Supplementary Information for

Synthesis of a Monocationic μ–Nitrido-Bridged Iron Porphycene Dimer and its Methane Oxidation Activity

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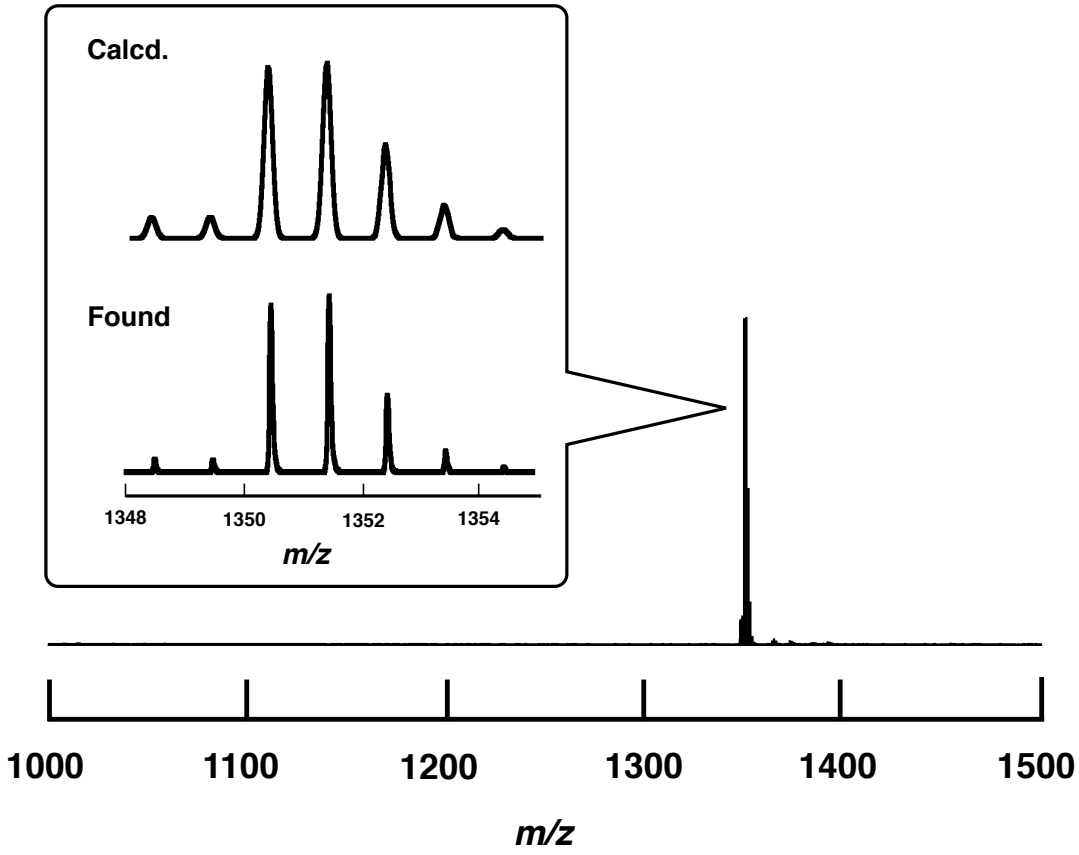

Figure S1. MALDI-TOF spectrum of $\mathbf{2}^{+}\cdot PF_6^{-}$. Inset: Comparison of the calculated and observed isotopic distribution patterns of $\mathbf{[2]}^{+}$.

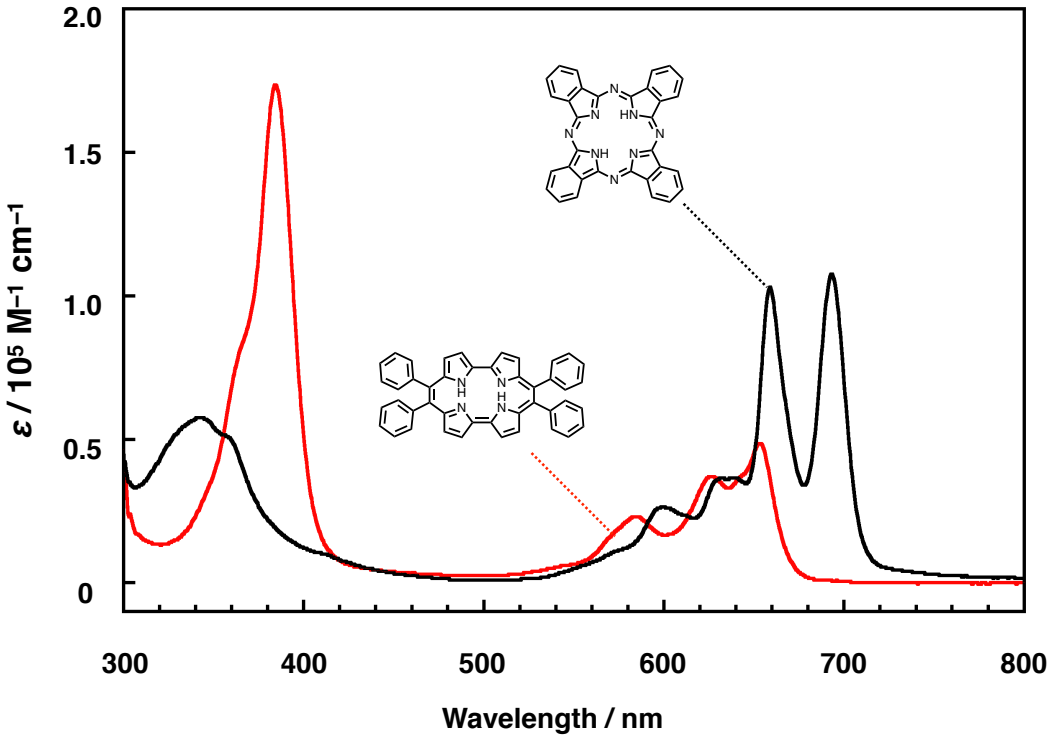

Figure S2. Comparison of UV-Vis spectra of a metal-free phthalocyanine and a metal-free porphycene in pyridine at 20 °C. [Substrate] = 2.0 μM.

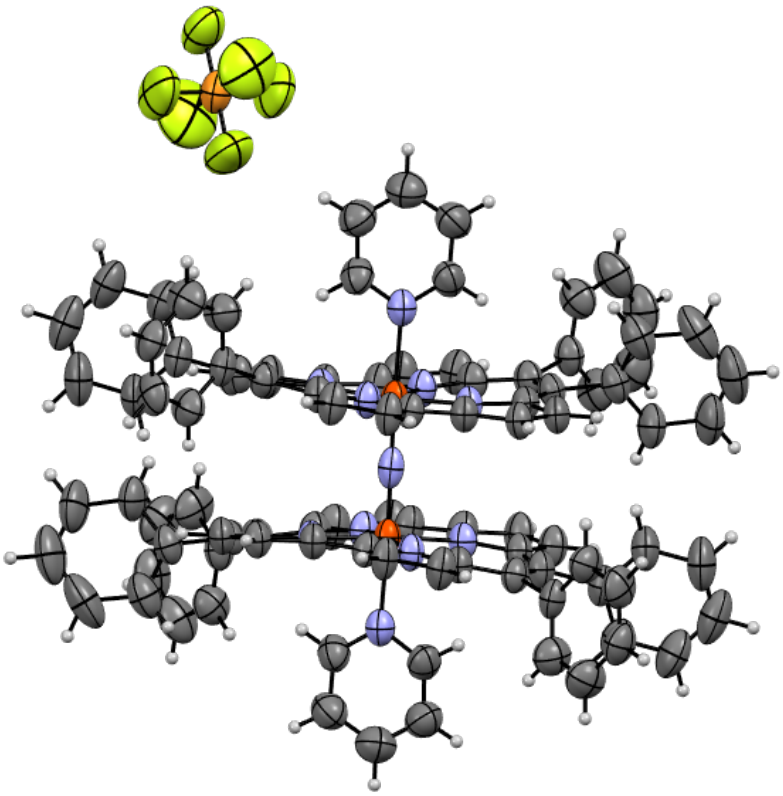

Figure S3. ORTEP representation of $\mathbf{2}^{+}\cdot PF_6^{-}$. Displacement ellipsoids are drawn at a 50% probability level. The solvents ($CHCl_3$) and a distorted coordinating pyridine were omitted for clarity.

Table S1. Amounts of the oxidized products observed in the reactions under methane (1.0 MPa) atmosphere using $\mathbf{2}^{+\cdot}PF_6^-/SiO_2$ as a catalyst.

Entry	Catalyst	Reaction Time / h	Gas	Additive	[CH_3OH] / mM	[HCHO] / mM	[HCOOH] / mM	TTN_{eff}
1	$\mathbf{2}^{+\cdot}I^-/SiO_2$	8	CH_4 (1.0 MPa)	•••	0.21	0.18	0.32	8
2	$\mathbf{2}^{+\cdot}I^-/SiO_2$	16	CH_4 (1.0 MPa)	•••	0.27	0.32	1.00	31
3	$\mathbf{2}^{+\cdot}I^-/SiO_2$	24	CH_4 (1.0 MPa)	•••	0.29	0.29	1.74	69
4	$\mathbf{2}^{+\cdot}I^-/SiO_2$	32	CH_4 (1.0 MPa)	•••	0.30	0.49	1.90	99
5	$\mathbf{2}^{+\cdot}I^-/SiO_2$	48	CH_4 (1.0 MPa)	•••	0.27	0.35	3.43	179
6	$\mathbf{2}^{+\cdot}I^-/SiO_2$	24	CH_4 (1.0 MPa)	100 mM Na_2SO_3	0.16	0.09	0.23	18

All reactions were performed in the presence of methane (1.0 MPa), H_2O_2 (189 mM), and TFA (51 mM) in H_2O (3.0 mL) containing a $\mathbf{2}^{+\cdot}PF_6^-/SiO_2$ (55 μM as $\mathbf{2}^{+\cdot}PF_6^-$). Concentrations of the oxidized products observed in the presence of methane are the mean values of three different reactions. TTN_{eff} values were calculated using equations (i) , (ii) in the main text.

Table S2. Amounts of the oxidized products observed in the reactions under N_2 (1.0 MPa) atmosphere (in the absence of methane) using $\mathbf{2}^{+}\cdot PF_6^{-}/SiO_2$ as a catalyst.

Entry	Catalyst	Reaction Time / h	Gas	Additive	[CH_3OH] / mM	[HCHO] / mM	[HCOOH] / mM	TTN(N_2)
1	$\mathbf{2}^{+}$-I^{-}/SiO_2	8	N_2 (1.0 MPa)	•••	0.11	0.15	0.23	20
2	$\mathbf{2}^{+}$-I^{-}/SiO_2	16	N_2 (1.0 MPa)	•••	0.13	0.08	0.64	39
3	$\mathbf{2}^{+}$-I^{-}/SiO_2	24	N_2 (1.0 MPa)	•••	0.11	0.10	0.64	40
4	$\mathbf{2}^{+}$-I^{-}/SiO_2	32	N_2 (1.0 MPa)	•••	0.11	0.05	0.40	25
5	$\mathbf{2}^{+}$-I^{-}/SiO_2	48	N_2 (1.0 MPa)	•••	0.10	0.06	0.34	22
6	$\mathbf{2}^{+}$-I^{-}/SiO_2	24	N_2 (1.0 MPa)	100 mM Na_2SO_3	0.11	0.06	0.16	12

All reactions were performed in the absence of methane (under N_2 (1.0 MPa) atmosphere), H_2O_2 (189 mM), and TFA (51 mM) in H_2O (3.0 mL) containing a $\mathbf{2}^{+}\cdot PF_6^{-}/SiO_2$ (55 μM as $\mathbf{2}^{+}\cdot PF_6^{-}$). Concentrations of the oxidized products observed in the presence of methane are the mean values of three different reactions. TTN(N_2) values were calculated using equation (ii) in the main text.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: FePpc2N

```
Bond precision:   C-C = 0.0103 A          Wavelength=0.41270

Cell:             a=29.2353(7)     b=18.6740(4)       c=19.5483(6)
                  alpha=90         beta=95.911(3)     gamma=90
Temperature:      123 K
```

	Calculated	Reported
Volume	10615.5(5)	10615.5(5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C98 H66 Fe2 N11, F6 P, 5.2(C H Cl3)	C98 H66 Fe2 N11, F6 P, 5.198(C H Cl3)
Sum formula	C103.20 H71.20 Cl15.60 F6 Fe2 N11 P	C103.20 H71.20 Cl15.60 F6 Fe2 N11 P
Mr	2275.00	2275.00
Dx,g cm-3	1.423	1.423
Z	4	4
Mu (mm-1)	0.170	0.171
F000	4614.4	4614.0
F000'	4619.00	
h,k,lmax	34,22,23	34,22,23
Nref	9394	9380
Tmin,Tmax	0.996,0.998	0.131,1.000
Tmin'	0.993	

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Correction method= # Reported T Limits: Tmin=0.131 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999           Theta(max)= 14.220
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R(reflections)= 0.0946(5611)

wR2(reflections)= 0.2853(9380)

S = 1.041 Npar= 946

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

RINTA01_ALERT_3_B The value of Rint is greater than 0.18
Rint given 0.186
PLAT020_ALERT_3_B The Value of Rint is Greater Than 0.12 ..... 0.186 Report

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Alert level C

CRYSC01_ALERT_1_C The word below has not been recognised as a standard identifier.
bluish

PLAT084_ALERT_3_C	High wR2 Value (i.e. > 0.25)		0.29	Report
PLAT088_ALERT_3_C	Poor Data / Parameter Ratio		9.93	Note
PLAT232_ALERT_2_C	Hirshfeld Test Diff (M-X) Fe1	--N5 .	5.7	s.u.
PLAT234_ALERT_4_C	Large Hirshfeld Difference C24	--C25 .	0.16	Ang.
PLAT234_ALERT_4_C	Large Hirshfeld Difference C36	--C37 .	0.18	Ang.
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	P1	0.165	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl1	0.140	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl4	0.150	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl7	0.138	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl10	0.123	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl13	0.247	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl19	0.145	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl22	0.155	Check
PLAT260_ALERT_2_C	Large Average Ueq of Residue Including	Cl25	0.110	Check
PLAT331_ALERT_2_C	Small Aver Phenyl C-C Dist C21	--C26 .	1.37	Ang.
PLAT341_ALERT_3_C	Low Bond Precision on C-C Bonds		0.01031	Ang.

Alert level G

ABSMU01_ALERT_1_G Calculation of _exptl_absorpt_correction_mu not performed for this radiation type.

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	55	Note
PLAT003_ALERT_2_G	Number of Uiso or Uij Restrained non-H Atoms ...	56	Report
PLAT013_ALERT_1_G	N.O.K. _shelx_hkl_checksum Found in CIF	Please	Check
PLAT042_ALERT_1_G	Calc. and Reported Moiety Formula Strings Differ	Please	Check
PLAT068_ALERT_1_G	Reported F000 Differs from Calcd (or Missing)...	Please	Check
PLAT083_ALERT_2_G	SHELXL Second Parameter in WGHT Unusually Large	24.67	Why ?
PLAT092_ALERT_4_G	Check: Wavelength Given is not Cu,Ga,Mo,Ag,In Ka	0.41270	Ang.
PLAT171_ALERT_4_G	The CIF-Embedded .res File Contains EADP Records	1	Report
PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	19	Report
PLAT174_ALERT_4_G	The CIF-Embedded .res File Contains FLAT Records	2	Report
PLAT175_ALERT_4_G	The CIF-Embedded .res File Contains SAME Records	1	Report
PLAT176_ALERT_4_G	The CIF-Embedded .res File Contains SADI Records	1	Report
PLAT177_ALERT_4_G	The CIF-Embedded .res File Contains DELU Records	11	Report
PLAT186_ALERT_4_G	The CIF-Embedded .res File Contains ISOR Records	11	Report
PLAT300_ALERT_4_G	Atom Site Occupancy of P1 Constrained at	0.5	Check

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PLAT300_ALERT_4_G Atom Site Occupancy of F1         Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F2         Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F3         Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F4         Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F5         Constrained at        0.5 Check
PLAT300_ALERT_4_G Atom Site Occupancy of F6         Constrained at        0.5 Check
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )        11% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  2  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  3  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  4  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  5  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  6  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  7  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  8  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd  9  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 10  )       100% Note
PLAT302_ALERT_4_G Anion/Solvent/Minor-Residue Disorder (Resd 11  )       100% Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  2  )       3.50 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  3  )       1.77 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  4  )       1.27 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  5  )       1.88 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  6  )       1.51 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  7  )       1.39 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  8  )       0.69 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd  9  )       2.12 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 10  )       1.17 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms in ..... (Resd 11  )       1.19 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  Cl1      ..C29             3.22 Ang.
                                          x,-y,-1/2+z  =      6_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  Cl6      ..C36             3.05 Ang.
                                        1/2-x,1/2-y,-z  =      7_555 Check
PLAT432_ALERT_2_G Short Inter X...Y Contact  Cl20     ..C31             3.22 Ang.
                                            x,y,z  =      1_555 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #         10 Check
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          2 Note
            F6 P
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          3 Note
            C H Cl3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          4 Note
            C H Cl3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          5 Note
            C H Cl3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #          9 Note
            C H Cl3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         10 Note
            C H Cl3
PLAT790_ALERT_4_G Centre of Gravity not Within Unit Cell: Resd.  #         11 Note
            C H Cl3
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............       580 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...         1 Note
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
PLAT984_ALERT_1_G The Cl-f'=    0.0382 Deviates from the B&C-Value     0.0553 Check
PLAT984_ALERT_1_G The  F-f'=   -0.0002 Deviates from the B&C-Value     0.0038 Check
PLAT985_ALERT_1_G The Fe-f"=    0.3079 Deviates from the B&C-Value     0.3056 Check
```

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

  9 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 19 ALERT type 2 Indicator that the structure model may be wrong or deficient
  7 ALERT type 3 Indicator that the structure quality may be low
 45 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
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It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/07/2021; check.def file version of 13/07/2021

Datablock FePpc2N - ellipsoid plot