Supplementary information

A polyurethane encapsulated benzo[2,3-*d*:6,7-*d'*]diimidazole organic down-converter for green hybrid LEDs

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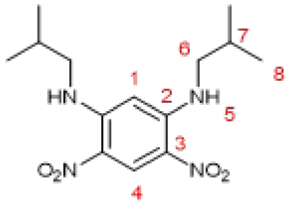
1. Synthesis.

General experimental

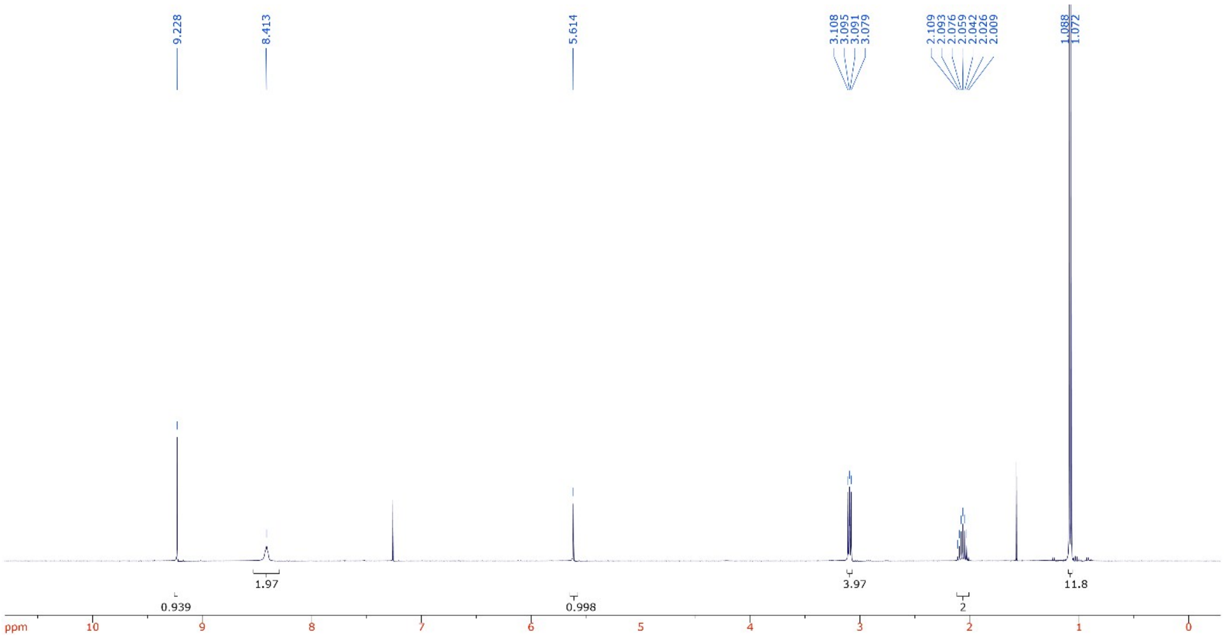
All starting materials and reagents were purchased from commercial suppliers (Aldrich, TCI or FluoroChem) and used without further purification. OPT4200 resin was purchased and used as per specifications from Intertronics.co.uk. Anhydrous solvents were obtained either from Innovative Technology inc. Pure Solv 400-5-MD solvent purification system or from Sigma Aldrich. Mass spectrometry was obtained from the mass spectrometry service at the University of Glasgow or the EPSRC UK National Mass Spectrometry Facility at Swansea University. NMRs were recorded on a Bruker Avance III 400 spectrometer. The ^{1}H and ^{13}C spectra were recorded at 400 MHz and 100 MHz, respectively, with TMS as internal standard. NMR spectra were analysed using iNMR 6.0. Solution state UV-vis spectroscopy was carried out on a Perkin Elmer Lambda 25 UV/Vis Spectrometer, while solution PL measurements were performed using a Shimadzu RF-5301PC spectro-fluorimeter. UV-vis and PL spectroscopy of the hardened films was recorded on a BMG labtech CLARIOstar plate reader. Absolute PLQY measurements were performed in a calibrated integrating sphere attached to an Ocean Optics USB2000+ spectrometer, and a Gooch & Housego double monochromator with a quartz halogen lamp. The samples were excited at 425 nm. TGA-DSC measurements were carried out on a TA Instruments SDT Q600. The optical measurements of the blue LEDs before and after deposition of the organic material were carried out using a calibrated integrating sphere system (Labsphere illumina®plus 600/610). Different parameters assessing the performance of the LEDs can be determined from the spectra, after correcting for system response, such as radiant and luminous flux, chromaticity coordinates (x, y) in the Commission internationale de l'éclairage (CIE) 1931 colour space chromaticity diagram and the luminous efficacy. As a constant current supply a Keithley 236 source measure unit was used. The pulsed current was supplied using a custom pulse driver with a duty cycle of 2% (500 µs period). All the spectroscopic, thermal analysis data and device characterisation were processed using Origin Pro software suite.

***N1,N3*-diisobutyl-4,6-dinitrobenzene-1,3-diamine (2).**

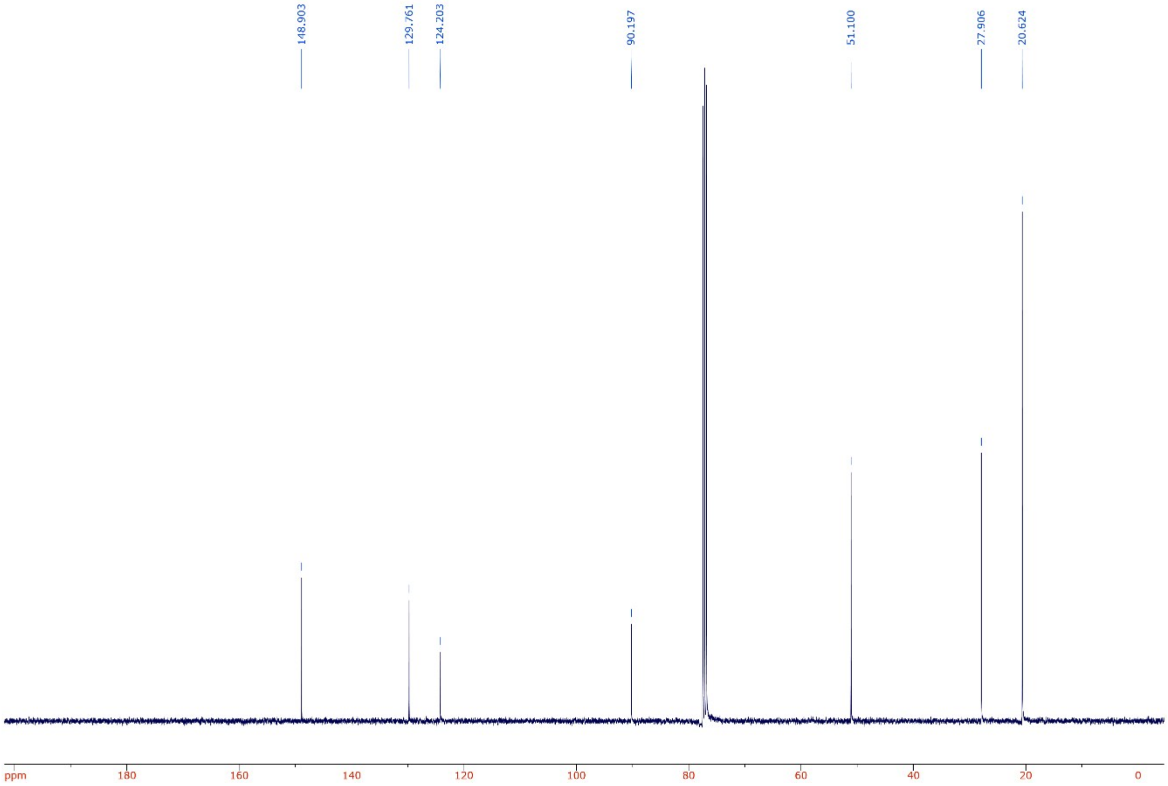


1,5-Difluoro-2,4-dinitrobenzene **1** (2.00 g, 9.80 mmol) and K_2CO_3 (2.98 g, 21.6 mmol) were dissolved in ethanol (100 ml) and the mixture was heated under reflux. Isobutylamine (2.13 ml, 21.56 mmol) in EtOH (50 ml) was added dropwise and the reaction was stirred under reflux for 24 hours. The mixture was allowed to cool to room temperature and concentrated under reduced pressure. Water (100 ml) was added and the mixture was extracted with dichloromethane (3 × 200 ml). The combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (SiO_2, dichloromethane:petroleum ether 40–60 °C; 6:4), affording compound **2** as a bright yellow solid (4.20 g, 90%). M.p. = 95–97°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ_H 9.23 (2H, s, C(4)$\underline{H}$), 8.44 (4H, s, N(5)$\underline{H}$), 5.61 (2H, s, C(1)$\underline{H}$), 3.09 (8H, dd, J = 6.7, 5.1, C(6)$\underline{H}$), 2.06 (4H, sept, J = 6.7, C(7)$\underline{H}$), 1.08 (24H, d, J = 6.7, C(8)$\underline{H}$). ^{13}C-NMR (100 MHz, $CDCl_3$) δ_C 148.9 ($\underline{C}$(3)), 129.8 ($\underline{C}$(2)), 124.2 ($\underline{C}$(4)), 90.2 ($\underline{C}$(1)), 51.1 ($\underline{C}$(6)), 27.9 ($\underline{C}$(7)), 20.6 ($\underline{C}$(8)). HRMS (NSI, *m/z*): $[M + H]^+$ calc. for $[C_{14}H_{23}O_4N_4]^+$ 311.1712; found 311.1712

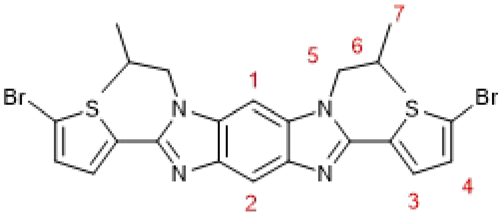
^{1}H NMR ($CDCl_3$, 400 MHz):



^{13}C NMR ($CDCl_3$, 100 MHz):

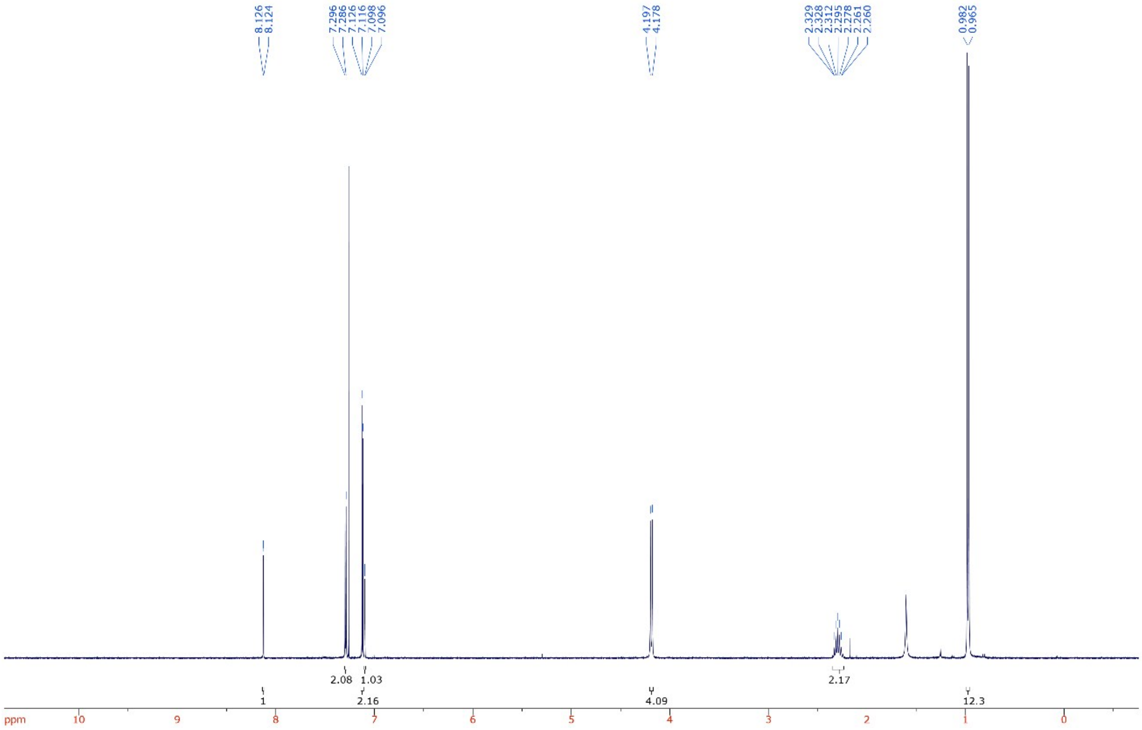


2,6-bis(5-bromothiophen-2-yl)-1,7-diisobutyl-1,7-dihydrobenzo [1,2-d:4,5- d']diimidazole (4)

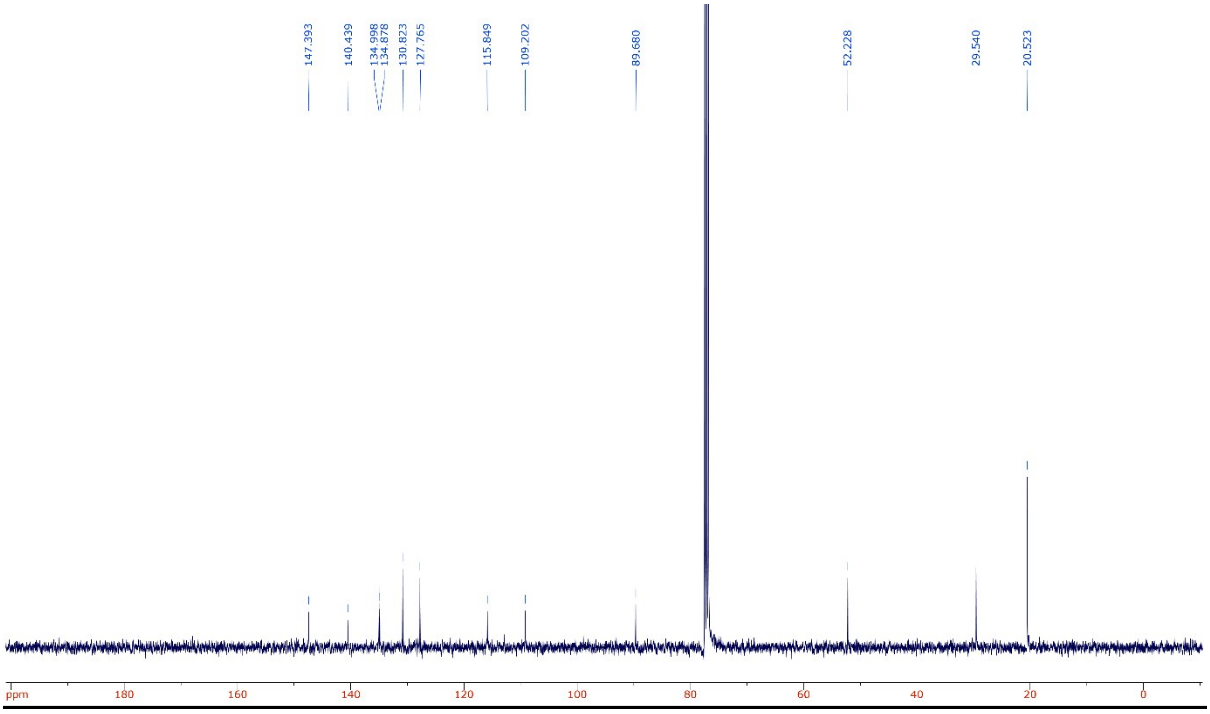


$LiAlH_4$ (1.47 g, 38.7 mmol) was added portion wise to a solution of compound **2** (2.00 g, 6.44 mmol) in dry tetrahydrofuran (75 ml). The reaction mixture was stirred for 16 hours under reflux, then allowed to cool to room temperature and quenched by the slow addition of water (5 ml). The resulting suspension was filtered and the solids were washed with ethyl acetate (100 ml). The filterate was washed with water (4 × 50 ml) and the organic phase was dried over $MgSO_4$, filtered and concentrated under reduced pressure to give *N1,N5*-diisobutylbenzene-1,2,4,5-tetraamine **(3)** as a crude product which was used without further purification. Compound **3** and 5-bromo-2-thiophenecarboxaldehyde (1.7 ml, 14.2 mmol) were dissolved in a mixture of glacial acetic acid (100 ml) and toluene (10 ml). The mixture was stirred for 72 hours, at 80 °C under N_2, then allowed to cool to room temperature. The solvent was evaporated under reduced pressure and the crude product was then purified by flash chromatography (SiO_2, dichloromethane:acetone; 9:1) to yield compound **4** as a pale-yellow solid (1.43 g, 47%). M.p. = 130 – 133°C. ^1H NMR (400 MHz, $CDCl_3$) δ_H 8.12 (2H, d, J = 0.77, C(2)$\underline{H}$), 7.29 (4H, d, J = 4.0, C(3)$\underline{H}$), 7.12 (2H, d, J = 4.0, C(4)$\underline{H}$), 7.10 (1H, d, J = 0.77 C(1)$\underline{H}$), 4.19 (4H, d, J = 7.6, C(5)$\underline{H}$), 2.29 (2H, sept, J = 6.7, C(6)$\underline{H}$), 0.97 (12H, d, J = 6.7, C(7)$\underline{H}$). ^{13}C-NMR (100MHz, $CDCl_3$) δ_C 147.4, 140.4, 135.0, 134.9, 130.8 ($\underline{C}$(4)), 127.8 ($\underline{C}$(3)), 115.9, 109.2 ($\underline{C}$(2)), 89.7 ($\underline{C}$1)), 52.2 ($\underline{C}$(5)), 29.5 ($\underline{C}$(6)), 20.5 ($\underline{C}$(7)). HRMS (NSI, *m/z*): $[M + H]^+$ calc. for $[C_{24}Br_2H_{25}N_4S_2]^+$ 590.9882; found 590.9878.

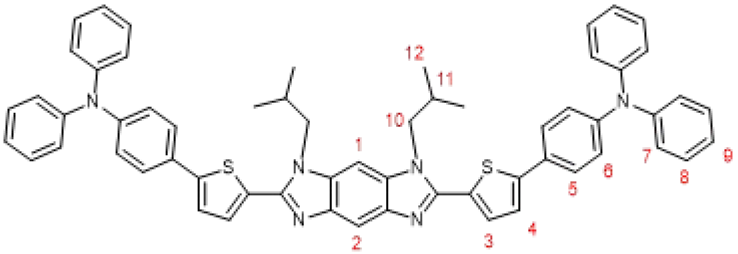
^{1}H NMR (CDCl$_3$, 400 MHz):



^{13}C NMR (CDCl$_3$, 100 MHz):

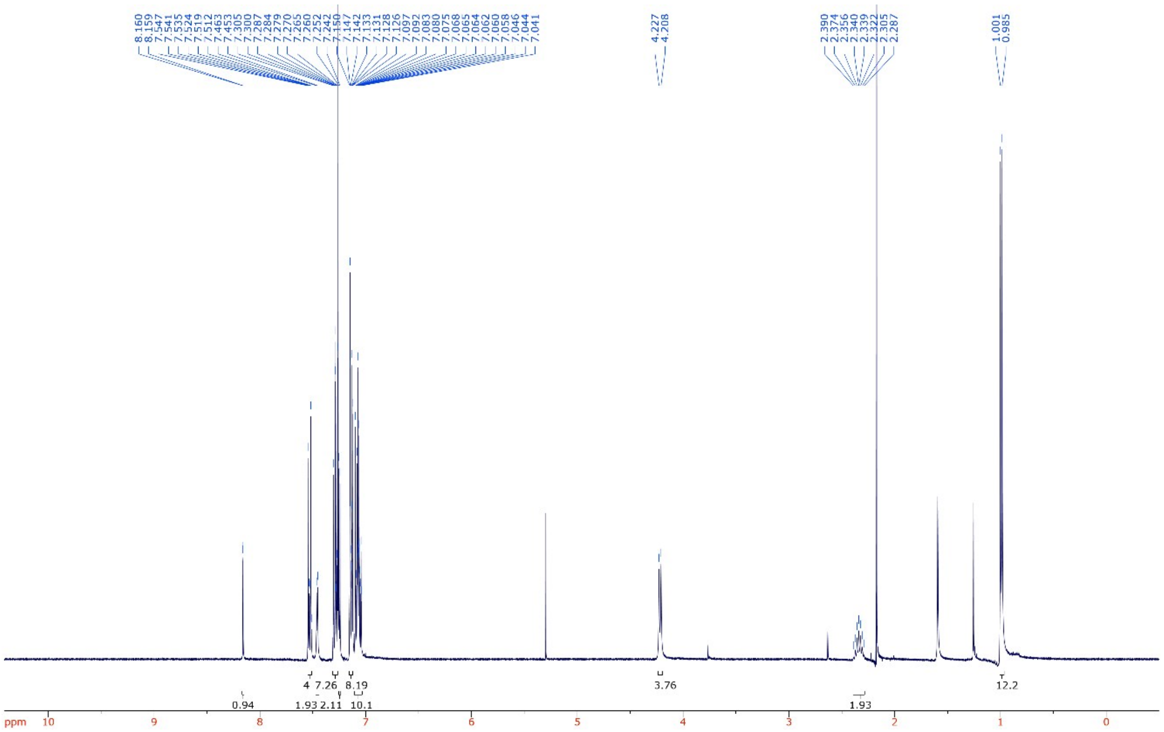


4,4'-(5,5'-(1,7-diisobutyl-1,7-dihydrobenzo[1,2-d:4,5-d']diimidazole-2,6-diyl)bis(thiophene-5,2-diyl))bis(*N,N*-diphenylaniline) (TPD-BDI).

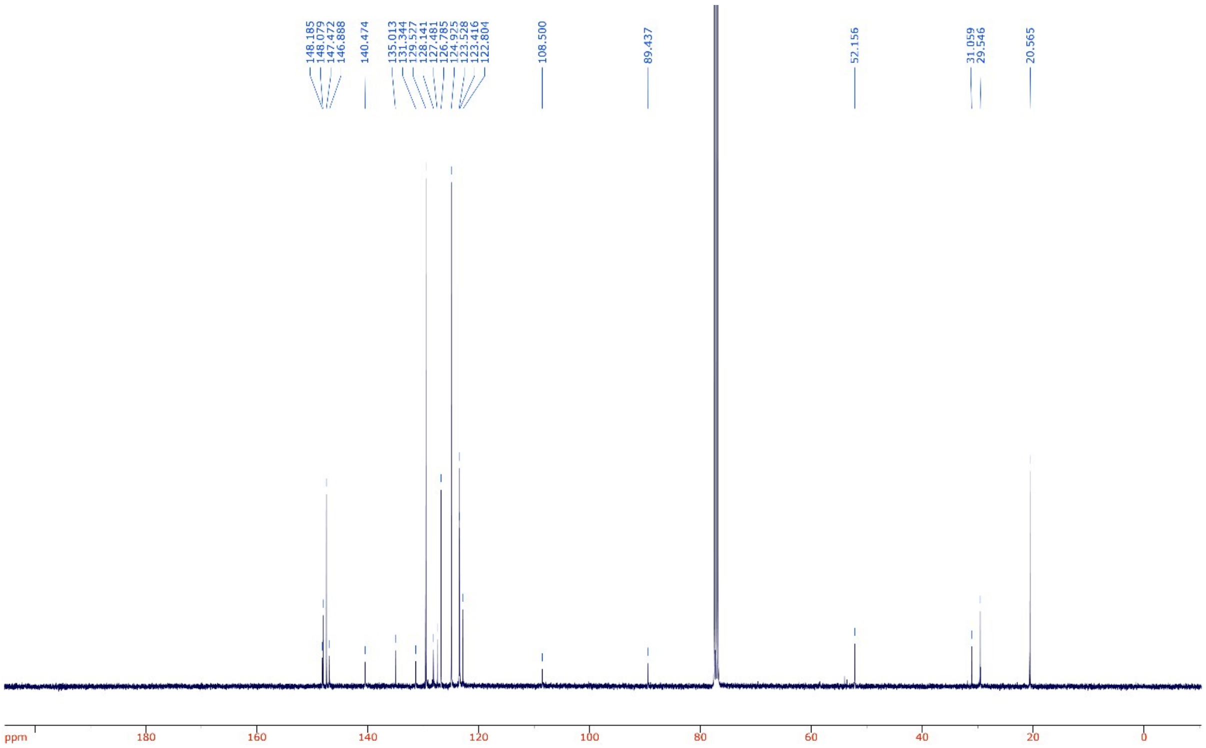


Compound **4** (0.200 g, 0.36 mmol), 4-(diphenylamino)phenylboronic acid pinacol ester (0.292 g, 0.79 mmol) and K_2CO_3 (0.199 g, 1.44 mmol) were dissolved in 1,4-dioxane (40 ml) under N_2. $Pd(PPh_3)_2Cl_2$ (0.01g, 0.014 mmol) was added and the mixture was stirred at 90 °C for 24 hours. After this time, the mixture was diluted with water (100 ml), extracted with dichloromethane (4 × 200 ml) and the combined organic extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography (SiO_2, dichloromethane:acetone; 9:1) to yield **TPA-BDI** as a yellow solid (0.214 g, 55%). M.p. > 300°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.16 (1H, d, *J* = 0.6, C(2)H), 7.55 - 7.51 (4H, m), 7.46 (4H, d, *J* = 3.9, C(3)H), 7.30 - 7.27 (7H, m), 7.25 (2H, d, *J* = 3.9), 7.15 – 7.13 (8H, m), 7.10 - 7.09 (10H, m), 4.22 (4H, d, *J* = 7.5, C(10)H), 2.34 (2H, sept, *J* = 6.9, C(11)H), 1.02 (12H, d, *J* = 6.7, C(12)H). ^{13}C-NMR (100MHz, $CDCl_3$) δ_C 148.2, 148.0, 147.3, 146.9, 140.3, 134.9, 131.2, 129.4 (C(7)),, 128.1 (C(3)), 127.3, 126.8 (C(6)), 124.9 (C(8)), 123.3, 123.2 (C(5, 9)), 122.7 (C(4)), 108,3 (C(2)), 88.7 (C(1)), 54 (C(10)), 29.1 (C(11)), 20.1 (C(12)). HRMS (NSI, *m/z*): $[M + H]^+$ calc. for $[C_{60}H_{53}N_6S_2]^+$ 921.3773; found 921.3778.

^{1}H NMR (CDCl$_3$, 400 MHz):



^{13}C NMR (CDCl$_3$, 100 MHz):



2. Optical characterisation of TPA-BDI in the poly(urethane) resin

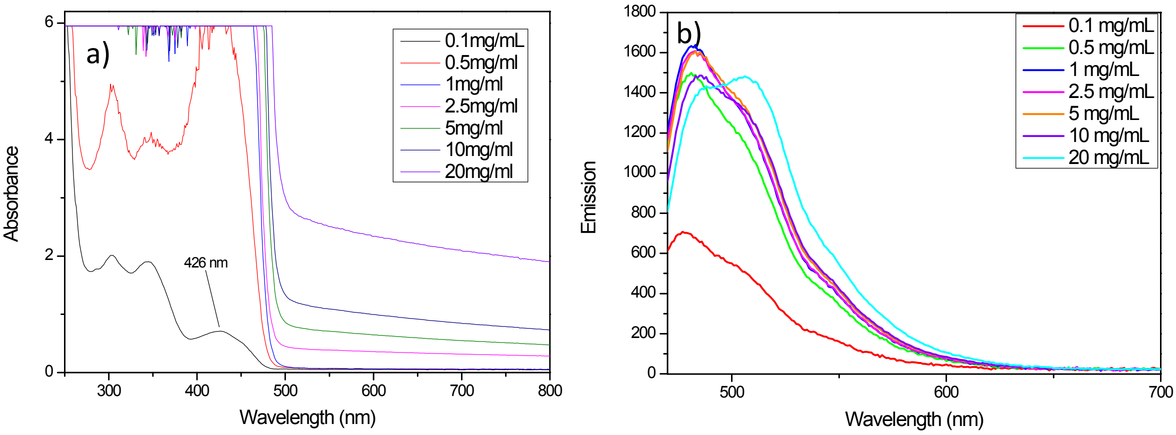
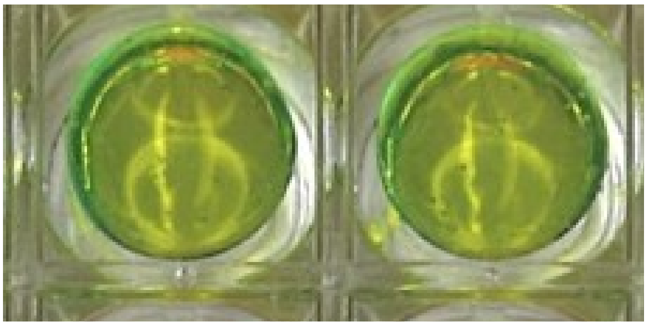
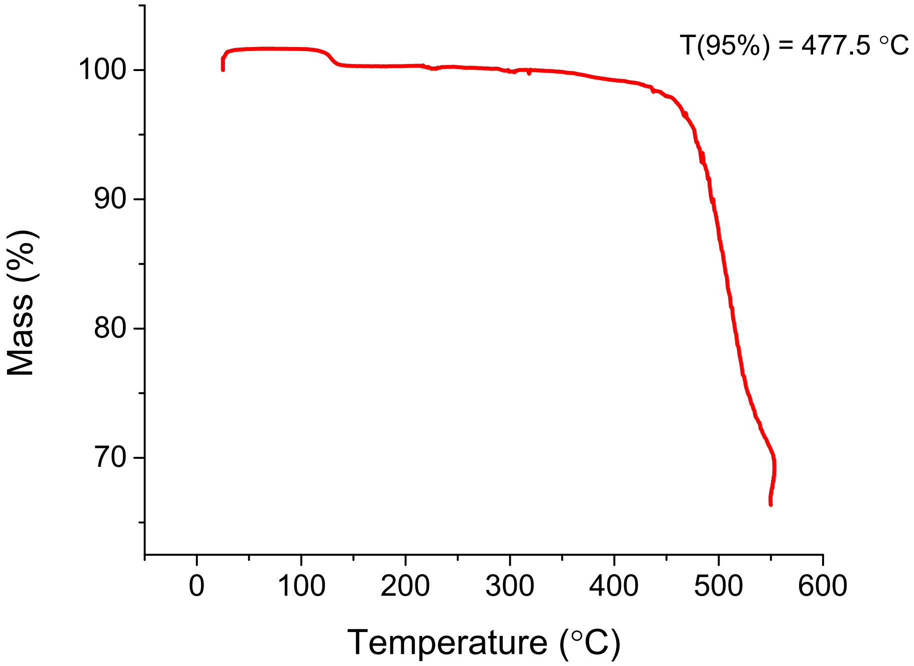


Figure S1: Thin film (a) absorbance and (b) emission characteristics of encapsulated **TPA-BDI**.



Figures S2: Optical microscope image of a sample film of **TPA-BDI** in Opti-tec™ 4200 showing good homogeneity and high transparency at 1 mg/ml.

3. Thermal analysis



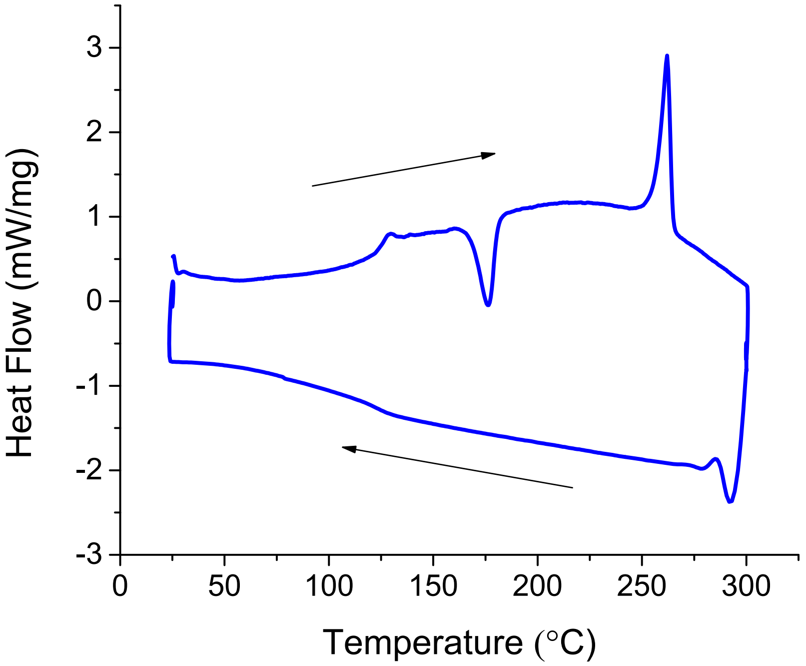


Figure S3: TGA (top) and DSC (bottom) traces of **TPA-BDI.**

4. Device lifetime and degradation study.

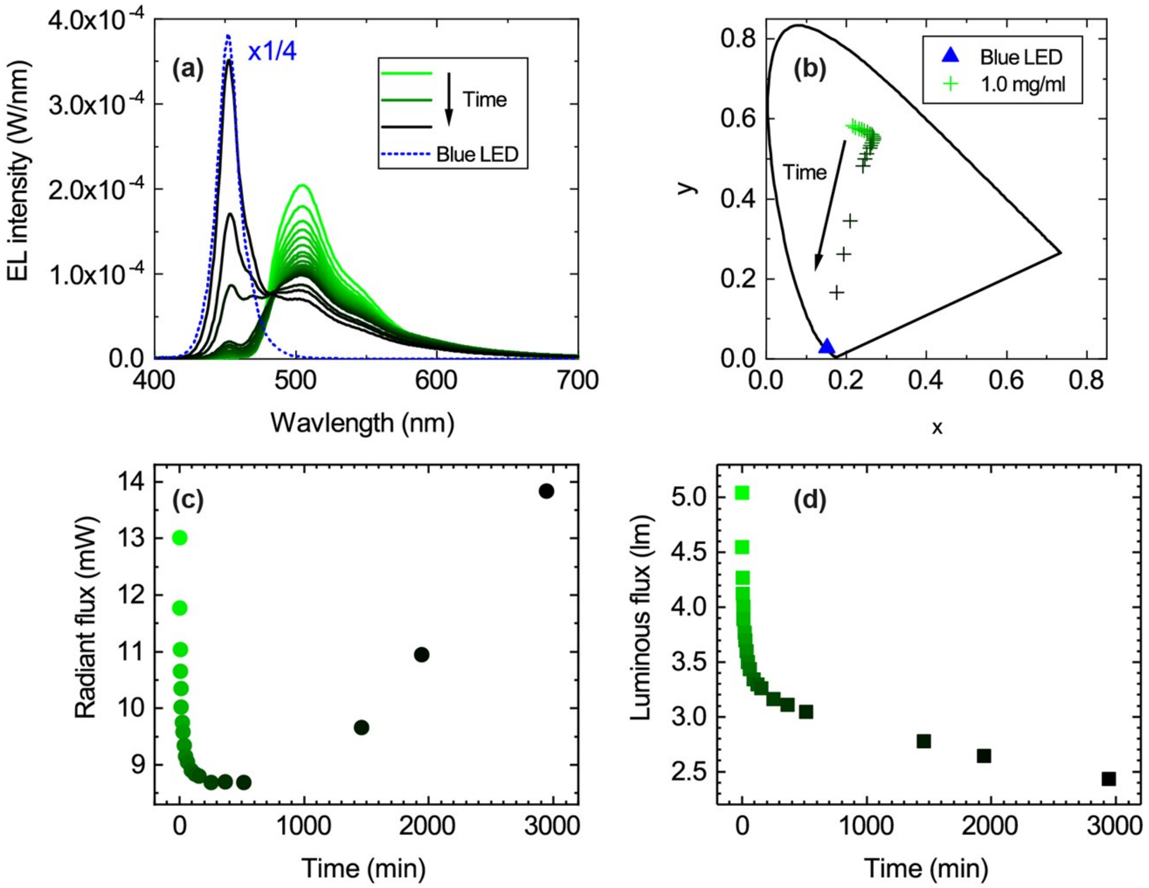


Figure S4: Lifetime measurements: The hybrid green LED with 1.0 mg/ml of the colour converter was continuously driven using 25 mA for 3000 minutes with EL spectra taken at different time intervals: (a) EL spectra, (b) CIE 1931 chromaticity coordinates (x, y), (c) radiant flux and (d) luminous flux. (a) and (c) are the same graphs as the ones used in the main manuscript in Figure 4.

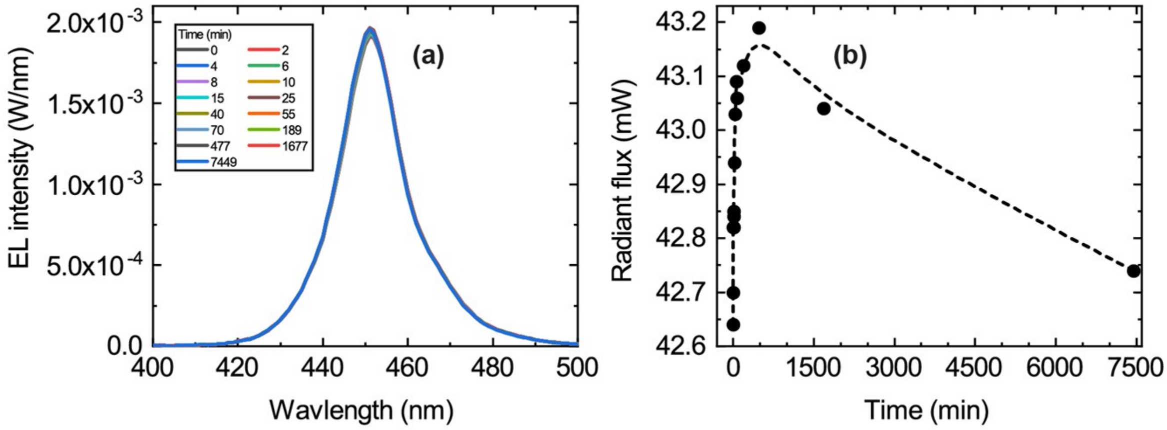


Figure S5: (a) EL spectra of a blue LED encapsulated with Opti-tec™ 4200. The LED was continuously operated at 25 mA for about 7500 minutes with EL spectra taken at different time intervals. (b) Radiant flux calculated from the EL spectra. The initial increase is due to the LED heating up in the first few minutes after switch-on. After 7500 minutes (125 hours) the radiant flux decreased by about 1% from its peak value.

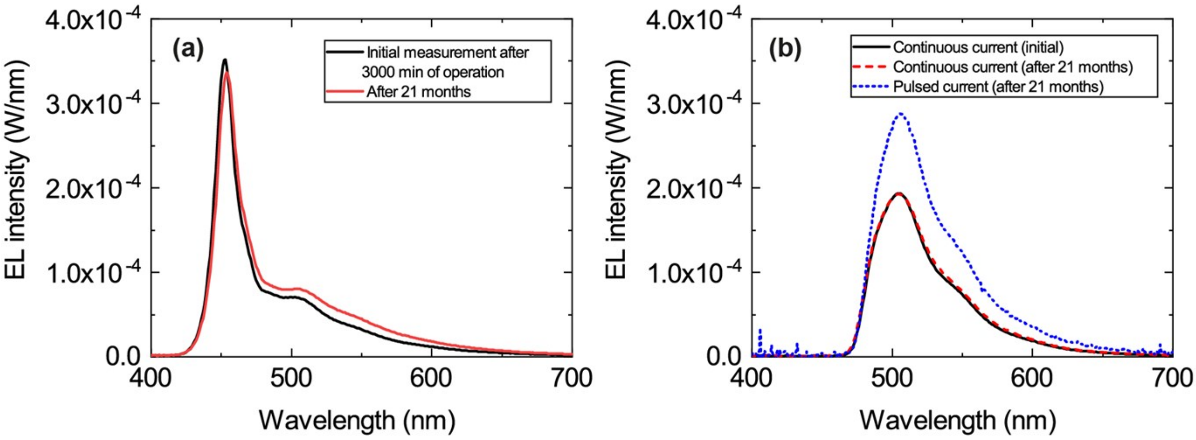


Figure S6: (a) Final EL spectrum of the LED from the lifetime series in Fig. S5 after 3000 min of constant irradiation compared with the EL spectrum of the same LED measured after 21 months at 25 mA. (b) EL spectra of a different hybrid LED (1 mg/ml concentration) using either a continuous (no more than 5 min) or pulsed current of 25 mA. The same LED was measured again after 21 months for comparison with the initial continuous current measurement. The pulsed current measurement was corrected according to the duty cycle of 2%.

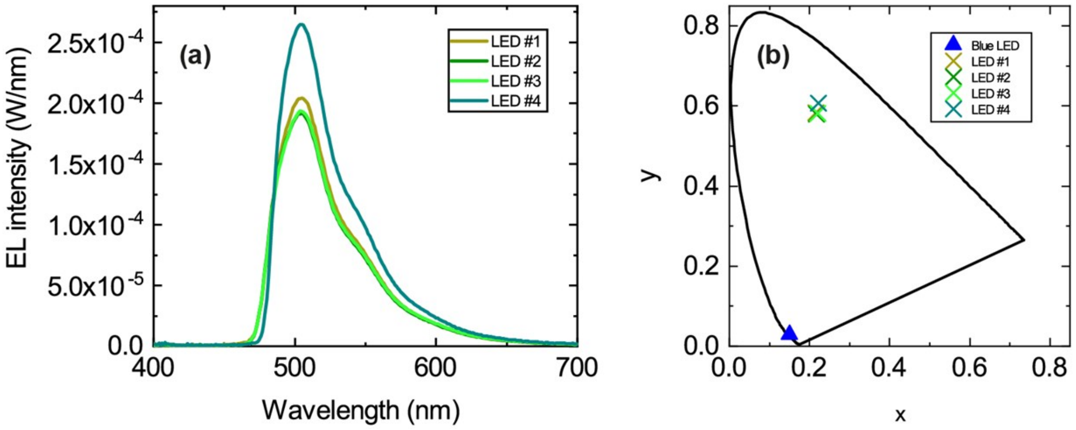


Figure S7: Reproducibility: Four blue LEDs were coated with 1.0 mg/ml of the organic material and the (a) EL spectra and (b) CIE 1931 chromaticity coordinates (x, y) were measured at 25 mA.

LED number	**Luminous efficacy (lm/W)**	**Radiant flux (mW) – hybrid LED (after)**	**Radiant flux (mW) – blue LED (before)**	**Radiant flux loss (%)**
#1	64	13	35	62
#2	68	12	32	61
#3	65	13	33	62
#4	96	16	34	53

Table S8: Luminous efficacy, radiant flux before and after depositing the organic material and loss in radiant flux for four hybrid LEDs using a concentration of 1.0 mg/ml.