Supporting Information

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

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Steady State Measurement

The steady state measurements were performed in solution and in solid state. Non–polar, polar– protic and polar–aprotic solvents were used for absorption and emission study. All spectroscopic measurements were carried out at room temperature (20°C). Concentrations used for the measurement was 10⁻⁵ M in solution. Solid samples were prepared on quartz plate by spincasting of dichloromethane compounds solution. λ_{max}^{Abs} : Absorption maxima presented in nm. λ_{max}^{Em} : Emission maxima presented in nm; Excitation wavelength used was absorption maxima of compounds in respective solvents for fluorescence mesurement. Quinine sulphate was used as standard for relative quantum yields evaluations.



Fig. S1 Steady state absorption spectra of compounds **6a–6d** (a) in toluene (b) in DMF (c) in methanol (d) in acetonitrile at room temperature



Fig. S2 Steady state emission spectra of compounds **6a–6d** (a) in toluene (b) in DMF (c) in methanol (d) in acetonitrile at room temperature



Fig. S3 Time resolved fluorescence decays of compounds **6a–6d** in chloroform monitored at 552 nm (a) **6a** (b) **6b** (c) **6c** (d) **6d**.



Fig. S4 Differential scanning calorimetry (DSC) data of compounds **6a–6d** (a) first cycle (b) second cycle.



Fig. S5 Powder-XRD data of compounds 6a-6d



Fig. S6 Thermal stability data of compounds 6a-6d



Fig. S7 X-ray crystal structures of **6b** (a) X-ray single crystal with hydrogen atoms (b) X-ray single crystal with ESIPT participating bond lengths and dihedral angles (c) Molecular packing (d) distances between N and O between two units (e) Planar nature of HBT unit.



Fig. S8 Optimized structure of *cis*-enol form at ground and S_1 state for **6a**.



Fig. S9 Photoelectron yield spectroscopy data of 6a–6d.



Fig. S10 Experimental energy levels of HOMO and LUMO of compounds 6a–6d.

X-ray Crystallography

Single crystal was obtained by the solvent diffusion of hexane into a solution of the compound **6b** in CH₂Cl₂. Data collections were performed on a Rigaku R–AXIS–RAPID diffractometer with Cu–K α radiation ($\lambda = 1.54187$ Å) at –150 °C. The non–hydrogen atoms were refined anisotropically. Hydrogen atoms except for OH groups were restrained to ride on the atom to which they are bonded. The two OH hydrogens were put by using reflection data. All the calculations were performed by using crystal structure crystallographic software package,¹ except for refinement, which was performed by using SHELXL–97.²

Empirical formula	$C_{51}H_{48}N_2O_2S_2$
Formula weight	785.07
T [°C]	-150
λ[Å]	1.54187
Crystal system	triclinic
Space group	P -1 (#2)
Z	2
<i>a</i> [Å]	11.7603(2)
<i>b</i> [Å]	14.1138(3)
<i>c</i> [Å]	14.5223(3)
α [°]	65.8221(8)
$\beta[\circ]$	86.8240(9)
γ [°]	70.2805(8)
$V[Å^3]$	2060.39(7)
$\rho_{\text{calcd}} [\text{g cm}^{-3}]$	1.265
Collected data	23668
Unique data / R_{int}	7367/ 0.0477
No. of parameters	522
Goodness-of-fit ^[a]	1.085
<i>R</i> 1 ($I > 2\sigma$), <i>wR</i> 2 (all reflections) ^[b]	0.0418, 0.1171
Residual density [e Å ⁻³]	0.29/-0.46

Table S1: X-ray crystallographic data for 6b

[a] GOF =
$$\left\{ \sum \left[w \left(F_0^2 - F_c^2\right)^2 \right] / (n-p) \right\}^2$$
, where *n* and *p* denote the number of data and parameters.
[b] R1 = $\sum \left(\|F_0\| - \|F_c\| \right) / \sum \|F_0\|$ and wR2 = $\left\{ \sum \left[w \left(F_0^2 - F_c^2\right)^2 \right] / \sum \left[w \left(F_0^2\right)^2 \right] \right\}^2$ where $w = 1 / \left[\sigma^2 \left(F_0^2\right) + (a \cdot P)^2 + b \cdot P \right]$ and $P = \left[\left(\text{Max}; 0, F_0^2 \right) + 2 \cdot F_c^2 \right] / 3$.

1. CrystalStructure 4.0, Crystal Structure Analysis Package, Rigaku Corporation (2000–2011). Tokyo 196-8666, Japan.

2. G. M. Sheldrick, Acta Cryst. A 2008, 64, 112–122.



Scheme S1. Structure of HBT, 6c and 6e





Scheme S2. ESIPT process (a) four level pathway (b) formation of hydrogen bonding and generation of phenoxide ion in polar aprotic and protic solvents.

NMR Spectra of compounds

¹H–NMR spectra of 6a



¹³C–NMR spectra of 6a



¹H–NMR spectra of 6b







¹H-NMR spectra of 6c



¹³C-NMR spectra of 6c



¹H-NMR spectra of 6d







¹H-NMR spectra of 6e



¹H-NMR spectra of 6e



¹H-NMR spectra of 4a



¹³C-NMR spectra of 4a



¹H-NMR spectra of 4b



¹³C-NMR spectra of 4b



¹H-NMR spectra of 4c



¹³C-NMR spectra of 4c



¹H-NMR spectra of 4d



¹³C-NMR spectra of 4d



¹H-NMR spectra of 2a



¹³C-NMR spectra of 2a



¹H-NMR spectra of 2b







¹H-NMR spectra of 2c



¹³C-NMR spectra of 2c

