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Conjugated Materials

Dithiolodithiole as a Building Block for Conjugated Materials**

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Abstract: *The development of new conjugated organic materials for dyes, sensors, imaging, and flexible light emitting diodes, field-effect transistors, and photovoltaics has largely relied upon assembling π-conjugated molecules and polymers from a limited number of building blocks. The use of the dithiolodithiole heterocycle as a conjugated building block for organic materials is described. The resulting materials exhibit complimentary properties to widely used thiophene analogues, such as stronger donor characteristics, high crystallinity, and a decreased HOMO–LUMO gap. The dithiolodithiole (C_4S_4) motif is readily synthetically accessible using catalytic processes, and both the molecular and bulk properties of materials based on this building block can be tuned by judicious choice of substituents.*

The importance of conjugated organic materials can hardly be overstated. They have proved invaluable to established applications such as dyes,[1] sensors,[2] and imaging[3] as well as emerging technologies including flexible light emitting diodes,[4] field-effect transistors,[5] and photovoltaics.[6] The development of new materials with desirable properties has largely relied upon assembling π-conjugated molecules and polymers from a limited number of building blocks.[7] We describe herein the use of the dithiolodithiole heterocycle as a conjugated building block for organic materials. The resulting materials exhibit complimentary properties to widely used thiophene analogues such as stronger donor characteristics, high crystallinity, and a decreased HOMO–LUMO gap.

As part of an ongoing research program dedicated to the development of novel conjugated materials[8] we seek new building blocks for conjugated materials which might serve to not only widen the scope of available building blocks, but also to introduce attractive properties to the resulting material. A rudimentary analysis of some commonly employed conjugated units is shown in Figure 1. Phenylene and thiophene units are aromatic in the ground state and upon absorption of a photon populate a formally non-aromatic quinoidal excited state. Thiophenes have a lower aromatic stabilization energy which contributes to lower HOMO–LUMO gaps in the resulting analogous materials, which is demonstrated by the difference in λ_{max} between *p*-terphenyl (274 nm) and 2,5-diphenylthiophene (326 nm). Substitution with 2-benzothiophene leads due a further reduction in HOMO–LUMO gap (369 nm), which can be attributed to the benzo-substitution leading to partial retention of aromatic character in the excited state. Additionally, (benzo)thiophenes can exhibit S–S contacts in the solid state, which can be crucial for favorable change transport characteristics.[9]

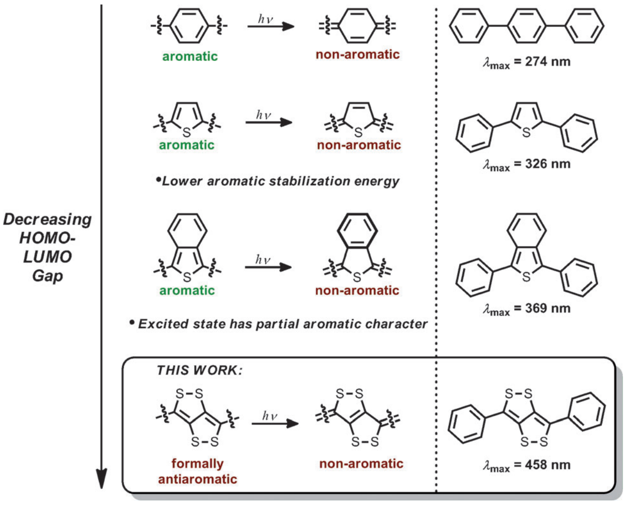

Figure 1. Comparison of various conjugated building blocks.

We were inspired by the successful implementation (benzo)thiophene-based materials for a variety of applications,[10] which are ascribable to the range of desirable properties they exhibit. Given that these properties can be attributed to the presence of a sulfur atom and/or fused ring system, we hypothesized that a heterocycle that contains multiple sulfur atoms in a fused ring systems may lead to a material with enhanced properties. A survey of possible atomic arrangements revealed that the dithiolodithiole (C_4S_4) heterocycle could be a viable candidate. Examination of the C_4S_4 unit reveals a 12e$^-$ (formally anti-aromatic by Hückel's rule) π system in the ground state and a non-aromatic π system in the quinoidal excited state, leading to potentially interesting optical and electronic properties. Illustratively, the absorption maximum of 3,6-diphenyldithiolodithiole (458 nm) is at significantly longer wavelength than the analogous (benzo)thiophene materials.

Despite the potential advantages of the C_4S_4 system, reports of examples are scant.[11] To study C_4S_4 derivatives in more detail, synthetic accessibility is required. A suitable approach was demonstrated by Blum and co-workers who reported the synthesis of a single example of a C_4S_4 derivative in 26% yield from 1,4-diphenylbutadiyne and elemental

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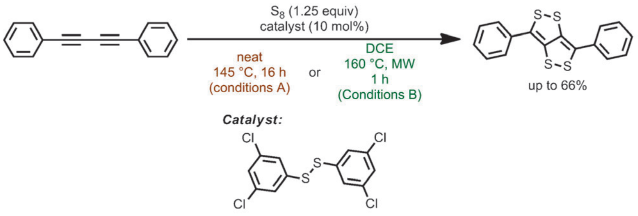
sulfur at 150 °C for 52 h.[11] Although butadiynes and elemental sulfur are convenient starting materials, a reduction of reaction times and increase in yields would be beneficial. Upon screening various reaction conditions, we identified two sets of conditions, using either thermal (conditions A) or microwave heating (conditions B), which improved both the reaction time and product yield (Scheme 1). In most cases, addition of a disulfide catalyst proved beneficial for achieving shorter reaction times and/or lower reaction temperatures.



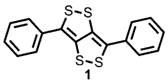
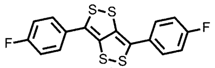
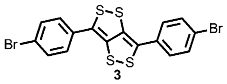
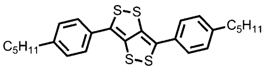
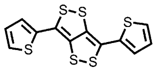
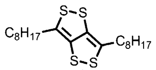
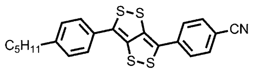
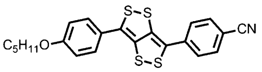
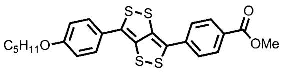
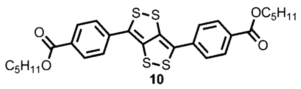
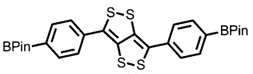
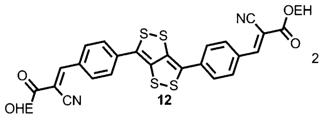
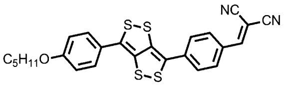
Scheme 1. Reaction conditions.

The reaction likely proceeds through sulfur-centered radicals with the disulfide catalyst acting as a radical mediator.[12]

The synthesis of a variety of different C_4S_4 derivatives was carried out using the newly developed conditions. The reaction is tolerant of a variety of functional groups, including halogens, alkyl, ester, cyano, and boronic esters.[13] The reaction yields are adequate (11–66 %) to obtain material to study the photophysical and electrochemical properties, which are shown in Table 1.[14] Substrates containing only strong electron-donating group lead to a complex mixture of products of which some have been completely characterized.[13] The C_4S_4 derivatives generally display a relatively broad absorption band with absorption maxima (λ_{max}) ranging from 449 nm to 649 nm with molar extinction coefficients (ε) ranging from 5700–26 300 $L\,mol^{-1}\,cm^{-1}$. Compounds with electron withdrawing groups generally exhibit a bathochromic shift as well as an increase in ε values, which is most likely due to the increased donor–π-acceptor nature of the chromophore. The ability of the C_4S_4 to act as a strong electron-donating group was also confirmed by the relatively low oxidation potential this family of compounds exhibits. Cyclic voltammetry of this series of compounds reveals two reversible oxidations with $E_{1/2}$ values ranging from 0.01 V to 0.21 V for the first oxidation and 0.62 V to 0.78 V for the second oxidation relative to a Fc/Fc^+ reference. The UV/Vis and CV data was used to estimate E_g and HOMO/LUMO values, which are also summarized in Table 1.

Materials that undergo significant redox induced changes in their absorption properties have demonstrated utility in electrochromic devices,[15] and electrochemical oxidation of C_4S_4 derivatives were studied using spectroelectrochemistry. An illustrative example using **7** is depicted in Figure 2. As shown, the radical cation produces the longest wavelength absorptions, whereas further oxidation to the closed shell dication produces a shift to a larger bandgap. Apart from the drastic change in UV/Vis absorption properties upon oxidation, further evidence for oxidation of the π-system as opposed to oxidation of sulfur atoms is provided by the fact that **6** does not undergo oxidation within the solvent window.

Table 1: Dithiolodithiole scope and photo/electrochemical properties.

Product	Yield[a]	λ_{max} (nm)[b]	ε ($M^{-1}cm^{-1}$)	$E_{1/2}$ vs. Fc/Fc^+ (V)[c]	E_g (eV)[d]	HOMO/LUMO (eV)[e]
 **1**	66%	458	8580	0.06, 0.67	2.38	-4.86/-2.48
 **2**	54%	449	5750	0.09, 0.68	2.41	-4.88/-2.48
 **3**	17%	463	5810	0.13, 0.71	2.32	-4.95/-2.63
 **4**	58%	455	6920	0.01, 0.62	2.40	-4.80/-2.40
 **5**	21%	370	12600	0.75	2.88	-5.59/-2.71
 **6**	16%	238	11100	--	3.40	--
 **7**	24%	517	26300	0.13, 0.71	2.14	-4.93/-2.79
 **8**	23%	518	18000	0.10, 0.65	2.15	-4.90/-2.75
 **9**	31%	507	13300	0.06, 0.63	2.19	-4.88/-2.69
 **10**	21%	520	21000	0.16, 0.74	2.13	-4.96/-2.83
 **11**	11%	503	9870	0.09, 0.69	2.24	-4.89/-2.65
 **12**	21%	630	24800	0.21, 0.76	1.73	-5.01/-3.28
 **13**	27%	649	14000	0.10, 0.63	1.65	-4.90/-3.25

[a] Yield of isolated product. [b] Measured in CH_2Cl_2. [c] CV measured in CH_2Cl_2 with 0.1 M nBu$_4$NPF$_6$ as supporting electrolyte using a Pt button working electrode, Pt counter electrode with Fc/Fc^+ reference. [d] Estimated from the absorption onset: $E_g = 1240/\lambda$. [e] Calculated from the first oxidation $E_{1/2}$: HOMO $= -(E_{1/2}^{ox} + 4.80)$; LUMO $=$ HOMO $- E_g$. EH = 2-ethylhexyl, Pin = pinacolato.

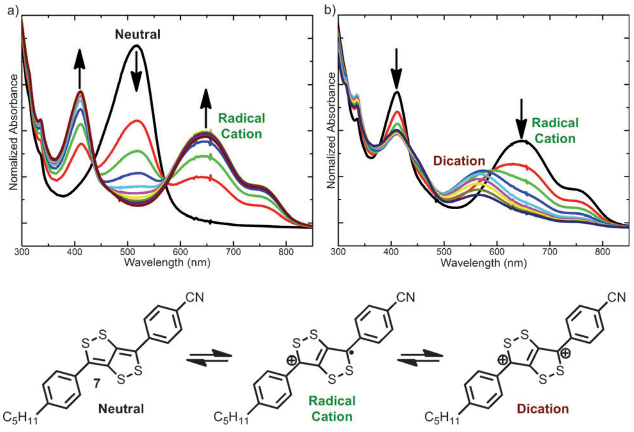


Figure 2. Spectroelectrochemistry of a solution of **7** in 0.1 м TBAPF$_6$ dichloromethane solution. Time between each absorption measurement is 15 s. a) At 450 mV. b) At 900 mV.

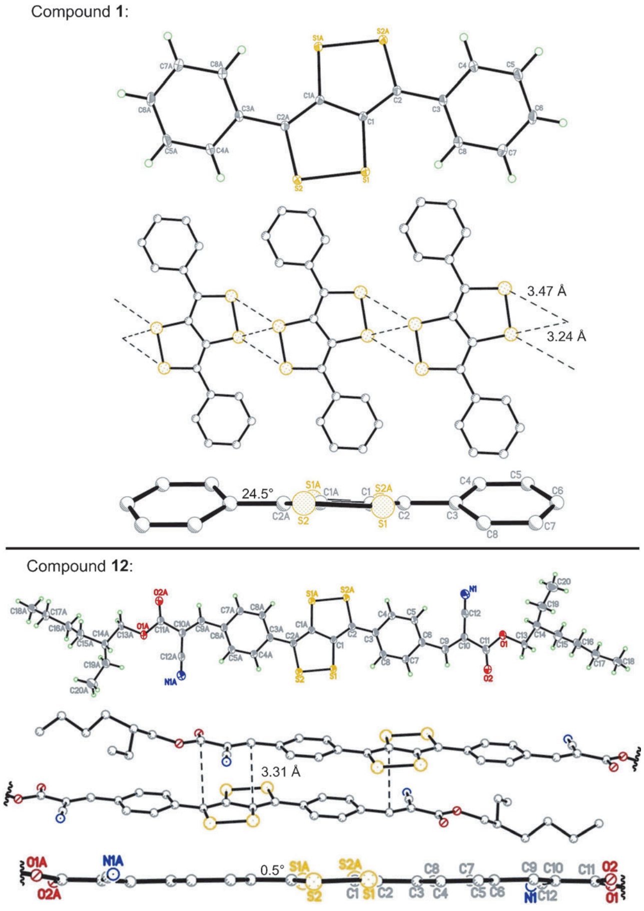


Figure 3. X-ray crystal structure of **1** and **12**. Ellipsoids are set at 50% probability. Characteristics of molecular packing for **1** and **12** are also depicted with hydrogen atoms and some alkyl groups omitted for clarity.[18]

Compound **6** would be expected to have similar $E_{1/2}$ values as other C$_4$S$_4$ compounds if oxidation occurred at the sulfur atom but very different $E_{1/2}$ values if oxidation occurs at the π-system given the disparate nature of the conjugated systems.

The X-ray crystal structures of compounds **1** and **12** are shown in Figure 3 along with some elements of their packing characteristics. The morphology of organic materials in the solid state is an important parameter that strongly affects performance in a variety of potential applications.[16] Thiophenes have been shown to exhibit favorable charge transport properties, due in part to their ability of form S–S contacts.[9,17] The presence of multiple sulfur atoms in the C$_4$S$_4$ heterocycle will likely lead to a higher degree of S–S contacts in the solid state and perhaps to favorable charge transport properties. Indeed, X-ray crystallography of **1** reveals multiple possible S–S contacts for the sulfur atoms of the C$_4$S$_4$ heterocycle. "Internal" sulfurs exhibit two S–S contacts, whereas the "external" sulfurs exhibit one S–S contact. Overall, this leads to six S–S contacts for a single molecule which compares favorably to analogous thiophene compounds.[9,17] Additionally, the presence of a large number of S–S contacts imparts highly crystalline character, thus not only aiding the ability to obtain suitable single crystals for X-ray analysis but perhaps leading to favorable properties attributed to crystalline organic materials. Moreover, the crystal structure of **1** reveals there is a significant dihedral angle of 24.54(4)° between the planes defined by the central C$_4$S$_4$ heterocycle and the pendant phenyl rings, presumably limiting the effective conjugation length of the molecule. However, other C$_4$S$_4$ derivatives can exhibit very different molecular packing depending on the nature of the substituents employed. For example, the molecular packing of **12**, which contains strong electron-withdrawing groups (2-cyanoacrylate), is dominated by intermolecular charge transfer interactions between electron-rich C$_4$S$_4$ heterocycle and electron poor 2-cyanoacrylate groups while not exhibiting any close S–S contacts. The intermolecular distance for **12** of 3.312 Å indicates the close proximity of the conjugated systems within the crystal packing which should be favorable for charge transport properties. Furthermore, the dihedral angle between the C$_4$S$_4$ heterocycle and the phenyl rings of **12** is 0.49(8)° which indicates a higher degree of π-orbital overlap and increased effective conjugation length than that of **1**, which is due to enhanced electronic communication between the electron-rich C$_4$S$_4$ heterocycle and electron-poor 2-cyanoacrylate group. These altering characteristics demonstrate the tunability of properties for this series of compounds by varying substituents.

Given that many high performance organic electronic materials include thiophene moieties, a direct comparison of a thiophene- with C$_4$S$_4$-based material would be germane. Figure 4 outlines a comparison of C$_4$S$_4$-based **7**, **9**, and **10** with thiophene-based **14**, **15**, and **16**, respectively. The compounds compared have the same substitution pattern and functional groups, the only difference being the central heterocycle. Additionally, both chromophores have equal π-conjugation lengths with both C$_4$S$_4$ and thiophene being a four carbon π-conjugated unit. However, the disparity of the resulting properties is striking. UV/Vis spectroscopy reveals that compounds **7**, **9**, and **10** exhibit much broader absorption than **14**, **15**, and **16**. Moreover, the absorption maximum and onset of absorption is, on average, red-shifted by 160 nm and 175 nm, respectively, when moving from thiophene to anal-

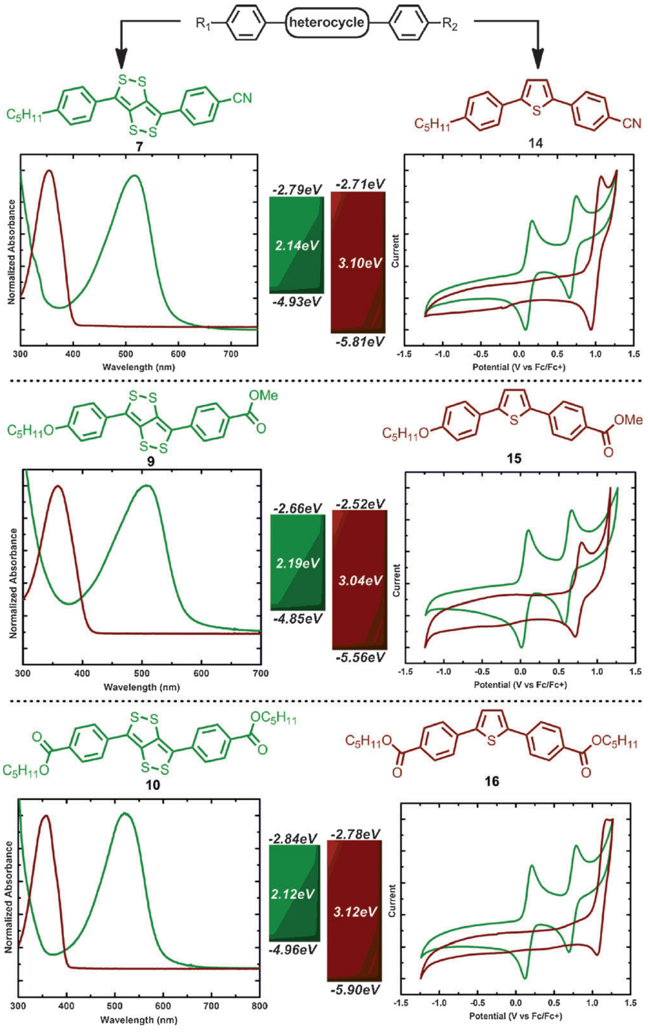


Figure 4. Comparison of dithiolodithiole to thiophene derivatives.

ogous C_4S_4-based materials. Cyclic voltammetry (CV) demonstrates that C_4S_4 donates electrons much more readily than thiophene since **14**, **15**, and **16** have an average 0.84 V higher $E_{1/2}$ value for the first oxidation event. Moreover, C_4S_4 derivatives will lose a second electron to form a dication at a lower oxidation potential than it takes analogous thiophene derivatives to lose the first electron. UV/Vis and CV data were also used to estimate the energy-level diagram for comparison between C_4S_4 and thiophene compounds. C_4S_4 derivatives have significantly smaller HOMO–LUMO gaps, ranging from than 0.85 eV difference between **9** and **15** to 1.00 eV difference between **10** and **16**. This difference is due mainly to a much higher lying HOMO level, but also in part a slightly lower lying LUMO level.

In conclusion, we have demonstrated the use of the dithiolodithiole heterocycle as a new building block for organic electronic materials. The dithiolodithiole motif is readily synthetically accessible using catalytic processes. Materials containing dithiolodithioles tend to be highly crystalline owing to multiple close S–S contacts or charge-transfer interactions in the solid state, and they exhibit complimentary optical and electronic properties compared to the analogous and widely used thiophene derivatives. The varying properties of C_4S_4 derivatives should lead to ability to fine-tune both the molecular and bulk properties of materials based on this building block by judicious choice of substituents. This work should contribute meaningfully to the repertoire of available building blocks for conjugated organic materials and lead to the discovery of new materials with exciting properties.

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Keywords: conjugated materials · heterocycles · sulfur · synthetic methods · thiophenes

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[12] TEMPO also served as a suitable radical mediator catalyst.

[13] See the Supporting Information for details.

[14] Raw UV/Vis and CV data can be found in the Supporting Information.

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[18] CCDC 996630 (**1**), 996631 (**2**), 996632 (**17**), and 996633 (1**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.