Triaryl Amine N-Functionalised 2,7-Linked Carbazole Polymers as a New Class of Blue Emitting Materials for LED Applications

Hunan Yi¹, Ahmed Iraqi *,¹ Mathew Stevenson², Claire J. Elliott² and David G. Lidzey²

¹ Department of Chemistry, University of Sheffield, Sheffield S3 7HF, United Kingdom.
² Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom.

*To whom correspondence should be addressed.
Fax: +44 (0)114 222 9303, E-mail: a.iraqi@sheffield.ac.uk

Experimental Details:

Measurements: NMR spectra were recorded on Bruker 250 MHz, AMX400 400 MHz or DRX500 500MHz NMR spectrometers at 22 °C in chloroform-d₆ or acetone-d₆ solutions with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet Model 205 FT-IR Spectrometer. Liquid samples were analysed neat, using NaCl–plate method and solid samples were analysed using the Diamond ATR attachment for solid samples. Melting points were obtained using Gallenkamp Melting Point Apparatus. GC-MS spectra were recorded on Perkin Elmer Turbomass Mass Spectrometer equipped with Perkin Elmer PE-5MS Capillary Column. Mass spectra were obtained by the electron impact method (EI) or the chemical ionisation method (CI). GPC curves were recorded on the equipment consisting of Waters Model 515 HPLC Pump, GILSON Model 234 Autoinjector,
MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5\(\mu\)m 500Å Column, and PLgel 10\(\mu\)m MIXED-B Column using THF as the eluate at the flow rate of 1 cm\(^3\) min\(^{-1}\). Polymer solutions in THF (2.5 mg cm\(^{-3}\)) were used as samples for GPC analysis. The GPC curves were obtained by the RI-detection method, which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Elemental analyses were carried out by the Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. UV-visible absorption spectra were measured by Hitachi U-2010 Double Beam UV / Visible Spectrophotometer. The absorbance of polymers was measured in solution in spectrophotometric grade solvents (dichloromethane, tetrahydrofuran and toluene) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma-Aldrich. Samples of pristine polymer thin films for UV-visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm\(^{-3}\) polymer solutions in dichloromethane (HPLC grade); and the measurements were carried out at ambient temperature. Photoluminescence spectra were obtained using Hitachi F-4500 Fluorescence Spectrophotometer equipped with Hamamatsu Photonics R928F Photomultiplier Tube (PMT). PL solution measurements were carried out using a Quartz Fluorescence Cuvette (light path length = 10 mm) purchased from Sigma-Aldrich. Photoluminescence spectra measurements of harmine, and quinine sulfate dihydrate solutions were carried out in respectively 0.05 mol dm\(^{-3}\) and 0.5 mol dm\(^{-3}\) sulfuric acid at 25 ºC in the air since both harmine and quinine sulfate dihydrate exhibit no oxygen quenching effect.

Photoluminescence spectra measurements of the polymer solutions were carried out in spectrophotometric grade toluene at 25 ºC. The oxygen quenching effects on polymer 4 was examined by comparing the photoluminescence spectra of their solution in the air with those under an argon atmosphere. Since the solutions exhibited oxygen quenching effect, photoluminescence spectra measurements of their solutions were carried out under nitrogen atmosphere. Samples of pristine polymer thin films for PL spectra measurements were prepared by dip coating quartz plates into 0.1 mg
polymer solutions in dichloromethane (HPLC grade), and the measurements were carried out at ambient temperature in air.

Absorbances at employed excitation wavelengths of the sample solutions were kept below 0.05 to obtain inner-filter-effect-free photoluminescence spectra. All photoluminescence spectra were corrected. The correction factors were obtained by excitation spectra measurement of the quantum counter (Rhodamine B standard solution) for the excitation side; and by synchronous wavelength scan using a light diffuser for the emission side. The light diffuser (parts No. 650-1576) was provided with the spectrophotometer as an accessory. The correction factors obtained were stored in the memory of the spectrophotometer. As a result, the spectrophotometer automatically gave corrected excitation and emission spectra when measurements were carried out.

Harmine and quinine sulfate dihydrate in 0.05 mol dm\(^{-3}\) (0.5 mol dm\(^{-3}\) for quinine sulfate dihydrate) sulfuric acid were employed as fluorescence standards. The quantum yields in diluted solutions were obtained by comparison with a fluorescence standard of a known quantum yield using the following equation:

\[
\Phi_x = \Phi_s \times \left( \frac{S_s}{A_s} \right)^{-1} \times \left( \frac{S_x}{A_x} \right) \times \left( \frac{n_s^2}{n_x^2} \right)
\]

where the subscripts s and x refer to the standard and the unknown sample solutions, \(\Phi\) is the quantum yield, A is the absorbance at the excitation wavelength, S is the integral intensity of the corrected photoluminescence spectra, and n is the refractive index of the solvent. The fluorescence standard solution and the unknown sample solution were excited at the same wavelength. Quinine sulfate dihydrate solution in 0.5 mol dm\(^{-3}\) sulfuric acid (\(\Phi_s = 0.546\)) was employed as the fluorescence standard solution. The refractive indexes of the solvents, were taken as 1.339, 1.334, and 1.4961 respectively for 0.5 mol dm\(^{-3}\) sulfuric acid, 0.05 mol dm\(^{-3}\) sulfuric acid, and toluene. (S/A) values of each sample in solution could simply be obtained by dividing the integral intensities of the spectra by the absorbances at the excitation wavelengths using a sample solution of a certain concentration. In
order to minimize experimental error, the final (S/A) values used in the calculations for each sample were obtained from the plots of the integral intensities of the spectra vs. the absorbances at the excitation wavelengths using sample solutions of various concentrations. The reliability of our measurements was confirmed upon measurement of the quantum yield of harmine using quinine sulfate dihydrate as a standard. The experimental value obtained was identical to that reported in the literature ($\Phi_s = 0.45$). [1] Solid-state quantum yield measurements were carried out on spin-cast thin films of polymer 4. The polymer was dissolved in toluene at a concentration of 20 mg cm$^{-3}$ and the films were spin-cast onto quartz substrates at 1000 rpm. The samples were mounted inside a LabSpec integrating sphere and excited using the 351 and 364 nm lines of an argon ion laser. To minimize the occurrence of photo-oxidation, the laser was attenuated and defocused to an approximate power density of 1 mW cm$^{-2}$ and the sphere was flushed with nitrogen. Light from within the sphere was collected via an optical fibre and detected using a scanning monochromator and photomultiplier tube. The spectral response of the combined sphere-fibre detector system was determined by measuring the emission from a tungsten halogen lamp that had been supplied and calibrated by the National Physical Laboratory. The quantum yield was calculated by measuring the relative number of photons emitted by the polymer compared to the relative number of photons absorbed. This technique is based upon the methodology of de Mello et al. [2] We have confirmed the calibration of our sphere system by measuring the quantum efficiency of thin films of a well characterized conjugated polymer poly(9,9’-dioctyl fluorene) [F8] supplied by the Dow Chemical Company. Here, we recorded a quantum efficiency of (0.46 ± 0.05); a value in excellent agreement with previous literature reports. [3]

Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2 ºC. 10 cm$^3$ of tetrabutylammonium perchlorate (TBAClO$_4$) solution in acetonitrile (0.1 mol dm$^{-3}$) was used as the electrolyte solution. A three electrode system was used consisting of an Ag/Ag$^{+}$ reference electrode
(silver wire in 0.01 mol dm$^{-3}$ silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm-diameter smooth platinum disc, area = $3.14 \times 10^{-2}$ cm$^2$), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm$^3$ of polymer solutions in dichloromethane (HPLC grade) (1 mg cm$^{-3}$) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC’s recommendation.$^{[4]}$


