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One-pot synthesis of 2-bromo-4,5-diazafluoren-9-one via a tandem oxidation–bromination-rearrangement of phenanthroline and its hammer-shaped donor–acceptor organic semiconductors

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ABSTRACT

An unexpected one-pot tandem procedure of 2-bromo-4,5-diazafluoren-9-one starting from phenanthroline with a yield of up to 50% has been described. The conversion mechanism involves three consecutive oxidation, bromination, and rearrangement reactions. A series of its hammer-shaped donor–acceptor organic semiconductors with solvent-dependent fluorescence have also been constructed via Ullman and/or Friedel–Crafts reaction. Diazafluorenes (DAFs) and derivatives are regarded as promising building blocks or candidates for donor–acceptor organic semiconductors.

1. Introduction

Donor–acceptor (D–A) molecules have attracted much attention in organic molecular and solid electronics after the discovery of frontier molecular orbital (FMO) theory and subsequently applications in the nonlinear optical materials.[1] D–A π-systems possess rectifying characteristics with the essence of intramolecular p–n junctions in molecular devices.[2] Huang's group proposed p–n π-conjugated copolymers to flexibly adjust highest occupied molecular orbital (HOMO) and lower unoccupied molecular orbital (LUMO) levels for red, green, and blue (RGB) light-emitting polymers in polymer light-emitting diodes (PLEDs).[3] Their charge transfer and energy transfer processes can be well tuned through the combination of various molecular segments to develop the high-efficient fluorescent red light-emitting materials[4] and ambipolar charge-transporting materials.[5] Furthermore, trap depth and trap density can be controlled via p–n components to develop polymeric dynamic random access memory (DRAM) cells.[6] Recently, D–A conjugated polymers were extensively applied to develop low-bandgap organic semiconductors with broad electronic absorption and high charge mobilities for solar cells.[7]

However, most of π-molecular segments exhibit electron-donating property in organic semiconductors,[8] it is significant to explore novel electron-withdrawing building blocks to fulfill various D–A π-systems for high-performance devices. Numerous efforts have been made to focus on pyridine,[9] oxadiazole,[10] benzothiadiazole,[11] perylene diimide,[12] and C_{60}[13] as electron-acceptors. Nevertheless, 4,5-diazafluorenes (DAFs) as popular chelate ligands[14] whose electron-deficient property have been ignored to a large extent.[15] DAFs are potential building blocks in organic electronics. 9,9′-Diaryl-DAFs exhibit excellent hole-blocking ability in comparison with the widely used 2,9-dimethyl-4,7-diphehyl-1,10-phenanthroline (BCP).[16] Moreover, spiro-DAF incorporated into blue terfluorene was demonstrated to enhance the ability of electron injection without changing the emission characteristics by Wong et al.[17] Besides, DAF-based photoinduced electron transfer (PET) chromophores were constructed to chelate with sense metal ions.[18] In this context, one challenge is to develop the key intermediates, such as halogen-substituted DAFs, which are significant to be introduced into the π-conjugated systems in organic electronics.

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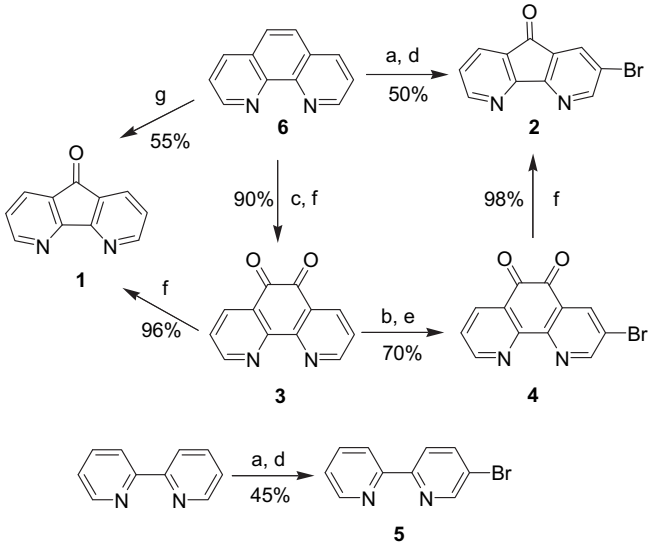
2. Results and discussion

It is known that halogenations of aromatic compounds have always been considered as key starting materials to actualize the connection of different π-molecular segments to construct semiconducting D–A molecules by various C–C, C–O or C–N cross-coupling reactions. The synthesis of diazafluorenone (**1**, Scheme 1) has been carried out under the condition of $KMnO_4$/KOH (0.24 M) and NaOH (0.1 M).[19] However, there are rarely reports on its halogen-substituted derivatives,[20] such as bromide substituted diazafluorenone **2**, in the last three decades. In this contribution, **2** was firstly synthesized and demonstrated by an unexpected one-pot tandem reaction in a yield of up to 50%, as shown in Scheme 1. We initially planned to prepare **3** from **6** in the condition of H_2SO_4/HNO_3/KBr for 2 h according to the literatures.[21] In fact, reaction time was occasionally prolonged to 24 h. As a result, after neutralizing the mixture with solid sodium hydroxide, two different compounds were monitored by thin-layer chromatography (TLC) after the rapid neutralization of the reactant with solid sodium hydroxide. GC–MS showed their molecular ion peaks of 182 and 260 g/mol, respectively, corresponding to diazafluorenone **1** and 2-bromo diazafluorenone **2**, respectively. Fortunately, the target compound **2** was unambiguously identified by single-crystal X-ray diffraction (Fig. 1).



Scheme 1. Synthesis of **1**,[19a,22] **2**, and **5**, and related intermediates. Conditions: (a) H_2SO_4/HNO_3/KBr, reflux, 24 h; (b) H_2SO_4/HNO_3/KBr, reflux, 12 h; (c) H_2SO_4/HNO_3/KBr, reflux, 2 h; (d) NaOH (s); (e) NaOH (aq); (f) NaOH (0.1 M); (g) $KMnO_4$; KOH (0.24 M).

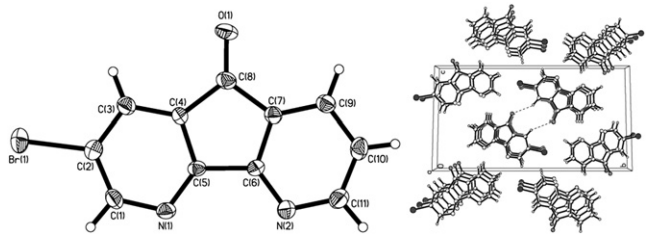
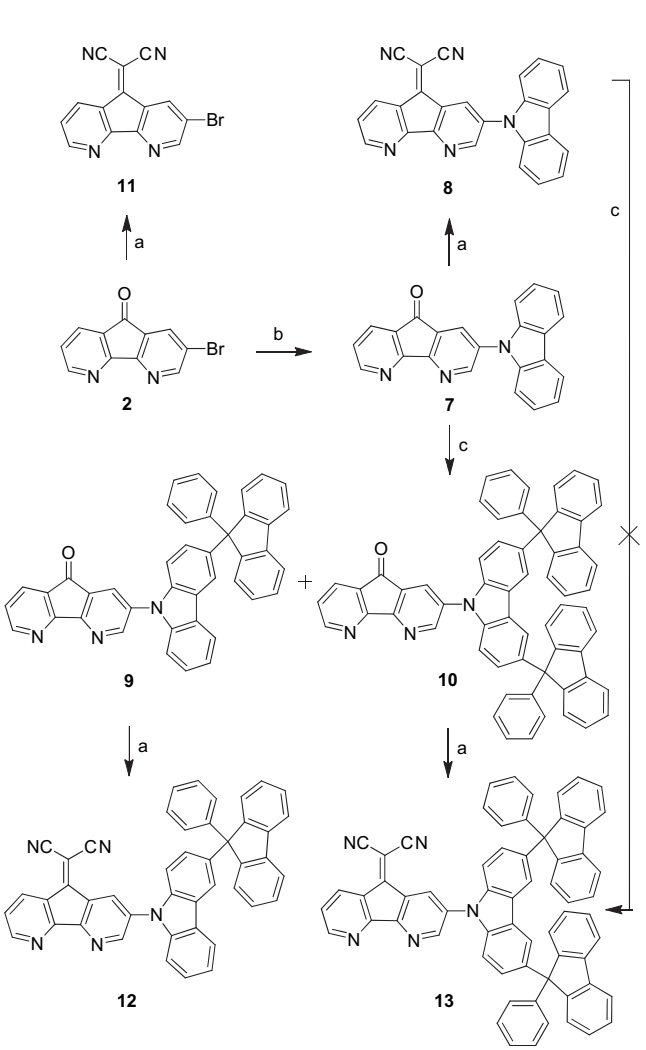


Fig. 1. X-ray crystal structure of **2** with ORTEP drawing and its molecular packing.

In order to profoundly understand the conversion mechanism, a series of experiments were designed and carried out with different reaction time. Compound **3** was obtained in 90% yield for 2 h, which is consistent with the literature.[21c] Then **4** was obtained in 70% yield after treating **3** in the same condition for 12 h. At last, **2** was smoothly synthesized with a yield of 98% after treating **4** in boiled sodium hydroxide solution undergoing a rearrangement reaction.[22] On the basis of these experiments above, we proposed a mechanism of one-pot three steps named as oxidation–bromination-rearrangement (OBR) procedure (Scheme 1) to this tandem reaction. In addition, we realized this useful alternative protocol for the facile synthesis of **5** successfully (Scheme 1),[23] which was obtained either by the troublesome bromination of 2,2′-bipyridine hydrobromide salt or Stille cross-coupling reaction in the literatures.[24]

Subsequently, a series of D–A type derivatives, among which DAF acting as acceptor and carbazole (Cz) as donor, were designed and constructed (Scheme 2). Compound **7** was obtained via C–N cross-coupling Ullman reaction in 71% yield. Then, dicyanovinyl group was introduced in the presence of malononitrile in dimethylsulfoxide (DMSO) giving **8** with the yield of 66% in order to further enhance the electron-withdrawing ability. The $BF_3 \cdot Et_2O$ catalyzed Friedel–Crafts (F–C) reaction[25] was carried out to generate CDAFs, monosubstituted **9** in 30% yield and disubstituted **10** in 68% yield. Similarly, dicyanovinyl group was also introduced giving **11**, **12**, and **13** in the yields of 70%, 63%, and 65%, respectively. It should be noted that **13** could not be effectively obtained by electrophilic F–C reaction starting from **11**. All the compounds were confirmed by ^1H NMR, ^{13}C NMR, GC–MS, MALDI-TOF MS, and elemental analysis.



Scheme 2. Synthesis of diazafluorenone-based D–A type derivatives. Conditions: (a) $CH_2(CN)_2$, DMSO, 5 h, 110 °C; (b) Carbazole, 1,2-dichlorobenzene, CuI, 18-crown-6, K_2CO_3, 24 h, 190 °C; (c) 9-phenyl-fluoren-9-ol, $BF_3 \cdot Et_2O$, CH_2Cl_2, rt, 24 h.

Fig. 2 displays electronic absorption UV–vis spectra of four DAF-based D–A type derivatives including **7**, **8**, **10**, and **13** in spin-coated films and THF solvent (10^{-5} mol/L) (inset). There are several distinct bands in all four compounds in both dilute THF solution and thin film. Among them, the high-energy absorption bands in the range of 200–300 nm is assigned to π–π* transition of π-conjugated backbone on account of the large absorption coefficients.[26] The lower-energy absorption band appearing in the range of 320–410 nm results from the intramolecular charge-transfer (ICT) transition. The lowest-energy absorption band of **10** appearing in the range of 420–510 nm with very small absorption coefficients is attributed to the symmetry-forbidden *n*–π* transition of the carbonyl groups in diazafluorenone.

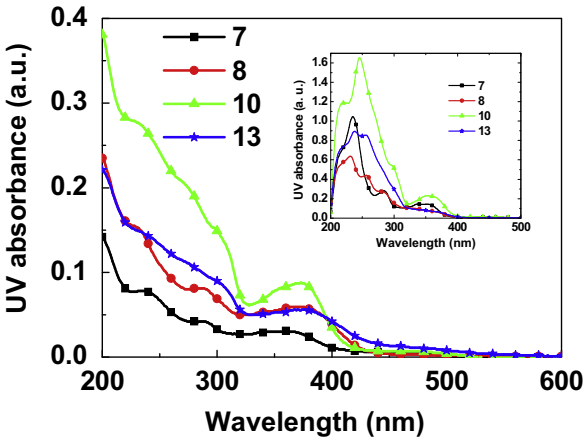


Fig. 2. The UV–vis spectra of **7** (black), **8** (red), **10** (green), and **13** (blue) in spin-coated films (a) and THF solvent (10^{-5} mol/L) (insert).

The electronic absorption and photoluminescence spectra of **10** in several different polar solvents, including toluene, benzene, tetrahydrofuran (THF), chloroform ($CHCl_3$), and DMSO, are shown in Fig. 3. The lower-energy bands in the range of 350–410 nm depend slightly on solvent polarity, as shown in Fig. 3a, revealing that weak electronic coupling existed between the donor (carbazole) and acceptor (diazafluorenone) moieties in the ground state. In contrast, it exhibits solvent-dependent fluorescence, indicating that the complicated excited states and energy transfer occur. There are two emission bands with the peaks of ca. 420 and 560 nm under the excitation of 360 nm in nonpolar toluene (420 and 561 nm) and benzene (431 and 566 nm) solvents (Fig. 3b), in which the intensity of yellow emission peak is relatively higher than that of blue emission. Blue and yellow emissions probably originated from ICT and the lowest excited state (*n*–π* state) via uncompleted energy transfer process, respectively. The emission wavelength of **10** altered with the different excitation wavelengths, also indicating that energy transfer from ICT to *n*–π* state is not completed. It is very interesting that two emission peaks at 433 and 572 nm remain in polar THF, while the yellow peak strength (572 nm) is weaker than that of blue peak (433 nm). This result further indicates that blue and yellow emissions probably originated from ICT excited state and diazafluorenone chromophores via uncompleted energy transfer process owing to the latter easily quenched by stronger polar solvent than the former. Furthermore, the long-wavelength emission disappeared in $CHCl_3$ (434 nm) and DMSO (451 nm). This result probably indicated that the stronger quenching effect of these polar solvents occur on the lowest excited state of *n*–π* state feature of diazafluorenone. The photograph shows the emission of **10** in different polar solvents under the irradiation of UV 365 nm (Fig. 3b, insert) matching well with the PL in different solvents. The similar solvent-dependent effect and incomplete energy transfer in the emission spectra of **7** were also found in the abovementioned solvents, but not clearly.

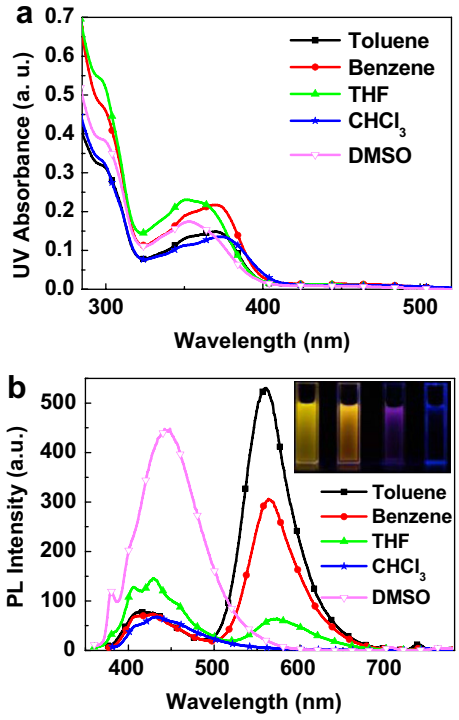


Fig. 3. The UV–vis (a) and PL spectra (b) of **10** in different solvents (10^{-5} mol/L), insert: the photograph (insert) of **10** in toluene, benzene, THF, and $CHCl_3$ under the irradiation of UV 365 nm.

It indicated that bulky 9-phenyl-fluoren-9-yl moieties (PFMs) of **10** also play a key role in tuning the energy transfer process and electronic behaviors (in Fig. S10).

The reductive and oxidative cyclic voltammograms (CV) were shown in Fig. 4 and Table 1. HOMO energy levels are estimated to be

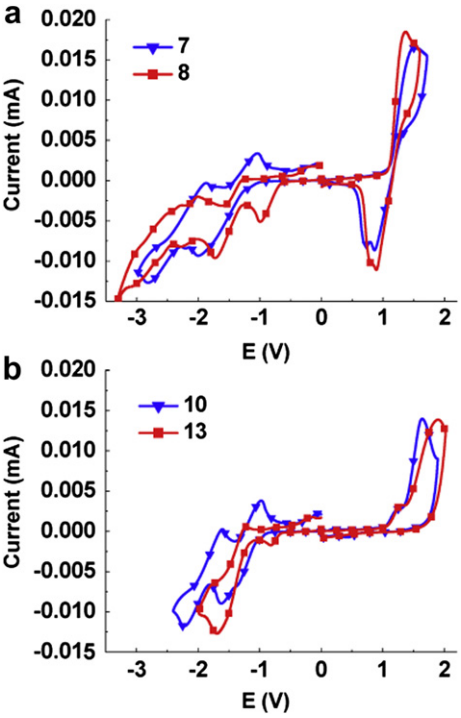


Fig. 4. Reductive and oxidative cyclic voltammograms of **7** (a, blue), **8** (a, red), **10** (b, blue), and **13** (b, red); 0.1 M *n*-Bu_4NPF_6 in THF (reduction) and 0.1 M *n*-Bu_4NPF_6 in CH_2Cl_2 (oxidation) were used as supporting electrolytes. A platinum sheet electrode was used as the working electrode; scanning rate was 100 mV/s, where $E^{+}_{(Fc/Fc)}$ is about 0.066 V for **7**, **8**, and **13**, and 0.14 V for **10**, respectively.

Table 1
Physical properties of target molecules

Compound	$\lambda_{abs,\ max}$/nm		$\lambda_{PL,\ max}$/nm	Cyclic voltammetry				
	Solution	Film	Solution	E_{ox}/(V)	E_{red}/(V)	HOMO (eV)	LUMO (eV)	E_g (eV)
7	235, 350	235, 359	402, 551	1.12	−1.25	−5.85	−3.48	2.37
8	231, 339	230, 372	419	1.10	−0.66	−5.83	−4.07	1.76
10	244, 353	234, 376	425, 563	1.07	−1.07	−5.73	−3.59	2.14
13	237, 346	235, 361	420, 560	1.06	−0.68	−5.79	−4.05	1.74

−5.85 eV for **7**, −5.83 eV for **8**, −5.73 eV for **10**, and −5.79 eV for **13** according to their turn-on voltages of oxidation processes, respectively, which probably is attributed to their electron-donating Cz groups.[27] Compared with **7** and **8**, the second peaks of **10** and **13** result from the fluorene groups. LUMO energy levels are estimated to be −3.48 eV for **7**, −4.07 eV for **8**, −3.59 eV for **10**, and −4.05 eV for **13** according to their turn-on voltages of reduction processes, respectively. Compared with **7** and **10**, the introduction of strongly electron-withdrawing dicyanovinyl groups in **8** and **13** greatly decreased their LUMO energy levels. It is worthy noting that **13** has the lowest HOMO/LUMO bandgap energy of 1.74 eV.

3. Conclusions

In summary, we have developed an effective protocol to synthesize 2-bromo-4,5-diazafluoren-9-one (**2**) and demonstrated the tandem oxidation–bromination-rearrangement mechanism. The one-pot synthesis method reveals that KBr is an efficient bromination reagent for electron-deficient diaza-aromatic hydrocarbons. A series of diazafluorenes-based derivatives also have been synthesized via Ullman and/or Friedel–Crafts reaction, which exhibit solvent-dependent fluorescence and low-energy bandgap. Diazafluorenes-based donor–acceptor systems are promising organic semiconductors and ligands in organic electronics and supramolecular chemistry.

4. Experimental section

4.1. General information

All the chemicals and reagents were purchased from Nanjing Fountain Global Displays. ^{1}H and ^{13}C NMR were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS 2010 PLUS. For the MALDI-TOF MS spectrum, it was recorded in reflective mode. Elemental analyses were carried out in an elementar Analysensysteme GmbH-vario EL III element analyzer. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25 °C, and emission spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A instrument. Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric analyzer under a heating rate of 10 °C/min and a nitrogen flow rate of 50 ml/min. CV studies were conducted using an CHI660C Electrochemical Workstation 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 (n-Bu_4NPF_6) in dichloromethane (oxidation process) and tetrahydrofuran (reduction process) at a sweeping rate of 100 mV/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO=−[E_{onset}−$E^{+}_{(Fc/Fc)}$+4.8] eV, where $E^{+}_{(Fc/Fc)}$ is about 0.066 V for **7**, **8**, and **13**, and 0.14 V for **10**, respectively. X-ray crystallographic data for **2** were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1 K CCD area detector (employing the program SMART) and a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ=0.71073 Å). Data processing was carried out 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 nonhydrogen atoms were refined using anisotropic thermal parameters and hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

*4.1.1. 2-Bromo-4,5-diazafluoren-9-one (**2**).* Mixture of 1,10-phenanthroline hydrate (2.93 g, 14.8 mmol), KBr (2.11 g, 17.8 mmol), and a mixed acid (18 ml of concentrated HNO_3 and 36 ml of concentrated H_2SO_4) was allowed to react for 24 h under reflux after the temperature ascending to 100 °C rapidly. The reaction mixture was poured into water (300 ml) and neutralized with solid sodium hydroxide until pH=7. The precipitate was filtered and washed with $CHCl_3$, then extracted with $CHCl_3$. The filtrate was dried over anhydrous $MgSO_4$. Then the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, EtOAc/petroleum ether, 1:2) to give **2** (1.93 g, 50%) as a straw yellow solid; mp 188–189 °C; R_f 0.35 (silica gel, EtOAc/petroleum ether, 1:3); [found: C, 50.62; H, 1.92. $C_{11}H_5BrN_2O$ requires C, 50.61; H, 1.93%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.84–8.83 (d, J=5.2 Hz, 1H), 8.13 (s, 1H), 8.04–8.02 (d, J=7.6 Hz, 1H), 7.42–7.39 (t, J=12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 162.7, 161.4, 156.0, 155.5, 134.2, 131.8, 130.4, 129.2, 125.0, 122.3. GC–MS (EI-m/z) calcd for $C_{11}H_5BrN_2O^+$ $[M]^+$ 261.07, found 261.15.

*4.1.2. 3-Bromo-1,10-phenanthroline-5,6-dione (**4**).* Mixture of Phenanthroline-5,6-dione (0.50 g, 2.38 mmol), KBr (0.34 g, 2.87 mmol), and a mixed acid (2.9 ml of concentrated HNO_3 and 5.6 ml of concentrated H_2SO_4) was allowed to react for 12 h under reflux after the temperature ascending to 100 °C rapidly. The reaction mixture was poured into water (300 ml) and neutralized with sodium hydroxide solution until pH=7. The precipitate was filtered and washed with $CHCl_3$, then extracted with $CHCl_3$. The filtrate was dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, EtOAc/petroleum ether, 2:1) to afford the desired product **4** (0.48 g, 70%) as a greenblack solid; mp 268 °C; R_f 0.25 (silica gel, EtOAc/petroleum ether, 2:1); [found: C, 49.90; H, 1.76. $C_{12}H_5BrN_2O_2$ requires C, 49.86; H, 1.74%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15–9.12 (s, 1H), 9.12–9.11 (d, J=4.8 Hz, 1H), 8.61 (s, 1H), 8.52–8.50 (d, J=7.6 Hz, 1H), 7.63–7.60 (t, J=12.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.98, 177.78, 157.46, 156.52, 152.35, 151.00, 139.34, 137.55, 128.56, 127.99, 125.87, 123.34. GC–MS (EI-m/z) calcd for $C_{12}H_5BrN_2O_2^+$ $[M]^+$ 289.08, found 289.95.

*4.1.3. Preparation of 5-bromo-2,2′-bipyridine (**5**).* The procedure is similar to the preparation of **2**. Mixture of 2,2′-bipyridine (0.5 g,

3.2 mmol), KBr (0.46 g, 3.87 mmol), and a mixed acid (3.9 ml of concentrated HNO_3 and 7.7 ml of concentrated H_2SO_4) was allowed to react for 24 h under reflux after the temperature ascending to 100 °C rapidly. The reaction mixture was poured into 50 ml water and neutralized with solid sodium hydroxide until pH=7. The precipitate was filtered and washed with $CHCl_3$, then extracted with $CHCl_3$. The filtrate was dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (EtOAc/petroleum ether, 1:5) to give desired product **5** (0.34 g, 45%) as a white solid; mp 74–75 °C; R_f 0.40 (silica gel, EtOAc/petroleum ether, 1:3); [found: C, 51.11; H, 2.94. $C_{10}H_7BrN_2$ requires C, 51.09; H, 3.00%]; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.74–8.743 (d, J=2 Hz, 1H), 8.70–8.69 (d, J=4 Hz, 1H), 8.40–8.38 (d, J=8 Hz, 1H), 8.35–8.33 (d, J=8 Hz, 1H), 7.97–7.95 (d, J=8 Hz 1H), 7.86–7.82 (t, J=8 Hz, 1H), 7.36–7.33 (t, J=8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.13, 154.59, 150.17, 149.23, 139.47, 137.00, 123.99, 122.33, 121.14. GC–MS (m/z) calcd for $C_{10}H_7BrN_2^+$ $[M]^+$, found 233.95. The compound is known and that the data obtained matches that of the literature values.[24b]

*4.1.4. 2-(Carbazol-9-yl)-4,5-diazafluorenone (**7**).* The samples of **2** (0.50 g, 1.1952 mmol), carbazole (0.74 g, 4.4293 mmol), potassium carbonate (0.32 g, 2.3153 mmol) a spot of 18-crown-6, and copper (I) iodide were dissolved in 1,2-dichlorobenzene, the mixture was refluxed for 24 h under the protection of N_2. Then remove the solvent by reduced pressure distillation, the remains were extracted with CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation, and the residue was purified by column chromatography (EtOAc/petroleum ether, 2:1) as eluent to obtain 0.47 g orange-red powder in the yield of (0.47 g, 71%); mp 172–173 °C; R_f 0.35 (silica gel, EtOAc/petroleum ether, 1:3); [found: C, 79.49; H, 3.79. $C_{23}H_{13}N_3O$ requires C, 79.53; H, 3.77%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10–9.09 (d, J=2.0 Hz, 1H), 8.9–8.89 (d, J=4.8 Hz, 1H), 8.26–8.25 (d, J=2.0 Hz, 1H), 8.18–8.16 (d, J=8.0 Hz, 2H), 8.1–8.08 (d, J=7.2 Hz, 1H), 7.51–7.45 (m, 4H), 7.44–7.42 (t, J=7.6 Hz, 1H), 7.40–7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.63, 162.91, 161.12, 155.6, 153.3, 140.1, 136.1, 131.8, 130.5, 129.9, 129.3, 126.60, 124.8, 124.1, 121.2, 120.7, 109.3. GC–MS (m/z) calcd for $C_{23}H_{13}N_3O^+$ $[M]^+$ 347.37, found 347.10.

*4.1.5. 2-(2-(Carbazol-9-yl)-4,5-diazafluoren-9-ylidene)malononitrile (**8**).* Mixture of **7** (0.2 g, 0.5758 mmol) and malononitrile (0.042 g, 0.6351 mmol) was dissolved in DMSO (5.0 ml). Then the mixture was stirred at 110 °C for 5 h. The carmine precipitation was then filtered and washed with MeCN to give **8** (0.15 g, 66%); [found: C, 78.93; H, 3.34. $C_{26}H_{13}N_5$ requires C, 78.97; H, 3.31%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.98 (s, 1H), 8.90–8.89 (d, J=4.4 Hz, 1H), 8.79–8.77 (d, J=8.4 Hz, 1H), 8.19–8.17 (d, J=8 Hz, 2H), 7.53–7.49 (m, 4H), 7.48–7.47 (t, J=4.8 Hz, 1H), 7.41–7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.2, 155.8, 155.5, 153.3, 140.0, 135.8, 133.7, 131.1, 130.1, 129.5, 126.8, 124.6, 124.2, 121.4, 120.8, 112.0, 109.2, 81.0. GC–MS (EI-m/z) calcd for $C_{26}H_{13}N_5^+$ $[M]^+$ 395.41, found 395.35.

*4.1.6. 2-(3,6-Bis(9-phenyl-fluoren-9-yl)-carbazol-9-yl)-9H-4,5-diazafluoren-9-one and 2-(3-(9-phenyl-9H-fluoren-9-yl)-9H-carbazol-9-yl)-9H-4,5-diazafluoren-9-one (**9** and **10**).* A sample of **7** (0.15 g, 0.4318 mmol) was dissolved in dry CH_2Cl_2 placed in the flask, 9-phenyl-fluorene-9-ol (PFOH) (0.25 g, 0.9678 mmol) was dissolved in dry CH_2Cl_2 in a constant dripping funnel, $BF_3\cdot Et_2O$ (0.4 ml) was injected in the flask, the aqueous turned into green from yellow immediately, stirred in room temperature, the PFOH was added in the flask by dropwise, the solution turned into purple accordingly, stirred at room temperature for 48 h, the reaction was quenched by water and ethanol, then extracted with CH_2Cl_2. The combined extracts were dried over anhydrous $MgSO_4$, concentrated, and the residue was purified by column chromatography (dichloromethane/petroleum ether, 4:1) to give **9** (0.076 g, 30%) as a yellow solid; R_f 0.32 (silica gel, dichloromethane/petroleum ether, 5:1); [found: C, 85.82; H, 4.27. $C_{42}H_{25}N_3O$ requires C, 85.84; H, 4.29%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.86–8.85 (d, J=3.6 Hz, 1H), 8.18 (s, 1H), 8.07–8.05 (d, J=7.6 Hz, 1H), 7.98–7.93 (t, J=19.2 Hz, 2H), 7.82–7.80 (d, J=7.6 Hz, 2H), 7.50–7.48 (d, J=7.6 Hz, 2H), 7.46–7.37 (m, 8H), 7.33 (t, 1H), 7.32–7.28 (m, 5H), 7.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.63, 162.92, 161.00, 155.59, 153.06, 151.55, 146.33, 140.35, 140.13, 139.17, 138.94, 136.10, 131.85, 130.43, 129.87, 129.08, 128.32, 128.18, 127.84, 127.55, 127.29, 126.73, 126.56, 126.25, 124.83, 124.05, 123.92, 121.11, 120.82, 120.28, 119.84, 109.26, 109.15, 65.53; MALDI-TOF MS (m/z) calcd for $C_{42}H_{25}N_3O^+$ $[M]^+$ 587.67, found 588.42. And **10** (0.24 g, 68%) as a yellow solid; R_f 0.30 (silica gel, dichloromethane/petroleum ether, 5:1); [found: C, 88.53; H, 4.47. $C_{61}H_{37}N_3O$ requires C, 88.49; H, 4.50%]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.87–8.85 (d, J=6.4 Hz, 1H), 8.13 (s, 1H), 8.06–8.04 (d, J=6 Hz, 1H), 7.83 (s, 2H), 7.81–7.79 (d, J=7.6 Hz, 4H), 7.47–7.45 (d, J=7.6 Hz, 4H), 7.42–7.36 (m, 6H), 7.30–7.25 (m, 16H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.54, 163.09, 155.55, 152.89, 151.57, 146.39, 140.07, 139.28, 138.96, 136.05, 131.81, 130.39, 129.86, 128.92, 128.30, 128.08, 127.77, 127.50, 127.25, 126.70, 126.26, 124.78, 123.99, 120.23, 120.09, 109.04, 65.53; MALDI-TOF MS (m/z) calcd for $C_{61}H_{37}N_3O^+$ $[M]^+$ 827.97, found 828.87.

*4.1.7. 2-(2-Bromo-4,5-diazafluoren-9-ylidene) malononitrile (**11**).* The procedure is similar to the preparation of **7**. A sample of **2** (0.10 g, 0.3830 mmol) and malononitrile (0.028 g, 0.4225 mmol) was dissolved in DMSO (1.4 ml), the mixture was stirred at 110 °C for 5 h. After reaction, the mixture was filtrated and washed with acetonitrile to give a brownish black precipitation as **11** (0.083 g, 70%); [found: C, 54.44; H, 1.58. $C_{14}H_5BrN_4$ requires C, 54.40; H, 1.63; Br, 25.85; N, 18.12]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.85–8.83 (d, J=5.2 Hz, 1H), 8.82 (s, 1H), 8.73–8.71 (d, J=8.4 Hz, 1H), 7.48–7.45 (t, J=13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.8, 157.7, 156.1, 155.5, 155.1, 135.9, 133.7, 130.3, 128.9, 124.8, 121.9, 111.9, 81.0. GC–MS (EI-m/z) calcd for $C_{14}H_5BrN_4^+$ $[M]^+$ 309.12, found 307.95.

*4.1.8. 2-(2-(3-(9-Phenyl-9H-fluoren-9-yl)-9H-carbazol-9-yl)-9H-4,5-diazafluoren-9-ylidene)malononitrile (**12**).* The procedure is similar to the preparation of **7** and **11**. Compound **9** (0.1 g, 0.1702 mmol) and malononitrile (0.01240 g, 0.1877 mmol) were dissolved in DMSO (0.62 ml), and then the mixture was stirred at 110 °C for 5 h. After filtration, **12** (0.68 g, 63%) was obtained as a brownish black precipitation; [found: C, 85.06; H, 3.91. $C_{45}H_{25}N_5$ requires C, 85.02; H, 3.96%]; ^{1}H NMR (100 MHz, $CDCl_3$, ppm) δ 9.02 (s, 1H), 8.89 (s, 1H), 8.86–8.85 (d, J=5.2 Hz, 1H), 8.75–8.73 (d, J=8 Hz, 1H), 7.99–7.95 (t, J=15.2 Hz, 2H), 7.82–7.80 (d, J=7.6 Hz, 2H), 7.50–7.48 (d, J=7.6 Hz, 2H), 7.74–7.75 (t, J=7.2 Hz, 1H), 7.44–7.33 (m, 8H), 7.32–7.30 (m, 5H), 7.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.01, 157.18, 155.73, 155.47, 153.20, 151.52, 146.33, 140.33, 140.13, 139.40, 138.94, 135.84, 133.67, 130.97, 130.08, 129.46, 128.32, 128.19, 127.85, 127.55, 127.33, 126.72, 126.27, 124.55, 124.17, 124.06, 121.45, 121.32, 120.91, 120.80, 120.28, 120.02, 111.98, 109.13, 108.94, 81.00, 65.54; MALDI-TOF MS (m/z) calcd for $C_{45}H_{25}N_5^+$ $[M]^+$ 635.71, found 635.91.

*4.1.9. 2-(2-(3,6-Bis(9-phenyl-fluoren-9-yl)-carbazol-9-yl)-9H-4,5-diazafluoren-9-ylidene)malononitrile (**13**).* The procedure is similar to the preparation of **11**. Compound **10** (0.2 g, 0.2416 mmol) and malononitrile (0.01756 g, 0.2658 mmol) were dissolved in DMSO (2.1 ml), then the mixture was stirred at 110 °C for 5 h. After washed with MeCN, the product **13** (0.14 g, 65%) was obtained as a brownish black precipitation; [found: C, 87.79; H, 4.23. $C_{64}H_{37}N_5$ requires C, 87.75; H, 4.26%]; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.99–8.96 (d, J=12.4 Hz, 1H), 8.85 (s, 1H), 8.13 (s, 1H), 8.06–8.04 (d, J=7.6 Hz, 1H),

7.87 (s, 1H), 7.83 (s, 1H), 7.81–7.79 (d, J=7.2 Hz, 4H), 7.47–7.45 (d, J=7.6 Hz, 4H), 7.39–7.36 (t, J=14.8 Hz, 6H), 7.30–7.26 (m, 16H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.09, 155.54, 151.58, 146.43, 140.08, 139.40, 139.29, 139.15, 138.97, 133.67, 131.81, 131.01, 130.39, 130.07, 129.85, 129.48, 128.92, 128.31, 128.10, 127.79, 127.52, 127.27, 126.71, 126.27, 124.14, 124.00, 120.25, 109.06, 81.01, 65.55; MALDI-TOF MS (m/z) calcd for $C_{64}H_{37}N_5^+$ $[M]^+$ 876.01, found 876.97.

4.2. X-ray crystallographic data

Crystallographic data for **2** are saved as the cif file, 2.cif. $C_{11}H_5BrN_2O$, M=261.08, colorless diamond 0.30×0.15×0.12 mm, monoclinic, $P2(1)/n$, Z=4, a=3.888 (3), b=21.646 (16), c=11.389 (9), α=90.00°, β=99.578 (10)°, γ=90.00°, V=945.2 (12) Å^3, $F(000)$=512, D_c=1.835 Mg m^{-3}, μ (Mo Kα)=4.317 mm^{-1}. Reflections collected/unique 3776/1647 (R_{int}=0.0336), Final R indices ($I>2\sigma$ (I)) $R1$=0.0990, $wR2$=0.2428, R indices (all data) $R1$=0.1067, $wR2$=0.2464. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication numbers CCDC 760634. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

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Supplementary data

^{1}H NMR, ^{13}C NMR, GC–MS, and MALDI-TOF MS spectral data for all corresponding products are provided. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.12.065. These data include MOL files and InChIKeys of the most important compounds described in this article.

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