Supporting Information

**Catalyst- and Template-Free Ultrafast Visible-Light-Triggered
Dimerization of Vinylpyridine-Functionalized Tetraarylamino-borane:
Intriguing Deep-Blue Delayed Fluorescence**

Kalluvettukuzhy K. Neena, Pagidi Sudhakar, and Pakkirisamy Thilagar*

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Experimental Section

Materials

The chemicals were purchased from commercial suppliers (Aldrich, USA; Merck, Germany; SDFCL, India) and used as received, unless otherwise mentioned. Standard Schlenk-line technique was used for reactions. THF was dried over sodium and distilled out under argon atmosphere.

Methods

^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 400 MHz NMR Spectrometer operating at a frequency of 400 MHz for ^1H and 100 MHz for ^{13}C . Chemical shift multiplicities are reported as singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), and multiplet (m). Solution ^1H NMR and ^{13}C NMR spectra were referenced internally to the solvent signals. ^{11}B NMR spectra were recorded at 25 °C on a JEOL 500 MHz NMR Spectrometer operating at a frequency of 160.5 MHz for ^{11}B . ^{11}B NMR chemical shift values were referenced to the external standard boron signal of $\text{BF}_3\cdot\text{Et}_2\text{O}$. High resolution mass spectra (HRMS) were recorded on a Micromass Q-ToF High Resolution Mass Spectrometer by electrospray ionization (ESI) method. Thermo-Gravimetric Analysis (TGA) curves of compounds were collected in a NETZSCH TG 209 F1 apparatus at a heating rate of 10 °C/min under argon atmosphere.

Solutions of all the compounds for spectral measurements were prepared using spectrophotometric grade solvents, microbalance (± 0.1 mg precision) and standard volumetric glass wares. Quartz cuvettes with sealing screw caps were used for the solution state spectral measurements. Electronic absorption spectra were recorded on a SHIMADAZU UV-2600 spectrophotometer. The emission and excitation spectra were recorded using an Edinburgh Instruments FLS980 spectrometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode and the highly sensitive photomultiplier tube (RED PMT in Cooled Housing) positioned after a double emission monochromator. All spectra were fully corrected for the spectral response of the instrument. Temperature dependent (77 and 298 K) measurements were performed using an Oxford Instruments OPTISTAT DN2 cryostat controlled by an Oxford Instruments Mercury iTC temperature controller connected to the FLS980 spectrometer. Samples were allowed to equilibrate at each temperature before measurements were conducted. Time gated emission spectra were excitation source was a pulsed microsecond flash lamp (μF1) with a pulse width of 1.1 μS . The delay time scale was 20 μS where in the shorter species having excited state lifetime of ~ 2 μS will be discarded by the time gated circuit attached to PMT detector. Fluorescence lifetimes were recorded using the time-correlated single photon counting (TCSPC) method using an Edinburgh Instruments FLS980 spectrometer described above. Measurements were made in right-angle geometry mode, and the emission was collected through a polarizer set to the magic angle. Solutions were excited with by a pulsed LED at 330 nm, at repetition rates of 10 MHz, as appropriate. The microsecond lifetimes were measured using the FLS980 spectrometer described above for steady-state measurements. The excitation source was a pulsed microsecond Flashlamp (μF1) with a pulse width of 1.1 μS . The quality of all decay fits was judged to be satisfactory, based on the calculated values of the reduced χ^2 and Durbin Watson parameters and visual

inspection of the weighted residuals. Absolute solid state quantum yields were measured using calibrated Horiba JOBIN YVON Integrating sphere. Solution state quantum yields were calculated with reference to anthracence ($\phi = 0.27$ in EtOH at 27 °C) as standard.⁸

Single-crystal X-ray diffraction (SCXRD) studies were carried out with a Bruker SMART APEX diffractometer equipped with 4-axis goniometer. The data were integrated using SAINT, and an empirical absorption correction was applied with SADABS.¹ The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL software.

Density functional theory (DFT/TD-DFT) calculations were done using B3LYP functional with 6-31G(d) basis set as incorporated in *Gaussian 09* package for all the atoms, mixing the exact Hartree-Fock-type exchange with Becke's exchange functional and that proposed by Lee-Yang-Parr for the correlation contribution.² The molecular structures obtained from SCXRD measurements were taken as the input for the calculations. The optimized structures and the frontier molecular orbitals (FMOs) were viewed using *Gaussview5.0*.

Synthesis

The synthesis and characterization of N,N-bis(4-bromophenyl)-B,B-bis(mesityl)borane (**1a**) was reported in our recent article³

Scheme S1. Synthesis of compounds **1** and **2**

Synthesis of compound 1

A pressure flask was charged with dry degassed toluene, N,N-bis(4-bromophenyl)-B,B-bis(mesityl)borane (**1a**) (1.00 g, 1.73 mmol), 4-vinylpyridine (400 μ L, 3.46 mmol), NEt₃ (960 μ L, 6.92 mmol), tri(*o*-tolyl)phosphine (25 mg, 0.05 mmol) and Pd(OAc)₂ (20 mg, 0.05 mmol) under argon atmosphere. The resultant reaction mixture was kept under heating conditions for 24 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, volatile organic materials were evaporated under reduced pressure to afford a crude product, which was purified by column chromatography on activated aluminium oxide (basic) using a mixture of hexane and EtOAc (3:7) as eluent to obtain **1** as a pale yellow solid. The compound was further recrystallized from diethylether to obtain an analytically pure pale yellow crystalline sample. Yield: 25%, (250 mg). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm) 8.54 (d, *J* = 6.12 Hz, 4H, *o*-CH of C₅H₄N), 7.30 (d, *J* = 6.08 Hz, 4H, *m*-CH of C₅H₄N), 7.25 (d, *J* = 8.24 Hz, 4H, *m*-CH of C₆H₄), 7.18 (d, *J* = 16.32 Hz, 2H, alkene CH), 6.94 (d, *J* = 8.64 Hz, 2H, *o*-CH of C₆H₄), 6.88 (d, *J* = 16.32 Hz, 2H, alkene CH), 6.59 (brs, 4H, CH of Mes), 2.16 (s, 18H, CH₃ of Mes). ¹¹B NMR (160.5 MHz, CDCl₃, 25 °C): δ (ppm) 49.2. ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 150.5 (*o*-carbon of C₅H₄N), 149.8 (*p*-carbon of C₅H₄N), 145.0 (Boron bound quaternary carbon of Mes), 139.0 (*o*-quaternary carbon of Mes), 138.0 (*p*-quaternary carbon of Mes), 133.1 (alkene carbon), 132.8 (*p*-carbon of C₆H₄), 128.4 (*o*-carbon of C₆H₄), 128.0 (*m*-carbon of C₆H₄), 127.2 (alkene carbon), 125.7 (*m*-carbon of Mes), 121.1 (*m*-carbon of C₅H₄N), 22.9 (*o*-CH₃ of Mes), 21.5 (*p*-CH₃ of Mes), Nitrogen bound quaternary carbons not observed. ESI-MS, (positive ion mode): calcd for C₄₄H₄₂BN₃ 623.3472 Da, observed 624.3548 Da (M+H)⁺. Anal.Cald. for C₄₄H₄₂BN₃: C, 84.74; H, 6.79; N, 6.74. Found C, 84.68; H, 6.60; N, 6.87.

Synthesis of 2: Sunlight induced SCSC transformation

Compound **2** was synthesized by exposing compound **1** (powder/crystals) to sunlight for ~ 1 h. The conversion was confirmed by ¹H NMR. The appearance of a new resonance at ~ 4.26 ppm corresponds to the ¹H resonance of cyclobutane and the appearance of two distinct resonances for the pyridyl protons in different magnetic environments indicates the formation of **2**. Yield: ~100%. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ (ppm). 8.52 (d, *J* = 6.04 Hz, 4H, *o*-CH of C₅H₄N of styryl pyridine), 8.37 (d, *J* = 5.92 Hz, 4H, *o*-CH of C₅H₄N attached to cyclobutane), 7.30-7.27 (m, 5H, *m*-CH of C₅H₄N of styryl pyridine and CH of C₆H₄), 7.20-7.19 (m, 4H, *m*-CH of C₅H₄N attached to cyclobutane), 7.16-7.12 (m, 2H, alkene CH), 6.93 (d, *J* = 8.6 Hz, 1H, CH of C₆H₄), 6.89-6.85 (m, 5H, CH of C₆H₄ and alkene), 6.83 (s, 1H, CH of C₆H₄), 6.78-6.70 (m, 10H, CH of C₆H₄), 6.57 (brs, 8H, aromatic CH of Mes), 4.26 (brs, 4H, C₄H₄), 2.21-2.01 (m, 36H, CH₃ of Mes). ¹¹B NMR (160.5 MHz, CDCl₃, 25 °C): δ (ppm) 45.9. ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ (ppm) 150.2 (*o*-carbon of C₆H₄N of styrylpyridine), 149.4 (*o*-carbon of C₆H₄N bound to cyclobutane), 149.0 (*p*-carbon of C₆H₄N of styrylpyridine), 147.6 (*p*-carbon of C₆H₄N bound to cyclobutane), 144.7 (Boron bound quaternary carbon of Mes), 138.6 (*o*-quaternary carbon of Mes), 138.4 (quaternary carbon of C₆H₄ bound to cyclobutane), 137.4 (quaternary carbon of C₆H₄ of styryl pyridine bound to N), 137.2 (quaternary carbon of Ph bound to N), 135.3 (*p*-quaternary carbon of Mes),

132.6 (alkene carbon), 132.5 (*p*-carbon of C₆H₄ of styryl pyridine unit), 127.9 (*o*-carbon of C₆H₄ bound to cyclobutane), 127.6 (*meta*-carbon of C₆H₄ bound to cyclobutane), 127.4 (*m*- carbon of Mes), 126.8 (*m*-carbon of Ph of styryl pyridine unit), 126.7 (*o*-carbon of C₆H₄ of styryl pyridine unit), 125.2 (alkene CH), 123.3 (*m*-carbon of C₆H₄N bound to cyclobutane), 120.7 (*o*-carbon of C₆H₄N to styrylpyridine), 46.4 (cyclobutane, C₄H₄), 22.5 (*o*-CH₃ of Mes), 21.1 (*p*-CH₃ of Mes). ESI-MS, (positive ion mode): calcd for C₈₈H₈₄B₂N₆ 1246.6944 Da, observed 1247.7021 Da (M+H)⁺. Anal.Cald. for C₈₈H₈₄B₂N₆: C, 84.74; H, 6.79; N, 6.74. Found C, 84.58; H, 6.63; N, 6.85.

NMR Spectral Characterization

Figure S1. ^1H NMR spectrum of **1** (top) and resonances are assigned to respective ^1H (bottom).

Figure S2. ^1H - ^1H COSY spectrum of **1**

Figure S3. ¹³C NMR spectrum (*N-bound quaternary carbons not observed, top) and ¹H-¹³C HSQC (bottom) of

Figure S4. ^{11}B NMR spectrum of **1**

Figure S5. ^1H NMR spectrum of **2** (top) and resonances are assigned to respective ^1H (bottom).

Figure S6. ^1H - ^1H COSY spectrum of 2

Figure S7. ^{13}C NMR spectrum (top) and ^1H - ^{13}C HSQC (bottom) of **2**

Figure S8. ^{11}B NMR spectrum of **2**

High Resolution Mass Spectral Characterization

Figure S9. HRMS of **1**

Figure S10. HRMS of **2**

Single Crystal X-ray Diffraction Studies

Table S1. Summary of X-ray crystallographic data of **1** and **2**

	1	2
Empirical formula	C ₄₄ H ₄₂ B ₁ N ₃	C ₈₈ H ₈₄ B ₂ N ₆
Formula weight	623.65	1247.30
Temperature (K)	100(2) K	100 (2) K
Wavelength/ Å	0.71073 Å	0.71073 Å
Crystal System	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>
<i>a</i> / Å	20.659(4)	24.887(2)
<i>b</i> / Å	16.640(3)	16.857(1)
<i>c</i> / Å	23.515(4)	19.151(1)
α [°]	90	90
β [°]	109.32 (10)	116.63(2)
γ [°]	90	90
<i>V</i> /Å ³	7629(2)	7181.9(1)
Crystal size (mm) ^[c]	0.18 x 0.15 x 0.10	0.18 x 0.15 x 0.10
<i>Z</i>	4	4
Crystal density, g cm ⁻³	1.084	1.153
^[a] <i>R</i> _{all} , <i>R</i> _{obs}	0.1692, 0.0909	0.0899, 0.0550
^[b] <i>wR</i> _{2_all} , <i>wR</i> _{2_obs}	0.3212, 0.2753	0.1367, 0.1252
Collected reflns	121626	53847
Unique reflns	13441	11595
Theta range for data collection	1.53 to 25.00 °	2.97 to 25.00 deg.
Absorption coefficient	0.064 mm ⁻¹	0.066 mm ⁻¹
Largest diff. peak and hole/ Å ⁻³	1.517 and -0.244	0.264 and -0.189
Goodness-of-fit on <i>F</i> ²	1.050	0.977
CCDC number	1554478	1554477

^[a] $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; ^[b] $wR_2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}$; ^[c] Same crystal have been used for measurements

Figure S11. Crystallographically distinct molecules present in the asymmetric unit of **1**

Table S2. Important bond lengths (Å), bond angles (°) and dihedral angles (°) of **1** from the crystal structure (atom numbering schemes are shown in Figure S9.)

Bond lengths (Å), bond angles (°) and dihedral angles (°)	1A	Bond lengths (Å), bond angles (°) and dihedral angles (°)	1A
B1-N1	1.408(4)	B2-N2	1.428(3)
B1-C1	1.596(5)	B2-C45	1.581(4)
B1-C7	1.581(5)	B2-C51	1.579(4)
N1-C19	1.438(4)	N2-C63	1.444(4)
N1-C32	1.454(4)	N2-C76	1.439(4)
C25-C26	1.256(6)	C69-C70	1.325(6)
C38-C39	1.307(6)	C82-C83	0.870(1)*
N1-B1-C1	117.9(3)	N2-B2-C45	118.4(3)
N1-B1-C7	121.4(3)	N2-B2-C51	120.2(3)
C1-B1-C7	120.7(3)	C45-B2-C51	121.3(3)
B1-N1-C19	125.8(3)	B2-N2-C63	121.7(2)
B1-N1-C32	120.9(3)	B2-N2-C76	123.6(2)
C19-N1-C32	113.4(2)	C63-N2-C76	114.7(2)
C1-B1-N1-C19	16.5(5)	C45-B2-N2-C63	17.0(4)
C1-B1-N1-C32	-163.6(3)	C51-B2-N2-C63	161.0(3)
C7-B1-N1-C19	-164.5(3)	C45-B2-N2-C76	-165.8(3)
C7-B1-N1-C32	15.3(4)	C51-B2-N2-C76	16.2(4)

* disordered

Table S3. Important bond lengths (Å), bond angles (°) and dihedral angles (°) of **2** from the crystal structure (atom numbering schemes are shown in the molecular structure)

Bond lengths (Å), bond angles (°) and dihedral angles (°)		Bond lengths (Å), bond angles (°) and dihedral angles (°)	
B1-N1	1.420(6)	B2-N2	1.416(6)
B1-C1	1.588(6)	B2-C45	1.604(6)
B1-C7	1.583(5)	B2-C51	1.575(4)
N1-C19	1.433(4)	N2-C63	1.428(4)
N1-C32	1.437(5)	N2-C76	1.445(5)
C25-C26	1.323(5)	C69-C70	1.300(4)
N1-B1-C1	120.1(3)	N2-B2-C45	121.4(3)
N1-B1-C7	118.3(3)	N2-B2-C51	118.2(3)
C1-B1-C7	121.5(3)	C45-B2-C51	120.4(3)
B1-N1-C19	123.6(3)	B2-N2-C63	124.6(3)
B1-N1-C32	122.2(3)	B2-N2-C76	122.0(3)
C19-N1-C32	114.3(3)	C63-N2-C76	113.3(3)
C1-B1-N1-C19	16.6(5)	C45-B2-N2-C63	-3.6(5)
C1-B1-N1-C32	-163.9(3)	C51-B2-N2-C63	179.8(3)
C7-B1-N1-C19	-165.4(3)	C45-B2-N2-C76	171.6(3)
C7-B1-N1-C32	14.2(5)	C51-B2-N2-C76	-5.1(5)

Figure S12. Intermolecular (C-H...N) Interactions (blue dotted lines) in the crystal lattice of compound **1**, which facilitates the face-to-face packing of olefin units following the Schmidt topochemical criteria for [2+2] cycloaddition reaction in the solid state (Atom colour codes: B-Orange, C-black, N-blue, H-grey; centroid of π -system–red)

Figure S13. Molecular structure of **2** showing the rctt regiochemistry of photodimerized product (Atom colour codes: B-Orange, C-black (C-red for cyclobutane), N-blue, H-grey; Hydrogen atoms except those of cyclobutane ring are omitted for clarity)

Figure S15. ^1H NMR spectrum of compound **1** (powder sample) after exposure to daylight for 1 h

Figure S16. Absorption spectrum of compound **1** irradiated with sun light at different time intervals (left) and plot of absorbance versus irradiation time showing first order kinetics (right).

Figure S17. ¹H NMR spectra of compound **2** recorded after heating the solid samples to different temperatures and then dissolving in CDCl₃.

Synthetic procedure for the photodimerization of 1 to 2 in presence of photosensitizer: The reaction was carried out by following a literature procedure.⁹ To a solution of compound **1** (0.08 mmol, 50 mg) in methanol (5 mL), [Ru(bpy)₃]Cl₂·6H₂O (5 mol %, 3 mg) was added and stirred for 10 min. The reaction mixture was exposed to sun light irradiation for 12 h. The reaction mixture was then filtered through a celite pad. Organic volatiles were removed under reduced pressure and the reaction was monitored by checking the ¹H NMR spectrum of the crude residue (Figure S18). From the ¹H NMR spectrum, the photodimerization reaction of **1** to **2** was found to be very slow and the calculated yield for conversion is only 7.5%.

Figure S18. ¹H NMR spectrum of compound **1** after exposing to sunlight in presence of [Ru(bpy)₃]Cl₂·6H₂O as photosensitizer

Figure S19. PXRD pattern of **1** and **2**

Theoretical Calculations: DFT/B3LYP/6-31G(d)-Gaussian09 programme

Figure S20. Ground state DFT optimized structures of **1** (left) and **2** (right); (atom colour codes, B-orange, C-black, N-blue).

Figure S21. Frontier molecular orbital energy level diagram of **1** and **2** (energies are not to scale).

Figure S22. Molecular orbitals of **1** (top) and **2** (bottom) from the ground state DFT optimized structure involved in electronic transitions.

Table S4. Summary of dominant electronic transitions of compounds **1** and **2** obtained from TD-DFT calculations

Compound	Excited State	E/eV	E/nm	f	Dominant transitions (percent contribution)
1	1	3.246	381.94	0.844	HOMO ->LUMO (99%)
	2	3.350	370.04	0.354	HOMO ->LUMO+1 (95%)
	7	3.919	316.34	0.519	HOMO-3 ->LUMO (47%)
	8	3.940	314.63	0.209	HOMO-2 ->LUMO (60%)
	9	3.970	312.30	0.342	HOMO-2 ->LUMO+1 (67%)
	11	4.037	307.07	0.2053	HOMO-3 ->LUMO+1 (44%)
2	1	3.392	365.48	0.808	HOMO-1 ->LUMO (96%)
	2	3.443	360.06	0.812	HOMO ->LUMO+1 (95%)
	3	3.531	351.10	0.000	HOMO ->LUMO (100%)
	7	3.925	315.84	0.1246	HOMO-2 ->LUMO+1 (48%)
	8	3.969	312.35	0.293	HOMO-6 ->LUMO+1 (41%)
	10	4.021	308.3	0.256	HOMO-1 ->LUMO+2 (53%)

Optical Properties

(* all the measurements were carried out in degassed solvents)

Figure S23. Absorption, emission and excitation spectra of compound **1** (left) and **2** (right); (Concentration: 1 μ M, solvent: THF, λ_{ex} = 340 nm)

Figure S24. Photographs of compound **1** before and after exposure to sunlight under UV light illumination (λ_{ex} = 365 nm).

Table S5. Summary of photophysical data of compounds **1** and **2** (Concentration: 1 μM , λ_{ex} = 340 nm and 330 nm pulsed led was used for TCSPC measurements).

	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$ (A %)	τ/ns (A %)
1 (THF solution)	470	$\tau_1 = 4.35$ (90); $\tau_2 = 10.87$ (10)	$\tau_1 = 1.07$ (25); $\tau_2 = 4.60$ (75)
2 (THF solution)	460	$\tau_1 = 4.41$ (90); $\tau_2 = 10.89$ (10)	$\tau_1 = 1.25$ (43); $\tau_2 = 5.78$ (57)
1 (solid state)	445	$\tau_1 = 3.82$ (85); $\tau_2 = 10.59$ (15)	$\tau_1 = 1.04$ (68); $\tau_2 = 3.09$ (32)
2 (solid state)	434	$\tau_1 = 4.25$ (92); $\tau_2 = 16.72$ (8)	$\tau_1 = 0.74$ (48); $\tau_2 = 2.42$ (52)

Table S6. Summary of photophysical data of compounds **1** and **2** at at 298 K and 77 K (Conc. 10 μM , solvent: 2-methyl THF, λ_{ex} = 340 nm for PL and μs life time measurements; and 330 nm pulsed led was used for TCSPC measurements)

	Temperature	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$ (A %)	τ/ns (A %)
1	77 K	410	$\tau_1 = 3.96$ (89); $\tau_2 = 11.29$ (11)	$\tau_1 = 1.45$
	298 K	469	$\tau_1 = 4.08$ (86); $\tau_2 = 10.98$ (14)	$\tau_1 = 0.84$ (8); $\tau_2 = 4.17$ (92)
2	77 K	409	$\tau_1 = 3.96$ (91); $\tau_2 = 11.05$ (9)	$\tau_1 = 1.51$
	298 K	455	$\tau_1 = 4.09$ (89); $\tau_2 = 11.57$ (11)	$\tau_1 = 1.05$ (34); $\tau_2 = 5.44$ (66)

Figure S25. Solid state emission spectra of compounds **1** (left) and **2** (right) at 298 K and 77K (λ_{ex} = 340 nm)

Table S7. Summary of photophysical data of compounds **1** and **2** in the solid state at 298 K and 77 K (λ_{ex} = 340 nm for PL and μs life time measurements; and 330 nm pulsed led was used for TSCPC measurements)

	Temperature	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$ (A %)	τ/ns (A %)
1	77 K	440	$\tau_1 = 3.59$ (78); $\tau_2 = 9.40$ (22)	$\tau_1 = 1.64$ (83); $\tau_2 = 5.37$ (17)
	298 K	445	$\tau_1 = 3.82$ (85); $\tau_2 = 10.59$ (15)	$\tau_1 = 1.04$ (68); $\tau_2 = 3.09$ (32)
2	77 K	420	$\tau_1 = 4.86$	$\tau_1 = 0.99$ (64); $\tau_2 = 2.39$ (36)
	298 K	434	$\tau_1 = 4.25$ (92); $\tau_2 = 16.72$ (8)	$\tau_1 = 0.74$ (48); $\tau_2 = 2.42$ (52)

Figure S26. Prompt and delayed emission spectra of compounds **1** (left) and **2** (right) at 298 K and 77K recorded in 2-MeTHF (Conc. 10 μM , λ_{ex} = 340 nm, delay time scale = 20 μs)

Figure S27. Prompt and delayed emission spectra of compounds **1** (left) and **2** (right) at 298 K and 77K (λ_{ex} = 340 nm, delay time scale = 20 μs) in the solid state.

Table S8. The calculated energy levels of compound **1** and **2** for the photophysical process

1	S ₀ - S ₁ transition = 3.2461 eV		
	n	S ₀ -T _n transition / eV	ΔE _{ST} (with respect to S ₁ state) / eV
	1	2.2132	1.0329
	2	2.2508	0.9953
	3	3.2513	-0.0052
	4	3.3402	-0.0941
	5	3.4220	-0.1759
2	S ₀ - S ₁ transition = 3.3924 eV		
	n	S ₀ -T _n transition/ eV	ΔE _{ST} (with respect to S ₁ state)/ eV
	1	2.2296	1.1628
	2	2.2300	1.1624
	3	3.2901	0.1023
	4	3.3285	0.0639
	5	3.4095	-0.0171

Figure S28. Luminescence spectra of compounds **1** (left) and **2** (right) in solvents of different polarity (Conc. 10 μ M, λ_{ex} = 340 nm)

Chart S1. Few of reported boron-nitrogen based DF materials⁴⁻⁷

References

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