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Assembly of annulated 1,3-diazapyrenes by consecutive cross-coupling and cyclodehydrogenation of (het)arene moieties

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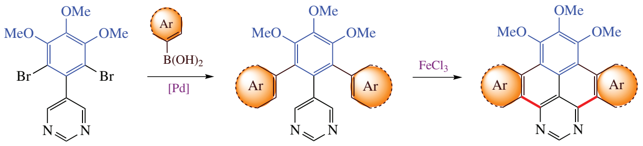
Di(het)areno[*e*,*l*][1,3]diazapyrene core was constructed by $FeCl_3$-mediated intramolecular oxidative cyclodehydrogenation of 5-[2,6-di(het)arylphenyl]pyrimidine precursors, which in turn were obtained by the Suzuki cross-coupling of 5-(2,6-dibromophenyl)pyrimidine derivative with the corresponding (het)arylboronic acids. Molecular orbital calculations as well as redox and photophysical measurements show that the fused products are promising for organic electronic application.



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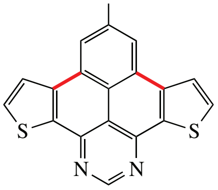
Pyrene[1,2] and its heterocyclic analogues[3–5] with π-expanded structures experience a renaissance due to their potential application in organic electronics, for example in light-emitting diodes, field-effect transistors and photovoltaic elements for solar cells. Several synthetic protocols for the preparation of these compounds from perimidines have been described,[6] including condensation with 2-ethoxymethylidene-1,3-dicarbonyl compounds, three-component coupling with 1,3,5-triazines and enols, electrophilic acylation with cinnamoyl chlorides accompanied by cleavage of the aromatic group, oxidative condensation with chalcones or cinnamic acids as well as *peri*-annulation with pyrimidines, or alternatively from benzo[*f*]quinazolines by their treatment with activated methylideneoxonium equivalents (for details, see Online Supplementary Materials, Figure S1). Note that only one approach has been reported for the synthesis of 8-substituted benzo[*g*,*h*]dithieno[2,3-*e*:3′,2′-*j*]perimidine (or dithieno[2,3-*e*:3′,2′-*l*][1,3]diazapyrene) system through oxidative photocyclization of the corresponding 5-(4-substituted phenyl)-4,6-di(2-thienyl)pyrimidines.[7]



Ref. 7

The intramolecular oxidative coupling of arenes has reached its preparative potential only recently, despite numerous notable examples known for a long time.[8–10] Motivated by these findings, we have adopted the strategy[11] consisting of the consecutive Suzuki cross-coupling and $FeCl_3$-mediated cyclodehydrogenation reactions for the synthesis of new fused 1,3-diazapyrenes (Scheme 1).

First, 5-{2,6-di[(het)aryl]-3,4,5-trimethoxyphenyl}pyrimidines **4a–c** were obtained in overall yields up to 53% using the microwave-assisted Suzuki cross-coupling of 5-bromopyrimidine **1** with 3,4,5-trimethoxyphenylboronic acid with formation of biaryl **2**, whose pyrogallol moiety was then exhaustively brominated leaving the pyrimidine ring untouched. Dibromide **3** thus obtained was subjected to the Suzuki cross-coupling with phenyl-, 3-thienyl- or 3-furylboronic acid affording *ortho*,*ortho*-tri-joined tetraarenes **4a–c**. For the final annulation, we employed our recently developed procedure[11] using 4 equiv. $FeCl_3$ as the oxidant in anhydrous CH_2Cl_2 at room temperature for 24 h under argon atmosphere. As a result, multi-fused hetarenes **5a–c** were obtained in yields up to 86% (see Scheme 1).[†]

[†] *General procedure of prepatation of 1,3-diazapyrene derivatives* **5a–c**. An appropriate 5-{2,6-di[(het)aryl]-3,4,5-trimethoxyphenyl}pyrimidine **4a–c** (0.5 mmol) was dissolved in dry $CHCl_3$ (5 ml), then the flask was flushed with argon and iron(III) chloride (324 mg, 2.0 mmol) was added to the solution. The mixture was stirred at room temperature for 24 h, then the solvent was evaporated. The residue was diluted with aqueous ammonia (10 ml), the formed precipitate was filtered off, washed with water, air-dried and purified by flash column chromatography using EtOAc–hexane as an eluent (1 : 3 to 1 : 1, v/v).

*8,9,10-Trimethoxytribenzo[*e*,*gh*,*j*]perimidine* **5a**. Yield 128 mg (65%), yellow solid, mp 200–202 °C. ^1H NMR (600 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 9.74 (ddd, 2H, *J* 8.5, 1.2, 0.6 Hz), 9.52 (ddd, 2H, *J* 8.0, 1.6, 0.6 Hz), 7.93 (ddd, 2H, *J* 8.5, 6.9, 1.6 Hz), 7.83 (ddd, 2H, *J* 8.0, 6.9, 1.2 Hz), 4.28 (s, 3H), 4.15 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ: 155.1, 153.4, 152.8, 148.3, 132.8, 131.3, 129.1, 127.8, 127.5, 125.5, 120.6, 119.0, 114.7, 61.7, 61.0. HRMS (ESI), *m*/*z*: 395.1389 $[M+H]^+$ (calc. for $C_{25}H_{19}N_2O_3$, *m*/*z*: 395.1390).

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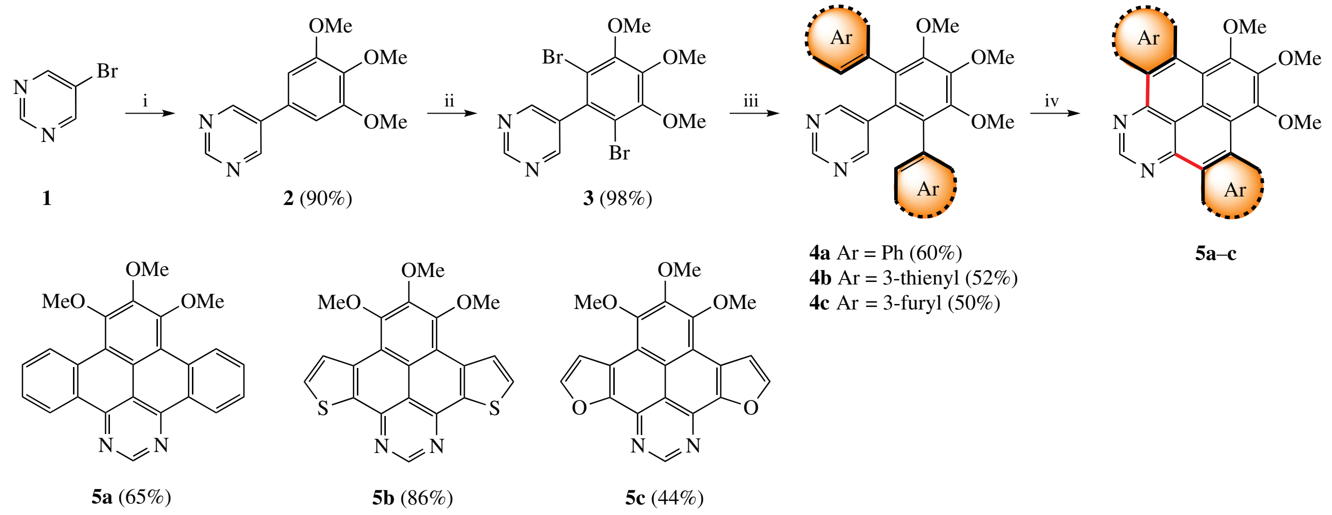

Scheme 1 *Reagents and conditions*: i, 3,4,5-$(MeO)_3C_6H_2B(OH)_2$ (0.9 equiv.), $Pd(PPh_3)_4$ (0.05 equiv.), K_3PO_4 (2.0 equiv.), 1,4-dioxane, MW, 165 °C, 30 min; ii, NBS (5.0 equiv.), DMF, room temperature, 18 h; iii, $ArB(OH)_2$ (6.0 equiv.), $Pd(PPh_3)_4$ (0.1 equiv.), K_3PO_4 (5.0 equiv.), 1,4-dioxane, MW, 165 °C, 30 min; iv, $FeCl_3$ (4 equiv.), CH_2Cl_2, room temperature, 24 h.

Table 1 UV-VIS and fluorescence data for compounds **5a–c** compared with pyrene.

Compound	λ/nm ($\varepsilon \times 10^3$/dm^3 mol^{-1} cm^{-1})	Excitation λ_{max}/nm	Emission[a] λ_{max}/nm	Φ_F[b]
5a	384 (24.3), 365 (23.0), 315 (48.1), 302 (54.3), 276 (153.7), 246 (75.7)	384, 362, 314, 302, 270, 247	446	0.22
5b	392 (26.7), 373 (21.4) 314 (39.3), 282 (24.1) 259 (31.2)	406, 343, 292, 249	434	0.15
5c	377 (18.7), 304 (32.5) 276 (21.7), 256 (28.4)	356, 281, 258, 241	418	0.33
Pyrene	337 (167.9), 321 (103.6) 308 (40.9), 274 (174.1) 263 (90), 242 (273.3)	345, 327, 312, 284, 267, 253	372, 393	0.07

[a] Excitation at 300 nm. [b] Fluorescence quantum yield (±10%) determined relative to 2-aminopyridine in 0.05 M H_2SO_4 as a standard with $\Phi_F = 0.60$.[12]

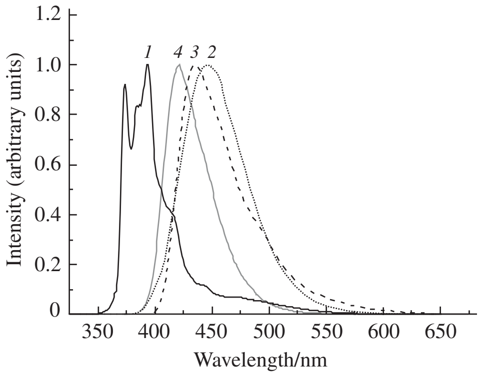

Figure 2 Normalized emission spectra of (*1*) pyrene as well as compounds (*2*) **5a**, (*3*) **5b** and (*4*) **5c** in CH_2Cl_2 at room temperature.

The optical properties of 8,9,10-trimethoxytribenzo[*e*,*gh*,*j*]perimidine **5a**, 7,8,9-trimethoxybenzo[*gh*]dithieno[2,3-*e*:3′,2′-*j*]perimidine **5b** and 7,8,9-trimethoxybenzo[*gh*]difuro[2,3-*e*:3′,2′-*j*]perimidine **5c** compared with unsubstituted pyrene as a standard were investigated using UV-VIS and photoluminescence spectroscopy in CH_2Cl_2 solutions at room temperature (Table 1, Figures 1 and 2). Incorporation of an electron-donating methoxy group and an increase in π-conjunction of polycyclic system by heteroannulation with 1,3-diazapyrene ring results in a bathochromic shift of absorption maxima in the series of compounds **5a–c** compared with pyrene. As well, in contrast to pyrene, compounds **5a–c** show single emission maxima in their fluorescence spectra with a bathochromic shift relative to pyrene, similarly to UV-VIS spectra (see Figure 2). The fluorescence efficiency of compounds **5a–c** (Φ_F = 0.15–0.33) is significantly higher than that for pyrene (Φ_F = 0.07).

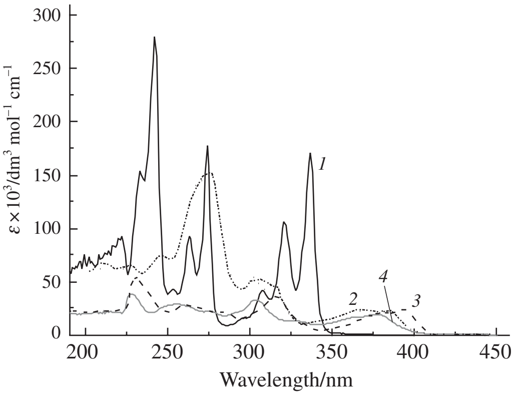

Figure 1 UV-VIS spectra of (*1*) pyrene as well as compounds (*2*) **5a**, (*3*) **5b** and (*4*) **5c** in CH_2Cl_2 at room temperature.

Cyclic voltammetry (CV) was performed for heteroannulated 1,3-diazapyrenes **5a–c** to determine their redox potentials (Table 2). Unfortunately, the cyclic voltammograms obtained demonstrate irreversible character of the oxidation. Since no cathodic behavior of compounds **5a–c** could be detected by CV, their excited state reduction potentials, corresponding to the LUMO energy levels, were calculated by addition of the energy gap E_g^{opt}, which was estimated from the long-wavelength absorption edge of the absorption spectra recorded in CH_2Cl_2 solution, to the HOMO energy values (see Table 2).

As expected, theoretically predicted energies of the HOMO, LUMO and the energy gap (see Table 2 and Figure S2) differ from those obtained experimentally due to approximate character of the exchange-correlation functional employed. Nevertheless, the trends calculated theoretically and determined experimentally for the series of compounds **5a–c**, appear to be the same from a qualitative point of view.

Unsubstituted pyrene was used as a reference in the following discussion on the relative changes in frontier orbital energies (see Table 2, entry 4). All compounds **5a–c** turned to be wide

Table 2 Electrochemical properties of heteroannulated 1,3-diazapyrenes **5a–c** compared with pyrene.

Entry	Compound	$E_{\mathrm{ox}}^{\mathrm{onset}\,a}$	E_{HOMO}/eV	E^{*}_{LUMO}/eV^{b}	$E_{\mathrm{g}}^{\mathrm{opt}}$/eV^{c}	$E_{\mathrm{HOMO}}^{\mathrm{calc}}$/eV^{d}	$E_{\mathrm{LUMO}}^{\mathrm{calc}}$/eV^{d}	$E_{\mathrm{g}}^{\mathrm{calc}}$/eV^{d}
1	**5a**	0.98	–6.08	–2.98	3.10	–5.97	–1.96	4.01
2	**5b**	0.84	–5.94	–2.92	3.02	–5.87	–2.17	3.70
3	**5c**	1.19	–6.29	–3.20	3.09	–5.80	–2.00	3.80
4	Pyrene	0.84	–5.94	–2.32	3.62	–5.63^{e}	–1.83^{e}	3.80^{e}

[a] $E_{\mathrm{ox}}^{\mathrm{onset}}$ – onset oxidation potential *vs*. Ag/AgNO$_3$ reference electrode. [b] $E^{*}_{\mathrm{LUMO}} = E_{\mathrm{HOMO}} + E_{\mathrm{g}}^{\mathrm{opt}}$. [c] Energy gap estimated from the onset of absorption spectra recorded in CH$_2$Cl$_2$ solution, $E_{\mathrm{g}}^{\mathrm{opt}} = 1240/\lambda_{\mathrm{onset}}$. [d] Calculation for compounds **5a–c** was performed using density-functional theory at the B3LYP/6-31G* level. [e] Calculation for pyrene was performed using density-functional theory at the B3LYP/6-31G** level.[13]

band gap semiconductors with emergy gap values of 3.02–3.10 eV, which is typical of semiconductor thienoacenes[14] (~3.0–3.5 eV) and much lower than for unsubstituted pyrene (3.62 eV). Thus, pyrimidine ring in polycycles **5** causes a relatively large reduction of the band gap value due to the donor–acceptor like structure. Moreover, incorporation of the nitrogen-rich ring leads to a much greater reduction in LUMO ($\Delta E = 0.60$–0.88) than in HOMO ($\Delta E = 0.00$–0.35). This finding suggests that increase in the nitrogen content in structurally similar compounds can lead to very low LUMO levels, which may be a useful strategy for the design of organic semiconductors. As a rule, air-stable *p*-channel field-effect transistor (FET) operation is implemented with organic semiconductors having the HOMO energy levels lower than 5.0 eV.[14] For this reason, 1,3-diazapyrenes **5a–c** seem to be promising for further development of air stable organic field-effect transistors (OFETs).

In summary, we have synthesized new benzo- and heteroannulated 1,3-diazapyrene derivatives *via* intramolecular oxidative cyclodehydrogenation of the corresponding 5-{2,6-di[(het)aryl]-3,4,5-trimethoxyphenyl}pyrimidines. This synthetic procedure provides a facile way to the family of nitrogen-containing polycyclic hetarenes that can be used in organic electronics and luminescent materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.03.003.

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