Structural Modulations: Unraveling the Impact of Benzothiazole Positions on the Optical Properties of Carbazole-Cyanostilbenes

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1. Materials and Measurements

The starting material for the synthetic scheme carbazole, and the chemicals including bromohexane. bis(pinacolato)diboron, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0), benzylcyanide, 5-bromobenzo[d]thiazole, 2-bromobenzo[d]thiazole, N-Bromosuccinimade, KOAc, NaOH, K2CO3, phosphorus oxychloride, dichloroethane, chloroform, tetrahydrofuran and methanol were purchased and used as received. DMF and Toluene was dried by storing it over 4 Å molecular sieves that had been activated by heating in a preheated 150 °C oven. Dichloroethane were dried over CaH₂, distilled and subsequently stored over 4 Å molecular sieves. Reactions sensitive to oxygen or moisture were conducted under a nitrogen atmosphere. Reflux reactions were carried out using a heating reaction block equipped with a temperature-controlled probe. All chromatographic purifications were done using silica gel (100–200 mesh). The ¹H and ¹³C NMR spectra of the synthesized compounds were recorded on a JEOL JNM-ECZ-500R/M1 (500 MHz) NMR spectrometer, using CDCl₃ as the solvent and tetramethylsilane (TMS) as an internal reference. High-resolution mass spectrometry (HRMS) data were acquired on a Waters Synapt XS spectrometer in positive ion mode, with a fragmentor voltage of 3.01 kV, cone voltage of 35 V, source offset of 4.0 V, source temperature of 120 °C, and cone gas flow rate of 50 L/h, and the ion values are reported as m/z. UV-visible absorption spectra were measured using a SHIMADZU-2600 spectrophotometer, maintaining a slit width of 2 nm. Fluorescence measurements were conducted on a PerkinElmer 6500 fluorescence spectrometer, with excitation and emission slit widths set at 5 nm and 20 nm, respectively. Lifetime measurements were performed on a time-correlated single-photon counting (TCSPC) setup (HORIBA, Deltaflex) using a 340 nm nano LED. X-ray diffraction (XRD) patterns in the 20 range of 0° to 90° were recorded on a PANalytical X'Pert3 powder X-ray diffractometer, employing a CuK α radiation source ($\lambda = 1.5406$ Å) at a scanning rate of 1° min⁻¹. Scanning electron microscopy (SEM) images were obtained using a ZEISS Gemini Sigma 300 instrument, while dynamic light scattering (DLS) measurements of aggregates were performed on the STABINO ZETA analyzer. Density functional theory (DFT) calculations were carried out at the B3LYP/6-311G(d,p) level using the Gaussian 09W software package. The single crystal X-ray diffraction analysis was performed using Bruker D8 Venture diffractometer equipped with Mo (K α) sources. Thermogravimetric analysis (TGA) was performed on a Thermal Analyzer STA 8000, and differential scanning

calorimetry (DSC) curves were recorded using a DSC Q20 V24.11 Build 124 model. Absolute quantum yields were determined using an integrating sphere.

2. Experimental Section

Synthesis of 9-hexyl-9H-carbazole (1)

To a solution of carbazole (20 g, 119.6 mmol) dissolved in DMF (75 mL), 1-bromohexane (25 mL, 179.4 mmol), and NaOH (6.5 g, 162.4 mmol) were added. The reaction mixture was stirred at 80 °C for 4 h, and the reaction progress was monitored via thin-layer chromatography (TLC) to ensure the complete consumption of the reactant. After complete consumption of reactant, the reaction mixture was cooled to room temperature, quenched with water, and extracted using ethyl acetate and brine multiple times. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude product was purified using silica gel column chromatography with hexane/ EtOAc (99:1) as the eluent, yielding the pure compound as a white solid (27.2 g, 90.6 %). ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 2H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.87 (m, 2H), 1.44 – 1.36 (m, 2H), 1.31 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H).

Synthesis of 9-hexyl-9H-carbazole-3-carbaldehyde (2)

A solution of dimethylformamide (DMF) (34 mL, 436.3 mmol) and POCl₃ (18 mL, 156.2 mmol) was added dropwise to an oven-dried Schlenk flask at 0 °C under an inert atmosphere, and the temperature was maintained 0 °C for 30 minutes. After allowing the mixture to reach room temperature, 9-hexylcarbazole (15.3 g, 61.2 mmol) dissolved in dry dichloroethane (DCE) (110 mL) was added and stirred at 85 °C for 16 h under inert conditions. The progress of the reaction was monitored using TLC, and upon confirming product formation, the reaction mixture was quenched with 2M NaOH solution and icecold water, followed by extraction with DCM. The combined organic layers were dried over anhydrous Na₂SO₄ and solvent was removed under reduced pressure. The crude product was purified using silica gel column chromatography with a hexane/ EtOAc (95:5) eluents, yielding the pure product as an off-white solid (15.1 g, 88.6 %). ¹H NMR (500 MHz, CDCl₃) δ 10.09 (s, 1H), 8.60 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 8.4, 4.7 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H), 4.31 (t, *J* = 7.3 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.39 (m, 2H), 1.35 – 1.25 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H).

Synthesis of 6-bromo-9-hexyl-9H-carbazole-3-carbaldehyde (3)

To a solution of 9-hexylcarbazole-3-carbaldehyde (15.1 g, 40.5 mmol) in CHCl₃ (220 mL), NBS (12.1 g, 67.9 mmol) was added portion wise, and stirred at room temperature for 12 h. The reaction progress was monitored using TLC, and upon confirming the formation of the product, the mixture was extracted with water, and brine solution. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/ EtOAc (95:5) as the eluent, yielding an off-white solid (14.7 g, 76.1 %). ¹H NMR (500 MHz, CDCl₃) δ 10.08 (s, 1H), 8.53 (s, 1H), 8.25 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 8.6 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.32 (d, *J* = 10.7 Hz, 1H), 4.29 (t, *J* = 9.1 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.36 (m, 2H), 1.33 – 1.25 (m, 4H), 0.86 (t, *J* = 7.1 Hz).

Synthesis of 9-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole-3carbaldehyde (4)

In a 100 mL oven-dried Schlenk flask, cooled under vacuum, 6-bromo-9-hexyl-9Hcarbazole-3-carbaldehyde (8.6 g, 24.1 mmol), bis(pinacolato)diboron (7.6 g, 30.1 mmol), potassium acetate (7.1 g, 72.2 mmol), and triphenylphosphine (253 mg, 0.96 mmol) were added and dissolved in dry toluene (110 mL) under a nitrogen atmosphere. The reaction mixture was degassed with N_2 for 30 minutes, after which gas dichlorobis(triphenylphosphine)palladium(II) (339 mg, 0.5 mmol) catalyst was added, and the reaction setup was purged with N₂ gas. The reaction was heated at 110 °C for 24 h and was monitored via TLC. Upon completion, the solvent was removed under reduced pressure, and the crude product was extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄, concentrated under vacuum, and purified by silica gel column chromatography using hexane/ EtOAc (96:4) as the eluent. This yielded the pure product as a yellow solid (8.3 g, 85 %).¹H NMR (500 MHz, CDCl₃) δ 10.06 (s, 1H), 8.66 (s, 1H), 8.61 (s, 1H), 8.00 (dd, J = 8.5, 1.5 Hz, 1H), 7.97 (dd, J = 8.3, 1.0 Hz, 1H), 7.43 (t, J = 8.5 Hz, 2H), 4.29 (t, J = 7.3 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.40 (s, 12H), 1.35 – 1.30 (m, 2H), 1.29 - 1.25 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H).

Synthesis of 6-(benzo[d]thiazol-5-yl)-9-hexyl-9H-carbazole-3-carbaldehyde (5)

To a 100 ml Schlenk flask 9-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9Hcarbazole-3-carbaldehyde (3 g, 7.4 mmol), 5-bromobenzo[d]thiazole (1.4 g, 6.7 mmol), were dissolved in tetrahydrofuran (40 mL) and potassium carbonate (2 M, 5 mL) were added. The reaction mixture was degassed using N₂ gas for 30 minutes then tetrakis (triphenylphosphine) palladium (0) Pd(PPh₃)₄ (75 mg, 0.06 mmol) catalyst was added to the reaction mixture. The reaction mixture was refluxed for 24 h under N₂ atmosphere. After removing the volatiles, the crude product was extracted using EtOAc/ H₂O and brine solution. The organic layer collected were dried over anhydrous Na₂SO₄. The crude product obtained upon concentrating under reduced pressured was purified using column chromatography with hexane/ EtOAc (90:10) as eluents. The pure product was obtained as white solid (2.3 g, 75.4 %). ¹H NMR (500 MHz, CDCl₃) δ 10.08 (s, 1H), 9.05 (s, 1H), 8.62 (s, 1H), 8.44 (s, 1H), 8.40 (s, 1H), 8.02 (t, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 10.2 Hz, 1H), 7.79 (d, *J* = 9.7 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 4.30 (t, *J* = 7.3 Hz, 2H), 1.93 – 1.83 (m, 2H), 1.41 – 1.36 (m, 2H), 1.30 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H).

Synthesis of (Z)-3-(6-(benzo[d]thiazol-5-yl)-9-hexyl-9H-carbazol-3-yl)-2phenylacrylonitrile (**5-BTCZCS**)

To a suspension of 6-(benzo[d]thiazol-5-yl)-9-hexyl-9H-carbazole-3-carbaldehyde (500 mg, 1.2 mmol) in 50 ml methanol, potassium tert-butoxide (543.6 mg,4.8 mmol) and the benzyl cyanide (210 µl, 1.8 mmol) were added. The reaction mixture was stirred at 65 °C up to the complete consumption of reactant. The reaction was monitored via thin layer chromatography (TLC) and the formation of product was confirmed. The hot reaction mixture was filtered and washed with methanol. The pure product was obtained as yellow solid. (320 mg, 62.6 %). ¹H NMR (500 MHz, CDCl₃) δ 9.05 (s, 1H), 8.68 (s, 1H), 8.45 (d, *J* = 16.1 Hz, 2H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 6.3 Hz, 3H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 4.35 (t, *J* = 7.2 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.46 – 1.39 (m, 2H), 1.38 – 1.29 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 155.0, 154.6, 143.9, 142.5, 141.1, 140.9, 135.7, 133.1, 132.5, 129.5, 129.0, 127.8, 126.6, 126.2, 126.0, 125.5, 123.9, 123.8, 123.2, 122.5, 122.4, 120.0, 119.6, 110.1, 109.8, 108.1, 44.0, 32.0, 29.5, 27.4, 23.0, 14.5. HRMS-ESI Calcd. for [M+H]⁺ C₃₄H₃₀N₃S Exact Mass: 512.2160; Found 512.2161.

Synthesis of (Z)-3-(6-bromo-9-hexyl-9H-carbazol-3-yl)-2-phenylacrylonitrile (6)

To a solution of bromocarbazole carbaldehyde (2 g and 5.6 mmol) dissolved in MeOH (80 ml) and NaOH (0.9 mg and 22.4 mmol) and benzyl cyanide (1 ml and 8.4 mmol) were added and stirred at 65 $^{\circ}$ C for 17 h, with the reaction progress monitored using TLC. Upon

confirming the complete consumption of reactant, the mixture was filtered, washed with methanol, and dried under vacuum, yielding the pure product as a yellow powder (2.00 g, 78.3 %). ¹H NMR (500 MHz, CDCl₃) δ 8.56 (s, 1H), 8.24 (d, *J* = 1.9 Hz, 1H), 8.12 (d, *J* = 10.4 Hz, 1H), 7.73 – 7.68 (m, 3H), 7.57 (d, *J* = 10.6 Hz, 1H), 7.47 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.38 (t, *J* = 6.9 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 4.27 (t, *J* = 7.3 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.39 – 1.33 (m, 2H), 1.33 – 1.25 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 143.6, 142.2, 140.1, 135.6, 129.5, 129.5, 129.1, 128.2, 126.2, 125.7, 124.9, 123.9, 123.0, 122.6, 119.5, 113.1, 111.1, 109.8, 108.5, 43.9, 32.0, 29.4, 27.4, 23.0, 14.5. HRMS-ESI Calcd. for [M+H]⁺ C₂₇H₂₆N₂Br Exact Mass: 457.1279; Found 457.1262.

Synthesis of (Z)-3-(9-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-3-yl)-2-phenylacrylonitrile (7)

To a 100 ml oven dried Schlenk flask cooled under vacuum, (Z)-3-(6-bromo-9-hexyl-9Hcarbazol-3-yl)-2-phenylacrylonitrile (3.2 g, 6.9 mmol), bis(pinacol-ato)diboron (2.1 g, 8.1 mmol), potassium acetate (2.1 g, 20.9 mmol), triphenylphosphine (73.3 mg,0.28 mmol) were added and dissolved using dry toluene (100 ml) under nitrogen atmosphere. And the reaction mixture is degassed using N₂ gas for 30 minutes. After that dichlorobis(triphenylphosphine)palladium(II) (50 mg, 0.07 mmol) catalyst were added and purged using N₂ gas and heated at 110 °C for 24 h. The solvent was evaporated under reduced pressure, crude product was extracted with EtOAc, and the organic volume were dried over Na₂SO₄. The crude product was obtained as a brown-black liquid upon removal of solvents under vacuo. The product was purified by column chromatography using hexane/ EtOAc (90:10) as eluents. The solvents were evaporated to obtain a yellow color solid (2.6 g, 73.6 %). ¹H NMR (500 MHz, CDCl₃) δ 8.66 (s, 1H), 8.61 (s, 1H), 8.16 (d, J =8.6 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.74 – 7.69 (m, 3H), 7.49 – 7.44 (m, 3H), 7.42 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 7.4 Hz, 1H), 4.31 (t, J = 7.2 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.41 (s, 12H), 1.36 - 1.26 (m, 6H), 0.87 (t, J = 7.0 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 144.0, 143.6, 142.1, 135.7, 133.3, 129.4, 128.9, 128.5, 127.3, 126.2, 125.6, 123.9, 123.3, 122.9, 119.5, 109.6, 109.0, 108.1, 84.2, 43.8, 31.9, 29.4, 27.3, 25.4, 22.9, 14.4. HRMS-ESI Calcd. for [M+H]⁺C₃₃H₃₈BN₂O₂ Exact Mass: 505.3026; Found 505.3047.

Synthesis of (Z)-3-(6-(benzo[d]thiazol-5-yl)-9-hexyl-9H-carbazol-3-yl)-2phenylacrylonitrile (**2-BTCZCS**)

To a 100 ml Schlenk flask 9 (Z)-3-(9-hexyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)-9H-carbazol-3-yl)-2-phenylacrylonitrile (0.5 g, 0.99 mmol), 5-bromobenzo[d]thiazole (254.6 mg, 1.2 mmol), and potassium carbonate (2 M, 5 mL) were dissolved in tetrahydrofuran (40 mL). The reaction mixture was degassed using N₂ gas for 30 minutes then tetrakis (triphenylphosphine) palladium (0) Pd(PPh₃)₄ (15 mg, 0.01 mmol) catalyst was added to the reaction mixture. The reaction mixture was refluxed for 24 h under N_2 atmosphere. After removing the volatiles, the crude product was extracted using DCM/H₂O and brine solution. The organic layer collected were dried over anhydrous Na₂SO₄. The pure product was obtained by recrystallisation using MeOH/ Et₂O (210 mg, 41.4 %). ¹H NMR (500 MHz, CDCl₃) δ 8.81 (s, 1H), 8.58 (s, 1H), 8.21 (m, 2H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.74 – 7.68 (m, 3H), 7.50 – 7.43 (m, 5H), 7.41 – 7.35 (m, 2H), 4.29 (t, J = 7.3 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.42 – 1.35 (m, 2H), 1.34 – 1.26 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 169.3, 154.7, 143.6, 142.9, 142.5, 135.5, 135.4, 129.5, 129.1, 127.6, 126.7, 126.5, 126.2, 126.1, 126.0, 125.2, 123.7, 123.6, 123.6, 123.2, 122.0, 120.7, 119.4, 110.0, 109.9, 108.6, 43.9, 31.9, 29.4, 27.3, 22.9, 14.4. HRMS-ESI Calcd. for [M+H]⁺ C₃₄H₃₀N₃S Exact Mass: 512.2160; Found 512.2161.

3. Characterisation Data



Figure S1. ¹H NMR spectrum (500 MHz) of 1 in CDCl₃







Figure S3. ¹H NMR spectrum (500 MHz) of 3 in CDCl₃







Figure S5. ¹H NMR spectrum (500 MHz) of 5 in CDCl₃



Figure S7. ${}^{13}C{}^{1}H$ NMR spectrum (126 MHz) of 6 in CDCl₃.



Figure S8. HRMS Spectra of compound 6.



Figure S9. ¹H NMR spectrum (500 MHz) of 7 in CDCl₃



Figure S10. ${}^{13}C{}^{1}H$ NMR spectrum (126 MHz) of 7 in CDCl₃.



Figure S11. HRMS Spectra of compound 7.



Figure S13. ¹³C{¹H} NMR spectrum (126 MHz) of 2-BTCZCS in CDCl₃.



Figure S15. ¹H NMR spectrum (500 MHz) of 5-BTCZCS in CDCl₃



Figure S16. ¹³C{¹H} NMR spectrum (126 MHz) of 5-BTCZCS in CDCl₃.



Figure S17. HRMS Spectra of compound 5-BTCZCS.

4. Optical Properties



Figure. S18: A) Normalized absorption (right) and B) Normalized emission spectra (left) of isomers **2-BTCZCS** and **5-BTCZCS** (Con. 10 μ M, $\lambda_{ex} = 385$ nm).

Isomers	$\lambda_{abs} (nm)/\epsilon^a (\times 10^4)$	λem (nm)	Φ _f ^b
2-BTCZCS	385 (3.3), 315 (3.5), 240 (2.3)	447	3.0 %
5-BTCZCS	385 (2.2), 290 (2.8), 250 (2.5)	460	3.7 %

Table S1. Photophysical Properties of isomers

^aMeasured in DCM (10⁻⁵ M). ^bAbsolute Quantum yields calculated in solution states using calibarated integrated sphere.



Figure S19. Normalised Absorption spectra of (A) 2-BTCZCS and (B) 5-BTCZCS in different polarity of solvents.

Compounds	Solvents	$\lambda_{max}^{[a]}(nm)$	$\lambda_{max}^{\left[b ight] }\left(nm ight)$	Δ ν ^[c]
	Hexane	372	425	3352
	Toluene	381	435	3258
2-BTCZCS	DCM	384	447	3670
	THF	380	444	3793
	ACN	378	465	4949
	DMF	383	461	4417
	Hexane	373	430	3553
	Toluene	381	438	3415
5-BTCZCS	DCM	384	459	4255
	THF	383	451	3936
	ACN	381	488	5755
	DMF	377	485	5906

Table S2. Photophysical properties of compounds **2-BTCZCS** and **5-BTCZCS** in different polarity of solvents ($\lambda_{ex} = 385$ nm for compounds).

[a] peak position of the maximum absorption band in nm. [b] Peak position of emission maxima in nm [c] Stokes shift in cm⁻¹.



Figure S20. Fluorescence life time decay profile of (A) **2-BTCZCS** and (B) **5-BTCZCS** in different polarity of solvents.

Table S3. Details of fluorescence decay profile of compounds 2-BTCZCS and 5-BTCZCSin different polarity of solvents

Compounds	Solvents	$A_1/A_2/A_3$	τ_1 (ns)	τ ₂ (ns)	τ3 (ns)	τ _{avr} (ns)
2-BTCZCS	Hexane	53.07/46.41/0.52	1.14	0.04	6.83	0.66
	Toluene	32.41/5.13/62.45	1.14	0.04	6.83	4.63
	THF	87.31/6.09/6.60	1.14	0.04	6.83	1.45

	DCM	33.77/63.07/3.16	1.14	0.04	6.83	0.63
	ACN	26.55/67.26/6.19	1.14	0.04	6.83	0.75
	DMF	25.81/66.84/7.35	1.14	0.04	6.83	0.83
5-BTCZCS	Hexane	66.11/33.06/0.82	1.14	0.04	6.83	0.82
	Toluene	33.17/3.76/63.06	1.14	0.04	6.83	4.68
	THF	90.06/0.09/9.85	1.14	0.04	6.83	1.70
	DCM	33.91/50.70/15.40	1.14	0.04	6.83	1.46
	ACN	15.54/64.55/19.91	1.14	0.04	6.83	1.56
	DMF	21.74/59.80/18.46	1.14	0.04	6.83	1.53

 τ_{avr} is calculated using the equation

$$\tau \, avr = \frac{(A1\tau 1 + A2\tau 2 + A3\tau 3)}{(A1 + A2 + A3)}$$

A is the percentage fraction of each life time component τ .

Table S4. Photophysica	l properties of Com	pounds in aggregated states
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Compounds	$\lambda_{\max}^{[a]}$ (Solution)	$\lambda_{max}^{[a]}$ (Aggregates)	Φ _f ^b (Solution)	Φ _f ^b (Aggregates)
2-BTCZCS	440 nm	475 nm	2.7 %	8 %
5-BTCZCS	450 nm	480 nm	2.1 %	9 %

[a] peak position of the emission maxima in nm. [b] Absolute quantum yield calculated.

5. SEM images



Figure S21. SEM images of (A) aggregates of **5** and (B) **6** (drop-casted from a 10^{-5} M THF/H₂O solution with $f_w = 90\%$.

6. Dynamic light Scattering studies



Figure S22. Size distributions of the aggregates of (A) 5 and (B) 6 THF-H₂O mixtures with $f_w = 90\%$ (Concentration: 1×10^{-5} mol/L).

7. Solid state Emission



Figure S23. Solid-state emission spectra of compounds (λ_{ex} = 385 nm). Digital images taken under UV lamp 365 nm are shown above the spectra.



5-BTCZCS

Figure S24. Digital images taken under UV lamp 365 nm of compounds 2-BTCZCS and 5-BTCZCS under annealing conditions.



Figure S25. Digital images taken under UV lamp 365 nm of compound **5-BTCZCS** under fuming with different solvents.

8. SCXRD Data



Figure S26. ORTEP diagram of compound **2-BTCZCS** with ellipsoids shown at the 50% probability level (Hydrogen atoms are omitted for clarity).

Table S5. Refined SCXRD data	a parameters of compound	2-BTCZCS
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Compound 2-BTCZCS			
Identification code	shelx		
Empirical formula	$C_{34}H_{29}N_3S$		
Formula weight	511.66		
Temperature	296(2) K		
Wavelength	0.71073 A		
Crystal system, space group	Triclinic, Pī		
Unit cell dimensions	$a = 9.1139(6)$ Å $\alpha = 101.387(4)$ deg.		
	$b = 10.7892(8)$ Å $\beta = 94.491(4)$ deg.		

	$c = 14.2581(10) \text{ Å} \gamma = 97.680(4) \text{ deg.}$
Volume	1354.17(17) A ³
Z, Calculated density	2, 1.255 Mg/m ³
Absorption coefficient	0.148 mm ⁻¹
F(000)	540
Crystal size	0.502 x 0.263 x 0.095 mm
Theta range for data collection	1.948 to 25.419 deg.
Limiting indices	-10<=h<=10, -12<=k<=12, -17<=l<=17
Reflections collected / unique	35611 / 4900 [R(int) = 0.1074]
Completeness to theta $= 25.242$	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8322
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4900 / 35 / 344
Goodness-of-fit on F ²	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0705, wR2 = 0.1672
R indices (all data)	R1 = 0.1792, WR2 = 0.2180
Extinction coefficient	n/a
Largest diff. peak and hole	0.439 and -0.320 e.A ⁻³

Table S6. Interactions present in the crystals.

Compound	Short contacts (D-HA)	d(HA) (Å)
2-BTCZCS	C(17)-H(17)N(2)	2.694
	C(16)-H(16)S(1)	3.499

9. DFT and TD-DFT Calculations

DFT calculation data of Compounds 2-BTCZCS and 5-BTCZCS.

Calculation method: B3LYP/6-311G(d, p) with Gaussian 09.

Table S7: Compound 2-BTCZCS

6	5.772118000	-2.980881000	0.424855000
6	6.491275000	-4.136793000	0.726608000
1	5.988611000	-5.078107000	0.911694000
6	7.878229000	-4.047698000	0.783979000
1	8.458349000	-4.933028000	1.016509000
6	8.534872000	-2.829862000	0.545394000
1	9.616602000	-2.788832000	0.596473000
6	7.817840000	-1.680268000	0.245683000
1	8.313685000	-0.735073000	0.060260000
6	6.419082000	-1.747278000	0.182683000
6	4.330655000	-1.032983000	-0.091121000

6	3.219595000	-0.115646000	-0.360089000
6	3.514277000	1.226131000	-0.700431000
1	4.553105000	1.524284000	-0.748404000
6	2.517256000	2.148748000	-0.966566000
1	2.772137000	3.169692000	-1.221216000
6	1.187895000	1.719634000	-0.893027000
6	0.867097000	0.379965000	-0.550739000
6	1.885504000	-0.531148000	-0.286543000
1	1.637866000	-1.553242000	-0.023042000
6	-1.482808000	-0.736811000	-0.326907000
1	-1.126163000	-1.726157000	-0.061649000
6	-0.578298000	0.290061000	-0.565756000
6	-1.056242000	1.580315000	-0.917373000
6	-2.428430000	1.834568000	-1.025280000
1	-2.804080000	2.814183000	-1.292223000
6	-3.311456000	0.797388000	-0.782120000
1	-4.368208000	1.000253000	-0.872405000
6	-2.867929000	-0.504200000	-0.425875000
6	-3.736523000	-1.638250000	-0.156603000
1	-3.187472000	-2.554160000	0.038426000
6	-5.090378000	-1.773839000	-0.085062000
6	-5.744363000	-3.086879000	0.176044000
6	-6.967618000	-3.152214000	0.861119000
1	-7.445736000	-2.239123000	1.196553000
6	-7.571274000	-4.377801000	1.126954000
1	-8.512588000	-4.404597000	1.663905000
6	-6.969918000	-5.563434000	0.708901000
1	-7.441786000	-6.517541000	0.913024000
6	-5.762011000	-5.511087000	0.013883000
1	-5.294600000	-6.425335000	-0.333838000
6	-5.158412000	-4.287122000	-0.256875000
1	-4.239457000	-4.264834000	-0.830313000
6	-5.981343000	-0.668490000	-0.232766000
6	-0.065291000	3.848927000	-1.447299000
1	-0.956695000	3.998188000	-2.060252000

1	0.791116000	4.096728000	-2.078683000
6	-0.105441000	4.758028000	-0.212024000
1	0.797198000	4.591059000	0.386019000
1	-0.955437000	4.465951000	0.411422000
6	-0.203328000	6.239824000	-0.596368000
1	0.629668000	6.487015000	-1.265107000
1	-1.120450000	6.405858000	-1.175908000
6	-0.178850000	7.205753000	0.598582000
1	0.731831000	7.030432000	1.185691000
1	-0.100807000	8.230140000	0.215334000
6	-1.401692000	7.120097000	1.520826000
1	-1.475636000	6.116327000	1.952655000
1	-2.310602000	7.264988000	0.923932000
6	-1.365226000	8.150641000	2.653646000
1	-0.481657000	8.011344000	3.284571000
1	-2.247340000	8.070316000	3.294813000
1	-1.332025000	9.170935000	2.258471000
7	5.581179000	-0.687097000	-0.101374000
7	-6.741502000	0.198035000	-0.341279000
7	0.017764000	2.427101000	-1.119181000
16	4.040957000	-2.761144000	0.277758000
Tab	ole S8: Compoun	d 5-BTCZCS	
6	-3.373556000	1.473575000	-0.612735000
6	-3.165033000	0.112148000	-0.296365000
6	-1.853719000	-0.369244000	-0.218509000
6	-0.781438000	0.492002000	-0.450119000
6	-1.022548000	1.852704000	-0.764846000
6	-2.323479000	2.351680000	-0.847655000
6	0.657425000	0.326037000	-0.438073000
6	1.212403000	1.597484000	-0.749137000
7	0.192430000	2.503936000	-0.952970000
6	1.500248000	-0.751951000	-0.200755000
6	2.898269000	-0.594695000	-0.267229000
6	3.419747000	0.691103000	-0.572990000
6	2.599797000	1.779641000	-0.811451000

6	3.696221000	-1.779750000	-0.004695000	
6	5.035662000	-2.028130000	-0.052488000	
6	-4.320126000	-0.790080000	-0.049807000	
6	-4.301388000	-2.112062000	-0.495933000	
6	-5.392066000	-2.951260000	-0.244966000	
6	-6.514900000	-2.456163000	0.453444000	
6	-6.552660000	-1.136063000	0.904123000	
6	-5.458342000	-0.323181000	0.649479000	
7	-5.482795000	-4.279376000	-0.643329000	
6	-6.607581000	-4.789404000	-0.272483000	
16	-7.708917000	-3.728057000	0.605201000	
6	5.609691000	-3.355521000	0.305874000	
6	6.783059000	-3.817216000	-0.310585000	
6	7.309255000	-5.067097000	0.002674000	
6	6.678861000	-5.880217000	0.942695000	
6	5.520983000	-5.426489000	1.573787000	
6	4.995367000	-4.175633000	1.265873000	
6	0.757369000	9.541084000	1.905644000	
6	0.744675000	8.665010000	0.649563000	
6	0.574233000	7.172923000	0.957320000	
6	0.555439000	6.286988000	-0.293409000	
6	0.385923000	4.798269000	0.028501000	
6	0.353785000	3.927866000	-1.234478000	
6	5.983212000	-1.046845000	-0.471709000	
7	6.787044000	-0.284984000	-0.809689000	
1	-4.387969000	1.845310000	-0.695709000	
1	-1.671081000	-1.404632000	0.045248000	
1	-2.522193000	3.387693000	-1.092045000	
1	1.084921000	-1.725061000	0.038115000	
1	4.488150000	0.841880000	-0.618190000	
1	3.034783000	2.745658000	-1.034775000	
1	3.094738000	-2.640879000	0.269710000	
1	-3.460910000	-2.503399000	-1.055786000	
1	-7.406072000	-0.751703000	1.448848000	
1	-5.469444000	0.695055000	1.019250000	

1	-6.904311000	-5.812182000	-0.467018000
1	7.281888000	-3.198504000	-1.047617000
1	8.212554000	-5.405722000	-0.491832000
1	7.090244000	-6.852226000	1.188880000
1	5.032579000	-6.041398000	2.321220000
1	4.116313000	-3.825846000	1.793730000
1	0.879164000	10.598159000	1.653732000
1	-0.176323000	9.437977000	2.467430000
1	1.578172000	9.261340000	2.573542000
1	1.676531000	8.813610000	0.090811000
1	-0.064951000	8.990833000	-0.014590000
1	-0.356941000	7.024390000	1.518767000
1	1.386004000	6.846291000	1.619709000
1	1.485718000	6.434461000	-0.856236000
1	-0.258275000	6.611335000	-0.954375000
1	-0.540216000	4.644552000	0.592604000
1	1.205691000	4.461883000	0.672408000
1	1.274047000	4.053969000	-1.808847000
1	-0.465601000	4.233954000	-1.889631000

 Table S9. DFT data of compounds 2-BTCZCS and 5-BTCZCS

Compounds	HOMO-	НОМО	LUMO	LUMO+1	HOMO-	HOMO-1-
	1 (eV)	(eV)	(eV)	(eV)	LUMO (eV)	LUMO (eV)
2-BTCZCS	-6.1704	-5.7300	-2.2426	-1.7337	3.49	3.92
5-BTCZCS	-6.1230	-5.6379	-2.1560	-1.3715	3.48	3.96

Table S10. TD-DFT simulated absorption values corresponding to major transitions

Compounds	λβ3Lyp ^a (nm)	λcam-b3lyp ^a (nm)	$\lambda_{M06^{a}}(\mathbf{nm})$	$\lambda_{M062X^a}(nm)$	$\lambda_{WB97XD^{a}}(\mathbf{nm})$
2-BTCZCS	390.02	338.86	378.82	339.19	333.66
	(1.0992)	(1.5019)	(1.2168)	(1.5088)	(1.5482)
5-BTCZCS	400.96	337.32	383.61	338.87	331.45
	(0.6694)	(1.129)	(0.8142)	(1.1262)	(1.1714)

^a Values obtained from various density functionals (B3LYP, CAM-B3LYP and M06-2X)/6-31G (d, p)/PCM (dichloromethane) levels of theory, and oscillator strength values are given in parenthesis.



Figure S27. Simulated absorption spectra of compound **2-BTCZCS** using different functionals with 6-311G (d, p) level of theory.



Figure S28. Simulated absorption spectra of compound **5-BTCZCS** using different functionals with 6-311G (d, p) level of theory.



Figure S29. Simulated absorption spectra of compound A) **2-BTCZCS** and B)**5-BTCZCS** using M06 with 6-311G (d, p) level of theory.

Table S11. Computed singlet vertical transitions involved in Compound 2-BTCZCS from TD-
DFT calculation using 6-311G (d, p) basis set M06 functional in Gaussian09.

Excited States	E (eV)	$\lambda_{max}(nm)$	f ^a	Major transitions (%)
S ₁	3.2729 eV	378.82 nm	1.2168	HOMO→LUMO (46.9 %)
S_2	3.6527 eV	339.43 nm	0.1139	HOMO-3 \rightarrow LUMO (2.5 %)
				HOMO-1→LUMO (30.7 %)
				HOMO→LUMO+1 (3.0 %)
				HOMO→LUMO+2 (12.29 %)
S ₃	3.8581 eV	321.36 nm	0.1783	HOMO-1→LUMO (5.1 %)
				HOMO-1→LUMO+1 (2.3 %)
				HOMO→LUMO (1.5 %)
				HOMO→LUMO+1 (39.78 %)
S 4	3.9266 eV	315.75 nm	0.3726	HOMO-3→ LUMO (1.92 %)
				HOMO-1→LUMO (8.7 %)
				HOMO-1→LUMO+1 (6.14 %)
				HOMO-1→LUMO+2 (1.87 %)
				HOMO→LUMO+1 (3.84 %)
				HOMO→LUMO+3 (24.0 %)
S ₅	4.0432 eV	306.65 nm	0.5949	HOMO-3→ LUMO (1.04 %)
				HOMO-1→LUMO (3.97 %)
				HOMO-1→LUMO+1 (32.86 %)

		HOMO-1→LUMO+2 (3.78 %)
		HOMO→LUMO+3 (5.16 %)

Table S12. Computed singlet vertical transitions involved in Compound **5-BTCZCS** from TD-DFT calculation using 6-311G (d, p) basis set M06 functional in Gaussian09.

Excited States	E (eV)	$\lambda_{max}(nm)$	f ^a	Major transitions (%)
S_1	3.2320 eV	383.61 nm	0.8142	HOMO-1→ LUMO (1.31 %)
				HOMO \rightarrow LUMO (47.2 %)
S ₂	3.6180 eV	342.69 nm	0.0797	HOMO-2→ LUMO (2.14 %)
				HOMO-1 \rightarrow LUMO (33.76 %)
				HOMO \rightarrow LUMO+1 (10.44 %)
S_3	3.8010 eV	326.18 nm	0.2357	HOMO-1 \rightarrow LUMO (11.65 %)
				HOMO-1 \rightarrow LUMO+1 (1.26 %)
				HOMO \rightarrow LUMO+1 (31.7 %)
				HOMO \rightarrow LUMO+1 (1.1 %)
S_4	4.1039 eV	302.11 nm	0.0466	HOMO-3→ LUMO+3 (1.54 %)
				HOMO-2→LUMO+2 (1.1 %)
				HOMO-1→LUMO+2 (3.88 %)
				HOMO→LUMO+1 (1.84 %)
				HOMO→LUMO+2 (37.9 %)
S ₅	4.2203 eV	293.78 nm	0.1228	HOMO-2 \rightarrow LUMO (1.0 %)
				HOMO-1 \rightarrow LUMO+1 (25.5 %)
				HOMO \rightarrow LUMO+3 (15.6 %)

10.Thermal properties



Figure S30. (A) TGA and (B) DSC curves of the compounds 5 and 6.

11. References

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