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Facile synthesis and self-assembly of diazafluorenone-based p-n (donor-acceptor) organic semiconductors

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1. Introduction

Donor-acceptor (D-A) molecules acting as organic semiconductors have been intensively investigated in the filed of organic and plastic electronics, such as organic light emitting diodes (OLED),¹ organic field effect transistors (OFET),² organic photovoltaics (OPV)³ owing to their unique charge transfer and energy transfer behaviors. However, the devices are affected not only by the properties of individual molecules but also the spatially intermolecular arrangement in the assembly.⁴ For example, Cho et al.^{4b} reported that the P3HT nanocrystals could adopt two different orientations-parallel and perpendicular to the insulator substrate, the results in the field-effect mobilities differ by more than a factor of four. In this context, a prerequisite for the development of high-performance devices is to adjust and control the spatial orientation and packing of molecules assemblies on the surface.⁵ Therefore, it is important to investigate self-assembly behaviors of the well-designed D-A structures.

Numerous efforts have been made to focusing on aza-aromatics,⁶ such as pyridine, tetrazine, oxadiazole, benzothiadiazole,

ABSTRACT

A mild and effective method to prepare 2,7-dibromo-4,5-diazafluoren-9-one (**3**) has been described involving tandem oxidation and rearrangement reactions. Diazafluorenone-based donor-acceptor (p-n) molecules via stille coupling reactions exhibit solvent-dependent fluorescence and excellent self-assembly behaviors at the solid-liquid interface according to the characterization of scanning tunnel-ing microscopy (STM).

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perylene diimide, diketopyrrolopyrrole, and 1,10-phenanthroline acting as electron-acceptor units in order to construct novel D–A organic molecules. As potential optoelectronic materials, diaza-fluorene derivatives (DAFs) have been investigated in many research fields, such as electron-transporting materials, organic light-emitters, solar sensitizers, and antibodies.⁷ Moreover, diaza-fluorene derivatives can smoothly form various complexes by co-ordination to many metals. However, due to the lack of convenient and effective synthetic routes to obtain the key intermediates,⁸ such as halogen-substituted DAFs, their electron-deficient properties have been rarely investigated to a large extent.⁹

In this work, a facile and mild method to prepare the intermediate-2,7-dibromo-4,5-diazafluoren-9-one has been well developed via tandem oxidation and rearrangement reactions. Based on that, a series of D–A molecules exhibiting solventdependent fluorescence have been obtained. Furthermore, their self-assemblies have been investigated on a highly oriented pyrolytic graphite (HOPG) surface.

2. Results and discussion

Two synthetic routes have been demonstrated to synthesize 2,7dibromo-4,5-diazafluoren-9-one (**3**) as shown in Scheme 1 (route I and route II). In the past, compound **3** was synthesized by direct



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bromination of 4,5-diazafluoren-9-one in the conditions of extremely excessive bromine and oleum with a low yield of 32% according to the literature (route I).⁸ In this study, an effective and smooth method to synthesize **3** is well developed and depicted as route II. The target compound was prepared starting from 1,10phenanthroline, which suffered bromination to give 3,8-dibromo-1,10-phenanthroline in 70% yield according to the literature.¹⁰ 3,8-Dibromo-1,10-phenanthroline was converted into the target compound **3** in the mixture of H₂SO₄/HNO₃/KBr, followed by solid sodium hydroxide with a moderate yield of 50%. The reaction is likely to involve tandem oxidation rearrangement processes similarly to our previous works,⁹ which has been unambiguously confirmed by the separated intermediate, 3,8-dibromo-1,10-phenanthroline-5,6dione (**2**).



 $\label{eq:scheme 1. Two synthetic routes to compound 3. Conditions: (a) Br_2/pyridine/S_2Cl_2/1-chlorobutane, reflux, 24 h; (b) H_2SO_4/HNO_3/KBr, reflux, 3 h; (c) solid sodium hydroxide.$

Subsequently, a series of D–A compounds were smoothly prepared as shown in Scheme 2. The target compounds **5** and **6**, were obtained via stille reactions between **3** and the tris(stannyl) derivatives in the presence of a catalytic amount of Pd(PPh₃)₂Cl₂ with the yields of 40% and 33%, respectively. Mono-substituted compound **7** was synthesized from compound **4** in the similar condition with a yield of 55%. In view of the toxicity of tin (II) reagents, we initially made attempt to construct these molecules by Suzuki cross-coupling reaction. Unfortunately, no target compounds were obtained probably due to instability of 2-thienylboronic acid derivatives,¹¹ along with the low reactivity of 4,5-diazafluorenone moiety.



All the compounds were confirmed by ¹H NMR, ¹³C NMR, X-ray crystallography, and/or element analysis. Single crystals of monomer **3**, grown by slow evaporation of the chloroform solution at

room temperature, were unambiguously characterized by X-ray crystallographic analysis as shown in Fig. 1. Compound **3**, crystallizes in a triclinic form with space group P-1. The molecule is planar as a whole and the dihedral angle between two pyridine planes is 2.41°. Excellent co-planarity of conjugated moiety enables the compound to be a high delocalized-electron system. In this crystal, the molecules form two sets of parallel layers that are linked by C3–H3…O1 intermolecular hydrogen bonds with the length of 2.468 Å along the *c* axis. Besides, Br…Br intermolecular bonds play a significant role in the packing of the molecules. The distance between Br1 and Br2 is 3.489 Å, which doubles the value of van der Waals radius of a bromine atom.¹²



Fig. 1. ORTEP drawing (30% probability) showing (a) the X-ray structure of monomer 3 and (b) packing program of the monomer 3.

Fig. 2 shows UV-vis spectra of compounds 5-7 in dichloromethane (DCM) solvent (10^{-5} mol/L) and spin-coated film. There are two absorption bands in all three compounds. The highenergy absorption bands appear in the range of 350–460 nm, which are attributed to $\pi - \pi^*$ transition and the intramolecular charge-transfer (ICT) transition. The low-energy absorption band in the range of 460-580 nm has small molar extinction coefficients, which is assigned to the symmetry-forbidden $n-\pi^*$ transition of the carbonyl groups in 4,5-diazafluoren-9-one units. In contrast to compounds 5 and 7, the absorption maximum (λ_{max}) of the absorption band of compound **6** is red-shifted approximately 40 nm, presumably because of the improved π conjugation by the addition of thiophene rings. The spectra broaden and extend to 576, 598, and 622 nm in the solid state with a peak emerging of 382, 395, and 420 nm for compounds 5, **6**, and **7**, respectively, indicating strong $\pi - \pi$ interactions in their crystalline forms.¹² From the absorption edges in the solid state, the optical energy gaps are estimated to be 2.15, 1.99, and 2.07 eV for 5, 6, and 7, respectively, which are also in close agreement with the data obtained from electrochemical measurements.



Fig. 2. UV-vis spectra of compounds **5–7** in solid film and solvent ($M=10^{-5}$ mol/L) (inset).

The absorption and emission spectra of compound 6 were investigated in different polar solvents, including toluene, dichloromethane (DCM), tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) (Fig. 3). The high-energy bands in the range of 350-460 nm are somewhat dependent on solvent polarity, indicating that there are very weak electronic coupling between donor (thiophene) and acceptor (4.5-diazafluoren-9-one) moieties in the ground state. However, it exhibits solvent-dependent fluorescence, suggesting the occurrence of complicated excited state and energy transfer process. There are two emission bands peaking at 481 nm and 595 nm under the excitation of 414 nm in non-polar solvent, such as toluene (Fig. 3), in which the intensity of blue emission is equivalent to that of yellow emission. The blue and yellow emission are attributed to ICT transition and $n-\pi^*$ state via limited energy transfer process. Furthermore, the long wavelength emissions vanish in polar solvents, such as DCM, THF, and DMF, revealing that the strong quenching effect of these polar solvents occurs on the lowest excited state of $n-\pi^*$ state feature of 4,5diazafluoren-9-one. In the emission spectra of compounds 5 and 7, the similarly incomplete energy transfer process and solventdependent effect are also found in the above-mentioned solvents (Supplementary data). While in the solid state, the emission spectra of these three compounds are quenched due to aggregation.



Fig. 3. The UV–vis (a) and PL spectra (b) of compound 6 in different solvents $(1 \times 10^{-5} \text{ mol/L})$.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate the thermal properties of these compounds. All of the present molecular materials demonstrate good thermal stability. The decomposition temperatures (lost 5% weight) of three compounds are 302, 335, and 321 °C, respectively (Supplementary data). Fig. 4 shows the DSC plots for compounds **5**–**7**. All the compounds exhibit crystalline-isotropic transitions with melting temperature (T_m) ranging from 167 to 223 °C. The melting temperature of compound **7** is 203 °C, much higher than the value of compound **5** (T_m =167 °C). T_m increases as the number of thiophene rings increases from two to four, which is confirmed by the highest melting temperature of compound **6** with a value of 223 °C.

The reduction and oxidation behavior of the compounds was investigated by cyclic voltammetry (CV) in anhydrous



Fig. 4. DSC curves for compounds 5-7.

tetrahydrofuran (THF) and dichloromethane (DCM), respectively (Fig. 5). A series of redox potentials are provided in Table 1. All the compounds present one quasi-reversible reduction peaks with $E_{\text{onset}}^{\text{red}}$ of -1.31 V for compound **5**, -1.23 V for compound **6**, and -1.26 V for compound **7**, respectively. In the oxidation region, the oxidation waves for three compounds were observed at 1.08, 0.87, and 1.02 V, respectively. The electrochemical gaps for compounds 5, 6, and 7 are 2.39, 2.10, and 2.28 V, respectively. The ability to adjust the oxidation and reduction properties of these compounds leads to the variation of electrochemical gaps from 2.39 V for compound 5 to 2.10 V for compound 6. DFT calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies are illustrated in Table 1. The HOMO is distributed to both 4,5-diazafluoren-9-one core and thiophene units for these compounds. While the LUMO is only localized on the 4,5diazafluoren-9-one core. The calculated ground-state singlet gaps for compounds 5, 6, and 7 are found to be 3.01, 2.60, 2.79 eV, respectively. The DFT calculations confirmed that the HOMO energy is increased by the addition of thiophene units owing to the increasing length of π -conjugation. The electrochemical measurements are also consistent with the results of the DFT calculations that the oxidation and reduction potentials of these compounds could be adjusted by varying the number of the thiophene units.



Fig. 5. Cyclic voltammetry of compounds 5 (black), 6 (red), and 7 (blue) measured in 0.1 M solution of $TBAPF_6/THF$ (reduction) and in 0.1 M solution of $TBAPF_6/DCM$ (oxidation).

Table 1Physical properties of compounds 5–7

Compound	E _g ^a (eV)	E _{ox} (V)	E _{red} (V)	Δ <i>E</i> (V)	HOMO (eV)	LUMO (eV)	HOMO— LUMO (DFT), eV
5	2.15	1.08	-1.31	2.39	-5.84	-3.45	3.01
6	1.99	0.87	-1.23	2.10	-5.63	-3.53	2.60
7	2.07	1.02	-1.26	2.28	-5.78	-3.5	2.79

^a From thin film.

The self-assembled monolayers (SAM) of compounds **6** and **7** were observed by scanning tunneling microscopy (STM) at the solid/liquid interface as shown in Fig. 6. The high-resolution STM image in Fig. 6a reveals the structural details of compound **6**, which turns out to be a striple feature, forming regular molecular rows. Owing to the large electronic density of aromatic rings, the aromatic part of the molecule appears in higher contrast than the alkyl chains in the image. The bright slices are attributed to π -conjugated molecular backbones, whereas the alkyl chains are darker.¹³ The slices stack in parallel with each other. The average length of the slices is measured to be 2.6±0.2 nm in the high-resolution STM image, which matches well with the theoretical length of π -conjugated backbone.



Fig. 6. (a) STM images on HOPG of **6.** 17.6 nm×17.6 nm, *I*=223. 3 pA, and V=-854.6 mV; (b) Tentative molecular models and unit cell vectors for the 2D packing of **6**; (c) STM images on HOPG of **7**. 18.6 nm×18.6 nm, *I*=221. 4 pA, and V=-857.6 mV; (d) Tentative molecular models and unit cell vectors for the 2D packing of **7**.

On the basis of molecular arrangement, a unit cell is determined and outlined by a black parallelogram in Fig. 6a. The lattice constants are $a=2.0\pm0.2$ nm, $b=8.4\pm0.2$ nm, and $\alpha=58\pm2^{\circ}$. According to the above observations, a plausible model is proposed in Fig. 6b, giving a visual representation of adlayer structure. In this model, the π -conjugated moieties of compound **6** stack with an angle of $\alpha=58\pm2^{\circ}$ to the molecular row. The distance between neighboring molecules within one molecular row is 2.0 ± 0.2 nm, indicating that four thiophene rings and diazafluorenone moieties are all adsorbed in parallel with the graphite plane. The alkyl chains ($-C_6H_{13}$) are interdigitated with each other between neighboring molecular rows.

In order to study the substituent effect. 2D self-assembly behaviors of compounds 7 were also taken into account. From the high-resolution STM image (Fig. 6c), large vague arrangements can be readily discerned among several ordered domains in this large area due to the solvent effect.¹⁴ Besides, several regular rows consist of bright sticks. Each bright stick represents a compound 7 molecule. All the sticks parallels to each other in the same row along the lamella axis. The intermolecular distance between the neighboring molecules along the lamella axis is ~ 1.0 nm. The length of the stick measured from Fig. 6c is about 1.4 ± 0.1 nm, which is identical to the theoretical length of π -conjugated moiety in this molecule. Considering the length of alkyl chain $(-C_6H_{13})$, they are probably interdigitated at the molecular side. A unit cell is marked by a black parallelogram in the high-resolution STM image (Fig. 6c), which includes four molecules from compound 7. The parameters are measured to be $a=1.0\pm0.1$ nm, $b=4.1\pm0.1$ nm, and α =84±2°. Based on the above observations, a plausible model is proposed and outlined by a black parallelogram in proportion marked in Fig. 6d. There are two different arrangement manners for the packing of compound 7: head-to-head or tail-to-tail. The reason for the resultant structure might be found in the relatively bulky characters in 4.5-diazafluoren-9-one moiety. The molecules prefer to adopt the energetically most favorable arrangement to shape the packing pattern. The molecule-substrate interactions may also play an important role in the 2D self-assembly patterns of compound 7. After further analysis and careful comparison of compounds 6 and 7, the packing structures are found to be distinct. The monolayer of compounds 6 is a large uniform and highly ordered assembly structure. The alkyl chains are interdigitated with each other between neighboring molecular rows. The van der Waals forces play a significant role in the formation of the molecular monolayers. While the STM image of compounds 7 reveals that the molecule-substrate interactions are probably dominant in the formation of 2D self-assembly patterns.

3. Conclusions

In summary, an effective and convenient protocol to synthesize 2,7-bromo-4,5-diazafluoren-9-one (**3**) has been proposed, involving tandem oxidation and rearrangement processes. A series of D–A molecules based on 4.5-diazafluoren-9-one units have been prepared via stille coupling reactions, which exhibit solvent-dependent fluorescence and low energy bandgaps. All three D–A compounds show good thermal stability and volatility. The results of their 2D self-assembly behaviors reveal that compound **6** tends to construct a highly ordered and uniform 2D structure while compound **7** is not very legible due to the competition of the van der Waals forces and the molecule–substrate interactions. Diazafluorenone-based donor–acceptor molecules are potential organic semiconductors for the application of solar cells, memory, and photodetectors.

4. Experimental section

4.1. General information

All the solvents and reagents were purchased from commercial suppliers and used without further purification, unless noted otherwise. All products were purchased by flash column chromatography, which was carried out with Kanto Silica Gel 60 N (40–63 µm). Spectrochemical-grade solvents were used for optical 1,10-Phenanthroline, measurements. thiophene, 2bromothiophene, dichlorobis(triphenylphosphine) palladium(II), and *n*-butyllithium were obtained from Aldrich Chemical Co, which were used without further purification. Sulfuric acids, nitric acid, bromine, sulfur monochloride, N,N-dimethylformamide, potassium carbonate, magnesium sulfate, chloroform, and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd without further purification. Tetrahydrofuran and toluene were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. 3,8-Dibromo-1,10phenanthroline,¹⁰ 2-bromo-4,5-diazafluoren-9-one (**4**),⁹ 2tributylstannyl-5-hexylthiophene, and 5-tributylstannyl-5'-hexyl-2,2'-bithiophene,¹⁵ were prepared according to the corresponding literature. ¹H NMR and ¹³C NMR were recorded on a Bruker 400 MHz spectrometer in CDCl₃-d or DMSO-d₆ with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GC-MS 2010 PLUS. Element analyses were carried out on an Elementar Analysensysteme GmbH Vario EL III Instrument. Absorption spectra were measured with a Shimadzu UV-3150 spectrometer at 25 °C, and emission spectra were recorded on a Shimadzu RF-530XPC luminescence spectrometer upon excitation at the absorption maxima. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric analyzer under a heating rate of 10 °C/min. Cyclic voltammetric (CV) studies were conducted at room temperature on the CHI660E system in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag⁺) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in CH₂Cl₂ at a sweeping rate of 0.1 V/s. According to the redox onset potentials of the CV measurements, the highest occupied molecular orbital (HOMO)/lowest unoccupied energy levels (LUMO) of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO= $-(E_{onset}-0.04 \text{ V})$ -4.8 eV, where the value 0.04 V is for ferrocene versus Ag/Ag⁺. X-ray crystallographic data for 3 were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector and a rotating anode utilizing graphite-monochromated Mo Ka radiation (λ =0.71073 Å). Data processing was carried out by using the program SAINT, while the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. The structures were solved by using the direct-method procedure in the Bruker SHELXL program library and refined by full-matrix least-squares methods on F^2 . All non-hydrogen atoms were treated with riding model at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded. The self-assembled monolayers (SAMs) of the compounds were prepared by placing a drop (ca. 3 µL) of solution (the concentration is ca. 10^{-4} M) on a freshly cleaved atomically flat surface of highly ordered pyrolytic graphite (HOPG, ZYB quality, Veeco Metrology). The solvent for preparing all solutions was octylbenzene. The samples were investigated at the liquid-solid interface. A nanoscope IIIa scanning probe microscope (Veeco Metrology) was employed to carry out the STM experiments using a standard constant-current mode under ambient conditions. STM tips were mechanically cut Pt/Ir wire (80/20). All the STM images shown herein are presented without further processing, except flattening. Experiments were repeated in several sessions using different tips to check for reproducibility and to avoid artifacts. The tunneling conditions used are given in the corresponding figure captions. The molecular models were built with a HyperChem software package.

4.1.1. 3,8-Dibromo-1,10-phenanthroline-5,6-dione (**2**). To a mixture of HNO₃ (1.4 g/mL, 1.35 mL, 19 mmol) and H₂SO₄ (1.84 g/mL, 2.70 mL, 50 mmol) were added 3,8-dibromo-l,10-phenanthroline (400 mg, 1.18 mmol) and KBr (170 mg, 1.42 mmol), the mixture was stirred at 90 °C for 3 h. After cooling to room temperature, the mixture was poured to 300 mL water and neutralized with diluted sodium hydroxide solution. The solution was extracted with chloroform (3×100 mL) and dried over anhydrous MgSO₄. After removing organic solvent, a yellow power was obtained in 70% yield. Mp: 308–312 °C; *R*_f 0.46 (silica gel, EtOAc/petroleum ether, 1:3); GC–MS (EI-*m*/*z*): 366 [M⁺]; ¹H NMR (400 MHz, CDCl₃-*d*): δ 8.61 (d, *J*=2.1 Hz, 1H), 9.14 (d, *J*=2.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃-*d*): δ 177.13, 157.60, 150.47, 139.53, 128.44, 123.58; Anal. Calcd for C₁₂H4Br₂N₂O₂: C, 39.17, H, 1.10, N, 7.61; found: C, 39.21; H, 1.29; N, 7.52.

4.1.2. 2,7-Dibromo-4,5-diazafluoren-9-one (**3**). To a blend solution of HNO₃ (1.4 g/mL, 1.35 mL, 19 mmol) and H₂SO₄ (1.84 g/mL, 2.70 mL, 50 mmol) was added 3,8-dibromo-l,10-phenanthroline (400 mg, 1.18 mmol) and KBr (170 mg, 1.42 mmol), the mixture was stirred at 90 °C for 3 h. After cooling to room temperature, the

mixture was poured to 300 mL water and neutralized with solid sodium hydrate quickly. The residue was extracted with chloroform (3×100 mL) and dried over anhydrous MgSO₄. Yellow organic layer was concentrated by rotary evaporation and washed with hexane to give 2,7-dibromo-4,5-diazafluoren-9-one (200 mg, 0.59 mmol) as a yellow solid in 50% yield. Mp: 257–259 °C; R_f 0.54 (silica gel, EtOAc/petroleum ether, 1:3); GC–MS (EI-*m*/*z*): 340 [M⁺]; ¹H NMR (400 MHz, CDCl₃-*d*): δ 8.88 (d, *J*=2.1 Hz, 1H), 8.11 (d, *J*=2.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃-*d*): δ 186.67, 160.61, 156.28, 134.44, 130.23, 122.58; Anal. Calcd for C₁₁H₄N₂Br₂O: C, 38.86; H, 1.19; N, 8.24; found: C, 39.01; H, 1.27; N, 8.13.

4.1.3. 2,7-Bis(5-hexylthiophen-2-yl)-4,5-diazafluoren-9-one (5). In a three-necked, oven-dried 250 mL round-bottom flask, 2,7dibromo-4,5-diazafluoren-9-one (340 mg, 1 mmol) and 2tributylstannyl-5-hexylthiophene (2.5 mmol, 2.5 equiv) was dissolved in 120 mL of anhydrous DMF. Bis(triphenylphosphine)palladium dichloride (40 mg, 0.06 mmol) was added quickly. After degassed for 30 min, the mixture was stirred at 80 °C for 24 h under nitrogen. The solvent was evaporated under vacuum. The residue was dissolved in a mixture of dichloromethane (200 mL) and THF (80 mL), and the resulting solution was washed with statured KF solution (100 mL), water and brine, respectively, and dried over anhydrous MgSO₄. The crude product was purified by column chromatography using dichloromethane as eluent to give a yellow solid (206 mg, 40%). Mp: 166–169 °C; Rf 0.52 (silica gel, EtOAc/ petroleum ether, 1:3); ¹H NMR (400 MHz, CDCl₃-d): δ 8.96 (d, *J*=2.2 Hz, 1H), 8.09 (d, *J*=2.1 Hz, 1H), 7.30 (d, *J*=3.6 Hz, 1H), 6.83 (d, *J*=3.6 Hz, 1H), 2.86 (t, *J*=7.6 Hz, 2H), 1.72 (dt, *J*=7.6 Hz, 2H), 1.42 (m, 6H), 0.90 (t, *I*=7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃-d): δ 189.60, 160.87, 151.55, 148.59, 136.55, 131.93, 129.90, 127.36, 125.72, 125.07, 31.55, 30.33, 28.75, 22.58, 14.09; Anal. Calcd for C₃₁H₃₄N₂OS₂: C, 72.33; H, 6.66; N, 5.44; found: C, 72.01; H, 6.70; N, 5.33; MALDI-TOF-MS (*m*/*z*) calcd for C₃₁H₃₄N₂OS₂ [M⁺] 514.21, found 513.77.

4.1.4. 2,7-Bis(5'-hexyl-[2,2'-bithiophen]-5-yl)-4,5-diazafluoren-9one (6). A mixture of compound 3 (340 mg, 1 mmol, 1 equiv), 5tributylstannyl-5'-hexyl-2,2'-bithiophene (1350 mg, 2.5 mmol, 2.5 equiv) and bis(triphenylphosphine)palladium dichloride (70 mg, 0.1 mmol, 0.1 equiv) was reacted in a similar fashion to that of preparing compound 5, except the reaction temperature was increased to 110 °C, and the reaction time was extended to 48 h. A brown power was obtained with a yield of 33%. Mp: 222–225 °C; R_f 0.51 (silica gel, EtOAc/petroleum ether, 1:3); ¹H NMR (400 MHz, CDCl₃-d): δ 9.00 (d, J=2.2 Hz, 1H), 8.12 (d, J=2.1 Hz, 1H), 7.38 (d, J=3.8 Hz, 1H), 7.13 (d, J=3.8 Hz, 1H), 7.07 (d, J=3.5 Hz, 1H), 6.72 (d, J=3.5 Hz, 1H), 2.81 (t, J=7.7 Hz, 2H), 1.67 (dt, J=7.7 Hz, 2H), 1.40–1.30 (m, 6H), 0.90 (t, J=6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃d): δ 189.25, 160.94, 151.48, 146.65, 139.92, 136.88, 133.87, 131.42, 129.94, 127.24, 125.99, 125.05, 124.16, 31.56, 31.54, 30.22, 28.76, 22.58, 14.08; Anal. Calcd for C₃₉H₃₈N₂OS₄: C, 68.99; H, 5.64; N, 4.13; found: C, 69.12; H, 5.83; N, 4.02; MALDI-TOF-MS (m/z) calcd for C₃₉H₃₈N₂OS₄ [M⁺] 678.19, found 678.12.

4.1.5. 2-(5'-Hexyl-[2,2'-bithiophen]-5-yl)-4,5-diazafluoren-9-one (7). A mixture of compound **4** (261 mg, 1 mmol, 1 equiv), 5-tributylstannyl-5'-hexyl-2,2'-bithiophene (650 mg, 1.2 mmol, 1.2 equiv) and bis(triphenylphosphine)palladium dichloride (0.1 mmol, 0.1 equiv, 70 mg) was reacted in a similar fashion to that of preparing compound **5**, except the reaction temperature was increased to 85 °C, and the reaction time was extended to 48 h. A red power was obtained in 55% yield. Mp: 201–204 °C; R_f 0.49; ¹H NMR (400 MHz, CDCl₃-d): δ 9.01 (d, J=2.1 Hz, 1H), 8.80 (d, J=4.7 Hz, 1H), 8.13 (d, J=2.2 Hz, 1H), 8.00 (d, J=7.6 Hz, 1H), 7.41–7.30 (m, 2H), 7.13 (d, J=3.8 Hz, 1H), 7.07 (d, J=3.6 Hz, 1H), 6.72 (d, J=3.5 Hz, 1H), 2.81 (t, J=7.6 Hz, 2H), 1.69 (dt, J=7.6 Hz, 2H), 1.53–1.19 (m, 6H), 0.90 (t, I=6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃-d): δ 189.35, 163.25, 161.07, 155.29, 151.28, 146.58, 139.86, 136.76, 133.83, 131.53, 129.60, 127.14, 126.00, 125.04, 124.30, 124.01, 31.55, 30.20, 28.77, 22.59, 14.10; Anal. Calcd for C₂₅H₂₂N₂OS₂: C, 69.73; H, 5.15; N, 6.51; found: C, 69.93; H, 5.25; N, 6.17; MALDI-TOF-MS (*m*/*z*) calcd for C₂₅H₂₂N₂OS₂ [M⁺] 430.12, found 430.42.

4.2. X-ray crystallographic data

Crystallographic data for **3** is saved as the cif file, 3 cif. C₁₁H₄Br₂N₂O, *M*=339.98, triclinic, space group *P*-1, *Z*=2, a=5.918(4) Å, b=8.445(6) Å, c=68.687(7) Å, $\alpha=68.687(7)$ (7)°, $\beta = 80.926(7)^{\circ}, \gamma = 83.203(9)^{\circ}, V = 527.7(6)^{\circ}, \Lambda^{3}, F(000) = 324,$ $D_c=2.140$ Mg/m³, μ (Mo K α)=7.656 mm⁻¹. Reflection collected/ 2383, Goodness of fit on $F^2(s)/1.062$, Final R indices $(I>2\sigma (I))$ *R*₁=0.0459, *wR*₂=0.1270, *R* indices (all data) *R*₁=0.0556, wR₂=0.1344. CCDC 832075 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Supplementary data

¹H NMR, ¹³C NMR, MALDI-TOF MS spectral data for all corresponding products are provided. Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/ j.tet.2012.07.066.

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