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Synthetic Routes to Fluorescent Dyes Exhibiting Large Stokes Shifts

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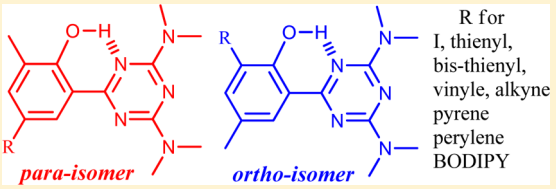
Supporting Information

ABSTRACT: Derivatives of isomeric 2-(hydroxytolyl)-4,6-dimethylamino-1,3,5-triazines have been synthesized in high yields in a controlled manner using a multistep reaction sequence. Iodination of either 2-(1′-hydroxy-6′-methylphen-2′-yl)- or 2-(1′-hydroxy-4′-methylphen-2′-yl)-4,6-dimethylamino-1,3,5-triazine with ICl provides species differing in the positioning of the iodo group relative to the hydroxyl which readily undergo Suzuki, Sonogashira, and Heck reactions under Pd(0) catalysis. Thus, thienyl, bisthienyl, and 3,4-ethylenedioxythienyl groups have been directly grafted, while unsubstituted polycyclic aromatics such as pyrene and perylene have been linked via alkyne bridges, as have ethynyldifluoroborondipyrromethane (BODIPY) dyes prepared in situ. The presence of a hydrogen bond in the ground state involving the hydroxyl substituent has been established by proton NMR and several X-ray structure determinations. All of the new dyes with a simple substituent (phenyl, thienyl) exhibited a pronounced green fluorescence resulting from an intramolecular proton transfer in the excited state (ESIPT) which produces a large Stokes shift (>10 000 cm^{-1}). With other dyes, the fluorescence of the keto form responsible for the ESIPT process could be used as the input energy in efficient intramolecular energy transfer processes. Replacing perylene with pyrene allowed reversal of the direction of energy transfer from the polyaromatic module to the keto form.



INTRODUCTION

The ever-increasing interest in fluorescent probes has propelled numerous research programs aimed at the discovery of new dyes displaying high photostability and emission wavelength tunability.[1,2] After years of intense interdisciplinary research, some basic rules have become clear for designing an effective fluorescence probe suited to applications in chemistry and biology. First, the dyes should possess large absorption cross sections and high fluorescence quantum yields. Second, it should be possible to tailor the probes at will in order to tune the spectroscopic properties and to use them in multiplexing experiments for tracking several targets.[3,4] Third, the energy offset between the dye and the medium of use should be well-controlled to avoid nonradiative deactivation channels. Finally, the dyes should have large Stokes shifts to provide high resolution and low detection limits. These shifts reflect the reorganization energy between the ground and excited state and are quite difficult to manipulate with singlet excited states.[5] One elegant recent solution was that of linking the dye (e.g., a difluoroboron dipyrromethene, BODIPY) with modules capable of intramolecular energy transfer (IMET).[6] Under these conditions, very large Stokes shifts (>10 000 cm^{-1}) result with anthracene-, pyrene-, and perylene-linked dyads or tryads.[7] A cascade energy transfer event is the result of favorable spectral overlap between the energy of the donor (e.g., pyrene) and the energy of the acceptor (e.g., BODIPY),[8] and in some specific cases, through-bond energy transfer has also been claimed.[9]

Another way to promote large Stokes shifts is to engineer molecules in which intramolecular proton transfer is promoted in the excited state (ESIPT process). Such dyes have become well-known since the discovery of this mechanism in methylsalicylate and related derivatives.[10,11] They include *o*-hydroxybenzophenones,[12] *o*-hydroxyphenylbenzotriazoles,[13] *o*-hydroxyphenylbenzoxazoles,[14] *o*-hydroxyphenylbenzothiazole,[15] and some more sophisticated species,[16] and they have found application as UV stabilizers in polymers and sun creams.[12b]

The anomalous emissions with large Stokes shifts displayed in solution and the solid-state spectra of 6-(2-hydroxy-5-methylphenyl)-1,3,5-triazine[17] attracted our attention to them as a potential platform for chemical transformations on the phenyl residue aimed at (i) shifting the emissive properties into the red; (ii) using the emission of the keto form (obtained by the ESIPT process), as input energy in more sophisticated multimodule systems; (iii) caging the photoluminescence by protective residues; and finally (iv) tuning the optical properties by changing the local environment of the dye (hydrophilic versus hydrophobic).

Access to 2,4,6-trifunctionalized 1,3,5-triazines is facile due to the well-known ease of displacement of the chloride atoms in cyanuric chloride by various nucleophiles in the presence of a base.[18] The substitution pattern is controlled mostly by the temperature and the kinetics but also depends on the structure of the nucleophile. The fact that with N-nucleophiles symmetrical and unsymmetrical mono-, di-, and trisubstituted

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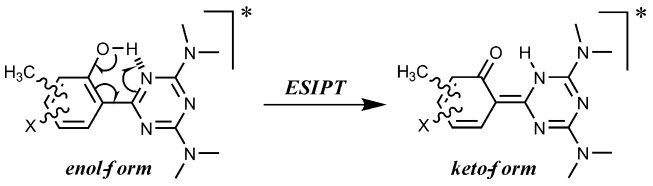
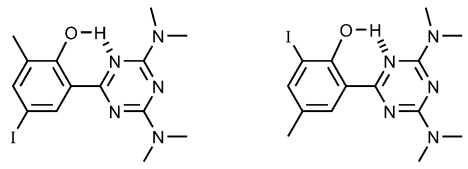
1,3,5-triazines can be easily prepared also opens up additional synthetic possibilities.[19]

Our present objective was to prepare 2-(hydroxy(methyl)-phenyl)-4,6-dimethylamino-1,3,5-triazine derivatives functionalized on the phenyl ring with various electron-rich modules so as to enable tuning of their fluorescence properties. In particular, we targeted the synthesis of two regioisomers of each in order to determine the influence of the substituents on proton transfer in the excited state (Chart 1).

Chart 1





RESULTS AND DISCUSSION

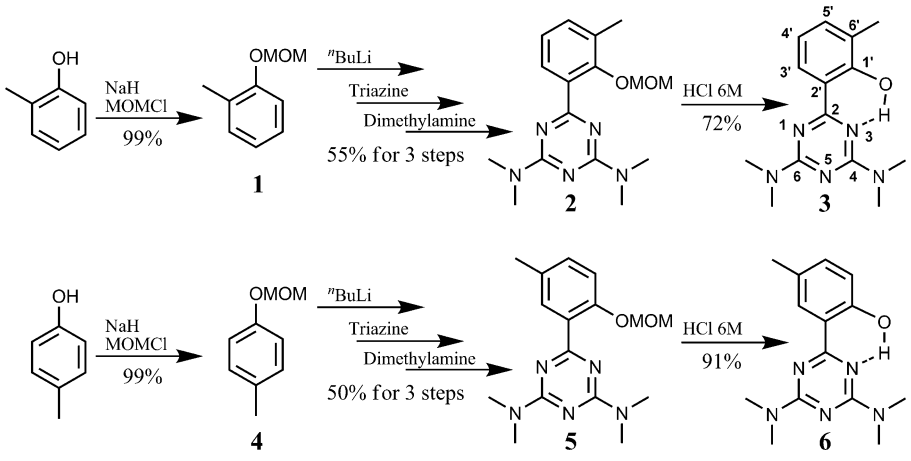
The molecules of interest were prepared according to Scheme 1. Five steps are required to produce the pivotal compounds **3** and **6** in good yields. The sequence includes the protection of the phenolic hydroxyl group of *o*- and *p*-cresol by methoxymethyl chloride (MOMCl), using sodium hydride in dimethylformamide to afford the substitution products **1** and **4** in quantitative yields. The protected phenols were then treated with *n*-butyllithium in tetrahydrofuran at −78 °C to generate the 2-lithio-aromatics. These were reacted with 1 equiv of cyanuric chloride to give the monoaryl derivative and the remaining chloro substituents then displaced by reaction with dimethylamine (40 wt % in water) to produce compounds **2** and **5** in fair yields. Finally, removal of the MOM groups in acid gave the desired compounds **3** and **6** (Scheme 1). In both cases, a very strong hydrogen bond[20] was apparent from the chemical shift of the phenolic proton at δ 14.4 and 14.0, respectively, in neutral $CDCl_3$.

Iodination of compound **3** using a solution of iodine monochloride in methanol led to introduction of an iodo group exclusively in the 4′ position of the phenyl ring as shown in structure **7**. For this compound, the phenyl protons resonate as doublets at δ 8.48 and 7.50 with a $^4J_{H-H}$ coupling constant of ca. 2.4 Hz. The X-ray structures of the functionalized derivatives **8** confirmed the regioselectivity of the iodination reaction (vide infra). The iodo derivatives were then submitted to different Pd-catalyzed cross-coupling reactions (Suzuki, Sonogashira, Heck) in order to extend the aromatic functionality of the phenyltriazine compounds and, thereafter, compare their photophysical properties (Scheme 2). Initially, comparison was made of aryl derivatives with vinyl or acetylene tethers with those having an aryl unit directly linked to the phenyl core. Suzuki cross-coupling reaction with $[Pd(PPh_3)_4]$ as the catalyst precursor and K_2CO_3 as base was used to insert different thienyl units (Scheme 2).[21]

Styrene was used in a Heck coupling using Pd(II) and K_2CO_3 in benzene/DMF to afford compound **11**.[22] The Z-conformation of the double bond was confirmed by the 16.9 Hz proton−proton coupling constant. A Sonogashira cross-coupling reaction $[Pd(PPh_3)_4]$ catalyst, triethylamine as base was used to insert a tolylacetylene residue. 4,4-Difluoro-1,3,5,7,8-pentamethyl-2-iodo-4-bora-3a,4a-diaza-s-indacene (BODIPY)[23] was also linked to compound **7** via a one-pot synthetic protocol. The instability of the corresponding BODIPY-C≡CH under the conditions used forced us to produce this intermediate in situ by (i) cross-coupling trimethylsilyl acetylene to the iodo-BODIPY derivative and then (ii) removing the TMS group with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in the presence of substoichiometric amounts of water (40 mol %)[24] and finally (iii) cross-linking the resultant and nonisolated alkyne derivative to compound **7** to produce the target dyes **14** in acceptable yields.

Iodination of compound **6** was realized under the same conditions using a solution of iodine monochloride in methanol and led to introduction of an iodo group exclusively in the 6′ positions of the phenyl ring as shown in structure **17**. For this isomer, the phenyl protons resonate as doublets at δ 8.16 and 7.68 ppm with a $^4J_{H-H}$ coupling constant of ca. 2.0 Hz. The X-ray structures of the functionalized derivatives **18** confirmed the

Scheme 1. Preparation of the Triazine Starting Materials 3 and 6



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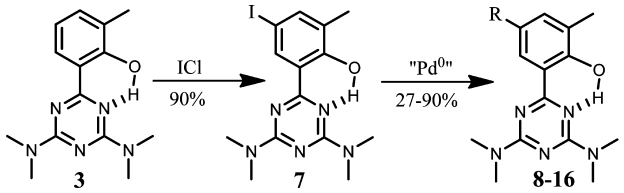
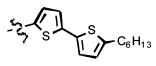
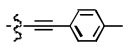
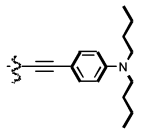
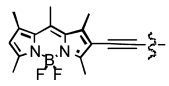
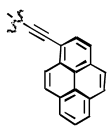
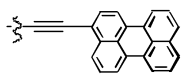
Scheme 2. Preparation of the *para*-Substituted Derivatives



R	Reaction Conditions	Isolated Yields	Compounds
	2-Thienylboronic acid (2eq.) [Pd(PPh$_3$)$_4$] (10mol%) K_2CO_3 (5eq.) Toluene, 80 °C	31%	**8**
	4,4',5,5'-Tetramethyl-1,3,2-dioxaboronic of 3,4-ethylenedioxy-thiophene (2eq.) [Pd(PPh$_3$)$_4$] (10mol%) K_2CO_3 (5 eq.) Toluene, 60 °C	27%	**9**
	5′-Hexyl-2,2′-bithiophene-5-boronic acid pinacol ester (2eq.) [Pd(PPh$_3$)$_4$] (10mol%) K_2CO_3 (5eq.) Toluene, 60 °C	41%	**10**
	Styrene (2eq.) [Pd(PPh$_3$)$_2$Cl$_2$] (10+10% mol) K_2CO_3 (1.5eq.) Benzene/DMF, 80 °C	28%	**11**
	4-Ethynyltoluene (2eq.) [Pd(PPh$_3$)$_2$Cl$_2$] (10 mol%) CuI (12 mol%) Benzene/TEA, 60 °C	90%	**12**

R	Reaction Conditions	Isolated Yields	Compounds
	*p*-(Dibutylamino) phenylacetylene (1.2 eq.) [Pd(PPh$_3$)$_4$] (10 mol%) CuI (12 mol%) Benzene/TEA, 60 °C	40%	**13**
	1) Bod-I (1eq.) Ethynyltrimethylsilane (1.05eq) [Pd(PPh$_3$)$_2$Cl$_2$] (5mol%) CuI (6mol%) Benzene/Diisopropylamine, rt 2) DBU (12eq), H_2O (40mol%)	66%	**14**
	1-Ethynylpyrene (1.1 eq.) [Pd(PPh$_3$)$_4$] (10mol%) CuI (12mol%) Benzene/TEA, 60 °C	41%	**15**
	3-Ethynylperylene (1.05 eq.) [Pd(PPh$_3$)$_4$] (10mol%) CuI (12mol%) Benzene/TEA, 60 °C	48%	**16**

regioselectivity of the iodination reaction (vide infra). This iodo derivative was then submitted to different Pd-catalyzed cross-coupling reactions (Suzuki, Sonogashira) in order to extend the aromatic functionality of the phenyltriazine compounds and, thereafter, compare their photophysical properties with the other isomers described in Scheme 2. BODIPY was also linked to isomer **17** via a similar one-pot synthetic protocol described above for compound **14**, involving the in situ preparation of ethynyl-BODIPY derivative following a controlled cross-coupling reaction with **17** in the presence of low valent palladium(0) to produce the target dye **20** in acceptable yields (Scheme 3).

X-ray Structure Determinations. The structures of the isomers **8** and **18** provide an indication of the consequences of the differences in location of a relatively small (thienyl) substituent on the properties of the molecule in the solid state. In both, it is apparent that the H-bond between the hydroxyl group and a triazine-N[25] plays an important role in maintaining the planarity of the hydroxyphenyltriazine core (Figures 1 and 2).

The dihedral angle between the ethynylaniline phenyl ring and the triazine unit of compound **13** is 26.52(7)°, a significant deviation from an overall planar conformation (Figure 3). The molecules **8** and **18** have a thienyl ring flip disorder, the thiophene ring being disordered over two conformations about the C5−C1 (C15, respectively) bond with a major−minor ratio refined to values of 0.675(4):0.325(4) (0.515(3):0.485(3), respectively). Compound **13** (Figure 3) also displays disorder of one of the two alkyl chains over two sets of positions with occupancies refined to 0.661(6) and 0.339(6) for the major and minor conformations, respectively.

Although all three compounds have an overall conformation which is close to planar, only the lattice of **8** shows a layered structure with sheets parallel to the (20−1) plane having a mean separation of 3.4 Å and centroid−centroid distance between parallel triazine and adjacent rings (a triazine at position 1−*x*, 2−*y*, 1−*z* and the phenyl at position −*x*, 2−*y*, 1−*z*) along the *a* direction of 3.76 Å (Figure 4).

Within a layer in which molecules are separated by normal van der Waals interactions, those which are not related by an inversion center assemble preferentially into strips running along [001] through formation of C−H···O hydrogen bonds (H···O 2.3 Å; CHO 163.7°) (Figure 5).

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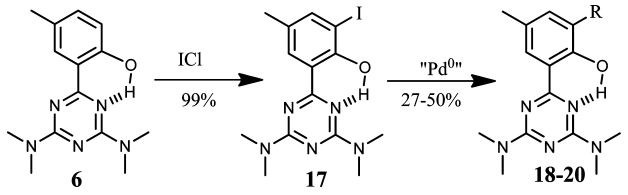
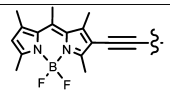
Scheme 3. Preparation of the *ortho*-Substituted Derivatives



R	Reaction Conditions	Isolated Yields	Compounds
	2-Thienylboronic acid (2.5 eq.) $[Pd(PPh_3)_4]$ (10mol%) K_2CO_3 (5eq.) Toluene, 60 °C	47%	**18**
	4,4',5,5'-Tetramethyl-1,3,2-dioxaboronic of 3,4-ethylenedioxy-thiophene (1.5eq.) $[Pd(PPh_3)_4]$ (10mol%) K_2CO_3 (5eq.) Toluene, 60 °C	27%	**19**
	1) Bod-I (1eq.) Ethynyltrimethylsilane (1.05eq.) $[Pd(PPh_3)_2Cl_2]$ (5mol%) CuI (6mol%) Benzene/Diisopropylamine, rt 2) DBU (12eq.), H_2O (40mol%)	50%	**20**

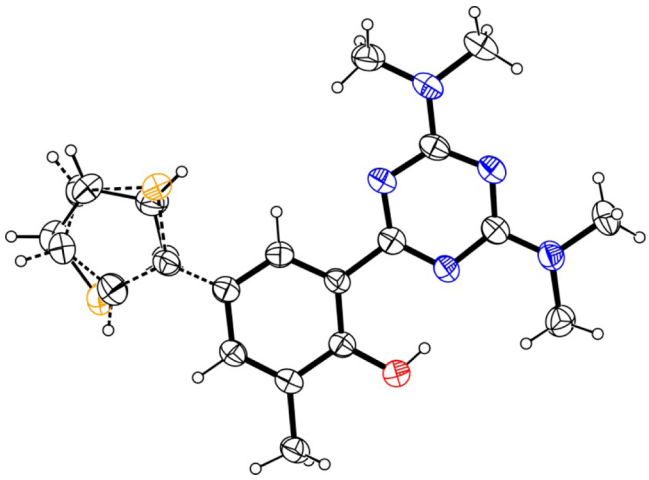


Figure 1. ORTEP view (30% probability ellipsoids) of the molecular unit found in the crystal lattice of **8**. Dashed lines represent a minor conformation of disordered atoms.

The structure **18** features a herringbone packing motif evident in a projection along the *c* axis with a dihedral angle of 70.1° between inverted molecules and those generated by the mirror glide or helicoidal two-fold axis (Figure 6).

This arrangement results from $\pi-\pi$ stacking interactions, slightly offset and with centroid separation of 3.56 Å between molecules at general position and those at 3−*x*, 1−*y*, 2−*z*, and by triazine methyl hydrogen interactions with phenyl or thiophene rings. In the case of **13**, the inversion-related molecules are segregated into undulating stripes running along the [101] direction and stacking along the *b* direction with a relative orientation of 35° between adjacent molecules (Figure 7). Interestingly, $\pi-\pi$ stacking interactions mainly involve two phenyl rings related by a center of inversion with a centroid distance of 3.72 Å.

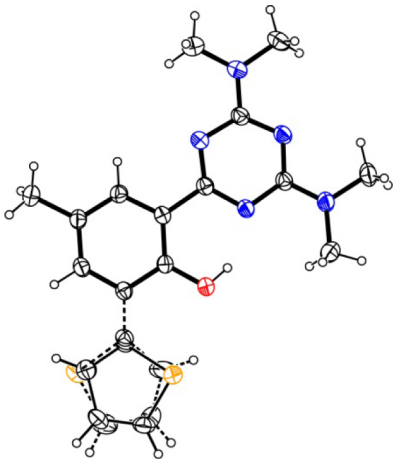


Figure 2. ORTEP view (30% probability ellipsoids) of the molecular unit found in the crystal lattice of **18**. Dashed lines represent a minor conformation of disordered atoms.

Optical Properties. The principal spectroscopic data relevant to the present discussion are given in Table 1, and typical examples are given in Figures 8−10. Generally, all dyes exhibit absorption patterns typical for substituted 1,3,5-triazine derivatives with an unstructured absorption band in the 320−400 nm range depending on the substitution patterns and more intense $\pi-\pi^*$ absorption at about 260 nm characteristic of the phenyl fragments.[25] Additional absorption transitions are found as expected by grafting BODIPY (λ_{abs} 529 nm), pyrene (λ_{abs} 392 nm), or perylene (λ_{abs} 472 nm) modules. Interestingly, in most cases, by irradiation in the triazine absorption around 350 nm, we did not observe the fluorescence expected for a classical organic dye (such as emission profiles which mirror the absorption, weak Stokes shift, etc.).[5a] Instead, we observed only a green emission with a maximum lying in the 490−550 nm range, with a large Stokes shift of about 10 000 cm^{-1} or 170 nm (Figures 8−10).

This green fluorescence with large Stokes shifts is assigned to that of the species resulting from intramolecular proton transfer (excited keto form, $S_1'^*$) of the triazine derivatives (Chart 2).[16a,26] In all present cases, the normal fluorescence of the excited enol form (S_1^*) was not observed. This indicates that either the lifetime of the fluorescent state S_1 (excited enol form) was extremely short ($<10^{-12}$ s^{-1}) or that a strong intramolecular hydrogen bond was involved in the ground state of the starting material. This has clearly been observed by NMR spectroscopy in the severe deshielding of the phenolic signal (see above).[20] This shows that with the present 1,3,5-triazine derivatives there is no hydrogen bond broken form (open-ring conformer) in contrast to those of other aromatic compounds such as salicylates giving ESIPT systems.[11b]

The fluorescence decay is monoexponential in all cases, and the lifetime is on the nanosecond time scale (Table 1). The corrected excitation spectrum matches well with the absorption spectrum over the entire spectral window. In addition, the fluorescence quantum yields and the excited-state lifetime

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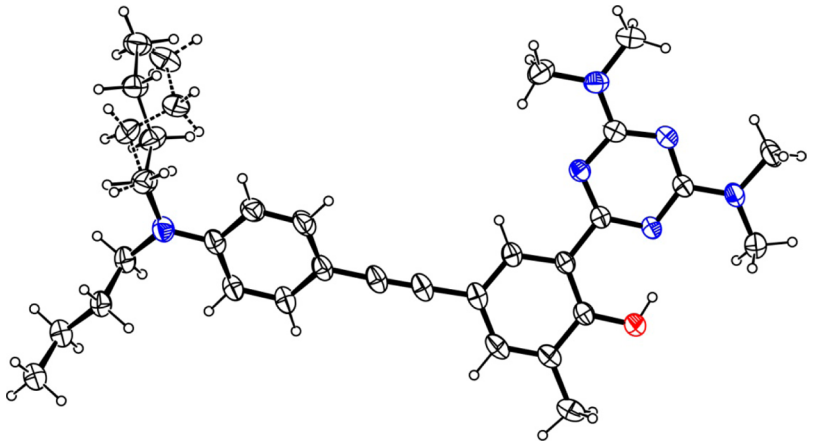

Figure 3. ORTEP view (30% probability ellipsoids) of the molecular unit found in the crystal lattice of **13**. Dashed lines represent a minor conformation of disordered atoms.

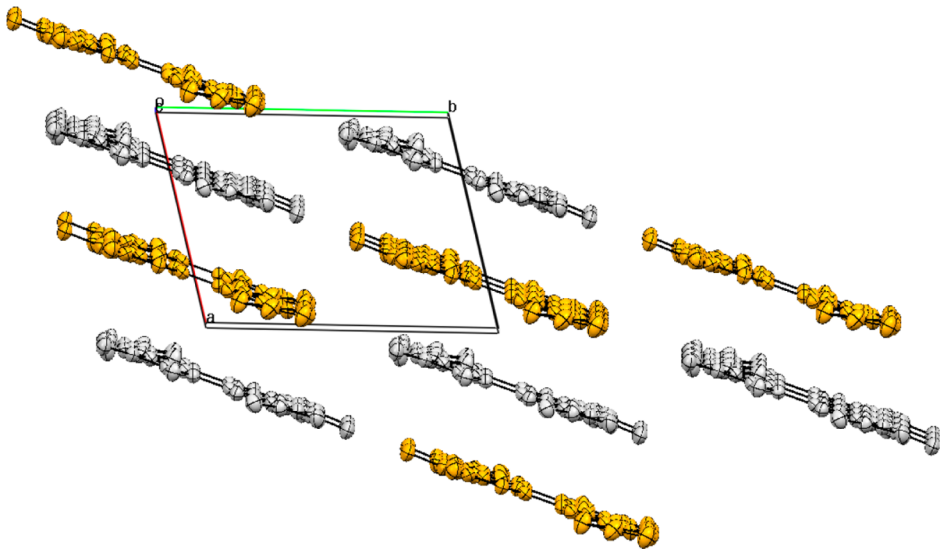

Figure 4. Packing of molecules **8** in layers viewed down the *c* direction.

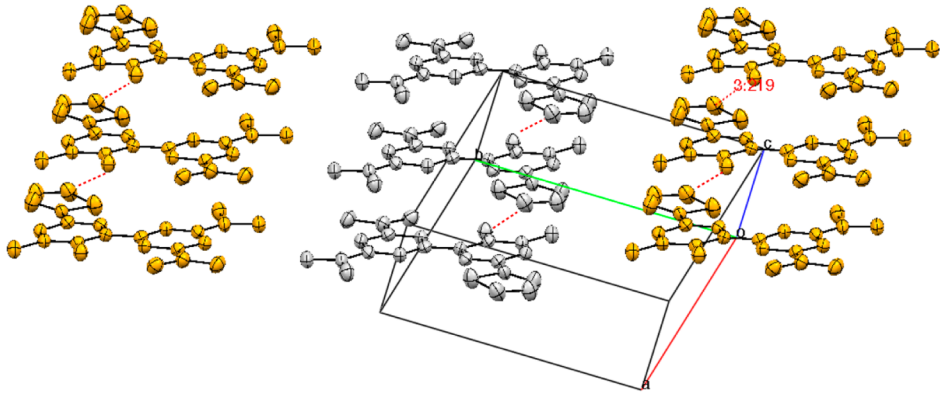

Figure 5. Packing of molecules **8** along the *a* direction. Molecules at general position (gray) and those related by an inversion center (gold).

recorded for the new dyes are independent of excitation wavelength.

The nature of the isomer has a relatively minor influence on the energy of the low energy absorption band. A weak 8 nm bathochromic shift was found in the absorption and emission spectra of the *para*-isomer **3** with respect to the *ortho*-isomer **6** (for unsubstituted derivatives). In comparing both substituted isomers, no effect was observed with thienyl compounds **8** and **18** and only a weak hypsochromic shift (5 nm) in absorption was found for the 3,4-ethylenedioxythienyl (EDOT)-substituted compounds **9** and **19**.

However, within a given isomer series, noticeable differences were observed. Replacing an iodo group by a thienyl unit causes 25 and 38 nm bathochromic shifts, respectively, in the

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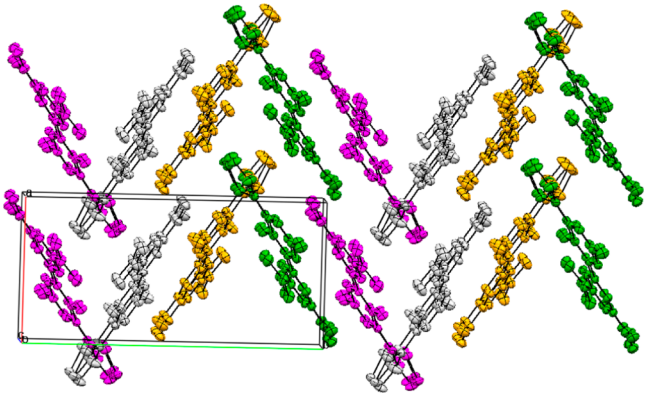

Figure 6. Packing of molecules **18** along the *c* axis. Molecules at general position (gray), related by a center of inversion (gold), by a 2_1 axis (green), by a glide mirror *c* (magenta).

absorption and emission spectra (Figure 9). Increasing the electronic density by using EDOT had little effect on the optical properties, whereas grafting of a bisthienyl unit (compound **10**) had detrimental effects on both the wavelengths of the absorption and emission and also on the quantum yield (Figure 9). The increase of the nonradiative rate for **10** may be due to the flexibility of the bisthienyl unit. Free rotation along the C−C linkage favors nonradiative deactivation channels.

The linking of a tolyl moiety through an ethynyl bond provided a greater bathochromic shift and a higher quantum yield than with an ethenyl bond (λ_{abs} 341 nm, ϕ_F 23% for **12** compared to λ_{abs} 316 nm, ϕ_F 9% for **11**, Figure 10). Switching from a methyl group to a dibutylamino function had little effect on the ϕ_F but induced a hypsochromic shift of 16 nm (compare dyes **12** and **13**, Table 1). The dibutylamino-functionalized 1,3,5-triazine is an interesting case because the spectroscopic properties were sensitive to the environment and, in particular, to acidic conditions. By spiking the solution with anhydrous HCl vapor, the absorption and emission bands of dye **13** were hypsochromically shifted by 14 and 50 nm, respectively (Figure 11). In situ deprotonation of the dibutylamino fragment using triethylamine restored the initial absorption and emission spectrum, proving the excellent stability of dye **13** under acidic, neutral, and basic conditions. Note that the excitation spectra perfectly match the absorption spectra in both situations.

Table 1. Selected Spectroscopic Data for the New Dyes[a]

dyes	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Δ_{SS} (cm^{-1})	τ_F (ns)	Φ_F (%)[b]	k_r[c] (10^8 s^{-1})	k_{nr}[c] (10^8 s^{-1})
3	319	7870	489	10900	4.5	28	0.6	1.6
6	327	7550	497	10500	5.3	30	0.6	1.3
7	332	6060	492	9800	1.1	7	8.7	0.5
8	357	5560	530	9100	4.7	25	0.5	1.6
9	360	4500	546	9500	4.1	18	0.4	2.0
10	355	43600	552	10100	1.8	5	0.3	5.4
11	316	39500	536	13000	3.4	9	0.3	2.7
12	300	31600	510	9700	5.8	23	0.4	1.3
	341	5600						
13	325	47000	533	12000	4.9	21	0.4	1.6
14	529	52000	600	2200	2.0	10	0.5	4.4
	350	10100						
15	392	36700	512	6000	4.5	46	0.1	1.2
16	472	50500	485	570	2.0	46	2.3	2.8
17	333	9030	499	10100	1.2	6	0.5	7.8
18	356	9170	551	9900	2.5	12	0.5	3.5
19	355	7650	558	10300	2.3	11	0.5	3.9
20	532	57000	586	1700	1.3	16	1.2	6.5
	350	14600						

[a]Measured in dichloromethane at rt except for dyes **14** and **20**, which were measured in toluene to limit aggregation. [b]Using Rhodamine 6G as reference, Φ = 0.78 in water,[27] λ_{ex} = 488 nm. [c]Calculated using the following equations: $k_r = \Phi_F/\tau_F$, $k_{nr} = (1 - \Phi_F)/\tau_F$, assuming that the emitting state is produced with unit quantum efficiency.

We next investigated the spectroscopy of the dyads, in particular, the BODIPY-linked 1,3,5-triazine (Figure 12). As would be expected based on literature data,[28] the major absorption at low energy was the BODIPY-centered $S_0 \rightarrow S_1$ transition. At higher energy, the main absorption bands of the substituted 1,3,5-triazine were seen at 348 and 364 nm, and the structureless absorption at about 380 nm was assigned in the light of previous data to the $S_0 \rightarrow S_2$ transition of the BODIPY subunit.[29] By excitation into the BODIPY absorption band at

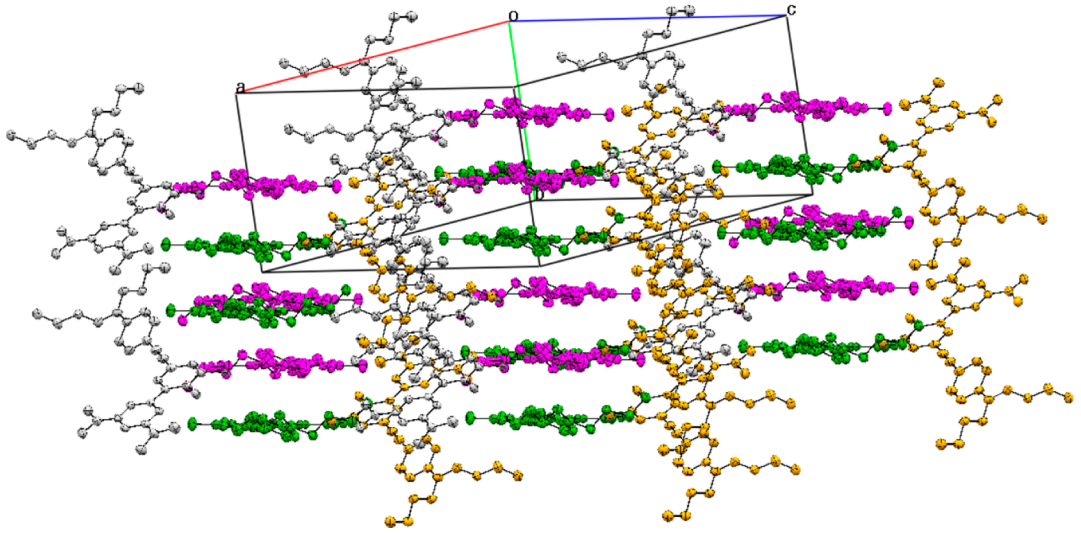

Figure 7. Packing of molecules **13** along the *b* direction. Molecules at general position (gray), related by a center of inversion (gold), by a 2_1 axis (green), by a glide mirror *c* (magenta).

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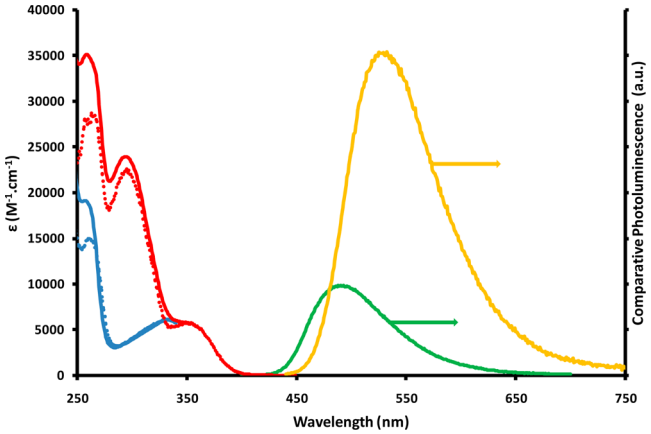
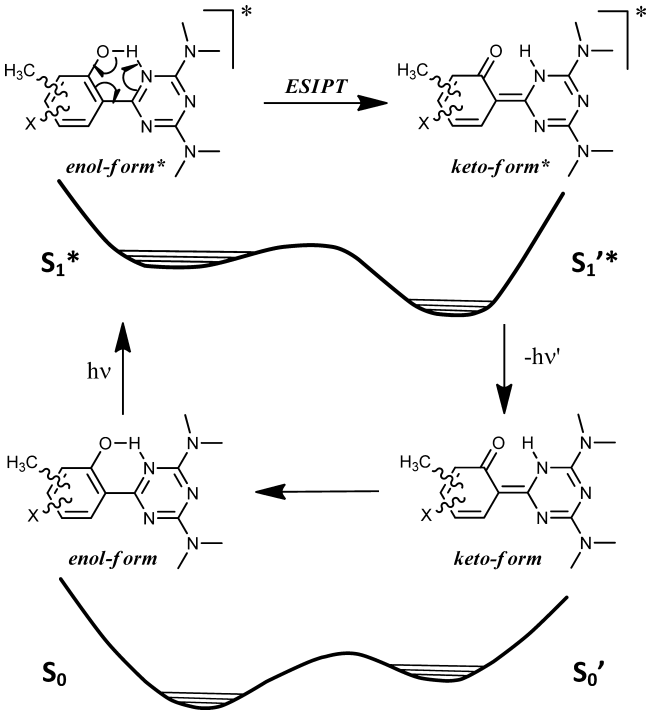


Figure 8. Absorption, emission, and excitation spectra of dyes **7** and **8**. Absorption (blue line for **7**, red for **8**), emission (green for **7**, yellow for **8**), and excitation (dashed blue line for **7**, red for **8**). For absorption, [*c*] ~2 × 10^{-5} M for both dyes; for emission, [*c*] ~2 × 10^{-6} M for both dyes (λ_{exc} = 310 nm for **7** and 350 nm for **8**); for excitation, [*c*] ~2 × 10^{-6} M for both dyes (λ_{exc} = 450 nm for **7** and **8**) in CH_2Cl_2 at rt .

Chart 2. Schematic Representation of the Energy-State Diagram for the Ground and Excited State of Triazine Derivatives during the Intramolecular Proton Transfer Processes: S_0,S'_0 and S_1,S'_1 Denote, Respectively, the Ground and Excited States



500 nm, intense emission of the BODIPY was detected. Interestingly, the irradiation into the triazine fragment at 350 nm resulted exclusively in BODIPY emission with no residual emission of the triazine ESIPT form (below 550 nm). This interesting result indicates that almost quantitative energy transfer from the ESIPT excited state to the BODIPY was occurring and that the triazine module could be used as an input energy device in more sophisticated systems. This result also held true for the *ortho*-isomer triazine-BODIPY dyad, **20**

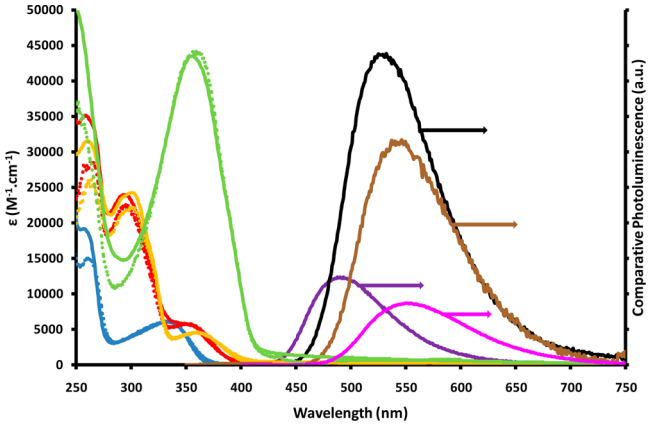


Figure 9. Absorption, emission, and excitation spectra of dyes **7**, **8**, **9**, and **10**. Absorption (blue line for **7**, red for **8**, yellow for **9**, and green for **10**), emission (purple for **7**, black for **8**, brown for **9**, and pink for **10**), and excitation (dashed blue line for **7**, red for **8**, yellow for **9**, and green for **10**). For absorption, [*c*] ~ 2 × 10^{-5} M for **7**, **8**, and **9**, [*c*] ~ 1.3 × 10^{-5} M for **10**; for emission, [*c*] ~ 2 × 10^{-6} M for **7**, **8**, and **9** and [*c*] ~ 1.3 × 10^{-6} M for **10** (λ_{exc} = 310 nm for **7**, 350 nm for **8** and **9**, 300 nm for **10**); for excitation, [*c*] ~ 2 × 10^{-6} M for **7**, **8**, and **9** and [*c*] ~ 1.3 × 10^{-6} M for **10** (λ_{em} = 450 nm for **7** and **8** and 500 nm for **9** and **10**) in CH_2Cl_2 at rt .

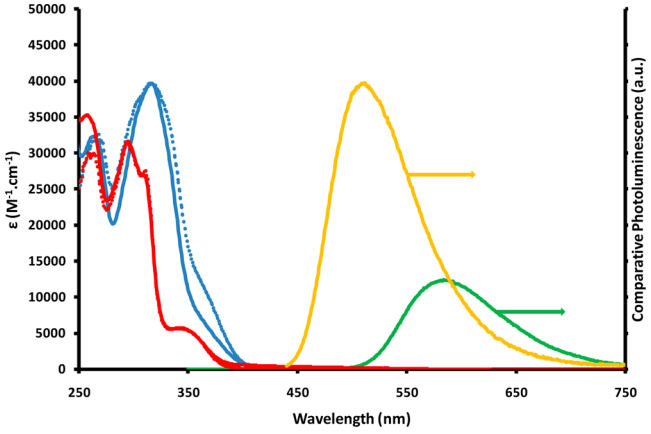


Figure 10. Absorption, emission, and excitation spectra of dyes **11** and **12**. Absorption (blue line for **11**, red for **12**), emission (green for **11**, and yellow for **12**), excitation (dashed blue line for **11**, and red for **12**). For absorption, [*c*] ~ 1.2 × 10^{-5} M for **11** and 1.8 × 10^{-5} M for **12**; for emission, [*c*] ~ 1.2 × 10^{-6} M for **11** and 1.8 × 10^{-6} M for **12** (λ_{exc} = 300 nm for both dyes); for excitation, [*c*] ~ 1.2 × 10^{-6} M for **11** and 1.8 × 10^{-6} M for **12** (λ_{em} = 480 nm for **11** and 460 nm for **12**) in CH_2Cl_2 at rt .

(Figure 12 and Table 1). From a mechanistic viewpoint, this is an interesting case because the emission of the keto form strongly overlaps with the absorption of the BODIPY singlet, and the hypothetical emission of the enol form should strongly overlap with the absorption of the second excited state of the BODIPY subunit. Keeping in mind that the excited state of the enol form is very short and that of the keto form is on the nanosecond time scale, we prefer the first hypothesis. These results are in keeping with previous results obtained with 4-alkyne-functionalized [2,2′-bipyridine]-3,3′-diol ESIPT dye types.[30]

It is instructive to take stock of the likely events that follow selective excitation into pyrene or perylene residues in the triazine dyads **15** and **16** (Figure 13). As would be expected

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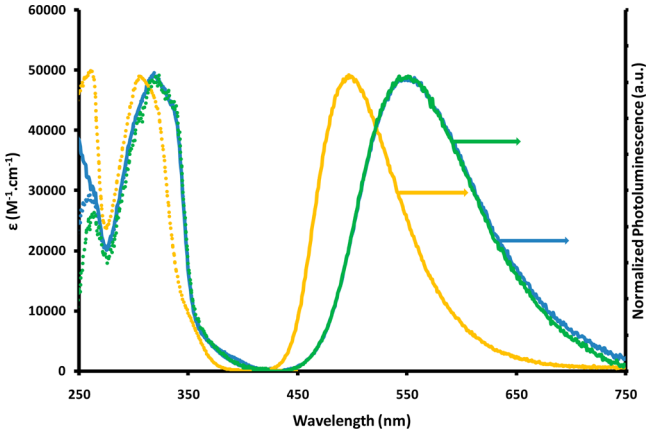

Figure 11. Absorption, emission, and excitation spectra of dye **13**. Absorption and emission (blue line), excitation (dashed line blue), emission with addition of anhydrous HCl vapors (yellow line), excitation with addition of anhydrous HCl vapors (dashed line yellow), emission after addition of anhydrous HCl vapors then triethylamine (green line) excitation after addition of anhydrous HCl vapors then triethylamine (dashed green line). For absorption, [*c*] ~ 1.4×10^{-5} M; for emission, [*c*] ~ 1.4×10^{-6} M (λ_{exc} = 300 nm); for excitation, [*c*] ~ 1.4×10^{-6} M for **11** and 1.8×10^{-6} M for **12** (λ_{em} = 500 nm) in EtOH at rt .

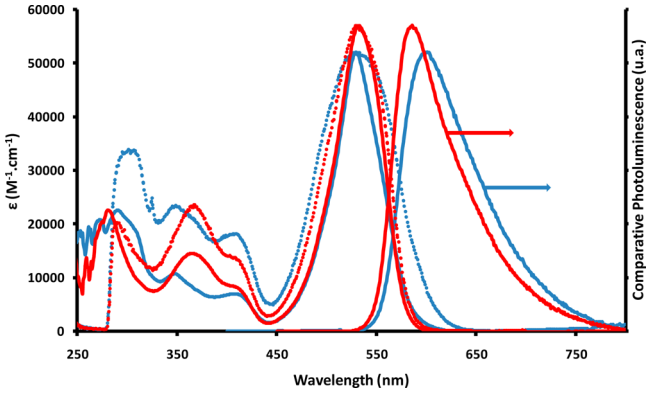

Figure 12. Absorption, emission, and excitation spectra of dyes **14** and **20**. Absorption (blue line for **14**, red for **20**), emission (blue for **14**, and red for **20**), excitation (dashed blue line for **14**, and red for **20**). For absorption, [*c*] ~ 1.5×10^{-5} M for **14** and 7.7×10^{-6} M for **20**; for emission, [*c*] ~ 1.5×10^{-6} M for **14** and 7.7×10^{-6} M for **20** (λ_{exc} = 500 nm for both dyes); for excitation, [*c*] ~ 1.2×10^{-6} M for **11** and 1.8×10^{-6} M for **12** (λ_{em} = 630 nm for both dyes) in toluene at rt .

based on the results described above with the BODIPY modules, the absorption spectrum of dyads **15** and **16** is almost a linear combination of the absorption of the triazine, pyrene, or perylene, respectively. The pyrene has a pronounced absorption which is overlapping with the absorption of the triazine. By irradiation in the pyrene band at ca. 400 nm, no residual emission of the pyrene was observed and only emission at 512 nm was triggered. This emission was assigned to the emission of the keto form of the triazine for which a marked ESIPT process is occurring (Chart 2). Interestingly, the quantum yield was the highest determined within this series of dyes (46%, Table 1). It is likely that the emission of the pyrene overlaps with the absorption of the triazine. The absorption of the latter is probably shifted bathochromically due to the high electron density imported by the pyrene moiety. Similar bathochromic shifts were observed by

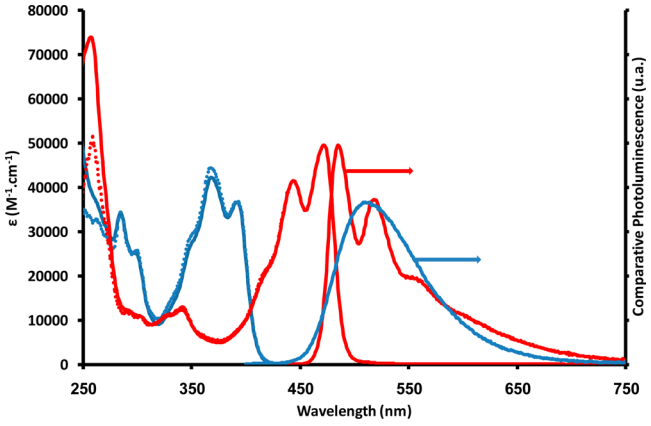

Figure 13. Absorption, emission, and excitation spectra of dyes **15** and **16**. Absorption (blue line for **15**, red for **16**), emission (blue for **15**, and red for **16**), excitation (dashed blue line for **15**, and red for **16**). For absorption, [*c*] ~ 1×10^{-5} M for **15** and 9×10^{-6} M for **16**; for emission, [*c*] ~ 1×10^{-6} M for **15** and 9×10^{-7} M for **20** (λ_{exc} = 340 nm for **15** and 430 nm for **16**); for excitation, [*c*] ~ 1×10^{-6} M for **15** and 9×10^{-7} M for **16** (λ_{em} = 450 nm for **15** and 500 nm for **16**) in CH_2Cl_2 at rt .

substitution of the iodo function in **7** or **17** with, for example, thienyl groups or by grafting electron-rich modules such as the bisthienyl or perylene fragments (Figure 13). Switching from pyrene to perylene (compound **16**) induced a pronounced shift of the main absorption of the polyaromatic moiety to lower energies (about 450 nm) and reduced the spectral overlap between the emission of the perylene and the absorption of the triazine. As a major consequence, excitation in the perylene subunit produced the characteristic structured emission of perylene.[31] This emission mirrored the absorption and is characteristic of a singlet excited state having a excited-state lifetime of 1.3 ns. By irradiation in the triazine absorption band in compound **16**, no emission of the keto form was found at 512 nm and the excited-state decay lifetime of the emission at 520 nm was monoexponential, excluding the presence of two overlapping emissive species. In the case of the perylene-grafted molecule **16** and contrary to the pyrene case **15**, energy transfer occurred from the keto form to the emissive state of perylene. Furthermore, the corrected excitation spectrum matched well with the absorption spectrum over the entire spectral window, and it is clear that photons collected by the pyrene subunit in the case of **15** and by the keto form of the triazine in the case of **16** were transferred quantitatively to the keto or perylene modules, respectively, under these conditions (Figure 13). This is interesting and has not been previously observed in related BODIPY dyads or tryads.[8]

In short, we have succeeded in extending the scope of 2-phenyl-functionalized 1,3,5-triazine platforms and have developed efficient routes to a variety of derivatives. Two series of constitutional isomers have been prepared and their spectroscopic properties studied. It was clearly established based on the chemical shift of the phenolic proton (>14.0 ppm) and confirmed by several X-ray diffraction studies that a very strong hydrogen bond favors the flat structure and a very efficient proton transfer in the excited state (ESPIT) provides a green fluorescence and a large Stokes shift. Absorption and emission are tunable by changing the nature of the substituent over a range of about 320 to 472 nm when comparing the unsubstituted triazine to the perylene-functionalized dye. The

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BODIPY modules extend the absorption to about 530 nm. In the case of the polyaromatic modules, interesting energy transfer pathways from the excited polycycles to the keto form of the excited triazine-phenol core or to the polycycle have been observed. All of these processes appear to be efficient and fast keeping in mind the short excited-state lifetimes. Many interesting features emerge from these studies, and solid-state spectroscopy should help the design of light-emitting devices.

These multifunctional molecules not only are promising as fluorophores but also provide a new prospect for dye innovation. The synthetic protocols and methodology pave the way for the design of more sophisticated scaffoldings in which multicascade energy transfer process could be used to concentrate photons to a large extent in order to promote chemical transformations or charge separation. Work along these lines is currently in progress.

EXPERIMENTAL SECTION

General Methods. All reactions were performed under a dry atmosphere of argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources without further purification unless otherwise stated. CH_2Cl_2 was distilled from P_2O_5 under an argon atmosphere. THF was distilled from sodium and benzophenone under an argon atmosphere. Toluene was distilled from sodium under an argon atmosphere. DMF was allowed to stand one night on KOH pellets prior to being distilled. The 200, 300, 400 (^{1}H) and 50, 75, 100 MHz (^{13}C) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards: ‰ (H) in parts per million relative to residual protiated solvent; ‰ (C) in parts per million relative to the solvent. Mass spectra were measured with a ESI-MS mass spectrometer. Chromatographic purifications were performed using 40−63 μm silica gel. TLC was performed on silica gel plates coated with a fluorescent indicator.

Electronic absorption and emission spectra were measured under ambient conditions using commercial instruments. Fluorescence spectra were recorded with a spectrofluorimeter. Solvents for spectroscopy were spectroscopic grade and were used as received after checking for impurities. A wide variety of excitation wavelengths were used, according to the species under investigation. Luminescence lifetimes were measured on a spectrofluorimeter, using software with time-correlated single photon mode coupled to a Stroboscopic system. The excitation source was a laser diode (λ 310 nm). No filter was used for the excitation. The instrument response function was determined by using a light-scattering solution (LUDOX).

The following equation was used to determine the relative fluorescence quantum yield:

$$\Phi_{cmp} = \Phi_{ref}\frac{I}{I_{ref}}\frac{OD_{ref}}{OD}\frac{n^2}{n_{ref}^2}$$

Here, I denotes the integral of the corrected emission spectrum, OD is the optical density at the excitation wavelength, and η is the refractive index of the medium. The reference fluorescence quantum yields were measured relative to Rhodamine 6G and cresyl violet[27] as standards.

Synthesis. All moisture-sensitive reactions were carried out under dry argon by using Schlenk tube techniques. All reagents were used directly as obtained commercially unless otherwise noted. *o*-Cresol, *p*-cresol, cyanuric chloride, butyllithium solution, dimethylamine solution 40 wt % in H_2O, sodium hybride 60% dispersion in mineral oil, 2,4-dimethylpyrrole, boron trifluoride etherate, copper(I) iodide, ethynyltrimethylsilane, 3,4-ethylenedioxythiophene, iodine monochloride, styrene, 1,8-diazabycyclo[4.5.0]undec-7-ene, diisopropylamine, and 4-ethynyltoluene were purchased from different commercial sources and used without further purification. [Pd(PPh$_3$)$_4$],[32] [Pd(PPh$_3$)$_2$Cl$_2$],[33] 3-ethynylperylene,[34] 1-ethynylpyrene,[35] compounds **1**[36] and **4**,[37] and 4,4-difluoro-1,3,5,7,8-pentamethyl-2-iodo-4-bora-3a,4a-diaza-s-indacene[23] were synthesized according to the literature procedures.

General Procedure 1 for the Synthesis of Hydroxyphenyl-1,3,5-triazine-2,4-dimethylamine Compounds. To a solution of the MOM-protected toluene derivatives in anhydrous THF was added *n*-BuLi (1.1 equiv, 1.6 M solution in hexane) at −78 °C under argon. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The resulting solution was slowly added to a solution of cyanuric chloride (1 equiv) in THF at −78 °C. The mixture was then warmed to rt and stirred for another 18 h. A 40% aqueous solution of dimethylamine (9 equiv) was added to the mixture and refluxed until TLC analysis showed that all starting material had been consumed. After being cooled to room temperature, the organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic phases were dried over $MgSO_4$, and the solvents were evaporated. The residue was then submitted to column chromatography separation on silica gel with petroleum ether/ethyl acetate (5:1) as eluant to give the desired compound in better than 50% yield.

General Procedure 2 for the Methoxymethylether Deprotection. Compound **2** or **5** was dissolved in a solution of CH_2Cl_2 (20 mL)/MeOH (20 mL)/EtOH (10 mL), and a solution of 6 M HCl was slowly added. The solution was stirred 12 h at rt. The mixture was poured into water (50 mL) and was extracted with CH_2Cl_2. The combined CH_2Cl_2 solution was washed with a saturated solution of $NaHCO_3$ and dried over $MgSO_4$. The residue was then submitted to column chromatography separation on silica gel.

General Procedure 3 for the Hydroxyphenyl-s-triazine-2,4-dimethylamine Iodinations. To a solution of hydroxyphenyl-1,3,5-triazine-2,4-dimethylamine (1 equiv) in a 50/50 mixture of DMF/MeOH was added dropwise a solution of ICl (1.5 equiv) in MeOH (10 mL). The reaction mixture was then stirred at room temperature, and the reaction progress was checked by TLC. After a period of time, TLC indicated that all starting material had been consumed. The reaction mixture was then diluted with CH_2Cl_2, washed with water, and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, and the solvents were evaporated. The crude product was recrystallized from EtOH/nonane to give white crystals.

General Procedure 4 for the Suzuki Cross-Coupling Reaction. A Schlenk tube was charged with a solution of appropriate iodo- and arylboronic acid or boronate derivatives in toluene. A mineral base (K_2CO_3) was also added. The solution was degassed with argon for 30 min, then [Pd(PPh$_4$)$_3$] was added. The mixture was stirred at 60 °C until complete consumption of the starting material (monitored by TLC). The solution was then extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography.

General Procedure 5 for the Sonogashira Cross-Coupling Reactions Using [Pd(PPh$_3$)$_4$]. A Schlenk tube was charged with a solution of appropriate iodo and ethynyl derivatives in a mixture of benzene/triethylamine (5/1). The solution was degassed with argon for 30 min, then [Pd(PPh$_3$)$_4$] (10 mol %) was added. The mixture was stirred at 60 °C overnight. After being cooled, the solution was extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography.

2-Thielnylboronic Acid.[38] A solution of thiophene (9.93 mL, 10.43 g, 0.124 mol) in dry THF (120 mL) cooled at −78 °C was treated dropwise with *n*-BuLi (100 mL, 1.6 mol/L). The reaction mixture was stirred at −78 °C for 30 min and then allowed to warm to −20 °C slowly. This 2-thienyllithium was again cooled to −78 °C and transferred by cannula into a solution of trisethylborate (28.1 mL, 24.08 g, 0.165 mol) in dry THF (80 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h before warming to room temperature. The mixture was then treated with 1 M aqueous HCl (200 mL) and the organic layer separated. The aqueous layer was then extracted with dichloromethane (5 × 120 mL), and the combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure to afford a white solid. Recrystallized of the white solid from water gave thiopheneboronic acid as a pure white solid (10.0 g, 63%): mp 126 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.59 (dd, 2H, ^3J = 18.4

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Hz, ^4J = 4.0 Hz), 7.14 (t, 1H, ^3J = 4.0 Hz), 6.55 (s, 2H); ^{13}C NMR (acetone, 75 MHz) δ = 140.7, 136.3, 130.4.

4,4,5,5-Tetramethyl-2-(2-thienyl)-1,3,2-dioxaborolane.[39] To a solution of 2-iodothiophene (210.0 mg, 1.00 mmol), copper iodine (19.0 mg, 0.01 mmol), and sodium hybride (60.0 mg, 1.50 mmol) in dry THF (4 mL) was added pinacolborane (192.0 mg, 1.50 mmol, 0.218 mL) via syringe under argon atmosphere. The resultant mixture was stirred at room temperature until the iodoaryl disappeared as monitored by TLC. After the reaction was quenched by adding 10 mL of saturated NH_4Cl, the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine and dried over $MgSO_4$. The solution was concentrated under vacuo, and the residue was chromatographed eluting with a mixture of petroleum ether/ethyl acetate (9:1) to give the desired compound as a white solid (182.8 mg, 87%): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.66−7.63 (m, 2H), 7.19 (dd, 1H, ^3J = 3.1 Hz, ^3J = 2.3 Hz), 1.35 (s, 12H).

4,4′,5,5′-Tetramethyl-1,3,2-dioxaboronic Ester of 3,4-Ethylenedioxythiophene.[40] A solution of 3,4-ethylenedioxythiophene (1.33 g, 9.36 mmol) in dry THF (25 mL) was cooled to −78 °C under argon, and 7.02 mL of *n*-BuLi solution (1.6 M, 11.2 mmol) was slowly added. The mixture was stirred at 0 °C for 30 min and then recooled to −78 °C. At this temperature, the reaction was treated with 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaborolane (5.34 mL, 26.2 mmol), and the mixture was stirred for one night. The reaction was poured into crushed ice/NH_4Cl, and the product was then extracted with Et_2O (3 × 30 mL). After being dried over $MgSO_4$, the solvent was removed at reduced pressure. The white solid product was used without further purification: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 6.65 (s, 1H), 4.31 (m, 2H), 4.21 (m, 2H), 1.35 (s, 12H).

4,4-Difluoro-1,3,5,7,8-pentamethyl-4-bora-3a,4a-diaza-s-indacene was synthesized according to a literature procedure[41] and recovered as orange needles: yield 44%; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.05 (s, 2H), 2.58 (s, 3H), 2.52 (s, 6H), 2.41 (s, 6H); UV−vis (CH_2Cl_2) λ nm (ε, M^{-1} cm^{-1}) 496 (94000), 467 (sh, 23000), 422 (6400), 356 (6200).

4,4-Difluoro-1,3,5,7,8-pentamethyl-2-iodo-4-bora-3a,4a-diaza-s-indacene was synthesized according to literature procedures[42] and recovered as orange needles: yield 66%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.12 (s, 1H), 2.60 (s, 6H), 2.53 (s, 3H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 156.2, 143.2, 141.3, 140.9, 84.4, 19.6, 17.7, 17.2, 15.9, 14.7; ^{11}B NMR ($CDCl_3$, 128 MHz) δ = 3.55 (t, ^1J = 32 Hz); UV−vis (CH_2Cl_2) λ (nm) (ε, M^{-1} cm^{-1}) = 509 (90000), 478 (sh, 27000), 421 (7000), 367 (9000); IR (KBr, cm^{-1}) 2963, 2923, 2853, 1782, 1547, 1528,1482, 1459, 1443, 1401, 1374, 1345, 1304, 1261, 1225, 1196, 1165, 1139, 1126, 1105, 1083, 1063, 1026, 975; FAB$^+$-MS *m*/*z* (nature of peak, relative intensity) 389.1 ($[M^+H]^+$, 100), 369.1 ($[M^-F]^+$, 15). Anal. Calcd for $C_{14}H_{16}BF_2IN_2$: C, 43.34; H, 4.16; N, 7.22. Found: C, 43.20; H, 3.92; N, 7.05.

***N,N*-Dibutyl-4-ethynylaniline.**[43] A 25 mL round-bottom flask equipped with a magnetic stir bar was charged with *N,N*-dibutyl-4-((trimethylsilyl)ethynyl)aniline (160.0 mg, 0.530 mmol), KOH (35.7 mg, 0.637 mmol), THF (1.0 mL), MeOH (5.0 mL), and water (1.0 mL). The reaction mixture was stirred for 90 min at 60 °C, diluted with Et_2O, washed with H_2O and brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was used without further purification (116.9 mg, 96% yield, green oil): ^{1}H NMR ($CDCl_3$, 200 MHz) 6.92 (ABsyst, 4H, ^3J = 9.0 Hz, $\upsilon_0\delta$ = 157.5 Hz), 3.26 (t, 4H, ^3J = 7.6 Hz), 2.96 (s, 1H), 1.56−1.28 (m, 8H), 0.95 (t, 6H, ^3J = 7.3 Hz).

1-Ethynylpyrene. To a solution 3-(pyren-1-yl)prop-2-yn-1-ol (400 mg, 1.56 mmol) in THF (30 mL) were added MnO_2 (1.36 g, 15.62 mmol) and KOH (438 mg, 7.81 mmol). The mixture was stirred for 1 h and filtered. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane/petroleum ether (v/v 5/95) to give 297 mg (84%) of 1-ethynylpyrene as a white solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.60 (d, 1H, ^3J = 9.0 Hz), 8.22−8.04 (m, 8 H), 3.63 (s, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 132.5, 131.6, 131.1, 131.0, 130.2, 128.6, 128.4, 127.2,126.6, 126.3, 125.7, 125.3, 124.4, 82.8, 82.6.

3-Ethynylperylene. To a solution 3-(perylen-3-yl)prop-2-yn-1-ol (300 mg, 0.98 mmol) in THF (50 mL) were added MnO_2 (852 mg, 9.80 mmol) and KOH (275 mg, 4.90 mmol). The mixture was stirred for 1 h and filtered. The solvent was removed by rotary evaporation. The residue was purified by chromatography on silica gel, eluting with dichloromethane/petroleum ether (v/v 15/85) to give 222 mg (82%) of 3-ethynylperylene as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24−8.17 (m, 4H), 8.11 (d, 1H, ^3J = 8.0 Hz), 7.72−7.68 (m, 3H), 7.57 (t, 1H, ^3J = 8.0 Hz), 7.47 (td, 2H, ^3J = 8.0, ^4J = 1.7 Hz), 3.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 134.9, 134.5, 132.3, 131.8, 131.4, 130.8, 130.5, 128.5, 128.4, 128.1, 127.3, 126.6, 125.9, 121.0, 120.7, 119.4, 118.9, 82.8, 82.1.

Compound 2. Prepared according to general procedure 1: 2-(methoxymethyl)toluene compound **1** (4 g, 25.1 mmol), dry THF (150 mL), *n*-Buli (17.25 mL, 1.77 g), cyanuric chloride (4.63 g, 25.1 mmol) in dry THF (80 mL), dimethylamine (28.6 mL, 25.5 g). Column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1) as eluant to give compound **2** as a white powder (4.41 g, 55%): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.66 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.8 Hz), 7.24 (d, 1H, ^3J = 7.8 Hz), 7.06 (m, 1H), 5.00 (s, 2H), 3.47 (s, 3H), 3.19 (s, 12H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 171.8, 165.3, 154.7, 143.4, 132.4, 132.0, 129.4, 123.6, 100.5, 57.1, 36.1, 17.1; EI-MS, *m*/*z* (%) 317.1 (100). Anal. Calcd for $C_{16}H_{23}N_5O_2$: C, 60.55; H, 7.30; N, 22.07. Found: C, 60.44; H, 6.97; N, 21.82.

Compound 3. Prepared according general procedure 3: compound **2** (1.0 g, 3.15 mmol), 6 M HCl (9 mL). Column chromatography on silica gel eluting with CH_2Cl_2 to give compound **3** as a white solid (787.5 mg, 91%): mp 161−162 °C; IR (ATR) ν in cm^{-1} 2921 (w), 2865 (w), 1561 (s), 1514 (s), 1407 (s), 1393 (s), 1368 (s), 1209 (m), 816 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 14.43 (s, 1H),[44] 8.25 (dd, 1H, ^3J = 7.8 Hz, ^4J = 1.5 Hz), 7.24 (d, 1H, ^3J = 8.8 Hz), 6.79 (t, 1H, ^3J = 7.8 Hz), 3.21 (s, 12H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 170.1, 163.6, 160.2, 134.0, 126.8, 126.1, 117.8, 117.7, 36.4, 16.0; EI-MS, *m*/*z* (%) 274.2 (100). Anal. Calcd for $C_{14}H_{19}N_5O$: C, 61.52; H, 7.01; N, 25.62. Found: C, 61.27; H, 6.64; N, 25.84.

Compound 5. Prepared according to general procedure 1: 4-(methoxymethyl)toluene compound **4** (2.5 g, 15.7 mmol), dry THF (125 mL), *n*-Buli (11.0 mL, 1.11 g), cyanuric chloride (2.89 g, 15.7 mmol) in dry THF (50 mL), dimethylamine (17.9 mL, 15.9 g). Column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1) as eluant to give compound **5** as a white powder (2.51 g, 50%): ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.53 (d, 1H, ^4J = 7.84), 7.11 (m, 2H), 5.16 (s, 2H), 3.50 (s, 3H), 3.18 (s, 12H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 171.5, 165.4, 153.5, 131.7, 131.4, 131.0, 130.3, 118.2, 96.4, 56.0, 36.2, 20.7; EI-MS, *m*/*z* (%) 318.1 (100). Anal. Calcd for $C_{16}H_{23}N_5O_2$: C, 60.55; H, 7.30; N, 22.07. Found: C, 60.37; H, 7.09; N, 21.79.

Compound 6. Prepared according general procedure 3: compound **5** (4.41 g, 13.89 mmol), 6 N HCl (40 mL). Column chromatography on silica gel eluting with CH_2Cl_2 to give compound **6** as a white solid (2.73 g, 72%): mp 162−163 °C; IR (ATR) ν in cm^{-1} 2921 (w), 2865 (w), 1561 (s), 1514 (s), 1407 (s), 1393 (s), 1368 (s), 1209 (m), 816 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 14.0 (s, 1H), 8.15 (d, 1H, ^3J = 1.9 Hz), 7.16 (dd, 1H, ^3J = 7.2 Hz, ^4J = 1.2 Hz), 6.86 (d, 1H, ^3J = 8.3 Hz), 3.20 (s, 12H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 170.0, 163.7, 159.7, 134.2, 129.0, 127.4, 118.1, 117.4, 36.4, 20.8; EI-MS, *m*/*z* (%) 274.2 (100). Anal. Calcd for $C_{14}H_{19}N_5O$: C, 61.52; H, 7.01; N, 25.62. Found: C, 61.38; H, 6.76; N, 25.35.

Compound 7. Prepared according general procedure 3: compound **3** (650.0 mg, 2.38 mmol), ICl (579.1 mg, 3.57 mmol), MeOH (50 mL), DMF (50 mL). The crude product was recrystallized from EtOH/nonane to give compound **7** as yellow powder (856.3 mg, 90%): mp 215−216 °C; IR (ATR) ν in cm^{-1} 2916 (w), 2863 (w), 1589 (s), 1557 (s), 1513 (s), 1460 (m), 1434 (m), 1403 (s), 1388 (s), 1357 (m), 1205 (m), 1053 (m), 866 (s), 805 (s); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 14.55 (s, 1H), 8.49 (d, 1H, ^3J = 2.4 Hz), 7.50 (d, 1H, ^3J = 2.0 Hz), 3.20 (s, 12H), 2.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 168.8, 163.4, 160.1, 141.9, 135.2, 129.1, 119.2, 79.4, 36.5, 16.7; EI-MS, *m*/*z* (%) 400.0 (100). Anal. Calcd for $C_{14}H_{18}IN_5O$: C, 42.12; H, 4.54; N, 17.54. Found: C, 41.80; H, 4.77; N, 17.49.

Compound 8. Prepared according to general procedure 4: compound **7** (50.0 mg, 0.125 mmol), 2-thienylboronic acid (0.500

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mmol, 64.2 mg, 4 equiv), and aqueous K_2CO_3 (86.5 mg, 0.626 mmol, 5 equiv) in toluene (10 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 4:6 to 1:9 as eluant to give compound **8** as a yellow powder (13.9 mg, 31%): mp 209−210 °C; IR (ATR) ν in cm^{-1} 3097 (w), 3058 (w), 2923 (m), 1613 (m), 1563 (s), 1510 (s), 1434 (m), 1384 (s), 1210 (m), 1054 (m), 807 (m); ^1H NMR (300 MHz, $CDCl_3$) δ =15.0 (s, 1H), 8.51 (d, 1H, ^3J = 2.4 Hz), 7.50 (d, 1H, ^3J = 2.4 Hz), 7.24 (m, 2H), 6.79 (dd, 1H, ^3J = 5.2 Hz, ^4J = 3.4 Hz), 3.22 (s, 12H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 169.3, 163.1, 159.9, 144.9, 132.1, 127.8, 126.9, 124.5, 123.4, 121.8, 117.6, 36.5, 16.1; EI-MS, *m*/*z* (%) 356.1 (100). Anal. Calcd for $C_{18}H_{21}N_5OS$: C, 60.82; H, 5.95; N, 19.70. Found: C, 60.66; H, 5.77; N, 19.52.

Compound 9. Prepared according to general procedure 4: compound **7** (100.0 mg, 0.250 mmol), 4,4′,5,5′-tetramethyl-1,3,2-dioxaboronic ester of 3,4-ethylenedioxythiophene (0.376 mmol, 100.7 mg, 1.5 equiv), and aqueous K_2CO_3 (69.2 mg, 0.500 mmol, 2 equiv) in toluene (10 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 4:6 to CH_2Cl_2 as eluant to give compound **9** as a yellow powder (28.1 mg, 27%): mp 227−229 °C; IR (ATR) ν in cm^{-1} 3097 (w), 3058 (w), 2923 (m), 2857 (w), 1613 (m), 1564 (s), 1511 (s), 1433 (m), 1393 (s), 1054 (m), 807 (m); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.57 (d, 1H, ^3J = 1.4 Hz), 7.64 (d, 1H, ^3J = 1.4 Hz), 6.22 (s, 1H), 4.30 (m, 2H), 4.25 (m, 2H), 3.24 (s, 12H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 162.6, 159.1, 142.4, 137.3, 132.9, 127.3, 125.0, 123.9, 117.9, 117.5, 96.4, 64.9, 64.7, 36.8, 16.6; EI-MS, *m*/*z* (%) 413.1 (100). Anal. Calcd for $C_{20}H_{23}N_5O_3S$: C, 58.09; H, 5.61; N, 16.94. Found: C, 57.74; H, 5.47; N, 16.79.

Compound 10. Prepared according to general procedure 4: compound **7** (50.0 mg, 0.125 mmol), 5′-hexyl-2,2′-bithiophene-5-boronic acid pinacol ester (0.250 mmol, 94.3 mg, 2 equiv), and aqueous K_2CO_3 (86.5 mg, 0.626 mmol, 5 equiv) in toluene (10 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 8:2 to 5:5 as eluant to give compound **10** as a yellow amorphous powder (26.6 mg, 41%): IR (ATR) ν in cm^{-1} 2923 (m), 2855 (w), 1611 (m), 1562 (s), 1508 (s), 1434 (m), 1394 (s), 1383 (s), 1209 (m), 1053 (m), 790 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.45 (d, 1H, ^3J = 2.2 Hz), 7.47 (d, 1H, ^3J = 2.2 Hz), 7.13 (d, 1H, ^3J = 3.9 Hz), 7.02 (d, 1H, ^3J = 3.6 Hz), 6.97 (d, 1H, ^3J = 3.6 Hz), 6.66 (d, 1H, ^3J = 3.9 Hz), 3.23 (s, 12H), 2.77 (t, 2H, ^3J = 7.4 Hz), 2.33 (s, 3H), 1.65 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H, ^3J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 170.0, 163.9, 160.7, 145.7, 143.5, 136.1, 135.4, 131.5, 127.4, 126.5, 125.2, 124.3, 124.2, 123.3, 122.6, 118.3, 36.7, 36.5, 32.1, 32.0, 30.6, 29.2, 23.0, 16.3, 14.3; EI-MS, *m*/*z* (%) 521.1 (100). Anal. Calcd for $C_{28}H_{35}N_5OS_2$: C, 64.46; H, 6.76; N, 13.42. Found: C, 64.22; H, 6.44; N, 13.18.

Compound 11. A Schlenk flask was charged with compound **7** (50.0 mg, 0.125 mmol), styrene (0.250 mmol, 0.029 mL, 2 equiv), and K_2CO_3 (26.0 mg, 0.188 mmol, 1.5 equiv) in a mixture of benzene (2 mL) and DMF (6 mL). The solution was degassed with argon for 30 min, then $[Pd(PPh_3)_2Cl_2]$ (10 + 10 mol %) was added. The mixture was stirred at 80 °C for 11 h (monitored by TLC). The solution was extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 8:2 to 6:4 as eluant to give compound **11** as a white powder (13.0 mg, 28%): mp 180−182 °C; IR (ATR) ν in cm^{-1} 3097 (w), 3058 (w), 2922 (m), 2850 (w), 1611 (m), 1563 (s), 1557 (s), 1509 (s), 1434 (m), 1384 (s), 1210 (m), 1056 (m), 810 (s); ^1H NMR (300 MHz, $(CD_3)_2CO$) δ = 8.43 (d, 1H, ^3J = 2.2 Hz), 7.61 (d, 1H, ^3J = 2.2 Hz), 7.57 (d, 2H, ^3J = 7.8 Hz), 7.35 (t, 2H, ^3J = 7.7 Hz), 7.22 (t, 1H, ^3J = 7.9 Hz), 7.22 (d, 1H, ^3J = 16.0 Hz), 7.1 (d, 1H, ^3J = 16.0 Hz), 3.24 (s, 12H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 160.2, 138.1, 132.1, 131.7, 131.6, 129.1, 129.0, 128.8, 128.7, 128.5, 128.2, 127.1, 126.3, 126.0, 125.8, 36.6, 16.4; EI-MS, *m*/*z* (%) 375.2 (100). Anal. Calcd for $C_{22}H_{25}N_5O$: C, 70.38; H, 6.71; N, 18.65. Found: C, 70.11; H, 6.54; N, 18.47.

Compound 12. Prepared according to general procedure 5: compound **7** (50.0 mg, 0.125 mmol), 4-ethynyltoluene (17.5 mg, 0.150 mmol, 2 equiv) in a mixture of benzene/triethylamine (5 mL/1 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 8:2 to 5:5 as eluant to give compound **12** as a pale yellow powder (43.7 mg, 90%): mp 218−219 °C; IR (ATR) ν in cm^{-1} 2924 (w), 2857 (w), 1612 (m), 1563 (s), 1511 (s), 1435 (m), 1390 (s), 1209 (m), 1055 (m), 810 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.41 (d, 1H, ^3J = 2.2 Hz), 7.41 (d, 1H, ^3J = 2.2 Hz), 7.28 (AB sys, 4H, J_{AB} = 7.9 Hz, $\upsilon_o\delta$ = 56.1 Hz), 3.23 (s, 12H), 2.36 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 169.4, 163.4, 160.6, 137.7, 136.8, 131.3, 130.4, 129.0, 126.6, 120.8, 117.8, 112.5, 89.4, 87.2, 36.4, 21.5, 15.9; EI-MS, *m*/*z* (%) 387.1 (100). Anal. Calcd for $C_{23}H_{25}N_5O$: C, 71.29; H, 6.50; N, 18.07. Found: C, 70.92; H, 6.32; N, 17.80.

Compound 13. Prepared according to general procedure 6: compound **7** (60.0 mg, 0.150 mmol), *p*-(dibutylamino)-phenylacetylene (41.4 mg, 0.180 mmol, 1.2 equiv) in a mixture of benzene/triethylamine (5 mL/1 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 7:3 to 3:7 as eluant to give compound **13** as a greenish amorphous powder (78.4 mg, 40%): IR (ATR) ν in cm^{-1} 2955 (m), 2923 (m), 2854 (m), 1736 (w), 1610 (m), 1562 (s), 1509 (s), 1466 (w), 1435 (m), 1398 (s), 810 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 8.39 (d, 1H, ^3J = 2.4 Hz), 7.38 (d, 1H, ^3J = 2.4 Hz), 6.96 (AB sys, 4H, J_{AB} = 5.6 Hz, $\upsilon_o\delta$ = 157.8 Hz), 3.30−3.12 (m, 4H), 3.16 (s, 12H), 2.28 (s, 3H), 1.56 (m, 4H), 1.39−1.31 (m, 4H), 0.95 (t, 6H, ^3J = 4.8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 169.8, 163.9, 160.7, 148.3, 136.9, 132.9, 130.2, 127.1, 118.2, 113.6, 111.7, 109.5, 88.6, 87.6, 51.1, 36.7, 36.5, 29.8, 20.7, 16.1, 14.2; EI-MS, *m*/*z* (%) 500.2 (100). Anal. Calcd for $C_{30}H_{40}N_6O$: C, 71.97; H, 8.05; N, 16.79. Found: C, 72.35; H, 8.41; N, 16.94.

Compound 14. A Schlenk tube was charged with a solution of 4,4-difluoro-1,3,5,7,8-pentamethyl-2-iodo-4-bora-3a,4a-diaza-s-indacene (190.0 mg, 0.490 mmol), trimethylsilylacetylene (50.6 mg, 0.515 mmol, 1.05 equiv) in a mixture of benzene/diisopropylamine (10 mL/2 mL). The solution was degassed with argon for 30 min, then $[Pd(PPh_2)_2Cl_2]$ (5 mol %, 18.1 mg) and CuI (6 mol %, 5.9 mg) were added. The mixture was stirred at rt for one night (monitored by TLC). Compound **7** (195.4, 0.490 mmol), DBU (895.6 mg, 5.88 mmol, 12 equiv), and 40 mol % of H_2O were then added, and the solution was stirred for an additional 3 days. The solution was then extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 8:2 to 0:10 as eluant to give compound **14** as a purple powder (181.1 mg, 66%): mp dec >270 °C; IR (ATR) ν in cm^{-1} 2923 (w), 2866 (w), 1556 (s), 1510 (s), 1467 (m), 1395 (s), 1199 (s), 1063 (s), 980 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.8 (s, 1H), 8.40 (d, 1H, ^3J = 2.0 Hz), 7.40 (d, 1H, ^3J = 2.0 Hz), 6.09 (s, 1H), 3.22 (s, 12 H), 2.67 (s, 3H), 2.62 (s, 3H), 2.56 (s, 3H), 2.54 (s, 3H), 2.43 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 169.4, 163.5, 155.3, 155.1, 142.1, 141.6, 104.4, 136.8, 133.5, 133.2, 130.2, 126.8, 126.7, 124.8, 121.9, 117.8, 112.7, 96.4, 79.5, 36.5, 36.3, 17.5, 16.7, 16.0, 15.9, 15.3, 14.6; EI-MS, *m*/*z* (%) 557.2 (100). Anal. Calcd for $C_{30}H_{34}BF_2N_7O$: C, 64.64; H, 6.15; N, 17.59. Found: C, 64.52; H, 5.82; N, 17.38.

Compound 15. Prepared according to general procedure 5: compound **7** (50.0 mg, 0.125 mmol), 1-ethynylpyrene (31.2 mg, 0.138 mmol, 1.1 equiv) in a mixture of benzene/triethylamine (5 mL/1 mL). The solution was degassed with argon for 30 min, then $[Pd(PPh_3)_4]$ (10 mol %, 15.0 mg) and CuI (12 mol %, 3.0 mg) were added. Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 7:3 to 5:5 as eluant to give an orange powder (79.0 mg, 41%): mp dec >250 °C; IR (ATR) ν in cm^{-1} 2920 (w), 1610 (m), 1569 (m), 1513 (s), 1389 (s), 845 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.85 (s, 1H), 8.70 (d, 1H, ^3J = 9.3 Hz), 8.59 (d, 1H, ^3J = 2.2 Hz), 8.26−8.00 (m, 8H), 7.61 (d, 1H, ^3J = 2.2 Hz), 3.25−3.19 (m, 12H), 2.33 (s, 3H); ^{13}C NMR (CD_2Cl_2, 75 MHz) δ = 168.8, 162.9, 160.7, 136.3, 131.1, 130.9, 130.7, 130.4, 130.0, 128.9, 127.7, 127.6, 127.4 126.8, 126.5, 125.8, 125.2, 125.0, 124.1, 123.8, 118.1, 117.5, 111.8, 95.6, 85.7, 35.9, 35.6, 15.3; EI-MS, *m*/*z* (%) 497.2 (100). Anal. Calcd for $C_{32}H_{27}N_5O$: C, 77.24; H, 5.47; N, 14.07. Found: C, 77.04; H, 5.25; N, 13.69.

Compound 16. Prepared according to general procedure 5: compound **7** (50.0 mg, 0.125 mmol), 1-ethynylperylene (36.3 mg,

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0.131 mmol, 1.05 equiv) in a mixture of benzene/triethylamine (5 mL/1 mL), [$Pd(PPh_3)_4$] (10 mol %, 14.5 mg), and CuI (12 mol %, 3.0 mg) were added. Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 9:1 to 4:6 as eluant to give compound **16** as an orange powder (32.6 mg, 48%): mp dec >270 °C; IR (ATR) ν in cm^{-1} 2922 (w), 1611 (m), 1574 (s), 1507 (s), 1403 (s), 1391 (s), 1382 (s), 809 (s), 761 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.91 (s, 1H), 8.53 (d, 1H ^3J = 2.0 Hz), 8.35 (d, 1H, ^3J = 8.2 Hz), 8.27−8.14 (m, 4H), 7.78−7.26 (m, 7H), 3.26−3.22 (m, 12H), 2.33 (s, 3H); due to the low solubility of the compound, the carbon NMR spectra have not been determined; EI-MS, *m*/*z* (%) 547.2 (100). Anal. Calcd for $C_{36}H_{29}N_5O$: C, 78.95; H, 5.34; N, 12.79. Found: C, 78.61; H, 5.12; N, 12.43.

Compound 17. Prepared according general procedure 3: compound **6** (600.0 mg, 2.19 mmol), ICl (534.6 mg, 3.29 mmol), MeOH (50 mL), and DMF (50 mL). The crude product was recrystallized from EtOH/nonane to give compound **17** as a pale yellow powder (871.4 mg, 99%): mp 211−213 °C; IR (ATR) ν in cm^{-1} 2916 (w), 2863 (w), 1600 (m), 1567 (s), 1511 (s), 1450 (m), 1391 (s), 1361 (m), 804 (s), 698 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 15.14 (s, 1H), 8.15 (d, ^1H, ^3J = 2.0 Hz), 7.67 (d, 1H, ^3J = 2.0 Hz), 3.20 (s, 12H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 168.9, 163.4, 158.5, 143.1, 129.6, 129.2, 118.3, 85.7, 36.6, 36.3, 20.2; EI-MS, *m*/*z* (%) 400.0 (100). Anal. Calcd for $C_{14}H_{18}IN_5O$: C, 42.12; H, 4.54; N, 17.54. Found: C, 41.94; H, 4.28; N, 17.27.

Compound 18. Prepared according to general procedure 4: compound **17** (50.0 mg, 0.125 mmol), 2-thienylboronic acid (0.500 mmol, 64.2 mg, 4 equiv), and aqueous K_2CO_3 (86.5 mg, 0.626 mmol, 5 equiv) in toluene (10 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 4:6 to 2:8 as eluant to give compound **18** as a yellow powder (21.0 mg, 47%): mp 227−228 °C; IR (ATR) ν in cm^{-1} 3097 (w), 3058 (w), 2923 (m), 2857 (w), 1611 (m), 1566 (s), 1506 (s), 1454 (w), 1434 (w), 1401 (s), 1383 (s), 1371 (s), 807 (s), 708 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.98 (s, 1H), 8.16 (d, 1H, ^3J = 2.4 Hz), 7.62 (dd, 1H, ^3J = 4.1 Hz, ^4J = 1.3 Hz), 7.55 (d, 1H, ^3J = 2.4 Hz), 7.31 (dd, 1H, ^3J = 5.3 Hz, ^4J = 1.3 Hz), 7.13−7.08 (m, 1H), 3.21 (s, 12H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 169.8, 163.4, 156.6, 140.0, 132.9, 128.5, 126.9, 125.3, 124.7, 122.6, 118.6, 36.5, 36.4, 20.8; EI-MS, *m*/*z* (%) 356.1 (100). Anal. Calcd for $C_{18}H_{21}N_5OS$: C, 60.82; H, 5.95; N, 19.70. Found: C, 60.72; H, 5.62; N, 19.42.

Compound 19. Prepared according to general procedure 4: compound **17** (100.0 mg, 0.250 mmol), 4,4′,5,5′-tetramethyl-1,3,2-dioxaboronic ester of 3,4-ethylendioxythiophene (0.376 mmol, 100.7 mg, 1.5 equiv), and aqueous K_2CO_3 (69.2 mg, 0.500 mmol, 2 equiv) in toluene (8 mL). Column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 5:5 to CH_2Cl_2 as eluant to give compound **19** as a yellow powder (26.9 mg, 27%): mp 237−239 °C; IR (ATR) ν in cm^{-1} 2923 (m), 2866 (w), 1611 (m), 1566 (s), 1510 (s), 1435 (m), 1403 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.90 (s 1H), 8.12 (d, 1H, ^3J = 2.2 Hz), 7.76 (d, 1H, ^3J = 2.2 Hz), 6.38 (s, 1H), 4.31−4.23 (m, 4H), 3.29 (s, 12H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 169.9, 163.5, 156.8, 141.2, 138.2, 134.1, 128.1, 126.7, 120.8, 118.1, 113.6, 99.0, 64.8, 64.5, 36.3, 20.9; EI-MS, *m*/*z* (%) 413.1 (100). Anal. Calcd for $C_{20}H_{23}N_5O_3S$: C, 58.09; H, 5.61; N, 16.94. Found: C, 57.89; H, 5.32; N, 16.64.

Compound 20. A Schlenk tube was charged with a solution of 4,4-difluoro-1,3,5,7,8-pentamethyl-2-iodo-4-bora-3a,4a-diaza-s-indacene (100.0 mg, 0.258 mmol), trimethylsilylacetylene (26.6 mg, 0.271 mmol, 1.05 equiv) in a mixture of benzene/diisopropylamine (10 mL/2 mL). The solution was degassed with argon for 30 min, then [$Pd(PPh_3)_2Cl_2$] (10 mol %, 18.0 mg) and CuI (12 mol %, 5.9 mg) were added. The mixture was stirred at rt for one night (monitored by TLC). Compound **17** (103.0, 0.258 mmol), DBU (470.8 mg, 3.09 mmol, 12 equiv), and 40 mol % of H_2O were then added and the solution was stirred for an additional 10 days. The solution was then extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and evaporated under vacuum. The residue was purified by column chromatography on silica gel eluting with petroleum ether/CH_2Cl_2 9:1 to CH_2Cl_2 as eluant to give compound **20** as a purple powder (72.1 mg, 50%): mp dec >270 °C; IR (ATR) ν in cm^{-1} 2923 (w), 2867 (w), 1556 (s), 1511 (s), 1479 (m), 1446 (w), 1398 (s), 1195 (s), 1057 (s), 979 (s); ^1H NMR (200 MHz, $CDCl_3$) δ = 14.72 (s, 1H), 8.17 (d, 1H, ^3J = 1.9 Hz), 7.40 (d, 1H, ^3J = 1.9 Hz), 6.09 (s, 1H), 3.23 (s, 12H), 2.71 (s, 3H), 2.63 (s, 3H), 2.61 (s, 3H), 2.54 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 168.9, 165.7, 155.4, 152.2, 151.6, 151.1, 142.6, 137.0, 140.0, 133.0, 131.9, 130.6, 128.9, 129.4, 126.3, 122.8, 122.1, 105.3, 35.8, 21.05, 17.3, 17.0, 15.4, 14.3, 13.5; TOF HR-MS EI, exact mass 557.2880, calcd 557.2886 for $C_{30}H_{34}BF_2N_7O$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystal structure determination parameters for **8**, **13**, and **18**, as well as proton and carbon NMR traces for all compounds. Absorption, emission, and excitation spectra for each compound are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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