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# Photoresponsive 2D Polymeric Langmuir–Blodgett Films of 2,3,6,7,10,11-Hexaiminotriphenylene

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2,3,6,7,10,11-Hexaiminotriphenylene (HATP) was connected via aerobic oxidative coupling to form large-area polymeric 2D films using Langmuir Blodget technique. These 2D polymers exihibited electronic transport property as a p-type semicondutor with high conductivity (0.91 S cm<sup>-1</sup>), high on/off current ratio (10<sup>3</sup>), and photo-responsivity (980nm) up to 160 mA W<sup>-1</sup>.

Two-dimensional (2D) materials are of considerable interest due to their potential applications in future electronics.<sup>1</sup> If these conductive/semi-conductive 2D materials also possess nanopores, new functional entities can be introduced into the pore. Moreover, emergent transport property can be expected taking advantage of unique physics of the 2D electronics and chemical tunability of the pores. It is thus of interest to develop conductive/semi-conductive 2D nets with diverse band structure and chemical versatility.<sup>2</sup>

In recent years, the polymerization of molecular monomers in restricted 2D space can lead to new types of 2D materials that are molecularly tunable using the machinery of synthetic chemistry. Based on shape and connection mode of the monomers, topology with regular nanopores can be designed,<sup>3</sup> as demonstrated by the development of 2D covalent organic frameworks (COF)<sup>4</sup> and 2D metal-organic frameworks (MOF).<sup>5</sup> Nevertheless, 2D COF and MOF with electronic conductivities are still limited, possibly due to the lack of conjugation and  $\pi$ orbital continuity of most of the known 2D COF and MOF structures.

Organic material such as polythiophene has been used in constructing field-effect transistors(FETs), as first demonstrated by Tsumura *et al.* in 1986.<sup>6</sup> Similarly, organic light emitting

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59 60 diodes (LEDs) and organic solar cells were developed.<sup>7</sup> Key advantages of organic electronic devices include the ease to prepare large area device and mechanical flexibility of these devices.<sup>8</sup> As a result, organic FETs have been extensively explored in soft and light-weight electronic devices.<sup>9</sup>

We aim to construct highly conjugated 2D polymers to promote in-plane charge transport property in these porous 2D materials for building new organic FETs.<sup>10</sup> In this work, we synthesize semiconductive centimeter-size polymeric films of 2,3,6,7,10,11-hexaiminotriphenylene (HATP) via aerobic oxidative coupling and condensation. To prepare the material in large area that is transferrable to device-relevant substrates,<sup>11</sup> we adopted Langmuir-Blodgett (LB) technique in the synthesis.<sup>12</sup> FETs based on such 2D films were realized by transferring the films to silicon wafers. These 2D polymers exihibited electronic transport property as a p-type semicondutor with high conductivity (0.91 S  $\mbox{cm}^{\mbox{-}1}\mbox{)}$  and high on/off current ratio (10<sup>3</sup>). Thanks to the wide optical absorption band of the 2D polymers, photo responsivity up to 160 mA W<sup>-1</sup> was observed. This work highlights opportunities to develop new 2D materials from molecular units.

Ultrathin 2D HATP centimeter-size polymeric films were synthesized using Langmuir-Blodgett (LB) technique. Ultrapure water (pH = 5.6 because of dissolved CO<sub>2</sub>) was used as subphase, and 2,3,6,7,10,11-hexaaminotriphenylene hexa-hydrochloride (HATP 6HCl) (0.375 mg ml<sup>-1</sup>) was dissolved in the organic solvent (CHCl<sub>3</sub>:DMF = 3:1, volume ratio) as organic phase. 2.34 μL of triethylamine was added into the organic solvent solution (4 mL) to neutralize HCl in order to increase solubility of monomers in organic solvent. After addition of the organic phase (300 µL, HATP: 0.375 mg ml<sup>-1</sup>) onto subphase (243 cm<sup>2</sup>) and waiting for 30 minutes to evaporate the organic solvent, two barriers on the LB sink moves towards each other (speed: 2 mm min<sup>-1</sup>) to restrict surface area between them (Fig. 1a). Surface pressure was monitored by measuring force excerted on a flat platinum wilhelmy plate half immersed in the liquid. An increase of the surface pressure can be detected during the formation of the 2D films (Fig. 1b). Repeated experiments

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<sup>†</sup>Electronic Supplementary Information (ESI) available: Experimental details, Raman, EM images, SEM-EDX, XPS and UV-Vis for ESI or other electronic format see DOI: 10.1039/x0xx00000x

#### COMMUNICATION

showed consistent surface pressure vs. area isotherms (Fig. S1, ESI<sup>+</sup>). The liquid surface was also monitored by a Brewster angle microscopy (BAM) to visualize film formation. When surface pressure reached 20 mN m<sup>-1</sup>, a flat film was clearly observed (Fig. 1a inset); when surface pressure reached 45 mN m<sup>-1</sup>, the flat films became plicated. As a result, we chose 20 mN m<sup>-1</sup> as target surface pressure. The size of prepared film was about 5.6 cm x 3.5 cm, so the area was about 19.6 cm<sup>2</sup>. When the films were formed, horizontal drawing-up method<sup>13</sup> was used to transfer the films onto substrates, in which the substrates were initially submerged in the subphase and then horizontally lifted for transferring after film formation on the surface.

Formation of the 2D HATP polymeric films require  $O_2$  as an oxidant. When synthesis was performed under  $N_2$  atmosphere by putting the LB device into a home-built glove box filled with  $N_2$  (Fig. S2, ESI<sup>+</sup>), no solid film formation can be observed (Fig. 1a, inset). Oxidative coupling of monomer can happen in two possible ways: 1) the oxidation of one monomer can produce an electron deficient N that forms an N-C bond to another unoxidized monomer with electron rich aromatic ring via electrophilic aromatic substitution, mimicking the formation of the N-C bond in polymerization of aniline (Fig. 1c, model 1)<sup>10</sup>; 2) the monomer can be oxidized to quinone imines that are further hydrolyzed to quinones and then undergo condensation with amine groups from unoxidized monomer to form N=C linkages (Fig. 1c, model 2).<sup>14</sup> Both paths lead to the formation of highly conjugated 2D polymers.



**Fig. 1** (a) Fabrication of 2D HATP polymeric films on the air-water interface using Langmuir-Blodgett (LB) technique and BAM images of the air-water interface in  $O_2$  and  $N_2$  atmosphere. (b) The surface pressure vs. area plot in the film formation. The LB machine was put into a home-built glove box to control the atmosphere. (c) Two possible models of HATP polymeric films.

Transmission electron microscopy (TEM) images (Fig. S3, ESI+) and scanning electron microscopy (SEM) images of the

# Journal Name

sample on silicon wafer (Fig. S4, Fig. S5a, ESI<sup>+</sup>), together with optical photograph of 2D HATP polymeric1911978/091139059/Si substrate (Fig. S5c) showed the macroscopic homogeneity of large-area 2D HATP polymeric films. Besides, no periodic fringes were observed for this 2D thin film by TEM using a voltage of either 75 kV or 200 kV (Fig. S3, Fig. S5d, ESI<sup>+</sup>). Energy dispersive X-ray spectroscopy (SEM-EDX) confirmed that the sample contain both C and N, which exhibited uniform distributions in the films as shown by the mapping (Fig. S6, ESI<sup>+</sup>). Thickness of the 2D HATP polymeric films (the one to construct the devices) was about 5.8 nm as measured by atomic force microscopy (AFM) (Fig. S5b). This thickness is about 17 times the thickness of the monomer (3.35 Å). We believe there were pleated packing structure in the film instead of a regular packing of flat monolayers. Atomic models of the connection in model 1 reveal significant steric interactions between adjacent groups if they lie on the same plane, indicating curvature formation in the conjugated  $\pi$  rings. More repeated experiments showed a thickness distribution in 3.6~5.9nm (Fig. S7, ESI<sup>+</sup>). We also tried to increase the volume of the organic phase on the subphase in hope to control the film thickness, but these changes had no effect on film thickness. Instead, larger film area was obtained when more monomers were added in the organic phase, as long as surface pressure was kept to 20 mN m<sup>-1</sup> at the point of film transfer. X-ray photoelectron spectroscopy (XPS) revealed composition of the films to contain C, N, and O<sup>15</sup> as shown in Fig. S8, ESI<sup>+</sup>. The O may come from guest water molecules and the Na may come from NaCl impurity.<sup>16</sup> There were two peaks on the XPS spectrum for C (1s) corresponding to C in two distinct chemical environments. There is only one single peak for N (1s). The HATP polymeric films showed Raman spectrum with peaks at similar positions to that of the HATP•6HCl monomer, but the Raman spectrum of HATP polymeric films also showed a fluorescence background that is absent in that of the monomer as shown in Fig. S9, ESI<sup>+</sup>. Fourier-transform infrared (FT-IR) absorption spectra (Fig. 2) showed aromatic C-H stretching vibrations at about 2924 cm<sup>-1</sup>, C-N stretching vibration at 1304 cm<sup>-1</sup>, and in-plane C-H bending at about 1095 cm<sup>-1</sup>, which are similar to corresponding bands of polyaniline. The bands at approximately 1523 cm<sup>-1</sup> and 1620 cm<sup>-1</sup> are due to the benzenoid and guinoid ring units.<sup>17</sup> Peak observed at 1456 cm<sup>-</sup> <sup>1</sup>was due to C=C vibration of aromatic polymer chain.<sup>18</sup> Compared with the monomer, the N-H stretching bands (primary amines) at 3338 cm<sup>-1</sup> and 3221 cm<sup>-1</sup>, as well as N-H bending band at 1634 cm<sup>-1</sup> and C-N stretching band (aromatic





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amines) at 1278 cm<sup>-1</sup> became weaker, which is consistent with

formation of the polymeric film. To investigate the charge transport property of the 2D HATP polymeric films, we employed field-effect transistors (FET) to measure their electrical behavior. In brief, the prepared ultrathin 2D HATP polymeric films on the surface of water were transferred onto silicon wafer covered with silicon dioxide of 300 nm in thickness. Two gold electrodes (40 nm, defined by hard masks) were then deposited on top of the film. The 300 nm layer of thermally grown oxide was used as an insulating layer, and the heavily doped silicon substrate served as the gate electrode.<sup>19</sup> We constructed a channel of 180 µm (L) X 1 mm (W) in size shown in Fig. 3a. The transfer characteristics (scanning gate voltage with a fixed drain voltage) of a representative HATP polymeric film device was shown in Fig. 3b. With the gate voltage ( $V_{gs}$ ) decreasing at a given drain voltage ( $V_{ds}$  = -5 V), the drain current  $(I_{ds})$  gradually increased, which confirms that the device is a typical p-type transistor. The p-type behavior indicates that 2D HATP film is a semiconductor with holes as the majority carrier.<sup>20</sup> The current on/off ratio in this device was approximately 10<sup>3</sup>. Even at such a high current, the devices are still in perfect condition with no carbonization, as demonstrated by a visual examination (Fig. S10, ESI<sup>+</sup>). The device currents increased with increased channel areas. However, once the HATP polymeric film was purposely damaged, the device lost the conductivity in Fig. 3b. These results consistently indicated that the high conductivity originated from 2D HATP film. Furthermore, the device characteristic is reproducible with the same structure as shown in Fig. S11, ESI<sup>+</sup>, and we also listed the repeated test results in Table S1, ESI<sup>+</sup>. Thus, we attributed the high conductivity of the 2D HATP films to long-range  $\pi$ -orbital overlapping in the network.<sup>21</sup> These devices based on 2D HATP polymeric films are stable and their properties do not degrade after many measurement cycles.



Fig.3 (a) A schematic of the back-gated FET. (b) Transfer characteristics of the FET device based on the HATP polymeric films (drain voltage  $V_{ds}$  = -5 V); Inset: optical micrograph of the representative FET.

We calculated the conductivity of the 2D HATP polymeric films using the  $I_{ds}$  vs.  $V_{ds}$  curve according to the following Equation of  $\sigma = L/R * s$ .  $\sigma$  is the conductivity of 2D HATP polymeric film, *R* is the resistance, s is the cross section area and *L* is the length of 2D HATP polymeric film. The calculated conductivity is about 0.91 S cm<sup>-1</sup>. Besides, we also measured currents at both drain and source terminals at the same time, the matching currents of which confirmed that the currents come from 2D HATP polymeric film and not from any leakage channel (Fig. S12, ESI<sup>+</sup>). Because the HATP polymeric films have a wide optical absorption band at UV-Vis-NIR region (Fig. S13, ESI<sup>+</sup>). The electrical photoresponse of the same device under the 980nm laser with a power density of 18.3 mW cm<sup>-2</sup> was shown in Fig. 4a. Meanwhile, we can observe an increase of current after illumination (Vgs = 0 V). The geversible and gener photoresponse was stable without obvious degradations over many measurement cycles, even in the presence of oxygen and moisture in the air (Fig. 4b).<sup>22</sup> We also measured I-V curve of a device after a storage of 10 days in air, which showed no loss of conductivity (Fig. S14, ESI<sup>+</sup>). To ensure that the photocurrent is through the HATP polymeric films, we tested a number of devices with the same metal channels but without the HATP polymeric films. All of these control devices behave as open circuits with no photoresponse (Fig. 4a). The photocurrent ( $I_{ph}$  = Ilight - Idark) increases with increasing light intensity (P) (Fig. 4c). The calculated responsivity  $(R)^{23}$  is up to 160 mA W<sup>-1</sup> under 980 nm light irradiation ( $R = I_{ph}/(P * S)$ ). With the increase of light power, a saturation of the drain current is observed. A fitting of the *I<sub>ph</sub>-P* curve in the sublinear region was obtained by equation of  $I_{ph} = b * P^{\alpha}$ . Here, b is a parameter related to responsivity, *P* is the laser power density and  $\alpha$  is an exponent, the value of which is between 0~1 and provides information of traps present in the device. The power function fitting gives  $\alpha$  equaling 0.69, which is consistent with models of surface trap states on the polymeric films.<sup>24</sup> In this model, the photocurrent comes from pumping electron to surface traps and thus leaving hole carriers in the valence band for conduction. Under high power illumination, saturation of the trap states and increased recombination rate of photoexcited carriers limit the photocurrent.<sup>22, 25</sup>



**Fig.4** Photocurrent characteristics of the HATP polymeric films. (a) *I–V* curves in dark and under 980 nm laser illumination with sweep voltage (-1~1 V). (b) Photoresponse of the HATP polymeric films at  $V_{ds} = -1$  V,  $V_{gs} = 0$  V and an illumination power of 18.3 mW cm<sup>-2</sup>. (c) Laser intensity-dependent photoresponse at  $V_{ds} = -1$  V,  $V_{gs} = 0$  V; inset: the corresponding fitting curve of photocurrent versus laser power intensity. (d) Comparison of the wavelength-dependent spectrum (red circle) with the UV-Vis absorption spectrum (blue line) of HATP thin films. The illumination wavelength was scanned from 200 to 1000 nm in 10 nm steps,  $V_{ds} = 1$  V,  $V_{gs} = 0$  V.

To confirm the important role of HATP polymeric films in device photoconductivity, we carried out wavelength-dependent measurements<sup>26</sup> using light from a xenon lamp with a monochromator to select the wavelength range. Based on the device photocurrent, we calculated the responsivities to represent the intrinsic photosensitivity of the device. The responsivity as a function of light wavelength from 200-1000 nm is shown in Fig. 4d ( $V_{gs} = 0$  V,  $V_{ds} = 1$  V, light intensity = 0.1~10

#### COMMUNICATION

mW cm<sup>-2</sup>, W = 1 mm,  $L = 180 \mu$ m). The peak in the responsivity spectrum (about 4 A W<sup>-1</sup>) of the device is at around 320 nm, roughly matching that of the UV-Vis absorption spectrum of the HATP polymeric films. Notably, the whole responsivity curve does not exactly match the shape of the UV-Vis spectrum, suggesting that lights of different wavelengths have different efficiencies in pumping electrons to the trap states.

### Conclusions

In summary, we synthesized a large-area 2D HATP polymeric film using Langmuir–Blodgett method and constructed a device of FET configuration. We systematically studied the photoelectric properties of the 2D HATP polymeric films. The device based on thin films of HATP exhibits a broad absorption spectrum from 200 to 1000 nm and a stable and fast response to light. This work highlights the opportunity in developing 2D polymeric organic semiconductors for constructing next generation electronic devices.

# **Conflicts of interest**

There are no conflicts to declare.

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