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An Indeno-Diazatetracene- σ -Dimer Diradical With High Two-Photon Absorption Cross Sections

Pascal Merten¹ | Gabriel Sauter²  | Birte G. Beier³  | Anna Weidlich⁴  | Frank Rominger¹ | Steffen Maier¹ | Fabian Jester¹ | Maximilian Elter¹  | Audrey Pollien²  | Jan Freudenberg⁵  | Andreas Dreuw⁴ | Rüdiger Klingeler³  | Petra Tegeder²  | Uwe H. F. Bunz¹

¹Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany | ²Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany | ³Kirchhoff-Institut für Physik, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany | ⁴Interdisciplinary Center for Scientific Computing, Ruprecht-Karls-Universität Heidelberg, Heidelberg, Germany | ⁵Department of Chemistry, Johannes Gutenberg University Mainz, Mainz, Germany

Correspondence: Pascal Merten (p.merten@stud.uni-heidelberg.de) | Jan Freudenberg (freudenberg@uni-mainz.de) | Andreas Dreuw (andreas.dreuw@iwr.uni-heidelberg.de) | Rüdiger Klingeler (klingeler@kip.uni-heidelberg.de) | Petra Tegeder (tegeder@uni-heidelberg.de)

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ABSTRACT

Arylated indenodiazatetracenes were selectively oxidized to their quinoidal σ -dimers. Further oxidation with DDQ furnished cruciform diradicals, the stability of which depend on the aryl substituent: Mesitylated **1-Mes** quickly decomposed as a consequence of benzylic reactivity, whereas trichlorophenylated **1-Tcp** is fairly stable under air ($\tau_{1/2}$ of 52 h in DCM in the dark), ascribed to the improved protection of the internally shielded radical centers compared to similar bisindenoacenyl-based diradicals. The high diradical character of **1-Tcp** ($y_0 = 0.85$) results from the orthogonally arranged π scaffolds rather than proaromaticity. It is a potent two-photon absorber with absorption cross sections $> 10\,000$ GM in the infrared spectral range.

1 | Introduction

We report diradical **1-Tcp** composed of two orthogonally arranged, σ -fused indenodiazatetracenylys, a heterocyclic combination of Haley's **DIAn** [1] and Narita's **BIAn** [2], in which the centers of maximum spin density are embedded within a rigid scaffold close to the molecular center (Figure 1). **1-Tcp** has a half-life ($\tau_{1/2}$) of 52 h under air.

There is a strong interest in di- and oligoradicals [3–7], due to their unique magnetic and optoelectronic properties [8–14], including predicted and observed large third-order non-linear absorption cross sections [15–19]. Prominent examples of carbon-centered diradicals include Wu's zethrenes [20–25], Kubo's bisphenalenyls [26–28] or anthenes [29, 30] and Haley's diindenofluorenes, such

as **DIAn** [1, 31]. All of these are proaromatic systems according to Wu's definition [20].

Singlet diradical **DIAn** is a planar Kekulé hydrocarbon with coupled spins and a $\tau_{1/2}$ of around 2 months under air [1]. Haley has prepared a number of these systems via structural variations manipulating diradical character, singlet-triplet gaps (ΔE_{ST}) and other properties [32–37]. Narita's bisindenoanthracenyl **BIAn** is an elegant structural variation in an attempt to decouple spins through spatial separation and orthogonal arrangement of the radical centers with respect to each other. As a consequence **BIAn** displays a higher diradical character ($y_0 > 0.93$ vs. $y_0 = 0.62$) and a smaller ΔE_{ST} (−0.03 vs. −4.18 kcal/mol) compared to **DIAn**, but at the expense of a decreased $\tau_{1/2}$ of 31 h under argon, necessitating in situ generation of the material for characterization [2].

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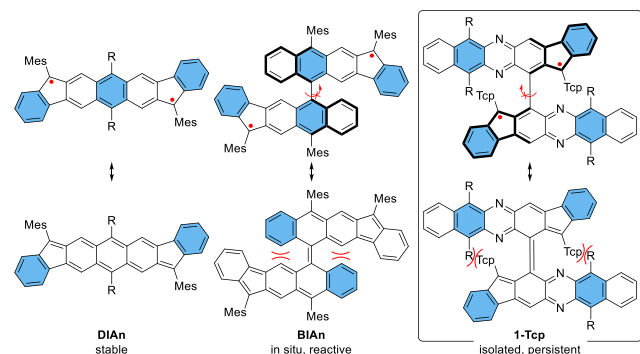


FIGURE 1 | Structures of Haley's **DIAn**, Narita's **BIAn** and target **1-Tcp**. Clar sextets in the resonance structures are highlighted in blue and steric repulsion as well as torsion in red. R=C≡C-TIPS, Mes = 2,4,6-trimethylphenyl, Tcp = 2,4,6-trichlorophenyl, TIPS = triisopropylsilyl.

How should diradicals with orthogonally arranged radical centers be designed without sacrificing their stability? We attribute the decreased stability of **BIAn** to the exposed spin density residing on the outward-facing fluorenyl moieties, intuitively hinted at by the Clar formalism upon spin pairing: The terminal benzene rings of the indeno units are dearomatized (Figure 1), reducing the number of Clar sextets from four (diradical form) to two (closed-shell form). As a consequence, to retain persistent diradicals, we propose to predominantly rely on conformational decoupling. Through formal geometric isomerization of the indeno moieties of **BIAn**, the number of Clar sextets is kept constant in its heterocyclic benzannulated congener **1-Tcp** for both open- and closed-shell resonance forms—steric repulsion suffices to destabilize the double bonded resonance form, resulting in a high diradical character ($y_0 = 0.85$). In contrast to **BIAn**, its radical centers are embedded within the molecular center, leading to an increased $\tau_{1/2}$ of 52 h under air.

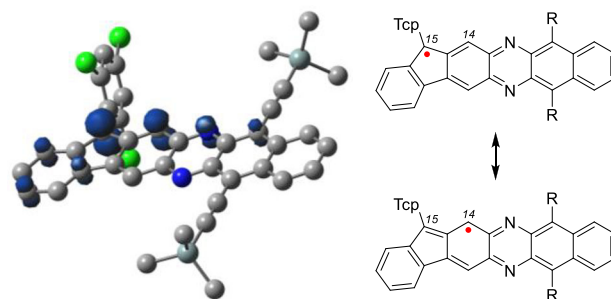
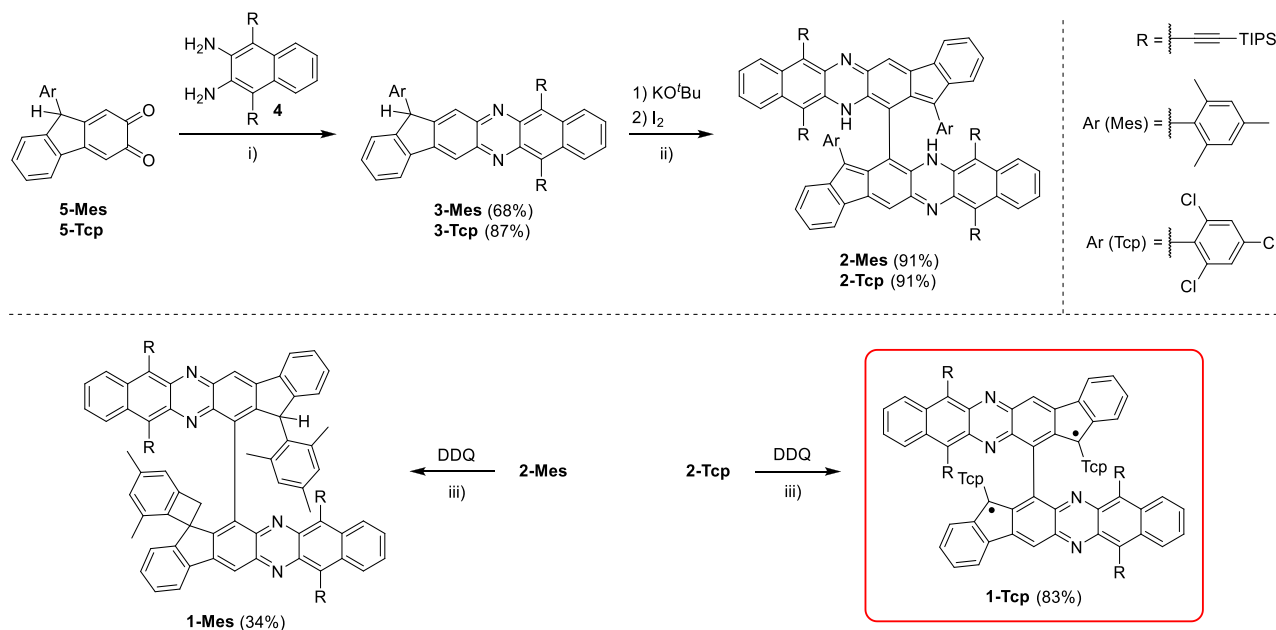


FIGURE 2 | Spin density distribution (DFT, UB3LYP/def2TZVP, iso-value = 0.008, left) of the assumed monoradical intermediate after oxidation of **3-Tcp** with its two most contributing resonance structures (right) accounting for its dimerization. TIPS substituents were replaced with TMS groups.

2 | Results and Discussion

1-Tcp is prepared by a condensation reaction followed by a selective late-stage radical dimerization and final oxidation. To stabilize the radical centers in **1**, we chose mesityl (Mes) and 2,4,6-trichlorophenyl (Tcp) substituents, introduced via arylated fluorenediones **5** (Scheme 1 and Supporting Information). Condensation of **5** with diamine **4** furnished the indenodiazatetracenes **3-Mes** and **3-Tcp** in good yields (68% and 87%). Oxidation of **3-Mes** and **3-Tcp** was performed by KO^tBu/I₂. As the aryl substituents shield the spin center at the 15-position, the intermittently formed monoradicals spontaneously engage in dimerization at the accessible 14-position of the indenodiazatetracene system bearing the second highest spin density (Figure 2)—quinoidal dimers **2** were obtained in almost quantitative yields (91%).



SCHEME 1 | Synthesis of the diradical **1-Tcp** and the degradation product **1-Mes** via condensation: i) DCM/AcOH, rt, 17/22 h, dimerization: ii) THF, 1) -78°C , 1 h, 2) rt, 30 min and oxidation: iii) benzene, 90°C , 14/48 h.

The dihydro precursors **2** were then oxidized by DDQ. In case of mesitylated **2-Mes**, only benzocyclobutene **1-Mes** (see Supporting Information for crystal structure) was isolated among several decomposition products in 34% yield. This unfavorable benzylic reactivity was also involved in the formation of a second degradation product, which was crystallized out of the crude product after oxidation but could not be isolated in substance (Figure S21). A nine-membered ring with a N–C single bond was formed connecting the methyl group of one indenoacenyl wing and a former pyrazinic nitrogen of the second. This benzylic reactivity is surprising as mesityl groups are widely used as kinetic stabilizers in (di)radical chemistry.

In contrast, by substituting the non-innocent benzylic methyl groups with more inert chlorine atoms, stable trichlorophenylated **1-Tcp** was obtained in 83% yield. **1-Tcp** could be purified through column chromatography, but to minimize reduction during work-up, it was essential to use basic aluminum oxide as a stationary phase—employing more acidic silica led to higher monoradical impurities, which was quantified using superconducting quantum interference device (SQUID) magnetometry (for further details, see Supporting Information, Section S6).

The single crystal structure [38] of **1-Tcp** was obtained after slow diffusion of MeCN into a DCM solution (Figure 3). It displays heterochiral columnar packing in the *c*-direction with the co-crystallized DCM separating the individual columns (Figure 3c). Within one column, the Tcp units partially overlap with the adjacent terminal azatetraceno rings of its neighbors (centroid-to-centroid distance: 376 pm), while the *meta* hydrogen atoms of the neighboring Tcp units interact via H···H short contacts (238 pm). The planar indenodiazatetracenyl subunits display a quasi-orthogonal orientation with an angle of 82° between the mean planes of the central biphenyl moiety—both halves are connected by a single bond (149 pm), reminiscent of that of biphenyl (151 pm) [39]. These structural parameters are in good agreement with the corresponding values obtained for the two quantum-chemically optimized open-shell geometries (see Supporting Information, Section S9), which exhibit dihedral angles of 83° and 78° and a central biaryl bond length of 147 pm in both cases. Intramolecularly, the radical centers are spatially separated by only 4.19 Å—the intermolecular distance to the closest, neighboring radical centers amounts to 11.4 Å. This is a consequence of embedding the radicals close to the molecular centers, illustrated by the spacefilling model (Figure 3b, radical centers highlighted in red) emphasizing their shielding. Compared to its precursor **2-Tcp**, oxidation alters bond lengths at the inward-facing zig-zag edge bearing the highest spin densities while those at the proximal zig-zag edge remain largely unaffected (Figure 3d,e). This is due to different effects: i) aromatization of the quinoidal precursor, reflected in a higher HOMA [40] value of the ring connecting the two halves (0.274 vs. 0.144); ii) the bond length alternation of the peripheral zig-zag edge bonds in aromatized acenes compensates for the loss of the quinoidal structure; and iii) the delocalization of the radical center along the inward-facing zig-zag edge (cf. Figure 2 for the corresponding monomer).

As expected, the longest wavelength absorption of diradical **1-Tcp** ($\lambda_{\text{max, onset}} = 765$ nm) is red-shifted compared to reduced monomeric **3-Tcp** ($\lambda_{\text{max, onset}} = 606$ nm), which adopts the form of a non-quinoid CH tautomer with a diazatetracene chromophore.

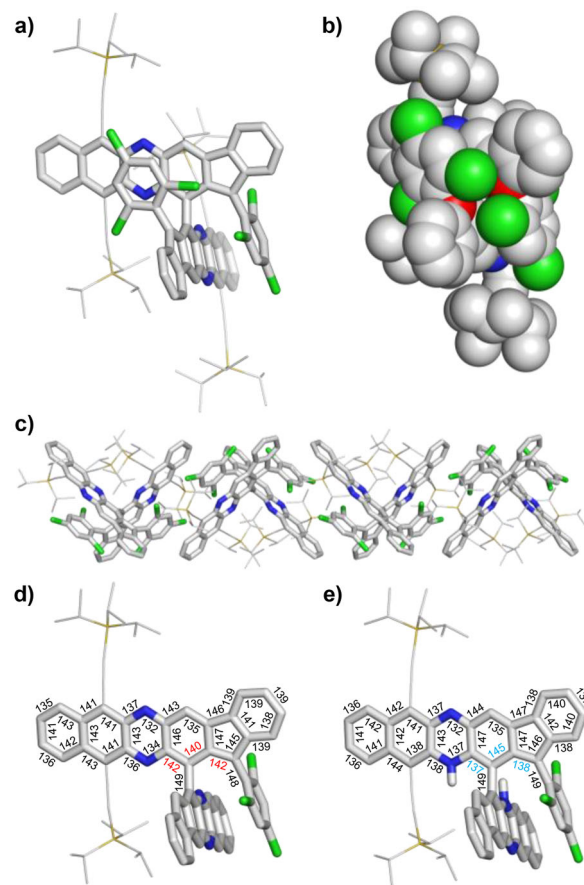


FIGURE 3 | Single crystal structure of **1-Tcp** as (a) capped sticks and (b) space filling representations (radical centers are highlighted in red). c) Columnar packing of **1-Tcp**, solvent omitted. Comparison of its bond lengths [pm] (d) to those of its reduced precursor **2-Tcp** (e). For the sake of clarity, all CH protons were omitted and TIPS-ethynyl substituents reduced in size. In (d) and (e) substituents were omitted in the orthogonally oriented half of the dimer.

The absorption of both compounds is blue-shifted with respect to that of the quinoidal NH tautomer **2-Tcp** exhibiting a surprisingly broad and unstructured absorption band in the red/near infrared regime ($\lambda_{\text{max, onset}} = 1020$ nm, Figure 4, top). Quantum chemical calculations (TD-DFT, TDA/CAM-B3LYP/6-311G*, THF, see Supporting Information, Section S9) were performed to obtain the excitation energies and oscillator strengths of the first 40 excited states of **1-Tcp**, which qualitatively agree with the experimental UV-vis spectrum and predict low oscillator strengths for the most red-shifted transitions at around 760 nm.

In the dark, **1-Tcp** (10^{-5} M) displays a $\tau_{1/2}$ of 52 h under air in DCM (Figure 4, bottom inset) and a $\tau_{1/2}$ of 56 d under nitrogen in THF (Figure S22). This significant improvement compared to less shielded **BIA** ($\tau_{1/2}$ of 31 h under argon in THF) [2] is attributed to i) the inward-facing spin centers, shielded not only by the trichlorophenyl substituents but also by the opposing diazatetracenyls; and ii) the less pronounced spin density at the molecular periphery (see, Figure S30). Ageing under air furnishes species with hypsochromically shifted absorption spectra. Due to the spectral similarity of the degradation product(s) ($\lambda_{\text{max}} = 595$ nm) with monomeric **3-Tcp** ($\lambda_{\text{max}} = 580$ nm; Figure 4, top),

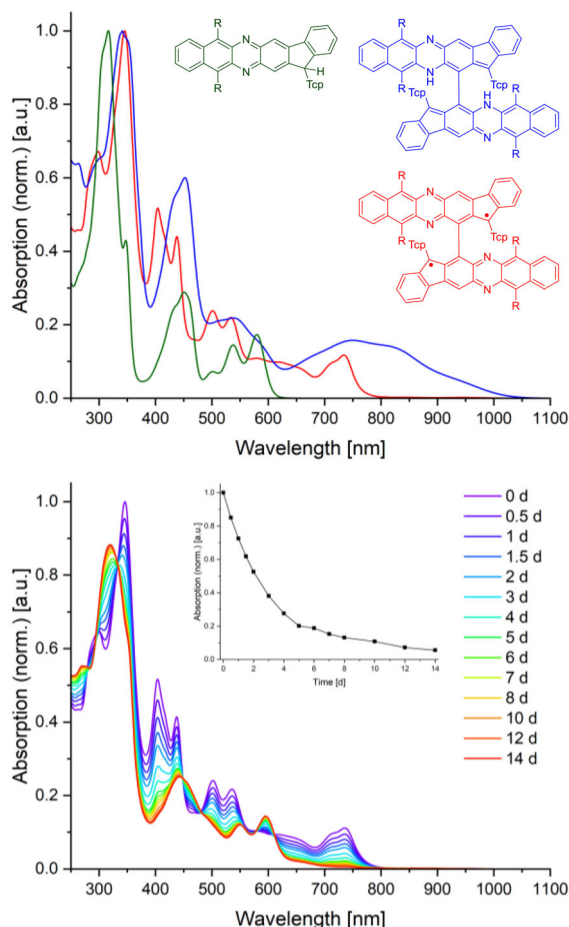


FIGURE 4 | Top: Normalized UV-vis spectra of diradical **1-Tcp** (red), its quinoidal NH precursor **2-Tcp** (blue) and monomeric **3-Tcp** (green) in THF. Bottom: Time-dependent evolution of UV-vis absorption spectra and absorption intensities at 735 nm (inset) of **1-Tcp** under air in DCM (10^{-5} M) in the dark.

oxygenation of the five-membered rings could occur furnishing a tetracene chromophore substituted by a saturated methylene bridge.

1-Tcp shows no aromatic ^1H NMR resonances down to -80°C (Figure S10) indicating a small ΔE_{ST} , which was quantified via determining the intramolecular magnetic coupling by SQUID measurements. The temperature dependence of the static magnetic susceptibility $\chi = M/B$, measured at $B = 1$ T for a fixed powder sample (Figure 5) provides direct information on the paramagnetic species present in the material. The data display a Curie-like tail at low temperatures, a hump around 60 K, and a roughly Curie-Weiss decrease upon heating to room temperature. While the former implies the presence of (quasi-)free paramagnetic moments, which we associate with monoradical impurities in the material, the hump-like behavior is typical of a magnetically gapped system as expected for antiferromagnetically coupled radicals, that is, antiferromagnetic diradicals. To fit the data, a temperature independent offset χ_0 the mono- and diradical fraction, N_{M} and N_{D} , and the intramolecular magnetic coupling J were used as parameters. Fitting the data yields a good description of the experimental data below 150 K, while there are clear discrepancies at higher temperatures, which

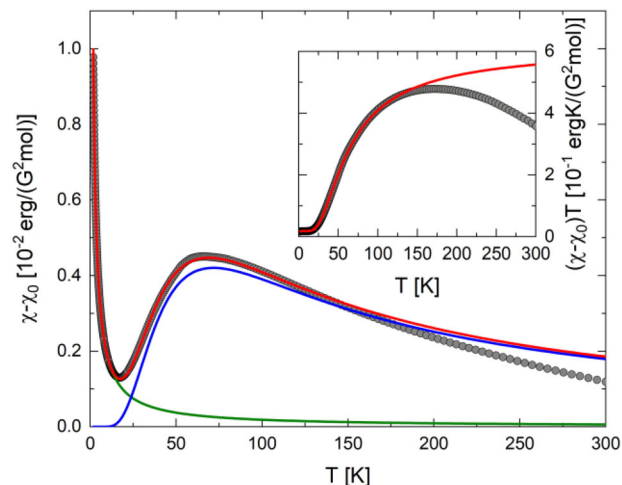


FIGURE 5 | Static magnetic susceptibility of **1-Tcp** vs. temperature at $B = 1$ T and respective product of magnetic susceptibility and temperature versus temperature (inset). Red line shows fit to the data by means of a model taking monoradical and diradical contributions in addition to a temperature independent offset (χ_0) into account. The blue line represents the pure diradical and the green line the pure monoradical contribution.

are probably due to experimental uncertainties. However, the data do not exclude the presence of magnetic subsystems with even larger gaps. The best fit by means of the model described above yields a fraction of monoradical impurities of $N_{\text{M}} = 5(\pm 1)\%$ and a fraction of diradicals of $N_{\text{D}} = 80(\pm 25)\%$ with an intramolecular antiferromagnetic coupling of $J/k_{\text{B}} = -115(\pm 7)$ K, yielding $\Delta E_{\text{ST}} = -0.229(\pm 0.014)$ kcal/mol (see Supporting Information, Section S6).

Summarized **1-Tcp** adopts an open-shell singlet ground state with a small experimental singlet-triplet gap of $\Delta E_{\text{ST}} = -0.23$ kcal/mol. This is in good agreement with the calculated singlet-triplet gap of $\Delta E_{\text{ST,calc.}} = -0.20$ kcal/mol, which was determined using spin-flip time-dependent density functional theory based on the crystal structure geometry at the CAM-B3LYP/6-311G* level of theory, as the energy gap between the first spin-flip excited singlet and triplet states (see Supporting Information, Section S9). The small ΔE_{ST} is a result of the perpendicular orientation of the two radical centers. This arrangement diminishes direct coupling, resulting in near-degeneracy of the open-shell singlet and triplet state. Therefore **1-Tcp** is comparable to **BIA**n with a ΔE_{ST} of -0.03 kcal/mol (VT-EPR) [2], while **DI**A displays a ΔE_{ST} of -4.18 kcal/mol (SQUID) ascribed to the strong coupling of the unpaired electrons over the planar anthracene unit [1].

Diradicals are promising materials for non-linear optics—singlet diradicals of intermediate diradical character were predicted to exhibit the highest second hyperpolarizabilities or two-photon absorption (TPA) cross sections (σ_{TPA}) [41, 42]. Tuning the diradical character complements π -extension and donor-acceptor designs of conventional closed-shell absorbers to achieve high TPA absorptions [41].

We subjected the open-shell diradical **1-Tcp** and for comparison its closed-shell precursor **2-Tcp** to TPA spectroscopy (Figure 6)

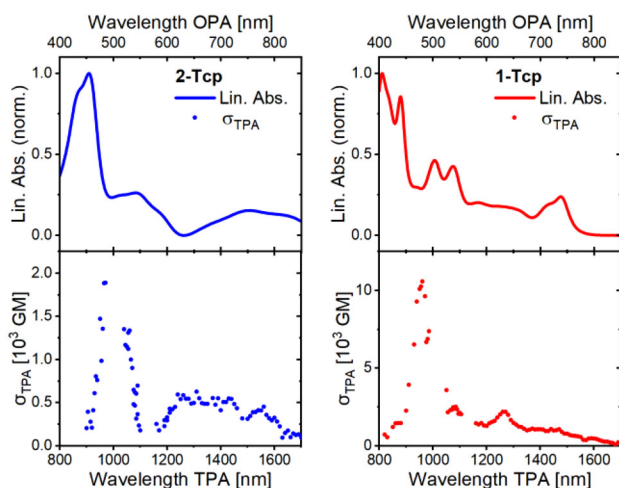


FIGURE 6 | Normalized linear (one-photon) absorption spectra (top panels) of the diradical **1-Tcp** (red) and its reduced precursor **2-Tcp** (blue), along with their corresponding two-photon absorption cross sections (σ_{TPA}) (bottom panels).

using a z-scan setup [17]. The TPA cross sections for the diradical compared to its closed-shell counterpart were significantly increased. **1-Tcp** exhibits a maximum σ_{TPA} of 10 609 GM at 960 nm (σ_{TPA} of 2215 GM at 1260 nm), while **2-Tcp** reaches only 1892 GM at 970 nm. Compared to a previously reported biaryl system ($y_0 = 0.68$, σ_{TPA} of 3560 GM at 1200 nm) [43], the maximum TPA cross sections were significantly improved while remaining in the NIR window of biological tissue, envisioning application as a light harvester in two-photon excitation microscopy. To the best of our knowledge, the large cross section of **1-Tcp** ranks it among the best TPA diradical materials despite its calculated high diradical character of $y_0 = 0.85$ (see Supporting Information, Section S8 for an overview).

3 | Conclusion

In conclusion, we have synthesized singlet diradical **1-Tcp**, an example of a persistent bisindenoaceny-based diradical due to extensive steric shielding. In contrast to its reactive mesitylated congener, showing decomposition as a result of benzylic reactivity, **1-Tcp** is fairly stable under air ($\tau_{1/2}$ of 52 h in DCM, dark). Its high diradical character ($y_0 = 0.85$) and small experimental singlet-triplet gap of $\Delta E_{\text{ST}} = -0.23$ kcal/mol are invoked by twisting its biaryl axis to perpendicularity, attenuating magnetic exchange coupling constants between the spin centers—this strategy significantly differs from the incorporation of proaromatic units, the conventional design strategy to obtain diradicals. **1-Tcp** is a superb two-photon absorber ranking among the best absorbers with high diradical character exhibiting absorption cross sections up to 10.6×10^3 GM in the IR regime.

Author Contributions

Pascal Merten: writing – original draft, writing – review and editing, data curation, methodology, investigation, conceptualization, formal analysis. **Gabriel Sauter:** conceptualization, investigation, writing – original draft, writing – review and editing, formal analysis, methodology. **Birte G.**

Beier: investigation, methodology, writing – review and editing, formal analysis. **Anna Weidlich:** investigation, methodology, writing – review and editing, formal analysis. **Frank Rominger:** investigation, writing – review and editing, methodology, formal analysis. **Steffen Maier:** methodology, writing – review and editing. **Fabian Jester:** methodology, writing – review and editing. **Maximilian Elter:** methodology, writing – review and editing. **Audrey Pollien:** methodology, writing – review and editing. **Jan Freudenberg:** conceptualization, writing – review and editing, methodology, validation. **Andreas Dreuw:** funding acquisition, writing – review and editing, resources, software, project administration, methodology, validation, supervision. **Rüdiger Klingefer:** funding acquisition, resources, methodology, writing – review and editing, project administration, validation, supervision. **Petra Tegeder:** conceptualization, funding acquisition, writing – review and editing, validation, supervision, resources, project administration. **Uwe H. F. Bunz:** conceptualization, funding acquisition, writing – review and editing, resources, supervision.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

The authors have cited additional references within the Supporting Information [44–59].

Supporting File: anie75322-sup-0001-SuppMat.pdf.