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1,4-Diaryl-7,10-dimethoxyquinoxalino[2,3-*b*]quinoxalines and Their Dihydro Derivatives: Redox Switching of NIR Absorption and Fluorescence

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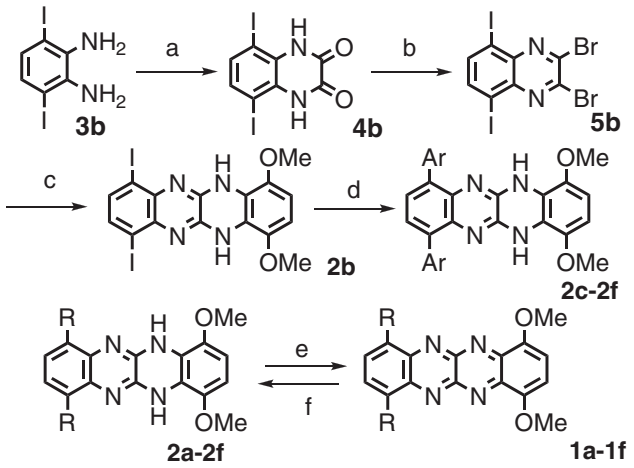
Due to the high-lying HOMO of the substituents and the low-lying LUMO inherited by the heterocyclic skeleton, the title quinoxalinoquinoxalines **1** exhibit absorption bands which extend to the NIR region, whereas the dihydro derivatives **2** are less colored but emit strong green fluorescence. Thus, the present pairs can serve as novel redox dyes for drastic spectral changes.

Linear azapolyacenes are an interesting class of compounds, for which not only the aromatic form with $[4n + 2]\pi$ electrons but also the antiaromatic ($[4n]\pi$) form can exist as stable species.[1] Some of them are attracting considerable recent attention as luminescent materials[2] or metal ligands[3] to gain advanced physical properties. During the course of our studies on redox active dyes exhibiting fluorescent switching,[4] we have found that the title heterocyclic pairs (**1**/**2**) are interesting Weitz-type redox systems,[5] whose properties can be modified by introduction of various aryl groups via the Suzuki–Miyaura coupling.[6] Noteworthy is that the electronic spectrum of aromatic form **1** extends to the NIR region whereas the antiaromatic dihydro derivatives **2** exhibit strong fluorescence, showing drastic spectral changes upon redox reactions. Here we report the preparation, X-ray structures, and spectral properties of **1** and **2**.

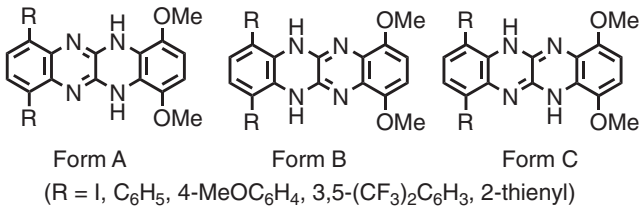
The parent quinoxalino[2,3-*b*]quinoxaline (QQ) is notorious for its low solubility[7] as are many linear polyacenes. This problem has been often overcome by introduction of substituents to prevent the skeleton from dense packing in the crystal. Electron-donating substituents such as methoxy groups are attractive in both aspects for increasing solubility and for raising the HOMO of the electron-deficient QQ derivatives. The latter effects would induce red shift of the absorption band toward the NIR region. With these in mind, we have designed here 1,4-diaryl-7,10-dimethoxy-QQs **1c**–**1f**, which would be interconvertible with the dihydro derivatives (H_2QQs) (**2c**–**2f**).

1,4-Diiodo-7,10-dimethoxy-H_2QQ (**2b**) was chosen as the key synthon, which was prepared as shown in Scheme 1, by following the preparation of 1,4,7,10-tetramethoxy-H_2QQ (**2a**).[8] Thus, 3,6-diiodo-1,2-phenylenediamine (**3b**)[9] and diethyl oxalate were condensed in the presence of sodium ethoxide. The resulting 2,3-dihydroxy-5,8-diiodoquinoxaline prefers to adopt the keto form **4b**, which was converted into 2,3-dibromo-5,8-diiodoquinoxaline (**5b**) by using PBr_3 (yield 66% over 2 steps). Upon condensation of **5b** and 3,6-dimethoxy-1,2-phenylenediamine (**3a**)[8] in refluxing ethanol, **2b** was obtained in 94% yield.

By adopting the standard conditions for the Suzuki–Miyaura coupling reaction between **2b** and $PhB(OH)_2$, phenyl groups can be attached at 1,4-positions of the H_2QQ skeleton to give **2c** in 90% yield. Diiodide **2b** was also converted into H_2QQs **2d**–**2f** smoothly having 4-methoxyphenyl, 3,5-bis(trifluoromethyl)phenyl, and 2-thienyl groups (yield 80, 95, and 76%, respectively) by using the corresponding arylboronic acids.[10,11] H_2QQs **2b**–**2f** thus obtained are stable yellow powders and easily oxidized upon treatment with DDQ to fully aromatized quinoxalinoquinoxalines QQs **1b**–**1f** (yield 96, 98, 90, 86, and 99%, respectively) exhibiting blue-black/green-black color. DDQ also works nicely to convert **2a** to **1a** (yield 93%); the latter was first prepared here by this method.



Scheme 1. Reagents and conditions: (a) $(COOEt)_2$, NaOEt, benzene, reflux; (b) PBr_3, reflux; (c) 3,6-dimethoxy-1,2-phenylenediamine (**3a**), EtOH, reflux; (d) arylboronic acid, $[Pd(PPh_3)_4]$, K_2CO_3, H_2O–THF, reflux; (e) DDQ, $CHCl_3$: (f) $Na_2S_2O_4$, THF–H_2O.



Scheme 2. Possible isomers of H_2QQs **2b**–**2f**.

There has been controversy concerning the structure of H_2QQs in terms of the positions of NH protons.[12] Thus, dihydro compounds **2b**–**2f** may adopt one of the three forms shown in Scheme 2. In the NMR spectrum of diphenyl derivative **2c** in DMSO-d_6, two sharp singlets are observed at 7.14 and 6.36 ppm for aromatic protons, thus ruling out the Form C, which had been

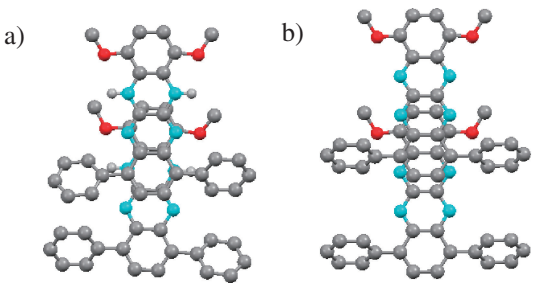


Figure 1. a) Molecular overlap in H_2QQ **2c** and b) that in QQ **1c**. In **2c**, there is another overlap in crystal, which is very close to that shown in a).

considered as the main contributor before. The higher-field resonance, which is close to that of **3a** (6.15 ppm), was assigned to those on the dimethoxybenzene nucleus of Form A. Preference of Form A over Form B could be rationalized by the intramolecular hydrogen bonding of N–H···O at the *peri*-positions. The same could be true for other H_2QQs **2b** and **2d**–**2f** as suggested by the similar NMR data shown in Table S1.[13]

In this way, it has been suggested that N–H protons localize on the 5,12-positions of **2c** in solution. According to X-ray analysis, this is also the case in the crystal (Figure 1a). The diphenyl-H_2QQ **2c** crystallizes in $P2_12_12_1$ space group ($Z = 8$), and there are two crystallographically independent molecules having quite similar structural parameters. The phenyl groups are rotated against the H_2QQ core with the torsion angles of 30–45°, and the three rings are arranged in a clockwise or an anticlockwise manner, respectively, in molecule **1** and molecule **2**. Although the location of N–H protons cannot be determined by differential fourier synthesis, the C–N bond lengths in the two diazahexagons are different enough [dihydropyrazine moiety: 1.358(9), 1.376(9), 1.383(9), and 1.394(9) Å in molecule **1**, 1.357(9), 1.367(8), 1.376(9), and 1.401(9) Å in molecule **2**; pyrazine moiety: 1.293(9), 1.305(9), 1.374(9), and 1.398(9) Å in molecule **1**, 1.292(9), 1.293(8), 1.349(9), and 1.385(8) Å in molecule **2**] to assure the structural assignment of the dihydropyrazine and pyrazine rings to confirm adoption of Form A (Table S2[13]). All methoxy groups in molecules **1** and **2** are located nearly on the same plane as the H_2QQ core, with the oxygen lone pair directing toward the N–H protons to make short O···H contacts (ca. 2.3 Å).

The intramolecular hydrogen bond is not the only factor that favors the observed geometry in terms of the methoxy groups to the core. As shown by the X-ray analysis on the corresponding oxidized form **1c**, the methoxy groups occupy quite similar positions despite the absence of hydrogen bonding (Figure 1b), which can be rationalized by considering the expected repulsion between the methyl groups and nitrogen lone pairs in the inward-directing conformer. In contrast to the case of H_2QQ **2c**, the C–N bond lengths in QQ **1c** fall in a narrow range of 1.334(5)–1.358(5) Å to indicate that both diazahexagons are the pyrazine rings. The molecules are lying on the crystallographic mirror plane that bisects the short axis of **1c**, so that the two phenyl rings are respectively attached in a clockwise and an anticlockwise manner to the core with the torsion angle of 54.0°.

In both crystals of **1c** and **2c**, the core skeleton is overlapped in a face-to-face manner to form one-dimensional columnar

Table 1. Redox potentials of QQs **1a**–**1f** and H_2QQs **2a**–**2f** measured by cyclic voltammetry in CH_2Cl_2

Compound	R	$E_1^{ox\,a}$/V	E_1^{red}/V	E_{sum}/V
1a	MeO	+1.47	−0.39	1.86
1b	I	+1.57	−0.15	1.72
1c	C_6H_5	+1.50	−0.36	1.86
1d	4-$MeOC_6H_4$	+1.44	−0.38	1.82
1e	3,5-$(CF_3)_2C_6H_3$	+1.57	−0.24	1.81
1f	2-thienyl	+1.27	−0.27	1.54
2a	MeO	+0.68		
2b	I	+0.87		
2c	C_6H_5	+0.75		
2d	4-$MeOC_6H_4$	+0.72		
2e	3,5-$(CF_3)_2C_6H_3$	+0.93		
2f	2-thienyl	+0.80		

[a]Irreversible wave.

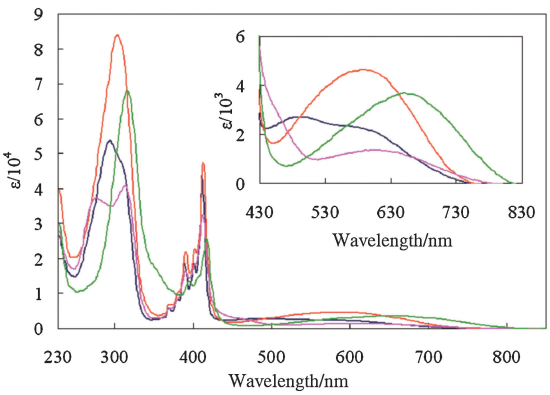


Figure 2. UV–vis–NIR spectra of QQs **1c**–**1f** in CH_2Cl_2 (**1c**: blue; **1d**: red; **1e**: pink; **1f**: green).

stacks, in which the electron-donating dimethoxybenzene moiety is overlapped with the electron-deficient quinoxaline skeleton (Figure 1). The columns are further packed in a herringbone motif exhibiting several short C–H···π contacts (Figure S1[13]). Not only by the packing arrangement in crystal but also by the redox potentials (E/V vs. SCE in CH_2Cl_2) in Table 1, the amphoteric character of **1** is clearly shown.

Thus, the present QQs undergo irreversible one-electron oxidation (E_1^{ox}) as well as reversible one-electron reduction (E_1^{red}). The second reduction process is irreversible, and the values of E_2^{red} are omitted in Table 1. The E_{sum} value defined as $E_1^{ox} - E_1^{red}$ is often used for evaluating the electrochemical amphotericity, and the small values (<2 V) indicate the narrow HOMO–LUMO gap for QQs **1**. The E_1^{ox} of **1f** (+1.27 V) is lower than phenyl derivative **1c** (+1.50 V) or tetramethoxy derivative **1a** (+1.47 V) due to the electron-rich thienyl rings. The highest electron-affinity is found in **1e** due to the electron-withdrawing 3,5-bis(trifluoromethyl)phenyl groups (E_1^{red}: −0.24 V). On the other hand, the dihydro derivatives **2** are not amphoteric. They are much weaker electron acceptors ($E_1^{red} <$ −2 V), but exhibit stronger electron-donating ability (E_1^{ox}: +0.68–+0.93 V) due to the dimethoxyphenylenediamine unit.

Such difference in electronic structure results in drastic changes in UV–vis–NIR spectra of QQs **1** and H_2QQs **2**. Due to

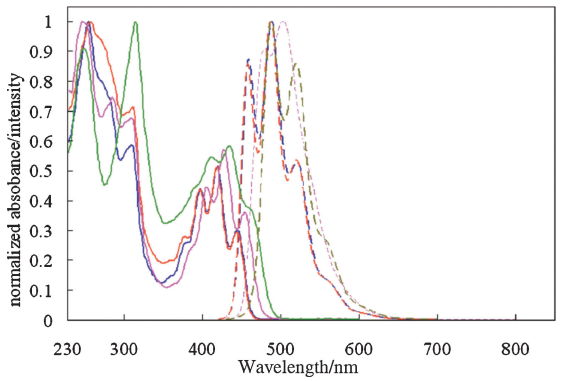


Figure 3. UV–vis (solid lines) and fluorescence spectra (dashed line) of H_2QQs **2c**–**2f** in CH_2Cl_2 (**2c**: blue; **2d**: red; **2e**: pink; **2f**: green).

Table 2. Fluorescence spectral data of H_2QQs **2c**–**2f** in CH_2Cl_2

Compound	Ar	Φ_{fl}[a]	$\lambda_{em\ max}$/nm
2c	C_6H_5	0.52	459, 488, 521
2d	4-$MeOC_6H_4$	0.49	458, 487, 520
2e	3,5-$(CF_3)_2C_6H_3$	0.38	480, 503
2f	2-thienyl	0.37	488, 521

[a]Determined by using *N*-methylacridinium salt ($\Phi = 0.84$) in MeCN as an external standard.

the high amphoteric nature, the electronic absorption bands of **1c**–**1f** extend to the NIR region ($\lambda > 700$ nm) with the absorption maxima at 590, 585, 609, and 651 nm, respectively (Figure 2). Such a band is also present in tetramethoxy derivative **1a** (616 nm) but absent in the parent QQ[12] without electron-donating substituents. The absorption is red-shifted in 3,5-bis(trifluoromethyl)phenyl (**1e**) and 2-thienyl derivatives (**1f**) due to the lower LUMO and higher HOMO, respectively, than phenyl derivative **1c**. These bands show intramolecular charge-transfer (CT), and the nonfluorescence of **1c**–**1f** can be also rationalized by considering facile nonradiative decay through CT interaction.

In contrast, strong green emission (450–600 nm) is evident for H_2QQs **2c**–**2f**. The fluorescence spectra exhibit fine structures as their absorption bands (350–450 nm) (Figure 3). Again, 3,5-bis(trifluoromethyl)phenyl (**2e**) and 2-thienyl derivatives (**2f**) show red-shifted absorption and emission, and the fluorescence quantum yields (Φ_{fl}) are marginally smaller in **2e** and **2f** than in **2c** and **2d** (Table 2). Due to the drastic spectral differences of the redox pairs of **1c**–**1f**/**2c**–**2f**, they can serve as novel redox dyes for drastic spectral changes. The reversible interconversion between **1c**–**1f**/**2c**–**2f** was demonstrated by high-yield reduction of **1c**–**1f** to **2c**–**2f** (yield 100, 95, 99, and 100%, respectively) using $Na_2S_2O_4$.

In summary, we have designed and efficiently prepared aryl-substituted QQ derivatives **1** by way of the Suzuki–Miyaura coupling reaction. They are electrochemically amphoteric and deeply colored dyes due to electron-donating methoxy groups, and their properties can be tuned by the electronic nature of aryl substituents. Noteworthy is the reversible interconversion with the dihydro **2** derivatives that emit strong fluorescence. Further modification are now in progress to attain unique properties of QQ and H_2QQ.

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