Method for the Large-Scale Synthesis of Multifunctional 1,4-Dihydro-pyrrolo[3,2-b]pyrroles

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ABSTRACT: A thorough investigation has enabled the optimization of the synthesis of 1,4-dihydro-pyrrolo[3,2-b]pyrroles. Although salts of such metals as vanadium, niobium, cerium, and manganese were found to facilitate the formation of 1,4-dihydro-pyrrolo[3,2-b]pyrroles from amines, aldehydes, and diacetyl, we confirmed that iron salts are the most efficient catalysts. The conditions identified (first step: toluene/AcOH = 1:1, 1 h, 50 °C; second step: toluene/AcOH = 1:1, Fe(ClO4)3·H2O, 16 h, 50 °C) resulted in the formation of tetraarylpyrrolo[3,2-b]pyrroles in a 66% yield. For the first time, very electron-rich substituents (4-MeNC6H4, 3-(OH)C6H4, pyrrol-2-yl) originating from aldehydes, and sterically hindered substituents (2-C6H4Cl, 2-BrC6H4, 2-CNC6H4, 2-(CO2Me)2C6H4, 2-(TMS-C≡C)C6H4) present on anilines can be appended to the pyrrolo[3,2-b]pyrrole core. It is now also possible to prepare 1,4-dihydro-pyrrolo[3,2-b]pyrroles bearing an ordered arrangement of N-substituents and C-substituents ranging from coumarin, quinoline, phthalimide to truxene. These advances in scope enable independent regulations of many desired photophysical properties, including the Stokes shift value and emission color ranging from violet-blue through deep blue, green, yellow to red. Simultaneously, the optimized conditions have finally allowed the synthesis of these extremely promising heterocycles in amounts of more than 10 g per run without a concomitant decrease in yield or product contamination. Empowered with better functional group compatibility, novel derivatization strategies were developed.

INTRODUCTION

The rising interest in conjugated heterocycles composed of two or more rings has its origin in organic electronics. Among various systems, heteropentalenes3–5 attract particular attention, with a special focus on thieno[3,2-b]thiophene.6–10 This chromophore, especially when embedded into larger, π-extended scaffolds, has been employed in research ranging from active high-efficiency organic solar cells11 to mechanosensitive fluorescent probes.12 1,4-Dihydro-pyrrolo[3,2-b]pyrroles are exceptionally electron-rich heteropentalenes, the chemistry of which has been developing very slowly for many years due to the lack of an efficient synthesis methodology.13 This situation changed dramatically in 2013, when we serendipitously found a method that allows rapid access to 1,4-dihydro-tetraarylpyrrolo[3,2-b]pyrroles (TAPPs).14 Since then, TAPPs have found multiple applications in research related to studying symmetry-breaking in the excited state,15 two-photon absorption,16 solvatofluorochromism13c,d direct solvent probing via H-bonding interactions,17 photochromic analysis of halocarbons,18 organic field-effect transistors,19 dye-sensitized solar cells,20 bulk heterojunction organic solar cells,21 organic light-emitting diodes,22 resistive memory devices,23 aggregation-induced emission,24 and MOFs.25 It has been also shown that TAPPs are an excellent platform for the synthesis of the π-expanded heteroanalogs of polycyclic aromatic hydrocarbons.26 Access to these aza-nanographenes hinges on the ability to prepare 1,4-dihydro-tetraarylpyrrolo[3,2-b]pyrroles possessing a suitable substitution pattern. In spite of significant efforts, many important functionalities have been so far incompatible with the multicomponent reaction leading to TAPPs. Simultaneously, the consequence of a growing interest in TAPPs is the increased demand for large quantities of these compounds. The possibility of large-scale preparation is also appreciated if industrial applications are seriously considered. Since our initial discovery,14 the reaction conditions for the multicomponent reaction of primary aromatic amines, aromatic aldehydes, and diacetyl, leading to TAPPs, have evolved. A few
years ago, we found that the addition of p-toluenesulfonic acid to the reaction mixture significantly increased the yields, with some limitations regarding the starting materials. More recently, we developed an improved procedure with an iron salt as the catalyst, leading to TAPPs in up to 77% yield with a reasonably broad substrate tolerance. The huge advantages of this protocol are its simplicity, the use of cheap starting materials, and straightforward workup as most TAPPs precipitate directly from the reaction mixture. Routinely, this methodology was tested on the scale of 1.0 mmol of diacetyl, with an amine, aldehyde, and diacetyl used in a 2:2:1 molar ratio, with 6 mol % of catalyst and carried out in an open flask. Increasing the scale by a factor of 4–5 usually leads to negligible changes in the reaction outcome; however, attempting to scale up this process even further (to 40 mmol of diacetyl) resulted in a significant drop in reaction yield (by a factor of at least 3) and the product being contaminated with the unreacted Schiff base. Reproducibility is a common problem associated with the scaling-up of chemical processes developed on a laboratory scale. The increasing interest in pyrrolo[3,2-b]pyrrole chemistry undoubtedly hinges upon better access to these heterocyclic compounds, and the problem of scalability might significantly hamper the further development of their applications. To solve these two challenges, we decided to re-examine all factors affecting the efficiency of TAPP synthesis, and herein, we present the results of our study.

**RESULTS AND DISCUSSION**

While re-examining the large-scale synthesis of TAPPs, the most important factors we took into consideration were reproducibility (in yield, impurity profile, reaction setup, course, and workup) and ease of operation (no chromatography, etc.), which determined the attractiveness of the small-scale method. Also important, but of lower significance, were cost (as necessary reagents are simple, inexpensive aromatic aldehydes and amines), and the reaction is catalyzed by a low-cost transition-metal salt), souring, waste handling (our method involves acceptable solvents), and safety (no exotherms, no bad decomposition profiles). Considering these, we analyzed the plausible mechanism of TAPP formation (Scheme 1).

Although some aspects of this reaction, including the role of the catalyst, are still not fully understood, the first stage, i.e., Schiff base formation, is definitely the most flexible, as it proceeds in a broad temperature and solvent range. The second stage, involving a Mannich reaction and cyclocondensations, followed by oxidation with air, offers much less control possibilities and, consequently, is probably much more sensitive to changes in reaction parameters. What we learned from previous optimization processes is that the highest yields are obtained when reactions are carried out in acidic media, preferably in acetic acid, while the addition of toluene as a cosolvent enables bulky, lipophilic starting materials to participate in the reaction, due to much better solubility in the reaction media.

We decided to conduct the optimization of TAPPs’ synthesis at a relatively large scale (4 mmol of diacetyl), 4 times larger than for previous optimizations, to find optimal conditions more adequate for larger scales. Another factor that we decided to keep constant was the reaction setup, and all optimization steps were performed in 25 mL round-bottom flasks equipped with magnetic stirring bars of the same size (length 20 mm). We also decided to carry out the reactions in open flasks because the addition of a condenser would slow down the diffusion of air into the reaction flask. For the optimization studies, we selected the synthesis of TAPP 3 from diacetyl, 4-cyanobenzaldehyde (1) and 4-tert-butylaniline (2). Compound 3 is known in the literature and had been prepared with a low 12% yield using TsOH as the catalyst. We repeated this reaction and obtained the product in an 18% yield (Table 1, entry 1). In the second experiment, we applied our recently optimized conditions; namely, we changed the catalyst to iron(III) perchlorate hydrate (6 mol %) and the solvent to a toluene/AcOH mixture (1:1 v/v). As expected, after stirring the reactants at 90 °C for 3 h, we witnessed a large 3-fold increase in the reaction yield to 54% (Table 1, entry 2). As suggested by the proposed reaction mechanism (Scheme 1), oxidation takes place in the final stage of the formation of TAPPs. Thus, we examined an effect of the presence of oxygen on the reaction outcome (Table 1, entries 3–7). Indeed, the reaction performed in a sealed Schlenk flask under an argon atmosphere with a catalytic amount of iron(III) perchlorate gave product 3 in a 14% yield (Table 1, entry 3). Although the yield is significantly lower, it is not indiscernible, which is reasoned by the oxidative nature of perchlorate. Indeed, in the case of the reaction conducted under an ambient atmosphere with solvents bubbled with argon prior to use, without the addition of any catalyst, the yield dropped even lower to 4% with a noticeably slower reaction rate (Table 1, entry 4). Most likely, a trace amount of the product is formed, due to the presence of the unreacted Schiff base, which also can react as an oxidant. Concurrently, the air atmosphere facilitated the formation of 3 in a 12% yield (Table 1, entry 5). These results show a significant role of oxygen as well as a complexity of the multicomponent reaction mechanism. On the other hand, under pure oxygen gas, the reaction yield was comparable to that of the experiment under air as an oxygen source (Table 1, entry 6). In addition, the reaction rate under oxygen seemed to be much faster, judged from the speed of color changes of the reaction mixture. However, after the fast formation of a bright yellow suspension of the product, we observed a quick darkening of the reaction mixture, which after 3 h of stirring appeared almost black, whereas under air at this point, the reaction mixture was still a brownish-orange suspension. This suggested that pure oxygen is too aggressive and may have caused further oxidation of the formed TAPP to some dark decomposition products. Hence, we shortened the reaction time to 0.5 h but the yield was not improved (Table 1, entry 7). Therefore, it can be concluded that for the synthesis of TAPP, air is a more optimal oxygen source than pure oxygen gas, owing to the reduced risk of...
overoxidation of sensitive products and ease of operation, not to mention safety matters. Having this established, wanting to keep other parameters unchanged, we then decided to focus mostly on reaction temperature and time. Our analysis of this problem led us to propose that one of the key factors in the synthesis of TAPPs is the accessibility of oxygen. It can be easily estimated that to form 4.0 mmol of the product, roughly 96 mL of pure oxygen gas or over 450 mL of air (under normal conditions) is required. While at small-scale reactions this factor is negligible, scaling up the process may lead to decreased and inefficient access to oxygen and a potential drop in the reaction yields, as a consequence of the square-cube law. Hence, to ensure good contact between the reactants and oxygen, in the next optimization steps, we decided to perform the reactions at lower temperatures and for longer times. We reasoned that lowering the temperature should lead to increased solubility of oxygen gas in the reaction system. Moreover, the lower temperature should also prevent a potential loss of diacetyl via evaporation (boiling point of 88 °C). In our previous studies, it turned out that this reaction occurs even at room temperature, although it is heterogeneous and the obtained yields are slightly lower. We expected that it could cause some problems with less soluble substrates; therefore, we decided to set up the reaction at 50 °C for 16 h. To our delight, under these conditions, the reaction of 4-tert-butylaniline with 4-cyanobenzaldehyde and diacetyl in a 2:2:1 molar ratio in the presence of 6 mol % iron(III) perchlorate hydrate as the catalyst in a mixture of toluene and acetic acid (1:1 v/v) as solvent provided the desired.

Table 1. Optimization Experiments Using 4-Cyanobenzaldehyde (1, 8 mmol), 4-tert-Butylaniline (2, 8 mmol), and Diacetyl (4 mmol)

| entry | catalyst (mol %) | solvent (mL/mL) | temp. (°C) | time (h) | oxidant | yield (%) |
|-------|-----------------|-----------------|------------|----------|---------|-----------|
| 1     | TsOH (10)       | AcOH (8)        | 90         | 3        | air     | 18        |
| 2     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 90         | 3        | air     | 54        |
| 3     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 90         | 3        | a       | 14        |
| 4     | —                | AcOH/toluene (6/6) | 50         | 16       | a       | 4         |
| 5     | —                | AcOH/toluene (6/6) | 50         | 16       | air     | 12        |
| 6     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 90         | 0.5      | O2      | 45        |
| 7     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 50         | 16       | air     | 69        |
| 8     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 50         | 16       | air     | 69        |
| 9     | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 50         | 16       | air     | 24        |
| 10    | Fe(ClO4)2·H2O (6) | AcOH/toluene (8/8) | 50         | 16       | air     | 67        |
| 11    | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | rt         | 16       | air     | 46        |
| 12    | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | rt         | 16       | O2      | 37        |
| 13    | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 50         | 3        | O2      | 67        |
| 14    | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 50         | 6        | air     | 69        |
| 15    | Fe(ClO4)2·H2O (10)| AcOH/toluene (6/6) | 50         | 16       | air     | 50        |
| 16    | Fe(ClO4)2·H2O (2) | AcOH/toluene (6/6) | 35         | 64       | air     | 65        |
| 17    | Fe(ClO4)2·H2O (6) | AcOH/toluene (6/6) | 35         | 64       | air     | 65        |
| 18    | Fe(ClO4)2·H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 65        |
| 19    | Fe2O3 (6)        | AcOH/toluene (3/3) | 50         | 16       | air     | 13        |
| 20    | Fe3(SO4)2·H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 21        |
| 21    | FeCl3 (6)        | AcOH/toluene (3/3) | 50         | 16       | air     | 21        |
| 22    | Fe(TTf)3 (6)     | AcOH/toluene (3/3) | 50         | 16       | air     | 64        |
| 23    | Fe(TTf)2 (6)     | AcOH/toluene (3/3) | 50         | 16       | air     | 51        |
| 24    | Fe(OAc)2 (6)     | AcOH/toluene (3/3) | 50         | 16       | air     | 47        |
| 25    | Fe(TTf)2·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 26    | Fe(TTf)2·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 27    | Fe(TTf)2·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 28    | Fe(acac)3·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 29    | Fe(acac)3·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 30    | Fe(acac)3·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 31    | Fe(acac)3·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |
| 32    | Fe(acac)3·6H2O (6) | AcOH/toluene (3/3) | 50         | 16       | air     | 63        |

“Reaction conducted under an argon atmosphere. *Reaction conducted under a constant air flow (rate: 4 mL/min). †Reaction conducted under a constant air flow (rate: 60 mL/min). ‡Twice smaller reaction scale, 2 mmol of diacetyl.
TAPP 3 in a 69% yield (Table 1, entry 8). It is worth mentioning that we tested the difference between dynamic and static air atmospheres (Table 1, entries 9 and 10). Product 3 was obtained in exactly the same yield (69%) under a constant air stream with a flow rate of 4 mL/min. Increasing the flow rate to 60 mL/min led to a noticeable drop of yield to 24%, due to evaporation of solvents. Dilution of the reaction mixture did not improve the yield (Table 1, entry 11), and a further decrease of the temperature to ambient conditions led to a significant drop in the reaction yields (entries 12 and 13). A good yield of TAPP 3 (65%) could still be obtained even at 35 °C, but the reaction time had to be elongated to 64 h (entry 17). Interestingly, at 50 °C, the reaction could be shortened to 3 h when pure oxygen was used as an oxidant without appreciable loss in efficiency (Table 1, entry 14). A catalyst loading of 6 mol % seems to be optimal since the increase of this amount to 10 mol % furnished the product in the same yield (69%, Table 1, entry 15), and the decrease to 2 mol % caused a drop in the reaction yield to 50% (Table 1, entry 16). We also investigated whether iron(III) perchlorate can be replaced with different iron sources (entries 19–26). The use of iron(III) oxide, iron(III) sulfate hydrate, iron(III) chloride, and iron(II) acetate provided poor yields of the product (13–22%), which in most cases was due to low solubility of these iron compounds in the reaction medium. Better results were obtained using iron(II) trifluoromethanesulfonate and iron(III) acetoacetonate; however, the yields of

Figure 1. Synthesis of TAPPs—substrate scope including challenging amines and aldehydes.
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approximately 50% were still considerably lower than with iron(III) perchlorate under the same conditions. Iron(III) trifluoromethanesulfonate and iron(III) p-toluenesulfonate hexahydrate proved almost as efficient as the perchlorate, leading to isolated yields of 64 and 63%, respectively. While due to much higher prices of these two reagents, iron(III) perchlorate still remains an optimal catalyst, they may be convenient replacements, e.g., for industrial-scale reactions where using large amounts of perchlorates may pose considerable safety hazards. Generally, iron(III) salts proved more effective catalysts than iron(II) salts. Furthermore, an experiment with the catalytic amount of perchloric acid gave 3 in a 48% yield (Table 1, entry 27), higher than the reaction without any catalyst and lower than the reaction with iron(III) perchlorate, indicating the importance of both cation and anion on the catalyst performance. Replacing the catalyst with VO(acac)$_2$, cerium(IV) fluoride, niobium(V) chloride, manganese(II) triflate, or addition of copper(II) salts did not improve the yields (Table 1, entries 28–32). The choice of catalysts was based on the assumption that an oxidant that was also a Lewis acid may facilitate the final oxidation step. It is worthwhile to add that in our hands NbCl$_5$ is not an efficient catalyst for TAPP formation under the originally published reaction conditions, i.e., in CH$_3$CN.

To prove the synthetic utility of the optimized reaction setup (first step: toluene/AcOH = 1:1, 1 h, 50 °C; second step: toluene/AcOH = 1:1, Fe(ClO$_4$)$_2$·H$_2$O, 16 h, 50 °C) (Table 1, entry 8), we subjected a range of sterically hindered and electronically diverse aldehydes and primary aromatic amines to these conditions, attempting to both increase the reaction scope and investigate if larger scale will deliver pure TAPPs in non-diminished yields (Figure 1).

The above-discussed modified method gives equal or higher yields of TAPPs than those previously reported for almost all substituted benzaldehydes and anilines trialed. Typically, pyrrolo[3,2-b]pyroles are obtained in good yields from electron-poor aldehydes (TAPPs 3–5, 7–9, 14, 36, 42, and 46; Figure 1). Importantly, lowering the reaction temperature allowed for the first time the use of electron-rich aldehydes; however, the obtained yields were reduced (TAPPs 11–13, 16, 19, 23, and 38; Figure 1). The most outstanding expansion of scope is TAPPs synthesized from sterically hindered primary aromatic amines. The attempts to prepare TAPPs from 2-chloroaniline or 2-bromoaniline under previously developed conditions$^{14a,15}$ gave yields below the detection limit. Under the new conditions, anilines with halo-, carboxy-, cyano-, or even (trimethylsilyl)ethyl substituents in the ortho position now lead to the corresponding TAPPs 6, 7, 8, 9, 31, 32, 33, 40, and 41 (Figure 1) in up to 32% yield, opening the door for their further functionalization. Exceptionally sterically hindered amines, for example, 2,4,6-trimethylamin, do not participate in this reaction; however, TAPP 34 bearing bulky 9-anthracenyl groups was obtained with acceptable yield from the corresponding anthracene-9-carboxaldehyde. In addition, pyrrolo[3,2-b]pyroles decorated with other polycyclic aromatic hydrocarbons, fluoranthene and truxene (TAPPs 37 and 14, respectively), could be obtained in surprisingly good yields, giving the possibility for significant expansion of the pyrrolo[3,2-b]pyrole π-electron system. This result may prove particularly important since the combination of electron-rich pyrrolo[3,2-b]pyrole core with extended π-electron substituents makes the discussed systems potentially hole-transporting materials.

Another valuable result is the possibility of transforming various heterocycle-derived aldehydes, both 5-membered heterocyclic aldehydes and 6-membered pyridine derivatives, into the corresponding products 19, 20, 24–27, 39, and 43 (Figure 1). These conditions also turned out to be effective for the synthesis of TAPPs from substituted 2-formylpyrrole and 2-formylthiophene.

Nevertheless, not all aromatic amines can form TAPPs. For example, the reaction of 4-cyanobenzaldehyde with 3-amino- or 3-aminoanisole did not lead to the desired product. Interestingly, 4-amino-2-hydroxytoluene, which contains a para-substituent, gave TAPP 28 under the same conditions.

In addition, we enriched the library of substrates with a set of hydroxybenzaldehydes, which under developed conditions afforded the corresponding products with moderate yields (TAPPs 11, 16, 21, 23, and 38; Figure 1). For these substrates, the best outcomes (up to 32%, TAPPs 16 and 23) were obtained for TAPPs bearing an electron-donating substituent on the N-aryl ring, while 4-cyanoalnine afforded the corresponding dye 11 in only a 13% yield. Alternatively, hydroxyphenyl-substituted pyrrolylpyroles are achievable via O-benzyl or O-(4-methoxybenzyl)-protected derivatives (TAPPs 17 and 22, respectively), which are available in good yields and can in principle be deprotected using known methods. Moreover, TAPP 45 possessing a phthalimide moiety can also be synthesized. One of the biggest breakthroughs was achieved with coumarins, bearing formyl or amino groups in various positions. The success of this attempt was not obvious, as various side reactions could be expected, including the Lewis acid-catalyzed Michael addition of pyrrolopyrrole and coumarin scaffolds. Indeed, early attempts of TAPP preparation from formyl-coumarins and amino-coumarins with TsOH as the catalyst failed. The first member of the coumarin-TAPP family, compound 35, was obtained in a fairly good 39% yield, which prompted us to test other coumarin derivatives as starting materials, and we found that coumarins can be used as both amine (as 6-amino-coumarin) and aldehyde components in the TAPP preparation. The resulting compound 44 was obtained in a 34% yield. It is noteworthy that TAPP 35 (Figure 1) is the first pyrrolo[3,2-b]pyrrole to date prepared from an aldehyde bearing CHO attached to the carbon—carbon double bond rather than to the aromatic ring.

With these results in hand, we attempted the large-scale synthesis of TAPPs. Aiming to keep the reaction setup and workup as simple as possible, we tested this methodology with selected amines, aldehydes, and diacetyl used in amounts of 80:80:40 mmol, with the reaction carried out in an open three-neck flask (to facilitate access to air; see the Supporting Information (SI) for further information). To our delight, the reaction was fully reproducible at large scale, giving products 3, 9, 15, and 24, with high purity and with virtually the same yield as in smaller-scale experiments, with all of the advantages of the latter, namely, simplicity of the reaction setup and workup (Figure 2).

To demonstrate the synthetic potential of the newly developed method, we decided to use 1,4-dihydro-pyrrolo[3,2-b]pyrrole obtained from 2-haloanilines in the preparation of heteroanalogues of polycyclic aromatic hydrocarbons (PAHs). Therefore, we obtained the dibromo-TAPP 49, which was subsequently transformed into the fused derivative 50 by palladium-catalyzed direct arylation (Scheme 2). Its structure was unambiguously confirmed by X-ray analysis (see the SI for further details; Figure S2). We recently described the synthesis of heterocycles possessing this skeleton either by direct arylation with TAPP obtained from ortho-bromo-substituted...
benzaldehydes or by 1,2-aryl shift in tetraarylpyrrolo[3,2-b]pyrroles. The present approach is an alternative route giving easy access to quite elaborated hetero-PAHs in just a two-step synthesis. Interestingly, the double intramolecular direct arylation proceeds regioselectivity at phenyl rings adjacent to positions 2 and 5. This underlines the strong influence of the pyrrolo[3,2-b]pyrrole core, which markedly increases the electron density on these substituents affecting their reactivity.

Aiming to further execute the advantages of this method, we took into consideration the annulation leading to π-expanded TAPPs. Such a strategy requires TAPPs decorated with a carbon–carbon triple bond located on the N-aryl ring and should afford a dye with improved conjugation between the core and substituents originating from parent aniline. Thus, we transformed parent pyrrolo[3,2-b]pyrrole 7a (Scheme 3) in the presence of indium(III) chloride into the fused analogue. The reaction leads predominantly to 7-endo-dig cyclization product 51, which was only isolated in a 35% yield due to limited stability. The preference for the 7-endo-dig pathway versus 6-exo-dig pathway seems to be related to both the nature of the catalyst and the structure of the substrate, which makes the formation of a seven-membered ring possible. It is likely, however, that the product containing a new six-membered ring forms albeit due to its reactivity, it reacts further under the reaction conditions. The plausible rationale behind the fact that the second annulation did not occur is the strong altering of electron distribution in molecule 51 compared to that in TAPP 50. A thorough analysis of one-dimensional (1D) NMR and two-dimensional (2D) NMR spectra provides sufficient structural information about compound 51. 1H NMR spectra show two singlets, originating from the core proton (6.22 ppm) and ethynyl proton (3.15 ppm), as well as two AA′XX′ systems (from substituents at positions 2 and 5). Such observations indicate the desymmetrization of the structure caused by monoannulation. Moreover, the number of correlations at 1H13C HSQC spectra, which is equal to the number of magnetically nonequivalent protons, can be rationalized only by the formation of the 7-endo-dig product (Figure S1) and excludes the 6-egzo-dig regioisomer. A thorough analysis of NOESY, 1H13C HSQC, and 13C13C HMBC spectra finally uncovers the structure of 51, supporting previous considerations. The formation of seven-membered rings was heretofore unreported for alkyne benzannulation.

As we mentioned in our previous papers, the extremely electron-rich character of the pyrrolo[3,2-b]pyrrole scaffold is sometimes manifested by its unexpected reactivity. In Scheme 4, we show another example of such a phenomenon. Looking for TAPPs with strongly polarized structures, we attempted the reaction of TAPP 18 with tetracyanoethylene (TCNE) in boiling toluene in the presence of pyridine, which in line with our expectation resulted in the formation of compound 52, however, only in a relatively small yield. To our surprise, the main product formed during this reaction was compound 53, apparently being a result of a tandem Diels–Alder reaction. Such a reaction was unexpectedly observed for the first time in the case of pyrrolo[3,2-b]pyrrole derivatives.
Having synthesized a library of new dyes, we investigated their fundamental photophysical properties. All measurements were performed in toluene as a solvent. Generally, unless decorated with strongly electron-withdrawing or electron-donating substituents at positions 2 and 5 of the central core, pyrrolopyrroles exhibit a broad, featureless absorption band at 350–375 nm with molar extinction coefficients ($\varepsilon$) of 10 000–40 000 M$^{-1}$ cm$^{-1}$ and emission maxima located at 400–420 nm with fluorescence quantum yields ($\Phi_f$) typically ranging from 0.30 to 0.70 (Table 2, Figures 3 and 4). Absorption and emission maxima are red-shifted to 400–410 and 450–460 nm, respectively, for compounds 3–9 bearing electron-withdrawing 4-cyanophenyl residues at positions 2 and 5. At the same time, these compounds exhibit higher $\varepsilon$ values of 40 000–60 000 M$^{-1}$ cm$^{-1}$ with larger $\Phi_f = 0.50–0.90$. Placing sterically hindered substituents at positions 1 and 4 does not influence the absorption and emission maxima underlying the relatively weak electronic coupling on N-substituents with the heterocyclic core. The most bathochromically shifted absorption (504 nm) and emission (647 nm) maxima among the synthesized dyes were exhibited by TAPP 11 bearing nitrophenyl substituents attached to the pyrrolopyrrole core through the thiophene linker (Figure 3). The remarkable red shift of both absorption and emission spectra is attributed to two factors, i.e., (1) extremely strong electron-withdrawing character of nitrophenyl substituents and (2) smaller dihedral angle between aryl substituents and the pyrrolo[3,2-b]pyrrole core (effect of the five-membered ring) leading to more effective $\pi$-conjugation. Conversely, substitution of the pyrrolo[3,2-b]pyrrole core with strong electron-donating groups at positions 2 and 5 (dyes 11–13 and 19) leads to only a slight red shift of absorption (349–395 nm), whereas a prominent red shift of emission (446–534 nm) resulting in large Stokes’ shifts of 6200–8300 cm$^{-1}$ suggests a notable difference in geometry of the $S_1$ excited state and $S_0$ ground state. The concomitant drop in fluorescence intensities ($\Phi_f = 0.04–0.08$) is likely due to the occurrence of charge-transfer processes.

As thoroughly discussed earlier, substituents located at positions 2 and 5 of pyrrolo[3,2-b]pyrrole scaffold have a significantly stronger impact on the optical features compared with those located at positions 1 and 4 (attached to nitrogen atoms). This is clearly manifested in the series of dyes 6–9 and 14 possessing sterically congested 2-halophenyl- or 2-carboxyphenyl- and truxene subunits attached to nitrogen atoms.
Undoubtedly, steric factors impose larger dihedral angles between N-aryl substituents and the central core, causing breakage of electronic communication between them. Nevertheless, the effect on both absorption and emission spectra is negligible in regard to sterically unencumbered 3, indicating a minor contribution of amine-originating substituents on the overall optical characteristics. As far as 14 is concerned, a deeper comparative analysis of absorption spectra indicates a clear increase of the molar absorption coefficient in the high-energy part of the spectrum, which is most likely caused by the presence of the truxene subunit. Of particular note is the strong blue fluorescence (Φfl reaching 0.93). One of the factors responsible for the observed excellent emissive properties could be symmetry-breaking within the truxene core.36

The new methodology allowed for the first time synthesis of coumarin-containing pyrrolopyrrole dyes 35 and 44. Their spectral features differ markedly, depending on the substitution pattern, giving the opportunity for fine-tuning the desired properties. In the case of TAPP 44, the fluorescence quantum yield is low, which is in agreement with the general trend observed for coumarins possessing electron-donating substituents at position 6.37 The bulky coumarin-4-yl substituent present at positions 2 and 5 of TAPP 35 results in the large difference in dihedral angles between ground- and excited-state geometries, which in turn manifests in the large Stokes shift. According to expectations, the π-extension of fused analogue 50 leads to a significant bathochromic shift of the absorption (442 nm) and emission (575 nm) maxima. In the absorption spectrum, two main bands with fine-vibronic features located at 370 and 420−440 nm are present, which is attributed to the rigidity of the structure. Surprisingly, a significant decrease of the fluorescent quantum yield is observed, most likely due to predominant radiationless de-excitation. We observed a similar tendency for the annulated dye 51, which shows a decreased fluorescence response when compared to that for the parent TAPP 7. Moreover, as for TAPP 50, the formation of a seven-
membered ring strongly shifts both absorption and emission maxima; however, for compound 51, it is in the opposite direction (hypsochromically $\lambda_{abs}$ and bathochromically $\lambda_{em}$), which results in a large Stokes’ shift of 5500 cm$^{-1}$.

**CONCLUSIONS**

Lowering the reaction temperature to 50 °C enabled more control of the course of the multicomponent reaction leading to tetraarylpypyrolo[3,2-b]pyrroles. This makes it possible to maintain high yields when increasing the scale to 4.0 and even 40 mmol. Simultaneously, the electron-rich aldehydes and sterically hindered anilines become compatible with this reaction and numerous corresponding TAPPs are obtained. Our findings expand the spectrum of possible tetraarylpypyrolo[3,2-b]pyrroles that can be prepared. These new reaction conditions proved to be extremely efficient in the synthesis of potentially useful halogen derivatives of pypyrolo[3,2-b]pyrroles, which was demonstrated by the synthesis of heteroanalogues of polycyclic aromatic hydrocarbons. The exceptionally high-lying occupied molecular orbitals (HOMO) is crucial in the synthesis of aza-nanographenes but also underpin the development of novel optoelectronic materials.

**EXPERIMENTAL SECTION**

**General Information.** All chemicals were used as received unless otherwise noted. Reagent-grade solvents (MeCN, CH$_2$Cl$_2$, hexane, toluene) were distilled prior to use. All reported NMR spectra were recorded on a 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ppm) for $^1$H and $^{13}$C NMR were determined with TMS as the internal reference; J values are given in Hz. UV–vis absorption and emission spectra were recorded in toluene. For all fluorescence measurements, spectrophotometer slits were set at 2.5 nm. Fluorescence spectra were obtained by excitation at 350 nm for compounds 3, 15–18, 22, 23, 25, 32, 39, and 52; 373 nm for compounds 5–14, 19, 21, 24, 28, 31, 33, 35, 40–42, 44–46, and 49–51; 450 nm for 54; and 460 nm for 43. Chemical character was performed on silica (Kieselgel 60, 200–400 mesh). Mass spectra were obtained with an EI ion source and the EBE double focusing geometry mass analyzer or spectrometer equipped with an electrospray ion source with a quadrupole time-of-flight (q-TOF)-type mass analyzer. The analytical data for compounds 3, 4, 15, 20, 26, 27, 29, and 34 have been described previously.

**Synthesis.** General Procedure for the Synthesis of Pyrrolo[3,2-b]pyrroles on a 20 mmol (Sum of All Starting Materials) Scale. Glacial acetic acid (6 mL), toluene (6 mL), aldehyde (8 mmol), and aniline (8 mmol) were placed in a 25 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 50 °C for 1 h. After that time, Fe(ClO$_4$)$_2$·6H$_2$O (85 mg) was added, followed by diacetyl (0.35 mL, 4 mmol). The resulting mixture was stirred at 50 °C (oil bath) in an open flask under 1 atm. The precipitate was filtered off, washed with cold methanol (in some cases, CH$_3$CN was used), and dried under vacuum. In the event that the product does not precipitate, the organic solvents are removed under reduced pressure, and then the product is obtained by crystallization from acetonitrile. In case the product contains pyridyl or amino substituent, the reaction mixture is quenched with saturated aqueous NaHCO$_3$ (60 mL). The precipitate was filtered off, washed with H$_2$O and CH$_3$CN, and dried under vacuum to afford the pure product.
7.39–7.29 (m, 5H), 7.19 (m, 8H), 6.39 (s, 1H), 6.38 (s, 1H) ppm. 13C NMR (126 MHz, CDCl3) δ = 138.9, 137.4, 136.6, 134.1, 134.1, 133.7, 133.5, 132.0, 132.0, 131.9, 129.6, 128.9, 128.6, 128.5, 127.2, 127.1, 121.8, 119.0, 109.1, 96.5, 96.1 ppm. HRMS (EI): m/z calcd for C32H24N6: 515.1888 [M–1H]−; found: 514.1895.

1.4-Bis(4-cyanophenyl)-2,5-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (10). Yellow solid. Yield: 0.27 g (14%) M.p. 197–200 °C (decomp.). 1H NMR (500 MHz, CDCl3) δ = 7.34 (d, J = 8.4 Hz, 4H), 7.05 (d, J = 8.4 Hz, 4H), 2.96 (s, 12H) ppm. 13C NMR (126 MHz, CDCl3) δ = 139.5, 137.3, 136.3, 135.7, 135.5, 129.4, 129.2, 128.4, 128.2, 127.8, 127.6, 126.7, 129.5, 128.6, 128.5, 127.8, 127.4, 127.2, 127.1, 123.5, 123.3, 123.1, 122.5, 122.3, 121.0, 119.0, 109.3, 96.6, 96.6, 29.5, 29.4, 29.2, 8.7, 8.6, 8.5 ppm. HRMS (ESI): m/z calcd for C58H34N6: 537.2614 [M + H]+; found: 537.2574.

2,5-Bis(4-cyanophenyl)-1,4-bis(4-methylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (11). Yellow solid. Yield: 0.24 g (13%) M.p. 197–200 °C (decomp.). 1H NMR (500 MHz, CDCl3) δ = 8.15 (d, J = 4.7 Hz, 2H), 7.38–7.45 (m, 2H), 7.22 (d, J = 8.2 Hz, 4H), 17.1 (t, J = 8.1 Hz, 4H), 7.02–6.95 (m, 4H), 6.77 (s, 2H), 2.38 (s, 1H), 2.35 (s, 1H) ppm. 13C NMR (126 MHz, CDCl3) δ = 151.9, 149.4, 139.8, 138.6, 135.8, 133.4, 132.9, 129.7, 129.0, 128.5, 128.3, 127.8, 127.3, 126.9, 126.5, 125.7, 124.6, 124.2, 123.7, 123.4, 123.2, 122.2, 121.0, 119.0, 109.3, 96.3, 96.5, 58.6, 58.6, 56.8, 58.9, 29.5, 29.4, 29.2, 8.7, 8.6, 8.5 ppm. HRMS (ESI): m/z calcd for C46H34N6: 470.2001 [M + H]+; found: 469.4438.

1.4-Bis(4-cyanophenyl)-2,5-bis(4-methylbenzyloxyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (12). Yellow solid. Yield: 0.27 g (14%) M.p. 197–200 °C (decomp.). 1H NMR (500 MHz, CDCl3) δ = 7.47 (m, 2H), 7.46 (m, 2H), 7.44 (m, 2H), 7.42 (m, 2H), 7.40 (m, 2H), 7.38 (m, 2H), 7.36 (m, 2H), 7.35 (m, 2H), 7.31–7.23 (m, 4H), 6.61 (s, 1H), 6.59 (s, 1H) ppm. HRMS (ESI): m/z calcd for C54H36N6O2: 722.2740 [M + H]+; found: 722.2707.

1.4-Bis(4-cyanophenyl)-2,5-bis(4-tert-butylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (13). Yellow solid. Yield: 0.18 g (6%) M.p. 268 °C. 1H NMR (500 MHz, CDCl3) δ = 7.38 (d, J = 8.4 Hz, 4H), 7.21 (d, J = 8.4 Hz, 4H), 7.14 (d, J = 8.4 Hz, 4H), 6.81 (d, J = 7.7 Hz, 2H), 6.69 (s, 2H), 6.65 (d, J = 8.2 Hz, 2H), 6.40 (s, 2H), 4.75 (s, 2H), 1.45 (s, 18H) ppm. 13C NMR (126 MHz, CDCl3) δ = 139.4, 137.8, 137.5, 137.3, 136.3, 135.8, 135.3, 135.3, 135.3, 135.3, 134.9, 125.8, 125.8, 124.5, 114.0, 96.8, 55.5, 34.5, 31.4 ppm. HRMS (ESI): m/z calcd for C66H60N6O2: 849.4235 [M + H]+; found: 849.4240.
2H), 2.21 (s, 6H) ppm; 13C{ 1H} NMR (126 MHz, THF-
39] d, 7.8 Hz, 4H), 7.11 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 8.5 Hz, 4H), 6.46 (s, 2H), 2.48 (t, J = 7.7 Hz, 4H), 1.56–1.46 (m, 4H), 1.32–1.18 (m, 28H), 0.87 (t, J = 6.7 Hz) ppm. 
13C{ 1H} NMR (126 MHz, CDCl3, δ = 151.7, 147.6, 140.0, 138.2, 137.4, 135.3, 132.0, 130.1, 128.7, 127.3, 123.9, 122.4, 121.7, 109.4, 96.6, 35.3, 31.8, 32.9, 29.2, 29.2, 22.6, 14.1 ppm. HRMS (EI): m/z calcld for C48H52N8: 740.4315 [M]+; found: 740.4292.

1.4-Bis(3,5-dii-(tet-butylphenyl)-2,5-bis-(fluoranthene-3-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (37). Compound was prepared starting from 0.25 mmol of parent aldehyde, 0.25 mmol of aniline, and 0.125 mmol of butan-2,3-dione. Orange solid. Yield: 45 mg (41%). Spectral and optical properties concur with literature data. 

1.4-Bis(3,5-dii-(tet-butylphenyl)-2,5-bis-(fluoranthene-3-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (38). Yellow solid. Yield: 0.32 g (10%). M.p. 251–252 °C. 1H NMR (500 MHz, CDCl3) δ = 8.71 (dd, J = 4.1, 1.5 Hz, 2H), 8.41 (dd, J = 8.6, 0.9 Hz, 2H), 7.38 (d, J = 7.9 Hz, 2H), 7.30 (dd, J = 8.6, 4.1 Hz, 2H), 7.11 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 8.4 Hz, 4H), 6.69 (d, J = 8.5 Hz, 4H), 6.46 (s, 2H), 2.48 (t, J = 7.7 Hz, 4H), 1.56–1.46 (m, 4H), 1.32–1.18 (m, 28H), 0.87 (t, J = 6.7 Hz) ppm. 
13C{ 1H} NMR (126 MHz, CDCl3, δ = 151.7, 147.6, 140.0, 138.2, 137.4, 135.3, 132.0, 130.1, 128.7, 127.3, 123.9, 122.4, 121.7, 109.4, 96.6, 35.3, 31.8, 32.9, 29.2, 29.2, 22.6, 14.1 ppm. HRMS (EI): m/z calcld for C52H56N4O2: 768.4403 [M]+; found: 768.4433.

1.4-Bis(3,4-diacyano-5-methyl-1H-pyrrole-2-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (39). Yellow solid. Yield: 0.85 g (29%). M.p. 325 °C (decomp.). 1H NMR (500 MHz, THF-d8) δ = 11.07 (s, 2H), 7.15, 7.07 (AA’BB’, J = 8.5 Hz, 8H), 6.51 (s, 2H), 2.55 (t, J = 7.0 Hz, 4H), 2.18 (s, 6H), 1.60–1.50 (m, 4H), 1.30–1.10 (m, 20H), 0.79 (t, J = 7.7 Hz, 6H) ppm. 
13C{ 1H} NMR (126 MHz, CDCl3, δ = 141.1, 138.9, 136.5, 131.8, 131.9, 129.2, 129.3, 129.7, 127.3, 117.5, 114.8, 104.9, 93.9, 86.3, 30.2 ppm. HRMS (EI): m/z calcld for C52H56N4O2: 768.4403 [M]+; found: 768.4433.
18.5, 152.8, 142.1, 135.2, 135.1, 134.1, 133.6, 131.3 (q, J = 131.5 Hz), 128.9, 127.3, 124.4, 122.2, 119.9, 119.3, 117.8, 117.7, 96.5 ppm; HRMS (EI): m/z calc for C_{29}H_{33}N-O; 580.1868 [M+]; found: 580.1685.

Synthesis of 2,5-Bis(2-methoxyphenyl)-1,4-bis(4-methylphenyl)-3-(tricyanovinyl)-1,4-dihydro[3,2-b]pyrrolo[3,2-b]pyrrole (53). Tyrrolopyrrole 30 (250 mg, 0.5 mmol) was dissolved in hot toluene (20 mL) and TCNE (256 mg, 2 mmol) was added, followed by pyridine (0.5 mL). The resulting brown mixture was heated at 110 °C (oil bath) for 3 h. Then, the solvent was removed and the residue was loaded onto the column and chromatographed (silica, DCM/hexanes, 3:2). The first two colored (yellow and black) bands were collected, evaporated separately, and triturated with hot MeOH to afford 52 (72 mg, 24%) and 53 (155 mg, 54%). Compound 52. Black solid. Yield: 73 mg (24%). M.p. 270–271 °C. H NMR (500 MHz, CDCl3) δ = 7.21 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 7.08–7.02 (m, 6H), 6.88 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 8.5 Hz, 2H), 6.24 (s, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.43 (s, 3H), 2.38 (s, 3H) ppm; 13C NMR (126 MHz, CDCl3) δ = 160.6, 158.9, 140.3, 138.8, 138.0, 137.9, 139.3, 135.0, 133.7, 132.4, 132.0, 130.4, 130.0, 129.3, 127.7, 125.6, 125.1, 124.9, 121.5, 114.5, 113.6, 112.9, 111.9, 111.6, 101.8, 93.5, 89.3, 85.5, 53.2, 52.1, 21.2, 21.1 ppm. HRMS (EI): m/z calc for C_{34}H_{24}N_{10}O_{2}: 592.2321 [M+]; found: 592.2323.

Synthesis of 1,4-Bis(4-cteylphenyl)-2,5-bis(4-methylphenyl)-1,4-dihydro[3,2-b]pyrrolo[3,2-b]pyrrole (53). Parent 151 (318 mg, 0.5 mmol) was dissolved in dry THF (45 mL) in a dried Schlenk flask. The mixture was cooled to −78 °C and n-BuLi (2.5 M solution in hexane, 0.4 mL, 1 mmol) was slowly added over a period of 5 min. After stirring at −78 °C for 1 h, BMe=Si (295 mg, 1 mmol) in THF (5 mL) was slowly added and the reaction mixture was allowed to warm to room temperature and stirred for 6 h. The solvents were removed under reduced pressure, and the resulting solid was dissolved in CHCl3 and quenched with 10 mL of H2O. The organic layer was separated and dried over MgSO4 and filtered. After CH2Cl2 was removed under reduced pressure, the residue was loaded onto the column and chromatographed (silica, DCM/hexanes, 3:2). A green fluorescent band was collected, evaporated, and crystallized from CHCl3/MeOH to give yellow crystals of 54. Yellow solid. Yield: 295 mg (67%). M.p. 89–90 °C. H NMR (500 MHz, CDCl3) δ = 8.43 (t, J = 6.5 Hz, 2H), 7.41–7.37 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.0 Hz, 2H), 6.88 (t, J = 8.5 Hz, 2H), 6.66 (t, J = 6.5 Hz, 2H), 6.53 (s, 4H), 6.22 (d, J = 8.0 Hz, 1H), 2.69 (t, J = 8.0 Hz, 2H), 2.59 (t, J = 8.0 Hz, 2H), 2.18 (s, 1H), 1.68 (s, 12H), 1.60–1.60 (m, 1H), 1.40–1.20 (m, 20H), 0.89 (dt, J = 7.0, 1.5 Hz, 6H) ppm; 13C NMR (126 MHz, CDCl3) δ = 152.1, 149.2, 145.3, 142.4, 141.5, 141.0, 139.9, 137.8, 136.3, 135.0, 134.6, 133.3, 129.6, 129.3, 129.2, 129.5, 125.0, 121.9, 120.4, 116.3, 115.7, 35.61, 35.58, 31.5, 31.4, 29.49, 29.47, 29.31, 22.7, 14.1 ppm. HRMS (ESI): m/z calc for C_{78}H_{65}N_{10}O_{2}: 885.6015 [M+H]+; found: 885.6007.
of perchlorate, butane-2,3-dione (3.45 g, 3.5 mL, 40 mmol, 1 equiv) was added, dropwise, over 3 min. The mixture was heated at 50 °C (temperature of the oil bath was 65 °C), and the thermometer immersed in the reaction mixture showed 50 °C. After few minutes, plenty of precipitates were formed and the resulting suspension was vigorously stirred for 16 h at 50 °C with all three necks uncapped throughout the whole reaction time to provide access of the oxygen from the air. Then, the oil bath was removed to allow the reaction mixture to cool to room temperature over 15 min. The resulting dark mixture was filtered, the precipitate was rinsed with methanol (2 × 250 mL) and a small amount of diethyl ether, and dried under vacuum (oil pump, argon/vacuum line, 0.80 mmHg) at 95 °C for 3 h to give the desired pyrrolypyrrole. In the case of pyrrolypyrroles synthesized from pyridinecarbaldehydes, the products do not precipitate; therefore, the workup was as follows: the reaction mixture was transferred to 500 mL RBF, and the solvents were removed under reduced pressure. Fifty milliliters of toluene was added to the obtained dark oil, and the mixture was boiled for 1 min, which caused the formation of large precipitates were formed and the resulting suspension was vigorously stirred for 16 h at 50 °C. Subsequent removal of traces of acetic acid, which facilitates crystallization. Fifty milliliters of acetonitrile was added to the obtained dark oil, and the mixture was evaporated again to remove traces of acetic acid, which facilitates crystallization. Fifty milliliters of toluene was added to the resulting dark oil, and the mixture was boiled for 1 min, which caused the formation of large quantities of precipitates. The flask was allowed to stand at r.t. for 15 min and then transferred to the fridge for 3 h. Subsequent filtration and drying under high vacuum afforded the desired pyridine-substituted pyrrolypyrrole.

Photophysical Measurements. All photophysical studies have been performed with freshly prepared air-equilibrated solutions at room temperature (298 K). A Perkin-Elmer Lambda 25 UV/vis spectrophotometer and a Hitachi F7000 fluorescence spectrometer were used to acquire the absorption and emission spectra. Spectroscopic-grade solvents were used without further purification. Quantum yields were estimated by measuring the fluorescence and absorbance of samples and a dye reference in DCM, MeCN, and EtOH and for selected examples in water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.joc.0c01665.

Optical properties; copies of 1H and 13C{1H} NMR data; determination of the structure of compound 51; X-ray crystallographic information; and photophysical data (PDF)

X-ray crystal data for 50 ( CIF)

X-ray crystal data for 53 ( CIF)

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M.T., O.V., and D.K. contributed equally. The manuscript was written through the contributions of all authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors would like to thank the Foundation for Polish Science (TEAM POIR.04.04.00-00-3CF4/16-00), COST (CHAOS CA 15106), and Global Research Laboratory Program (2014K1A12064569) through the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (Korea). The authors thank Dr. David C. Young for amending the manuscript.

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