Supporting Information

Simultaneous Harvesting of Triplet Excitons in OLEDs by both Guest and Host Materials with Intramolecular Charge-transfer Feature *via* Triplet-Triplet Annihilation†

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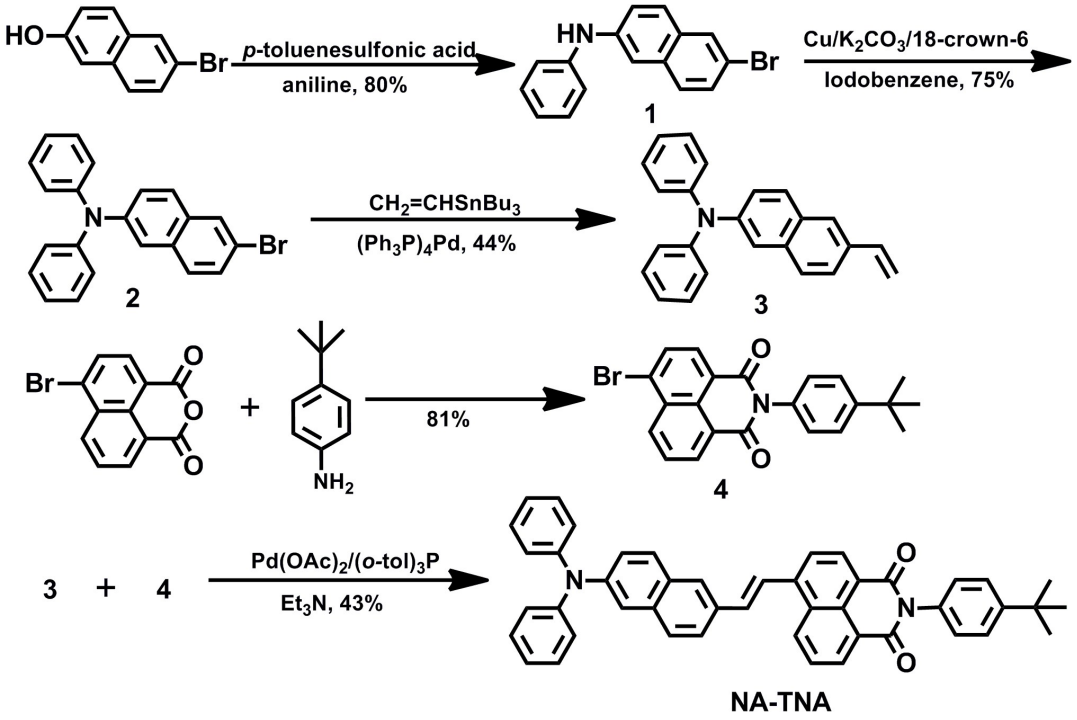
Contents

1) Synthetic procedures and characterization data



Scheme S1. Synthetic routes to **NA-TNA**.

Intermediates 6-bromo-*N*-phenylnaphthalen-2-amine (**1**),[1] 6-bromo-*N,N*-diphenylnaphthalen-2-amine (**2**),[1] and 6-bromo-2-(4-(*t*-butyl)phenyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (**4**)[2] were synthesized according to reported procedures. The objective molecule **NA-TNA** was synthesized through Heck coupling reaction between compounds **3** and **4**.

N,N-diphenyl-6-vinylnaphthalen-2-amine (3)

A flask was charged with a mixture of **2** (1.74 g, 4.66 mmol), $Pd(Ph_3P)_4$ (0.11 g, 0.094 mmol), tributylethenylstannane (1.78 g, 5.62 mmol), catalytic amount of 2,6-di-*t*-butylphenol and toluene (20 mL). The reaction mixture was refluxed for 24 h under argon in the dark. After cooled down to room temperature, saturated aqueous KF solution (20 mL) was added and the resulting mixture was stirred for 1 h at room temperature. The mixture was diluted with CH_2Cl_2 (20 mL × 3) and washed with brine, dried under anhydrous Na_2SO_4, then the solvent was removed in vacuum. The crude product was purified by column chromatography (eluent: petroleum ether) to render 0.66 g white solid. Yield: 44%. M.p.: 136.2-136.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.8 Hz, 2H), 7.58-7.49 (m, 2H), 7.37 (d, J = 2.0 Hz, 1H), 7.29 (t, J = 2.0 Hz, 1H), 7.28–7.24 (m, 4H), 7.20-7.08 (m, 4H), 7.08-7.00 (m, 2H), 6.84 (dd, J = 17.6 Hz, 11.2 Hz, 1H), 5.82 (dd, J = 17.6 Hz, 0.4 Hz, 1H), 5.33-5.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 145.6, 136.9, 134.1, 133.7, 129.9, 129.3, 129.0, 127.2, 126.1, 124.5, 123.6, 123.0, 119.8, 113.3.

(*E*)-2-(4-(*t*-butyl)phenyl)-6-(2-(6-(diphenylamino)naphthalen-2-yl)vinyl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (NA-TNA)

A flask was charged with a mixture of **3** (0.57 g, 1.80 mmol), **4** (0.86g, 2.11 mmol), $Pd(OAc)_2$ (0.008 g, 0.036 mmol), P(*o*-tolyl)$_3$ (0.022 g, 0.072 mmol), triethylamine (1.27 g, 12.6 mmol) and DMF (25 mL). The reaction mixture was stirred at 90 °C for 24 h under argon. After cooled to room temperature, the mixture was poured into water (40 mL), and the orange–red solid was collected, washed with water and dried in vacuo. The crude product was purified by column chromatography (eluent: petroleum ether/dichloromethane = 1/1, v/v) to obtain 0.51 g red solid. Yield: 43%. M.p.: 278 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.6 Hz, 2H), 8.64 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 1H), 7.99 (d, *J* = 16.0 Hz, 1H), 7.89 (s, 1H), 7.87-7.69 (m, 3H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.60 -7.46 (m, 3H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.34-7.23 (m, 7H), 7.17 (dd, *J* = 8.4 Hz, 1.2 Hz, 4H), 7.14-7.04 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 151.3, 147.5, 146.4, 141.9, 135.8, 134.7, 132.6, 132.5, 131.6, 131.5, 130.3, 129.7, 129.7, 129.4, 129.2, 127.9, 127.9, 127.6, 126.7, 126.4, 124.8, 124.4, 123.9, 123.7, 123.5, 123.3, 122.6, 121.4, 118.9, 34.8, 31.4. HRMS(ESI) for $C_{46}H_{36}N_2O_2$ $(M+H)^+$ Cacld: 649.2855, Found: 649.2852.

2) Photophysical and electrochemical properties.

Table S1 Photoluminescence lifetime data of **NA-TNA** in N_2–saturated Tol and DMSO solutions at room temperature (RT), and N_2–saturated DMSO solution at 77 K. Concentration: 5×10^{-6} M.

Solvent	λ_{em} (nm)	Lifetime (ns)	Content (%)	χ^2
Tol (at RT)	540	$\tau_1 = 0.22$ $\tau_2 = 2.26$	25.0 75.0	1.13
DMSO (at RT)	687	$\tau_1 = 0.08$ $\tau_2 = 0.45$ $\tau_3 = 1.82$	97.9 2.0 0.1	1.13
DMSO (at 77 K)	620	$\tau_1 = 530$ $\tau_2 = 1554$ $\tau_3 = 6369$	62.0 24.0 14.0	1.14

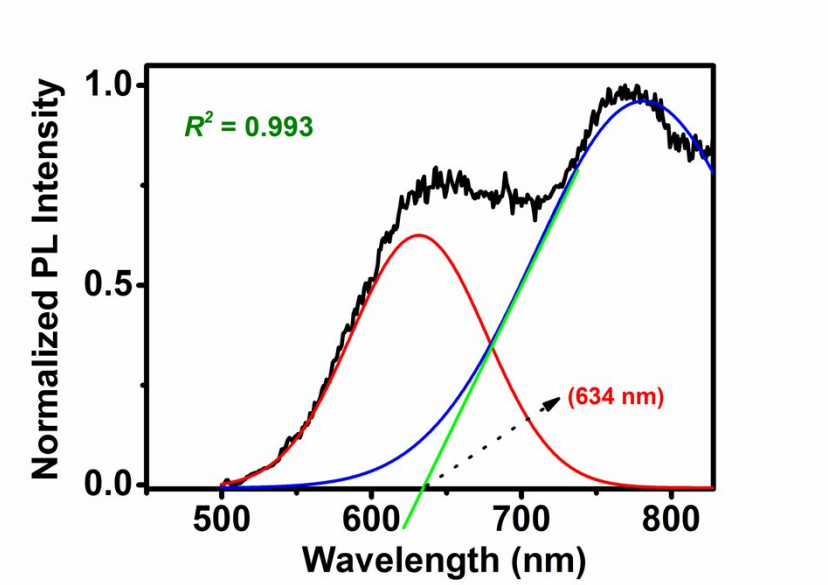


Fig. S1 Transient PL spectrum of **NA-TNA** measured at 77 K after 2 μs delay, and the spectral deconvolution results of the fluorescence and phosphorescence bands.

Table S2 Selected calculated absorption/emission energies (eV) and oscillator strength (f) along with the experimental data for **NA-TNA** in DMSO media at the levels of TD-M06-2X/6-311g(d, p) for the absorption and phosphorescence emission and TD-B3LYP/6-311g(d, p) for the fluorescence emission, based on their corresponding optimized geometries .

	ΔE_{cal}/eV	f	ΔE_{exp}/eV
Absorption	2.79	1.541	2.73
Fluorescence	1.87	0.482	1.80
Phosphorescence	1.33	-	1.74

Table S3 Fluorescence maximum data and PLQYs of CzPhONI, **NA-TNA**, and the blending films of **NA-TNA** in CzPhONI (1.4 wt%, 6.0 wt%, 10.0 wt%, and 15.0 wt%).

	λ_{PLmax} (nm)	PLQY
CzPhONI	496	0.069
NA-TNA (1.4 wt%)	566	0.802
NA-TNA (6.0 wt%)	575	0.668
NA-TNA (10.0 wt%)	583	0.605
NA-TNA (15.0 wt%)	592	0.336
NA-TNA (100 wt%)	635	0.068

λ_{PLmax}: PL emission maximum;

PLQY: absolute PL quantum yield, measured in an integrating sphere under ambient conditions (λ_{ex} = 380 nm).

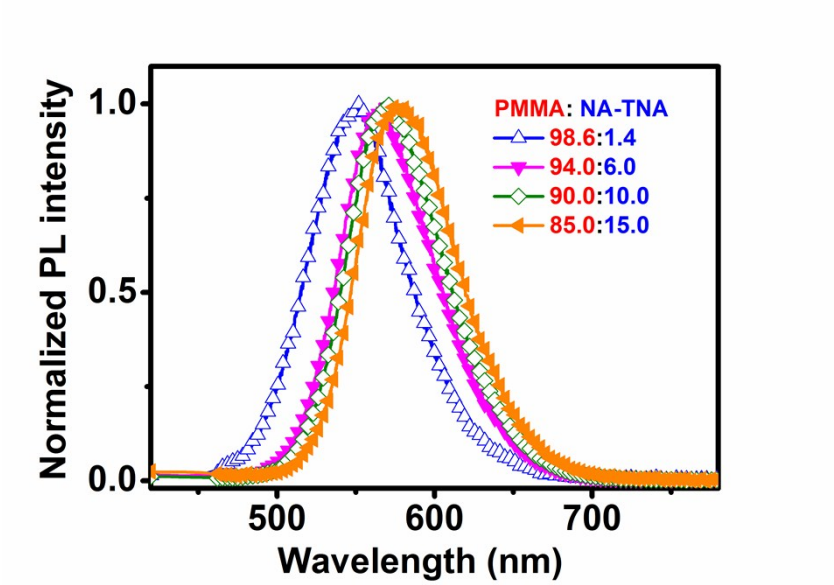


Fig. S2 Normalized fluorescence spectra of **NA-TNA** in PMMA with different doping levels in solid film state (λ_{ex} = 400 nm).

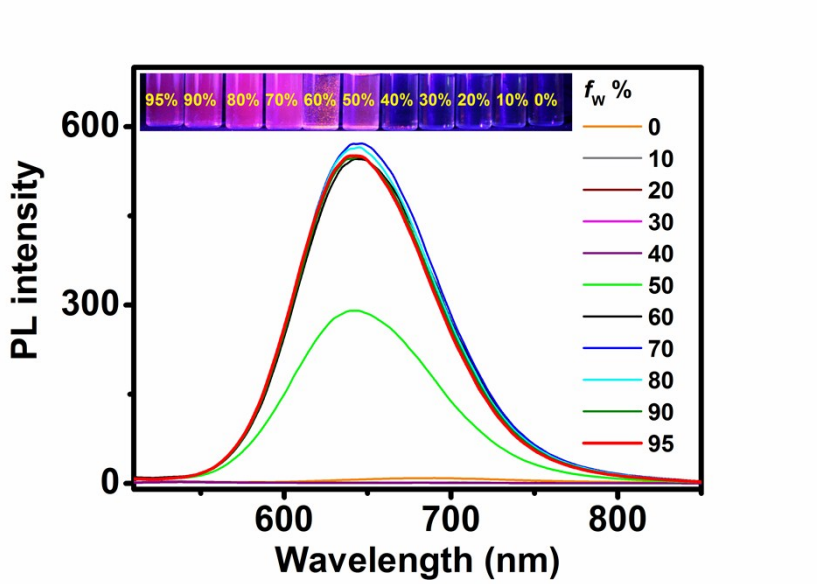


Fig. S3 PL spectra of **NA-TNA** (10 μM) in the MeCN/water mixtures with different water fractions (f_w, %)(λ_{ex} = 460 nm). Insets are the photographs of **NA-TNA** in MeCN/water mixture with different f_w (under irradiation at 365 nm).

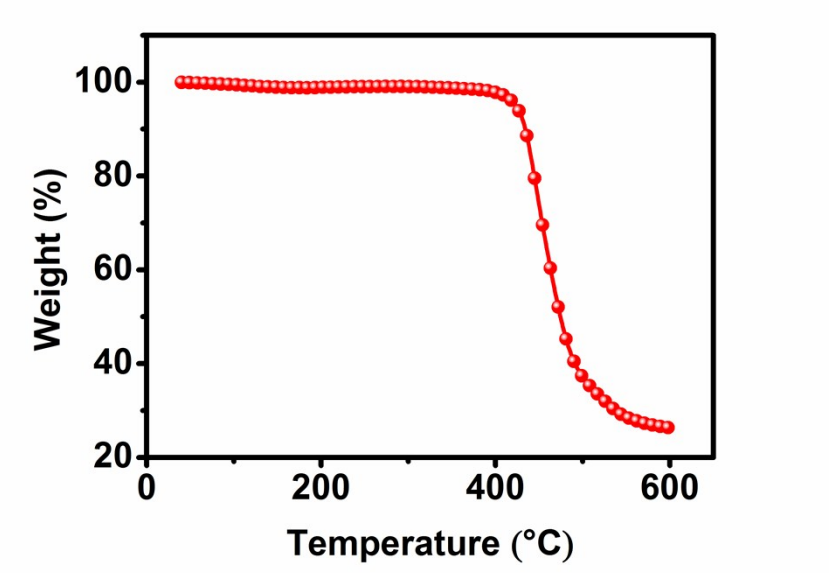


Fig. S4 TGA thermogram of **NA-TNA**.

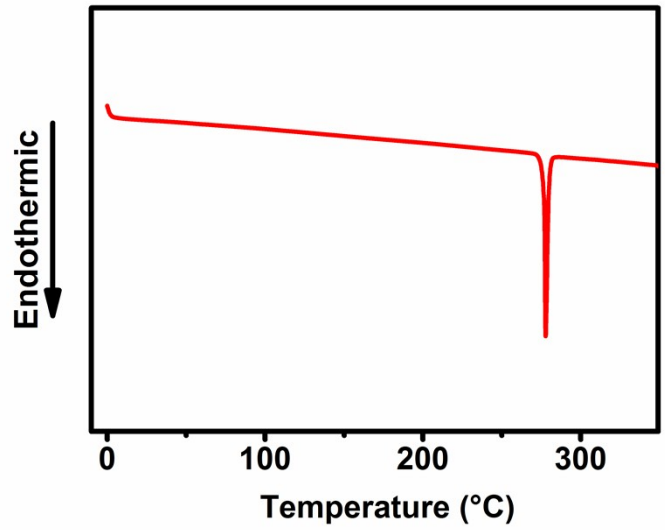


Fig. S5 DSC trace of **NA-TNA**.

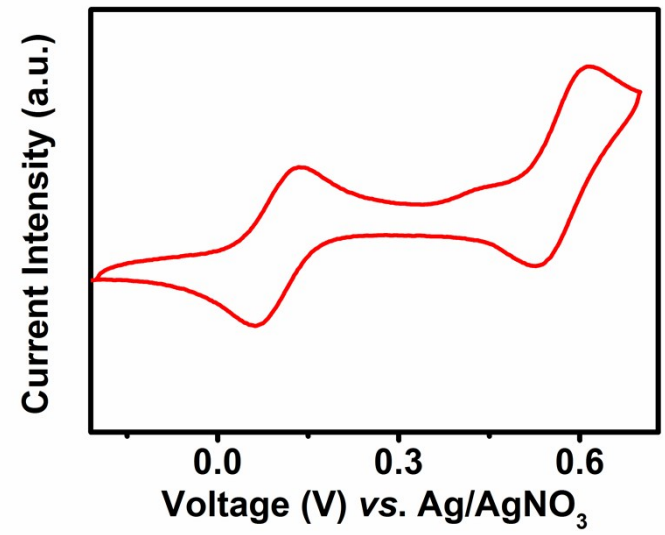


Fig. S6 Cyclic voltammogram of **NA-TNA**. The oxidation potential was determined relative to Ag/Ag^{+} in 5×10^{-4} mol·L^{-1} CH_2Cl_2 solution, using Fc/Fc^{+} as the internal reference.

3) Electroluminescence properties.

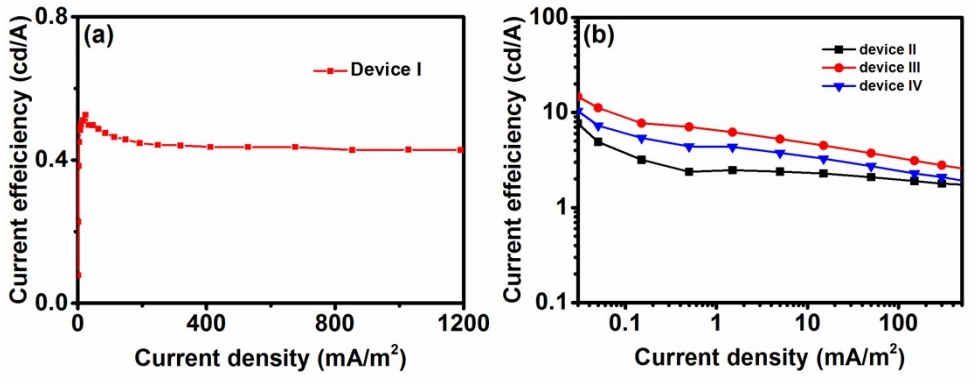


Fig. S7 Current efficiency–current density characteristics of devices I (a) and II-IV (b).

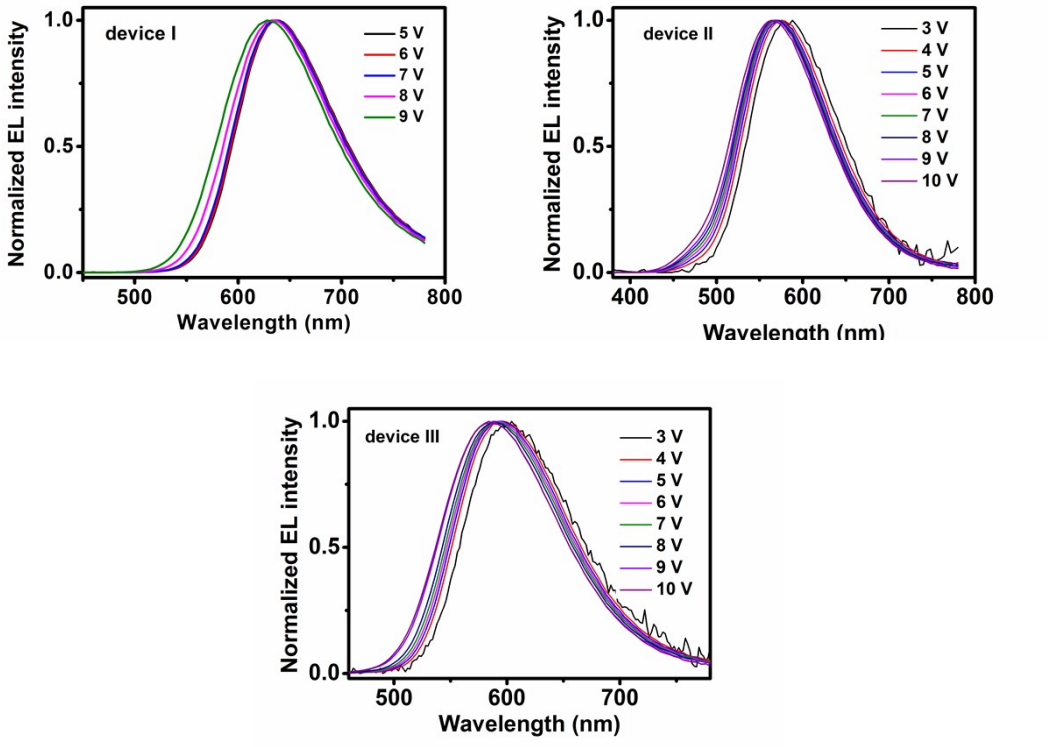


Fig. S8 The EL spectra of device I, II, and III under different driving voltages.

4) ^{1}NMR, ^{13}C NMR, FT-IR and HRMS spectra.

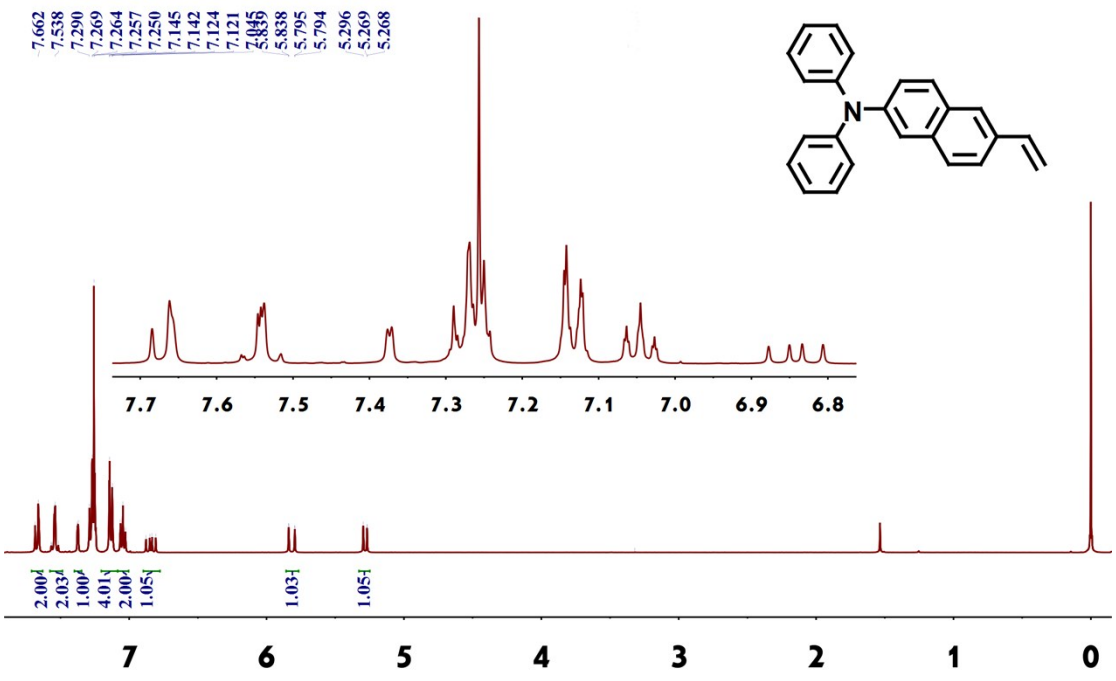


Fig. S9 The ^{1}H NMR spectrum of compound **3**.

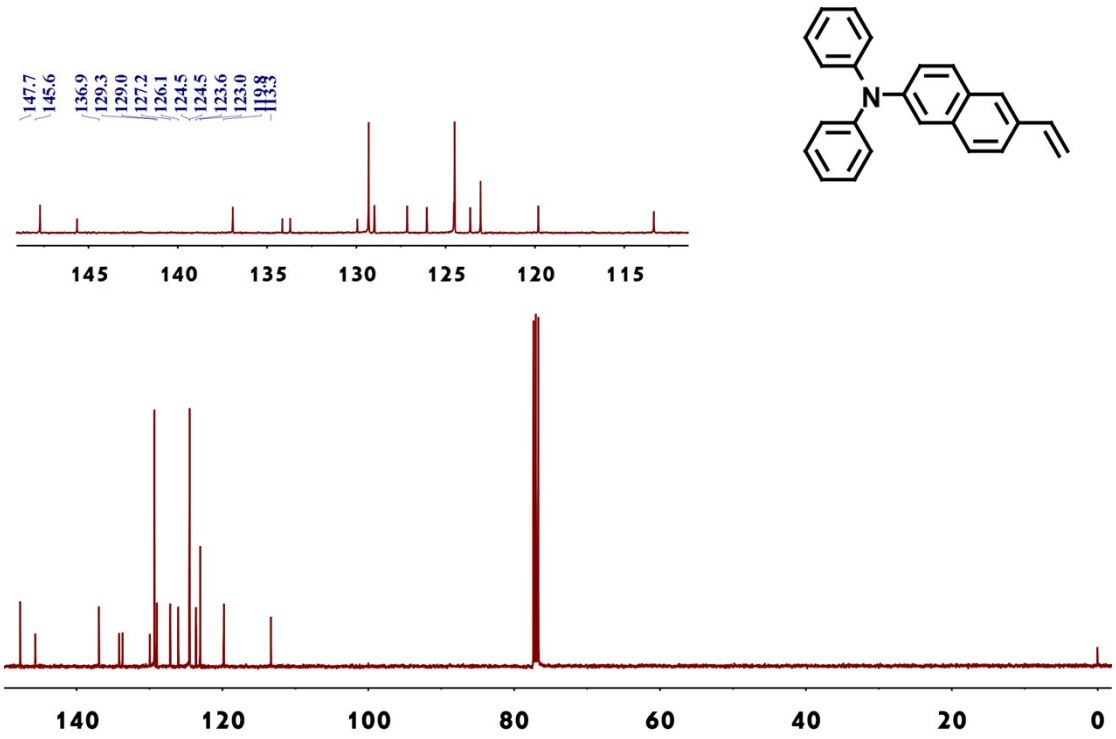


Fig. S10 The ^{13}C NMR spectrum of compound **3**.

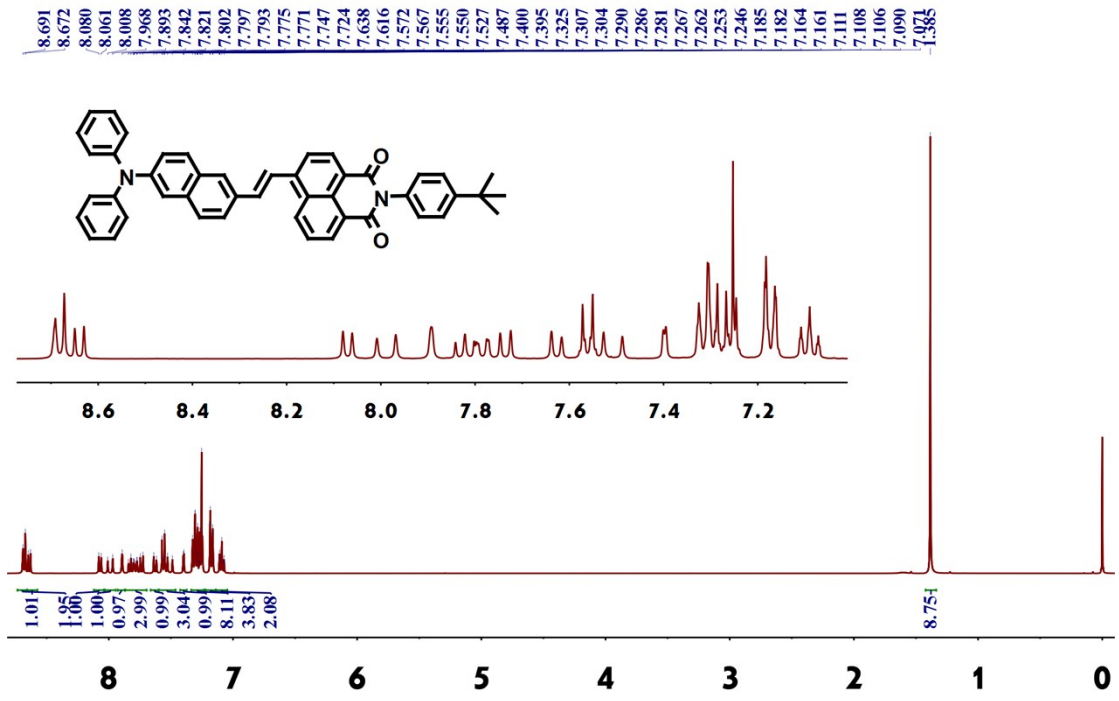


Fig. S11 The ^{1}H NMR spectrum of **NA-TNA**.

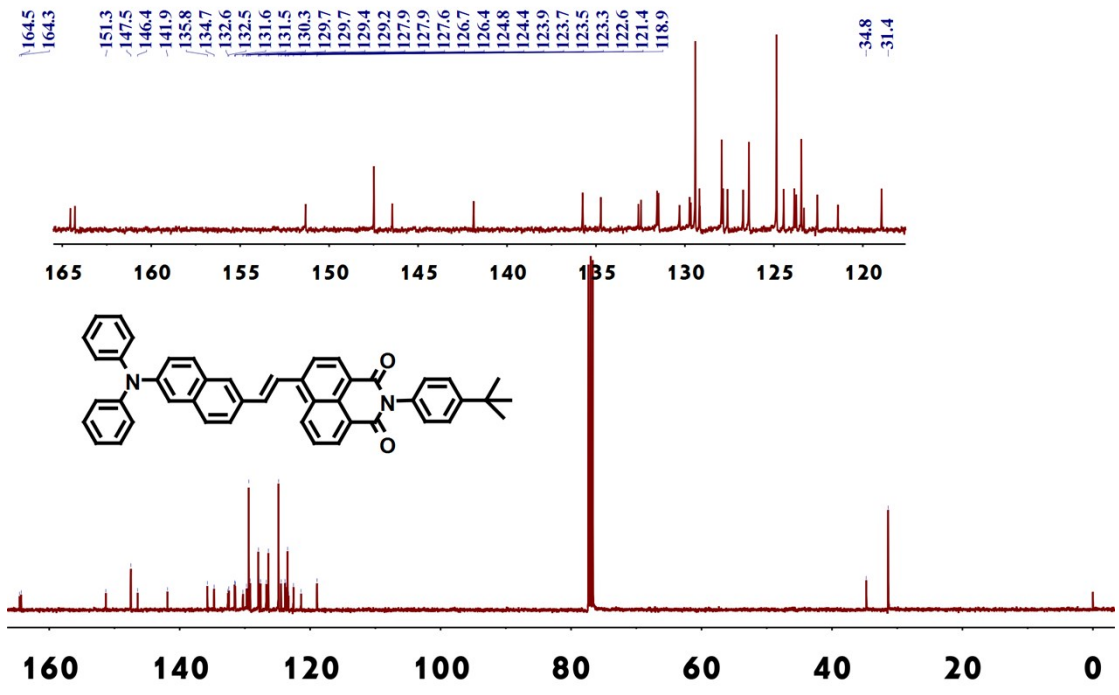


Fig. S12 The ^{13}C NMR spectrum of **NA-TNA**.

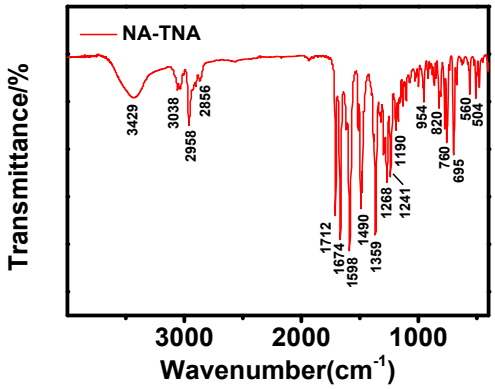


Fig. S13 The FT-IR spectrum of **NA-TNA**.

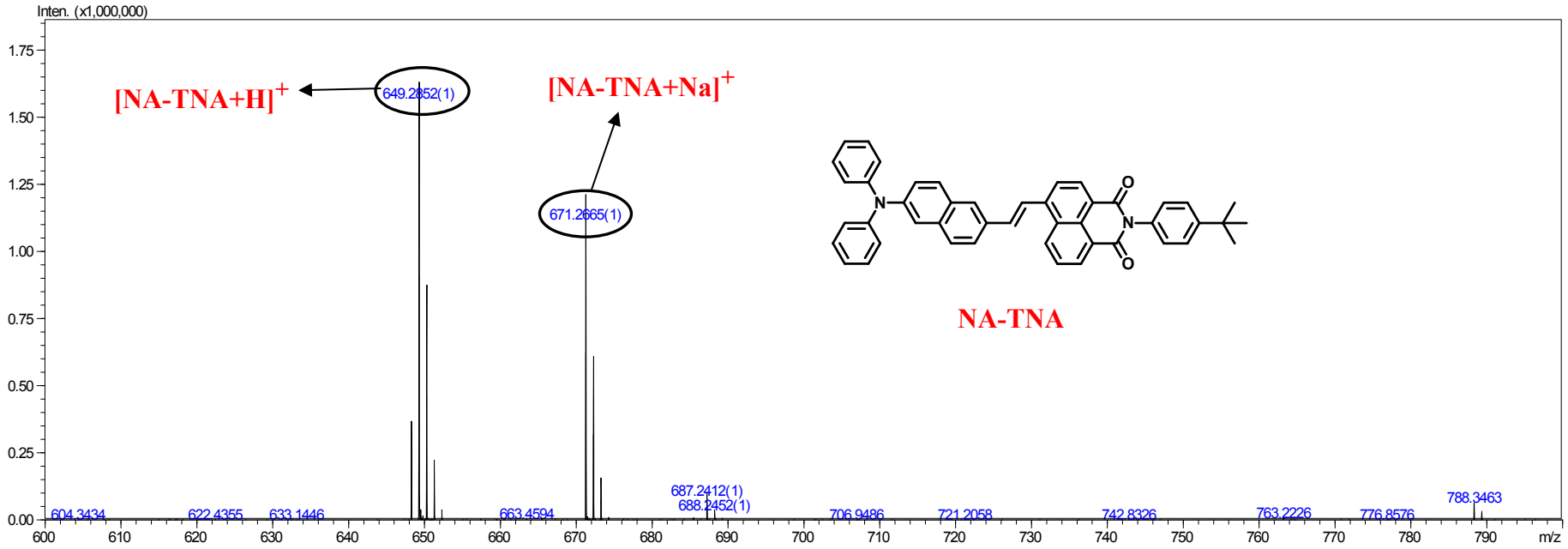


Fig. S14 The HRMS spectrum of **NA-TNA**.

5) References.

(1) B. A. Reinhardt, L. L. Brott, S. J. Clarson, A. G. Dillard, J. C. Bhatt, R. Kannan, L. X. Yuan, G. S. He and P. N. Prasad, *Chem. Mater*., 1998, **10**, 1863–1874.

(2) J. Zhou, P. Chen, X. Wang, Y. Wang, Y. Wang, F. Li, M. H. Yang, Y. Huang, J. S. Yu and Z. Y. Lu, *Chem. Commun*., 2014, **50**, 7586–7589.