Synthesis and Fluorescence Quenching of Copolymer Containing 3, 4, 9, 10-Perylenetetracarboxyl Diimide Side Chains

Zhao ZHANG[1]*, Zhao Bin CHEN[1], Feng Lian BAI[2], Yue Ping ZHANG[2], Yi Ming MO[2], Min ZHENG[2], Xiao Lin YAN[2], Yu liang LI[2]

[1]Department of Chemistry, Shanxi University, Taiyuan 030006
[2]Lab of Organic Solid, Institute of Chemistry, Academy Sinica, Beijing 100080

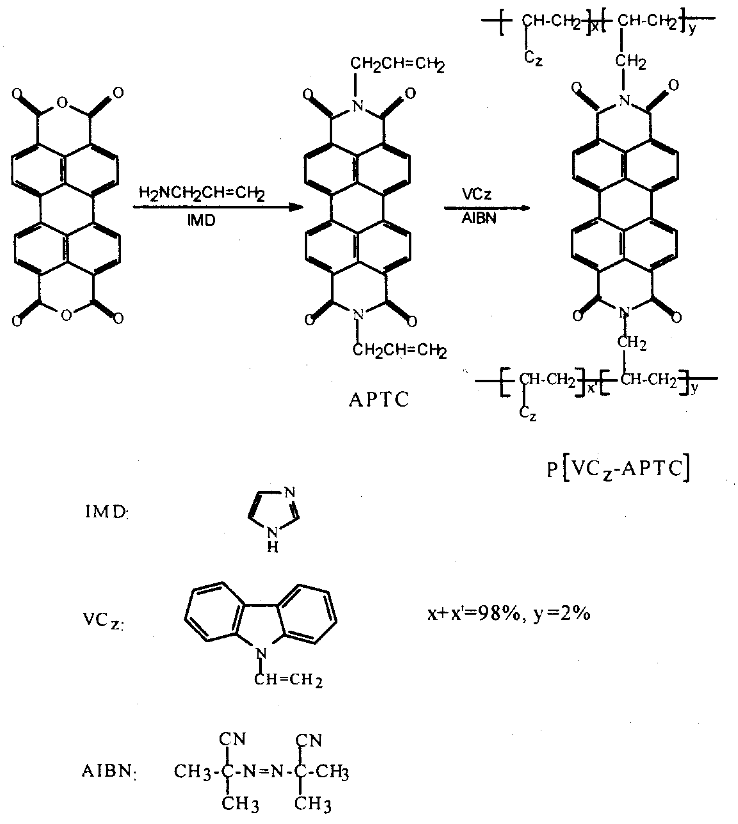
Abstract: A photoluminescence material, copolymer of N-vinylcarbazole (VCz) and N, N′ -bisallyl-3, 4, 9, 10-Perylenetetracarboxyl diimide (APTC) chromophores P(VCz-APTC) was synthesized. The fluorescence quenching of P(VCz-APTC) by fullerene (C_{60}) and triethylamine was also studied.

Keywords: 3, 4, 9, 10-Perylenetetracarboxyl diimide, copolymer, fluorescence quenching.

In recent years, the studies of various organic photo-luminous and photoconductive materials used in light emitting diodes (LED)[1], photodiodes, light emittinelectrochemical cells[2, 3] and plastic laser[4] have been an active area in both theoretical and practical research. As photosensitive electron transfer material, polyvinylcarbazole (PVK) possesses slow potentiality since it has only a slight sensitivity in the visible region. However, it is possible to sensitize the photo-conduction of PVK film by addition of a small amount of certain dyes or electron acceptor compounds. N, N′ -Bis –substituded-3, 4, 9, 10-perylenetetracarboxyl diimide (PTC) is one of fundamental organic compounds as photo-conductor, emitting dye for LED materials[5, 6]. A copolymer of N-vinylcarbazole (VCz) and N, N-bisallyl-3, 4, 9, 10-perylenetetracarboxyl diimide (APTC) chromophores P(VCz-APTC), which is a potential LED light emitting material, was synthesized. The photo-conductivity and photoluminescence active center doped with C_{60} in some polymers have been reported[7]. It is helpful to study the interaction between P(VCz-APTC) and C_{60} for understanding the mechanism of application in LED. The fluorescence quenching technique is an effective method for the study of the mechanism of molecular interaction, energy transfer and charge transfer[8]. The synthesis of P(VCz-APTC) are shown in **scheme 1.**

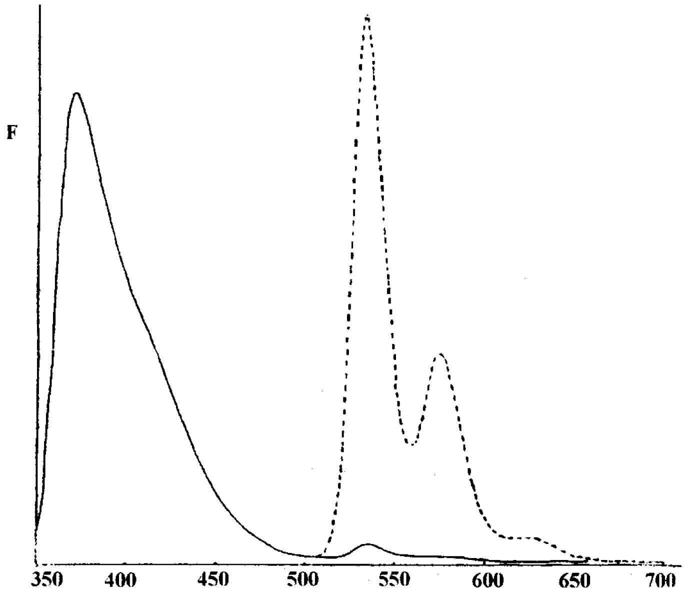
APTC was synthesized according to the literature[9] and the synthesis of P(VCz-APTC) are described as follows: Synthesis of APTC: the mixture of 3, 4, 9, 10-perylenetetracarboxylic dianhydride (1.0g), allylamine hydrochloride (10.2g) and IMD (5.0g) was heated at 160℃ for 4 hours (N_2 atmosphere). The ethanol (100mL) was added to the reaction solution, and the ethanol solution was acidified by addition of the hydrochloric acid (2mol/L, 300mL) to give APTC: 58% yield, mp>350℃, IR(cm^{-1}), 3050, 2925, 2850, 1695, 1660, 1590, 1575, 1530, 1470, 1430, 1370, 1345, 1310, 1300, 1270, 1170, 1125, 1002, 988, 915, 899, 850, 810, 795, 750. IR is identical with that described in literature. Synthesis of P(VCz-APTC): the solution of VCz (2.5g), APTC (0.12g) and benzene (100mL) was heated at 60℃ under N_2, and then AIBN (0.0025g) was added to the reaction mixture. The reaction was carried on 2 hours at 78℃. The reaction solution was cooled to room temperature and poured into 100mL methanol to precipitate P(VCz-APTC) 76% yield, M:1.6×10^5.

Scheme 1. The synthesis of P(VCz-APTC)



The fluorescence spectrum of P(VCz-APTC) was measured in THF solution. Two emission bands which emitted from carbazole rings (Cz) and PTC chromophores could be observed in P(VCz-APTC) THF solution when the excitation wavelength of 350 nm, the absorption wavelength of Cz, was used (**Figure.1**). The PTC emission at wavelength of 500~600 nm is due to the excited states energy which is transferred from Cz to PTC. When excitation wavelength was selected at 500 nm, the emission band of PTC could only be obtained. The charge transfer states was not observed.

Figure 1 The emission spectra of P(VCz-APTC) in THF solution.
— λ mex 350 nm
··· λ mex 500 nm



The fluorescence spectrum of PTC can be respectively quenched by adding C_{60} or Et_3N. Both quenching were following Stern-Volmer equation:

$$F_0/F=1+K_{sv}\,(Q)$$
$$K_{sv}=K_q\,\tau_0$$

The results are listed in **Table 1**

Table 1. The quenching results of P(VCz-APTC) by C_{60} and Et_3N

Quencher	$K_{sv}(M^{-1})$	$Kq(M^{-1}S^{-1})$	τ_0 of PTC(ns)
Et_3N	50.5	1.3×10^{10}	4.01
C_{60}	1.2×10^{4}	3.1×10^{12}	4.01

The lifetime of PTC were measured by single photon counting method. From **Table 1**, we can see that the fluorescence spectrum of PTC quenched by Et_3N is a dynamic process because lifetime of PTC was also quenched at the same time of the emission intensity quenched by Et_3N. The K_q of Et_3N is $1.3\times10^{10}\ M^{-1}S^{-1}$ which is a typical diffusion controlled quenching process. The lifetime remained unchanged when the fluorescence of PTC was quenched by C_{60}. So, this quenching is static. The K_q value of C_{60} is dramatically large in $10^{12}M^{-1}S^{-1}$ order, and is much greater than K_q of Et_3N. It indicated the existence of strong interaction between PTC chromophore and C_{60} molecular. The interaction force must come from the charge transfer and $\pi - \pi$ interaction between them. Further detailed studies on photo-luminous characteristics of P(VCz-APTC) will be reported shortly.

Acknowledgments

The project was supported by Foundation of CAS, Research Foundation of Director of ICCAS and Returned Student Foundation of Shanxi.

References

1. G. Yu, *Synth. Met.*, **1996**, *80*, 143.
2. O. Rafik, *Pure and Appl. Chem.*, **1982**, *60*, 1047.
3. J. H. Burroughes, D. D. C. Bradly, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature*, **1990**, *347*, 539.
4. F. Hide., M. A. Diaz Garcia, B. J. Schwartz, A. J. Heeger, *J.Chem. lett.*, **1996**, *256*, 424.
5. M.P.O′ Neil, M. P. Niemczyk, W. A. Svec, D. Gosztola, G. L. Gaines, M.R.Wa Sielewski, *Science*, **1992**, *257*, 63.
6. A. Rademacher, S. Markle and H. Langhals, *Chem. Ber.*, **1982**, *115*.2927.
7. Y. Wang, R.West, C.H. Yuan, *J. Am.Chem.Soc.*, **1993**, *115*, 3844.
8. F. Bai, X. Jia, L. Fan, Z. Chen, Z. Zhang and Z.Xia, *J.Photochem., Photobiol, A: Chem.*, **1992**, *63*, 187.
9. S. Demmig and H. Langhals, *Chem. Ber.*, **1988**, *121*, 225.

Received 12 July 1999