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

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1. Fig. 2 The one-photon absorption of T1-T2 in THF at a concentration of 1.0×10⁻⁵ M.

2. Fig. 3 The emission spectra of T1-T2 in different solvents at the concentration of 1.0×10⁻⁵ M.

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Fig. 2 The one-photon absorption of T1-T2 in THF at a concentration of $1.0 \times 10^{-5}$ M.

Fig. 3 The emission spectra of T1-T2 in different solvents at the concentration of $1.0 \times 10^{-5}$ M.

Fig. 8 The 2PA cross sections of T1-T2 in CH$_2$Cl$_2$. 
4. Experimental procedures for synthesis.

Scheme 1. Reagents and conditions: a) t-BuOK, DMF, 110°C, 10h; b) malononitrile, THF, Et$_3$N, 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$_2$Cl$_2$/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. El-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)$\delta$: 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.](image-url)
**Fig. S2** $^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of T1.

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

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**Fig. 9** (a, b) The PL spectra of T1-T2, in different pH values at a concentration of 1.0×10⁻⁵ 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 Na₂HPO₄ and C₄H₂O₇·H₂O; PH = 9.4, 10.7 were made by different buffer solutions being consisted of Na₂CO₃ and NaHCO₃.