

Communication

# Unexpected Strong Luminescence of Polysiloxanes Containing Carbazolyl and C<sub>60</sub> Moieties as Side Chains

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Two types of polysiloxanes, which contain both C<sub>60</sub> moieties and carbazolyl groups in the side chains with a difference in the numbers of the reacting site on C<sub>60</sub> molecules, were synthesized and their fluorescent properties were studied to distinguish the role of C<sub>60</sub> in the luminescent polymers. Our results demonstrated that when C<sub>60</sub> moieties are bonded to the polymers as multisubstituents but not linked to the luminescent moieties directly, the luminescence of the resultant polymers were still very strong instead of quenching, even the substituted degree is only 1.01.

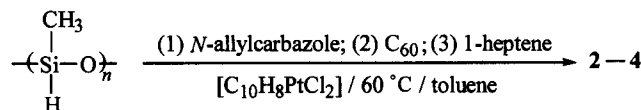
**Keywords** luminescence, C<sub>60</sub>, polysiloxane

As an electronic acceptor, C<sub>60</sub> was normally considered as an effective luminescence quencher,<sup>1</sup> and was utilized to study the quenching interaction between C<sub>60</sub> and the luminescent polymers.<sup>2-4</sup> On the other hand, a few multiadducts of C<sub>60</sub> are luminescent.<sup>5-7</sup> And as to the luminescent polymers, Tang *et al.*<sup>8</sup> recently described that the fluorescence intensity of C<sub>60</sub>-containing poly(1-phenyl-1-butyne) (C<sub>60</sub>-PPB) was about 1.5-fold higher than that of the pure poly(1-phenyl-1-butyne) (PPB) instead of quenching. However, the luminescent studies on C<sub>60</sub> moieties and C<sub>60</sub>-containing polymers are still very scarce. In this paper, a new kind of polysiloxanes (2-4, the structures are shown in Scheme 2) which contain both C<sub>60</sub> moieties and carbazolyl groups, as carbazole is a well known fluorescent molecules,<sup>9</sup> was prepared and also their photoluminescent properties were studied. For comparison, poly{methyl-[3-(9-carbazolyl)propyl]siloxane} (PSX) was also synthesized. The results showed that the fluorescence intensities of 2-4 are very strong instead of quenching.

The synthetic route to polysiloxanes 2-4 is shown in Scheme 1, and C<sub>60</sub> was bonded onto the polysiloxane backbone by the hydrosilylation reaction.<sup>10</sup> Thus, 1 was first reacted with *N*-allylcarbazole for a long period to ensure that carbazolyl molecules could react with 1 completely. The molar ratio of 1 to *N*-allylcarbazole was 2:1, so the resultant 2-4 all contain about 50% carbazolyl groups as side chains in molar ratio as expected. The different

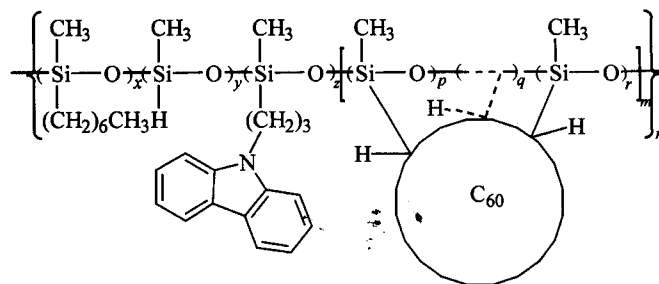
amount of C<sub>60</sub> was added to control the C<sub>60</sub> concentrations in 2-4. In the end, enough quantity of 1-heptene was added to react with the remaining Si-H bond to suppress the possible crosslinking of the polymer when exposed to air or water. Dichlorodicyclopentadiene platinum was chosen as the catalyst because it was soluble in toluene and its catalytic activity stays high during the period of the reaction.<sup>11</sup> PSX was synthesized according to the reported method.<sup>12</sup>

## Scheme 1



2-4 were easily dissolved in THF, toluene, chloroform, dimethylformide, *etc.*, and insoluble in water and alcohol. The contents of C<sub>60</sub> moieties in 2-4 could be easily estimated on the basis of the recovered unreacted C<sub>60</sub> as Sun<sup>13</sup> suggested. The structures of 2-4 were characterized by <sup>1</sup>H NMR, FT-IR, UV-Vis, and the speculated structures of 2-4 were demonstrated in Scheme 2.

## Scheme 2 Speculated structures of 2-4



The component concentrations in the polymer could be calculated from the <sup>1</sup>H NMR peak integration. As the weight concentration of C<sub>60</sub> was known, it could be calculated that how many Si-H bonds reacted with one C<sub>60</sub> molecule (Table 1).

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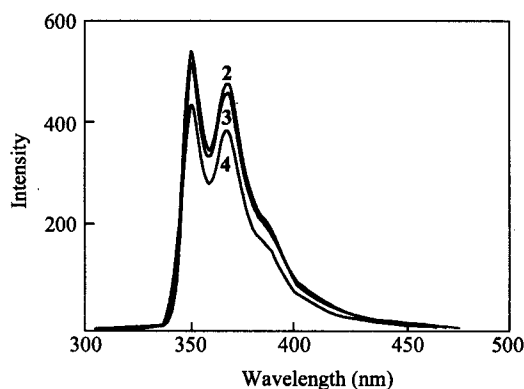
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**Table 1** The ratio of different moieties in polymers and the average number of adduct in one C<sub>60</sub>

Polysiloxane	Molar ratio (Carbazolyl:Si-H:C <sub>60</sub> -H:Heptynyl)	C <sub>60</sub> content (w/w)	Average number of adduct in one C <sub>60</sub> <sup>a</sup>
2	10:0.33:0.23:9.50	0.63%	8.25
3	10:3.28:0.21:6.50	1.25%	3.93
4	10:1.21:0.04:8.82	1.56%	1.01
5		2.1%	1.00

<sup>a</sup> The average number of Si—H bonds linked to one C<sub>60</sub> ball.

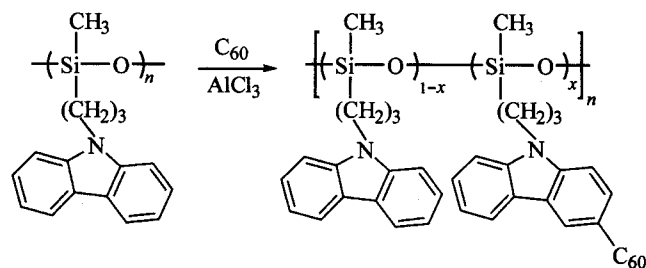
Fluorescence spectra of 2–4 were obtained in a dilute toluene solution at the concentration of  $8 \times 10^{-3}$  mg/mL, with the excited wavelength of 294 nm (Fig. 1). The polymers emit strong blue light readily observable by the naked eyes when excited at 294 nm. In 2–4, many Si—H bonds react with the C<sub>60</sub> cage, and largely perturb the electronic structure of the fullerene, leading to higher excitation energies and large singlet-triplet gaps.<sup>6,7</sup> Thus, 2–4, like the multiple adducts examples of C<sub>60</sub>-PPBs and some multiadducts of C<sub>60</sub> mentioned above, could emit stronger light. From Table 1, it is clear that the number of the Si—H bonds linked to the C<sub>60</sub> moieties decreased in the order of 2 > 3 > 4. This is a unique advantage of polysiloxanes, and also a reason why polysiloxanes were chosen for the research. Only when the substituted degree of C<sub>60</sub> moieties could be controlled in a system, the luminescent properties could be studied directly. Correspondingly, the fluorescence intensities of 2–4 decreased gradually in the same order. It seems that the more Si—H bonds reacted with C<sub>60</sub>, the larger it perturbs the electronic structure of the fullerene. Therefore, the intensities increase from 4 to 2 at the same concentration of the solution.



**Fig. 1** Fluorescent spectra of 2–4 in dilute toluene solutions at the concentration of  $8 \times 10^{-3}$  mg/mL excited at 294 nm with a slit width of 1.5 nm for the excited light and a slit width of 3 nm for the emission light.

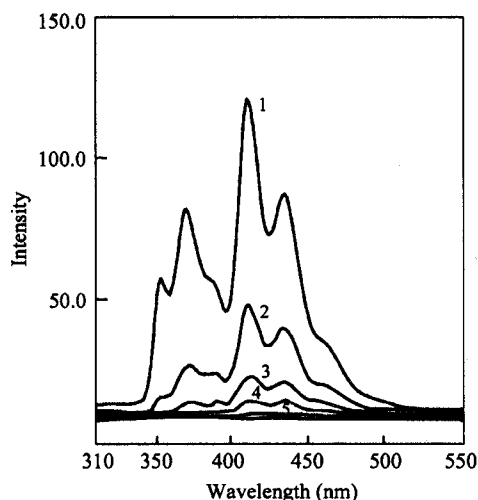
According to the previous reports, if the C<sub>60</sub> moieties are monosubstituents (sometimes even disubstituents) in the luminescent polymers, the photoluminescence of the polymers will be quenched.<sup>2,8</sup> In 4, the average number of Si—H bonds which linked to one C<sub>60</sub> ball is only 1.01, not much higher than 1, but its fluorescent intensity is still

very high. It is difficult to be understood. Therefore, another kind of C<sub>60</sub>-containing polysiloxane (5) was synthesized (Scheme 3), in which C<sub>60</sub> was directly linked to the carbazolyl side chains of PSX through Friedel-Crafts reaction in the solvent of CS<sub>2</sub>, and the C<sub>60</sub> moieties in 5 are monosubstituents similar to that in the cases of Gu<sup>4+</sup> and Thomas.<sup>14</sup> At the same measuring conditions, 5 emits no luminescence just like the cases reported before. The main difference between 4 and 5 lies in the different manner of C<sub>60</sub> linkage: in 4, C<sub>60</sub> moieties are not linked to the carbazolyl groups but directly to the polysiloxane backbone, while in 5, C<sub>60</sub> moieties are directly bonded to the carbazolyl moieties. This difference in the structure may lead to the opposite function of C<sub>60</sub> moieties in the polymers. Thus it may be difficult for the energy to be transferred from the carbazolyl groups to the C<sub>60</sub> moieties in 4, not like in the case of 5, in which this energy transfer results in the luminescence quenching.

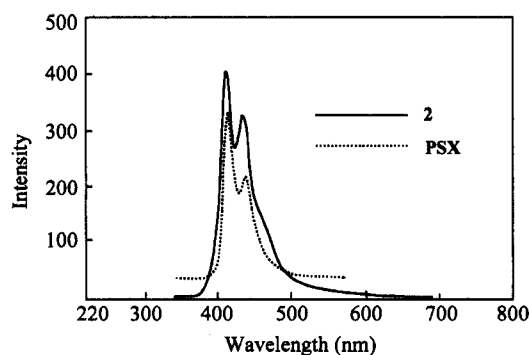
**Scheme 3**

To further investigate the different role of C<sub>60</sub> moieties bonded onto polysiloxane backbone from the doped C<sub>60</sub> molecules, we conducted the quenching experiment of PSX by C<sub>60</sub> (Fig. 2). The results indicate that the fluorescence of PSX can be quenched by C<sub>60</sub>. Namely, the fluorescence of PSX decreased rapidly as the concentration of C<sub>60</sub> increased. The quenching constant ( $K_{sv}$ ) was calculated to be  $6.50 \times 10^4$  M<sup>-1</sup> according to the Stern-Volmer equation. This suggested that the strong interaction between PSX and C<sub>60</sub> happens and leads to the fluorescence quenching.

The film fluorescent spectra of polymers were also conducted. In spite of the film thickness and the different excitation wavelength, the intensity of 2 was higher than that of PSX as demonstrated in Fig. 3. This showed that in solid state, the fluorescence was enhanced after linked with multisubstituent C<sub>60</sub> moieties.



**Fig. 2** Quenching spectra of PSX by  $C_{60}$  in toluene solution the concentration of  $C_{60}$  ( $\times 10^{-4}$  mol/L): (1) 0.8, (2) 1.60, (3) 2.4, (4) 3.2, (5) 4.0, (6) 8.0.



**Fig. 3** Film fluorescent spectra of **2** and PSX spin-coated from THF solutions (**2**: excited at 346 nm with a slit width of 3 nm for the excitation light and a slit width of 3 nm for the emission light; PSX: excited at 234 nm with a slit width of 3 nm for the excitation light and a slit width of 3 nm for the emission light).

In conclusion, two types of polysiloxanes (**2–5**), which contain both carbazolyl and  $C_{60}$  moieties in the side chains, were prepared. In one type (**2–4**), the substituted degree of  $C_{60}$  moieties can be adjusted, and the fluorescence intensities of **2–4** decreased gradually as the substituted degree decreased from **2** to **4**. The luminescent studies show that: when  $C_{60}$  moieties are doped in the lumi-

nescent polymers, or linked to the luminescent moieties of the luminescent polymers directly as monosubstituents, the luminescence of the resultant materials will be quenched as reported in the literatures. However, our results demonstrated that when they are bonded to the polymers as multisubstituents but not linked the luminescent moieties directly, the luminescence would be still strong, even the substituted degree is only 1.01. This phenomenon is unexpected, and not being reported yet. In the further study, we would test the above results by other polymeric systems.

## References

- 1 Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. *Science* **1992**, *258*, 1474.
- 2 Zheng, M.; Bai, F.; Li, Y.; Yu, G.; Zhu, D. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2587.
- 3 Wang, S.; Li, Y.; Zhu, D. *Fullerenes*, Vol. 9, Eds.: Maggini, M.; Martin, N.; Guldi, D. M., the Electrochemical Society, Toronto, Canada, **2000**, pp. 200–208.
- 4 Gu, T.; Chen, W.; Xu, Z. *Polym. Bull.* **1999**, *42*, 191.
- 5 Darwish, A. D.; Birkett, P. R.; Langley, G. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Fullerene Sci. Technol.* **1997**, *5*, 705.
- 6 Schick, G.; Levitus, M.; Kvetko, L.; Johnson, B. A.; Lamparth, I.; Lunkwitz, R.; Ma, B.; Khanm, S. I.; Garibay, M. A. G.; Rubin, Y. *J. Am. Chem. Soc.* **1999**, *121*, 3246.
- 7 Hutchison, K.; Gao, J.; Schick, G.; Rubin, Y.; Wudl, F. *J. Am. Chem. Soc.* **1999**, *121*, 5611.
- 8 Tang, B.; Xu, H.; Lam, J. W. Y.; Lee, P. P. S.; Xu, K.; Sun, Q.; Cheuk, K. K. L. *Chem. Mater.* **2000**, *12*, 1446.
- 9 Li, Z.; Qin, J.; Deng, X.; Cao, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3428.
- 10 Miller, M. L.; West, R. *Chem. Commun.* **1999**, 1797.
- 11 Stroehriegel, P. *Makromol. Chem. Rapid Commun.* **1986**, *7*, 771.
- 12 Wu, S.; Zeng, F.; Li, F.; Zhu, Y.; Li, J. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3854.
- 13 Liu, Y.; Bunker, C. E.; Sun, Y. *Chem. Commun.* **1996**, 1241.
- 14 Thomas, R. N. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 2727.