

Supplementary Information

A cross-linkable, organic down-converting material for white light emission from hybrid LEDs

Hao Yang,^a Jochen Bruckbauer,^b Lyudmyla Kanibolotska,^a Alexander L. Kanibolotsky,^{a,c} Joseph Cameron,^a David J. Wallis,^{d,e} Robert W. Martin*^b and Peter J. Skabara*^a

^aWestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK.

E-mail: peter.skabara@glasgow.ac.uk

^bDepartment of Physics, SUPA, University of Strathclyde, Glasgow, G4 0NG, UK.

E-mail: r.w.martin@strath.ac.uk

^cInstitute of Physical-Organic Chemistry and Coal Chemistry, 02160 Kyiv, Ukraine

^dDepartment of Materials and Metallurgy, University of Cambridge, Cambridge, CB3 0FS, UK

^eCentre for High Frequency Engineering, University of Cardiff, Cardiff, CF24 3AA, UK

Contents

1. Materials and instrumentation
2. Device fabrication
3. NMR spectra
4. Thermal analysis
5. GPC analysis of p(GC)

1. Materials and instrumentation

All reagents were purchased from Sigma Aldrich, Alfa Aesar, and Fluorochem. They were used without further purification.

All cinnamate-based materials were cross-linked under Vilber Lourmat handheld UV lamp that consists of two tubes that emit at 254 nm wavelength at 16 W of power. ¹H and ¹³C NMR spectra of samples were dissolved in deuterated chloroform and were both obtained from a Bruker AVIII 400 spectrometer at 400 MHz and 100 MHz, respectively. Mass spectra data were collected from Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) spectrometry with the instrumentation model of a Shimadzu Axima Performance spectrometer (mass range 1-500 000 Da in linear mode and 1-80 000 Da in reflectron mode). The spectra were taken in reflectron mode using dithranol and retinoic acid as matrices. Elemental analysis measurements were done with an Exeter CE-440 Elemental Analyser. TGA measurement was conducted on a Netzsch TG 209 F3 Tarsus thermogravimetric analyser. All melting points were measured with a Stuart Scientific Melting point apparatus. UV-vis absorption spectra were collected from a Shimadzu UV 2700 Spectrophotometer. For absorption spectroscopy, dilute solutions in dichloromethane (10^{-6} M) were prepared and were placed in a quartz cuvette with 1 cm path length. The scan range was set at 250-900 nm while the scan speed was set to normal. UV-vis absorption spectra of solid-state samples were measured by scanning GreenCin and GreenCin-TCM films that were spin-coated on quartz slides from toluene solutions at 2000 rpm speed. The instrumentation settings were kept the same as the measurements of solution-state samples. Emission spectra and PLQY values of GreenCin and GreenCin-TCM composite materials were obtained from an Edinburgh Instruments Spectrofluorometer FS5. For solution-state measurements, the concentrations were set to 10^{-6} M. The excitation wavelength for both emission spectra and PLQY measurements was set at 421 nm. The LEDs were characterised using a calibrated integrating sphere system (Labsphere illumina[®]plus 600/610) before and after deposition of the organic converter material. A Keithley 236 source measure unit was used as a constant current supply. All LEDs were driven with a constant forward current of 25 mA. Different parameters such as radiant and luminous flux, chromaticity coordinates (x, y), luminous and blue-to-white efficacy values were calculated from the recorded spectra, which are corrected for the system response. Parameters of hybrid devices were derived following standard methods described in Ref. 1 and 2.^{1,2}

Gel Permeation Chromatography was carried out using a chromatograph which consisted of the GPCmax VE-2001 solvent and sample delivery module as well as Viscotek 305 TDA temperature controlled analyser with an integrated refractive index (RI), dual low angle light scattering (LALS, 7°) and right angle scattering (RALS, 90°) detectors. The red laser source ($\lambda = 670$ nm) was used for light scattering measurements. The samples were run in THF with the flow rate of 1.0 ml/min at the temperature of 35 °C. The molecular weight determination was done assuming 100 % recovery. The calibration of the detectors was performed using a polystyrene (PS) standard with a low polydispersity index (PDI) (Mw=103 kDa, PDI=1.02). The results of calibration were checked by another PS standard with a higher molecular weight and PDI (Mw=245 kDa, PDI=2.28). The results of GPC analysis are shown on Figure S2.

2. Device fabrication

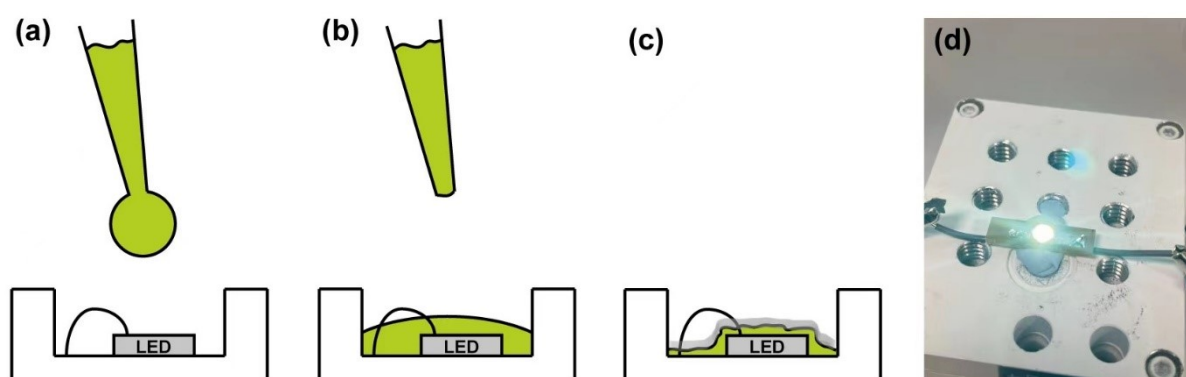
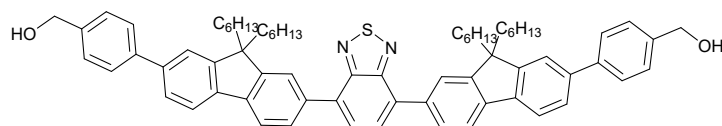


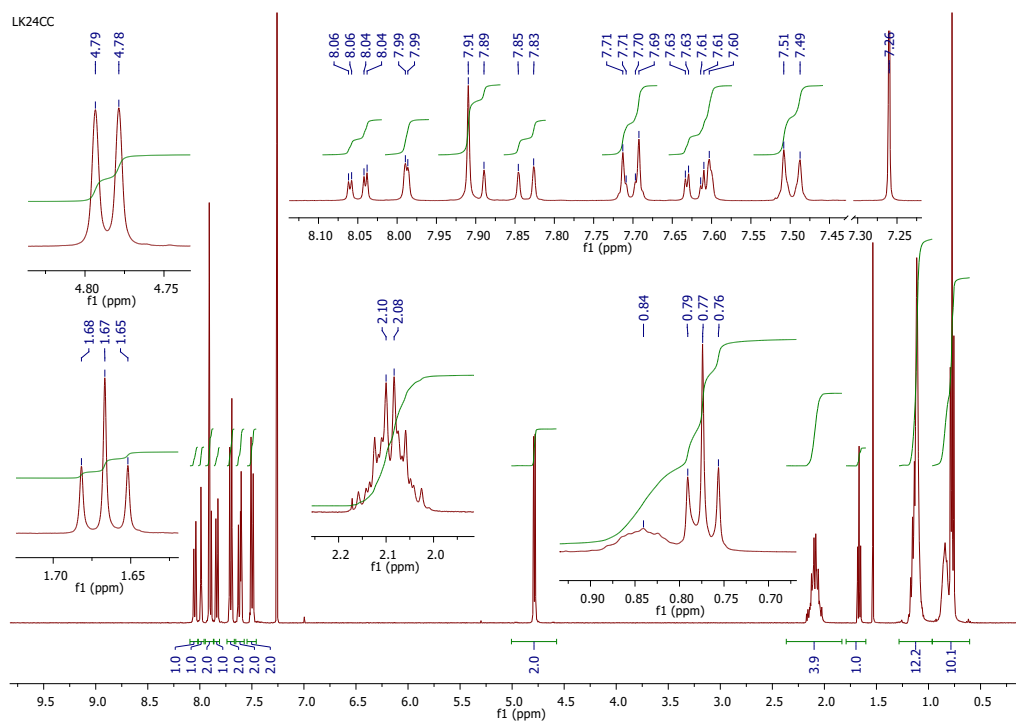
Fig. S1: Simplified schematic of the deposition process: (a) bare blue LED before drop-casting the organic colour converter using a pipette; (b) LED after deposition of several droplets of material inside the LED package on top of the LED die, (c) LED after organic down-converting material was cross-linked and washed followed by a second layer of cross-linked TCM film was applied to protect the emissive materials; (d) photo of a hybrid LED under operation inside the integrating sphere.

3. NMR spectra

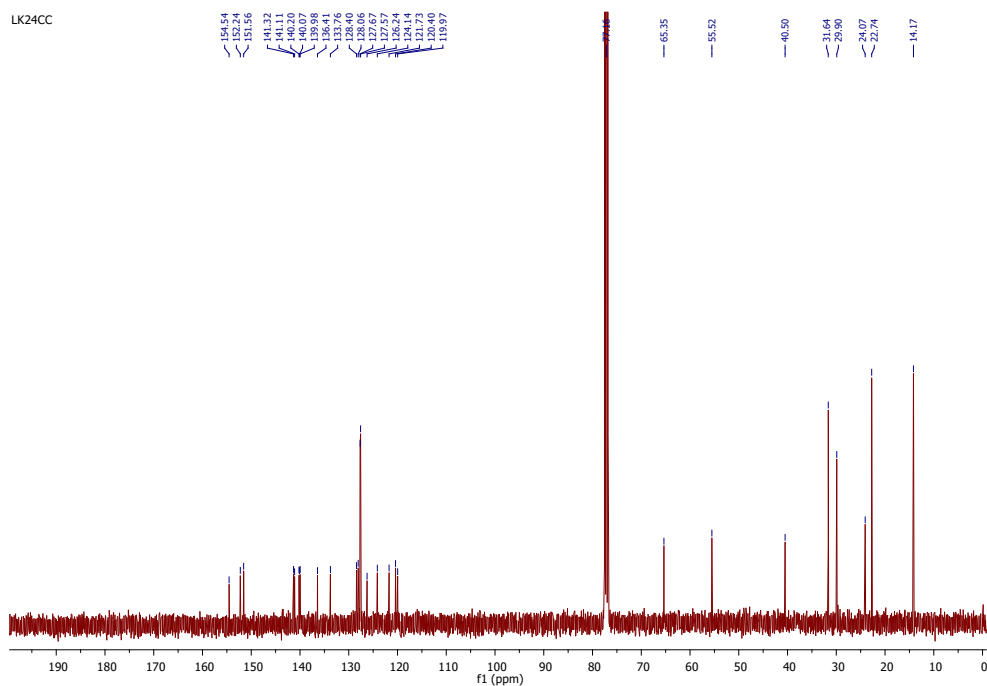
4,7-bis(7-(4-oxymethylphenyl)-9,9-dihexylfluoren-2-yl)-2,1,3-benzothiadiazole



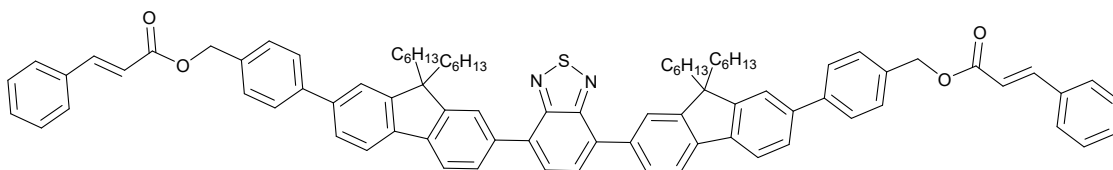
^1H NMR (CDCl₃, 400 MHz)



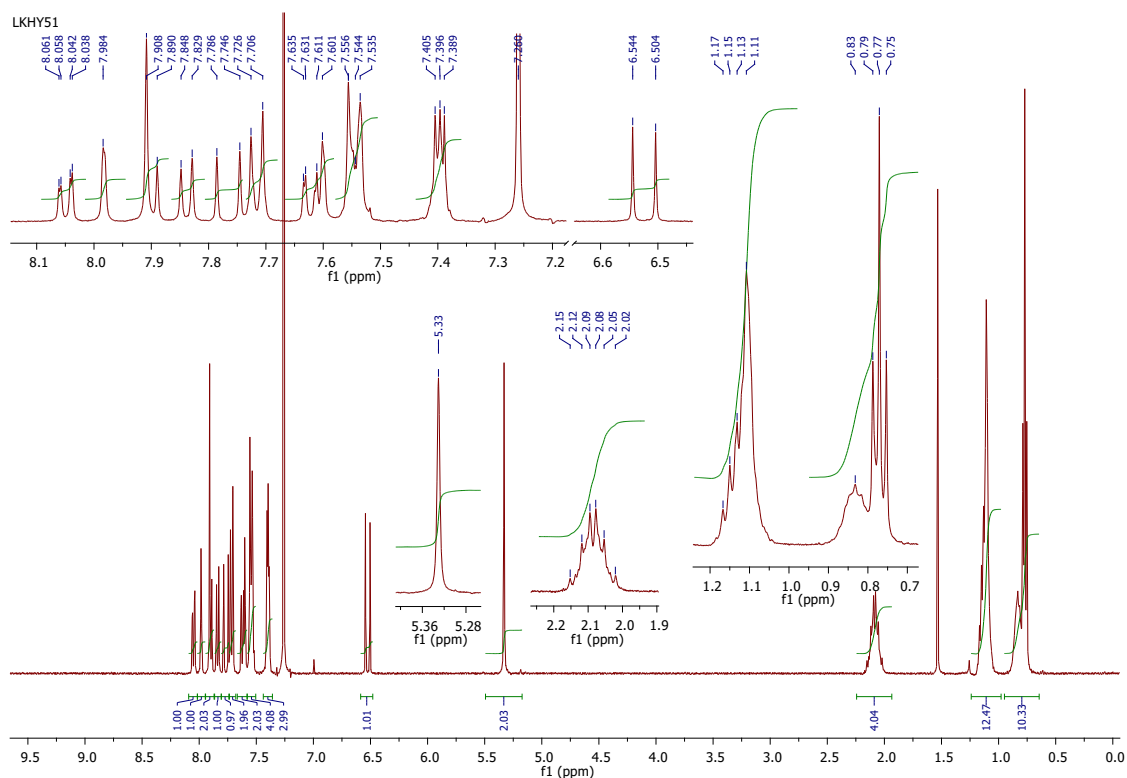
^{13}C NMR (CDCl₃, 100 MHz)



**4,7-bis(7-(4-cinnamoyloxymethylphenyl)-9,9-dihexylfluoren-2-yl)-2,1,3-benzothiadiazole
(GreenCin)**

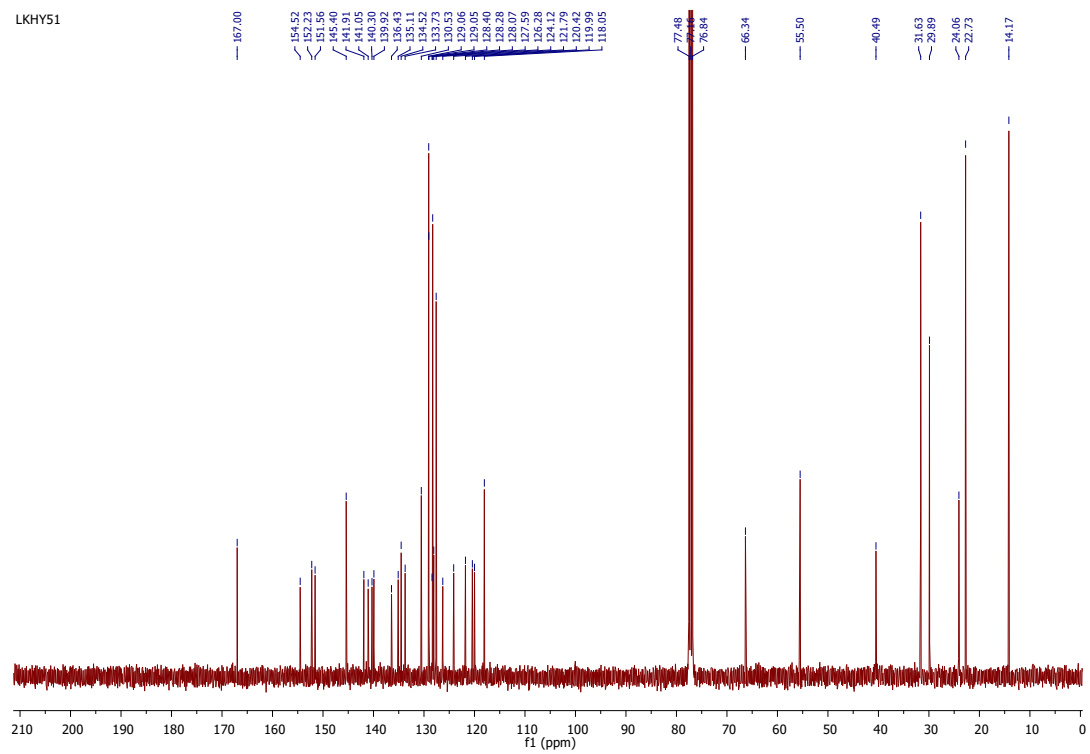


¹H NMR (CDCl₃, 400 MHz)



¹³C NMR (CDCl₃, 100 MHz)

LKHYS1



4. Thermal analysis

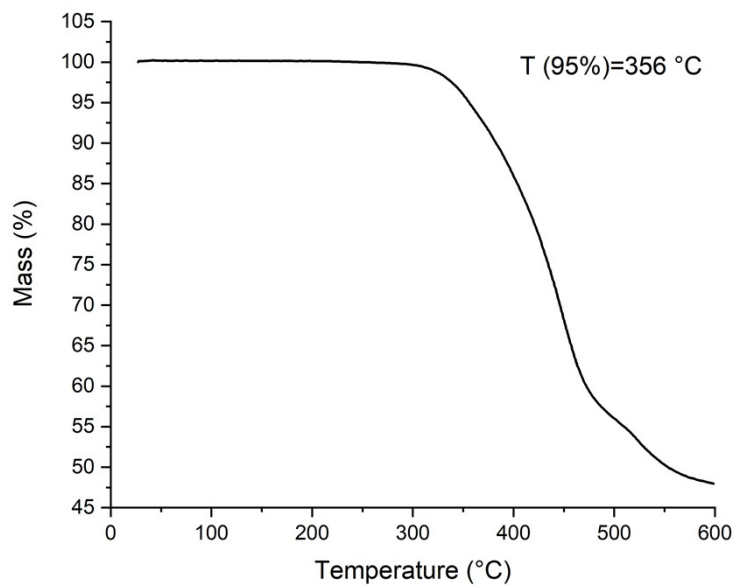


Fig. S2: Thermogravimetric analysis (TGA) of **GreenCin**

5. GPC analysis of p(GC).

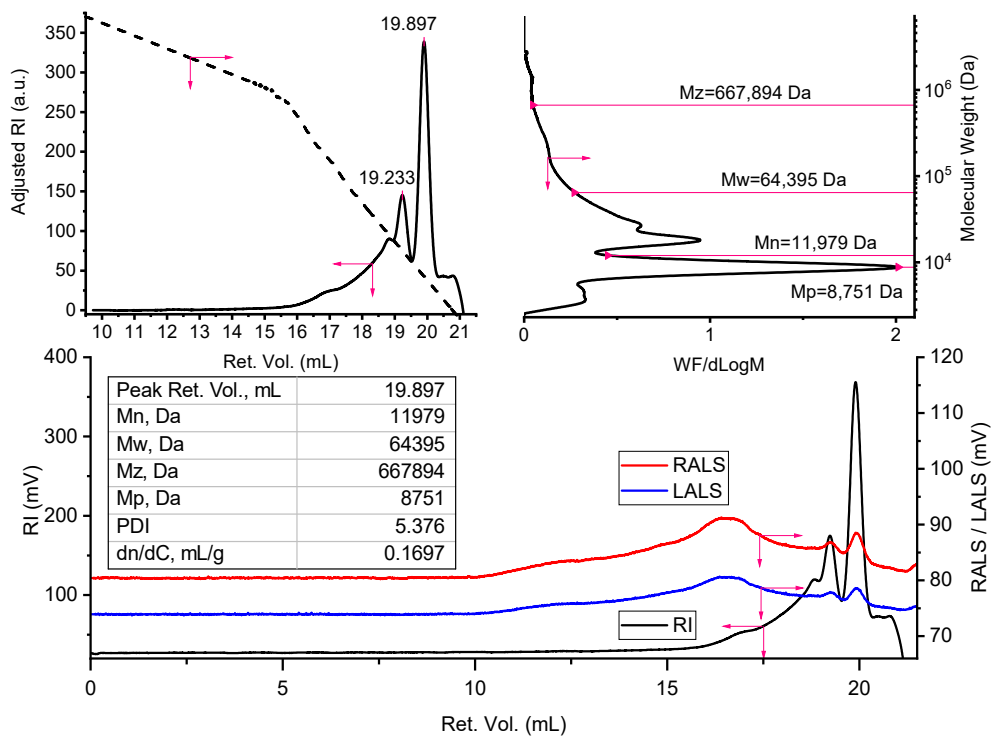


Fig. S3: GPC analysis of **p(GC)**

References:

1. J. Bruckbauer and N. J. Findlay, in *Optoelectronic Organic-Inorganic Semiconductor Heterojunctions*, ed. Y. Zhou, CRC Press, Boca Raton, 1st edn., 2021, ch. 10, pp. 231-266.
2. E. F. Schubert, *Light-Emitting Diodes*, Cambridge University Press, Cambridge, 2nd edn., 2006, ch. 16-19, pp. 275-331.