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# Knitting up 2,7-disubstituted Carbazole based Oligomers through Supramolecular Interactions for their Application in Organic Thin Film Transistors

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For the designing and development of organic electronic devices, the main focus is particularly on the synthesis of new organic semiconductors and dielectric materials. Molecular engineering is another effective strategy, in this direction which has been explored successfully in this study through synthesis of a  $\pi$ -conjugated oligomer CbzTPAU2, with  $M_w = 2169$ . This bow shaped oligomer with its core unit made from 2,7-disubstituted carbazole which further has been connected to its end-terminal unit TPAU2 by 1,4-bis(decyloxy)-2,5-diethynylbenzene. The presence of Uracil moiety on end terminals of CbzTPAU2 has triggered the self-assembly of CbzTPAU2 molecules through knitting up of each these single units through four Uracil-Uracil intermolecular hydrogen bonds (U---U) per CbzTPAU2 unit. Atomic Force Microscope (AFM) study was employed to explore the directionality of hydrogen bonding. Further, the effect of solvent polarity on the stability of U---U bonding in CbzTPAU2 oligomers has also been reported here in this study. The potential of these self-assembled CbzTPAU2 oligomers when explored as charge transporting layer in OTFTs has shown *p*-type behaviour. The OTFT device bottom-gate, top-contact when fabricated on the heavily doped *n*-type Si wafer with SiO<sub>2</sub> as gate dielectric (200 nm) has shown good on/off ratio  $3.43 \times 10^3$  and with average hole mobility of  $0.167 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .

## 1. Introduction

Research and development on new methodologies towards the advancement of organic thin film transistors (OTFTs) has become focus of interest for material chemists to replace the traditional expensive Silicon based technology.<sup>1</sup> In this direction, designing new organic semiconducting and dielectric materials or performing the semiconductor-dielectric interface study are the basic strategies that has been widely exploited for the electrical performance enhancement of OTFTs. Owing to the numerous benefits offered by organic semiconductors (OSCs) over their inorganic counterparts they are emerging as a material of choice for future organic electronic devices. The easy processability, low fabrication cost, and high flexibility are some of the main merits associated with OSCs.<sup>2</sup> Among OSCs  $\pi$ -conjugated materials, oligomer or polymer has shown a great potential for being their use as a charge transporting channel in OTFTs.<sup>3</sup> In last few decades, an exciting library of  $\pi$ -conjugated materials has been emerged, that has helped to establish a relation between their structure and charge carrier property.<sup>4</sup> In past various research groups have successfully achieved the

charge carrier mobility (or field effect mobility of  $\mu_{FE} \approx 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) by employing new OSCs.<sup>5</sup> However, tedious processes involved in their syntheses is one of the main drawback associated with this strategy. But still, the performance of OSCs is far away from their inorganic counterparts. Hence, instead of synthesis of new OSCs, there is a need for the development of new strategies that can help to harness maximum device performance from the present available library of OSCs. One such attractive approach is to use principles of supramolecular chemistry to organize the  $\pi$ -conjugated oligomers into well-defined polymeric structures.<sup>6</sup> This is because  $\pi$ -conjugated oligomers have numerous advantages over their parent counterpart  $\pi$ -conjugated polymers as they are easy to be synthesized and easy to be purified. However, in case of  $\pi$ -conjugated polymers, small impurities left in polymer backbones are known to affect the device performance significantly.<sup>7</sup> Further, employing the supramolecular-engineering in this respect, on  $\pi$ -conjugated system can open a new insight into the

charge-transport behaviour of these molecules.<sup>8</sup> This will push the electronic or molecular devices to new heights of application.

The  $\pi$ -conjugated oligomers has a potential to undergo self-assembly to form the nanostructures like nanowires, nanobelts which is much required for the device miniaturization as they require small channel material.<sup>9</sup> However, before employing them in OTFTs there is a strong desire to control their supramolecular organization because charge generation and transport is dictated by solid-state packing ( $\pi - \pi$  interactions) and nanoscale morphology.<sup>10</sup> Poly(para-phenylene ethynylene)s (PPE) are one such type of OSCs whose application in organic electronics has been demonstrated by Samori, Rabe, Müllen, Bunz and other distinguished scientists. Various nanostructures of PPEs such as nanoribbons, nanotubes, and nanotowers, etc. have been generated from them.<sup>11</sup> Among the various methods available for the synthesis of PPEs, Sonogashira coupling reaction is the most common strategy. However, this method has its own limitation *i.e.* dehalogenation side reactions, the ambiguity regarding the end-groups (dehalogenation, formation of phosphonium salts), the occurrence of diyne defects, formed by either reduction of Pd<sup>2+</sup> catalyst or by the presence of atmospheric oxygen and sometimes contamination with Pd catalyst residues containing phosphorus ligands. The synthesis of  $\pi$ -conjugated oligomers through a simple iterative and convergent Pd/Cu-coupling and alkyne deprotection protocol is an alternative method to design conjugated oligomers with free from above defects.<sup>12</sup> As compared to  $\pi$ -conjugated polymers these short oligo(phenylene acetylene) (OPA) derivatives, functional properties are easy to be tuned for their application in materials chemistry and molecular electronics.<sup>13</sup> The charge transport in these short length OPA takes place preferably through tunnelling as compared to incoherent hopping in their long chain parent analogue conjugated polymers. Additionally,  $\pi$ -conjugated polymers are typically longer than their persistence length, so a charge is not expected to be able to travel the full length of a molecule before having to hop to a neighbour.<sup>14</sup> Hence, self-assembly of  $\pi$ -conjugated oligomers is an effective bottom up strategy for the fabrication of  $\pi$ -conjugated polymer nanostructures which in turn have efficient charge separation and good charge transport properties as compared to their bulk counterparts.<sup>15</sup> A well-organized nanoarchitectures based on  $\pi$ -conjugated supramolecular assemblies is highly attractive for the OTFTs with tailor-made molecular arrangements. For example, polymer nanostructures prepared by oriented molecular assembly showed a mobility<sup>16</sup> up to 1.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Wang and co-workers also reported that when the molecular length is short enough, the conduction occurs dominantly by the tunnelling mechanism, but as the molecule gets longer, the hopping mechanism starts to contribute.<sup>17</sup> Hence, the study of supramolecularly-engineered assemblies of conjugated molecules can help to bridge the gap between functional properties of individual molecules and those of materials with high fidelity.<sup>18</sup>

In this study, our focus has been to explore the physical and electronic property of the OPA based on 2,7-disubstituted carbazole (6) scheme 1, through incorporation of suitable

substituents at its 2,7 position, which are capable of undergoing supramolecular polymeric structure formation at room temperature. These so formed supramolecular structures when employed as charge transporting layer in OTFTs has shown reasonable electronic properties for research. Owing to the selectivity and directionality of hydrogen bonds (H-bonds) we have employed the Uracil-Uracil (U---U) intermolecular hydrogen bonds for the formation of supramolecular structures in this study. In prior to formation of final charge transporting material, synthetic route of intermediate material (9) of OPA incorporated with 2,7-disubstituted carbazole subunit is demonstrated in scheme 2. It is the unique ability of Uracil molecules to undergo U---U intermolecular hydrogen bonds formation that has helped us to knit up the individual CbzTPAU2 (see scheme 4 and IUPAC name is disclosed in supporting information) units into supramolecular polymeric structure. To take advantage of U---U we have introduced the two U moieties on tris(4-iodophenyl)amine, (12, TPA) molecule through its reaction with two equivalents of U to form TPAU2 (13) scheme 3. It was further reacted through Sonogashira coupling with 2,7-bis(2-(2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-9*N*-(2-ethylhexyl)-carbazole (10, scheme 4) to finally get the target semiconducting molecule CbzTPAU2 (see scheme 4) as a bright red solid with a brownish tinge. It has good solubility in all common organic solvents like tetrahydrofuran (THF) or chloroform which makes it easily processable at room temperature for its study in organic electronics as reported here. The presence of triple bonds in CbzTPAU2 structure has provided the rigidity, which prevented it from aggregation when it was drop casted from its THF solution by following scheme 1. The presence of four U molecules per CbzTPAU2 finally has led to the formation of a rigid well-defined stable supramolecular structure as triggered by U---U all over the Si Substrate (5 × 5 cm<sup>2</sup>). The effect of solvent polarity on the stability of U---U intermolecular hydrogen bonds has also been evaluated in this study successfully. In together with 3D model as generated from ACD chemical lab, the morphology of the supramolecular structure formed by CbzTPAU2 was studied by the Atomic Force Microscopy (AFM). We further have explored the application of this supramolecular structure in the field of organic electronics by incorporating them as a conducting channel in bottom-gate top-contact OTFTs over *n*-type Si substrate.

## 2. Experimental Section

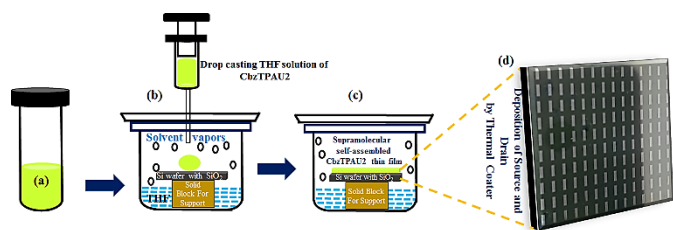
### 2.1 REAGENTS AND MATERIALS

All chemicals were procured from Sigma Aldrich and used as received. The dichloromethane, chloroform, tetrahydrofuran and dry dimethyl sulfoxide (DMSO) was obtained from Alfa Aesar were dried and distilled from sodium/benzophenone (except DMSO) prior to their use. Aluminium shots (Al, 99.999%, Admat Inc.) 3-5 nm in size, gold shots (Au, 99.999%, Admat Inc.) 1-2 nm in size, were purchased from Gredmann Taiwan Ltd. *n*-type Silicon wafers for fabrication of OTFTs were

purchased from local suppliers. All other reagents and solvents were purchased from commercial suppliers and used as such, unless specified. It should be noted that all experiments were performed under dry nitrogen atmosphere and in standard fume hood. The characterization of as synthesized compounds in this study was analysed by  $^1\text{H}$  NMR (300 MHz) and  $^{13}\text{C}$  NMR spectra (300 MHz) in respective deuterated solvents by employing Bruker spectrometer with tetramethylsilane as an internal standard.

## 2.2 THIN FILM PREPARATION OF CbzTPAU2 AND ITS CHARACTERIZATION

The silicon wafer was cleansed first by dipping it in HF solution for 5 minutes to remove the oxidized surface and then sequential washing of acetone and water was given to it. The as such cleaned Si wafer was then dried in oven at 70 °C. On the other side CbzTPAU2 (0.05 mg) solution was prepared in 10 ml of dry THF. A clear yellow solution of CbzTPAU2 with a greenish tinge was obtained in THF. The silicon wafer as cleaned by above method was allowed to come to room temperature, before being the CbzTPAU2 solution drop-casted over it. The detailed method of formation of self-assembled CbzTPAU2 layers as induced by U---U intermolecular hydrogen bonding between the CbzTPAU2 units is shown in scheme 1.<sup>19</sup> The supramolecular polymeric thin film of CbzTPAU2 were produced by slow-assembling from their solution (0.05 mg in 10 ml of THF) under a certain solvent pressure in a closed jar, as depicted in scheme 1. The solvent in the bottom of jar is THF as its vapour pressure is low, and this has given sufficient time to bow shaped CbzTPAU2 molecules to adjust and come closer together that has led to the formation of well self-assembled supramolecular structure through U---U intermolecular hydrogen bonding. It was annealed at 50 °C for 10 minutes before being studied their morphology by atomic force microscopy (AFM, Digital Instruments Nanoscope, D – 5000) with a scan size of  $1 \times 1 \mu\text{m}^2$  and a scan rate of 1 Hz.



Scheme 1. (a) THF solution of CbzTPAU2 (b) Drop casting the THF solution of CbzTPAU2 on Si wafer ( $\text{SiO}_2$  as a dielectric layer) as placed on solid block, in a beaker containing the THF solution under certain vapour pressure (c) CbzTPAU2 oligomers self-assemble from their THF solution into a supramolecular thin film through U---U intermolecular hydrogen bonding. This process takes 5-6 hours (d) Deposition of Source-Drain on Si wafer by thermal coater.

AFM measurements were performed under ambient conditions using a Veeco Multimode Nanoscope IV system operating in tapping mode in air. Silicon cantilevers (OMCL-AC160TS) with a resonance frequency of ~300 kHz were used.

## 2.3 OTFT DEVICE FABRICATION AND ELECTRICAL MEASUREMENTS

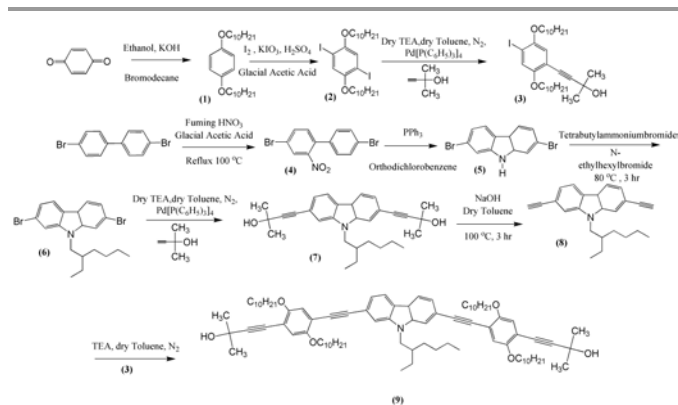
OTFT device with bottom-gate top-contact configuration were fabricated using heavily doped *n*-type Si wafers as the gate dielectric with thermally grown silicon dioxide ( $\text{SiO}_2$ ) layer 200 nm thick (capacitance = 172 nF  $\text{cm}^{-2}$ , contact area = 1.0  $\text{mm}^2$ ). The hydrogen bonded self-assembled semiconducting layer of CbzTPAU2 was fabricated next to  $\text{SiO}_2$  dielectric layer by following the scheme 1. The gold source and drain electrodes (100 nm thick) were deposited through shadow mask. The channel length and width were fixed at 82  $\mu\text{m}$  and 2000  $\mu\text{m}$  respectively.

The electrical characteristics of the transistors were measured in a nitrogen glove box on an Agilent-4156 probe station. The transistor parameters, such as charge carrier mobility, were calculated using the standard formalism of OTFTs in the linear and saturation regimes respectively. The CbzTPAU2 based OTFTs exhibits output characteristics with pinch off and current saturation. The electrical characteristics of the CbzTPAU2 based OTFTs were very stable during operation. The OTFT device measurements were performed using a semiconductor parameter analyser (Agilent 4155C probe station) at room temperature in a nitrogen glove box where the concentration of  $\text{H}_2\text{O}$  and  $\text{O}_2$  was less than 1 ppm. The  $\mu_{\text{FE}}$  value was obtained from the transfer characteristics in the linear region using equation 1. The mobility and threshold voltage of OTFTs in the linear regime are related by the equation,<sup>20</sup>

$$I_{\text{DS}} = \frac{WC_i}{L} \mu_{\text{FE}} (V_{\text{G}} - V_{\text{th}}) V_{\text{DS}} \quad (1)$$

where,  $I_{\text{DS}}$  and  $V_{\text{DS}}$  were the current and voltage bias between source and drain, respectively,  $V_{\text{G}}$  denoted the gate voltage at which the current starts to rise. Further,  $W$  and  $L$  denoted the source-drain width and length, respectively;  $\mu_{\text{FE}}$  was the field effect mobility;  $C_i$  was the capacitance per unit area of the insulator, and  $V_{\text{th}}$  was the threshold voltage.

## 3. Results and Discussion

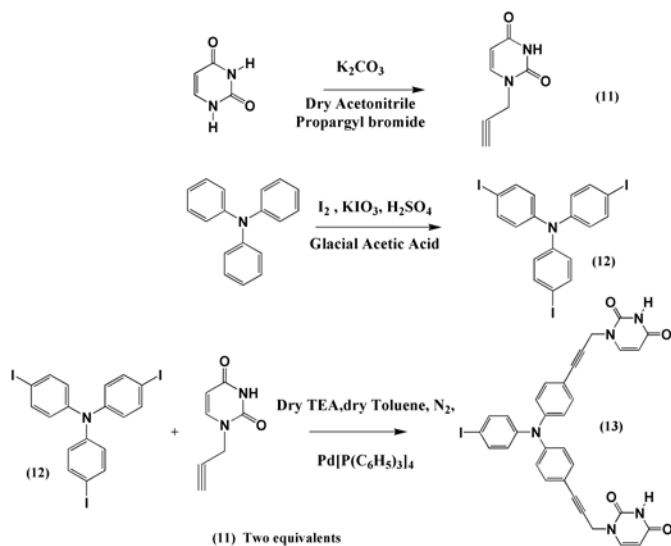


Scheme 2. Synthetic route of OPA (9) incorporated with 2,7-disubstituted carbazole subunit end terminated by 2-methyl-3-butyn-2-ol.

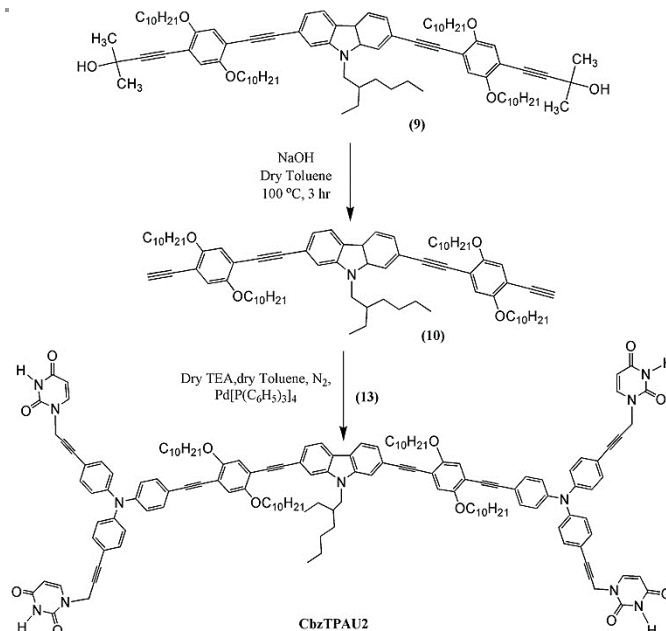


The syntheses of oligomer CbzTPAU2 is outlined in scheme 4 followed by scheme 2 and scheme 3. It was prepared by a Sonogashira coupling reaction between 2,7-bis((2,5-bis(decyloxy)-4-ethynylphenyl)ethynyl)-9-(2-ethylhexyl)-8a,9-dihydro-4bH-carbazole [10] and 1,1'-(3,3'-(4,4'-(4-iodophenylazanediy)bis(4,1-phenylene))bis(prop-2-yne-3,1-diyl))dipyrimidine 2,4(1H,3H)-dione, (TPAU2) [13]. The controlled elongation of OPA incorporated with 2,7-disubstituted carbazole unit through Sonogashira coupling reaction has played a crucial role in the synthetic strategy of CbzTPAU2. Further, the oligomer CbzTPAU2 as prepared by this strategy was easy to purify which involved repeated precipitation from THF in hexane. It offered an advantage to end-terminate the OPA, [10] at both its ends selectively with TPAU2 [13], (Scheme 4).

With this iterative synthesis strategy the end-termination of



Scheme 3. Synthetic route of TPAU2

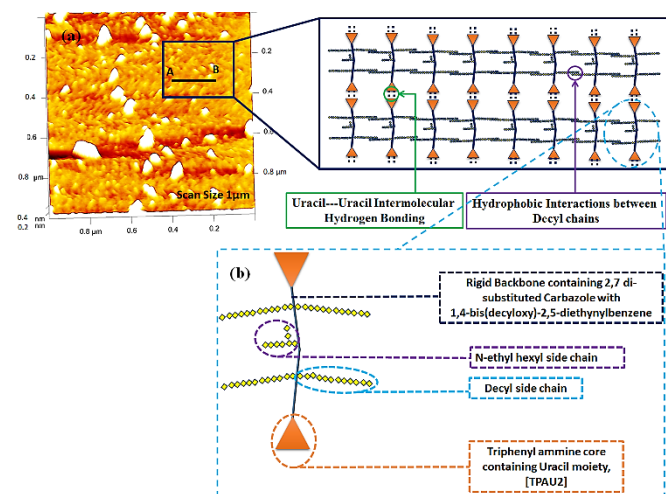


Scheme 4. Synthetic route of Oligomer CbzTPAU2

OPA (10) was more selective and specific as compared to their polymeric counterparts. Synthesis of TPAU2 is outlined in scheme 3. It was also prepared in reasonable yield 27.4% as a bright red solid by implementing Sonogashira coupling reaction between 1-(prop-2-ynyl)pyrimidine-2,4(1H,3H)-dione [11] and tris(4-iodophenyl)amine [12]. The presence of Uracil moiety and decyl chains on 4-(2,5-bis(decyloxy)-4-iodophenyl)-2-methylbut-3-yn-2-ol [3] in CbzTPAU2 has played a crucial role in its self-assembly through U---U intermolecular hydrogen bonds into a supramolecular polymeric structure.

### 3.1 THIN-FILM MORPHOLOGIES AND ORDERING STRUCTURES

The tapping mode AFM study was performed on the self-assembled monolayers of CbzTPAU2 for the better understanding of their morphology. The crucial role played by uracil moieties as present on the end terminals of CbzTPAU2



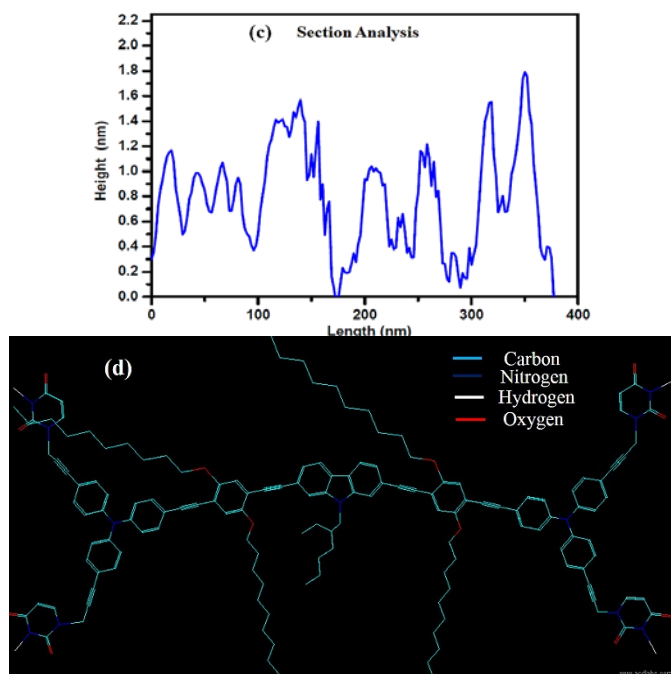


Figure 1. (a) AFM topographic image ( $1 \times 1 \mu\text{m}^2$ ) of the self-assembled oligomeric CbzTPAU2 thin film on Si wafer, as prepared by Scheme 1, (b) Cartoon representation of packing of CbzTPAU2 oligomers into their supramolecular thin film through U---U intermolecular hydrogen bonding, (c) Cross-sectional analysis of self-assembled layer of CbzTPAU2 corresponding to line AB in Fig. 1a, (d) Molecular model of Single CbzTPAU2 oligomer.

molecules has affected their self-assembly into supramolecular polymeric structure through U---U. The Uracil molecules are well known to form U---U intermolecular hydrogen bonding through  $-\text{NH}$  and  $-\text{CO}$  functional group present in their imide structure, which acts as donor and acceptor respectively. The role played by this type of intermolecular hydrogen bonding in self-assembly of CbzTPAU2 has been analysed by AFM imaging in topographic mode. On the basis of topographic AFM image (in Figure 1a) of self-assembled CbzTPAU2 supramolecular film, a cartoon structure has been designed as shown in Figure 1b. It has been found that the presence of Uracil moieties on the end terminals has triggered CbzTPAU2 molecules to self-assemble into its supramolecular thin film as shown in Figure 1b. Hence, it has been due to the presence of U---U intermolecular hydrogen bonding<sup>22</sup> the CbzTPAU2 molecules are able to form self-assembled supramolecular structure as shown in Figure 1b. Hence, it has been due to the presence of U---U intermolecular hydrogen bonding<sup>22</sup> the CbzTPAU2 molecules were able to form self-assembled supramolecular structure as shown in Figure 1b

which is in accordance with their corresponding AFM image Figure 1a. Further, the presence of decyl chains in its backbone structure on 1,4-bis(decyloxy)-2,5-diethynylbenzene has also helped in stabilizing this type of supramolecular architecture as shown in Figure 1b. The decyl chains in the backbone of CbzTPAU2 were involved in hydrophobic interactions with the decyl chains of penultimate CbzTPAU2 unit.<sup>23</sup> These hydrophobic interaction between decyl chains has helped the CbzTPAU2 molecules to self-assemble in the linear array while the U---U intermolecular hydrogen bonding has supported the molecules to get arranged in the vertical orientation as shown in cartoon structure Figure 1b. The AFM topographic image Figure 1a has supported the formation of this type of molecular arrangement as explained in this study. The presence of alkyl chains upto 10 carbons was found to be of sufficient length in forming a self-assembled array of CbzTPAU2 oligomers, Apart from maintaining their solubility in common organic solvents. It has been reported in previous research studies by various research groups that very long alkyl chains like dodecane or much longer alkyl chains can disturb the morphology of the oligomer or polymer on which they are attached. And hence in our case we choose alkyl carbon chain of 10 carbons only as it was expected that too long alkyl chains around the CbzTPAU2 oligomers would not allow them to self-assemble through U---U intermolecular hydrogen bonding.<sup>23b-d</sup>

Further, the cross-sectional analysis study has been performed on the self-assembled CbzTPAU2 oligomers to confirm whether these were single molecules or aggregation of CbzTPAU2 molecules from their THF solution. The sectional analysis study when performed on CbzTPAU2 self-assembled molecules as shown in Figure 1c has given their height of about 1.0 nm that is in accordance with the height of single molecule. Further, this AFM study also demonstrates the stability of this system as the CbzTPAU2 based supramolecular network covers the whole Si substrate when its solution in concentration of  $5 \times 10^{-5}$  M was drop casted on Si wafer by following the scheme 1.<sup>24</sup> Finally, on the basis of this AFM imaging study in topographic mode and the 3D model<sup>25</sup>, we were able to propose a cartoon model in Figure 1b which is in accordance with all our available data.

### 3.2 HYDROGEN-BONDING STABILITY STUDY OF CBZTPAU2 OLIGOMERS

As it has been shown in previous section in the form of AFM study that the strong and directional U---U intermolecular hydrogen bonding has guided the CbzTPAU2 oligomers to self-assemble them into their supramolecular structure. We further explored the effect of solvent polarity on the strength of U---U

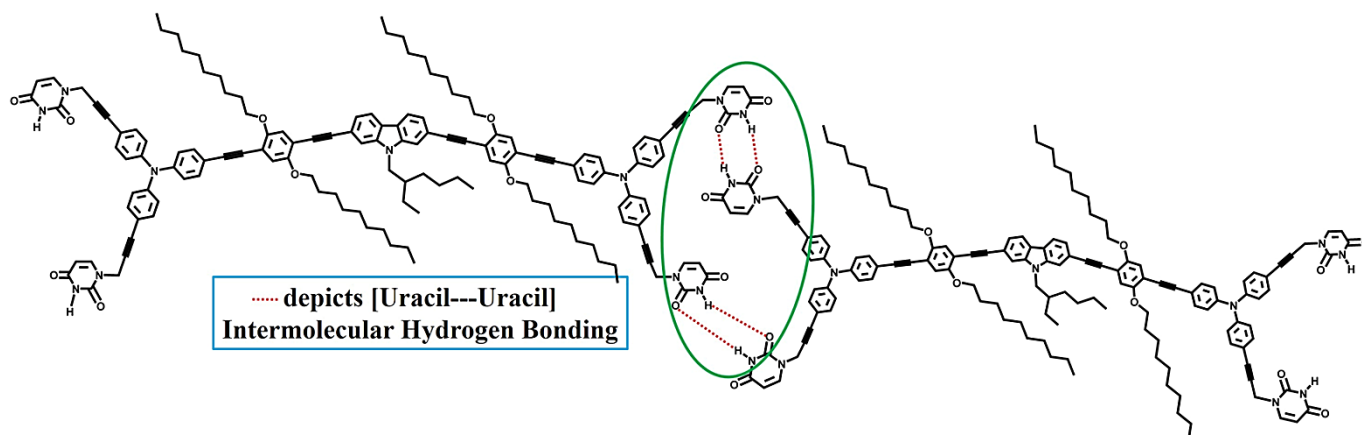


Figure 2. Schematic representation of U---U intermolecular hydrogen bonding between CbzTPAU2 units

intermolecular hydrogen bonding as that have prevailed in CbzTPAU2 based supramolecular structure in Figure 1a. The Figure 2 explains the chemical point of view of the involvement of uracil moieties which are present on the end terminals of CbzTPAU2 in U---U intermolecular hydrogen bonding. This type of supramolecular interaction in the form of hydrogen bonding has led to the formation of interesting supramolecular architecture by CbzTPAU2 small units.

The Figure 3a shows the THF solution of CbzTPAU2 and while Figure 3b shows the precipitation of the CbzTPAU2 as triggered by addition of few drops of DMSO in it. This shows that solvent polarity also has an important role in the formation of U---U intermolecular hydrogen bonding between CbzTPAU2 oligomers. Polar solvents are well known to break the intermolecular hydrogen bonds.<sup>26</sup> The precipitation effect of CbzTPAU2 molecules on addition of DMSO has been attributed to the disruption of U---U intermolecular hydrogen bonding in CbzTPAU2 based supramolecular structure.<sup>27e-f</sup> This has been attributed to the strong ability of U moieties to involve in U---

demonstrating the solvent effect on the formation and breakage of U---U intermolecular hydrogen bonding between CbzTPAU2 individual units.

DMSO intermolecular hydrogen bonding rather than in U---U intermolecular hydrogen bonding. This has led to the consequent precipitation of CbzTPAU2 from their THF solution on addition of few drops of DMSO in it. The Figure 3c explains the real situation chemically, how the DMSO solvent molecules interact with the CbzTPAU2 oligomers in their THF solution. In Figure 3c the green dots represent the THF solvent molecules while the red dots represent the DMSO solvent molecules (red dots) are leading to disruption of U---U intermolecular H-bonding through their binding with U moieties. This phenomena can further be explained in the form of equation 2 and equation 3.<sup>27</sup> Equation 2 represents, the CbzTPAU2 oligomers forming polymeric structure through U---U intermolecular hydrogen bonds. In favouring the shifts to the left hand side *i.e* leading to formation of precipitates [CbzTPAU2]<sub>n</sub>.DMSO on addition of few drops of DMSO. This has resulted in the disruption of CbzTPAU2 based supramolecular polymeric structure. Owing to the strong dipole moment (value of 3.960) of DMSO, preferential formation of intermolecular hydrogen bonds between the U---DMSO takes place and chemical equilibrium Figure 4 shows the formation of this type of U---DMSO intermolecular hydrogen bonds.

In this way, the subsequent precipitation of CbzTPAU2 has occurred on addition of polar solvent such as DMSO, as shown in Figure 3b.

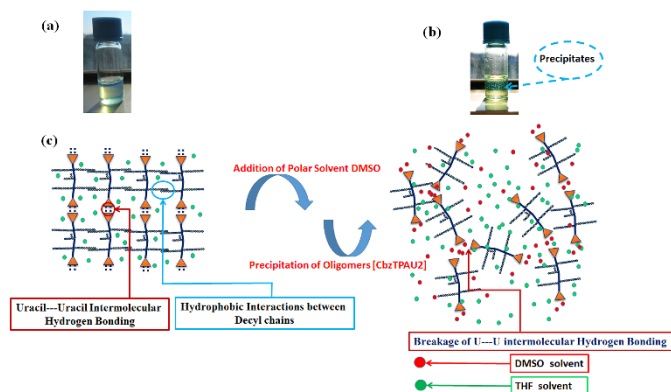
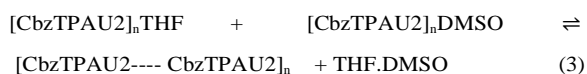
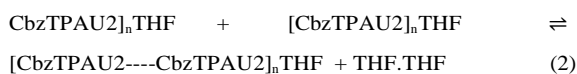


Figure 3. (a) THF solution of CbzTPAU2 (b) Addition of few drops of DMSO in THF solution of CbzTPAU2 leading to the precipitation of CbzTPAU2 (c) Cartoon Figure



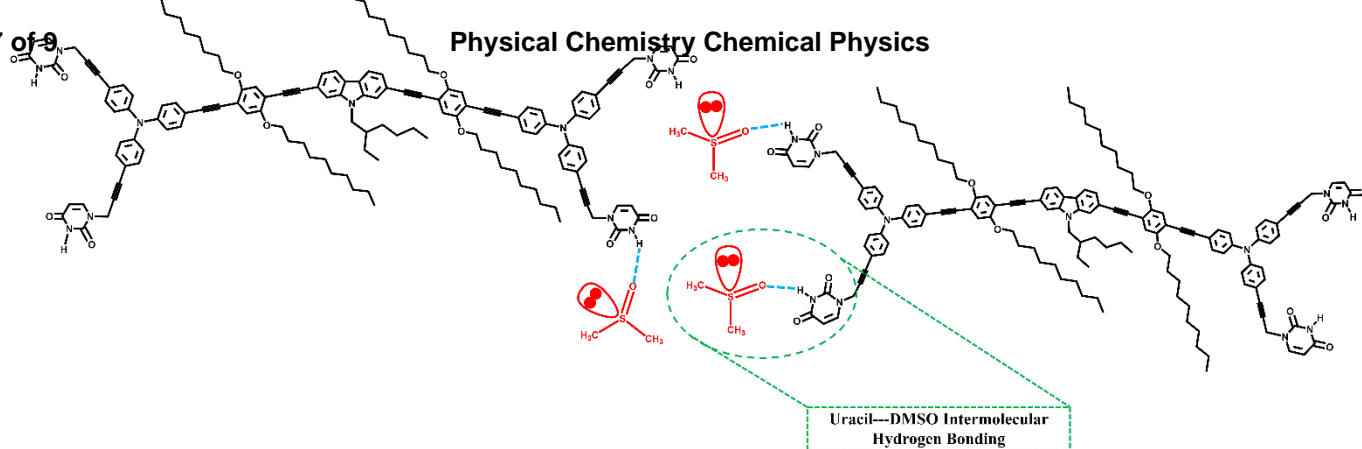


Figure 4. Schematic representation of U---DMSO intermolecular hydrogen bonds leading to interruption of self-assembled CbzTPAU2 supramolecular polymeric structure that was formed by U---U intermolecular hydrogen bonds.

### 3.3 FIELD-EFFECT TRANSISTOR PROPERTIES

We fabricated OTFT devices with a bottom gate and top contact (Figure 5a) for exploring the potential application of CbzTPAU2 self-assembled thin films as a charge transporting layer. The Figure 5b shows the photographic optical image of OTFTs as fabricated on *n*-type heavily doped Si wafer with its corresponding device configuration as shown in Figure 5a. The thermally grown 200 nm SiO<sub>2</sub> thick layer having a specific capacitance of 172 nFcm<sup>-2</sup> was employed as a gate dielectric layer in OTFTs as fabricated in this study. The supramolecular thin film of CbzTPAU2 was prepared by following the scheme 1 and Au source and drain electrodes were simultaneously deposited by vacuum evaporation on top of it through the homemade designed shadow mask. The resulting device had a channel length of 82 μm and a width of 2000 μm. The Figure 5c shows the transfer characteristics for the corresponding OTFT device. The Figure 5d presents the drain current-drain voltage (*I*<sub>DS</sub>-*V*<sub>DS</sub>) output curve as obtained from our OTFTs. The device demonstrated desirable OTFT characteristics (*p*-type) at an operating voltage within -40 V. The observed OTFT characteristics confirmed closely to conventional transistor models in both the linear and saturation regimes with *I*<sub>D</sub> increasing linearly at low drainage voltage, and clear saturation behaviour at high drain voltage. According to the drain current-gate voltage (*I*<sub>DS</sub>-*V*<sub>GS</sub>) transfer curve of Figure 5c, the OTFT with the CbzTPAU2 as semiconducting layer has displayed an average field hole mobility of 0.167 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at -40 V, with an on/off current ratio of 3.43 × 10<sup>3</sup>. The good hole transporting property along with the glassy film forming properties, offered by TPA has made us to choose it as an end capping agent<sup>29</sup> in the synthesis strategy of CbzTPAU2. The synthetic connection of two hole transporting materials, 2,7 disubstituted Carbazole and TPA through 1,4-bis(decyloxy)-2,5-diethynylbenzene by employing the Pd catalysed Sonogashira coupling reaction has helped to design this CbzTPAU2 oligomers for OTFTs. Owing to the better electrical and physical properties of 2,7 disubstituted

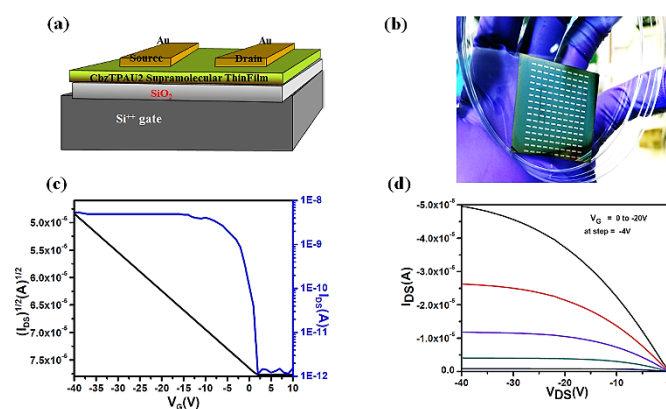


Figure 5. (a) Schematic diagram of bottom-gate OTFT device that features SiO<sub>2</sub> as a gate insulator and Self-assembled CbzTPAU2 polymeric structure as a semiconducting layer (b) photograph of the OTFT device on a 5 × 5 cm<sup>2</sup> area on a *n*-type heavily doped Si substrate and plots of OTFT; (c) transfer characteristic (*I*<sub>DS</sub>-*V*<sub>GS</sub>), when *V*<sub>DS</sub> = -2 V, and (d) output characteristic (*I*<sub>DS</sub>-*V*<sub>DS</sub>), where *V*<sub>GS</sub> ranges from 0 to -40 V at -3 V step.

carbazole as compared to their 3,6 counterparts we have introduced it into the main core of CbzTPAU2.<sup>30</sup> However, propeller like symmetry<sup>31</sup> of TPA moiety is known to affect the intermolecular packing of semiconducting materials, and consequently affects the electric performance of devices. Numerous strategies have been employed to meet this challenge for their better intermolecular packing towards the development of organic electronic devices as based on them. One such strategy here we have successfully employed in this directions is the extension of supramolecular chemistry. This is the packing of TPA based organic semiconductor CbzTPAU2 in the form of well-ordered polymeric architecture which has been triggered by U---U intermolecular hydrogen bonding. The presence of Uracil moieties on the end-terminals of TPA has guided the TPA molecules that has further triggered the CbzTPAU2 oligomers to self-assemble in a well described symmetry through U---U as shown in Figure 1. The comparison of OTFTs based on some of the common conventional organic semiconductor material with OTFTs as based on CbzTPAU2 as reported in this study has also been carried out and same has been reported in Table T1 (Supplementary Information). It has been found that OTFTs as based on this well-organized self-assembled CbzTPAU2 oligomers has average charge mobility when employed as a



charge transporting semiconductor layer in OTFTs as shown in Figure 5. It has been found that due to higher level of conjugation and better physical properties of 2,7 disubstituted carbazole over its 3,6 disubstituted carbazole counterparts, we incorporated it as core unit of CbzTPAU2. In term of the rigidity<sup>32</sup> of CbzTPAU2 oligomers, the presence of the couple of triple bond contributes to the figure-of-merit of poly(aryleneethylenes) system such as easy synthesis, with their rigid rod structure having an ability to self-assemble architectures. And also in the synthesis of CbzTPAU2 material, with incorporation of 2,7-dibromo-*N*-(2-ethylhexyl)carbazole and TPAU2 through Pd catalysed Sonogashira coupling reaction has helped us to achieve the final target molecule in an acceptable yield. This easy to follow synthetic approach was beneficial for the successful application of new type of semiconducting molecular material for OTFTs.

#### 4. Conclusions

The recent advances in OTFTs has highlighted the use of low cost technology and materials to replace the most commonly used semiconductors and dielectric materials. We have successfully demonstrated the advantage of supramolecular chemistry for designing of a new stable supramolecular architecture as formed by U---U intermolecular hydrogen bonds. This strategy was implemented for its application in organic electronics through synthesis of CbzTPAU2. The 2,7-disubstituted carbazole unit was used as a core unit in synthesis of CbzTPAU2 oligomer unit. To the best of our knowledge, it is less explored as compared to their 3,6 disubstituted carbazole counterparts. The two hole transporting materials 2,7 disubstituted carbazole and TPAU2 was easily connected by incorporating a rigid rod molecule 1,4-bis(decyloxy)-2,5-diethynylbenzene through easy-to-follow Pd catalysed Sonogashira coupling reaction. The presence of Uracil moieties has triggered the CbzTPAU2 units to self-assemble through U---U intermolecular hydrogen bonds. The self-assembled structure when employed as an active semiconducting layer in OTFTs has showed good *p*-type behaviour with a good on/off current ratio  $3.43 \times 10^3$  and average field hole mobility of  $0.167 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We have successfully explored the application of supramolecular chemistry in field of organic electronics. This study may show the potential of supramolecular chemistry to the material chemists to extract the better charge mobility from available vast library of OSCs as designing new novel organic semiconductor materials is tough and time consuming process.

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## GRAPHICAL ABSTRACT:

