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SYNTHESIS OF DIAZA-ANALOGUE OF FLUORENONE AND SPIROBIFLUORENE

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Abstract – The effective syntheses of diaza-analogue of fluorenone and spirobifluorene with N=N bond has been conducted with the using of ninhydrin and corresponding acetyl derivatives of arenes. Single-crystal X-ray diffraction of 2-(spirobifluoren-2-yl)- 3,4-dizaspirobifluorene (**4a**) proved the conformation.

INTRODUCTION

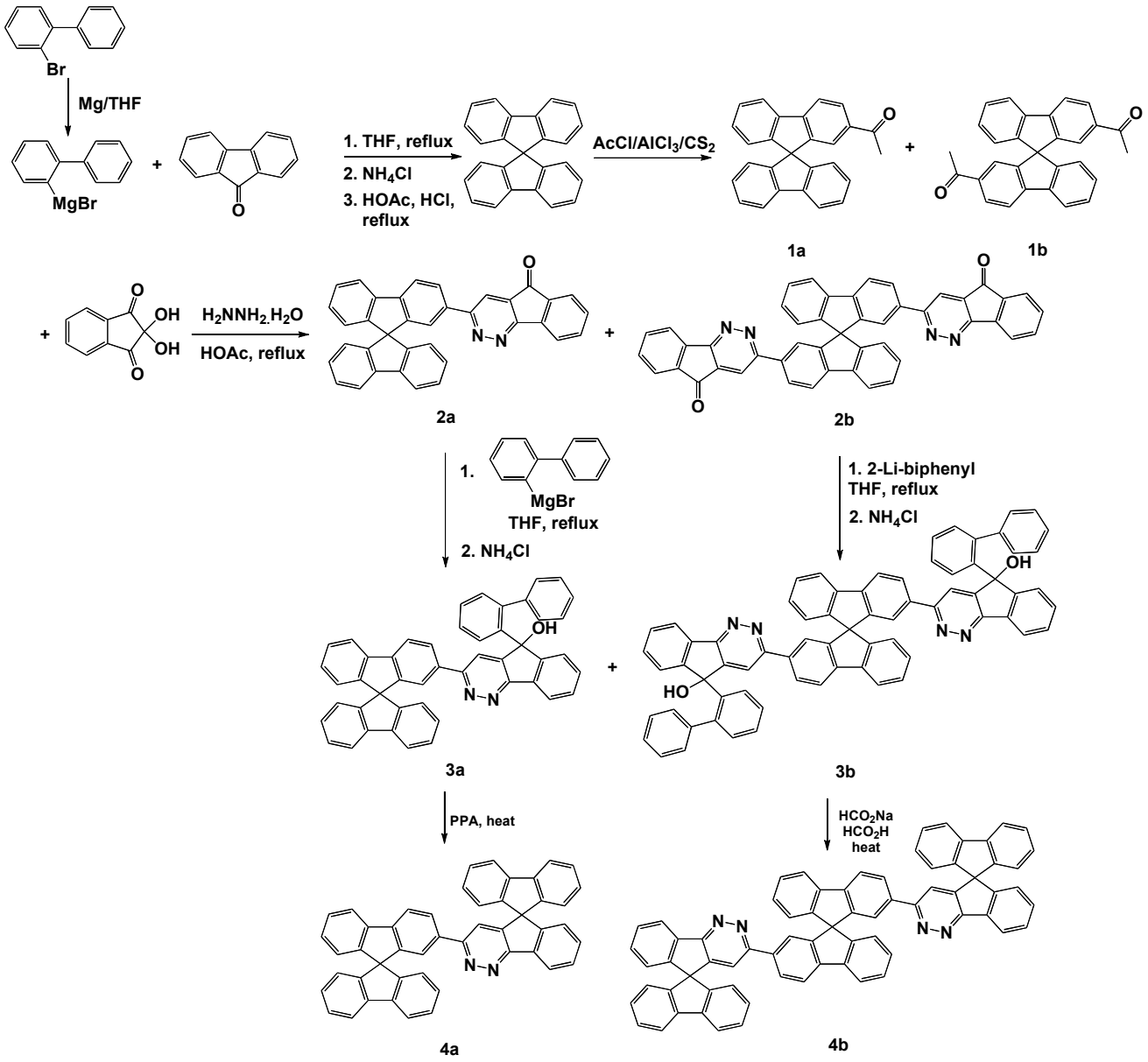
Polycyclic aromatic hydrocarbons (PAHs) have been of great interest especially in materials science because of their utilities in organic electronics, such as light-emitting diodes, field-effect transistors, and solar cells.[1] For this reason, development of an efficient and preparative method for simple or functionalized PAHs is considered to be highly important. In particular, fluorene derivatives are a notable structural motif for the diverse PAH derivatives having various applications as precursors for different materials.[2] In addition, some type of fluorene-bearing compounds especially aza- and diazafluorenones exhibit interesting bioactivities as monoamine oxidase (MAO) inhibitors.[3] They are also frequently utilized as effective ligands in organometallic chemistry.[4] Conventional multistep procedures were employed for the synthesis of fluorenes, spirobifluorene (SBF) and their derivatives, which have attracted considerable attention in recent years in the field of organic optoelectronics, owing to their intriguing electronic properties and aesthetic appeal.[5] Spirobifluorene could be considered as the joining of two fluorene units through a shared spiro sp^3-C atom which was first described by Gomberg in 1930.[6] This

non-planarity structure could effectively prevent crystals from forming,[7] and increase molecular amorphism. Therefore these kinds of compounds generally exhibit high T_g, good thermal stability and excellent solubility in common organic solvents.[8] Spiro compounds as organic molecular materials have become promising candidates for optoelectronic devices due to their high energy gap and low HOMO levels.[9] Mono-aza-spirobifluorene have been widely studied, however, as for heterocycle-fused spirobifluorene with N=N bond, 2-phenyl-3,4,4'- triazaspiribifluorene (3'-Phenylspiro-[4-azafluorene-9,5'-indeno[l,2-c] pyridazine]) is only sample reported so far.[10a]

Described herein are our most recent studies on the diaza-analogue of fluorenone, spirobifluorene derivatives, the scope and synthetic applicability were quite versatile. This led us to initiate our efforts on the detailed study of diazaspirobifluorenes, which are never studied in detail before. It was revealed that the employment of aromatic acetyl or diacetyl derivatives of aromatics or compounds with methylene-carbonyl moiety as templates through condensation reaction with ninhydrin and hydrazine hydrate in suitable solvents. The present synthetic route to a fluorene motif was quite general, thus allowing the synthesis of a wide range of diazafluorenones to take place smoothly to furnish the corresponding 2-arylfluorenones in moderate to excellent yields. They can be used as precursors for syntheses of previously unknown heterocycle-fused spirobifluorene compounds containing the 4-azafluorene and pyridazine fragments.

RESULTS AND DISCUSSION

Generally, synthsis of diaza-fluorenone could be accomplished by the reaction of ninhydrin with acetyl derivatives of arene and hydrazine hydrate in suitable solvents as described in literatures.[3] The reaction of 2-aryl-3,4-diazafluorenone with Grignard reagent or lithium salt generated by 2-bromobiphenyl afforded the tertiary fluoren-9-ol. The reaction conducted either under refluxing (for Grignard reaction) or at lower temperature (-78 °C for lithium salt reaction) afforded 2-aryl-3,4-diazafluoren-9-ol in good yields. Most of the fluoren-9-ol intermediates are separable and easily purified. However, their solubility vary upon different substituents. The conventional conditions with HCl/HOAc system didn't work for the ring closure reaction of fluoren-9-ols.[6] Many efforts were made in order to further convert them into 3,4-diazaspirobifluorene compounds effectively. Among conditions tested, we found that HCO_2H/ HCO_2Na and PPA systems both can serve as efficient catalysts for the ring closure reaction of fluoren-9-ols into 3,4-diazaspirobifluorenes. Synthesis of compounds **4a** and **4b** is outlined in Scheme 1.

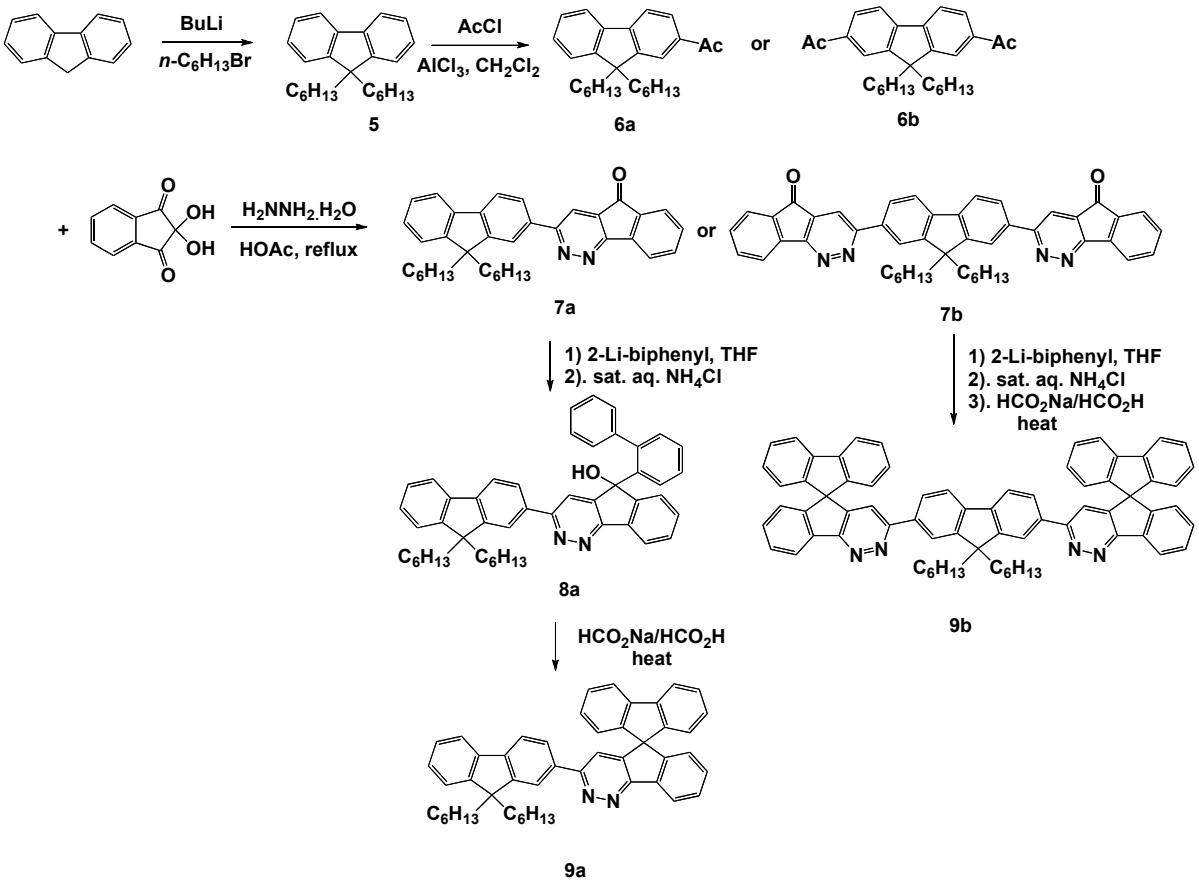


Scheme 1. Syntheses of Compounds **4a** and **4b**

The Grignard reagent, prepared *in situ* from 2-bromobiphenyl and Mg in THF, was reacted with fluorenone to form the tertiary fluoren-9-ol, which was cyclized with HCl/HOAc to form spirobifluorene following Gomberg's procedure.[6a] The acylation of spirobifluorene with $AlCl_3$ form 2-acetyl spirobifluorene (**1a**) and 2,2'-diacetylspirobifluorene (**1b**), which were easily separated by column chromatography. The reaction of **1a** or **1b** with ninhydrin and hydrazine hydrate in acetic acid under refluxing afford compound **2a** or **2b** in good yields (70 % and 73.8 % respectively), which could be purified by crystallization from EtOH or CH_2Cl_2. Again the Grignard reagent of 2-bromobiphenyl was employed to reaction with compounds **2a** or **2b** to form **3a** and **3b**. The ring closure reaction of **3a** could

be completed with PPA and higher temperature[10] or with HCO_2Na/HCO_2H to have better result. Compound **3b** was used to form compound **4b** directly due to the difficult to purify.

During this attempt, we found that the solubility of intermediates and final products **4a** and **4b** above are not so good, then we consider the more soluble 9,9-dihexylfluorene for our further targets (Scheme 2).



Scheme 2. Syntheses of compounds **9a** and **9b**

9,9-Dihexylfluorene (**5**) was synthesized by the reaction of fluorene and 1-bromohexane. The control acylation of 9,9-dihexylfluorene **(5)** led to the formation of 2-acetyl-9,9-dihexylfluorene **(6a)** and 2,7-diacetyl-9,9-dihexylfluorene **(6b)**, which were reacted with ninhydrin and hydrazine hydrate to form compounds **7a** and **7b** respectively. The lithium salt of 2-bromobiphenyl was used as nucleophilic reagent in order to synthesize alcohol compounds more effectively. Compound **8a** can be separated and further converted into compound **9a**. However, **8b** cannot be purified and thus converted to **9b** directly.

In order to have insight of their structure arrangements, the X-ray crystal structure of compound **4a** is established. The molecular structure of the title compound is shown in Figure 1.

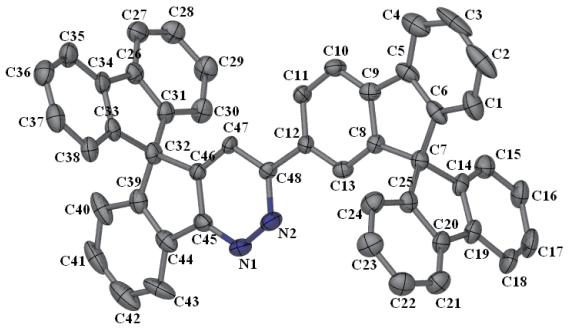


Figure1. Crystal structure of **4a**

As shown in Figure1, the title compound contains three fluorene units and one 3,4-diazafluorene moiety, 3,4-diazafluorene unit and one fluorene unit are almost coplanar, and 3,4-diazafluorene units are almost perpendicular to another fluorene unit. The rest of two fluorene units are also approximately perpendicular to each other. The spiro-junction of 2-(spirobifluorene-2-yl)-3,4-diazaspirobifluorene orthogonally arranges two conjugated molecular arms. The bond lengths of N=N and C=N are 1.324(6) Å (for N1-N2), 1.403(7) Å (for N1-C45), 1.370(5) Å (for N2-C48) Å, respectively. The dihedral angles of two fluorenyl rings of spirobifluorenes are 92.3 ° (with N-N bond)and 92.8 °**,** respectively.

EXPERIMENTAL

1. Instruments and materials

Melting point was measured on an X-4 micrographic melting point apparatus. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker DR × 500 spectrometer (^{1}H NMR 500 MHz, ^{13}C NMR 125 Hz). Data for X-ray structure analysis were collected on a Bruker-AXS detector with Mo *Ka* radiation (λ=0.71073Å). Structures were solved by direct methods with SHELXTL (version 6.10). Element analyses were measured on Vario EL III element analysis instrument. Mass spectra were measured either on Agilent 5973N mass spectrometer or micOTOF II (ESI) spectrometers.

2. Synthesis

Synthesis of 2-(spirobifluoren-2-yl)-3,4-diazafluorenone (2a)

Using 2-bromobiphenyl as starting material, the intermediates **1a** and **1b** was obtained by literature method.[11] The solution of 2-acetyl-9,9'-spirobifluorene (**1a**) (3.1 g, 8.65 mmol) and ninhydrin (1.54 g, 8.65 mmol) in 50 mL of glacial acetic acid was heated to reflux for 3-4 h. Then the reaction mixture was allowed to cool to room temperature and hydrazine hydrate (85%, 5.5 mL, 13 mmol) was added dropwise and the stirring was continued for 3 h. The resulting yellow solid was collected by filtration and

recrystallized from EtOH. Yield (70%). mp 263-265 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.25 (dd, *J* = 8Hz, *J* = 1.5Hz , 1H), 8.11 (d, *J* = 8Hz, 1H), 8.02 (d, *J* = 8Hz, 1H), 7.92 (d, *J* = 8Hz, 1H), 7.89 (d, *J* = 7.5Hz, 2H), 7.81 (d, *J* = 8.5Hz, 2H), 7.71 (t, *J* = 7Hz, 1H), 7.53 (t, *J* = 7.5Hz, 1H), 7.47 (s, 1H), 7.43-7.37 (m, 3H), 7.17 (t, *J* =7.5Hz, 1H), 7.13 (d, *J* = 7.5Hz, 2H), 6.77 (t, *J* = 7.5Hz, 3H). ^{13}C NMR ($CDCl_3$, 125MHz) δ: 190.35, 160.22, 159.79, 149.96, 149.57, 148.02, 144.37, 142.23, 141.87, 140.71, 136.37, 135.20, 134.73, 131.82, 130.71, 128.68, 127.96, 127.92, 127.89, 127.00, 125.12, 124.19, 123.95, 122.64, 122.19, 120.64, 120.57, 120.21, 117.29, 65.98. Anal. Calcd for $C_{36}H_{20}N_2O$: C, 87.08; H, 4.06; N, 5.64. Found: C, 87.22; H, 3.97; N, 5.56. MS (EI): m/z=496 [M^+].

Synthesis of 2,7-di-3,4-diazafluorenone-9,9'-spirobifluorene (2b)

The solution of 2,7-diacetyl-9,9'-spirobifluorene (**1b**) (4.09 g, 22.95 mmol) and ninhydrin (4.59 g, 11.47 mmol) in 150 mL of glacial acetic acid was heated to reflux for 3-4 h. Then the reaction mixture was allowed to cool to room temperature and hydrazine hydrate (85%, 1.46 mL, 33.41 mmol) was added dropwise and the stirring was continued for 3 h. The resulting yellow solid was collected by filtration and recrystallized from CH_2Cl_2.Yield (73.8%). mp 240 °C (dec.). ^{1}H NMR ($CDCl_3$, 500MHz) 8.25 (d, *J* = 8Hz, 2H), 8.09-8.03 (m, 4H), 7.96 (d, *J* = 8Hz, 2H), 7.83 (s, 2H), 7.79 (d, *J* = 7.5Hz, 2H), 7.69 (t, *J* =7.5Hz, 2H), 7.55 (s, 2H), 7.51 (t, *J* =7.5Hz, 2H), 7.44 (t, *J* = 7.0Hz, 2H), 7.18 (t, *J* = 7.5Hz, 2H), 6.82 (d, *J* = 8.0Hz, 2H). Anal. Calcd for $C_{47}H_{24}N_4O_2$: C, 83.42; H, 3.57; N, 8.28. Found: C, 83.02; H, 3.63; N, 7.96. MS (EI): m/z =676[M^+].

Synthesis of 2-(spirobifluoren-2-yl)-9-(2-biphenyl)-3,4-diazafluoren-9-ol (3a)

A flask charged with 2-biphenylmagnesium bromide, prepared in advance from 2-bromobiphenyl (4.29 g, 18.4 mmol) and magnesium (0.44 g, 18.4 mmol) in THF (50 mL), was added under refluxing a solution of **2a** (3.15 g, 6.14 mmol) in THF (40 mL) under N_2. The mixture was refluxed for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl after cooling to ambient temperature, and subsequently extracted with CH_2Cl_2. The combined organic extracts were washed and dried (Na_2SO_4) and filtered, and the solvents were concentrated by rotary evaporation. The resulting crude product was wash with hexanes and further purified by column chromatography on silica gel by using of CH_2Cl_2:AcOEt (20:1). Yield (61%). mp 198 °C (dec.). ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.43 (d, *J* = 7.5Hz, 1H), 8.17 (d, *J* = 8Hz, 1H), 8.11-8.05 (m, 4H), 7.62 (s, 1H), 7.60-7.57 (m, 2H), 7.46-7.38 (m, 5 H), 7.35 (t, *J* = 8.5Hz, 2H), 7.23-7.13 (m, 4H), 6.83 (d, *J* = 7 Hz, 1H), 6.75-6.65 (m, 4H), 6.58 (s, 1H), 6.51 (brs, 1H), 6.43 (brs, 1H), 6.11 (brs, 1H), 5.72 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 159.79, 156.82, 151.75, 149.48, 148.35, 143.21, 141.75, 141.02, 140.33, 139.26, 136.65, 136.61, 131.31, 129.57, 128.53, 127.84, 127.35, 126.37, 125.29, 124.00, 123.96, 121.98, 121.25, 121.07, 119.57, 80.11, 65.93. Anal. Calcd for $C_{48}H_{30}N_2O$: C, 88.59; H, 4.65; N, 4.30. Found: C, 88.24; H, 4.74; N, 4.25. MS (EI): m/z = 650 [M^+].

Synthesis of 2-(spirobifluoren-2-yl)-3,4-diazaspirobifluorene (4a)

A mixture of 1.5 g (0.97 mmol) of **3a** and 40 mL of polyphosphoric acid was heated for 10 h at 200 °C. After cooling water (250 mL) was added. The reaction products were repeatedly with CH_2Cl_2 and dried with Na_2SO_4 .The crude product was purified by column chromatography on a silica gel by using of CH_2Cl_2: AcOEt (10:1). Yield (60%). mp 388-390 °C. Single crystals of **4a** used for data collection were obtained by slowly evaporating a solution in acetone at room temperature. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.32 (d, *J* = 7.5Hz, 1H), 7.97 (dd, *J* = 7.5Hz, 1.5Hz, 1H), 7.87-7.82 (m, *J* = 7.5Hz, 6H), 7.49-7.42 (m, 2H), 7.40 (t, *J* = 7.5Hz, 2H), 7.37-7.33 (m, 3H), 7.27 (t, *J* = 7.5Hz, 1H), 7.13-7.05 (m, 6H), 6.73 (d, *J* = 7.65Hz, 1H), 6.74-6.68 (m, 5H); ^{13}C NMR ($CDCl_3$, 125MHz) δ: 157.42, 149.65, 149.05, 148.21, 147.91, 146.37, 143.56, 141.83, 141.78, 136.21, 131.21, 128.74, 128.33, 128.25, 127.80, 127.15, 124.07, 123.99, 123.96, 122.94, 121.94, 120.40, 120.34, 120.18, 120.08, 118.90, 65.98, 63.74. Anal. Calcd for $C_{48}H_{28}N_2$: C, 91.11; H, 4.46; N, 4.43. Found: C, 90.88; H, 4.96; N, 4.21. MS (EI): m/z=635 $[M+1]^+$.

2,2'-Bis(3,4-diaza-9,9'-spirobifluoren-2-yl)-9,9-spirobifluorene (4b)

A flask charged with 2-biphenylmagnesium bromide, prepared in advance from 2-bromobiphenyl (4.29 g, 18.4 mmol) and magnesium (0.44 g, 18.4 mmol) in THF (50 mL), was added under refluxing a solution of **2b** (3.15 g, 6.14 mmol) in THF (40 mL) under N_2. The mixture was refluxed for 12 h. After cooling to ambient temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. After workup, the residue was crystallized from petroleum ether, the solid was filtered and washed with CH_2Cl_2 to remove any trace of impurity and subsequently dissolved in the mixture of HCOONa and HCOOH with refluxing for few hours. The mixture was then cooled, diluted with water, and extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, water, brine. Then the organic phase was dried over Na_2SO_4, and filtered, the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel by using of CH_2Cl_2:EtOAc (10:1) to give a white solid which tends to turn to yellow on storage. mp 256 °C (dec.). ^{1}H NMR ($CDCl_3$, 500MHz) δ:8.29 (d, *J* = 7.8Hz, 2H), 7.92 (dd, *J* = 7.8Hz, *J* =1.5Hz, 2H), 7.83 (t, *J* = 8.3Hz, 8H), 7.46 (t, *J* = 7.1Hz, 4H), 7.39 (q, *J* = 7.3Hz, 4H), 7.33 (t, *J* = 7.2Hz, 2H), 7.27 (s, 1H), 7.12-7.05 (m, 9H), 6.72 (d, *J* = 7.7Hz, 2H), 6.68-6.66 (m, 6H). Anal. Calcd for $C_{71}H_{40}N_4$: C, 89.85; H, 4.25; N, 5.90. Found: C, 89.15; H, 4.55; N, 5.98. MS(ESI): Calcd for $C_{71}H_{40}N_4$ 949.1238; Found: 949.3325.

Synthesis of 9,9'-dihexylfluorene (5)

A solution of fluorene (8 g, 48.13 mmol) in THF (40 mL) was treated with BuLi (19.3 mL, 2.5 M in hexane, 48.13 mmol) under argon at -78 °C. The mixture was stirred at -78 °C for 45 min. A solution of 1-bromohexane (7.94 g, 48.13 mmol) in THF (20 mL) was added dropwise. After addition was complete,

the reaction mixture was left to stirred at -78 °C for 1.5 h and then left to room temperature. The reaction mixture was then re-cooled to -78 °C and 1-bromhexane (7.94 g, 48.13 mmol) was added. The reaction mixture was allowed to room temperature overnight and the whole lithiation and alkylation process repeated. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The organic fraction was dried $MgSO_4$ and the solvent was removed under reduced pressure. Yield (96%). ^{1}H NMR ($CDCl_3$, 500MHz) δ: 7.71 (dd, *J* = 6.5Hz, *J* = 1Hz, 2H), 7.36-7.29 (m, 6H), 1.99-1.96 (m, 4H), 1.14-1.08 (m, 4H), 1.05-1.03 (m, 8H), 0.79-0.76 (m, 6H), 0.66-0.61 (m, 4H).

Synthesis of 2-acetyl-9,9'-dihexylfluorene (6a)

A mixture of **5** (18 g, 53.8 mmol), anhydrous $AlCl_3$ (8.62 g, 64.56 mol) and 200 mL of dry CH_2Cl_2 was cooled below 0-5 °C with an ice-bath, and acetyl chloride (3.83 mL, 53.8 mol) was added dropwise. The mixture was heated to reflux for 6 h, then poured into 250 mL of ice-water containing 45 mL of conc HCl and stirred to reach room temperature. The organic phase was separated, and the aqueous layer was washed with CH_2Cl_2. The combined organic phase was washed with H_2O, 10% aqueous NaOH, H_2O and brine, dried over $MgSO_4$, then the solvent was removed. The residue was purified by column chromatography on silica gel by using of CH_2Cl_2:PE (1:3). Yield 8.7 g (43%) as a tan liquid. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 7.99 (s, 1H), 7.96 (d, *J* = 7.9Hz, 1H), 7.75-7.74 (m, 2H), 7.39-7.33 (m, 3H), 2.05-2.00 (m, 4H), 1.10-1.02 (m, 12H), 0.76-0.74 (m, 6H), 0.60-0.59 (m, 4H).

Synthesis of 2,7-diacetyl-9,9'-dihexylfluorene (6b)

A mixture of **5** (15.5 g, 46.33 mmol), anhydrous $AlCl_3$ (20 g, 0.15 mol) and 200 mL of dry CH_2Cl_2 was cooled below 0-5 °C with an ice-bath, and acetyl chloride (9.6 mL, 0.135 mol) was added dropwise. The mixture was heated to reflux for 12 h, then poured into 250 mL of ice-water containing 60 mL of conc HCl and stirred to reach room temperature. The organic phase was separated, and the aqueous layer was washed with CH_2Cl_2. The combined organic phase was washed with H_2O, 10% aqueous NaOH, H_2O and brine, dried over $MgSO_4$, then the solvent was removed. The residue was purified by column chromatography on silica gel with CH_2Cl_2:PE (1:3). Yield (30.9%) as a pale-yellow liquid. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.34 (s, 1H), 7.98-7.95 (m, 3H), 7.82 (d, *J* = 8.5Hz, 1H), 7.44 (d, *J* = 7.9Hz, 1H), 2.02-1.99 (m, 4H),1.06-0.96 (m, 12H), 0.71-0.68 (m, 6H), 0.53-0.52 (m, 4H).

Synthesis of 2-(9,9'-dihexylfluorenyl)-3,4-diazafluorenone (7a)

The solution of **6a** (5 g, 13.28 mmol) and ninhydrin (2.32 g, 13.28 mmol) in 150 mL of glacial acetic acid was heated to reflux for 3 h. Then the reaction mixture was allowed to cool to room temperature and hydrazine hydrate (85%, 0. 85 mL, 19.92 mmol) was added dropwise and the stirring was continued for 3 h. and further chromatographed on silica gel by using of CH_2Cl_2:PE (1:1). Yield (37.2%). mp 109-111 °C. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.25 (s, 1H), 8.22 (d, *J* = 7.5Hz, 1H), 8.13 (t, *J* = 7.5Hz, 2H), 7.89-7.87

(m, 2H), 7.80-7.76 (m, 2H), 7.58 (t, *J* = 7.4Hz, 1H), 7.43-7.38 (m, 3H), 2.10-2.06 (m, 4H), 1.14-1.06 (m, 12H), 0.78-0.75 (m, 6H), 0.70-0.68 (m, 4H). ^{13}C NMR ($CDCl_3$, 125MHz) δ: 190.53, 160.38, 160.23, 151.75, 151.47, 143.87, 142.38, 140.05, 136.42, 134.81, 134.33, 131.82, 130.92, 127.90, 126.92, 125.99, 125.15, 122.97, 122.21, 121.45, 120.29, 120.20, 117.42, 55.36, 40.32, 31.44, 29.63, 23.75, 22.51, 13.92. Anal. Calcd for $C_{36}H_{38}N_2O$: C, 84.01; H, 7.44; N, 5.44. Found: C, 84.31; H, 7.67; N, 5.50. MS (EI): m/z = 514 [M^+].

Synthesis of 2,7-di(3,4-diazafluorenonyl)-9,9'-dihexylfluorene (7b)

The solution of **6b** (3.34 g, 7.98 mmol) and ninhydrin (2.82 g, 15.96 mmol) in 150 mL of glacial acetic acid was heated to reflux for 3-4 h. Then the reaction mixture was allowed to cool to room temperature and hydrazine hydrate (85%, 1.19 mL, 27.93 mmol)) was added dropwise and the stirring was continued for 3 h. the mixture was then cooled, diluted with water, and extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, water, brine. After the organic phase was dried over Na_2SO_4, and filtered, the solvent was removed under reduced pressure, The residue was purified by column chromatography on silica gel using CH_2Cl_2:EtOAc (20:1). Yield (23.67%). mp 240-242 °C. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.59 (s, 1H), 8.27(s, 1H), 8.23 (t, *J* = 7.8Hz, 2H), 8.16 (dd, *J* = 7.5Hz, *J* = 1.5Hz, 1H), 8.13 (d, *J* = 7.5Hz, 3H), 7.99 (d, *J* = 8Hz, 1H), 7.90 (d, *J* = 7.5Hz, 2H), 7.91 (d, *J* = 7.5Hz, 2H), 7.61-7.57 (m, 3H), 2.10-2.05 (m, 4H), 1.12-1.03 (m, 12H), 0.76-0.69 (m, 10H). ^{13}C NMR ($CDCl_3$, 125MHz) δ: 189.28, 189.21, 159.37, 159.19, 159.07, 153.26, 150.79, 141.86, 141.14, 140.14, 135.27, 133.86, 133.76, 133.67, 133.65, 130.76, 130.73, 129.84, 129.79, 125.68, 125.10, 124.01, 122.54, 121.16, 121.09, 120.41, 119.51, 117.86, 116.31, 54.54, 39.15, 30.28, 28.45, 22.71, 21.34, 12.76. Anal. Calcd for $C_{47}H_{42}N_2O_2$: C, 81.24; H, 6.09; N, 8.06. Found: C, 81.22; H, 6.24; N, 7.86. MS (EI): m/z = 694[M^+].

Synthesis of 2-(9,9'-dihexylfluorenyl)-9-(2-biphenyl)-3,4-diazafluoren-9-ol (8a)

A solution of 2-bromobiphenyl (1.45 g, 6.22 mmol) in THF (20 mL) was treated with BuLi (2.74 mL, 2.5 M in hexane, 6.84 mmol) under argon at -78 °C. The mixture was stirred at -78 °C for 45 min. And a solution of **7a** (1.6 g, 3.11 mmol) in THF (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for 1 h, and at room temperature for 12 h. The organic layer was washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel by using of CH_2Cl_2:PE (5:1) as eluant to afford **8a**. Yield (33.4%). mp 186-188 °C. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.61(d, *J* = 8.1Hz, 1H), 7.96 (s, 1H), 7.70 (q, *J* = 8.5Hz, 3H), 7.58 (t, *J* = 7.7Hz, 1H), 7.53 (s, 1H), 7.40-7.30 (m, 5H), 7.21 (d, *J* =*7.5* Hz, 1H), 7.07 (t, *J* = 7.1Hz, 1H), 6.98 (t, *J* = 7.2Hz, 1H), 6.92 (d, *J* = 7.4Hz, 1H), 6 .77 (t, *J* = 7.3Hz, 1H), 6.53-6.47 (m, 2H), 6.11 (d, *J* = 6.8Hz, 1H), 5.73 (d, *J* = 6.1Hz, 1H), 5.07 (brs, 1H), 2.09-2.04 (m, 4H), 1.10-1.03 (m,

12H), 0.74-0.68 (m, 10H). ^{13}C NMR ($CDCl_3$, 125MHz) δ: 159.10, 157.65, 151.35, 151.33, 150.50, 149.06, 142.89, 140.53, 140.32, 139.66, 138.01, 135.51, 134.93, 131.12, 131.05, 129.34, 129.14, 128.60, 127.61, 127.54, 126.85, 126.76, 126.30, 126.01, 124.94, 122.96, 121.55, 121.31, 120.13, 119.77, 119.56, 80.27, 55.33, 40.35, 31.51, 29.66, 23.82, 22.52, 13.94. Anal. Calcd for $C_{48}H_{48}N_2O$: C, 86.19; H, 7.23; N, 4.19. Found: C, 86.46; H, 7.43; N, 4.19. MS (EI): m/z = 650 $[M\text{-}H2O]^+$.

Synthesis of 2-(9,9'-dihexylfluorenyl)-3,4-diazaspirobifluorene (9a)

A mixture of **8a**, HCOONa and HCOOH (50 mL) was refluxed for 20 h. The mixture was then cooled, diluted with water, and extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, water, brine. After workup, the residue was purified by column chromatography on silica gel using CH_2Cl_2 to give a white solid (0.35 g, yield 74.3%). mp 213-215 °C. ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.42 (d, *J* = 7.7Hz, 1H), 8.20 (s, 1H), 7.92 (d, *J* = 7.7Hz, 2H), 7.77 (dd, *J* = 8Hz, *J* = 1.4Hz, 1H), 7.69 (q, *J* = 5.8Hz, 2H), 7.54 (t, *J* = 7.5Hz, 1H), 7.46 (t, *J* = 7.5Hz, 2H), 7.34-7.29 (m, 5H), 7.19 (t, *J* = 7.5Hz, 2H), 6.81 (d, *J* = 7.6Hz, 3H), 2.02-1.96 (m, 4H), 1.06-0.96 (m, 12H), 0.72-0.69 (m, 6H), 0.59 (m, 4H). ^{13}CNMR ($CDCl_3$, 125MHz) δ: 161.59 , 157.89, 151.56, 151.41, 149.02, 148.19, 146.60, 142.96, 141.87, 140.29, 137.83, 135.11, 131.26, 128.87, 128.61, 128.33, 127.57, 126.76, 125.82, 124.19, 122.94, 122.03, 121.65, 120.4455, 120.07, 119.71, 118.79, 63.75, 55.34, 40.29, 31.44, 29.61, 23.70, 22.51, 13.93. Anal. Calcd for $C_{48}H_{46}N_2$: C, 88.57; H, 7.12; N, 4.30. Found: C, 88.61; H, 7.39; N, 4.25. MS (EI): m/z = 650 $[M^+]$.

Synthesis of 2,7-bis(3,4-diazaspirobifluoren-2-yl)-9,9'-dihexylfluorene (9b)

A solution of 2-bromobiphenyl (1.68 g, 7.21 mmol) in THF (20 mL) was treated with BuLi (2.88 mL, 2.5 M in hexane, 7.21 mmol) under argon at -78 °C. The mixture was stirred at -78 °C for 45 min. A solution of **7b** (1 g, 1.44 mmol) in THF (20 mL) was added dropwise. The resulting mixture was stirred at -78 °C for 2 h, and then kept at room temperature for 12 h. The organic layer was washed with water and brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using CH_2Cl_2:EtOAc (10:1). A mixture of fluoren-9-ol and HCOONa and HCOOH (30 mL) was refluxed for 24 h, cooled, diluted with water, and extracted with CH_2Cl_2. The combined organic extracts were washed with saturated aqueous $NaHCO_3$, water, brine. After workup, the residue was purified by column chromatography on silica gel using CH_2Cl_2:EtOAc (15:1) to give a solid (yield 32%). mp 197 °C (dec.). ^{1}H NMR ($CDCl_3$, 500MHz) δ: 8.42 (t, *J* = 7.8Hz, 2H), 8.20 (s, 1H), 8.31 (s, 1H), 7.93-7.89 (m, 5H), 7.76-7.71 (m, 2H), 7.54 (t, *J* = 7.5Hz, 2H), 7.45 (q, *J* = 6.6Hz, 4H), 7.37-7.28 (m, 5H), 7.17 (q, *J* = 6.5Hz, 4H), 6.82-6.78 (m, 6H), 2.02-1.96 (m, 4H), 1.03-0.96 (m, 10H), 0.69-0.66 (m, 4H), 0.58-0.55 (m, 8H). ^{13}C NMR ($CDCl_3$, 125MHz) δ: 161.72, 161.61, 157.86, 157.74, 153.35, 151.68, 149.00, 148.93, 148.37, 148.23, 146.51, 142.37, 141.84,

141.19, 137.78, 135.47, 131.29, 128.85, 128.61, 128.31, 126.69, 125.88, 124.23, 124.11, 123.22, 122.11, 122.01, 121.63, 120.44, 120.15, 118.97, 118.90, 118.80, 63.83, 63.80, 55.45, 40.25, 39.07, 31.37, 29.53, 23.70, 22.45, 22.39, 13.89. Anal. Calcd for $C_{71}H_{58}N_4$: C, 88.16; H, 6.04; N, 5.79. Found: C, 87.92; H, 6.13; N, 5.61. MS (ESI): Calcd for $C_{71}H_{58}N_4$ 967.2660. Found 967.4769.

Crystal data and structure determination

A single crystal of **4a** with dimensions of 0.55 mm × 0.47 mm × 0.12 mm was chosen for X-ray diffraction analysis performed on a Bruker-AXS diffractometer, equipped with Mo *Ka* radiation (λ= 0.71073 Å) at 296(2) K by using a φ-ω scan mode. In the ranges of 1.39≤θ≤25.01°, a total of 18678 reflections were collected including 5288 unique ones ($R\ int$ = 0.0327), of which 5288 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on $F2$ for the non-hydrogen atoms. **4a** ($C_{48}H_{28}N_2$, Mr = 632.72), crystallizes in the monoclinic system, space group C_C with a = 13.8523(6), b = 29.3297(13), c = 8.6397(4) Å, β =111.8760(10), V = 3257.4(3) Å^3, Z = 4, D_c = 1.290mg/m^3, μ = 0.075mm^{-1}, F(000) = 1320, the final R_1 = 0.0425 and wR_2 = 0.1110 for 5288 observed reflections ($I > 2\sigma(I)$). The hydrogen atoms were located from Fourier difference maps. The final R_1 = 0.0425, wR_2 = 0.1110 ($w = 1/[\sigma 2(Fo^2) + (0.0628P)^2 + 1.12P]$, where $P = (Fo^2 + 2Fc^2)/3$, (Δ/σ)max = 0.000, S = 1.025, (Δρ) max = 0.139 and (Δρ) min = –0.164 e/Å^3.

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