Supplementary Information

A new multitalented azine ligand: elastic bending, single-crystal-tosingle-crystal transformation and a fluorescence turn-on Al(III) sensor

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Experimental section

Materials

Commercially available starting materials and reagent grade solvents were used as received. The common reagents and solvents were procured from Merck and S. D. Fine Chem. Ltd. The solvents were dried and distilled following the standard literature procedures prior to their use. 2–Hydroxy–1–naphthaldehyde, 4-bromobenzaldehyde, ferrocenecarboxaldehyde and hydrazine hydrate were purchased from Sigma Aldrich Chemical Co., USA and used as received without further purifications. Compounds L_1 and L_2 were synthesized according to the previous literature.¹

Physical measurements

Single-crystal X-ray structural studies were conducted on a Rigaku Oxford SuperNova CCD Diffractometer equipped with a low-temperature attachment. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance (III) instrument by using DMSO-D6.¹H NMR chemical shifts are reported in parts per million(ppm) relative to the solvent residual peak. ¹³C NMR chemical shifts are reported relative to the solvent residual peak (DMSO-D6, 40.0 ppm). IR spectra [4000–400 cm⁻¹] were recorded with a Bio–Rad FTS 3000MX instrument on KBr pellets. Elemental analyses were carried out with a Thermo–Flash 2000 elemental analyzer. Spectrophotometric measurements were performed on a Varian UV/vis spectrophotometer (model: Cary 100) using a quartz cuvette with a path length of 1cm. Emission spectra were recorded in a fluoromax–4p fluorimeter from HoribaYovin (model: FM–100). The excitation and emission slits were 5/5 nm for the emission measurements. The mass spectra were recorded on Brucker–Daltonics, micro TOF–QII mass spectrometer.

Crystallographic data collection and structure determination

The single crystal of compound H_3L , H_3L^1 , L_1 and L_2 were mounted on a Rigaku Oxford SuperNova CCD Diffractometer and the single crystal X-ray data were collected at RT (293 K) using graphite–monochromated Mo K α ($\lambda_{\alpha} = 0.71073$ Å). The Data collections were evaluated using the CrysAlisPro CCD software. The data were collected by the standard φ – ω scan techniques and scaled as well as reduced by CrysAlisPro RED software. The crystal structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares with SHELXL-97 on $F^{2,2}$ The positions of all of the atoms were obtained by direct methods. All non-H atoms were refined anisotropically. All the H atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 × Ueq of their parent atoms. The hydrogen-bonding interactions, molecular drawings and mean-plane analyses were obtained using the Diamond program (*ver.* 3.1d).³ The crystal and refinement data are summarized in Table S1, and selected bond distances and angles are shown in Table S3. Despite several attempts we were not able to get better quality crystals for L₁ and L₂.

Synthesis of H₃L

10 mmol (1.38 g) of 2,3-dihydroxybenzaldehyde was dissolved in 40 mL of methanol by constant stirring. To this solution, an excess of hydrazine hydrate (5 mL) was added. The resulting solution was stirred for 8 h to obtain the pale yellow product which was collected by silica-gel column chromatography (Sheme 1, Step 1). In the next step 1.0 mmol (138 mg) of this product obtained in step 1 was dissolved in 20 mL of methanol with 1 mmol (172 mg) of 2hydroxy 1-napthaldehyde, and the reaction mixture was stirred for 15 h to obtain a deep vellow product which was washed two times with diethyl ether and then dried on high vacuum pump. Yellow flexible needle shaped single crystals of H₃L were grown from chloroform. Yield: 80%. Elemental analysis (found: C 71.94; H 4.69; N 8.93%; calc. for C₁₈H₁₄N₂O₃: C 70.58; H 4.61; N 9.15%. ¹H NMR (CDCl3, δH ppm):12.87(s, 1H), 10.87(s, 1H), 9.89(S, 1H), 9.36(s, 1H), 9.0(s, 1H), 8.64(d.d 1H), 8.04(d.d, 1H), 7.93(t, 1H), 7.62(d.d, 1H), 7.44(s, 1H), 7.28(t, 1H), 7.16(d, 1H), 6.97(d, 1H), 6.82(t, 1H). ¹³C NMR (CDCl₃, δc ppm): 163.61, 162.11, 160.59, 147.86, 146.17, 135.27, 132.74, 129.37, 128.51, 128.29, 124.30, 122.23, 121.97, 119.87, 119.36, 119.22, 188.91, 108.86. ESI-MS (m/z) 307.1 [M+1]. IR (KBr, cm⁻¹): 3448(br), 3057(w), 1917(s), 1621(m), 1586(vs), 1462(m), 1383(m), 1318(m), 1269(m), 1229(w), 1186(m), 1086(m), 956(m), 824(vs), 780(vs), 661(m).

Synthesis of H₃L-Al³⁺ Complex

Al(NO₃)₃·9H₂O (2.5 mmol, 9.37 mg) was added to a 40 mL methanolic solution of H_3L (5 mmol, 61. 2 mg) with constant stirring. The reaction mixture was stirred at room temperature for 8 h resulting the formation of dark yellow precipitate and then mixture was filtered, and washed with hexane. ESI–MS (m/z) 658.35 [M+Na].

Calculation of crystal elongation, translational motion and critical radius:

1. For H₃L

1.1 Change in length per molecule (elongation/contraction on bending)

A simple calculation was utilised to calculate the change in length Δl upon bending (elastic bending has been assumed). The model assumes bending of a crystal into a full loop (as shown in Fig. S19), with the perimeter along the neutral axis being represented by l_0 .

The length l_o is related to the radius r_o by the following relation:

$$r_0 = \frac{l_0}{2\pi}$$

(Equation 1)

Wherein l_0 is the measured length of the crystal as determined from SCXRD experiment.

The radius values for outer and inner arcs as shown in figure 1 would be given by:

$$r_{out} = r_0 + \frac{t}{2}$$
$$r_{in} = r_0 - \frac{t}{2}$$

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(Equation 2)

(Equation 3)

where 't' is the thickness of the crystal (defined as 30 μ m). From equations 1, 2 and 3, the values of r_{out} and r_{in} are calculated to be 86.65 μ m and 56.65 μ m respectively for the untouched crystal, and 86.15 μ m and 57.15 μ m for the crystal after bending.

The change in length (or perimeter), i.e. crystal elongation upon bending, is given by the following set of equations:

$$\begin{split} \Delta l_{out} &= 2 \pi (r_{out} - r_o) \\ \Delta l_{in} &= 2 \pi (r_o - r_{in}) \\ \Delta l_{in} &= \Delta l_{out} = \pi t \end{split}$$

(Equation 4, 5, 6)

For a crystal with a thickness of 30 μ m, the elongation is calculated to be 94.2 μ m. After bending, this value is 91.06 μ m.

Now, for monoclinic crystal, the formula unit is 4 and lattice parameter (a) is 14.649 Å, therefore 1 mm of crystal contains $10^7 \times (4/14.649)$ molecules.

So, for 0.43 mm length crystal, the number of molecules works out to be $10^7 \times (0.09 \text{ x } 4/14.649)$ molecules, which works out to be 1174141.5796 molecules.

1.2 Translational movement per molecule for 0.43 mm long crystal: This is given by the below equation:

$$\frac{\Delta l}{n} = 0.314 \times \frac{14.649}{10^7 \times 4 \times 0.43} = 2.6743 \text{ Å/molecule}$$
(Equation 7)

If the crystal length is halved, the translation movement will double. Thus, 1.33715 Å/molecule is the yield point for this crystal, i.e. translational movement beyond this value will induce breaking in the crystal if a full circle is attempted to be made by bending. The critical radius for this condition is given by the following equation:

$$r_c = \frac{0.215}{2\pi} = 0.0308 \ mm = 30.8 \ \mu m$$

(Equation 8)

1.3 Change in angle per molecule upon bending:

For a crystal of length 0.43 mm, the change in angle per molecule upon bending is given by 360/(number of molecules). Substituting appropriate values, the change in angle is found to be 0.0003067°/molecule. This quantity also doubles as the crystal size halves, meaning that the breaking strain is 0.0006134°/molecule.

2. For H₃L¹

2.1 Change in length per molecule (elongation/contraction on bending)

The obtained crystal had a length of 0.43 mm and a thickness of 22 μ m. From equations 1, 2 and 3, the values of r_{out} and r_{in} are calculated as 82.65 μ m and 60.65 μ m respectively. Based on equations 4, 5 and 6, the crystal elongation upon bending is calculated to be 69.08 μ m.

Now, as per the crystal structure and the parameters obtained for the axis, H_3L^1 displays enlargement of the a-axis. Keeping this and the formula unit for monoclinic space group (Z=4) into account, we can surmise that 1 mm of crystal contains $10^7 \times (4/28.115)$ molecules. The, given the crystal length, 0.43 mm of crystal would contain $0.43 \times 10^7 \times (4/28.115)$, i.e. 611773.07483 molecules.

2.2 Translational movement per molecule for 0.43 mm long crystal:

Equation 7 is modified as follows for this calculation:

$$\frac{\Delta l}{n} = 0.314 \times \frac{28.115}{10^7 \times 4 \times 0.43} = 5.1326 \text{ Å/molecule}$$

If the crystal length is halved, the translation movement will double. Thus, 2.5663 Å/molecule is the yield point for this crystal. Compared to H_3L , this represents an improvement in elastic property of H_3L^1 . The critical radius remains the same at 30.8 µm as determined by Equation 8.

2.3 Change in angle per molecule upon bending:

For a crystal of length 0.43 mm, the change in angle per molecule upon bending is given by 360/(number of molecules). Substituting appropriate values, the change in angle is found to be $0.0005884^{\circ}/molecule$. This quantity also doubles as the crystal size halves, meaning that the breaking strain is $0.001177^{\circ}/molecule$. This value is also an improvement over the value obtained for H₃L. The higher breaking strain indicates enhanced elastic property for H₃L¹ as compared to H₃L.

Table S1. Crystallographic parameters of H_3L and H_3L^1 .

Identification code	H ₃ L (293 K)	$H_{3}L^{1}(293 \text{ K})$
Empirical formula	$C_{18}H_{14}N_2O_3$	$C_{36}H_{28}N_4O_6$
Formula weight	306.31	612.62
Temperature	293(2) K	293(2) K
Wavelength	0.71073 A	0.71073 A
Crystal system, space group	Monoclinic, $P2_l/n$	Monoclinic, C2/c
Unit Cell Parameter		
a/Å	14.6490(13)	28.115(4)
b/Å	5.0010(4)	4.5482(5)
c/Å	21.4358(17)	23.970(4)
$\alpha/^{\circ}$	90	90
β/°	108.746(9)	93.065(11)
$\gamma/^{\circ}$	90	90
V/Å ³	1487.1(2)	3060.7(7)
$Z, d_{\text{calcd}}(\text{mg/m}^3)$	4, 1.368	4, 1.329
µ/ mm ⁻¹	0.095	0.092
F(000)	640	1280
θ range	2.894 to 24.996 deg.	3.285 to 24.999 deg.
Index ranges	-17<=h<=17,	-32<=h<=32,
	-5<=k<=5,	-5<=k<=5,
	-25<=1<=25	-16<=l<=28
Reflections collected /	13936 / 2606 [R(int) =	11501 / 2700 [R(int) =
unique	0.0742]	0.1370]
Data / restraints /	2606 / 1 / 217	2700 / 0 / 211
parameters	1.040	0.000
$\begin{array}{c} \text{GOF}, \text{F}^2 \\ \text{P1} \text{P2} \left[\text{I} > 2 - (1) \right] \end{array}$	1.049	0.966
$[K_1, WKZ [1 \ge 2\sigma(1)]]$	$K_1 = 0.0081, WKZ = 0.1722$	$K_1 = 0.0898, WKZ = 0.2037$
R1 wR2 (all data)	R1 = 0.1309 wR2 =	R1 = 0.2418 wR2 =
(un unu)	0.2189	0.2885
CCDC	1543797	1543798

Table S1a. Crystallographic parameters of L_1 and L_2

Identification code	L ₁ (293 K)	L ₂ (293 K)	
Empirical formula	$C_{14}H_{10}Br_2N_2$	$C_{22}H_{20}Fe_2N_2$	
Formula weight	366.06	424.10	
Temperature	293(2) K	293(2) K	
Wavelength	0.71073 A	0.71073 A	
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	
Unit Cell Parameter			
a/Å	3.8997(4)	7.5953(15)	
b/Å	7.1770(5)	10.1025(15)	
c/Å	24.082(3)	12.191(3)	
α/ [°]	90	90	
β/ [°]	90.434(10)	105.83(2)	
$\gamma/^{\circ}$	90	90	
$V/Å^3$	673.99(12)	899.9(3)	
$Z, d_{calcd}(mg/m^3)$	2, 1.804	2, 1.565	
u/ mm ⁻¹	5.996	1.619	
F(000)	356	436	
θ range	3.305 to 28.906 deg.	3.441 to 28.896 deg.	
Index ranges	-4<=h<=4,	-7<=h<=10, -	
C C	-9<=k<=9,	$13 \le k \le 13$,	
	-32<=1<=32	-16<=l<=15	
Reflections collected /	4630 / 4630 [R(int) =	6135 / 6135 [R(int) =	
unique	0.00]	0.00]	
Data / restraints /	4630 / 60 / 84	6135 / 183 / 119	
parameters			
GOF, F ²	1.171	1.094	
R1, wR2 [I>2σ(I)]	R1 = 0.1250, wR2 = R1 = 0.1166,		
	0.3152	0.3031	
R1, wR2 (all data)	R1 = 0.1737, wR2 =	R1 = 0.1614, wR2 =	
	0.3734 0.3725		
CCDC	1565839 1565840		
e S1h. Unit cell peremeters of I	and L hafara and after ill	humination of UV light	

Table S1b. Unit cell parameters of L_1 and L_2 before and after illumination of UV light

Compounds	Parameters	Before UV-	After UV-	
		illumination	illumination	
	Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	
	a/Å	3.8997(4)	3.882(15)	
	b/Å	7.1770(5)	7.164(9)	
	c/Å	24.082(3)	24.13(7)	
L_1	α/°	90	90	
	β/ [°]	90.434(10)	90	
	γ/°	90	90	
	V/Å ³	673.99(12)	671(18)	
	Crystal system, space	Monoclinic, $P2_l/c$	Monoclinic, $P2_1/c$	
	group			
	a/Å	7.5953(15)	7.584(19)	
	b/Å	10.1025(15)	10.07(5)	
L ₂	c/Å	12.191(3)	12.15(6)	
	α/°	90	90.02(4)	
	β/°	105.83(2)	105(1)	
	γ/°	90	90	
	V/Å ³	899.9(3)	894(17)	

Table S2. Comparison of crystal parameters of H_3L (original) and H_3L (Bending)

Parameter	H ₃ L	H ₃ L (Bending)	
a (Å)	14.649	14.641	
b (Å)	5.001	5.001	
c (Å)	21.4358	21.49	
α (°)	90	90	
β (°)	108.746	108.61	
γ (°)	90	90	
Space Group	$P2_{l}/n$	$P2_{l}/n$	
Crystal Dimensions ($L \times W$	$0.09 \times 0.03 \times 0.02$ (mm)	$0.09 \times 0.03 \times 0.02$ (mm)	
× H)			

Table S3. Hydrogen bonding of H_3L and H_3L^1 [Å and (°)].

	D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)		
	H ₃ L						
1	O(1)-H(101) ····N(1)#(0)	0.917(.003)	2.566(.004)	1.769(.000)	143.67(0.21		
2	O(2)-H(2)···N(2)#(0)	0.820(.000)	2.623(.000)	1.903(.000)	146.09(0.01)		
3	O(3)-H(103)····O(3)#(3)	0.838(.000)	2.806(.000)	1.998(.000)	161.49(0.01)		
Eq (0) (3)	Equivalent positions: (0) x,y,z (3) $-x+1/2+1,+y+1/2,-z+1/2+1$						
	1	1			1		
1	O(3)-H(101)····N(1)#(0)	0.820(.000)	2.555(.000)	1.830(.000)	146.63(0.02)		
2	O(2)-H(2)···N(2)#(0)	0.820(.004)	2.563(.004)	1.927(.000)	133.62(0.28)		
3	O(3)-H(103)····O(2)#(1)	0.820(.000)	2.107(.004)	2.899(.004)	162.65(0.12)		
3	C(12)-H(12) ····O(1)#(2)	0.930(.000)	2.603(.000)	3.479(.000)	157.29(0.02)		
Equivalent positions: (0) x,y,z (1) -x+1,+y,-z+1/2 (2) -x+1/2,+y-1/2,-z+1/2							

Table S4. Average Life time measurement of H_3L

τ_1 τ_2 α_1 α_2 χ^2 $<\tau>$

1.82 ns	4.12 ns	0.22	0.78	2.54	3.60 ns

 Table S5. Comparison with other available fluorescent chemosensors.

Serial	Туре	LOD	Dynamic	References

No.			range	
1	Rhodamine B-	$1.8 imes 10^{-7} M$	0-14 μM	Sensors and Actuators B., 2015,
	derivative			211 , 325.
2	Triphenylvinyl	21.6 nM	0-5 μΜ	Anal.Chem., 2015, 87, 1470.
	derivative			
3	Napthyridine-based	2.94 × 10 ⁻⁵ M	0-12 μM	<i>RSCAdv.</i> , 2014, 4 , 23428.
	rhodamine			
4	Coumarin based	$1.0 \times 10^{-7} \mathrm{M}$	0-2 μM	Inorg.Chem., 2010, 49 , 7229.
5	Napthelene-pyrazol	31.78 nM	0-1200	Analyst., 2014, 139, 4828.
	conjugate,		nM	
6	Furan derivative	6.03 × 10 ⁻⁷ M	0-8 µM	Analyst., 2012, 137, 3975.
7	Schiff base	4.79 × 10 ⁻⁸ M	0-50 μM	Sensors and Actuators B., 2015,
				216 , 86.
8	Naphthalene	1.0×10^{-7}	0-45 μM	Sensors and Actuators B., 2014,
	derivate	Μ		197 , 200.
9	Salen type schiff	86 nM	0-12 μM	Sci. Rep., 2016, 6, 34807.
	base			
10	Azine based	42 nM	0-22 μΜ	Present work



Scheme S1. Synthesis of L_1 and L_2



Scheme S2. Effect of UV light on L_1 and L_2 (No SCSC transformation).



Fig. S1 ¹H NMR spectrum of H_3L



Fig. S2 ¹³C NMR spectrum of H₃L



Fig. S3 ESI-MS spectrum of H₃L



Fig. S4 TGA curve of chemosensor H_3L



Fig. S5 DSC curve of chemosensor H_3L



Fig. S6 Molecular Structure of H_3L .



Fig. S7 Diffraction images (Exposure time = 20 s) obtained from the mounted crystal and the inset shows the (a) original form and (b) bent form.



Fig. S8 Illustrative diagrams: (a) elastic forces acting on crystal during bending and (b) crystal bending depicting critical radius.



Fig. S9 Intramolecular H-bonding interactions in, (a) H_3Land (b) H_3L^1



Fig. S10 (a) An intermolecular H-bonding interaction in H_3L along (100), (010) and (001) faces forming 1D- polymeric chain. (b) Dimer with *single hand shake* position



Fig. S11 (a) An intermolecular H-bonding interaction in H_3L^1 along (100), (010) and (001) faces forming 1D- polymeric chain. (b) Dimer with both *hand in hand handshake* position



Fig. S12 Absorption spectra of H_3L (3.0 × 10⁻⁵ M) with varying concentrations of Al³⁺ in aq. ACN (ACN/H₂O=7:3 v/v, 10 µM HEPES buffer, pH = 7.4) with Al³⁺ ion (c = 1.0 × 10⁻⁴ M). Inset: A = enlarge of peak A and B = enlarge of peak B.



Fig. S13 Fluorescence intensity at 555 nm for H_3L (3.0 × 10⁻⁴ M) in MeOH after addition of Al(III) (1.0 × 10⁻³ M) in aqueous solution.

The limit of detection (LOD) has been calculated using the equation,³

$$LOD = 3.3(\sigma/S),$$

where $\boldsymbol{\sigma}$ is standard error and S is the slope of calibration.



Fig. S14 (a) Fluorescence spectra of H_3L (3.0 × 10⁻⁵ M) ($\lambda ex = 382$ nm) with varying concentrations of Al³⁺ in aq. ACN (ACN/H₂O = 7:3 v/v, 10 μ M HEPES buffer, pH = 7.4) with Al³⁺ ion (c = 1.0 × 10⁻⁴ M). Inset: relative fluorescence intensity changes with respect to Al³⁺ concentration. (b) Effect of fluorescence intensity with addition of Al³⁺ along with other metal ions viz., Ag⁺, Na⁺, K⁺, Li⁺, Mn²⁺, Cd²⁺, Hg²⁺, Mg²⁺, Ca²⁺, Cr³⁺, Ni²⁺, Co²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Fe²⁺ and As³, (c) Histogram showing the relative fluorescence intensity of H₃L-Al³⁺ in presence of other cations. (d) Fluorescence Spectra of H₃L (20 μ M) in the presence of 20 equiv. of Al³⁺ before and after treatment with excess EDTA ($\lambda ex = 382$ nm).

The appearance of large bathochromic shift in the emission is a strong evidence for strong interaction between H_3L and Al(III).⁴ This may be due to the formation of a rigid system on binding with Al^{3+} ions.



Fig. 15 ¹H NMR spectra (400 MHz) of **H**₃L in DMSO-D6 at 25°C and the corresponding changes after the gradual addition of different equivalents of Al(NO₃)₃·9H₂O in D₂O from (**a**) H₃L, (**b**) H₃L + 0.2 equiv. Al³⁺, (**c**) H₃L + 0.4 equiv. Al³⁺, (**d**) H₃L + 0.6 equiv. Al³⁺, and (**e**) H₃L + 0.8 equiv. Al³⁺.



Fig. S16 Job's plot



Fig. S17 Mass spectrum of H₃L-Al³⁺ complex [M+Na⁺]. Inset showing H₃L-Al³⁺.



Fig. S18 (a) Average life time measurement of 1 in MeOH ($\lambda_{ex} = 375$ nm) (b) Fluorescence spectra of 1 in MeOH.



Fig. S19 Schematic diagram of full loop considered for calculation of changes in lengths and angles in an elastic crystal with thickness t and an initial length of $l_{o.}$

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