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RESEARCH ARTICLE

Variously Substituted Cyclopenta[2,1-*b*:3,4-*b*']difluorenyl Radicals: A Validation of *Clar*'s Rule

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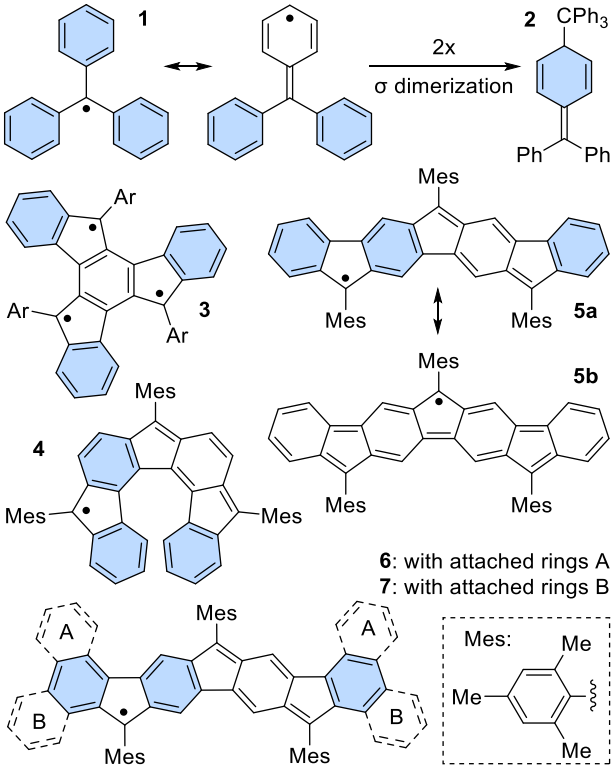
ABSTRACT

Two new cyclopenta[2,1-*b*:3,4-*b*']difluorenyl radicals were synthesized using *Suzuki* coupling to form a teraryl precursor, double *ortho* cyclization and reestablishment of conjugation as key steps. They were thoroughly characterized by electron paramagnetic resonance (EPR) and UV/Vis spectroscopy, as well as cyclic voltammetry, and complemented by quantum-chemical calculations. The latter provided insight into orbital energies and spin densities and gave simulated UV/Vis/NIR spectra. We previously proposed that these radicals are best described by resonance structures with the radical centers located in the outer five-membered rings. This interpretation is supported by calculated spin densities and follows *Clar*'s rule, favoring resonance formulas containing the maximum number of intact benzene rings. This suggestion is now further supported by experimental results: It turned out that the presumed centers of high spin density have mandatorily to be substituted by bulky aryl substituents, frequently used for the stabilization of carbon-centered radicals (i.e., mesityl or 2,6-dichlorophenyl) due to their orthogonal arrangement, and thus kinetic stabilization. In contrast, simple phenyl groups do not fulfill the needed criteria at these sites but can be introduced at the central ring, where calculated spin densities are lower. These results furthermore support the findings from quantum-chemical calculations that a triradical character of these radicals can be neglected.

1 | Introduction

Polyaromatic hydrocarbons (PHs) are π-conjugated systems typically composed of fused benzene rings. When these frameworks feature an alternating arrangement of six- and five-membered rings, as in indenofluorenes (IFs), they are classified as cyclopenta-fused polyaromatic hydrocarbons (CP-PAHs). While IFs display pronounced biradical character, systems incorporating an odd number of five-membered rings inevitably are radicals in their neutral and fully conjugated state. Organic carbon-centered radicals have been the subject of research for centuries; however, their intrinsic instability has long made them difficult to study. In the last decades, quite a number of remarkably stable carbon-centered hydrocarbon radicals have been reported since the proposal of the triphenylmethyl radical (**1**) by *Gomberg* (Scheme 1) [1].

However, only a small proportion of these radicals are sufficiently stable to be isolated and to withstand exposure to air, moisture, and solvents. In addition to their structural characteristics, they exhibit a range of promising electronic, optical, and magnetic properties, making them attractive for applications in organic electronics [2] and nonlinear optics [3]. Furthermore, their paramagnetic nature enables their use in spintronics [4, 5] and organic magnets [6–8], potentially enabling the development of fully organic spintronic devices [9]. Additionally, these systems show interesting aromatic behavior. While they are characterized by pronounced antiaromaticity, which is in accordance with their small calculated HOMO/LUMO gaps and the antiaromatic contribution arising from the indacene subunit. Nevertheless, our recent studies interestingly indicate that these compounds still exhibit a high degree of stability despite this significant antiaromatic character [10, 11].



SCHEME 1 | Triphenylmethyl radical (**1**), its σ dimer **2**, and a truxene-derived (tri-)radical **3**; **4**-**6**: helically and linearly arranged CP-PAH radicals, previously synthesized in our group. (Fully intact benzene rings are highlighted in blue).

The class of IFs has been extensively studied for the biradical character of its members, a pronounced antiaromaticity resulting from small HOMO/LUMO gaps, and its potential applications in organic electronic materials. On the contrary, derivatives containing an odd number of five-membered rings remain a relatively unexplored area of research. Early work in this area was reported by *Frantz* et al. [12], who synthesized the 10*H*,15*H*-–5,10,15-trimesityltruxen-5-yl radical, which was further investigated by *Yang* et al. and developed to a fully conjugated system **3**, where they claim a triradical structure for this compound [13].

Continuative studies in this field were conducted by our group. We synthesized, investigated, and reported a helical heptacyclic scaffold **4** composed of alternating six- and five-membered rings [14]. Subsequent work focused on linear scaffolds, including **5** as a constitutional isomer of **4** and π-extended nonacyclic radicals **6** and **7** [10, 11].

The synthesis of sufficiently stable radicals is a prerequisite for their further study and application. A common feature of these carbon-centered radicals is a kinetic stabilization of sites with highest spin densities by attaching bulky substituents and thereby preventing possible side reactions such as σ dimerization [15]. These substituents are mainly based on aromatic groups, such as the commonly used mesityl group. In addition, other sterically demanding substituents can be employed, including 2,4,6-trichlorophenyl, which additionally stabilizes the reactive sites through electronic effects, as well as substituents that are part of larger aromatic systems, such as 9-anthracenyl [13]. Other substituents have also been employed in connection with the biradicaloid IFs, such as unsubstituted phenyl [16] or less substituted groups like 2,6-dichlorophenyl [17, 18], pentafluorophenyl, and other fluorinated substituents, such as 3,5-bis(trifluoromethyl)phenyl [19]. While phenyl as a substituent usually does not provide sufficient stability, as evidenced by the decomposition of the corresponding products [16, 20, 21], the other listed groups usually give positive results.

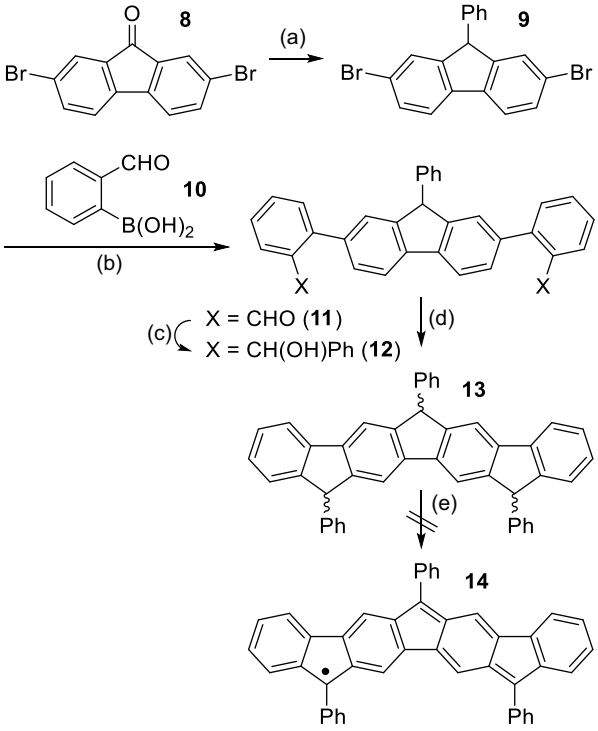
In this manuscript, we wish to report our results on the synthesis and investigation of diversely substituted cyclopenta[2,1-*b*:3,4-*b*']difluorenyl radicals, focusing on the influence of electronic and steric substituent effects on their stability.

2 | Results and Discussion

As previously mentioned, phenyl was rarely used as a bulky substituent in these systems due to an inherent instability of thus substituted radicals. It had been indicated that phenyl-substituted radicals were degraded under aerobic conditions. Although solutions kept under an inert atmosphere were reported to be stable, the duration of stability was not specified. Consequently, due to these air-sensitivity issues, no investigations of the electronic properties were conducted.

Our prior studies focused on the synthesis of an air- and moisture-stable hydrocarbon radical with four six- and three five-membered rings alternately fused to a heptacyclic system with bulky mesityl residues. Using our previously published synthetic route [10], we at first aimed for a phenyl-substituted radical **14** (Scheme 2).

The synthetic route started with commercially available 2,7-dibromofluoren-9-one (**8**), which was transferred into the respective phenyl-substituted fluorene **9** via a *Lewis* acid-mediated reduction/electrophilic aromatic substitution protocol. Subsequent double *Suzuki* coupling with 2-formyl-phenyl boronic acid (**10**) afforded dialdehyde **11**, which was subjected to a nucleophilic addition with a phenyl *Grignard* reagent (→ **12**), followed by a *Lewis* acid-induced *ortho* fusion to yield the heptacyclic scaffold **13**. The mixture of possibly formed diastereoisomers was deprotonated in the final step with potassium *tert*-butanolate and immediately oxidized with tetrachloro-*p*-benzoquinone (chloranil) yielding a light red solid. Initial analysis by ^{1}H NMR spectroscopy revealed resonances in conventional frequency ranges (0–12 ppm) in the respective spectrum, which is untypical for paramagnetic compounds. Identification of the radical was neither possible by mass spectrometry. These observations indicate that radical **14** was possibly formed but was not sufficiently stable. A possible explanation for this behavior can be traced back to the unhindered rotation of the phenyl units. If its orthogonal arrangement is no longer maintained, interactions between the orbitals of the molecular framework and those of the substituents may occur. This enables delocalization of the radical center, resulting in an increased spin density, e.g., at the *para* positions of the phenyl rings. Due to the inherent instability of phenyl-based radicals [22], subsequent reactions such as radical propagation [23] or, as observed for the *Gomberg* radical, dimerization via radical coupling (e.g., to **2**) are likely to occur [24].



SCHEME 2 | Attempted synthesis of a phenyl-substituted polyaromatic radical. Conditions: (a) $FeCl_3$, Me_3SiCl, Et_3SiH, benzene, 50°C, 5 h (89%); (b) cat. $Pd(dppf)_2$, Cs_2CO_3, toluene/H_2O (1:1), 105°C, 18 h (93%); (c) PhMgBr, THF, 0°C to rt, 15 min (not isolated); (d) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C to rt, 1 h (56%, two steps); and (e) 1) KO*t*Bu, 2) *p*-chloranil, THF, 60°C, 16 h (no product isolated).

We previously reported that calculated electron paramagnetic resonance (EPR) data for mesityl-substituted radical **5** indicate a strong delocalization of spin density over all carbon atoms, and calculated *Mulliken* atomic spin densities revealed highest spin densities at carbon atoms C-6, C-12, and C-15, with top values at positions C-12 and C-15 (0.41) and a comparatively smaller value at C-6 (-0.29) [10]. Additionally, calculation of natural orbital occupation numbers [25] and utilization of *Yamaguchi*'s scheme [26, 27] revealed a vanishingly small triradical character of the compound, indicating that the radical predominantly resides on one of the outer five-membered rings, more precisely at positions C-12 or C-15 (Figure 1; the most significant resonance formula **5a** and formula **5b** with minor relevance are given in Scheme 1). This is consistent with *Clar*'s rule, stating that the most stable isomer or (here) the most significant resonance formula is that with the maximum number of fully intact benzene rings [28, 29]. Although this rule was originally intended to cover only benzenoid compounds (i.e., consisting only of six-membered rings), it is in between used for the evaluation of polycyclic aromatic compounds of all kind [30, 31].

This raised the question of whether the framework can still be stable with a phenyl substituent at the position with smaller spin density (C-6), when positions C-12 and C-15 are substituted with a mesityl group. We started with dialdehyde **11**, whose synthesis was already described (*vide supra*). Nucleophilic addition with a mesityl *Grignard* reagent yielded diol **15**, which was then subjected to a *Lewis* acid-induced *ortho* fusion, yielding the heptacyclic scaffold **16**. In a finalizing step, the mixture of diastereoisomers **16** was

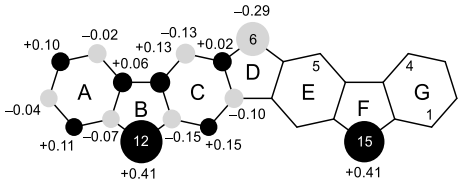
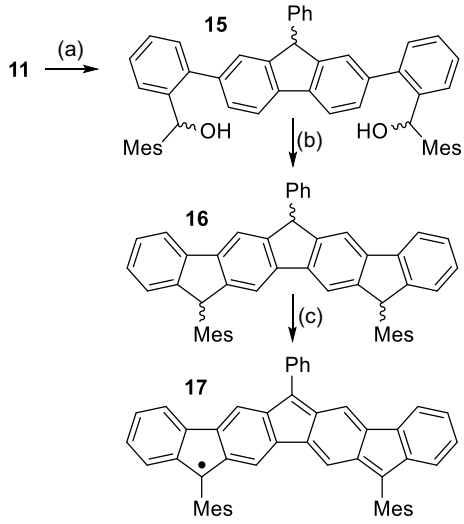


FIGURE 1 | Calculated spin densities of **5**, with highest spin densities at positions C-12 and C-15 (0.41) and a comparatively smaller value at C-6 (–0.29) [10].

deprotonated with potassium *tert*-butanolate and immediately oxidized with chloranil to yield the fully conjugated radical **17** as a dark green solid (Scheme 3).

Evidence for the radical nature of **17** was provided by the absence of resonances in conventional frequency ranges in the respective ^{1}H NMR spectrum and by the compound's EPR activity. A measured X-band EPR spectrum (Figure 2) showed a single line centered at $g = 2.0037$ without any discernible hyperfine couplings. A *Yamaguchi y* value of 0.26 was calculated, which is in good accordance with prior reports from our group. Generally, these calculated values depend to a non-negligible extent on the computational method used and, as reported recently, tend to be overestimated; they should thus be interpreted with caution [32].

The successful synthesis of this radical provides experimental evidence that the monoradical configuration is the most pronounced among the possible resonance formulas, giving a clear indication that the radical center is primarily localized on the outer five-membered rings, enabling the isolation of radical **17** as a stable compound. In contrast, a triradical configuration would locate an additional radical center at position C-6, thereby preventing sufficient stabilization, as observed for compound **14**. These observations are consistent with the relatively small calculated *y* value of 0.26. Generally, radical **17** demonstrates a sufficient stability behavior under ambient conditions, by showing resistance toward air, moisture, and solvents. However, compared to compound **5**,



SCHEME 3 | Synthesis of radical **17** with only one of the substituents being a phenyl group. Conditions: (a) MesMgBr, THF, 0°C to rt, 15 min (not isolated); (b) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C to rt, 1 h (84%, two steps); and (c) 1) KO*t*Bu, 2) *p*-chloranil, THF, 50°C, 30 min (81%).

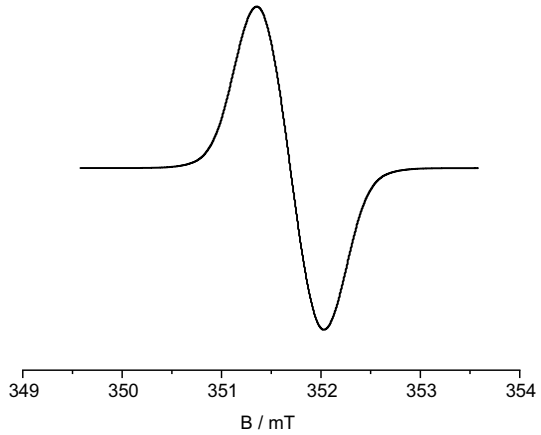


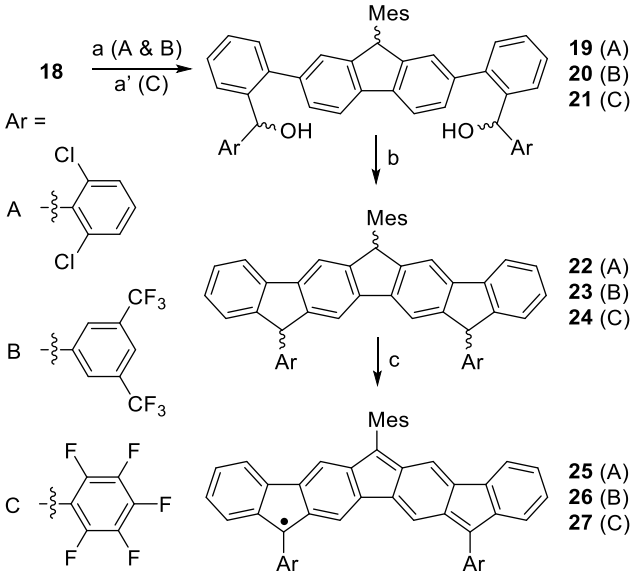
FIGURE 2 | Cw X-band (9.8630 GHz) EPR spectrum of **17** in toluene (1 mM) at ambient temperature showing a single resonance signal around $g = 2.0037$.

a noticeable decreased stability in solution is observed, which is evidenced by its visual decomposition within hours.

In principle, an instable core demands the use of bulky and electron-deficient substituents [33]. As the phenyl substituent does not fulfil these necessary criteria, this likely explains the observed instability of radical **14** [18] and the noticeable decreased stability for **17**. This key feature, more precisely the stabilization of the polyaromatic framework, allows the introduction and study of various functional groups and their influence on the radical character, and may help elucidate essential criteria for radical stabilization. For this purpose, a range of substituted groups was selected (Scheme 4, A-C). Since the effect of substituents was to be analyzed, it seemed advantageous to rely on the more stable systems featuring a mesityl group at position C-6. As realized in radical **17**, positions C-12 and C-15 can presumably be functionalized with various alternative stabilizing substituents.

Following the established synthetic route given in Schemes 2 and 3, these alternative substituents can again be introduced starting from dialdehyde **18**. Following a reported procedure by *Jiang* et al. [18] 2-bromo-1,3-dichlorobenzene was converted into the corresponding *Grignard* species in a proposed in situ approach and subsequently reacted with dialdehyde **18** to generate diol **19**. Treatment with $BF_3{\cdot}OEt_2$ furnished the heptacyclic scaffold **22**. Deprotonation with potassium *tert*-butanolate and immediate oxidation with chloranil yielded radical **25** as a dark green solid. The radical turned out to be stable under ambient conditions. Similarly, following a published procedure by *Sharma* et al. [19] either 1-bromo-3,5-bis(trifluoromethyl)benzene or 1-bromo-2,3,4,5,6-pentafluorobenzene were transferred into the corresponding *Grignard* species and reacted accordingly with dialdehyde **18** furnishing diols **20** and **21**. Subsequent *Lewis* acid-induced *ortho* fusion yielded the heptacyclic scaffolds **23** and **24**. However, treatment with potassium *tert*-butanolate and immediate oxidation with chloranil did not result in formation of the corresponding radicals **26** and **27**.

Initial evidence for the radical nature of **25** was again provided by the absence of resonances in the respective ^{1}H NMR spectrum. Similarly, a cw X-band (9.4214 GHz) EPR spectrum (Figure 3) in



SCHEME 4 | Synthesis of heptacyclic radicals with a variation of substituents. Conditions: (a) Ar-Br: 2-bromo-1,3-dichlorobenzene or 1-bromo-3,5-bis(trifluoromethyl)benzene, ^{i}PrMgCl, THF, 0°C to rt, 15 h (not isolated); (a') 1-bromo-2,3,4,5,6-pentafluorobenzene, Mg, THF, 40°C, 1 h or (pentafluorophenyl)magnesium bromide, THF, rt, 15 min (not isolated); (b) $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C to rt, 1 h [**22** (A): 65%, **23** (B): 33%, **24** (C): 43%, two steps]; and (c) 1) KO*t*Bu, 2) chloranil, THF, 60°C, 16 h [**25** (A): 52%, **26** (B) and **27** (C): no product isolated].

toluene (1 mM) measured at ambient temperature showed a broad single line centered at $g = 2.0038$ without any discernible hyperfine couplings and confirmed the compound's paramagnetic nature.

Calculated EPR data indicate that spin density is significantly delocalized across all carbon atoms of the heptacyclic framework, possibly explaining the observed unresolved hyperfine structure. This is further supported by calculated small coupling constants (Supporting Information). *Mulliken* atomic spin densities (Figure 4) are calculated for carbon atoms C-6, C-12, and C-15: For radical **17** highest spin densities are located at C-12 (0.43) and C-15(0.43),

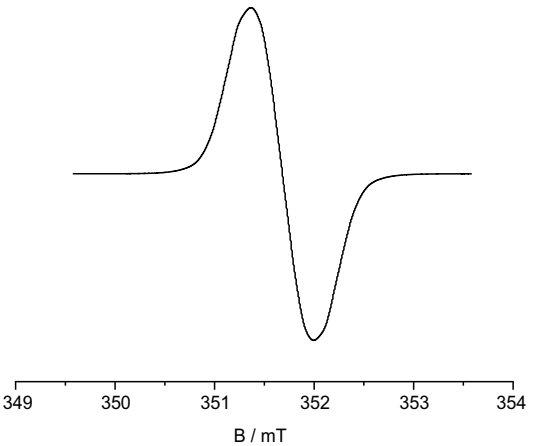


FIGURE 3 | Cw X-band (9.8633 GHz) EPR spectrum of **25** in toluene (1 mM) at ambient temperature showing a single resonance signal around $g = 2.0038$.

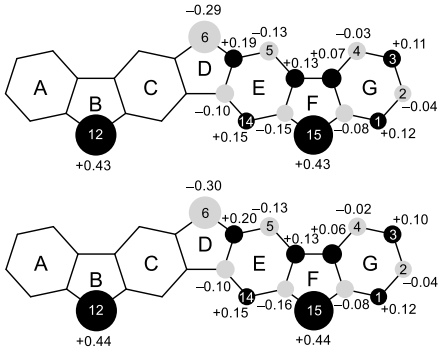


FIGURE 4 | Calculated spin densities of **17** (top) and **25** (bottom).

while a slightly lower value of -0.29 was calculated for C-6. Similar values were obtained for radical **25**, with spin densities of 0.44 at both C-12 and C-15, and a somewhat reduced value of -0.30 at C-6.

In contrast to **25**, a rather unusual behavior was observed during the analysis of the corresponding ^{1}H NMR spectra of **26** and **27**. While the spectrum of **25** showed virtually no resonances, the spectra of radicals **26** and **27** exhibited several distinct signals, suggesting a diamagnetic behavior. A more detailed analysis by mass spectrometry rather indicated the failure of both reactions. These observations provide strong evidence that the corresponding radicals were likely generated, but lacked persisting stability in analogy to the results obtained for **14**. A closer examination of these three compounds (**14**, **26**, and **27**) revealed structural similarities, particularly regarding the unhindered rotatability of the substituents. Although the CF_3 (**26**) groups and even the *ortho* fluorine substituents introduce steric hindrance, this appears insufficient to maintain a continuous orthogonal orientation, which possibly leads to a temporary orbital overlap with increase of spin density at the *para* positions of the corresponding substituents. Such an arrangement can facilitate secondary reactions, similar to those described for the *Gomberg* radical. A comparable behavior can also be proposed for structure **27**.

These valuable insights allow us to potentially establish criteria for the formation and stabilization of radical species: Bulky substituents only need to be present at sites of high spin density. These substituents are necessarily in an orthogonal arrangement relative to the core and the thus orthogonal π systems prevent spin delocalization into the periphery of the substituent, which would finally allow for σ dimerization, i.e., to a decomposition of the radical. Positions of medium spin density can be substituted even with phenyl substituents, where at least a temporary coplanarity can be assumed. No substituents at all are required at positions with hardly any significant spin density. These findings have always been implied to some extent in previous work, since bulky substituents in organic radicals have only been attached to positions of assumed high spin density, although some spin density is present at all positions of such compounds (c.f., Figure 4).

The energies of the SOMOs of radicals **17** (top) and **25** (bottom) are −5.07/−3.19 eV (**17**) and −5.21/−3.34 eV (**25**) for the α- and β spin, respectively (Figure 5).

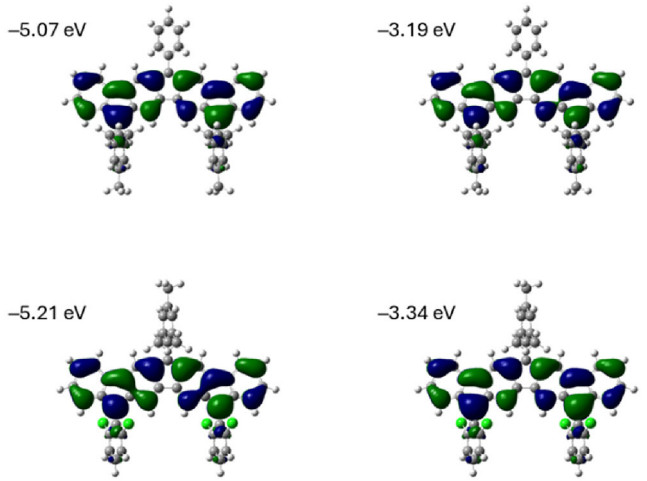


FIGURE 5 | Calculated SOMOs of α and β electrons for radicals **17** (top) and **25** (bottom; isovalue: 0.02 electrons$^{1/2}$ bohr$^{-3/2}$; calculated at the upbe0/def2tzvp/GD3BJ level).

Cyclic voltammetry enabled the electrochemical characterization of **17** and **25**, with redox potentials referenced to the ferrocene/ferrocenium couple Fc/Fc$^+$ (Figure 7) [34]. For radical **17**, we detected three quasi-reversible redox processes centered at $E^0_{½}(CH_2Cl_2)$ values of −2.04, −1.08, and 0.01 V. These results are in accordance with prior results. A direct comparison with prior findings from our group [10] (Figure 6) allows to potentially assign the observed potentials to the described redox processes, where the first two values indicate reductions to the di- and monoanion, respectively, whereas the last value most likely refers to oxidation to the monocation. In contrast, radical **25** displays six quasi-reversible redox processes centered at $E^0_{½}(CH_2Cl_2)$ values of −1.92, −1.82, −1.32, −0.98, −0.49, and 0.15 V. However, while for values −1.92 and −0.98 reduction to the di- and monoanion and for 0.15 V the oxidation to the monocation can again be assumed, values −1.82, −1.32, and −0.49 might be suspected to be part of another species. Nevertheless, analysis by ^{1}H NMR spectroscopy does not indicate the presence of a diamagnetic

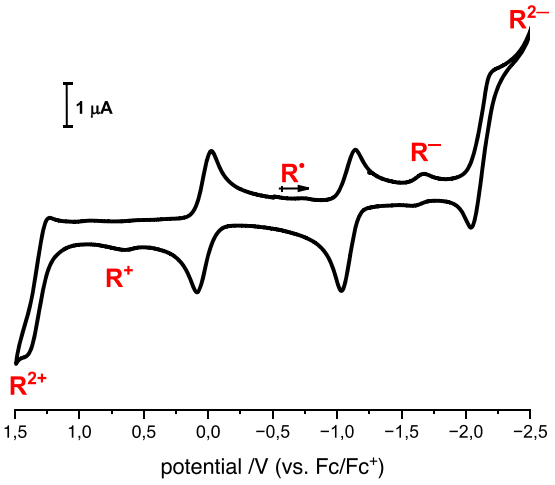


FIGURE 6 | Cyclic voltammogram of **5** recorded in CH_2Cl_2 at room temperature (vs. Fc/Fc$^+$, v (CH_2Cl_2) = 100 mV s^{-1}; Pt/[NBu_4][$Al(OC_4F_9)_4$]/Ag) as a reference plot [10].

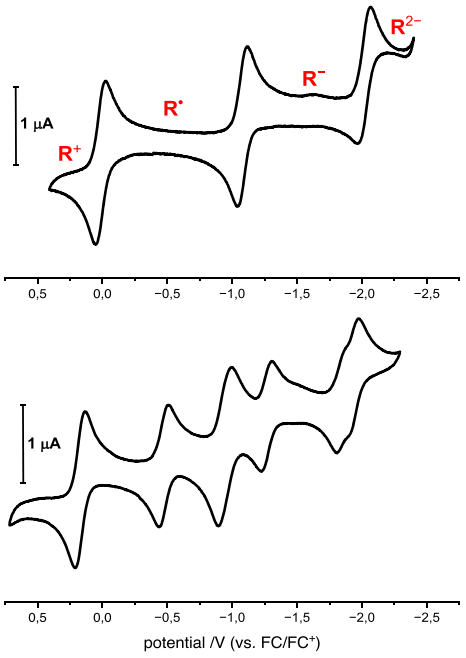


FIGURE 7 | Cyclic voltammograms of **17** (top) and **25** (bottom) recorded in CH_2Cl_2 at room temperature (vs. Fc/Fc^+, ν (CH_2Cl_2) = 100 mV s^{-1}; Pt/[NBu_4][PF_6]/Ag).

compound, nor does evaluation by EPR spectroscopy demonstrate the presence of another species. These additional redox cycles might in fact arise from the presence of the chlorine atoms in the substituents. Very similar values have been reported for 2,6-dichlorobiphenyl by *Farwell* et al. [35]. This interpretation is further supported by the closely separated virtual orbital energy levels of the chlorinated species (see Supporting Information), which should allow for further redox transitions observable in the cyclic voltammogram.

UV/Vis spectra of radicals **17** and **25** in CH_2Cl_2 were analyzed to evaluate substituent effects on the compounds' photochemical properties, with direct comparison to the reference system **5** (Figure 8). Comparison of **5**, **17**, and **25** shows only minor differences in their electronic transitions. All three compounds display closely aligned absorption bands. Specifically, the regions between 425–600, 600–725, and 750–930 nm display comparable band positions and intensities for **5**, **17**, and **25**. The only significant difference upon incorporation of the 2,6-dichlorophenyl substituents in **25** is observed at 750 nm, where a band/shoulder of low intensity, which is also present in the calculated spectrum, appears. Overall, these results indicate that the substituents do not significantly influence the absorption behavior, and that the observed transitions arise predominantly from the π orbitals of the heptacyclic core.

IFs are known to display extremely short excited-state lifetimes, potentially due to conical intersections, thereby suppressing fluorescence activity [36]. This inactivity was also observed for compounds **17** and **25**, which is in accordance with prior reports by our group [10, 11, 14].

Additionally, UV/Vis/NIR spectra of **17** and **25** were calculated using time-dependent density functional theory calculations [upbe0/def2tzvp/GD3BJ level] with a simulated solvent field

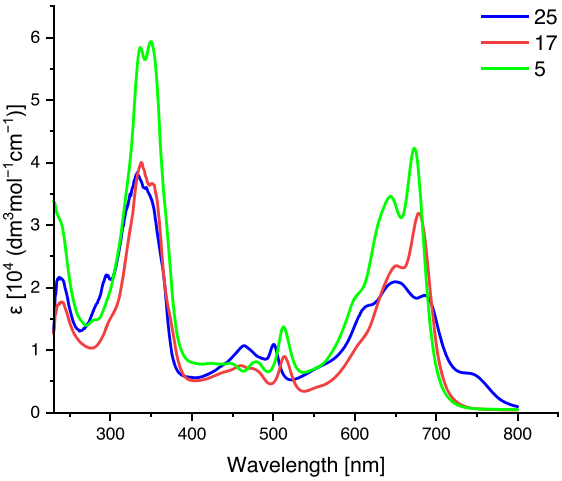


FIGURE 8 | Comparison of UV/Vis spectra of **5**, **17**, and **25** in CH_2Cl_2.

of methylene chloride (Figure 9). Only the π orbitals of the heptacyclic core are involved in these transitions, with negligible contribution from the aryl substituents. Significant transitions are listed in the Supporting Information.

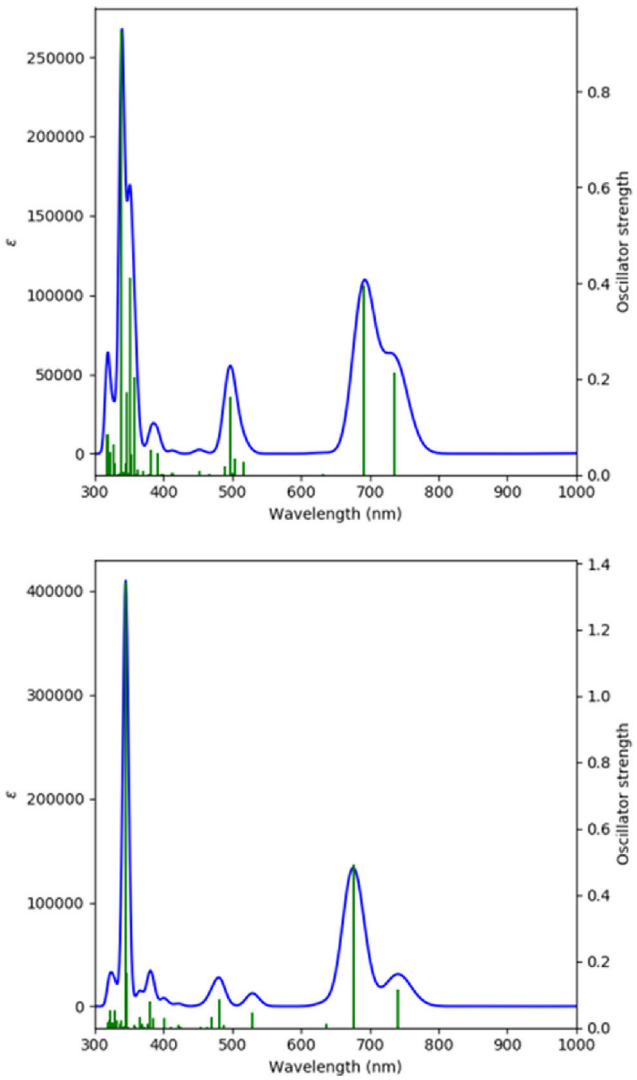


FIGURE 9 | Calculated UV/Vis/NIR spectra of **17** (top) and **25** (bottom) in CH_2Cl_2.

3 | Conclusion

We synthesized two further examples of cyclopenta[2,1-*b*:3,4-*b*']difluorenyl radicals using *ortho* cyclization and re-establishment of the conjugation as the key steps. Quantum-chemical calculations and the empirical rule by *Clar* already suggested that highest spin density is positioned in the outmost five-membered rings of these altogether three available compounds. This would leave a maximum number of fully intact benzene rings in the respective resonance formula. With the findings in this work, we now have further striking support for this claim by experimental findings. Radical-stabilizing substituents are mandatorily positioned at the outer cyclopentadiene rings (with high spin density), while a phenyl substituent, usually not sufficient for the stabilization of a radical, can be present at the central five-membered ring with significantly reduced spin density. As expected, we found that the frequently used mesityl and the 2,6-dichlorophenyl substituents meet the required conditions for a stabilization. Due to their steric hindrance, they keep an orthogonal orientation preventing spin delocalization to positions in the substituent, which would lead to destructive follow-up reactions at these positions. A phenyl group at the outer positions was not able to prevent a virtually immediate degradation of the radical. These experimental results furthermore support the findings from quantum-chemical calculations that a triradical character of these radicals can be neglected.

Acknowledgments

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Conflicts of Interest

The authors have no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. Experimental procedures, NMR and further spectra for new compounds, details of DFT calculations, and geometries for all calculated structures are included in the Supporting Information. The authors have cited additional references within the Supporting Information [37–76].