HLCT/HLCT-AIE-Enabled Donor-Acceptor System through Locking and Unlocking Strategy and Its Versatile Applications

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SI1. General information and measurements

^{1}H and ^{13}C NMR spectra were recorded using an AV 400 Avance-III FT-NMR Spectrometer (Bruker Biospin International, Switzerland) with spectrometer frequencies 400 MHz and 100 MHz respectively and Mass spectra of fluorophore were recorded on High Resolution Mass Spectrometer (HRMS) Waters, USA, XEVO G2-XS QTOF model. The FT-IR spectra were recorded on a Perkin–Elmer RX-I FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed using TA Instrument TGAQ50 thermal analysis system. UV-vis absorption was measured using UV-vis spectrophotometer (Shimadzu Corporation, japan/UV-2450 pekin Elmer, USA/Lamda 25) and photoluminescence (PL) spectra were recorded using an Edinburgh instrument FLS980 spectrofluorometer. The absolute PL Quantum yields (PLQY) were measured using an Edinburgh instrument spectrofluorometer, integrating sphere SC-30 model. The fluorophores' quantum yield is calculated using equation (1).

$$\Phi = \frac{L_n(\lambda) - L_i(\lambda)}{L_0(\lambda)} \quad (1)$$

$$\eta = \frac{E_i(\lambda) - (1-\Phi)_0(\lambda)}{E_0(\lambda)\Phi} \quad) \quad (2)$$

Where, $L_0(\lambda)$ is the integrated excitation profile (sample is directly excited by the incident beam) and $L_i(\lambda)$ are the integrated excitation profile attained from the empty integrated sphere. $E_0(\lambda)$ is the integrated luminescence of solid caused by direct excitation and $E_i(\lambda)$ is indirect illumination from the sphere, respectively. Photoluminescence lifetime of the dyes was measured at 298 K with an Edinburgh Instrument FLS 980 luminescence spectrometer based on the time correlated single photon counting technology for all the dyes. Cyclic voltammetry (CV) of the fluorophores was carried out by using AUTOLAB 302 Modular Potentiostat electrochemical analyzer at 298 ± 1 K. The tests were carried out in dimethylformamide (DMF) containing 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as a supporting electrolyte, and the scan rate was maintained at 100 $mV.s^{-1}$ with three conventional electrode configurations viz, a glassy carbon working electrode, a platinum plate auxiliary electrode, and an Ag/AgCl reference electrode.

SI2. Computational details:

The optimized geometries and relevant energies of the ImPy-Ac were obtained employing density functional theory (DFT) calculations using the hybrid B3LYP functional and 6-311G

(d, p) basis set. All geometries were confirmed to be minima by additional vibrational frequency calculations. The singlet and lowest triplet energies were evaluated via the Δ self-consistent field (ΔSCF) method based on optimized geometries. All the DFT and TD-DFT calculations were conducted using the Gaussian 09 software package and the Gauss View suite of programs for the studied system.

SI3. NMR (^{1}H and ^{13}C) spectra and HRMS spectra

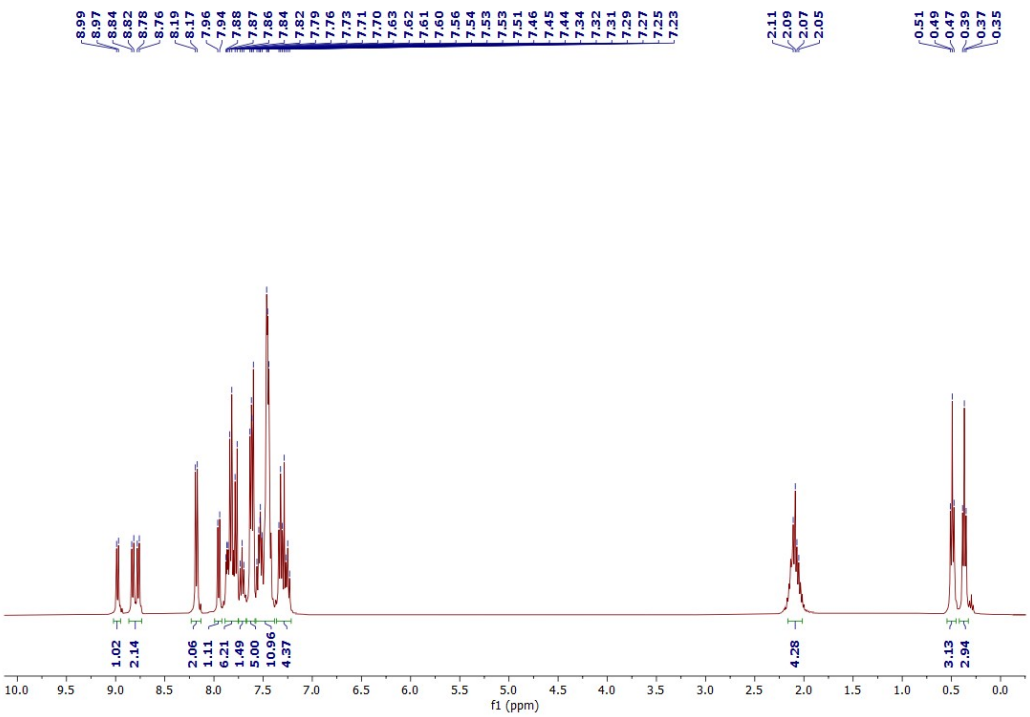

Figure S1. ^{1}H NMR spectra of PI-FLCBZ

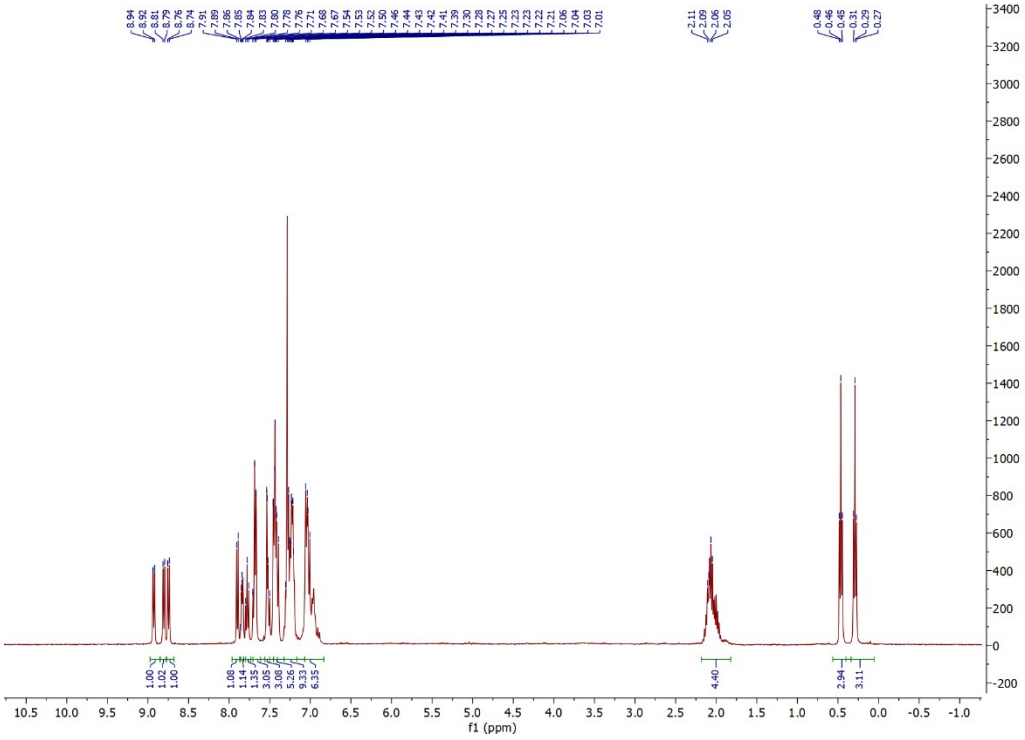

Figure S2. ^{1}H NMR spectra of PI-FLTPA.

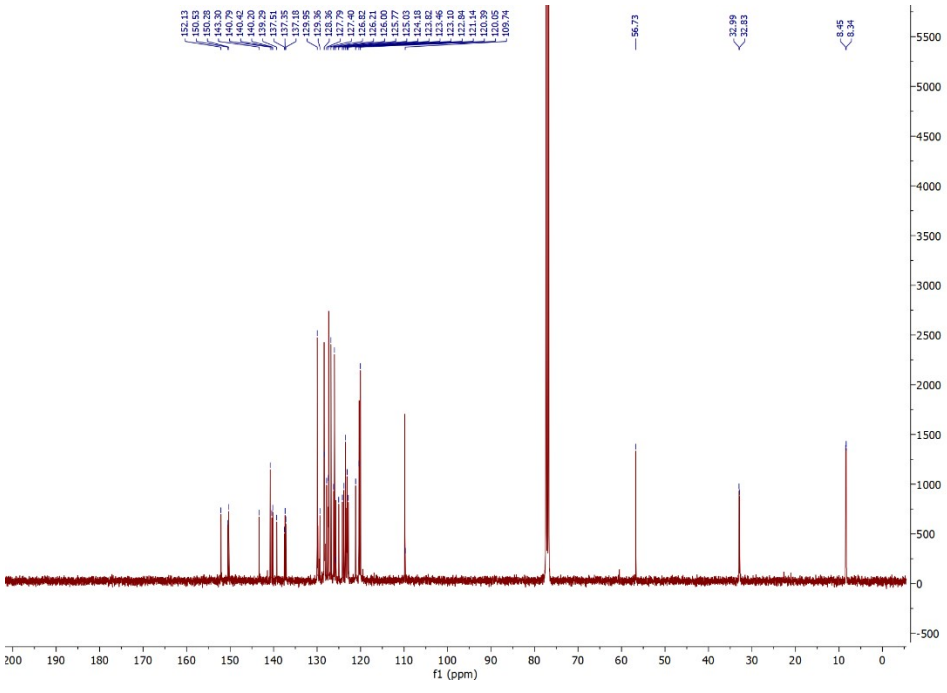

Figure S3. ^{13}C NMR spectra of PI-FLCBZ.

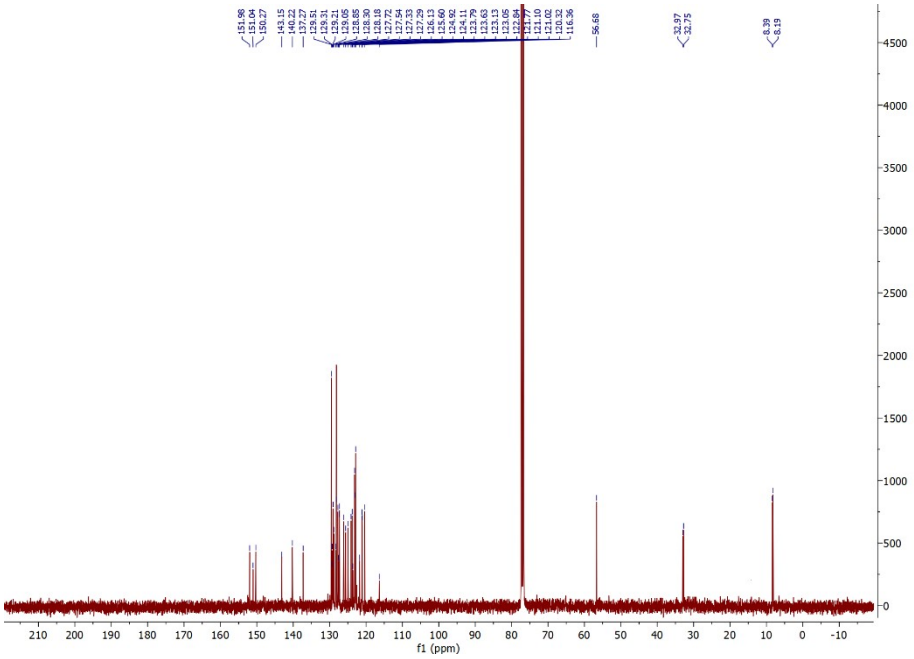

Figure S4. ^{13}C NMR spectra of PI-FLTPA.

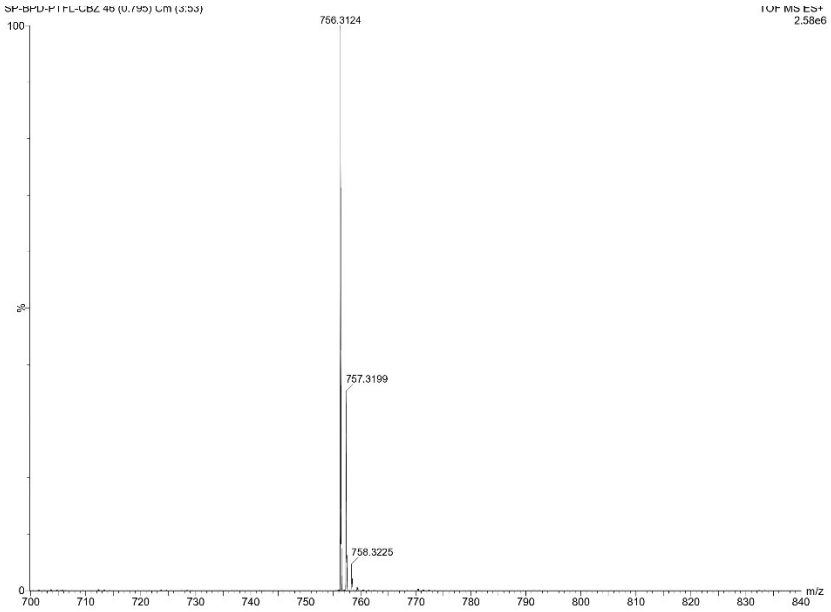

Figure S5. HRMS spectra of the PI-FLCBZ

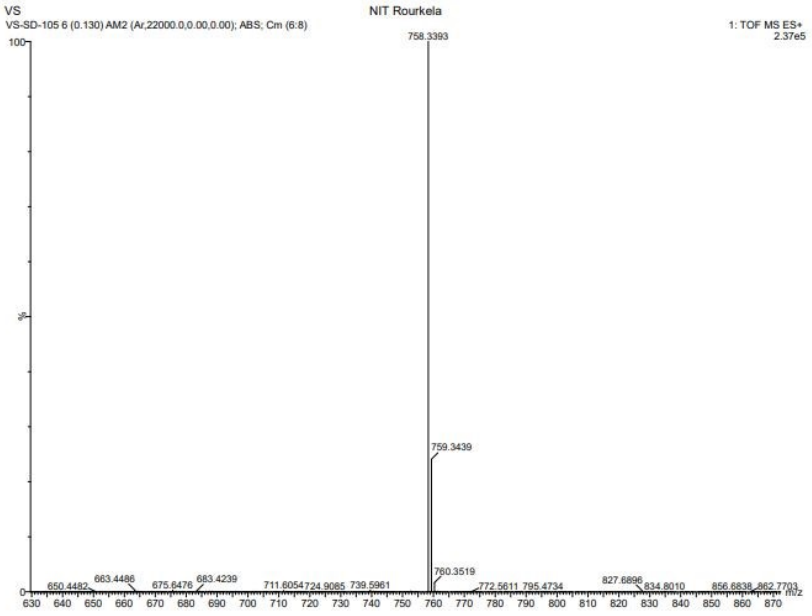

Figure S3. HRMS spectra of the PI-FLTPA.

SI4. Acidochromism properties of the fluorophore.

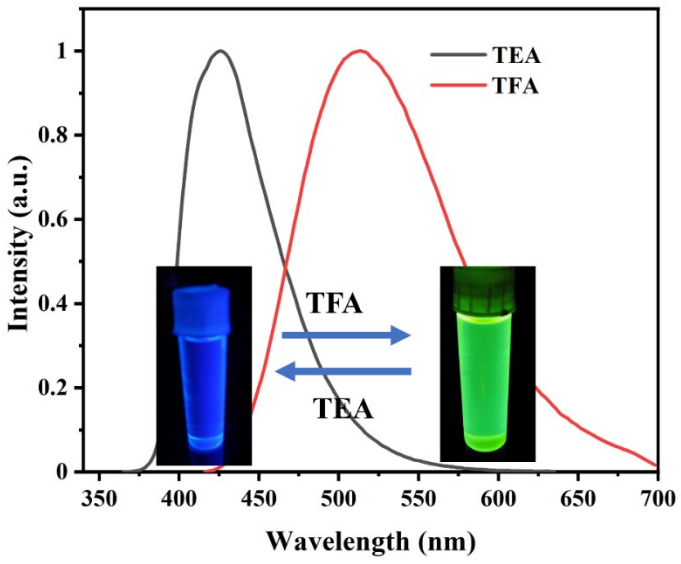

Figure S4. Fluorescence spectra of PI-FLCBZ with alternate addition of TFA and TEA

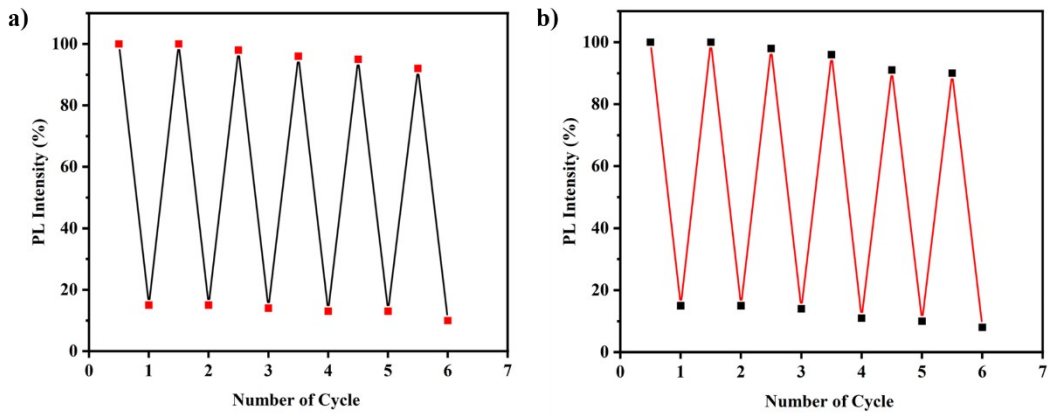

Figure S5. luminescence cycle of the fluorophores upon exposure to acid–base.

SI5. Theoretical Study.

The computed vertical transition and their oscillator strengths (*f*) and configuration of PI-FLCBZ.

Singlet

Excited State 1: Singlet-A 3.3327 eV 372.02 nm f=0.7715 <S**2>=0.000

198 -> 201 0.10070

199 -> 200 0.67956

199 -> 201 0.13366

Excited State 2: Singlet-A 3.3992 eV 364.75 nm f=0.3422 <S**2>=0.000

198 -> 200 0.12790

198 -> 201 0.11013

199 -> 200 -0.13353

199 -> 201 0.66648

Excited State 3: Singlet-A 3.6046 eV 343.97 nm f=0.0112 <S**2>=0.000

198 -> 200 0.66281

198 -> 201 -0.16189

Excited State 4: Singlet-A 3.7741 eV 328.52 nm f=0.0086 <S**2>=0.000

196 -> 200 -0.20188

196 -> 205 -0.15087

198 -> 200 0.11692

198 -> 201 0.20763

198 -> 202 -0.11833

198 -> 203 0.15346

199 -> 201 -0.10466

199 -> 202 -0.37627

199 -> 203 0.41449

Excited State 5: Singlet-A 3.8056 eV 325.79 nm f=0.0021 <S**2>=0.000

198 -> 200 0.13068

198 -> 201 0.61915

199 -> 201 -0.12618

199 -> 202 0.24147

Excited State 6: Singlet-A 3.8329 eV 323.47 nm f=0.0214 <S**2>=0.000

198 -> 201 -0.14126

198 -> 202 0.13161

198 -> 203 0.13469

199 -> 202 0.49028

199 -> 203 0.39655

199 -> 205 0.11704

Excited State 7: Singlet-A 3.9705 eV 312.26 nm f=0.0000 <S**2>=0.000

197 -> 200 0.67419

197 -> 201 -0.17584

Excited State 8: Singlet-A 3.9790 eV 311.60 nm f=0.0388 <S**2>=0.000

197 -> 210 0.14828

198 -> 204 -0.48140

199 -> 204 0.48664

Excited State 9: Singlet-A 4.0101 eV 309.18 nm f=0.0130 <S**2>=0.000

196 -> 200 0.46614

196 -> 203 -0.12096

198 -> 205 -0.11457

199 -> 203 0.24011

199 -> 205 -0.40268

Excited State 10: Singlet-A 4.1006 eV 302.36 nm f=0.0195 <S**2>=0.000

196 -> 200 0.38688

196 -> 201 0.48549

196 -> 203 0.11563

199 -> 205 0.28836

Triplet

Excited State 1: Triplet-A 2.5950 eV 477.77 nm f=0.0000 <S**2>=2.000

194 -> 200 0.14965

196 -> 203 0.12532

198 -> 200 0.11007

198 -> 205 0.12479

199 -> 200 0.55243

199 -> 201 -0.19074

199 -> 205 0.17175

Excited State 2: Triplet-A 2.9449 eV 421.01 nm f=0.0000 <S**2>=2.000

193 -> 200 0.12984

194 -> 200 -0.17632

196 -> 203 0.30359

198 -> 200 0.17549

198 -> 205 0.12088

198 -> 208 0.10712

199 -> 200 -0.19081

199 -> 202 -0.16037

199 -> 205 0.36258

Excited State 3: Triplet-A 3.0312 eV 409.02 nm f=0.0000 <S**2>=2.000

189 -> 202 -0.13553

190 -> 207 0.12578

195 -> 200 0.26688

195 -> 201 0.55968

Excited State 4: Triplet-A 3.1786 eV 390.06 nm f=0.0000 <S**2>=2.000

185 -> 215 -0.11676

192 -> 204 0.15494

192 -> 213 0.10511

197 -> 204 0.60055

198 -> 210 0.22709

199 -> 210 -0.11811

Excited State 5: Triplet-A 3.2363 eV 383.11 nm f=0.0000 <S**2>=2.000

188 -> 206 0.11608

196 -> 203 -0.24026

198 -> 200 0.46797

198 -> 201 -0.15101

198 -> 204 0.11007

198 -> 205 -0.11861

199 -> 208 -0.21983

Excited State 6: Triplet-A 3.3029 eV 375.37 nm f=0.0000 <S**2>=2.000

198 -> 201 0.14439

198 -> 203 0.18991

199 -> 200 0.13192

199 -> 201 0.45385

199 -> 202 -0.10369

199 -> 203 0.40103

Excited State 7: Triplet-A 3.3459 eV 370.56 nm f=0.0000 <S**2>=2.000

192 -> 210 0.12420

198 -> 204 0.55996

199 -> 204 -0.34378

Excited State 8: Triplet-A 3.4279 eV 361.69 nm f=0.0000 <S**2>=2.000

198 -> 203 -0.17940

199 -> 200 0.19675

199 -> 201 0.44670

199 -> 202 0.11323

199 -> 203 -0.38366

Excited State 9: Triplet-A 3.5335 eV 350.88 nm f=0.0000 <S**2>=2.000

194 -> 200 0.14077

196 -> 200 -0.23362

196 -> 201 0.16805

196 -> 203 0.36856

198 -> 200 0.17979

198 -> 205 -0.15919

199 -> 202 0.18324

199 -> 203 0.10759

199 -> 205 -0.25720

199 -> 208 -0.12607

Excited State 10: Triplet-A 3.7085 eV 334.32 nm f=0.0000 <S**2>=2.000

191 -> 209 0.10547

193 -> 200 -0.16154

193 -> 205 -0.12408

194 -> 200 0.27029

194 -> 205 -0.15286

196 -> 203 -0.15403

198 -> 200 0.15736

198 -> 208 0.15829

199 -> 200 -0.14456

199 -> 202 -0.16061

199 -> 208 0.18045

199 -> 211 -0.19706

The computed vertical transition and their oscillator strengths (*f*) and configuration of PI-FLTPA.

Singlet

Excited State 1: Singlet-A 3.2195 eV 385.10 nm f=0.8062 <S**2>=0.000

199 -> 201 0.11623

200 -> 201 0.65550

200 -> 202 0.21167

Excited State 2: Singlet-A 3.3049 eV 375.16 nm f=0.4132 <S**2>=0.000

199 -> 201 -0.15757

199 -> 202 0.12809

200 -> 201 -0.18056

200 -> 202 0.64673

Excited State 3: Singlet-A 3.5673 eV 347.56 nm f=0.0253 <S**2>=0.000

199 -> 201 0.66213

199 -> 202 -0.10061

200 -> 201 -0.17034

200 -> 202 0.13318

Excited State 4: Singlet-A 3.6550 eV 339.22 nm f=0.0509 <S**2>=0.000

198 -> 205 0.10833

199 -> 201 0.12036

199 -> 202 0.61513

199 -> 204 -0.13579

200 -> 203 0.10604

200 -> 204 -0.17403

Excited State 5: Singlet-A 3.7237 eV 332.96 nm f=0.0129 <S**2>=0.000

199 -> 202 -0.18784

199 -> 203 0.30293

200 -> 203 0.58025

Excited State 6: Singlet-A 3.7823 eV 327.81 nm f=0.0606 <S**2>=0.000

198 -> 205 -0.10594

199 -> 202 0.21576

199 -> 204 0.31743

200 -> 203 0.18345

200 -> 204 0.52469

Excited State 7: Singlet-A 3.8313 eV 323.61 nm f=0.0113 <S**2>=0.000

199 -> 206 -0.21287

200 -> 206 0.66074

Excited State 8: Singlet-A 3.9811 eV 311.43 nm f=0.0074 <S**2>=0.000

198 -> 201 -0.16840

198 -> 202 -0.21032

198 -> 204 0.14050

199 -> 205 0.22111

200 -> 204 -0.18329

200 -> 205 0.54424

Excited State 9: Singlet-A 4.0312 eV 307.56 nm f=0.1895 <S**2>=0.000

199 -> 207 -0.19129

200 -> 207 0.67084

Excited State 10: Singlet-A 4.0594 eV 305.42 nm f=0.0021 <S**2>=0.000

198 -> 201 0.17320

199 -> 203 0.56961

200 -> 203 -0.32484

200 -> 205 0.10451

Triplet

Excited State 1: 3.008-A 0.2686 eV 4615.73 nm f=0.0336 <S**2>=2.012

201A -> 203A 0.62567

201A -> 204A -0.19116

201A -> 208A -0.24679

201A -> 214A -0.10162

197B -> 200B -0.13768

198B -> 200B 0.10172

199B -> 200B 0.80317

201A <- 203A 0.29661

201A <- 208A -0.16284

199B <- 200B 0.24101

Excited State 2: 3.009-A 0.4641 eV 2671.37 nm f=0.0067 <S**2>=2.013

201A -> 202A 0.99120

Excited State 3: 3.008-A 0.7648 eV 1621.23 nm f=0.0043 <S**2>=2.012

201A -> 203A 0.11703

201A -> 204A 0.97174

201A -> 208A -0.10977

199B -> 200B 0.11410

Excited State 4: 3.010-A 0.8617 eV 1438.89 nm f=0.1805 <S**2>=2.014

201A -> 203A 0.66112

201A -> 205A -0.26074

201A -> 208A 0.41231

197B -> 200B -0.28332

198B -> 200B 0.26208

199B -> 200B -0.41754

199B <- 200B 0.10678

Excited State 5: 3.010-A 0.9659 eV 1283.64 nm f=0.0156 <S**2>=2.015

201A -> 205A 0.92636

201A -> 208A 0.18553

201A -> 210A -0.11220

197B -> 200B -0.10606

198B -> 200B 0.18087

199B -> 200B -0.11397

Excited State 6: 3.010-A 1.0297 eV 1204.12 nm f=0.0004 <S**2>=2.015

201A -> 205A 0.10001

201A -> 206A -0.40188

201A -> 207A 0.82040

201A -> 211A 0.35299

195B -> 200B -0.11485

Excited State 7: 3.014-A 1.1631 eV 1065.95 nm f=0.0040 <S**2>=2.020

201A -> 206A 0.82698

201A -> 207A 0.27601

201A -> 211A 0.12148

201A -> 212A -0.10179

201A -> 213A 0.29401

195B -> 200B -0.30524

198B -> 200B -0.12852

Excited State 8: 3.017-A 1.1834 eV 1047.68 nm f=0.0168 <S**2>=2.026

201A -> 203A -0.11417

201A -> 205A -0.15000

201A -> 206A 0.33477

201A -> 207A 0.32522

201A -> 211A -0.11919

201A -> 212A 0.13735

201A -> 213A -0.33396

195B -> 200B 0.41894

197B -> 200B 0.28028

198B -> 200B 0.57038

Excited State 9: 3.018-A 1.2039 eV 1029.86 nm f=0.0258 <S**2>=2.028

201A -> 203A -0.11458

201A -> 206A -0.13316

201A -> 207A -0.23982

201A -> 211A 0.15774

201A -> 212A -0.10351

201A -> 213A 0.41627

194B -> 200B 0.15881

195B -> 200B -0.39810

197B -> 200B 0.27310

198B -> 200B 0.64629

Excited State 10: 3.012-A 1.3893 eV 892.40 nm f=0.1008 <S**2>=2.018

201A -> 203A 0.38386

201A -> 208A 0.11482

201A -> 212A -0.40706

201A -> 213A -0.11897

201A -> 217A -0.13193

197B -> 200B 0.75267

198B -> 200B -0.23111

199B -> 200B -0.12237

201A <- 203A -0.10789

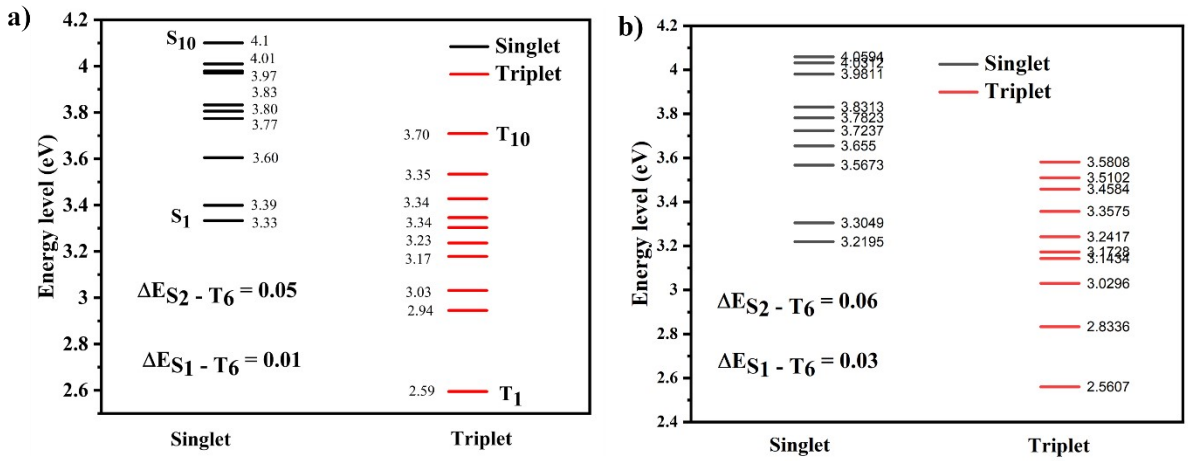

Figure S6. The energy difference between S_2-T_5 and S_2-T_4 for the fluorophore PI-FLCBZ

SI6. AIEE study of the fluorophore PI-FLCBZ.

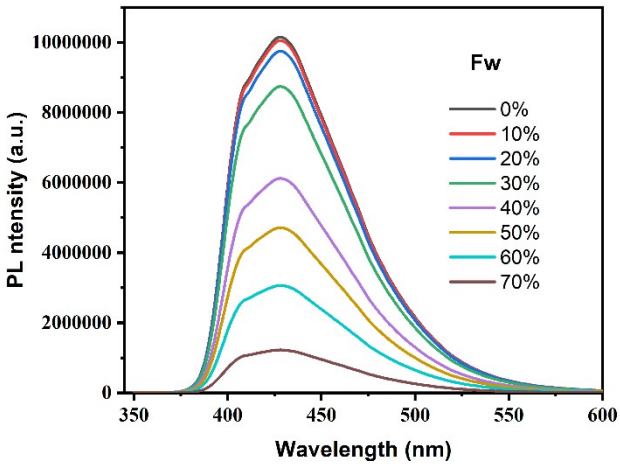

Figure S7. AIEE study of the fluorophore PI-FLCBZ

SI7. PLQY of the fluorophores.

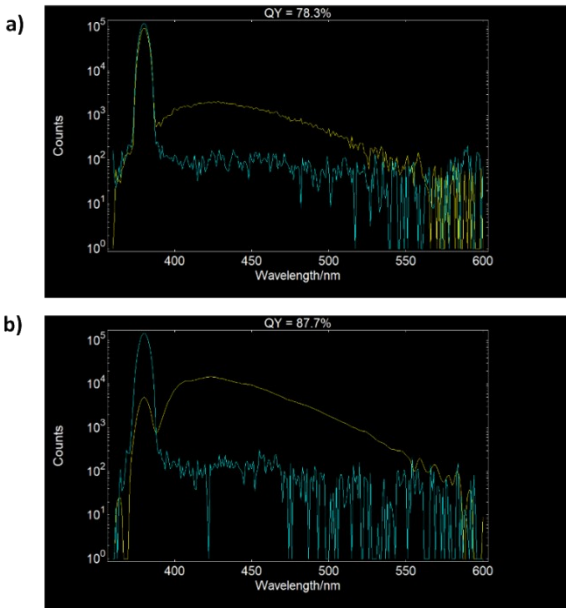

Figure S8. PLQY a) PI-FLCBZ b) PI-FLTPA

SI8. SXRD data of PI-FLTPA

Table S1. Crystallographic data of PI-FLCBZ.

Identification code	**mo_VS_NS_BB_2_0m**
Empirical formula	$C_{56}H_{41}N_3$
Formula weight	755.92
CCDC number	2493865
Temperature/K	298
Crystal system	monoclinic
Space group	C2/c
a/Å	19.8894(12)
b/Å	12.8546(9)
c/Å	32.966(2)
α/°	90
β/°	105.195(2)
γ/°	90
Volume/Å^3	8133.9(9)
Z	8
ρ_{calc}g/cm^3	1.235

μ/mm^{-1}	0.072
F(000)	3184.0
Crystal size/mm^3	0.29 × 0.25 × 0.19
Radiation	MoKα (λ = 0.71073)