

# Illuminating Metal Ion Sensors – Benzimidazolesulfonamide Metal Complexes

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## **SUPPORTING INFORMATION**

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**General.** Unless otherwise noted, starting materials were purchased from commercial suppliers (Sigma-Aldrich, Alfa Aesar) and were used without further purification.  $^1\text{H}$  NMR spectra were recorded on one of several Varian FT-NMR spectrometers, property of the Department of Chemistry and Biochemistry, University of California San Diego. Mass spectrometry was performed at the Small Molecule Mass Spectrometry Facility in the Department of Chemistry and Biochemistry, University of California San Diego.

The Cu, Ni, and Co TPBI complexes described below were stored in DMSO for ~2 months at room temperature with periodic exposure to light and showed no degradation based on the electronic spectra. However, the  $\text{Zn}(\text{TPBI})_2$  complex was found to degrade under the same conditions. In aqueous solution,  $\text{Zn}(\text{TPBI})_2$  was found to be stable for at least 3 days at room temperature with ambient light exposure.

**Synthesis of 2-(2'-Tosylaminophenyl)benzimidazole.** A solution containing 250 mg (1.20 mmol) of 2-(2-aminophenyl)-benzimidazole and 342 mg (1.79 mmol) of *p*-toluene sulfonyl chloride in 5 mL of pyridine was heated in a microwave reactor at 130 °C for 3 min (Power = 300W). The solution was then poured into 40 mL of water and extracted twice with chloroform. The organic layer was washed twice with a solution of 1M HCl, dried with anhydrous magnesium sulfate, and evaporated to give the product as a pale yellow solid (347 mg, 80%).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ , 400 MHz)  $\delta$  2.21 (s, 3H,  $\text{CH}_3$ ), 6.97 (d,  $J = 8.4$  Hz, 2H, ArH), 7.22 (dt,  $J_1 = 7.6$  Hz,  $J_2 = 0.8$  Hz, 1H, Hph), 7.30 (d,  $J = 3.2$  Hz, 1H, Hbenz), 7.31 (d,  $J = 3.2$  Hz, 1H, Hbenz), 7.40 (m, 1H, Hph), 7.42 (d,  $J = 8.4$  Hz, 2H, ArH), 7.63 (d,  $J = 3.2$  Hz, 1H, Hbenz), 7.64 (d,  $J = 3.2$  Hz, 1H, Hbenz), 7.70 (dd,  $J_1 = 8.0$

Hz,  $J_2 = 0.8$  Hz, 1H, Hph), 7.81 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 1.2$  Hz, 1H, Hph). ESI-MS(+):  $m/z$  364.13 (M+H)<sup>+</sup>.

**Synthesis of Zn(TPBI)<sub>2</sub>.** A solution of 20 mg (0.055 mmol) of TPBI in 3 mL of methanol was added dropwise with stirring to 6.0 mg (0.0275 mmol) of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O dissolved in 2 mL of methanol. The solution was allowed to stir for 1 h at which point Zn(TPBI)<sub>2</sub> was filtered off as a white precipitate. The product was dissolved in a 50:50 mixture of DMF and chloroform and crystallized by vapor diffusion using methanol as the precipitant. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ 8.15 (d, 1H, J = 8.0 Hz), 7.68 (d, 2H, J = 8.0 Hz), 7.61 (d, 1H, J = 8.0 Hz), 7.56 (d, 1H, J = 8.0 Hz), 7.2-7.3 (m, 2H), 7.08 (d, 2H, J = 8.0 Hz), 6.95-7.03 (m, 3H), 2.24 (s, 3H). Anal. Calcd. for C<sub>40</sub>H<sub>34</sub>N<sub>6</sub>O<sub>5</sub>S<sub>2</sub>Zn: C, 59.44%; H, 4.24%; N, 10.40%. Found: C, 59.07%; H, 4.44%; N, 10.39%.

**Synthesis of Ni(TPBI)<sub>2</sub>.** A solution of 20 mg (0.055 mmol) of TPBI in 3 mL of methanol was added dropwise with stirring to 6.8 mg (0.0275 mmol) of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O dissolved in 2 mL of methanol. The solution was allowed to stir for 1 h at which point Ni(TPBI)<sub>2</sub> was filtered off as a green precipitate. The product was dissolved in a 50:50 mixture of DMF and dichloromethane and crystallized by vapor diffusion using diethyl ether as the precipitant. Anal. Calcd. for C<sub>40</sub>H<sub>32</sub>N<sub>6</sub>O<sub>4</sub>S<sub>2</sub>Ni: C, 61.31%; H, 4.12%; N, 10.73%. Found: C, 61.11%; H, 4.10%; N, 11.00%.

**Synthesis of Co(TPBI)<sub>2</sub>.** A solution of 20 mg (0.055 mmol) of TPBI in 3 mL of methanol was added dropwise with stirring to 8.0 mg (0.0275 mmol) of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 2 mL of methanol. The solution was allowed to stir for 1 h before addition of 7.8 μL triethylamine. Co(TPBI)<sub>2</sub> was filtered off as a pink precipitate. The product

was dissolved in a 50:50 mixture of DMF and dichloromethane and crystallized by vapor diffusion using diethyl ether as the non-solvent. Anal. Calcd. for  $C_{40}H_{32}N_6O_4S_2Co$ : C, 61.30%; H, 4.12%; N, 10.73%. Found: C, 61.32%; H, 3.98%; N, 10.56%.

**Synthesis of Cu(TPBI)Cl.** A solution of 20 mg (0.055 mmol) of TPBI in 3 mL of methanol was added dropwise with stirring to 4.6 mg (0.0275 mmol) of  $CuCl_2 \cdot 2H_2O$  dissolved in 2 mL of acetonitrile. 55  $\mu$ L of 1M aqueous NaOH was added and the solution was allowed to stir for 1 h. The solvents were then evaporated and the residue was taken up in a 50:50 mixture of chloroform and acetone, then crystallized by vapor diffusion using diethyl ether as the precipitant. Anal. Calcd. for  $C_{20}H_{16}N_3O_2SCuCl$ : C, 52.06%; H, 3.50%; N, 9.11%. Found: C, 51.61%; H, 3.33%; N, 9.19%.

**Single-Crystal X-ray Diffraction.** Single crystals were mounted on a nylon loop with Paratone oil and placed under a nitrogen cold stream (100 K). Data was collected on a Bruker Apex Platform diffractometer using Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) controlled using the APEX 2.0 software package. A semiempirical method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL suite. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. Imidazole hydrogen atoms in all materials were found via Fourier difference maps and refined isotropically.

**Table S1.** Crystal and Structure Refinement Data for TPBI Complexes.

Compound	Zn(TPBI) <sub>2</sub> ·2CHCl <sub>3</sub>	Ni(TPBI) <sub>2</sub> ·2DMF	Co(TPBI) <sub>2</sub> ·2DMF	Cu(TPBI)Cl
Empirical Formula	C <sub>42</sub> H <sub>34</sub> N <sub>6</sub> O <sub>4</sub> S <sub>2</sub> Cl <sub>6</sub> Zn	C <sub>46</sub> H <sub>44</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Ni	C <sub>46</sub> H <sub>44</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Co	C <sub>20</sub> H <sub>16</sub> N <sub>3</sub> O <sub>2</sub> SClCu
Formula Weight	1028.94	927.72	927.94	461.4
Collection <i>T</i> (K)	100	100	100	100
$\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	C2/c	P-1
<i>a</i> (Å)	16.0240(6)	17.1240(12)	16.926(3)	8.0634(16)
<i>b</i> (Å)	16.9386(6)	16.2677(12)	16.313(3)	8.7327(17)
<i>c</i> (Å)	16.1452(6)	15.5935(11)	15.870(3)	13.168(3)
$\alpha$ (deg)	90	90	90	87.868(3)
$\beta$ (deg)	95.6920(10)	95.1570(10)	94.278(2)	89.634(2)
$\gamma$ (deg)	90	90	90	89.154(2)
<i>V</i> (Å <sup>3</sup> )	4360.6(3)	4326.3(5)	4369.7(12)	926.5(3)
<i>Z</i>	4	4	4	2
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.567	1.424	1.411	1.654
$\mu$ (mm <sup>-1</sup> )	1.077	0.605	0.548	1.458
min/max <i>T</i>	0.6149/0.8134	0.8635/0.8886	0.8529/0.9473	0.7494/0.8923
<i>hkl</i> ranges	-19< <i>h</i> <19	-20< <i>h</i> <20	-22< <i>h</i> <16	-10< <i>h</i> <10
	-20< <i>k</i> <20	-19< <i>k</i> <18	-21< <i>k</i> <21	-11< <i>k</i> <11
	-19< <i>l</i> <19	-18< <i>l</i> <18	-20< <i>l</i> <18	-17< <i>l</i> <17
total reflections	15629	18376	32469	10555
unique reflections	4000	3971	4996	3798
<i>R</i> (int)	0.0251	0.0503	0.0568	0.0448
parameters/restraints	279/0	298/0	278/0	257/0
<i>R</i> <sub>1</sub> (all data)	0.0340	0.0566	0.0852	0.0572
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0307	0.0448	0.0636	0.0427
<i>wR</i> <sub>2</sub> (all data)	0.0837	0.1240	0.1753	0.1125
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0809	0.1157	0.1596	0.1046
max/min residual (e <sup>-</sup> /Å <sup>3</sup> )	0.532/-0.476	0.612/-0.489	1.148/-0.634	0.631/-0.724
G.O.F.	1.007	1.069	1.070	1.065