*Supporting Information*

# Exploration of Fluorescence Behavior of Imidazolium-based Chemosensor in Solution and Solid-state and its Turn-on Response for $Al^{3+}$ in Pure Aqueous Medium

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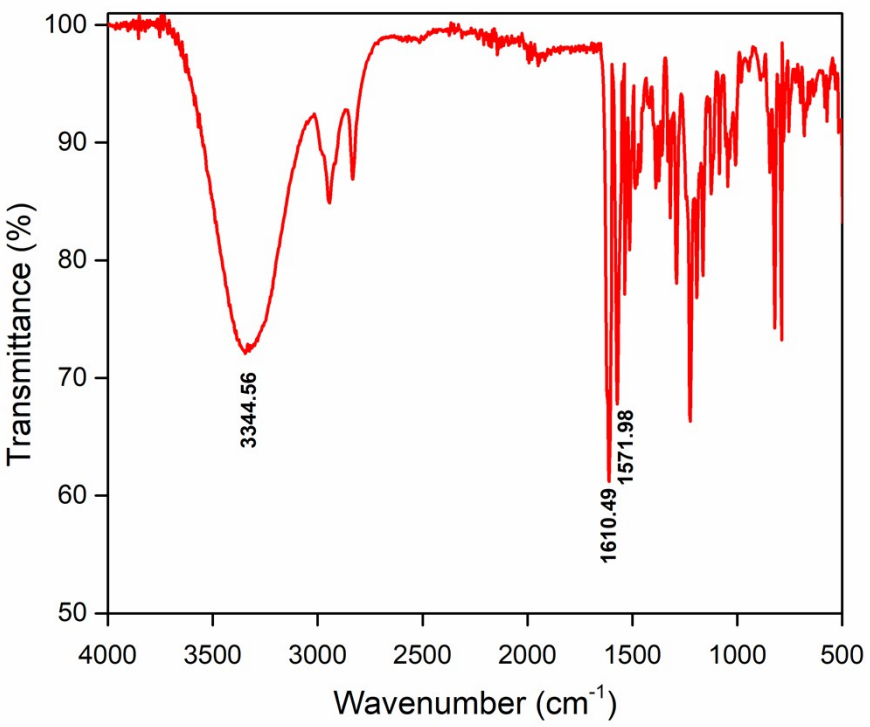


**Fig. S1** FT-IR spectra of **ImSB**.

## Cell parameters and structure data of ImSB:

**Table S1**. Crystal data and structure refinement of **ImSB**.

| | |
|---|---|
| Empirical formula | $C_{23}H_{25}BrN_4O_3$ |
| Formula weight | 485.38 |
| 3Temperature/K | 93(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.2780(3) |
| b/Å | 10.9501(2) |
| c/Å | 11.6256(3) |
| α/° | 87.339(2) |
| β/° | 68.312(2) |
| γ/° | 88.577(2) |
| Volume/Å$^3$ | 1096.27(5) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.470 |
| μ/mm$^{-1}$ | 1.908 |
| F(000) | 500.0 |
| Crystal size/mm$^3$ | 0.2 × 0.2 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 6.222 to 59.698 |
| Index ranges | -12 ≤ h ≤ 12, -13 ≤ k ≤ 14, -16 ≤ l ≤ 14 |
| Reflections collected | 16387 |
| Independent reflections | 5523 [$R_{int}$ = 0.0214, $R_{sigma}$ = 0.0219] |

| | |
|---|---|
| Data/restraints/parameters | 5523/0/289 |
| Goodness-of-fit on $F^2$ | 1.058 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0224, $wR_2$ = 0.0566 |
| Final R indexes [all data] | $R_1$ = 0.0264, $wR_2$ = 0.0582 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.38/-0.21 |

**Table S2**. Fractional Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$×$10^3$) of **ImSB**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***X*** | ***Y*** | ***Z*** | **U(eq)** |
|---|---|---|---|---|
| Br1 | 1046.6(2) | 2316.0(2) | 9186.8(2) | 20.79(5) |
| O1 | 6355.7(11) | 6727.2(9) | 6871.9(9) | 25.0(2) |
| O2 | 1783.2(10) | 5734.6(8) | 6136.1(9) | 22.86(19) |
| O3 | 2063.0(12) | 9518.3(10) | 9987.6(10) | 27.8(2) |
| N1 | 8696.9(12) | 7666.3(9) | 4945.3(10) | 18.9(2) |
| N4 | -4761.4(13) | 2725.0(10) | 9919.2(10) | 21.1(2) |
| N3 | -2982.6(12) | 4094.1(10) | 9158.3(10) | 19.2(2) |
| N2 | 9945.0(14) | 8294.7(10) | 6575.6(10) | 22.2(2) |
| C8 | 10150.3(15) | 8242.3(11) | 4464.8(12) | 18.5(2) |
| C13 | 10771.6(15) | 8591.5(11) | 5357.3(11) | 18.6(2) |
| C11 | 12972.6(15) | 9511.0(12) | 3660.7(13) | 22.4(2) |
| C12 | 12187.6(15) | 9239.3(11) | 4944.6(12) | 19.8(2) |
| C21 | -5180.7(15) | 3465.4(12) | 9097.8(11) | 20.9(2) |
| C7 | 7781.5(15) | 7500.9(11) | 4322.4(12) | 19.1(2) |
| C2 | 6285.2(14) | 7035.2(11) | 4846.2(11) | 18.3(2) |
| C1 | 5601.1(15) | 6668.9(11) | 6152.8(12) | 19.3(2) |
| C9 | 10951.1(15) | 8500.6(12) | 3221.1(12) | 20.7(2) |
| C19 | -1567.2(15) | 4797.9(12) | 8931.8(13) | 22.6(3) |
| C6 | 4039.7(15) | 6237.1(11) | 6591.4(12) | 20.8(2) |
| C4 | 3935.3(15) | 6514.7(12) | 4519.5(12) | 21.1(2) |
| C10 | 12365.5(15) | 9139.0(12) | 2826.1(12) | 22.3(2) |
| C5 | 3255.7(14) | 6152.8(11) | 5798.5(12) | 19.4(2) |
| C3 | 5408.1(15) | 6943.8(12) | 4071.3(12) | 21.1(2) |
| C18 | -608.0(15) | 4958.4(12) | 7553.9(13) | 23.5(3) |
| C15 | 11916.0(18) | 9285.3(13) | 7081.5(13) | 28.1(3) |
| C22 | -4070.8(15) | 4328.8(12) | 8617.6(12) | 20.6(2) |
| C16 | 10519.8(18) | 8640.7(13) | 7389.3(13) | 26.5(3) |
| C17 | 983.9(15) | 5411.3(12) | 7413.9(13) | 23.1(3) |
| C20 | -3429.2(15) | 3123.0(12) | 9935.9(12) | 22.0(2) |
| C14 | 12747.4(16) | 9584.0(12) | 5862.6(13) | 25.0(3) |
| C23 | -5658.5(18) | 1695.0(13) | 10685.0(14) | 29.1(3) |

**Table S3.** Anisotropic Displacement Parameters ($Å^2$×$10^3$) of **ImSB**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** |
|---|---|---|---|---|---|
| Br1 | 21.54(7) | 21.15(7) | 19.96(7) | 4.09(4) | -8.23(5) |
| O1 | 23.3(5) | 28.1(5) | 23.5(5) | 7.7(4) | -9.2(4) |
| O2 | 16.3(4) | 21.7(4) | 28.2(5) | 1.6(4) | -5.6(4) |

| | | | | | |
|---|---|---|---|---|---|
| O3 | 26.8(5) | 25.8(5) | 32.7(5) | 2.6(4) | -13.7(4) |
| N1 | 19.7(5) | 16.5(5) | 17.6(5) | 2.0(4) | -3.7(4) |
| N4 | 20.5(5) | 19.0(5) | 22.4(5) | -1.1(4) | -6.2(4) |
| N3 | 15.4(5) | 19.2(5) | 21.8(5) | -2.7(4) | -5.3(4) |
| N2 | 27.1(6) | 17.7(5) | 19.6(5) | 0.0(4) | -6.4(4) |
| C8 | 19.0(6) | 13.6(5) | 21.5(6) | 1.0(4) | -5.8(5) |
| C13 | 21.8(6) | 13.0(5) | 19.8(6) | 0.2(4) | -6.5(5) |
| C11 | 18.5(6) | 20.7(6) | 27.0(6) | 2.7(5) | -7.3(5) |
| C12 | 21.5(6) | 15.0(5) | 23.6(6) | -1.1(4) | -9.2(5) |
| C21 | 17.5(6) | 25.3(6) | 19.8(6) | -3.5(5) | -6.5(5) |
| C7 | 20.2(6) | 14.7(5) | 19.4(5) | -0.8(4) | -3.9(5) |
| C2 | 18.8(6) | 12.7(5) | 20.9(6) | -0.8(4) | -4.5(5) |
| C1 | 20.3(6) | 13.7(5) | 22.2(6) | 2.4(4) | -6.2(5) |
| C9 | 22.5(6) | 20.2(6) | 19.7(6) | 0.7(4) | -8.1(5) |
| C19 | 16.4(6) | 22.2(6) | 28.2(6) | -2.3(5) | -6.8(5) |
| C6 | 18.6(6) | 17.7(6) | 22.9(6) | 4.7(5) | -4.3(5) |
| C4 | 20.4(6) | 19.5(6) | 23.3(6) | -4.6(5) | -7.8(5) |
| C10 | 21.7(6) | 22.3(6) | 20.2(6) | 3.9(5) | -5.1(5) |
| C5 | 15.8(5) | 12.3(5) | 27.1(6) | -1.5(4) | -4.3(5) |
| C3 | 21.8(6) | 19.5(6) | 19.6(6) | -2.6(4) | -4.8(5) |
| C18 | 18.2(6) | 21.9(6) | 28.5(7) | 1.7(5) | -6.6(5) |
| C15 | 36.1(8) | 26.7(7) | 27.4(7) | -6.6(5) | -18.4(6) |
| C22 | 18.8(6) | 23.2(6) | 19.6(5) | -1.4(5) | -6.8(5) |
| C16 | 34.8(7) | 24.2(6) | 20.3(6) | -1.6(5) | -10.1(5) |
| C17 | 18.4(6) | 19.5(6) | 28.8(6) | 4.4(5) | -6.3(5) |
| C20 | 21.8(6) | 19.6(6) | 26.1(6) | -0.9(5) | -10.6(5) |
| C14 | 25.1(6) | 21.8(6) | 31.5(7) | -3.8(5) | -14.3(6) |
| C23 | 29.3(7) | 23.1(7) | 31.9(7) | 4.0(5) | -7.7(6) |

**Table S4**. Bond Lengths of **ImSB**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| O1 | C1 | 1.2779(16) | C11 | C12 | 1.4188(18) |
| O2 | C5 | 1.3595(15) | C11 | C10 | 1.3699(19) |
| O2 | C17 | 1.4255(16) | C12 | C14 | 1.4171(18) |
| N1 | C8 | 1.4075(16) | C21 | C22 | 1.3566(18) |
| N1 | C7 | 1.3241(17) | C7 | C2 | 1.3927(17) |
| N4 | C21 | 1.3811(17) | C2 | C1 | 1.4541(17) |
| N4 | C20 | 1.3279(17) | C2 | C3 | 1.4276(18) |
| N4 | C23 | 1.4708(17) | C1 | C6 | 1.4311(17) |
| N3 | C19 | 1.4709(16) | C9 | C10 | 1.4114(18) |
| N3 | C22 | 1.3862(16) | C19 | C18 | 1.5221(19) |
| N3 | C20 | 1.3325(17) | C6 | C5 | 1.3762(18) |
| N2 | C13 | 1.3663(16) | C4 | C5 | 1.4249(18) |
| N2 | C16 | 1.3186(18) | C4 | C3 | 1.3573(18) |
| C8 | C13 | 1.4300(18) | C18 | C17 | 1.5182(18) |
| C8 | C9 | 1.3788(17) | C15 | C16 | 1.408(2) |
| C13 | C12 | 1.4171(18) | C15 | C14 | 1.368(2) |

**Table S5**. Bond Angles of **ImSB**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C5 | O2 | C17 | 117.11(10) | C7 | C2 | C3 | 118.33(11) |
| C7 | N1 | C8 | 125.28(11) | C3 | C2 | C1 | 120.00(11) |
| C21 | N4 | C23 | 126.12(11) | O1 | C1 | C2 | 121.75(11) |
| C20 | N4 | C21 | 108.53(11) | O1 | C1 | C6 | 121.71(11) |
| C20 | N4 | C23 | 125.31(12) | C6 | C1 | C2 | 116.54(11) |
| C22 | N3 | C19 | 126.25(11) | C8 | C9 | C10 | 120.19(12) |
| C20 | N3 | C19 | 124.85(11) | N3 | C19 | C18 | 111.63(11) |
| C20 | N3 | C22 | 108.90(11) | C5 | C6 | C1 | 120.98(12) |
| C16 | N2 | C13 | 117.00(12) | C3 | C4 | C5 | 118.72(12) |
| N1 | C8 | C13 | 115.90(11) | C11 | C10 | C9 | 121.12(12) |
| C9 | C8 | N1 | 124.01(12) | O2 | C5 | C6 | 124.64(12) |
| C9 | C8 | C13 | 120.07(12) | O2 | C5 | C4 | 113.30(11) |
| N2 | C13 | C8 | 117.71(12) | C6 | C5 | C4 | 122.06(12) |
| N2 | C13 | C12 | 123.34(12) | C4 | C3 | C2 | 121.68(12) |
| C12 | C13 | C8 | 118.94(11) | C17 | C18 | C19 | 107.99(11) |
| C10 | C11 | C12 | 119.93(12) | C14 | C15 | C16 | 118.83(13) |
| C13 | C12 | C11 | 119.73(12) | C21 | C22 | N3 | 106.31(11) |
| C14 | C12 | C13 | 117.02(12) | N2 | C16 | C15 | 124.36(13) |
| C14 | C12 | C11 | 123.25(12) | O2 | C17 | C18 | 107.27(11) |
| C22 | C21 | N4 | 107.53(11) | N4 | C20 | N3 | 108.72(11) |
| N1 | C7 | C2 | 124.33(12) | C15 | C14 | C12 | 119.45(13) |
| C7 | C2 | C1 | 121.67(12) | | | | |

**Table S6** Hydrogen Bonds of **ImSB**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| N1 | H1 | O1 | 0.86 | 2.00 | 2.6634(14) | 133.2 |
| C22 | H22 | O1_$1[1] | 0.93 | 2.27 | 3.1837(16) | 165.6 |

[1]-1+X,+Y,+Z

**Table S7.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) of **ImSB**.

| Atom | *X* | *Y* | *Z* | U(eq) |
|---|---|---|---|---|
| H1 | 8377.65 | 7400.32 | 5705.02 | 23 |
| H11 | 13898.35 | 9941.14 | 3385.98 | 27 |
| H21 | -6063.16 | 3386.48 | 8908.34 | 25 |
| H7 | 8162.89 | 7709.35 | 3479.32 | 23 |
| H9 | 10558.07 | 8253.5 | 2640.82 | 25 |
| H19A | -946.75 | 4379.04 | 9343.45 | 27 |
| H19B | -1850.5 | 5595.51 | 9282.91 | 27 |
| H6 | 3547.43 | 6010.06 | 7424.55 | 25 |
| H4 | 3380.57 | 6457.96 | 4001.91 | 25 |
| H10 | 12894.31 | 9310.08 | 1984.97 | 27 |
| H3 | 5857.38 | 7184.32 | 3237.99 | 25 |
| H18A | -512.88 | 4185.45 | 7155.85 | 28 |
| H18B | -1106.73 | 5545.35 | 7167.63 | 28 |
| H15 | 12266.6 | 9504.02 | 7695.91 | 34 |

| | | | | |
|---|---|---|---|---|
| H22 | -4045.02 | 4953.62 | 8040.7 | 25 |
| H16 | 9966.35 | 8446.19 | 8221.88 | 32 |
| H17A | 884.86 | 6116.31 | 7913.82 | 28 |
| H17B | 1549.05 | 4774.64 | 7682.24 | 28 |
| H20 | -2896.04 | 2780.46 | 10411.57 | 26 |
| H14 | 13672.24 | 10009.78 | 5638.39 | 30 |
| H23A | -6358.72 | 1986.43 | 11461.43 | 44 |
| H23B | -4963.33 | 1099.44 | 10832.97 | 44 |
| H23C | -6238.98 | 1326.97 | 10260.63 | 44 |
| H3A | 1830(30) | 10240(20) | 9760(20) | 50(6) |
| H3B | 1210(30) | 9100(20) | 10240(20) | 48(6) |

## Crystal structure determination of ImSB:

Crystal Data for $C_{23}H_{25}BrN_4O_3$ ($M$ = 485.38 g/mol): triclinic, space group P-1 (no. 2), $a$ = 9.2780(3) Å, $b$ = 10.9501(2) Å, $c$ = 11.6256(3) Å, $\alpha$ = 87.339(2)°, $\beta$ = 68.312(2)°, $\gamma$ = 88.577(2)°, $V$ = 1096.27(5) Å$^3$, $Z$ = 2, $T$ = 93(2) K, μ(MoKα) = 1.908 mm$^{-1}$, $D_{calc}$ = 1.470 g/cm$^3$, 16387 reflections measured (6.222° ≤ 2Θ ≤ 59.698°), 5523 unique ($R_{int}$ = 0.0214, $R_{sigma}$ = 0.0219) which were used in all calculations. The final $R_1$ was 0.0224 (I >2σ(I)) and $wR_2$ was 0.0582 (all data).

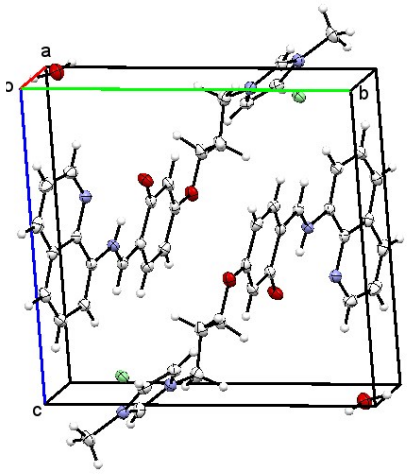


**Fig. S2** Unit cell packing of **ImSB**.

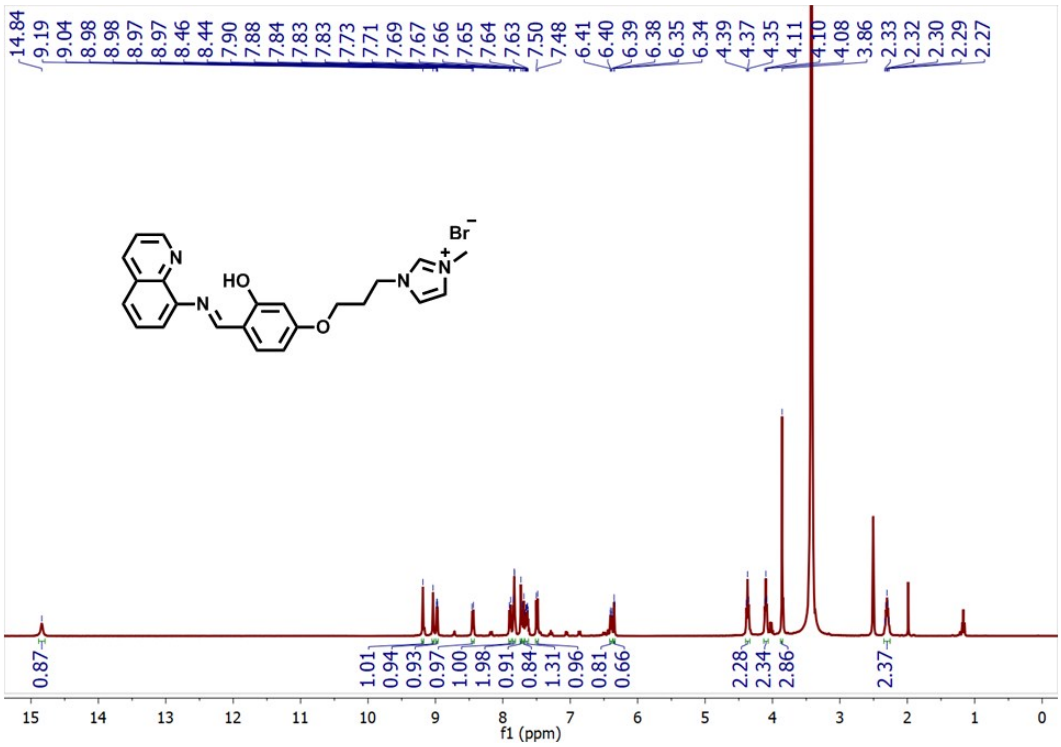


**Fig. S3** $^{1}$H NMR spectra of **ImSB**.

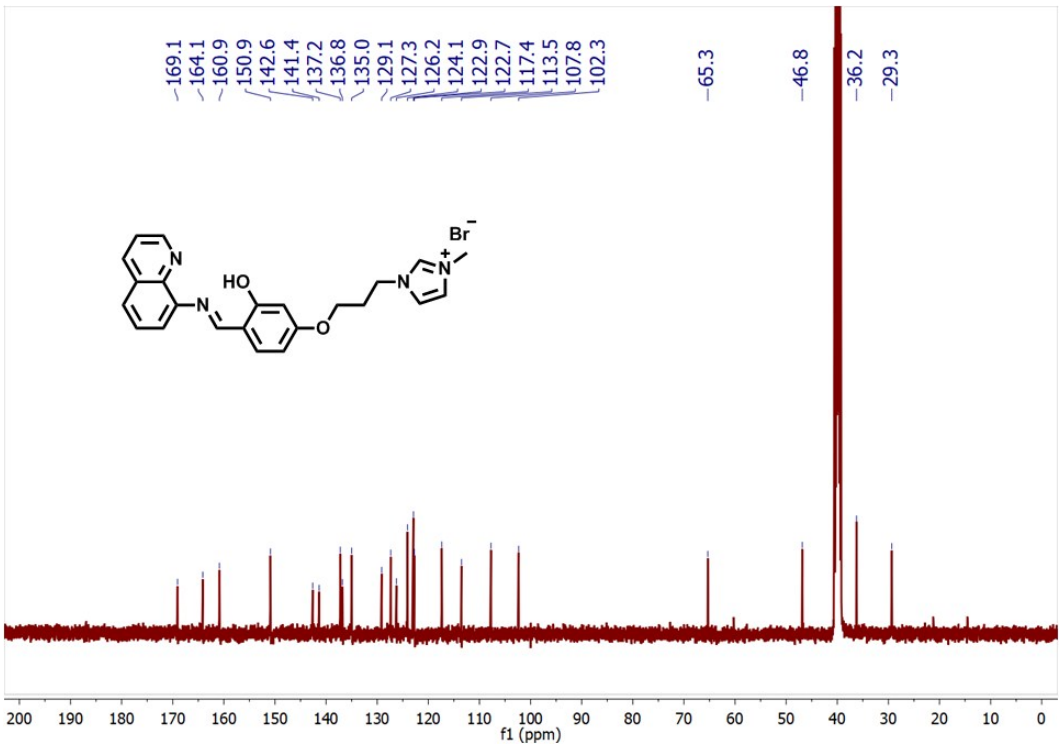


**Fig. S4** $^{13}$C NMR spectra of **ImSB**.

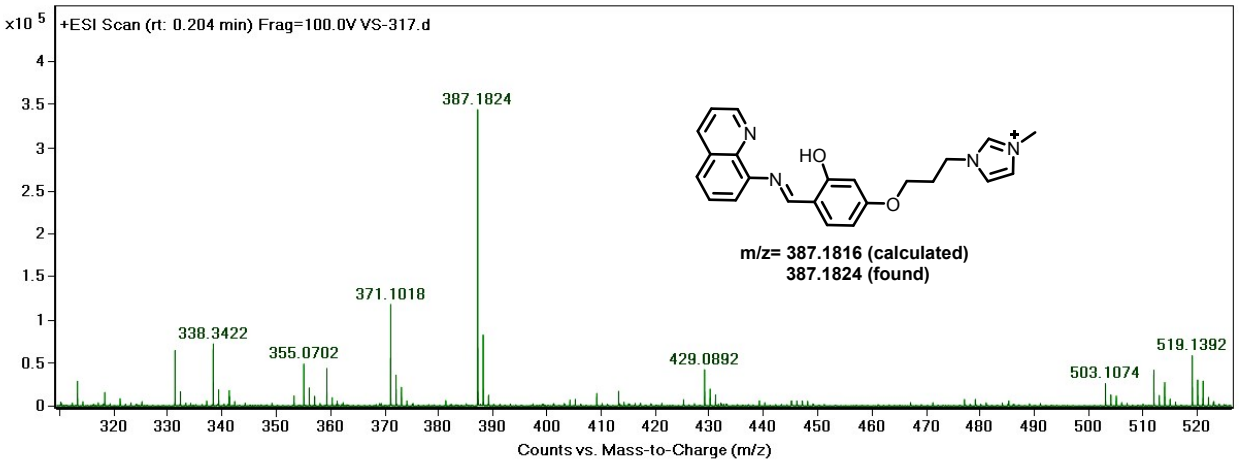


**Fig. S5** HRMS spectra of **ImSB**.

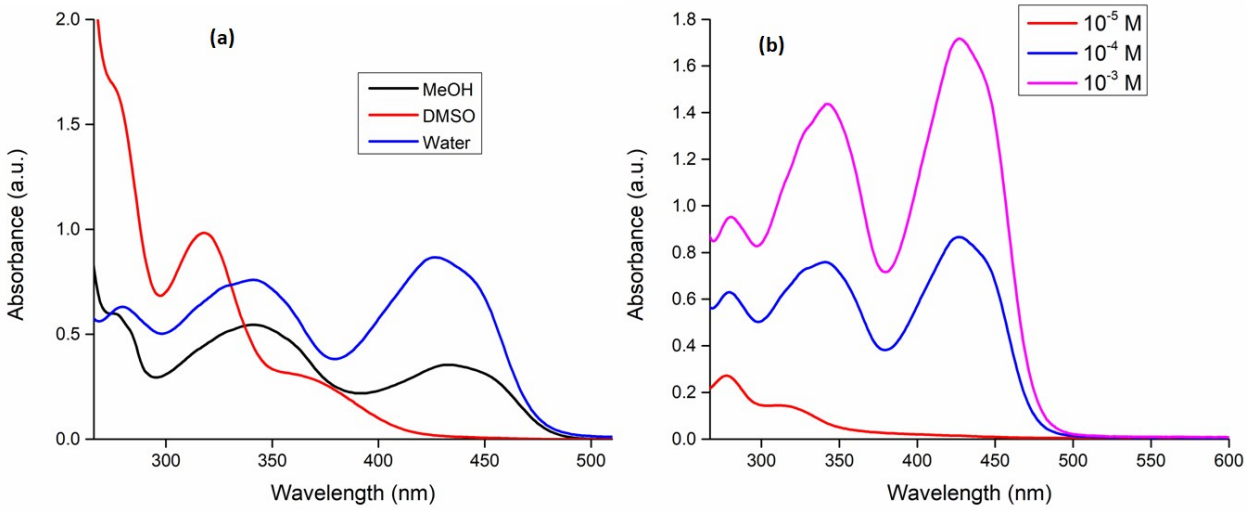


**Fig. S6** UV-visible spectra of **ImSB** (a) in different solvents at $10^{-4}$ M (b) at different concentrations.

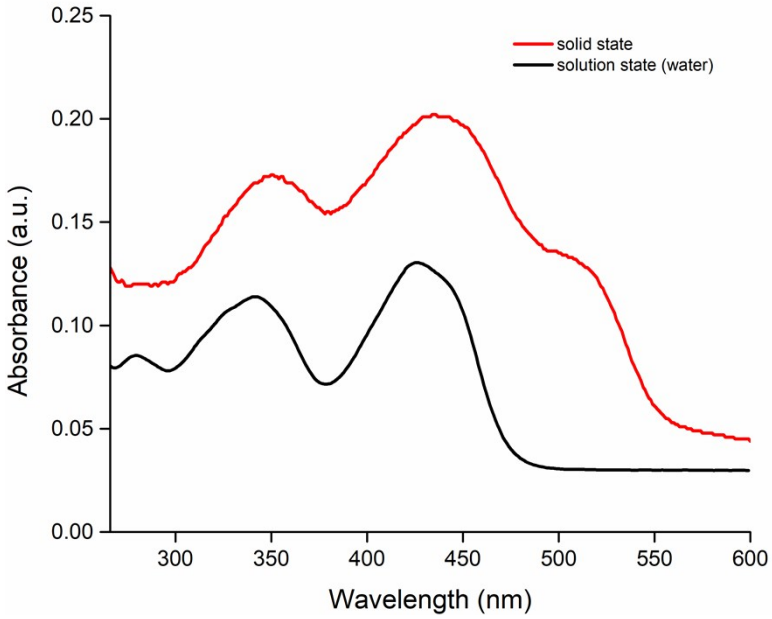


**Fig. S7** Solution ($10^{-4}$ M) and solid-state UV-visible spectra of **ImSB**.

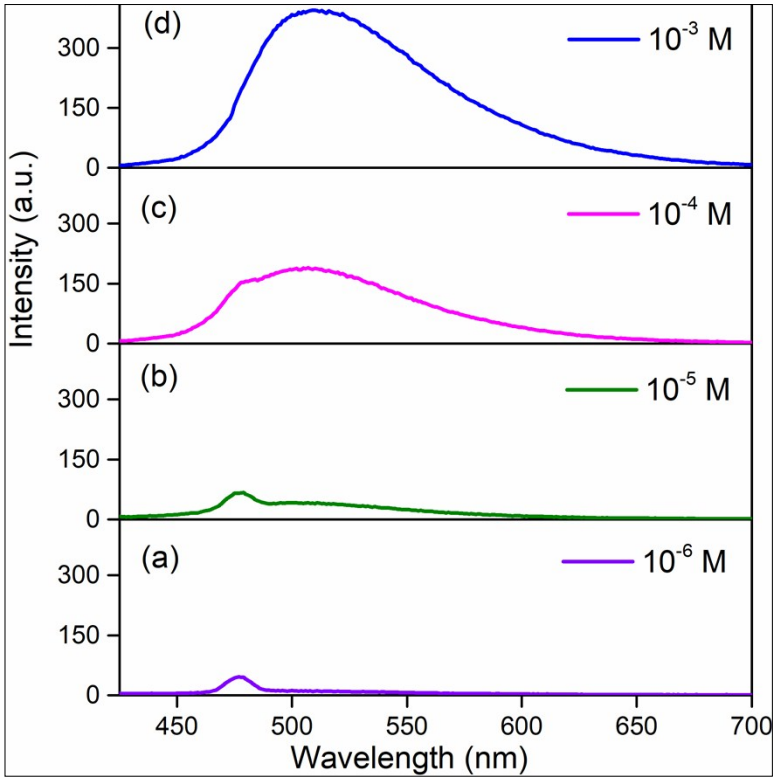


**Fig. S8** Fluorescence spectra at different concentrations of **ImSB**.

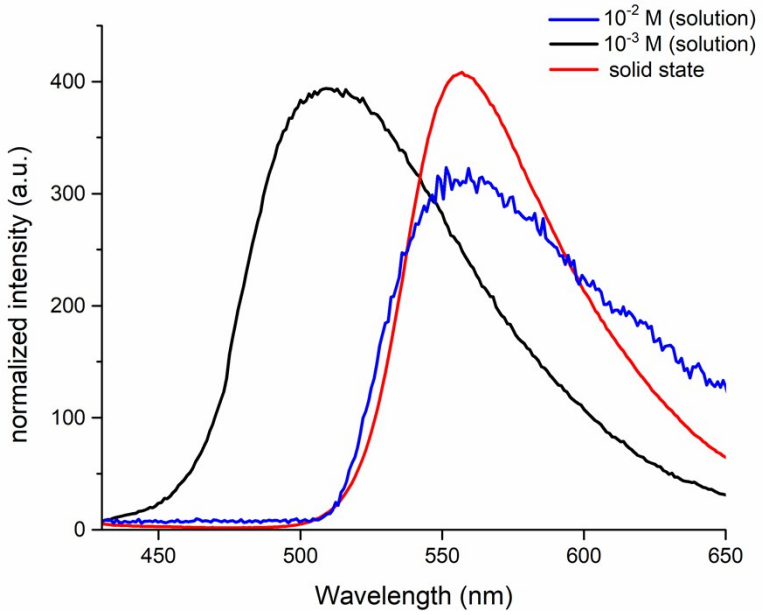


**Fig. S9** Solution and solid-state fluorescence spectra of **ImSB**.

**Table S8**. Fluorescence lifetime measurement data of **ImSB** and **ImSB**-$Al^{3+}$ in solution.

| **Entry** | Φ | $\tau_{avg}$ **(ns)** | $k_r$ (x $10^9$ $S^{-1}$) | $k_{nr}$ (x $10^9$ $S^{-1}$) | $\chi^2$ |
|---|---|---|---|---|---|
| **ImSB** | 0.01 | 0.172 | 0.058 | 5.755 | 0.816 |
| **ImSB**-$Al^{3+}$ | 0.49 | 2.996 | 0.163 | 0.171 | 1.253 |

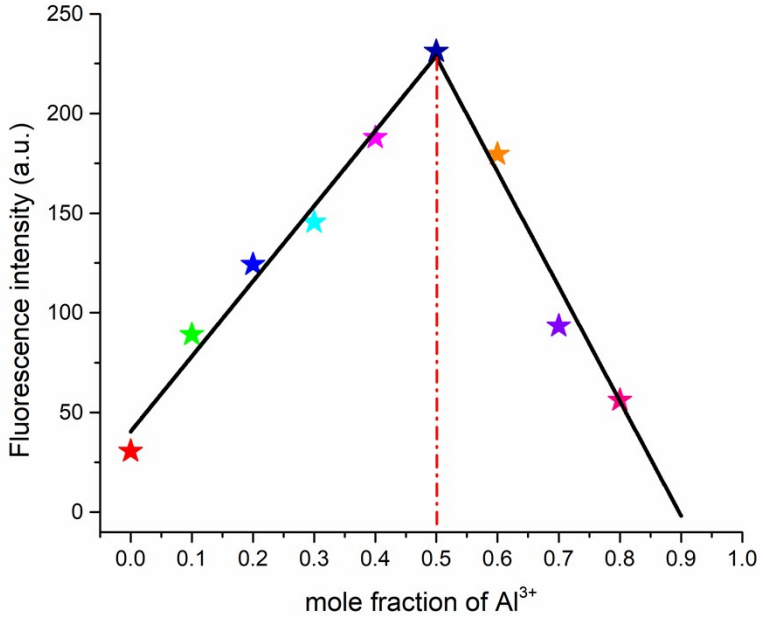


**Fig. S10** Job′s plot.

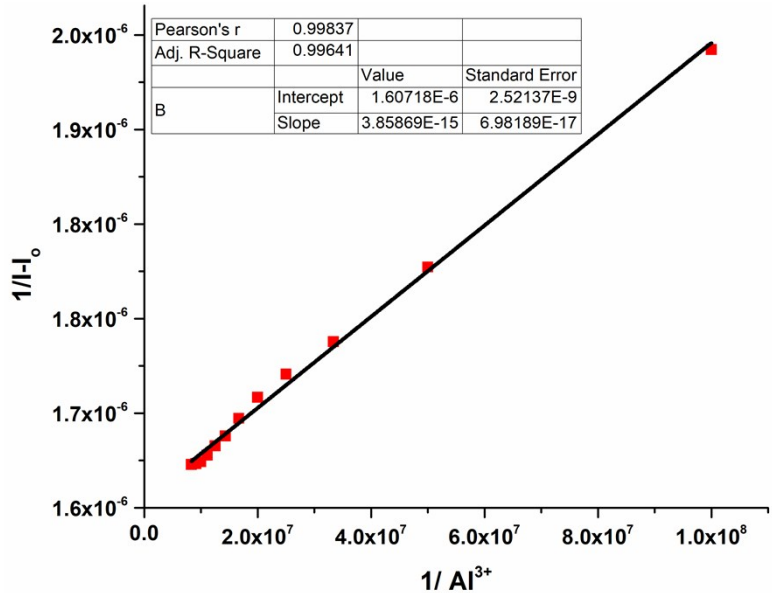


**Fig. S11** Benesi-Hildebrand plot of **ImSB** vs $Al^{3+}$ titration by fluorescence spectroscopy.

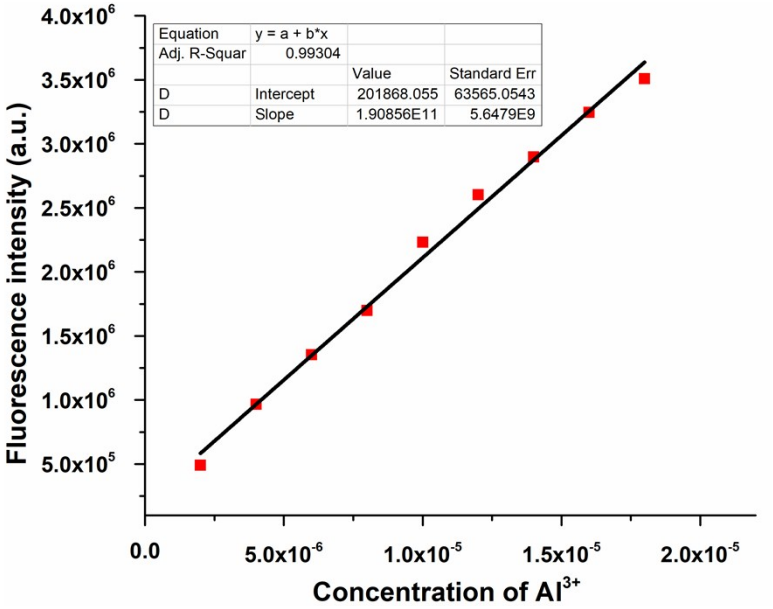


**Fig. S12** Detection limit calculation plot.

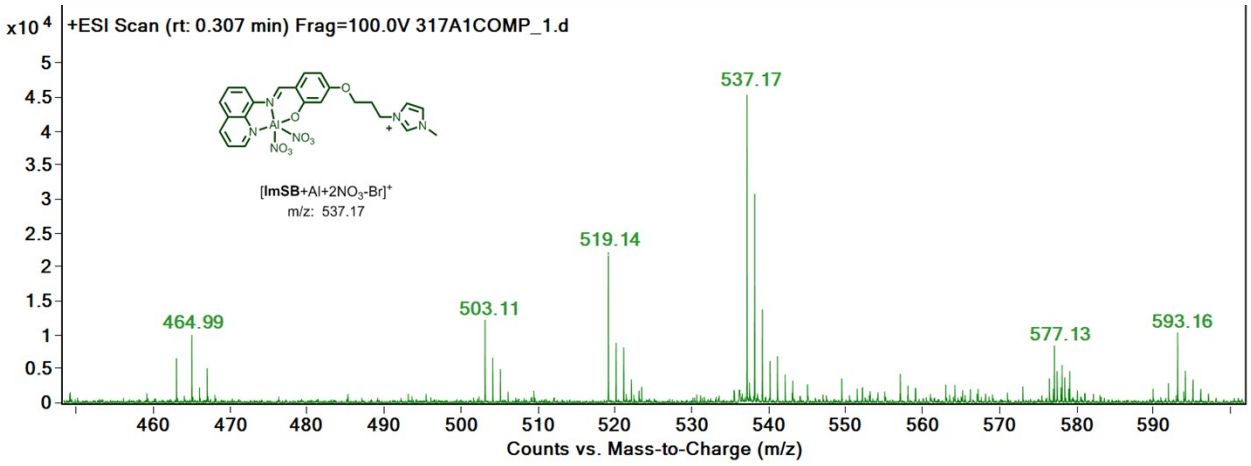


**Fig. S13** Mass spectra of **ImSB**-$Al^{3+}$.

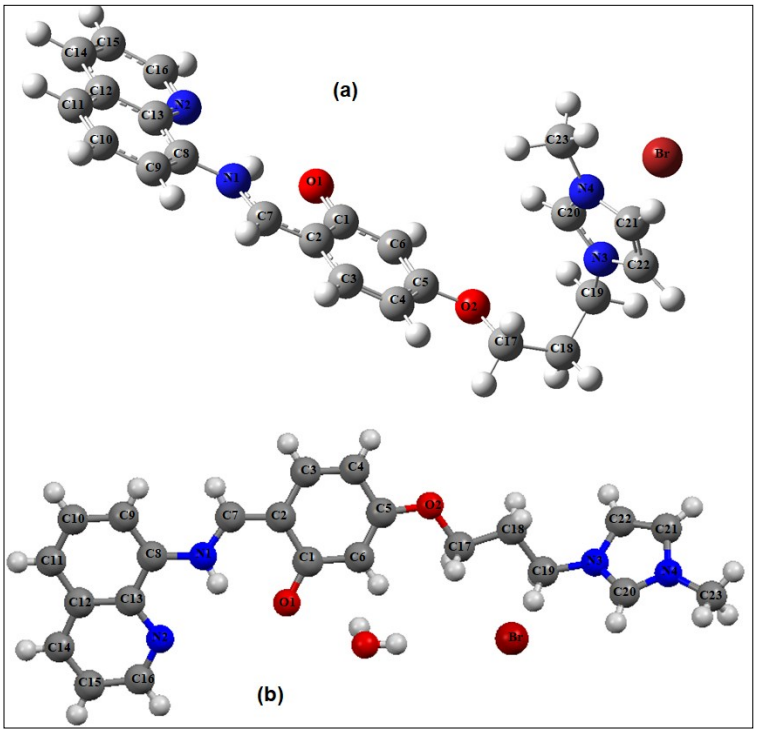


**Fig. S14** (a) DFT optimized structure of keto form and (b) crystal structure of **ImSB**.

**Table S9.** Comparison between some selected geometrical parameters of **ImSB** (keto form) by single crystal XRD and theoretical calculations.

| **Parameters** | **XRD** | **Calculated** |
|---|---|---|
| **Bond lengths** | | |
| O1-C1 | 1.2779 (16) | 1.25930 |
| O2-C5 | 1.3595 (15) | 1.37367 |
| O2-C17 | 1.4255 (16) | 1.42885 |
| N1-C8 | 1.4075 (16) | 1.40145 |
| N1-C7 | 1.3241 (17) | 1.33343 |

| | | |
|---|---|---|
| N4-C21 | 1.3811 (17) | 1.38468 |
| N4-C20 | 1.3279 (17) | 1.33784 |
| N4-C23 | 1.4708 (17) | 1.47687 |
| N3-C19 | 1.4709 (16) | 1.47010 |
| N3-C22 | 1.3862 (16) | 1.38711 |
| N3-C20 | 1.3325 (17) | 1.34238 |
| C21-C22 | 1.3566 (18) | 1.36602 |
| C7-C2 | 1.3927 (17) | 1.39543 |
| C2-C1 | 1.4541 (17) | 1.47554 |
| C2-C3 | 1.4276 (18) | 1.42672 |
| C1-C6 | 1.4311 (17) | 1.43995 |
| C19-C18 | 1.5221 (19) | 1.53586 |
| C6-C5 | 1.3767 (18) | 1.37544 |
| N2-C13 | 1.3663 (16) | 1.35855 |
| N2-C16 | 1.3186 (18) | 1.31908 |
| C8-C13 | 1.4300 (18) | 1.43632 |
| C8-C9 | 1.3788 (17) | 1.38597 |
| C4-C5 | 1.4249 (18) | 1.43397 |
| C18-C17 | 1.5182 (18) | 1.52495 |
| **Bond angles** | | |
| C5-O2-C17 | 117.11 (10) | 120.24763 |
| C7-N1-C8 | 125.28 (11) | 127.20193 |
| C21-N4-C23 | 126.12 (11) | 125.02697 |
| C20-N4-C21 | 108.53 (11) | 109.21709 |
| C20-N4-C23 | 125.31 (12) | 125.75498 |
| C22-N3-C19 | 126.25 (11) | 126.35761 |
| C20-N3-C19 | 124.85 (11) | 125.47373 |
| C20-N3-C22 | 108.90 (11) | 108.05887 |
| C16-N2-C13 | 117.00 (12) | 118.35100 |
| N1-C8-C13 | 115.90 (11) | 116.25799 |
| N1-C7-C2 | 124.33 (12) | 124.07009 |
| C7-C2-C1 | 121.67 (12) | 120.85822 |
| C7-C2-C3 | 118.33 (11) | 119.38750 |
| C3-C2-C1 | 120.00 (11) | 119.75395 |
| O1-C1-C6 | 121.71 (11) | 122.51688 |
| N3-C19-C18 | 111.63 (11) | 112.87054 |
| **O2-C5-C6** | **124.64 (12)** | **115.97064** |
| **O2-C5-C4** | **113.30 (11)** | **122.04984** |
| **C17-C18-C19** | **107.99 (11)** | **113.55552** |
| O2-C17-C18 | 107.27 (11) | 107.26271 |

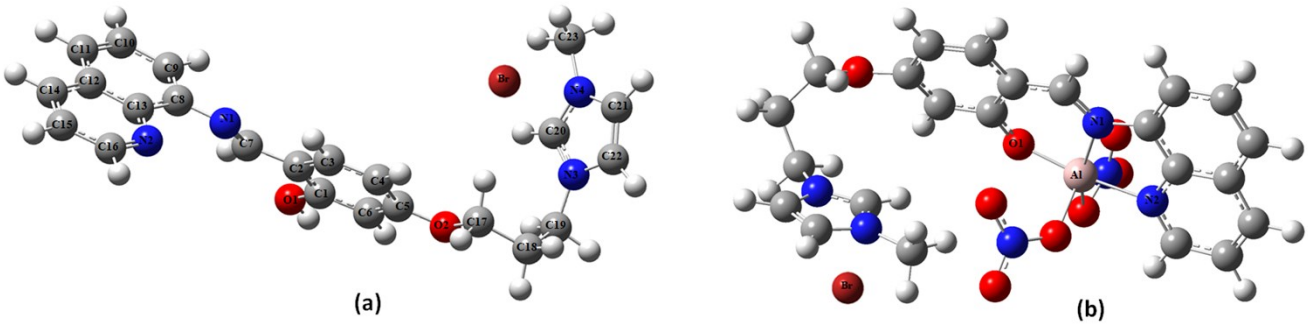


**Fig. S15** DFT optimized structures of (a) **ImSB** (enol form) and (b) its aluminium complex.

**Table S10. Selected bond lengths (Å) and bond angles (°) of DFT optimized structure of ImSB and its aluminium complex.**

| Parameters | ImSB (enol) (Calculated values) | Aluminium complex (Calculated values) |
|---|---|---|
| **Bond lengths** | | |
| C1-O1 | 1.354 | 1.303/1.364 |
| C7-N1 | 1.278 | 1.316 |
| N1-C8 | 1.396 | 1.411 |
| N2-C13 | 1.361 | 1.367 |
| N2-C16 | 1.319 | 1.328 |
| Al-O1 | - | 1.824 |
| Al-N1 | - | 2.008 |
| Al-N2 | - | 2.054 |
| **Bond angles** | | |
| O1-C1-C2 | 117.66 | 122.67 |
| C2-C7-N1 | 122.93 | 125.69 |
| C7-N1-C8 | 119.17 | 122.03 |
| N1-C8-C13 | 119.06 | 114.05 |
| N2-Al-N1 | - | 80.60 |
| N1-Al-O1 | - | 92.12 |

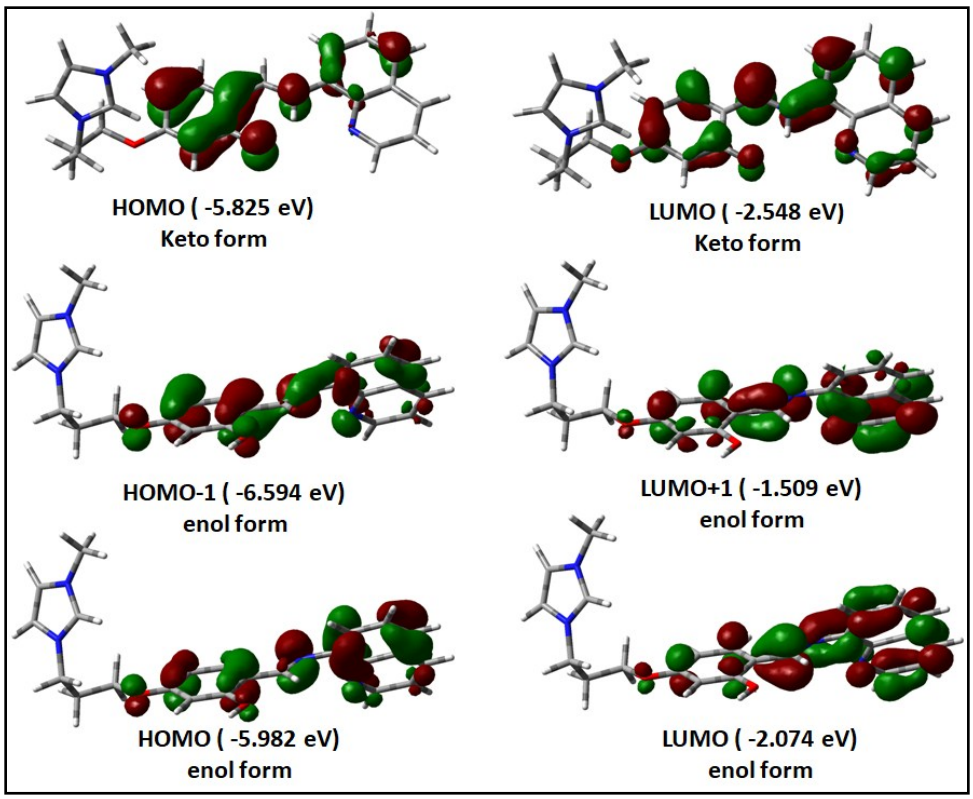


**Fig. S16** Energy of selected frontier molecular orbitals of **ImSB**$^{+}$.

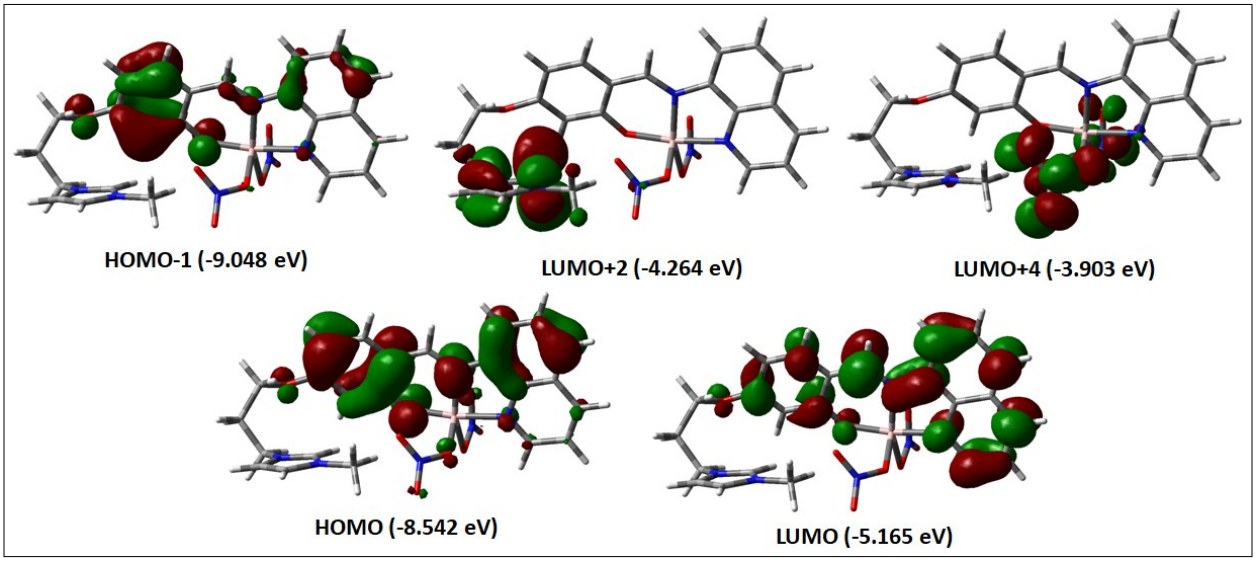


**Fig. S17** Energy of selected frontier molecular orbitals of aluminium complex.

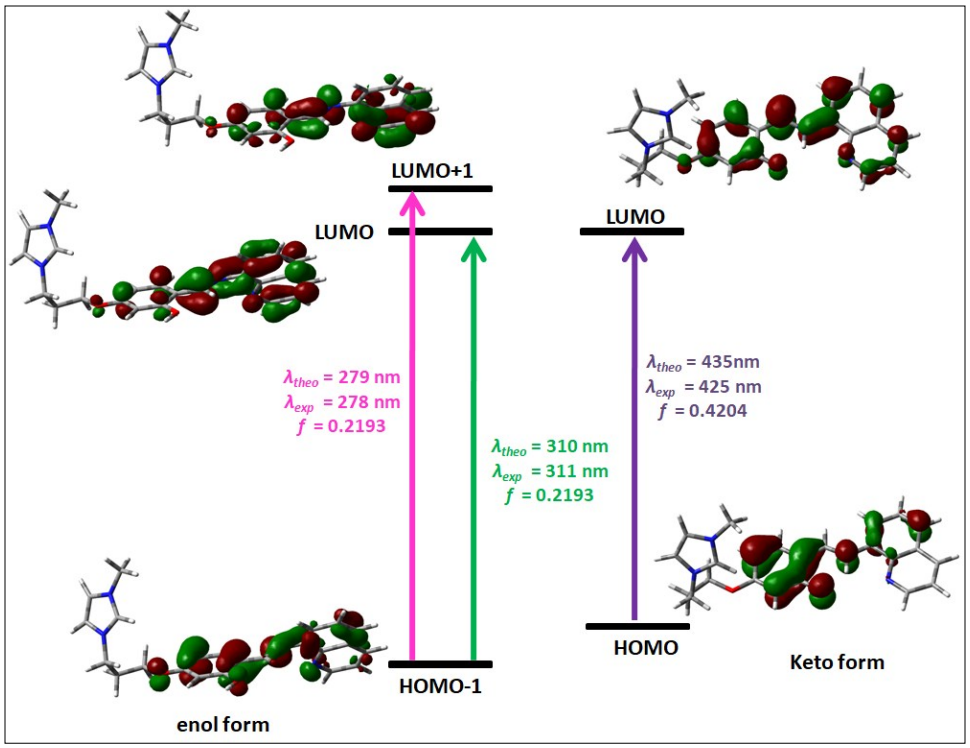


**Fig. S18** Pictorial representation of key transitions involved in the UV-visible spectra of **ImSB**$^{+}$.

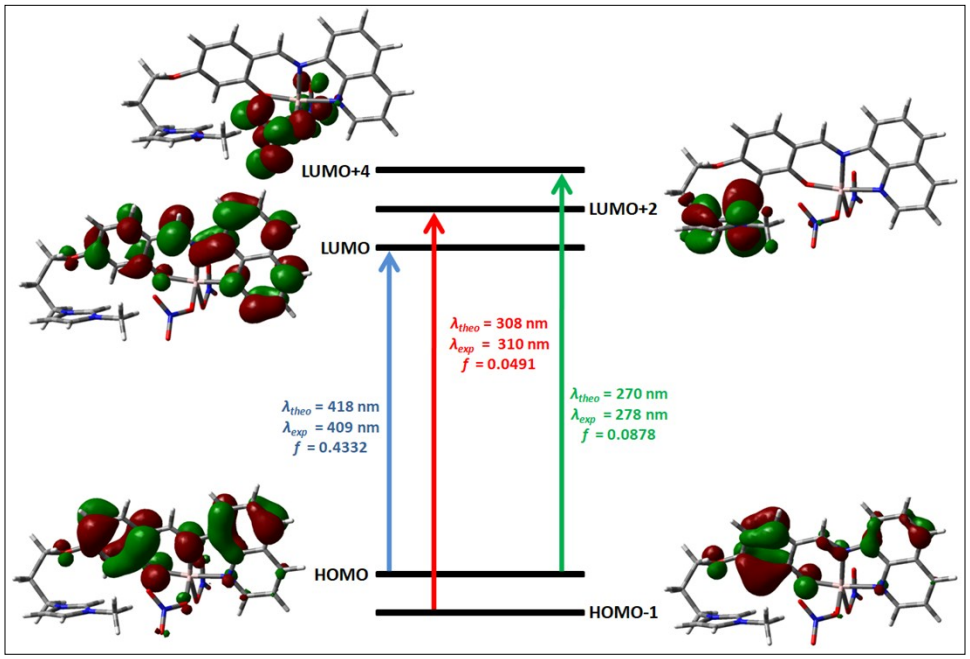


**Fig. S19** Pictorial representation of key transitions involved in the UV-visible spectra of aluminium complex.