

## **Supporting Information**

# Sterically Induced Polymorphism: ON-OFF Control of Excited-State Intramolecular Proton Transfer (ESIPT) Luminescence of 1-Methyl-2-(2'-Hydroxyphenyl)benzimidazole

Toshihide Shida, Toshiki Mutai\* and Koji Araki\*

*Department of Materials and Environmental Science, Institute of Industrial Science,  
the University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan*

*E-mail: [araki@iis.u-tokyo.ac.jp](mailto:araki@iis.u-tokyo.ac.jp), [mutai@iis.u-tokyo.ac.jp](mailto:mutai@iis.u-tokyo.ac.jp)*

## General procedures

UV-Vis absorption and fluorescence spectra in organic solutions were recorded using a Shimadzu UV-2500PC spectrophotometer and a JASCO FP-6600 spectrofluorophotometer, respectively. Fluorescence quantum yields (excitation wavelength 285 nm) in solution were determined by using 2-aminopyridine ( $\Phi = 0.37$  in ethanol) as a standard. Time-resolved emission decay was recorded using a Hamamatsu Photonics C11367-01 (Quantaaurus-Tau). The fluorescence spectra of solid samples were measured in an ILF-533 integral sphere attached to a JASCO FP-6600 spectrofluorophotometer, and the quantum yields were obtained using calculation software based on the literature method,<sup>1</sup> which was installed in the spectrofluorophotometer.

The repeating ON/OFF cycles shown in the inset of Figure 4 was measured as follows. ON→OFF process: The sample is placed onto a quartz plate with the approximate size of 20 mm x 4 mm, which covered the whole irradiated area by the excitation light. Then heated the quartz plate at 90 °C for 5 min and cooled to the room temperature. OFF→ON process: The sample is ground in a mortar for 5 min, then placed onto a quartz plate with the approximate size of 20 mm x 4 mm.

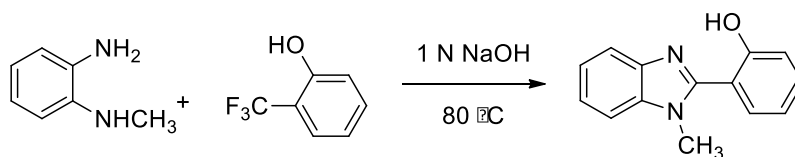
Differential scanning calorimetry (DSC) measurement was carried out on a PerkinElmer Pyris 1 thermal analyzers, respectively. A thermalgravimetric analysis (TG) was measured on a Rigaku ThermoPlus TG 8120 under N<sub>2</sub>.

Powder XRD measurements were conducted on a Rigaku RINT-2100 diffractometer (Cu  $K\alpha$ ) in the range  $0.7^\circ < 2\theta < 40^\circ$ .

The optimized ground-state geometries of HBI, MeHBI and tBuHBI were calculated by the *ab initio* HF method using 6-31G(d) basis set. These calculations were performed using a Gaussian 03W, Gaussian Inc. (Revision C.02) package,<sup>2</sup> and the results were processed on a GaussView 4.1

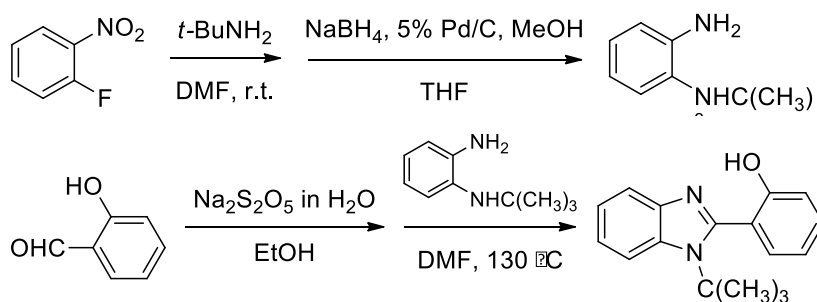
## Synthesis of 1-alkyl-2-(2'-hydroxyphenyl)benzimidazoles

### 1-methyl-2-(2'-hydroxyphenyl)benzimidazole (MeHBI)



To an aqueous NaOH solution (1 M, 30 mL) was added *o*-trifluoromethylphenol (1.67 g, 10.30 mmol) and *N*-methyl-1,2-phenylenediamine (1.37 mL, 12.05 mmol), and heated at 80 °C for 4 h. After cooling, hydrochloric acid (1 M, 30 mL) was added carefully with stirring. The precipitate was filtered off, washed with cold 1 M hydrochloric acid and H<sub>2</sub>O, and dried *in vacuo*. Purification by a silica gel column chromatography (CHCl<sub>3</sub>) to give a white powder (1.77 g, 77%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 11.26 (1H, s), 7.69 (1H, d, *J* = 7.3 Hz), 7.64 (2H, td, *J* = 5.3, 2.6 Hz), 7.42-7.38 (1H, m), 7.32 (1H, td, *J* = 7.6, 1.2 Hz), 7.27 (1H, td, *J* = 11.4, 3.7 Hz), 7.05 (1H, d, *J* = 8.2 Hz), 7.01-6.97 (1H, m), 3.83 (3H, s). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 156.7, 151.8, 141.4, 135.732, 131.4, 130.3, 122.4, 122.0, 119.0, 118.5, 116.5, 115.8, 110.3, 31.7. HRMS (FAB) (M+H)<sup>+</sup> Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: 225.1028, found: 225.1028. Anal. Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O: C, 74.98; H, 5.39; N, 12.49, Found: C, 74.74; H, 5.39; N, 12.51 %. M. p. 165.7–166.3 °C.

1-*tert*-Butyl-2-(2'-hydroxyphenyl)benzimidazole (tBuHBI)



To a dimethylformamide (5 mL) solution of 2-fluoronitrobenzene (2.2 mL, 20.89 mmol) in a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer was dropwise added *t*-butylamine (4.38 mL, 41.38 mmol, 2 eq.), and the mixture was stirred at room temperature over night. After dilution with water, the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , and then evaporated. The residue was applied to a silica gel column (hexane–ethyl acetate 9:1) to give *N*-*tert*-butyl-2-nitroaniline as yellow oil (2.74 g, 68 %). Then, to a cooled anhydrous THF (40 mL) solution of *N*-*tert*-butyl-2-nitroaniline (2.66 g, 13.7 mmol), 5 % Pd/C (360 mg) and  $\text{NaBH}_4$  (800 mg) was dropwise added methanol (20 mL), and stirred for 6 h. The catalyst was filtered off and the filtrate was poured into saturated aqueous solution of ammonium chloride, extracted with ethyl acetate. The organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , evaporated and dried *in vacuo* to give *N*-*tert*-butyl-1,2-diaminobenzene (1.63 g, 72 %).

As the second step of the reaction, sodium bisulfate (1.60 g, 8.5 mmol) in water (5 mL) was added in portions to a solution of salicylaldehyde (1.83 g, 15.0 mmol) in ethanol (50 mL) and the reaction mixture was stirred vigorously. The mixture was cooled to  $0\text{ }^\circ\text{C}$  and kept for several hours. The precipitate was filtered off, dried *in vacuo*, and then dissolved (3.02 g) in DMF (30 mL), to which was added *N*-*tert*-butyl-1,2-diaminobenzene (1.31 g, 8.0 mmol) and heated at  $130\text{ }^\circ\text{C}$  for 4 h. The reaction mixture was cooled to room temperature and poured into water. The precipitate was filtered off and dried *in vacuo* to give the product as white powder (2.08 g, 98 %).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  9.82 (1H, s), 7.82 (1H, dd,  $J = 7.1, 1.6$  Hz), 7.57 (1H, dd,  $J = 7.1, 2.1$  Hz), 7.31–7.16 (4H, m), 6.85–6.89 (2H, m), 1.55 (9H, s).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  155.8, 150.5, 143.3, 134.531, 130.9, 130.4, 123.7, 121.5, 121.0, 119.2, 118.5, 115.1, 114.8, 58.4, 29.7. FAB-MS ( $\text{M}+\text{H}$ ) $^+$  Calcd. for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$ : 267.1, Found: 267.3. Anal. Calcd. for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}$ : C, 76.66; H, 6.81; N, 10.52, Found: C, 76.71; H, 6.87; N, 10.29. M. p. 231.6–232.3.

### X-ray crystallographic analysis

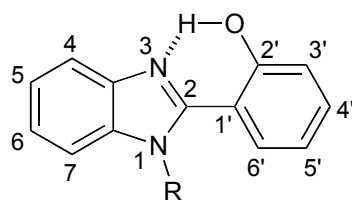
**MeHBI(L)** X-ray diffraction data were collected on a Rigaku Saturn 724 diffractometer equipped with a graphite-monochromatized Mo  $K\alpha$  source ( $\lambda = 0.71070 \text{ \AA}$ ) at 93 K. Data were processed using the CrystalClear program package and corrected for absorption. The structure was solved by direct method SHELXS-97<sup>3</sup> and expanded by subsequent Fourier synthesis. The refinement by full matrix least-squares calculations was performed using SHELXL-97.

**MeHBI(NL)** and **tBuHBI** X-ray diffraction data were collected on a MacScience DIP-Labo with graphite-monochromatized Cu- $K\alpha$  radiation was used. Calculations were performed using maXus<sup>4</sup> crystallographic software package. The crystal structures were solved by direct method using Shelxs-97<sup>3</sup> and the structure refinements were performed by a full-matrix least squares methods using Shelxl-97.

**Table S1.** Crystallographic data and structure refinement summary.<sup>a</sup>

	MeHBI		tBuHBI
	L	NL	
CCDC number <sup>b</sup>	924262	924263	924266
Molecular formula	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O	C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O	C <sub>17</sub> H <sub>18</sub> N <sub>2</sub> O
Molecular weight	224.26	224.26	266.33
Crystal size / mm <sup>3</sup>	0.40 × 0.30 × 0.04	0.53 × 0.15 × 0.13	0.37 × 0.22 × 0.19
Crystal system	Triclinic	Monoclinic	Rhombohedral
Space group	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>R</i> -3
<i>a</i> / Å	7.117(7)	7.516(1)	21.216(1)
<i>b</i> / Å	10.007(8)	15.318(1)	21.216
<i>c</i> / Å	16.788(16)	11.199(1)	17.221(1)
$\alpha$ / deg.	73.45(4)	90.00	90.00
$\beta$ / deg.	85.81(4)	114.615(2)	90.00
$\gamma$ / deg.	74.91(4)	90.00	120.00
<i>V</i> / Å <sup>3</sup>	1106.5(17)	1172.2(2)	6713.0(5)
<i>Z</i>	4	4	18
<i>d</i> <sub>calc.</sub> / g cm <sup>-3</sup>	1.346	1.271	1.186
$\mu$ / mm <sup>-1</sup> .	0.087	0.654	0.587
$\lambda$ / nm	0.71075	1.54184	
Temperature / K	93(2)	298(2)	298(2)
2 $\theta$ <sub>max</sub> / deg.	50.66	73.20	
<i>F</i> <sub>000</sub>	472	472	2556
Measured/independent reflections	6981/3853	10352/2305	21369/2958
<i>N</i> <sub>para</sub>	309	156	185
GOF	1.080	1.093	1.106
<i>R</i> <sub>int</sub>	0.1060	0.066	0.055
<i>R</i> <sub>1</sub>	0.1009	0.0607	0.0624
<i>wR</i> <sub>2</sub> (all data)	0.2949	0.1581	0.1504
Max/min residual electron density	0.627/-0.343	0.214/-0.384	0.185/-0.319

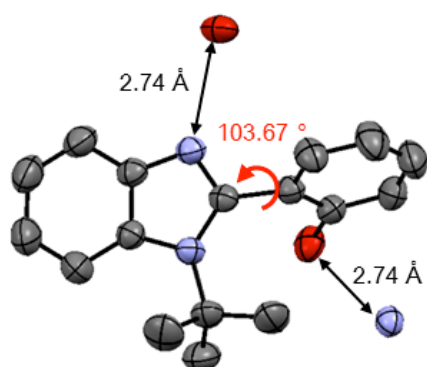
<sup>a,b</sup> These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



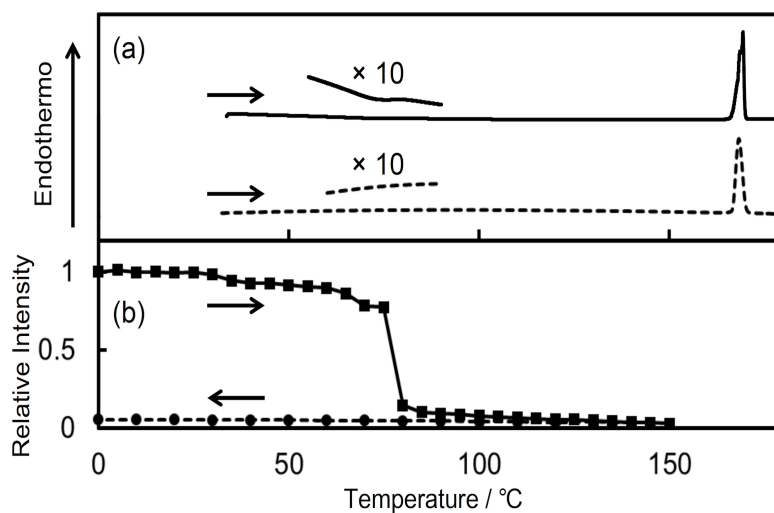
**Figure S1.** Chemical structure and the labeling scheme of HBI derivatives.

**Table S2.** Selected bond lengths and angles of the molecules in crystals.

	<b>MeHBI</b>			<b>tBuHBI</b>
	L <sub>Mol. A</sub>	L <sub>Mol. B</sub>	NL	NL
<b>Bond length / Å</b>				
N3-O (Intramol.)	2.562	2.558	3.869	3.609
N3-O (Intermol.)	4.714	4.750	2.697	2.736
N1-O (Intramol.)	4.208	4.207	3.080	3.204
N1-O (Intermol.)	3.738	3.754	4.870	4.672
O-C2'	1.361	1.356	1.348	1.354
C2'-C1'	1.436	1.425	1.399	1.389
C1'-C2	1.459	1.472	1.471	1.481
C2-N3	1.330	1.322	1.323	1.317
<b>Bond angle / deg.</b>				
N3-O-C2'	87.68	87.70	68.06	68.94
O-C2'-C1'	122.45	122.71	118.29	117.55
C2'-C1'-C2	117.89	117.84	122.10	120.57
C1'-C2-N3	121.67	121.43	124.01	118.38
C2-N3-O	88.43	88.64	31.11	42.15
N1-C2-C1'	125.91	126.18	123.48	128.58
C2-C1'-C6'	125.02	124.28	118.78	119.46
<b>Dihedral angle / deg.</b>				
N3-C2-C1'-C2'	15.27	14.88	126.84	-103.67
N3-C2-C1'-C6'	-164.33	-165.31	-53.27	67.96
N1-C2-C1'-C6'	18.47	16.77	121.44	-115.44
N1-C2-C1'-C2'	-161.95	-163.05	-58.45	72.93



**Figure S2.** ORTEP drawing of tBuHBI molecule in crystal. Thermal ellipsoids drawn at 50% probability level.



**Figure S3.** (a) DSC profiles of the MeHBI crystals, **L** (solid line) and **NL** (dashed line), on heating ( $10\text{ °C min}^{-1}$ ), and (b) relative emission intensities at 470 nm ( $\lambda_{\text{ex}} = 365\text{ nm}$ ) on heating (solid line;  $10\text{ °C min}^{-1}$ ) and cooling (dashed line;  $10\text{ °C min}^{-1}$ ).

## References

1. J. C. De Mello, H. F. Wittmann, R. H. Friend, *Adv. Mater.* **1997**, *9*, 230-232.
2. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.
3. G. M. Sheldrick, SHELX-97, Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
4. S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart and K. Shankland, maXus, Computer Program for the Solution and Refinement of Crystal Structures, Nonius, The Netherlands, MacScience, Japan, The University of Glasgow.