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Electronic Supplementary Information (ESI)

Triphenylamine-boron complexes: Molecular thermometer and alkyl chain controlled molecular fluorescent liquids



Scheme S1. Synthesis of **TPA-BF**₂ complexes.







¹H & ¹³C NMR of **TPA-BF₂-3**



¹H & ¹³C NMR of **TPA-BF₂-4**



¹H & ¹³C NMR of **TPA-BF₂-5**



¹H & ¹³C NMR of **TPA-BF₂-6**



 $^{1}\mathrm{H}$ & $^{13}\mathrm{C}$ NMR of $TPA\text{-}BF_{2}\text{-}7$



¹H & ¹³C NMR of **TPA-BF₂-8**

TPA-BF₂-2: m/z calculated $C_{21}H_{19}BF_2N_2O$ (M + H): 364.16, found: 364.10

 $\textbf{TPA-BF_2-3:}\ m/z\ calculated\ C_{22}H_{21}BF_2N_2O\ (M+H):$ 378.17, found: 377.90.

TPA-BF₂-4: m/z calculated $C_{23}H_{23}BF_2N_2O$ (M + H): 392.19, found: 392.10.

 $\textbf{TPA-BF}_2\textbf{-5}\text{:}\ m/z\ calculated\ C_{24}H_{25}BF_2N_2O\ (M+H)\text{:}\ 406.20,\ found:\ 407.00.$

 $\textbf{TPA-BF_2-6:}\ m/z\ calculated\ C_{25}H_{27}BF_2N_2O\ (M+H):$ 420.23, found: 420.20.

 $\label{eq:transform} \textbf{TPA-BF_2-7:} \ m/z \ calculated \ C_{26}H_{29}BF_2N_2O \ (M+H): 434.33, \ found: \ 434.20.$

 $\label{eq:TPA-BF2-8:m/z} \textbf{TPA-BF2-8:m/z} \ calculated \ C_{27}H_{31}BF_2N_2O \ (M+H): 448.25, \ found: \ 448.20.$

Table. Structure corresponding to the major two peaks of mass spectra.

Structure	Found M.wt.

TPA-BF ₂ -5	
	Fragment 1: Peak value: 372.900 M.wt: 372.51
	OH
TPA-BF ₂ -6	Fragment 2: Peak value (M + Na): 862.40
	Found (MI+ INa): 801.0
	Fragment 1: Peak value: 386.90 M.wt: 386.54
	Fragment 2:
$\mathbf{TPA}-\mathbf{BF}_{2-7}$	Peak value (M + Na): 890.40 Found (M+ Na): 889.65
2 2 -	N ⁻ ^B - ^F F ⁻ ^B - ^F F ⁻ ^B - ^N

	Quantum yield (%)				
TPA-BF ₂ -2	1.9				
TPA-BF ₂ -3	2.2				
TPA-BF ₂ -4	4.1				

	Fragment 1: Peak value: 401.00 M.wt: 400.57 Fragment 2: Peak value (M + Na): 918.50 Found (M+ Na): 917.70
TPA-BF ₂ -8	

Table S1. Fluorescence efficiency of TPA-BF₂ complexes.

TPA-BF ₂ -5	7.5
TPA-BF ₂ -6	7.8
TPA-BF ₂ -7	12.6
TPA-BF ₂ -8	8.2

Figure S1. Digital fluorescence images of TPA-BF₂ complexes. $\lambda_{exc} = 365$ nm.

Figure S2. FE-SEM images of TPA-BF₂-5 and TPA-BF₂-6 complexes.

TPA-BF2-2 TPA- BF2-3 TPA BF2-4 TPA- BF2-5 TPA- BF2-6 TPA- BF2-7 TPA- BF2-8

Figure S3. Digital images of TPA-BF₂ complexes.

Figure S4. Fluorescence spectra of TPA-BF₂-8 at RT and 77K.

Figure S5. HOMO-LUMO molecular orbital diagram of TPA-BF₂-4.

Figure S6. Disordered molecular structure and ORTEP (50% probability) structure of $TPA-BF_2-4$.

2θ (deg)

Figure S7. PXRD of TPA-BF₂-4.

Table S2. Quantum yield of $TPA-BF_2$ complexes in different solvent compared to quinine sulphate standard.

Figure S8. Fluorescence spectra of (a) TPA-BF₂-3, (b) TPA-BF₂-4, (c) TPA-BF₂-6 and (d) TPA-BF₂-8 in different solvent polarity.

Figure S9. Fluorescence spectra of (a) $TPA-BF_2-4$ and (b) $TPA-BF_2-7$ in different solvent polarity.

Figure S10. Absorption spectra of (a) $TPA-BF_2-2$, (b) $TPA-BF_2-3$, (c, h) $TPA-BF_2-4$, (d) $TPA-BF_2-5$, (e) $TPA-BF_2-6$, (f, h) $TPA-BF_2-7$ and (g) $TPA-BF_2-8$ in different solvent polarity.

Figure S11. Fluorescence tuning of (a) **TPA-BF₂-4**, (b) **TPA-BF₂-5** and (c) **TPA-BF₂-6** complexes in CHCl₃ while warming from 77K to RT. $\lambda_{exc} = 370$ nm.

Figure S12. Fluorescence tuning of **TPA-BF**₂ complexes in toluene while warming from 77K to RT. $\lambda_{exc} = 370$ nm.

Figure S13. Fluorescence lifetime decay (a) **TPA-BF₂-2**, (b) **TPA-BF₂-3**, (c) **TPA-BF₂-4**, (d) **TPA-BF₂-5**, (e) **TPA-BF₂-6**, (f) **TPA-BF₂-7** and (g) **TPA-BF₂-8** complexes in CHCl₃ at RT.

Table S3. Shows the χ^2 value and fluoresce+ence life time decay of ethyl, propyl, butyl, pentyl, hexyl, octyl respectively in solution state, B₁, B₂, B₃ are relative individual component contributions to τ_1, τ_2, τ_3 < τ > (ns) is the average lifetime from multiple decay profiles.

	B ₁	B ₂	B ₃	τ_1	τ ₂	τ ₃	<τ> (ns)	χ ²
TPA-2-BF ₂	0.26	0.09	0.65	1.935	5.079	0.554	2.64	1.10
TPA-3-BF ₂	0.38	0.14	0.49	2.264	4.654	0.354	2.99	1.09
TPA-4-BF ₂	0.27	0.10	0.63	2.06	6.248	0.397	3.60	1.17
TPA-5-BF ₂	0.25	0.10	0.65	2.104	6.043	0.293	3.64	1.31
TPA-6-BF ₂	0.28	0.11	0.61	2.419	6.816	0.316	4.20	1.07
TPA-7-BF ₂	0.26	0.15	0.59	2.061	6.331	0.319	4.29	1.12
TPA-8-BF ₂	0.28	0.13	0.60	1.946	6.396	0.338	4.08	1.03

Figure S14. Fluorescence tuning and digital images of (a) **TPA-BF₂-4**, (b) **TPA-BF₂-5** and (c) **TPA-BF₂-6** in CHCl₃ while warming from 77K to RT. λ exc = 370 nm.

Figure S15. CIE 1931 chromaticity plot with emission colour coordinates of fluorescence tuning in $CHCl_3$.

Figure S16. Fluorescence tuning of (a) **TPA-BF₂-2**, (b) **TPA-BF₂-3**, (c) **TPA-BF₂-4**, (d) **TPA-BF₂-5**, (e) **TPA-BF₂-6**, (f) **TPA-BF₂-7** and (g) **TPA-BF₂-8** in toluene while warming from 77K to RT. $\lambda_{exc} = 370$ nm.

Figure S17. CIE 1931 chromaticity plot with emission colour coordinates of fluorescence tuning in toluene.

Figure S18. Fluorescence spectra of TPA-BF₂ in PMMA matrix at RT and 77K.

Figure S19. Thermofluorochromism of (a, b) **TPA-BF₂-3**, (c, d) **TPA-BF₂-4** and (e, f) **TPA-BF₂-5** in toluene (Conc. = 10^{-5} M).

Figure S20. Thermofluorochromism of (a, b) **TPA-BF₂-6** and (c, d) **TPA-BF₂-7** in toluene (Conc. = 10^{-5} M).