Electronic Supplementary Information

Fluorescent azadipyrrinato zinc(II) complex: Hybridisation with a dipyrrinato ligand

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1. General

All commercially available chemicals were purchased and used without further purification. Dipyrrin **2**[1], and 1,3-di(4'-methoxy)phenyl-2-propene-1-one **3**[2] were synthesised according to the literature. Preparative gel permeation liquid chromatography (GPC) was performed by LC-918 with a JAIGEL 1H column (Japan Analytical Industry) using chloroform as solvent. ^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded on a Bruker-DRX500 spectrometer using residual $CDCl_3$ (δ_H 7.25, δ_C 77.00) as an internal standard. UV-vis spectra were recorded on a JASCO V-570 spectrometer. Fluorescence spectra were recorded on a HITACHI F-4500 fluorometer. Absolute quantum yields were measured by a HAMAMATSU C9920-01. For the measurement of absolute quantum yields, the excitation wavelengths were the absorption maxima and the concentrations were adjusted so that the largest absorbances were ~0.05 for each compound. High resolution mass spectroscopy (HRMS) was performed on a JEOL JMS-700MStation mass spectrometer using PEG600 as a matrix. X-ray diffraction data were collected at 113 K on a Rigaku Saturn CCD system with a graphite-monochromated MoK$_\alpha$ radiation (λ = 0.7107 Å) using Crystal Clear (Rigaku). The structure was solved by the direct method and refined by full-matrix least-squares using SHELXS-97.[3] DFT calculations were performed on Gaussian 09[4].

2. Material preparation

2.1 4-Nitro-1,3-di(4'-methoxy)phenyl-1-butanone (**4**)

This compound was synthesised according to the literature from **3**.[5]

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (m, 2H), 7.18 (m, 2H), 6.91 (m, 2H), 6.84 (m, 2H), 4.79 (m, 1H), 4.62 (m, 1H), 4.15 (m, 1H), 3.85 (s, 1H), 3.76 (s, 1H), 3.34 (m, 1H); ^{13}C{^{1}H} NMR (500 MHz, $CDCl_3$) δ = 195.42 (s), 163.75 (s), 158.97 (s), 131.09 (s), 130.30 (s), 129.43 (s), 128.45 (s), 114.32 (s), 113.81 (s), 79.85 (s), 55.46 (s), 55.18 (s), 41.22 (s), 28.71 (s).

2.2 Azadipyrrin **1**[6]

An EtOH (40 mL) solution of 4-Nitro-1,3-di(4'-methoxy)phenyl-1-butanone (**4**) (0.61 g, 1.86 mmol) and ammonium acetate (5.0 g, 65 mmol) was refluxed 24 h. While heating, the reaction solution turned into a blue suspension. After the reaction mixture was cooled to room temperature, precipitate was filtered, washed with EtOH and water, and dried *in vacuo*, to give azadipyrrin **1** (0.25 g, 47%) as a dark green solid.

HRMS(FAB+) [M+] calcd for $C_{36}H_{31}N_3O_4$: m/z 569.2315; found: m/z 569.2310.; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.9 Hz, 4H), 7.88 (d, *J* = 8.9 Hz, 4H), 7.04 (d, *J* = 8.9 Hz, 4H), 7.03 (s, 2H), 6.95 (d, *J* = 8.9 Hz, 4H), 3.90 (s, 6H), 3.87 (s, 6H), peak derived from pyrrolic proton could not be observed due to broadening; $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ = 161.12 (s), 159.53 (s), 154.10 (s), 149.20 (s), 141.78 (s), 130.31 (s), 128.04 (s), 126.88 (s), 125.20 (s), 114.59 (s), 113.69 (s), 112.96 (s), 55.49 (s), 55.35 (s).

2.2 Heteroleptic complex **1-Zn-2**

To a MeOH (10 mL) solution of $Zn(OAc)_2$ (9.4 mg, 0.051 mmol), a $CHCl_3$ (10 mL) solution of azadipyrrin **1** (29.1 mg, 0.051 mmol) and dipyrrin **2** (8.8 mg, 0.051 mmol) were added and stirred 1 h at room temperature. After removal of the solvent, the residue was purified by GPC followed by recrystallisation from MeOH/CH_2Cl_2 to give complex **1-Zn-2** (3.9 mg, 9.5%) as a gold metallic solid.

HRMS(FAB+) [M+] calcd for $C_{47}H_{41}N_5O_4Zn$: m/z 803.2450; found: m/z 803.2457.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.8 Hz, 4H), 7.48 (d, *J* = 8.8 Hz, 4H), 7.03 (s, 2H), 6.95 (d, *J* = 8.9 Hz, 4H), 6.91 (s, 1H), 6.87 (d, *J* = 3.8 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 4H), 6.01 (d, *J* = 3.8 Hz, 4H), 3.89 (s, 6H), 3.71 (s, 6H), 1.98 (s, 6H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ = 160.39 (s), 160.22 (s), 159.45 (s), 158.88 (s), 147.37 (s), 144.73 (s), 138.02 (s), 132.30 (s), 131.10 (s), 128.86 (s), 128.58 (s), 127.35 (s), 126.52 (s), 117.14 (s), 115.83 (s), 113.56 (s), 113.47 (s), 55.33 (s), 55.27 (s), 16.53 (s).

2.3 Homoleptic complex **1-Zn-1**

To a MeOH (20 mL) solution of $Zn(OAc)_2$, a CH_2Cl_2 solution of azadipyrrin 1 was added and stirred for 20 min. The reaction mixture was filtered through celite and evaporated. The residue was recrystallised from MeOH /CH_2Cl_2 to give **1-Zn-1** (14.5 mg) as a purple solid.

HRMS(FAB+) [M+] calcd for $C_{72}H_{60}N_6O_8Zn$: m/z 1200.3764; found: m/z 1200.3752.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.7 Hz, 8H), 7.42 (d, *J* = 8.7 Hz, 8H), 6.95 (d, *J* = 8.7 Hz, 8H), 6.61 (s, 4H), 6.59 (d, *J* = 8.7 Hz, 8H), 3.90 (s, 12H), 3.37 (s, 12H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ = 160.42 (s), 159.47 (s), 159.25 (s), 147.72 (s), 143.90 (s), 130.86 (s), 128.29 (s), 127.46 (s), 126.00 (s), 115.27 (s), 113.40 (s), 113.38 (s), 55.35 (s), 55.00 (s).

2.3 Homoleptic complex **2-Zn-2**

This compound was synthesised by the same procedure as that for **1-Zn-1**.

HRMS(FAB+) [M+] calcd for $C_{22}H_{22}N_4Zn$: m/z 406.1136; found: m/z 406.1134.; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.01 (d, *J* = 4.0 Hz, 2H), 7.00 (s, 1H), 6.21 (d, *J* = 4.0 Hz, 2H), 2.01 (s, 6H); $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$) δ = 159.45 (s), 138.35 (s), 132.26 (s), 129.67 (s), 117.15 (s), 16.41 (s).

3. X-ray crystallographic analysis

3.1 Heteroleptic complex **1-Zn-2**

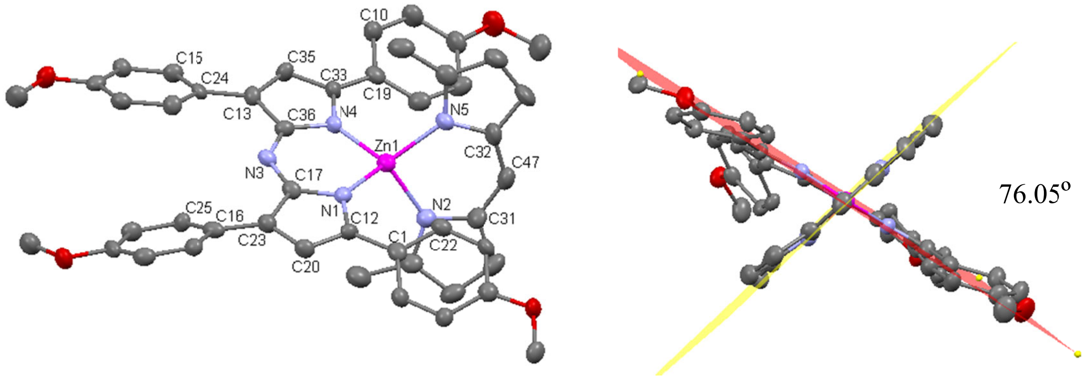

Fig. S1 (a) Thermal ellipsoid plot for **1-Zn-2** (50% probability) (b) Dihedral angle around Zn atom.

Table S1. Selected bond lengths **1-Zn-2**

Bond	Length (Å)	Bond	Length (Å)
Zn1 N1	1.999(5)	N3 C17	1.33(1)
Zn1 N2	2.011(6)	N1 C17	1.41(1)
Zn1 N4	2.008(7)	N2 C31	1.38(1)
Zn1 N5	1.992(5)	C31 C47	1.39(1)
N2 C3	1.356(8)	C32 C47	1.38(1)
N4 C36	1.416(9)	N5 C32	1.40(1)
N3 C36	1.324(7)		

Table S2. Selected bond angles for **1-Zn-2**

angle	degree (°)	angle	degree (°)
N1 Zn1 N4	96.4(2)	N4 Zn1 N5	111.5(2)
N1 Zn1 N2	105.8(2)	C17 N3 C36	129.9(6)
N2 Zn1 N5	94.8(2)	C31 C47 C32	130.3(7)

Table S3. Selected torsion angles around bonds for **1-Zn-2**

torsion angle	degree (°)	torsion angle	degree (°)
C17 N3 C36 N4	3(1)	C45 C19 C33 N4	14(**1**)
C36 N3 C17 N1	7(1)	C36 C13 C24 C44	23(**1**)
N5 C32 C47 C31	0(1)	C25 C16 C23 C17	30(**1**)
N2 C31 C47 C32	4(1)	C41 C1 C12 C20	16(**1**)

Table S4. Crystallographic data for **1-Zn-2**

chemical formula	$C_{47}H_{41}N_5O_4Zn$
formula weight	805.25
crystal system	monoclinic
space group	$P2_1/c$
a (Å)	25.194(8)
b (Å)	7.483(3)
c (Å)	22.121(8)
α (°)	90
β (°)	112.754(4)
γ (°)	90
V (Å^3)	3846(2)
Z	4
Dc (g cm^{-3})	1.391
F(000)	1680.00
reflections/parameters/constraints	6945/514/0
goodness of fit	1.083
μ	0.692
$R1$ [$I>2\sigma(I)$]	0.0881
$wR2$ [all data]	0.2336

3.2 Homoleptic complex **1-Zn-1**

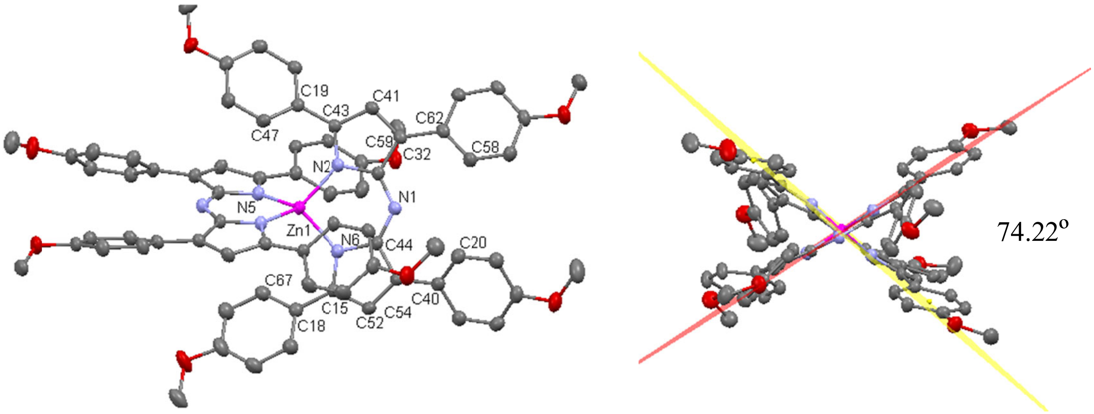

Fig. S2 Thermal ellipsoid plot for **1-Zn-1** (50% probability).

Table S5. Selected bond lengths for **1-Zn-1**

bond	length (Å)	bond	length (Å)
Zn1 N2	1.991(2)	N1 C59	1.322(3)
Zn1 N6	1.994(2)	N1 C44	1.327(4)
N2 C59	1.400(3)	N6 C44	1.398(3)

Table S6. Selected bond angles for **1-Zn-1**

angle	degree (°)	angle	degree (°)
N2 Zn1 N6	95.06(9)	C44 N1 C59	127.6(2)
N2 Zn1 N5	109.92(9)		

Table S7. Selected torsion angles around bonds for **1-Zn-1**

torsion angle	degree (°)	torsion angle	degree (°)
C44 N1 C59 N2	7.4(5)	C20 C40 C54 C44	33.2(5)
C59 N1 C44 N6	9.8(5)	C47 C19 C43 N2	22.2(5)
C59 C32 C62 C58	–13.6(5)	N6 C15 C18 C67	19.3(5)

Table S8. Crystallographic data for **1-Zn-1**

chemical formula	$C_{72}H_{60}N_6O_8Zn$
formula weight	1202.68
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	21.652(3)
b (Å)	11.8115(16)
c (Å)	22.608(3)
α (º)	90
β (º)	93.7316(15)
γ (º)	90
V (Å^3)	5769.6(14)
Z	4
Dc (g cm^{-3})	1.384
F(000)	2512.00
reflections/parameters/constraints	13099/784/0
goodness of fit	1.069
μ	0.492
$R1$ [$I>2\sigma(I)$]	0.0566
$wR2$ [all data]	0.1531

4. Optimised structures by DFT calculation

4-1. Heteroleptic complex **1-Zn-2**

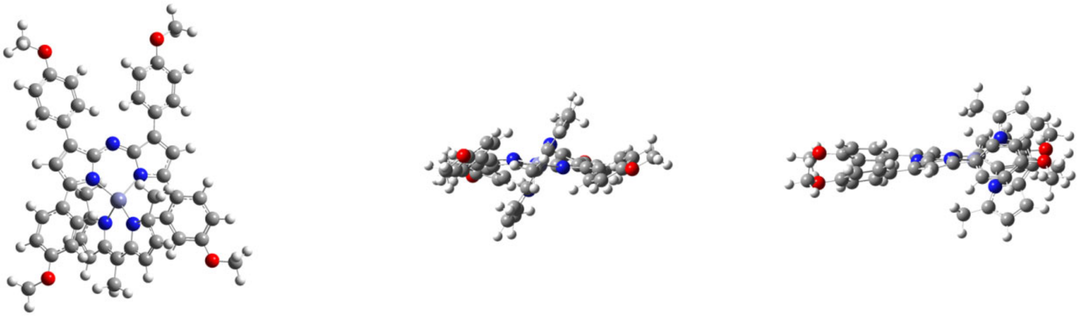

Fig. S3 Optimised structure of **1-Zn-2** (B97D/6-31G(d)).

Fig. S4 Optimised structure of **1-Zn-2** (B3LYP/6-31G(d)).

4-2. Homolpetic complex **1-Zn-1**

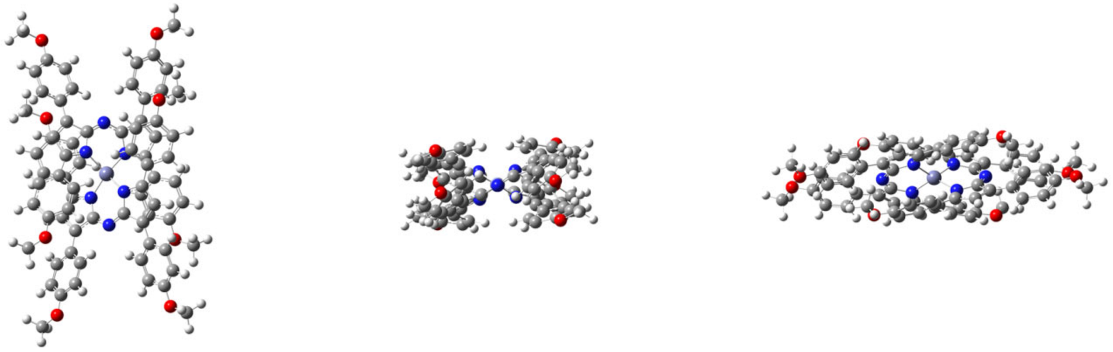

Fig. S5 Optimised structure of **1-Zn-1** (B97D/6-31G(d)).

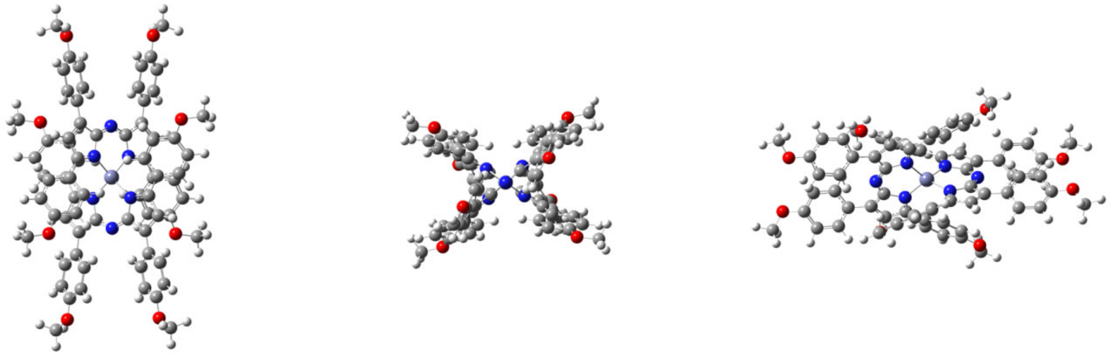

Fig. S6 Optimised structure of **1-Zn-1** (B3LYP/6-31G(d)).

References

1. L. Wu, K. Burgess, *Chem. Commun*., 2008, 4933.

2. Y. Qian, G. Y. Ma, Y. Yang, K. Cheng, Q. Z. Zheng, W. -J. Mao, L. Shi, J. Zhao, H. L. Zhu, *Bioorg*. *Med*. *Chem*., 2010, **18**, 4310.

3. G. M. Sheldrick, SHELX-97 Programs for Crystal Structure Analysis (Release 97-2); University of Göttingen, Germany, 1997.

4. Gaussian 09, Revision B.01,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci,
G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian,
A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada,
M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,
Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr.,
J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers,
K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand,
K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi,
M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross,
V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann,
O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski,
R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth,
P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels,
O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

5. W. Davey, D. J. Tivey, *J. Chem. Soc*., 1958, 2276.

6. S. O. McDonnell, D. F. O'Shea, *Org*. *Lett*., 2006, **8**, 3493.