Electroluminescence of anthracene-containing polyimides

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Electroluminescence has been revealed in a new class of electroactive polymers, the anthracene-containing aromatic polyimide derivatives; high thermal stability, ability to cast layers from solution and excellent film-forming properties make these materials of potential interest for technological applications.

Since the first report of efficient electroluminescence from conjugated polymers[1] this phenomenon has attracted attention due to its potential for use in wide-screen flat display technology. Conjugated polymers as emitting layers have become a subject of great interest. Currently, poly(*p*-phenylene vinylene) and its derivatives are the most studied electroactive polymers as conducting and light-emitting materials in electroluminescent light-emitting devices (ELEDs). However, certain nonconjugated polymers, *e.g.* polyimides, combined with electron transporting layers in the ELEDs, also rank as efficient electroluminophores.[2] Commonly used unilayer ELEDs consist of an electroactive polymer layer sandwiched between a transparent In–SnO_2 anode and a low work-function metal cathode. The basic electronic processes occurring in the operating ELEDs include electron–hole injection, transport of charges and their recombination in the bulk. The recombination leads to the formation of excitons which transfer their energy to the luminophore moieties (luminescent centres) of the polymer chains. The luminophore sites emit electroluminescent quanta.

Previously,[3–4] the synthesis of some new aromatic polyimides (API) based on 9,10-bis(*p*-aminophenyl)anthracene which exhibit photoluminescence was reported.[4] It should be stressed that the APIs are known as a class of polymers with high thermal stability and tolerance towards oxidation. In this communication we present results on the electroluminescence of one of the APIs whose structure is shown in Figure 1. This API is soluble and forms excellent films from solutions. Soluble anthracene-containing APIs with sulfur atoms in the back-bone have been shown previously to be efficient electron–hole conductors.[2] Bright electroluminescence (Figure 2, curve *2*) was observed in bilayer ELEDs based on the APIs in combination with tris(8-quinolinolato)aluminium complex (Alq_3) as an electron conducting layer. The photoluminescence of the anthracene-containing APIs has a strong pronounced exciplex character due to interchain electron donor–acceptor interaction of electron-excited anthracene groups with diimide fragments.[3–5]

The studied unilayer ELEDs with maximum brightness over 600 cd m^{-2} at 15 V consisted of an emitting API layer sandwiched in between transparent indium–tin oxide (ITO) and Mg:Ag electrodes. Polymer films 400–600 nm thick were formed on the ITO/glass by spin coating from a chloroform solution containing API under ambient conditions. The Mg:Ag electrodes were prepared by conventional vacuum vapour deposition at pressures below 5×10^{-6} Torr. All measurements were carried out at room temperature in ambient air. The experimental details are described elsewhere.[6]

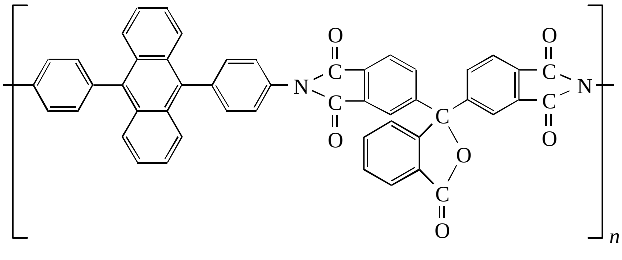

Figure 1 Chemical structure of aromatic polyimide anthracene derivatives.

The presence of diimide groups in the backbone makes APIs electronically conductive, while 9,10-diphenylanthracene (DPA) moieties play the role of hole-transporting sites in these polymers. At room temperature, the electron and hole drift mobilities directly measured by conventional time-of-flight (TOF) techniques[7] indicated effective bipolar transport in the APIs. Taking into account the comparatively high photoluminescent efficiency in these materials,[4] one would expect to observe electroluminescence in the API layers. We found experimentally that these polymers are excellent electroluminophores, being used in unilayer ELEDs.

The high brightness is achieved due to efficient hole and electron conductivity. For the API the electron and hole mobilities are of the same value $\mu_\mathrm{h} \cong \mu_\mathrm{e} = 2\times10^{-5}$ cm^2 V^{-1} s^{-1} for an electric field 3.3×10^5 V cm^{-1}.[7] On the other hand, the brightness is aided by the favourable relative positions of the energy levels providing an electron–hole injection balance in these polymers.

Figure 2 shows the absorption and photoluminescence spectra of the API films and electroluminescence spectra of typical ITO/API/Mg:Ag devices measured at 10 V. When illuminated at 350 nm, the API exhibited a photoluminescence spectrum at 540 nm while the electroluminescence band had a peak at 565 nm. Note that the electroluminescent peak position did not coincide with the λ_max of the photo-luminescence band. The essential difference in λ_max position between the photoluminescence and electroluminescence spectra observed for the API should presumably be accounted for by the difference in the mechanism of the two emission processes. In the case of photoluminescence, light is randomly absorbed by occasional luminescent centres in the polymer, whereas the mechanism of electroluminescence involves electron–hole recombination which gives rise to the formation of excitons. In API structures, in contrast to polyconjugated macromolecular systems, exciton states should be less moveable. If so,

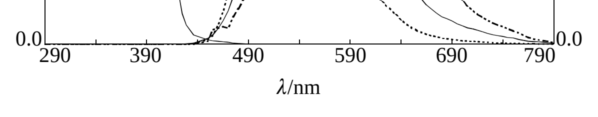

Figure 2 (*1*) Absorption spectrum of a polymer layer formed by spin-casting from a chloroform solution of API; (*2*) electroluminescence of bilayer ELED (ITO/API/Alq_3/Mg:Ag); (*3*) photoluminescence of API; (*4*) electroluminescence of unilayer ELED (ITO/API/Mg:Ag).

immediately after the formation they will transfer their energy to the nearest luminescent centre. Because charge carrier jumping through shallow traps is the most probable conduction mechanism for both types of carriers in these polymers,[7] it is reasonable to assume that trapped charges participate in the recombination. Trapped charge formation implies the initiation of electronic and dipole polarization of the medium. Polymer structure defects, polarized luminophore moieties or electron donor–acceptor inter- and/or intramolecular polymer complexes may be candidates for these traps. The latter are transport sites of reduced energy. Since the interchain electron donor–acceptor complex formed by the two transporting centres (diimide and DPA) may be a luminescent centre in the API, one may expect that the energy of emitting quanta should be reduced. The electroluminescence spectrum will have to shift towards the long-wave region when compared with the photoluminescence band. At the present time, efforts are underway on APIs of various chemical structure to elucidate the role of donor–acceptor interactions on the electroluminescence band location in the visible range in order to handle the problem of electroluminescence colour tuning for the API based ELEDs.

In summary, we have revealed electroluminescence in a new class of electroactive polymers, anthracene-containing aromatic polyimide derivatives. The high thermal stability, the ability to cast API layers directly from solution, excellent film-forming properties and efficient electroluminescence make APIs of potential interest for technological applications.

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