Supporting Information

Minute Torsional Reorganization Elicited Large Visible Range

Fluorescence Gain in Terphenyl Derived Crystals

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1. Experimental details

Materials: 3,5-bis(trifluoromethyl) phenylboronic acid, 3,5-dimethyl phenylboronic acid, and 1,4-dibromobenzene were purchased from TCI Chemicals (India) Pvt. Ltd and used without any further purification. All solvents and Silica gel (230-400 mesh) were purchased from Merck Life Science Pvt. Ltd. Solvents were dried and distilled before use by standard laboratory purification techniques. TLC analysis was performed on recoated Aluminium plates of silica gel 60 F254 plates (0.25 mm, Merck).

X-ray Crystal diffraction: High-quality crystals of **CF₃TP and MeTP** were chosen for the X-ray diffraction experiment. The crystal was mounted using oil (Infineum V8512) on a glass fibre. The data was collected in both 290 K and at 90 K using Rigaku Oxford diffractometer, XtaLAB Synergy, with Mo-K α radiation (λ = 0.71073 Å). Single crystal structures were solved using *Olex2* software package with the *ShelXT-2015* structure solution program and all the structures were refined with *ShelXT* refinement package in *Olex2*. All the crystallographic parameters for the compounds **CF₃TP** and **MeTP** were reported in Table S1.

Spectroscopic characterization: The ¹H NMR and ¹³C NMR spectra were recorded using 400 MHz JEOL and 500 MHz BRUKER NMR instruments. The Optical (Absorption and photoluminescence emission) spectra and basic fluorescence measurements and lifetime τ_f decay were performed in solution, powdered film, and single crystal of **CF₃TP and MeTP** derivatives. UV-Vis absorption (Abs) spectra were recorded on a UV-VIS spectrophotometer (PerkinElmer: Lambda-35 (for solution) and JASCO V-670 (for powder film)) using 1 cm quartz cuvette and plate, respectively. Room-temperature photoluminescence emission (PL) spectra were acquired on a spectrofluorometer (Fluoremax X and FLS-1000 EDINBURGH Instrument). The temperature dependency PL experiment of the compounds in solid-state was performed in FLS-1000 EDINBURGH Instrument with the cryostat setup, and temperature range were chosen 78 K-290 K. Absolute quantum yield were measured in the same instrument (FLS-1000 EDINBURGH) with Integrating sphere setup. In both cases, the lamp source was Xe-400, and the detector was PMT-400 and PMT-400+Integrating sphere. The fluorescence decay profile was performed using time-correlated single-photon counting (TCSPC) methods with HORIBA JOBIN

YVON (single photon counting controller: Fluorohub, precision photo multiplayer power supply: Fluoro3PS). For molecular excitation 280 nm (pulse duration <1 ns, repetition rate 1 MHz), Nano-LED was used as a light source and and an MCP photomultiplier tube (PMT) (Hamamatsu R3809U-50 series) was used as the detector.

Computational calculations were performed by density functional theory (DFT) method using the Gaussian 16 program package^[1]. The geometry of compounds were optimized employing B3LYP (Becke three parameters hybrid functional with Lee–Yang–Parr correlation functional) level of theory^[2]. The 6-31g (d,p) basis set^[3] was used for all atoms (C, H, and F) present in the compounds. Time-dependent density functional theory (TD-DFT) of the compounds were performed using the same basis set, B3LYP / def2-SVP for determining vertical electronic transitions. The molecular orbitals were visualized using the Avogadro molecular editor^[4]. Oscillator strength value obtained from TD DFT calculation using GaussView 6.0.16.

2. Synthesis of Triphenyl derivatives



Scheme S1: Synthetic step for obtaining the target molecules (A) CF₃TP and (B) MeTP.

Synthetic procedure:

CF₃TP and **MeTP** were synthesized by coupling the boronic acid derivatives (3,5-dimethyl phenylboronic acid and 3,5-bis(trifluoromethyl)phenylboronic acid) with dibromobenzene by Suzuki coupling reaction. In a 100 mL two neck Round Bottom (RB) flask, Dibromobenzene (1 mmol) and the boronic acid derivatives (2.4 mmol) were taken and to the mixture, dry toluene was added and stirred at room temperature. Then in the resultant mixture solution, a catalytic amount of Pd(PPh₃)₄ was treated in an inert condition, followed by the addition of aqueous

sodium carbonate solution (priorly degassing with Argon for 2 hours). The whole reaction mixture was refluxed for two days in a closed condensing setup with slow Argon gas flow. After completion of the reaction, the desired product was then separated and purified by column chromatography using a chloroform/hexane (4:1 v/v) mixture as an eluant. Further, the compounds were recrystallized in a chloroform/methanol (3:1) mixture.

A) CF₃TP:

¹H NMR (400 MHz, CDCl₃) δ [ppm]: 8.06 (s, 4H), 7.91 (s, 2H), 7.76 (s, 4H)

¹³**C NMR** (126 MHz, CDCl₃) δ [ppm]: 142.39 (s), 138.86 (s), 132.51 (q, *J* = 33.1 Hz), 128.25 (s), 127.28 (s), 123.41 (q, *J* = 272.7 Hz), 121.53 (s)

¹⁹**F NMR** (376 MHz, CDCl₃) δ[ppm]: -62.74 (s).

B) MeTP:

¹H NMR (400 MHz, CDCl₃) δ [ppm]: 7.63 (s, 4H), 7.25 (s, 4H), 7.00 (s, 2H), 2.39 (s, 12H).

 $^{13}\textbf{C}$ NMR (126 MHz, CDCl_3) δ [ppm]: 140.80 (s), 140.16 (s), 138.28 (s), 128.92 (s), 127.39 (s), 124.97 (s), 21.43 (s).



Figure S1: ¹H NMR spectrum of CF₃TP.



Figure S2: ¹³C NMR spectrum of CF₃TP.



Figure S3: ¹⁹F NMR spectrum of CF₃TP.



Figure S4: ¹H NMR spectrum of MeTP.



Figure S5: ¹³C NMR spectrum of MeTP.

3. Solvent dependent UV-Vis absorption spectra

Solution state absorption spectra of the Terphenyl derivatives were recorded in 10⁻⁵ M solution in different solvent polarities.



FigureS6: Solvent dependent UV-Vis absorption spectra of a) CF_3TP , b) MeTP. (ε in chloroform).

4. SCXRD analysis and crystallographic information of CF₃TP and MeTP

	CF₃TP		МеТР	
	290K	90 K	290 K	90 K
Crystal Formula	$C_{22}H_{10}F_{12}$	$C_{22}H_{10}F_{12}$	C ₂₂ H ₂₂	C ₂₂ H ₂₂
Molecular Weight	502.30	502.30	286.4	286.4
Temperature/K	293.15	90.0(3)	286(3)	89.9(3)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c
a/Å	5.013(4)	9.8389(3)	11.9931(4)	11.8877(2)
b/Å	23.68(2)	22.7414(7)	9.2234(3)	9.23230(10)
c/Å	8.514(8)	9.1352(3)	7.7551(3)	7.57030(10)

α/°	90.00	90.00	90.00	90.00
β/°	100.66(3)	111.238(3)	103.699(4)	106.230(2)
γ/°	90.00	90.00	90.00	90.00
Volume/Å ³	993.2(16)	1905.18(10)	833.44(5)	797.735(19)
Z	4	4	4	4
$\rho_{calc} mg/mm^3$	1.680	1.751	1.141	1.192
µ/mm ⁻¹	0.177	1.671	0.478	0.499
F(000)	500.0	1000.0	308.0	308.0
20 range for data collection/º	6.88 to 58.68	7.78 to 136.56	7.58 to 136.18	7.74 to 136.02
Index ranges	-5 ≤ h ≤ 6, -32 ≤ k ≤ 32, -11 ≤ l ≤ 11	-11 ≤ h ≤ 11, -27 ≤ k ≤ 23, -8 ≤ l ≤ 10	-14 ≤ h ≤ 14, -11 ≤ k ≤ 10, -8 ≤ l ≤ 9	-13 ≤ h ≤ 14, -11 ≤ k ≤ 7, -8 ≤ l ≤ 9
Reflections collected	18619	13111	6025	5708
Data/restraints/parameters	2653/0/230	3440/0/307	1501/0/102	1440/0/102
Independent reflections	2653 [R _{int} = 0.0616, R _{sigma} = 0.0408]	3440 [R _{int} = 0.0768, R _{sigma} = 0.0453]	1501 [R _{int} = 0.0287, R _{sigma} = 0.0195]	1440 [R _{int} = 0.0543, R _{sigma} = 0.0305]
Goodness-of-fit on F ²	1.185	1.038	1.116	1.064
Final R indexes [I>=2σ (I)]	$R_1 = 0.0997, wR_2$ = 0.2005	R ₁ = 0.0636, wR ₂ = 0.1778	$R_1 = 0.0482, wR_2$ = 0.1366	$R_1 = 0.0451, wR_2$ = 0.1215
Final R indexes [all data]	$R_1 = 0.1304, wR_2$ = 0.2148	R ₁ = 0.0681, wR ₂ = 0.1838	$R_1 = 0.0516, wR_2$ = 0.1406	$R_1 = 0.0461, wR_2$ = 0.1227
CCDC code	2117830	2117829	2117833	2117831

Table S1: Crystal structure and all refinement parameters of CF₃TP and MeTP.

5. Non-covalent interaction among the nearest molecule in crystalline form.

Non-covalent interaction among the nearest molecules (CF_3TP) in the molecular packing in both room temperature and low temperature were calculated from relevant crystallographic cif data files with help of Mercury 2021.1.0 software. Interaction in both vertical and longitudinal direction in molecular staking was presented and the interacting distance was also calculated.



Figure S7: Non-covalent interaction (green line) in (a) Vertical, (b) Longitudional direction and the interacting distance (c) in **CF₃TP** molecule in crystalline state at room temperature(**290 K**).



Figure S8: Non-covalent interaction (green line) in (a) Vertical, (b) Longitudinal direction, and the interacting distance (c) in the **CF₃TP** molecule in crystalline state at low temperature (**90 K**).

6. Computational details

The ground state geometry of the triphenyl derivatives (**CF**₃**TP** and **MeTP**) in the gas phase was optimized by employing B3LYP (Becke three parameters hybrid functional with Lee–Yang–Parr correlation functional) level of theory. The Molecular orbital and energy in different geometrical conditions were calculated and the molecular orbitals were visualized using the Avogadro molecular editor.



Figure S9: Optimized geometry of single molecules (CF₃TP and MeTP) in the gas phase.



Figure S10: Molecular orbital (HOMO/LUMO) of **CF₃TP** with geometry (i) varied the torsional angle for one of the terminal phenyl ring keeping the other two in the same plane, (ii) symmetric variation of the dihedral angle of the terminal phenyl rings and (iii) varying the dihedral angle of the terminal phenyl ring in the opposite direction with respect to the central phenyl ring.

7. PXRD and DSC data of CF₃TP



Figure S11: PXRD pattern of CF_3TP^{NL} from SXRD simulation and CF_3TP^{FL} as recorded.



Figure S12: DSC spectra of CF_3TP^{NL} (left) and CF_3TP^{FL} (right) respectively.

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