

## Dyes/Pigments | Hot Paper |

 Z-Shaped Pyrrolo[3,2-*b*]pyrroles and Their Transformation into  $\pi$ -Expanded Indolo[3,2-*b*]indolesRafał Stężycki,<sup>[a, b]</sup> Marek Grzybowski,<sup>[a]</sup> Guillaume Clermont,<sup>[c]</sup> Mireille Blanchard-Desce,<sup>\*[c]</sup> and Daniel T. Gryko<sup>\*[a]</sup>

Dedicated to Prof. Jonathan Lindsey on the occasion of his 60th birthday

**Abstract:** Sterically hindered 1,4-dihydropyrrolo[3,2-*b*]pyrroles possessing *ortho*-(arylethynyl)phenyl substituents at positions-2 and -5 were efficiently synthesized through a sila-Sonogashira reaction. These unique Z-shaped dyes showed relatively strong fluorescence in solution. Detailed optimization revealed that, in the presence of InCl<sub>3</sub>, these alkynes readily undergo an intramolecular double cyclization to give hexacyclic products bearing an indolo[3,2-*b*]indole skeleton in remarkable yields. Steady-state UV–visible spectroscopy revealed that upon photoexcitation, the prepared Z-shaped alkynes undergo mostly radiative relaxation leading to high fluorescence quantum yields. In the case of 7,14-

dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indoles, we believe that the substantial planarization of geometry in the excited state, is the underlying reason for the observed large Stokes shifts. The presence of additional electron-withdrawing groups makes it possible to further alter the photophysical properties. The two-photon absorption cross-section values of both families of dyes were found to be modest and the nature of the excited state responsible for two-photon absorption appeared to be strongly affected by the presence of peripheral groups. Serendipitous synthesis of unusual double-Z-shaped alkyne by Sonogashira and Glaser coupling is also reported.

## Introduction

Dihydroheteropentalenes are in the class of 10 $\pi$ -electron aromatic systems that play an important role in current optoelectronics. Thieno[3,2-*b*]thiophene<sup>[1]</sup> is the most widely studied member of this family, as it provides a basis for numerous ladder-type thiophene-based heterocycles.<sup>[2]</sup> The recent expansion of interest in this class of molecules has been fueled by research applications such as N-type field-effect transistors,<sup>[3]</sup> mechanosensitive membrane probes,<sup>[4]</sup> nonlinear optical materials,<sup>[5]</sup> in photovoltaic polymers,<sup>[6]</sup> hole-transport materials, polymer solar cells,<sup>[7]</sup> etc.<sup>[8]</sup> Consequently, novel ladder-type heteroacenes, such as dibenzothiopheno[6,5-*b*:6',5'-*f*]-thieno[3,2-*b*]thiophene,<sup>[9]</sup> and dithieno[2,3-*d*:2',3'-*d'*]-thieno[3,2-*b*:3',2'-*b'*]dipyrrole<sup>[10]</sup> have been recently prepared. Many strat-

egies for  $\pi$ -extension of the ladder-type acenes and heteroacenes have been proposed.<sup>[11]</sup> However, the thienothiophene core has only limited possibilities for  $\pi$ -expansion for two reasons: 1) lack of respective synthetic methods leading to unsymmetrically substituted derivatives possessing multiple aryl substituents, and 2) sulfur cannot accommodate the third substituent which controls secondary properties such as solubility. Taking advantage of the recent development of methodology for synthesis of ladder-type heteroacenes,<sup>[12,13]</sup> researchers have sought to include other heteroatoms, such as nitrogen.<sup>[14]</sup>

Although the first  $\pi$ -expanded pyrrole[3,2-*b*]pyrroles were synthesized by Golubev in the 19th century,<sup>[15]</sup> it was not until two years ago that this chemistry gained popularity.<sup>[16]</sup> An elegant study by Wan has shown that cyclic amides can be reductively transformed into indolo[3,2-*b*]indoles.<sup>[17]</sup>

We have previously reported that multicomponent condensation of aromatic amines, aromatic aldehydes, and diacetyl leads directly to pyrrole[3,2-*b*]pyrroles.<sup>[18]</sup> This methodology is the only procedure which allows the construction of both five-membered rings directly during the same synthetic operation, thus offering a unique possibility to quickly assemble large  $\pi$ -systems.<sup>[19]</sup> The goal of the current work was to further extend the limits of  $\pi$ -expansion among dihydroheteropentalenes in a search for functional dyes possessing unique combinations of properties.

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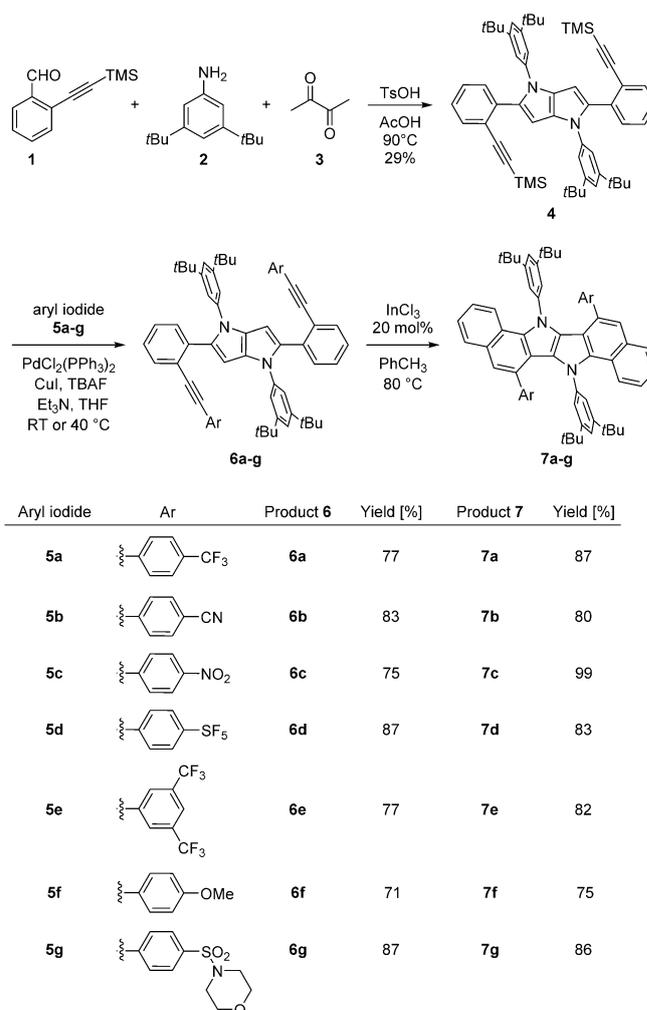
Supporting information for this article is available on the WWW under  
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## Results and Discussion

### Design and synthesis

In this study, we took advantage of the fact that our methodology leads to pyrrole[3,2-*b*]pyrroles having two unsubstituted core positions, while simultaneously exploiting the superb reactivity of the pyrrole ring versus electrophilic aromatic substitution. The designed approach comprises the Sonogashira coupling of 2-ethynylphenyl substituted pyrrolo[3,2-*b*]pyrroles followed by a double-annulation reaction. If successful, products of the first reaction would possess a unique Z-shape while the annulation would consist of a fully conjugated six-fused-rings system, that is, 7,14-dihydrobenzo[*g*]benzo[6,7]-indolo[3,2-*b*]indole.

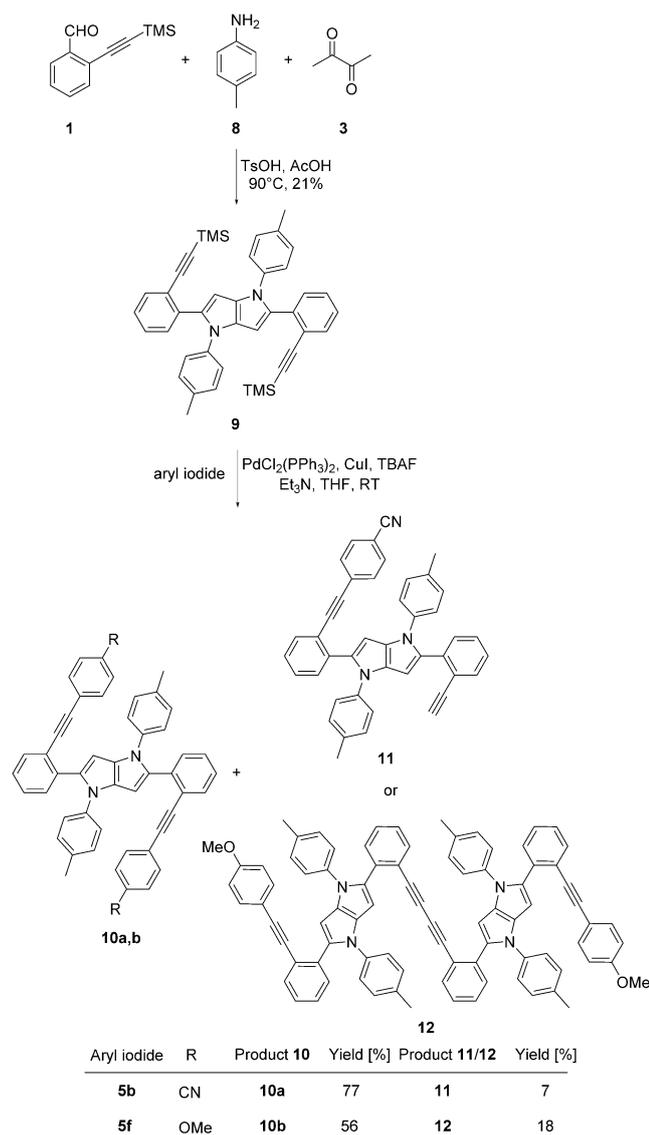
The construction of a pyrrolo[3,2-*b*]pyrrole core was achieved using the straightforward condensation of amine, aldehyde, and diacetyl discovered recently in our group.<sup>[18,19]</sup> This method provides the corresponding 1,2,4,5-tetraaryl-pyrrolopyrroles in one step in moderate yields and is tolerant for sterically hindered aldehydes.<sup>[18,19]</sup> We decided to use the aryl amine with two *tert*-butyl groups since these bulky substituents usually prevent  $\pi$ -stacking of large planar aromatic systems and should ensure a good solubility of the final products. 2-Trimethylsilylethynylbenzaldehyde (**1**) was chosen as the key starting material in our design. The condensation of the aldehyde with 3,5-bis(*tert*-butyl)aniline (**2**) and diacetyl (**3**) was conducted under standard conditions<sup>[18c]</sup> to afford pyrrolopyrrole **4** containing TMS-protected acetylene moieties in 29% yield (Scheme 1). Subsequently, this compound was subjected to the *sil*-Sonogashira coupling reaction<sup>[20]</sup> with a rationally chosen set of aryl iodides containing both electron-donating and electron-withdrawing substituents (Scheme 1). The resulting dyes **6a–g** were obtained in good yields ranging from 71 to 87%. In the context of the high electron density of the pyrrolo[3,2-*b*]pyrrole core, reaction with 1-iodo-4-methoxybenzene (**5f**) is worth mentioning since it led to an all-donor product **6f**, which, in principle, could be intrinsically unstable. In this case, the final reaction mixture was the most complex, but after purification of the desired compound, it proved to be sufficiently stable. The isolation of product **6b** containing two 4-cyanophenylethynyl substituents was extremely difficult. Very small amounts of impurities were observed (<sup>1</sup>H and <sup>13</sup>C NMR spectra) even after a laborious and lengthy purification process (including multiple chromatographies on silica gel, size-exclusion chromatography, and several crystallizations). We, therefore, decided to use it in the next step without further purification. The prepared compounds were mostly yellow solids, except **6c** (red) and **6f** (colorless). The annulation was first attempted in the presence of PtCl<sub>2</sub>, the most frequently used reagent in this reaction,<sup>[21a]</sup> but no product could be isolated. Eventually we applied alternative reaction conditions with indium(III) chloride as a catalyst.<sup>[21b]</sup> All reactions performed well in the presence of 20 mol% of InCl<sub>3</sub> and the whole set of indolo[3,2-*b*]indoles **7a–g** were obtained in excellent yields (75–99%, Scheme 1). Moreover, in all cases, the reaction led exclusively to the formation of 6-*endo-dig* cyclization products,



**Scheme 1.** Synthesis of Z-shaped dyes **6a–g** and  $\pi$ -expanded indoloindoles **7a–g**.

and the possible 5-*exo* isomers were not detected. It is noteworthy that, despite the inability to fully purify the compound **6b**, the product **7b** was obtained in 80% yield.

In parallel studies, we pursued the analogous synthetic route using *p*-toluidine (**8**) instead of 3,5-bis(*tert*-butyl)aniline (**2**). The pyrrole[3,2-*b*]pyrrole **9** was prepared without complications. However, its Sonogashira coupling with typical aryl iodides (i.e., 4-iodobenzonitrile (**5b**) and 4-iodoanisole (**5f**)) led to the formation of side products **11** or **12** in addition to the expected bis-arylethynes **10a,b** (Scheme 2). When iodoarene **5f** possessing the electron-donating methoxy groups was used, the product of Glaser coupling **12** was obtained, whereas iodoarene **5b**, with electron-withdrawing cyano substituents, gave the monocoupled product **11**. The subsequent reaction of **11** was probably stalled by its low solubility. However, when the reaction was repeated in the absence of aryl iodide **5f**, only the product resulting from removal of two TMS groups was obtained. The cyclization of compounds **10a** and **10b** in the presence of catalytic amounts of InCl<sub>3</sub> led to products the solubility of which was so low in common organic solvents that useful <sup>1</sup>H NMR spectra could not be recorded.



Scheme 2. Synthesis of compounds 10a, 10b, 11 and 12.

### Linear optical properties

With all targeted compounds in hand, we performed comprehensive investigations of their optical properties (Figure 1, Figure 2, Table 1). Because dye **6b** could not be prepared in pure form (see previous section), its optical characteristics are not presented.

Since solubility of compounds from all three series differed from case to case, we conducted optical measurements in a few different solvents such as toluene (the most versatile), cyclohexane, and  $\text{CH}_2\text{Cl}_2$ . The absorption spectra of dyes **6a–g** and **10a,b** (Z-shaped) displayed broad bands located typically between 380 and 480 nm, except for **6c** (400–520 nm) and **6f**, **10b** (350–430 nm). The molar absorption coefficients were in the range  $5600\text{--}18000\text{ M}^{-1}\text{ cm}^{-1}$ , that is, they were much lower than for analogous pyrrolopyrroles bearing arylethynyl substituents at *para* positions of benzene rings ( $40000\text{--}70000\text{ M}^{-1}\text{ cm}^{-1}$ ).<sup>[19c]</sup> This difference is undoubtedly an effect of

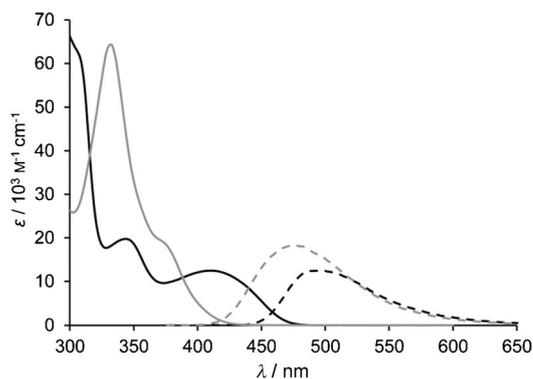


Figure 1. Absorption (solid) and emission (dashed) spectra of dyes **6d** (black) and **7d** (grey) measured in toluene.

Table 1. Photophysical properties of the prepared dyes.

Dye	Solvent	$\lambda_{\text{abs}}^{\text{max}}$	$\epsilon$ [ $\text{M}^{-1}\text{ cm}^{-1}$ ]	$\lambda_{\text{em}}^{\text{max}}$	$\Phi_{\text{fl}}^{\text{[a]}}$	$\Delta\lambda$ [ $\text{cm}^{-1}$ ]
<b>4</b>	toluene	384	23 000	440	0.73	3300
<b>6a</b>	toluene	406	13 000	482	0.65	3900
	$\text{CH}_2\text{Cl}_2$	397	11 000	522	0.40	6000
<b>6b</b>	toluene	$\approx 400$	10 000	502	0.60	6300
	toluene	444	7200	647	0.07 <sup>[b]</sup>	7100
<b>6c</b>	cyclohexane	452	7400	578	0.09	4800
	$\text{CH}_2\text{Cl}_2$	441	5600	–	–	–
<b>6d</b>	toluene	410	12 000	496	0.59	4200
	cyclohexane	419	12 000	477	0.57	2900
<b>6e</b>	$\text{CH}_2\text{Cl}_2$	403	10 000	541	0.04	6300
	toluene	400	8500	500	0.48	5000
<b>6f</b>	$\text{CH}_2\text{Cl}_2$	392	8500	538	0.25	6900
	toluene	383	18 000	452	0.64	4000
<b>6g</b>	cyclohexane	392	16 000	444	0.62	3000
	toluene	412	11 000	505	0.52	4500
<b>7a</b>	cyclohexane	418	9400	484	0.51	3300
	toluene	379	17 000	465	0.26	4900
<b>7b</b>	$\text{CH}_2\text{Cl}_2$	380	17 000	486	0.20	5700
	toluene	380	19 000	483	0.34	5600
<b>7c</b>	toluene	406	11 000	590	0.05 <sup>[c]</sup>	7800
	cyclohexane	401	10 000	533	0.22	6200
<b>7d</b>	$\text{CH}_2\text{Cl}_2$	409	10 000	–	–	–
	toluene	376	18 000	476	0.25	5600
<b>7e</b>	cyclohexane	373	17 000	465	0.27	5300
	$\text{CH}_2\text{Cl}_2$	378	18 000	504	0.02	6600
<b>7f</b>	toluene	373	14 000	467	0.43	5400
	$\text{CH}_2\text{Cl}_2$	377	20 000	484	0.24	5900
<b>7g</b>	toluene	377	20 000	484	0.24	4700
	toluene	358	37 000	431	0.24	4700
<b>9</b>	toluene	380	18 000	484	0.31	5700
	toluene	383	23 000	443	0.70	3500
<b>10a</b>	toluene	416	11 000	513	0.50	4500
<b>10b</b>	toluene	392	15 000	456	0.66	3600
<b>11</b>	toluene	400	18 000	526	0.46	6000
<b>12</b>	toluene	382	27 000	505	0.42	6400

[a] Reference: quinine sulfate in  $\text{H}_2\text{SO}_4$  (0.5 M;  $\Phi_{\text{fl}}=0.546$ ). [b] Reference: Cresyl Violet in Methanol ( $\Phi_{\text{fl}}=0.54$ ). [c] Rhodamine 6G in EtOH ( $\Phi_{\text{fl}}=0.96$ )

less extended conjugation of chromophores **6a–g** and **10a,b** possessing *ortho*-arylethynyl groups, due to their nonplanar conformation.<sup>[22]</sup> The presence of electron-withdrawing substituents at the periphery of the molecule formed A–D–A systems, which are known to have bathochromically shifted

absorption bands. The absorbance maxima ( $\lambda_{\text{max}}$ ) of the series **6a–g** were gradually red-shifted upon increasing the strength of the electron-withdrawing groups. Not surprisingly, the 4-nitrophenyl substituent led to the most bathochromically shifted absorption, so that  $\lambda_{\text{max}}$  reached 444 nm for compound **6c**.

Quite interestingly, all Z-shaped molecules, including compound **6c** bearing the nitro end-groups, were fluorescent in low to medium polarity solvents. The color of fluorescence ranged from blue (**6f** and **10a**) and turquoise to yellow (**6c**). Fluorescence quantum yields of these dyes were good in toluene ( $\Phi_{\text{fl}}=48\text{--}69\%$ ) and lower in  $\text{CH}_2\text{Cl}_2$ . Values in  $\text{CH}_2\text{Cl}_2$  were comparable to  $\Phi_{\text{fl}}$  previously determined for linear-type bis-arylethynyl-pyrrolopyrroles.<sup>[19c]</sup> This dependence of the fluorescence quantum yields on the polarity of the solvent for centrosymmetric compounds can be tentatively assigned to breaking of the symmetry in the excited state leading to a polar emissive excited state.<sup>[23]</sup> Such excited states are more stabilized by polar solvents, inducing a red shift of the fluorescence emission (as clearly observed in Table 1 with the variation of the maximum emission wavelengths from cyclohexane to toluene and DCM). This red-shift induces a decrease of the radiative rates and increases the non-radiative decay rates, subsequently yielding a marked decrease of fluorescence quantum yield. This property has been recently reported for A–D–A pyrrole[3,2-*b*]pyrroles.<sup>[24]</sup>

For the ladder-type dyes **7a–g**, hypsochromic shifts of both absorption (27–38 nm) and emission (17–33 nm) were observed as compared to Z-shaped dyes. This suggests that the angularly fused benzene rings had little effect on the HOMO/LUMO gap of the pyrrolo[3,2-*b*]pyrrole core and might be caused by the inefficiency of  $\pi$ -conjugation due to the angular fusion pattern.<sup>[25]</sup> Not surprisingly, ladder-type products displayed higher values of molar extinction coefficient in the range of 11 000–37 000  $\text{M}^{-1}\text{cm}^{-1}$ . Fluorescence quantum yields of the ladder-type compounds decreased ( $\Phi_{\text{fl}}=24\text{--}48\%$ , measured in toluene) in comparison to parent Z-shaped dyes. On the other hand, compounds **7a–g** exhibited larger Stokes shift values in low polarity solvents (the difference between **6d** and **7d** is 2400  $\text{cm}^{-1}$  in cyclohexane). Even though annulation leads to planarization and higher rigidity of the resulting molecules (six fused aromatic rings), a significant change of geometry seems to occur between the relaxed ground- and excited-states, that is, after excitation but prior to emission, for compounds of series **7a–g**. The dihedral angles between the four phenyl substituents and benzo[*g*]benzo[6,7]indolo[3,2-*b*]indole core are decreased in the emissive excited state. In typical low viscosity solvents, such as toluene, cyclohexane, and  $\text{CH}_2\text{Cl}_2$ , the rotation of the benzene ring along the linker is not disturbed and the co-planarity between the substituted phenyl ring and the indolo[3,2-*b*]indole core can be attained.

It is worth mentioning that despite the well-known quenching effect of the nitro group,<sup>[26,27]</sup> the fluorescence quantum yields of products **6c** and **7c** were found to be 9 and 22%, respectively, in cyclohexane. We also observed a bathochromic shift of the emission with increasing solvent polarity for derivatives **7a–g**. However, this shift was less marked than for derivatives **6a–g**. For instance, the emission of compound **6d**

was shifted by 64 nm on going from cyclohexane to DCM while it was shifted only by 39 nm for **7d**. This outcome suggests that the electronic redistribution (intramolecular charge transfer from the end-groups towards the indolo[3,2-*b*]indole core) occurring in the lowest excited state is less pronounced in derivatives **7a–g** compared to derivatives **6a–g**.

While maxima of absorption for dyes **7a–g** was the same as in the case of previously described  $\chi$ -shaped  $\pi$ -expanded pyrrole[3,2-*b*]pyrroles,<sup>[19a]</sup> their emission was markedly bathochromically shifted (460–530 nm vs. 420–460 nm). This outcome for dyes **7a–g** may be attributed to the negligible conjugation between the 7,14-dihydrobenzo[*g*]benzo[6,7]indolo[3,2-*b*]indole core and phenyl substituents in the ground state, whereas there is significant planarization of conformation in the excited state. Direct evidence for excited-state planarization among  $\pi$ -expanded thieno[3,2-*b*]thiophene derivatives has been reported recently by Matile and Vauthey.<sup>[28]</sup>

The dye **12** obtained by Glaser coupling showed hypsochromically shifted absorption and bathochromically shifted emission with regard to compound **10b**. This phenomenon caused the large Stokes-shift of **12** (6400  $\text{cm}^{-1}$  in toluene; Figure 2).

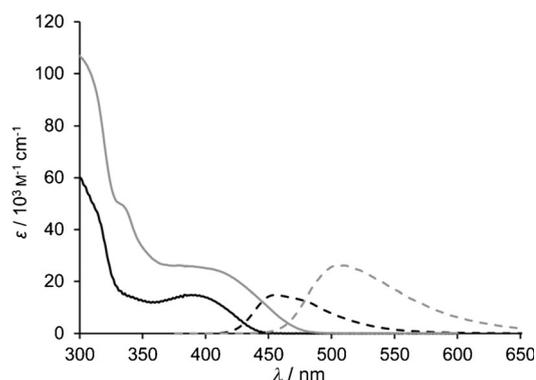


Figure 2. Absorption (solid) and emission (dashed) spectra of dyes **10b** (black) and **12** (grey) measured in toluene.

## Two-photon absorption

The unusual geometry and the structural similarity of these new compounds to previously published bis(arylethynyl)pyrrole[3,2-*b*]pyrroles,<sup>[18c]</sup> tetraaryl-pyrrolo[3,2-*b*]pyrroles,<sup>[23]</sup> and hexaaryl-pyrrolo[3,2-*b*]pyrroles<sup>[19c]</sup> prompted us to study the two-photon absorption (2PA) of all new dyes using two-photon induced fluorescence method (Table 2, and the Supporting Information). The measurements were conducted over the spectral range of 700–1000 nm. All the synthesized compounds showed modest 2PA cross-section ( $\sigma_2$ ) values. Z-shaped dyes bearing electron-withdrawing groups (EWG) exhibited lower  $\sigma_2^{\text{max}}$  values (38–66 GM) than intermediate **4** (92 GM) in almost all cases. This result was related to the difference in the nature of the states affected by the main 2PA band in the target spectral range. Whereas the lowest-energy excited state appeared to be both one and two-photon allowed in the case of compounds **6a–g** (see the Supporting Information), the 2PA band of compound **4** was observed at higher

energy, with the lowest excited state being only weakly allowed (see the Supporting Information). Hence, the nature of the excited state responsible for the 2PA response appeared to be strongly affected by the presence of the peripheral groups. Indeed, the 2PA response of compounds **6a–g** increased with increasing EW strength, confirming the role of the end-groups in the electronic transitions responsible for 2PA. Consequently, the strongest EWG, that is, the nitro group (compound **6c**), led to the maximum 2PA response ( $\sigma_2^{\max} = 129$  GM). Moreover, 2PA maximum of this compound was located at the longest wavelength (900 nm) among all examined dyes (Table 2). However, due to the very low values of fluorescence quantum yield, the critical figure of merit, that is, two-photon brightness ( $\sigma_2 \Phi_{\text{fl}}$ ), was the lowest for this dye (Table 2). Interestingly, compound **6d** bearing reasonably good electron-withdrawing substituents ( $\text{SF}_3$ ) exhibited as similar 2PA response to compound **6f** which had a reasonably good electron-donating substituent (OMe). However, in the case of compound **6f**, the excited state responsible for the 2PA response was found at higher energy than the lower one-photon-allowed excited state (see the Supporting Information), demonstrating the importance of the EWG in inducing 2PA in the lowest excited state. It is noteworthy that parallel linear-type dyes showed considerably higher 2PA cross-section values.<sup>[19c]</sup>

The annulation products **7a–g** showed even lower  $\sigma_2$  values than their non-annulated counterparts **6a–g**. This result contrasts with the observation of the larger 1PA of compounds **7a–g**, as compared to **6a–g**, but can be related to the less pronounced electronic redistribution in the lower excited states observed for derivatives **7a–g** as discussed earlier. However, similarly to the Z-shaped dyes **6a–g**, among the fused derivatives **7a–g**, the nitro-substituted dye **7c** showed the highest  $\sigma_2^{\max}$  value (100 GM at 820 nm). Interestingly, compound **7f** which contains the reasonably good electron-donating substituents (OMe) showed a similar 2PA response as the

compound having weak electron-withdrawing substituents ( $\text{CF}_3$ ).

Finally, 2PA extended Z-shaped compound **12** showed among the highest 2PA response and a broader 2PA spectrum, evidencing contributions from both the lower excited state and higher excited state which are only 2P allowed (see the Supporting Information).

## Conclusions

We have demonstrated that previously inaccessible Z-shaped arylethynylpyrrolopyrroles can be efficiently synthesized in two-steps from readily available 2-trimethylsilylethynylbenzaldehyde, aromatic amines, and various aryl iodides. The introduction of large substituents at the *ortho* positions of phenyl substituents offers a means for controlling the dihedral angle between the subunits, allowing for fine-tuning the optical properties. In spite of the bent conformation, absorption and emission reveals electronic interactions both in the ground and in the excited states, leading to a polar emissive excited state the emission state of which is red-shifted and fluorescence intensity is decreased with increasing solvent polarity. Subsequent reaction of these bis-alkynes with  $\text{InCl}_3$  resulted in double annulation to afford dyes with benzo[*g*]benzo[6,7]indolo[3,2-*b*]indole core. The approach presented here is general and thus can be used to introduce different functional groups onto the periphery of such  $\pi$ -expanded dyes. The two-photon absorption cross-section values were significantly increased when the intramolecular electronic redistribution from the substituents to the pyrrolo[3,2-*b*]pyrrole core, as provoked by peripheral EWGs, was enlarged. These findings demonstrate unexplored avenues for  $\pi$ -expanded fluorescent heteroatomics.

## Experimental Section

### General procedure for the synthesis of pyrrolo[3,2-*b*]pyrroles (**4**, **9**)

A 50 mL round-bottom flask equipped with a reflux condenser and magnetic stir bar was charged with glacial acetic acid (15 mL), arylamine (15 mmol), 2-((trimethylsilyl)ethynyl)benzaldehyde (15 mmol), and TsOH (0.75 mmol). The mixture was stirred at 90 °C for 30 min. After that, butane-2,3-dione (7.5 mmol) was slowly added by syringe, and the resulting mixture was stirred at 90 °C for 3 h. The mixture was then cooled to room temperature. The precipitate of the obtained dye was isolated by filtration and was washed with cold glacial acetic acid. The further purification of the individual products is described in Supporting Information.

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Dye	$2\lambda_{\text{OPA}}$ [nm] <sup>[a]</sup>	$\lambda_{2\text{PA}}^{\max}$ [nm] <sup>[b]</sup>	$\sigma_2^{\max}$ [GM] <sup>[c]</sup>	$\sigma_2^{\max} \Phi_{\text{fl}}$ [GM] <sup>[d]</sup>
<b>4</b>	772	710	92	67
<b>6a</b>	812	750	38	25
<b>6b</b>	800	800	48	27
<b>6c</b>	888	900	129	1
<b>6d</b>	820	770	63	37
<b>6e</b>	800	740	40	19
<b>6f</b>	776	720	66	42
<b>6g</b>	824	800	58	30
<b>7a</b>	746	710	19	5
<b>7b</b>	752	720	26	9
<b>7c</b>	812	820	100	4
<b>7d</b>	746	730	28	7
<b>7e</b>	752	720	12	5
<b>7f</b>	710	730	17	4
<b>7g</b>	754	730	13	4
<b>12</b>	764	740	90	37

[a] Maximum wavelength of linear absorption multiplied by 2. [b] Wavelength maximum of two-photon absorption. [c] Maximum value of two-photon absorption cross-section. [d] Two-photon brightness (product of two-photon absorption cross-section and fluorescence quantum yield).

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