

## Electronic Supplementary Information

# Synergetic enhancement of room-temperature phosphorescence via water molecules as hydrogen bonding bridge

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## Supplementary Figures

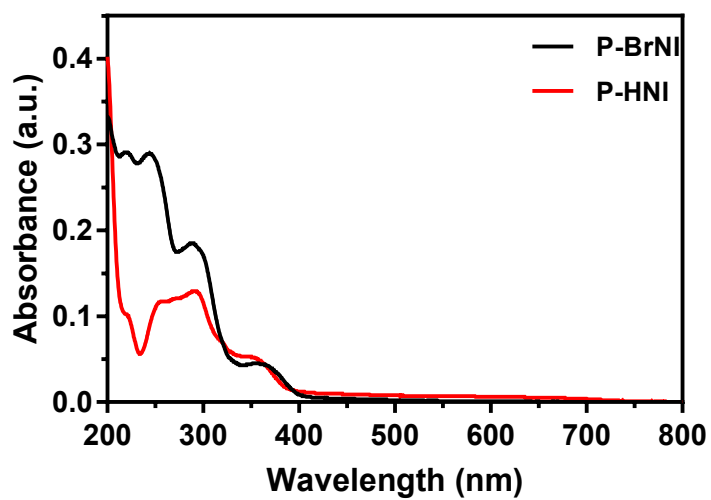


Figure S1. Solid-state absorbance spectra of P-BrNI and P-HNI powder.

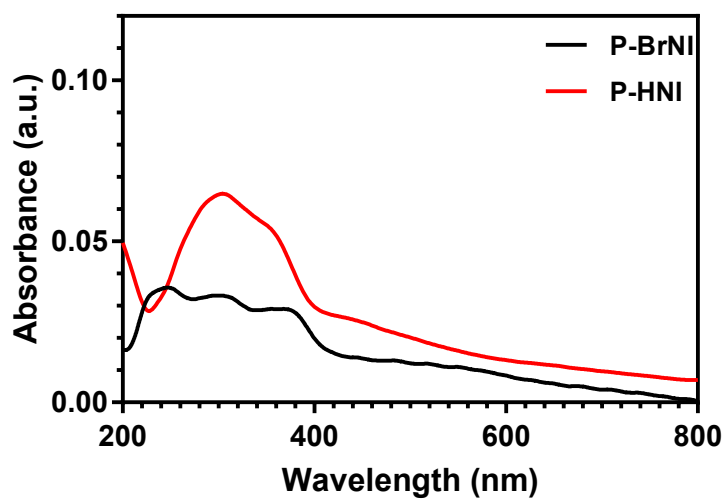


Figure S2. Solid-state absorbance spectra of P-BrNI and P-HNI film.

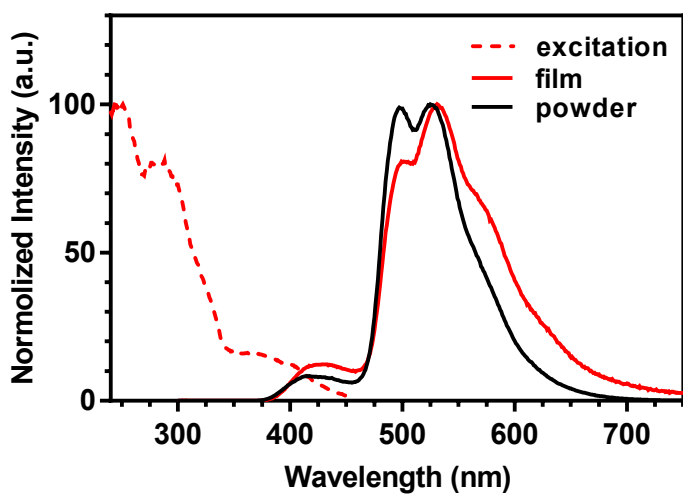


Figure S3. Excited spectrum (red dash line) and photoluminescence spectra of P-BrNI powder and P-BrNI film ( $\lambda_{\text{ex}}=280$  nm).

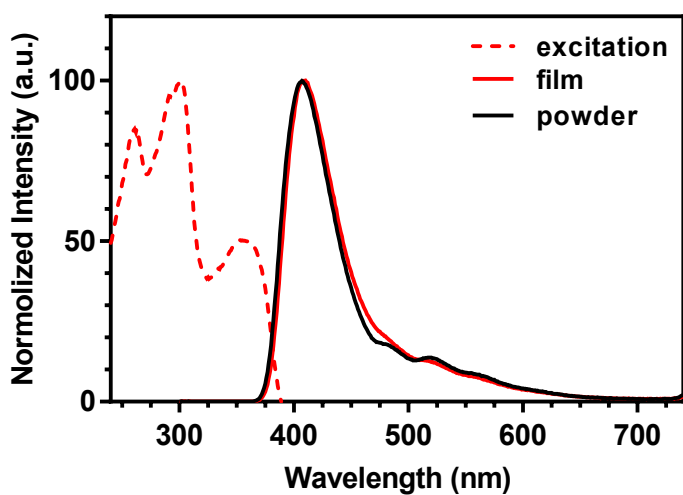


Figure S4. a) Excited spectrum (red dash line) and photoluminescence spectra of P-HNI powder and P-HNI film ( $\lambda_{\text{ex}}=280$  nm).

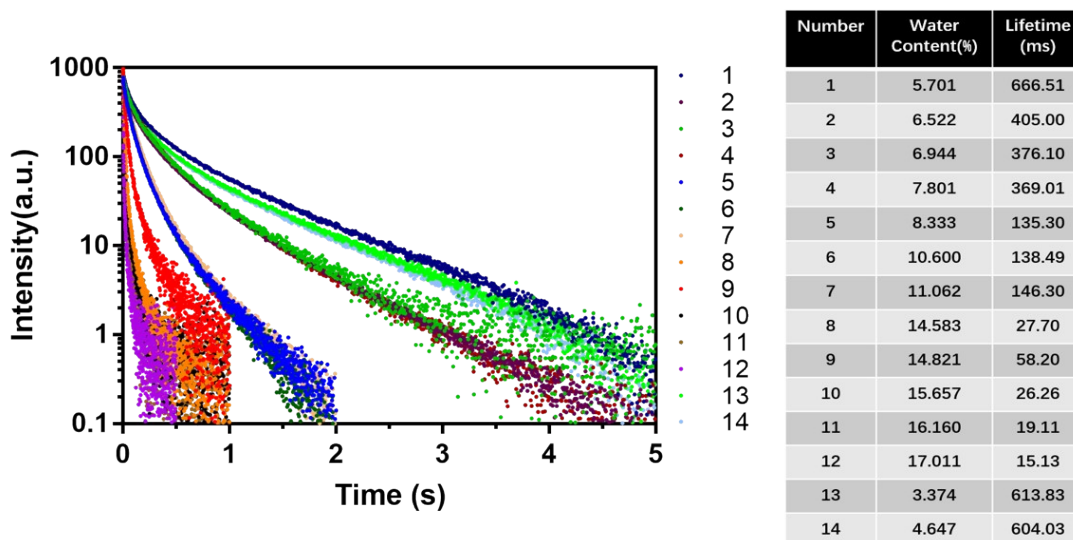


Figure S5. 14 groups of phosphorescence lifetimes of P-HNI powder with different water contents (The right table shows the specific data).

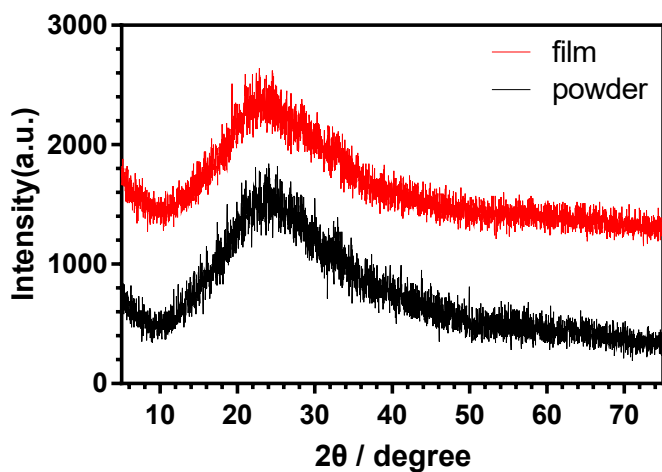


Figure S6. XRD patterns of P-HNI film (red) and powder (black).

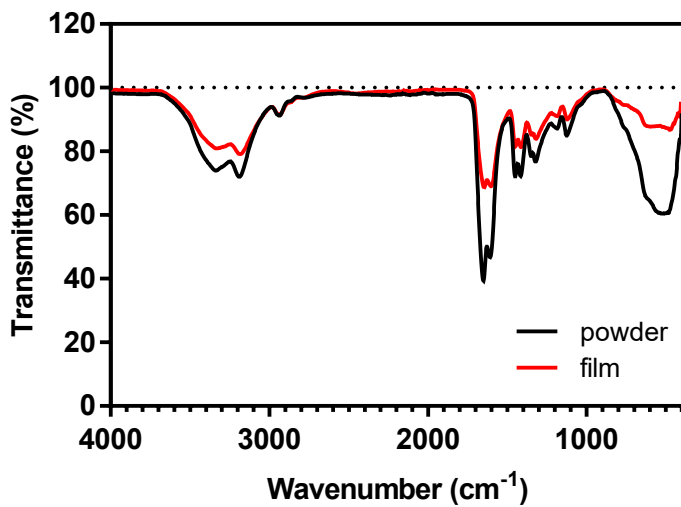


Figure S7. Infrared spectra of P-HNI powder and film.

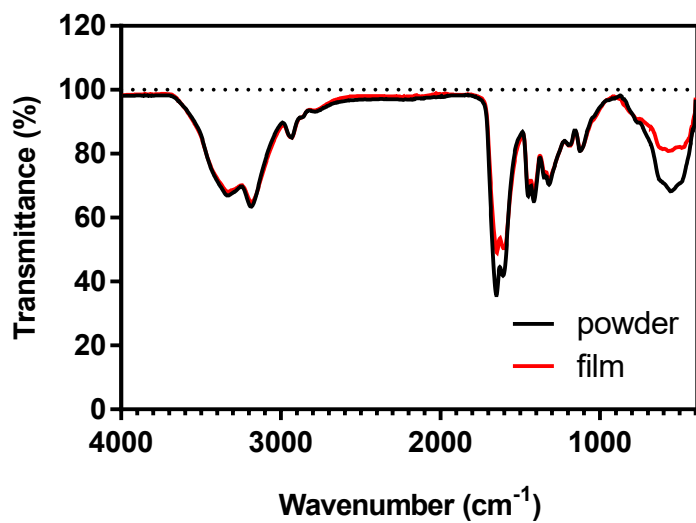


Figure S8. Infrared spectra of P-BrNI powder and film.

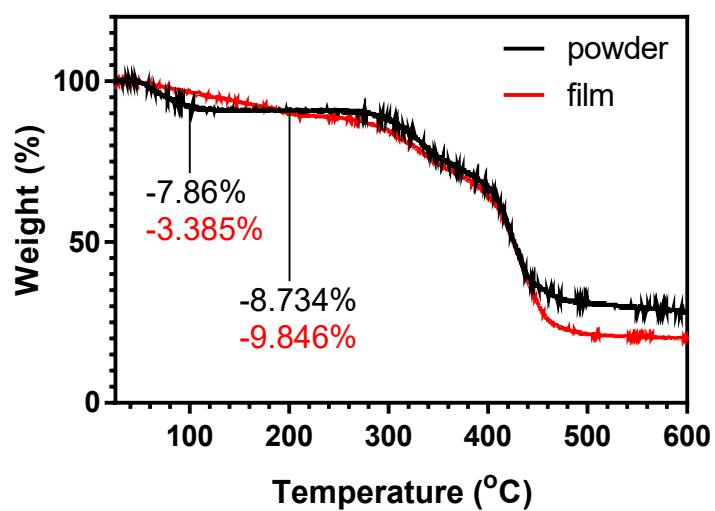


Figure S9. Thermogravimetric analysis of P-HNI powder and P-HNI film.

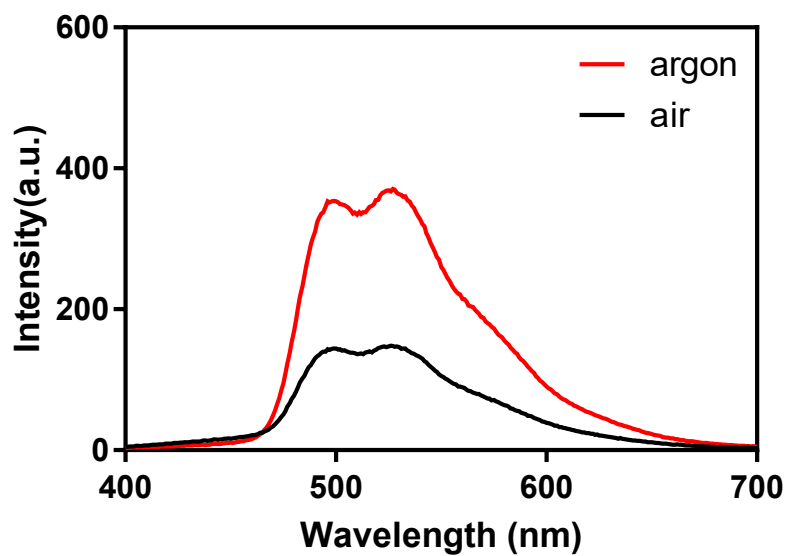


Figure S10. Phosphorescence spectra of P-BrNI powder in argon and air.

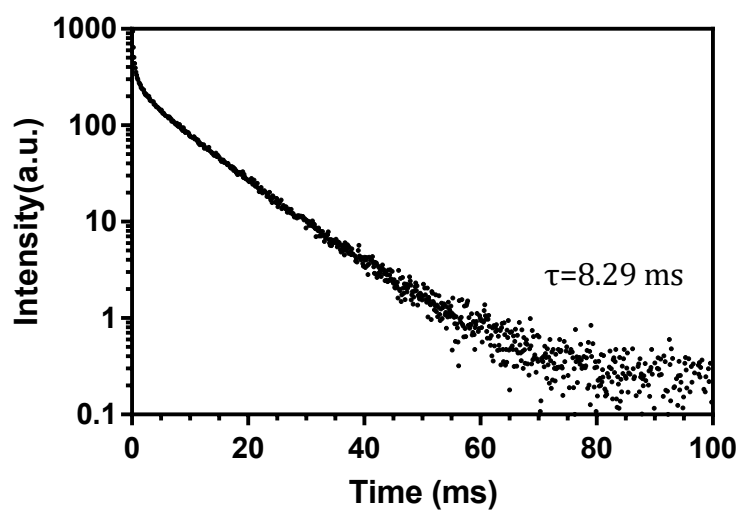


Figure S11. Phosphorescence lifetime of P-BrNI powder in argon.

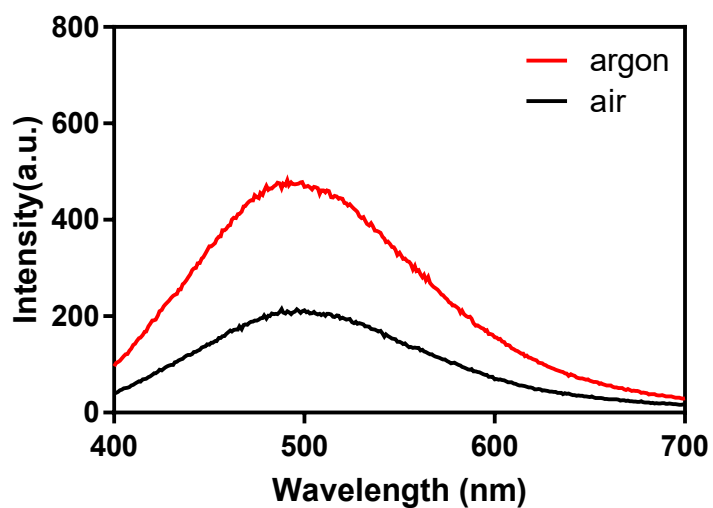


Figure S12. Phosphorescence spectra of P-HNI powder in argon and air.

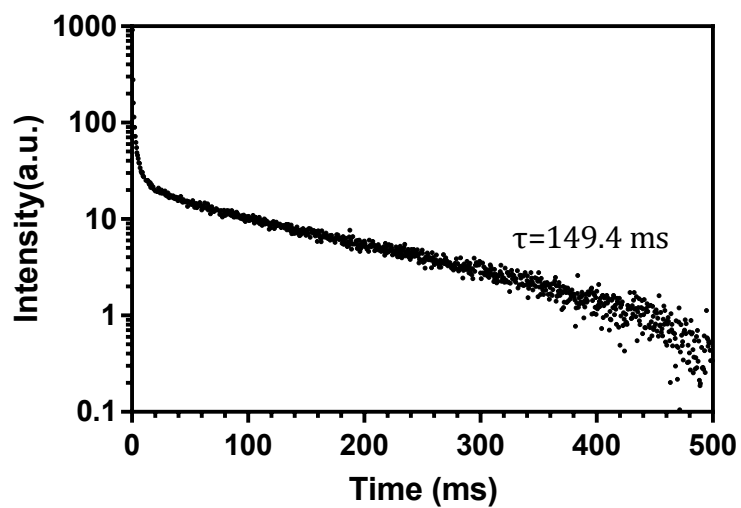


Figure S13. Phosphorescence lifetime of P-HNI Powder in argon.

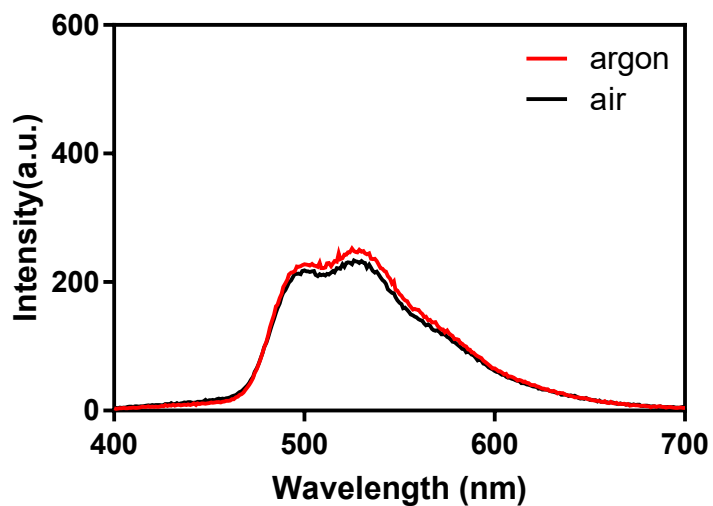


Figure S14. Phosphorescence spectra of P-BrNI film in argon and air.

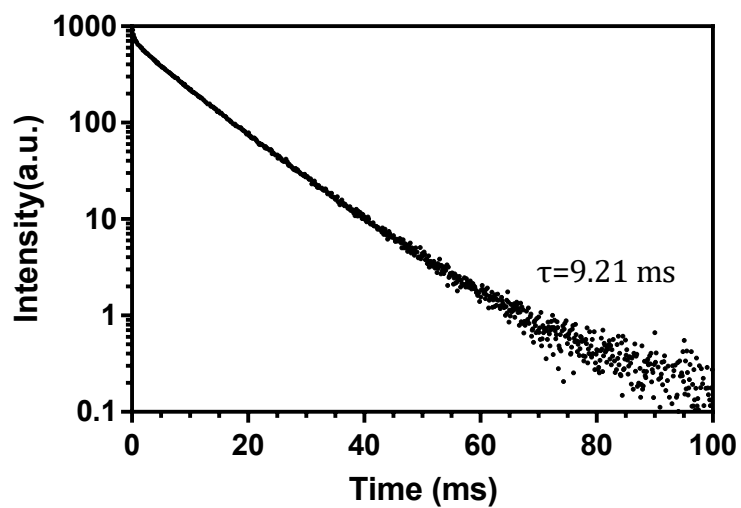


Figure S15. Phosphorescence lifetime of P-BrNI film in argon.



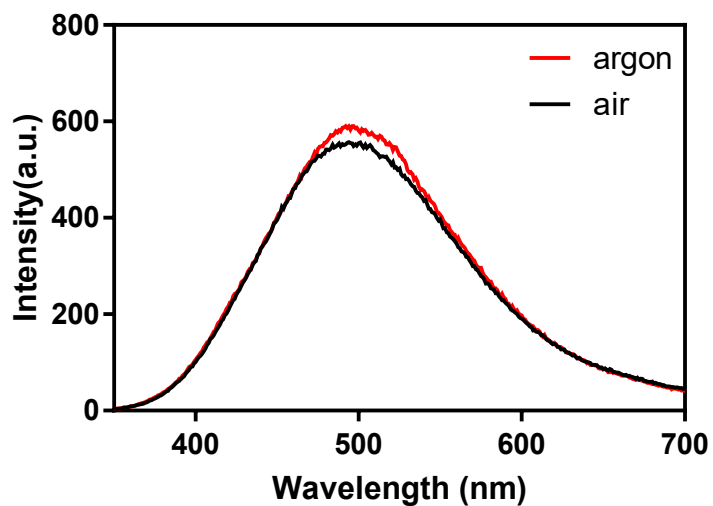


Figure S16. Phosphorescence spectra of P-HNI film in argon and air.

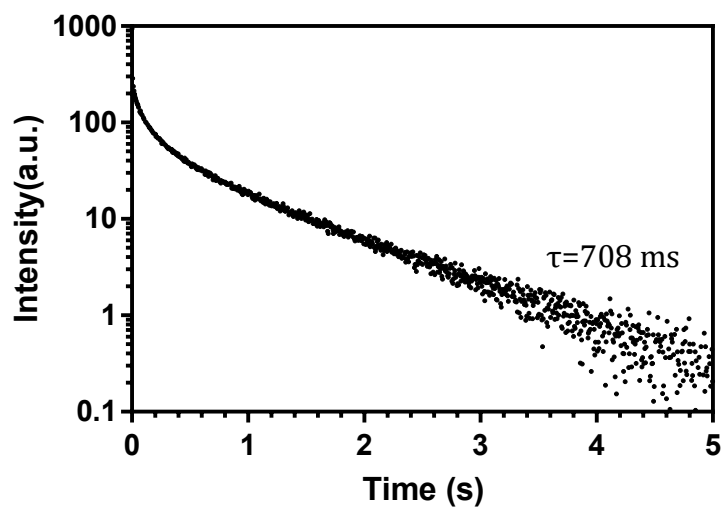


Figure S17. Phosphorescence lifetime of P-HNI film in argon.

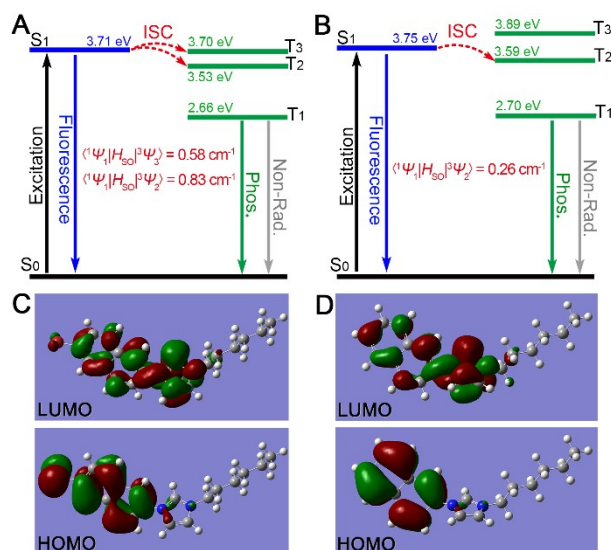


Figure S18. The Jablonski energy diagram of (A) P-BrNI and (B) P-HNI. The HOMO and LUMO of (C) P-BrNI and (D) P-HNI.

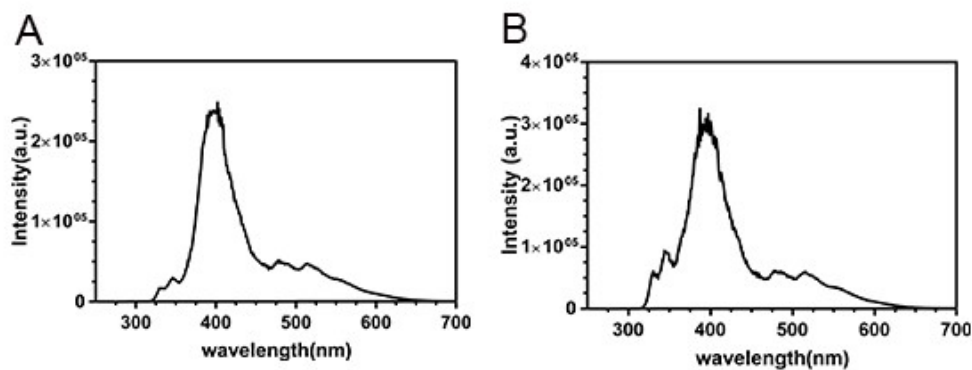


Figure S19. Photoluminescence spectra of (A) P-HNI film and (B) powder at 77K.

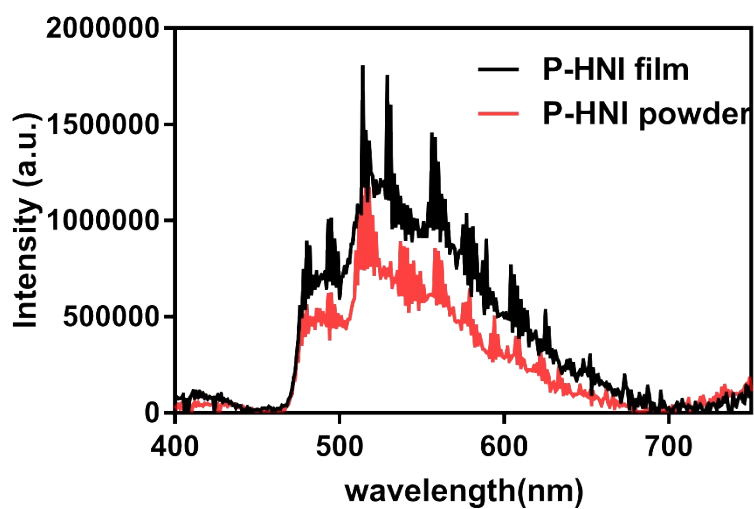


Figure S20. Phosphorescence spectra of P-HNI film(black) and powder(red) at 77K.

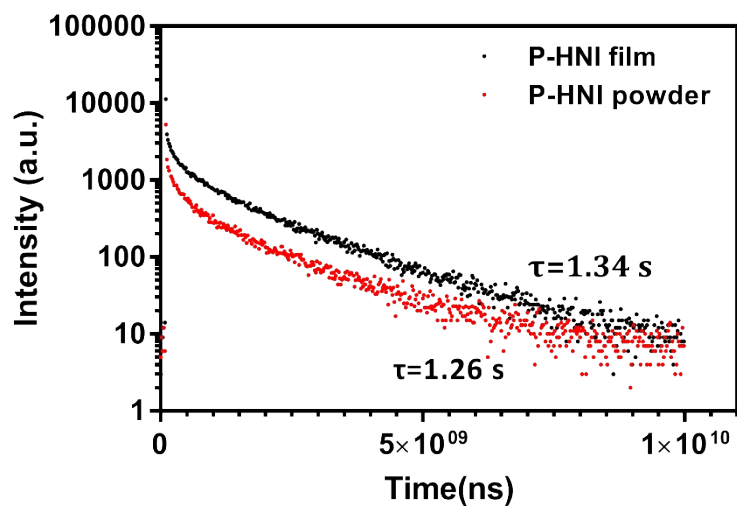
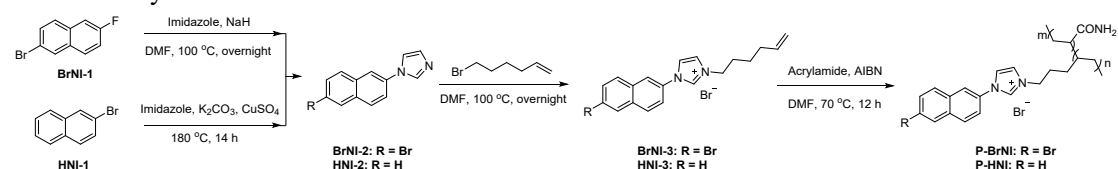


Figure S21. Phosphorescence lifetime of P-HNI film(black) and powder(red) at 77K.

## Chemistry

**Materials and Methods:** All the reagents and solvents were obtained commercially and used as supplied without further purification unless specified otherwise. The synthesized compounds were characterized by Nuclear Magnetic Resonance (NMR) spectrometer and high-resolution mass spectrometer (HRMS). The steady-state photoluminescence spectra at room temperature were measured using a Horiba FluoroMax-4 spectrofluorometer. The time-resolved photoluminescence spectra and lifetime at room temperature were recorded on an Agilent Cary Eclipse spectrophotometer. The photoluminescence quantum yields were measured using a HAMAMATSU absolute PL quantum yield spectrometer (C11347). The NMR spectra were measured on a Bruker AV-400 spectrometer and processing on MestReNova (Mestralab Research, version: 9.0.1) software. Reversed phase chromatography was performed on SepaBean™ machine (Santai Technology Inc., China) equipped with C18-bonded Sepaflash® columns. The electrospray ionization (ESI) HRMS was tested on a Waters GCT Premier spectrometer. The UV-Vis absorption spectra of solid sample were obtained on a PerkinElmer Lambda 950 spectrophotometer.

Scheme 1. Synthetic route of P-BNI and P-HNI.



**Synthesis of 1-(6-bromonaphthalen-2-yl)-1H-imidazole (BrNI-2):** Imidazole (204 mg, 3.0 mmol) was dissolved in anhydrous DMF (6 mL) followed by adding NaH (240 mg, 6.0 mmol) in portions at 0 °C. After stirred for 1 h at 0 °C, the reaction was added 2-bromo-6-fluoronaphthalene (672 mg, 3.0 mmol). The mixture was heated to 100 °C and stirred overnight. Then the reaction was poured into cold water (100 mL) and extracted with EA (3 × 30 mL). The organic phase was combined and dried under reduced pressure. **BrNI-2** (342 ms, Yield = 41.8%) was obtained as off-white solid through flash column chromatography on silica gel with EA as eluent. <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>, δ) 8.28 (s, 1H), 8.11 (s, 1H), 8.04 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.70 (s, 1H), 7.63 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.20 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, δ) 135.8, 135.1, 133.3, 132.1, 131.0, 130.7, 130.1, 129.5, 129.3, 121.4, 120.6, 119.1, 118.4; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>10</sub>BrN<sub>2</sub><sup>+</sup>, 273.0027; found, 273.0028.

**Synthesis of 1-(naphthalen-2-yl)-1H-imidazole (HNI-2):** Imidazole (409 mg, 6 mmol), 2-bromonaphthalene (621 mg, 3 mmol), K<sub>2</sub>CO<sub>3</sub> (622 mg, 4.5 mmol), and a catalytic amount of anhydrous CuSO<sub>4</sub> (2.5 mg) were stirred at 180 °C for 14 h. After cool to room temperature, the mixture was suspended by water (50 mL) and extracted with dichloromethane (3 × 20 mL). The organic phase was combined and dried under reduced pressure. **HNI-2** (223 ms, Yield = 40.8%) was obtained as off-white solid through flash column chromatography on silica gel with EA as eluent. <sup>1</sup>H NMR (400 MHz, Methanol-*d*<sub>4</sub>, δ) 8.23 (s, 1H), 8.01 – 7.95 (m, 2H), 7.90 (t, *J* = 7.3 Hz, 2H), 7.69 – 7.61 (m, 2H), 7.58 – 7.46 (m, 2H), 7.18 (s, 1H); <sup>13</sup>C NMR (101 MHz, Methanol-*d*<sub>4</sub>, δ) 137.1, 135.8, 135.0, 133.7, 131.2, 130.3, 129.0, 128.9, 128.3, 127.6, 120.8, 119.8, 119.7; HRMS (ESI) *m/z*: [M + H]<sup>+</sup> calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub><sup>+</sup>, 195.0922; found, 195.0911.

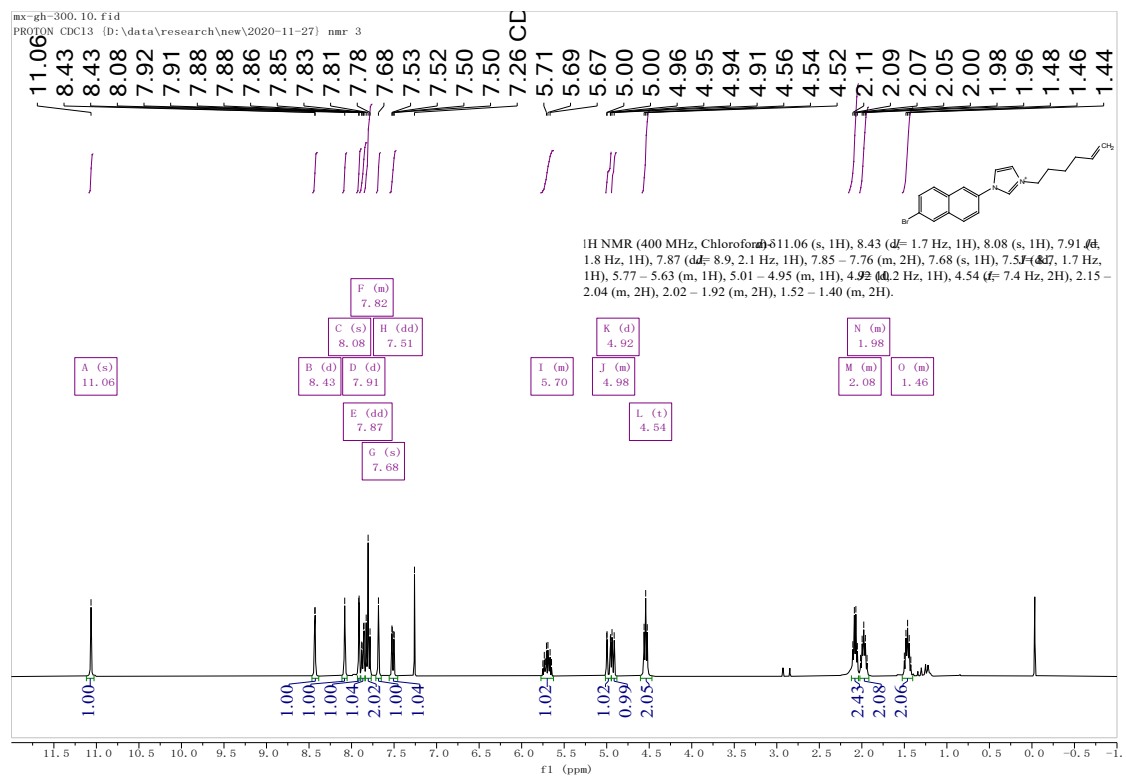
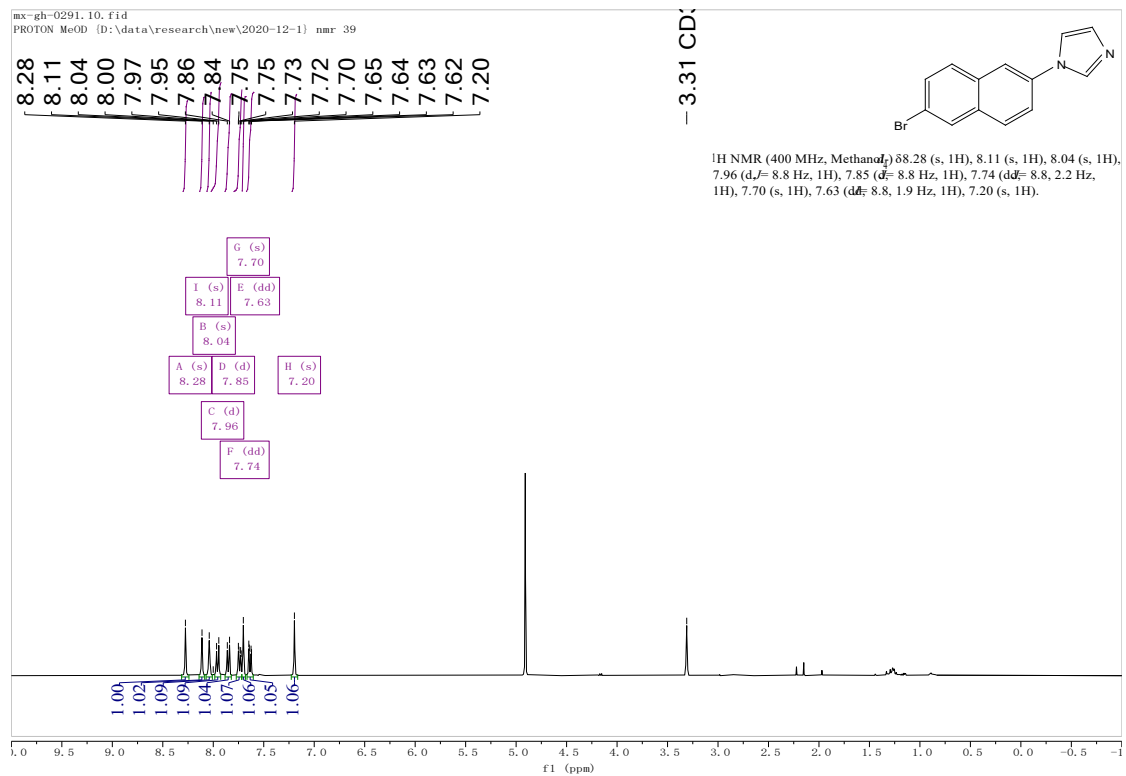
*Synthesis of 1-(6-bromonaphthalen-2-yl)-3-(hex-5-en-1-yl)-1H-imidazol-3-ium (BrNI-3) and 3-(hex-5-en-1-yl)-1-(naphthalen-2-yl)-1H-imidazol-3-ium (HNI-3):* The compound **BrNI-3** and **HNI-3** were synthesized by the same procedure using **BrNI-3** as a sample. BNI-2 (273 mg, 1.0 mmol) and 6-bromo-1-hexene (267  $\mu$ L, 2.0 mmol) were dissolved in anhydrous DMF (5 mL). The mixture was stirred at 100°C overnight under argon atmosphere. After cooled to room temperature, the reaction was poured into diethyl ether (50 mL) to precipitate oil droplet. After standing a while, the supernatant was carefully removed. The resulting liquid was purified by flash column chromatography on silica gel with DCM/MeOH = 30/1 as eluent to obtain **BrNI-3** as a white solid (305 mg, Yield = 69.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 11.06 (s, 1H), 8.43 (d,  $J$  = 1.7 Hz, 1H), 8.08 (s, 1H), 7.91 (d,  $J$  = 1.8 Hz, 1H), 7.87 (dd,  $J$  = 8.9, 2.1 Hz, 1H), 7.85 – 7.76 (m, 2H), 7.68 (s, 1H), 7.51 (dd,  $J$  = 8.7, 1.7 Hz, 1H), 5.77 – 5.63 (m, 1H), 5.01 – 4.95 (m, 1H), 4.92 (d,  $J$  = 10.2 Hz, 1H), 4.54 (t,  $J$  = 7.4 Hz, 2H), 2.15 – 2.04 (m, 2H), 2.02 – 1.92 (m, 2H), 1.52 – 1.40 (m, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ) 137.6, 136.0, 135.9, 134.0, 131.8, 131.5, 131.3, 130.2, 130.0, 123.2, 122.1, 121.0, 120.7, 119.9, 115.7, 50.4, 33.0, 29.7, 25.4; HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>20</sub>BrN<sub>2</sub><sup>+</sup>, 355.0804; found, 355.0796.

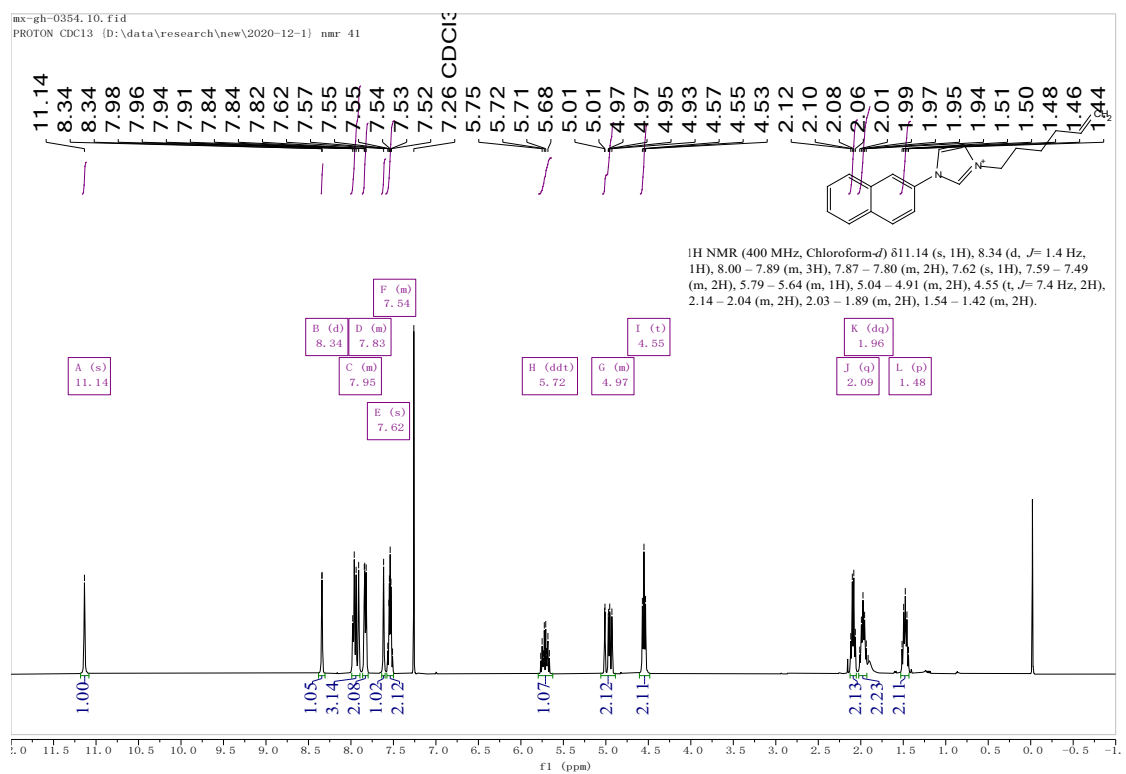
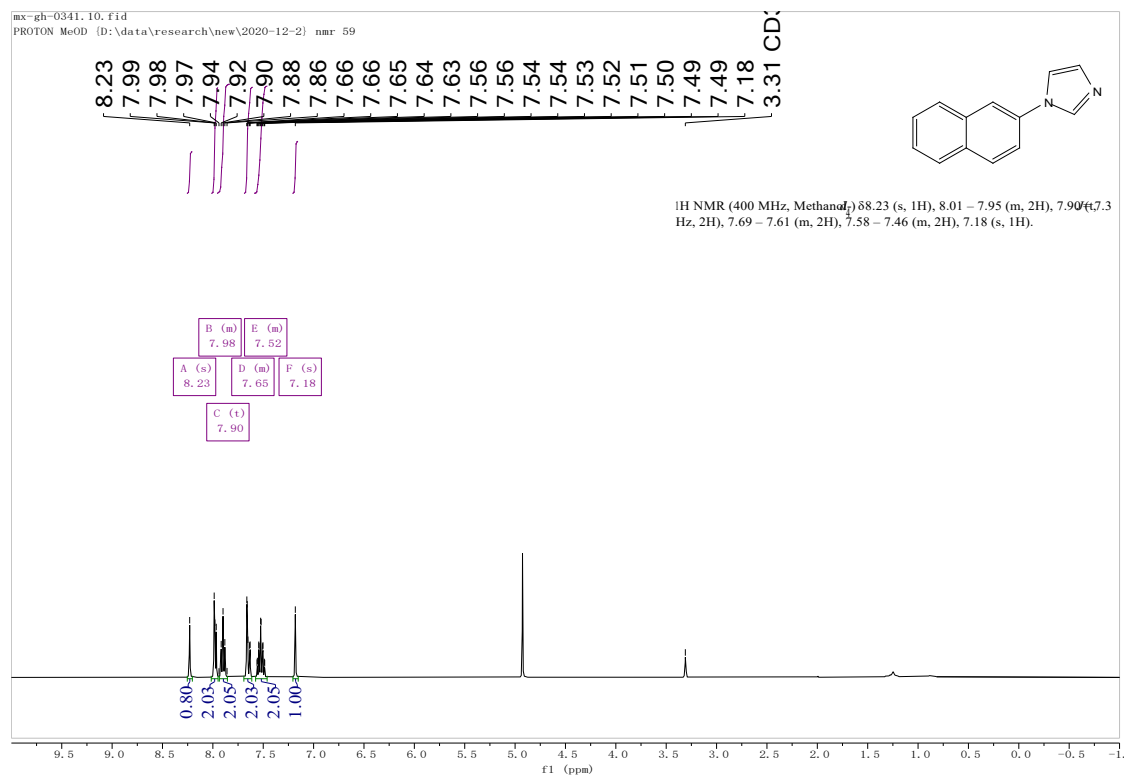
**HNI-3** was achieved following the similar procedure at 56.4% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ) 11.14 (s, 1H), 8.34 (d,  $J$  = 1.4 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.87 – 7.80 (m, 2H), 7.62 (s, 1H), 7.59 – 7.49 (m, 2H), 5.79 – 5.64 (m, 1H), 5.04 – 4.91 (m, 2H), 4.55 (t,  $J$  = 7.4 Hz, 2H), 2.14 – 2.04 (m, 2H), 2.03 – 1.89 (m, 2H), 1.54 – 1.42 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>,  $\delta$ ) 137.6, 136.0, 135.9, 133.2, 133.1, 131.6, 131.0, 128.6, 128.0, 123.1, 121.0, 120.6, 119.0, 115.6, 50.4, 33.0, 29.8, 25.4; HRMS (ESI)  $m/z$ : [M + H]<sup>+</sup> calcd for C<sub>19</sub>H<sub>21</sub>N<sub>2</sub><sup>+</sup>, 277.1699; found, 277.1709.

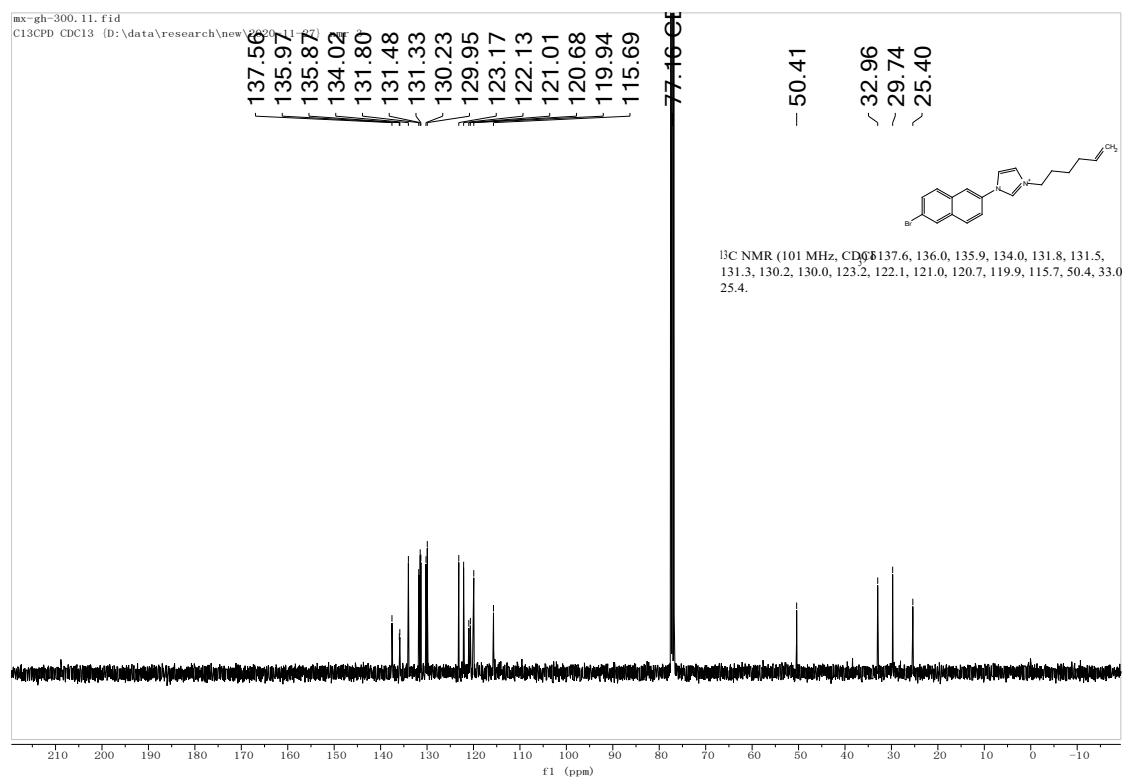
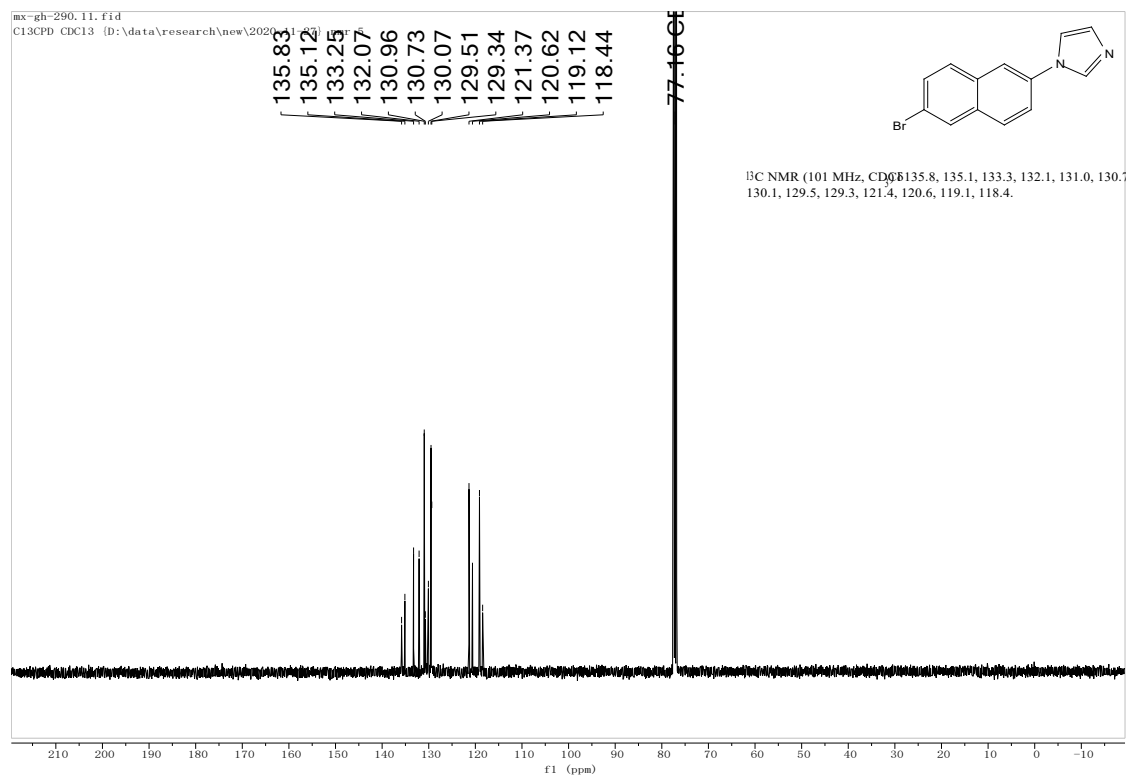
*Synthesis of P-BrNI:* Compound **BrNI-3** (44 mg, 0.1 mmol), acrylamide (356 mg, 5.0 mmol) and 2,2'-azobis(2-methylpropionitrile) (AIBN, 14 mg) was heat at 70°C under a nitrogen atmosphere in DMF (2 mL) for 12 h. After cooling to room temperature, the reaction was poured into MeOH (20 mL) to participate the polymer solid. The participate was filter off and washed with MeOH and dried to yield a white solid. GPC (H<sub>2</sub>O): Mn (PDI) = 3752 Da (3.313).

*Synthesis of P-HNI:* The **P-HNI** was achieved as a white solid follow a similar method as **P-BrNI**. GPC (H<sub>2</sub>O): Mn (PDI) = 4296 Da (3.143).

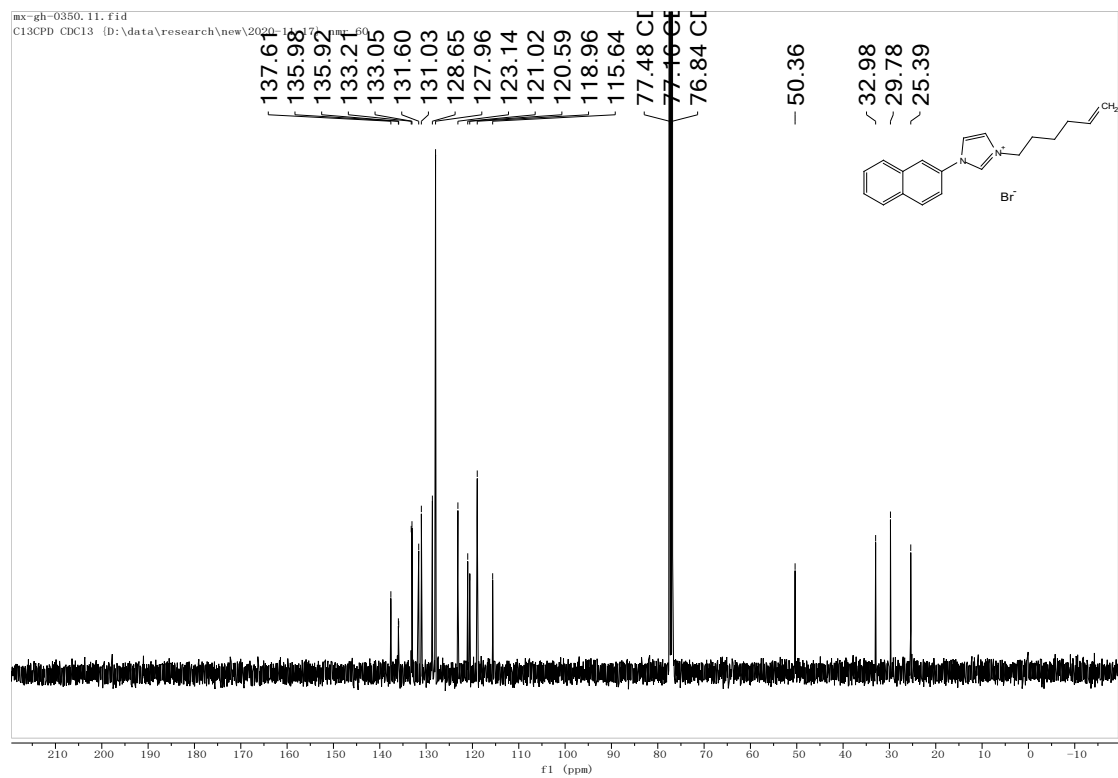
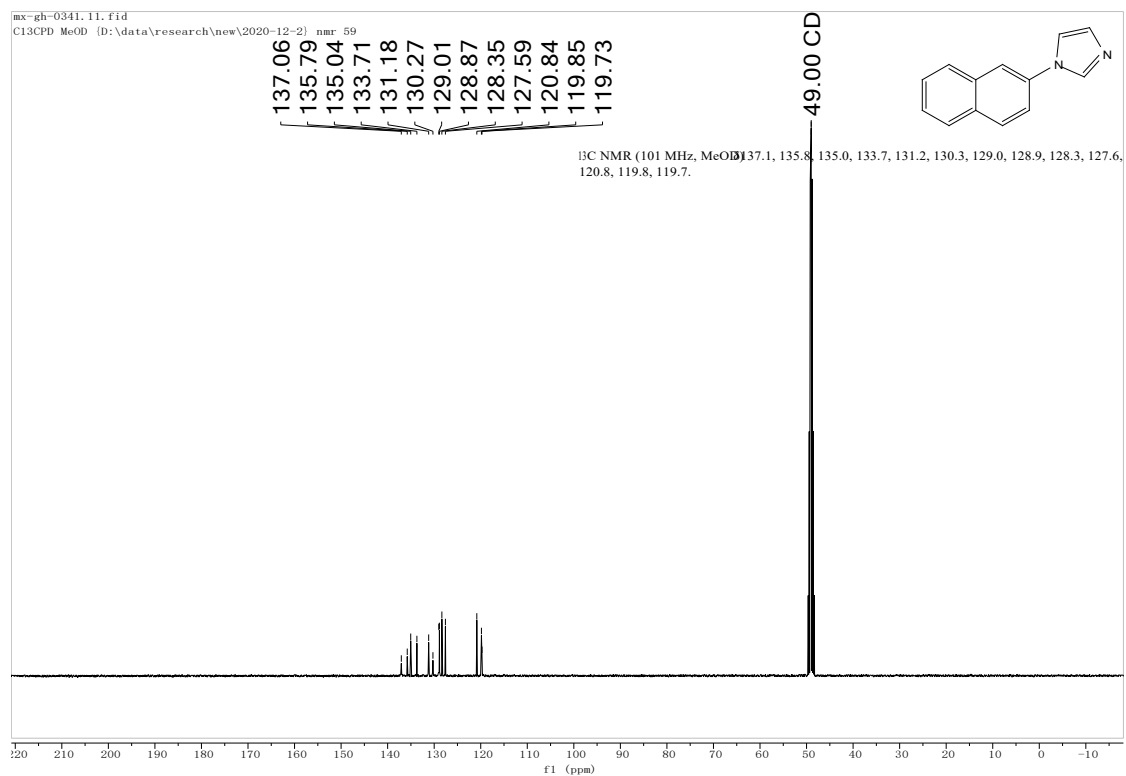
# <sup>1</sup>H, <sup>13</sup>C NMR and Mass Spectra











Elemental Composition Report

Single Mass Analysis

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Element prediction: Off

Number of isotope peaks used for i-FIT = 3

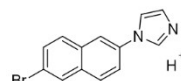
Monoisotopic Mass, Even Electron Ions

6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

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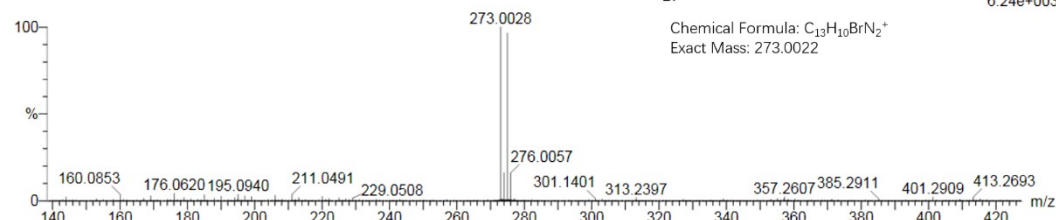
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X-MA  
MX-GH-029 17 (0.175) Cm (15:18)



Chemical Formula: C<sub>13</sub>H<sub>10</sub>BrN<sub>2</sub><sup>+</sup>  
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6.24e+003



Minimum: -1.5  
Maximum: 5.0 10.0 50.0

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HRMS(EI+) spectra of BrNI-2.

Elemental Composition Report

Single Mass Analysis

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Number of isotope peaks used for i-FIT = 3

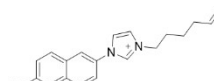
Monoisotopic Mass, Even Electron Ions

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Elements Used:

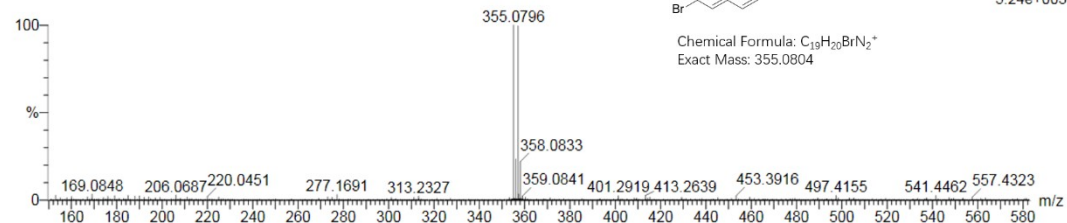
C: 0-19 H: 0-20 N: 0-2 Br: 0-1

X-MA  
MX-GH-030 89 (1.005) Cm (86:89)



Chemical Formula: C<sub>19</sub>H<sub>20</sub>BrN<sub>2</sub><sup>+</sup>  
Exact Mass: 355.0804

1: TOF MS ES+  
5.24e+003



Minimum: -1.5  
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
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HRMS(ESI+) spectra of BrNI-3.

Elemental Composition Report

Single Mass Analysis

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Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

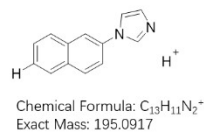
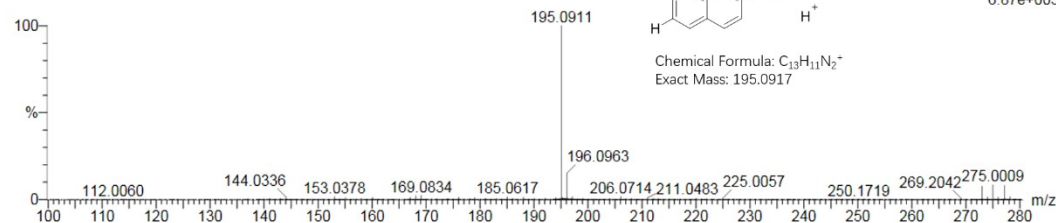
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Elements Used:

C: 0-19 H: 0-20 N: 0-2 Br: 0-1

X-MA

MX-GH-034- 54 (0.610) Cm (53.55)



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6.87e+03

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Maximum: 5.0 10.0 50.0

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195.0911	195.0922	-1.1	-5.6	9.5	311.2	0.0	C13 H11 N2

HRMS(ESI+) spectra of HNI-2.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

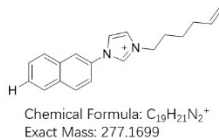
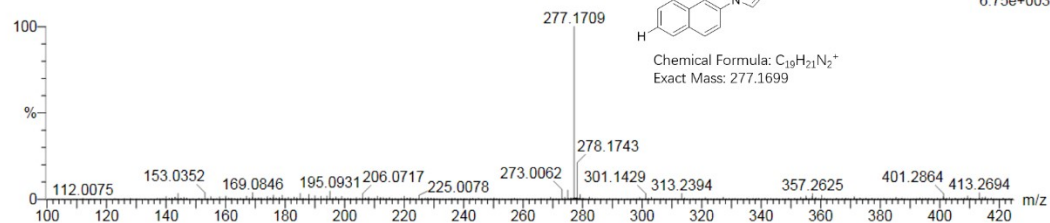
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Elements Used:

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X-MA

MX-GH-035 13 (0.129) Cm (12.18)



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6.75e+03

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Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
277.1709	277.1705	0.4	1.4	10.5	311.0	0.0	C19 H21 N2

HRMS(ESI+) spectra of HNI-3.