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Hyperbranched 3D oligophenylenes for blue electroluminescence

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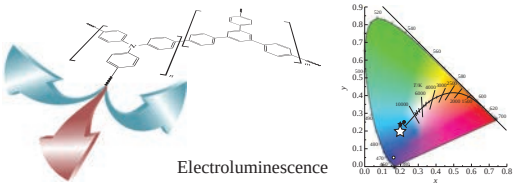
Hyperbranched 3-dimension (3D) oligophenylenes with a good electroluminescent external quantum efficiency (0.26%) in solution processed organic light-emitting devices were developed by a Ni⁰-catalyzed cross-coupling reaction of tribromo-substituted triphenylbenzene and triphenylamine.



Hyperbranched polymers are of increasing current interest since their peculiar 3D molecular architecture gives rise to the properties that cannot be achieved in linear macromolecules.[1] They possess a globular structure and low viscosity; moreover, their solubility in organic solvents, which is critical for low-cost processing techniques, essentially exceeds that of their linear analogues.[2]

Generally, the hyperbranched polymers do not have a clearly defined structure, and they exhibit a broad molecular-mass distribution. The branching of macromolecular chains can be irregular due to a single-step synthesis;[3] for this reason, its precise determination is very challenging since it could lead to unique morphological and optical properties.[4] A combination of both mass and optical spectroscopic techniques was proposed to investigate the building block model compounds and corresponding oligomers and polymers in order to characterize branched macromolecules.[5]

Once a synthetic protocol has been set for a specific branching structure, further chemical efforts are needed to successfully design soluble 3D macromolecules with properties suitable for optoelectronic applications, like a defined emission wavelength, electron or hole conductivity and good film-forming ability. The hyperbranched polymers are thereby synthesized with luminophores and groups endowing transport properties, embedded in the backbone or as ending groups of chain ramification.

Here, we present a novel hyperbranched oligophenylene as a potential blue emitter for organic light-emitting devices (OLEDs). Moreover, it is possible to explore it as a host for triplet emitters. The compound belongs to a family of hyperbranched oligophenylenes synthesized by the Ni⁰-catalyzed condensation[5,6] of 1,3,5-tris(4-bromophenyl)benzene and tris(4-bromophenyl)amine at different feed ratios, consequently forming blocks A and B (Figure 1).

We report preliminary elemental analysis data (Table 1) on N and Br contents and photoluminescence (PL) quantum yields (PLQYs) in solution for the hyperbranched oligophenylenes. We focus on the properties of the fully characterized A50/B50 compound (hereafter referred to as OPh3) with a good balance between film forming ability and optical properties.

The electronic absorption and PL spectra and PLQYs of OPh3 were measured in solution and in a solid state (a spin-coated thin film) (Figure 2). The absorption spectra of a solution and a film

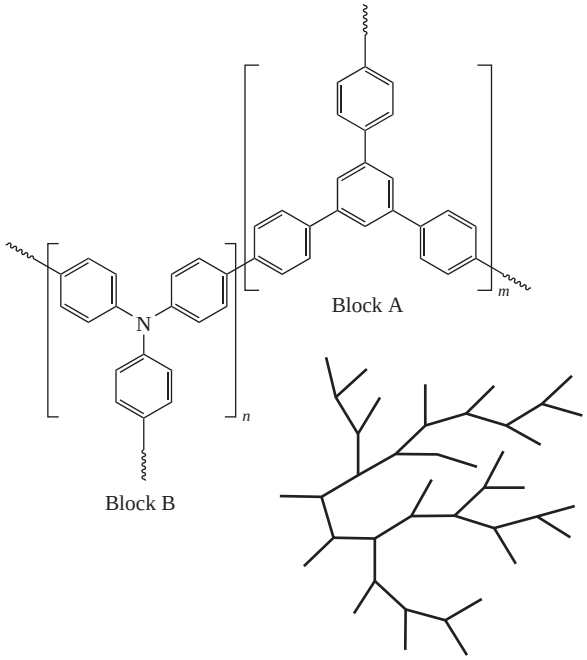


Figure 1 Chemical structure of OPhs and typical 3D structure of a branched polymer.

of OPh3 reveal contributions from 1,3,5-triphenylbenzene (TPB, band at 300 nm) and triphenylamine (TPA, band at 360 nm).[6,7] Similarly, in PL spectrum in solution, two distinct bands attributable to TPB (340–400 nm) and TPA (400–550 nm) are visible;[6,8] it is most likely that the 3D structure breaks conjugation between the two building blocks that maintain their individual properties.

Table 1 Properties of oligophenylenes.

Sample (ratio, mol%)	N (%)	Br (%)	PLQY (%) in CH_2Cl_2
OPh1 (A100)	0	–	81
OPh2 (A70/B30)	–	–	75
OPh3 (A50/B50)	0.91	3.80	62
OPh4 (B100)	2.86	9.75	37

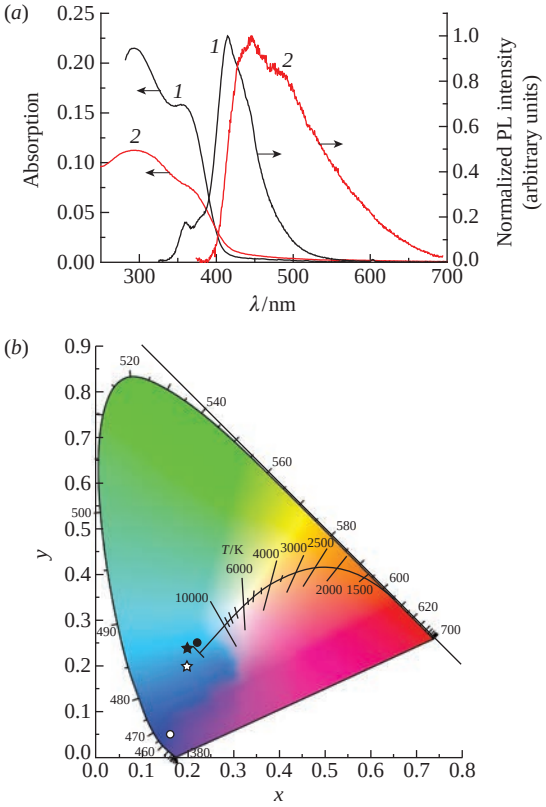


Figure 2 (*a*) Electronic absorption and PL spectra of OPh3 in (*1*) solution and (*2*) thin film. (*b*) CIE 1931 (*x*; *y*) chromaticity diagram for (○) solution (0.16, 0.05), (●) film (0.22, 0.25), (☆) single layer OLED (0.20, 0.20) and (★) triple layer OLED (0.20, 0.24).

This was confirmed by excitation spectra (ESI). Emission of TPB centered at 360 nm takes origin solely from an absorption band at 300 nm, while emission peaked at 420 nm is due to the excitation of the whole absorption spectrum. The latter can be explained by intra-chain energy transfer from TPB blocks to TPA units. PLQY in solution is as high as 62% in CH_2Cl_2 and

Table 2 Performance characteristics of OLEDs with single and triple layer architectures.

Device architecture	λ^{EL}_{max}/ nm	EQE_{max} (%)	LE_{max}/ cd A^{-1}	PE_{max}/ lm W^{-1}	L_{max}/ cd m^{-2}	CIE 1931 (x; y) @Voltage
Single layer	430	0.013	0.01	0.0025	130	(0.20; 0.20) @8V
Triple layer	445	0.26	0.25	0.09	275	(0.20; 0.24) @10V

decreases with increasing TPA content (Table 1). In a solid state, the PL of TPB is not visible and emission is red shifted with respect to solution. However, the excitation spectra suggest that OPh3 aggregates may be responsible for the broad emission peaked at 450 nm, having an absorption band at the tail of the absorption spectrum. Energy transfer from monomers to aggregates also can occur[9,10] (ESI). The strong PL quenching in a film (PLQY ~10%) can be ascribed to both aggregation and the presence of residual Br atoms that mainly influence the properties in a solid state.[11]

OPh3 was tested as an emitter in single and triple layer OLED architectures. It is well known that the efficiency of devices can be improved by introducing materials specialized in transporting of one type of charge carriers, either as a mixture[12] or in a multilayer configuration.[13] The multilayer prototype is fabricated using interfacial polymers with specific charge carrier transport properties: polyvinylcarbazole as a hole transporting/injecting layer (HIL) and the polar polymer poly([2,7-(9,9′-dioctyl)-fluorene]-alt{2,7-[9,9′-bis(5′′-trimethylammonium bromide)-pentyl]fluorene}) as an electron injecting layer (EIL).[14] All the organic layers of the device were prepared by a solution (spin-coating) technique due to the solubility of the materials creating the HIL and EIL in orthogonal solvents with respect to the emitting layer. The EL spectrum of ITO/PEDOT:PSS/OPh3/Ba/Al [ITO is indium tin oxide, PEDOT:PSS is poly(3,4-ethylene-dioxythiophene):poly(styrene sulfonate)] diodes is consistent with that measured for the film. The EL spectrum of the triple layer ITO/PEDOT:PSS/HIL/OPh3/EIL/Ba/Al device is peaked at 440 nm and slightly broader with respect to the single layer one [Figure 3(*a*),(*c*)], with a stronger and voltage dependent

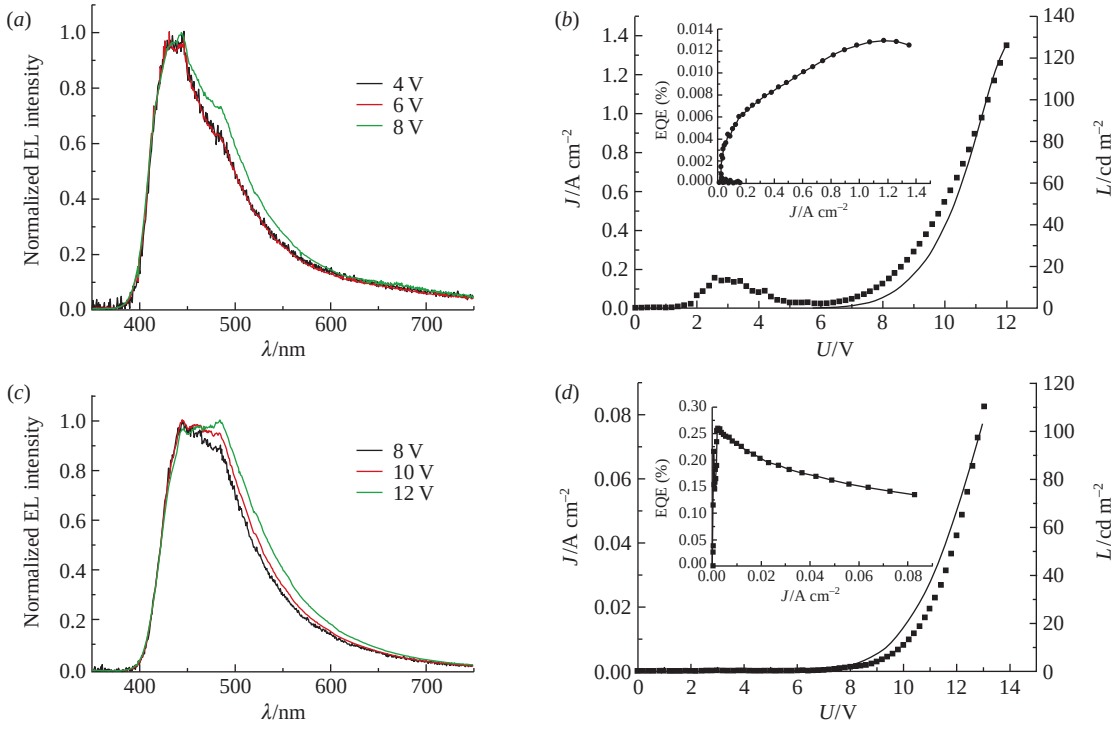


Figure 3 (*a*), (*c*) EL spectra at different voltages and (*b*), (*d*) the representative ILV characteristics of (*a*), (*b*) single and (*c*), (*d*) triple layer OLEDs (dots and lines denote current density and luminance, respectively). Insets: maximum EQE *vs.* current density.

contribution at longer wavelengths, probably, due to the formation of aggregates upon operation. The CIE 1931 chromaticity coordinates of the single and triple layer devices are located in the blue region and are (0.20; 0.20) and (0.20; 0.24), respectively. Onsets are at 6–7 V for both configurations. The best total external quantum efficiency (EQE) of 0.26%, with maximum luminance of 275 cd m^{-2}, was achieved for the triple layer device corresponding to almost 20 times the value obtained with single layer one [insets in Figure 3(*b*),(*d*)], accordingly to what is expected by the use of interlayers to control charge injection and exciton confinement.[14]

OPh3 was also tested as a host matrix for commercial red emitting bis[2-(9,9-dibutylfluorenyl)]-1-isoquinoline(acetylacetonate)iridium(III), or Ir^{III}-red.† To balance the hole transport properties typical of triphenylamine-based compounds,[15] an oxadiazole derivative OXD-7 (1,3-bis[5-(4-*tert*-butylphenyl)-1,3,4-oxadiazol-2-yl]benzene) was added to the blend. The composition of the active layer OPh3:OXD-7:Ir^{III}-red is 11 : 6 : 1 (by weight). The standard device architecture ITO/PEDOT:PSS/OPh3:OXD-7:Ir^{III}-red/Ba/Al exhibits poor performance. The total EQE is lower than 0.1%, and CIE coordinates (0.41; 0.26) are located in the orange-violet region due to the emission of OPh3 and Ir^{III}-red.

In conclusion, a series of 3D-hyperbranched oligophenylenes with different feed ratios of triphenylbenzene (A) and triphenylamine (B) building blocks has been synthesized. The materials obtained with an A:B ratio of 1:1 showed EQE = 0.26% in triple layer OLED architectures. The efficiency could be enhanced by reducing the residual Br content and by optimizing the A:B feed ratio in 3D-hyperbranched oligophenylenes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.07.027.

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