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Synthesis and photophysical processes of an anthracene derivative containing hole transfer groups

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ABSTRACT

A novel luminescent compound 9,10-di-(N-carbazovinylene)anthracene (DCVA) was synthesized by Heck reaction of 9,10-dibromoanthracene and N-vinylcarbazole. The structure was characterized by MS, ¹H NMR and Elemental analysis. The photoluminescent properties of DCVA have been carefully investigated by UV-vis absorption and fluorescence emission spectra. The results showed that the luminescent quantum yield of DCVA was 0.73 in THF and it emitted blue-light with the band gap of 3.60 eV estimated from the onset absorption. In addition, the light-emission of DCVA can be quenched by electron acceptor (dimethyl terephthalate), however, the fluorescent intensities of DCVA were slowly increased with the addition of electron donor (N,N-dimethylaniline). Furthermore, the molecular interactions of DCVA with fullerene (C_{60}) and carbon nanotubes (CNTs) were also investigated, which indicated the organic luminescent compound can be used as new fluorescent probe.

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1. Introduction

Organic light emitting diodes (OLEDs) have intrigued many researchers owing to their handing color turning and potential for application in display devices than inorganic semiconductors [1-3]. To date, although a great number of luminescent compounds which can be used for the OLEDs have been synthesized and investigated, the search for new compounds that possess the combined desirable properties, such as high brightness and luminescent efficiency, good film-forming properties, remains a big challenge in this area [4,5]. It is still urgent to design and synthesis luminescent organic compounds with high photoluminescence efficiency, excellent charge transport ability and film-forming property [6–8].

Anthracene has a blue emission and high fluorescence quantum yield and has been wildly applied as a photoluminescent compound in the fields of diode and battery [9]. Carbazole is not only an excellent hole-transfer molecule but also a blue-emission material with high luminescent efficiency. Introduced carbazole group to the compound consisting anthracene can give a well luminescent moiety which can contribute to the luminescent material [10,11].

Herein, our job combined anthracene and carbazole in one molecular and synthesis the following compound, DCVA, with blue emission and high fluorescence quantum yield unit and holetransfer unit. The optical properties were investigated by UV-vis absorption and fluorescence emission spectra. Additionally, the interactions of DCVA with electron donor or electron acceptor have been carefully studied. Moreover, the molecular interactions of DCVA with excellent semiconductor materials such as fullerene (C_{60}) and carbon nanotubes (CNTs) were also carefully investigated. The results showed that the photo-functional molecule DCVA was blue-light emission material for organic light emitting diodes.

2. Experimental

2.1. Materials and measurements

All the solvents were of analytic grade. Melting point was determined on a Sanyo Gallenkamp MPD350 melting point apparatus and melting point was uncorrected. ¹H NMR was measured on a Bruker ARX300 spectrometer with chemical shifts reported as ppm (in DMSO, TMS as an internal standard). Mass spectra were measured on a JEOL GC-MS D300 spectrometer. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). Absorption and fluorescence spectra were recorded on a Varian Cary 300 absorption spectrophotometer and a Hitachi F-4500 fluorescence spectrophotometer. Both excitation and emission bands were set at 10 nm. All the experiments were carried out at room temperature. The synthetic routes used are shown in Scheme 1.

2.2. Synthesis

2.2.1. Synthesis of 9,10-dibromoanthracene

9,10-Dibromoanthracene was synthesized according to the method previously reported [12].

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Scheme 1. The synthetic route of DCVA.

2.2.2. Synthesis of 9,10-di-(N-carbazovinylene)anthracene (DCVA)

The solution of $Pd(OAc)_2$ 0.056 g (0.25 mmol) and PPh_3 0.262 g (1.0 mmol) as catalyst in 20 mL [BMIM]BF₄ was stirred at 80 °C for 30 min under nitrogen atmosphere and then cooled to room temperature. A mixture of 9,10-dibromoanthracene 0.84 g (2.5 mmol), N-vinylcarbazole 1.05 g (5 mmol), and anhydrous sodium carbonate 0.4 g (5 mmol) was added. After stirred at 110 °C for 24 h, the mixture solution was extracted by 50 mL ether for 5 times. The organic solution was washed with water saturated solution of NaCl and dried over MgSO₄. Removal of the solvent in vacuo to give a yellow solid and purified by column chromatography on silica gel with petroleum ether: ethyl acetate (4:1) as the elutant to give slightly yellow crystals of 9,10-di-(N-carbazovinylene)anthracene (DCVA) in 58.8% yield, m.p. 167–168 °C. ¹H NMR(*d*-DMSO, ppm) δ : 7.26-8.10 (m, 28H); MS (EI, m/z): 560 (M⁺), 368 (C₁₄H₁₆N); Elemental analysis: Calcd (%) for C₄₂H₂₈N₂ (560.69) C, 89.97; H, 5.03. Found: C, 89.12; H, 4.86.

3. Results and discussion

3.1. The synthesis of DCVA

The luminescent compound DCVA was synthesized by Heck reaction of 9,10-dibromoanthracene and N-vinylcarbazole. Although this is a well-established method for C–C bond formation, but the contents of catalyst, reaction temperature and reaction medium have a significant influence on the Heck reaction. It has been found by experiment that the appropriate ratio of $Pd(OAc)_2$ to PPh₃ is 1:4 (mol), which can successfully form the reactive catalyst. The suitable reaction temperature is 110-120 °C. Noticeably, the reaction yield is more two times in [BMIM]BF₄ than in common solvents such as DMF, DMSO, etc.

3.2. UV-vis absorption and fluorescence emission spectrum

Fig. 1 shows the UV–Vis absorption spectra of DCVA in dilute THF solution. The maximum UV–Vis absorption peak of DCVA was 275 nm with shoulder peak 240 nm, which was similar with the absorption spectra of N-vinylcarbazole and it should mainly come from N-vinylcarbazole unit absorption. Meantime, the fluorescence emission peak of DCVA was 433 nm with shoulder peak 410 nm that also rooted in the emission peak of N-vinylcarbazole. Based on the fluorescent emission wavelength, the DCVA was a potential blue emission material compound.

3.3. Quantum yield of photoluminescence and the band gap

The photoluminescent quantum yield of DCVA was measured by relative method using the quinine sulfate as the standard (0.546 in 0.5 mol/L H₂SO₄) [13]. The quantum yield was calculated from the following equation:

$$\Phi_{\rm S} = \Phi_r \frac{F_{\rm S}}{F_r} \frac{A_r}{A_s} \left(\frac{n_r}{n_s}\right)^2$$

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 value of quantum yield of DCVA in THF was 0.73. The band gap (E_g^{opt}) of the complex can be estimated from the onset absorption (UV_{onset}) with E_g^{opt} $(eV) = hc/\lambda$ $(h = 6.626 \times 10^{-34}$ Js, $c = 3 \times 10^{17}$ nm/s, $1 \text{ eV} = 1.602 \times 10^{-19}$ J). The band gap of DCVA was 3.60 eV.

3.4. The interactions of DCVA with dimethyl terephthalate (DMTP) and N,N-dimethylaniline (DMA)

The fluorescence quenching technique was a helpful method for the study of the mechanism of molecular interaction, energy transfer or charge transfer. Dimethyl terephthalate (DMTP) was a typical electron acceptor and N,N-dimethylaniline (DMA) was a typical electron donor. As seen in Fig. 2, when DMTP was added to a solution of DCVA in THF, the fluorescence of DCVA was efficiently



Fig. 1. UV-vis absorption and fluorescence emission spectra of DCVA $(1.68\times 10^{-5}\,M)$ in THF.



Fig. 2. Fluorescence spectra of DCVA at different concentrations of DMTP. Concentration of DCVA, 1.50×10^{-5} M; concentration of DMTP (mol/L, M): 0, 0.00; 1, 7.14×10^{-7} ; 2, 2.13×10^{-6} ; 3, 4.96×10^{-6} ; 4, 8.97×10^{-6} ; 5, 2.65×10^{-5} ; 6, 8.16×10^{-5} ; 7, 1.27×10^{-4} .

quenched and the quenching process followed the Stern-Volmer equation: $F_0/F = 1 + K_{sv}[Q]$, where F_0 is the initial unquenched fluorescence, F is the fluorescence in the presence of quencher, K_{sv} is the static quenching coefficient, and [Q] is the quencher concentration (as shown in Fig. 2). The apparent quenching coefficient, K_{sv} , was $1.13\times 104\,M^{-1}$ (as shown in Fig. 3). The quenching process of DCVA with DMA was also examined and shown in Fig. 4. It can be seen that the fluorescence emission intensity of DCVA was increased with gradual adding of DMA in THF, which was obviously different phenomenon with DMTP adding to DCVA solution. From the experimental facts and references, an explanation is possible reasonable: N,N-dimethylaniline (DMA) is a rich electron group, while carbazole group is an hole transfer body, so the strong interaction between DMA and carbazole happens when DMA is gradually added into the solution of DCVA. The DMA molecule is associated by carbazole unit and the charge of DMA may then be transferred to DCVA, which would lead to increasing of fluorescence intensity of DCVA that are released from the actions of intramolecular or intermolecular carbazole units.

3.5. Interaction between DCVA and fullerene (C_{60})



Many researches show C_{60} bears many unusual electrochemical and electronic properties. One of the most remarkable properties of

Fig. 3. Dependence of F_0/F on the concentration of DMTP. [DCVA]: 1.50×10^{-5} M; F_0 is fluorescent intensity of DCVA without DMTP and *F* is fluorescent intensity of DCVA in the present with different concentrations of DMTP.



Fig.4. Fluorescence spectra of DCVA at different concentrations of DMA. Concentration of DCVA, 1.80×10^{-5} M; concentration of DMA(mol/L, M), 0, 0.00; $1, 5.12 \times 10^{-6}$; $2, 1.58 \times 10^{-6}$; $3, 9.24 \times 10^{-6}$; $4, 1.22 \times 10^{-5}$.

C₆₀ related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination [14]. In the experiment, the interactions of DCVA with C₆₀ were examined. The results were shown in Fig. 5. As we have seen in Fig. 5, '0' was DCVA in concentration $(1.68 \times 10^{-5} \text{ M})$ without C_{60} , '1–7' were DCVA in the present with different concentrations of C₆₀. With the gradual increasing of concentration of C₆₀, the fluorescence of DCVA was quenched efficiently and the process was also following the Stern-Volmer equation (Fig. 6). The apparent quenching constant was $1.85 \times 10^4 \, \text{M}^{-1}$, which suggests that the strong interactions between DCVA and C₆₀ happen in the excited state. This can be explained by two reasons. Firstly, both DCVA and C_{60} have a large π -conjugated system in which π - π interaction may change the configuration of DCVA [15]. Secondly, the photo-induced charge transfer from excited DCVA to C_{60} was rapid. Upon this charge transfer the conjugated system may be dramatically modified and distorted because of the strong electron-lattice interaction in the one-dimensional system [16].

3.6. Interaction between DCVA and carbon nanotubes (CNTs)

The investigation on the interaction between DCVA and carbon nanotubes (CNTs) was helpful to understand the optical property of DCVA and apply it to LEDs. The interaction between them in diluted solutions was examined by fluorescence spectrophotome-



Fig. 5. Fluorescence spectra of DCVA at different concentrations of C₆₀. Concentration of DCVA, 1.68×10^{-5} M; concentration of C₆₀ (mol/L, M), 0, 0.00; 1, 2.36×10^{-6} ; 2, 1.31×10^{-5} ; 3, 2.85×10^{-5} ; 4, 3.44×10^{-5} ; 5, 6.21×10^{-5} ; 6, 1.42×10^{-4} ; 7, 2.16×10^{-4} .



Fig. 6. Dependence of F_0/F on the concentration of C_{60} . [DCVA]: 1.50×10^{-5} M; F_0 is fluorescent intensity of DCVA without C_{60} and F is fluorescent intensity of DCVA in the present with different concentrations of C_{60} .



Fig. 7. Fluorescent spectra of DCVA at different concentrations of CNTs. Concentration of DCVA, 1.75×10^{-5} M; concentration of CNTs (mg mL^-1), 0, 0.00; 1, 5.36×10^{-6} ; 2, 8.21×10^{-6} ; 3, 9.67×10^{-6} ; 4, 3.08×10^{-5} ; 5, 7.23×10^{-5} ; 6, 3.87×10^{-4} ; 7, 9.33×10^{-4} .

ter and the result indicated that the fluorescence of DCVA can also be quenched by carbon nanotubes (Fig. 7). It can be seen that the emission peak intensities of DCVA were decreased with gradually increasing in concentration of CNTs in THF. The phenomenon indicated that the intense interaction of DCVA and CNTs in excited state was happened [17]. Due to the different space structures and optical properties of CNTs and C_{60} , the quenching interaction of C_{60} to DCVA was stronger than CNTs in dilute solution. Further research toward a better understanding of this action is currently in progress.

4. Conclusions

A novel luminescent compound DCVA containing anthracene blue-emitting photoluminescent group and carbazole hole transport group was designed and synthesized. The optical research showed the absorption had two absorptions peaks (275 nm, 240 nm) and the emission was located at 433 nm and 410 nm in THF. The luminescence quantum yield was 0.73 in THF. The lightemitting can be quenched by electron acceptor and the quenched processes followed the Stern–Volmer equation. The molecular interactions of DCVA with fullerene (C₆₀) and carbon nanotubes both happened in the excited state. It can be anticipated that DCVA will have a potential application as an emitting blue-light material.

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