Research Article

Diarylfluorene-Based Shape-Persistent Organic Nanomolecular Frameworks via Iterative Friedel-Crafts Protocol toward Multicomponent Organic Semiconductors

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We describe bottom-up fluorene approach to create soluble covalent organic nanomolecular architectures (ONAs) as potential multicomponent organic semiconductors (MOSs). BPyFBFFA as a typical model of ONAs and MOSs exhibits a persistent chair-shaped geometric structure that consists of hole-transporting triphenylamine (TPA), high-efficiency terfluorene, and high-mobility pyrenes. BPyFBFFA was synthesized via the intermediates PyFA and BPyFA with iterative Friedel-Crafts reactions and Suzuki cross-coupling reactions. BPyFBFFA behaves as an efficient blue light-emitter without the low-energy green emission band. Complex diarylfluorenes (CDAFs) are promising candidates for nanoscale covalent organic frameworks and MOSs. Friedel-Crafts protocols offer versatile toolboxes for molecular architects to frame chemistry and materials, nanoscience, and molecular nanotechnology as well as molecular manufactures.

1. Introduction

Multicomponent organic semiconductors (MOSs) are very important for the functional organic devices [1]. Until now, most of the typical electronic device functionality and performance optimization strongly depend on the synergic interactions among the contradictory components such as electron/hole, p/n, donor/acceptor and host/guest [2, 3]. To ingeniously arrange the opposite elements in the device space is a challenge that scientists face in organic electronics. Intramolecular contradiction-uniform systems via molecular engineering that have obvious advantages over physical contradictory systems have been explored such as p-n copolymerization [4, 5], bipolar light emitters and molecular heterojunction. The intrinsic merits originated from the molecular features such as efficient energy-transfer process. MOS fully has an advantage over semiconductor

blending systems with the drawback of phase separation. Recently, three-component red-green-blue (RGB) polymers show promising single-molecular white light-emitting materials [6–8]. The trend in organic semiconductors is to integrate various different functional moieties into single nanomolecules via covalent molecular engineering process. It is an emergent task to achieve stable and high-performance single-layer devices with MOSs equivalent to those in a multilayer device, although some issues are unresolved, such as unfoldable functionalities. For example, the unified p-n systems are still lagging behind the bulk heterojunction blending systems for polymer solar cells [9, 10].

The initial issues are that there are limited flexible methods to integrate various functional moieties into a robust system of MOSs with the suitable positions as well as controllable distance. Framework chemistry and materials offer the methodology to MOSs by means of state-of-the-art

models with several merits such as rigid shape persistence, cubic backbones, and mesh superstructures. However, the most reported metal-organic frameworks (MOFs) [11] and covalent organic frameworks (COFs) [12, 13] do not exhibit any solubility that severely hinders the entry to organic semiconductors. Soluble metal-organic polyhedron (MOPs) [14–16] and covalent organic polyhedron (COPs) [17, 18] do not easily access. In this background, it is necessary for molecular architects to create the designable organic intramolecular multicomponent systems that are suitable for the MOSs via a feature of facile, concise, green and sustainable syntheses.

Previously, we set up a $\text{BF}_3 \cdot \text{Et}_2\text{O}$ -mediated Friedel-Crafts reaction of tertiary alcohols [19–21], an atom-economic and classical C–H bond functionalization to synthesize a series of complex diarylfluorenes (CDAFs) [22]. Subsequently, this protocol has modified stacked polymer semiconductors for nonvolatile memory devices [23] and light-emitting devices [24, 25]. Hyperbranched conjugation-interrupted polymers have been made by means of Friedel-Crafts polymerization [26, 27]. More recently, morphology-directed molecular designs have been demonstrated using diarylfluorene-modified fullerenes for bulk heterojunction solar cells by our group [28]. Series of works from XIE-HUANG group demonstrate that this approach is effective for function-directed semiconducting materials in organic electronics. However, scientists have never started to explore fluorenol approach and Friedel-Crafts protocols as versatile toolbox toward structure-directed framework, porous, mesh nanomaterials in the realm of nanoscience, and molecular nanotechnology. To this end, we demonstrate the flexible fluorenol approach as an organic nanochemistry method for soluble covalent organic nanoframeworks (CONs). Diarylfluorene-based BPyFBFFA that is easily accessed from Friedel-Craft reaction has complex nanomolecular architecture with a nonplanar geometric shape of three-legged chair (Figure 3). The BPyFBFFA contains multicomponent blue emitting pyrene chromophores, terfluorene and hole-transporting triphenylamine (TPA), which exhibit a stable amorphous blue emitter with a low ionization potential of 5.32 eV.

2. Results and Discussion

We firstly carried out retrosynthesis analysis of BPyFBFFA as modeling MOSs that has an open framework (Scheme 1). So far, there are two typical divergent and convergent routes for dendrimers, multiarmed or starburst oligomers, and nanosized architectures. For this asymmetry BPyFBFFA, site-selective reaction that is a challenge in organic synthesis would be the prerequisite if the individual divergent route I or convergent route II is workable. To handle the thorny issue, we adopted a hybrid approach of divergent and convergent route to the target molecule, BPyFBFFA, as shown in Scheme 1. We found that $\text{BF}_3 \cdot \text{OEt}_2$ catalyzed electrophilic substitution reactions of 9-arylfluorenol with thiophene, TPA, and their derivatives in nearly quantitative yields that encouraged us exploring the complex BPyFBFFA via the Friedel-Crafts protocol.

BPyFBFFA was synthesized by the divergent and convergent mixture routes that are outlined in Scheme 1. First, we take three times of iterative Friedel-Crafts reactions to BPyFBFFA. In details, BPyFBFFA can be obtained by the Friedel-Crafts reactions of BPyPFBA with blue light-emitting tertiary alcohol (TFOH) at the yield of 70%. The key intermediate of BPyPFBA has been synthesized by the Suzuki cross-coupling reaction of compound 2 with 1-pyrenylboronic acid. Friedel-Crafts reactions of PyFA with bromo-substituted fluorene tertiary alcohol enable to synthesize compound 2. Similar processes of Friedel-Crafts reactions and Suzuki coupling reactions have been repeated to give the key intermediate, PyFA. The target BPyFBFFA can be accessed by the simplified two times of iterative Friedel-Crafts reactions that undergo the key intermediate of compound 3. The above effective route suggested that $\text{BF}_3 \cdot \text{OEt}_2$ -mediated Friedel-Crafts reaction, combining with the Suzuki reaction, is an efficient method to prepare different two-component or three-component complicated electroluminescent nanomolecules. The BPyFBFFA and the key intermediates have good solubility in common organic solvents such as dichloromethane, chloroform and THF that have been characterized by ^1H NMR, ^{13}C NMR and matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-tof-MS). The target compound has been unambiguously confirmed by the MALDI-tof-MS that exhibits a single peak with molecular weight of 2142.5 (Figure 1), well matched with the calculated molecular weight of 2143 Da.

The physical data that includes thermal, electrochemical and optical properties of these organic nanomolecules are collected in Table 1. The thermal properties of the nanomolecules were evaluated by thermogravimetric analyses (TGA) and differential scan calorimetry (DSC) (See Supplementary Material available online at <http://dx.doi.org/10.1155/2013/368202>). It is found that the decomposition temperatures (T_d) (5% weight loss) of nanomolecules are above 400°C. From DSC curves, two intermediates exhibited the glass transition in the second heating cycle with the T_g of 147°C for PyFA, 218°C for BPyFA and 130°C for BPyFBFFA. No crystallization exotherm and melting endotherm were observed. As expected, incorporation of diarylfluorenes is beneficial to raising morphological stability. CV measurement was employed by us to investigate the oxidation and reduction behavior of organic nanomolecular frameworks, in order to estimate their HOMO and LUMO energy levels. The reduction and oxidation behaviors of the nanomolecular PyFA, BPyFA and BPyFBFFA were investigated by cyclic voltammetry (CV) in anhydrous dichloromethane. BPyFBFFA has a bandgap of about 2.73 eV that is probably because pyrene causes the reduction of potential with LUMO of ~ -2.63 eV.

Figure 2 depicts the absorption and photoluminescence spectra of the compounds PyFA, BPyFA and BPyFBFFA in THF. The absorption and photoluminescence maxima of PyFA and BPyFA were very similar (Table 1). The peak at ~ 350 nm and ~ 298 nm in the absorption spectra of PyFA and BPyFA is ascribed to the most prominent $\pi-\pi^*$ vibration of chromophore pyrene and triphenylamine according to

SCHEME 1: Retrosynthesis analysis of BPyFBFFA: (a) divergent synthetic route, (b) convergent synthetic route, (c) mixture route to BPyFBFFA.

our previous observations [22], respectively. Therefore, compared with PyFA, BPyFA with double substitution of pyrene moieties exhibited the relatively increasing intensity of peak at 350 nm. The PL maxima of PyFA and BPyFA in film were obviously red shifted (c.a. 50 nm), relative to those in solution presumably because of the improved excimer emission that resulted from strongly π -stacking between pyrene planes. The absorption and PL maxima of BPyFBFFA in solution are about 350 nm and 422 nm, respectively. The photoluminescence maxima of BPyFBFFA in solid state thin films were slightly red shifted relative to those in solution presumably

because of different dielectric constants in microenvironment. The difference between the precursors and the target BPyFBFFA without excimers suggests the introduction of terfluorene backbone is favorable for the three-dimensional framework to overcome the intermolecular interactions by the increased distance among chromophores.

3. Conclusions

In summary, we proposed shape-persistent covalent organic frameworks, polyhedra, nanomolecular architectures as

TABLE 1: Physical data of PyFA, BPyFA and BPyFBFFA.

Compound	$\lambda_{\max}^a$ (nm/abs)	$\lambda_{\max}^a$ (nm/PL)	$\lambda_{\max}^b$ (nm/PL)	T_d ($^{\circ}\text{C}$) ^c	T_g ($^{\circ}\text{C}$) ^d	(HOMO/eV) ^e	(LUMO/eV) ^e	Band gap
PyFA	298, 350	405	454	430	147	-5.29	-2.51	2.78
BPyFA	298, 350	421	468	519	218	-5.36	-2.63	2.73
BPyFBFFA	349	401, 422	433	402	130	-5.32	-2.63	2.73

^a Measured in CHCl_3 solution; ^b film; ^c obtained from TGA measurements, T_d : decomposition temperature, the temperature was recorded corresponding to a 5% weight loss; ^d obtained from DSC measurements, T_g : glass transition temperature. ^e HOMO/LUMO = $-(E_{\text{onset}} - 0.05 \text{ V}) - 4.8 \text{ eV}$, where the value 0.05 V is for FOC versus Ag/Ag^+ .

FIGURE 1: MALDI-tof-MS spectrum of BPyFBFFA.

FIGURE 2: The UV and PL spectra of PyFA, BPyFA and BPyFBFFA.

FIGURE 3: The molecular structure of BPyFBFFA, optimized molecular configurations of BPyFBFFA without alkyl substitution, and its cartoon geometric shape that resembles chair.

alternative next-generation organic semiconductors and advanced organic nanomaterials. Fluorene approaches are one effective and atom-economic bottom-up synthesis to open nanomolecular covalent organic frameworks as organic nanosystems that have been made by retrosynthetic analysis of methodologies. Based on this strategy, BPyFBFFA has been fabricated by iterative Friedel-Crafts reaction combined with Suzuki coupling reactions. BPyFBFFA that contains the oligofluorene tethered with a core of hole-transporting triphenylamine exhibited stable amorphous blue emitting behaviors which is potential multicomponent electroluminescent material. Complex diarylfluorenes (CDAFs) will be potential candidate for organic/polymer porous materials and organic nanomaterials. Fluorene approaches would offer a versatile platform to organic framework semiconductors for plastic optoelectronics and organic mechatronics.

4. Experimental Section

4.1. Chemicals. All the solvents and reagents were purchased from commercial suppliers and were used without further purification, unless noted otherwise. All products were purchased by flash column chromatography which was carried out with Kanto Silica Gel 60N (40–63 μm). Spectrochemical-grade solvents were used for optical measurements. Tetra(triphenylphosphine) palladium(II), 1-pyrenylboronic acid, pyrene, 2-bromo-9-fluorenone, bromobenzene and TPA were obtained from Aldrich Chemical Co. Boron trifluoride etherate, potassium carbonate, magnesium sulphate, chloroform, and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. Dichloromethane as dried by anhydrous sodium under room temperature. THF and toluene were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. 2-bromo-9-phenylfluorene-9-ol and 2,7-dibromo-9-phenylfluorene-9-ol, 4-(2-bromo-9-phenyl-fluorene)-N-phenyl-N-(4-(9-phenyl-2-(pyren-1-yl)-fluorene) phenyl)aniline, and 9,9,9'',9''-tetraoctyl-9'-phenyl-[2,2':7',2''-terfluorene]-9'-ol were obtained according to our previous literatures [22, 24, 25].

4.2. Characterization. ^1H -NMR and ^{13}C -NMR were recorded on a Bruker 400 MHz spectrometer in d-CDCl_3 with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS-2010P. For the MALDI-TOF MS spectra, the spectra were recorded in reflective mode, and no substrates were used. Element analyses were carried out on an Elementa 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. DSC analyses were performed on a Shimadzu DSC-60A instrument at a heating rate of $10^\circ\text{C}/\text{min}$. TGA were conducted on a Shimadzu DTG-60H thermogravimetric analyzer under a heating rate of $10^\circ\text{C}/\text{min}$. 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 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in CH_2Cl_2 except that polymers were coated on platinum plate electrodes in acetonitrile 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): $\text{HOMO/LUMO} = -(E_{\text{onset}} - 0.05 \text{ V}) - 4.8 \text{ eV}$, where the value 0.05 V is for ferrocene versus Ag/Ag^+ .

4.3. General Procedure for Friedel-Crafts Reactions. A solution of boron trifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) in appropriate dichloromethane (20 mL) was added dropwise to a mixture solution of tertiary alcohols and aryl substrates in appropriate dichloromethane (100 mL). The reaction mixture was stirred at rt (25°C) under nitrogen until starting material is no longer detectable by TLC (2 hours 2 days). Ethanol (50 mL) and

water (150 mL) were successively added to quench the reaction. And then the phases were separated and the aqueous phase was extracted with dichloromethane. The combined dichloromethane layers were washed and dried (MgSO_4). After removal of the solvent, the remaining crude product was purified by silicone gel chromatography (petroleum ether-dichloromethane) to yield products.

4.4. Synthesis of 4-(2-Bromo-9-phenyl-fluoren-9-yl)-N,N-diphenylaniline (1). Three compounds were prepared following the general procedures above using 2-bromo-9-phenyl-fluoren-9-ol (0.34 g, 1 mmol, 1 equiv.), TPA (2.44 g, 10 mmol, 10 equiv.), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex (0.12 mL, 1 mmol). The reaction mixture was stirred under nitrogen at room temperature (25°C) for 30 min. The yield of 4-(2-bromo-9-phenyl-fluoren-9-yl)-N,N-diphenylaniline (**1**) is 90%. The yield of byproduct is 9%. GC-MS (m/z): 565 [M^+]. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.73–7.71 (d, $J = 7.6$ Hz, 1H), 7.62–7.60 (td, $J = 8.0$ Hz, 1H), 7.53–7.53 (s, 1H), 7.48–7.46 (dd, $J = 8.0$ Hz, $J = 2.0$ Hz, 2H), 7.42–7.38 (d, $J = 7.6$ Hz, 1H), 7.37–7.34 (t, $J = 7.2$ Hz, 1H), 7.32–7.25 (d, $J = 7.6$ Hz, 1H), 7.25–7.19 (m, 9H), 7.18–7.08 (d, $J = 8.0$ Hz, 4H), 7.08–6.97 (m, 4H), 6.91–6.89 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.63, 151.42, 147.79, 146.70, 145.49, 139.37, 139.17, 138.74, 130.87, 129.60, 129.43, 129.01, 128.57, 128.32, 128.23, 127.82, 127.06, 126.45, 124.71, 123.16, 123.12, 121.72, 121.53, 120.42, 65.31.

4.5. Synthesis of N-(4-(2-Bromo-9-phenyl-fluoren-9-yl)phenyl)-N-(4-(9-phenyl-2-(pyren-1-yl)-fluoren-9-yl)phenyl)aniline (2). The compound was prepared following the general procedures above using 2-bromo-9-phenyl-fluoren-9-ol (0.336 g, 1 mmol, 1 equiv.), PyFA (0.685 g, 1 mmol, 1 equiv.), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex (0.124 mL, 1 mmol). The yield of target product (**2**) is 89%. MALDI-TOF-MS (m/z): 1003.5 [M^+] calcd. Found: 1005. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.21–8.17 (m, 2H), 8.12–8.08 (m, 4H), 8.01–7.98 (m, 2H), 7.95–7.89 (m, 2H), 7.86–7.85 (d, $J = 7.6$ Hz, 2H), 7.72–7.64 (m, 3H), 7.59–7.57 (d, $J = 8.0$ Hz, 1H), 7.50–7.39 (m, 4H), 7.36–7.31 (m, 5H), 7.27–7.13 (m, 13H), 7.08–7.06 (d, $J = 7.6$ Hz, 2H), 6.99–6.88 (m, 7H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.62, 151.86, 151.77, 151.41, 147.62, 146.58, 146.29, 146.13, 145.47, 140.64, 140.09, 139.45, 139.36, 139.15, 138.81, 137.96, 131.70, 131.15, 130.85, 130.79, 130.17, 129.58, 129.44, 129.22, 128.99, 128.87, 128.65, 128.55, 128.48, 128.39, 128.29, 128.22, 128.02, 127.86, 127.81, 127.79, 127.63, 127.04, 126.88, 126.59, 126.43, 126.23, 125.46, 125.32, 125.27, 125.13, 125.04, 124.98, 124.86, 123.80, 123.28, 123.26, 121.67, 121.51, 120.53, 120.38, 65.40, 65.29.

4.6. Synthesis of N,N-Bis(4-(2-bromo-9-phenyl-fluoren-9-yl)phenyl)aniline (3). The compound was prepared following the general procedures above using 2-bromo-9-phenyl-fluoren-9-ol (3.36 g, 10 mmol, 2 equiv.), TPA (1.33 g, 5 mmol, 1 equiv.), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex (0.62 mL, 5 mmol). The yield of byproduct 4-(2-Bromo-9-phenyl-fluoren-9-yl)-N,N-diphenylaniline (**1**) is lower than 5%. The yield of N,N-bis(4-(2-bromo-9-phenyl-fluoren-9-yl)phenyl)aniline (**3**) is 83%. MALDI-TOF-MS (m/z): 883 [M^+]. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 7.72–7.70 (d, $J = 7.6$ Hz, 2H), 7.61–7.55 (d, $J =$

7.6 Hz, 2H), 7.51 (s, 2H), 7.47–7.45 (d, $J = 7.6$ Hz, 2H), 7.38–7.33 (m, 4H), 7.29–7.27 (d, $J = 7.6$ Hz, 2H), 7.24–7.16 (m, 12H), 7.08–7.06 (d, $J = 7.6$ Hz, 2H), 7.01–6.98 (d, $J = 7.6$ Hz, 5H), 6.90–6.88 (d, $J = 7.6$ Hz, 4H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.59, 151.38, 147.49, 146.47, 145.45, 139.37, 139.16, 139.01, 130.87, 129.54, 129.46, 129.02, 128.57, 128.32, 128.22, 127.82, 127.06, 126.44, 125.16, 123.49, 123.43, 121.71, 121.52, 120.41, 65.31.

4.7. Synthesis of N,N-Bis(4-(2-bromo-9-phenyl-fluoren-9-yl)phenyl)-4-(9-phenyl-2-(pyren-1-yl)-fluoren-9-yl)aniline. The compound was prepared following the general procedures above using 2-bromo-9-phenyl-fluoren-9-ol (0.672 g, 2 mmol, 2 equiv.), PyFA (0.685 g, 1 mmol, 1 equiv.), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex (0.124 mL, 1 mmol). The yield of target product is 75%. MALDI-TOF-MS (m/z): 1321.2 [M^+] calcd. Found: 1323. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.19–8.17 (d, $J = 8.0$ Hz, 2H), 8.11–8.04 (m, 4H), 8.01–7.96 (m, 2H), 7.94–7.89 (m, 2H), 7.85–7.83 (d, $J = 7.2$ Hz, 2H), 7.71–7.63 (m, 4H), 7.58–7.56 (d, $J = 8.0$ Hz, 2H), 7.49–7.39 (m, 6H), 7.34–7.29 (m, 7H), 7.24–7.12 (m, 17H), 6.98–6.96 (d, $J = 8.8$ Hz, 4H), 6.93–6.87 (m, 6H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 153.56, 151.83, 151.76, 151.36, 146.29, 146.09, 145.99, 145.42, 140.64, 140.36, 140.07, 139.44, 139.34, 139.16, 137.95, 128.92, 129.12, 131.69, 131.13, 130.85, 130.78, 130.19, 129.56, 129.22, 129.01, 128.84, 128.64, 128.5, 128.47, 128.38, 128.31, 128.25, 128.03, 127.87, 127.79, 127.61, 127.03, 126.87, 126.59, 126.42, 126.24, 125.46, 125.31, 125.26, 125.12, 125.01, 124.87, 124.17, 123.74, 121.66, 121.51, 120.53, 120.36, 65.39, 65.29.

4.8. Synthesis of N,N-Bis(4-(2-(pyren-1-yl)-9-phenylfluoren-9-yl)phenyl)-4-(2,7-bis(9,9-dioctylfluoren-2-yl)-9-phenylfluoren-9-yl)aniline (BPyFBFFA). The target molecule was prepared following the general procedures above using 9,9,9'',9''-tetraoctyl-9'-phenyl-[2,2':7',2''-terfluoren]-9'-ol (3.043 g, 2.94 mmol), BPyFA (3.307 g, 2.94 mmol), and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ complex (439.4 μL , 3.46 mmol). The reaction mixture was stirred at rt (25°C) under nitrogen for 48 h. The yield of BPyFBFFA is 70%. MALDI-TOF-MS (m/z): [M^+] calcd. For $\text{C}_{165}\text{H}_{147}\text{N}$, 2143 Found: 2142.

4.9. General Procedure for Suzuki Reactions, Taking N-phenyl-N-(4-(2-(pyren-1-yl)-9-phenyl-fluoren-9-yl)phenyl)aniline (PyFA) as an Example. A typical preparation procedure is as follows. In a three-necked schlenk flask (150 mL), 4-(2-bromo-9-phenyl-fluoren-9-yl)-N,N-diphenylaniline (**1**) (565 mg, 1 mmol), 1-pyrenylboronic acid (322 mg, 1.3 mmol, 1.3 eq), and tetra(triphenylphosphine) palladium (0) (80 mg) were added. The flask was evacuated and back filled with nitrogen atmosphere over three times, after which degassed toluene (30 mL) and K_2CO_3 aqueous solution (2 M, 5 mL, 10 e equiv.) were injected into the flask through syringe. The mixture was heated up to 90°C and stirred for 2 days. The solvent was removed under vacuum. The mixture was purified by silica gel chromatography (petroleum ether) to afford pale yellow powder (548 mg, 80%). MALDI-TOF-MS (m/z): [M^+] calcd. For $\text{C}_{53}\text{H}_{35}\text{N}$, 685.3; Found: 685.5. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.22–8.18 (t, $J = 7.6$ Hz,

2H), 8.16–8.18 (d, $J = 8.8$ Hz, 2H), 8.09 (s, 2H), 8.03–8.01 (t, 2H), 7.97–7.93 (t, $J = 7.6$ Hz, 2H), 7.89–7.87 (d, $J = 7.6$ Hz, 1H), 7.77 (s, 1H), 7.69–7.67 (d, $J = 7.6$ Hz, 1H), 7.52–7.50 (d, $J = 7.6$ Hz, 1H), 7.46–7.42 (t, $J = 7.6$ Hz, 1H), 7.37–7.34 (m, 3H), 7.27–7.21 (m, 7H), 7.19–7.17 (d, $J = 8.4$ Hz, 2H), 7.11–7.09 (d, $J = 7.6$ Hz, 2H), 7.02–6.96 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 151.88, 151.77, 147.91, 146.54, 146.21, 140.64, 140.11, 139.86, 139.46, 137.95, 131.711, 131.15, 130.79, 130.22, 129.45, 129.23, 128.91, 128.63, 128.53, 128.42, 128.05, 127.91, 127.86, 127.68, 126.98, 126.64, 126.28, 125.48, 125.37, 125.27, 125.16, 125.01, 124.92, 124.56, 123.51, 122.99, 120.61, 120.49, 65.41.

N,N-bis(4-(2-(pyren-1-yl)-9-phenyl-fluoren-9-yl)phenyl)aniline (BPYFA). The target molecule was prepared following the general procedures above. $R_f = 0.12$ (petroleum ether). MALDI-TOF-MS (m/z): $[M^+]$ calcd. For $\text{C}_{88}\text{H}_{55}\text{N}$, 1125.4, Found: 1125.6. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 8.17–8.14 (t, 4H), 8.09–8.04 (m, 8H), 7.96–7.91 (m, 6H), 7.88–7.83 (t, 4H), 7.71 (s, 2H), 7.64–7.62 (m, 2H), 7.46–7.44 (m, 2H), 7.42–7.38 (t, $J = 7.6$ Hz, 2H), 7.31–7.27 (m, 6H), 7.25–7.15 (m, 8H), 7.14–7.07 (m, 6H), 6.99–6.92 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 151.82, 151.74, 147.71, 146.36, 146.158, 140.61, 140.05, 139.87, 139.41, 137.89, 137.81, 131.64, 131.08, 130.72, 130.17, 129.43, 129.17, 128.85, 128.57, 128.55, 128.48, 128.37, 128.29, 128.01, 127.84, 127.80, 127.60, 126.88, 126.57, 126.21, 125.42, 125.23, 125.19, 125.05, 124.97, 124.89, 124.85, 123.57, 123.15, 120.54, 120.39, 65.37.

Authors' Contributions

G.- W. Zhang and L. Wang contributed equally to this work.

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