Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2015

Electronic Supporting Information for:

Structural Features and Near Infra-Red (NIR) Luminescence of Isomeric Yb(III) Bipyridyl-*N,N*'-Dioxide Coordination Polymers.

Gail M. Sequeira,[a] Wayne Y. Tan[a] and Evan G. Moore*[a]

School of Chemistry and Molecular Biosciences,

The University of Queensland, Brisbane, QLD, 4072, Australia.

Ph: +61 (0) 7 3365 3862, Fax: +61 (0) 7 3365 4273,

E-mail: egmoore@uq.edu.au.

Table of Contents:

1.1 Additional Crystallographic Refinement Details

1.2 Additional UV-Vis Spectra

1.3 Summary of Atomic Coordinates and ESP charges from DFT

1.4 References

1.1 Additional Crystallographic Refinement Details

Data were with collected using an Oxford Gemini Ultra employing either confocal mirror monochromated Cu-K_α radiation generated from a sealed tube (1.5418 Å) or graphite-monochromated Mo-K_α radiation generated from a sealed tube (0.71073 Å) with ω and ψ scans at 190(2) K.[1] Data integration and reduction were undertaken with CrysAlisPro.[1] Subsequent computations were carried out using the WinGX-32 graphical user interface.[2] Absorption corrections were applied to the data using CrysAlisPro.[1] Structures were solved by direct methods using SIR97[3] then refined and extended with SHELXL-2014.[4] In general, non-hydrogen atoms with occupancies greater than 0.5 were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Oxygen and nitrogen bound hydrogen atoms were first located in the difference Fourier map before refinement. Disorder was modelled using standard crystallographic methods including constraints, restraints and rigid bodies where necessary, with more specific details of the crystal data and structure refinement for each compound are given in Tables S1-S4 below.

Table S1. Crystal data and structure refinement details for $\{[Yb(4,4'\text{-bpdo})(NO_3)_3(CH_3OH)]\}_\infty$ (1)

No major difficulties were encountered during the refinement. One of the nitrate anions was disordered over two positions, which were modelled with 50% occupancy, with the coordinated MeOH molecule similarly disordered over two sites with 50% occupancy. The H atom of the coordinated MeOH could not be located on the difference map, and was not modelled.

Identification code	(**1**)
Empirical formula	C22 H24 N10 O24 Yb2
Formula weight	1158.56
Temperature	190(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, C 2/c
Unit cell dimensions	a = 15.319(2) A alpha = 90 deg.

	b = 8.1376(13) A	beta = 93.458(10) deg.
	c = 13.8906(16) A	gamma = 90 deg.
Volume	1728.4(4) A^3	
Z, Calculated density	2, 2.226 Mg/m^3	
Absorption coefficient	5.490 mm^-1	
F(000)	1116	
Crystal size	0.3 x 0.2 x 0.2 mm	
Theta range for data collection	2.835 to 28.899 deg.	
Limiting indices	-20<=h<=19, -11<=k<=10, -12<=l<=17	
Reflections collected / unique	6212 / 2045 [R(int) = 0.0759]	
Completeness to theta = 25.242	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.86961	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2045 / 0 / 160	
Goodness-of-fit on F^2	0.971	
Final R indices [I>2sigma(I)]	R1 = 0.0516, wR2 = 0.0918	
R indices (all data)	R1 = 0.0896, wR2 = 0.1036	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.882 and -1.085 e.A^-3	

Table S2. Crystal data and structure refinement details for $\{[Yb(3,3'\text{-bpdo})(NO_3)_3(CH_3OH)]\}_\infty$ (2)

No major difficulties were encountered during the refinement. One of the nitrate anions was disordered over two positions, which were modelled with ca. 80% and 20 occupancies. Only the major component was refined anisotropically. Similarly, the coordinated MeOH molecule was also disordered over two sites with 68% and 32% occupancy, and only the major component was refined anisotropically. The H atom of the coordinated MeOH could not be located on the difference map, and was not modelled.

Identification code	(**2**)	
Empirical formula	C22 H24 N10 O24 Yb2	
Formula weight	1158.57	
Temperature	190(2) K	
Wavelength	1.5418 A	
Crystal system, space group	Monoclinic, C 2/c	
Unit cell dimensions	a = 34.4809(13) A	alpha = 90 deg.
	b = 7.8110(17) A	beta = 124.9660(10) deg.
	c = 15.8568(6) A	gamma = 90 deg.
Volume	3499.8(8) A^3	
Z, Calculated density	4, 2.195 Mg/m^3	
Absorption coefficient	10.631 mm^-1	
F(000)	2224	
Crystal size	0.38 x 0.21 x 0.19 mm	
Theta range for data collection	3.128 to 62.494 deg.	
Limiting indices	-33<=h<=39, -8<=k<=8, -18<=l<=11	
Reflections collected / unique	11026 / 2772 [R(int) = 0.0359]	
Completeness to theta = 62.494	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.52678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2772 / 1 / 287	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0245, wR2 = 0.0630	
R indices (all data)	R1 = 0.0266, wR2 = 0.0652	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.707 and -1.078 e.A^-3	

Table S3. Crystal data and structure refinement details for $\{[Yb(4,4'\text{-bpdo})_4](CF_3SO_3)_3(CH_3OH)_2(CHCl_3)_2\}_\infty$ (3)

The anions and solvent within this structure were found to be extremely disordered. Only four of the nine triflate positions in the asymmetric unit could be successfully located. These were modeled over eight positions each with occupancies ranging from 0.25 to 0.75 and required the use of rigid body restraints and thermal parameter restraints to facilitate realistic modeling. Only one 0.25 occupancy chloroform solvent molecule could be successfully located and it required bond length constraints for realistic modeling. The remaining solvent and anions were smeared over a large region of volume and no satisfactory model could be found, despite multiple attempts including the use of rigid bodies. Accordingly, this contribution to the electron density was treated with the SQUEEZE[5] function of PLATON[6] which resulted in far more satisfactory residuals. Despite these minor problems the connectivity of the structure is unambiguous.

Identification code	(**3**)	
Empirical formula	C47 H42 Cl6 F9 N8 O19 S3 Yb	
Formula weight	1675.80	
Temperature	190(2) K	
Wavelength	1.5418 A	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	a = 24.260(11) A	alpha = 83.566(3) deg.
	b = 24.415(8) A	beta = 62.292(4) deg.
	c = 24.531(8) A	gamma = 61.717(4) deg.
Volume	11218(7) A^3	
Z, Calculated density	6, 1.488 Mg/m^3	
Absorption coefficient	5.843 mm^-1	
F(000)	4998	
Crystal size	0.3 x 0.3 x 0.3 mm	
Theta range for data collection	3.117 to 62.347 deg.	
Limiting indices	-21<=h<=26, -27<=k<=28, -27<=l<=26	
Reflections collected / unique	49687 / 30412 [R(int) = 0.0439]	

Completeness to theta = 67.680	74.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.51694
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	30412 / 87 / 1635
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0679, wR2 = 0.1854
R indices (all data)	R1 = 0.0790, wR2 = 0.1996
Extinction coefficient	n/a
Largest diff. peak and hole	2.653 and -1.825 e.A^-3

Table S4. Crystal data and structure refinement details for $\{[Yb(3,3'\text{-bpdo})_3(CF_3SO_3)](CF_3SO_3)_2(CH_3OH)_{0.5}(CHCl_3)_3\}_\infty$ (4)

No major difficulties were encountered during the refinement. One of the triflate anions was found to be disordered over two positions, which were modelled with ca. 67% and 43% occupancies, and required the use of rigid body restraints and thermal parameter restraints to facilitate realistic modeling. Two of the co-crystallised $CHCl_3$ solvent molecules were similarly refined using bond length constraints to obtain realistic modeling. The remaining MeOH solvent was satisfactorily modelled at 50% occupancy, with the C and O atoms occupying equivalent positions adjacent to an inversion centre. In this case, the H atom of the MeOH was first located on the difference map, and then refined using a riding model.

Identification code	(**4**)	
Empirical formula	C36.50 H29 Cl9 F9 N6 O15.50 S3 Yb	
Formula weight	1558.93	
Temperature	190(2) K	
Wavelength	1.5418 A	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	a = 11.2221(8) A	alpha = 65.394(7) deg.
	b = 16.3393(12) A	beta = 76.958(6) deg.

	c = 17.6442(11) A gamma = 74.365(6) deg.
Volume	2808.8(4) A^3
Z, Calculated density	2, 1.843 Mg/m^3
Absorption coefficient	8.944 mm^-1
F(000)	1532
Crystal size	0.40 x 0.20 x 0.19 mm
Theta range for data collection	3.035 to 61.669 deg.
Limiting indices	-12<=h<=11, -18<=k<=18, -20<=l<=12
Reflections collected / unique	16150 / 8516 [R(int) = 0.0683]
Completeness to theta = 61.669	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.32847
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8516 / 6 / 659
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0993, wR2 = 0.2689
R indices (all data)	R1 = 0.1181, wR2 = 0.2888
Extinction coefficient	n/a
Largest diff. peak and hole	3.147 and -1.694 e.A^-3

1.2 Additional UV-Vis spectra

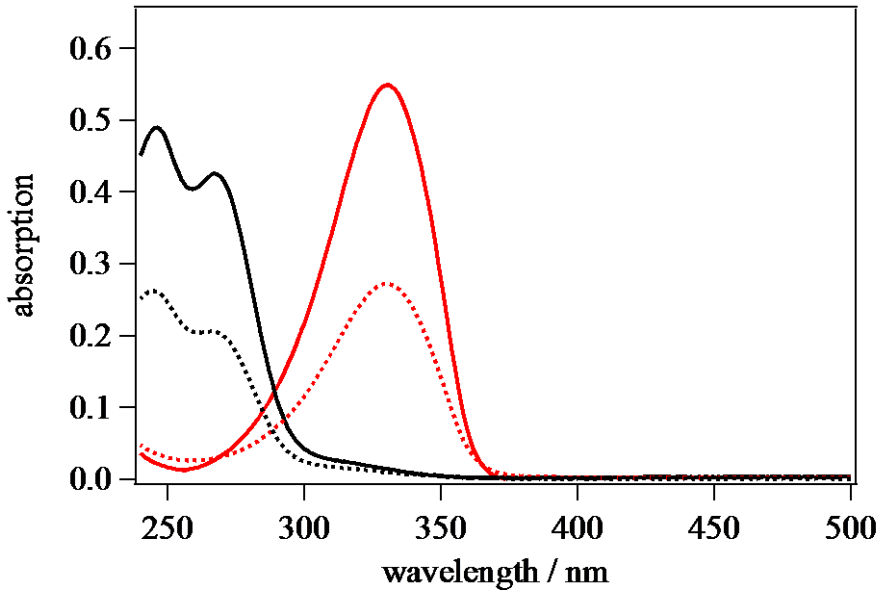

Fig S1. Observed UV-Vis absorption spectra of the *N*-oxide ligands (3,3'-bpdo, solid black line and 4,4'-bpdo, solid red line) in MeOH in comparison to spectra of samples of (**3**) (dashed black line) and (**4**) (dashed red line) after dissolution in MeOH.

1.3 Summary of Atomic Coordinates and ESP charges from DFT

1.3.1 4,4’-bpdo

Final Coordinates:

1	N	-3.0781056184,	0.0008573231,	-1.819552583
2	C	-3.0787974604,	0.0002649619,	-0.4455597514
3	C	-1.89526069,	0.0000589538,	0.2692280664
4	C	-0.635335846,	0.000248186,	-0.3750319883
5	C	-0.6778415167,	0.0004218489,	-1.7894617603
6	C	-1.8744170151,	0.0006681979,	-2.4821701162
7	C	0.6349106243,	-0.0002412057,	0.3757514195
8	C	1.8945327092,	0.0004495987,	-0.2690508559
9	C	3.0783775087,	0.000197265,	0.4451961804
10	N	3.0783059893,	-0.000855849,	1.8192154038
11	C	1.8749379978,	-0.0011319529,	2.4823624981
12	C	0.6780377461,	-0.0009306867,	1.7901845503
13	H	-1.9553999899,	0.0007675968,	-3.5593693111
14	H	0.2295493382,	0.0003371182,	-2.3795265918
15	H	-1.9752529554,	-0.0001361812,	1.3486126623
16	H	-4.0617294386,	-0.0000219886,	0.0025065596
17	H	1.9739199015,	0.001241146,	-1.3485098492
18	H	4.0611189772,	0.0007446922,	-0.003284873
19	H	1.9563759215,	-0.0014950195,	3.5595285161
20	H	-0.2289958033,	-0.0014450046,	2.3807434173
21	O	4.2235163934,	-0.0005304548,	2.4957314471
22	O	-4.2229980053,	0.0005262448,	-2.4966101636

Charges from ESP fit, RMS = 0.00221, RRMS = 0.08982:

1	N	0.486555	2	C	-0.094408
3	C	-0.208405	4	C	0.093116
5	C	-0.208375	6	C	-0.094434
7	C	0.096202	8	C	-0.220567
9	C	-0.077697	10	N	0.466857
11	C	-0.077651	12	C	-0.220618

13	H	0.154868	14	H	0.155281
15	H	0.155293	16	H	0.154869
17	H	0.162295	18	H	0.152297
19	H	0.152292	20	H	0.162304
21	O	-0.593479	22	O	-0.596594

Charge = 0.00000

Version=x86-Win32-G03RevB.04

State = 1-A

HF = -645.5548016

RMSD = 5.266e-009

RMSF = 2.864e-005

Dipole = -0.0004339, 0.000001, 0.0007482

PG = C01 [X(C10H8N2O2)]

THE GREAT THING ABOUT BEING IMPERFECT IS THE JOY IT BRINGS OTHERS.
-- SIGN OUTSIDE LAKE AGASSIZ JR. HIGH SCHOOL, FARGO, N.D.

Job cpu time: 0 days 0 hours 7 minutes 51.0 seconds.

File lengths (MBytes): RWF= 39 Int= 0 D2E= 0 Chk= 10 Scr= 1

Normal termination of Gaussian 03 at Tue May 19 13:20:14 2015.

1.3.2 3,3’-bpdo (transoid)

Final Coordinates:

1	C	0,	0,	0.
2	C	-0.7417799991,	0,	-1.2001509968
3	C	-1.0845260411,	-1. 237199832,	-1.7546914326
4	C	0.0003277545,	-2.4206201193,	0.0005302852
5	C	0. 3618187304,	-1.217715868,	0.5853987847
6	H	0.2962005432,	0.9227005538,	0.479232896
7	H	-1.6466299812,	-1.378762032,	-2.664138445
8	H	0.2387801491,	-3.4005167541,	0.3863304946
9	H	0.9315998278,	-1.235540056,	1.50726693
10	C	-1.1545444206,	1.2702228058,	-1.8679765415
11	C	-1.8896165396,	1.2403497306,	-3.0572746319
12	C	-0.8228470354,	2.5321927366,	-1.331312102

13	H	-2.2075406024,	0.3473592757,	-3.5716547463
14	C	-1.2337005096,	3.6922638204,	-1.9960458602
15	H	-0.256485535,	2.62351202,	-0.4149766385
16	C	-1.9610267727,	3.6151647518,	-3.1728116677
17	H	-0.9872969014,	4.6695870826,	-1.5973811128
18	H	-2.3152078323,	4.4590118549,	-3.7458532061
19	N	-0.7217990768,	-2.4227171636,	-1.1678231855
20	N	-2.2849221276,	2.3875679383,	-3.6968529381
21	O	-1.0719604894,	-3.5753783586,	-1.7343612007
22	O,	-2.9835548033,	2.3072766533,	-4.8271944183

Charges from ESP fit, RMS= 0.00216, RRMS= 0.08232:

1	C	-0.181827	2	C	0.072667
3	C	-0.174725	4	C	-0.095313
5	C	-0.156221	6	H	0.149423
7	H	0.173121	8	H	0.154544
9	H	0.162211	10	C	0.072667
11	C	-0.174725	12	C	-0.181827
13	H	0.173121	14	C	-0.156221
15	H	0.149423	16	C	-0.095313
17	H	0.162211	18	H	0.154544
19	N	0.490711	20	N	0.490711
21	O	-0.594592	22	O	-0.594592

Charge= 0.00000

Version=x86-Win32-G03RevB.04

State = 1-A1

HF = -645.5493417

RMSD = 3.930e-009

RMSF = 3.939e-005

Dipole = -1.7659934,0.,-2.8572605

PG = C02V [SGV(C10H8N2O2)]

THE LENGTH OF A MEETING IS PROPORTIONAL TO THE SQUARE OF THE PARTICIPANTS.

Job cpu time: 0 days 0 hours 1 minutes 52.0 seconds.

File lengths (MBytes): RWF= 36 Int= 0 D2E= 0 Chk= 9 Scr= 1

Normal termination of Gaussian 03 at Tue May 19 13:25:00 2015.

1.3.3 3,3’-bpdo (cisoid)

1	C	0.,	0.,	0.
2	C	0.0001689103,	1.4113440499,	0.0000031557
3	C	-1.1786088109,	2.0625858132,	0.3740503007
4	C	-2.3079781566,	0.0015289527,	0.7327950952
5	C	-1.1613155108,	-0.6866160901,	0.3686783524
6	H	0.8780040213,	-0.5658341467,	-0.278741897
7	H	-1.311984599,	3.1315924031,	0.4162445614
8	H	-3.2417920463,	-0.4522572743,	1.0294280964
9	H	-1.1787568097,	-1.7702838872,	0.3743338958
10	C	1.2033687948,	2.2090159714,	-0.3815763459
11	C	2.3822372126,	1.5577741971,	-0.755337529
12	C	1.2035377051,	3.6203600213,	-0.3815731903
13	H	2.5155271414,	0.4887676178,	-0.7978025003
14	C	2.3650714136,	4.3069760845,	-0.7495635508
15	H	0.3253907602,	4.1861941831,	-0.1032819173
16	C	3.5119597014,	3.6188310127,	-1.1129688906
17	H	2.3826091648,	5.3906438694,	-0.7549149847
18	H	4.4460490444,	4.0726172008,	-1.4087334128
19	N	-2.3092443639,	1.3744069598,	0.7327011553
20	N	3.5129199278,	2.2459530449,	-1.1138396833
21	O	-3.4071747926,	2.0439033823,	1.0810997636
22	O	4.6109367416,	1.576456612,	-1.4619659236

Version=x86-Win32-G03RevB.04

State=1-A

HF=-645.5503069

RMSD=3.229e-009

RMSF=2.414e-005

Dipole=0.0000001,0.0001523,0.

PG=C01 [X(C10H8N2O2)]

Charges from ESP fit, RMS= 0.00163 RRMS= 0.06802:

1	C	-0.232978	2	C	0.083046
3	C	-0.175920	4	C	-0.161740
5	C	-0.110774	6	H	0.182207
7	H	0.156408	8	H	0.177819
9	H	0.160790	10	C	0.131728
11	C	-0.188628	12	C	-0.255879
13	H	0.155666	14	C	-0.112316
15	H	0.183027	16	C	-0.143055
17	H	0.162556	18	H	0.171670
19	N	0.504607	20	N	0.491094
21	O	-0.591835	22	O	-0.587492

Charge= 0.00000

TO ERR IS HUMAN - AND TO BLAME IT ON A COMPUTER IS EVEN MORE SO.

Job cpu time: 0 days 0 hours 3 minutes 52.0 seconds.

File lengths (MBytes): RWF= 33 Int= 0 D2E= 0 Chk= 9 Scr= 1

Normal termination of Gaussian 03 at Tue May 19 13:31:04 2015.

1.4 References

(1) Technologies, A. *CrysAlisPro* Agilent Technologies Ltd: Yarton, Oxfordshire, UK, **2009-2011**

(2) Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837.

(3) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giocavazzo, C.; Gaugliardi, A.; Moliterni, G. C.; Polidori, G.; Spagna, S. *J. Appl. Cryst.* **1999**, *32*, 115.

(4) Sheldrick, G. M. *SHELX-2014: Programs for Crystal Structure Analysis* University of Göttingen: Göttingen, **2014**

(5) van der Sluis, P.; Spek, A. L. *Acta Crystallographica Section A* **1990**, *46*, 194.

(6) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool* Utrecht University: Utrecht, The Netherlands, **2008**