Supporting Information

Engineering TADF, Mechanochromism, and Second Harmonic Up-conversion Properties in Regioisomeric Substitution Space

Abhijit Chatterjee,^a Joy Chatterjee,^a Subrahmanyam Sappati,^b Riteeka Tanwar,^a Madan D. Ambhore,^c Habibul Arfin,^a Rintu M. Umesh,^d Mayurika Lahiri,^d Pankaj Mandal,^a and Partha Hazra^{*a}

^aDepartment of Chemistry, Indian Institute of Science Education and Research (IISER), Pune (411008), Maharashtra, India

^bDepartment of Pharmaceutical Technology and Biochemistry and Bio Tech Med Center, Gdańsk University of Technology, Gdańsk-80-233, Poland

^cDepartment of Chemistry, Yeshwant Mahavidyalaya Nanded, Nanded, PIN-431602, Maharashtra, India

^dDepartment of Biology, Indian Institute of Science Education and Research (IISER), Pune (411008), Maharashtra, India

* Corresponding author. E-mail: <u>p.hazra@iiserpune.ac.in</u>. Tel.: +91-20-2590-8077; Fax: +91-20-2589 9790.

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Instrumentation:

¹H NMR (at 400 MHz) and ¹³C NMR (at 100 MHz) data characterizations of all the synthesized compounds are performed using JEOL ECS-400 and Bruker Ascend TM 400 spectrometer using deuterated chloroform (CDCl₃) as solvent (having residual chloroform) and tetramethylsilane (TMS) as the internal standard. Chemical shift (δ) values are measured in ppm downfield from CDCl₃ (δ = 7.26 ppm) for ¹H NMR and relative to central CDCl₃ resonance (δ = 77.16 ppm) for ¹³C NMR. High-resolution mass spectra (HRMS) for all the compounds are recorded using ESI TOF in Water's SYNAPT G2 mass spectrometer.

Single-crystal diffraction analysis data were collected at 100K with a BRUKER KAPPA APEX II CCD Duo diffractometer (operated at 1500 W power: 50 kV, 30 mA) using graphite monochromatic Mo K α radiation (λ =0.71073 Å). The structures were solved by direct methods and refined by least-squares against F2 utilizing the software package SHELXL-97.¹⁻² More information on crystal structures can also be obtained from the Cambridge Crystallographic Data Centre under the CCDC deposition number. Powder XRD experiments are carried out using BRUKAR D8 advanced X-ray diffractometer with a Cu-K $_{\alpha}$ radiation source. Steady-state solution-based absorption spectra are recorded on Shimadzu, UV-2600 UV spectrophotometer. Steady-state emission spectra and time-gated emission spectra of all the samples in solution and solid state are carried out using Fluoromax-4C spectrofluorimeter and Fluorolog-3 phosphorimeter (HORIBA), respectively. TGA experiments were carried out using PerkinElmer STA 6000 instrument. Solid state UV-VIS absorption spectrum was collected using Shimadzu UV-3600i plus spectrophotometer.

Time-resolved PL decay profiles have been recorded either using a diode-laser source (for a total time window $<50 \ \mu$ s) or a microsecond flash lamp source (of 1.5-2.5 μ s bandwidth and in cases where the total time window $>50 \ \mu$ s) in Edinburgh FLS980 instruments. 800 nm mode-locked Ti-sapphire laser (Mai-Tai, Spectra-Physics) excitation source was focused on

the sample for the two-photon absorption experiment. Two-photon cell imaging and twophoton excitation-emission spectra collection are performed using a multiphoton microscope (Leica, Germany) at 63X & 10X oil immersion objectives, respectively.

For femtosecond fluorescence up-conversion measurements the samples are excited at 375 nm and 400 nm using the second harmonic of a mode-locked Ti-sapphire laser (Mai Tai, Spectra-Physics). The fundamental beams (760 nm or 800 nm) are frequency doubled in a nonlinear crystal of β-barium borate (BBO). Samples are loaded in a 1 mm thick rotating sample chamber. Fluorescence emitted from the sample is upconverted in another nonlinear crystal (BBO) using a gate pulse (760 nm or 800 nm) of the fundamental beam and passed through a variable delay line before up-conversion. The sum frequency of the fluorescence and gate pulse is detected as a function of the time delay between excitation and gate pulses. The angle between the polarization of the pump and gate pulses is maintained at the magic angle to eliminate effects from rotational diffusion. The upconverted signal is dispersed in a monochromator and detected using photon-counting electronics. A cross-correlation function obtained using the raman scattering from ethanol provided a full width at half-maximum (FWHM) of ~300 fs. Estimated uncertainties in the up-conversion measurements are ~15–20%. The average excitation power is varied but was around 8 ± 0.5 mW, and an average collection time of 2.5 s is used. No degradation of the sample is observed as the traces overlapped after each repetition, and the optical absorption measurements do not show any change before and after the measurements. The fluorescence decays are deconvoluted using a Gaussian-shaped excitation pulse by Igor Pro 6.0 analysis software. During analysis of upconverted decay profiles, the long component lifetime obtained from TCSPC is kept fixed.

Materials:

For synthesis purpose, all the important starting materials like tetrafluorophthalonitrile, tetrafluoroisophthalonitrile and tetrafluoroterephthalonitrile etc. are purchased from sigmaaldrich and were used without any further purification. For spectroscopic studies in solution, spectroscopic grade solvents were purchased from Spectrochem. Pvt. Ltd. India. For solid-state emission studies crystals or powdered samples were held in between two quartz slides purchased from TED PELLA INC.

Experimental Section:

Fabrication of emitter-doped PMMA films

Quantitative amounts of PMMA are dissolved in spectroscopic grade chloroform by heating at 50°C for 10 minutes and followed by sonication for another 5 minutes. Thereafter, a quantitative amount of emitters has been added to the PMMA solution and 0.2 ml of the resulting solution is used for spin-coating on a quartz plate at 2000 rpm for 30 seconds. The quartz plate was then kept in high vacuum for another 20 minutes prior to photophysical studies.

Density Functional Theory (DFT) calculation

Quantum chemical calculations are performed using the Gaussian 09 program³ using a highperformance cluster facility provided by IISER Pune. Initially, geometry optimization of all the luminogens is carried out in the gas phase and the nature of the stationary point (minima on the PE surface) is confirmed by frequency analysis⁴⁻⁵ at the CAM-B3LYP/6-311++G (d, p) level. Furthermore, TD-DFT calculations are carried out to visualize the spatial distribution of HOMOs and LUMOs as well as to get the energy information of several excited singlet and triplet states on equal no. of singlet and triplet states (td (50-50, n-states=10)) by CAM-B3LYP functional using TD-SCF method. Additionally, excited S_1 state geometry optimization is successfully performed at the B3LYP/6-31G (d, p) level after obtaining a frequency-analysed ground state optimized structure at the B3LYP/6-31G (d, p) level.

Spin-orbit coupling matrix element calculation

The spin-orbit coupling matrix between different excited singlet and triplet states was calculated using the zeroth-order regular approximation (ZORA) to the Dirac equation. In this approximation, the SOC operator, \hat{H}_{SOC} is described as⁶

$$\hat{H}_{SOC} = \frac{c^2}{\left(2c^2 - v\right)^2} \sigma \cdot \left(\nabla v \times p\right)$$

Where c, v, σ , and p signify the speed of light, Kohn-Sham potential, Pauli spin-matrix vector, and linear momentum operator respectively. The first-order perturbation is applied on scalar relativistic orbitals after the self-consistent field (SCF) and TD-DFT calculations to obtain SOC effects. CAM-B3LYP functional coupling with slater-type all-electron TZP basis is used to calculate SOC values. All such calculations are done using the PYSOC program.⁷

Fractional quantum yield calculation for film and powdered state

For fractional quantum yield calculation in solid state (film and pristine powdered state), the intensity of the emission at 0 delays has been measured (PF+DF), followed by a delayed emission (with delay time = 20 times of the average lifetime of prompt fluorescence or τ_{PF}) intensity measurement (only DF). The difference gives the quantitative estimate of the prompt fluorescence contribution.

Cell culture and drug treatments

MCF7 cells are obtained from the European Collection of Cell Cultures (ECACC). The cells are maintained in 100 mm dishes (Eppendorf or Corning) and are grown in high-glucose Dulbecco's Modified Eagle Medium (DMEM; Lonza) containing 10% heat-inactivated FBS (Invitrogen) and 100 units /mL penicillin-streptomycin (Invitrogen) and incubated at 37°C humidified 5% CO₂ incubators (Eppendorf or Thermo Scientific).

For multiphoton imaging experiments, $5X \ 10^4 \ MCF7$ (ECACC) cells are seeded on a coverslip and incubated at $37^{\circ}C$ with $5\% \ CO_2$ for 18hrs. Cells are treated with 10 μ M of compound (DPAOCN, DPAMCN, and DPAPCN) and incubated for 24 hrs. Post-treatment, cells are washed with 1X PBS twice and fixed with 4% paraformaldehyde for 20 minutes in dark. After fixation, cells are again washed with PBS and mounted onto slides. The cells are imaged in a multiphoton microscope (Leica, Germany) at 63X oil immersion objective.

For the MTT assay, 0.5 X 10^4 MCF7 cells are seeded in each well of a 96-well plate and incubated at 37°C with 5% CO₂ for 18 hours post-seeding. Cells are treated with different concentrations of the compound. 24 hrs post-treatment, drug-containing media is removed and, 0.5 mg/ml thiazolyl blue tetrazolium (MTT) containing DMEM is added to the cells and incubated at 37°C after covering with aluminum foil. 4 hours post MTT addition, the MTT-DMEM medium mixture is aspirated from the wells and 100 µl of DMSO is added to dissolve the purple MTT-formazan crystals. The absorbance is recorded at 570nm using the multimode Varioskan Flash plate reader (Thermo Scientific, USA).

Synthesis of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN:



Scheme S1: synthesis scheme of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN.

Synthesis of (a) DPAOCN: In a Schlenk RB flask equipped with a magnetic bead, diphenylamine (0.845 gm, 5 mmol) is taken and dissolved in 5 ml of anhydrous THF with argon flow. Vacuum-dried NaH (60% in oil, 300 mg, 7.5 mmol) is added slowly to the mixture and stirred at RT for 30 minutes. After that, tetrafluorophthalonitrile (0.2 gm, 1 mmol) is added to the reaction mixture, and the reaction is allowed to stir for another 48 hours at room temperature under argon (scheme S1). After 48 hours, the excess NaH is quenched by dropwise addition of distilled water. The mixture was then concentrated under a vacuum and washed

several times with water and DCM. Finally, the crude product is purified by SiO_2 column chromatography with a hexane/DCM solvent system. Yield: ~ 80%.

¹**H NMR (400 MHz, CHLOROFORM-D):** δ 7.19 (dd, *J* = 8.4, 7.5 Hz, 8H), 6.97 (dd, *J* = 10.6, 4.1 Hz, 4H), 6.85 (dd, *J* = 8.3, 7.5 Hz, 8H), 6.77 (dd, *J* = 8.5, 0.9 Hz, 8H), 6.69 (t, *J* = 7.3 Hz, 4H), 6.43 (dd, *J* = 8.5, 0.8 Hz, 8H).

¹³C NMR (100 MHz, CHLOROFORM-D): δ 150.43, 148.02, 144.92, 143.90, 128.96, 127.71, 123.86, 123.55, 122.41, 122.30, 116.96, 113.57.

HRMS (ESI TOF): *m*/*z* calcd. For C₅₆H₄₁N₆ [M+H]⁺ 797.3393 found 797.3394.

Synthesis of (b) DPAMCN: In a Schlenk RB flask equipped with a magnetic bead, diphenylamine (1.01 gm, 6 mmol) is taken and dissolved in 5 ml of anhydrous DMF with argon flow. Vacuum-dried NaH (60% in oil, 320 mg, 8 mmol) is added slowly to the mixture and stirred at 50°C for one hour. After 1 hour, tetrafluoroisophthalonitrile (0.2 gm, 1 mmol) is added to the reaction mixture, and the reaction is allowed to stir for another 4 hours at 50°C under argon (scheme S1). The completion of the reaction is confirmed by TLC. Excess NaH, is then quenched with a dropwise addition of distilled water. The mixture was then washed several times with water and ethyl acetate. Finally, the crude product is purified by SiO₂ flash column chromatography with a hexane/DCM solvent system. Yield: ~ 55%.

¹H NMR (400 MHz, CHLOROFORM-D): δ 7.32-7.22 (m, 4H), 7.13 – 7.06 (m, 12H), 7.02 (t, J = 7.4 Hz, 2H), 6.96-6.84 (m, 8H), 6.70 (d, J = 7.7 Hz, 10H), 6.56 (d, J = 7.8 Hz, 4H).
¹³C NMR (100 MHz, CHLOROFORM-D): δ 154.32, 151.91, 145.66, 144.80, 143.28, 140.4, 129.51, 128.73, 127.69, 124.31, 124.08, 123.06, 122.76, 122.72, 121.20, 113.28, 113.14.
HRMS (ESI TOF): *m/z* calcd. For C₅₆H₄₁N₆ [M+H]⁺ 797.3393 found 797.3385.

Synthesis of (c) DPAPCN: In a Schlenk RB flask equipped with a magnetic bead, diphenylamine (0.845 gm, 5 mmol) is taken and dissolved in 5 ml of anhydrous THF with argon flow. Vacuum-dried NaH (60% in oil, 300 mg, 7.5 mmol) is added slowly to the mixture and stirred at RT for 30 minutes. After that, tetrafluoroterephthalonitrile (0.2 gm, 1 mmol) is added to the reaction mixture, and the reaction is allowed to stir for another 4 hours at room temperature under argon (scheme S1). After 48 hours, the excess NaH is quenched by dropwise addition of distilled water. The mixture was then concentrated under a vacuum and washed several times with water and DCM. Finally, the crude product is purified by SiO₂ column chromatography with a hexane/DCM solvent system. Yield: \sim 50%.

¹**H NMR (400 MHz, CHLOROFORM-D):** δ 7.15 – 7.08 (m, 16H), 6.88 (t, *J* = 7.4 Hz, 8H), 6.82 – 6.76 (m, 16H).

¹³C NMR (100 MHz, CHLOROFORM-D): δ 146.05, 144.87, 128.89, 123.70, 122.67, 122.13, 113.34.

HRMS (ESI TOF): *m*/*z* calcd. For C₅₆H₄₁N₆ [M+H]⁺ 797.3393 found 797.3322.

¹<u>H NMR data of (a) DPAOCN</u>:



<u>¹H NMR data of (b) DPAMCN</u>:



1H NMR data of (c) DPAPCN:



13C NMR data of (a) DPAOCN:



195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 fl (ppm)

13C NMR data of (b) DPAMCN:



13C NMR data of (c) DPAPCN:



120 110 f1 (ppm)

HRMS data of (a) DPAOCN:



HRMS data of (b) DPAMCN:



HRMS data of (c) DPAPCN:



Crystallographic data



Identification code	DPAOCN	
CCDC No.	2287184	
Empirical formula	$C_{57}H_{42}Cl_2N_6$	
Formula weight	881.87	
Temperature/K	100(2)	
Crystal system	orthorhombic	
Space group	$P2_{1}2_{1}2_{1}$	
a/Å	9.771(3)	
b/Å	21.156(7)	
c/Å	22.933(8)	
α/°	90	
β/°	90	
γ/°	90	

Volume/Å ³	4741(3)
Z	4
ρcalc (g/cm ³)	1.235
µ/mm ⁻¹	0.182
F(000)	1840.0
Radiation	MoKa ($\lambda = 0.71073$)
20 range for data col	lection/° 3.85 to 58.53
Index ranges	$-11 \le h \le 13, -28 \le k \le 28, -31 \le 1 \le 30$
Reflections collected	87524
Independent reflectio	ns 12600 [$R_{int} = 0.1422, R_{sigma} = 0.1198$]
Data/restraints/parar	neters 12600/0/586
Goodness-of-fit on F ²	1.039
Final R indexes [I>=2	$R_{1} = 0.0670, wR_{2} = 0.1568$
Final R indexes [all d	ata] $R_1 = 0.1403, wR_2 = 0.1857$
Largest diff. peak/hol	le / e Å ⁻³ 0.68/-0.56
Flack parameter	0.15(3)



Table 2: Crystal data and structure refinement for DPAMCN.

Identification code	DPAMCN
CCDC No.	2271434
Empirical formula	C56H40N6O
Formula weight	812.94
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_l/C$
a/Å	13.956(3)
b/Å	13.033(3)
c/Å	23.580(5)
α/°	90
β/°	93.210(6)
γ/°	90
Volume/Å ³	4282.1(15)
Z	4

pcalc (g/cm ³)	1.261
μ/mm-1	0.077
F(000)	1704.0
Radiation	MoK α ($\lambda = 0.71073$)
20 range for data	collection /° 4.28 to 56.728
Index ranges	$-18 \le h \le 15, -17 \le k \le 16, -31 \le 1 \le 31$
Reflections collecto	e d 98411
Independent reflec	etions $10719 [R_{int} = 0.2496, R_{sigma} = 0.1347]$
Data/restraints/pa	rameters 10719/0/569
Goodness-of-fit on	F^2 1.060
Final R indexes [I>	≥=2σ (I)] $R_1 = 0.0882, wR_2 = 0.1764$
Final R indexes [al	ll data] $R_1 = 0.1629, wR_2 = 0.2104$
Largest diff. peak/	hole / e Å ⁻³ 0.57/-0.72



Table 3: Crystal data and structure refinement for DPAPCN.

Identification code DPAPCN

CCDC No. 2287185				
Empirical formula	$C_{58}H_{44}Cl_4N_6$			
Formula weight	966.79			
Temperature/K	100(2)			
Crystal system	monoclinic			
Space group	$P2_{l}/C$			
a/Å	12.415(2)			
b/Å	11.6613(19)			
c/Å	17.594(3)			
a/°	90			
β/°	109.655(5)			
γ/°	90			
Volume/Å ³	2398.9(7)			
Z	2			
ρcalc (g/cm³)	1.339			
µ/mm ⁻¹	0.294			
F(000)	1209.0			
Radiation	MoKa ($\lambda = 0.71073$)			
20 range for data c	ollection /° 4.272 to 48.998			
Index ranges $-14 \le h \le 14, -13 \le k \le 13, -20 \le l \le 19$				
Reflections collected	1 33520			
Independent reflect	ions 3995 [$R_{int} = 0.0645$, $R_{sigma} = 0.0373$]			
Data/restraints/para	ameters 3995/0/308			
Goodness-of-fit on l	F ² 1.339			
Final R indexes [I>=2σ (I)] R ₁ = 0.1161, wR ₂ = 0.3582				
Final R indexes [all data] $R_1 = 0.1258, wR_2 = 0.3634$				
Largest diff. peak/hole / e Å ⁻³ 1.21/-0.60				

Solution state photophysics and theoretical studies



Fig. S1 Ground state frequency analyzed optimized structures, HOMO, and LUMO orbitals of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN along with their energy gaps.



Fig. S2 Excitation spectra of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN in different solvents (10 µm concentration).



Fig. S3 Root mean square deviation (RMSD) between the ground state (S_0 state) and excited state (S_1 state) of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN; calculated and plotted using VMD software, here blue structures in all three cases denote the S_0 state and red structures denote the S_1 state. Optimized S_1 state molecular geometries of (d) DPAOCN, (e) DPAMCN, and (f) DPAPCN. For S_1 state optimization, TD-SCF method, and B3LYP/6-31G (d, p) level of theory have been used in all three cases prior to ground state optimization at B3LYP/6-31G (d, p). Co-ordinates of both ground state and excited state optimized geometries are given below:

DPAOCN ground state (S₀ state) optimized geometry:

- C 0.687000 -0.070000 -0.003000
- C -0.742000 -0.104000 0.040000
- C -1.495000 0.869000 -0.695000
- C -0.809000 1.904000 -1.360000

- C 0.594000 2.023000 -1.260000
- C 1.351000 1.040000 -0.589000
- N 2.763000 1.222000 -0.485000
- N 1.453000 -1.125000 0.587000
- N -1.435000 -1.011000 0.881000
- N -2.906000 0.786000 -0.790000
- C 3.639000 0.573000 -1.406000
- C 3.226000 2.357000 0.259000
- C 4.930000 0.205000 -0.993000
- C 5.805000 -0.411000 -1.883000
- C 5.410000 -0.682000 -3.196000
- C 4.131000 -0.315000 -3.609000
- C 3.253000 0.316000 -2.728000
- C 4.243000 3.187000 -0.239000
- C 4.680000 4.281000 0.503000
- C 4.103000 4.583000 1.737000
- C 3.081000 3.770000 2.225000
- C 2.648000 2.661000 1.500000
- C -3.737000 1.925000 -0.545000
- C -3.452000 -0.345000 -1.482000
- C -3.358000 2.894000 0.397000
- C -4.168000 4.001000 0.636000
- C -5.375000 4.163000 -0.044000
- C -5.752000 3.203000 -0.983000

- C -4.942000 2.099000 -1.242000
- C -4.552000 -1.033000 -0.954000
- C -5.094000 -2.116000 -1.644000
- C -4.544000 -2.529000 -2.861000
- C -3.453000 -1.839000 -3.391000
- C -2.914000 -0.746000 -2.712000
- C 1.253000 3.094000 -1.943000
- N 1.775000 3.958000 -2.522000
- C -1.506000 2.799000 -2.236000
- N -2.028000 3.508000 -2.996000
- C 2.127000 -0.886000 1.829000
- C 3.510000 -1.088000 1.954000
- C 4.147000 -0.856000 3.170000
- C 3.425000 -0.406000 4.279000
- C 2.051000 -0.207000 4.159000
- C 1.402000 -0.457000 2.948000
- C 1.759000 -2.279000 -0.188000
- C 2.242000 -3.445000 0.432000
- C 2.544000 -4.574000 -0.324000
- C 2.356000 -4.584000 -1.708000
- C 1.851000 -3.441000 -2.322000
- C 1.554000 -2.301000 -1.576000
- C -2.293000 -0.485000 1.894000
- C -3.444000 -1.191000 2.284000

- C -4.254000 -0.711000 3.309000
- C -3.947000 0.484000 3.963000
- C -2.809000 1.191000 3.578000
- C -1.984000 0.711000 2.560000
- C -1.271000 -2.435000 0.820000
- C -1.415000 -3.121000 -0.390000
- C -1.321000 -4.513000 -0.421000
- C -1.105000 -5.235000 0.751000
- C -0.962000 -4.550000 1.961000
- C -1.035000 -3.161000 1.997000

DPAOCN excited S₁ state optimized geometry:

С	-0.693000	-0.057000	0.006000

- C 0.767000 0.053000 0.061000
- C 1.530000 -0.837000 -0.728000
- C 0.910000 -1.887000 -1.457000
- C -0.508000 -2.162000 -1.264000
- C -1.266000 -1.149000 -0.614000
- N -2.722000 -1.280000 -0.639000
- N -1.568000 0.962000 0.544000
- N 1.394000 0.903000 1.027000
- N 2.943000 -0.691000 -0.815000
- C -3.446000 -0.638000 -1.681000
- C -3.333000 -2.183000 0.212000

- C -4.677000 -0.016000 -1.398000
- C -5.386000 0.616000 -2.414000
- C -4.885000 0.632000 -3.717000
- C -3.662000 0.017000 -3.997000
- C -2.936000 -0.609000 -2.989000
- C -4.607000 -2.743000 -0.091000
- C -5.197000 -3.638000 0.782000
- C -4.548000 -4.015000 1.966000
- C -3.280000 -3.496000 2.257000
- C -2.669000 -2.602000 1.397000
- C 3.823000 -1.798000 -0.633000
- C 3.451000 0.507000 -1.410000
- C 3.484000 -2.851000 0.231000
- C 4.352000 -3.922000 0.416000
- C 5.583000 -3.968000 -0.240000
- C 5.922000 -2.926000 -1.102000
- C 5.054000 -1.856000 -1.308000
- C 4.467000 1.236000 -0.779000
- C 4.973000 2.389000 -1.377000
- C 4.470000 2.830000 -2.603000
- C 3.464000 2.100000 -3.237000
- C 2.961000 0.938000 -2.650000
- C -1.134000 -3.299000 -1.803000
- N -1.698000 -4.225000 -2.250000

- C 1.615000 -2.607000 -2.448000
- N 2.152000 -3.209000 -3.295000
- C -2.177000 0.770000 1.818000
- C -3.545000 1.038000 2.012000
- C -4.141000 0.824000 3.253000
- C -3.395000 0.326000 4.323000
- C -2.040000 0.054000 4.135000
- C -1.432000 0.278000 2.900000
- C -1.833000 2.115000 -0.229000
- C -2.364000 3.286000 0.352000
- C -2.640000 4.400000 -0.431000
- C -2.384000 4.396000 -1.806000
- C -1.821000 3.257000 -2.379000
- C -1.540000 2.133000 -1.608000
- C 2.183000 0.324000 2.059000
- C 3.284000 1.019000 2.596000
- C 4.040000 0.468000 3.627000
- C 3.734000 -0.792000 4.147000
- C 2.656000 -1.494000 3.609000
- C 1.888000 -0.947000 2.582000
- C 1.235000 2.324000 1.000000
- C 1.356000 3.046000 -0.193000
- C 1.216000 4.434000 -0.195000
- C 0.967000 5.127000 0.989000

- C 0.840000 4.410000 2.181000
- C 0.962000 3.023000 2.189000

DPAMCN ground state (S₀ state) optimized geometry:

- C -0.063000 -1.219000 -0.132000
- C -0.787000 0.000000 -0.000000
- C -0.063000 1.220000 0.132000
- C 1.354000 1.201000 0.141000
- C 2.075000 0.000000 -0.000000
- C 1.354000 -1.201000 -0.141000
- N 3.493000 0.000000 -0.000000
- N -0.737000 2.461000 0.284000
- N -2.208000 0.000000 -0.000000
- N -0.737000 -2.461000 -0.284000
- C 2.088000 -2.415000 -0.339000
- N 2.703000 -3.386000 -0.518000
- C 2.088000 2.415000 0.339000
- N 2.703000 3.386000 0.518000
- C 4.183000 -0.271000 -1.217000
- C 5.358000 -1.037000 -1.217000
- C 6.023000 -1.293000 -2.413000
- C 5.520000 -0.814000 -3.626000
- C 4.344000 -0.065000 -3.627000
- C 3.681000 0.217000 -2.433000
- C 4.183000 0.271000 1.217000

- C 5.358000 1.037000 1.218000
- C 6.023000 1.293000 2.413000
- C 5.520000 0.814000 3.626000
- C 4.344000 0.065000 3.627000
- C 3.681000 -0.217000 2.433000
- C -0.479000 3.527000 -0.631000
- C -0.488000 4.865000 -0.207000
- C -0.246000 5.890000 -1.118000
- C 0.029000 5.609000 -2.457000
- C 0.055000 4.279000 -2.876000
- C -0.203000 3.246000 -1.978000
- C -1.379000 2.727000 1.534000
- C -2.633000 3.355000 1.564000
- C -3.246000 3.634000 2.783000
- C -2.627000 3.283000 3.986000
- C -1.379000 2.663000 3.959000
- C -0.750000 2.394000 2.742000
- C -2.923000 0.695000 -1.021000
- C -4.117000 1.373000 -0.720000
- C -4.827000 2.027000 -1.724000
- C -4.359000 2.034000 -3.040000
- C -3.173000 1.365000 -3.340000
- C -2.465000 0.692000 -2.345000
- C -2.923000 -0.695000 1.020000

- C -2.465000 -0.692000 2.345000
- C -3.173000 -1.365000 3.340000
- C -4.359000 -2.034000 3.040000
- C -4.826000 -2.027000 1.724000
- C -4.116000 -1.373000 0.720000
- C -1.379000 -2.727000 -1.534000
- C -0.750000 -2.394000 -2.742000
- C -1.379000 -2.663000 -3.959000
- C -2.627000 -3.283000 -3.986000
- C -3.245000 -3.634000 -2.783000
- C -2.632000 -3.356000 -1.564000
- C -0.479000 -3.526000 0.631000
- C -0.203000 -3.245000 1.978000
- C 0.055000 -4.278000 2.876000
- C 0.029000 -5.609000 2.458000
- C -0.246000 -5.890000 1.119000
- C -0.488000 -4.864000 0.208000

DPAMCN excited state (S₁ state) optimized geometry:

- C 1.175000 0.370000 -0.100000
- C 0.000000 0.000000 -0.798000
- C -1.175000 -0.370000 -0.100000
- C -1.149000 -0.429000 1.362000
- C 0.000000 0.000000 2.030000
- C 1.149000 0.429000 1.362000

- N 0.000000 0.000000 3.488000
- N -2.391000 -0.723000 -0.750000
- N 0.000000 0.000000 -2.228000
- N 2.391000 0.723000 -0.750000
- C 2.231000 0.948000 2.112000
- N 3.086000 1.372000 2.790000
- C -2.231000 -0.948000 2.112000
- N -3.086000 -1.372000 2.790000
- C -0.319000 1.177000 4.166000
- C 0.308000 1.472000 5.403000
- C 0.000000 2.647000 6.070000
- C -0.923000 3.545000 5.526000
- C -1.529000 3.266000 4.292000
- C -1.228000 2.103000 3.604000
- C 0.319000 -1.177000 4.166000
- C -0.308000 -1.472000 5.403000
- C 0.000000 -2.647000 6.070000
- C 0.923000 -3.545000 5.526000
- C 1.529000 -3.266000 4.292000
- C 1.228000 -2.103000 3.604000
- C -3.552000 0.056000 -0.499000
- C -4.842000 -0.503000 -0.536000
- C -5.961000 0.284000 -0.275000
- C -5.832000 1.636000 0.047000

- C -4.553000 2.190000 0.104000
- C -3.426000 1.416000 -0.165000
- C -2.497000 -2.006000 -1.365000
- C -3.148000 -2.149000 -2.601000
- C -3.249000 -3.401000 -3.203000
- C -2.694000 -4.529000 -2.596000
- C -2.044000 -4.391000 -1.369000
- C -1.952000 -3.144000 -0.752000
- C -0.853000 0.886000 -2.941000
- C -1.494000 0.465000 -4.120000
- C -2.307000 1.343000 -4.832000
- C -2.513000 2.649000 -4.381000
- C -1.882000 3.068000 -3.210000
- C -1.052000 2.202000 -2.500000
- C 0.853000 -0.886000 -2.941000
- C 1.052000 -2.202000 -2.500000
- C 1.882000 -3.068000 -3.210000
- C 2.513000 -2.649000 -4.381000
- C 2.307000 -1.343000 -4.832000
- C 1.494000 -0.465000 -4.120000
- C 2.497000 2.006000 -1.365000
- C 1.952000 3.144000 -0.752000
- C 2.044000 4.391000 -1.369000
- C 2.694000 4.529000 -2.596000

- C 3.249000 3.401000 -3.203000
- C 3.148000 2.149000 -2.601000
- C 3.552000 -0.056000 -0.499000
- C 3.426000 -1.416000 -0.165000
- C 4.553000 -2.190000 0.104000
- C 5.832000 -1.636000 0.047000
- C 5.961000 -0.284000 -0.275000
- C 4.842000 0.503000 -0.536000

DPAPCN ground state (S₀ state) optimized geometry:

- С -1.246000 -0.625000 0.332000 С -1.246000 0.625000 -0.333000 С 0.000000 1.208000 -0.672000 С 1.246000 0.625000 -0.333000 С 1.246000 -0.625000 0.332000 С -0.000000 -1.208000 0.671000 Ν 2.451000 -1.273000 0.700000 Ν 2.451000 1.273000 -0.700000 Ν -2.451000 1.273000 -0.700000 Ν -2.451000 -1.273000 0.700000С -0.000000 -2.346000 1.543000 Ν -0.000000 -3.223000 2.308000С 0.000000 2.346000 -1.544000
- N 0.000000 3.222000 -2.308000
- C 2.696000 -2.614000 0.273000

- C 3.314000 -3.540000 1.127000
- C 3.555000 -4.841000 0.692000
- C 3.167000 -5.250000 -0.585000
- C 2.535000 -4.335000 -1.427000
- C 2.307000 -3.026000 -1.010000
- C 3.291000 -0.666000 1.681000
- C 4.688000 -0.716000 1.547000
- C 5.504000 -0.140000 2.517000
- C 4.946000 0.504000 3.626000
- C 3.560000 0.551000 3.762000
- C 2.735000 -0.039000 2.804000
- C 3.292000 0.666000 -1.681000
- C 4.688000 0.715000 -1.547000
- C 5.504000 0.139000 -2.517000
- C 4.947000 -0.504000 -3.626000
- C 3.560000 -0.551000 -3.762000
- C 2.735000 0.039000 -2.804000
- C 2.696000 2.614000 -0.273000
- C 3.315000 3.540000 -1.127000
- C 3.556000 4.840000 -0.692000
- C 3.167000 5.250000 0.585000
- C 2.535000 4.335000 1.427000
- C 2.307000 3.026000 1.010000
- C -2.695000 2.615000 -0.273000

- C -2.307000 3.026000 1.010000
- C -2.535000 4.335000 1.427000
- C -3.166000 5.250000 0.585000
- C -3.554000 4.841000 -0.692000
- C -3.313000 3.541000 -1.127000
- C -3.292000 0.666000 -1.680000
- C -4.688000 0.716000 -1.546000
- C -5.505000 0.141000 -2.516000
- C -4.948000 -0.503000 -3.624000
- C -3.561000 -0.551000 -3.761000
- C -2.736000 0.039000 -2.803000
- C -2.696000 -2.614000 0.273000
- C -2.306000 -3.026000 -1.010000
- C -2.535000 -4.335000 -1.427000
- C -3.167000 -5.250000 -0.585000
- C -3.556000 -4.841000 0.691000
- C -3.315000 -3.540000 1.126000
- C -3.291000 -0.666000 1.681000
- C -2.735000 -0.040000 2.804000
- C -3.559000 0.550000 3.762000
- C -4.946000 0.503000 3.626000
- C -5.503000 -0.139000 2.517000
- C -4.687000 -0.715000 1.547000

DPAPCN excited state (S₁ state) optimized geometry:

- C 0.580000 0.380000 1.236000
- C -0.580000 -0.380000 1.236000
- C -1.212000 -0.769000 0.000000
- C -0.580000 -0.380000 -1.236000
- C 0.580000 0.380000 -1.236000
- C 1.212000 0.769000 0.000000
- N 1.144000 0.839000 -2.468000
- N -1.144000 -0.839000 -2.468000
- N -1.144000 -0.839000 2.468000
- N 1.144000 0.839000 2.468000
- C 2.284000 1.683000 0.000000
- N 3.162000 2.460000 0.000000
- C -2.284000 -1.683000 0.000000
- N -3.162000 -2.460000 0.000000
- C 2.456000 0.454000 -2.817000
- C 3.288000 1.295000 -3.584000
- C 4.572000 0.888000 -3.923000
- C 5.068000 -0.348000 -3.497000
- C 4.255000 -1.174000 -2.719000
- C 2.963000 -0.785000 -2.381000
- C 0.465000 1.863000 -3.189000
- C 0.369000 1.800000 -4.589000
- C -0.295000 2.804000 -5.289000
- C -0.878000 3.877000 -4.611000

- C -0.782000 3.941000 -3.220000
- C -0.111000 2.946000 -2.510000
- C -0.465000 -1.863000 -3.189000
- C -0.369000 -1.800000 -4.589000
- C 0.295000 -2.804000 -5.289000
- C 0.878000 -3.877000 -4.611000
- C 0.782000 -3.941000 -3.220000
- C 0.111000 -2.946000 -2.510000
- C -2.456000 -0.454000 -2.817000
- C -3.288000 -1.295000 -3.584000
- C -4.572000 -0.888000 -3.923000
- C -5.068000 0.348000 -3.497000
- C -4.255000 1.174000 -2.719000
- C -2.963000 0.785000 -2.381000
- C -2.456000 -0.454000 2.817000
- C -2.963000 0.785000 2.381000
- C -4.255000 1.174000 2.719000
- C -5.068000 0.348000 3.497000
- C -4.572000 -0.888000 3.923000
- C -3.288000 -1.295000 3.584000
- C -0.465000 -1.863000 3.189000
- C -0.369000 -1.800000 4.589000
- C 0.295000 -2.804000 5.289000
- C 0.878000 -3.877000 4.611000

- C 0.782000 -3.941000 3.220000
- C 0.111000 -2.946000 2.510000
- C 2.456000 0.454000 2.817000
- C 2.963000 -0.785000 2.381000
- C 4.255000 -1.174000 2.719000
- C 5.068000 -0.348000 3.497000
- C 4.572000 0.888000 3.923000
- C 3.288000 1.295000 3.584000
- C 0.465000 1.863000 3.189000
- C -0.111000 2.946000 2.510000
- C -0.782000 3.941000 3.220000
- C -0.878000 3.877000 4.611000
- C -0.295000 2.804000 5.289000
- C 0.369000 1.800000 4.589000



Fig. S4 Time-resolved fluorescence decay profiles of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN in solvents of varying polarity (concentration $10 \mu m$).

Solvent system	Decay type	Components
Toluene	Mono-exponential	3.57 ns
THF	Mono-exponential	5.35 ns
DMF	Mono-exponential	4.35 ns
Acetonitrile	Mono-exponential	4.34 ns
Methanol	Mono-exponential	1.25 ns

Table S1: Time-resolved fluorescence decay type and components in different solvents of DPAOCN (concentration $10 \ \mu m$).

Solvent system	Decay type	Components
Toluene	Mono-exponential	1.69 ns
THF	Mono-exponential	2.06 ns
DMF	Mono-exponential	3.03 ns
Acetonitrile	Mono-exponential	3.31 ns
Methanol	Mono-exponential	3.61 ns

Table S2: Time-resolved fluorescence decay type and components in different solvents of DPAMCN (concentration $10 \ \mu m$).

Solvent system	Decay type	Components
Toluene	Mono-exponential	1.73 ns
THF	Mono-exponential	1.83 ns
DMF	Mono-exponential	1.97 ns
Acetonitrile	Mono-exponential	2.01 ns

Table S3: Time-resolved fluorescence decay type and components in different solvents of DPAPCN (concentration $10 \ \mu m$).



Fig. S5 Fluorescence up-conversion decay profiles of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN in toluene (concentration $30 \ \mu m$).

Sample	λ_{em}	$ au_1$	α ₁	$ au_2$	α_2
DPAOCN	530 nm	3.5 ns	64.1 ± 0.7 %	6 ± 0 ps	37.2 ± 0.8 %
DPAOCN	550 nm	3.5 ns	93 ± 0.6 %	6.5 ± 0 ps	7 ± 1.1 %
DPAOCN	560 nm	3.5 ns	98.5 ± 1.1 %	9 ± 0 ps	1.4 ± 0.9 %
DPAMCN	500 nm	1.6 ns	64.8 ± 0.4 %	3.6 ± 0.1 ps	35.1 ± 0.7 %
DPAMCN	517 nm	1.6 ns	84.2 ± 0.3 %	$2.4\pm0.1~\mathrm{ps}$	15.7 ± 0.6 %
DPAMCN	540 nm	1.6 ns	100%	-	-
DPAPCN	550 nm	1.7 ns	62.4 ± 0.9 %	7.3 ± 0.4 ps	37.5 ± 1.54 %
DPAPCN	560 nm	1.7 ns	74 ± 1.8 %	8±1.1 ps	26 ± 2.45 %
DPAPCN	570 nm	1.7 ns	75.6 ± 1.5 %	7.6 ± 0.9 ps	24 ± 2.3 %

Table S4: Fluorescence up-conversion decay transients and their respective wavelength-based contributions for all three isomers in toluene. Shorter decay components and their respective contributions have been highlighted in bold.



Fig. S6 Delayed fluorescence lifetimes of (a) DPAOCN, (b) DPAMCN, (c) DPAPCN in degassed toluene (for 30 μm of luminogen concentration).



Fig. S7 Steady-state and time-gated emission spectra of (a) DPAOCN, (b) DPAMCN, (c) DPAPCN at room temperature (298 K) and 77 K in degassed toluene. At RT, for DPAOCN & DPAMCN, 50 μ s delay time and 2 ms sample windows have been used. For DPAPCN, 5 μ s delay time and 1 ms sample windows have been used. At 77 K(low-temperature), for DPAOCN & DPAMCN, 0.25 ms delay time and 10 ms sample windows have been used. For DPAPCN, due to its relatively lower lifetime, 0.1 ms delay time and 10 ms sample windows have been used.



Fig. S8 Energy diagram of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN obtained from TD-DFT (50-50) calculation using TD-SCF method at CAM-B3LYP/6-311++G (d, p) level of theory.



Fig. S9 Time-gated emission spectra at 77K of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN in toluene and polar glass-freezing alcoholic mixtures (GFM) (for DPAOCN and DPAMCN). For DPAPCN, DMSO has been used due to the isomer's poor solubility in GFM. Concentration= $30 \mu m$. For DPAOCN & DPAMCN, 0.25 ms delay time and 10 ms sample windows have been used. For DPAPCN, due to its relatively lower lifetime, 0.1 ms delay time and 10 ms sample windows have been used.



Photophysical properties in 10wt% PMMA film and powdered state

Fig. S10 (a) & (d) prompt fluorescence and delayed fluorescence lifetime of 10wt % DPAOCN doped PMMA film. (b) & (e) prompt fluorescence and delayed fluorescence lifetime of 10wt % DPAMCN doped PMMA film. (c) & (f) prompt fluorescence and delayed fluorescence lifetime of 10wt % DPAPCN doped PMMA film. Averaged prompt fluorescence lifetime (τ_{PF}) of DPAOCN, DPAMCN, and DPAPCN are found to be 4.39 ns, 1.19 ns, and 1.79 ns, respectively.



Fig. S11 Prompt fluorescence emission lifetime of (a) DPAOCN powder, (b) DPAMCN powder and (c) DPAPCN powder. Averaged prompt fluorescence lifetime (τ_{PF}) of DPAOCN, DPAMCN, and DPAPCN powder are found to be 2.1 ns, 1.1 ns, and 0.8 ns, respectively.



Fig. S12 Time-gated spectra of (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN powder at RT and at 77 K (50 μ s delay for RT spectra and 0.25 ms delay for 77 K spectra in case of DPAOCN and DPAMCN to remove residual TADF photon counts. For DPAPCN, due to its relatively lower lifetime, RT spectra were collected using a 10 μ s delay, and 77 K spectra were collected using a 0.1 ms delay. Sample windows for all room-temperature spectra measurements have been kept at 2 ms and for all low-temperature spectra measurements have been kept at 10 ms.



Fig. S13 Temperature-dependent PL decay of DPAOCN powder (collection wavelength at 600 nm) in (a) shorter time window (b) longer time window.

Mechanochromic luminescent (MCL) properties



Fig. S14 (a) & (b) Grinding effect on DPAMCN and DPAPCN pristine powder respectively (ex. 380 nm). (c) Photographic images (irradiated using 365 nm UV lamp) of grinding effect on DPAMCN (top) and DPAPCN (bottom) powder.



Fig. S15 (a) & (d) Effect of mechanical grinding on the prompt fluorescence and delayed fluorescence lifetime of DPAOCN powder. (b) & (e) Effect of mechanical grinding on the prompt fluorescence and delayed fluorescence lifetime of DPAMCN powder. (c) & (f) Effect

of mechanical grinding on the prompt fluorescence and delayed fluorescence lifetime of DPAPCN powder.



Fig. S16 Heating effect on the DPAOCN ground powder (O-form) to yield G-form.



Fig. S17 Hirshfeld surface analysis⁸⁻¹⁰ of DPAOCN crystal and fingerprint plot giving quantitative description regarding several non-covalent interactions using crystal explorer 3.1 software¹¹ with iso-value 0.5.



Fig. S18 Hirshfeld surface analysis of DPAMCN crystal and fingerprint plot giving quantitative description regarding several non-covalent interactions.



Fig. S19 Hirshfeld surface analysis of DPAPCN crystal and fingerprint plot giving quantitative description regarding several non-covalent interactions.



Fig. S20 Crystal unit cell packing of all three luminogens (a) DPAOCN (Z= 4, cell volume= 4740 Å³), (b) DPAMCN (Z= 4, cell volume= 4282 Å³), (c) DPAPCN (Z= 2, cell volume= 2398 Å³).



Fig. S21 Dihedral angles of each peripheral diphenylamine moiety with the central phthalonitrile core of DPAOCN.



Fig. S22 Simulated and experimental PXRD patterns of all forms of DPAOCN. Y-form = pristine form, O-form = ground form (obtained after mechanical grinding), reversibility to Y-form = exposing less DCM vapor on O-form or the ground powder, G-form= after prolonged exposure of DCM vapor on O-form or after heating the ground powder (O-form) at ~ 90°C.



Fig. S23 Simulated and experimental PXRD patterns of (a) DPAMCN, (b) DPAPCN powder under external stimuli.



Note 1: Large change in prompt and delayed emission lifetimes of DPAOCN:

Fig. S24 Optimized ground state (S_0 state) and excited state (S_1 state) structures of all three isomers in the gas phase at B3LYP/ 6-31G (d,p) level of theory.

Large changes in prompt and delayed fluorescence lifetime are attributed to large energy changes upon mechanical grinding in the case of mechano-active DPAOCN. Herein, we would like to draw the readers' attention to an intriguing aspect. Our theoretical outcomes from TDDFT calculation unambiguously indicate that the ICT excitation/emission processes of all

three isomers should be accompanied by variations of intramolecular D–A twisting (Figure S24). In powder form and especially in a system with large steric hindrance like DPAOCN, such structural relaxation would be strongly suppressed by constraints from the dense and rigid molecular packings that make the D and A units remain in the initial less twisted arrangements even in the excited state. However, upon grinding a large energy change is highly anticipated because the disordered amorphous states are generally less dense and possess a relatively large free volume which is accompanied by a large void volume of the DPAOCN molecule, in that case, the specific diphenyl amine donor units can more freely rotate to afford near orthogonal excited D–A structures with energetically different and more stabilized ICT excited state. Consequently, the PL spectra underwent conspicuous redshifts along with significant lifetime changes through the crystalline to amorphous transformation. On the contrary, such energy changes are less feasible in the other two isomers due to relatively lower steric hindrance and void volume and moreover, due to its centro-symmetric packing.

Note 2: Role of DCM adsorption and amount of DCM adsorbed by O-form (ground orange emissive powder) upon DCM vapour treatment:

Herein, adsorbed DCM is playing a crucial role in the modulation of crystallinity, as well as reversibility of the tri-color stimuli-responsiveness. Polar DCM molecules by creating a dipoledipole interaction alter the donor-acceptor dihedral angle of the molecule, thus changing the emission color of the system. We performed a control experiment to support this statementthe ground powder (O-form) was fumed with vapor of non-polar solvent like- hexane, and this time no color change was observed (Figure S25, below), supporting our claim of solventsample dipole-dipole interaction. It is worth noting that upon DCM vapour treatment a blue shift of the ground O-form is taking place, suggesting a lowering of the D-A dihedral angle of the luminogen by solvent dipole interaction. Moreover, analysis of the PXRD patterns of all the DCM-treated samples shows that the vapor treatment does not significantly change the crystalline phase as the position of the PXRD peaks remains nearly unchanged, the only change being the modulation of crystallinity of the samples. In order to quantify the amount of DCM adsorbed by the O-form (ground orange emissive powder) to revert back to Y-form and further forming the G-form, we conducted a TGA experiment using three samples: (a) ground powder (O-form), (b) a small amount of sample treated with DCM vapor (forming the Y-form), and (c) a large amount of sample treated with DCM vapor (forming the G-form). Samples b and c

exhibited a decrease in weight between 40-120°C (Figure S25, below), which is attributed to the adsorption of DCM vapor. It was further determined that sample b adsorbed approximately 2% of DCM vapor, while sample c adsorbed up to 6%, indicating varying levels of DCM adsorption.



Fig. S25 (a) No emission color change upon hexane fuming of the ground powder (O-form), (b) TGA data of ground powder (O-form), a small amount of sample treated with DCM vapor (forming the Y-form), and a large amount of sample treated with DCM vapor (forming the G-form).

Second Harmonic Generation (SHG) Properties and Instrumentation

Section A:

Experimental Setup for Second-Harmonic Generation:

For conducting SHG experiments, we have used ultrafast (~50 fs) pulses of different wavelengths from an optical parametric amplifier (OPA) as the excitation source. The OPA (TOPAS-C, Light Conversion) is pumped by a regenerative amplifier (Spitfire Pro XP, Spectra-Physics) with a pulse width of 45 fs (FWHM), 1 KHz repetition rate, and 800 nm center wavelength. Further, the amplifier was seeded with a mode-locked Ti: Sapphire oscillator (Tsunami, Spectra-Physics) of 80 MHz repetition rate and 800 nm central wavelength. The pump beam from the OPA passes through a neutral density (N. D.) filter for power-dependent measurements followed by an 850 nm of long-pass filter for the purity of the pump beam. The filtered output was then focused using a plano-convex lens of 200 mm focal length. To avoid damage, we kept the sample away from the focus where the spot size of the

beam is 400 μ m. The output SHG signal was then collimated using a 25 mm plano-convex lens and filtered using a 750 nm short-pass filter to remove any residual pump beam. The collimated output was then detected using a miniature spectrometer (USB4000, Ocean Optics) coupled to an optical fiber.



Scheme S1: experimental set-up for second harmonic generation.

Calculation of second-order nonlinear susceptibility ($\chi^{(2)}$):

To calculate the second-order nonlinear conversion efficiency of the DPAOCN crystals, we have relied on modified Maxwell's nonlinear equation of relative intensity given by equation (1):¹²

$$\chi_{S^{(2)}} = \chi_{R^{(2)}} \sqrt{\frac{I_S(2\omega)}{I_R(2\omega)}}$$
(1)

Where $\chi_{S^{(2)}}$ and $\chi_{R^{(2)}}$ are the second-order NLO susceptibilities of the sample and reference and $I_S^{(2\omega)}$ and $I_R^{(2\omega)}$ are the relative SHG intensities of the sample and reference, respectively. We have used potassium dihydrogen phosphate (KDP) as the reference for determining secondorder susceptibility from the SHG data. Our sample shows $\chi_{S^{(2)}} = 0.038$ pm/V at 1064 nm. Next, we determined the $\chi^{(2)}$ at 1220 nm of the sample from the SHG data of the sample and KDP at an excitation wavelength of 1220 nm by using the equation (2):

where $\chi_{\omega_{1}(2)}$ and $\chi_{\omega_{2}(2)}$ are the second-order susceptibilities at fundamental pump frequencies ω_{1} and ω_{2} and the $I(2\omega_{1})$ and $I(2\omega_{2})$ are their respective intensities. We have calculated $\chi^{(2)} = 0.19$ pm/V of DPAOCN at 1220 nm. As a result, our sample showed comparable SHG with that of the commercially available materials.¹³⁻¹⁴



Fig. SA1 $\chi^{(2)}$ value determination of DPAOCN crystals using KDP as reference.



Fig. SA2 Wavelength dependence of very weak third harmonic signal of DPAOCN crystals.

Calculation of Laser-Induced Damage Threshold (LIDT):

The laser-induced damage threshold (LIDT) is a measure of the optical stability of a nonlinear material used in NLO procedures. The sample's LIDT is determined by the pump strength at which the SHG response deviates from quadratic behavior. In our sample, the LIDT is the intensity corresponding to 3 mW.

 $Energy \ per \ pulse$ $Peak \ Intensity = Pulse \ width \times Effective \ Spot \ Area$ $Average \ Power$ $Where, \ Energy \ per \ pulse = Repetition \ Rate$ $LIDT = \ Peak \ Intensity = Average \ Power$ $Repetition \ Rate \times Pulse \ Width \times Effective \ Spot \ Area$ $3 \times 10^{-3} \ W$ $LIDT = \ Peak \ Intensity = 1000 \ Hz \times 45 \times 10^{-15} \ s \times \pi \times (400 \times 10^{-6} m)^2$

Using the aforementioned equation, we determined the LIDT for our sample, which is 13.27 GW/cm² with the necessary laser information.



Fig. SA3 Absorbance spectra of the DPAOCN crystals along with the maximum SHG signal at 610 nm. The absorbance spectrum is obtained by converting the diffuse reflectance spectrum using the Kubelka-Munk transformation, $\alpha/S = (1 - R)^2/2R$.

Applications

Section B: Converted LEDs (c-LEDs) fabrication

Drawing inspiration from three distinct emission properties of the isomers, we embarked on the creation of c-LEDs.¹⁵⁻¹⁸ For that, the samples were blended at a 10 wt% ratio with polymethyl methacrylate (PMMA) using chloroform as the solvent. This blend was subsequently applied as a coating atop InGaN chips (Fig. SB2), with an elaborate fabrication procedure outlined below. Intriguingly, when a 3V bias is applied, the c-LED coated with DPAOCN emits a captivating yellow light, while those coated with DPAMCN and DPAPCN radiate green and red, respectively (Fig. SB1c). It's noteworthy that these emission colors closely mirror the photoluminescent (PL) emissions from the 10 wt% doped PMMA films, mentioned in the earlier section (Fig. SB1a). This observation points to the potential utilization of these three regio-isomers in the creation of OLEDs for three distinct color regimes—green, yellow, and red.



Fig. SB1 (a) Emission spectra of all three fabricated c-LEDs, (b) CIE-chromaticity plots (GO-CIE, CIE-1931) of the emission spectra obtained in all three isomers, (c) emission glow from all three c-LEDs in three different color regimes and the schematic of the c-LED devices fabricated.

Fabrication of converted LEDs and related measurements:

Commercially available InGaN chips (power = 3W, λ_{EL} = 390-395 nm, V_F = 3.1 V, I_F = 700 mA) were purchased from ASIAN ELECTRONICS, India (Figure SB2). The optimal sample, at 10 wt% doped with poly (methyl methacrylate) or PMMA was mixed in chloroform and heated at 50°C with stirring for 10 minutes. After that, the mixture was coated on top of the UV chip, dried under an IR lamp source, and was used further for emission measurement.



Fig. SB2: Electroluminescence spectra of the InGaN chip centered at 390-395 nm region. Inset shows its photo under daylight and its electroluminescence under a 3 V bias.

Section C: Two-photon absorption properties



Fig. SC1 Two-photon excited emission spectra of (a) DPAOCN crystals, (b) DPAMCN crystals and (c) DPAPCN crystals (excitation wavelength kept at 830 nm and emission collected in 400-780 nm region, in the inset, two-photon confocal microscopy images (at 10X objective) of two-photon illuminated emission from DPAOCN, DPAMCN and DPAPCN crystals (excitation 840 nm). Two-photon excitation spectra of (d) DPAOCN crystals, (e) DPAMCN crystals, and (f) DPAPCN crystals. The wavelength range window for data collection is 690 nm- 1290 nm in all cases. The emission window is as follows: 580 nm-625 nm for DPAOCN, 522 nm-598 nm for DPAMCN, and 590 nm- 660 nm for DPAPCN. For both excitation and emission spectra, 20 nm step size has been used.



Fig. SC2 Two-photon absorption properties of all three regio-isomers in solution (DCM) and crystal state. For solution, an 800 nm laser source is used; crystals' confocal two-photon excited microscopic images have been collected using an 840 nm laser excitation source at 10X objective.



Fig. SC3 MTT viability assay of MCF7 in the presence of different concentrations of dye (a) DPAOCN, (b) DPAMCN, and (c) DPAPCN.



Section D: Rewritable device fabrication



The reversible tri-color emission characteristics of DPAOCN hold promise for a variety of potential applications, such as rewritable media¹⁹ To demonstrate this, a Whatman filter paper is dipped into a stock solution of DCM, kept there for 30 minutes, and then dried for another 30 minutes in vacuum. An orange background was found to be created after the drying process. After that, the word 'OL' (abbreviation of organic light) was written on it using DCM vapor. Initially, we intentionally spread out DCM vapor on the letters 'L' and 'O' was left incomplete to showcase the device's writing improvement potential. Thereafter, the writing was further improved with DCM vapor. The word 'OL' is now complete. To remove the word, a metal spatula was used to scratch it away, leaving only the orange background visible (Figure SD1). Consequently, this smart stimuli-responsive material enables a convenient cycle of writing and erasing.

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