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Novel *meso*-Polyarylamine-BODIPY Hybrids: Synthesis and Study of Their Optical Properties

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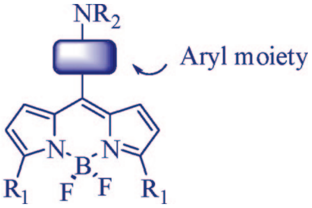

A series of 14 *meso*-polyarylamine-BODIPY (borondipyrromethene) hybrids of the general structure **A** were synthesized. Two methods were used to prepare them. The first protocol involved a direct Liebeskind−Srogl cross-coupling of thiomethylbodipys **1−2** with arylaminoboronic acids (4 examples, 75−98%). The second method involves a two-step sequence: a Liebeskind−Srogl reaction to prepare 6 *meso*-bromoarylbodipys (58−83%) followed by a Suzuki coupling of these Br-containing BODIPYs with arylaminoboronic acids (10 examples, 44−84%). Seven of these derivatives displayed emission in the near-infrared region. The optical properties of compound **18** were rationalized in terms of its crystal structure.

Introduction

Owing to the many applications and interesting properties, push−pull (also termed D-π-A systems, D = donor, A = acceptor) molecular systems have attracted significant attention.[1] One of the more interesting properties that these compounds may display is the emission in the near-IR (NIR) region, which may offer potential application in medicine.[2] In particular, polyarylamine derivatives are attractive electron-donor moieties. These compounds are standard hole-transport materials and studies on magnetic materials have been done based on the generation of high-spin triarylamine polyradicals.[3] Similarly, there are reports in the literature of polyarylamines used in the fabrication of red OLEDs.[4] With respect to the electron-accepting fragment, boradiazaindacene (BODIPY)[5] derivatives were chosen in this work due to their well-documented properties and applications which include labeling reagents, fluorescent switches, chemosensors, and laser dyes.[6] For the reasons mentioned above, hybrids that contain both polyarylamine and BODIPY moieties might display useful properties such as Twisted Intramolecular Charge Transfer (TICT) behavior.[7] This phenomenon is of particular importance in the design of chemosensors since its understanding would allow control of both the degree of electron transfer and the change of molecular geometry.[8] Prompted by our recent report on the

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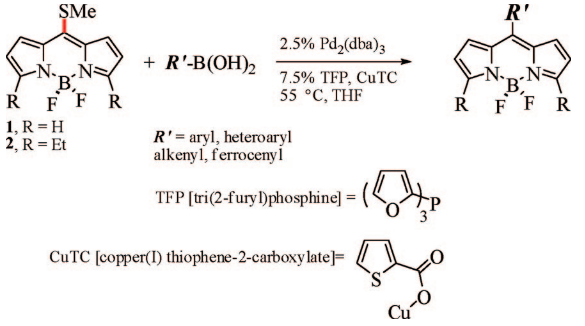
SCHEME 1. General Synthesis of 8-Substituted BODIPYs with the Liebeskind−Srogl Cross-Coupling



synthesis of *meso*-substituted BODIPY dyes[9] based on the Liebeskind−Srogl (L-S) cross-coupling, we decided to prepare a series of novel polyarylamine-BODIPY hybrids of the general structure **A** and study their properties.

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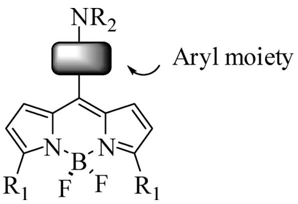


Herein we report our results.

Results and Discussion

Synthesis of the Polyarylamine-BODIPY Hybrids. The key step relies on the cross-coupling reaction of thioorganics with organoboron derivatives mediated by Cu(I) and catalyzed by Pd(0) *under neutral conditions* (the Liebeskind−Srogl reaction) (eq 1).[10]

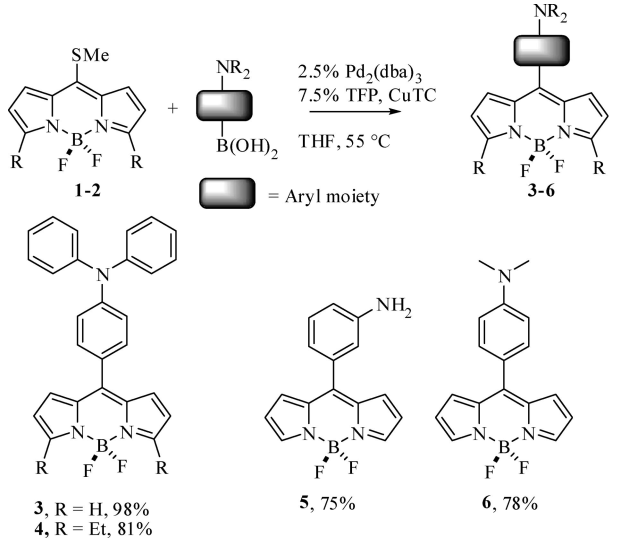
$$R_1\text{-SR}' + R_2\text{-B(OH)}_2\text{CuI)} \xrightarrow[\text{cat . Pd}]{\text{OCOR}} R_1\text{-}R_2 + \text{Cu-SR}' + \text{RC(O)O-B(OH)}_2 \quad (1)$$

As we have recently demonstrated, this protocol can be used in a very efficient manner to prepare 8-subtituted BODIPYs starting from 8-thiomethylbodipys **1**−**2** (Scheme 1).[11]

Accordingly, we envisioned that this process could be used to prepare a family of novel polyarylamine-BODIPY hybrids in two ways, either directly using the L-S cross-coupling, or by a sequential L-S/Suzuki process. Thus, hybrids **3**−**6** were prepared via a direct L-S cross-coupling according to Scheme 2.

In this fashion, amino-containing commercially available boronic acids were reacted with **1**−**2** following the literature procedure to yield hybrids **3**−**6** in 75−98% isolated yields. It is important to emphasize that the commercial form of *m*-aminophenylboronic acid used to prepare **5** is the monohydrate. This result further demonstrated the high tolerance of the L-S cross-coupling to the reaction conditions since **5** was produced in 75% *even in the presence of 1 equiv of water*.

SCHEME 2. Synthesis of Hybrids 3−6 via a Direct L-S Reaction



For the L-S/Suzuki approach, **1**−**2** were reacted with the corresponding bromoarylboronic acids in order to prepare the bromoarylbodipys **7**−**12** (Scheme 3).

Building blocks **7**−**12** were uneventfully synthesized in 58−83% isolated yield providing a series of brominated derivatives with an excellent handle for additional elaboration. The series **7**−**10** will allow structure−properties studies with systematic variations of not only the electronic features of the different analogues, but also the steric aspects of them. It is easily envisioned as well the possibility to prepare dendrimeric materials starting from dibromoarylbodipy **11** via the rich plethora of transition metal-catalyzed reactions. Similarly, bromothienylbodipy **12** will serve to prepare other thiophene-containing derivatives interesting for material science.[12] Two of such systems have been recently published.[13]

Once **7**−**12** were prepared, they were further functionalized with amino-containing boronic acids under the Suzuki conditions (Scheme 4).

Except for hybrids **13** (44% yield) and **16** (47% yield) which were prepared in modest yields, the Suzuki coupling worked efficiently for the rest of the derivatives yielding at the end a family of 10 additional polyarylamine-BODIPY hybrids in 69−84% isolated yields.

Optical Properties of the Hybrids. Boradiazaindacene (BODIPY) derivatives have found an array of applications in molecular biology, as chemical sensors, and as molecular devices (such as fluorescent switches) owing to their unique optical properties. These include sharp absorption and fluorescence bands, high extinction coefficients, efficient light emission,

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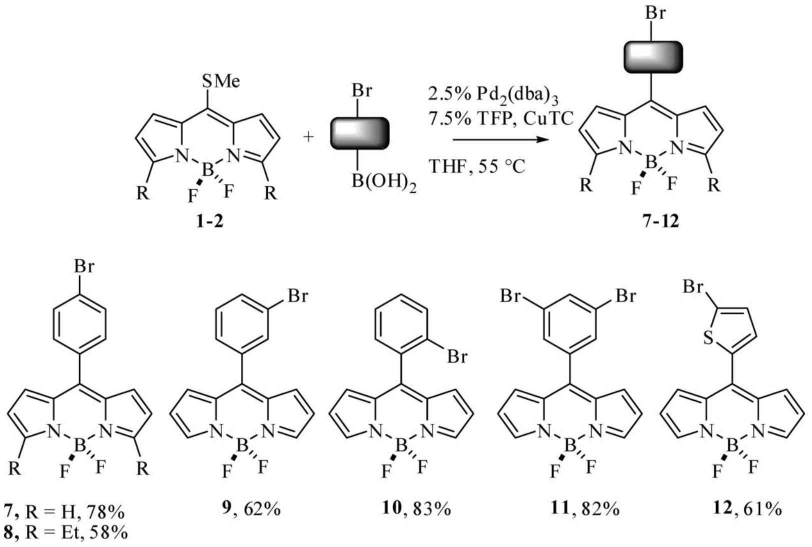
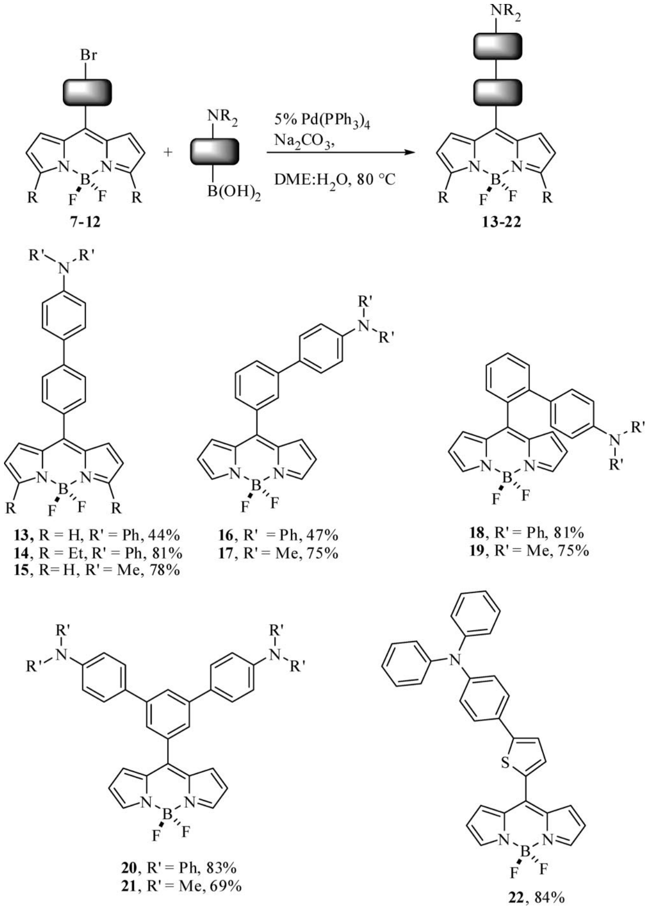
SCHEME 3. Synthesis of the Bromoarylbodipys 7−12



SCHEME 4. Synthesis of Hybrids 13−22



and high chemical and photolytic stability.[14] We are interested in investigating the optical properties of boradiazaindacenes with electron-donating amine groups because their interaction with the electron-withdrawing BODIPY group may enable them to exhibit intriguing twisted intramolecular charge transfer (TICT) behavior.[15] TICT has been known to greatly affect the emission properties of some chromophoric molecules containing donor and acceptor groups. The prime example of great interest is 4-*N*,*N*-dimethylaminobenzonitrile (DMABN). In the ground state, the molecule is almost planar, which corresponds to the maximum conjugation between the dimethylamino group and the phenyl ring. According to the Franck−Condon principle, the molecule in the locally excited state (LE) is still planar, but solvent relaxation takes place with a concomitant rotation of the dimethylamino group until it is twisted at right angles and the conjugation is lost. In the resulting TICT state, which is stabilized by the polar solvent molecules, there is a total charge separation between the dimethylamino group and the cyanophenyl moiety. In addition to the fluorescence band due to emission from the LE state, a largely red-shifted emission band corresponding to the emission from the TICT state is observed. In such systems, increasing the solvent polarity will lead to red shifts of their absrptions (λ_{ab}) and emissions (λ_{em}), its λ_{em} being more sensitive to the solvent polarity. Normally, in nonpolar solvent, there is only one emission peak from the LE state, while two emission peaks appear in polar solvent from the LE and TICT states, respectively, in which the latter peak is red-shifted by up to 100 nm from the former. TICT state is in most cases more likely to relax by nonradiative processes than by fluorescence emission, leading to the lower PL (photoluminescence) intensity and Φ_F (fluorescence quantum yield) value in polar environments. Thus, the emission properties of this group of molecules highly depend on the solvent polarity.

Figure 1 shows the UV absorption spectra of some BODIPYs in cyclohexane (CH) and THF solutions. All the molecules exhibit a similar spectral pattern and display a sharp absorption peak at about 500 nm in both solvents, although the spectra of **6**, **13**, and **15** are slightly broader in THF than those in CH. Due to the electron-donating ability, ethyl-substituted **4** and **14** exhibit better conjugation with the BODIPY core than the

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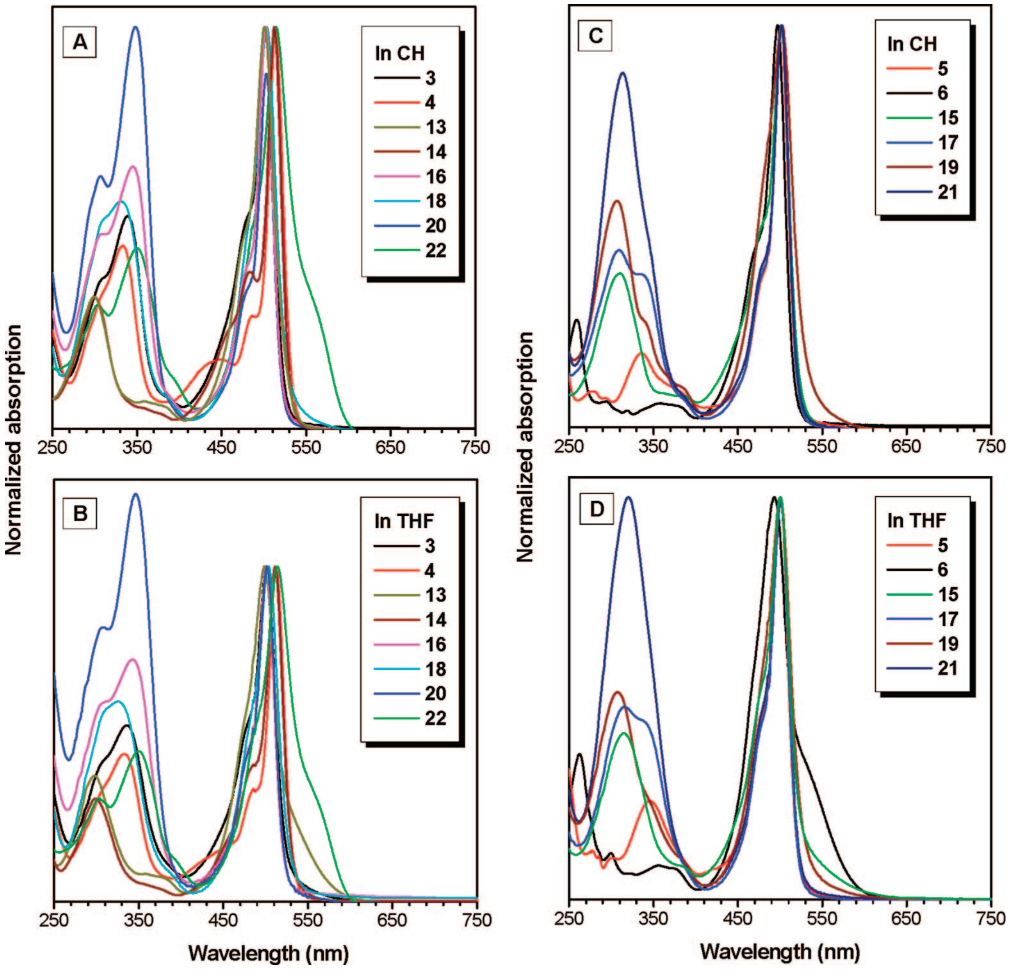

FIGURE 1. UV absorption of the polyarylamine-bodipy hybrids in cyclohexane (CH) and THF at a concentration of 10 μM.

nonsubstituted **3** and **13**, thus leading to a red shift of the absorption by ~10 nm. Dialkylamino groups in **6** and **15** have poorer electronic communication with the BODIPY core than the corresponding diphenylamino groups in **3** and **13**, thus resulting in slight blue shift of the absorption. Parts A and B of Figure 2 show the PL spectra of the para-substituted BODIPYs in CH and THF, respectively. Their emissions are strongly dependent on solvent polarity. The spectra measured in nonpolar CH display only one single sharp emission peak originating from the so-called LE state. A new peak, however, emerged at longer wavelengths in polar THF, which may be attributed to the emission from the TICT state. Table S1 (see the Supporting Information) shows the solvent polarity effect on the emission of **4** as a demonstration, which is of a typical TICT feature. Excitation of the molecules can lead to a fast transfer from the LE state to a weakly emissive TICT state in polar solvents, resulting in dual emission from both states. Compared with their para-substituted counterparts, the emissions of meta- and ortho-substituted amine-BODIPY hybrids in THF are only slightly redder than those in CH (Figure 2, parts C and D), suggesting that they exhibit little or no TICT behavior owing to the poorer electronic communication of the amine groups with BODIPY cores. Interestingly, **18** displays only one emission peak at 531 nm in THF, but two at 528 and 663 nm in CH. From the crystal structure of **18** (see the Supporting Information), we can see that it takes a very twisted conformation due to steric effects. It can be envisioned that the TICT state of **18** can occur in both nonpolar and polar solvents owing to its inherent twisted structure. However, in polar THF, the emission intensity from the TICT state is so low that it is not measurable, thus showing one apparent emission peak from the LE state. The photoimages of THF and CH solutions of some samples taken under normal room illumination and UV light are shown in parts E and F of Figure 2. The distinct emission color between the LE and ICT states enables us to distinguish them with the naked eye. Such dyes may thus be utilized as fluorescent probes for surface polarity detection of biological species. The quantum yields of these molecules in CH and THF are measured and given in Table 1. Due to the formation of the TICT state of para-substituted BODIPYs in THF, the values in this solvent are 10−50 times lower than those in CH. The quantum yields of meta-substituted BODIPYs in THF are in the range of 0.5−0.7%, which are 5−10 times lower than those in CH. For ortho-substituted ones, the values are also low and almost the same in both solvents. Among all the molecules, the values are in the order of para- > meta- > ortho-substituted ones. As can be seeen from both Figure 2 and Table 1, compounds **3**, **4**, **6**, **13**, **14**, **18**, and **22** display NIR emission.

Conclusions

Two general methods were developed to prepare polyarylamine-BODIPY hybrids. One involves the Liebeskind−Srogl cross-coupling and the other one consist of a L-S/Suzuki sequence. The optical properties of the hybrids were studied and it was found that seven of these analogues displayed NIR

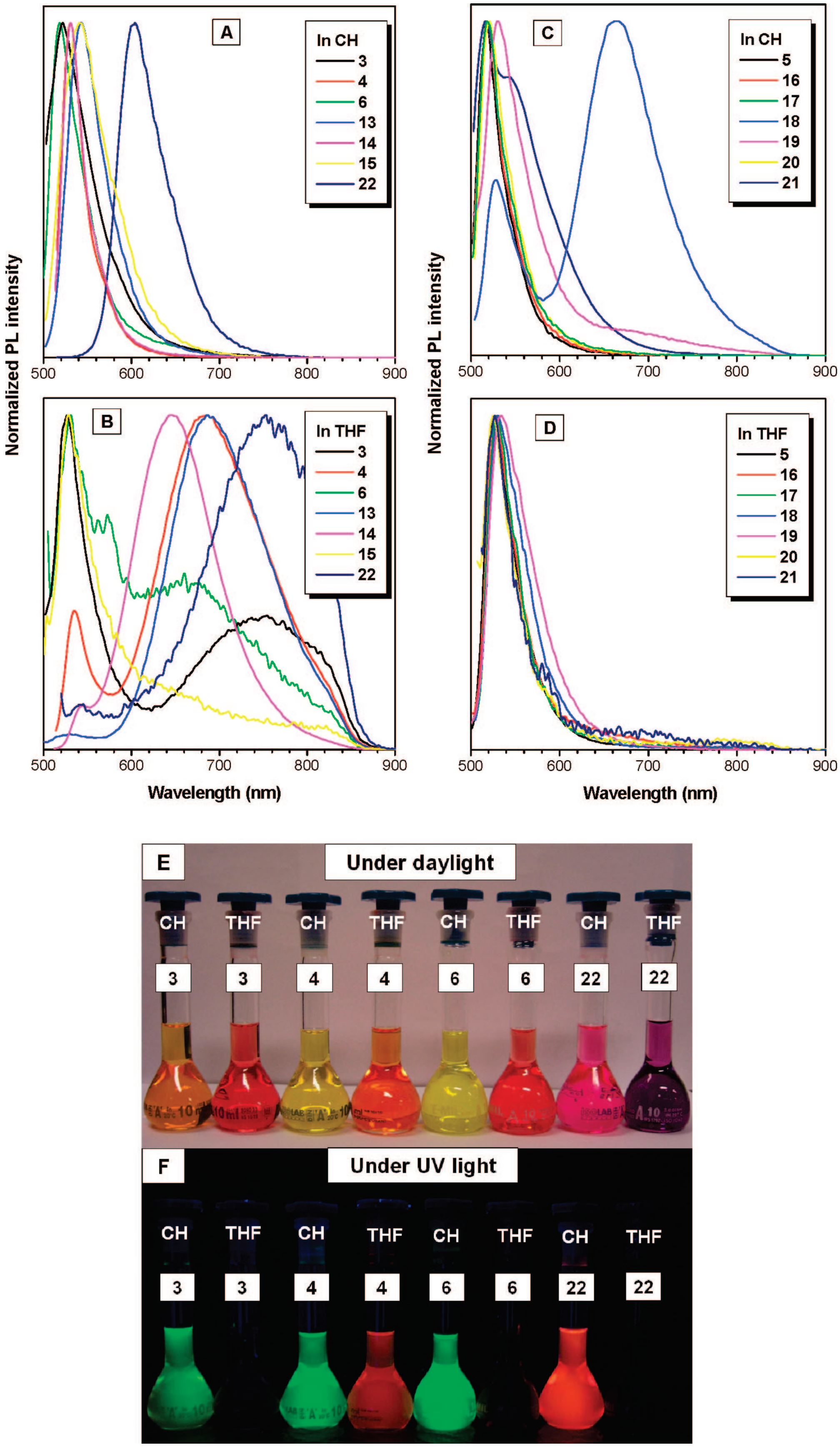

FIGURE 2. Photoluminescence (PL) spectra (A−D) and some photoimages (E and F) of the polyarylamine-BODIPY hybrids in cyclohexane (CH) and THF with a concentration of 10 μM.

TABLE 1. Optical Properties of the Polyarylamine-BODIPY Hybrids[a]

		λ_{ab} (nm)[b]		λ_{em} (nm)[c]		Φ_F[d]	
	compd no.	CH	THF	CH	THF	CH	THF
meta	**5**	501	501	517	526	0.0360	0.0066
	16	502	501	519	528	0.0447	0.0051
	17	501	501	518	530	0.0489	0.0058
	20	503	501	521	525	0.0548	0.0066
	21	502	501	517	527	0.0707	0.0070
ortho	**18**	503	504	528, 663	531	0.0061	0.0041
	19	502	500	530	534	0.0034	0.0048
para	**3**	501	498	542	530, 686	0.1233	0.0074
	4	512	511	531	544, 646	0.1394	0.0804
	6	497	493	519	530, 662	0.1498	0.0074
	13	502	501	521	527, 754	0.0283	0.0027
	14	514	513	531	535, 686	0.1609	0.0323
	15	501	501	541	528 (broad)	0.0690	0.0067
	22	514	512	604	545, 753	0.1704	0.0734

[a] In cyclohexane (CH) and THF solutions with a concentration of ~10 μM. [b] Absorption maximum. [c] Emission maximum. [d] Quantum yield estimated with fluorescein as standard (Φ_F = 79% in 0.1 N NaOH). Abbreviation: meta, ortho, and para = meta-, ortho-, and para-substituted BODIPYs.

emission. The optical behavior of compound **18** was rationalized based upon its crystal structure. Bromo-containing BODIPY derivatives **7**−**12** were prepared in an efficient fashion. These compounds will allow the construction of other architectures via the ever growing transition metal-based cross-coupling protocols. The methods developed herein are amenable for the synthesis of a second generation of the polyarylamine-BODIPY hybrids, especially because many of the compounds prepared in this work showed potentially useful properties. These new avenues are currently under investigation in our laboratories and will be disclosed in due course.

Experimental Section

General Procedure (GP) for the Liebeskind−Srogl Cross-Coupling: BODIPY 3. An oven-dry round-bottom flask, equipped with a stir bar, was charged with thiomethylbodipy **1** (40 mg, 0.168 mmol, 1 equiv), 4-(diphenylamino)phenylboronic acid (146 mg, 0.504 mmol, 3 equiv), and anhydrous THF (20 mL) under N_2. The stirred solution was sparged with N_2 for 10 mi., whereupon Pd_2dba_3 (3.8 mg, 4.2 μmol, 2.5 mol %), tri(2-furyl)phosphine (2.9 mg, 12.6 μmol, 7.5 mol %), and copper(I) thiophene-2-carboxylate (96 mg, 0.504 mmol, 3 equiv) were added followed by 5 min of N_2-purge. The reaction mixture was heated at 55 °C. The reaction was monitored by TLC (R_f 0.44, SiO_2-gel, 20% EtOAc/hexanes), which showed that the reaction was finished after 1.5 h. The reaction mixture was allowed to reach rt and was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, EtOAc/hexanes gradient) purification, followed by washings with petroleum ether (3 × 2 mL), **3** (72 mg, 0.165 mmol, 98%) was obtained as a purple solid (mp 212−214 °C): ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.49−7.31 (m, 6H), 7.24−7.05 (m, 10H), 6.55 (dd, J_1 = 4.0 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 151.1, 147.7, 146.6, 142.9, 134.8, 132.5, 131.3, 129.9, 126.4, 126.1, 124.9, 120.2, 118.2; IR (KBr, cm^{-1}) 3105 (w), 3059 (w), 3036 (w), 1587 (s), 1558 (s), 1533 (s), 1488 (s), 1412 (s), 1388 (s), 1332 (m), 1294 (m), 1261 (s), 1224 (m), 1192 (m), 1118 (s), 1076 (s), 980 (s), 911 (m), 757 (m), 742 (m), 696 (m). HRMS FABS (M + H$^+$) calcd for $C_{27}H_{21}BF_2N_3$ 436.1796, found 436.1791.

General Procedure (GP) for Suzuki Cross-Coupling: BODIPY 13. An oven-dry Schlenk tube, equipped with a stir bar, was charged with 8-(*p*-bromophenyl)bodipy **7** (40 mg, 0.115 mmol, 1 equiv), 4-(diphenylamino)phenylboronic acid (100 mg, 0.346 mmol, 3 equiv), Na_2CO_3 (73 mg, 0.692 mmol, 6 equiv), and DME/H_2O (4/1 v/v, 5 mL) under N_2. The stirred solution was sparged with N_2 for 10 min, whereupon $Pd(PPh_3)_4$ (8.0 mg, 6.92 μmol, 6 mol %) was added followed by 5 min of N_2-purge. The reaction mixture was heated at 80 °C. The reaction was monitored by TLC (R_f 0.38, SiO_2-gel, 20% EtOAc/hexanes), which showed that the reaction was finished after 30 min. The reaction mixture was allowed to reach rt and was adsorbed on SiO_2-gel. After flash-chromatography (SiO_2-gel, EtOAc/hexanes gradient) purification, followed by recrystallization from petroleum ether/toluene, **13** (26 mg, 0.0508 mmol, 44%) was obtained as a purple solid: mp 108−109 °C; IR (KBr, cm^{-1}) 3033 (w), 1590 (s), 1558 (s), 1537 (s), 1489 (s), 1412 (s), 1387 (s), 1261 (s), 1115 (s), 1077 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.95 (s, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.57−7.51 (m, 2H), 7.34−7.30 (m, 2H), 7.27−7.26 (m, 2H), 7.19−7.01 (m, 10H), 6.56 (dd, J_1 = 4.2 Hz, J_2 = 1.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.4, 147.6, 147.5, 144.0, 143.5, 135.0, 133.1, 132.3, 131.7, 131.4, 129.6, 128.0, 126.6, 125.0, 123.6, 123.5, 118.7; HRMS FABS (M + H$^+$) calcd for $C_{33}H_{25}BF_2N_3$ 512.2110, found 512.2114.

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Supporting Information Available: A complete description of the synthesis of all of the compounds described in the text, copies of their spectroscopic data (IR, ^{1}H, ^{13}C), and a CIF file and Ortep diagram of **18**. This material is available free of charge via the Internet at http://pubs.acs.org.

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