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Synthesis of bis-BN-naphthalene-fused Oxepins and Their Photoluminescence Including White-Light Emission

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Abstract. A series of novel bis-BN-naphthalene-fused oxepin derivatives were synthesized via a Pd-catalyzed tandem reaction from brominated 2,1-borazaronaphthalenes and cis-bis(boryl)alkenes. X-ray crystallographic analysis revealed that bis-BN-naphthalene-fused oxepins feature planar framework. The electronic and photophysical properties of the novel BN-naphthalene-fused oxepins were investigated by UV–vis and fluorescence spectroscopy, and DFT calculations, which disclosed the distinct electronic and photophysical properties from the

analogous hydrocarbon system. Interestingly, dual-fluorescent emissions were observed upon dissolving N-substituted derivatives **10-14** in dimethyl sulfoxide. Tunable emission colors especially for white-light emissions can be achieved by the control the ratio of solvents, concentration or temperature using only a single molecule compound.

INTRODUCTION

Incorporating heteroatoms into polycyclic aromatic hydrocarbons (PAHs) has proven to be a powerful tool to tune the properties of these functional materials.¹ Boron-containing π -conjugated materials have received considerable attention in recent years due to their unique optical and structural properties that result from the vacant *p*-orbital of the boron center.² In particular, substituting one or more C=C units in PAHs with isoelectronic B-N units is a promising way to expanding the PAHs family with distinctively different photophysical/chemical properties from their all carbon analogues.³⁻⁵ The chemistry of BN-PAHs, pioneered by Dewar and coworkers,⁶ has achieved rapid advances in the past decade.⁷ Although significant progress has been made in azaborine chemistry, the strategies for construction of BN-polycyclic aromatics are still quite limited and they usually rely on classical electrophilic borylations performed under harsh conditions or require multiple steps.⁸ Considering the interesting supramolecular chemistry and electronic properties of higher acenes,⁹ simple and efficient synthetic approach to BN heteroaromatics with large π -conjugated skeleton is highly desirable.

Heteropin has a seven-membered 8π conjugated system including a heteroatom (X) in the ring system. Dibenzoheteropins (Scheme 1, I) with saddle-shaped structures are more stable than heteropins. Moreover, dibenzoheteropins such as dibenzazepin (X = NR), dibenzoxepin (X = O), and dibenzosilepin (X = SiR₂) have

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been investigated in the development of new organic electronic materials.^{10, 11} Borepin, in which the 6π -electron seven-membered ring is planar and aromatic, is another class of boron-containing heteropin. A series of annulated borepins (Scheme 1, II) including π -expanded fused borepins that contain two borepin rings have been reported by the groups of Yamaguchi, Piers and Tovar.¹² The fundamental electronic properties, such as their intriguing fluorescence make them attractive candidates for organic electronic materials. Recently, Yan and co-workers reported the synthesis of planar dithienooxadiborepine (Scheme 1, III) and demonstrated that these compounds might be used as building block for electron-accepting materials.¹³ However, in all these cases sterically bulky groups are necessary to stabilize the electron deficient boron center which will prevent intermolecular π - π interaction. In response to these limitations, Yamaguchi and Piers have demonstrated that enforced planarity could stabilize boron-containing π -conjugated materials.¹⁴ In addition, the incorporation of an adjacent electron-donating atom to the boron center could further stabilize the boron-containing π -conjugated skeleton. These strategies have been applied to the synthesis of NBN units containing compounds.^{15, 16} Moreover, boronate esters have attracted considerable attention as novel materials for sensors and supramolecular assemblies.^[17] However, because of the lack of suitable synthetic methods, polycyclic aromatic compounds containing boronate substructures have not been well studied.¹⁸



Scheme 1 Heteropins discussed in this paper.

BN-naphthalenes, one of the smallest BN-PAHs, are excellent building blocks for construction of large functional BN-PAHs. However, the potential of this strategy in extending the π -conjugation and designing novel BN-polycyclic aromatics with improved properties is still relatively unexplored.¹⁹ Herein, we report the effecient synthesis of unprecedented bis-BN-naphthalene-fused oxepins (Scheme 1, **IV**) via a Pd-catalyzed tandem reaction from brominated 2,1-borazaronaphthalenes and cis-bis(boryl)alkenes. Interestingly, some of these BN-doped π -conjugated compounds exhibit dual-emission properties in DMSO, and white-light emission can be generated by controlling the solvent ratio, concentration or temperature with a single molecule. Since emission bands tend to be generated from the lowest excited state according to Kasha's rule,²⁰ achieving white-light emission from single molecules with simple structures is an exciting challenge in synthetic chemistry as well as in photochemistry and photophysics. This work not only presents a new strategy for the construction of larger BN-doped π -conjugated compounds, but also paves a new way for producing single molecular white-light organic compounds.

RESULTS AND DISCUSSION

As mentioned above, BN-naphthalenes are suitable building blocks to construct large functional BN-PAHs. Molander and co-workers recently reported that brominated N-alkyl B-aryl 2,1-borazaronaphthalenes undergo a selfarylation reaction in the presence of a catalytic amount of palladium and base, in which 2,1-borazaronaphthols and their respective anhydrides could be obtained.²¹ They postulated that the substituent on nitrogen is necessary to weak the B-C_{aryl} bond. We envisioned that the bulky substituent on 3-position will play the same role as one on nitrogen. Thus, this reaction mode can be used for constructing polycyclic aromatic compounds containing BN and BO units in one molecule. To test our hypothesis, the reaction of brominated B-phenyl-2,1-borazaronaphthalenes 1a and cis-bis(boryl)alkene 2a was evaluated initially (Table 1, entry 1). Using Pd(OAc)₂ (5 mol %) as catalyst, bis-BN-naphthalene-fused oxepin 3 was obtained in 51% yield after heating at 70 °C for 10 h in acetonitrile. After extensive screening of catalytic systems and reaction parameters the isolated yield of compound 3 can be increased to 84%, and the addition of appropriate amount water in the system can significantly improve the yield. The structure of 3 was unambiguously confirmed by X-ray single crystal analysis .

Table 1. Optimization of Reaction Conditions^a



entry	catalyst	base	solvent	H ₂ O	time	yield(%) ^b
1	$Pd(OAc)_2$	K ₂ CO ₃	MeCN		10h	51%
2	$Pd(OAc)_2$	K_2CO_3	MeCN	1.5µL	10h	68%
3	$Pd(OAc)_2$	K_2CO_3	MeCN	3.0µL	10h	70%
4	$Pd(OAc)_2$	K_2CO_3	MeCN	0.1mL	10h	38%
5	$Pd(OAc)_2$	K_2CO_3	MeCN	1.0mL	10h	31%
6	$Pd(dba)_2$	K_2CO_3	MeCN	3.0µL	10h	trace
7	PdCl ₂	K_2CO_3	MeCN	3.0µL	10h	44%
8	PdCl ₂ (dppf)	K_2CO_3	MeCN	3.0µL	10h	37%
9	$Pd(PPh_3)_4$	K_2CO_3	MeCN	3.0µL	10h	43%
10	PdCl ₂ (PPh ₃) ₂	K_2CO_3	MeCN	3.0µL	10h	56%
11	$Pd(OAc)_2$	K_2CO_3	Tol	3.0µL	10h	43%
12	$Pd(OAc)_2$	K_2CO_3	THF	3.0µL	10h	57%
13	$Pd(OAc)_2$	K_2CO_3	DMF	3.0µL	10h	67%
14	$Pd(OAc)_2$	КОН	MeCN	3.0µL	10h	68%
15	$Pd(OAc)_2$	NaOH	MeCN	3.0µL	10h	32%
16	$Pd(OAc)_2$	Cs_2CO_3	MeCN	3.0µL	10h	61%
17°	$Pd(OAc)_2$	K_2CO_3	MeCN	3.0µL	10h	45%

18	$Pd(OAc)_2$	K ₂ CO ₃	MeCN	3.0µL	15h	84%	
19	$Pd(OAc)_2$	K_2CO_3	MeCN	3.0µL	20h	66%	

^a Reaction conditions: **1a** (0.36 mmol), **2a** (0.18 mmol), Pd(OAc)₂ (5 mol%), base (4 equiv), solvent 3 mL at 70°C under Ar. ^b Isolated yields. ^c 5 equiv base was used.

We assumed that the cross coupling reaction will occurred initially to generate 2-phenyl-3-vinyl-2,1-borazaronaphthalene species (Scheme 2, **A**). The bulky vinyl substituent on the 3-position led to the phenyl groups on the boron atoms to rotate such that it is no longer in the same plane with the azaborine, thereby weakening the B-C_{phenyl} bond via decreasing the overlaps of the molecular orbitals between the empty *p*-orbital on the boron atom and phenyl group. And then Pd/water/base promoted B-C_{aryl} cleavage with subsequent intramolecular dehydration is very likely to take precedence. In addition, diphenyl was not found in this reaction. Trace amount of 2,3-diphenyl-2,1-borazaronaphthalene were obtained in this tandem reaction.



Scheme 2 Proposed mechanism for the formation of 3.

Single crystals of **3** were achieved from the *n*-hexane/dichloromethane solution through slowly evaporating the solvents. It shows a relatively planar main backbone with a fully zigzag-edged periphery (Figure 1). The largest dihedral angle of 8.65° was observed among the fused rings. Moreover, the phenyl groups on C9 and C9' were deviated from the main backbone by 82.78°. The short B-N bond lengths of **3** (1.414(3) Å) are consistent with those reported for BN-aromatic systems.^{4f, 4g, 5d} In

 addition, the B-C and N-C bond lengths (B-C = 1.535(3), N-C = 1.386(2) Å) in **3** are noticeably shorter than normal B-C (ca. 1.579(5) Å) and N-C (ca. 1.47 Å) single bonds, consistent with the electron delocalization over the C₄BN core.²² The sum of the inner angles of C₄B₂O seven-membered ring is 899.99°. The B-O bond lengths (1.382(3) Å) are comparable to those in arylboronic acids and their esters (1.35-1.38 Å).^{18d} Furthermore, substantial bond length alternations are observed for the C1-C9-C9'-C1' bonds. These observations indicated the nonaromativity of C₄B₂O ring. Many weak N-H···O intermolecular hydrogen bonds (3.684 Å) and π - π interactions with the distances of ~3.670 Å between the neighboring molecules can be detected in the crystals of **3** (Figure S1).



Figure 1. Molecular structure of **3** with thermal ellipsoids set at 30% probability: top view (left) and side view (right). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (deg): B1–N1 1.414(3), B1–C1 1.535(3), B1–O1 1.382(3), C1–C9 1.481(3), C9–C9' 1.372(3); B1–O1–B1 130.6(2), O1–B1–C1 128.2(2), B1–C1–C9 127.81(17), C1–C9–C9' 128.72(10).

TD-DFT (RB3LYP/6-31 (d, p)) calculations were performed to investigate the structure–property relationship of this new bis-BN-naphthalene fused oxepin. Since the corresponding hydrocarbon analogue **3'** (Figure 2) is not known, the same level

calculations were performed for 3' for comparison. A significant geometry difference can be found in 3'. The optimized structure of 3' is saddle-shaped, while 3 represent planar geometry, indicating the significant effects of the BN substitution (Figure S5, Figure S6). In addition, the HOMO of **3** is 0.53 eV higher than that of **3**' and the LUMO is 0.16 eV lower in energy (Figure 2). The plots of HOMO and LUMO orbitals for 3 and 3' are shown in Figure 2. Although they all are mainly corresponding to the π orbitals of the central fused rings with negligible contributions from the peripheral phenyl groups, the noticeable differences between the frontier orbitals of the two compounds can be seen due to the BN substitution. Nucleus-independent chemical shift (NICS) calculations (GIAO-B3LYP/6-311+G (d, p)) of **3** and **3'** were performed to investigate the aromaticity of each ring (Figure 2). Remarkably, the aromaticity of the fused peripheral benzo group and C₄BN ring in **3** is significantly reduced in comparison to the corresponding rings in 3'. These differences may partly due to the partially localized charge on the B and N atoms due to the polarization of the B-N bond. Notably, the seven-membered C_4B_2O ring in 3 indeed has a positive NICS (1) value of 3.5 ppm, supporting its nonaromaticity.



Figure 2. Calculated NICS (1) values (in ppm, calculated at the GIAO-B3LYP16-311+G (d. p) Level), and the calculated frontier orbitals and their energy levels of **3** (up) and its hydrocarbon analogue **3'** (down).

The synthesis of **3** prompted us to extend this methodology for the synthesis of the other derivatives. As shown in Table 2, both electron-donating and electron withdrawing groups on the phenyl rings of phenyl-substituted cis-bis(boryl)alkenes (**2**) were tolerated, furnishing the corresponding products in good to excellent yields. The molecular structures of **8** has also been determined by single-crystal X-ray analysis, and the crystal parameters are comparable to those of **3** (Figure S3, Table S1). In contrast, cis-bis(boryl)alkenes bearing 2-thienyl or ethyl groups is not effective and the cyclic product was not detected. In addition, N-substituted BN-naphthalenes also work well in this reaction (**10-14**). Compounds **3-14** were obtained as solids by chromatography on silica gel and could be stored in air for several months without any noticeable decomposition, as determined by ¹H NMR spectra. All compounds have been characterized by ¹H, ¹³C, ¹¹B NMR and HRMS spectroscopy. Overall, these results denominated that the tandem reaction is useful for the synthesis of diverse BN-naphthalene fused oxepin derivatives.

Table 2. Synthesis of bis-BN-naphthalene Fused Oxepins^a





^a Reaction conditions: 2.0 equiv of **1**, 1.0 equiv of **2**, 5 mol% of Pd(OAc)₂, 4 equiv of K_2CO_3 , 1 equiv of H₂O, CH₃CN (3 mL), 70 °C, 15 h.

Double bromination of **3** can be achieved by the reaction with 2.2 equivalent of bromine in CH₂Cl₂ at 0 °C, leading to the dibromination product 15 in quantitive yield (Scheme 3). The Suzuki cross-coupling reaction of with 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane produced compound 16 and 17 in moderate yield (Scheme 3). It should be mentioned that 10-20 eq of cross-coupling partners are needed for completeing the conversion. We tried to screening conditions to generate more effective conditions but failed. The structure of 16 has been confirmed by X-ray single crystal analysis (Figure S4, Table S1). The regioselectivity of the bromination of 3 is identical with that of 3-substituted 2,1-borazaronaphthalenes,²³ indicating the limited influence to electronic distribution in side BN-naphthalene ring by central nonaromatic C₄B₂O core. These results demonstrated that the diverse BN-PAH derivatives might be accessible following the synthetic methodologies.



Scheme 3. Bromination of 3 and subsequent cross-coupling reaction.

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The most prominent features of the bis-BN-naphthalene-fused oxepins can be seen in their UV-vis and emission spectra (Table 3, Figure S8). The bis-BN-naphthalene-fused oxepins 3-17 are fluorescent both in solution and in the solid state. The absorption and luminescence maxima measured in dichloromethane (DCM) and in the solid state are listed in Table 3. The UV-vis spectra of 3-17 in DCM all exhibited three structured absorption bands in the range of 372-419 nm. These absorption maxima are significantly red-shifted compared to that reported for dibenz[b,f]oxepin (300 nm).²⁴ In addition, DFT calculation showed that the HOMO and LUMO energy gap of 3 is 3.33 ev, which is in good agreement with the experimentally observed one (3.32ev, 374nm). Compounds 3-17 emitted intense blue luminescence (423-489 nm) and nearly holds mirrorimage relationship with the absorption bands with the quantum yields ($\Phi_{\rm F}$) ranging from 0.24 to 0.79. The narrow fluorescence maxima ranges indicated that the substituents on the five-ring fused system had a limited effect on their emission maxima. Compounds 3-17 are also luminescent in the solid state. Redshifts of the emission maxima and relatively large Stokes shifts in the solid state compared to their DCM solutions (Table 2, Figure S9) are generally observed. The $\Phi_{\rm F}$ of these compounds in the solid state were apparently affected by the substituents on the main backbone, and relatively high $\Phi_{\rm F}$ values (0.56, 0.64) for **3** and **7** were observed.

Table 3. Absorption and Emission Data for Compounds 3–17 in DCM and in theSolid State (in Parentheses)

Compounds	λ_{max}	λ_{max}	Φ_{F}	Stokes Shift
	(abs, nm) ^a	(em, nm) ^b	(%) ^c	(cm-1)
3	374, 390, 413	426, 451, 480 (498, 520)	79 (56)	739 (4133)

4	374, 391, 412	428, 452 (519, 553)	77 (13)	907 (5004)
5	374, 392, 413	427, 453, 479 (506)	79 (nd) ^[d]	794 (4450)
6	374, 392, 413	433, 455 (510)	69 (43)	1118 (4605)
7	374, 391, 413	427, 453, 480 (496)	73 (64)	794 (4052)
8	374, 392, 413	427, 454, 480 (509)	70 (nd)	794 (4567)
9	374, 392, 413	429, 454 (500)	71 (50)	903 (4213)
10	380, 397, 419	433, 460, 483 (516)	68 (42)	772 (4487)
11	378, 395, 415	431, 456 (513)	69 (nd)	895 (4603)
12	378, 396, 418	430, 457, 484 (508, 516)	78 (nd)	668 (4238)
13	372, 391, 412	423, 450, 477 (475, 500)	75 (28)	631 (3219)
14	381, 399, 421	434, 461, 489 (469, 495)	68 (34)	711 (2431)
15	380, 397, 420	433, 460, 486 (479, 508)	24 (nd)	715 (2933)
16	380, 397, 419	437, 463 (476, 506)	57 (nd)	983 (2858)
17	385, 403, 425	445, 471 (478, 509)	65 (5)	1058 (2609)

^a All experiments were performed in DCM solution at 10^{-5} M. ^b Emission maximum upon excitation at the absorption maximum wavelengths. (Samples were obtained as DCM solution 10^{-6} M or grinding crystals) ^c Absolute quantum yield determined by a calibrated integrating sphere system within $\pm 3\%$ errors. ^d nd = not determined.

The absorption and fluorescence properties of **3-17** were also investigated in toluene and negligible changes of absorption and fluorescence maxima were observed (Figure S10). Interestingly, dual-fluorescent emissions were observed when dissolving N-substituted derivatives **10-14** in dimethyl sulfoxide (DMSO), different emission colors especially for white-light emissions were observed (Figure 3a). In addition to the common emission at around 450 nm found for other derivatives, **10-14**

shows another broad emission band located at approximately 550 nm. The Φ_F for selected compounds in DMSO were comparable to those in DCM (**3**: 0.68, **10**: 0.66, **12**: 0.69, **17**: 0.73). Other solvents such as tetrahydrofuran, chloroform, dimethyl formamide, acetone, tetramethylene sulfone were investigated, and only DMSO had this interesting effect. We speculated that this interesting optical property originated from the aggregates between molecules induced by DMSO.²⁵ This was checked by measuring the fluorescence dependence on the concentration of **13** (Figure 3b). Long-wavelength emission around 530 nm decreased remarkably as the decrease of solution concentration. Using **12** as a prototype, the DMSO solution of **12** (10⁻⁵ M) presents colloidal behavior, which was verified by the typical Tyndall light-scattering effect (Figure 4a). Moreover, SEM experiments were carried out to get in detail about morphologies of **12** in DMSO which showed square particles were formed (Figure 4b).



Figure 3. a) Normalized fluorescence spectra of 3, 10-14 in DMSO solutions at 10^{-6} M and emission pictures of 3, 10-14 in DMSO and DCM solutions (10^{-6} M). b) Concentration-dependent emission spectra of 13 in DMSO.



Figure 4. a) Tyndall effect of **12** in DMSO solution (10⁻⁵ M) irradiated with a green laser beam igure Caption. b) SEM micrographsof **12** self-assembled microstructures deposited from DMSO solutions at 10⁻⁵ M.

Color-tunable emission could be conveniently achieved using the DMSO/DCM mixed solvent. Compound **12** were selected to investigate the color-tunable emission in mixed solvent. As shown in Figure 5a, long-wavelength emission declined with the increasing of DCM fraction. The Commission Internationale de l'Eclairege (CIE) color coordinate of the emission spectrum of the pure DMSO solution was calculated to be (0.35, 0.44), which is at the greenish yellow emission region. When the fraction of DCM was increased to 30%, luminescent color of the solution gradually turned white. At this state, the CIE coordinate was calculated to be (0.28, 0.33), which is very close to the coordinate (0.33, 0.33) of the standard white-light illumination. The CIE coordinate of the emission spectrum was shifted to (0.15, 0.13), while pure DCM was used, corresponding to the blue-emitting region in the chromaticity diagram (Figure 5b). Moreover, white-light emission could be achieved by other derivatives such as **10** in pure DMSO (0.30, 0.34) and **11** in DMSO/DCM (DCM = 30%) mixed system (0.28, 0.31) (see Figures S12 and S13).



Figure 5. a) Fluorescence photographs of DMSO solutions of **12** with varying DCM fractions (10⁻⁵ M). b) Calculated PL emission color coordinates in the CIE 1931 chromaticity diagram.

Temperature-dependent emission properties were also observed for **12** in DMSO. The emission was gradually turned from yellow to white as increasing temperature from room temperature to 65 °C, and then blue when rising to 100 °C (see Figures S15-18). The changes in emission color can be viewed with the naked eye. For a deeper understanding of the intermolecular interactions, temperature dependent ¹HNMR studies for **12** were carried out in DMSO- d_6 . Two broaden resonances at 5.11 ppm and 7.26 ppm were observed at 25 °C, corresponding to the CH_2 on the benzyl groups and aromatic ring respectively (Figures S15). At increasing temperature to 65 °C, the original broaden signal at 5.11 ppm shifted slightly downfield to 5.13 ppm with a sharper shape. Broaden signal at 7.26 ppm spited into structured triple peak (Figures S16). This trend is even more significant at elevated temperatures (Figures S17). The original spectrum could be regenerated when the temperature returned to 25 °C (Figures S18). These results indicated that the driving forces for the self-assembly process not only due to π - π stacking but also intermolecular C-H hydrogen bonding.

CONCLUSIONS

In summary, we have succeeded in the synthesis of novel air- and moisture-stable bis-BN-naphthalene-fused oxepins by Pd-catalyzed tandem reaction of brominated 2,1-borazaronaphthalenes with 1,2-Bis(pinacolatoboryl)alkenes, which represents a concise and new strategy for constructing large BN-doped π -conjugated compounds. Unlike it's carbonaceous analogues, bis-BN-naphthalene-fused oxepins represent a planar geometry. The nonaromaticity of planar C₄B₂O seven-membered ring has been confirmed by single crystal structure analysis and DFT calculations. These bis-BN-naphthalene-fused oxepin derivatives are luminescent in both solution and the solid state with moderate to high quantum yields. Interestingly, dual-fluorescent emissions were observed upon dissolving N-substituted derivatives **10-14** in DMSO, and tunable emission colors especially white-light emission can be generated by controlling the solvent ratio, concentration or temperature with a single molecule. We believe that this interesting optical property originates from the aggregates between molecules induced by DMSO.

EXPERIMENTAL SECTION

General Experimental Methods. All solvents were obtained from commercial sources and were purified according to standard procedures. Oil bath was used as heat source for all reactions require heating. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). The ¹H, ¹³C, ¹¹B and ¹⁹F NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are referenced against external BF₃· Et₂O (¹¹B), and CFCl₃(¹⁹F). HRMS were acquired in ESI mode with the TOF mass analyzer used. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Photoluminescence (PL) spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. Quantum yields in solutions were determined with an Edinburgh Analytical Instruments FL900CD calibrated integrating sphere system. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. The commercially

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available catalysts and reagents were purchased from J&K Scientific. The reaction schemes for compounds 1, 19 and 2 can be found in the supporting information (SI).

Procedures for the Synthesis of brominated B-phenyl-2,1-borazaronaphthalenes

1a, 1b, and 1d were synthesized as described in literature.²⁶ 1c, 1e, and 1f were prepared according to the process described below. Under argon atmosphere, to a dichloromethane solution (10 mL) of B-phenyl-2,1-borazaronaphthalenes (1.6 mmol, 1 equiv) was added a solution of Br_2 (1.8 mmol, 1.1 equiv) in dichloromethane (10 mL) over 30 min at 0 °C. After the completion of the dropwise addition, the reaction mixture was slowly returned to room temperature. The mixture was then suction filtered over Celite and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel with dichloromethane/hexanes (1:50).

3-bromo-1,2-diphenyl-2,1-borazaronaphthalene (**1c**). **1c** was obtained as a white solid (0.13 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.37–7.29(m, 3H), 7.28–7.27 (m, 1H), 7.25–7.20 (m, 3H), 7.17–7.14 (m, 3H), 7.09–7.06 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 1H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.4, 143.3, 141.9, 132.7, 129.2, 129.1, 129.0, 128.6, 127.3, 127.3, 126.8, 125.5, 122.1, 118.1; HRMS (ESI) Calcd for C₂₁H₁₆BBrNO₂ [M+COOH]⁻: 404.0457, found: 404.0467.

1-benzyl-3-bromo-7-fluoro-2-phenyl-2,1-borazaronaphthalene (**1e**). **1e** was obtained as a white solid (0.52 g, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.53–7.49 (m, 1H), 7.35–7.34(m, 2H), 7.25 (s, 2H), 7.27–7.25 (m, 2H), 7.21–7.12 (m, 4H), 6.96–6,85 (m, 4H), 5.17 (m, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.9 (d, *J* = 248.5 Hz), 144.8, 140.6, 140.5, 136.6, 130.6, 130.1 (d, *J* = 10.2 Hz), 127.9, 127.2, 126.6, 126.2, 124.6, 122.4, 109.4 (d, *J* = 23.7 Hz), 103.1 (d, *J* = 26.4 Hz), 52.8; HRMS (ESI) Calcd for C₂₂H₁₇BBrNFO₂ [M+COOH]⁻: 436.0520, found: 436.0527. 1-benzyl-3-bromo-7-methyl-2-phenyl-2,1-borazaronaphthalene (**1f**). **1f** was obtained as a white solid (1.89 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.35–7.33 (m, 1H), 7.26–7.24 (m, 2H), 7.20–7.10 (m, 4H), 7.04 (s, 1H), 6.98–6.94 (m, 3H), 5.21 (s, 2H), 2.22 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.2, 140.3, 139.3, 138.6, 131.7, 129.5, 128.8, 128.0, 127.6, 126.9, 125.7, 124.6, 123.5, 117.5, 53.4, 22.3; HRMS (ESI) Calcd for C₂₃H₂₀BBrNO₂ [M+COOH]⁻: 432.0770, found: 432.0762.

ProceduresfortheSynthesisof1-benzyl-2-phenyl-7-fluoro-2,1-Borazaronaphthalene (19)

To a toluene solution (40 mL) of allylpalladium(II) chloride dimer (37 mg, 0.1 mmol), JohnPhos (60 mg, 0.2 mmol) and *t*-BuONa (3.7 g, 39 mmol) was added 2-Bromo-4-fluoro-1-vinylbenzene (3.9 g, 19.5 mmol) and benzylamine (2.5 g, 23.4 mmol). The resulting mixture was heated to 100 °C for 12 hours. The reaction mixture was cooled, diluted with Et₂O (30 mL), and filtered over Celite. The solvent was removed in vacuo and the product was purified by flash column chromatography on silica gel with dichloromethane/hexanes (1:10). The product **18** was obtained as a yellow oil (3.42 g, 77%).

N-benzyl-5-fluoro-2-vinylaniline (**18**). ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.36 (m, 5H), 7.30–7.26 (m, 1H), 6.78–6.71(m, 1H), 6.51–6.47 (m, 1H), 6.40 (d, *J* = 11.6 Hz, 1H), 5.64 (d, *J* = 17.3 Hz, 1H), 5.35 (d, *J* = 10.9 Hz, 1H), 4.36 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 164.0 (d, *J* = 243.7 Hz), 146.7 (d, *J* = 10.7 Hz), 138.6, 132.1, 128.9, 128.7 (d, *J* = 10.1 Hz), 127.6, 120.3 (d, *J* = 2.0 Hz), 116.3, 103.9 (d, *J* = 21.8

Hz), 98.3 (d, *J* = 26.3 Hz), 48.3; HRMS (ESI) Calcd for C₁₅H₁₅FN [M+H]⁺: 228.1189, found: 228.1189.

To an oven-dried Schlenk bottle with a stir bar was added **18** (8.8 mmol, 1.0 equiv), and purged with Ar three times. CPME (20 mL) and toluene (20 mL) were added, followed by the PhBF₃K (13.2 mmol, 1.5 equiv) and SiCl₄ (8.8 mmol, 1.0 equiv) under Ar. The resulting mixture was heated to 80 °C for 16 hours , and then cooled to room temperature and diluted with hexanes (35 mL). The reaction mixture was filtered over Celite and removed in vacuo. The product was purified by column chromatography on silica gel with dichloromethane/hexanes (1:30). **19** was obtained as a white solid (1.10 g, 40%).

1-benzyl-7-fluoro-2-phenyl-2,1-borazaronaphthalene (**19**). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 11.4 Hz, 1H), 7.69–7.65 (m, 1H), 7.56–7.53 (m, 2H), 7.36–7.31 (m, 5H), 7.28–7.26 (m, 1H), 7.15–6.92 (m, 5H), 5.40 (s, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.9 (d, *J* = 245.9 Hz), 144.8, 142.6 (d, *J* = 10.4 Hz), 138.5, 132.5, 131.7 (d, *J* = 10.2 Hz), 128.9, 128.2, 127.8, 127.1, 125.7, 124.0 (d, *J* = 1.8 Hz), 109.4 (d, *J* = 22.9 Hz), 103.8 (d, *J* = 25.0 Hz), 52.7; HRMS (ESI) Calcd for C₂₂H₁₈BFNO₂ [M+COOH]⁻: 358.1415, found: 358.1411.

Procedures for the Synthesis of cis-Bis(boryl)alkenes

2a, 2b, 2d, and 2g were synthesized as described in literature.²⁷ 2c, 2e, and 2f were prepared according to the process described below. To a degassed solution of alkyne (1.0 mmol, 1.1equiv) and bis(pinacolato)diboron (0.9 mmol, 1.0 equiv) in DMF (5 mL) was added Pt(PPh₃)₄ (2.0 mol%). The reaction mixture was heated to 80 °C for 24 hours. After this time, the reaction was washed with saturated aqueous

NH₄Cl, and the aqueous phase is extracted with diethyl ether. The organic phase was dried over MgSO₄ and concentrated under reduced pressure to give the crude products, which were purified by recrystallisation from ethanol.

(Z)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2-di-m-tolylethene (**2c**). **2c** was obtained as a white solid (319 mg, 79%). ¹H NMR (400 MHz, CDCl₃) δ 6.94 (t, *J* = 7.6 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.77 (s, 2H), 6.72 (d, *J* = 7.6 Hz, 2H), 2.14 (s, 6H), 1.32 (s, 24H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 141.2, 136.6, 130.0, 127.2, 126.5, 126.3, 84.0, 24.9, 21.4; HRMS (ESI) Calcd for C₂₈H₃₉B₂O₄ [M+H]⁺: 461.3034, found: 461.3040.

(Z)-1,2-bis(4-fluorophenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan e (**2e**). **2e** was obtained as a white solid (535 mg, 88%). ¹H NMR (400 MHz, CDCl3) δ 6.89 (dd, J = 8.8, 5.6 Hz, 4H), 6.79 (t, J = 8.8 Hz, 4H), 1.32 (s, 24H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 161.2 (d, J = 245.0 Hz), 136.9 (d, J = 3.4 Hz), 130.8 (d, J = 7.8 Hz), 114.5 (d, J = 21.2 Hz), 84.2, 24.9; HRMS (ESI) Calcd for C₂₇H₃₃B₂F₂O₆ [M+COOH]⁻: 513.2431, found: 513.2429.

(Z)-1,2-bis(4-chlorophenyl)-1,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethen e (**2f**). **2f** was obtained as a white solid (413 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.08–7.06 (m, 4H), 6.88 – 6.85 (m, 4H), 1.31 (s, 24H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 139.3, 131.9, 130.6, 128.0, 84.3, 24.9; HRMS (ESI) Calcd for C₂₇H₃₃B₂Cl₂O₆ [M+COOH]^{-:} 545.1840, found: 545.1835.

Typical Procedures for the Synthesis of Compound 3-14.

Under argon atmosphere, to an acetonitrile solution (3 mL) of **1** (0.36 mmol, 2.0 equiv), **2** (0.18 mmol, 1.0 equiv), and Pd(OAc)₂ (5 mol%) was added K₂CO₃ (0.72 mmol, 4.0 equiv) and water (0.18 mmol, 1.0 equiv). The resulting mixture was heated

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to 70 °C for 15 hours. After completion of the reaction, the mixture was diluted with dichloromethane and washed twice with water. The aqueous phase was extracted with DCM, dried over MgSO₄, filtered and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel (dichloromethane/hexanes, 1:3).

13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (**3**). **3** was obtained as a yellow soild in 84% (68 mg). M.p.: > 300 °C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.4; ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.13–7.09 (m, 8H), 7.02–6.88 (m, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.8, 145.0, 144.0, 140.2, 130.8, 130.1, 128.6, 127.5, 125.3, 123.9, 120.0, 116.0; HRMS (ESI) Calcd for C₃₀H₂₂B₂N₂NaO [M+Na]⁺: 471.1816, found: 471.1820; IR (neat): *v* = 596, 659, 703, 755, 804, 1025, 1095, 1153, 1181, 1229, 1266, 1334, 1425, 1538, 1603, 2962, 3048, 3388 cm⁻¹.

13,14-di-p-tolyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (4). 4 was obtained as a yellow soild in 60% (52 mg). M.p.: 269–271°C;¹¹B NMR (128 MHz, CDCl₃) δ 30.9; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.20 (m, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.09 (s, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.92–6.87 (m, 8H), 6.81 (d, *J* = 8.0 Hz, 4H), 2.23 (s, 6H); ¹³C{¹H} NMR (101 MHz, (CD₃)₂SO) δ 146.7, 143.3, 141.0, 140.9, 133.7, 130.2, 129.2, 128.5, 128.1, 123.0, 119.6, 116.6, 20.7; HRMS (ESI) Calcd for C₃₂H₂₆B₂N₂O [M]⁺: 476.2231, found: 476.2236; IR (neat): *v* = 598, 656, 705, 749, 814, 1107, 1180, 1228, 1268, 1296, 1336, 1426, 1538, 1608, 2369, 3394 cm⁻¹.

13,14-di-m-tolyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (**5**). **5** was obtained as a yellow soild in 52% (45 mg). M.p.: 231–233°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.6; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.22 (m, 2H), 7.16 (d, *J* = 6.2 Hz, 4H), 7.01–6.97 (m, 4H), 6.92–6.88 (m, 4H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.74 (d, *J* = 8.8 Hz, 4H), 2.19 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.7, 144.0, 143.8, 140.2, 136.7, 131.6, 130.1, 128.5, 127.8, 127.1, 125.8, 124.0, 120.0, 116.0, 21.3; HRMS (ESI) Calcd. for

 $C_{32}H_{26}B_2N_2O$ [M]⁺: 476.2231, found: 476.2230; IR (neat): v = 465, 668, 714, 754,1229, 1271, 1336, 1425, 1542, 1606, 2363, 3022, 3373 cm⁻¹.

13,14-bis(4-methoxyphenyl)-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (6). 6 was obtained as a yellow soild in 83% (76 mg). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.6; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.21 (m, 2H), 7.15 (d, J = 7.4 Hz, 2H), 7.11 (s, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.92–6.88 (m, 4H), 6.85–6.83 (m, 4H), 6.68–6.66 (m, 4H), 3.75 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 156.9, 147.7, 144.0, 140.1, 136.7, 131.6, 130.1, 128.5, 123.9, 120.0, 116.0, 112.9, 55.1; HRMS (ESI) Calcd for C₃₂H₂₆B₂N₂O₃ [M]⁺: 508.2130, found: 508.2127; IR (neat): v = 755, 1112, 1173, 1234, 1278, 1340, 1428, 1500, 1538, 1608, 2365, 3397 cm⁻¹.

13,14-bis(4-fluorophenyl)-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (7). 7 was obtained as a yellow soild in 60% (52 mg). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.4; ¹⁹F NMR (376 MHz, CDCl₃) δ -117.1; ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.24 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.05 (s, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.94–6.81 (m, 12H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 160.6 (d, *J* = 244.5 Hz), 147.9, 143.4, 140.2, 139.8 (d, *J* = 3.6 Hz), 132.1 (d, *J* = 7.7 Hz), 130.1, 128.9, 123.7, 120.2, 116.1, 114.6 (d, *J* = 21.1 Hz); HRMS (ESI) Calcd for C₃₀H₂₀B₂F₂N₂O [M]⁺: 484.1730, found: 484.1727; IR (neat): *v* = 668, 712, 754, 829, 1211, 1271, 1344, 1426, 1498, 1541, 2364, 3409 cm⁻¹.

13,14-bis(4-chlorophenyl)-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (8). 8 was obtained as a yellow soild in 87% (81 mg). M.p.: > 300° C;¹¹B NMR (128 MHz, CDCl₃) δ 31.3; ¹H NMR (400 MHz, CDCl₃) δ 7.28–7.24(m, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.14–7.10 (m, 4H), 7.02–7.00 (m, 4H), 6.95–6.91 (m, 4H), 6.88–6.85 (m, 4H); ¹³C{¹H} NMR (101 MHz, (CD₃)₂SO) δ 147.4, 143.0, 142.9, 141.6, 132.8, 130.5, 129.9, 129.3, 128.2, 123.3, 120.2, 117.1; HRMS (ESI) Calcd for C₃₀H₂₀B₂Cl₂N₂O

 $[M]^+$: 516.1139, found: 516.1136; IR (neat): v = 597, 659, 708, 754, 821, 1012, 1089, 1229, 1270, 1336, 1425, 1481, 1539, 1608, 2366, 3395 cm⁻¹.

13-(4-methoxyphenyl)-14-(4-(trifluoromethyl)phenyl)-di-2,1-borazaronaphtho[2,3-b: 2',3'-f]oxepine (**9**). **9** was obtained as a yellow soild in 80% (78 mg). M.p.: 280-282°C;¹¹B NMR (128 MHz, CDCl₃) δ 31.6; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.3; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 7.9 Hz, 2H), 7.27–7.24 (m, 2H), 7.17–7.12 (m, 3H), 7.04 (dd, *J* = 7.8, 20.8 Hz, 4H), 6.94–690 (m, 5H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 157.3, 148.2, 148.1, 147.4, 144.0, 142.8, 140.2, 140.1, 135.7, 131.6, 131.0, 130.2, 130.0, 128.8, 127.3 (q, *J* = 32.2 Hz), 125.7, 124.5 (q, *J* = 3.6 Hz), 124.3 (q, *J* = 272.7 Hz), 123.8, 123.7, 120.2, 120.1, 116.1, 113.2, 55.1; HRMS (ESI) Calcd for C₃₂H₂₃B₂F₃N₂O₂ [M]⁺: 546.1898, found: 546.1895; IR (neat): *v* = 753, 1066, 1111, 1166, 1235, 1324, 1427, 1611, 2338, 2366, 3400 cm⁻¹.

5,7-dibutyl-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (**10**). **10** was obtained as a yellow soild in 63% (53 mg). M.p.: 231-234°C; ¹¹B NMR (128 MHz, CDCl₃) δ 31.9; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.32 (m, 2H), 7.27 (d, *J* = 7.6, 2H), 7.15–7.05(m, 8H), 7.00–6.90 (m, 8H), 4.21 (s, 4H), 1.87–1.79 (m, 4H), 1.60–1.53 (m, 4H), 1.06 (t, *J* = 7.3 Hz, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.4, 144.3, 143.8, 141.4, 131.0, 130.9, 128.6, 127.4, 125.2, 124.9, 119.4, 113.7, 43.4, 31.7, 20.8, 14.2; HRMS (ESI) Calcd for C₃₈H₃₈B₂N₂O [M]⁺: 560.3170, found: 560.3167; IR (neat): *v* = 595, 699, 740, 1232, 1324, 1348, 1404, 1634, 2365, 2927, 2955, 3438 cm⁻¹.

5,7,13,14-tetraphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (11). 11 was obtained as a yellow soild in 69% (58 mg). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.1; ¹H NMR (400 MHz, CDCl₃) δ 7.22–7.09 (m, 14H), 7.03–6.96 (m, 8H),

6.85–6.81 (m, 6H), 6.10 (d, J = 8.4 Hz, 2H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.8, 144.1, 143.5, 142.0, 130.9, 130.1, 129.6, 128.3, 128.2, 127.5, 126.8, 125.3, 123.9, 119.9, 115.9, 100.0; HRMS (ESI) Calcd for C₄₂H₃₀B₂N₂O [M]⁺: 600.2544, found: 600.2541; IR (neat): v = 536, 591, 696, 734, 906, 1070, 1120, 1235, 1296, 1328, 1402, 1490, 1538, 1585, 2367, 3054, 3435 cm⁻¹.

5,7-dibenzyl-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (12). 12 was obtained as a yellow soild in 78% (64 mg). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 31.4; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.20 (m, 8H), 7.15–7.11 (m, 9H), 7.06–6.94 (m, 11H), 6.87 (t, *J* = 7.4 Hz, 2H), 5.05 (s, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 147.9, 144.1, 143.9, 141.6, 138.4, 130.9, 130.8, 128.8, 128.5, 127.5, 126.6, 125.9, 125.3, 124.8, 119.9, 114.7, 47.3; HRMS (ESI) Calcd for C₄₄H₃₄B₂N₂O [M]⁺: 628.2857, found: 628.2855; IR (neat): *v* = 595, 697, 753, 1118, 1231, 1334, 1358, 1410, 1490, 1539, 1605, 2338, 2368, 3433 cm⁻¹.

5,7-dibenzyl-3,9-difluoro-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepin e (**13**). **13** was obtained as a yellow soild in 73% (63 mg). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 31.5; ¹⁹F NMR (376 MHz, CDCl₃) δ -110.4; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.21(m, 4H), 7.15–6.96 (m, 20H), 6.66–6.58 (m, 4H), 4.95 (s, 4H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 162.3 (d, *J* = 246.3 Hz), 146.2, 142.8, 142.5, 142.1 (d, *J* = 10.9 Hz), 136.6, 131.3 (d, *J* = 10.2 Hz), 129.7, 127.6, 126.5, 125.9, 124.7, 124.4, 120.4, 106.9 (d, *J* = 23.0 Hz), 100.6 (d, *J* = 26.2 Hz), 46.5; HRMS (ESI) Calcd for C₄₄H₃₂B₂F₂N₂O [M]⁺: 664.2669, found: 664.2667; IR (neat): *v* = 523, 1112, 1173, 1345, 1414, 1631, 2364, 3437 cm⁻¹.

5,7-dibenzyl-3,9-dimethyl-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepi ne (14). 14 was obtained as a yellow soild in 77% (66 mg). M.p.: 284–286°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.6; ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.19 (m, 4H),

7.13–6.97 (m, 20H), 6.76 (s, 2H), 6.69 (d, J = 7.9 Hz, 2H), 4.97 (s, 4H), 2.22 (s, 6H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.5, 143.2, 140.7, 138.0, 137.6, 129.9, 129.6, 127.4, 126.4, 125.5, 124.9, 124.1, 121.6, 120.2, 113.9, 76.3, 76.0, 75.7, 46.1, 21.1; HRMS (ESI) Calcd for C₄₆H₃₈B₂N₂O [M]⁺: 656.3170, found: 656.3166; IR (neat): v =669, 699, 1125, 1232, 1317, 1345, 1406, 1613, 2338, 2367, 3448 cm⁻¹.

Procedure for Double Bromination of 3

Under argon atmosphere, to a dichloromethane solution (10 mL) of **3** (148 mg, 0.33 mmol) was added a solution of Br_2 (117 mg, 0.73 mmol) in dichloromethane (10 mL) over 30 min at 0 °C. After the completion of the dropwise addition, the reaction mixture was slowly returned to room temperature. Solvent was then removed in vacuo to give **15** as a yellow solid in quantitive yield (178 mg).

2,10-dibromo-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxepine (15). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 31.7; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (dd, J = 8.6, 2.2Hz, 2H), 7.24 (d, J = 2.1 Hz, 2H), 7.11 (t, J = 7.4 Hz, 4H), 7.03–6.98 (m, 4H), 6.92–6.89 (m, 8H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 146.7, 144.4, 143.4, 138.9, 132.0, 131.3, 130.5, 127.6, 125.6, 125.5, 117.6, 112.3; HRMS (ESI) Calcd for C₃₀H₂₀B₂Br₂N₂O [M]⁺: 606.0108, found: 606.0105; IR (neat): v = 654, 702, 803, 1024, 1094, 1261, 1335, 1434, 2338, 2366, 2962, 3392 cm⁻¹.

Suzuki cross-coupling reaction of 15 with 4-methoxyphenylboric

To a pressure resistant tube under an atmosphere of Ar was sequentially added **15** (50 mg, 0.08 mmol), 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (188 mg, 0.6 mmol), Na₂CO₃ (50 mg, 0.48 mmol), Pd(PPh₃)₄ (28 mg, 0.024 mmol), THF (4 mL) and H₂O (0.26 mL). The reaction mixture was heated at 80 °C for 20 hours. After this time, the reaction mixture was cooled to room temperature, diluted

with dichloromethane and washed with water. The organic layer was separated, dried over MgSO₄ and removed in vacuo. The product was purified by flash column chromatography on silica gel with dichloromethane/hexanes (1:2), which is a yellow solid in 55% yield (28 mg).

2-bromo-10-(4-methoxyphenyl)-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f] oxepine (**16**). M.p.: 266–268°C; ¹¹B NMR (128 MHz, CDCl₃) δ 30.8; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.42 (m, 3H), 7.31–7.24 (m, 3H), 7.15–7.10 (m, 5H), 7.07–7.00 (m, 3H), 6.97–6.88 (m, 10H), 3.82 (s, 3H); ¹³C{¹H} NMR (101 MHz, CDCl₃) δ 158.7, 148.3, 146.3, 144.8, 143.7, 143.7, 143.6, 139.1, 139.0, 133.4, 133.1, 131.9, 131.1, 130.7, 127.9, 127.8, 127.6, 127.5, 125.5, 125.5, 125.4, 124.1, 117.6, 116.5, 114.1, 112.2, 55.4; HRMS (ESI) Calcd for C₃₇H₂₇B₂Br₁N₂O₂ [M]⁺: 632.1442, found: 632.1438; IR (neat): ν = 707, 1179, 1244, 1283, 1342, 1428, 1514, 1544, 1609, 2363, 3384 cm⁻¹.

To a pressure resistant tube under an atmosphere of Ar was sequentially added 15 (50 mg, 0.08 mmol), 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (384 mg, 1.6 mmol), Na₂CO₃ (52 mg, 0.49 mmol), Pd(PPh₃)₄ (29 mg, 0.025 mmol), THF (2 mL) and H₂O (0.26 mL).The reaction mixture was heated at 80 °C for 48h .After this time, the reaction mixture was cooled to room temperature, diluted with dichloromethane and washed with water. The organic layer was separated, dried over MgSO₄ and removed in vacuo.The product was purified by flash column chromatography on silica gel with dichloromethane/hexanes(1:1), which is a yellow solid in 72% yield (39 mg).

2,10-bis(4-methoxyphenyl)-13,14-diphenyl-di-2,1-borazaronaphtho[2,3-b:2',3'-f]oxep ine (17). M.p.: > 300°C; ¹¹B NMR (128 MHz, CDCl₃) δ 31.7; ¹H NMR (400 MHz, CDCl₃) δ 7.47–7.42 (m, 6H), 7.28 (s, 2H), 7.15–7.10 (m, 6H), 7.07–7.00 (m, 4H),

59 60

1	
2 3 4	6.97–6.90 (m, 10H), 3.81 (s, 6H); ¹³ C{ ¹ H} NMR (101 MHz, CDCl ₃) δ 158.6, 147.9,
5	144.1, 143.9, 139.2, 133.0, 130.8, 127.8, 127.7, 127.5, 127.4, 125.3, 124.1, 116.4,
7 8	114.1, 55.3; HRMS (ESI) Calcd for C ₄₄ H ₃₄ B ₂ N ₂ O ₃ [M] ⁺ : 660.2756, found: 660.2751;
9 10	IR (neat): $v = 818$ 1143 1178 1245 1294 1340 1436 1513 1608 2366 3432 cm ⁻¹
11 12	ACCOCIATED CONTENT
13	ASSOCIATED CONTENT
14 15	Supporting Information
16 17	The Supporting Information is available free of charge on the ACS Publications
18	website at DOI:10.1021/xxxxxxxxxxx.
19 20	UV-vis and emission spectra of 3-17
21	Temperature dependent ¹ HNMR spectra for 12
23	DFT calculations details for 3 and 3'
24 25	Copies of NMR spectra of all new compounds, and single crystal X-ray data
26 27	X-ray crystallography data for compound 3, 8 and 16 (CIF)
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36 37	Notes
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52 53	REFERENCES
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