Donor Positional Inversion in Carbazole-Cyanostilbene Conjugates: Reorienting Connectivity for Solid-State Color Modulation

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Table of Contents

1. **Materials and Measurements**……**S2**
2. **Experimental Section**……**S3**
3. **Characterisation Data**……**S4**
4. **SCXRD**……**S6**
5. **Optical Properties**……**S7**
6. **SEM images**……**S8**
7. **Dynamic Light Scattering studies**……**S8**
8. **VT-PXRD**……**S9**
9. **DFT data** ……**S9**
10. **Thermal properties**……**S12**
11. **References**……**S12**

1. Materials and Measurements

The starting material for the synthetic scheme Anthracene, carbazole and the chemicals including bromohexane, bis(pinacolato)diboron, triphenylphosphine, dichlorobis(triphenylphosphine)palladium(II), tetrakis(triphenylphosphine)palladium(0), 2-(4-bromophenyl)acetonitrile, N-Bromosuccinimade, KOAc, NaOH, K_2CO_3, dimethylformamide, 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 ºC oven. Dichloroethane were dried over CaH_2, 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 ^{1}H, ^{13}C NMR, spectra of the synthesized compounds were recorded on a JEOL JNM-ECZ-500R/M1 (500 MHz) NMR spectrometer, using $CDCl_3$ 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 ºC, 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 for liquid and 20 and 20 for solid, respectively. Data for SCXRD were collected on a Bruker D8 QUEST KAPPA diffractometer equipped with a PHOTON III C14 CPAD detector using Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. The structure was solved by Intrinsic Phasing (SHELXT-2018/2) and refined by full-matrix least-squares on F^2 (SHELXL-2019/2); all non-hydrogen atoms were refined anisotropically. X-ray diffraction (XRD) and VT-PXRD patterns in the 2θ range of 5º to 50º were recorded on a Rigaku SmartLab SE employing a CuKα radiation source (λ = 1.5406 Å). 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/6-31G(d,p) level using the Gaussian 09W software package. Thermogravimetric analysis (TGA) was performed on a TGAQ50V20.13 Build39 instrument,

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

The compounds **1-4** were synthesized accordingly from our previous study.[1]

Synthesis of (Z)-3-(anthracen-9-yl)-2-(4-bromophenyl)acrylonitrile (**5**)

Anthracene-9-carbaldehyde (1.00 g, 4.85 mmol) was dissolved in methanol (50 mL) in a 100 ml round-bottom flask. Sodium hydroxide (780 mg, 19.42 mmol) was added to the suspension, followed by the portionwise addition of 2-(4-bromophenyl)acetonitrile (1.43 g, 7.28 mmol). The reaction mixture was stirred at 65 ºC until complete consumption of the aldehyde, as monitored by thin-layer chromatography (TLC). Upon completion, the hot mixture was filtered to isolate the precipitated product, which was washed with hot methanol and dried under vacuum to obtain the pure product (1.86 g, 88 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.36 (s, 1H), 8.05 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.50 (m, 4H).

Synthesis of (Z)-3-(anthracen-9-yl)-2-(4-(9-hexyl-9H-carbazol-3-yl)phenyl)acrylonitrile (**AN-CZ-CS**)

In a 100 mL Schlenk flask, a mixture of (Z)-3-(anthracen-9-yl)-2-(4-bromophenyl)acrylonitrile (500 mg, 1.31 mmol), 9-hexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (590 mg, 1.56 mmol), and potassium carbonate (2 M aqueous solution, 5 mL) was dissolved in tetrahydrofuran (60 mL). The reaction mixture was degassed by bubbling nitrogen gas for 30 minutes. Subsequently, tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 15 mg, 0.013 mmol) was added under a nitrogen atmosphere. The reaction was refluxed for 24 hours under an inert atmosphere. Upon completion, the mixture was cooled to room temperature, and solvents were removed under reduced pressure. The resulting residue was extracted with dichloromethane and water. The organic layer was separated, dried over anhydrous sodium sulfate, and concentrated under vacuum to yield the crude product. The crude product was purified using flash column chromatography using DCM as the eluent. The final product was obtained by washing the solid with hot methanol and further washing with hexane, affording the purified compound as a yellow solid (390 mg, 54 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.46 (s, 1H), 8.42 (s, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.90 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.59

– 7.55 (m, 3H), 7.54 – 7.50 (m, 3H), 7.46 (d, J = 8.2 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 4.33 (t, J = 7.1 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.47 – 1.40 (m, 2H), 1.39 – 1.30 (m, 4H), 0.91 (t, J = 6.8 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 144.1, 141.4, 140.8, 139.6, 131.7, 131.6, 131.2, 130.0, 129.6, 129.4, 128.5, 128.3, 127.1, 127.0, 126.5, 126.0, 125.6, 125.4, 123.9, 123.3, 121.4, 121.0, 119.6, 119.3, 117.1, 109.6, 109.4, 43.7, 32.1, 29.4, 27.5, 23.0, 14.5. HRMS-ESI Calcd. for $[M+H]^+$ $C_{41}H_{34}N_2$ Exact Mass: 554.2713; Found 554.2722.

3. Characterisation Data

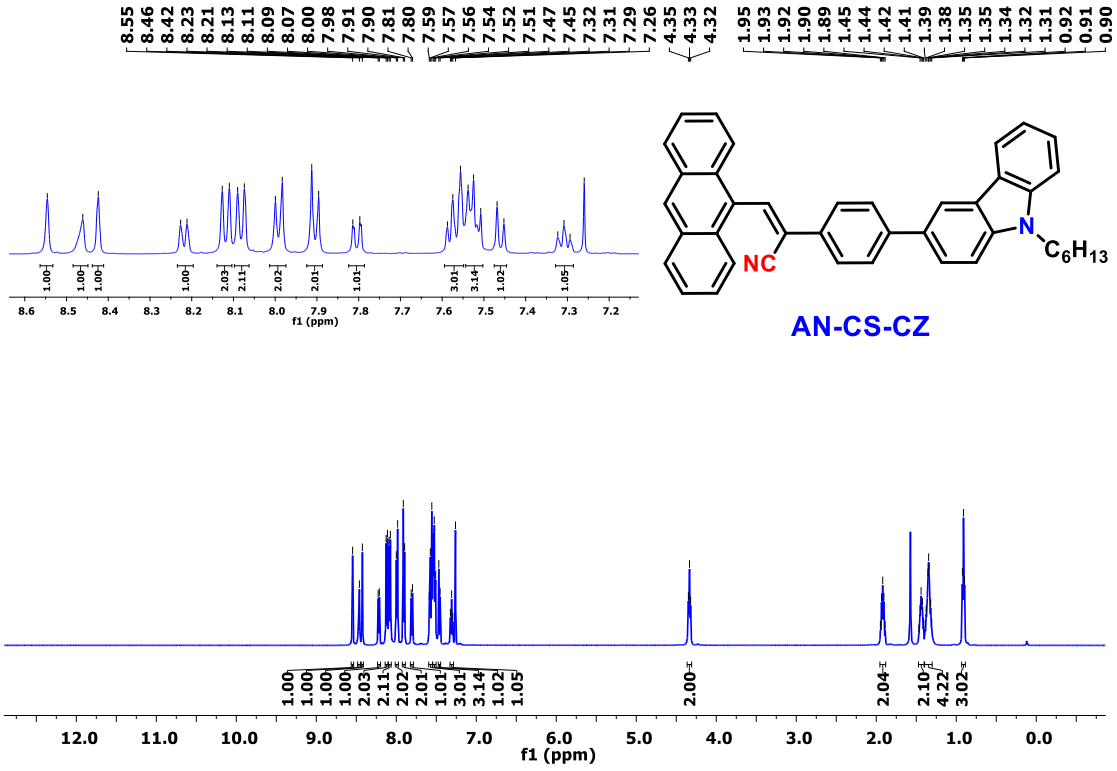

Figure S1. ^{1}H NMR spectrum (500 MHz) of **AN-CS-CS** in $CDCl_3$

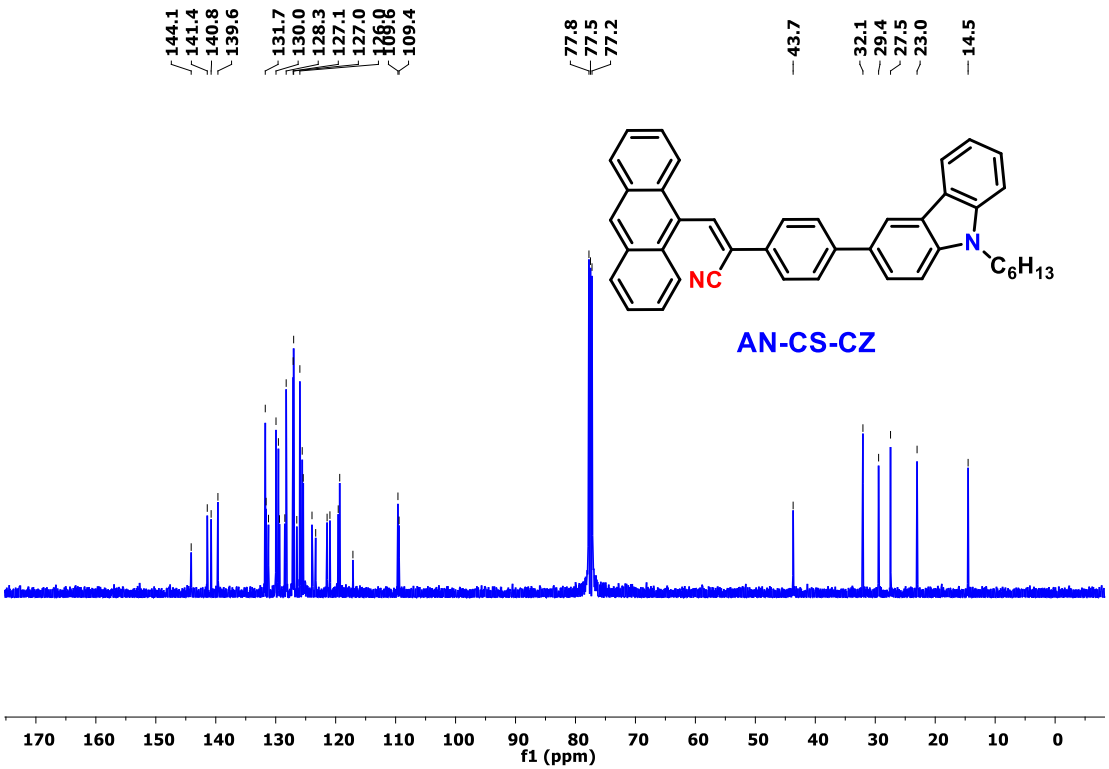

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz) of **AN-CS-CZ** in $CDCl_3$.

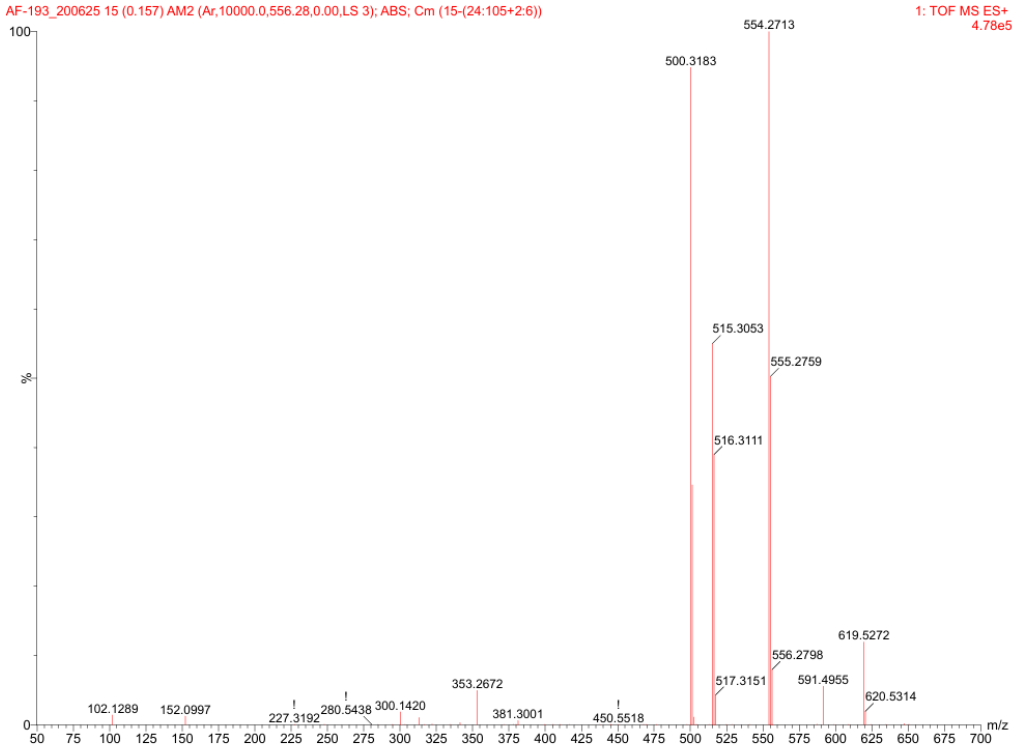

Figure S3. HRMS Spectra of compound **AN-CS-CZ**.

4. SCXRD Data

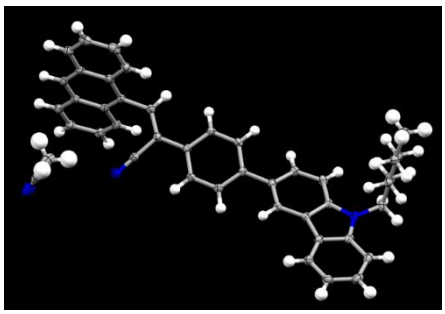

Figure S4. ORTEP diagram of compound **AN-CS-CZ** with ellipsoids shown at the 50% probability level.

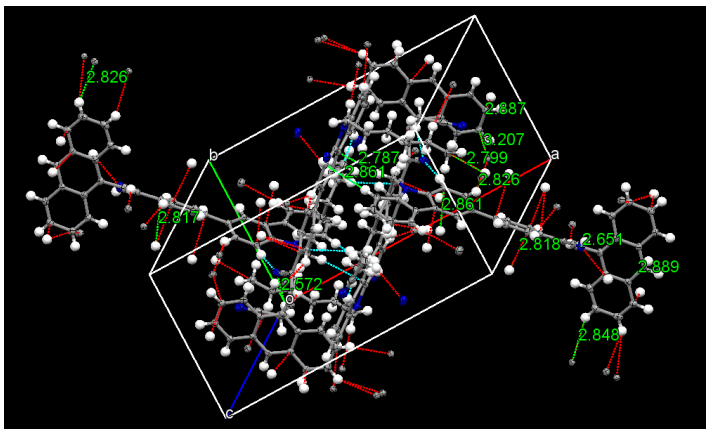

Figure S5. Interactions present in the crystal structure **AN-CS-CZ**.

Table S1. Refined SCXRD data parameters of compound **AN-CS-CZ**

CCDC number	2500771
Empirical formula	$C_{43}H_{37}N_3$
Formula weight	595.75
Temperature [K]	100(2)
Crystal system	monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	18.2101(8)
b [Å]	10.0951(4)
c [Å]	18.8354(9)
α [°]	90
β [°]	111.661(2)
γ [°]	90
Volume [Å^3]	3218.1(2)
Z	4
ρ_{calc} [gcm^{-3}]	1.23
μ [mm^{-1}]	0.072
F(000)	1264

Crystal size [mm^3]	0.04×0.1×0.251
Crystal colour	yellow
Crystal shape	block
Radiation	Mo K_α (λ=0.71073 Å)
2θ range [°]	3.92 to 56.73 (0.75 Å)
Index ranges	−24 ≤ h ≤ 24 −13 ≤ k ≤ 13 −25 ≤ l ≤ 25
Reflections collected	77474
Independent reflections	8017 R_{int} = 0.0429 R_{sigma} = 0.0231
Completeness to θ = 25.242°	99.9
Data / Restraints / Parameters	8016 / 0 / 417
Goodness-of-fit on F^2	1.019
Final R indexes [I≥2σ(I)]	R_1 = 0.0424 wR_2 = 0.1077
Final R indexes [all data]	R_1 = 0.0497 wR_2 = 0.1152
Largest peak/hole [eÅ^{-3}]	0.31/−0.26

5. Optical Properties

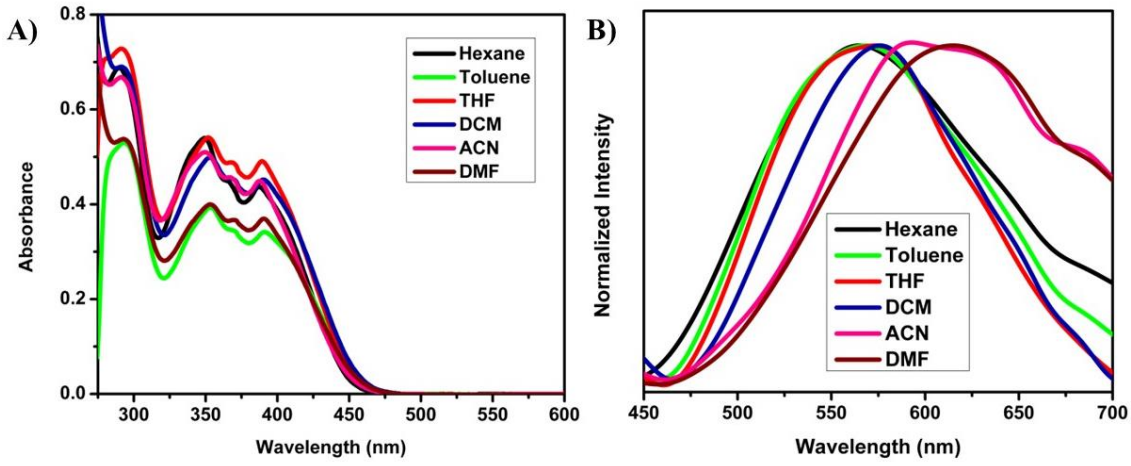

Figure S6. (**A**) Absorption and (**B**) Normalized emission spectra of compound **AN-CS-CZ** in different polarity of solvents. (Con. 3x10^{-5} M; λ_{ex} = 385 nm).

Table S2. Photophysical properties of compounds **AN-CS-CZ** in different polarity of solvents. (λ_{ex} = 385 nm).

Compounds	**Solvents**	$\lambda_{max}^{[a]}$ (nm)	$\lambda_{max}^{[b]}$ (nm)	$\Delta\nu$ [c]
	Hexane	388	560	7916

AN-CS-CZ	Toluene	391	568	7969
	THF	389	572	8224
	DCM	390	575	8249
	ACN	388	603	9189
	DMF	390	617	9433

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

6. SEM images

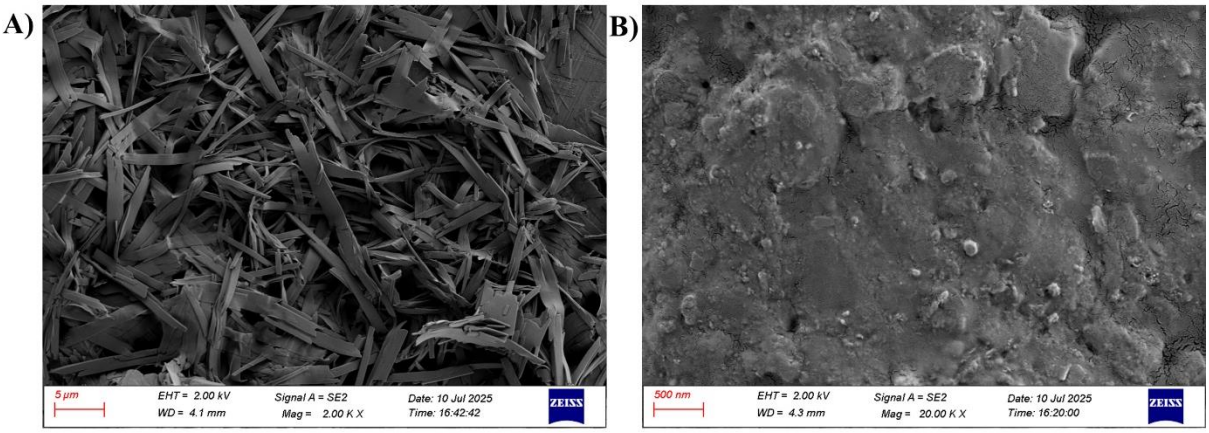

Figure S7. SEM images of (**A**) aggregates of **AN-CS-CZ** (drop-casted from a $3x10^{-5}$ M ACN/H_2O solution with f_w = 50 % (**B**) **AN-CS-CZ** (drop-casted from a $3x10^{-5}$ M ACN/H_2O solution with f_w = 90 %).

7. Dynamic light Scattering studies

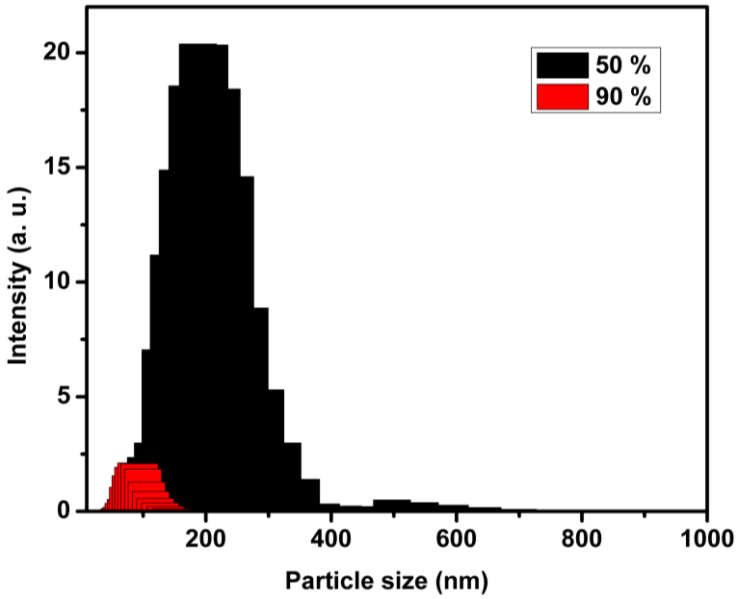

Figure S8. Size distributions of the aggregates of **AN-CS-CZ** (drop casted from a $3x10^{-5}$ M ACN/H_2O solution with f_w =50 % & 90 %).

8. VT-PXRD Studies

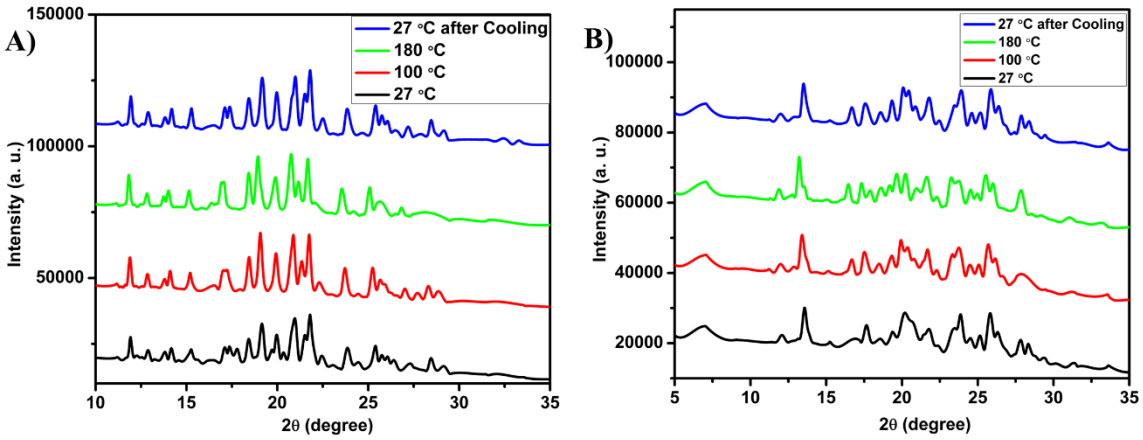

Figure S9. X-ray diffraction experiments at different temperatures of compound (**A**) D-D-A our previous study and (**B**) **AN-CS-CZ**.

9. DFT Data

Table S3. Compound **AN-CS-CZ**

6	-7.125516000	2.989999000	1.986929000
6	-8.544195000	2.892716000	2.021687000
6	-9.164554000	1.789234000	1.500327000
6	-8.409070000	0.718325000	0.930550000
6	-6.969485000	0.802791000	0.909170000
6	-6.366792000	1.985883000	1.441455000
6	-9.036547000	-0.405029000	0.383614000
6	-8.305954000	-1.463153000	-0.162387000
6	-6.860834000	-1.405933000	-0.173930000
6	-6.207664000	-0.255589000	0.343988000
6	-8.966437000	-2.615120000	-0.693801000
6	-8.254028000	-3.673814000	-1.185560000
6	-6.831550000	-3.642574000	-1.157759000
6	-6.161271000	-2.552547000	-0.668270000
6	-4.738777000	-0.142356000	0.386770000
6	-3.856541000	-0.202256000	-0.645088000
6	-2.384721000	-0.110879000	-0.470643000
6	-1.564563000	0.372882000	-1.503733000
6	-0.190590000	0.494105000	-1.329541000
6	0.429440000	0.136516000	-0.119706000
6	-0.394177000	-0.365460000	0.904120000

6	-1.766739000	-0.495370000	0.731504000
6	1.893246000	0.277182000	0.068690000
6	2.616080000	-0.676969000	0.823180000
6	3.987133000	-0.576961000	1.030273000
6	4.658454000	0.514387000	0.470317000
6	3.962813000	1.484999000	-0.299434000
6	2.586324000	1.358609000	-0.492767000
7	6.000395000	0.862240000	0.540727000
6	6.192370000	2.034725000	-0.185246000
6	4.946936000	2.461873000	-0.718165000
6	7.368572000	2.757083000	-0.407639000
6	7.280571000	3.922660000	-1.165918000
6	6.055475000	4.361067000	-1.696621000
6	4.887686000	3.635834000	-1.477072000
6	-4.332688000	-0.290096000	-1.999754000
7	-4.666573000	-0.336565000	-3.113582000
6	11.337724000	-4.578800000	0.162346000
6	10.613240000	-3.538241000	1.021324000
6	9.538715000	-2.760478000	0.252077000
6	8.814914000	-1.713254000	1.107706000
6	7.734651000	-0.939336000	0.343894000
6	7.039299000	0.109777000	1.224367000
1	-6.640513000	3.875631000	2.386742000
1	-9.128823000	3.699865000	2.452534000
1	-10.248178000	1.707142000	1.507503000
1	-5.289225000	2.098692000	1.394854000
1	-10.122607000	-0.460462000	0.389948000
1	-10.053011000	-2.630811000	-0.689167000
1	-8.766226000	-4.543547000	-1.585676000
1	-6.271075000	-4.496411000	-1.526383000
1	-5.078930000	-2.560460000	-0.643894000
1	-4.311683000	0.065064000	1.366030000
1	-2.009456000	0.651814000	-2.453861000
1	0.417025000	0.850182000	-2.155637000
1	0.047383000	-0.647297000	1.855019000

1	-2.362163000	-0.914526000	1.536600000
1	2.088336000	-1.534250000	1.229016000
1	4.511659000	-1.337499000	1.599612000
1	2.045062000	2.114362000	-1.053964000
1	8.322763000	2.426709000	-0.009955000
1	8.180453000	4.501554000	-1.351913000
1	6.022389000	5.273019000	-2.284498000
1	3.942377000	3.976683000	-1.889759000
1	12.095199000	-5.117389000	0.740719000
1	10.636850000	-5.319814000	-0.238437000
1	11.842305000	-4.108599000	-0.689261000
1	11.344959000	-2.830919000	1.434929000
1	10.150702000	-4.034673000	1.885257000
1	8.803169000	-3.466848000	-0.158055000
1	9.998952000	-2.265832000	-0.614912000
1	9.552321000	-1.005593000	1.513350000
1	8.361397000	-2.208382000	1.978470000
1	6.980023000	-1.633047000	-0.047473000
1	8.175359000	-0.437861000	-0.526778000
1	7.773462000	0.824881000	1.611987000
1	6.587277000	-0.369713000	2.099517000

Table S4. DFT data of compound **AN-CS-CZ**

Compound	**HOMO-1 (eV)**	**HOMO (eV)**	**LUMO (eV)**	**LUMO+1 (eV)**	**HOMO-LUMO (eV)**	**HOMO-1-LUMO (eV)**
AN-CS-CZ	-5.40	-5.19	-2.1	-1.33	3.09	3.31

10.Thermal properties

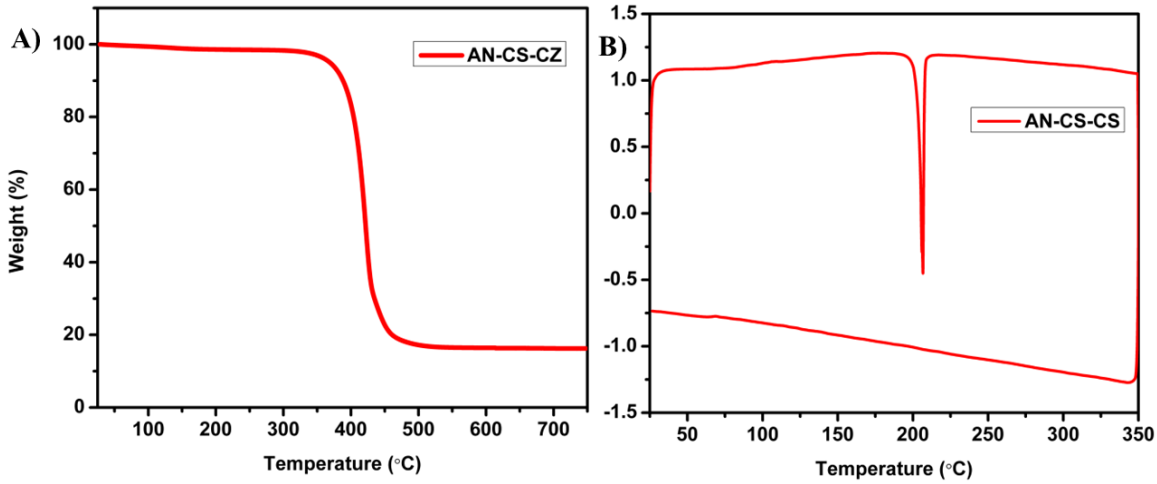

Figure S10. (**A**) TGA and (**B**) DSC curves of the compound.

11. References

1. Afrin, A.; Swamy, P, C. A. Aggregation induced emission and reversible mechanofluorochromism active carbazole–anthracene conjugated cyanostilbenes with different terminal substitutions. *New J. Chem*. **2023**, *47*, pp.18919-18932.