# Electronic Supplementary Information (ESI)

## Small molecules based on diphenylamine and carbazole with large two-photon absorption cross sections and extraordinary AIEE properties

Guojian Tian,[a] Wei Huang,[a] Shengyun Cai,[a] Haitao Zhou,[a] Bo Li,[b] Qiaochun Wang[a] and Jianhua Su *[a]

[a]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai, 200237, P. R. China. E-mail: bbsjh@ecust.edu.cn; Fax: +86-21-64252758

[b]Key Laboratory of Polar Materials and Devices, Ministry of Education, East China N ormal University, Shanghai, 200241, P. R. China.

1. **Fig. 2** The one-photon absorption of **T1-T2** in THF at a concentration of $1.0\times10^{-5}$ M.
2. **Fig. 3** The emission spectra of **T1-T2** in different solvents at the concentration of $1.0\times10^{-5}$ M.
3. **Fig. 8** The 2PA cross sections of **T1-T2** in $CH_2Cl_2$.
4. Experimental procedures for synthesis.
5. **Fig. S1-S6** $^{1}H$, $^{13}C$ NMR and EI-TOF spectrum of **T1-T2**.
6. **Fig. 9** The effect of pH on the one-photon fluorescence of **T1-T2**.

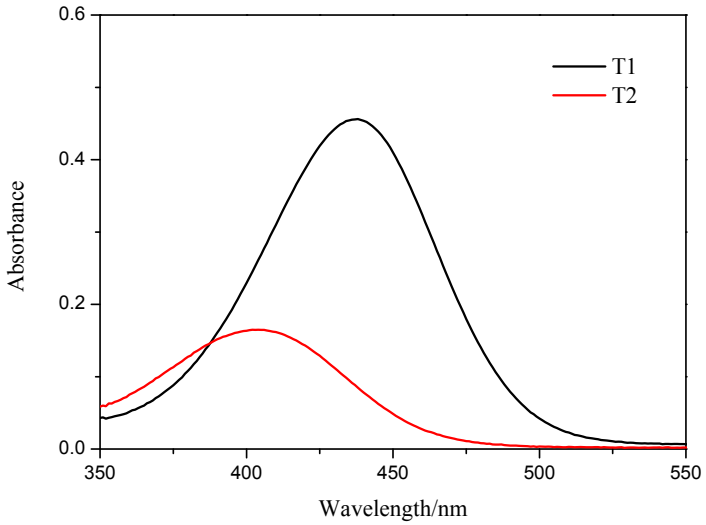



**Fig. 2** The one-photon absorption of **T1-T2** in THF at a concentration of $1.0\times10^{-5}$ M.

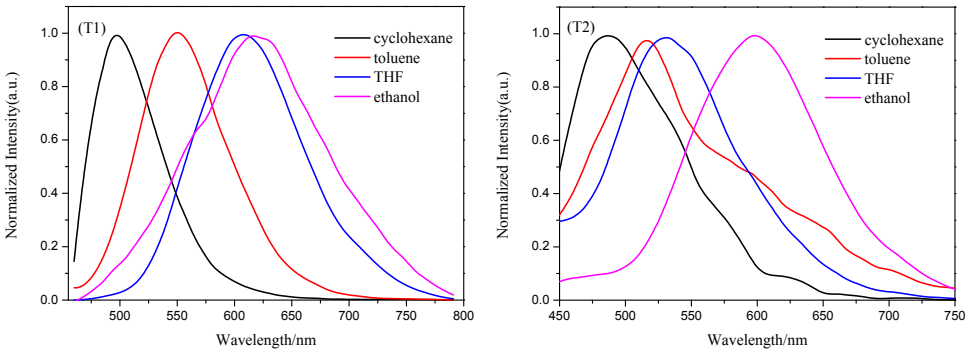



**Fig. 3** The emission spectra of **T1-T2** in different solvents at the concentration of $1.0\times10^{-5}$ M.

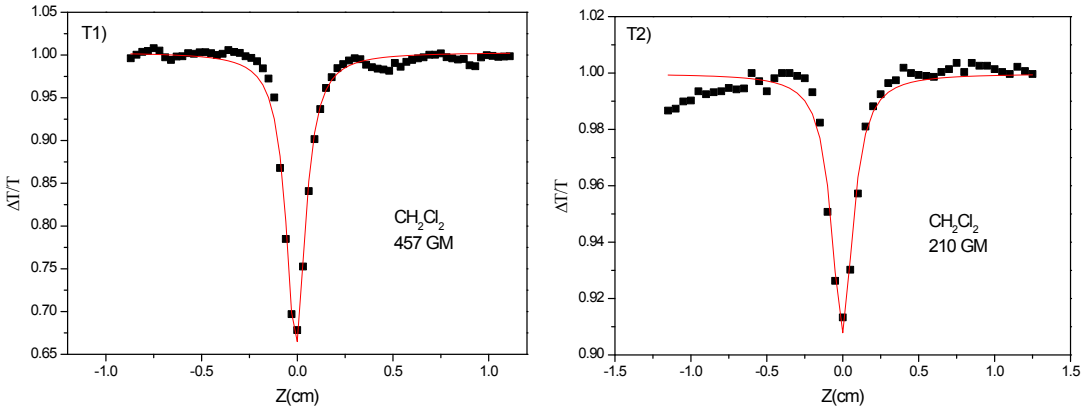
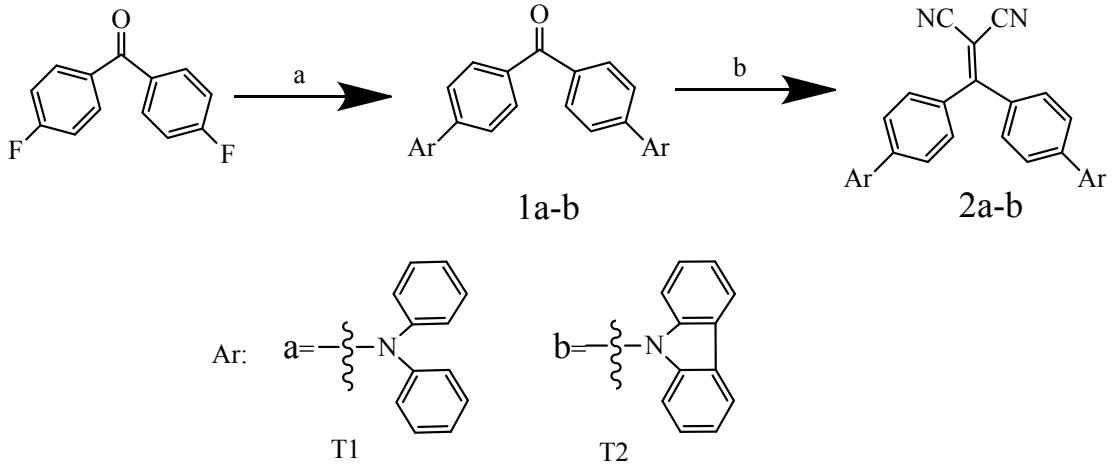



**Fig. 8** The 2PA cross sections of **T1-T2** in $CH_2Cl_2$.

## 4. Experimental procedures for synthesis.




**Scheme 1**. Reagents and conditions: a) t-BuOK, DMF, 110°C, 10h; b) malononitrile, THF, $Et_3N$, r.t, 2h.

### Synthesis

**Bis(4-(diphenylamino)phenyl)methanone(1a):** In a three-neck flask, diphenylamine (3.4g 20mmol) and potassium tertbutoxide (3.37g 30mmol) were dissolved in 100mL anhydrous DMF, the bis(4-fluorophenyl)-methanone (2.18g 10mmol) was slowly dropped into 30mL anhydrous DMF solution. The reaction mixture was refluxed for 10 h under $N_2$ atmosphere, when the mixture was cooled and then poured into 200 mL ice water, then a deep yellow solid precipitate was filtered off and washed with ethanol. After vacuum evaporated obtaining a 3.6 g yellow solid. Yield: 79.0 %. $^1$H NMR ($CDCl_3$, 400 MHz, TMS)δ: 7.74 (m, 4H), 7.35 (m, 8H), 7.22 (m, 8H), 7.14 (m, 4H), 7.02 (d, $J$ = 8.8 Hz, 4H).

**Bis(4-(9H-carbazol-9-yl)phenyl)methanone(1b):** Compound **1b** was synthesized by the same procedure as described above for **1a** using bis(4-fluorophenyl)methanone and carbazole. Yield: 85 %. $^1$H NMR ($CDCl_3$, 400 MHz, TMS)δ: 8.18 (dd, $J$ = 8.1, 3.1 Hz, 8H), 7.80 (d, $J$ = 8.5 Hz, 4H), 7.57 (d, $J$ = 8.2 Hz, 4H), 7.48 (m, 4H), 7.37 (m, 4H).

**2-(bis(4-(diphenylamino)phenyl)methylene)malononitrile (2a):** In a one-neck flask, bis(4-(diphenylamino)phenyl)methanone (208 mg, 0.5 mmol) and malononitrile(50 mg, 0.75 mmol) were dissolved in THF (30 mL). Then a few drops of triethylamine were added and which was stirred at room temperature for 2 h. After vacuum evaporated obtaining the crude product and purifying by column chromatography (silica gel. $CH_2Cl_2$/petroleum ether =1:1, v/v) to give a yellow solid (115 mg, 43.0 %); $^1$H NMR ($CDCl_3$, 400 MHz, TMS)δ: 7.68 (d, $J$ = 8.2 Hz, 4H), 7.31 (m, 8H), 7.17 (m, 8H), 7.12 (m, 4H), 7.02 (d, $J$ = 7.8 Hz, 4H). $^{13}$C NMR ($CDCl_3$, 100MHz, TMS), 151.95, 145.92, 132.73, 129.70, 127.43, 126.39, 125.22, 118.73, 116.04. EI-TOF: [M] calcd for $C_{40}H_{28}N_4$ : 564.2314, found: 564.2312. Anal. Calcd for $C_{40}H_{28}N_4$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.95; H, 5.03; N, 9.88 %.

**2-(bis(4-(9H-carbazol-9-yl)phenyl)methylene)malononitrile (2b):** Compound **2b** was synthesized by the same procedure as described above for **2a** using bis(4-fluorophenyl)methanone and carbazole. Yield: 41.0 %. $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS)δ: 8.17 (d, *J* = 4.2 Hz, 4H), 7.84 (s, 8H), 7.59 (d, *J* = 8.1 Hz, 4H), 7.48 (m, 4H), 7.36 (m, 4H). $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS), 142.38, 142.31, 139.94, 133.87, 132.44, 126.63, 126.38, 124.09, 121.04, 120.60, 114.03, 109.82. EI-TOF: [M] calcd for $C_{40}H_{24}N_4$ : 560.2001, found: 560.2002. Anal. Calcd for $C_{40}H_{24}N_4$: C, 85.69; H, 4.31; N, 9.99. Found: C, 85.52; H,4.23; N, 9.97 %.

## 5. Fig. S1-S6 $^{1}$H, $^{13}$C NMR and EI-TOF spectrum of T1-T2.

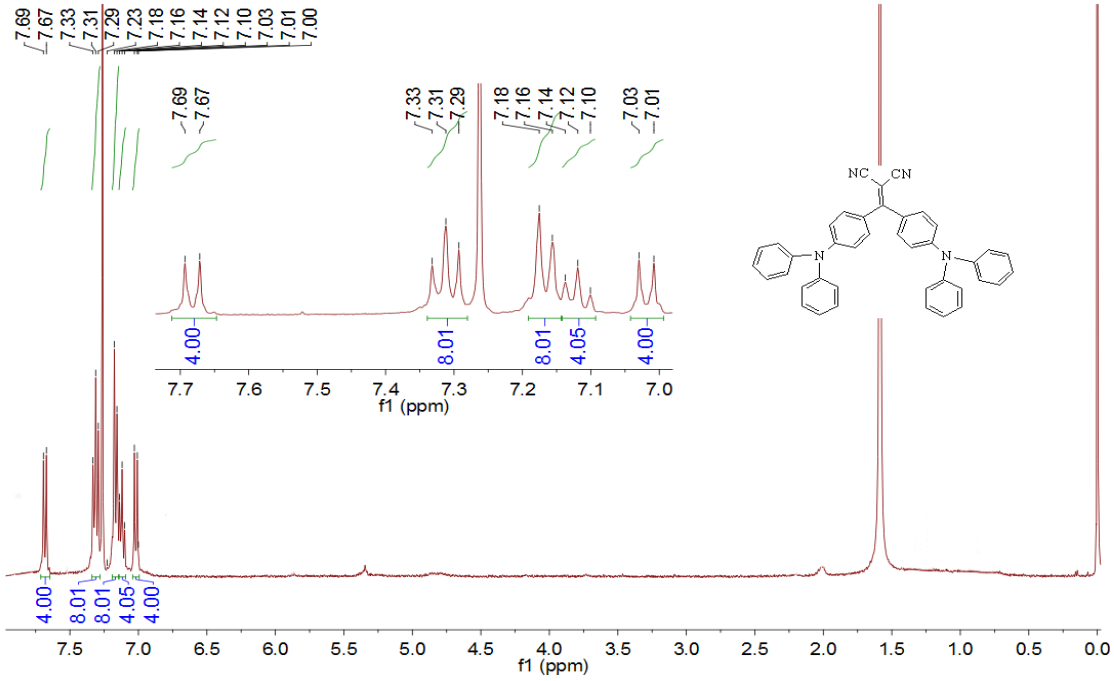



**Fig. S1** $^{1}$H NMR ($CDCl_3$, 400 MHz) spectrum of **T1.**

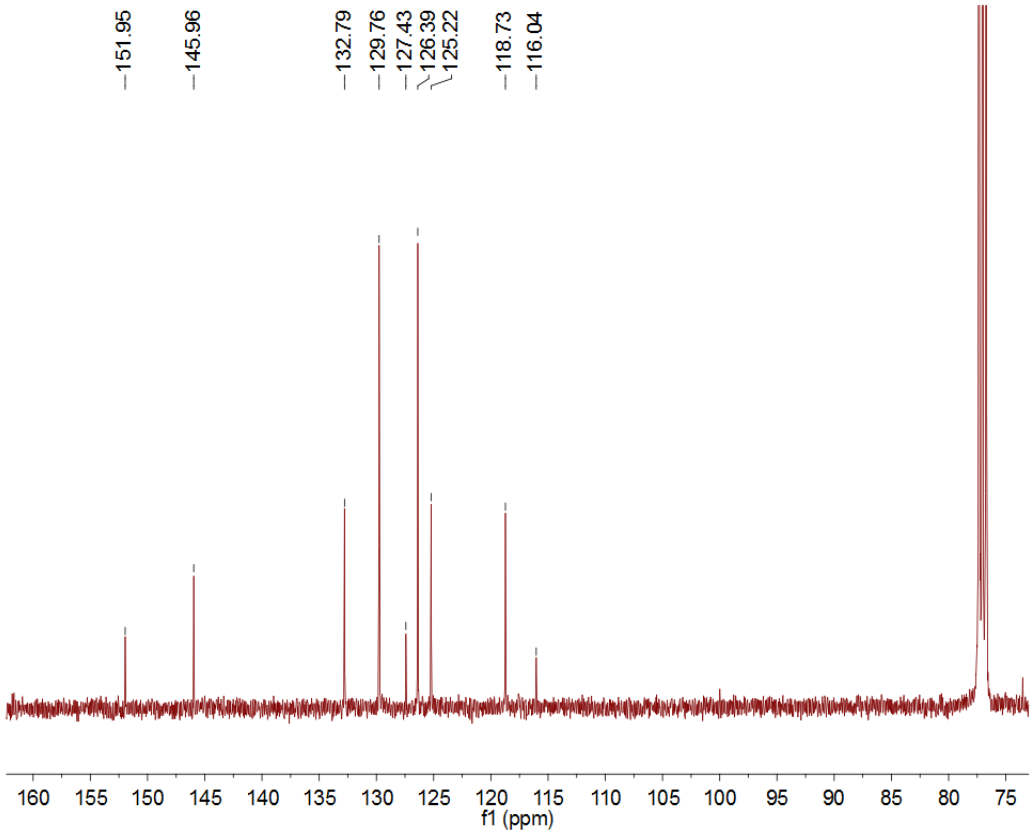
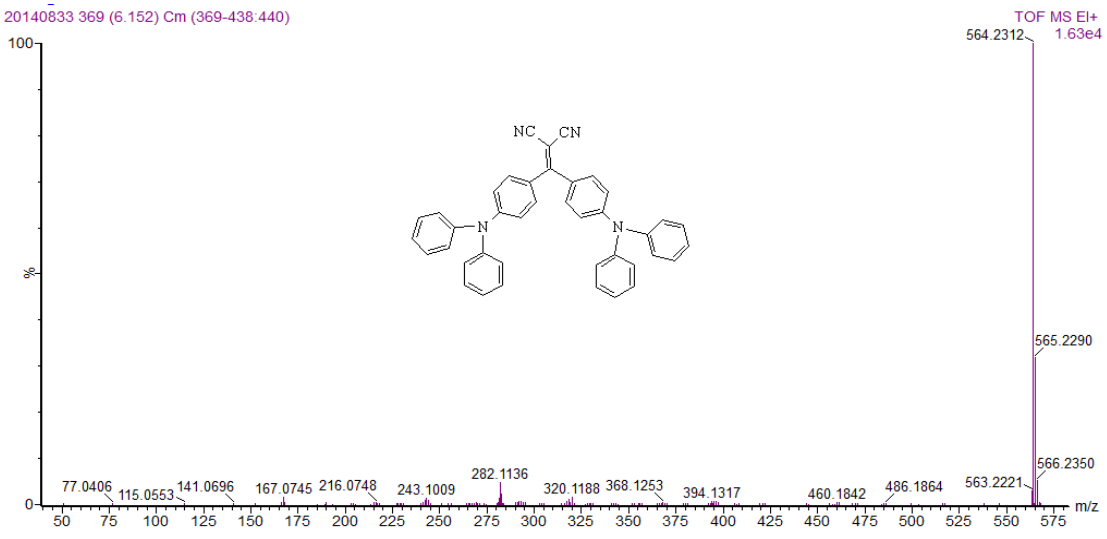



**Fig. S2** $^{13}C$ NMR ($CDCl_3$, 100 MHz) spectrum of **T1.**




| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|---|
| 564.2312 | 100.00 | 564.2314 | -0.2 | -0.4 | 29.0 | 544.1 | C40 H28 N4 |

**Fig. S3** EI-TOF spectrum of **T1.**

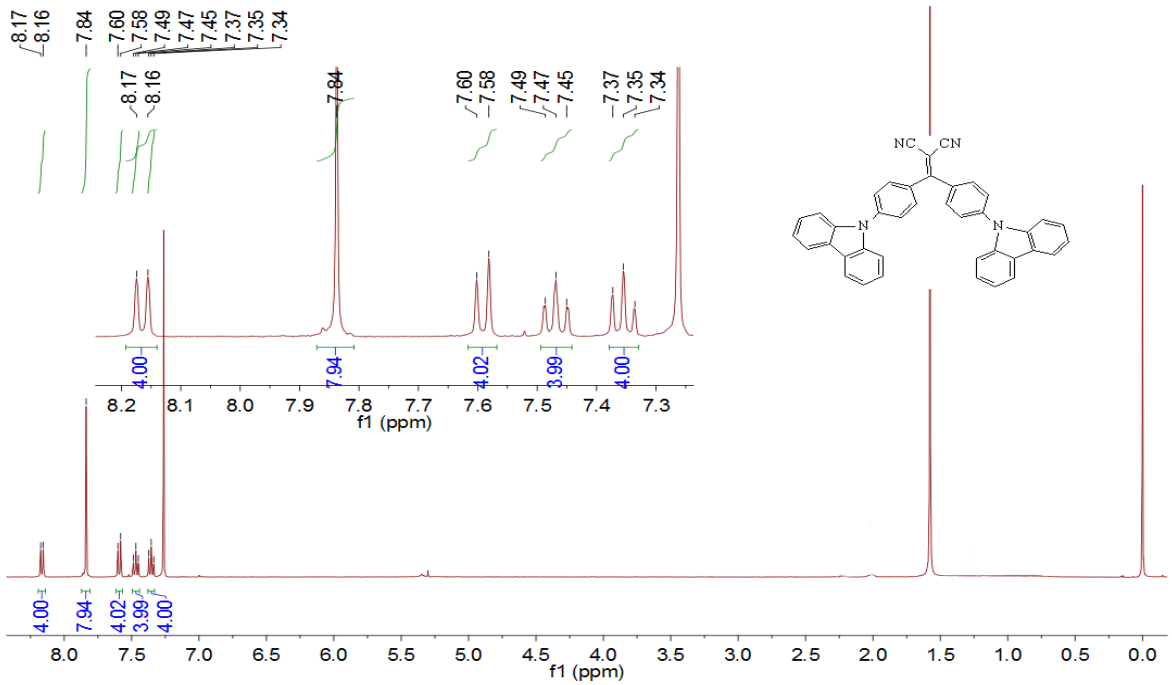



**Fig. S4** $^{1}$H NMR ($CDCl_3$, 400 MHz) spectrum of **T2.**

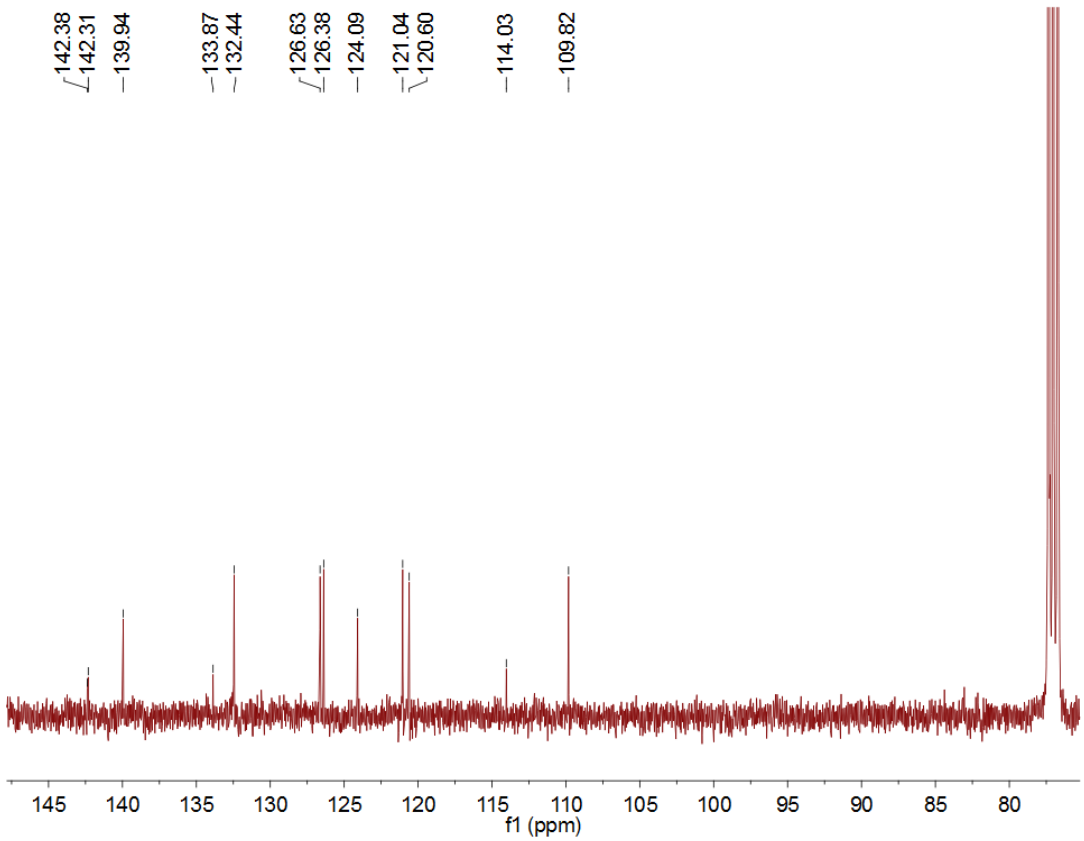
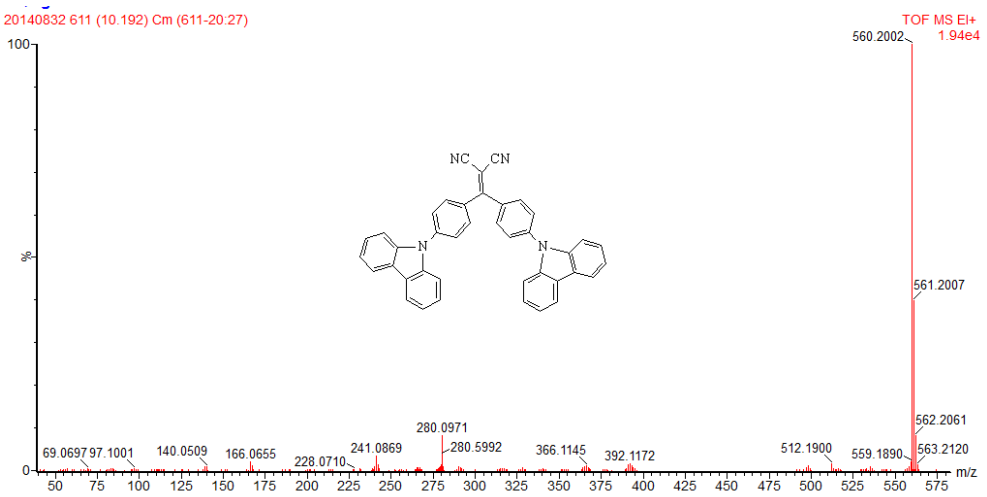



**Fig. S5** $^{13}$C NMR ($CDCl_3$, 100 MHz) spectrum of **T2.**




| Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|---|
| 560.2002 | 100.00 | 560.2001 | 0.1 | 0.2 | 31.0 | 102.8 | C40 H24 N4 |

**Fig. S6** EI-TOF spectrum of **T2.**

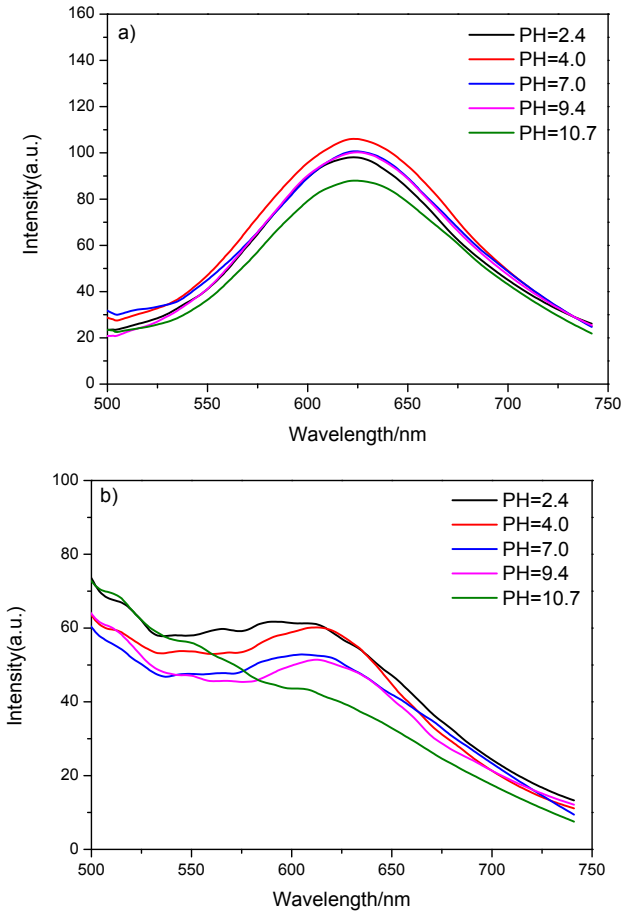



**Fig. 9** (a, b) The PL spectra of **T1-T2**, in different pH values at a concentration of $1.0\times10^{-5}$ M. Excitation wavelength: 443 nm (**T1**), 409 nm (**T2**). PH = 2.4, 4.0, 7.0 were made by different buffer solutions being consisted of $Na_2HPO_4$ and $C_4H_2O_7{\cdot}H_2O$; PH = 9.4, 10.7 were made by different buffer solutions being consisted of $Na_2CO_3$ and $NaHCO_3$.