SUPPORTING INFORMATION

High-Efficiency Pyrene-based Blue Light Emitting Diodes: Aggregation Suppression using Calixarene 3D-Scaffold

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1. General Experimental Methods

All the chemicals were purchased from Sigma-Aldrich and Strem and used without further purification. ¹H and ¹³C NMR data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to tetramethylsilane (TMS). Matrix assisted laser desorption /ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix. UV-Vis spectra were recorded on a Shimadzu model 2501-PC. Cyclic voltammetry (CV) experiments were performed using an Echochimie Autolab potentiostat (model PGSTAT30) in 0.1 M tetrabutylammonium hexafluorophosphate in dry dichloromethane at a scan rate of 100 mVs⁻¹. An Ag/AgCl in 3M KCl electrode, a platinum wire, and a platinum foil were used as the reference electrode, counter electrode, and working electrode, respectively. The compounds were measured in solution state by dissolving the compounds in the dichloromethane solution. The HOMO and LUMO energy level of the compounds were calculated from the onset oxidation and reduction potentials, respectively, using ferrocene as reference $(E_{HOMO} = 4.8 \text{ eV})$.^[1] Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument with a scan rate of 10 °C/min. Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument with a heating rate of 10°C/min.

2. Synthesis

Calix[4]arene was first di-butylated at the bottom rim via Williamson ether synthesis using K₂CO₃ as the base in the presence of butylbromide (2 equivalents), and further di-butylated using CsCO₃ to afford tetrabutoxycalix[4]arene in the 1,3-alternate conformation. Treatment of 1,3-alt tetrabutoxycalix[4]arene with excess N-bromosuccinimide provided 1,3-alt tetrabromotetrabutoxycalix[4]arene 4, which was then coupled with 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane under Suzuki-Miyaura conditions in the presence of $Pd(PPh_3)_4$ as the catalyst and K_2CO_3 as the base in a biphasic system of toluene and H_2O to provide 1 in 65% yield after purification. The cone conformer 2 was also prepared using a similar method but with the alkylation of calix[4]arene carried out in one step using NaH and an excess of butylbromide. Treatment of the resulting *cone* tetrabutoxycalix[4]arene with Nbromosuccinimide followed by coupling with 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2dioxaborolane 6 in the same Suzuki-Miyaura conditions as with the 1,3-alternate conformer afforded 2 in 53% yield after purification. The Suzuki-Miyaura coupling reactions were thin chromatography matrix-assisted monitored bv laver (TLC) and laser desorption/ionization-time-of-flight (MALDI-TOF) mass spectrometry for complete substitution of the pyrene chromophores on the calixarene cores.



Synthesis of 25,27-bis(n-butoxy)-26,28-hydroxycalix[4]arene:^[2] To a suspension of 25,26,27,28-tetrahydroxycalix[4]arene (10g, 23.5 mmol) and K₂CO₃ (9.75g, 70.6 mmol) in acetonitrile (500 ml) was added n-butyl iodide (9.53 g, 51.8 mmol) and the mixture was heated to reflux at 80 °C for 24 hours. The residue was redissolved in dichloromethane (about 200 ml) and the organic layer was washed with water (3 x 100 ml), dried over MgSO₄ and evaporated under reduced pressure. The crude product was dissolved in dichloromethane and precipitated into a swirling flask of methanol. The solid precipitate was filtered to yield the product as a white solid (9.26 g, 74%). ¹H NMR (400 MHz, CDCl₃): δ 1.11 (t, 6H), 1.83-1.74 (m, 4H), 2.09-2.01 (m, 4H), 3.37 (d, 4H), 4.01 (t, 4H), 4.34 (d, 4H), 6.66 (t, 2H), 6.76 (t, 2H), 6.91 (d, 4H), 7.05 (d, 4H), 8.25 (s, 2H) ppm.



Synthesis of 25,26,27,28-tetra(n-butoxy)-1,3-*alt*-calix[4]arene:^[2] To a suspension of 25,27bis(n-butoxy)-26,28-hydroxycalix[4]arene (3.95 g, 7.39 mmol) and Cs₂CO₃ (36.1 g, 111 mmol) in acetonitrile (240 ml) was added n-butylbromide (4.34 g, 31.7 mmol) and the mixture was heated to reflux at 80 °C for 24 hours. After cooling, the precipitate was filtered off and solution removed in vacuo. The residue was redissolved in dichloromethane (about 200 ml) and the organic layer was washed with water (3 x 100 ml), dried over MgSO₄ and evaporated under reduced pressure. The crude product was recrystallized from CHCl₃:MeOH (10:1) to yield the product as a white solid (2.44g, 51%). ¹H NMR (400 MHz, CDCl₃): δ 0.95 (t, 12H), 1.36-1.31 (m, 8H), 1.58-1.51 (m, 8H), 3.57 (t, 8H), 3.62 (s, 8H), 6.67 (t, 4H), 6.99 (d, 8H) ppm; MS (MALDI-TOF, m/z): calcd for C₄₄H₅₆O₄, 648.42; found, 648.52 [M⁺].



Synthesis of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-1,3-*alt*-calix[4]arene: 2-Butanone (40 ml) was added to 25,26,27,28-tetra(n-butoxy)-1,3-*alt*-calix[4]arene (1.28g, 1.98 mmol) and N-bromosuccinimide (2.82g, 15.8 mmol), and the mixture was stirred at room temperature for 24 hours. The solid suspension was filtered and dissolved in CHCl₃ (40 ml), and water (40ml) was added. The mixture was extracted with CHCl₃ (3 x 40 ml) and the organic layers combined, dried over MgSO₄, and concentrated under reduced pressure. The solid was washed with acetone and dried under vacuum to yield the product as off-white solids (1.10 g, 58%). ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, 12H), 1.33-1.25 (m, 8H), 1.43-1.38 (m, 8H), 3.53 (t, 8H), 3.61 (s, 8H), 7.14 (s, 8H) ppm. MS (MALDI-TOF, m/z): calcd for C₄₄H₅₂Br₄O₄, 964.06; found, 964.00 [M⁺].



Synthesis of 25,26,27,28-tetra(n-butoxy)-*cone*-calix[4]arene:^[3] To a suspension of 60% NaH in mineral oil (2.26 g, 56.5 mmol; washed with 3 x 30 ml of hexane) in anhydrous DMF (90 ml) was added tetrahydroxycalix[4]arene (3.0 g, 7.1 mmol). After the mixture was stirred for 10 min at 70 °C, 1-iodobutane (6.5 ml, 56.5 mmol) was added. The reaction mixture was stirred for an additional 1 h at 70 °C, cooled to room temperature, and then quenched by the dropwise addition of methanol (2 ml). After removal of solvent under reduced pressure, water (100 ml) was added followed by additional stirring (5 min). The solid organic product was then washed with methanol (2 x 50 ml) and recrystallized from acetone:methanol (5:1) to affording the product as pale yellow crystals (3.1 g, 68%). ¹H NMR (400 MHz, CDCl₃): δ 1.01 (t, 12H), 1.43-1.54 (m, 8H), 1.86-1.94 (m, 8H), 3.15 (d, 4H), 3.90 (t, 8H), 4.46 (d, 4H), 6.55-6.62 (t, 12H) ppm. MS (EI, m/z): calcd for C₄₄H₅₆O₄, 648.42; found, 648.3 [M⁺].



Synthesis of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-*cone*-calix[4]arene:^[3] 2-Butanone (40 ml) was added to 25,26,27,28-tetra(n-butoxy)-1,3-*alt*-calix[4]arene (2.0 g, 3.1 mmol) and N-bromosuccinimide (4.4g, 24.8 mmol), and the mixture was stirred at room temperature for 24 hours. The mixture was poured into water (40 ml), extracted with CHCl₃ (3 x 30 ml) and the organic layers combined, dried over MgSO₄, and concentrated under reduced pressure. The crude product was recrystallised in hexane:dichloromethane (5:1) to yield the product as colourless crystals (2.9 g, 86%). ¹H NMR (400 MHz, CDCl₃): δ 0.98 (t, 12H), 1.40-1.44 (m, 8H), 1.80-1.88 (m, 8H), 3.08 (d, 4H), 3.85 (t, 8H), 4.35 (d, 4H), 6.80 (t, 8H) ppm. MS (EI, m/z): calcd for C₄₄H₅₂Br₄O₄, 964.06; found, 964.5 [M⁺].



Synthesis of 5,11,17,23-tetrapyrene-25,26,27,28-tetrakis(n-butoxy)-*cone*-calix[4]arene: A mixture of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-*cone*-calix[4]arene (1.0 g, 1.04 mmol), 2-(pyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.73 g, 8.32 mmol) and Pd(PPh₃)₄ (0.092 g, 0.08 mmol) were prepared under argon atmosphere. Toluene (120ml) and 2M Na₂CO₃ (30ml) was added sequentially, and the mixture was stirred at 110 °C for 2 days. After cooling, the reaction was quenched with distilled water. The crude product was extracted with chloroform (3 x 50 ml) and the combined organic phases was dried over anhydrous MgSO₄ and evaporated under reduced pressure. Purification by column chromatography using dichloromethane:hexane (1:3) as the eluent to yielded the product as a light yellow solid (0.80 g, 53% yield). mp 120 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.15 (t, 12H), 1.70 (m, 8H), 2.05 (m, 8H), 3.48 (d, 4H), 3.92 (t, 8H), 4.45 (d, 4H), 7.99-8.25 (m, 36H), 8.53 (d, 4H), 9.07 (d, 4H) ppm. MS (MALDI-TOF, m/z): calcd for C₁₀₈H₈₈O₄, 1449.67; found, 1449.97 [M⁺].



Synthesis of 5,11,17,23-tetrapyrene-25,26,27,28-tetrakis(n-butoxy)-alt-calix[4]arene: A mixture of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-1,3-alt-calix[4]arene (1.0 g, 1.04 mmol), 2-(pyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.73 g, 8.32 mmol) and Pd(PPh₃)₄ (0.092 g, 0.08 mmol) were prepared under argon atmosphere. Toluene (120 ml) and 2M Na₂CO₃ (30 ml) was added sequentially, and the mixture was stirred at 110°C for 48 hours. After cooling, the reaction was quenched with distilled water. The crude product was extracted with chloroform (3 x 50 ml) and the combined organic phases was dried over anhydrous MgSO₄ and evaporated under reduced pressure. Purification by column chromatography using dichloromethane:hexane (1:3) as the eluent to yielded the product as a yellow solid (0.98 g, 65% yield). mp 118 °C; ¹H NMR (400 MHz, CDCl₃, δ): 0.87 (t, 12H), 1.35-1.32 (m, 8H), 2.07-2.04 (m, 8H), 3.98 (s, 8H), 4.14 (t, 8H), 7.60 (d, 8H), 8.22-7.99 (m, 20H), 8.53 (d, 8H), 9.07 (d, 8H) ppm; ¹³C NMR (100 MHz, CDCl₃, δ): 13.9, 19.3, 25.1, 33.2, 36.5, 123.5, 123.9, 124.1, 124.8, 125.2, 125.7, 126.1, 126.3, 126.5, 127.5, 127.7, 128.1, 128.5, 129.5, 130.8, 132.9, 133.5, 134.4, 137.5, 156.7; MS (MALDI-TOF, m/z): calcd for C₁₀₈H₈₈O₄, 1449.67; found, 1449.54 [M⁺]; Anal. calcd for C₁₀₈H₈₈O₄: C 89.47, H 6.12; found: C 89.88, H 6.43.



Synthesis of 1-(4-butoxyphenyl)pyrene: A mixture of 1-bromo-4-butoxybenzene (1.0g, 4.36 mmol), 2-(pyren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.57 g, 4.80 mmol) and Pd(PPh₃)₄ (0.046 g, 0.04 mmol) were prepared under argon atmosphere. Toluene (100ml) and 2M Na₂CO₃ (30ml) was added sequentially, and the mixture was stirred at 110 °C for 1 days. After cooling, the reaction was quenched with distilled water. The crude product was extracted with chloroform (3 x 50 ml) and the combined organic phases was dried over anhydrous MgSO₄ and evaporated under reduced pressure. Purification by column chromatography using dichloromethane:hexane (1:5) as the eluent to yielded the product as a light yellow solid (1.38 g, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.03 (t, 3H), 1.60 (m, 2H), 1.86 (m, 2H), 4.09 (d, 2H), 7.09 (d, 2H), 7.55 (d, 2H), 7.96-8.21 (m, 9H) ppm.

. .	PL λ _{max}		UV-vis [a]					
Emitter	Solution [eV]	Thin film	λ_{max} [nm]	Bandgap [b] [eV]	[eV]	LUMO [d] [eV]	T _g [e] [°C]	$T_d [f]$ [°C]
Pyrene-1,3- <i>alt</i> calixarene (1)	474	476	364	3.06	-5.74	-2.68	Not observed	250
Pyrene- <i>cone</i> calixarene (2)	473	475	357	3.13	-5.71	-2.58	Not observed	242

Table S1 Photophysical and thermal properties of calixarene-based emitters.

[a] Measured in thin film. [b] Measured from absorption onset of thin film UV-Vis spectrum. [c] Measured using photoelectron spectroscopy in air (PESA). [d] Calculated from $E_{LUMO} = E_{HOMO} + bandgap$. [e] Measured using DSC (20 °C min⁻¹ ramp rate). [f] Obtained from TGA measurement (temperature at 5% mass loss under nitrogen, 10 °C min⁻¹ ramp rate).

3. ¹H NMR spectra



Fig. S1. ¹H NMR spectrum of 25,27-bis(n-butoxy)-26,28-hydroxycalix[4]arene.



Fig. S2. ¹H NMR spectrum of 25,26,27,28-tetra(n-butoxy)-1,3-alt-calix[4]arene.



Fig. S3. ¹H NMR spectrum of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-1,3-alt-calix[4]arene.



Fig. S4. ¹H NMR spectrum of 25,26,27,28-tetra(n-butoxy)-*cone*-calix[4]arene.



Fig. S5. ¹H NMR spectrum of 5,11,17,23-tetrabromo-25,26,27,28-tetrakis(n-butoxy)-*cone*-calix[4]arene.



Fig. S6. ¹H NMR spectrum of 5,11,17,23-tetrapyrene-25,26,27,28-tetrakis(n-butoxy)-*cone*-calix[4]arene (2).



Fig. S7. 1H NMR spectrum of 5,11,17,23-tetrapyrene-25,26,27,28-tetrakis(n-butoxy)-*alt*-calix[4]arene (1).

4. Additional Figures



Fig. S8. Matrix-assisted laser desorption/ionization–time-of-flight (MALDI-TOF) spectrum for pyrene-*1,3-alt*-calix[4]arene **1**. Inset is an expanded view of the same spectrum showing the isotopic distribution of compound **1**.



Fig. S9. UV-vis absorption of pyrene-1,3-alt-calix[4]arene 1 in chloroform solution and in thin film. Also shown are photoluminescence emission spectra of 1 in solid state and in chloroform at different concentrations ranging from 10^{-2} to 10^{-7} M (excitation at 350 nm). No spectral shift was observed across all concentrations, and the absence of excimer band at higher concentrations and in solid state indicated that no ground state aggregation was taking place in 1.



Fig. S10. Photoluminescence emission spectra of pyrene-*1,3-cone*-calix[4]arene 2 in solid state and in chloroform at concentrations ranging from 10^{-2} to 10^{-6} M (excitation at 350 nm). No spectral shift was observed across all concentrations, and the absence of excimer band at higher concentrations and in solid state indicated that no ground state aggregation was taking place in 2.



Fig. S11. Photoluminescence spectra of model compound **3** in solid state and in chloroform at concentrations ranging from 10^{-2} to 10^{-7} M (excitation at 350 nm). Distinct bathochromic shift can be observed as concentration is increased. This indicates a transition from monomeric emission to excimer emission.

Fig. S12. Electroluminescence spectra of compounds 1 and 2 based on an organic light emitting device of the structure ITO/PEDOT:PSS/compound 1 or 2/TPBI/CsF/Al, obtained at a bias of 9 V (16.3 mA cm⁻² and 10.4 mA cm⁻² for compound 1 and compound 2, respectively) The emitting compounds were annealed at 80 °C for 30 minutes prior to deposition of TPBI and cathode.

Fig. S13. Current density (mA cm⁻² (log scale filled circles and squares)) and brightness (cd m², unfilled circles and squares) of electroluminescent devices of 1,3-alternating **1** (filled circles and squares) and cone **2** (unfilled circles and squares) as a function of voltage (V).

Fig. S14. Thermogravimetric analysis (TGA) spectrum of compounds 1 and 2 measured under nitrogen atmosphere at a ramp rate of $10 \,^{\circ}\text{C min}^{-1}$.

Fig. S15. Differential scanning calorimetry (DSC) spectrum of compounds **1** and **2** measured at a heating/cooling rate of 20 °C min⁻¹.

Reference List

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