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# Photoswitchable Organic Mixed Valence in Dithienylcyclopentene Systems with Tertiary Amine Redox Centers

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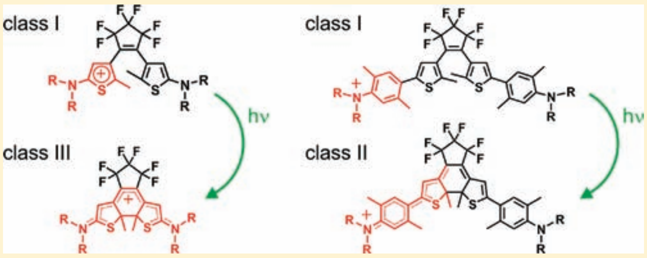
S Supporting Information

**ABSTRACT:** The electronic structures of the radical cations of two dithienylperfluorocyclopentene molecules with appended tertiary amine units were investigated by electrochemical and optical spectroscopic methods. The through-bond N−N distances in the photocyclized (closed) forms of the two systems are 9.3 and 17.6 Å, respectively, depending on whether the nitrogen atoms are attached directly to the two thienyl units or whether xylyl spacers are in between. In the case of the radical cation with the longer N−N distance, photocyclization of the dithienylperfluorocyclopentene core induces a changeover from class I to class II mixed valence behavior. In the case of the shorter system, the experimental data is consistent with assignment of the photocyclized form to a class III mixed valence species.



## INTRODUCTION

Mixed valence systems have played an important role in arriving at a detailed theoretical understanding of electron transfer reactions.[1] Although many chemists spontaneously associate the term “mixed valence” with coordination compounds, there have been investigations of purely organic mixed valence systems since the early days of this research field.[2] Aside from being of interest from a fundamental chemistry point of view, the extent of charge delocalization in organic mixed valence systems is relevant in the context of molecular electronics: Charge transfer across molecular wires longer than ∼25 Å usually cannot occur efficiently via the tunneling mechanism and consequently has to proceed via hopping from one molecular unit to the next.[3] It would be desirable to construct molecular units that permit large charge delocalization to minimize the distance over which charge carriers have to hop between individual units.[4] Among the many organic molecular wire systems that have been explored in the past, thiophene-based $\pi$-conjugated oligomers and polymers represent a particularly interesting class of materials since they are good hole transporters that have found application in organic light emitting diodes and other devices.[5] Recent experimental and theoretical works on bis(triarylamine) substituted oligothiophene (mixed valence) radical cations found that the extent of charge delocalization in these systems can indeed be very significant.[6] However, thienylene-bridged organic mixed valence systems are still poorly explored when compared to phenylene-bridged analogues.[2c]

In the context of molecular electronics, it may be desirable to develop molecules that exhibit reversibly switchable conductivity.[7] Among the many photoswitchable molecular units investigated so far,[8] dithienylcyclopentenes have received particular attention because of their favorable properties such as long-term chemical stability (including high reversibility) and pronounced photochromic behavior.[9] The issue of different charge and energy transfer properties of the open and the more $\pi$-conjugated photocyclized form of dithienylcyclopentenes is of long-standing interest and has stimulated much research.[10] However, among the many studies performed in this context, there are only a few that have employed dithienylcyclopentenes as bridging units between two identical redox centers to investigate mixed valence phenomena in the open and closed forms of the switchable spacer.[11] What is more, until now such work has focused exclusively on inorganic redox centers. There are two important arguments for investigation of dithienylcyclopentene-bridged mixed valence systems with organic redox moieties: (i) intervalence absorption bands of organic mixed valence systems are in many cases more easily detectable than those of coordination compounds and (ii) organic redox centers tend to exhibit inherently greater charge delocalization than coordination complexes.[2c] To underscore the importance of this latter point, in a series of (mixed valence) bis(triarylamine) radical cations, the effective diabatic electron transfer distance was found to be only roughly two-thirds of the N−N distance.[13]

Here, we report on the dithienylcyclopentene molecules with appended tertiary amine units shown in Scheme 1.

In the case of molecule **1**, two triarylamine redox centers are substituted to the photoswitchable core, while in molecule **3** the nitrogen atoms are connected directly to the thienyl rings. The electronic structures of the one-electron oxidized (mixed valence) forms of these molecules were investigated using optical absorption spectroscopy and cyclic voltammetry. Our results

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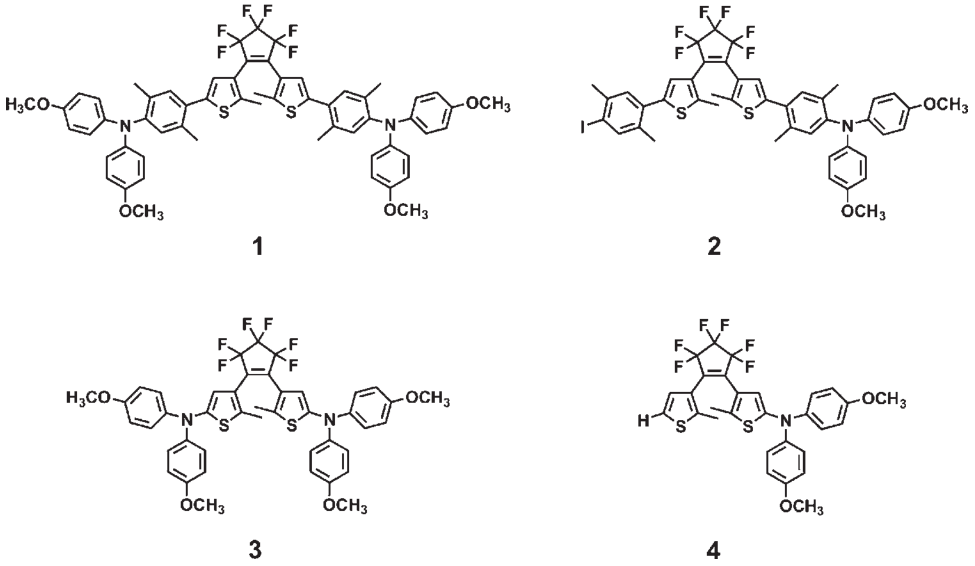
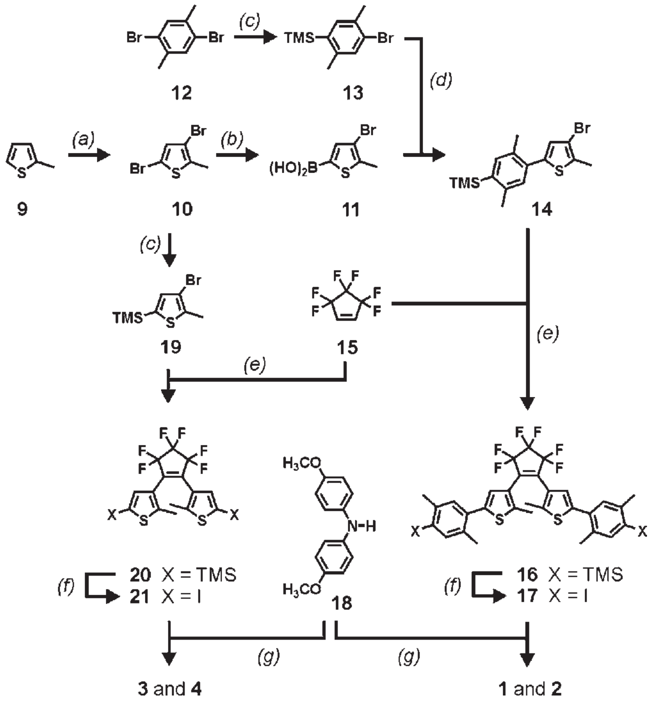
Scheme 1. Chemical Structures of the Molecules Investigated in This Work



Scheme 2. Synthetic Pathways to the Molecules from Scheme 1[a]



[a] (a) $Br_2$, $CH_3COOH$; (b) *n*-BuLi, THF, −78°C, triisopropyl borate, HCl; (c) *n*-BuLi, THF, −78°C, TMSCl; (d) THF/$H_2O$, $Pd(PPh_3)_4$, $Na_2CO_3$; (e) *n*-BuLi, THF, −78°C; (f) ICl, $CH_2Cl_2$; (g) *o*-dichlorobenzene, Cu, $K_2CO_3$.

demonstrate that in both systems the extent of charge delocalization depends very strongly on whether the dithienylcyclopentene unit is in its open or closed form. Molecules **2** and **4** served as reference systems that are chemically similar but unable to exhibit mixed valence phenomena.

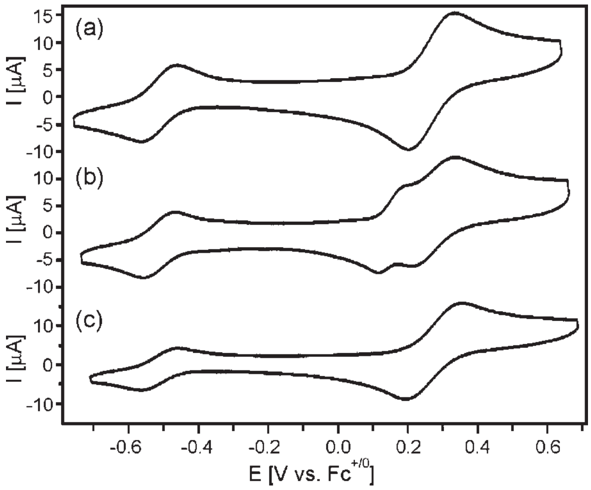


**Figure 1.** Cyclic voltammograms measured on acetonitrile solutions of (a) open form of molecule **1**; (b) closed form of molecule **1**; (c) closed form of reference molecule **2**. In all experiments, tetrabutylammonium hexafluorophosphate was used as an electrolyte at a concentration of 0.1 M. The waves at −0.51 V are due to decamethylferrocene ($Me_{10}Fc$), which was added to these solutions for internal voltage calibration.

## RESULTS AND DISCUSSION

The synthetic pathway to the molecules of central interest to this study is outlined in Scheme 2. Bromination of 2-methylthiophene (**9**)[14] yields 2,4-dibromo-5-methylthiophene (**10**), which can be converted to boronic acid **11**.[15] Reaction between the latter and 1-bromo-4-trimethylsilyl-2,5-dimethylbenzene (**13**)[16] yields coupling product **14**,[17] which can be reacted with perfluorocyclopentene (**15**) to the trimethylsilyl-protected dithienylperfluorocyclopentene **16**.[15] Deprotection of the trimethylsilyl-groups with iodine monochloride gives the diiodo-substituted analogue **17**, which can be reacted with 4,4′-dimethoxydiphenylamine (**18**) to the desired bis(triarylamine) **1**.[6a] Molecule **2** with only one amino-group is obtained as a

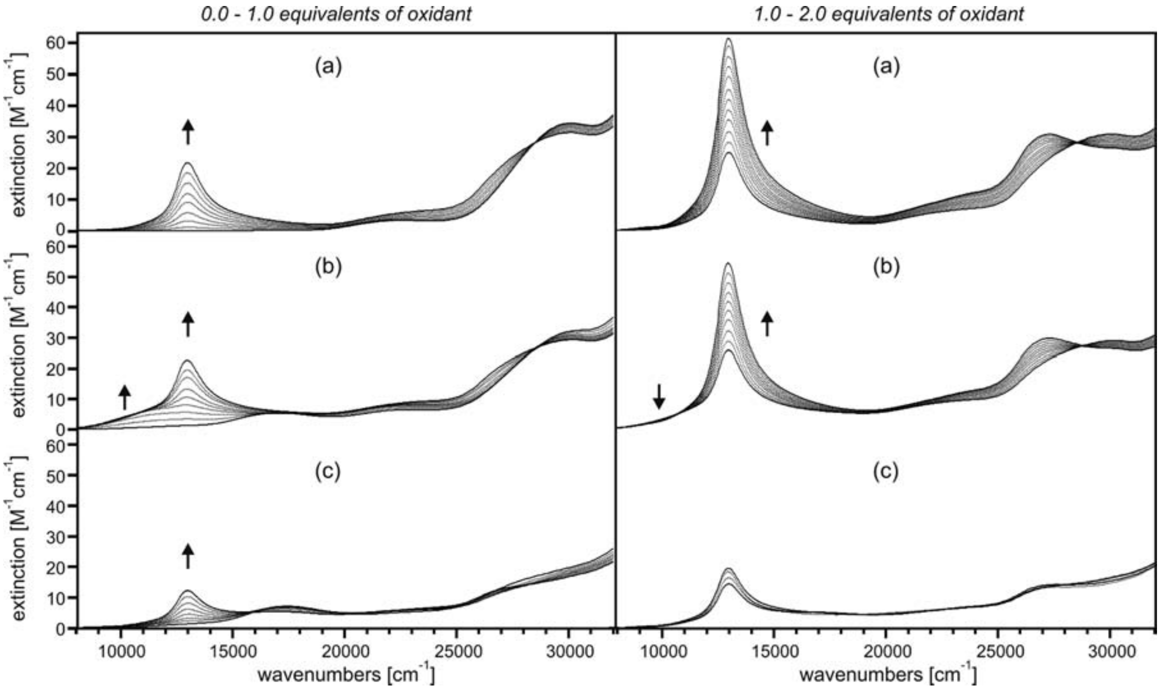


**Figure 2.** Optical absorption spectra of acetonitrile solutions of (a) open form of molecule **1**; (b) closed form of molecule **1**; (c) closed form of reference molecule **2** following addition of copper(II) perchlorate. (Left) Absorption spectra obtained after addition of 0.0−1.0 equivalents of copper(II) oxidant. (Right) Absorption spectra measured after addition of 1.0−2.0 equivalents of oxidant.

byproduct from the same reaction and can be separated from molecule **1** by column chromatography.

Synthesis of target molecules **3** and **4** departs from 3-bromo-2-methyl-5-trimethylsilylthiophene (**19**), which is put into reaction with perfluorocyclopentene (**15**) to yield dithienylperfluorocyclopentene **20**.[15] Trimethylsilyl-iodo exchange affords diiodo-substituted molecule **21**, which is reacted with 4,4′-dimethoxydiphenylamine (**18**) to obtain a mixture of target molecules **3** and **4**.[6a] This mixture is separable by column chromatography.

Figure 1a shows the cyclic voltammogram of the open form of molecule **1** (hereafter referred to as **1o**) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) as the electrolyte. The wave at −0.51 V is due to decamethylferrocene (Me$_{10}$Fc), which was used as a reference in all electrochemical experiments reported herein;[18] however, all experimentally determined potentials are reported relative to the ferrocenium/ferrocene (Fc$^{+/0}$) couple as is commonly done for electrochemistry in nonaqueous solvents. The wave centered at 0.27 V vs Fc$^{+/0}$ is readily assigned to oxidation of the two triarylamine units; this is evident both from comparison to literature data and from comparison to a tertiary amine reference molecule comprised of two anisyl- and one xylyl-substituent (Figure S1 in Supporting Information).[12a,19]

Irradiation of molecule **1** with UV light induces a photocyclization reaction as commonly observed for dithienylperfluorocyclopentenes. In the specific case of molecule **1**, this leads to a photostationary state containing a ratio between the closed isomer (hereafter denoted **1c**) and its open form (**1o**) greater than 20:1, as indicated by $^1$H NMR spectroscopy (Figure S4 in Supporting Information). The cyclic voltammogram of isomer **1c** is shown in Figure 1b. Instead of a single oxidation wave, two quasi-reversible oxidations are now observed in the potential range where triarylamine oxidations typically occur.[19,31]

The potential splitting between the two waves is 150 mV, suggesting that unlike in the open form, in the closed isomer of molecule **1** there is significant mutual interaction between the two triarylamine units. To eliminate any doubts that this splitting into two waves could have a different origin, reference molecule **2** with only one triarylamine unit was investigated. The cyclic voltammogram of the closed isomer (**2c**) is shown in Figure 1c and exhibits a single oxidation wave at 0.27 V vs Fc$^{+/0}$, in agreement with our expectation. The observation of a potential splitting of 150 mV between the two triarylamine oxidations in molecule **1c** is in line with a recent study of a ferrocene-disubstituted dithienylperfluorocyclopentene.[11c,d] At a comparable (geometrical) separation distance between the two redox-active units, a potential splitting of 160 mV has been reported for the closed form of the photoisomerizable bridging unit. Voltammetry sweeps to potentials more positive than 0.7 V vs Fc$^{+/0}$ that show the effect of photochemical ring-closure on dithienylperfluorocyclopentene-localized oxidations in a suitable reference molecule are given in Figure S7 of the Supporting Information. As commonly observed, the open dithienylcyclopentene moiety is oxidized irreversibly and at high potential, while the closed form exhibits a reversible wave at significantly less positive potential.

The optical absorption spectra shown in Figure 2 provide further evidence for significantly different extents of electronic communication between the triarylamine redox centers in the open and closed isomers of molecule **1**, but the evidence in this case is somewhat more subtle and requires more careful inspection of the experimental data. Figure 2a shows the result of a titration of molecule **1o** with copper(II) perchlorate in acetonitrile solution.

Upon addition of the copper oxidant, an absorption band at 12 900 cm$^{-1}$ becomes observable. This band is also observed for

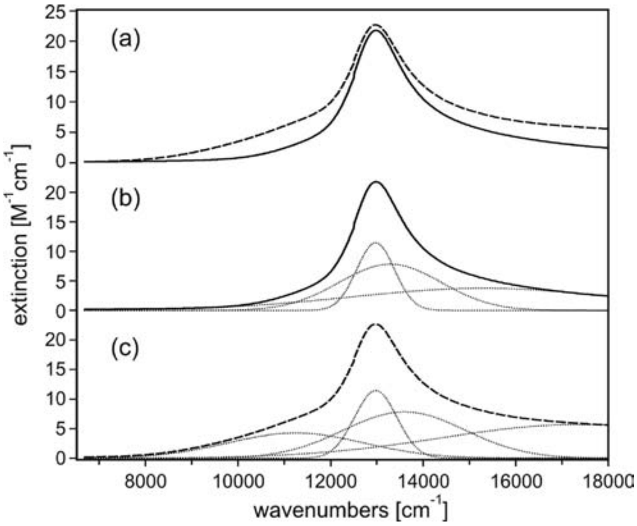


**Figure 3.** (a) Experimental optical absorption spectra of **1o**$^{\bullet+}$ (solid trace) and **1c**$^{\bullet+}$ (dashed trace), extracted from the titration end points in the left halves of Figure 2a and b (that is after addition of exactly 1 equivalent of oxidant). The same experimental data are also shown in (b) (**1o**$^{\bullet+}$) and (c) (**1c**$^{\bullet+}$), along with the results of multipeak fits with a minimal number of Gaussian functions (dotted traces).

the above-mentioned reference amine comprised of two anisyl- and one xylyl-substituents (Figure S2 in Supporting Information) and is typical for triarylamine radical cations.[19] Comparison of the titration end points in the left and right parts of Figure 2a shows that addition of 1 equivalent of oxidant to a solution of **1o** leads to an absorbance roughly half as large as addition of 2 equivalents of oxidant. This observation is in line with the expectation that in the dicationic form of **1o** there are two singly oxidized triarylamine radical cations with equal extinction coefficients at 12 900 cm$^{-1}$. The occurrence of an isosbestic point at 28 500 cm$^{-1}$ suggests that at any given titration point there are only two species which contribute significantly to the optical absorption spectrum.

Figure 2b shows analogous titration data for the closed isomer of molecule **1**. The data for **1c** is qualitatively similar to that shown for the open isomer, but with a subtle difference observable in the left part of Figure 2b: Underlying the triarylamine radical cation absorption at 12 900 cm$^{-1}$, there is a broad and somewhat weaker band (marked by an upward arrow) extending from 8000 cm$^{-1}$ to at least 15 000 cm$^{-1}$. The absorbance at 10 000 cm$^{-1}$ is caused to a significant extent by this broad band and is found to maximize after addition of 1 equivalent of oxidant. This becomes evident by the appearance of an isosbestic point at 10 800 cm$^{-1}$ in the right part of Figure 2b. It is to be noted that the triarylamine radical cation band centered at 12 900 cm$^{-1}$ does also contribute to the overall absorption at 10 000 cm$^{-1}$, hence the absorbance at this wavenumber decreases less significantly between 1 and 2 equivalents of oxidant than might be anticipated.

A direct superposition of the near-infrared absorption spectra of **1o**$^{\bullet+}$ and **1c**$^{\bullet+}$ is shown in Figure 3a, from which it can more clearly be seen that after addition of one equivalent of oxidant, **1c** exhibits significantly stronger absorption between 7800 cm$^{-1}$ and 12 600 cm$^{-1}$ than **1o**.[32] This falls into the spectral range in which intervalence absorption bands of bis(triarylamine) radical cations are commonly observed.[12a,b] The fact that the absorbance at 10 000 cm$^{-1}$ reaches its maximum exactly after addition of 1 equivalent of oxidant is in line with assignment of the broad near-infrared absorption of **1c**$^{\bullet+}$ to an intervalence transition. Indeed, Figure 2c (left) shows that for the closed form of molecule **2**, which is unable to exhibit mixed valence phenomena due to the presence of only a single triarylamine unit, an analogous near-infared absorption band cannot be detected. This eliminates the (theoretical) possibility that the additional near-infrared absorption intensity in Figure 2b is due to an electronic transition primarily associated with the bridging dithienylperfluorocyclopentene unit. There are no electronic absorptions at wavenumbers lower than 8000 cm$^{-1}$ in any of the species reported here; we measured absorption spectra down to 3700 cm$^{-1}$ on a suitable instrument.

In the middle and lower thirds of Figure 3, the experimental absorption data from Figure 3a are disentangled by multipeak fitting with Gaussian functions. The experimental spectrum of **1o**$^{\bullet+}$ between 7800 and 18 000 cm$^{-1}$ (solid trace in Figure 3b) can be fitted adequately with three Gaussian functions (dotted traces in Figure 3b). Albeit due to a single electronic transition, satisfactory fitting of the triarylamine radical cation absorption band at 12 900 cm$^{-1}$ requires the use of two Gaussians. These two Gaussians were kept fixed for the fit of the experimental spectrum of **1c**$^{\bullet+}$ (Figure 3c), because they describe absorptions that are localized on a given triarylamine unit and should therefore depend only little on whether the photoswitchable bridging unit is in its open or closed form. A total of four Gaussian functions is necessary to obtain a reasonable fit to the experimental spectrum in Figure 3c. The lowest energy Gaussian is of central interest here, as it describes the additional near-infrared intensity present in **1c**$^{\bullet+}$, which was attributed above to an intervalence transition.[33] The characteristics of this Gaussian are summarized in Table 1.

Even though the through-bond nitrogen—nitrogen distance ($d_{NN}$) is usually a bad measure for the effective electron transfer distance ($d_{AB}$) in bis(triarylamine) radical cations (and also in other organic mixed valence species),[2c] a brief comparison of $d_{NN}$ in our system to nitrogen—nitrogen distances in previously explored organic mixed valence systems appears useful for our analysis here. The radical cation of *N,N,N,′N′*-tetramethyl-*p*-phenylenediamine (TMPD) and the radical anion of 1,4-dinitrobenzene are both fully delocalized class III systems with $d_{NN}$ = 5.7 Å.[2c,20] The *N,N,N,′N′*-tetraanisyl-*p*-phenylenediamine radical cation has similar $d_{NN}$ and was also interpreted as a class III system.[21] Most systems with larger $d_{NN}$, for example a biphenyl-bridged bis(triarylamine) analogue with $d_{NN}$ = 10.0 Å or a tolane-bridged congener with $d_{NN}$ = 10.9 Å, are clear cases of class II systems.[12a] A bis(triarylamine) radical cation with a ladder-type pentaphenylene bridge and a nitrogen—nitrogen distance of 22 Å was described as a class II system with $H_{AB}$ = 548 cm$^{-1}$.[12d] Two bis(triarylamine) radical cations with [2.2]paracyclophane bridges and $d_{NN}$ = 9.9 and 15.1 Å, respectively, were also interpreted as class II species.[34] Among dinitroaromatic radical anions, there are a few examples of class III systems with $d_{NN}$ = 10.0 Å,[22] but these are clearly exceptions to the commonly observed behavior.[35] In molecule **1o**, $d_{NN}$ = 17.6 Å and consequently the expectation of a fully delocalized electronic structure for the radical cation of **1o**$^{\bullet+}$ appears unrealistic.[3c,12c]

Usually there are several experimental observables which can be used to distinguish between class II and class III mixed valence forms, but most of them are difficult to elucidate in the specific case of **1o**$^{\bullet+}$.[1b,d,f,h−j] For instance, the intervalence absorption

Table 1. Intervalence Band Data for the Radical Monocations of 1c and 3c along with Effective Electron Transfer Distances ($d_{AB}$) and Electronic Coupling Matrix Elements ($H_{AB}$)[a]

| compound | $\nu_{max}$ [cm$^{-1}$] | $\varepsilon_{max}$ [M$^{-1}$cm$^{-1}$] | $\Delta\nu_{1/2}$ [cm$^{-1}$] | $d_{AB}$ [Å] | $H_{AB}$ [cm$^{-1}$] |
|---|---|---|---|---|---|
| **1c**$^{\bullet+}$ | 11 250 | 4250 | 3500 | 17.6 | 476[b] |
| | | | | 0.66 × 17.6[d] | 722[b] |
| **3c**$^{\bullet+}$ | 11 100 | 18 400 | 2300 | 9.3 | 5550[c] |
| | | | | 9.3 | 1511[b] |
| | | | | 0.66 × 9.3[d] | 2289[b] |

[a] Parameters $\nu_{max}$, $\varepsilon_{max}$, and $\Delta\nu_{1/2}$ are defined in the text. [b] Calculated based on eq 1. [c] Calculated based on eq 3. [d] Multiplication factor 0.66 is used because prior studies on related bis(triarylamine) radical cations have led to the conclusion that $d_{AB} \approx 0.66 \times d_{NN}$.[13]

bands of class II systems commonly exhibit stronger solvent dependence than those of class III radicals, but in our case this effect is superimposed by the solvent dependence of the triarylamine radical cation band at 12 900 cm$^{-1}$. Likewise, an asymmetry of the intervalence absorption band, as reported for several systems near the borderline of class II and class III, is masked.[12a] Vibrational fine structure, frequently appearing in class III systems, is not observed. If occurring, this should be detectable even in our case since it would be expected close to the electronic origin of the near-infrared absorption band around 8000 cm$^{-1}$. Taken together, these facts support assignment of **1c**$^{\bullet+}$ to Robin-Day class II.[23] The potential splitting of 150 mV reported above and a comproportionation constant of 344 provides further support for this assignment. For reference, the potential splitting observed between the two oxidation waves of the class III system TMPD$^{\bullet+}$ amounts to 600 mV, resulting in a comproportionation constant of 1.4 × 10$^{10}$.[2c]

For class II systems with Gaussian-shaped intervalence absorption bands, an estimate of the matrix element $H_{AB}$ quantifying the electronic coupling between the two redox-active centers can be obtained using eq 1.[24]

$$H_{AB} = 2.05 \times 10^{-2} \times \sqrt{\varepsilon_{max} \times \tilde{\nu}_{max} \times \Delta\tilde{\nu}_{1/2}} \times d_{AB}^{\;-1} \qquad (1)$$

$\nu_{max}$ is the energy of the near-infared absorption band maximum in wavenumbers, $\Delta\nu_{1/2}$ is the full width at half-maximum (in cm$^{-1}$), $\varepsilon_{max}$ is the molar extinction coefficient at the band maximum, and $d_{AB}$ is the electron transfer distance. Using the Gaussian fit parameters given in Table 1 and $d_{AB} = d_{NN} = 17.6$ Å, one obtains $H_{AB} = 476$ cm$^{-1}$. However, as mentioned above, investigations of various kinds of organic mixed valence systems have demonstrated that $d_{AB}$ is usually significantly shorter than the distance between atoms which may formally be regarded as redox-active centers.[2c,13] For several dinitroaromatic radical anions, $d_{AB}$ was found to be only roughly 40% of $d_{NN}$,[35] while for a series of bis(triarylamine) radical cations $d_{AB}$ was estimated to be roughly two-thirds of $d_{NN}$.[13] When using $d_{AB} = 0.66 \times d_{NN} = 11.6$ Å, one obtains $H_{AB} = 722$ cm$^{-1}$ for **1o**$^{\bullet+}$. It appears appropriate to conclude that 476 and 722 cm$^{-1}$ represent reasonable lower and upper limits for the electronic coupling matrix element ($H_{AB}$) of the closed form of molecule **1** (Table 1, last column). $H_{AB}$ values on this order were previously reported for bis(triarylamine) radical cations with oligo-*p*-phenylene vinylene (OPV) and oligo-*p*-phenylene ethynylene (OPE) bridges and similar geometrical distance between redox-active centers.[2c,12a,12b] Oligo-*p*-phenylene bridged organic mixed valence systems exhibit significantly weaker electronic coupling at comparable geometrical distance between redox units,[12a,25] in line with the stronger distance dependence of electronic coupling matrix elements reported for these molecular bridges compared to OPVs or OPE wires.[3c,12b,26] Tunneling-energy gaps and bridge redox potentials play a key role in this context.[20,27]

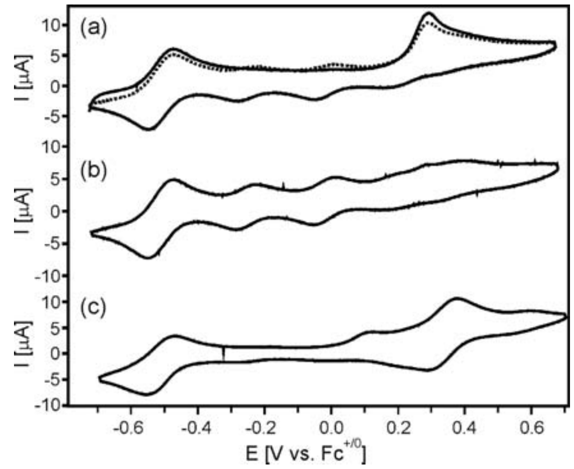


**Figure 4.** Cyclic voltammograms measured on acetonitrile solutions of (a) open form of molecule **3**; (b) closed form of molecule **3**; (c) closed form of reference molecule **4**. In all experiments, tetrabutylammonium hexafluorophosphate was used as an electrolyte at a concentration of 0.1 M. The waves at −0.51 V are due to decamethylferrocene (Me$_{10}$Fc), which was added to these solutions for internal voltage calibration.

Significantly stronger electronic couplings have been reported for mixed valence systems in which the nitrogen centers of tertiary amines are attached directly to bridging thiophene units.[6] This prompted our interest in molecule **3**, which differs from molecule **1** by the absence of two bridging xylyl units, resulting in a through-bond N−N distance of roughly 9.3 Å.

Figure 4a shows the result of a cyclic voltammetry experiment with the open form of molecule **3** (hereafter referred to as **3o**) in acetonitrile solution in the presence of tetrabutylammonium hexafluorophosphate electrolyte and Me$_{10}$Fc as a reference. The solid trace represents the initially recorded voltammogram. The first oxidation wave occurs at 0.29 V vs Fc$^{+/0}$, at essentially the same potential for which triarylamine oxidation was observed for molecule **1o** (Figure 1a). However, contrary to all other triarylamine oxidations reported in this work so far, the oxidation process considered here is irreversible. Instead, the subsequent voltage sweep from 0.7 to −0.7 V vs Fc$^{+/0}$ reveals two weaker reduction waves at −0.05 and −0.28 V vs Fc$^{+/0}$. In the subsequent second oxidative sweep from −0.7 to +0.7 V (dotted trace in Figure 4a), weak oxidation waves now occur at −0.22 and 0.01 V vs Fc$^{+/0}$, and at the same time the initially observed oxidation wave at 0.29 V has become less prominent.

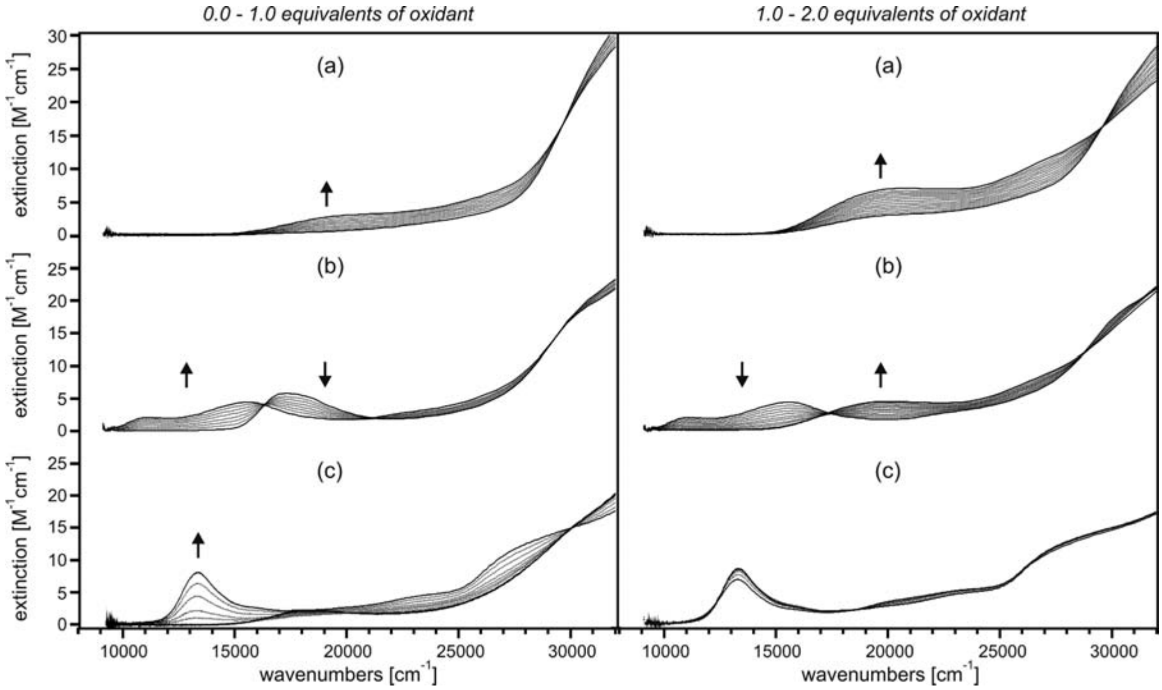


**Figure 5.** Optical absorption spectra of acetonitrile solutions of (a) open form of molecule **3**; (b) closed form of molecule **3**; (c) closed form of reference molecule **4** following addition of copper(II) perchlorate. (Left) Absorption spectra obtained after addition of 0.0−1.0 equivalents of copper(II) oxidant. (Right) Absorption spectra measured after addition of 1.0−2.0 equivalents of oxidant.

This behavior appears peculiar at first glance but can be understood readily upon inspection of the data in Figure 4b, measured on the closed form of molecule **3** (hereafter named **3c**). The voltammogram observed for this species exhibits two reversible oxidation waves centered at −0.25 and −0.02 V vs $Fc^{+/0}$. This is precisely at the potentials at which reduction and oxidation waves are observed after initial oxidation of molecule **3o** (Figure 4a). The conclusion which imposes itself is that application of electrochemical potentials more positive than 0.29 V vs $Fc^{+/0}$ to solutions of the open form of molecule **3** induces ring closure of the dithienylperfluorocyclopentene unit. This ring closure appears to be electrochemically irreversible, at least in the potential range considered here. From the decrease of the oxidation wave at 0.29 V in Figure 4a with increasing number of voltammetry cycles, one may estimate that ultimately more than 80% of all molecules undergo electrochemically induced ring closure.[36] Both tertiary amine redox units are oxidized simultaneously at 0.29 V vs $Fc^{+/0}$; hence, ring closure is likely to be the result of a two-electron oxidation process.

The observation of ring closure of dithienylcyclopentenes after two-electron oxidation is not without precedent, in fact there have been several very detailed investigations on this particular subject.[28] The efficiency of electrochemical ring closure has been found to increase with increasing electron-donating character of substituents attached to the $C_5$-position of the thienyl units,[28a,b] and therefore efficient electrochemical ring closure in the amino-substituted molecule **3o** is not a major surprise. The redox waves of the closed form fall into a potential range which is typical for thienyl-localized redox processes in dithienylcyclopentenes.[28a,b] Thus, after initial oxidation of the tertiary amine units of **3o**, ring closure occurs, and a species is formed for which the observed oxidation waves look like thienyl-localized redox processes. However, as will be discussed below, in the resulting species there is in fact significant charge delocalization between the amino-groups and the thienyl-rings. The potential splitting of 230 mV observed between the two oxidation waves of **3c** indicates that there is significant interaction between its two redox units. Thus, the one-electron oxidized form ($3c^{\bullet+}$) may potentially be considered a mixed valence system comprised of two thienyl/amine redox centers bridged by a perfluorocyclopentene unit.

The cyclic voltammogram of the closed form of reference molecule **4** in Figure 4c is in line with all observations and interpretations made above, although in this case the most important redox process appears to remain localized on the tertiary amine. Moreover, electrochemical cyclization of the open form of molecule **4** does not occur, indicating that electron-donating substituents on both thienyl units are necessary for efficient electrochemical ring closure.

The left part of Figure 5a shows the optical absorption spectra of an acetonitrile solution of molecule **3o** obtained after addition of up to 1 equivalent of copper(II) perchlorate. The initial solution is nearly colorless, and with increasing addition of oxidant there is only the build-up of a very broad absorption feature at wavenumbers higher than 15 500 cm$^{-1}$, and the solution turns red. Addition of a further equivalent of oxidant (Figure 5a, right) simply further increases the intensity of this absorption band. In other words, already the very first oxidation step in Figure 5a gives a spectrum that is essentially identical to that obtained at the titration end point, only with weaker overall intensity.

Figure 5b shows two analogous sets of data for the closed form of molecule **3**. Based on cyclic voltammetry data, it can be estimated that the photostationary state in this case contains more than 90% of **3c**, and this is corroborated by $^1$H NMR data (Figure S5 in Supporting Information). The initially present

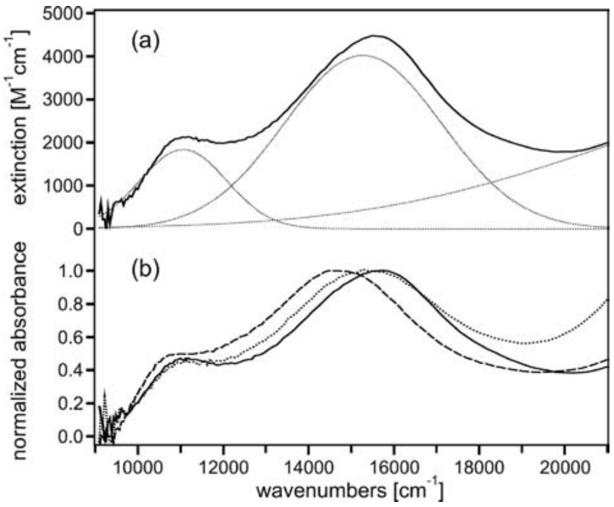


**Figure 6.** (a) Solid trace is the experimental absorption spectrum measured on an acetonitrile solution of **3c**$^{\bullet+}$ as extracted from the titration end point in the left part of Figure 5b. The dotted traces represent the result of a multipeak fit to the experimental data with a minimal number of Gaussian functions. (b) Solvent dependence of the experimental absorption spectrum of **3c**$^{\bullet+}$ (solid trace, acetonitrile; dotted trace, ethanol; dashed trace, dichloromethane).

absorption band in the visible spectral range ($\lambda_{\max}$ = 17 300 cm$^{-1}$) typical for the closed form of dithienylperfluorocyclopentenes decreases in intensity upon oxidation. Simultaneously, two new absorption bands at lower energies gain in intensity up to the titration point at which exactly one equivalent of oxidant has been added (left part of Figure 5b). Further addition of oxidant leads to a decrease of the intensity of the two low-energy absorptions, and at 2 equivalents of copper(II) added, they have disappeared completely (Figure 5b, right). The end points of the titrations of **3c** and **3o** yield nearly identical absorption spectra. The last absorption spectrum in the right part of Figure 5a essentially corresponds to the last absorption spectrum in Figure 5b, suggesting that the same species is probed in absorption in both cases. This finding is in line with the electrochemical results from above, which indicated that two-electron oxidation of **3o** leads to cyclization. It may be concluded that **3c**$^{2+}$ is the species that is detected at the end points of the two titrations in Figure 5a and b.

Above we noted already that the very first oxidation step performed on molecule **3o** (Figure 5a, left) results in an absorption spectrum which is nearly identical to that obtained at the titration end points of **3o** and **3c** (Figure 5a,b, right), only with weaker overall intensity. The logical conclusion is therefore that the **3c**$^{2+}$ species is formed already at the very first oxidation step of **3o**.[37] This interpretation is in agreement with the cyclic voltammetry data in Figure 4a which exhibits a single oxidation wave at 0.29 V vs Fc$^{+/0}$, indicating that **3o**$^{\bullet+}$ and **3o**$^{2+}$ are formed at very close potential. The latter reacts irreversibly to **3c**$^{2+}$, and thus neither **3o**$^{\bullet+}$ nor **3o**$^{2+}$ are observed in the optical absorption spectra of Figure 5a. The clean observation of monocationic **3c**$^{\bullet+}$ is certainly facilitated by the relatively large potential separation between the first and second oxidation process (230 mV, see above).

The occurrence of two near-infrared absorptions after addition of exactly 1 equivalent of oxidant to the closed form of molecule **3** (Figure 5b) suggests that **3c**$^{\bullet+}$ may indeed be considered a mixed-valence species with low-energy intervalence transitions. In order to test this hypothesis, an analogous titration was performed with the closed form of reference molecule **4**, which has only one amino-group attached to the dithienylperfluorocyclopentene core. The result of this titration is shown in Figure 5c. Instead of the two near-infrared absorptions seen in Figure 5b, there is only an absorption band at 13 300 cm$^{-1}$ for **4c**$^{\bullet+}$. Based on its great similarity to the absorption bands observed in Figure 2a/c, this band is attributed to absorption of a charge-localized tertiary amine radical cation. Consistent with this interpretation, this band remains essentially unaltered upon addition of a second equivalent of oxidant (Figure 5c, right). It is therefore plausible that the near-infrared bands of **3c**$^{\bullet+}$ in Figure 5b are indeed associated with the mixed valence character of this particular radical cation.

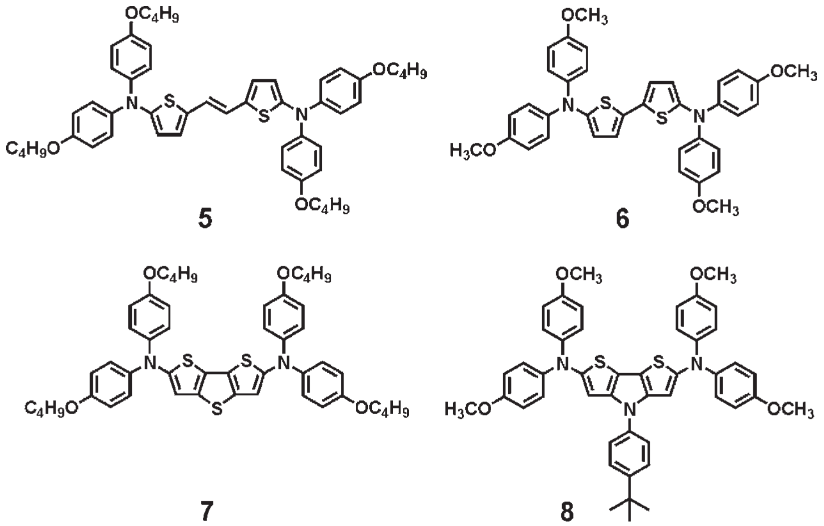
None of the forms of molecule **3** absorbs at wavenumbers lower than 9000 cm$^{-1}$ (absorption spectra were measured down to 3700 cm$^{-1}$), hence the unique absorptions between 9000 cm$^{-1}$ and 21 000 cm$^{-1}$ from the left part of Figure 5b, shown in more detail in Figure 6a, are indeed the lowest-energetic absorptions. The overall appearance of these two bands is reminiscent of the lowest energetic absorptions reported recently for the radical cations of (*E*)-1,2-bis[5-[bis(4-butoxyphenyl)-amino]-2-thienyl]ethylene (**5**) and 2,6-bis[bis(4-methoxyphenyl)amino]-2,2′-bithiophene (**6**) (Scheme 3).[6a] Time-dependent DFT calculations for **5**$^{\bullet+}$, **6**$^{\bullet+}$ and two related species (**7**$^{\bullet+}$, **8**$^{\bullet+}$) suggested that their near-infrared absorption bands have significant intervalence charge transfer character, while the absorptions occurring at shorter wavelengths are of different origin.[6a]

The solvent dependences of the two lowest-energetic absorptions of **3c**$^{\bullet+}$ are significantly different (Figure 6b): While the maximum of the higher energy absorption shifts from 15 700 cm$^{-1}$ in acetonitrile to 15 400 cm$^{-1}$ in ethanol and 14 700 cm$^{-1}$ in dichloromethane, the maximum of the weaker near-infrared absorption stays essentially constant at 11 100 cm$^{-1}$. Multipeak fitting with Gaussian functions reveals that the minor shift to lower wavenumbers of the near-infrared band is merely the result of the significant red-shift of the higher-energy absorption band. In acetonitrile, the characteristics of the Gaussian profile fitted to the near-infrared absorption band (dotted trace in Figure 6a) are as listed in Table 1. An important finding is that the fitted band profile is significantly narrower than what would be expected for a class II intervalence band: One would normally expect a class II intervalence band to satisfy eq 2,[1a] but in the present case the bandwidth $\Delta\nu_{1/2}$ is calculated to 5064 cm$^{-1}$, while the value obtained from the Gaussian fit amounts to only 2300 cm$^{-1}$.

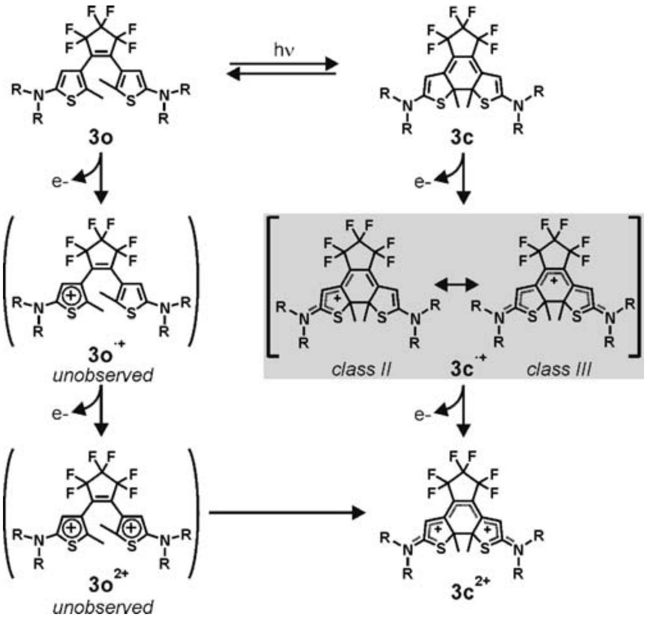
$$\Delta\tilde{\nu}_{1/2} = \sqrt{2310 \times \tilde{\nu}_{\max}} \qquad (2)$$

This, along with the observation of the solvent-independence of the near-infrared absorption band suggests that analysis in the framework of a fully delocalized class III system may be adequate for **3c**$^{\bullet+}$, similar to what has been done for the mixed valence radical cations of **5** and **6**.[6a] As noted above, in class III systems intervalence bands are frequently asymmetric or even exhibit vibrational fine structure.[1f,12a] Whether or not such asymmetry is present in the near-infrared absorption band of Figure 6a cannot be established based on the available data, and therefore the data is fitted with symmetric Gaussian functions which require a minimum of independent fit parameters. For fully delocalized

**Scheme 3. Chemical Structures of Four Molecules with Thienyl-linkers Previously Investigated in the Context of Organic Mixed Valence**[6a]



**Scheme 4. Graphical Summary of the Oxidation and Cyclization Processes Observed for Molecule 3**



systems, $H_{AB}$ may be calculated according to eq 3.[1a]

$$H_{AB} = \frac{\tilde{\nu}_{max}}{2} \tag{3}$$

For $3c^{\bullet+}$, this yields a value of 5550 cm$^{-1}$ (Table 1), which is similar to what has been reported for $6^{\bullet+}$ (5050 cm$^{-1}$) based on the same analysis.[6a] For $5^{\bullet+}$ a value of 4375 cm$^{-1}$ was reported, while for $7^{\bullet+}$ $H_{AB}$ = 5250 cm$^{-1}$ and for $8^{\bullet+}$ $H_{AB}$ = 6270 cm$^{-1}$.[6a] Alternatively, if one were to interpret the intervalence data of $3c^{\bullet+}$ in the framework of a class II mixed valence species, one would obtain $H_{AB}$ = 1511 cm$^{-1}$ based on eq 1 and $d_{AB} = d_{NN}$ = 9.3 Å, or $H_{AB}$ = 2289 cm$^{-1}$ for $d_{AB} = 0.66 \times d_{NN}$ = 6.1 Å. These values appear low both in comparison to those reported above for the radical cations of **5**−**8** as well as in comparison to the shorter system $1c^{\bullet+}$ discussed in the first half of this paper. Although it has been noted that in some cases the two-state model may be inadequate for analysis of intervalence bands in strongly coupled (class III) mixed valence system,[29] we restrict the current analysis to this model for the sake of simplicity. On a final note regarding the mixed valence character of $3c^{\bullet+}$, we point out that a comproportionation constant of 7.8 × 10$^3$ (based on $\Delta E$ = 230 mV, see above) is not in contradiction with interpretation of $3c^{\bullet+}$ as a class III system.

Scheme 4 summarizes our findings for molecule **3**. The open form (**3o**) photoisomerizes reversibly to the closed form (**3c**). The one-electron oxidized form of the open species ($3o^{\bullet+}$) and the corresponding two-electron oxidized species ($3o^{2+}$) are formed at very close potential, likely because the two amine units in molecule **3o** are only comparatively weakly interacting. Thus, in Scheme 4, radical monocation $3o^{\bullet+}$ is drawn as a charge-localized (class I) species. The dication $3o^{2+}$ undergoes spontaneous cyclization to $3c^{2+}$. One-electron oxidation of **3c** gives $3c^{\bullet+}$ which may be described adequately by two resonance structures: one implying full, the other implying partial delocalization of the odd electron. The discussion above leads to the conclusion that the fully delocalized structure is reasonable, although we cannot exclude definitively a significant contribution from the partially delocalized resonance structure. Further oxidation of $3c^{\bullet+}$ leads to $3c^{2+}$, which is the common two-electron oxidation product of both **3o** and **3c**. Interestingly, a solution containing a 1:1 ratio of **3o** and copper oxidant is photoswitchable to the $3c^{\bullet+}$ state (Figure S8 in Supporting Information).

## ■ SUMMARY AND CONCLUSIONS

Two dithienylperfluorocyclopentenes substituted symmetrically with two tertiary amino-groups have been explored from the perspective of mixed valence chemistry. While in molecule **1** it is possible to make a formal distinction between redox-active triarylamine groups and a dithienylperfluorocyclopentene bridging unit, this distinction is not meaningful for molecule **3**. Instead, when the nitrogen centers are attached directly to the thienyl rings, there is strong charge delocalization into the dithienylperfluorocyclopentene core, and one might consider the resulting radical monocations as partially "bridge-localized" species. Nevertheless, our study shows that thanks to the symmetrical nature of molecule **3** with its two easily oxidizable termini, the monocationic closed form of this compound exhibits spectroscopic and electrochemical properties that are typical for mixed valence species. For $\mathbf{3c}^{\bullet+}$, the experimental data is consistent with delocalization of the odd electron over the entire molecule (Robin-Day class III), while in the case of $\mathbf{1c}^{\bullet+}$, there is only partial charge delocalization (Robin-Day class II). In the open forms of both cations, the odd electron is localized on one branch of the otherwise symmetrical systems (Robin-Day class I). Because the open and closed forms can be interconverted by irradiation with UV and visible light, the extent of electronic communication is photoswitchable. Notably, intervalence absorptions in the molecules studied herein can be detected at long wavelengths (>900 nm) at which no photoisomerization reactions are induced, thereby allowing nondestructive interrogation of the cyclization state. This has been an important goal of much research on dithienylcyclopentenes.[30]

Attachment of the redox-active tertiary amine units directly to the thienyl-rings permits construction of molecular mixed valence systems with significantly shorter (geometrical and effective) electron transfer distances than what has previously been achieved for dithienylcyclopentene-based mixed valence molecules with inorganic redox centers.[11] What is more, it also introduces the interesting possibility of electrochemically inducing the cyclization reaction by a two-electron process.

In molecular wires, tertiary amine-substituted dithienylcyclopentenes may represent interesting photoswitchable building blocks. In their closed forms, they may serve as good hopping stations for long-range charge transfer between distant donors and acceptors because within these units, charge is strongly delocalized. In their open forms, by contrast, charge is localized and hopping events involving these molecular units as stations (also called stepping stones)[3b] have to occur over greater molecular distances.

## ■ EXPERIMENTAL SECTION

Commercially available chemicals were used as received without further purification. All reactions were carried out under nitrogen using solvents which were dried by routine methods. Thin-layer chromatography was performed using Polygram SIL G/UV254 plates from Machery-Nagel. For column chromatography, Silica Gel 60 from Macherey-Nagel was employed. Reaction products were characterized by $^1$H and $^{13}$C NMR spectroscopy (Avance DRX 300 spectrometer, using the deuterated solvent as the lock and residual solvent as an internal reference), by electron ionization mass spectrometry (EI-MS) using a Finnigan MAT8200 instrument, and by elemental analysis. Detailed synthetic protocols and product characterization data are given in the Supporting Information. Cyclic voltammetry was performed using a Versastat3−100 potentiostat from Princeton Applied Research equipped with a Pt disk working electrode, and a silver counter electrode. A silver wire did also serve as a quasi-reference electrode. Decamethylferrocene ($Me_{10}Fc$) was used as an internal reference,[18] but all experimentally determined potentials are reported relative to the ferrocenium/ferrocene ($Fc^{+/0}$) couple as is commonly done in electrochemistry. Prior to voltage scans at rates of 100 mV/s, nitrogen gas was bubbled through the dried solvent. The supporting electrolyte was a 0.1 M solution of tetrabutylammonium hexafluorophosphate. Optical absorption spectra were recorded on a Cary 5000 spectrometer from Varian or on a Cary 50 instrument from the same company. Copper(II) perchlorate was used as the preferred oxidant as described earlier.[19] Identical results were obtained with $NOBF_4$, but this compound is more difficult to handle and titration errors were generally larger.

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Synthetic protocols and characterization data for compounds **1**, **2**, **3**, **4**, **14**, **16**, **17** and for two reference compounds; optical absorption and cyclic voltammetry data for the two reference compounds mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) We note that the two oxidation waves have different intensities, suggesting that the photostationary state in the electrochemistry experiment differs from the 95% purity of **1c** derived from $^1$H NMR spectroscopy. We have made the observation that prolonged UV-irradiation of concentrated solutions of **1c** in acetonitrile (which are needed for cyclic voltammetry) leads to the appearance of an increasingly intense wave around 0.27 V vs Fc$^{+/0}$. This wave is likely due to increasing contamination of the solution with a photodegradation product. For the UV−vis experiments reported below, this problem does not occur because the respective solutions are less concentrated, and much shorter irradiation times can be employed.

(32) A subtraction of the near-infrared portions of the absorption spectra of **1c**$^{\bullet+}$ and **1o**$^{\bullet+}$ is shown in Figure S6 in the Supporting Information.

(33) Without in-depth computational work, the highest energy Gaussian cannot be assigned to a specific electronic transition with certainty. However, we note that the triarylamine radical cation band around 12 900 cm$^{-1}$ has been previously observed to exhibit a shoulder on its high energy side, see for example references 12a, 12b, and 34. The necessity to use a total of four Gaussians for the overall fit is therefore by no means unusual.

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(35) As pointed out by a reviewer, comparison to dinitroaromatic radical anions should be made with caution, not only because of their anionic nature but also because of the different amounts of ion-pairing in the bis(triarylamines) and the dinitroaromatic mixed valence species, as well as the different reorganization energies associated with intervalence charge transfer in the two types of systems.

(36) The remaining signal at 0.3 V vs Fc$^{+/0}$ is thus attributed to a remaining fraction of the open form of molecule **3**. The origin of the apparent wave at 0.4 V vs Fc$^{+/0}$ is unknown.

(37) An anonymous reviewer is acknowledged for correcting our initial interpretation of the experimental data in Figure 5a.