Electronic Supporting Information (ESI)

Synthesis, Characterization and Photophysical Studies of a Novel Polycyclic Diborane

Chang-Jiang Yao,[a] Kexiang Zhao,[a] Guankui Long,[b] Xinxiong Li,[a] Zhong-Liang Gong,[c] Yu-Wu Zhong,[c] Weibo Gao,[b] Yongxin Li,[d] Rakesh Ganguly,[d] Gang Li,[e] Qichun Zhang*[a]

[a] Dr. C.-J. Yao, Mr. K. Zhao, Dr. X. Li, Prof. Dr. Q. Zhang
School of Materials Science and Engineering, Nanyang Technological University Singapore
639798 Singapore (Singapore); E-mail: qczhang@ntu.edu.sg
[b] Dr. G. Long, Prof. Dr. W. Gao
Division of Physics & Applied Physics, School of Physical and Mathematics Science, Nanyang Technological University Singapore
639798 Singapore (Singapore)
[c] Dr. Z.-L. Gong, Prof. Dr. Y.-W. Zhong
CAS Key Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences
Beijing 100190, P. R. China
[d] Dr. Y. Li, Dr. R. Ganguly
Division of Chemistry & Biological Chemistry, School of Physical and Mathematics Science, Nanyang Technological UniversitySingapore
639798 Singapore (Singapore)
[e] Dr. G. Li
College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University
Jinan, 250014, P.R. China

1. Experimental Details.

Unless otherwise noted, the following conditions apply. All manipulations were performed under an inert atmosphere of dry argon. tetrakis(dimethylamino)diboron($B_2(NMe_2)_4$) was purchased from TCI Co. All solvents were freshly distilled and deoxygenated. Reaction progress was monitored using thin layer chromatography (TLC) plates pre-coated with a layer of silica with fluorescent indicator UV254. Column chromatography was performed using either Silica Gel 60 (40-63 microns) as the stationary phase and solvents as the mobile phase. Solvents were generally removed in vacuum using a rotary evaporator.

^{1}H NMR spectra was obtained at room temperature using a Bruker Advance 300 NMR spectrometer with tetramethylsilane (TMS, 0.00 ppm) as an internal standard and $CDCl_3$ as solvent. **Mass spectra** was measured on MALDI Shimadzu Performance (3,5-dimethoxy-4-hydroxycinnamic acid as matrix). **High resolution mass spectra (HRMS)** was recorded on a Water Q-Tof premier mass spectrometer. **Ultraviolet-Visible (UV-vis)** absorption spectra were recorded on a Shimadzu UV-2501 spectrophotometer. **Steady-state fluorescence** spectroscopic studies in solution were performed on a Shimadzu RF-5301 spectrofluorophotometer with a 150W Xenon lamp as light source. The slit width was set at 2.5 nm for excitation and 5.0 nm for emission. Samples for absorption and emission measurements were contained in 1 cm × 1 cm quartz cuvettes. Measurements were made using optically dilute solutions. The absolute emission quantum yields were determined on FLS980 spectrometer from Edinburgh Instruments Co., Ltd. **Single-crystal X-ray diffraction (XRD)**, X-ray diffraction data for **2** was collected on a Bruker APX3 and Bruker Photon III CPADs diffractometer with graphite-monochromated Mo $K\alpha$ (λ = 0.71073 Å) at 100 K.[1] The structure was solved by the direct method and refined on F^2 by full-matrix least-squares methods using the SHELXL program package.[2] All hydrogen atoms attached to carbon atoms in **2** were geometrically placed. **CCDC** 1866611 contains the supplementary crystallographic data for this paper.

Synthetic Procedures

1 was synthesized according to the previously-reported methods.[3-4]

The synthetic procedure for the preparation of compound **2** is depicted in **Scheme 1**. **^{1}H NMR** (300 MHz, $CDCl_3$): δ(ppm) = 8.33 (q, *J* = 3.0 Hz, 4H, Naphthal, naphthalene), 7.48 (q, *J* = 3.0 Hz , 4H, naphthalene), 7.42 (s, 4H, NH), 1.20-1.28 (m, 84H, ^{i}Pr). **^{13}C NMR** (75 MHz, $CDCl_3$): δ(ppm) = 138.74, 128.50, 124.83, 124.57, 124.46, 102.50, 101.42, 18.85, 11.39. **MALDI-TOF** Mass Spectra for: $C_{64}H_{96}B_2N_4Si_4$: 1054.20. HRMS-TOF for $[MH]^+$ calculated: 1055.6976; Found: 1055.7003. UV-vis, λ_{max}/nm, (CH_2Cl_2): 365 nm, 384 nm. PL, λ_{max}/nm, (CH_2Cl_2): 400 nm, 447 nm.

NMR Spectra

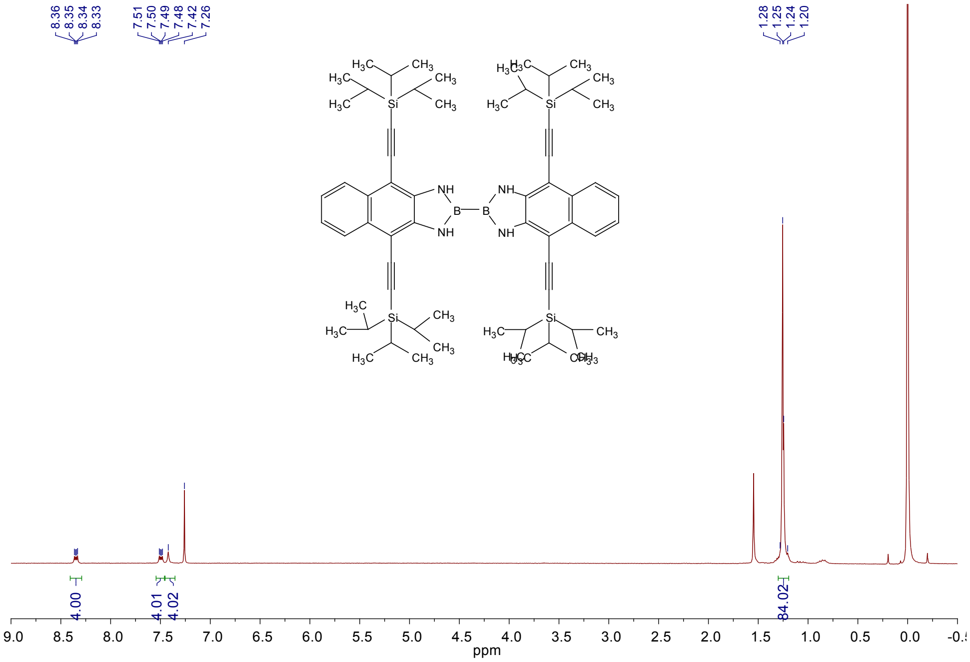


Figure S1. ^{1}H NMR spectrum of **$1,1$-$B_2\{2,3$-$(NH)_2$-$1,4$-$(^iPr_3SiC_2)_2C_{10}H_4\}$ (2)** in $CDCl_3$.

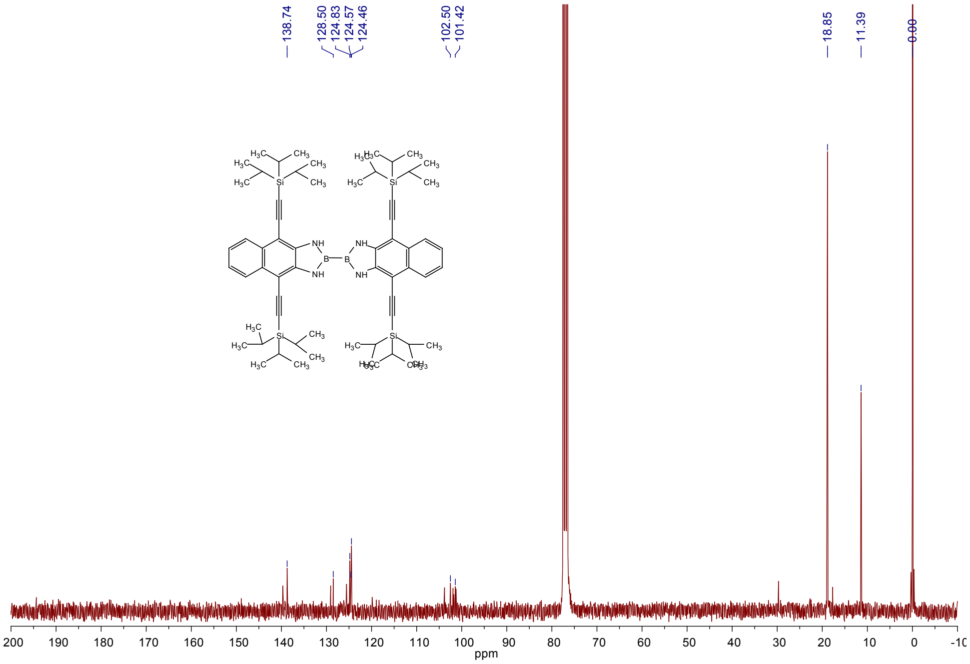
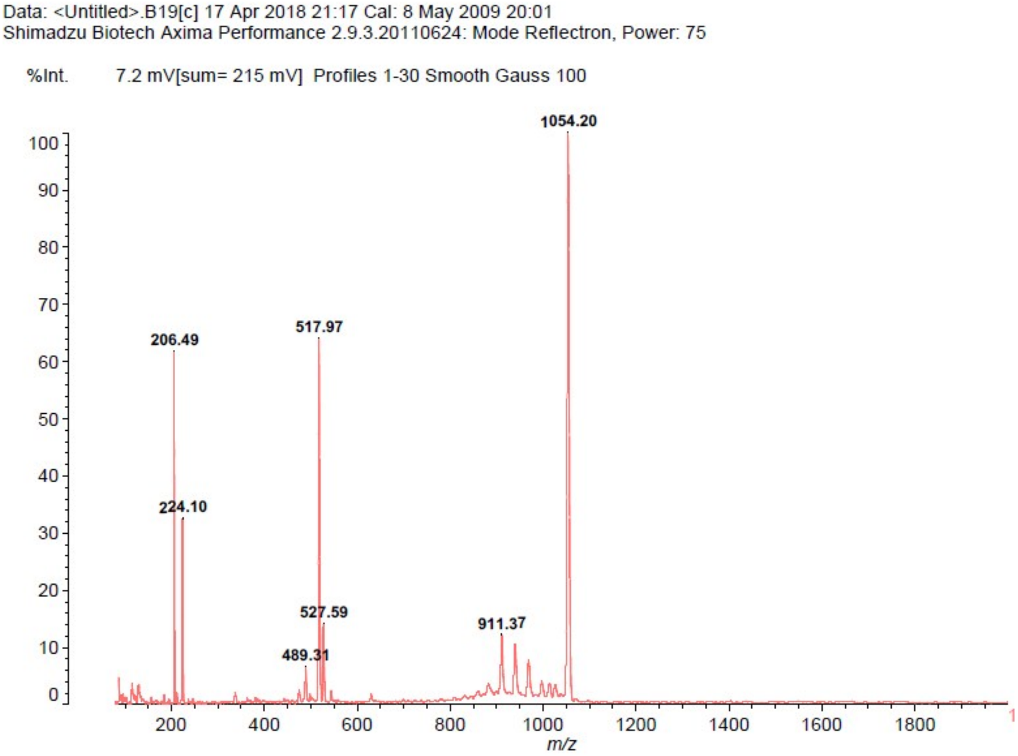


Figure S2. ^{13}C NMR spectrum of **1,1-$B_2\{2,3\text{-}(NH)_2\text{-}1,4\text{-}({}^iPr_3SiC_2)_2C_{10}H_4\}$ (2)** in $CDCl_3$.

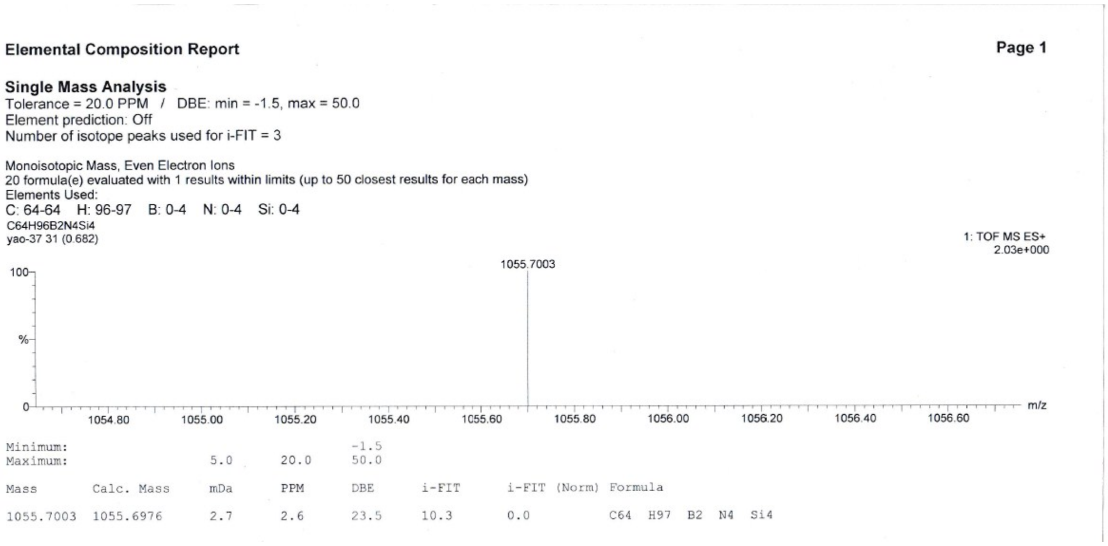
Mass Spectra



Data: <Untitled>.B19[c] 17 Apr 2018 21:17 Cal: 8 May 2009 20:01
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron, Power: 75

%Int. 7.2 mV[sum= 215 mV] Profiles 1-30 Smooth Gauss 100

Figure S3. MALDI-TOF spectrum of **1,1-B$_2${2,3-(NH)$_2$-1,4-(^{i}Pr$_3$SiC$_2$)$_2$C$_{10}$H$_4$} (2)**.



Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
20 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 64-64 H: 96-97 B: 0-4 N: 0-4 Si: 0-4
C64H96B2N4Si4
yao-37 31 (0.682)

1: TOF MS ES+
2.03e+000

```
Minimum:                              -1.5
Maximum:                5.0    20.0   50.0

Mass       Calc. Mass   mDa    PPM    DBE    i-FIT   i-FIT (Norm) Formula

1055.7003  1055.6976    2.7    2.6    23.5   10.3    0.0          C64  H97  B2  N4  Si4
```

Figure S4. HRMS-TOF spectrum of **1,1-B$_2${2,3-(NH)$_2$-1,4-(^{i}Pr$_3$SiC$_2$)$_2$C$_{10}$H$_4$} (2)**.

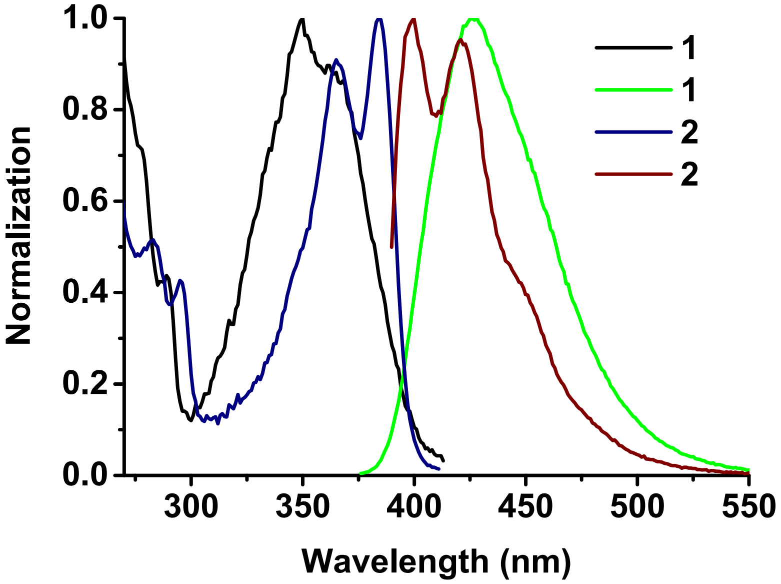


Figure S5. UV-vis spectra and PL emission spectra of dichloromethane solution of **1** and **2** (Absorption: black line for **1**, blue line for **2**; Emission: green for **1**, brown for **2**).

Single-crystal X-ray diffraction

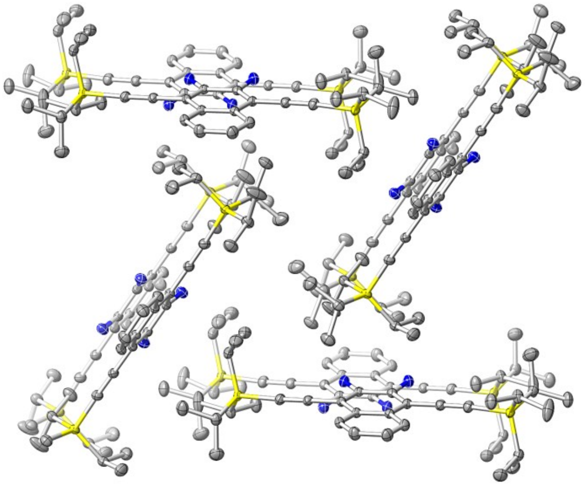


Figure S6. The side view of crystal stacking style of molecules in **2**. X-ray crystal structure of **2** at the 50% probability level, all hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data and structure refinement parameters of **2**.

Compound	**1,1-B_2\{2,3-$(NH)_2$-1,4-$(^iPr_3SiC_2)_2C_{10}H_4$\} (2)**
CCDC	1866611
T (K)	100
Formula	$C_{64}H_{96}B_2N_4Si_4$
Formula weight	1055.42
Crystal system	Triclinic
Space group	*P*-1
Z	4
a (Å)	14.598(2)
b (Å)	14.930(2)
c (Å)	31.428(5)
α (deg)	81.090(5)
β (deg)	82.566(5)
γ (deg)	89.760(5)
V ($Å^3$)	6709.3(18)
ρ calcd (g/cm^3)	1.045
λ (Mo Kα) (Å)	0.71073
F(000)	2296.0
μ/mm^{-1}	0.127
θ/range/deg	$2.23 \leq \theta \leq 27.72$
No. reflns collected	30958
No. unique reflns	20179
Parameters	1684
R (int)	0.0466
R_1 [I > 2σ(I)]	0.1123
wR^2 [I > 2σ(I)]	0.3736
Goodness-of-fit on F^2	1.079

Computational Methodology

The geometry structures of all as-prepared compounds were optimized by using DFT calculations (B3LYP/6-31G*),[5,6] and the frequency analysis was followed to assure that the optimized structures were stable states.

All calculations were carried out using Gaussian 09.[7]

References

[1] APEX2 (version 2009.9); Bruker AXS Inc., (Madison, WI, 2009).

[2] G. M. Sheldrick, A short history of SHELX. *Acta crystallogr*. A64, 112 (**2008**).

[3] B. D. Lindner, Y. X. Zhang, S. Höfle, N. Berger, C. Teusch, M. Jesper, K. I. Hardcastle, X. H. Qian, U. Lemmer, A. Colsmann, U. H. F. Bunz, M. Hamburger, *J. Mater. Chem. C*, 2013, **1**, 5718.

[4] S. J. Yang, B. W. Shan, X. M. Xu, Q. Miao, *Chem. Eur. J.* 2016, **22**, 6637-6642.

[5] A. Becke, Density-Functional Thermochemistry. III. The Role of Exact Exchange. *Journal of Chemical Physics* 1993, **98**, 5648.

[6] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B.,* 1988, **37**, 785-789.

[7] 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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.