# **Electronic Supplementary Information**

# Steric Hindrance Modulated Efficient Thermally Activated Delayed Fluorescence with Non-linear Optical, Piezoelectric, and Ferroelectric Properties

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#### Section S1: Instrumentation

All the synthesis are carried out in the nitrogen atmosphere in dry toluene as a solvent. The reaction was monitored by analytical thin layer chromatography (TLC) using Silica Gel 60/UV 254 purchased from Merck Specialties Pvt Ltd in a UV chamber containing 254 nm and 365 nm light source. The product was purified by column chromatography using silica gel with mesh 100-200. NMR spectra of the compounds are taken in chloroform-d6 solution and tetramethylsilane (TMS) as an internal standard. NMR spectra was recorded in Bruker Ascend<sup>TM</sup> 400 spectrometer. <sup>1</sup>H NMR spectra was recorded at 400 MHz and <sup>13</sup>C NMR was recorded at 100 MHz. Mass spectra was recorded in MALDI-TOF spectrometer with CHCA matrix. Single crystal X-ray data was collected in Bruker Kappa Apex II CCD duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) at 150K using graphite monochromatic Mo K $\alpha$  radiation ( $\lambda = 0.71$  Å). Crystal structures were solved in APEX software by direct method and refined by least-squares against F2 in SHELXL-97 package.<sup>1,2</sup> Absorption spectra in liquid state and in solid state were recorded in Shimadzu UV-2600 and Shimadzu UV-3600i plus double beam spectrometer. Fluorescence and phosphorescence spectra were collected in FluoroMax-4 and FluoroLog-3 (Horiba Jobin Yvon). Liquid nitrogen Dewar assembly (FL-1013) was used to record spectra at 77K. Quantum yield was measured by an integrating sphere (K-sphere, Horiba Jobin Yovn) connected with FluoroMax-4. Short lifetime (nanosecond range) of the sample was collected in FluoroCube system associated with FluoroHub and PPD-850 (Horiba Jobin Yvon) detector, 375 and 402 nm nanoLED were used as excitation source. Long lifetime (microsecond and above) was collected in DeltaFlex (Horiba Jobin Yvon) connected with DeltaHub and 355 nm spectraLED was used for excitation of the samples. For two-photon absorption, 800 nm mode-locked Ti-sapphire laser (Mai-Tai, Spectra-Physics) was used as the excitation source. Two-photon excitation and emission spectra were collected by using a multiphoton microscopy (Leica, Germany) at 63X and 10X oil immersion objectives.

#### Section S2: Materials

All the chemicals for synthesis were purchased from Sigma-Aldrich and TCI and were used without any further purification. For spectroscopic studies, spectroscopy grade solvents were purchased from Spectrochem Pvt Ltd, India. For solid state study, the quartz plates are purchased from Ted Pella INC.

## Section S3: Experimental Methods

### Preparation of 10 wt% CBP films

10 mg emitter and 90 mg CBP were weighed to make 10 wt% emitter-doped CBP. The compounds were dissolved in chloroform and pre-washed quartz plates were spin-coated with 80  $\mu$ L of solvent at 3000 rpm for 60 seconds. After that, those plates were kept in vacuum for 2 hours prior to photophysical measurements.

## Section S4: Synthesis and characterization

All the synthetic schemes are given in Scheme S1. All the reactions are performed in inert atmosphere and compounds are characterised by NMR, MALDI-TOF and SCXRD.



Scheme S1: Synthesis of CzPHCN, tCzPHCN and Cz2CzPHCN.

**Synthesis of 2,3-bis(4-bromophenyl)fumaronitrile (Br2FN)**<sup>3</sup>: Commercially available 4bromophenyl acetonitrile was taken as a precursor for the synthesis of 2,3-bis(4bromophenyl)fumaronitrile. A mixture of 4-bromophenyl acetonitrile (1.25 mmol) and molecular iodine (1.25 mmol) was purged with nitrogen, and dry diethyl ether (8 mL) was added via a syringe. After that, a solution of sodium methoxide (0.25 mmol) in methanol (2 mL) was slowly added to it at -78°C with continuous stirring over a period of 30 min. Then the resulting solution was further stirred for 30 min at -78°C. After that, the solution was kept in an ice bath for 5 h. The resulting mixture was quenched with 5% HCl (5 mL) solution below 10°C. The solution was filtered and washed with a cold methanol-water (1:1) solution and a white color compound was isolated. Finally, the structure of Br2FN was characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectroscopy.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.73 – 7.67 (m, 8H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 132.7, 130.6, 130.1, 126.8, 124.7, 116.1.

**MALDI-TOF:** *m*/*z* calcd. For C<sub>16</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub> 383.8898 found 383.3152.

**Synthesis of 3,6-dibromo-9,10-dicyanophenenthrene** (**Br2PHCN**)<sup>3</sup>: A solution of Br2FN (0.39 mmol) in chloroform (70 mL) was taken in a RB and then some crystals of molecular iodine was added to it. The mixture was irradiated with a 450W Mercury vapour lamp for 8 h and the reaction was monitored by checking TLC. Then the resulting solution was evaporated and the crude product was purified by silica gel column chromatography with hexane/ethyl acetate mixture. The structure of the photochemical product Br2PHCN was confirmed by NMR spectroscopy.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  8.82 (s, 2H), 8.27 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H). **HRMS:** m/z calcd. For C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>N<sub>2</sub> [M]+ 386.9132 found 386.944.

**General procedure for synthesis of CzPHCN, tCzPHCN and Cz2CzPHCN**: An oven dried Schlenk tube containing 3 mL of dry toluene was degassed by bubbling of nitrogen for 10 minutes. To this were added 3,6-dibromophenenthrene-9,10-dicarbonitrile (Br2PHCN) (300 mg), carbazole (for CzPHCN, 3,6-di-tert-butyl-9H-carbazole for tCzPHCN and 9'H-9,3':6',9"-tercarbazole for Cz2CzPHCN) (2.2 equiv), sodium *tert*-butoxide (157.44 mg), P(<sup>t</sup>Bu)<sub>3</sub> (0.279 mL) and Pd<sub>2</sub>(dba)<sub>3</sub> (45 mg). The Schlenk tube was heated at 100 °C for 24 hours. After completion of the reaction, the toluene was removed under vacuum and the crude product was purified by column chromatography with 230-400 mesh silica (40% DCM/hexane). The yield was 50-65%. The final product was confirmed by <sup>1</sup>H, <sup>13</sup>C, MALDI-TOF and single-crystal XRD analysis.

## **CzPHCN**

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (d, *J* = 2.0 Hz, 2H), 8.69 (d, *J* = 8.7 Hz, 2H), 8.19 (dd, *J* = 8.7, 1.9 Hz, 2H), 8.15 (d, *J* = 7.6 Hz, 4H), 7.57 – 7.53 (d, 4H), 7.43 (td, *J* = 7.7, 1.3 Hz, 4H), 7.34 (td, *J* = 7.5, 1.0 Hz, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 141.1, 140.3, 129.7, 128.5, 126.8, 126.7, 124.3, 121.4, 120.9, 120.7, 109.4.

**MALDI-TOF**: Calculated mass for  $C_{40}H_{22}N_4$  is 558.644, found 558.887.

#### tCzPHCN

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**: <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 8.86 (d, *J* = 2.0 Hz, 2H), 8.64 (d, *J* = 8.7 Hz, 2H), 8.21 – 8.12 (m, 6H), 7.54 – 7.44 (m, 8H), 1.45 (s, 36H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 144.4, 141.3, 138.4, 132.3, 129.4, 127.9, 126.3, 124.2, 119.8, 116.7, 115.9, 114.9, 108.8, 34.8, 31.9.

**MALDI-TOF**: Calculated mass for C<sub>56</sub>H<sub>54</sub>N<sub>4</sub> is 783.076, found 782.587.

#### Cz2CzPHCN

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  9.15 (d, J = 2.0 Hz, 2H), 8.86 (d, J = 8.7 Hz, 2H), 8.37 (d, J = 1.8 Hz, 2H), 8.33 (d, J = 2.0 Hz, 4H), 8.14 (d, J = 7.7 Hz, 8H), 7.78 (d, J = 8.7 Hz, 4H), 7.66 (dd, J = 8.7, 2.0 Hz, 4H), 7.40 – 7.30 (m, 16H), 7.29 – 7.23 (m, 8H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ 141.7, 140.6, 140.2, 131.8, 130.4, 129.1, 127.6, 126.9, 126.1, 124.9, 123.4, 121.4, 120.5, 120.4, 120.1, 117.1, 110.9, 109.6.

MALDI-TOF: Calculated mass for C<sub>56</sub>H<sub>54</sub>N<sub>4</sub> is 1218.416, found 1218.42.



<sup>1</sup>H NMR spectrum of **2,3-bis(4-bromophenyl)fumaronitrile** in CDCl<sub>3</sub> at 298K

<sup>13</sup>C NMR spectrum of **2,3-bis(4-bromophenyl)fumaronitrile** in CDCl<sub>3</sub> at 298K





Mass spectra of 2,3-bis(4-bromophenyl)fumaronitrile

<sup>1</sup>H NMR spectrum of **3,6-dibromo-9,10-dicyanophenenthrene** in CDCl<sub>3</sub> at 298K





Mass spectra of 3,6-dibromo-9,10-dicyanophenenthrene

<sup>1</sup>H NMR spectrum of **3,6-di(9H-carbazol-9-yl)phenanthrene-9,10-dicarbonitrile** 

(CzPHCN) in CDCl<sub>3</sub> at 298K



<sup>13</sup>C NMR spectrum of **3,6-di(9H-carbazol-9-yl)phenanthrene-9,10-dicarbonitrile** (CzPHCN) in CDCl<sub>3</sub> at 298K



Mass spectra of 3,6-di(9H-carbazol-9-yl)phenanthrene-9,10-dicarbonitrile (CzPHCN)



<sup>1</sup>H NMR spectrum of **3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)phenanthrene-9,10dicarbonitrile** (**tCzPHCN**) in CDCl<sub>3</sub> at 298K



<sup>13</sup>C NMR spectrum of **3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)phenanthrene-9,10dicarbonitrile (tCzPHCN)** in CDCl<sub>3</sub> at 298K



Mass spectra of **3,6-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)phenanthrene-9,10dicarbonitrile (tCzPHCN)** 



<sup>1</sup>H NMR spectrum of **3,6-di(9'H-[9,3':6',9''-tercarbazol]-9'-yl)phenanthrene-9,10dicarbonitrile** (Cz2CzPHCN) in CDCl<sub>3</sub> at 298K



<sup>13</sup>C NMR spectrum of **3,6-di(9'H-[9,3':6',9''-tercarbazol]-9'-yl)phenanthrene-9,10dicarbonitrile** (Cz2CzPHCN) in CDCl<sub>3</sub> at 298K



Mass spectra of **3,6-di(9'H-[9,3':6',9''-tercarbazol]-9'-yl)phenanthrene-9,10**dicarbonitrile (Cz2CzPHCN)



## Section S5: Computational Information

Quantum mechanical calculations were performed using Gaussian 09 package<sup>4</sup> in supercomputer (Param-Brahma facility, IISER Pune). The geometry of all the molecules was optimized, and frequencies are calculated at B3LYP/6-31g(d,p) level of theory in gas phase. With the optimized structure, TD-DFT calculations are carried out to see electronic distribution of electrons in molecular orbitals. Natural transition orbital (NTO) calculations are done to see the nature of excited states. The quantum mechanics/molecular mechanics (QM/MM) method is considered by using the two-layer ONIOM module based on the SCXRD crystallographic structure. A two-layer ONIOM model was constructed that separates the layers in the QM region for the central molecule of interest and the MM region for the surrounding environments. At first, using the QM/MM model, the system was optimized, and frequency calculation showed the absence of imaginary frequency. Then, TD-DFT calculations were performed to get the single point energies of the excited states. The spin-orbit coupling matrix element (SOCME) between singlets and triplets was calculated by using zeroth-order regular approximation (ZORA) to the Dirac equation<sup>5</sup>. All the calculations were done by PYSOC program<sup>6</sup>.



Fig. S1 Ground state energy scan of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN with respect to donor-acceptor dihedral angle ( $\theta_{DA}$ ).



**Fig. S2** Energy of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN with respect to donoracceptor dihedral angle ( $\theta_{DA}$ ) from TD-DFT.  $\Delta E_{ST_2}$  vs oscillator strength vs dihedral angle ( $\theta_{DA}$ ) plot of (d) CzPHCN, (e) tCzPHCN and (f) Cz2CzPHCN.



**Fig. S3** HOMO and LUMO of CzPHCN, tCzPHCN and Cz2CzPHCN obtained from TD-DFT calculation with 6-31g(d,p) level of theory.



**Fig. S4** Natural transition orbital analysis of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN of S<sub>1</sub>, T<sub>1</sub> and T<sub>2</sub> state.



**Fig. S5** (a) Conventional TADF mechanism for Cz2CzPHCN, RISC occurs via  $T_1$  state to  $S_1$  state. (b) RISC occurs through the upper triplet  $T_2$  state for CzPHCN and tCzPHCN.

Molecules	номо-	$f(S_0 \rightarrow$	$\Delta E_{ST}$	$\Delta E_{ST_2}$	<s<sub>1 Hso T<sub>1</sub></s<sub>	<s<sub>1 Hso T<sub>2</sub>&gt;</s<sub>	<s<sub>1 Hso </s<sub>
	LUMO	<b>S</b> <sub>1</sub> ) <sup>a</sup>	(eV) <sup>b</sup>	(eV) <sup>c</sup>	> ( <b>cm</b> <sup>-1</sup> ) <sup>d</sup>	( <b>cm</b> <sup>-1</sup> ) <sup>e</sup>	T3>
	overlap						( <b>cm<sup>-1</sup></b> ) <sup>f</sup>
CzPHCN	0.45	0.178	0.4423	0.039	0.23040	0.10460	0.37194
tCzPHCN	0.44	0.216	0.3847	0.0382	0.19792	0.10114	0.36719
Cz2CzPHCN	0.14	0.048	0.069	-	0.15651	0.07218	0.13053
				0.0322			

 Table S1 Theoretical parameters from TD-DFT calculations.

<sup>a</sup> oscillator strength of  $S_0 \rightarrow S_1$  absorption, <sup>b</sup> energy difference between  $S_1$  and  $T_1$  state, <sup>c</sup> energy difference between  $S_1$  and  $T_2$  state, <sup>d-f</sup> spin-orbit coupling matrix elements between  $S_1$  and triplet states.

# Section S6: Crystallographic Data

## **CzPHCN**



**Table S2** Crystal data and structure refinement for CzPHCN.

Identification code	CzPHCN
CCDC No.	2420130
Empirical Formula	$C_{40}H_{22}N_4$
Formula weight	558.62
Temperature/K	150
Crystal system	Cmc2(1)
Space group	Orthorhombic
a/Å	23.294(8)
b/Å	16.771(6)
c/Å	8.709(3)
α	90
β	90
γ	90
Volume/A <sup>3</sup>	3402(2)
Z	4
pcalc (g/cm <sup>3</sup> )	1.091
$\mu/mm^{-1}$	0.065
F(000)	1160.41
Radiation	MoK $a(\lambda=0.71073)$
$2\Theta$ range for data collection	2.43 to 19.06
Index ranges	-26 = < h = < 30,  -21 = < k = < 21,  -11 = < l = < 11,
Reflection collected	31967
Independent reflections	3977[R(int) = 0.1093  R(sigma) = 0.0891]
Data/restraints/parameters	3977/1/200
Goodness-of-fit on F <sup>2</sup>	0.837
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0653, wR_2 = 0.1748$
Final R indexes[all data]	$R_1 = 0.1729, wR_2 = 0.2485$
Largest diff. peak/hole/e Å <sup>-3</sup>	0.26/-0.17

## tCzPHCN



 Table S3 Crystal data and structure refinement for tCzPHCN.

Identification code	tCzPHCN
CCDC No.	2420153
Empirical Formula	$C_{56}H_{54}N_4$
Formula weight	783.03
Temperature/K	150
Crystal system	P 2 <sub>1</sub> /c
Space group	Monoclinic
a/Å	16.3865(11)
b/Å	10.2297(6)
c/Å	35.160(2)
α	90
β	103.138(2)
γ	90
Volume/A <sup>3</sup>	5739.6(6)
Z	4
pcalc (g/cm <sup>3</sup> )	0.906
$\mu/mm^{-1}$	0.053
F(000)	1672.0
Radiation	MoK\a(λ=0.71073)
20 range for data collection	2.32 to 25.03
Index ranges	-21 = < h = < 20,  -11 = < k = < 13,  -45 = < l = < 45,
Reflection collected	145179
Independent reflections	13157[R(int) = 0.1738  R(sigma) = 0.1048]
Data/restraints/parameters	13157/0/553
Goodness-of-fit on F <sup>2</sup>	1.023
Final R indexes $[I \ge 2\sigma(I)]$	$R_1 = 0.0856, wR_2 = 0.1963$
Final R indexes[all data]	$R_1 = 0.1583, wR_2 = 0.2287$
Largest diff. peak/hole/e Å-3	0.67/-0.29

## Cz2CzPHCN



Identification code	Cz2CzPHCN
CCDC Number	2420155
Empirical formula	$C_{88}H_{50}N_8$
Formula weight	1219.431
Temperature/K	150
Crystal system	triclinic
Space group	PĪ
a/Å	16.2336(13)
b/Å	17.0377(12)
c/Å	17.1281(14)
$\alpha/^{\circ}$	66.243(2)
β/°	67.979(2)
$\gamma/^{\circ}$	89.261(2)
Volume/Å <sup>3</sup>	3966.0(5)
Z	2
$\rho_{calc}g/cm^3$	1.021
$\mu/mm^{-1}$	0.061
F(000)	1268.7
Crystal size/mm <sup>3</sup>	$0.21\times0.15\times0.12$
Radiation	Mo Ka ( $\lambda = 0.71073$ )
$2\Theta$ range for data collection/	°4.12 to 50
Index ranges	$-21 \le h \le 21,  -18 \le k \le 22,  -21 \le l \le 22$
Reflections collected	82757
Independent reflections	13943 [ $R_{int} = 0.0770, R_{sigma} = 0.0831$ ]
Data/restraints/parameters	13943/234/936
Goodness-of-fit on F <sup>2</sup>	1.073
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0732,  wR_2 = 0.2183$
Final R indexes [all data]	$R_1=0.1005,wR_2=0.2449$
Largest diff. peak/hole / e Å-?	<sup>3</sup> 0.44/-0.50

**Table S4** Crystal data and structure refinement for Cz2CzPHCN.



Fig. S6 Molecular packing along a, b and c crystallographic axis.



**Fig. S7** Intramolecular interactions in (a) 4CzIPN and (b) 4CzTPN. Intermolecular interactions in (c) 4CzIPN and (d) 4CzTPN.



Fig. S8 Intermolecular interactions in (a-c) CzPHCN, (d) tCzPHCN and (e-f) Cz2CzPHCN.



**Fig. S9** Hirshfeld surface<sup>7</sup> analysis of a) CzPHCN, b) tCzPHCN and c) Cz2CzPHCN using Crystal Explorer software.<sup>8</sup>

Note 1: Effect of cyano group in layer formation

In CzPHCN, the nitrogen atom of CN interacts with one upper layer phenanthrene ring (N···C, 3.248 Å) and one lower layer carbazole ring (N···C, 3.180 Å) as shown in Fig. S10a and these interactions propagate (along with other non-covalent interactions) throughout the crystal facilitating the formation of layers. For tCzPHCN, CN group interacts with neighbouring tertbutyl carbazole group (N···C, 2.722 Å and N···H, 2.732 Å) as shown in Fig. S10c,d. For Cz2CzPHCN, nitrogen atom of cyano group interacts with neighbouring carbazole group (N···H) with a distance of 2.736 Å as shown in Fig. S10e,f. These interactions hold the structure and help in the formation of layers.



**Fig. S10** Interaction of -CN groups with other moieties of (a,b) CzPHCN, (c,d) tCzPHCN and (e,f) Cz2CzPHCN. Black dotted lines represent interaction of cyano groups with other moieties and different color codes represent different molecules.

## **Section S7: Photophysical Properties**



**Fig. S11** Solvent polarity-dependent steady-state PL of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN.



**Fig. S12** Prompt fluorescence lifetime of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in 10 μM toluene solution at room temperature.



**Fig. S13** Prompt fluorescence lifetime of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in neat films at room temperature (brown) and at 77K (blue).



**Fig. S14** Phosphorescence lifetime of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in neat films at 77K.



Fig. S15 Estimation of  $\Delta E_{ST}$  of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN from fluorescence spectra (black line) and phosphorescence spectra (blue line) onset.



Fig. S16 PLQY of CzPHCN in neat film taken in quartz plate at ambient condition.



Fig. S17 PLQY of tCzPHCN in neat film taken in quartz plate at ambient condition.



Fig. S18 PLQY of Cz2CzPHCN in neat film taken in quartz plate at ambient condition.



**Fig. S19** Steady state PL spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in neat films taken in ambient (red) and vacuum (black) conditions.



**Fig. S20** Prompt fluorescence lifetime of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in 10 wt% CBP film at room temperature.



Fig. S21 PLQY of CzPHCN in 10 wt% CBP taken in quartz plate at ambient condition.



Fig. S22 PLQY of tCzPHCN in 10 wt% CBP taken in quartz plate at ambient condition.



Fig. S23 PLQY of Cz2CzPHCN in 10 wt% CBP taken in quartz plate at ambient condition.



**Fig. S24** Steady state PL spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN in 10 wt% CBP films taken in ambient (red) and vacuum (black) conditions.

Table S5: Photophysical parameters in 10 wt% CBP films.

Molecules	PL	$\phi^{\mathrm{a}}$	$\phi_{ m PF}$	$\phi_{ m DF}$	$ au_{PF}$	$ au_{ m DF}$	$k_r (10^7 \text{ s}^{-1})$	$k_{\rm ISC}$ (10 <sup>7</sup>	k <sub>RISC</sub>
	(nm)				(ns)	(µs)	$(S_1 {\rightarrow} S_0)^b$	s <sup>-1</sup> )	$(10^5 \text{ s}^{-1})$
								$(S_1 \rightarrow$	$(T_1 \rightarrow$
								$T_1)^c$	$(\mathbf{S}_1)^d$
CzPHCN	520	0.78	0.71	0.07	10.6	1.4	6.78	2.66	2.18
CBP film									
tCzPHCN	530	0.94	0.73	0.21	9.6	0.9	7.64	2.78	11.6
CBP film									
Cz2CzPHCN	556	0.7	0.55	0.15	13.1	5.1	4.33	3.31	1.06
CBP film									

<sup>a</sup>  $\phi$  is the total PLQY measured in ambient condition. <sup>b</sup>  $k_r (S_1 \rightarrow S_0) = \phi_{PF} / \tau_{PF}$ . <sup>c</sup>  $k_{ISC} (S_1 \rightarrow T_1) = (1 - \phi_{PF}) / \tau_{PF}$ . <sup>d</sup>  $k_{RISC} (T_1 \rightarrow S_1) = \phi_{DF} / (k_{ISC} \phi_{PF} \tau_{DF} \tau_{PF})$ .

## Note 2: Effect of solvent and thickness in the preparation of neat film

Films from different solvents

0.5 mg of the compound was dissolved in 1 ml of THF and DCM, and spin-coated neat films of all the emitters were prepared on a pre-cleaned quartz substrate, which were dried for 4 hours in high vacuum to completely remove trapped solvent molecules before the experiment. Absorption spectra (Fig. S25) and emission spectra (Fig. S26) were collected to check the solvent effect on neat films. No significant spectral shift was observed in absorption and emission spectra, which indicates that the solvent has hardly any role in the absorption and emission profile of the compounds.



**Fig. S25** Normalized absorption spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN of spin-coated films prepared from 1 mM THF (green) and DCM (purple) solvent.



**Fig. S26** Normalized photoluminescence spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN of spin-coated films prepared from 1 mM THF (green) and DCM (purple) solvent.

#### Films of different thicknesses

To examine the influence of the thickness of the film, we prepared films of different thicknesses. We prepared a stock solution of 1 mg/mL in chloroform and from that 50 µL, 100 µL and 200 µL solutions were used to prepare the neat films of different thicknesses. As predicted, 50 µL spin-coated substrate will be the thinnest film and 200 µL spin-coated substrate will be the thickest. Again, the films were dried in high vacuum for 4 hours to ensure complete removal of the trapped solvents. Then, UV-vis absorption (Fig. S27) and emission

spectra (Fig. S28) were recorded, and no distinguishable changes were observed, signifying that the thickness has no role in the absorption and emission process.



Fig. S27 Normalized absorption spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN of spin-coated films prepared by spin-coating with 50  $\mu$ L, 100  $\mu$ L and 200  $\mu$ L solutions of CHCl<sub>3</sub> of concentration 0.5 mg mL<sup>-1</sup>. Cyan circle: 50  $\mu$ L, magenta circle: 100  $\mu$ L and olive circle: 200  $\mu$ L.



**Fig. S28** Normalized photoluminescence spectra of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN of spin-coated films prepared by spin-coating with 50  $\mu$ L, 100  $\mu$ L and 200  $\mu$ L solutions of CHCl<sub>3</sub> of concentration 0.5 mg mL<sup>-1</sup>. Cyan circle: 50  $\mu$ L, magenta circle: 100  $\mu$ L and olive circle: 200  $\mu$ L.

#### Section S8: Aggregation Induced Emission

The photophysics of aqueous solutions for molecules are the key to improving their application in biological systems and photonic technologies.<sup>9,10</sup> In the present work, we designed some charge-transfer-based molecules with reduced molecular interactions, and their emission properties were determined in aggregated states. Since the molecules are not soluble in water, a binary mixture of organic and aqueous solvents was used to induce aggregation. For all three of the molecules synthesized, an initial decrease in the PL intensity of the molecules was shown at lower fractions of water content, followed by a sharp rise at higher fractions, which confirmed their AIE properties (Fig. S29). The emission intensity of CzPHCN decreases by 15% at a fraction of water content compared to its pure acetonitrile solution. The intensity keeps decreasing until it reaches  $f_w = 30\%$ , where it begins to increase slightly until  $f_w = 70\%$ along with a blue shift in the emission from 600 nm to 586 nm. At  $f_w = 90\%$ , the emission intensity drastically increases with a further blue shift to 555 nm (Fig. S29a,d). The initial decrease in intensity at lower water fractions can be attributed to the stabilization of the CT state in the higher polarity of water, exhibiting solvatochromic behavior. The subsequent increase in intensity and blue-shifted emission are associated with aggregate formation, facilitated by the hydrophobic environment created at higher water content. For tCzPHCN, the emission intensity decreases down to  $f_w = 15\%$ , but with further water addition ( $f_w > 30\%$ ), the intensity rises dramatically (Fig. S29b,e). On the contrary, Cz2CzPHCN is almost nonemissive at  $f_w = 0-15\%$ , while it becomes emissive at  $f_w > 30\%$ . The intensity shoots up dramatically with additional water addition (Fig. S29c,f). These observations indicate an early onset of aggregation at reduced water fractions  $f_w = 30\%$  for both tCzPHCN and Cz2CzPHCN with respect to the case for CzPHCN where  $f_w$  was set at 70%. Presumably, an effect of excess hydrophobic end groups contributes toward earlier onset aggregation at smaller contents of a cosolvent (water, here). These results emphasize the crucial role of molecular structure and hydrophobicity in controlling aggregation and emission behavior, thus opening avenues for the design of tailored strategies for aqueous-compatible luminescent materials.



**Fig. S29**. Emission spectra of (a) CzPHCN and (b) tCzPHCN in different fractions of ACN/water binary mixture. Emission spectra of (c) Cz2CzPHCN in DMF/water binary mixture. PL intensity of (d) CzPHCN, (e) tCzPHCN and (f) Cz2CzPHCN with different water fractions and the inserted cuvette pictures are taken in the highest and lowest water fractions. PL spectra of CzPHCN and tCzPHCN were collected by 400 nm excitation and for Cz2CzPHCN, excitation was 430 nm.

#### Section S9: Two-Photon absorption

Organic luminogens that are excited by two photons have gained significant attention in the past few years because of their excellent optical properties, such as higher penetration depth, high spatial resolution, and minimal scattering of light.<sup>11</sup> Unlike one-photon-excited fluorophores, these luminogens are particularly advantageous in biological applications because they induce minimal damage to the target cells, making them ideal for cell imaging applications. All three luminogens- CzPHCN, tCzPHCN, and Cz2CzPHCN possess extensive  $\pi$ -conjugated structures and strong charge transfer capabilities, leading to significant hyperpolarizability and efficient two-photon absorption properties. In order to better appreciate these properties, we probed the two-photon absorption behavior of these luminogens. Our results show that all three luminogens have notable two-photon activity, in their molecular aggregates as shown in Fig. S30. The two-photon excited emission spectra, obtained upon excitation at 845 nm, were very similar to the single-photon excited emission spectra produced under 420 nm excitation (Fig. S30, S31). This similarity indicates stability and consistency in their emission characteristics. In addition, the emission spectra exhibit an anti-Stokes shift, with the excitation wavelengths ranging from 700 nm to 1100 nm (Fig. S30, S31). Powerdependent measurements of two-photon emission intensity, plotted on a log-log scale, present a slope of approximately 2 (Fig. S32). This result ensures that the observed emission is a predominantly two-photon process and contains minimal contributions from one-photon emissions.



**Fig. S30** Microscopic images of (a) CzPHCN, (d) tCzPHCN and (g) Cz2CzPHCN (c) in 80% organic/water mixture. (b,e,h) Two-photon excited emission spectra (excitation wavelength = 845 nm and power = 7.7 mW) (Onset: two-photon excited PL of aggregates, excitation: 800 nm). (c,f,i) Two-photon absorption spectra (emission window = 525-567 nm for CzPHCN and tCzPHCN and 525-650 nm for Cz2CzPHCN).



**Fig. S31** One-photon and two-photon emission profile of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN.



**Fig. S32** Power dependence study (excitation = 845 nm) of (a) CzPHCN, (b) tCzPHCN and (c) Cz2CzPHCN.

### Section S10: Second harmonic generation (SHG)

#### **Experimental Setup for Second-Harmonic Generation**

For second-harmonic generation (SHG) experiments, ultrafast (~50 fs) laser pulses of varying wavelengths from an optical parametric amplifier (OPA) were used as the excitation source. The OPA (TOPAS-C, Light Conversion) was pumped by a regenerative amplifier (Spitfire Pro XP, Spectra-Physics) with a pulse width of 45 fs (FWHM), a 1 kHz repetition rate, and a central wavelength of 800 nm. The amplifier was seeded by 35 fs pulses from a mode-locked Ti: Sapphire oscillator (Tsunami SP, Spectra-Physics) operating at 80 MHz with the same central wavelength (800 nm). The OPA was used to produce excitation wavelengths in the range of 1200–1440 nm, with a wavelength separator mounted on Mixer 3 for precise wavelength selection. For the experiments, the pump beam from the OPA passed through a neutral density (N.D.) filter to facilitate power-dependent measurements, followed by an 850 nm long-pass filter to ensure the purity of the pump beam. After passing through the half-wave plate, the pump pulses were focused on the sample using a 200 mm plano-convex lens. To prevent sample damage, the sample was positioned away from the focal point, resulting in a beam spot size of 400 µm at the sample. The SHG signal generated by the sample was collimated using a 25 mm plano-convex lens and passed through a 750 nm short-pass filter to eliminate any residual traces of the pump beam. The collimated output was subsequently detected using a miniature spectrometer (USB4000, Ocean Optics) coupled to a 400 µm optical fiber.



Fig. S33 Schematic of the SHG setup.

#### Calculation of second-order nonlinear susceptibility and LIDT

To quantify the second-harmonic generation (SHG) response, the second-order nonlinear susceptibility  $\chi^{(2)}$  of the material was calculated. The integrated intensity of the SHG spectrum of the sample was compared with that of a standard reference material, potassium dihydrogen phosphate (KDP), at 1064 nm. Using a modified version of Maxwell's nonlinear equation for relative intensity (Equation S1), the  $\chi^{(2)}$  value for CzPHCN was determined to be 0.128 pm V<sup>-1</sup> at 1064 nm. Subsequently, the SHG-integrated intensity of the sample was measured at the excitation wavelength of 1320 nm, where the SHG response was found to be at its maximum. The corresponding  $\chi^{(2)}$  value at 1320 nm was determined to be 0.21 pm V<sup>-1</sup>.<sup>12–14</sup>

Here,  $\chi_S^{(2)}$  and  $\chi_R^{(2)}$  represent the second-order nonlinear optical (NLO) susceptibilities of the sample and reference, respectively, while  $I_S(2\omega)$  and  $I_R(2\omega)$  denote the corresponding relative SHG emission intensities. Additionally,  $\chi_{(\omega 1)}^{(2)}$  and  $\chi_{(\omega 2)}^{(2)}$  correspond to the second-order susceptibilities at the fundamental pump frequencies  $\omega_1$  and  $\omega_2$ , while  $I(2\omega_1)$  and  $I(2\omega_2)$  represent their respective SHG intensities.<sup>15,16</sup>

The laser-induced damage threshold (LIDT) of CzPHCN was evaluated using Equation S3. At laser power levels exceeding 9.5 mW, the sample began to deviate from the expected quadratic behavior, indicating the onset of instability.<sup>17</sup> The LIDT was determined as the intensity corresponding to the maximum power level before this deviation. For CzPHCN, the LIDT was found to be 37.82 GW cm<sup>-2</sup>.

$$LIDT = Peak Intensity = 37.82 \text{ GW cm}^{-2}$$

#### Polarisation dependence of second harmonic generation:

When a strong electric field is applied to a dielectric material, it induces polarization, causing the material's response to deviate from linearity. This polarization is typically represented by a power series, where the second-order nonlinear polarization is mathematically related t o the incident electric field through the following equation.

$$P_i^{(2)} = \varepsilon_0 \sum_{jk} \chi_{ijk}^{(2)} E_j E_k$$

Here, i, j, and k represent the Cartesian indices.<sup>18</sup> The polarization-dependent SHG response of the pump light was recorded to investigate the structural anisotropy of the material. As depicted in Fig. 4d of the main manuscript, the two-lobed pattern represents the SHG response as a function of the pump polarization angle, with the polarization axis aligned orthogonal to the crystal axis.<sup>19</sup> The consistent SHG intensity, followed by a gradual decline, can be attributed to the pronounced nonlinearity along both axes. This interaction between polarized light and the crystal lattice demonstrates the pronounced anisotropic nature of the CzPHCN crystal. The polarization ratio of the CzPHCN crystal was determined to be 46% using the following equation.

$$\rho = \frac{(I_{max} - I_{min})}{(I_{max} + I_{min})} \times 100$$



Fig. S34 (a) Comparison of the SHG integrated intensity of CzPHCN with the reference KDP used for calculating  $\chi^{(2)}$ . (b) Power-dependent SHG response at the wavelength corresponding to the maximum SHG intensity.



**Fig. S35** Excitation wavelength (1200 nm to 1500 nm) dependent PL and THG signals for (a) tCzPHCN and (b) Cz2CzPHCN. Excitation power dependent PL and THG signals at the excitation wavelength of 1300 nm for (c) tCzPHCN and (d) Cz2CzPHCN. Excitation power dependence of two-photon excited PL intensities for (e) tCzPHCN and (f) Cz2CzPHCN.

Table SU SI	io propertie		ported ennu	er vs uns work	
Name	CCDC	Space	Highest	Corresponding	Second-
		group	SHG	excitation	order non-

Table SC SUC mean antiag of the new outed amitter are this aread

		group	SHG observed	excitation wavelength	order non- linear	induced damage
			at		susceptibility	threshold
					(χ <sup>(2)</sup> )	(LIDT)
DPAOCN	2287184	$P2_{1}2_{1}2_{1}$	610 nm	1220 nm	0.19 pm V <sup>-1</sup> at	13.27 GW
(Reported)					1220 nm	cm <sup>-2</sup> at
					excitation	1220 nm
						excitation
CzPHCN	2420130	$Cmc2_1$	660 nm	1320 nm	0.21 pm V <sup>-1</sup> at	37.82 GW
(This					1320 nm	cm <sup>-2</sup> at
work)					excitation	1320 nm
						excitation

# Section S11: Piezoelectricity and Ferroelectricity

## Preparation of CzPHCN Device for Piezoelectric Energy Harvesting Measurements

The tightly sandwiched nanogenerator devices of CzPHBN crystallites were prepared by attaching small (2 X 5 mm<sup>2</sup>) conductive adhesive copper tapes (Cu-lids in the schematic) at the corners of the ITO-coated PET sheets, which serve as the top and bottom. In the next step, adhesive Kapton tapes were placed on the borders of the ITO-coated PET sheets to avoid direct contact between the electrodes. Subsequently, CzPHBN crystallites were deposited on one of the ITO surfaces and then the other ITO-coated sheet with Cu tape with the Kapton border was placed above the crystal layer. In the last step, copper wires were soldered on the Cu-lids and the device was fully encapsulated with another layer of adhesive Kapton tapes to keep the sandwiched structure intact during measurements and reduce the static charge developed during the continuous impact on the device.

## **Ferroelectric Measurements**

To investigate the ferroelectric properties of CzPHBN, *P-E* hysteresis loop measurements were conducted on a thin film sample of approximately 2.21 µm thickness drop-casted on an Indium tin oxide (ITO)- coated glass surface, and Gallium Indium eutectic was used to the make top contact. These measurements were performed using the aixACCT TF-2000E model hysteresis loop analyzer. The experiments were conducted by applying the dynamic leakage current compensation (DLCC) mode to reduce the contributions from non-hysteretic components of the loop.

Laser-

Table S7	Reported	ferroelectric	materials v	s CzPHCN.
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Compounds	Ps	References
(R)- and (S)-(N,N-dimethyl-3-	0.4	20
fluoropyrrolidinium) iodide		
Amide-functionalized pyrene (Py) and naphthalene-diimide (NDI)	3.2	21
polyurethane (P1) and pyrene (Py)	0.8	22
DABCODA/LTa of DTa	0.42	23
DBCz-TCNQ complex	1.23	24
P1	2	25
[D55DMBP][Dia]	1.7	26
[H-55DMBP][Hia]	1.2	26
CzPHCN	0.32	This work

Composite Materials	Output voltage (V)	Current/ current- density	Active area (cm <sup>2</sup> )	Application/ input	References
γ-glycine	0.45	-	1.8 × 1.8	0.172 N, 0.5 Hz	27
L-Tyr	0.5	35nA	0.6 × 0.6	31 N, 0.2 Hz	28
L-AcW	1.46	-	1.0 × 1.0	52 N, 0.2 Hz	29
L-AcI	1.13	-	1.0 × 1.0	52 N, 0.2 Hz	29
L-AcC	0.27	-	1.0 × 1.0	52 N, 0.2 Hz	29
Pro-Phe-Phe	1.4	52 nA	0.7  imes 0.7	55 N, 0.2 Hz	30
Hyp-Phe-Phe	0.45	39.3 nA	0.7 × 0.7	23 N, 0.2 Hz	30
Phe-Phe	0.2	7.0 nA	-	55 N, 1 Hz	30
HFPD-PVA	18	-	$2 \times 2$	40 N, 4 Hz	31
AD <sub>2</sub> A-1	$0.05 \pm 0.01$	$0.89\pm0.05~nA/cm^2$	0.544	17 N, 5 Hz	32
AD <sub>2</sub> A-2	0.08 ± 0.01	$2.19 \pm 0.11 \text{ nA/cm}^2$	0.544	17 N, 5 Hz	32
AD <sub>1</sub> A	2.0 ± 0.10	$29.15 \pm 1.50 \text{ nA/cm}^2$	0.544	17 N, 5 Hz	32
AD <sub>2</sub> A	2.2 ± 0.11	$45.64 \pm 2.28 \text{ nA/cm}^2$	0.544	17 N, 5 Hz	32
AD <sub>3</sub> A	1.9 ± 0.10	$27.00 \pm 1.35 \text{ nA/cm}^2$	0.544	17 N, 5 Hz	32
CzPHCN	2.8	0.41 μΑ	$2 \times 5$ mm <sup>2</sup>	21N, 10 Hz	This work

 Table S8 Reported small organic-based piezoelectric materials vs CzPHCN

# Section S12: Literature Reported PLQY

Table S9	Literature re	ports of PLQ	Y vs	this work.

Structures	Name	PLQY (%)	State	Referen ces
	4CzIPN	35	Neat film	33
	4CzTPN	15.3	50% CBP film	34
	4CzPN	42	Neat film	35
	5CzBN or 5CzCN	21	Neat film	36

	_	18.1	0.05% PMM A film	37
$\begin{array}{c} \begin{array}{c} Ph \\ Ph $	4PhCz2BN	57	Neat films	38
$ \begin{array}{c}                                     $	4Cz2BN	13	Toluen e	38
CN tBu tBu tBu tBu tBu tBu tBu tBu	4tBuCz2BN	45	Toluen e	38

$\wedge$	2tCz2CzBN	66	Neat	39
			film	
TINN				
	C-DHCN	()	NI4	TL:
	CZPHCN	62	Neat filma	I his
			111115	WULK
CN				
	tCzPHCN	84	Neat	This
			films	work
N <sup>×</sup>				
TELL				
Y Y CN				
CN				
	Cz2CzPHCN	44	Neat	This
			films	work
CN				

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