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Synthesis and photoluminescent properties of some novel fluorene derivatives

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Abstract

Two novel fluorene compounds 9,9-bis[4′-(9″-carbazovinylene)-phenyl]fluorene (F-CZV) **4** and 9,9-bis{4′-[2″-phenyl-5″-(3‴-(methacrylamido)phenyl)]-1″,3″,4″-oxadiazolylphenyl}fluorene (F-MAOP) **6** were synthesized by the Heck reaction. The structures were characterized by MS, ^{1}H NMR, IR and UV–vis spectroscopy and the photoluminescent (PL) properties were investigated in ethyl acetate by UV–vis absorption and emission spectra. The spectroscopic properties of the two dyes were also analyzed in other solvents. By comparison with 9,9-bis(4′-iodophenyl)fluorene, the absorption and emission spectra of the two dyes showed a shift to higher wavelengths and displayed high fluorescence quantum yields (0.7–0.8), which can make these dyes very useful as new fluorescent probes.

Keywords: 2-Phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole; 9,9-Bis(4′-aminophenyl)fluorene; *N*-vinylcarbazole; Symmetrical dye

1. Introduction

In recent years, there has been considerable scientific interest in exploring organic materials for photoluminescent applications because their handling and color turning are easier than that of inorganic semiconductors [1]. Organic light emitting diodes (LEDs) have intrigued many researchers owing to their potential for application in display devices [2,3].

It is well known that to achieve good performance in LEDs, the injection of electrons and transport of holes should be balanced. The electron-withdrawing 1,3,4-oxadiazole unit is believed to have high electron affinity and should facilitate electron injection. Several organic molecules containing an oxadiazole unit, such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), have been used successfully as electron-injection materials to improve the balance of charge injection and to increase the photon/electron quantum efficiency [4–6]. *N*-vinylcarbazole is a prototypical hole transporting molecule with strong absorption in the ultraviolet spectral region together with blue-light emission as well [7–11].

In this paper, two novel fluorene derivatives that had electron-injection moieties, a 1,3,4-oxadiazole unit, and hole transport moieties, an *N*-vinylcarbazole unit, were synthesized and characterized. Their photophysical properties were also investigated.

2. Experimental

2.1. Materials and instruments

Reagent grade solvents were dried over a 4A molecular sieve and further distilled before use. Other chemicals were also of reagent grade and were used without further purification. The synthetic routes used are shown in Scheme 1.

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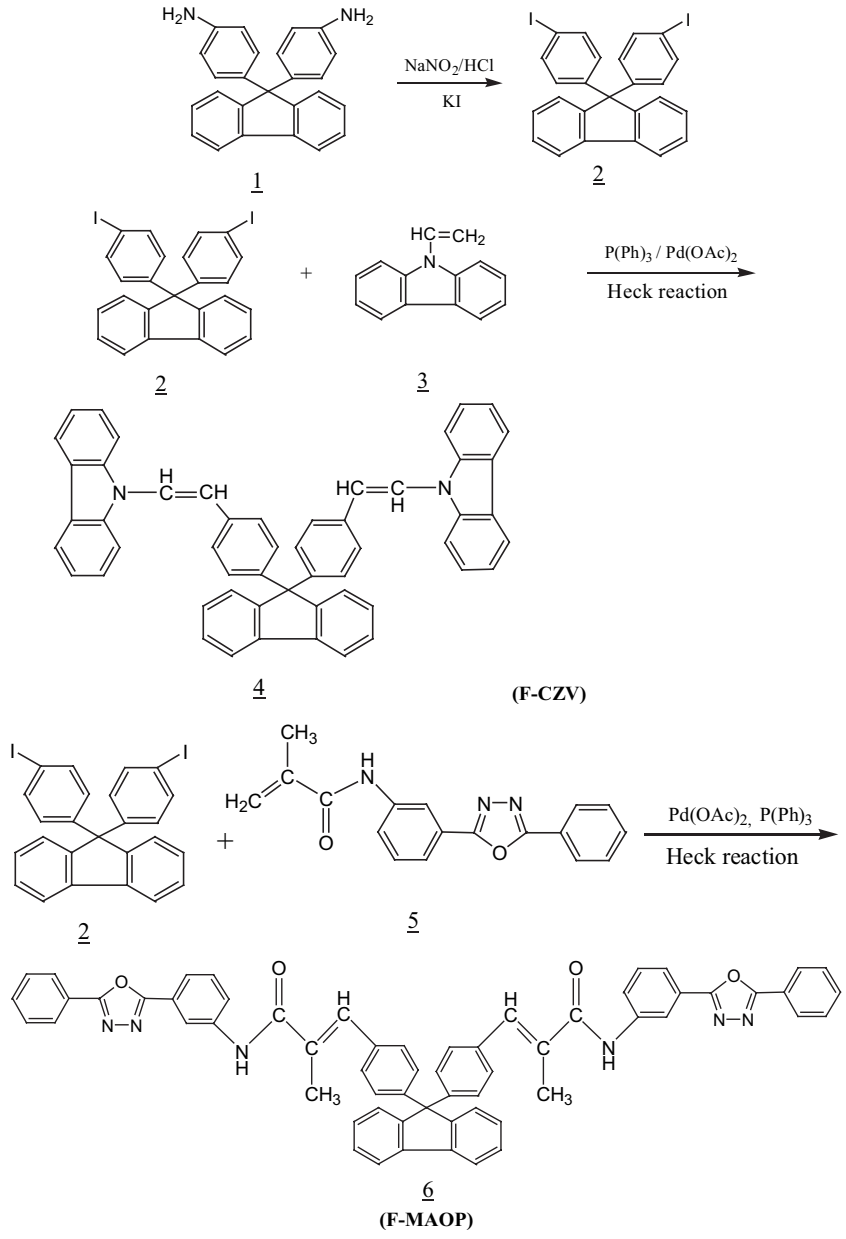

Scheme 1. The chemical structures of the dyes in the study.

Melting points were determined on a Sanyo Gallenkamp MPD350 melting point apparatus. All melting points were uncorrected. The IR spectra were determined on an IR-408 infrared spectrometer by dispersing samples in KBr disks. ^{1}H NMR spectra were measured on a R-24B Hitachi NMR spectrometer with DMSO as solvent. Mass spectrum data were obtained on a JEOL GC–MS D300 UV–vis spectrophotometer and fluorescence spectra were obtained on a Shimadzu UV 1601 SCM 3632 spectrophotometer and Perkin–Elmer LS-50B, luminescence spectrometer with a xenon lamp as the light source. Both excitation and emission bands were set at 10 nm. All the experiments were carried out at 25 ± 1 °C.

2.2. Synthesis of the compounds

2.2.1. 9,9-Bis(4′-iodophenyl)fluorene **2** [12]

9,9-Bis(4′-aminophenyl)fluorene (0.7 g/2.0 mmol) and concentrated hydrochloric acid (5 ml/0.06 mol) were refluxed for 2 h and then cooled to room temperature. This was added to a mixture of phosphoric acid (7 ml/0.11 mol), sodium nitrite (0.274 g/4.0 mol) and concentrated sulfuric acid (3 ml/0.054 mol) and stirred at −5 °C for 0.5 h. It was then poured into a solution of urea (0.3 g/5.0 mmol) and potassium iodide (0.664 g/4.0 mmol) in water (50 ml), and the reaction system was heated with stirring to 80 °C. A precipitate was formed by adding 40 ml water and this

was then dissolved in ethanol. After the insolubles were filtered off, the remaining liquid was poured into water, giving a white solid. The pure product, 9,9-bis(4′-iodophenyl) fluorene **2**, was produced in 81.5% yield by recrystallization from anhydrous ethanol. m.p.: 183–184 °C; MS (EI, *m*/*z*): 570 (M^+); ^{1}H NMR (DMSO, ppm) *δ*: 7.72–7.35 (16H, aromatic); IR (KBr, cm^{-1}): 1601, 1575, 1483, 1446 (⌔), 802 (-⌔-), 484 (C–I).

2.2.2. 9,9-Bis[4′-(9″-carbazovinylene)phenyl]fluorene (F-CZV) 4 [13,14]

A mixture of anhydrous palladium acetate (0.0112 g/0.05 mmol), 9,9-bis(4′-iodophenyl)fluorene (1.45 g/2.5 mmol), sodium acetate (0.4 g/5 mmol) and *N*-vinylcarbazole (1.05 g/5 mmol) was dissolved in 300 ml anhydrous DMF and stirred at 140 °C under a nitrogen atmosphere for 48 h. After addition of water to the reaction mixture, the precipitate was collected by filtration. The gray-white solid obtained was dissolved in ethanol, and poured into 300 ml distilled water. The solid product produced was isolated by filtration and purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:15) as the eluant to give slightly white crystals of F-CZV **4** in 16.4% yield. m.p.: 194–195 °C; MS (EI, *m*/*z*): 700 (M^+), 508 ($M-C_{14}H_{10}N$); ^{1}H NMR (DMSO, ppm) *δ*: 7.55–7.35 (32H, aromatic), 7.16 (4H, –CH=CH–); IR (KBr, cm^{-1}): 1600, 1558, 1506,1450 (⌔), 1326 (C–N).

2.2.3. 9,9-Bis{4′-[2″-phenyl-5″-(3‴-(methacrylamido)phenyl)]-1″,3″,4″-oxadiazolylphenyl}fluorene (F-MAOP) 6 [15]

A mixture of anhydrous palladium acetate (0.0112 g/0.05 mmol), 9,9-bis(4′-iodophenyl)fluorene (1.45 g/2.5 mmol), dry triethylamine (6 ml/0.043 mol) and 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole (1.525 g/5 mmol) was dissolved in DMF (30 ml) and stirred at 140 °C under nitrogen atmosphere for 56 h. The product was purified by column chromatography on silica gel with ethyl acetate:petroleum ether (1:10) to give yellow crystals of F-MAOP **6** in 14.3% yield. m.p.: 155–156 °C; MS (EI, *m*/*z*): 924 (M^+), 894 ($M-2CH_3$); ^{1}H NMR (DMSO, ppm) *δ*: 8.84 (2H, –NH–), 7.84–7.42 (26H, aromatic), 7.21 (2H, –CH=CH–), 2.12 (6H, $-CH_3$); IR (KBr, cm^{-1}): 3421 (N–H), 1683 (C=O), 1600, 1527, 1496, 1436 (⌔), 1403 ($-CH_3$).

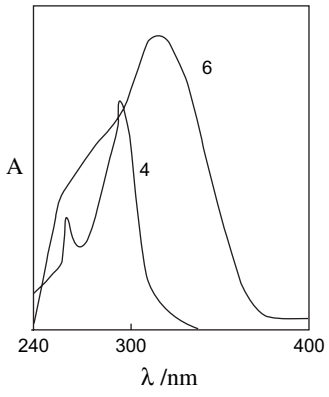

Fig. 1. Absorption spectra of compounds **4** and **6** in ethyl acetate. Concentration of **4**, 1.5×10^{-7} mg/ml. Concentration of **6**, 2.1×10^{-6} mg/ml.

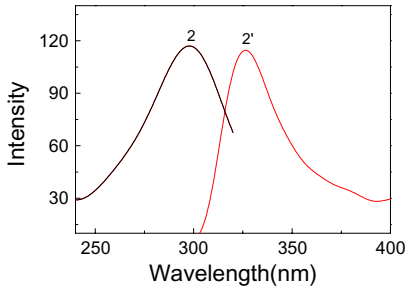

Fig. 2. Excitation and emission fluorescence spectra of compound **2** in ethyl acetate. Concentration of **2**, 2.5×10^{-5} mg/ml.

3. Results and discussion

3.1. The details of synthesis

9,9-Bis(4′-iodophenyl)fluorene **2** could be obtained via the diazotization reaction by employing the $NaNO_3$/H_2SO_4/KI, F-CZV **4** and F-MAOP **6** were prepared by Heck reaction of 9,9-bis(4′-iodophenyl)fluorene **2** with *N*-vinylcarbazole **3** and 2-phenyl-5-[3′-(methacrylamido)phenyl]-1,3,4-oxadiazole **5**, respectively. Although this is a well-established method for C–C bond formation, the contents of catalyst and reaction temperature have a significant influence on the Heck reaction. It has been found by our experiment that the appropriate ratio of $Pd(OAc)_2$ to $P(Ph)_3$ was 1:4 (mole) and the reaction temperature was 140 °C.

3.2. Absorption and fluorescence emission spectrum

The UV–vis absorption spectra of **4** and **6** in ethyl acetate are shown in Fig. 1. It can be seen from Fig. 1 that the maximum absorptions of **4** and **6** are at 290 nm and 305 nm, respectively. The excitation and emission spectra of **2**, **4** and **6** are shown in Fig. 2, Fig. 3 and Fig. 4, respectively. By comparison with compound **2**,

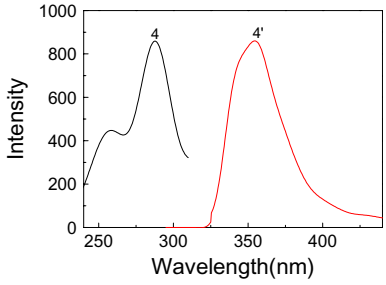

Fig. 3. Excitation and emission fluorescence spectra of compound **4** in ethyl acetate. Concentration of **4**, 5.5×10^{-8} mg/ml.

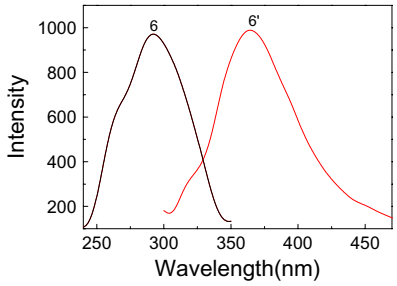

Fig. 4. Excitation and emission fluorescence spectra of compound **6** in ethyl acetate. Concentration of **6**, 7.2×10^{-7} mg/ml.

the emission spectra of **4** and **6** show a red-shift and the excitation spectra a blue-shift. These phenomena can be attributed to the greater π system conjugation length in **4** and **6** than that in **2**.

3.3. Quantum yield of photoluminescence

The fluorescence quantum yield was measured by a relative method using quinine sulfate as the standard (0.546 in 0.5 mol l^{-1} H_2SO_4) [16]. The quantum yield was calculated from the following equation:

$$\Phi_s = \Phi_r \frac{F_s}{F_r} \frac{A_r}{A_s} \left(\frac{n_r}{n_s}\right)^2.$$

In the above expression, Φ_s is the fluorescent quantum yield, F is the integration of the emission intensities, n is the index of refraction of the solution, and A is the absorbance of the solution at the exciting wavelength. The subscripts r and s denote the reference and unknown samples, respectively. The values of quantum yield of compounds **4** and **6** are 82% and 73%, respectively.

3.4. Solvent effect on photoluminescence

For a deeper understanding of the photoluminescence (PL) properties of **4** and **6**, the solvent effects on photoluminescence of the compounds were investigated. Compounds **4** and **6** have good solubility in common organic solvents, such as cyclohexane, dichloromethane, THF, ethyl acetate, ethanol, acetonitrile, methanol, etc. The fluorescence spectra of **4** and **6** were investigated in different solvents and all results are listed in Table 1. It can be seen from Table 1 that the emission spectra of **4** show a slight red-shift, but the emission spectra of **6** show a blue-shift as solvent polarity increases.

Table 1
The solvent effect of **4** and **6** (20 °C)

F-CZV **4**					
Solvent	C_6H_6	$CH_3COOC_2H_5$	CH_3CN	CH_3CH_2OH	CH_3OH
λ_{max}^{em} (nm)	235	356	357	358	359
F-MAOP **6**					
Solvent	THF	$CH_3COOC_2H_5$	CH_2Cl_2	CH_3CH_2OH	CH_3OH
λ_{max}^{em} (nm)	379	366	365	363	361

The red-shift of emission spectra of **4** with increase of solvent polarity can be due to dipole–dipole interaction of the excited state [17]. The blue-shift of emission spectra of **6** with increase of solvent polarity may be due to its different molecular structure containing the withdrawing electron group, 1,3,4-oxadiazole (OXD) unit. Further research toward a better understanding of this effect is currently in progress.

4. Conclusions

In summary, two new fluorene derivatives containing a hole-transfer moiety (*N*-vinylcarbazole) and an electron-injection moiety (oxadiazole), F-CZV **4** and F-MAOP **6**, respectively, were synthesized by the Heck reaction. The resulting compounds have excellent solubility in common organic solvents. The emission peaks of F-CZV **4** and F-MAOP **6** in ethyl acetate are at about 356 nm and 366 nm, respectively. They display high photoluminescence quantum yields (0.7–0.8) and are potential candidates as hole-transfer and electron-injection materials for organic photoluminescent devices.

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