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Efficient Synthesis of Dipyrrolobenzenes and Dipyrrolopyrazines via Bidirectional Gold Catalysis: a Combined Synthetic and Photophysical Study

Robin Heckershoff, Tobias Schnitzer, Tim Diederich, Lukas Eberle, Petra Krämer, Frank Rominger, Matthias Rudolph, and A. Stephen K. Hashmi*

ABSTRACT: New N-heterocyclic fluorophores are sought-after compounds for organic electronic devices. Here, we report on a straightforward synthesis to access meta/para-dipyrrolobenzenes and para-dipyrrolopyrazines in high yields using a bidirectional gold-catalyzed cyclization strategy. The versatility of our reaction protocol was showcased by preparing dipyrroloarenes with different substituents, various functional groups, and in a multitude of substitution patterns. Furthermore, we showed that the dipyrroloarenes can be post-modified by N-alkylation to improve the solubility or bromination to yield precursors for further derivatization via cross-coupling. Investigation of the photophysical properties of the—mostly unprecedented—dipyrroloarenes identified strong blue emitters such as the diphenyl meta-dipyrrolobenzene with a quantum yield of 98%. Moreover, we showed that changes in the solvent polarity or interactions with Lewis acids such as borane can be used to fine-tune the photophysical properties of the fluorophores.

INTRODUCTION

In recent years, extended N-heterocyclic arenes attracted increasing attention in the field of organic electronics.1,2 Their low band gap combined with high chemical and physical stability enable their use in various devices including organic field-effect transistors, 3–8 organic photovoltaics, 9,10 or organic light-emitting diodes (OLEDs).11,12 Constant evolution in the field of organic electronics and a need for higher energy efficacy emphasize the importance for synthetic strategies toward new N-heterocyclic arenes and the investigation of their photophysical properties.

A vastly unexplored and thus underappreciated class of organic emitters are dipyrrolobenzenes (Scheme 1a). This is surprising as the synthesis of dipyrrolobenzenes has been already described by Meldrum in 1899, 13 and Ruggli described a solution of diphenyl-m-dipyrrolobenzene as "magnificently blue fluorescent."14 Furthermore, seminal studies by Nakamura, 15–17 Geise, 18 and Wakamiya 19 suggest dipyrrolobenzenes as potential hole-injecting and near-infrared-absorbing, electroluminescent dyes. However, an in-depth photophysical analysis of dipyrrolobenzene derivatives has not been described, likely due to a lack of efficient and mild synthetic protocols that allow for implementation of different functional groups. 20–29

Since 2000, 30,31 gold catalysts have been established as a superior tool for the activation of alkynes, and many mild and high-yielding strategies to access N-heterocyclic five-membered...
rings are reported (Scheme 1b).\textsuperscript{32-47} The alkyne precursors are typically obtained via straightforward Sonogashira coupling, and the subsequent gold-catalyzed cyclization can be performed in the presence of various functional groups. Thus, we envisioned that a gold-catalyzed bidirectional cyclization of dianimidynes would provide access to a broad scope of dipyrrolobenzenes.

Here, we report on the gold-catalyzed synthesis of a series of meta- and para-dipyrrolobenzenes (mDPB/pDPB) and para-dipyrrolopyrazines (pDPP) (Scheme 1a) and their corresponding reaction precursors. Furthermore, we prove the synthetic utility of dipyrroloarenes in various post-modification reactions such as N-alkylation and brominations. Photophysical characterization identified multiple blue emitters with some of them having remarkably quantum yields of >95%.

**RESULTS AND DISCUSSION**

**Catalyst Screening.** We started our investigation by probing the bidirectional gold catalysis strategy on the synthesis of diphenyl-substituted meta-dipyrrolobenzene mDPBa. The alkyne precursor 1a was readily obtained in 81% yield by standard Sonogashira cross-coupling [5 mol % (Ph3P)2PdCl2 and 5 mol % CuI, THF/PrNEt2] of phenylacetylene and 4,6-diodobenzene-1,3-diamine. We tested a small set of different Au catalysts [SPhosAuNTf2 (I), Ph3PAuNTf2 (II), and IPrAuNTf2 (III)]. Table 1, entry 1-3 for the cyclization reaction of mDPBa in EtOH at room temperature. In the presence of 10 mol % of catalyst I and II, no clear product was obtained [probably induced by the in situ reduction of the sensitive gold(I) phosphane species, leading to ill-defined mixtures of gold species], while IPrAuNTf2 III showed 92% conversion and clean formation of product mDPBa. Remarkably, mDPBa precipitated from EtOH allowing for simple workup via centrifugation to isolate pure mDPBa in 87% yield.

Screening of other solvents did not improve the reaction as different alcohols (entry 4-7, here, e.g. in MeOH solubility problems prevented a good conversion) and aprotic solvents (entry 8-13) provided mDPBa in lower amounts (16-87% conversion, entry 8-11) or complicated the product isolation (entry 12-13). Finally, we lowered the catalyst loading and obtained mDPBa in 87% yield in the presence of 5 mol % III in EtOH within only 2 h. Pleasingly, crystals suitable for X-ray analysis were obtained by vapor diffusion (DMSO/H2O) that confirmed the dipyrrolobenzene structure of mDPBa (Scheme 3a).

**Synthesis of meta-Dipyrrolobenzenes.** With these conditions in hand, we challenged our reaction protocol using a series of dynes 1b−1i, which we obtained via Sonogashira cross-coupling of the corresponding acetylenes and 4,6-diodobenzene-1,3-diamine (Scheme 2). Besides mDPBa, the reported yields refer to that of the isolated products.

![Scheme 2. Synthesis of Dialkyne Precursors 1 via Sonogashira Cross-Coupling](image)

<table>
<thead>
<tr>
<th>entry</th>
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<th>conversion [%]</th>
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<td>SPhosAuNTf2</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>Ph3PAuNTf2</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>EtOH</td>
<td>IPrAuNTf2</td>
<td>92 (87)</td>
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</tr>
<tr>
<td>5</td>
<td>tPrOH</td>
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<td>73</td>
</tr>
<tr>
<td>6</td>
<td>BuOH</td>
<td>IPrAuNTf2</td>
<td>79</td>
</tr>
<tr>
<td>7</td>
<td>PhMe</td>
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<tr>
<td>9</td>
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<tr>
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<tr>
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<td>IPrAuNTf2</td>
<td>62</td>
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<tr>
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<td>EtOAc</td>
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<tr>
<td>13</td>
<td>DMF</td>
<td>IPrAuNTf2</td>
<td>95</td>
</tr>
</tbody>
</table>

*Conversion was determined by UPLC-MS. A mixture of products was observed. Yield of the isolated product.*

**meta-dipyrrolobenzenes bearing substituted aryl groups (mDPBb, mDPBc), heteroaromatic groups (mDPBd), and larger π-systems (mDPBe, mDPBF) were obtained in 0.5−18 h in excellent yields (92−99%) (Scheme 3a). However, substrates bearing electron-poor aromatic groups (mDPBb) or aliphatic substituents (mDPBc) did not engage in the reaction or showed decomposition, respectively [in this case also, AuCl3 and a series of gold(III) complexes were tested without any success]. Interestingly, starting material 1g, which contains amino groups on both, the central and the two peripheral benzene rings, did not form the dipyrrolobenzene but instead the diindole 1g'. In order to increase the solubility of the dipyrrolobenzenes for potential processing of electronic devices, we explored N-alkylation. Pleasingly, the initial attempt to form alkylated derivatives mDPBa' and mDPBc' by deprotonation of mDPBa and mDPBe with NaH and subsequent addition of 1-bromo-octane (DMF, rt, 4−24 h) succeeded without further optimization in moderate yields (31 and 40%, Scheme 3b).

**Synthesis of para-Dipyrrolobenzenes.** Next, we focused on the gold-catalyzed synthesis of para-dipyrrolobenzenes pDPB (Scheme 4). The synthesis of the alkyne precursor rendered more difficult than expected (Scheme 4a). Initial experiments to synthesize 2,5-diodobenzene-1,4-diamine failed, and the corresponding dibromide showed low reactivity and a
high rate of decomposition. Instead, the N-phenyl derivative 3 was prepared via a TiCl4-supported reductive amination of readily accessible diiodoquinone 2 and aniline.48 Sonogashira cross-couplings with different aryl alkynes and ethynyltrimethylsilane afforded the corresponding diyne compounds 4a−d. It is of note that all aryl-alkyne compounds show a high reactivity toward cycloisomerization, resulting in the partial conversion to the final dipyrrolobenzenes. This already occurs during the cross-coupling or during column chromatography on silica gel or aluminum oxide, which is problematic due to the low solubility of the final product. Therefore, we developed a protocol after which the ammonium salt, formed in the cross-coupling reaction, is removed by aqueous workup followed by treatment of the crude reaction mixture with minimal amounts of IPrAuNTf₂ (<1 mol % was sufficient for full conversion) and washing/recrystallizing of the resulting product. Using this simple workup, the desired para-dipyrrolobenzenes pDPBa−d (Scheme 4b) were obtained in high yields (76−87% over two steps). In contrast to 1g, the N-phenyl analogue 4b regioselectively forms the dipyrrolobenzene pDPBb and no diindole isomer (compare Scheme 3a, 1g′, which at the moment cannot yet be explained). Remarkably, even the halogenated substrate 4c—a substrate incompatible with most other cyclization methods (e.g., Pd/Rh catalysis or BuLi treatment)—did not interfere with the gold catalyst, providing the dibromo-dipyrrolobenzene pDPBc, which is a versatile compound for postfunctionalizations via cross-couplings. In order to obtain products with a smaller π-system, we faced the synthesis of unsubstituted pDPB. We therefore started from a silyl-protected alkyne precursor 4d-TMS, which showed a lower tendency to cycloisomerize and can be transformed to terminal diyne 4d-H using K₂CO₃ in MeOH/DCM. Surprisingly, under the reaction conditions for the cycloisomerization both, 4d-TMS and 4d-H, form the same product pDPBd, suggesting an in situ TMS-deprotection of 4d-TMS. Note, 4d-TMS reacts very cleanly, while 4d-H forms side products and provides pDPBd in a lower yield.

To access non-N-arylated para-dipyrrolobenzenes, we followed a reaction procedure recently established in our group that relies on the Boc-protected aniline 5 (Scheme 5).49 The Boc-protected para-dipyrrolobenzene pDPBe was obtained in excellent yield (94% in the final step). Heating of the compound to 200 °C led to deprotected pDPBe in almost quantitative yield (98%) and in an overall yield of 86% over three steps, which significantly outperforms previously reported syntheses.50−53

Synthesis of para-Dipyrrolopyrazines. Pyrazine is frequently found in organic functional materials, where its electronegative character has a significant influence on the optoelectronic and morphological properties of the com-
pounds, such as in, for example, thienopyrazines,54 diindenopyrazines,55 and azapentacenes.56,57 Replacing the benzene core of a DPB by a pyrazine results in the class of the dipyrrolopyrazines (DPPs, Figure 1a). Surprisingly, little is known about synthesis and photochemical properties of DPPs. Next to a few occurrences in annulated systems,58,59 only recently a method was developed to synthesize N-methylated DPPs.60 The readily available 2,5-dibromo-3,6-dichloropyrazine (Scheme 7a). For example, in the reaction of 8a, only small amounts of the non-cyclized product alongside with the single- and double-cyclized product (pDPPa) were observed. A major part (53% yield) of pDPPa was separated, and treatment of the residual product mixture with PdCl2(MeCN)2 (chlorobenzene, 110 °C, 2 d) provided the fully cyclized product and additional 25% yield, resulting in an overall yield of 78%. In comparison, the same reaction in the presence of IPrAuNTf2 was much slower; hence, more catalyst and longer reaction time were needed. We attribute the low reactivity to the formation of a stable pyrazine moiety,66,67 TIPS-protected substrate DPPb with TBAF in THF led almost exclusively to the double cyclized product (pDPBb) with 92% yield, which is a versatile precursor for further functionalizations via cross-couplings.6). However, the Buchwald–Hartwig coupling resulted in an inseparable mixture of mono-, di-, and tri-aminated products with different substitution patterns. To our delight, changing the reaction order and starting with the Sonogashira cross-coupling resulted in the corresponding alkylnyl pyrazines 8a–c in good yields of 87–90%.

The Buchwald–Hartwig amination of 8 with aniline did not result in the expected alkylnyl-N-phenyl derivatives due to partial in situ cyclization (Scheme 7a). For example, in the reaction of 8a, only small amounts of the non-cyclized product alongside with the single- and double-cyclized product (pDPPa) were observed. A major part (53% yield) of pDPPa was separated, and treatment of the residual product mixture with PdCl2(MeCN)2 (chlorobenzene, 110 °C, 2 d) provided the fully cyclized product and additional 25% yield, resulting in an overall yield of 78%. In comparison, the same reaction in the presence of IPrAuNTf2 was much slower; hence, more catalyst and longer reaction time were needed. We attribute the low reactivity to the formation of a stable pyrazine–gold complex, which was previously observed for the related pyridine moiety.66,67 TIPS-protected substrate 8b led to a chromatographically separable mixture of double cyclized pDPBb (9% yield) and single cyclized 9 (77% yield, see Supporting Information) with at most trace amounts of the non-cyclized product. In this case, treatment of 9 with 10 mol % IPrAuNTf2 in chlorobenzene at 110 °C for 2 days resulted in full conversion to pDPBb in 92% yield, resulting in an overall yield of 80% over two steps. The structure of pDPBb was unambiguously assigned by X-ray crystal structure analysis (Scheme 7c, crystals grown by evaporation of a solution of the compound in ethyl acetate). Treatment of pDPBb with TBAF in THF led almost quantitatively to pDPBc (Scheme 7b). The same product was also obtained from 8c, but an unselective formation of multiple products reduced the yield to only 10%. Finally, we postfunctionalized pDPBb with N-bromosuccinimide to the dibromide pDPBd (92% yield), which is a versatile precursor for further functionalizations via cross-couplings.

Photophysical Characterization. Next, we studied the photophysical properties of the synthesized compounds: mDPBb, pDPBb, pDPBc, and stable diarylalkyne precursors were studied by UV–Vis and fluorescence spectroscopy in DCM (Table 2, Figure 1). mDPBb−c, mDPBb′−e, and pDPBe were also studied in DMSO (mDPBe/f only in DMSO due to...
The absorption spectra of the dialkynyl compounds (1a−h, 4a, 6, and 8a) show a local maximum of the longest absorption wavelength (λ_{max,abs}) between 351 and 380 nm. Only the di-N-arylated dialkyne 4a absorbs at a higher wavelength of 427 nm. Based on the absorption onset, the optical gaps were determined between 3.02 and 3.25 eV for 1a−h, 6, and 8a and 2.55 eV for 4a, respectively. All compounds exhibit blue to blue-green fluorescence in solution (DCM) and blue to green fluorescence in the solid state (Figure 2). A larger influence of the substituents is observed for the emission spectra, where a higher bathochromic shift is displayed for systems with an extended π-system (1e/f, 4a). The maxima of the shortest emission wavelength (λ_{max,em}) lies at 390−518 nm, resulting in Stokes shifts of about 2000−4600 cm\(^{-1}\). Quantum yields (QY) are mostly in the single digit range and reach higher values (20−39%) for the larger systems 1e/f and 4a. mDPB−f and pDPB−e/e′ have similar absorption spectra with λ_{max,abs} ranging from 327 to 375 nm with larger bathochromic shifts for the π-extended compounds. The measurements in DMSO show higher values of about 10 nm corresponding to smaller optical gaps of 2.88−3.17 eV compared to that in DCM of 3.01−3.45 eV. The compounds are bright blue emitters in solution (DCM) and mostly show blue to green fluorescence in the solid state (Figure 2). The same trends as in the absorption spectra are also observed in the emission spectra with λ_{max,em} of 358−468 nm (Stokes shift of 885−7688 cm\(^{-1}\)) with expected shifts depending on the size of the π-system and electronic effects of the substituents. QY are strongly dependent on the substituents of the mDPB and pDPB core. Low values are observed for the bromine-substituted core (pDPBc, 2%) or on small π-systems.

**Figure 1.** Normalized absorption and emission spectra of the fluorogenic compounds.

**Scheme 6. Synthesis of Dialkyne Precursors 8 via Sonogashira Cross-Coupling**

Cl\(\text{N}^+\)Br + \(\text{R}^\text{−}\) → (PPh\(_3\))\(_2\)PdCl\(_2\) → Cl\(\text{N}^+\)Cl + \(\text{R}^\text{−}\)

7

Cl\(\text{N}^+\)Br + \(\text{TIPS}^\text{−}\) → Cl\(\text{N}^+\)TIPS + \(\text{TMS}^\text{−}\)

8

8a, 90%; 8b, 88%; 8c, 87%
(pDPBa, 5%). The other derivatives have medium to high QY of 37–79% in DCM and 14–83% in DMSO. The alkylated compounds mDPBa' and mDPBe' show only minor differences in the photophysical properties compared to the non-alkylated counterparts with exception of the QY. Alkylated mDPBe' shows a lower QY in DMSO compared to mDPBe (16–32%) and a QY of 39% in DCM. Remarkably, mDPBa' exhibits a boost of the QY from 79% (mDPBa) to 98% for the alkylated derivative (mDPBa') in DCM and thus topping established fluorescent dyes like fluorescein or rhodamin 6G.68,69 pDPBa has a $\lambda_{\text{max,abs}}$ of 373 nm and the Ph, TIPS, and TIPS/Br substituents of pDPBa/b/d result in a bathochromic shift of about 20–40 nm correlating to optical gaps between 2.80 and 3.10 eV. pDPPa–c show blue to green fluorescence in the solid state (Figure 2) and blue fluorescence in solution with $\lambda_{\text{max,em}}$ of 419–454 nm and corresponding Stokes shifts, ranging from 2358–3149 cm$^{-1}$. QY of pDPPa–d are comparable to their pDPB counterparts with higher values for the tetra phenyl compound pDPBa (56%), lower QY for pDPBa/b/c (23%/14%), and almost full fluorescence quenching due to the bromine substituents for pDPDd.

To study the effect of the different cores on the photophysical properties, we compared the absorption and emission spectra of the diphenyl derivatives of the C-substituted meta-dipyrrolobenzene (mDPBa) and para-dipyrrolobenzene (pDPBe) and the corresponding N-substituted para-dipyrrolobenzene (pDPBd) and para-dipyrrolopyrazine (pDPDc). In the absorption spectra, C- and N-substituted derivatives can be clearly differentiated: the C-substituted show a global maximum at ∼360 nm, the maxima of the N-substituted derivatives are blue-shifted to ∼275 nm. The fluorescence spectra of three of the four derivatives show maxima at a similar wavelength ∼415 nm, while the maximum of the N-substituted pDPBd is blue shifted by about 60 nm to a value of 358 nm. Similarly, also the QY differs significantly depending on the substitution pattern: the C-substituted show medium to high QY of 47–79%, while the QYs of the N-substituted derivatives are low 5–14%. The different effect of C- and N-substitution is underlined by the comparison to the tetra phenylated derivatives pDPBa and pDPBa. pDPBa exhibits similar absorption and emission spectra to mDPBa/pDPBe without N-arylation and therefore a large blue-shift compared to pDPDd. The additional C-arylation of the pyrazine compounds leads to a red-shift of both the absorption and emission spectra of about 40 nm and 20 nm, respectively. QYs are comparable to the C-arylated diphenyl derivatives, and the pyrazine core has only a minor influence on this property.

**Solvatochromy Study.** During the photophysical characterization of the meta-dipyrrolobenzenes, we realized interesting differences of the emission in DMSO versus DCM. We envisioned that the NH groups are potential coordinating sites for solvent molecules, thus giving rise to solvatochromic behavior. To study such a behavior, we focused on the diphenyl-substituted mDPBa and compared the absorption and emission spectrum in DCM, DMSO, THF, toluene, and MeOH (0.1 mM solutions). While no drastic changes in the shape of the absorption spectra were observed (Table 3a), a gradual increase in the emission maximum wavelengths was observed with increasing solvent polarity. The maxima range from $\lambda_{\text{max,em}}$ of 416 nm in toluene to 440 nm in DMSO. Furthermore, the QY of the mDPBa differs in the five solvents: the lowest QY was observed in MeOH (65%) and DMSO.

Scheme 7. (a) Buchwald Hartwig Amination and Subsequent Cyclization of 8 Forming pDPBa, (b) Postfunctionalizations of pDPBa, and (c) Crystal Structure of pDPBa.

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**The reported yields refer to that of the isolated products.**
Remarkably, an almost quantitative QY of 96% was observed in THF.

Effect of Lewis Acids on Photophysical Properties.

Based on the effect of different solvents on the emission of the dipyrrrolobenzene, we next focused on the interaction with Lewis acids, specifically BH₃. As the experiments were performed at slightly increased concentrations of 5 mM in DCM, we focused on the derivative mDPBb to ensure sufficient solubility. Upon addition of 10−50 equiv of BH₃ (1 M in THF), significant differences in the absorption and emission spectra are observed: the maxima in the absorption spectra at 316 and 356 nm shift to 340 and 369 nm, respectively, and the maximum at higher wavelength decreases in intensity with increasing amount of BH₃ present. Even more drastic effects were found in the emission spectra, where the maximum at 416 nm fully disappears, and a new maximum at 534 nm is observed. This is reflected in the visible fluorescence of the solutions (Table 3b), which changes from blue (0 equiv BH₃) over almost white (30 equiv BH₃) to greenish-yellow (50 equiv BH₃). The presence of an isosbestic point at ∼495 nm suggests the interconversion of two species upon addition of BH₃. We hypothesized that the changes in the optical properties are due to the formation of an N−BH₃ adduct. This was supported by NMR spectroscopic analysis of the reaction, in which addition of BH₃ solution to mDPBb in CD₂Cl₂ led to a downfield shift of the NH signals from 8.22 to 9.48 ppm and the appearance of new aromatic signals (see the

Table 2. Photophysical Properties of DPBs, DPPs, and Alkynyl Substrates in DCM at rt; Measurements in DMSO in Parenthesis

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<th>Compound</th>
<th>λₘₐₓₐbs[a] [nm]</th>
<th>λₘₐₓₐem[b] [nm]</th>
<th>Stokes Shift [cm⁻¹]</th>
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<td>4359(4745)</td>
<td>391(404)</td>
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<td>&lt;(4697)</td>
<td>&lt;(431)</td>
<td>&lt;(2.88)</td>
<td>&lt;(32%)</td>
</tr>
<tr>
<td>mDPBb</td>
<td>&lt;(383)</td>
<td>&lt;(474)</td>
<td>&lt;(5013)</td>
<td>&lt;(429)</td>
<td>&lt;(2.89)</td>
<td>&lt;(43%)</td>
</tr>
<tr>
<td>mDPBb</td>
<td>356(339)</td>
<td>416(437)</td>
<td>4051(6615)</td>
<td>3941(384)</td>
<td>3.15(2.23)</td>
<td>98%(71%)</td>
</tr>
<tr>
<td>mDPBb</td>
<td>342(340)</td>
<td>464(472)</td>
<td>7688(8225)</td>
<td>403(417)</td>
<td>3.08(2.97)</td>
<td>39%(15%)</td>
</tr>
<tr>
<td>mDPBb</td>
<td>375</td>
<td>418</td>
<td>2743</td>
<td>407</td>
<td>3.05</td>
<td>59%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>345</td>
<td>407</td>
<td>4415</td>
<td>390</td>
<td>3.18</td>
<td>49%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>351</td>
<td>468</td>
<td>7123</td>
<td>396</td>
<td>3.13</td>
<td>2%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>347</td>
<td>358</td>
<td>885</td>
<td>359</td>
<td>3.45</td>
<td>5%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>327</td>
<td>391</td>
<td>5066</td>
<td>369</td>
<td>3.36</td>
<td>59%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>392(408)</td>
<td>413(427)</td>
<td>1297(1091)</td>
<td>410(426)</td>
<td>3.01(2.91)</td>
<td>47%(54%)</td>
</tr>
<tr>
<td>mDPBb</td>
<td>388</td>
<td>442</td>
<td>3149</td>
<td>436</td>
<td>2.84</td>
<td>56%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>397</td>
<td>438</td>
<td>2358</td>
<td>417</td>
<td>2.97</td>
<td>23%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>373</td>
<td>419</td>
<td>2945</td>
<td>400</td>
<td>3.10</td>
<td>14%</td>
</tr>
<tr>
<td>mDPBb</td>
<td>405</td>
<td>454</td>
<td>2665</td>
<td>442</td>
<td>2.80</td>
<td>1%</td>
</tr>
</tbody>
</table>


Figure 2. Photographs of the compounds as solid and as solution in DCM under irradiation by UV light (365 nm).

(71%) followed by DCM (79%) and toluene (81%). Remarkably, an almost quantitative QY of 96% was observed in THF.
Supporting Information for 1H NMR spectra). Furthermore, addition of BH₃ to a solution of mDPBb in THF resulted in no changes of the fluorescence, presumably due to competitive coordination of the solvent to BH₃. Finally, we showed that the reaction is reversible: when adding THF to a yellow fluorescent solution of mDPBb/BH₃ (50 equiv), the original blue fluorescence of mDPBb was regained.

### Table 3. (a) Solvatochromy Study of mDPBa in Various Solvents and (b) Change of Absorbance and Fluorescence of mDPBa in the Presence of BH₃

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \lambda_{\text{max,abs}}[^{[a]}] ) [nm]</th>
<th>( \lambda_{\text{max,em}}[^{[b]}] ) [nm]</th>
<th>Stokes Shift [cm⁻¹]</th>
<th>( \lambda_{\text{onset,abs}} ) [nm]</th>
<th>( E_{\text{g(opt)}}[^{[c]}] ) [eV]</th>
<th>QY</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCM</td>
<td>355</td>
<td>420</td>
<td>4359</td>
<td>391</td>
<td>3.17</td>
<td>79%</td>
</tr>
<tr>
<td>DMSO</td>
<td>364</td>
<td>440</td>
<td>4745</td>
<td>404</td>
<td>3.07</td>
<td>71%</td>
</tr>
<tr>
<td>THF</td>
<td>360</td>
<td>426</td>
<td>4304</td>
<td>398</td>
<td>3.12</td>
<td>96%</td>
</tr>
<tr>
<td>toluene</td>
<td>357</td>
<td>416</td>
<td>3973</td>
<td>393</td>
<td>3.15</td>
<td>81%</td>
</tr>
<tr>
<td>MeOH</td>
<td>357</td>
<td>430</td>
<td>4755</td>
<td>395</td>
<td>3.14</td>
<td>65%</td>
</tr>
</tbody>
</table>

[^{[a]}]: Maximum of the longest absorption wavelength.[^{[b]}]: Maximum of the shortest emission wavelength.[^{[c]}]: Optical gap estimated from \( \lambda_{\text{onset,abs}} \): \( E_{\text{g(opt)}} = \frac{1239.8}{\lambda_{\text{onset,abs}}} \).

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**CONCLUSIONS**

In conclusion, we reported on a bidirectional gold-catalysis strategy to access a broad scope of mostly unprecedented dipyrroloarenes. These N-heterocyclic blue emitters show remarkable photophysical properties. We envision many applications for the—so far underappreciated—dipyrroloarenes and are convinced that our study marks a starting point for applications of these compounds as, for example, OLED...
emitters in the field of organic electronics. This is supported by their thermal stability; most of the target compounds without decomposition melt at temperatures above 300 °C.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c02394.

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**REFERENCES**


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CCDC 2155478−2155479 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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