Columnar Mesomorphism of Fluorescent Board-Shaped Quinoxalinophenanthrophenazine Derivatives with Donor−Acceptor Structure
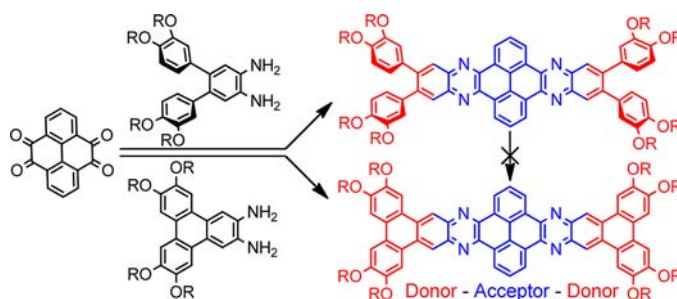
Shuai Chen,[†] Farah S. Raad,[†,‡] Mohamed Ahmida,[†] Bilal R. Kaafarani,*[,‡] and S. Holger Eichhorn*[,†]

Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada, and Department of Chemistry, American University of Beirut, Beirut 1107-2020, Lebanon

bilal.kaafarani@aub.edu.lb; eichhorn@uwindsor.ca

ABSTRACT

Quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine (QPP) dyes have been studied as electron acceptor materials, fluorophores, and building blocks for self-organizing organic semiconductors. Condensation of tetraketopyrene with electron-rich diamino-terphenylene and -triphenylene derivatives generates new donor−acceptor QPP derivatives that display columnar mesomorphism over wide ranges of temperature; are fluorescent in solution, liquid crystal, and solid phases; and have electron acceptor properties. Also reported are the synthesis and properties of the first diamino-(tetraalkoxy)triphenylene as a valuable new synthon.

The quinoxalino[2′,3′:9,10]phenanthro[4,5-*abc*]phenazine (QPP) core (**1**) has been used in the design of organic semiconductors,[1–3] sensors,[4,5] nanofibers,[6,7] and EPR spin labels[8] because of its high rigidity, thermal stability, electronic, and optical properties (Figure 1). A common goal of several reports has been the conversion of **1** into columnar liquid crystalline derivatives via the attachment of flexible side chains (**2**).[2,9–12] However, a large number of the reported derivatives display (lamellar) soft crystal rather than columnar liquid crystal phases because of their large

[†] University of Windsor.

[‡] American University of Beirut.

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aspect ratios and the attachment of only two side chains to each end of the molecule (tetracatenar motive). An advantage of columnar arrangements is the possible accommodation of $\pi-\pi$ stacking with a nonparallel orientation of the QPP cores that should enhance their emission properties and affects transport of charge carriers (e.g., may bias electron over hole transport).

To promote columnar mesomorphism over lamellar arrangements and to lower transition temperatures we decided to attach four side chains on each side by exchanging R with dialkoxy phenyl (3) and tetraalkoxyphenanthrene groups (4). Both the larger number of side chains and their orientation at an angle of about 60° relative to the long axis of the core increase the lateral packing volume of the side chains, which has been shown to disfavor lamellar and promote columnar mesomorphism in polycatenar-type liquid crystals.[13]
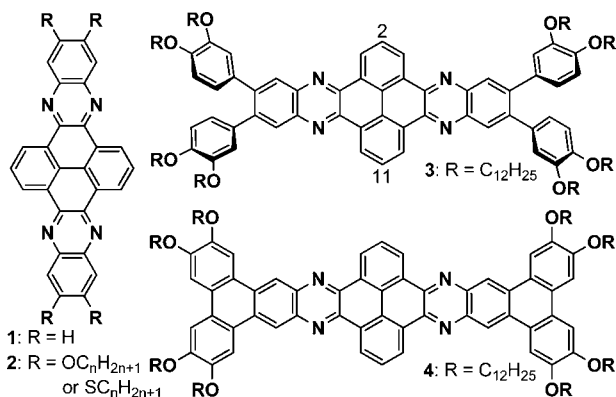
Figure 1. QPP core 1 and previously described tetraalkoxy and tetraalkylthio-substituted QPP derivatives 2. QPP derivatives 3 and 4 are new liquid crystalline derivatives reported here.

In our first synthetic attempt toward compounds 3 and 4 we followed a procedure recently reported by Lixiang Wang (Scheme 1).[2] Suzuki coupling between 4,5-dibromobenzene-1,2-diamine (5) and boronic acid 6 gave *ortho*-terphenyl 7, which was reacted with tetraketopyrene 8[5,14−16] to afford tetraphenyl QPP 3 in an overall yield of 54%. Unexpectedly, oxidative coupling of the dialkoxyphenyl rings to generate the planar QPP 4 was not successful. Instead a yellow insoluble compound was obtained that is likely a polymer of compound 3 according to its IR and UV−vis spectra.

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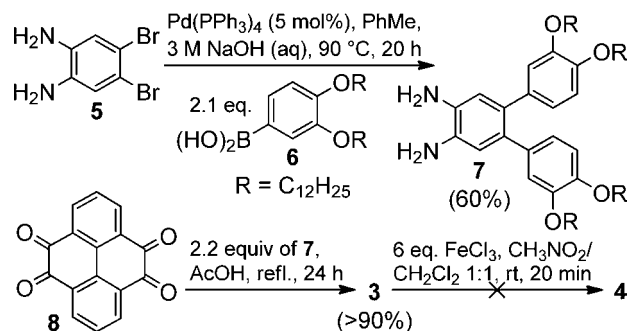
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Scheme 1. Synthesis of QPP 3

Our recent results on similar compounds showed that the oxidative coupling is successful when the 2 and 11 positions of QPP 3 are blocked by alkyl groups. This suggests that oxidative polymerization occurs via the 2 and 11 positions of QPP 3,[17,18] which is astonishing considering that the didodecyloxyphenyl groups should be more easily oxidized than the pyrene core (see topology of HOMO in Table S2, Supporting Information (SI)). However, we did not attempt protection of the 2 and 11 positions for the preparation of QPP 4 but, instead, decided to prepare 6,7,10,11-tetrakis(dodecyloxy)triphenylene-2,3-diamine 9 (Scheme 2) for a subsequent coupling to tetraketopyrene 8. Tetrakis(alkoxy)triphenylene-2,3-diamine derivatives have not been previously reported but are of broader interest as valuable building blocks for the synthesis of discotic liquid crystals and azaarenes.

Scheme 2. Synthesis of Diaminotetradodecyloxytriphenylene 9
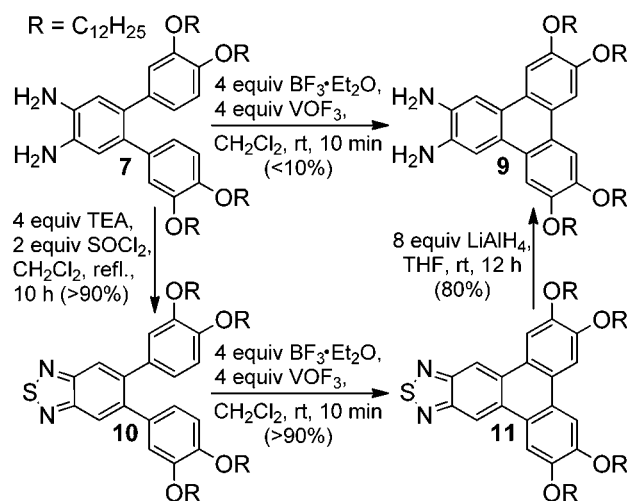
Diaminoterphenyl 7 is stable in air for months, but expectedly, the electron-rich diaminobenzene group causes many side reactions under oxidative coupling conditions.

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Consequently, the direct conversion of **7** to **9** is not feasible, although **9** was chromatographically isolated from a complex product mixture in yields of 5–8%. Protection of the two amino groups as a 2,1,3-thiadiazole ring renders the central phenyl group inert to the chosen oxidative coupling conditions (1:1 mixture of VOF_3 and $BF_3 \cdot Et_2O$), and triphenylene **11** was generated in close to quantitative yields. Only 2 equiv of VOF_3 are sufficient for this coupling, since product **11** is apparently not oxidized under these conditions.[19–21] Reduction of **11** with $LiAlH_4$ generates the desired diaminotriphenylene **9** in an overall yield of 65% starting from **7**.

Pure compound **9** is a white solid, but a brown solid is obtained when handled in air, which is attributed to the presence of oxidation products. However, the brown product gave satisfactory NMR spectra and was used without further purification for the subsequent condensation reaction with **8**. Samples of **9** that were stored for one month at −30 °C under argon gave identical yields.

Condensation of tetraketopyrene **8** with 2.2 equiv of diamine **9** in acetic acid did not generate QPP **4** but the monocondensation product **12** in close to quantitative yield based on **8** (Scheme 3). An excess of **9** was recovered from the reaction mixture, which confirms that no side reactions occurred. The formation of **12**, a valuable intermediate for the preparation of unsymmetrical QPP derivatives, is solely a result of its low solubility in acetic acid and does not require stoichiometric control.[2,3,6] QPP **4** was obtained in 80% yield when the reaction was conducted in a 1:8 mixture of acetic acid and THF.

Scheme 3. Condensation of **8** and **9** to **12** and QPP **4**
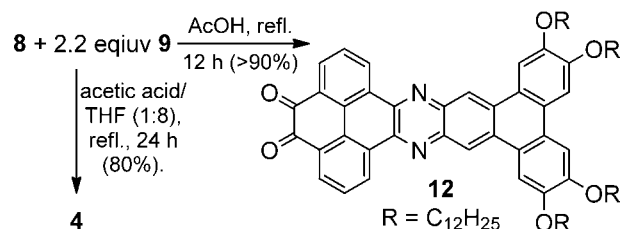
The thermal properties of compounds **3**, **4**, **7**, **9**, **10**, **11**, and **12** were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and variable temperature powder X-ray diffraction (pXRD) measurements. Mesomorphism was observed only for QPP derivatives **3** and **4** that display hexagonal and rectangular columnar mesophases over wide ranges of temperature (Figure 2).

QPPs **3** and **4** both display crystalline phases (Cr) and rectangular columnar mesophases (Col$_r$) while only QPP **3** also displays a high temperature hexagonal columnar
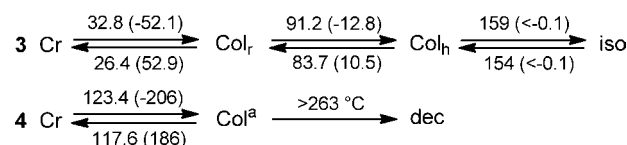
Figure 2. Phase behavior of QPPs **3** and **4** based on POM, DSC, and pXRD. Transition temperatures (onset) and enthalpies are given in °C (kJ/mol). [a] It is likely a Col$_r$-type mesophase (see SI).

mesophase (Col$_h$) and an isotropic liquid phase (Iso). The larger planar core of **4** clearly increases the thermal stability of its Cr and Col phases in comparison to **3** and suppresses the formation of Col$_h$ and Iso phases because thermal decomposition occurs first. Lower transition temperatures and the additional Col$_h$ and Iso phases most importantly benefit the processing of QPP **3** into aligned films for device applications. For example, **3** self-organizes into millimeter-sized domains of columnar stacks with vertical (homeotropic) alignment to a substrate when cooled from its isotropic liquid state between glass slides. This vertical self-alignment is particularly remarkable for a compound of a board shape rather than a disc shape and is only slightly disturbed at the transition into the biaxial Col$_r$ phase.

The electronic properties of QPPs **3** and **4** were probed by absorption spectroscopy, cyclic voltammetry, and DFT calculations (Table 1). Extension of the conjugated system in **4** decreases E_{gap} and E_{LUMO} by 0.2 eV with regard to **3**. A comparison of the red/ox potentials of QPPs **3** and **4** with the potentials of tetraalkoxy and tetraalkylthio substituted QPP derivatives **2**[9,15] reveals an increase of E_{HOMO} and a decrease of E_{LUMO} by 0.2 and 0.1 eV, respectively, for **3** and almost twice these values for **4**. Consequently, E_{gap} values of QPPs **3** and **4** are between 0.2 and 0.8 eV smaller than those for QPPs **2**. These properties qualify **3** and **4** as organic dyes with good electron acceptor properties.

Table 1. Red/Ox Potentials, $E_{HOMO/LUMO}$, and Optical HOMO−LUMO Gaps of QPPs **3** and **4**

	$E_{1/2}^{red}/E_{1/2}^{ox\,a}$	$E_{HOMO}/E_{LUMO}/E_{gap}^{d}$	$E_{HOMO}/E_{LUMO}/E_{gap}^{e}$	E_{gap}^{f}
3	−1.24/1.17[b]	−5.49/−3.08/2.41	−5.13/−2.18/2.95	2.48
4	n.a.[c]	n.a.[c]	−5.03/−2.28/2.75	2.21

[a] First potentials in V vs Ag/Ag$^+$ (CH_2Cl_2, glassy carbon working electrode. [b] Estimated from peak potential of irreversible oxidation at 1.20 V. [c] Insufficiently soluble for solution cyclic voltammetry. [d] Calculated based on $E_{1/2}^{ox}$ of ferrocene/ferrocenium as internal standard (0.48 V vs Ag/Ag$^+$ = 4.80 eV). [e] Based on DFT calculations (B3LYP/6-31g(d,p)) in vacuum. [f] Based on onset of longest wavelength absorption; Energy values are given in eV vs vacuum.[22]

The absorption and emission properties of QPPs **3** and **4** agree with the measured and calculated electronic properties and show the expected bathchromic shift of the absorption/emission maxima from 445/557 nm for **3** to

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475/654 nm for **4** because of its enlarged conjugated system (Figure 3). The observed large Stokes shifts of 112 and 179 nm for QPPs **3** and **4**, respectively, are probably generated by intramolecular charge transfer (ICT) states, and their formation is in agreement with the distinct spatial separation of HOMO and LUMO orbitals (donor−acceptor structure)[23] in calculated structures (see SI, Table S2).
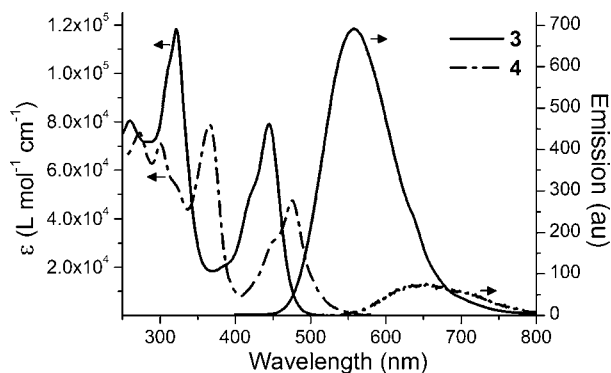

Figure 3. Absorption and fluorescence spectra of compounds **3** (1.0×10^{-5} M (absorption) and 1.0×10^{-6} M (fluorescence) in CH_2Cl_2) and **4** (8.7×10^{-6} M in $CHCl_3$ at 45 °C). Excitation wavelengths for **3** and **4** were 445 and 475 nm, respectively.

QPP **3** has a high fluorescence quantum yield of 31% in solution whereas QPP **4** only reaches 0.72%. Similarly, the fluorescence quantum yields of QPPs **2** are low with values below 0.3%,[24,25] and we hypothesize that the ether groups are involved in the more competitive nonradiative deactivation processes. The ether groups in QPP **3** only weakly electronically interact with the pyrene fluorophore since the phenyl groups are tilted out of plane.

Both QPPs **3** and **4** also fluoresce in their crystalline and columnar liquid crystal phases (see SI). This is rather unusual for $\pi−\pi$ stacking materials and suggests a weak interaction between the transition dipole moments, as it has been observed in columnar *J*-aggregates and compounds that stack orthogonally.[26,27]

In conclusion, we describe different synthetic approaches to new QPP derivatives **3** and **4** that display several types of columnar mesophases over wide ranges of temperature. Both compounds consist of donor−acceptor structures and can be categorized as organic dyes, electron acceptors, and fluorophores in liquid and solid phases. Their properties as organic semiconductors are presently under investigation.

Supporting Information Available. Synthesis and characterization of all compounds; UV−vis and fluorescence spectra, cyclic voltammetry, DFT calculations, POM, TGA, DSC, and pXRD of QPPs **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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