Supporting Information

Selective Fe^{2+} Ion Recognition Using a Fluorescent Pyridinyl-benzoimidazole-derived Ionophore

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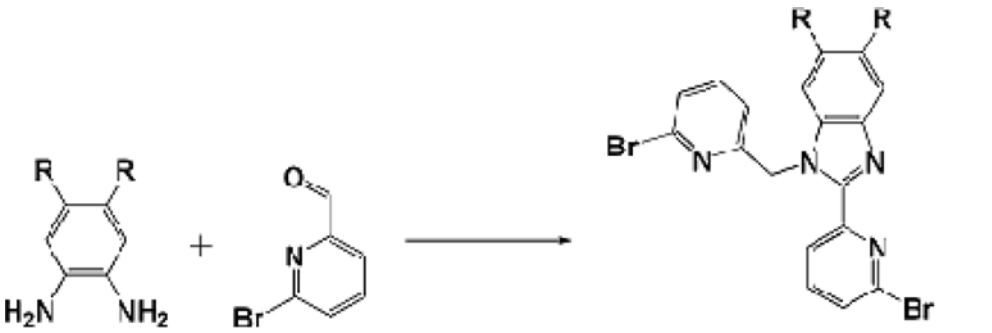
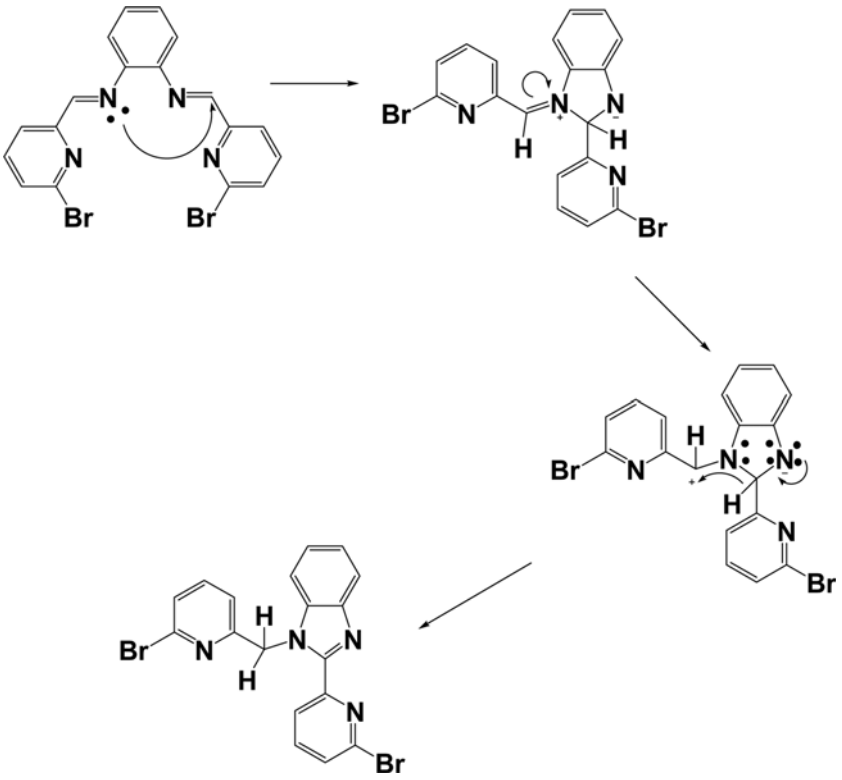


6-Br-ppmbi **for R = H**
6-Br-Me2-ppmbi **for R = CH_3**

Scheme 1



Scheme 2

Table S1. Summary of X-ray Crystallographic Data for **6Br-ppmbi** and **[Cu(6Br-Me2-ppmbi)(NO$_3$)$_2$]**

	6Br-ppmbi	**[Cu(6Br-Me2-ppmbi)(NO$_3$)$_2$]**
Empirical formula	$C_{18}H_{12}Br_2N_4$	$C_{20}H_{16}Br_2N_6CuO_6$
Formula weight	444.14	659.75
Space group	$P\bar{1}$	C2/c
a, Å	8.0316(8)	11.4709(8)
b, Å	9.4623(9)	14.0339(8)
c, Å	12.0952(11)	15.5854(10)
α, deg	71.450(3)	104.777(4)
β, deg	85.303(3)	90.997(3)
γ, deg	77.525(3)	107.114(3)
V, Å^3	841.83(14)	2306.9(3)
Z	2	4
Density (calculated) , g/cm^3	1.752	1.900
T, K	300	296(2)
Absorption coefficient, mm^{-1}	4.821	4.462
Total no. of data	12544	26244
No. of unique data points	3911	8386
No. of parameters	217	635
R1 (%)[a]	4.78	7.62
wR2 (%)[b]	15.47	20.79
Largest diff. peak and hole, e.Å^{-3}	0.504 and -0.893	0.817 and -0.555

[a] $R1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^1$

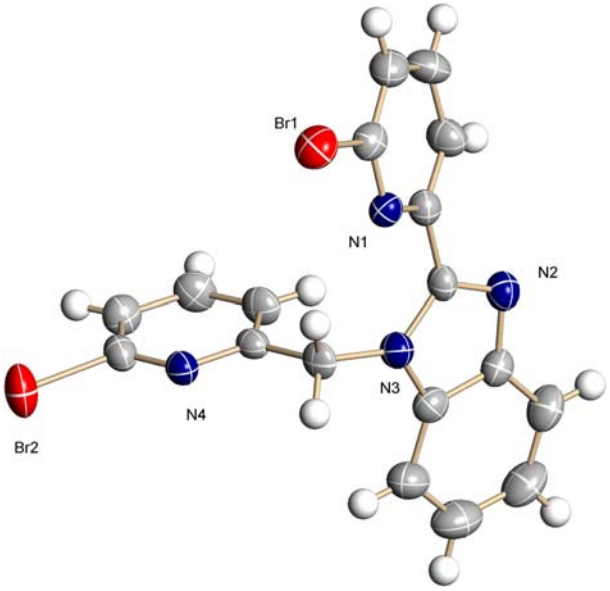


Fig. S1. ORTEP drawing of **6Br-ppmbi**, showing 50% probability thermal ellipsoids. It represents a highly hindered metal binding site composed with 6-bromo pyridine and imidazole motif

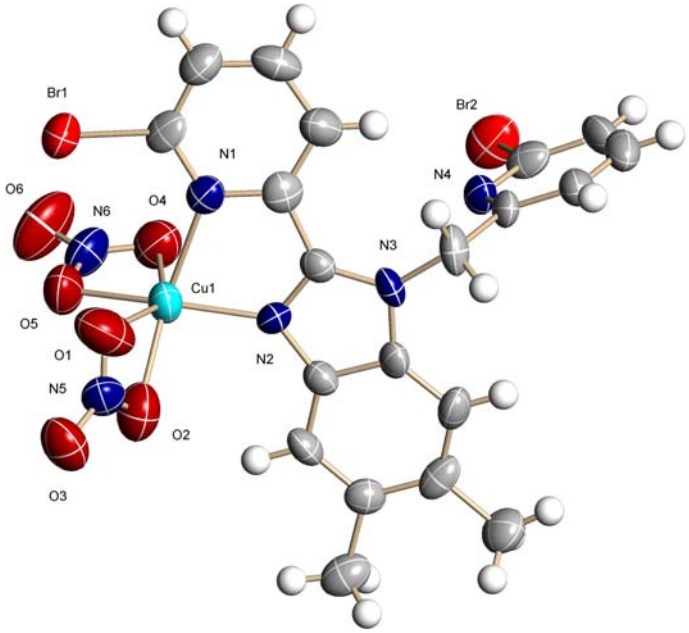


Fig. S2. ORTEP drawing of [Cu(6-Br-Me2-ppmbi)$(NO_3)_2$], showing 50% probability thermal ellipsoids.

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N12 N 0.1728(10) 0.5030(11) 0.2887(8) 0.055(3) Uani 1 1 d . . .
N6 N 0.0487(15) −0.1688(11) 0.1742(9) 0.074(4) Uani 1 1 d . . .
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C7 0.043(9) 0.041(7) 0.046(7) 0.016(6) 0.010(6) 0.010(7)
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C2 0.058(11) 0.074(11) 0.058(9) 0.021(8) 0.009(8) 0.034(9)
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C5 0.057(10) 0.060(9) 0.035(7) 0.010(7) −0.001(6) 0.015(8)
C9 0.035(8) 0.078(11) 0.057(8) 0.029(8) −0.001(6) 0.014(7)
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C25 0.042(9) 0.046(8) 0.040(7) 0.005(6) 0.012(6) 0.011(7)
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C35 0.037(8) 0.056(9) 0.052(8) 0.008(7) 0.011(6) 0.018(7)
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C11 0.058(10) 0.048(8) 0.039(7) 0.014(6) 0.002(7) 0.017(8)
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 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
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 used when they are defined by crystal symmetry.  An approximate (isotropic)
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 F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
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_refine_ls_number_restraints        0
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_refine_ls_R_factor_gt              0.0478
_refine_ls_wR_factor_ref            0.1836
_refine_ls_wR_factor_gt             0.1547
_refine_ls_goodness_of_fit_ref      1.190
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 _atom_site_symmetry_multiplicity
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Br1 Br 0.47384(8) 0.24642(7) 0.46918(5) 0.0541(2) Uani 1 1 d . . .
Br2 Br 1.01440(9) 0.76804(9) 0.53266(5) 0.0617(2) Uani 1 1 d . . .
N1 N 0.6046(5) 0.3855(5) 0.2571(3) 0.0344(9) Uani 1 1 d . . .
N2 N 0.7211(6) 0.5625(5) -0.0379(4) 0.0411(10) Uani 1 1 d . . .
N3 N 0.6816(6) 0.6733(5) 0.1054(3) 0.0386(10) Uani 1 1 d . . .
N4 N 0.8633(5) 0.7161(5) 0.3574(3) 0.0363(9) Uani 1 1 d . . .
C1 C 0.6064(7) 0.2475(6) 0.3315(4) 0.0402(11) Uani 1 1 d . . .
C2 C 0.6945(8) 0.1089(7) 0.3158(5) 0.0486(13) Uani 1 1 d . . .
H2 H 0.6905 0.0156 0.3713 0.058 Uiso 1 1 calc R . .
C3 C 0.7878(9) 0.1150(7) 0.2150(6) 0.0542(15) Uani 1 1 d . . .
H3 H 0.8498 0.0249 0.2007 0.065 Uiso 1 1 calc R . .
C4 C 0.7885(8) 0.2578(7) 0.1345(5) 0.0482(13) Uani 1 1 d . . .
H4 H 0.8510 0.2643 0.0656 0.058 Uiso 1 1 calc R . .
C5 C 0.6947(6) 0.3903(6) 0.1582(4) 0.0374(11) Uani 1 1 d . . .
C6 C 0.6969(6) 0.5420(6) 0.0748(4) 0.0343(10) Uani 1 1 d . . .
C7 C 0.7243(7) 0.7157(6) -0.0856(4) 0.0384(11) Uani 1 1 d . . .
C8 C 0.7468(8) 0.8008(8) -0.2013(5) 0.0528(15) Uani 1 1 d . . .
H8 H 0.7591 0.7566 -0.2610 0.063 Uiso 1 1 calc R . .
C9 C 0.7501(9) 0.9520(8) -0.2238(6) 0.0614(17) Uani 1 1 d . . .
H9 H 0.7643 1.0109 -0.3002 0.074 Uiso 1 1 calc R . .
C10 C 0.7326(9) 1.0194(8) -0.1345(6) 0.0652(18) Uani 1 1 d . . .
H10 H 0.7366 1.1216 -0.1530 0.078 Uiso 1 1 calc R . .
C11 C 0.7094(8) 0.9375(7) -0.0192(6) 0.0540(15) Uani 1 1 d . . .
H11 H 0.6980 0.9818 0.0403 0.065 Uiso 1 1 calc R . .
C12 C 0.7042(7) 0.7861(6) 0.0021(5) 0.0397(11) Uani 1 1 d . . .
C13 C 0.6827(6) 0.6906(6) 0.2208(4) 0.0370(11) Uani 1 1 d . . .
H13A H 0.6294 0.6155 0.2759 0.044 Uiso 1 1 calc R . .
H13B H 0.6141 0.7921 0.2189 0.044 Uiso 1 1 calc R . .
C14 C 0.8621(6) 0.6699(5) 0.2626(4) 0.0333(10) Uani 1 1 d . . .
C15 C 1.0118(7) 0.6075(6) 0.2125(5) 0.0430(12) Uani 1 1 d . . .
H15 H 1.0074 0.5781 0.1466 0.052 Uiso 1 1 calc R . .
C16 C 1.1678(7) 0.5894(7) 0.2616(5) 0.0486(13) Uani 1 1 d . . .
H16 H 1.2700 0.5478 0.2288 0.058 Uiso 1 1 calc R . .
C17 C 1.1717(7) 0.6332(7) 0.3596(5) 0.0460(13) Uani 1 1 d . . .
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H17 H 1.2749 0.6208 0.3955 0.055 Uiso 1 1 calc R . .
C18 C 1.0163(7) 0.6959(6) 0.4014(4) 0.0404(12) Uani 1 1 d . . .

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 _atom_site_aniso_U_33
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Br1 0.0595(4) 0.0588(4) 0.0395(3) -0.0075(3) 0.0090(3) -0.0194(3)
Br2 0.0590(4) 0.0906(5) 0.0508(4) -0.0387(4) -0.0028(3) -0.0226(4)
N1 0.033(2) 0.038(2) 0.030(2) -0.0100(16) 0.0024(16) -0.0061(17)
N2 0.046(3) 0.046(3) 0.034(2) -0.0137(19) 0.0012(18) -0.015(2)
N3 0.045(2) 0.041(2) 0.031(2) -0.0134(18) 0.0028(18) -0.010(2)
N4 0.041(2) 0.037(2) 0.033(2) -0.0132(17) 0.0005(17) -0.0096(18)
C1 0.035(3) 0.046(3) 0.039(3) -0.011(2) -0.001(2) -0.012(2)
C2 0.055(3) 0.043(3) 0.048(3) -0.010(2) -0.002(3) -0.017(3)
C3 0.062(4) 0.036(3) 0.066(4) -0.019(3) 0.000(3) -0.010(3)
C4 0.056(4) 0.047(3) 0.045(3) -0.020(3) 0.008(3) -0.013(3)
C5 0.036(3) 0.042(3) 0.036(3) -0.015(2) -0.001(2) -0.008(2)
C6 0.034(2) 0.042(3) 0.029(2) -0.016(2) 0.0005(19) -0.007(2)
C7 0.035(3) 0.045(3) 0.033(2) -0.009(2) -0.002(2) -0.010(2)
C8 0.054(4) 0.069(4) 0.032(3) -0.009(3) 0.001(2) -0.018(3)
C9 0.059(4) 0.066(4) 0.045(3) 0.004(3) 0.000(3) -0.018(3)
C10 0.062(4) 0.047(4) 0.075(5) -0.001(3) -0.002(3) -0.016(3)
C11 0.059(4) 0.044(3) 0.058(4) -0.013(3) -0.002(3) -0.013(3)
C12 0.035(3) 0.041(3) 0.040(3) -0.010(2) -0.002(2) -0.006(2)
C13 0.039(3) 0.045(3) 0.029(2) -0.021(2) 0.010(2) -0.008(2)
C14 0.042(3) 0.029(2) 0.029(2) -0.0090(18) 0.003(2) -0.010(2)
C15 0.048(3) 0.045(3) 0.038(3) -0.021(2) 0.010(2) -0.007(2)
C16 0.039(3) 0.051(3) 0.056(3) -0.023(3) 0.008(2) -0.007(3)
C17 0.036(3) 0.051(3) 0.051(3) -0.017(3) 0.001(2) -0.010(2)
C18 0.050(3) 0.042(3) 0.035(3) -0.014(2) 0.001(2) -0.018(2)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

loop_
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Br2 C18 1.915(5) . ?
N1 C1 1.326(6) . ?
N1 C5 1.340(6) . ?
N2 C6 1.320(6) . ?
N2 C7 1.386(7) . ?
N3 C6 1.378(6) . ?
N3 C12 1.396(6) . ?
N3 C13 1.457(6) . ?
N4 C18 1.323(7) . ?
N4 C14 1.353(6) . ?
C1 C2 1.383(8) . ?
C2 C3 1.371(9) . ?
C3 C4 1.393(8) . ?
C4 C5 1.388(8) . ?
C5 C6 1.473(7) . ?
C7 C8 1.399(7) . ?
C7 C12 1.401(8) . ?
C8 C9 1.376(10) . ?
C9 C10 1.399(10) . ?
C10 C11 1.387(9) . ?
C11 C12 1.384(8) . ?
C13 C14 1.511(7) . ?
C14 C15 1.379(7) . ?
C15 C16 1.377(8) . ?
C16 C17 1.380(8) . ?
C17 C18 1.367(8) . ?

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  _geom_angle_site_symmetry_3
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C1 N1 C5 117.0(4) . . ?
C6 N2 C7 104.9(4) . . ?
C6 N3 C12 105.5(4) . . ?
C6 N3 C13 129.3(4) . . ?
C12 N3 C13 123.7(4) . . ?
C18 N4 C14 116.4(4) . . ?
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```
N1 C1 C2 125.4(5) . . ?
N1 C1 Br1 115.5(4) . . ?
C2 C1 Br1 119.1(4) . . ?
C3 C2 C1 117.2(5) . . ?
C2 C3 C4 119.1(6) . . ?
C5 C4 C3 119.2(5) . . ?
N1 C5 C4 122.1(5) . . ?
N1 C5 C6 118.2(4) . . ?
C4 C5 C6 119.7(5) . . ?
N2 C6 N3 113.6(4) . . ?
N2 C6 C5 121.9(4) . . ?
N3 C6 C5 124.5(4) . . ?
N2 C7 C8 130.1(5) . . ?
N2 C7 C12 110.2(4) . . ?
C8 C7 C12 119.7(5) . . ?
C9 C8 C7 117.7(6) . . ?
C8 C9 C10 121.6(6) . . ?
C11 C10 C9 121.7(6) . . ?
C12 C11 C10 116.2(6) . . ?
C11 C12 N3 131.2(5) . . ?
C11 C12 C7 123.0(5) . . ?
N3 C12 C7 105.7(5) . . ?
N3 C13 C14 112.8(4) . . ?
N4 C14 C15 122.2(5) . . ?
N4 C14 C13 113.2(4) . . ?
C15 C14 C13 124.6(4) . . ?
C16 C15 C14 119.0(5) . . ?
C15 C16 C17 119.7(5) . . ?
C18 C17 C16 116.7(5) . . ?
N4 C18 C17 125.9(5) . . ?
N4 C18 Br2 115.5(4) . . ?
C17 C18 Br2 118.5(4) . . ?

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