

ORIGINAL ARTICLE

# New poly(4,4'-dicyano-4''-vinyl-triphenylamine) host material for single-layer Ir complex phosphorescent light-emitting devices

Yi-Kai Fang<sup>1</sup>, Wen-Ya Lee<sup>1</sup>, Chi-Shen Tuan<sup>2</sup>, Ling-Hui Lu<sup>2</sup>, Wan-Jung Teng<sup>2</sup> and Wen-Chang Chen<sup>1</sup>

We report a new host material for iridium complex light-emitting devices, poly(4,4'-dicyano-4''-vinyl-triphenylamine) (PCNVTPA), which was synthesized by nitroxide-mediated free radical polymerization. The incorporation of electron-withdrawing cyano groups led to a significant variation in electronic energy levels and luminescence characteristics in comparison with the parent poly(4-vinyltriphenylamine) (PVTPA). The prepared organosoluble PCNVTPA and PVTPA had number-average molecular weights ( $M_n$ ) of 10 200 and 23 400, respectively. PCNVTPA exhibited higher thermal stability ( $T_g=211$  °C) and photoluminescence (PL) quantum efficiency (PLQY) (20%) compared with PVTPA ( $T_g=140$  °C, PLQY=3%) because of enhanced rigidity from the cyano-substituted group. Cyano substitution also led to lower energy levels (HOMO, LUMO, unit: eV) in PCNVTPA (−5.63, −2.52) than in PVTPA (−5.35, −1.89). The emission peak of the Ir complexes was observed in the PL spectra of PVTPA or PCNVTPA/Ir complex blend through efficient energy transfer from the host polymer to the guest Ir complex. Single-layer phosphorescent electroluminescent devices of indium-tin oxide/PEDOT:PSS/PCNVTPA:Ir complexes/Ca:Al showed maximum luminance (2899 cd m<sup>−2</sup>) and luminance efficiency (8.84 cd A<sup>−1</sup>), respectively, which were much higher than those of PVTPA. Such an improvement was probably due to the more efficient hole trapping in Ir complexes by the lower HOMO level or better electron injection from the lower LUMO level of PCNVTPA. The results suggested that the new PCNVTPA could be a good host polymer for the electrophosphorescent device.

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**Keywords:** electron withdrawing; electrophosphorescent; energy level; light-emitting diodes; triphenylamine

## INTRODUCTION

Organic/polymer light-emitting diodes have attracted a lot of attention because of their potential application in flat-panel displays. They have the advantage of large-area low-cost fabrications through solution processing, such as spin casting, screen printing or inkjet printing.<sup>1–14</sup> However, the upper limit on the internal quantum efficiency of organic light-emitting diode or polymer light-emitting diode for electroluminescence is generally limited to 25% owing to the forbiddance of radioactive decay of triplet exciton. Phosphorescent materials based on heavy-metal complexes are particularly attractive, as both singlets and triplets can be harvested for light emission, approaching near 100% internal quantum efficiency.<sup>15,16</sup> Recently, highly efficient electrophosphorescent light-emitting diodes (LEDs) based on iridium,<sup>17</sup> platinum<sup>18</sup> and ruthenium<sup>19</sup> complexes as guests, and small molecules as hosts, have been reported. The heavy-metal complexes enhance phosphorescence, arising from the strong spin-orbit coupling at the metal atom, leading to rapid intersystem crossing and short triplet-state lifetime from the triplet-excited states to ground states.<sup>20</sup> In electrophosphorescent LEDs, charge carriers are injected

from corresponding electrodes into organic host materials, followed by excitation energy transfer to phosphorescent guest materials leading to electrophosphorescence. The transfer process of excited energy from host materials to heavy-metal complexes occurs through various mechanisms such as Förster and Dexter energy transfer.<sup>4,15</sup> In addition, the direct trapping of both holes and electrons on phosphorescent emitters also influences the efficiency of electrophosphorescent LEDs significantly.<sup>21</sup> Phosphorescent polymers consisting of host materials and heavy-metal complexes were reported.<sup>22–25</sup> However, the difficult synthesis procedures of phosphorescent polymers limit their commercial applications. Compared with complicated phosphorescent polymers, blending is a simple way to manipulate and optimize the composition ratio of host materials and guest organometallic complexes.

Triphenylamine-based derivatives have been used in photoreceptor devices<sup>26</sup> and organic light-emitting diodes<sup>27,28</sup> because of the good hole transporting ability of triphenylamine moieties. Small molecular triphenylamine derivatives as host materials have been developed, namely, 4,4',4''-tris(N-carbazole)triphenylamine, which is

<sup>1</sup>Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan and <sup>2</sup>Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsin-Chu, Taiwan

Correspondence: Dr W-C Chen, Institute of Polymer Science and Engineering, National Taiwan University, no. 1, sec. 4, Roosevelt Road, Taipei 106, Taiwan.

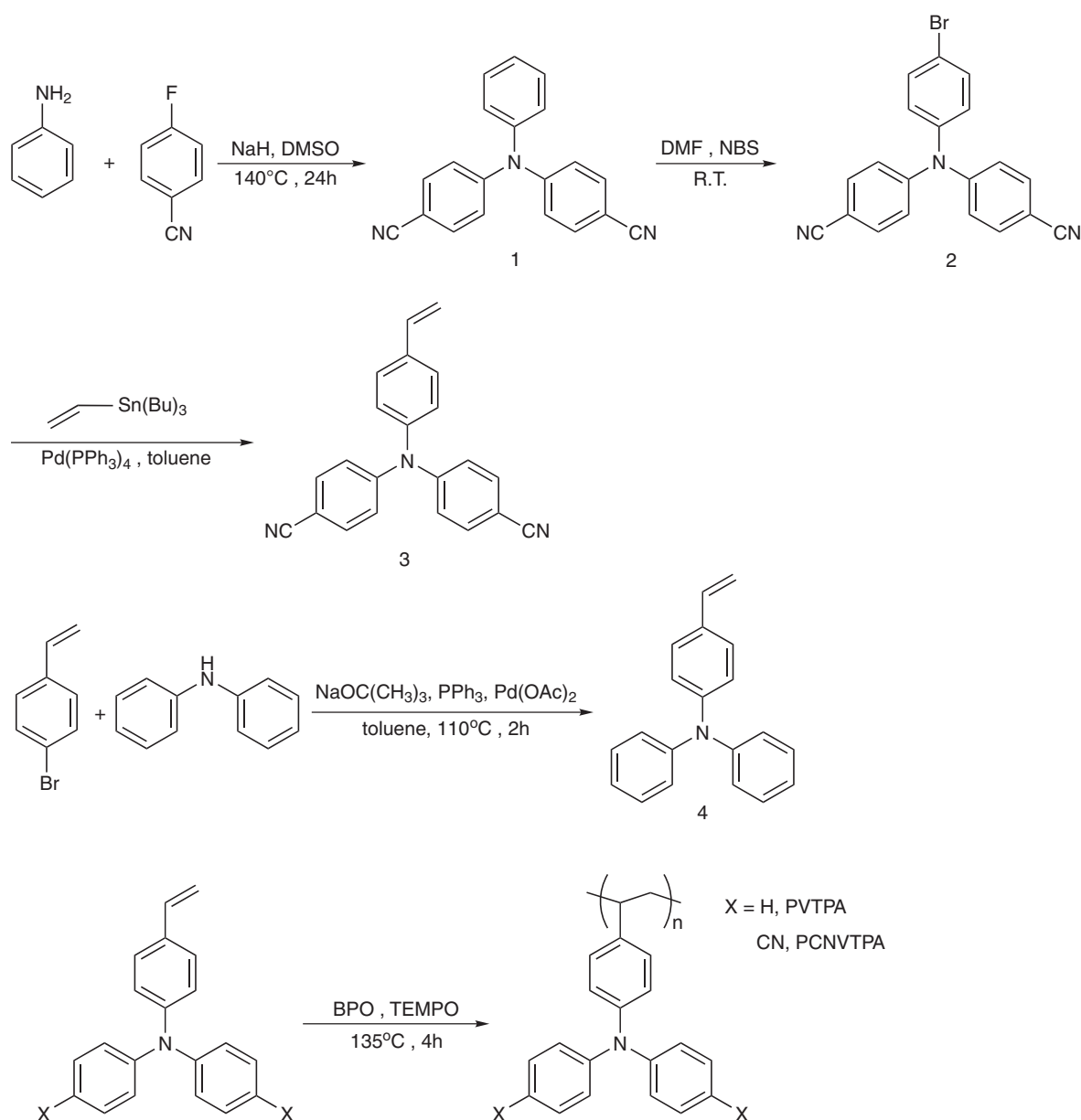
E-mail: chenwc@ntu.edu.tw

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a star-shaped molecule consisting of a triphenylamine unit and three carbazolyl groups.<sup>29,30</sup> Furthermore, polymeric materials with triphenylamine-based derivatives were demonstrated to act as a hole-transport layer in polymer light-emitting diodes.<sup>31</sup> However, there are rare reports for using a homopolymer on the basis of triphenylamine moieties as host materials for electrophosphorescent LEDs. Recently, Lee and co-workers<sup>15</sup> demonstrated that poly(4-vinyltriphenylamine) (PVTTPA) is a host material for electrophosphorescent LEDs, which introduced the triphenylamine moieties into side chains to improve the hole transporting characteristic. However, they reported that the high HOMO level of PVTTPA impeded the trapping of holes in iridium complexes, limiting the performance of the device.

In this study, we used nitroxide-mediated free radical polymerization<sup>32</sup> to synthesize a new host material, poly(4-vinyl-4,4'-dicyano-triphenylamine) (PCNVTPA), as shown in Scheme 1. Compared with

parent PVTTPA, a strong electron-withdrawing cyano group of PCNVTPA was expected to possess a lower HOMO level and lead to better hole trapping on organometallic emitters. In addition, the cyano group of PCNVTPA also provided a lower LUMO level for reducing the charge-injection barrier and enhancing electron transport. The photoluminescence (PL) spectra and performance of electrophosphorescent LEDs, based on the host materials of PVTTPA and PCNVTPA with various iridium complexes, were used to investigate the effect of energy transfer and charge trapping, including iridium (III) bis-(2-(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>) (FIrpic),<sup>33</sup> tris(2-phenylpyridine)iridium (III) (Ir(ppy)<sub>3</sub>)<sup>34</sup> and bis(1-phenylisoquinoline)-(acetylacetonate) iridium (III) (Ir(piql)<sub>2</sub>(acac)).<sup>35</sup> The optical, electrochemical properties and time-resolved lifetimes of PCNVTPA and PVTTPA were also investigated to realize the performance of these host polymers.



**Scheme 1** Synthetic schemes of monomers and polymers for PVTTPA and PCNVTPA.

## EXPERIMENTAL PROCEDURE

### Materials

Reagent-grade 4-fluorobenzonitrile (Matrix Scientific, Columbia, IN, USA), sodium hydride (Aldrich, Milwaukee, WI, USA), aniline (Acros, Geel, Belgium), *N*-bromosuccinimide (Acros), diphenylamine (Acros), 4-bromostyrene (Acros), vinyltributyltin (Acros), sodium tert-butoxide (Acros), triphenylphosphine, Pd(PPh<sub>3</sub>)<sub>4</sub> (Strem Chemicals, Newburyport, MA, USA), Pd(OAc)<sub>2</sub> (Strem Chemicals), toluene (TEDIA, Fairfield, CT, USA), dimethyl sulfoxide (TEDIA), dimethyl formamide (DMF) (TEDIA) and dimethyl acetamide (TEDIA) were used as received from commercial sources, and all other reagents were used without further purification. Benzoyl peroxide and 2,2,6,6-tetramethylpiperidine 1-oxyl were purchased from Acros and used after purification. Tetrabutylammonium perchlorate (TCI, Tokyo, Japan) was recrystallized twice from ethyl acetate and then dried in vacuum before use. 4,4'-Dicyanotriphenylamine was synthesized according to the reported method.<sup>36</sup> Ir(ppy)<sub>3</sub> and Ir(pi-q)<sub>2</sub>(acac) were purchased from American Dye Source (ADS, Baie D'Urfé, Quebec, Canada).

### Synthesis of monomers

**4,4'-dicyano-4''-bromo-triphenylamine (2).** *N*-Bromosuccinimide (7.80 g, 43.8 mmol) was added to the stirred solution of **1** (12.80 g, 43.4 mmol) in DMF (120 ml) at room temperature, and the mixture was stirred for 8 h. After the reaction mixture was poured into 120 ml of MeOH, 400 ml water was added slowly. The yellow solid was filtered and dried to give 15.71 g (96.80%) of product. <sup>1</sup>H NMR (dimethyl sulfoxide-*d*<sub>6</sub>, 300 MHz)  $\delta$  7.12–7.15 (m, 6H), 7.63 (d, 2H), 7.75 (d, 4H).

**4,4'-dicyano-4''-vinyl-triphenylamine (3).** Boronide **2** (7.30 g, 19.5 mmol), vinyltributyltin (6.66 g, 21 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.68 g, 0.6 mmol) were added to 120 ml toluene under nitrogen atmosphere and heated at 90 °C for 8 h. The cooled reaction mixture was concentrated under vacuum, washed with MeOH twice and dried to give a yellow powder. After drying the powder, the crude compound was purified by flash column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) to afford 5.40 g (86% yield) of pure **3** as a yellow powder solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  5.29 (d, 1H CH=CH), 5.75 (d, 1H, CH=CH), 6.69 (dd, 1H, ArCH=CH<sub>2</sub>), 7.03–7.11 (m, 6H), 7.41 (d, 2H), 7.52 (d, 4H).

**4-Vinyltriphenylamine (4).** A mixture of diphenylamine (16.92 g, 100 mmol), 4-bromostyrene (18.31 g, 100 mmol), sodium tert-butoxide (6.91 g, 120 mmol), Pd(OAc)<sub>2</sub> (0.71 g, 3wt%) and PPh<sub>3</sub> (5.25 g, 20 mmol) in 200 ml toluene under argon was heated at 110 °C for 2 h. Column chromatography (silica gel, hexanes) afforded 17.64 g (65%) of white solid product. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  5.16 (d, 1H CH=CH), 5.65 (d, 1H, CH=CH), 6.70 (dd, 1H, ArCH=CH<sub>2</sub>), 6.98–7.10 (m, 8H), 7.21–7.29 (d, 6H).

### Polymer synthesis

**Poly(4,4'-dicyano-4''-vinyl triphenylamine).** The monomer (**3**: 0.64 g, 2 mmol), initiator (benzoyl peroxide: 6.1 mg, 0.025 mmol) and free nitroxide (2,2,6,6-tetramethylpiperidine 1-oxyl: 5.1 mg, 0.0315 mmol) were dissolved in dry 1 ml DMF. The mixture was sealed under N<sub>2</sub> flow and placed into an oil bath at 135 °C for 4 h. After cooling, DMF (~1 ml per 0.2 g of polymer) was added to dissolve the polymer, and the solution was precipitated by methanol. Re-precipitation from DMF into acetone was carried out for further purification by Soxhlet extractor in acetone. The product was filtered and then dried at 60 °C under vacuum to give a yellow powder product. The yield was 50%. Anal. Calcd for (C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>)<sub>n</sub>: C, 82.22%; H, 4.70%; N, 13.08%. Found: C, 80.80%; H, 5.09%; N, 12.97%.

**Poly(4-vinyltriphenylamine).** A mixture of 4-vinyltriphenylamine (**4**: 0.61 g, 2 mmol), initiator (benzoyl peroxide: 6.1 mg, 0.025 mmol), free nitroxide (2,2,6,6-tetramethylpiperidine 1-oxyl: 5.1 mg, 0.0315 mmol) and dry 1 ml DMF was added to a glass tube fitted with a magnetic stirring bar. The mixture was sealed in N<sub>2</sub> and placed into an oil bath at 135 °C for 4 h. After cooling, DMF (~1 ml per 0.2 g of polymer) was added to dissolve the polymer, and the solution was precipitated by methanol. Re-precipitation from DMF into methanol was carried out for further purification by Soxhlet extractor in acetone. The product was collected by filtration and dried under vacuum at

60 °C to give a yellow powder product. The yield was 65%. Anal. Calcd for (C<sub>20</sub>H<sub>17</sub>N)<sub>n</sub>: C, 88.52%; H, 6.26%; N, 5.16%. Found: C, 86.83%; H, 6.33%; N, 4.68%.

### Characterization

<sup>1</sup>H and NMR spectra were measured on a Bruker Avance 300 MHz FT-NMR system (Bruker Avance, Karlsruhe, Germany). Gel permeation chromatographic analysis was performed on a Lab Alliance RI2000 instrument (one column, MIXED-D from Polymer Laboratories, Palo Alto, CA, USA) connected with one refractive index detector from Schambeck SFD GmbH (Bad Honnef, Germany). All gel permeation chromatographic analyses were performed on a polymer/tetrahydrofuran (or DMF) solution at a flow rate of 1 ml min<sup>-1</sup> at 40 °C (701C), and calibrated with polystyrene standards. Elemental analyses were performed with a Heraeus VarioEL-III-NCSH (Heraeus, Karlsruhe, Germany) instrument. Thermogravimetric analysis was conducted using a PerkinElmer Pyris 1 thermogravimetric analyser (PerkinElmer, Waltham, MA, USA). Experiments were carried out on 6–8 mg film samples heated in flowing nitrogen (flow rate 40 cm<sup>3</sup> per min) at a heating rate of 20 °C per min. Differential scanning calorimetry measurements were performed under a nitrogen atmosphere at a heating rate of 20 °C min<sup>-1</sup> from –50 to 250 °C using a TA instrument DSC-910S. Electrochemistry was performed with a CHI 611B electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. Cyclic voltammetry was performed with the use of a three-electrode cell in which indium-tin oxide (ITO) (polymer films area about 0.7 × 0.5 cm<sup>2</sup>) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a homemade Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra were measured with a Hitachi U4100 UV-Vis-NIR (Hitachi, Tokyo, Japan) spectrophotometer. Photoluminescence spectra were measured with a Fluorolog-3 spectrophotometer (Jobin Yvon, Edison, NJ, USA) spectrofluorometer. For thin film spectra, polymers were dissolved in chlorobenzene, dimethyl acetamide (for PCNVTPA) (~10 mg ml<sup>-1</sup>) and then placed in a quartz cell for measurement; the solution was then spin coated at a speed rate of 2000 r.p.m. for 60 s onto a quartz substrate. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra.

### Fabrication of electrophosphorescent LED

The electrophosphorescent devices were fabricated on ITO-coated glass substrate with sheet resistance of 7 Ω sq<sup>-1</sup>. The substrate was ultrasonically cleaned with detergent, deionized water, acetone and methanol subsequently. First, PEDOT:PSS was coated onto the pre-cleaned ITO glass as the hole-injection layer and dried in vacuum at 150 °C for 15 min. Afterward, a single-layer emissive layer was spin coated at 2000 r.p.m. from the polymer (10 mg) by doping with three different Ir complexes (6 wt%) in 1 ml of DMF solution. Finally, under a base pressure below 1 × 10<sup>-6</sup> Torr, a layer of Ca (40 nm) was vacuum deposited as cathode, and a thick layer of Al (200 nm) was deposited subsequently as the protecting layer. Thereafter, a device configuration of ITO/PEDOT:PSS/PVTPA or PCNVTPA:Ir complexes/Ca/Al was obtained. The refractive index of the thin films of polymer blends with Ir complexes was measured with an ellipsometer (SOPRA, GES-5E, Lausanne, Switzerland) analyzer. The thickness of the emissive layer was measured approximately 60–80 nm by the  $\alpha$ -stepper500/Tencor (Alpha-stepper500/Tencor, Milpitas, CA, USA). Current–voltage characteristics were analyzed with a computerized Keithley 2400 (Keithley Instruments, Cleveland, OH, USA) source measure unit. The luminance and CIE coordinate of the device were measured with a Topcon BM7 (Topcon, Tokyo, Japan) luminescent meter. The electroluminescent (EL) spectrum of the device was recorded on a Hitachi FL 4500 spectrophotometer.

## RESULTS AND DISCUSSION

### Polymer structure characterization

Compound (**3**) was synthesized by the aromatic nucleophile-attacked amination of 4-fluorobenzonitrile and aniline in dimethyl sulfoxide in the presence of sodium hydride, followed by *N*-bromosuccinimide in DMF, and then reacted by Stille coupling. Thereafter, the homopoly-

mer cyano-substituted aromatic polymer (PCNVTPA) was obtained by nitroxide-mediated free radical polymerization (Scheme 1). The polymer PVTPA was obtained from direct-living free radical polymerization of 4-vinyltriphenylamine (4). The molecular weight and thermal properties of polymers are summarized in Table 1.

Figure 1 shows the  $^1\text{H}$  NMR spectra of monomer (3) and polymer (PCNVTPA) in  $\text{CDCl}_3$  and  $d$ -DMF, respectively. In the spectrum of monomer (3), the signals at 5.29, 5.75 and 6.69 p.p.m. are assigned to the protons of the vinyl group. The signals in 7.03–7.52 p.p.m. are attributed to the protons on the triphenylamine aromatic moieties. The  $^1\text{H}$  NMR spectrum of PCNVTPA shows aromatic proton signals between 6.75 and 7.81 p.p.m. The experimental carbon, hydrogen and nitrogen contents are in fair agreement with the theoretical values.

Polymer PVTPA exhibited good solubility in various solvents such as tetrahydrofuran, toluene and chlorobenzene. However, PCNVTPA is only soluble in highly polar aprotic solvents such as DMF, dimethyl

acetamide and  $N$ -methylpyrrolidinone. The weight-average molecular weights ( $M_n$ ) of PVTPA and PCNVTPA are 10 200 and 23 400, with polydispersity index values of 1.27 and 1.24, respectively. The thermal properties of these polymers were evaluated by thermogravimetric analysis and differential scanning calorimetry, as shown in Figure 2, and the results are summarized in Table 1. As shown in Figure 2, PCNVTPA showed a higher  $T_d$  (404 °C) and  $T_g$  (211 °C) than the corresponding PVTPA ( $T_g=140$  °C,  $T_d=387$  °C). The high thermal stability can be attributed to the incorporation of the cyano-substituted groups, thereby increasing the rigidity of the pendant triphenylamine. Note that the high thermal stability of PCNVTPA could suppress the phase aggregation of phosphors in the blending process and enhance the performance and stability of electrophosphorescent LEDs further.

### Optical properties

The optical properties of PVTPA and PCNVTPA were investigated by ultraviolet-visible optical absorption and PL spectroscopy, as summarized in Table 2. Figure 3a shows the optical absorption spectra of PVTPA and PCNVTPA thin films on the quartz plate. The absorption peak maxima of PVTPA and PCNVTPA are observed at 306 and 353 nm, respectively. PCNVTPA has the main absorption peak maximum at 353 nm with the shoulder peak at 308 nm. The shoulder peak probably originated from the triphenylamine moiety, similar to that of PVTPA. The optical band gaps of PVTPA and PCNVTPA estimated from absorption edges are 3.46 and 3.11 eV, respectively. PCNVTPA shows a smaller band gap (3.11 eV) than PVTPA, probably due to intramolecular charge transfer in the cyano-substituted triphenylamine.<sup>37</sup>

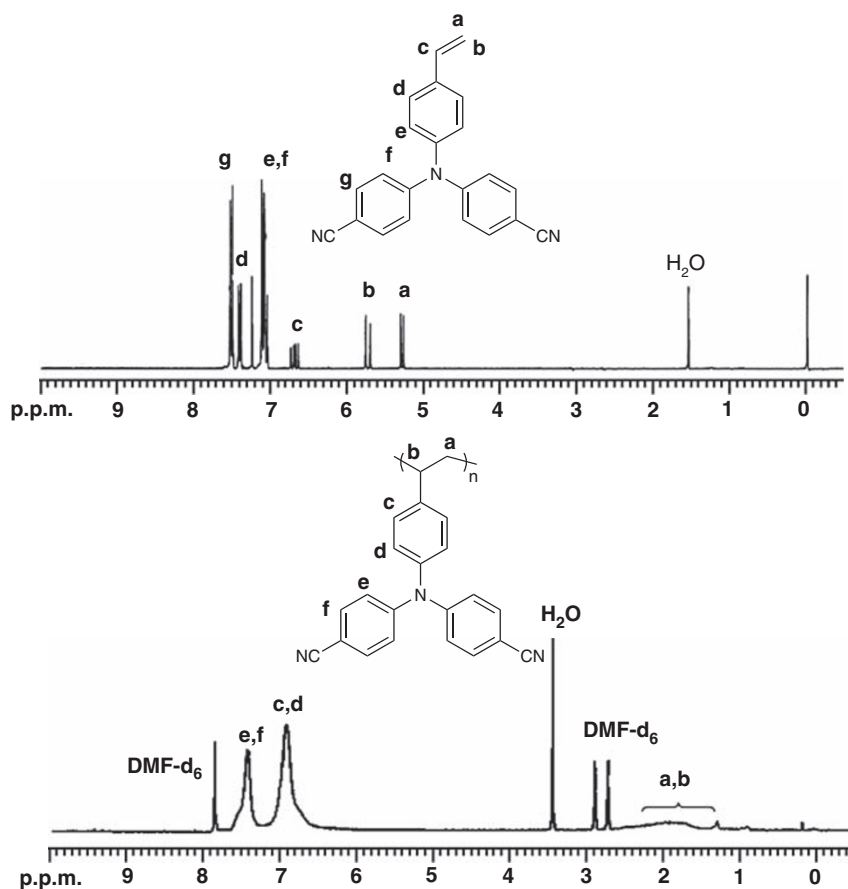
**Table 1** Molecular weights and thermal properties of PVTPA and PCNVTPA

Index	$M_n^a$	$M_w^a$	PDI <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	$T_d$ (°C) <sup>c</sup>
PVTPA	10 200	13 000	1.27	140	387
PCNVTPA	23 400	29 000	1.24	211	404

<sup>a</sup>Relative to polystyrene standards, with tetrahydrofuran (PVTPA), DMF (PCNVTPA) as the elute.

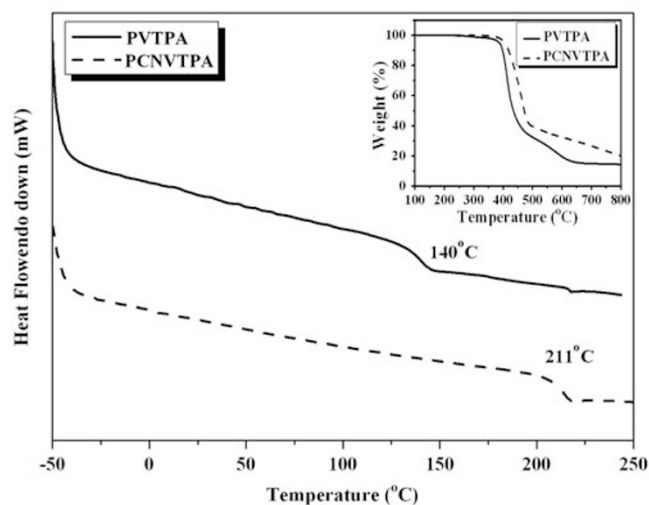
<sup>b</sup>Midpoint temperature of baseline shift on the second differential scanning calorimetry heating trace (rate 20 °C min<sup>-1</sup>) of the sample after quenching from 250 to -50 °C.

<sup>c</sup>Temperature at which 5 % weight loss occurred.



**Figure 1**  $^1\text{H}$  NMR spectra of monomer 3 and PCNVTPA in  $\text{CDCl}_3$  and  $\text{DMF-d}_6$ , respectively.

The normalized PL emission spectra of PVTPA and PCNVTPA in thin films are shown in Figure 3. The PL measurement was excited at a wavelength of 306 and 353 nm on the basis of the maximum optical absorption peaks. They showed blue emission peaks at 437 and 429 nm, respectively. Moreover, the PL quantum efficiencies of PVTPA and PCNVTPA films are 3.7 and 20.3%, respectively. It suggests that the cyano group not only decreases the band gap but also enhances the emission of PCNVTPA owing to increased rigidity.<sup>38</sup> The time-resolved PL decay time of PVTPA and PCNVTPA shown in Table 2 was obtained by exciting at 306 and 350 nm and monitoring at 437 and 429 nm, respectively. The absorption maxima ( $\lambda_{\max}$ ) of FIrpic, Ir(ppy)<sub>3</sub> and Ir(piq)<sub>2</sub>(acac) thin films are observed at 259, 290 and (296, 353) nm, respectively, which could be attributed to the ligand-centered  $\pi \rightarrow \pi^*$  transition as shown in Figure 3b. Furthermore, the absorption peak maxima (unit: nm) at (380, 381 and 483) and (408, 460 and 555) are attributed to singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) and triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) transitions, respectively. The PL peak maxima of FIrpic, Ir(ppy)<sub>3</sub> and Ir(piq)<sub>2</sub>(acac) thin films are exhibited at (476, 500), 517 and (622, 655, 702) nm, which are attributed to <sup>3</sup>MLCT transition, respectively. Two sets of decay times are obtained for both PVTPA (0.46 and 1.85 ns) and PCNVTPA (0.58 and 3.03 ns), where the short decay time is  $\tau_1$  and the other long decay time is  $\tau_2$ . The slow component ( $\tau_2$ ) of the lifetime might be attributed to the formation of excimers. The  $\tau_2$  of PCNVTPA exhibited a smaller fraction of 39% than that of PVTPA (79%), indicating that less excimers formed in the PCNVTPA thin film. It accounts for a higher quantum yield of PCNVTPA than PVTPA.



**Figure 2** Differential scanning calorimetry curves of PVTPA and PCNVTPA with a heating rate of 20 °C min<sup>-1</sup> under nitrogen. The inset shows the thermogravimetric analysis thermograms of PVTPA and PCNVTPA at a heating rate of 20 °C min<sup>-1</sup> under nitrogen.

**Table 2** Optical and electrochemical properties for homopolymer films

Polymer	$\lambda_{\max}$ (nm)	$E_g$ (eV) <sup>a</sup>	PL $\lambda_{\max}$ (nm)	$\phi^{PL}$ (%) <sup>b</sup>	HOMO <sup>c</sup>	LUMO <sup>d</sup>	$\tau_1$ (ns) <sup>e</sup>	$\alpha_1^f$	$\tau_2$ (ns)	$\alpha_2$
PVTPA	306	3.46	437	3.7	5.35	1.89	0.46	0.21	1.85	0.79
PCNVTPA	308, 353	3.11	429	20.3	5.63	2.52	0.58	0.61	3.03	0.39

<sup>a</sup>The data were calculated by the equation:  $\text{gap} = 1240/\lambda_{\text{onset}}$  of polymer film.

<sup>b</sup>PL quantum yield measured in the solid state.

<sup>c</sup>The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

<sup>d</sup>LUMO = HOMO - gap.

<sup>e</sup> $\tau$ , decay time.

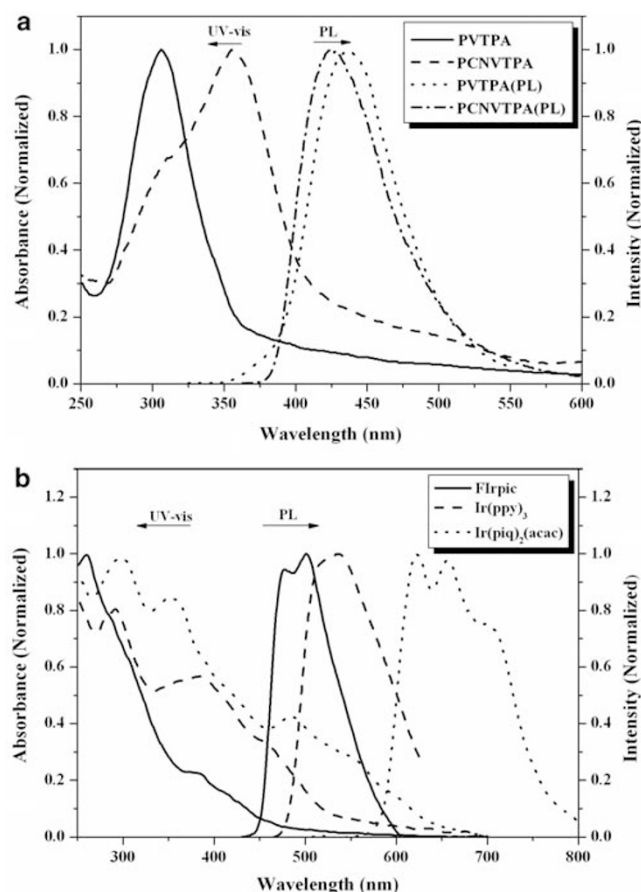
<sup>f</sup> $\alpha$ , decay time fraction.

### Förster energy transfer

The efficiency of Förster energy transfer was estimated from the PL quenching of host materials, as shown in Figures 4 and 5. The PL spectra of PCNVTPA/Ir(ppy)<sub>3</sub> blend films showed no further energy transfer after the composition of 6 wt% Ir(ppy)<sub>3</sub>, as shown in Figure 5a. Thus, we select 6 wt% of Ir phosphors for further luminescence characterization. The efficiency of Förster energy transfer from host to guest can be predicted through the analysis of the Förster radius. Long Förster radius induces more efficient energy transfer. The expression of Förster radius is given by equation (1):<sup>39</sup>

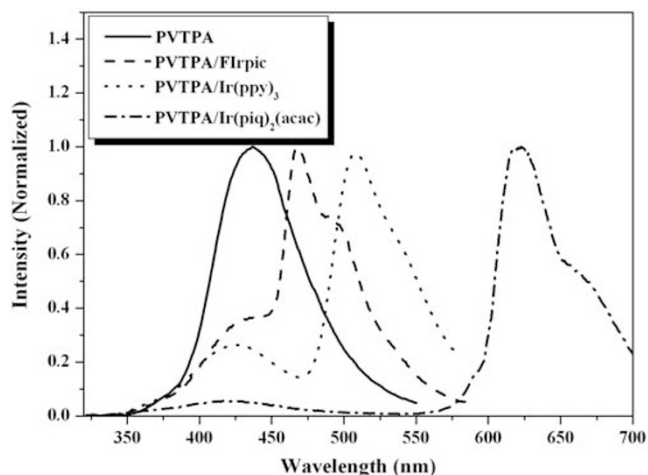
$$R_0^6 = \frac{9000(\ln 10)\kappa^2\Phi_D J}{128\pi^5 N_A V n^4} \quad (1)$$

where  $R_0$  is the characteristic Förster radius and  $\kappa^2$  is a configuration term with a value between 0 and 4 that takes into account the relative

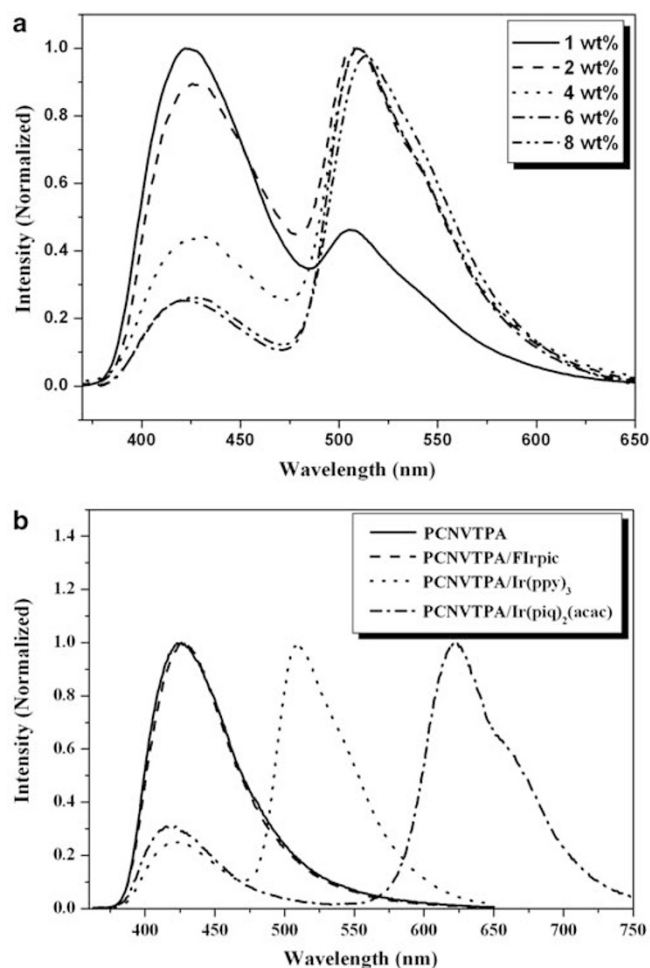


**Figure 3** (a) Normalized UV-vis absorption and PL spectra of PVTPA and PCNVTPA films. (b) Normalized UV-vis absorption and PL spectra of Ir complex films.

orientation of the transition dipole moments of a donor and an acceptor.  $\kappa^2$  is usually assumed to be equal to 2/3 for the dynamic random average of donors and acceptors.  $\Phi_D$  is the quantum yield of



**Figure 4** PL spectra of the films prepared from PVTPA blended with 6 wt% of various Ir complexes.



**Figure 5** (a) PL spectra of thin films from PCNVTPA blended with Ir(ppy)<sub>3</sub> phosphors from 1 to 8 wt%. (b) PL spectra of the thin films from PCNVTPA blended with 6 wt% Ir complexes.

fluorescence of the host,  $N_{AV}$  is Avogadro's number and  $n$  is the refractive index of the medium.  $J$  is the overlap integral that interprets the overlap of donor emission and acceptor absorption numerically, and is given by equation (2):

$$J = \int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \quad (2)$$

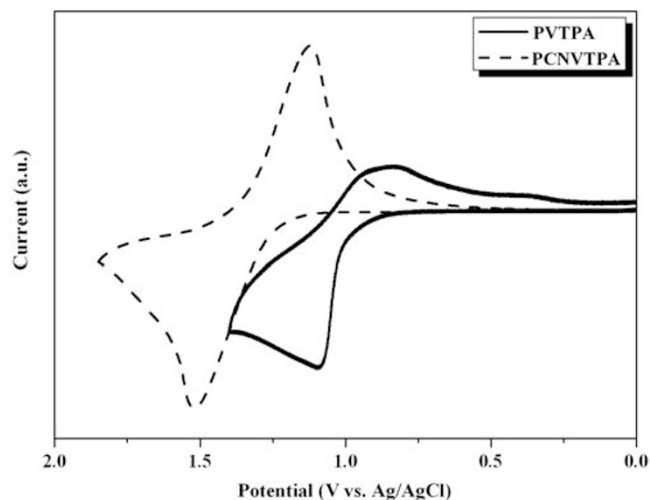
where  $F_D(\lambda)$  is the corrected fluorescence intensity of the host in the wavelength (nm) range from  $\lambda$  to  $\lambda+d\lambda$ , with the total intensity (area under the curve) normalized to unity, and  $\varepsilon_A(\lambda)$  is the molar absorption coefficient of the guest at  $\lambda$  (nm). We assume that  $\kappa^2$  and the density of the polymer blend with Ir complexes equal 2/3 and 1, respectively. The refractive index values of the PVTPA/Ir complex and PCNVTPA/Ir complex blend films measured from the ellipsometer are around 1.65 and 1.69. Hence, the Förster radii of PCNVTPA/Flrpic, Ir(ppy)<sub>3</sub> and Ir(piq)<sub>2</sub>(acac) blend films estimated by equations (1) and (2) are 2.06, 2.37 and 2.57 nm, respectively, whereas those of PVTPA blend films are 1.57, 1.81 and 1.98 nm. PCNVTPA possesses larger Förster radii with various dopant complexes than does PVTPA, indicating that the more efficient Förster energy transfer is in the PCNVTPA/Ir complexes blends. After blending with dopant Ir(ppy)<sub>3</sub> or Ir(piq)<sub>2</sub>(acac), the emission intensities of PVTPA and PCNVTPA decrease significantly but that of Ir complexes emerges, showing efficient Förster energy transfer. However, compared with the blend of PVTPA and Flrpic, the energy transfer of PCNVTPA and Flrpic is less efficient. It is presumably attributed to the fact that the quenching of the excited triplet state in Flrpic might occur through back energy transfer from the triplet state in Flrpic to that in PCNVTPA.<sup>15,40</sup>

### Electrochemical properties

The electrochemical properties of polymers were investigated by cyclic voltammetry, and the results are summarized in Table 2. The oxidation behaviors of PVTPA and PCNVTPA films on an ITO-coated glass substrate in dry acetonitrile containing 0.1 M of tetrabutylammonium perchlorate were investigated in atmosphere. The cyclic voltammograms of PVTPA and PCNVTPA are shown in Figure 6. The oxidation potential of PCNVTPA ( $E_{\text{onset}}=1.27$  V) is higher than that of PVTPA ( $E_{\text{onset}}=0.99$  V), because of the introduction of the electron-withdrawing cyano-substituted group. The HOMO levels of polymers were estimated from the onset of oxidation potentials ( $E_{\text{onset}}$ ), and the LUMO levels were determined by the extraction of band gaps from the HOMO levels. All electrochemical properties and energy levels are summarized in Table 2. The energy band diagrams of PVTPA, PCNVTPA and Ir complexes are shown in Figure 7. The HOMO energy level of host PCNVTPA (−5.63 eV) is lower than that of Ir(ppy)<sub>3</sub> (−5.5 eV) and Ir(piq)<sub>2</sub>(acac) (−5.0 eV). It would probably result in efficient hole trapping in Ir(ppy)<sub>3</sub> and Ir(piq)<sub>2</sub>(acac) and improve the efficiency of electrophosphorescent LEDs. However, the high HOMO energy levels of PVTPA (−5.35 eV) impede the hole trapping in Ir(ppy)<sub>3</sub> and Flrpic.

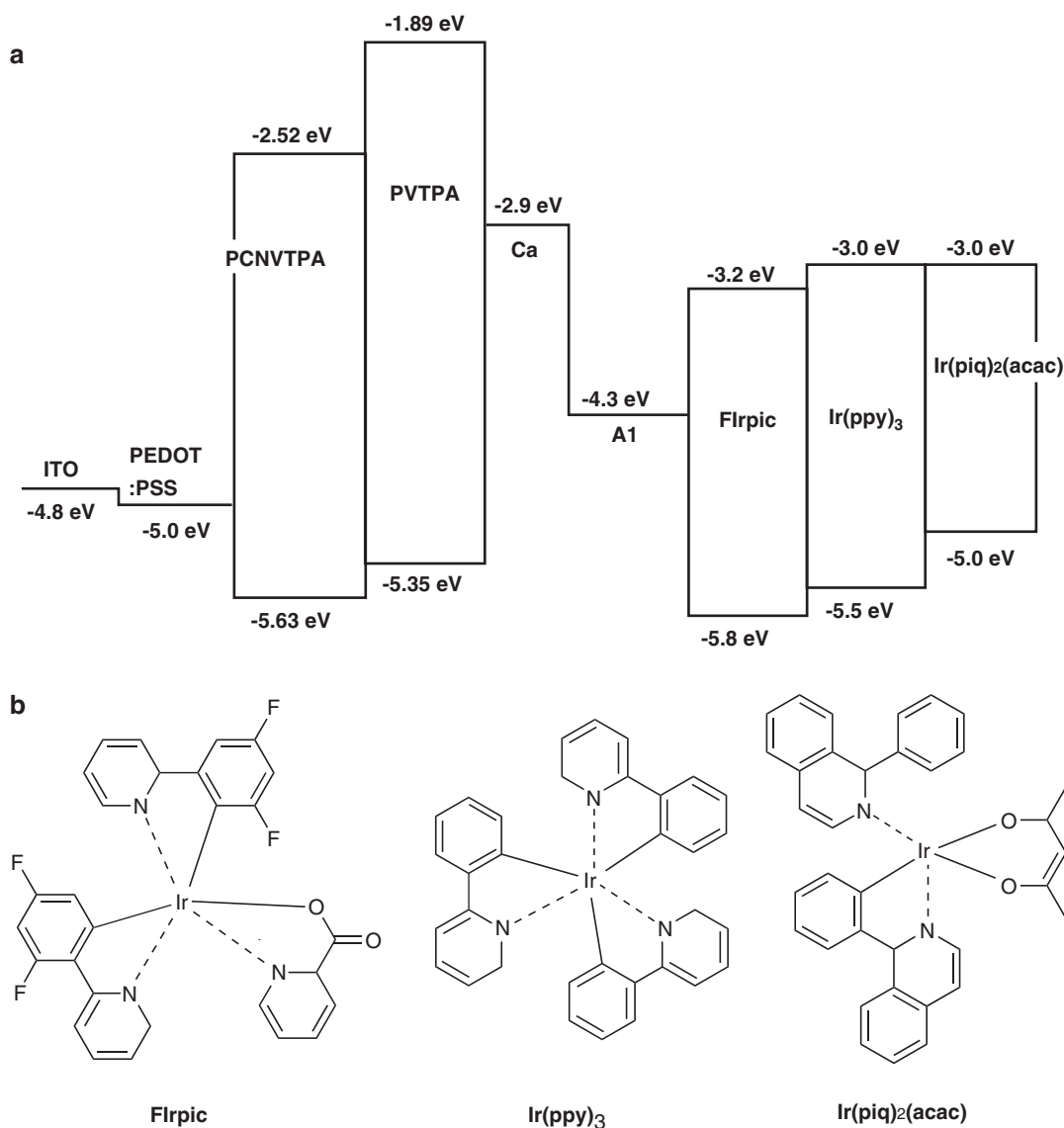
### Electroluminescence properties

To investigate the electrophosphorescent properties of polymers, single-layer electroluminescent devices based on the studied polymers as host materials were fabricated through a configuration of ITO/PEDOT:PSS/polymer:Ir complexes/Ca:Al. The corresponding emissive characteristics are listed in Table 3. As shown in Table 3, all devices of the PCNVTPA/Ir complex blends exhibited higher performance than those of PVTPA/Ir blends. The device based on PCNVTPA/Ir(ppy)<sub>3</sub>



**Figure 6** Cyclic voltammograms of the PVTPA and PCNVTPA film on an indium-tin oxide (ITO)-coated glass substrate in  $\text{CH}_3\text{CN}$  containing 0.1 M tetrabutylammonium perchlorate. Scan rate =  $0.1 \text{ V s}^{-1}$ .

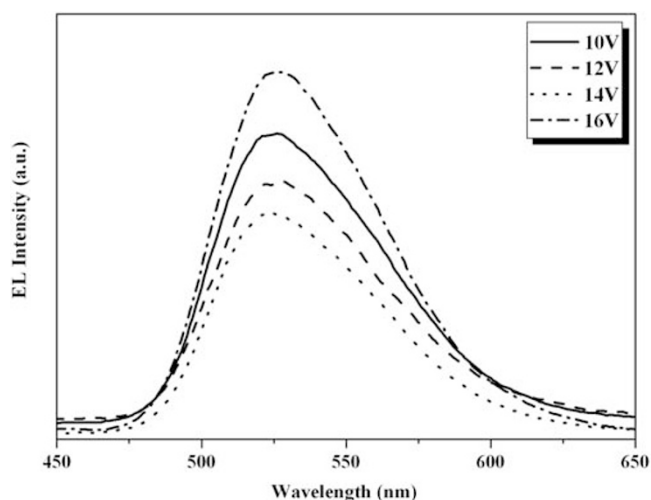
showed the highest luminance of  $2899 \text{ cd m}^{-2}$  and luminance efficiency of  $8.84 \text{ cd A}^{-1}$ . Figure 8 shows the EL spectra of the PCNVTPA/ $\text{Ir}(\text{ppy})_3$  blend film under various voltages, which exhibit a relatively stable EL emission. Compared with PL spectra, the EL spectra of the blends only exhibited a strong emission at  $\sim 525 \text{ nm}$ , which is attributed to the emission of  $\text{Ir}(\text{ppy})_3$ . It indicates the efficient energy transfer from PCNVTPA to  $\text{Ir}(\text{ppy})_3$ . However, the EL emission of PVTPA doped with  $\text{Flrpic}$  and  $\text{Ir}(\text{ppy})_3$  is not observed. It suggests that the trapping of holes and electrons on Ir complexes dominates the EL performance, instead of Förster energy transfer. As shown in Figure 6, the HOMO levels of  $\text{Ir}(\text{ppy})_3$  and  $\text{Ir}(\text{piq})_2(\text{acac})$  are higher than that of PCNVTPA. Thus, holes tend to trap-in  $\text{Ir}(\text{ppy})_3$  and  $\text{Ir}(\text{piq})_2(\text{acac})$ , and electrons can then sequentially hop onto phosphors to form excitons. In addition, the cyano-substituted group of PCNVTPA lowers the LUMO level ( $-2.52 \text{ eV}$ ) and facilitates electron injection from the cathode, making the single-layer devices possible without using further electron transporting materials. On the other hand, the higher HOMO level of PVTPA than that of  $\text{Flrpic}$  or  $\text{Ir}(\text{ppy})_3$  probably leads to the trapping of holes in PVTPA, whereby quenching of the triplet excited state occurs. Moreover, in the single-



**Figure 7** (a) HOMO and LUMO energy levels of PVTPA, PCNVTPA and Ir complexes. (b) The structures of Ir complexes.

**Table 3** Luminescent characteristics of single-layer light-emitting diodes on the basis of the polymer/Ir complex blend films

	$V_{\text{turn-on}}^a$ (V)	Bias <sup>b</sup> (V)	$L_{\text{max}}^c$ $\text{cd m}^{-2}$	$LE_{\text{max}}^d$ ( $\text{cd A}^{-1}$ )	CIE coordinates ( $x, y$ ) <sup>e</sup>
PVTPA/Flpic	— <sup>f</sup>	—	—	—	—
PVTPA/Ir(ppy) <sub>3</sub>	—	—	—	—	—
PVTPA/Ir(piq) <sub>2</sub> (acac)	6	11	34	0.02	(0.59, 0.33)
PCNVTTPA/Flpic	5	9	99	0.06	(0.22, 0.34)
PCNVTTPA/Ir(ppy) <sub>3</sub>	4	12.5	2899	8.84	(0.33, 0.61)
PCNVTTPA/Ir(piq) <sub>2</sub> (acac)	6	11	222	0.17	(0.67, 0.33)

<sup>a</sup>Voltage needed for a bcenterness of 1  $\text{cd m}^{-2}$ .<sup>b</sup> $L_{\text{max}}$ , maximum luminance.<sup>c</sup>Bias at maximum luminance.<sup>d</sup> $LE_{\text{max}}$ , maximum luminance efficiency.<sup>e</sup>CIE coordinates at maximum luminance.<sup>f</sup>No observation.**Figure 8** Normalized EL spectra of the PCNVTTPA under the different driving voltages (device structure: ITO/PEDOT:PSS/PCNVTTPA:Ir(ppy)<sub>3</sub>/Ca:Ag).

layer structure, the high-lying LUMO level ( $-1.89\text{ eV}$ ) of PVTPA could inhibit electron injection from the cathode. Hence, the maximum luminance of the blend of PVTPA and Ir(piq)<sub>2</sub>(acac) is an order of magnitude lower than that of the blend of PCNVTTPA and Ir(piq)<sub>2</sub>(acac). The good performance of electrophosphorescent LEDs based on PVTPA was only reported in the multilayer configuration using PBD (2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole) as electron transporting material and 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) as the exciton blocking layer.<sup>15</sup> However, the large injection barrier between PVTPA and the cathode reduces the application potential in single-layer devices. The present results show that cyano-substituted PCNVTTPA is a promising host material for single-layer phosphorescent devices.

## CONCLUSION

We have successfully synthesized a new host material PCNVTTPA by nitroxide-mediated free radical polymerization for high-performance iridium complex light-emitting devices. The incorporation of electron-withdrawing cyano groups led to a significant reduction in electronic energy levels and improved luminescent characteristics in comparison with parent PVTPA. Efficient energy transfer was observed from the host PCNVTTPA to the guest Ir complex. Single-

layer phosphorescent EL devices of ITO/PEDOT:PSS/PCNVTTPA:Ir complexes/Ca:Al exhibited the maximum luminance ( $2899\text{ cd m}^{-2}$ ) and luminance efficiency ( $8.84\text{ cd A}^{-1}$ ), respectively, which were much higher than those of PVTPA. Such an improvement was probably due to the more efficient hole trapping in Ir complexes or better electron injection from the lower energy levels of PCNVTTPA. The results suggested that PCNVTTPA could be a good host polymer for the electrophosphorescent device.

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- Heeger, A. J. Semiconducting and metallic polymers: the fourth generation of polymeric materials (nobel lecture). *Angew. Chem. Int. Ed.* **40**, 2591–2611 (2001).
- Pschenitzha, F. & Sturm, J. C. Three-color organic light-emitting diodes patterned by masked dye diffusion. *Appl. Phys. Lett.* **74**, 1913–1915 (1999).
- Sirringhaus, H., Kawase, T., Friend, R. H., Shimoda, T., Inbasekaran, M. & Wu, W. W. High-resolution inkjet printing of all-polymer transistor circuits. *Science* **290**, 2123–2126 (2000).
- Jin, Y., Song, S., Park, S. H., Kim, J., Woo, H. Y., Lee, K. & Suh, H. Novel electroluminescent PPV copolymers containing Si-phenyl and difluorovinylene units. *Polym. J.* **40**, 965–970 (2008).
- Lee, W. Y., Chen, C. W., Chueh, C. C., Yang, C. C. & Chen, W. C. Synthesis of new fluorene-indolocarbazole alternating copolymers for light-emitting diodes and field effect transistors. *Polym. J.* **40**, 249–255 (2008).
- Friend, R. H., Gymer, R. W., Holmes, A. B., Burroughes, J. H., Marks, R. N., Taliani, C., Bradley, D. D. C., Dos Santos, D. A., Brédas, J. L., Lögdlund, M. & Salaneck, W. R. Electroluminescence in conjugated polymers. *Nature* **397**, 121–128 (1999).
- McGehee, M. D., Bergstedt, T., Zhang, C., Saab, A. P., O'Regan, M. B., Bazan, G. C., Srdanov, V. I. & Heeger, A. J. Narrow bandwidth luminescence from blends with energy transfer from semiconducting conjugated polymers to europium complexes. *Adv. Mater.* **11**, 1349–1354 (1999).
- Lee, C. L., Lee, K. B. & Kim, J. J. Polymer phosphorescent light-emitting devices doped with tris(2-phenylpyridine) iridium as a triplet emitter. *Appl. Phys. Lett.* **77**, 2280–2282 (2000).
- O'Regan, M. B., Giebler, C., Fletcher, R. B., Cadby, J., Paliis, L. C., Lidzey, D. G., Lane, P. A., Bradley, D. D. C. & Blau, W. Electrophosphorescence from a doped polymer light emitting diode. *Synth. Met.* **116**, 379–383 (2001).
- Lamansky, S., Kwong, R. C., Nugent, M., Djurovich, P. I. & Thompson, M. E. Molecularly doped polymer light emitting diodes utilizing phosphorescent Pt(II) and Ir(III) dopants. *Org. Electron.* **2**, 53–62 (2001).
- Zhu, W. G., Mo, Y. Q., Yuan, M., Yang, W. & Cao, Y. Highly efficient electrophosphorescent devices based on conjugated polymers doped with iridium complexes. *Appl. Phys. Lett.* **80**, 2045–2047 (2002).
- Gong, X., Robinson, M. R., Ostrowski, J. C., Moses, D., Bazan, G. C. & Heeger, A. J. High-efficiency polymer-based electrophosphorescent devices. *Adv. Mater.* **14**, 581–585 (2002).
- Gong, X., Ostrowski, J. C., Moses, D., Bazan, G. C. & Heeger, A. J. Red electrophosphorescence from polymer doped with iridium complex. *Appl. Phys. Lett.* **81**, 3711–3713 (2002).
- Gong, X., Ostrowski, J. C., Moses, D., Bazan, G. C., Heeger, A. J., Liu, M. S. & Jen, A. K. Y. Electrophosphorescence from a conjugated copolymer doped with an iridium complex: high brightness and improved operational stability. *Adv. Mater.* **15**, 45–49 (2003).
- Lee, C. C., Yeh, K. M. & Chen, Y. New host homopolymers containing pendant triphenylamine derivatives: synthesis, optical, electrochemical properties and its blend with Ir(ppy)<sub>3</sub> for green phosphorescent organic light-emitting devices. *J. Polym. Sci. Part A: Polym. Chem.* **46**, 7960–7971 (2008).
- Yeh, K. M., Lee, C. C. & Chen, Y. Poly(4-vinyltriphenylamine): optical, electrochemical properties and its new application as a host material of green phosphorescent Ir(ppy)<sub>3</sub> dopant. *Synth. Met.* **158**, 565–571 (2008).
- Baldo, M. A., Thompson, M. E. & Forrest, S. R. High-efficiency fluorescent organic light-emitting devices using a phosphorescent sensitizer. *Nature* **403**, 750–753 (2000).
- Kavitha, J., Chang, S. Y., Chi, Y., Yu, J. K., Hu, Y. H., Chou, P. T., Peng, S. M., Lee, G. H., Tao, Y. T., Chien, C. H. & Carty, A. J. In search of high-performance platinum(II) phosphorescent materials for the fabrication of red electroluminescent devices. *Adv. Funct. Mater.* **15**, 223–229 (2005).
- Tung, Y. L., Lee, S. W., Chi, Y., Chen, L. S., Shu, C. F., Wu, F. I., Carty, A. J., Chou, P. T., Peng, S. M. & Lee, G. H. Organic light-emitting diodes based on charge-neutral Ru(II) phosphorescent emitters. *Adv. Mater.* **17**, 1059–1064 (2005).
- Klessinger, M. & Michl, J. *Excited States and Photochemistry of Organic Molecules* (Wiley-VCH, New York, 1995).



- 21 Gong, X., Ostrowski, J. C., Moses, D., Bazan, G. C. & Heeger, A. J. Electrophosphorescence from a polymer guest-host system with an iridium complex as guest: Förster energy transfer and charge trapping. *Adv. Funct. Mater.* **13**, 439–444 (2003).
- 22 Chen, X. W., Liao, J. L., Liang, Y. M., Ahmed, M. O., Tseng, H. E. & Chen, S. A. High-efficiency red-light emission from polyfluorenes grafted with cyclometalated iridium complexes and charge transport moiety. *J. Am. Chem. Soc.* **125**, 636–637 (2003).
- 23 Jiang, J., Jiang, C., Yang, W., Zhen, H., Huang, F. & Cao, Y. High-efficiency electrophosphorescent fluorene-*alt*-carbazole copolymers N-grafted with cyclometalated Ir complexes. *Macromolecules* **38**, 4072–4080 (2005).
- 24 You, Y., Kim, S. H., Jung, H. K. & Park, S. Y. Blue electrophosphorescence from iridium complex covalently bonded to the poly(9-dodecyl-3-vinylcarbazole): suppressed phase segregation and enhanced energy transfer. *Macromolecules* **39**, 349–356 (2006).
- 25 Schulz, G. L., Chen, X., Chen, S. A. & Holdcroft, S. Enhancement of phosphorescence of Ir complexes bound to conjugated polymers: increasing the triplet level of the main chain. *Macromolecules* **39**, 9157–9165 (2006).
- 26 Law, K. Y. Organic photoconductive materials: recent trends and developments. *Chem. Rev.* **93**, 449–486 (1993).
- 27 Mitschke, R. H. & Bauerle, P. The electroluminescence of organic materials. *J. Mater. Chem.* **10**, 1471–1507 (2000).
- 28 Forrest, S. R. Ultrathin organic films grown by organic molecular beam deposition and related techniques. *Chem. Rev.* **97**, 1793–1896 (1997).
- 29 Lkai, M., Tokito, S., Sakamoto, Y., Auzuki, T. & Taga, Y. Highly efficient phosphorescence from organic light-emitting devices with an exciton-block layer. *Appl. Phys. Lett.* **79**, 156–158 (2001).
- 30 Kuwabara, Y., Ogawa, H. & Shirota, Y. Thermally stable multilayered organic electroluminescent devices using novel starburst molecules, 4,4',4''-Tri(N-carbazolyl)triphenylamine (TCTA) and 4,4',4''-Tris-(3-methylphenylphenylamino)triphenylamine (m-MTDATA), as hole-transport materials. *Adv. Mater.* **6**, 677–679 (1994).
- 31 Feast, W. J., Peace, R. J., Sage, I. C. & Wood, E. L. Poly(4-vinyltriphenylamine): synthesis and application as a hole transport layer in light-emitting diodes. *Polym. Bull.* **42**, 167–174 (1999).
- 32 Fischer, A., Bremilla, A. & Lochon, P. Influence of initiator in controlled radical polymerization using nitroxide capping: the case of *N,N*-dimethylacrylamide.: synthesis of block copolymers of 4-vinylpyridine and *N,N*-dimethylacrylamide. *Euro. Polym. J.* **37**, 33–37 (2001).
- 33 Tsuboi, T., Murayama, H., Yeh, S. J. & Chen, C. T. Energy transfer between organic fluorescent CBP host and blue phosphorescent fipic and FIrN4 guests. *Optical Mater.* **29**, 1299–1304 (2007).
- 34 Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H. E., Adachi, C., Burrows, P. E., Forrest, S. R. & Thompson, M. E. Highly phosphorescent Bis-cyclometalated iridium complexes: synthesis, photophysical characterization, and use in organic light emitting diodes. *J. Am. Chem. Soc.* **123**, 4304–4312 (2001).
- 35 Lyu, Y. Y., Kwak, J., Jeon, W. S., Byun, Y., Lee, H. S., Kim, D., Lee, C. & Char, K. Highly efficient red phosphorescent OLEDs based on non-conjugated silicon-cored spirofluorene derivative doped with Ir-complexes. *Adv. Funct. Mater.* **19**, 420–427 (2009).
- 36 Chang, C. W. & Liou, G. S. Novel anodic electrochromic aromatic polyamides with multi-stage oxidative coloring based on *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine derivatives. *J. Mater. Chem.* **18**, 5638–5646 (2008).
- 37 Zhang, X., Jin, Y. H., Diao, H. X., Du, F. S., Li, Z. C. & Li, F. M. Synthesis of bismaleimides bearing electron-donating chromophores and their fluorescence behavior during copolymerization. *Macromolecules* **36**, 3115–3127 (2003).
- 38 Hong, Y., Lam, J. W. Y. & Tang, B. Z. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem. Commun.* **29**, 4332–4353 (2009).
- 39 Wu, W. C., Lee, W. Y., Pai, C. L., Chen, W. C., Tuan, C. S. & Lin, J. L. Photophysical and electroluminescent properties of fluorene-based binary and ternary donor-acceptor polymer blends. *J. Polym. Sci. Part B: Polym. Phys.* **45**, 67–78 (2007).
- 40 Adachi, C., Kwong, R. C., Djurovich, P., Adamovich, V., Baldo, M. A., Thompson, M. E. & Forrest, S. R. Endothermic energy transfer: a mechanism for generating very efficient high-energy phosphorescent emission in organic materials. *Appl. Phys. Lett.* **79**, 2082 (2001).