

**Electronic Supplementary Information (ESI)**

**Pyrene affixed triazoles: A new class of molecular semiconductors for robust, non-volatile resistive memory devices**

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**1. Experimental procedure- materials and methods:**

All chemicals were purchased from Sigma-Aldrich, Merck, Spectrochem Pvt. Ltd. and Alfa Aesar and used without further purification. All the solvents were purchased from Sigma-Aldrich, Merck, Spectrochem Pvt. Ltd. All the solvents were purified, degassed with argon and stored over activated molecular sieves (4 Å).<sup>1</sup> The FTIR spectra were recorded using a Perkin–Elmer Spectrum RX1 spectrophotometer. A KBr pellet was made by taking roughly 1 mg of the sample with 10 mg of KBr. NMR analysis of **1-DPY** and **2-DPY** were carried out with JEOL 400 MHz NMR in CDCl<sub>3</sub> at 25 °C. Coupling constants (J) are reported in Hertz (Hz). Coupling patterns are indicated as: s (singlet), d (doublet), t (triplet), or m (multiplet). The elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. HR-MS experiment were conducted using maXis impact BRUKER ESI-MS instrument and TGA was performed using a Mettler Toledo TGA/SDTA 851 thermogravimetric analyzer at a heating rate of 10°C min<sup>-1</sup> with a sample weight of ca 2–3 mg in nitrogen atmosphere. All experiments were carried out at room temperature (25 ± 1°C), unless otherwise mentioned.

## 2. Synthetic procedure and characterisation data:

**General Procedure:** In a 15 mL Schlenk tube, *N*-tosylhydrazone **1** (0.5 mmol, 2 equiv) was dissolved in 1.0 mL benzene. Next, B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst (6.4 mg, 0.0125 mmol, 5 mol %) dissolved in 0.5 mL of benzene was added at room temperature with continuous stirring under argon. After 10 minutes, 0.5 mL benzene solution of aniline **2** (0.25 mmol, 1 equiv) was slowly added to the mixture and the tube was sealed, heated at 80 °C for 48 h. Upon completion, the solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography to afford 1, 2, 4-triazoles **1-DPY** and **2-DPY**.

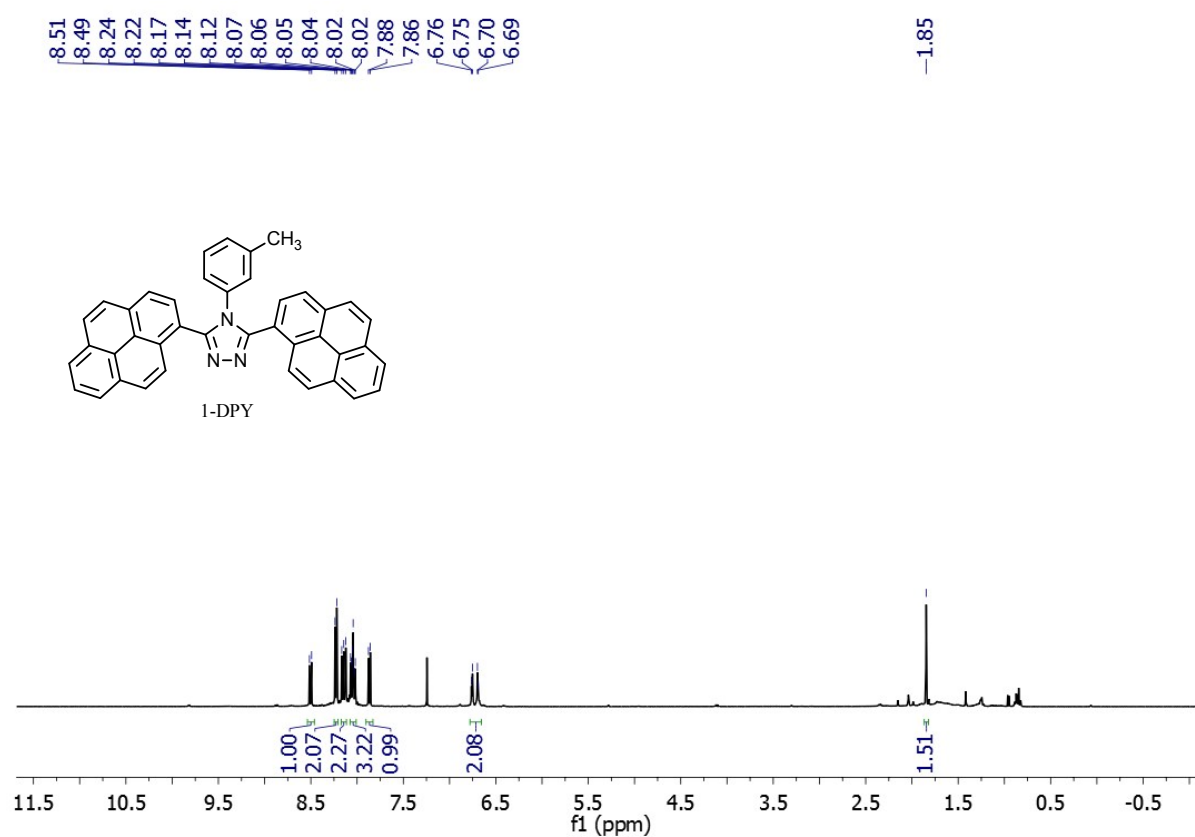
**3,5-Di(pyren-1-yl)-4-(*m*-tolyl)-4*H*-1,2,4-triazole (1-DPY):** Analytical TLC on silica gel, 1:1 ethyl acetate/hexane  $R_f = 0.20$ ; Yield 98.3 mg (0.175 mmol, 70%); <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 8.50 (d,  $J = 9.2$  Hz, 2H), 8.23 (d,  $J = 7.6$  Hz, 4H), 8.17 – 8.12 (m, 4H), 8.07 – 8.02 (m, 6H), 7.87 (d,  $J = 7.8$  Hz, 2H), 6.76 – 6.69 (m, 4H), 1.85 (s, 3H); <sup>13</sup>C NMR (101 MHz, CHLOROFORM-D) δ 154.3, 139.3, 134.4, 132.3, 131.1, 130.8, 129.5, 128.9, 128.8, 128.2, 127.3, 127.2, 126.4, 125.9, 125.8, 124.8, 124.7, 1234.3, 124.1, 124.0, 121.2, 20.9; Elemental Analysis. calcd. (%) for C<sub>41</sub>H<sub>25</sub>N<sub>3</sub>: C 87.99, H 4.50, N 7.51 Found: C 88.25, H 4.43, N 7.32. **HRMS (ESI<sup>+</sup>):** calcd for C<sub>41</sub>H<sub>26</sub>N<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> 560.2127, found 560.2106.

**Methyl 3-(3,5-di(pyren-1-yl)-4*H*-1,2,4-triazol-4-yl)benzoate (2-DPY):** Analytical TLC on silica gel, 1:1 ethyl acetate/hexane  $R_f = 0.20$ ; Yield 72.4 mg (0.120 mmol, 48%); <sup>1</sup>H NMR (400 MHz, CHLOROFORM-D) δ 8.43 (d,  $J = 9.2$  Hz, 2H), 8.24 (d,  $J = 7.6$  Hz, 4H), 8.18 – 8.14 (m, 4H), 8.10 –

8.03 (m, 6H), 7.92 (d,  $J = 7.8$  Hz, 2H), 7.60 – 7.58 (m, 2H), 7.05-7.03 (m, 1H), 6.93 (t,  $J = 7.9$  Hz, 1H), 3.50 (s, 3H);  $^{13}\text{C}$  NMR (126 MHz, CHLOROFORM-D)  $\delta$  165.0, 132.5, 131.1, 130.9, 130.82, 130.76, 129.6, 129.3, 129.0, 128.9, 128.2, 127.8, 127.2, 126.4, 126.0, 125.9, 124.7, 124.6, 124.3, 120.8, 52.1; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1725 (C=O stretching), 1083–717 (Ar–H stretching); Elemental Analysis. calcd. (%) for  $\text{C}_{42}\text{H}_{25}\text{N}_3\text{O}_2$ : C 83.56, H 4.17, N 6.96 Found: C 84.24, H 4.07, N 6.77. **HRMS (ESI<sup>+</sup>)**: calcd for  $\text{C}_{42}\text{H}_{26}\text{N}_3\text{O}_2^+ [\text{M}+\text{H}]^+$  604.2025, found 604.2021.

### Characterization data:

#### NMR data:



**Figure S1.**  $^1\text{H}$  NMR of **1-DPY** in CHLOROFORM-D ( $\text{CDCl}_3$ ).

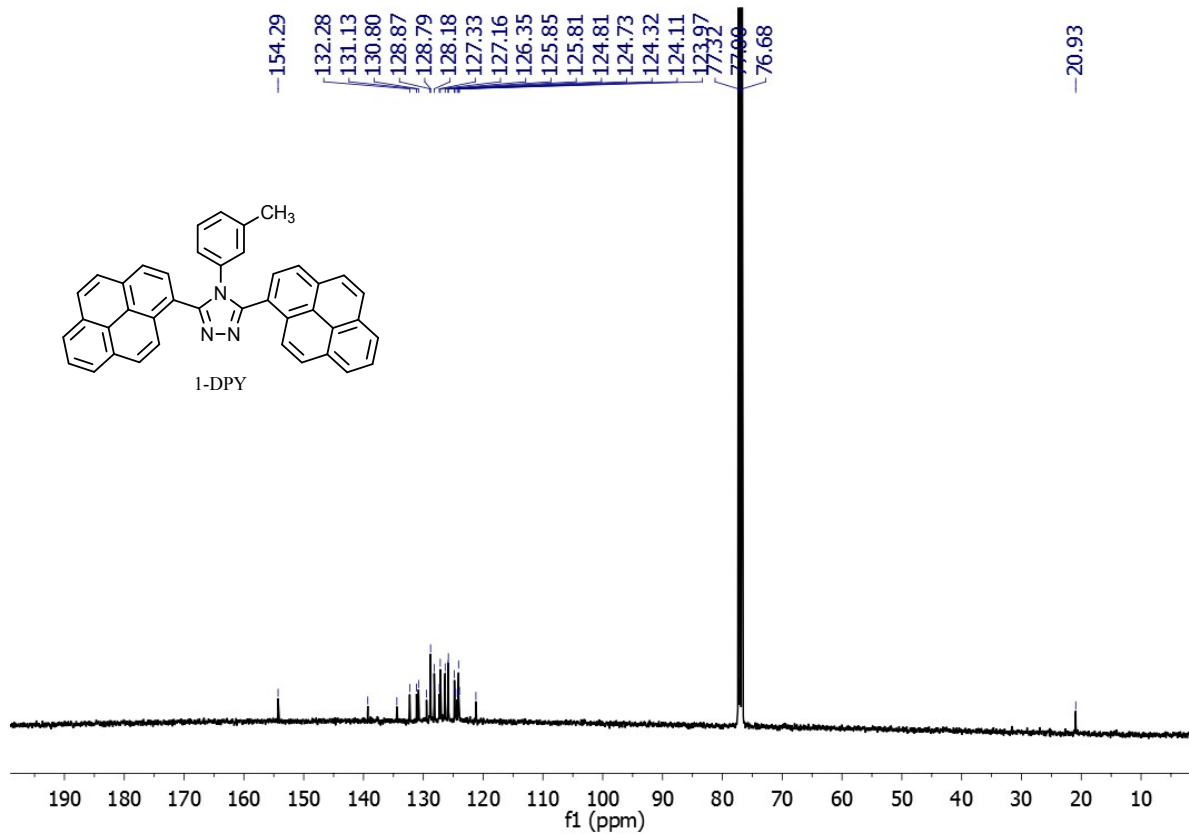


Figure S2. <sup>13</sup>C NMR of 1-DPY in CHLOROFORM-D (CDCl<sub>3</sub>).

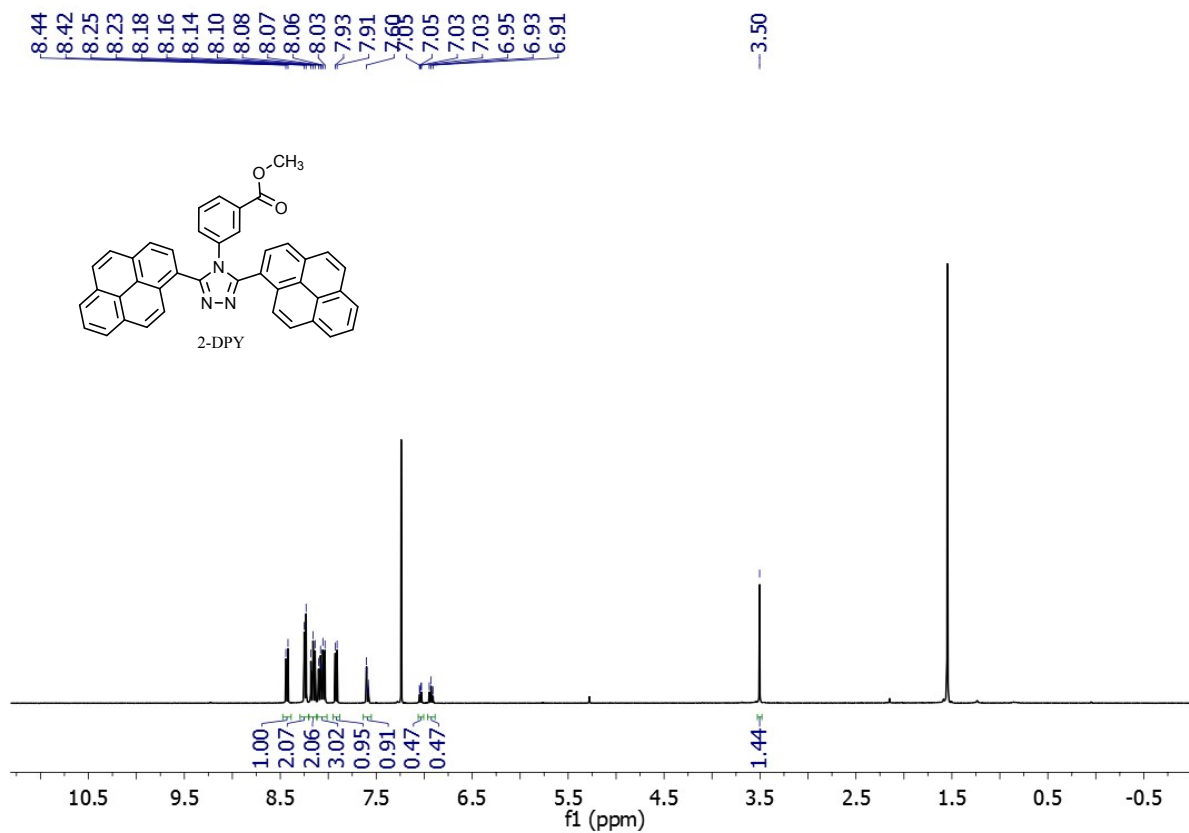


Figure S3. <sup>1</sup>H NMR of 2-DPY in CHLOROFORM-D (CDCl<sub>3</sub>).

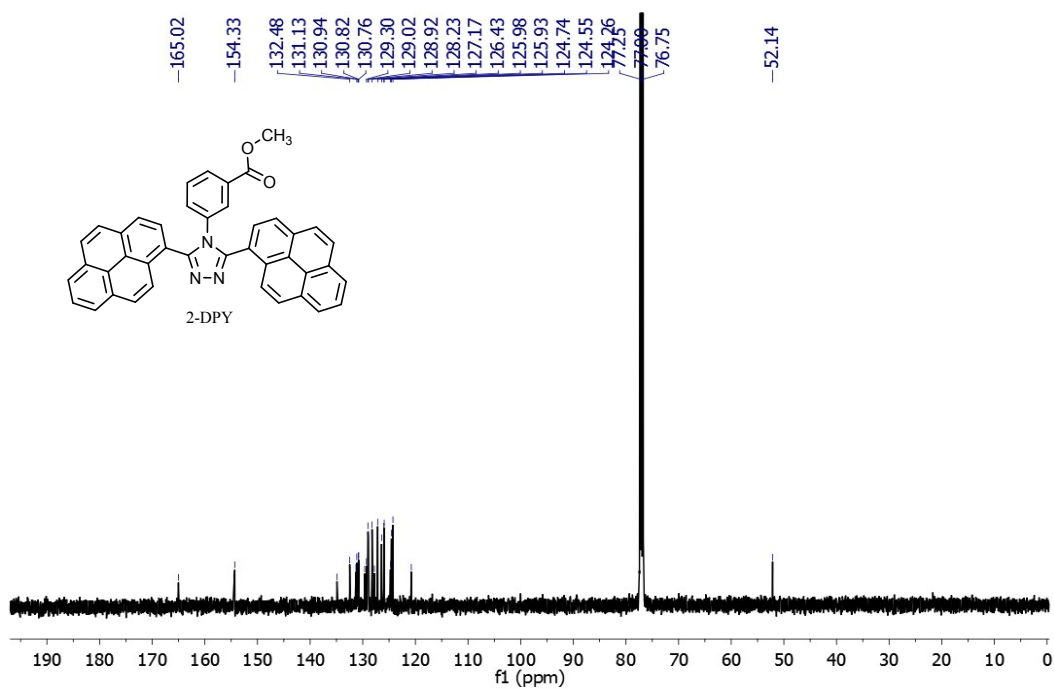


Figure S4. <sup>13</sup>C NMR of 2-DPY in CHLOROFORM-D (CDCl<sub>3</sub>).

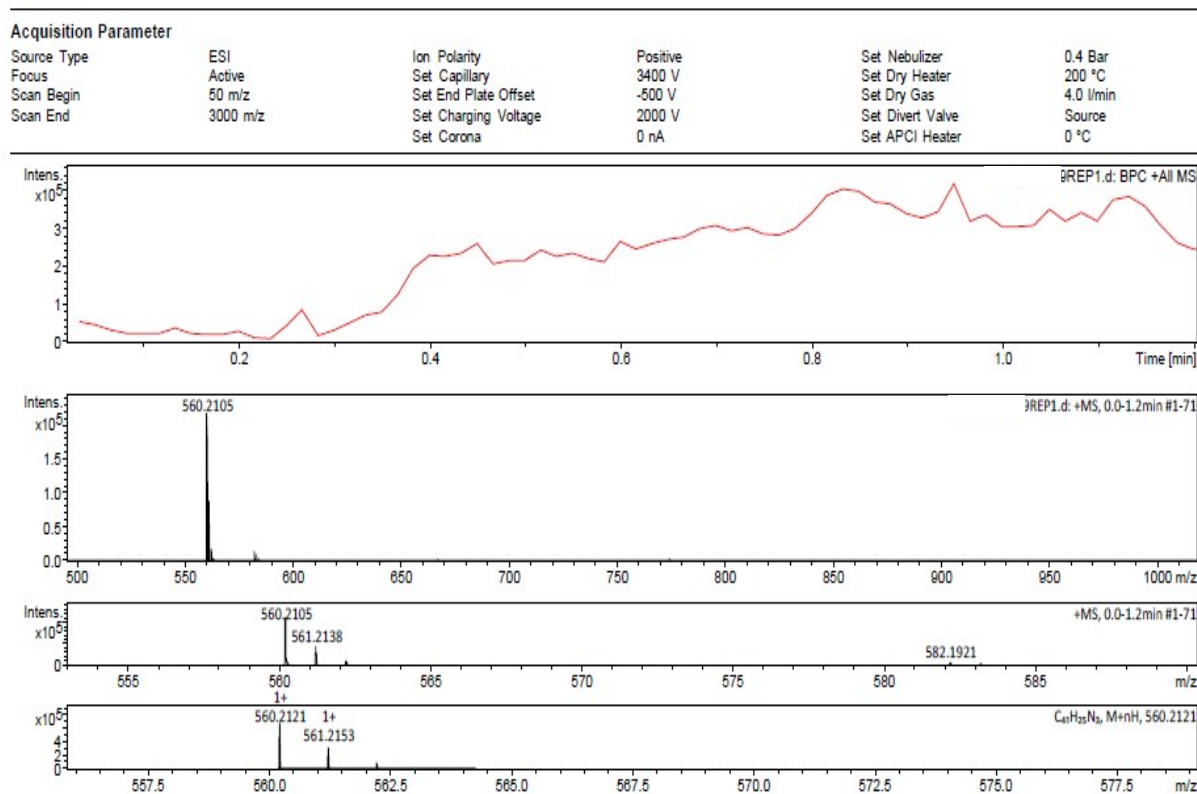
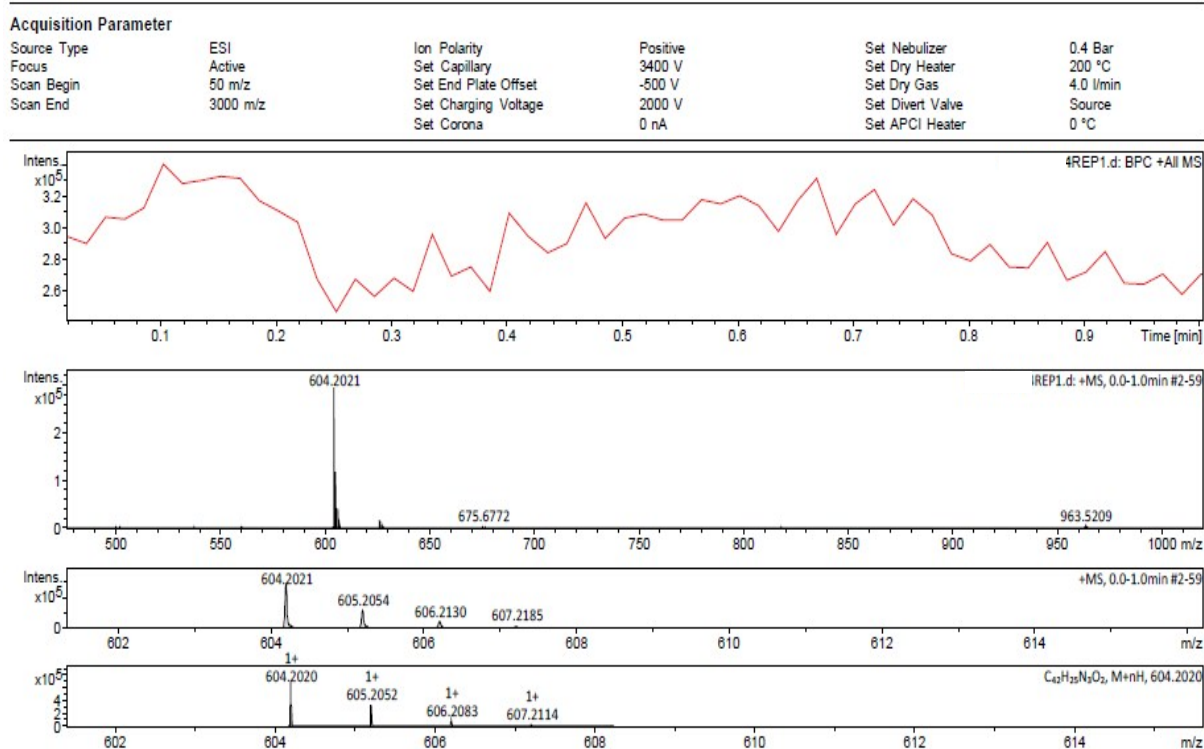
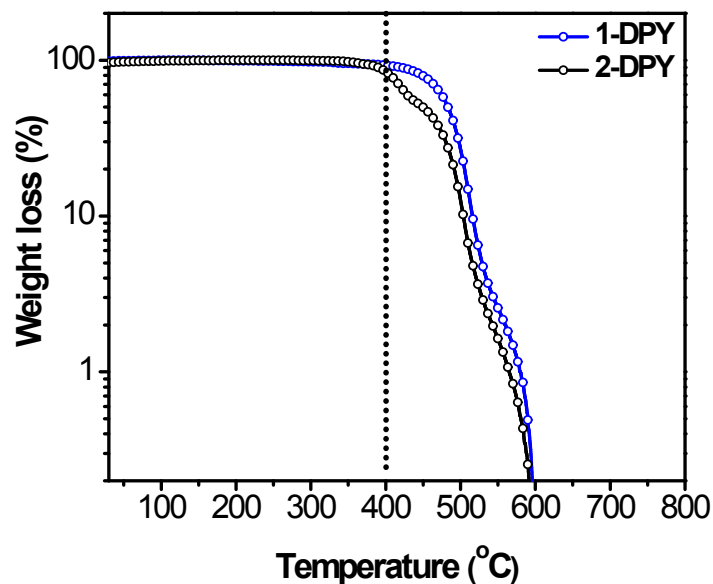


Figure S5. HR-MS spectrum of 1-DPY.



**Figure S6.** HR-MS spectrum of **2-DPY**.



**Figure S7.** TGA curves of **1-DPY** and **2-DPY** by heating the sample to 600°C at a rate of 10°C min<sup>-1</sup> under nitrogen atmosphere.

### 3. Optical and electrochemical properties:

UV-VIS absorption spectra were recorded with a PerkinElmer Lambda 35 spectrophotometer. Film state absorption spectra were recorded with PerkinElmer Lambda 25 spectrophotometer. Film is prepared by spin coating (1500 rpm, 60 sec) a solution (10 mM) of **1-DPY** and **2-DPY** on top of pre-cleaned quartz plate. Emission spectra were recorded using Fluoromax-4, Horiba Jobin Yvon spectrofluorimeter.

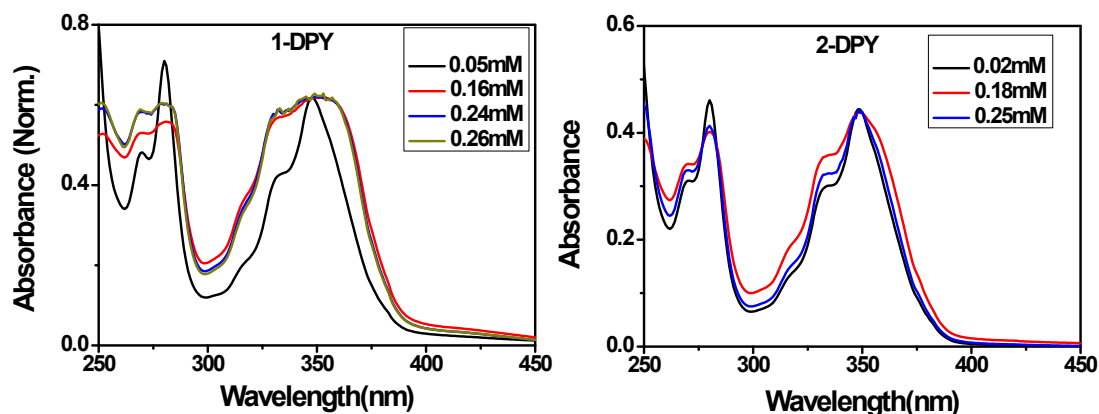


Figure S8. Concentration dependant absorption spectra of **1-DPY** and **2-DPY** in chloroform.

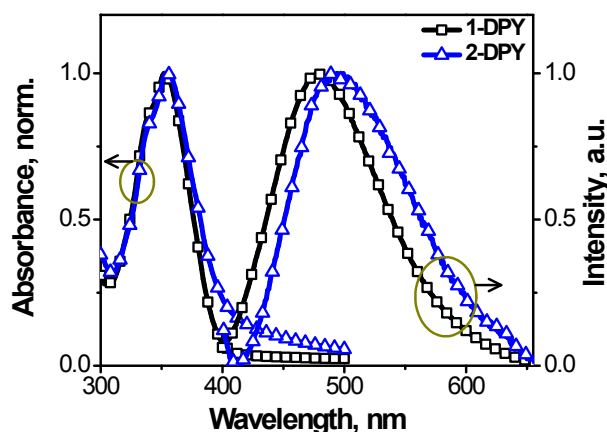


Figure S9. Film state absorption and fluorescence spectra of **1-DPY** and **2-DPY**.

**The cyclic voltammogram measurement:** Cyclic Voltammetry were recorded with CHI604D instrument. Cyclic Voltammetry for liquid state samples were determined at room temperature using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dry acetonitrile solvent under argon atmosphere with a scan rate of 100 mV/s, where gold wire used as the working electrode; platinum wire as the counter electrode; Ag/AgCl (saturated KCl) as the reference electrode. HOMO and LUMO energy levels of compound were calculated according to the inner reference ferrocene redox couple versus Ag/Ag<sup>+</sup> in acetonitrile by using the formula  $E_{\text{HOMO}} = - [ E_{\text{ox}}^{\text{onset}} + 4.8 - E_{\text{Fc}}^{1/2} ] .^2$



#### 4. Single crystal XRD Experiment:

The XRD measurements were recorded in Supernova model having Cu K $\alpha$  = 1.54059 Å radiation. The radiation probe was X-ray and radiation source was micro-focus sealed X-ray tube. The single crystal XRD data of **1-DPY** is shown below,

Molecular formula	C <sub>41</sub> H <sub>25</sub> N <sub>3</sub>
Formula weight	559.64
Temperature	100 K
Crystal system	Monoclinic
Space Group	C c(9)
Hall Group	C -2yc
Cell length, a	12.1102(8)Å
Cell length, b	10.0420(5)Å
Cell length, c	22.5616(11)Å
Cell Angle, $\alpha$	90°
Cell Angle, $\beta$	96.230(5)°
Cell Angle, $\gamma$	90°
Cell Volume	2727.53Å <sup>3</sup>
Density (CCDC)	1.363 g cm <sup>-3</sup>
Colour	Orange
Z, Z'	Z: 4 Z': 0
R-Factor(%)	5.28
Packing Coefficient	0.705609
h, k, l max	15,13,29
Nref	6318[ 3162]
Tmin, Tmax	0.935,0.961
Single Crystal size	79.6 nm

**Table S1.** Crystallographic data of **1-DPY** obtained from single crystal XRD experiment.

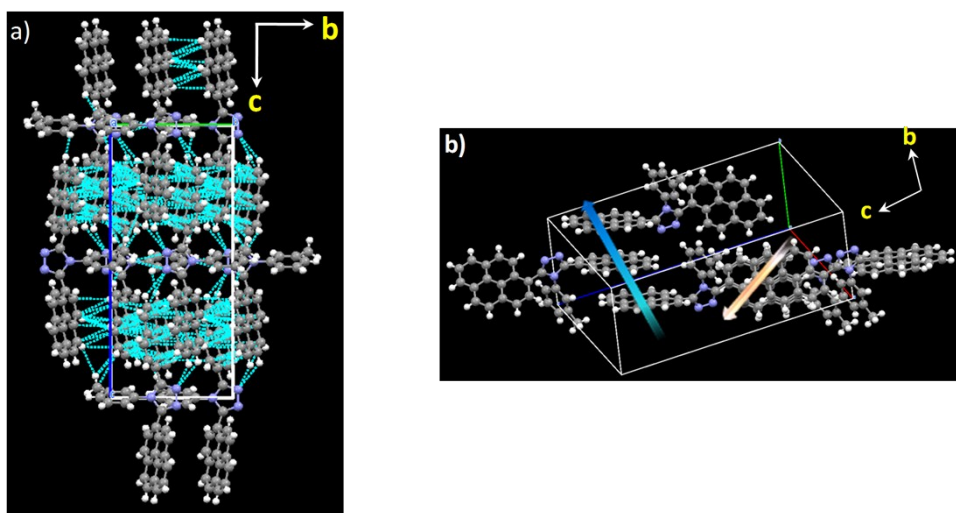
#### Fractional atomic coordinates of 1-DPY-

Number	Label	Xfrac + ESD	Yfrac + ESD	Zfrac + ESD
1	N001	0.5018(6)	0.1678(3)	0.5012(3)
2	C002	0.5656(5)	0.1375(6)	0.2936(2)
3	N003	0.5008(6)	-0.0406(5)	0.5318(3)
4	C004	0.3465(4)	0.1081(6)	0.7452(3)
5	C005	0.5835(5)	0.1023(6)	0.3555(2)
6	C006	0.3860(5)	0.2247(6)	0.3059(3)
7	H006	0.320536	0.26643	0.290524
8	C007	0.3633(5)	0.1403(7)	0.8077(2)
9	C008	0.7713(5)	0.0271(6)	0.3451(2)
10	H008	0.838916	-0.007255	0.361813
11	C009	0.5010(5)	0.0839(6)	0.5504(3)
12	C00A	0.4661(5)	0.1980(5)	0.2682(3)

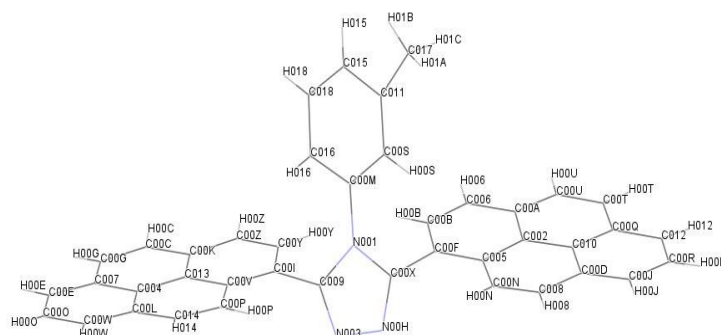
13	C00B	0.4005(5)	0.1914(6)	0.3654(3)
14	H00B	0.344791	0.211035	0.389367
15	C00C	0.5474(5)	0.2243(7)	0.7973(2)
16	H00C	0.613074	0.263056	0.814312
17	C00D	0.7549(5)	0.0587(6)	0.2813(3)
18	C00E	0.2769(5)	0.1185(7)	0.8414(2)
19	H00E	0.285939	0.141181	0.881652
20	C00F	0.4951(5)	0.1301(6)	0.3897(2)
21	C00G	0.4653(5)	0.1970(6)	0.8319(3)
22	H00G	0.476368	0.215982	0.872492
23	N00H	0.5030(6)	-0.0389(5)	0.4703(3)
24	C00I	0.5041(4)	0.1284(6)	0.6114(2)
25	C00J	0.8411(5)	0.0375(6)	0.2459(3)
26	H00J	0.909336	0.004992	0.262651
27	C00K	0.5336(5)	0.1936(6)	0.7339(2)
28	C00L	0.2435(4)	0.0543(6)	0.7192(3)
29	C00M	0.5011(8)	0.3109(3)	0.5005(4)
30	C00N	0.6886(6)	0.0478(6)	0.3795(3)
31	H00N	0.699851	0.026192	0.419806
32	C00O	0.1764(5)	0.0636(6)	0.8171(3)
33	H00O	0.120192	0.047211	0.841176
34	C00P	0.3149(5)	0.0462(6)	0.6227(3)
35	H00P	0.304465	0.022453	0.582606
36	C00Q	0.6378(4)	0.1415(6)	0.1956(3)
37	C00R	0.8234(5)	0.0657(6)	0.1851(3)
38	H00R	0.88075	0.051462	0.161587
39	C00S	0.5885(8)	0.3764(8)	0.4813(3)
40	H00S	0.647307	0.328924	0.468329
41	C00T	0.5324(5)	0.1984(6)	0.1709(3)
42	H00T	0.519988	0.216177	0.13027
43	C00U	0.4524(5)	0.2255(6)	0.2062(2)
44	H00U	0.386197	0.263459	0.18942
45	C00V	0.4190(4)	0.1036(6)	0.6471(2)
46	C00W	0.1610(5)	0.0336(6)	0.7571(3)
47	H00W	0.093173	-0.001686	0.741258
48	C00X	0.5036(5)	0.0852(6)	0.4539(2)
49	C00Y	0.6028(5)	0.1926(6)	0.6370(3)
50	H00Y	0.658291	0.213665	0.613139
51	C00Z	0.6167(5)	0.2240(6)	0.6968(2)
52	H00Z	0.681661	0.265661	0.712909
53	C010	0.6527(5)	0.1134(6)	0.2567(2)
54	C011	0.5897(12)	0.5129(10)	0.4810(4)
55	C012	0.7231(5)	0.1142(7)	0.1590(3)
56	H012	0.711722	0.128687	0.118032
57	C013	0.4320(4)	0.1347(6)	0.7083(2)

58	C014	0.2317(5)	0.0264(6)	0.6576(3)
59	H014	0.164213	-0.006928	0.640109
60	C015	0.5052(17)	0.5858(6)	0.5005(6)
61	H015	0.507894	0.67834	0.499979
62	C016	0.4133(7)	0.3803(9)	0.5217(3)
63	H016	0.354475	0.33552	0.536056
64	C017	0.6606(5)	0.6106(6)	0.4640(2)
65	H01A	0.736141	0.58215	0.47331
66	H01B	0.648773	0.691604	0.484996
67	H01C	0.645909	0.625705	0.421858
68	C018	0.4175(11)	0.5227(10)	0.5206(4)
69	H018	0.359868	0.57216	0.533645

**Table S2.** Atomic coordinates of **1-DPY** obtained from single crystal XRD experiment.



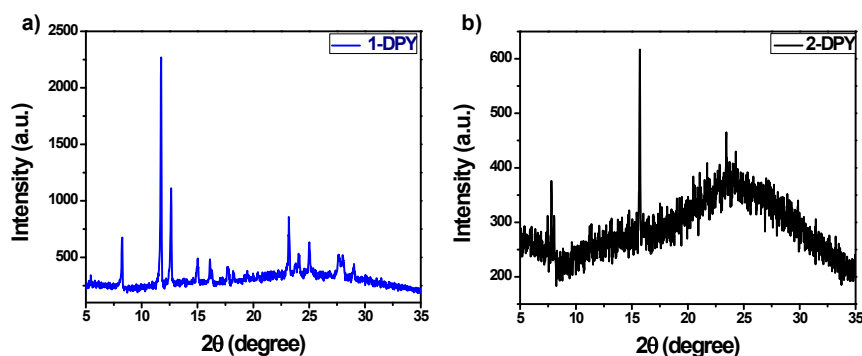
**Figure S10.** Molecular interaction and the growth direction of the single crystal from the molecular packing of **1-DPY** (a) and the unit cell diagram of **1-DPY** (b).



**Figure S11.** Labelling of atoms in **1-DPY** for understanding atomic coordinates.

## 5. Thin film XRD Experiment:

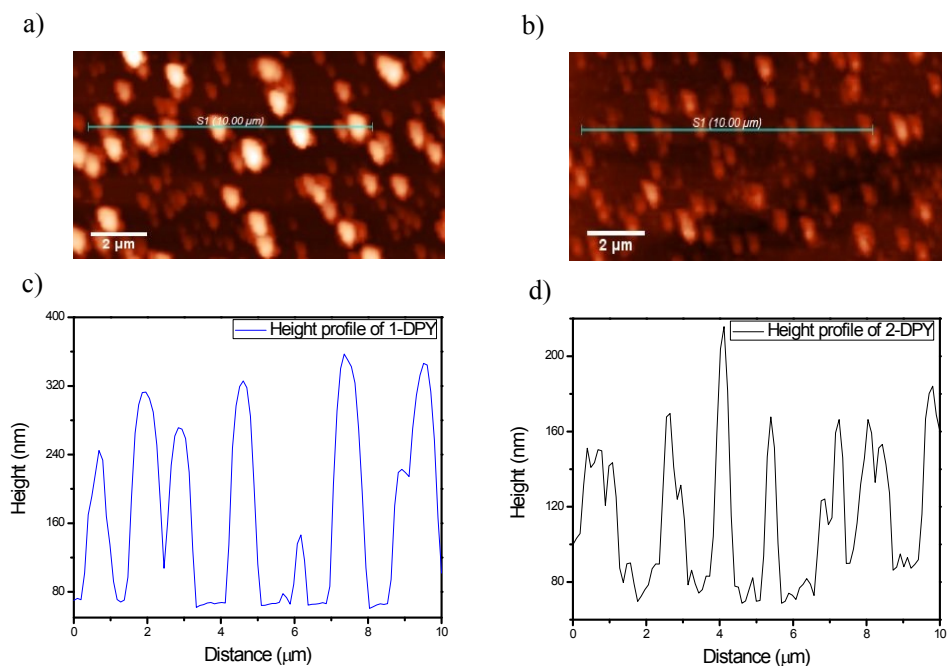
XRD measurements were recorded with a Rigaku (mini flex II, Japan) powder X-ray diffractometer with Cu  $K\alpha = 1.54059 \text{ \AA}$  radiation. The samples for X-ray measurement were prepared on glass cover slips by drop cast followed by drying at room temperature and after that vacuum for two day. Sample solution was prepared at 10mM concentration in  $\text{CHCl}_3$  solution.<sup>3</sup>



**Figure S12.** X-ray diffraction patterns of **1-DPY** (a) and **2-DPY** (b).

## 6. AFM Experiment:

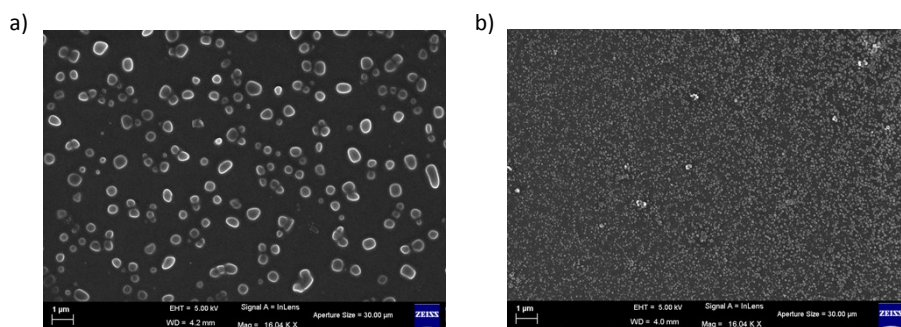
Atomic force microscopy was carried on NT-MDT (model no. AP-0100) in semicontact mode. The sample was prepared by spin casting the dilute solution (0.1mM) of compound in chloroform on top of mica surface, followed by drying in desiccators under vacuum for two days. The root-mean-square roughness ( $R_{RMS}$ ) of **1-DPY** and **2-DPY** were 7.42 nm and 8.74 nm. From roughness data it is confirm that both compounds have highly smooth surface and this smoothness increases charge transporting property of memory device. **1-DPY** have more smooth surface than **2-DPY** that gives idea about that **1-DPY** shows better memory characteristic property than **2-DPY**.<sup>4</sup>



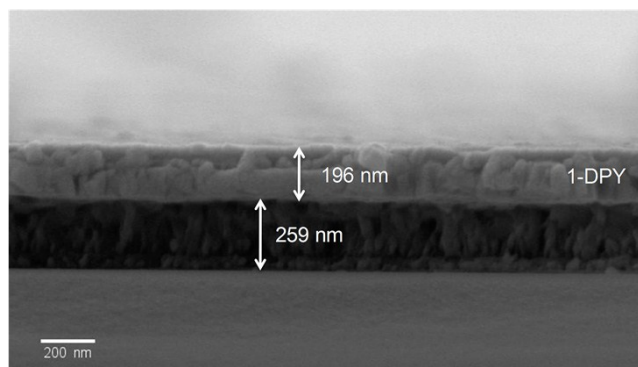
**Figure S13.** AFM image of **1-DPY** (a) and **2-DPY** (b) and their height profile (c) and (d) respectively.

## 7. SEM Experiment:

The morphology of the surfaces were investigated using field emission scanning electron microscopy (FE-SEM) The images were taken using an FE-SEM apparatus (ZEISS scanning microscope-ZSM-S 55 VP). The SEM samples were prepared by drop casting of 0.1 mM concentrated solution of **1-DPY** and **2-DPY** (chloroform solvent) on top of mica surface, followed by drying first in air for 10 hr at room temperature and then desiccators under vacuum for 2 days. From the SEM images it was observed that the particles were well shaped. Most of the particles were spherical in shape for both **1-DPY** and **2-DPY**. Some particles of **1-DPY** were rod like shape this is due to two or more particles were coagulated to form rod like shape. The particle size was calculated by using ImageJ software. Most of the particles were having size in the order of 350-400 nm for **1-DPY** and 70-80 nm range for **2-DPY**.<sup>5</sup>



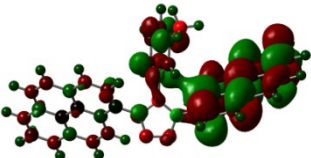
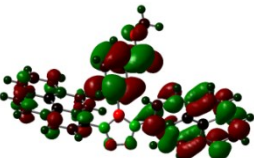
**Figure S14.** SEM images of **2-DPY** (a) and **1-DPY** (b).

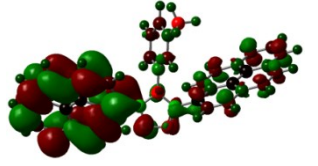
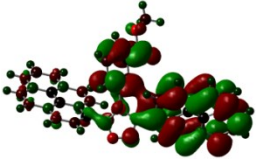
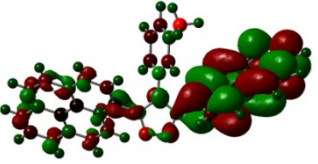
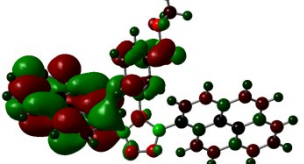
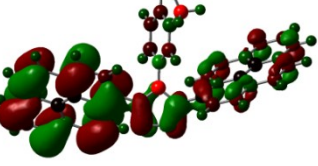
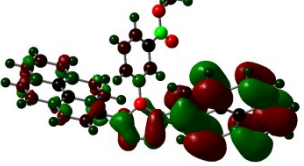
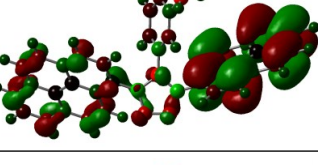
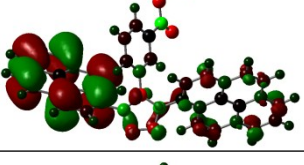
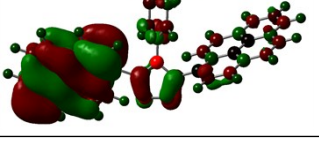
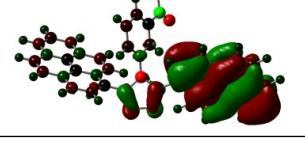


**Figure S15.** Cross-sectional scanning electron microscopic image of a thick film of **1-DPY** deposited on FTO.

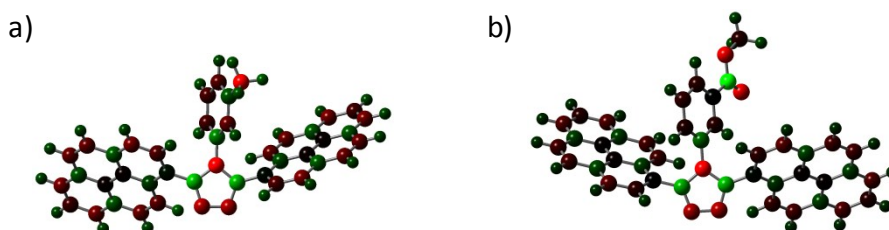
### 8. Computational calculations:

The geometric and electronic properties of **1-DPY** and **2-DPY** were obtained by computational methods using Gaussian 09 program package. The geometry was optimized by means of B3LYP (Becke three parameters hybrid functional with Lee–Yang–Parr correlation functional) with the 6–31G (d) atomic basis set. The molecular orbitals were visualized using GaussView 6.0.16.

1-DPY	2-DPY	Name of molecular orbitals
		LUMO+2

		LUMO+1
		LUMO
		HOMO
		HOMO-1
		HOMO-2

**Figure S16.** Molecular orbital diagrams obtained from theoretical calculation.



**Figure S17.** Optimised structure of **1-DPY** (a) and **2-DPY** (b) from theoretical calculation.

### 9. Device fabrication:

Memory devices were fabricated on indium tin oxide (ITO) coated PET substrates, which were cleaned by soap-water, acetone accordingly and finally keep it for 30 minutes in UV ozone cleaner. **1-DPY** and **2-DPY** solid powders were first dissolved in *o*-dichlorobenzene (3mg /0.3ml) at 120 °C for 30 min .This

solution was spin coated on ITO coated substrates at 750 rpm for 1 minutes to yield 220 nm thick films of **1-DPY** and **2-DPY**. Top electrode aluminium (Al) was vacuum evaporated on top of the films from a tungsten filament basket at a pressure below  $10^{-6}$  mbar. I-V characteristics were measured by KEITHLEY (2450 Source Meter). All the measurements were carried out at room temperature under ambient atmosphere in absence of light.

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