

Light-emitting dendrimer film morphology: A neutron reflectivity study

S. V. Vickers,¹ H. Barcena,¹ K. A. Knights,¹ R. K. Thomas,¹ J.-C. Ribierre,² S. Gambino,² I. D. W. Samuel,² P. L. Burn,^{3,a)} and Giovanna Fragneto⁴

¹Department of Chemistry, Chemistry Research Laboratory, University of Oxford, Mansfield Rd, Oxford OX1 3TA, United Kingdom

²Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, United Kingdom

³Centre for Organic Photonics and Electronics, The University of Queensland, Chemistry Building, Queensland 4072, Australia

⁴Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex 9, France

(Received 25 February 2010; accepted 29 May 2010; published online 29 June 2010)

We have used neutron reflectivity (NR) measurements to probe the physical structure of phosphorescent dendrimer films. The dendrimers consisted of *fac*-tris(2-phenylpyridyl)iridium(III) cores, biphenyl-based dendrons (first or second generation), and perdeuterated 2-ethylhexyloxy surface groups. We found that the shape and hydrodynamic radius of the dendrimer were both important factors in determining the packing density of the dendrimers. “Cone” shaped dendrimers were found to pack more effectively than “spherical” dendrimers even when the latter had a smaller radius. The morphology of the films determined by NR was consistent with the measured photoluminescence and charge transporting properties of the materials. © 2010 American Institute of Physics. [doi:10.1063/1.3457438]

Since the initial reports of light-emitting dendrimers being used in organic light-emitting diodes (OLEDs)^{1,2} they have now become an established materials class^{3,4} with phosphorescent dendrimers giving rise to highly efficient devices.⁵ For all light-emitting organic materials the morphology of the film can play a critical role in device performance as it governs the intermolecular interactions that control charge transport and photophysical properties. With dendrimers it has been found that the OLED performance is dependent on dendrimer generation and/or the number of dendrons attached to the core complex.^{6,7} Neutron reflectivity (NR) has been used to study the morphology of conjugated polymer films and the interface with the commonly used anode indium tin oxide (ITO).^{8–13} In this letter, we apply NR measurements to study the morphology of phosphorescent dendrimer films. The dendrimers are comprised of *fac*-tris(2-phenylpyridyl)iridium(III) cores, biphenyl-based dendrons, and 2-ethylhexyloxy surface groups (Fig. 1). Dendrimers **1** and **2** are first and second generation “singly dendronized” (one dendron per ligand) dendrimers, and because of the *facial* arrangement of the ligands are somewhat “cone” shaped. Dendrimer **3** differs from **1** and **2** in that it has two first generation dendrons attached per ligand, which we call “doubly dendronized,” and is consequently more spherical in shape. The results provide useful information on the crucial structure-semiconducting property relations in conjugated light-emitting dendrimer films.

The dendrimers contained perdeuterated 2-ethylhexyloxy surface groups, and were prepared by a similar method to the protonated versions.¹⁴ The deuterated surface groups provided contrast for the NR experiments but did not change their photoluminescence properties. For example, the film photoluminescence quantum yields (PLQYs) of the protonated and deuterated first generation dendrimer **1** measured using an integrating sphere¹⁵ were 65%¹⁶ and 63%,

respectively, while the double dendrimer **2** had a PLQY of 82% which is within the error of the material with the protonated surface groups (81%).¹⁶ Hydrodynamic diameters were calculated from the viscosity molecular weight obtained by gel permeation chromatography (GPC).¹⁷ GPC was carried out using PLgel Mixed-A columns (600 mm + 300 mm lengths, 7.5 mm diameter) from Polymer Laboratories calibrated with polystyrene narrow standards ($M_p = 580$ to 3.2×10^6) in tetrahydrofuran. The tetrahydrofuran was deoxygenated with helium and pumped with a rate of 1 cm³/min at 30 °C. The ITO on glass was from Merck Display Technologies (Part No: 255 645 XE, 20 Ω/sq) and consisted of (in order) soda lime glass, a silicon dioxide barrier layer and a layer of ITO. Before spin-coating, the ITO substrates were cleaned by sonication in tetrahydrofuran for 15 min at room temperature. For the NR experiments, neat films of **1**, **2**, and **3** were spin-coated from solutions of concentrations of 20 mg/mL in chloroform onto ITO substrates of dimensions 50 × 50 mm² at 2000 rpm for 60 s, and the NR profiles were collected under vacuum. NR measurements were carried out at the Institut Laue-Langevin, Grenoble, in the time-of-flight mode with a wavelength range of 2–20 Å at an incidence angle of 0.7° on the D17 reflectometer.¹⁸ The instrumental resolution [$\Delta(q)/q$] is equal to 2% as defined by the wavelength spread [$\Delta(\lambda)$] and beam divergence [$\Delta(\theta)$]. The specularly reflected beam at the solid/air interface was

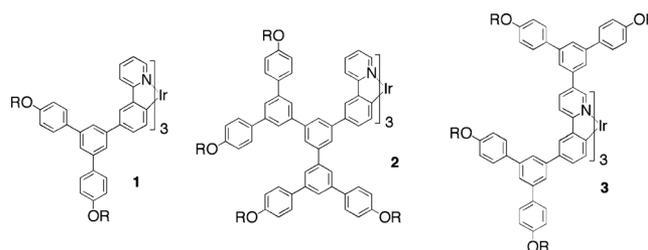


FIG. 1. Structures of the singly first generation **1** and second generation **2**, and doubly dendronised **3** dendrimers where R=(d₁₇)-2-ethylhexyl.

^{a)}Electronic mail: p.burn2@uq.edu.au.

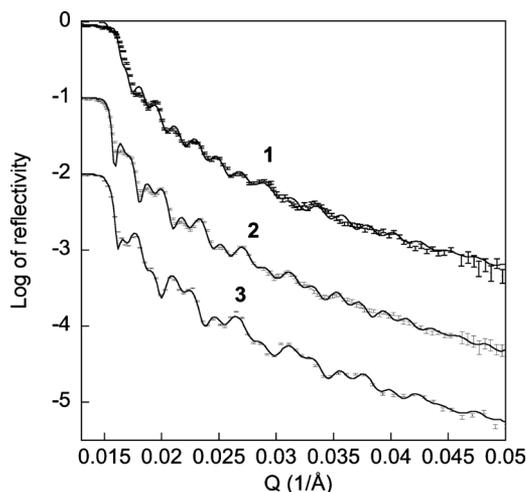


FIG. 2. Room temperature reflectivity profiles of dendrimers **1**, **2**, and **3**. The profiles are offset for clarity.

measured as a function of the wave vector transfer, Q , in a purpose built vacuum chamber. The model fitting method of analyzing the reflectivity profiles for layer thickness, scattering length density (SLD, given by the ratio of the scattering length, SL , of the material at the interfacial layer and its volume), and roughness has been described previously.¹⁰ For each of the layers the thickness is given to the nearest 10 Å and SLD is to the nearest $0.1 \times 10^{-6} \text{ \AA}^{-2}$. The fitting program errors were $\pm 5\%$ for thickness, $\pm 0.1 \times 10^{-6} \text{ \AA}^{-2}$ for SLD and $\pm 5\%$ for roughness in all fits. It should be noted that within the errors of the fitting parameters the NR profiles of the films could be fitted with zero roughness. The errors in the determined thicknesses and SLDs have been assessed as the range over which the fits, shown in the figure, are acceptable. The instrumental errors (reflectivity 10^{-8}) fall well below the sample background of the measurements (minimum reflectivity 10^{-4}) and are therefore negligible. NR measurements on the ITO on glass showed it was comprised of three layers excluding the bulk glass: the first layer immediately on the bulk glass had a thickness of 280 Å and SLD of $3.3 \times 10^{-6} \text{ \AA}^{-2}$; the second layer was 84 Å thick and had a SLD of $4.3 \times 10^{-6} \text{ \AA}^{-2}$; and the bulk layer of ITO was 1490 Å thick and had a SLD of $3.9 \times 10^{-6} \text{ \AA}^{-2}$. These parameters for the ITO were fixed during the analysis of the dendrimer films.

The room temperature reflectivity profiles for films of the first-generation, second-generation, and doubly dendronized dendrimers (**1**, **2**, and **3**, respectively) are shown in Fig. 2. In each case the solid markers represent the data points and the solid lines represent the fits achieved from

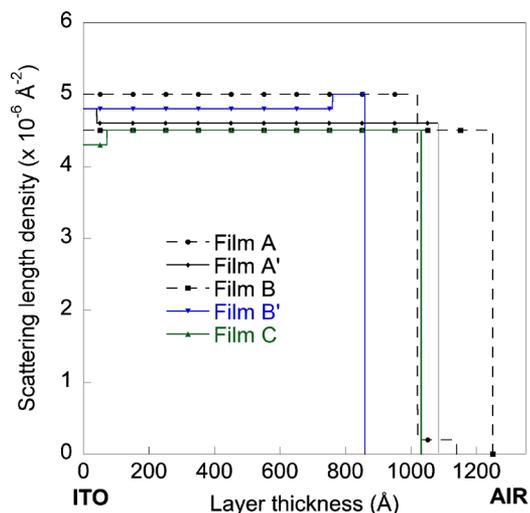


FIG. 3. (Color online) SLD vs position in the film for the five films from the ITO surface to the air interface.

modeling the film; the fitting parameters are summarized in Table I, and the SLD versus position in the film is shown pictorially in Fig. 3. When describing the dendrimer films the layer nearest the air interface is defined as layer-air and that nearest the ITO as layer-ITO. For dendrimers **1** and **2** two films (A and A' and B and B', respectively) were analyzed while a single film of the more difficult to form **3** was studied. As can be seen in Table I there were some minor differences between the SLDs of the bulk layers of the two films of dendrimer **1** (A and A'), with the average SLD for the bulk of the layer being $4.8 \times 10^{-6} \text{ \AA}^{-2}$. In addition to the slight differences between the bulk layers of films A and A', film A was found to have a thin (120 Å) layer-air of low SLD ($0.2 \times 10^{-6} \text{ \AA}^{-2}$), which was not present in the A' film. In contrast films A' had a thin (40 Å) slightly denser layer-ITO (SLD = $4.8 \times 10^{-6} \text{ \AA}^{-2}$). For the second-generation dendrimer **2** there were again very small differences between the bulk layers of the two films, which have an average SLD of the bulk layer of $4.7 \times 10^{-6} \text{ \AA}^{-2}$ (Table I). Film B could be fitted as a single layer while the best model of B' had two layers of similar SLD (layer-air: 100 Å and SLD = $5.0 \times 10^{-6} \text{ \AA}^{-2}$, and layer-ITO: 760 Å and SLD = $4.8 \times 10^{-6} \text{ \AA}^{-2}$). The differences in the parameters for the bulk layers between the two films of **1**, and also between the two films of **2** are outside the error of the fitting program implying that measurable but small structural differences can occur when films are prepared under slightly different environment conditions. Interestingly, the SLDs of the first and second-generation dendrimers are the same within error. Finally, the

TABLE I. Physical properties of the films of dendrimers **1**, **2**, and **3**. SLD is obtained from NR data analysis; MW and SL are calculated from the molecular formulas; and density and volume are derived from the SLD. D_H is obtained from GPC measurements. The errors shown are the fitting errors for a particular film.

| Dendrimer (film No.) | SLD of bulk material (10^{-6} \AA^{-2}) | MW of deuterated dendrimer (g/mol) | SL_{dend} (Å) | Density of bulk material (g/cm^3) | Volume per molecule (Å^3) | D_H of protonated dendrimer (Å) |
|----------------------|---|------------------------------------|------------------------|--|--------------------------------------|-----------------------------------|
| 1 (A) | 5.0 ± 0.1 | 2211 | 0.0145 | 1.26 ± 0.03 | 2900 ± 100 | 20.4 |
| 1 (A') | 4.6 ± 0.1 | 2211 | 0.0145 | 1.17 ± 0.03 | 3200 ± 100 | 20.4 |
| 2 (B) | 4.5 ± 0.1 | 3997 | 0.0280 | 1.07 ± 0.02 | 6200 ± 100 | 28.4 |
| 2 (B') | 4.8 ± 0.1 | 3997 | 0.0280 | 1.14 ± 0.02 | 5800 ± 100 | 28.4 |
| 3 | 4.5 ± 0.1 | 3768 | 0.0273 | 1.03 ± 0.02 | 6100 ± 100 | 25.6 |

NR profile for the film of dendrimer **3**, with the six first generation dendrons, was comprised of two layers with similar SLDs (layer-air: 960 Å and SLD= 4.5×10^{-6} Å⁻² and layer-ITO: 71 Å and SLD= 4.3×10^{-6} Å⁻²) with the SLD of the bulk layer being 4.5×10^{-6} Å⁻².

The physical density of the films (ρ_{film}) was determined using Eq. (1) as follows:

$$\rho_{\text{film}} = MW \times \text{SLD} / (0.602 \times \text{SL}_{\text{dend}}), \quad (1)$$

where MW=molecular weight of the dendrimer, SL_{dend} =scattering length of the dendrimer calculated from the molecular composition, and SLD=scattering length density of the bulk of the film determined by model fitting the NR data. The results are summarized in Table I. The films of dendrimer **1** were found to have an average density of 1.22 g/cm³, with that of dendrimers **2** and **3** being 1.11 g/cm³ and 1.03 g/cm³ respectively. Although these differences are close to the film-to-film differences between measurements (see Table I), they suggest that the density of films decreases on going from dendrimer **1** to dendrimer **2** to dendrimer **3**. The volume occupied by one dendrimer was calculated with Eq. (2) with results summarized in Table I as follows:

$$\text{Volume per dendrimer in film} = \text{SL}_{\text{dend}} / \text{SLD}. \quad (2)$$

The average volume occupied by each dendrimer in the film was 3100 Å³, 6000 Å³, and 6100 Å³ for **1**, **2**, and **3**, respectively. Assuming an error in these numbers due to film-to-film variation of $\pm 3\%$, these volumes correspond to diameters of 18.1 ± 0.2 , 22.5 ± 0.2 , and 22.6 ± 0.2 Å for **1**, **2**, and **3**. It is interesting to compare these values with the hydrodynamic diameter (D_{H}) obtained from GPC in which dendrimers **1**, **2**, and **3** were found to have D_{H} of 20.4 Å, 28.4 Å, and 25.6 Å, respectively (Table I). As would be expected from these results, in the film the second-generation dendrimer takes up more space than the singly dendronized first generation material but an important observation is that although dendrimer **2** has a larger hydrodynamic diameter than dendrimer **3** when measured in solution, in the film the volumes occupied by the dendrimers are very similar. This indicates that **3** is packing less efficiently than **2** within the film.

These physical results explain the experimental observations of the optoelectronic properties of the materials. In solution each of the protonated forms of the dendrimers have a PLQY of around 80%. However, in the solid state the PLQYs of the materials are different with the protonated forms of **1**, **2**, and **3** having PLQYs of 65%,¹⁶ 74%, and 81%¹⁶ respectively. The core of each dendrimer is emissive and hence the increase in PLQY across the series is due to the cores being less able to interact in the film. This is consistent with the average volume of each dendrimer in the film increasing from **1** to **3** in spite of **3** having the smaller hydrodynamic diameter than **2**. This is an important point as it shows that for dendrimers it is not only the size (either by generation or number of dendrons) that matters but also the distribution of the dendrons around the core. The results show that the more cone-like structure of the monodendronized materials can pack more efficiently than the more spherical doubly dendronized material. The effect of dendrimer packing in the films can also be seen to affect the hole mobilities (the cores are also responsible for charge transport). Time-of-flight experiments showed that, at the same

field (1 MV/cm), the first generation dendrimer had a hole mobility of 4.1×10^{-5} cm²/V s, which was an order of magnitude greater than that of the second generation dendrimer (6.6×10^{-6} cm²/V s).¹⁹ We find the hole mobility of the doubly dendronized material **3** to be 5×10^{-5} cm²/V s at the same field, which is similar to the first generation single dendron material, showing that molecular shape as well as molecular size influences the charge transporting properties. The high PLQY and good hole mobility explains why OLEDs with neat films of **3** perform well.⁷

We have shown that NR can give direct information about the physical structure of phosphorescent dendrimer films that explains their optoelectronic properties. The second generation and doubly dendronized dendrimers both dilute the active chromophores within the films when compared to the singly dendronized first generation material. The NR measurements also show that the shape and not just the volume of the dendrimer is important for the film morphology; second generation dendrimer **2** has a larger solution hydrodynamic diameter than the doubly dendronized dendrimer **3**, but in the solid state the cone-shaped nature of dendrimer **2** allows better packing than that seen for the film of the more spherical dendrimer **3**. Our results show that NR measurements are a powerful technique for the study of organic semiconductor thin films.

¹P. W. Wang, Y. J. Liu, C. Devadoss, P. Bharathi, and J. S. Moore, *Adv. Mater. (Weinheim, Ger.)* **8**, 237 (1996).

²M. Halim, J. N. G. Pillow, I. D. W. Samuel, and P. L. Burn, *Adv. Mater. (Weinheim, Ger.)* **11**, 371 (1999).

³P. L. Burn, S.-C. Lo, and I. D. W. Samuel, *Adv. Mater. (Weinheim, Ger.)* **19**, 1675 (2007).

⁴S.-C. Lo and P. L. Burn, *Chem. Rev. (Washington, D.C.)* **107**, 1097 (2007).

⁵S.-C. Lo, N. A. H. Male, J. P. J. Markham, S. W. Magennis, P. L. Burn, O. V. Salata, I. D. W. Samuel, and *Adv. Mater. (Weinheim, Ger.)* **14**, 975 (2002).

⁶J. P. J. Markham, S.-C. Lo, S. W. Magennis, I. D. W. Samuel, and P. L. Burn, *Appl. Phys. Lett.* **80**, 2645 (2002).

⁷S.-C. Lo, T. D. Anthopoulos, E. B. Namdas, I. D. W. Samuel, and P. L. Burn, *Adv. Mater. (Weinheim, Ger.)* **17**, 1945 (2005).

⁸G. R. Webster, W. J. Mitchell, P. L. Burn, R. K. Thomas, G. Fragneto, J. P. J. Markham, and I. D. W. Samuel, *J. Appl. Phys.* **91**, 9066 (2002).

⁹W. J. Mitchell, P. L. Burn, R. K. Thomas, and G. Fragneto, *Appl. Phys. Lett.* **82**, 2724 (2003).

¹⁰W. J. Mitchell, P. L. Burn, R. K. Thomas, G. Fragneto, J. P. J. Markham, and I. D. W. Samuel, *J. Appl. Phys.* **95**, 2391 (2004).

¹¹A. M. Higgins, P. C. Jukes, S. J. Martin, M. Geoghegan, R. A. L. Jones, and R. Cubitt, *Appl. Phys. Lett.* **81**, 4949 (2002).

¹²P. C. Jukes, S. J. Martin, A. M. Higgins, M. Geoghegan, R. A. L. Jones, S. Langridge, A. Wehrum, and S. Kirchmeyer, *Adv. Mater. (Weinheim, Ger.)* **16**, 807 (2004).

¹³A. M. Higgins, A. Cadby, D. C. Lidzey, R. M. Dalgliesh, M. Geoghegan, R. A. L. Jones, S. J. Martin, and S. Y. Heriot, *Adv. Funct. Mater.* **19**, 157 (2009).

¹⁴S.-C. Lo, E. B. Namdas, P. L. Burn, and I. D. W. Samuel, *Macromolecules* **36**, 9721 (2003).

¹⁵N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.* **241**, 89 (1995).

¹⁶J. C. Ribierre, S. G. Stevenson, I. D. W. Samuel, S. V. Staton, and P. L. Burn, *J. Disp. Technol.* **3**, 233 (2007).

¹⁷P. L. Burn, R. Beavington, M. J. Frampton, J. N. G. Pillow, M. Halim, J. M. Lupton, and I. D. W. Samuel, *Mater. Sci. Eng., B* **85**, 190 (2001).

¹⁸R. Cubitt and G. Fragneto, *Appl. Phys. A: Mater. Sci. Process.* **74**, S329 (2002).

¹⁹J. P. J. Markham, I. D. W. Samuel, S.-C. Lo, P. L. Burn, M. Weiter, and H. Bässler, *J. Appl. Phys.* **95**, 438 (2004).