# Electronic Supplementary Information

## Generating a three-dimensional non-fullerene electron acceptor by combining inexpensive spiro[fluorene-9,9'-xanthene] and cyanopyridone functionalities

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**DFT details**:

The Gaussian 09 ab initio/DFT quantum chemical simulation package was employed to acquire results represented in the present work.[S1] The geometry optimization of **A1** with truncated alkyl chains was carried out at the B3LYP/6-31G(d) level of theory. To ensure structures to be real, frequency calculations were carried out. Furthermore, the geometry of **A1** obtained at the B3LYP/6-31G(d) level was subjected to the time-dependent density functional theory (TD-DFT) studies for the observation of absorption properties (see Table S1). From the TD-DFT results it was seen that **A1** shows absorption bands at 539 nm and 512 nm. The frontier molecular orbitals (FMOs) were generated using Avogadro[S2,S3] and are depicted in Fig. S1. During the transition from HOMO to LUMO and HOMO-1 to LUMO+1, the electron density flows from the central part of molecule to the terminals.

**Table S1**: Calculated TD-DFT excitation properties of **A1**

| **Molecule** | **Excitation Energy (eV)** | **Excitation Wavelength (nm)** | **Oscillator Strength (f)** | **Excitations** | **% contribution for transition** |
|---|---|---|---|---|---|
| **A1** | 2.3015 | 539 | 1.6615 | 351 (H) → 352 (L) | 95% |
| | | | | 350 (H-1) → 352 (L) | 4% |
| | 2.4224 | 512 | 0.7807 | 350 (H-1) → 353 (L+1) | 95% |

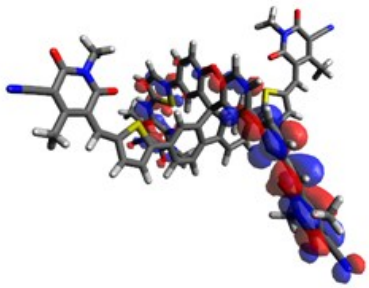
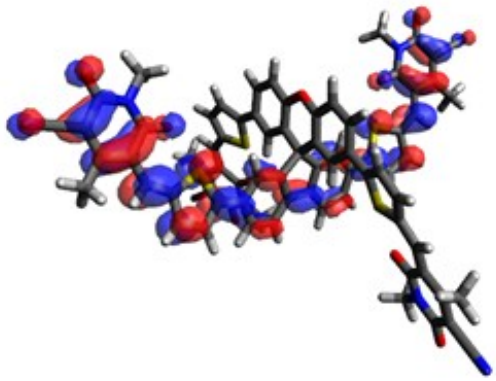
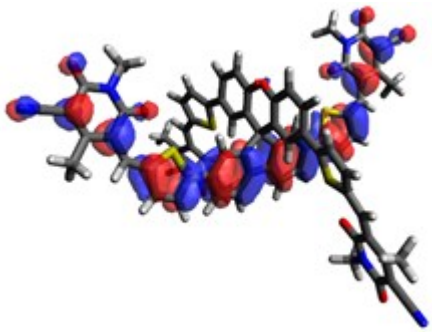
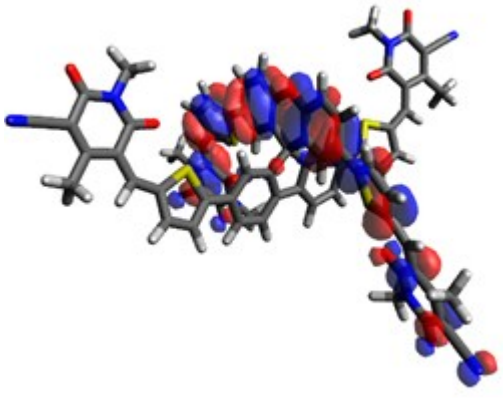
| **A1** | | eV | |
|---|---|---|---|
| 353 | L+1 | -3.3307 |  |
| 352 | L | -3.45179 |  |
| 351 | H | -5.99961 |  |
| 350 | H-1 | -6.01159 |  |

**Fig. S1** Frontier molecular orbitals of **A1** with energy levels in eV.

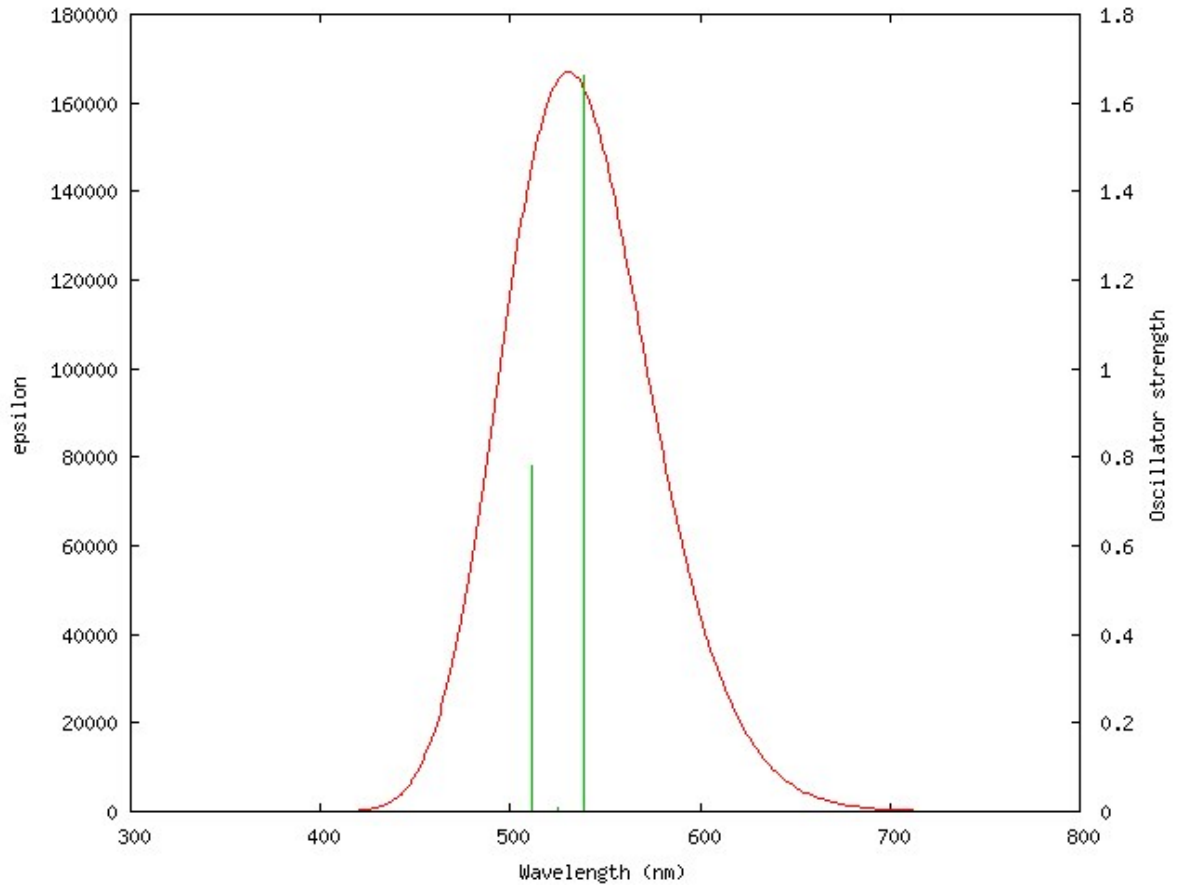



**Fig. S2** The computed absorption spectrum of **A1** showing transition peaks at 539 nm and 512 nm.

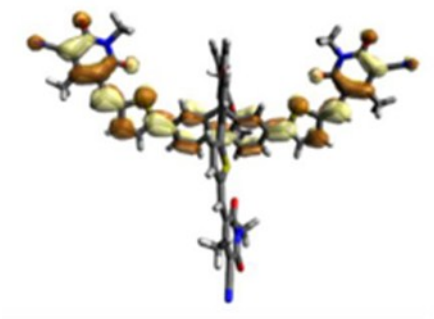
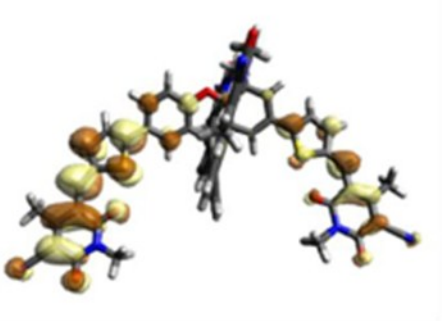
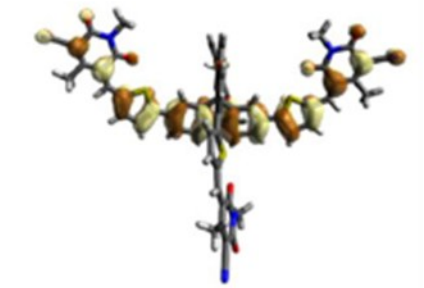
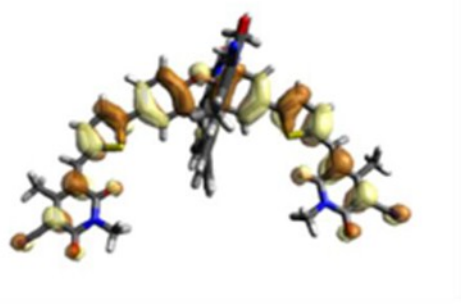
| | Dominant NTO pair corresponding to excitation energy 2.3015 eV | Dominant NTO pair corresponding to excitation energy 2.4224 eV |
|---|---|---|
| Electron |  |  |
| Hole |  |  |

**Fig. S3** The dominant natural transition orbital pair for the selected excited singlet states.

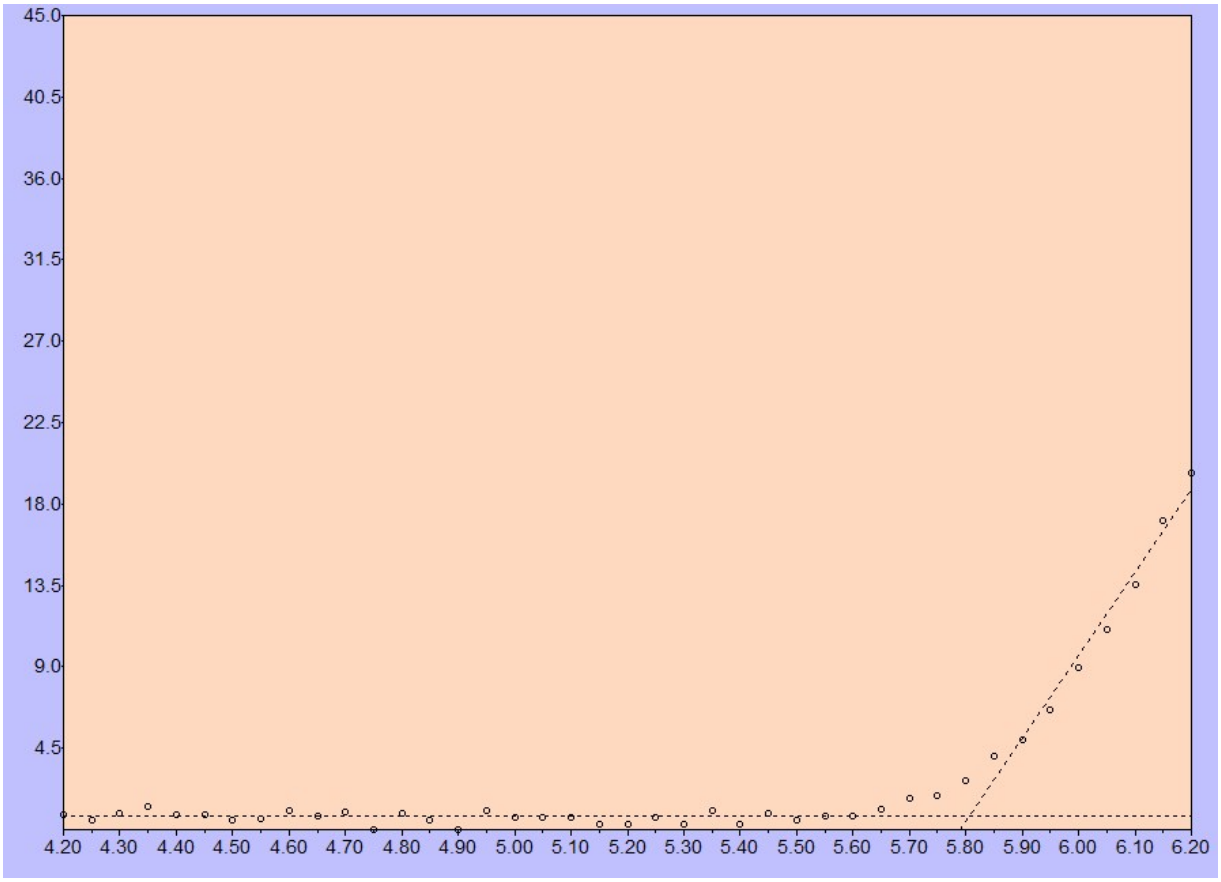



**Fig. S4** PESA spectrum of thin film of **A1**. The dashed-lines show the fits to extract ionisation potential (-5.81 eV) that corresponds to the HOMO energy level. [The PESA measurement was conducted using a Riken Keiki AC-2 PESA spectrometer with a power number setting of 0.5. Samples for PESA were prepared on ITO cleaned glass substrates and were run using the UV intensity of 10 nW (incident photon energy range = 4.2 eV to 6.2 eV)].

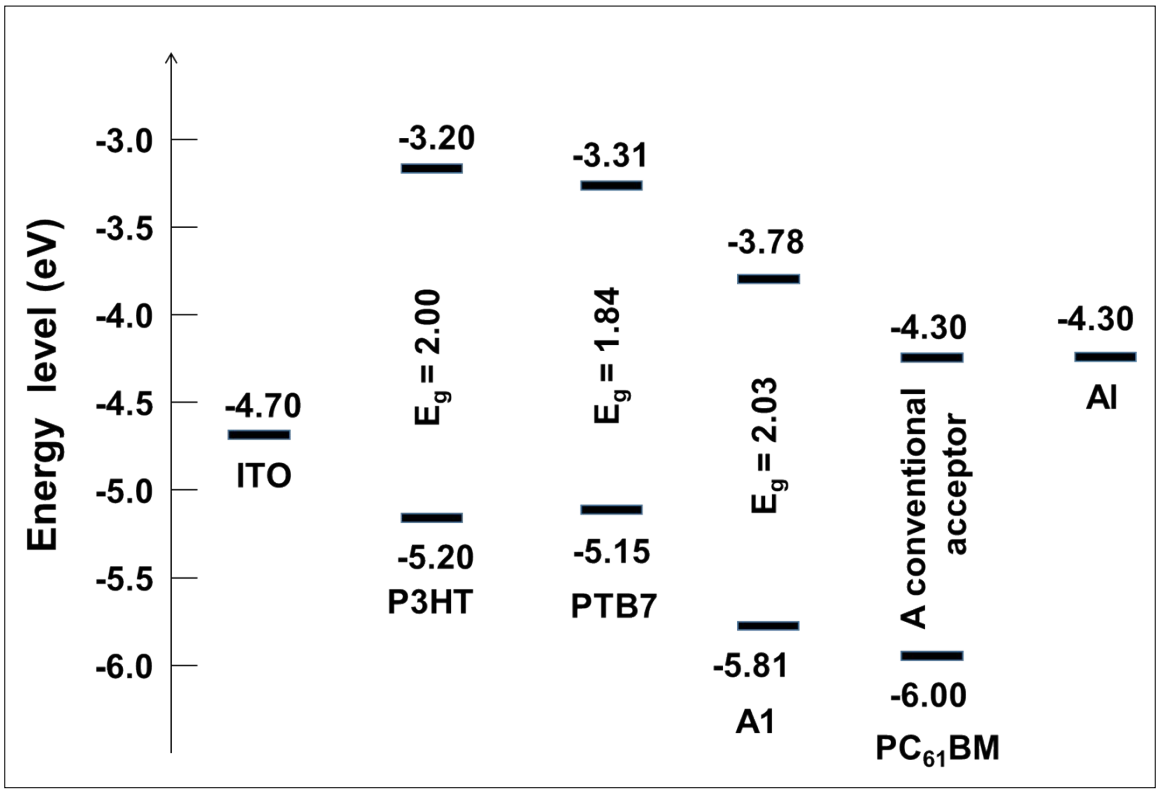



**Fig. S5** Energy level diagram showing alignments of different components of a BHJ device architecture. **Note**: The LUMO energy level was calculated using the method described in P. I. Djurovich *et al.*, *Org. Elect.*, 2009, 10, 515.

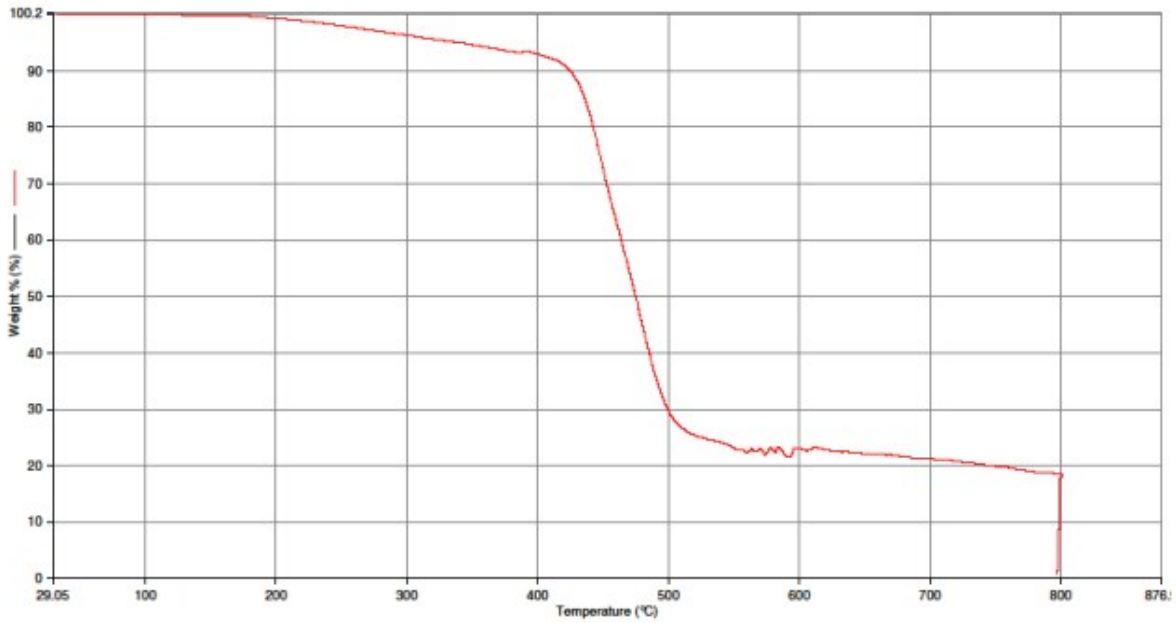



**Fig. S6** TGA curve showing thermal stability of **A1**.

**Table S2**. Photovoltaic cell parameters for **A1** blends

| Acceptor | Donor | Testing conditions (D: A)[a] | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | *FF* | Best PCE (%) | Average PCE (%) (± std dev)[c] |
|---|---|---|---|---|---|---|---|
| **A1** | P3HT | 1: 1.2 (annealed) | 1.01 | 9.56 | 0.61 | 5.84 | 5.80 (± 0.09) |
| **A1** | P3HT | 1: 1.2 (no annealing) | 0.88 | 8.01 | 0.58 | 4.13 | 4.09 (± 0.08) |
| **A1** | PTB7 | 1: 1.2 (annealed) | 1.04 | 11.01 | 0.63 | 7.21 | 7.18 (± 0.10) |
| **A1** | PTB7 | 1: 1.2 (no annealing) | 0.84 | 9.38 | 0.57 | 4.50 | 4.47 (± 0.06) |
| $PC_{61}BM$ | P3HT | 1: 1.2[b] | 0.57 | 8.28 | 0.64 | 3.03 | 2.99 (± 0.06) |

[a] BHJ devices with specified weight ratio. Device structure was ITO/PEDOT: PSS (38 nm)/active layer/Ca (20 nm)/Al (100 nm) with an active layer thickness of ~70 nm

[b] A standard P3HT: $PC_{61}BM$ device afforded 3.02% efficiency when tested under alike annealing conditions

[c] A total of ten devices were made for each combination; cell area = 0.1 cm$^2$.

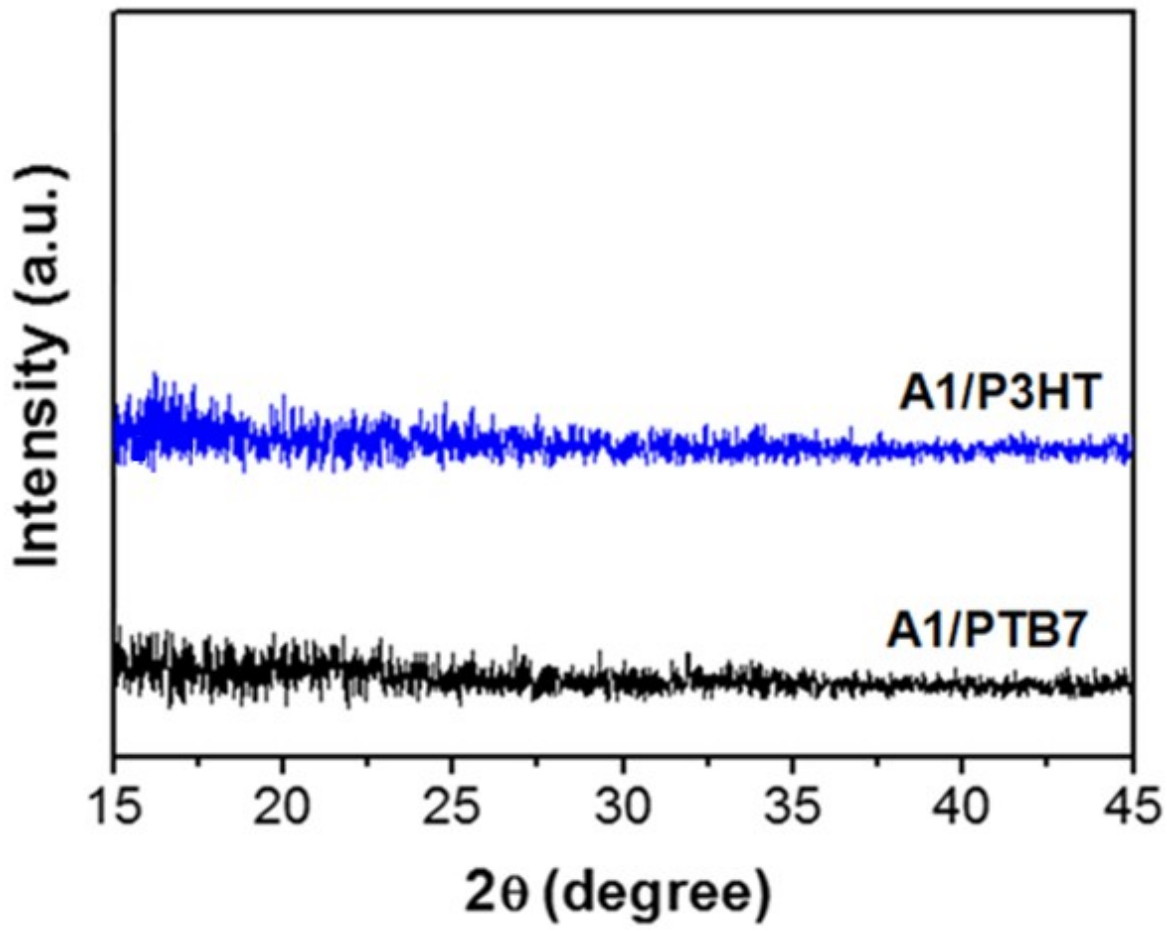



**Fig. S7** XRD spectra of the blend films of **A1** with PTB7 and P3HT showing the surfaces to be amorphous.

**References**:

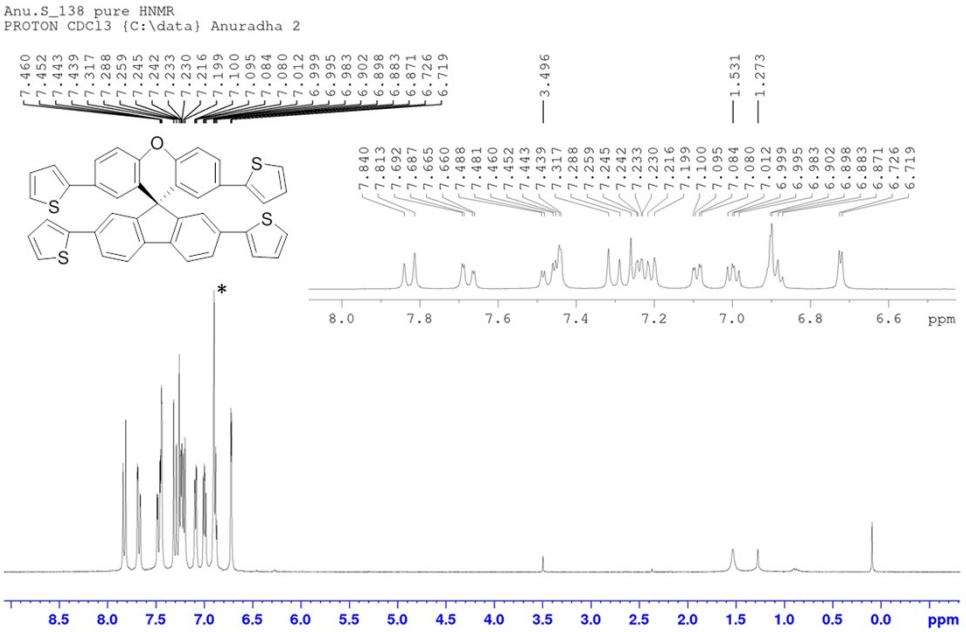
S1 M. J. Frisch, *et al.*, *Gaussian 09*, *Revision C.01*, Gaussian Inc., Wallingford CT, 2009.

S2 Avogadro: an open-source molecular builder and visualization tool, Version 1.1.0. http://avogadro.openmolecules.net/

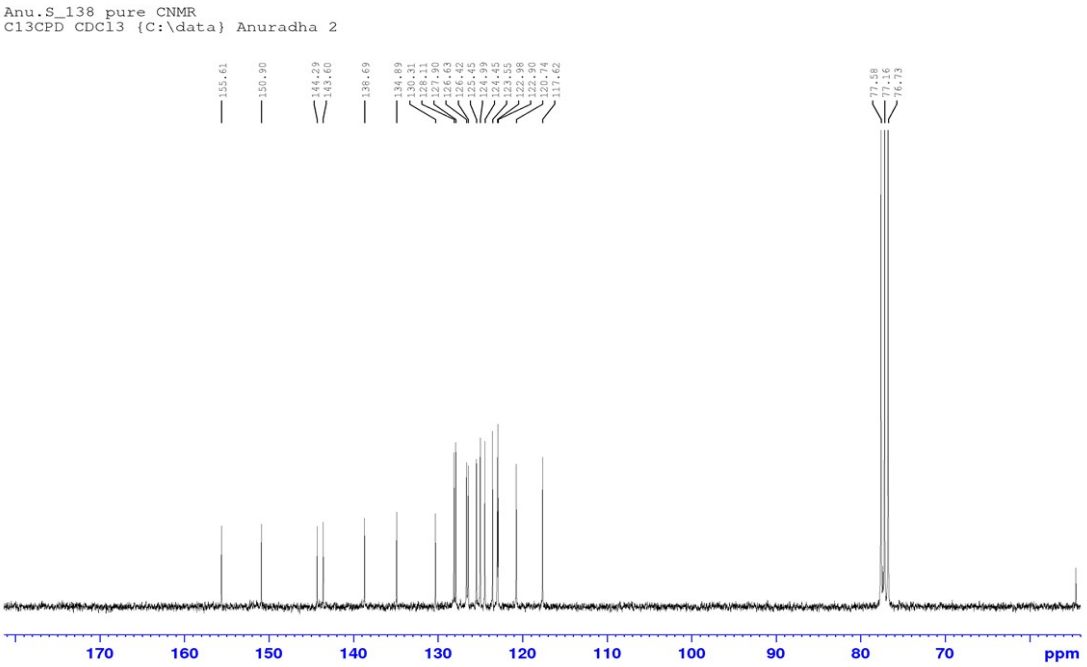
S3 M. D. Hanwell, *et al.*, *J. Cheminf.*, 2012, **4**, 17.

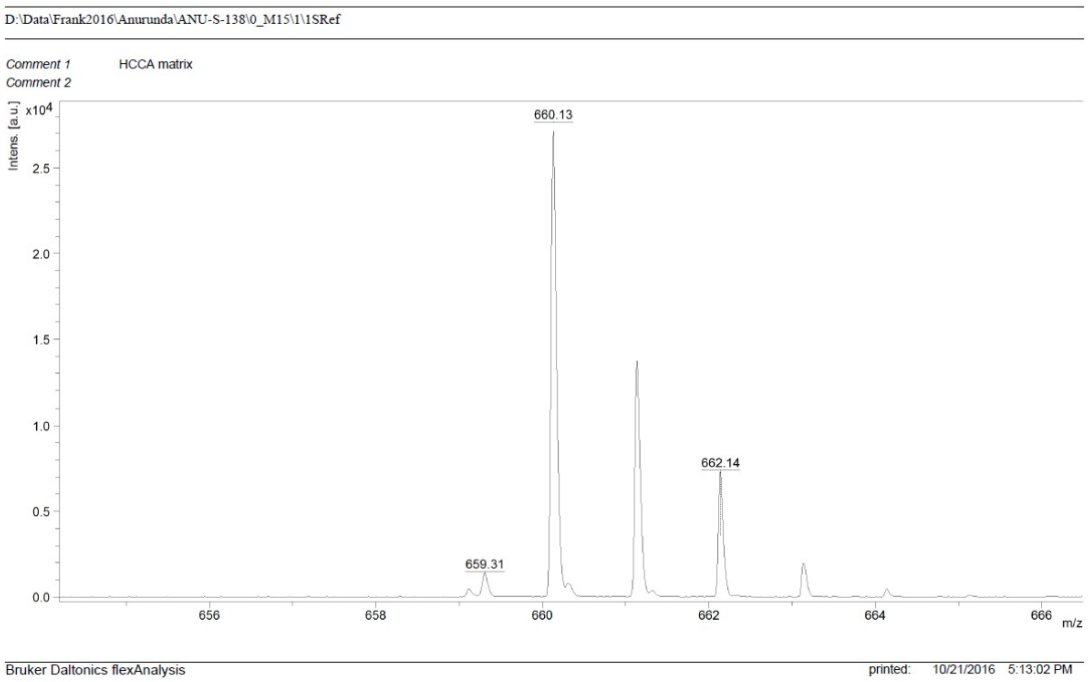
# Experimental Spectra

## Compound 1:




* $CDCl_3$

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HCCA matrix
Comment 2
Intens. [a.u.]
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662.14
659.31
m/z
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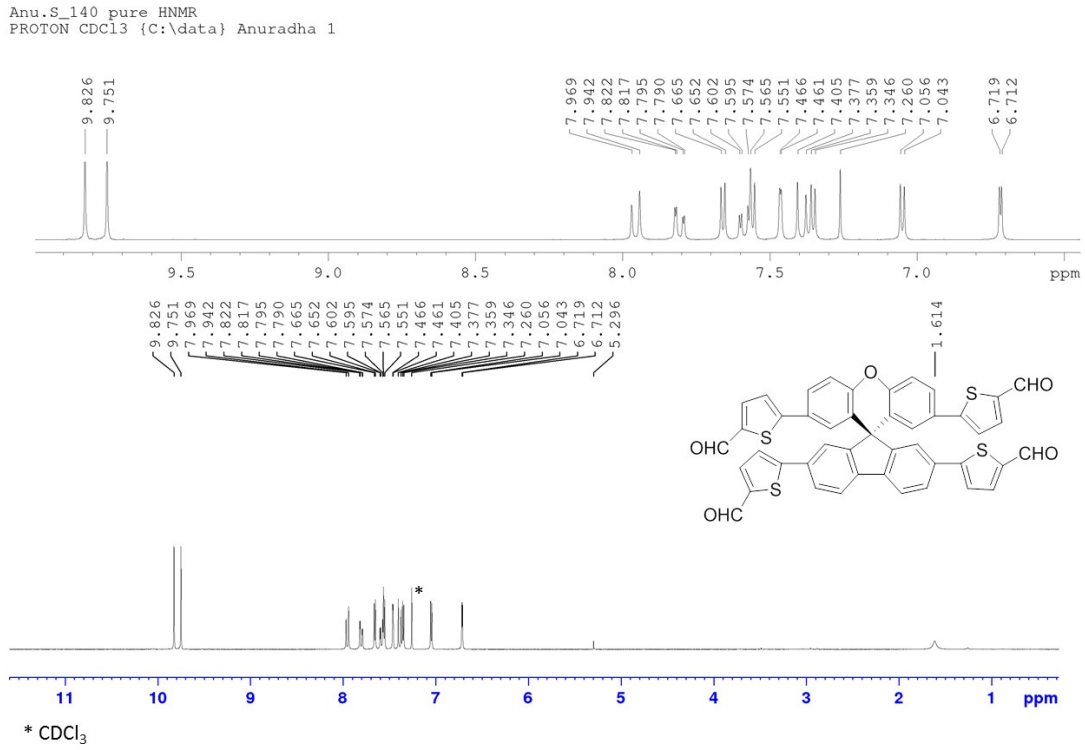
Anu.S_140 pure HNMR
PROTON CDCl3 {C:\data} Anuradha 1
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9.751
7.969
7.942
7.822
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7.795
7.790
7.665
7.652
7.602
7.595
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7.565
7.551
7.466
7.461
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7.359
7.346
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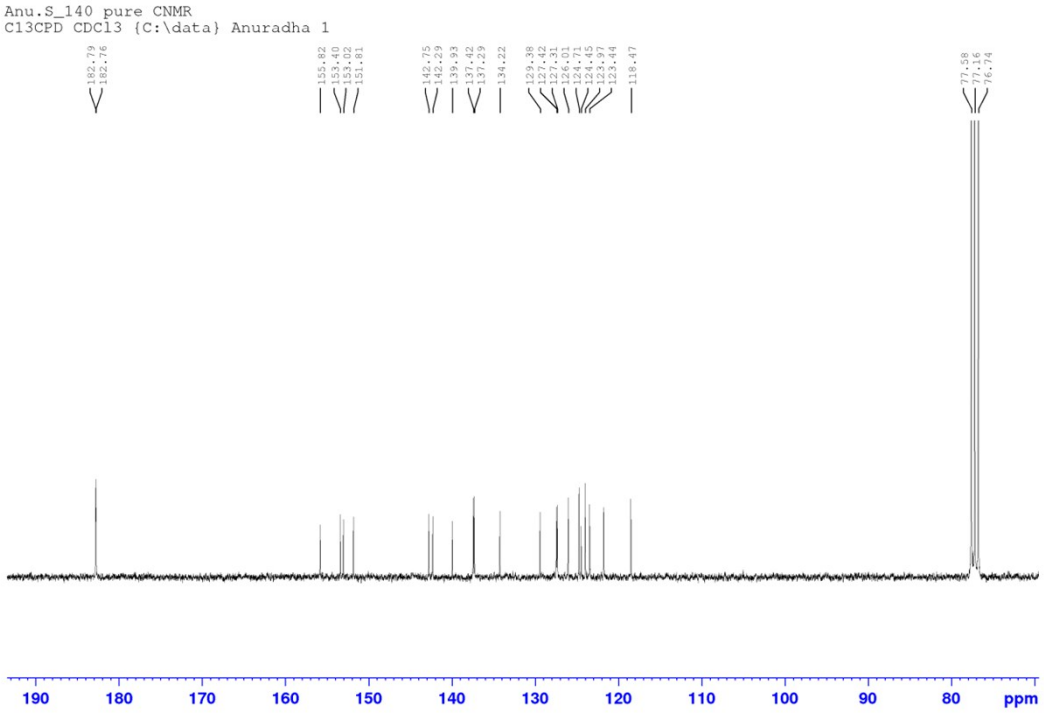
ppm
OHC
CHO
S
O
* CDCl3

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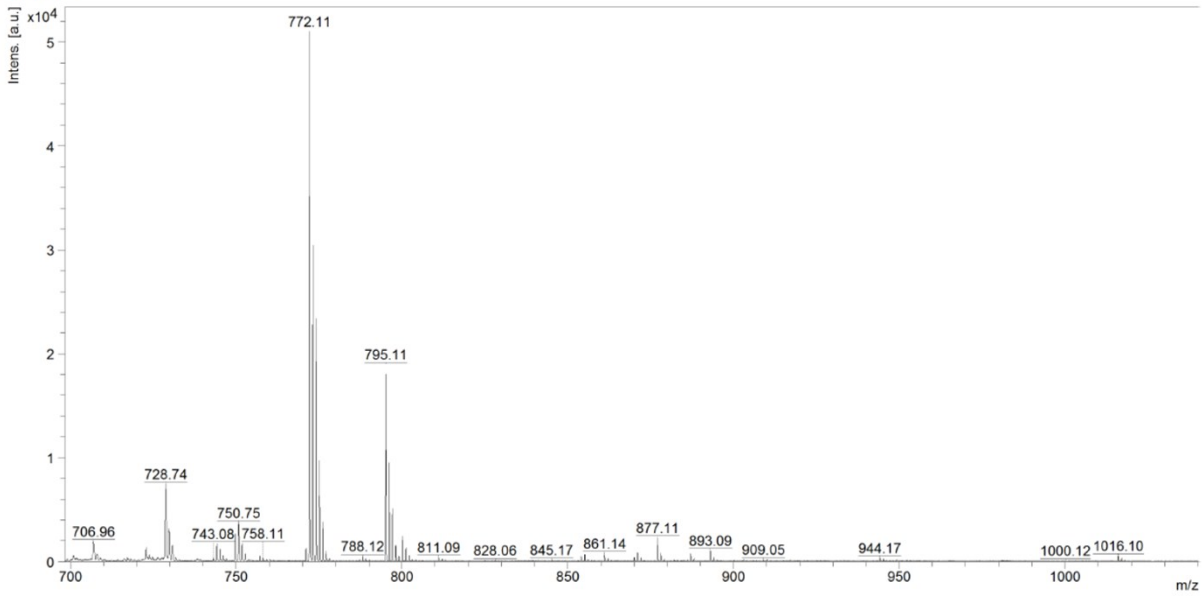
*Comment 1* HCCA matrix

*Comment 2*

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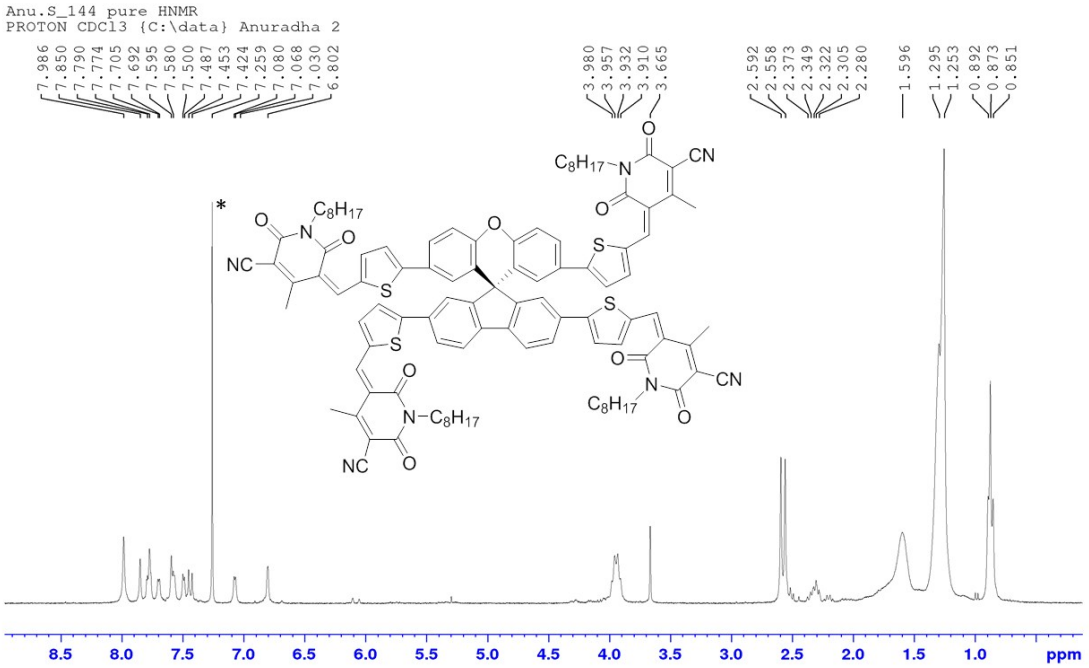
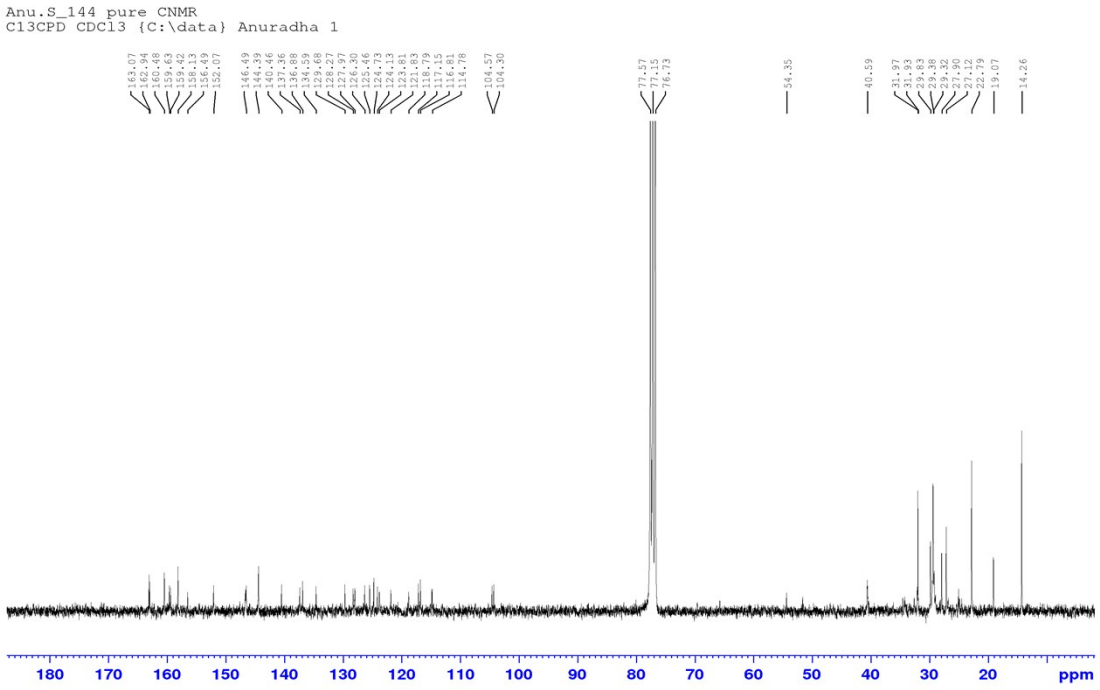
**Compound A1**:




*$CDCl_3$



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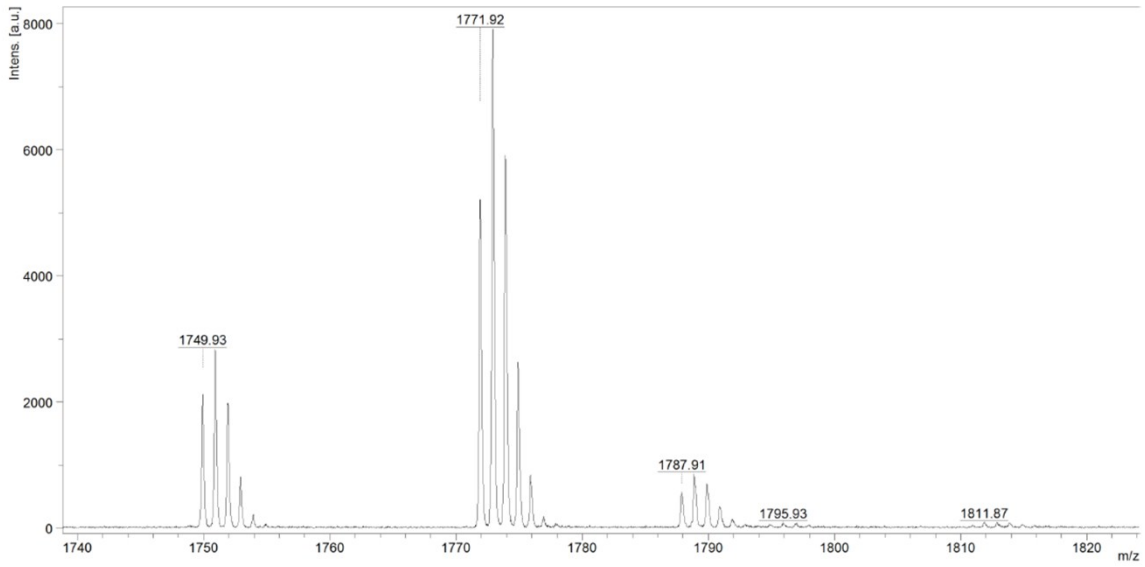
*Comment 1* HCCA matrix

*Comment 2*

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