

## Supporting Information

### **An ESIPT fluorophore with a switchable intramolecular hydrogen bond: for applications of solid-state fluorochromism and white light generation**

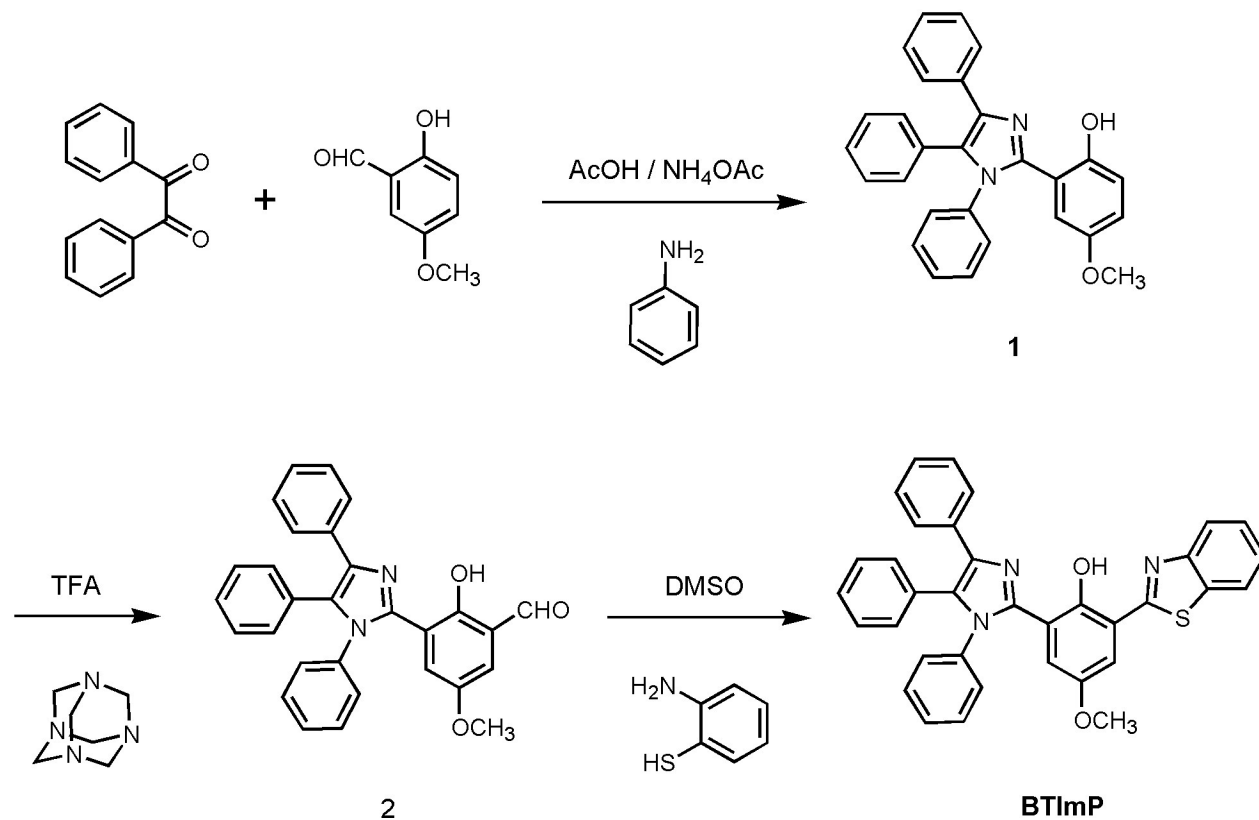
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## Synthetic Procedure



**4-methoxy-2-(1,4,5-triphenyl-1H-imidazol-2-yl)phenol (1).** **1** was prepared in a one-step reaction according to the previously reported method.<sup>1</sup> After reflux of benzil (4.2 g, 20 mmol), 5-methoxysalicylaldehyde (3.0 g, 20 mmol) and aniline (1.9 g, 20 mmol) in acetic acid (120 ml) with ammonium acetate (7.7 g), a white powder of **1** (6.0 g) was obtained in 71 % yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  3.26 (s, 3H), 6.21 (d, 1H, *J* = 2.9 Hz), 6.79 (dd, 1H, *J* = 8.9, 3.0 Hz), 6.88 (d, 1H, *J* = 9.0 Hz), 7.21-7.44 (m, 15H), 12.28 (s, 1H); MS (EI) calcd for C<sub>28</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> 418.49, found 418.

**2-hydroxy-5-methoxy-3-(1,4,5-triphenyl-1H-imidazol-2-yl)benzaldehyde (2).** Formylation of **1** at the 6 position was carried out by using a Duff reaction.<sup>2</sup> Hexamethylenetetramine (10 g) and **1** (2.9 g, 0.7 mmol) were dissolved in 50 ml of trifluoroacetic acid (TFA) and refluxed for 2 hours. After the addition of 4N HCl (90 ml), the resulting solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The obtained orange oil was solidified with methanol, giving yellow powder (1.9 g) in 61% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  3.42 (s, 3H), 6.45 (d, 1H, *J* = 3.2 Hz), 7.13 (d, 1H, *J* = 3.2 Hz), 7.24-7.52 (m, 15H), 10.47 (s, 1H). MS (EI) calcd for C<sub>29</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> 446.50, found 446.

**2-(1,3-benzothiazol-2-yl)-4-methoxy-6-(1,4,5-triphenyl-1H-imidazol-2-yl)phenol (BTImP).**

Benzothiazole ring formation was performed by a previously reported method.<sup>3</sup> **2** (1.0 g, 2.2 mmol) and 2-aminobenzenethiol (0.28 g, 2.2 mmol) were refluxed in DMSO (10 ml) for an hour. After cooling, methanol was added to the reaction mixture, and the resulting precipitate was filtered (1.0 g, yield 83 %). The crude product was recrystallized by 1,4-dioxane. The crystals of its HCl salt were obtained from the THF-HCl solution of BTImP. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  3.45 (s, 3H), 6.35 (d, 1H, *J* = 3.1 Hz), 7.27-7.57 (m, 17H), 7.88 (d, 1H, *J* = 2.9 Hz), 8.08 (d, 1H, *J* = 8.0 Hz), 8.17 (d, 1H, *J* = 8.1 Hz). MS (EI) calcd for C<sub>35</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub>S 551.66, found 552. Anal. calcd for C<sub>39</sub>H<sub>33</sub>N<sub>3</sub>O<sub>4</sub>S [(BTImP)(dioxane)]: C 73.22%, H 5.20%, N 6.57%; found: C 73.60%, H 5.17%, N 6.58%.

**Optical Measurements.** Absorption and fluorescence spectra were recorded on a Shimadzu UV2500PC spectrometer and a Jasco FP-8300 spectrofluorometer, respectively. The fluorescence quantum yield in solutions was determined by a relative method using fluorescein ( $\Phi_{\text{Fl}} = 0.97$ ) as a standard. <sup>1</sup>H-NMR spectra were measured using a JEOL JNM-ECP400 NMR spectrometer. Mass spectra were measured using a JEOL JMS-Q1050GS.

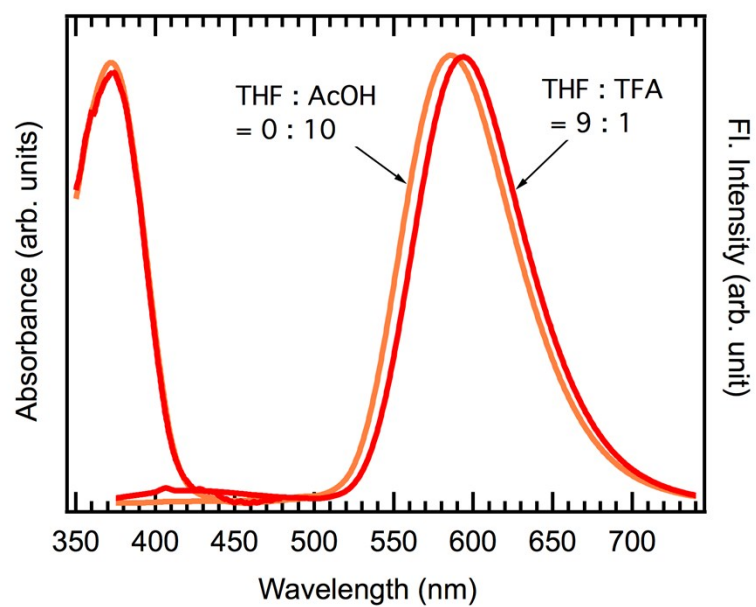
**X-ray Crystallography.** Temperature-dependent crystallographic data were collected using a diffractometer (Rigaku RAPID-II, Japan) equipped with a rotating anode fitted with a multilayer confocal optic, using Cu K $\alpha$  ( $\lambda = 1.54187 \text{ \AA}$ ) radiation from a graphite monochromator. Structure refinements were carried out using the full-matrix least-squares method on  $F^2$ . Calculations were performed using Crystal Structure software packages. Parameters were refined using anisotropic temperature factors, except for the hydrogen atom. The crystallographic data are shown in Table S1.

**Computational Method.** All calculations were performed with the GAUSSIAN 09W package.<sup>4</sup> Geometrical parameters were cited from the X-ray results. The single-point calculations without geometry optimization were performed using the DFT method with the B3LYP hybrid functional and the 6-311+G(d,p) basis sets.

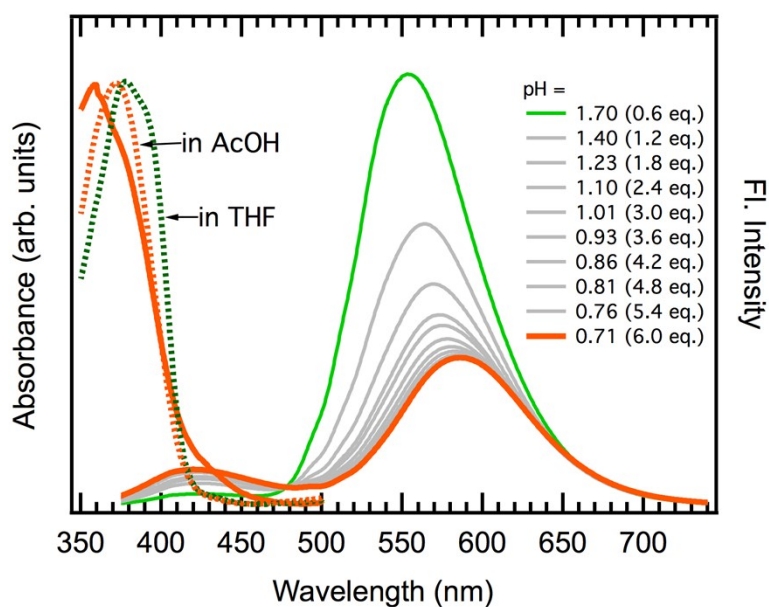
**Table S1.** Crystallographic Data for BTImP and the protonated BTImP.

	(BTImP)(dioxane)	(BTImP)(HCl)(H <sub>2</sub> O)
formula	C <sub>39</sub> H <sub>33</sub> N <sub>3</sub> O <sub>4</sub> S	C <sub>35</sub> H <sub>28</sub> N <sub>3</sub> O <sub>3</sub> ClS
F.W.	639.77	606.14
crystal system	triclinic	monoclinic
space group	<i>P</i> -1 (#2)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (#14)
<i>a</i> /Å	9.8090(3)	7.3303(3)
<i>b</i> /Å	12.1454(3)	23.9278(7)
<i>c</i> /Å	15.3153(4)	17.5078(6)
$\alpha$ /°	110.6219(15)	
$\beta$ /°	90.1616(17)	99.1818(17)
$\gamma$ /°	109.2305(14)	
<i>V</i> /Å <sup>3</sup>	1597.74(7)	3031.49(17)
<i>Z</i>	2	4
<i>D<sub>c</sub></i> /g·cm <sup>-3</sup>	1.330	1.328
<i>T</i> /K	100	100
$\mu$ /cm <sup>-1</sup>	12.81	20.86
total reflections	18296	34180
unique data ( <i>R</i> <sub>int</sub> )	5737(0.0913)	5533(0.0929)
<i>R</i> <sub>1</sub> <sup>a)</sup>	0.0661 ( <i>I</i> > 2.00σ( <i>I</i> ))	0.1044 ( <i>I</i> > 2.00σ( <i>I</i> ))
w <i>R</i> <sub>2</sub> <sup>a)</sup>	0.1624 (all reflections)	0.3273 (all reflections)
GOF	0.959	0.976

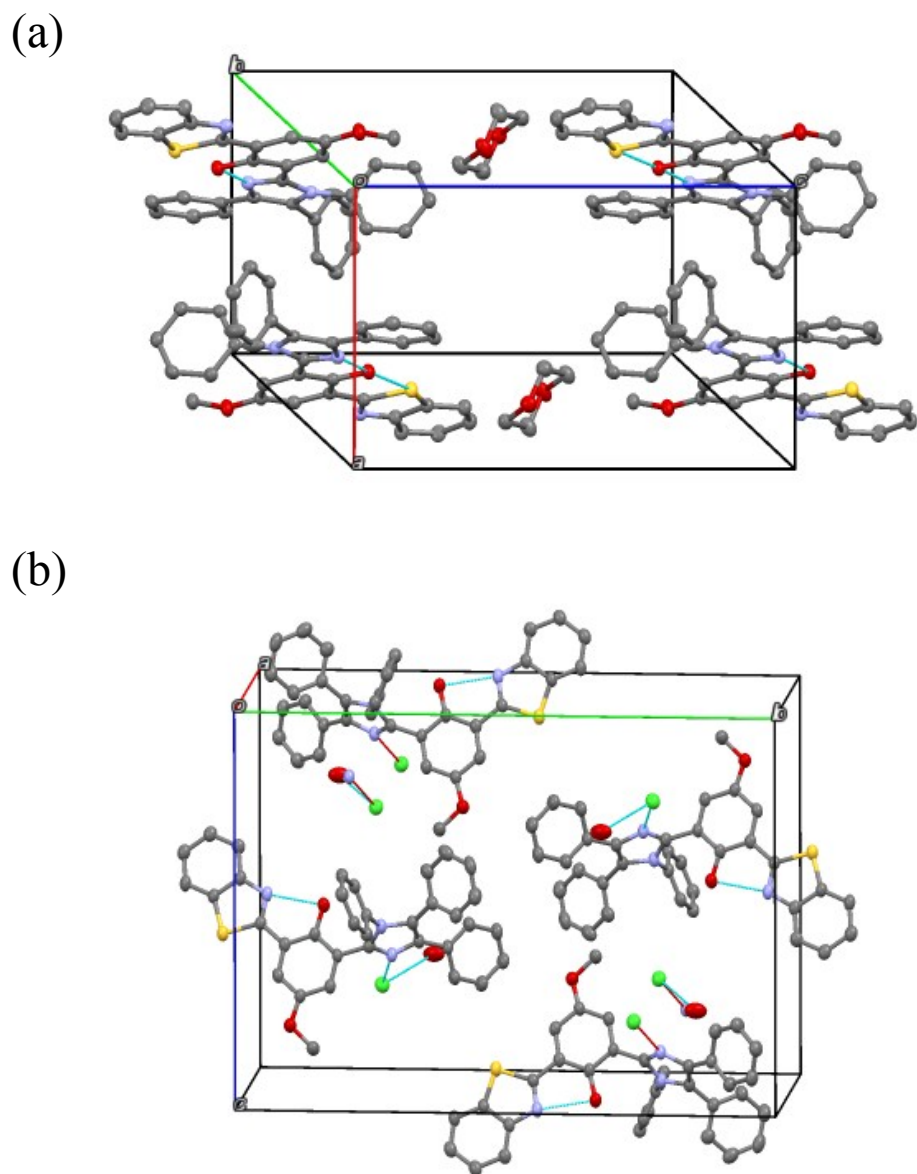
<sup>a)</sup> $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$  and  $R_w = (\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$ .



**Fig. S1** Absorption and fluorescence spectra of BTImP in the mixed solvent of THF and TFA (9:1, v:v) (red lines). Almost the same fluorescence spectrum as in AcOH (orange line) is obtained even by mixing a small amount of TFA to THF.  $\lambda_{\text{ex}} = 365 \text{ nm}$ .

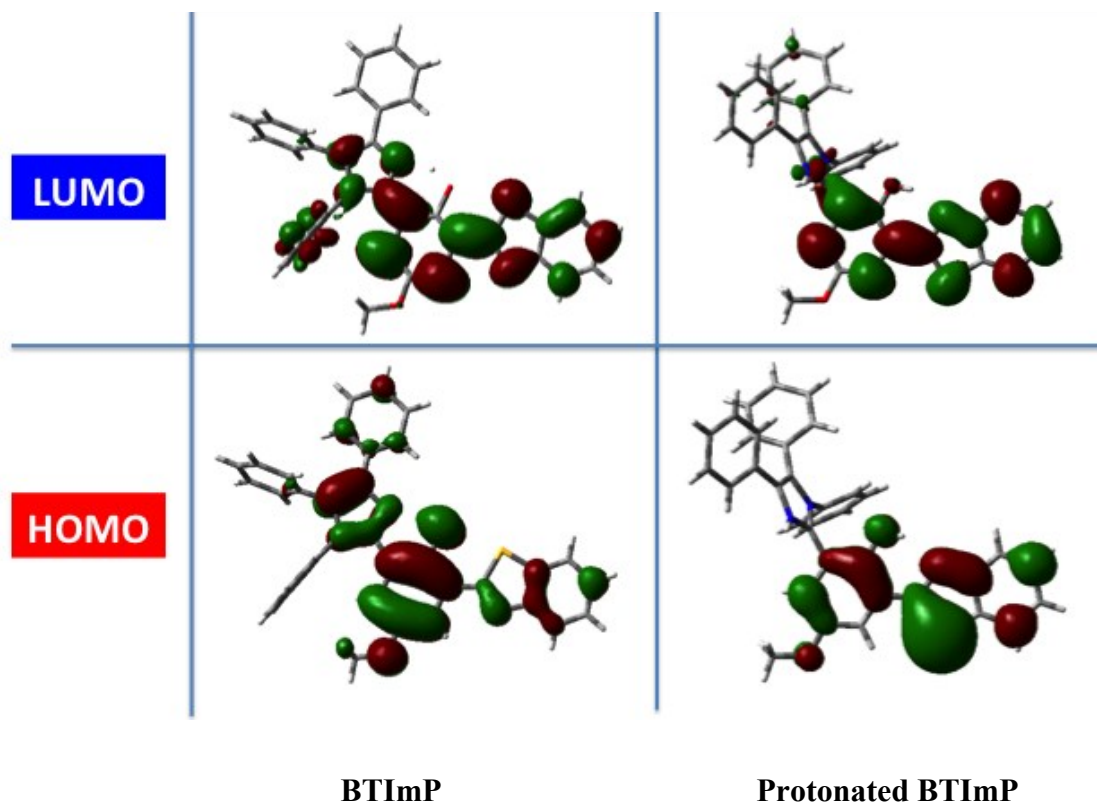


**Fig. S2** Fluorescence titration spectra of BTImP (0.1 mmol in 3 ml of THF) on gradual addition of 6 M HCl (10-100  $\mu$ l).  $\lambda_{\text{ex}}$  = 365 nm. Their absorption spectra (orange line at the left side) show a weak rise in the range 420-460 nm, although such a rise is not observed in AcOH and in THF (dotted lines).

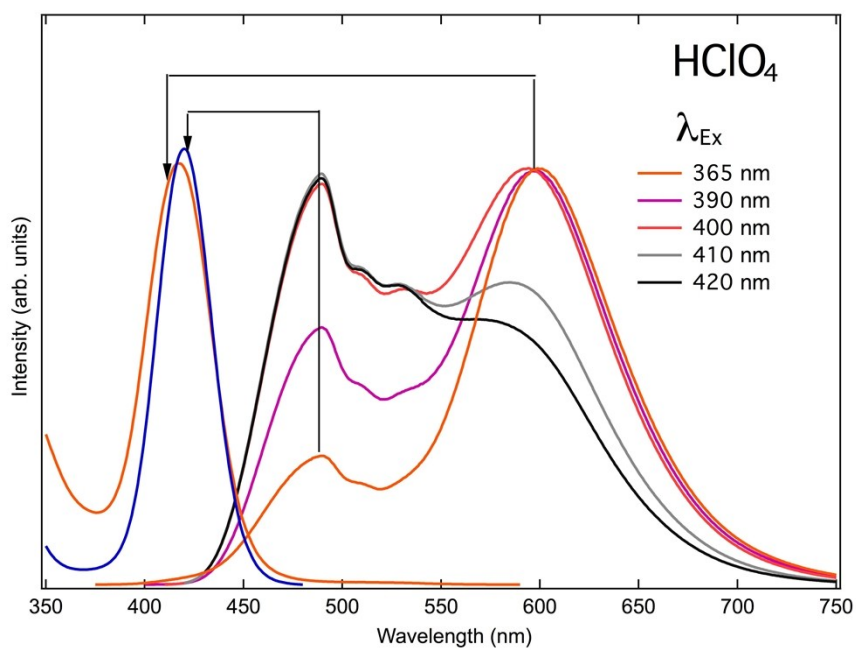


**Fig. S3** Crystal packing views of (a) BTImP and (b) its HCl salt. Hydrogen atoms are omitted for clarity.





**Fig. S4** DFT-calculated HOMO and LUMO of BTImP and the protonated BTImP.

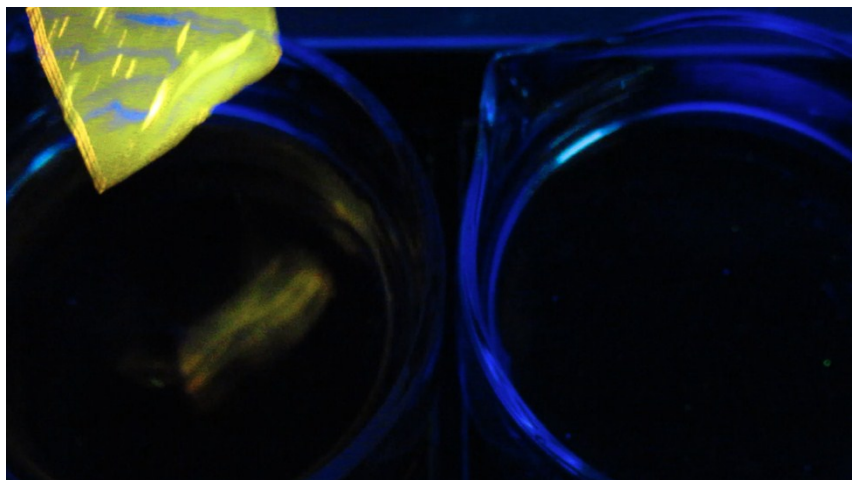


**Fig. S5** Excitation wavelength dependent fluorescence of BTImP in THF-HClO<sub>4</sub> solution. Arrows indicate the excitation spectra for each of the fluorescence peaks.

## References

1. S. Park, O.-H. Kwon, S. Kim, S. Park, M.-G. Choi, M. Cha, S. Y. Park and D.-J. Jang, *J. Am. Chem. Soc.*, 2005, **127**, 10070–10074.
2. L. F. Lindoy, G. V. Meehan and N. Svenstrup, *Synthesis*, 1998, 1029–1032.
3. T. G. Deligeorgiev, *Dyes Pigm.*, 1990, 243–248.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. GAUSSIAN 09W; Gaussian, Inc.; Wallingford CT, 2009.

## Note about the video clip



Left: 1N HCl solution. Right: 1N NaOH solution.