

Photophysical processes of some carbazole derivatives

Yiming Mo, Fenglian Bai *, Zhuting Wang

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Abstract

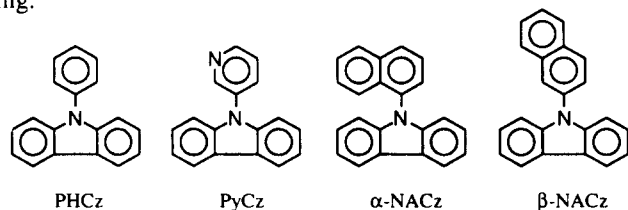
The photophysical properties of phenylcarbazole (PHCz), α -naphthylcarbazole (α -NACz), β -naphthylcarbazole (β -NACz) and *N*-(3-pyridyl)-carbazole (PyCz) were studied. α -NACz and β -NACz exhibit twisted intramolecular charge transfer fluorescence in polar solvents. The fluorescence of the carbazole derivatives can be quenched by electron donors and acceptors, and the quenching effects follow the Stern–Volmer equation. The existence of exciplexes is observed between the carbazole derivatives and electron acceptors, such as *p*-dicyanobenzene, dimethylterephthalate and benzanilide.

Keywords: Carbazole derivatives; Twisted intramolecular charge transfer; Stern–Volmer equation

1. Introduction

Carbazole and its derivatives have been studied extensively. The polymeric semiconductor poly(*N*-vinylcarbazole) can be used as a photoreceptor for copiers and photoconductive thermoplastic films. The charge transfer complex poly(*N*-vinylcarbazole)-2,4,7-trinitrofluorenone, which is characterized by a high sensitivity, broad spectral response and excellent stability, has been widely used in electrophotography [1]. Rettig [2] and Rettig and Zander [3] have found that the *N*-aryl-substituted derivatives of carbazole exhibit twisted intramolecular charge transfer (TICT) with an increase in the electron-accepting ability of the *N*-aryl moiety.

In this paper, we present the results of a study on the photophysical processes of phenylcarbazole (PHCz), α -naphthylcarbazole (α -NACz), β -naphthylcarbazole (β -NACz) and *N*-(3-pyridyl)-carbazole (PyCz). All of these carbazole derivatives were synthesized in our laboratory; the photophysical processes were studied using steady state and transient fluorescence spectroscopy and fluorescence quenching.



* Corresponding author.

2. Experimental details

All of the compounds were synthesized by copper-catalysed reactions of carbazole with iodoaromatic molecules; the compounds were purified by elution through a silica gel column [4] and characterized by IR spectroscopy, mass spectrometry (MS), nuclear magnetic resonance (NMR) spectroscopy, etc. Dimethylterephthalate (DMTP), *p*-dicyanobenzene (DCNB) and benzanilide (BZA) were of reagent grade (Beijing Chemical Plant) and were purified by recrystallization. Other reagents and solvents were all of reagent grade (Beijing Chemical Plant) and exhibited no fluorescence interference.

Steady state fluorescence spectra were recorded on a Hitachi MPF-4 fluorometer. The fluorescence decay was determined on a Horiba NAES-1100 nanosecond fluorometer. Absorption spectra were measured on an HP-8451A UV-visible spectrometer.

All experiments were carried out at 25 °C. For the fluorescence spectra, the excitation wavelength was 330 nm.

3. Results and discussion

The absorption and fluorescence spectra of PHCz, PyCz, α -NACz and β -NACz in polar and non-polar solvents were compared. The peak positions of the absorption spectra of the carbazole derivatives in different solvents are similar, without an obvious change as a function of the solvent polarity. The emission spectra of PHCz and PyCz exhibit a slight

Table 1

The maxima (λ_{\max} (nm)) and halfwidths ($\Delta\nu$ (cm^{-1})) of the fluorescence spectra (emission) of various *N*-aryl-carbazoles in different solvents

Solvent	PHCz	α -NACz	β -NACz	PyCz
	λ_{\max} ($\Delta\nu$)	λ_{\max} ($\Delta\nu$)	λ_{\max} ($\Delta\nu$)	λ_{\max}
Cyclohexane	344, 358 (2250)	367 (2710)	362 (2190)	336, 349
Benzene	349, 364 (2430)	378 (2910)	364 (2600)	340, 354
Ethyl acetate	347, 362 (2360)	383 (3280)	368 (3060)	338, 352
Dichloroethane	350, 364 (2420)	395 (3345)	378 (3240)	–
Ethanol	347, 361 (2415)	393 (3750)	373 (3515)	340, 383
Acetonitrile	348, 363 (2495)	406 (4350)	388 (3680)	341, 355

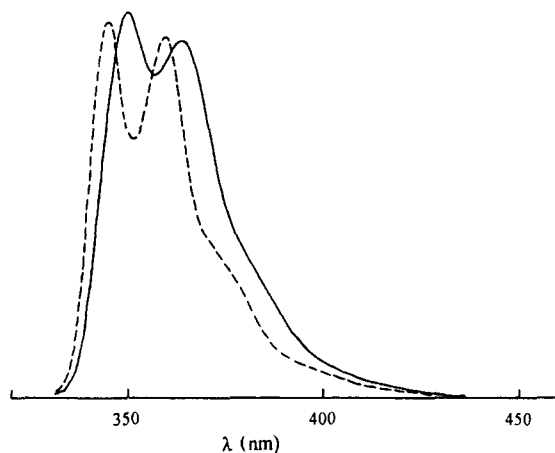


Fig. 1. Fluorescence spectra of PHCz in cyclohexane (broken line) and acetonitrile (full line).

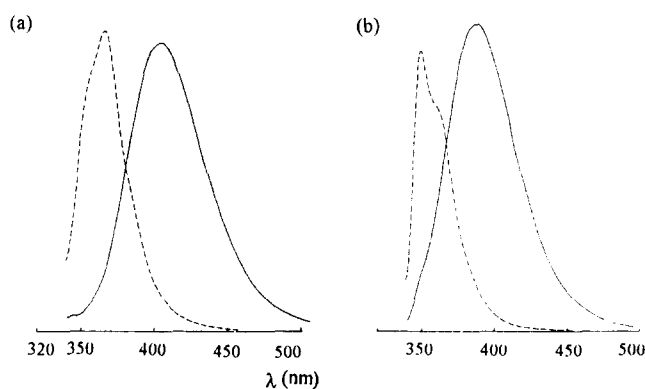
Fig. 2. Fluorescence spectra of α -NACz (a) and β -NACz (b) in cyclohexane (broken line) and acetonitrile (full line).

Table 2

The fluorescence lifetime τ (ns) of carbazole derivatives in different solvents

Solvent	PHCz	α -NACz	β -NACz	PyCz	EtCz
Cyclohexane	6.2	4.9	4.5	–	–
Benzene	6.3	4.8	4.0	3.1	7.8
Ethyl acetate	5.8	4.9	3.7	4.1	–
Dichloroethane	6.6	6.5	4.4	–	–

change in different solvents [5] (Fig. 1). In contrast, a large red shift, loss of fine structure and broadened band are

observed in the emission spectra of α -NACz and β -NACz, and the fluorescence halfwidth $\Delta\nu$ (Table 1) increases with increasing solvent polarity (Fig. 2). The spectral characteristics indicate the existence of a TICT state in α -NACz and β -NACz. The emission spectra of α -NACz and β -NACz exhibit only one fluorescence band arising from the TICT state [2,3] due to the steric hindrance by the naphthyl moiety.

Rettig and Zander [3] predicted that the TICT emission will be observed if the molecular system satisfies Eq. (1)

$$E(\text{TICT}) - E(\text{LE}) < 0 \quad (1)$$

$$E(\text{TICT}) \approx \text{IP}(\text{D}) - \text{EA}(\text{A}) + C + \Delta E_{\text{solv}} \quad (2)$$

$E(\text{TICT})$ and $E(\text{LE})$ are the energies of the lowest TICT state and the lowest locally excited state respectively. $\text{IP}(\text{D})$ and $\text{EA}(\text{A})$ are the ionization potential and electron affinity of the donor and acceptor moieties of the molecule respectively. C is the Coulomb energy and ΔE_{solv} is the interaction between the charge-separated molecule and the polar solvent. On going from PHCz to α -NACz and β -NACz, the donor moiety is the same, but the electron-accepting ability is enhanced. Therefore TICT emission of α -NACz and β -NACz can be seen in polar solvents. The temperature effect, i.e. the fluorescence emission shifts to the blue with increasing temperature, provides further support for the existence of a TICT state.

Table 2 lists the fluorescence lifetimes of the carbazole derivatives in different solvents. It can be seen that the fluorescence lifetimes of carbazole derivatives containing donating or accepting groups in the 9 position are shorter than that of *N*-ethyl carbazole (EtCz). It can also be seen that the solvent polarity has little effect on the lifetime.

The fluorescence of carbazole derivatives is quenched by electron donors, such as triethylamine (TEA), bipyridine (BPy) and diethylamine (DEA). The quenching effect follows the Stern–Volmer equation

Table 3

 $k_q \times 10^{-9}$ ($\text{M}^{-1} \text{s}^{-1}$) values of carbazole derivatives quenched by amines

Carbazole	TEA	BPy	DEA
PHCz	0.21	0.59	–
α -NACz	0.85	0.58	0.04
β -NACz	0.62	0.98	0.48

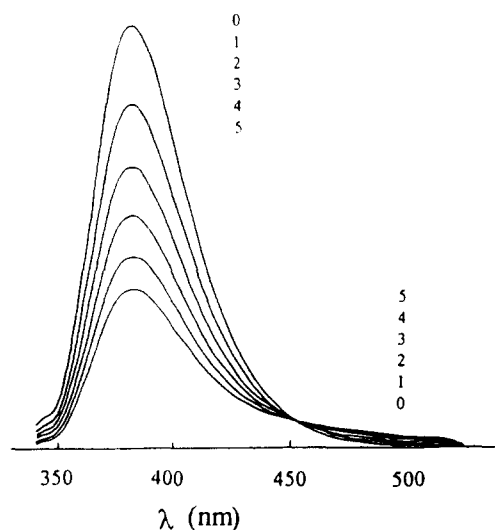


Fig. 3. Fluorescence spectra of α -NACz in ethyl acetate at different concentrations of DMTP (M): 0, 0; 1, 5.15×10^{-3} ; 2, 1.09×10^{-2} ; 3, 1.77×10^{-2} ; 4, 2.58×10^{-2} ; 5, 3.5×10^{-2} .

Table 4
 $k_q \times 10^{-9}$ ($M^{-1} s^{-1}$) values of carbazole derivatives quenched by acceptors

Carbazole	DMTP	DCNB	BZA
PHCz	15.4	18.4	124.1
PyCz	13.7	–	–
α -NACz	12.0	16.7	39.0
β -NACz	18.0	19.3	46.3
EtCz	13.1	–	–

Table 5
The change in dipole moment (D)

PHCz	α -NACz	β -NACz
–	15.2	10.1
PHCz–DMTP	α -NACz–DMTP	β -NACz–DMTP
13.1	20.0	19.2

$$F_0/F = 1 + K_{SV}[Q] \quad (3)$$

$$K_{SV} = k_q \tau \quad (4)$$

The quenching rate constants (k_q) were obtained according to the Stern–Volmer equation (Table 3). The ionization potentials of TEA, BPy and DEA are 7.50 eV, 9.3 eV and 8.01 eV respectively.

The fluorescence of carbazole derivatives can also be quenched by electron acceptors: DCNB, DMTP and BZA.

When DMTP is added to a solution of carbazole derivatives, the emission is quenched. Meanwhile, a new structureless emission band appears in the longer wavelength region. The emission intensity of the new band increases with increasing concentration of DMTP and the spectrum exhibits an isoemissive point (Fig. 3). The excitation spectra measured at different emission wavelengths with or without DMTP are identical. This indicates that exciplexes are formed between carbazole derivatives and DMTP. The addition of DCNB or BZA to a solution of carbazole derivatives produces the same results (Table 4). The k_q value of carbazole derivatives quenched by BZA is abnormally large; this is because BZA exhibits competitive absorption with the fluorescence of the carbazole derivatives at the excitation wavelength of 330 nm.

The dipole moment change accompanying the fluorescence transition of the exciplex was calculated using the Lippert equation [6] (Table 5).

4. Conclusions

The fluorescence of carbazole derivatives can be quenched by donor and acceptor molecules whether or not the TICT state exists. The quenching ability mainly depends on the ionization potential of the donors and the electron affinity of the acceptors.

Acknowledgments

This work was financially supported by the National Nature Science Foundation of China, the Foundation of the Chinese Academy of Sciences and the Photochemistry Laboratory, Institute of Photographic Chemistry, Academia Sinica.

References

- [1] R.H. Epping, W.F. Berg and K. Hanffe (eds.), *Current Problems in Electrophotography*, Walter de Gruyter, Berlin, 1972, p. 215.
- [2] W. Rettig, *Angew. Chem. Int. Ed. Engl.*, 25 (1986) 971.
- [3] W. Rettig and M. Zander, *Chem. Phys. Lett.*, 87 (1982) 229.
- [4] Z. Zhang, Z.B. Chen, Q.S. Du, Y.L. Feng and C.Z. Xia, *Youji Huaxue*, 9 (1989) 555 (in Chinese).
- [5] F.L. Bai, X.J. Jia, L. Fan, Z.B. Chen, Z. Zhang and Z.Z. Xia, *J. Photochem. Photobiol. A: Chem.*, 63 (1992) 187.
- [6] E. Lippert, *Z. Naturforsch., Teil A*, 10 (1955) 544.