

Phenylene Ethynylene Pentamers for Organic Electroluminescence

S. Anderson*^[a]

Abstract: An isomeric family of eighteen triisopropylsilyl-capped phenylene ethynylene pentamers (molecular formula $C_{60}H_{62}Si_2$) has been prepared by using fast parallel synthesis, for organic electroluminescence. Each pentamer was grown on a polymer support of propylaminomethylated polystyrene by using a series of palladium-catalysed reactions between aryl iodides and alkynes. "Tea bag" technology was used to carry out several different reactions simultaneously in the same flask. Here I present the syntheses of the materials, compare their photoluminescence both in solution and in the solid state (amorphous thin films) and describe the incorporation of the most promising pentamer into organic electroluminescence devices.

Keywords: combinatorial chemistry • luminescence • oligomers • organic electroluminescence • phenylene ethynylenes

Introduction

In less than a decade combinatorial chemistry has transformed drug discovery from a painstaking process of preparing compounds one at a time, to an industry where thousands of new compounds are created and screened simultaneously in a few hours.^[1] My goal is to use fast parallel synthesis,^[1b] a type of combinatorial chemistry, to discover new materials^[2] for organic electroluminescence (OEL).^[3] OEL is an emerging technology that allows the manufacture of efficient, low-voltage multicolour displays.^[4] An OEL display consists of thin films of organic materials sandwiched between electrodes. When an electric field is applied, holes are injected from the anode and electrons from the cathode. The holes and electrons combine to form excited states which then decay back to the ground state with the emission of light. Modifying the structure of the material may subtly control the colour of the emitted light. The luminescence characteristics of a molecule are important, but the success of a material for OEL also depends on its ability to form stable amorphous thin films, to transport charge, and to have suitable HOMO and LUMO energies for charge injection. By using fast parallel synthesis I hope to reduce the time needed to prepare a family of materials with related structures, so that the emission characteristics, and film-forming and transport properties of a material may be speedily optimised.

This fast parallel synthesis method relies on the use of polystyrene as a polymer support in synthesis.^[5] The polystyrene is functionalised so that molecules may be grown from

its surface and so that it swells when mixed with organic solvents allowing reagents to easily access the reactive sites. Excess reagents may be added to the polymer support to force reactions to go to completion, and workup is facilitated because isolation of the product bound to the polymer support may be carried out by filtration, followed by thorough washing to remove excess reagents. "Tea bag" technology is also used to allow several reactions to be carried out in the same reaction vessel simultaneously.^[6] In this method the polymer support is confined within a polyester bag; this is the "tea bag". The "tea bag" allows reagents to enter, but prevents polymer supports with different appended intermediates in different "tea bags" from mixing. Hence a chemical transformation may be carried out on various polymer supports in the same reaction vessel provided these polyester bags segregate them. Purification by chromatography is required only after the removal of the material from the polymer support, at the end of the synthesis. The synthetic strategy described in this paper uses polymer support and "tea bag" technology to greatly reduce the time and effort taken to purify intermediates.

I chose to explore a library of phenylene ethynylene oligomers to test the use of fast parallel synthesis in the search for new materials for OEL, for the following reasons:

- 1) This class of materials was already known to have promising properties for OEL. There are several literature reports on the photophysical properties of poly(2,5-dialkyl-*para*-phenylene ethynylene)s (PPEs) and several groups have successfully incorporated PPEs into OEL devices.^[7]
- 2) The synthesis of similar systems has been carried out on polymer supports^[8] and in solution,^[9] providing a wealth of synthetic methodology.

[a] Dr. S. Anderson

Sharp Laboratories of Europe Ltd
Oxford Science Park, Oxford, OX4 4GB (UK)
Fax: (+44)-1865-774436
E-mail: sally.anderson@sharp.co.uk

3) A series of different molecular geometries may be generated by incorporating *ortho*, *meta* and *para* links into the phenylene ethynylene chains. This will lead to materials with different conjugation lengths and shapes, so that one can assess the influence of these factors on the OEL characteristics of the materials. Conjugation length influences the charge transport properties of a material and the colour of emission, whereas molecular shape may determine OEL device performance in several ways: It influences how molecules interact with each other in the solid state, and, hence, the ability of a material to form thin films that transport charge efficiently and remain stable during device operation. It also influences whether emission occurs from an excited state localised on a single molecule or on a molecular aggregate.

In this paper I describe the preparation of an isomeric family of 18 triisopropylsilyl-capped phenylene ethynylene pentamers by using fast parallel synthesis. All the pentamers have the molecular formula $C_{60}H_{62}Si_2$, but have different shapes depending on whether the phenylene ethynylene chain contains *ortho*, *meta* or *para* links. Here I present the syntheses of the materials, compare their photoluminescence in solution and in the solid state (amorphous thin films) and describe some preliminary OEL device results.

Results and Discussion

Synthesis: The general structure of the phenylene ethynylene pentamers is shown in Figure 1. The three central phenyl units may be systematically varied to be *ortho*, *meta* or *para* substituted, leading to the 18 pentamers (**1–18**) illustrated. The pentamers were grown on a polymer support of alkynylphenyl-substituted propylaminomethylated polystyrene **22** by using a series of palladium-catalysed coupling reactions between alkynes attached to the polymer supports and aryl iodide building blocks in solution.^[10] The polymer support chemistry follows the methods of J. S. Moore et al.^[8a] and the preparation of pentamer **1** is outlined in Scheme 1. The syntheses of the three isomeric aryl iodide building blocks **29a–c**^[11] are outlined in Scheme 2. The common precursor **21** was prepared by the addition of diazonium salt **28a**^[12] to propylaminomethylated polystyrene **20**. The TMS group was then removed with tetrabutyl ammonium fluoride in tetrahydrofuran to generate the free alkyne **22**, which is the polymer support from which all the pentamers are grown. At this point a parallel synthetic method was used to generate the 18 pentamers as efficiently as possible. Eighteen “tea bags” were prepared each containing 1 g of substituted polystyrene **22**. Fine-mesh polyester “tea bags” allow reagents and building blocks to access the polymer support, but prevent cross contamination of polymer supports. Hence a common building block may be added to various polymer supports in

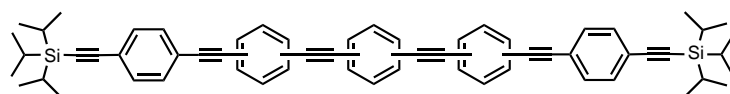


Figure 1. Generalised phenylene ethynylene pentamer.

the same reaction vessel. Each of the 18 bags was carefully labelled, so that the reaction histories could be easily identified, then three reaction flasks were set up:

- Flask 1: Building block **29a** was added to bags 1, 2 and 3.
- Flask 2: Building block **29b** was added to bags 4, 5, 6, 7, 8 and 9.
- Flask 3: Building block **29c** was added to bags 10, 11, 12, 13, 14, 15, 16, 17 and 18.

After 12 hours at 65 °C a sample of the polymer support was tested for free alkyne groups by placing a small amount of the polymer support (swollen with carbon tetrachloride) between two NaCl plates and recording the IR spectrum. Coupling was complete when no C–H alkyne stretch was observed. All 18 “tea bags” were then processed together; careful washing of the resin was required to remove traces of Pd catalyst. The trimethylsilyl groups were removed by treating all 18 bags with tetrabutyl ammonium fluoride (TBAF) in THF.

In the second round of coupling:

- Flask 1: Building block **29a** was added to bags 1, 4, 5, 10, 11 and 12.
- Flask 2: Building block **29b** was added to bags 2, 6, 7, 13, 14 and 15.
- Flask 3: Building block **29c** was added to bags 3, 8, 9, 16, 17 and 18.

Once again the bags were combined for workup and removal of the trimethylsilyl groups.

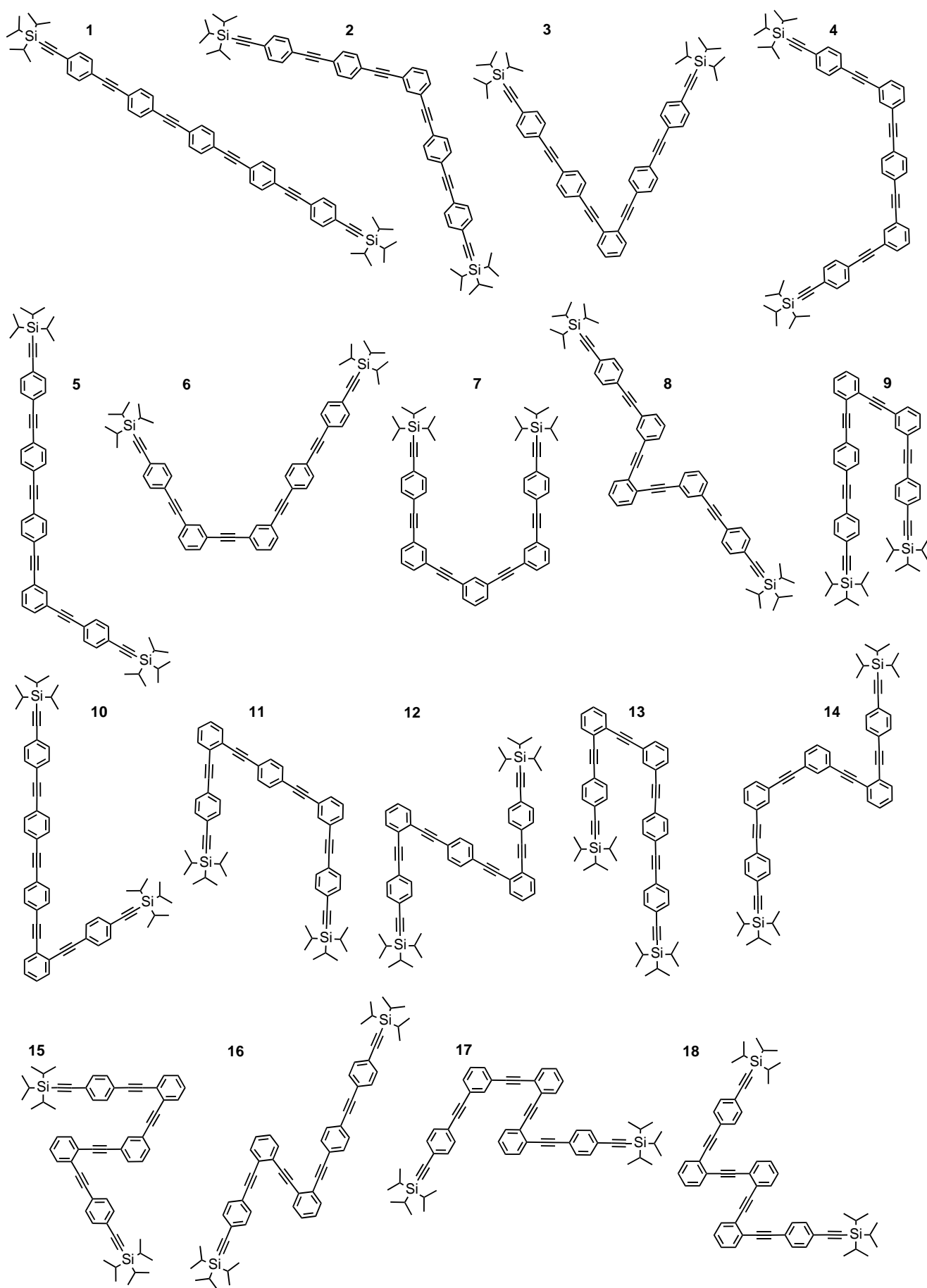
In the third round of coupling:

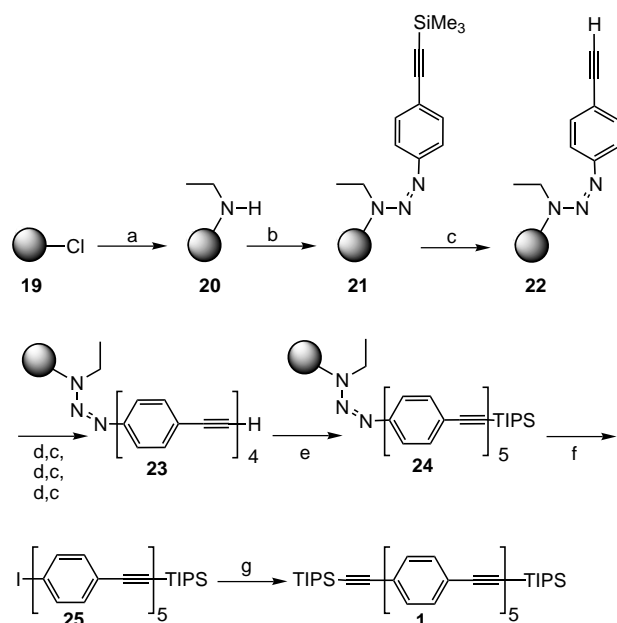
- Flask 1: Building block **29a** was added to bags 1, 2, 3, 5, 6, 9, 10, 13 and 16.
- Flask 2: Building block **29b** was added to bags 4, 7, 8, 11, 14 and 17.
- Flask 3: Building block **29c** was added to bags 12, 15 and 18.

Once again the “tea bags” were combined for workup and removal of the trimethylsilyl groups.

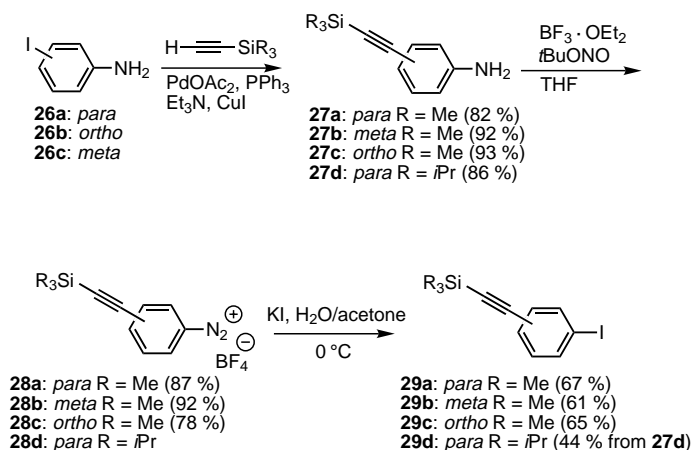
In the final coupling step aryl iodide **29d**, prepared as outlined in Scheme 2, was added to all eighteen bags in one reaction flask. The tedious part of the pentamer preparation came next: Polymer support from each bag had to be treated individually with methyl iodide to release the phenylene ethynylenes from the polymer supports, and then the resulting aryl iodides were treated with triisopropylsilylacteylene to yield the 18 pentamers. It was only at this final stage that the pentamers were purified by flash column chromatography and recrystallisation. This strategy allowed the 18 pentamers to be generated more quickly than would have been possible by using traditional solution phase methods. The pentamer sequences and yields are summarised in Table 1, for example, pentamer **1** contains the sequence **29a,29a,29a**, and was prepared in 42% overall yield. The yields for pentamer formation were calculated by comparing the theoretical yields calculated from the initial loading of the polymer support, determined by combustion analysis, with the mass of pen-

tamers isolated. Polymer supports **20** and **21** were found to contain 1.2×10^{-3} and 2.3×10^{-3} equivalents of nitrogen per gram of polymer support respectively. From these loadings





Scheme 1. Preparation of pentamer **1**. a) *n*-propylamine, 70 °C, 3 days; b) **11a**, K₂CO₃, DMF; c) Tetrabutylammonium fluoride, THF, RT, 5 min; d) **12a**, [Pd₂(dba)₃], CuI, PPh₃, Et₃N 70 °C, 12 h; e) **12d**, [Pd₂(dba)₃], CuI, PPh₃, Et₃N 70 °C, 12 h; f) MeI, 110 °C; g) triisopropylsilylacetylene, [Pd₂(dba)₃], CuI, PPh₃, Et₃N 70 °C, 12 h.



Scheme 2. Preparation of the trialkylsilicon-protected iodoalkynylphenyl building blocks **29a**, **29b**, **29c** and **29d** (yields are shown in brackets).

it was possible to calculate that polymer support **21** has 5.5×10^{-4} equivalents of triazene per gram of polymer support. Yields for pentamer formation were therefore calculated with this loading. The pentamers were characterised by ¹H and ¹³C NMR spectroscopy, mass spectrometry and elemental analysis. There was no evidence for the presence of any other oligomers, and the ¹³C NMR spectra clearly indicated the different symmetries of the systems; the oligomerisation process seems to be very efficient. As Moore reports^[8a] it seems that the yields of pentamers reflect the efficiency of the final methyl iodide liberation step, rather than the efficiency of the repeated palladium-catalysed coupling reactions, since the latter would reduce the purity of the pentamers. The isolated yields of the final products do not seem to reflect the efficiency of the coupling reaction, no shorter chains are

Table 1. Sequence information for pentamers **1–18**.

Bag no./ Pentamer no.	Round 1	Round 2	Round 3	Yield ([mg]) [%]
1	29a	29a	29a	(190) 42
2	29a	29b	29a	(150) 33
3	29a	29c	29a	(70) 16
4	29b	29a	29b	(210) 47
5	29b	29a	29a	(140) 31
6	29b	29b	29a	(180) 40
7	29b	29b	29b	(170) 38
8	29b	29c	29b	(100) 22
9	29b	29c	29a	(180) 40
10	29c	29a	29a	(160) 36
11	29c	29a	29b	(150) 33
12	29c	29a	29c	(170) 38
13	29c	29b	29a	(210) 47
14	29c	29b	29b	(160) 36
15	29c	29b	29c	(120) 27
16	29c	29c	29a	(130) 29
17	29c	29c	29b	(130) 29
18	29c	29c	29c	(70) 16

isolated and no terminal alkynes are detected after coupling. It is significant that the pentamers are readily isolated from the reaction mixtures by flash column chromatography and recrystallisation as pure compounds.

Photoluminescence measurements: The emission and absorption characteristics of the pentamers in dichloromethane are compared in Table 2. The solution quantum efficiencies for photoluminescence were found to vary from 0.75 to 0.3: pentamer **3** being the most emissive and pentamer **18** the least emissive. The pentamers with longer conjugation lengths showed red-shifted absorption and emission characteristics. Pentamer **1** had the longest wavelength absorption and emission as it has five conjugated *para* links in the chain, whereas pentamers **7** and **8** have the shortest wavelength absorption and emission characteristics, since they only have a diphenyl ethyne moiety before a *meta* link breaks the conjugation. Sublimation of the pentamers to form thin films proved difficult. A 20 nm thick film of pentamer **1** was prepared by sublimation at 300 °C and at 2×10^{-7} mbar over several hours. Differential scanning calorimetry (DSC) analysis of the pentamers showed that irreversible polymerisation occurs at temperatures above 300 °C. Pentamers with *ortho* links were the least stable, since they readily undergo intramolecular Bergman cyclisation.^[13] I was unable to prepare sublimed thin films of the other pentamers, so thin films of pentamers **2** to **18** on fused silica were prepared by spin-coating from toluene. Pentamer **1** is too insoluble in toluene, and too crystalline, to form good films, but the other pentamers seemed to form good amorphous films that did not recrystallise within one month of film deposition. The emission spectra of the thin films were broader and red-shifted relative to those measured in solution; pentamer **5** showed the largest red shift (52 nm). Presumably this material aggregates more strongly in the solid state. The absorption and emission characteristics of pentamer **3** in the solid state (amorphous thin film) and in solution are compared in Figure 2.

Table 2. Absorption and emission characteristics of pentamers 1–18.

	$\lambda_{\text{max(abs)}} (\log \epsilon)$ CH ₂ Cl ₂	$\lambda_{\text{max(em)}} (\phi)$ CH ₂ Cl ₂	$\lambda_{\text{max(abs)}}$ solid state	$\lambda_{\text{max(em)}}$ solid state
1	356 (5.15)	397, 418 (0.7)	370 ^[a]	420, 470, 485 ^[a]
2	335 (4.70), 343 (4.70), 359 (5.08)	367, 384, 399 (0.7)	338, 365	422, 446, 467
3	328 (5.11)	389, 410, 424 (0.75)	325, 373	420, 466
4	308 (5.13), 328 (5.19), 346 (4.76)	354, 371, 382, 401 (0.7)	311, 332	408, 425, 468
5	329 (5.05), 350 (5.03)	384, 404, 418 (0.65)	334, 382	436, 468
6	307 (5.05), 328 (5.10), 343 (4.87), 358 (4.75)	366, 383, 397 (0.65)	295, 310, 331, 363	418, 432, 467
7	297 (4.86), 281 (5.07), 287 (5.13), 307 (5.18), 327 (5.04)	333, 349, 357, 378 (0.65)	292, 310, 331	400, 471
8	281 (5.10), 307 (5.10), 328 (5.04)	350, 363, 377 (0.45)	289, 310, 332	397, 472
9	308 (5.08), 327 (4.97), 345 (4.75)	379, 399 (0.7)	296, 311, 331, 375	408, 468
10	328 (4.96), 344 (4.93)	392, 413 (0.7)	277, 303, 332	445, 471
11	309 (5.13), 328 (4.97)	377, 395 (0.5)	312, 332	428, 468
12	298 (5.09)	386, 407 (0.5)	303	427, 470
13	290 (4.95), 331 (4.99)	386, 407 (0.75)	294, 331	429, 468
14	290 (5.15), 307 (5.04), 327 (5.94)	360, 377 (0.5)	292, 310, 332	402, 469
15	289 (5.18), 326 (4.79), 338 (4.72), 351 (4.52)	360, 379 (0.5)	292, 332	404, 423, 468
16	297 (4.91), 333 (4.87)	382, 402 (0.65)	301, 334	428, 449, 469
17	280 (5.04), 307 (5.00), 328 (4.92)	371, 384, 400 (0.45)	283, 310, 331	402, 424, 469
18	279 (5.00), 296 (4.88), 318 (4.78)	378, 398 (0.3)	282, 326	482

[a] Pentamer film sublimed.

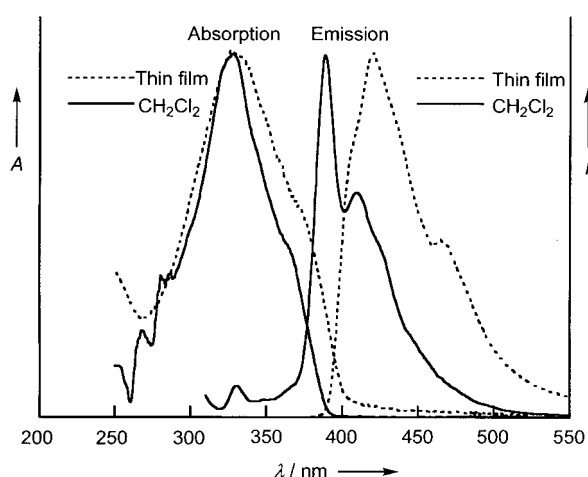


Figure 2. Normalised absorption and emission spectra of pentamer 3.

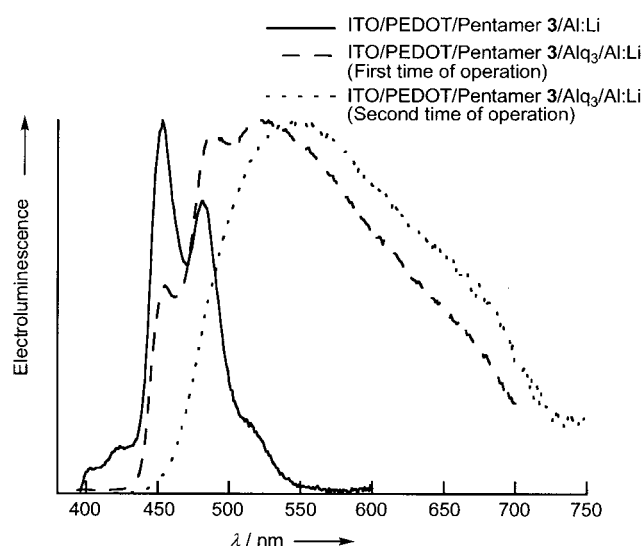


Figure 3. Normalised electroluminescence spectra from devices containing pentamer 3.

Electroluminescence: Pentamer 3 was found to be the most emissive material in solution (dichloromethane) and so was my first choice for incorporation into three simple test light emitting diodes (LEDs) to assess the suitability of these pentamers for OEL. A single-layer LED was prepared by spin-coating a 150 nm thick film of pentamer 3 onto indium tin oxide (ITO) glass ($20 \Omega \text{ square}^{-1}$), aluminium and lithium were then evaporated to form the cathode. Very faint blue electroluminescence was observed at voltages of greater than 20 V, but device performance seemed to be limited by a poor match between the electrode work functions and the HOMO and LUMO levels of pentamer 3. To improve hole injection a 50 nm thick film of PEDOT·PSS^[14] was spin-coated onto the ITO before deposition of pentamer 3. Device performance was improved significantly, a peak value of 5 cdm^{-2} was observed at 16 V. The EL spectrum of this device is shown in Figure 3, and the current-voltage-luminance characteristics are shown in Figure 4. The electroluminescence is red-shifted relative to the photoluminescence, presumably the emission observed originates from an aggregate of pentamer 3 or a

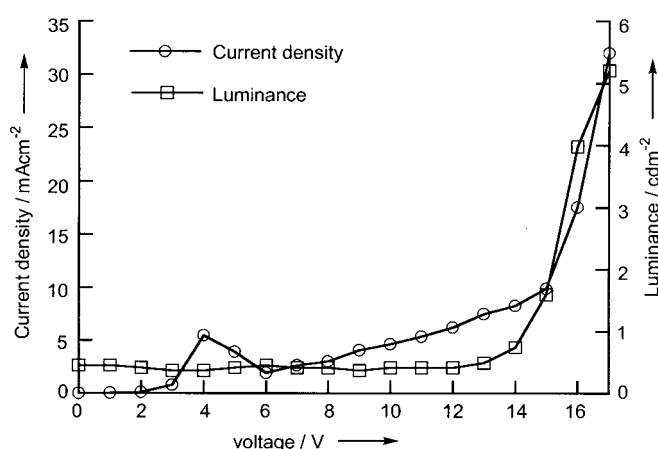


Figure 4. Voltage/current density/luminance characteristics for the two-layer device ITO/PEDOT·PSS (50 nm)/pentamer 3 (150 nm)/Al:Li.

species generated by pentamer **3** interacting with the cathode. To improve electron injection into the ITO/PEDOT/pentamer **3**/Al:Li device, a film of aluminium tris-8-hydroxyquinoline (Alq_3) (30 nm) was evaporated on top of pentamer **3**. Electron injection seemed to be improved but emission was observed from the pentamer **3**/ Alq_3 interface, so appeared blue-green in colour and became greener during device operation; therefore, some diffusion of the organic layers must take place. The current-density/voltage/luminance characteristics of this device are shown in Figure 5. Solid lines represent the characteristics for a previously untested device, when the emission is blue-green, and dashed lines the characteristics of a previously tested device when the emission had become green. The EL spectra for this device, initial run and then subsequent runs, are illustrated in Figure 3. Further device optimisation was not carried out.

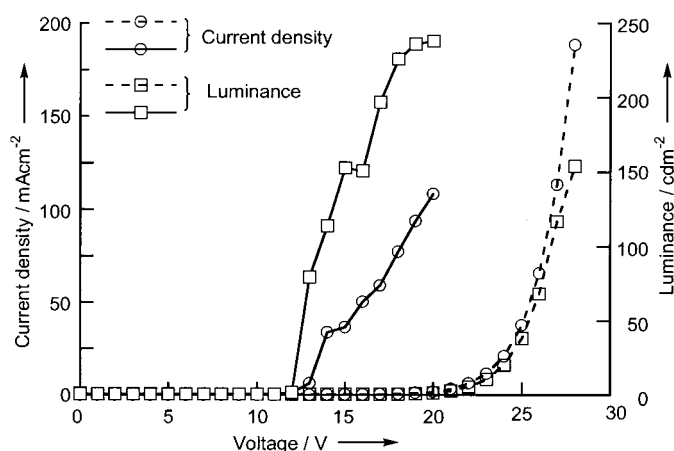


Figure 5. Voltage/current density/luminance characteristics for the three-layer device ITO/PEDOT:PSS (50 nm)/pentamer **3** (150 nm)/ Alq_3 (30 nm)/Al:Li, on first turning on the device (solid line), and on running the device a second time (dashed line).

Conclusion

A library of 18 triisopropylsilyl-capped phenylene ethynylene pentamers has been prepared by using fast parallel synthesis. All 18 pentamers have the same molecular formula but different geometries depending on whether the phenylene ethynylene links are *ortho*, *meta*, or *para*. The pentamer chains were grown on propylaminomethylated polystyrene by using “tea bag” technology, which greatly reduced the time required for the synthesis compared with using conventional solution phase techniques. The photophysical properties of the pentamers were measured in solution and then in thin films. The pentamers were found to form good quality thin films when spin-coated from toluene, and these films showed blue photoluminescence. Pentamer **3** was found to have the highest quantum efficiency in solution and, therefore, was incorporated into simple OEL devices; blue electroluminescence was observed from pentamer **3**. Three different device structures were prepared and tested, the best device performance was observed for the following device structure, ITO/PEDOT:PSS/pentamer **3**/ Alq_3 /Al:Li; unfortunately recombination

occurs at the pentamer **3**/ Alq_3 interface so the emission appears green. Pentamer **3** shows promising OEL, but further device optimisation to move the recombination zone into the pentamer **3** layer needs to be carried out.

Fast parallel synthesis facilitated the preparation of a family of phenylene ethynylene pentamers; however, to improve the process of searching for new materials for OEL, the screening of these materials needs to be accelerated. One needs to move away from one-by-one device preparation towards the manufacture of arrays of devices with varied device architectures.^[15]

Experimental Section

Unless otherwise stated the starting materials were purchased commercially and used without further purification. Flash column chromatography was performed with Merck silica gel 60 μm (230–400 mesh). Merrifield’s polymer support, chloromethyl polystyrene, 1% crosslinked with divinylbenzene (1.0–1.5 mequiv of chlorine per gram of polymer support, 200–400 mesh) was purchased from Aldrich. Dry triethylamine was obtained by distillation from calcium hydride under nitrogen. Mass spectrometry was carried out at the University of Southampton. Elemental analyses were carried out at The Inorganic Chemistry Laboratory, Oxford University. Infrared spectra were recorded on a Nicolet FTIR spectrometer. Infrared analysis of the polymer support was carried out by placing approximately 1 mg of the polymer support between two NaCl plates, swelling the polymer support by adding a drop of carbon tetrachloride and immediately recording an FTIR spectrum. ^1H NMR spectra in deuteriochloroform were recorded on a Bruker DPX300. Overlapping signals in ^{13}C NMR spectra (determined by integration comparison of similar environments) are denoted with an asterisk.

Preparation of building blocks **29a**, **29b** and **29c**

Compound 27a:^[11] 4-Iodoaniline (**26a**; 10 g, 4.57×10^{-2} mol), palladium(II) acetate (205 mg, 9.1×10^{-4} mol), copper(I) iodide (87 mg, 4.6×10^{-4} mol), and triphenylphosphine (480 mg, 1.8×10^{-3} mol) were dissolved in triethylamine (100 mL, freshly distilled ex. CaH_2), and the mixture degassed using two freeze-thaw-saturate-with-nitrogen cycles. Trimethylsilylacetylene (4.9 g, 7.1 mL, 5.0×10^{-2} mol) was then added by syringe, and the mixture carefully degassed by boiling briefly under reduced pressure and then flushing with nitrogen (trimethylsilylacetylene is rather volatile). After stirring at room temperature overnight hexanes was added, and the triethylaminehydrogen iodide removed by filtration through Celite. The filtrate was evaporated and then purified by chromatography on silica eluting with 1:1 dichloromethane/hexanes. Recrystallisation from hexanes (hot to cold) yielded **27a** as a pale brown solid (7.1 g, 82%). ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.27$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 6.57 (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 3.79 (s, 2H), 0.23 (s, 9H).

Compound 27b:^[11] See preparation of **27a** for experimental details. Yield: 8.0 g, 92% of a pale brown solid; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.08$ (t, $^3J(\text{H,H}) = 8$ Hz, 1H), 6.87 (dt, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 6.79 (t, $^4J(\text{H,H}) = 1$ Hz, 1H), 6.63 (ddd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 3.65 (s, 2H), 0.23 (s, 9H).

Compound 27c:^[11] See preparation of **27a** for experimental details. Yield: 8.1 g, 93%; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.29$ (dd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 7.08–7.14 (m, 1H), 6.60–6.70 (m, 2H), 4.23 (s, 2H), 0.26 (s, 9H).

Compound 27d: See preparation of **27a** for experimental details. Yield: 10.21 g, 86% of a pale yellow oil; ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.29$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 6.58 (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 3.78 (s, 2H), 1.12 (s, 21H).

Compound 28a:^[12] Boron trifluoride etherate (37.6 mL, 0.297 mol) was added to a chilled (ice/acetone bath (–20 °C)) three-necked round-bottomed flask fitted with a pressure equalising dropping funnel and a nitrogen inlet. When the solution had equilibrated to –20 °C compound **27a** (14 g, 7.39×10^{-2} mol) dissolved in THF (200 mL) was added dropwise over 5 mins. *tert*-Butyl nitrite (34.4 mL) in THF (100 mL, dry and nitrogen

saturated) was then added dropwise to the chilled mixture over 30 mins. The mixture was left at -20°C for a further 10 min before allowing the mixture to warm up to 5°C over 20 min in an ice/water bath. Diethyl ether (400 mL) was added to this mixture, and chilling this solution in an ice bath for 15 min yielded a cream crystalline solid, which was collected by filtration and washed with a minimum volume of cold diethyl ether. Yield of **28a** after drying in vacuo: 18.5 g, 87%; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 8.80$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 8.05 (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 0.28 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, $[\text{D}_6]\text{acetone}$, 25°C , TMS): $\delta = 136.00, 134.57, 133.57, 114.73, 107.69, 102.23, -0.70$.

Compound 28b: See preparation of **28a** for experimental details. Yield: 8.7 g, 92% of a white crystalline solid; $^1\text{H NMR}$ (300 MHz, $[\text{D}_6]\text{acetone}$, 25°C , TMS): $\delta = 8.87$ (t, $^4J(\text{H,H}) = 2$ Hz, 1H), 8.82 (dt, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 8.34 (dt, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 8.06 (t, $^4J(\text{H,H}) = 1$ Hz, 1H), 0.24 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, $[\text{D}_6]\text{acetone}$, 25°C , TMS): $\delta = 144.09, 135.23, 132.87, 132.48, 126.49, 117.22, 100.64, 100.17, -0.96$.

Compound 28c: See preparation of **28a** for experimental details. Yield: 8.3 g, 78% of a white crystalline solid; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 8.88$ (dd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 8.06–8.12 (m, 1H), 7.78–7.88 (m, 2H), 0.34 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, $[\text{D}_6]\text{acetone}$, 25°C , TMS): $\delta = 141.93, 134.67, 133.85, 131.96, 127.51, 117.69, 112.48, 95.41, -0.47$.

Compound 29a:^[16] Potassium iodide (0.9 g, 5.42 mmol) was dissolved in water/acetone (60:40, 5 mL), and the resulting solution cooled over ice/water. The diazonium salt **28a** (1 g, 3.47 mmol) was then added, followed by water (100 mL) and then the mixture extracted with diethyl ether (3×50 mL). The combined extracts were washed with sodium thiosulphate solution, dried over magnesium sulphate and then evaporated. Yield of **29a**: 0.7 g, 67%; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.63$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 7.18 (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 0.24 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 137.77, 133.84, 123.01, 104.36, 96.29, 94.89, 0.28$.

Compound 29b: See preparation of **29a** for experimental details. Yield: 6.3 g, 61% of a colourless oil; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.82$ (t, $^4J(\text{H,H}) = 2$ Hz, 1H), 7.64 (dt, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 2$ Hz, 1H), 7.41 (dt, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 2$ Hz, 1H), 7.03 (t, $^3J(\text{H,H}) = 8$ Hz, 1H), 0.24 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 140.93, 137.89, 131.42, 130.13, 125.56, 103.53, 96.29, 93.93, 0.27$.

Compound 29c: See preparation of **29a** for experimental details. Yield: 0.7 g, 65% of a colourless oil; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.83$ (dd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 7.47 (dd, $^3J(\text{H,H}) = 8$ Hz, $^4J(\text{H,H}) = 1$ Hz, 1H), 7.25–7.30 (m, 1H), 6.96–7.02 (m, 1H), 0.29 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 139.08, 133.10, 130.02, 129.96, 128.10, 106.91, 101.69, 99.19, 0.22$.

Compound 29d: Boron trifluoride etherate (37.6 mL, 0.297 mol) was added to a chilled (ice/acetone bath (-20°C)) three-necked round-bottomed flask fitted with a pressure equalising dropping funnel and a nitrogen inlet. When the solution had equilibrated to -20°C compound **27d** (10 g, 3.66×10^{-2} mol) dissolved in THF (70 mL) was added dropwise over 5 mins. *tert*-Butyl nitrite (15.3 mL, 13.3 g, 0.129 mol) in THF (30 mL, dry and nitrogen saturated) was then added dropwise to the chilled mixture over 30 min. The mixture was left at -20°C for a further 10 min before allowing the mixture to warm up to 5°C over 20 min in an ice/water bath. Hexanes (200 mL) was added to this mixture, and chilling this solution in an ice bath for 15 min yielded **28d** as a pale brown oil, which was separated from the reaction mixture, frozen in liquid nitrogen and dried in vacuo. Compound **28d** was used in the next step without any further purification. Potassium iodide (9 g, 0.054 mol) was dissolved in water/acetone (60:40, 50 mL), and the resulting solution cooled over ice/water. The diazonium salt **28d** (1 g, 3.47 mmol) was then added followed by water (100 mL). The resulting mixture was then extracted with diethyl ether (3×50 mL). The combined extracts were washed with sodium thiosulphate solution, dried over magnesium sulphate and then evaporated. Compound **29d** was purified by flash column chromatography on silica eluting with hexanes to yield **29d**, 6.2 g, 44%. $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.64$ (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 7.19 (d, $^3J(\text{H,H}) = 8$ Hz, 2H), 1.12 (s, 21H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C , TMS): $\delta = 137.73, 133.93, 123.41, 106.34, 94.56, 92.79, 19.04, 11.67$.

Compound 21: Compound **28b** (6.56 g, 2.28×10^{-2} mol) was added portionwise to a chilled suspension of propylaminomethyl polystyrene **20**^[8a] (20 g) potassium carbonate (finely powdered, 2.96 g) in DMF (250 mL). The addition was carried out at 0°C , and a sample was extracted and added to diethylamine periodically, the addition of **28b** was stopped when a trace of the diethyl triazine was observed. The polymer support **21** was decanted onto a frit with DMF and washed with methanol, water, methanol, THF, and methanol (800 mL of each), and then dried under reduced pressure to yield 22.82 g, 0.754 mequivs of triazine per gram of resin (determined by combustion analysis). IR indicated that no protodesilylation of the TMS group had taken place during the reaction. Polymer support **21** (20 g) was added to THF (180 mL) containing tetrabutylammonium fluoride (16 mL, 1M in THF, 5 wt% water). The mixture was stirred periodically for 5 mins, before transfer of the polymer support onto a frit and careful washing with THF (600 mL) and methanol (600 mL). Yield of **22** after careful drying: 18.6 g; IR (thin film): $\tilde{\nu} = 3310(\text{C}=\text{H})$, $2210\text{ cm}^{-1}(\text{C}=\text{C})$.

Generalised procedure for pentamer preparation: Eighteen 4 cm diameter polyester “tea bags” each containing 1 g of **22** were prepared. Freshly distilled (ex CaH_2) triethylamine was added to palladium dibenzylidene acetone (2.4 mm), copper(I) iodide (4 mm) and triphenylphosphine (20 mm) under nitrogen. The resulting mixture was stirred at 70°C for 2 h. The catalyst mixture was then allowed to settle, and the solution decanted; 10 mL of catalyst solution was added for each “tea bag”. Arylacetylene-TMS iodides **29a, b, c** (231 mg per “tea bag”) or arylacetylene-TIPS iodide **29d** (296 mg per “tea bag”) were added. All reactions were initially left for 12 h at 65°C before analysis of the resin by FT IR to estimate the degree of reaction.

Tetrabutylammonium fluoride protodesilylation: Protodesilylation was carried out on all eighteen “tea bags” simultaneously. The tea bags were placed in a beaker and covered with tetrahydrofuran. Tetrabutylammonium fluoride (20 mL, 1M solution in THF, 5 wt% water) was then added, and the mixture agitated. After 15 min the “tea bags” were thoroughly washed with THF and then methanol, before drying at 75°C under reduced pressure. A sample of resin from one bag was then tested by swelling with carbon tetrachloride and measuring the IR spectrum to check that complete protodesilylation had occurred.

Removal of the polystyrene-bound pentamers: Each “tea bag” was treated with methyl iodide (10 mL) in a sealed tube at 110°C for 12 hours. The methyl iodide was then removed by evaporation and 10 mL of the following catalyst solution added (palladium dibenzylidene acetone (2.4 mm), copper(I) iodide (4 mm) and triphenylphosphine (20 mm) in freshly distilled (ex CaH_2) pyridine and diethylamine (1:1)) along with triisopropylsilylacetylene (0.5 mL, 0.002 mol). The pressure tubes were sealed and heated to 110°C for 12 h. Each pentamer was then purified by flash column chromatography 5% dichloromethane in hexanes, followed by recrystallisation from dichloromethane with layered addition of methanol.

Pentamer 1: M.p. 286°C ; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.52$ (s, 12H), 7.46 (s, 8H), 1.14 (s, 42H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C): $\delta = 132.43, 132.01, 131.80, 123.97, 123.48, 123.44, 123.38, 123.20, 106.96, 93.41, 91.55, 91.50, 91.46, 91.25, 19.08, 11.69$; MS (MALDI-Tof, dihydroxybenzoic acid matrix): m/z : 839.5 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.35, H 7.56.

Pentamer 2: M.p. 90°C ; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.73$ (m, 1H), 7.40–7.50 (m, 18H), 7.35 (m, 1H), 1.13 (s, 42H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C): $\delta = 135.04, 132.43, 132.03, 132.00, 131.92, 131.81, 129.00, 123.98, 123.86, 123.49, 123.40, 123.25, 107.01, 93.40, 91.52, 91.27, 90.87, 90.17, 19.10, 11.72$; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1635.6 $[2M - iPr]^+$, 838.2 $[M]^+$, 795.2 $[M - iPr]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 86.01, H 7.93.

Pentamer 3: M.p. 169°C ; $^1\text{H NMR}$ (300 MHz, CDCl_3 , 25°C , TMS): $\delta = 7.40$ –7.60 (m, 18H), 7.34 (m, 2H), 1.41 (s, 42H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 25°C): $\delta = 132.43, 132.22, 132.03, 131.99, 131.81, 128.69, 126.07, 123.97, 123.63, 123.52, 123.24, 107.00, 93.81, 93.40, 91.57, 91.28, 90.67, 19.08, 11.71$; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.6 $[2M]^+$, 839.1 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.81, H 7.73.

Pentamer 4: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.72$ (m, 2H), 7.45–7.52 (m, 16H), 7.32–7.37 (m, 2H), 1.41 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.04$, 132.42, 132.03, 131.87, 131.82, 128.97, 123.97, 123.87, 123.82, 123.43, 123.20, 106.98, 93.36, 90.84, 90.64, 90.19, 90.10, 19.08, 11.70; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1678.1 $[2M]^+$, 839.4 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.61, H 7.62.

Pentamer 5: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.72$ (m, 1H), 7.40–7.53 (m, 18H), 7.35 (m, 1H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.04$, 132.42, 132.03, 132.00, 131.86, 131.82, 131.80, 128.98, 123.98*, 123.88, 123.82, 123.49, 123.44*, 123.40, 123.21, 123.20, 106.98*, 93.41, 93.37, 91.54, 91.45*, 91.25, 90.88, 90.63, 90.19, 90.11, 19.08, 11.70; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.6 $[2M]^+$, 839.3 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 86.03, H 7.07.

Pentamer 6: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.72$ (m, 2H), 7.60–7.74 (m, 16H), 7.30–7.36 (m, 2H), 1.26 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.07$, 132.42, 132.03, 131.99, 131.94, 131.90, 131.83, 131.81, 128.97, 123.97*, 123.88, 123.84*, 123.81, 123.48, 123.39, 123.24, 123.22, 107.00*, 93.40, 93.36, 91.50, 91.26, 90.86, 90.66, 90.20, 90.15, 89.57, 89.53, 19.08, 11.71; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.6 $[2M]^+$; MS (APCI): m/z : 880.0 $[M+K]^+$, 836.6 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2(\text{CH}_3\text{OH})_{0.5}$ (871.45): C 84.93, H 7.55; found: C 84.96, H 7.83.

Pentamer 7: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.72$ (m, 3H), 7.40–7.54 (m, 14H), 7.30–7.40 (m, 3H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.07$, 132.42, 131.93, 131.91, 131.88, 131.83, 128.97, 123.96, 123.86, 123.828, 123.21, 106.99, 93.35, 90.65, 90.18, 89.54*, 19.08, 11.73; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1678.9 $[2M]^+$; MS (APCI): m/z : 880.4 $[M+K]^+$, 839.1 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.48, H 7.70.

Pentamer 8: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.75$ (m, 2H), 7.30–7.59 (m, 18H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.17$, 132.35, 132.15, 131.86, 131.82, 129.01, 128.66, 126.16, 124.03, 123.92, 123.88, 123.21, 107.01, 93.27, 93.25, 90.64, 90.17, 89.34, 19.08, 11.71; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.6 $[2M]^+$, 839.3 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.51, H 7.23.

Pentamer 9: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.77$ (m, 1H), 7.30–7.60 (m, 19H), 1.14 (s, 21H), 1.12 (s, 21H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.25$, 132.43, 132.19, 132.14, 132.04, 131.86, 131.76, 131.69, 129.02, 128.68, 126.20, 126.05, 124.03, 123.96*, 123.90, 123.63, 123.51, 123.18*, 107.01, 106.96, 93.79, 93.31*, 93.28, 91.55, 91.25, 90.66, 90.60, 90.19, 89.38, 19.07, 18.86, 11.71, 11.68; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1678.6 $[2M]^+$, 839.3 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 86.11, H 7.45.

Pentamer 10: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.40$ –7.60 (m, 18H), 7.30–7.40 (m, 2H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 132.46$, 132.42, 132.23, 132.05, 132.00, 131.80, 128.69, 128.66, 126.07, 126.00, 124.00, 123.97, 123.68, 123.47, 123.44*, 123.42, 123.22, 106.99*, 93.81, 93.75, 93.41*, 91.53, 91.49*, 91.26, 90.67, 90.41, 19.08, 11.71; MS (APCI): m/z : 880.2 $[M+K]^+$, 838.0 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.76, H 7.17.

Pentamer 11: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.72$ (m, 1H), 7.40–7.60 (m, 16H), 7.30–7.40 (m, 3H), 1.14 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.06$, 132.46, 132.41, 132.23, 132.07, 131.97, 131.87, 131.82, 131.79, 128.97, 128.68, 128.65, 126.07, 126.01, 124.00, 123.96, 123.87, 123.84, 123.67, 123.44*, 123.21, 106.99*, 93.80, 93.74, 93.40, 93.35, 90.87, 90.65, 90.62, 90.41, 90.18, 90.15, 19.08, 11.71; MS (APCI): m/z : 880.0 $[M+K]^+$, 838.0 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2(\text{C}_6\text{H}_{14})_{0.76}$ (904.91): C 85.65, H 8.10; found: C 85.37, H 8.11.

Pentamer 12: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.40$ –7.60 (m, 16H), 7.30–7.40 (m, 4H), 1.13 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 132.46$, 132.25, 132.02, 131.78, 128.67, 128.64, 126.07, 126.01, 124.01, 123.68, 123.42, 106.97, 93.83, 93.77, 93.38, 90.64, 90.38, 19.08, 11.70; MS (APCI): m/z : 881.0 $[M+K]^+$, 839.0 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2(\text{CH}_3\text{OH})_{0.52}$ (856.07): C 84.90, H 7.56; found: C 84.90, H 7.48.

Pentamer 13: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.78$ (m, 1H), 7.40–7.60 (m, 16H), 7.30–7.40 (m, 3H), 1.14 (s, 21H), 1.13 (s, 21H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.20$, 132.46, 132.42, 132.28,

132.21, 132.01, 131.86, 131.78, 129.05, 128.67, 128.65, 126.18, 125.94, 124.07, 124.00, 123.94, 123.88, 123.48, 123.47, 123.36, 123.28, 107.00*, 93.78, 93.39*, 93.19, 91.45, 91.30, 90.83, 90.45, 90.17, 89.39, 19.09, 11.71; MS (APCI): m/z : 880.3 $[M+K]^+$, 838.2 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2$ (839.4): C 85.85, H 7.46; found: C 85.42, H 7.75.

Pentamer 14: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.69$ (m, 1H), 7.71 (t, $J = 1.6$ Hz, 1H), 7.6–7.4 (m, 14H), 7.4–7.3 (m, 4H), 1.14 (s, 21H), 1.12 (s, 21H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.12$, 135.05, 132.45, 132.41, 132.29, 131.93, 131.85, 131.83, 129.04, 128.99, 128.67, 128.65, 126.12, 125.94, 124.05, 123.99, 123.94, 123.86*, 123.79, 123.47, 123.25, 107.01*, 93.79, 93.36, 93.32, 93.15, 90.70, 90.43, 90.16, 89.58, 89.54, 89.33, 19.29, 11.71; MS (APCI): m/z : 880.3 $[M+K]^+$, 839.0 $[M]^+$; elemental analysis calcd (%) for $\text{C}_{60}\text{H}_{62}\text{Si}_2(\text{CH}_3\text{OH})_{0.31}$ (849.34): C 85.27, H 7.52; found: C 85.28, H 7.52.

Pentamer 15: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.83$ (m, 1H), 7.30–7.60 (m, 19H), 1.13 (s, 42H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.18$, 132.44, 132.29, 131.81, 129.10, 128.65, 126.10, 125.90, 124.10, 123.93, 123.43, 107.07, 93.78, 93.21, 93.15, 90.39, 89.37, 19.09, 11.90; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1678.6 $[2M]^+$, 795.1 $[M-iPr]^+$; MS (APCI): m/z : 880.0 $[M+K]^+$, 839.2 $[M]^+$.

Pentamer 16: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.30$ –7.63 (m, 20H), 1.14 (s, 21H), 1.13 (s, 21H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 132.44$, 132.40, 132.27, 132.25, 132.06, 131.87, 131.82, 131.77, 128.69, 128.65, 128.60, 126.26, 126.23, 125.99, 125.95, 123.91, 123.76, 123.64, 123.45, 123.29, 123.24, 107.12, 107.01, 93.89, 93.86, 93.35, 93.13, 92.70, 92.68, 91.38, 91.35, 90.65, 90.41, 19.08, 11.71; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1678.4 $[2M]^+$, 839.4 $[M]^+$; MS (APCI): m/z : 880.0 $[M+K]^+$, 839.2 $[M]^+$.

Pentamer 17: ^1H NMR (300 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.70$ (m, 1H), 7.20–7.65 (m, 19H), 1.14 (s, 21H), 1.12 (s, 21H); ^{13}C NMR (75 MHz, CDCl_3 , 25 °C): $\delta = 135.40$, 132.52, 132.40, 132.38, 132.25, 132.22, 131.86, 131.83, 131.81, 131.65, 128.79, 128.68, 128.63, 128.60, 126.36, 126.23, 125.97, 125.94, 107.11, 107.00, 93.88, 93.30, 93.13, 92.69, 90.77, 90.45, 89.96, 89.35, 19.07, 11.71; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.4 $[2M]^+$; MS (APCI): m/z : 879.9 $[M+K]^+$, 838.9 $[M]^+$.

Pentamer 18: ^1H NMR (CDCl_3 , 300 MHz): $\delta = 7.10$ –7.70 (m, 20H), 1.13 (s, 42H); ^{13}C NMR (CDCl_3 , 75 MHz): $\delta = 132.62$, 132.55, 132.22, 132.07, 131.81, 128.64, 128.47, 128.41, 126.19, 126.10, 125.88, 123.67, 123.50, 107.17, 93.72, 93.00, 92.82, 92.70, 90.47, 19.08, 11.70; MS (MALDI-Tof, α -cyano-4-hydroxycinnamic acid): m/z : 1677.4 $[2M]^+$, 839.1 $[M]^+$; MS (APCI): m/z : 838.9 $[M]^+$.

Photophysical experiments: Absorption spectra were measured on a Shimadzu 2401PC spectrophotometer. Photoluminescence spectra of materials in solution were measured with a Perkin–Elmer LS50B spectrophotometer. The photoluminescence quantum yields in dichloromethane were measured by comparison with anthracene in ethanol (27%).¹⁷ The solid-state photoluminescence spectra were measured by using an Edinburgh Instruments FS900CDT spectrofluorimeter.

Thin films (ca. 50 nm) of the pentamers for photoluminescence were prepared by spin-coating onto fused silica from toluene (15 mg mL⁻¹) at 4 krpm for 40 s, and their photoluminescence characteristics investigated in air.

Electroluminescence: ITO on glass with a sheet resistivity of 20 Ω square⁻¹ was obtained from Merck; it was cleaned by sonication in Decon, followed by 2% sodium hydroxide solution, washed with deionised water and then dried from *iso*-propanol. The ITO on glass was then patterned, by etching, into 2 mm width strips, and then cleaned again, before depositing any organic layers. The metal cathodes (2 mm width strips) were evaporated normal to the ITO strips, thus defining 2 mm \times 2 mm pixels. The luminance/current/voltage characteristics were measured by using a Topcon BM-7 luminance meter and a current/voltage measuring unit (Kiethley SM4236) under N₂. Electroluminescence spectra were measured by using an Edinburgh Instruments FS900CDT spectrofluorimeter.

ITO/pentamer 3 (150 nm)/Al:Li: Pentamer 3 (45 mg mL⁻¹) in toluene was deposited (150 nm) onto ITO-glass by spin-coating under nitrogen (2 krpm for 40 s); the substrate was then placed in the evaporation chamber without exposure to air and pumped overnight. The aluminium lithium cathode was evaporated at 10⁻⁷ mbar. $\leq 5\%$ lithium was incorporated into the aluminium cathode by coevaporating aluminium and lithium; the lithium was evaporated from a getter supplied by SAES Getters.

ITO/PEDOT·PSS (50 nm)/pentamer **3** (150 nm)/Al:Li: PEDOT·PSS (Baytron P, Bayer)^[14] was spin-coated onto ITO-glass under nitrogen; the resulting film was heated to 110 °C for 1 h under nitrogen, resulting in a film about 50 nm thick; after cooling pentamer **3** and aluminium were deposited as outlined above.

ITO/PEDOT·PSS (50 nm)/pentamer **3** (150 nm)/Alq₃ (30 nm)/Al:Li: In this device Alq₃ was evaporated at 10⁻⁷ mbar.

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