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Synthesis of 5,5′-Diarylimino Quinoidal 2,2′-Bithiazoles

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S Supporting Information

ABSTRACT: A Pd(0)-catalyzed double C−N coupling of 5,5′-dibromo-2,2′-bithiazoles with (het)arylamines and subsequent in situ Ag$_2$O-mediated oxidation provides access to cross-conjugated quinoidal 5,5′-diarylimino-2,2′-bithiazoles in moderate to high yield. The highly colored quinoidal 2,2′-bithiazoles were studied by UV/vis spectroscopy, cyclic voltammetry and computational methods.

Thiazole, which first appeared in the literature over 140 years ago,[1] is one of the most studied sulfur−nitrogen hetarenes. The chemistry and properties of thiazole-containing compounds have been extensively reviewed,[2] and there are regular updates on their biological properties[3] and their occurrence in natural products.[4]

2,2′-Bithiazoles, an important thiazole subclass, can exist at three oxidation levels: dithiadiazafulvalenes (DTDAFs), aromatic 2,2′-bithiazoles, and quinoidal 2,2′-bithiazoles (Figure 1).

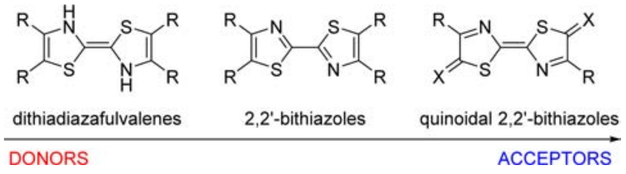

Figure 1. Structures of 2,2′-bithiazoles at three possible oxidation levels.

Aromatic 2,2′-bithiazoles are the most well studied, and several analogues display useful biological properties such as antiviral activity against hepatitis B[5] or HIV,[6] while others inhibit histone deacetylase.[7] Many aromatic 2,2′-bithiazoles also appear in small molecules, oligomers, and polymers with diverse uses in materials, e.g., as components in fluorescent chemosensors,[8] organic photovoltaics (OPVs),[9] and organic thin-film transistors (OTFTs)[10] and as liquid crystals,[11] macrocycles,[12] and ligands for metal coordination.[13]

DTDAFs and quinoidal 2,2′-bithiazoles are cross-conjugated, i.e., they possess at least "three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other".[14] Cross-conjugation can be used to modify both the optical and electronic properties of a molecule.[15] Furthermore, cross-conjugation can make molecules susceptible to quantum interference phenomena.[16] These features make cross-conjugated systems interesting for applications in organic electronics.

DTDAFs[17] are similar to tetrathiafulvalene (TTF)[18] and exhibit good electron-donating properties, making them useful components of conducting charge transfer salts. In contrast, quinoidal 2,2′-bithiazoles are electronically similar to quinones, i.e., the addition of one electron completes the π sextet required for Hückel aromaticity, potentially making them good redox-reversible electron acceptors.[19] To the best of our knowledge, there are only two reports on quinoidal 2,2′-bithiazoles: compounds **1**[20] and **2**[21] (Figure 2).

Quinoidal compounds have been used to design low-band-gap materials,[22] and quinoidal 2,2′-bithiophenes, which are structur-

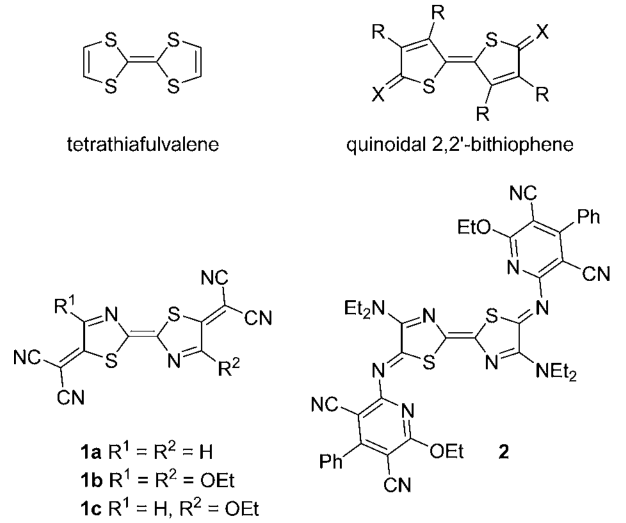

Figure 2. General structures of TTF and quinoidal 2,2′-bithiophenes and the structures of known quinoidal 2,2′-bithiazoles **1** and **2**.

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ally similar to the quinoidal 2,2′-bithiazoles reported herein, show n-type and/or ambipolar semiconductor properties.[23] The scarcity of studies on the aza analogues, quinoidal 2,2′-bithiazoles, can be attributed to the absence of a general and high-yielding synthesis of these systems.

Recently, we prepared highly functionalized pyrido[2,3-*b*]pyrimidines from dialkylamines and *N*-pyridyl-1,2,3-dithiazolimines [see Scheme S1 in the Supporting Information (SI)] and isolated as a minor side product the deep-green-colored quinoidal 2,2′-bithiazole **2** (Figure 2).[21] To facilitate its study, we needed a higher-yielding synthesis, but we failed to optimize its formation from 1,2,3-dithiazolimines. Nevertheless, a one-pot, two-step, chromatography-free route was developed that involved a Pd(0)-mediated double C−N coupling of available 5,5′-dibromo-2,2′-bithiazoles **3** with (het)arylamines to give 5,5′-diarylamino-2,2′-bithiazoles, which were then oxidized in situ to the analogous quinoidal 5,5′-diarylimino-2,2′-bithiazoles **4**.

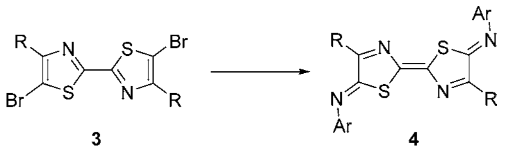
The study to identify and optimize a suitable C−N coupling protocol involved the use of 5,5′-dibromo-4,4′-diphenyl-2,2′-bithiazole (**3a**) and 4-*n*-butoxyaniline, as this combination gave products with good solubility that assisted with the workup. Extensive optimization of the C−N coupling invoked the use of different catalysts [Pd(Ph$_3$P)$_2$Cl$_2$, (PhCN)$_2$PdCl$_2$, PdCl$_2$, Pd(Ph$_3$P)$_4$, Pd$_2$dba$_3$, (MeCN)$_2$PdCl$_2$, [Pd(dppf)Cl$_2$]CH$_2$Cl$_2$, PEPPSI-IPr catalyst, Pd{P[3,5-(F$_3$C)$_2$C$_6$H$_3$]$_3$}$_3$ (Superstable Pd(0)), ligands [JohnPhos, *t*-BuX-Phos, (MeO)$_3$P, dppf, dppe, DPEPhos, BINAP, XantPhos], bases (K$_2$CO$_3$, Cs$_2$CO$_3$, K$_3$PO$_4$, NaOH), and solvents (THF, PhH, PhMe, MeCN, DMSO, DMF, 1,4-dioxane) (see SI section S2). Ultimately, a one-pot chromatography-free protocol was developed that gave the desired product **4d** in 86% yield. The optimized reaction conditions were as follows: (i) Pd{P[3,5-(F$_3$C)$_2$C$_6$H$_3$]$_3$}$_3$ (1.25 mol %), DPEPhos (5 mol %), K$_2$CO$_3$ (2.4 equiv), 1,4-dioxane, ca. 101 °C, argon; (ii) Ag$_2$O (1.2 equiv), ca. 101 °C. These conditions were then applied to prepare a range of 5,5′-diarylimino-4,4′-diaryl-5*H*,5′*H*-2,2′-bithiazolylidenes **4a−z** (Table 1). The reaction worked well with an electron-donating group (EDG) or electron-withdrawing group (EWG) on either the arylamine (entries 2−5 and 6−11, respectively) or the 4,4′-diaryl rings of the 2,2′-bithiazole (entries 13−17 and 18−23, respectively).

Worthy of note was that the reaction of **3a** with 4-nitroaniline (entry 8) led to the insoluble product **4h**, making its isolation and characterization difficult. Thus, 4-nitroaniline was reacted with 5,5′-dibromo-4,4′-bis[4-(*tert*-butyl)phenyl]-2,2′-bithiazole (**3b**), which gave the more soluble product **4n**.

The reaction of 4-*n*-butoxyaniline with 4,4′-dibromo-5,5′-di(pyrid-2-yl)-2,2′-bithiazole (**3g**) (entry 24) led to no reaction. This was not surprising, since pyridines can coordinate to palladium[24] and poison the catalytic cycle.[25] Also, the reaction of 2-, 3-, and 4-pyridylamines with **3a** proceeded only slowly (entries 9−11) and did not reach completion, often giving mixtures of unreacted dibromo- and/or monoamino bithiazoles (see SI section S4).

Electron-rich hetarenes were well-tolerated: the reaction of 4-*n*-butoxyaniline with 5,5′-dibromo-4,4′-bis(5-*n*-hexylthien-2-yl)-2,2′-bithiazole (**3h**) gave the desired product **4y** in 65% yield (entry 25), while the reaction of 3-amino-9-(2-ethylhexyl)-9*H*-carbazole with **3a** gave the desired product **4l** in a high 91% yield (entry 12). Both thienyl and carbazole moieties are frequently used as components in organic electronics because of their ease of structural modification, optical properties, electrochemical behavior, and environmental stability.[26]

Table 1. Coupling of 5,5′-Dibromo-2,2′-bithiazoles 3 (0.1 mmol) with (Het)arylamines[a]



3 **4**

entry	bithiazole (R)	Ar′	time t_1 (h)	time t_2 (min)	**4** (% yield)
1	**3a** (Ph)	Ph	25	25	**4a** (83)
2	**3a** (Ph)	4-*n*-BuC$_6$H$_4$	19	20	**4b** (75)
3	**3a** (Ph)	4-MeOC$_6$H$_4$	22	28	**4c** (85)
4	**3a** (Ph)	4-*n*-BuOC$_6$H$_4$	16	10	**4d** (86)
5	**3a** (Ph)	4-Et$_2$NC$_6$H$_4$	24	10	**4e** (68)
6	**3a** (Ph)	4-F$_3$CC$_6$H$_4$	24	20	**4f** (87)
7	**3a** (Ph)	4-NCC$_6$H$_4$	22	10	**4g** (92)
8	**3a** (Ph)	4-O$_2$NC$_6$H$_4$	16	10	**4h** (−)[b]
9	**3a** (Ph)	pyrid-2-yl	36	−	**4i** (ir)[c]
10	**3a** (Ph)	pyrid-3-yl	21	20	**4j** (57)[c]
11	**3a** (Ph)	pyrid-4-yl	21	15	**4k** (35)[c]
12	**3a** (Ph)	carbazol-3-yl[d]	17.5	30	**4l** (91)
13	**3b** (4-*t*-BuC$_6$H$_4$)	4-*n*-BuOC$_6$H$_4$	18	10	**4m** (66)
14	**3b** (4-*t*-BuC$_6$H$_4$)	4-O$_2$NC$_6$H$_4$	14	11	**4n** (83)
15	**3b** (4-*t*-BuC$_6$H$_4$)	pyrid-2-yl	21	10	**4o** (28)[b]
16	**3c** (4-MeOC$_6$H$_4$)	Ph	21	10	**4p** (76)
17	**3c** (4-MeOC$_6$H$_4$)	4-*n*-BuOC$_6$H$_4$	16	10	**4q** (55)
18	**3d** (4-FC$_6$H$_4$)	4-*n*-BuOC$_6$H$_4$	16	20	**4r** (76)
19	**3e** (4-F$_3$CC$_6$H$_4$)	Ph	16	25	**4s** (87)
20	**3e** (4-F$_3$CC$_6$H$_4$)	4-*n*-BuOC$_6$H$_4$	19	20	**4t** (84)
21	**3e** (4-F$_3$CC$_6$H$_4$)	4-Et$_2$NC$_6$H$_4$	17	10	**4u** (78)
22	**3f** (4-O$_2$NC$_6$H$_4$)	4-*n*-BuOC$_6$H$_4$	16	10	**4v** (74)[e]
23	**3f** (4-O$_2$NC$_6$H$_4$)	4-Et$_2$NC$_6$H$_4$	16	15	**4w** (69)[e]
24	**3g** (pyrid-2-yl)	4-*n*-BuOC$_6$H$_4$	12	−	**4x** (nr)[f]
25	**3h** (2′-*n*-hexylthien-2-yl)	4-*n*-BuOC$_6$H$_4$	20	10	**4y** (65)
26	**3i** (H)	4-*n*-BuOC$_6$H$_4$	72	−	**4z** (−)[g]
27	**3j** (Me)	4-*n*-BuOC$_6$H$_4$	72	−	**4aa** (−)[g]

[a]Reaction conditions: (i) ArNH$_2$ (2 equiv), Pd{P[3,5-(F$_3$C)$_2$C$_6$H$_3$]$_3$}$_3$ (1.25 mol %), DPEPhos (5 mol %), K$_2$CO$_3$ (2.4 equiv), 1,4-dioxane (2.5 mL), argon, ca. 101 °C, t_1 h; (ii) Ag$_2$O (1.2 equiv), ca. 101 °C, t_2 min. [b]Very insoluble product. [c]Incomplete reaction. [d]*N*-(2-Ethylhexyl). [e]A minor side product also obtained (see SI section S4). [f]No reaction. [g]Mainly unreacted starting material and brown baseline material.

Disapointingly, the reactions of 4-*n*-butoxyaniline with the 4,4′-unsubstituted and 4,4′-dimethyl-substituted 5,5′-dibromo-2,2′-bithiazoles **3i** (entry 26) and **3j** (entry 27), respectively, gave after 72 h mainly unreacted starting material and intractable brown baseline material (by TLC). Identifying conditions to enable these reactions will broaden the scope of this route and remains under investigation.

The synthesized quinoidal bithiazoles were studied with UV/vis spectroscopy, computational methods and cyclic voltammetry. All of the compounds exhibited strong absorption ranging from the visible to the NIR region, with $\lambda_{\mathrm{max,onset}}$ = 584 nm ($E_{\mathrm{g,opt}}$ = 2.12 eV) to 976 nm (1.27 eV) (e.g., compounds **4d**, **4e**, **4k**, **4l**, **4u**, and **4w** in Figure 3). The longest-wavelength absorption maxima (λ_{max}) were greatly influenced by the peripheral subsitution. The presence of EDGs on any of the aryl groups led to red shifts of λ_{max}, while EWGs led to red shifts when

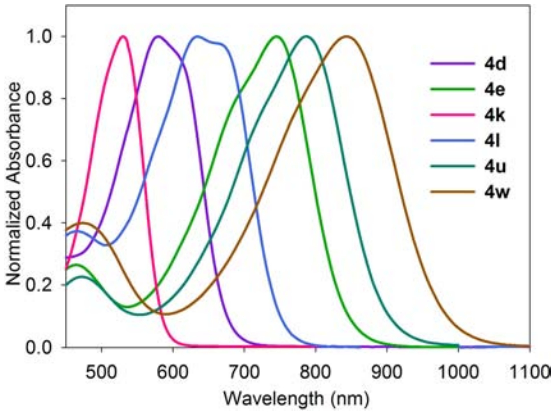


Figure 3. UV/vis spectra of selected bithiazoles **4d**, **4e**, **4k**, **4l**, **4u**, and **4w** in DCM.

attached at the 4,4′-diaryl positions but blue shifts when attached at the 5,5′-diarylimino positions. The observed shifts were greater when EDGs were attached to the 5,5′-diarylimino moieties and EWGs to the 4,4′-diaryl moieties; the greater effect exerted by the introduction of the substituents at the specified positions was evident from the orbital energy level changes as well as the topology of the frontier molecular orbitals (FMOs) (see SI section S5.4). The effects were additive, and combining a strong EDG with a strong EWG led to significant shifting of λ_{max} into the NIR region [e.g., bithiazole **4w** (λ_{max} = 842 nm)].

Exceptions were the pyrid-2-ylimine-bearing bithiazoles **4i** and **4o**, as the pyrid-2-yl group appeared to act as a weak EDG rather than a EWG. This was attributed to a N···S nonbonding interaction[27] (see SI section S5.4).

From TD-DFT RB3LYP/6-31G(d,p) studies, the longest-wavelength absorptions were assigned to the HOMO → LUMO transitions (e.g., Figure 4, compound **4a**). Gratifyingly, the computationally obtained optical band gaps were in good agreement with the experimental optical band gaps. The largest deviations (0.22−0.27 eV) were observed for compounds **4e**, **4u**, and **4w**. Analysis of the FMO representations of these compounds revealed that the first excitation has significant charge transfer character, i.e., the orbital density is localized on the EDG moiety in the HOMO but is mainly delocalized on the other moiety in the LUMO (Figure 5). This is reminiscent of the spatial separation of the HOMO and LUMO observed in related cruciforms.[28]

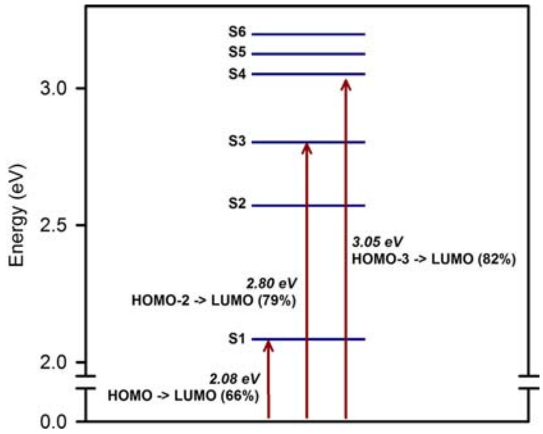


Figure 4. Energy diagram of singlet excited states for 2,2′-bithiazole **4a** from TD-DFT data at the RB3LYP/6-31G(d,p) level.

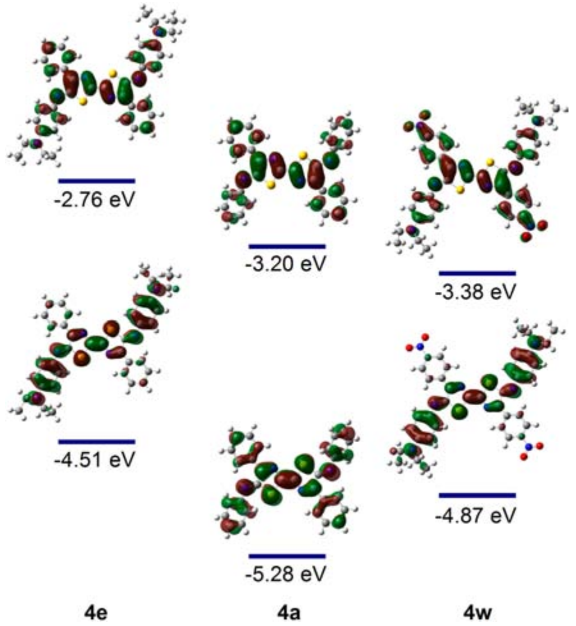


Figure 5. Frontier molecular orbitals (HOMO and LUMO) for compounds **4e**, **4a**, and **4w**.

Furthermore, cyclic voltammetry (CV) indicated that the quinoidal 2,2′-bithiazoles **4** display amphoteric redox behavior. Many of the compounds showed two reversible or quasi-reversible oxidation waves with onset values for the first oxidation in the range of 0.47 to 1.46 V vs SCE and two reversible or quasi-reversible reduction waves with onset values for the first reduction in the range of −0.29 to −0.68 V vs SCE (e.g., bithiazole **4a**, Figure 6).

Compounds **4** are weaker electron acceptors than Yamashita's bithiazoles **1**,[20] which displayed only reductions and no oxidations in the electrochemical window studied. This was expected as the latter possess the strongly electron-accepting dicyanomethylidene moiety.

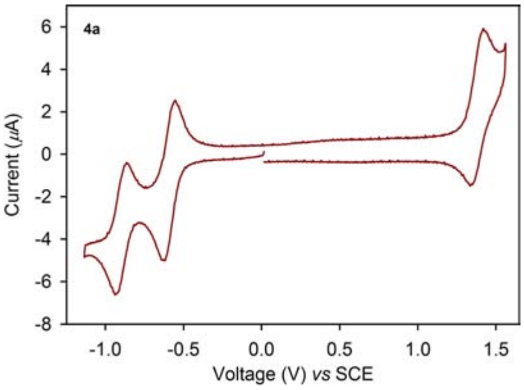


Figure 6. Cyclic voltammogram of **4a** in DCM (0.5 mM) containing *n*-Bu_4NPF_6 (0.1 M) as an electrolyte. A glassy carbon disk and Pt wire were used as the working and counter electrodes, respectively, and Ag/AgCl (1 M KCl) was used as the reference electrode. The scan rate was 100 mV/s, the temperature ca. 20 °C, and the external reference Fc/Fc^+ (0.475 V vs SCE).

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From the CV data, the energies E_{HOMO}, E_{LUMO} and $E_{g,electrochem}$ were also calculated and compared to the optical and computational data (see SI section S6). Interestingly, the HOMO and LUMO energies are similar to those of a recently reported quinoidal 2,2′-bithiophene that displayed ambipolar behavior in OFETs.[23b]

In conclusion, 22 new cross-conjugated quinoidal 5,5′-diarylimino 2,2′-bithiazoles were prepared via a double Pd(0)-catalyzed C−N coupling protocol and subsequent in situ oxidation in moderate to high yields. By manipulation of the peripheral substituents, the HOMO and LUMO energy levels can be altered and the optical band gap can be tuned up to the NIR region. Electrochemical studies revealed that quinoidal 2,2′-bithiazoles **4** display amphoteric redox behavior, in contrast to 2,2′-bithiazole **1a**, which showed only reductions in the electrochemical window studied.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03474.

Discussion of reaction optimization; extensive discussion of UV/vis, computational, and CV data; experimental section (PDF)

NMR spectra for all new compounds (PDF)

Computed atomic coordinates and total energies (PDF)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Prof. Robert C. Haddon who passed away on April 21, 2016.

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