Supporting Information for

Extended dipyrrin ligands: Candidates for optical metal ion detection under competitive conditions

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Experimental Section

General information: All reagents were purchased from different commercial sources and used directly without further purification. Solvents were purified by single distillation before use. NMR spectroscopy was performed with a Varian VNMRS 400 and 600 device and the chemical shifts were expressed in ppm. IR spectroscopy was achieved with a PerkinElmer Spectrum 100 device in KBr and ν_{max} were expressed in cm^{-1}. Mass spectrometry measurements were carried out with a LTQ Orbitrap XL device (ESI) or a Finnigan SSQ 7000 device (EI). A Vario EL Element Analyzer was used for measuring elementary analysis. UV-vis spectra were recorded on a PerkinElmer Lambda 35 UV/VIS spectrophotometer and fluorescence measurements were obtained of a PerkinElmer LS45 fluorescence spectrophotometer. Absorption maxima have been expressed in nm.

Synthesis of *meso*-Mesitylen-α,α-diformyldipyrrin(2):

To a solution of *meso*-Mesitylen-α,α-diformyldipyrrolmethan (**4**, 5.5 g, 17.2 mmol, 1.0 eq.) dissolved in dichloromethane (abs., 220 mL) DDQ (4.3 g, 18.9 mmol, 1.1 eq) was added. After 2 h of stirring at room temperature the product was isolated by column chromatography (dichloromethane (100): methanol (4)).

Product: 3.9 g (12.2 mmol, 71%, dark red solid). **^{1}H NMR (600 MHz, CDCl$_3$):** *δ* [ppm] = 12.65 (s, 1H), 9.98 (s, 2H), 6.95 (s, 2H), 6.92 (d, *J* = 4.4 Hz, 2H), 6.51 (d, *J* = 4.4 Hz, 2H), 2.36 (s, 3H), 2.06 (s, 6H); **^{13}C NMR (100 MHz, CDCl$_3$):** *δ* [ppm] = 185.10 (CHO), 152.68 (C), 146.41 (C), 144.90 (C), 138.68 (C), 136.23 (C), 131.91 (C), 129.13 (CH), 128.20 (CH), 121.73 (CH), 21.12 (CH$_3$), 19.99 (2xCH$_3$); **MS (EI (+)):** m/z = 320.4 (4%), 319.4 (27%), 318.3 (100%), 304.3 (17%), 303 (81%), 289 (18%), 261 (7%), 346 (12%), 235 (11%), 218 (7%); **MS (ESI (+), FTMS):** m/z = 351.17032 (26%, +MeO$^+$), 341.12601 (100%, +Na$^+$, 341.12605), 319.14426 (17%, +H$^+$, 319.14465); **CHN (%):** Calcd (1/2 H_2O) [%]: C 73.38, H 5.85, N 8.56; found [%]: C 73.18, H 5.696, N 8.444. **IR (KBr):** 3233 (m), 3103 (w), 3012 (w), 2929 (w), 2842 (m), 2718 (w), 2322 (w), 2101 (w), 1747 (m), 1694 (s), 1658 (s), 1570 (s), 1510 (m), 1439 (m), 1376 (vs), 1290 (m) 1226 (vs), 1143 (vs), 1047 (m), 1009 (m), 932 (s), 807 (vs), 718 (vs).

Synthesis of L1-H:

Semicarbazide hypochloride (210 mg, 1.88 mmol, 3.0 eq.) and NaOAc (154 mg, 1.88 mmol, 3.0 eq.) was dissolved in EtOH/H_2O (2 mL / 1 mL). *meso*-Mesitylen-α,α-diformyldipyrrin (200 mg, 0.63 mmol, 1.0 eq.) was added and the reaction mixture was stirred overnight at room temperature. The product was precipitated in ice water, filtered and dried.

Product: 236 mg (0.546 mmol, 87%, black solid). **^{1}H NMR (300 MHz, DMSO-*d_6*):** *δ* [ppm] = 10.58 (s, 2H), 7.83 (s, 2H), 6.97 (s, 2H), 6.86 (d, *J* = 4.2 Hz, 2H), 6.51 (s, 4H), 6.20 (d, *J* = 4.2 Hz, 2H), 5.72 (s, 1H), 2.29 (s, 3H), 1.98 (s, 6H). **^{13}C NMR (100 MHz, DMSO- *d_6*):** *δ* [ppm] = 156.71 (C=O), 142.10 (C), 142.02 (C), 137.64 (C), 136.92 (C), 136.38 (C), 133.46 (CH), 133.22 (C), 128.33 (CH), 127.33 (CH), 119.02 (CH), 21.17 (CH$_3$), 20.01 (2xCH$_3$). **^{1}H NMR (600 MHz, DMF-*d_7*):** *δ* [ppm] = 12.94 (s, 1H), 10.56 (s, 2H), 8.08 (s, 2H), 7.05 (s, 2H), 6.94 (d, *J* = 4.1 Hz, 2H), 6.67 (s, 4H), 6.32 (s, 2H), 2.36 (s, 3H), 2.10 (s, 6H). **^{13}C NMR (151 MHz, DMF-*d_7*):** *δ* [ppm] = 157.63 (C), 152.58 (br, C), 143.41 (br, C), 138.78 (C), 138.03 (C), 137.52 (C), 134.52 (CH), 134.28 (C), 129.09 (CH), 128.15 (CH), 119.70 (CH), 21.49 (CH$_3$), 20.39 (CH$_3$). **MS (ESI-, ITMS):** *m/z* = 431.130 (100%, -H$^+$, 431.195). **MS (ESI, ITMS, MS=431@cid30):** *m/z* = 414.084 (20%, -NH$_4^+$), 388.1333 (100%, -CONH$_2$), 345.1077 (25%, -CONH$_2$, -CONH$_1$). **CHN:** calcd (4 H_2O) [%]: C 52.37, H 6.39, N 22.21; found [%]: C 52.72, H 6.764, N 22.45. **IR (KBr):** 3490 (w), 3455 (m), 3133 (w), 2118 (w), 2085 (w), 1704 (vs), 1573 (vs), 1520 (m), 1444 (m), 1370 (s), 1291 (vs), 1242 (s), 1155 (vs), 1107 (s), 1029 (s), 966 (m), 941 (s), 900 (m), 860 (m), 820 (s), 795 (vs), 718 (s), 657 (w).

Synthesis of complex L1-ZnCl:

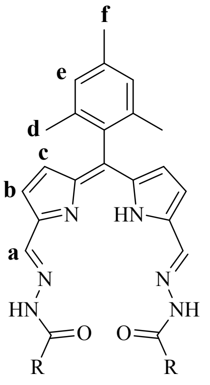
To a solution of L1-H (50 mg, 115 µmol, 1.0 eq.) in ethanol (40 mL) $ZnCl_2$ (31.4 mg, 230 µmol, 2.0 eq.) was added and stirred for 18 h at room temperature. The product was precipitated in ice water, filtered and dried.

^{1}H NMR (600 MHz, DMF-d_7): δ [ppm] = 10.60 (s, 2H), 8.20 (s, 2H), 7.04 (s, 2H), 6.94 (d, J = 4.2 Hz, 2H), 6.40 (d, J = 4.2 Hz, 2H), 2.37 (s, 3H), 2.08 (s, 6H). **^{13}C NMR (151 MHz, DMF-d_7):** δ [ppm] = 157.70 (C), 156.26 (C), 144.87 (C), 143.03 (C), 138.56 (C), 137.36 (C), 136.42 (C), 135.24 (CH), 132.10 (CH), 128.86 (CH), 120.31 (CH), 21.46 (CH_3), 20.29 (CH_3). **MS (ESI (-), FTMS):** m/z = 569.09058 (25%, -H$^+$ +$ZnCl_2$, 565.0570), 567.09283 (36%, -H$^+$ +$ZnCl_2$, 567.0583), 565.09583 (30%, -H$^+$, +$ZnCl_2$, 565.0612), 531.11346 (15%, -2H$^+$, +ZnCl$^+$, 531.0820), 529.11639 (16%, -2H$^+$, +ZnCl$^+$, 529.0851), 431.22009 (30%, -H$^+$, 431.1949), 296.92657 (100%). **MS (ESI (+), FTMS):** m/z = 929.32483 (7%,-H$^+$ +Zn^{2+}, 929.3227), 927.32837 (15%,-H$^+$ +Zn^{2+}, 927.3258), 497.12320 (11%, -H$^+$ +Zn^{2+}, 497.1199), 495.12408 (50%, -H$^+$ +Zn^{2+}, 495.1230), 433.21060 (40%, +H$^+$, 433.2095). **CHN:** calcd (L1-H -H$^+$ +ZnCl$^+$ +H_2O) [%]: C 48.02, H 4.58, N 20.36; found [%]: C 51.72, H 4.811, N 20.41.

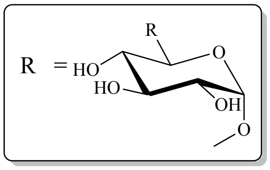
Synthesis of L2-H:

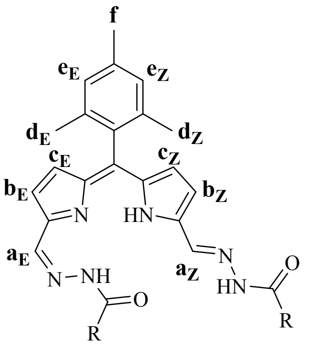
meso-Mesitylen-α,α-diformyldipyrrin (45 mg, 141 µmol, 1.0 eq.) was dissolved in MeOH (10 mL), treated with a catalytic amount of glacial acetic acid and allowed to stir for 5 min at room temperature. 1-O -Methyl-*α*-D-glucopyranuronic acid hydrazide (63 mg, 281 µmol, 2.0 eq.) was added and the reaction mixture was stirred overnight at room temperature. The product was obtained after removal of the solvent under reduced pressure.

Due to formation of 3 conformers in solution (in DMSO-d_6: E-E (55 %) Z-Z (5%) and E-Z conformer (40%)) proton signals of the carbohydrate moiety (3.0 – 4.5 ppm) overlapping and an exact assignment is not possible. The remaining proton signals were assigned with the help of COSY- and NOESY-experiments. In case of the anti-anti-conformer only the iminic proton (δ = 8.26 (s, 2H)) was assigned.



E-E conformer





E-Z conformer

Product: 98 mg (135 µmol, 96%, dark violet solid). **^{1}H NMR (600 MHz, MeOH-d_4): E-E** δ [ppm] = 8.32 (s, 2H, **a**), 6.99 (s, 2H, **e**), 6.89 (d, J = 4.2 Hz, 2H, **b**), 6.36 (br, 2H, **c**), 2.36 (s, 3H, **f**), 2.05 (s, 6H, **d**); **E-Z** δ [ppm] = 8.60 (s, 1H, **a_E**), 7.98 (s, 1H, **a_Z**), 7.09 (d, J = 4.4 Hz, 1H, **b_E**), 6.99 (s, 2H, **e**), 6.61 (d, J = 3.9 Hz, 1H, **b_Z**), 6.48 (d, J = 4.4 Hz, 1H, **c_E**), 6.21 (br, 1H, **c_Z**), 2.36 (s, 3H, **f**), 2.07 (s, 6H, **d_E or d_Z**) , 2.06 (s, 6H, **d_E or d_Z**). **MS (ESI (-), FTMS):** m/z = 725.27789 (100%, -H$^+$, 725.27879). **MS (ESI (+), FTMS):** m/z = 749.27417 (100%, +Na$^+$, 749.27529), 727.29352 (20%, +H$^+$, 727.29335). **CHN:** calcd (4 H_2O) [%]: C 51.12, H 6.31, N 10.52; found [%]: C 51.47, H 6.85, N 10.65. **IR (KBr):** 3834 (w), 3425 (s, broad), 2927 (m), 2656 (w), 2460 (w), 2283 (w), 2103 (w), 1982 (w), 1911 (w), 1738 (vs), 1678 (s), 1544 (s), 1437 (m), 1369 (vs), 1310 (m), 1220 (vs), 1106 (m), 1039 (vs), 973 (s), 800 (s), 718 (m).

Synthesis of complex L2-ZnOAc:

To a solution of L2-H (50.0 mg, 69 µmol, 1.0 eq.) in methanol (20 mL) $Zn(OAc)_2$*2H_2O (15.1 mg, 69 µmol, 1.0 eq.) was added and stirred for 18 h at room temperature. The product was obtained after removal of the solvent under reduced pressure.

Product: quantitative (dark purple solid). **^{1}H NMR (600 MHz, MeOH-d_4):** δ [ppm] = 8.38 (s, 2H), 6.98 (s, 2H), 6.86 (d, J = 4.4 Hz, 2H), 6.50 (d, J = 4.4 Hz, 2H), 4.81 (d, J = 3.7 Hz, 2H), 4.14 (d, J = 9.6 Hz, 2H), 3.70 (t, J = 9.2 Hz, 2H), 3.65 (t, J = 9.2 Hz, 2H), 3.53 (dd, J = 9.6, 3.7 Hz, 2H), 3.49 (s, 6H), 2.36 (s, 3H), 2.06 (s, 6H). **MS (ESI (-), FTMS):** m/z = 787.18146 (100%, - AcO$^-$, -2H$^+$, 787.19229). **CHN:** calcd (16 H_2O) [%]: C 37.98, H 6.73, N 7.38; found [%]: C 37.86, H 6.93, N 7.63. **IR (KBr):** 3850 (w), 3242 (s, broad), 2931(m), 2318, (w), 2098 (m), 1930 (w), 1742 (m), 1665 (m), 1522 (s), 1385 (m), 1254 (vs), 998 (vs), 840 (m), 787 (m), 723 (m).

Synthesis of complex L2-ZnCl:

To a solution of L2-H (25.0 mg, 34 µmol, 1.0 eq.) in methanol (15 mL) K_2CO_3 (4.8 mg, 34 µmol, 1.0 eq.) was added and stirred for 15 min at room temperature. After addition of $ZnCl_2$ (4.7 mg, 34 µmol, 1.0 eq.) stirring was continued for 24 h at room temperature. The product was obtained after removal of the solvent under reduced pressure.

Product: quantitative (purple solid). **^{1}H NMR (600 MHz, MeOH-d_4):** δ [ppm] = 8.47 (s, 2H), 6.98 (s, 2H), 6.94 (s, 2H), 6.49 (s, 2H), 4.82 (d, *J* = 9.5 Hz, 2H), 4.15 (d, *J* = 9.5 Hz, 2H), 3.71 (t, *J* = 9.2 Hz, 2H), 3.66 (t, *J* = 9.2 Hz, 2H), 3.54 (dd, *J* = 9.5, 3.7 Hz, 2H), 3.49 (s, 6H), 2.36 (s, 3H), 2.06 (s, 6H). **MS (ESI (-), FTMS):** m/z = 823.17023 (100%, -H^+, 823.16897). **MS (ESI (+), FTMS):** m/z = 789.20868 (100%, -Cl^-, 789.20684), 863.14130 (30%, +K^+, 863.13940). **IR (KBr):** 3836 (w), 3456 (w), 3012, (m), 2936 (m), 2692 (w), 2462 (w), 2282 (w), 2114 (w), 2031 (w), 1984 (w), 1739 (vs), 1516 (m), 1439 (m), 1366 (s), 1217 (vs), 1103 (w), 1044 (m), 992 (m), 837 (w), 784 (w), 722 (w).

Synthesis of complex L2-$LaCl_2$:

To a solution of L2-H (25.0 mg, 34 µmol, 1.0 eq.) in methanol (15 mL) K_2CO_3 (4.8 mg, 34 µmol, 1.0 eq.) was added and stirred for 15 min at room temperature. After addition of $EuCl_3$*7H_2O (12.8 mg, 34 µmol, 1.0 eq.) stirring was continued for 24 h at room temperature. The product was obtained after removal of the solvent under reduced pressure.

Product: quantitative (dark blue solid). **^{1}H NMR (600 MHz, MeOH-d_4):** δ [ppm] = 8.46 (s, 2H), 7.00 (s, 2H), 6.85 (d, *J* = 4.2 Hz, 2H), 6.58 (d, *J* = 4.2 Hz, 2H), 4.88 (d, *J* = 3.8 Hz, 2H), 4.31 (d, *J* = 9.5 Hz, 2H), 3.81 (t, *J* = 9.2 Hz, 2H), 3.77 (t, *J* = 9.2 Hz, 2H), 3.64 (dd, *J* = 9.5, 3.8 Hz, 2H), 3.51 (s, 6H), 2.38 (s, 3H), 2.05 (s, 6H). **^{13}C NMR (151 MHz, MeOH-d_4):** δ [ppm] = 173.56 (C), 156.30 (C), 152.57 (C), 147.46(CH), 146.61 (C), 139.24 (C), 137.56 (C), 137.22 (C), 134.09 (CH), 128.80 (CH), 122.94 (CH), 102.10 (CH), 74.28 (CH), 73.70 (CH), 72.73 (CH), 71.60 (CH), 56.53 (CH_3), 21.21 (CH_3), 20.24 (CH_3). **MS (ESI (-), FTMS):** m/z = 897.13403 (100%, - Cl^-, -2H^+, 897.13835). **MS (ESI (+), FTMS):** m/z = 899.15143 (10%, -Cl^-, 899.15290), 863.17468 (6%, -2Cl^-, -H^+, 863.17622). **CHN:** calcd (9 H_2O) [%]: C 37.20, H 5.42, N 7.66; found [%]: C 37.24, H 5.38, N 7.32. **IR (KBr):** 3837 (w), 3438 (m), 3381 (m), 3010, (w), 2935 (m), 2658 (w), 2460 (w), 2311 (w), 2103 (w), 1926 (w), 1739 (vs), 1612 (m), 1542 (m), 1433 (m), 1367 (s), 1225 (vs), 1105 (m), 1042 (s), 985 (vs), 833 (m), 791 (m), 723 (w).

UV-Vis spectra

UV-Vis measurements were carried out on a PerkinElmer Lambda 35 UV/Vis Spectrometer using Quartz cuvettes (200 - 900 nm) or PS/PMMA cuvettes (300 - 900 nm) purchased at VWR. For baseline calibration (auto zero) the corresponding solvents were measured as standard.

Metal ion sensing has been carried out with ligand **L1-H** ($1\cdot10^{-5}$ mol/L) in HEPES ($3\cdot10^{-4}$ mol/L) buffered methanol solution. Metal ion halides ($1\cdot10^{-4}$ mol/L) were added in 10-fold excess. In case of **L2-H** ($1\cdot10^{-5}$ mol/L) slightly basic solutions with 1 eq. of K_2CO_3 ($1\cdot10^{-5}$ mol/L) were prepared in water or methanol respectively. Again a 10-fold excess of metal ion halides ($1\cdot10^{-4}$ mol/L) was added.

Competitive studies were performed under similar condition for the respective ligand. In this case 10 eq. of a 1:1 mixture of two different metal salts were added.

Titration experiments were performed by using a standard ligand ligand solution of well defined concentration. Metal salts were added in varying ratios between 0 and 8 eq.

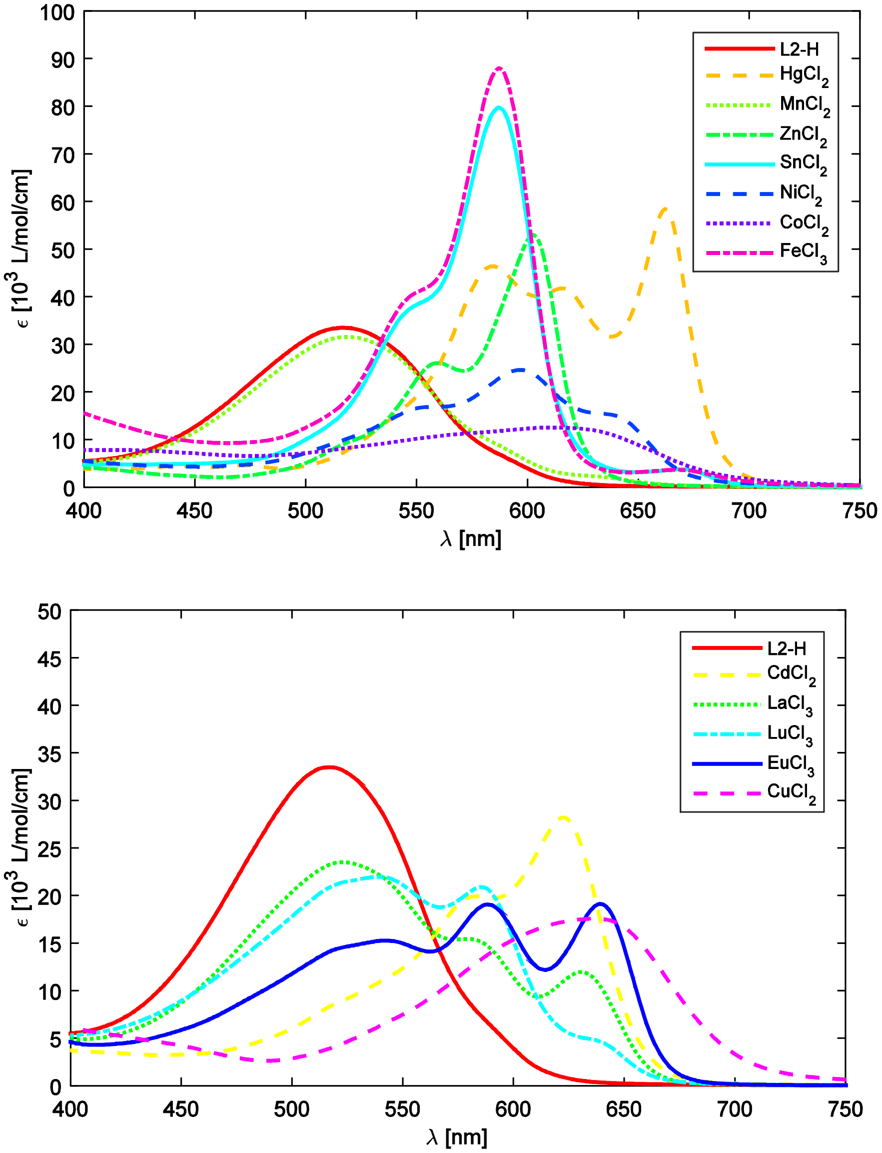


Figure 1. UV-vis spectra of aqueous ligand **L2-H** ($1\cdot10^{-5}$ mol/L) solutions containing 1 eq. of K2CO3 with different metal chlorides ($1\cdot10^{-4}$ mol/L) added.

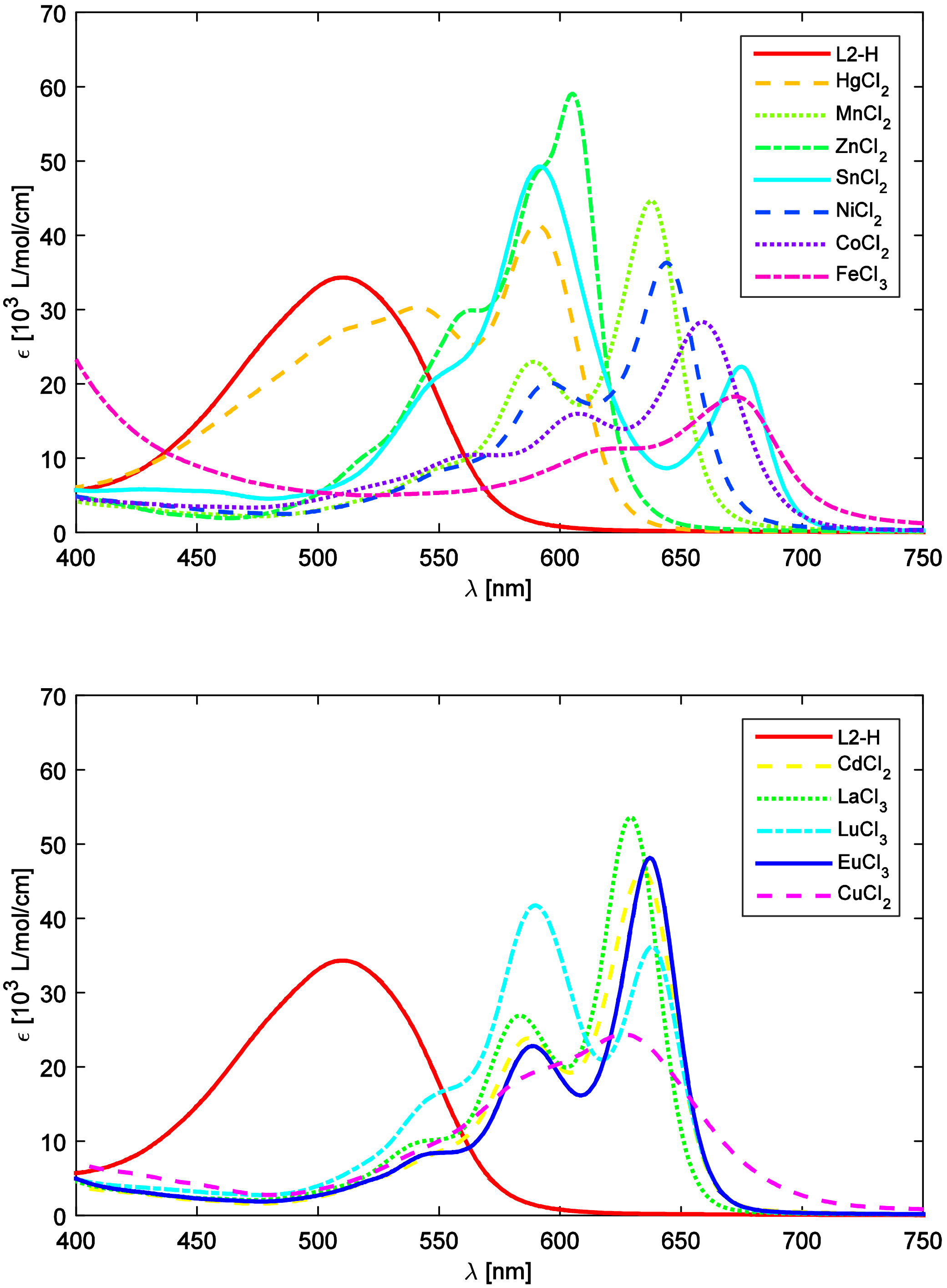


Figure 2. UV-vis spectra of methanolic ligand **L2-H** (1·10^{-5} mol/L) solutions containing 1 eq. of K2CO3 with different metal chlorides (1·10^{-4} mol/L) added.

		Cation A												
		Cu^{2+}	Lu^{3+}	Eu^{3+}	Sn^{2+}	Fe^{3+}	La^{3+}	Cr^{3+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Cd^{2+}	Mn^{2+}	Hg^{2+}
Cation B	Cu^{2+}		0.14	0.21	0.03	0.18	0.02	0.00	0.00	0.00	0.01	0.01	0.00	0.00
	Lu^{3+}	0.86		0.29	0.46	0.39	0.12	0.04	0.01	0.00	0.00	0.01	0.00	0.00
	Eu^{3+}	0.79	0.71		0.19	0.25	0.07	0.02	0.01	0.00	0.01	0.01	0.01	0.00
	Sn^{2+}	0.97	0.54	0.81		0.28	0.29	0.25	0.00	0.00	0.21	0.00	0.00	0.00
	Fe^{3+}	0.82	0.61	0.75	0.72		0.20	0.18	0.06	0.03	0.10	0.06	0.03	0.02
	La^{3+}	0.98	0.88	0.93	0.71	0.80		0.13	0.00	0.00	0.00	0.02	0.00	0.00
	Cr^{3+}	1.00	0.96	0.98	0.75	0.82	0.87		0.09	0.05	0.03	0.01	0.00	0.01
	Ni^{2+}	1.00	0.99	0.99	1.00	0.94	1.00	0.91		0.34	0.03	0.00	0.00	0.00
	Zn^{2+}	1.00	1.00	1.00	1.00	0.97	1.00	0.95	0.66		0.00	0.00	0.00	0.01
	Co^{2+}	0.99	1.00	0.99	0.79	0.90	1.00	0.97	0.97	1.00		0.06	0.00	0.00
	Cd^{2+}	0.99	0.99	0.99	1.00	0.94	0.98	0.99	1.00	1.00	0.94		0.28	0.05
	Mn^{2+}	1.00	1.00	0.99	1.00	0.97	1.00	1.00	1.00	1.00	1.00	0.72		0.16
	Hg^{2+}	1.00	1.00	1.00	1.00	0.98	1.00	0.99	1.00	0.99	1.00	0.95	0.84	

Table 1a. Ratio of complex A and B ($c_A/(c_A+c_B)$) formed in a HEPES buffered ligand (**L1-H**) solution from 1:1 mixtures of two different metal chlorides determined by UV-vis spectroscopy. **L1-H** ($1 \cdot 10^{-5}$ mol/L), $MACl_x$ ($1 \cdot 10^{-4}$ mol/L), MBClx ($1 \cdot 10^{-4}$ mol/L), HEPES ($3 \cdot 10^{-4}$ mol/L) in methanol. The numbers give the content of complex of cation A in the mixture.

H_2O

		Cation A									
		Sn^{2+}	Cu^{2+}	Fe^{3+}	Hg^{2+}	Zn^{2+}	Ni^{2+}	Co^{2+}	Cd^{2+}	Eu^{3+}	La^{3+}
Cation B	Sn^{2+}		0.13	0.32	0.05	0.00	0.00	0.00	0.00	0.00	0.00
	Cu^{2+}	0.87		0.58	0.03	0.00	0.00	0.00	0.00	0.00	0.00
	Fe^{3+}	0.68	0.42		0.21	0.08	0.35	0.41	0.21	0.33	0.22
	Hg^{2+}	0.95	0.97	0.79		0.00	0.00	0.00	0.00	0.00	0.00
	Zn^{2+}	1.00	1.00	0.92	1.00		0.23	0.17	0.06	0.04	0.01
	Ni^{2+}	1.00	1.00	0.65	1.00	0.77		0.32	0.22	0.10	0.09
	Co^{2+}	1.00	1.00	0.59	1.00	0.83	0.68		0.34	0.35	0.10
	Cd^{2+}	1.00	1.00	0.79	1.00	0.94	0.78	0.66		0.45	0.16
	Eu^{3+}	1.00	1.00	0.67	1.00	0.96	0.90	0.65	0.55		0.24
	La^{3+}	1.00	1.00	0.78	1.00	0.99	0.91	0.90	0.84	0.76	

MeOH

		Cation A									
		Fe^{3+}	Cu^{2+}	Eu^{3+}	La^{3+}	Sn^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Cd^{2+}	Hg^{2+}
Cation B	Fe^{3+}		0.31	0.29	0.05	0.07	0.03	0.06	0.00	0.01	0.00
	Cu^{2+}	0.69		0.35	0.09	0.08	0.00	0.05	0.00	0.00	0.00
	Eu^{3+}	0.71	0.65		0.19	0.15	0.06	0.03	0.01	0.00	0.00
	La^{3+}	0.95	0.91	0.81		0.41	0.03	0.04	0.03	0.00	0.00
	Sn^{2+}	0.93	0.92	0.85	0.59		0.10	0.09	0.00	0.08	0.00
	Ni^{2+}	0.97	1.00	0.94	0.97	0.90		0.26	0.13	0.12	0.02
	Co^{2+}	0.94	0.95	0.97	0.96	0.91	0.74		0.33	0.03	0.01
	Zn^{2+}	1.00	1.00	0.99	0.97	1.00	0.87	0.67		0.02	0.00
	Cd^{2+}	0.99	1.00	1.00	1.00	0.92	0.88	0.97	0.98		0.01
	Hg^{2+}	1.00	1.00	1.00	1.00	1.00	0.98	0.99	1.00	0.99	

Table 1b. Ratio of complex A and B ($c_A/(c_A+c_B)$) formed in a basic ligand (**L2-H**) solution from 1:1 mixtures of two different metal chlorides determined by UV-vis spectroscopy. **L2-H** ($1\cdot10^{-5}$ mol/L), K_2CO_3 ($1\cdot10^{-5}$ mol/L), M_ACl_x ($1\cdot10^{-4}$ mol/L), M_BCl_x ($1\cdot10^{-4}$ mol/L) in water or methanol. The numbers give the content of complex of cation A in the mixture.

Fluorescence measurements

Fluorescence measurements at 365 nm were carried out on a PerkinElmer LS45 Fluorescence Spectrometer using quartz cuvettes. For tested solutions the established concentrations of UV-Vis sensing experiments were chosen.

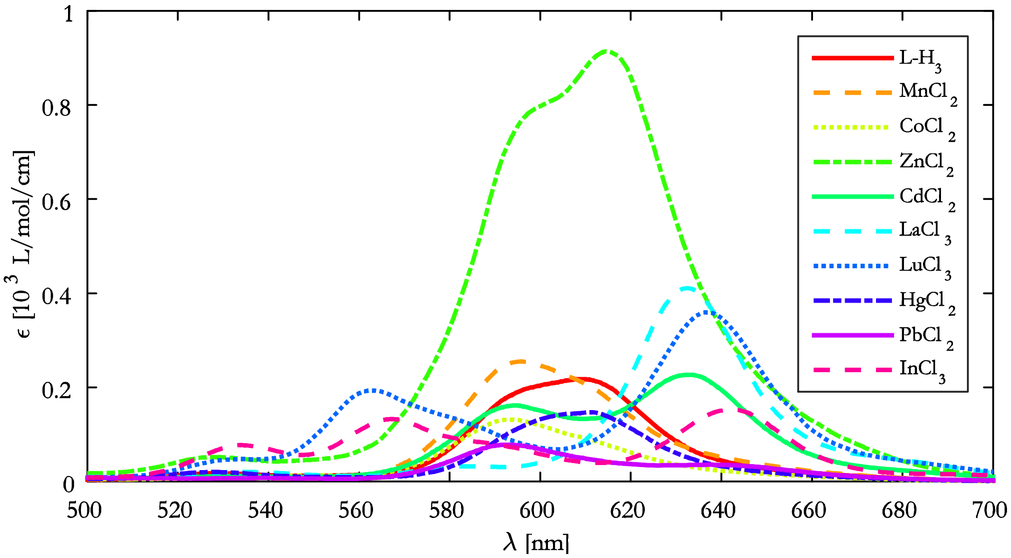


Figure 2. Emission spectra (excitation at 365 nm) of HEPES buffered ligand (**L1-H**) solution with different metal chlorides in methanol. **L1-H** ($1\cdot10^{-5}$ mol/L), MCl_x ($1\cdot10^{-4}$ mol/L), HEPES ($3\cdot10^{-4}$ mol/L) in methanol.

X-ray crystal structure.

Data for [ZnCl(H_2O)**L1**] were collected at 120 K on an Rigaku Oxford diffractometer equipped with an Atlas EoS CCD detector using mirror-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data collection and processing were performed using *CrysAlisPro*[1] program. The intensities were corrected with gaussian correction method[1]. The structure was solved by direct methods with the SHELXS[2] program. The structure was refined by full-matrix least squares calculations based on F^2 using SHELXL2014[2] module incorporated into the OLEX2[3] program package. Hydrogen atoms were included in calculated positions using 'riding model'. No attempt was made to locate the hydrogens for nitrogen and water molecules, and was added using ADDH command in OLEX2[3]. Crystal data for [ZnCl(H_2O)**L1**]: M = 1118.65, block, 0.26 x 0.17 x 0.11 mm^3, monoclinic, space group *C2/c*, *a* = 43.6763(10) Å, *b* = 14.1945(4) Å, *c* = 7.9006(2) Å, α = 90°, β = 92.268(3)°, γ = 90°, V = 4894.2(2) $Å^3$, Z = 4, D_c = 1.518 g/cm^3, F000 = 2312, μ= 1.157 mm^{-1}, T = 120 K, $2\theta_{max}$ = 55°, 33084 reflections with 4389 [$I_o > 2\sigma(I_o)$], R_{int} = 0.0485, reflections/parameters/restraints = 5619/326/1, GoF = 1.077, R = 0.0783 and wR= 0.2415 [$I_o > 2\sigma(I_o)$], R = 0.0928 and wR= 0.2561 (all reflections), 1.145 < ∆ρ < -0.761 e/$Å^3$. CCDC-1520476 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif;

References

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