Synthesis and photoluminescent properties of 7-*N*,*N*-diphenylamino-3- benzoheterocyclic coumarin derivatives

Tianzhi Yu · Ming Zhao · Aiwen Li · Yuling Zhao · Hui Zhang · Duowang Fan

Received: 9 June 2012/Accepted: 30 July 2012/Published online: 18 August 2012 © Springer Science+Business Media B.V. 2012

Abstract Two new 7-*N*,*N*-diphenylamino-3-benzoheterocyclic coumarin derivatives containing electron-transporting benzotriazolyl or benzoxazolyl moiety, 3-(1-benzotriazole)-7-*N*,*N*-diphenylaminocoumarin (BTDC) and 3-(2-benzoxazole)-7-*N*,*N*-diphenylaminocoumarin (BODC), were synthesized and characterized by element analysis, ¹H NMR and FT-IR spectra. The UV–vis and fluorescence spectra of these coumarin derivatives were investigated. The results show that BTDC and BODC exhibit strong blue and red emissions, respectively, under ultraviolet light excitation. The relationships between the chemical structure and the fluorescence characteristics of the 7-*N*,*N*-diphenylamino-3-benzoheterocyclic coumarin derivatives are discussed. It was found that the coumarin derivative will become a high-efficiency emitting material when an amino group is attached in 7-position of the coumarin ring, and 7- strong electron donors can improve the ability of the intramolecular charge transfer of the coumarin molecules.

Keywords Synthesis · 7-*N*,*N*-diphenylaminocoumarin derivative · Benzotriazole · Benzoxazole · Photoluminescence

Introduction

Coumarins are an important class of naturally occurring and synthetic compounds, which have been extensively investigated for electronic and photonic applications

M. Zhao \cdot A. Li \cdot Y. Zhao

School of Chemical and Biological Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

T. Yu (\boxtimes) \cdot M. Zhao \cdot A. Li \cdot H. Zhang \cdot D. Fan

Key Laboratory of Opto-Electronic Technology and Intelligent Control (Ministry of Education), Lanzhou Jiaotong University, Lanzhou 730070, China e-mail: yutianzhi@hotmail.com

[1–5], such as fluorescence probe, charge-transfer agents, solar energy collectors, and nonlinear optical properties, due to their characteristics of high emission yield, excellent photo-stability, extended spectral range, good solubility, and their relative ease of synthesis. As emitting materials, their fluorescent wavelength and fluorescence quantum yield strongly depend on the property and the position of the substituent and also on the rigidity of the molecule.

Highly efficient organic dyes often have a push-pull structure, which is composed of an electron-donating (D) unit, conjugated bridge (π) linker and electron-accepting (A) unit. The introduction of both an electron-donating substituent and an electronaccepting substituent to a core of the π system can also modulate the light-harvesting properties of the organic dyes [6–8]. The molecules with D- π -A structures are considered to be one of the most promising types of organic dyes, and have attracted intensive attention because of their great potential applications as electroactive and photoactive materials in molecular electronics, such as biochemical fluorescent technology [9], nonlinear optics [10], organic light-emitting diodes (OLEDs) [11] and photovoltaic cells [6-8, 12]. Among donor groups, triphenylamine and its derivatives have been widely used as sensitizers and have promising properties in the development of organic dyes, because the triphenylamine unit suppresses the aggregation of the dye due to its nonplanar structure. Moreover, triphenylamine derivatives were often used as light-emitting materials and hole transport materials due to their high hole mobility, solubility and the formation of amorphous film [13]. In order to achieve charge generating materials and charge transporting materials, many researchers have introduced several kinds of substituents in the rings of triphenylamine to improve the solubility of the compounds. This can not only enhance the molecular conjugated system but also effectively improve the hole mobility, the thermal stability and the resin compatibility [14–16].

In this communication, two new coumarin derivatives, 3-(1-benzotriazole)-7-*N*,*N*-diphenylaminocoumarin (BTDC) and 3-(2-benzoxazole)-7-*N*,*N*-diphenylaminocoumarin (BODC), were synthesized by introducing a diphenylamino group at 7-position of the coumarin ring as electron donor and a benzotriazole or a benzoxazole as electron acceptor. The chemical structures of 3,7-disubstituted coumarin derivatives in the present study are shown in Scheme 1. Their UV–vis absorption and photoluminescent (PL) properties were investigated. The substituent effects of the electron donors and the electron acceptors on the photoluminescent properties of the compounds are discussed.



Scheme 1 Molecular structures of 3,7-disubstituted coumarin derivatives in the present study

Experimental

Materials and methods

3-methoxybenzenamine from Acros Organics, 1H-benzotriazole (BTA) and boron tribromide from Aldrich were used without further purification. Bronze power, 18-crown-6, triethylamine (TEA), piperidine, chloroacetonitrile, iodobenzene, *o*-aminophenol, diphenylether and phosphorus oxychloride were analytical grade reagents from Tanjin Fuchen Chemical Reagent Factory. 7-*N*,*N*-diethylamino-3-(benzotriazol-1-yl)coumarin (DABTC-1) was synthesized according to the methods previously described [11].

IR spectra (400–4,000 cm⁻¹) were measured on a Shimadzu IRPrestige-21 FT-IR spectrophotometer. ¹H NMR spectra were obtained on Unity Varian-500 MHz. C, H and N analyses were measured on an Elemental Vario-EL automatic elemental analysis instrument. Melting points were measured by using an X-4 microscopic melting point apparatus made by Beijing Taike Instrument, and the thermometer was uncorrected. UV–vis absorption and fluorescence spectra were recorded on a Shimadzu UV-2550 spectrometer and on a Perkin Elmer LS-55 spectrometer, respectively.

Synthesis and characterization of BTDC and BODC

The synthetic routes were shown in Scheme 2. The intermediate, 2-(1*H*-benzotriazol-1-yl)acetonitrile, was obtained as previously described [11]. BTDC



Scheme 2 Synthetic routes of BTDC and BODC

and BODC were synthesized according to the methods previously described in [11] and [17], respectively.

4-(diphenylamino)-2-hydroxybenzaldehyde

4-(diphenylamino)-2-hydroxybenzaldehyde were obtained by two steps according to the method reported by Swanson et al. [16, 18].

Amounts of 7.468 g (0.06 mol) of 3-methoxybenzenamine, 28.494 g (0.14 mol) of iodobenzene, 14.99 g (0.24 mol) of copper powder, 0.440 g (1.6 mmol) of 18-crown-6 and 64.16 g (0.46 mol) of anhydrous potassium carbonate in 250 mL of diphenylether were placed into a 500-mL three -necked round-bottom flask. The reaction mixture was refluxed with stirring for 72 h under nitrogen atmosphere. The solids were removed by filtration and the solvents were removed by vacuum distillation. The crude was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:10, v/v) as the eluent, and 9.35 g of brown oil was 3-methoxytriphenylamine (yield 56 %). ¹H NMR (500 MHz, CDCl₃, δ , ppm): 6.85–7.31 (m, 11H, Ar–H), 6.62–6.66 (m, 2H, Ar–H), 6.53 (d, J = 7.2 Hz, 1H, Ar–H), 3.71 (s, 3H, OCH₃).

Next, 5 g (0.018 mol) of 3-methoxytriphenylamine was dissolved in dry CH₂Cl₂ (50 mL). 9 g (0.036 mol) of BBr₃ was added dropwise into the solution at -78 °C. The reaction mixture was further stirred overnight. Saturated aqueous Na₂CO₃ (100 mL) was added to quench the reaction. The organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (3 × 50 mL). The combined extracts were washed with water and dried over anhydrous MgSO₄. After filtering, the filtrate was evaporated to dryness under reduced pressure. The crude product was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:5, v/v) as the eluent to give 3-Hydroxytriphenylamine as absinthe-green solid (3.5 g, 73.76 %). m.p.: 98–100 °C. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 7.27–7.23 (m, 4H, Ar–H), 7.11–7.09 (m, 5H, Ar–H), 7.07–7.01 (m, 2H, Ar–H), 6.66–6.63 (d, J = 8.2 Hz, 1H, Ar–H), 6.52 (t, J = 1.8 Hz, 1H, Ar–H), 6.47–6.45 (d, J = 8.1 Hz, 1H, Ar–H), 4.61 (s, 1H).

A solution of POCl₃ (4.700 g, 30.7 mmol) in DMF (20 mL) was cooled at 0 °C. 3-Hydroxytriphenylamine (4.000 g, 15.33 mmol) was dissolved in another portion of DMF (20 mL). The POCl₃ solution was then added dropwise into 3-Hydroxytriphenylamine solution at 0 °C. The reaction mixture was reacted for 2 h and then hydrolyzed with water (40 mL) for 6 h. The crude product was extracted with CH₂Cl₂ (3 × 100 mL). The combined extracts were washed with water and dried over anhydrous MgSO₄. After filtering, the filtrate was evaporated to dryness under reduced pressure, and purified by chromatography on silica gel using ethyl acetate/ petroleum ether (1:4, v/v) as the eluent to give 4-(diphenylamino)-2-hydroxybenzaldehyde (3.29 g, 74.3 %). m.p.: 128–130 °C. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 11.40 (s, 1H, –CHO), 9.58 (s, 1H, Ar–OH), 7.34 (m, 4H, Ar–H), 7.25 (d, J =8.5 Hz, 1H, Ar–H), 7.25–7.18 (m, 6H, Ar–H), 6.45 (d, J = 8.5 Hz, 1H, Ar–H), 6.34 (d, J = 1.6 Hz, 1H, Ar–H).

3-(1-benzotriazole)-7-N,N-diphenylaminocoumarin (BTDC)

Under nitrogen atomosphere, 4-(diphenylamino)-2-hydroxybenzaldehyde (2.000 g, 6.91 mmol) and 2-(1*H*-benzotriazol-1-yl)acetonitrile (1.093 g, 6.91 mmol) was dissolved in 30 mL of anhydrous ethanol, and treated with piperidine (0.1 mL) at room temperature. The reaction mixture was refluxed with stirring for 50 h, and then acidized with hydrochloric acid (3.5 %) for 8 h. Ammonia was added to neutralize the acidity. The solution was extracted with CH₂Cl₂ (3 × 25 mL) and then dried over anhydrous MgSO₄. After filtering, the filtrate was evaporated to dryness under reduced pressure, and purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:10, v/v) as the eluent to give BTDC as solid (0.8 g, 26.9 %). m.p.: 210–212 °C. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 6.38 (s, 1H, Ar–H), 6.5–6.7(m, 12H, Ar–H), 6.95 (s, 1H, Ar–H), 7.1 (m, 2H, Ar–H), 7.25 (m, 2H, Ar–H). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 162.2, 150.8, 145.4, 141.1, 140.3, 132.1, 129.5, 127.3, 123.2, 122.6, 119.3, 118.2, 116.5, 113.0. IR (KBr pellet cm⁻¹): 3,031 (Ar–CH), 1,733 (C=O, lactone), 1,660 (C=C), 1,502, 1,457, 1,338, 1,253, 1,247, 1,164, 746. Anal. Calc. for C₂₇H₁₈N₄O₂ (%): C, 75.34; H, 4.21; N, 13.02. Found: C, 75. 41; H, 4.18; N, 12.95.

3-(2-benzoxazole)-7-N,N-diphenylaminocoumarin (BODC)

Under nitrogen atomosphere, a mixture of 4-(diphenylamino)-2-hydroxybenzaldehyde (2.000 g, 6.91 mmol), o-aminophenol (0.754 g, 6.91 mmol), benzoic acid (0.400 g, 3.09 mmol) and ethyl cyanoacetate (0.785 g, 6.91 mmol) was dissolved in 50 mL of 1-butanol. The mixture solution was refluxed for 12 h at 80 °C, and then 100 mL NaOH (2 %) was added to the mixture solution and stirred vigorously for 4 h at 80 °C. The mixture solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was washed with water and dried over anhydrous MgSO₄. After filtering, the filtrate was evaporated to dryness under reduced pressure, and purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:3, v/v) as the eluent to give BODC (1.2 g, 40.3 %). m.p: 216–218 °C. ¹H NMR (500 MHz, CDCl₃, δ , ppm): 6.8 (s, 1H, Ar-H), 7.21-7.50 (m, 12H, Ar-H), 7.60-7.80 (m, 4H, Ar-H), 8.14 (s, 1H, Ar-H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 162.1, 152.3, 151.2, 150.0, 146.1, 141.2, 140.5, 129.5, 127.6, 125.0, 123.6, 122.6, 119.1, 116.7, 113.0. IR (KBr pellet, cm⁻¹): 3,013 (Ar-CH), 1,737 (C=O, lactone), 1,653 (C=C), 1,626, 1,591, 1,328, 1,236, 1,238, 1,164, 1,155, 1,096, 746. Anal. Calc. for C₂₈H₁₈N₂O₃ (%): C, 78.13; H, 4.21; N, 6.51. Found: C, 78. 32; H, 4.16; N, 6.47.

Results and discussion

Absorption of BTDC and BODC

UV-vis absorption spectra of BTDC, BODC and DABTC-1 in dilute chloroform solutions are given in Fig. 1. It is shown that the absorption spectrum of BTDC exhibits absorptions at 228 and 284 nm. From the structures of BTDC and DABTC-1, they all have an electron-withdrawing benzotriazolyl moiety at



Fig. 1 UV-vis absorption spectra of the compounds in dilute chloroform solutions (C = 3.0×10^{-5} mol/L)

3-position of coumarin ring, but BTDC has an electron-pushing diphenylamino group at 7-position of the coumarin ring, while DABTC-1 has an electron-pushing diethylamino group at 7-position. Due to the $p-\pi$ conjugation effect, the electron density of the nitrogen atom in the diphenylamino group is smaller than that in the diethylamino group, and the electron-pushing power of the diphenylamine group is weaker than that of the diethylamino group. Compared with BTDC, the absorption bands of DABTC-1 were bathochromically shifted, in which the absorption bands were at 253 and 414 nm. This suggests that the molecular conjugation degree of DABTC-1 is larger than that of BTDC due to the strong electron-pushing power of the diethylamino group.

As shown in Fig. 1, the absorption spectrum of BODC gives four absorption bands which locate at 228, 289, 358 and 520 nm. Compared with BTDC, except that two shorter absorption bands at 228 and 289 nm were present in the absorption spectrum of BODC, an important feature of the absorption spectra of BODC is that two absorption bands were observed at 358 and 520 nm, which were absent in the spectrum of BTDC. From the structures of BTDC and BODC, it can be seen that they have the same electron-pushing diphenylamine group at 7-position of the coumarin ring and different electron-withdrawing groups at 3-position. BTDC possesses an electron-withdrawing benzotriazolyl moiety at 3-position of the coumarin ring, while BODC has an electron-withdrawing benzoxazolyl group. From the maximum absorption band at 284 nm for BTDC and 520 nm for BODC, it is deduced that the electron-withdrawing power of benzotriazole is larger than that of benzoxazole, and the molecular conjugation degree of BODC is larger than that of BTDC.

Photoluminescence of BTDC and BODC

Figure 2 shows the photoluminescent spectra of BTDC, BODC and DABTC-1 in dilute chloroform solutions. It is clear that BTDC and DABTC-1 exhibit bright blue

emissions in dilute solutions, and the emission peaks of them locate at around 420 and 447 nm, respectively. The emission peak of DABTC-1 was red-shifted by about 27 nm compared with that of BTDC due to the larger conjugation of molecule in DABTC-1.

As shown in Fig. 2, the compound BODC shows bright red emission with a peak at 630 nm in dilute solution. Compared with BTDC, the emission maximum peak of BODC was red-shifted by about 210 nm due to the larger conjugation of molecules in BODC.

From the above photoluminescent characteristics of the three compounds, it is further indicated that the electron-pushing power of the diphenylamine group is weaker than that of the diethylamino group and the electron-withdrawing power of benzotriazole is larger than that of benzoxazole.

In addition, the fluorescence quantum yields of BTDC and BODC in chloroform solutions were calculated according to the method described by Kaholek et al. [19] with anthracene as a standard ($\Phi_F = 0.25$ [19]). In the research, the $\Phi_{F,BTDC}$ and $\Phi_{F,BODC}$ are 0.38 and 0.46, respectively. The fluorescence quantum yields of BTDC and BODC in chloroform solutions are less than that of DABTC-1in chloroform solution [11].

Conclusions

Two new 3,7-disubstituted coumarin derivatives, 3-(1-benzotriazole)-7-*N*,*N*-diphenylaminocoumarin (BTDC) and 3-(2-benzoxazole)-7-*N*,*N*-diphenylaminocoumarin (BODC), were successfully synthesized and characterized. All synthesized compounds are fluorescent in solutions: BTDC exhibits bright blue emission with the peak at 420 nm and BODC emits bright red light with the peak at 630 nm.



Fig. 2 Photoluminescent spectra of the compounds in dilute chloroform solutions (C = 3.0×10^{-5} mol/L, $\lambda_{ex,BTDC} = 284$ nm, $\lambda_{ex,DABTC} = 414$ nm and $\lambda_{ex,BODC} = 520$ nm)

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Grant 61166003) and the Natural Science Foundation of Gansu Province (1010RJZA060), and also supported by the Program for Changjiang Scholars and Innovative Research Team in University (IRT0629).

References

- 1. R.P. Haugland, M.T.Z. Spence, I.D. Johnson, *Handbook of fluorescent probes and research chemicals*, 6th edn. (Molecular Probes, Eugene, 1996)
- H. Schwander, P. Hendrix, in *Ullmann's encyclopedia of industrial chemistry*, vol. A11, 5th edn., ed. by Y.S. Yamamoto (VCH, Weinheim, 1988), p. 280
- 3. O.S. Wolfbeis, E. Koller, P. Hochmuth, Bull. Chem. Soc. Jpn. 58, 731-734 (1985)
- 4. U. Tripathy, P.B. Bisht, J. Chem. Phys. 125, 144502-144509 (2006)
- 5. S.L. Gilat, A. Adronov, J.M.J. Fréchet, Angew. Chem. Int. Ed. 38, 1422-1427 (1999)
- 6. H. Imahori, T. Umeyama, S. Ito, Acc. Chem. Res. 42, 1809–1818 (2009)
- S. Franco, J. Garin, N.M. De Baroja, R. Pérez-Tejada, J. Orduna, Y.H. Yu, M. Lira-Cantú, Org. Lett. 14, 752–755 (2012)
- S.P. Singh, M.S. Roy, K.R. Justin Thomas, S. Balaiah, K. Bhanuprakash, G.D. Sharma, J. Phys. Chem. C 116, 5941–5950 (2012)
- 9. G.S. Jiao, L.H. Thoresen, K. Burgess, J. Am. Chem. Soc. 125, 14668-14669 (2003)
- K. Staub, G.A. Levina, S. Barlow, T.C. Kowalczyk, H.S. Lackritz, M. Barzoukas, A. Fortd, S.R. Marder, J. Mater. Chem. 13, 825–833 (2003)
- T.Z. Yu, P. Zhang, Y.L. Zhao, H. Zhang, J. Meng, D.W. Fan, L.L. Chen, Y.Q. Qiu, Org. Electron. 11, 41–49 (2010)
- 12. Z.J. Ning, Q. Zhang, W.J. Wu, H.C. Pei, B. Liu, H. Tian, J. Org. Chem. 73, 3791–3797 (2008)
- 13. Q. Xu, H.Z. Chen, M. Wang, J. Funct. Mater. 36, 1659-1663 (2005)
- 14. Y. Imai, M. Ishida, M.A. Kakimoto, High Perform. Polym. 15, 281-290 (2003)
- 15. C. Lambent, G. Noll, Synth. Met. 139, 57-62 (2003)
- S.A. Swanson, G.M. Wallraff, J.P. Chen, W.J. Zhang, L.D. Bozano, K.R. Carter, J.R. Salem, R. Villa, J.C. Scott, Chem. Mater. 15, 2305–2312 (2003)
- 17. Y.L. Zhao, T.Z. Yu, Y.Z. Wu, H. Zhang, D.W. Fan, Z.W. Gan, L.L. Yang, X.Q. Han, Y.M. Zhang, J. Fluoresc. 22, 631–638 (2012)
- C.T. Chen, C.L. Chiang, Y.C. Lin, L.H. Chan, C.H. Huang, Z.W. Tsai, C.T. Chen, Org. Lett. 5, 1261–1264 (2003)
- 19. M. Kaholek, P. Hrdlovič, J. Photochem. Photobiol. A Chem. 127, 45-55 (1999)