

Solvent-regulated fluorescence off-on signaling of Ni(II) and Zn(II) with the formation of two mononuclear complexes with ATP detection ability by Zn(II) assembly

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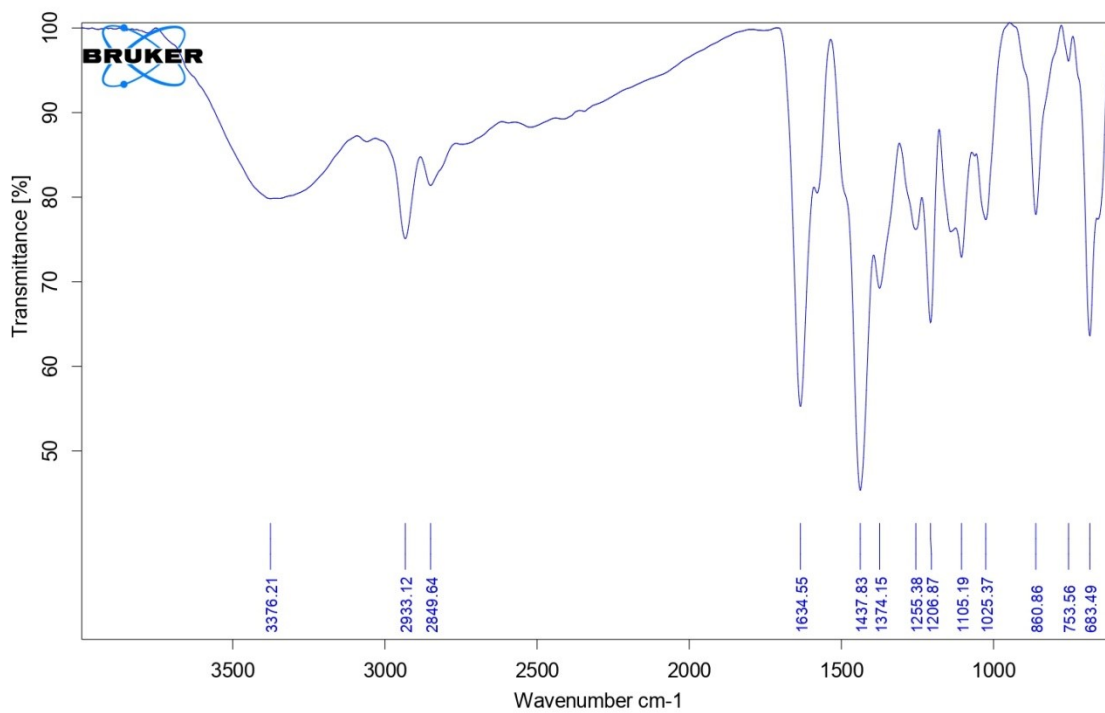


Fig. S1: FTIR spectrum of **HL**

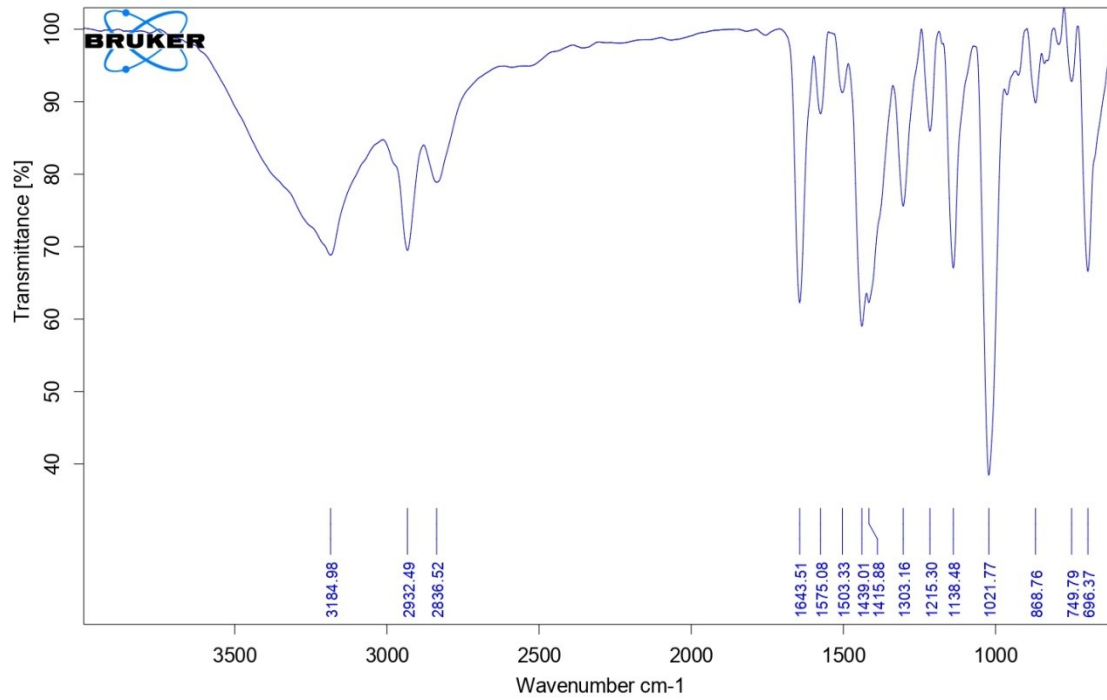


Fig. S2: FTIR spectrum of complex **1**

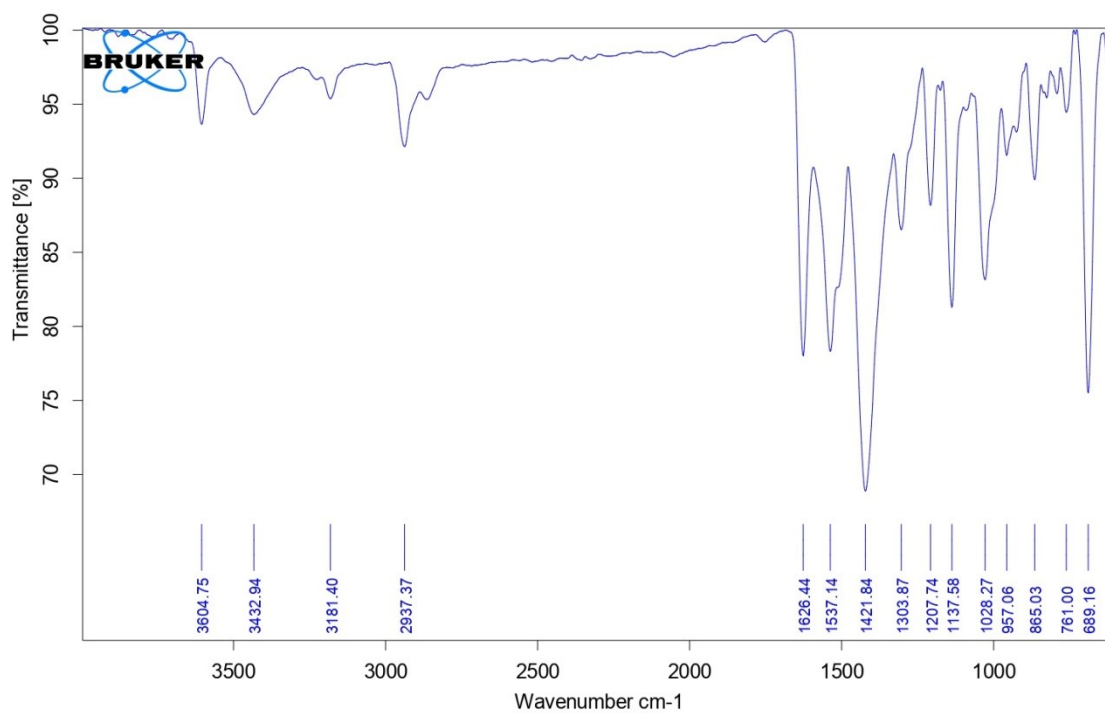


Fig. S3: FTIR spectrum of complex 2

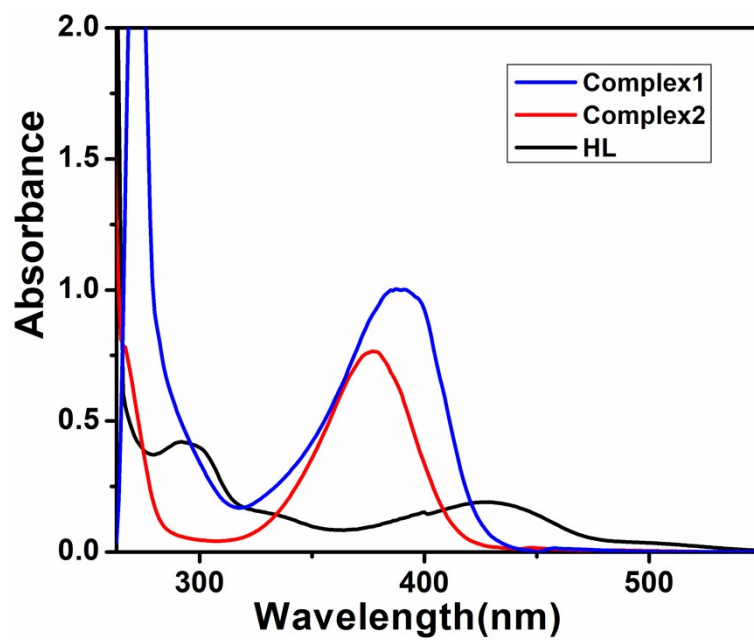


Fig.S4: UV spectrum of HL, complex 1 and complex 2

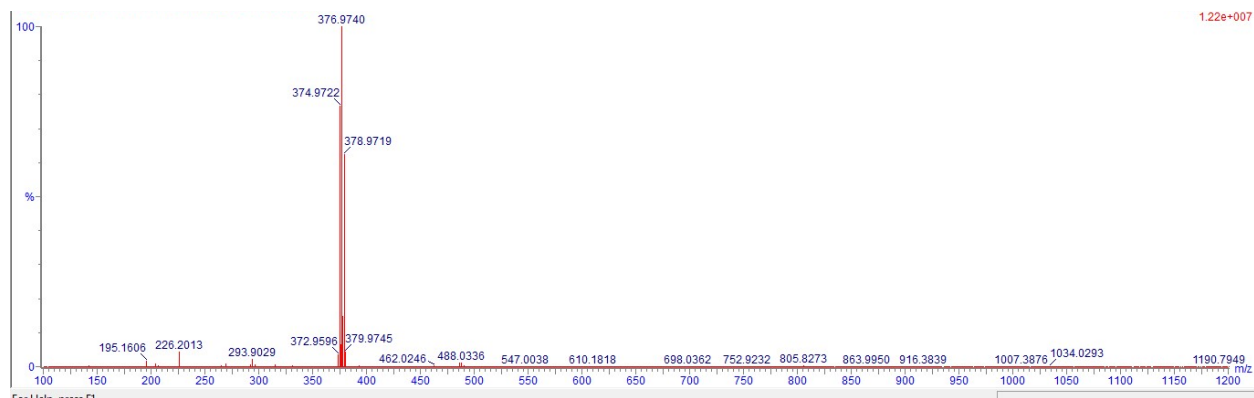


Fig. S5: Mass spectrum of HL

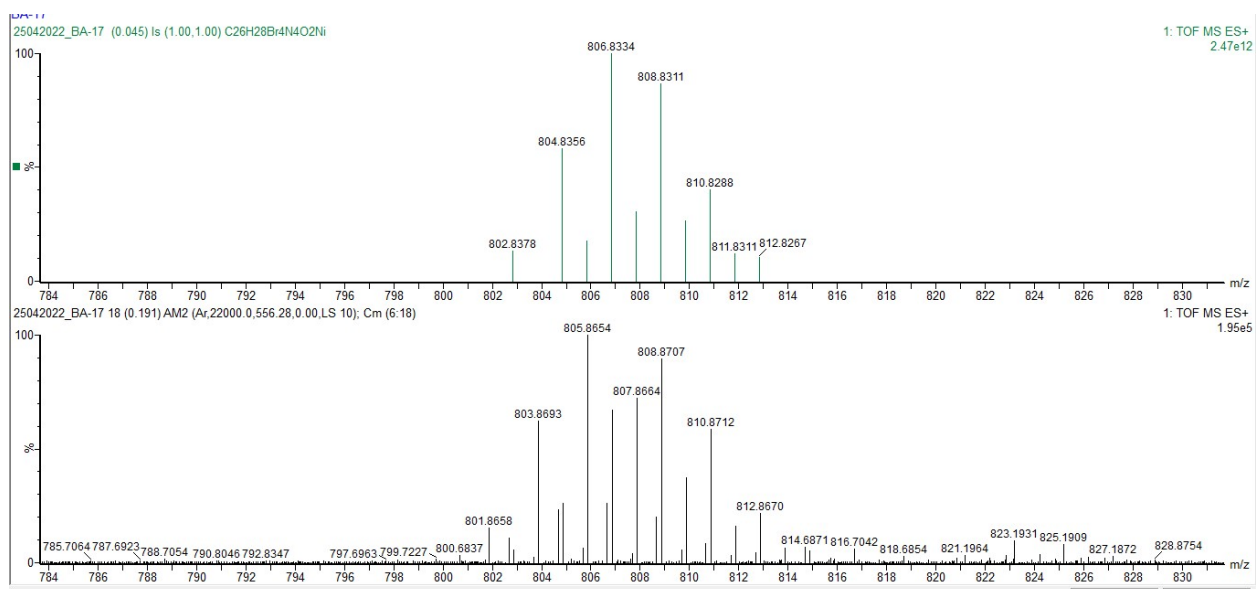


Fig. S6: FTIR spectrum of complex 1

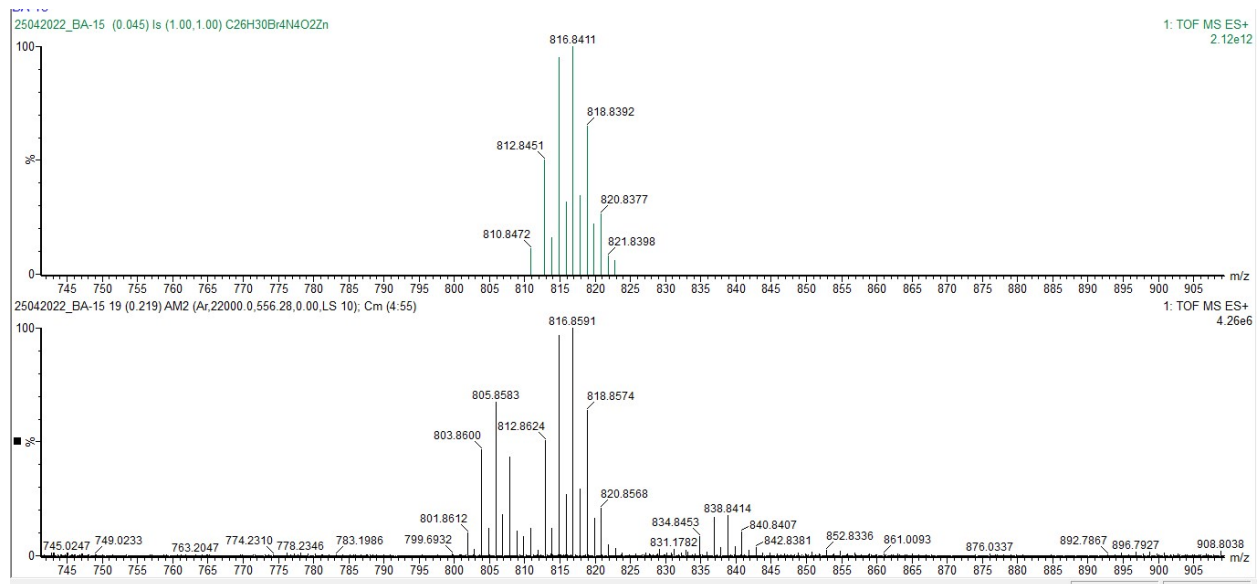


Fig. S7: Mass spectrum of complex 2

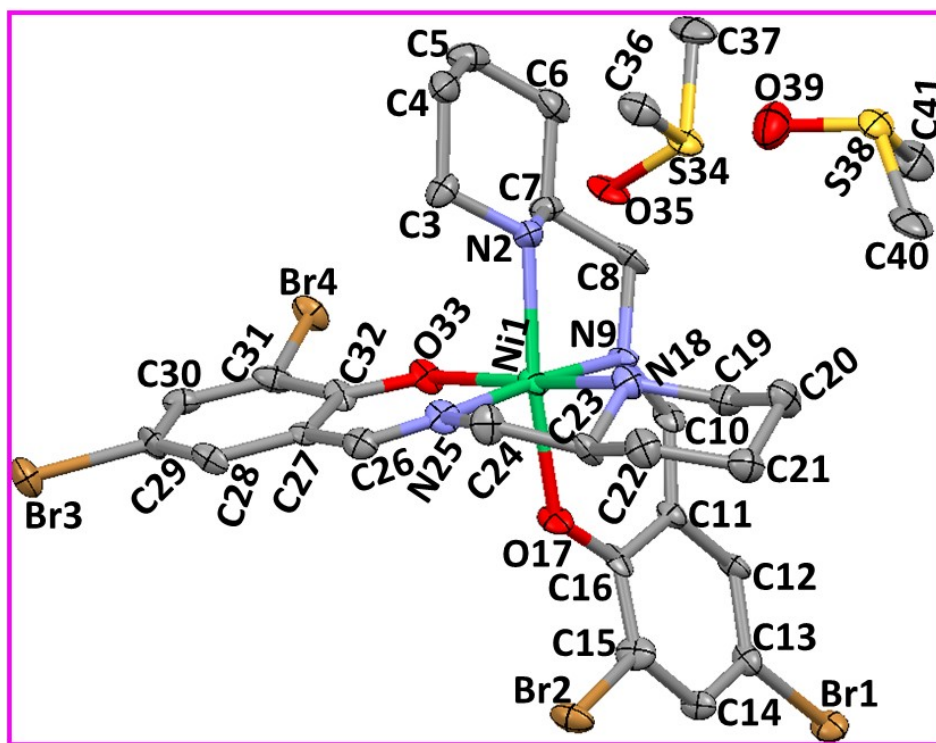


Fig. S8: Molecular plot of complex 1

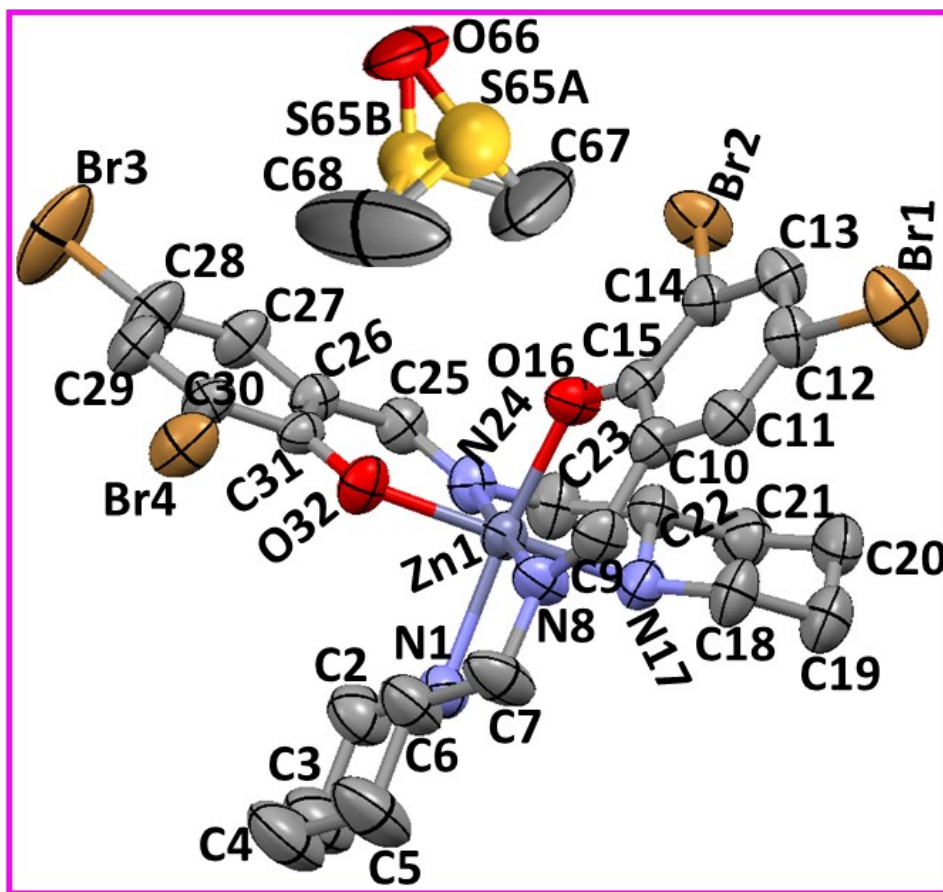


Fig. S9: Molecular plot of complex 2

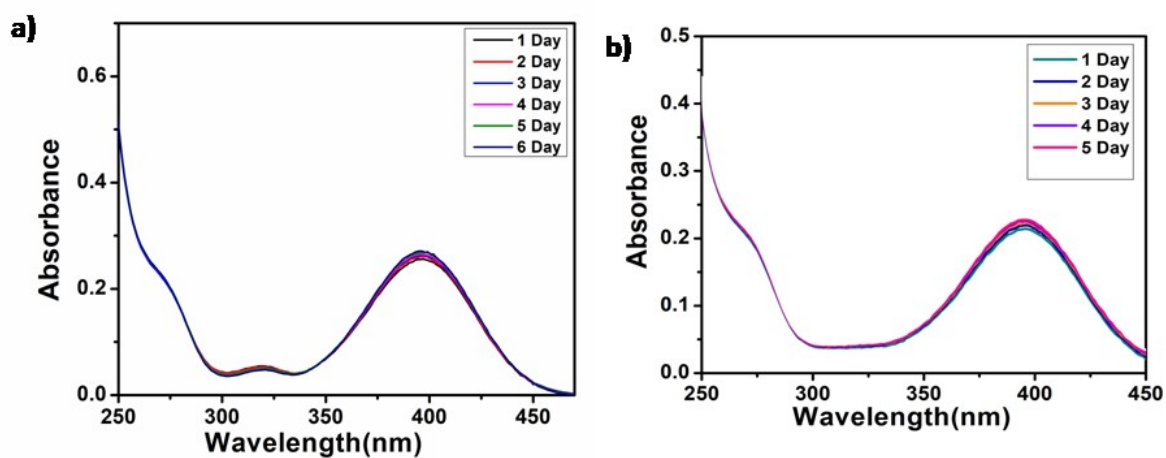


Fig. S10: Absorbance alteration of HL ($3 \times 10^{-5} \text{ M}^{-1}$) as a function of time in a) methanol: H_2O (9:1) HEPES buffer b) pure HEPES medium

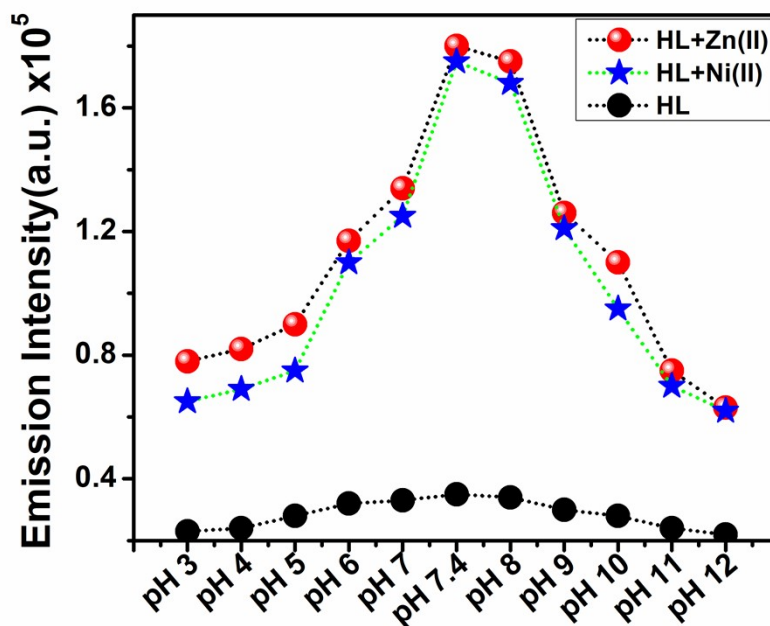


Fig. S11: In different pH the fluorescence intensity changes of free **HL** ($3 \times 10^{-5} \text{ M}^{-1}$) a) at 453 nm in the absence and presence (four equivalent) of Zn(II)/Ni(II) in methanol-water HEPES buffer medium.

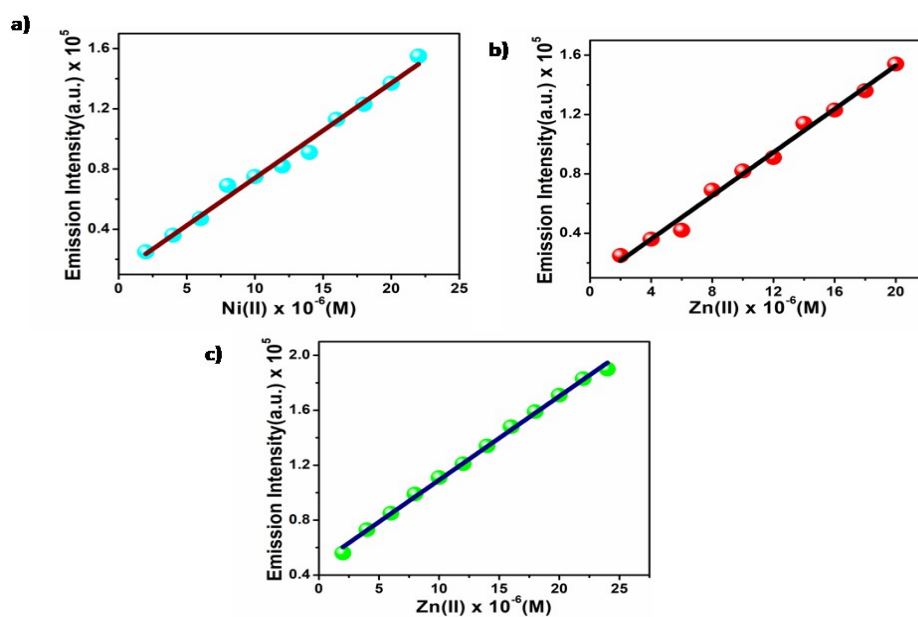


Fig. S12: Change of fluorescence emission intensity of **HL** as a function of a) Zn(II) and Ni(II) concentration for detection limit calculation in a) methanol /water 9:1 HEPES buffer medium b) Zn(II) only in pure HEPES buffer medium, used to measure limit of detection.

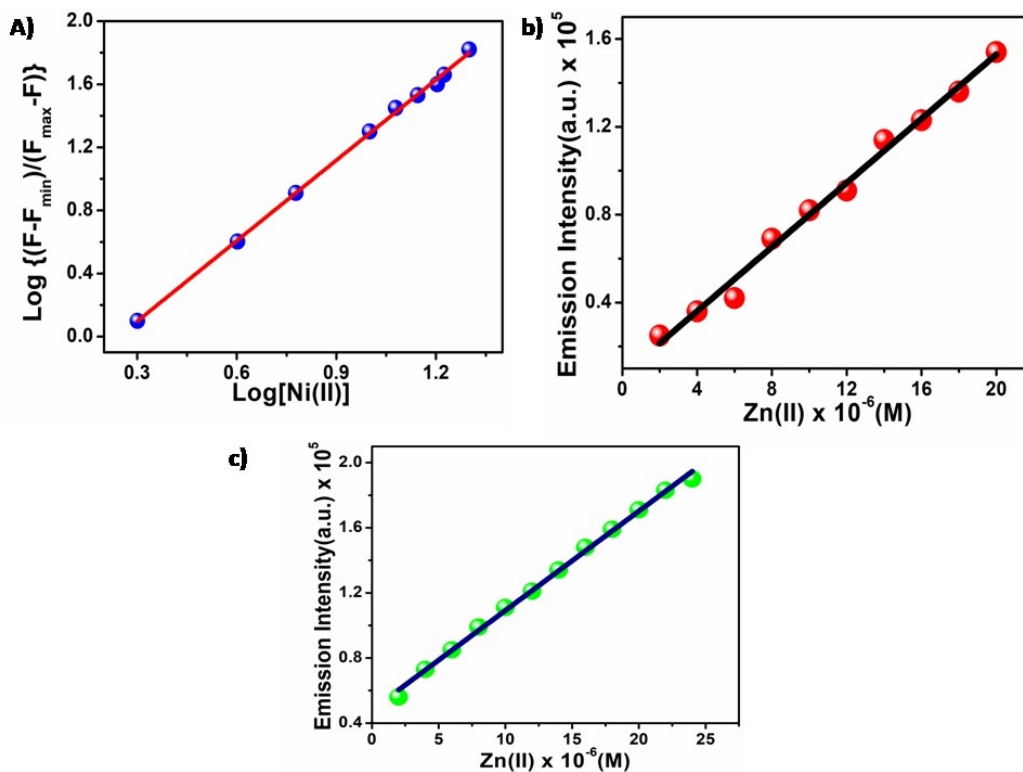


Fig. S13: a) During recognition of Zn(II) and Ni(II) in methanol-water medium b) Zn(II) in HEPES buffer medium by HL, the Binding constant measurement by utilizing probe-analyte fluoresce enhancement titration pictograph.

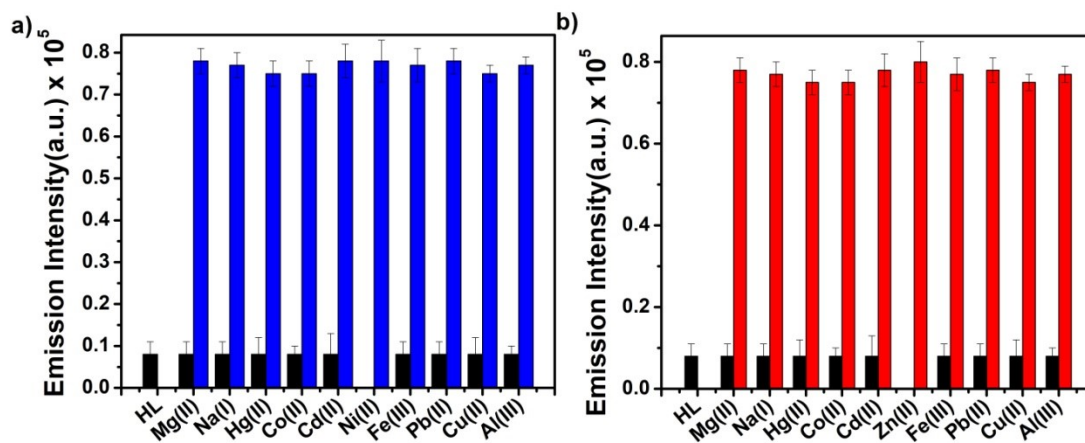


Fig. S14: Fluorescence intensity change of a) HL-Zn(II) b) HL-Ni(II) adduct in methanol water (9:1) HEPES buffer medium in the presence of four equivalent of various competitive cations.

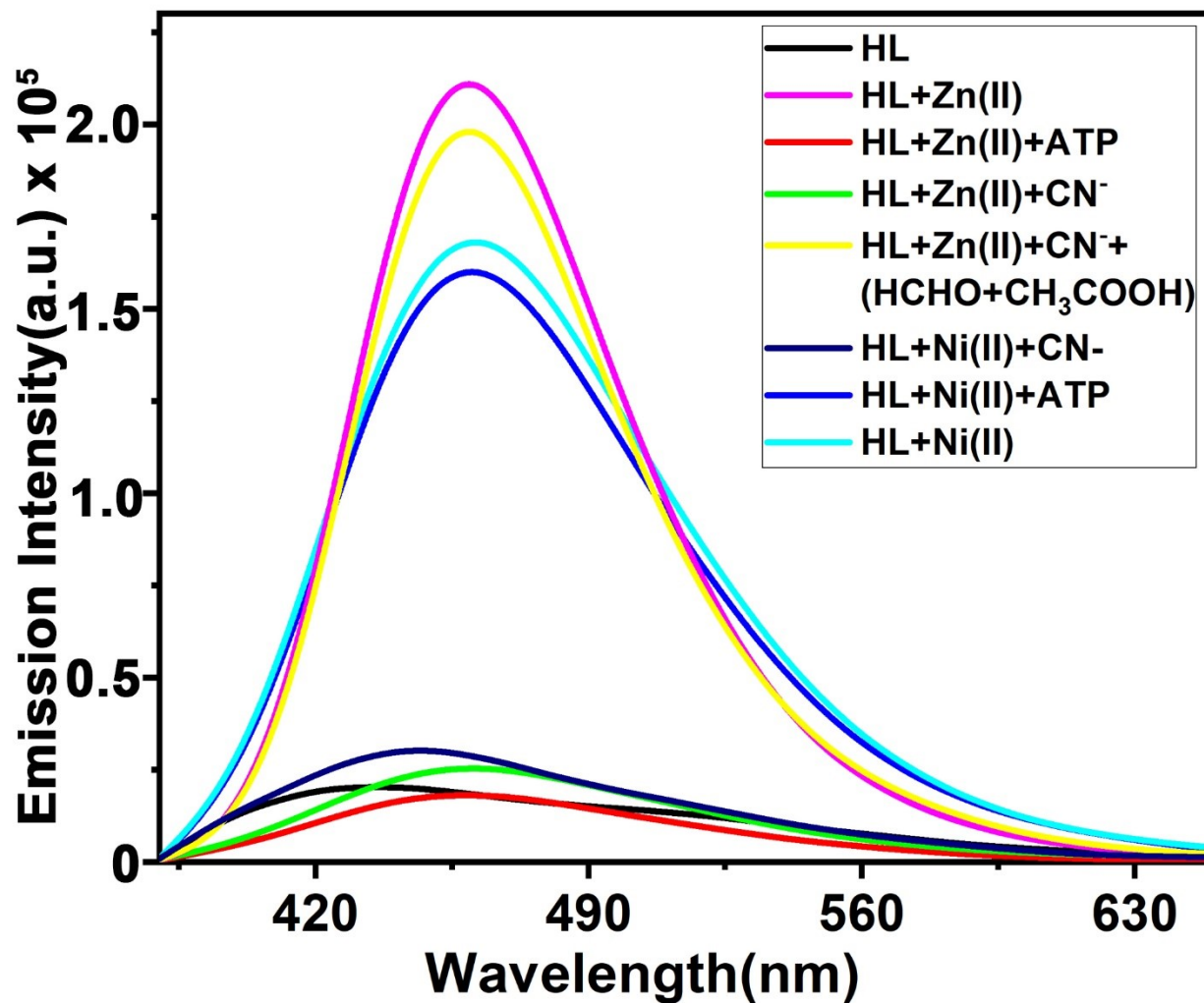


Fig. S15: Selective sensing of Zn(II) in presence of Ni(II) or vice versa in the semi-aqueous medium.

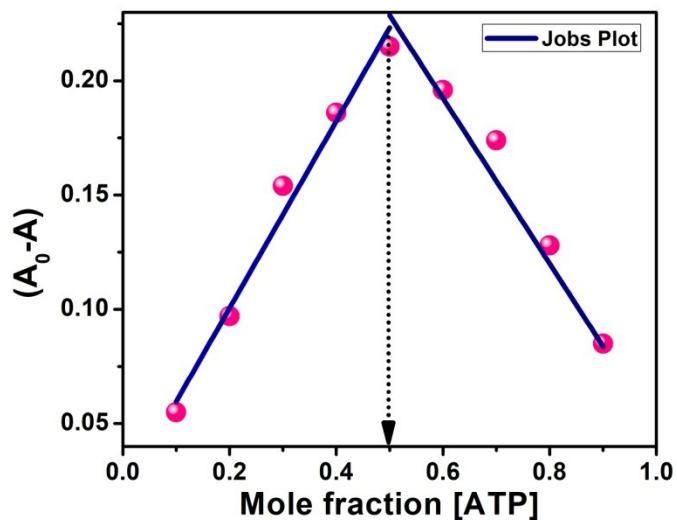


Fig. S16: Jobs plot of 1:1 probe-analyte adduct formation during sensing of ATP by complex 2 in purely HEPES buffer medium.

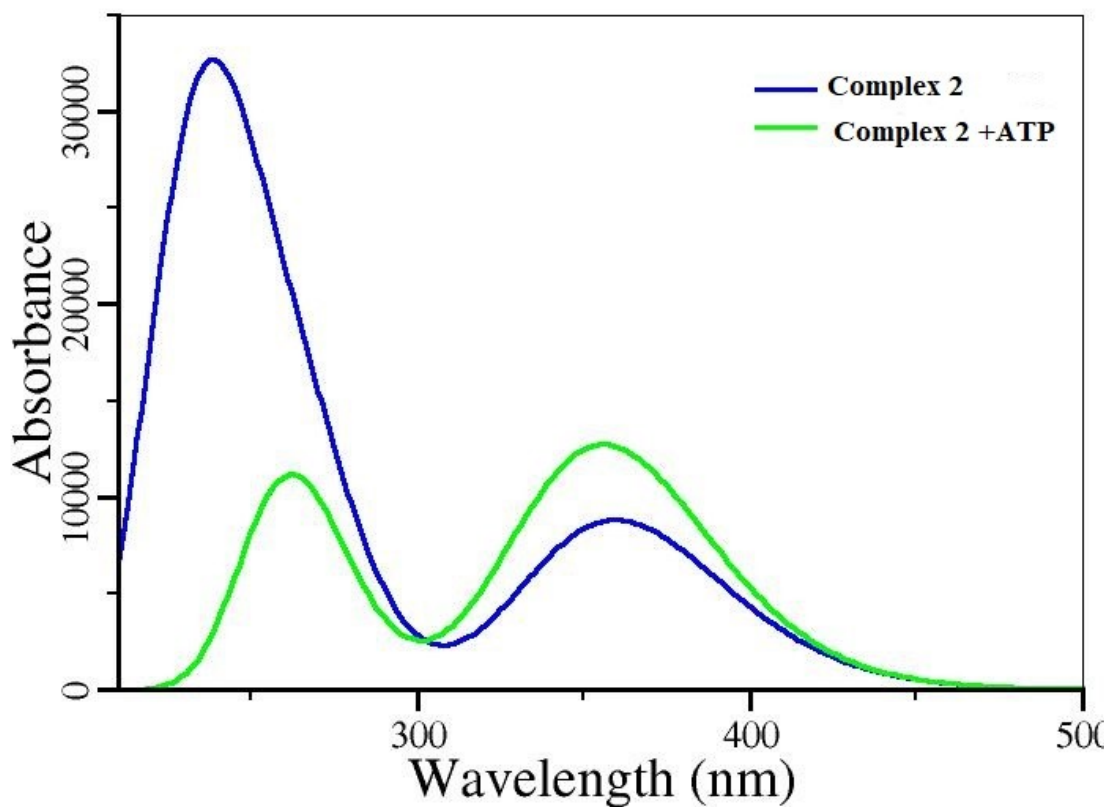


Fig. S17: The theoretically obtained (TDDFT) UV spectrum of complex 2 and complex 2-ATP adduct

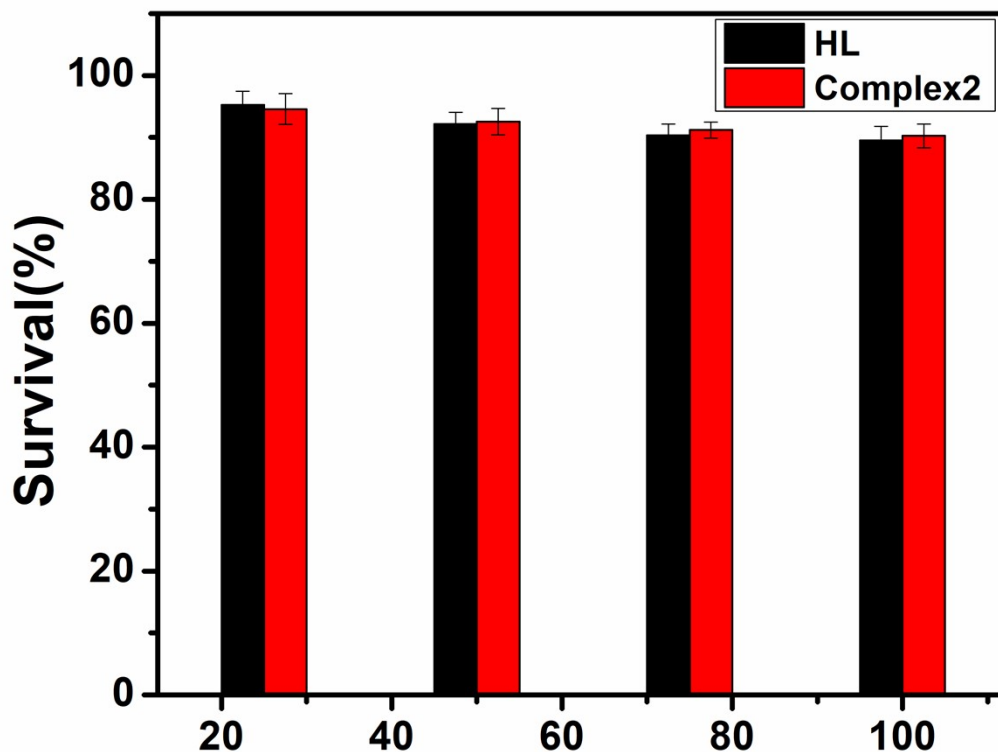


Fig. S18: Dose dependent suppression of cell viability of **HL** and complex **2** on HeLa cell line (24 hrs)

Table S1: C-H... Br interaction parameter of complex **1**

C-H...Br	C-H (Å)	H...Br (Å)	C...Br (Å)	C-H...Br (°)	Symmetry operation for A
C(40)-H(40A)...Br2	0.98	2.98	3.668(6)	128.3	$x, -y+3/2, z+1/2$
C(28)-H(28)... Br2	0.95	3.02	3.828(4)	143.9	$-x+1, -y+2, -z+1$

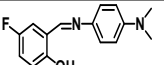
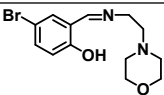
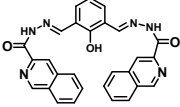
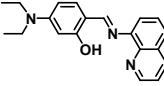
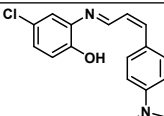
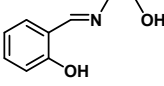
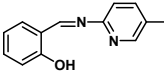
Table S2: Hydrogen bonding parameter of complex **2**

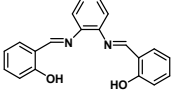
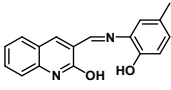
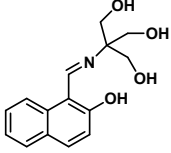
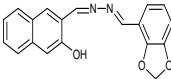
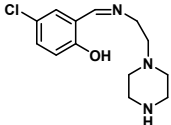
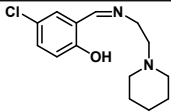
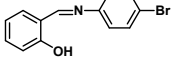
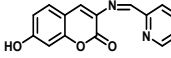
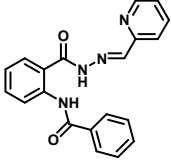
D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry operation for A
N(17)-H(17)...O66	0.87(5)	2.14(5)	2.959(7)	156(4)	$-x, y-1/2, -z+1/2$
N(33)-H(33)...O70	0.85(5)	2.15(6)	2.978(6)	165(5)	x, y, z
N(49)-H(49)...O70	0.79(7)	2.32(7)	3.025(7)	149(7)	x, y, z

Table S3: C-H... Br interaction parameter of complex 2

C-H...Br	C-H (Å)	H...Br (Å)	C...Br (Å)	C-H...Br (°)	Symmetry operation for A
C(13)-H(13)...Br8	0.93	2.97	3.839(5)	155.4	-x, y+1/2, -z+1/2
C(27)-H(27)...Br4	0.93	2.93	3.761(5)	149.5	x, -y+3/2, z+1/2
C(29)-H(29)...Br6	0.93	2.92	3.636(5)	134.9	-x+1, y+1/2, -z+1/2
C(59)-H(59)...Br6	0.93	3.00	3.881(5)	159.0	-x+1, -y+1, -z
C(34)-H(34)...Br3	0.97	2.97	3.830(6)	148.0	x, -y+3/2, z-1/2

Table S4: Reference table of the simple Schiff base ligand with their activity towards Zn(II) and Ni(II) sensing

Probe	Cation detection	LOD (M)	Crystal obtained	Solvent / solvent sensitivity for multi cation	Probe reversibility	Applications	Solid Metal-ligand complex for 2 nd step sensing	references
	Zn ²⁺	2.6×10 ⁻⁷	No	EtOH-H ₂ O (1:2)	No	No	No	1
	Zn ²⁺ ,	4.1×10 ⁻⁷	Yes	MeOH-H ₂ O (1:9)	No	live cells imaging	No	2
	Zn ²⁺ , Mg ²⁺	3.0×10 ⁻⁷ 2.9×10 ⁻⁸	No, No	DMF-H ₂ O (9:1) MeCN/Yes	No	live cells imaging, Tap water, Real sample	No	3
	Zn ²⁺ , Mg ²⁺ , Co ²⁺	1.8×10 ⁻⁶ 7.0×10 ⁻⁹ 2.9×10 ⁻⁸	No, No, No	MeCN-H ₂ O (9:1)/No	No	live cells imaging	No	4
	Ni ²⁺	1.0×10 ⁻⁷	No	DMSO-H ₂ O (1:1)	No	No	No	5
	Zn ²⁺	1.0×10 ⁻⁷	Yes	H ₂ O (HEPES buffer)	Yes	Fluorescence image in plant root	No	6
	Zn ²⁺ , Ni ²⁺	1.6×10 ⁻⁷ 6.9×10 ⁻⁷	No	DMSO-H ₂ O (9:1)/No	Yes	No	No	7

	Ni ²⁺	1.0×10 ⁻⁴	Yes	MeCN	No	No	No	8
	Zn ²⁺ , Ni ²⁺	7.2×10 ⁻⁸	No	DMSO-H ₂ O (9:1, v/v),	No	live cells imaging	No	9
	Al ³⁺ , Zn ²⁺	9.0×10 ⁻⁷ 6.6×10 ⁻⁹	No	MeOH-H ₂ O (9:1) DMF/H ₂ O (9:1)/Yes	No	No	No	10
	Zn ²⁺	9.6×10 ⁻⁸	No	DMSO/H ₂ O (9:1)	Yes	On-site detection , live cells imaging	No	11
	Zn ²⁺ , Cu ²⁺	3.2×10 ⁻⁸ 2.1×10 ⁻⁸	No	MeOH-H ₂ O (9:1) /No	Yes	live cells imaging	No	12
	Zn ²⁺	5.3×10 ⁻⁸	Yes	MeOH-H ₂ O (9:1)	Yes	live cells imaging	No	13
	Zn ²⁺	3.7×10 ⁻⁷	Yes	MeOH-H ₂ O (9:1)	Yes	DNA, HSA Interaction , Heavy metal detection	No	14
	Ni ²⁺	2.3×10 ⁻⁵	No	EtOH	No	Paper strip	No	15
	Ni ²⁺	1.8×10 ⁻⁶	Yes	MeOH/H ₂ O (1:1)	No	live cells imaging	No	16
Our Probe (HL)	Zn ²⁺ , Ni ²⁺		Yes (crystal obtained in both cases)	H ₂ O (1:1) MeO-H ₂ O (9:1)/Yes	Yes	live cells imaging, ,	Yes/ATP detection	