1. Tables

Table S1. Selected experimental crystal data for the orthorhombic (*Pccn*, PI) polymorph of $[Fe(PM\text{-}BiA)_2(NCS)_2]$ at different pressure points.

Chemical Formula	**Orthorhombic** $FeN_6S_2C_{38}H_{28}$					
Pressure(GPa)	**0.44**	**0.85**	**1.36**	**0.15**	**0.61**	**1.07**
a (Å)	12.7982(13)	12.7285(15)	12.6944(16)	12.9059(5)	12.7999(5)	12.735(3)
b (Å)	14.360(4)	13.881(6)	13.638(6)	14.8090(6)	14.221(6)	13.784(8)
c (Å)	17.650(6)	17.6348(18)	17.597(6)	17.6530(6)	17.680(6)	17.657(5)
V ($Å^3$)	3243.8(2)	3116.1(2)	3046.5(2)	3373.9(2)	3218.2(2)	3099(2)
Density ($g\ cm^{-1}$)	1.4113	1.4687	1.5027	1.3569	4.9746	5.1652
μ (mm^{-1})	0.147	0.154	0.157	0.615	2.236	2.322
Radiation Type	Synchrotron			Synchrotron		
Wavelength (Å)	0.413(3)			0.720(4)		
Diffractometer	κ-diffractometer using a Pilatus 1M CdTe			Multipurpose PILATUS @ SNBL diffractometer		
No. of measured,	13625	14040	13295	2436	3447	2274
symmetry independent,	1899	1855	1812	1057	1346	917
and observed $[I > 2\sigma(I)]$	1034	1116	1050	507	671	400
reflections						
R_{int}	0.1747	0.1389	0.1845	0.0582	0.0607	0.0863
$(\sin\theta\ /\ \lambda)\ (Å)^{-1}$	0.67	0.67	0.67	0.8	0.8	0.8
No. of parameters	113	103	95	213	213	213
$R[F^2 > 2\,\sigma(F^2)]$	0.1631	0.1221	0.1733	0.0557	0.0636	0.0384
$wR(F^2)$	0.0988	0.0934	0.1425	0.0403	0.0575	0.0275
S	3.3	3.52	4.54	2.1	2.65	1.33

Table S2. Selected experimental crystal data for the monoclinic ($P2_1/c$, PII) polymorph of [Fe(PM-BiA)$_2$(NCS)$_2$] at different pressure points.

Chemical Formula	**Monoclinic** $FeN_6S_2C_{38}H_{28}$					
Pressure(GPa)	**0.36**	**0.65**	**0.81**	**1.34**	**0.46**	**1.46**
a (Å)	16.885(3)	16.700(6)	16.528(2)	16.316(2)	16.867(2)	16.152(2)
b (Å)	12.3716(13)	12.2217(13)	12.1829(17)	12.1419(10)	12.3747(10)	12.1258(10)
c (Å)	17.219(2)	17.6348(18)	17.597(6)	16.848(2)	17.181(2)	16.7840(2)
β (°)	116.120(15)	115.85(15)	116.902(2)	115.86(15)	115.930(15)	115.936(15)
V (Å^3)	3225.8(7)	3111.1(2)	3062.3(2)	3003.5(7)	3225.07(7)	2956.17(7)
Density (g cm^{-1})	1.4183	1.4701	1.4937	1.5229	1.4183	1.5473
μ (mm^{-1})	0.147	0.152	0.155	0.158	0.638	0.695
Radiation Type	Synchrotron			Synchrotron		
Wavelength (Å)	0.413(3)			0.720(4)		
Diffractometer	κ-diffractometer using a Pilatus 1M CdTe			Multipurpose PILATUS @ SNBL diffractometer		
No. of measured, symmetry independent, and observed $[I > 2\sigma(I)]$ reflections	13763	13772	12592	1333	2627	2608
	3132	3054	1515	2917	1522	1470
	1317	1358	859	1376	1071	1231
R_{int}	0.227	0.2057	0.306	0.2481	0.0694	0.0455
(sin θ / λ) (Å)$^{-1}$	0.55	0.55	0.55	0.55	0.65	0.68
No. of parameters	153	155	152	155	204	204
R[F^2 > 2 σ(F^2)]	0.2145	0.1727	0.284	0.2078	0.1003	0.0735
wR(F^2)	0.1388	0.1275	0.2305	0.1791	0.1195	0.0867
S	3.43	3.27	5.97	4.19	6.75	5.55

2. Figures

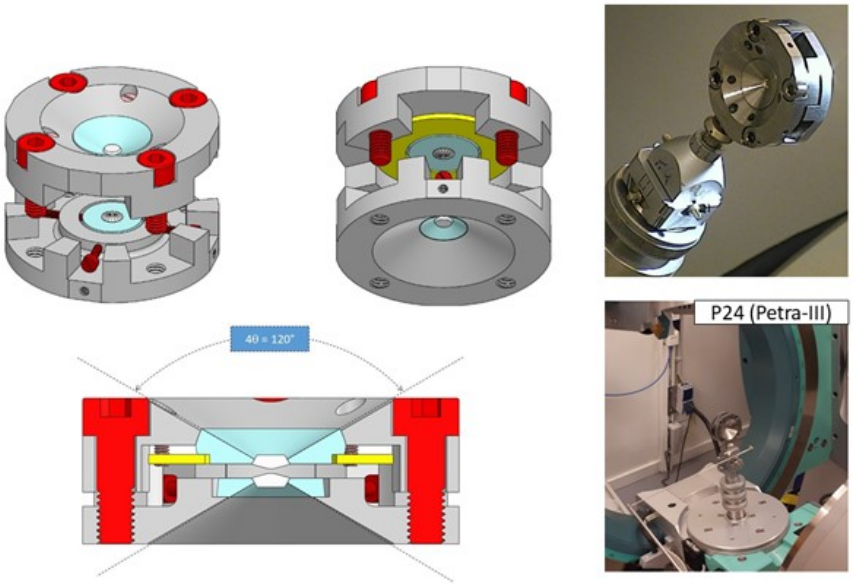


Figure S1. (left) **Yao-DAC for X-ray and neutron single-crystal diffraction**
The diamond anvil cell with an opening of 120° (Yao-DAC) is based on the design by Yao Cheng [1]. Its diameter is 40 mm. The body parts as well as the seats are made of the NiCrAl alloy allowing for using it both for X-ray and neutron single-crystal diffraction [2]. The body parts have matching crenel-like cuts. The screws (M4 and M1.6) and the locking ring for the rocker seat are made of titanium (grade 2). Both parallel and translational alignments of the diamonds are possible.

References

1. Cheng, Y. A Diamond Anvil Cell for Combined X-Ray and Neutron Single- Crystal Studies. Thesis, 2018.
2. Cheng, Y.; Brenk, J.; Friedrich, B.; Perßon, J.; Maraytta, N.; Gibson, J.S.K.L.; Korte-Kerzel, S.; Roth, G.; Su, Y.; Zhu, F.; et al. Ni–Cr–Al Alloy for neutron scattering at high pressures. *Materials Science and Technology* **2020**, *36*, 949–954. https://doi.org/10.1080/02670836.2019.1578077.