Poly(9,9-dialkyl-3,6-dibenzosilole)—a high energy gap host for phosphorescent light emitting devices†

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The preparation of the 3,6-disubstituted dibenzosilole monomers 4, 5 and 10 by two different routes is described; Suzuki copolymerisation afforded poly(9,9-dioctyl-3,6-dibenzosilole) 11 which has a sufficiently high triplet energy (2.55 eV) to function as a host for green electrophosphorescent emitters.

Electroluminescence from conjugated polymers[1] can be significantly improved by harnessing the energy of their non-emissive triplet states.[2] Continued advances in the use of phosphorescent metal complexes in organic light emitting diodes fabricated by vapour deposition have opened the way to very high efficiency devices.[3] To prevent triplet–triplet quenching, these phosphorescent emitters are dispersed in a suitable host material. Whilst considerable progress has been made using small organic molecules and dendritic materials,[4] few polymeric hosts exist that have appropriate energy levels for these phosphorescent complexes, particularly the green and blue emitters.[2] Polymers are attractive host materials for large area displays fabricated by solution deposition. Non-conjugated polymers such as poly(vinylcarbazole) (PVK) and polystyrene have been successfully used in devices with phosphorescent guests. However, these materials suffer from problems with charge injection and transport, and devices based on them are typically characterised by high turn-on and operating voltages.[5] In contrast, conjugated polymers have been shown to provide better charge transport and balanced charge injection in devices.[6] In order to reduce phase separation and/or aggregation in the blends, it is possible to use single component emitting materials in which the phosphorescent complexes are tethered to the polymer host.[7]

The key requirement of hosts for phosphorescent guests is that they must have a triplet energy level higher than the emitting material.[8] The search for conjugated materials with high triplet energies is a challenging one. To date only poly(*N*-alkyl-3,6-carbazole)s (PCaz) have been reported to be suitable hosts for green phosphorescent emitters.[9] In this paper we report a new polymer, poly(9,9-dioctyl-3,6-dibenzosilole) (**11**), and its use in an electroluminescent device as a host material for a green phosphorescent emitter. This new polymer contains 9,9-dialkylsilyl functionalities that modulate the electron affinity of the π-conjugated system.[10] A further feature is the relatively short conjugation path, which is limited by the 3,6-linkage.[9]

We report the synthesis of a 3,6-disubstituted dibenzosilole monomer precursor by two routes, the first employing selective transmetalation of 2,2′-diiodo-5,5′-dibromobiphenyl (**3**) followed by silacyclisation (as used for the corresponding 2,7-dibenzosilole),[11] and the second exploiting the displacement of methyl groups from a dibenzosilole **8**. The latter route demonstrates the versatility of the alkyl-displacement on silicon reaction in realising potential variations in the solubilising substituents on the bridging silicon. The poly(3,6-dibenzosilole) arising from these routes exhibits a suitable triplet energy level for green guest electrophosphorescence.

In the shorter route, the known[12] 2,2′-diiodobiphenyl (**2**) was brominated to give **3** in 48% yield (Scheme 1). The observed regioselectivity of the bromination reaction is consistent with the preferential stabilisation of the Wheland intermediate by the iodo substituents, presumably because the phenyl substituents are twisted out of conjugation by steric influences. Selective silacyclisation, as previously described for the analogous 4,4′-dibromobiphenyl derivative,[11] afforded the dibenzosilole **4** in 64% yield. The boronate counterpart for the cross-coupling reaction, **5a**, was readily prepared by double lithiation of **4** followed by boronation, as shown in Scheme 1. The structure of **5a** was confirmed by X-ray crystallography.†

A potentially more versatile route to a variety of 9,9-disubstituted dibenzosiloles is illustrated in the second route. Reversing the pattern of halogen substitution (**7**) and transmetallation, followed by silacyclisation as already described, afforded 9,9-dimethyl-3,6-bis(trimethylsilyl)dibenzosilole (**8**). The two methyl groups on the bridging silicon of **8** can be selectively displaced in the presence of the trimethylsilyl groups by treatment with a slight excess of alkyllithium (*e.g.* hexyllithium in this case) to give **9**. The transalkylation reaction presumably occurs *via* a pentacoordinated intermediate that is stabilised by the biphenyl rings as the hexyl anion attacks the silicon.[13] Subsequent departure of the more stable methyl anion leaving group afforded **9** in effectively quantitative yield. This method is a very versatile approach to a wide range of 9-substituted dibenzosiloles, given the limited commercial availability of disubstituted dichlorosilanes. By way of illustration, the 9,9-dioctyl analogue could also be made with octyllithium. Subsequent iododesilylation of **9** with iodine monochloride afforded the diiododibenzosilole **10**, which could be further boronated to give the corresponding monomer **5b**.

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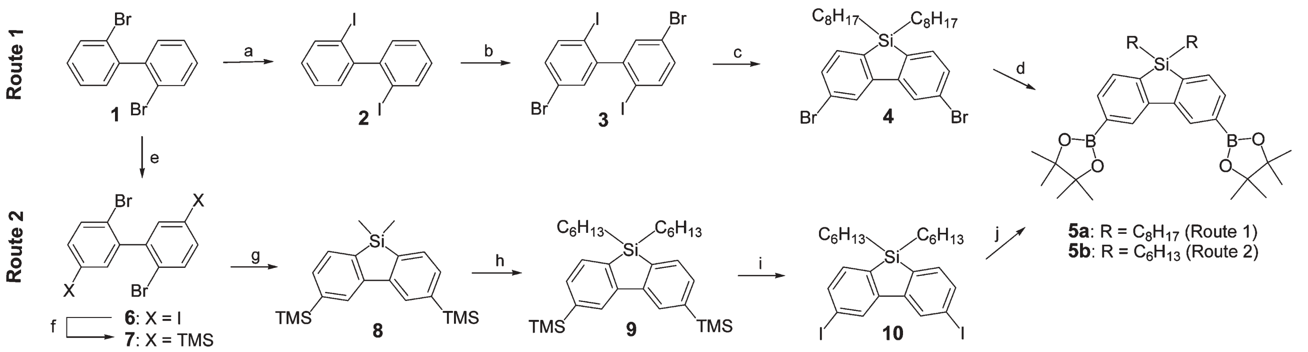
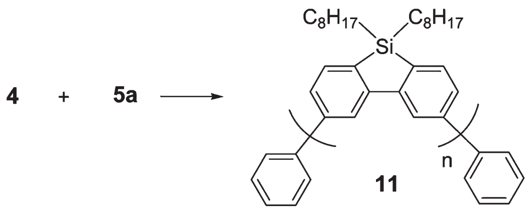
† Electronic Supplementary Information (ESI) available: Details of characterisation data and crystal structure determination for **5a**, experimental details for PL and EL measurements. See DOI: 10.1039/b511208g



Scheme 1 Reagents and conditions: (a) *n*BuLi, THF, −78 → 25 °C, 24 h, then I_2 in Et_2O, 0 °C, 2 h, 85%; (b) Br_2, Fe, $CHCl_3$, 50 °C, 24 h, 50%; (c) *t*BuLi (4.2 equiv.), THF, −90 °C, then $(C_8H_{17})_2SiCl_2$, 25 °C, 64%; (d) *t*BuLi, THF, −78 °C, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane, 25 °C, 75%; (e) I_2, $NaIO_4$, conc. H_2SO_4, AcOH, Ac_2O, 24 h, 40%; (f) *n*BuLi, −78 °C, 24 h, then TMSCl, −78 °C → 25 °C, 24 h, 84%; (g) *t*BuLi, −78 → 25 °C, 24 h, then $SiMe_2Cl_2$, −78 °C → 25 °C, 24 h, 81%; (h) *n*HexLi, −78 °C, 15 min, 95%; (i) ICl, CH_2Cl_2, 25 °C, 1 h, 90%; (j) *t*BuLi, THF, −78 °C, then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane, −78 → 25 °C, 24 h, 42%.

The Suzuki polycondensation of the dibromide **4** with the diboronic ester **5a** was carried out under basic conditions with the catalyst system $Pd(OAc)_2$–tricyclohexylphosphine in a biphasic system of toluene and aqueous tetraethylammonium hydroxide,[11] with phenyl group end-capping affording poly(9,9-dioctyl-3,6-dibenzosilole) (**11**) in 93% yield (Scheme 2); the molecular weight of **11** was determined by GPC analysis with polystyrene standards, M_w = 23 000 and M_n = 11 000 (degree of polymerisation ≈ 30, polydispersity = 2.1). Polymer **11** is completely soluble in common organic solvents such as toluene, chloroform and THF.

The photoluminescence (PL) spectrum of a thin film of **11** at 77 K exhibited a 0–0 transition at 3.5 eV and a second maximum at 3.3 eV (excitation at 4.4 eV). The corresponding room temperature measurement is overwhelmed by a broad emission band centering at 3.3 eV corresponding to the first vibronic sideband (Fig. 1a, b). The phosphorescence emission spectrum of **11** was conveniently obtained at 77 K using a cryostat fitted to a commercially available fluorescence spectrometer.[14] The emission consists of a broad band exhibiting vibronic structure (excitation at 3.9 eV) (Fig. 1c). The onset of the triplet emission of the homopolymer is measured at 2.55 eV, and this is taken as a measure of the homopolymer triplet energy level. We have found this method to be a reliable procedure for estimating triplet energies of conjugated polymers. The triplet energy of 2.55 eV implies that the polymer is a potential host for phosphorescent emitters that have a triplet energy level lower than 2.55 eV, without the risk of energy back-transfer onto the polymer. This triplet energy is significantly higher than that of commonly used polyfluorenes (2.1 eV),[15] and comparable with that of PCaz (2.6 eV).[9]



Scheme 2 Reagents and conditions: $Pd(OAc)_2$, tricyclohexylphosphine, Et_4NOH, toluene, 90 °C, then $PhB(OH)_2$, 2 h, then PhBr, 2 h, 93%.

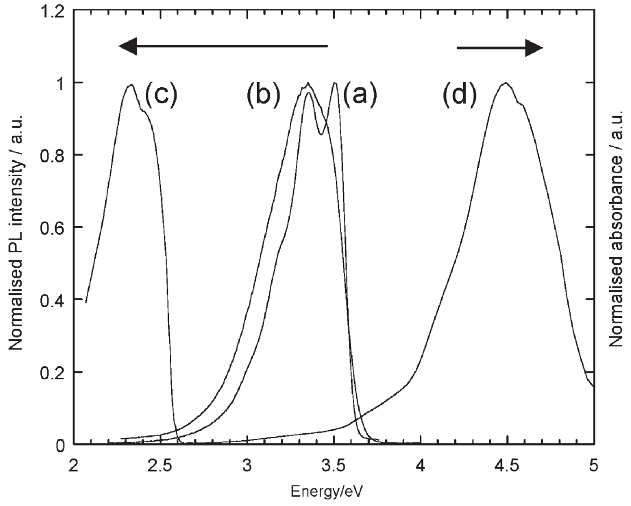


Fig. 1 The singlet photoluminescence spectra of a thin film of **11** on glass obtained at 77 K (a) and at room temperature (b), and the triplet photoluminescence spectrum of a thin film of **11** obtained at 77 K upon excitation at 3.9 eV (318 nm) (c). The room temperature absorption spectrum of a thin film of **11** is represented by (d).†

To investigate the capability of **11** as a high energy polymer host, *fac*-tris[2-(2-pyridyl-κ*N*)-5-methylphenyl]iridium(III), (Ir(m-ppy)$_3$) (**12**), which has a triplet energy of 2.4 eV,[16] was blended into a toluene solution of the polymer (8 wt%) to provide a green phosphorescent dopant. The electroluminescence emission from an unoptimised neat emissive layer device of configuration ITO/PEDOT:PSS/polymer blend/LiF/Al showed complete energy transfer from the polymer host to the green dopant at a drive voltage of 4 V (Fig. 2) and the absence of any emission from **11**. The efficient Förster energy transfer from the singlet π* state of the host to the metal-to-ligand charge transfer (MLCT) band of the guest points to the good overlap between the emission band of the homopolymer **11** and the absorption band of the Ir(m-ppy)$_3$. The electrophosphorescence is achieved by fast intersystem crossing to the corresponding emissive triplet state. Direct charge trapping and hopping of the holes between the Ir dopants, on the other hand, almost certainly also plays an important role in the electroluminescence at the present doping level.

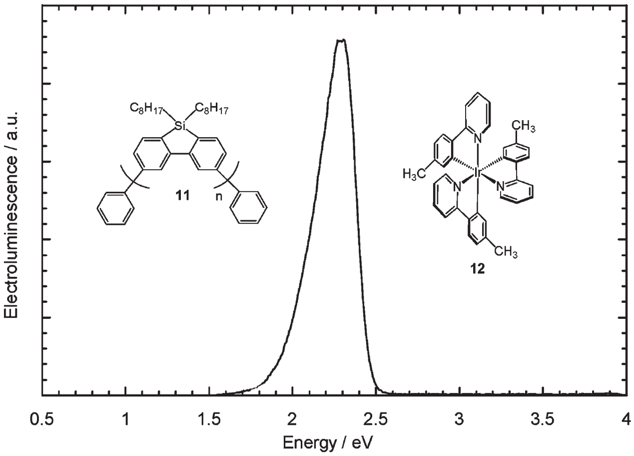


Fig. 2 Electroluminescence spectrum of a PLED containing a layer of the polymer **11**, into which the triplet emitter **12** is dispersed at a mass ratio of 8 wt%.†

The low turn-on voltage of the device can be related to the observed HOMO and LUMO energy levels of **11**. Cyclic voltammetry (CV) measurements put the LUMO energy of **11** at -2.15 eV (*cf.* PCaz at -2.0 eV), indicative of the electron withdrawing contributions from the bridging silicon atoms onto the phenyl rings due to σ^*–π^* conjugation,[10] which is often observed in molecular and polymeric siloles.[10,17] We were unable to observe an oxidation wave in the CV measurements, but we can use the optical band gap (3.5 eV, Fig. 1d) to deduce the HOMO level at -5.65 eV (*cf.* PVK at -5.8 eV).[18] The lower HOMO level in polymer **11** compared with that of PVK results in a reduced hole-injection barrier at the PEDOT:PSS interface. The positions of the HOMO and LUMO levels in **11** are therefore potentially favourable for both electron and hole injection into the device.

In summary, the successful synthesis of 3,6-functionalised dibenzosilole building blocks has opened the door to a new class of solution-processable, high energy gap, conjugated polymers.[19] The potential of such polymers as hosts for green phosphorescent emitters is evident from our preliminary EL studies, where complete energy transfer from the polymer to the guest at a low turn-on voltage was observed in a simple device.

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Notes and references

1 (*a*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539; (*b*) A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem.*, 1998, **110**, 416.

2 E. Holder, B. M. W. Langeveld and U. S. Schubert, *Adv. Mater.*, 2005, **17**, 1109.

3 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151.

4 J. P. J. Markham, E. B. Namdas, T. D. Anthopoulos, I. D. W. Samuel, G. J. Richards and P. L. Burn, *Appl. Phys. Lett.*, 2004, **85**, 1463.

5 For examples see: (*a*) X. Gong, M. R. Robinson, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2002, **14**, 581; (*b*) S. Lamansky, P. I. Djurovich, F. Abdel-Razzaq, S. Garon, D. L. Murphy and M. E. Thompson, *J. Appl. Phys.*, 2002, **92**, 1570.

6 X. Gong, J. C. Ostrowski, D. Moses, G. C. Bazan and A. J. Heeger, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 2691.

7 (*a*) X. W. Chen, J. L. Liao, Y. M. Liang, M. O. Ahmed, H. E. Tseng and S. A. Chen, *J. Am. Chem. Soc.*, 2003, **125**, 636; (*b*) A. J. Sandee, C. K. Williams, N. R. Evans, J. E. Davies, C. E. Boothby, A. Köhler, R. H. Friend and A. B. Holmes, *J. Am. Chem. Soc.*, 2004, **126**, 7041; (*c*) J. Jiang, C. Jiang, W. Yang, H. Zhen, F. Huang and Y. Cao, *Macromolecules*, 2005, **38**, 4072.

8 A. Köhler, J. S. Wilson and R. H. Friend, *Adv. Mater.*, 2002, **14**, 701.

9 (*a*) K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035; (*b*) A. van Dijken, J. J. A. M. Bastiaansen, N. M. M. Kiggen, B. M. W. Langeveld, C. Rothe, A. Monkman, I. Bach, P. Stössel and K. Brunner, *J. Am. Chem. Soc.*, 2004, **126**, 7718.

10 (*a*) S. Yamaguchi and K. Tamao, *Chem. Lett.*, 2005, **34**, 2; (*b*) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, 1998, 3693; (*c*) S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2327; (*d*) L. C. Palilis, A. J. Mäkinen, M. Uchida and Z. H. Kafafi, *Appl. Phys. Lett.*, 2003, **82**, 2209.

11 K. L. Chan, M. J. McKiernan, C. R. Towns and A. B. Holmes, *J. Am. Chem. Soc.*, 2005, **127**, 7662.

12 T. K. Dougherty, K. S. Y. Lau and F. L. Hedberg, *J. Org. Chem.*, 1983, **48**, 5273.

13 (*a*) M. Ishikawa, T. Tabohashi, H. Sugisawa, J. Nishimura and M. Kumada, *J. Organomet. Chem.*, 1983, **250**, 109; (*b*) A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, R. F. Schmitz and G. W. Klumpp, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1127; (*c*) A. H. J. F. de Keijzer, F. J. J. de Kanter, M. Schakel, V. P. Osinga and G. W. Klumpp, *J. Organomet. Chem.*, 1997, **548**, 29; (*d*) S. Deerenberg, M. Schakel, A. H. J. F. de Keijzer, M. Kranenburg, M. Lutz, A. L. Spek and K. Lammertsma, *Chem. Commun.*, 2002, 348.

14 The triplet energy of polymer **11** was measured by spin-coating a 10 mg cm^{-3} toluene solution of **11** at 2500 rpm onto a glass microscope slide. The slide was mounted on a glass holder and inserted into an Oxford Instruments Optistat DN cryostat. The cryostat was evacuated, the sample chamber was filled with helium gas and then cooled to 77 K. The cryostat was mounted on a baseplate inside the sample chamber of a Varian Cary Eclipse fluorescence spectrometer. The phosphorescence spectrum was recorded in "phosphorescence mode" with the number of flashes set to 50, a delay of 5 ms and a gate of 100 ms. This allowed the weak phosphorescence peak to be separated from the high intensity, but rapidly decaying, fluorescence signal. A low temperature phosphorescence spectrum identical to that reported by Bässler *et al.*[15] was obtained using this technique on a sample of poly(dioctylfluorene).

15 (*a*) D. Hertel, S. Setayesh, H.-G. Nothofer, U. Scherf, K. Müllen and H. Bässler, *Adv. Mater.*, 2001, **13**, 65; (*b*) U. Scherf and E. J. W. List, *Adv. Mater.*, 2002, **14**, 477.

16 (*a*) D. Kolosov, V. Adamovich, P. Djurovich, M. E. Thompson and C. Adachi, *J. Am. Chem. Soc.*, 2002, **124**, 9945; (*b*) C.-H. Yang, K.-H. Fang, C.-H. Chen and I.-W. Sun, *Chem. Commun.*, 2004, 2232.

17 (*a*) S. Yamaguchi, T. Endo, M. Uchida, T. Izumizawa, K. Furukawa and K. Tamao, *Chem.–Eur. J.*, 2000, **6**, 1683; (*b*) L. C. Palilis, A. J. Mäkinen, M. Uchida and Z. H. Kafafi, *Appl. Phys. Lett.*, 2003, **82**, 2209.

18 Y. Kawamura, S. Yanagida and S. R. Forrest, *J. Appl. Phys.*, 2002, **92**, 87.

19 Since the submission of this manuscript, a closely related UV-emitting polymer has been synthesised *via* a different route. See: Y. Mo, R. Tian, W. Shi and Y. Cao, *Chem. Commun.*, 2005, 4925.