Supporting Information

A Polymer Rigidity Probe Based on Ultralong Organic Room Temperature Phosphorescence of A New Skeleton Benzo[4,5]imidazo[1,2-a]pyridine

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1. Materials and General Methods

All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

^{1}H NMR was recorded on the 400 MHz (Bruker ARX400) and ^{13}C NMR spectra were recorded on the Bruker 101 MHz spectrometer at room temperature with $CDCl_3$ and DMSO-d_6 as the solvents and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HR-MS) were acquired on a Waters Xevo G2 Qt of mass spectrometer. Transient and delayed photoluminescence spectra were performed on the Hitachi F-4600 or Edinburgh Instruments FLS1000 fluorescence spectrophotometer. Luminescence lifetime were acquired on the Edinburgh Instruments FLS1000 fluorescence spectrophotometer or Deltaflex Fluorescence Lifetime Instrument (λ_{ex}=365 nm). The lifetimes are fitted with the software that comes with the Edinburgh Instruments FLS1000 instrument to give the appropriate order of fit. The program uses a double exponential function fit. The lifetime fitting equation is $\tau=(B_1\tau 2\ 1+B_2\tau 2\ 2)/(B_1\tau_1+B_2\tau_2)$.

TD-DFT calculations were conducted on Gaussian 09 program with a method similar to previous literature.[1] Ground state (S_0) geometries of BNPy, BNPy-1and BNPy-2 monomer were directly optimized in vacuum condition. On the basis of this, exciton energies in singlet (S_n) and triplet states (T_n) were estimated through a combination of TDDFT and B3LYP at the 6-311+G (p, d) level. We have to emphasize that the computed singlet and triplet levels in this article refer to emission (excited state optimization). Kohn-Sham frontier orbital analysis was subsequently performed based on the results of theoretical calculation to elucidate the mechanisms of possible singlet-triplet intersystem crossings, in which the channels from S_1 to T_n were believed to share part of the same transition orbital compositions. Herein, energy levels of the possible T_n states were considered to lie within the range of ES_1±0.3 eV.[2] Spin-orbital couplings (SOC) matrix elements were conducted through the Beijing Density Functional (BDF) program based on optimized or single crystal structures at the B3LYP/6-311G* level.

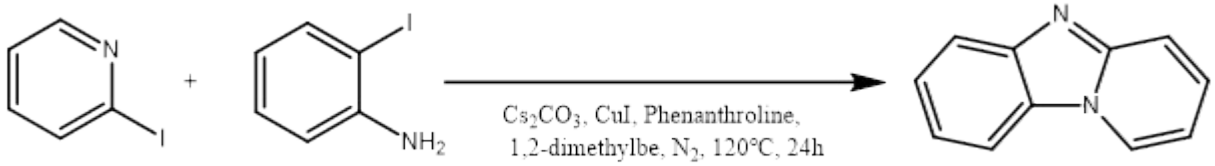
2. Syntheses and characterizations

BNPy: 2-iodoaniline (2.5 mmol, 548.0 mg), Cs_2CO_3 (7.5 mmol, 2444.0 mg), CuI (0.5 mmol, 95.0 mg), 1,10-phenanthroline (1.0 mmol, 180.0 mg) were added to a 100 mL Shrek bottle. Fill the Shrek bottle with nitrogen, and then add 2-iodopyridine (3.0 mmol, 615.0 mg) and xylene (5 ml, AR grade). The mixed solution was refluxed at 120 ℃ for 48 h in nitrogen atmosphere. After the reaction was over, the resultant mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by silica gel column using petroleum ether and ethyl acetate as the eluent to obtain pure product as white powder. Yield: 82%.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.50 (dt, J = 6.9, 1.2 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.74 (dt, J = 9.3, 1.2 Hz, 1H), 7.57 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.51 – 7.37 (m, 2H), 6.89 (td, J = 6.7, 1.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 148.42, 144.36, 129.41, 125.72, 121.07, 119.90, 118.00, 110.42, 110.35.

HR-ESI-MS Calcd. For $C_{11}H_8N_2$ $[M+H]^+$: 169.0766. Found: 169.0813.



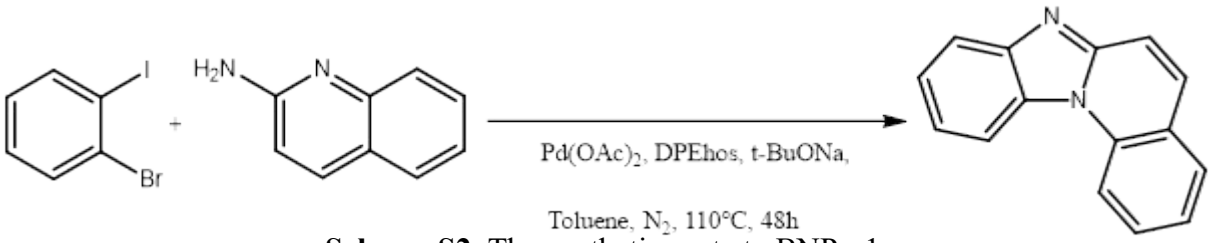
Scheme S1. The synthetic route to BNPy.

BNPy-1: Quinolin-2-amine (2.4 mmol, 345.6 mg), Sodium tert-butoxide (4.0 mmol, 384.4 mg), $Pd(OAc)_2$ (0.06 mmol, 13.5 mg), (oxybis(2,1-phenylene))bis(diphenylphosphine) (0.06 mmol, 32.3 mg) were added to a 100 mL shrek bottle. Fill the Shrek bottle with nitrogen, and then add 1-bromo-2-iodobenzene (2.0 mmol, 564.0 mg) and toluene (8 ml, AR grade). The mixed solution was refluxed at 110 ℃ for 48 h in nitrogen atmosphere. After the reaction was over, the resultant mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by silica gel column using petroleum ether and ethyl acetate as the eluent to obtain pure product as yellow powder. Yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.54 (d, J = 8.5 Hz, 1H), 8.40 – 8.33 (m, 1H), 8.05 – 7.98 (m, 1H), 7.81 (dd, J = 7.8, 1.6 Hz, 1H), 7.72 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.67 (d, J = 9.5 Hz, 1H), 7.61 (d, J = 9.4 Hz, 1H), 7.53 (td, J = 8.1, 7.7, 1.2 Hz, 1H), 7.47 (qd, J = 8.1, 1.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 148.26, 144.74, 135.72, 131.23, 130.91, 129.69, 129.56, 124.46, 124.20, 123.46, 122.69, 120.53, 117.79, 115.27, 114.01.

HR-ESI-MS Calcd. For $C_{15}H_{10}N_2$ $[M+H]^+$: 219.0922. Found: 219.0916.



Scheme S2. The synthetic route to BNPy-1.

N-(naphthalen-2-yl)pyridin-2-amine: Naphthalen-2-ylboronic acid (2.0 mmol, 344.0 mg), Pyridin-2-amine (2.4 mmol, 225.6 mg), $Cu(OAc)_2$ (0.2 mmol, 180.0 mg) and Dichloromethane (5 ml, AR grade) were added to a 50 mL round bottom flask. The mixed solution was reacted at room temperature for 10 h in air conditions. After the reaction was over, the crude product was purified by silica gel column using petroleum ether and ethyl acetate as the eluent to obtain pure product as light brown powder. Yield: 78%.

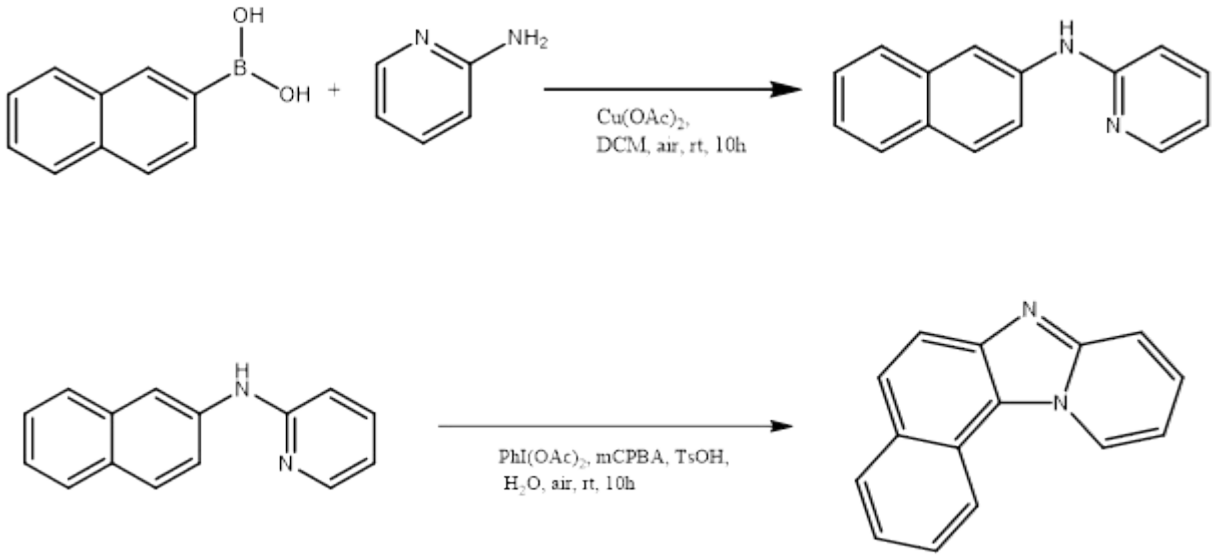
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.28 (d, J= 4.0 Hz, 1H), 7.84 - 7.74 (m, 4H), 7.55 - 7.51 (m, 1H), 7.47 - 7.36 (m, 3H), 7.00 (d, J= 8.4 Hz, 1H), 6.78 (dd, J= 6.8 Hz, J= 5.2 Hz, 1H).

BNPy-2: Add $PhI(OAc)_2$ (0.2 mmol, 64.4 mg) and mCPBA (1.0 mmol, 172.57 mg) and p-toluenesulphonic acid monohydrate (2.0 mmol, 380.4 mg) to a solution of N-aryl-2-aminopyridine (1.0 mmol, 220.0 mg) in water 4 mL. The mixed solution was reacted at room temperature for 6 h in air conditions. After the reaction was over, the crude product was purified by silica gel column using petroleum ether and ethyl acetate as the eluent to obtain pure product as yellow powder. Yield: 10%.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.15 (d, J = 6.9 Hz, 1H), 8.51 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.94-7.89 (m, 2H), 7.75 (dd, J = 7.6, 7.4 Hz, 1H), 7.57 (dd, J = 7.5, 7.4, 1H), 7.48 (dd, J= 8.4, 7.2, 1H), 7.07 (dd, J= 6.7, 6.7, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 147.70, 143.23, 130.27, 129.93, 127.61, 126.96, 126.87, 126.78, 123.92, 122.92, 121.53, 120.12, 119.08, 118.24, 111.78.

HR-ESI-MS Calcd. For $C_{15}H_{10}N_2$ $[M+H]^+$: 219.0922. Found: 219.0948.



Scheme S3. The synthetic route to BNPy-2.

Preparation of doped PMMA film: Dissolve chromophore (2 mg) and polymethyl methacrylate (200 mg) in dichloromethane (2 ml); ultrasonicate the mixture for about 30 min to obtain a homogeneous mixed solution; and finally pour it into a petri dish, and wait for the solvent to evaporate naturally to obtain the colourless and transparent PMMA film.

Preparation of doped PVA film: The chromophore (0.2 mg) was dissolved in dimethyl sulfoxide (20 µl) . 4 ml aqueous PVA (200 mg) solution was added and the mixture was kept being stirred for 30 minutes at 100 degrees Celsius. The resulting solution was then sonicated at 60 degrees Celsius for 1 hour to complete the doping process. Transparent films were made by dropping the solution into the prepared petri dishes and kept at 70 degree Celsius for 8 hours.

Preparation of copolimerized PAA-PMA film: MA, AA, BNPy-1/BNPy-2 (0.1 wt%) and photoinitiator (ethoxy benzoin, 1.0 wt%) were accurately weighed and thoroughly mixed, and the mixed solution was injected into a closed transparent mould with a syringe, and then irradiated with a 365 nm UV lamp (5 W) for about 3 minutes to obtain a transparent copolymer film. Excitingly, phosphorescence intensity and phosphorescence lifetime of BNPy-1/BNPy-2 varied significantly along with the increasing AA weight ratio.

3. NMR spectra and HR-MS of the mentioned molecules

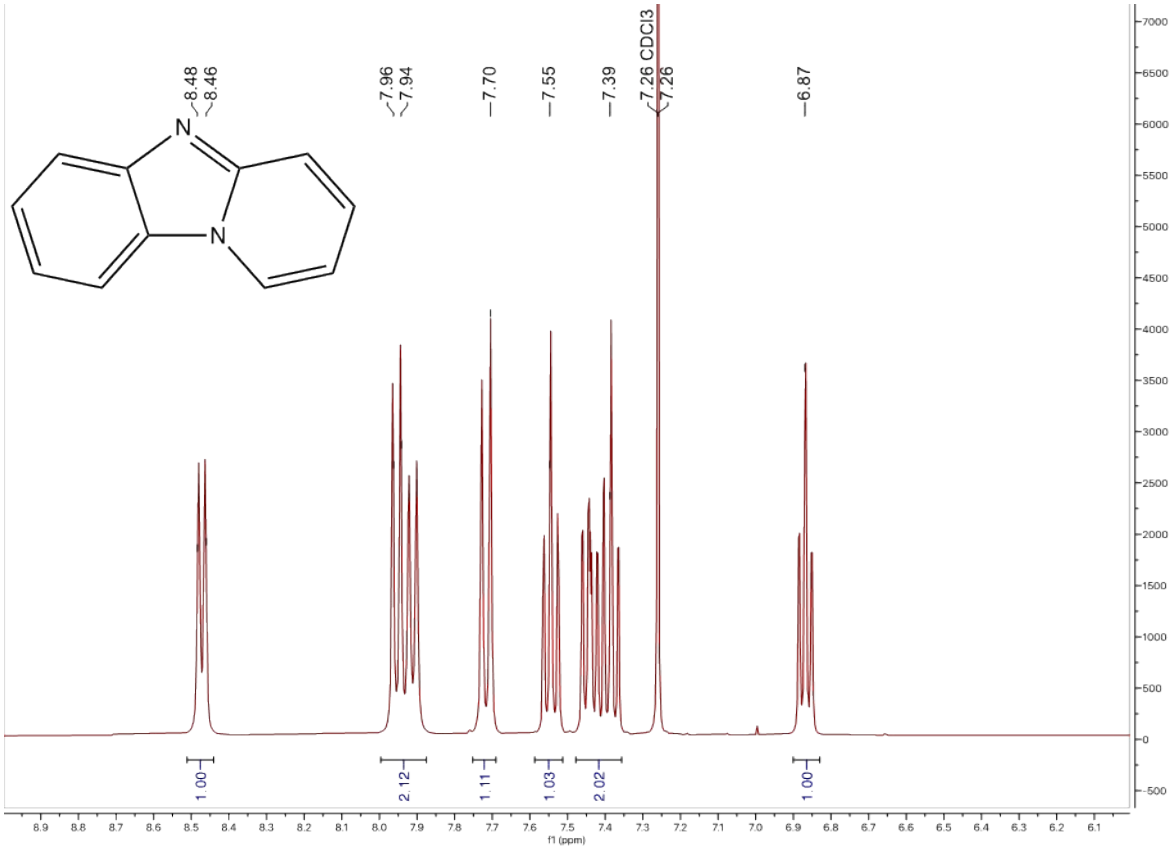


Figure S1. ^{1}H NMR spectrum of BNPy in Chloroform-*d*.

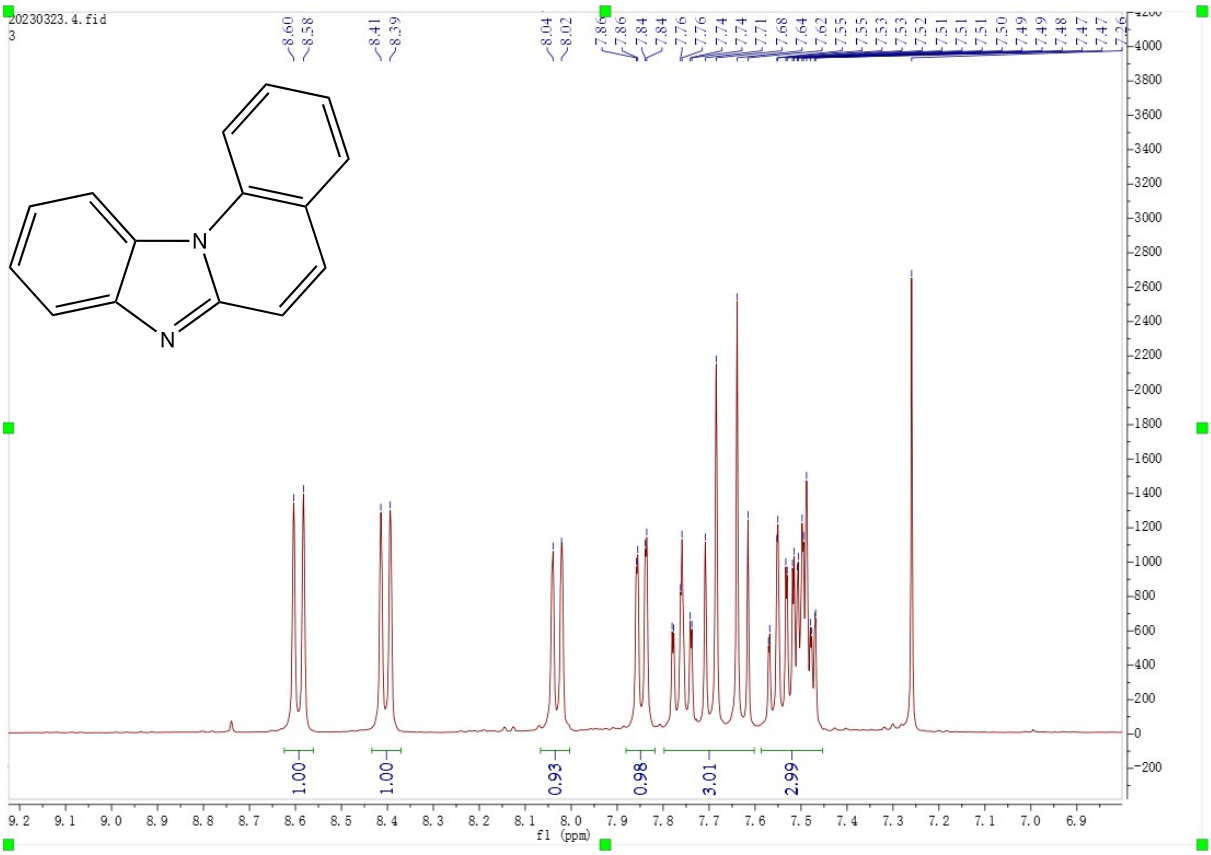


Figure S2. ^{1}H NMR spectrum of BNPy-1 in Chloroform-*d*.

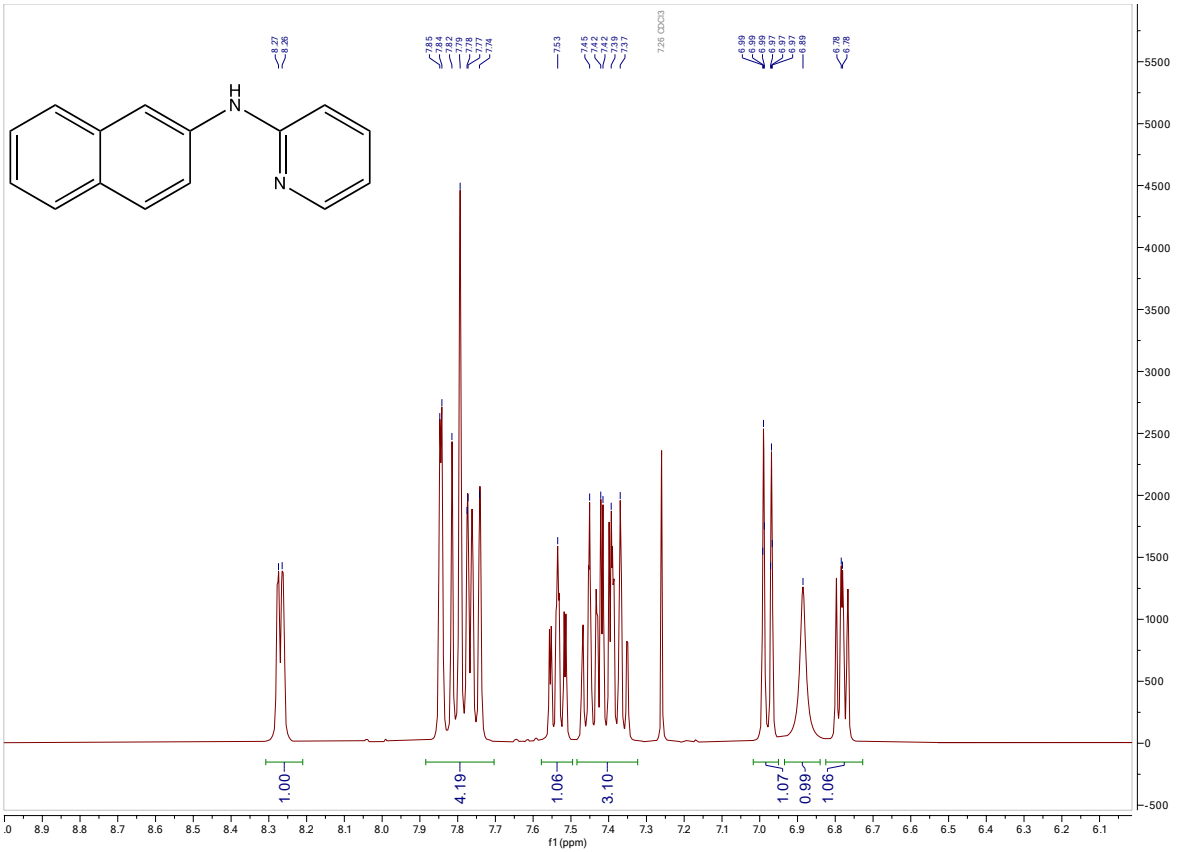


Figure S3. ^{1}H NMR spectrum of N-(naphthalen-2-yl)pyridin-2-amine in Chloroform-*d*.

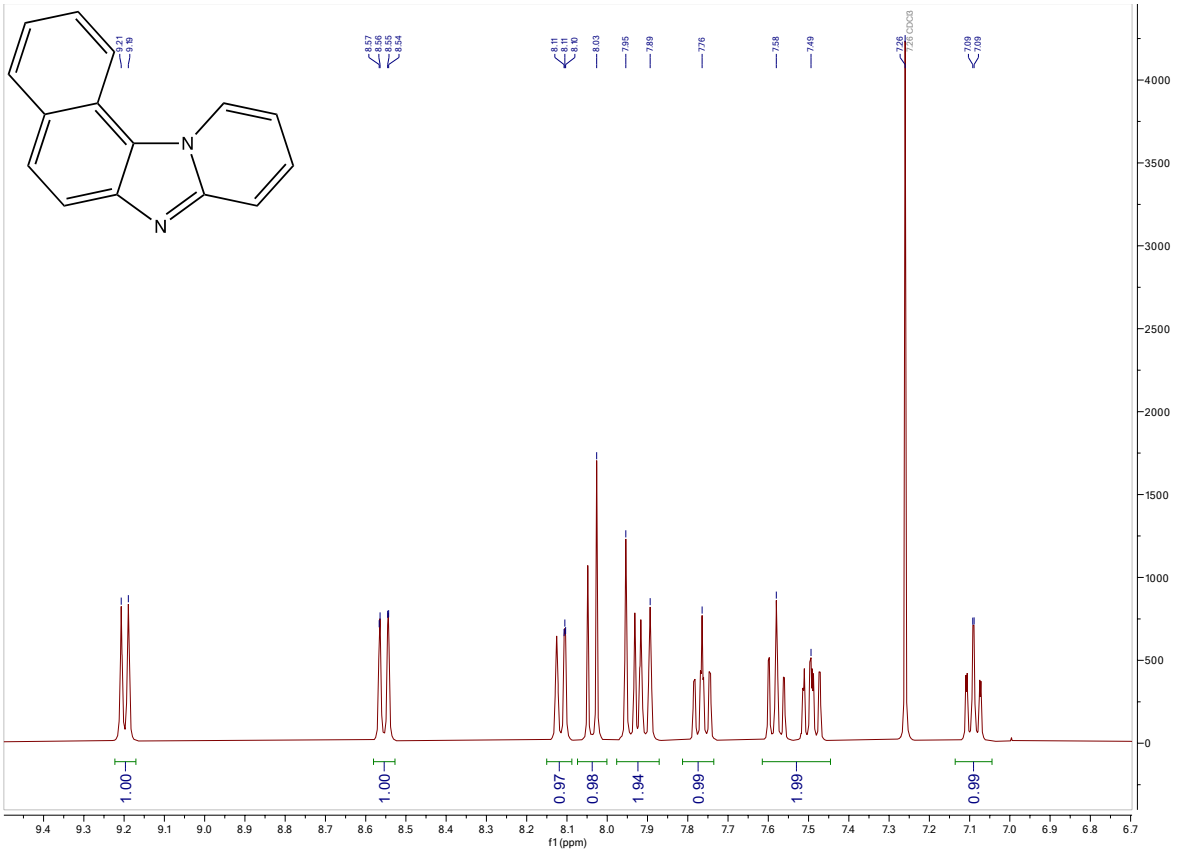


Figure S4. ^{1}H NMR spectrum of BNPy-2 in Chloroform-*d*.

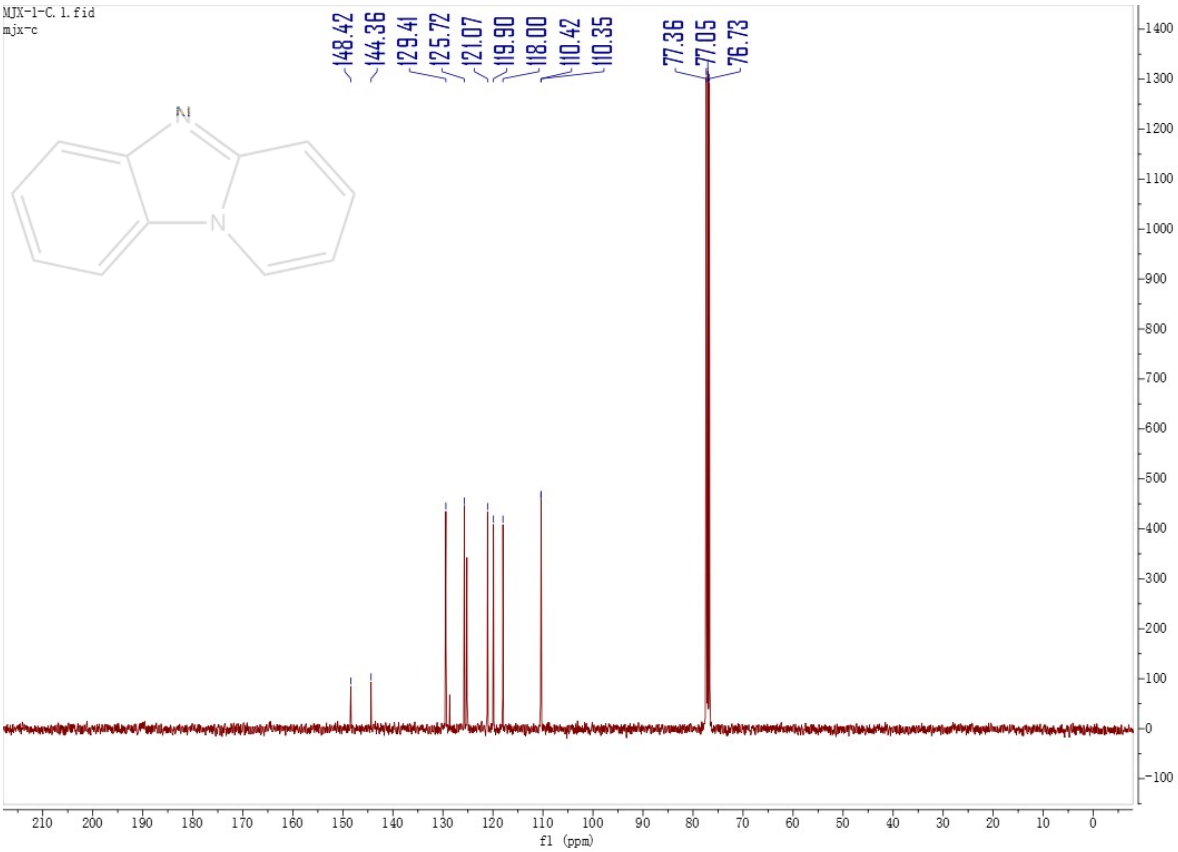


Figure S5. ^{13}C NMR spectrum of BNPy in $CDCl_3$.

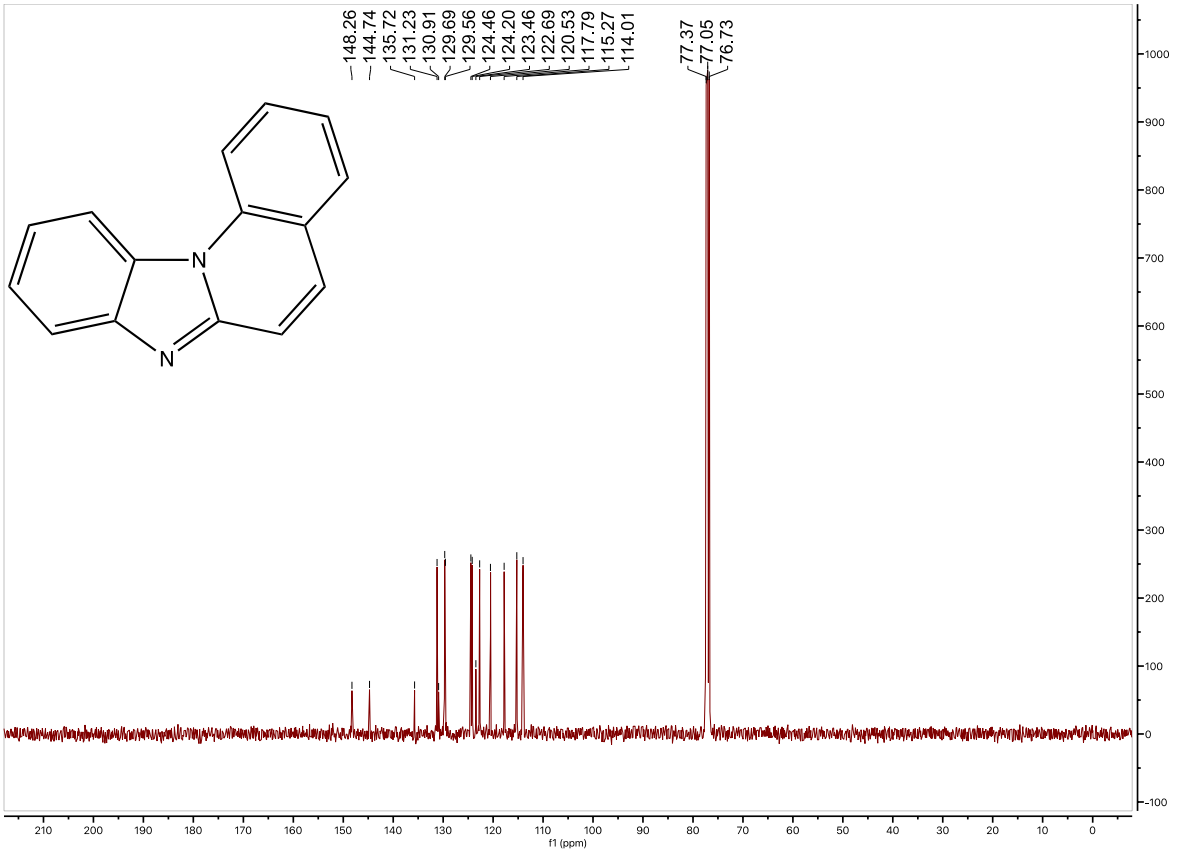


Figure S6. ^{13}C NMR spectrum of BNPy-1 in $CDCl_3$.

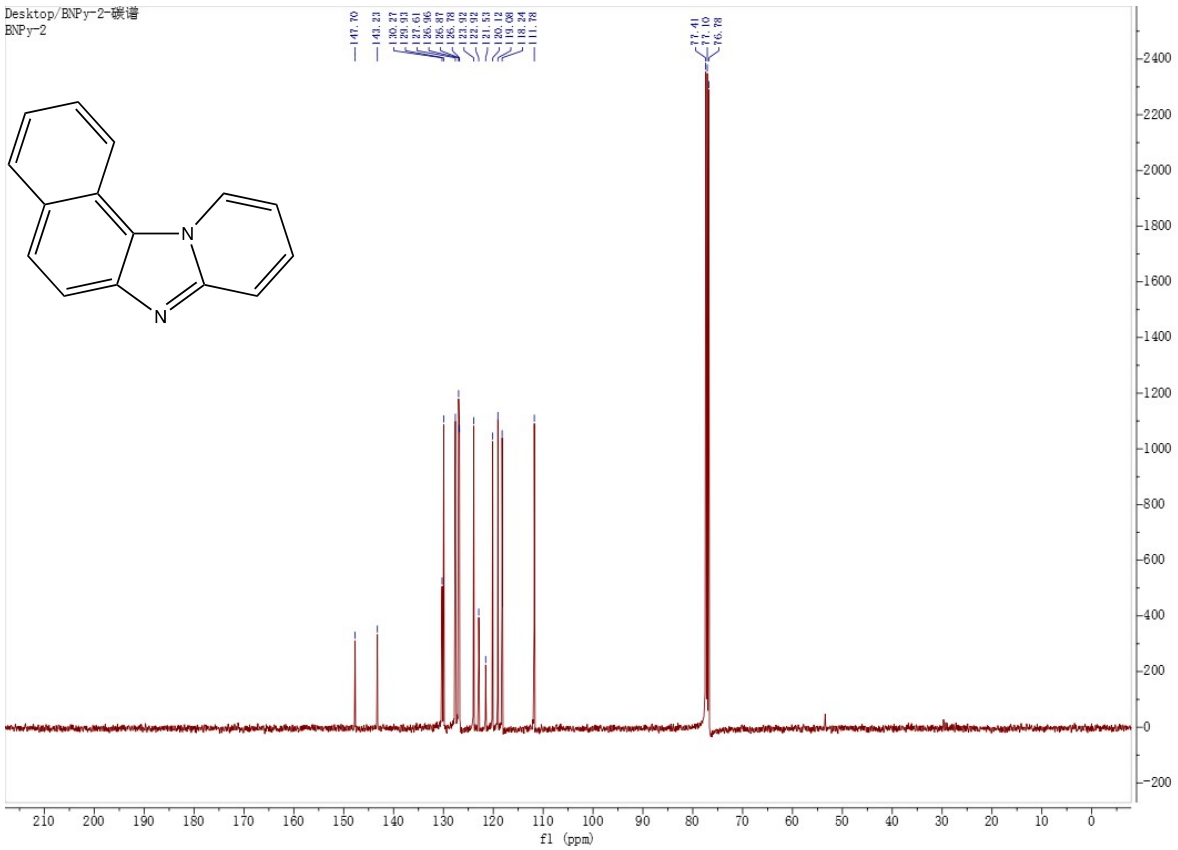


Figure S7. ^{13}C NMR spectrum of BNPy-2 in $CDCl_3$.

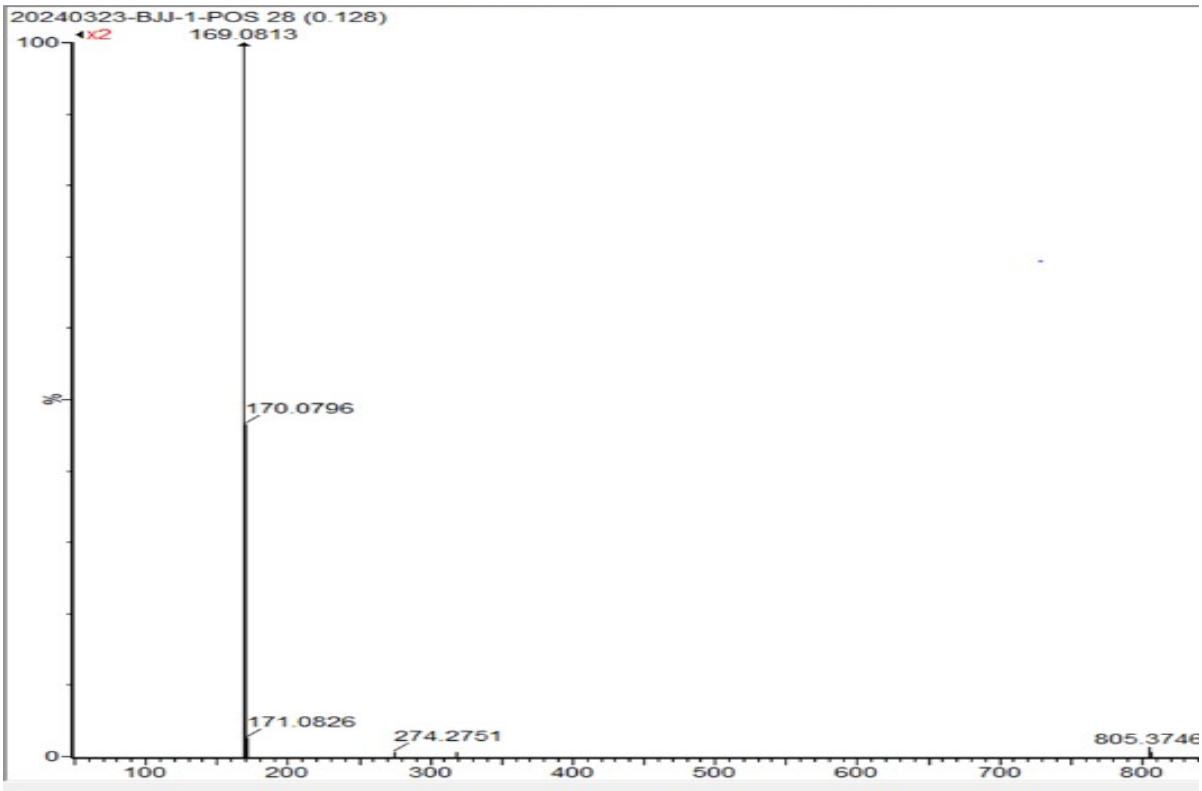


Figure S8. HR-MS spectrum of BNPy.

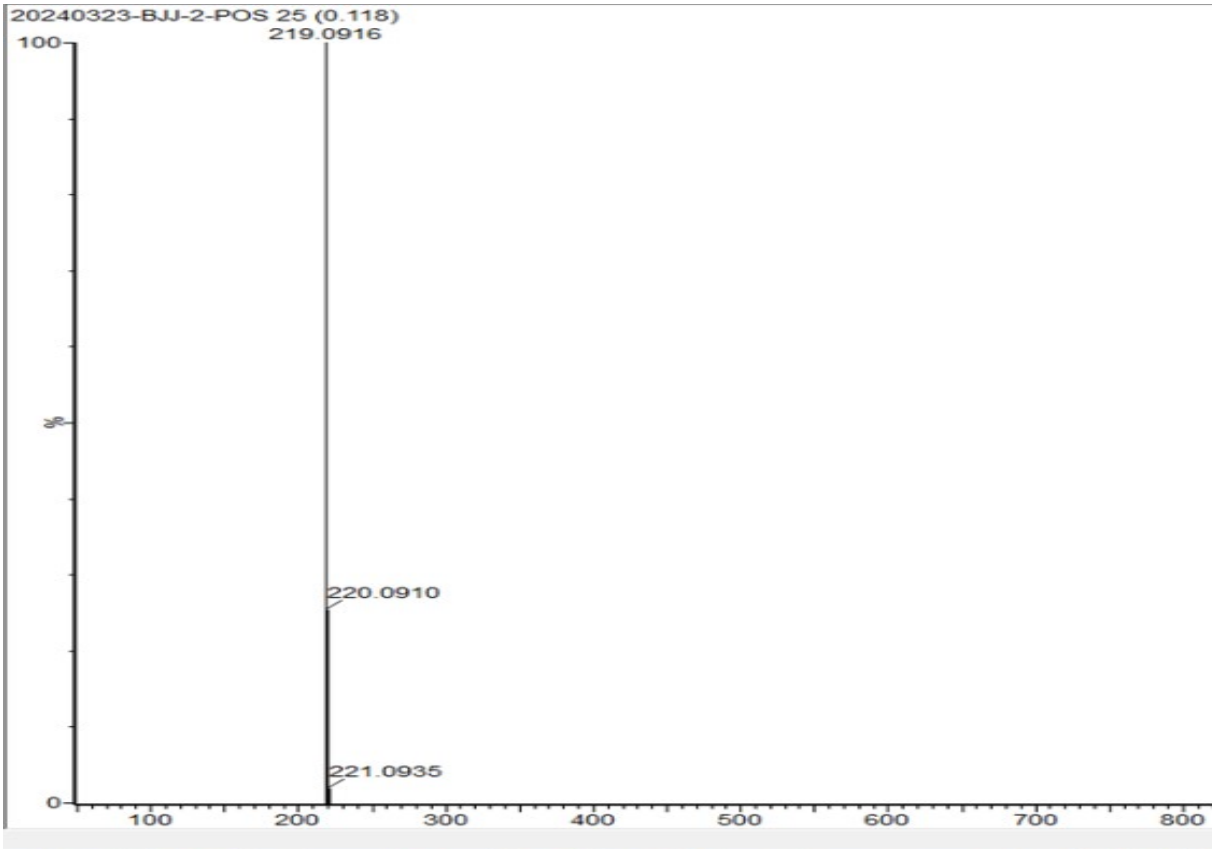


Figure S9. HR-MS spectrum of BNPy-1.

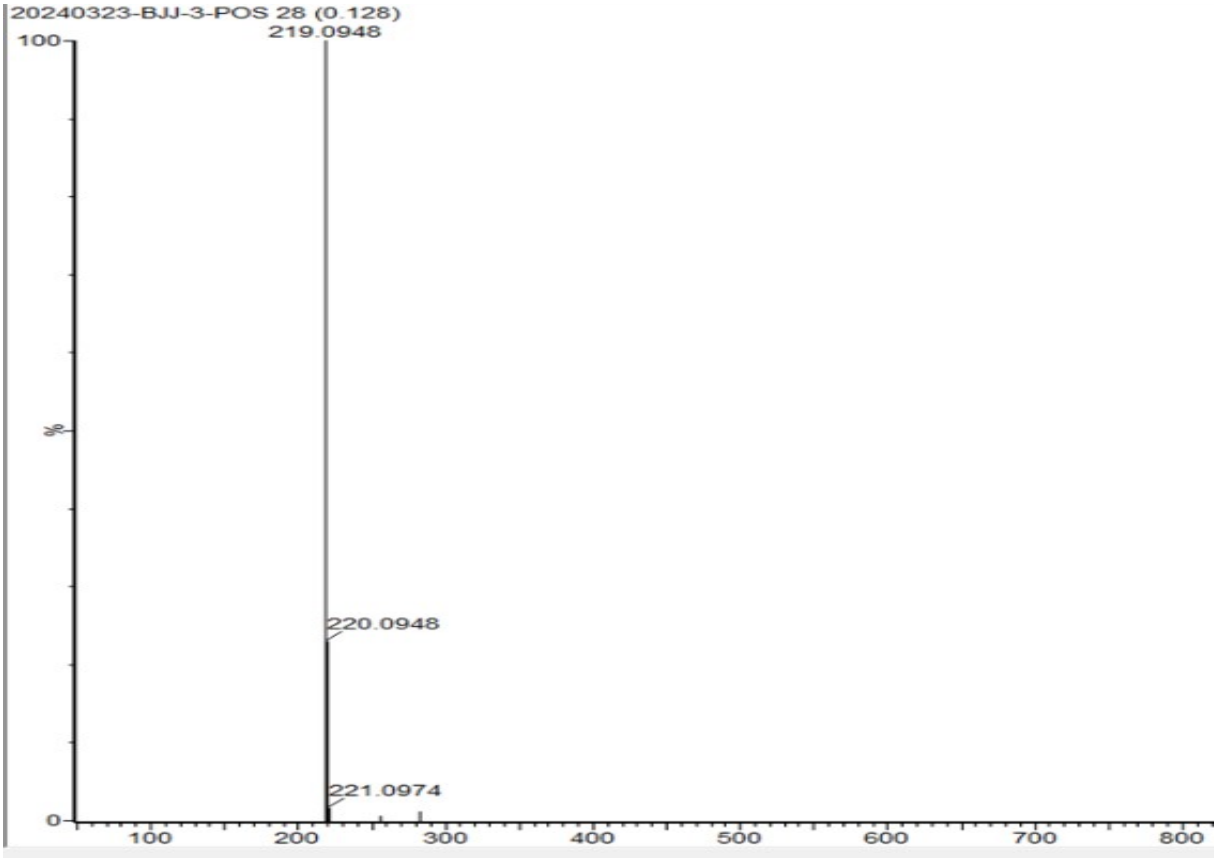


Figure S10. HR-MS spectrum of BNPy-2.

4. Photophysical properties in solution

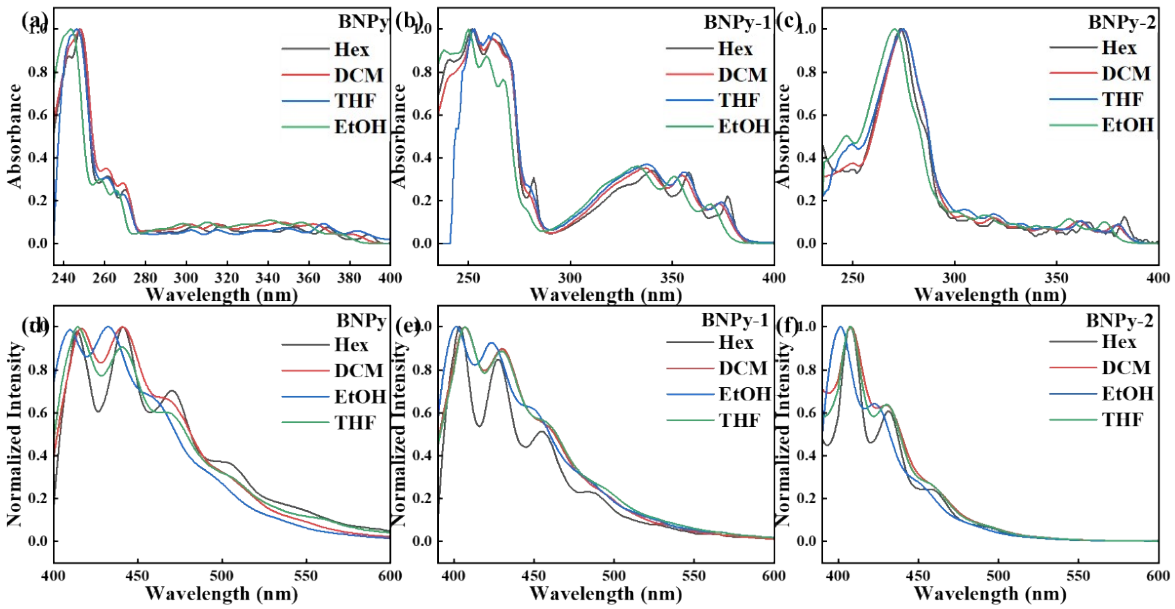


Figure S11. Absorption spectra of (a) BNPy, (b) BNPy-1 and (c) BNPy-2 in hexane, DCM, EtOH and THF solution; PL spectra of (d) BNPy, (e) BNPy-1 and (f) BNPy-2 in hexane, DCM, EtOH and THF solution.

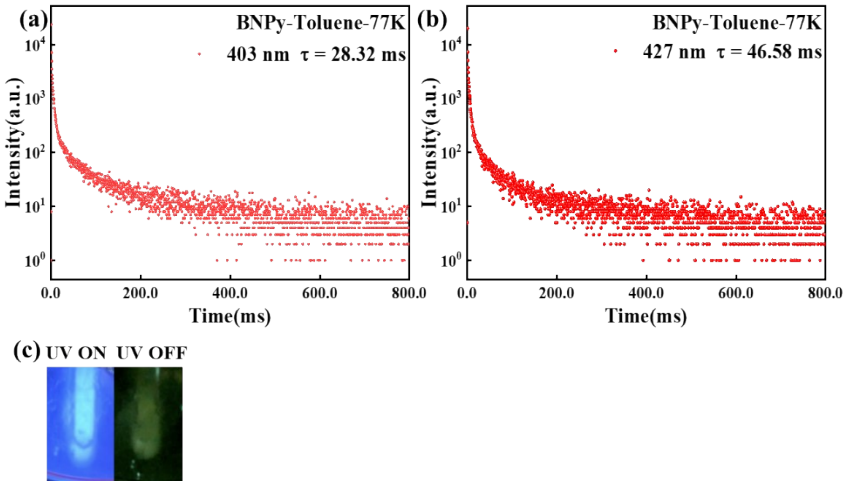


Figure S12. (a-b) Decay spectra of the BNPy toluene solution at 77 K; (c) phosphorescent images of the BNPy toluene solution in liquid nitrogen. (λ_{ex} = 365 nm).

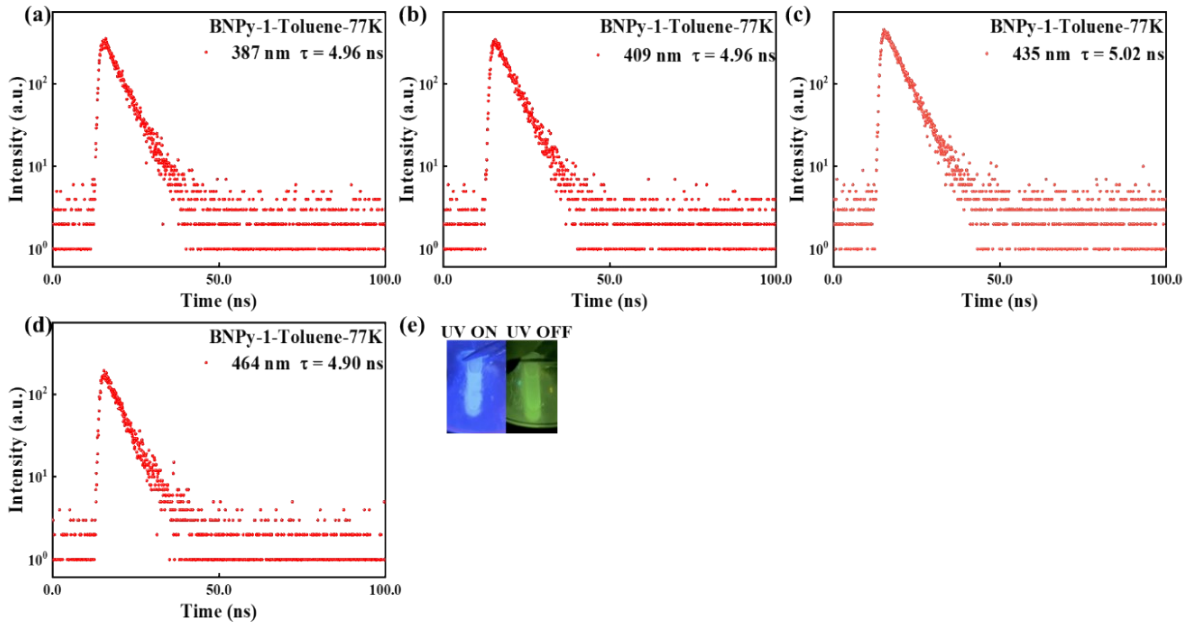


Figure S13. (a-d) Decay spectra of the BNPy-1 toluene solution at 77 K; (e) phosphorescent images of the BNPy-1 toluene solution in liquid nitrogen. (λ_{ex} = 365 nm).

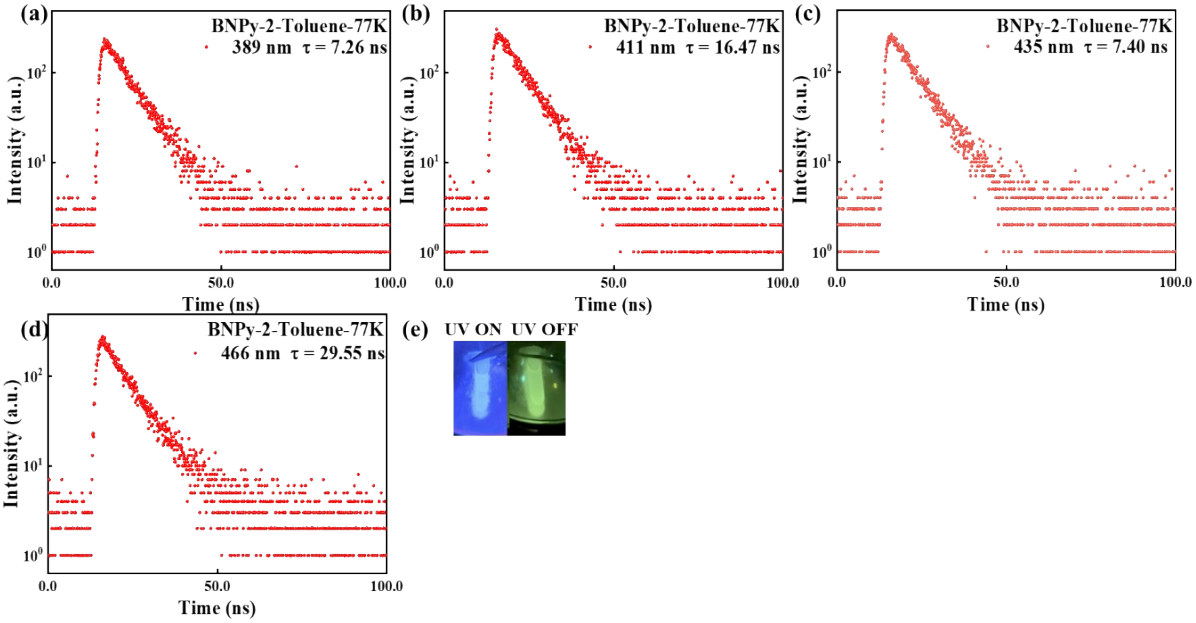


Figure S14. (a-d) Decay spectra of the BNPy-2 toluene solution at 77 K; (e) phosphorescent images of the BNPy-2 toluene solution in liquid nitrogen. (λ_{ex} = 365 nm).

5. Photophysical properties in the solid state.

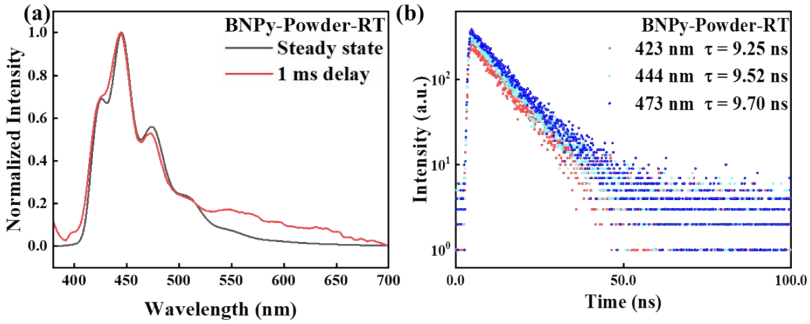


Figure S15. (a) Steady-state and 1 ms-delayed PL spectra of BNPy powder at RT; and (b) decay spectra at ambient condition.

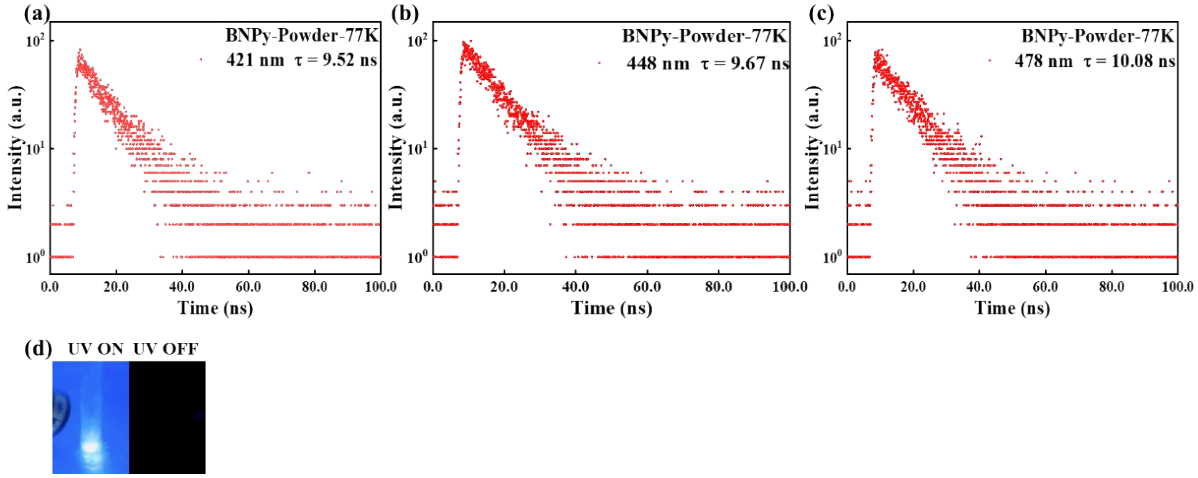


Figure S16. (a-c) Decay spectra of BNPy powder at 77K; (d) phosphorescent images of the BNPy powder in liquid nitrogen. (λ_{ex} = 365 nm).

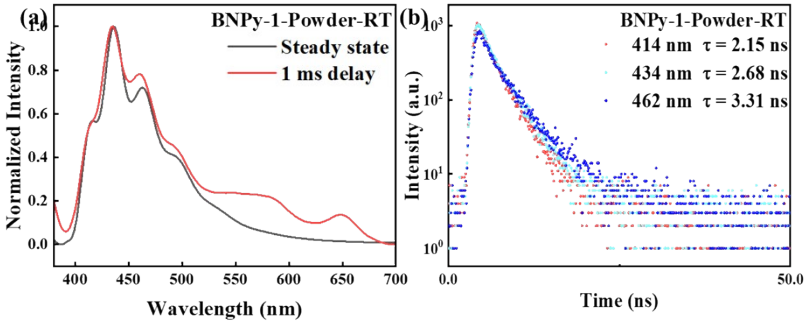


Figure S17. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1 powder at RT; and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

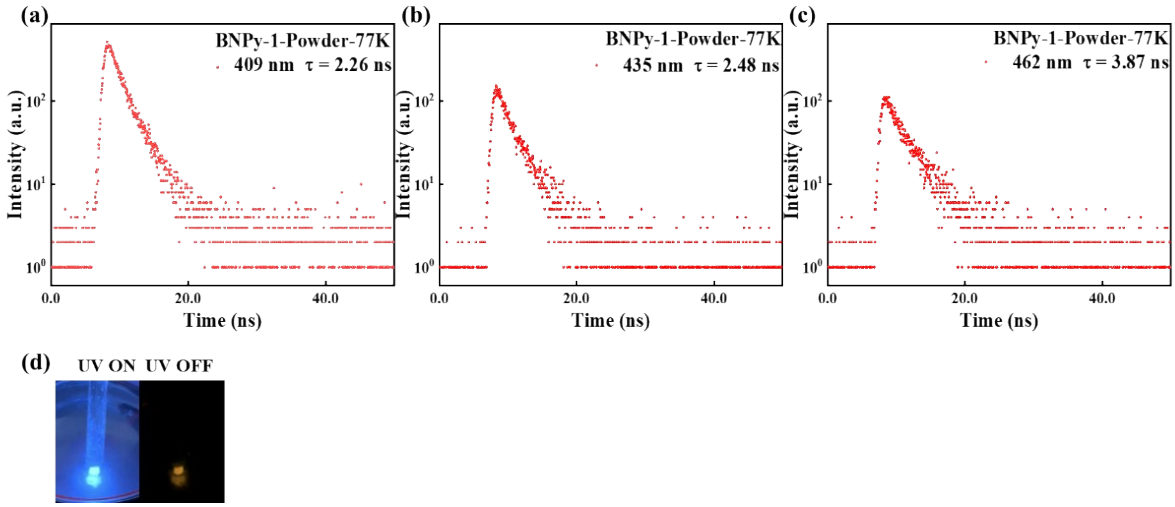


Figure S18. (a-c) Decay spectra of the BNPy-1 powder at 77 K; (d) phosphorescent images of the BNPy-1 powder in liquid nitrogen. (λ_{ex} = 365 nm).

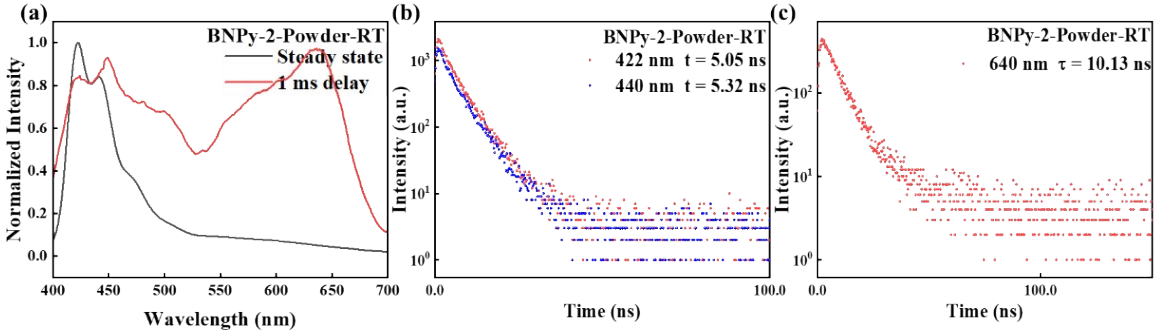


Figure S19. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2 powder at RT; and (b-c) decay spectra at ambient condition. (λ_{ex} = 365 nm).

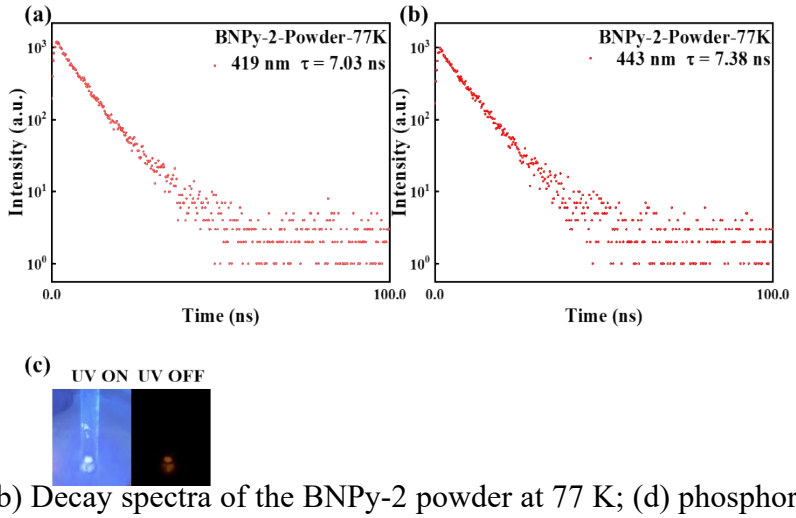


Figure S20. (a-b) Decay spectra of the BNPy-2 powder at 77 K; (d) phosphorescent images of the BNPy-2 powder in liquid nitrogen. (λ_{ex} = 365 nm).

6. Photophysical properties in PMMA film and PVA film.

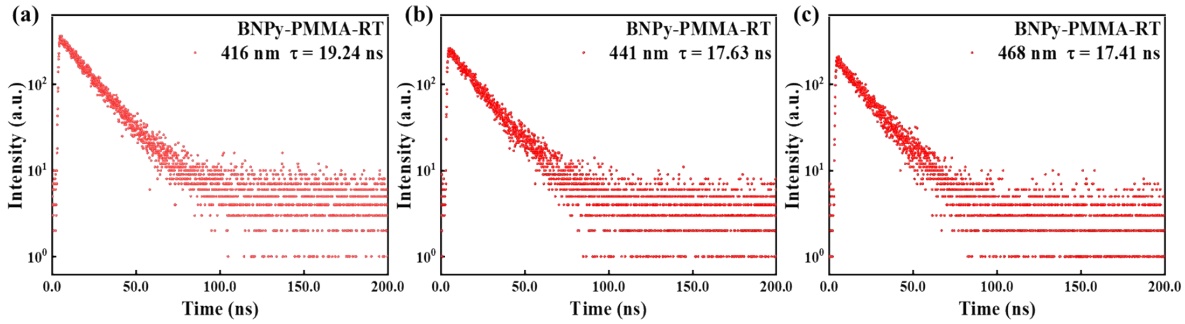


Figure S21. (a-c) Decay spectra of the BNPy@PMMA film (1 wt%) at ambient condition. (λ_{ex} = 365 nm).

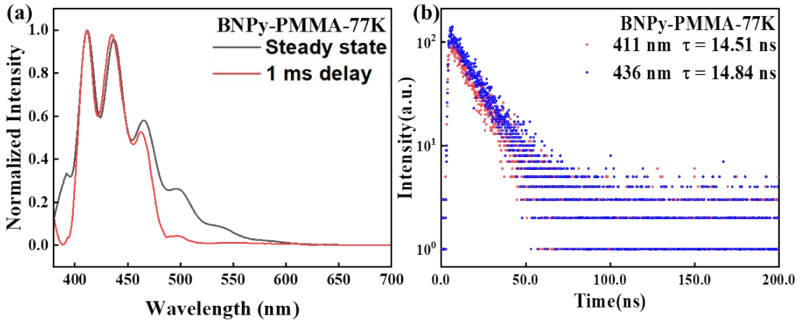


Figure S22. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy@PMMA film (1 wt%); and (b) decay spectra at 77 K. (λ_{ex} = 365 nm).

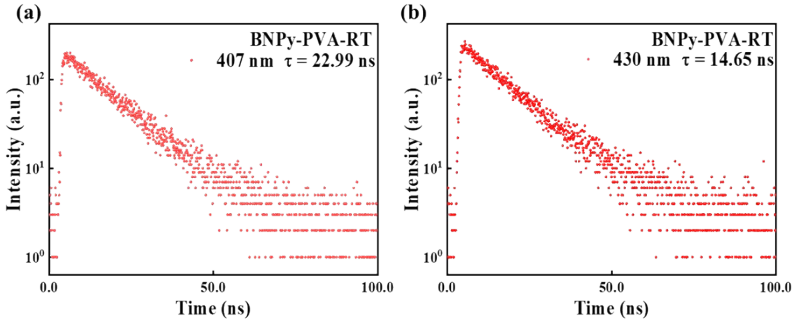


Figure S23. (a-b) Decay spectra of the BNPy@PVA film (0.1 wt%) at ambient condition. (λ_{ex} = 365 nm).

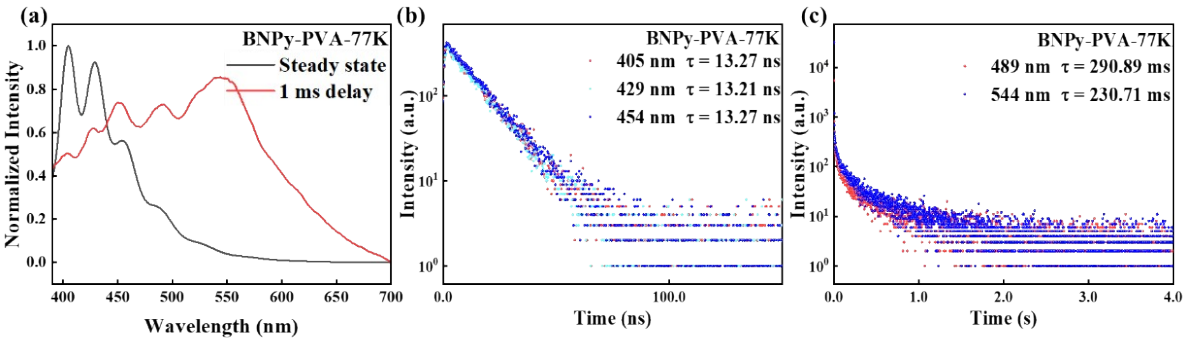


Figure S24. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy@PVA film (0.1 wt%); and (b-c) decay spectra at 77 K. (λ_{ex} = 365 nm).

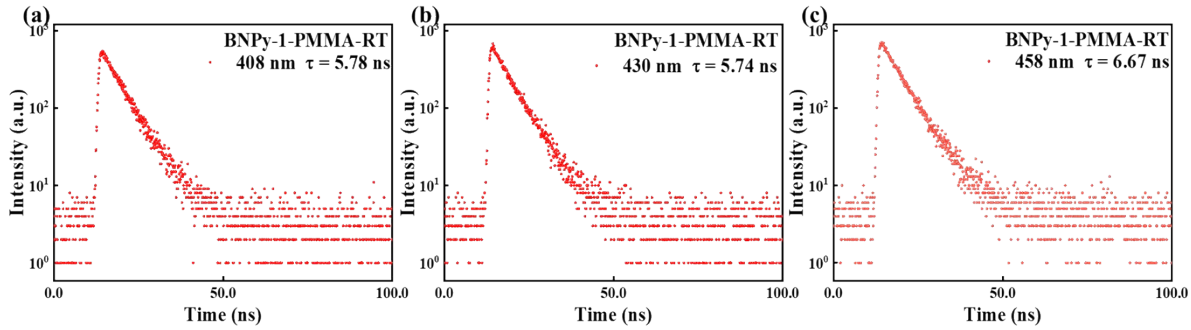


Figure S25. (a-c) Decay spectra of the BNPy-1@PMMA film (1 wt%) at ambient condition. (λ_{ex} = 365 nm).

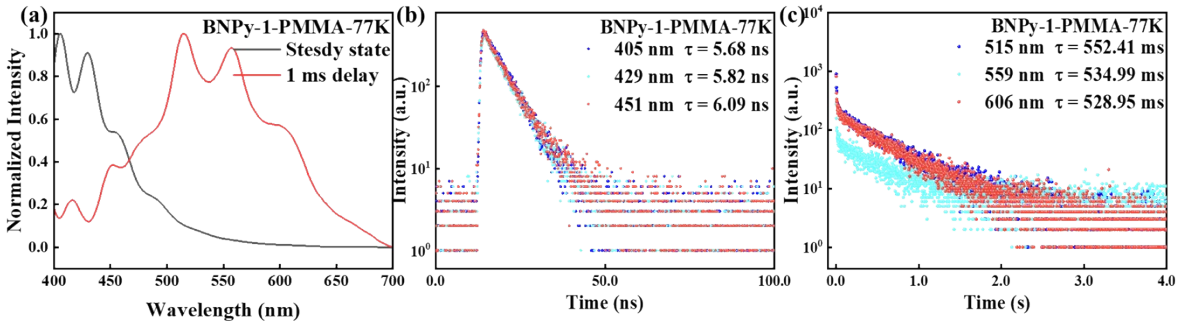


Figure S26. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy-1@PMMA film (1 wt%); and (b) decay spectra at 77 K. (λ_{ex} = 365 nm).

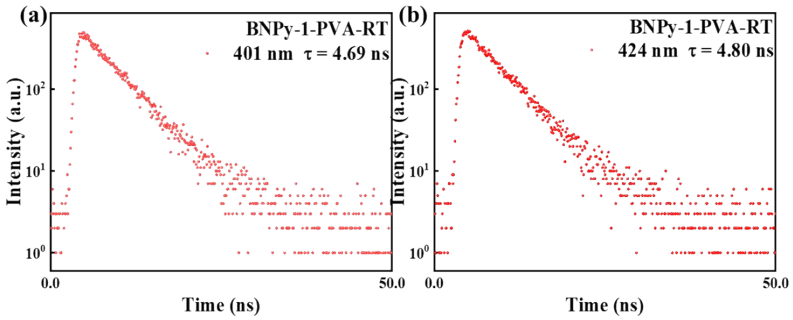


Figure S27. (a-b) Decay spectra of the BNPy-1@PVA film (0.1 wt%) at ambient condition. (λ_{ex} = 365 nm).

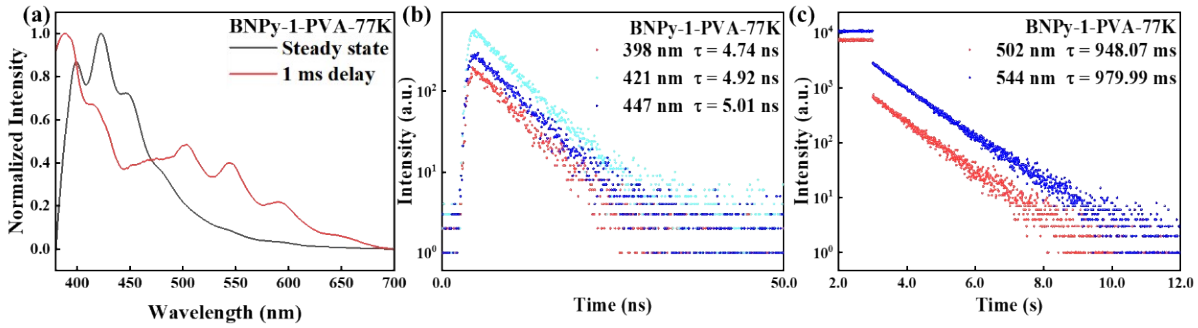


Figure S28. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy-1@PVA film (0.1 wt%); and (b-c) decay spectra at 77 K. (λ_{ex} = 365 nm).

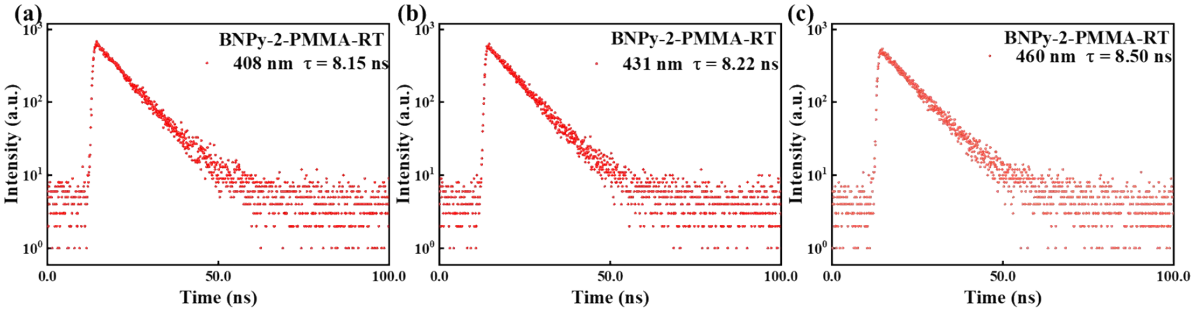


Figure S29. (a-c) Decay spectra of the BNPy-2@PMMA film (1 wt%) at ambient condition. (λ_{ex} = 365 nm).

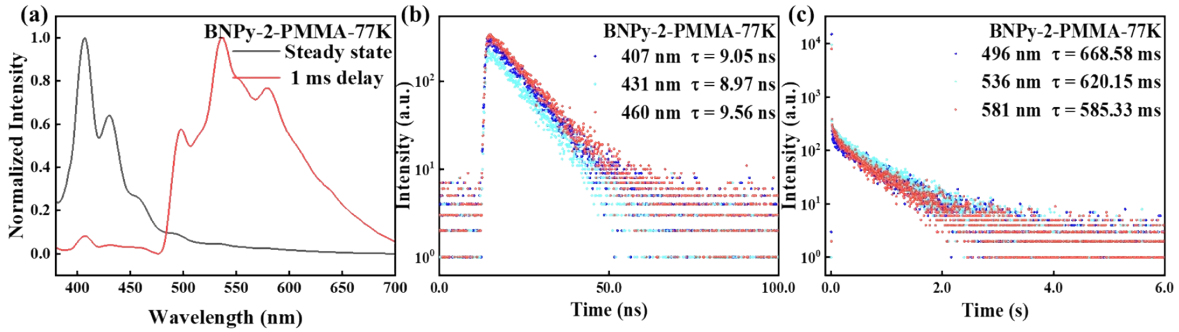


Figure S30. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy-2@PMMA film (1 wt%); and (b-c) decay spectra at 77K. (λ_{ex} = 365 nm).

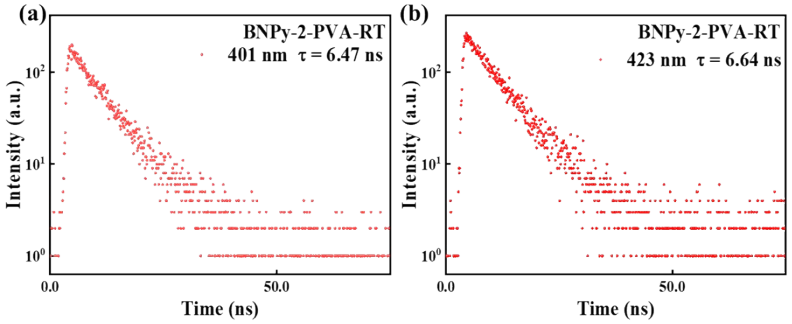


Figure S31. (a-b) Decay spectra of the BNPy-2@PVA film (0.1 wt%) at ambient condition. (λ_{ex} = 365 nm).

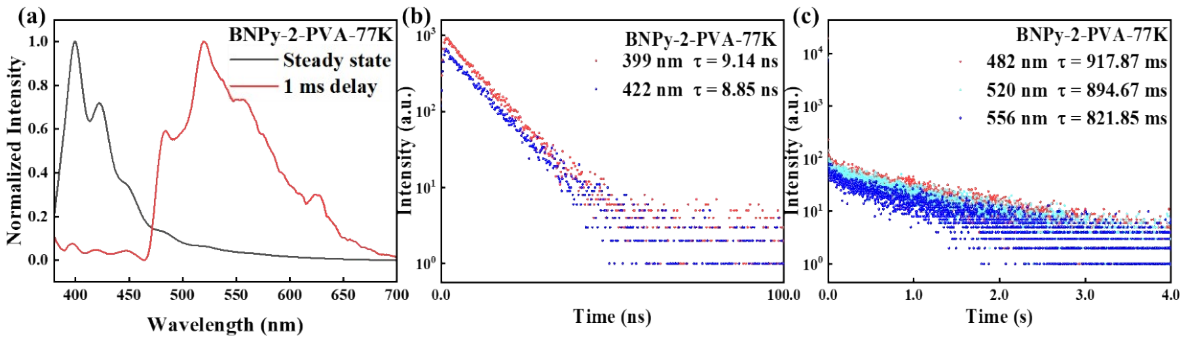


Figure S32. (a) Steady-state and 1 ms-delayed PL spectra of the BNPy-2@PVA film (0.1 wt%); and (b-c) decay spectra at 77 K. (λ_{ex} = 365 nm).

7. Photophysical properties of BNPy-1/BNPy-2 doped into DMAP

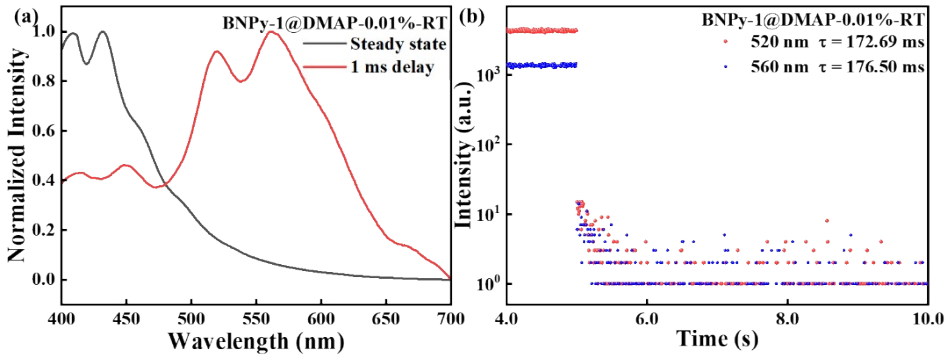


Figure S33. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.01 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

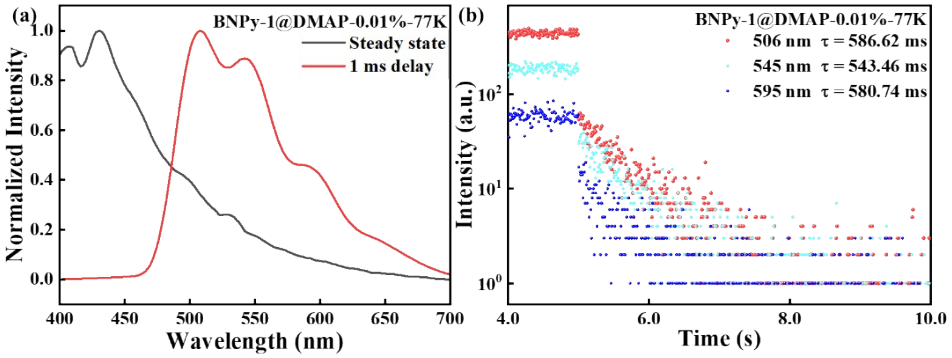


Figure S34. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.01 wt%); and (b) decay spectra at 77 K. (λ_{ex} = 365 nm).

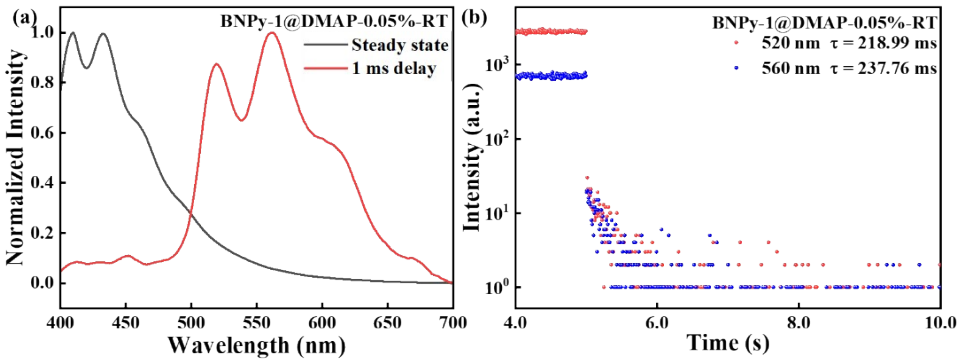


Figure S35. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.05 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

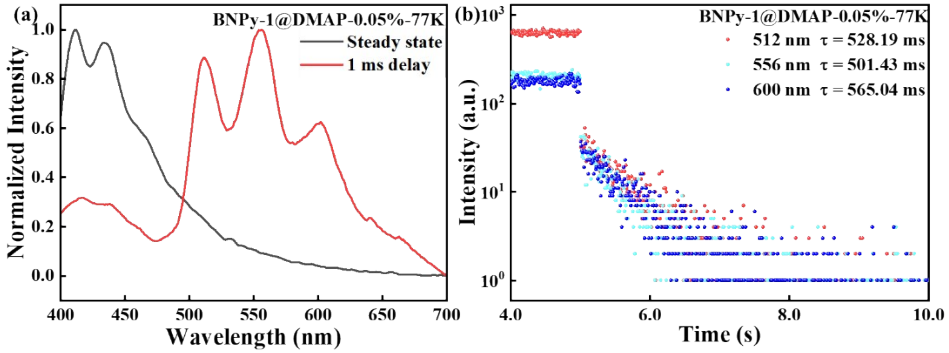


Figure S36. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.05 wt%); and (b) decay spectra at 77K. (λ_{ex} = 365 nm).

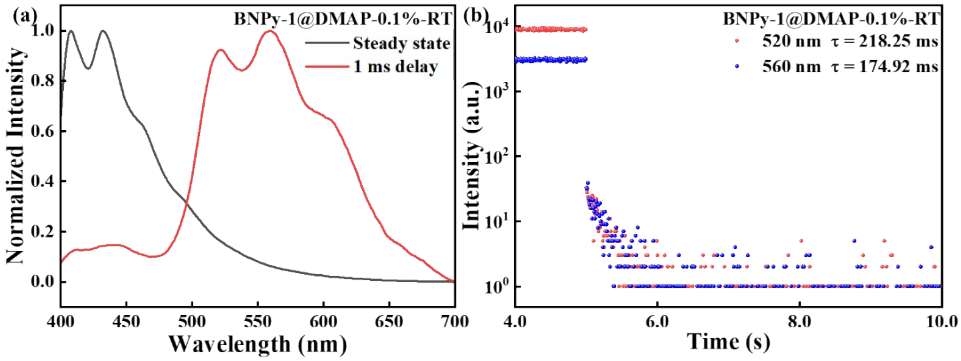


Figure S37. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

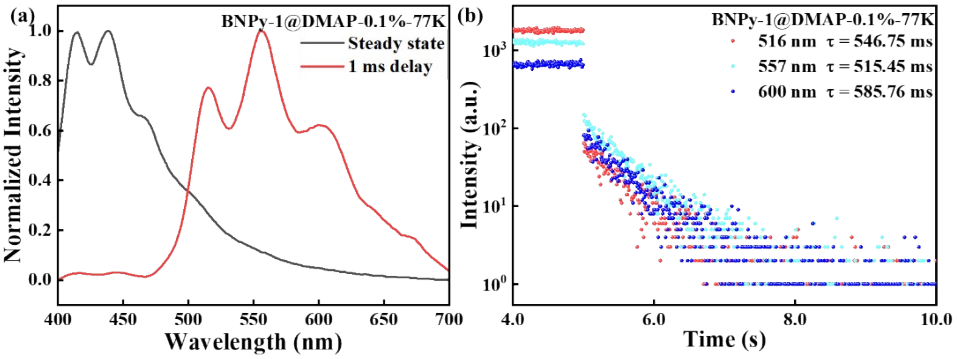


Figure S38. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.1 wt%); and (b) decay spectra at 77K. (λ_{ex} = 365 nm).

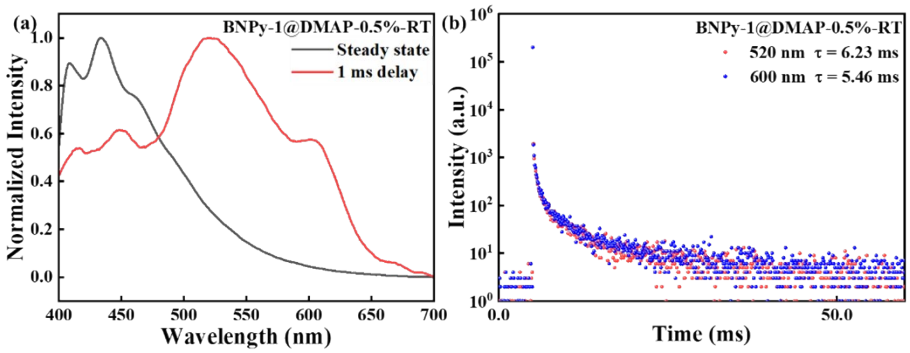


Figure S39. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.5 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

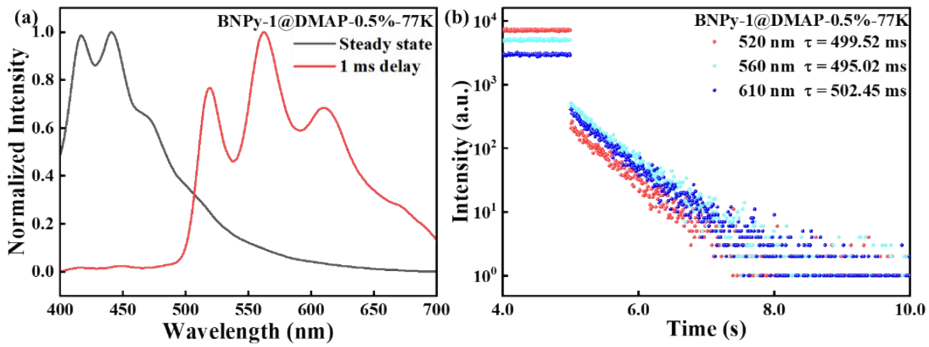


Figure S40. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (0.5 wt%); and (b) decay spectra at 77 K. (λ_{ex} = 365 nm).

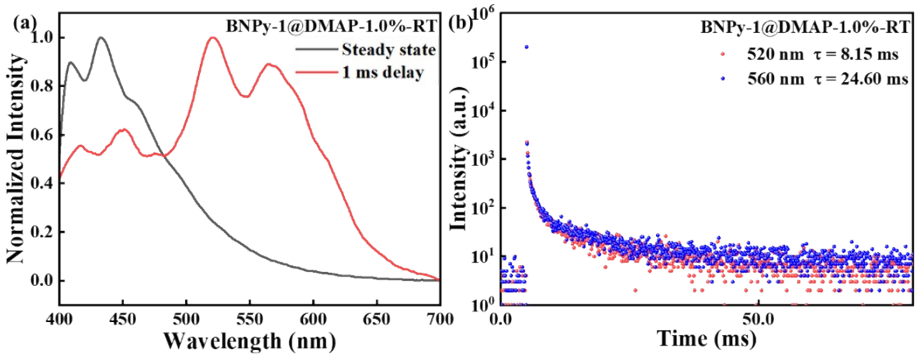


Figure S41. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (1.0 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

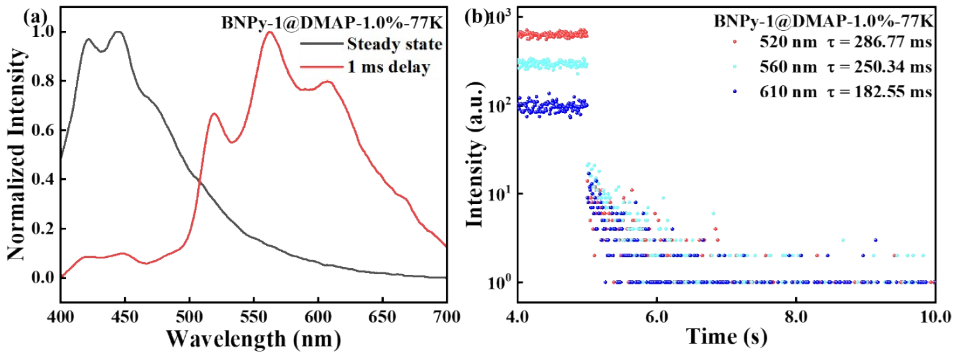


Figure S42. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@DMAP (1.0 wt%); and (b) decay spectra at 77 K. (λ_{ex} = 365 nm).

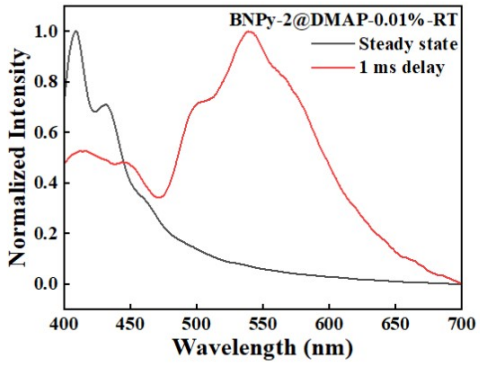


Figure S43. Steady-state and 1 ms-delayed PL spectra of BNPy-2@DMAP (0.01 wt%) at ambient condition. (λ_{ex} = 365 nm).

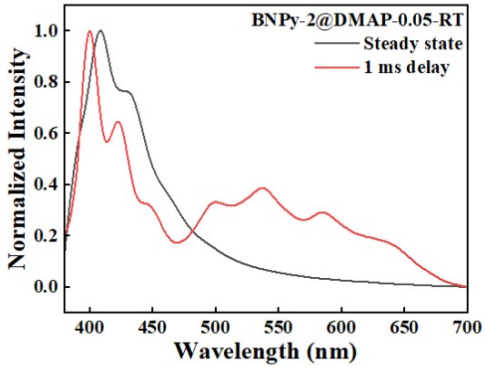


Figure S44. Steady-state and 1 ms-delayed PL spectra of BNPy-2@DMAP (0.05 wt%) at ambient condition. (λ_{ex} = 365 nm).

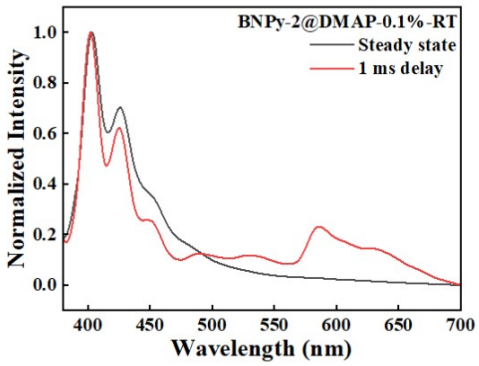


Figure S45. Steady-state and 1 ms-delayed PL spectra of BNPy-2@DMAP (0.1 wt%) at ambient condition. (λ_{ex} = 365 nm).

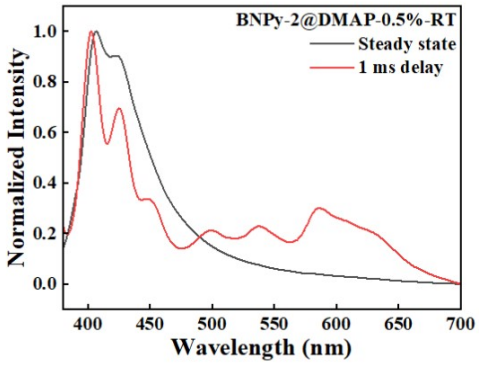


Figure S46. Steady-state and 1 ms-delayed PL spectra of BNPy-2@DMAP (0.5 wt%) at ambient condition. (λ_{ex} = 365 nm).

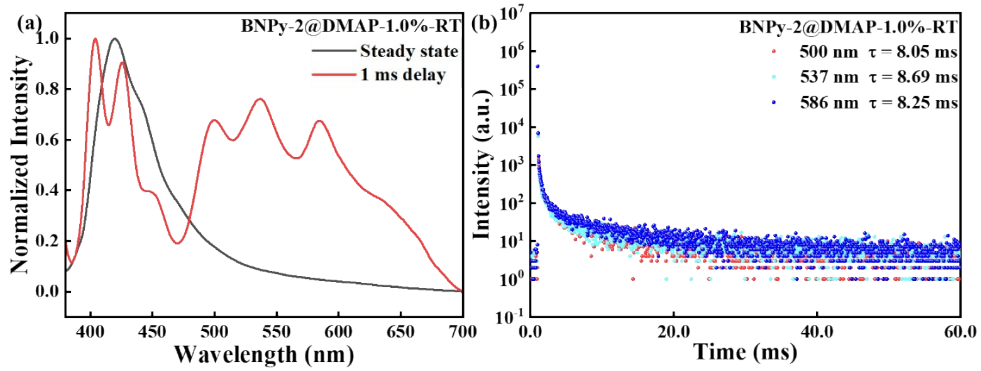


Figure S47. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@DMAP (1.0 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

8. Photophysical properties in the AA/MA copolymerized film

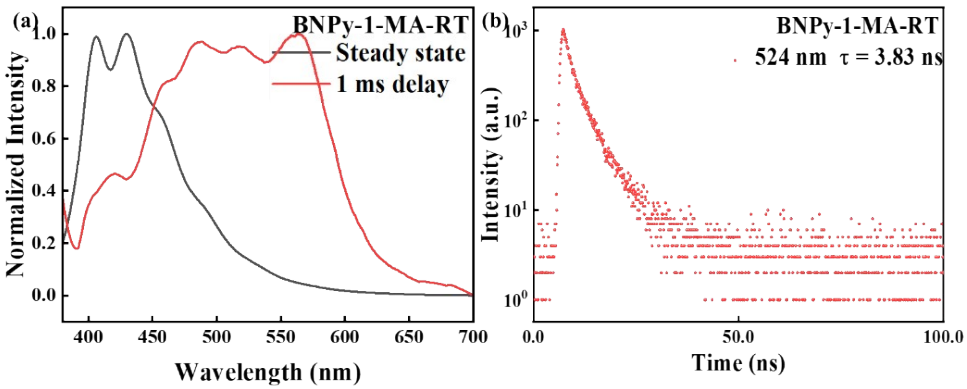


Figure S48. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

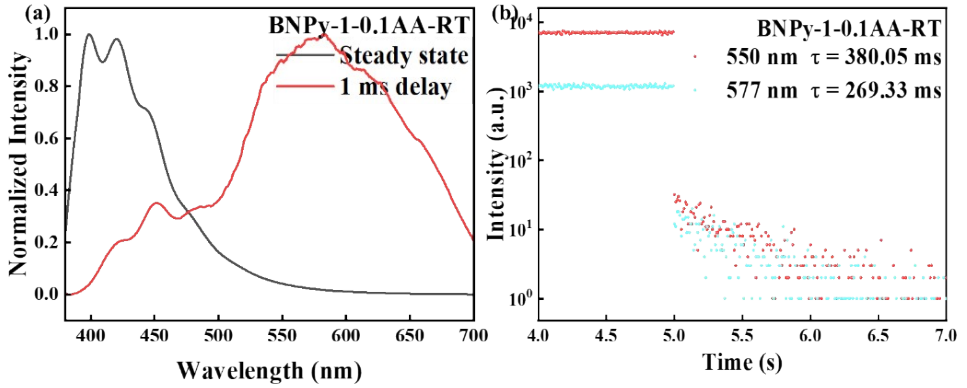


Figure S49. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.1PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

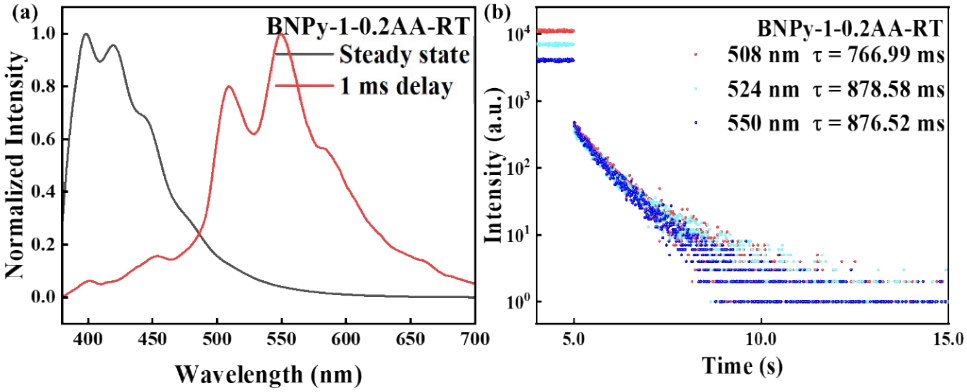


Figure S50. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.2PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

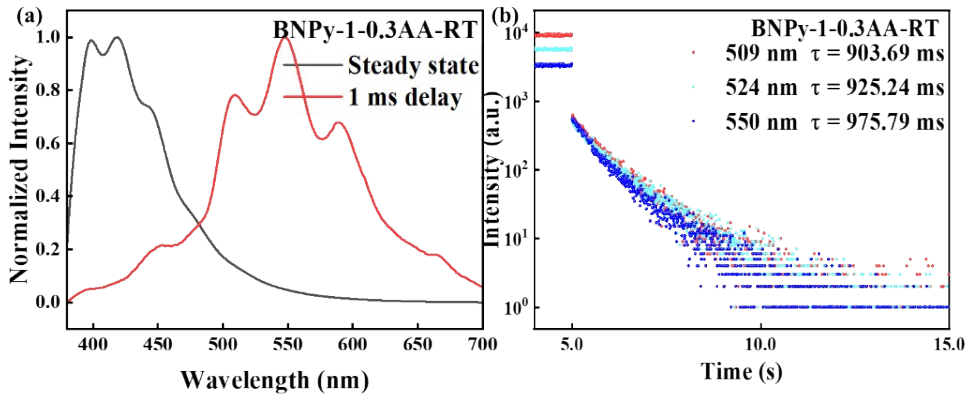


Figure S51. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.3PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

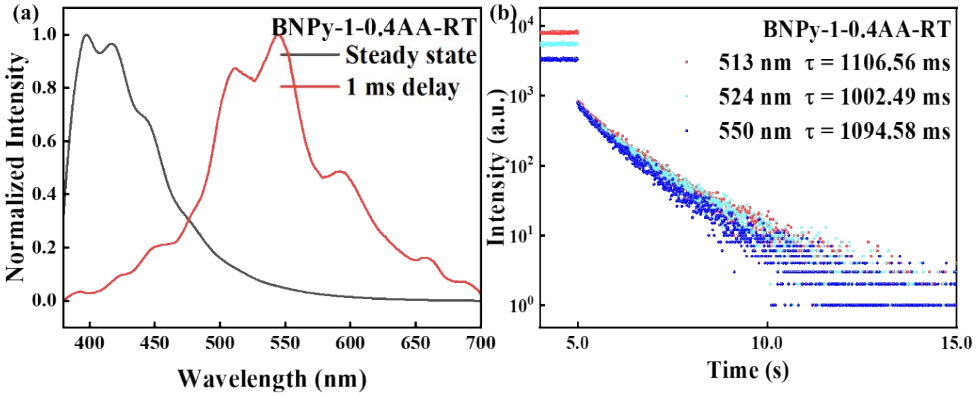


Figure S52. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.4PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

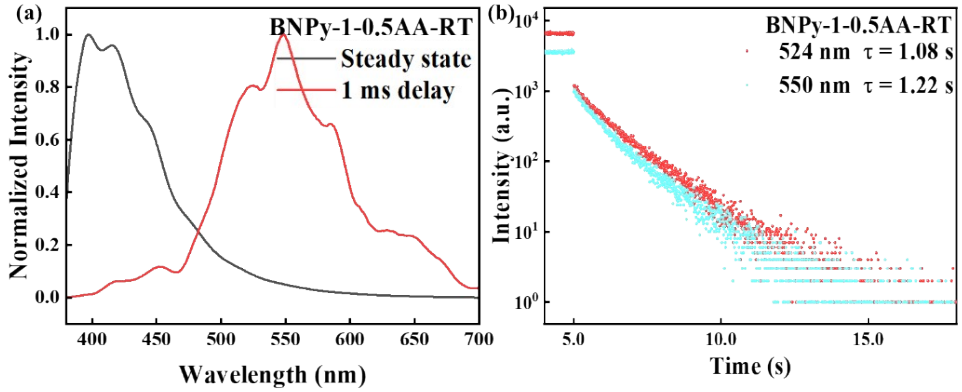


Figure S53. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.5PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

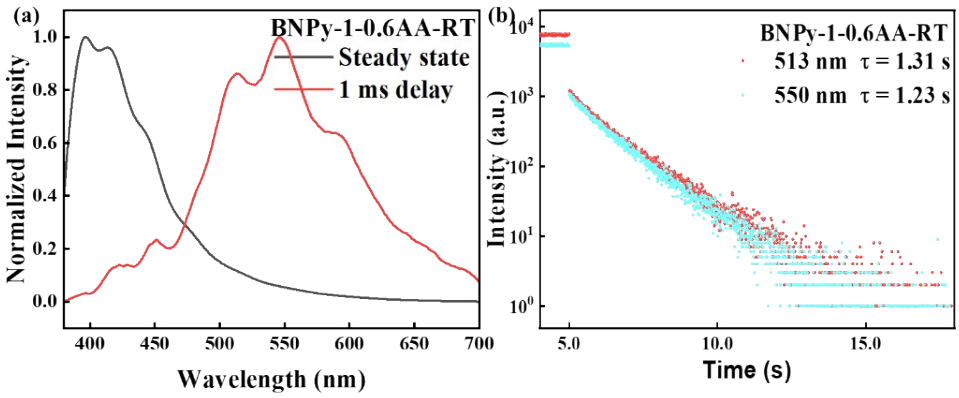


Figure S54. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.6PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

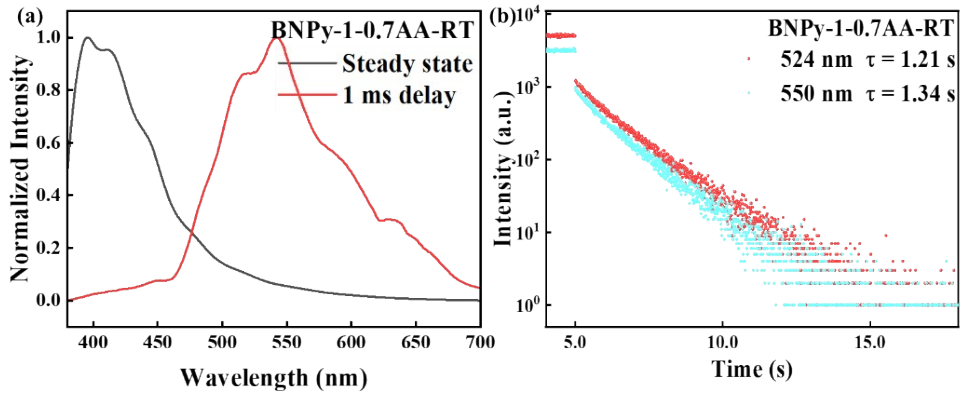


Figure S55. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.7PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

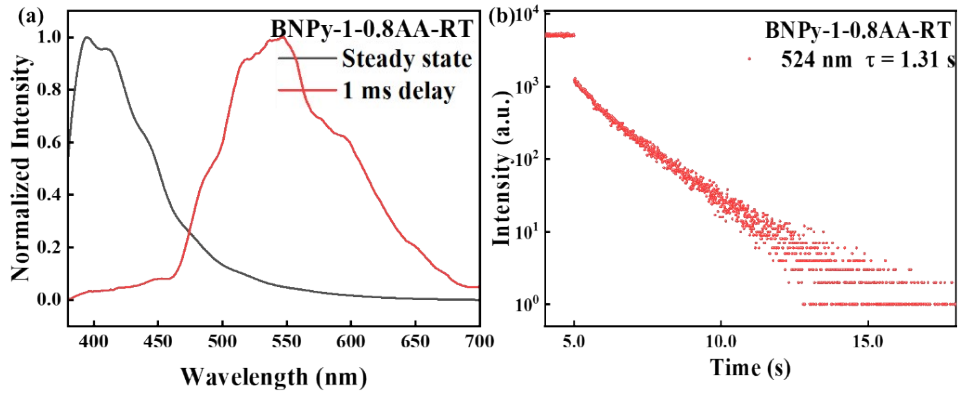


Figure S56. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.8PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

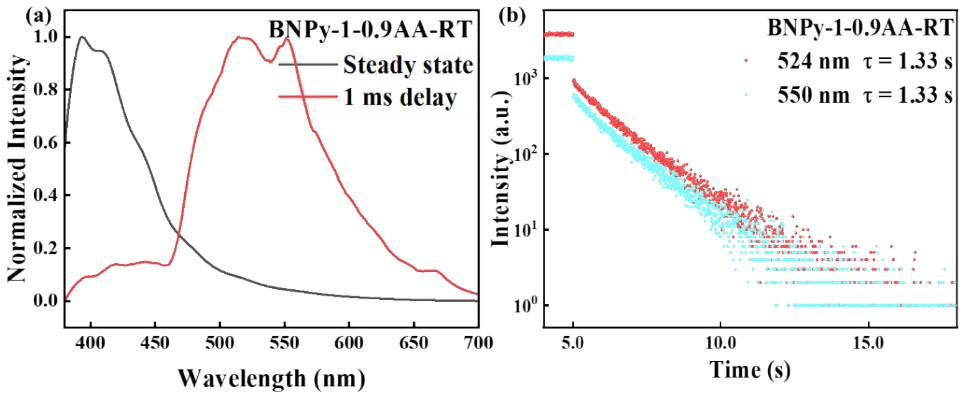


Figure S57. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@0.9PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

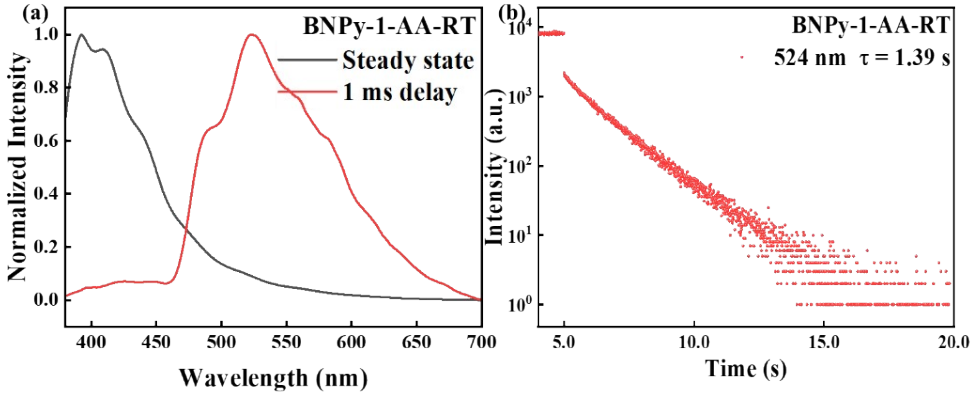


Figure S58. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-1@1.0PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

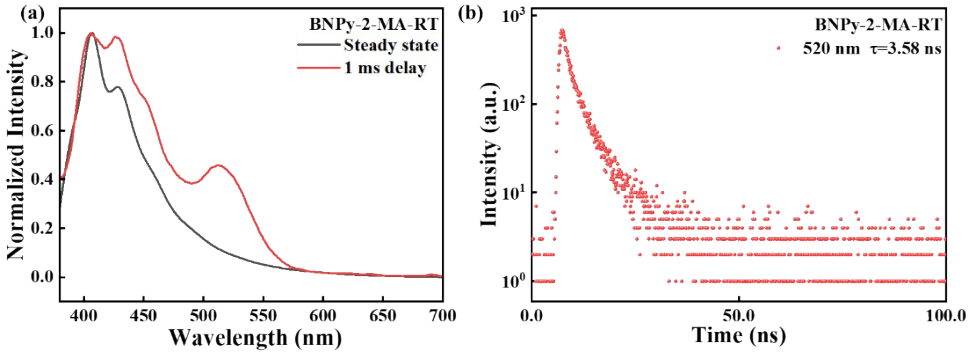


Figure S59. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

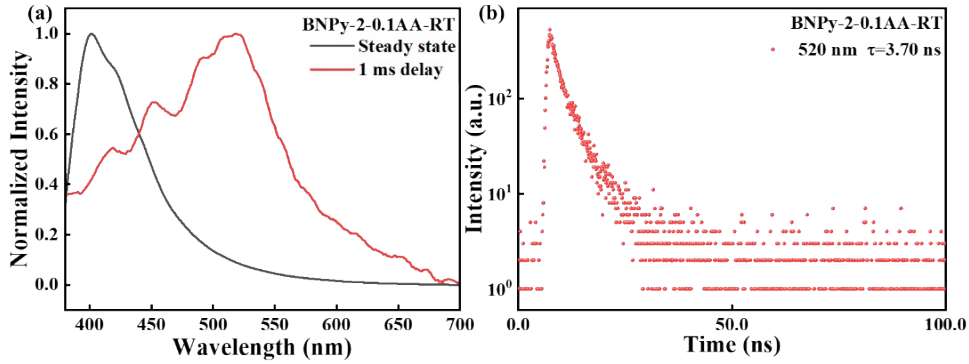


Figure S60. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.1PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

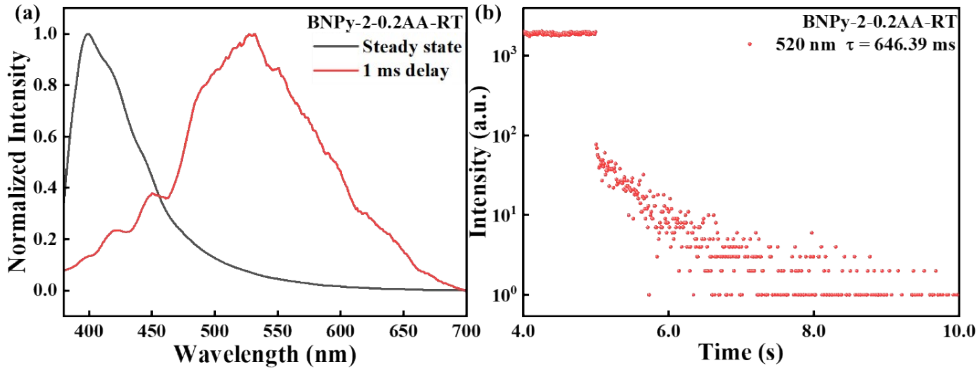


Figure S61. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.2PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

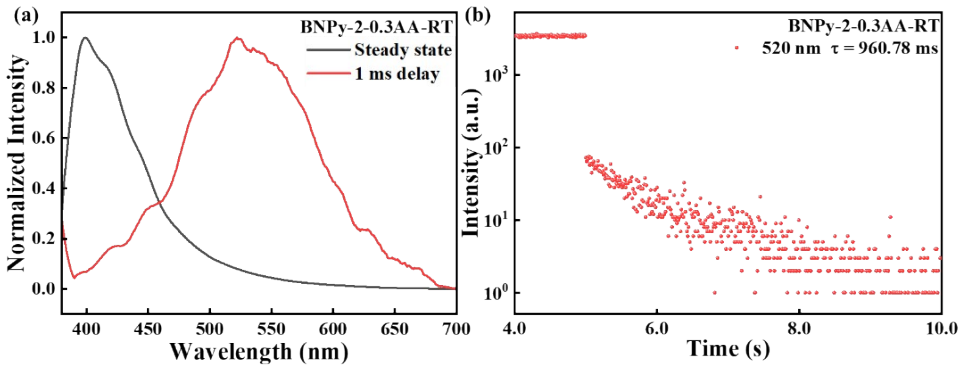


Figure S62. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.3PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

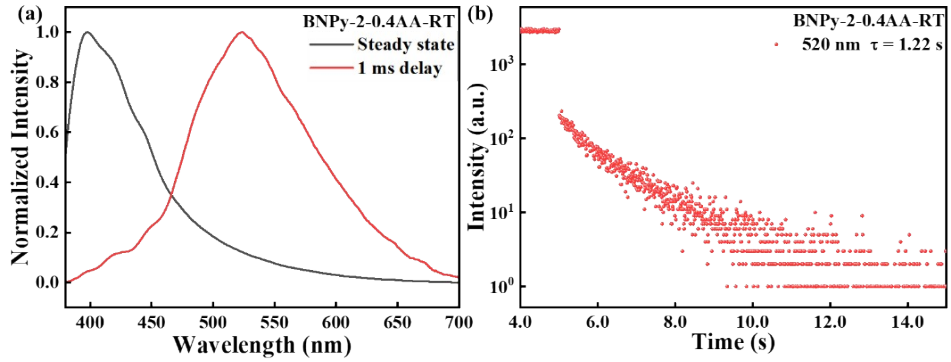


Figure S63. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.4PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

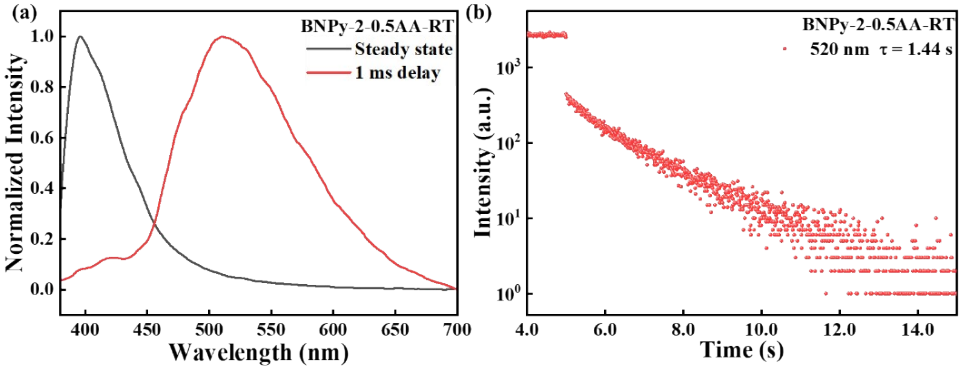


Figure S64. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.5PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

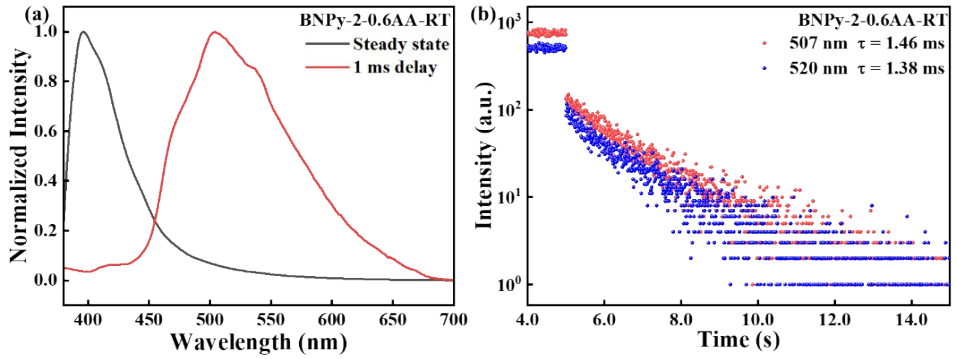


Figure S65. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.6PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

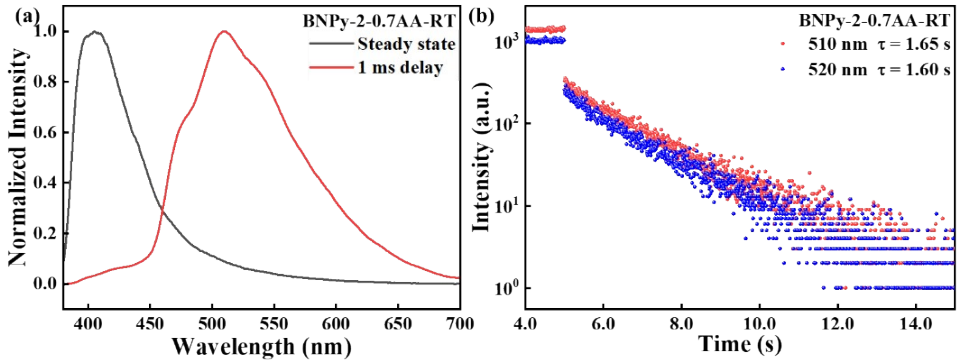


Figure S66. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.7PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

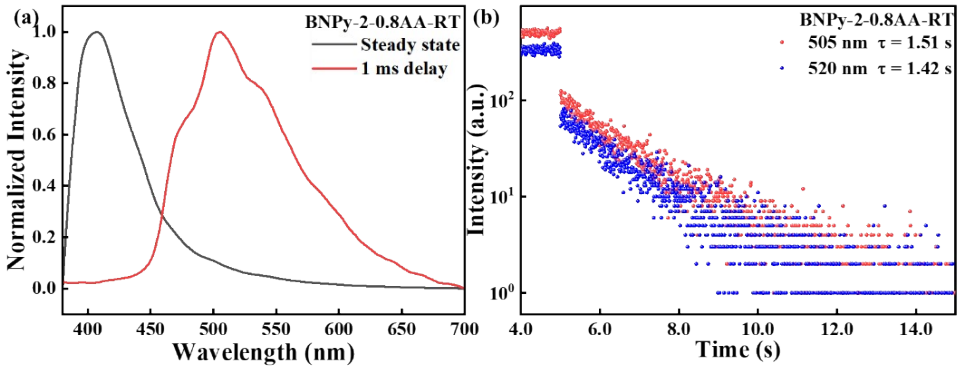


Figure S67. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.8PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

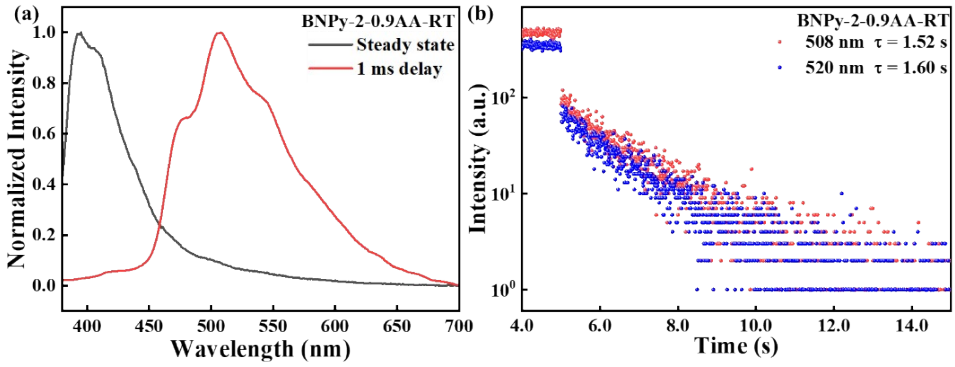


Figure S68. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@0.9PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

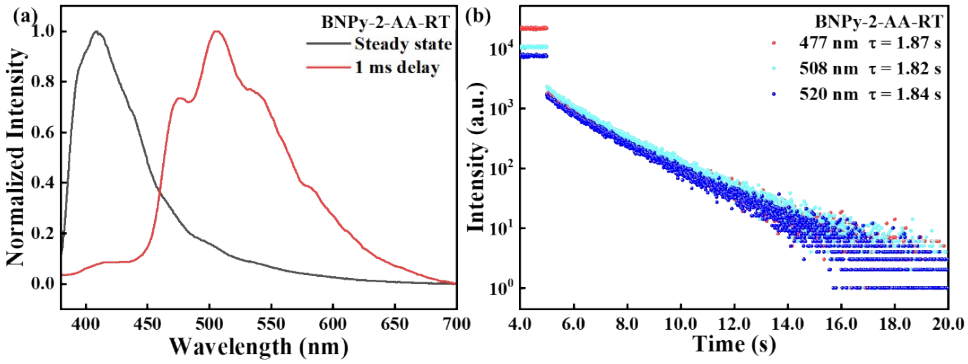


Figure S69. (a) Steady-state and 1 ms-delayed PL spectra of BNPy-2@1.0PAA-PMA film (0.1 wt%); and (b) decay spectra at ambient condition. (λ_{ex} = 365 nm).

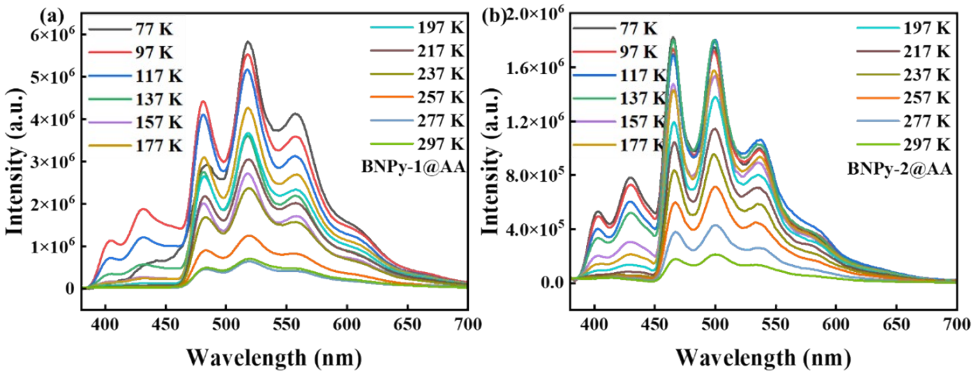


Figure S70. Variable-temperature 1 ms-delayed spectra of (a) BNPy-1@1.0PAA-PMA film (0.1 wt%), (b) BNPy-2@1.0PAA-PMA film (0.1 wt%).

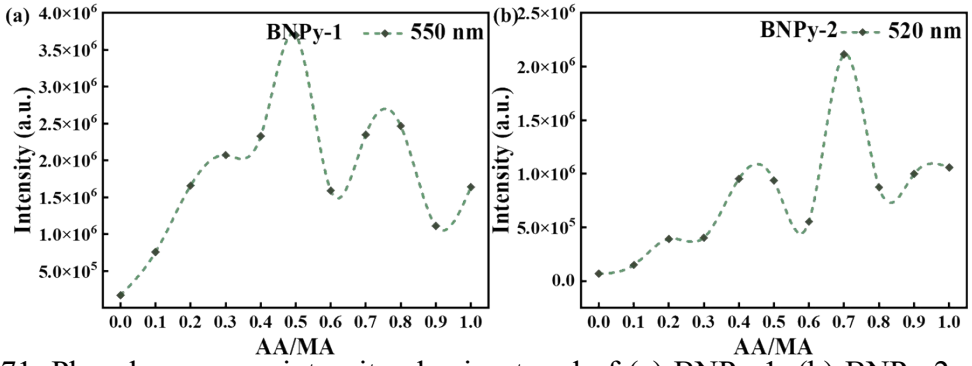


Figure S71. Phosphorescence intensity chaning trend of (a) BNPy-1, (b) BNPy-2 along with AA concentration.

Table S1. Quantum yields and associated rate constants of BNPy-1@1.0PAA-PMA film and BNPy-2@1.0PAA-PMA film.

Sample	λ_{ex}/nm	φ_{FL}/%	φ_{PL}/%	K_{ISC}/s^{-1}	K_r^{Phos}/s^{-1}	K_{nr}^{Phos}/s^{-1}
BNPy-1@1.0PAA-PMA	365	14.56	1.74	2.18×10^6	0.013	0.71
BNPy-2@1.0PAA-PMA	365	13.68	0.20	2.22×10^5	0.001	0.55

9. TD-DFT results

Table S2. The singlet and triplet excited state transition configurations of BNPy monomer. The matched excited states that contain the same orbital transition components of S_1 are shown in red.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.4463	H-2→L (2.38), **H→L (92.85)**
T_2	3.4089	H-2→L (17.89), H-2→L+3 (2.11), H-1→L (35.33), H-1→L+3 (3.66), H→L+1 (32.09), H→L+3 (3.96)
S_1	**3.4894**	**H→L (96.50)**
T_3	3.5948	H-2→L (7.86), H-1→L (57.41), H→L+1 (30.29)

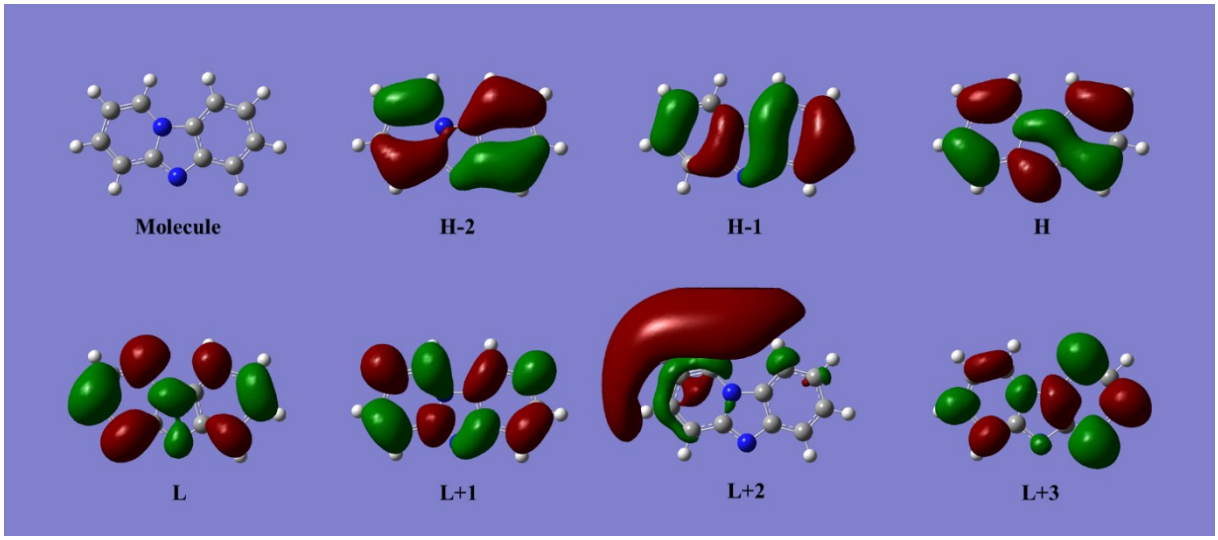


Figure S72. Plots of BNPy monomer visualized orbitals.

Table S3. The singlet and triplet excited state transition configurations of BNPy -1 monomer. The matched excited states that contain the same orbital transition components of S_1 are shown in red.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.4757	H-2→L (2.62), H-2→L+2 (2.04), **H→L (89.13)**
T_2	3.2404	H-3→L+1 (2.48), H-3→L+2 (3.11), H-2→L (7.09), H-1→L (72.65), H→L+2 (4.94)
S_1	**3.5083**	**H-1→L+1 (3.05), H→L (94.34)**
T_3	3.5249	H-3→L+1 (3.85), H-2→L (24.59), H-1→L (19.92), H→L+1 (23.68), H→L+2 (20.16),
T_4	3.7518	H-3→L (12.38), H-3→L+1 (3.07), H-3→L+4 (3.01), H-2→L (5.35), H-2→L+2 (4.07), **H-1→L+1 (32.08),** H-1→L+2 (5.43), H→L+1 (10.67), H→L+2 (9.31), H→L+4 (4.01) H→L+7 (2.68)

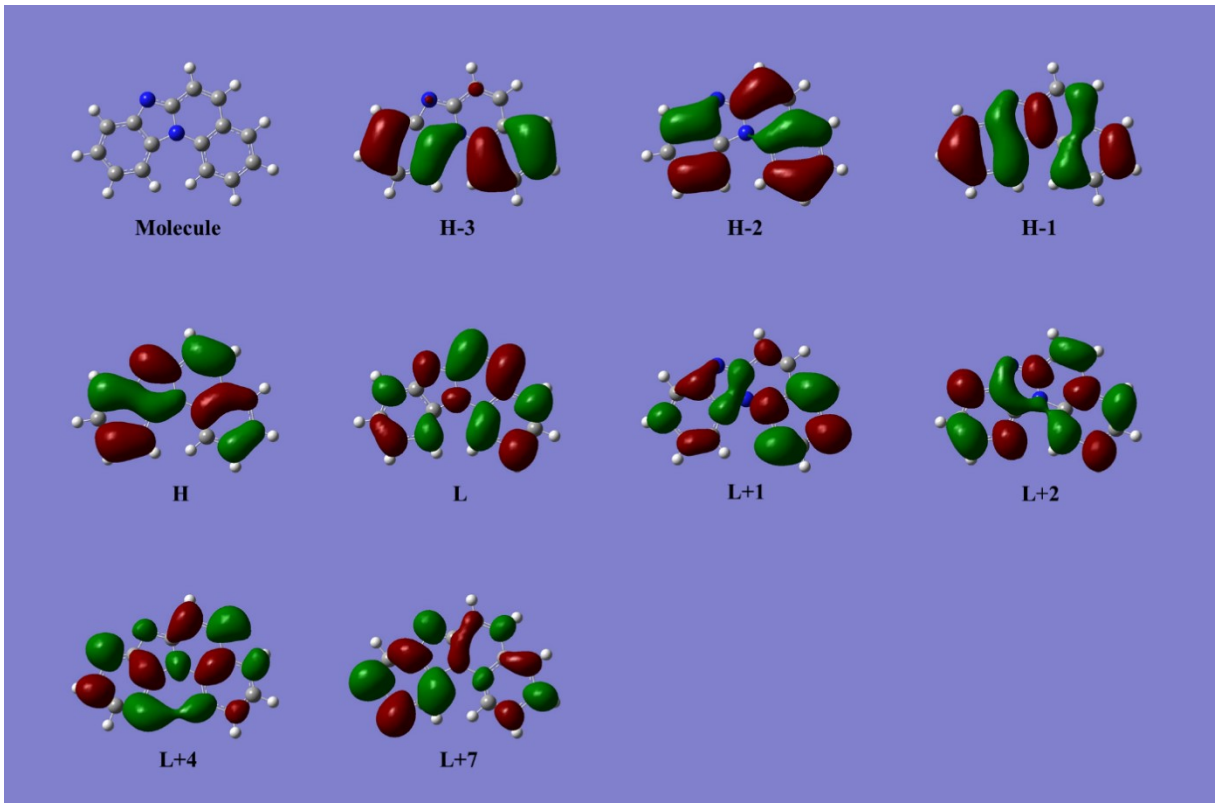


Figure S73. Plots of BNPy -1 monomer visualized orbitals.

Table S4. The singlet and triplet excited state transition configurations of BNPy-2 monomer. The matched excited states that contain the same orbital transition components of S_1 are shown in red.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.5840	H-2→L (2.51), H-2→L+2 (3.24), H-1→L (18.95), **H→L (61.99),** H→L+1 (9.05)
T_2	2.8600	H-1→L (31.56), **H-1→L+1 (13.70),** H-1→L+2 (4.23), **H→L (24.62),** H→L+1 (17.11)
T_3	3.3267	H-1→L (36.70), H→L+1 (55.04),
S_1	**3.4756**	**H-1→L+1 (6.47), H→L (89.31)**
T_4	3.5983	H-2→L (24.61), H-1→L (3.36), **H-1→L+1 (32.21),** H-1→L+2 (6.56), **H→L (8.22),** H→L+1 (11.42), H→L+2 (8.66)
S_2	3.7660	H-1→L (68.37), H→L+1 (27.91),
T_5	3.7718	H-4→L (2.01), H-2→L (8.47), H-2→L+5 (2.53), **H-1→L+1 (37.11),** H-1→L+2 (7.34), H→L+2 (33.80),

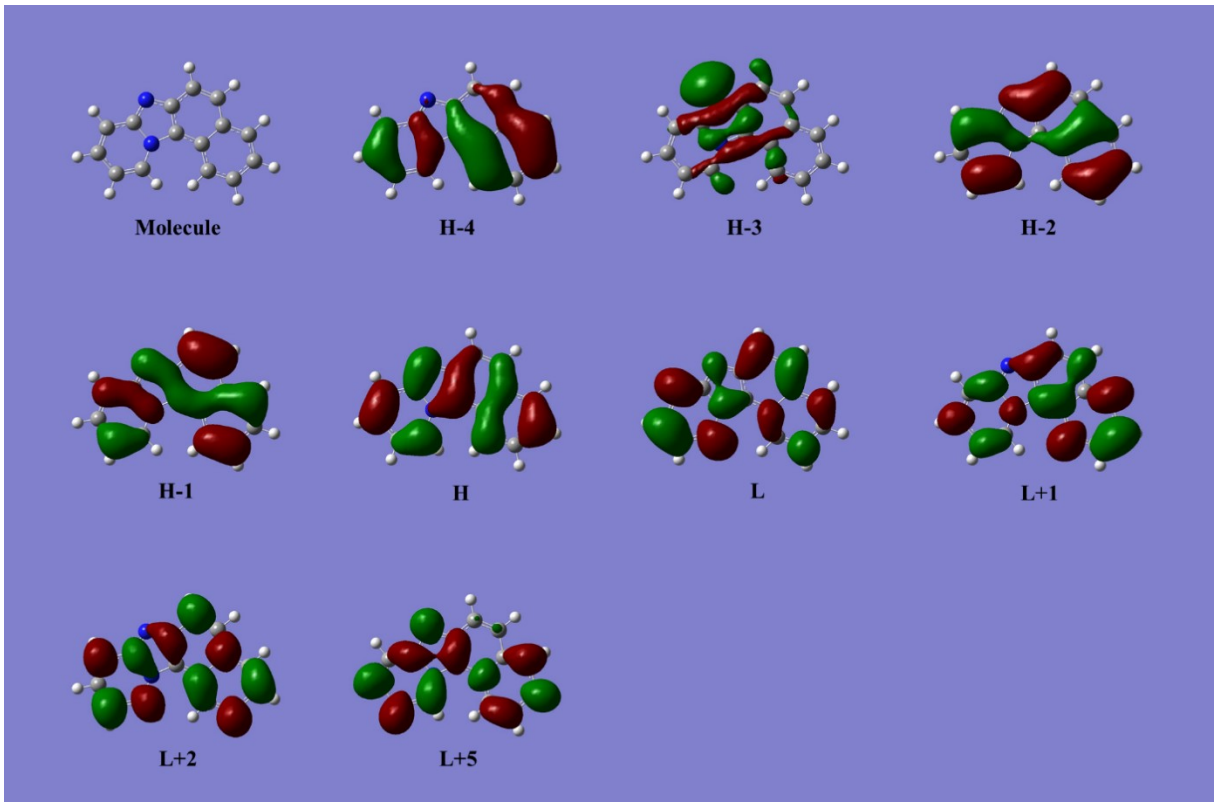


Figure S74. Plots of BNPy -2 monomer visualized orbitals.

Table S5. Spin-orbit coupling (SOC) values between S_n and T_n of BNPy, BNPy-1 and BNPy-2 monomer.

$<S_n\|Hso\|T_n>$	BNPy(cm^{-1})	BNPy-1(cm^{-1})	BNPy-2(cm^{-1})
S_0/T_1	0.65029	0.77972	0.67206
S_0/T_2	0.52085	0.11534	0.19256
S_0/T_3	0.14017	0.02878	0.74625
S_0/T_4	-	0.99845	0.68549
S_0/T_5	-	-	0.33774
S_1/T_1	0.25484	0.03605	0.94941
S_1/T_2	1.01411	0.95545	1.04353
S_1/T_3	0.19761	0.23127	0.31038
S_1/T_4	-	0.37207	0.29305
S_1/T_5	-	-	0.59606
S_2/T_1	-	-	0.96683
S_2/T_2	-	-	0.25318
S_2/T_3	-	-	0.22028
S_2/T_4	-	-	1.07443
S_2/T_5	-	-	0.66820

Table S6. Total energy of BNPy, BNPy-1 and BNPy-2 monomer.

	BNPy	BNPy-1	BNPy-2
Monomer ($E_{M,\mathrm{HF}}$)	-533.631096906	-687.313231224	-687.307999930

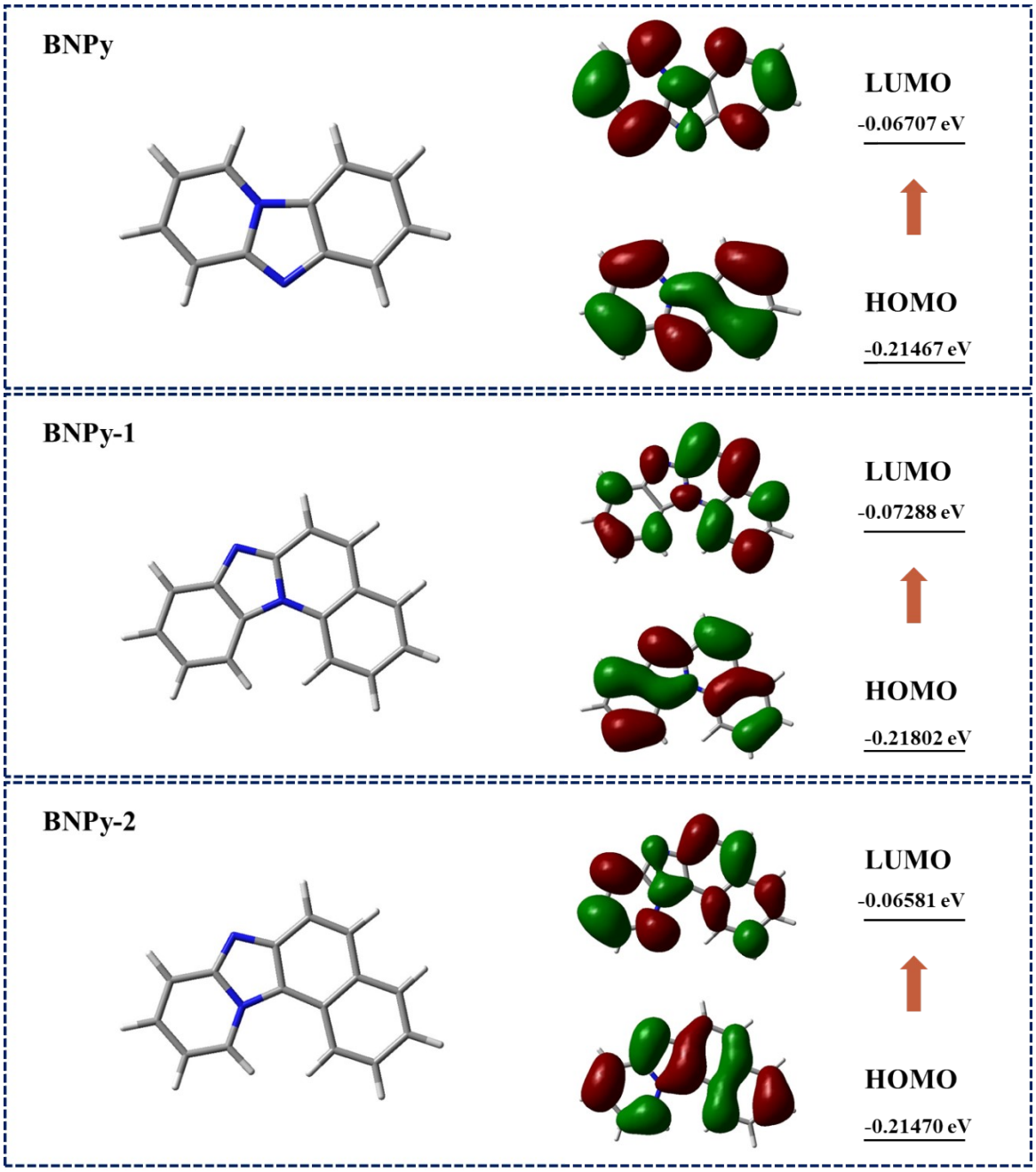


Figure S75. Plots of BNPy, BNPy-1 and BNPy-2 monomer and radical visualized orbitals.

References

1. Li, J.-A., Zhou, J., Mao, Z., Xie, Z., Yang, Z., Xu, B., Liu, C., Chen, X., Ren, D., Pan, H., et al. (2018). Transient and Persistent Room-Temperature Mechanoluminescence from a White-Light-Emitting AIEgen with Tricolor Emission Switching Triggered by Light. Angew. Chem. Int. Ed. *57*, 6449-6453.
2. An, Z., Zheng, C., Tao, Y., Chen, R., Shi, H., Chen, T., Wang, Z., Li, H., Deng, R., Liu, X., and Huang, W. (2015). Stabilizing triplet excited states for ultralong organic phosphorescence. Nat. Mater. *14*, 685-690.