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# Molecular Weight Engineering in High Performance Ambipolar Emissive Mesopolymers

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Abstract: Mesopolymers, with structural defects free, high solubility and negligible batch-to-batch variation of conjugated polymers, open a new avenue for organic optoelectronics. For example, organic light emitting transistors (OLETs) that integrate the functions of organic light-emitting diodes (OLEDs) and organic fieldeffect transistors (OFETs) together, and are promising devices for next generation display technology and organic electrically pumped laser. However, in most cases, charge transport ability and light emitting strength are contradictory within one conjugated polymer. Therefore, the development of polymeric materials with high carrier mobility and light emitting ability becomes a key challenge. Herein, three low molecular weighted mesopolymers with thienopyrroledione-benzothiadiazole repeating units (meso-TBTF) were obtained by direct arylation polymerization of monomers. Resultant mesopolymers display strong solid state emission and high ambipolar carrier mobility, making them competitive candidates for light-emission devices. The molecular weights of meso-TBTF can be tuned by polymerization temperature, affording products with molecular weights of 3.8 kDa, 6.7 kDa, and 9.9 kDa for device characterization. All mesopolymers exhibit undetectable homo-coupling defects with gradiently-tunable energy levels and better electrical performance over the corresponding high molecular weight polymer. It is found that meso-TBTF with molecular weight of 6.7 kDa has the best electrical performance with an average mobility of 5.65 x 10<sup>-3</sup> cm<sup>2</sup> V<sup>1</sup> s<sup>-1</sup> for electrons and 1.50 x 10<sup>-2</sup> cm<sup>2</sup>  $V^1$  s<sup>-1</sup> for holes, which are among the highest ambibipolar luminescent polymers. In summary, all mesopolymers have photoluminescence quantum yields (PLQY) of about 50% in solution and 10% in solid state. Polymer light emitting diodes of this material are fabricated to explore its potential use in optoelectronic devices.

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#### Introduction

Semiconducting polymers can be used in multiple fields<sup>[1]</sup> such as organic photovoltaics (OPV),<sup>[2]</sup> field-effect transistors,<sup>[3]</sup> thermoelectricity<sup>[4]</sup> and light-emitting diodes. Organic light emitting transistors (OLETs) that integrate electroluminescent function of OLED and logic function of OFET, are promising device architecture for next generation display technology and organic electrically pumped laser.<sup>[5]</sup> However, in most cases, charge transport ability and light emitting strength are contradictory within one conjugated polymer.<sup>[6]</sup> Therefore, the development of polymeric materials with high carrier mobility and light emitting ability becomes a key challenge. Recently, fruitful results have been achieved by adjusting molecular packing of emissive small molecules<sup>[7]</sup> and enhancing intermolecular charge transfer in emissive polymers,<sup>[8]</sup> e.g., Anthopoulos et al. have achieved a record of 2.4 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for high mobility emissive unipolar polymer.<sup>[8a]</sup> However, there are relatively few examples of ambipolar emissive polymers.<sup>[9]</sup> For example, commercially available materials F8BT possesses well balanced ambipolar mobility with high PLQY around 50%, while OC1C10-PPV possess moderate PLQY with ambipolar mobility which is tested in asymmetric FET devices. Moreover, both materials suffer from relatively low charge carrier mobility. (Scheme 1, for other examples of optoelectronic materials, see Table S1)

Traditional polymerization methods, such as Suzuki, Stille or Negishi cross coupling, suffer from complicated monomer functionalization steps and homo-coupling defects, which may cause performance degradation. Contrast to traditional transition metal catalyzed C-C cross coupling polymerization, direct arylation polymerization (DArP)<sup>[10]</sup> avoids additional steps for preparation of organometallic reagents. Recently, we synthesized mesopolymers with precisely controlled molecular weights, undetectable structural defects and high ambipolar mobility by ligand modulated DArP reactions.<sup>[11]</sup>

Among the characteristics that influence the electrical and optical performance of polymers, molecular weight is one of the most essential parameters.<sup>[12]</sup> Research in different fields such as OFETs,<sup>[11, 13]</sup> and OPVs<sup>[14]</sup> has shown that the change of molecular weight has a great impact on the device performance of semiconducting polymers and oligomers.<sup>[15]</sup> Herein, we carried out molecular weight engineering strategy in thienopyrroledione (TPD), fluorene and benzothiadiazole (BTz) based mesopolymers meso-TBTF. Three mesopolymers with number-average molecular weights of 3.8 kDa, 6.7 kDa, and 9.9 kDa and their corresponding polymer with number-average molecular weight of 15 kDa were synthesized and characterized. All mesopolymers exhibit fine-tuned energy levels with better ambipolar carrier mobility with hole and electron mobilities up to  $1.65 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for holes and  $1.10 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electrons, which is an order-ofmagnitude higher than TBTF polymer. Besides, meso-TBTF (6.7 kDa) exhibits the best performance, which is among the Angewandte Chemie International Edition

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highest in ambipolar luminescent conjugated polymers. Meanwhile, all mesopolymers emitted light with the photoluminescence quantum yields (PLQY) of about 50% in solution and 10% in solid state.



Scheme1. Emissive polymeric materials with field effect mobility in literatures and this work, mobility of OC<sub>1</sub>C<sub>10</sub>-PPV was characterized in organic light emitting transistor with asymmetric architecture.

#### **Results and discussion**

We initiate our study by using the highly planner TPD-based monomer<sup>[16]</sup> thienopyrroledione-benzodiathiadiazole-thieno pyrroledione (TBT) (Scheme S1). To investigate the best DArP reaction condition,<sup>[10a, 17]</sup> the TPD monomer was chosen as the model substrate, instead of the more complicated monomer TBT. We tested the influence of Pd catalyst, ligand and reaction temperature (Table 1). We first optimized the Pd catalysts and ligands that can promote the DArP reactions. Results show that the combination of an activated Pd catalyst, Herrmann's catalyst, and an electron donating ligand, tris(omethoxyphenyl)phosphine, provide the most efficient polymerization. This might due to the activated catalyst favours the C-H activation steps and the electron rich metal centre favours the oxidative addition steps to the electron rich fluorene system. Moreover, results show that reaction temperature can also significantly influence reaction yields and molecular weights.

The desired products were obtained through the aforementioned DArP conditions with dihexyl-dibromofluorene and thienopyrroledione-benzodiathiadiazole-thienopyrroledione segments (Figure 1a). Mesopolymers with number-average molecular weights of 3.8 kDa, 6.7 kDa, and 9.9 kDa were

synthesized by varying reaction temperature from 70  $^{\circ}$ C, 90  $^{\circ}$ C to 110  $^{\circ}$ C. Three mesopolymers possess narrow polydispersity index (PDI) of 1.65, 2.33 and 2.46, respectively. Thermogravimetric analysis (TGA) results show that all materials possess good thermo stability with decomposition temperature over 350  $^{\circ}$ C (Figure S12).

To synthesize the corresponding polymer, bromination of monomer TBT and pinacolboration of monomer fluorene was carried out (Scheme S8 and Scheme S9). After preparing the new monomers, the corresponding polymer was obtained through Suzuki coupling. The number average molecular weight of the polymers was 15 kDa with PDI of 3.1, which is larger than that of mesopolymers (Figure S13).

To gain insight into structural defects in polymer and mesopolymers, a difluorene compound diF was synthesized as the model molecule of the homo-coupling defects. By analysing <sup>1</sup>H NMR, <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy (COSY) spectra, chemical structure of diF was confirmed (**Figure S7** and **Figure S14**). Then the <sup>1</sup>H NMR spectra of **poly-TBTF** and **meso-TBTF** were collected to carry out defect analysis (**Figure 1b**). Mesopolymers synthesized by DArP possess sharp peaks without detectable defects from 7.0 to 7.8 ppm. Meanwhile, **poly-TBTF** has broad peaks with obvious defect peaks. **RESEARCH ARTICLE** 

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Table 1. Optimization of DArP reaction conditions.



<sup>a</sup> Yields are measured from CHCl<sub>3</sub> extracted after standard Soxhlet extraction. <sup>b</sup> No reaction



Figure 1.(a) The synthesis of the meso-TBTF and poly-TBTF.(b) <sup>1</sup>H NMR in aromatic region of diF(In 1,1,2,2-tetrachloroethane-D2), high temperature <sup>1</sup>H NMR in aromatic region of poly-TBTF and meso-TBTF (100 °C in 1,1,2,2-tetrachloroethane-D2).

In order to characterize the optical properties of the materials, we performed the ultraviolet-visible absorption spectra (UV-vis) and photoluminescence (PL) spectra of materials in dilute chloroform solution and on spin-coated thin film on quartz substrates, respectively (Figure 2 and Table 2). According to the UV spectra, redshift in both the absorption peak and absorption edge from solution and film were observed upon the

increase of molecular weight of TBTF, while **poly-TBTF** possesses the highest absorption edge and the narrowest optical band gap. For mesopolymers, the absorption peaks of mesopolymers in solution increased from 514 nm for **meso-TBTF-1** to 540 nm for **meso-TBTF-3**. Similar trend was observed in thin films, which redshifts from 540 nm to 576 nm.

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Figure 2. (a) UV-visible absorption and (b) Photoluminescence spectra of polymer and mesopolymers (s = solution in CHCl<sub>3</sub>, f = spin coated film on quartz). (c) UPS spectra of polymer and mesopolymers on silicon. (d) TBTF in the optimized structures with the values for the LUMO and HOMO performing 5.23 eV and 5.40eV based on B3LYP/6-31G(d).

Table 2.Summarization of optical properties and energy levels										
TBTF	λ <sub>abs</sub> <sup>sol a</sup> (nm)	λ <sub>abs</sub> <sup>film b</sup> (nm)	λ <sub>em</sub> <sup>sol</sup> (nm)	λ <sub>em</sub> <sup>film</sup> (nm)	PLQY <sup>sol</sup> (%)	PLQY <sup>film</sup> (%)	λ <sub>abs</sub> <sup>edge</sup> (nm)	Eg <sup>c</sup> (eV)	LUMO (eV)	HOMO (eV)
Meso-TBTF-1	514	540	613	628	52	10	660.21	1.878	3.916	5.794
Meso-TBTF-2	540	573	618	642	51	9	653.57	1.897	3.973	5.793
Meso-TBTF-3	543	576	611	643	40	9	668.12	1.856	4.017	5.867
Poly-TBTF	510	550	625	660	40	8	674.08	1.839	3.904	5.743

<sup>a</sup> Materials were dissolved in chloroform to form dilute solution of about concentration of 1×10<sup>5</sup>mol/L. <sup>b</sup> 10mg/mL solution of materials in o-DCB were spin coated on quartz to form thin films.  ${}^{c}E_{g}$ = 1240/ $\lambda_{abs}$  edge

The luminance peaks of PL spectra for polymer and mesopolymers with high molecular weight materials also showed obvious redshift both in solution and thin film, which is similar to that of the absorption spectra. Moreover, from the analysis of full width at half maximum (FWHM), all mesopolymers possess red emission with narrower emission bands in solution and thin film relative to poly-TBTF (Figure S15, which is beneficial for light emitting devices with high colour purity. Besides, absolute PLQY value was tested using an integrating sphere are listed (Table 2), the luminescent properties of the polymer and mesopolymers are similar, with about 50% in solution and nearly 10% in solid state.<sup>[18]</sup>

In addition, in order to characterize the band structure of the materials, we combined the results of optical band gap calculated from absorption spectra and ultraviolet photoelectron spectroscopy (UPS) spectra (Figure 2c). All polymer and mesopolymers have similar energy level with low lying LUMO

around -4.0 eV below vacuum and HOMO around 5.8 eV below vacuum, which matches the need of high performance ambipolar or n-type semiconductors. (Cyclic Voltammetry test show similar results. See Figure S17). Furthermore, it was found that molecular weight can affect band gaps and energy levels. Meso-TBTF-2 has the widest, while meso-TPTF-3 has the narrowest band gap among three mesopolymers, with the band gap of 1.897 eV and 1.856 eV respectively. Besides, poly-TBTF possess narrower band gap than all the mesopolymers, reaching a value of 1.839 eV. Meanwhile, with the increase of molecule weights, the LUMO levels of mesopolymers and polymer downshifted from 3.916 eV and 3.973 eV to 4.017 eV. These results demonstrate that by controlling molecular weights, fine tuning of band structure can be achieved in mesopolymers, which is helpful to construct ambipolar or n-type optical electronic devices.

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Figure 3. Transfer (top) and output (bottom) curves of TG/BC OFET devices based on (a, e) poly-TBTF, (b, f) meso-TBTF-1, (c, g) meso-TBTF-2 and (d,h) meso-TBTF-3. Device parameters: channel width/length (W/L) = 10,  $C_i = 3.5 \text{ nF/cm}^2$ .

TBTF	Annealing temperature (°C)	μ <sub>e</sub> (10 <sup>-3</sup> cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	μ <sub>h</sub> (10 <sup>-3</sup> cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	V <sub>T</sub> (V)	I <sub>on</sub> / I <sub>off</sub>
	as cast	0.45	-	+44.0; -	2.6×10 <sup>3</sup> ; -
	150	1.14	0.16	+21.8; -28.5	3.84×10 <sup>3</sup> ; 5.39×10 <sup>3</sup>
Meso-TBTF-1	200	1.70	9.55	+28.4; -58.7	1.52×10 <sup>3</sup> ; 4.88×10 <sup>2</sup>
	250	3.30	12.50	+30.1;-23.5	3.03×10 <sup>3</sup> ; 2.68×10 <sup>2</sup>
Meso-TBTF-2	250	5.65	15.00	+31.1; -36.6	1.07×10 <sup>3</sup> ; 3.29×10 <sup>2</sup>
Meso-TBTF-3	250	6.38	4.83	+30.1; -40.2	1.52×10 <sup>3</sup> ; 3.56×10 <sup>2</sup>
Poly-TBTF	250	0.78	1.17	+17.7; -35.5	3.82×10 <sup>1</sup> ; 1.89×10 <sup>1</sup>

(a) Device parameters: channel width/length (W/L) = 10,  $C_i = 3.5 \text{ nF/cm}^2$ .

Table3. Optimization of annealing temperature and FET performance of polymer and mesopolymers.

To evaluate the charge transport performance of the semiconducting materials, devices with a top-gate/bottomcontact (TGBC) architecture were fabricated. Firstly, 20 nm thick gold electrodes with a channel width/length ratio of 10 were patterned on glass substrates by thermal evaporation. Then in a glove box, *o*-DCB solutions of materials with a concentration of 10 mg/mL were spin coated on source-drain electrodes patterned glass substrates. Then, it was subjected to thermal annealing at certain temperature. After that, PMMA insulating layer<sup>[19]</sup> with the capacitance of 3.5 nF/cm<sup>2</sup> was prepared by spin coating and thermal annealing. Lastly, 150 nm of patterned aluminum as the gate electrode was deposited on PMMA insulating layer in vacuum.

We chose **meso-TBTF-1** as an example of **meso-TBTF**, and tested the charge transporting properties of as cast and annealed thin films (**Table 3** and **Figure S19**).The mesopolymer in as cast thin film only showed unipolar electron mobility of less than  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. As the annealing

temperature increased to 150 °C, the material exhibited average hole mobility of  $1.60 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the n-type performance is also improved by an order of magnitude to 1.14  $\times$  10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. When the material was annealed and treated at 200 °C, average hole mobility of 1.0  $\times$  10<sup>-2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and electron mobility of 1.70 x  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was observe. The annealing temperature of 250 °C produced the most remarkable performance of the p-type average mobility of 1.25  $\times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and n-type of 3.30  $\times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The best condition was introduced into other polymer and mesopolymers (Figure 3 and Table 3). Results show that all mesopolymers have better mobility than poly-TBTF, and mesopolymers meso-TBTF-2 and meso-TBTF-3 with molecular weights of 6.7 kDa and 9.9 kDa possess the average mobility up to  $6.38 \times 10^{-3}$  $\text{cm}^2$  V<sup>-1</sup> s<sup>-1</sup> for electrons and 1.5 × 10<sup>-2</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes, which is one order of magnitude higher than the performance of poly-TBTF.

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This result is likely due to the fact that mesopolymers have lower homo-coupling defect sites than poly-TBTF. Besides, meso-TBTF-2 with the molecular weight of 6.7 kDa showed the best hole transporting ability with the average mobility of 5.65 x  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for electrons and 1.50 ×  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for holes. Meso-TBTF-3 with the molecular weight of 9.9 kDa showed the charge transporting ability with the average hole-electron mobility both reaching 10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. For meso-TBTF-3 with a molecular weight of 9.9 kDa, the n-type performance is enhanced, while the p-type mobility decreases obviously. Results show that molecular weights influence the properties of ambipolar emissive mesopolymer mainly in the way that influencing the balance of electron and hole mobility. With the increase of molecular weight, n-type mobility of mesopolymer increases and p-type mobility decreases. This phenomenon matches the changing trends of band structures characterized by UPS experiments. In general, several mesopolymers with various molecular weights of TBTF showed balanced ambipolar mobility with the the average hole and electron mobility are up to  $5.65 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and  $1.50 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and the best performance of hole-electron mobilities are over  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. which is the best performance of ambipolar red emissive conjugated polymers<sup>[20]</sup> (For comparison of FET performance between commercially available F8BT and meso-TBTF-2, see Figure S20 and Table S4).

In order to further demonstrate the electroluminescence properties of TBTF molecules, OLED devices based on meso-TBTF-2, which had good photoluminescence efficiency and charge transporting properties, was fabricated. We chose Indium Tin Oxide (ITO, 25 nm) and Lig/AI (100 nm) as anode and cathode, while poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT-PSS, 25 nm) and 2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole (TPBi, 25 nm) as the holetransporting layer and electron-transporting layer, respectively. The active layer was formed by spin-coating the 10 wt % solution of TBTF in 4,4'-bis(9-carbazolyl)-1,1'-biphenyl (CBP, 25 nm) (Figure 4a). Figure 4 shows the current density-voltageluminance curve and electroluminescence spectrum of the OLED device. The threshold voltage of the device was 15.1 V, and the maximum brightness was 296.6 cd m<sup>-2</sup>. EL spectrum (Figure 4b) shows that the device exhibited EL with the maximum wavelength of about 680 nm which is red-shifted and broadened relative to the PL spectra (618 nm in solution and 642 nm in solid state, Figure 2b). These results show that TBTF polymer and mesopolymers have the potential of being further used in optoelectronic devices such as organic light emitting transistors.[21]

The surface morphology of the films was characterized by atomic force microscopy (AFM) and two-dimensional grazing incidence wide-angle X-ray diffraction (GIWAXS). Figure S21 shows the AFM bright field images of the material films at device fabricating conditions. All film samples from mesopolymers show ultra smooth surfaces with Rq values between 0-0.60 nm, while polymer films are uneven with the Rq of 0.83 nm. More specifically, as the annealing temperature increases, the roughness of the **meso-TBTF** decreases and the Rq values decreases from about 0.6 nm at untreated to 0.40 nm at 250 °C, which shows that annealing is beneficial to the improvement of device performance and the result is consistent with the characterization of OFETs. In GIWAXS analysis (Figure S22),all annealed mesopolymer films showed an obvious (010) diffraction peaks in out-of-plane direction, while the annealed

polymer film has weaker (010) peaks. These results show that the polymer does not prefer to form a highly crystalized thin film compared to mesopolymers and all polymer and mesopolymers prefer to form thin film with face-on orientation.



Figure 4.(a) The current density-voltage-luminance curve (inner picture: device structure and energy level of OLED device. Energy levels: ITO -4.8 eV, PEDOT:PSS HOMO -5.2 eV, LUMO -3.3 eV, TBTF:CBP HOMO -5.8 eV, LUMO -4.0 eV, TPBI HOMO -6.2 eV, LUMO -2.7 eV, Liq/Al -4.3 eV) and (b) electroluminescence curve (inner picture: photos of working OLED devices) of the OLED devices.

#### Conclusions

Herein we carried out direct arylation polymerization for ambipolar emissive polymers comprising TPD, fluorene and BTz units, which possess less homo-coupling structural defects and better performance over Suzuki-reaction-synthesized polymer. Meanwhile, molecular weight engineering strategy was carried out and three mesopolymers with the molecular weight of 3.8 kDa, 6.7 kDa and 9.9 kDa were synthesized and characterized. Three mesopolymers show similar red emissive properties with PLQY up to 52 % in solution and 10 % in solid thin film. Moreover, band structures and energy levels of three mesopolymers can be finely-tunable, which finally influence the OFET device performance. The average hole and electron mobility are up to 5.65 x  $10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 1.50 x  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup>  $s^{-1}$  and the best hole and electron mobility are up to  $1.10 \times 10^{-2}$  $cm^2 V^{-1} s^{-1}$  and 1.65 x 10<sup>-2</sup>  $cm^2 V^{-1} s^{-1}$  for meso-TBTF-2, which is the best performance in red emissive ambipolar conjugated polymers. Besides. OLED device fabricating shows excellent potential in optoelectronic devices for these mesopolymers.

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### **Conflict of interest**

The authors declare no conflict of interest.

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# **Entry for the Table of Contents**

# **Research Article**

Molecular weight engineering of redemissive mesopolymer with no detectable homo-coupling defects, fine-tuned energy level and better bipolar mobility was carried out. OFET and OLED based on the materials mark application potential in optoelectronic devices.



XiaofeiGuo, Yihan Zhang, Yongxu Hu, Jiaxin Yang, Yang Li, Zhenjie Ni, Huanli Dong, Wenping Hu

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