

Fine-tuning the optoelectronic chattels of fluoreno-thiophene centred molecular semiconductors through symmetric and asymmetric push-pull switch

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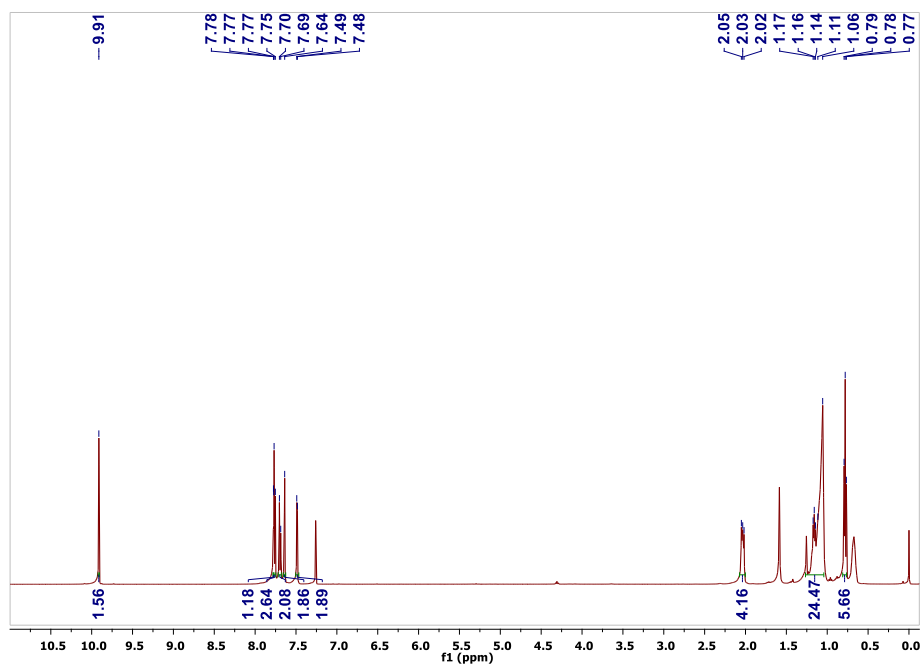
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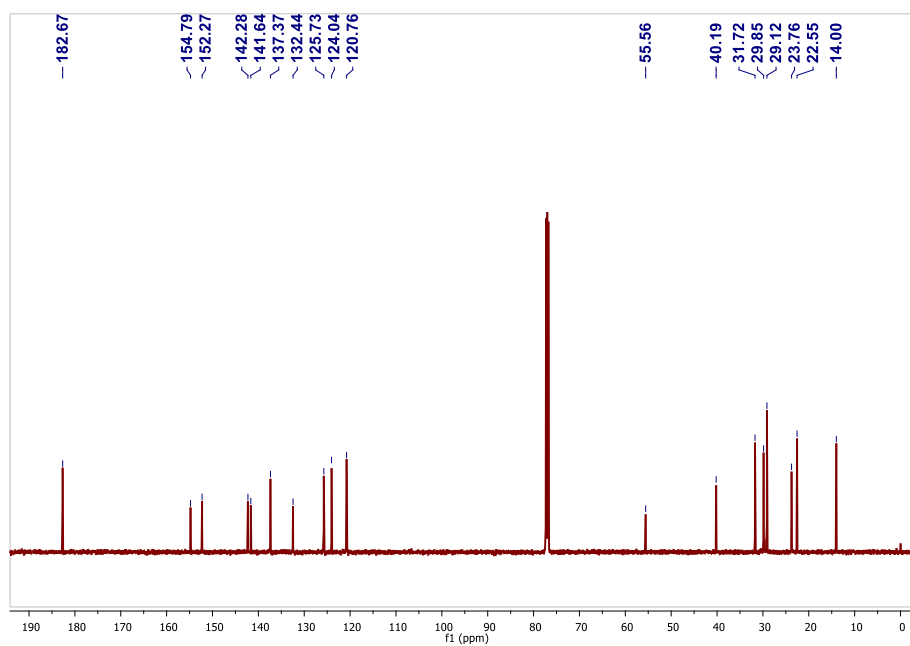
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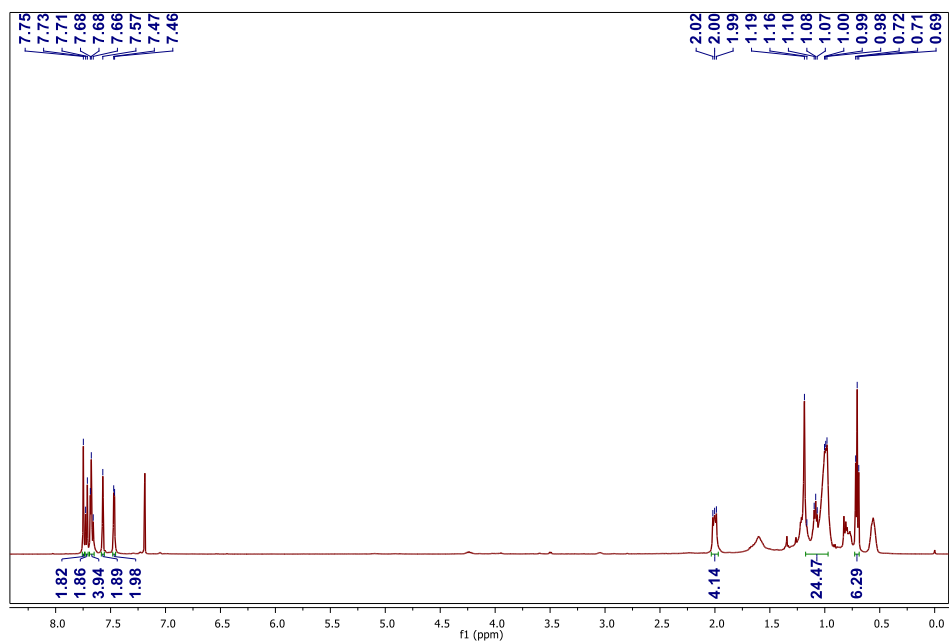
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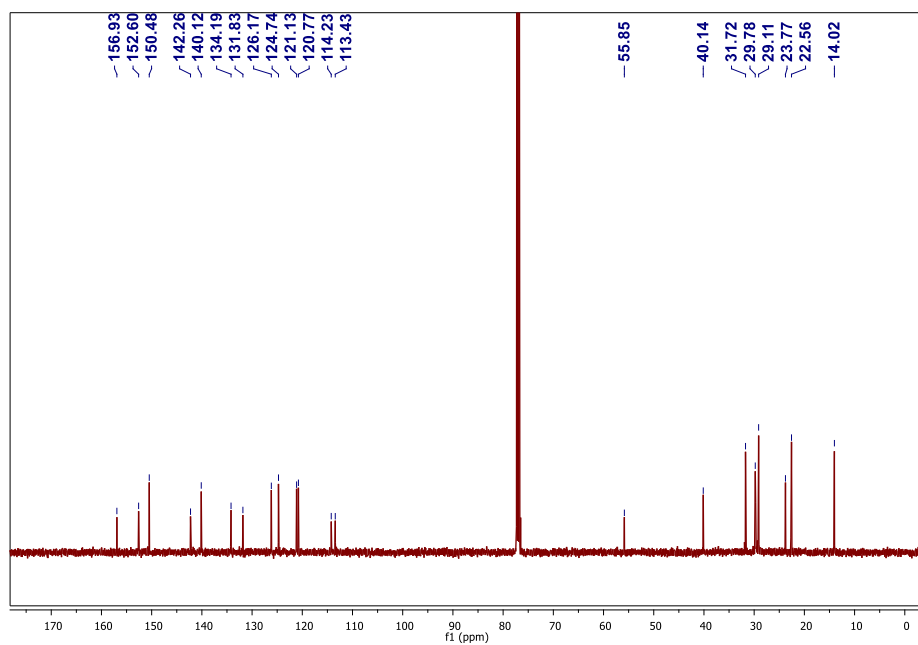
¹H NMR spectrum of **CHO-CHO** in CDCl₃



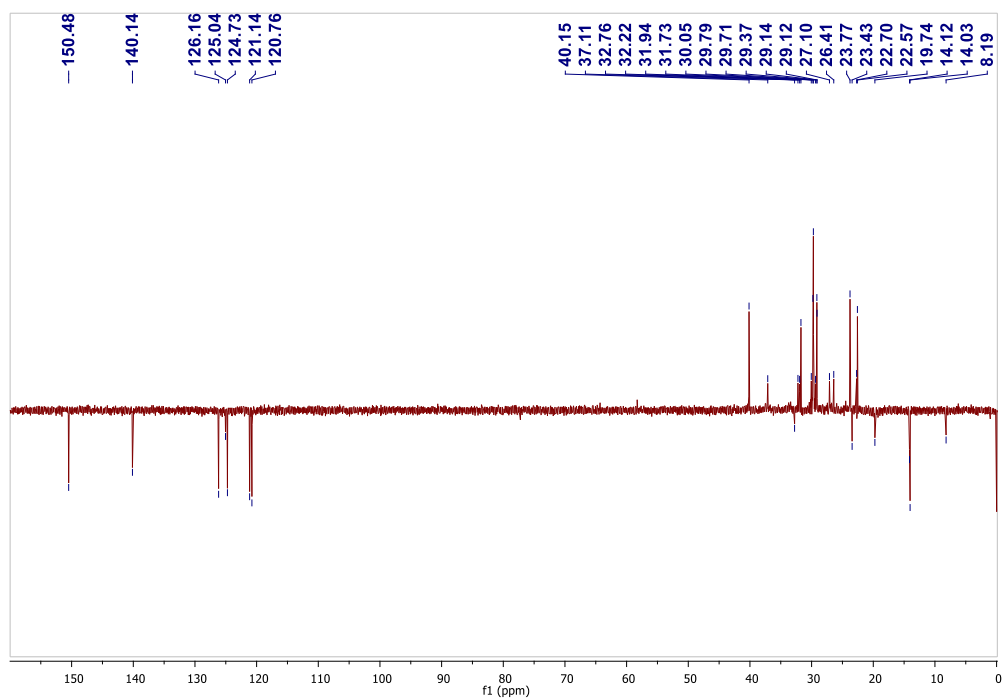
¹³C NMR spectrum of **CHO-CHO** in CDCl₃



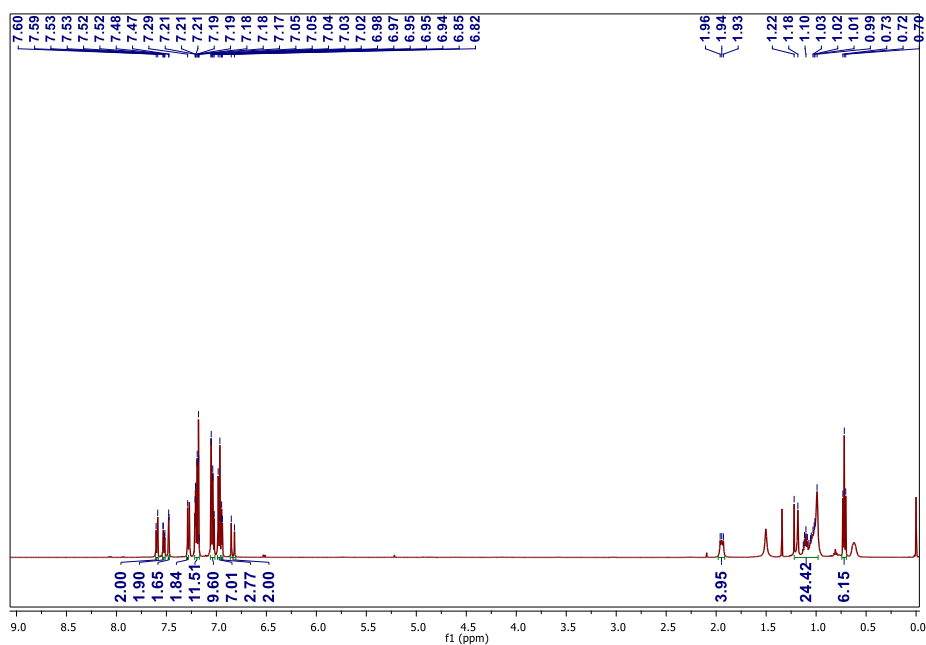
¹H NMR spectrum of CN-CN in CDCl₃



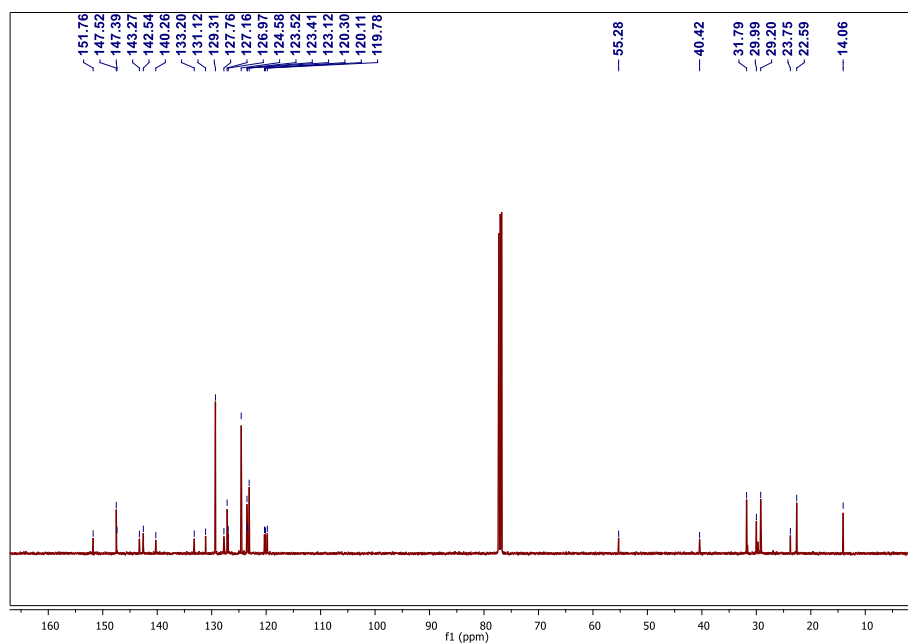
¹³C NMR spectrum of CN-CN in CDCl₃



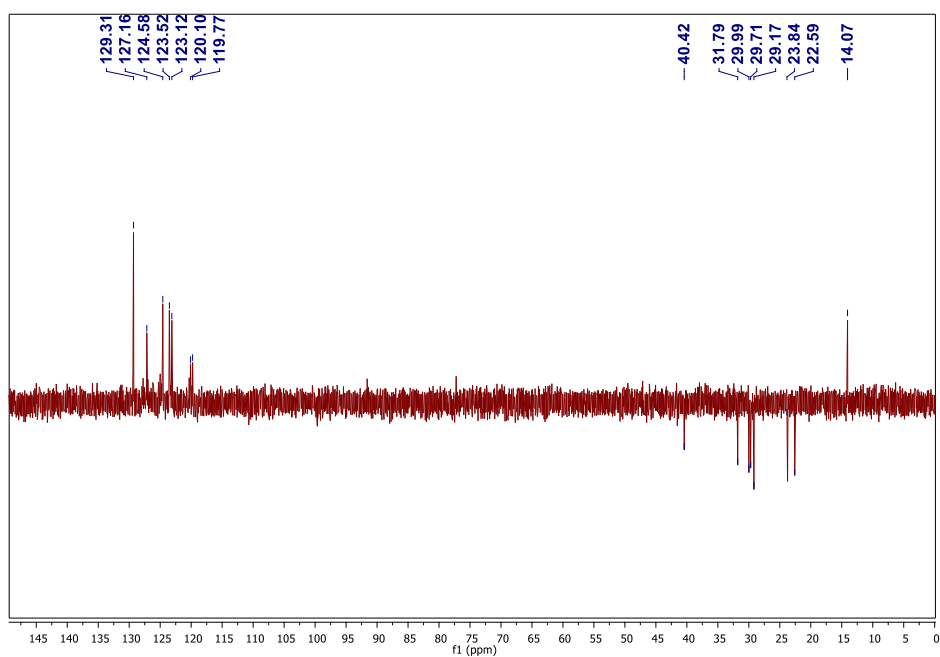
DEPT-135 spectrum of **CN-CN** in CDCl_3



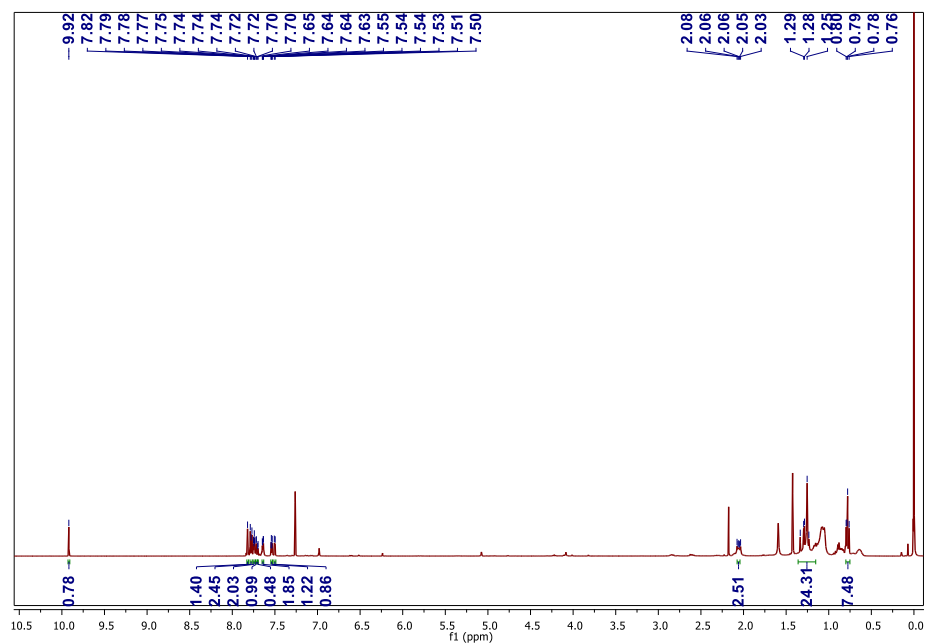
^1H NMR spectrum of **TPA-TPA** in CDCl_3



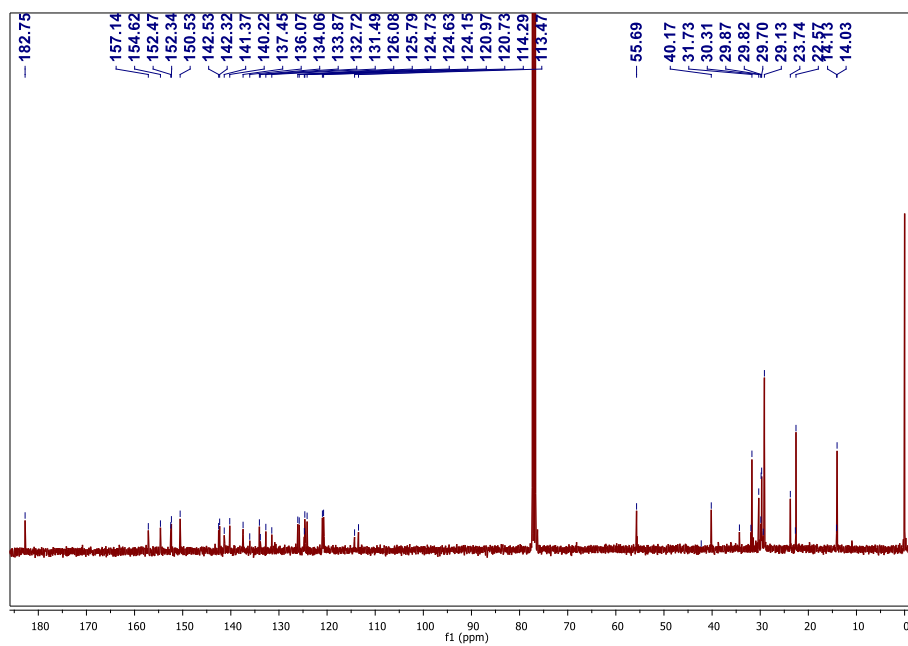
¹³C NMR spectrum of **TPA-TPA** in CDCl₃



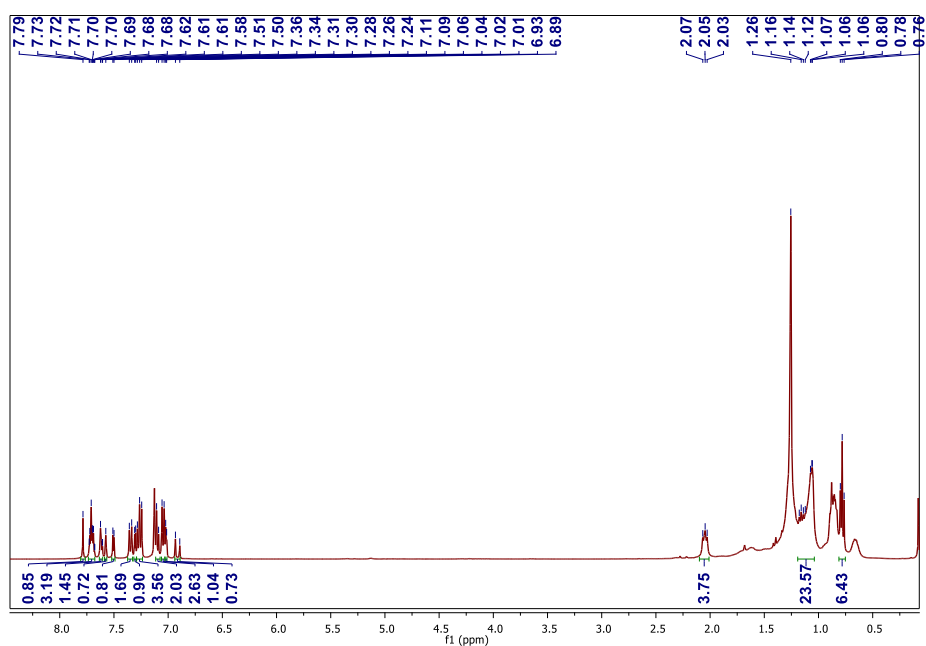
DEPT-135 spectrum of **TPA-TPA** in CDCl₃



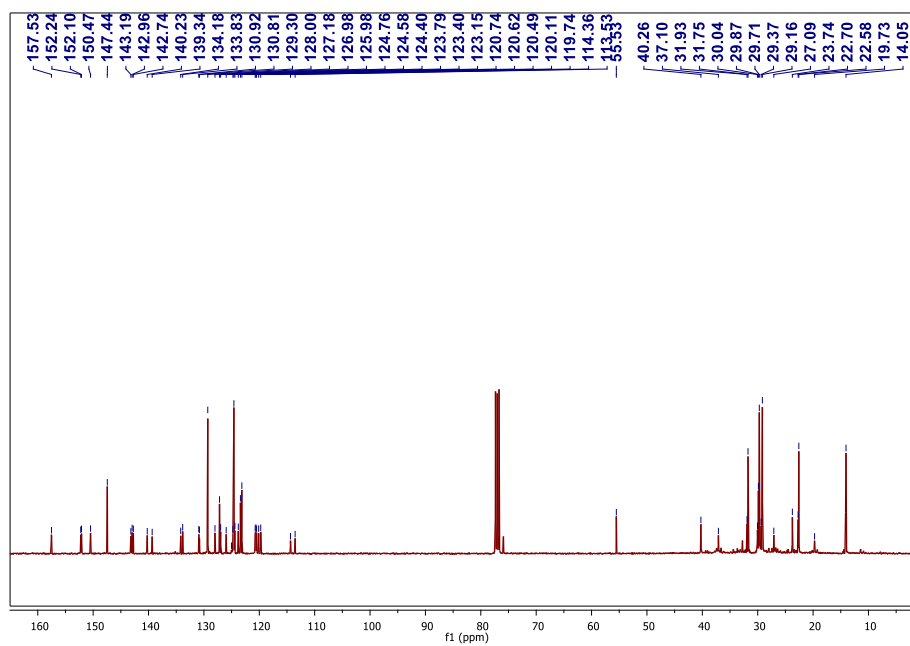
¹H NMR spectrum of **CN-CHO** in CDCl₃



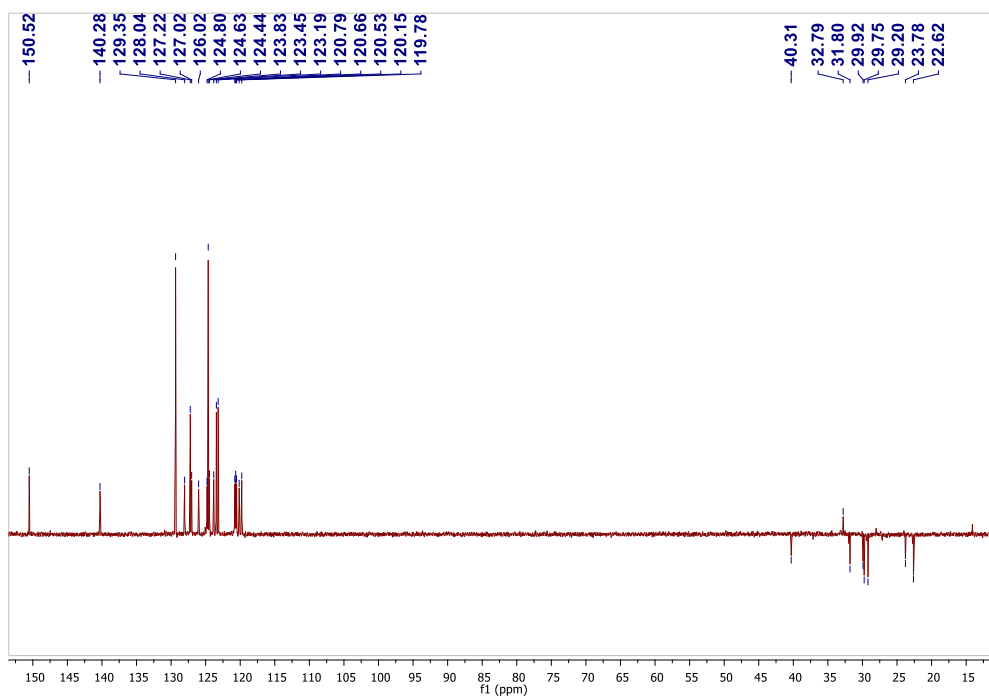
¹³C NMR spectrum of **CN-CHO** in CDCl₃



¹H NMR spectrum of **TPA-CN** in CDCl₃



¹³C NMR spectrum of **TPA-CN** in CDCl₃



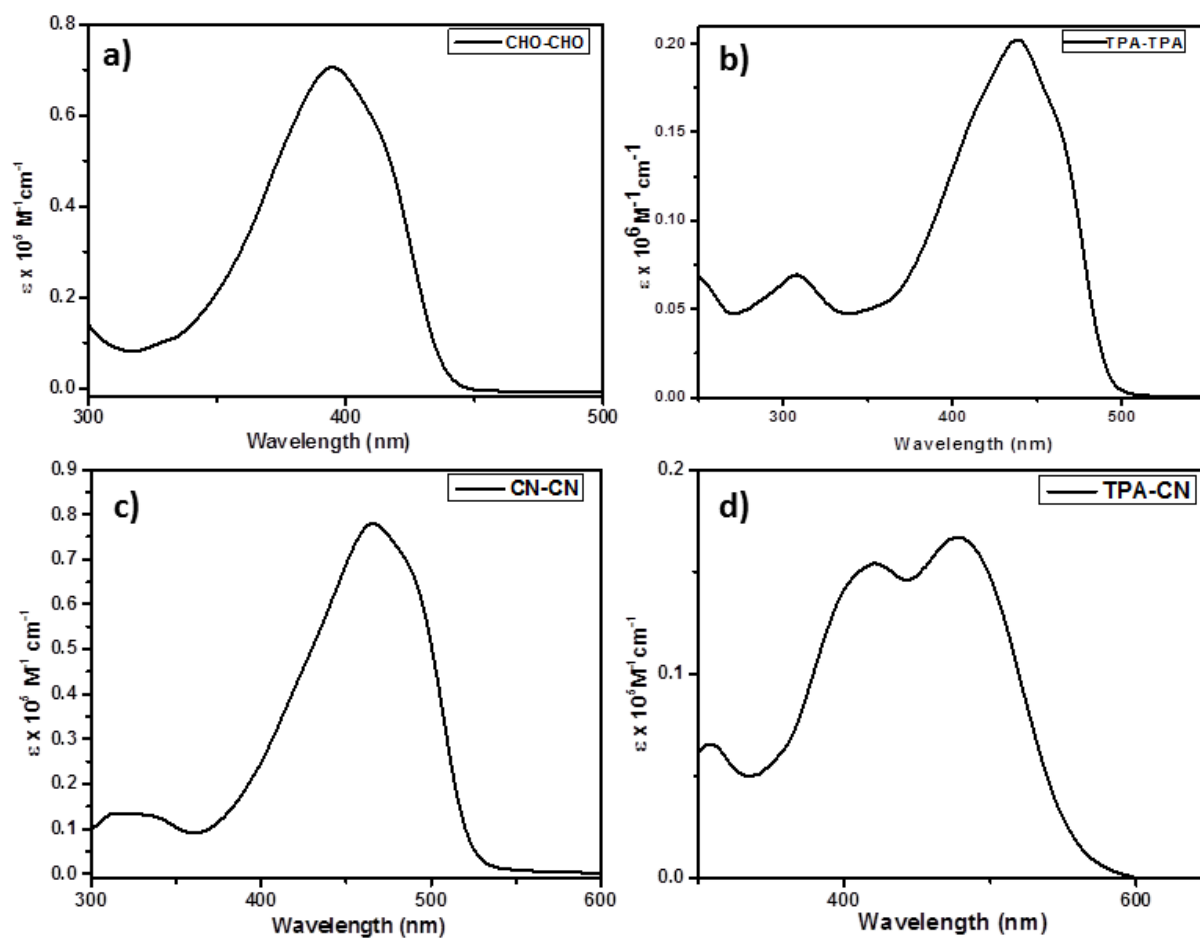


Fig S1. UV-vis spectra of compounds in CHCl_3 at different concentration

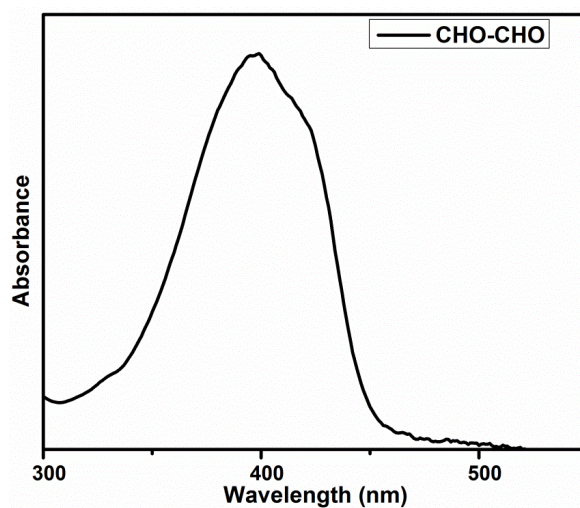


Fig S2. UV-vis spectra of **CHO-CHO** as thin film

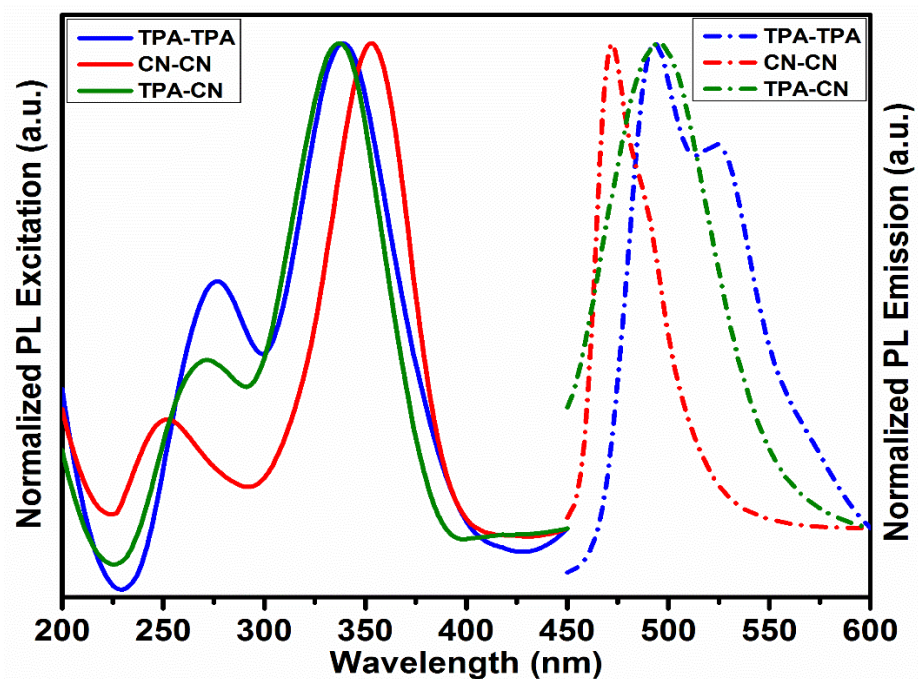


Fig S3. PL emission and excitation spectra of compounds in CHCl_3 at different concentration

Table S1 Photoexcitation and emission data

	λ_{em} (nm) ^a	λ_{ex} (nm) ^b	C (M) ^c	Stokes shift (cm^{-1})	ϕ (%) ^d
TPA-TPA	493	339	5.0×10^{-6}	178600	18.3
CN-CN	529	353	1.0×10^{-5}	169500	14.2
TPA-CN	584	337	3.0×10^{-5}	94300	21.1

^aEmission in solution; ^bExcitation from emission in solution; ^cConcentration used for UV-vis was retained;
^dQuantum yields were measured using quinine sulphate ($\phi = 55\%$) as reference

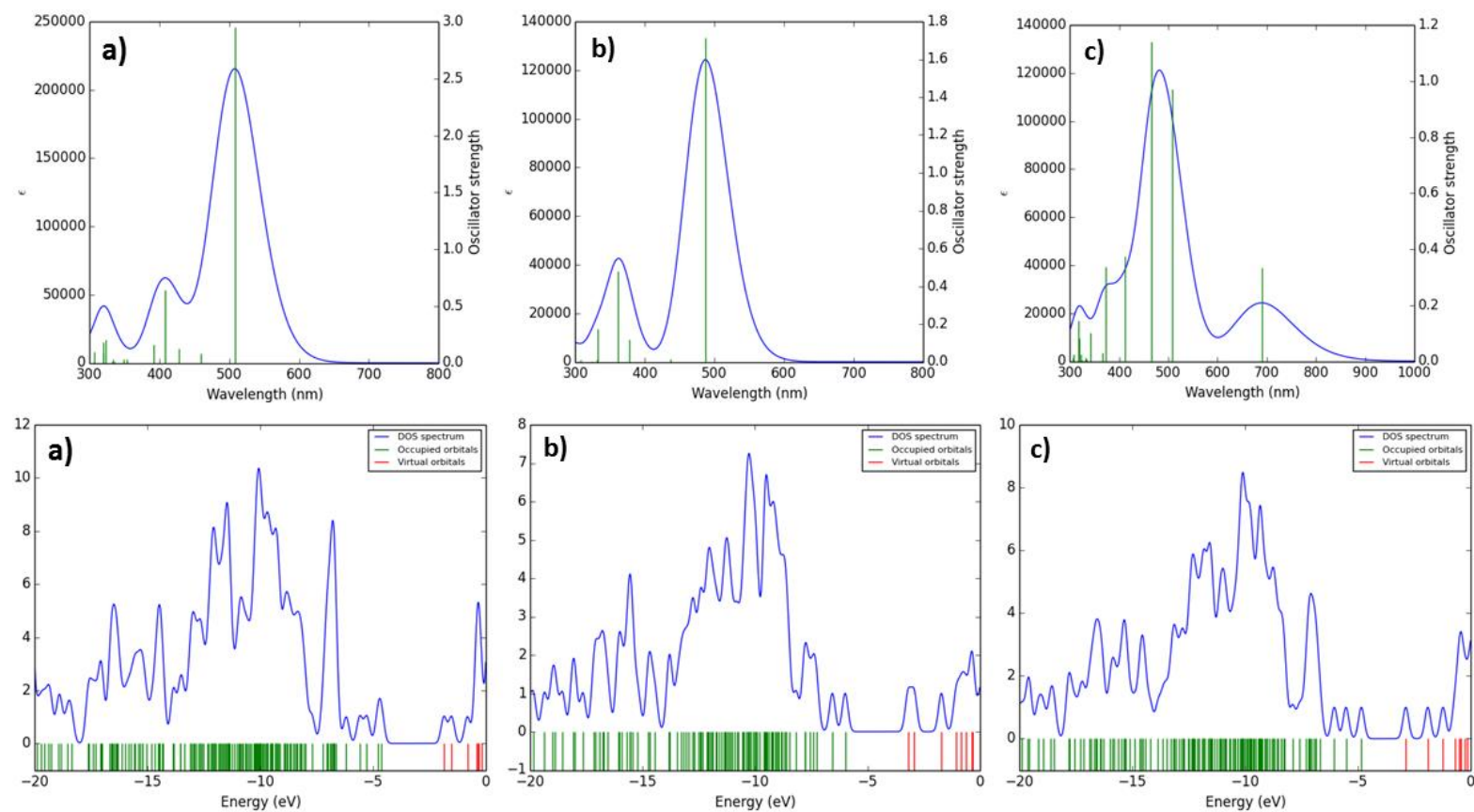


Fig S4. Computed gas phase UV-vis spectrum of a) **TPA-TPA**; b) **CN-CN**; c) **TPA-CN** (top); Total Density of states (TDOS) & band structure of a) **TPA-TPA**; b) **CN-CN**; c) **TPA-CN** obtained at B3LYP/6-31G** (d,p) basis set

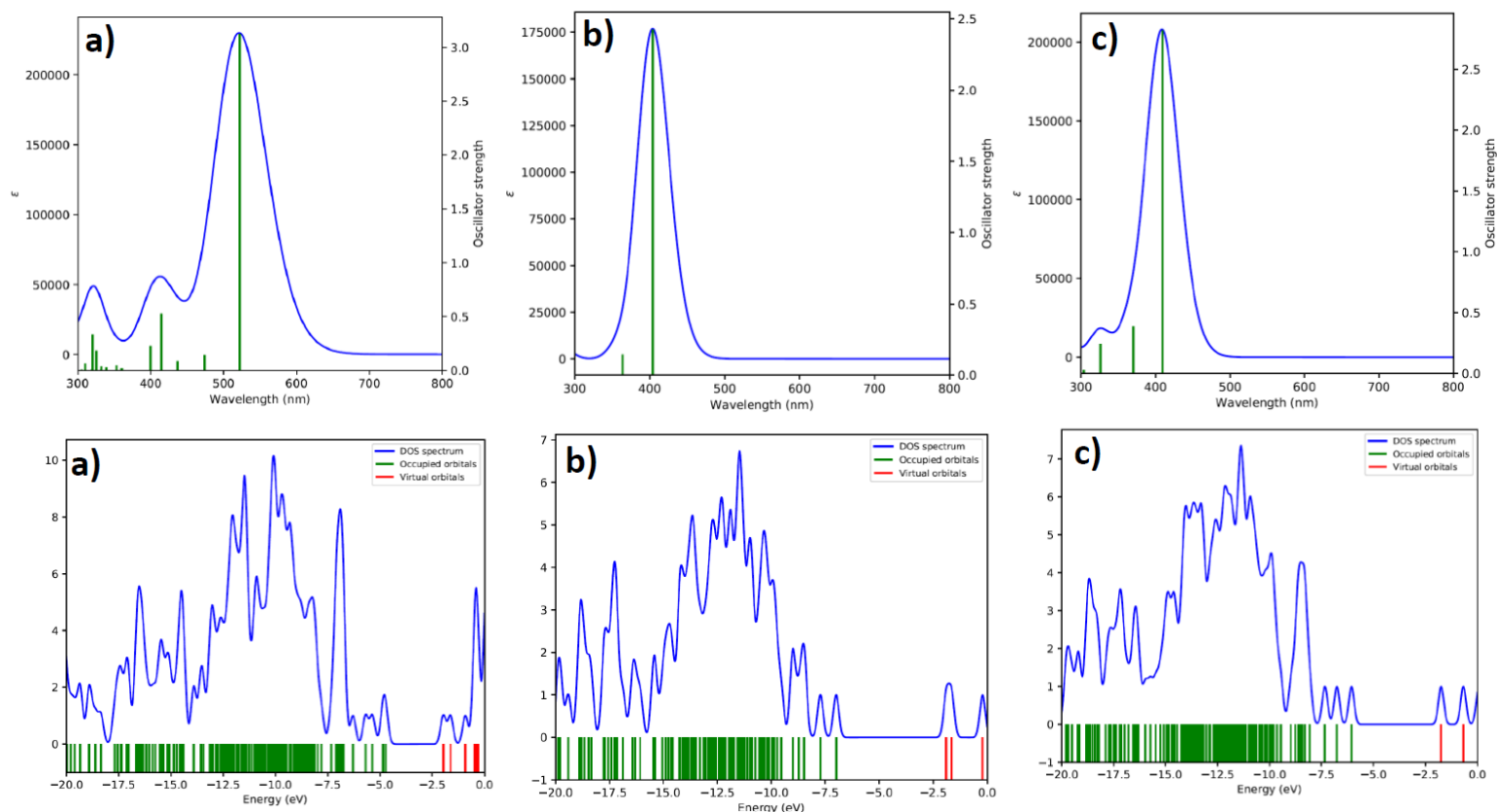
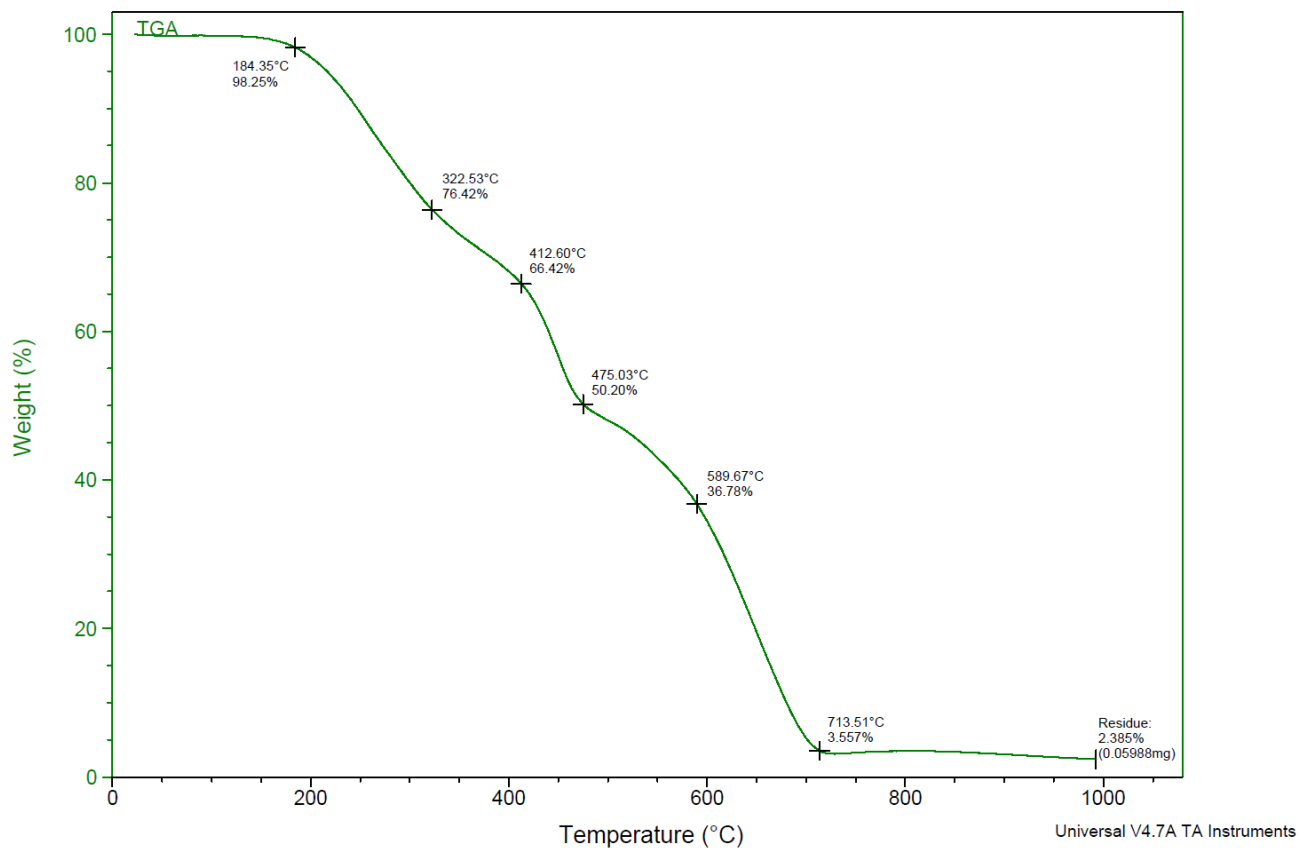


Fig S5. Theoretical UV-vis spectrum in chloroform under IEFPCM model of a) **TPA-TPA**; b) **CN-CN**; c) **TPA-CN** (top); Total Density of states (TDOS) & band structure of a) **TPA-TPA**; b) **CN-CN**; c) **TPA-CN** obtained at CAM-B3LYP functional

Sample: S-1[VNC010]
Size: 2.5110 mg
Method: N2
Comment: K.Chitra

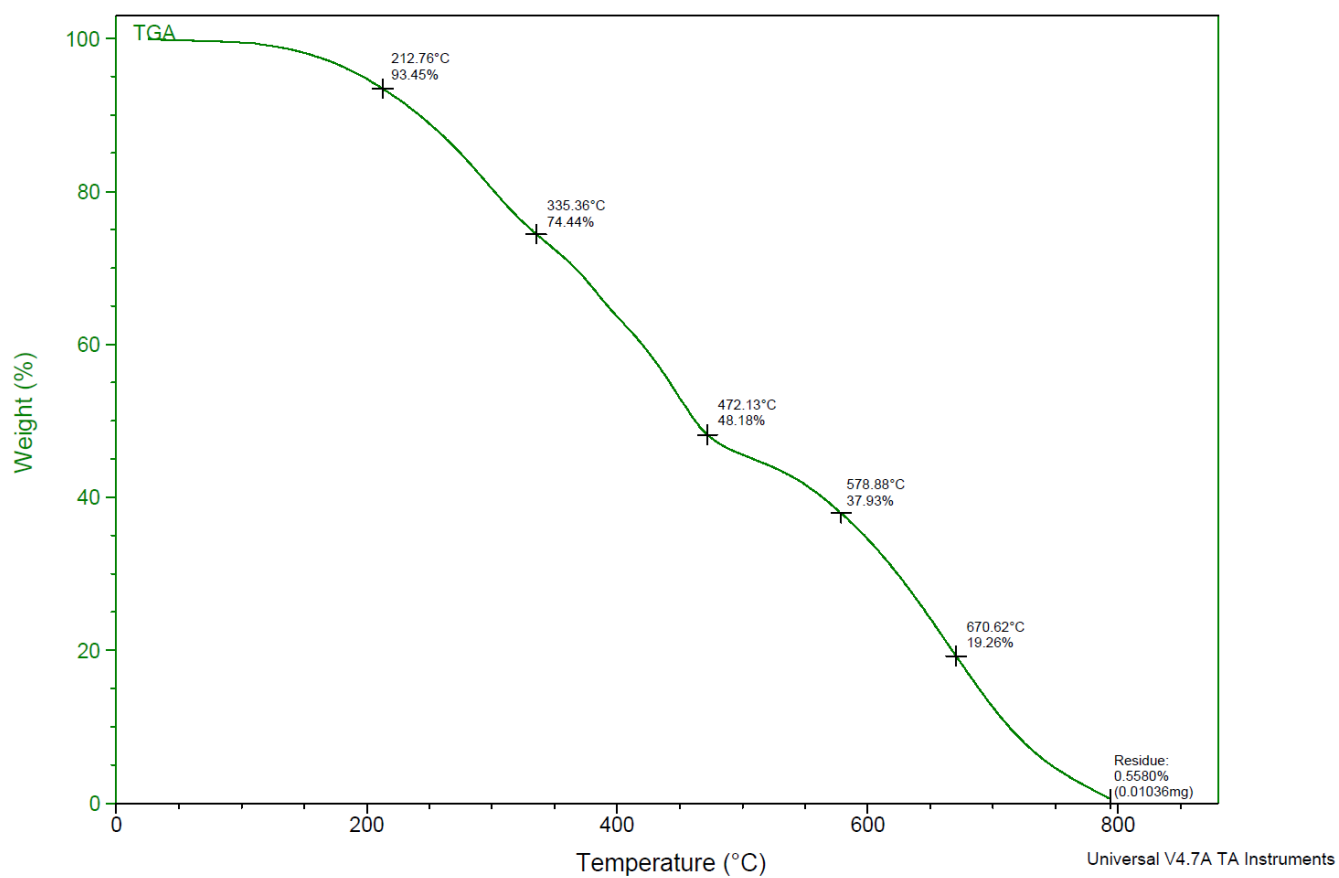
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Operator: Er P.Murugesan
Run Date: 11-Jul-2018 12:27
Instrument: SDT Q600 V8.3 Build 101



TPA-TPA

Sample: S-1[PCR 55]
Size: 1.8560 mg
Method: N2
Comment: K.Chitra

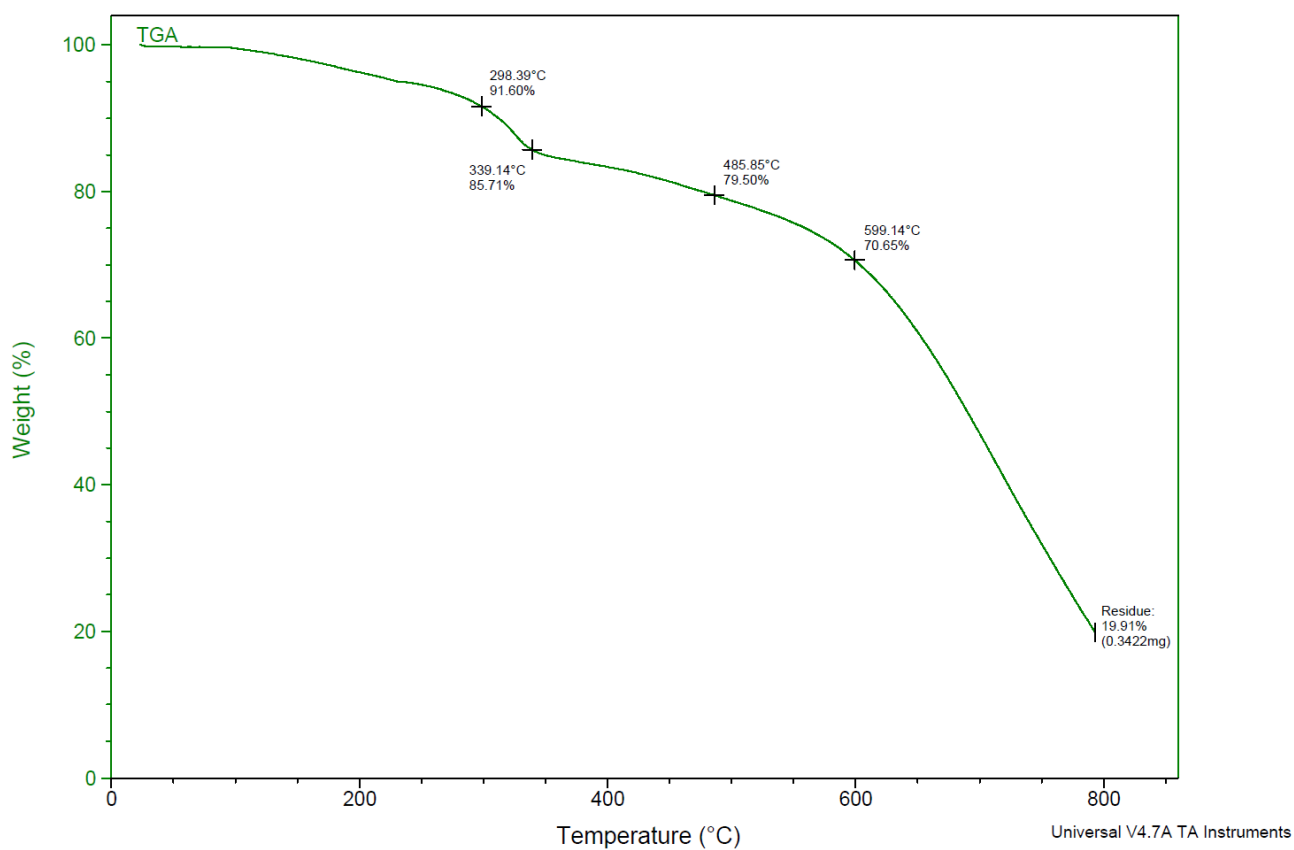
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CN-CN

Sample: S-1
Size: 1.7190 mg
Method: N2
Comment: Chitra

Directory: C:\DATA\October 2018
Operator: Er P.Murugesan
Run Date: 04-Oct-2018 13:13
Instrument: SDT Q600 V8.3 Build 101

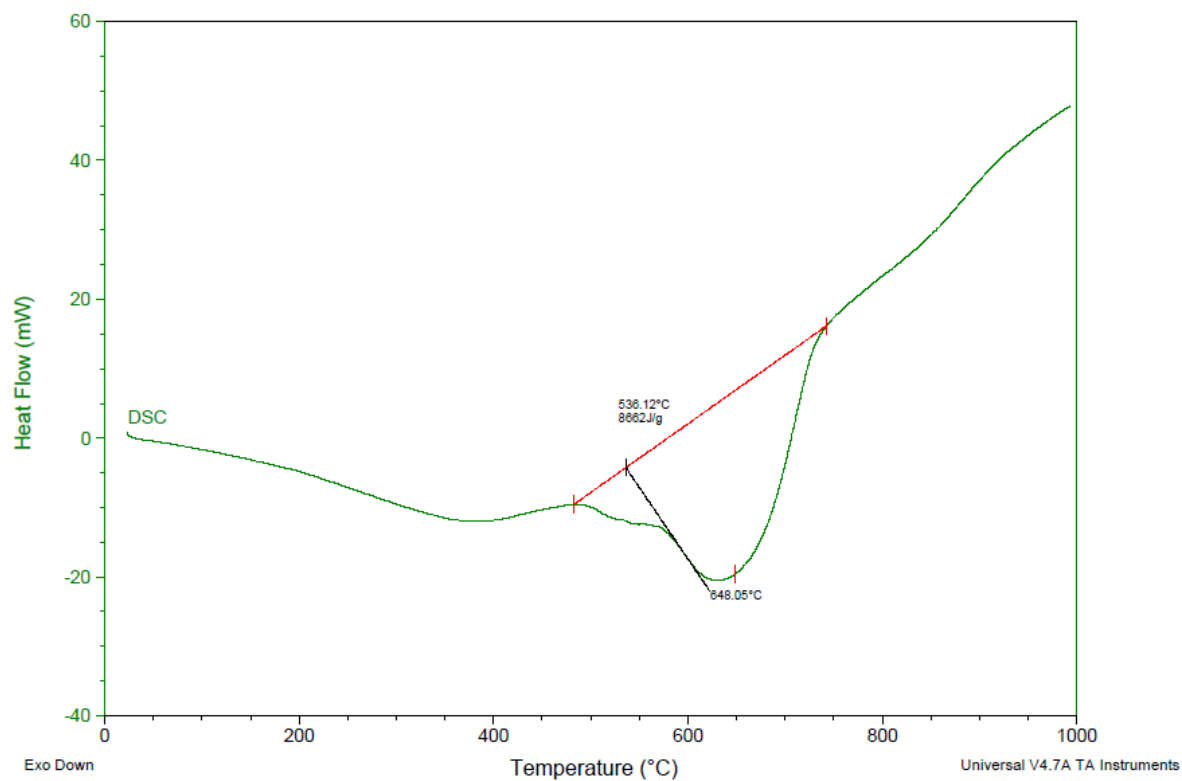


TPA-CN

Fig S6. TGA curves **TPA-TPA** (top); b) **CN-CN** (middle) and c) **TPA-CN** (centre)

Sample: S-1[VNC010]
Size: 2.5110 mg
Method: N2
Comment: K.Chitra

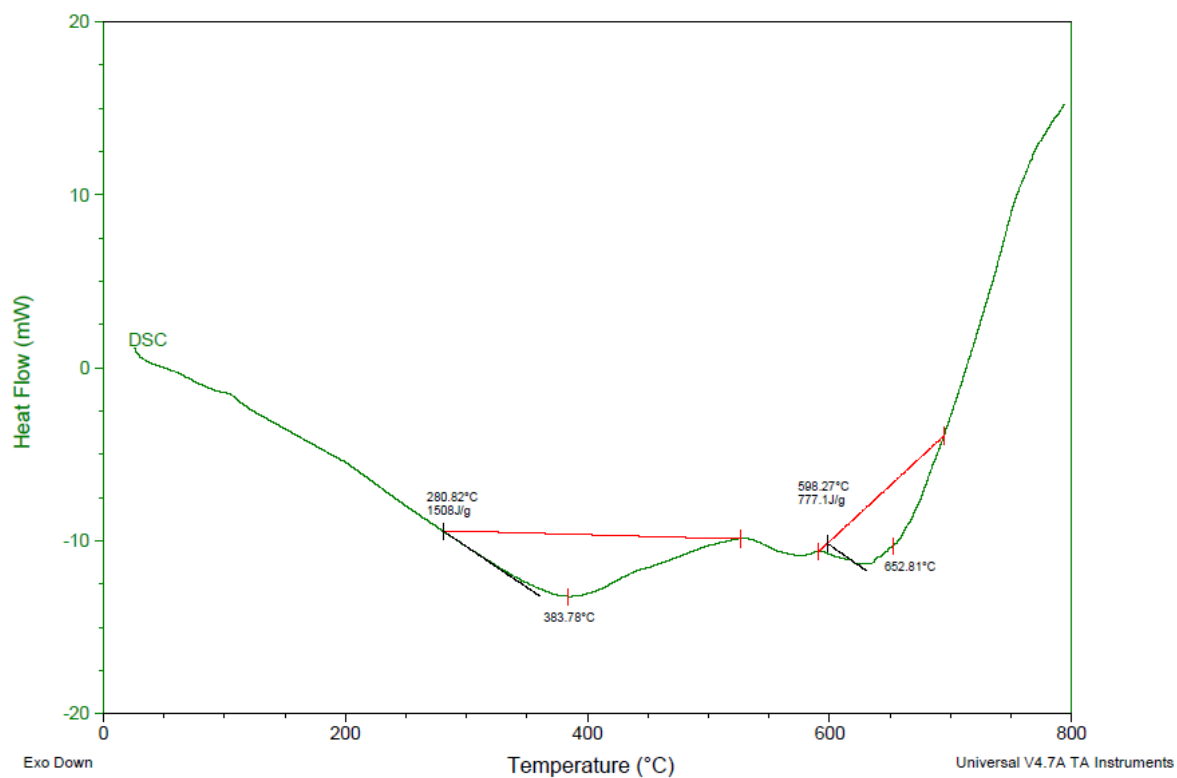
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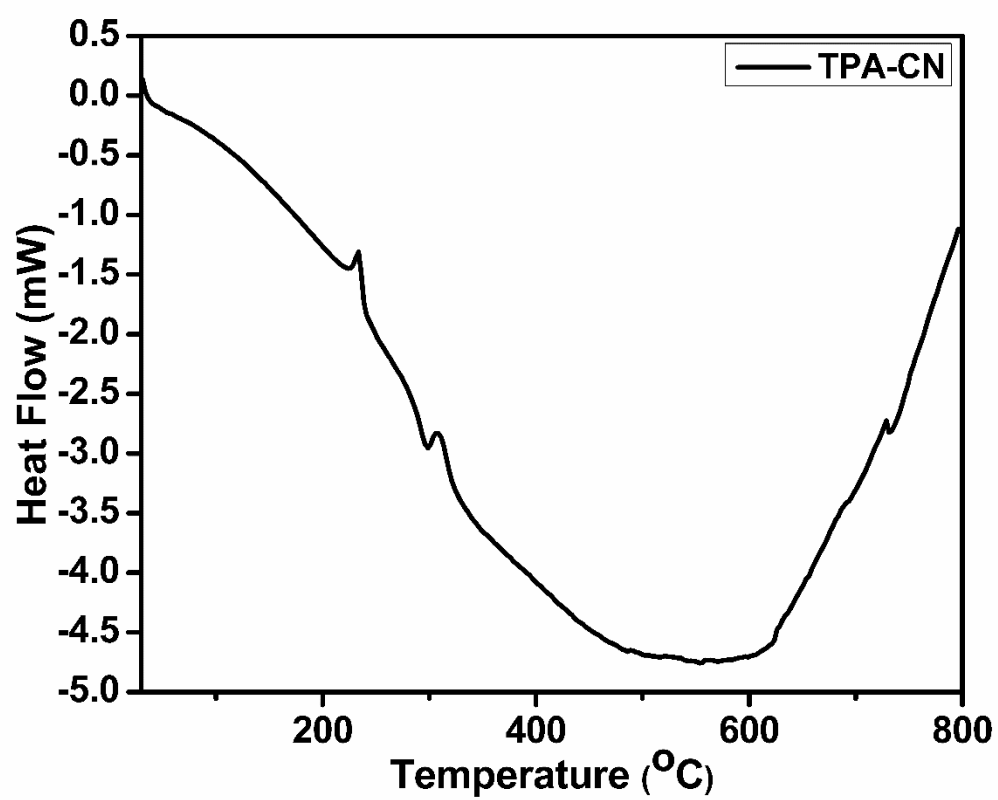
TPA-TPA

Sample: S-1[PCR 55]
Size: 1.8560 mg
Method: N2
Comment: K.Chitra

Directory: C:\DATA\July 2018
Operator: Er P.Murugesan
Run Date: 05-Jul-2018 15:11
Instrument: SDT Q600 V8.3 Build 101



CN-CN



TPA-CN

Fig S7. DSC thermogram of **TPA-TPA** (top); b) **CN-CN** (middle) and c) **TPA-CN** (centre)

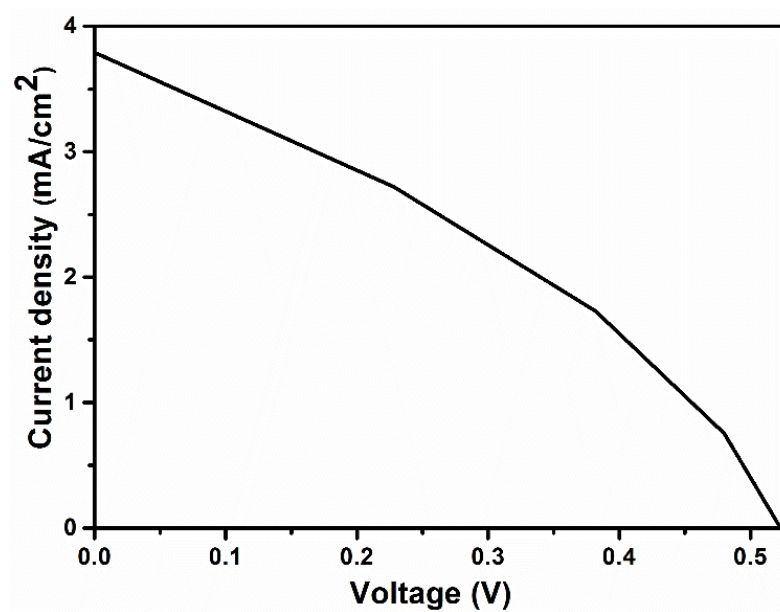


Fig S8. *J*-*V* curve of 1:1 blend of as-cast **TPA-CN:PCBM**

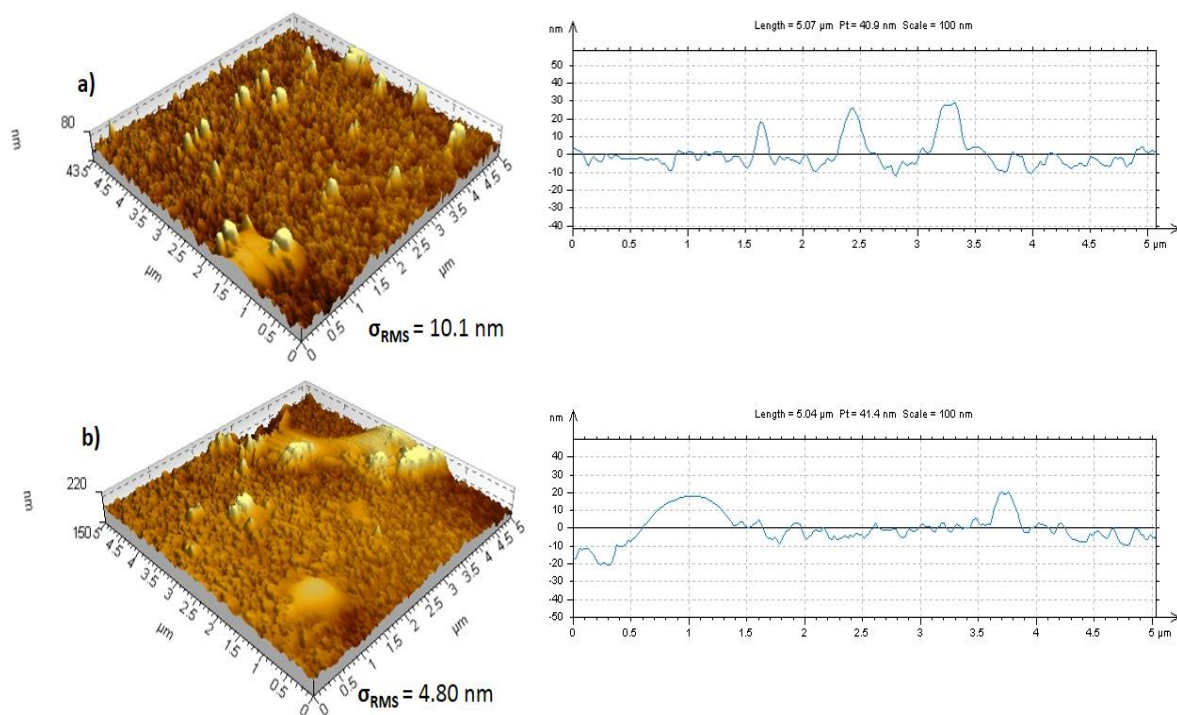


Fig S9 Tapping mode AFM height images (5 X 5 μm) of TPA-TPA:PCBM: (a) pristine film; (b) annealed film at 120 $^{\circ}\text{C}$ for 5 min

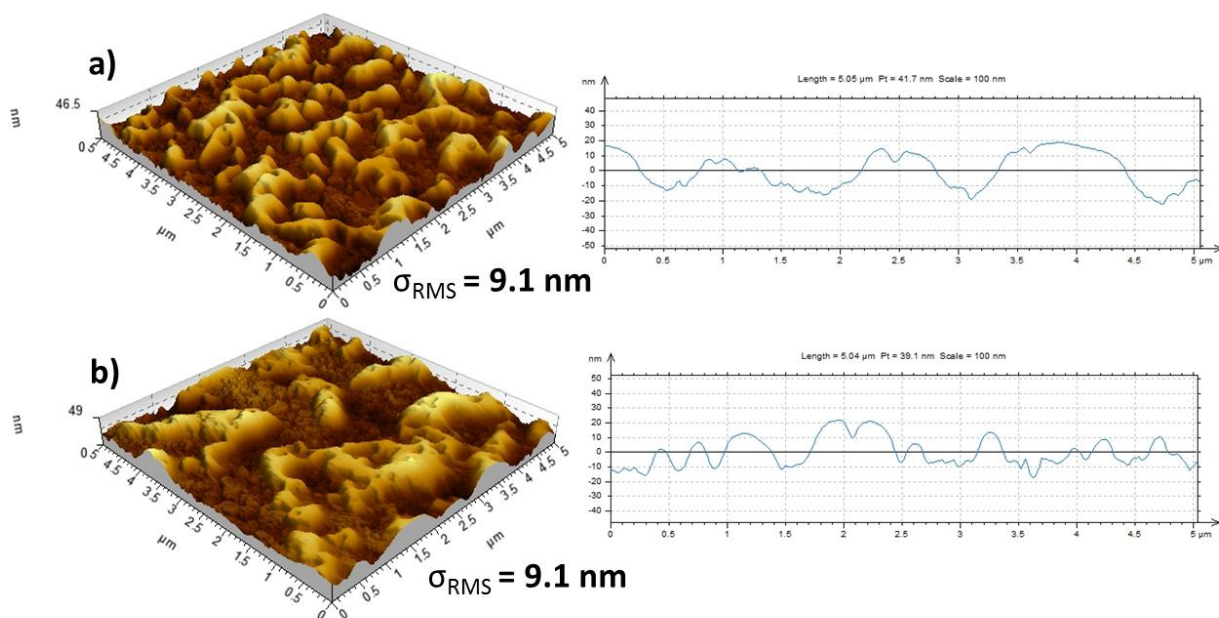


Fig S10 Tapping mode AFM height images (5 X 5 μm) of CN-CN:PCBM: (a) pristine film; (b) annealed film at 120 $^{\circ}\text{C}$ for 5 min

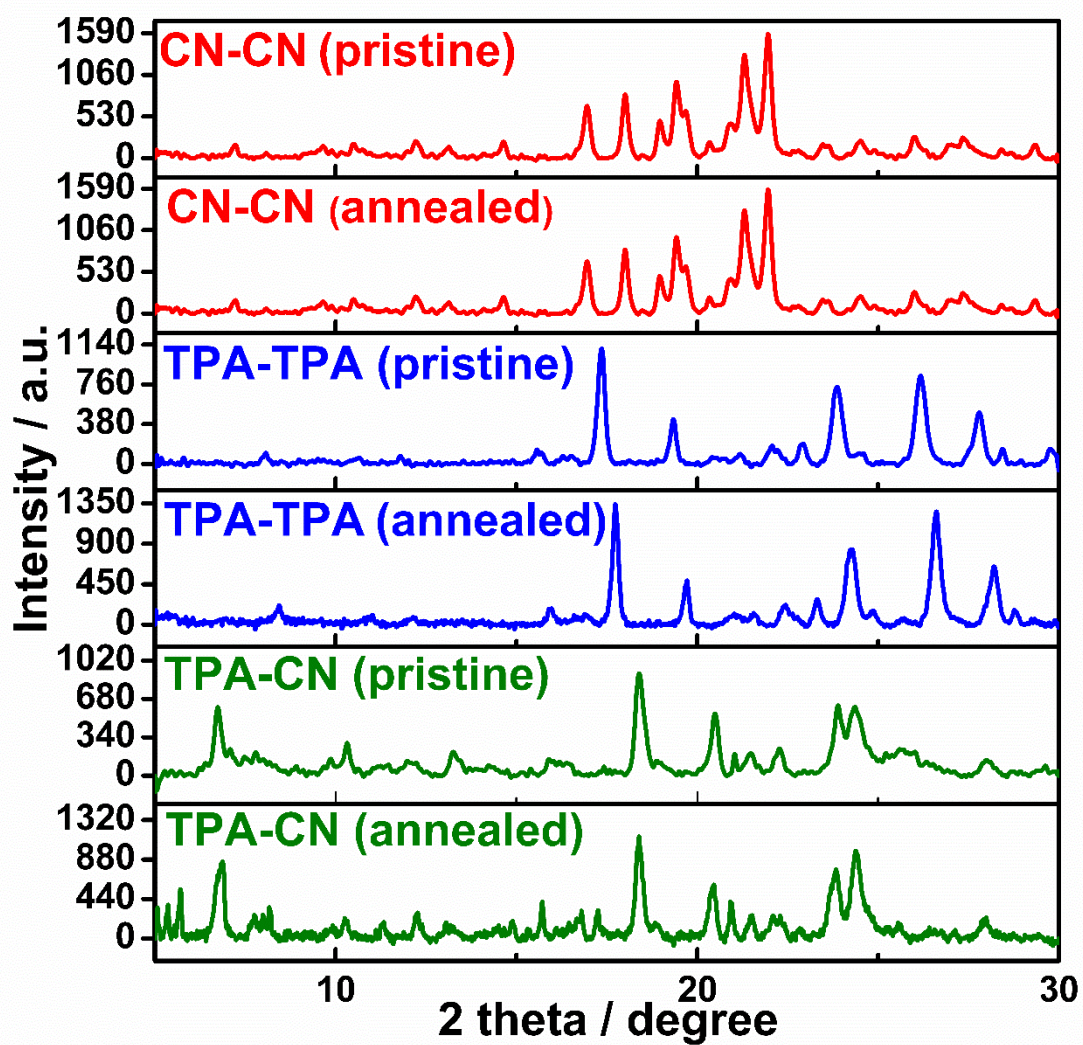


Fig S11 XRD of pristine and annealed films at 120 °C for 5 min

Table S2 Cartesian coordinates**TPA-TPA**

Symbol	X	Y	Z
C	2.95771	-1.3135	-0.3904
C	3.43248	0.00323	-0.5583
C	2.50304	1.06757	-0.5261
C	1.14964	0.81264	-0.3587
C	0.70063	-0.5117	-0.1675
C	1.60682	-1.5743	-0.1858
C	-0.0195	1.80465	-0.2709
C	-1.1896	0.84681	-0.0003
C	-0.7427	-0.4911	0.04792
C	-2.5426	1.12982	0.12063
C	-3.4729	0.0895	0.34296
C	-3.001	-1.237	0.41036
C	-1.6505	-1.5322	0.25514
C	0.25069	2.78152	0.91523
C	-0.2894	2.53852	-1.621
C	-0.795	3.86603	1.20786
C	0.76291	3.54083	-2.1133
C	-0.3485	4.78721	2.35399
C	0.33177	4.23015	-3.4176
C	-1.3068	5.94859	2.66636
C	1.37369	5.19317	-4.01
C	-2.6819	5.51976	3.20434
C	1.61973	6.45904	-3.1725
C	-3.6039	6.68734	3.62409
C	2.60232	7.47454	-3.7981
C	4.07573	7.33765	-3.3752
C	-3.5491	7.08486	5.11028
C	-2.2016	7.61368	5.61336
C	4.76928	6.03028	-3.7737
C	-4.8941	0.40219	0.49729
C	4.85441	0.28264	-0.7604
C	-5.4748	1.58018	0.91895
C	-6.8895	1.54149	0.95274
C	-7.4293	0.33186	0.55812
S	-6.1406	-0.7809	0.12476
C	5.43938	1.38232	-1.3535
C	6.85366	1.33457	-1.3804
C	7.38954	0.1951	-0.8104
S	6.09728	-0.8355	-0.215
C	-8.8305	-0.0032	0.49378

C	8.78954	-0.1312	-0.6968
C	-9.3634	-1.1867	0.10984
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C	10.7307	-1.5979	-0.0406
C	-10.777	-1.5389	0.04216
C	11.0928	-2.824	0.55085
C	12.4198	-3.2024	0.7078
C	13.4559	-2.3666	0.25987
C	13.1101	-1.1413	-0.3419
C	11.7825	-0.7671	-0.4803
C	-11.146	-2.8079	-0.4447
C	-12.475	-3.2	-0.5445
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C	-13.151	-1.0669	0.36072
C	-11.822	-0.6802	0.44158
N	14.8131	-2.7439	0.40517
C	15.7926	-1.7711	0.75003
C	15.2029	-4.1003	0.22303
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C	-15.854	-1.7829	-0.619
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H	18.4802	0.88757	1.69548
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H	14.5665	-0.8171	2.24302
H	16.5088	-4.1293	1.93648
H	17.2039	-6.4805	1.61067
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H	14.6606	-6.7501	-1.8456
H	13.9903	-4.3897	-1.5343

CN-CN

Symbol	X	Y	Z
C	2.96556	-2.9102	0.2229
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C	2.53016	-0.5395	-0.1082
C	1.16685	-0.7956	-0.1021
C	0.70164	-2.1124	0.10224
C	1.60092	-3.1701	0.26085
C	-0.0048	0.18943	-0.2192
C	-1.1959	-0.7645	-0.0516
C	-0.7568	-2.0945	0.12535
C	-2.5542	-0.4914	-0.1214

C	-3.4969	-1.5332	0.02715
C	-3.036	-2.851	0.22568
C	-1.6766	-3.1368	0.26735
C	0.10839	1.23038	0.93817
C	-0.1004	0.8487	-1.6309
C	-0.9825	2.30465	1.03973
C	1.01337	1.81934	-2.0451
C	-0.7042	3.30406	2.17413
C	0.73925	2.45135	-3.4192
C	-1.7431	4.42999	2.30683
C	1.86512	3.35713	-3.9443
C	-3.148	3.96032	2.71939
C	2.07094	4.65056	-3.1384
C	-4.1742	5.09625	2.93365
C	3.14813	5.60538	-3.7005
C	4.56632	5.4366	-3.1271
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C	8.76442	-1.6379	0.58809
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C	9.36961	-2.6752	1.25368
C	-10.856	-2.8033	-1.041
N	-12.014	-2.8137	-1.158
C	10.7929	-2.6879	1.39996
N	11.9514	-2.6901	1.5146
C	8.65716	-3.7742	1.82471
N	8.07787	-4.6709	2.29034
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H	-2.9062	0.51333	-0.3257
H	-3.7527	-3.6551	0.36111
H	-1.3427	-4.16	0.41
H	1.0815	1.72841	0.84538
H	0.1491	0.67441	1.88296
H	-0.162	0.04124	-2.371
H	-1.0601	1.37711	-1.6886
H	-1.9523	1.82532	1.2074
H	-1.0641	2.85799	0.09459
H	1.12549	2.60902	-1.2927
H	1.97243	1.28877	-2.089
H	0.28441	3.75449	2.01188
H	-0.6351	2.76009	3.12691
H	0.5655	1.64756	-4.147
H	-0.197	3.02611	-3.3738
H	-1.3721	5.15951	3.03498
H	-1.8157	4.97037	1.35197
H	1.63496	3.63271	-4.982
H	2.79798	2.78143	-3.9888
H	-3.5309	3.28397	1.94476
H	-3.0769	3.35378	3.63386
H	2.31258	4.41488	-2.0931
H	1.10856	5.17915	-3.1078
H	-5.164	4.74227	2.61939
H	-3.9332	5.93483	2.26488
H	3.18322	5.5107	-4.7951
H	2.83788	6.63866	-3.5022
H	5.19532	6.24021	-3.5312
H	4.5302	5.60195	-2.0414
H	-5.1377	6.33756	4.40074
H	-4.6207	4.78306	5.02252
H	-3.2767	6.68639	5.96454
H	-2.2384	5.56565	5.08592
H	-2.709	7.10064	4.34234
H	6.27901	4.09485	-3.0379
H	4.72766	3.26151	-2.921
H	5.28221	3.8787	-4.4821
H	-5.026	0.85496	0.57525
H	-7.616	0.757	0.27005
H	5.02337	0.53061	-1.1157
H	7.61198	0.46552	-0.7977
H	-9.4662	-0.7657	-0.3542
H	9.43704	-0.8737	0.20577

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Symbol	X	Y	Z
C	-5.9026	-3.2086	-0.2753
C	-6.6355	-2.0334	-0.0108
C	-5.9442	-0.8039	0.08859
C	-4.5657	-0.7642	-0.0526
C	-3.8543	-1.9499	-0.3409
C	-4.524	-3.172	-0.4479
C	-3.6215	0.44575	-0.0169
C	-2.2773	-0.2316	-0.3207
C	-2.442	-1.6221	-0.4977
C	-1.0067	0.32462	-0.3585
C	0.12008	-0.4866	-0.6216
C	-0.0722	-1.8699	-0.8196
C	-1.3381	-2.4402	-0.7504
C	-4.0652	1.4468	-1.1286
C	-3.5304	1.10116	1.39643
C	-3.2355	2.72418	-1.3153
C	-4.7779	1.80829	1.94242
C	-3.84	3.64658	-2.3859
C	-4.5097	2.46559	3.30564
C	-3.0835	4.96814	-2.6008
C	-5.7452	3.09492	3.97037
C	-1.6683	4.80913	-3.1806
C	-6.3316	4.29319	3.20802
C	-0.9325	6.13648	-3.473
C	-7.4188	5.09907	3.94217
C	-8.7571	4.37385	4.20142
C	-1.0838	6.69198	-4.9007
C	-2.5016	7.09686	-5.3179
C	-8.8336	3.57678	5.51015
C	1.45296	0.11308	-0.6773
C	-8.0868	-2.0655	0.15521
C	1.79795	1.41604	-0.9711
C	3.19096	1.66221	-0.9315
C	3.94935	0.55341	-0.6044
S	2.89831	-0.828	-0.3361
C	-8.8927	-1.1453	0.81347
C	-10.255	-1.4779	0.78665
C	-10.536	-2.6618	0.10845
S	-9.0485	-3.3596	-0.5187
C	5.38525	0.50111	-0.4802
C	-11.847	-3.1948	-0.0374

C	6.12864	-0.5782	-0.1412
C	-12.286	-4.3408	-0.6557
C	7.57829	-0.6456	-0.0063
C	8.17117	-1.8383	0.45189
C	9.54398	-1.9608	0.61998
C	10.3974	-0.8871	0.31493
C	9.82064	0.30733	-0.16
C	8.44757	0.42329	-0.3092
N	11.7982	-1.0011	0.47354
C	12.5631	0.10997	0.92837
C	12.4553	-2.2323	0.18981
C	13.793	0.41773	0.32588
C	14.5465	1.49786	0.78051
C	14.0822	2.29749	1.82675
C	12.8556	1.9979	2.42269
C	12.1032	0.90885	1.98738
C	13.4352	-2.7311	1.062
C	14.0866	-3.9289	0.77471
C	13.7618	-4.6562	-0.372
C	12.7816	-4.1658	-1.2372
C	12.1377	-2.9599	-0.968
C	-13.683	-4.6505	-0.6603
N	-14.821	-4.8943	-0.6591
C	-11.422	-5.2708	-1.3106
N	-10.721	-6.0319	-1.8452
H	-6.4198	-4.1615	-0.3336
H	-6.5095	0.10871	0.23977
H	-3.9811	-4.0877	-0.6619
H	-0.8565	1.37855	-0.1527
H	0.78419	-2.4996	-1.0407
H	-1.4584	-3.5103	-0.8933
H	-5.1048	1.73326	-0.9257
H	-4.089	0.89804	-2.0783
H	-3.226	0.32104	2.10509
H	-2.7031	1.82117	1.37615
H	-2.2119	2.45742	-1.597
H	-3.1668	3.27902	-0.37
H	-5.1257	2.56656	1.23083
H	-5.5958	1.08613	2.05676
H	-4.8772	3.87697	-2.1066
H	-3.8987	3.10322	-3.3397
H	-4.0924	1.70933	3.98379
H	-3.7305	3.2327	3.19138
H	-3.6814	5.60572	-3.2613

H	-3.0172	5.5071	-1.6446
H	-5.4687	3.42008	4.98233
H	-6.5111	2.31917	4.09926
H	-1.0661	4.22411	-2.4747
H	-1.7151	4.20709	-4.0997
H	-6.7393	3.95747	2.24473
H	-5.5089	4.97977	2.96186
H	0.1399	5.99146	-3.2924
H	-1.2548	6.89831	-2.7488
H	-7.0173	5.47128	4.89549
H	-7.6227	5.99154	3.33717
H	-9.5599	5.12154	4.21557
H	-8.9822	3.71503	3.35089
H	-0.4257	7.56548	-4.9966
H	-0.6985	5.94741	-5.6108
H	-2.4977	7.55929	-6.3106
H	-3.1766	6.23647	-5.3642
H	-2.9319	7.82135	-4.6169
H	-9.8242	3.12702	5.6376
H	-8.0971	2.76975	5.55224
H	-8.6548	4.22853	6.37285
H	1.06704	2.16979	-1.2403
H	3.63919	2.62647	-1.1452
H	-8.4981	-0.2767	1.32564
H	-11.033	-0.8867	1.25851
H	5.8761	1.45193	-0.6792
H	-12.624	-2.5863	0.41971
H	5.60928	-1.513	0.06859
H	7.53305	-2.6826	0.70029
H	9.96326	-2.8894	0.99114
H	10.4632	1.14232	-0.417
H	8.04631	1.35758	-0.6897
H	14.1509	-0.193	-0.4961
H	15.4961	1.72248	0.30335
H	14.6689	3.14239	2.17375
H	12.4857	2.6057	3.24346
H	11.1577	0.67049	2.4629
H	13.6813	-2.1751	1.96044
H	14.8426	-4.3012	1.46001
H	14.2663	-5.5925	-0.5891
H	12.5247	-4.7166	-2.1375
H	11.3873	-2.5752	-1.6505