Supplementary Material (ESI) for Chemical Communications

Inhibition of Twisting of a Green Fluorescent Protein-like Chromophore by Metal Complexation

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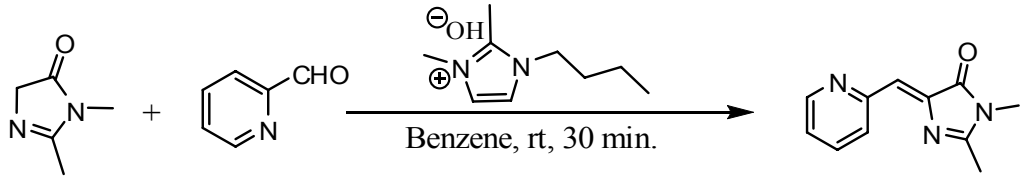
SUPPORTING INFORMATION

1. Synthesis and characterization of PyMDI.



The title compound (**PyMDI**) was conveniently obtained in a 76% yield via a Knoevenagel-type condensation of 2-pyridinecarbaldehyde with 1,2-dimethyl-1*H*-imidazol-5(4*H*)-one.[1] The reaction was catalyzed using 3-butyl-1,2-dimethyl-1*H*-imidazol-3-ium hydroxide, a recently developed ionic liquid with literature precedence for use with aldol condensation reactions[2], Michael additions[3] and Knoevenagel condensations.[4] It is critical that the reaction product, (*Z*)-1,2-dimethyl-4-(pyridin-2-ylmethylene)-1*H*-imidazol-5(4*H*)-one immediately be purified, flushed with nitrogen, and stored at 0^{o}C in the dark. For purification, column chromatography on alumina was used with ethyl acetate as the eluent.

Experimental

The 1,2-dimethyl-1*H*-imidazol-5(4*H*)-one was synthesized according to Wu and Burgess,[5] while the 3-butyl-1,2-dimethyl-1*H*-imidazol-3-ium hydroxide was obtained following the Ranu and Banerjee procedure.[6]

Synthesis of (*Z*)-1,2-dimethyl-4-(pyridin-2-ylmethylene)-1H-imidazol-5(4*H*)-one

To a solution of 1,2-dimethyl-1*H*-imidazol-5(4*H*)-one (2.18 g, 19.5 mmol) in benzene (15 mL), 2-pyridinecarbaldehyde (2.09 g, 19.5 mmol) was added followed by 3-butyl-1,2-dimethyl-1*H*-imidazol-3-ium hydroxide (0.23 g, 1.35 mmol). The solution was stirred at room temperature for 30 min. Solvent was removed under vacuum (rotovap), followed by re-dissolving the residue in ethyl acetate. The solution was applied on top of a neutral alumina column and elution was

continued with ethyl acetate (ca. 250 mL). The chromatographically homogeneous fractions containing (**PyMDI**) were combined and the solvent was removed under vacuum to yield yellow solid. Yield: 3.0 g (15.9 mmol, 76%); mp 115–117 ^{o}C (decomp.)

^{1}H NMR (500 MHz, $CDCl_3$)[7] δ = 8.68 (ddd, 1H, J_{HH} = 0.9 Hz, 1.7 Hz, 4.8 Hz); 8.57 (dt, 1H, J_{HH} = 0.9 Hz, 8.0 Hz); 7.72 (dt, 1H, J_{HH} = 1.8 Hz, 7.6 Hz); 7.22 (s, 1H); 7.20 (ddd, 1H, J_{HH} = 1.1 Hz, 4.8 Hz, 7.5 Hz); 3.18 (s, 3H); 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.51, 164.68, 153.40, 150.05, 140.77, 136.22, 127.43, 126.76, 123.34, 26.60, 15.82.

EIMS: m/z 201.1(66); 173.1(10); 118.1(13); 56(100).

Anal. Calcd for $C_{11}H_{11}N_3O$: C, 65.66; H, 5.51; N, 20.88.

Found: C, 65.73; H, 5.62; N, 20.71.

Synthesis of Zn complex of (*Z*)-1,2-dimethyl-4-(pyridin-2-ylmethylene)-1H-imidazol-5(4*H*)-one

To a solution of (*Z*)-1,2-dimethyl-4-(pyridin-2-ylmethylene)-1H-imidazol-5(4*H*)-one (60 mg, 0.3 mmol) in methanol (4 mL) a zinc nitrate hexahydrate (92 mg, 0.31 mmol) in methanol (4 mL) solution was added. Crystallization ensued almost immediately. The reaction mixture was left for crystallization at 4^{o}C for 24 h., The solid was filtered and washed with cold methanol to yield 56 mg of yellow solid, mp 214-216 ^{o}C (decomp.)

^{1}H NMR (300 MHz, CD_3OD) δ = 8.68 (d, 1H, J_{HH} = 5.4 Hz); 8.26 (dt, 1H, J_{HH} = 1.8 Hz, 7.8 Hz); 8.10 (d, 1H, J_{HH} = 7.8 Hz); 7.74 (t, 1H, J_{HH} = 6.3 Hz); 7.34 (s, 1H); 3.33 (s, 3H); 2.55 (broad s, 3H).

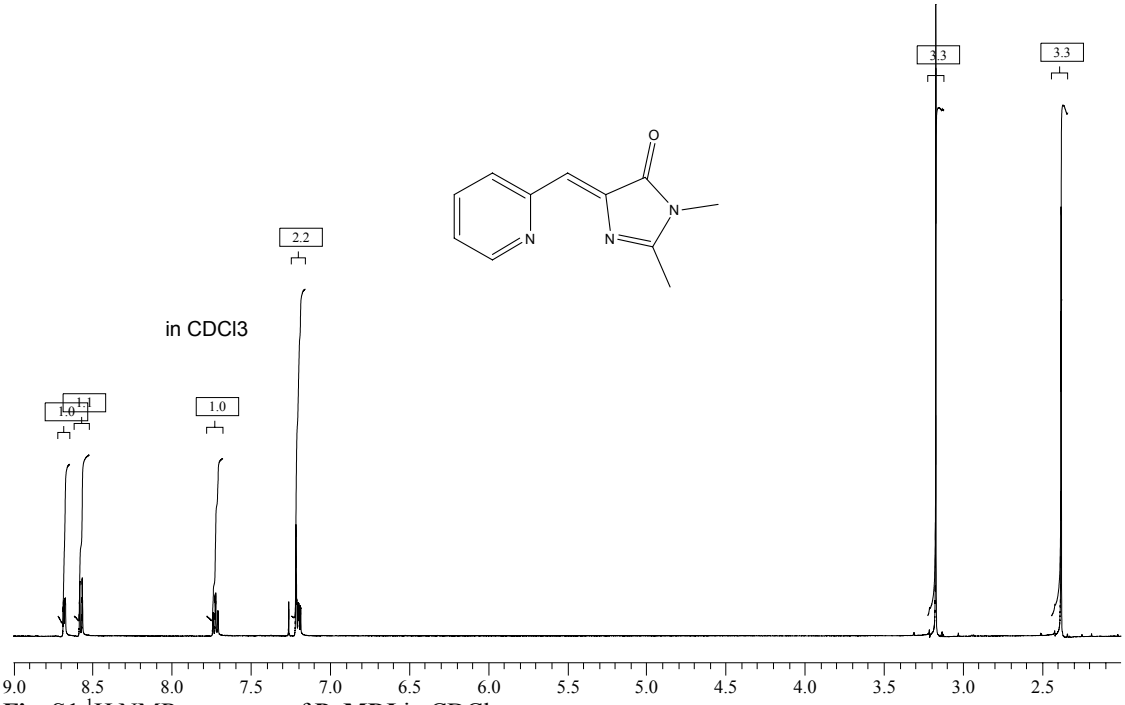


Fig. S1 ^{1}H NMR spectrum of **PyMDI** in $CDCl_3$

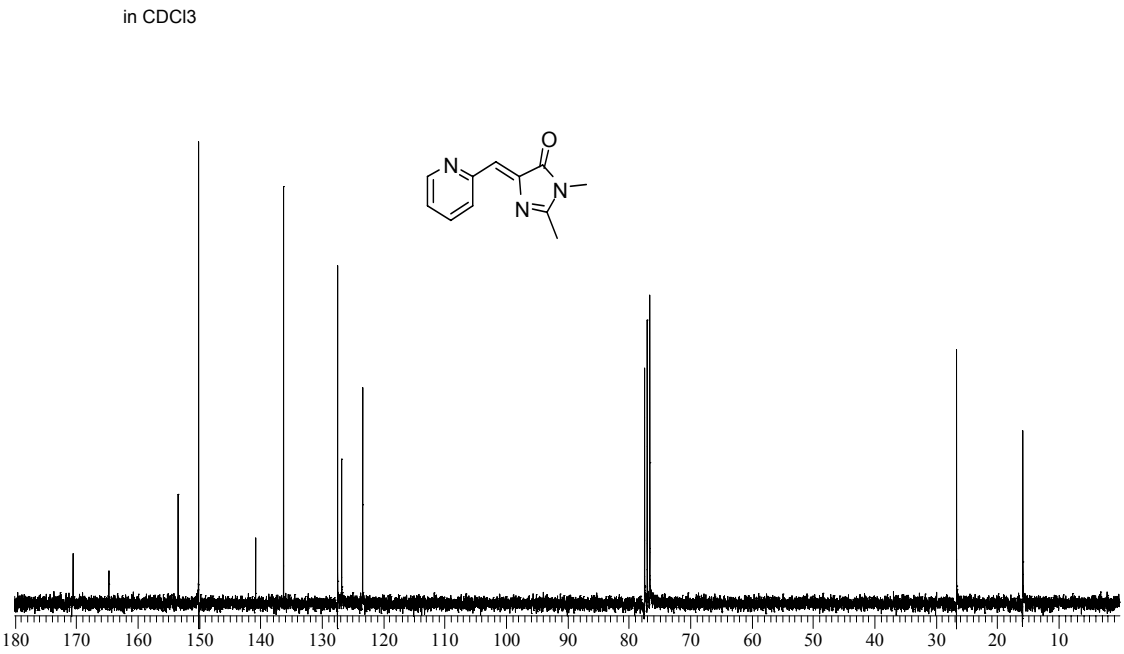


Fig. S2. ^{13}C NMR spectrum of **PyMDI** in $CDCl_3$.

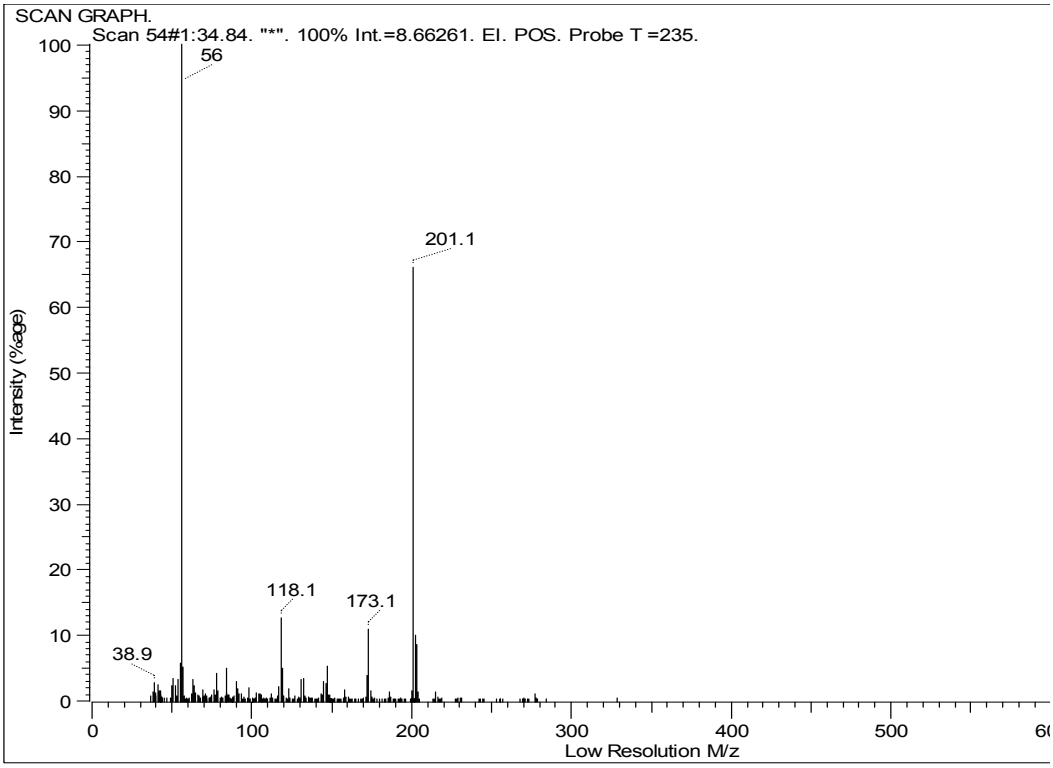


Fig. S3. Mass spectrum of **PyMDI** taken in EI mode.

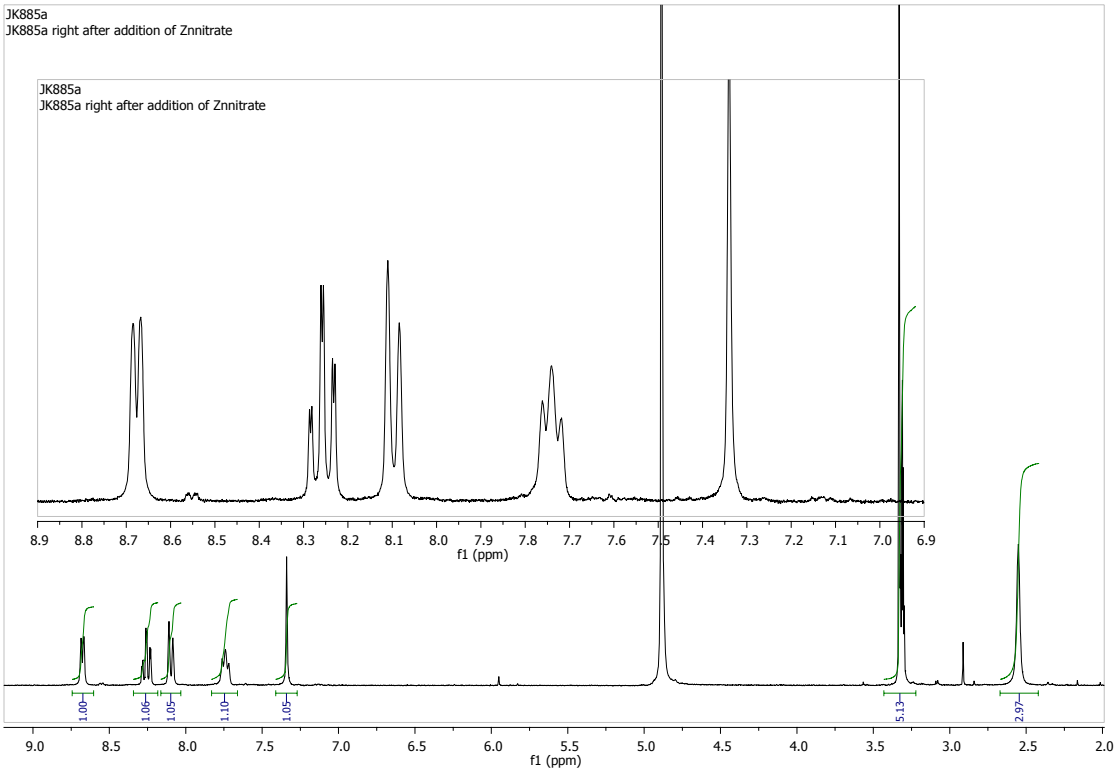


Fig. S4. ^{1}H NMR spectrum of **Zn-PyMDI** in CD_3OD. The N-methylamide resonance, a singlet at 3.33 ppm is superimposed on solvent signals while a singlet at 4.89 ppm belongs to water.

2. Stoichiometry of Zn(II) binding to PyMDI in solution.

The stoichiometry of complexation in solution was determined using a Job plot according to method described in Ref 8. Referring to Fig. S5, the maximum occurs at a mole fraction of 0.5, implying a 1:1 complex.

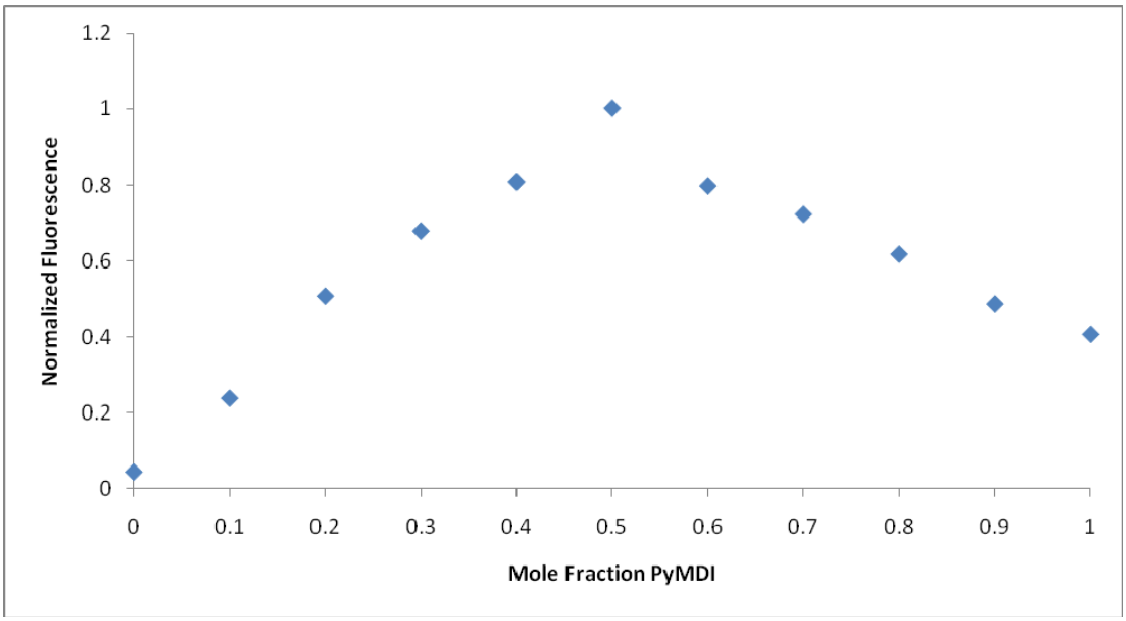


Fig. S5 Job Plot. Fluorescence was monitored at 424 nm,

Given a 1:1 stoichiometry, a Benesi-Hildebrand plot can be created to determine the binding constant of the complex. It should be noted that Benesi-Hildebrand plots are only applicable to 1:1 complexes. The Benesi-Hildebrand equation for fluorescence spectroscopy is given by:[9]

$$1/(I-I_0) = 1/(I_1-I_0) + 1/(K_f(I_1-I_0)) \times 1/[Zn^{2+}]. \qquad (S1)$$

where I_0 is the emission intensity of a free ligand, and I is the emission intensity of the complex at some Zn(II) concentration. Additionally, it is noted that the Benesi-Hildebrand plot confirms the assumptions made from the Job plot with respect to the 1:1 stoichiometric relationship. The

Benesi-Hildebrand plot in Fig. S6 (shown below) yields an R^2 = 0.997 and gives a binding constant for **Zn(PyMDI)** of 1892 M^{-1}.(Table S1).

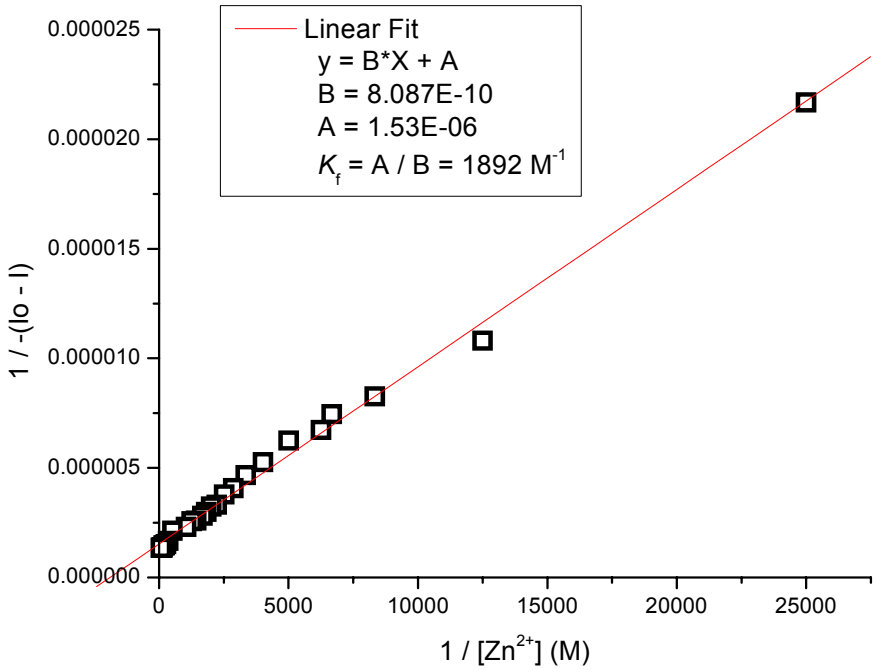


Fig. S6 Benesi-Hildebrand plot for titration of **PyMDI** with Zn^{2+} in solution.

Table S1. Formation and stability constants of various Zinc(II) complexes.

Compound	K_f (M^{-1})	K_d (M)
Zn(PyMBDI)	1.89E+03	5.29E-04
Zn(en)	5.13E+05	1.95E-06[10]
$Zn(en)_2$	2.35E+10	4.26E-11[10]
$Zn(en)_3$	1.23E+12	8.12E-13[10]
Zn(phen)	2.70E+06	3.70E-07[11]
$Zn(phen)_2$	3.70E+12	2.70E-13[11]
$Zn(phen)_3$	1.00E+17	1.00E-17[11]
Zn(acac)	1.18E+05	8.50E-06[12]
$Zn(acac)_2$	1.05E+09	9.50E-10[12]

3. Spectral behavior of PyMDI in methanol/water mixtures.

In order to detect possible **PyMDI** photobasicity dependence on water concentration in methanol/water mixtures, absorption and emission spectra of **PyMDI** were obtained for 5% increments. It is noted that as water concentration increases, the absorption maximum demonstrate a bathochromic shift (Fig S7). At the same time, in all cases only emission from the neutral species was observed (Fig S8). The intensity decreased as the water concentration increased, due to an unestablished quenching mechanism that may involve a diabatic protonation of the chromophore.

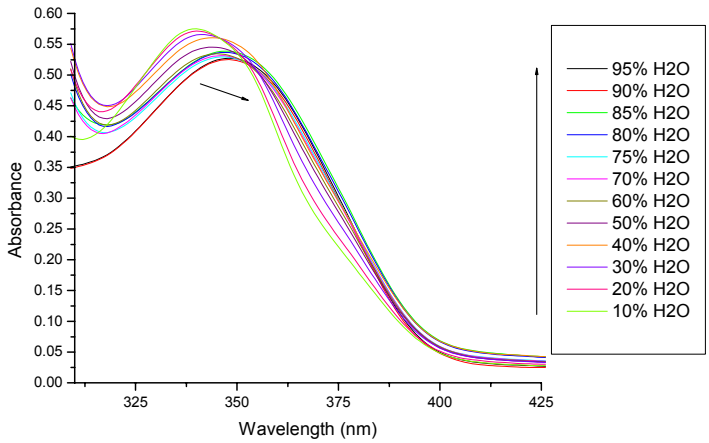


Fig. S7. Absorption Spectra of **PyMDI** in MeOH/H_2O.

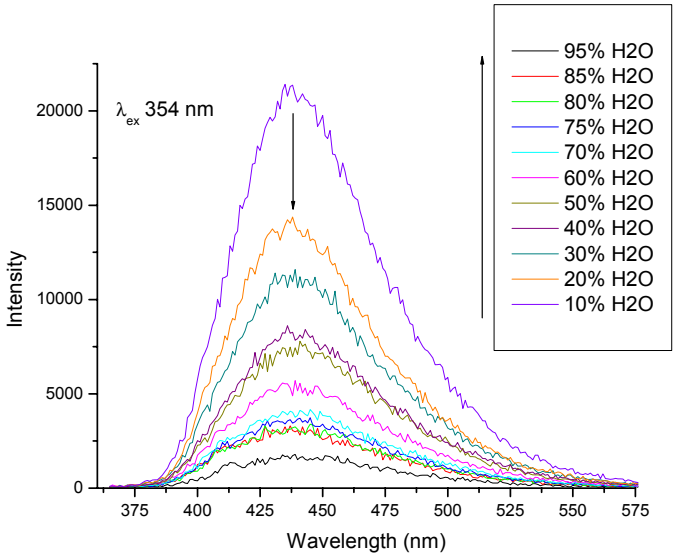


Fig. S8: MeOH/H_2O Emission Spectra of **PyMDI.**

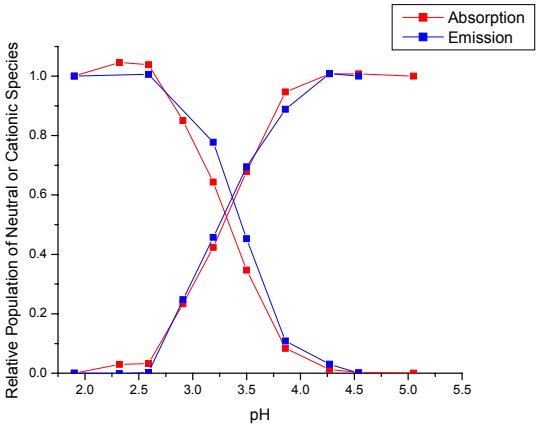


Fig. S9. pH titration curves of **PyMDI** with Zn^{2+} in 1/1 vol MeOH/H_2O solution.

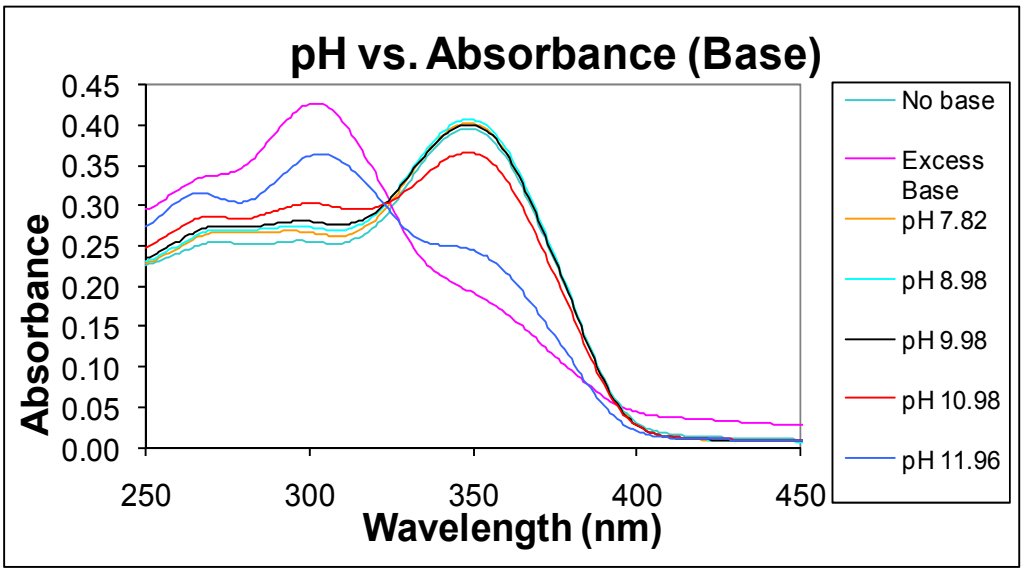


Fig. S10. Absorption spectra of **PyMDI** in MeOH/H_2O (1/1 vol) at basic pH values.

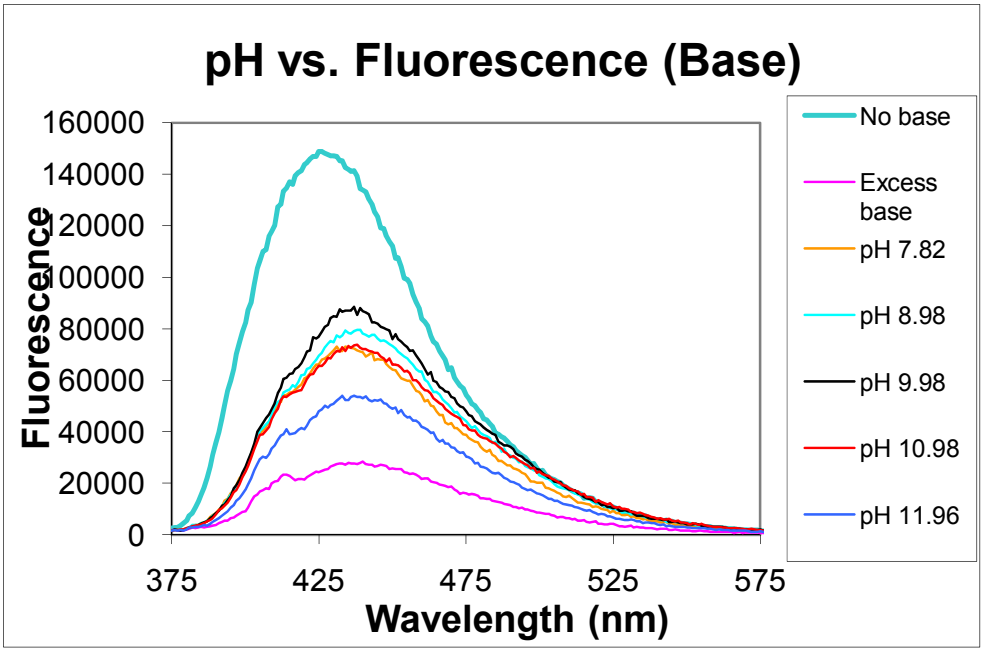


Fig. S11. Emission spectra of **PyMDI** in MeOH/H_2O (1/1 vol) at basic pH values (λ_{ex} = 344nm).

4. pH-stability of Zn-PyMDI complex.

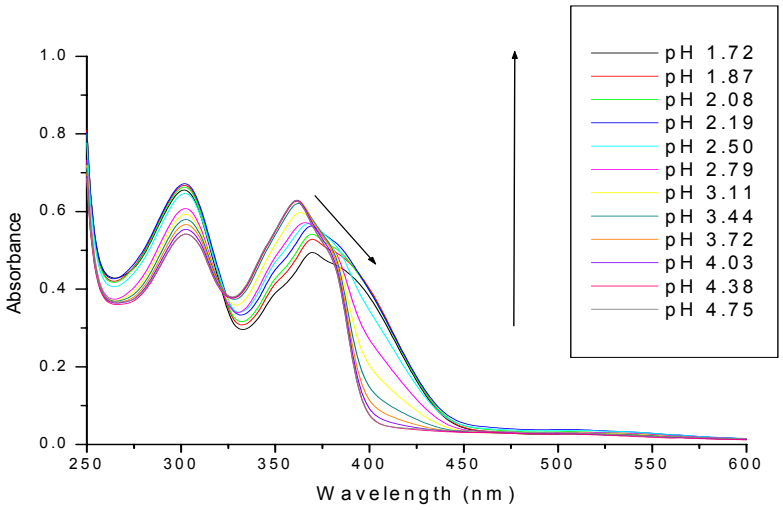


Fig. S12 Absorption Spectra of **PyMDI** at various pH and 20 mM Zn(II) mixture.

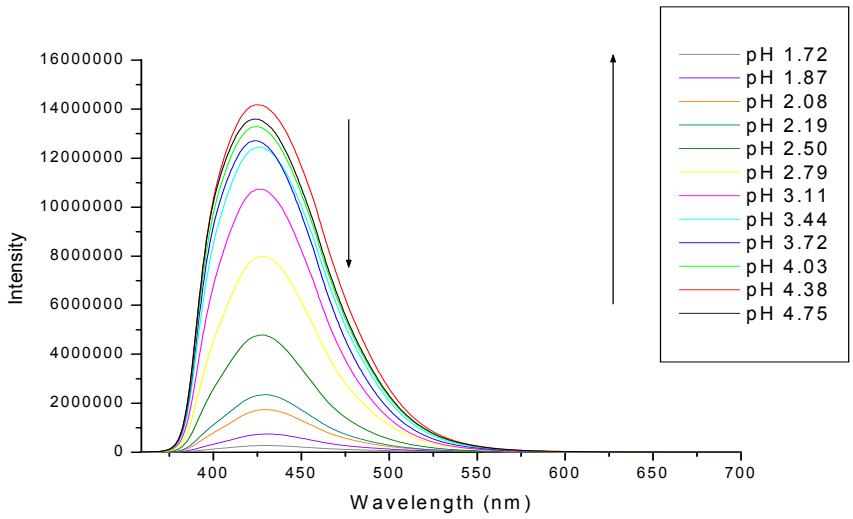


Fig. S13. Emission Spectra of **PyMDI** and 20 mM Zn(II) mixture at various pH (λ_{ex} = 344nm).

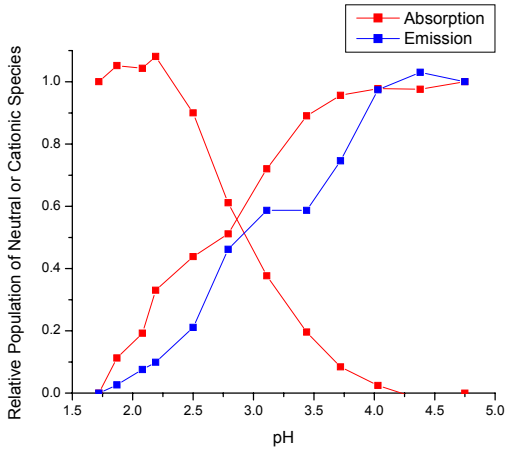


Fig. S14. Titration curve for **PyMDI**:20 mM Zn(II) mixture.

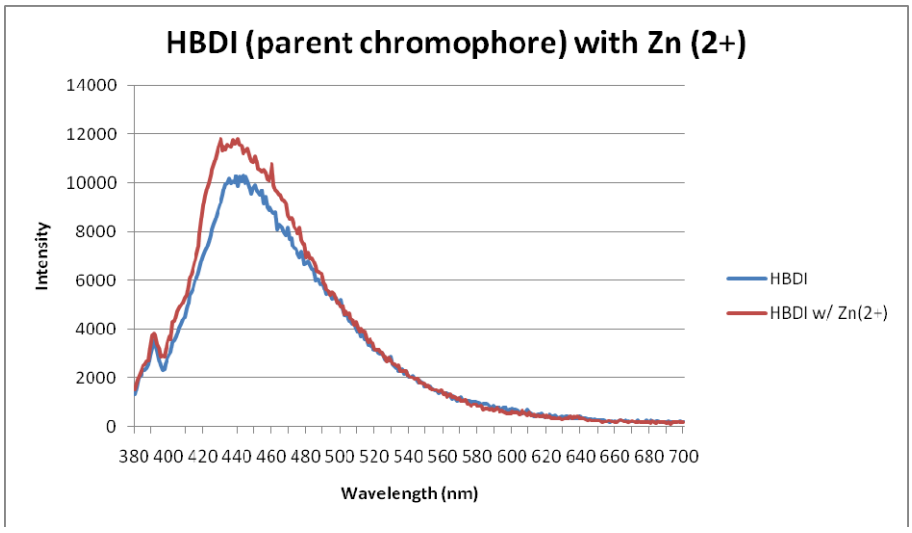


Fig. S15. Fluorescence spectra of parent chromophore (HBDI) in the presence of 15 mM Zn^{2+}

5. Crystallography Data for Zn-PyMDI complex.

Note:

The best crystals obtained for crystal structure determination were twinned and disordered. The data would not support refining all atoms as anisotropic. In finding the solution, several space groups were tried including orthorhombic and P2/n, however, no solution could be found. We believe that the disordered methanol solvent molecules--one full molecule and 0.7 additional molecule complicate the structure refinement in addition to the asymmetry of the coordinated NO_3 groups on the Zn atoms. There is pseudo 2/c or 2/n symmetry but this is not satisfied by all the atoms.

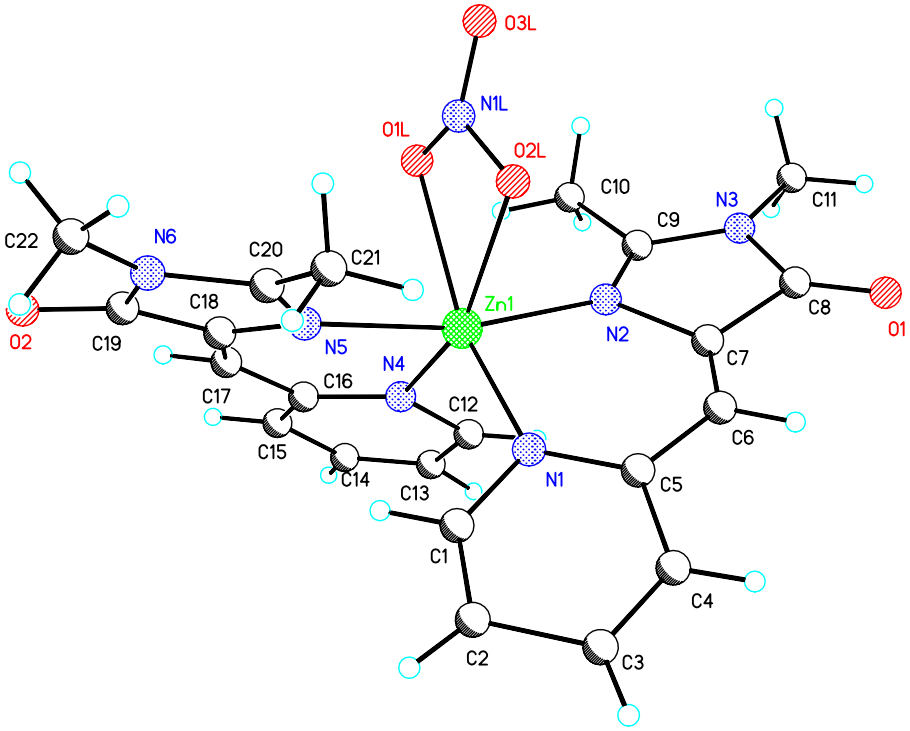


Fig. S16. Molecular structure of **Zn-PyMDI.**

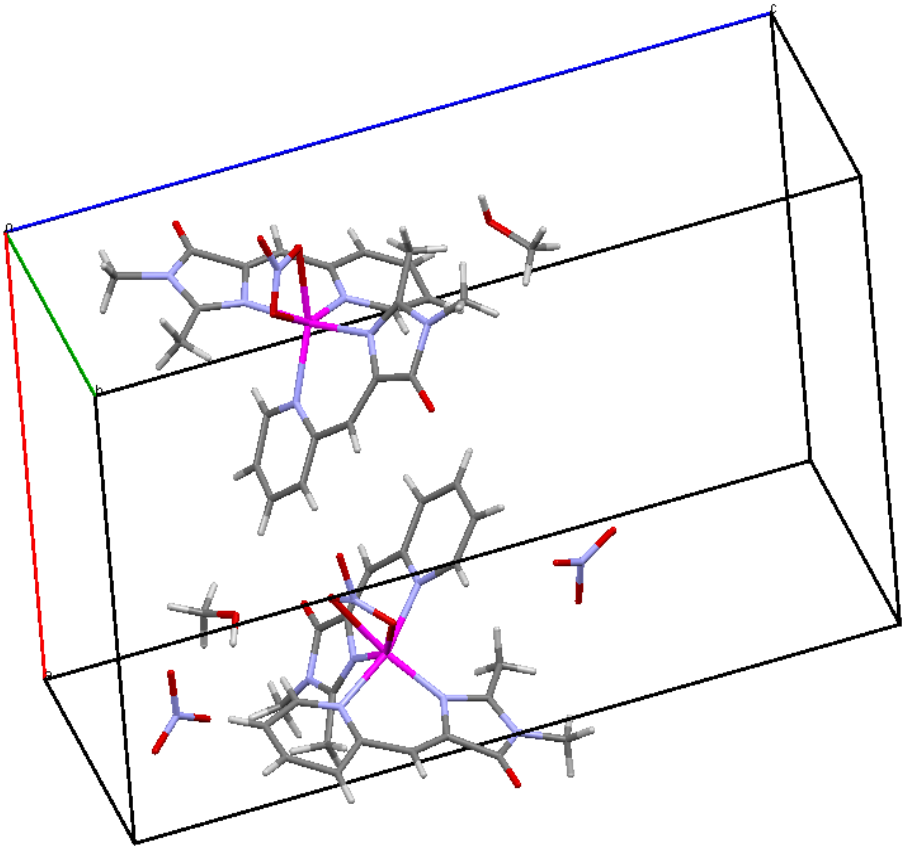


Fig. S17. Crystal structure of **Zn-PyMDI** complex. The asymmetric crystal unit contains two molecules of the complex compensated by two nitrate ions placed outside the coordination sphere of zinc in addition to 1.7 molecules of methanol. Stick style was selected for clarity.

Table S2. Crystal data and structure refinement for JK885a.

Identification code	jk885a	
Empirical formula	C45.70 H50.80 N16 O17.70 Zn2	
Formula weight	1238.16	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	Pn	
Unit cell dimensions	a = 15.4288(11) Å	α= 90°.
	b = 7.6422(6) Å	β= 90.335(6)°.
	c = 22.522(2) Å	γ = 90°.
Volume	2655.5(4) $Å^3$	
Z	2	
Density (calculated)	1.548 Mg/m^3	
Absorption coefficient	1.873 mm^{-1}	
F(000)	1277	
Crystal size	0.12 x 0.09 x 0.02 mm^3	
Theta range for data collection	3.46 to 66.59°.	
Index ranges	-18<=h<=18, -9<=k<=9, -26<=l<=26	
Reflections collected	9768	
Independent reflections	6142 [R(int) = 0.0627]	
Completeness to theta = 66.59°	91.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9635 and 0.8134	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6142 / 0 / 611	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0634, wR2 = 0.1399	
R indices (all data)	R1 = 0.1316, wR2 = 0.1730	
Absolute structure parameter	0.23(9)	
Largest diff. peak and hole	0.342 and -0.395 e.$Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for JK885a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2787(12)	3230(20)	4553(8)	54(5)
C(2)	2314(11)	4300(20)	4904(8)	54(5)
C(3)	1395(12)	4510(20)	4700(7)	50(4)
C(4)	1185(12)	3600(20)	4194(8)	52(5)
C(5)	1768(13)	2470(20)	3865(8)	54(5)
C(6)	1468(11)	1660(20)	3326(7)	45(4)
C(7)	1886(11)	870(20)	2938(8)	52(5)
C(8)	1530(11)	70(30)	2333(7)	53(5)
C(9)	2974(13)	-270(30)	2392(8)	55(5)
C(10)	3835(13)	-880(30)	2191(10)	74(6)
C(11)	2172(10)	-1290(30)	1464(7)	65(6)
C(12)	4262(12)	3260(30)	2816(9)	64(6)
C(13)	4925(15)	4200(30)	2531(10)	78(7)
C(14)	5734(16)	4220(30)	2684(11)	79(7)
C(15)	5965(13)	3350(30)	3178(9)	64(6)
C(16)	5369(11)	2510(30)	3476(9)	56(6)
C(17)	5615(12)	1700(30)	4009(10)	67(6)
C(18)	5158(11)	830(20)	4482(7)	40(4)
C(19)	5554(14)	300(30)	4986(10)	64(6)
C(20)	4153(11)	-390(30)	4963(9)	58(5)
C(21)	3327(10)	-950(20)	5221(8)	60(5)
C(22)	4915(15)	-1350(30)	5894(9)	84(7)
N(1)	2610(9)	2280(20)	4029(7)	57(4)
N(2)	2851(9)	420(19)	2924(8)	57(4)
N(3)	2224(11)	-610(20)	2091(8)	60(4)
N(4)	4544(10)	2397(19)	3278(6)	46(4)
N(5)	4306(10)	460(20)	4486(6)	46(4)
N(6)	4873(9)	-590(20)	5336(7)	49(4)
O(1)	818(9)	150(20)	2163(6)	75(4)
O(2)	6338(9)	430(20)	5187(6)	76(4)
N(1L)	3637(15)	-2746(13)	3689(10)	65(3)

O(1L)	4214(9)	-1860(20)	3493(7)	77(4)
O(2L)	2936(8)	-1878(17)	3896(5)	48(3)
O(3L)	3510(20)	-4285(13)	3647(13)	151(6)
Zn(1)	3563(4)	736(2)	3687(3)	50(1)
C(1B)	7563(15)	5950(30)	4791(11)	86(7)
C(2B)	6920(12)	5410(30)	5142(9)	61(5)
C(3B)	6035(9)	5511(19)	4936(7)	44(4)
C(4B)	5939(11)	6140(20)	4421(7)	52(4)
C(5B)	6568(10)	7030(20)	4034(7)	48(4)
C(6B)	6383(10)	7904(19)	3501(7)	42(4)
C(7B)	6935(11)	8600(20)	3094(8)	47(4)
C(8B)	6624(11)	9620(20)	2627(7)	41(4)
C(9B)	8073(10)	9720(20)	2720(7)	42(4)
C(10B)	8944(11)	10230(20)	2543(9)	66(5)
C(11B)	7327(13)	11430(30)	1877(9)	93(6)
C(12B)	9555(10)	6050(20)	2604(7)	38(4)
C(13B)	10207(14)	5270(30)	2246(11)	76(6)
C(14B)	10969(14)	5390(30)	2462(10)	90(7)
C(15B)	11247(11)	6330(20)	3012(8)	59(5)
C(16B)	10506(10)	6770(20)	3298(7)	44(4)
C(17B)	10698(13)	7670(20)	3868(9)	64(5)
C(18B)	10216(11)	8540(20)	4239(8)	46(4)
C(19B)	10521(16)	9650(30)	4776(10)	75(6)
C(20B)	9102(13)	9840(30)	4688(9)	61(5)
C(21B)	8193(11)	10470(20)	4810(9)	63(5)
C(22B)	9680(10)	11810(20)	5449(7)	58(4)
N(1B)	7409(9)	6820(20)	4218(6)	45(4)
N(2B)	7875(9)	8736(19)	3123(6)	43(3)
N(3B)	7358(10)	10380(20)	2374(7)	64(5)
N(4B)	9682(10)	6680(20)	3090(7)	57(4)
N(5B)	9318(9)	8640(20)	4229(7)	58(4)
N(6B)	9774(10)	10467(19)	4949(7)	53(4)
O(1B)	5869(7)	9927(15)	2438(6)	49(3)
O(2B)	11217(10)	9740(20)	4974(7)	104(6)
N(1BL)	8652(18)	3739(17)	3672(11)	78(4)
O(1BL)	9007(9)	4670(20)	4050(8)	70(4)

O(2BL)	8134(10)	4510(20)	3302(7)	71(4)
O(3BL)	8253(8)	2187(12)	3685(7)	100(5)
Zn(1B)	8568(4)	7224(2)	3686(3)	52(1)
N(1A)	8909(11)	6520(30)	1015(7)	67(4)
O(1A)	8659	7773	1280	144(7)
O(2A)	9459	6738	678	128(5)
O(3A)	8619	4895	1141	121(6)
N(2A)	8242(12)	6150(30)	6369(9)	94(7)
O(4A)	8584	4993	6167	99(5)
O(5A)	8424	7735	6148	92(5)
O(6A)	7780	6071	6825	146(6)
O(1S)	11(8)	6720(20)	5534(6)	65(4)
C(1S)	610(12)	7320(30)	5991(8)	91(7)
O(2S)	7082(13)	6540(30)	1877(8)	65(5)
C(2S)	6610(15)	7090(30)	1413(9)	50(6)

Table S4. Bond lengths [Å] and angles [°] for JK885a.

C(1)-C(2)	1.35(2)	C(15)-C(16)	1.31(3)
C(1)-N(1)	1.41(2)	C(15)-H(15A)	0.9500
C(1)-H(1A)	0.9500	C(16)-N(4)	1.35(2)
C(2)-C(3)	1.50(2)	C(16)-C(17)	1.40(3)
C(2)-H(2)	0.9500	C(17)-C(18)	1.44(3)
C(3)-C(4)	1.37(2)	C(17)-H(17A)	0.9500
C(3)-H(3A)	0.9500	C(18)-N(5)	1.345(19)
C(4)-C(5)	1.45(2)	C(18)-C(19)	1.35(3)
C(4)-H(4A)	0.9500	C(19)-O(2)	1.29(2)
C(5)-N(1)	1.36(2)	C(19)-N(6)	1.48(2)
C(5)-C(6)	1.44(2)	C(20)-N(5)	1.28(2)
C(6)-C(7)	1.24(2)	C(20)-N(6)	1.40(2)
C(6)-H(6A)	0.9500	C(20)-C(21)	1.47(2)
C(7)-N(2)	1.53(2)	C(21)-H(21A)	0.9800
C(7)-C(8)	1.59(2)	C(21)-H(21B)	0.9800
C(8)-O(1)	1.164(18)	C(21)-H(21C)	0.9800
C(8)-N(3)	1.31(2)	C(22)-N(6)	1.39(2)
C(9)-N(2)	1.32(2)	C(22)-H(22A)	0.9800
C(9)-N(3)	1.36(2)	C(22)-H(22B)	0.9800
C(9)-C(10)	1.48(3)	C(22)-H(22C)	0.9800
C(10)-H(10A)	0.9800	N(1)-Zn(1)	2.040(15)
C(10)-H(10B)	0.9800	N(2)-Zn(1)	2.050(17)
C(10)-H(10C)	0.9800	N(4)-Zn(1)	2.184(15)
C(11)-N(3)	1.51(2)	N(5)-Zn(1)	2.137(12)
C(11)-H(11A)	0.9800	N(1L)-O(3L)	1.197(14)
C(11)-H(11B)	0.9800	N(1L)-O(1L)	1.20(2)
C(11)-H(11C)	0.9800	N(1L)-O(2L)	1.35(2)
C(12)-N(4)	1.30(2)	O(1L)-Zn(1)	2.270(16)
C(12)-C(13)	1.41(3)	O(2L)-Zn(1)	2.270(13)
C(12)-H(12A)	0.9500	C(1B)-C(2B)	1.34(3)
C(13)-C(14)	1.29(3)	C(1B)-N(1B)	1.47(3)
C(13)-H(13A)	0.9500	C(1B)-H(1BA)	0.9500
C(14)-C(15)	1.34(3)	C(2B)-C(3B)	1.44(2)
C(14)-H(14A)	0.9500	C(2B)-H(2BA)	0.9500

C(3B)-C(4B)	1.26(2)	C(18B)-C(19B)	1.55(3)
C(3B)-H(3BA)	0.9500	C(19B)-O(2B)	1.16(2)
C(4B)-C(5B)	1.47(2)	C(19B)-N(6B)	1.37(2)
C(4B)-H(4BA)	0.9500	C(20B)-N(6B)	1.28(2)
C(5B)-N(1B)	1.370(19)	C(20B)-N(5B)	1.42(3)
C(5B)-C(6B)	1.40(2)	C(20B)-C(21B)	1.51(3)
C(6B)-C(7B)	1.36(2)	C(21B)-H(21D)	0.9800
C(6B)-H(6BA)	0.9500	C(21B)-H(21E)	0.9800
C(7B)-C(8B)	1.39(2)	C(21B)-H(21F)	0.9800
C(7B)-N(2B)	1.46(2)	C(22B)-N(6B)	1.53(2)
C(8B)-O(1B)	1.259(17)	C(22B)-H(22D)	0.9800
C(8B)-N(3B)	1.40(2)	C(22B)-H(22E)	0.9800
C(9B)-N(2B)	1.22(2)	C(22B)-H(22F)	0.9800
C(9B)-N(3B)	1.44(2)	N(1B)-Zn(1B)	2.181(14)
C(9B)-C(10B)	1.46(2)	N(2B)-Zn(1B)	2.017(14)
C(10B)-H(10D)	0.9800	N(4B)-Zn(1B)	2.226(16)
C(10B)-H(10E)	0.9800	N(5B)-Zn(1B)	1.997(16)
C(10B)-H(10F)	0.9800	N(1BL)-O(1BL)	1.23(3)
C(11B)-N(3B)	1.38(2)	N(1BL)-O(2BL)	1.29(2)
C(11B)-H(11D)	0.9800	N(1BL)-O(3BL)	1.337(19)
C(11B)-H(11E)	0.9800	O(1BL)-Zn(1B)	2.224(15)
C(11B)-H(11F)	0.9800	O(2BL)-Zn(1B)	2.346(15)
C(12B)-N(4B)	1.212(19)	N(1A)-O(2A)	1.153(17)
C(12B)-C(13B)	1.42(3)	N(1A)-O(1A)	1.193(19)
C(12B)-H(12B)	0.9500	N(1A)-O(3A)	1.351(19)
C(13B)-C(14B)	1.27(2)	N(2A)-O(4A)	1.13(2)
C(13B)-H(13B)	0.9500	N(2A)-O(6A)	1.25(2)
C(14B)-C(15B)	1.49(3)	N(2A)-O(5A)	1.34(2)
C(14B)-H(14B)	0.9500	O(1S)-C(1S)	1.453(18)
C(15B)-C(16B)	1.36(2)	O(1S)-H(1S)	0.8400
C(15B)-H(15B)	0.9500	C(1S)-H(1S1)	0.9800
C(16B)-N(4B)	1.354(19)	C(1S)-H(1S2)	0.9800
C(16B)-C(17B)	1.49(2)	C(1S)-H(1S3)	0.9800
C(17B)-C(18B)	1.30(2)	O(2S)-C(2S)	1.34(3)
C(17B)-H(17B)	0.9500	O(2S)-H(2S)	0.8400
C(18B)-N(5B)	1.39(2)	C(2S)-H(2S1)	0.9800

C(2S)-H(2S2)	0.9800	N(3)-C(11)-H(11A)	109.5
C(2S)-H(2S3)	0.9800	N(3)-C(11)-H(11B)	109.5
		H(11A)-C(11)-H(11B)	109.5
C(2)-C(1)-N(1)	134.2(17)	N(3)-C(11)-H(11C)	109.5
C(2)-C(1)-H(1A)	112.9	H(11A)-C(11)-H(11C)	109.5
N(1)-C(1)-H(1A)	112.9	H(11B)-C(11)-H(11C)	109.5
C(1)-C(2)-C(3)	113.5(16)	N(4)-C(12)-C(13)	112.4(18)
C(1)-C(2)-H(2)	123.3	N(4)-C(12)-H(12A)	123.8
C(3)-C(2)-H(2)	123.3	C(13)-C(12)-H(12A)	123.8
C(4)-C(3)-C(2)	114.7(17)	C(14)-C(13)-C(12)	126(2)
C(4)-C(3)-H(3A)	122.7	C(14)-C(13)-H(13A)	117.0
C(2)-C(3)-H(3A)	122.7	C(12)-C(13)-H(13A)	117.0
C(3)-C(4)-C(5)	125.6(17)	C(13)-C(14)-C(15)	118(2)
C(3)-C(4)-H(4A)	117.2	C(13)-C(14)-H(14A)	121.1
C(5)-C(4)-H(4A)	117.2	C(15)-C(14)-H(14A)	121.1
N(1)-C(5)-C(6)	119.2(16)	C(16)-C(15)-C(14)	118.9(19)
N(1)-C(5)-C(4)	121.3(16)	C(16)-C(15)-H(15A)	120.6
C(6)-C(5)-C(4)	119.2(16)	C(14)-C(15)-H(15A)	120.6
C(7)-C(6)-C(5)	129.5(16)	C(15)-C(16)-N(4)	122(2)
C(7)-C(6)-H(6A)	115.3	C(15)-C(16)-C(17)	117.9(17)
C(5)-C(6)-H(6A)	115.3	N(4)-C(16)-C(17)	120.3(18)
C(6)-C(7)-N(2)	129.3(15)	C(16)-C(17)-C(18)	134.8(17)
C(6)-C(7)-C(8)	127.7(15)	C(16)-C(17)-H(17A)	112.6
N(2)-C(7)-C(8)	103.0(15)	C(18)-C(17)-H(17A)	112.6
O(1)-C(8)-N(3)	131.0(18)	N(5)-C(18)-C(19)	111.7(15)
O(1)-C(8)-C(7)	125.6(17)	N(5)-C(18)-C(17)	125.7(15)
N(3)-C(8)-C(7)	103.3(13)	C(19)-C(18)-C(17)	122.6(17)
N(2)-C(9)-N(3)	113.6(17)	O(2)-C(19)-C(18)	134(2)
N(2)-C(9)-C(10)	122.3(16)	O(2)-C(19)-N(6)	120.9(17)
N(3)-C(9)-C(10)	123.4(17)	C(18)-C(19)-N(6)	105.4(16)
C(9)-C(10)-H(10A)	109.5	N(5)-C(20)-N(6)	114.2(16)
C(9)-C(10)-H(10B)	109.5	N(5)-C(20)-C(21)	130.1(17)
H(10A)-C(10)-H(10B)	109.5	N(6)-C(20)-C(21)	114.9(17)
C(9)-C(10)-H(10C)	109.5	C(20)-C(21)-H(21A)	109.5
H(10A)-C(10)-H(10C)	109.5	C(20)-C(21)-H(21B)	109.5
H(10B)-C(10)-H(10C)	109.5	H(21A)-C(21)-H(21B)	109.5

C(20)-C(21)-H(21C)	109.5	N(2)-Zn(1)-N(4)	94.8(5)
H(21A)-C(21)-H(21C)	109.5	N(5)-Zn(1)-N(4)	92.5(5)
H(21B)-C(21)-H(21C)	109.5	N(1)-Zn(1)-O(1L)	154.1(6)
N(6)-C(22)-H(22A)	109.5	N(2)-Zn(1)-O(1L)	88.3(6)
N(6)-C(22)-H(22B)	109.5	N(5)-Zn(1)-O(1L)	80.9(5)
H(22A)-C(22)-H(22B)	109.5	N(4)-Zn(1)-O(1L)	96.8(5)
N(6)-C(22)-H(22C)	109.5	N(1)-Zn(1)-O(2L)	97.0(5)
H(22A)-C(22)-H(22C)	109.5	N(2)-Zn(1)-O(2L)	80.9(5)
H(22B)-C(22)-H(22C)	109.5	N(5)-Zn(1)-O(2L)	88.2(5)
C(5)-N(1)-C(1)	110.6(15)	N(4)-Zn(1)-O(2L)	153.7(5)
C(5)-N(1)-Zn(1)	130.6(13)	O(1L)-Zn(1)-O(2L)	57.3(2)
C(1)-N(1)-Zn(1)	118.5(11)	C(2B)-C(1B)-N(1B)	122.8(19)
C(9)-N(2)-C(7)	104.7(15)	C(2B)-C(1B)-H(1BA)	118.6
C(9)-N(2)-Zn(1)	136.6(13)	N(1B)-C(1B)-H(1BA)	118.6
C(7)-N(2)-Zn(1)	118.2(11)	C(1B)-C(2B)-C(3B)	119.8(19)
C(8)-N(3)-C(9)	114.3(16)	C(1B)-C(2B)-H(2BA)	120.1
C(8)-N(3)-C(11)	119.2(15)	C(3B)-C(2B)-H(2BA)	120.1
C(9)-N(3)-C(11)	124.9(15)	C(4B)-C(3B)-C(2B)	115.0(16)
C(12)-N(4)-C(16)	122.7(17)	C(4B)-C(3B)-H(3BA)	122.5
C(12)-N(4)-Zn(1)	113.7(12)	C(2B)-C(3B)-H(3BA)	122.5
C(16)-N(4)-Zn(1)	123.6(13)	C(3B)-C(4B)-C(5B)	130.1(15)
C(20)-N(5)-C(18)	107.2(13)	C(3B)-C(4B)-H(4BA)	114.9
C(20)-N(5)-Zn(1)	131.0(13)	C(5B)-C(4B)-H(4BA)	114.9
C(18)-N(5)-Zn(1)	119.5(10)	N(1B)-C(5B)-C(6B)	120.2(14)
C(22)-N(6)-C(20)	128.5(16)	N(1B)-C(5B)-C(4B)	113.2(13)
C(22)-N(6)-C(19)	130.2(15)	C(6B)-C(5B)-C(4B)	126.5(13)
C(20)-N(6)-C(19)	101.3(15)	C(7B)-C(6B)-C(5B)	129.5(14)
O(3L)-N(1L)-O(1L)	130(2)	C(7B)-C(6B)-H(6BA)	115.2
O(3L)-N(1L)-O(2L)	112(2)	C(5B)-C(6B)-H(6BA)	115.2
O(1L)-N(1L)-O(2L)	116.5(10)	C(6B)-C(7B)-C(8B)	120.8(15)
N(1L)-O(1L)-Zn(1)	95.2(11)	C(6B)-C(7B)-N(2B)	128.7(15)
N(1L)-O(2L)-Zn(1)	90.9(8)	C(8B)-C(7B)-N(2B)	109.4(14)
N(1)-Zn(1)-N(2)	90.0(6)	O(1B)-C(8B)-C(7B)	132.2(16)
N(1)-Zn(1)-N(5)	97.0(6)	O(1B)-C(8B)-N(3B)	122.5(15)
N(2)-Zn(1)-N(5)	167.7(3)	C(7B)-C(8B)-N(3B)	105.3(14)
N(1)-Zn(1)-N(4)	109.1(3)	N(2B)-C(9B)-N(3B)	115.2(14)

N(2B)-C(9B)-C(10B)	127.2(16)	O(2B)-C(19B)-C(18B)	128(2)
N(3B)-C(9B)-C(10B)	117.6(14)	N(6B)-C(19B)-C(18B)	102.6(17)
C(9B)-C(10B)-H(10D)	109.5	N(6B)-C(20B)-N(5B)	112.5(17)
C(9B)-C(10B)-H(10E)	109.5	N(6B)-C(20B)-C(21B)	123.1(18)
H(10D)-C(10B)-H(10E)	109.5	N(5B)-C(20B)-C(21B)	124.1(17)
C(9B)-C(10B)-H(10F)	109.5	C(20B)-C(21B)-H(21D)	109.5
H(10D)-C(10B)-H(10F)	109.5	C(20B)-C(21B)-H(21E)	109.5
H(10E)-C(10B)-H(10F)	109.5	H(21D)-C(21B)-H(21E)	109.5
N(3B)-C(11B)-H(11D)	109.5	C(20B)-C(21B)-H(21F)	109.5
N(3B)-C(11B)-H(11E)	109.5	H(21D)-C(21B)-H(21F)	109.5
H(11D)-C(11B)-H(11E)	109.5	H(21E)-C(21B)-H(21F)	109.5
N(3B)-C(11B)-H(11F)	109.5	N(6B)-C(22B)-H(22D)	109.5
H(11D)-C(11B)-H(11F)	109.5	N(6B)-C(22B)-H(22E)	109.5
H(11E)-C(11B)-H(11F)	109.5	H(22D)-C(22B)-H(22E)	109.5
N(4B)-C(12B)-C(13B)	124.6(17)	N(6B)-C(22B)-H(22F)	109.5
N(4B)-C(12B)-H(12B)	117.7	H(22D)-C(22B)-H(22F)	109.5
C(13B)-C(12B)-H(12B)	117.7	H(22E)-C(22B)-H(22F)	109.5
C(14B)-C(13B)-C(12B)	114(2)	C(5B)-N(1B)-C(1B)	117.8(16)
C(14B)-C(13B)-H(13B)	123.0	C(5B)-N(1B)-Zn(1B)	126.6(11)
C(12B)-C(13B)-H(13B)	122.9	C(1B)-N(1B)-Zn(1B)	114.7(12)
C(13B)-C(14B)-C(15B)	128(2)	C(9B)-N(2B)-C(7B)	105.4(13)
C(13B)-C(14B)-H(14B)	116.2	C(9B)-N(2B)-Zn(1B)	133.4(12)
C(15B)-C(14B)-H(14B)	116.2	C(7B)-N(2B)-Zn(1B)	120.7(11)
C(16B)-C(15B)-C(14B)	105.9(15)	C(11B)-N(3B)-C(8B)	123.3(15)
C(16B)-C(15B)-H(15B)	127.0	C(11B)-N(3B)-C(9B)	131.9(15)
C(14B)-C(15B)-H(15B)	127.0	C(8B)-N(3B)-C(9B)	104.8(13)
N(4B)-C(16B)-C(15B)	128.0(15)	C(12B)-N(4B)-C(16B)	118.6(16)
N(4B)-C(16B)-C(17B)	120.2(15)	C(12B)-N(4B)-Zn(1B)	119.9(13)
C(15B)-C(16B)-C(17B)	111.1(14)	C(16B)-N(4B)-Zn(1B)	120.6(11)
C(18B)-C(17B)-C(16B)	132.8(17)	C(18B)-N(5B)-C(20B)	105.2(15)
C(18B)-C(17B)-H(17B)	113.6	C(18B)-N(5B)-Zn(1B)	123.7(13)
C(16B)-C(17B)-H(17B)	113.6	C(20B)-N(5B)-Zn(1B)	131.0(12)
C(17B)-C(18B)-N(5B)	126.2(17)	C(20B)-N(6B)-C(19B)	112.2(17)
C(17B)-C(18B)-C(19B)	127.4(18)	C(20B)-N(6B)-C(22B)	120.6(16)
N(5B)-C(18B)-C(19B)	106.4(16)	C(19B)-N(6B)-C(22B)	126.7(16)
O(2B)-C(19B)-N(6B)	130(2)	O(1BL)-N(1BL)-O(2BL)	117.1(12)

O(1BL)-N(1BL)-O(3BL)	134(2)	O(2S)-C(2S)-H(2S3)	109.8
O(2BL)-N(1BL)-O(3BL)	98(2)	H(2S1)-C(2S)-H(2S3)	109.5
N(1BL)-O(1BL)-Zn(1B)	96.8(11)	H(2S2)-C(2S)-H(2S3)	109.5
N(1BL)-O(2BL)-Zn(1B)	89.4(11)		
N(5B)-Zn(1B)-N(2B)	112.2(3)		
N(5B)-Zn(1B)-N(1B)	102.4(6)		
N(2B)-Zn(1B)-N(1B)	89.6(5)		
N(5B)-Zn(1B)-O(1BL)	94.4(6)		
N(2B)-Zn(1B)-O(1BL)	153.4(6)		
N(1B)-Zn(1B)-O(1BL)	85.5(5)		
N(5B)-Zn(1B)-N(4B)	91.4(6)		
N(2B)-Zn(1B)-N(4B)	97.8(6)		
N(1B)-Zn(1B)-N(4B)	160.7(3)		
O(1BL)-Zn(1B)-N(4B)	79.9(6)		
N(5B)-Zn(1B)-O(2BL)	150.3(6)		
N(2B)-Zn(1B)-O(2BL)	97.2(6)		
N(1B)-Zn(1B)-O(2BL)	81.0(5)		
O(1BL)-Zn(1B)-O(2BL)	56.2(3)		
N(4B)-Zn(1B)-O(2BL)	80.4(5)		
O(2A)-N(1A)-O(1A)	117.0(16)		
O(2A)-N(1A)-O(3A)	121.1(15)		
O(1A)-N(1A)-O(3A)	121.6(13)		
O(4A)-N(2A)-O(6A)	124(2)		
O(4A)-N(2A)-O(5A)	117.4(17)		
O(6A)-N(2A)-O(5A)	118.0(17)		
C(1S)-O(1S)-H(1S)	113.3		
O(1S)-C(1S)-H(1S1)	109.7		
O(1S)-C(1S)-H(1S2)	113.1		
H(1S1)-C(1S)-H(1S2)	109.5		
O(1S)-C(1S)-H(1S3)	105.6		
H(1S1)-C(1S)-H(1S3)	109.5		
H(1S2)-C(1S)-H(1S3)	109.5		
C(2S)-O(2S)-H(2S)	106.2		
O(2S)-C(2S)-H(2S1)	105.4		
O(2S)-C(2S)-H(2S2)	113.1		
H(2S1)-C(2S)-H(2S2)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for JK885a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	63(10)	41(10)	56(11)	-21(9)	2(9)	-23(8)
C(2)	49(8)	73(12)	39(8)	18(8)	-3(7)	-15(8)
C(3)	68(11)	47(9)	35(8)	-2(7)	7(8)	4(8)
C(4)	68(10)	40(9)	49(10)	15(8)	27(9)	8(8)
C(5)	77(13)	51(12)	34(9)	2(8)	7(9)	8(10)
C(6)	58(9)	50(10)	26(7)	4(7)	12(7)	28(8)
C(7)	37(8)	63(12)	56(11)	17(9)	-22(8)	-19(8)
C(8)	31(8)	101(14)	28(7)	5(8)	-2(7)	5(8)
C(9)	67(12)	64(13)	34(9)	18(9)	-5(9)	3(10)
C(10)	73(12)	80(15)	68(13)	-25(11)	6(11)	16(11)
C(11)	30(7)	128(17)	39(9)	2(11)	-6(7)	5(9)
C(12)	56(10)	81(14)	56(11)	-14(11)	19(9)	-22(10)
C(13)	110(16)	61(13)	62(12)	15(9)	16(11)	-40(11)
C(14)	87(14)	71(14)	80(15)	-33(11)	46(13)	-35(11)
C(15)	57(11)	74(14)	61(13)	-11(10)	-2(10)	-17(10)
C(16)	33(9)	72(14)	64(12)	-19(10)	8(9)	11(9)
C(17)	40(9)	69(14)	93(15)	-25(12)	-2(10)	16(9)
C(18)	41(8)	51(11)	27(7)	-6(7)	15(7)	-10(7)
C(19)	72(12)	44(10)	77(14)	-6(9)	15(11)	15(9)
C(20)	36(9)	72(14)	67(13)	-2(11)	8(9)	10(9)
C(21)	36(8)	81(14)	62(11)	-35(10)	-1(8)	-12(9)
C(22)	133(17)	60(13)	59(13)	16(11)	9(12)	16(13)
N(1)	29(6)	73(10)	69(10)	20(8)	5(6)	11(6)
N(2)	43(7)	49(10)	80(11)	16(8)	18(7)	-3(7)
N(3)	67(10)	56(10)	56(9)	-14(7)	12(8)	-12(8)

N(4)	63(9)	48(8)	26(6)	2(6)	6(6)	11(7)
N(5)	49(8)	68(11)	21(6)	4(6)	-16(6)	6(8)
N(6)	40(7)	77(11)	32(7)	-12(7)	-4(6)	-14(7)
O(1)	44(6)	123(11)	60(8)	-5(7)	14(6)	1(7)
O(2)	49(7)	119(12)	59(8)	2(7)	-23(6)	-3(7)
N(1L)	84(8)	57(6)	54(5)	-14(11)	12(6)	-28(10)
O(1L)	60(8)	92(12)	79(10)	15(9)	6(8)	-2(9)
O(2L)	43(6)	66(9)	34(6)	-1(6)	13(6)	4(6)
O(3L)	212(12)	67(7)	174(12)	-44(14)	113(9)	17(15)
Zn(1)	42(1)	60(1)	47(1)	1(2)	0(1)	-5(2)
N(1B)	41(7)	57(9)	38(7)	1(6)	7(6)	5(6)
N(2B)	36(6)	51(8)	40(7)	3(7)	0(6)	-13(6)
N(3B)	52(8)	99(13)	42(8)	15(8)	10(7)	-5(9)
N(4B)	64(9)	49(9)	58(9)	-7(7)	0(7)	15(7)
N(5B)	46(7)	74(11)	53(9)	20(8)	16(7)	-12(7)
N(6B)	63(9)	50(9)	45(8)	-13(7)	-5(8)	-5(8)
O(1B)	28(4)	46(6)	72(7)	-11(5)	-6(5)	8(4)
O(2B)	84(9)	158(16)	68(9)	-38(9)	-6(8)	-19(9)
N(1BL)	98(10)	81(9)	54(6)	35(12)	29(7)	3(13)
O(1BL)	48(7)	79(10)	85(10)	-4(8)	-8(7)	0(7)
O(2BL)	72(9)	87(11)	55(8)	-2(8)	13(7)	-7(8)
O(3BL)	156(13)	49(6)	96(7)	-11(7)	17(11)	1(6)
Zn(1B)	41(1)	56(1)	58(1)	1(2)	-1(1)	1(2)
N(1A)	67(10)	83(11)	50(9)	14(8)	8(8)	4(8)
O(1A)	195(18)	136(18)	102(13)	-11(11)	17(13)	35(14)
O(2A)	134(11)	125(12)	126(13)	12(9)	50(10)	4(9)
O(3A)	127(12)	74(11)	162(15)	10(11)	-44(11)	-20(10)
N(2A)	56(10)	135(19)	91(15)	-26(12)	-7(10)	-34(11)
O(4A)	117(12)	87(12)	91(10)	-27(9)	22(9)	-14(10)
O(5A)	58(7)	51(9)	167(15)	0(9)	-1(8)	1(6)
O(6A)	97(9)	284(19)	56(7)	-54(9)	39(7)	-91(11)
O(1S)	53(7)	94(10)	47(6)	-20(6)	-8(6)	1(6)
C(1S)	88(12)	113(18)	72(12)	13(11)	-50(10)	-24(11)
O(2S)	79(12)	71(12)	47(10)	6(9)	34(9)	-7(10)
C(2S)	63(13)	55(13)	33(11)	-2(10)	37(10)	-9(11)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
H(1A)	3367	3094	4688	64
H(2)	2544	4857	5247	64
H(3A)	988	5221	4904	60
H(4A)	610	3710	4047	63
H(6A)	862	1747	3254	54
H(10A)	4267	-642	2501	111
H(10B)	3995	-251	1827	111
H(10C)	3813	-2135	2110	111
H(11A)	1570	-1250	1325	98
H(11B)	2380	-2502	1454	98
H(11C)	2533	-566	1205	98
H(12A)	3675	3255	2686	77
H(13A)	4763	4881	2196	93
H(14A)	6151	4832	2455	95
H(15A)	6552	3338	3308	77
H(17A)	6224	1718	4073	80
H(21A)	2851	-629	4953	89
H(21B)	3247	-375	5606	89
H(21C)	3332	-2223	5276	89
H(22A)	4364	-1939	5978	127
H(22B)	5023	-448	6194	127
H(22C)	5386	-2211	5903	127
H(1BA)	8144	5768	4918	103
H(2BA)	7045	4955	5526	74
H(3BA)	5560	5134	5170	52
H(4BA)	5372	6027	4258	62
H(6BA)	5784	8035	3411	50
H(10D)	9370	9673	2808	98
H(10E)	9002	11501	2568	98
H(10F)	9047	9847	2134	98
H(11D)	6722	11620	1759	140

H(11E)	7638	10864	1552	140
H(11F)	7599	12560	1967	140
H(12B)	8980	6077	2451	46
H(13B)	10083	4708	1879	92
H(14B)	11414	4810	2248	108
H(15B)	11824	6578	3136	71
H(17B)	11289	7608	3984	77
H(21D)	8203	11281	5146	95
H(21E)	7823	9466	4904	95
H(21F)	7964	11068	4458	95
H(22D)	9075	12194	5473	88
H(22E)	10050	12827	5366	88
H(22F)	9856	11284	5827	88
H(1S)	-121	5662	5566	97
H(1S1)	343	8262	6221	136
H(1S2)	1165	7722	5832	136
H(1S3)	708	6304	6249	136
H(2S)	7602	6738	1792	98
H(2S1)	6020	7242	1565	75
H(2S2)	6602	6263	1082	75
H(2S3)	6830	8226	1275	75

Table S7. Torsion angles [°] for JK885a.

N(1)-C(1)-C(2)-C(3)	1(3)
C(1)-C(2)-C(3)-C(4)	0(2)
C(2)-C(3)-C(4)-C(5)	1(3)
C(3)-C(4)-C(5)-N(1)	-3(3)
C(3)-C(4)-C(5)-C(6)	-176.9(17)
N(1)-C(5)-C(6)-C(7)	-6(3)
C(4)-C(5)-C(6)-C(7)	168.7(18)
C(5)-C(6)-C(7)-N(2)	3(3)
C(5)-C(6)-C(7)-C(8)	-177.2(18)
C(6)-C(7)-C(8)-O(1)	2(3)
N(2)-C(7)-C(8)-O(1)	-178.4(19)
C(6)-C(7)-C(8)-N(3)	179.8(19)
N(2)-C(7)-C(8)-N(3)	-0.5(18)
N(4)-C(12)-C(13)-C(14)	1(3)
C(12)-C(13)-C(14)-C(15)	-4(4)
C(13)-C(14)-C(15)-C(16)	1(3)
C(14)-C(15)-C(16)-N(4)	5(3)
C(14)-C(15)-C(16)-C(17)	-176.4(19)
C(15)-C(16)-C(17)-C(18)	173(2)
N(4)-C(16)-C(17)-C(18)	-9(3)
C(16)-C(17)-C(18)-N(5)	6(4)
C(16)-C(17)-C(18)-C(19)	-173(2)
N(5)-C(18)-C(19)-O(2)	-177(2)
C(17)-C(18)-C(19)-O(2)	2(3)
N(5)-C(18)-C(19)-N(6)	3(2)
C(17)-C(18)-C(19)-N(6)	-177.4(16)
C(6)-C(5)-N(1)-C(1)	177.1(16)
C(4)-C(5)-N(1)-C(1)	3(2)
C(6)-C(5)-N(1)-Zn(1)	-9(3)
C(4)-C(5)-N(1)-Zn(1)	176.9(13)
C(2)-C(1)-N(1)-C(5)	-2(3)
C(2)-C(1)-N(1)-Zn(1)	-177.1(18)
N(3)-C(9)-N(2)-C(7)	-10(2)
C(10)-C(9)-N(2)-C(7)	179.4(18)

N(3)-C(9)-N(2)-Zn(1)	162.1(13)
C(10)-C(9)-N(2)-Zn(1)	-8(3)
C(6)-C(7)-N(2)-C(9)	-174.1(19)
C(8)-C(7)-N(2)-C(9)	6.2(18)
C(6)-C(7)-N(2)-Zn(1)	12(2)
C(8)-C(7)-N(2)-Zn(1)	-167.7(10)
O(1)-C(8)-N(3)-C(9)	172(2)
C(7)-C(8)-N(3)-C(9)	-6(2)
O(1)-C(8)-N(3)-C(11)	6(3)
C(7)-C(8)-N(3)-C(11)	-171.9(15)
N(2)-C(9)-N(3)-C(8)	11(2)
C(10)-C(9)-N(3)-C(8)	-178.7(19)
N(2)-C(9)-N(3)-C(11)	176.2(17)
C(10)-C(9)-N(3)-C(11)	-13(3)
C(13)-C(12)-N(4)-C(16)	4(3)
C(13)-C(12)-N(4)-Zn(1)	-174.9(13)
C(15)-C(16)-N(4)-C(12)	-8(3)
C(17)-C(16)-N(4)-C(12)	173.5(18)
C(15)-C(16)-N(4)-Zn(1)	171.4(15)
C(17)-C(16)-N(4)-Zn(1)	-7(2)
N(6)-C(20)-N(5)-C(18)	4(2)
C(21)-C(20)-N(5)-C(18)	172.7(19)
N(6)-C(20)-N(5)-Zn(1)	166.0(12)
C(21)-C(20)-N(5)-Zn(1)	-25(3)
C(19)-C(18)-N(5)-C(20)	-4(2)
C(17)-C(18)-N(5)-C(20)	176.4(18)
C(19)-C(18)-N(5)-Zn(1)	-169.0(12)
C(17)-C(18)-N(5)-Zn(1)	12(2)
N(5)-C(20)-N(6)-C(22)	176(2)
C(21)-C(20)-N(6)-C(22)	5(3)
N(5)-C(20)-N(6)-C(19)	-2(2)
C(21)-C(20)-N(6)-C(19)	-172.5(16)
O(2)-C(19)-N(6)-C(22)	1(3)
C(18)-C(19)-N(6)-C(22)	-178.8(19)
O(2)-C(19)-N(6)-C(20)	179.1(18)
C(18)-C(19)-N(6)-C(20)	-0.9(19)

O(3L)-N(1L)-O(1L)-Zn(1)	168(3)
O(2L)-N(1L)-O(1L)-Zn(1)	2(2)
O(3L)-N(1L)-O(2L)-Zn(1)	-170(2)
O(1L)-N(1L)-O(2L)-Zn(1)	-2(2)
C(5)-N(1)-Zn(1)-N(2)	17.5(16)
C(1)-N(1)-Zn(1)-N(2)	-168.7(14)
C(5)-N(1)-Zn(1)-N(5)	-152.3(16)
C(1)-N(1)-Zn(1)-N(5)	21.4(14)
C(5)-N(1)-Zn(1)-N(4)	112.6(15)
C(1)-N(1)-Zn(1)-N(4)	-73.7(15)
C(5)-N(1)-Zn(1)-O(1L)	-69(2)
C(1)-N(1)-Zn(1)-O(1L)	105.1(17)
C(5)-N(1)-Zn(1)-O(2L)	-63.3(16)
C(1)-N(1)-Zn(1)-O(2L)	110.4(13)
C(9)-N(2)-Zn(1)-N(1)	171.7(19)
C(7)-N(2)-Zn(1)-N(1)	-16.9(12)
C(9)-N(2)-Zn(1)-N(5)	-63(4)
C(7)-N(2)-Zn(1)-N(5)	108(3)
C(9)-N(2)-Zn(1)-N(4)	62.6(19)
C(7)-N(2)-Zn(1)-N(4)	-126.0(12)
C(9)-N(2)-Zn(1)-O(1L)	-34.1(19)
C(7)-N(2)-Zn(1)-O(1L)	137.3(12)
C(9)-N(2)-Zn(1)-O(2L)	-91.2(19)
C(7)-N(2)-Zn(1)-O(2L)	80.2(12)
C(20)-N(5)-Zn(1)-N(1)	71.5(19)
C(18)-N(5)-Zn(1)-N(1)	-127.8(13)
C(20)-N(5)-Zn(1)-N(2)	-53(5)
C(18)-N(5)-Zn(1)-N(2)	108(3)
C(20)-N(5)-Zn(1)-N(4)	-179.0(18)
C(18)-N(5)-Zn(1)-N(4)	-18.3(14)
C(20)-N(5)-Zn(1)-O(1L)	-82.4(18)
C(18)-N(5)-Zn(1)-O(1L)	78.3(14)
C(20)-N(5)-Zn(1)-O(2L)	-25.3(18)
C(18)-N(5)-Zn(1)-O(2L)	135.4(14)
C(12)-N(4)-Zn(1)-N(1)	-65.3(15)
C(16)-N(4)-Zn(1)-N(1)	115.3(13)

C(12)-N(4)-Zn(1)-N(2)	26.3(14)
C(16)-N(4)-Zn(1)-N(2)	-153.0(14)
C(12)-N(4)-Zn(1)-N(5)	-163.7(14)
C(16)-N(4)-Zn(1)-N(5)	17.0(14)
C(12)-N(4)-Zn(1)-O(1L)	115.2(13)
C(16)-N(4)-Zn(1)-O(1L)	-64.1(14)
C(12)-N(4)-Zn(1)-O(2L)	105.5(15)
C(16)-N(4)-Zn(1)-O(2L)	-73.8(18)
N(1L)-O(1L)-Zn(1)-N(1)	5(2)
N(1L)-O(1L)-Zn(1)-N(2)	-81.3(14)
N(1L)-O(1L)-Zn(1)-N(5)	92.7(14)
N(1L)-O(1L)-Zn(1)-N(4)	-175.9(14)
N(1L)-O(1L)-Zn(1)-O(2L)	-1.0(14)
N(1L)-O(2L)-Zn(1)-N(1)	-176.4(11)
N(1L)-O(2L)-Zn(1)-N(2)	94.8(11)
N(1L)-O(2L)-Zn(1)-N(5)	-79.5(11)
N(1L)-O(2L)-Zn(1)-N(4)	12.3(17)
N(1L)-O(2L)-Zn(1)-O(1L)	0.9(12)
N(1B)-C(1B)-C(2B)-C(3B)	6(3)
C(1B)-C(2B)-C(3B)-C(4B)	0(3)
C(2B)-C(3B)-C(4B)-C(5B)	-10(3)
C(3B)-C(4B)-C(5B)-N(1B)	14(3)
C(3B)-C(4B)-C(5B)-C(6B)	-170.5(18)
N(1B)-C(5B)-C(6B)-C(7B)	2(3)
C(4B)-C(5B)-C(6B)-C(7B)	-172.9(17)
C(5B)-C(6B)-C(7B)-C(8B)	-171.7(17)
C(5B)-C(6B)-C(7B)-N(2B)	-5(3)
C(6B)-C(7B)-C(8B)-O(1B)	-10(3)
N(2B)-C(7B)-C(8B)-O(1B)	-179.1(17)
C(6B)-C(7B)-C(8B)-N(3B)	168.9(16)
N(2B)-C(7B)-C(8B)-N(3B)	0(2)
N(4B)-C(12B)-C(13B)-C(14B)	-5(3)
C(12B)-C(13B)-C(14B)-C(15B)	-4(4)
C(13B)-C(14B)-C(15B)-C(16B)	11(3)
C(14B)-C(15B)-C(16B)-N(4B)	-11(3)
C(14B)-C(15B)-C(16B)-C(17B)	178.2(16)

N(4B)-C(16B)-C(17B)-C(18B)	-3(3)
C(15B)-C(16B)-C(17B)-C(18B)	168(2)
C(16B)-C(17B)-C(18B)-N(5B)	10(4)
C(16B)-C(17B)-C(18B)-C(19B)	-170.5(19)
C(17B)-C(18B)-C(19B)-O(2B)	-9(4)
N(5B)-C(18B)-C(19B)-O(2B)	171(2)
C(17B)-C(18B)-C(19B)-N(6B)	171.0(19)
N(5B)-C(18B)-C(19B)-N(6B)	-9(2)
C(6B)-C(5B)-N(1B)-C(1B)	177.5(16)
C(4B)-C(5B)-N(1B)-C(1B)	-7(2)
C(6B)-C(5B)-N(1B)-Zn(1B)	-14(2)
C(4B)-C(5B)-N(1B)-Zn(1B)	161.8(12)
C(2B)-C(1B)-N(1B)-C(5B)	-2(3)
C(2B)-C(1B)-N(1B)-Zn(1B)	-171.7(17)
N(3B)-C(9B)-N(2B)-C(7B)	0(2)
C(10B)-C(9B)-N(2B)-C(7B)	-177.3(17)
N(3B)-C(9B)-N(2B)-Zn(1B)	172.1(12)
C(10B)-C(9B)-N(2B)-Zn(1B)	-6(3)
C(6B)-C(7B)-N(2B)-C(9B)	-167.9(18)
C(8B)-C(7B)-N(2B)-C(9B)	0(2)
C(6B)-C(7B)-N(2B)-Zn(1B)	19(2)
C(8B)-C(7B)-N(2B)-Zn(1B)	-173.2(12)
O(1B)-C(8B)-N(3B)-C(11B)	-4(3)
C(7B)-C(8B)-N(3B)-C(11B)	176.9(18)
O(1B)-C(8B)-N(3B)-C(9B)	179.5(16)
C(7B)-C(8B)-N(3B)-C(9B)	0.2(19)
N(2B)-C(9B)-N(3B)-C(11B)	-177(2)
C(10B)-C(9B)-N(3B)-C(11B)	1(3)
N(2B)-C(9B)-N(3B)-C(8B)	0(2)
C(10B)-C(9B)-N(3B)-C(8B)	177.6(15)
C(13B)-C(12B)-N(4B)-C(16B)	5(3)
C(13B)-C(12B)-N(4B)-Zn(1B)	-164.3(15)
C(15B)-C(16B)-N(4B)-C(12B)	5(3)
C(17B)-C(16B)-N(4B)-C(12B)	174.7(16)
C(15B)-C(16B)-N(4B)-Zn(1B)	173.7(14)
C(17B)-C(16B)-N(4B)-Zn(1B)	-17(2)

C(17B)-C(18B)-N(5B)-C(20B)	-175(2)
C(19B)-C(18B)-N(5B)-C(20B)	5(2)
C(17B)-C(18B)-N(5B)-Zn(1B)	7(3)
C(19B)-C(18B)-N(5B)-Zn(1B)	-172.5(13)
N(6B)-C(20B)-N(5B)-C(18B)	2(2)
C(21B)-C(20B)-N(5B)-C(18B)	174.9(18)
N(6B)-C(20B)-N(5B)-Zn(1B)	178.6(13)
C(21B)-C(20B)-N(5B)-Zn(1B)	-8(3)
N(5B)-C(20B)-N(6B)-C(19B)	-8(2)
C(21B)-C(20B)-N(6B)-C(19B)	178.3(19)
N(5B)-C(20B)-N(6B)-C(22B)	178.7(14)
C(21B)-C(20B)-N(6B)-C(22B)	5(3)
O(2B)-C(19B)-N(6B)-C(20B)	-169(3)
C(18B)-C(19B)-N(6B)-C(20B)	11(2)
O(2B)-C(19B)-N(6B)-C(22B)	3(4)
C(18B)-C(19B)-N(6B)-C(22B)	-177.0(15)
O(2BL)-N(1BL)-O(1BL)-Zn(1B)	-8(2)
O(3BL)-N(1BL)-O(1BL)-Zn(1B)	-143(3)
O(1BL)-N(1BL)-O(2BL)-Zn(1B)	7(2)
O(3BL)-N(1BL)-O(2BL)-Zn(1B)	156.6(13)
C(18B)-N(5B)-Zn(1B)-N(2B)	-117.7(13)
C(20B)-N(5B)-Zn(1B)-N(2B)	65.9(19)
C(18B)-N(5B)-Zn(1B)-N(1B)	147.6(14)
C(20B)-N(5B)-Zn(1B)-N(1B)	-28.9(18)
C(18B)-N(5B)-Zn(1B)-O(1BL)	61.3(15)
C(20B)-N(5B)-Zn(1B)-O(1BL)	-115.2(17)
C(18B)-N(5B)-Zn(1B)-N(4B)	-18.7(15)
C(20B)-N(5B)-Zn(1B)-N(4B)	164.8(17)
C(18B)-N(5B)-Zn(1B)-O(2BL)	54(2)
C(20B)-N(5B)-Zn(1B)-O(2BL)	-122.4(17)
C(9B)-N(2B)-Zn(1B)-N(5B)	65(2)
C(7B)-N(2B)-Zn(1B)-N(5B)	-124.2(12)
C(9B)-N(2B)-Zn(1B)-N(1B)	168.4(18)
C(7B)-N(2B)-Zn(1B)-N(1B)	-20.9(13)
C(9B)-N(2B)-Zn(1B)-O(1BL)	-112.4(19)
C(7B)-N(2B)-Zn(1B)-O(1BL)	58(2)

C(9B)-N(2B)-Zn(1B)-N(4B)	-29.5(18)
C(7B)-N(2B)-Zn(1B)-N(4B)	141.1(13)
C(9B)-N(2B)-Zn(1B)-O(2BL)	-110.7(18)
C(7B)-N(2B)-Zn(1B)-O(2BL)	59.9(13)
C(5B)-N(1B)-Zn(1B)-N(5B)	133.5(14)
C(1B)-N(1B)-Zn(1B)-N(5B)	-57.8(14)
C(5B)-N(1B)-Zn(1B)-N(2B)	20.8(14)
C(1B)-N(1B)-Zn(1B)-N(2B)	-170.4(14)
C(5B)-N(1B)-Zn(1B)-O(1BL)	-133.0(15)
C(1B)-N(1B)-Zn(1B)-O(1BL)	35.8(13)
C(5B)-N(1B)-Zn(1B)-N(4B)	-92(2)
C(1B)-N(1B)-Zn(1B)-N(4B)	77(3)
C(5B)-N(1B)-Zn(1B)-O(2BL)	-76.5(14)
C(1B)-N(1B)-Zn(1B)-O(2BL)	92.2(14)
N(1BL)-O(1BL)-Zn(1B)-N(5B)	-171.2(14)
N(1BL)-O(1BL)-Zn(1B)-N(2B)	7(2)
N(1BL)-O(1BL)-Zn(1B)-N(1B)	86.7(14)
N(1BL)-O(1BL)-Zn(1B)-N(4B)	-80.6(14)
N(1BL)-O(1BL)-Zn(1B)-O(2BL)	4.6(14)
C(12B)-N(4B)-Zn(1B)-N(5B)	-167.9(15)
C(16B)-N(4B)-Zn(1B)-N(5B)	23.4(14)
C(12B)-N(4B)-Zn(1B)-N(2B)	-55.3(15)
C(16B)-N(4B)-Zn(1B)-N(2B)	136.0(14)
C(12B)-N(4B)-Zn(1B)-N(1B)	56(3)
C(16B)-N(4B)-Zn(1B)-N(1B)	-112(2)
C(12B)-N(4B)-Zn(1B)-O(1BL)	97.8(15)
C(16B)-N(4B)-Zn(1B)-O(1BL)	-70.8(14)
C(12B)-N(4B)-Zn(1B)-O(2BL)	40.7(14)
C(16B)-N(4B)-Zn(1B)-O(2BL)	-127.9(14)
N(1BL)-O(2BL)-Zn(1B)-N(5B)	4.3(18)
N(1BL)-O(2BL)-Zn(1B)-N(2B)	176.6(12)
N(1BL)-O(2BL)-Zn(1B)-N(1B)	-94.9(12)
N(1BL)-O(2BL)-Zn(1B)-O(1BL)	-4.3(13)
N(1BL)-O(2BL)-Zn(1B)-N(4B)	79.9(12)

Symmetry transformations used to generate equivalent atoms:

References and Notes

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7 Note: The ^{1}H NMR spectra of (*Z*)-1,2-dimethyl-4-(pyridin-2-ylmethylene)-1*H*-imidazol-5(4*H*)-one and of its Zn(II) complex were not of the first order and the coupling constants were not optimized but were identified by visual inspection.
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