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Highly Emissive Excited– State Intramolecular Proton Transfer (ESIPT) Inspired 2–(2′–Hydroxy) Benzothiazole –Fluorene Motifs: Spectroscopic and Photophysical Properties Investigation

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Tuning or switching of the solid state luminescence of organic materials is an attractive target for both basic research and practical applications. In the present study, solid state emissive compounds with very high quantum efficiencies (Φ_f up to 68%) were achieved by chemical alteration of excited state intramolecular proton transfer (ESIPT) 2–2′–hydroxy benzothiazole (HBT) unit. Five ESIPT inspired compounds based on fluorene were synthesized via Suzuki coupling reaction. Their photophysical properties were studied by means of steady state absorption, emission spectra and time resolved emission method in solid as well as in solution of different polarities. The fluorophores showed absorption in UV region and emission in visible region with large Stokes shift (~ 232 nm). Efficient yellow emissive compounds showed very high quantum yields ($\Phi_f = 55–68\%$) in solid state, which are the highest quantum yields in solid state to the best of our knowledge, for fluorene based ESIPT molecules. The fluorescence lifetime in solid state is between 3.48–5.21 ns, while it is 5–10 fold less in chloroform (0.52–0.75 ns) solution. The optical properties of these compounds are sensitive towards the polarity of the medium. The structural properties, such as X–ray single crystal analyses, DSC and TGA were studied, and the lack of stacking and/or hydrogen bonding interactions around HBT motifs reveals enough room for ESIPT in the series of molecules even in their solid state. The DFT computations were performed to support experimental results and the calculations are well in line with the experimental results. These suggest high quantum efficiency ascribed to the large orbital energy difference between HOMOs and LUMOs of *enol* and *keto* forms transformed via ESIPT, and hence, singlet energy localization onto the *keto* form. The intra–molecular charge transfer nature between fluorene and HBT units plays a key role for the localization of energy on HBT motifs in their excited states.

Introduction

Organic solid–state luminescent materials have been attracting considerable interest since past two decades in various fields because of their potential use in high–tech applications^{1–7}. Most of the solid–state luminescent materials reported so far are used as organic light emitting diodes^{8–11}, organic solid state lasers^{12,13}, organic field–effect transistor¹⁴, nonlinear optics^{15,16}, organic photovoltaics (OPV)¹⁷, and

fluorescent sensors^{18,19}. These materials are generally designed from the fluorophores that exhibit excellent fluorescence properties in solution^{20,21}. It is well known that in solid state, intermolecular interaction enhances nonradioactive deactivation which quenches the luminescence properties of the materials²². This phenomenon is called aggregation–caused quenching (ACQ)^{22,23}. Modulating the π –conjugated framework to a twisted packing is an ideal approach to avoid ACQ since molecules with twisted solid–state conformations restrict face–to–face arrangement and avoid strong intermolecular interaction in solid phase^{22,23}. Recently a new class of luminescent materials has been reported^{20,24–28}. These are non–fluorescent in solution or as an individual molecule but are highly emissive in the solid state after formation of aggregates^{20,24–28}. This novel class of compounds is referred to as aggregation–induced emission/aggregation–induced emission enhancement (AIE/AIEE)^{20,24–28}. AIE/AIEE fluorophores are however limited and still remain a challenge for new fluorophore development because unclear mechanism allows aggregation²⁹. Organic compounds which are highly emissive in rigid media but non emissive in solution (or weakly emissive) have been raising a lot of interest

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Electronic Supplementary Information (ESI) available: NMR spectra, steady state measurements, DSC, TGA and photoelectron yield spectroscopy data of compounds **6a–6e**. DFT calculation using B3LYP/6–31G**(d,p) of compound **6a** (optimized structure of *cis*–enol form: S_0 and S_1 state), experimental energy levels of HOMO and LUMO of compounds **6a–6d** and X–ray crystallographic data of **6b** CCDC 1410376. See DOI: 10.1039/x0xx00000x

optoelectronic devices^{20,30}. To obtain highly emissive solid state fluorophores, it is essential to suppress radiationless deactivation of the excited state of the compounds. Various strategies including RIR, RTICT, RCT, AIE /AIEE and ESIPT process used to obtained solid state emission by controlling non-radiative process^{20,22,23,25,31-41}.

Excited state intramolecular proton transfer (ESIPT) is a photochemical process that produces a tautomer with a different electronic structure from the original excited form^{5,42-44}. It is a four level process in which *enol* form (E) can be changed to *keto* form (K) after photo-excitation by transfer of a proton to the neighboring electronegative atoms through intramolecular hydrogen bonding⁴². On relaxation of excited state *keto* form to the ground state, the *enol* form is recovered by ground state proton transfer (GSIPT)⁴⁵. The pre-requisite for ESIPT is the presence of intramolecular hydrogen bonding between acidic proton (–OH and –NH₂) and basic moiety (=N– and –C=O) with suitable geometry⁴⁶. Large Stokes shift (~6000–10000 cm⁻¹)⁴², dual emission³⁴, ultrafast process⁴⁷ and spectral sensitivity to the surrounding medium⁴⁸ are the remarkable properties of the ESIPT fluorophores. Dual emission originating from both initial excited form and the proton-transfer tautomer or single emission with large Stokes shift covering the whole visible domain can result in the production of white light^{49,50}. White light emitters are used as chemical sensors^{43,51-53}, lightening materials⁵⁴, optoelectronic devices⁵⁵ and for fundamental photophysical studies⁵⁶⁻⁵⁸. Recently, solid state ESIPT chromophores have been reported by several groups for above maintained applications^{21,30,34,59,60}. Till date, commonly used and most studied ESIPT fluorophores are derivatives of 2-(2'-hydroxyphenyl) benzimidazole (HBI)⁶¹⁻⁶³, 2-(2'-hydroxyphenyl) benzoxazole (HBO)⁶⁴⁻⁶⁶ and 2-(2'-hydroxyphenyl) benzothiazole (HBT)^{46,67-69} due to chemical simplicity and efficient ESIPT properties.

Fluorene and its derivatives are among the most studied electroluminescent materials due to desirable electron transporting properties⁷⁰⁻⁷³. These materials are used in optoelectronic devices as well as in newer arenas of biotechnology⁷⁰⁻⁷⁴. The emission properties of fluorene and its derivatives are tunable by controlling the molecular packing through substitution at 9, 9 or 7, 7' -positions⁷¹. In present study fluorene has been chosen as luminescent electron donor motif and HBT unit as acceptor. HBT unit helps to achieve the solid state emission by reducing self-absorption due to large Stokes shift between absorption and keto-emission⁷⁵. Two HBT units are introduced at 7,7' -position of fluorene through single bonds. This can help in enhancing emission by restricting the intramolecular rotation around the single bonds between two aromatic rings^{21,22}. The purpose of two HBT units is to obtain appropriate molecular packing (*slip-stacking*) instead of face-face-stacking (*H*-packing) for enhancement of solid state emission²².

Experimental

Materials

2,7-Dibromo-9,9-dimethylfluorene, 2,7-dibromo-9,9-dihexylfluorene, 2,7-dibromo-9,9-dioctylfluorene, 9,9-didecylfluorene-2,7-diboronic acid, 5-bromosalicylaldehyde, 2-aminothiophenol, 1,2-benzenediamine, 1,3-propanediol, Pd(PPh₃)₄, K₂CO₃, *n*-BuLi and trimethylborate were purchased from Tokyo Chemical Industries (TCI), Japan. All the solvents used for the synthesis were from Wako Pure Chemical Industries Ltd., Japan. All the reagents were used without further purification.

Characterizations

All the synthesized compounds were purified by column chromatography on silica gel. Compounds **6a-6d** and **6e** were purified by column chromatography followed by recycle preparative HPLC system (Japan Analytical Industry Co., Ltd.) LC-9210NEXT with JaiGel-1H/-2H) using chloroform as eluent. The compounds **6a-6e** were characterized by ¹H-NMR, ¹³C-NMR, MALDI-TOF (Matrix-assisted laser desorption ionization time-of-flight) and elemental analysis techniques. The ¹H-NMR spectra were recorded on a JEOL 400SS (400 MHz) spectrometer and ¹³C-NMR spectra on a JEOL 400SS (100 MHz) spectrometer, and all spectra were recorded in a CDCl₃ and DMSO-d₆ solvent using TMS as an internal reference standard at room temperature (20 °C). Chemical shifts of NMR spectra are given in parts per million (ppm). Low and high resolution matrix-assisted-laser-desorption/ionization (MALDI) mass spectra (MS) were obtained on Bruker Daltonics FLEX-PC using α-phenylcinnamic acid as a matrix. All steady state absorption spectra were recorded on a JASCO V-570 UV-Vis spectrophotometer. Fluorescence spectra were measured on fluorescence spectrophotometer (F-2700, Hitachi High-Technologies). Relative quantum yield measurements were performed using FP-6500 spectrofluorometer (JASCO). Absolute quantum yields in solid state were measured on FP-6500 spectrofluorometer with an ISF-513 fluorescence integrate sphere unit (JASCO). Photoelectron yield spectroscopy (PYS) experiments were performed on RIKEN Keiki Co., Ltd., model AC-3. The single crystals were obtained by slow evaporation of a mixed solution (CH₂Cl₂: Hexane) for **6b** and data collections were performed on a Rigaku R-AXIS-RAPID diffractometer with Cu-Kα radiation (λ = 1.54187 Å) at -150 °C. Thermogravimetric analysis (TGA) was performed with an EXSTAR TG/DTA-7200 system (SII Nano Technology Inc.) using a Pt pan at the ramp rate of 10 °C/min under N₂ flow. DSC measurements were performed on a PerkinElmer model DSC 8000 differential scanning calorimeter. Powder-XRD measurements were performed on MiniFlex 600, Rigaku make in the range of 2θ = 2–30°. All theoretical calculations were performed using Gaussian 09 package.

Synthesis Details**9,9-Dimethylfluorene-2,7-bis(trimethylene boronates) 2a**

n-BuLi (1.6 M in hexane, 14.49 mL, 22 mmol) was added dropwise into a solution of 2,7-dibromo-9,9-dimethylfluorene **1a** (2 g, 5.71 mmol) in anhydrous THF (40 mL) at -78°C . The reaction mixture was stirred for 3 h prior to the addition of trimethyl borate (6.31 mL, 57 mmol) in one portion. The mixture was stirred at -78°C for 1h after addition of tri-methyl borate and warmed to room temperature and stirred for 20 h. The reaction mass was poured into crushed ice containing 2M HCl (100 mL) with constant stirring. The reaction mixture was extracted with diethyl ether (100 mL \times 2) and the combined extracts were evaporated to give yellow colored solid. The obtained solid was refluxed with 1,3-propanediol (0.63 mL, 8.71 mmol) in 60 mL toluene for 12 h. The reaction mass was concentrated under vacuum and the obtained liquid was purified by column chromatography (with silica gel and *n*-hexane-ethyl acetate as the eluent) to obtain a yellow liquid **2c** (Yield after column chromatography: 1.8 g, 89%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 7.83–7.76 (m, 2H), 7.74–7.70 (m, 4H), 4.20–4.17 (t, 8H), 2.10–2.04 (m, 4H), 1.48 (s, 6H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 153.4, 141.6, 132.6, 127.7, 127.5, 119.6, 62.1, 46.7, 27.5, 27.1.

MALDI-TOF (m/z): calculated: 362.03, found: 362.36.

9,9-Dihexylfluorene-2,7-bis(trimethylene boronates) 2b

n-BuLi (1.6 M in hexane, 7.5 mL, 12.0 mmol) was added dropwise into a solution of 2,7-dibromo-9,9-dihexylfluorene **1b** (2 g, 4.0 mmol) in anhydrous THF (40 mL) at -78°C . The reaction was stirred for 3 h prior to the addition of methyl borate (4.5 mL, 40 mmol) in one portion. The mixture was stirred at -78°C for 1h after addition of tri-methyl borate and warmed to room temperature and stirred for 20 h. The reaction mass was poured into crushed ice containing 2M HCl (100 mL) with constant stirring. The reaction mixture was extracted with diethyl ether (100 mL \times 2) and the combined extracts were evaporated to give yellow colored solid. The obtained solid was refluxed with 1,3-propanediol (0.76 mL, 10 mmol) in 60 mL toluene for 12 h. The reaction mass was concentrated under vacuum and the obtained solid was purified by column chromatography (with silica gel and *n*-hexane-ethyl acetate as the eluent) to obtain a yellow colored solid **2b** (Yield after column chromatography: 1.4 g, 69%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 7.73–7.66 (m, 6H), 4.20–4.18 (t, 8H), 2.09–2.06 (m, 4H), 1.99–1.95 (m, 4H), 1.15–0.97 (m, 12H), 0.74–0.70 (m, 6H), 0.70–0.50 (m, 4H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 150.3, 143.6, 132.5, 127.9, 127.6, 119.2, 62.1, 54.9, 40.6, 40.4, 31.6, 29.8, 27.5, 23.7, 22.7, 14.1.

MALDI-TOF (m/z): calculated: 502.34, found: 503.12.

9,9-Dioctylfluorene-2,7-bis(trimethylene boronates) 2c

n-BuLi (1.6 M in hexane, 6.7 mL, 10.8 mmol) was added dropwise into a solution of 2,7-dibromo-9,9-octylfluorene **1c** (2 g, 3.6 mmol) in anhydrous THF (40 mL) at -78°C . The reaction was stirred for 3 h prior to the addition of methyl borate (4.0 mL, 36 mmol) in one portion. The mixture was

stirred at -78°C for 1h after addition of tri-methyl borate and warmed to room temperature and stirred for 20 h. The reaction mass was poured into crushed ice containing 2M HCl (100 mL) with constant stirring. The reaction mixture was extracted with diethyl ether (100 mL \times 2) and the combined extracts were evaporated to give yellow colored solid. The obtained solid was refluxed with 1,3-propanediol (0.63 mL, 8.71 mmol) in 60 mL toluene for 12 h. The reaction mass was concentrated under vacuum and the obtained liquid was purified by column chromatography (with silica gel and *n*-hexane-ethyl acetate as the eluent) to obtain a yellow liquid **2c** (Yield after column chromatography: 1.8 g, 89%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 7.74–7.66 (m, 6H), 4.20–4.17 (t, 8H), 2.08–2.06 (m, 4H), 1.98–1.94 (m, 4H), 1.27–0.98 (m, 20H), 0.84–0.52 (m, 10H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 150.3, 143.6, 132.3, 127.9, 119.2, 62.1, 54.9, 40.4, 31.8, 30.1, 29.4, 29.3, 22.6, 14.1.

MALDI-TOF (m/z): calculated: 558.41, found: 558.76.

9,9-Didecylfluorene-2,7-diboronic acid 2d

9,9-Didecylfluorene-2,7-diboronic acid was purchased from Tokyo Chemical Industries (TCI), Japan and used for next step without purification.

9,9-Dimethylfluorene-2,7-bis(5-salicylaldehyde) 4a

9,9-Dimethylfluorene-2,7-bis-trimethylene boronate **2a** (2.0g, 5.5 mmol), 5-bromosalicylaldehyde **3** (3.36 g, 16.7 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.016 g, 0.013 mmol) were added to a mixture of 50 mL degassed toluene (three times) and aqueous (degassed water 10 mL) 2 M K_2CO_3 under nitrogen atmosphere. The mixture was stirred at 110°C for 24 h. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with dichloromethane. The combined organic layers were washed with water and dried over sodium sulfate. The organic layer was concentrated under vacuum, to obtain a white colored solid. The crude product was purified by column chromatography (with silica gel and dichloromethane as the eluent) (Yield after column chromatography: 2.1 g, 88%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 11.02 (s, 2H), 10.02 (s, 2H), 7.83–7.82 (m, 6H), 7.60–7.53 (m, 4H), 7.11–7.09 (d, 2H), 1.59 (s, 6H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 196.8, 161.0, 154.8, 138.7, 138.1, 135.9, 133.7, 131.9, 125.9, 120.9, 120.8, 120.7, 118.2, 47.2, 27.4.

MALDI-TOF (m/z): calculated: 434.15, found: 434.37.

9,9-Dihexylfluorene-2,7-bis(5-salicylaldehyde) 4b

9,9-Dihexylfluorene-2,7-bis-trimethylene boronate **2b** (1.0 g, 1.9 mmol), 5-bromosalicylaldehyde **3** (0.79 g, 3.9 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.020 g, 0.017 mmol) were added to a mixture of 50 mL degassed toluene (three times) and aqueous (degassed water 10 mL) 2 M K_2CO_3 under nitrogen atmosphere. The mixture was stirred at 110°C for 24 h. After completion of reaction (monitored by TLC), the mixture was cooled to room temperature, and poured into deionized water (200 mL). The

aqueous layer was extracted thrice with dichloromethane. The combined organic layers were washed with water and dried over sodium sulfate. A white colored solid was obtained after the concentration of organic layers. The crude product was purified by column chromatography (with silica gel and dichloromethane as the eluent) (Yield after column chromatography: 1.0 g, 88%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 11.02 (s, 2H), 10.02 (s, 2H), 7.85–7.76 (m, 6H), 7.55–7.49 (m, 4H), 7.12–7.10 (d, 2 H), 2.06–2.02 (m, 4H), 1.15–1.05 (m, 12H), 0.74–0.72 (m, 10H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 196.8, 161.0, 151.9, 140.0, 138.4, 135.9, 133.8, 131.9, 125.6, 120.9, 120.8, 120.3, 118.2, 55.4, 40.5, 31.5, 29.7, 23.8, 22.6, 14.2, 14.1.

MALDI-TOF (m/z): calculated: 574.31, found: 574.65.

9,9-Dioctylfluorene-2,7-bis(5-salicylaldehyde) 4c

9,9-Dioctylfluorene-2,7-bis-trimethylene boronate **2c** (3.0g, 5.3 mmol), 5-bromosalicylaldehyde **3** (2.77 g, 13.7 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.026 g, 0.022 mmol) were added to a mixture of 50 mL degassed toluene (three times) and aqueous (degassed water 10 mL) 2 M K_2CO_3 (10 mL) under nitrogen atmosphere. The mixture was stirred at 110 °C for 24 h. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with dichloromethane. The combined organic layers were washed with water and dried over sodium sulfate. A white colored solid was obtained after the concentration of organic layers. The crude product was purified by column chromatography (with silica gel and ethylacetate and hexane as eluent) (Yield after column chromatography: 3.0 g, 89%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 11.03 (s, 2H), 10.03 (s, 2H), 7.84–7.78 (m, 6H), 7.56–7.51 (m, 4H), 7.13–7.11 (d, 2 H), 2.07–2.03 (m, 4H), 1.21–1.07 (m, 20H), 0.80–0.76 (m, 10H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 196.8, 161.0, 151.9, 140.0, 138.4, 135.9, 133.8, 131.9, 125.6, 120.9, 120.8, 120.3, 118.2, 55.4, 40.4, 31.8, 30.0, 29.2, 23.8, 22.6, 14.1.

MALDI-TOF (m/z): calculated: 630.37, found: 630.86.

9,9-Didecylfluorene-2,7-bis(5-salicylaldehyde) 4d

9,9-Didecylfluorene-2,7-diboronic acid **2d** (3.0 g, 5.0 mmol), 5-bromosalicylaldehyde **3** (2.24 g, 11.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.015 g, 0.012 mmol) were added to a mixture of 50 mL degassed toluene (three times) and aqueous (degassed water 10 mL) 2 M K_2CO_3 (12 mL) under nitrogen atmosphere. The mixture was stirred at 110 °C for 24 h. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature, and poured into deionized water (200 mL). The aqueous layer was extracted thrice with dichloromethane. A white colored solid was obtained after the concentration of organic layers. The crude product was purified by column chromatography (with silica gel and ethylacetate and hexane as eluent 5:95) (Yield after column chromatography: 3.54 g, 94%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 11.02 (s, 2H), 10.02 (s, 2H), 7.86–7.76 (m, 6H), 7.55–7.50 (m, 4H), 7.12–7.10 (d, 2 H), 2.06–2.02 (m, 4H), 1.30–1.05 (m, 36H), 0.85–0.81 (m, 10H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 196.8, 161.0, 151.9, 140.0, 138.3, 135.9, 133.8, 131.9, 125.6, 120.9, 120.8, 120.3, 118.2, 55.4, 40.5, 29.8, 29.7, 29.6, 29.3, 14.1.

MALDI-TOF (m/z): calculated: 743.07, found: 744.21.

4,4'-(9,9-Dimethyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) 6a

A mixture of 9,9-dimethylfluorene-2,7-bis(5-salicylaldehyde) **4a** (2.0 g, 4.6 mmol), aminothiophenol **5** (1.38 g, 11.0 mmol), aq. H_2O_2 (3.1 g, 92.0 mmol) and conc. HCl (2.52 g, 69.0 mmol) was stirred in ethanol (50 mL) for 24 h at room temperature (22 °C). After completion of reaction, (monitored by TLC) the brown colored reaction mixture was filtered under vacuum, washed with ethanol and dried. The crude product was purified by column chromatography (ethyl acetate: hexane as eluent). The obtained pure yellow colored solid was further purified by HPLC to obtain **6a** (chloroform as mobile phase), abbreviated as **MF-ESIPT**. (Yield after column chromatography: 1.2 g, 59%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 12.60 (s, 2H), 8.03–8.01 (d, 2H), 7.95–7.92 (m, 4H), 7.85–7.83 (d, 2H), 7.72–7.69 (dd, 2H), 7.65(d, 2H), 7.61–7.59 (dd, 2H), 7.53–7.51 (m, 2H), 7.45–7.43 (m, 2H), 7.22–7.21 (d, 2H) 1.63 (s, 6H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 169.4, 157.5, 154.7, 151.9, 139.4, 137.9, 133.4, 132.7, 131.9, 126.8, 126.0, 125.7, 122.3, 121.6, 121.1, 120.5, 118.4, 117.0, 47.2, 27.4.

MALDI-TOF (m/z): calculated: 644.80, found: 645.65.

Elemental Analysis; Mol. Formula: $\text{C}_{41}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$ (Actual: C: 76.37, H: 4.38, S:9.95, N:4.34; Found: C: 76.07, H:4.56, S:9.85, N:4.34)

4,4'-(9,9-Dihexyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) 6b

A mixture of 9,9-dihexylfluorene-2,7-bis(5-salicylaldehyde) **4b** (0.75 g, 1.3 mmol), aminothiophenol **5** (0.65 g, 5.2 mmol), aq. H_2O_2 (0.28 g, 7.8 mmol) and conc. HCl (0.53 g, 1.5 mmol) was stirred in ethanol (20 mL) for 24 h at room temperature (22 °C). After completion of reaction, (monitored by TLC) the yellow colored reaction mixture was filtered under vacuum, washed with ethanol and dried. The crude product was purified by column chromatography (ethyl acetate: hexane as eluent). The obtained pure pale yellow colored solid was further purified by HPLC to obtain **6b** (chloroform as mobile phase) abbreviated as **HF-ESIPT**. (Yield after column chromatography: 0.4 g, 45%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ ppm 12.60 (s, 2H), 8.03–8.02 (d, 2H), 7.95–7.92 (m, 4H), 7.81–7.80 (d, 2H), 7.72–7.69 (dd, 2H), 7.61–7.58 (dd, 2H), 7.55–7.53(m, 4H), 7.45–7.43 (m 2H), 7.23–7.21 (d, 2H), 2.09–2.05 (m, 4H), 1.20–1.05 (m, 12 H), 0.79–0.77 (m, 10H).

$^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ ppm 169.4, 157.4, 151.9, 139.9, 139.0, 133.5, 132.7, 131.8, 126.8, 125.7, 122.3, 121.6, 121.1, 120.2, 118.4, 117.0, 55.4, 40.4, 31.5, 29.8, 23.9, 22.7, 14.1.

MALDI-TOF (m/z): calculated: 785.07, found: 786.00.

Elemental Analysis; Mol. Formula: $\text{C}_{51}\text{H}_{48}\text{N}_2\text{O}_2\text{S}_2$ (Actual: C: 78.02, H:6.16, S:8.17, N:3.57; Found: C:77.61, H:6.11, S:8.15, N:3.51)

4,4'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) 6c

A mixture of 9,9-dioctylfluorene-2,7-bis(5-salicylaldehyde) **4c** (2.0 g, 3.1 mmol), aminothiophenol **5** (0.95 g, 7.6 mmol), aq. H₂O₂ (1.7 g, 50.0 mmol) and conc. HCl (1.15 g, 31.0 mmol) was stirred in ethanol (30 mL) for 24 h at room temperature (22 °C). After completion of reaction, (monitored by TLC) the brown-yellow colored reaction mixture was filtered under vacuum, washed with ethanol and dried. The crude product was purified by column chromatography (ethyl acetate: hexane as eluent). The obtained pure pale yellow colored solid was further purified by HPLC to obtain **6c** (chloroform as mobile phase) abbreviated as **OF-ESIPT**. (Yield after column chromatography: 1.0 g, 37%).

¹H-NMR (400 MHz, CDCl₃): δ ppm 12.60 (s, 2H), 8.03–8.02 (d, 2H), 7.95–7.92 (m, 4H), 7.81–7.80 (d, 2H), 7.71–7.69 (dd, 2H), 7.61–7.53 (m, 6H), 7.45–7.41 (m, 2H), 7.23–7.21 (d, 2H), 2.08–2.05 (m, 4H), 1.20–1.05 (m, 20 H), 0.77–0.76 (m, 10H).

¹³C-NMR (100 MHz, CDCl₃): δ ppm 169.4, 157.4, 151.9, 139.9, 139.0, 133.5, 131.8, 126.9, 126.8, 125.7, 122.3, 121.6, 121.1, 120.2, 118.4, 117.0, 55.4, 40.4, 31.8, 30.1, 29.3, 29.2, 22.7, 14.1.

MALDI-TOF (*m/z*): calculated: 841.18, found: 842.08.

Elemental Analysis; Mol. Formula: C₅₅H₅₆N₂O₂S₂; Elemental Analysis (Actual: C: 78.53, H:6.71, S:7.62, N:3.33; Found: C: 78.46, H:6.74, S:7.62, N:3.39)

4,4'-(9,9-Didecyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenol) 6d

A mixture of 9,9-didecylfluorene-2,7-bis(5-salicylaldehyde) **4d** (2.0 g, 2.6 mmol), aminothiophenol **5** (0.75 g, 6.0 mmol), aq. H₂O₂ (1.3 g, 32.5 mmol) and conc. HCl (0.91 g, 24.9 mmol) was stirred in ethanol (40 mL) for 24 h at room temperature (22 °C). After completion of reaction, (monitored by TLC) the brown colored reaction mixture was filtered under vacuum, washed with ethanol and dried. The crude product was purified by column chromatography (ethyl acetate: hexane as eluent). The obtained pure pale yellow colored solid was further purified by HPLC to obtain **6d** (chloroform as mobile phase) abbreviated as **DF-ESIPT**. (Yield after column chromatography: 0.8 g, 31%).

¹H-NMR (400 MHz, CDCl₃): δ ppm 12.60 (s, 2H), 8.03–8.02 (d, 2H), 7.95–7.92 (m, 4H), 7.81–7.79 (d, 2H), 7.69 (dd, 2H), 7.61–7.51 (m, 6H), 7.43–7.40 (m, 2H), 7.21–7.23 (d, 2H), 2.05–2.09 (m, 4H), 1.23–1.09 (m, 36 H), 0.80–0.73 (m, 10H).

¹³C-NMR (100 MHz, CDCl₃): δ ppm 169.4, 157.4, 151.9, 139.9, 139.0, 133.4, 131.8, 126.9, 126.8, 125.7, 122.3, 121.6, 121.1, 120.2, 118.4, 117.0, 55.4, 40.4, 31.9, 31.0, 30.1, 29.7, 29.4, 29.3, 23.9, 22.7, 14.1.

MALDI-TOF (*m/z*): calculated: 953.39, found: 954.22.

Elemental Analysis; Mol. Formula: C₆₃H₇₂N₂O₂S₂; (Actual: C: 79.39, H: 7.61, S: 6.73, N: 2.94; Found: C: 79.08, H: 7.59, S: 6.53, N: 2.99)

4,4'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]imidazol-2-yl)phenol) 6e

A mixture of 9,9-dioctylfluorene-2,7-bis(5-salicylaldehyde) **4c** (0.1 g, 0.15 mmol), 1,2-benzenediamine **5b** (0.048 g, 0.44 mmol), aq. H₂O₂ (0.053 g, 1.55 mmol) and conc. HCl (0.030 g, 0.82 mmol) were stirred in ethanol (10 mL) for 24 h at room temperature (22 °C). After completion of reaction, (monitored by TLC) the brown colored reaction mixture was filtered under vacuum, washed with ethanol and dried. The crude product was purified by column chromatography (ethyl acetate: hexane as eluent). The obtained pure pale yellow colored solid was further purified by HPLC to afford **6e** (chloroform as mobile phase). (Yield after column chromatography: 0.050 g, 39%).

¹H-NMR (400 MHz, DMSO-d₆): δ ppm 13.37 (s, 2H), 13.29 (s, 2H), 8.52 (s, 2H), 7.98–7.96 (d, 2H), 7.84–7.68 (m, 10H), 7.34–7.29 (m, 4H), 7.18–7.16 (d, 2H), 2.08–2.05 (m, 4H), 1.27–1.05 (m, 20 H), 0.68–0.64 (m, 10H).

¹³C-NMR (100 MHz, CDCl₃): δ ppm 158.0, 152.2, 151.8, 139.8, 138.6, 133.6, 131.9, 130.6, 124.6, 123.0, 120.8, 118.2, 113.4, 112.1, 55.5, 31.6, 29.6, 28.9, 23.8, 21.5, 21.4, 14.3.

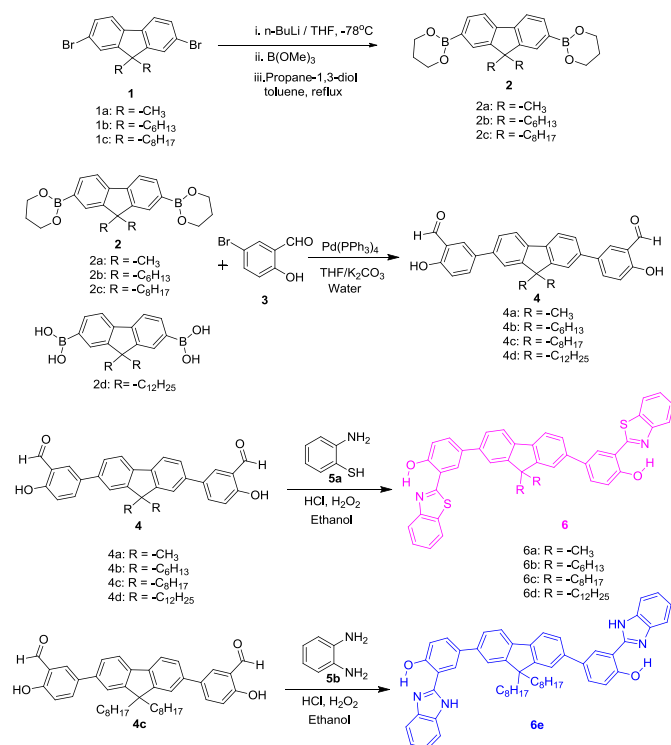
MALDI-TOF (*m/z*): calculated: 806.46, found: 807.94.

Result and Discussion

Design and Synthesis of Compounds

Scheme 1 illustrates the chemical structures and synthetic route of HBT **6a–6d** and HBI **6e** derivatives. Five ESIPT fluorophores were designed according to the following procedure. HBT and HBI units were introduced into 7,7'-positions of fluorene unit via Suzuki coupling and cyclisation reactions.

9,9-Dialkylfluorene-2,7-bis(trimethylene boronates) **2a–2c** were synthesized from 2,7-dibromo-9,9-dialkylfluorene by *n*-BuLi reaction at –78 °C followed by substitution reaction of trimethylborate and 1,3-propanediol. Boronate esters **2a–2c** and boronic acid **2d** were coupled with 5-bromosalicylaldehyde **3** via Suzuki coupling using Pd(PPh₃)₄ catalyst under basic medium to obtain 9,9-dialkylfluorene-2,7-bis(5-salicylaldehyde) **4a–4d**. The condensation followed by cyclisation of 9,9-dialkylfluorene-2,7-bis(5-salicylaldehyde) **4a–4d** with *o*-aminothiophenol **5a** or 1,2-benzenediamine **5b** in acidic catalyzed reaction obtained **6a–6d** and **6e** with good yields. All compounds were found to have good solubility in organic solvents; as a result they could be well purified by chromatography techniques for spectral and optical studies (NMR spectra of all compounds are included in the supplementary information).



Scheme 1: Synthesis of 4,4'-(9,9-dialkyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]thiazol-2-yl)phenyl) **6a–6d** and 4,4'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(2-(benzo[d]imidazole-2-yl)phenyl) **6e**.

Optical Properties

Steady State measurements

A summary of the steady state absorption and emission of the compounds **6a–6e** is provided in **Table 1**. Compounds **6a–6d** have the same core and differ only by the length of the alkyl chain attached to 9,9-position of the fluorene unit. Initially absorption and emission properties were studied for **HBT**, **6c** and **6e** (**Scheme S1**) to understand the effect of conjugation as well as strength of electron acceptor group on optical properties. **HBT**, **6c** and **6e** showed similar absorption pattern (λ_{abs} around 335 nm in chloroform ($\pi-\pi^*$ transition)) (**Fig. 1**, **Table 1**). However, the emission pattern is totally different. Compound **6c** showed emission at 552 nm which is 62 and 27 nm red shifted emission as compared to benzimidazole **6e** ($\lambda_{\text{em}} = 490$ nm, **Fig. 1**) and **HBT** ($\lambda_{\text{em}} = 525$ nm) respectively in chloroform. The red shift is explained in terms of more delocalization of the π -electron in **HBT** derivative **6c**, which has more aromatic character in comparison to **HBI** derivative⁷⁶. In ESIPT process, fluorescence properties depend on intra-molecular hydrogen bonding, which occurs at the excited state. In hydroxy-azoles family, the intra-molecular hydrogen bond (OH---N) in **HBI** was reported to be weak in comparison to **HBT**⁷⁷. More aromatic character and strong intra-molecular hydrogen bonding enhances the fluorescence properties of the ESIPT fluorophores^{21,22,29}. The emission wavelength of **HBT** is almost identical to its derivatives **6a–6d** in chloroform. However it is reported that **HBT** is weakly or non-emissive in crystalline state due to face-face stacking⁷⁸. In present study, synthesized compounds **6a–**

6d are highly emissive in crystalline state. This can be assigned for RIR effect and molecular packing of fluorene and HBT unit. Considering the solid state emission with high quantum efficiencies, only HBT based ESIPT fluorophores **6a–6d** were explored for deeper study. The steady state absorption spectra of compounds **6a–6d** in various solvents and on solid film at room temperature are shown in **Fig. 2** and **Fig. S1**.

The absorption spectra of all these compounds in various solvents and on solid film were at 325–344 nm, which can be assigned to the $\pi-\pi^*$ transition of the fluorene–benzothiazole conjugated backbone of these molecules. In non-polar (toluene and chloroform), polar-protic (methanol) and polar-aprotic (DMF and acetonitrile) solvents, the spectral position of absorption spectra were almost same for all compounds (**Fig. 2** and **Fig. S1**) implying the little influence of solvent polarity on the ground state of these compounds. The similar absorption band of these compounds indicate that they are maintained their *enol* forms at the ground state⁶⁷. In chloroform and toluene absorption maxima was 334 nm, while slightly blue shifted absorption was observed in acetonitrile and methanol solvents. The compounds **6b**, **6c** and **6d** showed 5 nm red shifted absorption in DMF ($\lambda_{\text{abs}} = 338$ nm) as compared to other studied solvents. In the solid state, **6a** showed absorption at 344 nm, which is slightly red shifted (~ 5 nm) compared to **6b**, **6c** and **6d** (**Fig. 2**).

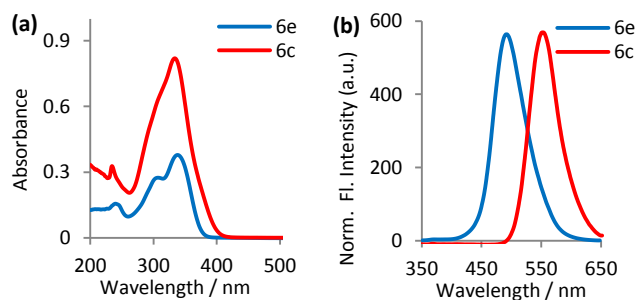


Fig. 1 (a) Steady state absorption spectra; (b) fluorescence spectra of compounds **6c** and **6e** in chloroform at room temperature (10^{-5} M concentration; $\lambda_{\text{exc}} = 330$ nm for fluorescence measurement).

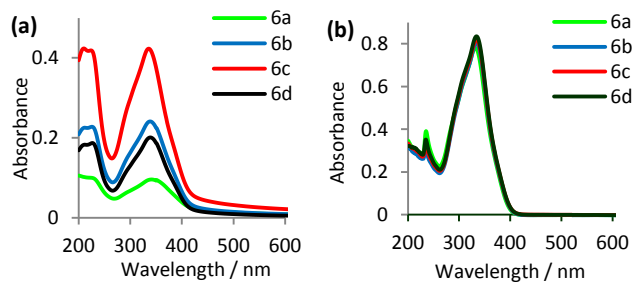


Fig. 2 Steady state absorption spectra of compounds **6a–6d** (a) in solid state (1 wt %) (b) in chloroform (10^{-5} M concentration) at room temperature.

Table 1: Summary of optical properties of the compounds **6a-6e** and **HBT**.

Comps	Medium	$\lambda_{\text{max}}^{\text{Abs}}$ (nm)	ϵ ($\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)	$\lambda_{\text{max}}^{\text{Em}}$ (nm)	Stoke shift (nm)	Stoke shift (cm^{-1})	Quantum efficiency Φ (%)	Fluorescence lifetime (ns)
6a	^a Solid Film	344	<i>g</i>	544	200	10687	^c 60.12	5.21
	^b Chloroform	332	78000	552	220	12004	^d 1.80, ^e 4.60	0.52
	^b Toluene	333	91500	551	218	11881	^d 1.00, ^e 2.90	<i>f</i>
	^b DMF	336	28500	415	79	5665	^d 7.90, ^e 7.50	<i>f</i>
	^b Methanol	329	400	426 527 555	97 198 226	6920 11419 12377	<i>f</i>	<i>f</i>
	^b Acetonitrile	331	3880	407 430 552	76 99 221	5641 6955 12095	<i>f</i>	<i>f</i>
6b	^a Solid Film	338	<i>g</i>	551	213	11436	^c 67.21	3.56
	^b Chloroform	334	80400	552	218	11824	^d 1.80, ^e 4.40	0.74
	^b Toluene	335	69400	551	216	11701	^d 1.50, ^e 3.10	<i>f</i>
	^b DMF	338	21900	415	77	5489	^d 7.50, ^e 7.30	<i>f</i>
	^b Methanol	325	2100	412 431 557	87 106 232	6497 7567 12815	<i>f</i>	<i>f</i>
	^b Acetonitrile	333	2300	407 430 543	74 97 210	5460 6774 11613	<i>f</i>	<i>f</i>
6c	^a Solid Film	336	<i>g</i>	552	216	11645	^c 54.65	3.48
	^b Chloroform	334	81900	552	218	11824	^d 1.70, ^e 4.30	0.75
	^b Toluene	336	72200	551	215	11613	^d 1.40, ^e 2.90	<i>f</i>
	^b DMF	338	47200	405	67	4894	^d 7.20, ^e 11.50	<i>f</i>
	^b Methanol	333	1560	431 543	98 210	6828 11613	<i>f</i>	<i>f</i>
	^b Acetonitrile	331	6230	407 430 552	76 99 221	5641 6955 12095	<i>f</i>	<i>f</i>
6d	^a Solid Film	339	<i>g</i>	552	213	11382	^c 62.94	3.51
	^b Chloroform	334	83500	552	218	11824	^d 1.60, ^e 4.10	0.55
	^b Toluene	335	70600	551	216	11701	^d 1.40, ^e 3.10	<i>f</i>
	^b DMF	339	33300	406	67	4894	^d 7.00, ^e 7.40	<i>f</i>
	^b Methanol	329	3700	431 540	102 211	7193 11876	<i>f</i>	<i>f</i>
	^b Acetonitrile	328	1940	407 429 552	79 101 224	5917 7177 12371	<i>f</i>	<i>f</i>
6e	^b Chloroform	335	37300	490	155	9442	<i>f</i>	<i>f</i>
HBT ^h	^b Chloroform	338	<i>f</i>	525	187	10538	<i>f</i>	<i>f</i>
	^b Toluene	337	20100	514	177	10218	0.5	<i>f</i>
	^b Methanol	332	20800	373	41	3310	<i>f</i>	<i>f</i>

^a Measured on thin film, spin-cast from (1 wt %) dichloromethane solution. ^b Measured from 10^{-5} M solution. ^c Absolute quantum yields in solid state. ^{d, e} Quantum yields measured by relative methods using quinine sulphate standard (^d 10^{-5} M and ^e 10^{-6} M concentration). ^f Not measured. ^g Not calculated, ^h Literature data^{68,88}

Interestingly, the fluorescence properties are solvent dependent. In non-polar organic solvents (toluene and chloroform), compounds showed single broad emission around 552 nm, which is similar to solid state emission (Fig. 3 and Fig. S2). The single broad emission with large Stokes shift can be assigned to the excited state *cis-keto* form (III) (ESIPT emission)⁷⁹. In chloroform and toluene, the strong intramolecular hydrogen bonding stabilizes the ground state (S_0) *cis-enol* form (I) and makes up the major population at S_0 state. After photoexcitation, *cis-enol* undergoes ESIPT at S_1 state to form (II) the excited state *cis-keto* tautomer which then emits at longer wavelength (ESIPT emission) (Scheme S2). In polar aprotic and protic solvents (acetonitrile, methanol and DMF) all compounds show significant dual or triple emission (Fig. S2). The short wavelength and long wavelength can be assigned to the excited *cis-enol* form (II) and *cis-keto* tautomer (III) respectively. In addition to *cis-enol* and *cis-keto* emission extra emission peak was observed in polar protic and aprotic solvents. The third emission band in methanol could be ascribed to the phenoxide species generated due to deprotonation induced by intermolecular hydrogen bonding between the acidic phenol hydrogen and the solvent molecules form (C)⁴⁸ (Scheme S2). In acetonitrile, additional peak can be assigned for protonated *cis-enol* form (B)⁶⁷. In polar aprotic solvent (DMF), compounds showed intense emission between 405–415 nm and shoulder peak between 470–480 nm (Fig. S2). The *cis-enol* emission was between 405–415 nm and *cis-keto* emission was between 470–480 nm. The short wavelength emission band at 407 nm and long wavelength emission band between 543–552 nm was observed in acetonitrile.

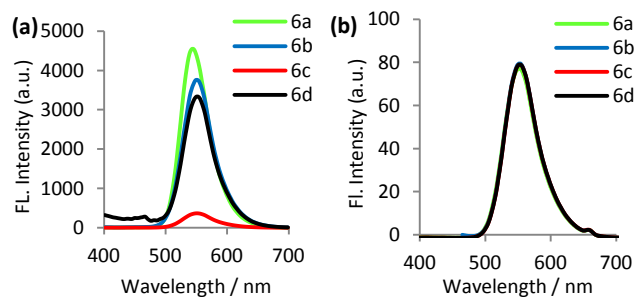


Fig. 3 Steady state emission spectra of **6a-6d** (a) in solid state (spin coated: 1 wt %) (b) in chloroform (10^{-5} M concentration) at room temperature, $\lambda_{\text{exc}} = 330$ nm for fluorescence measurement.

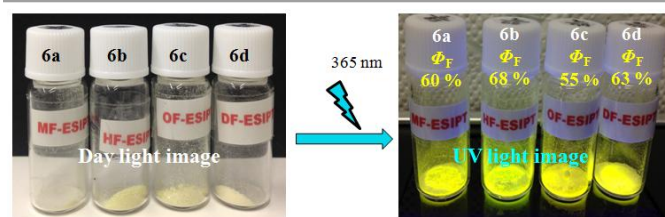


Fig. 4 Day light and UV light images of compounds **6a-6d**.

A third emission band at 430 nm was also observed along with normal ESIPT process emissions in acetonitrile due to protonated *cis-enol*. Similar spectral observations were observed for all compounds in methanol solvent.

Compounds are highly emissive in solid state and weakly emissive in solvents of different polarity after photoexcitation. This quenching in fluorescence in solution can be assigned to intramolecular rotation or conformational changes due to solvation effect⁸⁰. The compounds **6a-6d** are yellow colored emissive in solid state upon photoexcitation (Fig. 4). The compound **6a** showed broad emission maxima at 544 nm, which is blue shifted emission as compared to **6b** ($\lambda_{\text{em}} = 551$ nm), **6c** ($\lambda_{\text{em}} = 552$ nm) and **6d** ($\lambda_{\text{em}} = 552$ nm).

Recently Wang and coworkers reported ultra-high quantum yield (91.68%) in solid state with desirable Stokes shift for carbazole based hydroxy benzothiazole ESIPT derivative⁶⁹. A large Stokes shift is a desirable property of the compounds having ESIPT unit⁴². Remarkably large Stokes shift was observed for the compounds **6a-6d** in solid state as well as in solution. In solid state, Stokes shift was higher for **6c** ($11,645 \text{ cm}^{-1}$) in comparison to **6d** ($11,382 \text{ cm}^{-1}$), **6b** ($11,430 \text{ cm}^{-1}$) and **6a** ($10,687 \text{ cm}^{-1}$). Similar Stokes shifts were observed in solvents of different polarity (Table 1). Interestingly, here along with large Stokes shift we have achieved very high quantum efficiencies by incorporating rigid fluorene core between two benzothiazole units. Compound **6b** showed highest absolute quantum yield (67.21%) as compared to **6d** (62.94%), **6a** (60.12%) and **6c** (54.65%) in solid state. The high quantum yields in solid state can be assigned to slip-stacking and strong intramolecular hydrogen bonding²². The 10–15 fold quenching in quantum efficiency was observed in solution as compared to solid state. The relative quantum yields of compounds were studied in chloroform, toluene and DMF at different concentrations. Except in DMF (for **6a** and **6b**), at lower concentration compounds showed high quantum efficiency. In DMF, the quantum yields were almost same for 10^{-5} and 10^{-6} M concentration for all compounds except **6c**. Compound **6c** showed 1.5 fold more quantum yield at 10^{-6} M concentration in comparison to 10^{-5} M concentration. However, **6a** and **6b** showed more quantum yields at 10^{-5} M concentration in comparison to 10^{-6} M concentration. In chloroform and toluene, 3–4 fold enhancement in quantum yields were observed for dilute solution. In short, compounds showed higher quantum yields in DMF in comparison to chloroform and toluene. Lowering of quantum yields in chloroform can be assigned to quenching effect of heavy chlorine atoms and ACQ in toluene by observing fluorescence color.

A detailed study was carried out to study the effect of phase transition or polymorphism (upon heating) on fluorescence properties. In further experiment, spin coated samples **6a-6d** were heated up to 250 °C slowly, and the emission spectra were recorded in molten state as it cooled to room temperature (20 °C). The emission spectra were similar in molten state and crystalline state. In both the states the compounds emit at same wavelength with change in the fluorescence intensity (Fig. 5).

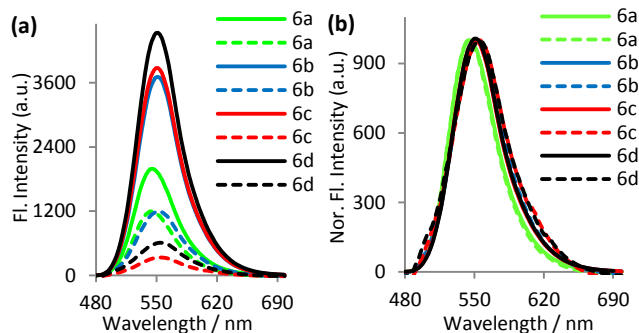


Fig. 5 Steady state emission spectra of compounds **6a–6d** in crystalline state and molten state (a) Fluorescence spectra in solid state (solid line) and molten state (dotted line) (b) Normalized fluorescence spectra in solid state (solid line) and molten state (dotted line), (concentration 1 wt %, $\lambda_{\text{exc}} = 330$ nm).

Time-resolved fluorescence measurements

The fluorescence lifetimes in chloroform solution and in solid state were evaluated by monitoring the peak at 552 nm upon 377 nm excitation (Fig. 6 and Fig. S3). The fluorescence decays were fitted to a multi (bi or tri)-exponential decay function. The average lifetimes of **6a** ($\Phi_{\text{F}} = 1.8\%$), **6b** ($\Phi_{\text{F}} = 1.8\%$), **6c** ($\Phi_{\text{F}} = 1.7\%$) and **6d** ($\Phi_{\text{F}} = 1.6\%$) in chloroform were 0.52, 0.74, 0.75 and 0.55 ns respectively (Table 2). In contrast, all of the ESIPT molecules showed 5–10 times longer lifetime in solid state than those in the solutions, **6a** ($\Phi_{\text{F}} = 60.12$; $\tau_{\text{F}} = 5.21$ ns), **6b** ($\Phi_{\text{F}} = 67.21$; $\tau_{\text{F}} = 3.56$ ns), **6c** ($\Phi_{\text{F}} = 54.65$; $\tau_{\text{F}} = 3.48$ ns), and **6d** ($\Phi_{\text{F}} = 62.94$; $\tau_{\text{F}} = 3.15$ ns). Interestingly, the decays in solutions were mostly dominated by the single exponential function (78–89%), while those in the solid states were partly composed of primary bi-exponential functions (48–78%). In particular, **6b** and **6d** indicate almost equal contributions of ca. 4.5–4.8 ns and 2.7–3.1 ns decays. Based on the steady-state electronic absorption properties summarized in Table 1, radiative lifetimes τ_{R} from the compounds are calculated as $\tau_{\text{R}} = 0.54$, 0.53, 0.58, 0.51 for **6a**, **6b**, **6c**, and **6d**, respectively based on their oscillator strength f estimated by the numerical integrations of their steady state absorption spectra. The relative strength of f (= 2.9, 3.0, 2.7, and 3.1 respectively) for **6a**, **6b**, **6c**, and **6e** in these series of compounds was well represented by the TD-DFT calculations ($f = 1.1$, 0.8, and 1.2, respectively for **6b**, **6c**, and **6d**) relative to **6a**. The values of τ_{R} are consistent with fluorescence lifetimes in solutions (Table 1). In the solid state, the lifetime exhibit considerable elongation up to 5 ns, suggesting that the emission can be attributed to the keto forms with the smaller polarizability (ESIPT emission) through relatively slow structural relaxation from the ground state enol form.

Aggregation Induced Emission (AIE) study

In order to have more information about fluorescence properties in the aggregate state, AIE study was performed for representative compound **6b** in THF and THF–water mixture (various ratios).

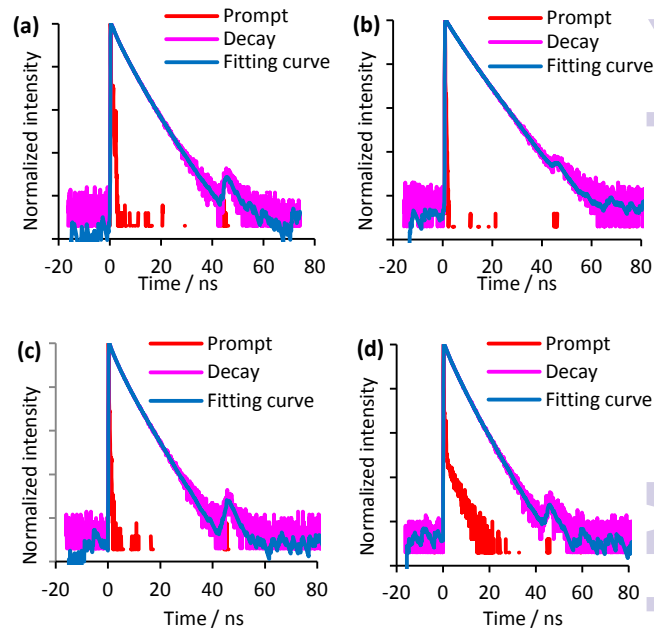


Fig. 6 Time resolved fluorescence decays of compounds in solid state (a) **6a** (b) **6b** (c) **6c** (d) **6d** ($\lambda_{\text{exc}} : 377$ nm).

Table 2: Summary of excited state lifetimes (a) solid state (b) in chloroform of compounds **6a–6d**

Comps.	τ_1/ns (A_1 %)	τ_2/ns (A_2 %)	τ_3/ns (A_3 %)	Average τ_{F} (ns)
^a 6a	5.75 (78)	3.31 (22)	-	5.21
^b 6a	0.57 (88)	0.13 (12)	-	0.52
^a 6b	3.06 (48)	4.82 (42)	0.68 (10)	3.56
^b 6b	0.60 (78)	0.23 (13)	2.89 (9)	0.74
^a 6c	4.22 (65)	2.14 (32)	0.34 (3)	3.48
^b 6c	0.52 (89)	2.56 (11)	-	0.75
^a 6d	4.56 (48)	2.70 (47)	0.63 (5)	3.15
^b 6d	0.60 (84)	0.25 (16)	-	0.55

The absorption and emission spectra of **6b** in THF and THF–water mixture at different water fractions are shown in Fig. 7. In THF solution, **6b** showed dual emissions at 404 and 553 nm corresponding to the enol (E^*) and keto (K^*) emission respectively. Upon increasing water fraction from 0 to 60 %, a slight change was observed in fluorescence intensity. This slight shift is not due to aggregation but caused by the solvent effect^{31,81,82}. When the water fraction was further increased from 70 to 90%, the significant change in the absorption and emission spectra were observed. The sudden change in the emission and absorption spectra becomes the evidence for the formation of nano-particles^{31,81,82}. This sudden spectral change indicates the transition from the homogenous solution to the nanoaggregates and is not due to solvent effect^{81,82}. When the water fraction is between 0–60 %, the absorption peaks are almost identical at around 334 nm, similar to absorption peak in THF solution.

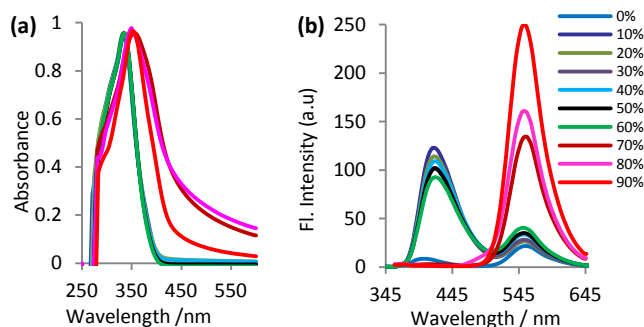


Fig. 7 (a) Normalized absorption spectra (b) Steady state emission spectra of compound **6b** in THF and THF-water mixture (Concentration 10^{-5} M concentration, room temperature, $\lambda_{\text{ex}} = 330$ nm, water fraction (vol %)).

However, in fluorescence spectra the intensity of enol and keto emission is comparatively higher as compared to emission peaks in THF. In aggregated state (water 70–90 %), 20 nm red shift in absorption was observed. This red shift is assigned to *J*-aggregation which is a typical characteristic of AIE²⁰. The formation of *J*-aggregates was further conformed by single crystal data. In the aggregate state, the enol emission around 415–420 nm gradually disappeared and keto emission (554 nm) became the dominant emission. The maximum fluorescence efficiency was obtained at 90 % water content, upto 7 fold enhancements ($\Phi_{\text{F}} = \sim 10$) in quantum efficiency was observed in aggregate state in comparison to molecularly dispersed THF solution ($\Phi_{\text{F}} = 1.5$).

Structural Properties

To have further in depth knowledge of structural properties of compounds, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), powder-XRD and single X-ray analyses were carried out. DSC analyses were performed on the neat material under nitrogen atmosphere. The summarized results of DSC are shown in **Fig. S4**.

On the first heating cycle by differential scanning calorimeter, very sharp melting endothermic transitions were observed for **6b**, **6c** and **6d**. The compound **6a** did not show endothermic transition up to 300 °C for both cycles of DSC. The melting transitions were observed at 216 °C, 175 °C and 135 °C for **6b**, **6c** and **6d** respectively, which indicates presence of molecular order within the crystalline state. In case of **6d** small endothermic peaks were observed (at 36 °C and 76 °C) before melting endothermic transition. These can be assigned to slight disorder (or phase change) in the crystalline state. After melting, crystalline materials undergo phase transition to isotropic liquid. The materials then appear to become kinetically trapped in the amorphous phase (glass state). Phase transition was not observed upon cooling to room temperature (no recrystallisation occurs) in first DSC cycle for **6c** and **6d**. Compound **6b** showed small phase transition peak at 30 °C in first cooling cycle. This is due to slight change in amorphous phase. In second cycle of DSC, melting endothermic transition was not observed for **6c** and **6d** upon heating. This clearly indicates that materials remain in glass

state after first melting endothermic transition. In case of **6b**, broad exothermic phase transition (160 °C) was observed before melting endothermic transition (216 °C). This transition is a phase change from glass state to crystalline state (recrystallisation occur in second DSC heating cycle). After melting endothermic transition, **6b** remained in glass state after cooling. Similar to first cooling cycle, small phase transition peak was observed at 37 °C for second cooling cycle for **6b**. The DSC data concludes that phase transition of the materials is irreversible in nature for **6c** and **6d**, but it is reversible for **6b**. The compounds **6a–6d** are crystalline in nature which were confirmed by powder-XRD experiments **Fig. S5**.

Thermogravimetric analysis (TGA) technique is used for evaluation of thermal stability of emissive compounds. Thermogravimetric analysis were carried out under nitrogen atmosphere using alumina/ Pt pans at the ramp rate of 10 °C/min for temperature range between 40 to 1000 °C. Compounds **6a–6d** are thermally stable up to 400 °C. The compounds **6b** and **6d** showed 5% weight loss at 415 °C while **6a** and **6c** showed 5% weight loss at 424 °C. The degradation of compounds started after 415 °C, and significant weight loss was observed between 415–540 °C, however after 540 °C the % weight loss was very slow. Except **6c**, 80% degradation was observed around 540 °C for the compounds. Compound **6b** showed 70% degradation up to 550 °C and did not degrade completely even up to 1000 °C (75% weight loss observed) and other compounds showed 87–95% weight loss at 1000 °C. The TGA data clearly indicates that the T_{d} is not dependent on length of alkyl chain attached to 9,9–position of fluorene. The high thermal stability is due to the rigid fluorene and benzothiazole unit. Overall, all compounds showed almost same and very high thermal stability. The thermal stability data are summarized in **Fig. S6**.

X-Ray crystallographic analysis of **6b** was performed (other compounds we are unable to obtained single crystal ever after many attempts) to study structural parameters. The crystal structure of **6b** is shown in **Fig. 8**, **Fig. S7** and **Table S1**.

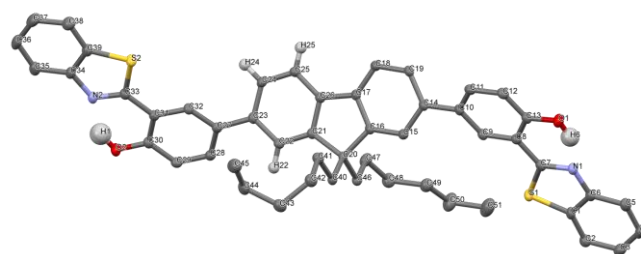


Fig. 8 X-ray crystal structure of **6b**. Hydrogen atoms (except for –OH groups) are omitted for clarity. Thermal ellipsoids are set at 50% probability. Hydrogen atoms except OH groups were restrained to ride on the atom to which they are bonded. The two OH hydrogen atoms were put by using reflection data.

The distances between the oxygen and nitrogen (O_1-N_1 and O_2-N_2) were 2.593 Å and 2.612 Å respectively, indicating the formation of an intramolecular hydrogen bond ($O_1-H_6---N_1$ and $O_2-H_1---N_2$). The O–H bond lengths of phenolic hydroxy group (O_1-H_6 and O_2-H_1) were 0.881 Å and 0.910 Å respectively. The bond lengths between acidic hydrogen atoms and basic nitrogen atoms (intramolecular hydrogen bonds; N_1-H_6 and N_2-H_1) were 1.788 Å for each bond. The small torsion angle between the two aromatic rings was ($N_1-C_7-C_8-C_{13}$ and $N_2-C_{33}-C_{31}-C_{30}$) 4.5° and 2.5° respectively, confirming the coplanar configuration which fulfills the requirement of ESIPT (Fig. S7). A small twisting ($C_{11}-C_{10}-C_{14}-C_{19}$ and $C_{32}-C_{27}-C_{23}-C_{24}$, 39° and 36° respectively) was observed between fluorene and hydroxy benzothiazole (HBT) in the crystal. The crystal had slip-stacked packing with interplanar distance of about 3.617 Å (Fig. S7). The 2-(2-hydroxyphenyl) benzothiazole part of molecule overlapped with phenyl and imidazole part of the neighboring molecule. The distance between an oxygen atom and the nearest nitrogen atom (O_1-N_1) of neighboring molecule was 4.756 Å, which confirms the absence of inter-molecular hydrogen bonding (Fig. S7). The high quantum yields can be explained by conformational fixating in the photo-excited state due to strong intramolecular hydrogen bonding which suppresses the molecular rotation and non-radiative decay²².

Theoretical calculation

Geometric structure

The compounds **6a–6d** contains two HBT units separated by fluorene motif. In order to study the proton transfer process in detail, DFT computations were performed⁸³. The ground and excited state of *cis-enol* were optimized using B3LYP functional and 6-31G**(d,p) basis set. Theoretical calculation was carried out for the *cis-enol* form for **6a** (small alkyl chain compound was considered for simplicity). In the ground state, the O–H bond length of phenolic hydroxy group ($O_{27}-H_{57}$ and $O_{41}-H_{65}$) was found to be 0.992 Å. At the same time, the bond lengths between acidic hydrogen atoms and basic nitrogen atoms (intramolecular hydrogen bond; $N_{74}-H_{57}$ and $N_{75}-H_{65}$) were found to be 1.733 Å. At the excited state (S_1 state), the O–H bond lengths ($O_{27}-H_{57}$ and $O_{41}-H_{65}$) extended to 1.022 Å and 0.998 Å respectively, while N–H ($N_{74}-H_{57}$ and $N_{75}-H_{65}$) bond lengths decreased to 1.611 Å and 1.706 Å respectively (Fig. S8). The increase in O–H bond lengths and the decrease in N–H bond lengths suggest the increase in intramolecular hydrogen bond strength at S_1 state, which favor ESIPT process. However the shorting of (N–H) distance and elongation of bond length (O–H) in the S_1 state is more dramatic on one side than the other (Table 3).

Table 3. Calculated bond lengths (Å) and angles (°) of **6a** in the S_0 and S_1 states

Bond lengths/ angle	Electronic State		Bond lengths/ angle	Electronic State	
	S_0	S_1		S_0	S_1
$O_{27}-H_{57}$	0.992	1.022	$O_{41}-H_{65}$	0.992	0.998
$N_{74}-H_{57}$	1.733	1.611	$N_{75}-H_{65}$	1.733	1.706
$\delta(O_{27}-H_{57}-N_{74})$	147.0	151.6	$\delta(O_{41}-H_{65}-N_{75})$	147.0	147.2

The concomitant enlargement of the $O_{27}-H_{57}-N_{74}$ angle from 147° in the S_0 state to 151° in the S_1 state indicate that strong intramolecular hydrogen bond is strengthened in the S_1 state. Moreover, in the case of $O_{41}-H_{65}-N_{75}$ angle enlargement of bond angle is not significant. This result clearly indicates that proton transfer in the excited state is not occurs simultaneously for both HBT units^{84–86}. This observation is supported by degenerate LUMOs energies in next section. Similar to single crystal data, the calculated torsion angles $N_{74}-C_{20}-C_{18}-C_{17}$ and $N_{75}-C_{34}-C_{32}-C_{31}$ (phenyl and imidazole ring) at ground state were 0.4 and 0.2° respectively, which support the experimental results about planarity between phenyl and benzothiazole unit. The computed dihedral angles between the fluorene and HBT unit $C_{15}-C_{14}-C_{11}-C_{12}$ and $C_{33}-C_{28}-C_2-C_1$ were 37° each at ground state, which is in accordance with experimental results. In the S_1 state, the computed dihedral angles $C_{15}-C_{14}-C_{11}-C_{12}$ and $C_{33}-C_{28}-C_2-C_1$ were 23° and 2° respectively, implying that compound is more planar in the excited state in comparison to ground state. The experimental and computed dihedral angle values of compounds clearly indicate that compounds have efficient conjugation between the fluorene core and HBT units.

Frontier molecular orbitals

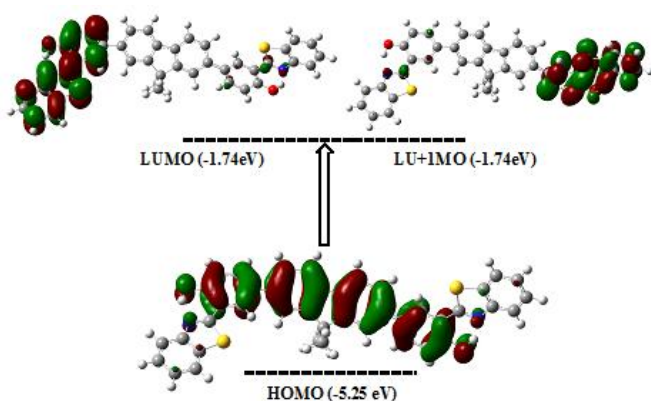
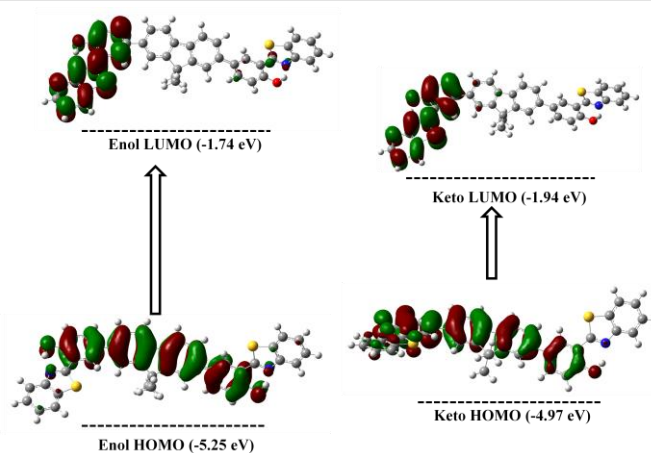
Photoelectron yield spectroscopy (PYS) was used for experimental HOMOs level determination of the compounds **6a–6d** (Fig. S9). All the compounds showed a comparatively same HOMO level (Fig. S10, Table 4). The compound **6c** showed a slightly deeper HOMO level (-6.06 eV) in comparison to **6d** (-6.00 eV), **6b** (-6.00 eV), and **6a** (-6.02 eV). The deeper HOMO level of the compounds is due to two electron withdrawing benzothiazole units attached to fluorene unit. The LUMO levels of the compounds **6a–6d** were calculated from HOMO energy levels and optical band gap (E_g^{opt}). The optical band gaps of the compounds were calculated from the onset value of thin film UV-Vis absorption spectrum. The E_g^{opt} were found to be 3.09, 3.19, 3.18 and 3.19 eV for **6a**, **6b**, **6c** and **6d** respectively. The LUMO level of compounds is similar to HOMO level (Fig. S10, Table 4). The LUMO of **6a** and **6d** were found to be -2.97 eV, and **6b** and **6c** showed decreased LUMO levels (-2.81 and -2.88 eV respectively) in comparison to **6a** and **6d**. The energy gap between HOMO and LUMO is almost same for all the compounds due to similar backbone of the compounds. Results indicate that alkyl change attached to fluorene core did not involve significantly in electron distribution.

In order to have more understanding of the nature of the electronically excited state, the calculated MOs of **6a** are shown in Fig. 9. Only the highest occupied molecular orbital and degenerate lowest unoccupied molecular orbitals are shown here. Fig. 9 illustrates that the HOMO and the LUMO are localized on different part of the **6a**. In HOMO the electron density is concentrated on fluorene motif, while the electron density is distributed over benzothiazole for LUMO and degenerate LU+1MO orbitals.

Table 4. Absorption maxima, band gap and HOMO/LUMO energies of compounds **6a-6d**

Comp	$\lambda_{\text{max}}^{\text{Abs}}$ thin film ^a (nm)	Onset ^a (nm)	$E_{\text{g}}^{\text{opt}}$ (eV) ^b	HOMO Expt. ^c [Calc.] ^d (eV)	LUMO Expt. ^e [Calc.] ^d (eV)
6a	344	401	3.09	-6.02 [-5.25]	-2.97 [-1.74]
6b	338	389	3.19	-6.00 [-5.25]	-2.81 [-1.74]
6c	336	389	3.18	-6.06 [-5.25]	-2.88 [-1.74]
6d	339	389	3.19	-6.00 [-5.25]	-2.97 [-1.74]

^a Prepared on quartz plate by spin-casting of dichloromethane compounds solution (1 wt %). ^b Determined by onset of optical absorption. ^c Measured by photoelectron yield spectroscopy. ^d DFT calculation by B3LYP/6-31G**(d,p) during DFT calculation side alkyl chains were replaced by methyl group for simplicity. ^e Calculated by adding $E_{\text{g}}^{\text{opt}}$ to HOMO.

**Fig. 9** Frontier molecular orbitals (HOMO, LUMO and LU+1MO) of **6a** (Enol form).**Fig. 10** Frontier molecular orbitals with energies (HOMO and LUMO) of **6a** (Enol and Keto form).

This clearly indicates that charge transfer from fluorene core to benzothiazole unit resulted after photo-excitation on both side of HBT units. The energies of **LUMO** and **LU+1MO** conclude that change of charge density takes place with equal probability but not simultaneously. The experimental results of HOMO and LUMO energies are well in agreement with theoretical results computed by DFT.

The HOMO and LUMO energies of the **6a** were evaluated for both *enol* and *keto* form **Fig. 10**. The *enol* form showed deeper HOMO level in comparison to HOMO level of *keto* form, while LUMO of *keto* form is deeper than that of *enol* form. There is large orbital energy difference between HOMOs and LUMOs of *enol* and *keto*. This condition is not favorable for effective orbital interaction between excited state *enol* and ground state *keto* form^{59,87}. The energy transfer from excited state *keto* to ground state *enol* is forbidden due to large mismatch of their molecular orbital's energy levels. This suppressed the fluorescence quenching process leading to high quantum yields.

Conclusion

In summary, we have succeeded in preparation of solid state emissive compounds by tuning 2-(2'-hydroxy) benzothiazole unit by facial and straight forward chemical alteration. Very high quantum efficiency (~ 68%) of small fluorene based ESIPT molecules is a very striking feature of the present protocol. The X-ray single crystal analysis and DFT computations confirm the suitability of ESIPT process. Intra-molecular charge transfer nature between the donor (fluorene) and the ESIPT acceptor molecules conduct the large mismatch of HOMO and LUMO levels in their ground and excited states, leading to the design of ESIPT based highly emissive solid state compound. High quantum yield, large Stokes shift, micro-environmental sensitive emission, high fluorescence life time together with their known structural properties, make these materials exciting candidates for many solid state optoelectronic applications.

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Notes and references

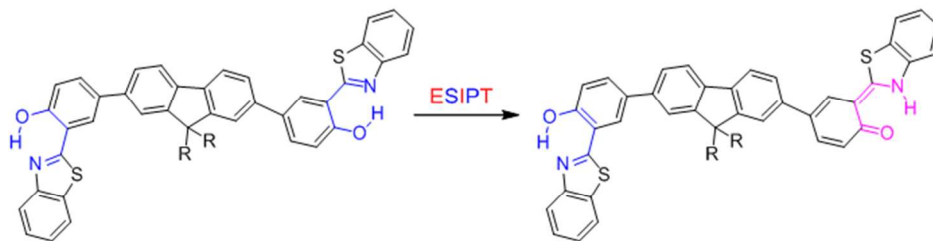
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Table of contents

Efficient Solid State Emission of fluorene–benzothiazole motifs via ESIPT process have been discussed experimentally and theoretically.



ESIPT Process; Φ_{FL} : 55-68 % in solid state; τ_F : 3.15-5.21 ns; λ_A : $\sim 12377 \text{ cm}^{-1}$

