

Synthesis of 9-ethynyl-9-fluorenol and its derivatives for crystallographic and optical properties study

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Abstract—A series of compounds derived from multifunctional 9-ethynyl-9-fluorenol were synthesized and their structures were characterized by spectroscopic methods. Some derivatives were luminescent with high quantum yields, which might be used as optoelectronic materials based on their optical property investigation.

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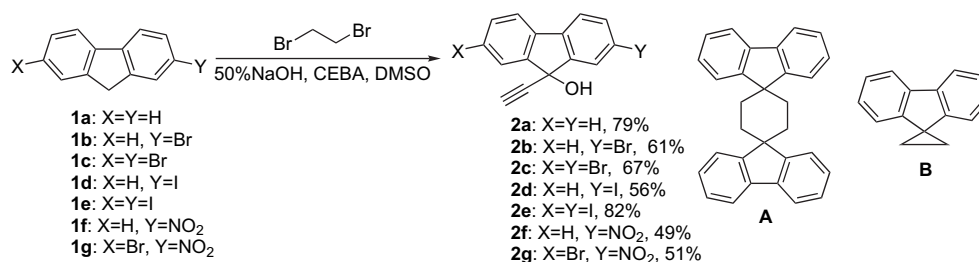
1. Introduction

Organic fluorescent compounds are currently attracting a great deal of attention because of their versatile applications in the fields of biochemistry, organic electronics, and supramolecular chemistry. For example, fluorescent temperature sensors,¹ solvent polarity sensors,² metal ions sensors,³ and pH sensors⁴ are widely applied in biochemistry. Additionally, in the field of organic electronics, research has not only focused on the optimization of electroluminescence cell structure but also on developing new optoelectronic materials.⁵ Many of organic molecules have been designed and synthesized as potential candidates for optoelectronic materials, such as diarylfluorene derivatives,⁶ tetra(aryl)silane,⁷ star shaped truxene or isotruxene derivatives,⁸ multichromophoric polyphenylene dendrimers,⁹ polycyclic aromatic hydrocarbons,¹⁰ and so on. One of the reasons for wide application of organic fluorescent compounds is the easier chemical modification of organic structures over inorganic ones. Therefore, designing new fluorophores with multifunctional groups are challenging and might open a new way to obtain unknown organic fluorophores with unique

and interesting optoelectronic properties.¹¹ 2,7-Dihalo-9-ethynyl-9-fluorenol is such an intermediate with four functional groups, from which numerous fluorescent organic compounds could be constructed.

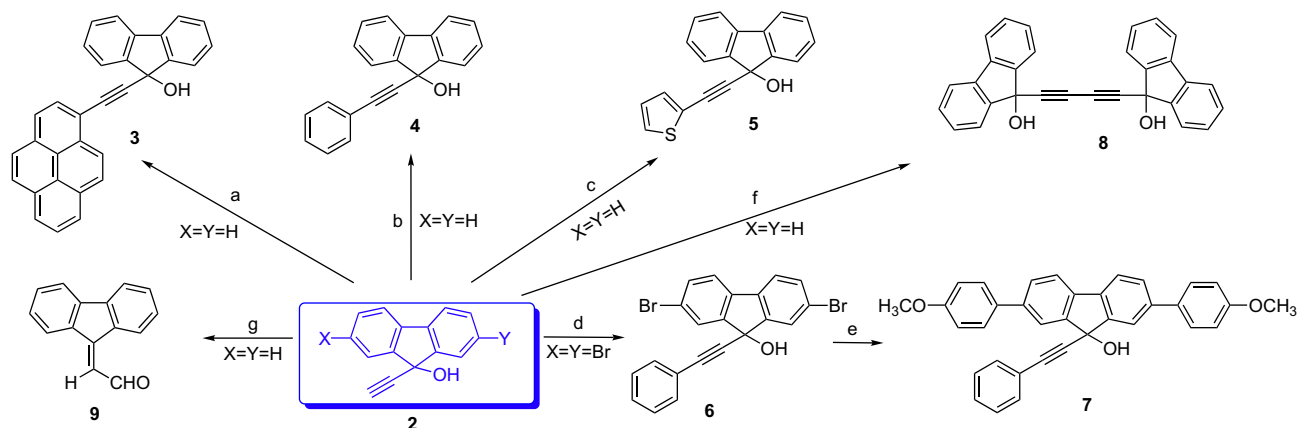
9-Ethynyl-9-fluorenol and its derivatives were useful compounds in synthetic organic chemistry. They were used for the synthesis of photochromic material molecules,¹² aryl-substituted cumulenes or extended [4]-radialenes,¹³ ruthenium carbonyl clusters,¹⁴ novel fluorene based host compounds,¹⁵ fluorenyl substituted naphthocyclobutene, and anthrodcyclobutene derivatives.¹⁶ There are hitherto several synthetic methods leading to 9-ethynyl-9-fluorenol and its derivatives in literatures. Most of them involve organometallic reagents, such as sodium acetylide,^{12b,17} lithium acetylide,¹⁸ and ethynylmagnesium bromide¹⁹ in which inert atmosphere reaction conditions could not be avoided.

Here, we would like to report a simple and efficient method for preparation of 9-ethynyl-9-fluorenol (**2a**) and its derivatives (**Scheme 1**). Initially, we would like to have bisprobi-fluorene framework (**A**²⁰ in **Scheme 1**) function as light



Scheme 1. General procedure for synthesis of 9-ethynyl-9-fluorenol and its derivatives.

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Scheme 2. Syntheses of compounds **3–9**: (a) 1-iodopyrene, PdCl₂(PPh₃)₂, PPh₃, CuI, triethylamine. (b) Iodobenzene, PdCl₂(PPh₃)₂, PPh₃, CuI, triethylamine. (c) 2-Iodothiophene, PdCl₂(PPh₃)₂, PPh₃, CuI, triethylamine. (d) Iodobenzene, PdCl₂(PPh₃)₂, PPh₃, CuI, triethylamine. (e) 4-Methoxyphenylboronic acid, Pd(PPh₃)₄, K₂CO₃, 18-crown-6, toluene/ethanol. (f) PdCl₂(PPh₃)₂, CuI, I₂, *i*-Pr₂NH and (g) TsOH, grinding.

emitting materials in order to investigate and solve the ‘green-emission tail’, which was the key issue in electroluminescence based on polyfluorene emitters. But eventually, spirofluorene framework (**B** in Scheme 1) was constructed.²¹ And the reason for ‘green-emission tail’ was thereby ascribed to fluorenone defects by crystallographic analysis based on those compounds with framework **B**. Interestingly, by changing the sequence of sample addition, 9-ethynyl-9-fluorene (**2a**) was obtained in 79% yield. Moreover, from **2a** and **2c**, some fluorescent compounds with high emission efficiencies (**3–9**) (Scheme 2) were constructed in moderate yields. Optical properties of these synthesized compounds were investigated and their structure–property relationship regarding fluorescence is hereby discussed.

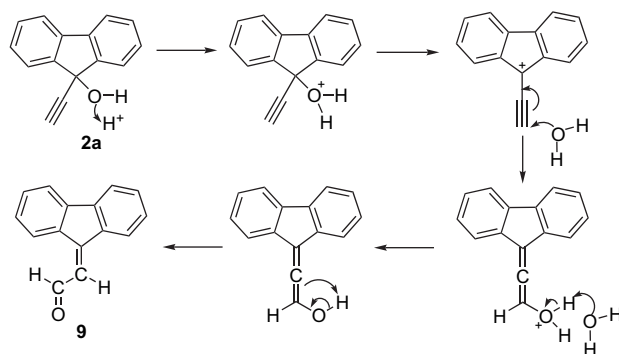
2. Results and discussion

2.1. Synthesis

2-Bromo-9H-fluorene (**1b**),²² 2,7-dibromo-9H-fluorene (**1c**),²³ 2-iodo-9H-fluorene (**1d**),²⁴ 2,7-diiodo-9H-fluorene (**1e**),²⁴ 2-nitro-9H-fluorene (**1f**),²⁵ and 2-bromo-7-nitro-9H-fluorene (**1g**)²⁶ were prepared by literature procedures. A simple way to synthesize compounds (**2a–2g**) is illustrated in Scheme 1. In this procedure, 50% NaOH aqueous solution was used as base to generate the acetylenic anion by elimination of 2 M HBr followed by abstracting the proton from the terminal triple bond, while a catalytic amount of cetyltrimethylammonium bromide (CEBA) was used as phase transfer catalyst. In this way, inert atmosphere and acetylene gas could be avoided. Not only the bare fluorene (**1a**) could be used as the starting material, but also fluorene derivatives with electron withdrawing groups (**1b–1g**). Yields were moderate, varying from 49% to 82%. Moreover, DMSO played a key role in this transformation. For instance, when either DMF or THF was used as solvent instead of DMSO, no desired product (**A**, **B** or **2**) was obtained.

Due to the multifunctionality of **2**, many compounds with versatile applications could be designed and prepared. For instance, conjugation system could be well extended through 2,7 positions of fluorene by Suzuki or Ullmann reaction (compound **7** as an example). Hydroxy group at 9 position

of fluorene could be protonated along with the ease of formation of benzylic cation. Further, the acetylenic group at 9 position of fluorene also allowed for facile formation of various kinds of compounds (compounds **3**, **4**, **5**, **6**, and **8**). Thus, compounds **3–9** were synthesized (Scheme 2) as we predicted except compound **9**. Grinding compound **2a** with either *o*-dihydroxyphenol or *p*-dihydroxyphenol catalyzed by *p*-TsOH was supposed to form benzopyrans according to Tanaka’s publication.^{12a} However, neither *o*-dihydroxyphenol nor *p*-dihydroxyphenol was involved in the product, 2-(9H-fluoren-9-ylidene)acetaldehyde (**9**). The possible mechanism is drawn in Scheme 3.



Scheme 3. Proposed mechanism from **2a** to **9**.

2.2. X-ray crystallographic analysis: solid-state conformation and molecular packing

Structures of **2a** and **3** were confirmed by X-ray crystallographic analysis. Single-needle crystal of **2a** or **3** suitable for X-ray diffraction was obtained by very slow evaporation of a CH₂Cl₂/hexane solution. A numbering guide and the derived crystal structures are shown in Figures 1 and 2. The selected molecular parameters are provided in Table S1.

Both **2a** and **3** crystallize in a monoclinic crystal system with a centrosymmetric space group *P2₁/c* (No. 14). However, the number of molecule in a unit cell was different. Compound **2a** contains 16 molecules in a unit cell, while **3** contains only 4 molecules in a unit cell.

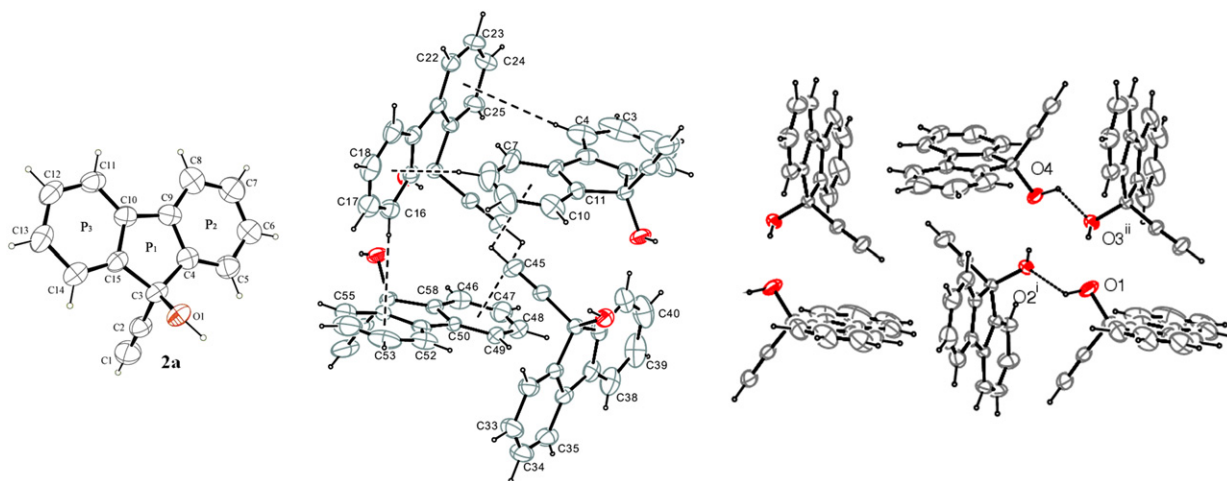


Figure 1. Left: the molecular structure of **2a** with labeling schemes, 30% thermal ellipsoids, and defining planes. Middle: the C–H \cdots π interaction (dashed lines) between neighboring **2a**. Right: the crystal packing of **2a**, showing the intermolecular hydrogen bonding (dashed lines). [Symmetry codes: (i) $-1+x,y,z$ and (ii) $1+x,y,z$].

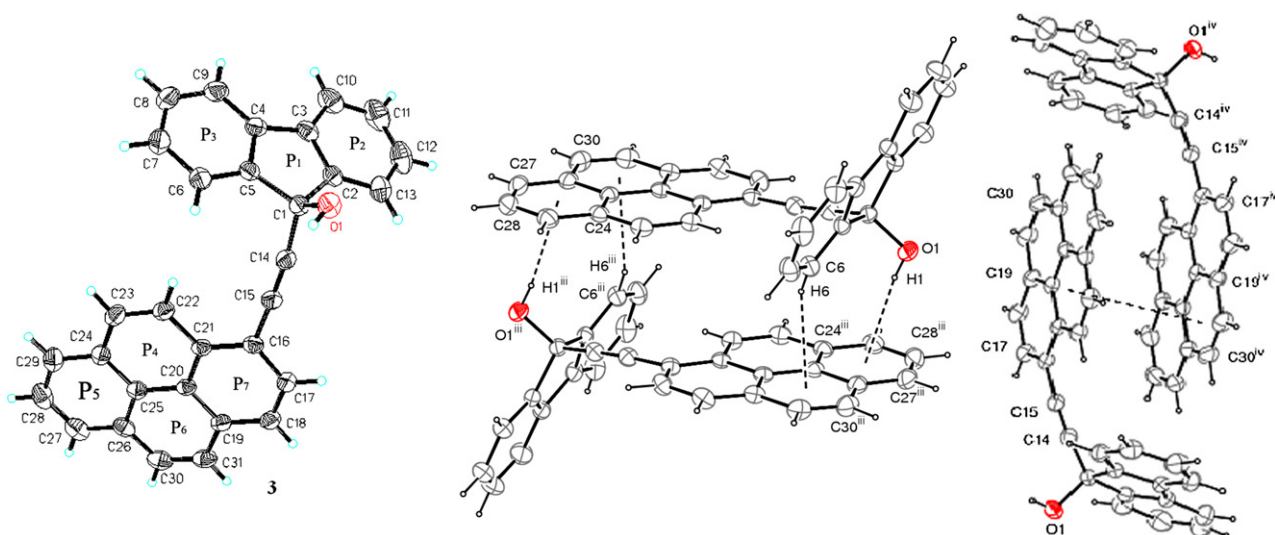


Figure 2. Left: the molecular structure of **3** with labeling schemes, 30% thermal ellipsoids, and defining planes. Middle: the C–H \cdots π interaction (dashed lines) between neighboring **3**. [Symmetry codes: (iii) $-x,1-y,2-z$]. Right: the $\pi\cdots\pi$ interaction (dashed lines) between neighboring **3**. [Symmetry code: (iv) $-x,1-y,1-z$].

Several CH \cdots π interactions occur in compound **2a**, which are shown in Figure 1 (middle). The H(4) \cdots Cg(8) separation (Cg(8) is the centroid of C21 benzene ring) and C(4)–H(4) \cdots Cg(8) angle are 3.35 Å and 177.15°, respectively. The H(8) \cdots Cg(7) separation (Cg(7) is the centroid of the C16 benzene ring) and C(8)–H(8) \cdots Cg(7) angle are 3.15 Å and 131.25°, respectively. The H(16) \cdots Cg(12) separation (Cg(12) is the centroid of the C51 benzene ring) and C(16)–H(16) \cdots Cg(12) angle are 2.86 Å and 156.17°, respectively. The H(30) \cdots Cg(11) separation (Cg(11) is the centroid of the C46 benzene ring) and C(30)–H(30) \cdots Cg(11) angle are 3.24 Å and 98.95°, respectively. The H(45) \cdots Cg(6) separation (Cg(6) is the centroid of the C1 benzene ring) and C(45)–H(45) \cdots Cg(6) angle are 3.14 Å and 92.42°, respectively. Neighboring complexes are linked to each other via an O(1)–H(10) \cdots O(2) hydrogen bonding with the separation 2.74 Å [symmetry code: (i) $-1+x,y,z$] and an O(4)–H(40) \cdots O(3) hydrogen bonding with the separation 2.82 Å [symmetry code: (ii) $1+x,y,z$] to form a supramolecule.

No face-to-face intermolecular π interaction between fluorene groups was observed in the orientational stacking of compound **2a**. The major two effects are CH \cdots π and hydrogen bonding intermolecular attractions.

The CH \cdots π interactions also occur in compound **3**, which is shown in Figure 2 (middle). The H(1) \cdots Cg(7) separation (Cg(7) is the centroid of P₅) and O(1)–H(1) \cdots Cg(7) angle are 2.58 Å and 171.00°, respectively. The H(6) \cdots Cg(5) separation (Cg(5) is the centroid of P₆) and C(6)–H(6) \cdots Cg(5) angle are 2.65 Å and 148.37°, respectively [symmetry code: (iii) $-x,1-y,2-z$]. According to the calculated result, no hydrogen bonding exists in **3**. As shown in Figure 2 (right), the pyrene groups of the neighboring compounds (**3**) were parallel to reach the cofacial arrangement and the distance between them was 3.30 Å (less than 3.60 Å). Therefore, the major two effects are CH \cdots π and $\pi\cdots\pi$ intermolecular attractions.

Although the stabilization arising from a single intermolecular CH \cdots π interaction or hydrogen bonding is weak, the

sum of multiple intermolecular CH $\cdots\pi$ interaction or hydrogen bonding can become significant. In addition, they may influence the optical properties of materials, especially for organic molecules bearing π -groups.²⁷

2.3. Optical properties

Solvents used in spectroscopic measurements were spectrograde and purified by distillation before use. The absorption and emission spectra of **2a–9** in solutions were measured in THF with a concentration of 10^{-6} M. All absorption and emission properties in THF solutions are summarized in Table 1.

Generally speaking, maximum absorption wavelengths obtained from spectroscopic recording were related to the energy gap ($E_{\text{LUMO}}-E_{\text{HOMO}}$) calculated by PM3 method to a certain extent (Table 1). The larger energy gap was, the shorter maximum absorption wavelength observed.

In THF solutions, absorption and emission spectra of **2a** and **3** are given in Figure 3. Maximum absorption wavelengths for them were 276 nm and 366 nm, respectively, while the maximum emission wavelengths for them were 312 nm and 383 nm, respectively. Absorption of **2a** was the typical fluorene absorption, that of **3** was the simple combination of absorptions of fluorene and pyrene due to the interruption of sp^3 hybridized carbon. Absorption and emission of **2a** were structureless, while those of **3** were vibronic. Compound **3** gave a smaller Stokes' shift.

In order to investigate the structure–property relationship of optical properties, the absorption and emission spectra of **3** were compared with those of 1-ethynylpyrene (**10**), which were prepared by literature procedure.²⁹ As shown in Figure 4, absorption spectrum of **3** was red-shifted compared to that of **10**, while emission spectra of both were nearly the same. In a word, the emission of **3** could be simply ascribed to the emission from pyrene and presented a single molecular emission in its dilute solution.

It is important to survey the emission performance in solid state because the real state for their functions as optoelectronics materials is the solid state. By examining emissions from thin film, powder, and crystal of **3** it was noticeable that

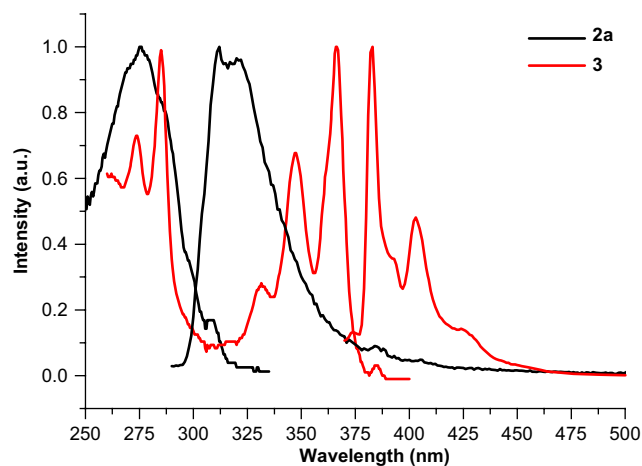


Figure 3. Normalized absorption and fluorescence spectra of **2a** and **3** in THF.

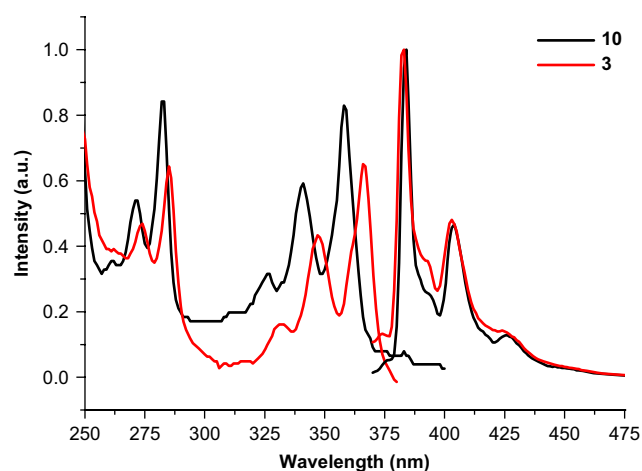


Figure 4. Normalized absorption and fluorescence spectra of **3** and **10** in THF.

molecular packing played a critical role in emission character. As the molecule got closer, from dilute solution ($C=1\times 10^{-5}$ M) (**3**-THF-LC in Fig. 5) to highly concentrated solution ($C=2\times 10^{-3}$ M) (**3**-THF-HC in Fig. 6), to film (**3**-film in Fig. 5) or powder (**3**-powder in Fig. 5), and finally

Table 1. Optical properties of compounds

Compounds	Abs. (nm) ($\epsilon\times 10^{-4}$)	Em. (nm)	Quantum yield Φ (%)	Stokes' shift (nm)	HOMO ^d (eV)	LUMO ^d (eV)	Gap ^d (eV)	μ_g (D) ^d	T_m ^e (°C)	T_d ^e (°C)
2a	276 (1.19)	312	0.44 ^b	36	-8.95	-0.47	8.48	1.41	106.1	—
3	366 (3.70)	383, 406	13.29 ^a	40	-8.25	-1.24	7.01	1.73	184.7	292.8
4	251 (1.21)	320	3.43 ^b	69	-9.02	-0.55	8.47	1.38	81.4	244.2
5	275 (2.47)	312	0.36 ^b	37	-9.05	-0.58	8.47	2.00	101.4	267.8
6	291 (1.90)	349	6.96 ^c	58	-9.18	-0.88	8.30	1.78	173.6	278.4
7	333 (3.45)	387	19.5 ^a	54	-8.51	-0.74	7.77	1.18	204.8	323.0
8	269 (1.81)	322	0.24 ^b	53	-8.94	-0.60	8.34	2.10	—	144.3
9	267 (3.70)	313	0.54 ^b	46	-9.15	-1.31	7.84	3.25	115.9	—
10	358	383	22.19 ^a	25	-8.23	-1.12	7.11	0.14	—	—

^a Quantum yields were calculated on the basis of 9,10-diphenylanthracene as standard ($\Phi=1.0$ in cyclohexane).²⁸

^b Quantum yields were calculated on the basis of *p*-terphenyl ($\Phi=0.93$ in cyclohexane).²⁸

^c Quantum yields were calculated on the basis of 1,4-diphenylbutadiene ($\Phi=0.42$ in hexane).²⁸

^d The energy level of HOMO or LUMO and the ground-state dipole moment is calculated by PM3 method.

^e Melting points of **2a** and **9** were recorded on a BÜCHI 535. Others were measured by DSC. Decomposition temperatures were measured by TGA.

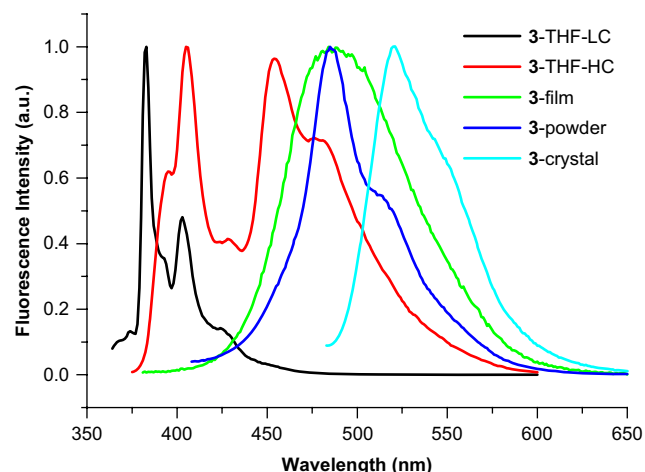


Figure 5. Normalized emission spectra of **3** in different existing appearances.

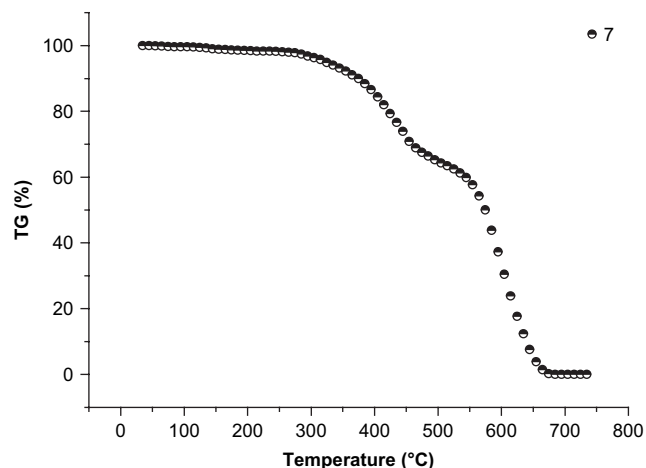


Figure 6. TGA chart of compound **7** in N_2 at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

to crystal (**3-crystal** in Fig. 5), the excimer emissions³⁰ of **3** were gradually red-shifted. The more oriented molecular packing was, the more red-shifted emission observed.

2.4. Thermal stabilities

Thermal stabilities of the compounds (**3–8**) were measured by the DSC and TGA analyses. Melting points of these compounds were obtained and listed in Table 1. TGA analysis showed that these compounds exhibited decomposition temperatures (T_d) in the range of $244.2\text{--}323.0\text{ }^\circ\text{C}$ with 5% weight loss excepted for **8** (Table 1). TGA chart of **7** is given in Figure 6 as an example.

3. Conclusion

In conclusion, we described a facile synthetic route to 9-ethynyl-9-fluorene. Several fluorescent compounds derived from it were thereafter synthesized. Emission properties were not only relative to the molecular structure, but also molecular packing. Further studies about their fluorescent applications are under investigation.

4. Experimental

4.1. General methods

^1H and ^{13}C NMR spectra were obtained on a Bruker AVANCE DMX500 spectrometer operating in the FT mode. Five percent w/v solutions in chloroform-*d* or DMSO-*d* were used to obtain NMR spectra. TMS was used as an internal standard. Hewlett Packard 5989B electron impact mass spectrometer with 70 eV and IonSpec HiResMALDI were used to obtain mass spectra. Melting points were recorded on a BÜCHI 535. Fluorescence measurements were made with a RF-5301pc spectrofluorometer (Shimadzu, Kyoto, Japan) equipped with a xenon lamp. UV–vis absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. NETZSCH STA 409 PG/PC was used to measure the thermal performances of the compounds. Solvents were distilled before use. Commercially available reagents were used without further purification unless otherwise stated.

XRD measurements were carried out at room temperature on a rotating-anode Rigaku RASIX-RAPID diffractometer by using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Measurements for **2a** and **3** were carried out on a charge-coupled device (CCD) area detector diffractometer under the same conditions. In these two cases, intensity data were collected in the ω scan mode. Crystal structure of **2a** was solved by direct methods where the SIR92 program was used,³¹ while the crystal structure of compound **3** was solved by the SIR97 program.³²

4.1.1. General procedure for synthesis of 9-ethynyl-9-fluorene derivatives (2). 1,2-Dibromoethane (25 mmol), 12.5 mL of 50% NaOH aqueous solution, and a catalytic amount of CEBA in 80 mL DMSO were mixed at room temperature, the solution of fluorene derivative (5 mmol) in 30 mL DMSO was added drop wise. After solution was stirred vigorously at room temperature for 10 h, the mixture was poured into water and extracted with dichloromethane (30 mL \times 3). The organic layers were combined, washed with water, and dried over anhydrous MgSO_4 . After filtration, filtrate was evaporated under reduced pressure. The crude products were purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent). In this way, the 9-ethynyl-9-fluorene derivatives were obtained.

4.1.1.1. 9-Ethynyl-9-fluorene (2a). Application of above procedure to fluorene (**1a**) (831 mg, 5 mmol) afforded compound **2a** (815 mg, 79%) as a white solid: mp $105.7\text{--}106.4\text{ }^\circ\text{C}$. ^1H NMR δ CDCl_3 : 2.47 (s, 1H, $\text{C}\equiv\text{CH}$), 2.59 (s, 1H, OH), 7.36 (t, 2H, $J = 7.5\text{ Hz}$), 7.41 (t, 2H, $J = 7.5\text{ Hz}$), 7.61 (d, 2H, $J = 7.5\text{ Hz}$), 7.70 (d, 2H, $J = 7.5\text{ Hz}$) ppm; ^1H NMR δ $\text{CDCl}_3/\text{D}_2\text{O}$: 2.48 (s, 1H), 7.36 (t, 2H, $J = 7.4\text{ Hz}$), 7.41 (t, 2H, $J = 7.5\text{ Hz}$), 7.62 (d, 2H, $J = 8.0\text{ Hz}$), 7.71 (d, 2H, $J = 7.5\text{ Hz}$) ppm; ^{13}C NMR δ CDCl_3 : 71.60, 74.80, 84.07, 120.48, 124.48, 128.86, 130.10, 139.34, 146.82 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_{10}\text{O}$: 206.2, found: 228.7 (100%, $\text{M} + \text{Na}^+$).

4.1.1.2. 2-Bromo-9-ethynyl-9H-fluorene-9-ol (2b). Application of above procedure to 2-bromo-9H-fluorene (**1b**)

(123 mg, 0.5 mmol) afforded compound **2b** (87 mg, 61%) as a pale yellow solid: mp 128.1–128.9 °C. ^1H NMR δ CDCl_3 : 2.48 (s, 1H, C \equiv CH), 2.74 (s, 1H, OH), 7.37 (m, 2H), 7.44 (d, 1H, $J=8.0$ Hz), 7.51 (dd, 1H, $J_1=8.0$ Hz and $J_2=1.5$ Hz), 7.56 (d, 1H, $J=6.5$ Hz), 7.66 (d, 1H, $J=7.0$ Hz), 7.81 (d, 1H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 72.27, 74.45, 83.36, 120.55, 121.81, 122.36, 124.54, 128.04, 129.23, 130.29, 133.12, 138.28, 138.32, 146.46, 148.62 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_9\text{BrO}$: 284.0, found: 306.7 (91.7%, $\text{M}+\text{Na}^+$), 308.7 (100%, $\text{M}+2+\text{Na}^+$).

4.1.1.3. 2,7-Dibromo-9-ethynyl-9H-fluoren-9-ol (2c).

Application of above procedure to 2,7-dibromo-9H-fluorene (**1c**) (162 mg, 0.5 mmol) afforded compound **2c** (122 mg, 67%) as a pale yellow solid: mp 199.7–200.8 °C. ^1H NMR δ CDCl_3 : 2.55 (s, 1H, C \equiv CH), 2.63 (s, 1H, OH), 7.46 (d, 2H, $J=8.0$ Hz), 7.54 (dd, 2H, $J_1=8.0$ Hz, $J_2=1.5$ Hz), 7.82 (d, 2H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 72.97, 74.25, 82.86, 121.92, 122.84, 128.14, 133.40, 137.34, 148.29 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_8\text{Br}_2\text{O}$: 361.9, found: 384.6 (44.7%, $\text{M}+\text{Na}^+$), 386.6 (100%, $\text{M}+2+\text{Na}^+$), 388.5 (36.7%, $\text{M}+4+\text{Na}^+$).

4.1.1.4. 9-Ethynyl-2-iodo-9H-fluoren-9-ol (2d). Application of above procedure to 2-iodo-9H-fluorene (**1d**) (146 mg, 0.5 mmol) afforded compound **2d** (93 mg, 56%) as a dark yellow solid: mp 135.8–137.4 °C; ^1H NMR δ CDCl_3 : 2.50 (s, 1H, C \equiv CH), 2.64 (s, 1H, OH), 7.38 (m, 3H), 7.58 (m, 1H), 7.67 (m, 1H), 7.72 (dd, 1H, $J_1=8.0$ Hz, $J_2=1.5$ Hz), 8.02 (d, 1H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 72.28, 74.38, 83.40, 93.62, 120.61, 122.14, 124.49, 129.43, 130.30, 133.85, 138.43, 138.95, 139.05, 146.29, 148.73 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_9\text{IO}$: 332.0, found: 354.8 (100%, $\text{M}+\text{Na}^+$).

4.1.1.5. 9-Ethynyl-2,7-diiodo-9H-fluoren-9-ol (2e). Application of above procedure to 2,7-diiodo-9H-fluorene (**1e**) (209 mg, 0.5 mmol) afforded compound **2e** (188 mg, 82%) as a yellow solid: mp 236.3–237.1 °C. ^1H NMR δ CDCl_3 : 2.55 (s, 1H, C \equiv CH), 2.61 (s, 1H, OH), 7.33 (d, 2H, $J=8.5$ Hz), 7.74 (dd, 2H, $J_1=7.8$ Hz, $J_2=1.8$ Hz), 8.01 (d, 2H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 72.99, 74.06, 82.71, 94.22, 122.23, 133.85, 138.05, 139.29, 148.09 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_8\text{I}_2\text{O}$: 457.9, found: 456.7 (100%, $(\text{M}-1)^+$).

4.1.1.6. 9-Ethynyl-2-nitro-9H-fluoren-9-ol (2f). Application of above procedure to 2-nitro-9H-fluorene (**1f**) (106 mg, 0.5 mmol) afforded compound **2f** (62 mg, 49%) as a brown solid: mp 171.9–173.5 °C. ^1H NMR δ CDCl_3 : 2.56 (s, 1H, C \equiv CH), 2.81 (s, 1H, OH), 7.49–7.50 (m, 2H), 7.71–7.77 (m, 3H), 8.33 (dd, 1H, $J_1=15.8$ Hz, $J_2=2.3$ Hz), 8.56 (d, 1H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 72.90, 74.29, 82.62, 120.36, 120.76, 121.88, 124.92, 126.16, 130.72, 130.95, 137.06, 145.67, 148.05, 148.08, 148.31 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_9\text{NO}_3$: 251.1, found: 273.8 (100%, $\text{M}+\text{Na}^+$).

4.1.1.7. 2-Bromo-9-ethynyl-7-nitro-9H-fluoren-9-ol (2g). Application of above procedure to 2-bromo-7-nitro-9H-fluorene (**1g**) (145 mg, 0.5 mmol) afforded compound **2g** (84 mg, 51%) as a brown solid: mp 206.9–208.3 °C. ^1H NMR δ CDCl_3 : 2.60 (s, 1H, C \equiv CH), 2.92 (s, 1H, OH),

7.60 (dd, 2H, $J_1=25.5$ Hz, $J_2=8.0$ Hz), 7.72 (d, 1H, $J=8.5$ Hz), 7.90 (s, 1H), 8.33 (d, 1H, $J=7.0$ Hz), 8.53 (s, 1H) ppm; ^{13}C NMR δ CDCl_3 : 73.57, 73.92, 82.00, 120.41, 120.88, 123.12, 124.90, 126.31, 128.55, 133.86, 135.96, 144.70, 147.75, 148.47, 149.71 ppm. MS (ESI) (m/z): calcd for $\text{C}_{15}\text{H}_8\text{BrNO}_3$: 329.0, found: 351.7 (100%, $\text{M}+\text{Na}^+$), 353.7 (66.7%, $\text{M}+2+\text{Na}^+$).

4.1.1.8. 9-(Pyren-1-ylethynyl)-9H-fluoren-9-ol (3).

Compound **2a** (206 mg, 1 mmol), 1-iodopyrene (328 mg, 1 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis-(triphenylphosphine)palladium(II) (3.5 mg, 0.005 mmol), triphenylphosphine (5 mg, 0.02 mmol), and dry triethylamine 100 mL were placed in a 150-mL round bottom flask equipped with a Teflon covered magnetic stir bar. After the solution was purged with nitrogen for half an hour, it was refluxed under nitrogen for 4 h. The reaction mixture was filtered and filtrate was evaporated under reduced pressure. The residue was purified through column chromatography (silica gel, hexane/dichloromethane as eluent). In this way, 305 mg (75% yield) of **3** was obtained as a yellow solid: mp 184.7 °C. ^1H NMR δ CDCl_3 : 2.83 (s, 1H), 7.40–7.45 (m, 4H), 7.66 (d, 2H, $J=7.0$ Hz), 7.92–8.05 (m, 8H), 8.11–8.13 (m, 2H), 8.40 (d, 1H, $J=8.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 75.88, 82.66, 94.80, 116.97, 120.61, 124.40, 124.51, 124.71, 125.55, 125.81, 125.87, 126.41, 127.39, 128.48, 128.66, 128.97, 130.03, 130.18, 131.19, 131.38, 131.67, 132.60, 139.45, 147.60 ppm. MS (MALDI) (m/z): calcd for $\text{C}_{31}\text{H}_{18}\text{O}$: 406.1, found: 406.2 (100%, M^+).

4.1.1.9. 9-(Phenylethynyl)-9H-fluoren-9-ol (4).³³ Compound **4** was prepared by a similar method as the preparation of **3**. When **2a** (824 mg, 4 mmol) was reacted with iodobenzene (816 mg, 4 mmol) and purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent), 903 mg (80% yield) of **4** was obtained as a brown solid: mp 81.4 °C. ^1H NMR δ CDCl_3 : 2.73 (s, 1H), 7.20–7.25 (m, 3H), 7.30–7.33 (m, 2H), 7.35–7.40 (m, 4H), 7.59 (d, 2H, $J=7.0$ Hz), 7.74 (d, 2H, $J=7.5$ Hz) ppm.

4.1.1.10. 9-(Thiophen-2-ylethynyl)-9H-fluoren-9-ol (5). Compound **5** was prepared by a similar method as the preparation of **3**. When **2a** (206 mg, 1 mmol) was reacted with 2-iodothiophene (210 mg, 1 mmol) and purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent), 236 mg of **5** (82% yield) was obtained as a brown solid: mp 101.4 °C. ^1H NMR δ CDCl_3 : 2.83 (s, 1H), 6.84–6.86 (m, 1H), 7.13–7.15 (m, 2H), 7.27–7.35 (m, 4H), 7.55 (d, 2H, $J=7.5$ Hz), 7.69 (d, 2H, $J=7.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 75.40, 76.61, 92.93, 120.38, 122.41, 124.59, 127.02, 127.64, 128.74, 129.87, 132.92, 139.15, 146.95 ppm; MS (ESI) (m/z): calcd for $\text{C}_{19}\text{H}_{12}\text{OS}$: 288.4, found: 311.0 (100%, $\text{M}+\text{Na}^+$).

4.1.1.11. 2,7-Dibromo-9-(phenylethynyl)-9H-fluoren-9-ol (6). Compound **6** was prepared by a similar method as the preparation of **3**. When **2c** (728 mg, 2 mmol) was reacted with iodobenzene (408 mg, 2 mmol) and purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent), 687 mg of **6** (78% yield) was obtained as a yellow solid: mp 173.6 °C. ^1H NMR δ CDCl_3 : 2.70 (s, 1H), 7.28–7.34 (m, 3H), 7.43–7.46 (m, 3H), 7.47 (s, 1H), 7.53 (d, 1H, $J=1.5$ Hz), 7.55 (d, 1H, $J=2.0$ Hz), 7.87 (d,

2H, $J=1.5$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 74.92, 84.61, 87.59, 121.93, 122.82, 128.18, 128.56, 128.23, 132.27, 133.25, 137.29, 148.89 ppm. MS (ESI) (m/z): calcd for $\text{C}_{21}\text{H}_{12}\text{Br}_2\text{O}$: 437.9, found: 436.7 (47.7%, (M-1) $^+$), 438.8 (100%, (M+1) $^+$), 440.7 (33.2%, (M+3) $^+$).

4.1.1.12. 2,7-Bis(4-methoxyphenyl)-9-(phenylethynyl)-9H-fluoren-9-ol (7). A mixture of **6** (330 mg, 0.75 mmol), 4-methoxyphenylboronic acid (342 mg, 2.25 mmol), K_2CO_3 (1.05 g, 7.5 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (10 mg, 0.08 mmol) in 70 mL toluene/ethanol (10:1, v/v) was refluxed for 40 h.³⁴ After cooling and filtering, the filtrate was evaporated under reduced pressure. The crude products were purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent). In this way, 260 mg (70% yield) of **7** was obtained as a dark yellow solid: mp 204.8 °C. ^1H NMR δ CDCl_3 : 2.70 (s, 1H), 3.86 (s, 6H), 7.00 (d, 4H, $J=8.5$ Hz), 7.24–7.28 (m, 3H), 7.43–7.45 (m, 2H), 7.61–7.63 (m, 6H), 7.67 (s, 1H), 7.69 (s, 1H), 7.98 (d, 2H, $J=1.0$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 55.61, 75.49, 83.69, 89.13, 114.53, 120.74, 122.54, 122.91, 128.37, 128.40, 128.46, 128.78, 132.22, 133.55, 137.58, 141.47, 148.32, 159.56 ppm. MS (MALDI) (m/z): calcd for $\text{C}_{35}\text{H}_{26}\text{O}_3$: 494.2, found: 492.7 (100%, (M-1) $^+$).

4.1.1.13. 9,9'-(Buta-1,3-diyne-1,4-diyl)bis(9H-fluoren-9-ol) (8).^{12a,35} Compound **2a** (206 mg, 1 mmol), cuprous iodide (10 mg, 0.05 mmol), dichlorobis(triphenylphosphine)palladium(II) (10 mg, 0.015 mmol), I_2 (126 mg, 0.5 mmol), and dry *i*-Pr $_2\text{NH}$ (80 mL) were placed in a 150-mL round bottle flask equipped with a Teflon covered magnetic stir bar.³⁶ The mixture was stirred at room temperature for 6 h and then poured into 50 mL of water with some sodium bisulfite. The mixture was extracted with dichloromethane (20 mL \times 3). Solvent was removed by evaporation. The residue was purified through column chromatography (silica gel, *n*-hexane/ethyl acetate as eluent), 152 mg of **8** (yield, 74%) was obtained as a brown solid. ^1H NMR δ ($\text{CD}_3)_2\text{SO}$: 6.86 (s, 2H), 7.34 (t, 4H, $J=7.5$ Hz), 7.42 (t, 4H, $J=7.5$ Hz), 7.60 (d, 4H, $J=7.5$ Hz), 7.78 (d, 4H, $J=7.5$ Hz) ppm.

4.1.1.14. 2-(9H-Fluoren-9-ylidene)acetaldehyde (9). A mixture of **2a** (330 mg, 1.6 mmol), *p*-TsOH (0.1 equiv), and a small amount of silica gel was well ground for 30 min at room temperature in the solid state and purified through column chromatography (silica gel, *n*-hexane/dichloromethane as eluent), 124 mg (37.5% yield) of **9** was obtained as a yellow solid: mp 115.6–116.3 °C (lit.^{36a} mp 116 °C). ^1H NMR δ CDCl_3 : 6.84 (d, 1H, $J=8.0$ Hz), 7.29–7.33 (m, 2H), 7.42–7.48 (m, 2H), 7.63 (d, 1H, $J=7.5$ Hz), 7.66–7.68 (m, 2H), 8.03 (d, 1H, $J=8.0$ Hz), 10.86 (d, 1H, $J=8.0$ Hz) ppm; ^{13}C NMR δ CDCl_3 : 120.39, 120.75, 122.57, 123.21, 127.85, 128.21, 131.66, 131.78, 135.77, 138.40, 141.34, 142.94, 151.55, 190.41 ppm. ^1H NMR and ^{13}C NMR are consistent with the previous report.³⁷

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Supplementary data

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