Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2019

Figure/Table	Content	Page number
Figure S1	FT-IR spectrum of complex 1	3
Figure S2	FT-IR spectrum of complex 2	3
Figure S3	FT-IR spectrum of complex 3	4
Figure S4	¹ H NMR spectrum of complex 1 recorded in (CDCl ₃ +	4
	DMSO-d ₆)	
Figure S5	$^{13}C{^{1}H}$ NMR spectrum of complex 1 recorded in	5
	$(CDCl_3 + DMSO-d_6)$	
Figure S6	¹¹⁹ Sn NMR spectrum of complex 1 recorded in CDCl ₃	5
Figure S7	¹ H NMR spectrum of complex 2 recorded in CDCl ₃	6
Figure S8	$^{13}C{^{1}H}$ NMR spectrum of complex 2 recorded in CDCl ₃	6
Figure S9	¹¹⁹ Sn NMR spectrum of complex 2 recorded in CDCl ₃	7
Figure S10	¹ H NMR spectrum of complex 3 recorded in CDCl ₃	7
Figure S11	$^{13}C{^{1}H}$ NMR spectrum of complex 3 recorded in CDCl ₃	8
Figure S12	¹¹⁹ Sn NMR spectrum of complex 3 recorded in CDCl ₃	8
Figure S13	Absorption spectral variation of complex 1 (1.1 x 10 ⁻⁵ mol	9
	dm ⁻³) with the addition of 1-5 equivalent of nitrate salts	
	$(1.6 \text{ x } 10^{-4} \text{ mol dm}^{-3}) \text{ of } (\mathbf{a}) \text{ Ba}^{2+} (\mathbf{b}) \text{ Cr}^{3+} (\mathbf{c}) \text{ Co}^{2+} (\mathbf{d}) \text{ Fe}^{3+}$	
	in methanol	
Figure S14	Absorption spectral variation of complex 1 (1.1 x 10 ⁻⁵ mol	10
	dm^{-3}) with the addition of 1-5 equivalent of nitrate salts	
	$(1.6x \ 10^{-4} \ \text{mol} \ \text{dm}^{-5}) \text{ of } (\mathbf{e}) \ \text{Cd}^{2+} (\mathbf{f}) \ \text{Mn}^{2+} (\mathbf{g}) \ \text{Ni}^{2+} (\mathbf{h}) \ \text{Ag}^{+}$	
5. 645	(i) Zn^{2+} in methanol	
Figure S15	Absorption spectral variation of complex 2 (1.1 x 10^{-5} mol	11
	dm ³) with the addition of 1-5 equivalent of nitrate salts $(1 - 10^{-4} - 11^{-3}) = f(2) = 2^{+4} + 12^{-3} + 12$	
	$(1.6 \times 10^{-1} \text{ mol dm}^{\circ}) \text{ of } (\mathbf{a}) \text{ Ba}^{-1} (\mathbf{b}) \text{ Cr}^{-1} (\mathbf{c}) \text{ Co}^{-1} (\mathbf{d}) \text{ Fe}^{-1}$	
Eiguna S16	In methanol Absorption spectral variation of complex $2(1.1 \times 10^{-5} \text{ mol})$	10
Figure 510	Absorption spectral variation of complex 2 (1.1 x 10 mol dm^{-3}) with the addition of 1.5 equivalent of nitrate salts	12
	(1.6 \times 10 ⁻⁴ mol dm ⁻³) of (a) Cd ²⁺ (f) Mn ²⁺ (g) Ni ²⁺ (h) A g ⁺	
	(i) $7n^{2+}$ in methanol	
Figure S17	Absorption spectral variation of complex $3(11 \times 10^{-5} \text{ mol})$	13
1 iguie 517	dm^{-3}) with the addition of 1-5 equivalent of nitrate salts	15
	(1.6 x 10^{-4} mol dm ⁻³) of (a) Ba ²⁺ (b) Cr ³⁺ (c) Co ²⁺ (d) Fe ³⁺	
	in methanol	
Figure S18	Absorption spectral variation of complex $3(1.1 \times 10^{-5} \text{ mol})$	14
0	dm ⁻³) with the addition of 1-5 equivalent of nitrate salts	
	$(1.6 \times 10^{-4} \text{ mol dm}^{-3}) \text{ of } (\mathbf{e}) \text{ Cd}^{2+} (\mathbf{f}) \text{ Mn}^{2+} (\mathbf{g}) \text{ Ni}^{2+} (\mathbf{h}) \text{ Ag}^{+}$	
	(i) Zn^{2+} in methanol	
Figure S19	(a) Absorption spectral variation of complex 1 (1.1 x 10 ⁻⁵	15
	mol dm ⁻³) with the addition of 1-5 equivalent of copper(II)	
	nitrate trihydrate (1.6 x 10^{-4} mol dm ⁻³) in methanol. (b)	
	Stoichiometric plot of complex 1 with copper(II) nitrate	
	trihvate (c) Joh's plot of Complex 1 with copper(II) nitrate	
1	uniyad. (C) JOB'S PIOL OF COMPLEX I with copper(II) Intrate	<u> </u>

	trihydrate. (d) Benesi-Hildebrand plot Complex 1 with	
	addition of copper(II) nitrate trihydrate	
Figure S20	(a) Absorption spectral variation of complex 2 (1.1 x 10^{-5}	16
	mol dm ⁻³) with the addition of 1-5 equivalent of copper(II)	
	nitrate trihydrate $(1.6 \times 10^{-4} \text{ mol dm}^{-3})$ in methanol. (b)	
	Stoichiometric plot of complex 2 with copper(II) nitrate	
	trihyate. (c) Job's plot of Complex 2 with copper(II) nitrate	
	trihydrate. (d) Benesi-Hildebrand plot Complex 2 with	
	addition of copper(II) nitrate trihydrate	
Figure S21	Changes in partial ¹ H NMR spectra of complex 3 with the	17
	addition of an equivalent amount of selected metal ions in	
	DMSO-d ₆ .	
Figure S22	Graph between absorbance and concentration of guest	18
	(Cu^{2+}) for calculation of slope for complex 1	
Figure S23	Graph between absorbance and concentration of guest	19
	(Cu^{2+}) for calculation of slope for complex 2	
Figure S24	Graph between absorbance and concentration of guest	19
	(Cu^{2+}) for calculation of slope for complex 3	
Figure S25	Powder XRD pattern of complex 1	21
Figure S26	Powder XRD pattern of complex 1	22
Figure S27	Powder XRD pattern of complex 1	23



Figure S1: FT-IR spectrum of complex 1.



Figure S2: FT-IR spectrum of complex 2.



Figure S3: FT-IR spectrum of complex 3.



Figure S4: ¹H NMR spectrum of complex **1** recorded in (CDCl₃+ DMSO-d₆).



Figure S5: ¹³C{¹H} NMR spectrum of complex **1** recorded in (CDCl₃+ DMSO-d₆).



Figure S6: ¹¹⁹Sn NMR spectrum of complex 1 recorded in CDCl₃.



Figure S7: ¹H NMR spectrum of complex 2 recorded in CDCl₃.



Figure S8: ¹³C{¹H} NMR spectrum of complex **2** recorded in CDCl₃.



Figure S9: ¹¹⁹Sn NMR spectrum of complex 2 recorded in CDCl₃.



Figure S10: ¹H NMR spectrum of complex 3 recorded in CDCl₃.



Figure S11: ${}^{13}C{}^{1}H$ NMR spectrum of complex 3 recorded in CDCl₃.



Figure S12: ¹¹⁹Sn NMR spectrum of complex 3 recorded in CDCl₃.



Figure S13: Absorption spectral variation of complex 1 ($1.1 \times 10^{-5} \text{ mol dm}^{-3}$) with the addition of 1-5 equivalent of nitrate salts ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) of (**a**) Ba²⁺ (**b**) Cr³⁺ (**c**) Co²⁺ (**d**) Fe³⁺ in methanol.



Figure S14: Absorption spectral variation of complex **1** ($1.1 \times 10^{-5} \text{ mol dm}^{-3}$) with the addition of 1-5 equivalent of nitrate salts ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) of (**e**) Cd²⁺ (**f**) Mn²⁺ (**g**) Ni²⁺ (**h**) Ag⁺ (**i**) Zn²⁺ in methanol.



Figure S15: Absorption spectral variation of complex 2 ($1.1 \times 10^{-5} \text{ mol dm}^{-3}$) with the addition of 1-5 equivalent of nitrate salts ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) of (**a**) Ba²⁺ (**b**) Cr³⁺ (**c**) Co²⁺ (**d**) Fe³⁺ in methanol.



Figure S16: Absorption spectral variation of complex **2** ($1.1 \times 10^{-5} \text{ mol dm}^{-3}$) with the addition of 1-5 equivalent of nitrate salts ($1.6 \times 10^{-4} \text{ mol dm}^{-3}$) of (**e**) Cd²⁺ (**f**) Mn²⁺ (**g**) Ni²⁺ (**h**) Ag⁺ (**i**) Zn²⁺ in methanol.



Figure S17: Absorption spectral variation of complex **3** (1.1 x 10^{-5} mol dm⁻³) with the addition of 1-5 equivalent of nitrate salts (1.6 x 10^{-4} mol dm⁻³) of (a) Ba²⁺ (b) Cr³⁺ (c) Co²⁺ (d) Fe³⁺ in methanol.



Figure S18: Absorption spectral variation of complex **3** ($1.1 \times 10^{-5} \mod \text{dm}^{-3}$) with the addition of 1-5 equivalent of nitrate salts ($1.6 \times 10^{-4} \mod \text{dm}^{-3}$) of (**e**) Cd²⁺ (**f**) Mn²⁺ (**g**) Ni²⁺ (**h**) Ag⁺ (**i**) Zn²⁺ in methanol.



Figure S19: (a) Absorbance of complex $1 (1.1 \times 10^{-5} \text{ mol dm}^{-3})$ with the addition of 1-5 equivalent of copper(II) nitrate trihydrate (1.6 x $10^{-4} \text{ mol dm}^{-3})$ in methanol. (b) Stoichiometric plot of complex 1 with copper(II) nitrate trihydre. (c) Job's plot of complex 1 with copper(II) nitrate trihydrate. (d) Benesi-Hildebrand plot of complex 1 with addition of copper(II) nitrate trihydrate.



Figure S20: (a) Absorbance of complex $2(1.1 \times 10^{-5} \text{ mol dm}^{-3})$ with the addition of 1-5 equivalent of copper(II) nitrate trihydrate $(1.6 \times 10^{-4} \text{ mol dm}^{-3})$ in methanol. (b) Stoichiometric plot of complex 2 with copper(II) nitrate trihydre. (c) Job's plot of complex 2 with copper(II) nitrate trihydrate. (d) Benesi-Hildebrand plot of complex 2 with addition of copper(II) nitrate trihydrate.





LOD (Limit of Detection) for complexes 1-3 with Cu²⁺ ion.

LOD for all complexes with Cu^{2+} ion was calculated from the absorption data. It was calculated by considering the band at wavelength 366 nm in all complexes **1-3** which gradually decreases on titration with 10 μ L Cu²⁺ ion solution.

To determine the standard deviation for the absorbance, the absorbance of the individual receptors without any cation was measured by 15 times and the standard deviation of blank measurements was calculated.

The limit of detection (LOD) of the complexes for sensing of Cu^{2+} was determined from the following equation:

$LOD = K \times SD/S$

Where K = 3 (according to IUPAC consideration); SD is the standard deviation of the blank receptor (complex 1-3) solution; S is the slope of the calibration curve. From the linear fit of the graphs S22, S23 and S24, slope (S) for all complexes are determined.



Figure S22: Graph between absorbance and concentration of guest (Cu^{2+}) for calculation of slope for complex 1.



Figure S23: Graph between absorbance and concentration of guest (Cu^{2+}) for calculation of



slope for complex 2.

Figure S24: Graph between absorbance and concentration of guest (Cu^{2+}) for calculation of

slope for complex **3**.

Complex 1: K = 3; SD = 0.027; S = -32385.78; LOD = $2.5 \times 10^{-6} M$ Complex 2: K = 3; SD = 0.028; S = -31632.92; LOD = $2.6 \times 10^{-6} M$ Complex 3: K = 3; SD = 0.023; S = -46664.01; LOD = $1.47 \times 10^{-6} M$

The binding constant K can be calculated for complexes 1-3.

we got intercept (C) and slope (m) value by linear fitting the graph (Benesi-Hildebrand plot) for complex **1**, **2** and **3** from plot **S19(d)**, **S20(d)** and **3(d)** respectively. K can be calculated by formula C/m. Complex **1**: C = 0.477; $m = 2.386 \times 10^{-5}$; $K = 0.19 \times 10^5 M^{-1}$ Complex **2**: C = 0.631; $m = 2.391 \times 10^{-5}$; $K = 0.26 \times 10^5 M^{-1}$

Complex 3: C = 0.433; $m = 1.183 \times 10^{-5}$; $K = 0.40 \times 10^{5} M^{-1}$

X-ray crystallography

The intensity data of **1-3** were collected on a Rigaku SuperNova diffractometer equipped with an Eos S2 CCD detector, using MoK α radiation with graphite monochromator ($\lambda = 0.71073$ Å) at T = 293(2) K. The structure was solved by SHELXT and refined on F^2 by full-matrix least-squares methods using SHELXL using Olex2 as the graphical interface.¹⁻ ² Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized F_0^2 from counting statistics. The function R_1 and wR_2 were ($\sigma ||F_0| - |F_c||$) / $\sigma |F_0|$ and [σw ($F_0^2 - F_c^2$)² / $\sigma(wF_0^4)$]^{1/2}, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1862874-1862876. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: <u>deposit@ccdc.cam.ac.uk</u>



Figure S25: Powder XRD pattern of complex 1.



Figure S26: Powder XRD pattern of complex 2.



Figure S27: Powder XRD pattern of complex 3.

References:

1. Sheldrick, G.M., Crystal structure refinement with ShelXL, Acta Cryst., (2015), C71, 3-8.

 O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), 42, 339-341.