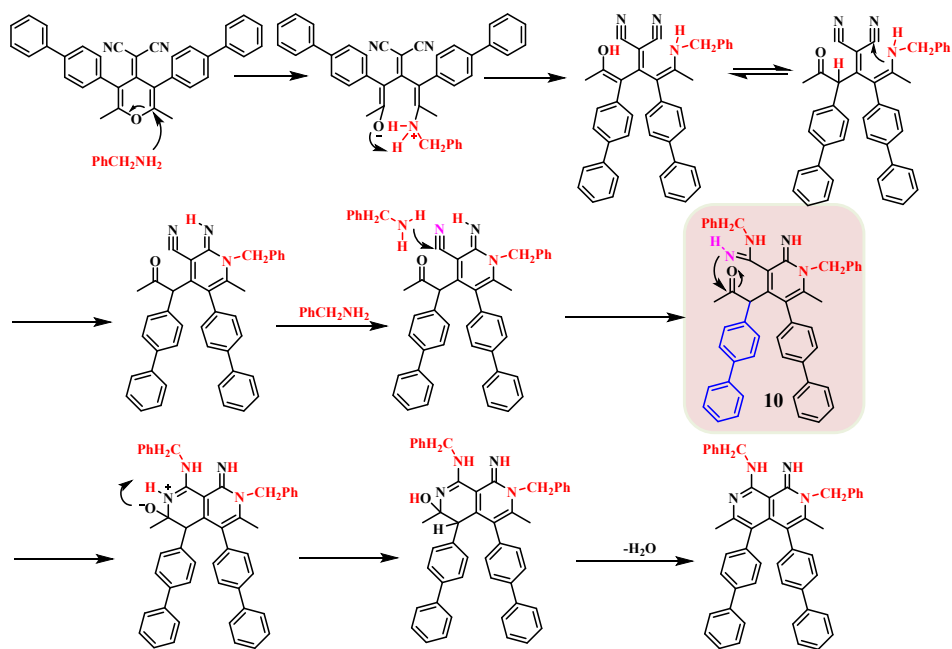


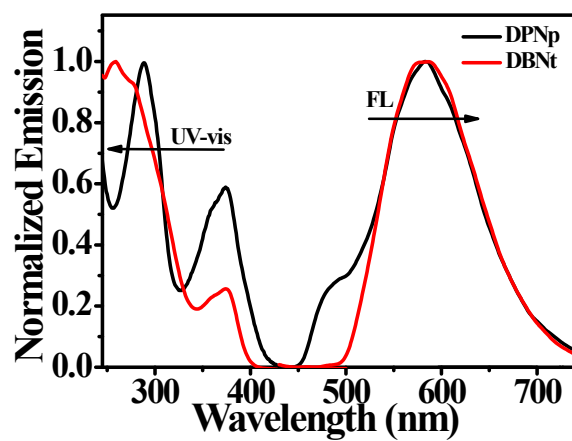
Fig. S1 Single crystal structure of compound 8.



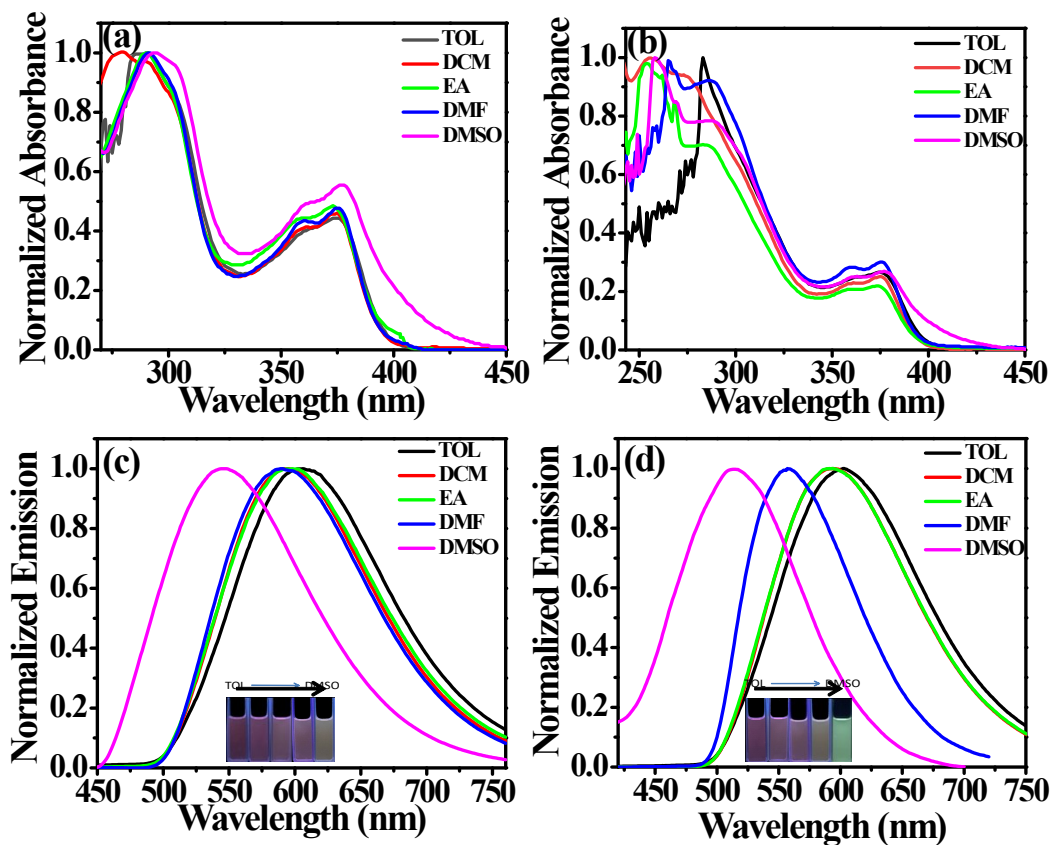
Scheme S2 Possible reaction mechanism of DPNp obtained from compound 3 and benzylamine.



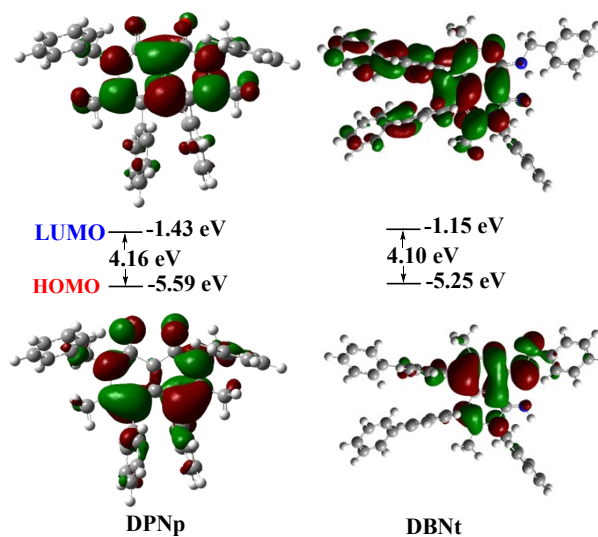
**Scheme S3** Possible reaction mechanism of **DBNt** obtained from compound **8** and benzylamine.



**Fig. S2** UV-vis absorption and fluorescence spectra of **DPNp** and **DBNt** in chloroform at a concentration of  $1 \times 10^{-5}$  mol/L.



**Fig. S3** Absorption and fluorescence spectra of **DPNp** (a, c) and **DBNt** (b, d) in various solvents ( $1 \times 10^{-5}$  mol/L). Inset: fluorescence pictures of **DPNp** and **DBNt** in various solvents. TOL: toluene; DCM: dichloromethane; EA: ethyl acetate; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide.



**Fig. S4** LUMO/HOMO distributions and energy gaps of **DPNp** and **DBNt**.

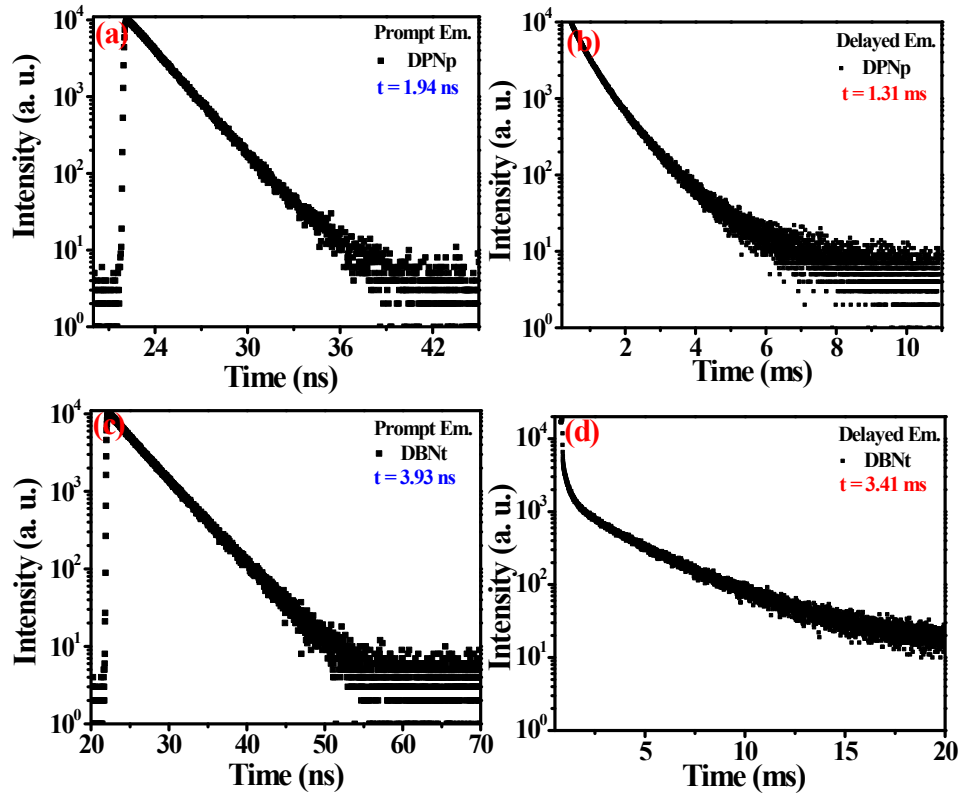


Fig. S5 Prompt and Delayed emission intensities of DPNp (a, b) and DBNt (c, d) solids.

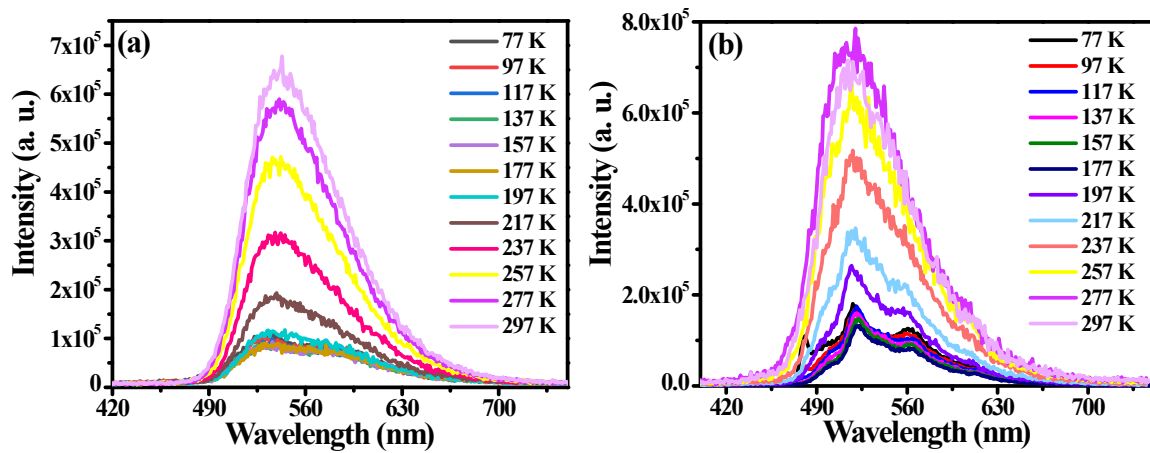
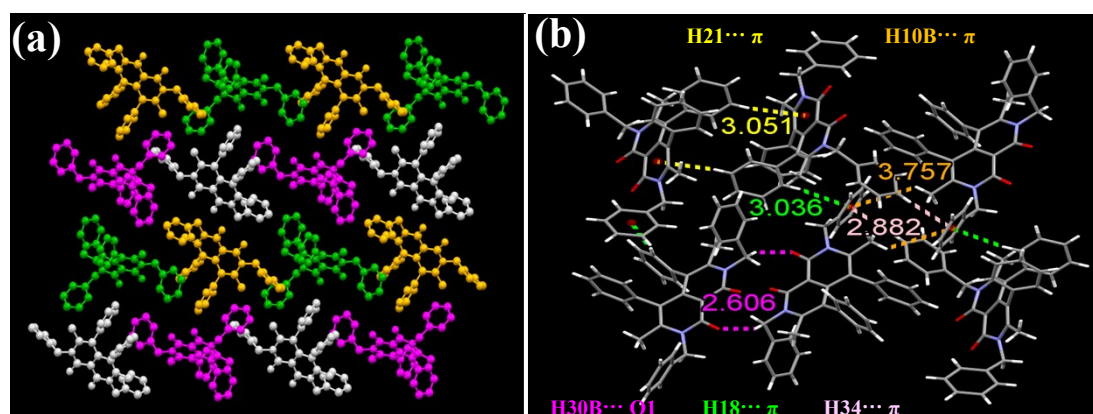


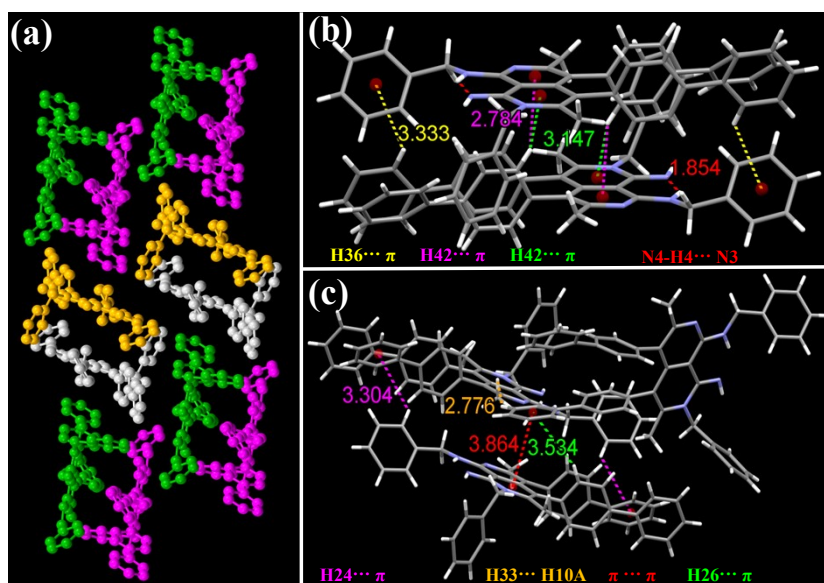
Fig. S6 Delayed emission intensity of DPNp (a) and DBNt (b) solids at different temperatures (Delayed time: 0.5 ms).

**Table S1.** Crystal data and details of collection and refinement for compound **8**, **DPNp**, and **DBNt**.

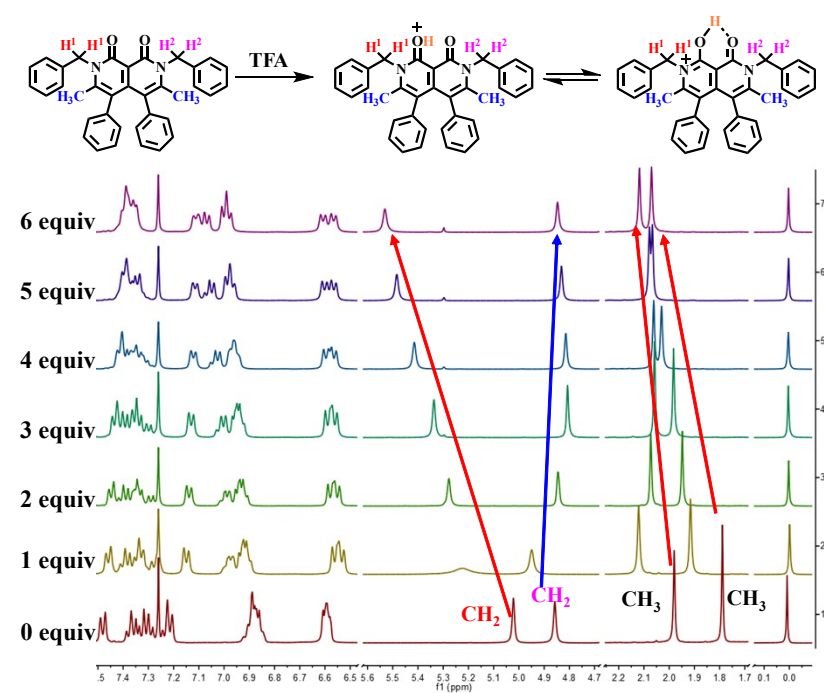
	<b>8</b>	<b>DPNp</b>	<b>DBNt</b>
CCDC (no.)	2173593	2173594	2173595
Empirical formula	C <sub>68</sub> H <sub>48</sub> N <sub>4</sub> O <sub>2</sub>	C <sub>36</sub> H <sub>30</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>48</sub> H <sub>40</sub> N <sub>4</sub>
Formula weight	953.10	522.62	672.84
Temperature (K)	293(2)	296(2)	213(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
<i>Z</i>	4	4	4
<i>D</i> <sub>calcd</sub> [Mg/m <sup>3</sup> ]	1.214	1.242	1.256
<i>F</i> (000)	2000	1104	1424
$\theta$ range [°]	2.499-25.000	2.106-26.000	2.253-25.500
<i>R</i> <sub>1</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.0825	0.0492	0.0603
<i>wR</i> <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.1572	0.1302	0.1344
<i>a</i> [Å]	30.271(3)	13.9488(4)	18.9851(13)
<i>b</i> [Å]	19.1087(18)	11.7242(3)	9.8420(7)
<i>c</i> [Å]	9.0450(9)	17.1824(4)	19.9967(16)
$\alpha$ [deg]	90	90	90
$\beta$ [deg]	94.914(3)	95.7400(10)	107.793(2)
$\gamma$ [deg]	90	90	90
<i>V</i> [Å <sup>3</sup> ]	5212.8(9)	2795.90(13)	3557.7(5)
GOF	1.002	1.011	1.053
<i>R</i> (int)	0.1164	0.0434	0.0819
No. of reflns collected	23606	32271	16646
No. of unique reflns	9146	5482	6568
<i>R</i> <sub>1</sub> (all data)	0.2503	0.0714	0.1008
<i>wR</i> <sub>2</sub> (all data)	0.2425	0.1503	0.1634

**Fig. S7** Crystal structure of **DPNp**: (a) stacking mode; (b) C–H $\cdots$  $\pi$  interactions and C–H $\cdots$ O bond in the crystal structure.

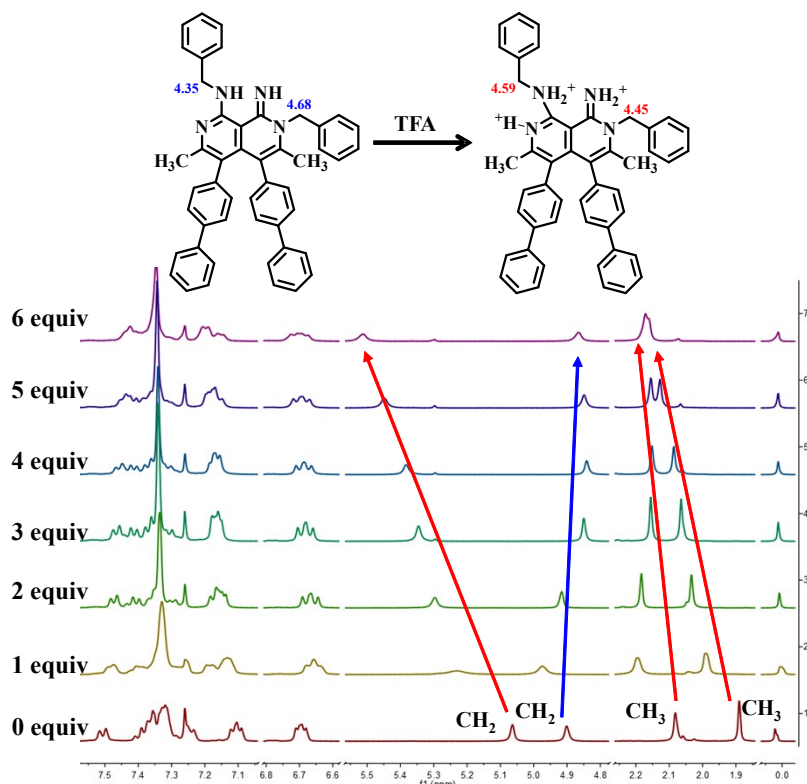




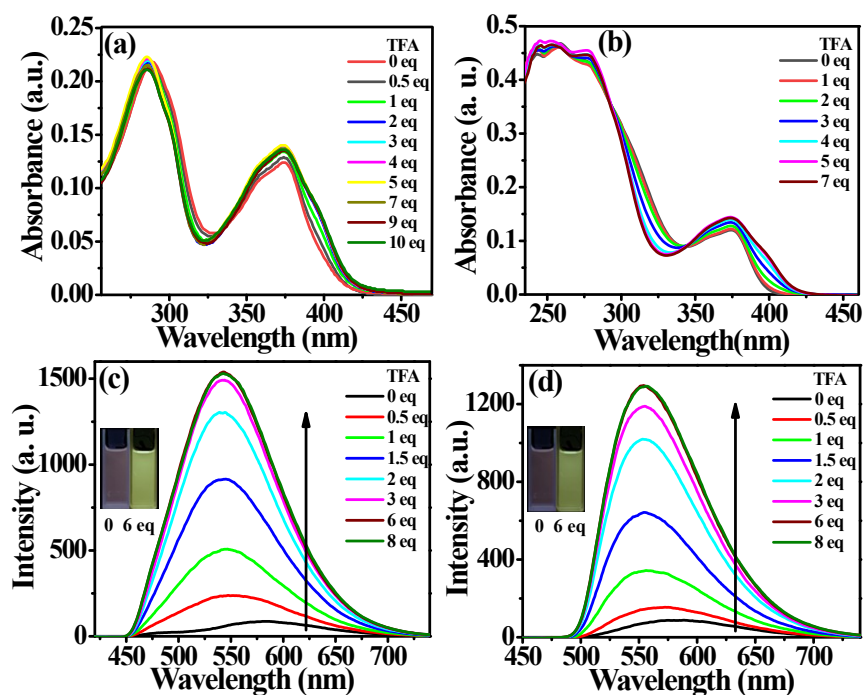
**Fig. S8** Crystal structure of **DBNT**: (a) stacking mode; (b) intermolecular interactions in dimer; (c) intermolecular interactions between dimers.



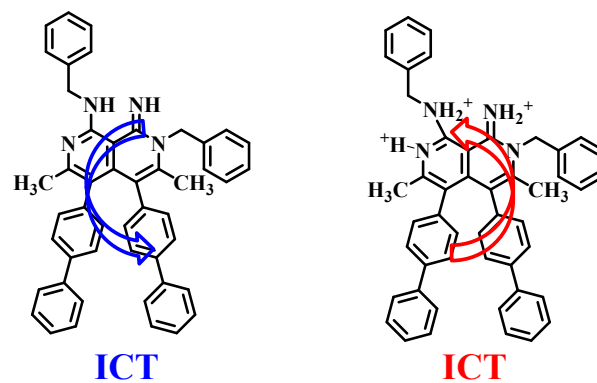
**Fig. S9** Protonation process (up) and  $^1\text{H}$  NMR spectra (down) of **DPNp** in  $\text{CDCl}_3$  with the addition of TFA.



**Fig. S10**  $^1\text{H}$  NMR spectra of **DBNt** in  $\text{CDCl}_3$  with the addition of TFA. Chemical shifts of protons of **DBNt** obtained from the simulation of ChemDraw software.

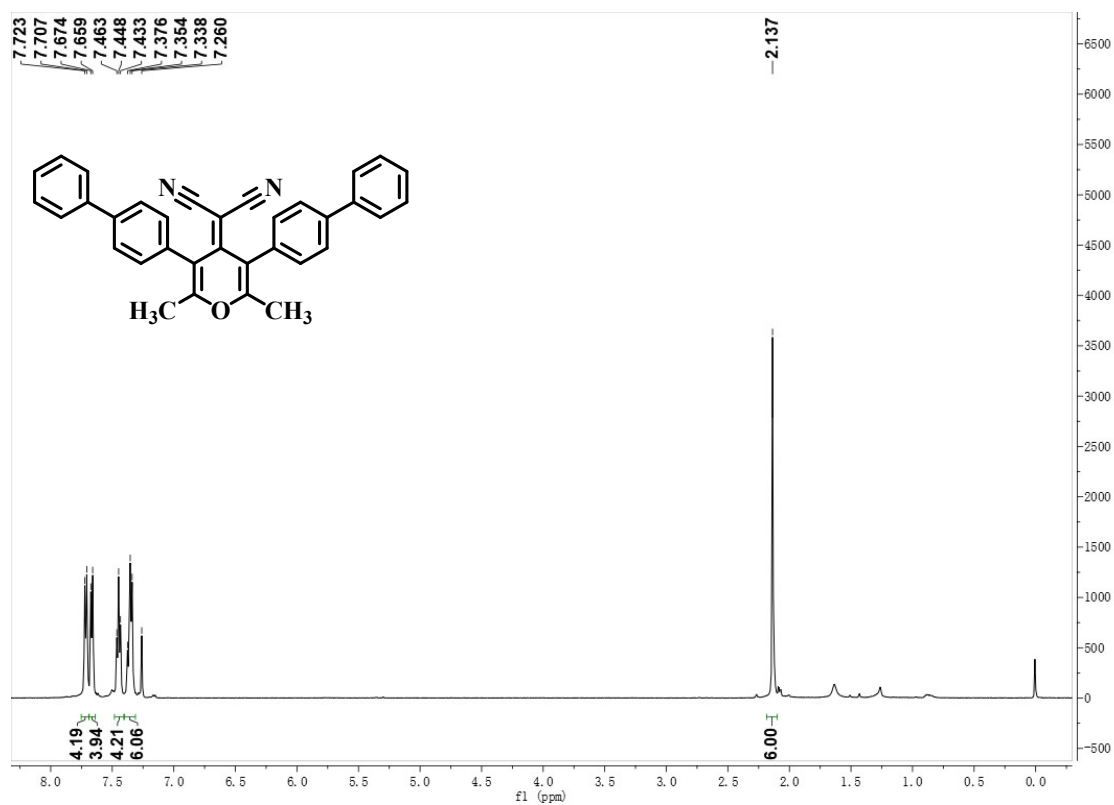


**Fig. S11** Absorption and fluorescence spectra of **DPNp** (a, c) and **DBNt** (b, d) in chloroform ( $1 \times 10^{-5}$  mol/L) with the addition of TFA. Inset: fluorescence pictures of **DPNp** and **DBNt** before and after the addition of TFA.



**Fig. S12** Flow direction of electron cloud in ICT process of solid **DBNt** sample before and after the fumigation of TFA vapor.

### 3. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, and HRMS spectra



**Fig. S13**  $^1\text{H}$  NMR of compound **8** ( $\text{CDCl}_3$ , 500 MHz).

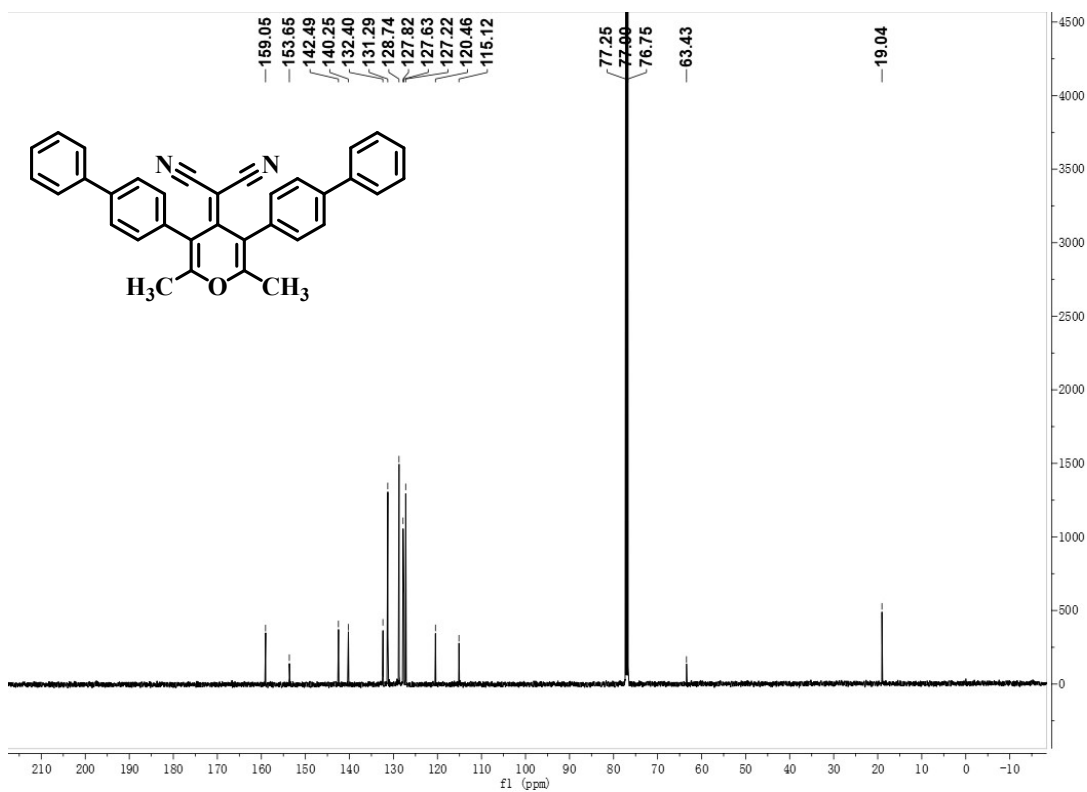


Fig. S14 <sup>13</sup>C NMR of compound 8 (CDCl<sub>3</sub>, 125 MHz).

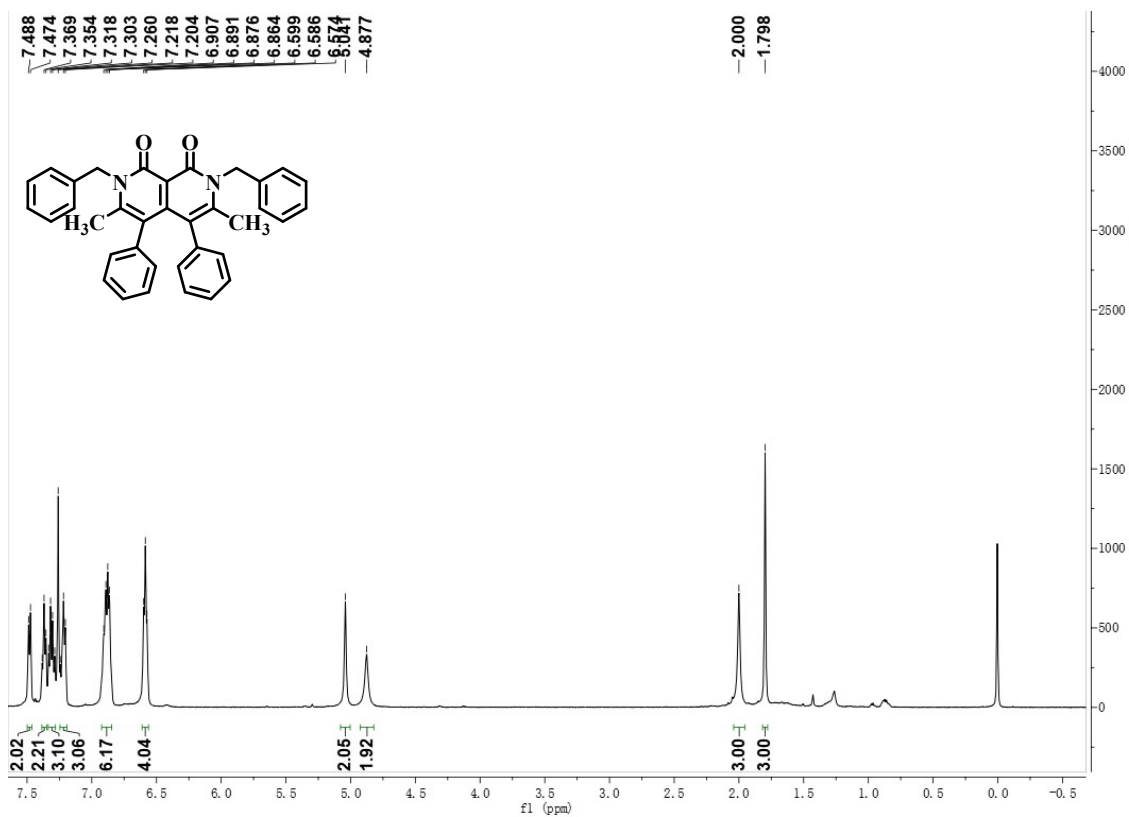


Fig. S15 <sup>1</sup>H NMR of DPNp (CDCl<sub>3</sub>, 500 MHz).

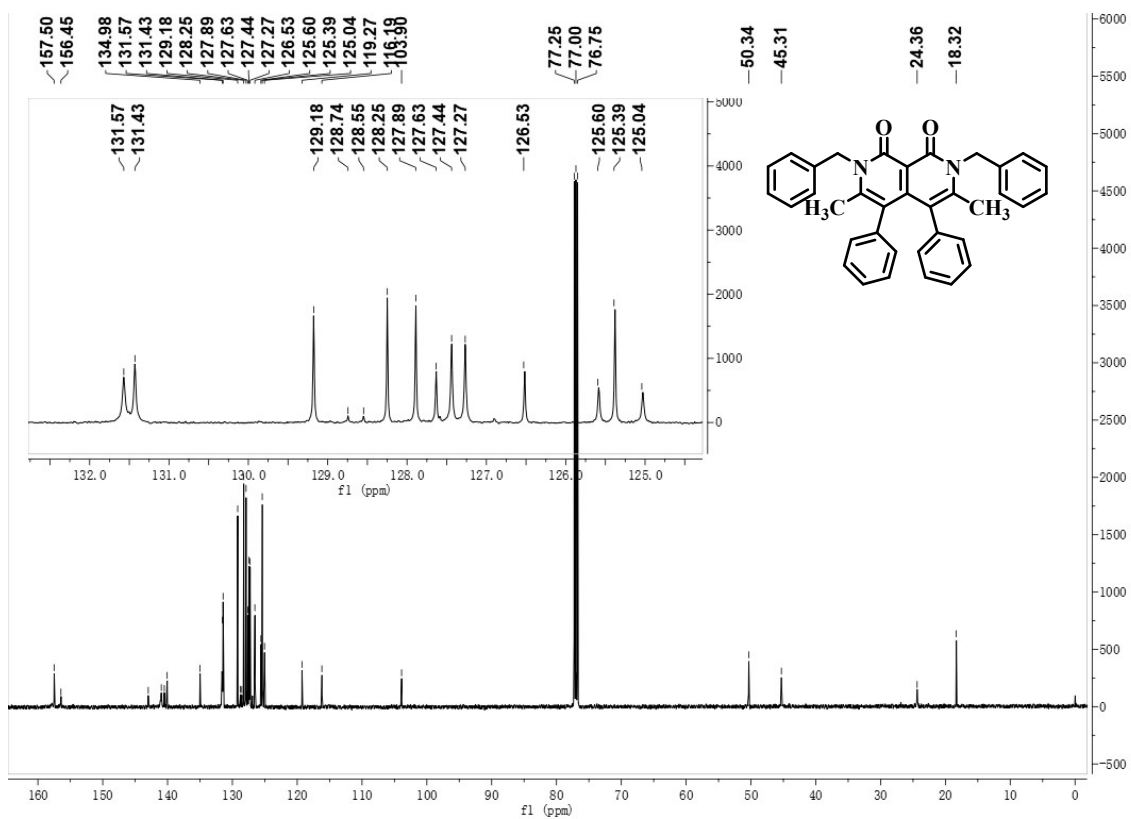


Fig. S16  $^{13}\text{C}$  NMR of DPNp ( $\text{CDCl}_3$ , 125 MHz).

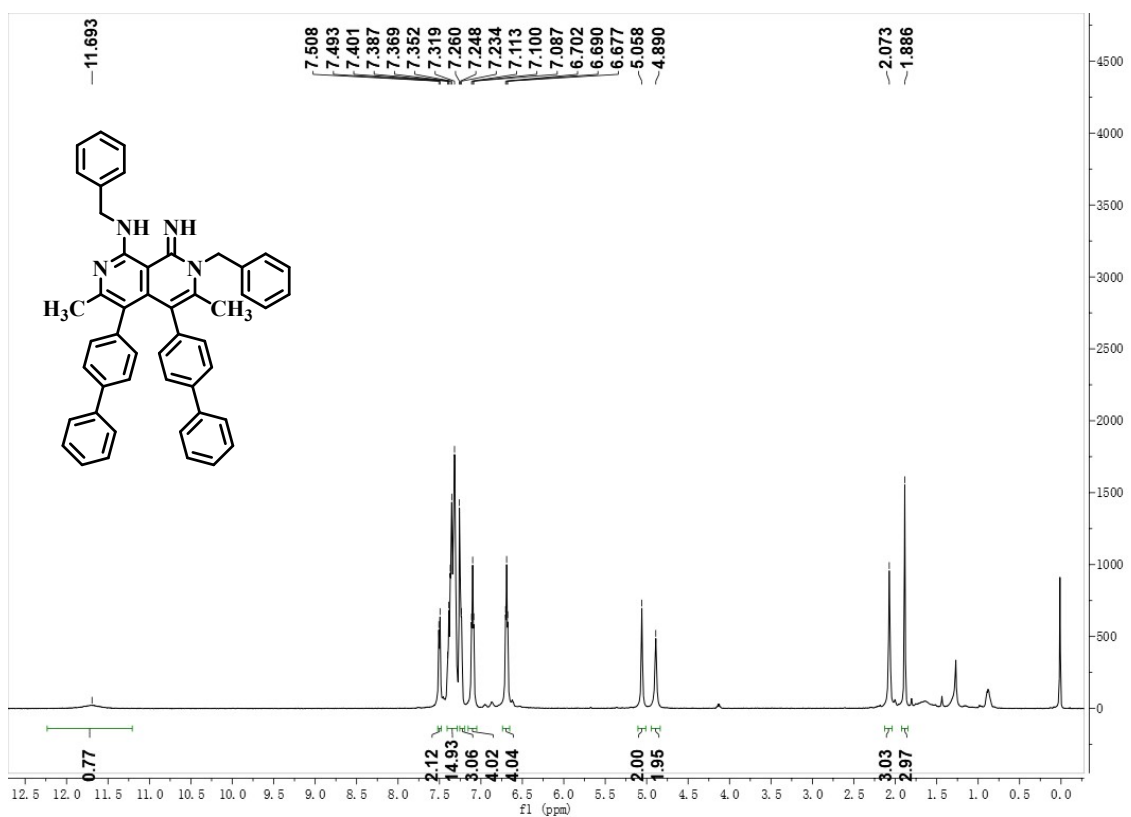
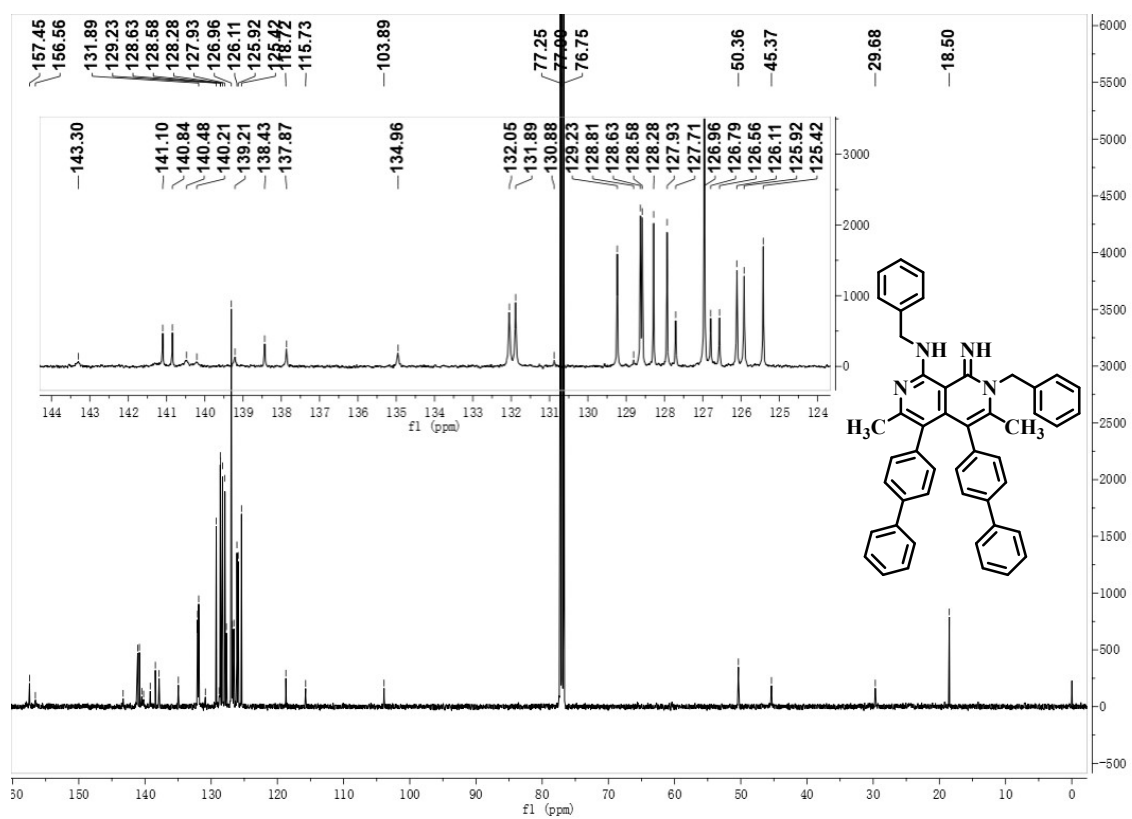


Fig. S17  $^1\text{H}$  NMR of DBNt ( $\text{CDCl}_3$ , 500 MHz).



**Fig. S18**  $^{13}\text{C}$  NMR of DBNt ( $\text{CDCl}_3$ , 125 MHz).