Comparison of the electroluminescence and its related properties of two cyclopentadiene derivatives

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Abstract

In order to fully understand the dependence of device electroluminescence (EL) on the chemical structure of two light-emitting materials: 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (TPCP) and 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (PPCP), their properties in solution and as evaporated thin films of UV-Vis absorption, geometric structures, photoluminescence (PL), electrochemistry, glass transition temperature and EL were compared. Compared with that of TPCP, the first absorption band of PPCP shifts to the shorter wavelength region both in solution and thin film state; the photoluminescence in solution exhibits lower quantum efficiency but in thin film state has a higher intensity; the electrochemical oxidation happens at a higher potential; the solid powder exhibits higher glass transition temperature; and the electroluminescent device shows higher luminescence and efficiency. Reasons responsible for the differences were analyzed.
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1. Introduction

Substantial interest in the development of electroluminescence (EL) as a new promising display technique has been aroused by the pioneer work done by Tang and Vanslyke [1], Adachi et al. [2], Burroughs et al. [3] and Sheats et al. [4]. Based upon formation of emissive states through direct injection of electrical charge into single layer or multilayer thin films, many small organic molecules, metal chelates and extended conjugation polymers have been tested for EL use. Structure–effect relationship analyses of the EL materials prove to be useful, e.g. remarkable structural modifications of the widely used light-emitter and electron transporter aluminum-quinolate (ALQ) [5–7] and the hole transporter, *N,N′*-bis(3-methylphenyl)-*N,N′*-diphenyl benzidine (TPD) [8–10], have been carried out. These structural modifications have been proved to have substantial effect on PL and EL performance, stability and charge transport ability, etc.

We previously reported the effect of electric field strength on the EL spectra of a blue-emitting device based on 1,2,3,4-tetraphenyl-1,3-cyclopentadiene

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(TPCP) [11]. Addition of another phenyl group to the cyclopentadiene backbone creates 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene (PPCP). It was ever used as a dopant in an EL device based on poly(3-alkylthiophene) [12]. In this paper, we choose TPCP and PPCP as the light-emitting materials and compare the structural induced differences in their absorption, photoluminescence, electrochemistry, stability and electroluminescence to study the structure–effect relationships.

2. Experimental details

TPD and PPCP were used as purchased from Aldrich. ALQ was synthesized by the reaction of 8-hydroxyquinoline with aluminum chloride and was recrystalized three times and purified by sublimation. TPCP was synthesized according to [11].

In photoluminescence quantum efficiency measurement, quinine bisulfate in 1N H_2SO_4 was used as a standard whose quantum yield is 56% (excited at 334.1 nm) [13]. The determination of the fluorescence quantum efficiency of the molecules in the form of solid powder is always difficult because complicated instrument is needed to deduct the interference and measure precisely the input of the excitation light and the output of the emission light. Nevertheless, turning the solid powder into a thin solid film to make a smooth surface should eliminate the effect of light scattering fairly well. Then, if we use the same excitation light and compare the integration of the emission light, we can obtain the relative magnitude of a series of samples. In our experiment, we prepare the thin solid film by vacuum evaporating the solid materials on the quartz substrate. By comparing the integration of the photoluminescence emission and counting the absorption value, the fluorescence intensity of TPCP and PPCP can also be compared. The reproductivity error is within negligible range.

The UV-Vis absorption spectrum measurements were completed at a Shimadzu UV-3100 spectrophotometer. Photoluminescence and electroluminescence were measured with a Hitachi model 850 fluorescence spectrophotometer. Cyclic voltammetric (CV) experiments were performed at a CH Instruments Voltammetric Analyzer model 600. For solution CV, the working, auxiliary and reference electrode was a $0.5\,cm^2$ glass-carbon disk, a Pt wire and a Ag/AgCl

wire, respectively; 0.1 M Bu_4NClO_4 in *N,N*-dimethylformamide (DMF) was used as the supporting electrolyte. Film state CV was recorded by using the evaporated thin film on ITO substrate as the working electrode, a saturated calomel electrode (SCE) as the reference and a Pt wire as the auxiliary electrode in 0.1 M KCl aqueous solution. EL devices were fabricated by thermally evaporating the organics and the aluminum cathode on to ITO below a pressure of 1×10^{-5} Torr. The geometric structures of TPCP and PPCP were simulated at the RHF/STO-3G level by *Gaussian 94* suite of programs on a PII-400 personal computer. All measurements were completed at room temperature under ambient atmosphere.

3. Results and discussion

3.1. Absorption spectra

Fig. 1(a) and (b) compares the absorption spectra of TPCP and PPCP in acetonitrile solution and as thin films. Film state absorption spectra have a "flat" feature and shift to the red wavelength region more than 10 nm, compared with their corresponding spectra in solution. In thin film state, the distance of the molecules is decreased and the interaction between molecules increases. The wave functions of the molecules are so overlapped that they form coupled indiscrete band gaps [14]. Compared with the difference between the discrete lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the molecules in solution, the band gap of the molecules in thin film state is smaller (see Fig. 2(a)). So, the thin film state absorption spectra move towards the red wavelength region. In solid state, molecules become rigid and cannot move freely as in solution, so the vibration and rotation structure will disappear. There is also Coulombic interaction and intramolecular electron transfers between the excited state of one molecule and the ground state of the other, so the excitation energy is not limited in a single molecule but move within the entire crystal. This results in the flattening of the thin film spectra.

There is also a difference (nearly 8 nm) between the first band of the absorption spectra of TPCP and PPCP. The structure optimization data simulated by molecular mechanics show that all the phenyl groups in
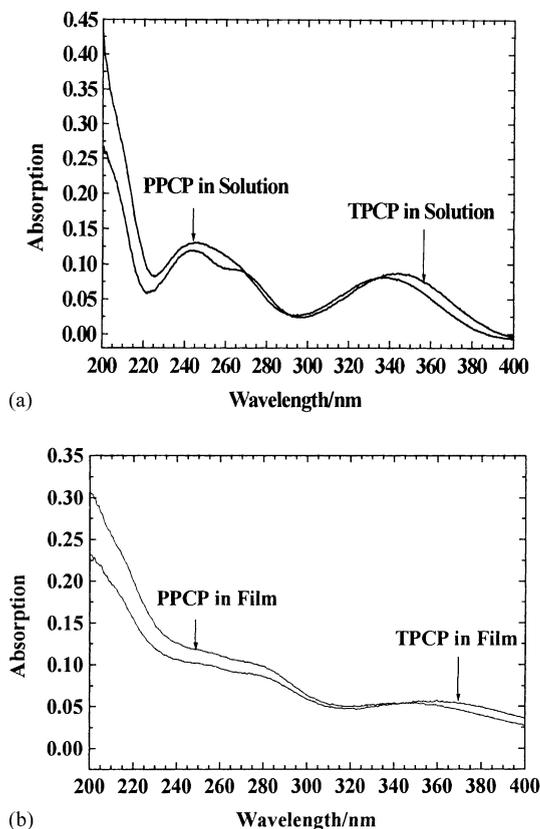
Fig. 1. Absorption spectra of TPCP and PPCP in solution (a) and as thin films (b).

both TPCP and PPCP connecting with the cyclopentadiene plane are non-planar because of steric hindrance (Fig. 2(b)). In PPCP, the addition of another phenyl group which is nearly perpendicular to the cyclopentadiene plane makes the two phenyl groups adjacent to it deviate more from the cyclopentadiene plane (in PPCP the deviation angles between the cyclopentadiene plane and the two phenyl groups adjacent to the additional phenyl group is 56.5 and 43.4°, respectively while in TPCP, they are all 40.9° correspondingly) than the other two phenyl groups move close to the cyclopentadiene plane (in PPCP the deviation angle between the cyclopentadiene plane and the two phenyl groups one C atom next to the additional phenyl group is 53.5 and 54.5° while in TPCP they are all 55.7° correspondingly). So the addition of another phenyl group reduces the conjugation effect among the non-planar π systems by steric

hindrance. This reduced conjugation effect is responsible for the rise of the LUMO and the fall of the HOMO therefore increases the transition energy of $S_0 \rightarrow S_1$ [15] and results in a blue shift of the first absorption band for PPCP in solution and in film compared with TPCP.

3.2. PL spectra and efficiency

Fig. 3 shows the PL spectra of TPCP and PPCP in acetonitrile solution and thin film state. Similar to the absorption spectra, the PL spectra in film also shift towards the red wavelength region compared with those of their counterparts in solution.

Table 1 shows the photoluminescence quantum yield of TPCP and PPCP in different solvents and the relative fluorescence intensity as thin films. In toluene solution, the quantum efficiency for TPCP is 5.73%, much higher than that of PPCP (3.09%). In acetonitrile and methanol, the PL quantum yield of TPCP is still larger than that of PPCP but to a less extent. However, the fluorescence intensity of TPCP in thin film state is more than two times lower than that of PPCP. How to interpret this phenomenon? The reason may be as follows. In the absorption spectra measurement, we observed that with the decrease of the solvent polarity, the first peak of both TPCP and PPCP shift toward the longer wavelength region. So, it can be concluded that the polarity of the excited state of both TPCP and PPCP is lower than that of the ground state as the solvent with a lower polarity stabilizes the excited singlet state and result in a decrease in the transition energy [16]. This depolarized excited state will favor non-polar solvents. So as the polarity of the solvent decreases, the PL quantum yield increases. As

Table 1
PL quantum yields of TPCP and PPCP in different solutions and their relative fluorescence intensities as thin films

	Acetonitrile (%)	Methanol (%)	Toluene (%)	Film state
TPCP	2.54	3.10	5.73	0.37
PPCP	1.97	2.93	3.09	1

The excitation wavelength for the comparison of fluorescence intensity is 345 nm, at which the absorbance is the same for TPCP and PPCP. The luminance integration area is 970 for TPCP and 2638 for PPCP. The latter is normalized to 1.

Single TPCP or PPCP
molecule in solution

Amorphous TPCP or PPCP
molecules in solid film state

(a)

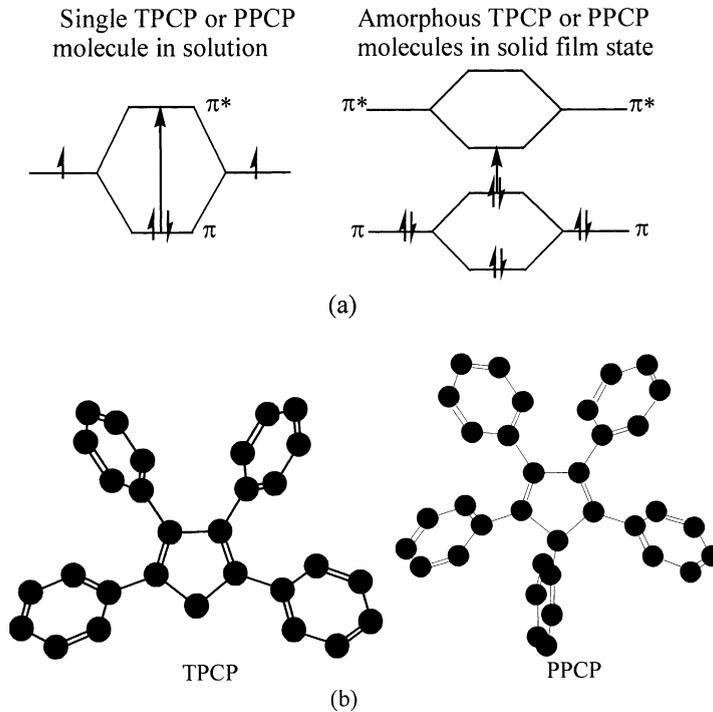TPCP   PPCP

(b)

Fig. 2. (a) A diagram showing that the discrete energy levels of TPCP or PPCP in solution as a single molecule become coupled bands in solid state as aggregated molecules. (b) Geometric structure of TPCP and PPCP.

can be seen in Table 1, in toluene, even a small difference in the polarity of TPCP and PPCP results in remarkable difference in PL efficiency. However, in a solvent with a higher polarity, the influence of the small difference in the polarity of TPCP and PPCP on

Fig. 3. PL spectra of TPCP and PPCP in solution and in thin film.

PL quantum yield becomes less important as can be seen in acetonitrile and methane. To the extreme, in thin film state where the influence of solvent disappears and the molecules become rigid, the fluorescence intensity is solely related with the intrinsic property responsible for the PL emission, the lifetime of the first excited singlet state.

3.3. Electrochemical behaviors

Fig. 4(a) and (b) show the cyclic voltammograms of TPCP and PPCP in DMF solution and in thin film state. In both conditions, the oxidation peak of PPCP appears at a higher potential than that of TPCP. This means that PPCP needs a higher energy to remove an electron out of its HOMO. Similar to the case in the absorption spectra, this peak shift is the result of the decreased HOMO level of PPCP compared with that of TPCP due to the reduced conjugation effect. So, the ionization potential (IP, defined as the energy needed to remove an electron out of the HOMO to an infinite remote place of a molecule in gas state) of PPCP is
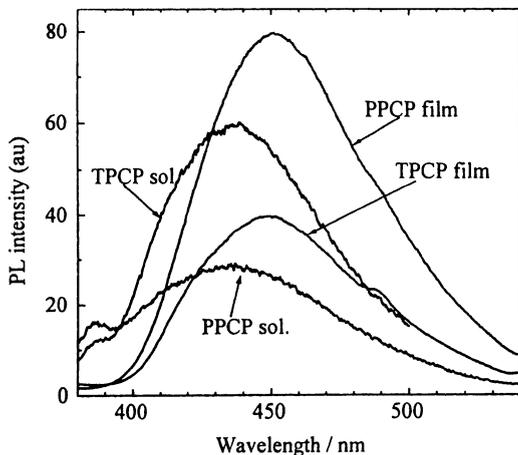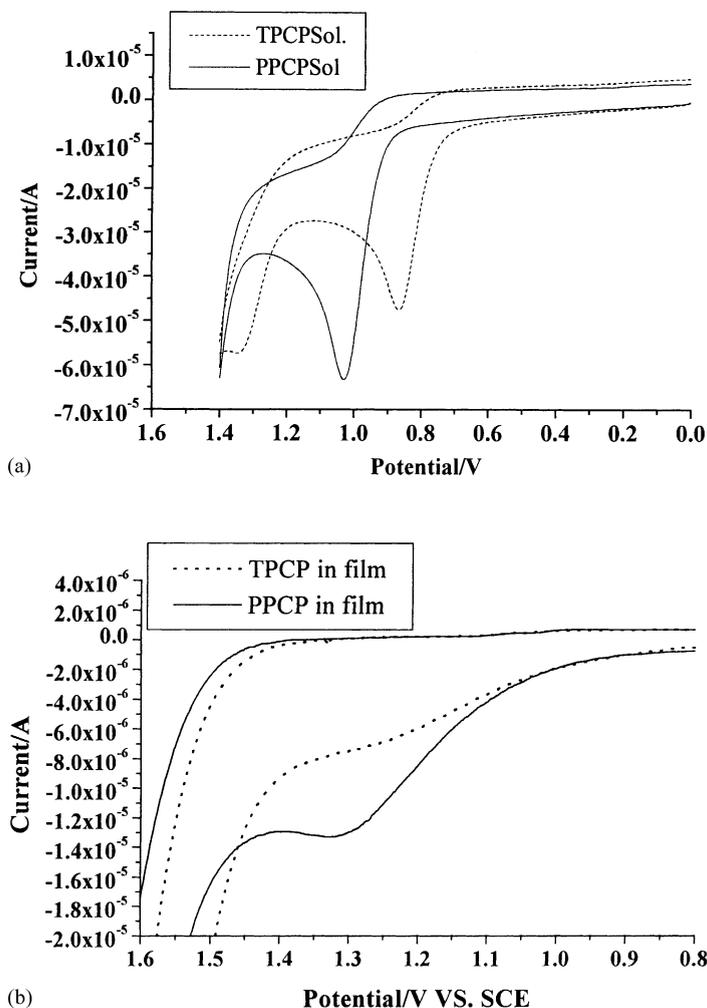
Fig. 4. Cyclic voltammograms of TPCP and PPCP in DMF solution and as evaporated thin films on ITO substrate.

higher than that of TPCP. Based on a simple calculation of the oxidation potentials in solution [17], IP for TPCP and PPCP is 5.60 and 5.75 eV, respectively.

3.4. Glass transition temperature

We measured the glass transition temperature (T_g) of TPCP and PPCP by differential scanning calorimetry (DSC). PPCP has a higher T_g of 188 °C (mp = 255 °C) than that of TPCP (T_g = 130 °C, mp = 182 °C). It is also higher than most of the hole transporting materials which is currently in use. For example, T_g for TPD, 4,4′,4″-tris(3-methylphenylphe-nylamino)-trisphenylamine (*m*-TDATA) and *N,N′*-bis(3-naphthyl)-*N,N′*-diphenyl benzidine (NPB) is 60, 75 and 95 °C, respectively [18]. Higher T_g is desirable for the formation of an amorphous film and the stability of an EL device.

3.5. Electroluminescence

Using TPD as the hole transport layer, TPCP as the light-emitting layer and ALQ as the electron transport layer, we previously reported the effect of electric field strength (EFS) on the EL spectra of the triple layer EL devices [11]. At higher EFS, the device shows an
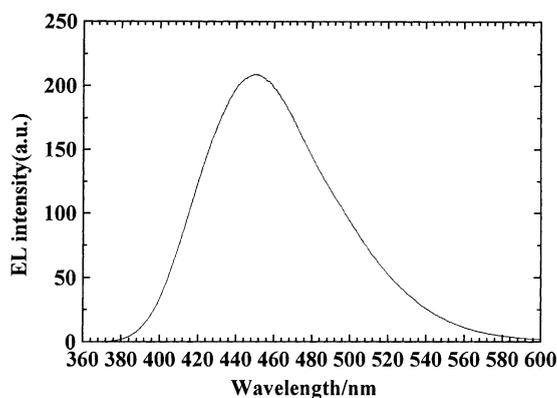
Fig. 5. Electroluminescence of PPCP. The position of the peak is the same for devices with varying thicknesses and drive voltages: (1) ALQ layer being 22 nm, the PPCP layer is 11, 21 and 27 nm; (2) PPCP layer being 10 nm, the ALQ layer is 15 and 30 nm; (3) the drive voltage can range from 6 to 16 V.

emission of 460 nm which arise from the light-emitting layer TPCP; at lower EFS, electrons are blocked in the electron transport layer 8-hydroxyquinoline aluminum (ALQ) and the device emits light at 517 nm characteristic of ALQ; at medium EFS, electrons are gradually injected from ALQ layer into TPCP layer resulting in a wide-banded emission composed of both TPCP and ALQ; this emission peak shifts from initial 517 nm to final 460 nm when the drive voltage is slowly increased. In this study, unlike the EL behavior of TPCP, the EL emission based upon PPCP is EFS independent. As Fig. 5 shows, at a low drive voltage of 10 V, all devices inspite of the thickness of PPCP (11, 22 and 27 nm) and ALQ layer (15, 22 and 30 nm) exhibit EFS independent EL emission of PPCP, excluding the emission of ALQ. Why is the emission not EFS dependent? It may be due to the better amorphous film forming ability of PPCP which enables the formation of a better interface between PPCP and ALQ. This well-formed interface together with the reduced conjugation of PPCP will reduce the interaction between the molecules of PPCP and ALQ thus reduce the possibility of the movement of the recombination zone which is the result of the tunneling effect.

Because the decreased conjugation effect not only increases the LUMO but also decreases the HOMO of PPCP, the IP will increase and the electron affinity (EA) will decrease relative to the vacuum level. So,

theoretically, it would become more difficult for the holes from TPD layer and electrons from ALQ layer to be injected to the PPCP layer. This will reduce the performance of the EL device. However, the result turned out to be contrary to the expectation. The maximum EL luminance we obtained is 950 cd m^{-2} and efficiency 0.12 lm W^{-1}, higher than those of the EL device based on TPCP (maximum luminance 600 cd m^{-2} and efficiency 0.1 lm W^{-1} [11]). This increased luminance and efficiency is the compromise of the energy level and the other two factors of PPCP: higher fluorescence intensity and amorphous film forming ability. Perhaps, this is the reason why efficiencies in PL for thin films are two times higher for PPCP while in EL the difference is only 20% (from 0.1 to 0.12%).

4. Conclusion

PPCP was chosen to compare its EL properties with those of its analogue, TPCP. Compared with TPCP, the additional phenyl group in PPCP reduces the conjugation effect and results in the increase of the LUMO as well as the decrease of the HOMO which are proved by the blue shift of the first absorption band of PPCP in solution. Correspondingly, the first oxidation peak of the electrochemical reaction of PPCP needs a higher potential both in solution and in film state. Thin film state PPCP exhibits higher PL intensity but in nonpolar solution, it exhibits a lower PL quantum efficiency. PPCP has a higher T_g as much as 188 °C, so it is more likely for it to form an amorphous film which can reduce the interaction at the interface between PPCP and ALQ when fabricated into an EL device. As a result of the higher photoluminescence intensity and higher T_g, the EL device with thin film PPCP as the light-emitting layer exhibits higher electroluminescence and higher efficiency.

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