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Synthesis of conjugated 2,7-bis(trimethylsilylethynyl)-(phenylethynyl)$_n$fluoren-9-one and 9-(*p*-methoxyphenyl)-9-methyl derivatives: optical properties

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Abstract—2,7-Substituted 9-fluorenones and 9,9-disubstituted fluorene have been synthesized and their fluorescence properties analyzed. The synthesis of conjugated 2,7-bis(trimethylsilylethynyl)-(phenylethynyl)$_n$fluoren-9-one (or the 9-(*p*-methoxyphenyl)-9-methyl) structures was carried out by the heterocoupling reaction between the 2,7-di(halo)fluoren-9-one (or 2,7-dibromo-9-(*p*-methoxyphenyl)-9-methylfluorene) and *p*-trimethylsilylethynyl(phenylethynyl)$_n$ ($n=1,2$), catalyzed by the dichloro bis(triphenylphosphine)palladium and cuprous iodide system, in a divergent synthesis.The π-extended conjugated compounds exhibit fluorescence radiation emission (blue light-emitting), with important quantum yield for the 9-(*p*-methoxyphenyl)-9-methyl-2,7-bis(trimethylsilylethynyl)-(phenylethynyl)$_n$fluorenes which increases with the conjugation.

1. Introduction

In the last decade the research on the synthesis of carbon-rich organic and organometallic compounds for the widespread applications in the field of materials science as remarkably increased.[1]

In this context, the use of π-conjugated rigid fluorenyl chromophores and their derivatives offers exciting perspectives for the design of new molecular oligomeric and polymeric materials for various optoelectronic applications.[2] The fluorene ring has been used to prepare conjugated 2,7- and 9-one or 9,9-disubstituted compounds because the conjugated ring exhibits fluorescence radiation emission (fluorene, Φ, 0.80 in cyclohexane).[3]

Synthesis of conjugated co-polymers including fluorenyl-acetylene–arylidene,[4] and a family of poly(2,7-diethynyl)-9,9-disubstituted fluorenes,[5] showing electroluminescent properties, have been reported.

Polyfluorenes (PFs) are a class of conjugated polymers, which are used as the blue light-emitting diodes (PLEDs).[6] The PFs exhibit high photoluminescence (PL) efficiency, good charge transport and thermal stability by chemical modification and copolymerization. Moreover, as a host material, the PFs can enable full color (blue, green, and red) via energy transfer, to longer wavelength emitters in blends with other conjugated polymers with phosphorescent dyes.[7]

However, the presence of the carbonyl group in fluoren-9-one considerably stabilizes the ring system but decreases the quantum yield of the fluorescent emission (Φ, 0.02 in dichloromethane). Thus, the PFs structure suffers photoxidation in the solid state in short times giving 9-fluorenone keto defects, which show guest emitters behaviour,[8] that produces an important decreasing in the fluorescence quantum yield.[9] Some key constitutional aspects have been considered.[10]

Moreover, the 2,7-disubstituted fluoren-9-one derivatives can present electrical and nonlinear optical properties.[11]

On the other hand, substituent derivatization at the C-9 position of the monomeric fluorenes offers the prospect of controlling polymer properties such as solubility, emission wavelengths, processability, and potential interchain interactions in films.[1]

Keywords: 2,7-Di(ethynylphenyl)$_x$fluoren-9-one; 9,9-Disubstituted fluorene; *p*-(Trimethylsilyl)phenylethynyl; π-Extended conjugation; Fluorescence; Sonogashira reaction.

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We report the synthesis of the 2,7-bis(trimethylsilylethynyl)-fluoren-9-one and their 9,9-disubstituted conjugated compounds, to verify the effect of the chains on the fluorescence emission.

2. Results and discussion

A relevant starting unit with synthetic versatility to prepare oligomeric fluorenone structures including the fluoren-9-one ring was the 2,7-di(halo)fluoren-9-one (Br, **1** or I, **3**). Compound **1** was obtained by treatment of 2,7-dibromofluorene with chromium oxide in anhydrous acetic acid at room temperature, in practically quantitative yield, Scheme 1. The more active 2,7-diiodofluoren-9-one (**3**) has been obtained by direct fluorene iodination followed by chromic oxidation.[12] We have synthesized the diiodo **3** from 2,7-dinitrofluoren-9-one, by reduction with stannous chloride in ethyl acetate, to 2,7-diaminofluoren-9-one (**2**),[13] as a brown solid, in excellent yield (97%). Finally **2** was treated with sodium nitrite in concentrated sulfuric acid to prepare the double diazonium salt, which by reaction with potassium iodide gives 2,7-diiodofluoren-9-one (**3**), yellow solid, in good yield (62%), Scheme 1.

No fluorescence radiation emission was observed for the 2,7-di(halo)fluoren-9-one (**1** or **3**), due to the presence of heavy-atoms on the 2,7-positions and the 9-carbonyl group. In this way, were prepared the 2,7-dibromo derivatives without the 9-carbonyl group by treatment of **1** with methylmagnesium iodide to give the 9-hydroxy-9-methyl **4** or the elimination product 9-methylidene **5**, which do not emit fluorescence radiation. The 9-(*p*-methoxyphenyl)-9-methyl compound **6** was obtained by sulfuric acid catalyst treatment of the methylidene compound **5** with anisole, Scheme 1. Compound **6** shows very low fluorescence quantum yield, Table 1. All these data accord well with that reported in advance for aromatic rings containing heavy-atoms.[14]

On the other hand, to prove the effect of the conjugated carbonyl group on the fluorescence emission, the conjugated 2,7-bis(trimethylsilylethynyl)fluoren-9-one (**7**),[2,15] and their 9-(*p*-methoxyphenyl)-9-methyl derivative **9**, were obtained. The heterocoupling between trimethylsilylacetylene and 2,7-dibromofluoren-9-one (**1**) (or **6**) in triethylamine at 50 °C, catalyzed by the palladium–copper system, gives a pale-yellow solid in good yield (78%), (or **9**, a white solid, 94% yield). Scheme 2.

Catalytic deprotection of the trimethylsilylethynyl group in compound **7** (or **9**) was carried out with potassium carbonate in tetrahydrofuran–methanol (4/1), at room temperature, giving 2,7-diethynylfluoren-9-one (**8**),[2,16] pale-yellow solid in 98% yield, (or **10**, white solid in quantitative yield).

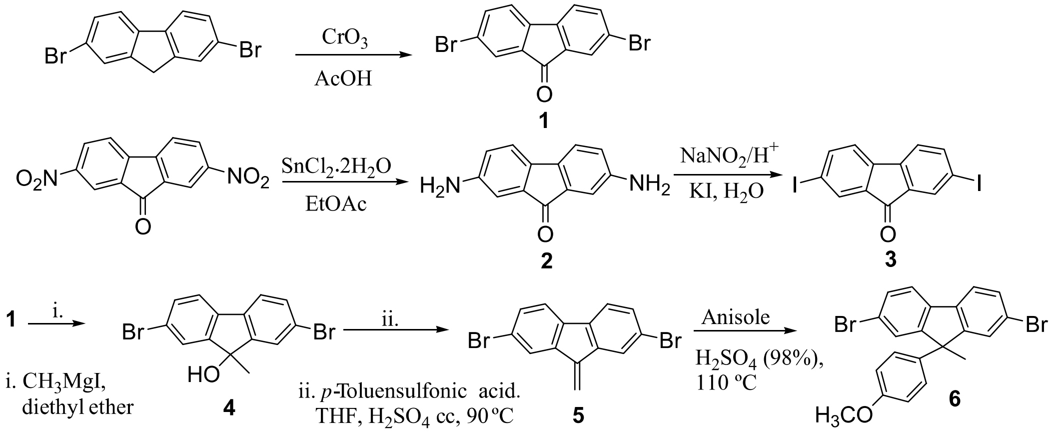
Compounds **7**–**10** exhibit fluorescence radiation emission in dichloromethane, the 9,9-disubstituted **9** and **10** show a very important quantum yield, Table 1.

Afterwards, the more extended conjugated 2,7-di[(*p*-trimethylsilylethynylphenyl)ethynyl]fluoren-9-one (**14**) was synthesized by double heterocoupling reaction between *p*-(trimethylsilylethynyl)phenylacetylene (**13**) and 2,7-diiodo derivative **3** (2,7-dibromofluoren-9-one, fails), in triethylamine at 50 °C, catalyzed by the palladium–copper system. Compound **14** was obtained as an orange solid, in good yield (73%), Scheme 3.

The monoacetylene **13** was obtained by specific deprotection[17] of the propargylic compound **12** with powdered sodium hydroxide in dry toluene at reflux temperature, as a white solid in quantitative yield.

The specific method for deprotection of 2-methyl-3-butyn-2-ol in dry toluene, in presence of the trimethylsilyl protector group, requires rigorous dry conditions. There are many references for trimethylsilyl deprotection with different bases such as aqueous sodium hydroxide.[18] Under dry conditions, sodium hydroxide dissociation is avoided and thus, the sodium hydroxide can only behave as a basic group abstracting the acid proton of the alcohol with elimination of acetone. In contrast, in presence of a little amount of water or MeOH, the sodium hydroxide is partially dissociated and a nucleophilic attack of the OR anion to the silicon atom takes place, with formation of Me_3Si-OR and the elimination of the trimethylsilyl group.[17]

The doubly protected 4-[*p*-(trimethylsilylethynyl)phenyl]-2-methyl-3-butyn-2-ol (**12**) was prepared by heterocoupling between the iodo derivative **11** and trimethylsilylacetylene



Scheme 1.

Table 1. UV–vis and fluorescence spectra of the fluorene compounds

Compound	UV–vis (CH_2Cl_2) λ_{max} (nm)[a]	ε (M^{-1} cm^{-1})	F (CH_2Cl_2) λ_{max} (nm)[b]	Φ_f
6	318	26,300	334	0.4×10^{-2}[c]
7	340	6620	527	0.04[d]
8	334	21,800	523	0.03[d]
9	344	93,000	351 and 363	0.79[c]
10	332	58,100	355	0.52[c]
14	358	15,800	531	0.03[d]
17	374	25,900	531	0.03[d]
18	337	6600	502	0.10[d]

[a] At room temperature.

[b] At room temperature and $[c]\cong10^{-8}$ M.

[c] Fluorescence quantum yield was in dichloromethane relative to 2-aminopyridine in 0.1 N H_2SO_4.

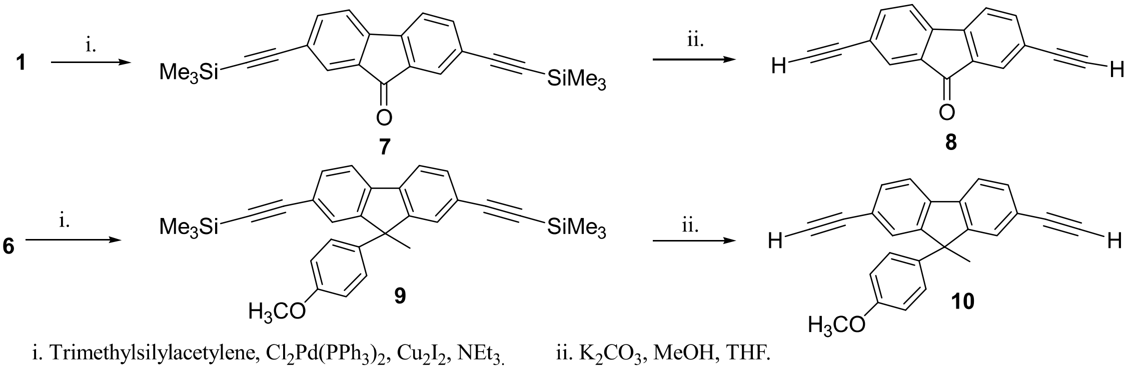
[d] Fluorescence quantum yield in dichloromethane relative to quinine sulfate in 1 N H_2SO_4.

in triethylamine, catalyzed by the palladium–copper system, in practically quantitative yield, as a white solid.

Compound **11** was prepared by the monoheterocoupling between 1,4-diiodobenzene and 2-methyl-3-butyn-2-ol, in triethylamine, catalyzed by the palladium–copper system, as a white solid in good yield (78%).[19]

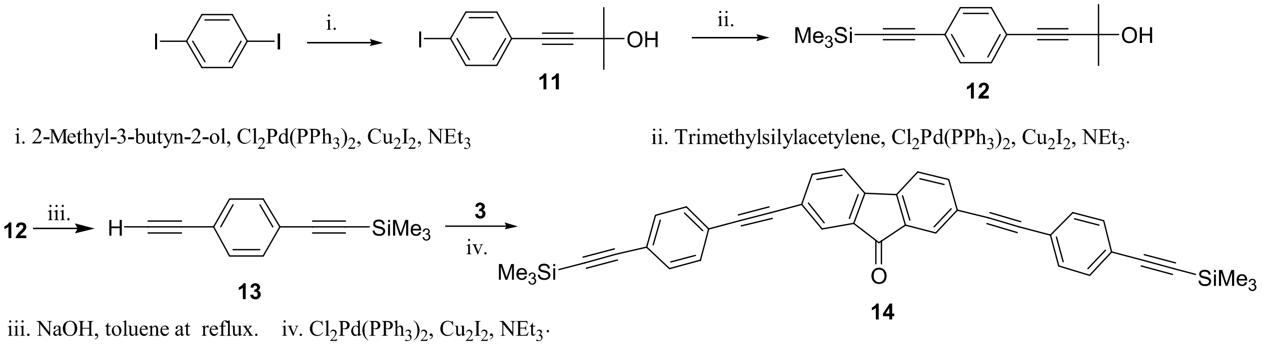
Moreover, the conjugated 2,7-di[*p*-(*p*-{trimethylsilylethynyl}phenylethynyl)phenylethynyl]fluoren-9-one (**17**), was synthesized by heterocoupling between the terminal acetylene **16** and 2,7-diiodo derivative **3** in triethylamine at 60 °C, in presence of the palladium–copper system, as an orange solid in good yield (82%), Scheme 4.

The terminal acetylene **16** was quantitatively obtained as a white solid, by treatment of **15** with catalytic powdered sodium hydroxide in dry toluene at the reflux temperature.



i. Trimethylsilylacetylene, $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3. ii. K_2CO_3, MeOH, THF.

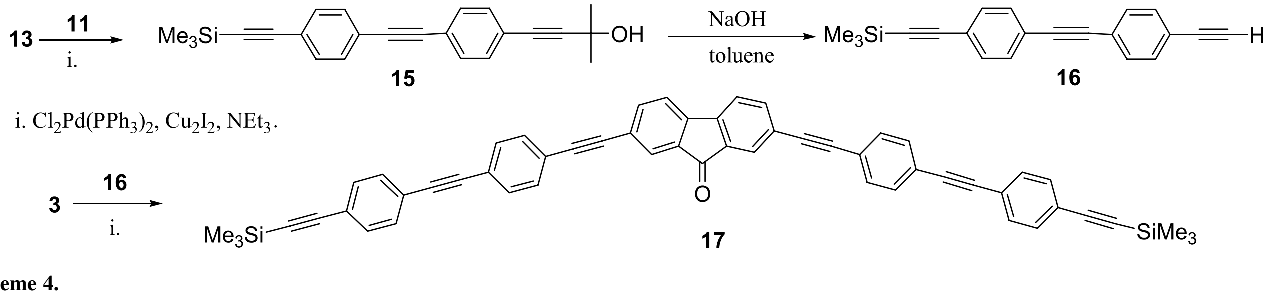
Scheme 2.



i. 2-Methyl-3-butyn-2-ol, $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3 ii. Trimethylsilylacetylene, $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3.

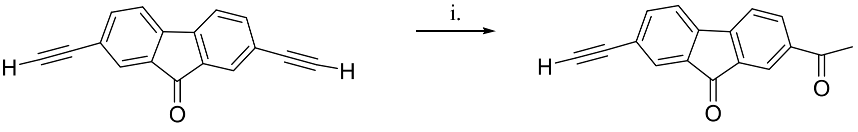
iii. NaOH, toluene at reflux. iv. $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3.

Scheme 3.



i. $Cl_2Pd(PPh_3)_2$, Cu_2I_2, NEt_3.

Scheme 4.



8 i. *p*-Toluensulfonic ac. / H_2O. **18**

Scheme 5.

The precursor 4-[*p*-(*p*-{trimethylsilylethynyl}phenylethynyl)phenyl]-2-methyl-3-butyn-2-ol (**15**) was prepared by heterocoupling between the terminal acetylene **13** and the iodoarene **11**, in triethylamine, catalyzed by the palladium–copper system, giving a white solid in practically quantitative yield.

All the 2,7-di(ethynylphenyl)$_n$fluoren-9-one compounds show fluorescence emission radiation with low quantum yields, by the presence of the 9-carbonyl group and also by the homo diethynyl 2,7-substitution. The last effect can be proved by the partial mild hydrolysis of the terminal acetylene **8**, with *p*-toluensulfonic acid with a little amount of water, to obtain 2-acetyl-7-ethynylfluoren-9-one (**18**), as a pale-yellow solid in 88% yield. Compound **18** shows fluorescence radiation emission with the quantum yield increasing significantly with respect to **8**, Scheme 5, Table 1.

Table 1, shows the UV–vis absorption of **17**, red-shifted by 18 nm compared to **14** and 34 nm respect **7**, due to the extended conjugation, while the fluorescent emission of the same compounds do not show or red-shifted by only 4 nm, respectively. Hence, the UV–vis absorption and the weak fluorescent emission are dominated from different transitions. The fluorescent emission of these fluorenones should be attributed to the n-π transition, which is not so substituent dependent. The 9-(*p*-methoxyphenyl)-9-methyl compounds **9** and **10** show fluorescence emission (blue light-emitting) with very important quantum yield.

Moreover, it was noticeable the large Stokes shift of the fluorescent wavelength emission for the fluoren-9-ones, in contrast with the moderate shift for the 9,9-disubstituted compounds **9** and **10**.

3. Conclusions

Conjugated 2,7-disubstituted 9-fluorenones and 9,9-disubstituted fluorene compounds have been efficiently synthesized and their fluorescence properties analyzed. The conjugated 2,7-bis(trimethylsilylethynyl)-(phenylethynyl)$_n$-fluoren-9-one structures have been satisfactory synthesized by means of the Sonogashira heterocoupling reaction between the 2,7-di(halo)fluoren-9-one (or 2,7-di(halo)-9-(*p*-methoxyphenyl)-9-methylfluorene) and *p*-trimethylsilylethynyl(phenylethynyl)$_n$ ($n=1,2$), catalyzed by the dichloro bis(triphenylphosphine)palladium, in a divergent synthesis. The starting 2,7-dibromo-9-(*p*-methoxyphenyl)-9-methylfluorene was obtained in good yield by reaction of the appropriate 9-one derivative with methylmagnesium iodide followed the acid catalysis reaction on *p*-methoxybenzene. The π-extended conjugated compounds exhibit fluorescence radiation emission with significant quantum yield for the 9-(*p*-methoxyphenyl)-9-methyl-2,7-bis(trimethylsilylethynyl)-(phenylethynyl)$_n$fluorenes.

4. Experimental

4.1. General

Melting points were determined in open capillaries using a Buchi or Reichert hot stage microscope and are uncorrected. IR spectra of solids were recorded as KBr pellets and IR spectra of oils were recorded as thin films on NaCl plates with a Bruker Vector 22 spectrophotometer, and the wave numbers are given in cm^{-1}. ^1H NMR spectra and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker Aspect spectrometer. Chemical shifts are given in δ with TMS as an internal reference and constants coupling J are given in Hz, the solvent is $CDCl_3$. Mass spectra were recorded on a VG AutoSpec spectrometer at 70 eV and the MALDI-TOF spectra were recorded on a Bruker Reflex III spectrometer. Elemental analyses were performed with a LECO CHN-900. The UV–vis spectra were recorded on a Hewlett Packard 8453 spectrometer, frequencies are given in nm and ε in $L\,mol^{-1}\,cm^{-1}$. All fluorescence spectra were recorded at room temperature at 10^{-8} M on a SLM Aminco Bowman series 2, the fluorescence quantum yield was determined in dichloromethane on freshly prepared samples (air-equilibrated) with absorbances at the excitation wavelength (365 nm for the standard quinine sulfate). The samples quinine sulfate in 1 N H_2SO_4 and 2-aminopyridine in 0.1 N H_2SO_4 were employed as a standard ($\Phi_f=0.55$ and 0.66, respectively) to measure the fluorescence quantum yields, which were corrected taking into account the refractive indices of the solvents used. Yields are given after chromatography column separation on silica gel 60 (200–400 mesh) using the indicated solvents or solvent crystallization.

4.1.1. 2,7-Dibromofluoren-9-one (1). To a suspension of 2,7-dibromofluorene (5 g, 15 mmol) in anhydrous acetic acid (50 mL), was added a solution of chromium oxide in anhydrous acetic acid (50 mL, 10%). The mixture was stirred at room temperature for 6 h and then, the pH of the mixture was neutralized by addition a solution of sodium bicarbonate. The yellow solid was filtered through a Büchner funnel and was washed with H_2O to give a residue, which was purified by recrystallization in ethanol/toluene, giving 2,7-dibromofluoren-9-one (**1**) as a yellow solid, mp 205–206 °C, 5.1 g (98%) yield, which agrees well with a commercial sample.

4.1.2. 2,7-Diaminofluoren-9-one (2). To a solution of 2,7-dinitrofluoren-9-one (2.7 g, 10 mmol) in ethyl acetate (freshly distilled) (200 mL), was added $SnCl_2$–$2H_2O$ (7.5 g, 33 mmol), under argon atmosphere. The mixture was stirred for 24 h at the reflux temperature and then poured onto ice (100 g). The pH of the mixture was made basic (9–10) by addition of aqueous sodium hydroxide and finally was extracted with AcOEt. The organic layer was dried over anhydrous sodium sulfate and after filtration the solvent was removed. The residual brown solid was purified by silica gel column chromatography eluting with hexane–ethyl acetate (2/1), giving **2** as a brown solid, mp 276–278 °C (lit. 278–279 °C),[13] 2.0 g (97%) yield.

4.1.3. 2,7-Diiodofluoren-9-one (3). To a solution of sodium nitrite (304 mg, 4.4 mmol) in concentrated sulfuric acid (20 mL) at 0 °C, was added dropwise a solution of compound **2** (400 mg, 1.9 mmol) in glacial acetic acid (10 mL). The mixture was stirred for 15 min and after poured onto ice (8 g) and urea (47.3 mg, 0.78 mmol) and then, a solution of potassium iodide (43 g, 269 mmol) in water (40 mL) was added and stirred overnight under reduced pressure. The solid was filtered, dried, and extracted with dichloromethane. The combined extracts were refluxed with charcoal and finally purified by silica gel column chromatography (hexane/dichloromethane, 2:1) giving **3** as a yellow solid, mp 198–199 °C (lit. 201–202 °C),[12] 508 mg (62%) yield.

4.1.4. 2,7-Dibromo-9-hydroxy-9-methylfluorene (4). To a solution of compound **1** (100 mg, 0.3 mmol) in dry Et_2O (20 mL), under argon atmosphere at 0 °C, was added dropwise a solution of methylmagnesium iodide (100 mg, 0.6 mmol). The white solution was stirred for 3 h and then, was added a saturated aqueous ammonium chloride solution. The mixture was stirred for 15 min and extracted with Et_2O. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a white solid, which was purified by silica gel column chromatography (dichloromethane). Compound **4** was isolated as a white solid, mp 161–162 °C, 104 mg (98%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 289 (ε, 21,600), 305s (ε, 14,400). IR (KBr, cm^{-1}): 3314, 1100, 1061, 886, 865, 818. ^{1}H NMR ($CDCl_3$): δ 7.63 (d, 2H, $J=1.7$ Hz), 7.48 (dd, 2H, $J=8.0$, 1.7 Hz), 7.43 (d, 2H, $J=8.0$ Hz), 2.20 (s, 1H), 1.66 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 151.4, 136.1, 132.3, 126.7, 122.2, 121.5, 86.2, 26.1. $C_{14}H_{10}Br_2O$ (354.04). Anal. Calcd: C 47.50, H 2.85. Found: C 47.42, H 2.98.

4.1.5. 2,7-Dibromo-9-methylidenefluorene (5). To a solution of compound **4** (100 mg, 0.28 mmol) and *p*-toluensulfonic acid (96 mg, 0.56 mmol) in dry THF (20 mL), under argon atmosphere, was added concentrated sulfuric acid (1 mL). The mixture was stirred for 30 h at 90 °C and then, the solvent was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution, and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a solid residue, which was purified by silica gel column chromatography (hexane/dichloromethane, 4:1). Compound **5** was isolated as a pale-yellow, mp 209–210 °C, 92 mg (98%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 256 (ε, 40,000), 264 (ε, 58,000), 280 (ε, 17,700), 299 (ε, 20,000), 312 (ε, 21,300). IR (KBr, cm^{-1}): 1850, 1055, 914, 878, 852, 806. ^{1}H NMR ($CDCl_3$): δ 7.81 (s, 2H), 7.48 (s, 4H), 6.08 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 141.5, 139.5, 138.0, 131.8, 124.4, 121.3, 121.1, 110.4. $C_{14}H_8Br_2$ (336.02). Anal. Calcd: C 50.04, H 2.40. Found: C 50.38, H 2.62.

4.1.6. 2,7-Dibromo-9-(*p*-methoxyphenyl)-9-methylfluorene (6). To a solution of compound **5** (100 mg, 0.3 mmol) in anisole (10 mL), under argon atmosphere, was added concentrated sulfuric acid (85%, 1 mL). The mixture was stirred for 24 h at 110 °C and then, the solvent was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution, and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a solid, which was purified by silica gel column chromatography (hexane/dichloromethane, 1:1). Compound **6** was isolated as a white solid, mp 115–116 °C, 100 mg (75%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 289 (ε, 40,000), 306 (ε, 18,700), 318 (ε, 26,300). Fluorescence (CH_2Cl_2), λ_{max} (nm): 334 ($\phi=0.4\times10^{-2}$). IR (KBr, cm^{-1}): 2926, 1253, 1061, 881, 867, 809, 834. ^{1}H NMR ($CDCl_3$): δ 7.58 (d, 2H, $J=8.2$ Hz), 7.47 (dd, 2H, $J=8.2$, 1.8 Hz), 7.32 (d, 2H, $J=1.8$ Hz), 7.03 (d, 2H, $J=8.9$ Hz), 6.78 (d, 2H, $J=8.9$ Hz), 3.77 (s, 3H), 1.83 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.5, 155.8, 137.5, 135.1, 130.5, 127.47, 127.45, 121.8, 121.5, 113.9, 55.2, 54.4, 25.2. $C_{21}H_{16}Br_2O$ (446.16). Anal. Calcd: C 56.79, H 3.63. Found: C 56.61, H 3.45.

4.1.7. 2,7-Bis(trimethylsilylethynyl)fluoren-9-one (7). General procedure for the heterocoupling reaction. To a solution of 2,7-dibromofluoren-9-one (**1**) (750 mg, 2.2 mmol) and trimethylsilylacetylene (0.69 mL, 4.9 mmol) in freshly distilled triethylamine (50 mL), under argon atmosphere and 50 °C, was added dichloro bis(triphenylphosphine)palladium (78 mg, 0.11 mmol) and cuprous iodide (4.2 mg, 0.03 mmol). The mixture was stirred for 15 h and then, the amine was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution with a little amount of KCN, and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a brown solid, which was purified by silica gel column chromatography (hexane/dichloromethane, 2:1). Compound **7** was isolated as a pale-yellow solid, mp 165–168 °C (lit. 164–168 °C),[2] 645 mg (78%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 277 (ε, 17,400), 287 (ε, 26,100), 312 (ε, 3830), 326 (ε, 5950), 340 (ε, 6620). Fluorescence (CH_2Cl_2), λ_{max} (nm): 527 ($\phi=0.04$).

4.1.8. 2,7-Diethynylfluoren-9-one (8). General procedure. To a solution of 2,7-bis(trimethylsilylethynyl)fluoren-9-one (**7**) (480 mg, 1.28 mmol) in THF–MeOH (80 mL/40 mL), under argon atmosphere, was added potassium carbonate (709 mg, 5.13 mmol). The mixture was stirred at room temperature for 4 h and then, the solvent was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a residue, which was purified by silica gel column chromatography (hexane/dichloromethane, 2:1). Compound **8** was isolated as a pale-yellow solid, mp 237–239 °C (lit. 239–241 °C),[2] 290 mg (98%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 269 (ε, 134,800), 279 (ε, 242,300), 308 (ε, 24,100), 321 (ε, 31,200), 334 (ε, 21,800). Fluorescence (CH_2Cl_2), λ_{max} (nm): 523 (ϕ=0.03).

4.1.9. 9-(*p*-Methoxyphenyl)-9-methyl-2,7-bis(trimethylsilylethynyl)fluorene (9). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (16 mg, 0.02 mmol), Cu_2I_2 (0.4 mg, 0.002 mmol), compound **6** (50 mg, 0.11 mmol), trimethylsilylacetylene (24 mg, 0.24 mmol), and NEt_3 (30 mL) was stirred for 16 h at 50 °C. By silica gel flash column chromatography (hexane/dichloromethane, 2:1) was isolated **9** as a white solid, mp 195–196 °C, 50 mg (94%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 301 (ε, 35,400), 311 (ε, 56,800), 328 (ε, 50,800), 344 (ε, 83,000). Fluorescence (CH_2Cl_2), λ_{max} (nm): 351 and 363 (ϕ=0.79). IR (KBr, cm^{-1}): 2959, 2154, 1253, 1250, 1061, 893, 859, 760. ^1H NMR ($CDCl_3$): δ 7.66 (d, 2H, J=7.9 Hz), 7.47 (dd, 2H, J=7.9, 1.4 Hz), 7.31 (d, 2H, J=1.4 Hz), 7.04 (d, 2H, J=8.9 Hz), 6.77 (d, 2H, J=8.9 Hz), 3.76 (s, 3H), 1.82 (s, 3H), 0.24 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 158.3, 154.4, 139.2, 135.7, 131.4, 127.7, 127.6, 122.4, 120.1, 113.8, 105.6, 94.6, 55.2, 54.0, 25.1, −0.1. $C_{31}H_{34}OSi_2$ (478.77). Anal. Calcd: C 77.77, H 7.16. Found: C 77.95, H 7.02.

4.1.10. 2,7-Diethynyl-9-(*p*-methoxyphenyl)-9-methylfluorene (10). Following the general method used for the synthesis of **8**, a mixture of potassium carbonate (304 mg, 2.2 mmol), compound **9** (50 mg, 0.11 mmol), and THF–MeOH (16 mL/4 mL) was stirred at room temperature for 3 h. By silica gel flash column chromatography (hexane/dichloromethane, 2:1) was isolated **10** as a white solid, mp 183–184 °C, 37 mg (99%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 293 (ε, 42,700), 304 (ε, 61,500), 321s (ε, 34,200), 332 (ε, 58,100). Fluorescence (CH_2Cl_2), λ_{max} (nm): 355 (ϕ=0.52). IR (KBr, cm^{-1}): 2103, 2934, 2103, 1263, 894, 825. ^1H NMR ($CDCl_3$): δ 7.69 (d, 2H, J=7.9 Hz), 7.49 (d, 2H, J=7.9 Hz), 7.35 (s, 2H), 7.04 (d, 2H, J=8.9 Hz), 6.77 (d, 2H, J=8.9 Hz), 3.76 (s, 3H), 3.08 (s, 2H), 1.84 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 158.3, 154.4, 139.4, 135.5, 131.5, 127.9, 127.5, 121.5, 120.3, 113.8, 84.1, 77.6, 55.2, 54.0, 25.2. MS (70 eV): 334 (M^+, 75), 319 (100), 276 (20), 250 (6), 226 (9), 159 (15). $C_{25}H_{18}O$ (334.41). Anal. Calcd: C 89.79, H 5.43. Found: C 89.88, H 5.68.

4.1.11. 4-(*p*-Iodophenyl)-2-methyl-3-butyn-2-ol (11). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (21 mg, 0.03 mmol), Cu_2I_2 (0.6 mg, 0.003 mmol), 1,4-diiodobenzene (1 g, 3.03 mmol), 2-methyl-3-butyn-2-ol (255 mg, 3.03 mmol), and NEt_3 (100 mL) was stirred at room temperature for 12 h. By silica gel flash column chromatography (hexane/ethyl acetate, 4:1) was obtained **11** as a white solid, mp 89–90 °C, 676 mg (78%) yield.

^1H NMR ($CDCl_3$): δ 7.63 (d, 2H, J=8.1 Hz), 7.12 (d, 2H, J=8.1 Hz), 1.60 (s, 6H).

4.1.12. 4-[*p*-(Trimethylsilylethynyl)phenyl]-2-methyl-3-butyn-2-ol (12). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (400 mg, 0.73 mmol), Cu_2I_2 (14 mg, 0.073 mmol), compound **11** (2.1 g, 7.32 mmol), trimethylsilylacetylene (718 mg, 7.31 mmol), and NEt_3 (100 mL) was stirred at room temperature for 12 h. By silica gel column chromatography (hexane/dichloromethane, 2:1) was obtained **12** as a white solid, mp 108–109 °C, 1.8 g (98%) yield.

IR (KBr, cm^{-1}): 3286, 2157, 1497, 1250, 833, 759. ^1H NMR ($CDCl_3$): δ 7.40 (d, 2H, J=8.6 Hz), 7.33 (d, 2H, J=8.6 Hz), 1.6 (s, 6H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 131.7, 131.4, 122.8, 122.7, 104.5, 96.0, 95.6, 81.7, 65.5, 31.3, −0.1.

4.1.13. *p*-(Trimethylsilylethynyl)phenylacetylene (13). General procedure. To a solution of 4-[*p*-(trimethylsilylethynyl)phenyl]-2-methyl-3-butyn-2-ol (**12**) (204 mg, 0.8 mmol) in dry toluene (40 mL) was added finely powdered sodium hydroxide (3.2 mg, 0.08 mmol), under argon atmosphere, and the mixture was warmed at the reflux temperature for 2 h, and then filtered. The solvent was removed at reduced pressure and the solid residue was purified by silica gel column chromatography (hexane/dichloromethane, 1:1) giving **13** as a white solid, mp 52–53 °C, 158 mg (99%) yield.

IR (KBr, cm^{-1}): 3302, 2162, 1580, 1413, 1250, 760. ^1H NMR ($CDCl_3$): δ 7.45 (s, 4H), 3.20 (s, 1H), 0.30 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 131.8, 131.7, 123.5, 122.1, 104.3, 96.4, 83.1, 78.9, −0.1. $C_{13}H_{14}Si$ (189.34). Anal. Calcd: C 78.72, H 7.11. Found: C 78.86, H 7.04.

4.1.14. 2,7-Di[(*p*-trimethylsilylethynylphenyl)ethynyl]-fluoren-9-one (14). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), Cu_2I_2 (1 mg, 0.005 mmol), compound **3** (100 mg, 0.25 mmol), compound **13** (99 mg, 0.5 mmol), and NEt_3 (30 mL) was stirred for 12 h at 50 °C. By silica gel flash column chromatography (hexane/dichloromethane, 5:1), was obtained **14** as an orange solid, mp > 300 °C, 104 mg (73%) yield.

IR (KBr, cm^{-1}): 3012, 2157, 1592, 1473, 1254, 759. UV–vis (CH_2Cl_2), λ_{max} (nm): 310 (ε, 11,200), 358 (ε, 15,800). Fluorescence (CH_2Cl_2), λ_{max} (nm): 531 (ϕ=0.03). ^1H NMR ($CDCl_3$): δ 7.80 (dd, 2H, J=6.2, 1.6 Hz), 7.64 (dd, 2H, J=6.2, 1.6 Hz), 7.53 (m, 8H), 7.35 (d, 2H, J=6.2 Hz), 0.26 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 189.7, 141.2, 135.4, 132.5, 132.0, 131.1, 127.5, 123.5, 122.3, 121.8, 120.7, 103.8, 97.4, 85.1, 78.3, −0.1. $C_{39}H_{32}OSi_2$ (572.84). Anal. Calcd: C 81.77, H 5.63. Found: C 81.50, H 5.85.

4.1.15. 4-[*p*-(*p*-{Trimethylsilylethynyl}phenylethynyl)-phenyl]-2-methyl-3-butyn-2-ol (15). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), Cu_2I_2 (1.2 mg, 0.005 mmol), compound **11** (143 mg, 0.5 mmol), compound **13** (100 mg, 0.5 mmol), and NEt_3 (100 mL) was stirred at room temperature for 12 h. By silica gel flash column chromatography (hexane/ethyl acetate, 3:1) gives **15** as a white solid, mp > 300 °C, 176 mg (99%) yield.

IR (KBr, cm^{-1}): 3355, 2154, 1576, 1511, 1250, 1161, 840, 758. ^1H NMR ($CDCl_3$): δ 7.56–7.37 (m, 8H), 1.64 (s, 6H), 0.28 (s, 9H).

4.1.16. 4-[*p*-(Trimethylsilylethynyl)phenylethynyl]-phenylacetylene (16). Following the general method used for the synthesis of **13**, a mixture of compound **15** (100 mg, 0.28 mmol), dry toluene (25 mL), and finely powdered sodium hydroxide (1.1 mg, 0.03 mmol) was stirred for 5 h and then filtered. The residual solid was purified by silica gel column chromatography (hexane/dichloromethane, 1:1) giving **16** as a white solid, mp 72–75 °C, 82 mg (98%) yield.

IR (KBr, cm^{-1}): 2148, 1582, 1521, 1246, 836, 752. ^1H NMR ($CDCl_3$): δ 7.48 (s, 8H), 3.18 (s, 1H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.5, 133.4, 131.9, 131.6, 123.4, 122.9, 122.6, 104.8, 96.8, 94.2, 89.3, 88.9, 85.8, 79.0, −0.1. MS (70 eV): 298 (M^+, 100), 297 (20), 224 (15), 125 (8). $C_{21}H_{18}Si$ (298.12). Anal. Calcd: C 84.51, H 6.08. Found: C 84.79, H 6.21.

4.1.17. 2,7-Di[*p*-(*p*-{trimethylsilylethynyl}phenyl-ethynyl)phenylethynyl]fluoren-9-one (17). Following the general method used for the synthesis of **7**, a mixture of $Cl_2Pd(PPh_3)_2$ (35 mg, 0.05 mmol), Cu_2I_2 (1 mg, 0.005 mmol), compound **3** (100 mg, 0.25 mmol), compound **16** (149 mg, 0.5 mmol), and NEt_3 (30 mL) was stirred for 48 h at 50 °C. By silica gel flash column chromatography (hexane) was obtained **14** as an orange solid, mp > 300 °C, 158 mg (82%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 260 (ε, 7600), 323 (ε, 16,800); 374 (ε, 25,900). Fluorescence (CH_2Cl_2), λ_{max} (nm): 531 ($\phi = 0.03$). IR (KBr, cm^{-1}): 2178, 1597, 1531, 1256, 830, 748. ^1H NMR ($CDCl_3$): δ 7.67 (s, 6H), 7.44 (s, 8H), 7.23 (s, 8H), 0.27 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 143.9, 137.5, 136.9, 134.5, 133.0, 131.9, 131.3, 127.3, 124.7, 123.4, 122.8, 122.4, 122.2, 104.5, 96.4, 94.4, 90.3, 90.2, 86.5, 78.3, −0.2. MS (70 eV): 773 (M^+, 100). $C_{55}H_{40}OSi_2$ (773.08). Anal. Calcd: C 85.45, H 5.22. Found: C 85.27, H 5.45.

4.1.18. 2-Acetyl-7-ethynylfluoren-9-one (18). To a solution of the compound **8** (80 mg, 0.35 mmol) and *p*-toluensulfonic acid (181 mg, 1.01 mmol) in CCl_4 (20 mL), under argon atmosphere, was added H_2O (1 mL). The mixture was warmed at the reflux temperature for 24 h and then, the solvent was removed under reduced pressure. The crude residue was washed with a saturated aqueous ammonium chloride solution, and extracted with dichloromethane. The extracts were dried on anhydrous sodium sulfate and after filtration; the solvent was removed to give a solid residue, which was purified by silica gel column chromatography (hexane/dichloromethane, 1:3). Compound **18** was isolated as a pale-yellow solid, mp 228–230 °C, 77 mg (88%) yield.

UV–vis (CH_2Cl_2), λ_{max} (nm): 281 (ε, 62,100), 308 (ε, 8700), 324 (ε, 9700), 337 (ε, 6600). Fluorescence (CH_2Cl_2), λ_{max} (nm): 502 ($\phi = 0.096$). IR (KBr, cm^{-1}): 3247, 2159, 1715, 1682, 1661, 882, 838, 804. ^1H NMR ($CDCl_3$): δ 8.21 (d, 2H, $J = 1.7$ Hz), 8.16 (d, 2H, $J = 7.0$ Hz), 7.81 (s, 1H), 7.68 (dd, 2H, $J = 7.0$, 1.7 Hz), 7.64 (d, 2H, $J = 7.0$ Hz), 7.58 (d, 2H, $J = 7.0$ Hz), 3.22 (s, 1H), 2.64 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 196.4, 191.7, 147.7, 143.0, 138.5, 138.1, 135.1, 134.9, 134.5, 128.1, 124.3, 124.2, 121.2, 120.8, 82.4, 79.6, 29.7. MS (70 eV): 246 (M^+, 75), 231 (100), 203 (31), 175 (52), 149 (12). $C_{17}H_{10}O_2$ (246.26). Anal. Calcd: C 82.91, H 4.09. Found: C 83.10, H 4.35.

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