Temperature Controlled Locally Excited and Twisted Intramolecular Charge Transfer
State Dependent Fluorescence Switching in Triphenylamine-benzothiazole Derivatives

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Scheme S1. Synthesis of TPA-benzothiazole derivatives.
Figure S1. $^1$H and $^{13}$C NMR spectrum of NTPP.
Figure S2. $^1$H and $^{13}$C-NMR spectrum of NTMP.
Figure S3. $^1$H and $^{13}$C-NMR spectrum of BDTP.
Figure S4. **NTPP**: m/z calcd for C\textsubscript{25}H\textsubscript{18}N\textsubscript{2}S (M + H): 378.1, found: 378.1.
Figure S5. **NTMP**: m/z calcd for C_{26}H_{20}N_{2}O_{5} (M + H): 408.1, found: 408.1.
Figure S6. **BDTP**: m/z calcd for C\textsubscript{26}H\textsubscript{20}N\textsubscript{2}OS (M + H): 394.1, found: 394.2.
Figure S7. Absorption spectra of (a) NTPP (b) NTMP and (c) BDTP in different solvents (10⁻⁵ M)
Figure S8. Fluorescence spectra of BDTP in different solvents (10^{-5} M)
Figure S9. Emission decay profiles of NTPP in different solvents.
Figure S10. Temperature dependent $\lambda_{\text{max}}$ variation of (a) NTPP and (b) NTMP in DMF.

Figure S11. Temperature dependent fluorescence modulation of BDTP in DMF. The fluorescence intensity at -196°C was divided by a factor of 3.
Figure S12. Fluorescence spectra of (a) NTPP (b) NTMP and (c) BDTP at liquid N$_2$ temperature.
Figure S13. Fluorescence spectra of (a) NTPP and (b) NTMP at 30°C in the forward heating and reverse cooling of DMF solution.
Figure S14. Excitation spectra of (a) NTPP, (b) NTMP and (c) BDTP at different temperature in DMF.

Table S1. Solid state excited state lifetime.

|      | $\tau_1$ (ns) | $\tau_2$ (ns) | $\tau_3$ (ns) |
|------|---------------|---------------|---------------|
| NTPP | 0.12          | 0.78          | 2.22          |
| NTMP | 0.20          | 0.92          | 2.15          |
| BDTP | 0.17          | 0.77          | 1.99          |
Figure S15. Emission decay profiles in the solid state of (a) NTPP, (b) NTMP and (c) BDTP.
Figure S16. Fluorescence spectra of (a) NTPP, (b) NTMP and (c) BDTP solids at room and liquid nitrogen temperature.
Figure S17. Comparison of molecular packing of NTPP crystal lattice for data collected at (a) 100K and (b) 298K.
Figure S18. Comparison of molecular packing of NTMP crystal lattice for data collected at (a) 100K and (b) 298K.
Figure S19. Comparison of molecular packing of BDTP crystal lattice for data collected at (a) 100K and (b) 298K.

Table S1. Calculated optical band gap using Gaussian 09 program package.

|       | HOMO (eV) | LUMO (eV) | Band gap (eV) |
|-------|-----------|-----------|---------------|
| NTPP  | -5.394    | -1.631    | 3.76          |
| NTMP  | -5.253    | -1.424    | 3.83          |
| BDTP  | -5.376    | -1.724    | 3.65          |