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# 1, 6- and 2, 7-*Trans*- $\beta$ -Styryl Substituted Pyrenes Exhibiting Both Emissive and Semiconducting Properties in the Solid State

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**ABSTRACT:** Molecular materials that are both emissive and semiconducting are highly demanding for organic optoelectronics. In this paper, we report the synthesis, emissive and semiconducting properties of 1, 6 and 2, 7-*trans-β*-styryl substituted pyrenes (**16PyE** and **27PyE**). The results reveal that both **16PyE** and **27PyE** are emissive and semiconducting in the solid state. The fluorescence quantum yields of crystalline solids of **16PyE** and **27PyE** were determined to be 28.8% and 27.4%, respectively. Microrods of **16PyE** and output curves of the respective organic field effect transistors (OFETs), thin films of **16PyE** and **27PyE** were found to show *p*-type semiconducting property with hole mobility up to  $1.66 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Such dual functions (emissive and semiconducting) of **16PyE** and **27PyE** can be ascribed to the unique intermolecular interactions and packing within crystals of **16PyE** and **27PyE**.

## ■ INTRODUCTION

Various conjugated molecules and macromolecules have been investigated for either highly emissive materials or semiconductors with high charge mobilities.<sup>1–19</sup> Such emissive materials and organic semiconductors have been utilized to fabricate OLEDs (organic light-emitting diodes) and OFETs (organic field-effect transistors), respectively. The performances of OLEDs and OFETs have been improved significantly thanks to the developments of i) the emissive materials with high quantum yields and tunable emitting colors<sup>20–26</sup> and ii) p-, nand ambipolar semiconductors with high charge mobilities.<sup>1–8,</sup>  $^{27-43}$  Meanwhile, molecular materials that are both emissive and semiconducting are highly demanding for applications in organic light emitting field-effect transistors15-17, 44-47 and organic lasers.48,49 However, it still remains challenging to rationally devise such dual functional materials. This is because organic semiconductors usually entail intermolecular  $\pi$ - $\pi$ stacking to generate conducting pathways, but such  $\pi$ - $\pi$  interactions are normally detrimental to light-emissions due to the formation of excimers or exciplexes.<sup>50–53</sup> Nevertheless, a number of dual functional materials with both emissive and semiconducting properties have been reported in recent years.54-58 For instance, some of us found that the cruciform molecule, 2,2'-((5,5'-(3,7-dicyano-2,6-bis(dihexylamino)benzo-[1,2*b*:4,5*b*']-difuran-4.8 divl)bis(thiophene-5,2diyl))bis(methanylylidene)) dimalono- nitrile (BDFTM)<sup>55</sup> and the naphthalene diimide derivatives<sup>56, 57</sup> exhibited both emissive and semiconducting properties in the solid states, but their

charge mobilities were low. Heeger, Hu and their coworkers

reported 2,6-substituted anthracene molecules which were

found to be not only highly emissive, but also p-type semicon-

ducting with single crystal mobility of  $34 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ .<sup>58</sup> These results clearly demonstrate that intermolecular interactions and orientations are critical for molecular solids to be strongly emissive and semiconducting simultaneously. But, the clear structure-property correlation has been not yet established for such dual functional materials.

In this paper, we report 1, 6- and 2, 7-trans- $\beta$ -styryl substituted pyrenes (16PyE and 27PyE in Scheme 1) for the development of molecular materials exhibiting both emissive and semiconducting properties. The molecular design is based on the following considerations: i) pyrene derivatives can be emissive in both solution and solid state, and they can also exhibit excimer emission under certain conditions, <sup>59-60</sup> ii) semiconductors with high hole mobilities have been reported with pyrene derivatives,  $^{61-67}$  and iii) the incorporation of  $\beta$ -styryl units into the pyrene core can alter the intermolecular interactions so that the resulting solids show both emissive and semiconducting properties simultaneously.<sup>67</sup> The results reveal that the crystalline solids of 16PyE and 27PyE are dual functional with fluorescence quantum yields and hole charge mobilities up to 28.8% and 1.66 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, respectively. Moreover, emissive microrods of 16PyE and microplates of 27PyE exhibit outstanding optical waveguide behaviors.

# RESULTS AND DISCUSSIONS

Synthesis and crystal structures. Compounds 16PyE and 27PyE were successfully obtained by the respective Pd-catalyzed coupling reactions (see Scheme 1) of 1, 6-dibromopyrene and 2, 7-dibromopyrene with *trans-\beta*-styryl boronic acid, followed by recrystallization from toluene, in high yields (>80%). Both 16PyE and 27PyE show poor solu-

bility in most organic solvents, and they are only dissolved in hot DMF and aromatic solvents. The thermogravimetric analysis (see Figure S1) reveals that both **16PyE** and **27PyE** are thermally stable below 250 °C.

Scheme 1. Chemical structures of 16PyE and 27PyE and their synthetic approaches.



Single crystals of 16PyE and 27PyE suitable for X-ray analvsis were obtained and their crystal structures were successfully determined. Figure 1 shows their molecular structures and intermolecular arrangements. Both 16PyE and 27PyE adopt *E*-conformations, and the phenyl groups in **16PyE** and **27PyE** are not coplanar with the respective pyrene rings, forming dihedral angles of 18.46° and 32.42°, respectively. As shown in Figure S2, short interatomic C...H' and C...C' contacts in the range of 2.855-3.260 Å are observed for 16PyE. Apart from the multiple short interatomic C...H' (2.811-2.850 Å) contacts, intermolecular C-H... $\pi$  (2.848 Å) interactions are observed for 27PyE (see Figure S3). Notably, the neighboring pyrene units are not parallel and no intermolecular *face-to-face* arrangements are detected; instead the neighboring pyrene units are inclined to each other with dihedral angles ranging from 25.51° to 34.30°. Molecules are relatively densely packed with packing indexes of 0.686 and 0.715 within crystals of 27PyE and 16PyE, respectively.<sup>68</sup> As to be discussed below, such intermolecular interaction and arrangements make these molecular materials be semiconducting and emissive simultaneously. The multiple intermolecular interactions can endow 16PyE and 27PyE in the solid state with semiconducting property, whereas the fact that the neighboring pyrene and phenyl units are not in *face-to-face* orientations is expected to keep 16PyE and 27PyE being emissive in the solid state.



Figure 1. (From *left* to *right*) Molecular structures, dihedral angles between the respective benzene ring and the pyrene core, and the intermolecular arrangements of 16PyE (*up*, a-c) and 27PyE (*down*, d-f).

**HOMO/LUMO energies.** As shown in Figure S4, **16PyE** and **27PyE** show one quasi-reversible oxidation wave at 0.82 V and 0.98 V ( $E_{ox}$ .<sup>1/2</sup>, vs. Fc/Fc<sup>+</sup>), respectively. The respective

onset oxidation potentials ( $E_{ox}$ , onset, vs. Fc/Fc<sup>+</sup>) of **16PyE** and **27PyE** were measured to be 0.84 V and 0.86 V, respectively. Based on the onset potentials, HOMO energies were estimated to be -5.64 eV for 16PyE and -5.66 eV for 27PyE, respectively. Figure S5B shows the absorption spectra of 16PyE and 27PyE in the solid states. 16PyE absorbs strongly at 420 nm and 468 nm, whereas the maxima absorptions of 27PyE are blue-shifted to 336 nm and 351 nm (see Table 1). Furthermore, the onset absorptions of 16PyE and 27PyE were determined to be 521 and 465 nm, respectively. Thus, the respective optical bandgaps of 16PyE and 27PyE were estimated to be 2.38 eV and 2.67 eV. Accordingly, the LUMO energies of 16PyE and 27PyE were calculated to be -3.26 eV and -2.99 eV, respectively, by using the equation LUMO = HOMO +  $E_{g}^{opt}$ . Obviously, **16PyE** shows lower LUMO level than 27PyE, which can be rationalized as follows: the styryl substitution at 2,7-positions is expected to have less perturbation on the electronic properties of pyrene since nodal planes pass through the 2,7-positions in both the HOMO and LUMO orbitals of pyrene.<sup>59</sup> However, the styryl substitution at the 1,6positions of pyrene as in 16PyE will elongate the conjugation, and as a consequence the LUMO orbital can be stabilized.



Figure 2. Normalized fluorescence spectra of DMF solutions (A,  $10 \ \mu$ M) and thin films (B) of **16PyE** and **27PyE**.

Emissive and optical waveguiding properties. Both 16PyE and 27PyE are emissive in solutions and solid states. As depicted in Figure 2, solutions and thin films of 16PyE and 27PyE exhibit structured emission bands, and the respective emission maxima, quantum yields and lifetimes are listed in Table 1. The respective emission maxima of 16PyE in solution and solid state are red-shifted in comparison with those of 27PyE. As discussed above, this can be attributed to the fact that substitution at 2,7-positions has less pronounced effects on the electronic structure of pyrene, but the styryl substitution at the 1,6-positions of pyrene can prolong the conjugation which will lead to the red-shift of the fluorescence spectrum. The structured emission bands of 16PyE and 27PyE in the

Table 1. The absorp	tion and fluorescence da	ta of 16PyE and 27PyE
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		Solution				Solid Sta	ite	
	Abs.	PL	$\Phi^{a}$	$<\tau>^b$	Abs.	PL	$\Phi^{c}$	$<_{\tau}>^{d}$
	$\lambda$ (nm)	$\lambda_{em.}(nm)$	(%)	(ns)	$\lambda$ (nm)	$\lambda_{em.}\left(nm\right)$	(%)	(ns)
16PyE	302, 410, 434	463, 485	81.4	2.0	420, 468	526, 565	28.8	2.9
27PyE	323, 338	437, 465, 497	15.2	27.6	336, 351	446, 474, 502	27.4	46.7

 $^{a, c}$  The quantum yields in solutions (5.0  $\mu$ M in DMF) and in the solid states were measured with the Hamamatsu spectrometer C11347 Quantaurus-QY;  $^{b, d}$  Fluorescence lifetimes in solutions (5.0  $\mu$ M in DMF) and in the solid state were measured with the Hamamatsu spectrometer C11367.



**Figure 3.** a, d) PL images of microrods of **16PyE** (a) and microplates of **27PyE** (d) upon excitation with mercury lamp; b, e) PL images upon excitation of microrods of **16PyE** (b) and microplates of **27PyE** (e); c) the corresponding spatially resolved PL spectra of the emissions that are out-coupled at the end of the microrod of **16PyE**; insets show the variation of the peak intensity at 530 nm vs. the propagation distance for microrods of **16PyE**; f) the corresponding spatially resolved PL spectra of the four edges (marked with 1–4) for **27PyE**.

solid states may be relevant to the fact that there is no face-toface intermolecular  $\pi$ - $\pi$  interactions within the crystals of **16PyE** and **27PyE**, and as a result the formation of excimers is not favorable. As listed in Table 1, the average fluorescence lifetimes of **16PyE** and **27PyE** are prolonged in the solid states by comparing with those of **16PyE** and **27PyE** in the respective solutions.

The emission quantum yields ( $\Phi$ ) of **16PyE** in DMF solution and solid state are 81.4% and 28.8%, respectively. Thus, **16PyE** exhibits aggregation caused quenching emission. In the contrary, **27PyE** displays aggregation induced enhanced emission because the emission quantum yield of **27PyE** increase from 15.2% in DMF solution to 27.4% in the solid state. The multiple intermolecular interactions within crystal of **27PyE** are expected to fix the conformation of **27PyE**, thus inhibiting the intramoleuclar motions and enhancing the emission according to previous studies.

The solid state emissions of **16PyE** and **27PyE** endow the crystalline microrods or micro-plates of **16PyE** and **27PyE** with promising optical waveguilding properties. Microrods of

**16PyE** and microplates of **27PyE** were successfully obtained by slowly cooling the respective hot solutions. As shown in Figure 3, the microrods of **16PyE** exhibit intense yellow-green emission when excitation with mercury lamp. Moreover, bright photo-luminescence spots are detected at the ends of the microrods, while the remaining surfaces emit weakly. Such photoluminescence images reveal that these microrods can employ as active optical waveguides. On the basis of electron diffraction pattern shown in Figure S7a, molecules of **16PyE** are packed along the [100] direction (*a*-axis) to form the 1D microrods. Such intermolecular arrangements will enable the emission light generated upon excitation at certain position of the microrod to be propagated along the microrod via energy transfer mechanism.<sup>21, 24, 55, 57</sup>

To investigate the light waveguiding efficiency, the spatially resolved PL spectra were measured by locally exciting the microrod of **16PyE** with a 375 nm laser. Figure 3c shows the photo-luminescence spectra at the end of a single microrod of **16PyE** under the excitations at different positions (Figure 3b, labeled as 1–6). Obviously, the emissions at the

microrod-ends become gradually weak with increasing propagation distances. As depicted in the inset of Figure 3c, the intensity of the out-coupled emission decays almost exponentially by prolonging the propagation distance. By fitting the data,<sup>70, 71</sup> the optical loss coefficient at 530 nm for microrods of **16PyE** was estimated to be 64 dBmm<sup>-1</sup>. Such optical loss can be ascribed to Rayleigh scattering due to defects within microrods; such defects can induce the local variation of refractive index along the microrods.<sup>72–76</sup> As displayed in Figures 2B and S5B, the corresponding absorption and fluorescence spectral overlap is small for **16PyE** in the crystalline state, thus self-absorption can not contribute largely to the optical loss during the light propagation.

The microplates of 27PyE contains two pairs of parallel edges along the [110] and [110] directions, respectively, based on the electron diffraction pattern (see Figure S7c). Figure 3d shows the photoluminescence (PL) image of the microplates of 27PyE. It is clear that the edges of these microplates show brighter blue-emissions than the respective surfaces, indicating that efficient optical waveguiding occurs within microplates of 27PyE. Bright out-coupled blueemissions were detected around the respective mid-points of four edges (marked with 1-4) when the laser beam was focused on the center of the microplate. The PL spectra from the respective areas around the mid-points of four edges were collected (see Figure 3f). As shown in Figure 3f, the emission intensity from the mid-point of edge 1 is almost the same as that of edge 3. Similarly, the emission intensity from edge 2 is rather close to that from edge 4. But, the emission intensities from edges 1 and 3 are slightly higher than those from edges 2 and 4. Figure S7d shows the intermolecular arrangements of 27PvE in the *ab* plane together with PL image of the microplate upon the excitation at the center of the microplate. The photo-luminescence energy from the molecule located at the center of the microplate can be transferred to molecules at the edges. The molecule at the center of the microplate is closer to molecules around the mid-points of the edges, leading to

strong emissions around the mid-points of four edges. The propagation distances from the center of the microplate to the mid-points of edges 1 and 3 are the same. This agrees well with the observation that emission intensity from the mid-point of edge 1 is almost the same as that from edges 3. This also holds true for edges 2 and 4. But, the propagation distance from the center of the microplate to either mid-points of edges 2 or 4 is slightly longer than that from the center of the microplate to either mid-points of edges 1 or 3. This may interpret the observation that emission intensities from the mid-points of edges 1 and 3 are slightly stronger than those from edges 2 and 4.

Thin film semiconducting properties. The semiconducting properties of 16PyE and 27PyE were explored by fabrication of the bottom-gate/bottom-contact OFETs with thin films of 16PyE and 27PyE on OTS (octadecyltrichlorosilane) modified SiO<sub>2</sub>/Si substrate. Thin-films of 16PyE and 27PyE of about 50 nm in thickness were prepared by vapor deposition at different substrate temperatures. The output and transfer curves were measured and the semiconducting performance data were summarized in Table 2.

As shown in Figure 4,  $I_{DS}$  increases by applying the negative  $V_{GS}$ . Thus, both thin-films of **16PyE** and **27PyE** behave as *p*-type semiconductor, being in agreement with the HOMO and LUMO energy levels of **16PyE** and **27PyE** as discussed above. As listed in Table 2, hole mobilities of **16PyE** and **27PyE** increase by enhancing the substrate temperature from 25 °C to 50 °C, but they decrease by further increasing the substrate temperature to 70 °C for both **16PyE** and **27PyE**.<sup>77</sup> In comparison with those of **16PyE**, thin film of **27PyE** exhibits higher mobility and higher  $I_{on/off}$  ratio. The hole mobility can reach 1.66 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> with  $I_{on/off}$  ratio up to 10<sup>8</sup> for thin film of **27PyE** prepared on substrate at 50 °C, whereas the maxima hole mobility for thin film of **16PyE** is only 0.17 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> (see Table 2).

In order to understand the different semiconducting properties of **16PyE** and **27PyE**, their thin films were characterized

Table 2. Hole mobility ( $\mu$ ) including the average and maximum values, current on/off ratio ( $I_{on}/I_{off}$ ) and threshold voltage				
(V <sub>th</sub> ) of OFETs with thin-films of 16PyE and 27PyE at different substrate temperatures.				

	Temp. (Sub.)	$I_{on}/I_{off}$	$V_{th}$	$\mu_{\rm h}({\rm ave.})^{\rm a}$	$\mu_{\rm h}({\rm max.})$	
	[°C]		[V]	$[\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}]$	$[\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}]$	
 16PyE	25	10 <sup>7</sup>	-1520	0.040	0.046	
	50	$10^{6}$	-1520	0.14	0.17	
	70	$10^{6}$	-1015	0.13	0.15	
27PyE	25	10 <sup>7</sup>	-6065	0.56	0.74	
	50	10 <sup>8</sup>	-5560	1.44	1.66	
	70	10 <sup>7</sup>	-5560	0.72	0.89	

<sup>a</sup> The average mobilities were obtained based on more than 10 OFET devices.



**Figure 4.** Output and transfer characteristics of OFETs with thin films of **16PyE** (A, B) and **27PyE** (D, E) deposited on OTS-modified SiO<sub>2</sub>/Si substrate at 50 °C; the channel width (W) and the lengths (L) were 1440 nm and 40 nm, respectively; histograms of device mobility for thin films of **16PyE** (C) and **27PyE** (F) deposited on OTS-modified SiO<sub>2</sub>/Si substrate at 50 °C.

with AFM and XRD. As depicted in Figure 5A, one diffraction peak at  $2\theta$ =5.02° was detected for thin film of **27PyE** deposited at 25 °C. When the substrate temperature was enhanced to 50 °C, the diffraction intensity 5.02° increased, and high order diffractions at  $2\theta = 10.04^{\circ}$ ,  $15.08^{\circ}$  and  $20.22^{\circ}$ emerged concomitantly. The *d*-spacing corresponding to the diffraction at  $2\theta$ =5.02° is 17.5 Å, which is shorter than the molecular length of 27PyE (20.2 Å). Thus, molecules of 27PyE are probably tilted onto the surface of the substrate. The emergence of more diffractions up to fourth orders reveals that the thin film crystallinity increases for 27PyE upon increasing the substrate temperature. The thin film XRD pattern of 27PyE was also compared with that simulated from its crystal structural data (see Figure S9). The signals at  $2\theta$ =5.02°,  $10.04^{\circ}$ ,  $15.08^{\circ}$  and  $20.22^{\circ}$  match well with the 002, 004, 006 and 008 diffractions, respectively. The appearance of these diffractions manifest that molecules of 27PyE are orderly stacked along the c-axis within thin film on substrate at 50 °C. However, these diffractions were weakened after further increasing the substrate temperature to 70 °C (see Figure 5A). These XRD data are in good agreement with the fact that thin film hole mobility firstly increases by enhancing the substrate temperature to 50 °C, but it decreases after further boosting the

substrate temperature to 70 °C. In comparison, no diffractions were observed for thin films of **16PyE** deposited at different temperatures as shown in Figure 5B. This agrees with the fact that thin film of **16PyE** possesses relatively low hole mobility.

Figure 6 depicts the AFM images of thin films of **27PyE** and **16PyE** deposited at different temperatures. It is clear that layered structures were formed after the substrate was heated to 50 °C, and grain size was incremented from ca. 450 nm for thin film deposited at 25 °C to ca. 1100 nm. However, the grain size was reduced to ca. 600 nm and moreover boundary areas emerged among the grains for thin film of **27PyE** deposited at 70 °C (see Figure 6). Such thin-film morphological alteration agrees well with the thin film semiconducting performance of **27PyE** at different substrate temperatures (see Table 2).

For thin films of **16PyE** at different substrate temperatures, no layered structures were detected. But, the grain size increased by enhancing the substrate temperatures. It is expected that large grains are beneficial for charge transporting. For thin film of **16PyE** deposited at 70 °C, there are obviously boundary areas among the grains. The presence of boundary areas is detrimental for charge transporting.



Figure 5. XRD patterns of thin-films of 27PyE (A) and 16PyE (B) deposited at different substrate temperatures.



Figure 6. AFM images of thin-films of 27PyE and 16PyE deposited on OTS-modified SiO<sub>2</sub>/Si substrates at different temperatures.

In addition, the bottom-gate/top-contact OFETs with crystalline microrods of 16PyE and microplates of 27PyE were fabricated with the technique reported previously<sup>78,79</sup> (see Supporting Information), and the respective transfer and output characteristics were depicted in Figure S10. As expected, both microrods of 16PyE and microplates of 27PyE display typical *p*-type semiconducting behavior. As listed in Table S2, the averge/highest hole mobilities were measured to be 0.054/0.13 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the microrods of **16PyE** along [100] direction (a-axis) of the crystal. For microplates of 27PyE, the averge/highest hole mobilities along [110] direction were deduced to be  $0.14/0.32 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ , whilst those along [110] direction were  $0.11/0.27 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ . Thus, the chargetransporting along [110] and [110] directions is almost isotropic for microplates of 27PyE. It is noted that hole mobilities of OFETs with crystalline microrods of 16PyE and microplates of 27PyE are lower than the respective ones of thin films of 16PyE and 27PyE. This is likely owing to the high bulk resistances induced by the relatively large thicknesses' (80-115 nm, see Figure S10) for microrods of 16PyE and microplates of 27PyE.

Furthermore, intermolecular transfer integrals and hole reorganization energies were calculated on the basis of crystal structures of **16PyE** and **27PyE** (see Figure S11), aiming to understand the correlation between the semiconducting property and intermolecular packing. As listed in Table S3, intermolecular transfer integrals along the molecular long axis of **16PyE** (pathways 3 and 4 in Figure S11) are small, but the intermolecular transfer integrals along pathways 1 and 2 (along the *a*-axis) are large (see Table S3). These data indicate that the crystal of **16PyE** is expected to exhibit anisotropic charge transporting behavior with high charge mobility along the *a*-axis, corresponding to the long axis of the microrod (see Figure S10). For **27PyE**, however, intermolecular transfer integrals along different pathways are almost the same (see Figure S11 and Table S3), indicating that charge transporting within the crystal of **27PyE** is almost isotropic. This is consistent with the fact that charge mobilities measured along the two microplate edges are almost identical (see Table S2). Table S3 also shows that **27PyE** exhibits smaller hole reorganization energy than **16PyE**. This can interpret the fact that hole mobilities of both thin film and crystalline object for **27PyE** are higher than those for **16PyE**.

## CONCLUSION

Two *trans*- $\beta$ -styryl substituted pyrenes **16PyE** and **27PyE** were synthesized and characterized. The results reveal that the incorporation of styryl groups in 16PyE and 27PyE alters the intermolecular arrangements largely; multiple intermolecular interactions exist within crystals of 16PvE and 27PvE, but neighboring pyrene units are not arranged in face-to-face modes. Such unique intermolecular arrangements endow 16PyE and 27PyE with both emissive and semiconducting properties in the solid state. 16PyE and 27PyE are fluorescent in solutions and solid states, and interestingly 27PyE exhibits aggregation induced enhanced emission with quantum yield of 27.4% in the solid state. Furthermore, microrods of 16PvE and microplates of 27PyE possess promising optical waveguiding properties. Thin films of 16PyE and 27PyE deposited at different substrate temperatures were utilized to fabricate OFETs, and the results manifest that i) thin films of 16PyE and **27PyE** are *p*-type semiconducting, ii) hole mobility of thin film of 27PyE is generally higher than that of 16PyE, and iii) the maxima charge mobility is 1.66 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for thin film of 27PyE deposited at 50 °C. It is intended to explore the correlation between molecular structure and intermolecular interactions and packing with the emissive and semiconducting properties in further studies. Such structureemissive/semiconducting property correlation will aid us to optimize the structural design for molecular materials with high emission quantum yields and charge mobility.

# EXPERIMENTAL SECTION

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59 60 **Materials and characterization techniques.** Chemicals and solvents were purchased from Alfa-Aesar, Sigma-Aldrich, J&K and used without further purification. Solvents and other common reagents were obtained from Beijing Chemical Co..

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker AVANCE III 500 MHz spectrometer using tetramethylsilane as internal standard. EI-MS spectra were recorded with APEX II spectrometer (FT-ICR-MS). Elemental analysis was performed on a Carlo Erba model 1160 elemental analyzer. TGA-DTA measurements from room temperature to 500 °C were carried out on a SHIMADZU DTG-60 instrument under a dry nitrogen flow with a heating rate of 10 °C/min. Cyclic voltammograms were measured on a computer-controlled CHI660C instruments at room temperature; the measurements were performed in a conventional threeelectrode cell using a Pt working electrode, a Pt counter electrode and a Ag/AgCl (saturated KCl) reference electrode, and *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) as the supporting electrolyte with a scan rate of 100 mV·s<sup>-1</sup>. To calibrate the redox potentials, the cyclic voltammogram of ferrocene was measured under the same conditions.

Single crystals of **16PyE** and **27PyE** were cultivated by slowly cooling their hot solutions in toluene. The diffraction data of single crystals were collected on Rigaku Saturn diffractometer with CCD area detector. All calculations were performed with the SHELXS-97 programs. The crystallographic data were deposited in the Cambridge Crystallographic Data Center (CCDC) as CCDC 1473291, CCDC 1473294 for **16PyE** and **27PyE**, respectively.

JASCO V-570 UV-Vis spectrophotometer was utilized to measure the solution and thin-film absorption spectra, while Hitachi (F4500) spectrophotometer was used to record the solution and solid-state fluorescence spectra at 25 °C. Fluorescence quantum yields and fluorescence lifetimes were measured with a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus-OY and the compact fluorescence lifetime spectrometer C11367 of Hamamatsu, respectively. PL images were recorded with an Olympus research inverted system microscope equipped with a CCD camera; a mercury lamp equipped with a band-pass filter ( $\lambda$ =330–380 nm) was utilized as the excitation source. To measure the microarea PL spectra, microrods and microplates dispersed on a glass cover slip were excited with a UV laser  $(\lambda=375 \text{ nm}, \text{ semiconductor laser})$ . The excitation laser which was filtered with a band-pass filter (330-380 nm) was focused to excite the microrods and microplates with an objective lens ( $50\times$ , N.A.=0.80). The light was subsequently coupled to a grating spectrometer (Acton SP-2358) and recorded by a thermal-electrically cooled CCD (Princeton Instruments, ProEm: 1600B). TEM and SAED measurements were carried out using a JEOL-1011 transmission electron microscope.

For the fabrication of bottom-gate/bottom-contact OFETs, a *n*type Si wafer with a SiO<sub>2</sub> layer of 300 nm and a capacitance of 11 nF cm<sup>-2</sup> were used as the gate and dielectric, respectively. Photolithography was employed to prepare the drain-source (D-S) gold contacts. Molecules of **16PyE** and **27PyE** (about 50 nm in thickness) were deposited (0.1 Å/s) under vacuum onto the Si/SiO<sub>2</sub> substrate, which was modified by OTS at different substrate temperatures (25 °C, 50 °C and 70 °C). The measurements were contacted under nitrogen atmosphere with a Keithley 4200 SCS semiconductor parameter analyzer at room temperature. The mobility was extracted with the following equation:

$$I_{DS} = \frac{W}{2L} \mu C_i (V_{GS} - V_{ih})^2$$

where  $\mu$  is the field-effect mobility, *L* and *W* are the channel length and width, respectively, C<sub>i</sub> is the insulator capacitance per unit area, and *V*<sub>GS</sub> and *V*<sub>th</sub> is the gate and threshold voltages, respectively.

The reflection mode X-ray diffraction (XRD) measurements were performed with a 2-kW Rigaku X-ray diffraction system at room temperature. The thin film surfaces were analyzed with tapping-mode AFM using Digital Instruments Nanoscope III and V atomic force microscope in ambient conditions in the dark. Thin films for AFM investigation were identical to those employed for the fabrication of organic filed-effect transistors.

General procedure for the synthesis of 16PyE and 27PyE. To a degassed THF solution (10 mL) of 1, 6-dibromopyrene or 2, 7-dibromopyrene (1.0 mmol) and *trans-β*-styrylboronic acid (5.0 mmol), a catalytic amount of  $[Pd(PPh_3)_4]$  and 3.0 mL of  $K_2CO_3$  aqueous solution (2.0 M) were added. The mixture was heated at 80 °C overnight under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, the precipitate was filtered and washed with water. The residue was collected, dried and then recrystallized from toluene.

**16PyE** was obtained as yellow solids in 82% yield. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 80 °C, TMS)  $\delta$ /ppm: 8.67 (d, J= 9.0, 2H), 8.45 (d, J = 8.0, 2H), 8.33-8.29 (m, 4H), 8.22 (d, J = 9.0, 2H), 7.82 (d, J = 7.5, 4H), 7.51-7.43 (m, 6H), 7.33 (t, J = 7.3, 2H); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ , 80 °C):  $\delta$ /ppm: 138.04, 132.56, 132.48, 130.77, 129.17, 128.88, 128.29, 128.09, 127.41, 125.83, 125.74, 124.35, 123.62; EI-MS m/z = 406 [M<sup>+</sup>]; Anal. Calcd for C<sub>32</sub>H<sub>22</sub>: C, 94.55; H, 5.45; found: C, 94.29; H, 5.71.

**27PyE** was obtained as white solids in 85% yield. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ , 80 °C)  $\delta$ /ppm: 8.49 (s, 4H), 8.19 (s, 4H), 7.74 (d, J = 10, 4H), 7.64 (d, J = 9.2, 3H), 7.46 (t, J = 10, 4H), 7.34 (t, J = 10, 2H); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ , 80 °C):  $\delta$ /ppm: 137.73, 135.71, 129.22, 128.22, 127.65, 127.10, 123.71; EI-MS m/z = 406 [M<sup>+</sup>]; Anal. Calcd for C<sub>32</sub>H<sub>22</sub>: C, 94.55; H, 5.45; found: C, 94.53; H, 5.47.

### ASSOCIATED CONTENT

#### **Supporting Information**

TGA analysis, crystallographic data, short interatomic contacts within the crystal structures, cyclic voltammograms, absorption spectra, fluorescence lifetime fitting curves, TEM images and intermolecular packings, output and transfer characteristics of OFETs of thin film deposited on OTS-modified SiO<sub>2</sub>/Si substrate at 25 °C and 75 °C, XRD patterns of thin film of **27PyE** and its simulated XRD patterns from crystal structural data, single crystal OFET measurement, theoretical calculation and NMR spectra. The Supporting Information is available free of charge on the ACS Publications website.

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All authors have given approval to the final version of the manuscript.

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Both 1, 6 and 2, 7-*trans*- $\beta$ -styryl substituted pyrenes show relatively strong emissions in the solid state, and their microcrystalline samples exhibit promising optical waveguilding behavior. Moreover, their thin films exhibit *p*-type semiconducting property with hole mobilities up to 1.66 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>.