Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supplementary Information

Ground-State Conformers Enable Bright Single-Fluorophore Ratiometric Thermometers with Positive Temperature Coefficients

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Computational Results

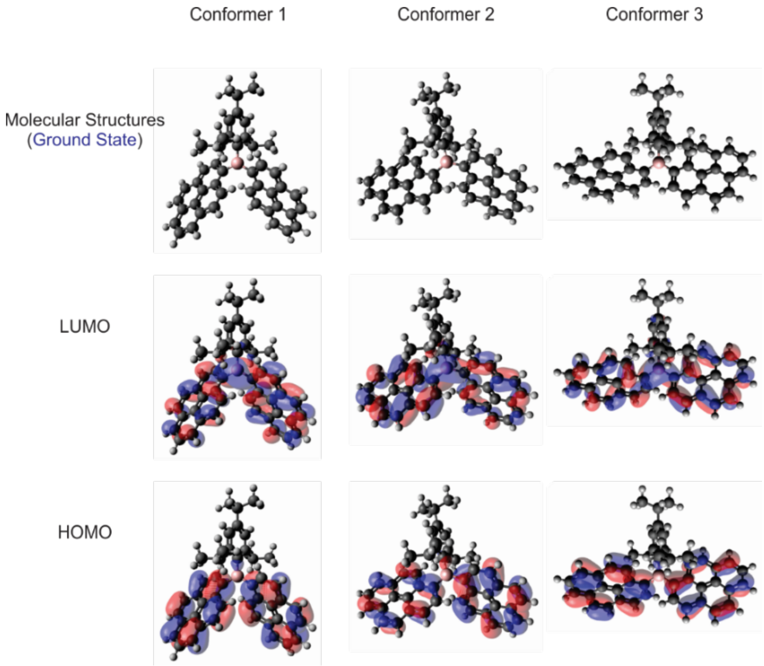


Fig. S1 *Optimized molecular structures and their LUMO and HOMO for three conformational isomers of* ***DPTB*** *in the* ***ground*** *state in vacuo.*

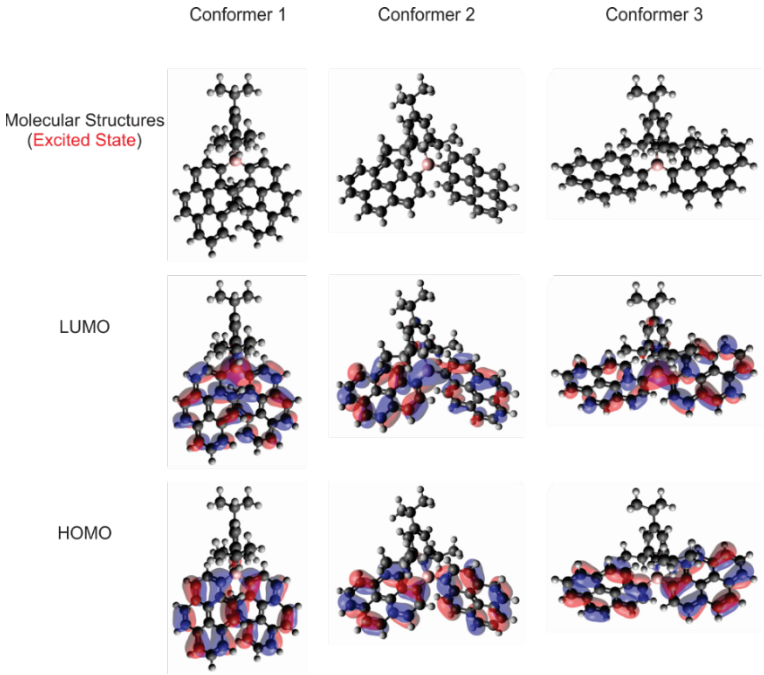


Fig. S2 *Optimized molecular structures and their LUMO and HOMO for three conformational isomers of* ***DPTB*** *in the* ***excited*** *state in vacuo. Only Conformer 1 exhibits a large geometry relaxation with respect to its ground state structure.*

Crystallographic Experiments

A single crystal of **DPTB** was obtained by slow solvent evaporation at room temperature from its n-hexane/chloroform solution (Fig. S3a), which enables further confirmation of the molecular structure by the crystallographic analysis (Table S1, Supporting Information). The single crystal belongs to the monoclinic system, with the space group C2/c. Fig. S3b shows the ORTEP drawings (50% probability ellipsoids) for the **DPTB** crystal. **DPTB** molecule has a propeller conformation. The torsion angles between two pyrene planes and the central boron plane are ~36.70° and ~35.18°. The increased steric hindrance caused by two isopropyl and two pyrene moieties of **DPTB** leads to a significant torsion angle (78.81°) between the benzene ring and the central boron plane (Fig. S3c). Additionally, each unit cell consists of six independent molecules (Fig. S3d). This crystal is mainly formed via intermolecular face-to-face π-π interactions between the adjacent pyrene moieties (Fig. S3e). The distance between adjacent pyrene planes amounts to ~3.44 Å (Fig. S3f).

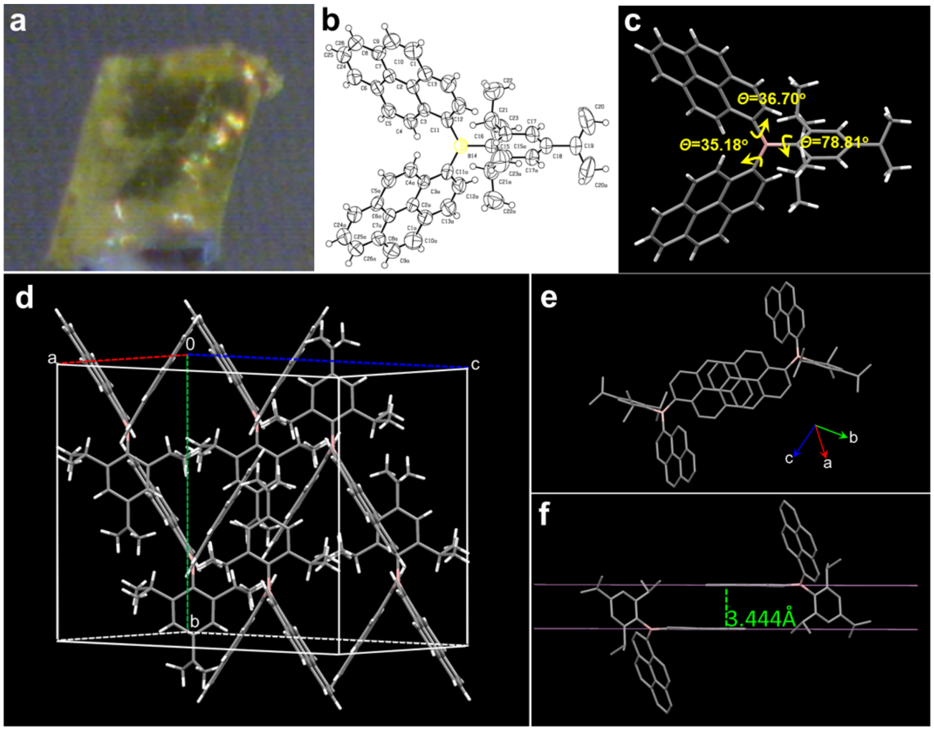


Fig. S3 *(a) Photography of the single crystal of **DPTB**. (b) Crystallographic asymmetric unit of **DPTB** at room temperature with anisotropic displacement ellipsoids drawn at the 50% probability level. (c) Selected torsion angles of **DPTB** in its single crystal. c) Unit cell structure of the **DPTB** single crystal. (d) Face-to-face π-π interactions between two neighboring **DPTB** molecules. (e) Distance between two pyrene planes.*

Table S1 *Single-crystal X-ray diffraction experimental details of* ***DPTB****.*

Identification code	**DPTB**
Empirical formula	$C_{47}H_{43}B$
Formula weight	618.34
Crystal system	monoclinic
Space group	C2/c
a, Å	10.3419(12)
b, Å	16.4056(15)
c, Å	20.936(2)
α, deg	90.00
β, deg	100.537(11)
γ, deg	90.00
Volume, $Å^3$	3492.2(6)
Z	8
$D_{calcd.}$, g/cm^3	1.171
F_{000}	1308.0
Temp, (K)	293(2)
M(Mo Kα), mm^{-1}	0.066
θ range, deg	6.36 to 58.07
Index ranges	$-14 \leq h \leq 10$, $-20 \leq k \leq 20$, $-25 \leq l \leq 26$
No. of collected reflns.	9530
No. of unique reflns.	4149
R(int)	0.0317
Data/restraints/parameters	4149/0/222
R_1, wR_2 [obs I>= 2σ (I)]	0.0829, 0.2097
R_1, wR_2 (all data)	0.1682, 0.2768
Residual peak/hole e. Å^{-3}	0.28/-0.20
Goodness-of-fit on F^2	1.027
CCDC number	1564212

Fluorescence Lifetime Measurements

Table S2 *Double-exponential fitting to the fluorescence decay dynamics of* ***DPTB*** *in DMSO at various emission wavelengths* (*λ_{em}*). ***DPTB*** *was excited at 370 nm; τ: lifetime; RC: relative contribution.*

λ_{em}	τ_1 (ns)	RC (%)	τ_2 (ns)	RC (%)	χ^2
460	1.27	3.44	11.02	96.56	1.14
520	7.14	15.45	11.56	84.55	1.22
580	7.43	19.27	11.66	80.73	1.12
640	8.95	44.46	12.39	55.54	1.18

690	9.39	60.86	13.30	39.14	1.25

Fluorescence and Spectral Properties

To ensure that fluorescence excitation spectra were not affected by molecular aggregation, we probed these spectral data in both 0.5 µM (Fig. S4) and 5 µM (Fig. 3b) ethanol solution of **DPTB**, as well as 5 µM EA solution of **DPTB** (Fig. S5). All these spectral data consistently show that different conformers are present in the ground-state of **DPTB**.

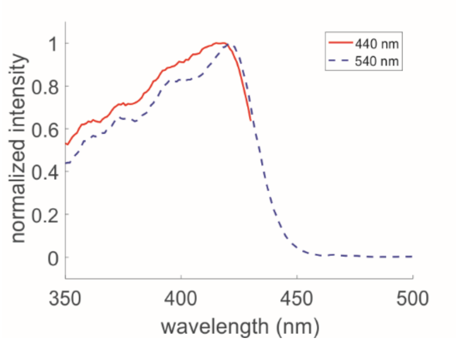


__Fig. S4__ Normalised fluorescence excitation spectra of __DPTB__ in ethanol at room temperature, monitored at emission wavelengths of 440 and 540 nm, respectively. ([__DPTB__] = 0.5µM).

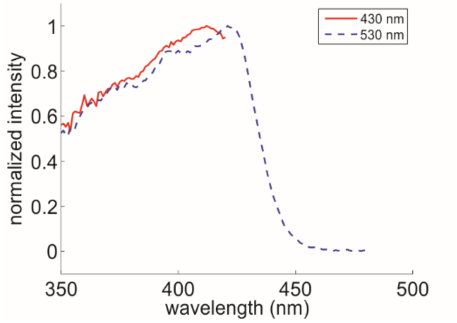


__Fig. S5__ Normalised fluorescence excitation spectra of __DPTB__ in EA at room temperature, monitored at emission wavelengths of 430 and 530 nm, respectively. ([__DPTB__] = 5µM).

__Table S3__ Quantum yields of __DPTB__ in different solvents at various temperatures.

Solvent	75 °C	65 °C	55°C	45°C	35°C	25°C	15°C
Cyclohexane	-	0.7649	0.7760	0.7840	0.7909	0.811	-
EA	-	0.7615	0.8142	0.7969	0.7817	0.7696	0.7523
Ethanol	-	0.5415	0.5547	0.5643	0.5743	0.5825	-
DMSO	0.4431	0.4344	0.4351	0.4331	0.4307	0.4261	-

Table S4 *Temperature coefficients of* ***DPTB*** *peak emission intensities in various solvents.*

Solvent	DMSO	EA	Ethanol	Cyclohexane
Temperature coefficient (%/°C)	0.06	0.11	-0.31	-0.28

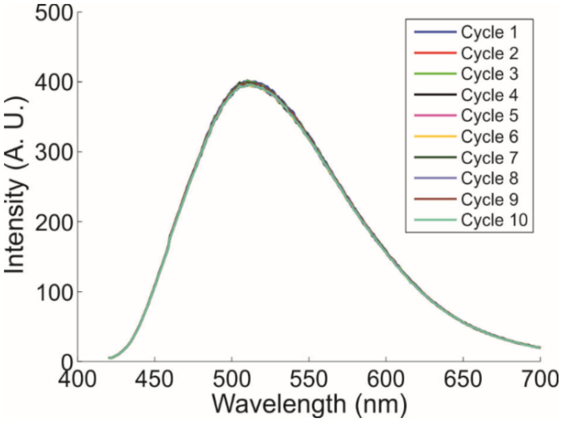
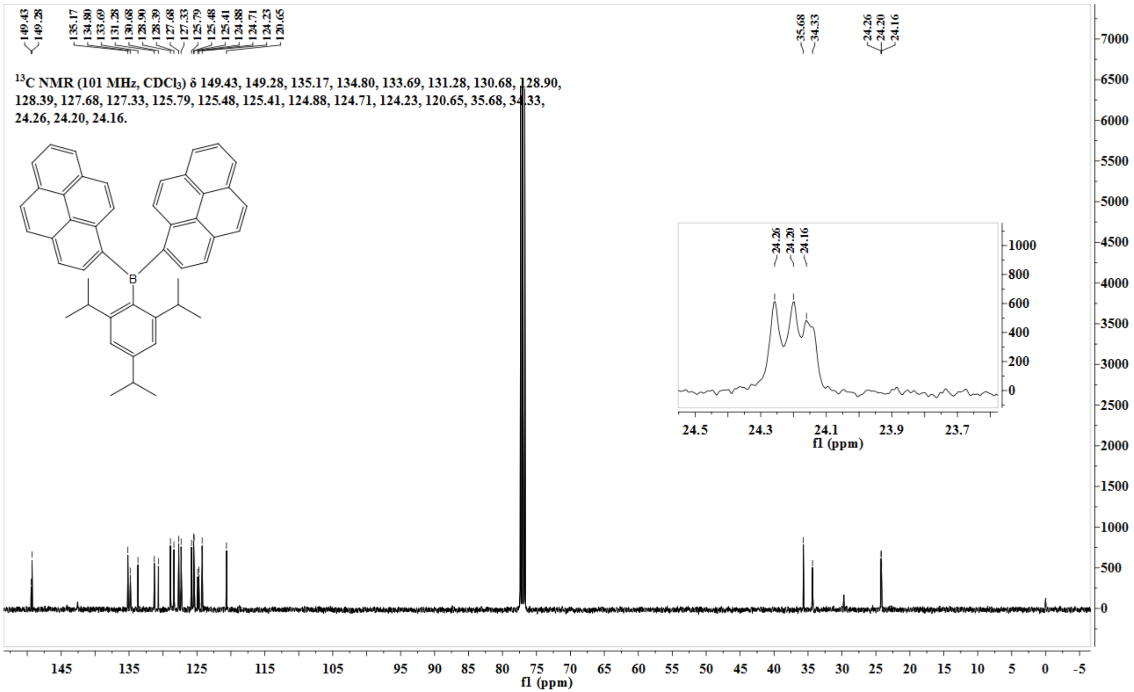


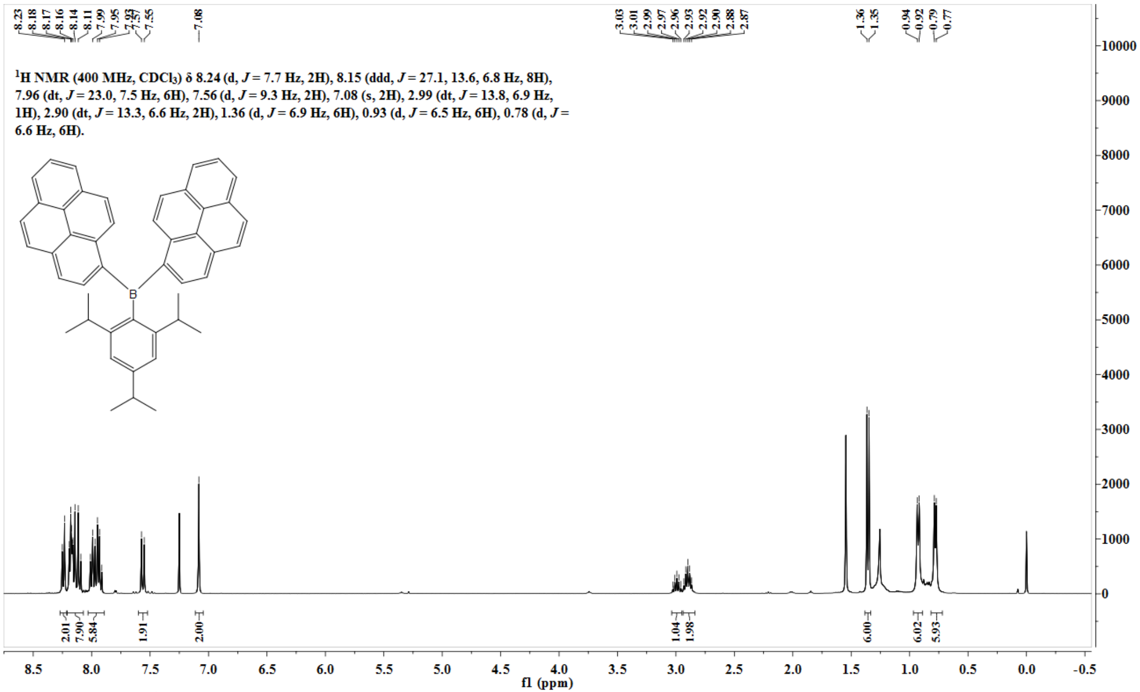
Fig. S6 *The emission spectra of DPTB measured at 45°C in 10 heating/cooling cycles from 25 °C to 75 °C.*

NMR Spectra



^{13}C NMR (101 MHz, $CDCl_3$) δ 149.43, 149.28, 135.17, 134.80, 133.69, 131.28, 130.68, 128.90, 128.39, 127.68, 127.33, 125.79, 125.48, 125.41, 124.88, 124.71, 124.23, 120.65, 35.68, 34.33, 24.26, 24.20, 24.16.

Fig. S7 *^{13}C-NMR spectrum of* ***DPTB*** *in $CDCl_3$.*



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.7 Hz, 2H), 8.15 (ddd, *J* = 27.1, 13.6, 6.8 Hz, 8H), 7.96 (dt, *J* = 23.0, 7.5 Hz, 6H), 7.56 (d, *J* = 9.3 Hz, 2H), 7.08 (s, 2H), 2.99 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.90 (dt, *J* = 13.3, 6.6 Hz, 2H), 1.36 (d, *J* = 6.9 Hz, 6H), 0.93 (d, *J* = 6.5 Hz, 6H), 0.78 (d, *J* = 6.6 Hz, 6H).

Fig. S8 *^{1}H-NMR spectrum of **DPTB** in $CDCl_3$.*