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Novel Molecular Building Blocks Based on the Boradiazaindacene Chromophore: Applications in Fluorescent Metallosupramolecular Coordination Polymers

Ö. Altan Bozdemir,^[a] Onur Büyükcakir,^[a, b] and Engin U. Akkaya*^[a]

Abstract: We designed and synthesized novel boradiazaindacene (Bodipy) derivatives that are appropriately functionalized for metal-ion-mediated supramolecular polymerization. Thus, ligands for 2-terpyridyl-, 2,6-terpyridyl-, and bipyridyl-functionalized Bodipy dyes were synthesized through Sonogashira couplings. These fluorescent building blocks are responsive to metal ions in a stoichiometry-dependent

manner. Octahedral coordinating metal ions such as Zn^{II} result in polymerization at a stoichiometry corresponding to two terpyridyl ligands to one Zn^{II} ion. However, at increased metal ion

Keywords: coordination polymers • dyes/pigments • polymerization • self-assembly • Sonogashira coupling

concentrations, the dynamic equilibria are re-established in such a way that the monomeric metal complex dominates. The position of equilibria can easily be monitored by ^1H NMR and fluorescence spectroscopies. As expected, although open-shell Fe^{II} ions form similar complex structures, these cations quench the fluorescence emission of all four functionalized Bodipy ligands.

Introduction

Coordination polymers represent a distinct group of supramolecular polymers,^[1–6] which have attracted great attention in recent years.^[7–12] The degree of polymerization in such polymers is primarily controlled by the concentration of the building blocks in solution and the strength of interaction between the ligand and the metal ion. The dynamic nature of the equilibria governing the extent of polymerization provides enormous potential in manipulating the macroscopic properties of these polymers, whether in solution or in other phases. Recent studies in the groups of Würthner^[13–15] and Schubert^[16,17] established the viability of the terpyridyl–metal coordinative bond as a promising strategy for the preparation of such self-assembled supramolecular polymers. In these studies, fluorescent supramolecular coordina-

tion polymers were obtained by utilizing terpyridyl– Zn^{II} coordination.

Boradiazaindacene^[18–19] dyes (also known as bodipy dyes, boron-dipyrin dyes, and BDPs) are bright fluorophores with many desirable properties, including very versatile chemistry of the parent fluorophore.^[20–23] In recent years, there has been a flurry of activity investigating many derivatives and numerous applications of these dyes. Among these, fluorescent chemosensors,^[24–27] molecular logic gates,^[28] fluorescent organogels,^[29] sensitizers in dye-sensitized solar cells,^[30,31] cellular imaging,^[32] and applications in photodynamic therapy^[33,34] are particularly noteworthy. There have also been previous reports of bipyridyl^[35,36] and terpyridyl^[37–39] derivatives of bodipy dyes and their Zn^{II} complexes, although the monomeric derivatives were not designed for self-assembled polymerization. Herein, we report 2- and 2,6-derivatized bodipy dyes with one or two ligands per bodipy unit, placed on opposite ends of the fluorophore core. In the case of the bis(terpyridyl) derivative, clear signals of polymerization are observed by using ^1H NMR spectroscopy upon gradual addition of Zn^{II} . The additional data obtained from the monoterpyridyl derivative also corroborates the interpretation of the spectral changes observed by using NMR spectroscopy. In addition, the ligand is attached to the bodipy core through triple bonds, and any changes in charge density distribution are transmitted to the core. The result is a significant enhancement in

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the emission intensity upon Zn^{II} binding, which is accompanied by a small blueshift in the absorption spectrum. Thus, formation of the coordination polymers were also evidenced by fluorescence changes of the fluorophores. To the best of our knowledge, signaling of metal-ion-mediated polymerization through a clear and observable change in the emission intensity was unprecedented.

Results and Discussion

Synthesis of the building blocks: To improve solubility in organic solvents, our synthetic approach required the initial synthesis of a bodipy derivative with 3,5-bis(decyloxy)phenyl groups at the *meso* positions. We started our synthesis with 3,5-bis(decyloxy)benzaldehyde **1**, which can be obtained by a two-step conversion from commercially available 3,5-dihydroxybenzyl alcohol. Standard procedures yielded bright green emitting bodipy dye **2** in 30 % yield. Addition of different molar ratios of I_2/HIO_3 to bodipy **2** resulted in either monoiodinated **3**, or diiodinated **4** bodipy derivatives.^[40] Ligands were tethered to the fluorophore unit through Sonogashira couplings using either 4-ethynylphenylterpyridyl or bis(ethynylbipyridyl), both of which were described by Ziesel and co-workers.^[39,41] The reactions proceeded smoothly, yielding target compounds **5**, **6**, **7**, and **8**. Maximal absorption peaks showed larger redshifts in the cases of 2,6-bis-substituted products (571 and 577 nm, **8** and **7** respectively). Compound **6** was designed as the monomeric building block for a fluorescent supramolecular coordination polymer. Compound **5** is a reference compound, expected to assist us in identifying spectral changes on polymer formation. Bipyridyl derivatives **7** and **8** are different types of building block that might be useful in the construction of gridlike structures and metal-ion-coordination-mediated energy transfer and light-harvesting systems. Compound **8** (Scheme 1) is

Abstract in Turkish: *Bu çalışmada, metal iyonları aracılığıyla supramoleküler polimerizasyon için uygun şekilde fonksiyonlandırılmış yeni boradiazaindasen (Bodipy) türevleri tasarlanmış ve sentezlenmiştir. Bu amaçla, ligand olarak Sonogashira reaksiyonu ile 2- ve 2,6-terpiridil ve bipiridil gruplarını içeren Bodipy boyarmaddeleri sentezlenmiştir. Bu floresan yapı blokları stokiyometriye bağlı bir biçimde metal iyonlarına duyarlılık gösterirler. Zn^{II} gibi oktahedral koordinasyon eğilimi olan metal iyonları, iki terpiridil ligandına bir Zn^{II} iyonu tekabül edecek bir stokiyometride polimerizasyona yol açmaktadırlar. Bununla beraber, yüksek metal iyonu derişimlerinde monomerik metal kompleksinin baskın olacağı bir biçimde, dinamik dengeler yeniden kurulmaktadır. Bu dengelelerin pozisyonu ^1H NMR ve floresans spektroskopileriyle kolaylıkla izlenebilmektedir. Beklenildiği gibi, benzer kompleks yapılar oluşturmaya rağmen Fe^{II} iyonu, sentezlenen tüm fonksiyonallaştırılmış Bodipy ligandlarının emisyonlarını sönmüldirmektedir.*

particularly relevant in ion-sensing applications based on earlier literature data in which chromophores were tethered by bipyridyl linkages.^[39]

NMR spectroscopic study of the complexation and coordination polymer formation: Metal ion complexation results in characteristic signal changes in the ^1H NMR spectra (Figure 1). First, the monoterpyridyl-bodipy compound **5** is

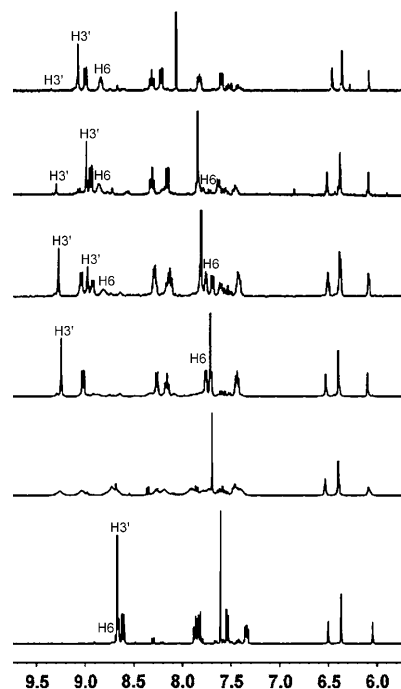
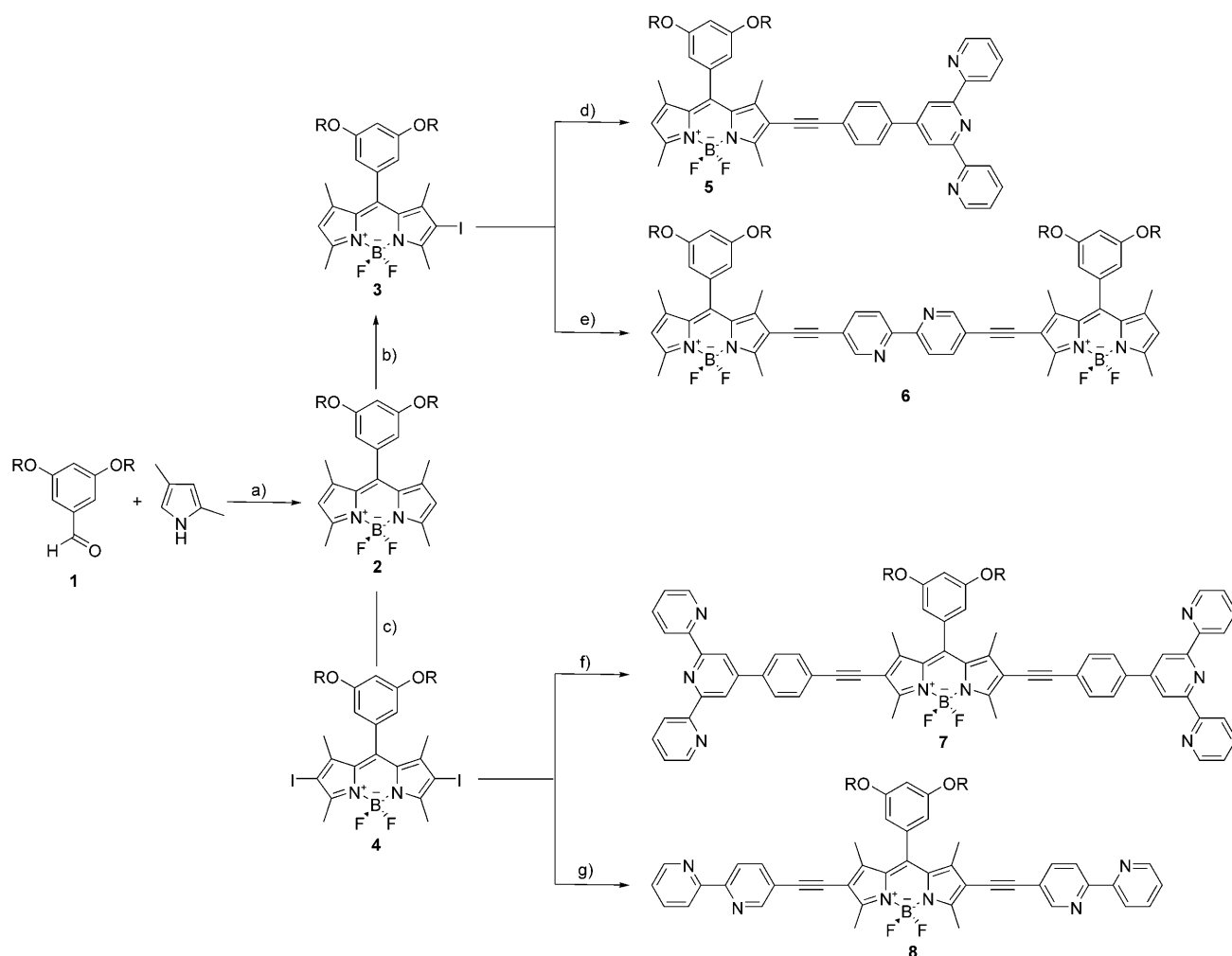
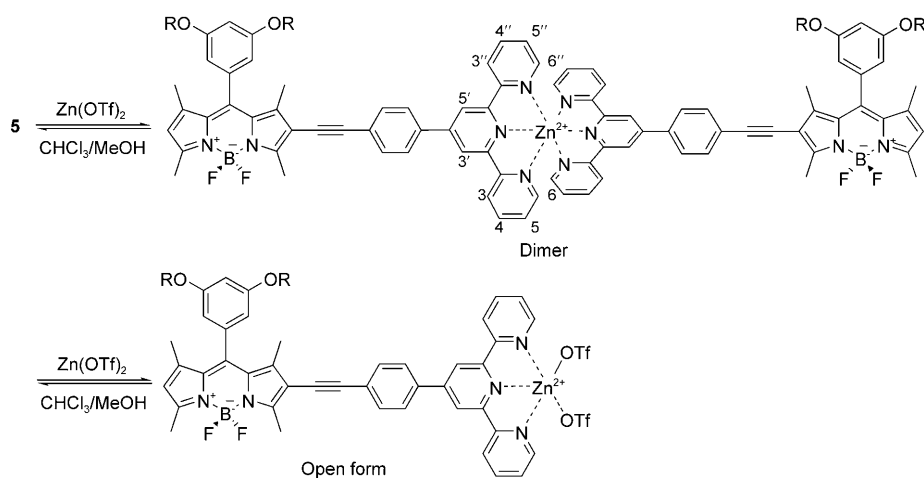


Figure 1. ^1H NMR spectra obtained by the titration of **5** in 60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$ (13 mm) with $\text{Zn}(\text{OTf})_2$. $\text{Zn}^{\text{II}}/\mathbf{5}$ ratio varies from bottom to top as 0:1, 0.25:1, 0.5:1, 0.75:1, 1:1, 1:1.5.

highly instructive. As expected, whereas the ^1H NMR signals corresponding to the bodipy core are not noticeably shifted upon complexation, terpyridyl signals shift to low field on Zn^{II} complex formation. Addition of 0.25 equivalents of Zn^{II} to **5** results in some signal broadening together with a downfield shift. When the amount of Zn^{II} is increased to 0.5 equivalents, the molar ratio is just right for the 2:1 (**5**– Zn^{II}) complex. The most downfield sharp signal has been identified as the $\text{H}3'$ singlet. In the 2:1 complex, it appears at $\delta = 9.3$ ppm. The most characteristic change is that of the $\text{H}6$ (and $\text{H}6'$) signal: complex formation induces a significant upfield shift because those hydrogen nuclei will be brought into the shielding zone of the pyridine rings of the other terpyridyl. As a result, in the metal-free ligand **5**, the $\text{H}6$ nuclei resonate at $\delta = 8.7$ ppm, but in the 2:1 complex, this signal moves to $\delta = 7.7$ ppm. As previously demonstrated, further addition of Zn^{II} decreases the equilibrium concentration of the dimeric 2:1 complex in favor of the “open form” (Scheme 2). As a result, the sharp downfield $\text{H}3'$ singlet decreases in intensity as more and more Zn^{II} is added. At 1:1.5 equivalents of Zn^{II} , the signal at $\delta = 9.3$ ppm practi-



Scheme 1. a) i) **1**, 2,4-dimethyl pyrrole, trifluoroacetic acid (TFA), CH_2Cl_2 , RT, 1 d, ii) 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), NEt_3 , $\text{BF}_3\cdot\text{OEt}_2$, CH_2Cl_2 , RT, 2 h; b) **2**, I_2 (1 equiv), HIO_3 , $\text{EtOH}/\text{H}_2\text{O}$, 60°C , 1 h; c) **2**, I_2 (2 equiv), HIO_3 , $\text{EtOH}/\text{H}_2\text{O}$, 60°C , 1 h; d) **3**, 4'-ethynyl-2,2',6'2''-terpyridine, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, THF/diisopropylamine, 50°C , 40 min then RT, 1 d; e) **3**, 5,5'-diethynyl-2,2'-bipyridine, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, THF/diisopropylamine, 50°C , 40 min then RT, 1 d; f) **4**, 4'-ethynyl-2,2',6'2''-terpyridine, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, THF/diisopropylamine 50°C , 40 min then RT, 1 d; g) 5-ethynyl-2,2'-bipyridine, $[\text{PdCl}_2(\text{PPh}_3)_2]$, CuI, THF/diisopropylamine, 50°C , 40 min then RT, 1 d. R = decyl.



Scheme 2. Formation of dimeric and open-form structures by the addition of $\text{Zn}(\text{OTf})_2$.

cally disappears and a new singlet at $\delta=9.1$ ppm becomes prominent. That particular signal corresponds to the open 1:1 Zn^{II} complex, **5-Zn^{II}**. In this complex, other coordination sites of Zn^{II} should be occupied with DMSO molecules or triflate ions. Bis(terpyridyl) compound **7** displays very clear signs of polymerization on addition of Zn^{II} (Figure 2). Upon addition of 0.25 equivalents of Zn^{II} , the ^1H NMR signals become very broad. The addition of one equivalent of Zn^{II} should generate the largest polymer chain lengths, and this is

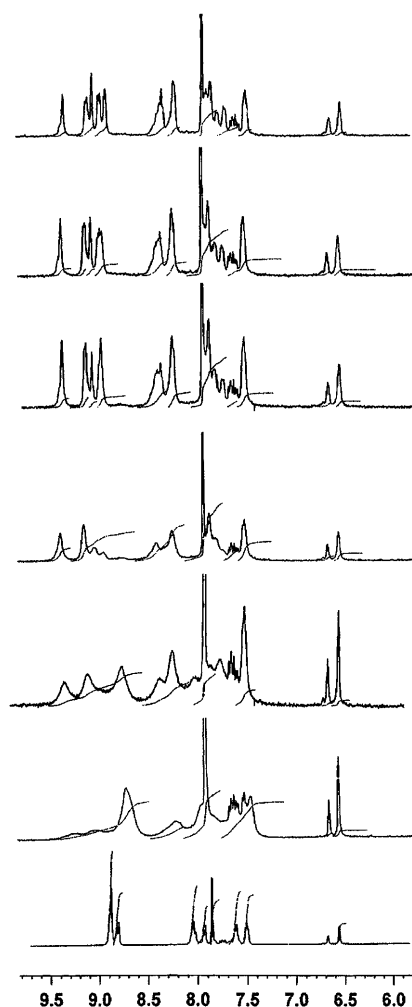
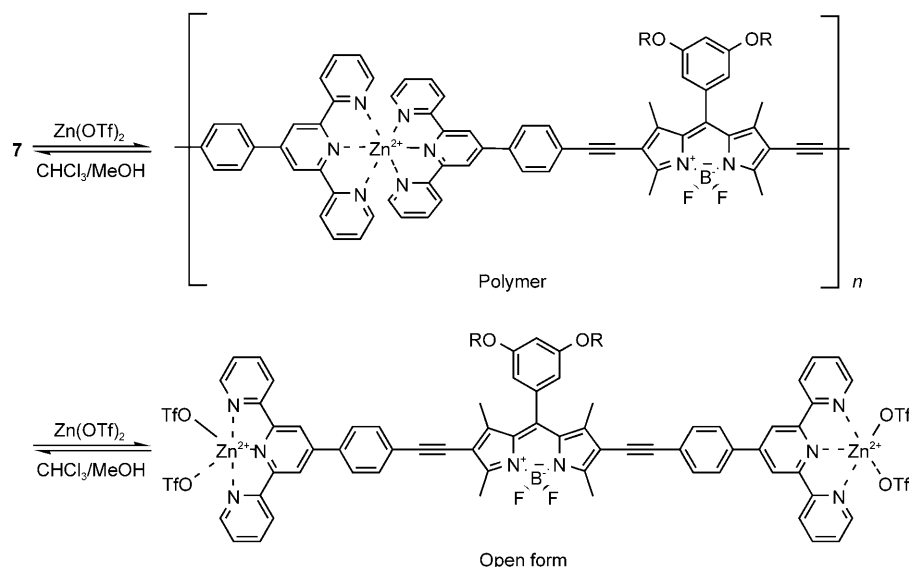


Figure 2. ^1H NMR spectra obtained by the titration of **7** in 60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$ (13 mm) with $\text{Zn}(\text{OTf})_2$. $\text{Zn}^{II}/\mathbf{7}$ ratio varies from bottom to top as 0:1, 0.25:1, 0.5:1, 0.75:1, 1:1, 2:1, 3:1.

clearly reflected in the broadness of the signals. As expected, the pyridine ring protons of the terpyridyl group shifted downfield. Most interestingly, addition of more than 0.5 equivalents of Zn^{II} to ligand **7** results in sharpening of the ^1H NMR signals of the aromatic protons. Upon addition of one or more equivalents of Zn^{II} , the NMR spectra display a clear predominance of the 1:1 open-form complex, with very distinctively sharper monomeric aromatic hydrogen signals (Scheme 3).

Absorbance and steady-state fluorescence spectroscopic in-

vestigation of the complexation and coordination polymer formation: To synthesize the building blocks, terpyridyl-phenyl and bipyridyl groups have been attached to the fluorophore core through ethynyl spacers; there is some conjugation and thus electronic communication between the ligand moieties and the bodipy cores. As a result, we observe spectral changes not only in peaks that correspond to $\pi-\pi^*$ transitions in the oligopyridine moieties, but in bodipy S_0-S_1 transitions as well. For example, in the reference compound **5**, the increase in the absorption of the peak at 325 nm peak and the shoulder at 400 nm are due to terpyridyl ligand– Zn^{II} coordinative interactions. As the inset in Figure 3 clearly shows, above 0.5 equivalents of Zn^{II} , the change in the absorption levels off very quickly, indicating a strong affinity between the ligand and the Zn^{II} in this particular solvent system (80:20 $\text{CHCl}_3/\text{MeOH}$). In addition, there is a small increase of the bodipy absorption peak at 536 nm as the added amount of Zn^{II} is increased (the extinction coefficient (ϵ) changes from 95 000 to 104 000 $\text{cm}^{-1}\text{M}^{-1}$). Zn^{II} titration of the monotopic ligand **5** shows a gradual increase in the emission intensity (Figure 4) and at saturation the intensity of the bodipy emission is nearly doubled. There is a concomitant small blueshift in the emission intensity in this peak, from 572 to 563 nm. The equilibrium constant (K_1) for the first binding event (**5**– Zn^{II}), determined by following the absorbance changes at 325 nm, is $6.8 \times 10^6 \text{ M}^{-1}$. Zn^{II} titration of the ditopic bis(terpyridyl) bodipy ligand **7** shows similar changes. There are increases in the absorption peaks at 325, 400 (shoulder), and 577 nm (bodipy S_0-S_1 transition) (Figure 5). As expected, the absorption changes at 325 nm (Figure 5, inset) level off only after one equivalent of Zn^{II} ions were added (1:1). In the fluorescence spectrum (Figure 6), there is a minor increase (+30 %) in the intensity with just a few nanometers of blueshift in the peak position (from 608 to 602 nm). As expected, the bipyridyl– Zn^{II} interaction is weaker, and coordination stoichiometry and spatial arrangement of the bodipy chromophores should be differ-



Scheme 3. Formation of polymeric and open-form structures by the addition of $\text{Zn}(\text{OTf})_2$.

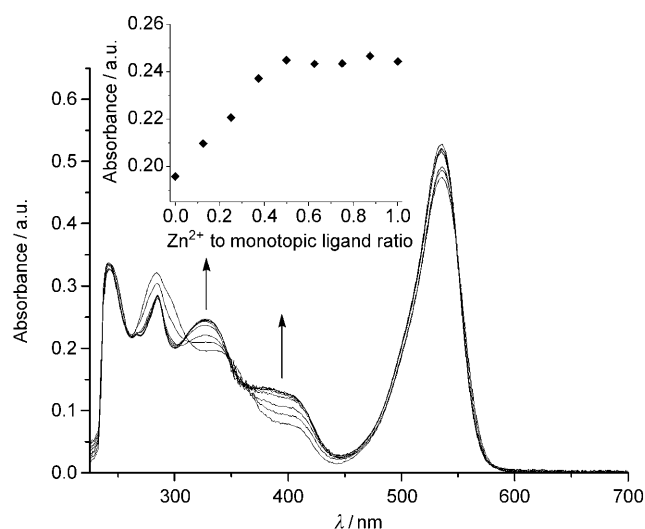


Figure 3. UV/Vis spectra obtained by the titration of **5** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂. The inset shows the absorption coefficient at 325 nm as a function of the Zn^{II}/**5** ratio.

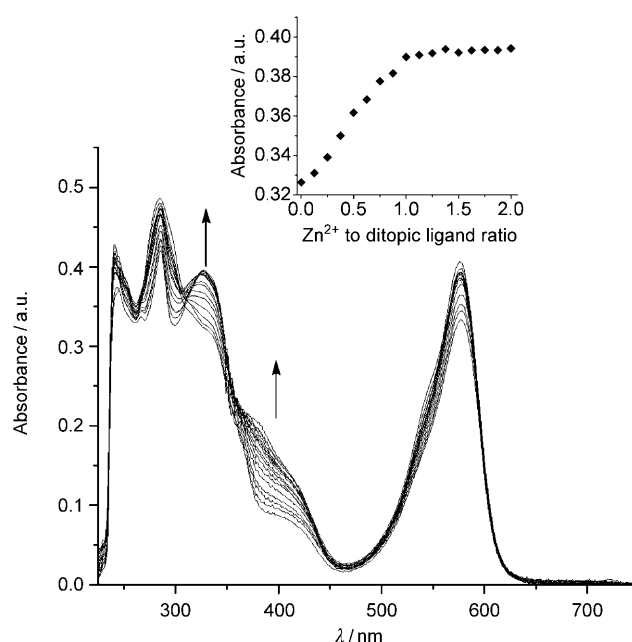


Figure 5. UV/Vis spectra obtained by the titration of **7** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂. The inset shows the absorption coefficient at 325 nm as a function of Zn^{II}/**7** ratio.

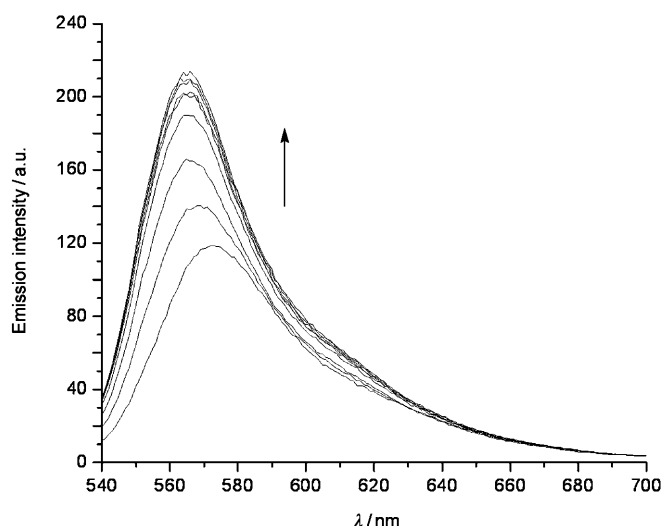


Figure 4. Fluorescence spectra obtained by the titration of **5** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

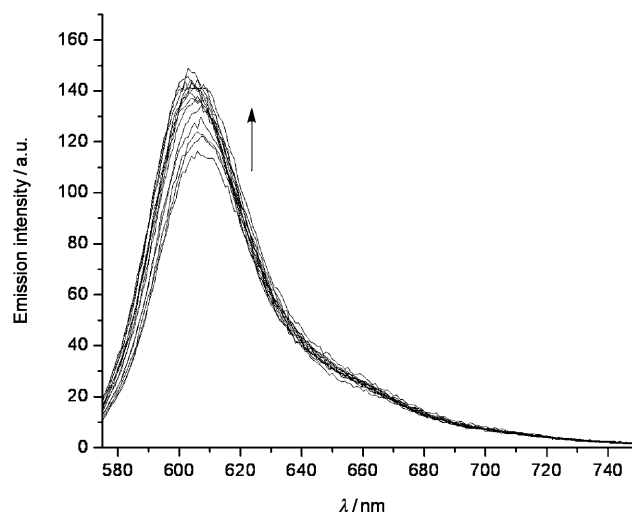


Figure 6. Fluorescence spectra obtained by the titration of **7** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

ent from the terpyridine derivatives. On saturation with Zn^{II}, the absorption spectra of compound **6** (Figure 7) display minor changes at 380 (decrease) and 541 nm (increase), the emission peak intensity increases (+44%, Figure 8), and the peak shifts blue (from 567 to 558 nm). The K_1 value for the first binding event (**6**–Zn^{II}), determined by following the emission changes at the peak wavelength (558 nm), is $2.2 \times 10^5 \text{ M}^{-1}$. In contrast, bis(bipyridylbodipy) **8** shows a somewhat complicated response in absorption spectra during titration (Figure 9). Whereas the peak at 400 nm behaves normally (an increase with an expected saturation behavior), the bodipy peak shows an increase: growth of a shoulder at 530 nm and then disappearance of the shoulder with a final increase at 562 nm. We speculate that the growth of a shoulder is suggestive of interchromophoric stacking with

lower Zn^{II} to ligand ratios, in which two bodipys might be brought together in an octahedral arrangement. Increasing Zn^{II} concentration would of course favor an open form resembling that of the terpyridine derivatives. The K_1 value for the first binding event (**8**–Zn^{II}), determined by following the emission changes at the peak wavelength (588 nm), is $1.7 \times 10^6 \text{ M}^{-1}$. Emission spectra (Figure 10) are supportive of this speculation; at lower Zn^{II} concentrations, binding causes more spectral blueshift rather than intensity change, but at larger proportions of Zn^{II}, bodipy groups are removed from each other with the formation of open-form structures, de-

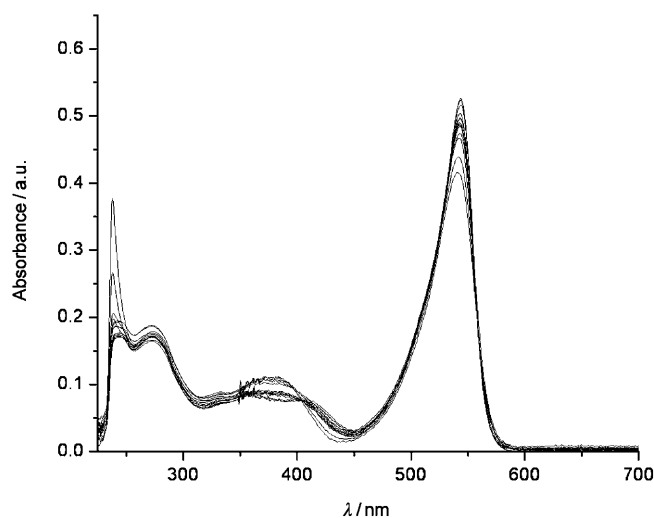


Figure 7. UV/Vis spectra obtained by the titration of **6** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

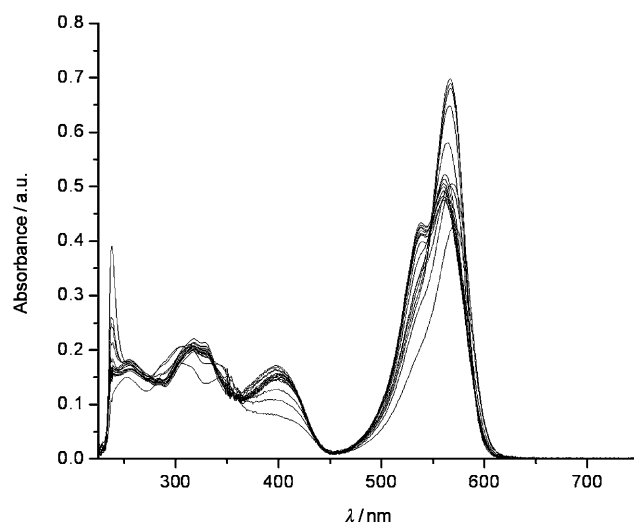


Figure 9. UV/Vis spectra obtained by the titration of **8** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

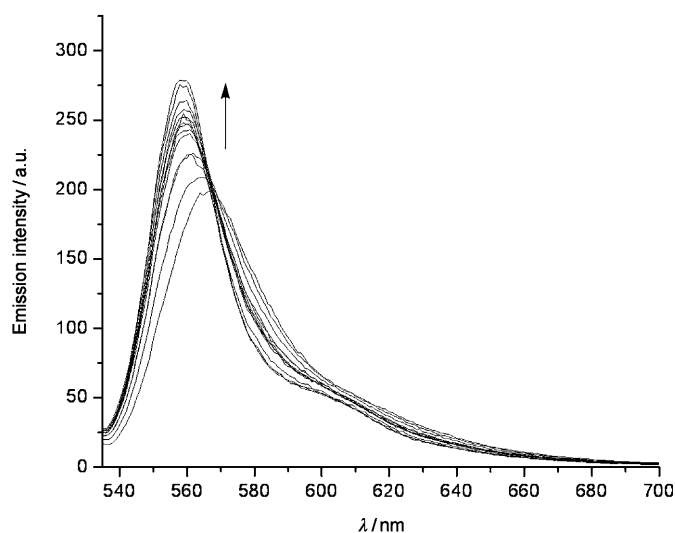


Figure 8. Fluorescence spectra obtained by the titration of **6** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

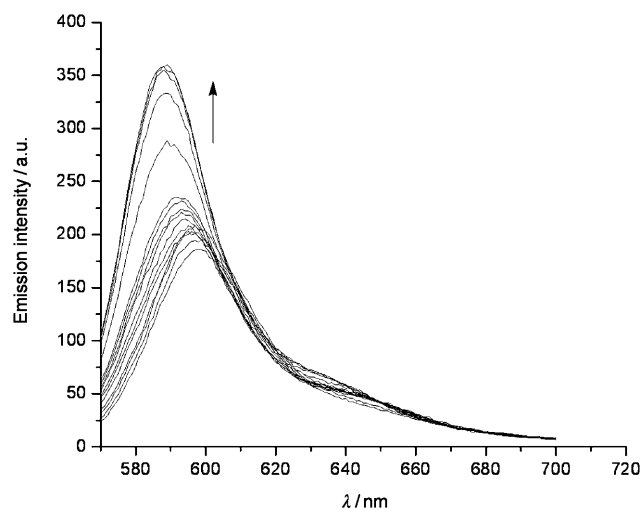


Figure 10. Fluorescence spectra obtained by the titration of **8** in 80:20 CHCl₃/MeOH (5.0×10^{-6} M) with Zn(OTf)₂.

creasing the effects of self-quenching of the bodipy fluorophores. The complex formation with Fe^{II} quenches the fluorescence emission in all cases (see the Supporting Information), which is not surprising considering that Fe^{II} is an open-shell cation with available oxidation states. Spectroscopic data for the free ligands and their Zn^{II} complexes are presented in Table 1.

Mass spectrometric studies of the metal complexes: Mass spectrometry of the polymeric species does not yield large molecular weight peaks, in accordance with previous reports on metallosupramolecular polymers.^[10] However, at any ratio near 1:2 equivalency between the Zn^{II} ions and **5**, four easily identifiable peaks are observed by using MALDI-TOF spectrometry: **5**₂-Zn at 1999.4 amu, **5**-Zn(OTf)₂ at 1918.8 amu, **5**-Zn(OTf) at 1183.7 amu, and **5** at 968.7 amu.

Table 1. Spectroscopic^[a] data for free and Zn^{II}-complexed ligands.

	λ_{abs} [nm]	$\lambda_{\text{abs}}^{[b]}$ [nm]	λ_{f} [nm]	$\lambda_{\text{f}}^{[b]}$ [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	$\epsilon_{\text{max}}^{[b]}$ [M ⁻¹ cm ⁻¹]	ϕ_{f}	$\phi_{\text{f}}^{[b]}$
5	536	535	572	563	95 000	104 000	0.27 ^[c]	0.29 ^[c]
6	541	543	567	558	67 000	81 000	0.29 ^[c]	0.32 ^[c]
7	577	576	608	602	83 200	98 000	0.47 ^[d]	0.49 ^[d]
8	571	567	598	588	86 000	136 000	0.53 ^[d]	0.67 ^[d]

[a] Determined in 80:20 CHCl₃/MeOH solution. [b] Recorded in the presence of Zn^{II}. [c] Rhodamine 6G in water ($\phi_{\text{f}}=0.95$) was used as reference. [d] Sulforhodamine 101 hydrate in ethanol ($\phi_{\text{f}}=0.90$) was used as reference.

Both the open form with the triflate counterions, and the dimeric complex shown in Scheme 2 appear on the mass spectrum (see the Supporting Information).

Conclusion

Through the use of Sonogashira couplings, four functional building blocks carrying bodipy fluorophores were synthesized. Ter- and bipyridyl ligands have been repeatedly shown to be very useful in the construction of supramolecular structures. Terpyridyl is a strong enough ligand for Zn^{II} ions, and the addition of zinc triflate forms a fluorescent coordination polymer. This polymerization process can be easily followed by the observation of fluorescence characteristics. Ditopic bis(terpyridyl) bodipy ligand **7** shows clear evidence of polymerization when 0.5 equivalents of Zn^{II} ions were added. The addition of Zn^{II} changes the dynamic equilibrium concentration of the polymer, and the ^1H NMR signals become more sharp as more Zn^{II} ions are added, which indicates a monomeric complex (open form). With their lower affinities, bipyridyl derivatives can also be useful as fluorescent chemosensors when considering that intracellular Zn^{II} concentrations can vary by six orders of magnitude. A fluorescent coordination polymer may find utility in electrochromic devices or in other device applications in which reversible changes between states of different physical properties is an asset.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer (operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) in CDCl_3 and $[\text{D}_6]\text{DMSO}$ with tetramethylsilane as an internal standard. All spectra were recorded at 25°C and coupling constants (J values) are given in Hz. Chemical shifts are given in parts per million (ppm). Absorption spectra were obtained by using a Varian Cary-100 spectrophotometer. Fluorescence measurements were conducted on a Varian Eclipse spectrofluorimeter. Mass spectra were recorded at the Ohio State University Mass Spectrometry and Proteomics Facility, Ohio, USA. Reactions were monitored by TLC using Merck TLC Silica gel 60 F_{254} and Merck Aluminium Oxide 60 F_{254} . Silica gel column chromatography was performed over Merck Silica gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM). Aluminium oxide column chromatography was performed using Merck Aluminium Oxide 90 active neutral. 4'-(4-Ethynylphenyl)-2,2',6',2''-terpyridine, 5,5'-diethynyl-2,2'-bipyridine, and 5-ethynyl-2,2'-bipyridine were synthesized according to literature procedures.^[42,43] Anhydrous tetrahydrofuran was obtained by heating at reflux over sodium/benzophenone prior to use. All other reagents and solvents were purchased from Aldrich and used without further purification.

UV/Vis and fluorescence titration experiments: UV/Vis and fluorescence titrations were conducted at 25°C as constant host titrations. Aliquots of $\text{Zn}(\text{OTf})_2$ (0.025 mm in 80:20 $\text{CHCl}_3/\text{MeOH}$) and solvent mixture (80:20 $\text{CHCl}_3/\text{MeOH}$) were added to a solution of **5**, **6**, **7**, or **8** (0.025 mm in 80:20 $\text{CHCl}_3/\text{MeOH}$) to obtain the desired metal to ligand ratio. After each addition, UV/Vis absorption and fluorescence spectra were recorded. (λ_{ex} = 535 nm for **5** and **6**, and 570 nm for **7** and **8**).

^1H NMR titration experiments: Aliquots of $\text{Zn}(\text{OTf})_2$ (13 mm and 10 mm in 60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$), respectively) and solvent mixture (60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$) were added to a solution of **5** (13 mm in 60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$) or **7** (10 mm in 60:40 $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$) to obtain the desired metal-to-ligand ratio, and after each addition, ^1H NMR spectra were recorded at 25°C.

3,5-Bis(decyloxy)benzaldehyde (1): 3,5-Bis(decyloxy)benzyl alcohol (21.40 mmol, 9.00 g) and PCC (53.49 mmol, 11.53 g) were added to a

500 mL round-bottomed flask containing CH_2Cl_2 (250 mL), and the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was then washed with water and the organic phase was evaporated at reduced pressure. Silica gel column chromatography using CHCl_3 as the eluant gave **1** as a waxy solid (8.1 g, 90%). ^1H NMR (400 MHz, CDCl_3): δ = 9.80 (1H, s; CHO), 6.93 (2H, s; ArH), 6.60 (1H, s; ArH), 3.92 (4H, t, J = 6.49 Hz; OCH_2), 1.75–1.65 (4H, m; CH_2), 1.41–1.32 (4H, m; CH_2), 1.20 (24H, s; CH_2), 0.80 ppm (6H, t, J = 6.59 Hz; CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 192.0, 160.8, 138.4, 108.1, 107.1, 68.5, 31.9, 29.6, 29.5, 29.3, 29.1, 26.0, 22.7, 14.1 ppm.

4,4-Difluoro-8-[3',5'-bis(decyloxy)phenyl]-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (2): 2,4-Dimethyl pyrrole (15.8 mmol, 1.50 g) and **1** (7.17 mmol, 3 g) were added to a 1 L round-bottomed flask containing argon-degassed CH_2Cl_2 (400 mL). One drop of TFA was added and the solution was stirred under nitrogen at room temperature for 1 d. After addition of a solution of DDQ (7.17 mmol, 1.628 g) in CH_2Cl_2 (100 mL), stirring was continued for 30 min. Et_3N (6 mL) and $\text{BF}_3\cdot\text{OEt}_2$ (3 mL) were successively added and after 30 min, the reaction mixture was washed three times with water and dried over anhydrous Na_2SO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography using 2:1 $\text{CHCl}_3/\text{hexane}$ as the eluant to give **2** as a red waxy solid (1.381 g, 30%). ^1H NMR (400 MHz, CDCl_3): δ = 6.45 (1H, s; ArH), 6.35 (2H, s; ArH), 5.90 (2H, s; H2, H6), 3.85 (4H, t, J = 6.56 Hz; OCH_2), 2.47 (6H, s; CH_3), 1.72–1.62 (4H, m; CH_2), 1.49 (6H, s; CH_3), 1.40–1.30 (4H, m; CH_2), 1.20 (24H, s; CH_2), 0.80 ppm (6H, t, J = 6.53 Hz; CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.2, 155.4, 143.2, 136.4, 131.2, 121.0, 106.4, 102.3, 68.4, 31.9, 29.6, 29.5, 29.3, 29.2, 26.0, 22.7, 14.6, 14.2, 14.0 ppm; HRMS (TOF-ESI): m/z calcd for $\text{C}_{39}\text{H}_{59}\text{BF}_2\text{N}_2\text{O}_2\text{Na}$: 658.4572 [$M+\text{Na}$] $^+$; found: 658.4542 [$M+\text{Na}$] $^+$.

4,4-Difluoro-8-[3',5'-bis(decyloxy)phenyl]-2-iodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (3): Compound **2** (1.91 mmol, 1.21 g) and iodine (1.52 mmol, 0.387 g) were added to a 500 mL round-bottomed flask and to this solution iodic acid (1.52 mmol, 0.268 g) dissolved in water (2 mL) was added. The reaction mixture was stirred at 60°C and was monitored by TLC (1:1 $\text{CHCl}_3/\text{hexanes}$). When TLC indicated that all the starting material had been consumed, the reaction was quenched by the addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) and the product was extracted into CHCl_3 . The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:1 $\text{CHCl}_3/\text{hexane}$ as the eluant to give **3** as a red waxy solid (0.98 g, 67%). ^1H NMR (400 MHz, CDCl_3): δ = 6.48 (1H, s; ArH), 6.32 (2H, d, J = 1.90 Hz; ArH), 5.97 (1H, s; H2), 3.85 (4H, t, J = 6.60 Hz; OCH_2), 2.55 (3H, s; CH_3), 2.49 (3H, s; CH_3), 1.72–1.62 (4H, m; CH_2), 1.49 (6H, s; CH_3), 1.40–1.30 (4H, m; CH_2), 1.20 (24H, s; CH_2), 0.8 ppm (6H, t, J = 6.60; CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.3, 157.7, 154.4, 145.1, 143.2, 141.5, 136.2, 131.6, 130.7, 122.1, 106.2, 102.5, 84.1, 68.4, 38.2, 33.8, 32.9, 31.9, 31.3, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.8, 28.2, 26.1, 26.0, 25.8, 22.7, 16.5, 15.7, 14.7, 14.5, 14.1 ppm; HRMS (TOF-ESI): m/z calcd for $\text{C}_{39}\text{H}_{58}\text{BF}_2\text{I}_2\text{N}_2\text{O}_2\text{Na}$: 784.3538 [$M+\text{Na}$] $^+$; found: 784.3513 [$M+\text{Na}$] $^+$.

4,4-Difluoro-8-[3,5-bis(decyloxy)phenyl]-2,6-diiodo-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (4): Compound **2** (2.47 mmol, 1.57 g) and iodine (6.18 mmol, 1.57 g) were added to a 500 mL round-bottomed flask. A solution of iodic acid (4.93 mmol, 0.87 g) in water (2 mL) was added and the reaction mixture was stirred at 60°C and monitored by TLC (1:1 $\text{CHCl}_3/\text{hexane}$). When all the starting material had been consumed, the reaction was quenched by the addition of a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) and the product was extracted into CHCl_3 . The solvent was evaporated and the residue was purified by silica gel column chromatography using 1:1 $\text{CHCl}_3/\text{hexane}$ as the eluant to give **4** as a red waxy solid (2.09 g, 95%). ^1H NMR (400 MHz, CDCl_3): δ = 6.49 (1H, s; ArH), 6.28 (2H, s; ArH), 3.85 (4H, t, J = 6.45 Hz; OCH_2), 2.55 (6H, s; CH_3), 1.73–1.63 (4H, m; CH_2), 1.49 (6H, s; CH_3), 1.40–1.30 (4H, m; CH_2), 1.20 (24H, s; CH_2), 0.80 ppm (6H, t, J = 6.32 Hz; CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 161.4, 156.7, 145.4, 141.4, 136.1, 131.0, 106.1, 102.7, 85.5, 68.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 16.9, 16.0, 14.1 ppm; HRMS (TOF-ESI): m/z calcd for $\text{C}_{39}\text{H}_{57}\text{BF}_2\text{I}_2\text{N}_2\text{O}_2\text{Na}$: 910.2505 [$M+\text{Na}$] $^+$; found: 910.2495 [$M+\text{Na}$] $^+$.

4,4-Difluoro-8-[3',5'-bis(decyloxy)phenyl]-2-[p-(2'',2''',6''',2''''-terpyridin-4''-yl)ethynylphenyl]-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (5): Compound **3** (0.30 mmol, 0.23 g), 4'-ethynyl-2,2':6'2''-terpyridine (0.60 mmol, 0.20 g), [PdCl₂(PPh₃)₂] (0.018 mmol, 12.64 mg), CuI (0.03 mmol, 5.71 mg), and freshly distilled THF (10 mL) were added to a 50 mL Schlenk tube. Diisopropylamine (5 mL) was added and the resulting suspension was extensively deaerated by bubbling with argon at 50 °C for 40 min. The reaction mixture was stirred at room temperature for 1 d. The solvent was removed under reduced pressure and the residue was washed with water (100 mL) and extracted into CHCl₃. The organic layer was evaporated and column chromatographic separation of the residue on neutral alumina using 1:1 CHCl₃/hexane as the eluant gave **5** as a purple solid. (0.203 g, 70 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.67 (2H, s; H3'', H5'''), 8.65 (2H, d, *J* = 5.78 Hz; H6'', H6'''), 8.58 (2H, d, *J* = 7.94 Hz; H3'', H3'''), 7.82–7.75 (4H, m; H4'', H4'''), ArH), 7.51 (2H, d, *J* = 8.23 Hz; ArH), 7.30–7.25 (2H, m; H5'', H5'''), 6.48 (1H, s; H4'), 6.37 (2H, d, *J* = 1.93 Hz; H2', H6'), 5.97 (1H, s; H6), 3.87 (4H, t, *J* = 6.57 Hz; OCH₂), 2.66 (3H, s; CH₃), 2.52 (3H, s; CH₃), 1.73–1.63 (4H, m; CH₂), 1.65 (3H, s; CH₃), 1.52 (3H, s; CH₃), 1.40–1.30 (4H, m; CH₂), 1.20 (24H, s; CH₂), 0.80 ppm (6H, t, *J* = 6.63 Hz; CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 161.3, 156.1, 156.0, 149.4, 149.1, 137.7, 137.0, 136.1, 131.7, 127.2, 124.5, 123.9, 121.4, 118.6, 106.2, 102.4, 95.6, 83.8, 68.5, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.8, 14.1 ppm; HRMS (TOF-ESI): *m/z* calcd for C₆₂H₇₂BF₂N₅O₂Na: 989.5661 [*M*+Na]⁺; found: 989.5676 [*M*+Na]⁺.

4,4-Difluoro-8-[3',5'-bis(decyloxy)phenyl]-2,6-bis[p-(2'',2''',6''',2''''-terpyridin-4''-yl)ethynylphenyl]-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (7): Compound **4** (0.338 mmol, 0.30 g), 4'-ethynyl-2,2':6'2''-terpyridine (1.182 mmol, 0.394 g), [PdCl₂(PPh₃)₂] (0.0203 mmol, 14.23 mg), CuI (0.034 mmol, 6.44 mg), and freshly distilled THF (10 mL) were added to a 50 mL Schlenk tube. Diisopropylamine (5 mL) was added and the resulting suspension was extensively deaerated by bubbling with argon at 50 °C for 40 min. After degassing, the reaction mixture was stirred at room temperature for 1 d. Solvents were removed under reduced pressure and the residue was washed with water (100 mL) and extracted into CHCl₃. The organic layer was evaporated and separation by column chromatography on neutral alumina using 1:1 CHCl₃/hexane as the eluant gave **7** as a blue solid. (0.382 g, 87 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.68 (4H, s; H3'', H5'''), 8.64 (4H, d, *J* = 6.55 Hz; H6'', H6'''), 8.61 (4H, d, *J* = 7.94 Hz; H3'', H3'''), 7.86–7.79 (4H, m; H4'', H4'''), 7.82 (4H, d, *J* = 8.03 Hz; ArH), 7.52 (4H, d, *J* = 8.15 Hz; ArH), 7.33–7.27 (4H, m; H5'', H5'''), 6.52 (1H, brs; H4'), 6.39 (2H, d, *J* = 1.78 Hz; H1', H6'), 3.88 (4H, t, *J* = 6.52 Hz; OCH₂), 2.68 (6H, s; CH₃), 1.74–1.64 (4H, m; CH₂), 1.69 (6H, s; CH₃), 1.43–1.33 (4H, m; CH₂), 1.20 (24H, s; CH₂), 0.80 ppm (6H, t, *J* = 5.26 Hz; CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 161.4, 156.2, 155.9, 149.3, 149.1, 141.0, 137.7, 136.9, 132.1, 132.0, 131.9, 131.6, 131.1, 128.6, 128.4, 127.2, 124.2, 123.9, 121.4, 118.6, 106.2, 96.4, 83.0, 68.5, 31.9, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1, 13.9 ppm; HRMS (MALDI-TOF): *m/z* calcd for C₈₈H₈₈BF₂N₈O₂: 1298.686 [*M*]⁺; found: 1298.830 [*M*]⁺.

5,5'-Bis[4'',4''-difluoro-8''-(3''',5''',bis(decyloxy)phenyl)-1'',3'',5'',7''-tetramethyl-4''-bora-3''a,4''a-diaza-s-indacene-2''-ethynyl-2,2'-bipyridine (6): Compound **3** (0.265 mmol, 0.202 g), 5,5'-diethynyl-2,2'-bipyridine (0.0256 mmol, 18 mg), [PdCl₂(PPh₃)₂] (0.032 mmol, 22.3 mg), CuI (0.0265 mmol, 5.05 mg), and freshly distilled THF (10 mL) were added to a 50 mL Schlenk tube. Diisopropylamine (5 mL) was added and the resulting suspension was extensively deaerated by bubbling with argon at 50 °C for 40 min. After degassing, the reaction mixture was stirred at 50 °C for 1 d. After removal of the solvents under reduced pressure, the residue was washed with water (100 mL) and extracted into CHCl₃. The organic layer was evaporated and separation by column chromatography on silica gel using CHCl₃ as the eluant gave **6** as a purple solid (0.215 g, 55 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.65 (2H, d, *J*_{H6-H4} = 1.44 Hz; H6, H6'), 8.28 (2H, d, *J*_{H3-H4} = 8.28 Hz; H3, H3'), 7.73 (2H, dd, *J*_{H4-H3} = 8.28, *J*_{H4-H6} = 1.04 Hz; H4, H4'), 6.47 (2H, t, *J* = 2.20 Hz; H4'''), 6.32 (4H, d, *J* = 2.20 Hz; H2'', H6'''), 5.98 (2H, s; H2''), 3.82 (8H, t, *J* = 6.62 Hz; OCH₂), 2.63 (6H, s; CH₃), 2.50 (6H, s; CH₃), 1.71–1.61 (8H, m; CH₂), 1.60 (6H, s; CH₃), 1.52 (6H, s; CH₃), 1.38–1.29 (8H, m; CH₂), 1.20 (48H, brs; CH₂), 0.78 ppm (12H, t, *J* = 5.28 Hz; CH₃); ¹³C NMR (100 MHz,

CDCl₃): δ = 161.3, 158.0, 156.2, 153.9, 151.2, 145.5, 142.2, 138.7, 136.0, 132.6, 129.9, 122.2, 120.5, 114.1, 106.2, 102.5, 93.1, 87.1, 68.5, 31.9, 29.7, 29.5, 29.3, 29.2, 29.1, 26.0, 22.7, 14.8, 13.5 ppm; HRMS (MALDI-TOF): *m/z* calcd for C₉₂H₁₂₂B₂F₄N₆O₄: 1472.965 [*M*]⁺; found: 1473.120 [*M*]⁺.

4,4-Difluoro-8-[3',5'-bis(decyloxy)phenyl]-2,6-bis(2'',2'''-bipyridine-5''-ethynyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (8): Compound **4** (0.161 mmol, 143 mg), 5-ethynyl-2,2'-bipyridine (0.972 mmol, 175 mg), [PdCl₂(PPh₃)₂] (0.096 mmol, 6.74 mg), CuI (0.016 mmol, 3 mg), and freshly distilled THF (10 mL) were added to a 50 mL Schlenk tube. Diisopropylamine (5 mL) was added and resulting suspension was extensively deaerated by bubbling with argon at 50 °C for 40 min. After degassing, the reaction mixture was stirred at 40 °C for 1 d. After removal of the solvents under reduced pressure, the residue was washed with water (100 mL) and extracted into CHCl₃. The solvent was removed and separation by column chromatography on silica gel using 1 % methanol/CHCl₃ as the eluant gave **8** as a blue solid. (0.128 g, 80 %). ¹H NMR (400 MHz, CDCl₃): δ = 8.68 (2H, s; H6''), 8.61 (2H, d, *J* = 4.52 Hz; H6'''), 8.40–8.30 (4H, m; H3'', H3'''), 7.80–7.75 (4H, m; H4'', H4'''), 7.30–7.20 (2H, m; H5'', H5'''), 6.51 (1H, s; H4'), 6.38 (2H, d, *J* = 1.63 Hz; H2', H6'), 3.88 (4H, t, *J* = 6.54 Hz; OCH₂), 2.68 (6H, s; CH₃), 1.74–1.64 (4H, m; CH₂), 1.67 (6H, s; CH₃), 1.41–1.31 (4H, m; CH₂), 1.20 (24H, brs; CH₂), 0.79 ppm (6H, t, *J* = 6.19 Hz; CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 161.4, 159.2, 155.9, 153.0, 151.3, 149.3, 145.3, 143.1, 140.6, 138.9, 135.9, 131.5, 124.2, 121.4, 120.4, 116.2, 106.0, 102.7, 93.5, 86.0, 68.5, 31.9, 29.5, 29.4, 29.3, 29.1, 26.0, 22.7, 14.1, 13.8, 13.4 ppm; HRMS (MALDI-TOF): *m/z* calcd for C₆₃H₇₁BF₂N₆O₂: 992.570 [*M*]⁺; found: 992.741 [*M*]⁺.

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