

Spectroscopic and electrical characteristics of highly stable ultra-violet emitting tetraphenylsilane-carbazole organic compound

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Abstract

Optical absorption and photoluminescence (PL) are investigated for organic small molecule of ultra-violet (344 nm) fluorescence emitting bis (3,5-di (9H-carbazol-9-yl) phenyl)diphenylsilane (SimCP2), together with the glass transition temperature T_g and carrier mobility. SimCP2 is morphologically more stable than the other ultra-violet light emitting materials 1,3-bis (9-carbazolyl) benzene (mCP) and 3,5-bis (9-carbazolyl) tetraphenylsilane (SimCP) because of higher T_g of 148 °C. The electron and hole mobilities are higher (4.8×10^{-4} and $2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, at electric field of $9 \times 10^4 \text{ Vcm}^{-1}$) than those of mCP and SimCP. From the PL spectra of SimCP2 doped in polystyrene, the most intense 0-0 vibrational T_1 emission band was observed at 412 nm. SimCP2 has a wide band gap of highest occupied molecular orbital (HOMO) energy of 6.12 eV and lowest unoccupied molecular orbital (LUMO) energy of 2.56 eV. These results indicate that SimCP2 is expected to be efficient host material for blue phosphorescence emitters in organic light emitting diodes.

1. Introduction

Since organic light emitting diode (OLED) was discovered in late 1980's, researchers in both academia and industry have been working very hard to improve its performance. Successful improvements were obtained using new emissive materials and modifying device structure. Organic phosphorescent emitters show much higher efficiency than fluorescent ones. Of various OLEDs, phosphorescent OLEDs based on cyclometalated iridium complexes are well known

because of their high efficiency.

Phosphorescent materials are used as dopants and are dispersed in a host material. Greater difference of the triplet energies of fluorescent host and the phosphorescent guest materials is required in order to confine the electro-generated triplet excitons in the dopant molecules. Arylamino-containing organic substances such as 4,4'-bis (9-carbazolyl)-2,2'-biphenyl (CBP) are usually chosen as host materials and are proved working reasonably well for phosphorescent green or red emitters.

CBP has the T_1 energy of 2.56 eV (corresponding to 484 nm), therefore it does not have sufficient high triplet-state energy to prohibit T_1 - T_1 energy-transfer from the blue dopant to host. Having T_1 energy of 2.90 eV (~428 nm), 1,3-bis (9-carbazolyl)benzene (mCP) is better than CBP for blue phosphorescent dopant iridium bis (4,6-difluorophenylpyridinato) picolate (FIrpic) [1]. We have found that 3,5-bis (9-carbazolyl)tetraphenylsilane (SimCP) is even better than mCP for blue phosphorescent dopants [2].

Effective host materials for blue emitter are requested to have not only high band gap energy but also high glass transition temperature (T_g) and carrier mobility. SimCP has a significantly higher T_g than that of mCP (55 °C vs. 101 °C). High T_g of the host material is beneficial to avoid the molecular crystallization or aggregation [3, 4]. However, SimCP shows morphologically instability as mentioned later. Therefore it is necessary to synthesize new materials which have higher T_g and higher stability and high carrier mobility than SimCP. The present work was undertaken to find new host materials with higher T_1 energy level, higher T_g and hence longer-term stability of amorphous thin film, which are suitable as a host material for blue phosphorescent emitters in OLEDs.

In the present paper, we report the optical and electrical properties of new material, bis (3,5-di (9H-carbazol-9-yl) phenyl)diphenylsilane $C_{72}H_{48}N_4Si$ (named SimCP2). From its optical absorption and photoluminescence (PL) spectra, its charge carrier mobility, and its morphological stability, we show that SimCP2 is a better host material for blue emitters than SimCP and mCP.

2. Experimental method

SimCP2 was synthesized as follows. Bis (4- (3,5-dibromophenyl) diphenylsilane) (4.17 g, 6.4 mmol) [5]) and carbazole (5.34 g, 30.7 mmol) were dissolved in dry xylenes (40 mL) containing potassium carbonate (12.72 g, 92.0 mmol) and palladium acetate (0.057g, 0.25 mmol). After the injection of tri-tert-butylphosphine (0.20 mL, 0.8 mmol), the resulting mixture was stirred for 16 h at refluxing temperature under the protection of nitrogen atmosphere. After cooling to ambient

temperature, the reaction was quenched with excess water (100 mL). The mixture was extracted with dichloromethane. The organic phase was washed with water and dried by magnesium sulfate. After the removal of magnesium sulfate, the mixture was evaporated to dryness and the residual was subjected for flash column chromatography (silica gel, dichloromethane/hexanes, 2/8). The product was isolated as a white powder and became a faint yellow glassy solid after sublimation. The molecular structure of SimCP2 is shown in inset of Fig. 1. Two 3,5-di (9H-carbazol-9-yl) phenyl ligands are attached to Si in SimCP2, which is different from SimCP with only one 3,5-di (9H-carbazol-9-yl) phenyl ligand.

The glass transition temperature was measured with a differential scanning calorimetry (DSC) method. It was estimated to be 148 °C from the DSC thermograms (Fig. 2). The highest occupied molecular orbital (HOMO) energy was measured with a Riken Keiki AC-2 photoelectron emission spectrometer. The carrier mobility was measured with the time of flight (TOF) method [3].

For optical study, thin films of neat SimCP and polystyrene (PS) doped with 3, 5, 10, 15, and 20 wt% SimCP2 were prepared by thermal vacuum deposition and spin-coating on to quartz substrates at ambient temperature, respectively. The deposition was performed using ULVAC cryogenics at a chamber pressure of 10^{-6} Torr. Thickness of film is 30 nm. The doped films were prepared by co-evaporation of the dopant and host material by controlling the individual evaporation rate through quartz thickness monitor (ULVAC CRTM-6000).

Optical absorption spectra were measured with a Shimadzu UV-3100PC spectrophotometer. The PL and photoluminescence excitation (PLE) spectra were measured at various temperatures between 10 K and 300 K with a Spex Fluorolog-3 fluorophotometer. The excitation source was a 450 W Xe-lamp. Filters were used to avoid the half and second harmonics of the excitation light.

3. Experimental results and discussion

The HOMO energy of SimCP2 was estimated to be 6.12 eV from the photoelectron spectra of the neat film without any heat treatment (Fig. 1). Its energy was also measured at room temperature after the neat film was heated at 70, 120, and 150 °C, but no change was observed compared with the case without thermal annealing. The neat film, which was kept in open air at room temperature after annealing at 150 °C, shows morphological stability, i.e., neither aggregation nor crystallization was observed after 60 days when we look the film by eyes as shown in Fig. 3. In cases of mCP and SimCP neat films, quick morphology degradation was found after annealing at 70 °C. The degradation was also observed even for thermally unannealed film more strongly in mCP than in SimCP [3]. This indicates that the SimCP2 film is morphologically more stable and more

robust to water and oxygen molecules than mCP and SimCP.

Carrier mobilities of electrons and holes of SimCP2 are plotted against electric field in Fig. 4, and compared with those of mCP and SimCP. Like the cases of various organic semiconductors [6, 7], the electron and hole mobilities of SimCP2, mCP and SimCP follow the linear relationship of the Poole-Frenkel model with applied electric field when the mobility is log-plotted against square root of electric field. The hole and electron mobility in SimCP2 is found to be 4.8×10^{-4} and $2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, at electric field of $9 \times 10^4 \text{ V cm}^{-1}$ at room temperature. This indicates that SimCP2 has a balanced bipolarity although the hole mobility is a little higher than the electron mobility. These mobilities are higher for SimCP2 than for mCP and much higher than for SimCP. High charge carrier mobility of the material is one of the factors that can reduce the driving voltage of OLED and hence increase the power efficiency (lm/W) of the device. Based on the Poole-Frenkel model, the mobility at zero-field (called zero-field mobility) is obtained by extraction. Table 1 summarizes the zero-field electron and hole mobilities for SimCP2, mCP, and SimCP. For comparison, the two kinds of mobilities are also shown for neat CBP [8,9], N, N'-bis (1-naphthyl)-N, N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB, i.e., α -NPD) [10] and tris (8-hydroxyquinoline) aluminum (Alq₃) [10] films. Although the two zero-field mobilities of SimCP2 are lower than those of CBP, they are higher than those of NPB and Alq₃. It is noted for CBP that the hole mobility is higher than the electron mobility under the electric field, but the zero-field mobilities are reversed [9].

Figure 5 shows absorption and emission spectra of SimCP2 diluted in dichloromethane (CH₂Cl₂) solution and absorption spectrum of neat SimCP2 film at room temperature. Similar absorption spectrum was also obtained from SimCP2 diluted in chloroform (CHCl₃) solution. Absorption peaks due to SimCP2 are observed at 339, 325, 311, 292, 285, and about 255 nm for the SimCP2 (transparent range of wavelength $\lambda > 240$ nm). On the other hand, absorption peaks are observed at 342, 328, 313, 296, 290, 240, 227, and 207 nm from the neat film. Although the two absorption spectral line shapes are quite similar to each other, the neat film shows a red shift. It is suggested that this shift is caused by different dipole-dipole interaction of the SimCP2 molecule and its neighboring molecule between the solution and neat film (i.e., solvation effect). The emission spectrum consists of three vibronic peaks at 349, 363 and 378 nm where their intensities decrease with decreasing photon energy. Small Stokes shift is found for the emission. This emission is attributed to the S₁ emission, i.e., emission due to electronic transition from the lowest singlet state S₁ to the ground state ¹S₀. The lowest unoccupied molecular orbital (LUMO) energy is approximated by the difference of the HOMO energy and the absorption edge of the UV absorption spectra [11-13]. We observe the absorption edge (i.e., onset) at about 348 nm (3.56 eV). Therefore,

from the HOMO energy of 6.12 eV, the LUMO energy of SimCP2 is determined to be 2.56 eV.

We compare the absorption spectrum of SimCP2 between the neat and doped films. The spectral line shape is very similar among PS film doped with 5 wt% SimCP2, PS film doped with 15 wt% SimCP2, and neat SimCP2 film as shown in Fig. 6. This indicates that no aggregation is formed with increasing concentration of the dopant. Unlike the neat film, a weak absorption band appears at about 260 nm in the doped film. This is due to absorption from polystyrene host.

Figure 7 shows the PL and PLE spectra for PS films doped with 3, 15, and 20 wt% SimCP2 at 10 K. Intense emission peaks are observed at 343.8, 360.1, and 378 nm for 3 wt% film and weak PL bands are observed at 412.2, 433, and 441.8 nm. Like the case of mCP and SimCP [3, 4], the latter bands are attributed to the T_1 emission. Although the T_1 emission is enhanced with decreasing temperature (discussed later), it is too weak to observe clearly for 20 wt% doped film even at 10 K. It is noted that the T_1 emission intensity decreases with increasing concentration. The PLE spectra observed for 370 nm emission (curves 4 and 5 of Fig. 7) consist of peaks at 338.1, 324.1, 311.0, and 293.0 nm, which are quite similar to the absorption spectra of Fig. 5. The PLE line shape of the 338.2, 325.1, and 311 nm bands shows a mirror image for the PL line shape of the 343.8, 360.1, and 376 nm bands when the overlapping 293.0 nm PLE band tail is subtracted from the 311 nm band. Such a mirror image is also observed for the absorption and PL spectra of SimCP2 in solution (Fig. 5). This means that the three absorption bands at $\lambda > 310$ nm belong to the same S_1 state.

From the PL line shape with vibrational progression, the 412.2, 433, and 441.8 nm PL bands are assigned to the vibronic 0-0, 0-1, and 0-2 bands, respectively, which mean the transitions from the energy level of vibrational quantum number $n=0$ of the S_1 state to the energy levels of vibrational quantum numbers $m=0, 1, \text{ and } 2$ of the 1S_0 ground state. From the mirror image the 338.1, 324.1, and 311.0 nm PLE bands are attributed to the vibronic transitions from the energy level of $m=0$ of the 1S_0 state to the energy levels of $n=0, 1 \text{ and } 2$ of the S_1 state. The PL and PLE spectra exhibit the vibrational progression with energy of about 1316 and 1270 cm^{-1} , respectively. The energy is larger for the PL bands than for the PLE bands, indicating that the vibrational energy is higher for the 1S_0 state than for the excited S_1 state.

Temperature dependence of the PL spectra is shown in Fig. 8 for the PS film doped with 5 wt% SimCP2 excited at 305 nm. The intensity of S_1 emission decreases with decreasing temperature from 296 K to about 170 K and then leveling off down to 17 K, whereas the intensity of emission bands with $\lambda > 400$ nm increases with decreasing temperature down to 10 K (see Fig. 9). This T_1 emission appear in a spectral region of $410 \text{ nm} < \lambda < 500 \text{ nm}$, with peaks at 412, 425, 433, 442, 467, and 480 nm. Enhancement of additional low-energy emission band with vibronic structure at low temperatures has been observed for the T_1 emission in several fluorescent materials such as mCP

and SimCP [3]. Therefore the emission bands at $\lambda > 400$ nm are confirmed to be the T_1 emission with vibronic structure. The most intense band locates at 412 nm, which corresponds to the 0-0 vibrational transition. Therefore the T_1 energy is estimated to be 3.01 eV.

It was very difficult to locate the absorption bands of $^1S_0 \rightarrow T_1$ transition in the absorption spectra. Alternatively, we measured the PLE spectrum for 470 nm T_1 emission at 13 K. This spectrum is shown in Fig. 10. A very weak PLE band is observed at about 400 nm at the low-energy tail of the 340 nm intense PLE band ($^1S_0 \rightarrow S_1$ transition). This is attributable to the T_1 absorption bands because the low-energy tail of the 400 nm PLE band extends to about 410 nm which is close to the intense T_1 0-0 vibrational emission band at 412 nm. From the observation of the intense $^1S_0 \rightarrow S_1$ PLE bands, it is thus confirmed that the T_1 emission is caused by the intersystem crossing from the S_1 state to the T_1 state after excitation into the S_1 state. The intensity ratio of the T_1 absorption to the S_1 absorption is approximately estimated as 0.02 : 1.00.

Figure 11 illustrates the concentration dependence of the S_1 emission intensity (integrated area) for the PS films with various SimCP2 dopant concentrations and neat film at room temperature, together with the absorption intensities at 340 nm. Absorption intensity increases linearly with increasing concentration, whereas the saturation is observed at high dopant concentrations for emission intensity (i.e., emission concentration quenching). The linearity of the absorption intensity supports our suggestion, which is derived from absorption spectra of Fig. 6, that no aggregation is formed in the films. At dopant concentration of higher than 5 wt%, emission concentration quenching does happen, indicating the energy transfer among the neighboring SimCP2 molecules.

4. Summary

It was found that UV-emitting SimCP2 is morphologically more stable than mCP and SimCP because of higher T_g of 148 °C, and SimCP2 has higher mobility for both electron and hole (4.8×10^{-4} and 2.7×10^{-4} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, respectively, at electric field of $9 \times 10^4 \text{V cm}^{-1}$) than mCP and SimCP. The HOMO and LUMO energies of SimCP2 are determined to be 6.12 and 2.56 eV, respectively. The most intense 0-0 vibrational S_1 emission band was observed at 344 nm, while the T_1 emission band at 412 nm. Therefore the T_1 energy was estimated to be 3.01 eV. It is thus conceivable that SimCP2 with balanced bipolarity and high morphological stability will be one of highly efficient host materials for blue phosphorescence emitter in OLEDs.

Acknowledgements

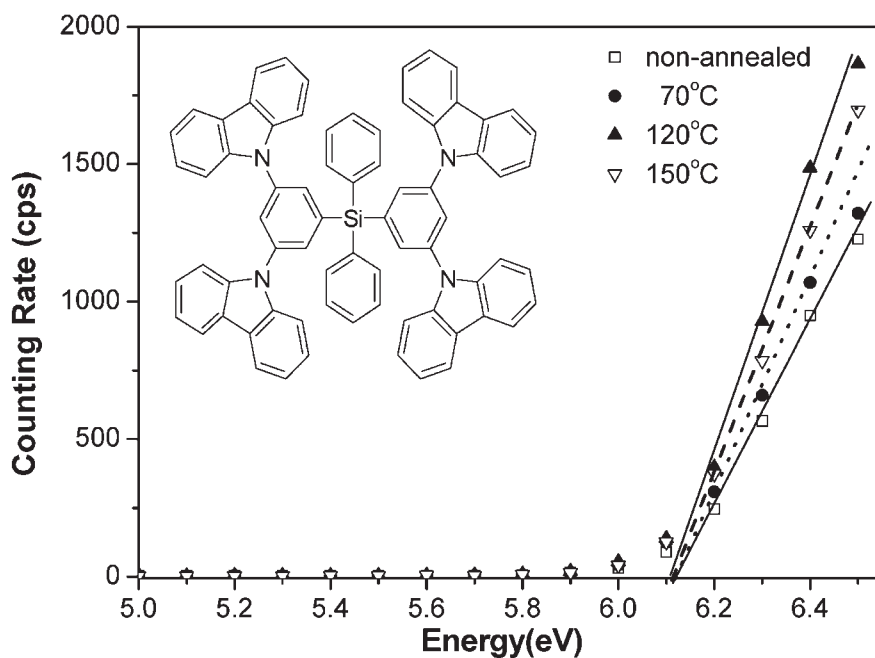
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Table 1 Zero-field mobilities, μ_{oh} and μ_{oe} for holes and electrons, respectively, in neat SimCP2, mCP, SimCP, CBP, NPB and Alq₃ films.

	μ_{oh} (cm ² V ⁻¹ s ⁻¹)	μ_{oe} (cm ² V ⁻¹ s ⁻¹)
SimCP2	2.4×10^{-4}	1.3×10^{-4}
mCP	1.2×10^{-4}	3.4×10^{-5}
SimCP	5.8×10^{-5}	5.0×10^{-5}
CBP	3.8×10^{-4} [8, 9]	4.4×10^{-4} [8, 9]
NPB	1.8×10^{-4} [10]	1.0×10^{-5} [10]
Alq ₃	7.0×10^{-10} [10]	8.0×10^{-8} [10]

**Fig. 1** The HOMO energy of SimCP2 obtained from the photoelectron emission spectroscopy for neat non-annealed SimCP2 film and neat SimCP2 films annealed at 70, 120 and 150 °C. Molecular structure of SimCP2 is shown in inset.

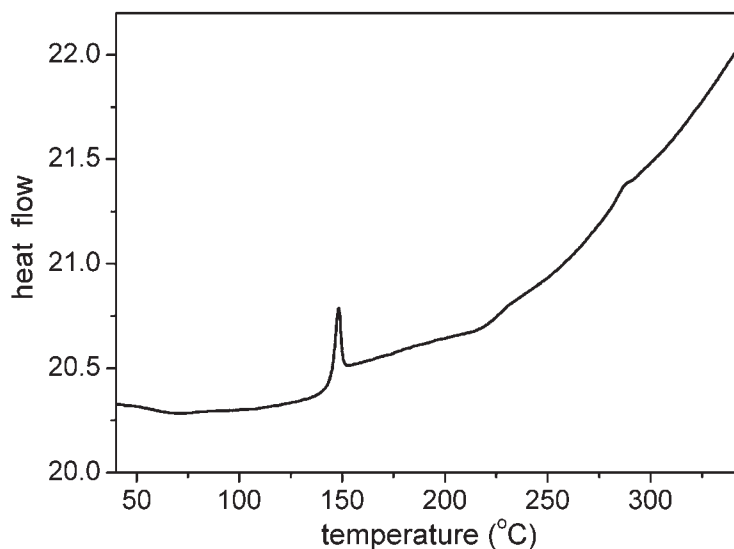


Fig. 2 DSC (differential scanning calorimetry) thermogram of SimCP2 which was obtained during heating of the neat SimCP2 film from 40 °C to 350 °C

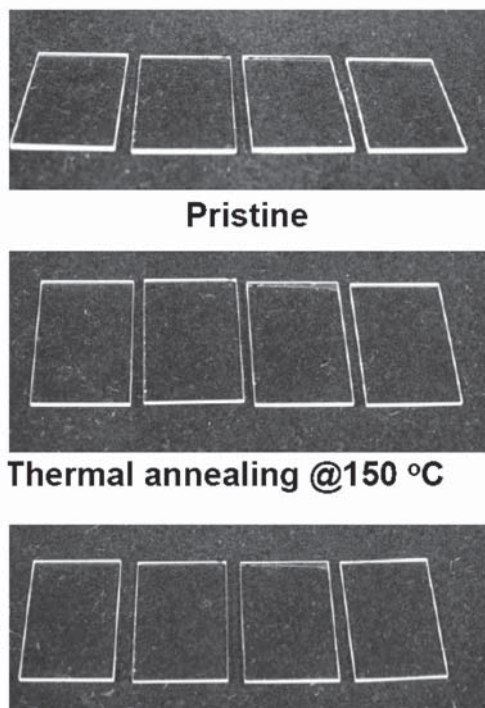


Fig. 3 Photographs of four neat SimCP2 films on glass plate (size is 10x20 mm) taken 10 minutes after thermal annealing at 150 °C (middle) and in 60 days after annealing at 150 °C (bottom). Non-thermally annealed films are shown at top. The four film samples were all fabricated in a same run of the thermal-vacuum-deposition. No difference was observed among them before and after thermal annealing.

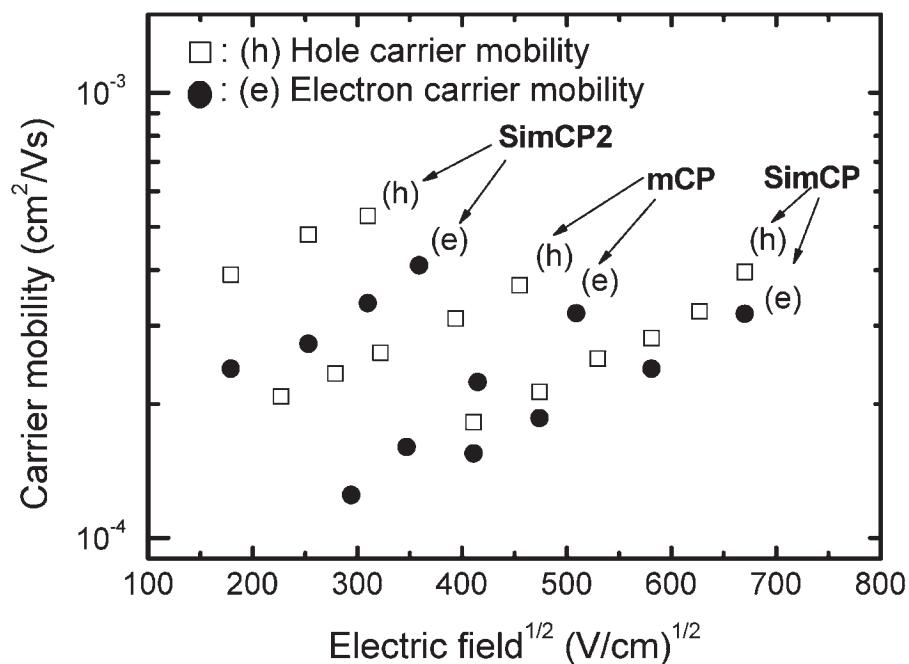


Fig. 4 Plot of electron and hole mobilities of SimCP2 against the electric field, compared with those of mCP and SimCP.

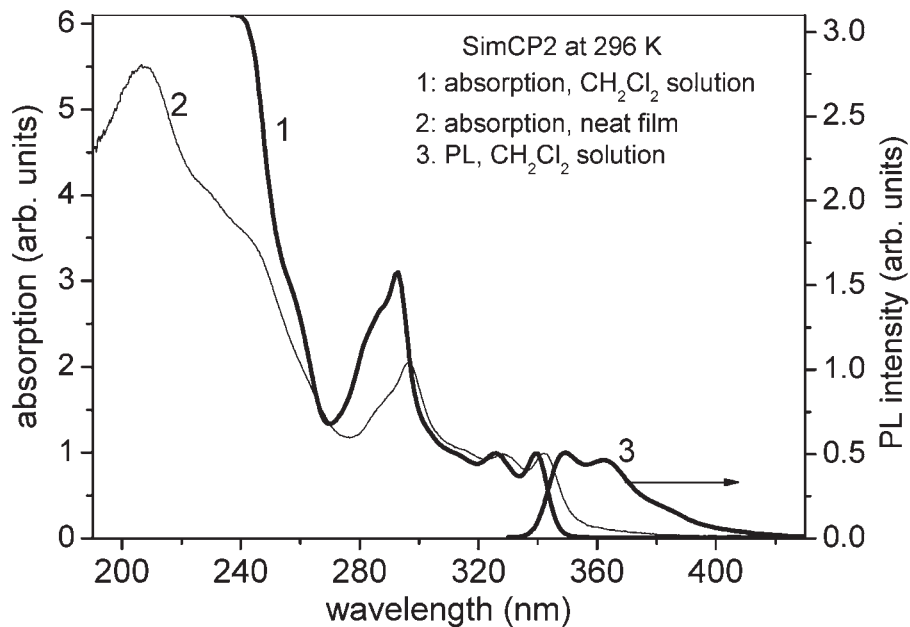


Fig. 5 Absorption and PL spectra of SimCP2 in CH_2Cl_2 and absorption spectrum of neat SimCP2 film. Absorption spectrum is cut at $\lambda < 240$ nm for the case of solution because of strong absorption by the solvent.

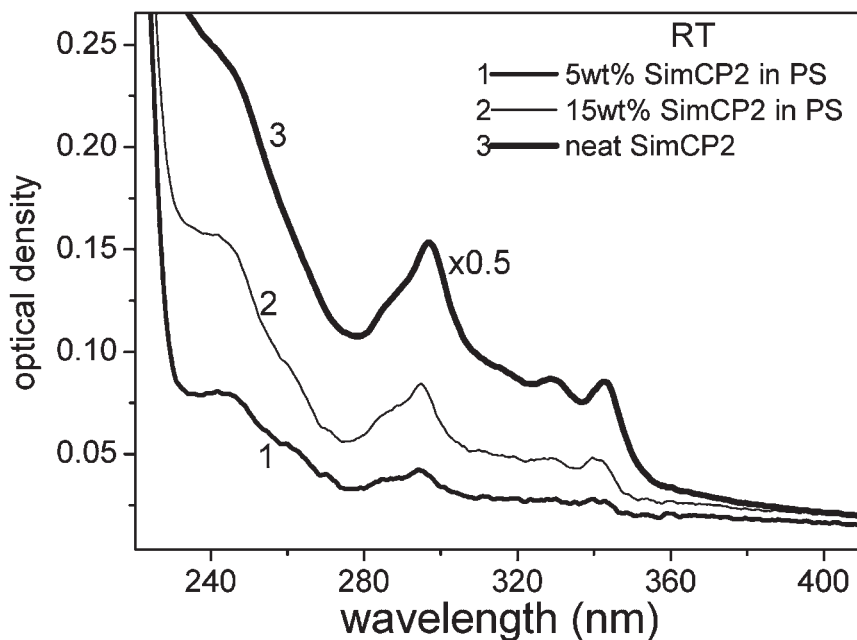


Fig. 6 Absorption spectra of SimCP2 which are measured using PS films with 5 and 15 wt % SimCP2 and using neat SimCP2 film at 296 K.

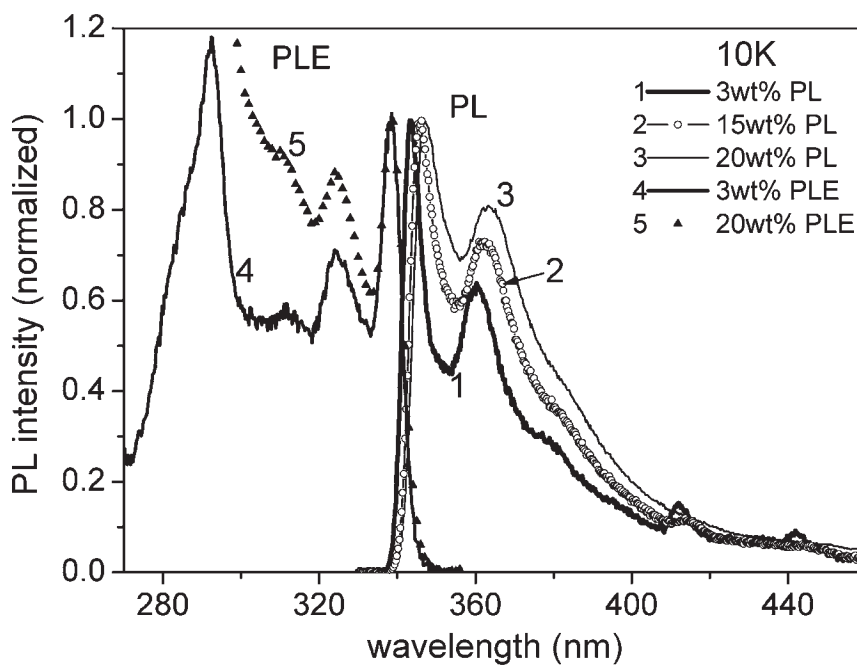


Fig. 7 PL spectra of SimCP2 which are measured using PS films with 3, 15, and 20 wt % SimCP2 excited at 305nm at 10 K, and PLE spectra of SimCP2 for 370 nm emission which are measured using PS films with 3 and 20 wt % SimCP2 at 10 K.

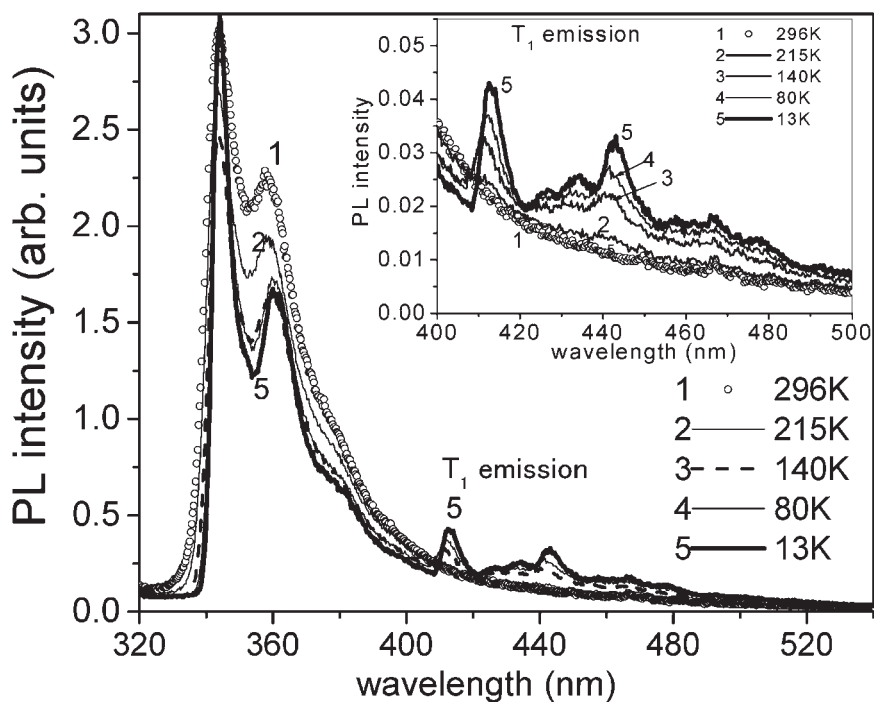


Fig. 8 PL spectra of SimCP2 in a polystyrene film doped with 5 wt% SimCP2, which was excited at 305 nm at various temperatures. Inset is the enlarged T_1 emission spectra.

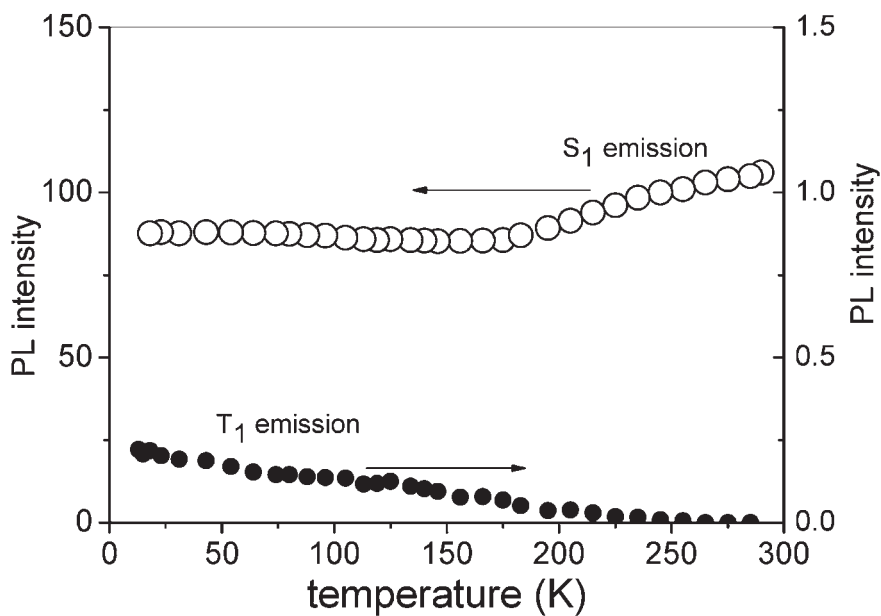


Fig. 9 Temperature dependence of the S_1 and T_1 emission intensities which we obtained from PS film with 5 wt% SimCP2 excited at 305 nm.

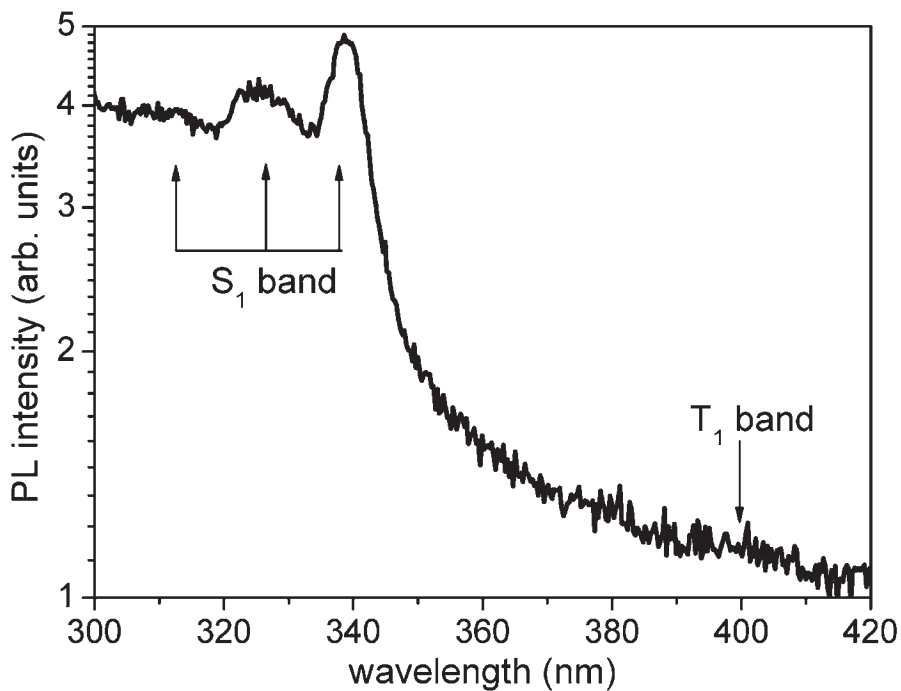


Fig. 10 Logarithmic plot of the PLE spectrum for 470nm T_1 emission in PS film with 15 wt% SimCP2 at 13 K.

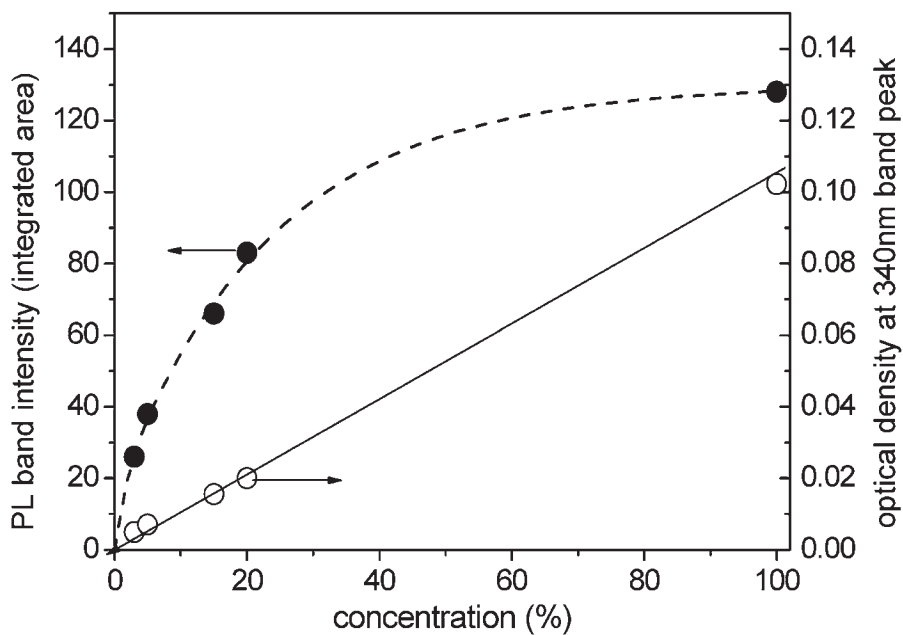


Fig. 11 Concentration dependence of the PL and absorption intensities of SimCP2 in SimCP2-doped PS films. The dotted line is meant as guide to the eye.

