Electronic Supplementary Material (ESI) for CrystEngComm.

ESI

Pressure-induced Phase-Separation of Miscible Liquids: 1:1 n-pentane/isopentane

Pressure-induced and time-dependent liquid-liquid phase separation (LLPS) of the mixture of n-pentane/isopentane (1:1) is highly reproducible and observed in multiple cases during the in-house high-pressure X-ray single crystal diffraction (HP XRSD) experiments.

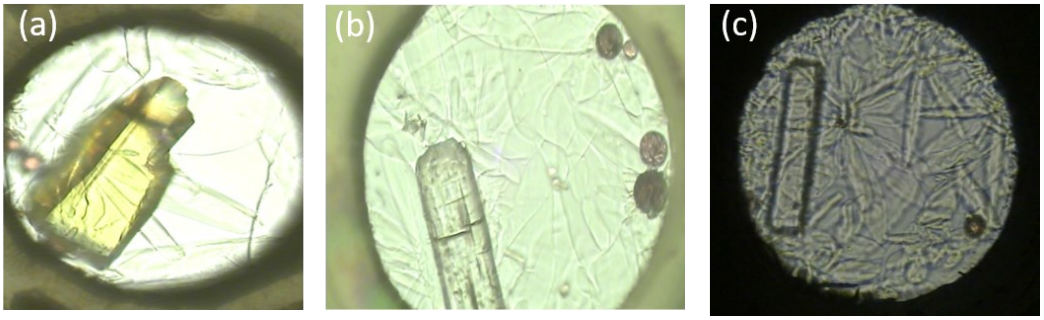

Figure S1. Microscopic images of DAC cells loaded with a single crystal and few ruby spheres as pressure calibrants, using the mixture of n-pentane and isopentane as PTM. PTM crystallised at pressure above ca 2.5 GPa. (a) a single crystal sample A at *ca* 3.3 GPa; (b) a single crystal sample B at *ca* 2.9 GPa, and (c) a single crystal sample C at *ca* 2.6 GPa.

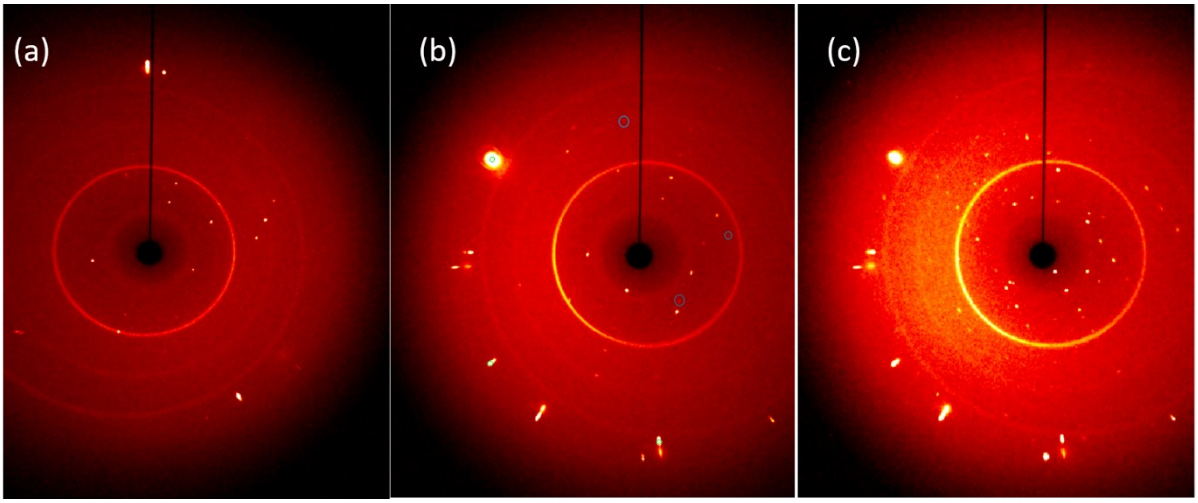

Figure S2. 2D images of HP-XRSD data of co-crystal of *Bipy:NTO* at different pressure conditions, using the mixture of n-pentane/isopentane as PTM, recorded on the lab X-ray diffractometer. Images are shown frames collected from the same sample and detector angles. (a) co-crystal of *Bipy:NTO* at *ca* 1.2 GPa. No PTM crystal observed optically, diffraction data shown on the frame are mainly from co-crystal of *Bipy:NTO*. (b) co-crystal of *Bipy:NTO* at *ca* 2.8 GPa. Multiple crystals of PTM formed in the DAC. Most diffraction from PTM crystals are overwhelmed by that from *Bipy:NTO*. only few diffraction from PTM crystal is shown on the frame (highlighted by black circles). (c) co-crystal of *Bipy:NTO* at *ca* 3.3 GPa. The crystal of *Bipy:NTO* converted into amorphous at 3.3 GPa . Diffraction from PTM crystals can be clearly observed on the frame.

Table S1. Crystallographic and Structural Refinement Parameters of n-pentane at 3.3 GPa.

Temperature (K)	297
Pressure (GPa)	3.3
Formula	C_5H_{12}
Formula Weight	432.24
Crystal System	Orthorhombic
Space group	*Pbcn*
a/ Å	3.7996(7)
b/Å	8.2477(13)
c/ Å	14.205(4)
α/°	90
β/°	90
γ/°	90
V/ Å^3	445.16(17)
Z	4
D_c/ g cm^{-3}	1.076
μ /mm^{-1}	0.058
F(000)	168.0
θ range/°	4.6-28.53
Reflections collected	2022
Unique reflections	864
Reflections $I > 2\sigma(I)$	233
R_{int}	0.0367
goodness-of-fit (F^2)	1.190
$R1$ ($I > 2\sigma(I)$)	0.0437
$wR2$($I > 2\sigma(I)$)	0.1270
CCDC No.	2026696

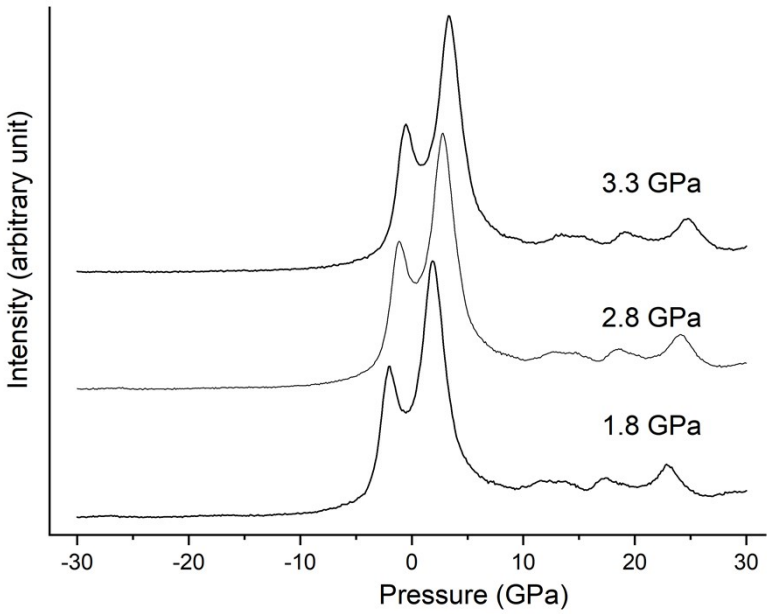

Figure S3. Multiplots of ruby R lines from the DAC sample of Bipy:NTO at select pressure conditions. 1:1 n-pentane and isopentane was used as PTM. Lack of significant broadening of Ruby R lines confirmed that the *iso*-pentane remained in liquid phase.

Table S2. Crystallographic Parameters of Bipy:NTO

	a (Å)	*b* (Å)	*c* (Å)	*β*(°)	V (Å)^3
Ambient pressure (120 K)	7.8212(2)	5.78560(10)	27.3363(5)	92.192(2)	1236.07
High Pressure (2.8 GPa & 298 K)	7.2747(16)	5.6382(6)	26.176(3)	93.556(12)	1071.57