Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

SI01 - XRD of non-templated FePc

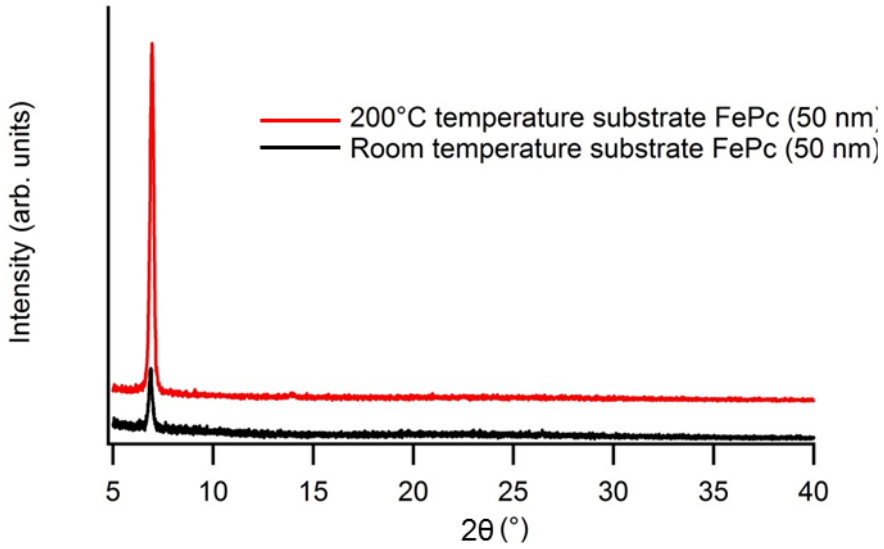


Figure SI01 –XRD traces for 50 nm FePc at room temperature and 200°C substrate growth conditions

SI02 – Surface roughness vs FePc thickness

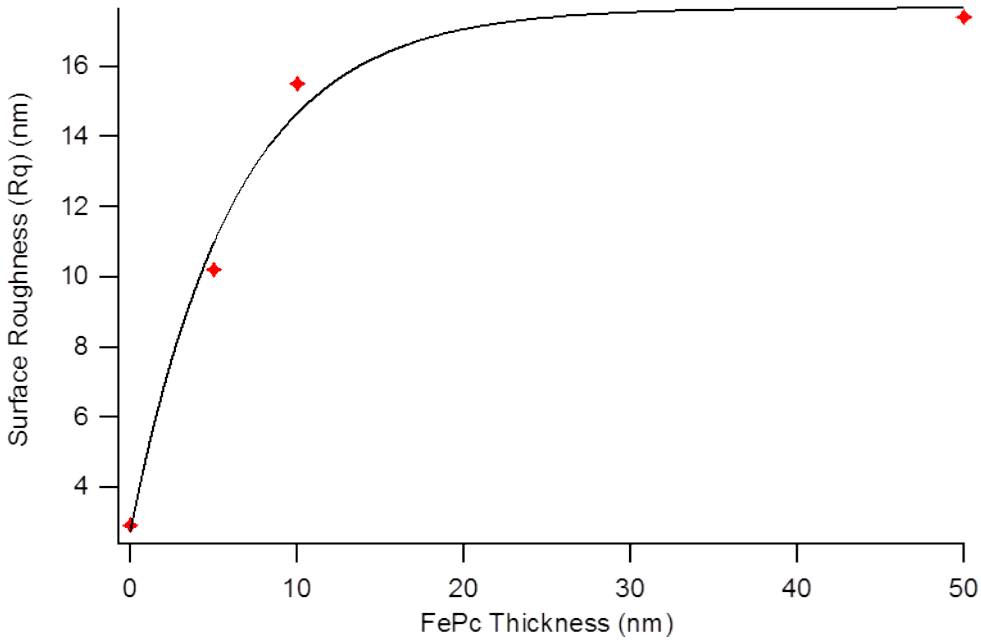


Figure SI02 – Surface roughness vs. FePc thickness (red points) - an exponential fit (black line) is included as a guide for the eye

SI03 – Expanded high angle XRD

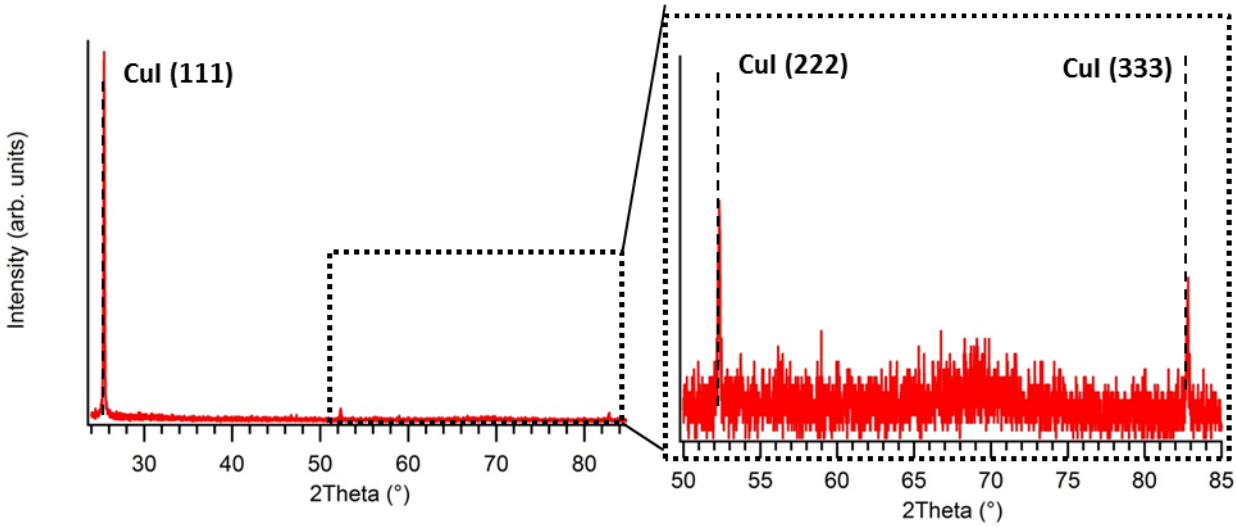
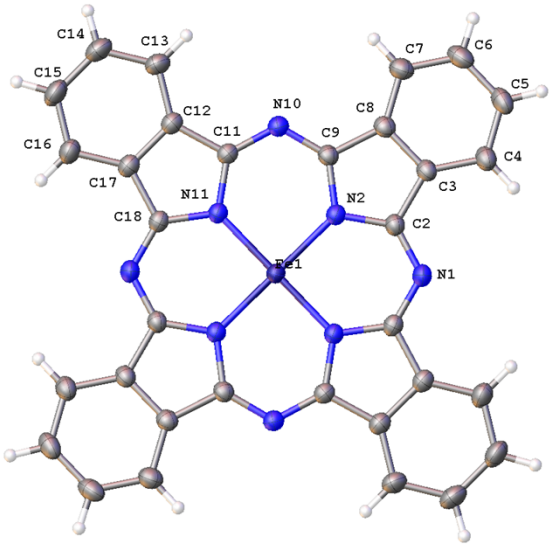
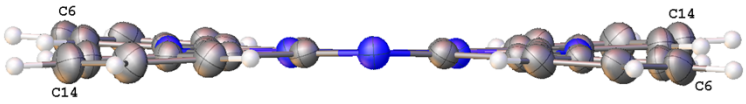


Figure SI03 – Expanded higher-angle XRD

SI04 - Crystal Structure of FePc



Solid state structure of FePc test_3 with only the asymmetric unit of the structure labeled. Atoms are drawn at 50% probability. The molecule lies on an inversion centre at Fe1



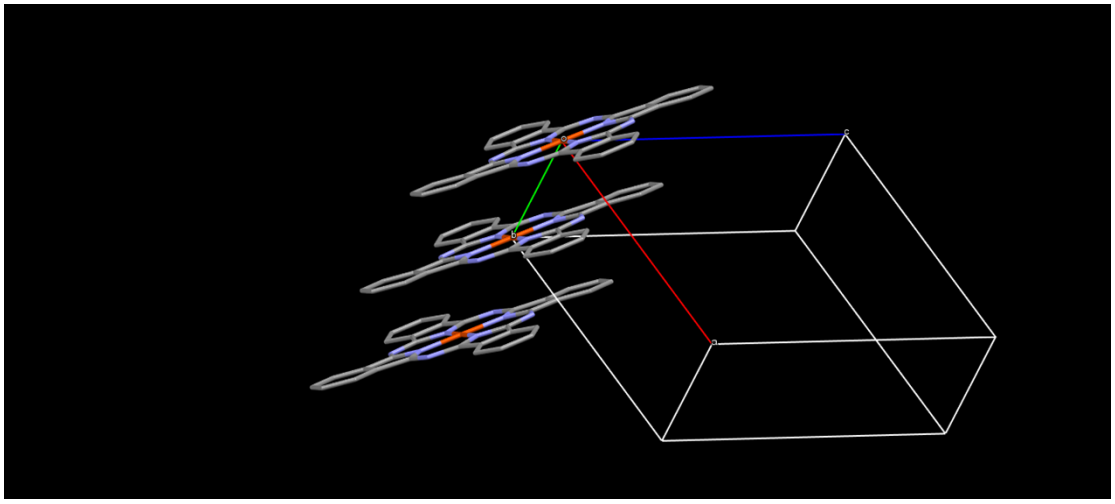
Picture looking along the plane of the PC core through N1-Fe1-N1 to highlight how the phenyl ring C12-C17 (labeled with a C14) lies much more above and below the plane of the PC core compared to phenyl C3-C8

The asymmetric unit contains half a PC core with Fe1 lying on an inversion centre on special position 2a

The Pc ring is not perfectly flat but ring C12-C17 lies above and below the Pc core. This is highlighted by the data below where the first 9 atoms (the Fe and the nitrogens) define a mean plane and the other atoms show their deviation from this plane

* 0.0000 (0.0000) Fe1
* -0.0057 (0.0006) N1
* 0.0069 (0.0010) N2
* 0.0001 (0.0006) N10
* -0.0071 (0.0010) N11
* 0.0057 (0.0006) N1_$3
* -0.0069 (0.0010) N2_$3
* -0.0001 (0.0006) N10_$3
* 0.0071 (0.0010) N11_$3
0.1812 (0.0028) C5
0.1913 (0.0028) C6
-0.1968 (0.0030) C14
-0.1817 (0.0029) C15

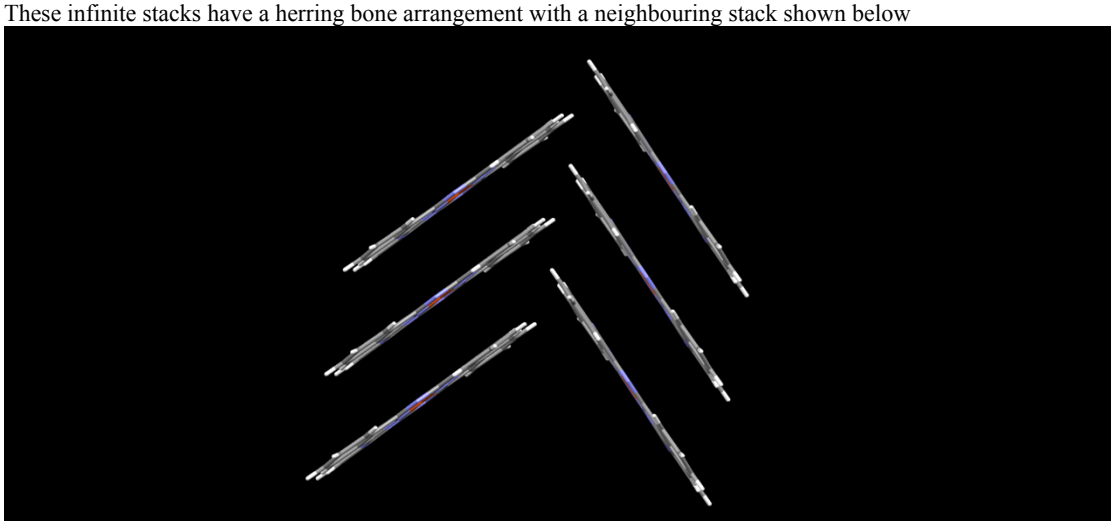
The packing has an off set pi stack with symmetry related Pc rings that travels along the c axis of the cell shown below (using Mercury)



Closest atomic contact between these stacked Pcs is

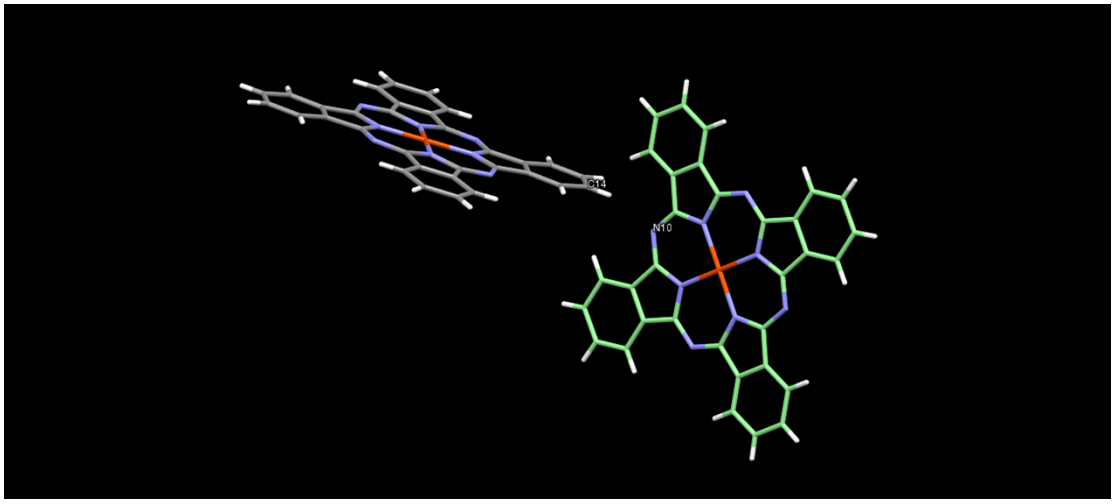
3.2394 (0.0013) Fe1 - N1_$1
3.3274 (0.0021) C9 - C4_$1

These infinite stacks have a herring bone arrangement with a neighbouring stack shown below

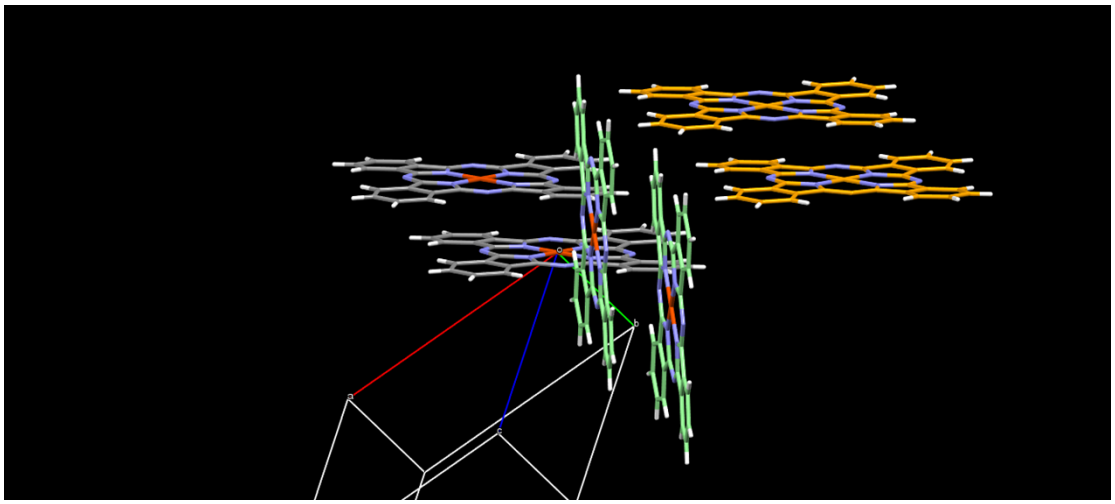


The atoms used to define the mean planes through the interacting systems and the angle between them was
Fe1 C2 C4 C6 C8 C12 C14 C16 C18 to Fe1_$2 C2_$2 C4_$2 C6_$2 C8_$2 C12_$2 C14_$2 C16_$2 C18_$2
88.319 (0.016) degrees

There is also a slightly different orientation where another symmetry related stack is orthogonal to the original stack. This interaction is characterized by one of the phenyl rings (C12-C17) poking into the bay area (C7-N10_C13) of symmetry related Pc ring shown below



The two interactions are shown together below. Orange Pcs with green is the herring bone style interaction. Green with grey Pcs is the alternative interaction. The grey and the orange Pcs are related by glide planes. The green stack is related by a 2(1) screw axis to the other two stacks.



The angle between means planes through these stacks is

Fe1 C2 C4 C6 C8 C12 C14 C16 C18 to Fe1_$2 C2_$2 C4_$2 C6_$2 C8_$2 C12_$2 C14_$2 C16_$2 C18_$2 is 88.319 (0.016) degrees (it's the same angle for mean planes from orange to green and from green to grey as the orange and grey stacks are related by a translation)

Symmetry operators used to define symmetry related atoms in above discussion are

$1 +X,1+Y,+Z
$2 0.5-X,0.5+Y,0.5-Z
$3 -X,-Y,-Z

Experimental

Single crystals of $C_{32}H_{16}FeN_8$ [Fe-Pc_test3] were grown by sublimation. A suitable crystal was selected and mounted on a Mitigen loop with silicon oil on an Oxford Diffraction Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-

341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122
Crystal structure determination of [Fe-Pc_test3]

Crystal Data for $C_{32}H_{16}FeN_8$ (M =568.38): monoclinic, space group $P2_1/n$ (no. 14), a = 14.6133(4) Å, b = 4.78734(11) Å, c = 17.2977(4) Å, β = 105.582(3)°, V = 1165.65(6) Å^3, Z = 2, T = 293(2) K, μ(MoKα) = 0.691 mm^{-1}, *Dcalc* = 1.619 g/mm^3, 13513 reflections measured (6.498 ≤ 2Θ ≤ 75.18), 5517 unique (R_{int} = 0.0325, R_{sigma} = 0.0432) which were used in all calculations. The final R_1 was 0.0513 (I > 2σ(I)) and wR_2 was 0.1227 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

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1. Fixed Uiso
At 1.2 times of:
All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
C4(H4), C5(H5), C6(H6), C7(H7), C13(H13), C14(H14), C15(H15), C16(H16)
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This report has been created with Olex2, compiled on 2013.11.15 svn.r2839 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Fe-Pc_test3. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Fe1	0	0	0	22.82(8)
N1	1512.4(9)	-5160(2)	788.2(8)	27.7(2)
C2	916.1(10)	-4247(3)	1188.1(8)	25.5(3)
N2	242.0(9)	-2183(2)	969.1(7)	24.3(2)
C3	913.9(11)	-5364(3)	1968.4(9)	26.3(3)
C4	1469.5(11)	-7402(3)	2443.1(9)	32.8(3)
C5	1297.4(12)	-7953(4)	3178.5(10)	37.4(4)
C6	592.1(12)	-6529(4)	3424.4(9)	38.2(4)
C7	33.6(13)	-4513(4)	2947.5(10)	34.4(3)
C8	206.6(11)	-3933(3)	2210.6(8)	27.2(3)
C9	-209.3(10)	-1966(3)	1573.8(8)	25.4(3)
N10	-919.6(9)	-283(2)	1601.3(7)	27.0(2)
C11	-1277.9(10)	1507(3)	1013.8(8)	25.0(3)
N11	-986.9(9)	1954(2)	327.2(7)	24.2(2)
C12	-2065.2(11)	3356(3)	1017.2(9)	27.6(3)
C13	-2618.3(12)	3699(4)	1554.2(10)	35.5(3)
C14	-3342.4(13)	5668(4)	1361.7(11)	41.4(4)
C15	-3501.4(13)	7265(4)	663.1(11)	41.1(4)
C16	-2949.9(12)	6952(3)	131.4(10)	34.3(3)
C17	-2230.9(11)	4952(3)	321.4(9)	27.5(3)
C18	-1543.8(10)	4051(3)	-94.8(8)	25.2(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Fe-Pc_test3. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	22.82(15)	22.47(13)	23.75(13)	1.70(9)	7.25(10)	2.61(10)
N1	25.9(6)	28.1(6)	28.4(5)	3.4(4)	6.3(5)	5.1(5)
C2	23.5(7)	25.7(6)	25.8(6)	2.1(5)	4.4(5)	0.9(5)
N2	23.3(6)	24.2(5)	25.6(5)	0.7(4)	6.7(4)	1.4(4)
C3	23.3(7)	27.4(6)	27.1(6)	3.8(5)	4.8(5)	-1.1(5)

C4	27.4(7)	34.3(7)	35.0(7)	8.6(6)	5.3(6)	1.9(6)
C5	31.7(8)	39.9(8)	36.0(7)	14.6(7)	1.2(7)	-1.0(7)
C6	37.3(9)	46.9(9)	29.9(7)	10.6(7)	8.0(6)	-5.5(7)
C7	35.7(9)	38.5(8)	31.2(7)	5.3(6)	12.5(7)	-1.0(6)
C8	25.8(7)	28.1(6)	27.8(6)	2.6(5)	7.1(5)	-2.3(5)
C9	24.8(7)	24.8(6)	26.4(6)	2.0(5)	6.6(5)	-1.1(5)
N10	26.6(6)	28.0(6)	27.4(5)	1.8(4)	9.3(5)	1.5(5)
C11	23.5(6)	25.3(6)	26.6(6)	-1.5(5)	7.7(5)	0.0(5)
N11	23.5(6)	23.7(5)	25.8(5)	0.9(4)	7.0(4)	2.0(4)
C12	26.1(7)	27.7(6)	29.9(6)	-2.0(5)	8.8(5)	1.1(5)
C13	36.5(9)	38.7(8)	35.8(7)	-1.0(6)	17.5(7)	4.0(7)
C14	37.1(9)	46.6(9)	46.1(9)	-5.1(8)	20.8(8)	7.1(8)
C15	35.0(9)	42.5(9)	47.8(9)	-3.1(7)	14.6(8)	13.3(7)
C16	32.3(8)	34.6(8)	36.0(7)	-0.5(6)	9.4(6)	8.9(6)
C17	25.0(7)	27.7(6)	29.6(6)	-3.3(5)	7.1(5)	1.1(5)
C18	22.7(7)	25.3(6)	27.0(6)	-1.2(5)	5.5(5)	1.7(5)

Table 4 Bond Lengths for Fe-Pc_test3.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Fe1	N2[1]	1.9259(11)	C8	C9	1.453(2)
Fe1	N2	1.9259(11)	C9	N10	1.3247(18)
Fe1	N11[1]	1.9271(11)	N10	C11	1.3251(18)
Fe1	N11	1.9271(11)	C11	N11	1.3815(17)
N1	C2	1.3239(18)	C11	C12	1.453(2)
N1	C18[1]	1.3234(18)	N11	C18	1.3727(18)
C2	N2	1.3747(18)	C12	C13	1.395(2)
C2	C3	1.4525(19)	C12	C17	1.391(2)
N2	C9	1.3823(17)	C13	C14	1.389(3)
C3	C4	1.388(2)	C14	C15	1.396(3)
C3	C8	1.395(2)	C15	C16	1.384(2)
C4	C5	1.387(2)	C16	C17	1.394(2)
C5	C6	1.394(3)	C17	C18	1.4493(19)
C6	C7	1.384(2)	C18	N1[1]	1.3235(18)
C7	C8	1.393(2)			

[1]-X,-Y,-Z

Table 5 Bond Angles for Fe-Pc_test3.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N2[1]	Fe1	N2	180.00(9)	N2	C9	C8	109.72(12)
N2[1]	Fe1	N11[1]	89.12(5)	N10	C9	N2	127.64(13)
N2	Fe1	N11[1]	90.88(5)	N10	C9	C8	122.64(13)
N2[1]	Fe1	N11	90.88(5)	C9	N10	C11	121.19(12)
N2	Fe1	N11	89.12(5)	N10	C11	N11	127.59(13)
N11[1]	Fe1	N11	180.00(9)	N10	C11	C12	122.78(12)
C18[1]	N1	C2	121.96(13)	N11	C11	C12	109.64(12)
N1	C2	N2	128.07(12)	C11	N11	Fe1	127.22(10)
N1	C2	C3	122.02(13)	C18	N11	Fe1	125.62(9)
N2	C2	C3	109.90(12)	C18	N11	C11	107.16(11)
C2	N2	Fe1	125.49(9)	C13	C12	C11	132.47(14)
C2	N2	C9	107.32(11)	C17	C12	C11	106.57(12)
C9	N2	Fe1	127.19(10)	C17	C12	C13	120.96(14)
C4	C3	C2	131.40(14)	C14	C13	C12	117.40(15)
C4	C3	C8	122.03(13)	C13	C14	C15	121.22(15)
C8	C3	C2	106.56(12)	C16	C15	C14	121.64(16)
C5	C4	C3	117.06(15)	C15	C16	C17	117.03(15)
C4	C5	C6	121.20(15)	C12	C17	C16	121.75(14)
C7	C6	C5	121.67(15)	C12	C17	C18	106.48(13)
C6	C7	C8	117.49(16)	C16	C17	C18	131.77(14)
C3	C8	C9	106.48(12)	N1[1]	C18	N11	127.97(13)
C7	C8	C3	120.55(14)	N1[1]	C18	C17	121.88(13)
C7	C8	C9	132.96(15)	N11	C18	C17	110.14(12)

[1]-X,-Y,-Z

Table 6 Torsion Angles for Fe-Pc_test3.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Fe1	N2	C9	C8	-178.10(10)	C8	C9	N10	C11	179.37(14)
Fe1	N2	C9	N10	2.4(2)	C9	N10	C11	N11	-1.4(2)
Fe1	N11	C18	N1[1]	-0.9(2)	C9	N10	C11	C12	179.10(13)
Fe1	N11	C18	C17	177.94(10)	N10	C11	N11	Fe1	2.5(2)
N1	C2	N2	Fe1	-0.9(2)	N10	C11	N11	C18	-178.29(14)
N1	C2	N2	C9	179.89(14)	N10	C11	C12	C13	-1.8(3)
N1	C2	C3	C4	0.6(3)	N10	C11	C12	C17	178.79(14)
N1	C2	C3	C8	179.78(14)	C11	N11	C18	N1[1]	179.88(15)
C2	N2	C9	C8	1.14(16)	C11	N11	C18	C17	-1.28(16)
C2	N2	C9	N10	-178.36(14)	C11	C12	C13	C14	-178.77(17)
C2	C3	C4	C5	178.64(16)	C11	C12	C17	C16	179.62(14)
C2	C3	C8	C7	-179.30(15)	C11	C12	C17	C18	0.04(16)
C2	C3	C8	C9	-0.06(16)	N11	C11	C12	C13	178.61(16)
N2	C2	C3	C4	-178.43(15)	N11	C11	C12	C17	-0.83(16)
N2	C2	C3	C8	0.77(17)	C12	C11	N11	Fe1	-177.90(9)
N2	C9	N10	C11	-1.2(2)	C12	C11	N11	C18	1.30(16)
C3	C2	N2	Fe1	178.08(10)	C12	C13	C14	C15	-0.8(3)
C3	C2	N2	C9	-1.18(16)	C12	C17	C18	N1[1]	179.69(14)
C3	C4	C5	C6	0.4(2)	C12	C17	C18	N11	0.77(16)
C3	C8	C9	N2	-0.66(16)	C13	C12	C17	C16	0.1(2)
C3	C8	C9	N10	178.87(13)	C13	C12	C17	C18	-179.48(14)
C4	C3	C8	C7	0.0(2)	C13	C14	C15	C16	0.3(3)
C4	C3	C8	C9	179.23(14)	C14	C15	C16	C17	0.4(3)
C4	C5	C6	C7	0.1(3)	C15	C16	C17	C12	-0.6(2)
C5	C6	C7	C8	-0.5(3)	C15	C16	C17	C18	178.84(16)
C6	C7	C8	C3	0.5(2)	C16	C17	C18	N1[1]	0.2(3)
C6	C7	C8	C9	-178.50(16)	C16	C17	C18	N11	-178.75(16)
C7	C8	C9	N2	178.44(17)	C17	C12	C13	C14	0.6(2)
C7	C8	C9	N10	-2.0(3)	C18[1]	N1	C2	N2	2.0(2)
C8	C3	C4	C5	-0.5(2)	C18[1]	N1	C2	C3	-176.79(14)

[1]-X,-Y,-Z

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Fe-Pc_test3.

Atom	*x*	*y*	*z*	U(eq)
H4	1937	-8355	2275	39
H5	1659	-9297	3514	45
H6	494	-6944	3921	46
H7	-439	-3582	3113	41
H13	-2507	2649	2023	43
H14	-3728	5928	1705	50
H15	-3990	8573	552	49
H16	-3055	8027	-332	41

This report has been created with Olex2, compiled on 2013.11.15 svn.r2839 for OlexSys.