A novel triarylamine-based conjugated polymer and its unusual light-emitting properties

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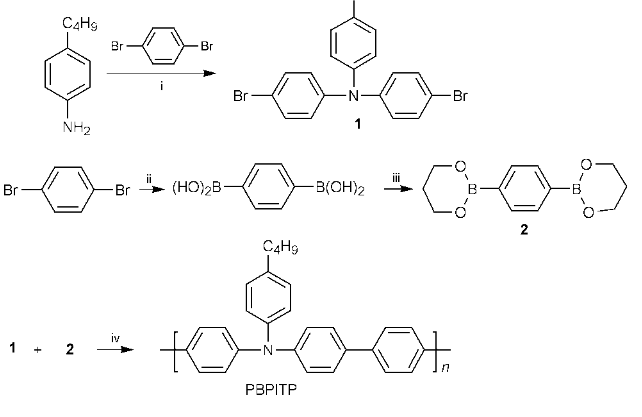
A new soluble triphenylamine-based conjugated polymer, poly[*N*-(4′-butylphenyl)imino(1,1′:4′,1″-terphenyl-4′4″-ylene)], (PBPITP), has been synthesized, which emits blue photoluminescence (PL) with high absolute PL quantum efficiency (45 ± 3%) but exhibits red electroluminescence (red shifted by as much as 157 nm from the PL spectrum).

In the last two decades, conjugated polymers have attracted considerable attention because of their promising applications in optoelectronic devices.[1] In particular, significant progress has been achieved in the development of light-emitting diodes (LEDs) based on conjugated polymers.[2] The important molecular structures for light-emitting applications have been reviewed recently.[3,4] In the past few years, some effort has also been devoted to introducing group 13 and 15 elements, such as boron and nitrogen, into backbones of conjugated polymers to explore new functional materials.[5–8] Although the conjugation is limited because of the introduction of B or N atoms, in which the B or N atoms are connected with C atoms with three σ covalent bonds, extension of π-conjugation along the backbones *via* the vacant p-orbitals of boron atoms or the lone-paired electrons of nitrogen atoms is observed. Some attractive properties, such as improved solubility, high PL efficiency and high stability toward air oxidation, have been demonstrated in such polymers.[5,6] Among the new developed polymers, triarylamine-based ones are particularly interesting because they have low ionization potentials (I_p) and exhibit good hole transporting properties in organic LEDs.[9,10] Here, we report the synthesis of a new triarylamine-based conjugated polymer, poly[*N*-(4-butylphenyl)imino(1,1′:4′,1″-terphenyl-4′,4″-ylene)](PBPITP), and its unusual light-emitting properties.

The chemical structure and the synthetic route to the new polymer PBPITP are depicted in Scheme 1. Monomer **1** was synthesized (30% yield) through a modified Hartwig–Buchwald coupling reaction between 4-butylaniline and a 5-fold excess of 1,4-dibromobenzene in toluene in the presence of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$], 1,1′-bis(diphenylphosphino)ferrocene (dppf) and $NaOBu^t$.[11,12] Monomer **2** was synthesized (overall yield 60%) in two steps from 1,4-dibromobenzene. 1,4-Dibromobenzene was first converted to *p*-phenylenediboronic acid following the procedure in the literature.[13] *p*-Phenylenediboronic acid was then refluxed with propane-1,3-diol in toluene to afford monomer **2**. Polymerization was performed by a Suzuki coupling reaction using K_2CO_3 as base and toluene as solvent. The polymer was isolated by pouring the hot (*ca.* 60 °C) reaction mixture into stirred methanol and was washed with water, methanol and acetone successively. The polymer was further purified by re-dissolving in THF and then precipitated from methanol twice prior to drying *in vacuo* at room temperature. The polymer was finally obtained as a pale yellow powder (yield 36%). The structure of the polymer was confirmed by ^1H and ^{13}C NMR and elemental analysis.†



Scheme 1 Synthetic route to PBPITP. *Reagents and conditions*: i, $Pd_2(dba)_3$, dppf, toluene, $NaOBu^t$, 90 °C; ii, (1) Mg, THF, (2) $B(OMe)_3$, THF, −78 °C, (3) H^+, 0 °C; iii, $HO(CH_2)_3OH$, toluene, reflux; iv, $Pd(0)(PPh_3)_4$, $K_2CO_3(aq)$, toluene, *ca.* 100 °C.

The polymer readily dissolves in highly polar solvents, such as THF, chlorobenzene and 1,3-dichlorobenzene, but shows low solubility in low polar solvents, such as toluene and xylene (dissolves upon heating). Uniform and pinhole-free thin films on substrates can be obtained by spin-coating chlorobenzene solutions of the polymer. Poor solubility in toluene and xylene allows the deposition of additional polymer on such films from these solvents. The molecular weight of the polymer was measured by gel permeation chromatography (GPC), using polystyrenes as standard and THF as eluent. The number-average molecular weight (M_n) and polydispersity (PD) were determined as 6400 and 1.75, respectively.

Polymer films on a variety of substrates (micro slides, ITO-coated glasses and quartz plates) emit intense blue light upon exposure to UV light. Fig. 1 shows the UV-VIS absorption and fluorescence (excited at 375 nm) spectra (curves 1 and 2) of the polymer measured from a film on a quartz plate at room temperature. The absorption spectrum peaks at 375 nm and onsets at 448 nm. The π–π* band gap, E_g, is estimated from the

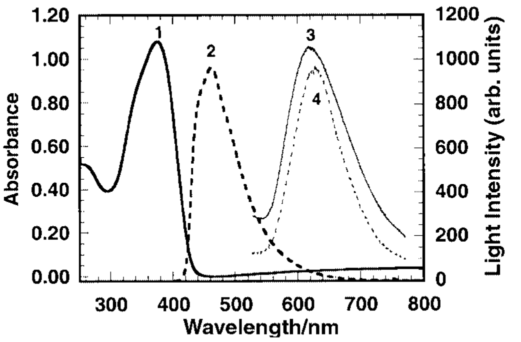


Fig. 1 UV–VIS absorption (1) and photoluminescence (excitation at 375 nm) (2) spectra of PBPITP, and EL spectra recorded from ITO/PBPITP/Ca (3) and ITO/PBPITP/PDHFDDOP/Ca (4).

onset wavelength as 2.77 eV. The fluorescence spectrum exhibits a maximum at 461 nm with a shoulder around 440 nm. The absolute PL efficiency of the polymer as a neat film was measured in an integrating sphere as 45 ± 3%. These results indicate that PBPITP is an efficient blue emissive polymeric PL material.

The redox behavior of the polymer was investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.10 M tetrabutylammonium perchlorate solution in acetonitrile at room temperature. The anodically scanned cyclic voltammogram is shown in Fig. 2. The oxidative process starts at *ca.* 0.6 V (*vs.* standard calomel electrode, SCE) and gives a sharp oxidative peak at 1.04 V. The oxidation is highly reversible, and the corresponding reduction peak appears at 0.77 V. The energy level of the highest occupied molecular orbital (HOMO) of the polymer, E_{HOMO}, can be estimated from the oxidative onset potential, to be -5.0 eV.[14] In the cathodic scan, no reduction peak (down to -2.5 V *vs.* SCE was observed). The energy level of the lowest unoccupied molecular orbital (LUMO), E_{LUMO}, can be estimated by subtracting the optical band gap energy, E_g, from E_{HOMO} as determined by the electrochemistry. This leads to an estimate of E_{LUMO} of -2.17 eV.

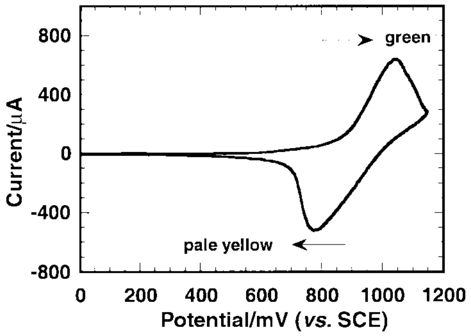


Fig. 2 Cyclic voltammogram of PBPITP. Working electrode: PBPITP film-coated platinum plate (square, *ca.* 1 cm^2); counter electrode: platinum wire; reference electrode: Ag/$\mathrm{AgNO_3}$ (0.10 M). Scan rate: 20 mV.s^{-1} room temperature. The arrows indicate the film color change during scan.

Single-layered electroluminescent (EL) cells, ITO|PBPITP(1000 –1500 Å)|Ca (1500 Å), were fabricated. The devices emitted bright red light above *ca.* 15 V under a forward bias (ITO wired positive). The EL spectrum is shown in Fig. 1 (curve 3) and exhibits a maximum at 618 nm. The EL spectrum is red-shifted by 157 nm (0.7 eV) in comparison with the PL spectrum. A layer (1000–1500 Å) of poly(9,9-dihexylfluorene-*alt-co*-2,5-didecyloxy-*para*-phenylene) (PDHFDDOP), an efficient blue EL polymer,[10] was further deposited on the PBPITP film to fabricate double polymer-layer ITO|PBPITP|PDHFDDOP|Ca devices, in which the PBPITP film was kept from direct contact with the calcium electrode by the PDHFDDOP layer. The double-layered devices also emitted red light. The EL spectrum (curve 4 in Fig. 1) is almost the same with that recorded from the single-layered devices. The results reveal that an interface effect is not the cause of the large red-shift of EL compared with PL. In addition, the threshold voltages for current flow and light emission were dramatically decreased to *ca.* 5 V upon addition of the PDHFDDOP layer. The external EL quantum efficiency was increased from *ca.* 0.01 to *ca.* 0.025% by the addition of the PDHFDDOP layer. It is evident that the role of the PDHFDDOP film is to serve as an electron-transporting rather than as an emissive layer. The improved EL performance can be attributed to the lower LUMO energy level of PDHFDDOP ($-$ 2.6 eV)[15] compared with that of PBPITP, which results in a smaller energy barrier for electron injection. Also, the improved EL demonstrates the good hole transporting property of PBPITP.

It can be concluded from the results that PBPITP is a promising red EL polymeric material.

In conventional conjugated polymers, PL and EL normally originate from the same molecular excitation, *i.e.* singlet excitons. This results in the EL emission spectrum of a conjugated polymer closely resembling its PL spectrum. The large difference between the PL and EL spectra here implies that the recombination mechanisms of charge carriers for PL and EL in PBPITP are different. A similar phenomenon was reported most recently in a binaphthalene-containing conjugated polymer.[16] Excimer emission might be responsible for the unusual emissive phenomenon.[17] Further investigation is required in order to understand the origin of the unusual emissive phenomenon and what mechanisms are responsible for it, and are actively being pursued.

In summary, a new soluble triarylamine-containing conjugated polymer has been synthesized through a Suzuki coupling reaction. The polymer in the form of a film exhibits high absolute PL efficiency and good hole transporting properties. The PL emission of the polymer is blue whereas its EL emission is red. The wavelength difference between the PL and EL spectrum is as large as 157 nm. It is evident that the PL and EL spectrum correspond to different molecular excitations. Such a polymer provides a good opportunity to understand the PL and EL processes in conjugated polymers.

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Notes and references

† *Selected data* for PBPITP: $\delta_{\mathrm{H}}(\mathrm{CDCl_3})$ δ 7.76–7.44 (m, 10H), 7.22–7.01 (m, 6H), 2.75–2.49 (t, 2H), 1.74–1.49 (m, 2H), 1.49–1.24 (m, 2H), 1.03–0.86 (t, 3H). $\delta_{\mathrm{c}}(\mathrm{CDCl_3})$ 147.06, 144.88, 138.91, 138.23, 134.33, 129.27, 128.97, 128.16, 127.27, 126.81, 125.06, 123.67, 35.04, 33.61, 22.39, 13.95. Anal. Calc. for $\mathrm{C_{28}H_{25}N}$: C, 89.56; H, 6.71; N, 3.73. Found: C, 88.17; H, 6.84; N, 3.46%.

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