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SUPPLEMENTARY MATERIAL TO

Spectral characterization and antimicrobial activity studies of 5,6-dichloro-1*H*-benzimidazol-2-yl-(4'/5'/6'-substituted)-phenols (HL_1–HL_{20}) and Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) complexes of HL_1

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EXPERIMENTAL

Chemistry and apparatus

All chemicals and solvents were of reagent grade and they were used without further purification.

Analytical data were obtained with a Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined using a Buchi M-560 melting-point apparatus. Molar conductivity of the complexes was measured on a WTW Cond315i conductivity meter in DMF at 25 °C. Magnetic measurements: MK1 Sherwood Scientific apparatus (at room temperature by Gouy's method). NMR spectra were run on a Varian Unity Inova 500 NMR spectrometer. FT-IR spectra were recorded on a Bruker Optics Vertex 70 spectrometer using Attenuated Total Reflection (ATR) techniques between 400 and 4000 cm^{-1}. The Electron Spray Ionization-Mass Spectrometry (ESI-MS) analysis was carried out in positive ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS. Fluorescence spectra were performed on a Shimadzu RF-5301 PC Spectrofluorophotometer in EtOH (c = ~1×10^{-4} mol L^{-1}).

$[Co(\mathbf{L_1})_2(H_2O)_2]$: Light brown solid. Yield: 71 %; dec. p.: 168 °C; Combustion analysis for $C_{26}H_{18}Cl_4N_4O_4Co$ (FW: 651.19): Calculated. C 47.95, H 2.79, N 8.60; found C 48.42, H 3.04, N 8.48. Magnetic moment, μ_{eff}: 3.47μ_B. Λ_M (DMF, 25 °C, S m^2 mol^{-1}): 21.3. IR (ATR, cm^{-1}): 3225m,br ν(H_2O+NH), 3107m ν$(CH)_{ar.}$,1607m ν(C=N), 1599m ν(C=C), 1485m, 1453m, 1372m, 1245m ν(C–O), 1098m, 960m, 864m δ$(CH)_{ar.}$, 813m, 751s ν(C–Cl), 677m, 578m, 545m, 502m ν(Co–O), 462m ν(Co←N), 428m. TGA (t / °C: weight loss, %): 100: 1.1; 150: 5.7; 200: 6.7; 300: 19.4; 400: 53.1; 500: 85.2; 600: 87.5; 700: 89.1; 800: 89.1 (Theoretical value of CoO: 11.5 %). Fluorescence spectra (EtOH, c = 1×10^{-4} mol L^{-1}, λ_{max}/ nm): 469m.

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[Ni($\mathbf{L_1}$)$_2$]·2H$_2$O: Light brown solid. Yield: 73 %; dec. p.: 165 °C; Combustion analysis for $C_{26}H_{18}Cl_4N_4O_4Ni$ (FW: 650.95): Calculated. C 47.97, H 2.79, N 8.61; found C 48.33, H 2.96, N 8.44. Magnetic moment, $\mu_{eff.}$: 2.05 μ_B. Λ_M (DMF, 25 °C, S m^2 mol^{-1}): 31.5. IR (ATR, cm^{-1}): 3356m ν(OH), 3269m ν(NH), 3068m ν(CH)$_{ar.}$, 1609m ν(C=N), 1595m ν(C=C), 1503m, 1456m, 1387m, 1246m ν(C–O), 1103m, 1039m, 854m δ(CH)$_{ar.}$, 815m, 754s ν(C–Cl), 680m, 616m, 537m, 504m ν(Ni–O), 449m ν(Ni←N), 416m. TGA (t / °C: weight loss, %): 100: 5.8; 150: 6.0; 200: 6.5; 300: 18.2; 400: 51.6; 500: 86.5; 600: 88.2; 700: 88.8; 800: 88.8 (Theoretical value of NiO: 11.5 %). Fluorescence spectra (EtOH, c = 1×10^{-4} mol L^{-1}, λ_{max}/ nm): 417sh, 462m.

[Cu($\mathbf{L_1}$)$_2$]·H$_2$O: Brown solid. Yield: 80 %; dec. p.: 332 °C; Combustion analysis for $C_{26}H_{16}Cl_4N_4O_3Cu$ (FW: 637.80): Calculated. C 48.96, H 2.53, N 8.78; found C 48.60, H 2.54, N 8.41. Magnetic moment, $\mu_{eff.}$: 1.62 μ_B. Λ_M (DMF, 25 °C, S m^2 mol^{-1}): 7.1. IR (ATR, cm^{-1}): 3357m,br ν(H$_2$O+NH), 3130m,br, 3054w ν(CH)$_{ar.}$, 1617m ν(C=N), 1588m ν(C=C), 1556m, 1451m, 1355m, 1244sν(C–O), 1197m, 1100m, 975m, 868m δ(CH)$_{ar.}$, 759m, 742m ν(C–Cl), 691m, 573m, 546m, 503m ν(Cu–O), 443m ν(Cu←N), 420m. TGA (t / °C: weight loss, %): 100: 2.7; 150: 3.3; 200: 6.3; 300: 18.0; 400: 49.5; 500: 85.5; 600: 87.3; 700: 87.5; 800: 87.7 (Theoretical value of CuO: 12.5 %). Fluorescence spectra (EtOH, c = 1×10^{-4} mol L^{-1}, λ_{max}/ nm): 469w,br.

[Zn($\mathbf{L_1}$)Cl(H$_2$O)]·2H$_2$O: Dirty white solid. Yield: 71 %; dec.p.: 270 °C; Combustion analysis for $C_{13}H_{13}Cl_3N_2O_4Zn$ (FW: 433.02): Calculated. C 36.06, H 3.03, N 6.47; found C 35.84, H 2.88, N 6.32. Λ_M (DMF, 25 °C, S m^2 mol^{-1}): 45.8. IR (ATR, cm^{-1}): 3365m,br ν(OH), 3203m,br ν(NH), 3042w ν(CH)$_{ar.}$, 1620m ν(C=N), 1609m ν(C=C), 1558m, 1483m, 1456m, 1321m, 1233s ν(C–O), 1147m, 969m, 856m δ(CH)$_{ar.}$, 740s ν(C–Cl), 692m, 577m, 541s, 505m ν(Zn–O), 443m ν(Zn←N), 421m. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 12.81 (*brs*, 1H, NH), 7.89 (*brs*, 2H, H4+H7), 7.84 (*dd*, 1H, J_1 = 7.9, J_2 = 1.6, H3'), 7.15 (*dt*, 1H, J_1 = 8.3, J_2 = 1.4, H4'), 6.71 (*dd*, 1H, J_1 = 7.7, J_2 = 3.7, H6'), 6.52 (*td*, 1H, J_1 = 7.2, J_2 = 7.1, J_3 = 1.2, H5'). TGA (t / °C: weight loss, %): 100: 8.6; 150: 11.7; 200: 16.4; 300: 25.1; 400: 53.5; 500: 79.4; 600: 82.2; 700: 82.4; 800: 82.5 (Theoretical value of ZnO: 18.8 %). Fluorescence spectra (EtOH, c = 1×10^{-4} mol L^{-1}, λ_{max}/ nm): 425sh, 450m,br.

[Pd($\mathbf{L_1}$)$_2$]·2H$_2$O: Soil colored solid. Yield: 66 %; dec. p. >350 °C; Combustion analysis for $C_{26}H_{18}Cl_4N_4O_4Pd$ (FW: 698.70): Calculated. C 44.41, H 3.01, N 7.21; found C 44.70, H 2.60, N 8.02. Λ_M (DMF, 25 °C, S m^2 mol^{-1}): 14.3. IR (ATR, cm^{-1}): 3269m,br ν(NH+OH$_2$), 3117w ν(CH)$_{ar.}$, 1602m ν(C=C), 1588m ν(C=N), 1531m, 1476m, 1310m, 1239s ν(C–O), 1144m, 1034m, 969m, 870m δ(CH)$_{ar.}$, 753s ν(C–Cl), 702m, 672m, 568m, 503m ν(Pd–O), 443m ν(Pd←N). ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.43 (*s*, 1H, NH), 7.94 (*brs*, 1H, H7), 7.87 (*s*, 1H, H4), 7.68 (*dt*, 1H, J_1 = 8.0, J_2 = 1.7, H5'), 7.45 (*dt*, 1H, J_1 = 7.8, J_2 = 7.1, J_3 = 1.0, H4'), 7.22 (*d*, 1H, J = 7.6, H6'), 7.05 (*dt*, 1H, J_1 = 8.0, J_2 = 1.0, H3'). TGA (t / °C: weight loss, %): 100: 5.4; 150: 5.7; 200: 6.1; 300: 19.9; 400: 49.7; 500: 74.6; 600: 77.3; 700: 81.1; 800: 81.2 (Theoretical value of PdO: 17.5 %). Fluorescence spectra (EtOH, c = 1×10^{-4} mol L^{-1}, λ_{max}/ nm): 415sh, 459m.

*2-(5,6-Dichloro-1H-benzimidazol-2-yl)phenol (**HL$_1$**)*: Yield: 80 %. Slightly yellow solid. Decomposition point (Dec. p.): 331 °C. (+)ESI-MS (*m/z*): calculated for [$C_{13}H_8Cl_2N_2O$]$^+$ 279.1, observed 279.3 (100 %) and 281.3 for ([$C_{13}H_8Cl_2N_2O$ + 2H]$^+$ (73.9 %). Combustion analysis for $C_{13}H_8Cl_2N_2O$: Calculated. C 55.94, H 2.89, N 10.04; found C 56.15, H 3.03, N 9.97. IR (ATR): 3333m ν(NH+OH), 3101m ν(CH)$_{ar.}$, 1639m ν(C=N), 1600m ν(C=C), 1578m, 1487s, 1370m, 1256m ν(C–O), 1136m, 1106m, 960m, 865m δ(CH)$_{ar.}$, 739s ν(C–Cl), 678m, 580m, 553m, 422m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.30 (*s*, 1H, NH), 12.42 (*s*, 1H, OH), 8.08 (*dd*, 1H, J_1 = 7.9, J_2 = 1.6, H3'), 8.00 (*brs*, 1H, H4), 7.84 (*brs*, 1H, H7), 7.41 (*dt*, 1H, J_1 =

1.6, J_2 = 7.2, J_3 = 8.4, H5'), 7.06 (*dd*, 1H, J_1 = 8.3, J_2 = 1.0, H6'), 7.03 (*dt*, 1H, J_1 = 7.6, J_2 = 1.1, H4'). Fluorescence spectra (λ_{max} / nm): 394w, 466s.

*2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4-fluorophenol (**HL$_2$**)*: Yield: 71 %. Light yellow solid. Dec. p.: 352 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_7Cl_2FN_2O]^+$ 297.1, observed 297.3 (100 %) and 299.3 for $([C_{13}H_7Cl_2FN_2O + 2H]^+$ (66.0 %). Combustion analysis for $C_{13}H_7Cl_2FN_2O$: Calculated. C 52.55, H 2.37, N 9.43; found C 52.71, H 2.53, N 9.27. IR (ATR, cm^{-1}): 3341m ν(NH+OH), 3078m $\nu(CH)_{ar.}$, 1650m ν(C=N), 1600m ν(C=C), 1583m, 1498m, 1448m, 1304m, 1255m ν(C–O), 1168m, 1096m, 976m, 859m, 814s $\delta(CH)_{ar.}$, 780m, 743m ν(C–Cl), 665m, 561s, 470m, 443m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.27 (*s*, 1H, NH), 12.21 (*s*, 1H, OH), 8.02 (*brs*, 1H, H4), 7.93 (*d*, 1H, J = 3.1, H3'), 7.91 (*brs*, 1H, H7), 7.28 (*dd*, 1H, J_1 = 9.0, J_2 = 3.1, H5'), 7.08 (d, 1H, J = 9.1, H6'). Fluorescence spectra (λ_{max} / nm): 393w, 480s.

*4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_3$**)*: Yield: 85 %. Yellowish grey solid. Dec. p.; 220 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_7BrCl_2N_2O + H]^+$ 359.0, observed 359.3 (100 %) and 357.3 for $([C_{13}H_7BrCl_2N_2O – H]^+$ (53.3 %). Combustion analysis for $C_{13}H_7BrCl_2N_2O$: Calculated. C 43.61, H 1.97, N 7.82; found C 43.45, H 1.91, N 7.74. IR (ATR, cm^{-1}): 3341m ν(NH+OH), 3075m $\nu(CH)_{ar.}$, 2960m,br, 1719m ν(C=O), 1620m ν(C=N), 1609m ν(C=C), 1482m, 1372m, 1249s ν(C–O), 1136m, 965m, 866m, 801s $\delta(CH)_{ar.}$, 739m ν(C–Cl), 632m, 565m ν(C–Br), 487m, 420m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.31 (*brs*, 1H, NH), 12.51 (*brs*, 1H, OH), 8.16 (*d*, 1H, J = 2.4, H3'), 7.92 (*brs*, 2H, H4+H7), 7.43 (*dd*, 1H, J_1 = 8.8, J_2 = 2.4, H5'), 7.10 (*d*, 1H, J = 8.8, H6'). Fluorescence spectra (λ_{max} / nm): 393w, 474s.

*4-Chloro-2-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_4$**)*: Yield: 81 %. Yellowish grey solid. Dec. p.: 221 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_7Cl_3N_2O]^+$ 313.5, observed 313.2 (100 %) and 315.2 for $([C_{13}H_7Cl_3N_2O + 2H]^+$ (90.1 %). Combustion analysis for $C_{13}H_7Cl_3N_2O$: Calculated. C 49.79, H 2.25, N 8.93; found: C 49.64, H 2.16, N 8.80. IR (cm^{-1}): 3338m ν(NH+OH), 3077m $\nu(CH)_{ar.}$, 2960m,br, 1723m ν(C=O), 1621m ν(C=N), 1602m ν(C=C), 1576m, 1474m, 1444m, 1355m, 1278m, 1249m ν(C–O), 1136m, 1095m, 965m, 866m, 800m $\delta(CH)_{ar.}$, 745m ν(C–Cl), 720m ν(C–Cl), 648m, 564m, 543m, 490m, 420m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.32 (*brs,* 1H, NH), 12.52 (*brs,* 1H, OH), 8.29 (*d,* 1H, J = 2.4, H3'), 8.01 (*brs*, 1H, H4), 7.88 (*brs*, 1H, H7), 7.54 (*dd,* 1H, J_1 = 8.8, J_2 = 2.4, H5'), 7.03 (*d,* 1H, J = 8.8, H6'). Fluorescence spectroscopy (λ_{max}/nm): 394w, 475m.

*2-(5,6-dichloro-1H-benzimidazol-2-yl)-4-iodophenol (**HL$_5$**)*: Yield: 65 %. Light orange solid. Dec. p.: 231 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_7Cl_2IN_2O]^+$ 405.1, observed 405.1 (100 %) and 407.1 for $([C_{13}H_7Cl_2IN_2O + 2H]^+$ (73.9 %). Combustion analysis for $C_{13}H_7Cl_2IN_2O$: Calculated. C 38.55, H 1.74, N 6.92; found: C 38.41, H 1.63, N 6.84. IR (cm^{-1}): 3351m ν(NH+OH), 3094m $\nu(CH)_{ar.}$, 2930m,br, 1656m ν(C=N), 1605m ν(C=C), 1565m, 1466s, 1366m, 1273m ν(C–O), 1181m, 1128m, 1095m, 961m, 865m, 814s $\delta(CH)_{ar.}$, 760m ν(C–Cl), 678m, 564m, 540m ν(C–I), 508m, 419m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.22 (*s,* 1H, NH), 12.51 (*s,* 1H, OH), 8.38 (*d,* 1H, J = 2.0, H3'), 8.00 (*brs,* 1H, H4), 7.84 (*brs,* 1H, H7), 7.64 (dd, 1H, J_1 = 8.7, J_2 = 2.0, H5'), 6.87 (*d,* 1H, J = 8.7, H6'). Fluorescence spectroscopy (λ_{max}/nm): 393w, 476m.

*2-Chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_6$**)*: Yield: 80 %. Matte yellow solid. Dec. p.: 373 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_7Cl_3N_2O]^+$ 313.5, observed 313.2 (100 %), 315.2 ($[C_{13}H_7Cl_3N_2O + 2H]^+$ (100 %) and 317.2 for ($[C_{13}H_7Cl_3N_2O + 4H]^+$ (47.6 %). Combustion analysis for $C_{13}H_7Cl_3N_2O$: Calculated. C 49.79, H 2.25, N 8.93; found: C 49.63, H 2.33, N 8.77. IR (cm^{-1}): 3336m,br ν(NH+OH), 3075w $\nu(CH)_{ar.}$, 1624m ν(C=N), 1601m

ν(C=C), 1464m, 1441m, 1373m, 1252m ν(C–O), 1094m, 968m, 860m δ(CH)$_{ar.}$, 785m, 747m ν(C–Cl), 736m ν(C–Cl), 665m, 611m, 571s, 427m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.72 (*brs,* 1H, NH), 13.38 (*s,* 1H, OH1'), 8.08 (*brs,* 1H, H4), 8.02 (*dd,* 1H, J$_1$ = 7.9, J$_2$ = 1.5, H3'), 7.87 (*brs,* 1H, H7), 7.59 (*dd,* 1H, J$_1$ = 7.9, J$_2$ = 1.5, H5'), 7.06 (*t,* 1H, J$_1$ = J$_2$ = 7.9, H4'). Fluorescence spectroscopy (λ$_{max}$/nm): 394w,br, 463m,br.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (***HL$_7$***): Yield: 90 %. Creamy colored solid. Dec. p.: 343 °C. (+)ESI-MS (*m/z*): calculated for [C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$]$^+$ 309.0, observed 309.1 (100 %), 311.1 ([C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$ + 2H]$^+$ (69.7 %). Combustion analysis for C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.25, H 3.37, N 8.95. IR (cm^{-1}): 3294m,br ν(NH+OH), 3058w ν(CH)$_{ar.}$, 2943m ν(CH)$_{al.}$, 1623m ν(C=N), 1591m ν(C=C), 1476m, 1420m, 1372m, 1249s ν(C–O), 1182m ν(C–O), 1095m, 1056m, 967m, 857m δ(CH)$_{ar.}$, 776m ν(C–Cl), 731m, 603m, 545m, 425m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.33 (*brs,* 1H, NH), 12.50 (*brs,* 1H, OH'), 7.92 (*brs,* 2H, H4+H3'), 7.63 (*d,* 1H, J = 2.9, H7), 7.12 (*dd,* 1H, J$_1$ = 8.0, J$_2$ = 1.1, H5'), 6.97 (*t,* 1H, J$_1$ = J$_2$ = 8.0, H4'), 3.84 (*s,* 3H, OCH$_3$). Fluorescence spectroscopy (λ$_{max}$/nm): 394w,br, 481s.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-5-methoxyphenol (***HL$_8$***): Yield: 80 %. Slightly yellow solid. Dec. p.: 292 °C. (+)ESI-MS (*m/z*): calculated for [C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$]$^+$ 309.0, observed 309.3 (100 %), 311.2 ([C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$ + 2H]$^+$ (64.7 %). Combustion analysis for C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.24, H 3.41, N 8.94. IR (cm^{-1}): 3344m,br ν(NH+OH), 3102m ν(CH)$_{ar.}$, 2971m ν(CH)$_{al.}$, 1640m ν(C=N), 1600m ν(C=C), 1453m, 1388s, 1267m ν(C–O), 1200m ν(C–O), 1134m, 1026m, 951m, 865m, 817m δ(CH)$_{ar.}$, 796m ν(C–Cl), 672m, 568m, 548m, 475m, 425m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.17 (*s,* 1H, NH), 12.68 (*s,* 1H, OH), 7.96 (*d,* 1H, J = 8.8, H3'), 7.94 (*s,* 1H, H4), 7.77 (*s,* 1H, H7), 6.64 (*dd,* 1H, J$_1$ = 8.8, J$_2$ = 2.5, H4'), 6.59 (*d*, 1H, J = 2.4, H6'), 3.81 (*s,* 3H, OCH$_3$). Fluorescence spectroscopy (λ$_{max}$/nm): 394w,br, 452m.

2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4-methoxyphenol (***HL$_9$***): Yield: 71 %. Slightly yellow solid. Dec. p.: 352 °C. (+)ESI-MS (*m/z*): calculated for [C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$]$^+$ 309.0, observed 309.2 (100 %), 311.2 ([C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$ + 2H]$^+$ (59.9 %). Combustion analysis for C$_{14}$H$_{10}$Cl$_2$N$_2$O$_2$: Calculated. C 54.39, H 3.26, N 9.06; found: C 54.25, H 3.43, N 8.95. IR (cm^{-1}): 3306m ν(NH+OH), 3076m ν(CH)$_{ar.}$, 2974m ν(CH)$_{al.}$, 1619m ν(C=N), 1598m ν(C=C), 1493m, 1450m, 1370m, 1273m ν(C–O), 1214m ν(C–O), 1171m, 1042m, 968m, 866m, 809m δ(CH)$_{ar.}$, 758m ν(C–Cl), 726m, 673m, 573m, 512m, 438m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.24 (*s,* 1H, NH), 11.92 (*s,* 1H, OH), 8.01 (*brs,* 1H, H4), 7.85 (*brs,* 1H, H7), 7.66 (*d,* 1H, J = 2.4, H3'), 7.03 (*dd,* 1H, J$_1$ = 8.9, J$_2$ = 2.6, H5'), 6.99 (*d,* 1H, J$_1$ = 8.9, J$_2$ = 7.9, H6'), 3.80 (*s,* 3H, OCH$_3$). Fluorescence spectroscopy (λ$_{max}$/nm): 389s,br, 508m,br.

2-(5,6-dichloro-1H-benzimidazol-2-yl)-4-methylphenol (***HL$_{10}$***): Yield: 72 %. Slightly yellow solid. Dec. p.: 326 °C. (+)ESI-MS (*m/z*): calculated for [C$_{14}$H$_{10}$Cl$_2$N$_2$O]$^+$ 293.0, observed 293.2 (69.9 %), 295.2 ([C$_{14}$H$_{10}$Cl$_2$N$_2$O + 2H]$^+$ (100 %). Combustion analysis for C$_{14}$H$_{10}$Cl$_2$N$_2$O: Calculated. C 57.36, H 3.44, N 9.56; found: C 57.47, H 3.30, N 9.49. FT-IR (cm^{-1}): 3467m ν(OH), 3376m ν(NH), 3062m ν(CH)$_{ar.}$, 2925m ν(CH)$_{al.}$, 1614m ν(C=N), 1584m ν(C=C), 1485s, 1354m, 1284m ν(C–O), 1257m, 1134m, 962m, 855m, 812s δ(CH)$_{ar.}$, 780m ν(C–Cl), 685m, 554m, 476m, 442m, 421m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d$_6$, δ): 13.20 (*brs,* 1H, NH), 12.16 (*brs,* 1H, OH), 7.95 (*brs,* 1H, H4), 7.89 (*d,* 1H, J = 1.7, H3'), 7.84 (*brs,* 1H, H7), 7.21 (*dd,* 1H, J$_1$ = 8.3, J$_2$ = 1.8, H5'), 6.95 (*d*, 1H, J = 8.3, H6'), 2.32 (*s,* 3H, CH$_3$). Fluorescence spectroscopy (λ$_{max}$/nm): 375w,br, 394w,br, 482m.

2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methylphenol (***HL$_{11}$***): Yield: 94 %. Slightly bright yellow solid. Dec. p.: 357 °C. (+)ESI-MS (*m/z*): calculated for [C$_{14}$H$_{10}$Cl$_2$N$_2$O]$^+$ 293.0,

observed 293.3 (100 %), 295.2 ($[C_{14}H_{10}Cl_2N_2O + 2H]^+$ (92.7 %). Combustion analysis for $C_{14}H_{10}Cl_2N_2O$: Calculated. C 57.36, H 3.44, N 9.56; found: C 57.50, H 3.55, N 9.42. IR (cm^{-1}): 3323m,br ν(NH+OH), 3054m ν$(CH)_{ar.}$, 2951m ν$(CH)_{al.}$, 1628m ν(C=N), 1601m ν(C=C), 1475m, 1445m, 1415m, 1370m, 1300m, 1252m ν(C–O), 1094m, 1013m, 966m, 886m, 863m δ$(CH)_{ar.}$, 786s ν(C–Cl), 665m, 573s, 518m, 428m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.52 (*s,* 1H, NH), 13.01 (*s,* 1H, OH), 8.03 (*s,* 1H, H4), 7.87 d (1H, J = 7.6, H3'), 7.81 s (1H, H7), 7.31 d (1H, J = 7.3, H5'), 6.95 dd (1H, J_1 = 7.5, J_2 = 7.6, H4'), 2.26 (*s,* 3H, CH_3). Fluorescence spectroscopy (λ_{max}/nm): 379w,br, 473s.

*2-Bromo-4-chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_{12}$**)*: Yield: 82 %. Mate light yellow solid. Dec. p.: 228 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6BrCl_3N_2O + H]^+$ 393.5, observed 393.1 (100 %), 395.1 ($[C_{13}H_6BrCl_3N_2O + 3H]^+$ (64.5 %), 391.1 $[C_{13}H_6BrCl_3N_2O – H]^+$ (55.7 %). Combustion analysis for $C_{13}H_6BrCl_3N_2O$: Calculated. C 39.78, H 1.54, N 7.14; found: C 39.75, H 1.66, N 7.01. IR (cm^{-1}): 3403m ν(NH+OH), 3085m ν$(CH)_{ar.}$, 1669s ν(C=O), 1624m ν(C=N), 1601m ν(C=C), 1448m, 1373m, 1256m ν(C–O), 1096m, 970m, 853m δ$(CH)_{ar.}$, 754m ν(C–Cl), 722m ν(C–Cl), 669m, 610m, 554m ν(C–Br), 498m, 423m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.80 (*brs,* 1H, NH), 13.44 (*s,* 1H, OH), 8.18 (*brs,* 1H, H4), 8.05 (*brs,* 1H, H7), 7.95 (*s,* 1H, H3'), 7.84 (*brs,* 1H, H5'). Fluorescence spectroscopy (λ_{max}/nm): 393w,br, 479s,br.

*4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-fluorophenol (**HL$_{13}$**)*: Yield: 74 %. Dirty yellow solid. Dec. p.: 284 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6BrCl_2FN_2O + H]^+$ 376.0, observed 377.2 (100 %), 375.1 ($[C_{13}H_6BrCl_2FN_2O – H]^+$ (65.6 %). Combustion analysis for $C_{13}H_6BrCl_2FN_2O$: Calculated. C 41.53, H 1.61, N 7.45; found: C 41.43, H 1.73, N 7.27. IR (cm^{-1}): 3398m ν(NH+OH), 3084m ν$(CH)_{ar.}$, 2872m,br, 1662s ν(C=O), 1614m ν(C=N), 1577m ν(C=C), 1489s, 1374m, 1265s ν(C–O), 1233m, 1095m, 972m, 916m, 855s δ$(CH)_{ar.}$, 807m, 754m ν(C–Cl), 666m, 553m ν(C–Br), 427m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.58 (*brs,* 1H, NH), 13.15 (*brs,* 1H, OH), 8.10 (*d,* 1H, J = 2.3, H5'), 7.96 (*brs,* 1H, H4), 7.94 (*brs,* 1H H7), 7.66 (*d,* 1H, J = 2.4, H3'). Fluorescence spectroscopy (λ_{max}/nm): 393w, 418sh, 469s.

*2-Chloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)-4-fluorophenol (**HL$_{14}$**)*: Yield: 89 %. Slightly yellow solid. Dec. p.: 341 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6Cl_3FN_2O]^+$ 331.5, observed 331.3 (100 %), 333.3 ($[C_{13}H_6Cl_3FN_2O + 2H]^+$ (73.9 %). Combustion analysis for $C_{13}H_6Cl_3FN_2O$: Calculated. C 47.09, H 1.82, N 8.45; found: C 47.21, H 1.96, N 8.27. IR (cm^{-1}): 3420m ν(NH+OH), 3089m ν$(CH)_{ar.}$, 1662m ν(C=O), 1622m ν(C=N), 1577m ν(C=C), 1466m, 1444s, 1370m, 1264m ν(C–O), 1209m, 1100m, 999m, 867s δ$(CH)_{ar.}$, 793m ν(C–Cl), 741m ν(C–Cl), 666m, 573m, 507m, 425m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.69 (*brs,* 1H, NH), 13.48 (*brs,* 1H, OH), 8.06 (*brs,* 1H, H5'), 7.92 (*d,* 1H, J = 3.0, H4), 7.90 (*d,* 1H, J = 3.0, H7), 7.61 (*d,* 1H, J = 3.0, H3'). Fluorescence spectroscopy (λ_{max}/nm): 394w,br, 482m,br.

*2,4-Dichloro-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_{15}$**)*: Yield: 86 %. Mate yellow solid. Dec. p.: 344 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6Cl_4N_2O + H]^+$ 349.0, observed 349.3 (100 %), 347.3 ($[C_{13}H_6Cl_4N_2O – H]^+$ (64.2 %), 351.3 ($[C_{13}H_6Cl_4N_2O + 3H]^+$ (54.8 %). Combustion analysis for $C_{13}H_6Cl_4N_2O$: Calculated C 44.87, H 1.74, N 8.05; found: C 44.71, H 1.87, N 8.16. IR (cm^{-1}): 3408m ν(NH+OH), 3078m ν$(CH)_{ar.}$, 1722m ν(C=O), 1657m ν(C=N), 1623m ν(C=C), 1576m, 1477m, 1442s, 1365m, 1259m ν(C–O), 1187m, 1099m, 974m, 869m, 817m δ$(CH)_{ar.}$, 766m ν(C–Cl), 728m ν(C–Cl), 667m, 614m, 558m, 501m, 427m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.78 (*brs,* 2H, NH+OH), 8.15 (*d,* 1H, J = 2.5, H3'), 8.07 (*brs,* 1H, H4), 8.03 (*brs,* 1H, H7), 7.73 (*d,* 1H, J = 2.5, H5'). Fluorescence spectroscopy (λ_{max}/nm): 393w,br, 478m,br.

*2,4-Dibromo-6-(5,6-dichloro-1H-benzimidazol-2-yl)phenol (**HL$_{16}$**)*: Yield: 75 %. Orangey yellow solid. Dec. p.: 275 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6Br_2Cl_2N_2O]^+$ 437.0, observed 437.3 (100 %), 439.3 ($[C_{13}H_6Br_2Cl_2N_2O + 2H]^+$ (98.9 %), 435.3 ($[C_{13}H_6Br_2Cl_2N_2O – H]^+$ (41.6 %). Combustion analysis for $C_{13}H_6Br_2Cl_2N_2O$: Calculated. C 35.74, H 1.38, N 6.41; found: C 35.65, H 1.47, N 6.55. IR (cm^{-1}): 3354w ν(NH), 3313w ν(OH), 3069m $\nu(CH)_{ar.}$, 1637m ν(C=N), 1604m ν(C=C), 1558m, 1458s, 1445s, 1364m, 1259m ν(C–O), 1097m, 973m, 855s, 836m $\delta(CH)_{ar.}$, 733m ν(C–Cl), 684m, 599m, 550m ν(C–Br), 447m, 420m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.88 (*brs,* 1H, NH), 13.82 (*brs,* 1H, OH), 8.32 (*s,* 1H, J = 2.2, H3'), 8.08 (*brs,* 1H, H4), 8.03 (*brs,* 1H, H7), 7.94 (*d,* 1H, J = 2.1, H5'). Fluorescence spectroscopy (λ_{max}/nm): 479s.

*2-(5,6-Dichloro-1H-benzimidazol-2-yl)-4,6-diiodophenol (**HL$_{17}$**)*: Yield: 76 %. Yellowish orange solid. Dec. p.: 203 °C. (+)ESI-MS (*m/z*): calculated for $[C_{13}H_6Cl_2I_2N_2O]^+$ 531.0, observed 531.3 (100 %), 533.2 ($[C_{13}H_6Cl_2I_2N_2O + 2H]^+$ (64.1 %). Combustion analysis for $C_{13}H_6Cl_2I_2N_2O$: Calculated. C 29.41, H 1.14, N 5.28; found: C 29.57, H 1.07, N 5.37. IR (cm^{-1}): 3472m ν(NH), 3375m ν(OH), 3059m $\nu(CH)_{ar.}$, 1665m ν(C=O), 1622m ν(C=N), 1594m ν(C=C), 1440s, 1356m, 1257m ν(C–O), 1136m, 1093m, 965m, 860s, 825m $\delta(CH)_{ar.}$, 736m ν(C–Cl), 662m, 595m, 541m ν(C–I), 426m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.73 (*brs,* 1H, NH), 12.64 (*s,* 1H, OH), 8.39 (*d,* 1H, J = 2.0, H5'), 8.13 (*s,* 1H, H4), 7.99 (*d,* 1H, J = 2.0, H3'), 7.95 (*s,* 1H, H7). Fluorescence spectroscopy (λ_{max}/nm): 393w,br 486s.

*4-Chloro-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (**HL$_{18}$**)*: Yield: 85 %. Matte yellow solid. Dec. p.: 274 °C. (+)ESI-MS (*m/z*): calculated for $[C_{14}H_9Cl_3N_2O_2]^+$ 343.5, observed 343.2 (100 %), 345.2 ($[C_{14}H_9Cl_3N_2O_2 + 2H]^+$ (92.9 %). Combustion analysis for $C_{14}H_9Cl_3N_2O_2$: Calculated. C 48.94, H 2.64, N 8.15; found: C 48.79, H 2.80, N 8.00. IR (cm^{-1}): 3359m ν(NH+OH), 3102m $\nu(CH)_{ar.}$, 2951m $\nu(CH)_{al.}$, 2858m,br, 1665m ν(C=N), 1614m ν(C=C), 1579m, 1488m, 1442s, 1405m, 1315m, 1249s ν(C–O), 1095m, 1051m, 974m, 836m, 807m $\delta(CH)_{ar.}$, 730m ν(C–Cl), 725m ν(C–Cl), 621m, 552m, 433m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.40 (*s,* 1H, NH), 12.62 (*s,* 1H, OH), 7.98 (*brs,* 1H, H4), 7.89 (*brs,* 1H, H7), 7.73 (*d,* 1H, J = 2.4, H3'), 7.18 (*d,* 1H, J = 2.0, H5'), 3.87 (*s,* 3H, OCH_3). Fluorescence spectroscopy (λ_{max}/nm): 393w, 482s.

*4-Bromo-2-(5,6-dichloro-1H-benzimidazol-2-yl)-6-methoxyphenol (**HL$_{19}$**)*: Yield: 75 %. Skin color solid. Dec. p.: 229 °C. (+)ESI-MS (*m/z*): calculated for $[C_{14}H_9BrCl_2N_2O_2 + H]^+$ 389.0, observed 389.1 (100 %), 387.1 ($[C_{14}H_9BrCl_2N_2O_2 – H]^+$ (61.2 %). Combustion analysis for $C_{14}H_9BrCl_2N_2O_2$: Calculated. C 43.33, H 2.34, N 7.22; found: C 43.51, H 2.23, N 7.03. IR (cm^{-1}): 3356m ν(NH), 3279m ν(OH), 3083m $\nu(CH)_{ar.}$, 2852w,br, 1675m ν(C=O), 1621m ν(C=N), 1602m ν(C=C), 1440m, 1372m, 1254s ν(C–O), 1238m ν(C–O), 1093m, 1058m, 972m, 838m, 806m $\delta(CH)_{ar.}$, 710m ν(C–Cl), 640m, 551m ν(C–Br), 487m, 428m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.42 (*s,* 1H, NH), 12.66 (*s,* 1H, OH), 8.04 (*s,* 1H, H4), 7.87 (*s,* 1H, H7), 7.86 (*d,* 1H, J = 2.2, H5'), 7.25 (*d,* 1H, J=2.2, H3'), 3.87 (*s,* 3H, OCH_3). Fluorescence spectra (λ_{max} / nm): 393w, 486s.

*2,4-Dibromo-6-(5,6-dichloro-1H-benzimidazol-2-yl)-3-methoxyphenol (**HL$_{20}$**)*: Yield: 88 %. Yellowish orange solid. Dec. p.: 234 °C. (+)ESI-MS (*m/z*): calculated for $[C_{14}H_8Br_2Cl_2N_2O_2]^+$ 467.0, observed 467.1 (100 %), 469.1 ($[C_{14}H_8Br_2Cl_2N_2O_2 + 2H]^+$ (83.2 %). Combustion analysis for $C_{14}H_8Br_2Cl_2N_2O_2$: Calculated. C 36.01, H 1.73, N 6.00; found: C 36.35, H 1.93, N 5.87. IR (ATR, cm^{-1}): 3367w ν(OH), 3126m ν(NH), 3088m $\nu(CH)_{ar.}$, 2938m $\nu(CH)_{al.}$, 1665m ν(C=O), 1632m ν(C=N), 1600m, ν(C=C), 1564m, 1429m, 1372s, 1260m ν(C–O), 1230m ν(C–O), 1096m, 1061m, 970m, 863m $\delta(CH)_{ar.}$, 774m, 753m ν(C–Cl), 664m, 627m, 551m ν(C–Br), 460m, 412m, cm^{-1}. ^{1}H-NMR (500 MHz, DMSO-d_6, δ): 13.76 (*brs*, 2H,

NH+OH), 8.38 (*s*, 1H, H3'), 7.97 (*s*, 1H, H4), 7.95 (*s*, 1H, H7), 3.86 (*s*, 3H, OCH_3). Fluorescence spectra (λ_{max} / nm): 393w,br, 467m,br.

TABLE SI. Selected bond distances and angles for **HL_{18}** (Å, º)

C7—N1	1.367(3)	C7—N2	1.323(3)
C2—Cl1	1.739(3)	C3—Cl2	1.740(3)
C1—C2	1.377(4)	C2—C3	1.401(4)
C7—C8	1.461(3)	C9—O1	1.353(3)
C10—O2	1.368(3)	C14—O2	1.428(3)
C12—Cl3	1.740(3)	C9—C10	1.402(4)
C10—C11	1.376(4)	C11—C12	1.391(4)
C9-O1-H1A	109.5	N2-C7-N1	111.8(2)
N1-C5-C6	105.4(2)	C1-C2-Cl1	119.3(2)
C3-C2-Cl1	119.6(2)	C2-C3-Cl2	119.9(2)
C4-C3-Cl2	118.2(2)	N1-C5-C6	105.4(2)
N2-C7-N1	111.8(2)	C10-O2-C14	116.1(2)
C11-C12-Cl3	117.8(2)	C13-C12-Cl3	120.6(2)

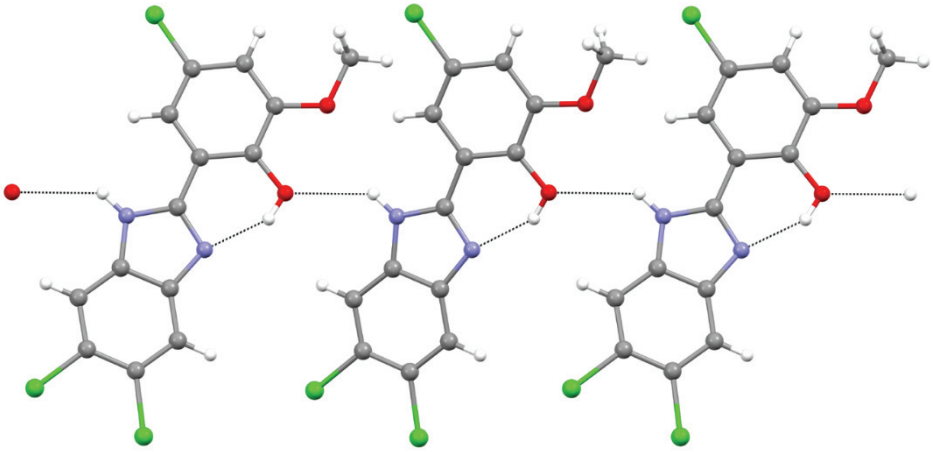

Fig. S1. Part of the crystal structure of **HL_{18}**, showing the formation of C(6) chain.