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Dyes/Pigments

Luminescent Materials: Locking π-Conjugated and Heterocyclic Ligands with Boron(III)

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boron · dyes/pigments · energy transfer · fluorescence · ligands

Multidisciplinary research on novel organic luminescent dyes is propelled by potential applications in plastic electronics and biomedical sciences. The construction of sophisticated fluorescent dyes around a tetrahedral boron(III) center is a particular approach that has fueled the creativity of chemists. Success in this enterprise has been readily achieved with simple synthetic protocols, the products of which display unusual spectroscopic behavior. This account is a critical review of recent advances in the field of boron(III) complexes (excluding BODIPYs and acetylacetonate boron complexes) involving species displaying similar coordination features, and we outline their potential development in several disciplines.

1. Introduction

The continuing development of fluorescent dye systems is the result of intense interest, from chemists, physicists, and biochemists, which is motivated by their use as molecular probes in biomedical analysis, microscopy, genotyping assays, trace-chemical analysis, and materials science. Major applications in the field of organic electronics and photonics involving liquid-crystal displays, OLEDs, organic photovoltaic devices, solar energy concentrators, bioimaging, and nanoemitters, for example, have been developed as a result of this interest. The history of synthetic dyestuffs extends back over more than 150 years, with a primary interest over this period being the search for molecules with exceptional chemical, photochemical, and thermal stability, thus allowing their exposure to harsh sunlight conditions and heat. Families of dyes that have been engineered systematically include polyaromatics (pyrene, tetracene, pentacene, etc.),[1–3] porphyrins,[4] coumarins,[5] xanthenes (rhodamines, fluorescein, etc.),[6] cyanines (Cy2, Cy3 and Cy5, etc.),[7] squaraines,[8] and peryleneimides (including rylenes, etc.).[9] A workhorse family in recent times has been that based on 4,4′-difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives, with interest having been particularly strong over the past decade.[10–12] Intense efforts to improve their photochemical stability have proved particularly rewarding when the fluoro ligands on boron are replaced by functionalized alkynides.[13,14] In many instances, BODIPY dyes display relatively narrow absorption and emission bands, high molar absorption coefficients, and outstanding fluorescence quantum yields. Furthermore, they are resistant to triplet formation, thus avoiding detrimental singlet oxygen generation under photolysis. Also remarkable is their redox activity in the ground and excited states, activity which makes them attractive materials for electron transfer, charge separation, excimer formation, and near-infrared (NIR) emission.[15–17]

One major drawback of BODIPY dyes, despite their intense fluorescence in solution, is their weak emission in the solid state, and this limits optoelectronic applications. This weak emission is mostly caused by self-absorption resulting from very narrow Stokes shifts inducing a strong overlap of the dye absorption and emission spectra. Also detrimental is the flat conjugated core, which facilitates tight packing in the most cases, and thus significant luminescence quenching. Decorating dyes with bulky substituents is one effective strategy for decreasing intermolecular aggregation.[18] Nevertheless, aggregation-induced fluorescence enhancement can also be a useful strategy to produce fluorescent nano-objects from nonfluorescent molecules in solution.[19] In specific cases, controlled aggregation can facilitate formation of

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specific aggregates with NIR absorption and emission properties.[20]

Another straightforward means of producing photoresponsive materials in the solid state is intramolecular proton transfer in the excited state (ESIPT).[21–23] This process is ultrafast (sub-picosecond timescale) and produces an emitting state different in nature from that of the ground state (e.g. keto form rather than the enol form). In this way the Stokes shift of the emitted light is very large and the materials are emissive in the solid state. This feature has been exploited to engineer libraries of smart molecules with large emissive quantum yields.[24,25]

Tailoring of neutral boron dyes for fine-tuning of their optical and physical properties has been explored in energy conversion devices (organic light-emitting diodes, OLEDs, and organic photovoltaics, OPV),[26–28] cascade-energy-transport devices,[29] solar concentrators,[30] and NIR-absorbing systems.[31] It has recently been demonstrated that strengthening the molecular interactions by supramolecular means (hydrogen bonding, halogen or CH interactions) favors the organization of dyes in thin films, which is a key point in the intrinsic control of the morphology of a photoactive layer when charge separation is concerned, such as in organic solar cells produced by solution processing.[32]

The search for novel dyes is by no means complete and remains a challenging target for an increasing number of chemists. This minireview focuses upon the use of a central four-coordinate B^{III} atom to configurationally lock N,N and N,O ligands, thus inducing rigidification of the cyanine or merocyanine core (Figure 1). The pivotal roles of the B^{III} are to stabilize the ligand by coordination and to render the π system planar, thereby enhancing conjugation and charge transfer along the main molecular axis with appropriate substituents. The chelating ligands are usually charged (O^- and/or N^- sites), and two additional anions (usually F^- or Ar^-) on the boron center ensure neutrality of the resulting dyes (Figure 1). All these features are beneficial for the spectroscopic properties inducing well-defined and sharp absorption and emission transitions, high quantum yields, and suitable excited-state lifetimes. These novel dyes can be classified by the number of atoms present in the ring formed after complexation. Their postfunctionalization and optical properties in solution and in the solid state are discussed together with interesting potential applications. BODIPY dyes have been covered in recent comprehensive review articles and will not be discussed herein.[10–12,15–17,33] Other borate complexes of N,C, C,C, C,O, O,O, and tritopic ligands will be the subject of a separate compilation.

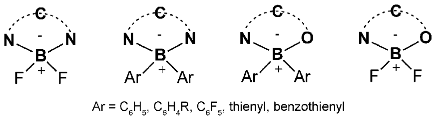

Figure 1. Configurational locking of ligands by chelation of boron(III). The bridge between the chelating donor atoms contains at least one carbon atom and is usually conjugated.

Denis Frath (left) obtained his Ph.D. the University of Strasbourg under the supervision of Dr. G. Ulrich and Dr. R. Ziessel. His doctoral work was focused on organic/inorganic catalysts for the light-driven production of hydrogen from water and on the synthesis and spectroscopic properties of novel organoboron fluorescent dyes. He is currently working on the elaboration of photochromic devices as a post-doctoral fellow with Prof. K. Matsuda at Kyoto University in Japan.

Julien Massue (center left) received his Ph.D. from the University of Rennes in 2005 under the guidance of Prof. D. Lorcy and Dr. N. Bellec. After postdoctoral research in the groups of Prof. T. Gunnlaugsson (2005–2007), Prof. D. Sames (2008–2009), and Drs. C. Andraud/C. Monnereau (2010), he obtained a permanent CNRS position at the ICPEES-LCOSA in Strasbourg. His current research interests lie in the development of solution- and solid-state emitting functional fluorophores for biological imaging, bioconjugation, biodetection of substrates, and solar cells.

Gilles Ulrich (center right) obtained his Ph.D. from the University Louis Pasteur of Strasbourg under the guidance of Dr. R. Ziessel in 1996. After postdoctoral research with Prof. H. Iwamura (1996–1997), Dr. J. J. Wolff (1997–1998), and Dr. F. Arnaud-Neu (1998–1999) he joined the CNRS at Paul Sabatier University of Toulouse. He moved in 2002 to Strasbourg and was promoted in 2009 to "Directeur de Recherche CNRS". His interests are the development of new organic functional fluorescent dyes, including luminescent borate complexes for a broad panel of applications.

Raymond Ziessel (right) obtained his Ph.D. from the University Louis Pasteur of Strasbourg under the guidance of Prof. J.-M. Lehn and Dr. J.-P. Sauvage. He is the Director of the Laboratoire de Chimie Organique et Spectroscopies Avancées (LCOSA) in Strasbourg. This team is part of the ICPEES-LCOSA and focused on molecular synthesis and spectroscopy. Recent research interests focus on the preparation of novel liquid crystals, organogelators, and ionic liquids from π–π and electrostatic interactions, metallo-polyacetylenes, and lanthanides complexes for biomaterial labeling and time-resolved fluorescence imaging.

2. Luminescent N,N π-Conjugated Boron(III) Complexes.[*]

Five types of boron(III) chelation modes providing an efficient rigidification of π-conjugated ligands, while maintaining an overall neutrality, have been identified in the literature (Figure 2). These five types are those where, for five-membered rings, the boron center is chelated to two nitrogen atoms incorporated in either one or two aromatic systems (Types I and II, respectively) and where, for six-membered rings, the two donor atoms are connected to the

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[*] Each family of borate complexes is described by a number for example, **1**, **2**, **3**.... and members of the same family are labeled **1a**, **1b**, **1c**.......

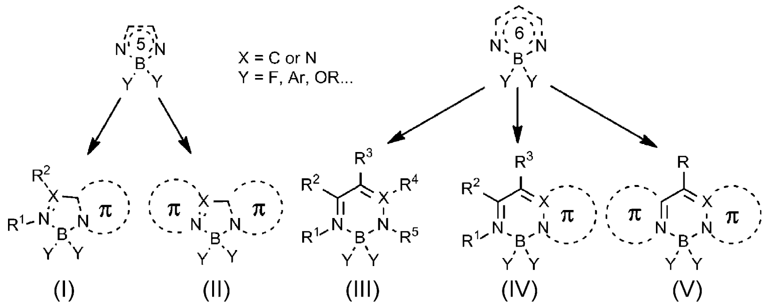


Figure 2. Various N,N chelation modes. For X = N no substituent is present.

boron center as part of a non-aromatic system (Type III) or as part of one (Type IV) or two (Type V) aromatic systems.

2.1. Five-Membered Rings: Type I Complexes

The various synthetic routes to Type I structures are described in Figure 3. Hohaus et al. were the first to report the formation of the highly fluorescent quinoline-based boron(III) complexes **2** in the late sixties,[34] and this scaffold was later utilized by Chujo et al. in organoboron polymers.[35] Other Type I structures are more recent, with examples including the complex **1**, which is obtained through cyclization of acetylacetone onto 2,6-diaminopyridine with subsequent oxidation to give a ditopic ligand.[36] The azo complex **3** contains a functionalized quinolone ligand which undergoes reversible *trans*/*cis* isomerization under visible-light irradiation.[37] Arterburn et al. reported the facile preparation of a whole family of dyes based on a triazaborolopyridinium motif with the general formula **4**, some of them being water-soluble and of use as protein-conjugated imaging agents.[38] The complexes **5** are the products of BPh_2 complexation with an iminopyrrole skeleton; the R group on the imine site may vary from phenyl to different extended aromatic bridges, thus allowing the formation of dinuclear boron complexes suited to efficient insertion in single-layer nondoped OLEDs.[39]

2.2. Five-Membered Rings: Type II Complexes

The different synthetic paths reported in the literature for the formation of Type II structures are described in Figure 4. Lin et al. recently described a new family of dyes based on a phenanthro[9,10-*d*]imidazole-quinoline scaffold (**6**) as low-band-gap materials which are highly emissive in both solid and solution states.[40] Boron 2-(2′-pyridyl)imidazole (BOPIM) complexes (**7**[41,42] and **8**[43–45]) were obtained by BF_2 complexation with the organic products formed through condensation in acidic media. Diphenyl boron complexes of 2-(2′-pyridyl)indole derivatives (**9**) were synthesized by a two-step Fischer procedure from substituted phenylhydrazine derivatives and acetylpyridine.[46] Pyridine-pyrazole-based complexes (**10**)[47,48] were obtained in three steps, the last of which involved a reaction with $B(C_6F_5)_3$, whereas pyridine indole or pyridine azaindole BPh_2 complexes (**11**) were obtained through a key step involving a palladium-catalyzed Negishi cross-coupling.[49,50] Substituted pyridine pyrrole scaffolds have also been utilized in the efficient construction of emissive boron(III) complexes (BF_2 or BPh_2 entities) such as **12**[50] or **13**.[51] Finally, the dyes **14** were obtained by an initial condensation between phenylene- or naphthalenediamine and 2-carboxypyridine derivatives.[52,53]

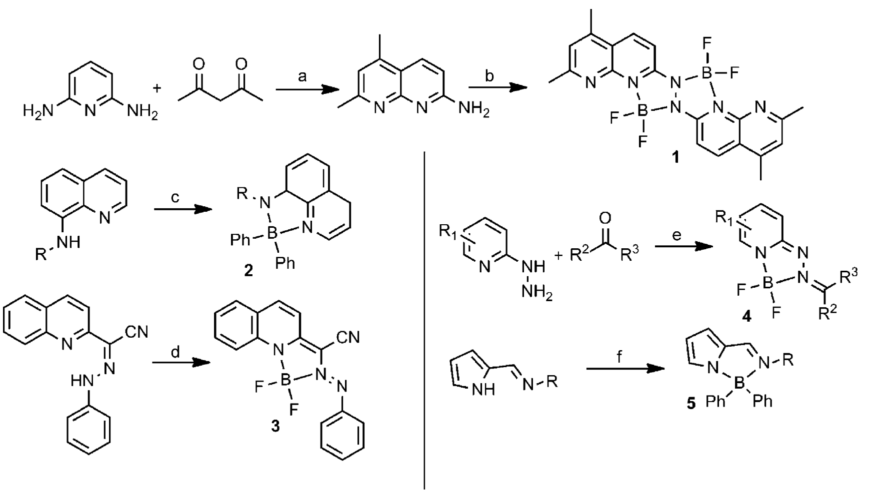


Figure 3. Synthesis of Type I borate complexes. a) AcOH, H_2SO_4; b) 1. NaClO, 2. AcOH, 3. $BF_3{\cdot}OEt_2$, 2,6-lutidine; c) $(Ph_2B)_2O$ or BPh_3; d) $BF_3{\cdot}Et_2O$; e) 1. pyridine, 2. $BF_3{\cdot}OEt_2$, DBU; f) BPh_3. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

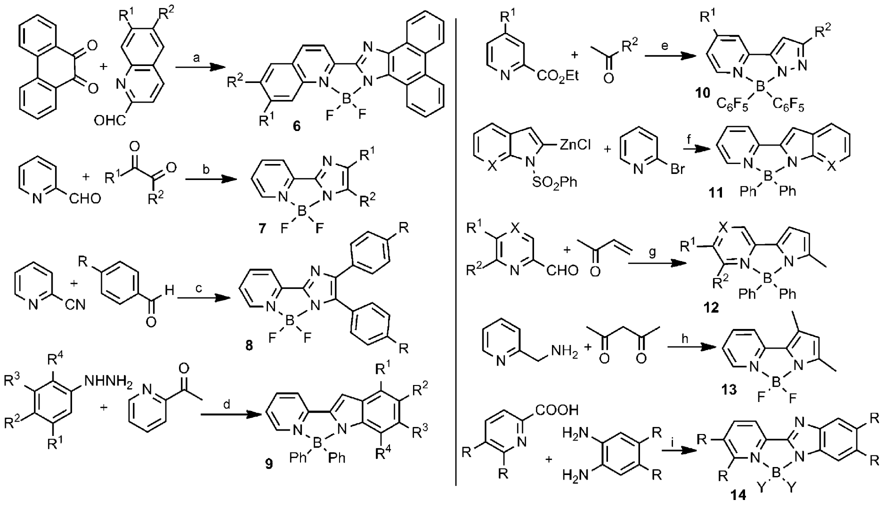


Figure 4. Synthesis of Type II borate complexes. a) 1. AcONH$_4$, 2. BF$_3$·OEt$_2$, DIEA; b) 1. AcONH$_4$, AcOH, 2. BF$_3$·OEt$_2$; c) 1. AcOH, 2. BF$_3$·OEt$_2$; d) 1. EtOH, 2. AcOH or polyphosphoric acid, 3. BPh$_3$; e) 1. NaH, 2. NH$_2$NH$_2$·H$_2$O, 3. B(C$_6$F$_5$)$_3$; f) 1. [Pd(PPh$_3$)$_2$Cl$_2$], DIBAH, 2. NaOH, 3. BPh$_3$, g) 1. Et$_3$N, 2. (NH$_4$)$_2$CO$_3$, EtOH, HCl, 3. BPh$_3$; h) 1. TsOH, 2. BF$_3$.Et$_2$O, 2,4,6-collidine; i) 1. PPA, 2. BY$_3$. DIBAH = diisobutylaluminum hydride, DIEA = diisoprpylethylamine, PPA = polyphosphoric acid, Ts = 4-toluenesulfonyl.

2.3. Six-Membered Rings: Type III Complexes

Among the six-membered-ring Type III complexes (Figure 5), some like **15** are the result of the condensation of aniline derivatives with subsequent chelation of the resulting Schiff base,[54,55] whereas others like complexes **16**,[56] **17**,[56] and **19**[57] rely on the formation of an iminoenamine ligand as a key step. It is worth noting that the dyes **19** exhibit weak fluorescence quantum yields in solution because of vibrational deactivation but brighten in the solid state as a result of aggregation-induced emission (AIE). The restriction of intramolecular rotation of the substituted phenyl groups is due to tight π–π stacking interactions in the aggregate and is the main cause for the observed AIE effect.[58,59] Finally, Svobodová et al. recently described the formation of oxazaborines which can rearrange at 200 °C in DMF or DMSO to selectively yield the isomeric triazaborines **18**, which exhibit fluorescence properties at low temperature both in solution and in the solid state.[60]

2.4. Six-Membered Rings: Type IV Complexes

Known routes to Type IV structures are described in Figure 6. A recent breakthrough was reported by Piers et al., who described three distinct families of dyes (**20**–**22**).[61] These scaffolds were constructed using various palladium-catalyzed cross-coupling reactions as a key step. The resulting rigidified

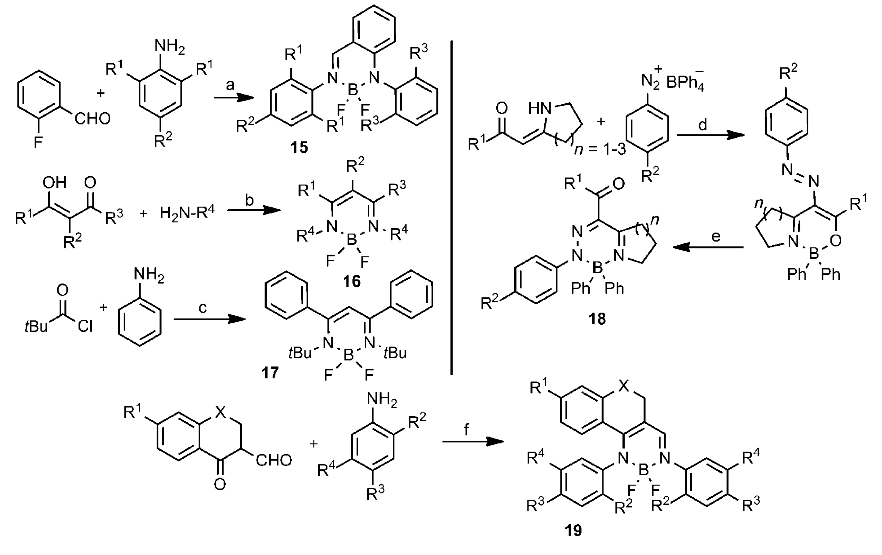


Figure 5. Synthesis of Type III borate complexes. a) 1. *n*-hexane, 2. LiNHAr(R^3)$_2$ (R^3 = Et or *i*Pr), 3. *n*BuLi, BF$_3$·OEt$_2$; b) 1. TsOH, Dean–Stark apparatus, 2. BF$_3$.OEt$_2$; c) 1. Et$_3$N, 2. PCl$_5$, 3. LiMe, 4. *n*BuLi, TMEDA, *t*BuC(NPh)Cl; d) CH$_2$Cl$_2$/toluene; e) DMF or DMSO; f) 1. Et$_3$N, CH$_2$Cl$_2$, 2. BF$_3$·OEt$_2$. X = C, O, S. DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsulfoxide, TMEDA = *N*,*N*,*N'*,*N'*-tetramethylethylenediamine.

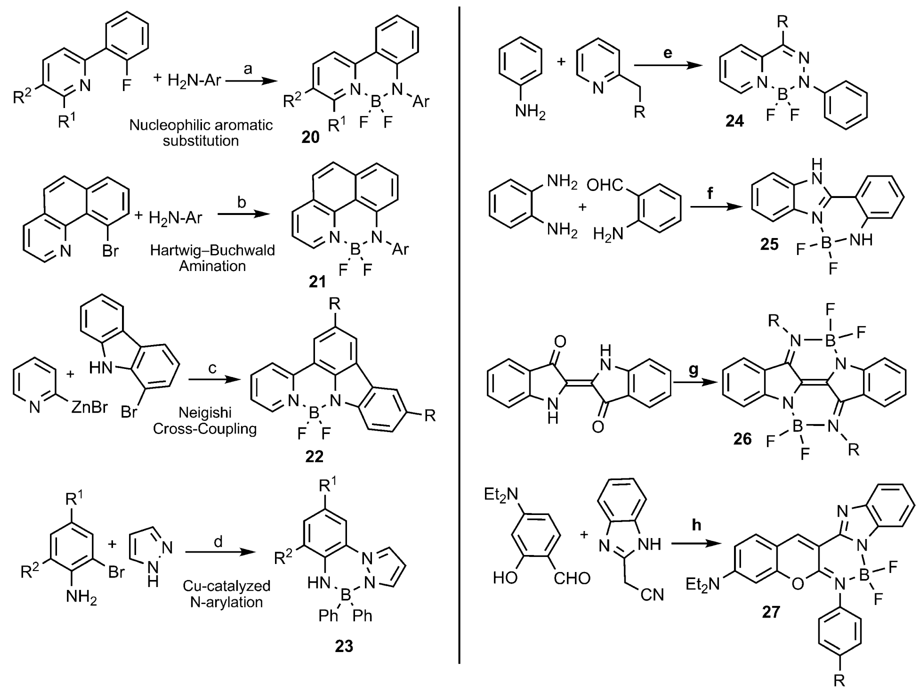


Figure 6. Synthesis of Type IV borate complexes. a) 1. *n*BuLi, THF, 2. $BF_3{\cdot}Et_2O$; b) 1. *t*BuONa, $[Pd_2(dba)_3]$, diphenylphosphinoferrocene, 2. $BF_3{\cdot}Et_2O$; c) 1. KH, 2. $[Pd(PPh_3)_4]$, 3. $BF_3{\cdot}Et_2O$; d) 1. K_2CO_3, *N,N'*-dimethylethylenediamine, CuI, 2. BPh_3; e) 1. K_2CO_3, 2. BPh_2OH; f) 1. $KHSO_4$, 2. I_2, *o*-dichlorobenzene, 3. BPh_3; g) 1. $TiCl_4$, DABCO, R-NH_2 (R = Me, Et, *i*Pr), bromobenzene, 2. $BF_3{\cdot}Et_2O$; h) 1. piperidine, 2. TsOH, R-ArNH_2, 3). $BF_3{\cdot}Et_2O$, DIEA. DABCO = 1,4-diazabicyclo[2.2.2]octane, dba = dibenzylideneacetone.

BF_2 complexes display large Stokes shifts along with high quantum yields both in solution and in the solid state, and make efficient biological membrane probes. The organic scaffold 2-(pyrazolyl)aniline complexed to diphenylboron (**23**; BORAZAN) has been synthesized using a copper-catalyzed N-arylation reaction between pyrazole and aniline derivatives.[62,63] BF_2 hydrazone complexes (**24**; BODIHY) exhibit enhanced emission in the solid state and can act as solid-state acid/base sensors when appropriately substituted.[64] In addition, 2-aniline-benzimidazole coordinates boron, thus leading to the complex **25** but no photophysical studies have been reported.[65] Another recent trend is the chemical modification of familiar fluorophores such as indigos or coumarins to provide chelating sites for efficient boron complexation. This is the case for the BF_2 complexes **26**[66] and **27** (BORICO)[67] which display interesting spectroscopic properties.

2.5. Six-Membered Rings: Type V Complexes

A selection of Type V complexes is shown in Figure 7. Daltrozzo, Zumbusch et al. and Kobayashi et al. independently prepared the complexes **28** and **29** which are based on modified diketopyrrolopyrroles (DPP)[68–70] and azapyrrolopyrroles,[71] respectively. These highly colored dyes display pronounced electronic delocalization over the π-conjugated backbone and are highly fluorescent in the red and NIR regions. Even more pronounced π delocalization has recently been seen in tetracoordinated boron bis(pyrrolopyrrole)cyanines.[72] The complex **30** displays strong visible fluorescence and reversible redox properties along with a well-ordered molecular packing favorable for use as an electron-transport material in electroluminescence devices.[73] Other examples include quinolone indole BPh_2, quinolone azaindole BPh_2 (**31**),[74] naphthyridine BF_2 complexes (**32**),[75] or pyridomethene BF_2 complexes (**33**).[76] Curiel et al. developed indolocarbazole-based ligands for the efficient coordination of a boron diphenyl fragment. The complex **34** exhibits a narrow HOMO–LUMO band gap suited to efficient insertion in optoelectronic devices.[77] Finally, azaboron diquinomethene complexes (**35**) were recently described as highly fluorescent emitters.[78]

The team of Arterburn[38] has demonstrated the stability of triazaborolopyridinium fluorophores by undertaking several postsynthetic modifications (Figure 8). In particular, the fluorine on the boron could be replaced by methoxy groups. The resulting complex was further modified by a Sonogashira cross-coupling reaction, then acylation with a cysteine derivative to produce a biological inhibitor for fluorescence imagery.

In the same vein, numerous Suzuki couplings have been performed on fluorophores bearing reactive bromo groups, thus leading to new substituents on the pyridomethene framework (Figure 9).[76]

3. Luminescent N,O π-Conjugated Boron(III) Complexes

In the case of fluorescent boron(III) complexes with N,O chelates, we define five categories in which the chelate

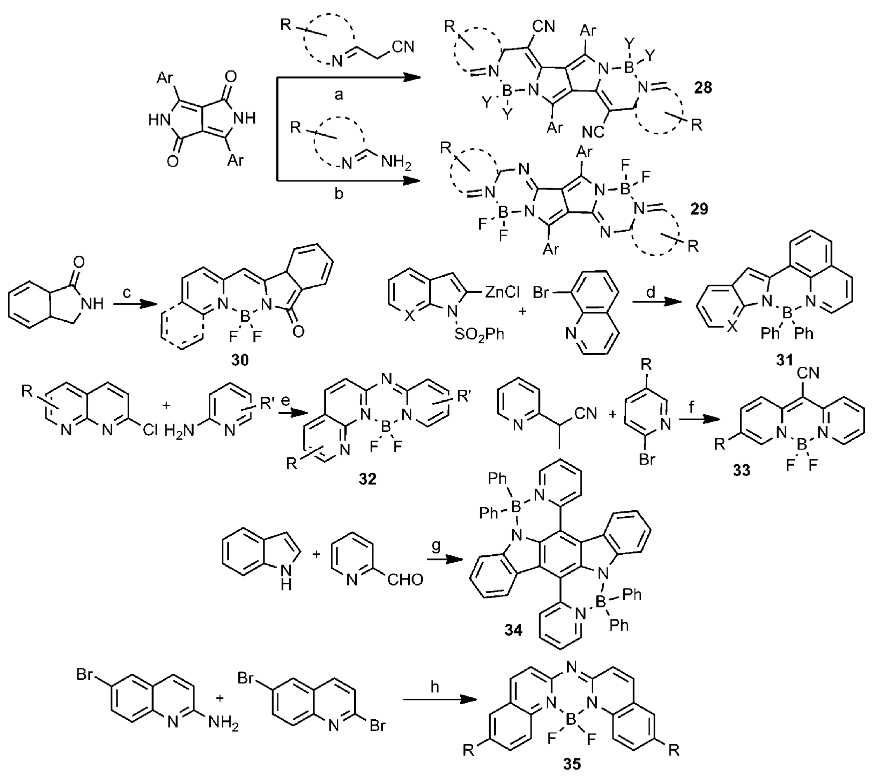
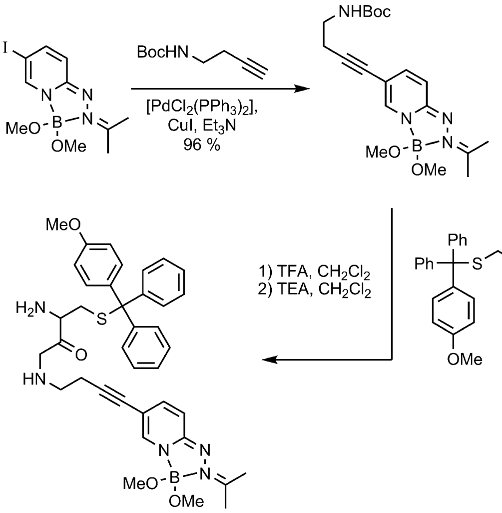
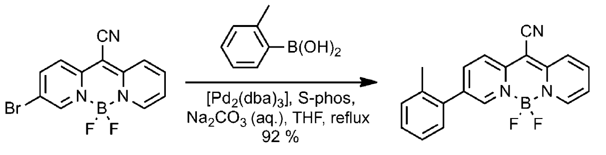


Figure 7. Synthesis of Type V borate complexes. a) 1. $POCl_3$, 2. $BF_3{\cdot}OEt_2$, DIEA, or BPh_2Cl; b) 1. $TiCl_4$, Et_3N, 2. $BF_3{\cdot}$ Et_2O; c) 1. 2-pyridinecarboxaldehyde or 2-quinolinecarboxaldehyde, 2. K_2CO_3, 3. $BF_3{\cdot}$ Et_2O, DIEA; d) 1. NaH, 2. $BF_3{\cdot}Et_2O$ (X=C, N); e) 1. $[Pd(PPh_3)Cl_2]$, DIBAH, 2. NaOH, EtOH, 3. BPh_3; f) 1. NaH, 2. $BF_3{\cdot}Et_2O$; g) 1. $NaNO_2$, H_2O/HCl, 2. AcONa, 3. $BF_3{\cdot}Et_2O$, DIEA; h) 1. $Pd(OAc)_2$, *t*BuONa, bis(2-diphenylphosphinophenyl)ether, 2. $[Pd(dppf)_2Cl_2]$ $RB(OH)_2$, 3. $BF_3{\cdot}$ Et_2O, DIEA. dppf=1,1′-bis(diphenylphosphanyl)ferrocene.



4a: λ_{abs} = 400 nm; λ_{em} = 486 nm; $\Phi_{DMSO/PBS}$ = 0.29

Figure 8. Functionalization of a triazaborolopyridinium. Boc=*tert*-butoxycarbonyl, PBS=phosphate-buffered saline, TEA=triethylamine, TFA=trifluoroacetic acid. λ_{abs}=absorption wavelength, λ_{em}=emission wavelength, Φ=quantum yield.



33a: λ_{abs} = 324, 458 nm; λ_{em} = 465 nm; Φ_{hexane} = 0.25

Figure 9. Suzuki cross-coupling on a pyridomethene BF_2 complex. S-phos=2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl.

ring has a rigid, near-planar form (Figure 10). For five-membered chelate rings, the nitrogen atom ligated to the boron may be either part of an aromatic ring (Type VII) or not (Type VI). For six-membered rings, the coordinating nitrogen atom is either not included (Type VIII) or included (Type IX) in an aromatic system. Also, some seven-membered ring complexes have been described with the coordinating nitrogen atom included in an aromatic system (Type X).

3.1. Five-Membered Rings: Type VI Complexes

Up to now, few examples of Type VI complexes have been described in the literature (Figure 11). They can be constructed by an aldehyde (e.g. cinnamaldehyde) condensation with 2-aminophenol.[79,80] These compounds have nonlinear optical properties, and structural studies have shown signifi-

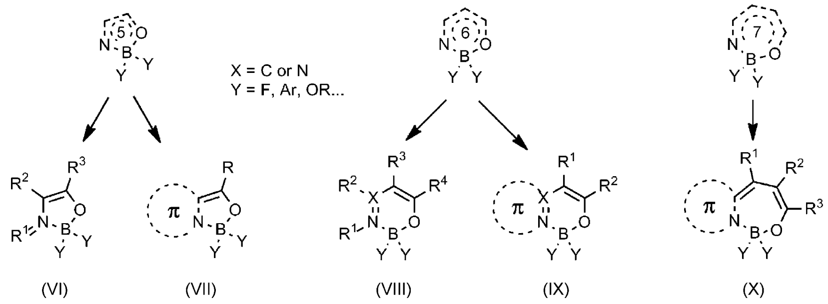


Figure 10. Various N,O chelation modes. For X = N no substituent is present.

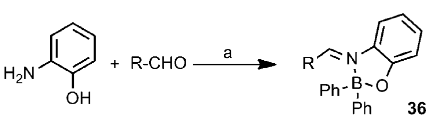


Figure 11. Synthesis of Type VI borate complexes a) 1. MeOH, 2. BPh_2OH, AcOEt or Et_2O.

cant effects on the delocalization of the aromatic systems because of conformational changes induced by boron(III) coordination.

3.2. Five-Membered Rings: Type VII Complexes

The motivation for engineering 8-hydroxyquinoline boron complexes such as **37** (Figure 12), was to find alternatives to Alq_3 derivatives studied in the early 2000s for OLED applications .[81,82] The central quinoline core tolerates different functional groups, and structural variations are also possible on the boron center. At boron, for instance, perfluorophenyl ligands[83] as well as unsymmetrically substituted diaryl acid carrying various functional groups (CHO, trimethylsilyl, SMe, amides, halides) have been used.[84] Other Type VII complexes involve pyridine, quinoline (e.g. **38**),[34] or ketopyrrole (e.g. **39**) derivatives.[85]

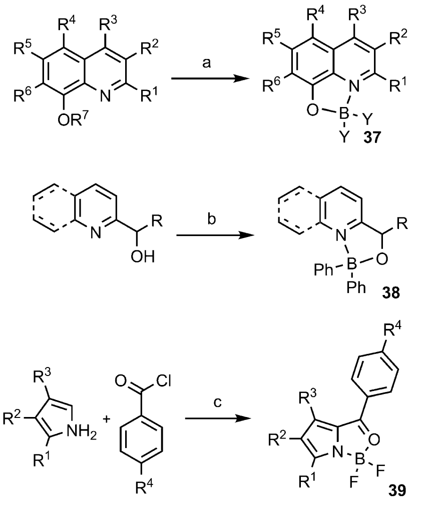
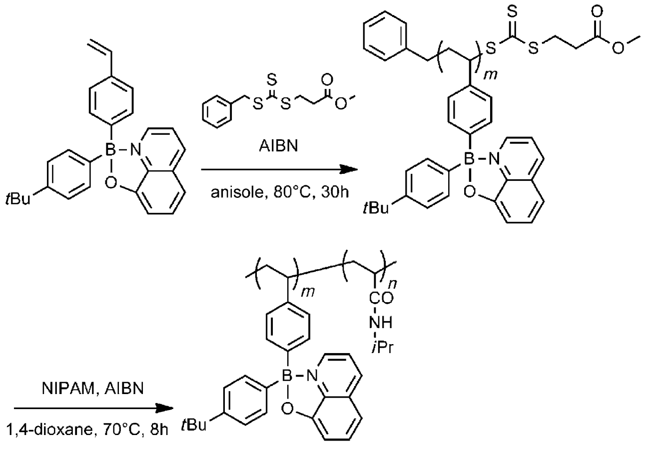


Figure 12. Synthesis of Type VII borate complexes. a) Various reaction conditions; see original publications; b) $Ph_2B\text{-}O\text{-}BPh_2$; c) 1. $C_2H_4Cl_2$, reflux, 2. $BF_3.OEt_2$.

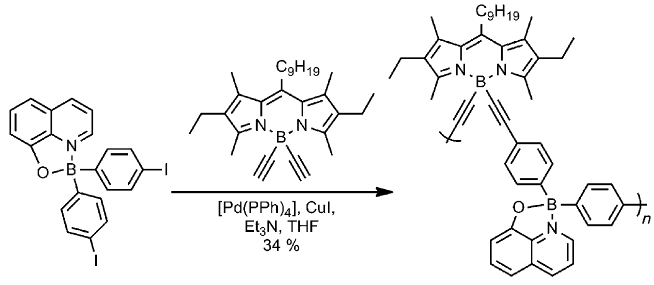
It is interesting to note that the good chemical stability of these dyes allow modification to tune their physical properties (solubility, polarity, chirality, filmability, crystallinity, etc.) and their optical properties, as well as permit inclusion into mesophases or polymers. Both Jäkle et al.[86,87] and Chujo et al.[88] have incorporated luminescent boron complexes into specific polymers. Thus, a quinoline boron complex bearing a styrene group has been used to construct a fluorescent copolymer (Figure 13),[89] while a hybrid polymer made up with two types of fluorophores has been created from an *E*-BODIPY by using a Sonogashira cross-coupling (Figure 14).[90]



40: λ_{abs} = 395 nm; λ_{em} = 507 nm; Φ_{THF} = 0.17

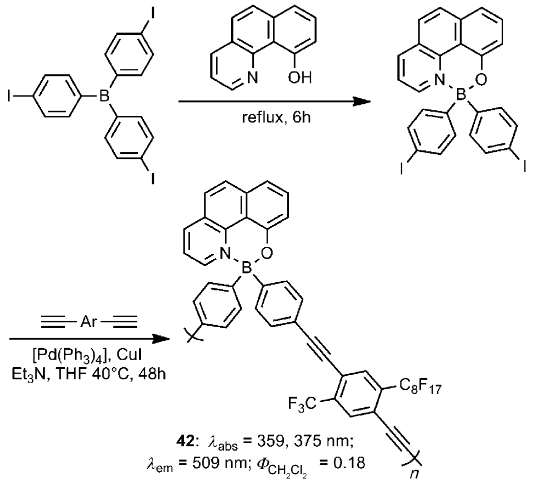
Figure 13. A luminescent polymer described by Jäkle et al.[87] AIBN = 2,2′-azobis(2-methylpropionitrile), NIPAM = *N*-isopropylacrylamide.

More recently, Chujo et al.[91] described several boron complexes bearing iodophenyl groups which can be used to assemble a polyacetylene polymer by a palladium-catalyzed cross-coupling reaction (Figure 15).



14: λ_{abs} = 264, 376, 516 nm; λ_{em} = 525 nm; $\Phi_{CH_2Cl_2}$ = 0.67

Figure 14. A luminescent polymer described by Hewavitharanage et al.[90] THF = tetrahydrofuran.



42: λ_{abs} = 359, 375 nm; λ_{em} = 509 nm; $\Phi_{CH_2Cl_2}$ = 0.18

Figure 15. Synthesis of a benzoquinolinol-based luminescent polymer described by Chujo et al.[91]

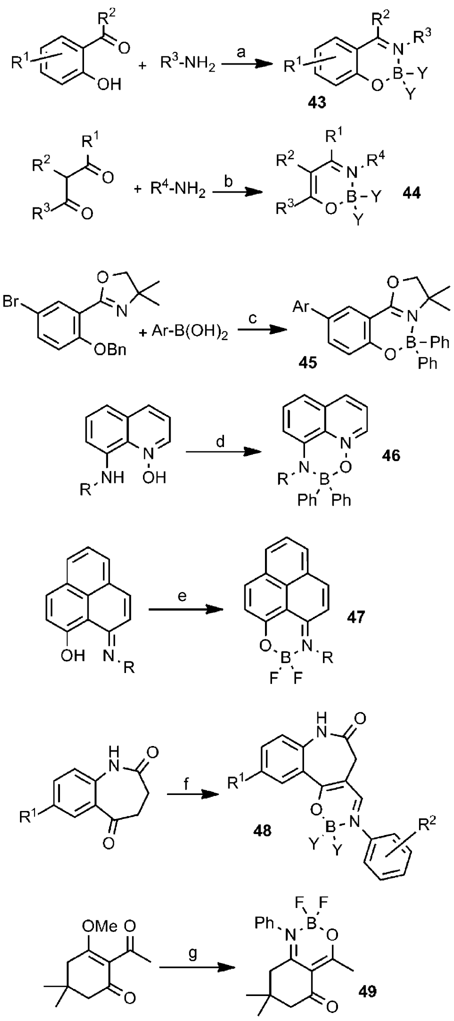


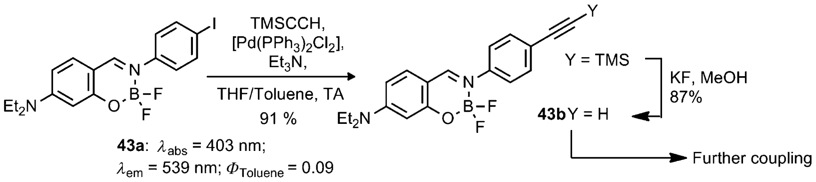
Figure 16. Synthesis of Type VIII borate complexes. a) 1. alcohol, 2. BY_3 ou BY_2Y', Y = F or Ar; b) 1. TsOH, Dean–Stark apparatus, 2. $BF_3{\cdot}OEt_2$, or iPrB(OC_6H_4O) (derived from *ortho*-hydroxyphenol); c) 1. Pd(OAc)$_2$, K_3PO_4, P(PhOMe)$_3$, 2. H_2, Pd/C, 3. BPh_3; d) Ph_2B-O-BPh_2; e) $BF_3{\cdot}OEt_2$; f) 1. DMF/DMA, 2. $R^2C_6H_4NH_2$, AcOH, 3. BPh_3, or $BF_3{\cdot}OEt_2$, DIEA; g) 1. $PhNH_2$, 2. $BF_3{\cdot}OEt_2$. DMA = *N,N*-dimethylacetamide.

3.3. Six-Membered Rings: Type VIII Complexes

Hohaus et al. were first to prepare Type VIII complexes (e.g. **43**, Figure 16),[92,93] but did not investigate their optical properties in detail.[94–96] We recently conducted such studies in the process of optimizing the fluorescence properties of the chelates by varying the nature of the R^3 substituents on the aniline.[97] A system with three boron centers, analogous to **43**, but based on a central 1,3,5-substituted phenyl ring, was described with interesting self-assembly and luminescence properties.[98] Other complexes, based on a ketoiminate pattern with a bidentate (**44**)[56,99,100] or tridentate[101] chelation mode, are known. The dyes **45** can be obtained from oxazolylphenolates ligands functionalized by Suzuki coupling.[102] The compounds **46**,[34] **47**,[103] **48**,[104] and **49**[105] have novel molecular structures but their luminescence properties remain modest.

To examine the impact of post-synthetic functionalization on the optical properties of BORANIL dyes (boron-complexed ANILs)[97] we made use of a Sonogashira cross-coupling reaction starting from the pivotal iodophenyl derivative **43a** (Figure 17). Excellent yields, with no significant decomplexation during the coupling reaction or deprotection steps, were obtained.[97] The resulting acetylenic **43b** was coupled to either subphthalocyanine or BODIPY derivatives to obtain cassettes for intramolecular energy-transfer studies.

In addition, the nitrophenyl analogue **43c** could be easily reduced to the corresponding aniline **43d** in high yield,



43a: λ_{abs} = 403 nm; λ_{em} = 539 nm; $\Phi_{Toluene}$ = 0.09

Figure 17. Sonogashira coupling on salicylalcdimine boron complex. TMS = trimethylsilyl.

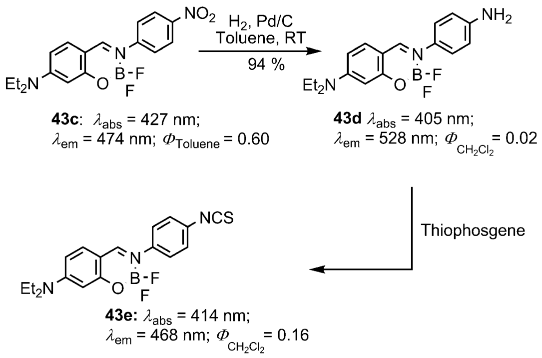


Figure 18. Reduction of a nitro salicylaldimine boron complex.

without reduction of the imino group (Figure 18). This strategy was used to prepare the stable isothiocyanate **43e**, which can be used as precursor for the synthesis of fluorescent amides, urea, and thiourea derivatives. The compound **43e** proved to be a useful labeling probe for a model BSA protein.[106]

The value of the capacity to functionalize boron chelates is highlighted in oxazaborine derivatives which do not exhibit significant luminescence, although the greater degree of conjugation imparted by the cyanine framework generates interesting optical properties (Figure 19).[105] The ketoenamine unit, when complexed to boron(III), has a methyl group sufficiently acidic to participate in a Knoevenagel condensation with various aldehydes, thus providing the compounds **49a**,**b**.

3.4. Six-Membered Rings: Type IX Complexes

A plethora of structures based on hydroxybenzazole has been described and prototypical examples are shown in Figure 20. This generic family is based on the coordination of a phenoxide O and the N of either a benzimidazole (**50**),[107,108] benzoxazole (**51**),[109–113] or benzothiazole (**52**)[114,115] derivative. A more extended structure is found in the phenanthroimidazole derivative **53**,[108] and the complexes **54**,[116,117] **55**,[118,119] and **56**[120] are monotopic or ditopic analogues of pyridine phenol, mostly studied for their use in electroluminescent devices. Interestingly, the generic family of compounds **56** was synthesized by a cascade reaction starting from the ethynyl derivative.[121] The compounds **57** stem from complexation of boron with ligands prepared from a coupling of quinoline and either phenalene or perylene derivatives.[122,123] The dimeric complexes **58** were engineered from a thiazolothiazole skeleton conjugated to two phenol subunits.[124] Furthermore, amide formation between a naphthyridine, bearing an amino group, and various benzylic esters leads to ligands for the boron(III) complexes **59**.[125] The compounds **60** can be obtained from pyrazine and benzylic esters.[126] The fluorophore **61** was produced from a coumarin modified with a benzoxazole substituent.[127]

3.5. Seven-Membered Rings: Type X Complexes

Only a few examples have been described, based on boron complexation to a pyrrole nitrogen atom and to an oxygen atom of a salicylaldehyde (**62**),[128] imidazolinone (**63**),[129] or modified coumarin (**64**)[130] (Figure 21).

4. Optical Properties of Borate Complexes

Detailed optical properties of selected compounds are gathered in Table 1.

4.1. Solution Fluorescence

In most cases, the fluorescence of these molecules has been assigned to a strong π→π* transition localized on the conjugated chelating backbone. The reported radiative deactivation processes are typical of singlet emitters of highly rigid and aromatic structures having short excited-state lifetimes and weakly polarized excited states, thus giving emission profiles which mirror the absorption of the molecules. When the organic cores incorporate strong donor/acceptor modules (push/pull character), an emissive excited charge-transfer state, sensitive to the dipolar moment of the solvent, can be observed. The lifetimes remain short but with Stokes shifts increasing markedly with solvent polarity. The absence of heavy atoms (except for some compounds bearing I or Br) excludes intersystem crossing and most dyes are resistant to triplet formation, an interesting situation which also excludes formation of the very reactive singlet oxygen which could lead to photodegradation of the fluorophores under aerobic conditions.

The rigidification of **1a**[36] resulting from a double boron complexation leads to highly structured absorption and emission bands (Figure 22). This immobilization of the structure disfavors the vibrational and rotational nonradiative deactivation channels, thus leading to exceptionally high fluorescence quantum yields, for example, 97 % for **1a** in

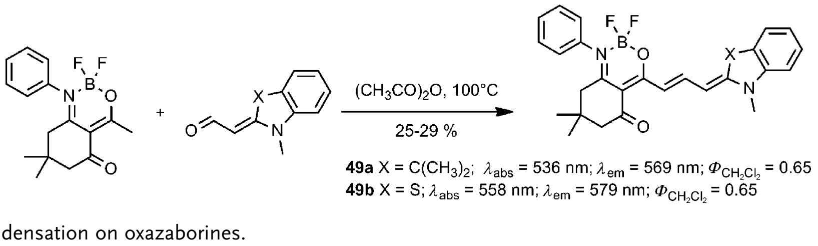


Figure 19. Knoevenagel condensation on oxazaborines.

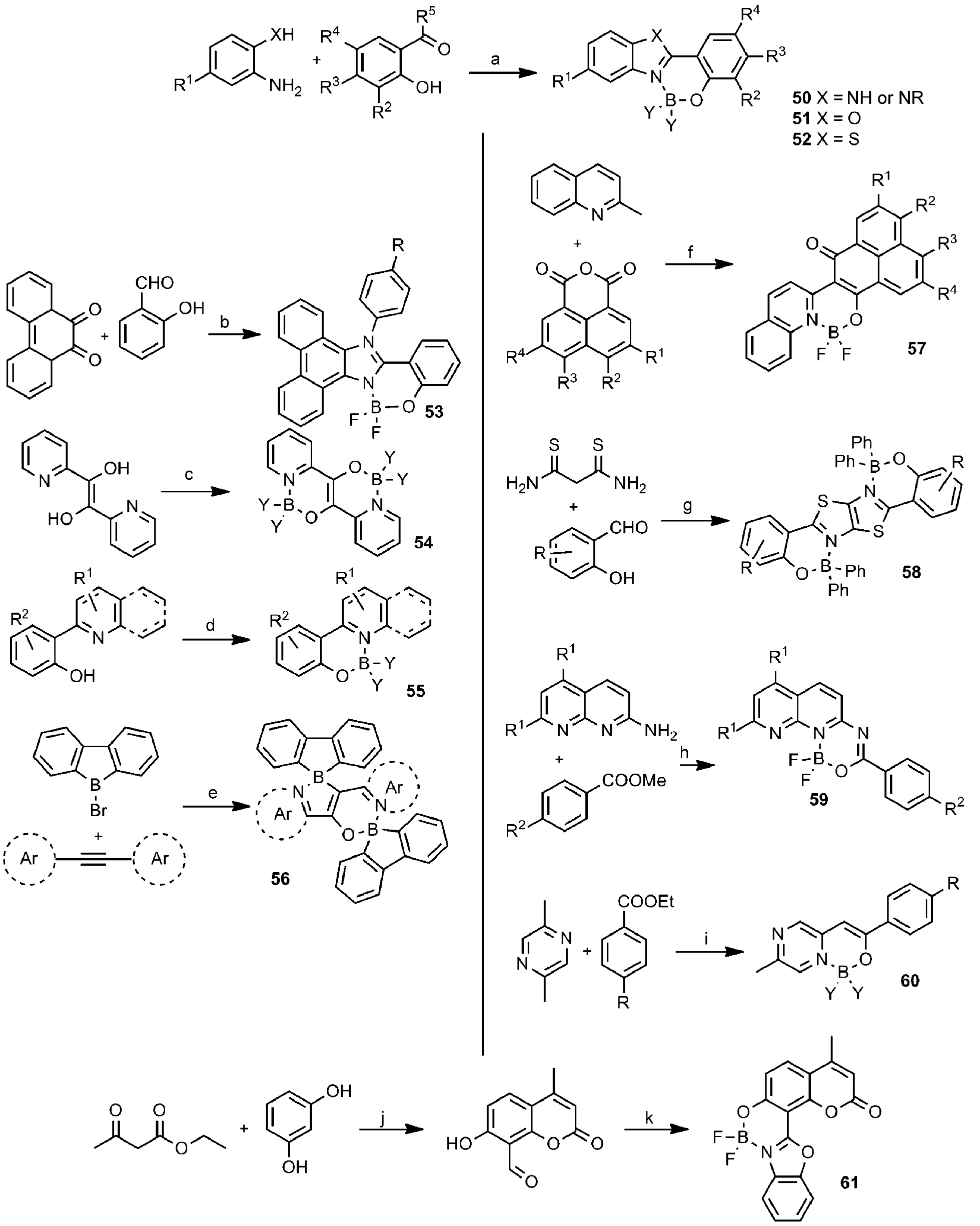


Figure 20. Synthesis of Type IX borate complexes. a) Various reaction conditions; see original publications; b) 1. $AcONH_4$, $RC_6H_4NH_2$, AcOH, 2. $BF_3{\cdot}OEt_2$, DIEA; c) $BY_3{\cdot}OEt_2$, BPh_3 or $B(OR)_3$; d) $BY_3{\cdot}OEt_2$ or BPh_3; e) 1. THF, 2. H_2O; f) 1. $ZnCl_2$, 2. $BF_3{\cdot}OEt_2$, DIEA; g) 1. phenol, 2. BPh_3; h) 1. NaH, 2. $BF_3{\cdot}OEt_2$; i) 1. NaH, 2. $BF_3{\cdot}OEt_2$, or BPh_3, THF; j) 1. H_2SO_4, 2. acetic acid, hexamethylenetetramine, 3. HCl, 70 °C; k) 1. ethyl cyanoacetate, benzoic acid, 2. $BF_3{\cdot}OEt_2$

CH_2Cl_2. In addition, **4b**[38] shows a similar chelating pattern and quantum yields, and a relatively large Stokes shift (3000 cm^{-1}). Switching from a hydrazone to a five-membered ring such as in **7a**,[41] **10a**,[47] and **13a**,[51] leads to intense emission in the blue-green region, and results from destabilization of the LUMO imposed by the steric constraints of the five-membered ring.

Complexes with iminoenamine ligands are often weakly fluorescent because of nonradiative deactivation pathways promoted by rotation of the side groups. In some cases, steric hindrance slows down these processes and allows good fluorescent properties, such as found for **15a** (Figure 23).[54] Interestingly, significant Stokes shifts were found for the unsymmetrical compounds **20a** (Δ_{ss} of 5100 cm^{-1}), **21a**, and **22a** (Δ_{ss} 3900 cm^{-1} in both cases).[61] The BORAZAN derivative **23**, described by Gardinier et al., shows emission mostly in the $\lambda = 470$–500 nm range.[62] The complex **23b** displays a bathochromic shift for both transitions as well as an increase of the quantum yield compared to the precursor **23a**. This difference is likely due to an intramolecular hydrogen bond between the imidazole and coordinated NH function, thus rigidifying the structure.[63] The complex **30a** also shows interesting emissive properties.[73]

Wang et al.[131] and Jäkle et al.[132] have developed several boron(III) precursors which enable facile variation of the substituent on 8-hydroxyquinoline chelates such as **37a**,**b**

Table 1: Compilation of the optical properties of a selection of boron(III) complexes.[a]

Dye	Solvent	λ_{abs} [nm]	ε [$M^{-1}cm^{-1}$]	λ_{em} [nm]	Δ_{ss} [cm^{-1}]	Φ_F	τ [ns]	Ref.
1a	CH_2Cl_2	392, 415, 440, 470	30000	478, 512	–	0.97	121	[36]
4a	DMSO/PBS	400	13000	486	4400	0.29	–	[38]
4b	MeOH	472	29000	551	3000	0.75	–	[38]
7a	Cyclohexane	392	20000	463	3900	0.47	–	[41]
8a	THF	420	11000	560	6000	0.25	–	[43]
8a	solid	420	–	572	6300	0.37	–	[43]
10a	CH_3CN	319	14000	380	5000	0.88	6.40	[47]
13a	THF	405	11000	505	4300	0.22	–	[51]
15a	*n*-hexane	440	10000	512	3200	0.57	–	[54]
20a	CH_2Cl_2	417	10000	531	5100	0.33	2.00	[61]
21a	CH_2Cl_2	466	6000	569	3900	0.66	11.1	[61]
22a	CH_2Cl_2	416	11000	496	3900	0.75	5.50	[61]
23a	CH_2Cl_2	358	7000	467	6500	0.66[b]	–	[63]
23b	CH_2Cl_2	252, 292, 372	6000	474	5800	0.75[b]	–	[63]
24a	CH_2Cl_2	413	–	512	4700	0.06	–	[64]
24a	solid	–	–	497	–	0.52	–	[64]
26a	CH_2Cl_2	752	26000	819	1100	–	–	[66]
27a	CH_2Cl_2	420, 496	85000, 46000	550, 550	5600, 1900	0.56, 0.59	4.06	[67]
28a	CH_2Cl_2	732	190000	749	300	0.69	–	[69]
29a	$CHCl_3$	655	110000	676	470	0.81	5.29	[71]
30a	CH_2Cl_2	395	–	454	3300	0.47	–	[73]
32a	CH_2Cl_2	379, 399, 422	95000	431, 454, 485	500	0.83	3.5	[75]
32a	solid	–	–	466, 491, 527	–	0.44	6.4	[75]
32b	CH_2Cl_2	396, 419, 445	84000	451, 476, 509	300	0.74	3.9	[75]
32b	solid	–	–	503, 518, 557	–	0.64	7.3	[75]
33a	*n*-hexane	324, 458	48000	465	330	0.25	–	[76]
33a	solid	–	–	507	–	0.04	–	[76]
34a	CH_2Cl_2	643	19000	695	1200	0.03	–	[77]
36a	$CHCl_3$	552	32000	–	–	–	–	[79]
37a	CH_2Cl_2	294, 304, 320, 336, 354, 380	–	496	6200	0.37	–	[131]
37b	THF	394	3000	508	5700	0.16	–	[132]
37c	THF	389	5000	485	5100	0.39	–	[133]
37d	CH_2Cl_2	258, 306, 406	–	529	5700	0.23	–	[134]
40	THF	395	–	507	5600	0.17	–	[87]
41	CH_2Cl_2	264, 376, 516	–	525	330	0.67	–	[90]
42	$CHCl_3$	359, 375	48000	509	7000	0.18	–	[91]
43a	toluene	403	69000	455	2900	0.09	0.27	[97]
43c	toluene	427	66000	474	2300	0.60	1.61	[97]
43d	CH_2Cl_2	405	48000	528	5800	0.02	0.21	[106]
43e	CH_2Cl_2	414	71000	468	2800	0.16	0.49	[106]
43f	toluene	428	68000	506	3600	0.90	1.14	[97]
43h	toluene	414, 567	60000, 76000	574, 574	6700, 215	0.15, 0.17	2.02	[97]
50a	CH_2Cl_2	375	72000	393	1200	0.13	1.94	[108]
51a	CH_2Cl_2	376	8000	452	4500	0.38	2.92	[111]
51b	CH_2Cl_2	371	44000	420	3100	0.53	1.00	[111]
51c	CH_2Cl_2	383	14000	457	4200	0.32	3.02	[111]
51d	CH_2Cl_2	362, 503	15000, 63000	513, 513	8100, 390	0.48, 0.50	2.43	[111]
52a	CH_2Cl_2	413	60000	430	1000	0.98	–	[115]
52b	CH_2Cl_2	456	6000	597	5200	0.28	–	[115]
52c	CH_2Cl_2	515	17000	660	4300	0.34	–	[136]
53a	CH_2Cl_2	364	21000	393	2000	0.53	1.86	[108]
56a	CH_2Cl_2	428	15000	510	3800	0.85	–	[121]
57a	CH_2Cl_2	368, 427	17000	588	6400	0.50	–	[122]
57b	CH_2Cl_2	616	–	655	970	0.50	5.45	[123]
59a	CH_2Cl_2	252, 313, 440	63000	537	4100	0.22	3.05	[125]
59a	solid	–	–	542	–	0.04	3.7/1.06	[125]
60a	CH_2Cl_2	429	17000	520	4100	0.71	–	[126]
60a	solid	–	–	540	–	0.18	–	[126]
64a	MeCN	290, 385, 472, 509	–	538	1100	0.50	–	[130]
65	CH_2Cl_2	379	92000	456	4500	0.60	1.50	[139]
66	*n*-hexane	406	19000	510	5000	0.49	3.00	[142]
66	solid	–	–	527	–	0.50	–	[142]

[a] For a given structure see Figure in the text. [b] In toluene.

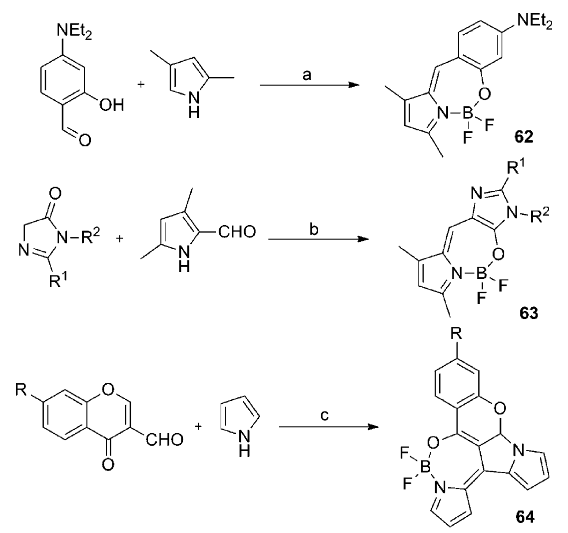
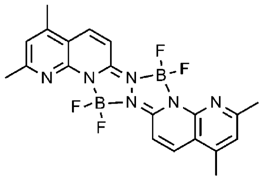
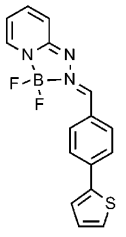


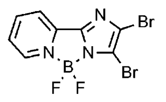
Figure 21. Synthesis of Type X borate complexes. a) 1. DDD, 2. $BF_3\cdot OEt_2$; b) 1. Piperidine or HBr/TFA, 2. $BF_3\cdot OEt_2$; c) 1. TFA, 2. DDQ, 3. $BF_3\cdot OEt_2$. DDD = Dichlorodiphenyldichloroethane, DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.



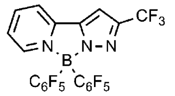
1a: λ_{abs} = 392, 415, 440, 470 nm; λ_{em} = 478, 512 nm; $\Phi_{CH_2Cl_2}$ = 0.97



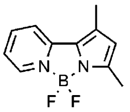
4b: λ_{abs} = 472 nm; λ_{em} = 551 nm; Φ_{MeOH} = 0.75



7a: λ_{abs} = 392 nm; λ_{em} = 463 nm; $\Phi_{cyclohexane}$ = 0.47

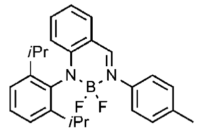


10a: λ_{abs} = 319 nm; λ_{em} = 380 nm; Φ_{CH_3CN} = 0.88

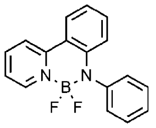


13a: λ_{abs} = 405 nm; λ_{em} = 505 nm; Φ_{THF} = 0.22

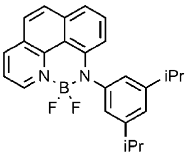
Figure 22. Optical properties of a selection of five-membered ring N,N borate complexes. Inset: absorption and emission of **1a** in dichloromethane solution (from Ref. [36]).



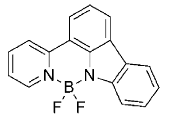
15a: λ_{abs} = 440 nm; λ_{em} = 512 nm; Φ_{hexane} = 0.57



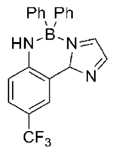
20a: λ_{abs} = 417 nm; λ_{em} = 531 nm; $\Phi_{CH_2Cl_2}$ = 0.33



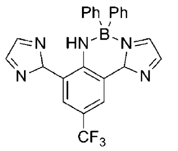
21a: λ_{abs} = 466 nm; λ_{em} = 569 nm; $\Phi_{CH_2Cl_2}$ = 0.66



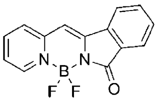
22a: λ_{abs} = 416 nm; λ_{em} = 496 nm; $\Phi_{CH_2Cl_2}$ = 0.75



23a: λ_{abs} = 358 nm; λ_{em} = 467 nm; $\Phi_{toluene}$ = 0.66

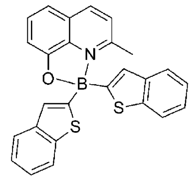


23b: λ_{abs} = 372 nm; λ_{em} = 474 nm; $\Phi_{toluene}$ = 0.75

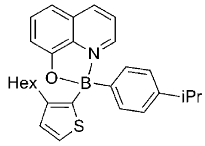


30a: λ_{abs} = 395 nm; λ_{em} = 454 nm; $\Phi_{CH_2Cl_2}$ = 0.47

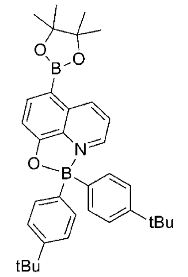
Figure 23. Optical properties of a selection of six-membered ring N,N borate complexes.



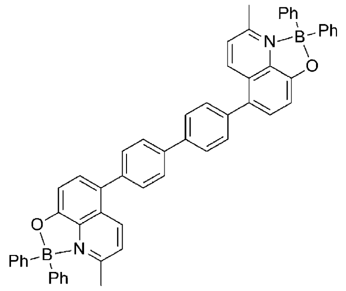
37a: λ_{abs} = 294, 304, 320, 336, 354 380 nm; λ_{em} = 496 nm; $\Phi_{CH_2Cl_2}$ = 0.37



37b: λ_{abs} = 394 nm; λ_{em} = 508 nm; Φ_{THF} = 0.16



37c: λ_{abs} = 389 nm; λ_{em} = 485 nm; Φ_{THF} = 0.39



37d: λ_{abs} = 258, 306, 406 nm; λ_{em} = 529 nm; $\Phi_{CH_2Cl_2}$ = 0.23

Figure 24. Optical properties of a selection of 8-hydroxyquinoline-based borate complexes.

(Figure 24). The same groups worked on the substitution at the 8-position to obtain **37c**[133] and **37d**.[134] This synthetic methodology enabled tuning the emission wavelength from blue to yellow without perturbing the quantum yields to a great extent.

To further illustrate the fluorescence features of BOR-ANIL dyes, we choose two systems developed in our laboratory.[97] The basic compound **43c**, bearing a strong donor on one side (diethylamino) and a strong acceptor on the other side (nitro), shows minor changes in its absorption spectra in various solvents, but a drastic perturbation of the emission (Figure 25). Indeed, in a solvent with a weak dipole moment (toluene) an intense ($\Phi = 60\,\%$) structured emission with a small Stokes shift is observed, and is characteristic of a singlet-state emission. When the dipole moment of the solvents is increased, the emission is bathochromically shifted

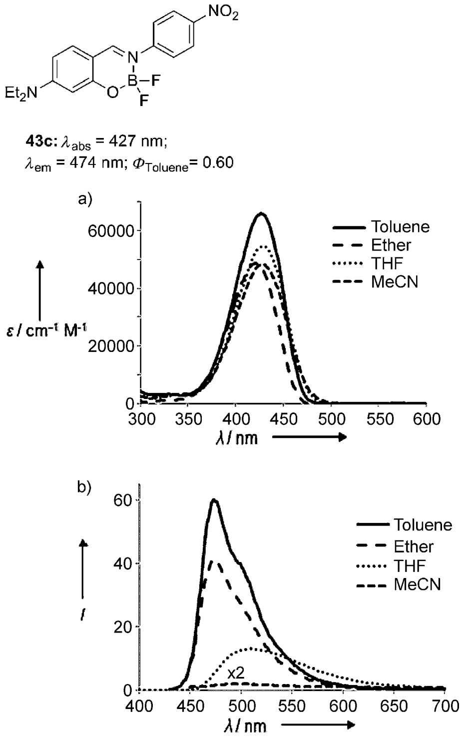


Figure 25. Absorption (a) and emission (b) spectra of **43c** in various solvents.

and the quantum yield falls to 13% in THF, and to almost zero in MeCN. This behavior is characteristic of an emissive charge-transfer excited state.

For the diboron complex **43f** the structured emission observed in toluene, with a high quantum yield (90%), is weakly dependent on the solvent dielectric constant as acetonitrile gives a quantum yield at 68% (Figure 26). However, for both of these solvents there is a nanosecond scale emission lifetime, and a weak Stokes shift. In this case, the emission is safely assigned to a singlet excited state.

Several boron complexes based on benzazole derivatives have been synthesized and studied (Figure 27). The benzimidazole (**50**) and phenanthroimidazole (**53**) series display fluorescence at relatively high energies[108,135] while the benzoxazole series **51** exhibit a significant bathochromic shift in emission.[111] Switching the oxygen for a sulfur atom further stabilizes the LUMO through d-orbital hybridization, which leads to fluorescence at lower energies in the benzothiazole series **52**. The HOMO–LUMO energetic gap correlates with the structure of the chelating core, with a continuous decrease along the benzimidazole > benzoxazole > benzothiazole series of dyes. Interestingly, the photophysical properties of benzazole derivatives are highly dependent on the nature and the position of the functionalization on the phenol ring. For example, the presence of a dimethylamino group at the 4-position in **52a** engenders a blue fluorescence at $\lambda = 430$ nm while the presence of the same group at the 5-position leads to a strong red-shift in **52b** ($\lambda_{em} = 597$ nm).[115] It is noteworthy that some of these dyes display interesting fluorescence and filmability in the solid state.[108,111,113,115]

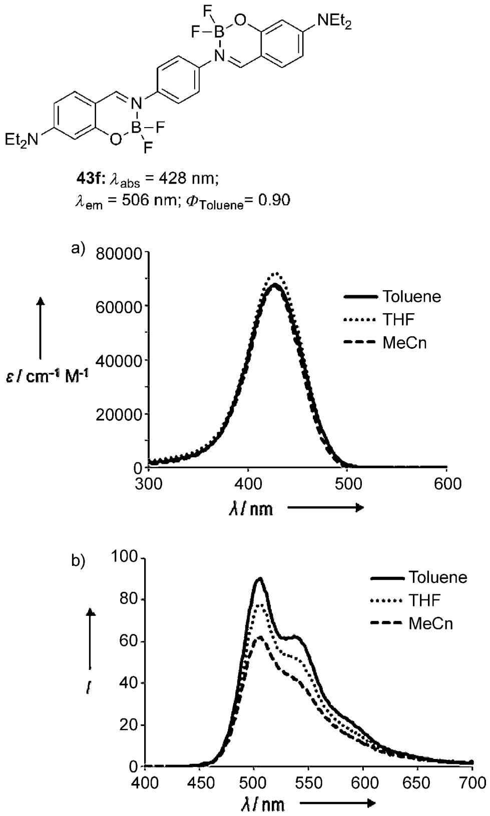


Figure 26. Absorption (a) and emission (b) spectra of **43f** in various solvents.

Several families of six-membered-ring borate complexes have been described, with most of them exhibiting interesting fluorescence properties and impressive quantum yields (Figure 28). Most of these compounds are unsymmetrical and polarized, thus favoring large Stokes shifts: 3800 cm^{-1} for **56a**,[121] 6400 cm^{-1} for **57a**,[122] 4100 cm^{-1} for **59a**,[125] and 4100 cm^{-1} for **60a**.[126]

Worth noting is the fact that among the few examples of seven-membered-ring borate complexes, only **64a**[130] exhibits attractive physical properties, wherein both absorption and emission red-shifted with respect to smaller chelate ring sizes (Figure 29).

4.2. Red and NIR Emitters

Increasing the degree of π conjugation of organic frameworks is a useful strategy for stabilizing the LUMO and provoking a bathochromic shift of both absorption and emission, thereby reaching, in some cases, the red/NIR window. Emission maxima beyond $\lambda = 650$ nm are often observed and can even reach $\lambda = 819$ nm (e.g., **26a**; Figure 30). In keeping with the energy-gap-law theory, the quantum yields can be extremely weak.[66] To rigidify the structure and extend the delocalization a common strategy has been to engineer ditopic ligands capable of offering two chelation sites such as in a dipyridinephenyl backbone (**34a**)[77] or a fused dipyrrole (**28a**).[69] Note that the replace-

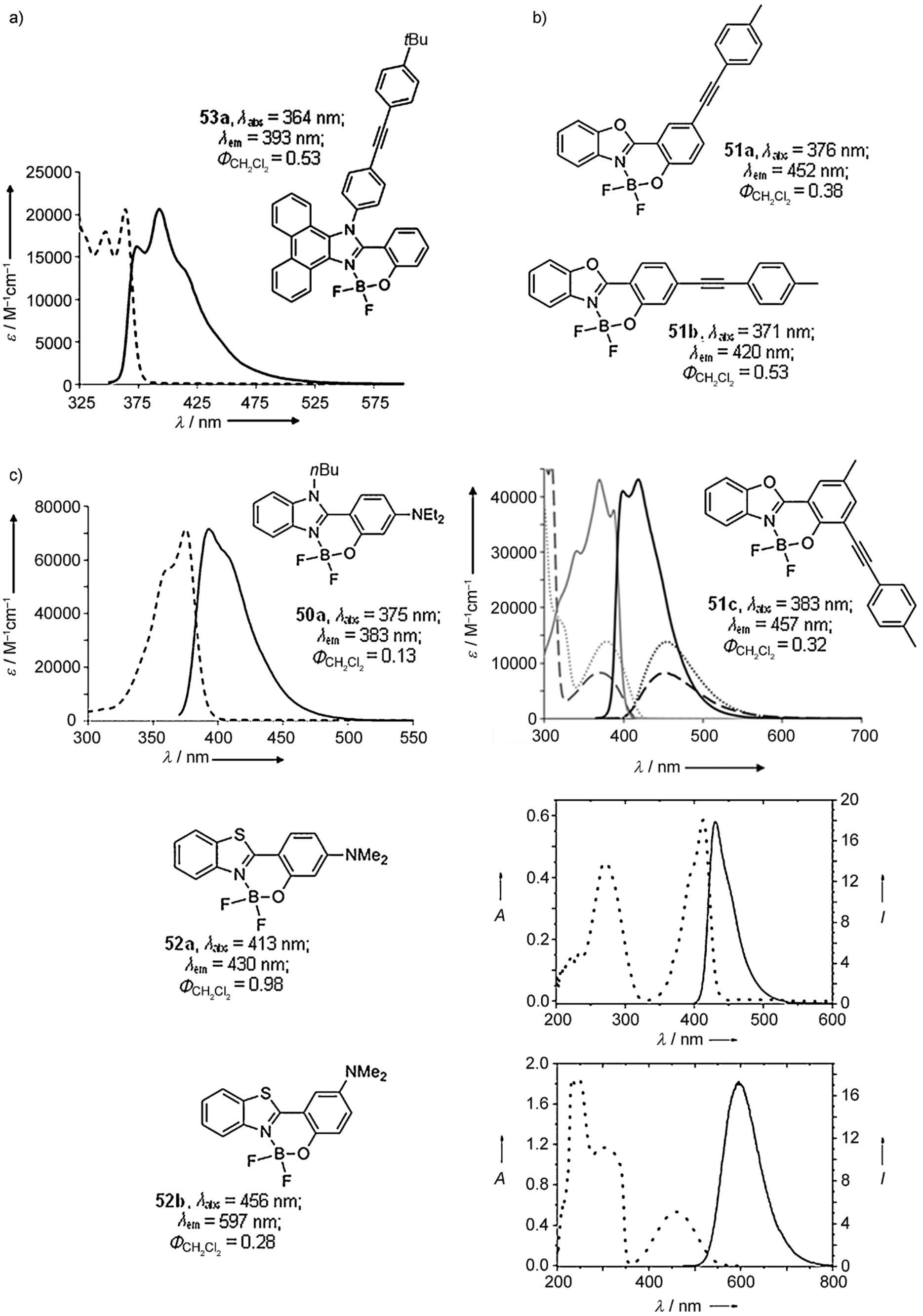
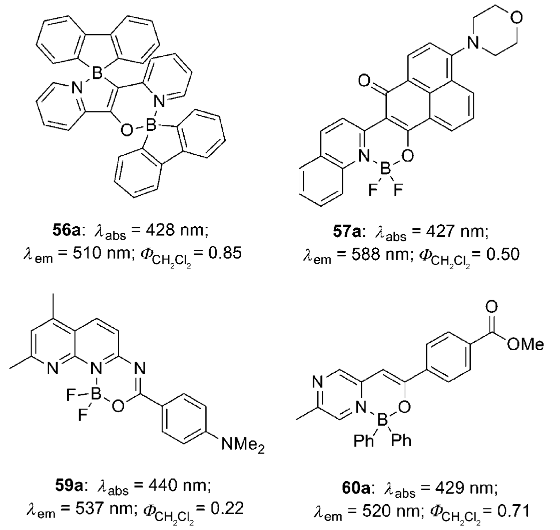


Figure 27. Optical properties of a selection of benzazole borate complexes [benzimidazoles (a), benzoxazoles (b) and benzothiazoles (c)].

ment of the electroattractive cyano group in **28a** by a bridging nitrogen atom in **29a** in the cyanine-type of arrangement causes a marked hypsochromic shift in both absorption and emission properties.[71] Compounds emitting above λ = 700 nm have been obtained by using a rigid pyrrolopyrrole core.[72] Frameworks displaying similar emissive properties have been constructed from the rigid matrices of quinolone perylene (**57b**)[123] or bis(hydroxybenzothiazol) (**52c**) framework.[136]

4.3. Photoinduced Energy Transfer

There is a constant interest in the study of energy transfer between fluorophores displaying different energy levels, as such models are of paramount importance to an understanding of energy concentration in natural photosynthesis and for the possible use of such fluorophores in luminescent solar energy concentrators.[29] Appropriate dyads are quite easy to prepare by linking the popular BODIPY or subphthalocyanine (SubPc) units to HBO-borates, BORICOs, or BORANILs by unsaturated tethers. The compounds **51d**,[111] **27a**,[67] and **43h**[97] show a high efficiency (> 95 %) of energy transfer



56a: λ_{abs} = 428 nm; λ_{em} = 510 nm; $\Phi_{CH_2Cl_2}$ = 0.85

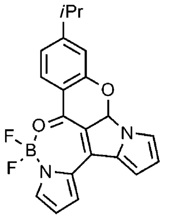
57a: λ_{abs} = 427 nm; λ_{em} = 588 nm; $\Phi_{CH_2Cl_2}$ = 0.50

59a: λ_{abs} = 440 nm; λ_{em} = 537 nm; $\Phi_{CH_2Cl_2}$ = 0.22

60a: λ_{abs} = 429 nm; λ_{em} = 520 nm; $\Phi_{CH_2Cl_2}$ = 0.71

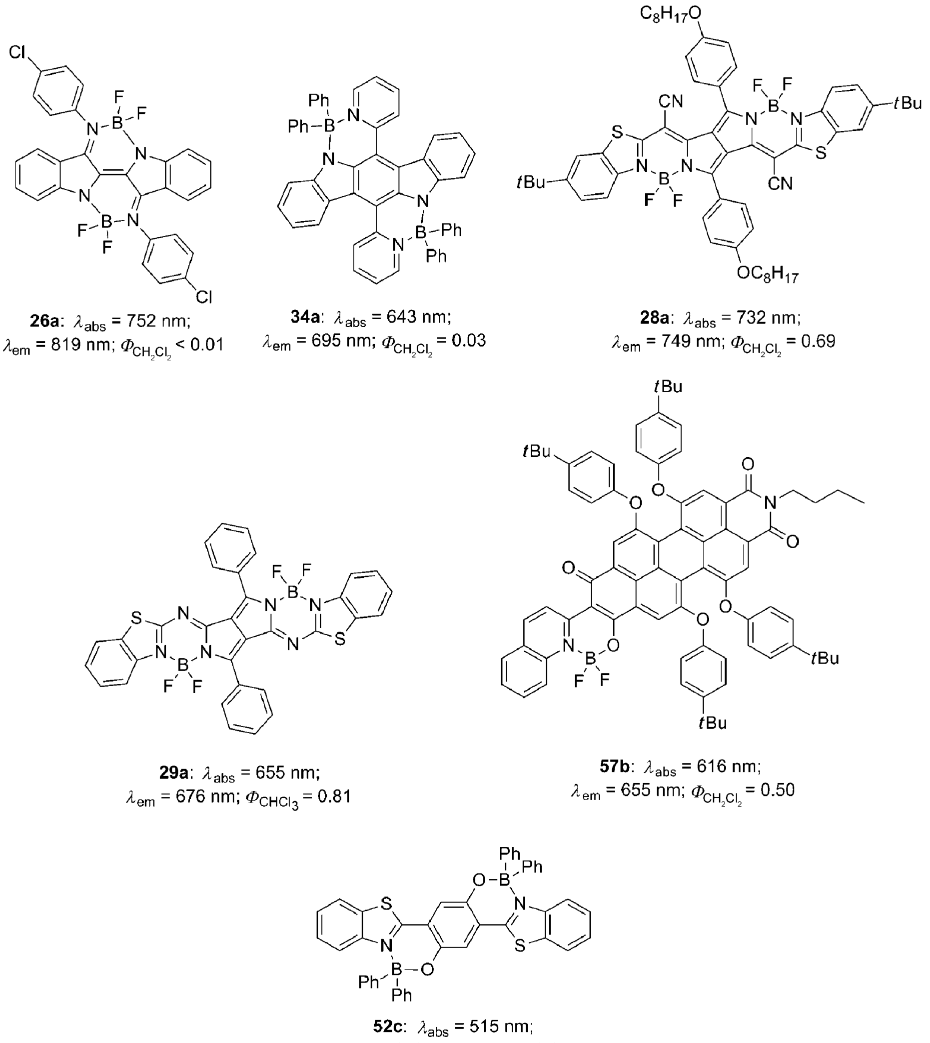
Figure 28. Optical properties of a selection of six-membered ring N,O borate complexes.

from the N,N or N,O borate subunits to the linked BODIPY or SubPc energy acceptors, thus providing in all cases virtual Stokes shifts larger than 8000 cm^{-1} (Figure 31). The efficiency of the energy transfer is evident in the very weak residual emission of the energy donor (borate complex) observed in the steady-state emission spectrum. This favorable intramolecular energy-transfer process is facilitated by an efficient spectral overlap between the emission of the donor and the spectral absorption of the acceptor (Förster resonance energy transfer process). The large Stokes shift engendered by this process is of fundamental interest in bioanalysis to avoid reabsorption of the emitted light by the ground state of the fluorescent probe.



64a: λ_{abs} = 509 nm; λ_{em} = 538 nm; Φ_{MeCN} = 0.50

Figure 29. Unusual seven-membered ring coordination and its optical properties.



26a: λ_{abs} = 752 nm; λ_{em} = 819 nm; $\Phi_{CH_2Cl_2}$ < 0.01

34a: λ_{abs} = 643 nm; λ_{em} = 695 nm; $\Phi_{CH_2Cl_2}$ = 0.03

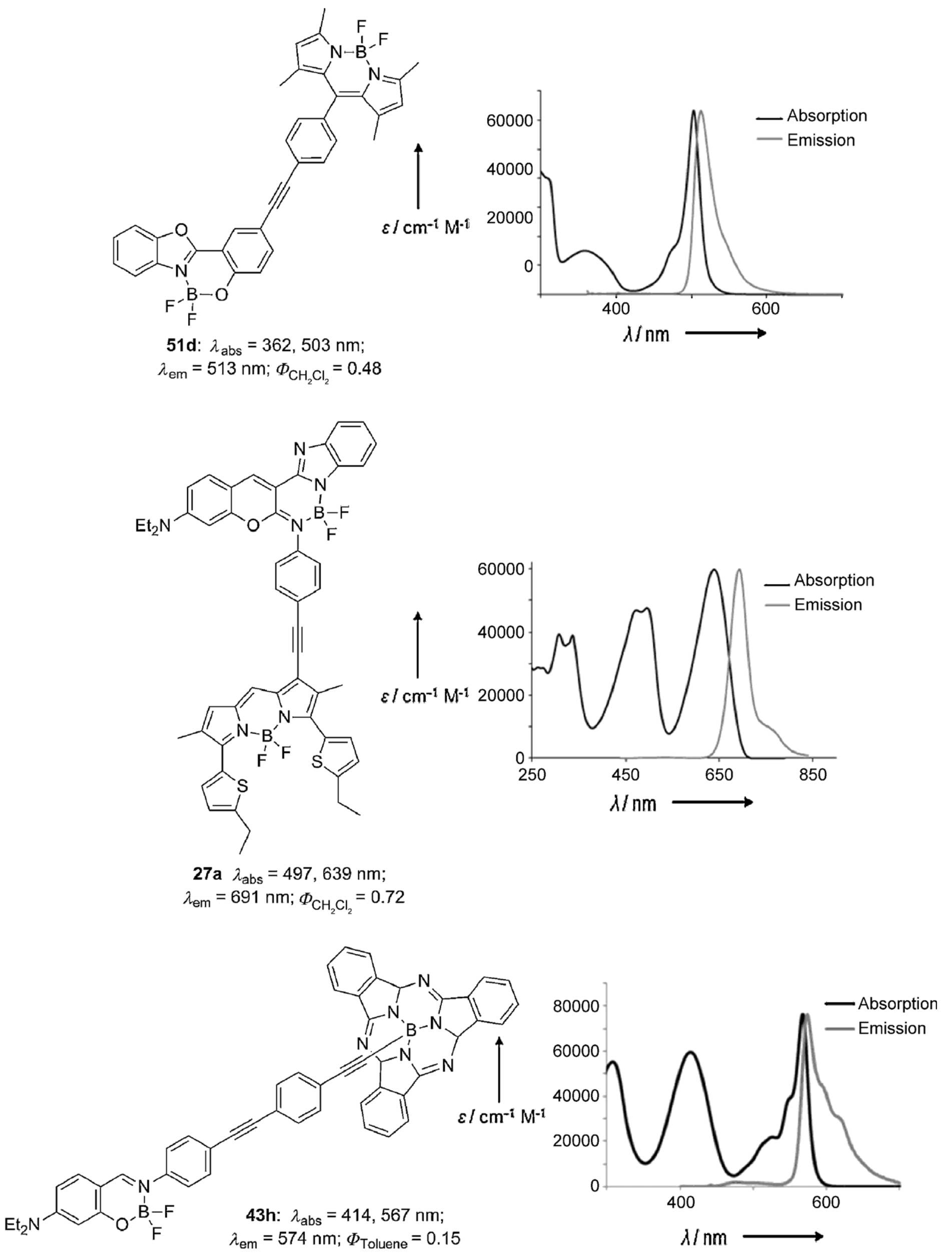
28a: λ_{abs} = 732 nm; λ_{em} = 749 nm; $\Phi_{CH_2Cl_2}$ = 0.69

29a: λ_{abs} = 655 nm; λ_{em} = 676 nm; Φ_{CHCl_3} = 0.81

57b: λ_{abs} = 616 nm; λ_{em} = 655 nm; $\Phi_{CH_2Cl_2}$ = 0.50

52c: λ_{abs} = 515 nm; λ_{em} = 660 nm; $\Phi_{CH_2Cl_2}$ = 0.34

Figure 30. Optical properties of a selection of N,N and N,O borate complexes emitting in the red/NIR region.



51d: λ_{abs} = 362, 503 nm; λ_{em} = 513 nm; $\Phi_{CH_2Cl_2}$ = 0.48

27a λ_{abs} = 497, 639 nm; λ_{em} = 691 nm; $\Phi_{CH_2Cl_2}$ = 0.72

43h: λ_{abs} = 414, 567 nm; λ_{em} = 574 nm; $\Phi_{Toluene}$ = 0.15

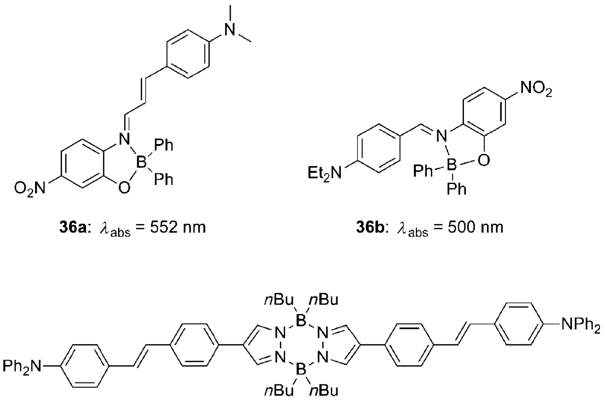
Figure 31. Selection of dyads including luminescent borate complexes and corresponding absorption and emission spectra measured under high dilution in dichloromethane.

4.4. Nonlinear Optical (NLO) Properties

It has previously been established that push-pull organic or inorganic structures exhibit unusual nonlinear optical properties, thus leading to interesting applications in optical devices aimed at data storage, communication, switching, computing, and image processing. Some of the borate complexes described in this account are decorated with strong donor or acceptor groups, and have significant dipolar or quadrupolar moments (Figure 32). For instance, **36a** shows a second-order hyperpolarizability, thus allowing generation of a second harmonic ($\beta\mu = 1562\times10^{-30}\,\mathrm{cm^5\,esu^{-1}\,D^{-1}}$) along with a third harmonic ($\chi^{(3)} = 8.4\times10^{-12}$ esu).[79] The complex **36b** also shows a third harmonic generation ($\chi^{(3)} = 4.1\times10^{-12}$ esu).[80] The salicylaldimine derivative **41a** also exhibits second- ($\beta\mu = 497.9\times10^{-30}\,\mathrm{cm^5\,esu^{-1}\,D^{-1}}$) and third-order phenomena ($\chi^{(3)} = 5.01\times10^{-12}$ esu).[137] Surprisingly, only a second-order effect was observed for **41b** ($\beta_{vec}\mu = 497.9\times10^{-30}\,\mathrm{cm^5\,esu^{-1}\,D^{-1}}$).[138] Interestingly, **65** has been found to be an efficient two photon absorber at $\lambda = 800$ nm ($\sigma_2 = 314$ GM).[139]

4.5. Solid-State Fluorescence

One of the most striking properties of luminescent borate complexes is that they retain their strong fluorescence in the solid state (Figure 33).[43,64,75] Several potential applications

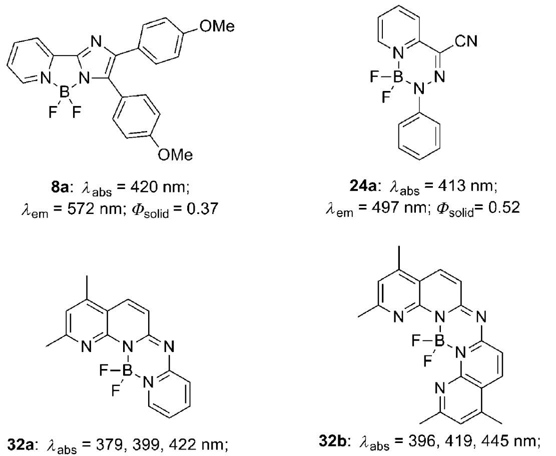


36a: λ_{abs} = 552 nm

36b: λ_{abs} = 500 nm

65: λ_{abs} = 379 nm; λ_{em} = 456 nm; $\Phi_{CH_2Cl_2}$ = 0.60

Figure 32. Borate complexes with NLO activity.



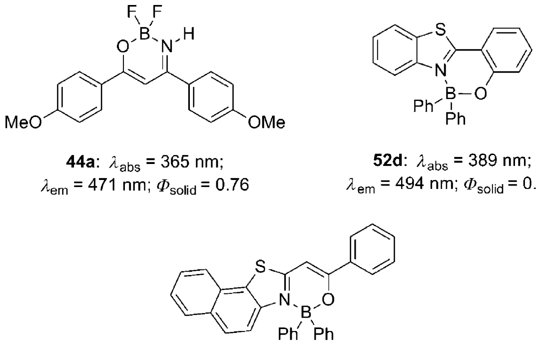
8a: λ_{abs} = 420 nm; λ_{em} = 572 nm; Φ_{solid} = 0.37

24a: λ_{abs} = 413 nm; λ_{em} = 497 nm; Φ_{solid} = 0.52

32a: λ_{abs} = 379, 399, 422 nm; λ_{em} = 466, 491, 527 nm; Φ_{solid} = 0.44

32b: λ_{abs} = 396, 419, 445 nm; λ_{em} = 503, 518, 557 nm; Φ_{solid} = 0.64

Figure 33. Solid-state optical properties of some N,N borate complexes.



44a: λ_{abs} = 365 nm; λ_{em} = 471 nm; Φ_{solid} = 0.76

52d: λ_{abs} = 389 nm; λ_{em} = 494 nm; Φ_{solid} = 0.60

66: λ_{abs} = 406 nm; λ_{em} = 527 nm; Φ_{solid} = 0.50

Figure 34. Optical properties in solid state of some N,O borate complexes.

such as emitters in OLEDs, solid-state lasers, sensors, reversible solid-state mechanochromic dyes, and in optoelectronic device technologies to achieve switchable and tunable fluorescence in the organic solid state are the stimulus to research on such materials.[140,141]

Other fluorophores based on N,O ligands also exhibit fluorescence properties in the solid state. The compound **44a** is a member of a family which is not fluorescent in solution, but displays intense fluorescence in the solid state because of restriction of rotation in the condensed phase (Figure 34).[100] The same behavior is found with **66**.[142] The compound **52d**[136] is fluorescent in solution and keeps excellent fluorescence properties in the solid state. Nowadays solid-state luminescence is one of the most promising application domains for N,N and N,O borate complexes.

5. Electroluminescent Devices

A good overview of the utilization of N,N and N,O complexes in electroluminescent devices up to 2011 may be found in a recent comprehensive review by Rao and Wang.[143] Thummel et al.[74] have synthesized numerous borate complexes used in this field.[74] For instance, **5a**[39] was used as pure emitting layer in devices with a brilliance around 1000 $\mathrm{cd\,m^{-2}}$ (Figure 35). Other N,N borate complexes such as **15a**[144] and **16b**[55] are not electroactive by themselves but have been used as dopants in standard devices exhibiting then a brilliance of respectively 320 and 457 $\mathrm{cd\,m^{-2}}$.

As a result of their strong analogy with the popular Alq3 [aluminium(III) tris(8-hydroxyquinolinate)] numerous hydroxyquinoline-based boron complexes were tested early on in OLEDs (Figure 35). The main advantage of boron complexes versus aluminium complexes is the much stronger covalency of B–O and B–N bonds than that of the corresponding Al–O and Al–N bonds, and thus results in a greater stability of the boron compounds. This is indeed observed quite generally, thus allowing the engineering of numerous high-performance fluorescent borate emitters for use in OLED devices. The devices using **37e**,[145] **37f**,[146] and **37g**[82] have brilliance values of over 1000, 2600, and 4000 $\mathrm{cd\,m^{-2}}$, respectively. More recently, devices based on the salicylaldimine complexes **43g**[147] and **43h**[148] were tested but the brilliance was weak (respectively 195 and 100 $\mathrm{cd\,m^{-2}}$). To date, the best results obtained with electroluminescent borate complexes have been with compounds based on pyridine phenol chelates (Figure 35). The compounds **55a**[149] and **55b**[119] have brilliance values around 10000 $\mathrm{cd\,m^{-2}}$. The compound **58a**,[124] based on a thiazolothiazole backbone, used pure as an emitting layer allows attainment of a brilliance value of 18000 $\mathrm{cd\,m^{-2}}$. The compound **51f**, bearing a diphenylamine donor group on the phenol side, gives an outstanding brilliance of 31000 $\mathrm{cd\,m^{-2}}$.[114]

6. Other Applications

A small number of other applications of luminescent borate complexes have been reported, some of which are based on their very interesting photophysical properties. One example is the use of borate complexes as photosensitizers in photovoltaic cells.[150] A flexible macrocycle based on an

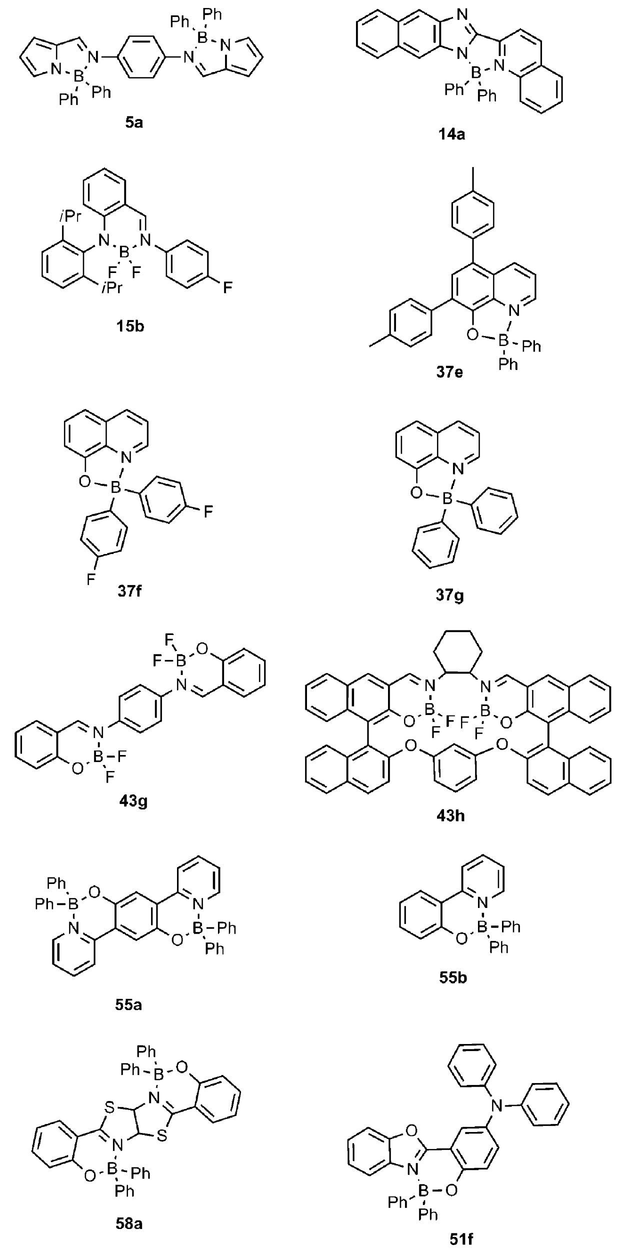


Figure 35. Panel of N,N and N,O borate complexes used in electroluminescent devices.

assembly of salicylaldimine borate complexes allowed inclusion of various ionic species within the receptor.[151] Some studies on the toxicology and the pharmacologic activity of salicylaldimine-based borate complexes as antifungal compounds have been carried out.[152,153] Other complexes have been used to generate singlet oxygen, and are potentially useful for photodynamic therapy,[44] and as photoinitiators in radical polymerization reactions.[154]

7. Conclusions and Perspectives

Of the numerous new dyes characterized over the past few years, those based on neutral, four-coordinate boron(III) complexes offer many advantages over those commonly prepared by multistep and tedious synthetic protocols. The issues of purification, stability, and handling (toxicity), and cost are crucial for potential commercialization. Although this stage has not been reached yet for the borate complexes, very attractive optical properties such as high absorption coefficients, red-shifted emission wavelengths, and high quantum yields are evident. In this minireview we have considered the most promising systems based on anionic N,N or N,O ligands. Each family of complexes may be distinguished by the number of atoms in the ring systems and the number of aromatic systems in the π conjugation. This classification gives five categories for the N,N borate complexes and five for the N,O borate complexes. Especially important features of these dyes in general are their intrinsic chemical stability, the availability of large amounts, and resistance to aggressive reagents, thus making them suitable for extended functionalization. In most cases the synthesis of given compounds is straightforward and amenable to gram-scale preparation. This aspect is true in the particular case of BORANILs and related derivatives. Under appropriate functionalization conditions, several cases of efficient cascade energy transfer from the locked boron(III) center to an energy-acceptor unit (e.g. a BODIPY or a SubPc) or from one heterocyclic boron(III) center to another one have been established. That the dyes can be decorated with reactive isocyanate reactive groups offers the possibility of linking them to proteins in aqueous media, a reaction of obvious bioanalytical interest. These new dyes seem to be stable under biological conditions without noticeable loss of the fluorescence over a period of one day. More work is needed to assess the stability in vivo. Some are sensitive to the dipolar field of the solvent and their environment, thus making them attractive for specific applications in the field of medical imaging. Many of the groups termed BORANILs[97] and BORICOs[67] dyes are so readily prepared that they may be suitable for large-scale applications as photoresponsive materials in solution and in the solid state (for example, in solar cells).

Another interesting application of neutral boron(III) complexes is that in light emitting devices (OLEDs), the high and enduring brilliance of these devices indicate the exceptional chemical and optical stability of the dyes in air in the presence of electric fields. Various borate complexes have been screened for antifungal activities and are known to inhibit the growth of some microorganisms.[153] This is important in relation to both biodegradation of any devices incorporating the dyes and to the possible toxicity of the devices themselves.

Clearly, these novel borate complexes display many attractive features, with some aspects of their spectroscopy awaiting full theoretical elucidation. Their possible applications as probes of membrane structure and function are also yet to be investigated. There is little doubt that development of the use of these new compounds carries the promise of revealing and deciphering properties of all forms of condensed matter.

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