Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information (ESI) for Chemical Communication

A Boron-Centered Radical: Potassium-Crown-Ether Stabilized Boryl Radical Anion

Ningning Yuan,[a] Wenqing Wang,[a] Ziye Wu,[b] Sheng Chen,[a] Gengwen Tan,[a] Yunxia Sui,[a] Xinping Wang,*[a] Jun Jiang,*[b] and Philip P. Power*[c]

Caption of Content

Experimental Section

All experiments were carried out under a nitrogen or argon atmosphere by using standard Schlenk techniques and a glovebox. Solvents were dried prior to use. Mes_2BF, 4-Bromo-3,5-dimethylpyridine hydrochloride, *n*-BuLi and 18-Crown-6 were purchased and used upon arrival. Cyclic voltammetry was performed on a CHI660E electrochemical workstation with platinum as the working and a saturated calomel electrode as reference. Freshly distilled THF was used as a solvent and n-Bu_4NPF_6 (10^{-1}M) was used as electrolyte. EPR spectra were obtained using Bruker EMX plus-6/1 X-band variable-temperature apparatus and was simulated with the software of WINEPR SimFonia. UV-Vis spectra were recorded on Lambda 750 spectrometer. Element analyses were performed at Shanghai Institute of Organic Chemistry, the Chinese Academy of Sciences. X-ray crystal structures were obtained by using Bruker D8 CMOS detectors. ^{1}H、^{13}C and ^{11}B NMR spectra were recorded on a Bruker DPX 400. Infrared spectra were collected on a VECTOR22 FT-IR spectrometer. Mass spectrometry (MS) was performed on Shimadzu LC-MS 2010.

Synthesis of 1: To a suspension of 4-Bromo-3,5-dimethylpyridine hydrochloride (3.05 g, 13.7 mmol) in dry ether (80 mL) was added *n*-BuLi in *n*-hexane (2.5 M, 14 mL, 35 mmol) at –78°C under argon. After 1 hour, Dimesitylfluoroborane (4.34 g, 16.2 mmol) in dry ether was added. The mixture was allowed to warm to room temperature and stirred for 24h. The pale yellow solid obtained by evaporation of the solvent was subjected to chromatography on SiO_2 eluting with hexane/EtOAc (10:1) to **1** (1.20 g, 27%) as a Colorless solid; ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.16 (s, 2H), 6.75 (s, 4H), 2.27(s, 6H), 2.01 (s, 6H), 1.97 (s, 6H), 1.94 (s, 6H). ^{13}C NMR($CDCl_3$, 100 MHz, ppm) δ 148.20, 140.84, 140.38, 140.14, 133.75, 133.60, 128.82, 22.85, 21.23, 19.35. IR(KBr): 3010, 2978, 2855, 1604, 1443, 1417, 1373, 1267, 1239, 1220, 1203, 1174, 1154, 1033, 869, 844, 750, 734, 702, 671, 520. ^{11}B NMR ($CDCl_3$, 128 MHz, ppm) 73.25. MS: *m/z* 356.25 [M^+]. Elemental analysis (%) Calcd: C 84.51; H 8.51; N 3.94; Found: C 84.32, H 8.61, N 3.82.

Synthesis of 1K: Under anaerobic and anhydrous conditions, a mixture of **1** (0.208 g, 0.636 mmol), 18-Crown-6 (0.176g, 0.667 mmol) and potassium (0.026 g, 0.667 mmol) in THF (≈ 30 mL) was stirred at room temperature for 1 day. The resultant

blue solution was filtered and the filtrate was then concentrated and stored at around -20 ^{o}C for 1 day to afford blue X-ray-quality crystals of **1K**. Yield: 0.138 g, 29.7 %. Elemental analysis (%) Calcd: C 67.38; H 8.55; N 1.92; Found: C 67.06, H 8.49, N 2.07.

Computational details

All the geometry optimizations were carried out at the (U)B3LYP/6-31G(d, (p)) level of theory. The obtained stationary points were characterized by frequency calculations. The molecular orbitals and spin densities were calculated at the level of (U)B3LYP/6-31G(d, p) at the optimized geometries. Time-dependent density functional theory (TDDFT) calculations at the same level were performed to calculate the excited states. The solvent effect of THF was considered with the polarizable continuum model (PCM). The UV-vis absorption spectrum was calculated for **1k** using time-dependent DFT (TD-DFT) method at UB3LYP/6-31g(d, p).The EPR spectrum was calculated at the UB3LYP/6-311g(d) level using the optimized geometry. All calculations were performed with the Gaussian 09 program suite.

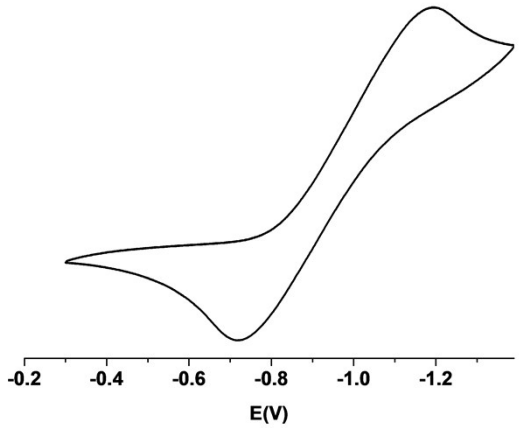


Figure S1. Cyclic voltammogram of **1** (1×10^{-3} M) in THF, containing 0.1 M $^{n}Bu_4NPF_6$, measured at 100 mV s^{-1} at 25 ^{o}C

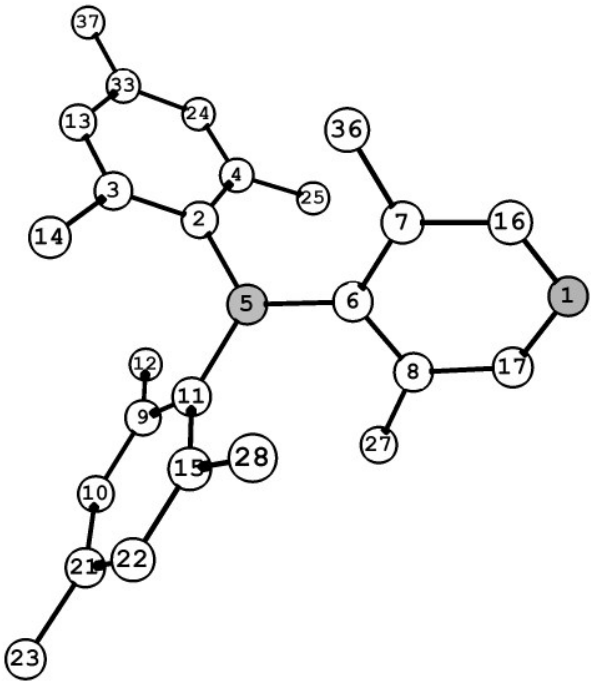
Table S1. Experimental and Calculated Structural Parameters (avg.) for **1**, **1K** and free **1**$^{\bullet-}$.

Experimental		
	1	**1K**
B–C_{mes} (Å)	1.572(3)	1.603(3)
B–$C_{pyridine}$ (Å)	1.594(3)	1.553(3)

Calculated			
	1	**1K**	free **1**$^{\bullet-}$
B–C_{mes} (Å)	1.582	1.603	1.597
B–$C_{pyridine}$ (Å)	1.594	1.554	1.577
Electron spin density		0.53	0.64

Selected Mulliken atomic spin densities for some atoms in free $1^{\bullet-}$

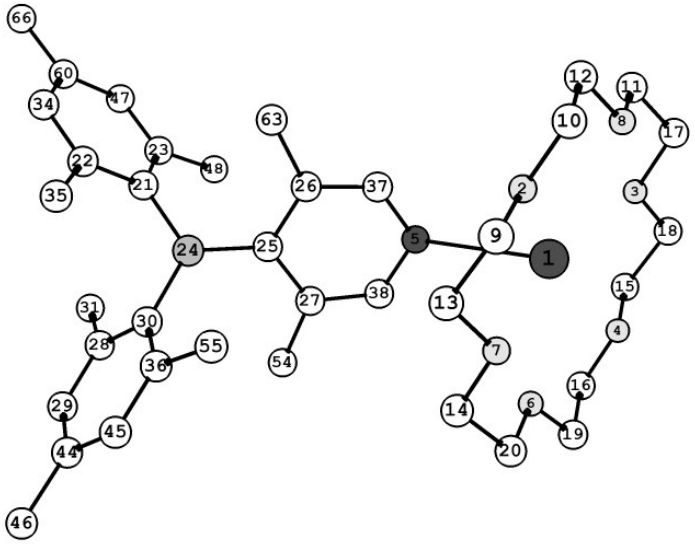
1	N	0.105979
2	C	-0.062888
3	C	0.053328
4	C	0.057479
5	B	0.638825
6	C	-0.021964
7	C	0.073643
8	C	0.073732
9	C	0.053036
10	C	-0.027978
11	C	-0.062673
12	C	-0.001817
13	C	-0.027981
14	C	-0.001744
15	C	0.057146
16	C	-0.028378
17	C	-0.028430
21	C	0.070744
22	C	-0.030198
23	C	-0.005984
24	C	-0.030491
25	C	-0.001067
26	H	0.001373
27	C	-0.004083
28	C	-0.000965
33	C	0.071104
36	C	-0.004059
37	C	-0.006011



Sum of Mulliken atomic spin densities = 1.00000

Selected Mulliken atomic spin densities for some atoms in 1K

1	K	0.000146
2	O	-0.000009
3	O	0.000004
4	O	0.000002
5	N	0.178410
6	O	-0.000014
7	O	0.000233
8	O	0.000001
9	C	0.000011
10	C	-0.000005
11	C	0.000004
12	C	0.000000
13	C	0.000197
14	C	0.000413
15	C	0.000003
16	C	0.000004
17	C	-0.000003
18	C	-0.000002
19	C	-0.000005
20	C	0.000038
21	C	-0.058184
22	C	0.031771
23	C	0.034172
24	B	0.532946
25	C	0.083380
26	C	0.077140
27	C	0.071508
28	C	0.030829
29	C	-0.014186
30	C	-0.056105
31	C	-0.001002
34	C	-0.014638
35	C	-0.000980
36	C	0.035366
37	C	-0.008785
38	C	-0.010094
44	C	0.035153
45	C	-0.017038
46	C	-0.002908
47	C	-0.016701
48	C	0.001031



54	C	-0.005692
55	C	0.000975
60	C	0.034444
63	C	-0.006219
66	C	-0.002837

Sum of Mulliken atomic spin densities = 1.0000

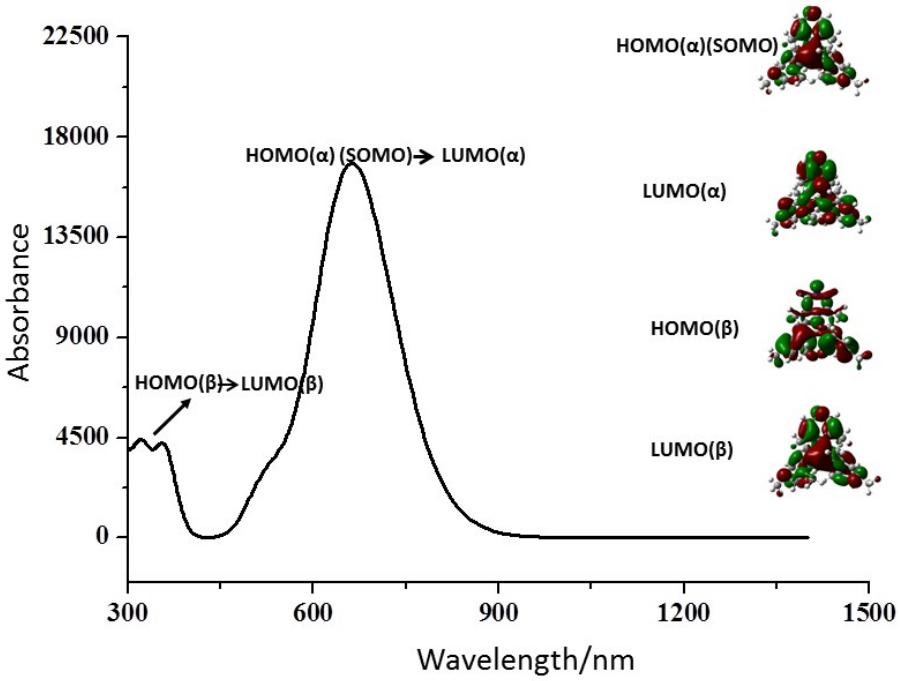


Figure S2. Calculated absorption spectrum of $\mathbf{1}^{\bullet-}$ and related molecular obtials.

Coordinates for optimized geometries of 1, 1K and free $1^{\bullet-}$

Neutral **1**

B	0.00000300	0.22954800	0.00001500
C	1.37786900	-0.54782900	-0.01278600
C	1.63365900	-1.59236900	0.91980700
C	2.86768400	-2.25030400	0.91575800
H	3.04653400	-3.03408500	1.64879100
C	3.61278800	-0.92960400	-0.92994200
H	4.37325000	-0.67950300	-1.66687500
C	2.40633600	-0.22330700	-0.94028200
C	2.24850600	0.86058400	-1.98943100
H	2.29525100	1.86100200	-1.54870800
H	1.29624100	0.79389100	-2.52378400
H	3.04554400	0.78933500	-2.73468100
C	0.62232500	-2.02449900	1.96484200
H	-0.24782200	-2.50932900	1.51403400
H	0.24415200	-1.18260900	2.55377100
H	1.07630100	-2.73194000	2.66428800
C	-0.00003200	1.82333300	-0.00000300
C	-0.75987100	2.56688800	-0.93869700
C	-1.62061200	1.93302400	-2.00963700
H	-1.06994900	1.20028100	-2.60897200
H	-1.99772000	2.69718900	-2.69538300
H	-2.48019300	1.40955800	-1.58178000
C	-0.70293500	3.96507200	-0.89019500
H	-1.26958600	4.54653100	-1.61756700
N	-0.00009600	4.66882600	-0.00003000
C	3.87250200	-1.94060400	-0.00261000
C	5.20170300	-2.65504300	0.02225400
H	5.93049800	-2.11135300	0.63665400
H	5.62812100	-2.74358500	-0.98155900
H	5.10833500	-3.66049900	0.44318600
C	-1.37784300	-0.54787200	0.01281800
C	-1.63359600	-1.59239400	-0.91980000
C	-2.86761000	-2.25035000	-0.91578900
H	-3.04643800	-3.03410900	-1.64885100
C	-3.61276300	-0.92971600	0.92994100
H	-4.37324100	-0.67964700	1.66686900
C	-2.40632500	-0.22339700	0.94031400
C	-2.24851000	0.86046800	1.98949300
H	-2.29526500	1.86089900	1.54879800
H	-1.29624400	0.79376100	2.52384100
H	-3.04554600	0.78919300	2.73474300

C	-0.62220600	-2.02454600	-1.96477400
H	0.24753800	-2.51009500	-1.51394000
H	-0.24337400	-1.18259600	-2.55317600
H	-1.07636600	-2.73141000	-2.66468500
C	0.75976900	2.56694100	0.93868000
C	1.62053200	1.93313400	2.00963700
H	1.06992200	1.20032400	2.60893600
H	1.99754600	2.69731800	2.69541200
H	2.48017700	1.40976100	1.58179100
C	0.70277200	3.96512000	0.89015200
H	1.26938800	4.54662000	1.61751800
C	-3.87244500	-1.94069400	0.00257500
C	-5.20163700	-2.65514900	-0.02232800
H	-5.93046800	-2.11138400	-0.63661900
H	-5.62801000	-2.74383500	0.98149100
H	-5.10827100	-3.66054500	-0.44340200

1K

K	-3.77426100	0.03180600	0.11785600
O	-3.05782300	-0.88742000	2.67867000
O	-5.67781700	-1.51173200	-1.36627300
O	-5.38607700	1.26246400	-1.99033900
N	-1.24141700	-0.44629200	-0.76042500
O	-3.46648900	2.76787300	-0.54450600
O	-2.63670700	1.86539900	2.03703200
O	-5.01075000	-2.37240900	1.27083700
C	-2.52865900	0.05855400	3.59996800
C	-3.79401600	-1.93315500	3.28728100
C	-5.37635500	-3.26904800	0.23109600
C	-4.14085900	-2.96176600	2.23143000
C	-1.73825000	1.10099600	2.83857700
C	-1.97901200	2.90805400	1.32152700
C	-5.71015200	0.27526100	-2.96006000

C	-4.70253600	2.38160400	-2.54416300
C	-6.34472700	-2.57678800	-0.70410900
C	-6.50553100	-0.82892400	-2.29709400
C	-4.38680200	3.36776700	-1.43913100
C	-2.99756300	3.64202600	0.47594600
C	4.12424700	-1.46475900	-0.34630800
C	5.08948300	-1.75511800	0.65972300
C	4.05038000	-2.37844600	-1.43676800
B	3.19848600	-0.15771700	-0.29451000
C	1.65597000	-0.25596000	-0.45252400
C	0.87344700	-1.37206300	0.03698400
C	0.85621400	0.75553000	-1.11155700
C	5.02843000	1.67500000	-0.87508100
C	5.67106600	2.89334100	-0.63294200
C	3.92711600	1.25324800	-0.07492700
C	5.52539200	0.84760400	-2.04270000
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H	-3.19680500	-2.42461900	4.07135500
C	5.91330900	-2.88195300	0.56549600
C	5.24142900	-0.88569400	1.89132000
C	3.53072200	2.13683800	0.96871800
C	-0.50240400	-1.39468200	-0.13724600
C	-0.51685800	0.59792000	-1.23204000
H	4.70616400	0.56422300	-2.71269800
H	5.99264100	-0.08512200	-1.71393500
H	6.26084800	1.40679200	-2.63040600
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C	6.01788200	5.04002900	0.66865400
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C	3.06610900	-2.19086800	-2.57416600
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H	-0.97901000	0.61437400	2.21104100
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H	-1.86106300	-0.44213600	4.31771600
H	-3.34271700	0.54015100	4.16395600
C	1.46167300	1.97158100	-1.77623100
C	2.37424500	1.81138000	1.89282700
H	3.31883200	-2.84308300	-3.41700400
H	3.05051300	-1.15697300	-2.93155600
H	2.03900900	-2.42149400	-2.26939300
H	6.49887300	3.18688500	-1.27749100
C	5.84287400	-3.76573600	-0.51376000
H	6.62833200	-3.07864300	1.36356800
H	4.81750200	-4.16291400	-2.35758100
C	1.47733500	-2.51903700	0.81571500
H	-4.79499400	-0.13971000	-3.40926500
H	-6.31926100	0.71284700	-3.76662000
C	6.77206000	-4.95224300	-0.61813300
H	0.68886200	-3.13847400	1.25981500
H	2.12389100	-2.15669900	1.62267700
H	2.10393400	-3.16757900	0.19680400
H	-5.86556600	-4.16373900	0.64750400
H	-4.48617100	-3.59574800	-0.32786000
H	5.41207600	5.73076500	1.26407700
H	6.28961600	5.54860800	-0.26311900
H	6.95113100	4.86772600	1.22121400
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H	-7.38309300	-0.40071600	-1.78834800
H	-6.86493200	-1.52357800	-3.07245700
H	-1.09054800	1.36356000	-1.75773600
H	5.89534800	-1.36487900	2.62745500
H	4.27513900	-0.69814800	2.37247700
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H	2.36334900	2.48789400	2.75489800
H	2.42782500	0.78239600	2.26150000
H	1.40844000	1.90013300	1.38110900
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H	6.33066600	-5.75677300	-1.21556400
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H	-1.06707100	-2.23843300	0.26607400
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H	-3.95557700	4.27556800	-1.88965400
H	-5.31145700	3.65463600	-0.91362300
H	0.70783500	2.49961500	-2.37223500
H	2.28311000	1.68687900	-2.44302200
H	1.88797500	2.68118700	-1.06142700
H	-5.33057700	2.87665900	-3.30136600
H	-3.76882800	2.05894500	-3.02830100

free **1**$^{\bullet-}$

N	0.02092500	4.76146200	-0.00682800
C	1.37302400	-0.53455500	-0.01514000

C	1.59502000	-1.64163600	-0.89254900
C	2.44836200	-0.21824000	0.87144000
B	0.00059100	0.28101800	-0.00001700
C	0.00832500	1.85845400	-0.00205800
C	0.91437900	2.63740700	-0.79769100
C	-0.89066600	2.64788400	0.79137300
C	-1.61416200	-1.61806000	0.90484300
C	-2.82305900	-2.32116900	0.88727400
C	-1.37968300	-0.52109200	0.01793000
C	-0.58427000	-2.04088400	1.93237100
C	2.79691300	-2.35660400	-0.87067300
C	0.55624400	-2.06915200	-1.90919200
C	-2.45226600	-0.19822800	-0.86919700
C	0.86096800	4.03067600	-0.75590800
C	-0.82523800	4.04048300	0.74485500
H	-0.19844000	-1.17783900	2.48583800
H	0.28593200	-2.52058700	1.47351500
H	-1.01898500	-2.74439300	2.65198300
C	-3.86151400	-1.99814600	0.00931800
C	-3.64867700	-0.92548300	-0.85827600
C	-5.14431100	-2.79578700	-0.01987000
C	3.63742600	-0.95739700	0.86485200
C	2.33974800	0.90237800	1.88482000
H	-4.43606400	-0.65021000	-1.56041600
C	-1.88935800	2.03438400	1.74645000
C	-2.33618700	0.92139000	-1.88294200
H	3.14377400	0.83443400	2.62690900
H	1.37879900	0.87294500	2.40927400
H	2.39650400	1.89142000	1.41754100
H	-2.96475500	-3.14057200	1.59255000

C	3.84153700	-2.03399900	0.00003800
H	2.92640900	-3.18730400	-1.56496900
H	4.42526400	-0.69033800	1.56971400
C	1.90857000	2.01206600	-1.74976200
C	5.14464800	-2.79831000	-0.01572900
H	2.33561600	2.77254800	-2.41437400
H	1.43327400	1.24142600	-2.36718500
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H	-5.42667700	-3.14165900	0.98155100
H	-5.05962800	-3.69118800	-0.65263500
H	-1.50480500	4.61960600	1.37523800
H	0.98402400	-2.77843000	-2.62730700
H	0.16847900	-1.20880700	-2.46523200
H	-0.31171100	-2.54377000	-1.44078500
H	-3.14158000	0.85946600	-2.62405900
H	-1.37618300	0.88361600	-2.40858200
H	-2.38414900	1.91121300	-1.41632000
H	4.98585300	-3.86378600	-0.21998400
H	5.66770600	-2.71643500	0.94372100
H	5.83262000	-2.42590200	-0.78855300
H	1.54569300	4.60174800	-1.38806800
H	-2.30904200	2.80075700	2.40896500
H	-1.41988300	1.26188100	2.36597100
H	-2.72113900	1.54340800	1.23074800