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Light-emitting conjugated molecule containing 1,3,4-oxadiazole, carbazole and naphthalene units

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Abstract

A novel π -conjugated small molecule VNCO, 2,5-bis{3'-[3"-vinyl-9"-(α -naphthyl)carbazolyl]phenyl}-1,3,4-oxadiazole, containing holetransporting carbazole moieties, electron-injecting 1,3,4-oxadiazole moieties and chromophore naphthalene was designed and synthesized by Wittig reaction of 2,5-bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole and 3-formyl-9-(α -naphthyl)carbazole. The UV–vis absorption, fluorescence excitation and emission spectra have been obtained in solution for VNCO. The photoluminescence (PL) of VNCO were examined in different solvents and the luminescence quantum yield was 0.746 in chloroform. It emitted blue and blue–green light, with the band gap of 3.30 eV estimated from the onset absorption. In addition, the light-emitting can be quenched by both electron donor (*N*,*N*-dimethylaniline) and electron acceptor (dimethylterephalate). Furthermore, the molecular interactions of VNCO with fullerene (C₆₀) or carbon nanotubes (CNTs) were also carefully investigated.

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Keywords: Light-emitting; Wittig reaction; Fullerene (C₆₀); Carbon nanotubes (CNTs)

1. Introduction

Organic semiconducting materials including polymers, oligomers, and small molecules are a subject of high interest as potential active materials in optoelectronic devices [1]. These materials are characterized by a low driving voltage, uniform luminance, the manifestation of various colors, the ability to easily form patterns and nanoscale films, and the capacity for mass production [2,3]. Since the found of polymer light-emitting diodes (PLEDs) based on poly (pphenylenevinylene) (PPV) by the Cambridge group, many researchers have made some efforts to develop light-emitting (LE) molecules that exhibit both high LE efficiency and high stability, properties that are directly related to the performance and reliability of LED [4,5]. Low LE efficiency in LEDs is attributed mainly to an imbalance in the transportation rates of the electrons and holes in LE layer [6-9]. To overcome the problem of low LE efficiency, it is desired for combining the electron-injecting group, hole-transporting group and chromophore in the same molecule.

Many researches show that carbazole and its derivatives are good hole-transport materials and have been used in construction of light-emitting device (LEDs) [10,11]; several 1,3,4-oxadiazole (OXD) derivatives, such as 2-(4'-biphenylyl)-5-(4'-tert-butylphenyl)-1,3,4-oxadi-azole (PBD) have been actually used as electron-injection materials to improve the balance of charge carrier and to increase the photon/electron quantum efficiency [12-15]. In this study, we designed and synthesized π -conjugated small molecule VNCO bearing hole-transporting carbazole moieties, electroninjecting 1,3,4-oxadiazole moieties and chromophore naphthalene. The synthesis was carried out by Wittig reaction of 2,5-bis(3-tolylene-triphenylphosphonium bromide)-1,3,4oxadiazole and 3-formyl-9-(α -naphthyl)carbazole. The absorption, fluorescence excitation and emission spectra have been obtained in solution for VNCO. The photoluminescence (PL) of VNCO were examined in different solvents. The quenching processes of VNCO with electron donor N,N-dimethylaniline (DMA), and electron acceptor, dimethylterephthalate (DMTP) were studied. Moreover, the

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molecular interactions of VNCO with fullerene (C_{60}) or carbon nanotubes (CNTs) were also investigated.

2. Experimental

2.1. Materials and instruments

The reagents and chemicals for preparation of compounds were used as received unless noted otherwise. Ethanol, dichloromethane, toluene, chloroform, ethyl acetate, petroleum ether, etc. were purchased from Beijing Chemical Plant and treated according to standard methods used before, which were all applied to measurement of the light-emitting properties. The synthetic route used is shown in Scheme 1.

Melting points were determined on a Sanyo Gallenkamp MPD350 melting point apparatus and uncorrected. The IR spectra were determined on a PE-1700 IR spectrophotometer by dispersing samples in KBr disks. ¹H NMR spectra were measured on a Bruker ARX300 spectrometer with DMSO as solvent. Mass spectrum dates were obtained on a JEOL GC- MS D300. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) UV–vis and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer and Shimadzu RF-540 spectrofluorothotometer, respectively. Luminescence spectrometer was with a xenon lamp as the light source. Both excitation and emission bands were set at 5 nm. All the experiments were carried out at 15 ± 1 °C.

2.2. Preparation of materials

2.2.1. Preparation of 9-(α -naphthyl)carbazole [16]

Place 0.05 mol of carbazole, 0.054 mol of α -bromonaphthanlene, 50 mol of potassium carbonate, 0.008 mol of copper powder and 100 ml of nitrobenzene in three-necked flask equipped with a mechanical stirrer, dropping funnel and a Claisen still-head which was fitted with a thermometer and a condenser. The reaction mixture was stirred vigorously and heated on an oil hath to gentle reflux. The water produced from the reaction together with some nitrobenzene was distilled from the reaction system. After refluxing for 10 h, the



Scheme 1. The synthetic routes of compounds.

reaction mixture was cooled and the solvent, nitrobenzene, with the unreacted halides were removed by steam distillation. The residue was filtered at the pump, washed well with water and dried in the air. The crude products were purified by recrystallization or silica gel column chromatography (eluent: ethyl acetate:*n*-hexane = 1:10). Yield: 71%, m.p. 123–124 °C, IR (KBr pellet) cm⁻¹: 3020, 1600, 1580, 1470, 775, 765, 750,725; ¹H NMR (CDCl₃): δ : 6.88–8.24 (m, 15H). Anal. Calcd for C₂₂H₁₅N: C, 90.06; H, 5.16; N, 4.77. Found: C, 89.76; H, 5.03; N, 4.41.

2.2.2. 3-Formyl-9-(α -naphthyl)carbazole [17]

To 0.2 mol of N,N-dimethyl formamide cooled to 0°C was added dropwise 0.2 mol of phosphorous oxychloride. The mixture was left to stand for 1 h at room temperature to complete the formation of the complex reagent. 0.02 mol of 9-(α -naphthyl)carbazole in the reaction solvent were then added. The reaction mixture was heated to 110 °C with stirring for 24 h and poured into broken ice. After neutralizing with base, the mixture was extracted with chloroform and dried with anhydrous magnesium sulfate. The solvent was removed by distillation in vacuum, giving the solid residue. The crude product was purified by silica gel column chromatography (eluent: ethyl acetate:n-hexane = 1:3). Yield: 42%, m.p. 168–169 °C. IR (KBr pellet) cm⁻¹: 3015, 2754, 1690, 1600, 1238, 820, 800, 770. ¹H NMR (CDCl₃): δ 7.5-8.6(m, 14H), 10.05(s, 1H). MS (m/z): 321(M⁺), 292, 127.

2.2.3. 2,5-Bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole

2,5-Bis(3-tolylene-triphenylphosphonium bromide)-1,3, 4-oxadiazole was synthesized by the previous work [18].

2.2.4. 2,5-Bis{3'-[3"-vinyl-9"-(αnaphthyl)carbazolyl]phenyl}-1,3,4-oxadiazole (VNCO) [19]

The freshly prepared sodium ethoxide (0.24 mol) were added at 0°C to a well stirred solution of appropriated 3-formyl-9-(α-naphthyl)carbazole (0.04 mol) and 2,5-bis(3tolylene-triphenyl-phosphonium bromide)-1,3,4-oxadiazole (0.02 mol) in anhydrous THF (30 mL) under nitrogen atmosphere. After the resulting suspension was stirred at 0°C for 1 h, the corresponding reaction mixture was stirred at 70 °C for 12 h; the solvent was removed under reduced pressure. Then, the mixture was diluted with ethyl acetate and washed with 1N HCl and water. The organic extract was dried (MgSO₄) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (1:7) mixture gave analytically pure compounds. Yield: 52%, IR (KBr pellet) cm⁻¹: 2934, 2865, 1610, 1500, 1480, 1418, 1074, 804, 696; ¹H NMR (DMSO): δ: 7.54–8.72(m, aromatic and olefinic). Anal. Calcd for C₆₂H₄₀N₄O: C, 86.91; H, 4.67; N, 6.55. Found: C, 86.98; H, 4.66; N, 6.52.

3. Results and discussion

3.1. The synthesis of compounds

9-(α -Naphthyl)carbazole could be obtained via the C–N coupling reaction, Cu(0) as catalyst, by employing α -bromonaphthanlene and carbazole. 3-Formyl-9-(α -naphthyl)carbazole was synthesized by two-step strategy, and reaction temperature have a significant influence on the reaction. It have been found by experiment that the suitable reaction temperature was 110 °C. 2,5-Bis{3'-[3''-vinyl-9''-(α -naphthyl)carbazolyl]-1,3,4-oxadiazole was synthesized by 3-formyl-9-(α -naphthyl)carbazole 2,5-bis(3-tolylene-triphenylphosphonium bromide)-1,3,4-oxadiazole via Wittig reaction.

Comparing the IR spectrum of 3-formyl-9-(α -naphthyl)carbazole with that of 9-(α -naphthyl)carbazole evidences the formation of the aldehyde group. The most obvious change of the IR after Vilsmeier reaction is the appearance of a new peak at 1690 cm⁻¹, which indicates that C=O structure is introduced into 3-formyl-9-(α -naphthyl)carbazole. In addition, from IR spectrum of 2,5-bis{3'-[3"-vinyl-9"-(α -naphthyl)carbazolyl]-1,3,4-oxadiazole, the disappearance of 1690 cm⁻¹ (C=O) and the appearance of 1602 cm⁻¹ (\bigcirc -c=C) indicate that the target compound VNCO is successfully synthesized by Wittig reaction.

3.2. UV–vis absorption and fluorescence excitation and emission spectrum

Fig. 1 shows the UV–vis absorption, photoluminescence (PL) excitation and the PL emission spectra of VNCO in dilute chloroform solution. The UV–vis absorption spectra of VNCO solution in chloroform showed absorption peak (λ_{ab}) around 240 nm attributable to the naphthalene, carbazole and oxadizole rings and a shoulder 273 nm that is assigned to the π – π^* transition of the conjugation backbone. The



Fig. 1. The UV-vis absorption and fluorescence excitation, emission spectrum of VNCO.



Fig. 2. The emission spectra of VNCO in different solvents.

PL excitation spectra were overlapped with the absorption spectra and displayed maximum ($\lambda_{ex,max}$) at 283 nm. VNCO emitted blue and blue–green light with emission maximum ($\lambda_{f,max}$) at 375 nm.

3.3. Solvent effects on photoluminescence (PL)

The compound VNCO has good solubility in common organic solvents, such as ethanol, acetonitrile, chloroform, toluene, etc. The emission spectra of VNCO are investigated in different solvents and all results are showed in Fig. 2. It can be seen from Fig. 2 that with the increase of the solvents polarity, the emission spectra of VNCO are red shift from 364 to 394 nm and half-peak breadth are gradually widened. It is well known that the emission spectra of chromophore red shift with the increase of the solvents polarity due to the dipole–dipole interaction of the excited state.

3.4. Quantum yield of photoluminescence and the band gap

The fluorescence quantum yield was measured by relative method using the quinine sulfate as the standard (0.546 in $0.5 \text{ mol } L^{-1} \text{ H}_2 \text{SO}_4$) [20]. The quantum yield was calculated from the following equation:

$$\Phi_{\rm s} = \Phi_{\rm r} \frac{F_{\rm s}}{F_{\rm r}} \frac{A_{\rm r}}{A_{\rm s}} \left(\frac{n_{\rm r}}{n_{\rm s}}\right)^2$$

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 VNCO in chloroform is 0.746. The band gap (E_g^{opt}) of the VNCO can be estimated from the onset absorption (UV_{onset}) with E_g^{opt} (eV)= hc/λ (h=6.626 × 10⁻³⁴ J s, c=3 × 10¹⁷ nm/s, 1 eV=1.602 × 10⁻¹⁹ J). The band gap of the VNCO is 3.30 eV.



Fig. 3. Fluorescence spectra of VNCO at different concentration of DMA. Concentration of VNCO, 8.63×10^{-6} mol/L; concentration of DMA (mol/L), 0, 0.00; (1) 1.34×10^{-5} ; (2) 3.36×10^{-5} ; (3) 7.39×10^{-5} ; (4) 1.55×10^{-4} ; (5) 3.13×10^{-4} .

3.5. The quenching processes of fluorescence of VNCO with N,N-dimethylaniline (DMA) and dimethylterephthalate (DMTP)

N,*N*-dimethylaniline (DMA) is a typical electron donor and dimethylterephalate (DMTP) is a typical electron acceptor. When DMA is added to a solution of VNCO in chloroform, the fluorescence of VNCO is efficiently quenched and the quenching process follows the Stern–Volmer equation. The apparent quenching coefficient, K_{sv} , is $1.46 \times 10^4 \text{ M}^{-1}$ (as shown in Fig. 3). In order to go further into the fluorescence quenching of VNCO, the quenching process of VNCO with DMTP is also examined and shown in Fig. 4. It can be seen that the emission intensity of fluorescence are initially increased and then decreased with gradual increasing in concentration of VNCO in chloroform. Meanwhile, the emission peaks show red-shifted about 15 nm. From the experimental facts and references, an explanation is proposed: carbazole



Fig. 4. Fluorescence spectra of VNCO at different concentration of DMTP. Concentration of VNCO, 3.72×10^{-6} mol/L; concentration of DMTP (mol/L), 0, 0.00; (1) 5.88×10^{-4} ; (2) 8.76×10^{-4} ; (3) 5.52×10^{-2} ; (4), 6.93×10^{-2} ; (5) 8.32×10^{-2} ; (6) 9.22×10^{-2} .

unit is an electron donor group and a typical hole-transporting molecule while dimethylterephalate (DMTP) is a good electron acceptor, so the strong interaction between carbazole and DMTP happens when DMTP is gradually added into the solution of VNCO, the potential energy of VNCO that results from the action between VNCO and solvent is delivered, which would lead to increasing of fluorescence intensity of carbazole units. When the concentration of DMTP goes beyond a certain scope, the excess DMTP units would act as quencher to quench gradually the fluorescence of VNCO.

3.6. Interaction between VNCO and fullerene (C_{60})

C₆₀ bears many unusual electrochemical and electronic properties. One of the most remarkable properties of C_{60} related to electron transfer phenomena is that it can efficiently induce a rapid charge separation and a further slow charge recombination [21]. In the experiment, the interactions of VNCO with C_{60} are examined. The results are shown in Fig. 5. As we have seen in Fig. 5, '0' is VNCO in concentration (5.89 \times 10⁻⁶ mol/L) without C₆₀, '1–5' are VNCO in the present in different concentration of C₆₀. With the gradual increasing of concentration of C₆₀, the fluorescence of VNCO is quenched efficiently and the process is also following the Stern-Volmer equation (Fig. 6). The apparent quenching constant is $3.52 \times 10^5 \,\mathrm{M}^{-1}$, which suggests that the strong interactions between VNCO and C₆₀ happen in the excited state. The interactions are mainly coming from the stronger charge-transfer process of the long π electron system (VNCO) with the electron acceptor (C_{60}).

3.7. Interaction between VNCO and carbon nanotubes (CNTs)

Carbon nanotubes are unique tubular structures of nanometer diameter and have large length/diameter ratio [22]. It shows promise for a wide range of applications due



Fig. 5. Fluorescence spectra of VNCO at different concentration of C_{60} . Concentration of VNCO, 5.89 × 10⁻⁶ mol/L; concentration of C_{60} (mol/L), 0, 0.00; (1) 1.39 × 10⁻⁶; (2) 2.32 × 10⁻⁶; (3) 3.24 × 10⁻⁶; (4) 4.63 × 10⁻⁶; (5) 6.02 × 10⁻⁶.



Fig. 6. Dependence of $F^{0/F}$ on concentration of C₆₀. Concentration of VNCO 5.89 × 10⁻⁶ mol/L.



Fig. 7. Fluorescence spectra of VNCO at different concentration of CNTs. Concentration of VNCO, 8.63×10^{-6} mol/L; concentration of CNTs (mg/ml), 0, 0.00; (1) 2.10×10^{-6} ; (2) 4.22×10^{-6} ; (3) 7.32×10^{-5} ; (4) 9.15×10^{-5} .

to a combination of their unusual structural, mechanical and electronic properties [23]. The investigation on the interaction between VNCO and carbon nanotubes (CNTs) is helpful to understand the optical property of VNCO and apply it to LEDs. The quenching process of VNCO with carbon nanotubes is shown in Fig. 7. It can be seen that the fluorescence of VNCO is quenched. Similarly, the strong interacting between VNCO and CNTs are initiated in the excited state. The strong interaction may be caused by the photoinduced charge transfer and stacking processes of initiated $\pi-\pi$ system. Further research toward a better understanding of this action is currently in progress.

4. Conclusions

A new π -conjugated VNCO, 2,5-bis{3'-[3"-vinyl-9"-(α -naphthyl)carbazolyl]phenyl}-1,3,4-oxadiazole, bearing

hole-transporting carbazole moieties, electron-injecting 1,3,4-oxadiazole moieties and chromophore naphthalene was successfully synthesized by Wittig reaction. The optics researches showed VNCO emitted blue and blue–green light, with the band gap of 3.30 eV estimated from the onset absorption, the luminescence quantum yield was 0.746 in chloroform, and displayed the emission spectra are red-shifted with the increase of the solvents polarity. Moreover, the light-emitting can be quenched by both electron donor (N,N-dimethylaniline) and electron acceptor (dimethylterephalate), the molecular interactions of VNCO with fullerene (C_{60}) or carbon nanotubes happened in the excited state.

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References

- J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, A.B. Holmes, Nature 347 (1990) 539.
- [2] A. Kraft, A.C. Grimsdale, A.B. Holmes, Angew. Chem. Int. Ed. 37 (1998) 402.
- [3] D.Y. Kim, H.N. Cho, C.Y. Kim, Prog. Polym. Sci. 25 (2000) 1089.

- [4] C. Adach, S. Tokoto, T. Tsutsui, S. Saito, Jpn. J. Appl. Phys. 27 (1998) 713.
- [5] X.C. Li, G.C.W. Spencer, A.B. Holmes, S.C. Moratti, F. Cacialli, R.H. Friend, Synth. Met. 76 (1996) 153.
- [6] D.D.C. Bradley, Synth. Met. 54 (1993) 401.
- [7] G.M. Wang, C.W. Yuan, H.W. Wu, Y. Wei, J. Appl. Phys. 78 (1995) 2679.
- [8] A.R. Brown, D.D.C. Bradley, J.H. Burrouthes, R.H. Friend, N.C. Greenham, P.L. Burn, A.B. Holmes, A. Kraft, Appl. Phys. Lett. 61 (1992) 2793.
- [9] C. Adachi, S. Tokito, T. Tsutsui, S. Satio, Jpn. J. Appl. Phys. 31 (1992) 1812.
- [10] F.L. Bai, M. Zheng, G. Yu, D.B. Zhu, Thin Solid Films 363 (2000) 118–121.
- [11] D.B. Romero, M. Schaer, M. Leclerc, D. Ades, A. Siove, L. Zuppiroli, Synth. Met. 80 (1996) 271.
- [12] S. Aratani, C. Zhang, K. Palbaz, S. Hoger, F. Wudl, A.J. Heeger, J. Electron. Mater. 23 (1994) 453.
- [13] C. Zhang, H. von Seggern, K. Pakbaz, B. Kraabel, H.W. Schmidt, A.J. Heeger, Synth. Met. 62 (1994) 35.
- [14] Y.Q. Liu, X.Z. Jiang, Q.L. Li, D.B. Zhu, Synth. Met. 4 (1997) 36.
- [15] C. Hosokawa, N. Kawasaki, S. Sakamoto, T. Kusumoto, Appl. Phys. Lett. 61 (1992) 2503.
- [16] T. Ahn, H.K. Shim, Macromol. Chem. Phys. 202 (2001) 3180.
- [17] Z. Arnold, A. Hoy, Collection Czech. Chem. Commun. 27 (1962) 2886.
- [18] S.Y. Song, M.S. Jang, H.K. Shim, D.H. Hwang, T. Zyung, Macromolecules 32 (1999) 1482.
- [19] Y.L. Lin, H.S. Kuo, Y.W. Wang, S.T. Huang, Tetrahedron 59 (2003) 1277.
- [20] J.N. Dmas, G.A. Crobys, J. Phys. Chem. 71 (1971) 991.
- [21] B.W. Jing, D.Q. Zhang, D.B. Zhu, Tetrahedron Lett. 41 (2000) 8559.
- [22] H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.
- [23] M.S. Dresselhaus, G. Dresselhaus, R. Saito, Carbon 33 (1995) 883.