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Synthesis of Quinolino[4,3-*j*]phenanthridines and their Photophysical Characterization

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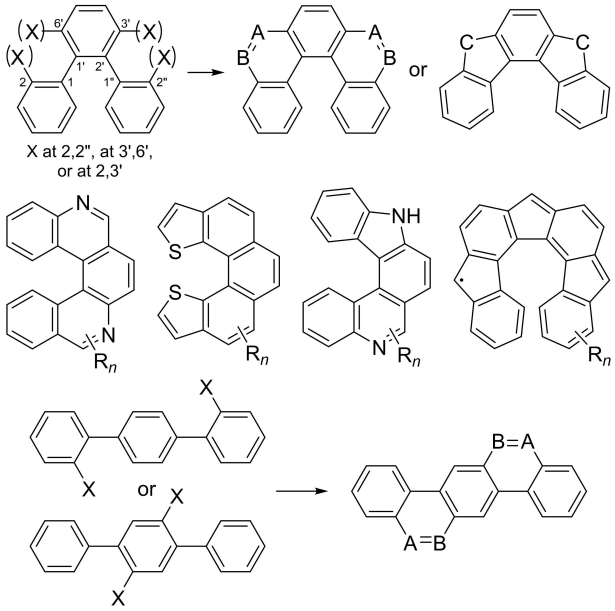
Quinolino[4,3-*j*]phenanthridines were synthesized from *para*-terphenyl-2,2′′-diamines, which were obtained by cross-coupling reactions. The diamines were converted into amides and *ortho*-cyclized to quinolino[4,3-*j*]phenanthridines using *Morgan-Walls* reactions. Prolonged reaction times were required in these electrophilic substitution reactions to overcome the respective deactivated intermediates formed after the first *ortho* fusion. Optophysical properties were determined by UV/Vis and fluorescence spectroscopy and calculated by quantum chemical calculations. The compounds exhibit rather small HOMO/LUMO gaps and a remarkable bathochromic shift of luminescence upon protonation, what makes these compounds promising candidates for optoelectronic applications.

Introduction

Polycyclic aromatic hydrocarbons (PHs of PAHs)[1] are of significant interest since their extended π systems lead to small HOMO/LUMO gaps and thus to quite special electronic and optoelectronic properties. When these compounds contain nitrogen atoms in their core, they are occasionally called PANHs (polycyclic aromatic nitrogen-containing hydrocarbons).[2] Position and number of nitrogen atoms allow for a fine tuning of the properties and further characteristics like electron acceptor abilities might allow for applications in field effect transistors (FETs), photo transistors, organic light diodes (OLEDs), solar cells, sensors, and memory devices.[3] A possible intercalation of these compounds (or of their *N*-alkylated derivatives) into DNA opens up further possibilities in chemical biology and medicinal applications.[4]

We developed a method for the synthesis of helicenes, where we used *ortho* fusions in *ortho*-teraryls and obtained various nitrogen-[5] and sulfur-containing helicenes[6] as well as helicene radicals (Scheme 1).[7] We considered this method similarly suitable for the synthesis of roughly linearly arranged PANHs by *ortho* fusion of *para*-terphenyls. The thus accessible quinolino[4,3-*j*]phenanthridines (QPs) have occasionally been reported as side products,[8] as products in test reactions,[9] as intermediates for polymer syntheses,[10] and as sporadic examples in different synthetic approaches.[11] One patent proposed utilization of these compounds in OLEDs.[12] Here, we wish to report their synthesis by *ortho* fusion and their (opto)electronic properties.



Scheme 1. Top row: *ortho* fusion in *ortho*-terphenyl; middle: examples of helicenes synthesized by *ortho* fusion; bottom: possible approaches to PANHs by *ortho* fusion in *para*-terphenyls (X: suitable substituents for coupling; A, B, and C: various atoms and atom groups).

Results and Discussion

Synthesis of 7,14-Unsubstituted Quinolino[4,3-j]phenanthridines

We started the synthesis of QPs **9** from commercially available methyl- and methoxy-substituted nitroanilines **1** (Scheme 2). *Sandmeyer* reaction according to *Wetzel et al.* furnished the respective iodides **2**,[13] which were transformed into stannanes **3** by palladium-catalyzed reaction with bis(tributyltin).[14]

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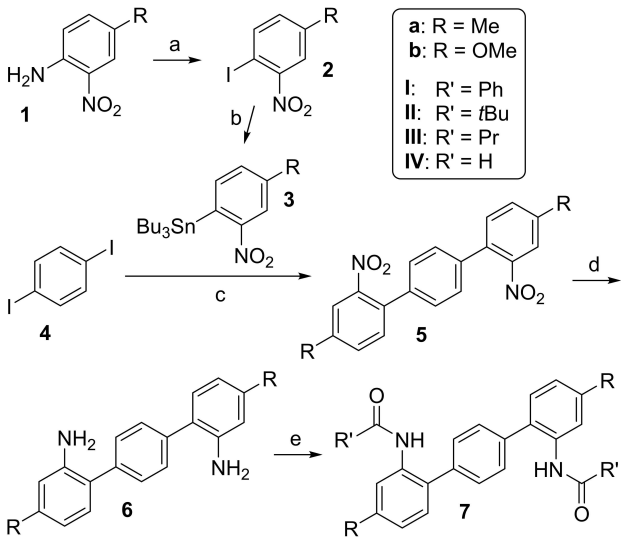
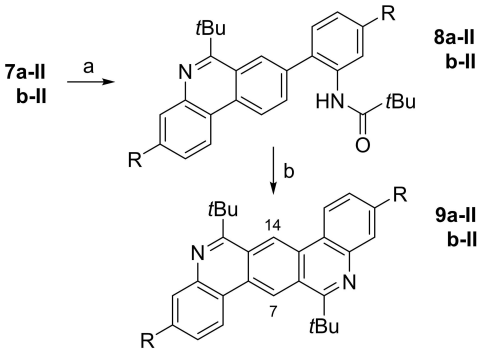


Scheme 2. Synthesis of acylamido-terphenyls **7**. Conditions: a) $NaNO_2$, HCl, 0 °C, 30 min, then KI, 0 to 70 °C, 1.5 h, **2a**: 79%, **2b**: 81%; b) Sn_2Bu_6, cat. $Pd[(PPh_3)_2]Cl_2$, PPh_3, *o*-xylene, 100 °C, 4 d, **3a**: 64%, **3b**: 74%; c) **3a**/**3b**, cat. $Pd(PPh_3)_4$, cat. CuI, CsF, DMF, 55 °C, 4 d, **5a**: 93%, **5b**: 97%, d) KBH_4, CuCl, MeOH, 0 to 50 °C, 1.5 h, **6a**: 86%, **6b**: 95%, e) see Table 1.

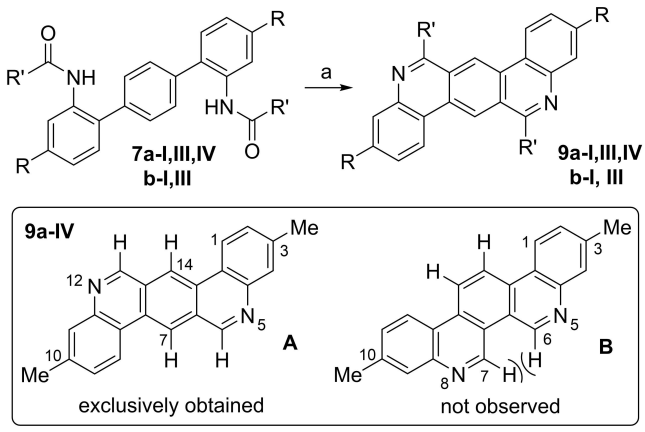
Table 1. Conditions for the formation of amides **7**.

Starting material	Acid derivative	Method[a]	Product (yield)
6a	benzoyl chloride	A	**7a-I** (99%)
6a	pivaloyl chloride	A	**7a-II** (quant.)
6a	butyryl chloride	A	**7a-III** (quant.)
6a	formic acid	B	**7a-IV** (90%)
6b	benzoyl chloride	A	**7b-I** (97%)
6b	pivaloyl chloride	A	**7b-II** (85%)
6b	butyryl chloride	A	**7b-III** (quant.)

[a] A: Et_3N, CH_2Cl_2, 0 °C to rt, 16 h; B: pyridine, PPAA, EtOAc/MeCN, −15 °C to rt, 16 h.



Scheme 3. Synthesis of QPs. Conditions: a) see Table 2, b) P_4O_{10}, $POCl_3$, 110 °C, 3 d, **9a-II**: 14%, **9b-II**: 26%.



Scheme 4. One-step synthesis of QPs. Conditions: a) P_4O_{10}, $POCl_3$, 110 °C, 3 d, **9a-I**: 41%, **9a-III**: 26%, **9a-IV**: 9%, **9b-I**: 31%, **9b-III**: 41%.

Double *Stille* coupling with 1,4-diiodobenzene (**4**) gave rise to dinitroterphenyls **5**. This cross coupling was performed using conditions described by *Mee* et al.,[15] where we took advantage of the rate-accelerating effects of copper salts[16] and cesium fluoride.[17] The latter was reported to lead to the precipitation of the formed organotin halides by conversion into the respective organotin fluorides. Dinitroterphenyls **5** were thus obtained in excellent yields. Based on a protocol from *He et al.*, reduction of the nitro groups was carried out with potassium borohydride in the presence of copper(I) chloride[18] furnishing diaminoterphenyls **6** with high yields. The synthetic steps of stannylation, *Stille* coupling, and subsequent reduction to diamine **6** can be shortened by *Suzuki* coupling according to *Herzog et al.* with commercially available starting materials.[5b] This was exemplarily demonstrated using terphenyldiamine **6a** as a target. Further details and reaction conditions are given in the SI. Reaction with benzoyl, pivaloyl, or butyryl chloride, respectively, led to a virtually quantitative formation of the respective bisamides **7** (Table 1). We furthermore reacted diamine **6a** with formic acid by using propanephosphonic acid anhydride (PPAA)[19] as coupling agent according to a published protocol from *Dunetz et al.* and obtained formamide **7a-IV**.

For the *ortho* fusions with installation of the required imine subunits, we used a method that proved in our group to be well suited for the realization of similar transformations: Double S_EAr reaction with concomitant dehydration of bisamides **7** was expected to be possible with a double *Morgan-Walls* cyclization furnishing quinolino[4,3-*j*]phenanthridines (Schemes 3 and 4). Nevertheless, a first S_EAr would lead to phenanthridine **8**, which is deactivated for a further attack of an electrophile. Together with an evolving steric hindrance, this led to a sluggish reaction. (Substituents R′ might interfere with hydrogen atoms at positions C-7 and C-14 in the final product.) When we reacted pivaloyl amides **7a-II** and **7b-II** (Scheme 3), it turned out that the reaction stopped after the first cyclization when standard conditions like the combination of phosphorus pentoxide (P_4O_{10}) and phosphoryl chloride ($POCl_3$)[20] or heating with the latter in nitrobenzene[21] (Table 2) were applied. Fortunately, the reaction could be forced to completion, when phenanthridines **8** were again reacted with $P_4O_{10}/POCl_3$ and with a prolonged reaction time of three days instead of 16 hours. *tert*-Butyl-substituted

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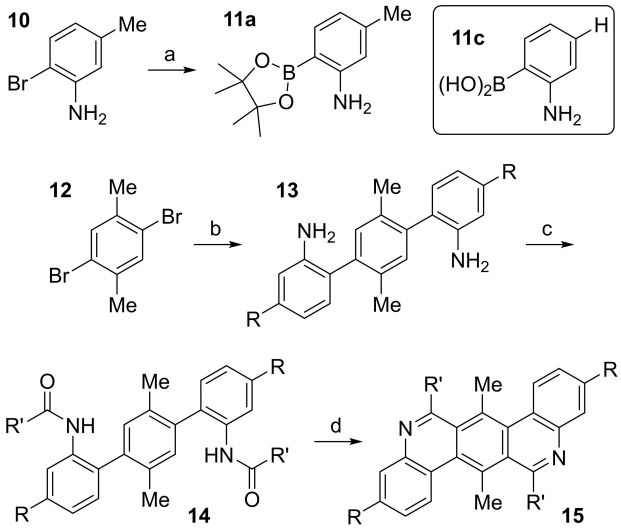
Table 2. Conditions for cyclization to phenanthridines **8**.

Starting material	Conditions	Product (yield)
7a-II	P_4O_{10}, $POCl_3$, 110 °C, 16 h	**8a-II** (76%)
7b-II	$POCl_3$, nitrobenzene, 150 °C, 3 d	**8b-II** (46%)

derivatives **9a-II** and **9b-II** were thus obtained, albeit with yields not exceeding 26%.

Transformations of further terphenyl derivatives were thus performed with conditions established by *Gong et al.*[20] but with longer reaction times. QPs were here obtained in only one step with yields ranging from 26 to 41% for phenyl and propyl derivatives **9a-I,III** and **9b-I,III** (Scheme 4). A rather poor yield of 9% in the transformation of formamide derivative **7a-IV** is most likely due to a partial thermal decomposition of the formyl group. Nevertheless, the latter reaction gives further insight in the regioselectivity of the *ortho* fusions. Both the amide groups (each being positioned in one of the terminal benzene rings) are neighbored by two *ortho* positions in the central benzene ring, which could give rise to two different isomers **A** and **B** (see inlay in Scheme 4) during the second S_EAr reaction. It seemed to be quite unlikely that two alkyl or aryl substituents could be present at positions C-6 and C-7 (i.e., in the bay region) of isomer **B**, but the formation of this isomer could not be excluded when it is unsubstituted at these positions. However, it turned out that even formamide **7a-IV** exclusively reacted to isomer **A** (**9a-IV**); the isomeric structure **B** was not observed. This could be confirmed by careful evaluation of 2D NMR experiments (ROESY, HMBC, HSQC), where further details are given in the SI.



Scheme 5. Synthesis of 7,14-dimethyl-substituted QPs **15**. Conditions: a) B_2Pin_2, cat. $Pd[(PPh)_3]_2Cl_2$, KOAc, 1,4-dioxane, 110 °C, 16 h, **11a**: 66% (containing minor impurities); b) **11a**/**11c**, cat. $Pd[(PPh_3)_2]Cl_2$, Na_2CO_3, THF/H_2O (1:1), 80 °C, 16 h, **13a**: 71% (containing minor impurities), **13c**: 99%; c) see Table 3; d) P_4O_{10}, $POCl_3$, 110 °C, 3 d, **15a-I**: 39%, **15c-I**: 23%, no product **15c-III** or **15c-IV** was isolated in the cyclization of **14c-III** or **14c-IV**, respectively.

Table 3. Conditions for the formation of amides **14**.

Starting material	Conditions	Product (yield)
13a	benzoyl chloride, Et_3N, CH_2Cl_2, 0 °C to rt, 16 h	**14a-I** (83%)
13c	benzoyl chloride, Et_3N, CH_2Cl_2, 0 °C to rt, 16 h	**14c-I** (95%)
13c	butanoyl chloride, Et_3N, CH_2Cl_2, 0 °C to rt, 16 h	**14c-III** (96%)
13c	formic acid, pyridine, PPAA,[a] EtOAc/MeCN (1:1), −15 °C to rt, 16 h	**14c-IV** (82%)

[a] Propanephosphonic acid anhydride.

Synthesis of 7,14-Dimethyl-Substituted Quinolino[4,3-j]phenanthridines

In order to further investigate the interference of substituents introduced with the amide group and further substituents present in the terphenyl moiety, we synthesized and investigated 7,14-dimethyl-substituted QPs. For this, we used a modified synthetic strategy with a *Suzuki* coupling as key reaction (Scheme 5).

We started with 2-bromo-5-methylaniline (**10**), which was boronated in a *Miyaura* reaction with bis(pinacolato)diboron (B_2pin_2). The corresponding (2-aminophenyl)boronic acid (**11c**), lacking the methyl substituent, was commercially available. *Suzuki* coupling with 1,4-dibromo-2,5-dimethylbenzene (**12**) afforded diaminoterphenyls **13** with good to excellent yields. Minor impurities in methyl-substituted derivative **13a** (which might have been present already in boronate **11a**) could be removed after the next step. The 4,4''-dimethyl-substituted derivate **13a** was benzoylated and the unsubstituted diaminoterphenyl **13c** was converted into the respective benzamide, butyramide, and formamide. All bisamides **14** were obtained in good to excellent yields (Table 3). As expected, the methyl groups in the central benzene ring give rise to a significantly increased steric hindrance, which prevented *ortho* fusion in some cases. *Morgan-Walls* reactions were again carried out with $P_4O_{10}/POCl_3$ within three days, but even with these conditions no cyclisation was observed for butyramide **14c-III** and formamide **14c-IV**. Phenyl-substituted QPs **15a-I** and **15c-I** could be obtained, but only with yields not exceeding 39%.

Photophysical Characterization of the Quinolinophenanthridines

Of the nine successfully synthesized QPs, we selected a set of five representatives (**9a-I**, **9a-III**, **9b-I**, **15a-I**, and **15c-I**) for further investigations. Their photophysical properties, i.e., their absorption and emission were measured by UV/Vis and fluorescence spectroscopy. Measurements during titration

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with acids and quantum chemical calculations augmented these investigations.

Although absorbance patterns in measured UV/Vis spectra of the compounds are quite similar, there are still some remarkable differences (Figure 1): 7,14-Dimethylated QPs **15a-l** and **15c-l** showed a significant redshift as compared with the non-methylated compounds (**9a-l**, **9a-III**, and **9b-l**). Within the latter compounds, **9a-l** and **9a-III** showed a higher extinction for the prominent bands at 280–320 nm as compared with methoxy-substituted substrate **9b-l**. Bands of low intensities were observed in the 380–510 nm region. TD-DFT calculations indicate that the latter can predominantly (92 to 97%) be associated with HOMO→LUMO transitions. Calculated UV/Vis spectra are given in Figure 2; they are in rather good agreement with the respective measured spectra. The most prominent bands, which are detected in the range of 300–340 nm (experimental) and 304–322 nm (calculated), are mainly due to H−1→LUMO (24–35%) and HOMO→L+1 transitions (62–71%). Further transitions for each of the investigated compounds are given in the SI. Energies of frontier orbitals and the respective HOMO/LUMO gaps are summarized in Table 4.

QPs as virtually all pyridine-derived PANHs were expected to be quite basic and their protonated derivatives might show deviating absorption and emission properties. In order to quantify the basicity of the herein investigated compounds, their pK_a values were calculated by comparing solvent-dependent free energies of the compounds and that of a reference acid. We chose phenanthridinium as a suitable reference.[22] Details of these calculations are given in the SI; the results are summarized in Table 5. pK_a values range from 4.48 (**15c-l**) to 5.94 (**9a-III**), where phenyl-substituted derivatives show less pronounced basicities. The terminal substituents R (OMe, Me, or H) have no clear influence on the compounds' acidities.

We recorded UV/Vis spectra after addition of 0–25 equivalents of trifluoroacetic acid (TFA). Figure 3 shows the spectra, where arrows indicate absorption trends during acidification. Successive bathochromic shifts and changes in the respective low-energy absorbances are clearly visible, while an unambiguous trend in the low-wavelength region around 300 m cannot be identified.

Emissions were measured in 20 μM CH_2Cl_2 solutions using excitation at 330 nm. The spectra exhibit distinct *Stokes* shifts (Figure 4). Emission maxima are in the range of 440–503 nm, where addition of TFA leads to a significant bathochromic shift of 73–96 nm resulting in emission maxima at 502–600 nm for the protonated species.

We finally estimated aromaticities for a selection of quinolinophenanthridines by performing NICS-XY-scans.[23] As expected, the outer and the central rings showed a benzene-like aromatic behavior, while the aromaticity of the pyridine rings is somewhat reduced. The respective scans are given in the SI.

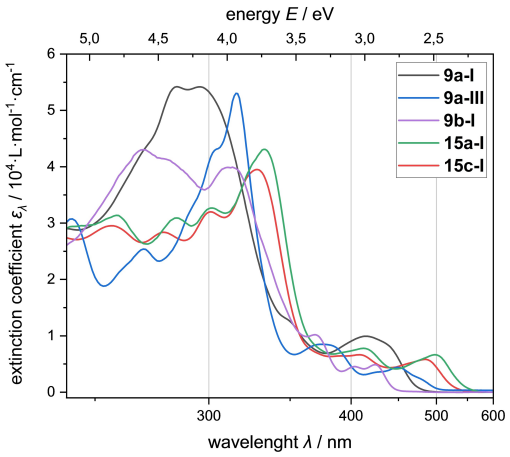

Figure 1. Quantitative experimental UV/Vis spectra of selected QPs in CH_2Cl_2 at 20 °C.

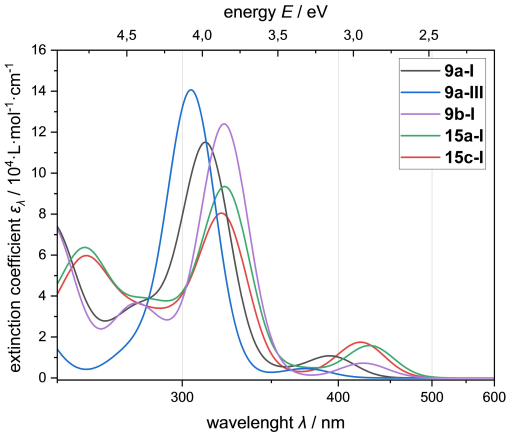

Figure 2. Calculated UV/Vis spectra of selected QPs (implicit solvent field of CH_2Cl_2).

Table 4. Calculated energies of frontier orbitals and HOMO/LUMO gaps.

Compound	E_{FMO} (eV; DFT)		$\Delta E_{LUMO-HOMO}$ (eV)
	HOMO	LUMO	
9a-l	−6.20	−2.34	3.86
9a-III	−6.21	−2.17	4.04
9b-l	−5.97	−2.33	3.64
15a-l	−6.07	−2.42	3.65
15c-l	−5.96	−2.38	3.58

Table 5. Calculated pK_a values of quinolinophenanthridinium ions.[a]

Comp.	pK_a	Comp.	pK_a	Comp.	pK_a
9a-l·H^+	4.70	**9b-l**·H^+	4.82	**15c-l**·H^+	4.48
9a-III·H^+	5.94	**15a-l**·H^+	5.16	*phenanthridinium*	*4.47*[b]

[a] Details on these calculations are given in the SI. [b] Experimental value used as reference [22].

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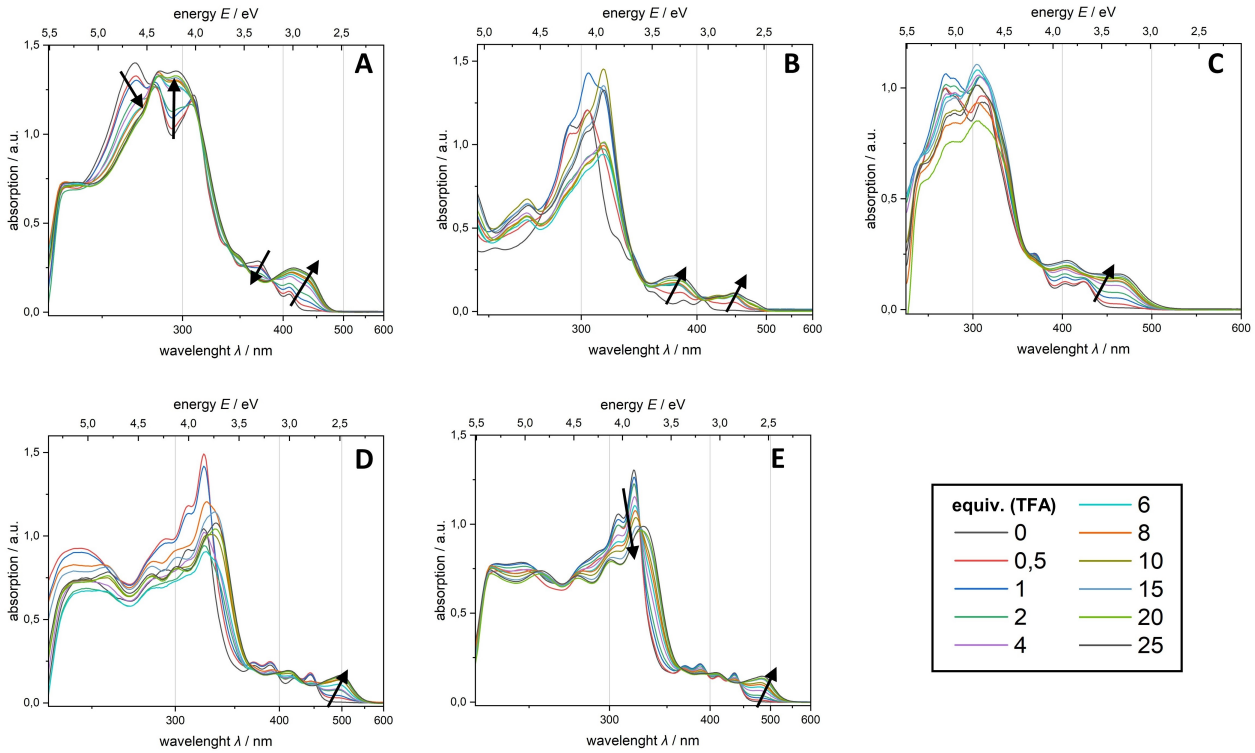

Figure 3. Absorption behavior of QPs during titration with TFA in CH_2Cl_2 at 20 °C. **9a-I** (A), **9a-III** (B), **9b-I** (C), **15a-I** (D), and **15c-I** (E). Enlarged figures are given in the SI.

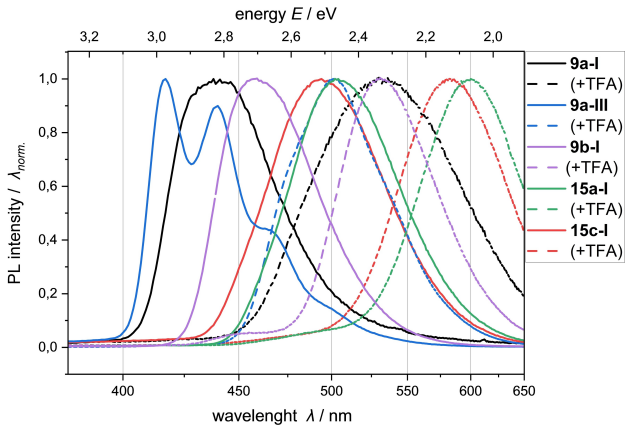

Figure 4. Normalized fluorescence spectra of selected QPs (CH_2Cl_2 at 20 °C, 20 µmol, λ_{ex} = 330 nm). Spectra measured after addition of 25 eq. TFA are given as dashed curves.

Conclusions

We developed a concise synthesis of linear nitrogen-containing heterocycles, where we obtained nine novel QPs using double *ortho* fusion in suitably substituted *para*-terphenyls. We overcame the problem of intermediately formed deactivated species arising after a first *ortho* fusion by utilization of adapted reaction conditions. Only one of the two possible *ortho* fusions occurred, even when the steric differentiation is only ruled by a small hydrogen atom. It thus became obvious that the pseudo-*syn* isomer is favored over the pseudo-*anti* isomer due to steric hindrance in the bay region. Selected QPs were extensively photophysically characterized by UV/Vis and fluorescence spectroscopy and by titration experiments. The experimental findings were complemented by quantum chemical calculations. The influence of the methyl groups at the central benzene ring turned out to be particularly striking, leading to smaller HOMO/LUMO gaps and to a bathochromic shift in the UV/Vis and fluorescence spectra.

Experimental Section

General Procedure 1 (GP 1): Synthesis of Amides with Acid Chlorides

According to a published protocol,[24] the amine and Et_3N were dissolved in anhydrous CH_2Cl_2 under an argon atmosphere and cooled to 0 °C. The acid chloride was dissolved separately in 1 mL CH_2Cl_2 and then slowly dripped into the ice-cooled solution. The reaction mixture was stirred at 0 °C for 1 h, warmed to room temperature, and stirred overnight. Saturated aqueous $NaHCO_3$ solution (20 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with brine (100 mL) and dried (Na_2SO_4). The solvent was then removed at reduced pressure. The crude product was purified by column chromatography or recrystallization.

General Procedure 2 (GP 2): Cyclization of Amides with P_4O_{10} in $POCl_3$

According to a published protocol,[20] the amide and P_4O_{10} were suspended in phosphoryl chloride in a pressure tube under an argon atmosphere and stirred at 110 °C for 3 d. After cooling, the reaction mixture was carefully poured onto 300 mL of ice-cooled 5 M NaOH solution. The suspension was mixed with 250 mL CH_2Cl_2, stirred for 15 min, and filtered. The organic layer was separated, dried (Na_2SO_4), and concentrated at reduced pressure. The crude product was purified by column chromatography or recrystallization.

1-Iodo-4-methyl-2-nitrobenzene (2 a)

Following a published protocol,[13b] 4-methyl-2-nitroaniline (**1 a**; 6.00 g, 39.4 mmol, 1.00 equiv.) was suspended in concentrated HCl (15 mL) and heated to 100 °C for 10 min. After cooling to 0 °C, a solution of $NaNO_2$ (3.26 g, 47.3 mmol, 1.20 equiv.) in H_2O (5 mL) was added dropwise. The mixture was stirred for 30 min at 0 °C and a solution of KI (10.5 g, 63.1 mmol, 1.60 equiv.) in H_2O (10 mL) was slowly added. The resulting mixture was heated to 70 °C for 1.5 room temperature, $Na_2S_2O_5$ solution was added until the mixture turned colorless. The aqueous layer was extracted with CH_2Cl_2 (3×100 mL) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, concentrated at reduced pressure, and purified by column chromatography (silica gel, n-hexane/CH_2Cl_2 10:1→2:1) to yield **2 a** as a red solid (8.15 g, 31.0 mmol, 79 %). The NMR data are in agreement with published data.[13b] R_f = 0.31 (n-hexane/CH_2Cl_2 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.39 (s, 3 H, CH_3), 7.07 (dd, ^3J = 8.1 Hz, ^4J = 2.1 Hz, 1 H, 5-H), 7.66 (d, ^4J = 2.1 Hz, 1 H, 3-H), 7.87 (d, ^3J = 8.1 Hz, 1 H, 6-H).

Tributyl(4-methyl-2-nitrophenyl)stannane (3 a)

Following a published protocol,[14] 1-iodo-4-methyl-2-nitrobenzene (**2 a**, 1.00 g, 3.80 mmol, 1.00 equiv.), Sn_2Bu_6 (2.9 mL, 3.31 g, 5.70 mmol, 1.50 equiv.), $PdCl_2(PPh_3)_2$ (26.7 mg, 38.0 μmol, 0.01 equiv.), and PPh_3 (49.9 mg, 190 μmol, 0.05 equiv.) were dissolved in anhydrous *o*-xylene (20 mL). The reaction mixture was degassed (ultrasonication, 15 min) and heated to 100 °C for 4 d. The solvent was removed at reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL) and treated with saturated KF solution (60 mL). After stirring for 1 h, the mixture was filtered over *Celite*® and the organic layer was dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, n-hexane) to yield **3 a** as a yellow oil (1.04 g, 2.42 mmol, 64 %). The NMR data are in agreement with published data.[25] R_f = 0.25 (n-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 0.86 (t, ^3J = 7.3 Hz, 9 H, 3×4′-CH_3), 1.04–1.19 (m, 6 H, 3×1′-CH_2; with Sn satellites), 1.24–1.36 (m, 6 H, 3×3′-CH_2), 1.42–1.56 (m, 6 H, 3×2′-CH_2; with Sn satellites), 2.44 (s, 3 H, 4-CH_3), 7.39–7.46 (m, 1 H, 5-H), 7.54 (d, ^3J = 7.3 Hz, 1 H, 6-H; with Sn satellites), 8.11–8.15 (m, 1 H, 3-H).

4,4′′-Dimethyl-2,2′′-dinitro-1,1′:4′,1′′-terphenyl (5 a)

Following a published protocol,[15b] 1,4-diiodobenzene (**4**; 650 mg, 1.97 mmol, 1.00 equiv.), stannane **3 a** (1.81 g, 4.24 mmol, 2.15 equiv.), $Pd(PPh_3)_4$ (227 mg, 197 μmol, 0.10 equiv.), CuI (75.0 mg, 394 μmol, 0.20 equiv.), and CsF (1.20 g, 7.88 mmol, 4.00 equiv.) were dissolved in DMF (12 mL). After degassing with argon (ultrasonication, 15 min), the reaction mixture was heated to 55 °C for 72 h. After cooling to room temperature, CH_2Cl_2 (300 mL) was added to the reaction mixture. The organic layer was washed with water (2×200 mL) and brine (400 mL), dried (Na_2SO_4), concentrated at reduced pressure, and purified by column chromatography (silica gel, n-hexane/ CH_2Cl_2 1:1→1:3) and recrystallization (n-hexane/EtOAc 5:1) to yield **5 a** as a yellow solid (640 mg, 1.84 mmol, 93 %). R_f = 0.35 (n-hexane/CH_2Cl_2 1:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 2.45 (s, 6 H, 2×CH_3), 7.39 (s, 4 H, 2′-H, 3′-H, 5′-H, 6′-H), 7.50 (d, ^3J = 7.8 Hz, 2 H, 6-H, 6′′-H), 7.60 (dd, ^3J = 7.8 Hz, ^4J = 1.9 Hz, 2 H, 5-H, 5′′-H), 7.84 (d, ^4J = 1.6 Hz, 2 H, 3-H, 3′′-H); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 20.2 (2×CH_3), 124.3 (2×CH), 128.2 (4×CH), 131.6 (2×CH), 131.6 (2×C_q), 133.5 (2×CH), 136.6 (2×C_q), 139.3 (2×C_q), 148.7 (2×C_q); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2918 (vs), 1522 (vs), 1480 (s), 1433 (vs), 1351 (s), 1096 (vs), 1004 (vs), 916 (vs), 857 (s), 825 (s), 799 (s), 757 (s); MS (FAB): *m/z* (%) = 350 (30) $[M+2]^+$, 349 (100) $[M+1]^+$, 348 (89) $[M]^+$, 332 (33) $[M-O]^+$; HRMS (FAB): *m/z* ($[M+1]^+$) calcd. for $C_{20}H_{17}N_2O_4^+$: 349.1183; found: 349.1184.

4,4′′-Dimethyl-[1,1′:4′,1′′-terphenyl]-2,2′′-diamine (6 a)

Following a published protocol,[18] dinitroterphenyl **5 a** (420 mg, 1.21 mmol, 1.00 equiv.) and freshly prepared CuCl (955 mg, 9.65 mmol, 8.00 equiv.) were suspended in anhydrous MeOH (20 mL). KBH_4 (963 mg, 19.3 mmol, 16.0 equiv.) was slowly added with stirring. The reaction mixture was carefully heated to 50 °C and stirred for 90 min. Ice was added and the aqueous layer was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine (100 mL), dried (Na_2SO_4), filtered (*Celite*®), concentrated at reduced pressure, and purified by column chromatography (silica gel, CH_2Cl_2) to yield **6 a** as a colorless solid (300 mg, 1.04 mmol, 86 %). R_f = 0.21 (CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 2.33 (s, 6 H, 2×CH_3), 3.78 (s, 4 H, 2×NH_2), 6.63 (d, ^4J = 1.4 Hz, 2 H, 3-H, 3′′-H), 6.68 (dd, ^3J = 7.6 Hz, ^4J = 1.7 Hz, 2 H, 5-H, 5′′-H), 7.08 (d, ^3J = 7.6 Hz, 2 H, 2-H, 2′′-H), 7.52 (s, 4 H, 2′-H, 3′-H, 5′-H, 6′-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 21.4 (2×CH_3), 116.5 (2×CH), 119.8 (2×CH), 124.7 (2×C_q), 129.6 (4×CH), 130.5 (2×CH), 138.3 (2×C_q), 138.6 (2×C_q), 143.5 (2×C_q); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3412 (s), 3312 (s), 1613 (s), 1567 (s), 1525 (s), 1488 (s), 1424 (s), 1392 (vs), 1296 (s), 1273 (vs), 1244 (s), 1007 (vs), 945 (s), 847 (vs), 796 (m); MS (FAB): *m/z* (%) = 290 (16) $[M+2]^+$, 289 (75) $[M+1]^+$, 288 (100) $[M]^+$, 287 (22) $[M-1]^+$; HRMS (FAB): *m/z* ($M^{\bullet+}$) calcd. for $C_{20}H_{20}N_2^{\bullet+}$: 288.1621; found: 288.1622.

N,N′-(4,4′′-Dimethyl-[1,1′:4′,1′′-terphenyl]-2,2′′-diyl)dibutyramide (7 a-III)

GP 1: A solution of diamine **6 a** (180 mg, 624 μmol, 1.00 equiv.) and Et_3N (331 μL, 240 mg, 2.37 mmol, 3.80 equiv.) in CH_2Cl_2 (15 mL) was reacted with butyryl chloride (206 μL, 213 mg, 2.00 mmol, 3.20 equiv.). Purification by column chromatography (silica gel, CH_2Cl_2→CH_2Cl_2 + 2 % MeOH) yielded **7 a-III** as a colorless solid (267 mg, 623 μmol, quant.). R_f = 0.26 (CH_2Cl_2 + 2 % MeOH); ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 0.85 (t, ^3J = 7.4 Hz, 6 H, 2×4′′′-CH_3), 1.54 (qt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 4 H, 2×3′′′-CH_2), 2.15 (t, ^3J = 7.3 Hz, 4 H, 2×2′′′-CH_2), 2.34 (s, 6 H, 4-CH_3, 4′′-CH_3), 7.12 (d, ^3J = 8.0 Hz, 2 H, 5-H, 5′′-H), 7.24 (d, ^3J = 7.8 Hz, 2 H, 6-H, 6′′-H), 7.31 (s, 2 H, 3-H, 3′′-H), 7.40 (s, 4 H, 2′-H, 3′-H, 5′-H, 6′-H), 9.12 (s, 2 H, 2×NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 13.6 (2×4′′′-CH_3), 18.5 (2×CH_2), 20.6 (2×CH_2), 37.6 (4-CH_3, 4′′-CH_3), 126.7 (2×CH), 127.8 (2×CH), 128.7 (4×CH), 129.8 (2×CH), 133.5 (2×C_q), 134.7 (2×C_q), 137.1 (2×C_q), 137.5 (2×C_q), 171.5 (2×CO); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3227 (s), 2960 (s), 1657 (s), 1571 (s), 1534 (s), 1515 (s), 1475 (s), 1421 (vs), 1377 (vs), 1289 (s), 1203 (s), 1096 (vs), 1008 (vs), 959 (vs), 880 (vs), 853 (s), 805 (s); MS (FAB): *m/z* (%) = 430 (31) $[M+2]^+$, 429 (100) $[M+1]^+$, 428 (43) $[M]^+$, 359 (21) $[M+2-C_4H_7O]^+$, 358 (14) [M+

1–C_4H_7O]$^+$; HRMS (FAB): *m/z* ([M + 1]$^+$) calcd. for $C_{28}H_{33}N_2O_2^+$: 429.2537; found: 429.2538.

3,10-Dimethyl-6,13-dipropylquinolino[4,3-*j*]phenanthridine (9 a-III)

GP 2: A suspension of diamide **7 a-III** (200 mg, 467 μmol, 1.00 equiv.) and P_4O_{10} (4.64 g, 16.3 mmol, 35.0 equiv.) in $POCl_3$ (30 mL) was reacted. Purification by column chromatography (silica gel, CH_2Cl_2→CH_2Cl_2 + 2% MeOH) yielded **9 a-III** as a yellow solid (48.5 mg, 124 μmol, 26%). R_f = 0.17 (CH_2Cl_2 + 1% MeOH); ^{1}H NMR (400 MHz, CD_2Cl_2 + TFA-d_1): δ (ppm) = 1.26 (t, ^3J = 7.3 Hz, 6 H, 2×3′-CH_3), 2.20 (qt, ^3J = 7.3 Hz, ^3J = 7.3 Hz, 4 H, 2×2′-CH_2), 2.74 (s, 6 H, 3-CH_3, 10-CH_3), 3.97 (t, ^3J = 7.3 Hz, 4 H, 2×1′-CH_2), 7.98 (dd, ^3J = 8.4 Hz, ^4J = 1.7 Hz, 2 H, 2-H, 9-H), 8.32 (s, 2 H, 4-H, 11-H), 8.84 (d, ^3J = 8.5 Hz, 2 H, 1-H, 8-H), 9.83 (s, 2 H, 7-H, 14-H); ^{13}C NMR (100 MHz, CD_2Cl_2 + TFA-d_1): δ (ppm) = 14.4 (2×CH_3), 22.7 (2×CH_3), 25.1 (2×CH_2), 35.0 (2×CH_2), 122.1 (2×C_q), 122.9 (2×CH), 123.5 (2×CH), 125.9 (2×CH), 126.9 (2×C_q), 132.7 (2×C_q), 133.7 (2×C_q), 134.0 (2×CH), 145.5 (2×C_q), 166.2 (2×C_q); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2959 (s), 2865 (vs), 1616 (vs), 1579 (s), 1492 (s), 1464 (s), 1421 (vs), 1369 (s), 1315 (s), 1262 (s), 1190 (s), 1157 (vs), 1040 (vs), 887 (s), 863 (s), 812 (s), 780 (s), 745 (s); MS (FAB): *m/z* (%) = 394 (14) [M + 2]$^+$, 393 (39) [M + 1]$^+$, 392 (10) [M]$^+$, 154 (100) [3-NBA]$^+$; HRMS (FAB): *m/z* (M$^+$) calcd. for $C_{28}H_{29}N_2^+$: 393.2325; found: 393.2324.

Supporting Information

The authors have cited additional references within the Supporting Information (Ref. [26–38]).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aromatic compounds · absorption · fluorescence · cross-coupling · cyclization

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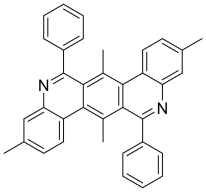
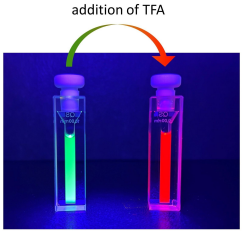
RESEARCH ARTICLE

Quinolino[4,3-*j*]phenanthridines

- 9 synthesized derivatives
- titration experiments
- UV/Vis and fluorescence spectra
- quantum chemical calculations





*M. Sc. F. R. Schumann, Prof. Dr. J. Podlech**

1 – 9

Synthesis of Quinolino[4,3-*j*]phenanthridines and their Photophysical Characterization

Nine novel quinolino[4,3-*j*]phenanthridines were successfully synthesized. UV/Vis and fluorescence spectroscopy revealed remarkable optoelectronic properties. Large Stokes shifts were especially observed for the protonated substrates. The experimental results were compared and complemented with quantum chemical calculations, providing further insights into the compounds' properties.