Electronic Supplementary Information

A sandwich-type zinc complex from rhodamine dye based ligand: a potential fluorescent chemosensor for acetate in human blood plasma and a molecular logic gate with INHIBIT function

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IR spectrum of Zn-R1

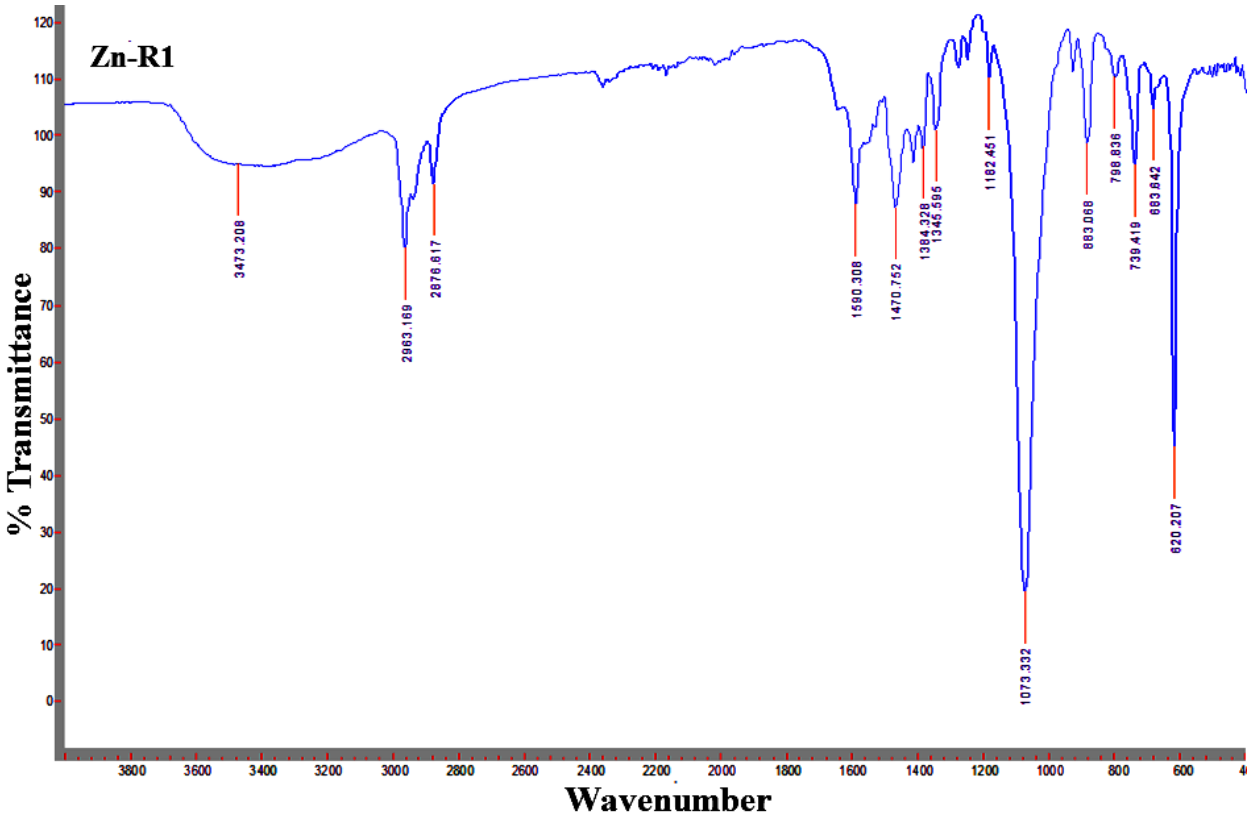

Figure S1 IR spectrum of **Zn-R1**.

^{1}H NMR spectrum of Zn-R1

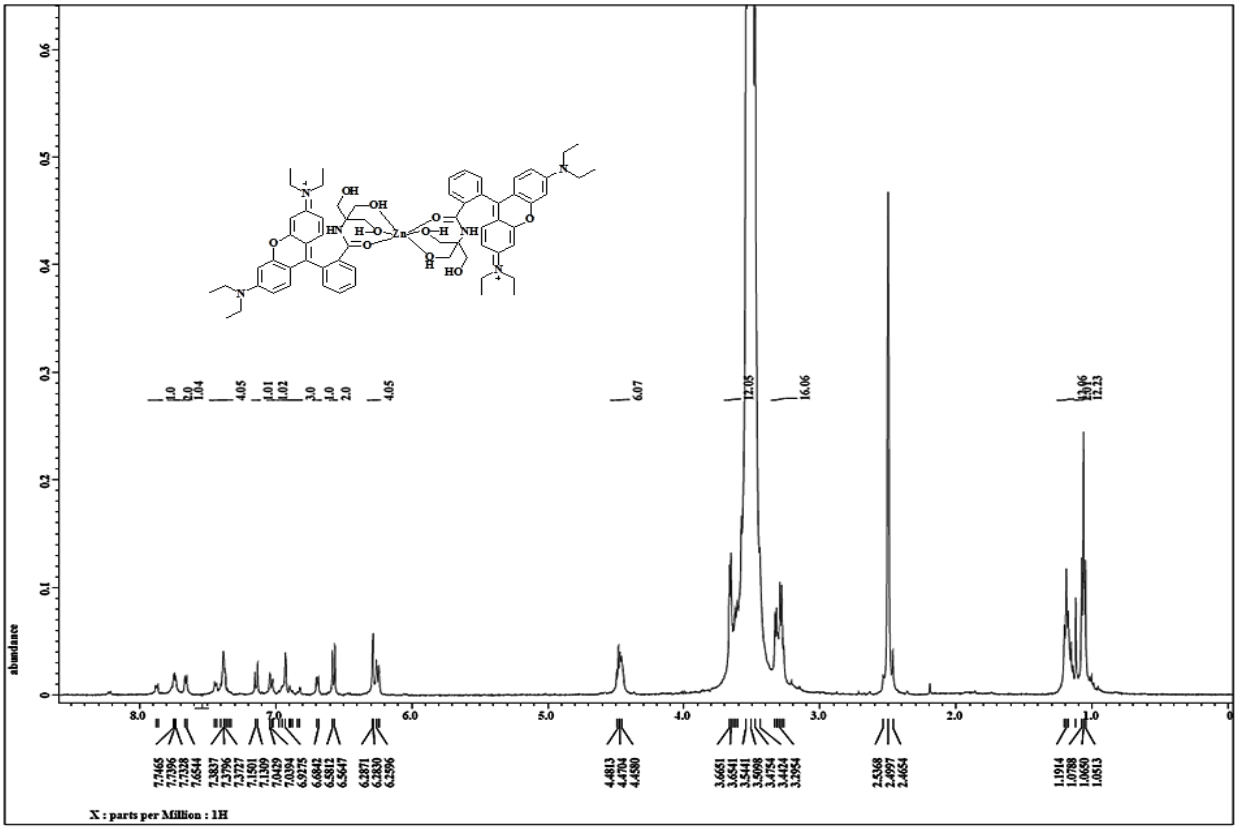

Figure S2(a) ^{1}H NMR spectrum of **Zn-R1**.

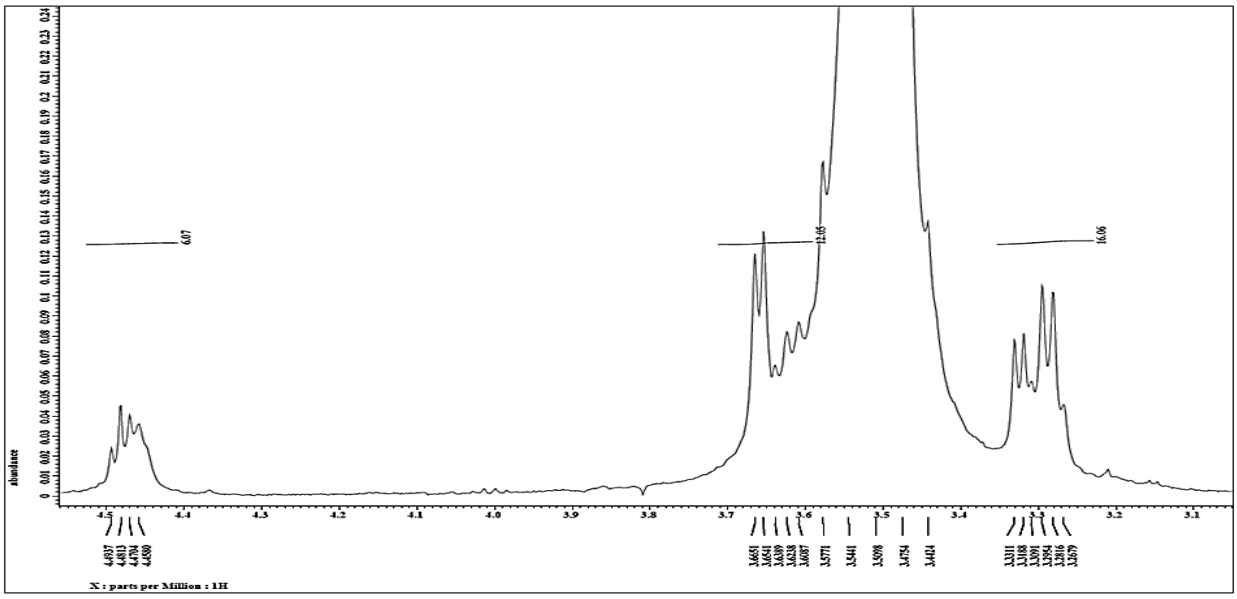

Figure S2(b) Expanded region of ^{1}H NMR spectrum of **Zn-R1**.

^{13}C NMR spectrum of Zn-R1

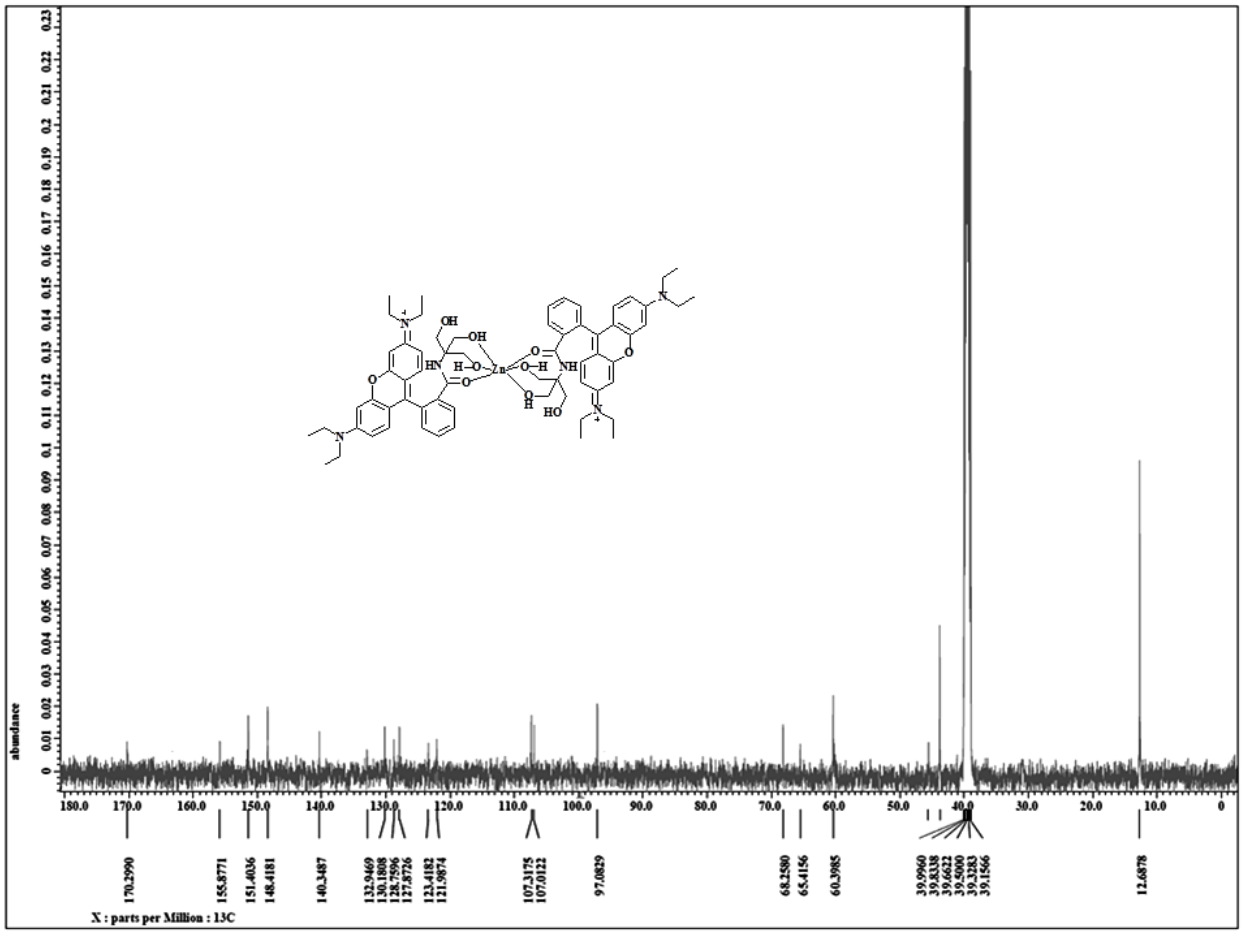

Figure S3 ^{13}C NMR spectrum of **Zn-R1**.

Mass spectrum of Zn-R1

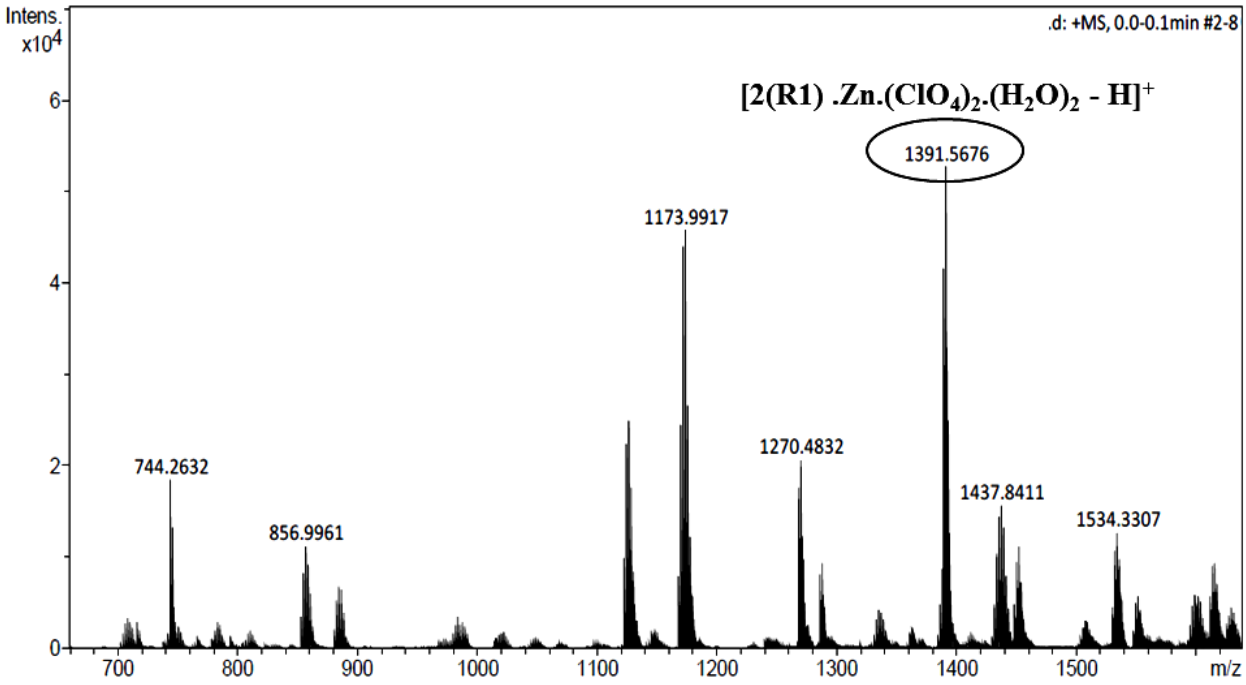

Figure S4 Mass spectrum of **Zn-R1**.

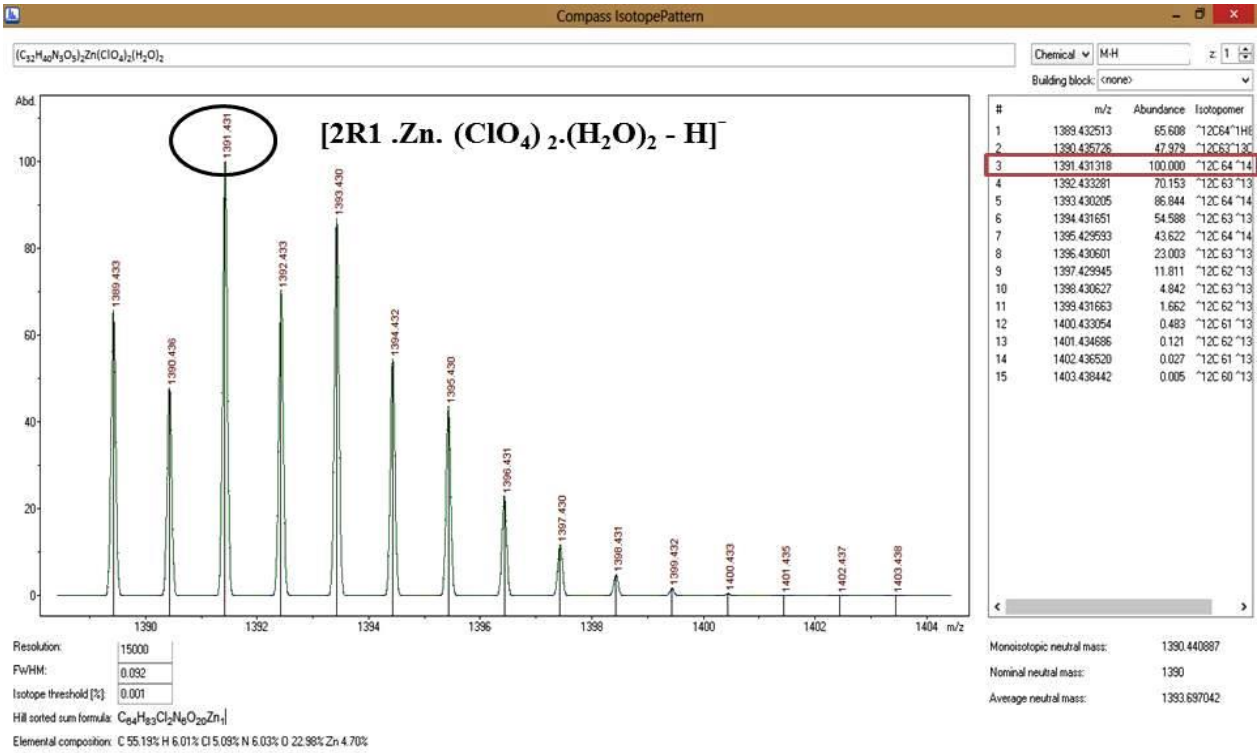

Figure S5(a) Theoretical isotopic pattern of m/z 1391.43 peak representing **Zn-R1** $(C_{32}H_{40}N_3O_5)_2Zn(ClO_4)_2.2H_2O$-H**)** calculated using compass isotope pattern.

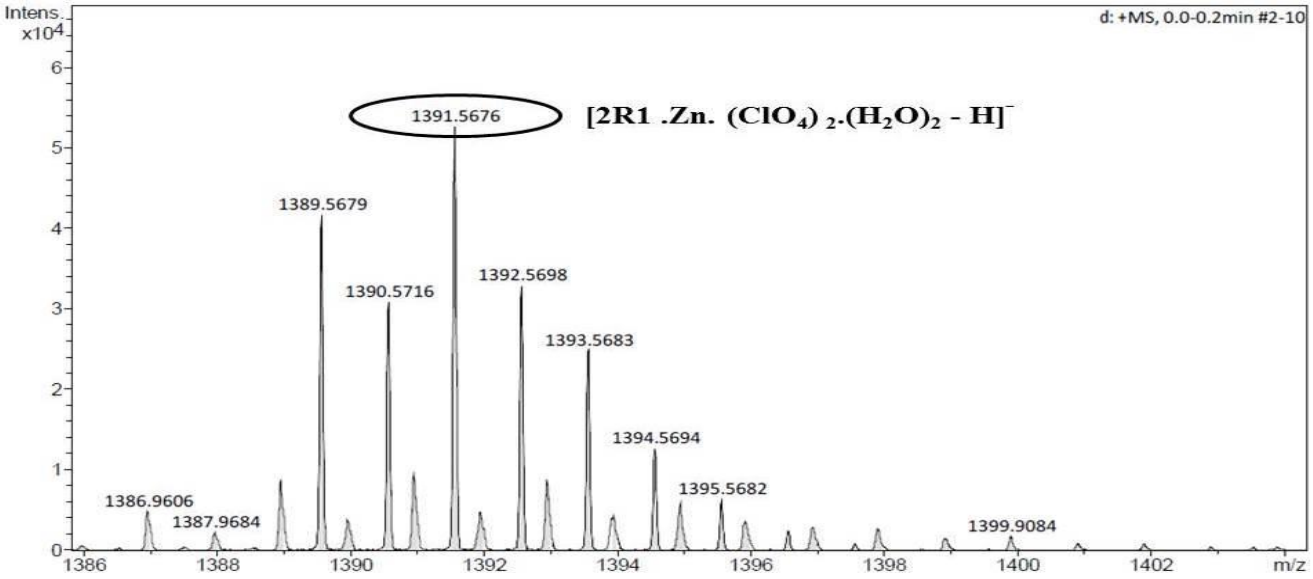

Figure S5(b) Experimental isotopic pattern of m/z 1391.56 peak representing **Zn-R1** $(C_{32}H_{40}N_3O_5)_2Zn(ClO_4)_2.2H_2O$-H**)**.

Determination of the stoichiometry of R and Zn^{2+}

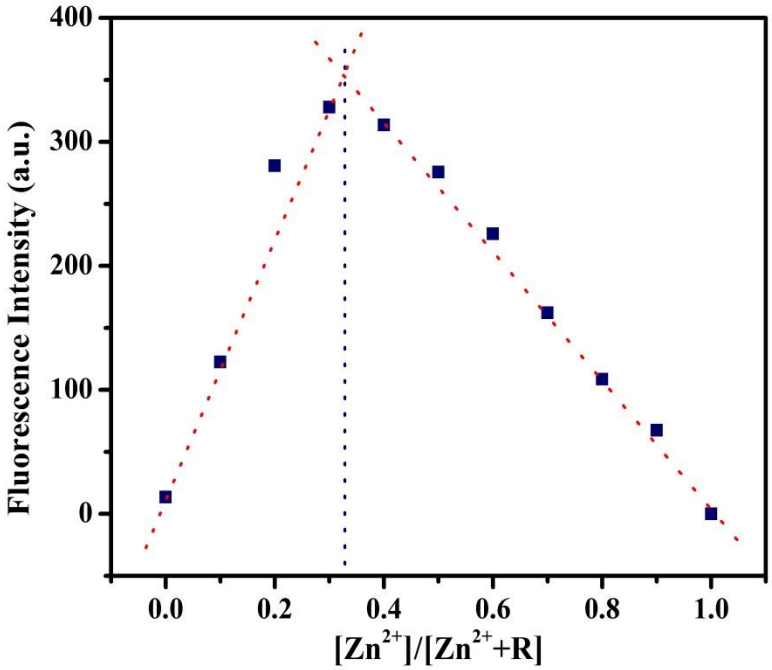

Figure S6 Job's plot for the determination of the stoichiometry of interaction of **R** with Zn^{2+}. λ_{ex} = 530 nm. 10 μm solutions of **R** and Zn^{2+} were used for this study.

Determination of the detection limit of R towards Zn^{2+}

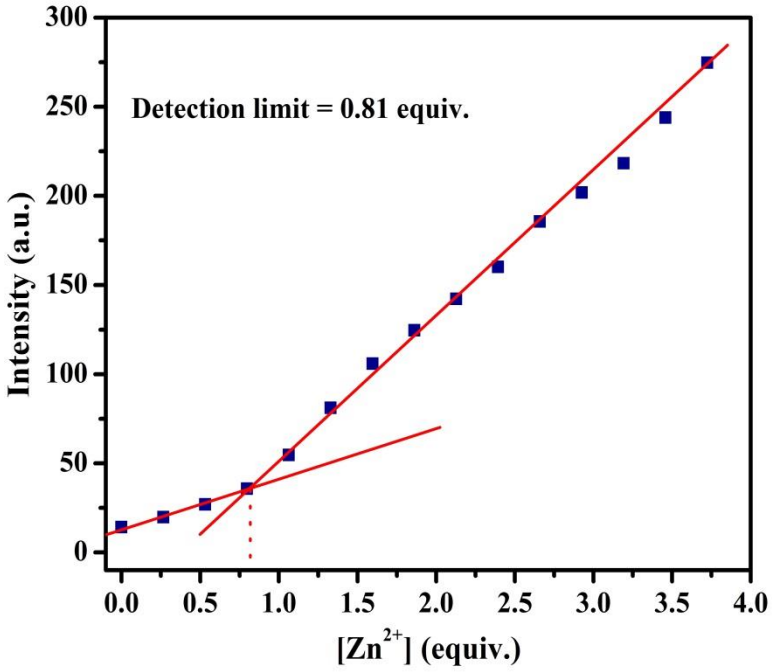

Figure S7 Fluorescence intensity at 585 nm of **R** in CH_3CN with different amounts of Zn^{2+}. λ_{ex} = 530 nm.

Absorption spectra of R on addition of Zn^{2+}

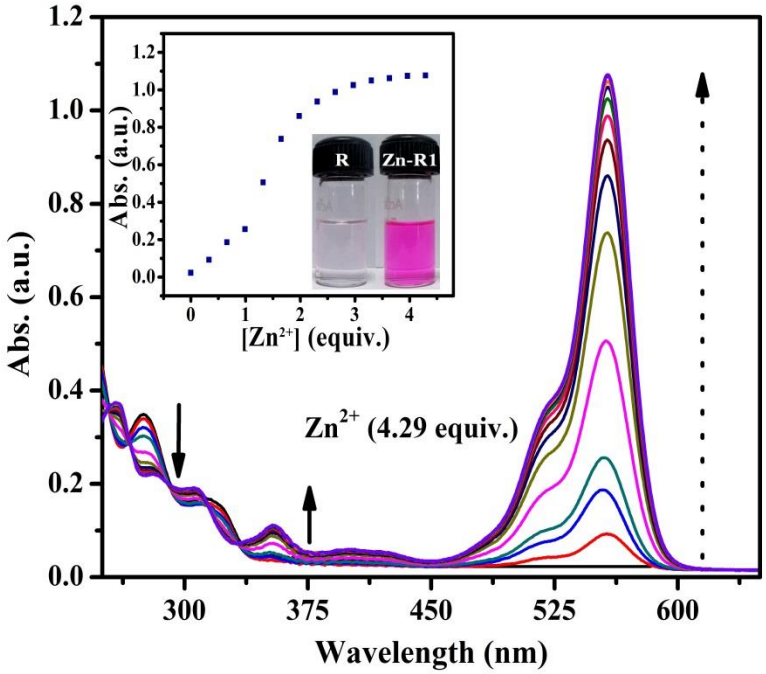

Figure S8 Absorption spectra of **R** (5×10^{-6} M) upon addition of Zn^{2+} (4.29 equivalents). Inset shows change in color & absorbance with the addition of increasing amounts of Zn^{2+}.

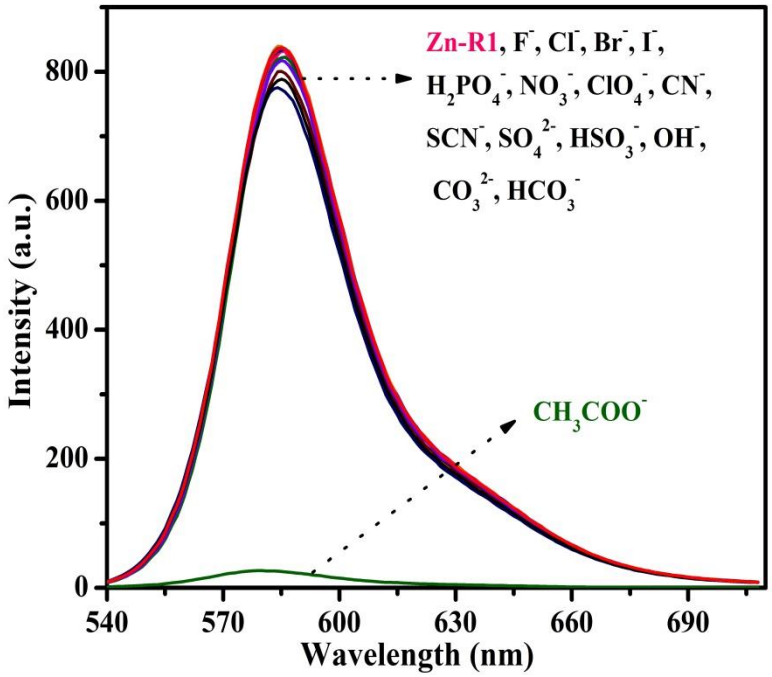

Figure S9(a) Fluorescence spectra of **Zn-R1** (5×10^{-6} M) upon addition of 6.0 equiv. of various anions (F^-, Cl^-, Br^-, I^-, CH_3COO^-, $H_2PO_4^-$, NO_3^-, ClO_4^-, CN^-, SCN^-, SO_4^{2-}, HSO_3^-, OH^-, CO_3^{2-} and HCO_3^-) in CH_3CN:H_2O (9.5:0.5 %, *v*/*v*); λ_{ex}= 530 nm.

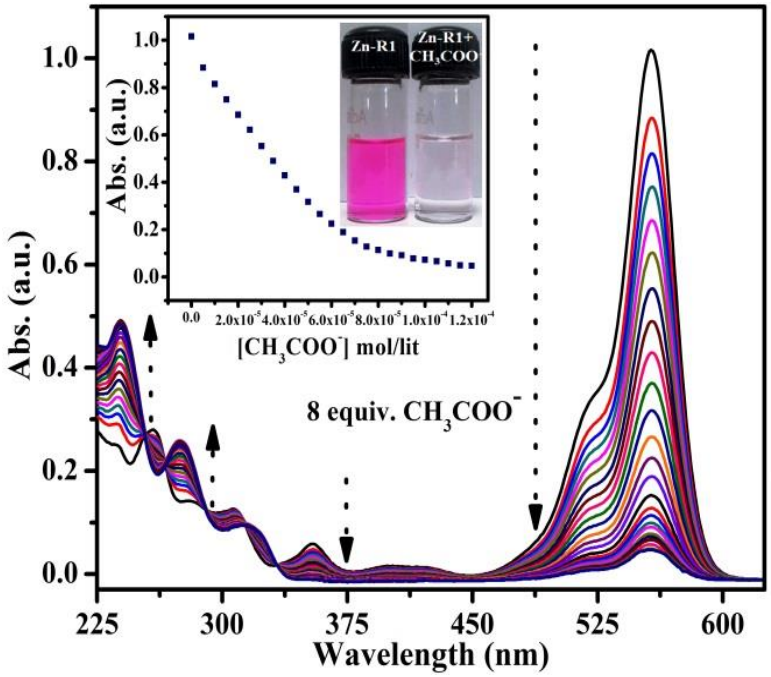

Figure S9(b) UV-vis spectra of **Zn-R1** (5×10^{-6} M) upon addition of 6.0 equiv. of CH_3COO^- in CH_3CN:H_2O (9.5:0.5 %, *v*/*v*). Inset shows the colour change as well as the changes in absorbance values on addition of various equivalents of acetate ions.

Stern-Volmer constant

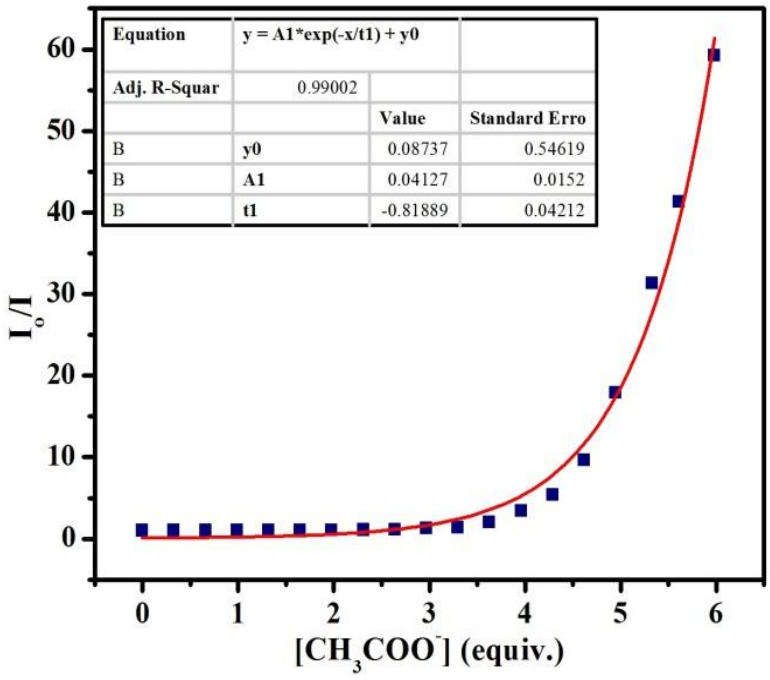

Figure S10 Stern-Volmer plot of the fluorescence response of **Zn-R1** to [CH_3COO^-].

$I/Io=Ae^{Kx}+B$

Quenching Constant = A×K, where K = 1/t

Determination of the stoichiometry of interaction between Zn-R1 and CH_3COO^-

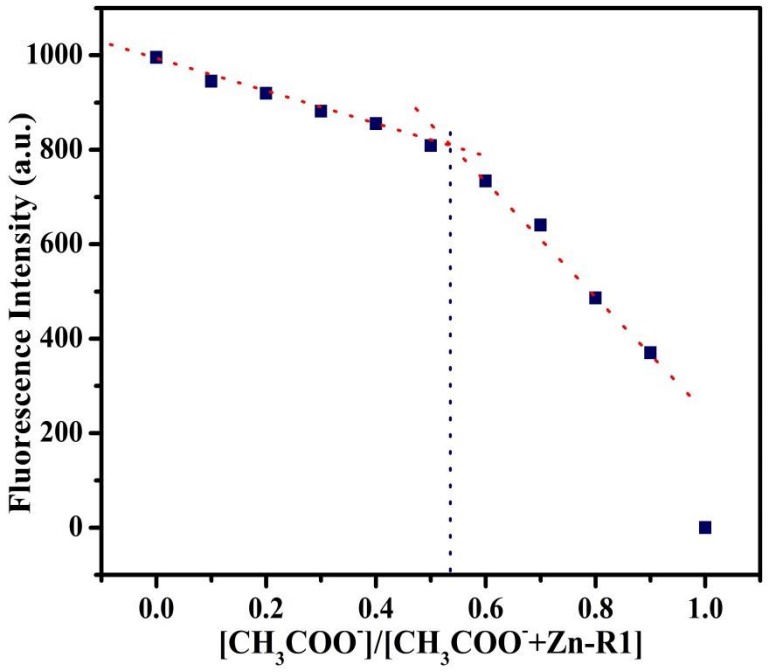

Figure S11 Job's plot for the determination of the stoichiometry of interaction between **Zn-R1** and CH_3COO^-. λ_{ex} = 530 nm. 10 μm solutions of **Zn-R1** and CH_3COO^- were used for this study.

Determination of the detection limit of Zn-R1 towards CH_3COO^-

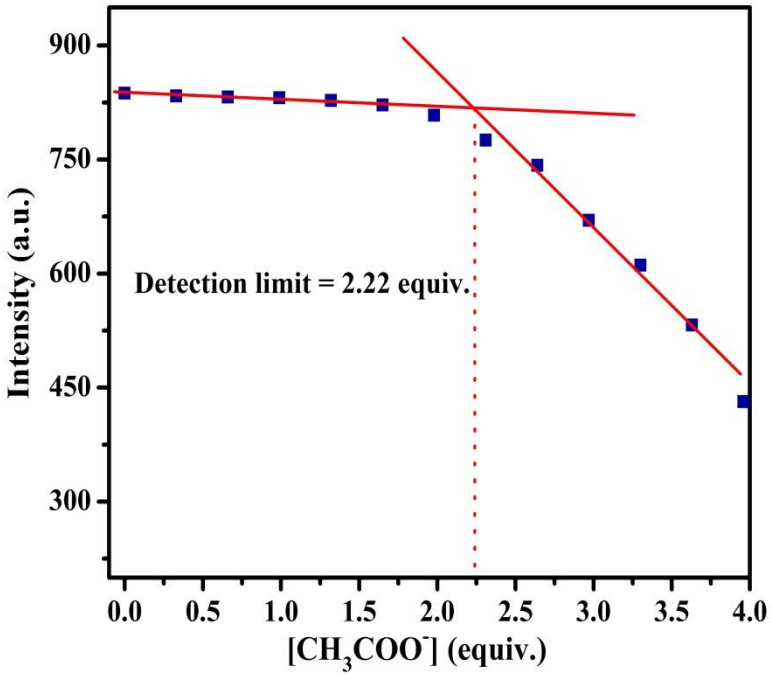

Figure S12 Fluorescence intensity at 585 nm of **Zn-R1** in CH_3CN:H_2O (9.5:0.5 %, *v*/*v*) with different amounts of CH_3COO^-. λ_{ex} = 530 nm.

Fluorescence spectra of Zn-R1 on the addition of CH_3COO^- in DMSO:H_2O mixed solvent system

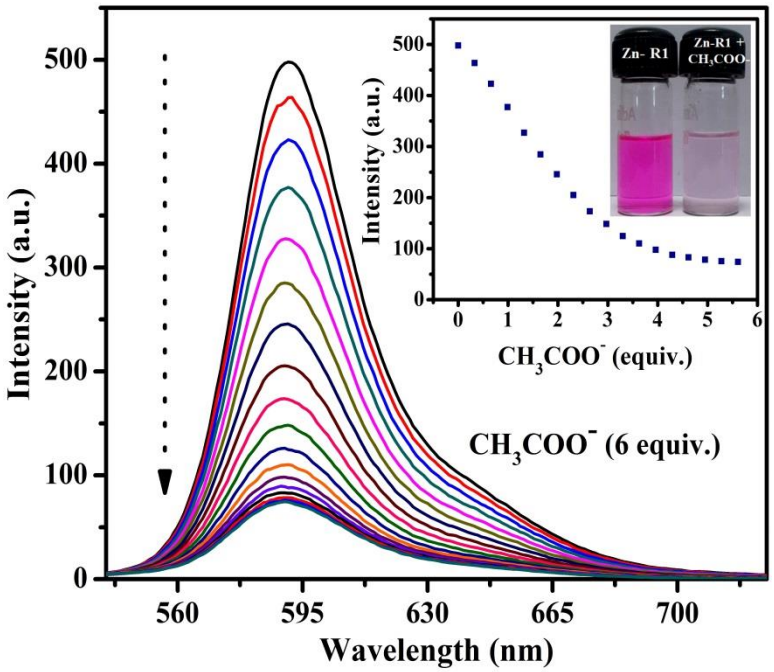

Figure S13(a) Fluorescence spectra of **Zn-R1** (5×10^{-6} M) upon addition of 6.0 equiv. of CH_3COO^- in DMSO:H_2O (9.5:0.5 %, *v*/*v*). Inset shows the colour change as well as the changes in absorbance values on addition of various equivalents of acetate ions.

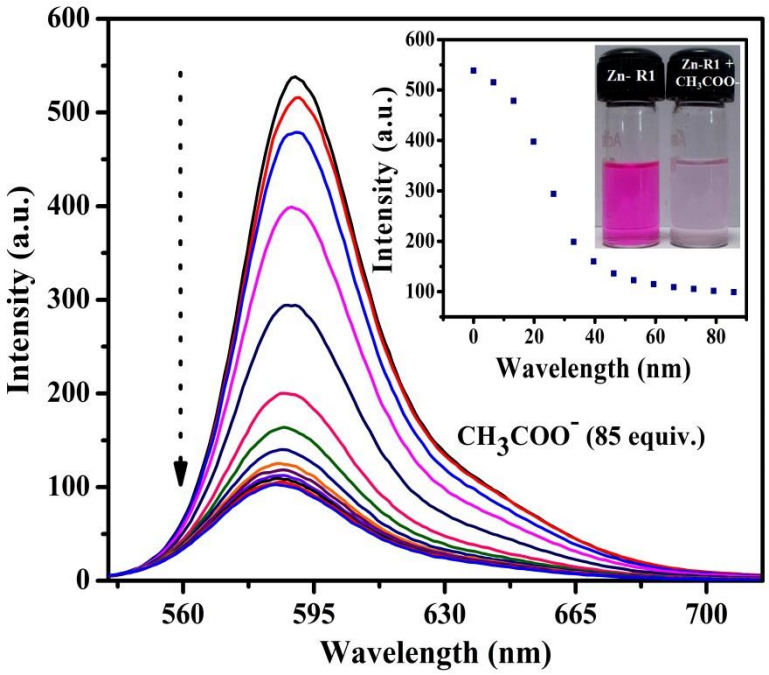

Figure S13(b) Fluorescence spectra of **Zn-R1** (5×10^{-6} M) upon addition of 6.0 equiv. of CH_3COO^- in DMSO:H_2O (7:3 %, *v*/*v*). Inset shows the colour change as well as the changes in absorbance values on addition of various equivalents of acetate ions.

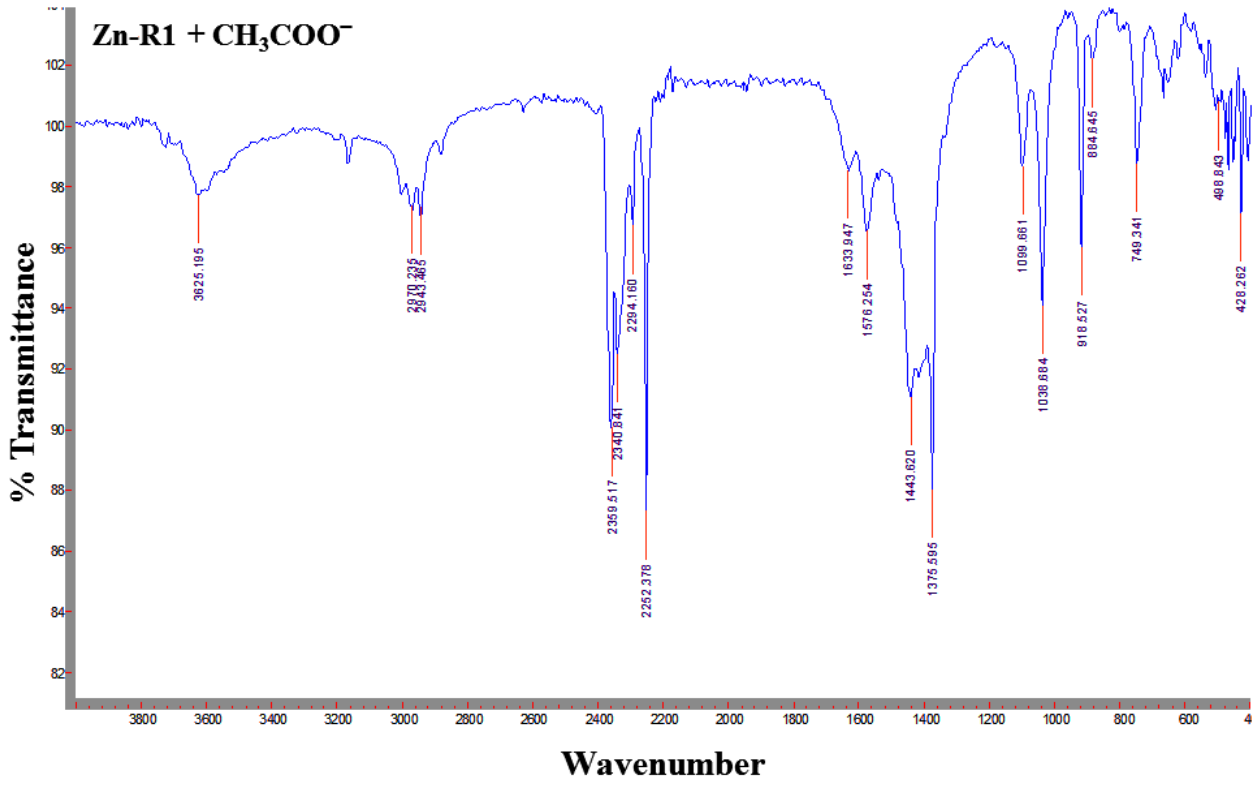

Figure S14 IR spectrum of **Zn-R1** after addition of CH_3COO^-.

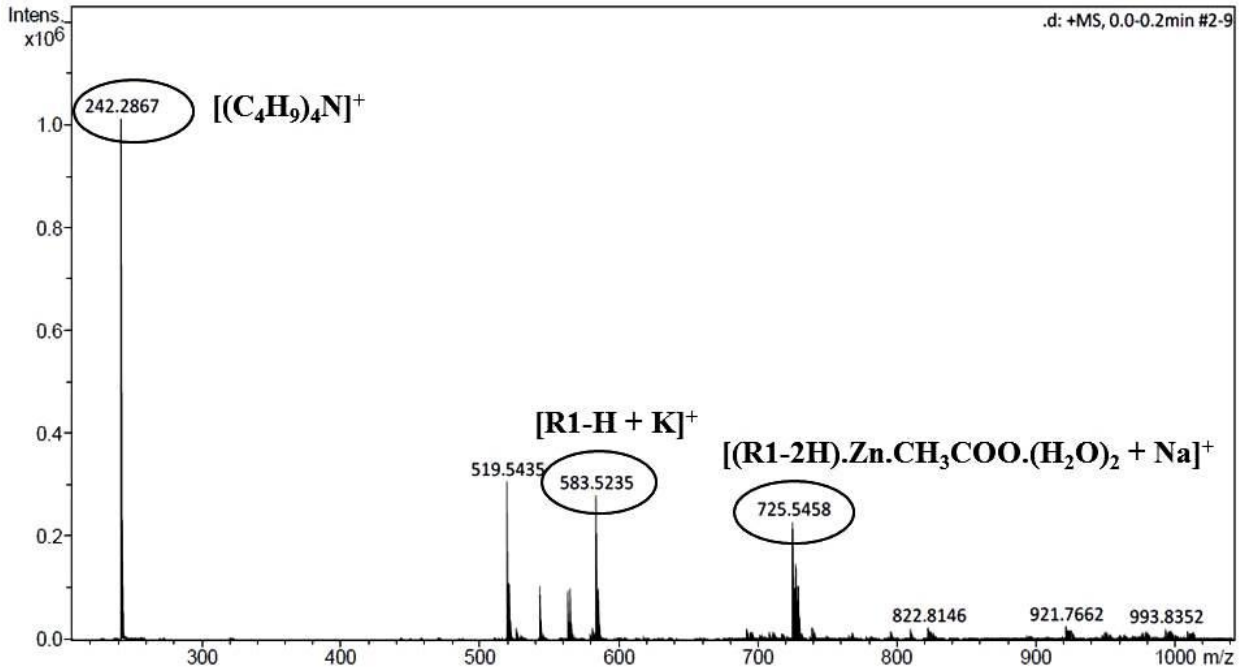

Figure S15(a) Mass spectrum of **Zn-R1** after addition of CH_3COO^- (m/z range 200-1100 is shown).

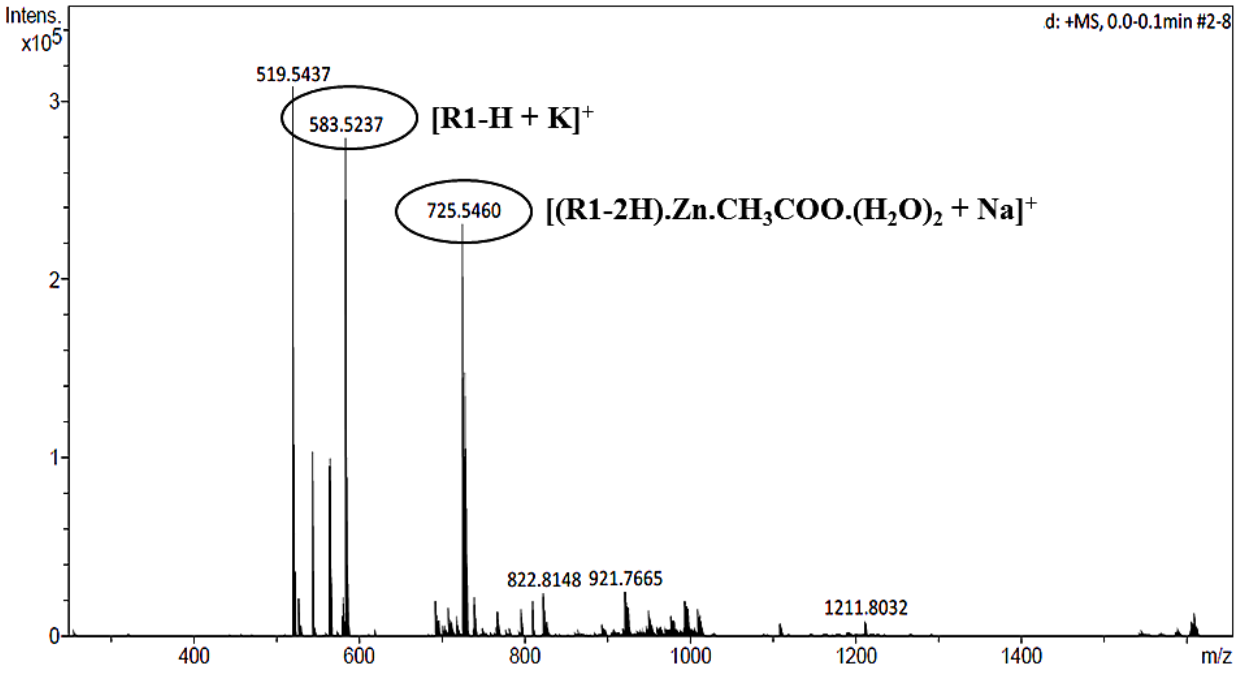

Figure S15(b) Mass spectrum of **Zn-R1** after addition of CH_3COO^- (m/z range 300-1700 is shown).

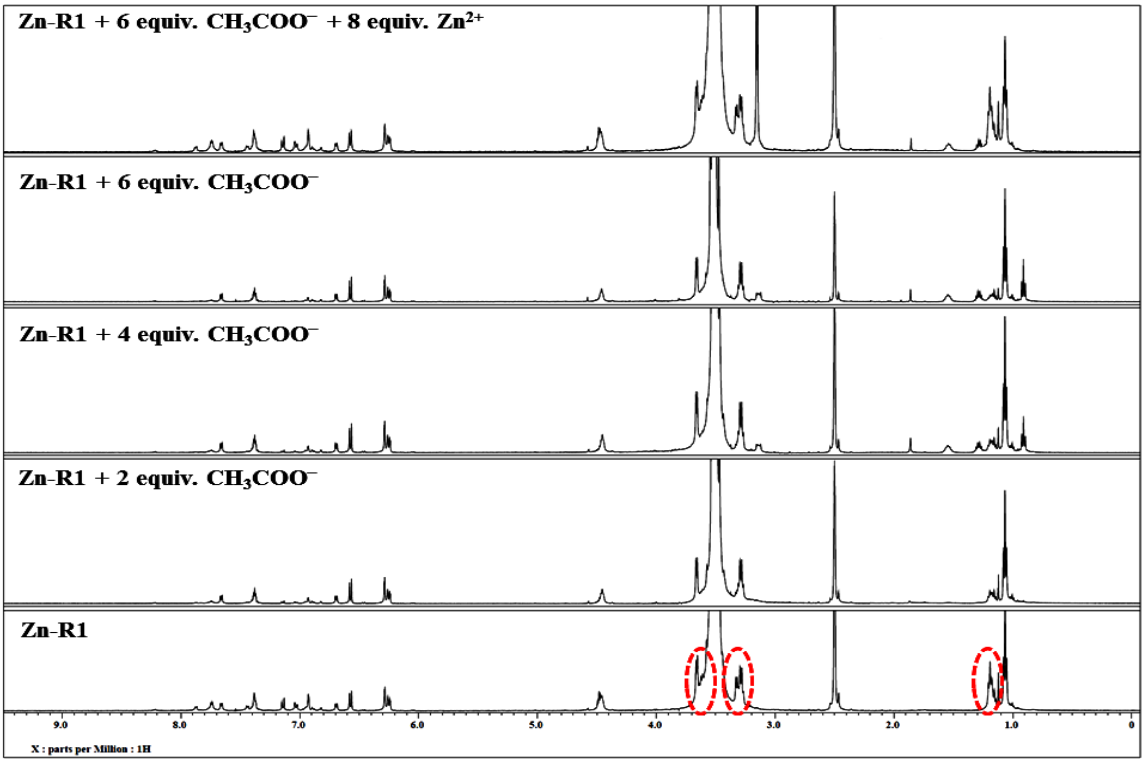

Figure S16(a) ^{1}H NMR spectra of **Zn-R1** in DMSO-d_6 after addition of CH_3COO^-.

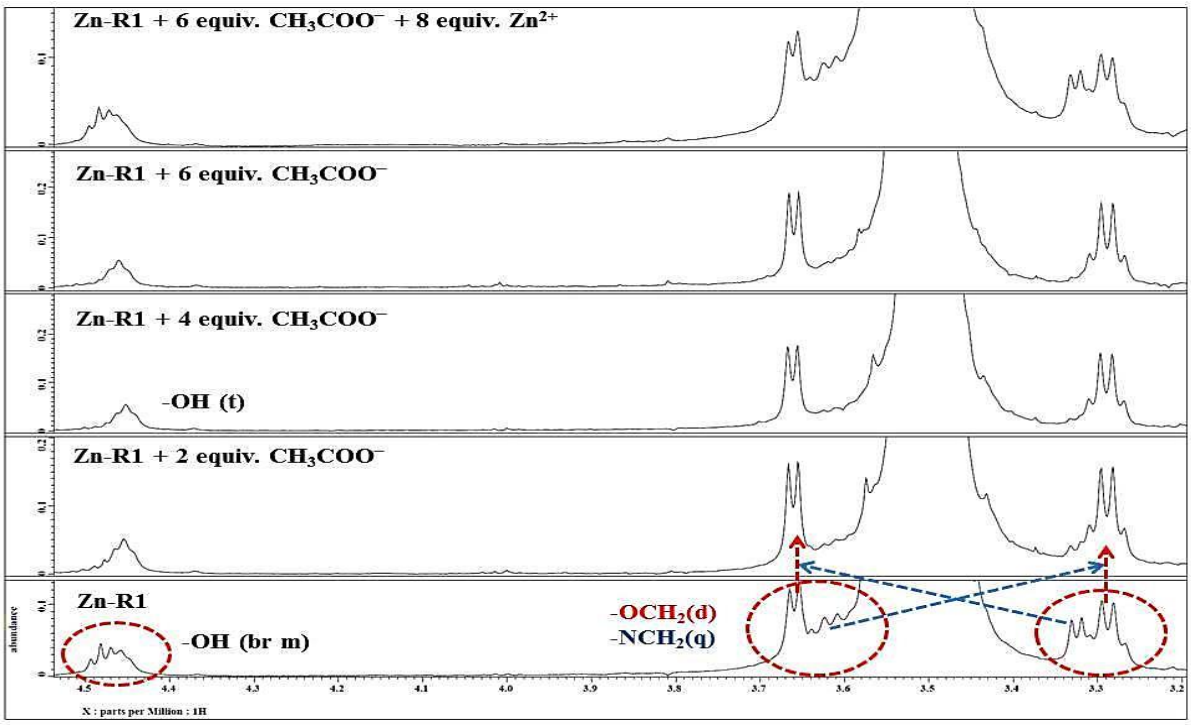

Figure S16(b) Expansion of ^{1}H NMR spectra of **Zn-R1** in DMSO-d_6 after addition of CH_3COO^- in the region of 4.55 to 3.2 ppm.

Table S1: Fluorescence life time measurement data of **R**, **Zn-R1** and **Zn-R1** in presence of CH_3COO^-.

Components	**R**	**Zn-R1**	**Zn-R1 +CH_3COO^-**
τ_1 [ns]	0.211	0.581	0.156
f_1	80%	15%	89%
τ_2 [ns]	1.311	1.184	1.381
f_2	20%	85%	11%
χ^2	1.175885	1.048132	1.171815

Absorption spectra of Zn-R1 on addition of CH_3COO^- present in artificial blood plasma

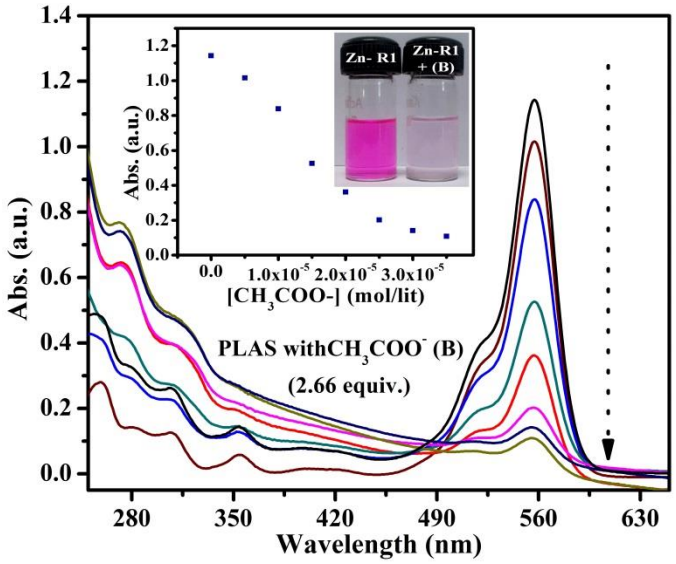

Figure S17 Absorption spectra of **Zn-R1** (5×10^{-6} M) upon addition of PLAS (B) (2.66 equivalents). Inset shows change in colour & absorbance with the addition of increasing amounts of PLAS (B).

Determination of the detection limit of Zn-R1 towards CH_3COO^- present in artificial blood plasma

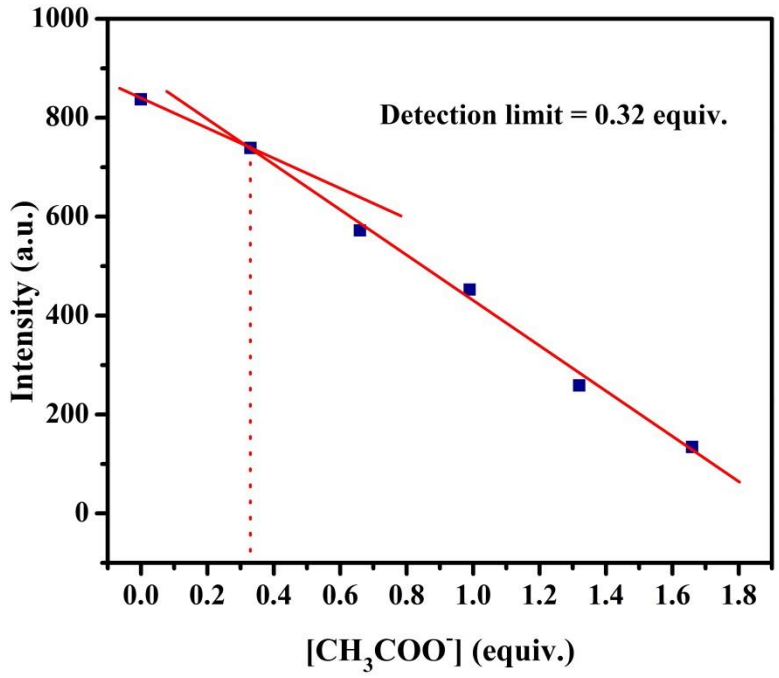

Figure S18 Fluorescence intensity at 585 nm of **Zn-R1** in CH_3CN:H_2O (9.5:0.5 *v/v*) with different amounts of PLAS (B). λ_{ex} = 530 nm.

Stern-Volmer constant

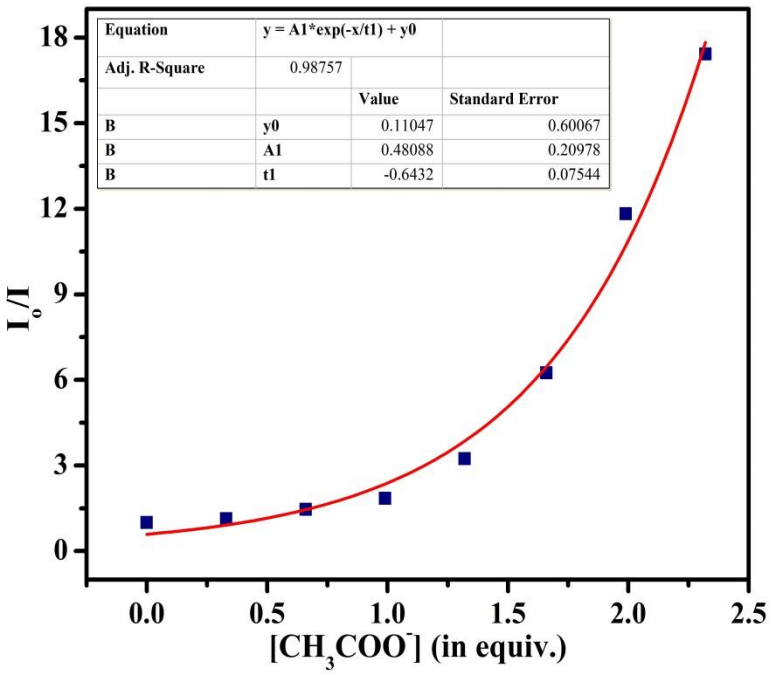

Figure S19 Stern-Volmer plot of the fluorescence response of **Zn-R1** to [CH_3COO^-] present in PLAS (B).

I/Io = Ae^{Kx}+B

Quenching constant = A×K, where K = 1/t

X-ray crystallography and structure analysis

Table S2: The crystallographic data and structure refinement parameters of **Zn-R1**

Empirical formula	C64 H88 Cl4 N6 O30 Zn	
Formula weight	1628.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.3279(12) Å	α = 104.215(6)°
	b = 12.8597(9) Å	β = 100.333(7)°
	c = 13.1221(9) Å	γ = 105.122(7)°
Volume	1879.7(3) $Å^3$	
Z	1	
Density	1.439 Mg/m^3	
Absorption coefficient	0.556 mm^{-1}	
F(0 0 0)	852	
Crystal size	0.2907 × 0.26 × 0.1383	
Θ range for data collection	1.724 to 28.337°.	
Limiting indices	-16<=h<=10, -12<=k<=16, -14<=l<=16	
Refinement method	Full-matrix least-squares on F^2	
Reflections collected	10473	
Data/restraints/parameters	7861 / 4 / 489	
Goodness of fit on F^2	1.053	
Final R indices [I >2σ(I)]	R1 = 0.0827, wR2 = 0.2386	
R indices (all data)	R1 = 0.1081, wR2 = 0.2735	
Largest diff. peak and hole	0.803 and -0.518 $e.Å^{-3}$	

Table S3: Selected bond lengths [Å] and angles [°] for **Zn-R1**.

Bond	Bond length[Å]	Bond	Bond length[Å]
Zn(1)-O(4)	2.031(4)	C(1)-C(2)	1.364(5)
Zn(1)-O(4)#1	2.031(4)	C(20)-C(19)	1.501(5)
Zn(1)-O(2)#1	2.055(3)	C(19)-C(18)	1.393(5)
Zn(1)-O(2)	2.055(3)	C(19)-C(14)	1.399(5)
Zn(1)-O(3)	2.115(3)	C(14)-C(15)	1.381(5)
Zn(1)-O(3)#1	2.115(3)	C(14)-C(7)	1.488(5)
Cl(3)-O(11)	1.372(7)	C(12)-C(11)	1.419(6)
Cl(3)-O(10)	1.377(6)	C(7)-C(8)	1.398(5)
Cl(3)-O(9)	1.398(6)	C(11)-C(10)	1.431(6)
Cl(3)-O(7)	1.404(6)	C(8)-C(9)	1.418(5)
Cl(7)-O(14)	1.211(10)	N(2)-C(3)	1.338(5)
Cl(7)-O(13)	1.307(9)	N(2)-C(31)	1.478(6)
Cl(7)-O(12)	1.357(11)	N(2)-C(29)	1.486(7)
Cl(7)-O(8)	1.389(8)	C(5)-C(4)	1.356(6)
O(2)-C(20)	1.232(4)	C(3)-C(2)	1.410(6)
O(1)-C(1)	1.369(4)	C(3)-C(4)	1.430(6)
O(1)-C(13)	1.371(4)	C(18)-C(17)	1.376(6)
O(3)-C(23)	1.414(6)	C(10)-C(9)	1.351(5)
N(3)-C(20)	1.330(5)	C(15)-C(16)	1.378(6)
N(3)-C(21)	1.475(5)	C(17)-C(16)	1.377(6)
O(4)-C(22)	1.434(6)	O(5)-C(24)	1.359(8)
C(13)-C(12)	1.360(5)	C(27)-C(28)	1.515(9)
C(13)-C(8)	1.414(5)	C(21)-C(23)	1.520(7)
N(1)-C(11)	1.346(5)	C(21)-C(22)	1.521(7)
N(1)-C(27)	1.461(6)	C(21)-C(24)	1.553(7)
N(1)-C(25)	1.480(6)	C(31)-C(32)	1.495(10)
C(6)-C(7)	1.403(5)	C(26)-C(25)	1.501(8)
C(6)-C(5)	1.413(5)	C(30)-C(29)	1.512(12)
C(6)-C(1)	1.415(5)		

Bond Angle	Bond Angle [°]	Bond Angle	Bond Angle [°]
O(4)-Zn(1)-O(4)#1	180	C(18)-C(19)-C(14)	119.6(3)
O(4)-Zn(1)-O(2)#1	91.52(14)	C(18)-C(19)-C(20)	121.2(3)
O(4)#1-Zn(1)-O(2)#1	88.48(14)	C(14)-C(19)-C(20)	119.2(3)
O(4)-Zn(1)-O(2)	88.48(14)	C(15)-C(14)-C(19)	118.8(3)
O(4)#1-Zn(1)-O(2)	91.52(14)	C(15)-C(14)-C(7)	119.7(3)
O(2)#1-Zn(1)-O(2)	180.00(10)	C(19)-C(14)-C(7)	121.4(3)
O(4)-Zn(1)-O(3)	84.39(15)	C(13)-C(12)-C(11)	119.8(3)
O(4)#1-Zn(1)-O(3)	95.61(15)	C(8)-C(7)-C(6)	119.4(3)
O(2)#1-Zn(1)-O(3)	93.28(12)	C(8)-C(7)-C(14)	120.9(3)
O(2)-Zn(1)-O(3)	86.72(12)	C(6)-C(7)-C(14)	119.7(3)
O(4)-Zn(1)-O(3)#1	95.61(15)	N(1)-C(11)-C(12)	122.1(4)
O(4)#1-Zn(1)-O(3)#1	84.39(15)	N(1)-C(11)-C(10)	120.5(4)
O(2)#1-Zn(1)-O(3)#1	86.72(12)	C(12)-C(11)-C(10)	117.4(3)
O(2)-Zn(1)-O(3)#1	93.28(12)	C(7)-C(8)-C(13)	119.6(3)
O(3)-Zn(1)-O(3)#1	180	C(7)-C(8)-C(9)	124.6(3)
O(11)-Cl(3)-O(10)	107.4(5)	C(13)-C(8)-C(9)	115.7(3)
O(11)-Cl(3)-O(9)	116.9(7)	C(3)-N(2)-C(31)	122.2(4)
O(10)-Cl(3)-O(9)	106.6(5)	C(3)-N(2)-C(29)	120.2(4)
O(11)-Cl(3)-O(7)	108.1(5)	C(31)-N(2)-C(29)	117.3(4)
O(10)-Cl(3)-O(7)	112.0(6)	C(4)-C(5)-C(6)	122.0(4)
O(9)-Cl(3)-O(7)	105.9(4)	N(2)-C(3)-C(2)	122.2(4)
O(14)-Cl(7)-O(13)	103.3(8)	N(2)-C(3)-C(4)	120.5(4)
O(14)-Cl(7)-O(12)	119.2(14)	C(2)-C(3)-C(4)	117.3(4)
O(13)-Cl(7)-O(12)	102.1(11)	C(17)-C(18)-C(19)	120.3(4)
O(14)-Cl(7)-O(8)	109.8(10)	C(9)-C(10)-C(11)	121.2(4)
O(13)-Cl(7)-O(8)	123.4(10)	C(16)-C(15)-C(14)	121.3(4)
O(12)-Cl(7)-O(8)	100.0(6)	C(5)-C(4)-C(3)	121.2(4)
C(20)-O(2)-Zn(1)	134.8(2)	C(18)-C(17)-C(16)	120.2(4)
C(1)-O(1)-C(13)	120.5(3)	C(10)-C(9)-C(8)	122.2(4)
C(23)-O(3)-Zn(1)	120.3(3)	C(1)-C(2)-C(3)	120.3(4)
C(20)-N(3)-C(21)	127.6(3)	C(17)-C(16)-C(15)	119.8(4)
C(22)-O(4)-Zn(1)	122.9(3)	N(1)-C(27)-C(28)	111.8(5)
C(12)-C(13)-O(1)	115.9(3)	N(3)-C(21)-C(23)	111.1(4)
C(12)-C(13)-C(8)	123.6(3)	N(3)-C(21)-C(22)	111.6(4)
O(1)-C(13)-C(8)	120.5(3)	C(23)-C(21)-C(22)	113.6(4)

C(11)-N(1)-C(27)	122.3(4)	N(3)-C(21)-C(24)	105.8(4)
C(11)-N(1)-C(25)	121.9(4)	C(23)-C(21)-C(24)	105.7(4)
C(27)-N(1)-C(25)	115.8(4)	C(22)-C(21)-C(24)	108.5(4)
C(7)-C(6)-C(5)	124.5(3)	N(2)-C(31)-C(32)	112.1(5)
C(7)-C(6)-C(1)	119.4(3)	N(1)-C(25)-C(26)	112.8(5)
C(5)-C(6)-C(1)	116.0(3)	O(3)-C(23)-C(21)	113.7(4)
C(2)-C(1)-O(1)	116.6(3)	O(5)-C(24)-C(21)	114.9(5)
C(2)-C(1)-C(6)	123.0(3)	O(4)-C(22)-C(21)	112.5(4)
O(1)-C(1)-C(6)	120.4(3)	N(2)-C(29)-C(30)	113.3(6)
O(2)-C(20)-N(3)	124.4(4)		
O(2)-C(20)-C(19)	119.1(3)		
N(3)-C(20)-C(19)	116.5(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1