

# Conjugated dendrimers: a modular approach to materials for full colour displays

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## ABSTRACT

Conjugated dendrimers provide an excellent molecular architecture for tuning material properties for organic light emitting diodes. Here we demonstrate a modular approach allowing highly efficient fluorescent and phosphorescent emissive chromophores to be used to make red, green and blue solution-processed light emitting diodes. The choice of a common dendritic architecture ensures good solubility and film forming properties irrespective of the choice of core unit. In addition, this architecture allows blending of dendrimers with different cores without phase separation. We show that blending provides a simple but powerful way of tuning the colour of dendrimer LEDs from deep blue to blue-green, and from green to red with little impact on the device properties.

## 1. INTRODUCTION

Organic light emitting diodes (OLEDs) are a highly efficient alternative technology for flat panel display applications. Their low cost and ever increasing efficiency and reliability is appealing for the marketplace, along with the versatility of chemical synthesis to tune their chemical and optical properties. Solution processing of OLEDs is an attractive route to fabrication of these devices, which offers flexibility and low cost of fabrication and also opens up exciting possibilities such as inkjet printing of displays. Conjugated polymers are the most widely established and studied class of solution processible light-emitting materials, however conjugated dendrimers have recently also shown much promise in this field<sup>1-3</sup>. Efficient dendrimer LEDs reported so far have been green emitters<sup>2-3</sup> based on electrophosphorescence. We now show that the modular nature of dendrimers allows us to change the colour of emission of the dendrimers by use of alternative core moieties. The use of the dendritic structure allows a wide choice of core molecules including, for example, dye molecules, phosphors and repeat units of conjugated polymers. In this paper we show how red, green and blue emission can be achieved using a common dendritic architecture, and how through use of this structure, blending of dendrimers with different cores can lead to precise tuning of the emission colour whilst maintaining solubility and film forming properties.

The facility to tune the emission colour of OLEDs is also an important goal to achieve desired emission properties for light emitting diodes. This can be achieved in organic electroluminescent materials by systematic modification of the chemical structure<sup>4</sup>. However, instead of chemical modification, an alternative method is a physical approach by blending materials. For evaporated small molecular OLEDs, co-evaporation of dyes and dopants into a wider energy gap host matrix is the mainstay of efficient small molecular devices<sup>5</sup>. This technique allows use of materials that in neat form would show little or no emission, and gives the possibility of tuning the emission colour by choice and concentration of dopant in the host.

In direct contrast, when attempting to blend solution processible materials, many other factors need to be considered. Blends can suffer from detrimental effects due to the different solubility of each component in the spinning solvent. Blends of polymers are well known to intrinsically phase separate<sup>6</sup>, and studies performed on conjugated polymer blends have shown that the degree of phase separation is highly dependent on the doping ratio of the two polymers and spinning solvent used<sup>7,8</sup>. Moving to dye doped polymer systems, it has been shown that the film forming properties of many systems are highly reliant upon the particular combination of host polymer and solvent used<sup>9</sup>. Many small molecule EL

materials, often used as dopants, are generally difficult to process from solution, limiting the choice of dye and the concentration used in the host polymer.

We demonstrate that the above problems can be overcome using conjugated dendrimers with different cores but identical surface groups. The modular construction of dendrimers enables their processing and electronic properties to be tuned independently. This is a significant advantage when forming a blend of materials as we can encapsulate different cores within the same shell and surface groups, avoiding phase separation effects.

## 2. RGB DENDRIMER MATERIALS

Our approach to tuning the emission colour of solution processible LEDs involves the use of dendrimers with red, green and blue emitting core chromophores. The cores can be either phosphorescent or fluorescent, and wide ranges of organic molecules are available which emit efficiently at these wavelengths. Conjugated dendrons are then attached to the selected core *via a meta* linkage. The advantage of this method is that the electronic properties of the core remain unperturbed by the addition of the bulky dendrons. To the outer extremities of the dendrons are attached solubilising, or surface, groups. They can be tuned to specific applications and can be chosen independently of the core, so as not to affect the emission properties. This contrasts with many conjugated polymer systems, where attachment of side groups to improve site isolation or solubility can have large effects on the wavelength of the emitted light. An example of this is the attachment of alkoxy substituents to the precursor polymer *para*-poly(phenylene-vinylene) (PPV)<sup>10</sup> in order to give a directly solution processible material. The result is a large shift in emission wavelength from the green-yellow (for PPV) to orange-red (as in the case of a dialkoxy derivative, MEH-PPV)<sup>11,12</sup>

Recent advances in the performance of organic electroluminescent materials and devices have led to very high efficiencies<sup>13-17</sup>. Many of these materials are potentially suitable for incorporation into a dendrimer structure. The structures of blue **1**, green **2** and red **3** emitting dendrimers are shown in Fig. 1, and their electroluminescence spectra in Fig. 2. All of these dendrimers share first generation biphenyl dendrons and 2-ethyl-hexyloxy surface groups. Only the core chromophore is changed in each case to give blue, green and red emission. The photopic response of the eye is shown in Fig. 2 (dotted line). This indicates the perceived intensities of the emitted light. Fig. 2 also shows the CIE coordinates of the materials in electroluminescence, indicating that the three dendrimers are close to the vertices of the RGB triangle, thus providing a full colour gamut for display applications.

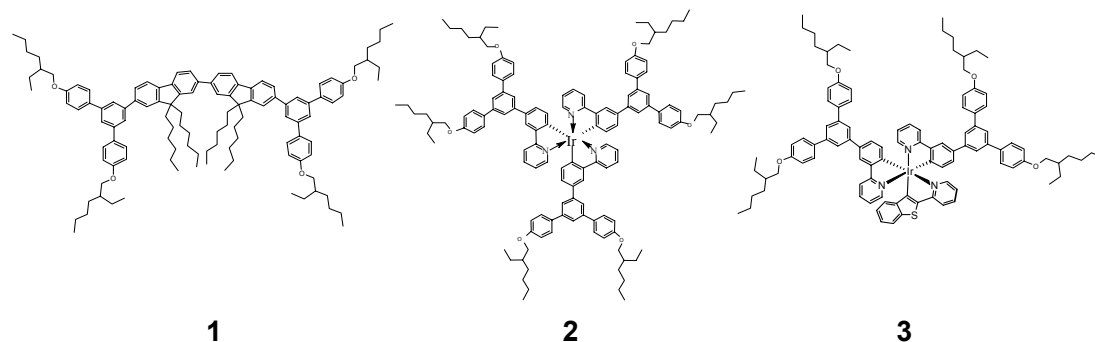
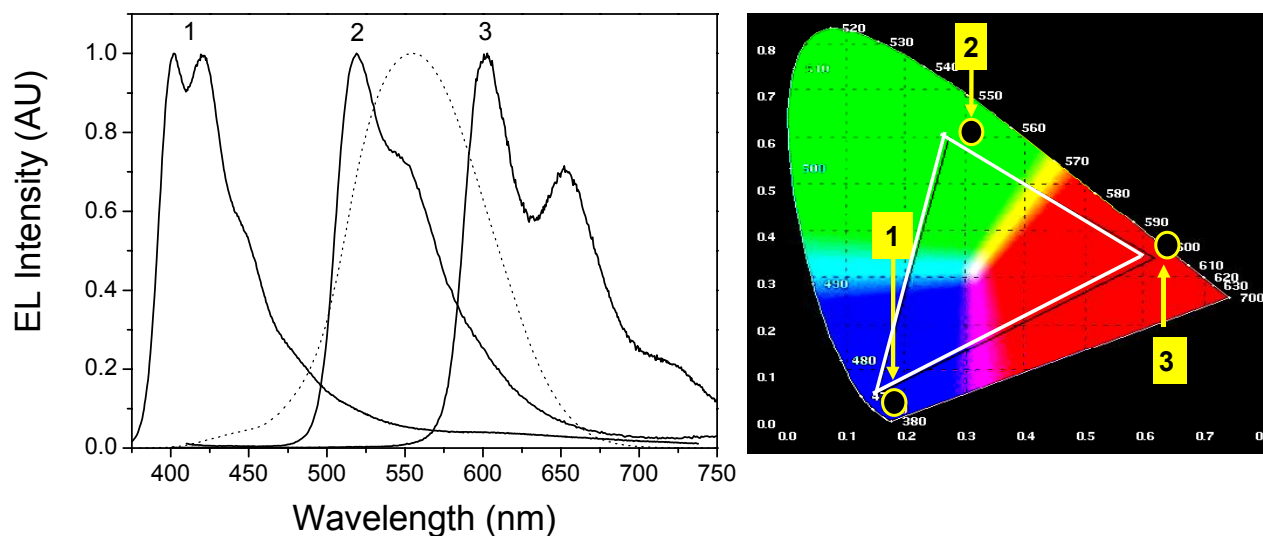


Fig. 1. The structures of the blue (1), green (2) and red (3) dendrimers studied

For blue light emission, the best colour purity currently requires fluorescent materials. Although highly efficient blue phosphorescent OLEDs exist<sup>13</sup> their colour purity is not high due to the peak of emission occurring at a wavelength around 470 nm. Thus the devices appear blue green and are not yet suitable for full colour displays. Many highly efficient fluorescent materials are known to emit throughout the blue spectral range, and one of the more successful families are poly(fluorene) based materials<sup>14</sup>. Thus this core was chosen as the basis for a deep blue emitting dendrimer. The first generation *bis*-fluorene **1** contains a *bis*-fluorene-*bis*-phenyl core with hexyl side groups, phenylene dendrons and 2-ethylhexyloxy surface groups. The emission is in the deep blue and shows significant vibronic structure. Peaks are visible at 401 nm and 421 nm, with a shoulder at 440 nm. CIE coordinates of (0.16, 0.06) show that the blue emission is

very pure. However, the photopic response of the eye is very poor in this region so low brightnesses and power efficiencies when compared to sky blue or green materials are expected.



**Fig. 2. Left: EL spectra of 1, 2 and 3 together with CIE photopic response curve (dotted line). Right: CIE colour chart for 1, 2 and 3.**

For red and green light emission, phosphorescent materials have shown outstanding device performance, with very high external quantum efficiencies for green and red phosphors based on *bis* cyclometallated iridium complexes<sup>15-17</sup>. The green emitter **2** contains a *tris*-2-phenylpyridine iridium ( $\text{Ir}(\text{ppy})_3$ ) core which has been used successfully in both evaporated<sup>15,16</sup> and solution processed<sup>2,3</sup> OLEDs. Biphenylene dendrons are then attached to the core unit in the *meta* position, thus preventing further electron delocalisation. This can be seen in the identical nature of the solution photoluminescence when compared to the parent core  $\text{Ir}(\text{ppy})_3$ <sup>18</sup>. The emission is a vibrant green with a luminescence maximum at 518 nm and CIE coordinates of (0.32, 0.64). This is similar to that reported for  $\text{Ir}(\text{ppy})_3$  based devices<sup>15</sup>.

It has been demonstrated that the colour of emission of the iridium phosphors can be tuned by changing the ligand attached to the metal core<sup>19</sup>, and so we used an  $\text{Ir}(\text{ppy})_2(\text{btp})$  core to make a red emitting dendrimer. It contains one benzothienylpyridine (btp) ligand and two phenylpyridine ligands attached to the metal at the centre of the molecule. Biphenylene dendrons are attached to the phenylpyridine ligands in the *meta* position. The addition of a lower energy btp ligand moves the emission maximum from 518 nm (green) to 600 nm (red)(CIE coordinates (0.64, 0.36)). Similar results for  $(\text{btp})_2$  iridium based phosphors have been reported<sup>17</sup> however the emission in those cases is more redshifted to 610 – 620 nm. In this respect a material possessing one btp unit is interesting, as it implies that a change to just one ligand is sufficient to cause a large change in the emission properties, and gives a pure primary red colour.

In order to determine the potential of these materials for LEDs, the photoluminescence quantum yields (PLQYs) of neat films of dendrimers **1**, **2** and **3** were measured. This was done in an integrating sphere following excitation at 325 nm from a Helium-Cadmium laser using the method of Greenham et al<sup>20</sup>. The blue emitting dendrimer **1** was found to have the highest PLQY of 42% in thin film. Thin films of green and red emitting **2** and **3** were found to have PLQYs of 22% and 7% respectively. The lower efficiency of the red emitter is due to the presence of only two dendrons on this material, reducing the inter-chromophore separation and leading to greater intermolecular interactions. High efficiencies in both photoluminescence and electroluminescence have been reported for phosphorescent dendrimers dispersed into wide-gap carbazole containing host materials<sup>2,3</sup> and this has been shown to produce optical quality films with no phase separation<sup>21</sup>. Thus **2** and **3** were doped into 4-4'-*N,N'*-dicarbazolyl-biphenyl (CBP) at concentrations of 20wt% and the respective PLQYs measured. They were found to be very high, with 20wt% of **2** in CBP giving 78% and the same quantity of **3** giving 49%. Coupled with the advantages of phosphorescence, these results are expected to lead to high efficiency in electroluminescence.

### 3. RGB DENDRIMER DEVICES

It was found that all dendrimers could be spin-coated to form optical quality, pinhole free films. All devices were fabricated using a bilayer structure, however the optimum device configuration is dependent on the particular material. The best device performance of **1** came from the use of an oxygen plasma treated ITO anode coated with a layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT/PSS). In view of the large bandgap of **1** a significant barrier to hole injection is expected, so a thin (25 nm) layer of Poly(N-vinyl Carbazole) (PVK) was spun onto the PEDOT/PSS layer in order to assist hole injection and block electron extraction. The layer of dendrimer **1** was then spin coated from toluene solution, which does not dissolve the PVK layer. A calcium-aluminium cathode is used, with a thin (0.4 nm) layer of lithium fluoride between the dendrimer and the calcium. This is an effective electron injecting contact for wide band-gap organic materials. For the green and red dendrimers **2** and **3** PEDOT/PSS has been found to be detrimental to the efficiency of LEDs and therefore plasma treated ITO was used to inject holes. In this case the dendrimers function as hole transport and emitting layers and an electron transport layer of 1,3,5-tri(phenyl-2-benzimidazole)-benzene (TPBI) is thermally evaporated onto the spin-coated dendrimer layer. A lithium fluoride (1 nm)-aluminium contact completes the devices.

All devices were efficient, and the external quantum efficiencies (EQEs) at 100 Cd/m<sup>2</sup> are 1% for blue, 16% for green and 5.4% for red. The lower efficiency of **1** and **2** is partly due to the use of a fluorescent blue which leads to losses associated with triplet formation, and the lower PLQYs of the blue and red materials. The turn on voltages (defined here as the voltage at which the device emits 1 Cd/m<sup>2</sup>) are low: 4.4 V for the blue system, 3.6 V for the red and 2.9 V for the green emitters.

Fig. 3. shows the luminous efficiencies and brightnesses of the blue, green and red LEDs as a function of applied bias. A very high luminous efficiency of 46 lm/W at 100 Cd/m<sup>2</sup> and 3.7 V for the green system is the highest reported for OLEDs with a solution processed emissive layer. Luminous efficiencies at 100 Cd/m<sup>2</sup> of 0.2 lm/W at 6.6 V for the blue system and 3.85 lm/W at 5.6 V for the red are also competitive<sup>4,5,14,22</sup>. The much lower luminous efficiency of red and blue when compared with green is a product of the lower EQEs of these colours and the poorer photopic response of the eye at blue and red wavelengths. For example, the brightness of **1** is a factor of 7 lower than **2** when emitting the same optical power. The decrease in luminous efficiency at high brightnesses is primarily due to the increase in drive voltage.

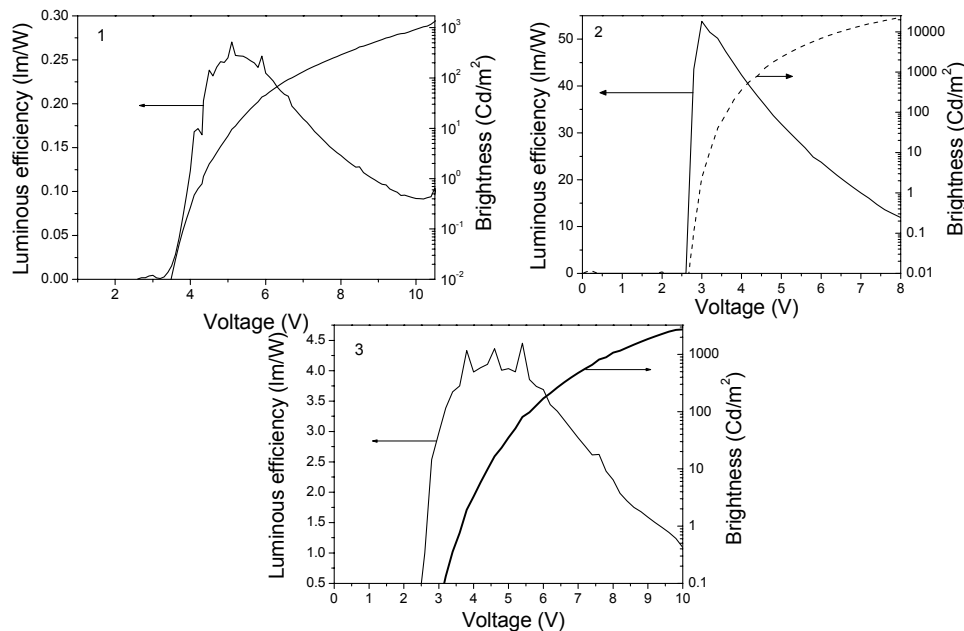


Fig. 3. Power efficiencies and brightnesses of blue (1) green (2) and red (3) devices

#### 4. COLOUR TUNING BY DENDRIMER BLENDING

So far we have demonstrated that by judicious choice of core chromophore we are able to tune the colour of dendrimer LEDs to produce blue, green and red emitting devices without affecting the processing properties. The three systems investigated here all possess identical surface groups and first generation dendrons. In contrast to many blend systems, this allows dendrimers with different cores to be intermixed without phase separation. In addition, due to this structural similarity, film forming properties are not dependent upon blend ratio, so much larger regimes of concentrations can be explored. This method has hence been used to tune the colour of efficient dendrimer LEDs to lead to desired emission coordinates. We have used two different sets of materials to demonstrate colour tuning. The first set are fluorescent blue materials, and the second set are phosphorescent materials.

As discussed earlier, the colour purity of **1** was very high, however its deep blue colour leads to poor power efficiencies. Thus a new dendrimer was investigated to provide a red-shifted emission. The first generation fluorene-thiophene dendrimer (G1FT) is similar to **1** but contains a thiophene unit in place of one of the fluorene units, and is shown in the inset to Fig. 4. The electron donating thiophene ring is expected to lead to a bathochromic shift of the material relative to **1**. Indeed, in solution (data not shown) this substitution results in an emission peak at 415 nm, as compared to 396 nm measured for **1**. However, when G1FT is spin coated to form a neat film it shows a heavily redshifted emission with a peak at 477 nm. The emission appears blue-green to the eye. The large difference between solution (deep blue) and film (blue-green) suggests that the redshifted emission originates from concentration dependent intermolecular interactions, and that it could be controlled by dilution in a suitable host material. Given the common surface groups of **1** and G1FT, blends can be formed without phase separation, and this has been verified by atomic force microscopy (AFM). It can be seen from Fig. 4 that by changing the blend ratio from neat films to 80:20 and 50:50 blends of **1**:G1FT, the CIE coordinates can be changed from deep blue (0.16,0.06) (neat **1**) to blue green (0.18,0.13) (neat G1FT). There is little impact on device performance, with all blends showing EQEs of 1%. However, there is an increase in power efficiency of a factor of four (from 0.3 to 1.2 lm/W) in moving from a neat film of **1** to one of G1FT due to the change of spectrum. Hence blending of dendrimers provides a convenient way of fine-tuning emission colour. This has application in systems where the greater power efficiency of a less saturated blue could be used to save on battery life, for example. A mains powered display, however, has no stringent energy demands and thus a deeper blue could be used to provide a greater colour gamut.

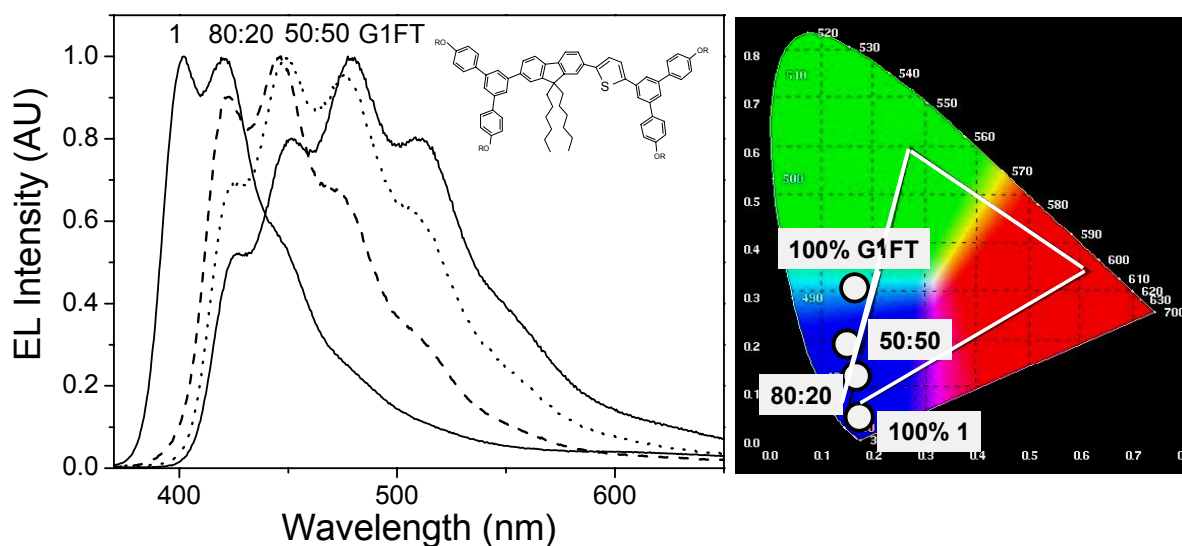


Fig. 4. EL spectra and CIE coordinates of blends of **1** and G1FT. Inset: structure of G1FT

We have also explored tuning over a wider range of emission colours by blending phosphorescent dendrimers **2** and **3**. Different blend ratios of **2** and **3** were used at in a total of 20wt% in a CBP host. Films of **2** have been shown not to phase separate when blended into CBP at 20wt%, and give a surface roughness of  $\sim 1 \text{ nm}^{21}$ . Similar film quality has been

observed for films of **3** at the same doping ratio. It should be noted that without the dendrimer, CBP does not form good quality spin-coated films and is prone to recrystallisation and inhomogeneous film formation. Given the similar properties of the two dendrimers, blends of red and green at a total of 20wt% in CBP can form excellent quality thin films irrespective of blend ratio.

Colour tuning has been achieved in electrophosphorescent polymer based devices<sup>22</sup> however the efficiencies reported are much lower than those for evaporated systems. The use of PVK as a host material in these systems often leads to high operating voltages and consequently low power efficiencies. However, by use of a dendrimer blend layer and a TPBI electron transporting layer (as for the highly efficient red and green devices discussed earlier) low voltages and high efficiencies can be achieved, with good tuning of the emission colour. Fig. 5 shows the EL spectra and CIE coordinates of three blends of **2** and **3**, with neat films for comparison. Good colour tuning from green to red is possible, all blends share external quantum efficiencies between 5 and 10%. As the amount of red is increased the EQE decreases due to the lower PLQY of **3**, but the efficiencies are all in excess of that measured for the neat red. This illustrates that the concept of dendrimer blending using a common surface architecture can lead to highly efficient and colour tunable LEDs.

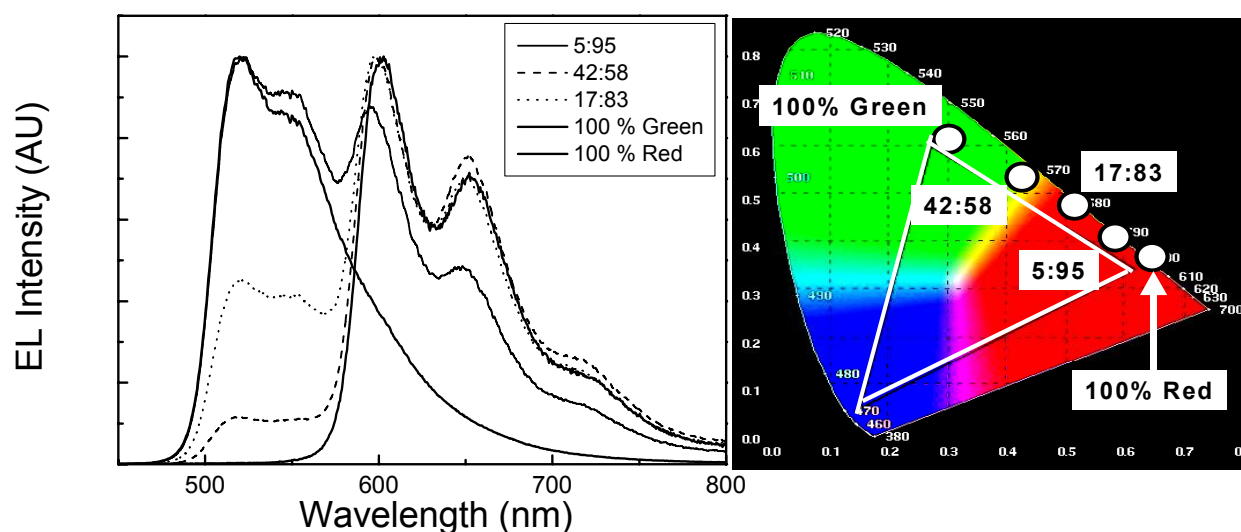


Fig. 5. EL spectra and CIE coordinates of blends of **2** and **3**.

## 5. CONCLUSIONS

In conclusion we have demonstrated that by choice of a common dendrimer shell and surface groups we are able to form efficient red, green and blue emitting dendrimer LEDs via solution processing. The processing properties of the dendrimers are independent of the emissive chromophore. In addition, we have also demonstrated that blending provides a simple way of tuning colour.

## 6. ACKNOWLEDGEMENTS

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