

SUPPLEMENTARY MATERIAL TO
**Synthesis and spectral characterization of
1,2-bis(5-methyl/chloro-1*H*-benzimidazol-2-yl)ethanols and
their Co(II), Pd(II) and Zn(II) complexes**

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*1,2-Bis(5-methyl-1*H*-benzimidazol-2-yl)ethanol (1)*. Yield: 2.17 g, 71 %; colourless solid; m.p.: 190 °C (decomp.); Anal. Calcd. for C₁₈H₁₈N₄O (FW: 306.36): C, 70.57; H, 5.92; N, 18.29 %. Found: C, 70.26; H, 5.81; N, 18.02 %; Mid- and far-IR (ATR, cm⁻¹): 3120*m,br*, 3033*m,br*, 2923*m*, 2860*m*, 2733*m,br*, 1631*m*, 1594*w*, 1537*m*, 1447*s*, 1409*m*, 1307*m*, 1279*m*, 1224*m*, 1089*m*, 1048*m*, 1020*m*, 856*m*, 794*s*, 597*m*, 430*m*, 410*m*, 374*m*, 253*m*. Raman (cm⁻¹): 3059*m*, 2925*m*, 2861*w*, 1645*w*, 1589*m*, 1539*m*, 1442*m*, 1376*w*, 1276*s*, 1129*w*, 1021*w*, 944*w*, 882*w*, 759*m*, 597*w*, 439*w*, 300*w*, 200*w*. ¹H-NMR (500 MHz, DMSO-*d*₆, δ / ppm): 12.17 (2H, *brs*, exchangeable with D₂O, NH & NH'), 7.26 (2H, *brs*, H4 & H7), 6.92 (1H, *brs*, H6), 6.13 (1H, *brs*, exchangeable with D₂O, OH), 5.32 (1H, *brs*, CH–OH), 3.33 (2H, *brs*, splits into two broad singlets after D₂O: 3.49, *brs*, & 3.67, *brs*, CH₂), 2.36 (3H, *s*, CH₃); ¹³C-NMR (APT, 125 MHz, DMSO-*d*₆, δ / ppm): quaternary carbons: 157.0 (C2), 152.6 (C2'), 141.1 (C9+C9'), 138.2 (C8+C8'), 131.5 (C5+C5'); H-bonded carbons (CHs): 123.2, 122.4, 67.2 (C–OH); 36.7 (CH₂); 22.0 (CH₃). Fluorescence spectra (EtOH, *c* = 1×10⁻⁴ mol L⁻¹, λ_{max} / nm): 406*m,br*, 428*m*, 456*sh*. ESI-MS (*m/z*): 307.2 ([M+1]⁺, 100), 308.5 ([M+2]⁺, 32.2), 310.0 ([M+4]⁺, 7.5), 289.5 ([M–OH–1]⁺, 10.4).

*1,2-Bis(5-chloro-1*H*-benzimidazol-2-yl)ethanol (2)*. Yield: 2.05 g 59 %; colourless solid; m.p.: 212 °C (decomp.); Anal. Calcd. for C₁₆H₁₂Cl₂N₄O (FW: 347.20): C, 55.35; H, 3.48; N, 16.14 %. Found: C, 55.26; H 3.31; N, 16.11 %; Mid- and far-IR (ATR, cm⁻¹): 3145*m,br*, 3046*m,br*, 2986*w*, 1623*w*, 1585*w*, 1542*w*, 1473*m*, 1444*m*, 1414*m*, 1300*w*, 1086*s*, 1024*s*, 927*m*, 848*m*, 803*m*, 599*m*, 561*s*, 537*m*, 475*w*, 423*w*, 390*m*, 272*m*, 175*m*, 132*m*. Raman (cm⁻¹): 3085*m*, 2943*m*, 2900*w*, 1584*m*, 1539*m*, 1469*w*, 1291*w*, 1276*w*, 1056*m*, 998*w*, 960*w*,

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886w, 805w, 705w. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ / ppm): 12.57 (1H, *brs*, exchangeable with D_2O , NH'), 12.50 (1H, *brs*, exchangeable with D_2O , NH), 7.56 (1H, *brm*, H7), 7.53 (1H, *s*, H4), 7.14 (1H, *brd*, $J = 8.3$ Hz, H6), 6.25 (1H, *s*, exchangeable with D_2O , OH), 5.37 (1H, *dd*, $J = 8.3$ & 4.9 Hz, CH-OH), 3.55 (2H, *dd*, $J = 14.9$ & 4.9 Hz, CH_2); $^{13}\text{C-NMR}$ (125 MHz, APT, $\text{DMSO-}d_6$, δ / ppm): quaternary carbons: 159.2 (C2), 154.6 (C2'), 144.7 (C9), 142.7 (C9'), 135.7 (C8), 133.8 (C8'), 126.9 (C5), 126.1 (C5'); H-bonded carbons (CHs): 122.7, 120.6, 118.8, 113.5, 112.9, 111.5, 67.0 (C-OH); 36.8 (CH_2). Fluorescence spectra (EtOH , $c = 1 \times 10^{-4}$ mol L^{-1} , λ_{max} / nm): 401*m,br*, 423*m*, 451*sh*. ESI-MS (m/z): 347.3 ($[\text{M}]^+$, 100), 348.3 ($[\text{M}+1]^+$, 16.7), 349.2 ($[\text{M}+2]^+$, 61.7), 350.3 ($[\text{M}+3]^+$, 11.7), 351.2 ($[\text{M}+4]^+$, 11.4), 369.1 ($[\text{M}+23(\text{Na})-1]^+$, 17.1), 313.4 ($[(\text{M}-\text{Cl})+1]^+$, 6.8), 279.3 ($[(\text{M}-2\text{Cl})+1]^+$, 3.2).

$[\text{Co}(\mathbf{1})_2(\text{H}_2\text{O})]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**1a**). Yield: 0.188 g, 93 %; purple–blue solid; m.p.: 253 °C (decomp.); Anal. Calcd. for $\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{N}_8\text{O}_4\text{Co}$ (FW: 778.61): C, 55.53; H, 5.18; N, 14.39 %. Found: C, 54.96; H, 5.05; N 14.03 %; Mid- and far-IR (ATR, cm^{-1}): 3112*m,br*, 3036*m,br*, 2918*m*, 1630*m,br*, 1597*m,br*, 1538*m,br*, 1455*s*, 1416*m*, 1320*m*, 1283*m*, 1224*m*, 1075*m*, 1056*m*, 864*m*, 802*s*, 597*m*, 478*w*, 432*m*, 429*m*, 413*m*, 372*w*, 122*s*. Raman (cm^{-1}): 3055*m*, 2923*m*, 2865*w*, 1648*w*, 1594*m*, 1539*s*, 1460*m*, 1379*w*, 1283*s*, 1142*w*, 1081*w*, 942*w*, 763*m*, 506*w*, 451*w*, 242*w*, 175*m*. Fluorescence spectra (EtOH , $c = 1 \times 10^{-4}$ mol L^{-1} , λ_{max} / nm): 405*m,br*, 428*m,br*, 456*sh*. ESI-MS (m/z): 307.2 ($[\text{M}_L+1]^+$, 100), 670.2 ($[(2\text{L}+\text{Co})-1]^+$, 26.9), 705.8 ($[(2\text{L}+\text{Co}+\text{Cl})-1]^+$, 16.3), 764.0 ($[(\text{M}-\text{H}_2\text{O})+3]^+$, 5.3); A_M (DMF , 25 °C, $\text{S m}^2 \text{mol}^{-1}$): 86; Magnetic moment, μ_{eff} : 4.47 μ_B .

$[\text{Pd}(\mathbf{1})\text{Cl}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**1b**). Yield: 0.180 g, 71 %; slightly khaki solid; m.p.: >350 °C (decomp.); Anal. Calcd. for $\text{C}_{36}\text{H}_{40}\text{Cl}_4\text{N}_8\text{O}_4\text{Pd}_2$ (FW: 1003.41): C, 43.09; H, 4.02; N, 11.17 %. Found: C, 42.93; H, 4.44; N, 10.89 %; Mid- and far-IR (ATR, cm^{-1}): 3353*m,br*, 3303*m,br*, 3227*s,br*, 3087*w*, 2923*m*, 1662*w*, 1631*m*, 1600*m*, 1537*m*, 1469*s*, 1285*m*, 1250*m*, 1170*m*, 1075*m*, 1054*m*, 857*m*, 803*s*, 674*m*, 597*m*, 413*m*, 295*m,br*, 271*s*, 134*s*. Raman (cm^{-1}): 3058*m*, 2926*m*, 1598*m*, 1544*s*, 1451*m*, 1381*w*, 1288*s*, 1230*w*, 1056*w*, 1002*w*, 956*w*, 890*w*, 762*m*, 650*w*, 465*w*, 213*w*. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ / ppm): 13.47 (2H, *brs*, exchangeable with D_2O , NH & NH'), 8.73 (1H, *brs*, H7), 8.06 (1H, *brs*, H4), 7.24 (1H, *brs*, H6), 7.22 (*brs*, 1H, exchangeable with D_2O , OH), 6.77 (1H, *brs*, CH-OH), 4.77 (2H, *brs*, CH_2), 2.47 (3H, *s*, CH_3). $^{13}\text{C-NMR}$ (125 MHz, APT, $\text{DMSO-}d_6$, δ / ppm): quaternary carbons: 155.4 (C2), 150.5 (C2'), 140.2 (C9), 138.3 (C9'), 134.1 (C8), 133.0 (C8'), 132.5 (C5'), 131.2 (C5); H-bonded carbons (CHs): 125.9, 125.1, 119.4, 112.7, 112.2, 64.8 (C-OH); 35.3 (CH_2); 19.0 (CH_3). Fluorescence spectra (EtOH , $c = 1 \times 10^{-4}$ mol L^{-1} , λ_{max} / nm): 373*w*, 393*w*. ESI-MS (m/z): 481.0 ($[(\text{M}/2-\text{H}_2\text{O})-3]^+$, 100), 479.0 ($[(\text{M}/2-\text{H}_2\text{O})-4]^+$, 82.6), 477.9 ($[(\text{M}/2-\text{H}_2\text{O})-6]^+$, 69.1), 482.9 ($[(\text{M}/2-\text{H}_2\text{O})-1]^+$, 48.7), 480.0 ($[(\text{M}/2-\text{H}_2\text{O})-3]^+$, 42.1), 476.8 ($[(\text{M}/2-\text{H}_2\text{O})-5]^+$, 21.6), 481.9 ($[(\text{M}/2-\text{H}_2\text{O})-2]^+$, 19.5), 484.9

($[(M/2-H_2O)+1]^+$, 12.1), 307.1 (M_L , 6.1), 717.1 ($[M-PdCl_2]^+$, 11.25), 964.02 ($[M-2H_2O-3]^+$, 6.21); A_M (DMF, 25 °C, S m² mol⁻¹): 123.

$[Zn(I)Cl_2] \cdot 2H_2O$ (**1c**). Yield: 0.235 g, 88 %; colourless solid; m.p.: 309 °C (decomp.); Anal. Calcd. for C₁₈H₂₂Cl₂N₄O₃Zn (FW: 478.71): C, 45.16; H, 4.63; N, 11.70 %. Found: C, 44.63; H, 3.76; N, 11.13 %; Mid- and far-IR (ATR, cm⁻¹): 3298*m,br*, 3218*m,br*, 3059*m,br*, 2921*m*, 1627*m*, 1597*m*, 1537*m*, 1463*s*, 1416*m*, 1303*m*, 1228*m*, 1075*m*, 1046*s*, 861*m*, 798*s*, 669*m*, 596*m*, 550*m*, 421*m*, 320*s,br*, 178*m*, 142*m*, 114*m*. Raman (cm⁻¹): 3065*m*, 2960*w*, 2922*s*, 2867*w*, 1629*w*, 1598*m*, 1532*s*, 1470*w*, 1424*w*, 1377*w*, 1293*s*, 1231*w*, 1138*w*, 1064*w*, 1018*w*, 948*w*, 871*w*, 770*m*, 325*m*, 290*w*, 182*m*. ¹H-NMR (500 MHz, DMSO-*d*₆, δ / ppm): 13.43 (2H, *brs*, exchangeable with D₂O, NH & NH'), 8.08 (1H, *brs*, H7), 7.44 (1H, *brs*, H4), 7.21 (1H, *dd*, $J = 7.0$ & 4.2 Hz, H6), 6.93 (1H, *s*, exchangeable with D₂O, OH), 5.51 (1H, *d*, $J = 8.3$ Hz, CH-OH), 3.82 (1H, *dd*, $J_1 = 15.6$ Hz, $J_2 = 9.3$ Hz, CH₂), 3.64 (1H, *dd*, $J = 15.6$ & 3.82 Hz, CH₂), 2.46 (3H, *s*, CH₃); ¹³C-NMR (125 MHz, APT, DMSO-*d*₆, δ / ppm): quaternary carbons: 158.2 (C2), 152.8 (C2'), 140.7 (C9), 138.3 (C9'), 134.1 (C8), 133.1 (C8'), 131.0 (C5); H-bonded carbons (CHs): 126.3, 125.2, 118.5, 112.7, 64.7 (C-OH), 35.5 (CH₂), 22.0 (CH₃). Fluorescence spectra (EtOH, $c = 1 \times 10^{-4}$ mol L⁻¹, λ_{max} / nm): 375*w*, 421*sh*, 442*m,br*. ESI-MS (m/z): 307.3 ($[M_L+1]^+$, 100), 405.3 ($[(L+ZnCl)-2]^+$, 99.6), 848.9 ($[(2L+2Zn+3Cl)-1]^+$, 66.3), 409.3 ($[(L+ZnCl)+2]^+$, 65.0), 713.2 ($[2L+ZnCl]^+$, 51.3), 813.1 ($[(2L+2Zn+2Cl)-1]^+$, 25.0), 441.3 ($[M-(2H_2O)-1]^+$, 8.9); A_M (DMF, 25 °C, S m² mol⁻¹): 9.0.

$[Co(2)_2]Cl_2 \cdot 2H_2O$ (**2a**). Yield: 0.186 g, 85 %; purple solid; m.p.: 222 °C (decomp.); Anal. Calcd. for C₃₂H₂₈Cl₆N₈O₄Co (FW: 860.30): C, 44.68; H, 3.28; N, 13.03 %. Found: C, 44.09; H, 3.43; N, 12.82 %; Mid- and far-IR (ATR, cm⁻¹): 3102*m,br*, 3036*m,br*, 2891*m*, 1624*m*, 1590*m*, 1531*m*, 1446*s*, 1409*m*, 1320*m*, 1280*m*, 1215*m*, 1072*m*, 1049*s*, 931*m*, 855*m*, 801*s*, 709*m*, 597*m*, 541*m*, 476*m*, 423*m*, 367*m*, 288*m*, 258*m*, 198*m*, 122*m*. Raman (cm⁻¹): 3071*m*, 2922*m*, 1590*m*, 1530*s*, 1450*m*, 1427*m*, 1334*s*, 1276*s*, 1231*m*, 1064*m*, 708*w*, 220*w*, 150*m*. Fluorescence spectra (EtOH, $c = 1 \times 10^{-4}$ mol L⁻¹, λ_{max} / nm): 399*m,br*, 424*m,br*, 453*sh*. ESI-MS (m/z): 347.3 ($[M_L+1]^+$, 100), 349.2 ($[M_L+2]^+$, 64.0), 381.1 ($[M_L+23+1]^+$, 38.3), 408.1 ($[(L+Co)+2]^+$, 16.1), 752.0 ($[(2L+Co)-1]^+$, 4.8), 476.0 ($[(L+CoCl_2)-1]^+$, 4.2); A_M (DMF, 25 °C, S m² mol⁻¹): 105; magnetic moment, μ_{eff} (μ_B): 4.05.

$[Pd(2)Cl]_2Cl_2 \cdot 2H_2O$ (**2b**). Yield: 0.219 g, 89 %; soil-coloured solid; m.p.: >350 °C (decomp.); Anal. Calcd. for C₃₂H₂₈Cl₈N₈O₄Pd₂ (FW: 1085.08): C, 35.42; H, 2.60; N, 10.33 %. Found: C, 35.13; H, 2.86; N, 9.97 %; Mid- and far-IR (ATR, cm⁻¹): 3393*m,br*, 3189*m,br*, 3053*m,br*, 1624*m*, 1590*m*, 1534*m*, 1448*m*, 1406*m*, 1307*m*, 1247*m*, 1184*m*, 1082*m*, 1046*m*, 947*m*, 854*m*, 805*s*, 713*m*, 597*m*, 470*m*, 415*m*, 345*m*, 296*s*, 223*s,br*, 129*s,br*. Raman (cm⁻¹): 3078*w*, 2931*w*, 1590*w*, 1526*m*, 1457*w*, 1422*w*, 1282*w*, 1228*w*, 1073*w*, 987*w*, 875*w*,

790w, 712w, 506w, 386w, 234w. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ / ppm): 13.77 (1H, *brd*, $J = 11.2$ Hz, exchangeable with D_2O , NH'), 13.71 (1H, *brd*, $J = 9.8$ Hz, exchangeable with D_2O , NH), 8.19 (1H, *m*, H7), 7.70 (1H, *m*, H4), 7.49 (1H, *m*, H6), 7.17 (1H, *s,br*, exchangeable with D_2O , OH), 6.65 (1H, *s*, CH-OH), 4.73 (1H, *d*, $J = 4.9$ Hz, CH_2), 4.69 (1H, *dd*, $J_1 = 4.9$ Hz, $J_2 = 2.4$ Hz, CH_2). $^{13}\text{C-NMR}$ (APT, 125 MHz, $\text{DMSO-}d_6$, δ / ppm): quaternary carbons: 157.4 (C2), 152.8 (C2'), 140.9 (C9), 138.8 (C9'), 133.8 (C8), 132.0 (C8'), 129.0 (C5), 127.8 (C5'); H-bonded carbons (CHs): 124.7, 123.7, 121.4, 119.4, 114.8, 112.8; 64.6 (C-OH); 35.1 (CH_2). Fluorescence spectra (EtOH , $c = 1 \times 10^{-4}$ mol L^{-1} , λ_{max} / nm): 375w,*br*, 393m, 461m,*br*. ESI-MS (m/z): 520.9 ($[(\text{M}/2-\text{H}_2\text{O})-4]^+$, 100), 519.9 ($[(\text{M}/2-\text{H}_2\text{O})-5]^+$, 62.8), 522.9 ($[(\text{M}/2-\text{H}_2\text{O})-2]^+$, 62.7), 518.9 ($[(\text{M}/2-\text{H}_2\text{O})-6]^+$, 60.1), 522.1 ($[(\text{M}/2-\text{H}_2\text{O})-3]^+$, 40.5), 524.9 ($[(\text{M}/2-\text{H}_2\text{O})]^+$, 28.2), 508.5 ($[(\text{M}/2-\text{H}_2\text{O}-\text{OH})]^+$, 21.6), 712.9 ($2\text{L}+\text{H}_2\text{O}$, 28), 347.3 (M_L , 8.2), 1046.5 ($[\text{M}-2\text{H}_2\text{O}-3]^+$). Λ_M (DMF , 25 °C, $\text{S m}^2 \text{mol}^{-1}$): 122.

$[\text{Zn}(2)\text{Cl}_2]$ (**2c**). Yield: 0.204 g, 94 %; slightly yellow solid; m.p.: >350 °C (decomp.); Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{Cl}_4\text{N}_4\text{OZn}$ (FW: 483.51): C, 39.74; H, 2.50; N, 11.59 %. Found: C, 40.33; H, 2.65; N, 11.70 %; Mid- and far-IR (ATR, cm^{-1}): 3189m,*br*, 3109m,*br*, 3043m,*br*, 2897m, 1624m, 1594m, 1535m, 1449s, 1429m, 1300m, 1223m, 1194m, 1046s, 931m, 851m, 801s, 716m, 597m, 419m, 319m,*br*, 254m, 205m, 173m, 133m, 107s. Raman (cm^{-1}): 3076m, 2922m, 1629w, 1590m, 1536m, 1428m, 1355w, 1285m, 1246w, 1130w, 1067m, 940w, 716m, 325m, 299m, 167w. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$, δ / ppm): 13.68 (2H, *brs*, exchangeable with D_2O , NH & NH'), 7.90 (2H, *brs*, H4 & H7), 7.41 (1H, *m*, H6), 6.94 (1H, *s*, exchangeable with D_2O , OH), 5.55 (1H, *d*, $J = 7.3$ Hz, CH-OH), 3.85 (2H, *dd*, $J_1 = 16.0$ Hz, $J_2 = 9.0$ Hz, CH_2), 3.66 (2H, *d*, $J = 14.6$ Hz, CH_2). $^{13}\text{C-NMR}$ (APT, 125 MHz, $\text{DMSO-}d_6$, δ / ppm): quaternary carbons: 159.9 (C2), 154.8 (C2'), 137.7 (C9 & C9'), 133.5 (C8 & C8'), 128.4 (C5), 124.5 (C5'); H-bonded carbons (CHs): 124.3, 122.3, 64.8 (C-OH); 35.4, (CH_2). Fluorescence spectra (EtOH , $c = 1 \times 10^{-4}$ mol L^{-1} , λ_{max} / nm): 394w,*br*, 425w,*br*, 453sh; ESI-MS (m/z): 815.1 ($[2\text{M}-\text{ZnCl}_2-\text{OH}]^+$, 100), 837.8 ($[(2\text{M}-\text{ZnCl}_2-\text{OH})+\text{Na}]^+$, 44), 723.9 ($[(2\text{L}+\text{Na})+6]^+$, 42.2), 827.1 ($[2\text{M}-\text{ZnCl}_2-4]^+$, 30.7), 714.2 ($[(2\text{L}+\text{Na})-3]^+$, 12.7), 347.7 ($[\text{M}_\text{L}]^+$, 16.9), 477.8 ($[\text{M}-6]^+$, 11.1). Λ_M (DMF , 25 °C, $\text{S m}^2 \text{mol}^{-1}$): 6.0.

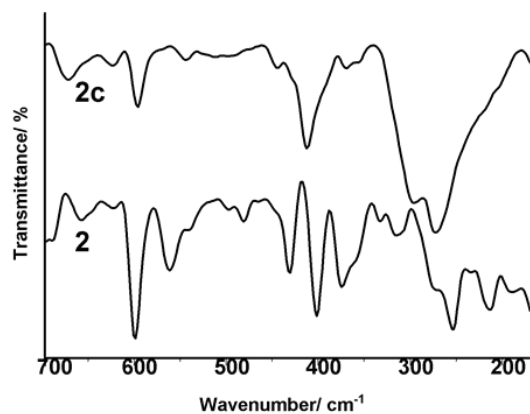


Fig. S-1. Far IR spectra of **2** and $[\text{Zn}(\mathbf{2})\text{Cl}_2]$ (**2c**) in the 100–700 cm^{-1} range.

TABLE S-I. TGA data (mass loss, %) of the complexes (thermal decomposition)

Complex	Temperature, °C												
	100	150	200	250	300	350	400	450	500	550	600	650	700
1a	2.9	5.0	5.3	8.4	11.1	12.8	14.5	17.6	34.6	63.2	85.3	86.2	86.1
1b	2.8	4.2	4.9	5.6	6.8	8.2	10.9	56.1	71.8	73.1	74.6	75.1	75.0
1c^a	6.5	6.8	7.0	7.4	8.3	9.6	10.5	14.1	16.4	20.6	30.1	49.4	80.1
2a	3.4	4.9	5.3	8.3	10.4	15.5	19.2	23.6	28.4	36.2	75.7	86.5	90.2
2b	3.9	5.3	5.6	6.0	8.4	13.8	18.3	26.1	38.0	78.2	78.2	78.3	78.3
2c	0.8	1.1	1.5	1.9	4.4	8.0	12.7	18.3	37.6	55.6	71.3	85.7	86.1

^a750 °C: 85.1 %