

Cite this: *Chem. Commun.*, 2012, **48**, 5106–5108

www.rsc.org/chemcomm

COMMUNICATION

High-efficiency pyrene-based blue light emitting diodes: aggregation suppression using a calixarene 3D-scaffold†

Khai Leok Chan,^{*a} Jacelyn Pui Fong Lim,^a Xiaohui Yang,^b Ananth Dodabalapur,^c Ghassan E. Jabbour^{*b} and Alan Sellinger^{*d}

Received 10th February 2012, Accepted 29th March 2012

DOI: 10.1039/c2cc30995e

An efficient blue light emitting diode based on solution processable pyrene-1,3-*alt*-calix[4]arene is demonstrated, providing a record current efficiency of 10.5 cd A^{−1} in a simple non-doped OLED configuration. Complete suppression of pyrene aggregation in the solid state is achieved by controlling chromophore dispersion using the 1,3-*alt*-calix[4]arene scaffold.

Organic light emitting diodes (OLEDs) have gained enormous attention in the scientific community due to their potential applications in next-generation flat panel displays and solid-state lighting.^{1–5} The development of highly efficient, color-stable and readily processable organic emitters, especially blue, constitutes a critical component in the technology roadmap of OLEDs.^{6,7} Blue emitting dopants dispersed in host matrices have been demonstrated to provide efficient fluorescent and phosphorescent blue OLEDs, but such systems suffer from potential phase segregation and associated color stability issues when subjected to prolonged operation.⁸ The alternative system that consists of a single layer of non-doped emitter is advantageous for its reliability and simplicity in fabrication, but organic chromophores tend to take on a planar construct at the molecular level that display high tendency towards aggregation/excimer formation in a condensed state, and this can lead to a red-shift of emission and quenching of fluorescence.

Pyrene is a classical example of a conjugated aromatic chromophore that emits deep blue with high quantum efficiency in dilute solution, but aggregates in the condensed state.^{9–12} Its long fluorescence lifetime,¹³ high charge carrier mobility^{14,15} and chemical stability make it a potentially good candidate for OLED applications. Despite this, many reports have shown

progress in using the pyrene moiety as a blue emitter with moderate success.^{16–21}

We have been exploring the use of multi-functionalised 3-D hybrid cores such as octavinylsilsesquioxane and cyclic triphosphazenes as platforms from which organic chromophores, such as pyrene, can be attached to provide OLED materials.^{22–24} These inert rigid platforms serve to electronically isolate the intramolecular chromophores and disperse them in radial directions so as to minimise aggregation. Monodispersed star-shaped materials that are prepared in this way, such as pyrene-functionalised octavinylsilsesquioxane, have demonstrated high solution processability, high purity, and excellent OLED properties.²³ Calix[4]arene, a 3-D organic platform, that exists in one of four possible conformational isomers—cone, partial-cone, 1,2-alternate, and 1,3-alternate—has been extensively used as molecular scaffolds in the design of supramolecular guest–host systems and in the construction of novel molecular architectures because of its tunable and unique three-dimensional structures together with the ease of chemical functionalisations.^{25–27} However the use of calix[4]arene for light emitting applications has been limited, and only the *cone* conformer has been deployed, with chromophores substituted non-conjugatively to the bottom rim to give low efficiency OLEDs.^{28–30}

In this report, we present a novel pyrene-functionalised calix[4]arene **1** in Scheme 1 in which pyrene chromophores are attached to a 1,3-*alt*-calix[4]arene scaffold. The scaffold forces intramolecular pyrene units to be arranged radially orthogonal to each other, thus ensuring complete suppression of chromophore aggregation in the solid state. The solution-processable **1** provides a blue OLED with a current efficiency of 10.5 cd A^{−1} and a maximum external quantum efficiency (EQE) of 6.4% that exceeds the classical 5% upper limit for fluorescent-based OLEDs. We demonstrate the importance of the 1,3-*alt*-calix[4]arene scaffold in suppressing aggregation by comparing with the *cone*-calix[4]arene conformer **2** and model compound **3**. In the latter cases, significantly lower efficiencies were observed in electroluminescent devices. These observations highlight the effectiveness of 1,3-*alt*-calix[4]arene as a scaffold in dispersing and suppressing aggregation between chromophores, and in enhancing the performance of OLEDs.

The synthesis of pyrene-substituted calix[4]arene **1** follows 3 simple synthetic steps depicted in Scheme 1.^{31,32} A detailed description of the synthesis can be found in the ESI.†

^a Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 3 Research Link, Singapore 117602, Singapore.

E-mail: chankl@imre.a-star.edu.sg

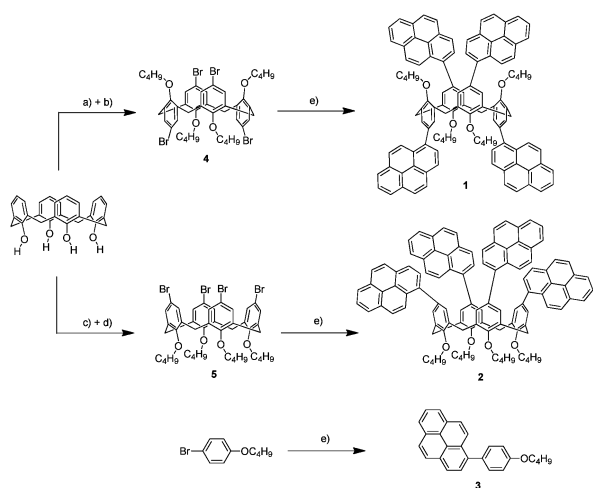
^b Solar and Alternative Energy Engineering Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia.

E-mail: ghassan.jabbour@kaust.edu.sa

^c Microelectronics Research Center, University of Texas at Austin, Austin, TX 78758, USA

^d Center for Advanced Molecular Photovoltaics (CAMP), 476 Lomita Mall, Stanford University, Stanford, CA 94305-4045, USA. E-mail: aselli@stanford.edu

† Electronic supplementary information (ESI) available: Synthetic procedures and characterisation of molecules, and OLED device data. See DOI: 10.1039/c2cc30995e



Scheme 1 Synthesis of pyrene-functionalised calix[4]arenes in the 1,3-*alternate* (**1**) and *cone* (**2**) conformations. *Reagents and conditions*: (a) *n*-butyl iodide, K_2CO_3 , acetonitrile, 80 °C then *n*-butyl iodide, Cs_2CO_3 , acetonitrile, 80 °C, 37%; (b) *N*-bromosuccinimide, acetonitrile, room temperature, 58%; (c) *n*-butyl iodide, NaH, DMF, 70 °C, 68%; (d) *N*-bromosuccinimide, 2-butanone, room temperature, 86%; (e) 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane, $\text{Pd}(\text{PPh}_3)_4$, 2 M Na_2CO_3 , toluene, 100 °C, 65% (**1**), 53% (**2**) and 90% (**3**).

Both calix[4]arenes **1** and **2** were found to exhibit high solubility in common organic solvents such as THF, chloroform and toluene, and readily purified *via* column chromatography. The conformations of the calix[4]arene cores **1** and **2** were confirmed by ^1H NMR. Two broad bands were observed in the spectrum of **2** at 3.50 and 4.15 ppm which corresponds to the bridging *exo*- and *endo*-hydrogen atoms, respectively, of the *cone*-calix[4]arene core. On the other hand, a single broad band at 3.98 ppm is observed in the spectra of **1** corresponding to the stereoscopically identical bridging hydrogens of the 1,3-*alt*-calix[4]arene core (Fig. S6 and S7, ESI†).

The photophysical properties of both calix[4]arene cores **1** and **2** were examined by UV-Vis absorption and emission (PL) spectroscopy in dilute chloroform solutions (10^{-7} M) and in thin films (Table S1, Fig. S9 and S10, ESI†). The UV-vis and PL spectra of **1** and **2** in solution and thin film state are very similar indicating that aggregation is minimized in the solid state. For example, no appreciable change in peak positions or emission band widths was detected as solution concentrations were varied over six orders of magnitude from 10^{-2} to 10^{-7} M in chloroform. In contrast, model compound **3** displayed a distinct bathochromic shift of emission of about 70 nm on going from solution to solid state (Fig. S11, ESI†). This bathochromic shift is well documented for pyrene derivatives transitioning from single molecules to calix[4]arene cores (both 1,3-*alt* and *cone*).³³

To better understand how the 1,3-*alt* calixarene scaffold suppresses aggregation, molecular modeling was carried out on pyrene-1,3-*alt*-calix[4]arene **1** (Fig. 1).³⁴ The modeling shows a pair of pyrene chromophores on each of the top and bottom rims of the calix[4]arene scaffold, and all the intramolecular chromophores directed away from the core and aligned orthogonal ($\sim 90^\circ$) to one other. This arrangement is the result of the square geometry of the calixarene

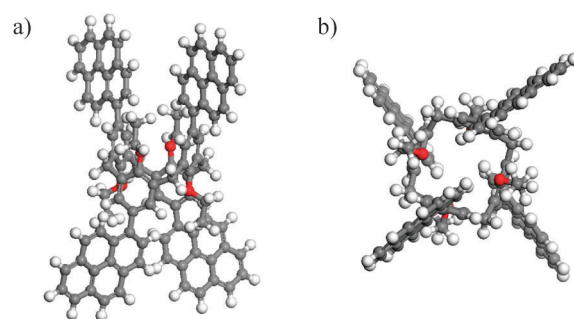


Fig. 1 The geometrically optimized 3D molecular model of compound **1** from (a) side view and (b) top view clearly showing the orthogonal and radial arrangements of the pyrene chromophores that are attached to the 1,3-*alt* calix[4]arene scaffold.

scaffold, and the 1,3-*alternate* directionality of the substitution around the scaffold. The chromophore orientation clearly prevents pyrene units from π -stacking with each other, and this therefore reduces the likelihood of intramolecular aggregate or excimer formation.

The thermal properties of pyrene-1,3-*alt*-calix[4]arene **1** were evaluated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S14 and S15, ESI†). The melting temperatures and decomposition temperatures were measured at 120 °C and 250 °C, respectively, and no glass transition was observed. Similar values (118 °C and 260 °C, respectively) were observed for pyrene-*cone*-calix[4]arene **2**. The HOMO energy levels of **1** and **2** were measured by cyclic voltammetry and found to be the same at -5.2 eV (Table S1, ESI†).

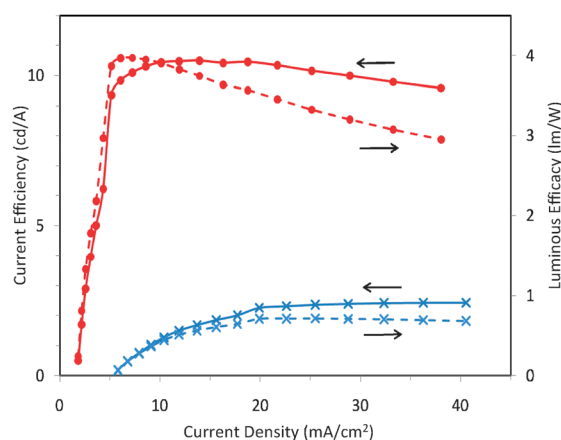
Light emitting diodes (OLEDs) with the architecture ITO/PEDOT:PSS/compound **1**, **2** or **3** (80 nm)/TPBI (30 nm)/CsF/Al were fabricated by spin-coating solutions of the pyrene-emitters in chloroform (10 mg ml^{-1}) over the PEDOT:PSS-coated ITO substrate followed by a hole blocking TPBI layer and CsF/Al cathode evaporation. Blue emission was observed in both **1** and **2**, with Commission Internationale de l'Eclairage (CIE) coordinates measured at (0.15, 0.24) and (0.17, 0.23), respectively. The EL profiles of each compound showed remarkable similarity to its PL profiles in both solution and solid state, with the emission peaks of all EL and PL spectra for each compound observed to fall within a 5 nm spectral range of one another (Fig. S12, ESI†). This indicates that the chromophore species of **1** (and **2**) are similar in the various environments and are independent of the mode of excitation.

The EL performances of the devices are summarized in Table 1. The device from pyrene-1,3-*alt*-calix[4]arene **1** shows a maximum current efficiency of 10.5 cd A^{-1} at 14 mA cm^{-2} ($\text{EQE} = 6.4\%$) and a maximum luminous efficacy of 4 lm W^{-1} at 6.1 mA cm^{-2} (Fig. 2). Moreover, the current efficiency remained a high 9.5 cd A^{-1} ($\text{EQE} = 5.8\%$) when the brightness was increased to *ca.* 5000 cd m^{-2} (11 V). The turn on voltage is 6 V. The system shows a five-fold improvement in efficiency (at 100 cd m^{-2}) over the leading solution-processed pyrene-based OLED,¹⁹ and represents among the most efficient non-doped, solution processed fluorescent blue OLED reported to date. The remarkable OLED performance of pyrene-1,3-*alt*-calix[4]arene **1** is attributed to the unique ability of the 1,3-*alt*-calix[4]arene scaffold at dispersing pyrene units that are otherwise prone to aggregation and the luminescent

Table 1 Performances of pyrene-calix[4]arenes **1** and **2** and model compound **3** in an OLED device of the structure ITO/PEDOT:PSS/Emitter/TPBI/CsF/Al

| Device | Emitter | At maximum current efficiency, η_c | | | | At maximum luminous efficacy, η_p | | | |
|--------|---|---|--------------------|-----------|-------------------------------|--|----------------------------|-----------|-------------------------|
| | | η_c^a /cd A ⁻¹ | η_{ext}^b (%) | Voltage/V | Brightness/cd m ⁻² | η_p^c /lm W ⁻¹ | J^d /mA cm ⁻² | Voltage/V | CIE ^e [x, y] |
| 1 | Pyrene-1,3- <i>alt</i> -calixarene (1) | 10.5 | 6.4 | 8.8 | 1460 | 4.0 | 6.1 | 7.8 | (0.15, 0.24) |
| 2 | Pyrene- <i>cone</i> -calixarene (2) | 2.4 | 1.5 | 11.2 | 984 | 0.71 | 20.0 | 10.0 | (0.17, 0.23) |
| 3 | Model compound (3) | No electroluminescent emission | | | | | | | |

^a Current efficiency. ^b External quantum efficiency (EQE). ^c Luminous efficacy. ^d Current density. ^e Commission Internationale de L'Eclairage (CIE) coordinates at 9 V.

**Fig. 2** The current efficiency (cd A⁻¹, solid) and luminous efficacy (lm W⁻¹, dashed) of electroluminescent devices of compound **1** (red, circle) and compound **2** (blue, cross) as a function of current density.

quenching of excited states. In comparison, the device based on pyrene-*cone*-calix[4]arene **2** was significantly less efficient; the maximum current efficiency achieved was 2.5 cd A⁻¹, that was less than 25% the efficiency of compound **1**. The clustering of all pyrene units on one face of the *cone*-calix[4]arene scaffold in compound **2** likely led to significant aggregation quenching. On the other hand, the device with model compound **3** as the emitter showed no electroluminescence. Varying the charge injection/transport layers in the device and increasing bias voltage also did not yield any emission. This clearly demonstrates the significant role played by the calix[4]arene scaffolds in suppressing chromophore aggregation.

In summary, a highly efficient solution processable blue OLED based on pyrene-1,3-*alt*-calixarene **1** has been developed, providing an excellent luminous efficiency of 10.5 cd A⁻¹ and an external quantum efficiency of 6.4% at 1460 cd m⁻². This, to our knowledge, represents the most efficient non-doped solution-processable blue fluorescent OLED reported to date. This simple strategy is synthetically straightforward to deploy, has demonstrated its utility on traditionally poor-emitting systems such as pyrenes, and may provide higher efficiencies for chromophore systems that are not inherently prone to aggregation.

Notes and references

- A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz and A. B. Holmes, *Chem. Rev.*, 2009, **109**, 897–1091.
- J. W. Park, D. C. Shin and S. H. Park, *Semicond. Sci. Technol.*, 2011, **26**, 034002.
- S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234–239.
- Y. Sun, N. C. Giebink, H. Kanno, B. Ma, M. E. Thompson and S. R. Forrest, *Nature*, 2006, **440**, 908–912.
- S. Tonzani, *Nature*, 2009, **459**, 312–314.
- A. R. Duggal, C. M. Heller, J. J. Shiang, J. Liu and L. N. Lewis, *J. Disp. Technol.*, 2007, **3**, 184–192.
- Z. Ma, S. Prashant and Z. K. Chen, *Curr. Org. Chem.*, 2010, **14**, 2034–2069.
- J. R. Gong, L. J. Wan, S. B. Lei, C. L. Bai, X. H. Zhang and S. T. Lee, *J. Chem. Phys. B*, 2005, **109**, 1675–1682.
- J. B. Birks, D. J. Dyson and I. H. Munro, *Proc. R. Soc. London, Ser. A*, 1963, **275**, 575–588.
- P. Reynnders, W. Kuhnle and K. A. Zachariasse, *J. Am. Chem. Soc.*, 1990, **112**, 3929–3939.
- K. A. Zachariasse, *Trends Photochem. Photobiol.*, 1994, **3**, 211–227.
- K. A. Zachariasse, A. Macanita and W. Kuhnle, *J. Phys. Chem. B*, 1999, **103**, 9356–9365.
- J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- N. Karl, *Synth. Met.*, 2003, **133–134**, 649–657.
- L. Zophel, D. Beckmann, V. Enkelmann, D. Chercka, R. Rieger and K. Mullen, *Chem. Commun.*, 2011, **47**, 6960–6962.
- T. M. Figueira-Duarte, P. G. Del Rosso, R. Trattnig, S. Sax, E. J. W. List and K. Mullen, *Adv. Mater.*, 2010, **22**, 990–993.
- F. Liu, W. Y. Lai, C. Tang, H. B. Wu, Q. Q. Chen, B. Peng, W. Wei, W. Huang and Y. Cao, *Macromol. Rapid Commun.*, 2008, **29**, 659–664.
- J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D. F. Huang and T. J. Chow, *Org. Lett.*, 2007, **9**, 5215–5218.
- P. Sonar, M. S. Soh, Y. H. Cheng, J. T. Henssler and A. Sellinger, *Org. Lett.*, 2010, **12**, 3292–3295.
- W. Sotoyama, H. Sato, M. Kinoshita, T. Takahashi, A. Matsuura, J. Kodama, N. Sawatari and H. Inoue, *SID Digest*, 2003, **45**, 1294–1295.
- Z. Zhao, J. H. Li, X. Chen, X. Wang, P. Lu and Y. Yang, *J. Org. Chem.*, 2009, **74**, 383–395.
- M. Y. Lo, K. Ueno, H. Tanabe and A. Sellinger, *Chem. Rec.*, 2006, **6**, 157–168.
- M. Y. Lo, C. Zhen, M. Lauters, G. E. Jabbour and A. Sellinger, *J. Am. Chem. Soc.*, 2007, **129**, 5808–5809.
- S. Sudhakar and A. Sellinger, *Macromol. Rapid Commun.*, 2006, **27**, 247–254.
- Z. Asfari, V. Bohmer, J. Harrowfield and J. Vicens, *Calixarenes 2001*, Kluwer Academic Publishers, Dordrecht, the Netherlands, 2001.
- D. M. Homden and C. Redshaw, *Chem. Rev.*, 2008, **108**, 5086–5130.
- A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713–1734.
- P. Peng, J. Zou, G. Zeng, Z. Wen and W. Zheng, *Synth. Met.*, 2009, **159**, 1944–1949.
- X. Q. Wei, G. Yang, J. B. Cheng, Z. Y. Lu and M. G. Xie, *Opt. Mater.*, 2007, **29**, 936–940.
- X. Q. Wei, G. Yang, J. B. Cheng, Z. Y. Lu and M. G. Xie, *Mater. Chem. Phys.*, 2007, **102**, 214–218.
- M. Conner, V. Janout and S. L. Regen, *J. Org. Chem.*, 1992, **57**, 3744–3746.
- W. Verboom, S. Datta, Z. Asfari, S. Harkema and D. N. Reinhoudt, *J. Org. Chem.*, 1992, **57**, 5394–5398.
- J. R. Lackowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York, 1999.
- J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244–13249.