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 spin-casting of dichloromethane compounds solution. $\lambda_{\text{Abs max}}$: Absorption maxima presented in nm. $\lambda_{\text{Em max}}$: Emission maxima presented in nm; Excitation wavelength used was absorption maxima of compounds in respective solvents for fluorescence measurement. 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 CH$_2$Cl$_2$. Data collections were performed on a Rigaku R–AXIS–RAPID diffractometer with Cu–K$_\alpha$ 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, except for refinement, which was performed by using SHELXL–97.

Table S1: X–ray crystallographic data for 6b

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{51}$H$</em>{48}$N$_2$O$_2$S$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>785.07</td>
</tr>
<tr>
<td>$T$ [°C]</td>
<td>$-150$</td>
</tr>
<tr>
<td>$\lambda$ [Å]</td>
<td>1.54187</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1 (#2)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$a$ [Å]</td>
<td>11.7603(2)</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>14.1138(3)</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>14.5223(3)</td>
</tr>
<tr>
<td>$\alpha$ [°]</td>
<td>65.8221(8)</td>
</tr>
<tr>
<td>$\beta$ [°]</td>
<td>86.8240(9)</td>
</tr>
<tr>
<td>$\gamma$ [°]</td>
<td>70.2805(8)</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
<td>2060.39(7)</td>
</tr>
<tr>
<td>$\rho$ calc’d [g cm$^{-3}$]</td>
<td>1.265</td>
</tr>
<tr>
<td>Collected data</td>
<td>23668</td>
</tr>
<tr>
<td>Unique data / $R_{int}$</td>
<td>7367/ 0.0477</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>522</td>
</tr>
<tr>
<td>Goodness-of-fit$^{[b]}$</td>
<td>1.085</td>
</tr>
<tr>
<td>$R1$ ($I &gt; 2\sigma(I)$), $wR2$ (all reflections)$^{[b]}$</td>
<td>0.0418, 0.1171</td>
</tr>
<tr>
<td>Residual density [e Å$^{-3}$]</td>
<td>0.29/ -0.46</td>
</tr>
</tbody>
</table>

[a] GOF = $\sqrt{\sum w(F_0^2 - F_c^2)^2 / (n - p)}$, where $n$ and $p$ denote the number of data and parameters.

[b] $R1 = \sum ||F_o|| - ||F_c|| / \sum ||F_o||$ and $wR2 = \sqrt{\sum w(F_0^2 - F_c^2)^2 / (n - p)}$ where $w = 1/\left[\sigma^2(F_0^2) + (a\cdot P)^2 + b\cdot P\right]$ and $P = \left[\text{Max}(0,F_0^2) + 2\cdot F_c^2\right]/3$.

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

\(^1\)H–NMR spectra of 6a

\(^{13}\)C–NMR spectra of 6a
$^1$H–NMR spectra of 6b

$^{13}$C–NMR spectra of 6b
$^1$H-NMR spectra of 6c

$^{13}$C-NMR spectra of 6c
$^{1}$H-NMR spectra of 6d

$^{13}$C-NMR spectra of 6d
$^1$H-NMR spectra of 6e
$^1$H-NMR spectra of 4a

$^{13}$C-NMR spectra of 4a
$^1$H-NMR spectra of 4b

$^{13}$C-NMR spectra of 4b
$^1$H-NMR spectra of 4c

$^{13}$C-NMR spectra of 4c
$^1$H-NMR spectra of 4d

$^{13}$C-NMR spectra of 4d
\textbf{\textsuperscript{1}H-NMR spectra of 2a}

![\textbf{\textsuperscript{1}H-NMR spectra of 2a}]

\textbf{\textsuperscript{13}C-NMR spectra of 2a}

![\textbf{\textsuperscript{13}C-NMR spectra of 2a}]
$^1$H-NMR spectra of 2b

$^{13}$C-NMR spectra of 2b
$^{1}$H-NMR spectra of 2c

$^{13}$C-NMR spectra of 2c