

# The Interaction Between Conjugated Polymer and Fullerenes

MIN ZHENG, FENGLIAN BAI, FENGYING LI, YULIANG LI, DAOBEN ZHU

Institute of Chemistry, Laboratory of Organic Solids, Chinese Academy of Sciences, P.O. Box 2709, Group 108, Beijing 100080, People's Republic of China

Received 14 August 1997; accepted 4 November 1997

**ABSTRACT:** The fluorescence of Poly(2-methoxy,5-(2'-ethylhexyloxy)-p-phenylene-vinylene) (MEH-PPV) quenched by fullerenes was examined, and the results indicate that this quenching is not dynamic. Strong interaction in the excited state between them may be caused by the photoinduced charge transfer and  $\pi$ - $\pi$  conjugated system interaction. More direct and convincing evidence of the charge transfer complex are presented. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 599–603, 1998

**Key words:** MEH-PPV; fullerenes; fluorescence quenching; charge transfer complex

## INTRODUCTION

Recently, conducting polymers have received much attention due to their rich photophysics and potential applications, such as nonlinear optical and light-emitting devices.<sup>1–4</sup> Among these conjugated polymers, the class of substituted polyphenylene-vinylens are known to exhibit relatively strong photoluminescence (PL). MEH-PPV especially has been proven to be a very interesting material because of its high PL efficiency and its solubility in common organic solvents. The photoconductivity and fluorescence of MEH-PPV film doped with C<sub>60</sub> have already been reported.<sup>5,6</sup> The study of the mechanism of the interaction between MEH-PPV and fullerenes is helpful to understand the optical property of MEH-PPV. So far, there is not any report on the interaction of fullerenes and MEH-PPV diluted solutions by fluorescence spectrophotometry. The

fluorescence quenching technique is an effective method for the study of the mechanism of molecular interaction, energy transfer, or charge transfer.

In this article the fluorescence quenching of MEH-PPV by C<sub>60</sub> and its derivatives were examined, and the results showed that strong interaction exists between MEH-PPV and C<sub>60</sub>. More direct and convincing evidence of the photoinduced charge transfer complex formation in the excited state between MEH-PPV and 1,2-(1',1',2',2'-Tetracyanomethanoxymethano)-C<sub>60</sub> (TCM-C<sub>60</sub>) were presented.

## EXPERIMENTAL

### Materials

MEH-PPV (Scheme 1) was synthesized in this laboratory according to the reported method<sup>7</sup> and characterized by elemental analysis, IR, NMR, etc. The molecular weight (GPC vs. polystyrene) is about 200,000. The preparation method of C<sub>60</sub> and its derivative TCM-C<sub>60</sub> (Scheme 1) was described in elsewhere.<sup>8</sup>

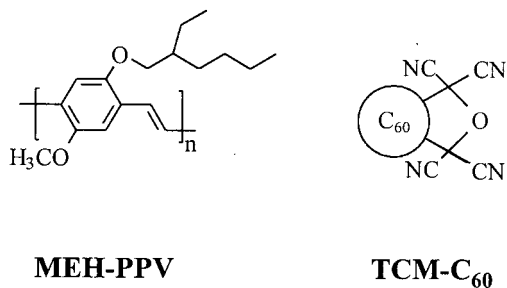
Correspondence to: F. Bai.

Contract grant sponsors: National Natural Science Foundation of China, Foundation CAS, Photochemistry Lab IPC-CAS, and Research Foundation of Molecular Science Centre.

*Journal of Applied Polymer Science*, Vol. 70, 599–603 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/030599-05



**Scheme 1** The chemical structure of MEH-PPV and TCM-C<sub>60</sub>.

MEH-PPV was dissolved in benzene, and the concentration of this solution was  $7.5 \times 10^{-5} M$ . Then the solution was diluted with benzene containing different contents of C<sub>60</sub>. The final concentration of MEH-PPV was  $2.5 \times 10^{-5} M$  with different amounts of C<sub>60</sub>, which were indicated in the text. The mixed solution was stirred for about 10 min then stood by for fluorescence measurement.

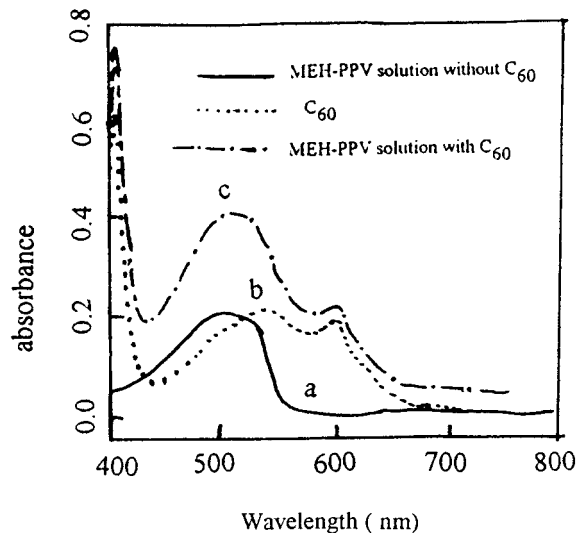
## INSTRUMENTATION

The UV-visible absorption spectra were taken on a Hitachi 340 UV-VIS spectrometer. The steady-state PL emission and excitation spectra were obtained on a Hitachi MPF-4 fluorescence spectrophotometer. The fluorescence lifetimes of MEH-PPV were recorded on an Horiba NAES-1100ns spectrometer with an excitation wavelength of 490 nm. All the spectra were obtained at room temperature.

## RESULTS AND DISCUSSIONS

Figure 1 shows the comparison of UV-VIS spectra of C<sub>60</sub> and MEH-PPV solution in benzene with and without C<sub>60</sub> solution. The concentration of MEH-PPV and C<sub>60</sub> are  $1.3 \times 10^{-5} M$  and  $2.3 \times 10^{-4} M$ , respectively.

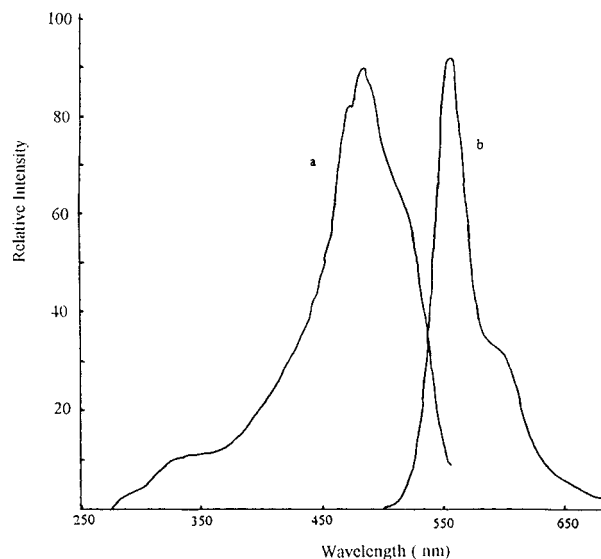
From Figure 1 one can see that although the intensity of every peak of mixed solution (c) is slightly higher than the sum of the intensity of the corresponding peak of MEH-PPV (a) and C<sub>60</sub> (b), the absorption spectrum of the mixed solution (c) is almost overlapped on both spectra. The new absorption band of the charge transfer complex of MEH-PPV and C<sub>60</sub> was not observed directly in



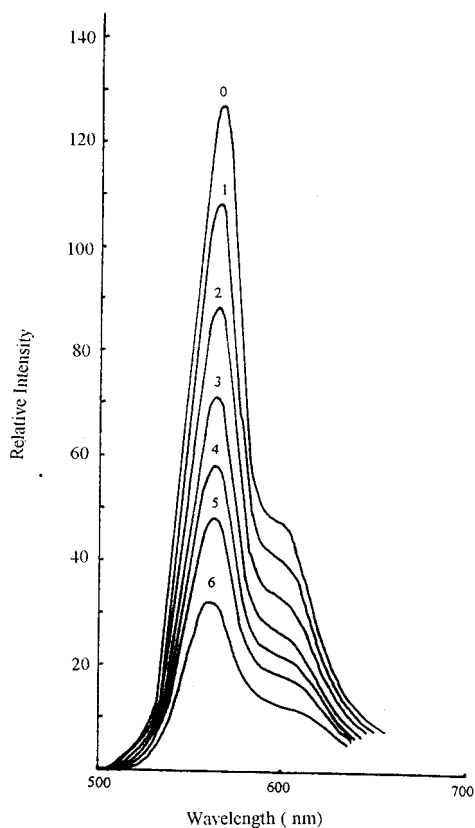
**Figure 1** UV spectra of C<sub>60</sub> ( $2.3 \times 10^{-4} M$ ) and MEH-PPV ( $1.3 \times 10^{-5} M$ ) solution in benzene. (a) MEH-PPV solution without C<sub>60</sub>; (b) C<sub>60</sub>; (c) MEH-PPV solution with C<sub>60</sub>.

the ground state in our experiment. This may be due to the low concentration and the small value of the molar extinction coefficient of the charge transfer complex. Further study is being carried out.

Figure 2 shows the excitation and emission spectra of MEH-PPV in benzene solution with the concentration of  $1.3 \times 10^{-5} M$ . The peak of



**Figure 2** The excitation (a) and emission (b) spectra of MEH-PPV solution in benzene ( $1.3 \times 10^{-5} M$ ).



**Figure 3** The fluorescence of MEH-PPV solution ( $2.5 \times 10^{-5}M$ ) quenched by  $C_{60}$  solution in benzene. The concentration of  $C_{60}$  is 0.  $0M$ ; 1.  $0.69 \times 10^{-4}M$ ; 2.  $1.38 \times 10^{-4}M$ ; 3.  $2.07 \times 10^{-4}M$ ; 4.  $2.76 \times 10^{-4}M$ ; 5.  $3.45 \times 10^{-4}M$ ; 6.  $4.6 \times 10^{-4}M$ .

emission is at about 560 nm, with a shoulder at about 600 nm.

The fluorescence of MEH-PPV can be quenched by  $C_{60}$ . Keeping the concentration of MEH-PPV unchanged, the concentrations of  $C_{60}$  are increased gradually. The quenched fluorescence are shown in Figure 3.

Due to the competition absorption of  $C_{60}$  at the excitation and emission wavelength of MEH-PPV, an equation to calibrate the fluorescence intensity to be used is shown below:

$$F = F_{em} \cdot \frac{1 - e^{-\epsilon_1 C_1 l}}{\epsilon_1 C_1} \times \frac{\epsilon_1 C_1 + \epsilon_2 C_2}{1 - e^{-(\epsilon_1 C_1 + \epsilon_2 C_2)l}} \cdot \frac{\epsilon_3 C_3 l}{1 - e^{-\epsilon_3 C_3 l}} \quad (1)$$

where  $F_{em}$  is the experimental fluorescence intensity;  $F$  is the fluorescence intensity after calibra-

tion;  $C_1$ ,  $\epsilon_1$  and  $C_2$ ,  $\epsilon_2$  are the concentration and molar extinction coefficients of MEH-PPV and  $C_{60}$  at excitation wavelength ( $\lambda_{ex} = 490$  nm), respectively, while  $C_3$  and  $\epsilon_3$  are the concentration and molar extinction coefficient of  $C_{60}$  at emission wavelength of MEH-PPV ( $\lambda_{em} = 560$  nm).  $l$  is the thickness of the cell. The intensity of fluorescence was quenched remarkably after  $C_{60}$  was added. The quenching follows Stern-Volmer equation:

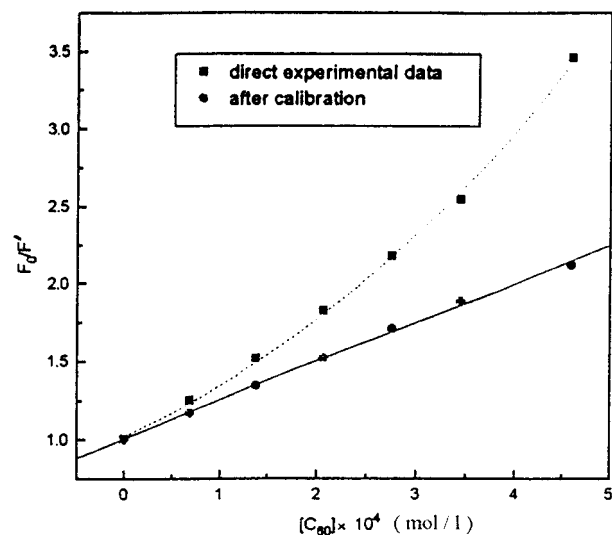
$$F_0/F = 1 + K_{SV}[Q] \quad (2)$$

$$K_{SV} = K_q \times \tau_0 \quad (3)$$

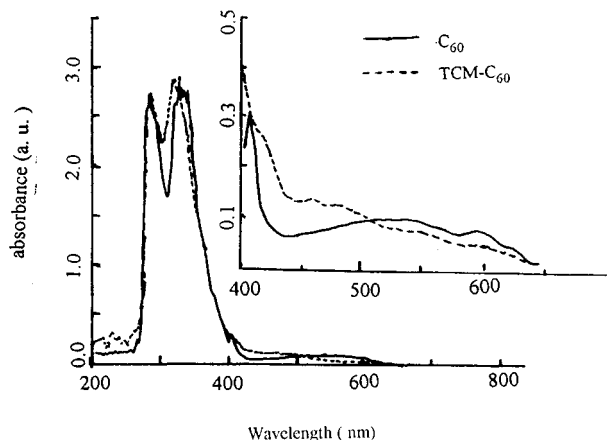
where  $F_0$  is the fluorescent intensity of MEH-PPV without addition of  $C_{60}$ ;  $F$  is the fluorescent intensity with addition of  $C_{60}$ ;  $[Q]$  is the concentration of  $C_{60}$ ;  $K_{sv}$  is the quenching constant;  $K_q$  is the bimolecular quenching constant; and  $\tau_0$  is the lifetime of fluorescent agent without  $C_{60}$ .

Figure 4 demonstrates the dependence of calibrated  $F_0/F'$  on the concentration of  $C_{60}$ .

The quenching constant ( $K_{SV}$ ) of  $C_{60}$  is very large ( $2.5 \times 10^3 M^{-1}$ ), suggesting that strong interaction between MEH-PPV and  $C_{60}$  happens in the excited state. This can be explained by two reasons. On one hand, both MEH-PPV and  $C_{60}$  have a large  $\pi$ -conjugated system in which  $\pi$ - $\pi$  interaction may change the configuration of MEH-PPV.<sup>9</sup> On the other hand, the photo-induced charge transfer from excited MEH-PPV to  $C_{60}$  was rapid. Upon this



**Figure 4** The dependence of  $F_0/F'$  on the concentration of  $C_{60}$ .



**Figure 5** The UV-VIS spectra of  $C_{60}$  (solid) and TCM- $C_{60}$  (dashed) concentration:  $1 \times 10^{-5}M$ .

charge transfer the conjugated polymer system may be dramatically modified and distorted because of the strong electron-lattice interaction in the one-dimensional system.<sup>10</sup> In this system, the process of charge transfer from the  $\pi^*$  band of the photo-excited MEH-PPV to  $C_{60}$  competes with the radiative emission of MEH-PPV.<sup>11</sup> The fluorescence lifetimes of MEH-PPV solution in benzene before and after adding  $C_{60}$  were determined, and the results show that they are independent of the concentration of  $C_{60}$ . This implies that no dynamic quenching happened. The bimolecular quenching constant ( $K_q$ ) of  $C_{60}$  is  $6.6 \times 10^{12}M^{-1}s^{-1}$ .

To verify this interpretation, we also measured the fluorescent quenching of TCM- $C_{60}$  (Scheme 1) to MEH-PPV. TCM- $C_{60}$  has four symmetric strong acceptor groups  $-C\equiv N$ . The electron-accept ability of TCM- $C_{60}$  is much stronger than that of  $C_{60}$ . Figure 5 shows the UV-VIS spectra of  $C_{60}$  and TCM- $C_{60}$ . The concentrations of  $C_{60}$  and TCM- $C_{60}$  in benzene are  $1 \times 10^{-5}M$ . The UV-VIS spectra of cyanated  $C_{60}$  changes little except the reduced molar extinction coefficient from wavelength 500 nm to 700 nm, which is due to the change of the conjugation system.

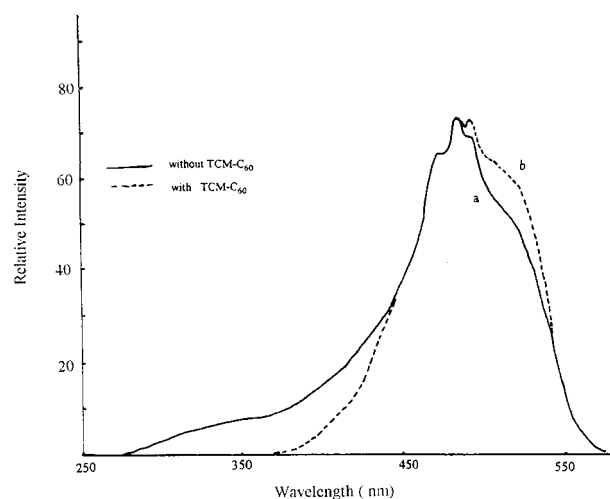
With the same experimental condition as  $C_{60}$ , the fluorescent quenching of TCM- $C_{60}$  was consistent with  $C_{60}$ . However, the quenching ability of TCM- $C_{60}$  is much stronger than that of  $C_{60}$ . Its  $K_{SV}$  and  $K_q$  are  $1.8 \times 10^4M^{-1}$  and  $4.7 \times 10^{13}M^{-1}s^{-1}$ , respectively, and they are larger than that of  $C_{60}$  by almost one order of magnitude due to its stronger ability of accepting electron.

The results above clearly show that the strong interaction between TCM- $C_{60}$  and MEH-PPV ex-

ists in the excited states because TCM- $C_{60}$  has similar  $\pi$ -system structure with  $C_{60}$  and also has more strong electron-accept ability. With the increase of the concentration of TCM- $C_{60}$ , the photo-induced charge transfer complex could be observed. This can be seen from Figure 6. Normalized, the intensity of peak 485 nm, the intensity of peak 520 nm, obviously increases when TCM- $C_{60}$  was added to MEH-PPV. Peak 520 nm partly belongs to the photo-induced charge transfer complex. This is the direct evidence of the charge transfer complex. However, this phenomenon has not been found in the UV-VIS spectrum of the mixed solution of MEH-PPV and TCM- $C_{60}$ , and it is still simply overlapped in the concentration we used.

## CONCLUSION

In summary, the fluorescence of MEH-PPV in solution can be quenched by fullerenes, and this quenching is not dynamic. When MEH-PPV is in the excited state, a strong interaction happens by photo-induced charge transfer. This was verified by the difference of quenching constants of  $C_{60}$  and TCM- $C_{60}$ . The formation of charge transfer complex may distort the conjugation system of polymer in the excited state, but in the ground state further study of this work is still being carried on.



**Figure 6** The normalized PL excitation spectra of MEH-PPV solution ( $2.0 \times 10^{-5}M$ ) (a) without TCM- $C_{60}$  (solid), (b) with TCM- $C_{60}$  ( $0.87 \times 10^{-4}M$ ) (dashed).

This work was financially supported by the National Nature Science Foundation of China and Foundation of CAS, partly supported by Photochemistry Lab IPCCAS and Research Foundation of Molecular Science Centre and Director of ICCAS.

## REFERENCES

1. J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature*, **347**, 539 (1990).
2. D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, **58**, 1982 (1991).
3. G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, **357**, 477 (1992).
4. H. Tomozawa, D. Braun, and A. J. Heeger, *Synth. Met.*, **22**, 63 (1987).
5. C. H. Lee, G. Yu, N. S. Sariciftci, A. J. Heeger, and C. Zhang, *Synth. Met.*, **75**, 127 (1995).
6. K. Lee, N. S. Sariciftci, and A. J. Heeger, *Synth. Met.*, **69**, 445 (1995).
7. U.S. Pat. 5,189,136. Feb. 23, 1993.
8. (a) N. Jagerovic, J. Elguero, and J. L. Aubagnac, *J. Chem. Soc., Perkin Trans.*, **1**, 499 (1996); (b) F. Li, Y. Li, F. Bai, and D. Zhu, *Fullerene Sci. Technol.*, to appear.
9. S. H. Gallagher, R. S. Armstrong, P. A. Lay, and C. A. Reed, *J. Phys. Chem.*, **99**, 5817 (1995).
10. S. Morita, A. A. Zakhidov, and K. Yoshino, *Solid State Commun.*, **82**, 249 (1992).
11. N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, *Science*, **258**, 1474 (1992).