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First synthesis of new polycyclic systems from *ortho*-di(heteroaryl)-substituted furazanopyrazine derivatives by the Scholl reaction

Egor V. Verbitskiy,*[a,b] Yuriy A. Kvashnin,[a,b] Margarita V. Medvedeva,[b] Tatiana S. Svalova,[b]
Alisa N. Kozitsina,[b] Oleg S. Eltsov,[b] Gennady L. Rusinov[a,b] and Valery N. Charushin[a,b]

[a] *I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 620108 Ekaterinburg, Russian Federation. E-mail: Verbitsky@ios.uran.ru*
[b] *Institute of Chemical Engineering, Ural Federal University, 620002 Ekaterinburg, Russian Federation*

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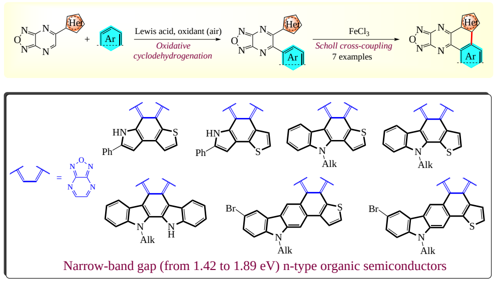
A facile synthetic protocol to hard-to-get polycyclic (hetero)aromatic compounds annulated to [1,2,5]oxadiazolo[3,4-*b*]pyrazine scaffold *via* the $FeCl_3$-mediated intramolecular Scholl cross-coupling has been developed. Based on the electrochemical and photophysical measurements, the synthesized polycyclic systems may be regarded as narrow band-gap (from 1.42 to 1.89 eV) n-type organic semiconductors whose energy levels are comparable to those of the commercially available n-type semiconductors.



Keywords: furazanopyrazines, Scholl reaction, organic semiconductors, C–H functionalization, S_N^H-reaction, polycyclic aromatic hydrocarbons, iron trichloride.

Polycyclic aromatic hydrocarbons (PAHs) and heterocyclic nanographenes have been considered as engaging subjects in interdisciplinary research connected with materials science.[1] Although many synthetic procedures[2] have been elaborated to prepare this kind of compound, the Scholl reaction and related oxidative dehydrogenative couplings appear to be the most powerful tool for the synthesis of heterocyclic PAHs.[3] The mechanism of the Scholl reaction is not definite and still controversial, but it is connected with some electrophilic aromatic processes (Figure 1). These reactions are facilitated by the presence of electron-donating substituents[3] (for example, when R^1 and R^2 are alkyl or alkoxy groups) on the aromatic rings, whereas electron-withdrawing groups R^1 and R^2 strongly deactivate the substrate.[4] Examples of using only pyrimidine derivatives as an electron acceptor aryl moiety (see Figure 1, Ar is substituted pyrimidine) are documented.[5] As a part of our ongoing studies on polycyclic systems, we envisaged that 5,6-di(hetero)aryl-containing [1,2,5]oxadiazolo[3,4-*b*]pyrazines equipped with various electron-donating parts should be active in the Scholl coupling.[6] Thus, herein, we report a new synthetic protocol for the preparation of various unsymmetrical polycyclic systems annulated to furazanopyrazine core and study of their photophysical and electrochemical properties.

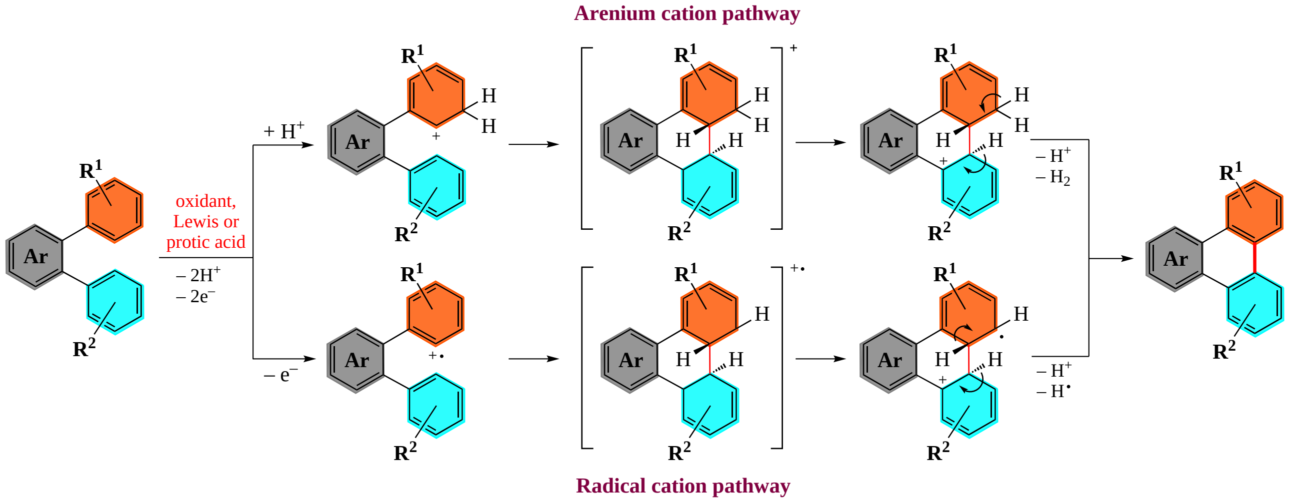
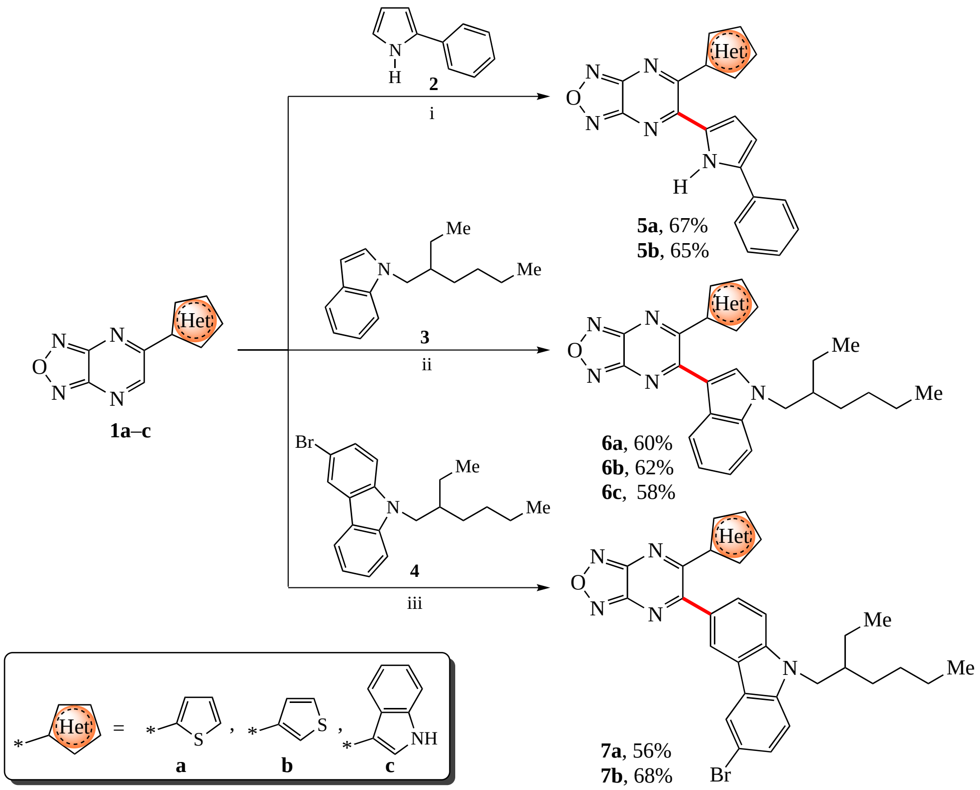


Figure 1 Two plausible pathways for Scholl reaction.

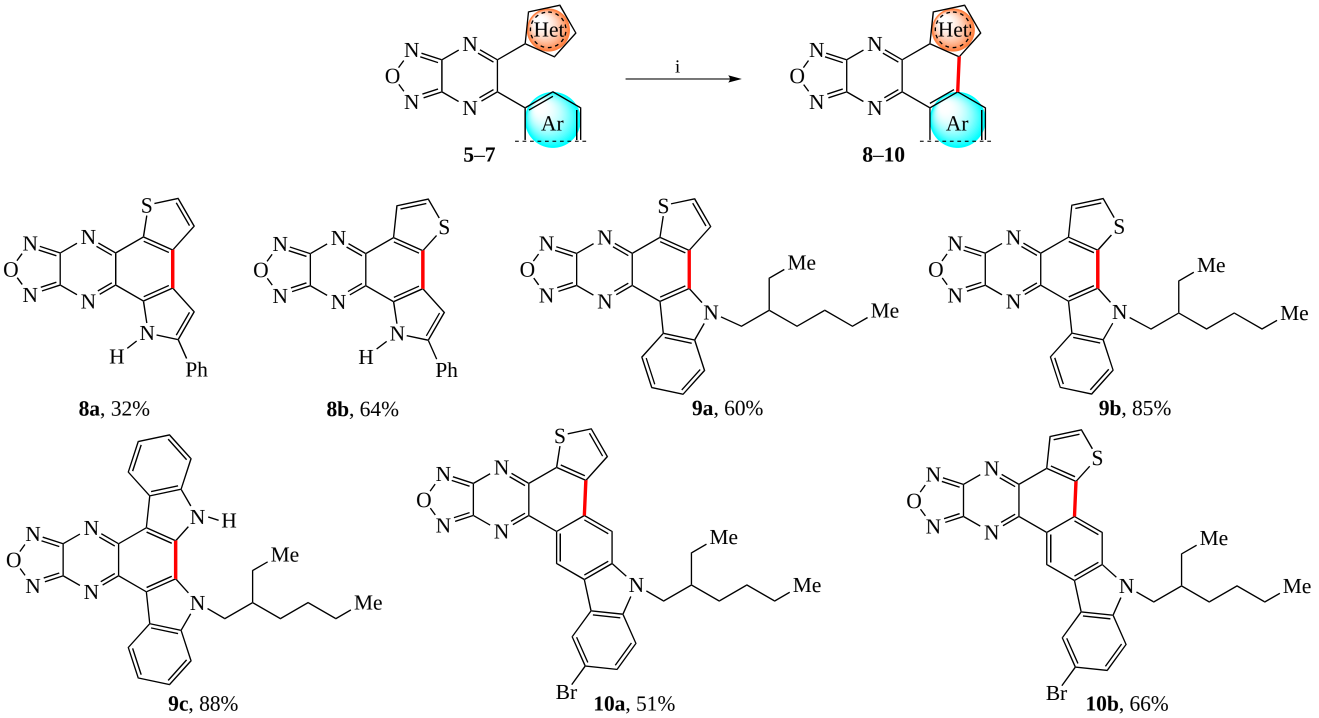


Scheme 1 *Reagents and conditions*: i, CF_3COOH (1 equiv.), room temperature, 24 h; ii, AcOH, room temperature, 24 h; iii, $BF_3{\cdot}Et_2O$ (1 equiv.), MeCN, room temperature, 24 h.

The synthesis of required starting compounds is outlined in Scheme 1. Unsymmetric 5,6-di(hetero)aryl-[1,2,5]oxadiazolo[3,4-*b*]pyrazines **5–7** were accessed employing the nucleophilic aromatic substitution (S_N^H-reaction) from our previous report.[7] The most reasonable conditions were used for each type of nucleophiles. Reactions of 5-heteroaryl[1,2,5]oxadiazolo[3,4-*b*]pyrazines **1a–c** with 2-phenyl-1*H*-pyrrole **2** and 1-(2-ethylhexyl)-1*H*-indole **3** were carried out in the presence of trifluoroacetic and acetic acids, respectively. On the contrary, furazanopyrazines **1a**,**b** reacted with 3-bromo-9-(2-ethylhexyl)-

Table 1 Optimization of conditions for the synthesis of 12-bromo-9-(2-ethylhexyl)-9*H*-[1,2,5]oxadiazolo[3′,4′:2,3]thieno[2′,3′:7,8]quinoxalino[6,5-*b*]carbazole **10b** from precursor **7b**.

Entry	Oxidant	Acid	Yield (%)[a]
1	$FeCl_3$ (4 equiv.)	H_2SO_4 (1 equiv.)	29
2	$FeCl_3$ (4 equiv.)	CF_3SO_3H (1 equiv.)	51
3	DDQ (2.5 equiv.)	CF_3SO_3H (1 equiv.)	12
4	$MoCl_5$ (2.5 equiv.)	–	21
5	$FeCl_3$ (8 equiv.)	–	66



Scheme 2 *Reagents and conditions*: i, $FeCl_3$ (8 equiv.), $CHCl_3$, room temperature, 10 h. For optimization, see Table 1.

9*H*-carbazole **4** only in the presence of $BF_3{\cdot}Et_2O$ giving the corresponding S_N^H-products in yields up to 68% (see Scheme 1).

Compound **7b**, 5-[6-bromo-9-(2-ethylhexyl)-9*H*-carbazol-3-yl]-6-(thiophen-3-yl)[1,2,5]oxadiazolo[3,4-*b*]pyrazine, was obtained in the highest yield, so it was chosen to optimize the Scholl cross-coupling conditions (Table 1, Scheme 2). Initially, we tried to carry out the reaction according to the described procedure[6(*d*)] using $FeCl_3$ (4 equiv.) as the oxidant and H_2SO_4 (1 equiv.) in anhydrous $CHCl_3$ at room temperature for 24 h under an argon atmosphere (entry 1). A study of various oxidants and Lewis acids demonstrated that the optimal conditions comprised 8-fold excess of anhydrous iron(III) chloride under aerobic conditions, which afforded the desired 12-bromo-9-(2-ethylhexyl)-9*H*-[1,2,5]oxadiazolo[3′,4′:2,3]thieno[2′,3′:7,8]-quinoxalino[6,5-*b*]carbazole **10b** in the best 66% yield (entry 5).

The found reaction conditions were extended to the scope of *ortho*-di(heteroaryl)substituted furazanopyrazines **5**–**7** to convert them into a diversity of new polycyclic systems such as substituted [1,2,5]oxadiazolo[3,4-*b*]pyrrolo[2,3-*f*]thienoquinoxalines **8a**,**b**, [1,2,5]oxadiazolo[3′,4′:5,6]pyrazino[2,3-*c*]-thienocarbazoles **9a**,**b**, [1,2,5]oxadiazolo[3′,4′:5,6]pyrazino[2,3-*c*]-indolo[2,3-*a*]carbazole **9c**, and [1,2,5]oxadiazolo[3′,4′:2,3]-thienoquinoxalino[6,5-*b*]carbazoles **10a**,**b** in 32–88% yields.

Photophysical properties were studied in dichloromethane (Figure 2, Table 2). All polycyclic systems **8**–**10** are deeply coloured (from violet to black in the solid state) compounds that do not fluoresce in the visible range. The first maximum wavelength absorption in the range 250–350 nm could be attributed to the localized π–π* transitions, while the broad absorption band at 450–530 nm may occur due to an intramolecular charge transfer inside the polycyclic system. On moving from **8** to **10** chemotype, a pronounced bathochromic shift of the absorption maxima due to an increase in the π-conjugated polycyclic system due to the introduction of a more extended carbazole fragment is observed.

To study the electrochemical properties of the prepared compounds we used cyclic voltammetry (CV) (see Table 2 and Online Supplementary Materials, Figures S26–S32). A similar character of redox behavior was observed for all compounds **8**–**10**, generally, one irreversible anodic peak in 1.5–2 V potential range and one or two close to reversible independent redox processes in –0.5 and –1.3 V potential range. The HOMO and LUMO energy values were estimated based on electrochemical data (see Table 2).

Frontier molecular orbital energies and HOMO/LUMO energy gap (E_g) are important criteria that impact the electronic and conducting properties of materials. On a direct metal–semiconductor junction, the barrier height at the metal–semiconductor interface is given by the difference between metal work function and semiconductor HOMO/LUMO energy. In addition, the existence of a direct correlation between charge carrier types in the organic thin-film transistors (OTFTs) and experimentally estimated frontier molecular orbital levels was revealed. Particularly, for OTFTs with Au source-drain electrodes, n-type materials should possess low LUMO levels, such that they lie close to the work function potential of the Au electrode (–5.1 eV).[8] A common conclusion derived from this study means that materials with LUMO < –3.15 eV and HOMO < –5.60 eV exhibit strictly n-type semiconductor behavior, which is attributed to high barriers to hole injection.[9] Thus, based on the HOMO and LUMO data on the energies obtained from electrochemical studies (see Table 2), the synthesized polycyclic systems may be regarded as narrow-gap (from 1.42 to 1.89 eV) n-type organic semiconductors [the energy levels compare favorably to the commercially available n-type semiconductor such as fullerene C_{60}[10] and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA),[11] Figure 3].

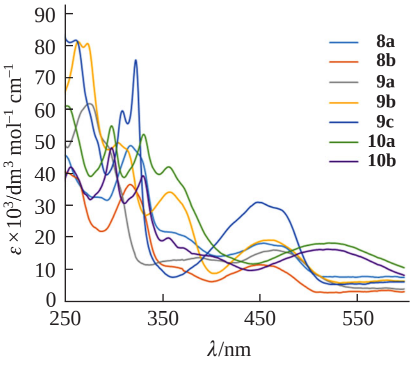


Figure 2 UV/VIS spectra of polycycles **8**–**10** (5×10^{-6} M) in dichloromethane at room temperature.

Table 2 Absorption maxima λ_{abs}, extinction coefficient (ε), and HOMO–LUMO energies of the polycycles **8**–**10** estimated in dichloromethane.

Compound	λ_{abs}/nm ($\varepsilon \times 10^3$/dm^3 mol^{-1} cm^{-1})	E_{Ox}^{onset}/V	E_{Red}^{onset}/V	E_{HOMO}/ eV	E_{LUMO}/ eV	E_g^{el}/ eV
8a	315 (46) 455 (18)	1.20	–0.26	–5.64	-4.18	1.46
8b	326 (34) 450 (9)	1.47	–0.23	–5.91	-4.21	1.70
9a	274 (60) 473 (13)	1.59	–0.28	–6.03	-4.16	1.87
9b	265 (80) 304 (46) 360 (33)	1.55	–0.34	–5.99	-4.10	1.89
9c	262 (80) 311 (58) 325 (74) 450 (30)	1.40	–0.36	–5.84	-4.08	1.76
10a	255 (60) 300 (53) 333 (50) 360 (40) 527 (17)	1.14	–0.28	–5.58	-4.16	1.42
10b	260 (41) 300 (46) 330 (38) 525 (15)	1.15	–0.34	–5.59	-4.10	1.49

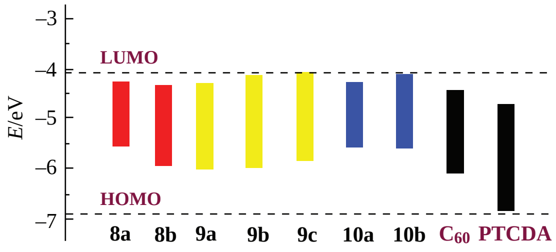


Figure 3 HOMO/LUMO energy levels of compounds **8a**,**b** (red), **9a**–**c** (yellow) and **10a**,**b** (blue) and popular n-type organic semiconductor materials (black) for comparison.

To summarize, we have developed a convenient Scholl reaction-based synthetic approach to a series of novel unsymmetrical polycyclic systems annulated to furazanopyrazine scaffold. The compounds obtained can be useful as new n-type semiconductors for organic electronic applications.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.11.005.

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