Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A platform with connections in many directions - further remarkable facets to the multifaceted Methylbiquinoxen dication

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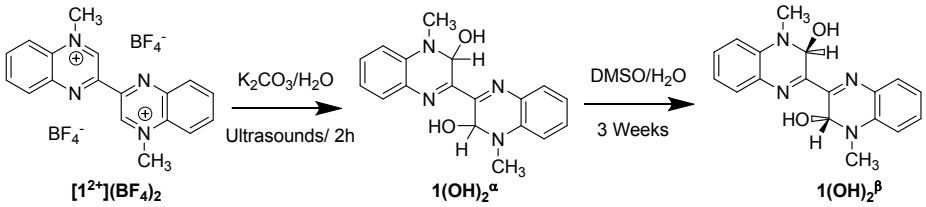
Supporting Information

Summary table

Supplementary Figures and tables

A. Synthesis

A_1- Synthesis of the pseudo-base $1(OH)_2$ (α and β phases)



$[1^{2+}](BF_4)_2$ $1(OH)_2^{\alpha}$ $1(OH)_2^{\beta}$

A_{11}- $(1^{2+})[BF_4]_2$

According to literature,[1] a stirred solution of trimethyloxonium tetrafluoroborate (14.32 g; 96.8 mmol) in acetonitrile (500 mL) is treated portion wise with biquinoxaline (5 g; 19.3 mmol) at 0 °C. The resultant dark green mixture is then left stirring for 5 d at ambient temperature. The resulting solid is filtered, washed with Et_2O and dried in air. The crude powder (7.67g) was added to 400 mL of water. After boiling the mixture and hot filtration, the yellow/brown solution was cooled and stored overnight at 0°C. The resulting yellow/off-white crystals were collected by filtration, washed with water and dried under vacuum. Yield: 4.69 g (52%) Anal. Calcd for $C_{18}H_{16}B_2N_4F_8$: C, 46.80; H, 3.49; N, 12.13. Found: C, 47.38; H, 4.05; N, 12.19. ^{1}H NMR (500 MHz, CD_3CN): δ = 10.35 (s, 2H), 8.72 (dd, *J* = 8.3, 1.3 Hz, 2H), 8.62 (d, *J* = 8.6 Hz, 2H), 8.52 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 2H), 8.49 – 8.45 (m, 1H), 4.91 (s, 6H)

A_{12} - $1(OH)_2^{\alpha}$

In a 500 mL flask were mixed $(\mathbf{1^{2+}})[BF_4]_2$ (1.5 g, 3.25 mmol) and K_2CO_3 (2 g, 14.5 mmol) with 400 mL of distillate water. The mixture is then inserted in an ultrasound bath and left for 2h. After turning into a homogeneous orange powder, the mixture is filtered, cleaned with distillated water, and dried under vacuum. The product $\mathbf{1(OH)_2^{\alpha}}$ (1.015 g, 97%) is obtained as an orange crystalline powder.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.47 (d, *J* = 7.5 Hz, 2H), 7.31 (ddd, *J* = 7.5 Hz, *J* = 1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 2H), 6.17 (d, *J* = 6.1 Hz, 2H), 6.09 (d, *J* = 6.1 Hz, 2H), 3.20 (s, 6H).

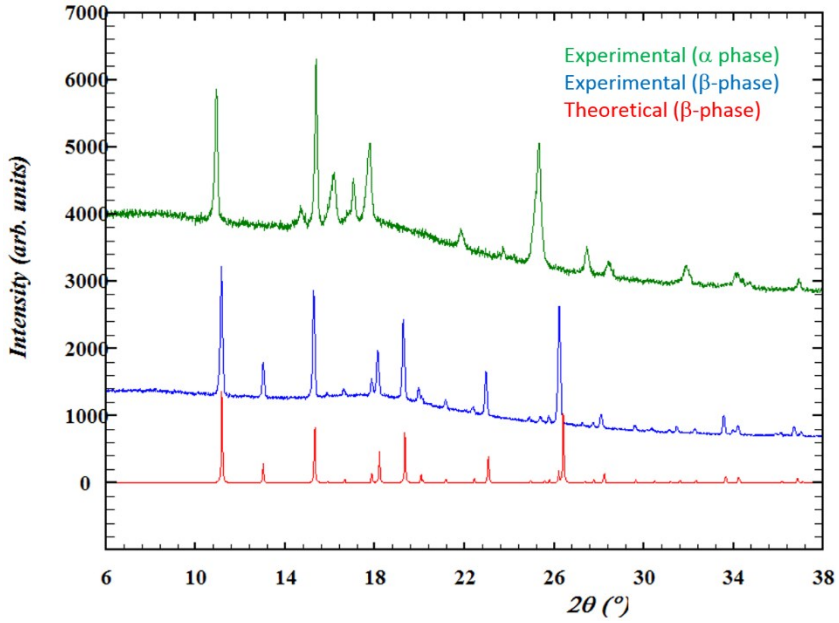
E.A: [calc. (C, 67.07; H, 5.63; N, 17.38) / meas. (C, 66.81; H, 5.44; N, 17.46)

A_{13} - $1(OH)_2^{\beta}$

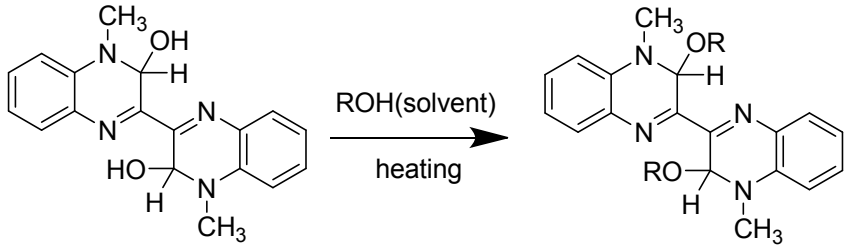
Pure crystals of $\mathbf{1(OH)_2^{\beta}}$ were obtained as follow. In a pillbox, 100 mg of $\mathbf{1_{OH}^{\alpha}}$ are dissolved in 12 mL of DMSO leading to a dark yellow solution. The pillbox was covered with an aluminium foil perforated with needles holes, and inserted in a flask containing 200 mL of distillate water. The flask was then sealed and left standing over three weeks, thereafter red blocks-like crystals formed. The crystals were filtered, cleaned with water and dried under vacuum, leading to $\mathbf{1(OH)_2^{\beta}}$ as a pure phase (88 mg, 88 %).

[1] N. Leblanc, S. Sproules, K. Fink, L. Sanguinet, O. Aleveque, E. Levillain, P. Rosa, A. K. Powell, *Chem. Sci.* **2016**, *7*, 3820-3828.

XRPD of $1(OH)_2^{\alpha}$ and $1(OH)_2^{\beta}$



A_2- Bis-σ^H-adducts $1(OR)_2$ (R=Me, Et, OEtOEt)

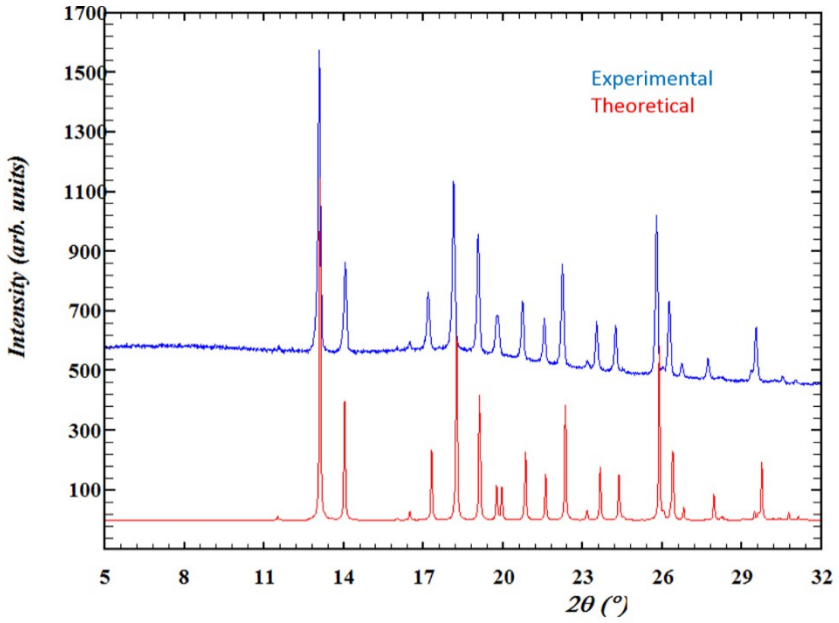


$1(OH)_2$ (α or β phases) R=Me, Et, OEtOEt **$1(OR)_2$**

A_{21} -$1(OMe)_2$

160 mg (0.5 mmol) of **$1(OH)_2^{\alpha}$** were completely dissolved in 100 mL of hot MeOH. After cooling down, the bright yellow solution was then left to slowly evaporate. After three weeks, the orange crystals formed are filtered from the solution (reduced to ≈ 50 mL), washed with a small amount of MeOH and dried under vacuum, leading to 135 mg (77%) of **$1(OMe)_2$** as a pure crystalline phase.
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (dt, *J* = 7.8, 1.3 Hz, 2H), 7.34 (m, 2H), 6.97 (m, 4H), 6.34 (s, 1H), 6.26 (s, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 3.37 (s, 3H), 3.33 (s, 3H).
E.A: [calc. (C, 68.55; H, 6.33; N, 15.99) / meas. (C, 68.34; H, 6.45; N, 15.84)

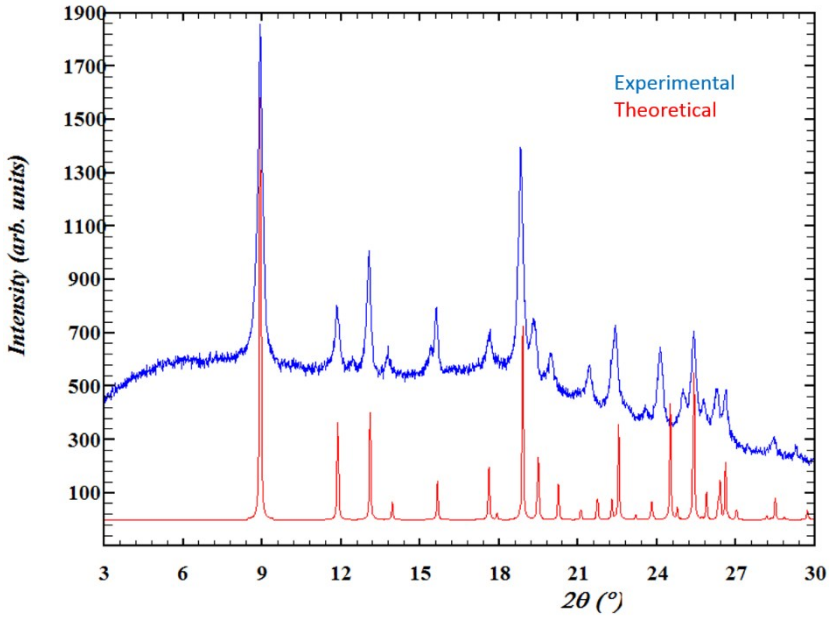
XRPD of $1(OMe)_2$



A_{22} - 1(OEt)$_2$

Same procedure as described above for **1(OMe)$_2$**, (**1(OH)$_2^{\alpha}$**: 50 mg) but EtOH (30 mL) is used instead of MeOH. Yield (31 mg, 52%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60 (m, 2H), 7.33 (td, *J* = 7.32, 7.30, 1.23 Hz, 2H), 6.95 (m, 4H), 6.39 (s, 1H), 6.26 (s, 1H), 3.63 (M, 4H), 3.38 (s, 3H), 3.35 (s, 3H), 1.13 (t, 3H), 1.06 (t, 3H). E.A: [calc. (C, 69.82; H, 6.92; N, 14.80) / meas. (C, 69.49; H, 7.13; N, 14.78)

XRPD of 1(OEt)$_2$



A_{23} - 1(OEtOEt)$_2$

Same procedure as described above for **1(OMe)$_2$**, (**1(OH)$_2^{\alpha}$**: 50 mg) but 2-Ethoxyethanol is used instead of MeOH. Yield (35 mg, 48%). ^{1}H NMR (500 MHz, THF-d^8): δ = 7.53 (dd, *J* = 7.6, 0.7 Hz, 2H), 7.29 (t, *J* = 8.0 Hz , 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 2H), 6.28 (s, 2H), 3.79 (m, 2H), 3.71 (m, 2H), 3.41 (s, 6H), 3.33 (m, 8H), 1.05 (t, 6H). E.A: [calc. (C, 66.35; H, 7.13; N, 12.38) / meas. (C, 68.78; H, 7.36; N, 12.04)

B. Single crystal X-ray diffraction analysis for $1(OH)_2^{\beta}$, $1(OMe)_2$, $1(OEt)_2$ and $1(OEtOEt)_2$.

B_1-$1(OH)_2^{\beta}$

Table 1. Crystal data and structure refinement.

Empirical formula	C18 H18 N4 O2
Formula weight	322.36
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 5.8457(6) A alpha = 90 deg. b = 13.5935(14) A beta = 98.476(9) deg. c = 9.8497(11) A gamma = 90 deg.
Volume	774.14(14) A^3
Z, Calculated density	2, 1.383 Mg/m^3
Absorption coefficient	0.093 mm^-1
F(000)	340
Crystal size	0.3 x 0.2 x 0.1 mm
Theta range for data collection	2.572 to 27.332 deg.
Limiting indices	-7<=h<=7, -17<=k<=15, -12<=l<=12
Reflections collected / unique	4612 / 1717 [R(int) = 0.0266]
Completeness to theta = 25.242	97.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1717 / 0 / 146
Goodness-of-fit on F^2	0.962
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0964
R indices (all data)	R1 = 0.0558, wR2 = 0.1034
Extinction coefficient	0.084(15)
Largest diff. peak and hole	0.164 and -0.116 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	3540(3)	6654(1)	2287(2)	53(1)
C(9)	690(2)	7325(1)	3636(1)	45(1)
C(8)	911(2)	8285(1)	3166(2)	52(1)
C(7)	-429(3)	9028(1)	3585(2)	57(1)
C(6)	-2029(3)	8839(1)	4465(2)	57(1)
C(5)	-2304(2)	7895(1)	4911(2)	52(1)
C(4)	-961(2)	7131(1)	4518(1)	45(1)
C(3)	181(2)	5508(1)	4795(1)	42(1)
C(2)	2414(2)	5774(1)	4284(1)	44(1)
N(1)	1943(2)	6533(1)	3277(1)	48(1)
N(2)	-1354(2)	6169(1)	4936(1)	43(1)
O(1)	3965(2)	6063(1)	5468(1)	50(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.4560(16)
C(1)-H(1A)	0.979(19)
C(1)-H(1B)	0.983(19)
C(1)-H(1C)	0.971(19)
C(9)-N(1)	1.3764(18)
C(9)-C(8)	1.397(2)
C(9)-C(4)	1.4157(17)
C(8)-C(7)	1.378(2)
C(8)-H(8)	1.008(17)
C(7)-C(6)	1.390(2)
C(7)-H(7)	0.984(19)
C(6)-C(5)	1.374(2)
C(6)-H(6)	0.95(2)
C(5)-C(4)	1.391(2)
C(5)-H(5)	1.001(17)
C(4)-N(2)	1.3991(18)
C(3)-N(2)	1.2926(17)
C(3)-C(3)#1	1.462(3)
C(3)-C(2)	1.5111(16)
C(2)-O(1)	1.4232(17)
C(2)-N(1)	1.4299(19)
C(2)-H(2)	0.958(14)
O(1)-H(9)	0.91(2)

N(1)-C(1)-H(1A)	110.6(10)
N(1)-C(1)-H(1B)	110.1(10)
H(1A)-C(1)-H(1B)	111.5(15)
N(1)-C(1)-H(1C)	106.6(10)
H(1A)-C(1)-H(1C)	107.9(14)
H(1B)-C(1)-H(1C)	110.1(15)
N(1)-C(9)-C(8)	124.51(12)
N(1)-C(9)-C(4)	116.64(12)
C(8)-C(9)-C(4)	118.84(13)
C(7)-C(8)-C(9)	120.06(13)
C(7)-C(8)-H(8)	119.8(10)
C(9)-C(8)-H(8)	120.2(10)
C(8)-C(7)-C(6)	121.08(15)
C(8)-C(7)-H(7)	120.4(10)
C(6)-C(7)-H(7)	118.5(9)
C(5)-C(6)-C(7)	119.56(14)
C(5)-C(6)-H(6)	121.8(11)
C(7)-C(6)-H(6)	118.7(11)
C(6)-C(5)-C(4)	120.75(13)
C(6)-C(5)-H(5)	123.9(10)
C(4)-C(5)-H(5)	115.3(10)

C(5)-C(4)-N(2)	119.46(11)
C(5)-C(4)-C(9)	119.68(13)
N(2)-C(4)-C(9)	120.75(12)
N(2)-C(3)-C(3)#1	119.75(12)
N(2)-C(3)-C(2)	121.13(12)
C(3)#1-C(3)-C(2)	119.03(13)
O(1)-C(2)-N(1)	113.73(12)
O(1)-C(2)-C(3)	105.69(10)
N(1)-C(2)-C(3)	108.43(11)
O(1)-C(2)-H(2)	110.7(8)
N(1)-C(2)-H(2)	107.4(8)
C(3)-C(2)-H(2)	110.9(8)
C(9)-N(1)-C(2)	116.25(10)
C(9)-N(1)-C(1)	120.11(12)
C(2)-N(1)-C(1)	117.96(11)
C(3)-N(2)-C(4)	118.13(10)
C(2)-O(1)-H(9)	106.6(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	48(1)	64(1)	49(1)	5(1)	17(1)	0(1)
C(9)	40(1)	49(1)	45(1)	2(1)	6(1)	-1(1)
C(8)	51(1)	55(1)	50(1)	6(1)	7(1)	-3(1)
C(7)	61(1)	48(1)	62(1)	7(1)	6(1)	1(1)
C(6)	56(1)	49(1)	67(1)	-2(1)	12(1)	5(1)
C(5)	47(1)	52(1)	59(1)	-2(1)	13(1)	1(1)
C(4)	39(1)	47(1)	48(1)	0(1)	7(1)	-1(1)
C(3)	37(1)	48(1)	43(1)	-3(1)	9(1)	-2(1)
C(2)	38(1)	46(1)	49(1)	-1(1)	12(1)	0(1)
N(1)	45(1)	51(1)	50(1)	5(1)	17(1)	1(1)
N(2)	37(1)	47(1)	47(1)	-1(1)	10(1)	-1(1)
O(1)	37(1)	58(1)	54(1)	1(1)	10(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic
displacement parameters (A^2 x 10^3) for nle717.

	x	y	z	U(eq)
H(1A)	4850(30)	7068(13)	2667(18)	60(4)
H(1B)	2720(30)	6928(13)	1425(19)	60(4)
H(1C)	4130(30)	6004(14)	2126(18)	59(5)
H(8)	2060(30)	8438(13)	2523(17)	60(4)
H(7)	-240(30)	9709(14)	3284(18)	64(5)
H(6)	-2910(30)	9368(15)	4733(19)	70(5)
H(5)	-3470(30)	7700(13)	5510(18)	58(4)
H(2)	3020(20)	5222(11)	3845(14)	39(3)
H(9)	5410(40)	6015(15)	5240(20)	83(6)

Table 6. Torsion angles [deg].

N(1)-C(9)-C(8)-C(7)	179.88(13)
C(4)-C(9)-C(8)-C(7)	1.4(2)
C(9)-C(8)-C(7)-C(6)	-0.6(2)
C(8)-C(7)-C(6)-C(5)	-0.9(2)
C(7)-C(6)-C(5)-C(4)	1.6(2)
C(6)-C(5)-C(4)-N(2)	-177.02(14)
C(6)-C(5)-C(4)-C(9)	-0.7(2)
N(1)-C(9)-C(4)-C(5)	-179.37(13)
C(8)-C(9)-C(4)-C(5)	-0.8(2)
N(1)-C(9)-C(4)-N(2)	-3.12(19)
C(8)-C(9)-C(4)-N(2)	175.49(13)
N(2)-C(3)-C(2)-O(1)	86.36(15)
C(3)#1-C(3)-C(2)-O(1)	-90.29(17)
N(2)-C(3)-C(2)-N(1)	-35.93(17)
C(3)#1-C(3)-C(2)-N(1)	147.43(15)
C(8)-C(9)-N(1)-C(2)	149.39(14)
C(4)-C(9)-N(1)-C(2)	-32.08(17)
C(8)-C(9)-N(1)-C(1)	-3.5(2)
C(4)-C(9)-N(1)-C(1)	175.00(13)
O(1)-C(2)-N(1)-C(9)	-68.11(14)
C(3)-C(2)-N(1)-C(9)	49.13(16)
O(1)-C(2)-N(1)-C(1)	85.41(15)
C(3)-C(2)-N(1)-C(1)	-157.35(12)
C(3)#1-C(3)-N(2)-C(4)	-179.30(14)
C(2)-C(3)-N(2)-C(4)	4.07(18)
C(5)-C(4)-N(2)-C(3)	-166.65(13)
C(9)-C(4)-N(2)-C(3)	17.10(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Datablock: I

Bond precision: C-C = 0.0019 A Wavelength=0.71073
Cell: a=5.8457(6) b=13.5935(14) c=9.8497(11)
alpha=90 beta=98.476(9) gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	774.14(14)	774.14(14)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C18 H18 N4 O2	C18 H18 N4 O2
Sum formula	C18 H18 N4 O2	C18 H18 N4 O2
Mr	322.36	322.36
Dx,g cm-3	1.383	1.383
Z	2	2
Mu (mm-1)	0.093	0.093
F000	340.0	340.0
F000'	340.13	
h,k,lmax	7,17,12	7,17,12
Nref	1756	1717
Tmin,Tmax	0.978,0.991	
Tmin'	0.972	

Correction method= Not given
Data completeness= 0.978 Theta(max)= 27.332
R(reflections)= 0.0371(1194) wR2(reflections)= 0.1034(1717)
S = 0.962 Npar= 146

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

.Alert level B

PLAT415_ALERT_2_B Short Inter D-H..H-X H2 .. H9 .. 2.06 Ang.

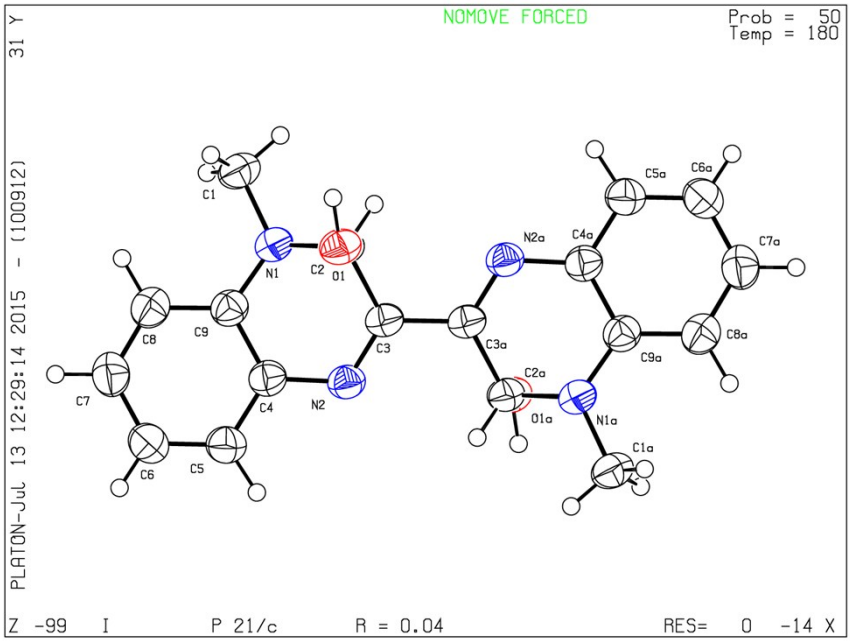
Alert level C

PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ..... 0.977 Note

Alert level G

PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) S Verify

0 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
1 **ALERT level G** = General information/check it is not something unexpected



B_2-1(OMe)$_2$

Table 1. Crystal data and structure refinement.

Empirical formula	C20 H22 N4 O2
Formula weight	350.41
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pcab
Unit cell dimensions	a = 10.2451(8) A alpha = 90 deg. b = 11.0740(7) A beta = 90 deg. c = 15.3632(11) A gamma = 90 deg.
Volume	1743.0(2) A^3
Z, Calculated density	4, 1.335 Mg/m^3
Absorption coefficient	0.089 mm^-1
F(000)	744
Crystal size	0.24 x 0.222 x 0.194 mm
Theta range for data collection	3.016 to 27.370 deg.
Limiting indices	-9<=h<=13, -14<=k<=14, -19<=l<=19
Reflections collected / unique	8828 / 1941 [R(int) = 0.0545]
Completeness to theta = 25.242	98.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1941 / 0 / 163
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1214
R indices (all data)	R1 = 0.0683, wR2 = 0.1326
Extinction coefficient	0.066(6)
Largest diff. peak and hole	0.184 and -0.198 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	5921(2)	3016(2)	3433(1)	40(1)
C(9)	4367(2)	1414(2)	3042(1)	31(1)
C(8)	4152(2)	1882(2)	2207(1)	36(1)
C(7)	3286(2)	1317(2)	1649(1)	40(1)
C(6)	2631(2)	266(2)	1893(1)	39(1)
C(5)	2899(2)	-245(2)	2693(1)	35(1)
C(4)	3771(2)	308(2)	3269(1)	31(1)
C(3)	4744(2)	314(2)	4618(1)	30(1)
C(2)	4919(2)	1661(2)	4547(1)	31(1)
C(10)	3809(2)	3426(2)	5045(2)	44(1)
N(1)	5162(1)	1953(1)	3652(1)	32(1)
N(2)	4121(1)	-295(1)	4032(1)	31(1)
O(1)	3742(1)	2161(1)	4893(1)	36(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.450(2)
C(1)-H(1A)	1.04(3)
C(1)-H(1B)	0.98(2)
C(1)-H(1C)	0.99(2)
C(9)-N(1)	1.378(2)
C(9)-C(8)	1.400(2)
C(9)-C(4)	1.412(2)
C(8)-C(7)	1.383(3)
C(8)-H(8)	0.99(2)
C(7)-C(6)	1.394(3)
C(7)-H(7)	1.02(2)
C(6)-C(5)	1.381(2)
C(6)-H(6)	1.02(2)
C(5)-C(4)	1.398(2)
C(5)-H(5)	1.05(2)
C(4)-N(2)	1.396(2)
C(3)-N(2)	1.293(2)
C(3)-C(3)#1	1.462(3)
C(3)-C(2)	1.507(2)
C(2)-O(1)	1.429(2)
C(2)-N(1)	1.435(2)
C(2)-H(2)	1.03(2)
C(10)-O(1)	1.421(2)
C(10)-H(10A)	1.02(3)
C(10)-H(10B)	1.01(3)
C(10)-H(10C)	1.00(3)
N(1)-C(1)-H(1A)	111.8(14)
N(1)-C(1)-H(1B)	111.1(13)
H(1A)-C(1)-H(1B)	104.1(18)
N(1)-C(1)-H(1C)	109.1(12)
H(1A)-C(1)-H(1C)	111.5(17)
H(1B)-C(1)-H(1C)	109(2)
N(1)-C(9)-C(8)	123.72(16)
N(1)-C(9)-C(4)	117.57(14)
C(8)-C(9)-C(4)	118.68(16)
C(7)-C(8)-C(9)	120.03(18)
C(7)-C(8)-H(8)	118.9(12)
C(9)-C(8)-H(8)	120.9(12)
C(8)-C(7)-C(6)	121.35(17)
C(8)-C(7)-H(7)	119.0(12)
C(6)-C(7)-H(7)	119.6(12)
C(5)-C(6)-C(7)	119.01(17)
C(5)-C(6)-H(6)	118.5(11)

C(7)-C(6)-H(6)	122.5(11)
C(6)-C(5)-C(4)	120.73(17)
C(6)-C(5)-H(5)	121.3(12)
C(4)-C(5)-H(5)	117.8(12)
N(2)-C(4)-C(5)	119.11(15)
N(2)-C(4)-C(9)	120.75(15)
C(5)-C(4)-C(9)	119.93(15)
N(2)-C(3)-C(3)#1	119.25(19)
N(2)-C(3)-C(2)	121.65(14)
C(3)#1-C(3)-C(2)	119.07(18)
O(1)-C(2)-N(1)	114.54(14)
O(1)-C(2)-C(3)	104.89(13)
N(1)-C(2)-C(3)	108.20(13)
O(1)-C(2)-H(2)	110.3(10)
N(1)-C(2)-H(2)	106.7(10)
C(3)-C(2)-H(2)	112.3(10)
O(1)-C(10)-H(10A)	114.0(13)
O(1)-C(10)-H(10B)	108.4(16)
H(10A)-C(10)-H(10B)	110(2)
O(1)-C(10)-H(10C)	112.2(16)
H(10A)-C(10)-H(10C)	103(2)
H(10B)-C(10)-H(10C)	109(2)
C(9)-N(1)-C(2)	116.88(14)
C(9)-N(1)-C(1)	120.77(14)
C(2)-N(1)-C(1)	119.82(14)
C(3)-N(2)-C(4)	117.54(15)
C(10)-O(1)-C(2)	113.67(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for nle740g.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	37(1)	37(1)	45(1)	5(1)	5(1)	-6(1)
C(9)	27(1)	33(1)	33(1)	0(1)	3(1)	4(1)
C(8)	37(1)	38(1)	34(1)	5(1)	3(1)	5(1)
C(7)	39(1)	48(1)	32(1)	1(1)	-1(1)	10(1)
C(6)	38(1)	44(1)	35(1)	-4(1)	-3(1)	5(1)
C(5)	32(1)	35(1)	37(1)	-4(1)	-2(1)	3(1)
C(4)	32(1)	29(1)	31(1)	1(1)	-1(1)	2(1)
C(3)	27(1)	31(1)	31(1)	2(1)	2(1)	-1(1)
C(2)	30(1)	31(1)	33(1)	1(1)	1(1)	0(1)
C(10)	47(1)	35(1)	51(1)	-4(1)	2(1)	7(1)
N(1)	32(1)	30(1)	34(1)	3(1)	1(1)	-3(1)
N(2)	30(1)	31(1)	32(1)	2(1)	0(1)	0(1)
O(1)	34(1)	33(1)	41(1)	-2(1)	5(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for nle740g.

	x	y	z	U(eq)
H(1A)	5330(20)	3770(20)	3332(13)	52(6)
H(1B)	6490(20)	3250(20)	3917(15)	51(6)
H(1C)	6460(20)	2839(18)	2915(15)	45(5)
H(8)	4560(20)	2645(19)	2022(13)	40(5)
H(7)	3100(20)	1695(19)	1059(14)	45(5)
H(6)	1980(20)	-156(19)	1494(12)	40(5)
H(5)	2420(20)	-1030(20)	2905(14)	47(6)
H(2)	5710(20)	1964(15)	4895(11)	30(4)
H(10A)	3880(30)	3930(20)	4491(16)	63(7)
H(10B)	3010(30)	3680(20)	5382(18)	78(8)
H(10C)	4610(30)	3660(20)	5382(16)	68(8)

Table 6. Torsion angles [deg] for nle740g.

N(1)-C(9)-C(8)-C(7)	-176.69(16)
C(4)-C(9)-C(8)-C(7)	5.3(3)
C(9)-C(8)-C(7)-C(6)	-1.2(3)
C(8)-C(7)-C(6)-C(5)	-2.8(3)
C(7)-C(6)-C(5)-C(4)	2.7(3)
C(6)-C(5)-C(4)-N(2)	-173.39(15)
C(6)-C(5)-C(4)-C(9)	1.4(3)
N(1)-C(9)-C(4)-N(2)	-8.8(2)
C(8)-C(9)-C(4)-N(2)	169.32(15)
N(1)-C(9)-C(4)-C(5)	176.50(15)
C(8)-C(9)-C(4)-C(5)	-5.3(2)
N(2)-C(3)-C(2)-O(1)	83.65(18)
C(3)#1-C(3)-C(2)-O(1)	-94.3(2)
N(2)-C(3)-C(2)-N(1)	-39.0(2)
C(3)#1-C(3)-C(2)-N(1)	143.00(19)
C(8)-C(9)-N(1)-C(2)	156.98(16)
C(4)-C(9)-N(1)-C(2)	-25.0(2)
C(8)-C(9)-N(1)-C(1)	-5.0(3)
C(4)-C(9)-N(1)-C(1)	173.11(16)
O(1)-C(2)-N(1)-C(9)	-70.86(19)
C(3)-C(2)-N(1)-C(9)	45.72(19)
O(1)-C(2)-N(1)-C(1)	91.26(19)
C(3)-C(2)-N(1)-C(1)	-152.17(16)
C(3)#1-C(3)-N(2)-C(4)	-173.25(17)
C(2)-C(3)-N(2)-C(4)	8.8(2)
C(5)-C(4)-N(2)-C(3)	-168.46(16)
C(9)-C(4)-N(2)-C(3)	16.8(2)
N(1)-C(2)-O(1)-C(10)	-73.30(19)
C(3)-C(2)-O(1)-C(10)	168.23(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Datablock: I

Bond precision: C-C = 0.0023 A Wavelength=0.71073
Cell: a=10.2451(8) b=11.0740(7) c=15.3632(11)
alpha=90 beta=90 gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	1743.0(2)	1743.0(2)
Space group	P c a b	P c a b
Hall group	-P 2bc 2ac	-P 2bc 2ac
Moiety formula	C20 H22 N4 O2	C20 H22 N4 O2
Sum formula	C20 H22 N4 O2	C20 H22 N4 O2

Mr	350.42	350.41
Dx,g cm-3	1.335	1.335
Z	4	4
Mu (mm-1)	0.089	0.089
F000	744.0	744.0
F000'	744.29	
h,k,lmax	13,14,19	13,14,19
Nref	1973	1941
Tmin,Tmax	0.979,0.983	
Tmin'	0.979	

Correction method= Not given
Data completeness= 0.984 Theta(max)= 27.370
R(reflections)= 0.0476(1339) wR2(reflections)= 0.1326(1941)
S = 1.015 Npar= 163

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level G

PLAT128_ALERT_4_G Alternate Setting for Input Space Group Pcab Pbca
Note
PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) S
Verify

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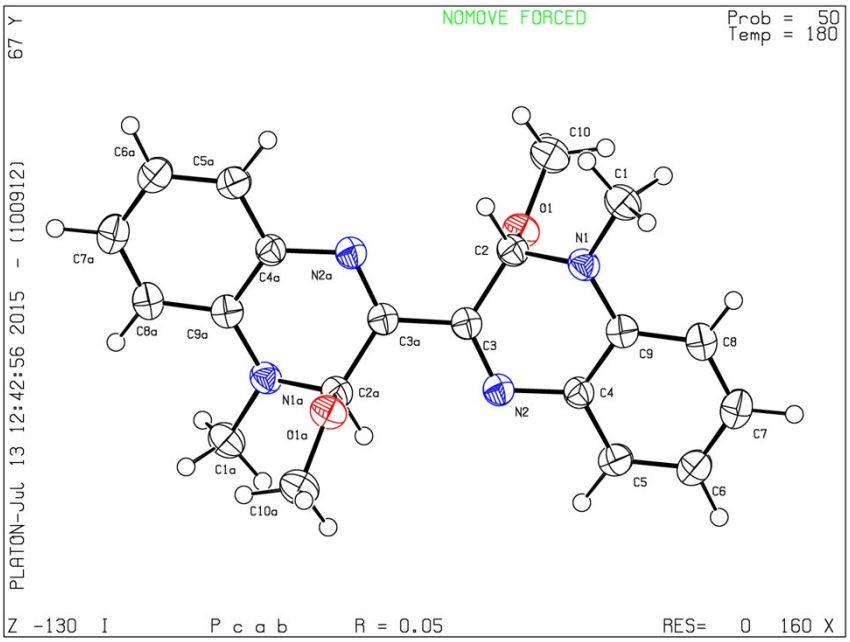
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
0 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected



B_3-1$(OEt)_2$

Table 1. Crystal data and structure refinement.

Empirical formula	C22 H26 N4 O2
Formula weight	378.47
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/a
Unit cell dimensions	a = 8.8290(11) A alpha = 90 deg. b = 11.3130(16) A beta = 107.834(9) deg. c = 10.4030(13) A gamma = 90 deg.
Volume	989.1(2) A^3
Z, Calculated density	2, 1.271 Mg/m^3
Absorption coefficient	0.083 mm^-1
F(000)	404
Crystal size	0.378 x 0.353 x 0.156 mm
Theta range for data collection	2.734 to 27.402 deg.
Limiting indices	-11<=h<=11, -14<=k<=14, -13<=l<=10
Reflections collected / unique	4943 / 2205 [R(int) = 0.0256]
Completeness to theta = 25.242	98.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2205 / 0 / 180
Goodness-of-fit on F^2	0.927
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.0968
R indices (all data)	R1 = 0.0622, wR2 = 0.1075
Extinction coefficient	0.094(10)
Largest diff. peak and hole	0.186 and -0.154 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	793(2)	1345(1)	4605(2)	63(1)
C(9)	1451(1)	2924(1)	3229(2)	52(1)
C(8)	2066(2)	2144(2)	2465(2)	62(1)
C(7)	2469(2)	2556(2)	1367(2)	72(1)
C(6)	2249(2)	3724(2)	976(2)	73(1)
C(5)	1609(2)	4505(2)	1691(2)	63(1)
C(4)	1229(1)	4122(1)	2826(1)	52(1)
C(3)	381(1)	4596(1)	4643(1)	47(1)
C(2)	1012(2)	3449(1)	5322(2)	49(1)
C(10)	3075(2)	3080(2)	7418(2)	65(1)
C(11)	4522(2)	3654(2)	8339(2)	71(1)
N(1)	1001(1)	2581(1)	4325(1)	53(1)
N(2)	532(1)	4921(1)	3498(1)	49(1)
O(1)	2573(1)	3730(1)	6196(1)	53(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.4522(18)
C(9)-N(1)	1.3735(19)
C(9)-C(8)	1.403(2)
C(9)-C(4)	1.414(2)
C(8)-C(7)	1.377(3)
C(7)-C(6)	1.379(3)
C(6)-C(5)	1.382(2)
C(5)-C(4)	1.393(2)
C(4)-N(2)	1.3955(17)
C(3)-N(2)	1.2922(18)
C(3)-C(3)#1	1.466(3)
C(3)-C(2)	1.4997(18)
C(2)-N(1)	1.4264(18)
C(2)-O(1)	1.4350(16)
C(10)-O(1)	1.4166(18)
C(10)-C(11)	1.491(2)
N(1)-C(9)-C(8)	123.56(14)
N(1)-C(9)-C(4)	117.88(11)
C(8)-C(9)-C(4)	118.52(14)
C(7)-C(8)-C(9)	119.97(16)
C(8)-C(7)-C(6)	121.38(15)
C(7)-C(6)-C(5)	119.82(18)
C(6)-C(5)-C(4)	120.13(17)
C(5)-C(4)-N(2)	118.71(14)
C(5)-C(4)-C(9)	120.14(13)
N(2)-C(4)-C(9)	121.02(12)
N(2)-C(3)-C(3)#1	118.84(14)
N(2)-C(3)-C(2)	123.52(11)
C(3)#1-C(3)-C(2)	117.58(15)
N(1)-C(2)-O(1)	113.85(10)
N(1)-C(2)-C(3)	109.53(12)
O(1)-C(2)-C(3)	104.71(10)
O(1)-C(10)-C(11)	108.78(14)
C(9)-N(1)-C(2)	118.01(11)
C(9)-N(1)-C(1)	121.72(12)
C(2)-N(1)-C(1)	119.38(13)
C(3)-N(2)-C(4)	117.54(11)
C(10)-O(1)-C(2)	115.45(11)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	63(1)	43(1)	76(1)	0(1)	12(1)	3(1)
C(9)	42(1)	56(1)	54(1)	-9(1)	8(1)	0(1)
C(8)	49(1)	66(1)	65(1)	-18(1)	9(1)	4(1)
C(7)	56(1)	89(1)	66(1)	-28(1)	15(1)	1(1)
C(6)	72(1)	94(1)	58(1)	-16(1)	27(1)	-8(1)
C(5)	64(1)	70(1)	56(1)	-7(1)	20(1)	-8(1)
C(4)	47(1)	56(1)	51(1)	-8(1)	13(1)	-3(1)
C(3)	43(1)	45(1)	49(1)	-1(1)	10(1)	-3(1)
C(2)	45(1)	46(1)	54(1)	0(1)	13(1)	0(1)
C(10)	72(1)	65(1)	53(1)	10(1)	10(1)	0(1)
C(11)	65(1)	87(1)	53(1)	5(1)	8(1)	5(1)
N(1)	53(1)	43(1)	60(1)	-3(1)	14(1)	1(1)
N(2)	49(1)	47(1)	50(1)	-3(1)	14(1)	-2(1)
O(1)	49(1)	58(1)	49(1)	6(1)	10(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(1A)	200(20)	891(16)	3680(20)	79(5)
H(1B)	1790(20)	926(16)	5040(20)	83(5)
H(1C)	60(30)	1310(18)	5260(20)	100(6)
H(8)	2210(20)	1265(16)	2741(18)	74(5)
H(7)	2940(20)	1975(16)	820(20)	88(6)
H(6)	2480(20)	4011(16)	220(20)	86(6)
H(5)	1383(19)	5353(16)	1444(18)	67(4)
H(2)	338(16)	3139(11)	5899(15)	50(4)
H(10A)	3290(20)	2230(20)	7190(20)	94(6)
H(10B)	2140(20)	3061(15)	7854(19)	82(5)
H(11A)	5340(20)	3706(16)	7910(20)	89(6)
H(11B)	4880(20)	3234(18)	9190(20)	94(6)
H(11C)	4280(20)	4521(19)	8590(20)	92(6)

Table 6. Torsion angles [deg].

N(1)-C(9)-C(8)-C(7)	179.09(13)
C(4)-C(9)-C(8)-C(7)	1.3(2)
C(9)-C(8)-C(7)-C(6)	-1.4(2)
C(8)-C(7)-C(6)-C(5)	-0.1(2)
C(7)-C(6)-C(5)-C(4)	1.8(2)
C(6)-C(5)-C(4)-N(2)	-177.74(13)
C(6)-C(5)-C(4)-C(9)	-1.9(2)
N(1)-C(9)-C(4)-C(5)	-177.59(12)
C(8)-C(9)-C(4)-C(5)	0.31(19)
N(1)-C(9)-C(4)-N(2)	-1.81(18)
C(8)-C(9)-C(4)-N(2)	176.09(12)
N(2)-C(3)-C(2)-N(1)	-30.26(16)
C(3)#1-C(3)-C(2)-N(1)	152.63(13)
N(2)-C(3)-C(2)-O(1)	92.19(14)
C(3)#1-C(3)-C(2)-O(1)	-84.92(15)
C(8)-C(9)-N(1)-C(2)	155.14(12)
C(4)-C(9)-N(1)-C(2)	-27.07(17)
C(8)-C(9)-N(1)-C(1)	-14.0(2)
C(4)-C(9)-N(1)-C(1)	163.80(13)
O(1)-C(2)-N(1)-C(9)	-76.27(15)
C(3)-C(2)-N(1)-C(9)	40.56(14)
O(1)-C(2)-N(1)-C(1)	93.12(14)
C(3)-C(2)-N(1)-C(1)	-150.06(12)
C(3)#1-C(3)-N(2)-C(4)	-178.53(13)
C(2)-C(3)-N(2)-C(4)	4.39(18)
C(5)-C(4)-N(2)-C(3)	-171.14(12)
C(9)-C(4)-N(2)-C(3)	13.02(18)
C(11)-C(10)-O(1)-C(2)	-167.02(13)
N(1)-C(2)-O(1)-C(10)	-93.61(15)
C(3)-C(2)-O(1)-C(10)	146.80(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Datablock: I

Bond precision: C-C = 0.0023 A Wavelength=0.71073
Cell: a=8.8290(11) b=11.3130(16) c=10.4030(13)
alpha=90 beta=107.834(9) gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	989.2(2)	989.1(2)
Space group	P 21/a	P 21/a
Hall group	-P 2yab	-P 2yab
Moiety formula	C22 H26 N4 O2	C22 H26 N4 O2
Sum formula	C22 H26 N4 O2	C22 H26 N4 O2
Mr	378.47	378.47
Dx,g cm-3	1.271	1.271
Z	2	2
Mu (mm-1)	0.083	0.083
F000	404.0	404.0
F000'	404.15	
h,k,lmax	11,14,13	11,14,13
Nref	2249	2205
Tmin,Tmax	0.969,0.987	
Tmin'	0.969	

Correction method= Not given
Data completeness= 0.980 Theta(max)= 27.402
R(reflections)= 0.0379(1399) wR2(reflections)= 0.1075(2205)
S = 0.927 Npar= 180

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

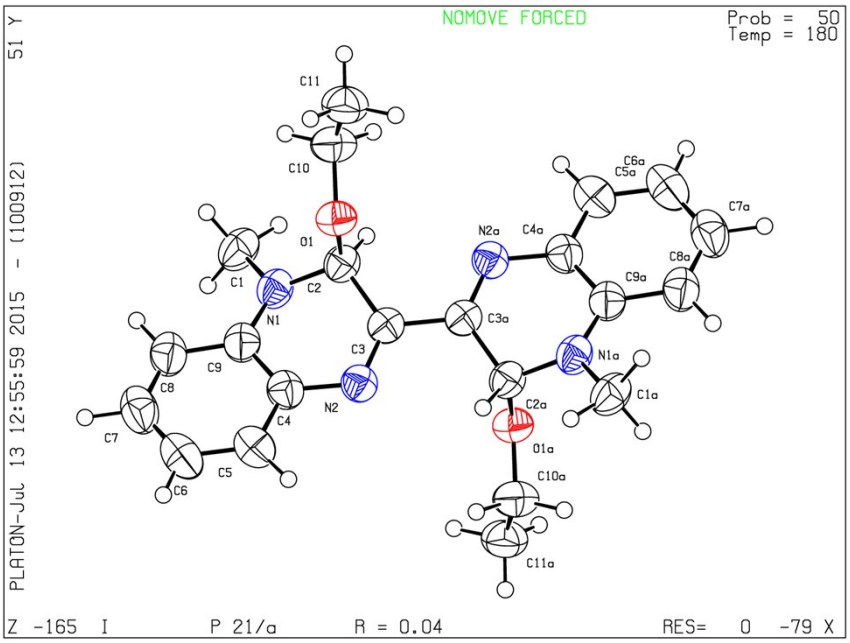
Alert level C

PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT128_ALERT_4_G Alternate Setting for Input Space Group P21/a P21/c Note
PLAT180_ALERT_4_G Check Cell Rounding: # of Values Ending with 0 = 3
PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) S Verify

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
3 **ALERT level G** = General information/check it is not something unexpected



B_4-1(OEtOEt)$_2$

Table 1. Crystal data and structure refinement.

Empirical formula	C26 H34 N4 O4
Formula weight	466.57
Temperature	180(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P21/a
Unit cell dimensions	a = 8.6751(8) A alpha = 90 deg. b = 11.2503(10) A beta = 94.681(7) deg. c = 13.3424(10) A gamma = 90 deg.
Volume	1297.84(19) A^3
Z, Calculated density	2, 1.194 Mg/m^3
Absorption coefficient	0.081 mm^-1
F(000)	500
Crystal size	0.3 x 0.2 x 0.1 mm
Theta range for data collection	2.371 to 27.453 deg.
Limiting indices	-11<=h<=8, -14<=k<=14, -17<=l<=17
Reflections collected / unique	7771 / 2890 [R(int) = 0.0578]
Completeness to theta = 25.242	98.5 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2890 / 0 / 157
Goodness-of-fit on F^2	0.878
Final R indices [I>2sigma(I)]	R1 = 0.0498, wR2 = 0.1279
R indices (all data)	R1 = 0.0819, wR2 = 0.1460
Extinction coefficient	0.193(18)
Largest diff. peak and hole	0.154 and -0.145 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3).
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	4216(2)	6301(2)	10262(2)	69(1)
C(9)	3108(2)	7847(2)	11291(1)	61(1)
C(8)	2334(2)	7030(2)	11863(1)	68(1)
C(7)	1612(2)	7407(2)	12681(1)	75(1)
C(6)	1660(2)	8588(2)	12981(1)	75(1)
C(5)	2450(2)	9399(2)	12446(1)	69(1)
C(4)	3167(2)	9048(2)	11601(1)	60(1)
C(3)	4523(2)	9579(1)	10256(1)	56(1)
C(2)	4140(2)	8422(1)	9741(1)	58(1)
C(10)	2673(2)	7932(2)	8196(1)	68(1)
C(11)	1545(2)	8492(2)	7431(1)	73(1)
C(12)	117(3)	8028(3)	5896(2)	101(1)
C(13)	-300(4)	7014(4)	5219(2)	133(1)
N(1)	3873(2)	7535(1)	10469(1)	61(1)
N(2)	4024(2)	9883(1)	11106(1)	59(1)
O(1)	2822(1)	8680(1)	9050(1)	62(1)
O(2)	1148(2)	7623(1)	6696(1)	85(1)

Table 3. Bond lengths [A] and angles [deg].

C(1)-N(1)	1.452(2)
C(9)-N(1)	1.373(2)
C(9)-C(8)	1.400(2)
C(9)-C(4)	1.413(2)
C(8)-C(7)	1.370(3)
C(7)-C(6)	1.386(3)
C(6)-C(5)	1.376(3)
C(5)-C(4)	1.389(2)
C(4)-N(2)	1.396(2)
C(3)-N(2)	1.293(2)
C(3)-C(3)#1	1.463(3)
C(3)-C(2)	1.497(2)
C(2)-N(1)	1.424(2)
C(2)-O(1)	1.439(2)
C(10)-O(1)	1.4140(19)
C(10)-C(11)	1.494(3)
C(11)-O(2)	1.408(2)
C(12)-O(2)	1.412(3)
C(12)-C(13)	1.481(4)
N(1)-C(9)-C(8)	123.47(16)
N(1)-C(9)-C(4)	117.98(15)
C(8)-C(9)-C(4)	118.48(16)
C(7)-C(8)-C(9)	120.05(18)
C(8)-C(7)-C(6)	121.50(19)
C(5)-C(6)-C(7)	119.33(18)
C(6)-C(5)-C(4)	120.55(19)
C(5)-C(4)-N(2)	118.92(16)
C(5)-C(4)-C(9)	120.05(16)
N(2)-C(4)-C(9)	120.90(15)
N(2)-C(3)-C(3)#1	118.72(18)
N(2)-C(3)-C(2)	123.71(15)
C(3)#1-C(3)-C(2)	117.54(17)
N(1)-C(2)-O(1)	114.42(13)
N(1)-C(2)-C(3)	109.80(13)
O(1)-C(2)-C(3)	104.66(13)
O(1)-C(10)-C(11)	108.14(15)
O(2)-C(11)-C(10)	106.99(16)
O(2)-C(12)-C(13)	108.7(2)
C(9)-N(1)-C(2)	118.83(14)

C(9)-N(1)-C(1)	121.09(14)
C(2)-N(1)-C(1)	119.52(13)
C(3)-N(2)-C(4)	117.76(14)
C(10)-O(1)-C(2)	114.31(13)
C(11)-O(2)-C(12)	113.99(18)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2

Table 4. Anisotropic displacement parameters (A^2 x 10^3).
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	67(1)	50(1)	90(1)	-2(1)	2(1)	0(1)
C(9)	55(1)	57(1)	69(1)	4(1)	1(1)	0(1)
C(8)	64(1)	62(1)	77(1)	9(1)	0(1)	-6(1)
C(7)	68(1)	79(1)	78(1)	13(1)	5(1)	-9(1)
C(6)	73(1)	84(1)	71(1)	4(1)	12(1)	1(1)
C(5)	71(1)	66(1)	70(1)	2(1)	9(1)	7(1)
C(4)	56(1)	58(1)	66(1)	4(1)	4(1)	1(1)
C(3)	54(1)	48(1)	66(1)	-2(1)	3(1)	2(1)
C(2)	54(1)	51(1)	68(1)	-1(1)	5(1)	1(1)
C(10)	72(1)	67(1)	66(1)	-9(1)	4(1)	-1(1)
C(11)	77(1)	74(1)	68(1)	-3(1)	4(1)	-6(1)
C(12)	85(2)	151(2)	66(1)	-1(1)	-4(1)	-10(2)
C(13)	110(2)	206(4)	81(1)	-36(2)	-1(1)	-36(2)
N(1)	63(1)	47(1)	73(1)	-1(1)	7(1)	0(1)
N(2)	58(1)	52(1)	68(1)	1(1)	4(1)	2(1)
O(1)	58(1)	59(1)	67(1)	-7(1)	2(1)	2(1)
O(2)	85(1)	98(1)	70(1)	-12(1)	-2(1)	-7(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

	x	y	z	U(eq)
H(1A)	4572	5909	10877	103
H(1B)	5004	6263	9798	103
H(1C)	3297	5914	9974	103
H(8)	2310	6230	11686	81
H(7)	1078	6860	13044	90
H(6)	1163	8828	13539	91
H(5)	2505	10189	12652	83
H(2)	5008	8177	9362	69
H(10A)	2306	7154	8380	82
H(10B)	3668	7837	7923	82
H(11A)	632	8754	7743	88
H(11B)	2009	9175	7129	88
H(12A)	603	8649	5527	121
H(12B)	-806	8353	6156	121
H(13A)	625	6649	5016	199
H(13B)	-915	7294	4636	199
H(13C)	-880	6442	5567	199

Table 6. Torsion angles [deg].

N(1)-C(9)-C(8)-C(7)	179.20(16)
C(4)-C(9)-C(8)-C(7)	2.2(3)
C(9)-C(8)-C(7)-C(6)	-1.8(3)
C(8)-C(7)-C(6)-C(5)	0.0(3)
C(7)-C(6)-C(5)-C(4)	1.3(3)
C(6)-C(5)-C(4)-N(2)	-176.83(16)
C(6)-C(5)-C(4)-C(9)	-0.9(3)
N(1)-C(9)-C(4)-C(5)	-178.06(15)
C(8)-C(9)-C(4)-C(5)	-0.9(2)
N(1)-C(9)-C(4)-N(2)	-2.2(2)
C(8)-C(9)-C(4)-N(2)	174.99(15)
N(2)-C(3)-C(2)-N(1)	-28.8(2)
C(3)#1-C(3)-C(2)-N(1)	153.19(17)
N(2)-C(3)-C(2)-O(1)	94.46(17)
C(3)#1-C(3)-C(2)-O(1)	-83.5(2)
O(1)-C(10)-C(11)-O(2)	-166.81(14)
C(8)-C(9)-N(1)-C(2)	157.90(16)
C(4)-C(9)-N(1)-C(2)	-25.1(2)
C(8)-C(9)-N(1)-C(1)	-13.5(3)
C(4)-C(9)-N(1)-C(1)	163.56(15)
O(1)-C(2)-N(1)-C(9)	-79.18(18)
C(3)-C(2)-N(1)-C(9)	38.1(2)
O(1)-C(2)-N(1)-C(1)	92.33(18)
C(3)-C(2)-N(1)-C(1)	-150.34(15)
C(3)#1-C(3)-N(2)-C(4)	-177.47(17)
C(2)-C(3)-N(2)-C(4)	4.5(2)
C(5)-C(4)-N(2)-C(3)	-171.83(15)
C(9)-C(4)-N(2)-C(3)	12.3(2)
C(11)-C(10)-O(1)-C(2)	-165.02(15)
N(1)-C(2)-O(1)-C(10)	-86.79(17)
C(3)-C(2)-O(1)-C(10)	152.98(13)
C(10)-C(11)-O(2)-C(12)	-178.10(17)
C(13)-C(12)-O(2)-C(11)	-175.76(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+2

Datablock: I

Bond precision: C-C = 0.0026 A Wavelength=0.71073
Cell: a=8.6751(8) b=11.2503(10) c=13.3424(10)
alpha=90 beta=94.681(7) gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	1297.84(19)	1297.84(19)
Space group	P 21/a	P 21/a
Hall group	-P 2yab	-P2yab
Moiety formula	C26 H34 N4 O4	C26 H34 N4 O4
Sum formula	C26 H34 N4 O4	C26 H34 N4 O4
Mr	466.57	466.57
Dx,g cm-3	1.194	1.194
Z	2	2
Mu (mm-1)	0.081	0.081
F000	500.0	500.0
F000'	500.21	
h,k,lmax	11,14,17	11,14,17
Nref	2974	2890
Tmin,Tmax	0.981,0.992	
Tmin'	0.976	

Correction method= Not given
Data completeness= 0.972 Theta(max)= 27.453
R(reflections)= 0.0498(1622) wR2(reflections)= 0.1460(2890)
S = 0.878 Npar= 157

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

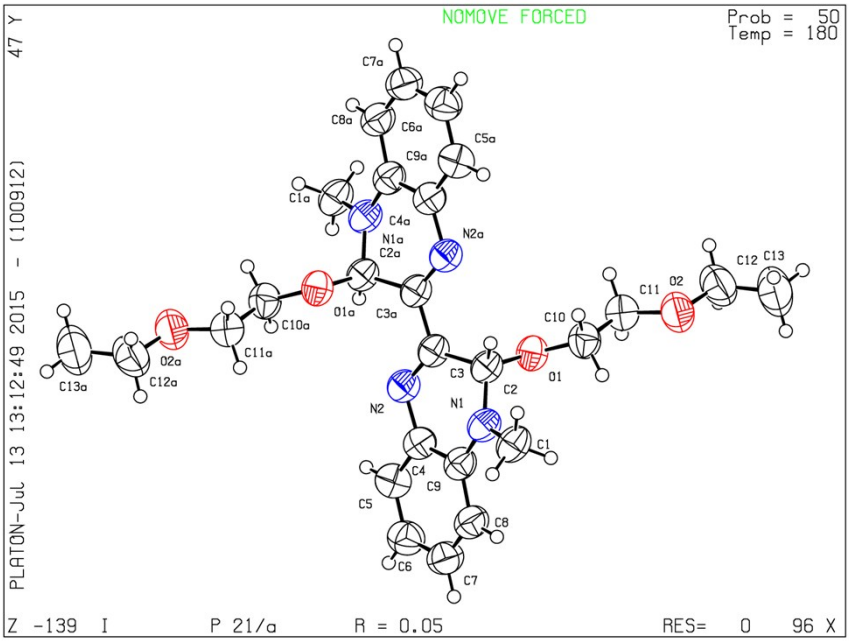
Alert level C

PLAT761_ALERT_1_C CIF Contains no X-H Bonds ..... Please Check
PLAT762_ALERT_1_C CIF Contains no X-Y-H or H-Y-H Angles ..... Please Check

Alert level G

PLAT128_ALERT_4_G Alternate Setting for Input Space Group P21/a P21/c Note
PLAT793_ALERT_4_G The Model has Chirality at C2 (Centro SPGR) S Verify

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
2 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
2 **ALERT level G** = General information/check it is not something unexpected



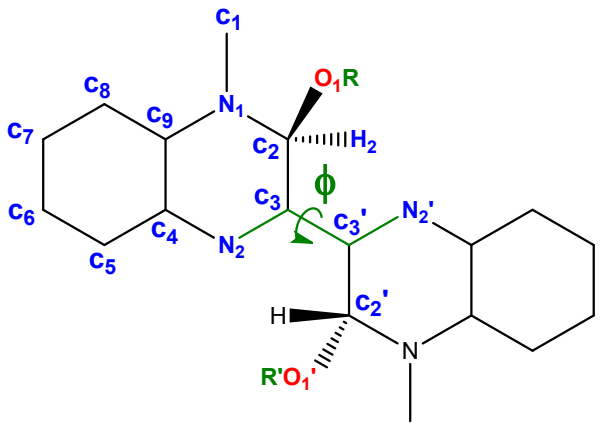
C. Structural parameters of 1^{2+}, $1(OH)_2^{\beta}$ and $1(OR)_2$ (R=Me, Et and EtOEt).

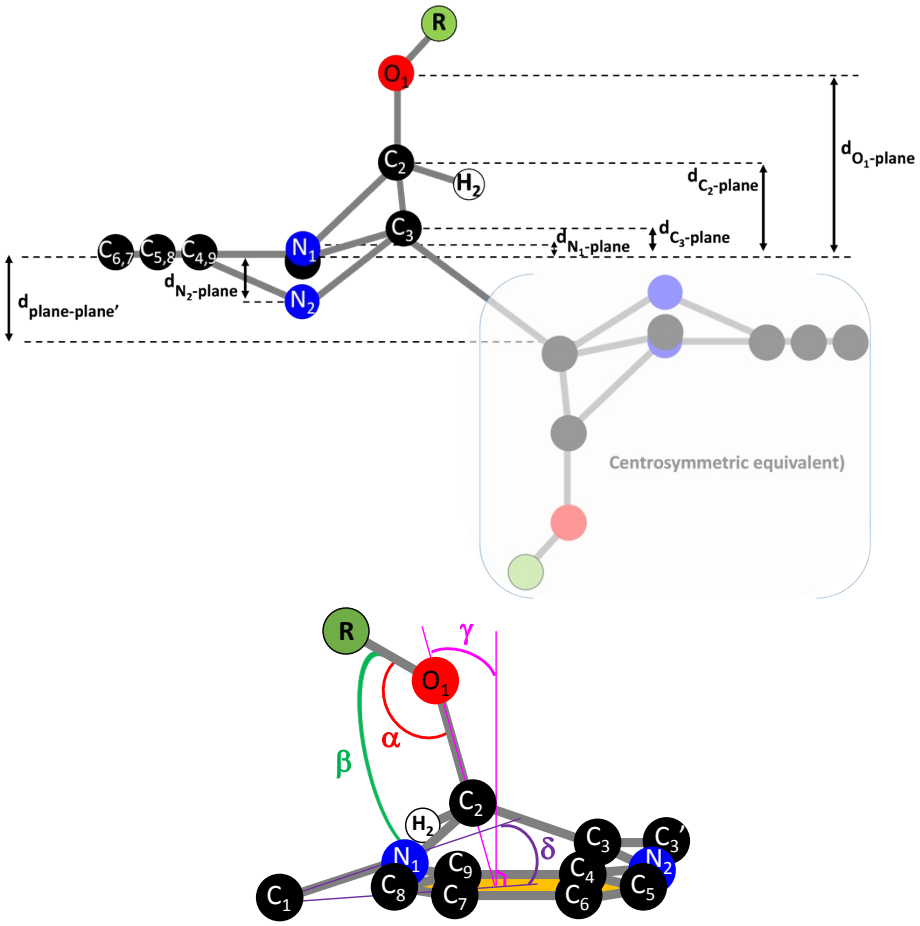
In all asymmetric units, the organic part is made of two equivalent half moieties related by an inversion centre, which are of *N*-methylquinoxalinium, 2-hydroxy-1-methyl-1,2-dihydroquinoxaline and 2-methoxy-1-methyl-1,2-dihydroquinoxaline type for $\mathbf{1}^{2+}$, $\mathbf{1(OH)_2^{\beta}}$ and $\mathbf{1(OMe)_2}$ respectively. All atoms including hydrogens were identified from Fourier difference maps. All atoms occupy general positions.

The structure of the dication $\mathbf{1}^{2+}$ is made of a fully aromatic π-conjugated system with full electron delocalization. The average C–C bond length in the benzene ring is of about 1.39-1.40 Å and C–C and C–N bond distances in the pyrazinium moiety are of about 1.41Å and 1.32–1.40 Å respectively. In spite of the rotation freedom around the central C_3–C_3' bond, $\mathbf{1}^{2+}$ is perfectly planar with a *trans*-geometry (ϕ=180°), the dihedral angle being defined such as ϕ=N_2–C_3–C_3'–N_2'.

Both $\mathbf{1(OH)_2^{\beta}}$ and $\mathbf{1(OMe)_2}$ are isostructural and can be described as originating from the planar *trans*-dication $\mathbf{1}^{2+}$, with a subsequent nucleophilic addition of either the hydroxide or methoxide anions only on C_2 and C_2' atoms. Consequently, while keeping the same *trans*-conformation geometry (ϕ=180° for all), the C_2 and C_2' atoms lose their sp^2 character becoming sp^3, with the C_2–O_1 (C_2'–O_1') bonds being almost perpendicular to the mean plane of the molecules (see γ angles in Table S1). These are in line with a significant increase of the N_1–C_2 (N_1'–C_2') and C_2–C_3 (C_2–C_3') bond distances to d=1.428 (2) Å (+0.12 Å) and to d=1.503 (2) Å (+0.1 Å) respectively, and with C_2(C_2')-centred angles values close to 109.4° (Table S1), as compared to $\mathbf{1}^{2+}$. Furthermore, due to their asymmetric environment C_2 and C_2' define two chiral centres (their absolute configurations are here chosen as C_2 (S) and C_2' (R)) which are related by an inversion centre between the C_3–C_3' central bond so that the whole molecules remain achiral.

The presence of these two sp^3 carbons also disrupt the planarity of the molecules. Indeed, whereas $\mathbf{1}^{2+}$ is fully planar, in $\mathbf{1(OH)_2^{\beta}}$ and $\mathbf{1(OMe)_2}$, the "*N*-methylpyrazine" cores adopt a distorted geometry which vary depending on the OR substituent (Table S1 and S2). For a precise description and comparison, some specific parameters such as the offset distances of N_1, N_2 and C_3 from the benzene planes (d_X-plane with X=N_1, N_2, C_3) and the deviation angle (δ) between the vector C_1-N_1 and the benzene plane have been also identified. Regarding the environment around the oxygen atom, the C_2-O_1-R angle (α) and the dihedral N_1-C_2-O_1-R angle (β) have been also reported. Globally for all $\mathbf{1(OH)_2^{\beta}}$ and $\mathbf{1(OR)_2}$ compounds, N_1 atom exhibits no offset (0.002(1) Å <$d_{N1\text{-plane}}$< 0.090(1) Å) but its π-orbital can slightly deviates from the π-conjugated plane (4°<δ<14°). N_2 and C_3 atoms can strongly deviate from the benzene planes with 0.064(1) Å <$d_{N2\text{-plane}}$< 0.192(1) Å and 0.026(1) Å <$d_{C3\text{-plane}}$< 0.186(1) Å). From the previous parameters, nevertheless no real common difference can be observe between $\mathbf{1(OH)_2^{\beta}}$ and $\mathbf{1(OR)_2}$ species, instead of the fact that more the length of the **R** substituent increase, better planar is the whole π-conjugated system. However, regarding the O_1 environment we noticed a similar α angle for each $\mathbf{1(OR)_2}$ species (<α>=114.5°) whereas for $\mathbf{1(OH)_2^{\beta}}$ it is tighter with α=106.3°.





Scheme of the common structure of **1(OH)$_2^{\beta}$** and **1(OR)$_2$**. (Top) Basic skeleton of the molecule introducing important atoms labels and the dihedral angle ϕ= abs (N_2-C_3-C_3'-N_2'). (Middle) Projection along the N_1-C_1 vector and collinear to the benzene moieties (C_4 to C_9); Important distance parameters are reported. (Down) View of half of the molecule where important angles are reported (complete definition of the angle in Table S1).

Table S1: Specific parameters (distance in Å, angle in degree) of $\mathbf{1}^{2+}$, $\mathbf{1(OH)_2^{\beta}}$, $\mathbf{1(OMe)_2}$, $\mathbf{1(OEt)_2}$ and $\mathbf{1(OEtOEt)_2}$.

	$\mathbf{1}^{2+1}$	$\mathbf{1(OH)_2^{\beta}}$	$\mathbf{1(OMe)_2}$	$\mathbf{1(OEt)_2}$	$\mathbf{1(OEtOEt)_2}$
$d_{plane-plane'}$[a]	0.177 (2)	0.284 (1)	0.258 (1)	0.160 (1)	0.038 (1)
$d_{N_1-plane}$	0.018 (1)	0.002 (1)	0.090 (1)	0.030 (1)	0.022 (1)
$d_{C_2-plane}$	0.009 (1)	0.665 (1)	0.638 (1)	0.513(1)	0.469 (1)
$d_{C_3-plane}$	0.055 (1)	0.186 (1)	0.026 (1)	0.129 (1)	0.089 (1)
$d_{N_2-plane}$	0.038 (1)	0.081 (1)	0.192 (1)	0.064 (1)	0.083 (1)
$d_{O_1-plane}$		2.077 (1)	2.047 (1)	1.948 (1)	1.902 (1)
α[b]		106.3 (1)	113.7(1)	115.4 (1)	114.3 (1)
β[c]		80.7 (1)	73.2 (1)	93.6 (1)	86.7 (1)
γ[d]		7.0 (1)	9.5 (1)	1.5 (6)	4.8 (1)
δ[e]		4.1 (1)	3.8 (1)	14.0 (1)	13.9 (1)
ϕ[f]	180	180	180	180	180

[a] Plane defined by the benzene rings (C_4-C_9 and C_4'-C_9')
[b] Angle defined as α=abs (C_2-O_1-R)
[c] Dihedral angle defined as β=abs (N_1-C_2-O_1-R)
[d] Angle between vector C_2-O_1 and the normal of the benzene plane
[e] Deviation angle between vector C_1-N_1 and the benzene plane
[f] Dihedral angle defined as ϕ=abs (N_2-C_3-C_3'-N_2')

Table S2: Main Geometrical parameters (distance in Å, angle in degree) of $\mathbf{1}^{2+}$, $\mathbf{1(OH)_2^{\beta}}$, $\mathbf{1(OMe)_2}$, $\mathbf{1(OEt)_2}$ and $\mathbf{1(OEtOEt)_2}$.

	$\mathbf{1}^{2+1}$	$\mathbf{1(OH)_2^{\beta}}$	$\mathbf{1(OMe)_2}$	$\mathbf{1(OEt)_2}$	$\mathbf{1(OEtOEt)_2}$
C_1-N_1	1.476	1.456 (2)	1.450 (2)	1.452 (2)	1.452 (2)
C_9-N_1	1.383	1.376 (2)	1.378 (2)	1.373 (2)	1.373 (2)
C_8-C_9	1.402	1.397(2)	1.400 (2)	1.403 (2)	1.400 (3)
C_7-C_8	1.368	1.378(2)	1.383 (2)	1.377 (3)	1.370 (3)
C_6-C_7	1.404	1.390 (3)	1.394 (3)	1.373 (3)	1.387 (3)
C_5-C_6	1.366	1.374 (2)	1.381 (2)	1.382 (3)	1.376 (3)
C_5-C_4	1.415	1.391 (2)	1.398 (2)	1.393 (2)	1.389 (2)
C_4-C_9	1.416	1.416 (2)	1.412 (2)	1.414 (2)	1.413 (2)
C_4-N_2	1.352	1.399 (2)	1.396 (2)	1.396 (2)	1.396 (2)
N_2-C_3	1.315	1.293 (2)	1.293 (2)	1.292 (2)	1.293 (2)
N_1-C_2	1.311	1.430 (2)	1.435 (2)	1.426 (2)	1.424 (2)
C_3-C_2	1.410	1.511 (2)	1.507 (2)	1.500 (2)	1.497 (2)
C_3-C_3'	1.476	1.462 (2)	1.462 (2)	1.466 (2)	1.463 (2)
C_2-O_1		1.423 (2)	1.429 (2)	1.435 (1)	1.439 (2)
O_1-R		0.908 (24)	1.421 (2)	1.417(2)	1.414 (2)
		N_1 hybridization			
C_1-N_1-C_9	119.7 (1)	120.1 (1)	120.8 (1)	121.7 (1)	121.0 (1)
C_1-N_1-C_2	119.8 (1)	117.9 (1)	119.8 (1)	119.3 (1)	119.5 (1)
C_9-N_1-C_2	120.4 (1)	116.2 (1)	116.8 (1)	118.0 (1)	118.8 (1)
<Angle> =	**119.9 (1)**	**118.0 (1)**	**118.9 (1)**	**119.6 (1)**	**119.8 (1)**

[1] N. Leblanc, S. Sproules, K. Fink, L. Sanguinet, O. Aleveque, E. Levillain, P. Rosa, A. K. Powell, *Chem. Sci.* **2016**. DOI. 10.1039/C5SC04904K

		C_2 hybridization			
N_1-C_2-H_2	117.1 (1)	107.3 (8)	106.7 (9)	108.2 (7)	109.2 (1)
N_1-C_2-C_3	119.8 (1)	108.4 (1)	108.2 (1)	109.5 (1)	109.8 (1)
H_2-C_2-C_3	122.9 (1)	110.9 (7)	112.2 (9)	111.8 (7)	109.2 (1)
C_3-C_2-O_1		105.6 (1)	104.8 (1)	104.7 (1)	104.6 (1)
N_1-C_2-O_1		113.7 (1)	114.5 (1)	113.8 (1)	114.4 (1)
H_2-C_2-O_1		110.6 (8)	110.2 (1)	108.7 (8)	109.2 (1)
<Angle> =	**119.9 (1)**	**109.4 (1)**	**109.4 (1)**	**109.4 (1)**	**109.4 (1)**
		C_3 hybridization			
C_2-C_3-N_2	122.6 (1)	121.1 (1)	121.6 (1)	123.5 (1)	123.7 (1)
C_2-C_3-C_3'	119.2 (1)	119.0 (1)	119.0 (1)	117.5 (1)	117.5 (1)
N_2-C_3-C_3'	118.1 (1)	119.7 (1)	119.2 (1)	118.8 (1)	118.7 (1)
<Angle> =	**119.9(1)**	**119.9 (1)**	**119.9 (1)**	**119.9 (1)**	**119.9 (1)**
		N_2 hybridization			
C_3-N_2-C_4	117.4 (1)	118.1 (1)	117.1 (1)	117.5 (1)	117.7 (1)

D. Additional UV-Vis, Fluorescent, NMR and IR studies

Absorption peak λ_{max}	**H_2O**	**MeCN**	**DCM**
1^{2+}	449 nm	440 nm	441 nm
$1(OH)^{+}$	360 nm	360 nm	368 nm
$1(OH)_2$	490 nm	500 nm	540 nm

Table S3: Absorption maxima of **1^{2+}**, **$1(OH)^{+}$** and **$1(OH)_2$** in different solvent (H_2O, MeCN and DCM)

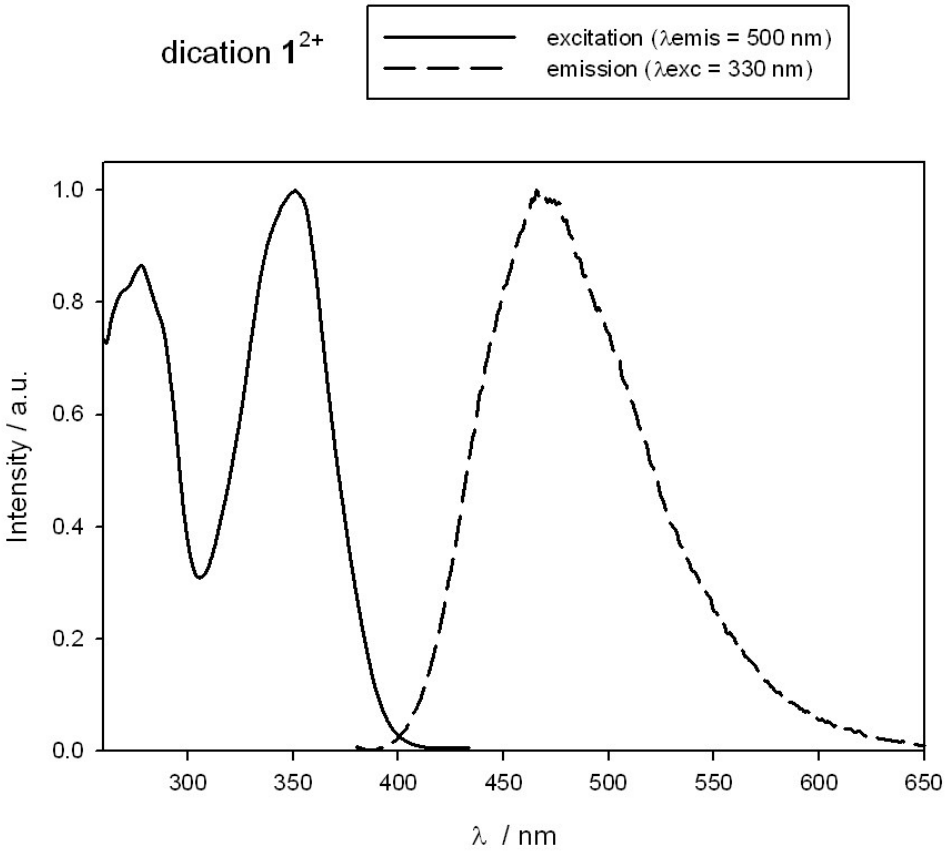


Figure S1: Excitation spectrum of 1^{2+} in dilute acetonitrile solution (emission wavelength 500 nm, black solid line) and emission spectrum (excitation wavelength 330 nm, dashed line).

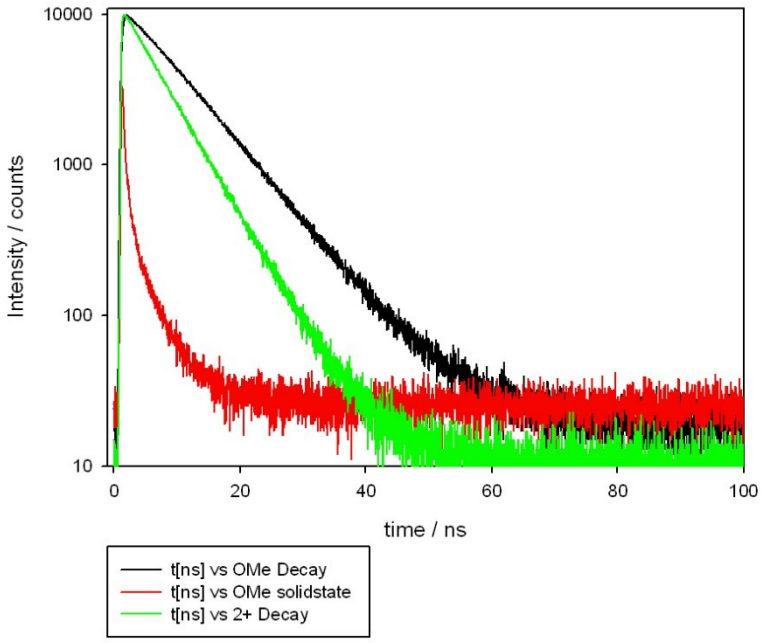


Figure S2: Fluorescence decay curves of the dication $\mathbf{1}^{2+}$ in acetonitrile solution (green) and of the bis-σ^H- adduct $\mathbf{1(OMe)_2}$ in acetonitrile dilute solutions (black) and in solid state (red).

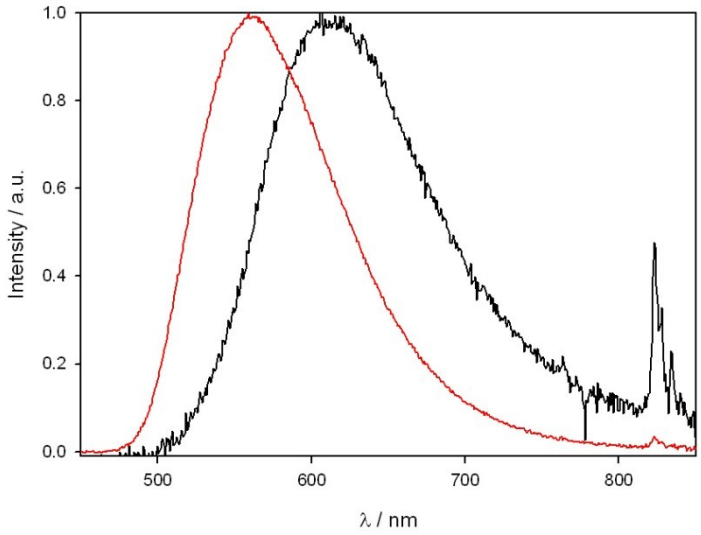


Figure S3: Emission spectra of bis-σ^H- adduct $\mathbf{1(OMe)_2}$ in acetonitrile dilute solutions ($1*10^{-5}$M, red line) and in the solid state (black line), excitation wavelength 410 nm.

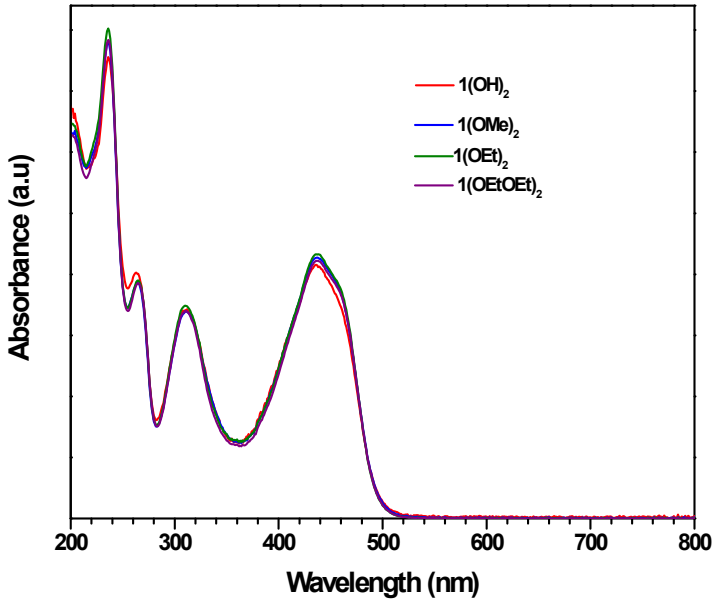


Figure S4: Solution state UV-Visible spectra of **1(OH)$_2^{\beta}$**, **1(OMe)$_2$**, **1(OEt)$_2$** and **1(OEtOEt)$_2$**

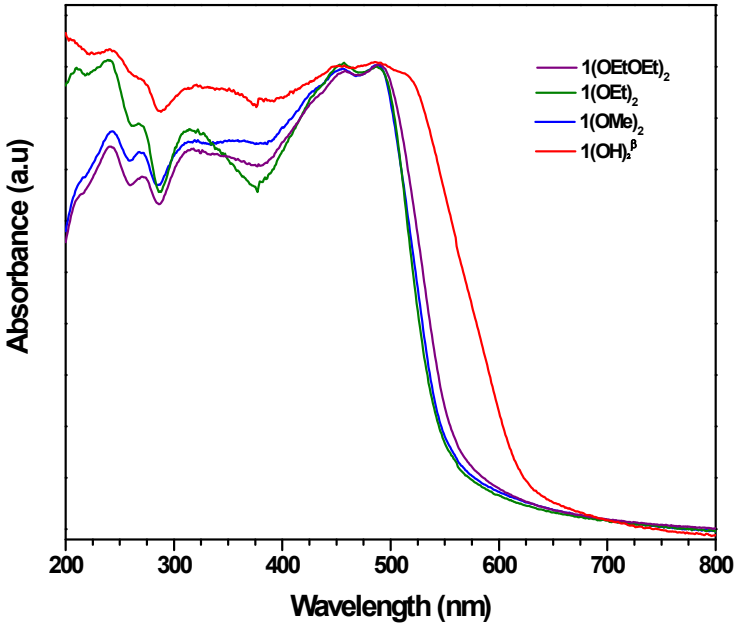


Figure S5: Solid state UV-Visible spectra of **1(OH)$_2^{\beta}$**, **1(OMe)$_2$**, **1(OEt)$_2$** and **1(OEtOEt)$_2$**

R =	**OEt** (MeCN)	**OEt** (SS)	**OEtOEt** (MeCN)	**OEtOEt** (SS)
Φ_{fluo}	0.67	0.15	0.59	0.16

Table S4: Quantum yields of the bis-σ^H- adducts **1(OR)$_2$** (R=Et, OEtOEt) , in acetonitrile dilute solutions (1*10^{-5}M, MeCN) and in solid state (SS).

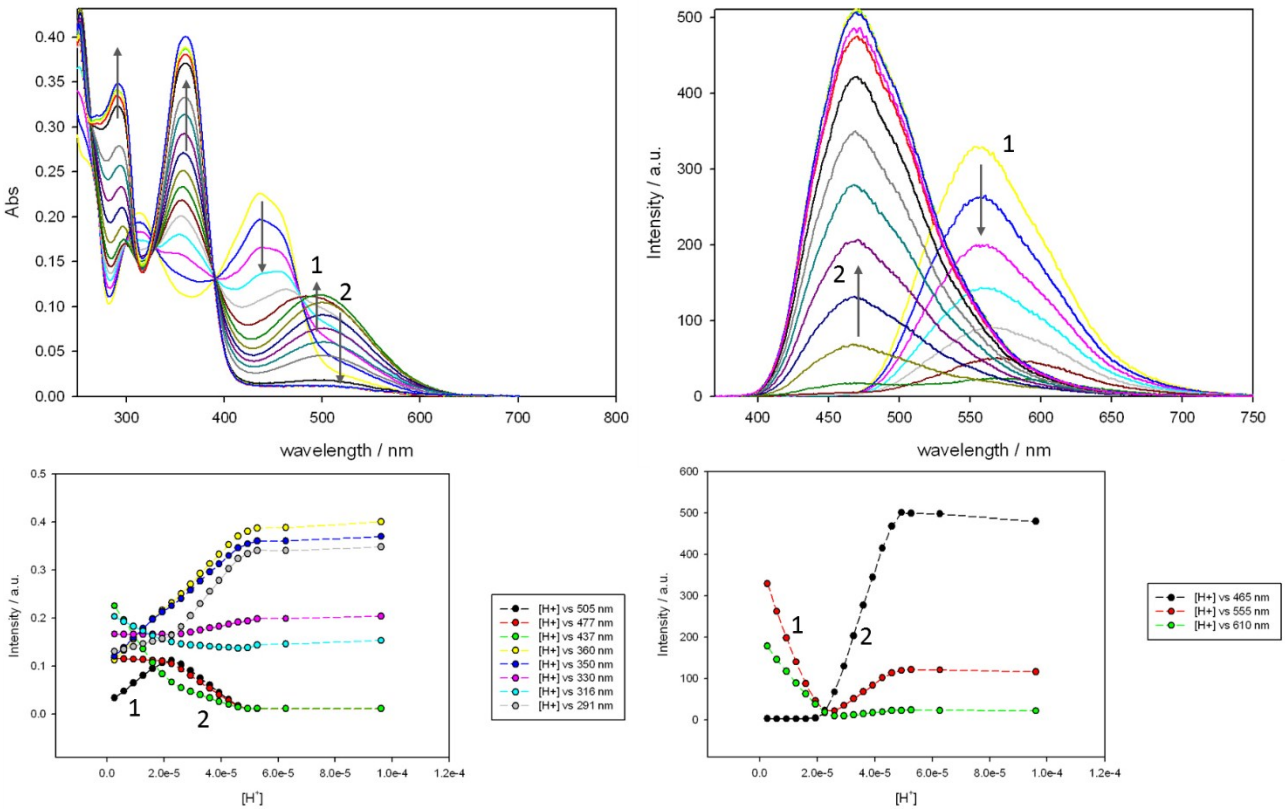


Figure S6: Absorption (left) and emission (right) spectra of titration of **1(OMe)$_2$** with HCl (in Et_2O, diluted in Acetonitrile, to avoid presence of water). The 2-steps mechanism is highlighted by the absorption and emission trends at individual wavelengths (bottom graphs, left and right respectively).

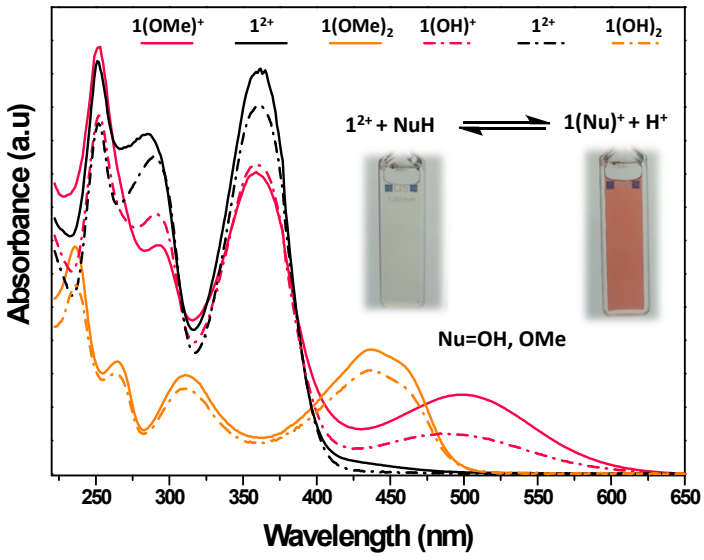


Figure S7: UV-Vis spectrum of **1(OD)**$^+$ (**1**$^{2+}$ dissolved in D_2O at pH=6.46 – pink solid line) and **1(OMe)**$^+$ (**1**$^{2+}$ dissolved in MeOH-d_4 – pink dashed line) overlaid with the spectra of **1**$^{2+}$ (black solid and dashed lines) after mild acidification. The spectra of the neutral bis-σ^H-adduct **1(OMe)$_2$** (orange solid line) and dipseudobase **1(OH)$_2$** (orange dashed line) have been added for comparison.

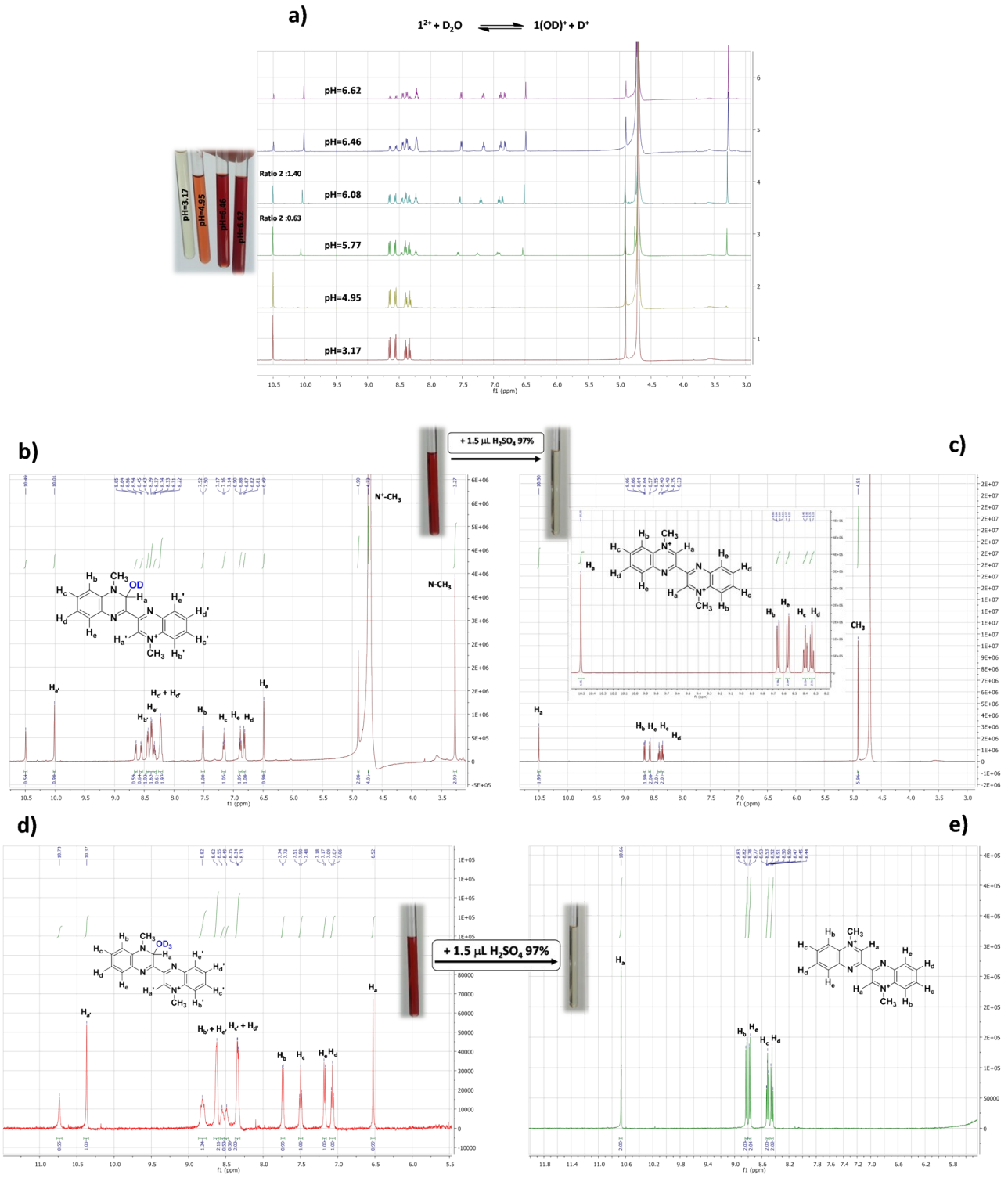
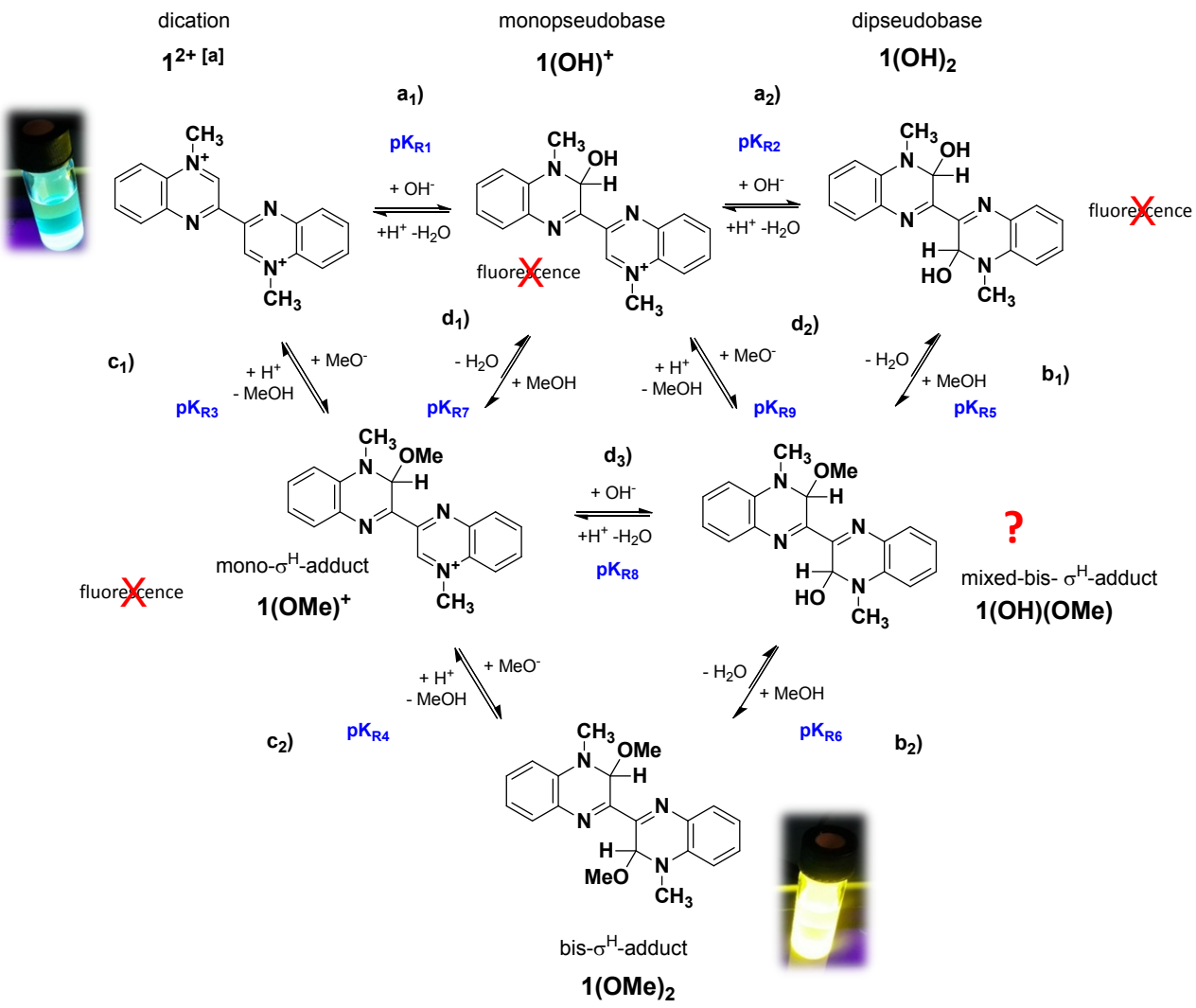


Figure S8: (a) Overlay of the NMR spectra of $\mathbf{1}^{2+}$ dissolved in D_2O at different pH (using Na_3PO_4) showing the appearance of the monopseudobase **1(OD)**$^+$, as the major product, by increasing the pH. (b) NMR spectrum of $\mathbf{1}^{2+}$ dissolved in D_2O at pH=6.46 showing the typical signature of the monopseudobase **1(OD)**$^+$, as the major product. (c) NMR spectrum of the solution used in (b) after in situ mild acidification (1.5mL H_2SO_4 97%), showing the typical signature of the dication $\mathbf{1}^{2+}$. (d) NMR spectrum of $\mathbf{1}^{2+}$ dissolved in MeOH-d_4 showing the typical signature of the mono-σ^H-adduct **1(OMe-d$_3$)**$^+$, as the major product. (e) NMR spectrum of the solution used in (d) after in situ mild acidification (1.5mL H_2SO_4 97%), showing the typical signature of the dication $\mathbf{1}^{2+}$.



Scheme S1: Complete view of the different pH-dependent species identified and their corresponding equilibria in solution: **1^{2+}**, **$1(OH)^{+}$**, **$1(OH)_2$**, **$1(OMe)^{+}$** and **$1(OMe)_2$**. The sixth hypothetical species, the mixed bis-σ^H-adduct **1(OH)(OMe)**, is also represented.

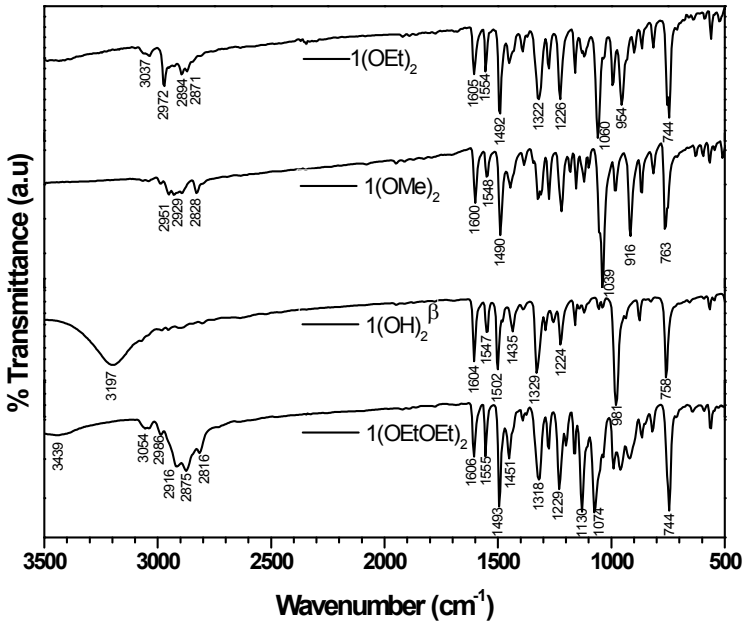


Figure S9: Solid state infrared spectra of **$1(OH)_2^{\beta}$**, **$1(OMe)_2$**, **$1(OEt)_2$** and **$1(OEtOEt)_2$**

E. Experimental details

Single crystals X-Ray diffraction data of **1(OH)$_2^{\beta}$**, **1(OMe)$_2$**, **1(OEt)$_2$** and **1(OEtOEt)$_2$** were collected at 180 K on a STOE IPDS II diffractometer equipped with a graphite monochromatised Mo Kα radiation (λ = 0.71073 Å), and mounted with an Oxford Nitrogen Cryostream. Structures were solved and refined using the Shelxl2013[2] and WingX2013[3] packages and molecular diagrams were prepared using Diamond 3.2k.[4] Positions, atomic displacement parameters, and hydrogens were refined by full-matrix least-squares routines against F^2.

Photophysical measurements. Absorption spectra were measured on a Shimadzu UV-3600 double-beam UV–VIS–NIR spectrophotometer and baseline corrected. Steady-state emission and excitation spectra and time resolved emission decays were recorded on a Picoquant FT300 fluorometer with a 450 W xenon arc lamp, and a 375nm diode laser, respectively. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. The absolute photoluminescence quantum yields (PLQY) and the solid state emission spectra were measured on a Hamamatsu Quantaurus-QY integrating sphere in air-equilibrated condition using an empty quartz tube as a reference.

Procedure for the polymer functionalization: 200 μL of 1mM of the oligomers and polymers in acetonitrile (concentration of hydroxyl terminations) were mixed with 50 μL of 0.5mM **1(OH)$_2$** in acetonitrile solution, and allowed to react overnight to ensure that kinetics were also allowed for slowly diffusing polymers (though luminescence is mostly observed within few minutes). A blank was prepared by mixing 50 μL of 0.2mM of **1(OH)$_2$** in acetonitrile solution with 200 μL of acetonitrile. Then, 100 μL of the reaction crude was diluted in 2 mL of acetonitrile and absorption, emission, excitation spectra and emission decays were measured.

[2] G. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122
[3] L. Farrugia, *J. Appl. Cryst.*, 2012, **45**, 849-854
[4] H. Putz and K. Brandenburg, Diamond - Crystal and Molecular Structure Visualization, Kreuzherrenstr. 102, 53227 Bonn, Germany