Supporting Information

A supramolecular H-bond driven light switch sensor for small anions

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1. General Information

Materials and Methods

4,4',5,5'-Tetramethyl-2,2'-bibenzimidazole and Tetrakis(2-phenylpyridine-C^2,N)bis(μ-chloro)diiridium were synthesized according to published procedures.[1–3] IrBBI was synthesized as published recently.[4] Technical grade solvents were purchased from VWR/Prolabo and redistilled under reduced pressure at 40°C. Dry solvents were obtained from a MBraun MB SPS-800 system. All chemicals were purchased from Merck Millipore, Sigma Aldrich, ABCR, Acros Organics, Alfa Aesar or VWR/Prolabo and used as purchased (≥95%). ^{1}H-NMR spectra were recorded at ambient temperature, unless otherwise stated, with a Bruker 400 MHz spectrometer. All spectra were referenced to the corresponding solvent residual signal, i.e. 1.940 ppm for acetonitrile, 7.260 for chloroform, 5.320 for dichloromethane and 4.870 for methanol. Mass spectra were recorded on a Finnigan MAT SSQ 710 or on a Thermoquest-Finnigan MAT 95XL. Elemental analysis was performed on an Elementar vario MICRO cube.

General spectroscopic Methods

Solvent chloroform used for spectral experiments was redistilled under reduced pressure at 40°C and kept over molecular sieves. Tetrabutylammonium (TBA) salts of F^-, Cl^-, Br^-, I^-, and $HSO4^-$ were purchased from Alfa Aesar and Merck Chemicals and dissolved in chloroform. Binding constants were performed in duplicate, and the average is reported. All data were manipulated with the OriginLab software package.

Emission spectroscopy

Emission spectra were performed on a JASCO Spectrofluorometer FP-8500 at room temperature. Cuvettes with a 1 cm path length and a 3mL volume were used for all measurements. For the DNBA quenching experiment aliquots of the TBA-DNBA salt (c = 2 x 10^{-5} M) were added stepwise to a 2 mL solution of IrBBI-H_2 (c = 9.04 x 10^{-7} M) in chloroform by a syringe. Thereby the TBA salt was dissolved in a solution of IrBBI-H_2 (c = 9.04 x 10^{-7} M), so no effect of dilution has to be regarded. For the anion sensor titration we prepared a mixture of IrBBI-H_2 (c = 9.04 x 10^{-7} M), quenched with 6.86 equivalents of the 3,5-dinitrobenzoate salt. For a typical anion sensor titration experiment 10 μL aliquots of a TBA salt (c = 3 x 10^{-4} M) were added stepwise to a 2 mL solution of IrBBI-H_2···DNBA (c = 9.04 x 10^{-7} M) in chloroform by a syringe. Thereby the TBA salt was dissolved in a solution of IrBBI-H_2···DNBA (c = 9.04 x 10^{-7} M), so no effect of dilution has to be regarded. The excitation wavelengths were fixed at 378 nm with the slit width of 5 nm and repeated at least twice times.

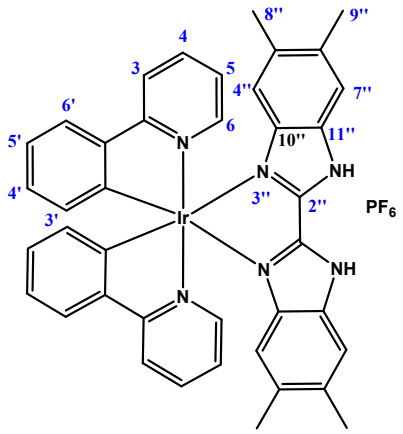
^{1}H NMR Titration

^{1}H NMR spectra were recorded at ambient temperature, unless otherwise stated, with a Bruker 400 MHz spectrometer with $CDCl_3$ as a solvent and TMS as an internal standard. For the titration experiment, aliquots of the TBA salt of 3,5-dinitrobenzoate (0 – 400 μL, 0.0225 M in dichloromethane-d^2) were added to a solution of IrBBI-H_2(200 μL, 4.5 mM in dichloromethane-d^2). The complex concentration was kept constant (1.5 mM).

2. Additional information

Hexafluorophosphate to 3,5-dinitro benzoate anion exchange was effected by adding the respective tetrabutylammonium benzoate salts to a solution of IrBBI-H_2 in dichloromethane. The resulting ion mixture were stirred at room temperature for 5 hours, then evaporated to dryness. The resulting solid was treated with acetonitrile and filtered. Slow addition of diethyl ether to the filtrate induced precipitation of the pure benzoate salts of the iridium complex.

Single crystals of IrBBI-H_2 + (3,5-dinitrobenzoate)- were grown at room temperature by layering diethyl ether above a dichloromethane solution of the iridium complex.



Scheme S2 Numbering scheme for the assignment of the ^{1}H NMR signals of Ir(tmBBI)-H_2.

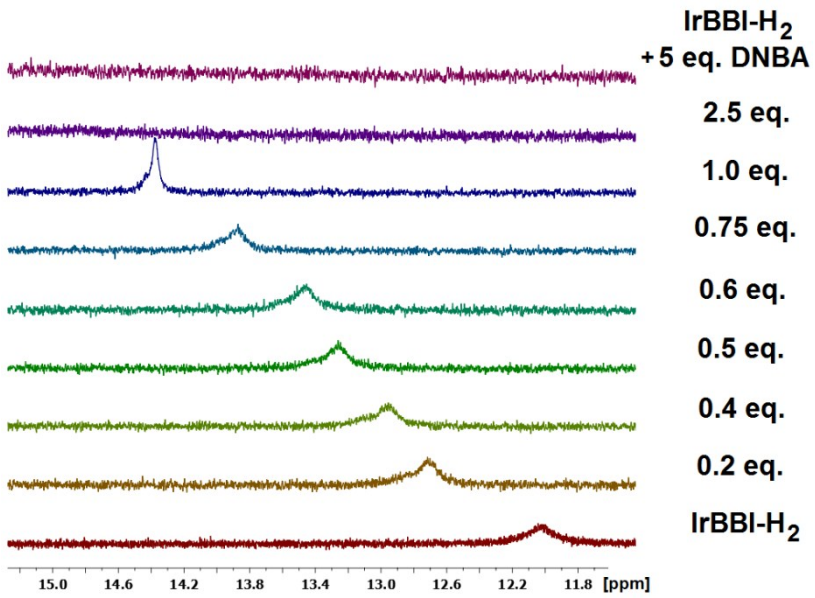


Fig. S1 ^{1}H NMR titration of IrBBI-H_2 (bottom) in $CDCl_3$ with increasing equivalents of 3,5-dinitro benzoate anion. The N-H signal of IrBBI-H_2 is shifting into the lowfield with increasing amount of DNBA. After 1.0 eq. the signal vanishes.

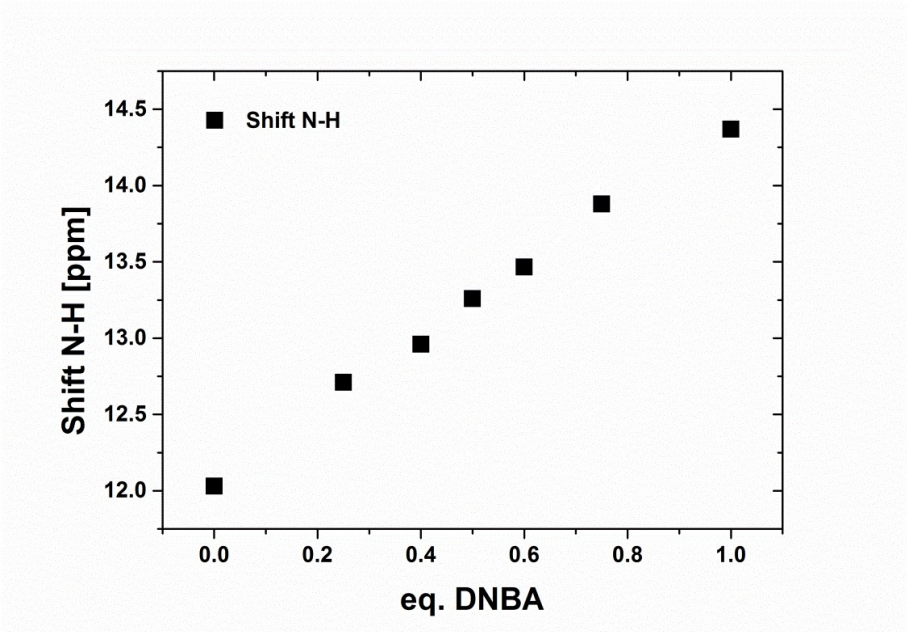


Fig. S2 Plot of the shift of the NH signal in the ^{1}H NMR titration of IrBBI-H_2 in $CDCl_3$ with increasing equivalents of 3,5-dinitro benzoate anion.

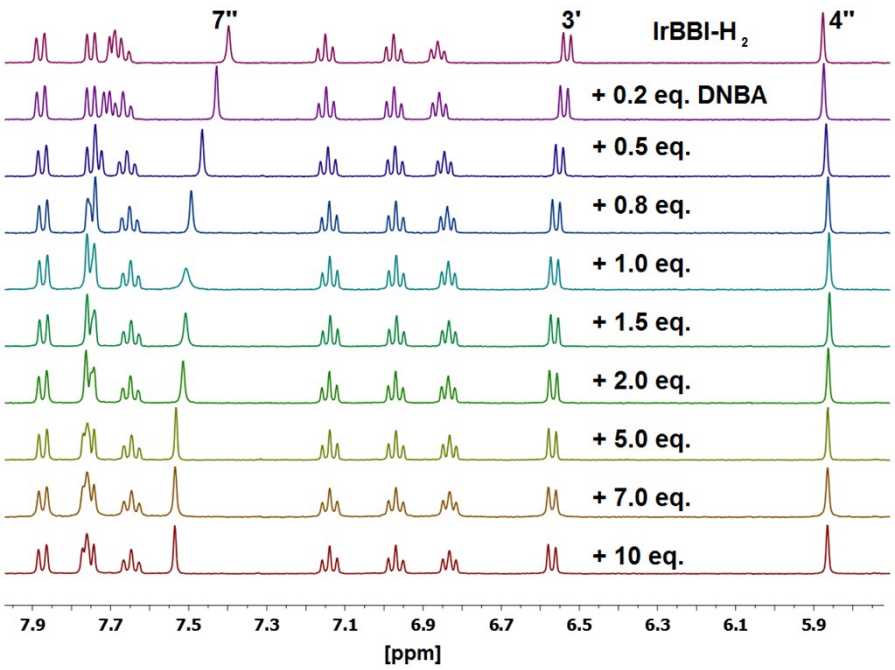


Fig. S3 ^{1}H NMR titration of IrBBI-H_2 (bottom) in deuterated DCM with increasing equivalents of 3,5-dinitro benzoate anion. The proton signals H-7'', H-3' and H-4'' are marked (host concentration = 1.5mM).

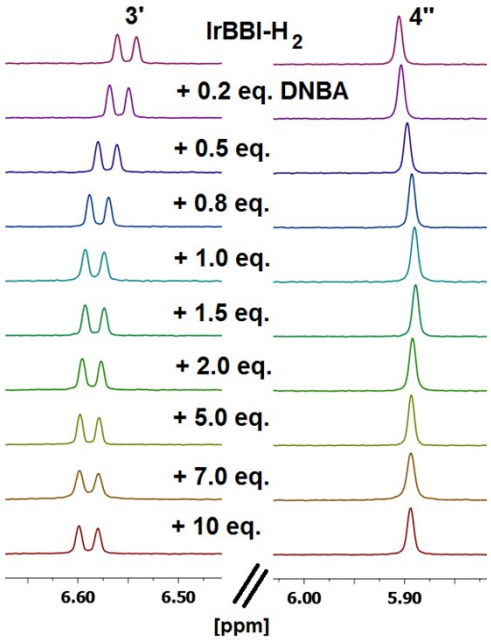


Fig. S4 ^{1}H NMR titration of IrBBI-H_2 in deuterated DCM with increasing equivalents of 3,5-dinitro benzoate anion. Depicted are the proton signals H-3' and H-4'' (host concentration = 1.5mM).

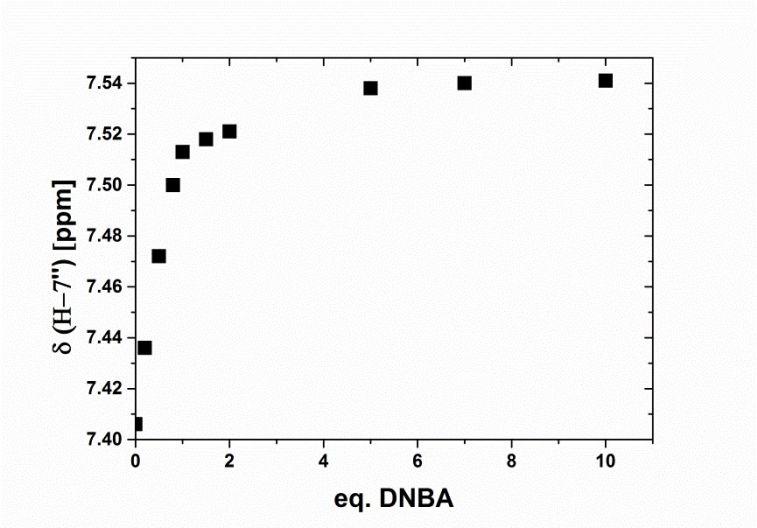


Fig. S5 ^{1}H NMR titration of IrBBI-H_2 in deuterated DCM with increasing equivalents of 3,5-dinitro benzoate anion. Depicted is the shift of the proton signal H-7'' (host concentration = 1.5mM).

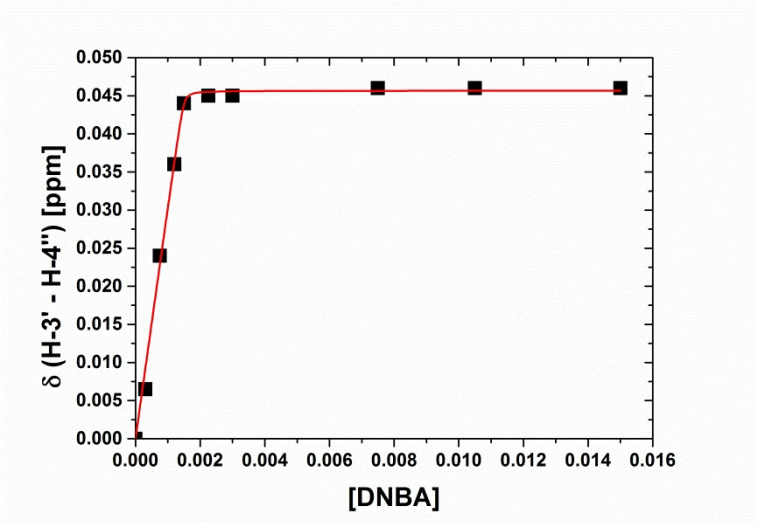


Fig. S6 ^{1}H NMR titration of IrBBI-H_2 in deuterated DCM with increasing equivalents of 3,5-dinitro benzoate anion. Depicted is the difference of the shifts of the proton signals H-3' and H-4''[δ(H-3' – H-4'')]; (host concentration = 1.5mM).

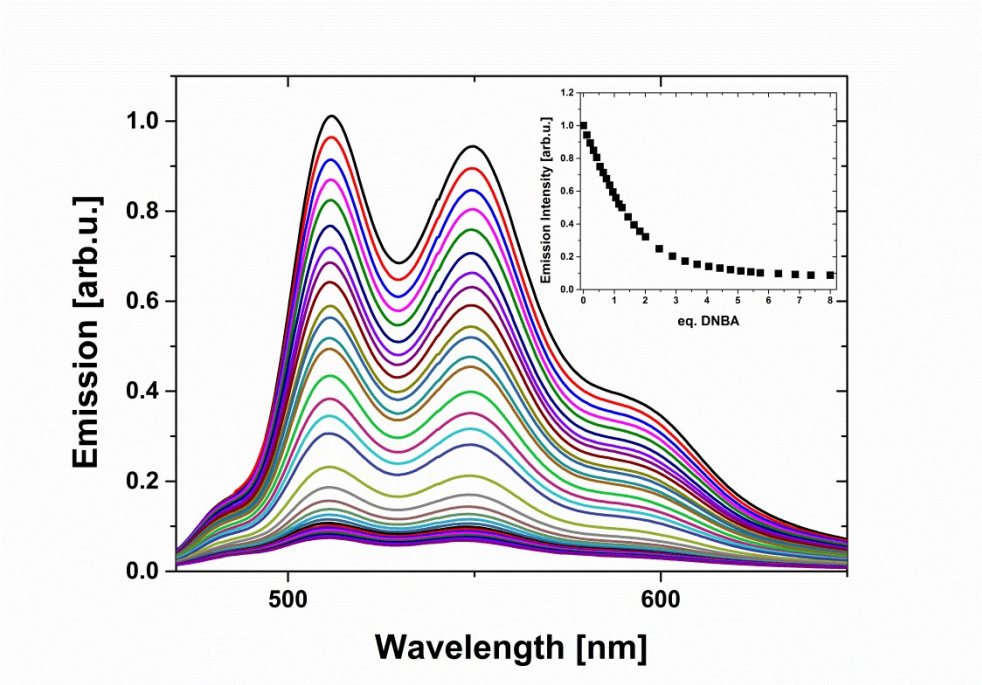


Fig. S7 Main: luminescence of IrBBI-H_2 as a function of increasing amounts of DNBA (depicted is only one measurement of three, average can be found in Fig.S8); inset: plot of the normalized iridium luminescence intensity as a function of number of equivalents of DNBA added.

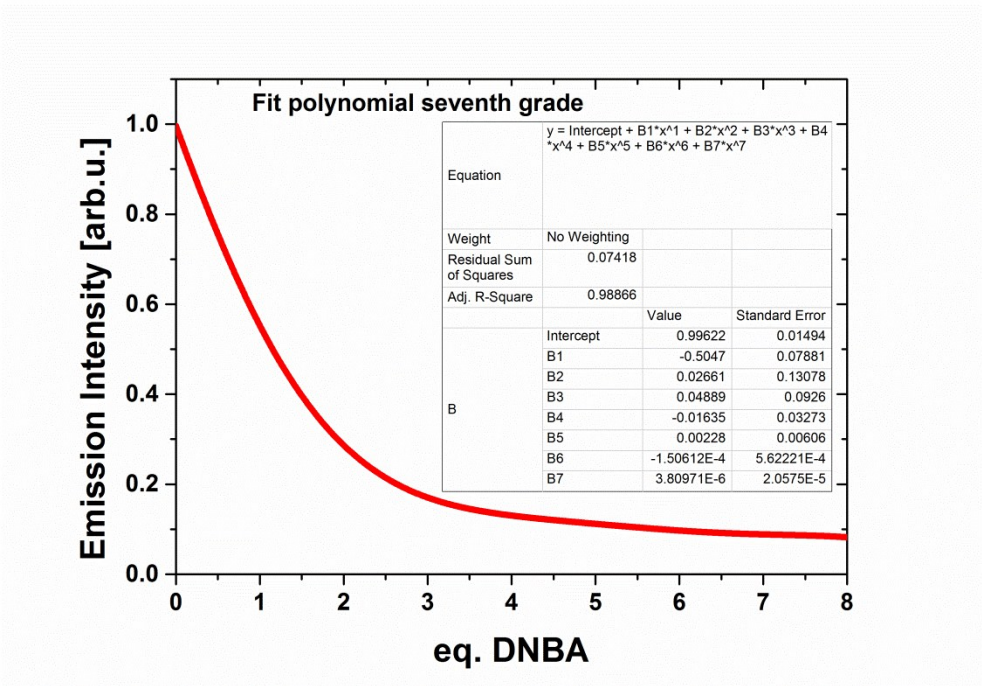


Fig. S8 Plot (polynomial 7th grade) of the average of three measurements of the normalized luminescence intensity of IrBBI-H_2 as a function of number of equivalents of DNBA added.

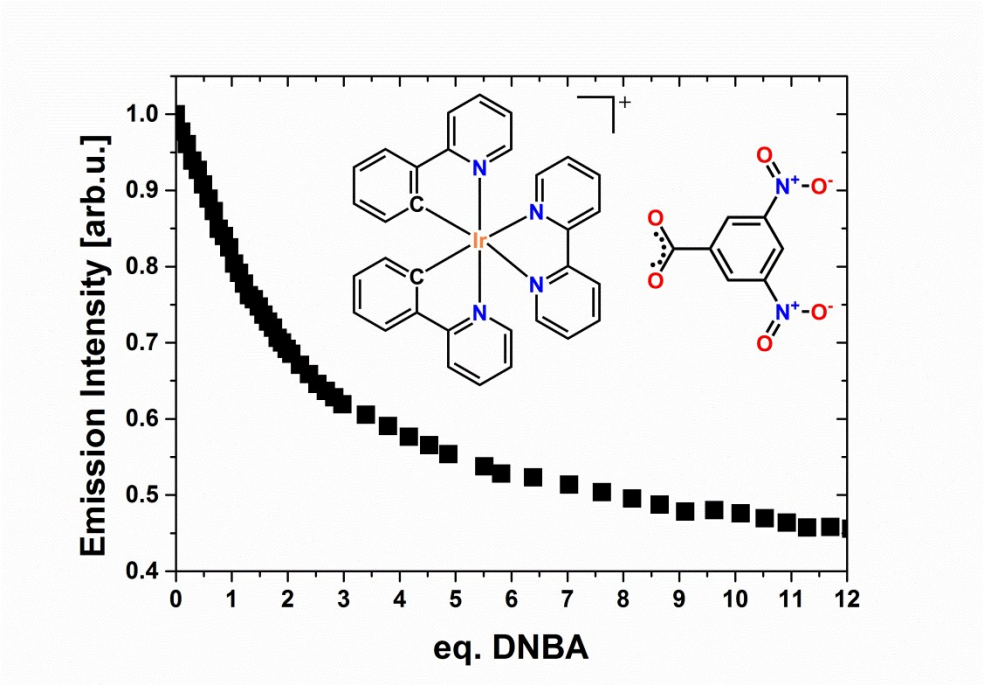


Fig. S9 Main: plot of the normalized luminescence intensity of $[Ir(ppy)_2(bipy)][PF_6]$ (**R2**) as a function of number of equivalents of DNBA added; Inset: scheme of the reagents involved.

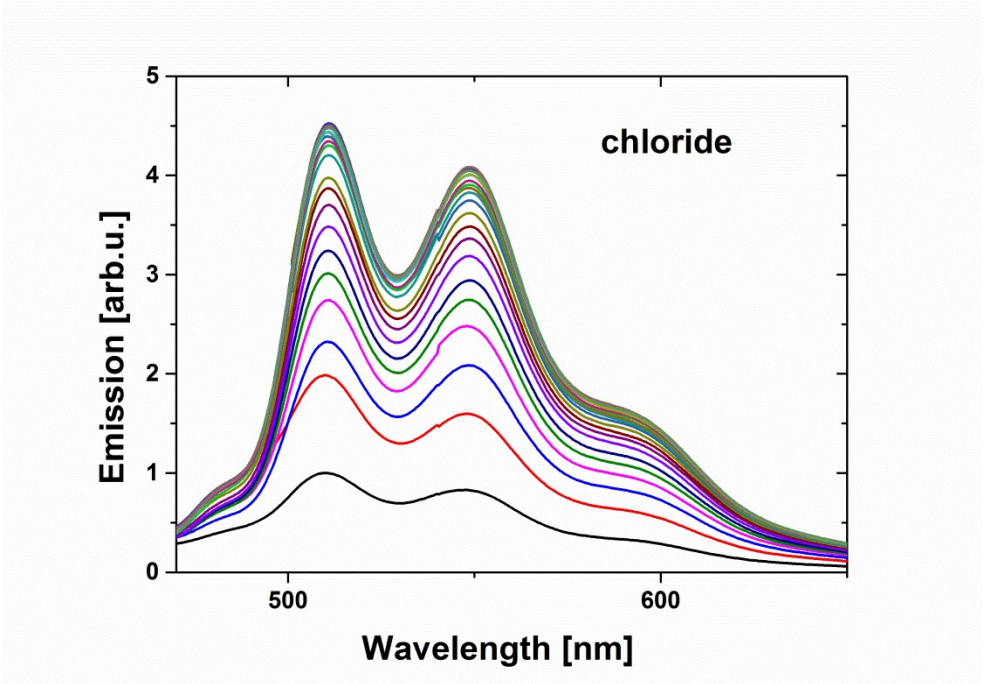


Fig. S10 Luminescence of IrBBI-H_2···DNBA as a function of increasing amounts of chloride (depicted is only one of at least two distinct measurements).

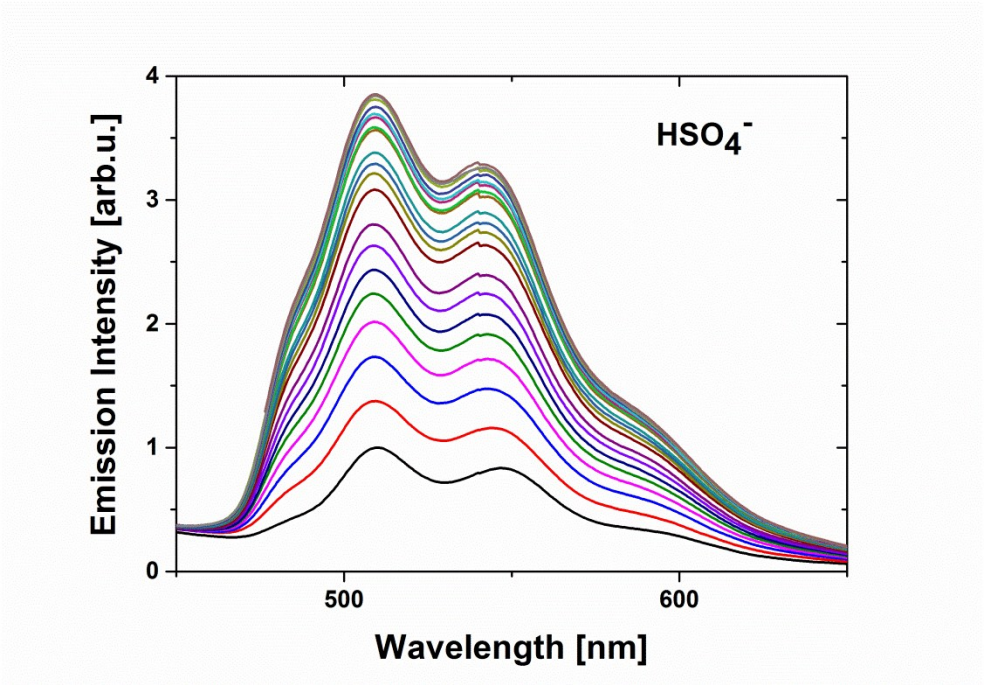


Fig. S11 Luminescence of IrBBI-H_2···DNBA as a function of increasing amounts of hydrogen sulfate (depicted is only one of at least two distinct measurements).

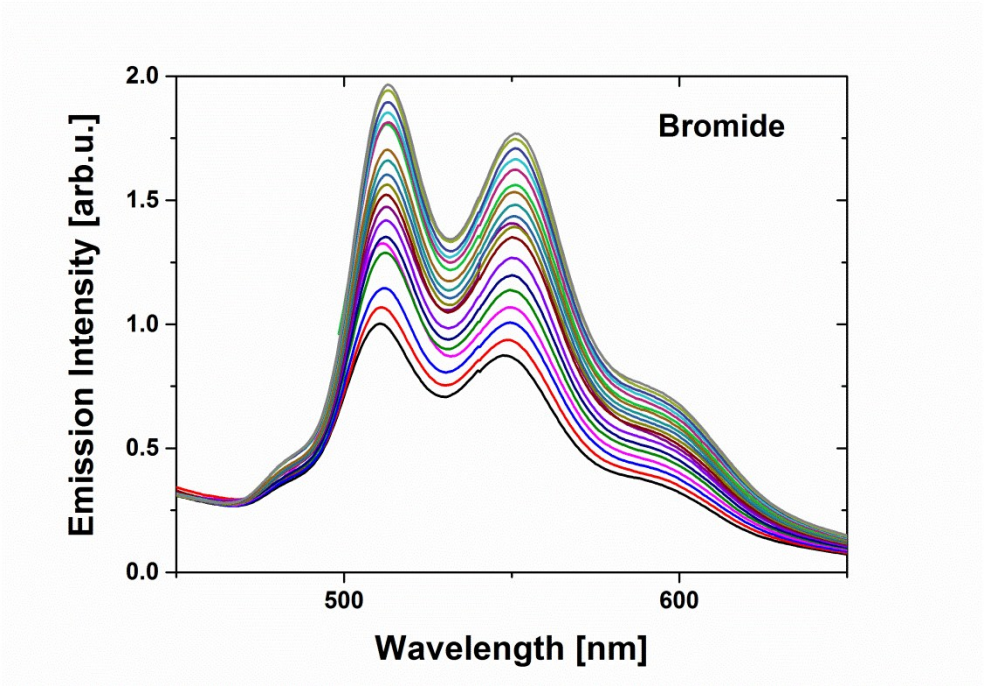


Fig. S12 Luminescence of IrBBI-H_2···DNBA as a function of increasing amounts of bromide (depicted is only one of at least two distinct measurements).

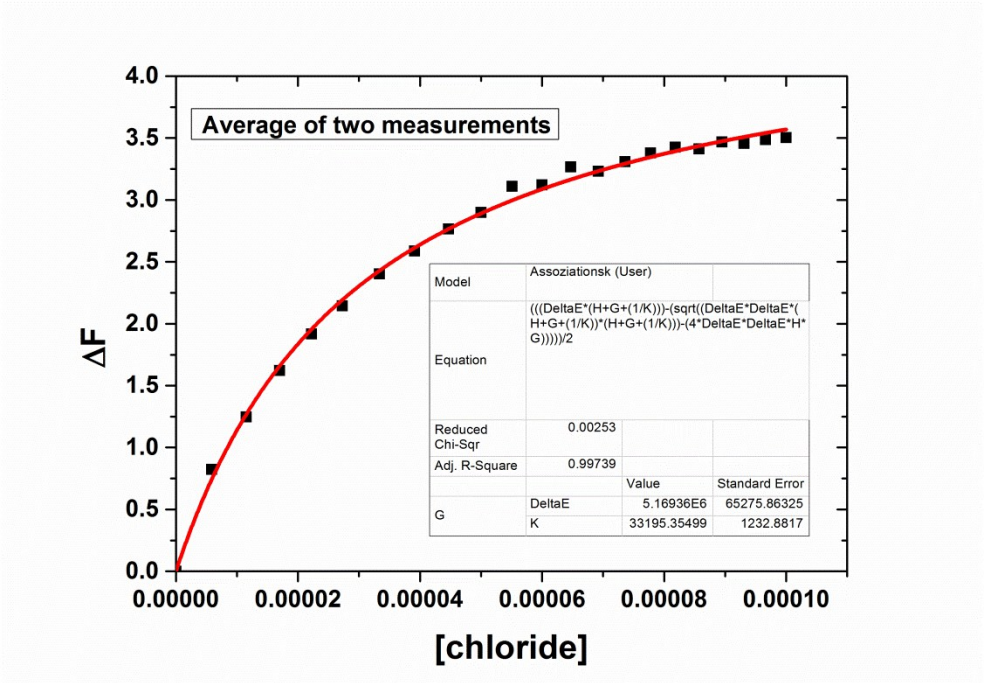


Fig. S13 Plot of the normalized luminescence intensity of IrBBI-H_2···DNBA as a function of increasing amounts of chloride (depicted is the average of two distinct measurements) and fit according to fit function FF1 (*vide infra*).[5]

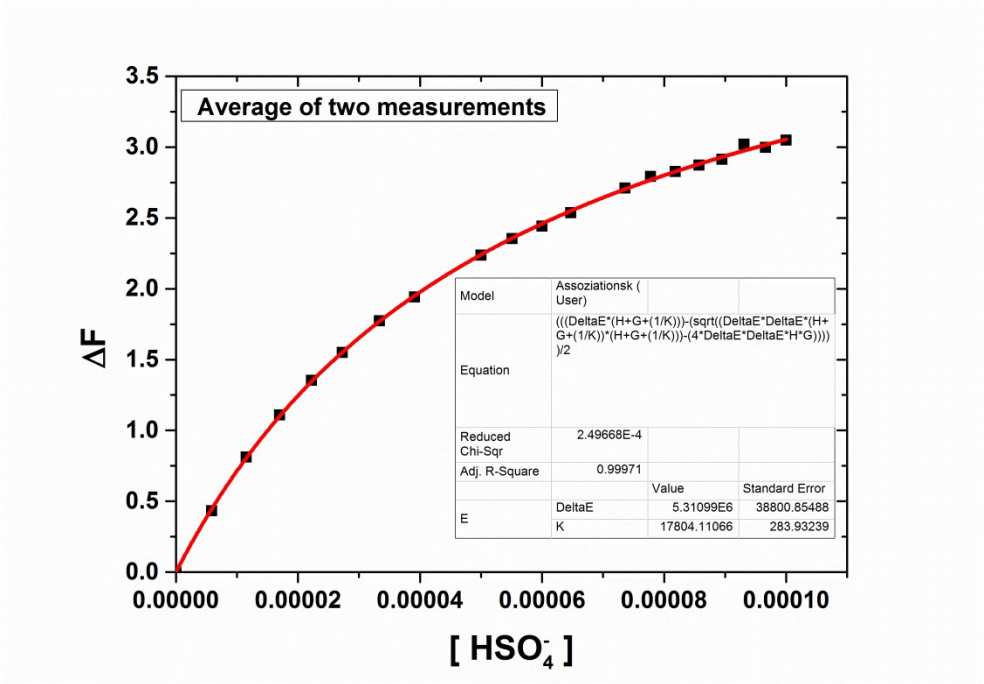


Fig. S14 Plot of the normalized luminescence intensity of IrBBI-H_2···DNBA as a function of increasing amounts of hydrogen sulfate (depicted is the average of two distinct measurements) and fit according to fit function FF1 (*vide infra*).[5]

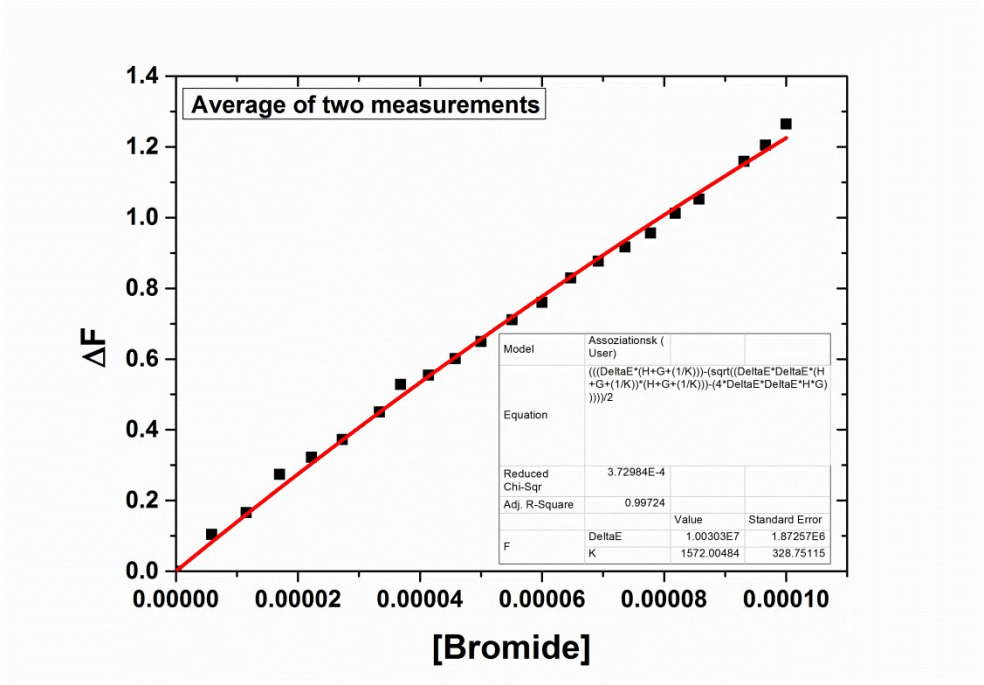


Fig. S15 Plot of the normalized luminescence intensity of IrBBI-H_2···DNBA as a function of increasing amounts of bromide (depicted is the average of two distinct measurements) and fit according to fit function FF1 (*vide infra*).[5]

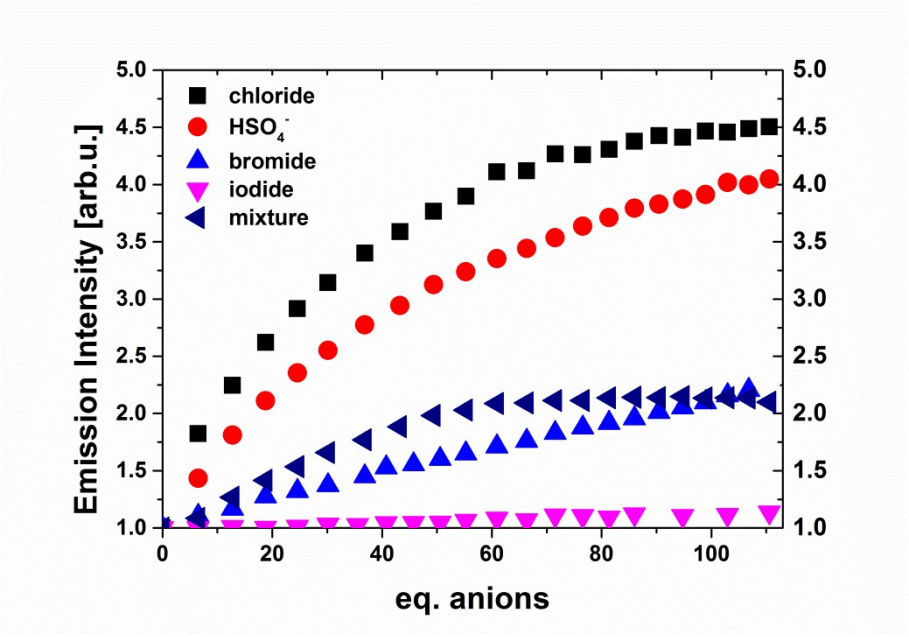
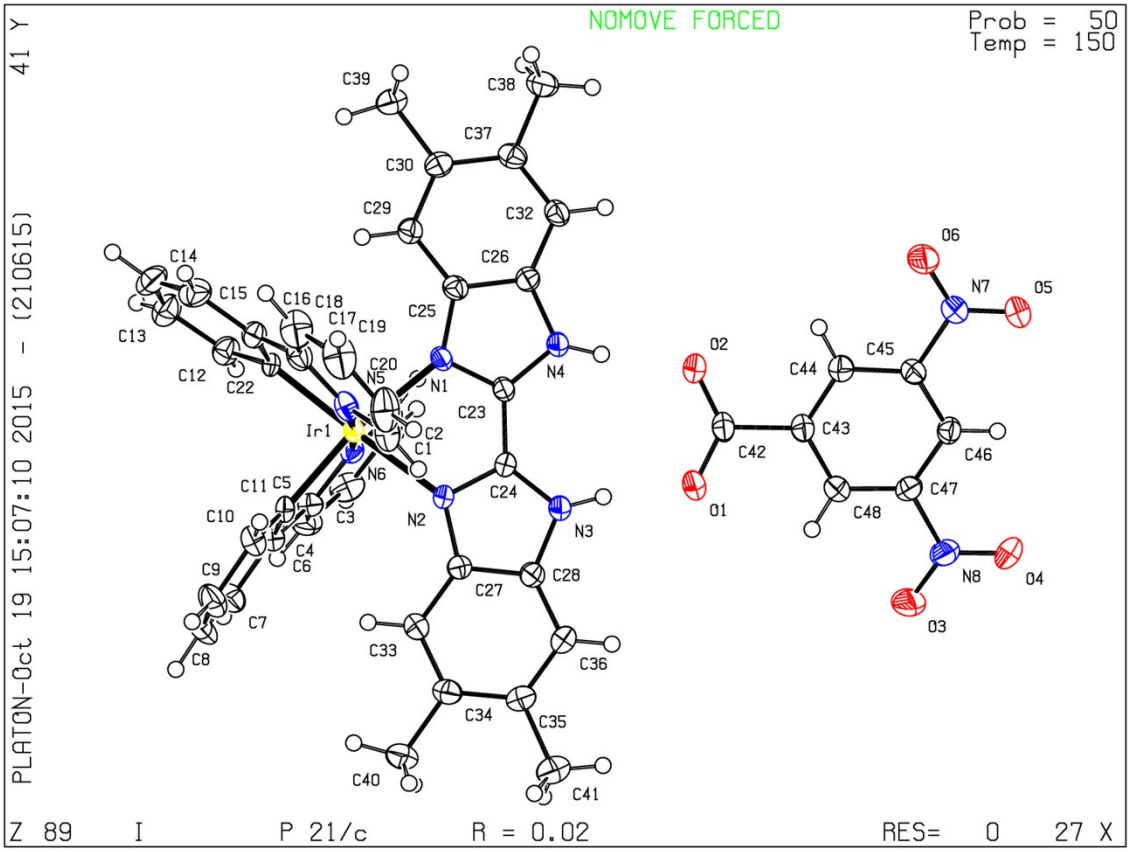


Fig. S 16 Plot of the normalized luminescence intensity of IrBBI-H_2···DNBA (S) as a function of number of equivalents anions added; the "mixture" consists of equal amounts of Cl^-, Br^-, I^-, HSO_4^- anions; the total ion concentration is 3 x 10^{-4} M.

Fit function FF1. Aforementioned binding constants were calculated to the fit function below with respect to literature[5]

$$\Delta F = \frac{\Delta\varepsilon([H] + [G] + K^{-1}) \pm \sqrt{\Delta\varepsilon^2([H] + [G] + K^{-1})^2 - 4\Delta\varepsilon^2[H][G]}}{2}$$

3. Crystallographic data



Crystal data for **[(ppy)$_2$Ir(tmBBI)](DNBA)**: C_{47} H_{37} Ir N_8 O_6, M_r = 1002.04 g mol^{-1}, yellow fragment, crystal size 0.1186 x 0.0535 x 0.0246 mm^3, monoclinic, space group P 2$_1$/c, a = 12.14320(10) Å, b = 30.0046(4) Å, c = 11.12950(10) Å, β= 92.4390(10)°, V = 4051.38(7) Å^3, T = 150(2) K, Z = 4, $\rho_{calcd.}$ = 1.643 Mg/m^3, μ (Cu-Kα) = 6.897 mm^{-1}, F(000) = 2000, altogether 33117 reflexes up to h(-6/15), k(-35/37), l(-13/13) measured in the range of 7.450° ≤ Θ ≤ 74.469° , completeness Θ_{max} = 99.7 %, 8244 independent reflections, R_{int} = 0.0333, 7209 reflections with $F_0 > 4$ σ(Fo), 563 parameters, 0 restraints, $R1_{obs}$ = 0.0239, $wR2_{obs}$ = 0.0540, $R1_{all}$ = 0.0299, $wR2_{all}$ = 0.0564, GOOF = 1.052, largest difference peak and hole: 0.787/-0.504 e·Å^{-3}. CCDC 1432106 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Bond angles

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
H1	C1	C2	119.0(3)	C12	C22	Ir1	128.0(2)	C35	C41	H41C	109.5(3)
H1	C1	N6	118.8(3)	C16	C22	Ir1	114.6(2)	H41A	C41	H41B	109.5(4)
C2	C1	N6	122.2(3)	C24	C23	N1	117.5(2)	H41A	C41	H41C	109.5(4)
C1	C2	H2	120.5(3)	C24	C23	N4	128.8(3)	H41B	C41	H41C	109.4(4)
C1	C2	C3	118.8(3)	N1	C23	N4	113.6(2)	C23	N1	C25	105.2(2)
H2	C2	C3	120.6(3)	C23	C24	N2	116.1(2)	C23	N1	Ir1	114.6(2)
C2	C3	H3	120.3(3)	C23	C24	N3	130.1(3)	C25	N1	Ir1	140.1(2)
C2	C3	C4	119.4(3)	N2	C24	N3	113.8(2)	C24	N2	C27	104.8(2)
H3	C3	C4	120.3(3)	C26	C25	C29	121.3(2)	C24	N2	Ir1	115.9(2)
C3	C4	H4	120.0(3)	C26	C25	N1	108.1(2)	C27	N2	Ir1	139.2(2)
C3	C4	C5	120.1(3)	C29	C25	N1	130.6(2)	C24	N3	C28	106.3(2)
H4	C4	C5	119.9(3)	C25	C26	C32	120.9(2)	C24	N3	H3A	126.8(3)
C4	C5	C6	126.5(3)	C25	C26	N4	107.2(2)	C28	N3	H3A	126.9(3)
C4	C5	N6	119.6(3)	C32	C26	N4	131.9(2)	C23	N4	C26	105.8(2)
C6	C5	N6	113.9(3)	C28	C27	C33	120.1(3)	C23	N4	H4A	127.1(3)
C5	C6	C7	124.0(3)	C28	C27	N2	108.6(2)	C26	N4	H4A	127.1(3)
C5	C6	C11	115.0(3)	C33	C27	N2	131.3(3)	C17	N5	C21	119.7(3)
C7	C6	C11	120.8(3)	C27	C28	C36	121.6(3)	C17	N5	Ir1	115.3(2)
C6	C7	H7	120.1(3)	C27	C28	N3	106.5(2)	C21	N5	Ir1	124.8(2)
C6	C7	C8	119.6(3)	C36	C28	N3	131.9(3)	C1	N6	C5	119.7(2)
H7	C7	C8	120.3(4)	C25	C29	H29	120.8(3)	C1	N6	Ir1	124.3(2)
C7	C8	H8	119.7(4)	C25	C29	C30	118.4(3)	C5	N6	Ir1	116.0(2)
C7	C8	C9	120.5(3)	H29	C29	C30	120.8(3)	C11	Ir1	C22	87.4(1)
H8	C8	C9	119.8(4)	C29	C30	C37	120.1(3)	C11	Ir1	N1	169.8(1)
C8	C9	H9	119.7(4)	C29	C30	C39	119.8(3)	C11	Ir1	N2	94.6(1)
C8	C9	C10	120.7(3)	C37	C30	C39	120.0(3)	C11	Ir1	N5	97.8(1)
H9	C9	C10	119.6(4)	C26	C32	H32	120.8(3)	C11	Ir1	N6	80.5(1)
C9	C10	H10	119.8(3)	C26	C32	C37	118.4(3)	C22	Ir1	N1	102.3(1)
C9	C10	C11	120.3(3)	H32	C32	C37	120.8(3)	C22	Ir1	N2	176.1(1)
H10	C10	C11	119.8(3)	C27	C33	H33	120.7(3)	C22	Ir1	N5	80.1(1)
C6	C11	C10	118.0(3)	C27	C33	C34	118.5(3)	C22	Ir1	N6	95.2(1)
C6	C11	Ir1	114.5(2)	H33	C33	C34	120.8(3)	N1	Ir1	N2	75.82(9)
C10	C11	Ir1	127.2(2)	C33	C34	C35	120.9(3)	N1	Ir1	N5	86.94(9)
H12	C12	C13	119.4(3)	C33	C34	C40	119.2(3)	N1	Ir1	N6	95.43(9)
H12	C12	C22	119.5(3)	C35	C34	C40	120.0(3)	N2	Ir1	N5	96.31(9)
C13	C12	C22	121.1(3)	C34	C35	C36	120.5(3)	N2	Ir1	N6	88.40(9)
C12	C13	H13	119.7(3)	C34	C35	C41	119.6(3)	N5	Ir1	N6	175.1(1)
C12	C13	C14	120.7(3)	C36	C35	C41	119.8(3)	O4	N8	O3	124.2(3)
H13	C13	C14	119.6(4)	C28	C36	C35	118.4(3)	O4	N8	C47	118.3(3)
C13	C14	H14	120.1(4)	C28	C36	H36	120.8(3)	O3	N8	C47	117.5(3)
C13	C14	C15	119.8(3)	C35	C36	H36	120.8(3)	O5	N7	O6	124.6(3)
H14	C14	C15	120.1(4)	C30	C37	C32	120.8(3)	O5	N7	C45	118.0(2)
C14	C15	H15	120.1(4)	C30	C37	C38	119.4(3)	O6	N7	C45	117.4(2)
C14	C15	C16	119.8(3)	C32	C37	C38	119.8(3)	C44	C43	C48	119.5(3)
H15	C15	C16	120.1(3)	C37	C38	H38A	109.5(3)	C44	C43	C42	120.8(3)
C15	C16	C17	123.4(3)	C37	C38	H38B	109.4(3)	C48	C43	C42	119.6(3)
C15	C16	C22	121.5(3)	C37	C38	H38C	109.5(3)	C43	C44	H44	120.6(3)
C17	C16	C22	114.9(3)	H38A	C38	H38B	109.5(3)	C43	C44	C45	118.9(3)
C16	C17	C18	125.6(3)	H38A	C38	H38C	109.4(3)	H44	C44	C45	120.5(3)
C16	C17	N5	114.4(3)	H38B	C38	H38C	109.5(3)	N8	C47	C48	119.0(3)
C18	C17	N5	120.0(3)	C30	C39	H39A	109.5(3)	N8	C47	C46	118.1(3)
C17	C18	H18	120.2(4)	C30	C39	H39B	109.5(3)	C48	C47	C46	122.9(3)
C17	C18	C19	119.6(3)	C30	C39	H39C	109.4(3)	C43	C48	C47	119.3(3)
H18	C18	C19	120.2(4)	H39A	C39	H39B	109.5(3)	C43	C48	H48	120.3(3)
C18	C19	H19	120.0(4)	H39A	C39	H39C	109.5(3)	C47	C48	H48	120.4(3)
C18	C19	C20	119.9(4)	H39B	C39	H39C	109.5(3)	O1	C42	O2	127.5(3)
H19	C19	C20	120.1(4)	C34	C40	H40A	109.5(3)	O1	C42	C43	115.6(3)
C19	C20	H20	120.7(4)	C34	C40	H40B	109.5(3)	O2	C42	C43	116.9(3)
C19	C20	C21	118.6(4)	C34	C40	H40C	109.5(3)	C47	C46	H46	121.8(3)
H20	C20	C21	120.6(4)	H40A	C40	H40B	109.4(4)	C47	C46	C45	116.4(3)
C20	C21	H21	119.0(4)	H40A	C40	H40C	109.6(4)	H46	C46	C45	121.8(3)
C20	C21	N5	122.1(3)	H40B	C40	H40C	109.4(4)	N7	C45	C44	119.2(3)
H21	C21	N5	119.0(3)	C35	C41	H41A	109.5(3)	N7	C45	C46	117.8(3)
C12	C22	C16	117.1(3)	C35	C41	H41B	109.5(3)	C44	C45	C46	123.0(3)

Bond lengths

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
C1	H1	0.930(3)	C18	C19	1.376(6)	C37	C38	1.508(5)
C1	C2	1.379(5)	C19	H19	0.929(4)	C38	H38A	0.959(4)
C1	N6	1.349(4)	C19	C20	1.380(6)	C38	H38B	0.960(3)
C2	H2	0.929(4)	C20	H20	0.930(4)	C38	H38C	0.960(4)
C2	C3	1.379(5)	C20	C21	1.378(5)	C39	H39A	0.959(4)
C3	H3	0.930(3)	C21	H21	0.929(4)	C39	H39B	0.959(4)
C3	C4	1.381(5)	C21	N5	1.343(4)	C39	H39C	0.959(3)
C4	H4	0.930(3)	C22	Ir1	2.020(3)	C40	H40A	0.961(4)
C4	C5	1.395(5)	C23	C24	1.454(4)	C40	H40B	0.961(4)
C5	C6	1.459(4)	C23	N1	1.330(4)	C40	H40C	0.960(4)
C5	N6	1.364(4)	C23	N4	1.348(4)	C41	H41A	0.960(4)
C6	C7	1.398(5)	C24	N2	1.337(4)	C41	H41B	0.960(4)
C6	C11	1.416(5)	C24	N3	1.335(4)	C41	H41C	0.960(4)
C7	H7	0.931(3)	C25	C26	1.399(4)	N1	Ir1	2.175(2)
C7	C8	1.377(5)	C25	C29	1.395(4)	N2	Ir1	2.150(2)
C8	H8	0.931(4)	C25	N1	1.393(3)	N3	H3A	0.860(2)
C8	C9	1.377(5)	C26	C32	1.397(4)	N4	H4A	0.861(2)
C9	H9	0.928(4)	C26	N4	1.383(4)	N5	Ir1	2.054(2)
C9	C10	1.396(5)	C27	C28	1.404(4)	N6	Ir1	2.038(2)
C10	H10	0.930(3)	C27	C33	1.404(4)	O1	C42	1.251(4)
C10	C11	1.396(4)	C27	N2	1.386(4)	O2	C42	1.252(4)
C11	Ir1	2.000(3)	C28	C36	1.387(4)	O5	N7	1.218(4)
C12	H12	0.930(3)	C28	N3	1.383(4)	O4	N8	1.225(4)
C12	C13	1.391(5)	C29	H29	0.930(3)	O6	N7	1.220(4)
C12	C22	1.399(4)	C29	C30	1.392(4)	N8	O3	1.227(5)
C13	H13	0.931(3)	C30	C37	1.430(5)	N8	C47	1.465(4)
C13	C14	1.382(5)	C30	C39	1.505(5)	N7	C45	1.475(4)
C14	H14	0.930(4)	C32	H32	0.929(3)	C43	C44	1.393(5)
C14	C15	1.379(5)	C32	C37	1.386(4)	C43	C48	1.389(4)
C15	H15	0.930(3)	C33	H33	0.929(3)	C43	C42	1.522(4)
C15	C16	1.398(5)	C33	C34	1.383(5)	C44	H44	0.929(3)
C16	C17	1.461(5)	C34	C35	1.421(5)	C44	C45	1.387(4)
C16	C22	1.408(4)	C34	C40	1.516(5)	C47	C48	1.380(5)
C17	C18	1.391(5)	C35	C36	1.386(5)	C47	C46	1.383(5)
C17	N5	1.362(4)	C35	C41	1.507(5)	C48	H48	0.930(3)
C18	H18	0.931(4)	C36	H36	0.931(3)	C46	H46	0.931(3)
						C46	C45	1.380(4)

*All bond lengths are given in Å.

Hydrogen bond distances

Atom 1	Atom 2	Length*
N3	O1	2.616(3)
N4	O2	2.690(3)

*All distances are given in Å.

4. References

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