Electronic Supplementary Material (ESI) for New Journal of Chemistry

Photophysical property trends for a homologous series of bis-ethynyl-substituted benzochalcogendiazoles

Electronic Supporting Information

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Experimental Details

Chemicals

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Fluka, Merck, ABCR) or kindly donated by Prof. G. Helmchen and used without further purification. Solvents such as THF and DCM were dried in drying apparatus MB SPS-800. Air- and moisture-sensitive reactions were carried out in heat-gun-dried glassware under an atmosphere of nitrogen. Deuterated solvents were purchased from Deutero GmbH.

All NMR spectra were recorded in $CDCl_3$ at room temperature on a Bruker Avance 300 (300 MHz) spectrometer. The chemical shifts are reported in ppm downfield to TMS and referenced using the residual $CHCl_3$ ($\delta = 7.26$) resonance for ^{1}H-NMR and the central $CHCl_3$ ($\delta = 77.16$) resonance for ^{13}C-NMR. ^{1}H-NMR spectra assignments are reported as follows (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad signal; coupling constant(s) in Hz; integration). Mass spectra were recorded on an Bruker ApexQe FT-ICR Instrument or an JOEL JMS-700. Elemental Analysis was performed by the Microanalytical Laborarory of the University of Heidelberg. For column chromatography silica gel from Macherey, Nagel & Co. KG, Düren (Germany) (particle size: 0.04-0.063 mm) was used. Thin layer chromatography was performed on Polygram Sil G/UV 254 plates from Macherrey, Nagel & Co. KG, Düren (Germany).

Photophysical Properties

All photophysical measurements were made using GPR grade solvents. UV-visible absorption spectra were recorded in quartz cuvettes of path length $l = 1$ cm with an absorbance, A, < 0.3 at 400 nm and were measured on a Jasco V-660 or V-670 spectrometer operated with the Jasco provided software. Baseline correction was achieved by reference to pure solvent in the same cuvette.

Excitation and emission photoluminescence spectra were recorded on a PTI QuantMaster™ 40 spectrofluorometer. Samples were held in quartz fluorescence cuvettes, $l = 1$ cm x 1 cm and fluorescence was detected at 90^o to the excitation beam. Solutions had $A = 0.10–0.15$ at the excitation wavelength to minimise inner filter effects. PLQYs were measured using the PTI QuantaMaster™ and the comparative method, employing the fluorescent standard quinine sulphate in 0.1 M sulphuric acid ($\Phi_f = 0.577$ at $\lambda_{ex} = 350$ nm). Data was obtained using the PTI-provided software, but exported, analyzed and plot in Microsoft Excel.

Fluorescence lifetime measurements were made using the time-correlated photon counting method. Briefly this was achieved as follows: a pulsed IBH NanoLED diode (371 nm or 396 nm) was used as an excitation source with emission detected in a 90° geometry by a Perkin Elmer

SPCM-AQR single-photon counting avalanche diode at a wavelength selected by a monochromator (Jobin-Yvon Triax 320) set to a 1 nm bandpass. The signal was digitised by a National Instruments (NI) USB-5133 (8 bit, 100 Ms/s) digitiser and processed and recorded by in-house NI LabVIEW software.

Raman Spectroscopy

Raman spectra were obtained on a Jobin-Yvon LabRAM-HR, with excitation at 633 nm.

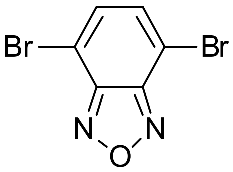
Ab initio Calculation Details

Geometry optimisation calculations were carried out using the Spartan '10 package.[1] Density functional theory (DFT) ground-state optimised structures were calculated using Becke's three parameter Lee-Yang-Parr (B3LYP) exchange-correlation functional with a basis set of 6-311++G**. TD-DFT calculations were performed using Gaussian '09,[2] employing the Becke's three parameter Lee-Yang-Parr (B3LYP) or the Cambridge-B3LYP exchange-correlation functional with a basis set of 6-311++G**.

Orbital surfaces generated from the DFT calculations were visualised in Spartan. The initial geometry input for optimisation was based on a chemically intuitive geometry, when experimental data were not available, to maximise the probability of locating the global minimum on the potential energy surface.

Synthesis of Intermediates

4,7-Dibromobenzofurazan[3]

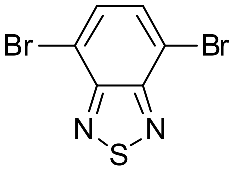


Chemical Formula: $C_6H_2Br_2N_2O$
Molecular Weight: 277.90

Benzofurazan (2.41 g, 20.1 mmol) and iron powder (230 mg, 4 mmol) were placed in a round bottom flask and the materials heated to 90 °C. Elemental bromine (9.6 g, 60 mmol) was added dropwise over an hour, and upon complete addition the reaction mixture was heated at reflux for 2 h. The reaction mixture was allowed to cool, which caused it to solidify. The residue was dissolved in DCM (20 mL) and washed with brine (50 mL). The organic fraction was separated and washed with saturated sodium bicarbonate solution (4 × 50 mL), with brine (3 × 50 mL) and with water (3 × 50 mL). The organic fraction was dried over magnesium sulfate and reduced in vacuo. The brown crude product was chromatographed on silica gel (hexane/ethyl acetate 9:1 eluant) to afford 4,7-dibromobenzofurazan (4.4 g, 78 %) as a cream powder.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51 (s). ^{13}C{^{1}H}NMR ($CDCl_3$, 101 MHz): δ 149.4, 134.2, 108.7. GCMS (EI): m/z 276-278-280 [M including splitting characteristic of isotopic abundances of dibrominated species $C_6H_2Br_2N_2S$].

4,7-Dibromobenzothiadiazole[4]

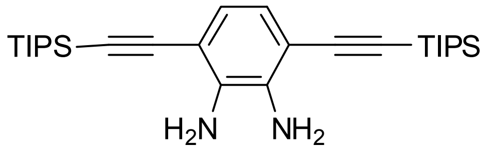


Chemical Formula: $C_6H_2Br_2N_2S$
Molecular Weight: 293.97

o-Phenyldiamine (5 g, 46 mmol) was added to a mixture of DCM and Et_3N (220 mL, v/v 10:1) and the solid totally dissolved by sonication. Thionyl chloride (6.7 mL, 92 mmol) was added drop–wise and the mixture refluxed for 3 h. The solvent was removed *in vacuo* and water was added (100 mL). Hydrochloric acid (5 M) was added slowly to achieve a pH of 1, and then the product was extracted with DCM and the organic layer dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product purified by recrystallisation from hot hexane to yield an orange crystalline solid (5.3 g, 85 %). A portion of this product (1.5 g, 11 mmol) was reacted on immediately by taking into HBr (48 %, 30 mL), then bromine (2 mL) in HBr (30 mL) was added slowly. The reaction mixture was refluxed for 3 h. An orange solid precipitated during the reaction. The mixture was allowed to cool and the solid removed by filtration. The filtrate was washed with aqueous sodium bisulfite, and the product extracted with DCM. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure, affording 4,7-dibromobenzothiadiazole as a yellow solid (2.9 g, 90 %).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (s). MS (EI): (m/z) 292-294-296 [M including splitting characteristic of isotopic abundances of dibrominated species $C_6H_2Br_2N_2S$].

3,6-bis(triisopropylsilylethynyl)benzene-1,2-diamine[5]



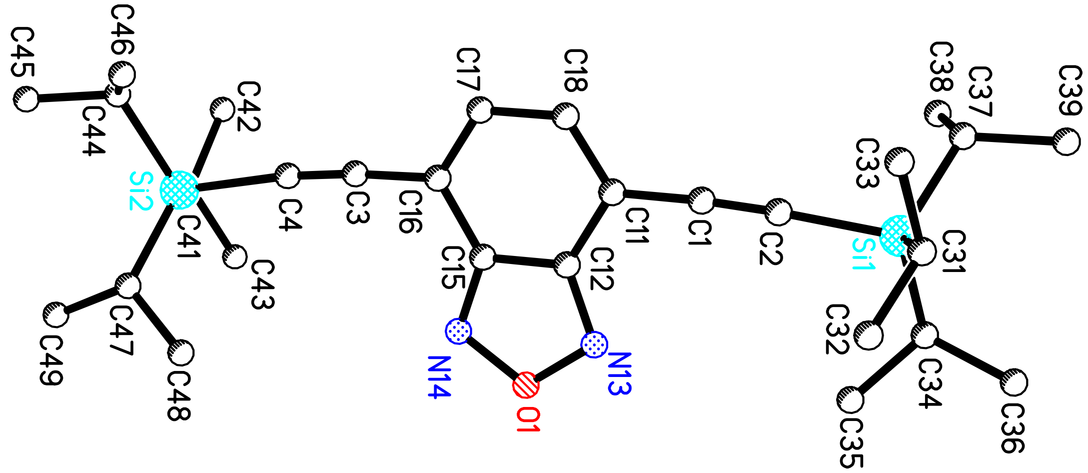
Chemical Formula: $C_{28}H_{48}N_2Si_2$
Molecular Weight: 468.87

To a heatgun-dried Schlenk flask was added **2** (4.00 g, 8.05 mmol) and dry THF (80 mL). After cooling to 0°C under N_2, $LiAlH_4$ (1.53 g, 40.25 mmol) was added in small portions. The yellowish solutions changes directly to a deep violet suspension. After 70 min at room temperature the mixture was quenched with a saturated NH_4Cl-solution. After adding water and EtOAc, the aqueous phase was separated and washed with EtOAc. The combined organic layers were evaporated. Purification by flash column chromatography gave a orange, air sensitive solid (silica gel, petrolether/EtOAc, 40:1, 89%), m.p. 127°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.10-1.19 (m, 42H), 3.77 (brs, 4H), 6.80 (s, 2H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 11.41, 18.85, 97.26, 103.82, 110.10, 122.29, 136.68; IR: υ = 3433 3338, 2941, 2890, 2863, 2143, 1609, 1452, 997, 882, 788; MS (Electrospray ionization, ESI): *m/z* calcd. for $C_{28}H_{49}N_2Si_2$ $[M+H]^+$: 469.34288, found: 469.34310, correct isotope distribution; calcd. for $C_{28}H_{48}N_2Si_2$ C 71.73, H 10.32, N 5.97, found: C 71.29, H 10.38, N 6.04.

Crystallographic Structure Determination

The structures determined here exhibit high degrees of disorder – specifically around the iso-propyl groups. The structures are only included as a proof of constitution, and as such no discussion is included regarding these systems' molecular structures.

4,7-bis-(triisopropylsilylethynyl)benzofurazan (1)



Crystal data for **1**: $C_{28}H_{44}N_2OSi_2$, $M = 480.83$, monoclinic, $a = 14.8274(3)$ Å, $b = 15.2591(3)$ Å, $c = 14.0991(3)$ Å, $\alpha = 90.00°$, $\beta = 106.703(1)°$, $\gamma = 90.00°$, $V = 3055.37(11)$ Å^3, $T = 200(2)$ K, space group $P2(1)/c$, $Z = 4$, 18484 reflections measured, 3523 independent reflections ($R_{int} = 0.0599$). The final R_1 values were 0.0628 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1687 ($I > 2\sigma(I)$). The final R_1 values were 0.0906 (all data). The final $wR(F^2)$ values were 0.1935 (all data).

We have found severe disorder in one of the TIPS (=Si(iPr)3) groups (the one around Si2). It's not only the isopropyl groups, but the complete TIPS group including the Si atom that suffers from the disorder. In the model we have tried to describe the electron density distribution by a superposition of two different representations of the TIPS group. We are aware that this is probably not the complete truth, but the limited quality data for this structure does not justify the modelling of more than twofold disorder. In order to input more information into the data base we applied appropriate restraints to the model that consider the full local symmetry of the TIPS groups. The used restraints are "equivalent bond length (1,2-distances) restraints" and "equivalent bond angle (1,3-distances) restraints" for all chemically equivalent bonds and angles in all representations of the TIPS groups. The standard deviations for these restraint were 0.01 in all cases.

Furthermore we applied delta-U (rigid bond) restraints with a standard deviation of 0.01 for all atom pairs in the disordered TIPS group for both orientations. The same atoms were also moderated by isotropic restraints with a standard deviation of 0.1.

```
XL cards used to generate the used restraints:

DELU SI2 > C49B
ISOR SI2 > C49B
SAME 0.01 0.01 SI1 C34 C35 C36 C37 C38 C39 C31 C33 C32
SAME 0.01 0.01 SI2 C41 > C49
SAME 0.01 0.01 SI2B C41B > C49B
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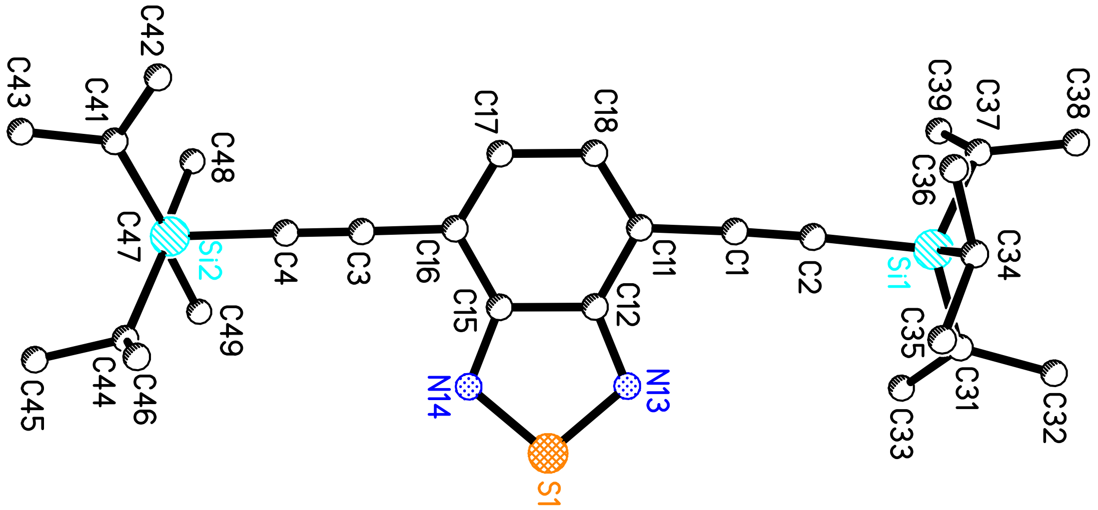
4,7-bis-(triisopropylsilylethynyl)benzothiadiazole (2)



Crystal data for 2: $C_{28}H_{44}N_2SSi_2$, M = 496.89, monoclinic, a = 14.3360(14) Å, b = 14.9701(15) Å, c = 14.9722(16) Å, α = 90.00°, β = 97.892(2)°, γ = 90.00°, V = 3182.8(6) $Å^3$, T = 200(2) K, space group P2(1)/n, Z = 4, 14129 reflections measured, 2647 independent reflections (R_{int} = 0.0491). The final R_1 values were 0.0728 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2099 ($I > 2\sigma(I)$). The final R_1 values were 0.1112 (all data). The final $wR(F^2)$ values were 0.2437 (all data).

For the same reasons and with the same justification as for (**1**) we used restraints to improve the data/parameter ratio. The used restraints are again "equivalent bond length (1,2-distances) restraints" and "equivalent bond angle (1,3-distances) restraints" for all chemically equivalent bonds and angles in the structure, thus implying full local symmetry to the model. The standard deviations for these restraint were 0.01 in all cases.

Furthermore we applied delta-U (rigid bond) restraints with a standard deviation of 0.01 for all bonded atom pairs in the structure.

```
XL cards used to generate the used restraints:

DELU 0.01
FMAP 2
PLAN 9
SAME 0.01 0.01 SI2 SI1 C3 C4 C1 C2 C16 C15 N14 S1 N13 C12 C11 C18 C17 =
     C41 > C49 C34 > C39 C31 C33 C32
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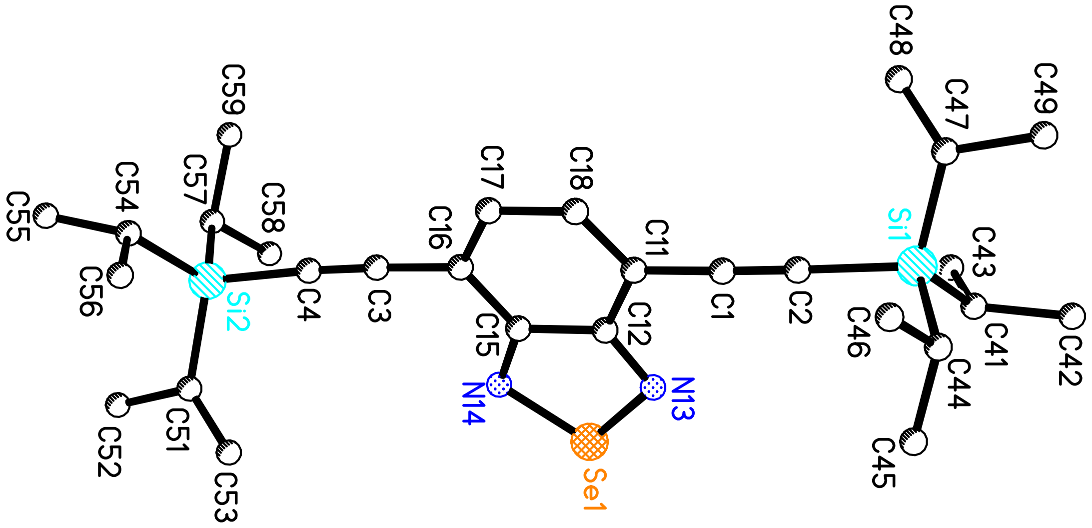
4,7-bis-(triisopropylsilylethynyl)benzoselenadiazole (3)



Crystal data for **3**: $C_{28}H_{44}N_2SeSi_2$, $M = 543.79$, monoclinic, $a = 14.751(3)$ Å, $b = 14.938(3)$ Å, $c = 15.035(3)$ Å, $\alpha = 90.00°$, $\beta = 105.604(5)°$, $\gamma = 90.00°$, $V = 3190.8(12)$ Å^3, $T = 200(2)$ K, space group $P2(1)/n$, $Z = 4$, 16265 reflections measured, 3148 independent reflections ($R_{int} = 0.0514$). The final R_1 values were 0.0485 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1217 ($I > 2\sigma(I)$). The final R_1 values were 0.0711 (all data). The final $wR(F^2)$ values were 0.1348 (all data).

The used restraints are again "equivalent bond length (1,2-distances) restraints" and "equivalent bond angle (1,3-distances) restraints" for all chemically equivalent bonds and angles in the TIPS groups. The standard deviations for these restraint were 0.02 for 1,2-distances and 0.04 for 1,3-distances.

Furthermore we applied delta-U (rigid bond) restraints with a standard deviation of 0.01 for all bonded atom pairs in the structure.

```
XL cards used to generate the used restraints:

DELU
SAME SI1 C41 C43 C42
SAME SI1 C44 C45 C46 C47 C48 C49 C41 C42 C43
SAME SI2 C51 > C59
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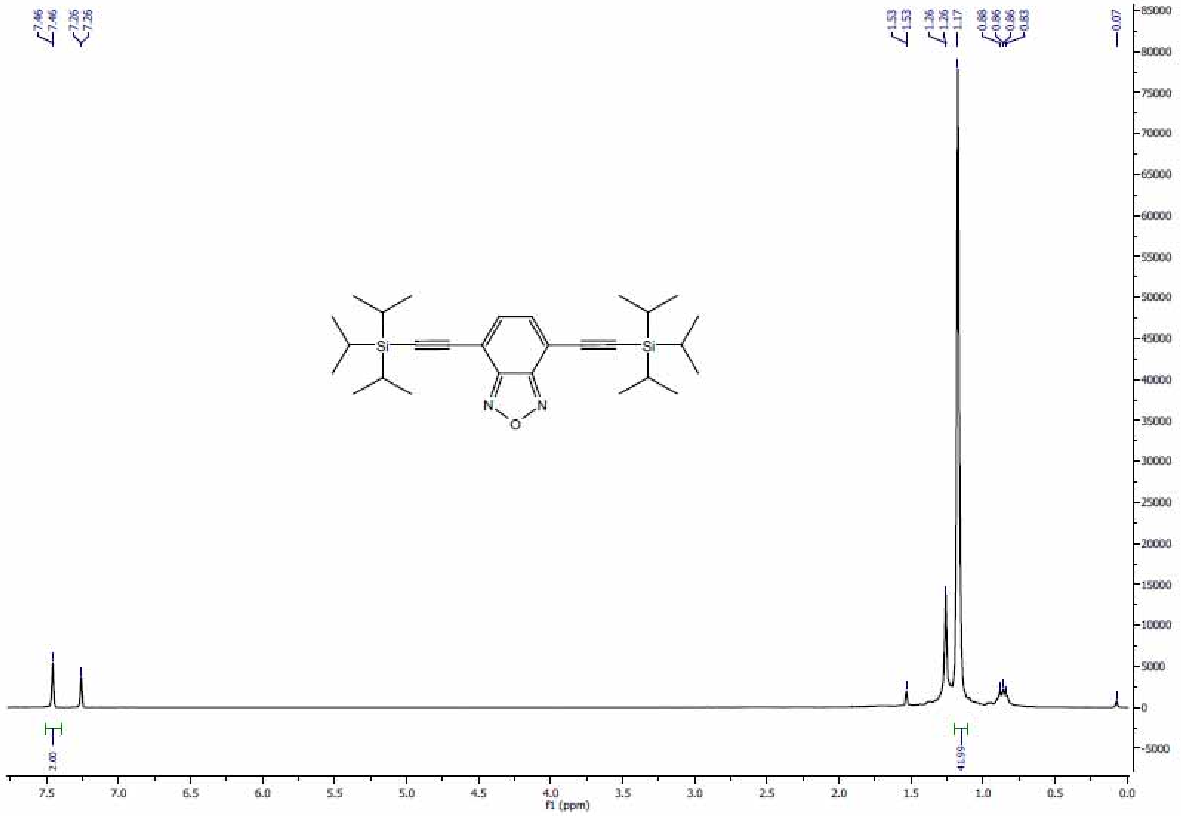
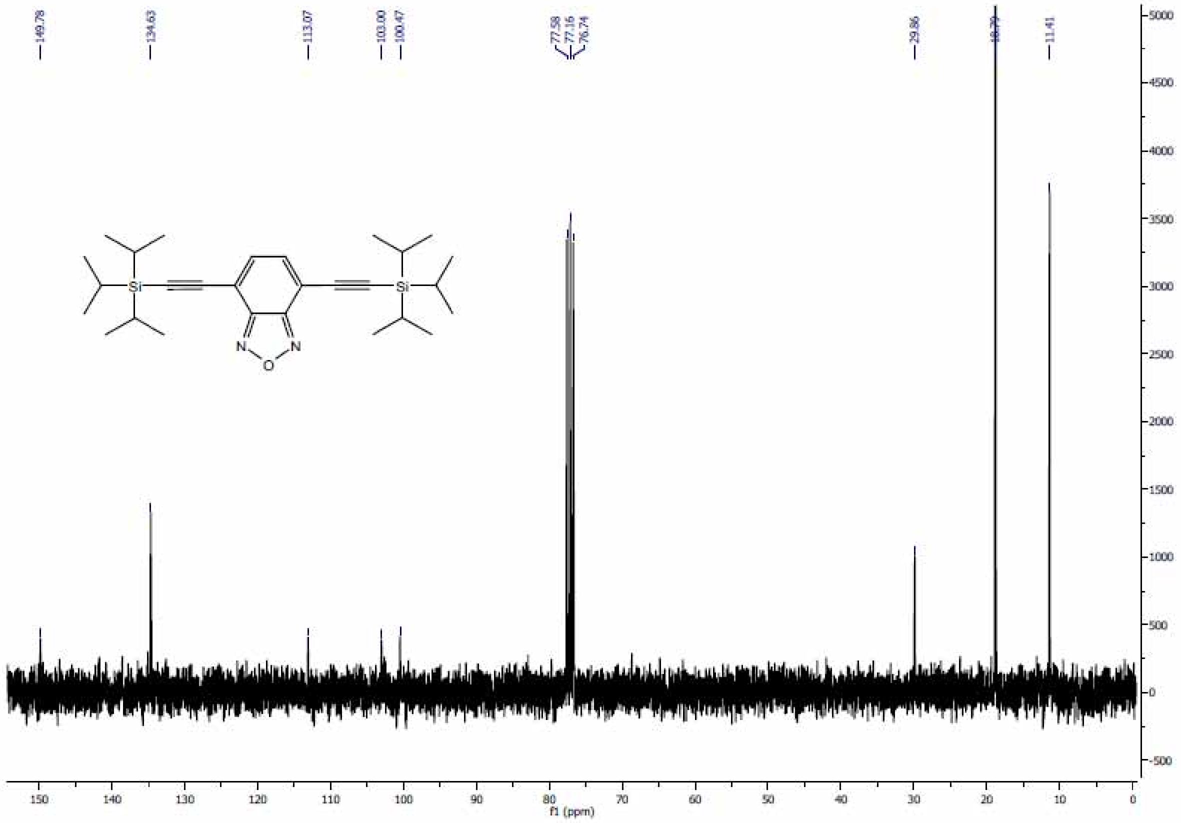

7.46
7.46
7.26
7.26
1.53
1.53
1.26
1.26
1.17
0.88
0.86
0.86
0.83
0.07
Si
Si
N
N
O
2.00
41.99
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


149.78
134.63
113.07
103.00
100.47
77.58
77.16
76.74
29.86
18.79
11.41
Si
Si
N
N
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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[1] Spartan'10; Wavefunction, Inc. Irvine, CA.

[2] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A.Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G.Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009

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[4] B. Neto, A. Lopes, M. Wuest, V. Costa, G. Ebeling, and J. Dupont, *TetrahedronLett.*, 2005, **46**, 6843–6846.

[5] R. Yang, R. Tian, J. Yan, Y. Zhang, J. Yang, Q. Hou, W. Yang, C. Zhang, and Y. Cao, *Macromolecules*, 2005, **38**, 244–253.