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Syntheses, structures, two-photon absorption cross-sections and computed second hyperpolarisabilities of quadrupolar A–π–A systems containing *E*-dimesitylborylethenyl acceptors†‡

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A series of bis(*E*-dimesitylborylethenyl)-substituted arenes, namely arene = 1,4-benzene, 1,4-tetrafluorobenzene, 2,5-thiophene, 1,4-naphthalene, 9,10-anthracene, 4,4′-biphenyl, 2,7-fluorene, 4,4′-*E*-stilbene, 4,4′-tolan, 5,5′-(2,2′-bithiophene), 1,4-bis(4-phenylethynyl)benzene, 1,4-bis(4-phenylethynyl)tetrafluorobenzene and 5,5″-(2,2′:5′,2″-terthiophene), have been synthesised *via* hydroboration of the corresponding diethynylarenes with dimesitylborane. Their absorption and emission maxima, fluorescence lifetimes and quantum yields are reported along with the two-photon absorption (TPA) spectra and TPA cross-sections for the 5,5′-bis(*E*-dimesitylborylethenyl)-2,2′-bithiophene and 5,5′-bis(*E*-dimesitylborylethenyl)-2,2′:5′,2″-terthiophene derivatives. The TPA cross-section of the latter compound of *ca.* 1800 GM is the largest yet reported for a 3-coordinate boron compound and is in the range of the largest values measured for quadrupolar compounds with similar conjugation lengths. The X-ray crystal structures of 1,4-benzene, 2,5-thiophene, 4,4′-biphenyl and 5,5″-(2,2′:5′,2″-terthiophene) derivatives indicate π-conjugation along the BC═C–arene–C═CB chain. Theoretical studies show that the second molecular hyperpolarisabilities, γ, in each series of compounds are generally related to the HOMO energy, which itself increases with increasing donor strength of the spacer. A strong enhancement of γ is predicted as the number of thiophene rings in the spacer increases.

Introduction

Three-coordinate boron has many interesting properties, due to its vacant p-orbital, and can be incorporated into organic molecules, particularly π-conjugated ones, where it acts as a π-acceptor, whilst remaining a σ-donor.[1,2] However, such boron centres are susceptible to attack by nucleophiles, such as water, including that present as moisture in the atmosphere. This can be circumvented through the use of bulky substituents, such as mesityl (2,4,6-trimethylphenyl) groups, which provide steric protection for the boron centre. Although it is usually assumed that two mesityl substituents are necessary to provide air-stability for extended periods,[3] recent work on dibenzoborins including main-group atoms suggested that only one mesityl moiety on the boron is sufficient in certain cases,[4] which appear not to require the use of bulkier groups, such as triptyl (2,4,6-triisopropylphenyl) or supermesityl (2,4,6-tri-*tert*-butylphenyl), which have been employed in closely related systems.[5,6]

Early work focused largely on the electrochemistry of such boron-containing materials, as examined by cyclic voltametry.[7] However, in recent years, there has been considerable interest in the optical properties of three-coordinate boron compounds. Such materials have been shown to display significant emission solvatochromism,[8,9] as well as substantial second-[10,11] and third-order[11d] non-linear optical (NLO) coefficients, and inclusion into coordination networks provides second-order coefficients up to 35 times that of urea.[12] Recently, several conjugated molecules with boron-containing side groups were shown to display very large Stokes shifts and very high quantum yields, even in the solid state, which was ascribed to the lack of intermolecular quenching, due to the absence of close packing.[13] A number of boron-containing molecular materials have been shown to exhibit large

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‡ Electronic supplementary information (ESI) available: Measured absorption and emission spectra, computed absorption spectra and TD_DFT computed electronic transitions for compounds **1j** and **1m**. CCDC reference numbers 724814–724818. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905719f.

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two-photon absorption (TPA) cross-sections.[14,15] Recently, two three-coordinate boron-containing pyridine systems have been shown to undergo reversible B–C bond breaking/C–C bond formation upon irradiation by UV light.[16]

Additional applications of conjugated three-coordinate boron-containing materials include use in electron-transport and/or emissive layers in organic light-emitting diodes (OLEDs),[17–20] or as dopants in non-emissive hosts,[21] such as a boron-substituted phenylpyridyl-based iridium complex which was found to be an efficient red triplet emitter,[21b] and as colourimetric or luminescent sensors for anions, most commonly fluoride ions.[22–27]

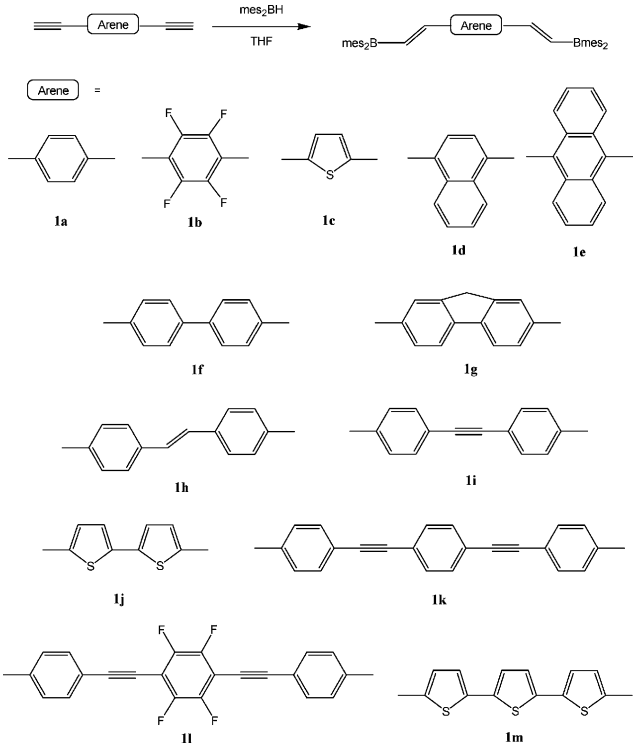
For several years, we have been investigating the properties of conjugated molecular materials containing dimesitylboryl groups,[1a,b,11,15,21b] including those based on the *E*-dimesitylborylethenyl motif.[11a,d–f] These are readily synthesised by hydroboration of ethynylarenes with dimesitylborane, which we recently showed to exhibit a monomer–dimer equilibrium in solution.[28] Whilst this hydroboration reaction usually proceeds in an anti-Markovnikov manner, we recently observed one instance of Markovnikov addition in the hydroboration of 2,5-diethynylpyridine.[29]

Herein, we present details of the synthesis, characterisation, and optical properties of a series of bis(*E*-dimesitylborylethenyl)arenes: *viz.*, 1,4-bis(*E*-dimesitylborylethenyl)benzene (**1a**), 1,4-bis(*E*-dimesitylborylethenyl)tetrafluorobenzene (**1b**), 2,5-bis(*E*-dimesitylborylethenyl)thiophene (**1c**), 1,4-bis(*E*-dimesitylborylethenyl)naphthalene (**1d**), 9,10-bis(*E*-dimesitylborylethenyl)anthracene (**1e**), 4,4′-bis(*E*-dimesitylborylethenyl)biphenyl (**1f**), 2,7-bis(*E*-dimesitylborylethenyl)fluorene (**1g**), 4,4′-bis(*E*-dimesitylborylethenyl)-*E*-stilbene (**1h**), 4,4′-bis(*E*-dimesitylborylethenyl)tolan (**1i**), 5,5′-bis(*E*-dimesitylborylethenyl)-2,2′-bithiophene (**1j**), 1,4-bis(4-(*E*-dimesitylborylethenyl)phenylethynyl)benzene (**1k**), 1,4-bis(4-(*E*-dimesitylborylethenyl)phenylethynyl)tetrafluorobenzene (**1l**) and 5,5″-bis(*E*-dimesitylborylethenyl)-2,2′:5′,2″-terthiophene (**1m**). The molecular structures of **1a**, **1c**, **1f** and **1m** in the solid state have been determined *via* single-crystal X-ray diffraction. We have previously reported third-order NLO coefficients for compounds **1a** and **1f**,[11d] and the TPA behaviour of **1a**, **1b**, **1c**, **1f**, **1g** and **1h**[15a] as well as the synthesis and optical properties of the related compound, 3,6-bis(*E*-dimesitylborylethenyl)-*N*-*n*-butylcarbazole (**1n**).[15c] In the current paper, we report a theoretical study of second molecular hyperpolarisabilities of the series of boron compounds as well as TPA spectra and cross-sections of **1j** and **1m**, which allows a discussion of the increase in TPA as a function of the number of thienyl units in the linker group.

Results and discussion

Synthesis

The bis(dimesitylborylethenyl)arenes **1a–m** were prepared by hydroboration of 1,4-diethynylbenzene, 1,4-diethynyltetrafluorobenzene, 2,5-diethynylthiophene, 1,4-diethynylnaphthalene, 9,10-diethynylanthracene, 4,4′-diethynylbiphenyl, 2,7-diethynylfluorene, 4,4′-diethynyl-*E*-stilbene, 4,4′-diethynyltolan, 5,5′-diethynyl-2,2′-bithiophene, 1,4-bis(4-ethenylphenylethynyl)benzene, 1,4-bis(4-ethenylphenylethynyl)tetrafluorobenzene and 5,5″-diethynyl-2,2′:5′,2″-terthiophene, respectively, with one equivalent of dimesitylborane dimer in dry THF, under an inert atmosphere, at room temperature, in moderate to good yields as shown in Scheme 1. Only *syn*-, anti-Markovnikov monohydroboration occurred owing to the steric hindrance of the two mesityl groups, as is usually the case. Some of these compounds undergo discolouration over a period of months if left exposed to the air. They can be re-purified by filtration through a silica plug with an appropriate solvent system. The discolouration can be prevented by storage under an inert atmosphere. We were not able to obtain satisfactory elemental analyses for **1j** and **1m**, but were able to obtain satisfactory accurate mass measurements.



Scheme 1 The syntheses of **1a–m**.

Crystal structures

Single crystals of **1a** were grown by cooling a solution in hexane–DCM; however, they desolvated within seconds, whereas single crystals formed overnight from an equimolar solution of **1a** and 1,4-bis(*N*,*N*-dimethylamino)benzene in hexane–DCM contained neither solvent nor diamine and were indefinitely air-stable. Whilst it is clear that the diamine somehow induced crystallisation, the nature of this involvement is unclear, and numerous attempts to grow crystals of other symmetric bis(dimesitylborylethenyl)arenes in the presence of various diamines were unsuccessful. Crystallisation of **1a** from toluene produced the toluene solvate **1a**·3PhMe (**1a′**). Crystals of **1c** and **1m** were grown from hexane–DCM solution (**1c** by refrigeration) and both contained DCM of crystallisation. Though these crystals desolvated rapidly, they could be handled by the oil-drop technique. Crystals of **1f**, obtained by cooling a toluene solution, and containing toluene of crystallisation, desolvated over 10–20 min. It proved impossible to obtain suitable crystals of any of the other

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bis(*E*-dimesitylborylethenyl)arenes despite repeated attempts; cooling solutions resulted in the formation of powders, whereas solvent evaporation resulted in amorphous films.

The crystal of solvent-free **1a** has one independent molecule in a general position. In **1a′** the diboryl molecule lies on a crystallographic inversion centre; of the two crystallographically non-equivalent toluene molecules, one is disordered between two overlapping inversion-related positions and the other between two symmetrically unrelated orientations (also overlapping). Thus, the asymmetric unit contains half of the host molecule and 3/2 of a solvent molecule. The asymmetric unit of **1c** comprises two molecules (*i* and *ii*) with substantially different conformations, and one dichloromethane molecule whose CH_2 group is disordered between two positions. Molecule **1f** lies on a crystallographic inversion centre; the structure also contains two symmetrically non-equivalent toluene molecules, one of which has crystallographic twofold symmetry and the other is disordered between two positions related by a twofold axis. The asymmetric unit of **1m** contains one host molecule, the packing of which leaves elongated voids around inversion centres (one void of 396 $Å^3$ per unit cell, which amounts to *ca.* 16% of the total crystal volume), filled with chaotically disordered solvent. The estimated[30] electron density in each void totals *ca.* 112 electrons. From this, we assumed the void to contain three dichloromethane molecules, *i.e.* 3/2 molecule per formula (asymmetric unit), which were approximated by a set of partially occupied Cl and C positions.

Molecular structures (Fig. 1; selected geometrical parameters are listed in Table 1 and 2) are consistent with those of mono-(dimesitylborylethenyl)arenes.[11a,f] All molecules have *E*,*E*-configurations about the olefinic bonds. Borylethenyl groups adopt transoid configurations in both pseudo-polymorphs of **1a**, in **1f** and in molecule *ii* of **1c**, whereas in molecule *i* of **1c** and in compound **1m**, these groups are cisoid to each other and to the sulfur atom (in **1c**, *i*) or the *adjacent* sulfur atom (in **1m**). Boron atoms have trigonal planar geometries. The planes of the two mesityl rings (*M*1 and *M*2, see Fig. 1) and the ethene B–C=C–C moiety (*En*) are inclined to the boron trigonal plane (BC_3 plane)

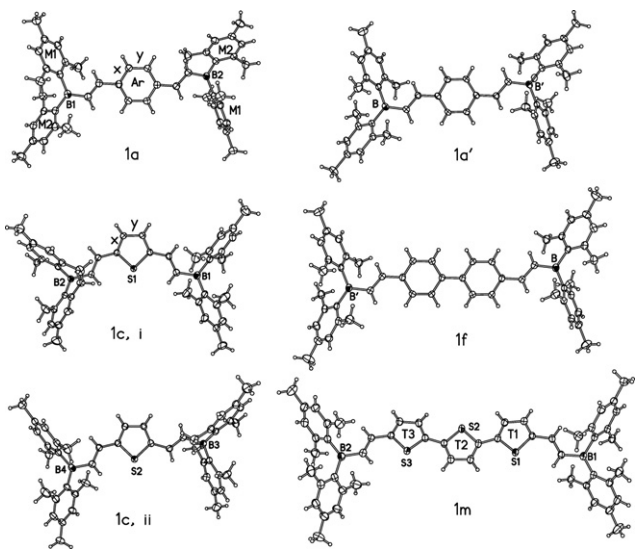

Fig. 1 Molecular structures of **1a**, **1a′** (toluene solvate omitted), **1c** (two independent molecules), **1f** and **1m**. Thermal ellipsoids are drawn at the 50% probability level. Primed atoms are generated by the inversion centre.

Table 1 Interplanar and torsion angles (°)[a]

		$BC_3/M1$	$BC_3/M2$	BC_3/En	*En*/Ar	τ
1a	B(1)	65.2(1)	48.4(1)	9.6(2)	13.7(2)	2.7(1)
	B(2)	66.5(1)	54.9(1)	21.9(2)	14.1(2)	15.2(1)
1a′		60.2(1)	48.1(1)	13.1(2)	3.7(2)	0.1(2)
1c, *i*	B(1)	63.6(1)	52.2(1)	14.6(4)	7.6(4)	3.1(2)
	B(2)	47.7(1)	51.7(1)	30.0(2)	10.2(1)	0.8(2)
1c, *ii*	B(3)	48.4(1)	62.0(1)	24.6(3)	19.8(2)	7.4(2)
	B(4)	61.0(1)	57.0(1)	15.1(4)	1.1(4)	4.2(2)
1f		65.5(1)	50.8(1)	9.1(3)	8.1(3)	0.5(3)
1m	B(1)	59.2(1)	42.5(1)	28.8(1)	12.5(1)	5.1(2)
	B(2)	58.4(1)	53.7(1)	23.1(3)	3.8(3)	6.6(2)

[a] τ =|180° − torsion angle B–C=C–C(Ar)|; *En* = ethene moiety B–C=C–C(Ar).

Table 2 Average bond distances (Å)

	B–C(Mes)	B–C(*En*)	C=C (*En*)	C(*En*)–C(Ar)	*x*	*y*
1a	1.582(2)	1.547(2)	1.3445(18)	1.464(2)	1.400(2)	1.380(2)
1a′	1.576(2)	1.555(2)	1.346(2)	1.463(2)	1.402(2)	1.379(2)
1c	1.576(3)	1.552(3)	1.341(3)	1.447(3)	1.372(3)	1.412(3)
1f	1.584(4)	1.548(4)	1.341(4)	1.461(4)	1.386(4)	1.380(4)
1m	1.574(3)	1.556(3)	1.345(3)	1.451(3)	1.371(3)	1.415(3)

in a propeller-like fashion. The BC_3/M angles are consistently large (48–67°) which must be attributed to intramolecular steric crowding. Such conformation precludes any efficient stacking arrangements in the solid state and generally makes compounds **1** very awkward for crystal packing (see Fig. 2 and ref. 11*d*), which explains why most of them crystallise as solvates or not at

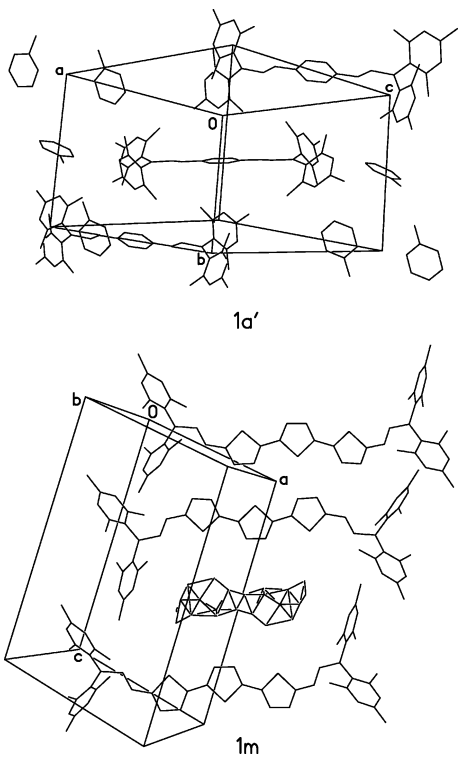

Fig. 2 Crystal packing of **1a′** (omitting the solvent disorder) and **1m**, showing the solvent-occupied cavity.

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all. The link between (and including) the two boron atoms always remains sufficiently planar for π-conjugation, albeit undergoing various minor distortions which can be attributed to the demands of crystal packing rather than any intramolecular effects. Thus, the BC_3/*En* angle varies widely (9–30°), even in the same molecule. The twist between the central arene (Ar) and the ethene moieties ranges from 3 to 20°. In some structures, there is also a small but significant twist around the olefinic bond, which is as high as 15.2° in **1a**; incidentally, this is the only unsolvated structure. In **1f**, the biphenyl group is rigorously planar. In **1m**, the tri(thiophene) moiety adopts a conformation usual for oligothiophenes:[31] roughly planar, with opposite orientations of adjacent rings (inter-ring dihedral angles *T*1/*T*2 6.2°, *T*2/*T*3 10.9°).

Bond distances do not change significantly with conformation. As in mono-(dimesitylborylethenyl)arenes,[11a,f] the B–C(ethenyl) bonds in **1** are slightly shorter than B–C(mes) (Table 3), which is probably due to π-delocalisation along the chain, *vide infra*. Indeed, the central arene ring in both **1a** and **1a′** shows a slight quinoidal distortion with $\Delta = \langle x \rangle - \langle y \rangle = 0.02$ Å, although Δ is insignificant in **1f**. The ethenyl group forms a slightly shorter C–C bond with a thiophene than with a benzene ring; the bonds between thiophene rings in **1m** [1.450(3) and 1.455(3) Å] are also shorter than that between the benzene rings in **1f** [1.485(4) Å]; however, the B–C and ethenyl (C=C) bond lengths remain practically identical.

Optical properties

The absorption maxima, extinction coefficients, fluorescence maxima and quantum yields were measured for compounds **1a–i** and **1k–l** in cyclohexane solutions, and **1j** and **1m** in toluene solutions. The data are given in Table 3, together with results for some of the compounds for which spectra had been measured in DCM solutions for comparison.[15a] The compounds exhibit absorption maxima in the range 362–469 nm. The longest wavelength absorptions are observed for compound **1m**, which is attributed to the better conjugation which occurs in the thienyl systems. It is notable that compound **1f** has a shorter wavelength maximum than **1a**, indicating that the biphenylene group is effectively less conjugated than the phenylene group. This is probably a consequence of the distribution of rotamers in solution. This postulate is corroborated by noting the much longer wavelength absorption of compound **1g**, which contains the rigidly planar fluorenylene group. The most intense absorption of compound **1h** occurs at a longer wavelength than that of **1i**, indicating that conjugation in the stilbenyl system is more efficient than that in the tolan-based one. The BPEB-based systems **1k** and **1l** do not have significantly longer wavelength absorptions than **1i**, again likely due to the distribution of rotamers present in solution, a phenomenon we have discussed previously.[32] The extinction coefficients of the most intense absorption maxima of compounds **1a–h** are in the range 42 000–89 000 M^{-1} cm^{-1}. They generally increase as the conjugated system becomes longer.

The fluorescence maxima, upon excitation at 340 nm, are in the range 406–565 nm. They generally follow a similar pattern to the absorption maxima. The quantum yields, measured in hydrocarbon solvents, range from below 0.005 for **1e** to 0.38 for **1h**. They are generally larger for the extended systems **1h–m**, and have similar values to those measured in DCM solutions. The quantum yield of compound **1b** is almost five times that of **1a**, which must result from its fluorination, and is 1.5 times greater than in DCM. Compound **1c** has a much lower fluorescence quantum yield, which may be attributable to the presence of the heavier sulfur atom in the thiophene ring, enhancing the intersystem crossing rate. The quantum yield of **1e** is the lowest, which could be a result of it being unable to adopt a planar conformation required for efficient fluorescence, due to steric interaction between the vinylic hydrogen and the anthracenyl moiety, and can be contrasted with the very large quantum yield of 9,10-bis(dimesitylboryl)anthracene in toluene (0.68).[11d] The naphthalene-based compound **1d** has a quantum yield nearly eight times larger than that of **1e** probably because it is able to achieve planarity in its cisoid configuration.

Their Stokes shifts range from 700 cm^{-1} for **1g** to 5200 cm^{-1} for **1e**. For some of the compounds which also had their optical properties measured in DCM solution (**1a–c** and **1f–h**),[15a] significant variations in their Stokes shifts with solvent were observed. For compounds **1a** and **1g**, this can be explained by variation of the respective emission intensities and extinction coefficients of their vibrational bands. Such an explanation cannot be invoked to explain the solvent-dependent shift in emission of **1b**, in which only one broad band is observed, the

Table 3 Optical properties of **1a–m** in cyclohexane solution (unless otherwise stated)[a]

Compound	λ_{max} (abs)/nm	ε/M^{-1} cm^{-1}	λ_{max} (em)/nm	Stokes shift/cm^{-1}	Φ
1a	372 (373)	42 000 (45 000)	406 (433)	2300 (3700)	0.015 (0.032)
1b	362 (360)	47 000 (38 000)	440 (505)	4900 (8000)	0.073 (0.045)
1c	411	48 000	452	2200	0.010
1d	396	67 000	454	3200	0.038
1e	436	70 000	565	5200	<0.005
1f	365 (370)	58 000 (52 000)	408 (419)	2900 (3200)	0.054 (0.084)
1g	406 (386)	75 000 (57 000)	417 (430)	700 (2700)	0.098 (0.043)
1h	397 (399)	83 000 (70 000)	434 (447)	2200 (2700)	0.38 (0.55)
1i	377	64 000	410	2100	0.22
1j[b]	449	48 000	506	2500	0.13
1k	380	89 000	412	2100	0.16
1l	376	85 000	410	2200	0.21
1m[b]	469	51 000	537	2700	0.20

[a] Values obtained in DCM solution given in parentheses (ref. 15*a*). [b] Measured in toluene solution.

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maximum of which in cyclohexane solution is blue-shifted by 65 nm in the latter, compared to the values obtained in DCM solution. The very large Stokes shift of **1b** in DCM solution (8000 cm^{-1}) was attributed to a highly reorganised excited state, possibly a twisted intramolecular charge-transfer (TICT) state.[15a] Therefore, it can be assumed that its reorganisation energy is significantly lower in cyclohexane solution. (Note: the absorption and emission spectra of **1c** were remeasured in DCM and were found to be very similar to those obtained in cyclohexane. It would appear that there was an impurity present in the original samples, leading to an erroneously high energy value previously reported by us for λ_{max}(abs).)[15a] In addition, the fluorescence lifetimes of **1j** and **1m** were measured in toluene solution and found to be 0.62 ns and 0.96 ns, respectively. These values are similar to that of **1n** measured in toluene,[15c] and to the values for several of these compounds measured in DCM, which, with the exception of **1b**, were all below 1 ns.[15a]

Two-photon absorption measurements

Two-photon processes are rapidly becoming the focus of much attention due to their potential applications in laser scanning microscopy,[33] 3-D optical data storage,[34] localised photodynamic therapy,[35] microfabrication and optical power limitation.[36] A comprehensive review of the two-photon properties of conjugated molecular materials has recently been published.[37]

The two-photon absorption (TPA) cross-sections, σ_2, of **1j** and **1m** were measured in toluene solution, at 5 nm intervals from 750 nm to *ca.* 930 nm. A plot of TPA cross-section, *vs.* half of the excitation wavelength for both **1j** and **1m** is shown in Fig. 3, together with their linear absorption spectra for comparison. The TPA maximum, σ_2^{max}, of **1j** occurs at <750 nm, and is likely to be >800 GM, which is significantly greater than that reported for **1c** in DCM, which was found to be only *ca.* 20 GM (although, in light of the discrepancies found for the previously reported absorption and emission spectra of **1c**, *vide supra*, this value may be inaccurate).[15a] The σ_2^{max} of **1m** was found to occur at *ca.* 800 nm and to be *ca.* 1800 GM. The fact that both of these maxima occur at significantly shorter wavelengths than twice those of their respective one-photon absorption maxima indicates excitation to higher energy states than the S_1 state, most likely to S_2 which is consistent with the selection rules for quadrupolar molecules such as these.[38] Indeed, the TD-DFT UV-vis computed spectra of **1j** and **1m** (see Fig. S1 and Table S1 in ESI‡) show high energy one-photon excitations, with lower oscillator strengths than that of the excitation to the S_1 state. The lowest energy absorption involves mainly a HOMO → LUMO transition (leading to the S_1 state) computed to occur at 561 nm for **1m**. This value is significantly lower in energy than the experimental value of λ_{max} at 469 nm, as expected. Thus, the computed value is based on a gas-phase optimised structure which is close to planar, whereas in solution an ensemble of rotamers is present, *vide supra*.[32] Several higher energy transitions with low oscillator strengths are computed around or below 400 nm; HOMO − 1 → LUMO and HOMO − 3 → LUMO transitions at 410 nm ($S_0 \rightarrow S_2$), and HOMO − 1 → LUMO + 1 and HOMO − 2 → LUMO + 1 transitions at 336–331 nm arise for **1m**. Similarly, in the case of **1j**, high energy one-photon transitions arise at 413 nm (HOMO − 2 → LUMO, $S_0 \rightarrow S_2$) and 316–310 nm (HOMO − 1 → LUMO + 1 and HOMO − 3 → LUMO + 1), largely separated in energy from the intense HOMO–LUMO transition which is computed to occur at 515 nm in simulated toluene solvent using the PCM model (see Computational details), corresponding to the experimentally observed absorption band centred at 449 nm.

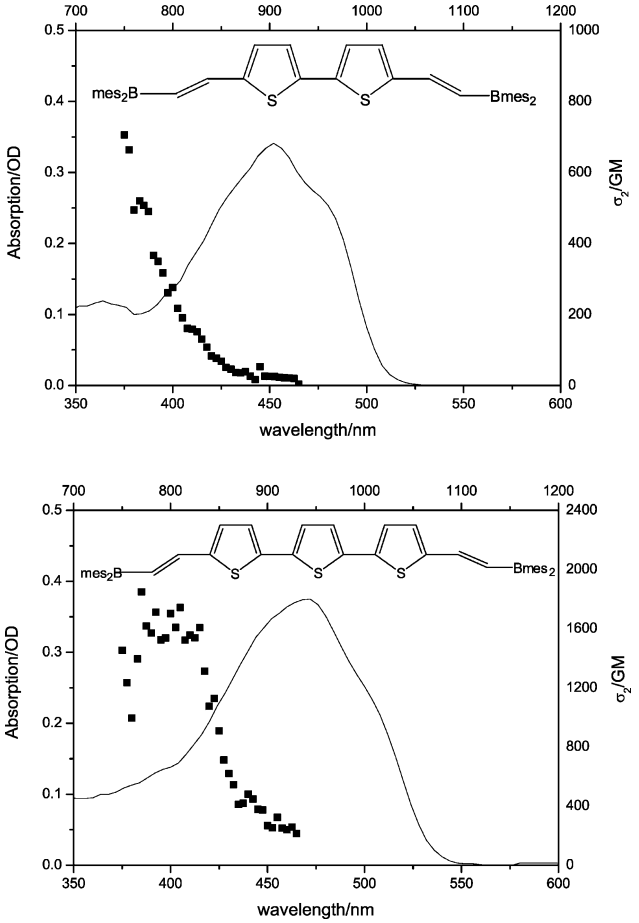

Fig. 3 Plots of one-photon absorption *vs.* wavelength (solid lines, left-hand side and bottom axes) and two-photon absorption cross-section *vs.* wavelength (filled squares, right-hand side and top axes) for **1j** and **1m** in toluene.

To the best of our knowledge, σ_2^{max} for **1m** represents the highest value for a boron-containing molecule, significantly exceeding that of the related compound, *E*,*E*-1,4-bis(2′-[5′-(dimesitylboryl)thiophen-2-yl]ethenyl)benzene (1340 GM),[14d] as well as several bis(dioxaborine) compounds.[39] There are only a few reports on the TPA of thiophene-containing molecules, although several such molecules, shown in Fig. 4, have been found to exhibit large σ_2 values.[40,41] Compound **A** was found to have a σ_2^{max} value of 2560 GM at 740 nm,[40a] whereas the related compounds **B** and **C** have σ_2 values of 3040 GM and 5480 GM, respectively, at 705 nm, and probably even higher values at shorter wavelengths.[40b] Interestingly, the related compound **D**, which contains terminal thienyl moieties instead of phenylene ones, has a σ_2 value of only 850 GM at 705 nm (although again, probably larger values at lower wavelengths). Compound **E** was found to have a σ_2^{max} value of *ca.* 3700 GM, which occurs at *ca.* 650 nm.[41]

The σ_2^{max}/MW value for **1m** is *ca.* 2.26 GM, and its σ_2^{max}/N_{eff} value, where N_{eff} is the effective number of conjugated electrons,[42] is *ca.* 90 GM, which is larger than the corresponding

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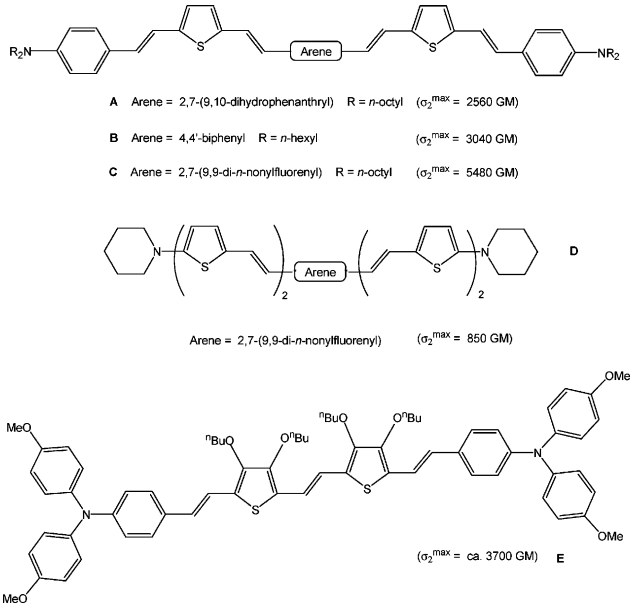

Fig. 4 Structures of thiophene-containing compounds for which TPA cross-sections have been reported.

values for all of the above compounds, except for **C** and **E**, which have values of 137 GM and *ca.* 130 GM, respectively. However, a better method of comparison is to use σ_2^{max}/N_{eff}^2 values, as this quotient has been found to be relatively constant in systems composed of similar units, such as dendrimers, a result that is predicted by a theoretical approach using the Thomas–Kuhn sum rules.[42b] The σ_2^{max}/N_{eff}^2 value of **1m** is *ca.* 4.5 GM, which can be compared with values of *ca.* 3.4 GM for **C** (for the largest σ_2 value observed) and *ca.* 4.5 GM for **E**. These results indicate that the terminally substituted dimesitylborylethenyl-oligothiophene motif is an excellent one for induction of large TPA cross-sections, with extended analogues likely to show significantly higher σ_2^{max} values.

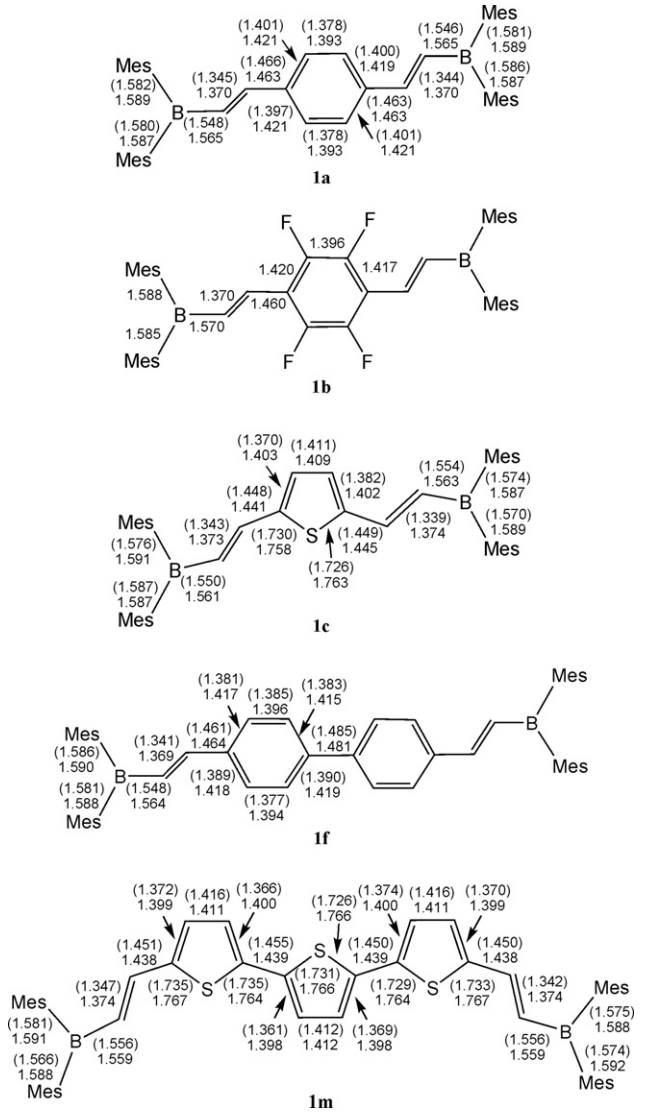

Fig. 5 Computed bond lengths for compounds **1a–c** and **1f**. Experimental distances are given in parentheses for **1a**, **1c** (transoid form *ii*), **1f**, and **1m**.

Computational studies on the molecular and electronic structures and second hyperpolarisabilities

Semi-empirical calculations at the AM1 level and more sophisticated density functional theory (DFT) calculations (see Experimental section for computational details) were conducted on the whole series of compounds **1a–n**.

Their ground state geometries were first optimised at the DFT level. Pertinent calculated bond lengths for a selected group of compounds (**1a–c**, **1f** and **1m**) representative of the whole set of compounds studied are given in Fig. 5 and are compared to their corresponding crystallographically measured values where available. A rather good agreement is observed between theory and experiment, with overestimations not larger than a few hundredths of an Å. This gives confidence in the computed bond distances in molecules such as **1b** for instance, for which no X-ray diffraction data are available yet. The nature of the spacer barely affects the B–C bond distances, which are very similar in all the compounds considered, *ca.* 1.56 Å. Fluorine substitutions on the central phenyl do not affect the external C–C bonds (1.46 Å and 1.37 Å; compare **1a** and **1b** in Fig. 5). As observed experimentally, some distortion of the aryl rings towards a quinoidal structure is computed ($\Delta \sim 0.03$ Å).

Both dynamic and static second-order hyperpolarisabilities, γ_{stat} and γ_{THG} (Table 5), have been computed at the AM1 level for the whole series of symmetrical compounds. Only two experimental values[43] are available, namely for **1a** and **1f**, which are 155×10^{-36} and 229×10^{-36} esu, respectively, whereas the computed values are 357×10^{-36} and 611×10^{-36} esu. The agreement between the measured and the computed values is qualitatively correct.

Because of their structural similarities, four series of compounds are considered for discussion. The **1a–1e** series of compounds differs by the nature of the central ring: benzene (**1a**), tetrafluorobenzene (**1b**), thiophene (**1c**), naphthyl (**1d**) and anthryl (**1e**). The **1f–1i** and **1n** series includes compounds with two phenyl rings linked by a single bond (biphenyl, **1f**, **1g** and **1n**), a double bond (stilbene, **1h**), and a triple bond (tolan, **1i**). We will add **1a** with one phenyl group, and **1k** and **1l** with three

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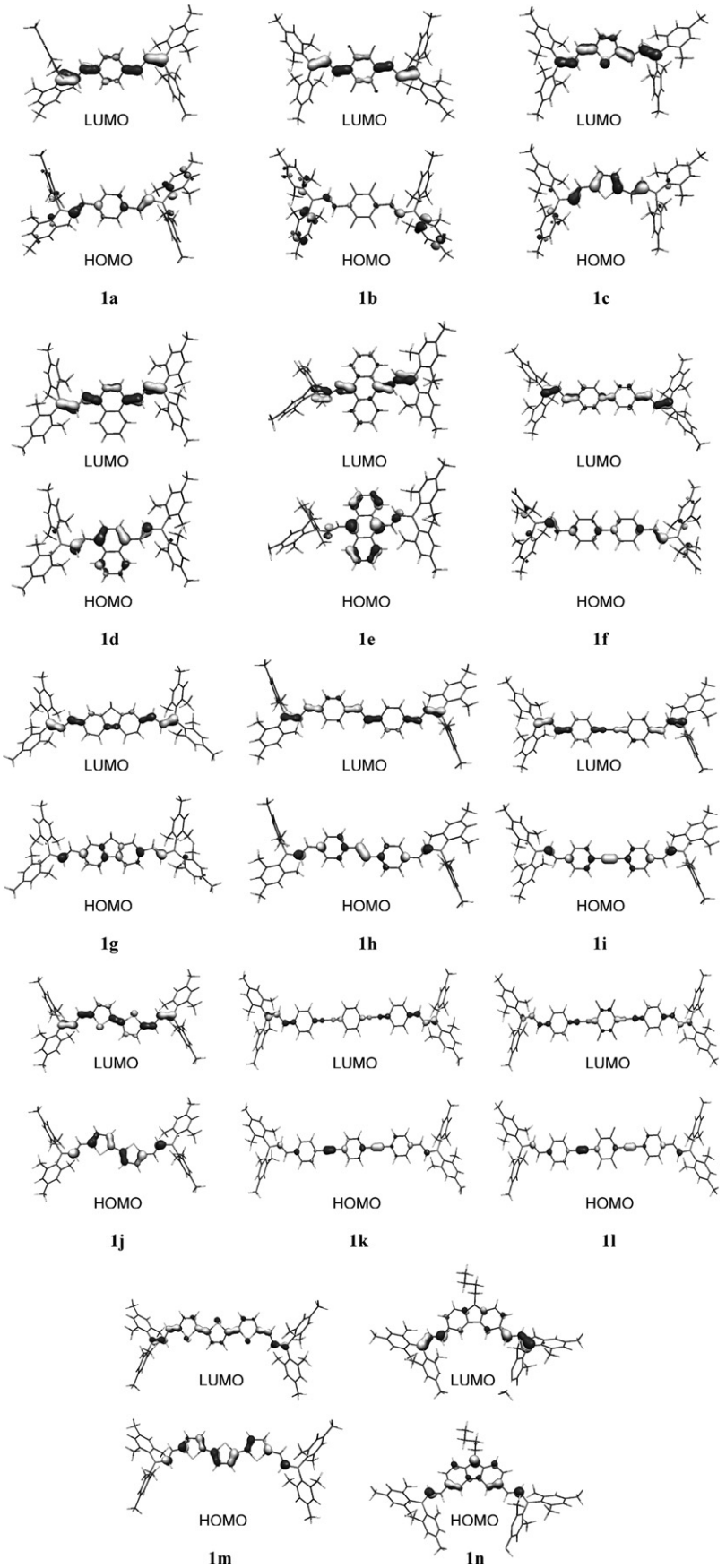

Fig. 6 HOMO and LUMO plots for compounds **1a–n**.

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Table 4 Static (γ_{stat}), dynamic (γ_{THG}) second-order hyperpolarisabilities (10^{-36} esu), HOMO–LUMO gaps (ΔE_{HL}, eV) and HOMO energies (E_H, eV) computed for the **1a–n** series. Experimental values are given in parentheses where available

Compound	γ_{stat}	γ_{THG}	ΔE_{HL}	E_H
1a	205	357 (155)	2.09	−5.22
1b	210	385	2.01	−5.34
1c	235	483	1.83	−5.09
1d	217	433	1.90	−5.03
1e	196	535	1.55	−4.72
1f	332	611 (229)	2.14	−5.14
1g	362	757	2.06	−5.06
1h	641	1418	1.84	−4.98
1i	529	1053	1.97	−5.12
1j	530	1528	1.63	−4.90
1k	1031	2231	1.83	−5.14
1l	1160	2752	1.83	−4.98
1m	983	3812	1.49	−4.76
1n	252	448	2.25	−4.90

phenyl rings (**1k**) and two phenyls and one tetrafluorobenzene ring (**1l**) to this series. Another series, **1c**, **1j** and **1m**, contains compounds with one thiophene ring (**1c**), two thiophene rings (**1j**) and three thiophene rings (**1m**). Indeed, in all of the compounds, the spacer plays the role of the donor vis-à-vis the two dimesitylborylethenyl fragments.

The calculated second hyperpolarisabilities, γ_{THG}, for the hydrogenated and fluorinated species are almost equal; $\gamma_{THG} = 357 \times 10^{-36}$ esu and 385×10^{-36} esu for **1a** and **1b**, respectively. Replacement of a phenyl ring (**1a**) by a naphthyl (**1d**) or an anthryl (**1e**) group leads to γ values of the same order of magnitude with a slight increase for γ_{THG} from **1a** (357×10^{-36} esu) to **1d** (433×10^{-36} esu) to **1e** (535×10^{-36} esu). Finally, with thiophene (**1c**) instead of benzene (**1a**), a slightly higher γ_{THG} value is computed (483×10^{-36} esu).

More importantly, the magnitude of γ is more strongly dependent on the length of the bridge. A comparison of **1a** and **1f** shows that the incorporation of a second phenyl ring roughly doubles γ_{THG} (357×10^{-36} *vs.* 611×10^{-36} esu). Comparable values for the related compounds **1g** (fluorene) and **1n** (carbazole) are obtained (757×10^{-36} esu and 448×10^{-36} esu, respectively). Moreover, the addition of double (**1h**) or triple (**1i**) C–C bonds between the phenyl rings greatly increases the second-order hyperpolarisabilities (1418×10^{-36} esu and 1053×10^{-36} esu, respectively). Interestingly, the second-order hyperpolarisabilities increase to over 2000×10^{-36} esu upon incorporation of three phenyl rings (**1k**) or two phenyl and one tetrafluorobenzene ring (**1l**) separated by ethynyl groups (2231×10^{-36} esu and 2752×10^{-36} esu, respectively).

Increasing the number of thiophene rings in the bridge leads to a very strong enhancement of γ_{THG}, which rises from 483×10^{-36} esu with one ring (**1c**) to 1528×10^{-36} esu with two rings (**1j**) to 3812×10^{-36} esu with three rings (**1m**). We note that the rise is more dramatic when thiophene units, rather than phenyl groups, are added in the spacer. For example, γ_{THG} changes from 357×10^{-36} esu for **1a** (one phenyl) to 2231×10^{-36} esu for **1k** (three phenyls + two ethynyl groups), but goes from 483×10^{-36} esu for **1c** (one thiophene) to 3812×10^{-36} esu for **1m** (three thiophenes).

It is worth considering whether the characteristics of the HOMO → LUMO excitation affect the γ values of these symmetrical molecules. Energy and nodal properties of the HOMO and LUMO for the whole series, computed at the DFT level, are shown in Fig. 6. Overall, the LUMOs are highly delocalised over the boron atoms and the spacer, whereas the HOMOs are mainly localised on the spacer, except for **1a**, **1b** and **1f** where they are localised on the mesityl groups. HOMO → LUMO transitions thus represent quadrupolar charge-transfer from the centres to the ends of the molecules.

As can be seen in Table 4, HOMO–LUMO gaps are not very different in the whole series. However, it is noteworthy that overall HOMO–LUMO energy gaps (ΔE_{HL}) vary inversely with γ_{THG} for each series, *i.e.*, the latter becomes larger as ΔE_{HL} diminishes, but it is just a crude correlation, which is not strictly respected in all series. Some deviations are observed. For example, for the **1a**, **1f**, **1h**, and **1i** series, γ values vary as γ (**1a**) < γ (**1f**) < γ (**1i**) < γ (**1h**), whereas the HOMO–LUMO gaps change as ΔE_{HL} (**1f**) > ΔE_{HL} (**1a**) > ΔE_{HL} (**1i**) > ΔE_{HL} (**1h**). The inversion between **1a** and **1f** may be related to geometrical factors. Indeed, **1f**, with two phenyl groups, is not fully planar in the gas-phase optimised structure, due to steric repulsion between the *ortho*-hydrogen atoms of the two phenyl neighbours. The loss of planarity leads to a larger calculated ΔE_{HL}. It is thus intriguing that in the experimental solid state structure, *vide supra*, the two phenyl rings are coplanar.

More interestingly, we note that the increase in γ within each series of compounds is somewhat related to the HOMO energy, which itself depends upon the donor strength of the spacer. Indeed, the higher the HOMO energy is (which increases with increasing donating capabilities of the spacer), the larger the γ values are, in general.

For the **1a–1e** series, γ (**1a**) < γ (**1b**) < γ (**1d**) < γ (**1c**) < γ (**1e**) whereas the energies of the HOMO (E_H) vary as E_H (tetrafluorobenzene, **1b**) < E_H (benzene, **1a**) < E_H (thiophene, **1c**) ~ E_H (naphthyl, **1d**) < E_H (anthryl, **1e**). This is less satisfactory than that for the **1a**, **1f**, **1h**, and **1i** series, γ (**1a**) < γ (**1f**) < γ (**1i**) < γ (**1h**) < γ (**1k**) but E_H (benzene, **1a**) < E_H (biphenyl, **1f**) = E_H (bisphenylethynylbenzene, **1k**) ~ E_H (tolan, **1i**) < E_H (stilbene, **1h**). In the case of the **1c**, **1j**, and **1m** series, we note that the ranking γ (**1c**) < γ (**1j**) < γ (**1m**) strictly matches that of E_H, *i.e.* E_H (thiophene, **1c**) < E_H (bithiophene, **1j**) < E_H (terthiophene, **1m**).

Conclusions

A series of bis(*E*-dimesitylborylethenyl)arenes have been synthesised *via* hydroboration of the appropriate diethynylarenes with dimesitylborane. Theoretical studies show that the increase of γ in each series of compounds is generally related to the HOMO energy, which itself depends upon the donor strength of the spacer. The higher the HOMO energy is the larger the γ values are, in general. A strong enhancement of γ is predicted and the TPA cross-sections increase dramatically as the number of thiophene rings in the spacer increases. The terthiophene compound, **1m**, shows a very large TPA cross-section of *ca.* 1800 GM.

Experimental

General manipulations and synthetic techniques

All reactions were carried out under an inert atmosphere in an Innovative Technology System 1 glovebox. THF solvent was

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either distilled under nitrogen from sodium–benzophenone, or dried and deoxygenated by passage through columns of activated alumina and R311 catalyst under argon pressure using an Innovative Technology SPS-400 solvent purification system. All other solvents were GPR grade and used as received. Dimesitylborane was prepared according to the literature procedure.[44] The starting materials 1,4-diethynylbenzene,[45] 1,4-diethynyltetrafluorobenzene,[46] 2,5-diethynylthiophene,[47] 1,4-diethynylnaphthlalene,[48] 9,10-diethynylanthracene,[49] 4,4′-diethynylbiphenyl,[50] 2,7-diethynylfluorene,[51] 4,4′-diethynyl-*E*-stilbene,[52] 4,4′-diethynyltolan,[53] 5,5′-diethynyl-2,2′-bithiophene,[47] 1,4-bis(4-ethynylphenylethynyl)benzene[54] and 5,5″-diethynyl-2,2′:5′,2″-terthiophene[47] were prepared according to literature procedures. The synthesis of 1,4-bis(4-ethynylphenylethynyl)tetrafluorobenzene will be reported in due course.

NMR experiments were performed in $CDCl_3$, CD_2Cl_2 or d_6-benzene on a Varian Mercury-200, Inova-500 or Bruker Avance-400 instrument at the following frequencies: ^{1}H: 200, 400, 500 MHz; ^{13}C: 50, 100 MHz; ^{11}B: 96 MHz and ^{19}F: 188 MHz. Proton and ^{13}C NMR spectra were referenced to residual protons in the solvent relative to external $SiMe_4$. ^{19}F NMR spectra were referenced to $CFCl_3$ as the external standard. ^{11}B NMR spectra were referenced to external $BF_3 \cdot Et_2O$. All coupling constants, *J*, are given in Hz. All ^{13}C NMR spectra are ^{1}H decoupled. Due to the exceptionally broad nature of peaks in the ^{11}B NMR spectra of these compounds, it often proved impossible to obtain suitable spectra. Standard MS (EI) analyses were obtained on a Micromass Autospec in EI operation, except for **1a** and **1f**, which were obtained using negative CI with argon gas. Accurate mass HRMS analyses were performed either by ESI$^+$ on a 0.01 mg ml^{-1} solution in DCM–methanol (9 : 1 v/v) using a Thermo-Finnigan LTQFT spectrometer (**1j**) or as a powder using an ASAP probe attached to a Waters LCT spectrometer (**1m**). Elemental analyses were carried out on an Exeter Analytical CE-440 analyzer at Durham University.

Preparation of bis(*E*-dimesitylborylethenyl)arenes

1,4-Bis(*E*-dimesitylborylethenyl)benzene 1a. To a solution of 1,4-diethynylbenzene (0.12 g, 0.95 mmol) in THF (15 ml) was added dropwise with rapid stirring, at room temperature, a solution of dimesitylborane (0.50 g, 2.0 mmol) in THF (25 ml). The colourless mixture was stirred for 2 h, during which time a pale yellow colour evolved. GC-MS analysis revealed no sign of either diethynylbenzene or dimesitylborane. The solvent was removed *in vacuo* and residual THF was removed by stirring in ether followed by removal of solvent *in vacuo* (3 times), resulting in a pale yellow powder. After checking for purity by ^{1}H NMR spectroscopy, the powder was recrystallised from DCM–hexane as the 1 : 1 DCM solvate to give **1a** (0.51 g, 75%).

(Found: C, 79.89; H, 7.55. Calc. for $C_{46}H_{52}B_2 \cdot CH_2Cl_2$: C, 79.40; H, 7.65%); δ_H (200 MHz, C_6D_6) 7.53 (2H, d, *J* 18), 7.34 (2H, d, *J* 18), 7.18 (4H, s), 6.85 (8H, s), 2.35 (24H, s), 2.20 (12H, s); δ_C (50 MHz, C_6D_6) 152.4, 142.1, 140.7, 138.7, 138.2, 136.0, 128.8, 128.7, 23.5, 21.1; δ_B (96 MHz, $CDCl_3$) 40; *m*/*z* (CI$^-$) 626 (M$^+$), 506 (−mesitylene), 275, 164.

1,4-Bis(*E*-dimesitylborylethenyl)tetrafluorobenzene 1b. The electronegativity of the attached fluorine atoms results in a low reactivity of diethynyltetrafluorobenzene towards hydroboration. For this reason, an extended reaction time was required for complete conversion. Similar to the preparation of **1a**, a solution of 1,4-diethynyltetrafluorobenzene (0.18 g, 0.91 mmol) in THF (15 ml) was reacted with a solution of dimesitylborane (0.5 g, 2.0 mmol) in THF (25 ml) for 3 d. The yellow powder was recrystallised from DCM to give **1b** (0.55 g, 87%).

(Found: C, 79.25; H, 7.02. Calc. for $C_{46}H_{48}B_2F_4$: C, 79.10; H, 6.93%); δ_H (400 MHz, $CDCl_3$) 7.75 (2H, d, *J* 18), 7.03 (2H, d, *J* 18), 6.83 (8H, s), 2.29 (12H, s), 2.17 (24H, s); δ_C (100 MHz, $CDCl_3$) 147.8, 145.1 (d, *J* 260), 141.5, 140.7, 139.1, 135.6, 128.4, 117.4, 23.4, 21.2; δ_F (188 MHz, $CDCl_3$) −143.8; *m*/*z* (EI) 698 (M$^+$), 578 (−mesitylene), 448.

2,5-Bis(*E*-dimesitylborylethenyl)thiophene 1c. Similar to the preparation of **1a**, a solution of 2,5-diethynylthiophene (0.25 g, 1.9 mmol) in THF (10 ml) and ether (5 ml) was reacted with a solution of dimesitylborane (1.0 g) in THF (25 ml). Over 12 h, the solution evolved an intense yellow colour. After removal of THF, the resulting orange oil was mixed with ether (10 ml), and hexane (20 ml) was added to precipitate the product as a bright yellow powder to give **1c** (0.44 g, 35%).

(Found: C, 83.45; H, 8.04. Calc. for $C_{44}H_{50}B_2S$: C, 83.55; H, 7.97%); δ_H (500 MHz, C_6D_6) 7.28 (4H, m), 6.80 (8H, s), 6.26 (2H, s), 2.29 (24H, s), 2.18 (12H, s); δ_C (50 MHz, C_6D_6) 146.7, 144.3, 142.4, 140.7, 139.4, 138.6, 131.2, 128.7, 23.4, 21.1; δ_B (96 MHz, $CDCl_3$) 55; *m*/*z* (EI) 632 (M$^+$), 512 (−mesitylene).

1,4-Bis(*E*-dimesitylborylethenyl)naphthalene 1d. To a solution of freshly prepared 1,4-diethynylnaphthalene (0.10 g, 0.57 mmol) in THF (20 ml) was added solid dimesitylborane (0.265 g, 0.57 mmol). The solution was stirred for 2 d before being concentrated to dryness and washed with hexane (3 × 10 ml). The resulting yellow powder was recrystallised from ether to give **1d** (0.25 g, 64%).

(Found: C, 88.84; H, 8.10. Calc. for $C_{50}H_{54}B_2$: C, 88.76; H, 8.04%); δ_H (500 MHz, C_6D_6) 8.26 (2H, d, *J* 17), 8.01 (2H, br s), 7.77 (2H, s), 7.64 (2H, d, *J* 17), 6.94 (2H, br s), 6.83 (8H, s), 2.36 (24H, s), 2.16 (12H, s); δ_C (100 MHz, C_6D_6) 148.8, 140.7, 138.6, 128.3, 128.0, 127.5, 127.0, 126.5, 125.7, 124.5, 123.9, 23.5, 21.3; δ_B (96 MHz, C_6D_6) 70; *m*/*z* (EI) 676 (M$^+$), 556 (−mesitylene).

9,10-Bis(*E*-dimesitylborylethenyl)anthracene 1e. Similar to the preparation of **1a**, a solution of freshly recrystallised 9,10-diethynylanthracene (0.226 g, 1.0 mmol) in THF (25 ml) was reacted with a solution of dimesitylborane (0.5 g, 2.0 mmol) in THF (25 ml) for 3 d. Removal of solvent and washing with hexane (4 × 15 ml) gave a red–orange powder, which contained various unidentified impurities (by ^{1}H NMR spectroscopy). Column chromatography (silica, eluted with 20 : 1 v/v hexane–acetone) and removal of solvent resulted in an orange powder. It proved impossible to recrystallise this powder in reasonable yield.

(Found: C, 90.01; H, 8.24. Calc. for $C_{54}H_{56}B_2$: C, 89.26; H, 7.77%); δ_H (400 MHz, C_6D_6) 8.16 (4H, m), 8.05(2H, d, *J* 18), 7.30 (2H, d, *J* 18), 7.36 (4H, m), 6.79 (8H, s), 2.27 (24H, s), 2.23 (12H, s); δ_C (100 MHz, $CDCl_3$) 149.4, 140.9, 138.9, 138.8, 134.3, 134.0, 127.8, 127.3, 127.2, 119.3, 22.4, 21.0; *m*/*z* (EI) 726 (M$^+$), 606 (−mesitylene).

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Table 5 Crystallographic data

Compound	**1a**	**1a′**	**1c**	**1f**	**1m**
Formula	$C_{46}H_{52}B_2$	$C_{46}H_{52}B_2 \cdot 3PhMe$	$C_{44}H_{50}B_2S \cdot ½CH_2Cl_2$	$C_{52}H_{56}B_2 \cdot 2PhMe$	$C_{52}H_{54}B_2S_3 \cdot \frac{3}{2}CH_2Cl_2$
Formula weight	626.50	902.90	674.98	886.86	924.14
T/K	120	110	120	120	120
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$I2/a$ (#15)	$P\bar{1}$ (#2)
a/Å	8.3031(7)	15.144(2)	12.479(1)	15.354(1)	11.719(1)
b/Å	28.945(2)	11.4882(15)	17.769(2)	16.332(1)	12.093(1)
c/Å	15.803(1)	16.240(2)	18.516(2)	21.522(2)	18.175(1)
α/°	90	90	79.05(2)	90	84.011(3)
β/°	92.37(1)	99.46(2)	80.04(2)	90.75(2)	78.787(2)
γ/°	90	90	78.07(3)	90	81.317(2)
V/Å^3	3794.8(6)	2787.1(6)	3905.5(7)	5396.3(7)	2490.2(3)
Z	4	2	4	4	2
ρ_{calcd}/g cm^{-3}	1.097	1.076	1.148	1.092	1.232
μ/mm^{-1}	0.06	0.06	0.18	0.06	0.35
2θ max/°	60	55	58	55	61
Total reflections	78 404	28 754	48 948	31 814	34 061
Unique reflections	11 080	6398	20 654	6191	15 077
Parameters	463	392	926	309	607
R_{int}	0.056	0.054	0.070	0.078	0.030
R (F, $I>2\sigma(I)$)	0.047	0.052	0.060	0.077	0.058
wR (F^2, all data)	0.141	0.142	0.168	0.228	0.175

4,4′-Bis(*E*-dimesitylborylethenyl)biphenyl 1f. Similar to the preparation of **1a**, a solution of 4,4′-diethynylbiphenyl (0.19 g, 0.94 mmol) in THF (15 ml) was reacted with a solution of dimesitylborane (0.50 g, 2.0 mmol) in THF (25 ml). The pale yellow powder was recrystallised from DCM–hexane to give **1f** (0.62 g, 90%).

(Found: C, 88.95; H, 8.00. Calc. for $C_{52}H_{56}B_2$: C, 88.89; H, 8.03%); δ_H (200 MHz, $CDCl_3$) 7.63 (8H, s), 7.46 (2H, d, J 18), 7.18 (2H, d, J 18), 6.86 (8H, s), 2.33 (12H, s), 2.22 (24H, s); δ_C (50 MHz, C_6D_6) 151.4, 142.0, 141.4, 140.6, 138.4, 138.2, 137.0, 128.8, 128.5, 128.3, 23.3, 21.1; δ_B (96 MHz, $CDCl_3$) 46; m/z (CI$^-$) 702 (M$^+$), 582 (−mesitylene), 386.

2,7-Bis(*E*-dimesitylborylethenyl)fluorene 1g. Similar to the preparation of **1a**, a solution of 2,7-diethynylfluorene (0.20 g, 0.94 mmol) in THF (15 ml) was reacted with a solution of dimesitylborane (0.50 g, 2.0 mmol) in THF (25 ml). The pale yellow powder was recrystallised from diethyl ether (0.6 g, 86%).

(Found: C, 89.01; H, 8.02. Calc. for $C_{53}H_{56}B_2$: C, 89.08; H, 7.90%); δ_H (400 MHz, $CDCl_3$) 7.75 (4H, m), 7.57 (2H, m), 7.45 (2H, d, J 18), 7.24 (2H, d, J 18), 6.86 (8H, s), 3.91 (2H, s), 2.33 (12H, s), 2.23 (24H, s); δ_C (100 MHz, $CDCl_3$) 152.8, 144.4, 142.8, 142.3, 140.6, 138.4, 137.3, 137.0, 128.2, 127.7, 127.0, 124.5, 120.4, 31.6, 23.3, 21.2; m/z (EI) 714 (M$^+$), 594 (−mesitylene), 468, 248.

4,4′-Bis(*E*-dimesitylborylethenyl)-*E*-stilbene 1h. Similar to the preparation of **1a**, a solution of *trans*-4,4′-diethynylstilbene (0.23 g, 1.0 mmol) in THF (25 ml) was reacted with a solution of dimesitylborane (0.50 g, 2.0 mmol) in THF (25 ml). The bright yellow powder was recrystallised from DCM–hexane to give **1h** (0.60 g, 82%).

(Found: C, 88.94; H, 7.99. Calc. for $C_{54}H_{58}B_2$: C, 89.01; H, 8.02%); δ_H (200 MHz, CD_2Cl_2) 7.46 (8H, s), 7.33 (2H, d, J 18), 7.09 (2H, s), 7.04 (2H, d, J 18), 6.75 (8H, s), 2.21 (12H, s), 2.10 (24H, s); δ_C (50 MHz, CD_2Cl_2) 151.1, 141.4, 138.4, 138.2, 137.7, 137.6, 136.8, 136.5, 128.0, 127.8, 127.3, 126.1, 22.2, 20.1; m/z (EI) 728 (M$^+$), 608 (−mesitylene), 480, 248.

4,4′-Bis(*E*-dimesitylborylethenyl)tolan 1i. Similar to the preparation of **1a**, a solution of 4,4′-diethynyltolan (0.23 g, 1.0 mmol) in THF (20 ml) was reacted with a solution of dimesitylborane (0.5 g, 2.0 mmol). The bright yellow powder was recrystallised from DCM–hexane to give **1i** (0.55 g, 75%).

(Found: C, 89.54; H, 7.95. Calc. for $C_{54}H_{56}B_2$: C, 89.26; H, 7.77%); δ_H (400 MHz, $CDCl_3$) 7.51 (8H, s), 7.41 (2H, d, J 18), 7.11 (2H, d, J 18), 6.84 (8H, s), 2.31 (12H, s), 2.20 (24H, s); δ_C (100 MHz, $CDCl_3$) 151.3, 140.6, 138.6, 137.7, 131.9, 128.3, 128.0, 127.3, 126.9, 124.1, 91.2, 23.3, 21.2; m/z (EI) 726 (M$^+$), 606 (−mesitylene), 248.

5,5′-Bis(*E*-dimesitylborylethenyl)-2,2′-bithiophene 1j. A solution of 5,5′-diethynyl-2,2′-bithiophene (0.04 g, 0.2 mmol) in THF (10 ml) was reacted with a solution of dimesitylborane (0.10 g, 0.4 mmol) in THF (25 ml) for 3 d. Removal of solvent with the assistance of additional ether gave a bright orange powder which was recrystallised from hexane–ether (2 : 1 v/v) to give **1j** (0.04 g, 30%).

δ_H (400 MHz, $CDCl_3$) 7.24–6.99 (8H, m), 6.82 (8H, s), 2.29 (12H, s), 2.19 (24H, s); δ_C (100 MHz, $CDCl_3$) 144.2, 144.1, 140.6, 139.5, 138.9, 138.5, 138.0, 130.9, 128.2, 125.3, 23.2, 21.2; m/z (ESI$^+$) 712.37500 (M$^+$). Calc. for $C_{48}H_{52}{}^{10}B_2S_2$: 712.37637.

1,4-Bis(4-(*E*-dimesitylborylethenyl)phenylethynyl)benzene 1k. Similar to the preparation of **1a**, a solution of 1,4-bis(4-ethynylphenylethynyl)benzene (0.16 g, 0.5 mmol) in THF (15 ml) was reacted with a solution of dimesitylborane (0.25 g, 1.0 mmol) in THF (25 ml). The yellow powder was applied to a pad of silica, and elution with hexane initially, then with DCM, to remove impurities, and recrystallisation from DCM gave **1k** (0.34 g, 84%).

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(Found: C, 89.86; H, 7.54. Calc. for $C_{62}H_{60}B_2$: C, 90.07; H, 7.31%); δ_H (400 MHz, $CDCl_3$) 7.51 (12H, s), 7.41 (2H, d, *J* 18), 7.011 (2H, d, *J* 18), 6.84 (8H, s), 2.31 (12H, s), 2.20 (24H, s); δ_C (100 MHz, $CDCl_3$) 151.2, 142.1, 140.6, 138.6, 137.8, 131.9, 131.6, 128.2, 128.0, 127.3, 124.0, 123.1, 91.4, 90.9, 23.3, 21.2; *m*/*z* (EI) 826 (M^+), 606 (−mesitylene), 248.

1,4-Bis(4-(*E*-dimesitylborylethenyl)phenylethynyl)tetrafluorobenzene 1l. Similar to the preparation of **1a**, a solution of 1,4-bis(4-ethynylphenylethynyl)tetrafluorobenzene (0.10 g, 0.5 mmol) in THF (15 ml) was reacted with a solution of dimesitylborane (0.25 g, 1.0 mmol) in THF (25 ml). After removal of solvent and washing with ether, the yellow powder was applied to a pad of silica, and elution with hexane initially, then with DCM, to remove impurities, and recrystallisation from DCM gave **1l** (0.34 g, 84%).

(Found: C, 83.04; H, 6.59. Calc. for $C_{62}H_{56}B_2F_4$: C, 82.86; H, 6.28%); δ_H (400 MHz, $CDCl_3$) 7.57 (8H, m), 7.46 (2H, d, *J* 18), 7.12 (2H, d, *J*, 18), 6.85 (8H, s), 2.32 (12H, s), 2.21 (24H, s); δ_C (100 Hz, $CDCl_3$) 150.6, 140.6, 139.0, 132.3, 128.3, 128.0, 127.5, 127.3, 126.9, 122.4, 103.6, 23.3, 21.2; δ_F (188 MHz, $CDCl_3$) −137.4; *m*/*z* (EI) 898 (M^+), 778 (−mesitylene), 248.

5,5″-Bis(*E*-dimesitylborylethenyl)-2,2′:5′,2″-terthiophene 1m. A solution of 5,5″-diethynyl-2,2′:5′,2″-terthiophene (0.04 g, 0.14 mmol) in THF (10 ml) was reacted with a solution of dimesitylborane (0.07 g, 0.28 mmol) in THF (25 ml) for 3 d. Removal of solvent with additional ether gave a dark red powder which was recrystallised from hexane–ether (2 : 1 v/v) to give **1m** (0.04 g, 37%).

δ_H (400 MHz, $CDCl_3$) 7.13–6.99 (10H, m), 6.82 (8H, s), 2.29 (12H, s), 2.20 (24H, s); δ_C (100 MHz, $CDCl_3$) 144.3, 143.7, 140.7, 139.4, 138.4, 136.7, 130.9, 128.2, 125.3, 124.7, 23.2, 21.2; *m*/*z* ($ASAP^+$) 794.3651 (M^+). Calc. for $C_{52}H_{54}{}^{10}B_2S_3$: 794.3646.

X-Ray crystallography

X-Ray diffraction experiments were carried out on Bruker 3-circle diffractometers with CCD area detectors SMART 6K (**1a**, **1m**) or SMART 1K (**1a′**, **1c**, **1f**), using graphite-monochromated Mo-K_α radiation ($\bar{\lambda}$ = 0.71073 Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Crystallographic data and other experimental parameters are listed in Table 5. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software,[55] packing and solvent content were analysed using *SQUEEZE* program of the *PLATON* software package.[56]

Optical measurements

UV-vis absorption spectra were obtained using a Hewlett-Packard 8453 diode array spectrophotometer using standard 1 cm quartz cells. Fluorescence spectra and quantum yields were obtained using a Fluoromax-3-22 spectrophotometer. Quantum yields were measured against quinine sulfate in 0.1 M H_2SO_4 ($\Phi = 0.54$) and norharmane in 0.1 M H_2SO_4 ($\Phi = 0.58$) standards for all compounds, except **1j** and **1m**, which were measured against fluorescein in 0.1 M NaOH (Φ = 0.9). Fluorescence lifetimes were measured by time-correlated single photon counting (TCSPC) using a 396 nm pulsed laser diode.

Two-photon absorption methodology

Two-photon absorption measurements were performed as described previously.[57] The TPA excitation spectra were calculated using fluorescein in 0.1 M NaOH as a reference using the relation:

$$\frac{\sigma_2^S(\lambda_{exc})\phi^S}{\sigma_2^R(\lambda_{exc})\phi^R} = \frac{C_R n_S F^S(\lambda_{em})}{C_S n_R F^R(\lambda_{em})}$$

where σ_2 is the TPA cross-section for sample and reference, ϕ is the photo-luminescence quantum yield (PLQY), *C* is the concentration, *n* is the refractive index and $F(\lambda_{em})$ is the corrected integrated PL spectrum. The TPA values for fluorescein at various excitation wavelengths have been determined by Albota *et al.*[58] with the following modification. The TPA cross-section curve of Albota *et al.* was extrapolated to 5 nm steps corresponding to the measured spectra of this current work. Each spectrum was averaged over 10 separate measurements to accommodate for any fluctuations of the laser excitation source or local heating in the sample and reference materials.

Computational details

The computed molecular structures were optimised at the BP86/6-31G* level using the GAUSSIAN 03 package.[59] Second hyperpolarisability calculations were carried out at the AM1 level[60] using the linear-scaling semi-empirical program MOPAC program.[61] Dynamic hyperpolarisabilities were calculated at 1907 nm ($\hbar\omega$ = 0.65 eV). Representations of the molecular orbitals were plotted using MOLEKEL4.3.[62] Standard TD-DFT PBE0/6-31G* calculations,[63] including solvent effects (toluene) *via* the PCM model, have been carried out using the GAUSSIAN 03 package.

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