JOC The Journal of Organic Chemistry

Article

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Tetraaryl-, Pentaaryl-, and Hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles: Synthesis and Optical Properties

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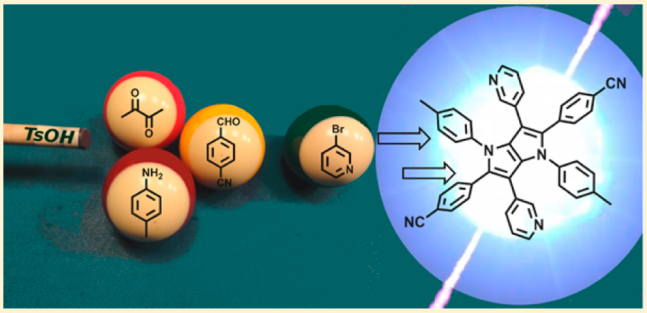
Supporting Information

ABSTRACT: Efficient conditions for the synthesis of tetra-, penta-, and hexasubstituted derivatives of 1,4-dihydropyrrolo-[3,2-*b*]pyrrole were developed. The tetraaryl derivatives were obtained in a novel one-pot reaction among aromatic aldehydes, aromatic amines, and butane-2,3-dione. After a thorough examination of various reaction parameters (solvent, acid, temperature) *p*-toluenesulfonic acid was identified as the crucial catalyst. As a result, 1,4-dihydropyrrolo[3,2-*b*]pyrroles were obtained in the highest yields reported to date. The scope and limitation studies showed that this new method was particularly efficient for sterically hindered aldehydes (yields 45−49%). Pentaaryl- and hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles were prepared from tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles via direct arylation by employing both electron-poor and electron-rich aromatic and heteroaromatic haloarenes. Strategic placement of electron-withdrawing substituents at the 2-, 3-, 5-, and 6-positions produced an acceptor−donor−acceptor type fluorophore. The resulting multiply substituted heteropentalenes displayed intriguing optical properties. The relationship between the structure and photophysical properties for all compounds were directly compared and thoroughly elucidated. All synthesized products displayed strong blue fluorescence and exhibited moderate to large Stokes shifts (3000−7300 cm^{-1}) as well as high quantum yields of fluorescence up to 88%. Two-photon absorption cross-section values measured in the near-IR region were surprisingly high (hundreds of GM), given the limited conjugation in these propeller-shaped dyes.



INTRODUCTION

The ongoing development of new fluorescent dyes has proved to be an applicable and relevant field of organic chemistry. Over recent years, applications for fluorescent probes have expanded and the need for dyes with diverse spectral and physicochemical properties has increased. Despite numerous available fluorophores, new dyes for more specialized applications including single-photon fluorescence imaging,[1] two-photon absorption, and two-photon fluorescence microscopy are still required.[2,3] In addition to classic fluorescent chemical platforms such as coumarins,[4−6] fluorescein,[7,8] and BODIPYs,[9−11] investigators continue to seek new scaffolds.[12−15]

1,4-Dihydropyrrolo[3,2-*b*]pyrroles are the least elaborated compounds among the family of 10-π-electron heterocycles called diheteropentalenes. The analogous thieno[3,2-*b*]-thiophene[16,17] and thieno[3,2-*b*]pyrrole[18] cores are well-known and have been thoroughly studied and widely utilized in diverse fields of research. Their electronic structures make them interesting from both theoretical and synthetic perspectives. They have attracted the greatest interest in such fields as optoelectronics[19] and polymers for organic light emitting diodes (OLEDs) and for other photovoltaic applications,[20] as well as organic dyes in dye-sensitized solar cells.[21] In addition to their ubiquity in materials science, thieno[3,2-*b*]thiophenes and thieno[3,2-*b*]pyrroles can be applied in biology and medicine.[22−24]

The 1,4-dihydropyrrolo[3,2-*b*]pyrrole scaffold was discovered in 1972 by Hemetsberger and Knittel.[25] Only a few methods for the synthesis of these cores were known until 2013, and they all require multiple-step syntheses and produce low overall yields. Mukai and co-workers obtained a derivative of 1,4-dihydropyrrolo[3,2-*b*]pyrrole in the reaction between 1,4-bis(trimethylsilyl)benzene and methyl azidoformate followed by subsequent oxidation by DDQ.[26,27] Dieck and co-workers reported the interesting methodology of treating diazasilacyclopentene with alcohol to generate N,N-disubstituted 1,4-dihydropyrrolo[3,2-*b*]pyrrole.[28] Suzukamo et al. developed the synthesis of asymmetrical 1,4-dihydropyrrolo[3,2-*b*]pyrroles utilizing derivatives of pyrrole-2-carboxyaldehyde in the Knoevenagel reaction with ethyl azidoacetate followed by thermal cyclization to form a new five-membered ring.[29] This method was improved by utilizing ruthenium salts to close the second pyrrole ring.[30] Recently, a new, versatile method for the

Received: February 3, 2014
Published: March 12, 2014

dx.doi.org/10.1021/jo5002643 | *J. Org. Chem.* 2014, 79, 3119−3128

synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles was discovered.[31] Despite numerous advantages such as the striking simplicity of this one-pot synthesis, inexpensive starting materials, and no requirement for tedious column chromatography purification, this method was hampered by low to mediocre yields.

The high fluorescence quantum yield of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles combined with their facile one-pot synthesis[31] have encouraged investigators to broaden the scope of their physicochemical properties and to extend their practical applications. However, to achieve this aim, more efficient synthetic methods are needed, and while there has been dramatic progress in past years,[29−31] we still have much to learn. For functional dyes based on an 1,4-dihydropyrrolo[3,2-*b*]pyrrole core to fulfill their full potential, we must address the issues of both stability and the ability to fine-tune the fluorescence. The multicomponent character of this process, as well as the promising optical properties of tetrasubstituted pyrrolo[3,2-*b*]pyrroles, prompted us to investigate whether they could be effectively arylated via direct arylation with aryl halides.

Herein, we present an enhanced protocol for the synthesis of tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles together with synthesis of pentaaryl- and hexaaryl-1,4-dihydropyrrolo[3,2-*b*]-pyrroles by means of a direct arylation reaction.

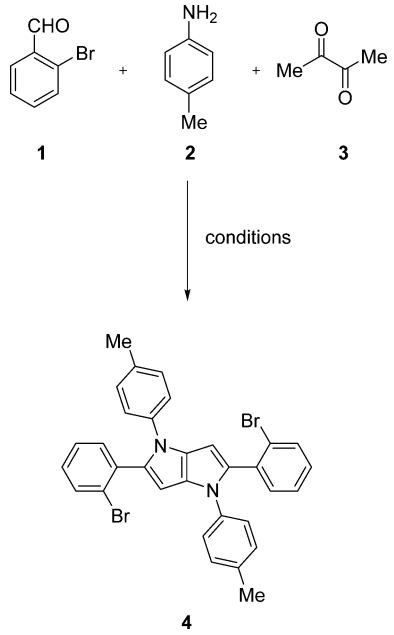
RESULTS AND DISCUSSION

To optimize the multicomponent reaction leading to tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles, 2-bromobenzaldehyde and *p*-toluidine were chosen as model substrates (Table 1). The reaction carried out under standard conditions (AcOH, 90 °C, 3 h) resulted in the formation of compound **4** in 35% yield (Table 1, entry 1). Conducting the reaction without solvent at elevated temperature (150 °C) using very strong acids such as triflic acid and *p*-toluenesulfonic acid led to tarry products, whereas reactions conducted with trifluoroacetic acid at 80 °C did not produce pyrrolo[3,2-*b*]pyrrole and the reaction stopped at the formation of the Schiff base (Table 1, entries 2−4). Since the proposed reaction mechanism[31] involved both acid- and base-catalyzed steps, we attempted to add various bases such as Et_3N, DBU, and KOAc with detrimental effect. On the other hand, the addition of a strong acid (either Brønsted or Lewis) in a catalytic amount (10 mol %) to the reaction mixture increased the yield of product **4**. While the utilization of sulfuric acid or TfOH as catalyst gave a rather negligible improvement, the addition of $AlCl_3$ and TFA, however, notably increased the yields (Table 1, entries 5−8). The best result was obtained for reactions in which *p*-toluenesulfonic acid was added in a 10 mol % amount—the yield of product **4** was improved to 49% (Table 1, entry 9). Addition of 20 mol % of TsOH did not increase the yield of heterocycle **4**. Finally, a control experiment under optimized conditions with equimolar amounts of TsOH led to a black tarry material (Table 1, entry 11).

After the optimal conditions (entry 9, AcOH, 90 °C for 3 h, 10 mol % of TsOH) were established for the desired transformation, the scope and limitations of this approach were investigated by testing a broad range of aldehydes and a variety of amines (Table 2). Aldehydes **5**−**11**, bearing either electron-withdrawing or electron-donating groups, and amines **2**, **12**, and **13** were employed (Table 2). The results showed that pyrrolo[3,2-*b*]pyrroles **14**−**23** could be obtained regardless of the substrate structures in yields of 22−49%.

The improved yields of desired heterocycles in comparison to the former protocol without TsOH[31] were even more significant

Table 1. Optimization of Reaction Conditions of Synthesis of Pyrrolo[3,2-*b*]pyrrole 4



entry	solvent	catalyst[a]	temp, °C	yield, %
1	AcOH		90	35
2	TfOH		150	tar
3	TsOH		150	tar
4	TFA		80	0
5	AcOH	TFA	90	46
6	AcOH	H_2SO_4	90	36
7	AcOH	$AlCl_3$	90	43
8	AcOH	TfOH	90	39
9	**AcOH**	**TsOH**	**90**	**49**
10	AcOH	TsOH[b]	90	49
11	AcOH	TsOH[c]	90	tar

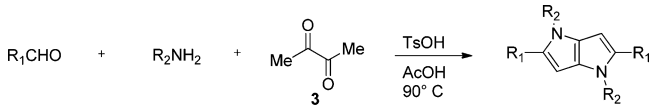
[a]10 mol % catalyst. [b]20 mol % catalyst. [c]Equimolar with aldehyde and amine.

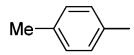
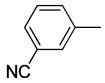
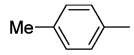
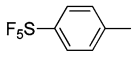
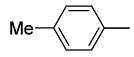
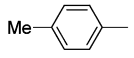
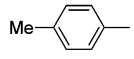
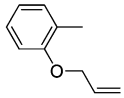
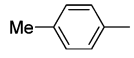
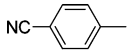
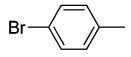
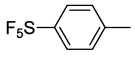
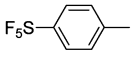
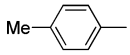
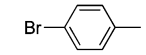
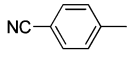
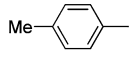
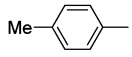
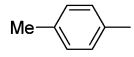
in some cases than in the model reaction. The biggest increase was observed in the reaction between 4-cyanobenzaldehyde (**10**) and 4-bromoaniline (**12**), in which the yield of compound **19** after addition of TsOH was almost 3-fold higher than in the reaction without catalyst (Table 2). Apparently, the electronic character of the group attached to the benzaldehydes and anilines strongly influenced the catalytic cycle of the reaction. For neutral and slightly electron donating groups such as H and CH_3, adding TsOH to the reaction mixture produced no relevant improvement of reaction yield (Table 2, compounds **16** and **23**), whereas for either electron-donating (methoxy, allyloxy) or electron-withdrawing (CN, SF_5) groups, yields were appreciably higher when catalyst was added (Table 2, compounds **15** and **17**−**20**). Surprisingly, sterically hindered benzaldehydes **1**, **8**, and **9** afforded high yields. The synthesis of compound **19** has been repeated on a 10 mmol scale, without decrease in the yield, affording ∼1.5 g of the product in one batch.

In contrast to thieno[3,2-*b*]thiophenes and furo[3,2-*b*]-furanes, the skeleton of pyrrolo[3,2-*b*]pyrroles offers the possibility to introduce a total of six (rather than four) different substituents at the heterocyclic core. This possibility allows the fine-tuning of the properties via, for example, addition of additional aryl substrates. Traditionally, Suzuki[32] or Stille[33]

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

Table 2. Synthesis of Compounds 4 and 14−23



Aldehyde	R_1	Amine	R_2	Pyrrolopyrrole	Yield[a]	Yield[b]
1		2		4	35%	49%
5		2		14	28%[c]	34%
6		2		15	21%	35%
7		2		16	33%[c]	34%
8		2		17	29%	45%
9		2		18	26%	45%
10		12		19	8%	23%
6		13		20	14%	26%
11		12		21	15%[c]	22%
10		2		22	30%[c]	37%
11		2		23	34%[c]	34%

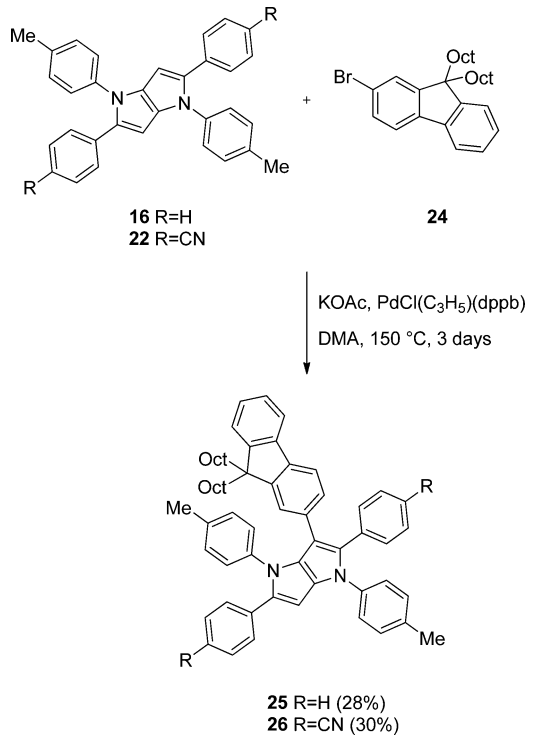
[a]Isolated yield without catalyst. [b]Isolated yield after addition of 10 mol % of TsOH. [c]Reference 31.

coupling would be employed to achieve this goal; however, we resolved to prepare these compounds by one of the newest methodologies, direct arylation of aromatic systems.[34−40] Various electron-rich aromatic heterocycles, such as pyrrole, indole, thiophene, imidazole, etc., have been successfully arylated to smoothly furnish biaryl linkages.[41−46]

Initially, the two heterocycles **16** and **22** were subjected to direct arylation with 2-bromo-9,9-dioctylfluorene (**24**) (Scheme 1). Compound **22** possesses peripheral cyano substituents, which are strong electron withdrawing groups, whereas dye **16** bears hydrogen atoms which are considered as neutral. Pyrrole[3,2-*b*]pyrrole with an electron-donating group in this position was intentionally omitted because of the intrinsic low stability of such donor−donor−donor systems.[31] In the direct arylation of electron-rich heterocycles, relatively simple conditions based on palladium catalysts such as $Pd(OAc)_2$ and $PdCl_2(PPh_3)_2$ are ubiquitous.[47,48] Unfortunately, these conditions were ineffective in the case of arylation of

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

Scheme 1



tetraarylpyrrolo[3,2-*b*]pyrroles. Steric hindrance may account for the reaction failure. Doucet and co-workers reported a method of direct arylation of sterically congested pyrroles in which the $PdCl(C_3H_5)$(allyl) complex was utilized as catalyst.[49−51] The application of this catalyst to reaction of heterocycles **16** and **22** with **24** generated monoarylated products **25** and **26** with reasonable yields (Scheme 1). Attempts to force this reaction to completion (i.e., bis-arylation) by increasing the reaction time failed.

Significantly the higher stability of **22** and **26** vs **16** and **25**, as well as the much higher fluorescence quantum yield of **26** as compared to that **25**, prompted us to use **22** as the exclusive substrate in further investigations.

Since the optical goal corroborated the synthetic objective, our particular choice of substrates was mostly based on the desire to investigate the reactivity of pyrrolo[3,2-*b*]pyrroles as well as on modulating the photophysical processes. Given these objectives, we chose the following aryl halides as pivotal building blocks: 2-bromo-9,9-dioctylfluorene (**24**), 4-pentafluorosulfanylbromobenzene (**27**), 4-nitrobromobenzene (**28**), 4-bromobenzonitrile (**29**), 3-bromopyridine (**30**), 4-bromopyridine hydrochloride (**31**), 4-bromoanisole (**32**), and 3,5-dimethoxybromobenzene (**33**) (Table 3). These bromoarenes were tested in reactions with pyrrolo[3,2-*b*]pyrrole **22**, under optimized reaction conditions. All reactions led to products of direct arylation (Table 3).

In the case of electron-donating bromoarenes, monoarylation products were almost exclusively formed. The opposite situation emerged when haloarenes with electron-withdrawing substituents were used. Substrates possessing electron-withdrawing groups such as 4-pentafluorosulfanylbromobenzene (**27**) and 4-nitrobromobenzene (**28**) displayed higher reactivity, and the main products formed were the bisarylated derivatives **39** and **40** of parent compound **22** (Table 3). 4-Bromobenzonitrile was the only exception. In this example the only product of direct arylation was the pentaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole **35**, which is the product of monoarylation. The replacement of 4-bromobenzonitrile (**29**) with 4-iodobenzonitrile had no significant effect on the final outcome (Table 3). Still, the higher yield of **35** (48% for iodide versus 37% for bromide) was observed as iodides are generally more reactive than the corresponding bromides.[40]

Given the significant interest in heteroacenes in the field of organic electronics[52−55] (especially organic thin-film transistors), we decided to investigate electrochemical properties of exemplary pyrrolo[3,2-*b*]pyrroles **15**, **16**, **18**, and **41** by cyclic voltammetry (Table 4 and the Supporting Information). Compounds **16** and **18** underwent two reversible oxidations, whereas **41** showed only one reversible oxidation at 0.32 V. Interestingly, for compound **15** the first reversible process is followed by a second quasi-reversible oxidation and then finally a third nonreversible oxidation (at 2.2 V). The last oxidation may be associated with electro-polymerization, which is often observed for pyrrole, thieno[3,2-*b*]thiophene, and analogous compounds. The decrease of first oxidation potentials follows (**15** > **16** > **18**) the intuitive increase in electron density imparted by the presence of electron-donating substituents in positions 2 and 5. No reduction of the pyrrolo[3,2-*b*]pyrrole core has been observed in the potential window scanned (±2.0 V). Negligible reduction peaks at −1.46 V for **18** and **41** are probably associated with reduction of pyridine etc. The HOMO energy levels (E_{HOMO}) were estimated from the first oxidation potentials (Table 4). They are slightly higher than those for indolo[3,2-*b*]carbazoles and for *S*,*N*-heterohexacenes reported by Bäuerle and Würthner.[54,55]

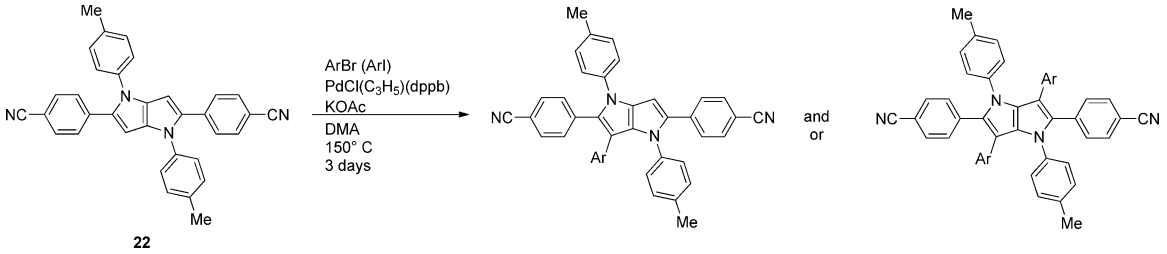
Optical Properties. We examined the effects of structural variations on the photophysical properties of all new pyrrolo[3,2-*b*]pyrroles. All compounds were dissolved in dichloromethane, and their optical properties were analyzed to assess the effect of each architectural modification (Table 5 and Figures 1−3).

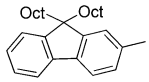
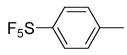
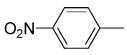
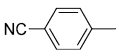
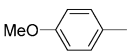
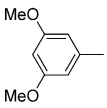
All of the dyes possessed strong absorption bands, which were typically located between 300 and 450 nm. These compounds exhibited molar extinction coefficients in the range of 18000−54000 M^{-1} cm^{-1}. The presence of electron-withdrawing substituents at positions 2 and 5 formed quadrupole-like push−pull systems, which are known to have bathochromically shifted absorption bands. Insertion of further substituents at positions 3 and 6 (either electron withdrawing or electron donating) to the 1,4-dihydropyrrolo[3,2-*b*]pyrrole core did not produce a further red shift of the absorption. In contrast, a slightly hypsochromic shift was observed. A rational interpretation of these findings may be based on the intrinsic tendency of the molecules to adopt a minimum energy state. Compounds **39**−**44** contained six aryl substituents in close proximity to each other, causing the steric hindrance, which in turn results in a nonplanar arrangement of these benzene rings. This orientation would break the conjugation and prevent an efficient overlapping of the orbitals, which is manifested as a hypsochromic shift of absorption and lowered molar extinction coefficient ε.

All investigated molecules, excluding compounds bearing the 4-nitrophenyl substituent (**34** and **40**) and one compound bearing a bromine atom (**4**), emitted violet, blue, or bluish green light. The absence of fluorescence for dyes **34** and **40** was expected due to the known quenching effect of the nitro group.[56] Intriguingly, pyrrole[3,2-*b*]pyrroles **4**, **19**, and **21** possessing bromine displayed different optical properties. The fluorescence of compound **4** was quenched due to the heavy-atom effect of Br,[56] whereas compound **21** possessed low but measurable fluorescence. On the other hand, product **19** with a bromine

dx.doi.org/10.1021/jo5002643 | *J. Org. Chem.* 2014, 79, 3119−3128

Table 3. Direct Arylation of Pyrrolo[3,2-*b*]pyrrole 22



Aryl halide	Ar	Monoarylation product	Yield (%)	Bisarylation product	Yield (%)
24		**26**	30	-	-
27		-	-	**39**	35
28		**34**	24	**40**	53
29		**35**	37 (48)[a]	-	-
30		**36**	21	**41**	47
31		-	-	**42**	56
32		**37**	34	**43**	11
33		**38**	29	**44**	12

[a]4-Iodobenzonitrile was used.

Table 4. Redox Potentials (V versus Fc/Fc$^+$) of Compounds 15, 16, 18, and 41

	$E^{1/2}_{ox1}$, V	$E^{1/2}_{ox2}$, V	E_{HOMO}, eV
15	0.40	1.00	−5.20
16	0.20	0.91	−5.00
18	−0.01	0.62	−4.81
41	0.32		−5.07

Cyclic voltammograms of compounds **15**, **16**, **18**, and **41** were measured in deoxygenated 0.1 M solutions of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane, using a glassy-carbon working electrode, a Ag/AgCl reference electrode, and a platinum-foil auxiliary electrode (scan rate v = 50 mV s^{-1}, Ar, 20 °C). All values of E (in V) are reported with respect to the Fc/Fc$^+$ redox potential.

atom in the same position as dye **21**, but with two cyano groups, exhibited an extremely high fluorescence quantum yield (86%). In contrast to absorption, attaching additional aryl or heteroaryl moieties directly to the parent core affected the slight bathochromic shift of fluorescence. We concluded that the geometry of such molecules allows for a higher degree of planarization in the excited state,[57] which translates to stronger emission shifts and hence larger Stokes shifts for these compounds. Additionally, pentaaryl- and hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles **34**−**44** exhibited fluorescence quantum yields (48−64%) that approached the values of the parent compound **22** (Table 5).

The location of the strongly electron withdrawing $F_5SC_6H_4$ substituent markedly affected the optical properties. Its presence at position 2 led to sharp decreases in fluorescence quantum yields (dyes **15** and **20**). On the other hand, the same substituent at position 3 (compound **39**) had no detrimental effect on Φ_{fl}. The presence of an additional 4-cyanophenyl substituent at position 3 red-shifted the emission ∼15 nm (**22** → **35**).

Two-photon absorption spectra of selected compounds were measured using TPFM (Figure 4). The measurements were conducted over the range of 700−1020 nm (corresponding to the relevant biological spectral window). In the spectral range of interest, two-photon absorption cross sections were strongly dependent on the magnitude of charge transfer. Indeed, dyes **26**, **35**, **39**, and **41** containing the strongly electron-withdrawing 4-cyanophenyl substituent gave relatively intense 2PA signals. Interestingly, the two-photon absorption of these quadrupolar molecules was typically within 300−700 GM at 700−720 nm.

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

Table 5. Spectroscopic Properties of Synthesized Dyes

compd	λ_{abs}, nm	λ_{em}, nm	Stokes shift, cm^{-1}	molar abs coeff ε_{max}, M^{-1} cm^{-1}	fluorescence quantum yield Φ_{fl}[a]
4	333			18000	
14[b]	368	462	5500	33000	0.17
15	382	434	3100	47000	0.01
16[b]	347	408	4300	33 000	0.62
17	338	414	5400	27000	0.40
18	336	414	5600	28000	0.62
19	399	454	3000	50000	0.86
20	378	426	3000	43000	0.05
21[b,c]	348	437	5800	33000	0.10
22[b]	405	459	3000	54000	0.88
23[b]	348	410	4300	37000	0.37
25	331	437	7300	40000	0.30
26	404	472	3600	40000	0.57
34	393			40000	
35	400	474	3900	43000	0.48
36	393	453	3400	43000	0.36
37	406	467	3200	43000	0.75
38	401	461	3200	43000	0.79
39	395	463	3800	36000	0.64
40	381			45000	
41	396	465	3800	36000	0.64
42	405	467	3300	30000	0.59
43	405	467	3300	48000	0.69
44	402	465	3400	38000	0.52

[a]Determined with quinine sulfate in H_2SO_4 (0.5 M) as a standard. [b]Reference 31. [c]Spectra measured in toluene.

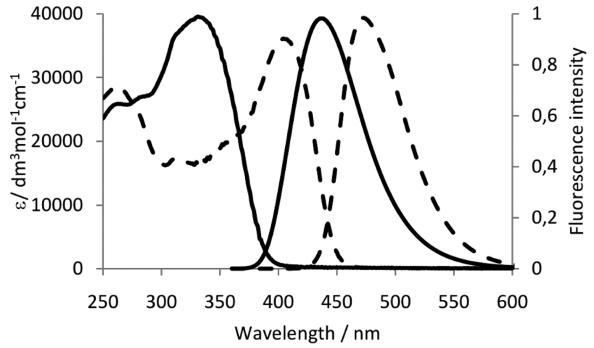


Figure 1. Absorption and emission spectra of compounds **25** (solid line) and **26** (dashed line) measured in dichloromethane.

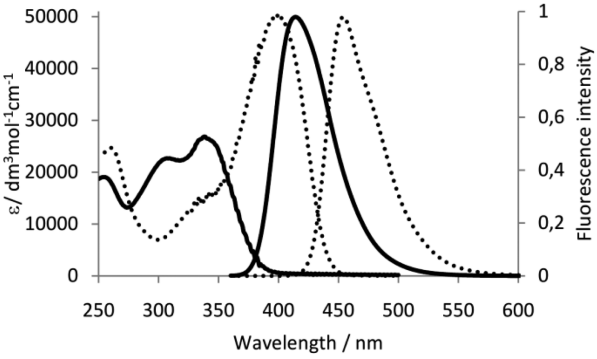


Figure 2. Absorption and emission spectra of PP **17** (solid line) and PP **19** (dotted line) measured in dichloromethane.

Indeed, the highest values σ_2 in the near-IR region of the spectrum were obtained for compounds **26** and **35** possessing

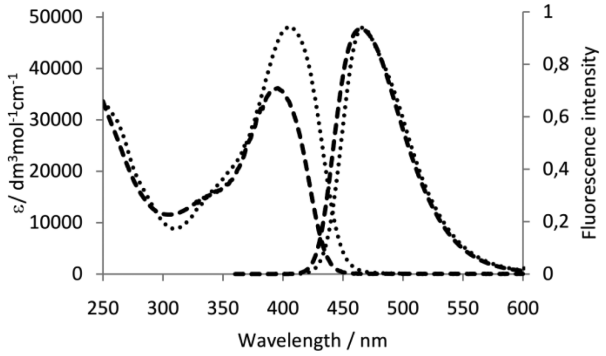


Figure 3. Absorption and emission spectra of compounds **41** (dashed line) and **43** (dotted line) measured in dichloromethane.

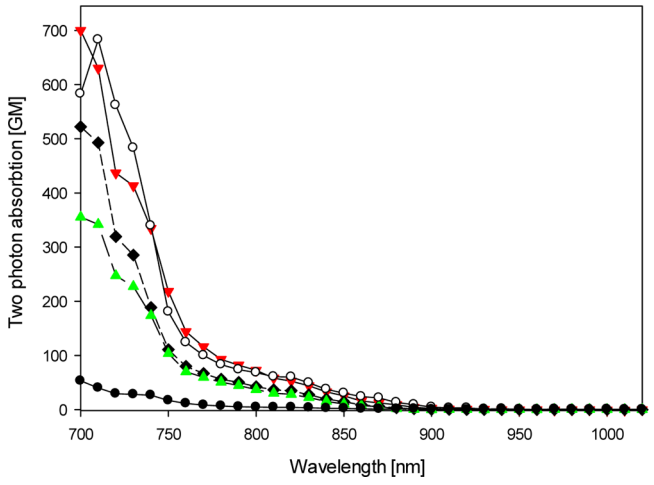


Figure 4. Two-photon absorption of compounds **35** (red ▼), **41** (black ◆), **39** (green ▲), **26** (black ○), and **25** (black ●).

either the additional strongly electron-withdrawing 4-cyanophenyl substituent or the fluorene moiety known to increase 2PA (Figure 4).[58] Ultimately, the critical figure of merit, i.e., the two-photon brightness, was the highest for dye **26** (~400 GM).[59] As illustrated in Figure 4 for compounds **25**, **26**, **35**, **39**, and **41**, the lowest (strongly one-photon allowed) excited state is moderately intense and the higher (only weakly one-photon allowed) state, responsible for the large 2PA response, is located below 700 nm. This feature is reminiscent of the behavior of typical symmetrical quadrupolar derivatives.[2]

■ CONCLUSION

In conclusion, we have developed a refined and versatile procedure for the preparation of pure tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles directly from readily available aromatic aldehydes and primary aromatic amines. By identifying the issue of the activation of one of the substrates by sulfonic acids and by tailoring the reaction conditions accordingly, yields of a broad range of pyrrolo[3,2-*b*]pyrroles have been improved by as much as a factor of 3. This one-pot methodology is particularly efficient for substrates possessing strong electron-withdrawing groups such as CN and SF_5 and for sterically hindered aldehydes. The yields of products (up to 49%) were satisfactory, considering the complex mechanism of this process. Straightforward purification by filtration and recrystallization, without the need for column chromatography, makes this an optimal reaction method for the synthesis of tetrasubstituted pyrrolo[3,2-*b*]pyrroles.

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

Pentaaryl- and hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles were synthesized directly from the parent tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrrole and various aryl and heteroaryl bromides. The scope and limitations of this reaction were studied. Our observation confirmed the general trend that electron-poor aryl bromides are more reactive than electron-rich ones. In the case of the former, hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles were formed as the main product, while pentaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles were favored in the latter case. Almost all derivatives exhibited strong blue fluorescence (Φ_{fl} up to 88%). Other notable findings are as follows. (1) The propeller-like conformation of hexaarylpyrrolo[3,2-*b*]pyrroles translates to limited conjugation in the ground state and hence hypsochromic shifts of absorption/emission. (2) The heavy-atom effect of bromine is somehow neutralized by the quadrupolar nature of heteropentalenes bearing two 4-CNC_6H_4 substituents. (3) In spite of limited conjugation, the two-photon absorption cross section is rather high, most probably due to the strongly electron rich character of the pyrrolo[3,2-*b*]pyrrole core. These results are significant in that they provide a comprehensive study of the optical properties of tetraaryl, pentaaryl, and hexaaryl derivatives of 1,4-dihydropyrrolo[3,2-*b*]pyrroles and may also open the door to practical applications.

EXPERIMENTAL SECTION

General Remarks. All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes) were distilled prior to use. DMF was dried over magnesium sulfate and then distilled and stored under argon. Transformations with moisture- and oxygen-sensitive compounds were performed under a stream of argon. The reaction progress was monitored by means of thin-layer chromatography (TLC), which was performed on aluminum foil plates, covered with silica gel 60 F_{254} or aluminum oxide 60 F_{254} (neutral). Product purifications were done by means of column chromatography with Kieselgel 60 or aluminum oxide. Occasionally, dry column vacuum chromatography (DCVC) was performed for purification of products using silica gel Type D 5F. The identity and purity of prepared compounds were proved by ^{1}H NMR and ^{13}C NMR spectrometry as well as by mass spectrometry (via EI-MS or ESI-MS). HRMS (ESI-TOF) and HRMS (EI): double-focusing magnetic sector instruments with EBE geometry were utilized. NMR spectra were measured on 500, 600, or 200 MHz instruments with TMS as internal standard. All chemical shifts are given in ppm. All melting points for crystalline products were measured with an automated melting point apparatus and are given without correction. The absorbance and fluorescence spectra were measured in dichloromethane.

General Procedure for the Synthesis of Pyrrolo[3,2-*b*]pyrroles 4 and 14−23. In a 25 mL round-bottom flask equipped with a reflux condenser and magnetic stir bar, glacial acetic acid (2 mL) was placed followed by the addition of arylamine (2 mmol), aldehyde (2 mmol), and TsOH (0.2 mmol). The mixture was stirred at 90 °C for 30 min. After that time, butane-2,3-dione (1 mmol) was slowly added via syringe and the resulting mixture was stirred at 90 °C for 3 h. The reaction mixture was then cooled to room temperature. The precipitate of the obtained dye was isolated by filtration and washed with cooled glacial acetic acid. Recrystallization from AcOEt and drying under vacuum afforded pure product.

*2,5-Bis(2-bromophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**4**).* Yellowish solid. Yield: 291 mg (49%). R_f = 0.68 (SiO_2, AcOEt/hexanes, 1/4). Mp: 239−241 °C (AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, *J* 8.1, 1.1 Hz, 2H), 7.28 (dd, *J* 7.6, 1.7 Hz, 2H), 7.20 (dt, *J* 7.5, 1.1 Hz, 2H), 7.11−7.09 (m, 10H), 6.45 (s, 2H), 2.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.4, 135.1, 134.7, 133.4, 133.1, 133.0, 129.8, 129.5, 128.6, 126.9, 124.4, 124.0, 96.3, 20.9. HRMS (EI): calcd for $C_{32}H_{24}N_2Br_2$ 594.0306 [M^+], found 594.0305. Anal. Calcd for $C_{32}H_{24}Br_2N_2$: C, 64.45; H, 4.06; Br, 26.80; N, 4.70. Found: C, 64.51; H, 4.24; Br, 26.78; N, 4.52. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 306 (19), 333 (18) nm.

*2,5-Bis(3-cyanophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**14**).* Yellow solid. Yield: 166 mg (34%). R_f = 0.52 (SiO_2, AcOEt/hexanes, 1:2). Mp: 314−316 °C (AcOEt). Spectral and physical properties concurred with published data.[31]

*1,4-Bis(4-methylphenyl)- 2,5-bis(4-(pentafluoro-λ^6-sulfanyl)-phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**15**).* Yellowish solid. Yield: 241 mg (35%). R_f = 0.70 (SiO_2, AcOEt/hexanes, 1/4). Mp: 322−324 °C (AcOEt, decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, *J* 8.8 Hz, 4H), 7.26−7.21 (m, 8H), 7.16 (d, *J* 8.2 Hz, 4H), 6.43 (s, 2H), 2.41 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.9, 136.8, 136.4, 134.5, 133.0, 130.1, 127.3, 125.8, 125.2, 95.6, 21.1. HRMS (EI): calcd for $C_{32}H_{24}F_{10}N_2S_2$ 690.1221 [M^+], found 690.1230. Anal. Calcd for $C_{32}H_{24}F_{10}N_2S_2$: C, 55.65; H, 3.50; F, 27.51; N, 4.06; S, 9.29. Found: C, 55.64; H, 3.50; N, 4.12; F, 27.41; S, 9.18. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 381 (41) nm.

*2,5-Diphenyl-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**16**).* Beige solid. Yield: 145 mg (34%). R_f = 0.86 (SiO_2, EtOAc/hexanes, 1/4). Mp: 239−244 °C (AcOEt). Spectral and physical properties concurred with published data.[31]

*2,5-Bis(2-methoxyphenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**17**).* Beige solid. Yield: 224 mg (45%). R_f = 0.61 (SiO_2, AcOEt/hexanes, 1/4). Mp: 286−289 °C (AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, *J* 7.4 Hz, *J* 1.3 Hz, 2H), 7.23 (dt, *J* 8.8 Hz, *J* 1.4 Hz, 2H), 7.13 (d, *J* 8.2 Hz, 4H), 7.06 (d, *J* 8.2 Hz, 4H), 6.92 (t, *J* 7.4 Hz, 2H), 6.75 (d, *J* 8.2 Hz, 2H), 6.37 (s, 2H), 3.37 (s, 6H), 2.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 138.6, 134.1, 131.8, 131.6, 130.0, 129.1, 128.4, 123.7, 123.4, 120.5, 111.0, 95.0, 54.9, 20.9. HRMS (EI): calcd for $C_{34}H_{30}N_2O_2$ 498.2307 [M^+], found 498.2309. Anal. Calcd for $C_{34}H_{30}N_2O_2$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.62; H, 6.28; N, 5.39. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 309 (23), 338 (27) nm.

*2,5-Bis(2-(allyloxy)phenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**18**).* Beige solid. Yield: 248 mg (45%). R_f = 0.65 (SiO_2, AcOEt/hexanes, 1/4). Mp: 203−204 °C (AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, *J* 7.5 Hz, *J* 1.7 Hz, 2H), 7.20 (dt, *J* 7.5 Hz, *J* 1.7 Hz, 2H), 7.14 (AA′XX′, 4H), 7.05 (d, *J* 8.2 Hz, 4H), 6.92 (dt, *J* 7.4 Hz, *J* 0.6 Hz, 2H), 6.76 (d, *J* 8.2 Hz, 2H), 6.39 (s, 2H), 5.64−5.55 (m, 2H), 5.10−5.04 (m, 4H), 4.20−4.16 (m, 4H), 2.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 138.7, 134.1, 133.8, 131.8, 130.1, 129.2, 128.3, 124.0, 123.3, 120.6, 116.8, 112.5 95.4, 68.9, 20.9. HRMS (EI): calcd for $C_{38}H_{34}N_2O_2$ 550.2620 [M^+], found 550.2635. Anal. Calcd for $C_{38}H_{34}N_2O_2$: C, 82.88; H, 6.22; N, 5.09. Found: C, 83.05; H, 6.32; N, 5.09. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 308 (24), 336 (28) nm.

*1,4-Bis(4-bromophenyl)-2,5-bis(4-cyanophenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**19**).* Yellow solid. Yield: 142 mg (23%). R_f = 0.56 (SiO_2, AcOEt/hexanes, 1/4). Mp: 351−353 °C (AcOEt, dec). ^{1}H NMR (500 MHz, $CDCl_3$,): δ 7.55 (AA′XX′, 4H), 7.52 (AA′XX′, 4H), 7.27 (AA′XX′, 4H), 7.13 (AA′XX′, 4H) 6.47 (s, 2H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.2, 137.1, 135.1, 133.1, 132.8, 132.2, 128.0, 126.7, 120.2, 118.8, 109.8, 96.6. HRMS (EI): calcd for $C_{32}H_{18}N_4Br_2$ 615.9898 [M^+], found 615.9924. Anal. Calcd for $C_{32}H_{18}Br_2N_4$: C, 62.16; H, 2.93; Br, 25.85; N, 9.06. Found: C, 62.11; H, 3.03; Br, 25.94; N, 9.15. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 399 (50) nm.

*1,2,4,5-Tetrakis(4-(pentafluoro-λ^6-sulfanyl)phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**20**).* Yellowish solid. Yield: 238 mg (26%). R_f = 0.67 (SiO_2, AcOEt/hexanes, 1/4). Mp: 329−331 °C (AcOEt). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* 8.2 Hz, 4H), 7.68 (d, *J* 8.2 Hz, 4H), 7.34 (d, *J* 8.1 Hz, 4H), 7.28 (d, *J* 8.1 Hz, 4H) 6.54 (s, 2H) ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.2, 141.7, 135.7, 134.8, 132.5, 127.7, 127.6, 126.4, 124.6, 97.9. HRMS (EI): calcd for $C_{30}H_{18}F_{20}N_2S_4$ 914.0034 [M^+], found 914.0029. Anal. Calcd for $C_{30}H_{18}F_{20}N_2S_4$: C, 39.39; H, 1.98; F, 41.54; N, 3.06; S, 14.02. Found: C, 39.57; H, 2.06; F, 41.32; N, 3.09; S, 14.18. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 319 (23), 376 (42) nm.

*1,4-Bis(4-bromophenyl)-2,5-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**21**).* White solid. Yield: 133 mg (22%). R_f = 0.71 (SiO_2, AcOEt/hexanes, 1/4). Mp: 297−298 °C (AcOEt). Spectral and physical properties concurred with published data.[31]

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**22**).* Yellow-green solid. Yield: 180 mg (37%). R_f

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

= 0.65 (SiO_2, CH_2Cl_2). Mp: 319−321 °C (AcOEt). Spectral and physical properties concurred with published data.[31]

*1,2,4,5-Tetra(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**23**).* White solid. Yield: 158 mg (34%). R_f = 0.71 (SiO_2, AcOEt/hexanes, 1/4). Mp: 261−262 °C (AcOH). Spectral and physical properties concurred with published data.[31]

General Procedure for the Synthesis of Pentaaryl- and Hexaaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles 25, 26, and 34−44. The parent 1,4-dihydropyrrolo[3,2-*b*]pyrrole (0.25 mmol), aryl bromide (or iodide) (1 mmol), KOAc (1 mmol), and $PdCl(C_3H_5)$-(dppb) (0.01 mmol) were placed in a 25 mL Schlenk flask, which was flushed with argon prior to use. Then 8 mL of dry DMA was added and the resulting mixture was stirred at 150 °C for 3 days. The product was purified by means of flash column chromatography and then recrystallized from toluene or ethyl acetate. The obtained crystals were dried under reduced pressure.

*3-(9,9-Dioctyl-9H-fluoren-2-yl)- 2,5-diphenyl-1,4-bis(4-methylphenyl)dihydropyrrolo[3,2-b]pyrrole (**25**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1/1). Yield: 140 mg (28%). R_f = 0.73 (SiO_2, AcOEt/hexanes, 1:2). Mp: 67−68 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* 7.5 Hz, 1H), 7.31−7.26 (m, 1H), 7.26−7.22 (m, 2H), 7.19−7.10 (m, 10H), 7.05−6.97 (m, 5H), 6.86 (d, *J* 0.9 Hz, 1H), 6.83−6.79 (AA′XX′, 2H), 6.73 (d, *J* 8.2 Hz, 1H), 6.63 (dd, *J* 7.8 Hz, *J* 1.4 Hz, 1H), 6.46 (s, 1H), 2.35 (s, 3H), 2.21 (s, 3H), 1.75 (dt, *J* 12.7 Hz, *J* 4.8 Hz, 2H), 1.59 (dt, *J* 12.7 Hz, *J* 4.8 Hz, 2H), 1.25−1.17 (m, 4H), 1.17−1.07 (m, 8H), 1.06−0.98 (m, 4H), 0.97−0.90 (m, 4H), 0.82 (t, *J* 7.0 Hz, 6H), 0.53−0.39 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.8, 149.7, 141.4, 138.5, 137.5, 136.5, 136.3, 135.8, 135.0, 133.8, 133.1, 132.6, 132.3, 131.0, 130.0, 129.9, 129.55, 129.49, 128.7, 128.4, 128.0, 127.6, 127.2, 126.50, 126.46, 126.04, 125.97, 125.3, 125.1, 122.7, 119.2, 118.1, 110.8, 93.3, 54.6, 40.4, 31.8, 30.1, 29.42, 29.39, 23.6, 22.6, 21.0, 14.1. HRMS (ESI) calcd for $C_{61}H_{66}N_2$ 826.5226 [M^+], found 826.5225. Anal. Calcd for $C_{61}H_{66}N_2$: C, 88.57; H, 8.04; N, 3.39. Found: C, 88.36; H, 8.14; N, 3.24. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 331 (40) nm.

*2,5-Bis(4-cyanophenyl)-3-(9,9-dioctyl-9H-fluoren-3-yl)-1,4-bis(4-methylphenyl)dihydropyrrolo[3,2-b]pyrrole (**26**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1/1). Yield: 66 mg (30%). R_f = 0.66 (SiO_2, AcOEt/hexanes, 1/4). Mp: 229−231 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* 7.2 Hz, 1H), 7.42 (AA′XX′, 2H), 7.35−7.31 (m, 1H), 7.30−7.27 (m, 3H), 7.27−7.25(m, 1H), 7.22−7.17 (m, 5H), 7.11 (AA′XX′, 2H), 7.07 (AA′XX′, 2H), 6.85 (s, 1H), 6.78 (s, 4H), 6.64 (dd, *J* 7.7 Hz, *J* 1.3 Hz, 1H), 6.54 (s, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 1.84−1.76 (m, 2H), 1.66−1.60 (m, 2H), 1.24−1.18 (m, 4H), 1.18−1.12 (m, 8H), 1.08−1.01 (m, 4H1.01−0.93 (m, 4H), 0.82 (t, *J* 7.0 Hz, 6H), 0.49 (quint, *J* 7.8 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 150.2, 140.9, 139.4, 137.8, 137.0, 136.9, 136.7, 136.2, 135.6, 131.9, 131.72, 131.69, 131.5, 131.4, 131.3, 130.8, 130.0, 129.7, 129.2, 127.9, 127.1, 127.0, 126.7, 125.3, 125.0, 122.8, 119.4, 119.1, 118.8, 118.6, 112.3, 109.1, 109.0, 94.7, 54.8, 40.3, 31.8, 30.0, 29.5, 29.3, 23.7, 22.6, 21.0, 14.1. HRMS (ESI) calcd for $C_{63}H_{64}N_4$ 876.5131 [M^+], found 876.5124. Anal. Calcd for $C_{63}H_{64}N_4$: C, 86.26; H, 7.35; N, 6.39. Found: C, 86.02; H, 7.38; N, 6.30. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 404 (40) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3-(4-nitrophenyl)dihydropyrrolo[3,2-b]pyrrole (**34**).* Orange solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1/1). Yield: 36 mg (24%). R_f = 0.51 (SiO_2, AcOEt/hexanes, 1/4). Mp: 344−346 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (AA′XX′, 2H), 7.44 (AA′XX′, 2H), 7.39 (AA′XX′, 2H), 7.20 (t, *J* 8.5 Hz, 4H), 7.08 (AA′XX′, 2H), 7.03 (AA′XX′, 2H), 6.95 (d, *J* 8.0 Hz, 2H), 6.84−6.81 (m, 2H), 6.51 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.9, 140.4, 138.0, 137.4, 136.9, 136.22, 136.19, 136.1, 135.9, 131.9, 131.8, 131.1,, 130.1, 129.6, 128.0, 127.5, 125.5, 122.7, 119.0, 118.6, 110.3, 109.4, 94.5, 21.1. HRMS (EI): calcd for $C_{40}H_{27}N_5O_2$ 609.2165 [M^+], found 609.2184. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 393 (40) nm.

*2,3,5-Tris(4-cyanophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**35**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1/1−3/1). Yield: 71 mg (48%). R_f = 0.41 (SiO_2, AcOEt/hexanes, 1/4). Mp: 325−326 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, *J* 8.2 Hz, 2H), 7.38 (d, *J* 8.2 Hz, 2H), 7.24−7.16 (m, 6H), 7.07 (d, *J* 8.1 Hz, 2H), 7.00 (d, *J* 8.2 Hz, 2H), 6.94 (d, *J* 7.9 Hz, 2H), 6.82−6.77 (m, 4H), 6.50 (s, 1H), 2.39 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 137.8, 137.4, 136.8, 136.3, 136.10, 136.08, 135.9, 131.9, 131.79, 131.75, 131.19, 131.18, 131.1, 130.7, 130.1, 129.5, 128.0, 127.4, 125.4, 118.96, 118.95, 118.7, 110.1, 109.5, 109.4, 109.3, 94.5, 21.08, 21.04. HRMS (EI): calcd for $C_{41}H_{27}N_5$ 589.2266 [M^+], found 589.2259. Anal. Calcd for $C_{41}H_{27}N_5$: C, 83.51; H, 4.62; N, 11.88. Found: C, 83.47; H, 4.63; N, 11.72. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 400 (43) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3-(pyridin-3-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**36**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/MeOH 95/5). Yield: 30 mg (21%). R_f = 0.71 (SiO_2, CH_2Cl_2/MeOH, 95/5). Mp: 319−320 °C (toluene, dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (d, *J* 2.0 Hz, 1H), 8.02 (s, 1H), 7.43 (d, *J* 7.8 Hz, 2H), 7.36 (d, *J* 7.8 Hz, 2H) 7.23−7.17 (m, 4H), 7.09 (d, *J* 7.6 Hz, 2H), 7.04−6.98 (m, 3H), 6.95−6.88 (m, 3H), 6.80 (d, *J* 7.5 Hz, 2H), 6.52 (s, 1H), 2.39 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 147.0, 137.9, 137.6, 137.5, 136.6, 136.3, 136.2, 136.0, 135.6, 132.1, 131.9, 131.8, 131.7, 131.3, 131.0, 130.1, 129.6, 129.3, 127.9, 127.3, 125.4, 122.4, 119.0, 118.8, 109.9, 109.2, 107.2, 94.5, 21.09, 21.04. HRMS (EI): calcd for $C_{39}H_{27}N_5$ 565.2266 [M^+], found 565.2280. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 395 (33) nm.

*2,5-Bis(4-cyanophenyl)-3-(4-methoxyphenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**37**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, AcOEt/hexanes 1/4). Yield: 50 mg (34%). R_f = 0.45 (SiO_2, AcOEt/hexanes, 1/4). Mp: 298−300 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, *J* 8.3 Hz, 2H), 7.33 (d, *J* 8.3 Hz, 2H), 7.20 (d, *J* 8.3 Hz, 2H), 7.17 (d, *J* 8.3 Hz, 2H), 7.08 (d, *J* 8.1 Hz, 2H), 7.03 (d, *J* 8.2 Hz, 2H), 6.89 (d, *J* 8.0 Hz, 2H), 6.78 (d, *J* 8.1 Hz, 2H), 6.62 (d, *J* 8.5 Hz, 2H), 6.52 (d, *J* 6.8 Hz, 2H), 6.51 (s, 1H), 3.75 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 137.8, 137.1, 136.8, 136.7, 136.1, 135.8, 135.6, 131.9, 131.7, 131.7, 131.6, 131.4, 130.9, 130.0, 129.2, 129.0, 128.2, 127.9, 127.2, 125.3, 125.0, 113.1, 111.3, 109.1, 108.9, 94.6, 55.2, 21.04, 21.02. HRMS (EI): calcd for $C_{41}H_{30}N_4O$ 594.2420 [M^+], found 594.2430. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 406 (43) nm.

*2,5-Bis(4-cyanophenyl)-3-(3,5-dimethoxyphenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**38**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, AcOEt/hexanes 1/4). Yield: 45 mg (29%). R_f = 0.43 (SiO_2, AcOEt/hexanes, 1/4). Mp: 340−342 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (AA′XX′, 2H), 7.35 (AA′XX′, 2H), 7.21 (AA′XX′, 2H), 7.17 (d, *J* 8.0 Hz, 2H), 7.08 (m, 4H), 6.92 (AA′XX′, 2H), 6.80 (AA′XX′, 2H), 6.51 (s, 1H), 6.23 (t, *J* 2.2 Hz, 1H), 5.89 (d, *J* 2.2 Hz, 2H), 3.43 (s, 6H), 2.39 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 137.8, 137.0, 136.6, 136.3, 135.9, 135.6, 134.6, 131.9, 131.7, 131.5, 131.4, 131.0, 130.9, 130.0, 129.2, 128.0, 127.3, 125.4, 119.08, 119.05, 111.6, 109.3, 109.2, 108.8, 99.3, 94.8, 54.8 21.02, 20.93. HRMS (EI): calcd for $C_{42}H_{32}N_4O_2$ 624.2525 [M^+], found 624.2542. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 401 (43) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3,6-bis(4-(penta-fluoro-λ^6-sulfanyl)phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**39**).* Yellow-greenish solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 1/1−3/1). Yield: 78 mg (35%). R_f = 0.56 (SiO_2, AcOEt/hexanes, 1/4). Mp: 330−331 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (AA′XX′, 4H), 7.30 (AA′XX′, 4H), 7.01 (AA′XX′, 4H), 6.86 (d, *J* 8.0 Hz, 4H), 6.78 (d, *J* 8.5 Hz, 4H), 6.70 (AA′XX′, 4H), 2.29 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.6 (m), 137.8, 136.8, 135.9, 135.2, 132.3, 131.8, 131.1, 130.4, 129.5, 129.4, 127.4, 125.2 (m), 125.1, 118.7, 110.2, 108.0, 20.8. HRMS (EI): calcd for $C_{46}H_{30}N_4F_{10}S_2$ 892.1752 [M^+], found 892.1734. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 395 (33) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3,6-bis(4-nitrophenyl)dihydropyrrolo[3,2-b]pyrrole (**40**).* Orange solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/hexanes 2/1) Yield: 97 mg (53%). R_f = 0.42 (SiO_2, AcOEt/hexanes, 1/4). Mp: 354−356 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79 (AA′XX′, 4H), 7.35 (AA′XX′, 4H), 6.98 (AA′XX′, 4H), 6.91 (d, *J* 8.0

dx.doi.org/10.1021/jo5002643 | J. Org. Chem. 2014, 79, 3119−3128

Hz, 4H), 6.82 (AA′XX′, 4H), 6.77 (AA′XX′, 4H), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8, 140.0, 138.2, 135.8, 135.2, 133.3, 131.8, 131.4, 131.0, 129.5, 129.2, 127.6, 124.8, 122.8, 118.5, 110.6, 108.0, 21.1. HRMS (EI): calcd for $C_{46}H_{30}N_6O_4$ 730.2329 [M^+], found 730.2345. Anal. Calcd for $C_{46}H_{30}N_6O_4$: C, 75.60; H, 4.14; N, 11.50. Found: C, 75.56; H, 4.20; N, 11.41. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 381 (45) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3,6-bis(pyridin-3-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**41**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/MeOH 95/5). Yield: 76 mg (47%). R_f = 0.55 (SiO_2, CH_2Cl_2/MeOH, 95/5). Mp: 345−347 °C (toluene, dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, *J* 3.0 Hz, 2H), 8.01 (s, 2H), 7.32 (d, *J* 8.2 Hz, 4H), 7.01 (d, *J* 7.6 Hz, 2H), 6.97 (d, *J* 8.2 Hz, 4H), 6.93−6.86 (m, 6H), 6.75 (d, *J* 8.0 Hz, 4H), 2.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 147.0, 137.8, 137.6, 136.1, 135.1, 133.1, 131.7, 131.2, 129.5, 129.4, 129.2, 127.4, 122.5, 118.7, 110.1, 106.1, 21.1. HRMS (EI): calcd for $C_{44}H_{30}N_6$ 642.2532 [M^+], found 642.2521. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 396 (36) nm.

*2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-3,6-bis(pyridin-4-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**42**).* Yellow solid. Product was purified by means of flash column chromatography (SiO_2, CH_2Cl_2/MeOH 95/5). Yield: 91 mg (56%). R_f = 0.56 (SiO_2, CH_2Cl_2/MeOH, 95/5). Mp: 345−347 °C (toluene, dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (s, 4H), 7.35 (d, *J* 6.9 Hz, 4H), 7.00 (d, *J* 6.9 Hz, 4H), 6.93 (d, *J* 6.2 Hz, 4H), 6.77 (d, *J* 6.2 Hz, 4H), 6.57 (s, 4H), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 141.4, 138.1, 135.9, 135.3, 133.3, 131.8, 131.4, 129.5, 129.1, 127.7, 125.3, 118.5, 110.6, 107.3, 21.0. HRMS (EI): calcd for $C_{44}H_{30}N_6$ 642.2532 [M^+], found 642.2529. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 405 (30) nm.

*2,5-Bis(4-cyanophenyl)-3,6-bis(4-methoxyphenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**43**).* Yellow solid. The product was purified by means of flash column chromatography (SiO_2, AcOEt/hexanes 1/4). Yield: 21 mg (12%). R_f = 0.39 (SiO_2, AcOEt/hexanes, 1/4). Mp: 292−294 °C (toluene). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.45 (AA′XX′, 4H), 7.05 (AA′XX′, 4H), 6.86 (AA′XX′, 4H), 6.77 (AA′XX′, 4H), 6.64 (AA′XX′, 4H), 6.51 (AA′XX′, 4H), 3.67 (s, 6H), 2.22 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 137.2, 136.5, 135.8, 132.3, 131.8, 131.3, 131.1, 129.7, 129.0, 127.5, 125.3, 119.1, 113.1, 110.1, 109.0, 55.2, 21.0. HRMS (EI): calcd for $C_{48}H_{36}N_4O_2$ 700.2838 [M^+], found 700.2860. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 405 (48) nm.

*2,5-Bis(4-cyanophenyl)-3,6-bis(3,5-dimethoxyphenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**44**).* Yellow solid. Product was purified by means of flash column chromatography (SiO_2, AcOEt/hexanes 1/4). Yield: 21 mg (11%). R_f = 0.37 (SiO_2, AcOEt/hexanes, 1/4). Mp: 329−331 °C (toluene). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (AA′XX′, 4H), 7.01 (AA′XX′, 4H), 6.88 (AA′XX′, 4H), 6.74 (AA′XX′, 4H), 6.23 (t, *J* 2.2 Hz, 1H), 5.89 (d, *J* 2.2 Hz, 2H), 3.42 (s, 12H), 2.30 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 136.9, 136.8, 135.7, 134.6, 132.3, 131.4, 131.2, 129.2, 129.0, 127.6, 119.1, 110.5, 109.3, 108.8, 99.3, 54.8, 20.9. HRMS (EI): calcd for $C_{50}H_{40}N_4O_4$ 760.3050 [M^+], found 760.3065. λ_{abs} (CH_2Cl_2, $\varepsilon \times 10^{-3}$): 402 (38) nm.

Linear Optical Measurements. Steady-state fluorescence measurements were performed on dilute solutions (ca. 10^{-6} M, optical density <0.1) contained in standard 1 cm quartz cuvettes. Compounds were dissolved in dichloromethane unless otherwise noted. Emission spectra were obtained, for each compound, under excitation at the wavelength of 350 nm. Fluorescence quantum yields were measured using quinine hemisulfate hydrate in 0.5 M sulfuric acid as a standard.

Two-Photon Fluorescence Intensity Measurements. Dichloromethane (CHROMASOLV, for HPLC, ≥99.9%), methanol (CHROMASOLV, for HPLC, ≥99.9), 5-Carboxyfluorescein (99% (HPLC)), Rhodamine B, and Rhodamine 6G were purchased from Sigma-Aldrich, Denmark. The samples were dissolved in dichloromethane, and Rh B and Rh 6G were dissolved in methanol. The fluorescein was dissolved in a CAPS buffer (*N*-cyclohexyl-3-aminopropanesulfonic acid), pH 11. Concentrations of the samples and references where determined by a dilution series in a spectrophotometer (Perkin-Elmer Lambda 35) using quartz cuvettes. Single-photon fluorescence emission spectra were measured using a spectrofluorometer (ChronosFD from ISS, Champaign, IL, USA). The two-photon absorption measurements were performed using a custom-built multiphoton excitation spectrofluorometer.[60] In short, the excitation source was a Ti:Sa laser (HPeMaiTai DeepSee, Spectra Physics, Mountain View, CA). The laser power was controlled using a motorized half-wave plate together with a polarizer. The laser was focused on the sample using a CFI S Plan Fluor ELWD 60X objective (Nikon). The laser power was monitored by a power meter (PM100D with a S142C head, Thorlabs Sweden AB Goteborg, Sweden). The two-photon emission was collected through the objective and passed through a Multiphoton-Emitter HC 680/SP (AHF analysentechnik AG, Tuebingen, Germany) to a multimode optical fiber (M200L02S-A, Thorlabs Sweden AB Goteborg, Sweden). The emission was then sent to a monochromator (ARC-SP2155, BFi OPTiLAS, Sweden), and the spectra were imaged by a cooled CCD camera (PIXIS 400B, Princeton Instruments, Princeton NJ, USA). A motorized XY stage (Nikon) was used as a sample holder. The laser, laser power, camera, and XY stage were controlled using ImageJ[61] and custom scripts. Calculations of the two-photon cross sections were done using custom Matlab code (MathWorks, Natick, MA, USA). The absolute two-photon absorption cross sections were calculated using a relative fluorescence intensity technique as described previously.[61] Flourescein in a CAPS buffer, (pH 11) and Rh 6G and Rh B in methanol were used to reference the system, using the references' well-characterized spectra.[62] The measurements for the two-photon cross sections were carried out at least five times for the different samples with excitation wavelengths from 700 to 1020 nm.

To eliminate artifacts, due to photobleaching or linear absorption, we tested that the fluorescence signal increased as the square of the excitation intensity at the different excitation wavelengths for the different samples.

Electrochemistry. Cyclic voltammograms of compounds **15**, **16**, **18**, and **41** were measured in deoxygenated 0.1 M solutions of tetrabutylammonium hexafluorophosphate in anhydrous dichloromethane, using a glassy-carbon working electrode, a Ag/AgCl reference electrode, and an auxiliary platinum foil (scan rate v = 50 mV s^{-1}, Ar, 20 °C). All values of E (V) are reported with respect to the Fc/Fc^+ redox potential.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving normalized absorption spectra for dyes **4**, **15**, **17**−**20**, **25**, **26**, and **34**−**44**, ^{1}H NMR and ^{13}C NMR spectra for compounds **4**, **14**−**23**, **25**, **26**, and **34**−**44**, and cyclic voltammetry plots for compounds **15, 18**, and **41**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support of our work from the Foundation for Polish Science (Mistrz programme) is gratefully acknowledged. The research leading to these results has received partial funding from the European Community's Seventh Framework Programme under the TOPBIO project, grant agreement no. 264362. J.B. gratefully acknowledges support from the Danish Molecular Biomedical Imaging Center (DaMBIC) and the Carlsberg Foundation. We thank Anita Janiga and Yevgen Poronik for useful suggestions and Jillian Larsen (UC Riverside) for amending the manuscript.

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