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Electronic Supplementary Information

Tunable luminescence of novel organic co-crystal based on intermolecular charge transfer under pressure

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1. Crystallographic data

Table S1. Crystallographic data of 9ACA-TFP derived from single-crystal X-ray diffraction measurements.

9-Acetylanthracene-Tetrafluoroterephthalonitrile	
Formula	$C_{40}H_{24}F_4N_2O_2$
Formula weight	640.61 g/mol
Crystal system	monoclinic
Space-group	P 1 21/n 1 (14)
Lattice parameter a (Å)	11.6109(4)
Lattice parameter b (Å)	10.4279(4)
Lattice parameter c (Å)	13.0037(5)
Lattice parameter β(degree)	95.052(1)
Cell ratio a/b	1.1134
Cell ratio b/c	0.8019
Cell ratio c/a	1.1200
Cell volume ($Å^3$)	1568.34(10)
Formula units per cell Z	2
Calculated density (g cm^{-3})	1.35646
Rall	0.1001
F(000)	660.0
R reflections	0.0539
wR2	0.1539(3836)
CCDC NO	1829909

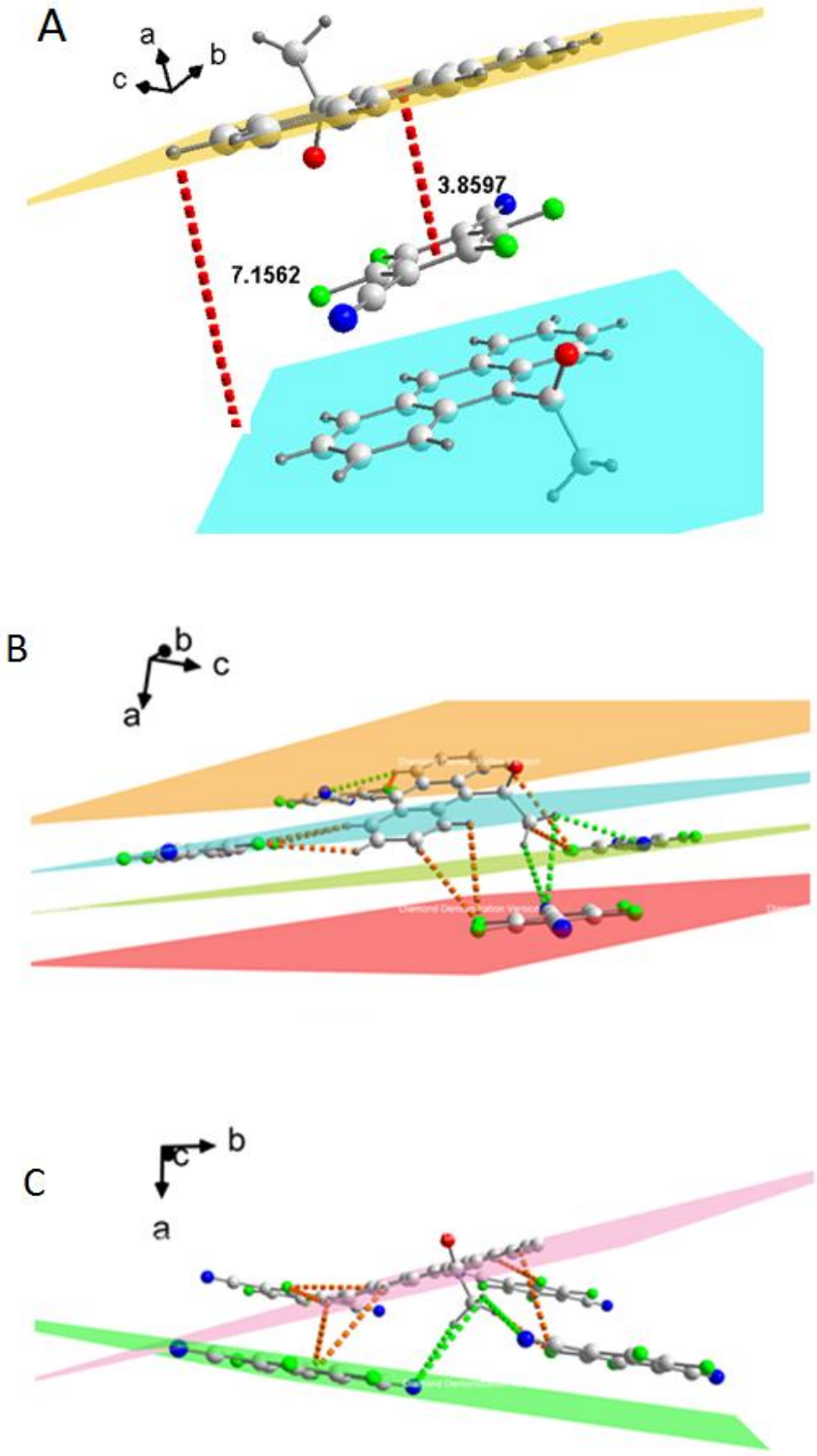

Fig. S1. (A) Two 9ACA molecules are in parallel with each other (distance is 7.1562 Å) and one TFP molecule is filled at an angle of 6.640 °. The distance of benzene ring in the middle of 9ACA and TFP molecule is estimated to about 3.8597 Å. (B) The planes of the four TFP molecules are paralleled to each other with the distance 1.9293 Å. (C) The planes of the four TFP molecules Intersected with the plane of the 9ACA molecule at an angle of 25.169 °

2. The effect of the pressure on the luminescence of 9ACA single crystal.

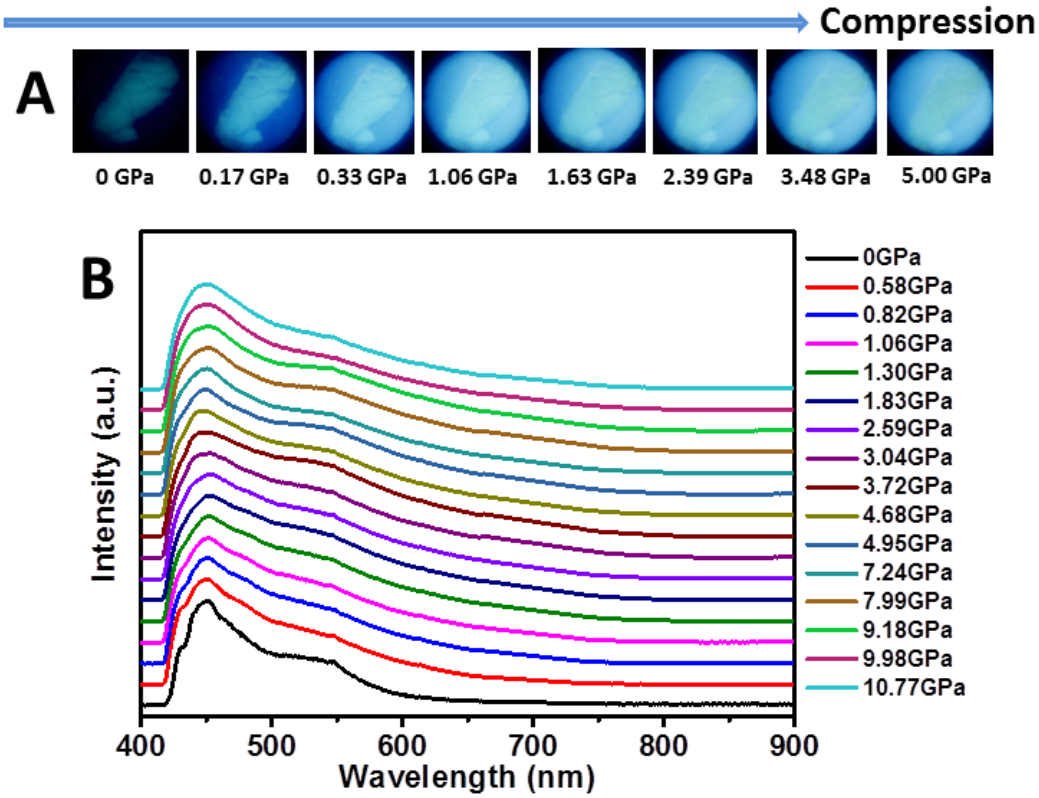

Fig. S2. Fluorescent images (A) and spectra (B) of the 9ACA single crystal under compression.

3. Peak fitting

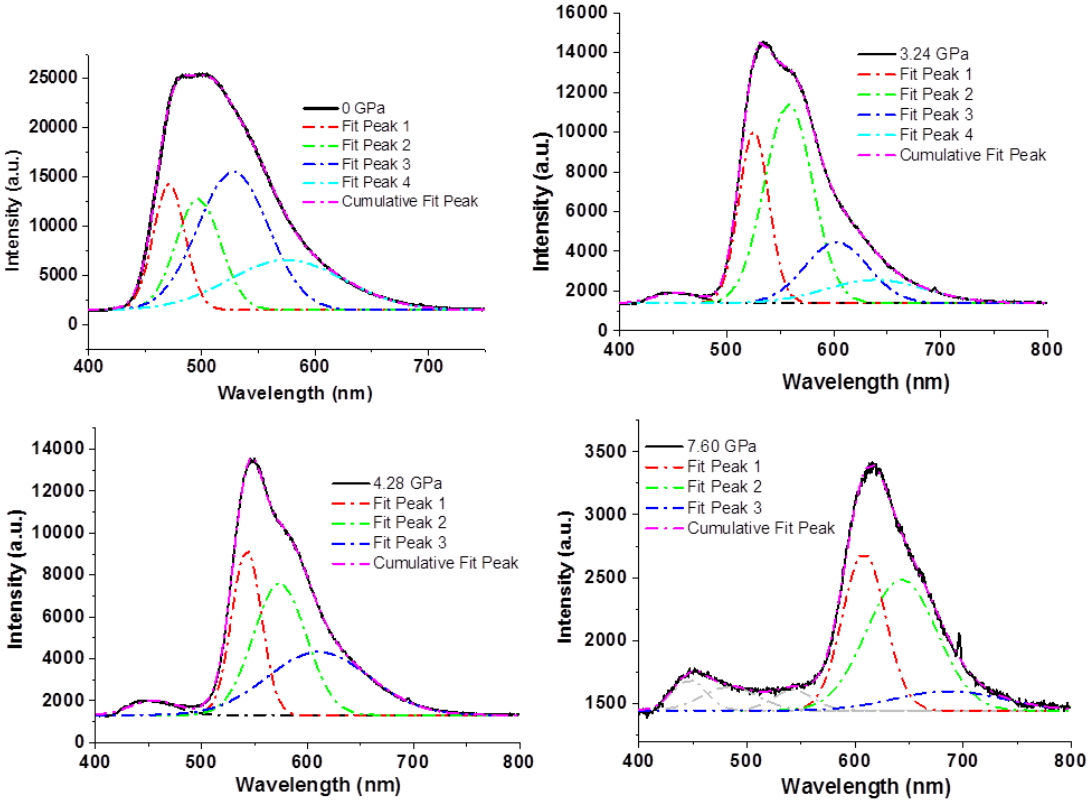

Fig. S3 Fluorescent emission spectra of the 9ACA-TFP co-crystal under the pressures of 0, 3.24, 4.28 and 7.60 GPa, respectively. Dashed lines depict the fitted fluorescent bands

Table S2. The analysis of the emission bands of the 9ACA-TFP crystal under compression.

Peak 1				
Pressure (GPa)	Wavelength (nm)	Area	FWHM	Intensity (a.u.)
0.00	471	449816.27	33.07	12778.03
0.25	474	384050.37	34.73	10388.29
0.46	479	286433.55	31.45	8555.61
1.02	487	315892.26	32.08	9255.6
1.67	499	366530.4	31.84	10815.25
2.39	511	343021.59	32.45	9929.06
3.24	525	303095.99	33.03	8619.66
4.28	542	276327.54	32.99	7868.14
5.24	582	173562.26	41.76	3904.03
6.6	584	106556.23	43.44	2303.97
7.6	611	37374.3	48.18	728.6

Peak 2				
Pressure (GPa)	Wavelength (nm)	Area	FWHM	Intensity (a.u.)
0.00	496	182452.87	46.31	11312.56
0.25	502	557669.81	35.83	4783.74
0.46	507	462391.01	50.24	8645.18
1.02	520	629483.60	50.16	11788.35
1.67	532	664498.76	47.67	13093.49
2.39	544	660111.05	49.66	12485.24
3.24	557	563595.74	52.89	10010.2
4.28	573	392365.55	58.77	6271.68
5.24	617	188874.57	68.04	2607.43
6.6	621	110495.37	67.12	1546.48
7.6	641	67805.63	88.8	717.33

Peak 3				
Pressure (GPa)	Wavelength (nm)	Area	FWHM(nm	Intensity (a.u.)
0.00	523	1091780	72.69	14056.65
0.25	527	808764.58	73.7	10308.85
0.46	533	742135.1	74.3	9382.45
1.02	551	574010.82	72.55	7432.31
1.67	566	523153.91	73.24	6693.57
2.39	583	338615.21	70.15	4534.57
3.24	602	225408.65	68.99	3069.21
4.28	610	362830.91	112.86	3019.97
5.24	651	104499.73	101.75	964.8
6.6	653	56024.56	112.42	466.5
7.6	685	18845.5	171.18	80.04

Peak 4				
Pressure (GPa)	Wavelength (nm)	Area	FWHM	Intensity (a.u.)
0.00	574	646374.15	119.53	5080.01
0.25	570	483558.68	118.02	3848.91
0.46	570	621869.69	126.16	4630.56
1.02	592	430720.93	116.01	3487.66
1.67	611	348613.14	119.3	2745.17
2.39	619	266240.96	115.6	2163.57
3.24	639	134806.21	108.04	1172.14
4.28				
5.24				
6.6				
7.6				

Table S3. The analysis of the emission bands of the 9ACA-TFP crystal under decompression.

Peak 1

Pressure (GPa)	Wavelength (nm)	Area	FWHM (nm)	Intensity (a.u.)
7.60	611	37374.3	48.18	728.6
6.83	589	59412.55	42.23	1321.42
6.00	574	61866.84	38.51	1509.13
4.80	547	40073.71	31.58	1192.02
3.76	535	94409.25	34.14	2597.3
2.39	510	85964.91	34.8	2320
0.94	492	112165.24	30.98	3400.78
0.00	471	211202.33	27.8	7135.38

Peak 2

Pressure (GPa)	Wavelength (nm)	Area	FWHM (nm)	Intensity (a.u.)
7.60	641	67805.63	88.8	717.33
6.83	623	105835.06	76.33	1302.56
6.00	610	90257.3	65.1	1381.95
4.80	582	113503.47	65.4	1630.27
3.76	570	199839.08	57.37	3272.09
2.39	546	359782.81	57.49	5878.84
0.94	526	407982.45	57.59	6654.36
0.00	493	404815.77	46.84	8117.78

Peak 3

Pressure (GPa)	Wavelength (nm)	Area	FWHM(nm)	Intensity (a.u.)
7.60	685	18845.5	171.18	80.04
6.83	668	38762.45	135.97	267.8
6.00	653	41717.95	109.33	358.46
4.80	629	56485.54	93.57	567.07
3.76	615	107835.02	80.35	1260.77
2.39	588	261626.25	80.65	3047.36
0.94	558	575918.8	87.34	6194.52
0.00	529	2820	79.03	12871.3

Peak 4

Pressure (GPa)	Wavelength (nm)	Area	FWHM (nm)	Intensity (a.u.)
7.60				
6.83				
6.00				
4.8	693	17561.1	154.96	106.45
3.76	652	62304.19	121.98	479.82
2.39	635	227307.32	123	1736.06
0.94	606	640989.46	145.2	4146.75
0.00	584	715586.57	132.52	5072.76

4. The absorption edges wavelength - pressure relationship.

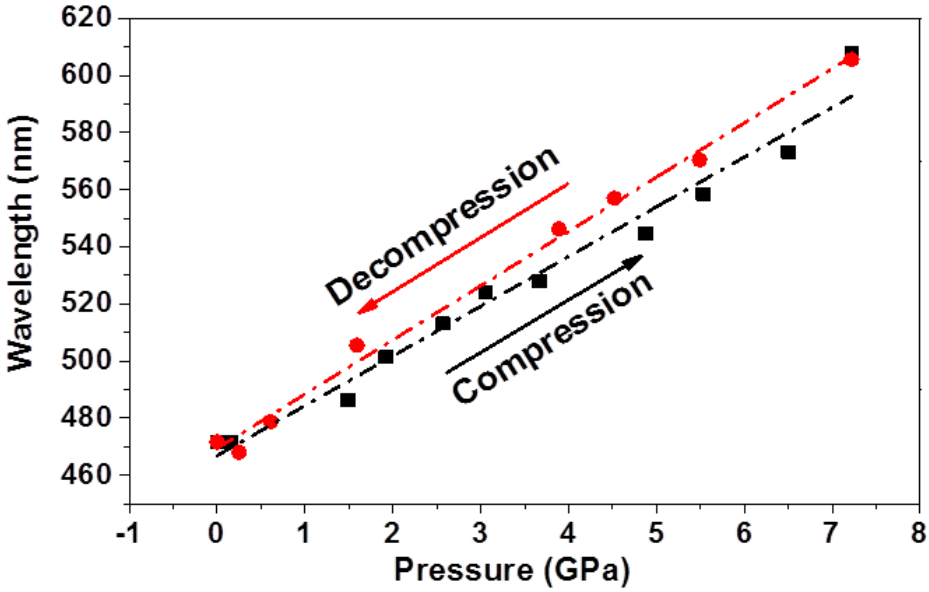

Fig. S4 The absorption edges wavelength-pressure relationship of the 9ACA-TFP cocrystal, upon compression and decompression.

5. Raman band assignments of 9ACA-TFP cocrystal.

Fig. S4 presents the Raman spectra of 9ACA-TFP cocrystal obtained from calculation and experiment. The excitation wavelength was 633 nm. We take the single-crystal X-ray data of the 9ACA-TFP co-crystal as models to compute the Raman spectrum of 9ACA-TFP cocrystal, at the B3LYP method with the 6-31 G (d, p) basis set. All the calculations were carried out by using the GAUSSIAN 09 program package. The assignment of Raman bands were shown in Table S5.

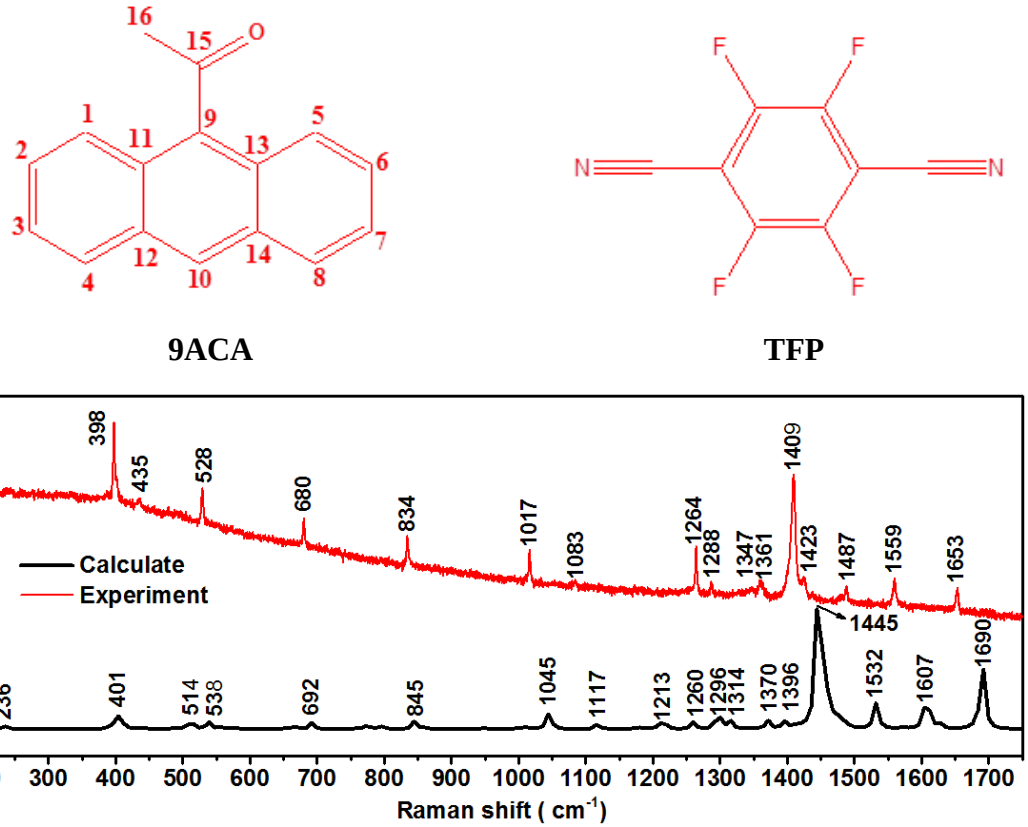

Fig. S5 Raman spectra of the 9ACA-TFP co-crystal achieved from DFT calculation and experiment (excited with a 633 nm laser).

Table S4 Raman shift assignments of 9ACA-TFP cocrystal.

calculations (ν/cm^{-1})	Experiment (ν/cm^{-1})	Assignments
1690	1653	(F)C=C(F) in of plane stretching and C≡N rotating of TFP
1607	1559	C-H in of anthracene plane banding, C_2-C_3, C_6-C_7, C_{11}-C_{12}, C_{13}-C_{14} in plane sym-stretching of 9ACA
1532	1487	C-H in of anthracene plane bending, C_2-C_3, C_6-C_7 in plane sym-stretching of 9ACA
1462	1423	In plane ring breathing of TFP and C≡N rotating of TFP
1445(s)	1409(s)	C-H in of anthracene plane banding, C-H in CH3 banding and C_1-C_2, C_3-C_4, C_5-C_6, C_7-C_8, C_{11}-C_{12}, C_{13}-C_{14}, C_9-C_{15} in plane sym-stretching, of 9ACA
1396	1361	CH_3 stretching of 9ACA
1370	1347	C≡N rotating of TFP; C-H in of anthracene plane bending, C-H in of CH3 banding, C_9-C_{15}, C_{10}-C_{12}, C_{10}-C_{14}, C_9-C_{13}, C_6-C_{11} in plane antisym -stretching, of 9ACA
1314	1288	C-H in of anthracene plane bending, in plane ring (C_9-C_{11}-C_{12}-C_{10}-C_{14}-C_{13}) breathing and C-CH_3 stretching of 9ACA
1296		C-H in of anthracene plane bending and in plane ring (C_9-C_{11}-C_{12}-C_{10}-C_{14}-C_{13}) breathing of 9ACA
1260	1264	C-H in of anthracene plane bending and C_1-C_{11}, C_5-C_{13} in plane sym-stretching of 9ACA
1213		C-H in of anthracene plane bending of 9ACA
1117	1083	C-CN in of plane stretching, in plane ring breathing of TFP, and C≡N rotating of TFP
1045	1017	ν(C_2-C_3), ν(C_6-C_7), C-H in of anthracene plane bending of 9ACA
845	834	ν(CH_3), C-H out of plane bending, ∠C_1-C2-C3, ∠C5-C6-C7 scissoring vibration of 9ACA
692	680	ν(CH_3), ν(C=O), ring (C_1-C_2-C_3-C_4-C_{12}-C_{11}), ring (C_5-C_6-C_7-C_8-C_{14}-C_{13}) and ring (C_9-C_{11}-C_{12}-C_{10}-C_{14}-C_{13}) breathing in of anthracene plane
538	528	In plane ring breathe and C≡N rotating of TFP
514		C≡N out of plane antisym-stretching and ring out of plane stretching of TFP
401	398	C_1-C_2-C_3-C_4 and C_5-C_6-C_7-C_8 in of anthracene plane sym-stretching, ν(CH_3), ν(C=O) of 9ACA; C≡N rotating of TFP
236		Ring (C_1-C_2-C_3-C_4-C_{12}-C_{11}) and ring (C_5-C_6-C_7-C_8-C_{14}-C_{13}) out of anthracene plane deformation of 9ACA, C≡N rotating of TFP

6. The Raman spectra of 9ACA-TFP co-crystal under decompression

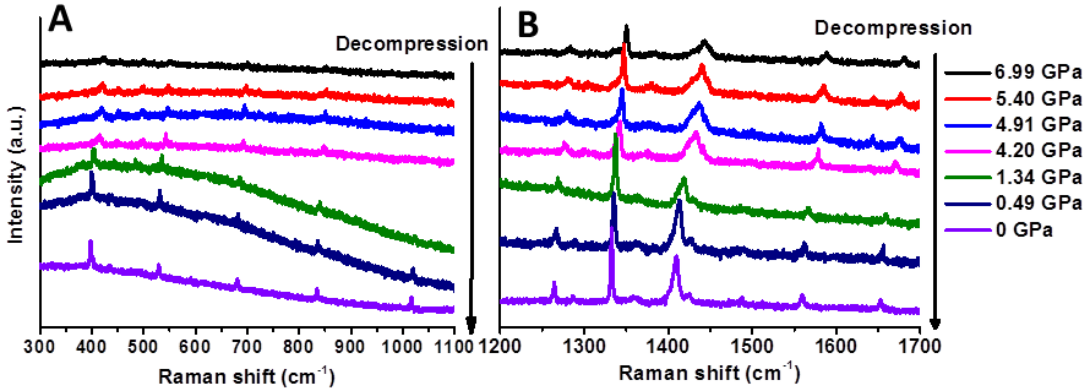

Fig. S6 Raman spectra of the 9ACA-TFP co-crystal under decompression, in frequency region (A) 300 ~ 1100 cm^{-1} and (B) 1200 ~ 1700 cm^{-1}. The excitation wavelength is 785 nm.