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Bonding and Electronic Properties of Linear Diethynyl Oligothienoacene-Bridged Diruthenium Complexes and Their Oxidized Forms

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Abstract

A series of five diruthenium diethynyl complexes based on α,β -fused oligothienoacenes in the core of the bridging ligands (BL), $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{C-L-C}\equiv\text{C})]$ (dppe = 1,2-bis(diphenylphosphino)ethane, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), L = thieno[3,2-*b*]thiophene (**4**), thieno[2,3-*b*]thiophene (**5**), 3,4-dimethylthieno[2,3-*b*]thiophene (**6**) dithieno[3,2-*b*:2',3'-*d*]thiophene (**7**) and thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8**), have been synthesized and fully characterized electrochemically and spectroscopically. Elongation of the redox non-innocent oligothienoacene bridge core causes a smaller potential difference

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3 between the initial two anodic steps, not seen for free dialkyl oligothienoacenes, and
4 increased positive charge delocalization over the conjugated bridge backbone. The
5 HOMO of the parent complexes resides predominantly on the oligothienoacene core,
6 with strong participation of the ethynyl linkers and slightly smaller contribution from
7 the metallic termini. This bonding character makes the initial one-electron oxidation
8 symmetrical, as revealed by combined voltammetric and spectroscopic (IR,
9 UV-vis-NIR and EPR) methods as well as DFT and TD-DFT calculations of truncated
10 and selected non-truncated models of the studied series. The remarkable gradual
11 appearance of two C≡C stretching absorptions in the IR spectra of the monocationic
12 diethynyl complexes is ascribed to increasing vibronic coupling of the IR-forbidden
13 $\nu_s(\text{C}\equiv\text{C})$ mode of the oxidized $-\text{[C}\equiv\text{C-core-C}\equiv\text{C}]^+-$ bridge with a low-lying
14 $\pi-\pi^*(\text{intra-bridge})$ / MLCT electronic transition in the NIR-mid-IR spectral region.
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28 Introduction

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30 Numerous redox-active di- and oligonuclear transition metal complexes exhibit a
31 wide range of important electronic, magnetic and optical properties^[1] that can be
32 varied reversibly along readily accessible multiple redox states. Certain physical
33 properties of bimetallic complexes, such as luminescence and non-linear optical
34 (NLO) activity, may display larger variability compared to the monometallic
35 congeners.^[2] Specifically in molecular electronics, carefully designed symmetric
36 bimetallic complexes with conjugated bridging ligands and two or more redox centers
37 featuring a variable degree of electronic communication are of central importance to
38 study the mixed-valence (MV) electronic coupling^[3] and develop a variety of
39 functional materials. The ability of the molecular bridge to mediate electronic
40 communication has been investigated by a wide range of methods including
41 voltammetric techniques and spectroelectrochemistry (UV-vis-NIR-IR, Raman, EPR,
42 etc.) and theoretical calculations.^[4-11]
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55 Diruthenium complexes based on a few classical types of redox-active metallic
56 termini supported by ancillary ligands are often explored to test diverse types of
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3 carbometalated bridging ligands in symmetric MV systems.^[12] The electronic
4 coupling between the metal centers strongly depends on the key properties of the
5 bridging ligand, such the degree of conjugation, coplanarity and length. In the earlier
6 literature, researchers have mainly focused on bridging conjugated polyaromatic
7 hydrocarbons (PAHs),^[13] such as oligophenylene.^[14] Thiophene-based heteroacenes
8 have emerged as excellent building blocks in the synthesis of a variety of
9 opto-electronic materials. These organic semiconductor materials exhibit considerable
10 potential for application as photoswitches^[15], DSSC^[16] and OFETs,^[17] owing to their
11 good conjugation. In the field of organometallic chemistry, α,β -fused
12 oligothiencene moieties have been applied as organic bridging units and introduced
13 to gold- and platinum-containing ethynyl complexes; their physical and luminescent
14 properties were investigated^[18]. Recently, Lapinte and co-workers^[19] have described
15 magnetic communication between two [Fe(dppe)Cp*] units mediated by the
16 2,5-diethynylthiophene spacer. Chen and co-workers^[20] have also reported
17 thiophene-based bimetallic ruthenium complexes and studied their electron-transfer
18 properties. Subsequently, Liu and co-workers investigated the electronic coupling
19 properties of oligothiophene-bridged binuclear ruthenium complexes (Chart 1) and
20 their charge transfer ability^[11a]. Recent studies^[21] document that the charge transport
21 ability across a molecular wire reduces and even drops exponentially with increasing
22 their length. In overall consideration,^[22] the fused molecular framework of
23 thienoacenes represents one of the most attractive candidates for low-resistance
24 molecular-scale wires featuring favorable electrical conductance characteristics.

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26 Systematic investigation of thiophene-based heteroacenes with higher
27 conjugation may reveal excellent charge transfer properties. With this in mind, we
28 have synthesized and characterized a series of diethynyl oligothiencenes as bridging
29 ligands carbometalated to Ru(dppe)Cp* terminal groups, viz. complexes **4-8** (Chart 1)
30 based on thieno[3,2-*b*]thiophene (**4**), thieno[2,3-*b*]thiophene (**5**),
31 3,4-dimethylthieno[2,3-*b*]thiophene (**6**) dithieno[3,2-*b*:2',3'-*d*]thiophene (**7**) and
32 thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8**) in the bridge core. We aimed
33 (i) to probe with spectro-electrochemistry and quantum chemical calculations how the
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elongation of the oligothiophene bridge core in complexes **1**, **4**, **7** and **8** affects their redox and electronic coupling properties, (ii) to evaluate the effect of the positional isomerism and methyl substitution of the dithienoacene bridge core in complexes **4-6** on their electronic properties, and (iii) to compare the new experimental results with those previously reported^[11a] for closely related complexes **1-3** with oligothiophenes in the bridge core.

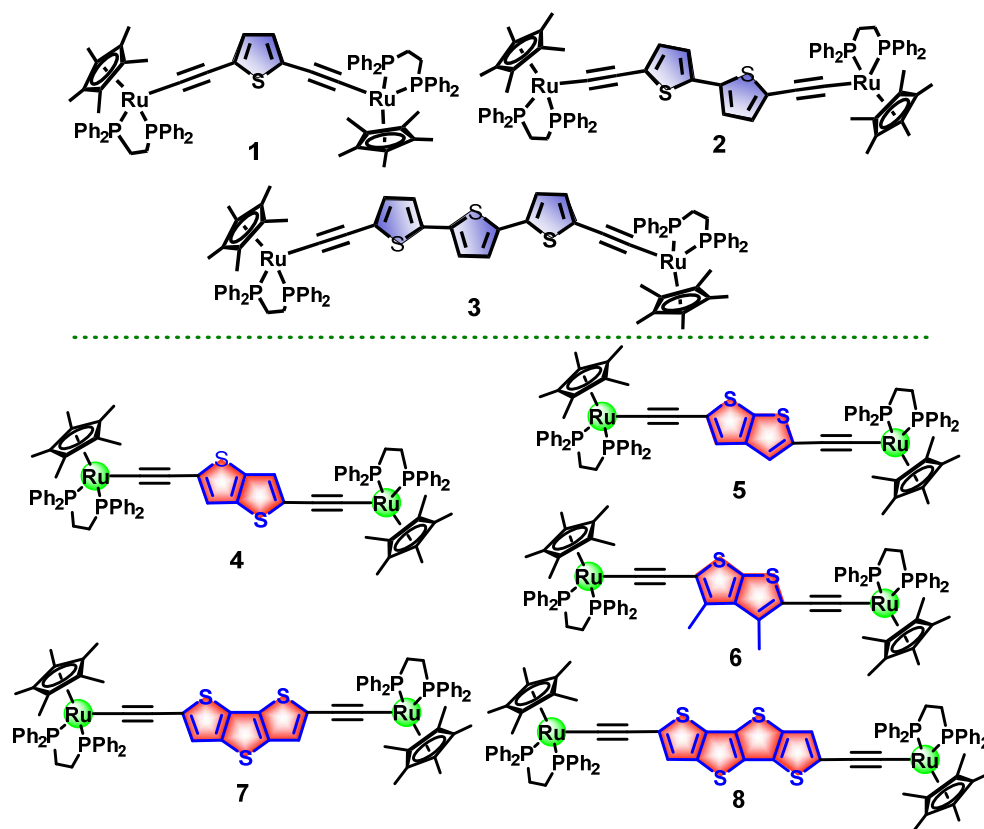


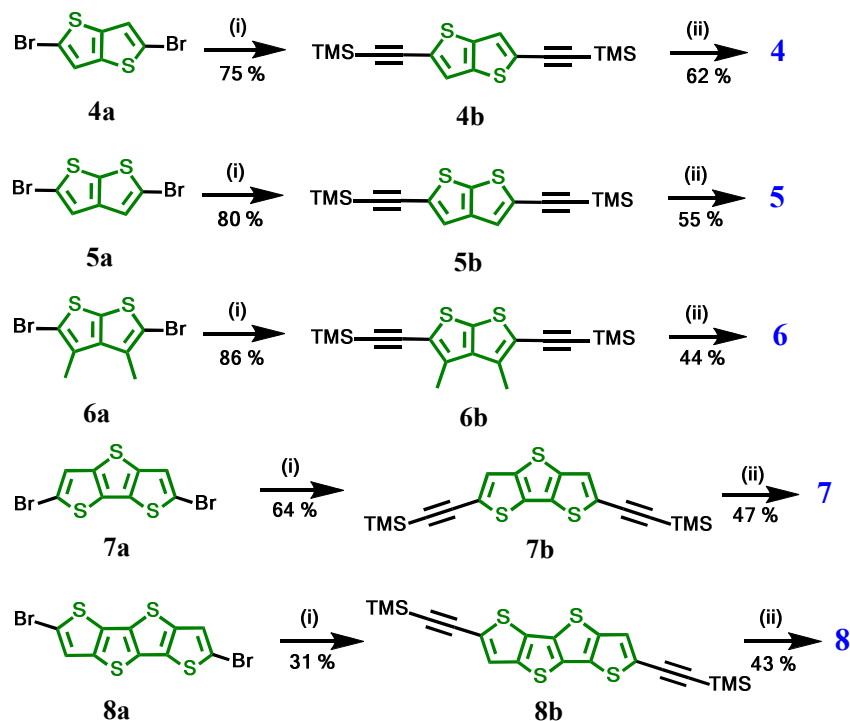
Chart 1. Previously published^[11a] diethynyl oligothiophene-bridged diruthenium complexes **1-3** and the target new series of diethynyl oligothienoacene-bridged diruthenium complexes **4-8**. Complex **1** links both groups. Diethynyl dithienoacene isomers **4-6** form a separate sub-group.

Results and Discussion

Syntheses and Characterization

The general synthetic route toward diethynyl oligothienoacene-bridged

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3 diruthenium complexes **4-8** is outlined in Scheme 1. Bridge-core precursors **4a**^[23],
4 **5a**^[23], **6a**^[24], **7a**^[17, 23b], **8a**^[25] were prepared by the literature methods. Intermediates
5 **4b-8b** were obtained in moderate to high yields by palladium(0)/copper(I)-catalysed
6 cross-coupling reactions^[26] of trimethylsilylthyne with
7 2,5-dibromothieno[3,2-*b*]thiophene (**4a**), 2,5-dibromothieno[2,3-*b*]thiophene (**5a**),
8 2,5-dibromo-3,4-dimethylthieno[2,3-*b*]thiophene (**6a**),
9 5,5'-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (**7a**) and
10 2,6-dibromo-thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8a**), respectively.
11 Low solubility of compound **8a** resulted in lower yields (31%) of complex **8b**. Finally,
12 compounds **4b-8b** were deprotected by the removal of the TMS group in a methanolic
13 KF solution, and reacted with [RuCl(dppe)Cp*] for 24 h at 60 °C. Target complexes
14 **4-8** were collected by filtration and characterized by conventional spectroscopic
15 methods. However, low solubility precluded the collection of sufficiently resolved ¹³C
16 NMR spectra of complexes **4** and **5**. The studied diruthenium complexes exhibit some
17 characteristic ¹H NMR signals. For example, complex **7** shows the proton chemical
18 shifts (in ppm) for C₅(CH₃)₅ at δ 1.55, CH₂/dppe at δ 2.06 and 2.68, and
19 heptathienoacene-*H* at δ 6.42. Tetrathienoacene-*H* and CH₂/dppe signals of complex **4**
20 coincide. Characteristic ¹³C NMR resonances of Ru-C≡C- in **6-8** are observed at δ
21 117. The ³¹P NMR spectra of complexes **4-8** display only one signal at δ 80.00,
22 reflecting the molecular symmetry. The ν_{as}(C≡C) wavenumber in the IR spectra of the
23 solid diethynyl complexes **1**, **4**, **7** and **8** (in the Nujol mull) gradually decreases from
24 2064 cm⁻¹ to 2041 cm⁻¹ as the conjugated bridge core elongates. This trend is in line
25 with the increasing electron-withdrawing power of the oligothienoacene bridge core,
26 reflected in the less negative oxidation potentials (see below).
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Scheme 1. Reaction paths to diethynyl oligothienoacene-bridged diruthenium complexes **4-8**, and corresponding reaction yields. Reagents and conditions: (i) TMSA, $[\text{Pd}(\text{PPh}_3)_4]$, CuI, THF/ $(i\text{-Pr})_2\text{NH}$; (ii) $[\text{RuCl}(\text{dppe})\text{Cp}^*]$, KF, $\text{CH}_3\text{OH}/\text{THF}$. TMSA = trimethylsilylacetylene, dppe = 1,2-bis(diphenylphosphino)ethane, Cp^* = pentamethylcyclopentadiene.

X-ray Structure Determination

Single crystals of complexes **7** and **8** suited for X-ray structural analyses were grown by layering the solution in dichloromethane with hexane. The molecular structures of **7** and **8**, including top and side views, are shown in Figure 1, respectively. Details of the data collection and refinement are presented in Table S1 (Supporting Information). Selected parameters (bond lengths (Å) and angles (deg)) from the crystal structures of parent **7** and **8** are collected in Tables 1 and S2 (Supporting Information). Both diruthenium complexes are symmetrical and exhibit a planar rigid structure over the entire bridge (Figure 1). As encountered in other $\text{Ru}(\text{dppe})\text{Cp}^*$ -based complexes^[13], the ethynyl linker and the Cp^* and dppe ligands at the Ru center form a pseudo-octahedral environment. The P(1)–Ru(1)–P(2) angles in complexes **7** and **8** reach 83.35° and 83.57°, respectively, falling within the range of

83-84° reported for a number of ruthenium phenylacetylide complexes.^[13b,27] The bonding parameters of the planar oligothienoacene core, viz. thieno[3,2-*b*:2',3'-*d*]thiophene in **7** and thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene in **8**, do not deviate significantly from those reported for free triisopropylsilyl octathienoacene.^[28] The Ru(1)–C(37)–C(38) angles in complexes **7** and **8** are 174.63° and 168.81°, respectively.

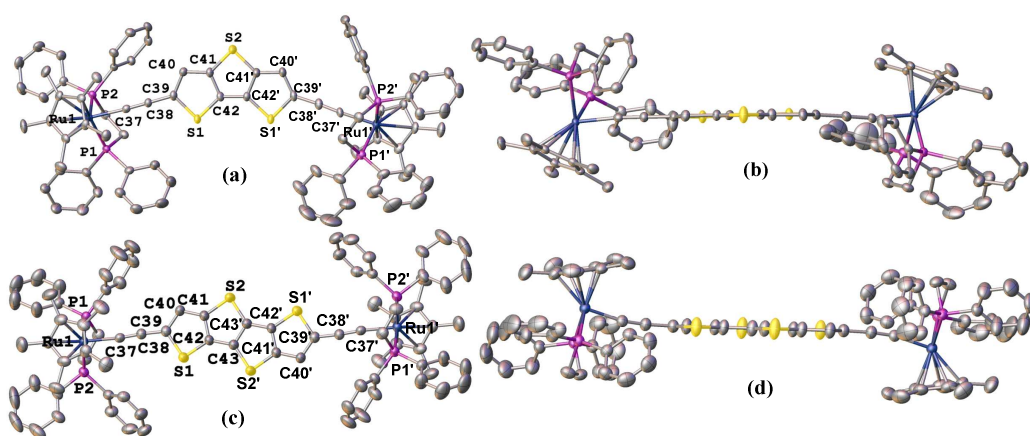


Figure 1. X-ray structures of complexes **7** (a, b) and **8** (c, d) with thermal ellipsoids at the 50% probability level: (a, c) top view, (b, d) side view. Hydrogen atoms and solvent molecules have been removed for clarity.

Table 1. Selected bond lengths (Å), angles (deg) and interatomic distance (Å) from the crystal structure of complex **7** and the DFT-optimized structures of models $[7-H]^{n+}$ ($n = 0, 1, 2$) and *trans-7*⁺.^a

| Parameter | 7 | <i>trans-7</i> ⁺ (BLYP35) ^b | [7-H] (B3LYP) | [7-H] ⁺ (B3LYP) | [7-H] ²⁺ (B3LYP) | |
|-----------|--------------------|--|------------------|-------------------------------|--------------------------------|--------------|
| Ru1–C37 | 1.986(3) | 1.913 | 1.910 | 2.011 | 1.966 | 1.921 |
| Ru1–P1,2 | 2.262(7), 2.276(7) | 2.281, 2.273 | 2.287, 2.277 | 2.280, 2.279 | 2.301, 2.301 | 2.323, 2.322 |
| C37–C38 | 1.219(4) | 1.206 | 1.205 | 1.230 | 1.242 | 1.256 |
| C38–C39 | 1.416(4) | 1.336 | 1.338 | 1.401 | 1.373 | 1.351 |
| C39–C40 | 1.372(4) | 1.363 | 1.363 | 1.385 | 1.410 | 1.437 |
| C40–C41 | 1.414(4) | 1.343 | 1.347 | 1.418 | 1.391 | 1.369 |
| C41–S2 | 1.745(3) | 1.697 | 1.697 | 1.757 | 1.756 | 1.757 |

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|-------------|----------|--------|--------|--------|--------|--------|
| C41–C42 | 1.382(4) | 1.373 | 1.373 | 1.402 | 1.428 | 1.453 |
| C42–C42' | 1.407(4) | 1.349 | 1.349 | 1.418 | 1.392 | 1.371 |
| S1–C42 | 1.722(3) | 1.679 | 1.680 | 1.736 | 1.736 | 1.739 |
| S1–C39 | 1.757(3) | 1.719 | 1.719 | 1.787 | 1.789 | 1.793 |
| P1–Ru1–P2 | 83.35(3) | 83.35 | 83.09 | 93.08 | 92.57 | 91.18 |
| Ru1–C37–C38 | 174.6(2) | 174.99 | 173.80 | 178.41 | 178.00 | 177.53 |
| C37–C38–C39 | 179.7(3) | 179.53 | 179.50 | 178.90 | 178.07 | 176.71 |
| Ru...Ru' | 15.2 | 14.9 | 14.9 | 15.4 | 15.3 | 15.2 |

^aThe values are identical for the molecule halves, with the exception of slightly asymmetric *trans-7*⁺. ^bThe values for *trans-7*⁺ in the right column correspond to the atom numbering with apostrophes in Figure 1(a).

Electrochemical Studies

Electronic properties of complexes **4-8** were first studied by electrochemistry revealing differences in their stepwise one-electron oxidation. The separation of two reversible redox waves ($\Delta E_{1/2}$) is known to be potentially influenced by several factors such as electrostatic interaction, solvation, ion pairing with the electrolyte and structural distortions caused by an electron transfer process^[29-32]. The anodic responses of the complexes were obtained in CH₂Cl₂/10⁻¹ M Bu₄NPF₆ with cyclic voltammetry (CV) and square-wave voltammetry (SWV); the corresponding data are listed in Table 2. The oxidation potentials of reference complexes **1-3** have been reported in the literature^[11a].

Cyclic and square-wave voltammograms (CVs and SWVs) of complexes **1** and **4-8** are depicted in Figures 2 and 3, and Figures S1-S4 (Supporting Information). All the complexes readily undergo two consecutive fully reversible one-electron oxidations. Figure 3a reveals that the $E_{1/2}(2)$ potential in the oligothienoacene series **1**, **4**, **7** and **8** changes only slightly with the increasing length of the bridge core, while the $E_{1/2}(1)$ values increase profoundly, from -0.387 V for **1** to -0.180 V for **8**. The potential difference $\Delta E_{1/2}$ decreases almost linearly from 320 mV to 135 mV with the number (1-4) of the α,β -fused thiophene rings (Figure 4) and the distance between the terminal ruthenium centers (Figure S5). The increasing delocalization of the unpaired electron/hole over the longer redox non-innocent diethynyl oligothienoacene bridge decreases the further input of energy required to place the other hole into the

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3 monocationic system. Notably, previously reported diethynyl oligothiophene-bridged
4 complexes **1-3**^[11a] exhibit more pronounced changes in $\Delta E_{1/2}$ because of the larger
5 amplitude of the chain length variation from single thiophene to bithiophene and
6 linear terthiophene. The comproportionation constants K_c for complexes **1**, **4**, **7** and **8**,
7 dwindle along the series from 2.25×10^5 to 191 (Table 2), marking the gradually
8 decreasing thermodynamic stability of the electrochemically generated open-shell
9 monocations.
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17 In contrast to the studied oligothienoacene series with the ruthenium ethynyl
18 termini, the oxidation potentials of free (alkyl)disubstituted oligothienoacenes,
19 $R-T_n-R$ ($n = 4-8$), strongly decrease with the chain length and the $\Delta E_{1/2}$ values do not
20 decline below 300 mV.^[33] This difference in the anodic behavior is one of the
21 characters reflecting the involvement of the conjugated (Ru-)ethynyl units in the
22 stepwise oxidation.
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29 The differences in the anodic potentials are marginal in the series of diethynyl
30 dithienoacene complexes **4**, **5** and **6** (Figure 3b and Table 2). The isomerization of the
31 bridge core from thieno[3,2-*b*]thiophene in **4** to thieno[2,3-*b*]thiophene in **5** (with the
32 sulfur atoms located on the same side of the unit) caused a slight positive shift of the
33 anodic potentials and a twice as large K_c value. Even higher stability was observed for
34 **6**⁺ with two methyl substituents attached to the thieno[2,3-*b*]thiophene isomer in the
35 bridge core. In contrast to the minor variability of the anodic voltammetric behavior,
36 the structural changes in the dithienoacene series have profound consequences for the
37 NIR-mid-IR electronic and IR vibrational absorption of **4**⁺-**6**⁺, as presented in the
38 following section.
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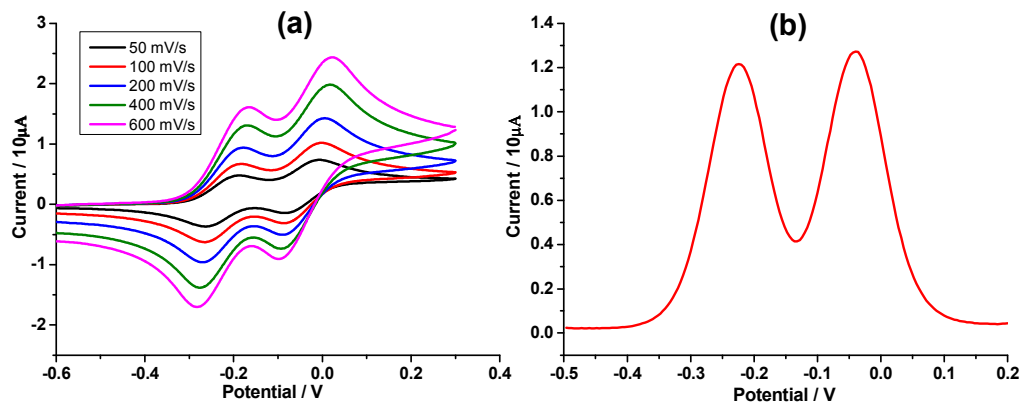


Figure 2. Anodic voltammetric responses of complex **7** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$. (a) Cyclic voltammograms (CVs) at a different scan rate (0.05, 0.1, 0.2, 0.4, 0.6 V s^{-1}); (b) the square-wave voltammogram (SWV) at $f = 10 \text{ Hz}$ ($t_p = 25 \text{ mV}$). The potential scale is referenced vs Fc/Fc^+ .

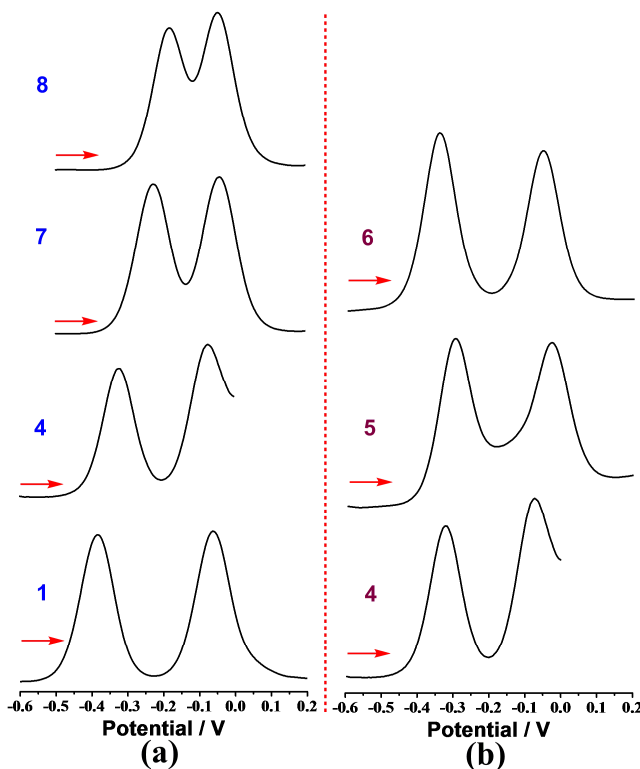


Figure 3. Anodic square-wave voltammograms (SWVs) of (a) the series of oligothiophene complexes **1**, **4**, **7**, **8**, and (b) the series of dithienoacene complexes **4**, **5**, **6** in $\text{CH}_2\text{Cl}_2/\text{Bu}_4\text{NPF}_6$, $f = 10 \text{ Hz}$ ($t_p = 25 \text{ mV}$). The potential scale is referenced vs Fc/Fc^+ .

Table 2. Electrochemical data determined for complexes **1-8**.^a

| Complex | $E_{1/2}(1)$ (V) | $E_{1/2}(2)$ (V) | $\Delta E_{1/2}$ (mV) ^b | K_c ^c |
|-------------------------|------------------|------------------|------------------------------------|--------------------|
| 1 ^c | -0.387 | -0.067 | 320 | 2.25×10^5 |
| 2 ^c | -0.224 | -0.087 | 137 | 207 |
| 3 ^{c,d} | -0.052 | -0.132 | 80 | 22.5 |
| 4 | -0.320 | -0.072 | 248 | 1.56×10^4 |
| 5 | -0.296 | -0.026 | 270 | 3.66×10^4 |
| 6 | -0.343 | -0.055 | 288 | 7.61×10^4 |
| 7 | -0.224 | -0.040 | 184 | 1.29×10^3 |
| 8 | -0.180 | -0.045 | 135 | 191 |

^a Electrode potential values vs the Fc/Fc^+ standard redox couple recorded at 25 °C in dry dichloromethane containing 10^{-1} M Bu_4NPF_6 . Additional anodic waves observed at higher potentials, most likely due to the oligothiophene bridge core, were not examined further. ^b $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1)$. ^c Ref.^{11a}. The comproportionation constants, $K_c = \exp(\Delta E_{1/2}/25.69)$ at 298 K. ^d Calculated according to ref.^[34] for the experimental value $E_p = -0.092$ mV (unresolved maxima) and width of 154 mV (the differential-pulse method).

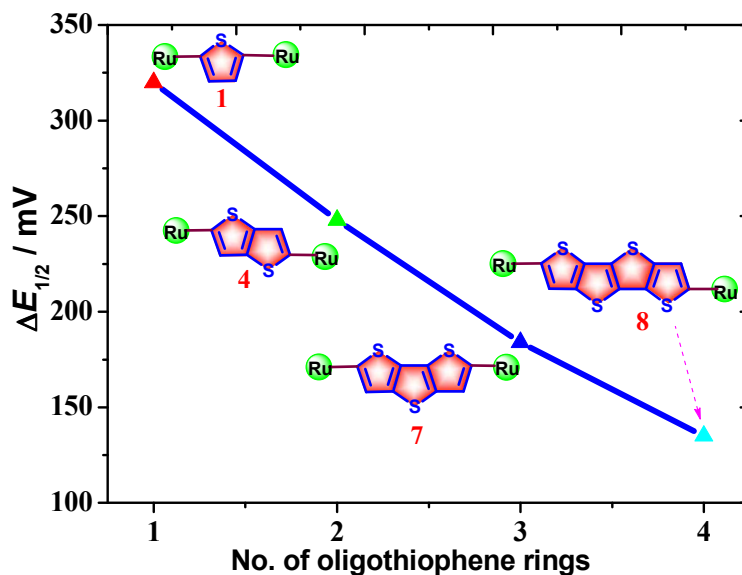


Figure 4. Plot of anodic potential difference $\Delta E_{1/2}$ for diruthenium complexes **1**, **4**, **7** and **8** versus the number of the α,β -fused thiophene rings in the bridge core.

Chemical Oxidation Monitored by IR and UV-vis-NIR Spectroscopy

The characteristic infrared C≡C stretching absorption can conveniently be used to monitor structural changes accompanying the strongly bridge-localized oxidation of the studied series of complexes (Chart 1). The CV and SWV studies have revealed that both the first and second oxidation potentials of complexes **1-8** are lower compared to $E_{1/2}$ of the ferrocene standard (Table 2). Ferrocenium hexafluorophosphate, FcPF₆, therefore served conveniently as a mild oxidizing agent to selectively generate the corresponding mono- and dications both in the oligothiophene-core series **1-3**^[11a] and the new oligothienoacene-core series **4-8**.

The $\nu_{\text{as}}(\text{C}\equiv\text{C})$ vibrational frequencies recorded for complexes **1**^{*n*+}-**8**^{*n*+} ($n = 0-2$) in dichloromethane are presented in Table 3. In the oligothienoacene-core series **1, 4, 7** and **8** (Figure 5), the experimental IR spectra in the $\nu(\text{C}\equiv\text{C})$ region exhibit a single band of low to medium intensities, with absorption maxima shifting gradually to a larger wavenumber for the shorter bridge core, viz. from 2043 cm⁻¹ (for **8**) to 2056 cm⁻¹ (for **1**). This trend, which is also seen^[11a] in the diethynyl oligothiophene-bridged series **1-3** (Table 3), indicates less π -conjugation between the ethynyl linker and the shorter bridge core. As a result, the HOMO energy rises in this direction and the oxidation potential becomes more negative (vide supra). In contrast, the corresponding dications do not display any obvious trend in the main ethynyl stretching wavenumber values, all lying close to 1910 cm⁻¹ (Table 3), in line with the conjugated symmetric {M=C=C}₂=C(core)²⁺ backbone. This observation complies with the stagnant electrode potentials for the mono-/dication redox couples (Table 2).

Most interesting observations in the infrared $\nu(\text{C}\equiv\text{C})$ region have been made for the singly-oxidized cationic species divided into the oligothiophene series **1, 4, 7** and **8**, and the dithienoacene series **4-6**. Except for **1**⁺ absorbing at 1961 cm⁻¹, the cations with the elongated oligothienoacene core feature two $\nu(\text{C}\equiv\text{C})$ absorption bands with increasing separation: **4**⁺ ($\Delta\tilde{\nu} = 26$ cm⁻¹), **7**⁺ ($\Delta\tilde{\nu} = 42$ cm⁻¹) and **8**⁺ ($\Delta\tilde{\nu} = 55$ cm⁻¹); the average wavenumber value however remains close to 1961 cm⁻¹ (Table 3). At the same time, the increased band separation is accompanied by rising intensity of the $\nu(\text{C}\equiv\text{C})$ band at the larger wavenumber. Notably, this trend reaches the maxima in the

dithienoacene series where 5^+ ($\Delta\tilde{\nu} = 69 \text{ cm}^{-1}$) and 6^+ ($\Delta\tilde{\nu} = 91 \text{ cm}^{-1}$) largely exceed the values obtained for 8^+ . In this case, the remarkable IR spectral changes in the $\nu(\text{C}\equiv\text{C})$ region cannot be explained the co-existence of different rotamers of the monocations, modelled by DFT calculations,^[35-37] as the one-electron oxidation largely resides on the oligothiophene bridge core (see below). Instead, it is important to consider the variable energy of lowest NIR-mid-IR $\pi\text{-}\pi^*$ (intra-bridge) electronic absorption accompanying the conversion of the neutral parent complexes to the monocations, as highlighted hereinafter.

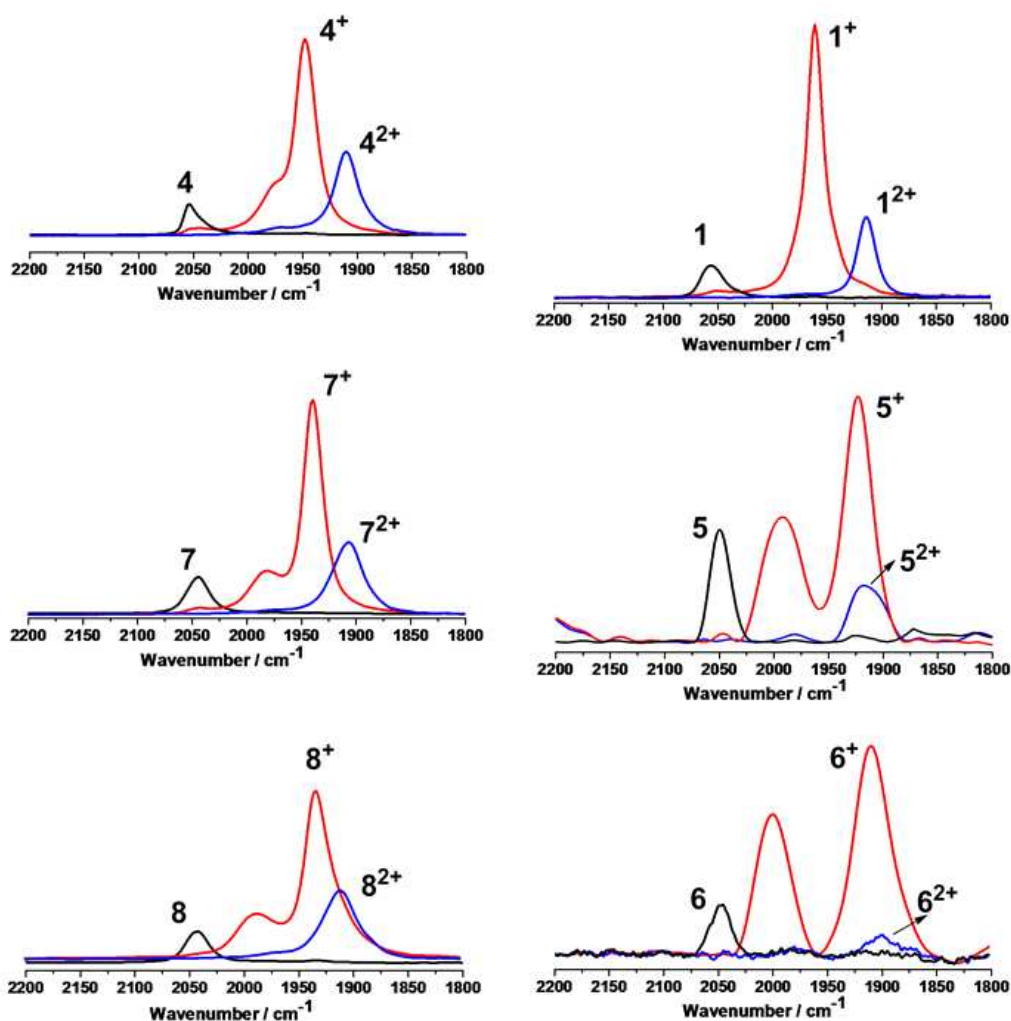


Figure 5. IR spectra in the $\nu(\text{C}\equiv\text{C})$ region of complexes **1** and **4-8** in dichloromethane and their corresponding mono- and dications formed by addition of equivalent amounts of FcPF_6 .

Table 3. IR $\nu(\text{C}\equiv\text{C})$ wavenumbers (cm^{-1}) [av. = the average value] recorded for complexes $[\mathbf{1-8}]^{n+}$ ($n = 0, 1, 2$) in dichloromethane.^{a,b}

| Complex | $n = 0$ | $n = 1$ | $n = 2$ |
|---------------------|----------|--------------------------------|--------------------|
| $\mathbf{1}^{n+ c}$ | 2056 (w) | 1961 (s) [av. 1961] | 1914 (m-w) |
| $\mathbf{2}^{n+ c}$ | 2055 (w) | 1982 (sh), 1933 (s) [av. 1958] | 1909 (m-w) |
| $\mathbf{3}^{n+ c}$ | 2046 (w) | 2007 (w), 1920 (m) [av. 1964] | 1971 (w), 1917 (w) |
| $\mathbf{4}^{n+}$ | 2052 (w) | 1974 (sh), 1948 (s) [av. 1961] | 1912 (m-w) |
| $\mathbf{5}^{n+}$ | 2050 (m) | 1992 (m), 1923 (s) [av. 1958] | 1916 (w) |
| $\mathbf{6}^{n+}$ | 2047 (w) | 2000(m-s), 1909 (s) [av. 1955] | 1900 (vw) |
| $\mathbf{7}^{n+}$ | 2045 (w) | 1981 (w), 1939 (s) [av. 1960] | 1907 (m-w) |
| $\mathbf{8}^{n+}$ | 2043 (w) | 1988 (w), 1933 (s) [av. 1961] | 1911 (m-w) |

^a Oxidation of the neutral parent complexes to corresponding mono- and dications was carried out by addition of exact equivalent amounts of ferrocenium hexafluorophosphate. ^b The low-intensity $\nu_s(\text{C}\equiv\text{C})$ mode was not detected in the experimental IR spectra of neutral parent complexes and corresponding dications. For $\mathbf{7}$ and $\mathbf{7}^+$, both $\nu_s(\text{C}\equiv\text{C})$ and $\nu_{as}(\text{C}\equiv\text{C})$ wavenumbers were obtained by harmonic frequency IR and Raman calculations, see the DFT section. ^c Ref.^[11a]

Changes in the electronic UV-vis-NIR-IR absorption recorded for complexes $\mathbf{1}$, $\mathbf{4-8}$ upon gradual addition of one and two equivalents of the ferrocenium hexafluorophosphate oxidant to their solutions in dichloromethane are depicted in Figure 6 and Figures S6-S8 (Supporting Information). The corresponding electronic absorption data for the neutral parent complexes and their mono- and dications are listed in Table 4. The UV-vis-NIR spectral responses to the two initial oxidation steps within the diruthenium diethynyl oligothienoacene series $\mathbf{1}$, $\mathbf{4-8}$ are very similar and will be demonstrated in detail for complex $\mathbf{7}$ with alternating trithienoacene in the bridge core (Figure 6). Neutral parent $\mathbf{7}$ exhibits an intense absorption at 445 nm that corresponds to the HOMO→LUMO (π - π^*) transition characteristic for free oligothienoacenes^[33], with participation of the π -system of the ethynylene linkers. The one-electron oxidation to $\mathbf{7}^+$ generates two intense subgap absorption bands at 683 nm and 1800 nm with a shoulder around 1375 nm. This new visible and asymmetric NIR absorption is typical for radical cations of free oligothienoacenes and can be ascribed to SOMO→LUMO and HOMO→SOMO (π - π^*) transitions, respectively.^[33] It is

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2
3 evident that the oxidation of **7** to **7⁺** is largely localized on the trithiophene bridge core.
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5 The participation of the (Ru–)ethynyl linkers, revealed by the IR spectral monitoring
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7 and anomalous voltammetric responses (see above), will be discussed in greater detail
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9 in the following TD-DFT section. Continued oxidation of **7⁺** to **7²⁺** led to the
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11 appearance of a new intense absorption band at 909 nm, which also complies with the
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13 dominantly terthiophene-localized anodic steps; in spectra of free oligothiophene
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15 dications this band is attributed to a HOMO→LUMO (π - π^*) transition^[33].

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17 All three members of the diethynyl tetrathienoacene redox series, **8ⁿ⁺** ($n = 0, 1, 2$),
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19 exhibit the intra-bridge electronic transitions red-shifted compared to **7ⁿ⁺**, while the
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21 opposite blue shift is encountered for the two shorter members **4ⁿ⁺** and **1ⁿ⁺** ($n = 0, 1, 2$).
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23 The descendent trends for the elongated oligothienoacene bridge core in each
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25 oxidation state are visualized in Figures 6a ($n = 0$), 6b ($n = 1$) and 6c ($n = 2$).

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27 Focusing on the remarkable spectral changes observed in the infrared $\nu(\text{C}\equiv\text{C})$
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29 region of the monocationic ($n = 1$) series (see Figure 5), the analysis of the
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31 corresponding NIR electronic absorption provides a strong support for vibronic
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33 coupling^{13b} of the $\nu(\text{C}\equiv\text{C})$ modes of the oxidized $-\text{[C}\equiv\text{C-core-C}\equiv\text{C}]^+$ bridge to the
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35 low-lying electronic transition. The stronger coupling, taking place on decreasing
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37 significantly the excitation energies, activates the $\nu_s(\text{C}\equiv\text{C})$ mode of the bridge in terms
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39 of both gained intensity and wavenumber difference from the asymmetric stretching
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41 mode. Thus, for singly oxidized **1⁺**, **4⁺**, **7⁺** and **8⁺**, the absorption maxima of the lowest
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43 NIR absorption bands shift from 7195 to 6370, 5555 and 4930 cm^{-1} , respectively,
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45 resulting in the pronounced activation of the symmetric stretching mode of the
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47 oxidized diethynyl oligothienoacene bridge in the same direction (Figure 5). A strong
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49 support for this explanation is obtained from monitoring the oxidation of the diethynyl
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51 dithienoacene series, **4-6**. Whereas the redox properties in this series are very similar
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53 (see Table 2), the energy of the lowest electronic transition further decreases from
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55 6370 cm^{-1} for **4⁺** to 4000 cm^{-1} for **5⁺** and even 3825 cm^{-1} for **6⁺** that is the minimum
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57 value in the studied diethynyl oligothienoacene series. Accordingly, the strongest
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59 effect on the $\nu(\text{C}\equiv\text{C})$ modes is observed for **6⁺** (Figure 5) showing the largest energy
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61 gap $\Delta\tilde{\nu} = 91 \text{ cm}^{-1}$ between the $\nu(\text{C}\equiv\text{C})$ absorption maxima, and comparable band

intensities. These characteristics nicely correspond with a very similar situation reported for another singly oxidized Ru diethynyl complex, viz. $[\{\text{Ru}(\text{dppe})\text{Cp}^*\}_2(\mu\text{-C}\equiv\text{C-L-C}\equiv\text{C})]^+$, L = benzo[1,2-*b*;4,3-*b'*]-dithiophene (bent).^[35] In the latter case, the lowest electronic absorption (featuring a mixed ML(bridge)-CT and $\pi\text{-}\pi^*$ (benzodithiophene) character) lies at 3200 cm^{-1} and the separation of the two $\nu(\text{C}\equiv\text{C})$ absorption maxima of comparable intensities reaches $\Delta\tilde{\nu} = 86 \text{ cm}^{-1}$. The substitution with L = benzo[1,2-*b*;4,5-*b'*]dithiophene (linear) caused a blue shift of the NIR absorption to 4540 cm^{-1} , accompanied by a significant decrease of the $\nu(\text{C}\equiv\text{C})$ separation to $\Delta\tilde{\nu} = 41 \text{ cm}^{-1}$ and reduced relative intensity of the symmetric stretching mode. The closely related diethynyl oligothiophene series^[11a] **1**⁺-**3**⁺ represents another example of the vibronic coupling affecting the $\nu_s(\text{C}\equiv\text{C})$ vibrations of the singly oxidized bridge.

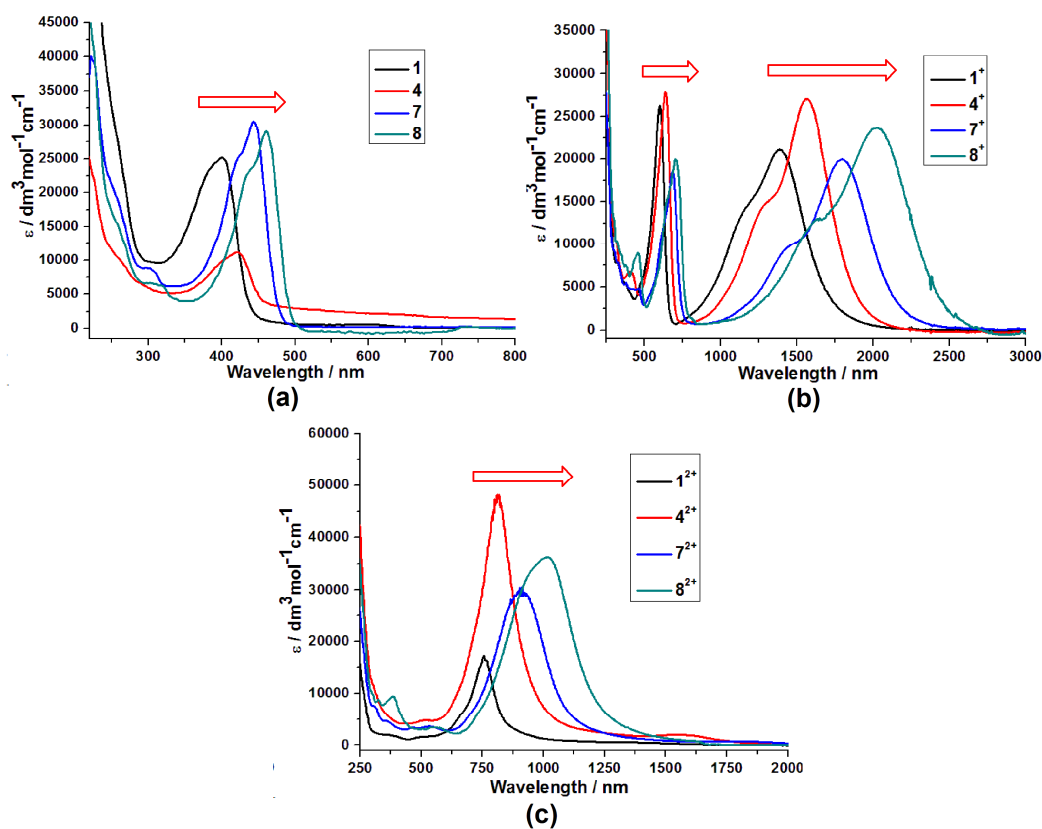


Figure 6. Red shift of the corresponding (generally intra-bridge) electronic transitions in the UV-vis-NIR absorption spectra recorded for the diruthenium diethynyl oligothiophenoacene redox

series $\mathbf{1}^{n+}$, $\mathbf{4}^{n+}$, $\mathbf{7}^{n+}$ and $\mathbf{8}^{n+}$ ($n = 0, 1, 2$), with the increasing length of the oligothienoacene bridge core. (a) $n = 0$; (b) $n = 1$; (c) $n = 2$. Conditions: CH_2Cl_2 , 298 K.

Table 4. Electronic absorption of complexes **1** and **4-8** in their mono- and dicationic forms in CH_2Cl_2 at 298 K.^a

| Complex | $\lambda_{\text{max}}(\text{nm}) (10^{-4} \epsilon_{\text{max}} (\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}))$ |
|-----------------------|--|
| 1 | 400 (2.51) |
| 1⁺ | 600 (2.63), 1390 (2.11) |
| 1²⁺ | 754 (1.73) |
| 4 | 421 (1.15) |
| 4⁺ | 639 (2.81), 1569 (2.75) |
| 4²⁺ | 812 (4.86) |
| 5 | 336 (2.06) |
| 5⁺ | 341 (1.56), 767 (0.52), 2500 (0.72) |
| 5²⁺ | 446 (1.37), 820 (0.93), 1237 (0.39) |
| 6 | 329 (2.25), 841 (0.14) |
| 6⁺ | 425 (1.11), 799 (0.88), 2614 (0.68) |
| 7 | 445 (3.12) |
| 7⁺ | 683 (1.89), 1800 (2.04) |
| 7²⁺ | 909 (3.05) |
| 8 | 461 (2.97) |
| 8⁺ | 707 (2.06), 2028 (2.42) |
| 8²⁺ | 1017 (3.67) |

^a Oxidized species $\mathbf{6}^{2+}$ was poorly soluble under the given experimental conditions.

DFT and TD-DFT Calculations

In order to assist the analysis of the molecular and electronic structures in the diethynyl oligothienoacene series $[\mathbf{1}]^{n+}$, $[\mathbf{4}]^{n+}$, $[\mathbf{7}]^{n+}$ and $[\mathbf{8}]^{n+}$ ($n = 0, 1, 2$), truncated model complexes $[\mathbf{1-H}]^{n+}$, $[\mathbf{4-H}]^{n+}$, $[\mathbf{7-H}]^{n+}$ and $[\mathbf{8-H}]^{n+}$ were selected for density functional theory (DFT) calculations at the B3LYP/6-31G* level. The extension “-H” indicates the replacement of the Cp* and dppe ligands in the parent complexes by Cp and two PH_3 ligands, respectively. Representative non-truncated model complex $\mathbf{7}^+$

has been selected for DFT calculations based on the global hybrid BLYP35 functional and the 6-31G* basis set, following examples in the literature^[13,35-38]. Key frontier orbitals of $[\mathbf{4-H}]^{n+}$ - $[\mathbf{8-H}]^{n+}$ ($n = 0, 1, 2$) with electron density distribution are shown in and Figures S9-S13 (Supporting Information). The lists of frontier molecular orbital energies and compositions resulting from Mulliken analysis are provided in Tables S3-S17 (Supporting Information).

DFT (G09-B3LYP)-optimized truncated model structures $[\mathbf{7-H}]^{n+}$ and $[\mathbf{8-H}]^{n+}$ ($n = 0, 1, 2$) reveal significant changes in the bond lengths accompanying the sequential one-electron oxidation of the conjugated bridging ligands (see below), i.e., gradual lengthening of the C≡C and C=C bonds and shortening of the C–C bonds (Chart 1). The bridge core in the dication obtains a markedly quinoid structure, much like the crystalline dication of free triisopropylsilyl octathienoacene^[28]; the Ru–C≡C–C(core) moiety converted to delocalized $\{\text{Ru}=\text{C}=\text{C}\}_2=\text{C}(\text{core})^{2+}$. More accurate bond lengths and angles in singly oxidized $\mathbf{7}^+$ have been obtained with the G09-BLYP35 DFT method (Table 1). The highest occupied molecular orbitals (HOMOs) of complexes $[\mathbf{4-H}]$ - $[\mathbf{8-H}]$ are indeed largely delocalized over the diethynyl oligothienoacene bridge, with contributions rising from 76% to 84% on elongating the bridge core; the metallic termini become less involved in the same direction.

The calculated spin-density distribution in monocations $[\mathbf{1-H}]^+$, $[\mathbf{4-H}]^+$, $[\mathbf{7-H}]^+$ and $[\mathbf{8-H}]^+$ reveals, in line with the parent HOMO characters, that the oxidation is increasingly localized on the elongated diethynyl oligothienoacene bridge, viz. from 72% in $[\mathbf{1-H}]^+$ to 80% in $[\mathbf{8-H}]^+$. However, the participation of the ethynyl linkers decreases along this series from 36% in $[\mathbf{1-H}]^+$ to 24% in $[\mathbf{8-H}]^+$, whereas the involvement of the oligothienoacene core rises from 36% in $[\mathbf{1-H}]^+$ to 56% in $[\mathbf{8-H}]^+$ (Figure 7). These changes have a strong implication for the $\nu(\text{C}\equiv\text{C})$ wavenumbers in the IR spectra (see below). For the dicationic species, $[\mathbf{1-H}]^{2+}$, $[\mathbf{4-H}]^{2+}$, $[\mathbf{7-H}]^{2+}$ and $[\mathbf{8-H}]^{2+}$, the HOMO and LUMO are also largely delocalized over ethynyl–core backbone with some participation of the Ru centers, having a very similar composition as the HOMO-1 and HOMO of the neutral parents (Figures S9-S13, Supporting Information). The LUMO+1 and LUMO are different, except those of

[8-H]²⁺ and [8-H], respectively.

The B3LYP DFT calculations yielded single IR $\nu(\text{C}\equiv\text{C})$ wavenumbers for both neutral [1-H], [4-H], [7-H] and [8-H] and the corresponding dications: [1-H]ⁿ⁺ – 2118 cm⁻¹ ($n = 0$) and 1980 cm⁻¹ ($n = 2$); [4-H]ⁿ⁺ – 2113 cm⁻¹ ($n = 0$) and 1981 cm⁻¹ ($n = 2$); [7-H]ⁿ⁺ – 2111 cm⁻¹ ($n = 0$) and 1982 cm⁻¹ ($n = 2$); [8-H]²⁺ – 2110 cm⁻¹ ($n = 0$) and 1986 cm⁻¹ ($n = 2$) (scaled by 0.9614, see the Computational Details). The large $\Delta\delta(\text{C}\equiv\text{C})$ values of 143, 137, 134 and 129 cm⁻¹ along the series, which are very close to the experimental values of 142, 140, 138 and 132 cm⁻¹, respectively (Table 3), reveal significant weakening of the C≡C bond upon the two-electron oxidation. The smaller $\Delta\delta(\text{C}\equiv\text{C})$ values reflect the declining involvement of the ethynyl linkers in the oxidation that becomes increasingly localized on the elongated, strongly conjugated oligothienoacene bridge core. The same descending trend applies for the corresponding cationic series [1-H]⁺, [4-H]⁺, [7-H]⁺ and [8-H]⁺. The calculated $\Delta\delta(\text{C}\equiv\text{C})$ values of 91, 87, 85 and 82 cm⁻¹, respectively, are consistent with the changing spin-density distribution in the model cationic complexes, as shown in Figure 7.

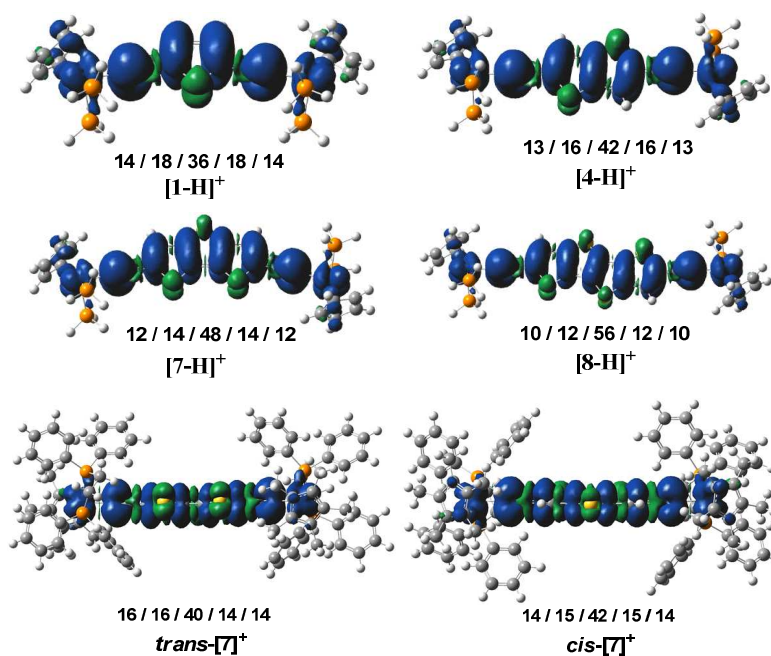


Figure 7. Spin-density distributions in oligothienoacene (T_n)-bridged diruthenium monocations [1-H]⁺, [4-H]⁺, [7-H]⁺, [8-H]⁺ and *trans*-7⁺ and *cis*-7⁺ (Ru/CH≡CH/ T_n /CH≡CH/Ru) with the

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2
3 corresponding compositions. Contour values: ± 0.0004 e/bohr³.
4

5 A number of earlier reported singly oxidized diruthenium diethynyl complexes
6 with a planar aromatic bridge core show multiple $\nu(\text{C}\equiv\text{C})$ absorption bands assigned
7 to different rotamers with a variable degree of a mixed-valence state.^[13,28] Within the
8 studied diethynyl oligothiencene series, three principal conformations, viz. *trans*-,
9 *cis*- and *perp*-, were modelled for representative non-truncated cation 7^+ , having
10 employed the expedient global hybrid functional BLYP35 introduced recently by
11 Kaupp, Low and co-workers.^[35-38] The basis set 6-31G* (Lanl2dz for the Ru atom)
12 was used in combination with the conductor polarizable continuum model (CPCM) in
13 CH_2Cl_2 . Notably, the DFT method has only afforded potential minima for slightly
14 asymmetrical *trans*- 7^+ (Table 1) and symmetrical *cis*- 7^+ conformations while several
15 optimization programs failed to obtain a stable perpendicular conformation, *perp*- 7^+ .
16 In this regard, 7^+ resembles the electronically closely related diethynyl
17 benzodithiophene-bridged diruthenium complexes.³⁶ The DFT results obtained for
18 non-truncated isomers *trans*- 7^+ and *cis*- 7^+ within the harmonic approach show strong
19 $\nu_{\text{as}}(\text{C}\equiv\text{C})$ absorption at 2231 cm^{-1} ; in addition, a very weak $\nu_{\text{s}}(\text{C}\equiv\text{C})$ band at 2239 cm^{-1}
20 was obtained for *trans*- 7^+ (scaled by 0.95, see the Computational Details). In addition,
21 the calculated Raman wavenumbers of the symmetric and asymmetric C≡C stretching
22 modes for *trans*- 7^+ are identical with the IR results; their absorption intensities are
23 inverted. For comparison, harmonic frequency IR and Raman calculations for parent
24 **7** also yielded $\nu_{\text{as}}(\text{C}\equiv\text{C})$ and $\nu_{\text{s}}(\text{C}\equiv\text{C})$ absorptions at 2294 cm^{-1} and 2298 cm^{-1} ,
25 respectively. The $\Delta\tilde{\nu}(\text{C}\equiv\text{C})$ value calculated for parent **7** and corresponding *trans*- 7^+ is
26 smaller than the experimental value of 106 cm^{-1} for $\nu_{\text{as}}(\text{C}\equiv\text{C})$, see Table 3. Both
27 *trans*- 7^+ and *cis*- 7^+ isomers show almost symmetric distribution of the spin density
28 over the bridge core and ethynyl linkers, viz. *trans*- 7^+ : 70%; *cis*- 7^+ : 72% (Figure 7),
29 thereby closely resembling truncated $[\mathbf{7-H}]^+$. This outcome supports the assumption
30 that the proximity of the electronic absorption in the NIR region is the main factor
31 responsible for the appearance of the two significantly separated IR-active $\nu(\text{C}\equiv\text{C})$
32 modes of 7^+ , as discussed in the preceding spectroscopic section. The origin of the
33 low-energy electronic absorption has been unraveled with TD-DFT (BLYP35)
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calculations carried out on the structurally fully optimized non-truncated models of 7^+ (Figure S14). The major electronic excitations in *trans*- 7^+ and *cis*- 7^+ are listed in Table 5. The corresponding isosurface plots of molecular orbitals involved in the major electronic excitations are displayed in Figure S15. Both cationic isomers of 7^+ exhibit an intense absorption band near 7000 cm^{-1} and two smaller bands between 17000 and 21000 cm^{-1} (*trans*- 7^+ : 7047 , 17605 , and 20790 cm^{-1} ; *cis*- 7^+ : 7077 , 17391 , and 20833 cm^{-1} , Table 5), thereby reproducing well the absorption maxima in the NIR and visible region of the experimental electronic absorption spectrum (Figure 6, Table 4). Thus, the strong NIR absorption corresponds to the β -HOSO \rightarrow β -LUSO excitation having a dominant π - π^* (diethynyl trithienoacene) character mixed with some ML(bridge)CT. The direct involvement of the ethynyl linkers in the low-energy electronic excitation is not surprising, having a big impact on their vibrational behavior (Figure S15). The visible region features an intense absorption band below 600 nm , largely due to α -HOSO \rightarrow α -LUSO displaying very similar π - π^* (intra-bridge)/MLCT characteristics (Figure S15). Finally, the fairly weak electronic absorption of the cationic complexes in the blue spectral region, 400 - 500 nm (Figure 6b), belongs mainly to L(Cp*, dppe)MCT, also directed to the β -LUSO.

Table 5. Major electronic excitations of *trans*- and *cis*- 7^+ determined by TD-DFT methods.

| Rotamer | λ/nm [cm^{-1}] | Oscillator strength (f) | Major contributions | Assignment |
|----------------------|---|--------------------------------|--|---|
| <i>trans</i> - 7^+ | 1419 [7047] | 1.1214 | β -HOSO \rightarrow β -LUSO (98%) | π - π^* (diethynyl trithienoacene) ML(bridge)CT |
| | 568 [17605] | 0.8393 | α -HOSO \rightarrow α -LUSO (76%) | π - π^* (diethynyl trithienoacene) ML(bridge)CT |
| | 481 [20790] | 0.1787 | β -HOSO-6 \rightarrow β -LUSO (88%) | L(Cp*, dppe)MCT |
| <i>cis</i> - 7^+ | 1413 [7077] | 1.1727 | β -HOSO \rightarrow β -LUSO (98%) | π - π^* (diethynyl trithienoacene) ML(bridge)CT |
| | 575 [17391] | 0.8892 | α -HOSO \rightarrow α -LUSO (83%) | π - π^* (diethynyl trithienoacene) ML(bridge)CT |

| | | | |
|----------------|--------|--|-----------------|
| 480 [20833] | 0.1975 | β -HOSO-6 \rightarrow β -LUSO (92%) | L(Cp*, dppe)MCT |
|----------------|--------|--|-----------------|

EPR studies

The contribution of the terminal metal centers and bridging ligands to the one-electron anodic processes was further explored by the EPR spectroscopy for monocations 1^+ , 4^+ , 7^+ and 8^+ in CH_2Cl_2 at 298 and 150 K. The EPR signals were recorded after having added 1 equiv. of the ferrocenium hexafluorophosphate oxidant (see Figures S16-S19 in Supporting Information). Detailed data are summarized in Table S18. The solutions of the monocations exhibit at 298 K isotropic singlets with no apparent hyperfine coupling to ^{31}P nuclei of the ancillary dppe ligands. All determined g_{iso} -values in Table S18 are close to 2.04. This value is close to the g -values for radical cations of free oligothiеноacenes^[33b,c] and free electron ($g_e = 2.0023$); the cationic complexes therefore exhibit certain organic radical characters.^[39] Importantly, at 150 K, the EPR spectra of the cations displayed broad signals showing only small g -tensor anisotropy. The EPR spectra are close to those reported for cationic oligothiophene complexes $1^+ \text{-} 3^+$.^[11a] The total g -tensor anisotropy (Δg) values for complexes 1^+ , 4^+ , 7^+ and 8^+ are 0.042, 0.040, 0.030 and 0.033, respectively, falling apparently out of the range of Δg values for paramagnetic organometallic complexes with ruthenium(III) centers (0.3~0.6)^[40-43]. The small g_{iso} and Δg values in this series of complexes therefore comply with the dominant participation of the diethynyl oligothiеноacene bridge in the one-electron oxidation, which is fully consistent with the results of the DFT calculations (vide supra).

Conclusions

In this work, we describe successful syntheses and full characterization of five redox-responsive diruthenium complexes, **4-8**, having thieno[3,2-*b*]thiophene (**4**), thieno[2,3-*b*]thiophene (**5**), 3,4-dimethylthieno[2,3-*b*]thiophene (**6**) dithieno[3,2-*b*:2',3'-*d*]thiophene (**7**) and

1
2
3 thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8**) in the core of the diethynyl
4 oligothienoacene bridge. Differently from free oligothienoacenes, the elongation of
5 the bridge core leads to positive potential shifts a reduced potential difference, $\Delta E_{1/2}$,
6 between the two anodic steps. This behavior reflects the involvement of ethynyl
7 linkers, and to a small extent even the ruthenium centers, in line with the presented
8 DFT calculations and EPR spectra. In the monocationic series, the spin density is
9 localized symmetrically on the bridge, with an increasing contribution of the
10 elongated oligothienoacene core. This trend for 4^+ , 7^+ and 8^+ cannot explain the
11 appearance of two IR $\nu(\text{C}\equiv\text{C})$ absorption bands with increasing wavenumber
12 difference along this series and varied intensity ratio. According to the frequency DFT
13 calculations, the IR spectrum of non-truncated model *trans*- 7^+ , electronically very
14 close to the *cis*-isomer but showing small asymmetry, exhibits one intense $\nu_{\text{as}}(\text{C}\equiv\text{C})$
15 band while the $\nu_{\text{s}}(\text{C}\equiv\text{C})$ absorption is vanishingly low. Other theoretical rotamers on
16 the potential energy landscape with asymmetric localization of the spin density along
17 the molecular backbone have not been obtained. This behavior can be explained by
18 considering a strong vibronic coupling of the $\nu_{\text{s}}(\text{C}\equiv\text{C})$ mode of the oxidized
19 $-\text{[C}\equiv\text{C}-\text{core}-\text{C}\equiv\text{C}]^{+-}$ bridge to a low-lying $\pi-\pi^*$ (intra-bridge) / MLCT electronic
20 transition observed in the NIR-IR spectral region. Indeed, the significant red shift of
21 the NIR-IR absorption maxima is accompanied by the conspicuous appearance of the
22 dual $\nu(\text{C}\equiv\text{C})$ absorption. A strong support for this plausible explanation comes from
23 the diethynyl dithienoacene series 4^+-6^+ showing otherwise very similar redox
24 properties. The likely general nature of this phenomenon is proposed, based on the
25 literature data for other dinuclear diethynyl complexes with a readily oxidized
26 conjugated bridge core. Our study provides further helpful information for potential
27 applications of redox-responsive conjugated oligothienoacene systems as components
28 of molecular electronic devices.
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Experimental section

General Materials. All manipulations were carried out at room temperature under a dry nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were pre-dried, distilled, and degassed prior to the use. The main reagents 3-bromothiophene, thieno[2,3-*b*]thiophene, acetylacetone, [Pd(PPh₃)₄] and TMSA were commercially available. The starting materials [RuCl(dppe)Cp*]^[44], 2,5-dibromothieno[3,2-*b*]thiophene (**4a**)^[23], 2,5-dibromothieno[2,3-*b*]thiophene (**5a**)^[23], 2,5-dibromo-3,4-dimethylthieno[2,3-*b*]thiophene (**6a**)^[24], 5,5'-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (**7a**)^[17,23b] and 2,6-dibromo-thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8a**)^[25] were prepared by the literature methods.

Syntheses of bis((trimethylsilyl)ethynyl)thienoacenes^[26]

2,5-Bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (**4b**).

Trimethylsilylacetylene (392 mg, 4.00 mmol) was added to a stirred solution of 2,5-dibromothieno[3,2-*b*]thiophene **4a** (300 mg, 1.0 mmol), CuI (19 mg, 0.10 mmol), and [Pd(PPh₃)₄] (116 mg, 0.10 mmol) in (*i*-Pr)₂NH (10 mL) and THF (10 mL) under an argon atmosphere; the mixture was heated at 60 °C for 24 h. The solution was then cooled down and filtered through a bed of Celite. The filtrate was evaporated under reduced pressure and purified by silica gel column chromatography (petroleum ether) to give of a light-yellow powder. Yield: 251 mg, 75%. ¹H NMR (400 MHz, CDCl₃): δ 0.26 (s, 18H, SiCH₃), 7.29 (s, 2H, thiophene-H), as reported in ref.^[45].

2,5-Bis(trimethylsilylethynyl)thieno[2,3-*b*]thiophene (**5b**). This compound was synthesized by the same method as **4b**, having used 2,5-dibromothieno[2,3-*b*]thiophene (**5a**) (600 mg, 2.00 mmol), CuI (38 mg, 0.20 mmol), and [Pd(PPh₃)₄] (524 mg, 0.46 mmol), (*i*-Pr)₂NH (30 mL), THF (30 mL), trimethylsilylacetylene (1772 mg, 18.08 mmol). Yield: 535 mg (80%) of a light-yellow powder. ¹H NMR (400 MHz, CDCl₃): δ 0.27 (s, 18H, SiCH₃), 7.16 (s, 2H, thiophene-H). EI-MS: *m/z* = 332.11 [M]⁺. Note: the compound was thermally unstable and hence used directly in the next reaction step after the characterization

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3 and purity check with NMR and MS.

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5 2,5-Bis(trimethylsilylethynyl)-3,4-dimethylthieno[2,3-*b*]thiophene (**6b**). This
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7 compound was synthesized by the same method as **4b**, having used
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9 2,5-dibromo-3,4-dimethylthieno[2,3-*b*]thiophene (**6a**) (100 mg, 0.31 mmol), CuI
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11 (5.85 mg, 0.20 mmol), [Pd(PPh₃)₄] (35.5 mg, 0.41 mmol), triethylamine (NEt₃) (5
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13 mL), THF (15 mL), trimethylsilylacetylene (196 mg, 2.00 mmol). Yield: 95 mg (86%)
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15 of a light-yellow powder. ¹H NMR (400 MHz, CDCl₃): δ 0.26 (s, 18H, SiCH₃), 2.51
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17 (s, 6H, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ 0.0 (SiMe₃), 14.3 (CH₃), 97.4, 102.2,
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19 121.2, 136.5, 137.2, 144.0. Anal. Calcd for C₁₈H₂₄S₂Si₂: C, 59.94; H, 6.71. Found: C,
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21 59.78; H, 6.65.

22 5,5'-Bis(trimethylsilylethynyl)dithieno[3,2-*b*:2',3'-*d*]thiophene (**7b**). This
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24 compound was synthesized by the same method as **4b**, having used
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26 5,5'-dibromodithieno[3,2-*b*:2',3'-*d*]thiophene (**7a**) (800 mg, 2.26 mmol), CuI (43 mg,
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28 0.23 mmol), [Pd(PPh₃)₄] (262 mg, 0.23 mmol), (*i*-Pr)₂NH (30 mL), THF (30 mL),
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30 trimethylsilylacetylene (886 mg, 9.04 mmol). Yield: 562 mg (64%) of a light-yellow
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32 powder. ¹H NMR (400 MHz, CDCl₃): δ 0.28 (s, 18H, SiCH₃), 7.40 (s, 2H,
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34 thiophene-H), as reported in ref.^[46].

35 2,6-Bis(trimethylsilylethynyl)thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene
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37 (**8b**). This compound was synthesized by the same method as **4b**.
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39 2,6-dibromo-thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8a**) (300 mg, 0.73
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41 mmol), CuI (14 mg, 0.073 mmol), and [Pd(PPh₃)₄] (85 mg, 0.073 mmol), (*i*-Pr)₂NH
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43 (30 mL), THF (30 mL), trimethylsilylacetylene (358 mg, 3.66 mmol). Yield: 100 mg
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45 (31%) of a yellow powder. ¹H NMR (400 MHz, CDCl₃): δ 0.28 (s, 18H, SiCH₃), 7.42
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47 (s, 2H, thiophene-H). Anal. Calcd for: C₂₀H₂₀S₄Si₂: C, 54.01; H, 4.53. Found: C,
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49 53.87; H, 4.61. Note: the compound has poor solubility in many deuterated solvents
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51 including CDCl₃, and the ¹³C NMR spectrum could not be collected.

52 53 54 **General Syntheses of Diruthenium Complexes**^[11]

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56 Preparation of **4**. A solution of [RuCl(dppe)Cp*] (381 mg, 0.57 mmol),
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58 2,5-bis(trimethylsilylethynyl)thieno[3,2-*b*]thiophene (**4b**) (90 mg, 0.27 mmol), and
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KF (188 mg, 3.24 mmol) in 20 mL CH₃OH and 5 mL THF was heated to reflux under nitrogen atmosphere for 24 h. The crude product was collected by filtration, washed with methanol and hexane. The solid was dissolved in dichloromethane, precipitated by slow diffusion of hexane, then filtered and dried to give **4** as a yellow powder. Yield: 250 mg, 60%. Note: the compound is poorly soluble in many deuterated solvents including CDCl₃, and its ¹³C NMR spectrum could not be collected. ¹H NMR (400 MHz, CDCl₃): δ 1.57 (s, 30H, 2C₅(CH₃)₅), 2.04 (br, 4H, CH₂/dppe), 2.66 (br, 4H, CH₂/dppe), 7.21-7.37 (m, 32H+2H, H_{Ar}/dppe+H_{thiophene}), 7.74 (br, 8H, H_{Ar}/dppe). ³¹P NMR (160 MHz, CDCl₃): δ 79.9 (s, dppe). IR (Nujol/cm⁻¹): ν(C≡C) 2052 (s). Anal. Calcd for C₈₂H₈₀P₄Ru₂S₂: C, 67.66; H, 5.54. Found: C, 67.71; H, 5.49.

Preparation of **5**. The synthetic procedure applied to **5** mirrored that for **4**, having used [RuCl(dppe)Cp*] (381 mg, 0.57 mmol), 2,5-bis(trimethylsilylethynyl)thieno[2,3-*b*]thiophene (**5b**) (90 mg, 0.27 mmol), KF (188 mg, 3.24 mmol), CH₃OH (20 mL), THF (5 mL). Yield: 221 mg (55%) of a yellow solid. Note: the compound is poorly soluble in many deuterated solvents including CDCl₃, and its ¹³C NMR spectrum could not be collected. ¹H NMR (400 MHz, CDCl₃): δ 1.54 (s, 30H, 2C₅(CH₃)₅), 2.05 (br s, 4H, CH₂/dppe), 2.67 (br s, 4H, CH₂/dppe), 6.27 (s, 2H, H_{thiophene}), 7.21-7.37 (m, 43H, H_{Ar}/dppe), 7.74 (br s, 8H, H_{Ar}/dppe). ³¹P NMR (160 MHz, CDCl₃): δ 79.1 (s, dppe). IR (Nujol/cm⁻¹): ν(C≡C) 2050 (s). Anal. Calcd for C₈₂H₈₀P₄Ru₂S₂: C, 67.66; H, 5.54. Found: C, 67.59; H, 5.56.

Preparation of **6**. The synthetic procedure applied to **6** mirrored that for **4**, having used [RuCl(dppe)Cp*] (195 mg, 0.29 mmol), 2,5-bis(trimethylsilylethynyl)-3,4-dimethylthieno[2,3-*b*]thiophene (**6b**) (50 mg, 0.14 mmol), KF (97 mg, 1.67 mmol), CH₃OH (20 mL), THF (5 mL). Yield: 97 mg (44%) of a yellow solid. ¹H NMR (400 MHz, CDCl₃): δ 1.55(s, 30H, 2C₅(CH₃)₅), 2.01(s, 6H, CH₃), 2.11 (br, 4H, CH₂/dppe), 2.73(br, 4H, CH₂/dppe), 7.17-7.33 (m, 32H, H_{Ar}/dppe), 7.74 (br, 8H, H_{Ar}/dppe). ¹³C NMR (100 MHz, CDCl₃): δ 10.1 (CH₃), 13.6 (thiophene-CH₃), 29.4 (t, *J* = 23.00 Hz, CH₂/dppe), 92.8 (CH/C₅Me₅), 102.3 (thiophene-C≡CH), 117.2 (Ru-C≡CH), 126.5, 127.4, 128.8, 128.8, 133.2, 133.7, 136.7, 137.2, 138.7, 139.1. ³¹P NMR (160 MHz, CDCl₃): δ (ppm) 79.9 (s, dppe). IR (Nujol/cm⁻¹): ν(C≡C) 2049 (s). Anal. Calcd for

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$C_{84}H_{86}P_4Ru_2S_2$: C, 67.91; H, 5.83. Found: C, 67.87; H, 5.88.

Preparation of **7**. The synthetic procedure applied to **7** mirrored that for **4**, having used $[RuCl(dppe)Cp^*]$ (289 mg, 0.43 mmol), 5,5'-bis(trimethylsilylethynyl)dithieno[3,2-*b*:2',3'-*d*]thiophene (**7b**) (80 mg, 0.21 mmol), KF (143 mg, 2.47 mmol), CH_3OH (20 mL), THF (5 mL). Yield: 155 mg (47%) of a brown solid. 1H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 30H, $2C_5(CH_3)_5$), 2.06 (br, 4H, $CH_2/dppe$), 2.68 (br, 4H, $CH_2/dppe$), 6.42 (s, 2H, thiophene), 7.22-7.40 (m, 32H, $H_{Ar/dppe}$), 7.75 (br, 8H, $H_{Ar/dppe}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0 (CH_3), 29.4 (t, $J = 22.80$ Hz, $CH_2/dppe$), 92.8 (CH/C_5Me_5), 102.9 (thiophene- $C\equiv CH$), 117.1 (Ru- $C\equiv CH$), 126.5, 127.4, 129.0, 133.2, 133.5, 136.3, 136.8, 138.3, 138.6, 140.2. ^{31}P NMR (160 MHz, $CDCl_3$): δ 79.9 (s, dppe). IR (Nujol/ cm^{-1}): $\nu(C\equiv C)$ 2044 (w). Anal. Calcd for $C_{84}H_{80}P_4Ru_2S_3$: C, 66.74; H, 5.33. Found: C, 66.69; H, 5.41.

Preparation of **8**. The synthetic procedure applied to **8** mirrored that for **4**, having used $[RuCl(dppe)Cp^*]$ (158 mg, 0.24 mmol), 2,6-bis(trimethylsilylethynyl)thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (**8b**) (50 mg, 0.11 mmol), KF (78 mg, 1.35 mmol), CH_3OH (20 mL), THF (5 mL). Yield: 80 mg (43%) of a dark brown solid. 1H NMR (400 MHz, $CDCl_3$): δ 1.55 (s, 30H, $2C_5(CH_3)_5$), 2.08 (br, 4H, $CH_2/dppe$), 2.67 (br, 4H, $CH_2/dppe$), 6.43 (s, 2H, thiophene), 7.31-7.39 (m, 32H, $H_{Ar/dppe}$), 7.75 (br, 8H, $H_{Ar/dppe}$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0 (CH_3), 29.6 (t, $J = 22.80$ Hz, $CH_2/dppe$), 93.0 (CH/C_5Me_5), 103.0 (thiophene- $C\equiv CH$), 117.1 (Ru- $C\equiv CH$), 126.7, 127.4, 129.0, 131.5, 132.3, 133.2, 133.5, 136.3, 136.8, 137.7, 138.6, 142.0. ^{31}P NMR (160 MHz, $CDCl_3$): δ 79.9 (s, dppe). IR (Nujol/ cm^{-1}): $\nu(C\equiv C)$ 2041 (w). Anal. Calcd for $C_{86}H_{80}P_4Ru_2S_4$: C, 65.88; H, 5.14. Found: C, 65.95; H, 5.01.

Crystallographic Details. Single crystals of complexes **7** and **8** suitable for X-ray analysis, were grown by slow diffusion of hexane into a solution of dichloromethane. Crystals with approximate dimensions of $0.16 \times 0.12 \times 0.10$ mm³ for **7** and $0.12 \times 0.10 \times 0.10$ mm³ for **8** were mounted on a glass fibre for diffraction experiments. Intensity data were collected on a Nonius Kappa CCD diffractometer with Mo K α

radiation (0.71073 Å) at low temperature (100 K) for **7** and room temperature (296 K) for **8**. The structures were solved by a combination of direct methods (SHELXS-97)^[47] and Fourier difference techniques and refined by full-matrix least squares (SHELXL-97)^[48]. All non-H atoms were refined anisotropically. The hydrogen atoms were placed in ideal positions and refined as riding atoms. The partial solvent molecules have been omitted. Further crystal data and details of the data collection are summarized in Table S1. Selected bond distances and angles are given in Tables 1 and S2 (Supporting Information), respectively. CCDC number 1504782 & 1504783 for **7** and **8**.

Physical Measurements. ¹H, ¹³C, and ³¹P NMR spectra were collected on a Varian Mercury Plus 400 spectrometer (400 MHz). ¹H and ¹³C NMR chemical shifts are given relative to TMS, and ³¹P NMR chemical shifts to 85% H₃PO₄. Elemental analyses (C, H, N) were performed with a Vario EIII Chnso instrument. UV-vis-NIR spectra were recorded using a Shimadzu UV-3600 spectrophotometer and liquid-sample cells of the 0.2-mm optical path. IR spectra of solid samples dispersed in Nujol between KBr discs, and solutions in 0.2-mm optical cells were obtained with a Nicolet Avatar spectrometer. Electrochemical measurements were conducted with a CHI 660C potentiostat. A single-compartment electrochemical cell contained a pre-polished platinum disk working electrode (*d* = 0.5 mm), a platinum wire counter electrode, and a silver wire pseudo-reference electrode. Dry CH₂Cl₂, deaerated by bubbling with argon for 10 min, was used to prepare solutions of 10⁻³ M complexes and 10⁻¹ M *n*-Bu₄NPF₆ (dry, recrystallized) added as the supporting electrolyte. Ferrocene served as an internal reference for *E*_{1/2} values and rapid electron transfer at the anode reflected in identical Δ*E*_p values for each reversible redox couple. Chemical oxidation of parent complexes to corresponding mono- and dications was carried out by adding equivalent amounts of ferrocenium hexafluorophosphate.^[11a] EPR spectra was recorded on a Bruker BioSpin spectrometer, using a microwave frequency of about 9.84 GHz, 100 kHz modulation frequency, 1 G modulation amplitude, and ca 20 mW power of the microwave.

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3 **Computational Details.** Density functional theory (DFT) calculations were
4 performed using the Gaussian 09 software^[49] at the B3LYP/6-31G* (Lan12dz for the
5 Ru atom) and BLYP35^[38]/6-31G* (Lan12dz for the Ru atom) levels of theory.
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7 Geometry optimizations and full geometry optimizations were performed without any
8 symmetry constraints, and frequency calculations on the resulting optimized
9 geometries showed no imaginary frequencies. Electronic transitions were calculated
10 by the time-dependent DFT (TD-DFT) method. The MO contributions were generated
11 using GaussView 5.0. The solvation effects in dichloromethane were included for a
12 part of the calculations with the conductor-like polarizable continuum model
13 (CPCM)^[50]. Calculated harmonic vibrational frequencies were scaled by an empirical
14 factor of 0.95 (BLYP35) and 0.9614 (B3LYP).^[51,52]
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51 **Notes**

52 The authors declare no competing financial interest.
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55 † **Electronic supplementary information (ESI) available:** IR and UV-vis-NIR
56 spectra, calculated DFT data, and NMR information. CCDC number 1504782 &
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1504783 for 7 and 8. ESI and crystallographic data in CIF or other electronic format are available free of charge via the Internet at <http://pubs.acs.org>.

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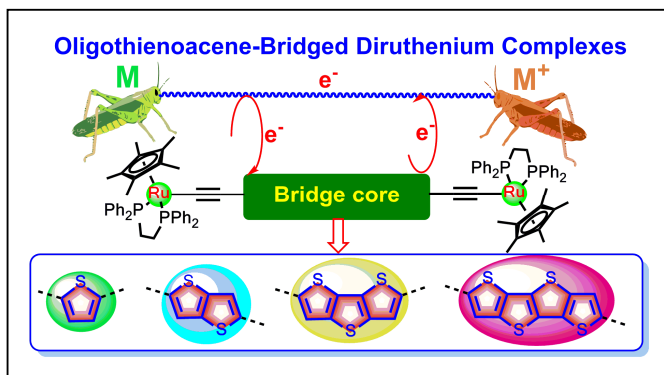
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TOC and Graphical Abstract



Ya-Ping Ou, Jing Zhang, Ming-Xing Zhang, Fuxing Zhang, Daizhi Kuang, František Hartl, Sheng Hua Liu**

Page No. – Page No.

Title: Bonding and electronic properties of linear diethynyl oligothienoacene-bridged diruthenium complexes and their oxidized forms

The localization of the HOMO of the parent diruthenium complexes on the redox non-innocent oligothienoacene bridge core with strong participation of the ethynyl linkers and a limited contribution from the metallic termini makes the initial one-electron oxidation symmetrical. The remarkable appearance of a dual IR $\nu(\text{C}\equiv\text{C})$ absorption in the cationic complexes is ascribed to a vibronic coupling of the IR-forbidden $\nu_s(\text{C}\equiv\text{C})$ mode of the oxidized $-\text{C}\equiv\text{C}-\text{core}-\text{C}\equiv\text{C}-$ bridge to the low-lying $\pi-\pi^*$ (intra-bridge) / MLCT electronic transition in the NIR-mid-IR spectral region.