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Electronic Supplementary Information

Intriguing emission properties of triphenylamine-carborane systems

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Experimental

General Procedures

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in the glove box under the vacuum atmospheres. Solvents were purchased from Samshun pure chemical company and used without purification. Glassware, syringe, magnetic stirring bar, and needle were dried in a convection oven overnight. Decaborane ($B_{10}H_{14}$) was purchased from Katchem and used after sublimation. The starting materials **1**, **2**, **3** and **4** were synthesized according to the literature procedure.[S1,S2]

The ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Buruker 300 spectrometer operating at 300.1 and 100.5, 128.4 MHz, respectively. ^{1}H, ^{11}B and ^{13}C NMR chemical shifts were measured relative to internal residual peaks from the lock solvent (99.9% $CDCl_3$), and then referenced to TMS ($Si(CH_3)_4$, 0.00 ppm). The HR-MS analysis was performed by high sensitive LC/MS/MSn (n=10) spectrometer (Thermo Fisher Scientific, LCQ Fleet Hyperbolic Ion Trap MS/MSn Spectrometer). An UV-Vis-NIR spectrophotometer (Agilent Technologies, Cary 5000) and a fluorescence spectrophotometer (Varian, Cary Eclipse) were used to measure the absorption and emission spectra, respectively.

Synthetic details

1-(4-triphenylamine)-2-phenyl-*o*-carborane (1a)

A mixture of **1** (2.0 g, 4.40 mmol), diphenylamine (1.79 g, 10.56 mmol), K_2CO_3 (1.82 g, 13.20 mmol), $Pd(PPh_3)_4$ (0.30 g, 0.33 mmol) and 1,1'-Bis(diphenylphosphino)ferrocene (0.3 g, 0.54 mmol) were dissolved in dry toluene (50 mL). The mixture was stirred under N_2 atmosphere for overnight at 110 ˚C. The mixture solution was cool to the room temperature, and then organic layer was extracted with CH_2Cl_2 (3 times with 20 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using CH_2Cl_2/hexane (1:3) eluent to afford (0.92 g, 53% yield) as a yellowish solid. ^{1}H NMR ($CDCl_3$): δ 7.48 (d, J = 7.5 Hz, 2H), 7.34-7.21 (m, 9H), 7.08 (t, J =7.2 Hz, 2H), 7.99 (d, J = 7.8 Hz, 4H), 6.74 (d, J = 9.3 Hz, 2H). ^{11}B NMR ($CDCl_3$): δ -0.81, -9.00. ^{13}C NMR ($CDCl_3$): δ 149.35, 146.68, 132.62, 132.35, 131.72, 130.82, 130.75, 130.54, 130.30, 130.00, 129.24, 128.71, 127.60, 126.15, 125.54, 125.12, 124.71, 124.40, 123.18, 123.11, 121.48, 120.17, 119.76, 86.12, 85.57. The ESI-MS calculated for $C_{26}H_{29}B_{10}N$ was 465.3231. Found: 466.3309 $[M+H]^+$.

1,2-*bis*(4-triphenylamine)-*o*-carborane (1b)

The compound was synthesized according to a procedure similar to that for 1a, using 2 instead of 1, to give 0.73 g of white powder (66.7% yield). ^{1}H NMR ($CDCl_3$): δ 7.29-7.20 (m, 10H), 7.10-7.01 (m, 14H), 6.78 (d, J = 9.3 Hz, 4H). ^{11}B NMR ($CDCl_3$): δ -0.90, -8.86. ^{13}C NMR ($CDCl_3$): δ 149.44, 146.84, 131.74, 129.65, 125.37, 124.20, 123.39, 120.62, 86.36. The ESI-MS calculated for $C_{38}H_{38}B_{10}N_2$ was 632.3966. Found: 633.4057 $[M+H]^+$.

1-(3-triphenylamine)-2-phenyl-*o*-carborane (2a)

The compound was synthesized according to a procedure similar to that for **1a**, using **3** instead of **1**, to give 1.46 g of white powder (72% yield). ^{1}H NMR ($CDCl_3$): δ 7.40 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 6.6 Hz, 1H), 7.26-7.21 (m, 6H), 7.11-6.97 (m, 5H), 6.85 (t, J = 10.2 Hz, 5H). ^{11}B NMR ($CDCl_3$): δ -0.83, -8.87. ^{13}C NMR ($CDCl_3$): δ 147.82, 147.14, 131.55, 131.18, 130.78, 130.59, 130.43, 130.24, 129.53, 129.10, 128.81, 128.60, 128.39, 127.66, 127.42, 126.29, 125.97, 125.70, 125.34, 124.78, 124.52, 123.97, 123.63, 122.64, 85.30, 85.10. The ESI-MS calculated for $C_{26}H_{29}B_{10}N$ was 465.3231. Found: 466.3271 $[M+H]^+$.

1,2-*bis*(4-triphenylamine)-*o*-carborane (2b)

The compound was synthesized according to a procedure similar to that for **1a**, using **4** instead of **1**, to give 1.03 g of white powder (79.2% yield). ^{1}H NMR ($CDCl_3$): δ 7.27-7.22 (m, 3H), 7.16 (s, 1H), 7.09-7.03 (m, 4H), 7.01-6.91 (m, 7H). ^{11}B NMR ($CDCl_3$): δ -0.84, -8.92. ^{13}C NMR ($CDCl_3$): δ 147.87, 147.16, 131.71, 130.59, 130.34, 130.26, 130.08, 129.72, 128.85, 128.77, 128.62, 126.33, 126.01, 125.51, 124.60, 124.57, 123.71, 122.72, 85.11. The ESI-MS calculated for $C_{38}H_{38}B_{10}N_2$ was 632.3966. Found: 633.4016 $[M+H]^+$.

References

S1 M. J. Mio, L. C. Kopel, J. B. Braun, T. J. Kadzikwa, K. L. Hull and R. G. Brisbois, *Org. Lett.*, 2002, 4, 3199.

S2 J. O. Huh, H. Kim, K. M. Lee, Y. S. Lee, Y. Do, M. H. Lee, *Chem. Commun*. 2010, 46, 1138–1140.

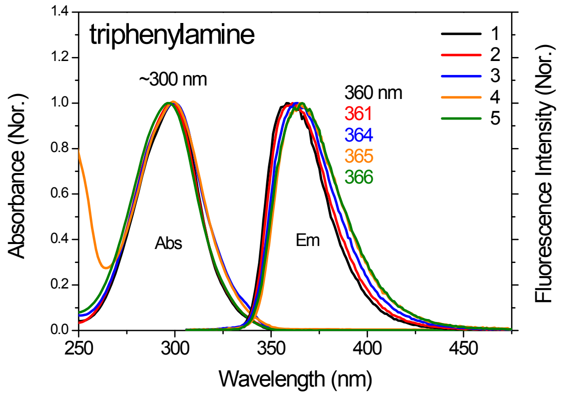

Fig. S1. Absorption and emission spectra of triphenylamine in various solvents: 1, *n*-hexane; 2, ethyl ether; 3, THF; 4, CH_2Cl_2; 5, CH_3CN.

Table S1. Absorption and emission maxima (nm), and extinction coefficient (*ε*) for *para*-substituted dyads measured in different solvents

	1a		**1b**	
	λ_{abs} (log ε)	λ_{em}	λ_{abs} (log ε)	λ_{em}
n-hexane	302 (4.3)	399	302 (4.5)	372
	328 (4.4)	590	321 (4.5)	590
Ethyl ether	301 (4.3)	422	302 (4.6)	393
	329 (4.4)		324 (4.6)	
THF	303 (4.2)	432	304 (4.4)	382
	330 (4.3)		325 (4.5)	
CH_2Cl_2	306 (4.3)	446	307 (4.5)	393
	331 (4.3)		326 (4.5)	
CH_3CN	304 (4.3)	461	304 (4.5)	399
	332 (4.3)		322 (4.5)	

Table S2. Absorption and emission maxima (nm), and extinction coefficient (*ε*) for *meta*-substituted dyads measured in different solvents

	2a		**2b**	
	abs (log *ε*)	em	abs (log *ε*)	em
n-hexane	300 (4.4)	409	299 (nd)	362
		683		412
				661
Ethyl ether	298 (4.4)	436	297 (4.6)	362
				436
THF	300 (4.4)	448	299 (4.6)	366
				454
CH_2Cl_2	301 (4.4)	459	300 (4.6)	369
				462
CH_3CN	297 (4.4)	471	297 (nd)	369
				474

nd: Exact values were not determined owing to poor solubility

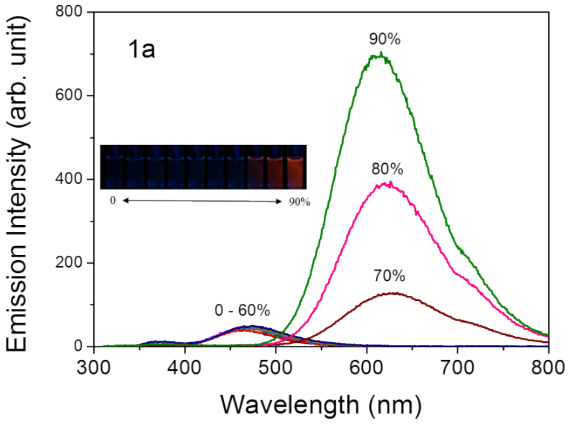

Fig. S2. Emission spectra of **1a** (2 μM) in H_2O-CH_3CN. λ_{ex} = 300 nm. Inset photograph: Emission images of **1a** in CH_3CN (0 %) and aqueous mixtures (10—90%, interval fraction is 10 %) under 365 nm-UV illumination.