Electronic Supplementary Information

A new biphenol-dipicolylamine based ligand and its dinuclear Zn^{2+} complex as fluorescent sensors for ibuprofen and ketoprofen in aqueous solution

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1. Synthesis of the ligand

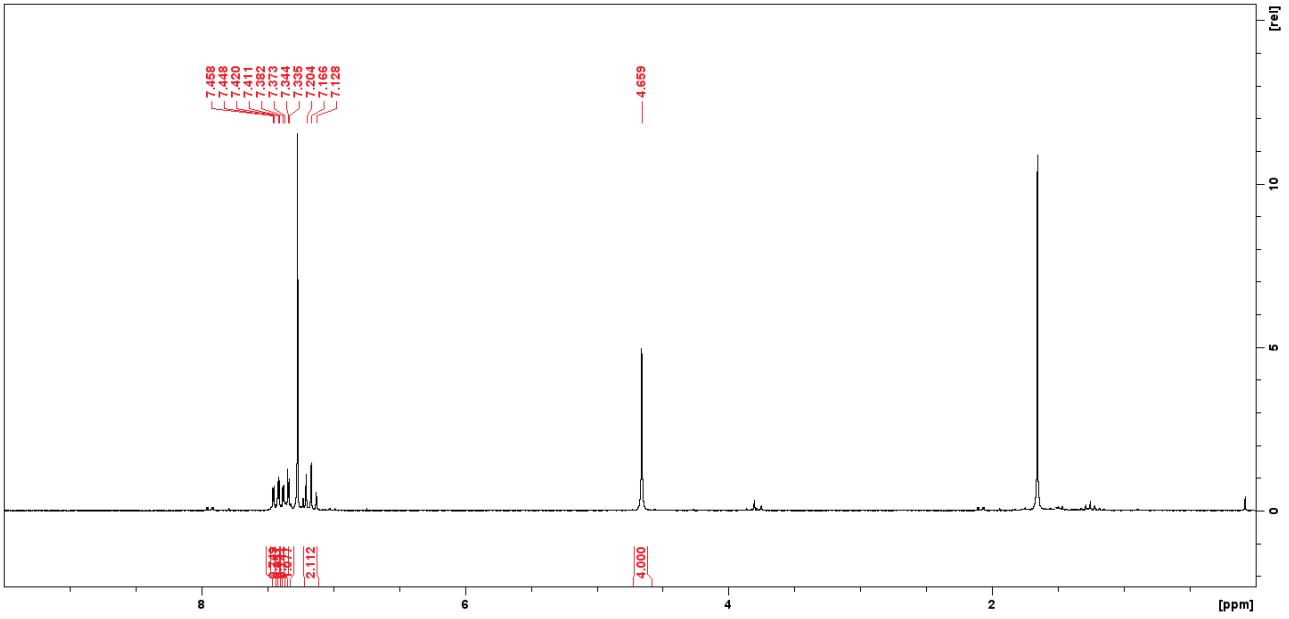

Figure S1. ^{1}H NMR spectrum of **2** in $CDCl_3$ at 25 °C.

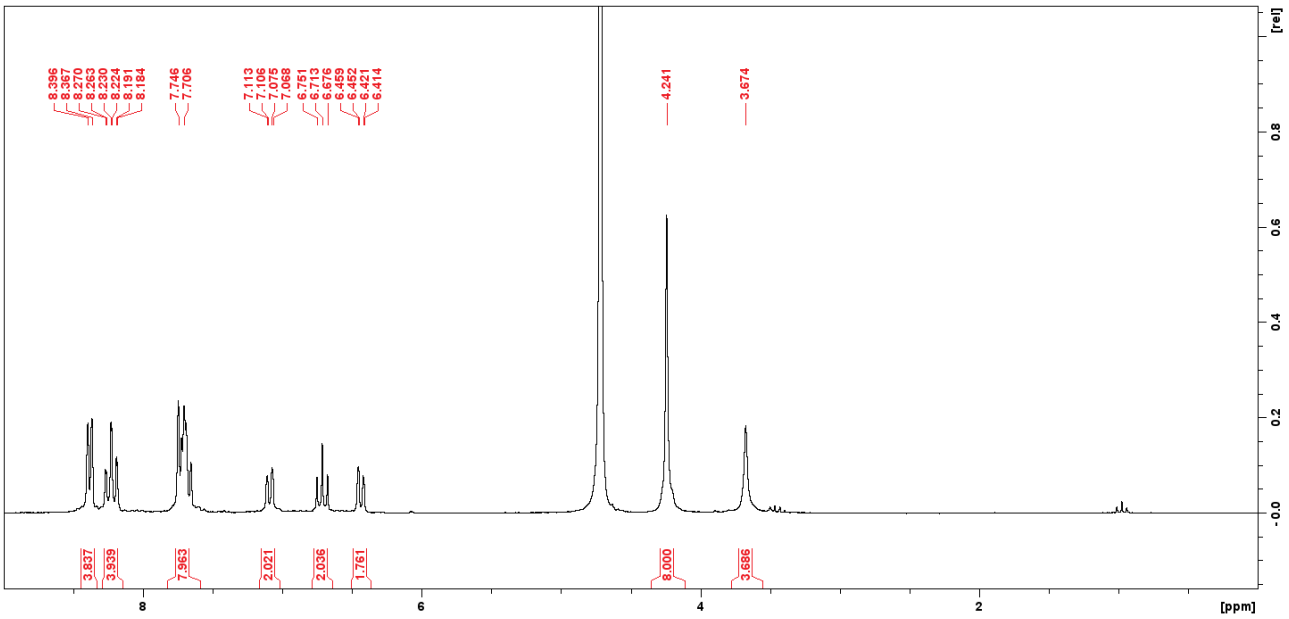

Figure S2. ^{1}H NMR spectrum of **L** in D_2O at 25 °C.

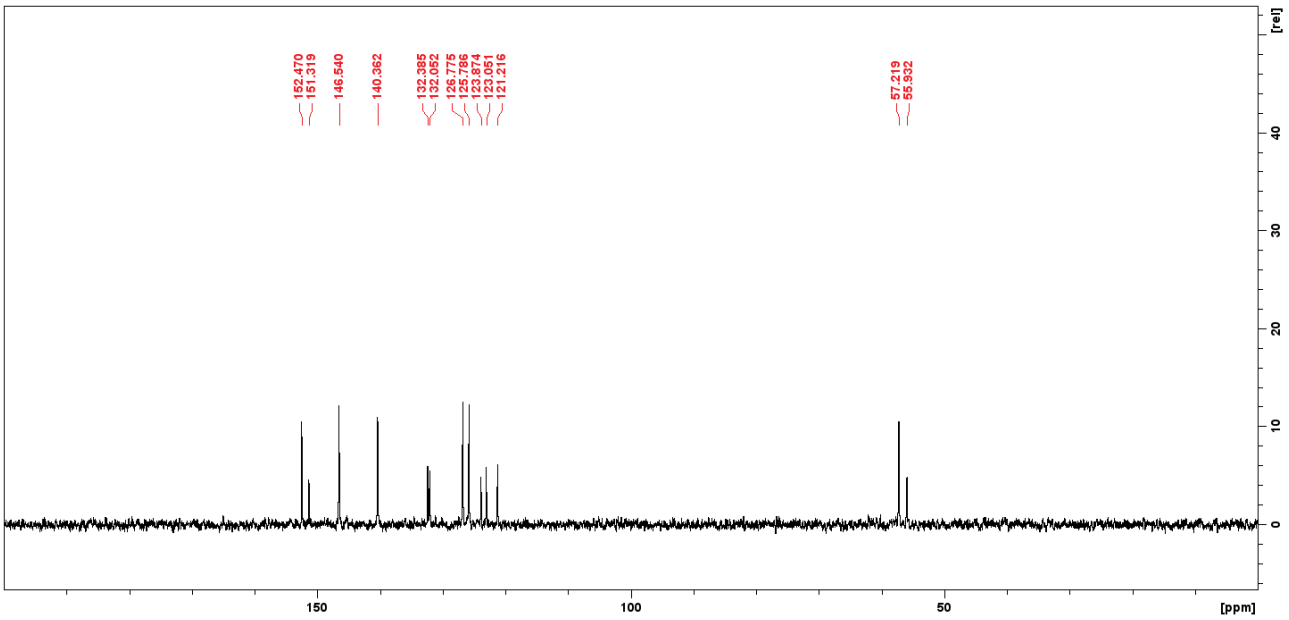

Figure S3. ^{13}C NMR spectrum of **L** in D_2O at 25 °C.

2. Solid state structure of the ligand

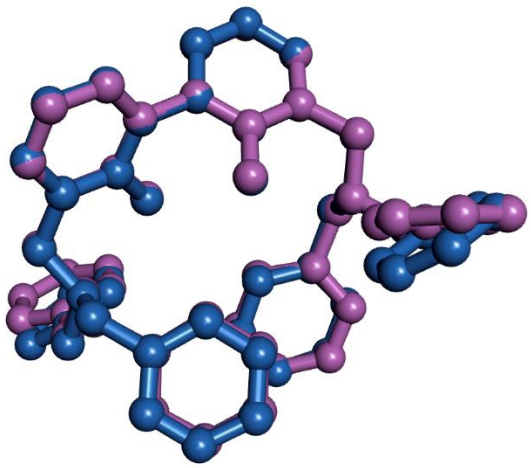

Figure S4. Superimposition of the two independent molecules of L.

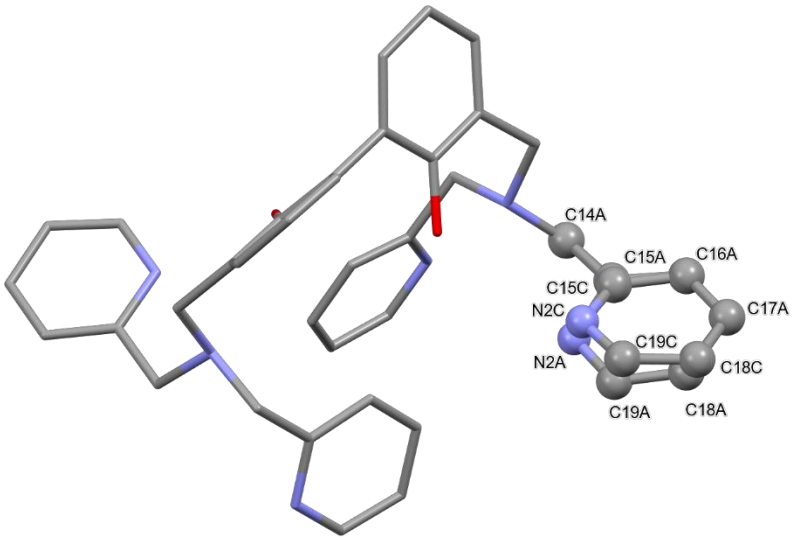

Figure S5. Disordered **L** molecule in the asymmetric unit. Hydrogen atoms have been omitted for the sack of clarity.

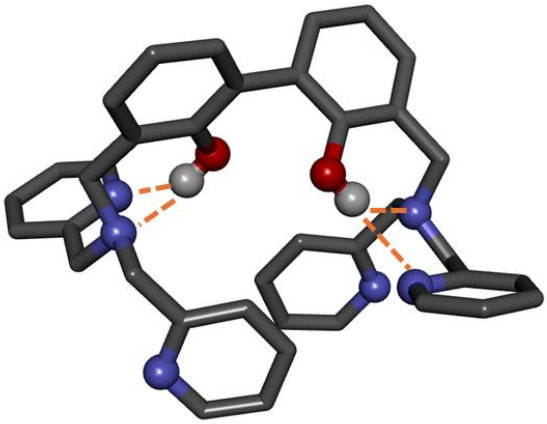

Figure S6. Bifurcated H-bond in **L** (independent molecule B).

Table S1. Crystallographic data and refinement parameters of **L**.

empirical formula	$C_{38}H_{36}O_2N_6$
formula weight	608.73
T (K)	100
Crystal system, space group	Monoclinic, P2/c
Unit cell dimensions (Å, °)	a = 21.2572(5) b = 14.9463(4), β = 90.088(2) c = 20.1478(5)
V (Å3)	6401.3(3)
Z, dcalc(g/cm^3)	8, 1.263
μ (mm-1)	0.636
F(000)	2576
Reflections collected/unique/Rint	119791 / 11753 / 0.1006
Data/parameters	11753 / 878
Final R indices [I>2σ(I)]	R1 = 0.0503, wR2 = 0.1198
R indices all data	R1 = 0.0667, wR2 = 0.1308

Table S2. Selected torsion angles and angles between planes of **L**.

	Angle (°)	
Torsion	**A**	**B**
C2-C1-C7-C12	-63.0(2)	-65.6(2)
N1-C14-C15-N2*	61(2) / 44(1)	33.3(3)
N1-C20-C21-N3	-100.6(2)	-88.1(2)
N4-C27-C28-N5	-104.5(2)	-105.3(2)
N4-C33-C34-N6	40.5(2)	53.2(2)
Angle between planes	**Angle (°)**	
	A	**B**
(C1-C6)//C7-C12)	60.22(6)	63.35(5)
(N2-C19)//(N3-C25)*	76.8(2) / 77.9(2)	64.5(1)
(N5-C32)//(N6-C38)	73.48(8)	68.42(7)

* Due to the presence of disorder two values have been reported.

3. Acid-base properties of the ligand

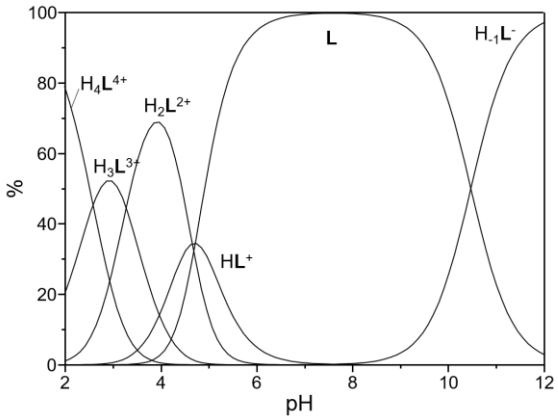

Figure S7. Distribution diagram of the species present in solution of **L** ([**L**] = 1 x 10^{-3} M) obtained via potentiometric measurements in H_2O/CH_3CN 80:20 (v/v) NMe_4Cl 0.1 M at 298 ± 0.1 K.

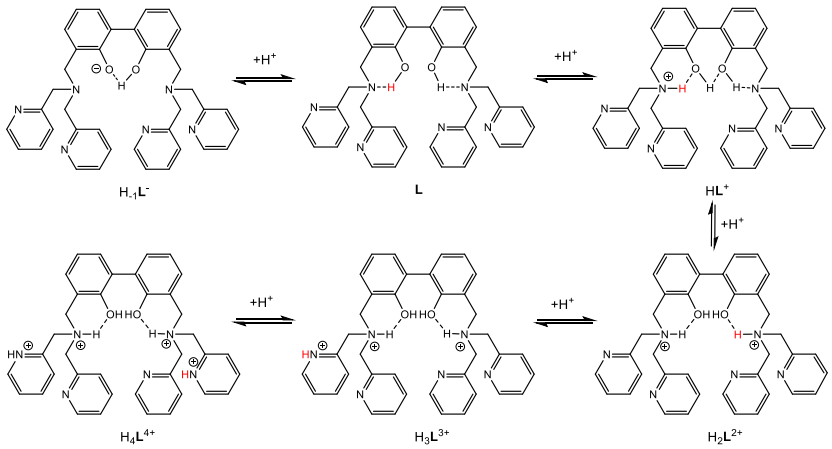

Figure S8. Proposed distribution of the acidic hydrogen atoms in the protonated species of **L**.

4. Zn^{2+} binding properties.

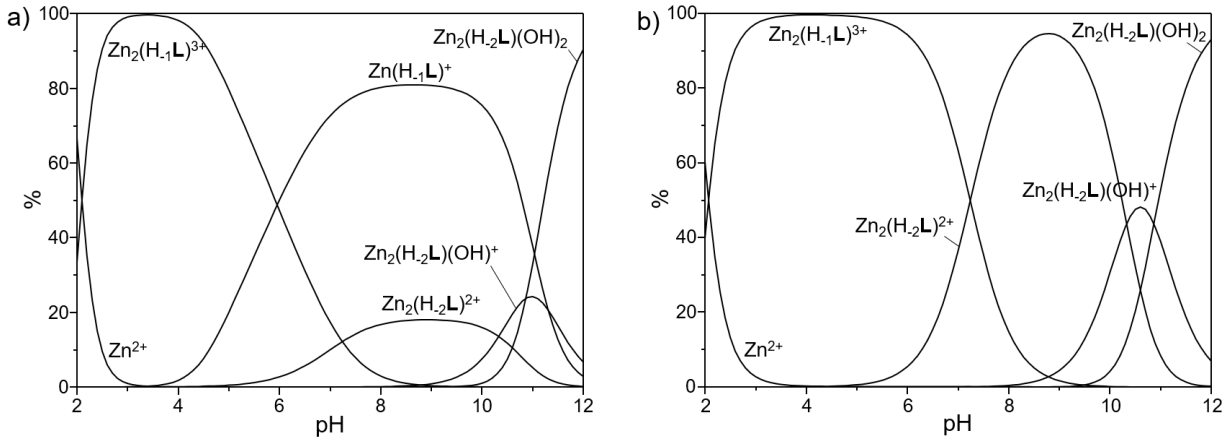

Figure S9. Distribution diagrams of the species present in solution for the **L**/Zn^{2+} system in 1:1 (a) and 1:2 (b) molar ratios as a function of pH in aqueous solution ([**L**] = 1 x 10^{-3} M, H_2O/CH_3CN 80:20 (v/v) NMe_4Cl 0.1 M, 298 ± 0.1 K).

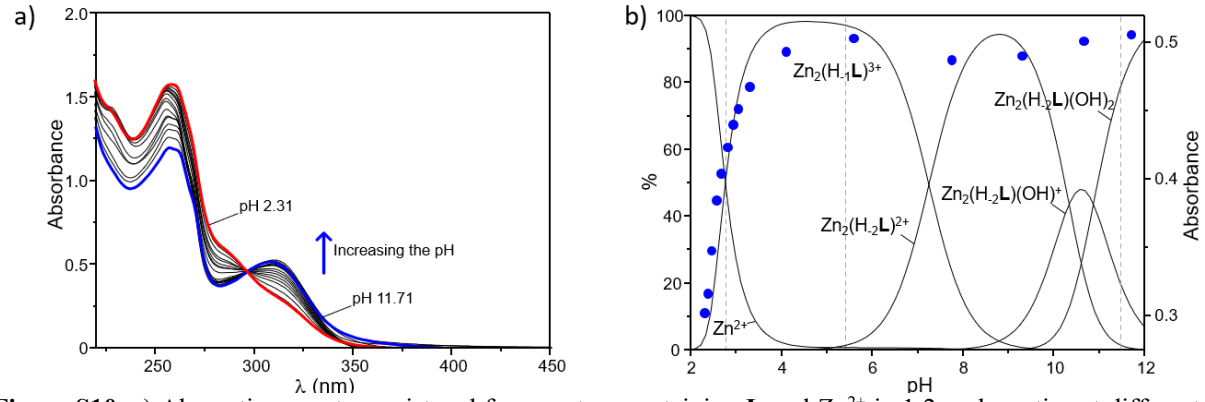

Figure S10. a) Absorption spectra registered for a system containing **L** and Zn^{2+} in 1:2 molar ratios at different pH values and b) variation of the absorbance at 313 nm as a function of pH overlapped with the distribution diagram of the species present in solution ([**L**] = 3.3 x 10^{-5} M (a, b) 1 x 10^{-4} M, H_2O/CH_3CN 80:20 v/v).

5. DFT calculations

Table S3. Selected optimized bond distances (Å) and angles (°) for $Zn(H_{-1}\mathbf{L})^{+}$ (species 1 and 2, differing for the initial placement of Zn^{2+} with respect to the BPH oxygen atoms), $Zn_2(H_{-2}\mathbf{L})^{2+}$ and $Zn_2(H_{-1}\mathbf{L})^{3+}$ (species 1 and 2, differing for the presence of an *intra*-BPH H-bond).

	$Zn(H_{-1}\mathbf{L})^{+}_{(1)}$	$Zn(H_{-1}\mathbf{L})^{+}_{(2)}$	$Zn_2(H_{-2}\mathbf{L})^{2+}$	$Zn_2(H_{-1}\mathbf{L})^{3+}_{(1)}$	$Zn_2(H_{-1}\mathbf{L})^{3+}_{(2)}$
Zn1-O1	1.944	1.936	1.868	1.903	2.149
Zn1-O2	2.107	2.169	/	/	/
Zn1-N1	2.280	**2.352**	2.030	2.090	2.000
Zn1-N2	2.081	2.050	2.097	2.035	2.040
Zn1-N3	2.104	2.086	2.044	2.016	2.057
O1-Zn1-N1	86.40	81.20	102.08	101.22	88.26
O1-Zn1-N2	94.92	115.05	118.29	124.01	155.44
O1-Zn1-N3	153.18	127.15	127.18	121.00	136.25
O1-Zn1-O2	85.22	85.34	/	/	/
O2-Zn1-N2	136.68	123.14	/	/	/
O2-Zn1-N3	92.21	95.07	/	/	/
O2-Zn1-N1	140.51	156.69	/	/	/
N1-Zn1-N2	82.47	79.98	85.72	84.79	82.30
N1-Zn1-N3	78.69	78.37	84.24	114.89	79.42
N2-Zn1-N3	104.94	108.53	114.45	86.47	64.06
Zn2-O1	/	/	/	/	/
Zn2-O2	/	/	1.874	2.003	**2.651**
Zn2-N4	/	/	2.095	2.055	1.993
Zn2-N5	/	/	2.030	1.998	2.050
Zn2-N6	/	/	2.045	1.994	2.057
O2-Zn2-N4	/	/	102.38	97.96	80.37
O2-Zn2-N5	/	/	119.54	121.91	155.74
O2-Zn2-N6	/	/	126.01	114.73	65.10
N4-Zn2-N5	/	/	85.78	87.01	77.13
N4-Zn2-N6	/	/	84.31	88.06	84.22
N5-Zn2-N6	/	/	114.33	123.29	103.39
C2-C1-C7-C12	50.11	51.80	-44.78	-51.11	47.90
O1---O2	2.745	2.787	4.771	4.637	2.610

Table S4. Intramolecular hydrogen bonds and angles between mean planes containing aromatic BPH rings.

	L	$H_{-1}\mathbf{L}^{-}$	$Zn(H_{-1}\mathbf{L})^{+}_{(1)}$	$Zn(H_{-1}\mathbf{L})^{+}_{(2)}$	$Zn_2(H_{-2}\mathbf{L})^{2+}$	$Zn_2(H_{-1}\mathbf{L})^{3+}_{(1)}$	$Zn_2(H_{-1}\mathbf{L})^{3+}_{(2)}$
D-H···A	**O2-H2o···N4**	**O2-H2o···O1**	**O2-H2o···N6**	**O2-H2o···N4**	/	/	**O2-H2o···O1^{-}**
H···A (Å)	1.856	1.291	1.568	1.664	/	/	1.763
D···A (Å)	2.738	2.409	2.613	2.619	/	/	2.610
D-H···A (°)	144.70	167.01	168.62	150.56	/	/	145.27
BPH angles (°)	62.68	34.29	49.56	51.17	45.33	51.34	45.11