Available online at www.sciencedirect.com

ScienceDirect

Chinese Chemical Letters 21 (2010) 9–12

CHINESE CHEMICAL LETTERS

www.elsevier.com/locate/cclet

A novel carbazole-based fluorescent probe: 3,6-Bis-[(*N*-ethylcarbazole-3-yl)-propene-1-keto]-*N*-ethylcarbazole

Li Ling Hao, Jun Fen Li, Pei Hua Lin, Rui Feng Dong,
Du Xin Li, Shao Min Shuang, Chuan Dong *

Research Center of Environmental Science and Engineering, School of Chemistry and Chemical Engineering,
Shanxi University, Taiyuan 030006, China

Received 24 March 2009

Abstract

A novel carbazole-based compound **5**, 3,6-bis[(*N*-ethylcarbazole-3-yl)-propene-1-keto]-*N*-ethylcarbazole has been designed, synthesized and characterized. The absorption and fluorescence spectra in solvents of different polarities prove that the compound has a distinct intramolecular charge transfer character. Compound **5** can be used as a new class of fluorescent probe or biosensor due to its sensitivity to the local microenvironment such as solvent polarity.

Keywords: Carbazole; Fluorescent probe; Intramolecular charge transfer; Synthesis

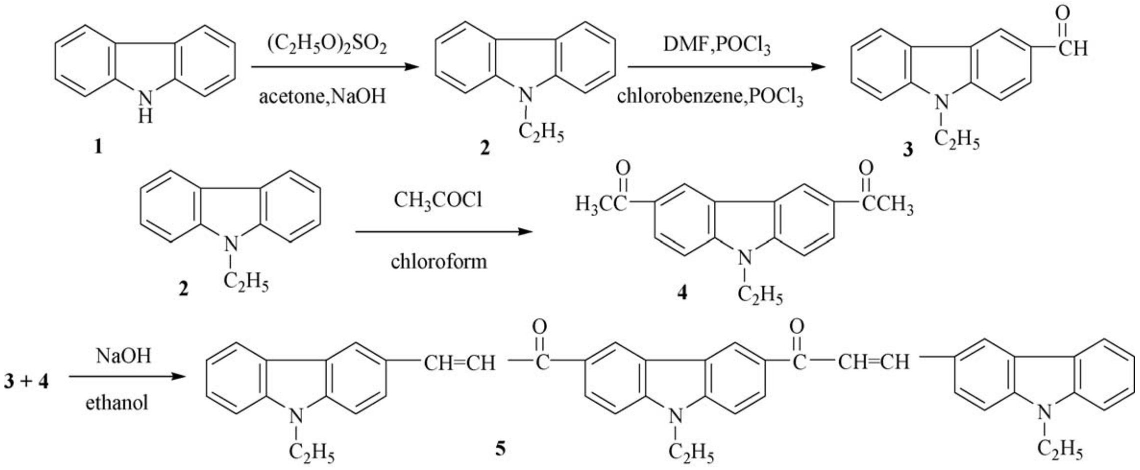
An intramolecular charge transfer (ICT) compound has an electron-donating group and an electron-accepting group connected through a π-conjugated linker [1,2]. ICT is a fundamental process and has always been attracting considerable attention as a topic of central importance in various photophysical, photochemical and biochemical processes [3,4], e.g. fluorescent probe or biosensor for studying different microenvironment [5–7], organic light-emitting diodes [8–10], organic material for non-linear optics [11,12] and two-photon absorption materials [13,14]. Carbazole and its derivatives are one of the most important fundamental structures in the field of organic electrical and optical materials [15]. It is well known that carbazole and its derivatives exhibit large π-conjugation system, special rigid structure and good hole transporting properties and can be easily modified at the 3- and 6-positions to tune the optical properties [16–18]. In addition, carbazole and its derivatives can be used as a strong electron-donating chromophore [19,20]. Up to now, the studies on synthesis and the photoluminescence properties of new carbazole-containing compounds are yet a significant subject [21].

Herein, we design and synthesize a novel carbazole-based molecule: 3,6-bis[(*N*-ethylcarbazole-3-yl)-propene-1-keto]-*N*-ethylcarbazole (compound **5**, shown in Scheme 1). In this compound, the *N*-ethylcarbazole group is used as the central core to connect with the other two *N*-ethylcarbazole units in one molecule. The absorption and fluorescence spectra in solvents of different polarities prove that compound **5** has a distinct ICT character.

---

* Corresponding author.
E-mail address: dc@sxu.edu.cn (C. Dong).

doi:10.1016/j.cclet.2009.07.003



Scheme 1. Synthetic route of compound **5**.

1. Experimental

Melting points were determined on x-5 melting point detector. IR spectra were recorded with an FTIR 1730. ^{1}H NMR spectra and ^{13}C NMR spectra were obtained on a Bruker 300 MHz instrument. The absorption spectra were recorded on a TU-1901 dual-beam UV–vis spectrophotometer and fluorescence spectra were obtained on a Carry Eclipse fluorescence spectrofluorometer (Varian, USA) equipped with a 150 W xenon lamp source.

Compounds **2** and **3** were synthesized according to literature [2]. A mixture of $AlCl_3$ (3.2 g), CH_3COCl (3.2 g, 40.76 mmol) and $CHCl_3$ (150.0 mL) were added in a 250 mL 3-necked flask equipped with a stirrer. Then the solution which was obtained from compound **2** (2.0 g, 10.26 mmol) and $CHCl_3$ (20.0 mL) was added in drop-by-drop. After stirring for 16 h at room temperature, the reaction mixture was poured into 200 mL of ice water under vigorous stirring and was kept stirring for 5 h. Yellow needle-like crystals of compound **4** were obtained after being recrystallized from ethanol (1.83 g, 64.0% yield). The melting point was 183–185 °C. The synthesis method was improved based on literature [22]. IR (KBr) cm^{-1}: 3417, 3126, $\nu_{\mathrm{C–H}}$ (carbazole and –$COCH_3$); 3051, 2970, $\nu_{\mathrm{C–H}}$ (–CH_2CH_3); 1662, 1625, $\nu_{\mathrm{C=O}}$ (–$COCH_3$); 1487, 1427, $\nu_{\mathrm{C=C}}$ (carbazole); 1392, 1348, $\nu_{\mathrm{C–N}}$ (carbazole); 802, $\delta_{\mathrm{C–H}}$ (carbazole). ^{1}H NMR ($CDCl_3$): δ 1.44–1.19 (3H, –CH_3), 2.70 (6H, –$COCH_3$), 4.38–4.31(2H, –CH_2–), 8.71–7.21 (6H, carbazole). Compound **3** (1.0 g, 4.48 mmol), **4** (0.5 g, 1.79 mmol) and ethanol (100.0 mL) were added in a 250 mL round-bottomed flask, and the solution was obtained by stirring at room temperature. Then 10% NaOH aqueous solution (3.0 mL) was dropped in. The reaction solution was stirred for 36 h at room temperature. Yellow powder of compound **5** was obtained (0.64 g, 51.8% yield). The melting point was 210–213 °C. IR (KBr) cm^{-1}: 3413, 3126, $\nu_{\mathrm{C–H}}$ (carbazole); 3056, 2970, $\nu_{\mathrm{C–H}}$ (–CH_2CH_3); 1674, 1647, $\nu_{\mathrm{C=O}}$ (–COCH=CH–); 1624, 1593, $\nu_{\mathrm{C=C}}$ (–COCH=CH–); 1492, 1475, $\nu_{\mathrm{C=C}}$ (carbazole); 1390, 1348, $\nu_{\mathrm{C–N}}$ (carbazole); 1018, $\nu_{\mathrm{C–H}}$ (–COCH=CH–); 804, 744, $\delta_{\mathrm{C–H}}$ (carbazole). ^{1}H NMR ($CDCl_3$): δ 1.46 (9H, –CH_3), 4.39 (6H, –CH_2–), 2.74 (4H, –CH=CH–CO–), 8.91–7.22 (20H, carbazole). ^{13}C NMR ($CDCl_3$, δ ppm): 18.26 (–CH_3), 42.54 (–CH_2–), 31.12 (–CH=CH–), 113.26–150.11 (carbazole), 201.99 (–CO–). In general, the typical δ ^{13}C value of –CH=CH– in the region of from 80 to 160, but the region is wider with a substituent group of O- or N-atom [23].

2. Results and discussion

The fluorescence quantum yield (φ_f) of compound **5** in different solvents are: carbon tetrachloride, 0.0045; diethyl ether, 0.0138; tetrahydrofuran, 0.0333; chloroform, 0.135; dimethyl sulfoxide, 0.428; ethanol, 0.516, water, 0.0446. It is obvious that compound **5** shows good luminescence in ethanol.

Typical absorption spectra of compound **5** in solvents of different polarities are shown in Fig. 1. The spectra exhibit two main bands, whose maxima are located in the between 220 and 350 nm, and larger than 350 nm. The short wavelength bands between 220 and 350 nm are attributed to carbazole moiety whereas the long wavelength bands

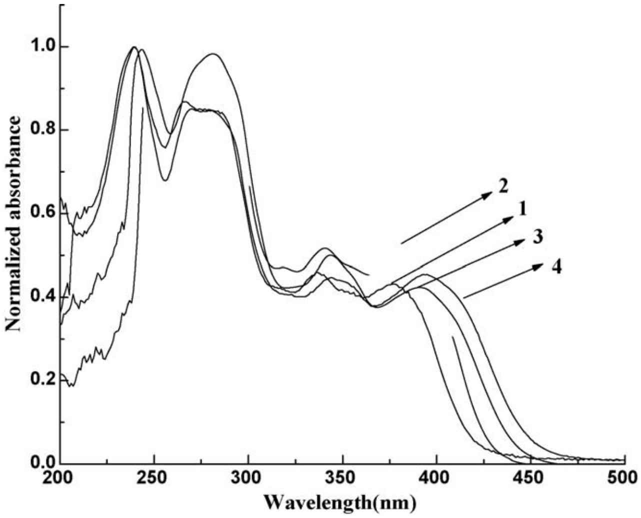


Fig. 1. Normalized absorption spectra of compound **5** in various solvents: (1) diethyl ether, (2) tetrahydrofuran, (3) chloroform, (4) ethanol.

larger than 350 nm are assigned to ICT transitions from carbazole moiety to carbonyl group moiety. The absorption spectra of larger than 350 nm show minimal dependence on the solvent polarity with red shift of about 17 nm from 378 nm in diethyl ether to 395 nm in ethanol. So, the solvatochromism displayed by the absorption spectra is negligible.

Typical fluorescence emission spectra of compound **5** are shown in Fig. 2. It is noted that with the increasing of the solvent polarity, the fluorescence emission spectra dramatically shift from 430 nm in non-polar cyclohexane to 542 nm in a strongly polar solvent, methanol. The shift of fluorescence spectra is larger than that of the absorption spectra, which indicates that intensively photoinduced ICT takes place (refer to Scheme 2) within the molecule in the singlet excited state. The distinctly solvatochromic effect can be attributed to the decrease of the energy in the excited singlet state with the increase of the solvent polarity.

In summary, carbazole-based compound **5** with ICT character is successfully synthesized and characterized. The solvatochromism exhibited by the compound is also discussed. Compound **5** can be used as a new class of fluorescent probe or biosensor due to its sensitivity to the local microenvironment such as solvent polarity.

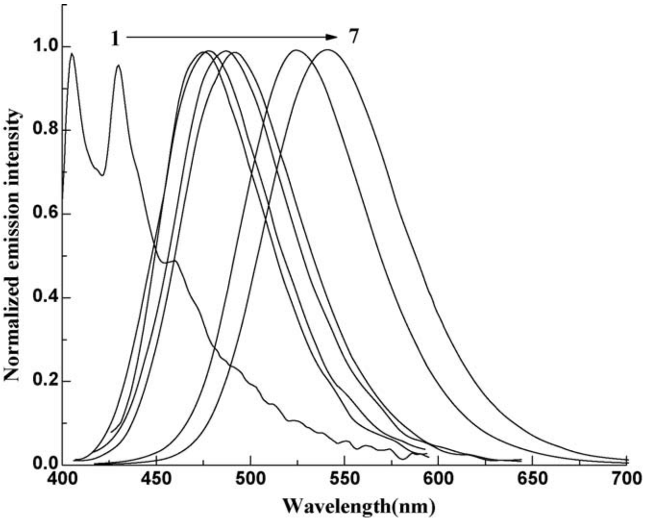
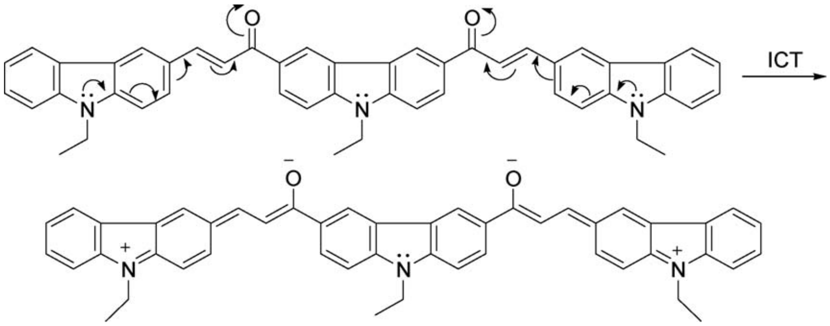


Fig. 2. Normalized emission spectra of compound **5** in various solvents: (1) cyclohexane, (2) chloroform, (3) acetone, (4) *N*,*N*-dimethylformamide, (5) acetonitrile, (6) ethanol, (7) methanol. The arrow direction indicates increasing solvent polarity.



Scheme 2. ICT process of compound **5**.

Acknowledgments

This work was supported by the National Science Foundation of China (No. 20875059) and the Youth Science Foundation of Shanxi Province (No. 20051005).

References

[1] H.X. Shao, X.P. Chen, Z.X. Wang, et al. J. Lumin. 127 (2007) 349.
[2] S.M. Song, D. Ju, J.F. Li, et al. Talanta 77 (2009) 1707.
[3] A. Mallick, P. Purkayastha, N. Chattopadhyay, J. Photochem. Photobiol. C: Photochem. Rev. 8 (2007) 109.
[4] S.L. Wang, T.I. Ho, J. Photochem. Photobiol. A: Chem. 135 (2000) 119.
[5] S.L. Wang, J.M. Lin, Chem. Phys. Lett. 444 (2007) 71.
[6] J.F. Callan, A.P. de Silva, J. Ferguson, et al. Tetrahedron 60 (2004) 11125.
[7] J. Kim, T. Morozumi, H. Nakamura, Tetrahedron 64 (2008) 10735.
[8] A.P. Kulkarni, Y. Zhu, A. Babel, et al. Chem. Mater. 20 (2008) 4212.
[9] A.P. Kulkarni, P.T. Wu, T.W. Kwon, et al. J. Phys. Chem. B 109 (2005) 19584.
[10] P.F. Wang, Z.Y. Xie, S.W. Tong, et al. Chem. Mater. 15 (2003) 1913.
[11] G. Kwak, S. Wang, M.S. Choi, et al. Dyes Pigments 78 (2008) 25.
[12] J.L. Xu, X.F. Liu, J. Lv, et al. Langmuir 24 (2008) 4231.
[13] S.J.K. Pond, O. Tsutsumi, M. Rumi, et al. J. Am. Chem. Soc. 126 (2004) 9291.
[14] A. Abbotto, L. Beverina, R. Bozio, et al. Org. Lett. 4 (2002) 1495.
[15] I.K. Moon, C.S. Choi, N. Kim, Polymer 48 (2007) 3461.
[16] S.S. Palayangoda, X. Cai, R.M. Adhikari, et al. Org. Lett. 10 (2008) 281.
[17] S. Grigalevicius, Synthetic Met 156 (2006) 1.
[18] Y. Liu, M. Nishiura, Y. Wang, et al. J. Am. Chem. Soc. 128 (2006) 5592.
[19] Y. Qian, G.M. Xiao, G. Wang, et al. Dyes Pigments 71 (2006) 109.
[20] D.X. Cao, Z.Q. Liu, G.Z. Li, et al. J. Mol. Struct. 874 (2008) 46.
[21] L.H. Feng, C.H. Zhang, H.Y. Bie, et al. Spectrochim. Acta A 61 (2005) 1171.
[22] C.H. Deng, M. Ding, Z.B. Wang, et al. Chin. J. Hefei Univ. (Nat. Sci.) 14 (2004) 48.
[23] E. Pretsch, P. Bühlmann, C. Affolter, G.B. Rong, Rong Translated Structure Determination of Organic Compounds Tables of Spectral Data, East China University of Science and Technology Publishing House, 2002, p. 82.