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ARTICLE TYPE

A series of blue supramolecular polymers with different counterions for polymer light-emitting diodes **†**

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A series of blue supramolecular polymers with different counterions based on host-guest interactions was developed for polymer light-emitting diodes. It was found that the counterions play important roles on the resulting materials' ¹⁰ supramolecular interactions as well as the device performance.

Supramolecular polymers have attracted considerable attention due to their unique properties and potential applications in the past decade. ¹ Different from traditional polymers, the ¹⁵ supramolecular polymers are generally formed from the monomeric units through noncovalent, mechanically interlocked structures, but show good solution processibility and comparable mechanical properties in the bulk as those traditional polymers.² Consequently, the supramolecular polymers can be potentially ²⁰ promising candidates for solution processed organic devices, such as polymer light-emitting diodes,³ polymer solar cells⁴ *etc.*, which can combine both the advantages of small molecular ⁵ and polymer optoelectronic materials.⁶ For example, supramolecular light-emitting polymers (SLEPs), based on the host-guest ²⁵ interaction between dibenzo[24]crown-8 (DB24C8) and

- dibenzylammonium salt (DBA) derivatives, have been developed and applied as emission layer in PLEDs, where the SLEPs exhibited good film forming ability and comparable device performances to those traditional light-emitting polymers.⁷ Since ³⁰ the DBA are usually used as the guests, there are a lot of
- ³⁰ the DBA are usually used as the guests, there are a for or compensating counterions among these host-guest supramolecular polymers. It has been reported that these counterions can not only affect the supramolecular interactions of these supramolecular materials,⁸ but also play important roles on

³⁵ the device performance of the optoelectronic materials.⁹ Thereby, to further develop high performance host-guest interaction based supramolecular optoelectronic materials, it is critical to understand the insight of the impact of counterions on the resulting materials' supramolecular interactions and the device ⁴⁰ performance.

Herein, we developed a series of blue-emitting SLEPs based on the host-guest interaction of DB24C8 and DBA functionalized conjugated oligomers.^{7, 10} The DB24C8 functionalized fluorenedibezothiophene-S,S-dioxide (SO) co-oligomer FSO was 45 developed as the host. The SO unit is a promising building block

for organic blue-emitting materials, because it can greatly enhance the efficiency and electroluminescence (EL) spectra stability of the resulting materials.¹¹ The DBA functionalized fluorene-based oligomers FX with different counterions (FP6-, ⁵⁰ Br-, BIm4-) were developed as the guests. The influences of different counterions on the resulting linear supramolecular polymer FSO-FX's supramolecular interactions, thermal properties, optical physical properties as well as device performance were studied.



Scheme 1. Chemical structures of host momomer FSO and guest momomers FX and Schematic illustration of the formation of FSO-FX at high concentration by self-assembly.

The details of the synthesis of the host and guest oligomers ⁶⁰ were demonstrated in the supporting information, where a palladium-catalyzed Suzuki cross-coupling reaction produced the host monomer FSO in a high yield of 72%. The guest monomer FPF6 was prepared according to the reported procedure.7a The guest monmomers FX with different counterions were obtained ⁶⁵ from a ion-exchange procedure by adding an excess of a salt with the counterion of interest into a FPF6 methanol/tetrahydrofuran (THF) solution with vigorous stirring, followed by dialysis in water, yielding FBr, and FBIm4 in 80%, and 74%, respectively. 1H NMR studies analysis confirmed quantitative replacement by

⁷⁰ Br- and BIm4-(Fig. S1, ESI*). FPF6 and FBr have excellent solubility in common organic solvents such as THF, CH3CN, and dimethylsulfoxide (DMSO), etc., however, the solubility of FBIm4 was poor. More than 10 mg of FPF6 and FBr can be readily dissolved in 1 mL of DMSO at room temperature to give a clear solution, while 1 mL of DMSO is only able to solve around 1 mg of FBIm4. The concentration-dependent 1H NMR studies of FSO and FX (Fig. 1, S2 and S3, ESI*) provided important insights into their self-assembly behavior by host-guest interaction in solution. The interactions of FSO and FX were fast-s0 exchange complexations.¹² As shown in Fig. 1, S2 and S3, at low

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concentrations, the benzyl protons H had one set of well-defined signals for the cyclic and linear species. As the concentrations increased, the signals for the cyclic dimer decreased, and the signals for the linear increased. At high concentrations, all the ⁵ signals become broad, confirming the formation of high molecular weight aggregates driven by host-guest interactions.^{7, 12, 13}



Fig. 1 The stacked ¹H NMR spectra (600 MHz, CDCl₃/CD₃CN 1/1, v/v, ¹⁰ 25 □) of solutions of FSO and FBr at different concentrations: a) FSO, h) FBr, and equimolar solutions b) 1, c) 2, d) 5, e) 10, f) 20, and g) 30mM. u: uncomplexed monomer, c: cyclic polymer, and l: linear supramolecular polymer.

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- The thermal properties of the resulting FSO-FX were studied 15 by the differential scanning calorimetry (DSC). FSO-FPF₆ exhibited a high glass transition temperature (T_{p}) of 103.2 °C, which was comparable to those of similar traditional conjugated polymers.^{11a} Interestingly, the T_g of FSO-FBr and FSO-FBIm₄ was dramatically lower than those of FSO-PF₆. The concentration 20 dependence of the solution viscosity provides important information on the aggregation behavior of the supramolecular polymers. The double logarithmic plots of specific viscosity vs. the monomer concentration of all the resulting FSO-FX were shown in Fig S5, ESI*. At low concentrations, the curves for 25 FSO-PF₆, FSO-FBr, and FSO-FBIm₄ had slopes of 0.18, 0.19, and 0.32, respectively, which is characteristic for noninteracting assemblies of constant size.¹⁴ As the concentrations increase, the curves exhibited a sharp rise with slopes of 2.14, 2.02, and 2.35 for FSO-PF₆, FSO-FBr, and FSO-FBIm₄, respectively, indicating
- ³⁰ the formation of linear supramolecular polymers. The critical polymerization concentrations (CPC), corresponding to the transition from the cyclic species to linear supramolecular polymers, are approximately 13, 18, and 15 mmol L⁻¹ for FSO-PF₆, FSO-FBr, and FSO-FBIm₄, respectively. The viscosity study ³⁵ results show that the resulting FSO-FX exhibit good film
- formation capabilities for solution processed PLEDs applications. The absorption and photoluminescent (PL) spectra of the monomers FSO and FX and the supramolecular polymer FSO-FX in solid films are shown in Fig. 2. The host FSO exhibited similar
- ⁴⁰ UV-visible absorption and PL spectra to those of typical fluorene-SO co-oligomers.^{11a} The guest monomers FX showed similar absorption, but more pronounced emission tails at around 500-600 nm compared to those of typical fluorene trimmers,¹⁵ which is probably due to the strong intermolecular interactions

45 caused by the ionic groups among them.^{3b, 16} Compared to FPF₆ and FBIm₄, the FBr showed a much broader emission, indicating a much stronger interchain interaction corresponding to the smaller size of Br, while the interchain interactions of FPF₆ and FBIm₄ are largely suppressed by the "spacer" effect of larger FP_6 ⁵⁰ and BIm₄⁻ counterions.^{9b} The photophysical properties of the resulting supramolecular polymer FSO-FX were also investigated. Interestingly, despite of different counterions, all the FSO-FX exhibited similar Uv-vis and PL spectra, and the emission tails at around 500-600 nm of the FX guests completely disappeared. 55 That indicates the strong intermolecular interactions of FX were greatly suppressed in FSO-FX, probably due to the host-guest interactions, which were desirable for PLEDs application. Consequently, the counterion-dependent PL quenching of those traditional conjugated polyelectrolytes was not observed among 60 these supramolecular materials,^{16a} and all the FSO-FX show similar high quantum efficiencies, which are 53, 47, and 50% for FSO-FPF₆, FSO-FBr, and FSO-FBIm₄, respectively.



Fig. 2 (a) UV-visible absorption and (b) PL spectra of host FSO, guest FX and FSO-FX in thin films.

- The EL properties of the FSO-FX were investigated in OLEDs with device configuration of indium tin oxide (ITO)/ poly(3,4ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS)/FSO-FX/Al, where PSO-FX were used as the 70 emission layer and the high work-function metal Al was used as the cathode. It should be noted that most of traditional lightemitting materials exhibited very poor device performance in the devices with stable high work-function metal cathodes (such as Au, Ag, Al etc.) due to the large electron injection barrier.^{16, 17} 75 Nevertheless, the highly polar charged groups and counterions among FSO-FX may endow them good interface modification capabilities and thus allow the using of high work-function metals as the cathode in devices.9 Indeed, as shown in Table 1 and Fig. 3, all the FSO-FX exhibited good device performance 80 with maximum luminance efficiencies (LEs) more than 1 cd/A,
- which is much higher than that of their polyfluorene analogue in the same device configuration (~0.01 cd/A). ¹⁷ Moreover, compared to previously reported all-fluorene based blue-emitting SLEP,^{7a} all the FSO-FX also exhibited much improved device
- ⁸⁵ performance. For example, the device with FSO-FPF₆ as emission layer exhibited a turn voltage (V_{on}) of 5.5 V, a maximum brightness (L_{max}) of 281 cd m⁻², and a maximum *LE* of 2.60 cd A⁻¹, which is much better than those of our previously reported fluorene-based SLEP with a V_{on} of 10.0 V, a L_{max} of 79.6 ⁹⁰ cd m⁻², and a maximum *LE* of 0.49 cd A^{-1,7a} This is due to the
- incorporation SO building blocks, which will cause efficient charge transfer among the SLEPs and enhance the hole/electron recombination ratios in the devices, resulting in the greatly

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improved device shown in Fig. 3, F at around 474 polyfluorene h 5 disappeared, ¹⁸ wh conjugated polym	performances a FSO-FPF ₆ exhib nm and the omopolymers tich is similar thers. ¹¹ In order to	is well as colour ited a pure blue-en excimer emission in the long to those SO-based to investigate the	stability. ^{11c} As mission peaked on of typical wavelength I blue-emitting colour stability	of the FSO-F current were of accelerating ap 10 of FSO-FPF ₆ at 474 nm, ind	X, EL spectra de carried out (Fig. S pplied current fron were almost uncha licating its exceller	ependences upon 7, ESI*). It was f a 2 mA to 20 mA, inged with emission at colour stability.	varied applied ound that with the EL spectra on peak located
Table 1 EL Perfor	rmance of the F	SO-FX in the devi	ces with configu	ration of ITO/PEI	OOT:PSS/emission	layer/Al.	
	$V_{\rm on}[{ m V}]^{ m a)}$	$L[cd m^{-2}]^{b)}$	LE $[cd A^{-1}]^{c)}$	$L_{max}[cd m^{-2}]$	$LE_{max}[cd A^{-1}]$	EQE _{max} (%)	$V_{\rm oc}[V]$
FSO-FPF ₆	5.5	86	0.92	281	2.60	1.78	0.96
FSO-FBr	6.0	85	0.84	435	1.14	0.74	0.82
FSO-FBIm ₄	4.7	151	1.51	777	1.53	1.24	1.02
^{a)} The turn-on vol at a current densit	tage at which luty around 10 mA	iminescence reach A cm ⁻² .	1 cd m ⁻² . ^{b)} Brig	htness at current of	density around 10	mA cm ⁻² . ^{c)} Lumin	ous efficiency
The EL proper ¹⁵ were also investig PF ₆ and FSO-FB FSO-FBr showed its PL emission,	rties of the FSC gated. It was fo BIm_4 were simil a largely red-s which were attr	D-FX with differe und that the EL s ar with their PL hifted EL emission ibuted to the stron	ent counterions pectra of FSO- spectra, while on compared to ng electrostatic	50 further develo supramolecula applications.	op high performar ar optoelectronic	nce host-guest int materials for	eraction based optoelectronic

attractions in FSO-FBr. Since it has been found that counterions 20 can largely affect the electron injection properties of those traditional conjugated polyelectrolytes,9 photovoltaic measurements were performed to determine the build-in potential across the devices, which can reflect the barrier height of the charge injection in devices and hence the charge injection 25 properties of the corresponding materials.¹⁶ It was found that the open-circuit voltage (V_{oc}) ranked in the order of FSO-FBr (0.82 V) < FSO-FPF₆ (0.96 V) < FSO-FBIm₄ (1.02V), which is consistent with the turn-on voltage (V_{on}) order of the OLED devices (Table 1). Among all the FSO-FX, FSO-FBIm₄ exhibited ³⁰ the best comprehensive device performance with the lowest V_{on} of 4.7 V, a LE of 1.51 cd A^{-1} with a L of 281 cd m^{-2} at the current density around 10 mA cm⁻² and a more pure blue-emission compared to FSO-PF₆ and FSO-Br. Considering the relative high PL quantum efficiencies of these materials, their device 35 performance may be further improved if used in the multilayer

PLEDs with suitable carrier transporting and blocking layers.



Fig.3 a) J-L-V and b) EL spectra in the device with configuration of ITO/PEDOT:PSS/FSO-FX/Al.

- In summary, a series of supramolecular polymers incorporating 40 SO units and containing different counterions were developed by exploiting host-guest interactions. It was found that both the supramolecular interaction behaviour and the device performance of the resulting supramolecular polymers are strongly influenced
- 45 by the counterions. Moreover, it was interestingly found that counterion-dependent PL quenching, which is a common phenomenon in the traditional conjugated polyelectrolytes, can be effectively suppressed among these supramolecular polymers. Our these preliminary studies provide useful information to

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Notes and references

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