

A Stable Open-Shell Peri-hexacene with Remarkable Diradical Character

Corresponding Author: Professor Wangdong Zeng

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

Referee Report for "Stable Peri-hexacene: A Long-Waited Open-Shell Graphene Fragment"

This manuscript reports the successful synthesis, isolation, characterization, and theoretical studies of a stable peri-hexacene derivative. The structure was confirmed by X-ray crystallography, and its properties were thoroughly analyzed through an impressive set of experimental techniques complemented by theoretical calculations.

The work provides significant insights into the design of stable zigzag-edged graphene-like molecules with large diradical character. The experimental and computational analysis give detailed information about the molecule's stability and electronic properties, including local and global aromaticity as well as spin density distribution.

The synthesis of peri-hexacene represents an important advancement in the field of nanographenes, particularly due to the difficulty in stabilizing such large acenes. Despite the high diradical character of the parent peri-hexacene, the derivative shows stability under ambient conditions. Due to its diradical nature, the compound has an open-shell singlet ground state, a small singlet-triplet energy gap, a narrow HOMO-LUMO gap, and amphoteric redox behavior. The reported molecule's stability and unique electronic properties make it a valuable contribution to the fields of nanoelectronics and spintronics. There are a number of reasons to fully support publication of these results. I list them below.

Novelty: The successful synthesis and stabilization of peri-hexacene is a notable achievement in synthetic organic chemistry.

Experimental validation: The work is supported by comprehensive experimental data, including X-ray crystallography, UV-vis-NIR spectroscopy, CV, and SQUID measurements.

Theoretical insights: The manuscript integrates detailed theoretical calculations that complement the experimental findings, particularly regarding the molecule's diradical character and aromaticity.

Impact on the field: The research opens new pathways for designing stable open-shell graphene-like materials.

There are no significant weaknesses. The work is done well and presented clearly. However, I have a few minor suggestions for improvement:

Please check references for typos: see ref. 3g, for example.

Change "firsty" to "firstly" in "The monobrom CP-fused perylene 3 was firsty synthesized by regio-selective bromination with bromine under controlled condition"

I feel that the title may be a bit too dramatic. In particular, the phrase "long-awaited" is subjective and could be reconsidered. One of the radicals is misplaced in the top right structure of Figure 1.

The importance of Clar's sextets in emergence of diradical and polyradical character is an essential part of the discussion. While only 6 out of 17 benzene rings of the peri-hexacene correspond to the Clar sextet, it is enough to generate significant diradical character. In this context, I would like to draw the attention of authors to the discussion of how the number of Clar's sextets leads to the emergency of diradical character recently analyzed in JACS, 2022, 144, 23448, which is currently not cited.

It is intriguing that the additional Clar sextet in the right-hand structure in Figure 1d appears to introduce tetradical character. This raises the question of how high the quintet states might be. It would be interesting to evaluate this computationally as well.

In summary, this manuscript presents a significant advancement in the synthesis and study of peri-hexacene. The conclusions are well-supported by rigorous experimental and theoretical analysis. This is a beautiful and important molecule! I believe this paper will be a valuable contribution to the field. Congratulations to the authors!

(Remarks on code availability)

Reviewer #2

(Remarks to the Author)

The authors report a beautiful zig-zag peri-hexacene, including synthesis, crystal structure, magnetic property, aromaticity calculations as well as electronic absorption and redox behaviors. The studies were well performed. But, the synthetic strategy and ways of structural and magnetic studies were not innovative. No particular structural and physical insights were provided. Thus, I cannot recommend its publication in the present form. However, this work can be publishable after major revisions.

1. The comparisons with the analogues of this hexacene in terms of aromaticity, electronic absorption and S-T energy gap are necessary.
2. They fitted the magnetic data with S-T model. But, the four-radical state should also make contribution to magnetic property.
3. The aromaticity analysis can be carried out by analyzing the ¹H NMR spectra and bond lengths.
4. It is also interesting to investigate the excited state behavior by using ultra-fast absorption spectroscopy.

(Remarks on code availability)

Reviewer #3

(Remarks to the Author)

In this paper, Zhang et al. reported the synthesis and isolation of a peri-hexacene derivative. The structure of peri-hexacene is confirmed via single-crystal analysis, and its electronic and magnetic properties are fully characterized using means of techniques. Additionally, the ACID and NICS analyses also revealed the aromaticity of the target molecule. While this is a well-executed study, this reviewer feels that the paper lacks the importance and novelty to be published in Nature Communication by considering the following points. Synthetic strategy: The synthetic route employed in this work is largely an extension of strategies previously developed for peri-tetracene and peri-heptacene by Feng and Wu. The difference here lies in the use of perylene units instead of biphenyl on the outer edges. The authors should comment on and provide insights into this strategy, particularly whether other larger periacenes could also be synthesized by changing the related building blocks. Properties: The characterization of peri-hexacene here follows standard techniques used for other reported [n,m]periacenes, including UV-Vis spectroscopy, CV, EPR, and SQUIDs. While the addition of this new member to the periacene family is commendable, the authors are encouraged to introduce new measurements (i.e. pulsed EPR) to demonstrate the unique aspects of stable periacene diradicaloids in comparison to other reported diradicaloids. Other comments: a) The EPR signal for the target molecule in the solid state is very broad, it will be helpful to include the simulated EPR data and also provide the VT EPR in the solution phase; b) Regarding the oxidized species, the authors claimed that "All absorption spectra are in agreement with the time-dependent (TD) DFT calculations (see SI)". However, this is not accurate, as the simulated spectra differ significantly from the experimental results, such as in Figure S7; c) To improve clarity, the authors should consider adding resonance structures "Form B" and "Form C" of peri-hexacene to Figure 1d; d) Some typos in the paper, i.e. "(UB3LYP/6-31G(d,p)" "procedre" "monobrom". A thorough proofreading is recommended.

(Remarks on code availability)

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

(Remarks on code availability)

Version 1:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

The authors have addressed my concerns in an acceptable way and thus I recommend its publication.

Reviewer #3

(Remarks to the Author)

This reviewer appreciates the author's efforts to address the previously raised concerns. However, some issues remain unresolved.

1. As noted in previous comments, the synthetic strategy employed in this study lacks innovation, a point also raised by another reviewer. In the rebuttal, the authors referred to the unique nature of "peri-hexacene as a star molecule," highlighted the "reasonable stability of the peri-hexacene derivative ($t_{1/2} = 24$ h under ambient conditions)," and defended "the selection of the CP-Perylene building block". However, these points do not adequately address the novelty of the synthetic approach. A recent publication in *J. Am. Chem. Soc.* 2024, 146, 27293–27298, reported the synthesis of both peri-pentacene and peri-hexacene derivatives using a similar method. Although this reported work did not employ bay position protection for target diradicaloids, it achieved better stability with a $t_{1/2}$ of 72 hours. The authors are encouraged to discuss this reference in relation to their studies.

2. Following the above comment, this reviewer would suggest that the authors focus more closely on the physical and magnetic properties of this peri-hexacene derivative. While the addition of TA and pulsed EPR data is appreciated, essential details regarding the measurements are missing. For instance, what is the device information? was the pulsed EPR measured in solution or in the solid state of the sample? What solvent and concentration were used? Did the authors conduct temperature-dependent measurements? Additionally, how do the spin properties compare with other reported radicaloids?

Version 2:

Reviewer comments:

Reviewer #3

(Remarks to the Author)

The manuscript appears acceptable for publication since the authors have now clarified the synthetic approach employed in this study and properly addressed my previous comments. One additional point is that some relevant references in the table comparing spin coherence times are missing, such as *Chem. Commun.*, 2022, 58, 3019; *J. Am. Chem. Soc.* 2023, 145, 14064, etc.

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Point-by-point response to the reviewers' comments

We would like to express our sincere appreciation to the referees for taking the time to review this paper and providing helpful comments which have improved the quality of the paper. We have revised the manuscript in accordance with their suggestions.

Reviewer 1

Comments:

This manuscript reports the successful synthesis, isolation, characterization, and theoretical studies of a stable peri-hexacene derivative. The structure was confirmed by X-ray crystallography, and its properties were thoroughly analyzed through an impressive set of experimental techniques complemented by theoretical calculations.

The work provides significant insights into the design of stable zigzag-edged graphene-like molecules with large diradical character. The experimental and computational analysis give detailed information about the molecule's stability and electronic properties, including local and global aromaticity as well as spin density distribution.

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There are a number of reasons to fully support publication of these results. I list them below.

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Theoretical insights: The manuscript integrates detailed theoretical calculations that complement the experimental findings, particularly regarding the molecule's diradical character and aromaticity.

Impact on the field: The research opens new pathways for designing stable open-shell graphene-like materials.

There are no significant weaknesses. The work is done well and presented clearly. However, I have a few minor suggestions for improvement:

(1) Please check references for typos: see ref. 3g, for example.

Change "firsty" to "firstly" in "The monobrom CP-fused perylene 3 was firsty synthesized by regio-selective bromination with bromine under controlled condition"

Response: The correction has been done accordingly in the revised manuscript.

(2) *I feel that the title may be a bit too dramatic. In particular, the phrase "long-awaited" is subjective and could be reconsidered.*

Response: According to the reviewer's suggestion, the title has been changed to "Peri-hexacene: A Stable Open-Shell Graphene Fragment with Remarkable Diradical Character" in the revised manuscript.

(3) *One of the radicals is misplaced in the top right structure of Figure 1.*

Response: The correction has been done in the revised manuscript.

(4) *The importance of Clar's sextets in emergence of diradical and polyradical character is an essential part of the discussion. While only 6 out of 17 benzene rings of the peri-hexacene correspond to the Clar sextet, it is enough to generate significant diradical character. In this context, I would like to draw the attention of authors to the discussion of how the number of Clar's sextets leads to the emergency of diradical character recently analyzed in JACS, 2022, 144, 23448, which is currently not cited.*

Response: According to the reviewer's suggestion, the importance of Clar's aromatic sextets in emergence of diradical and polyradical character has been discussed in the revised manuscript: "The Clar's aromatic π -sextet rule is a fundamental concept in the chemistry of polycyclic aromatic hydrocarbons (PAHs) and posits that the Kekulé resonance structure with the highest number of disjoint benzene-like aromatic π -sextets—referred to as "Clar's sextets"—has the most contribution to the properties of the PAH. Generally, an isomeric PAH with more Clar's sextets is expected to exhibit higher stability. Recent studies have highlighted the importance of additional aromatic sextet rings on stabilizing the diradical structure. Specifically, the gain of one or more additional Clar's sextets in the open-shell form is crucial for achieving a stable ground-state singlet diradicaloid with high diradical character. According to this rule, the molecule can be drawn in at least three different resonance forms: a closed-shell form with two aromatic sextet rings (the hexagons shaded in blue, form A), an open-shell diradical form with five aromatic sextet rings (form B), and an open-shell tetraradical form with six aromatic sextet rings (form C). The gain of three/four Clar's aromatic sextet rings in the open-shell resonance forms B/C implies a large diradical character and moderate tetraradical character." The discussion has been added to the revised manuscript (see page 3). The reference (JACS, 2022, 144, 23448) has been cited in the revised manuscript as ref. 32.

(4) *It is intriguing that the additional Clar sextet in the right-hand structure in Figure 1d appears to introduce tetraradical character. This raises the question of how high the quintet states might be. It would be interesting to evaluate this computationally as well.*

Response: We performed the broken-symmetry DFT calculations at the theory level of UB3LYP/6-31G(d,p) and a triplet-quintet energy gap (ΔE_{T-Q}) was

estimated to be -21.79 kcal/mol, a large ΔE_{T-Q} value, in consistence with small tetraradical character. This information has been added to the revised manuscript (see page 10).

In summary, this manuscript presents a significant advancement in the synthesis and study of peri-hexacene. The conclusions are well-supported by rigorous experimental and theoretical analysis. This is a beautiful and important molecule! I believe this paper will be a valuable contribution to the field. Congratulations to the authors!

Response: We sincerely appreciate your recognition and strong recommendation. Your valuable comments and suggestions have significantly enhanced the quality of our paper.

Reviewer 2

Comments:

The authors report a beautiful zig-zag peri-hexacene, including synthesis, crystal structure, magnetic property, aromaticity calculations as well as eletronic absorption and redox behaviors. The studies were well performed. But, the synthetic strategy and ways of structural and magnetic studies were not innovative. No particular structural and physical insights were provided. Thus, I cannot recommend its publictaion in the present form. However, this work can be publishable after major revisions.

Response: We sincerely appreciate your recognition and recommendation. Your valuable comments and suggestions have significantly enhanced the quality of our paper.

(1) *The comparisons with the analogues of this hexacene in terms of aromaticiy, electronic absorption and S-T enegy gap are necessary.*

Response:

(1) The calculated harmonic oscillator model of aromaticity (HOMA) values based on the X-ray structures revealed that the four benzenoid rings at the termini (rings A/F/L/Q) have largest HOMA values (0.87/0.84, Figure 2c), indicating a large aromatic character. The rings C/D/N/O have much smaller HOMA values (0.38~0.44, Figure 2c) while the other benzenoid rings have a HOMA value of 0.65~0.80 (Figure 2c), indicating significant contribution of the open-shell diradical form **B** with five localized aromatic sextet rings shown in Figure 1d to the ground-state structure. On the other hand, nucleus independent chemical shift (NICS) calculations show that these five benzenoid rings have large negative NICS(1)_{zz} values (-20.49 ppm ~ -22.20 ppm), the rings B/E/H/J/M/P have moderate negative NICS(1)_{zz} values (-11.93 ppm ~ -16.00 ppm) while the rings C/D/N/O are almost non-aromatic (Figure 3a). All these suggest that [6]PA possesses a large diradical character, which can be stabilized by five aromatic sextet rings. ACID plot shows obvious clockwise diatropic ring current circuit along the periphery

(Figure 3b), indicating that the molecule is globally aromatic and the two hexacene units are coupled well with each other, in accordance with the bond length analysis. Notably, the central anthracene units show clockwise diatropic ring current (Figure 3b), in agreement with the HOMA value and NICS analysis. Furthermore, the calculated 2D ICSS map also shows that the rings A/F/L/Q have the strongest shielding, the rings B/E/H/J/M/P have moderate shielding, and there is the least shielding in other benzenoid rings (Figure 3c), consistent with the NICS and ACID calculations. For comparison, although the open-shell diradical form of [4]PA exhibits a localized aromatic character (Figure 1a), the central benzenoid ring connecting the two tetracene units in [4]PA is almost non-aromatic. The central benzenoid rings connecting the two hexacene/heptacene units in [6]PA and [7]PA are aromatic. This difference could be ascribed to the much larger diradical character of [6]PA and [7]PA compared to [4]PA. Therefore, the lateral extension in [6]PA and [7]PA provides the opportunity to form local aromatic sextets along the central row of the backbone, resulting in different electronic structure (see pages 7 and 8).

- (2) The *peri*-hexacene **1** shows a weak absorption band in the NIR region with maximum (λ_{\max}) at 1090 nm along with a shoulder (λ_{sh}) at 1197 nm (Figure 5a). **1** also displays multiple intense absorption bands in the visible region. The NIR absorption band has a similar structure to that in [4]PA derivative and [7]PA derivative, however, the intensity is much weaker. Furthermore, the characteristic long-wavelength shoulder peak for **1** is strong indication that it has an open-shell singlet ground state, and the band is originated from the ground-state HOMO,HOMO \rightarrow LUMO,LUMO double excitation. The optical band gap ($E_{\text{g}}^{\text{opt}}$) of **1** from the onset of its UV/Vis absorption is roughly estimated to be 0.99 eV, which is smaller than that of [4]PA derivative (1.12 eV) due to the π -extension (see page 10 and 11).
- (3) we also carried out superconducting quantum interference device (SQUID) measurement for the microcrystalline powder sample of **1** at 2–300 K. The magnetic susceptibility increased with increasing temperature, and the singlet-triplet energy gap ($\Delta E_{\text{S-T}}$) was estimated to be -1.33 kcal/mol by careful fitting of the data by using the Bleaney–Bowers equation (Figure 4). All these indicate that compound **1** is an open-shell singlet diradicaloid and exhibits a large diradical character with a small singlet-triplet energy gap. For comparison, the [4]PA derivative (-2.5 kcal/mol) showed a larger $\Delta E_{\text{S-T}}$ value, in consistence with its smaller diradical character (see page 9).

We have mentioned all key points clearly in the manuscript.

(2) *They fitted the magnetic data with S-T model. But, the four-radical state should also make contribution to magnetic property.*

Response: The diradical character (y_0) and tetraradical character (y_1) of the parent [6]PA were calculated to be 94.5% and 24.5%, respectively. Based on this, the four-radical state should also make certain contribution to magnetic property. However, the bond length analysis shows that the open-shell diradical form with five localized aromatic sextet rings contributes the most to the

properties of **1**. On the other hand, DFT calculations suggests that compound **1** has a large triplet-quintet energy gap ($\Delta E_{T-Q} = -21.79$ kcal/mol), in consistence with small tetraradical character (γ_1) of 24.5%. All these indicate that the contribution from the tetraradical form is negligible. So we fitted the magnetic data with S-T model.

(3) The aromaticity analysis can be carried out by analyzing the ¹H NMR spectra and bond lengths.

Response: The ¹H NMR spectrum of **1** in THF-*d*₈ at room temperature exhibited one almost flat baseline, and cooling of sample to -80 °C also did not obtain full resolution (Figure S3). But, the structure of **1** was unequivocally confirmed by X-ray crystallographic analysis. Based on the crystal structures, the local aromaticity of individual rings was analyzed using the harmonic oscillator model of aromaticity (HOMA) values, which are a representative index for the assessment of the bond alternation. A HOMA value of 1 indicates a typical aromatic ring, while a smaller HOMA value is associated with lower aromaticity. The four benzenoid rings at the termini (rings A/F/L/Q) have largest HOMA values (0.87/0.84, Figure 2c), indicating a large aromatic character. The rings C/D/N/O have much smaller HOMA values (0.38~0.44, Figure 2c) while the other benzenoid rings have a HOMA value of 0.65~0.80 (Figure 2c), indicating significant contribution of the open-shell diradical form **B** with five localized aromatic sextet rings shown in Figure 1d to the ground-state structure (see page 7).

(4) It is also interesting to investigate the excited state behavior by using ultra-fast absorption spectroscopy.

Response: According to the reviewer's suggestion, we further investigated the excited state behavior of **1** by using ultra-fast absorption spectroscopy. To reveal the excited-state dynamics of compound **1**, its femtosecond transient absorption (fs-TA) spectra have been recorded in degassed DCM (Figure 1). As shown in Figure 1A, upon photoexcitation, two photo-induced bleaching (PIB) bands centered at ~600 and ~644 nm were observed for fs-TA spectra of **1**. The proximity of these two bands to the position of the ground-state absorption peak suggests they are originated from ground-state bleaching (GSB). Furthermore, two excited-state absorption (ESA) bands centered at ~470 and ~520 nm at blue region, as well as a broad band after 660 nm at the red region were observed, which should be originated from its singlet state. With the delay of the time, the TA signal recovered into the ground state without no further spectral evolution, suggesting that no new excited state was formed. From the fitting result of the single-wavelength dynamics of 470 nm (Figure 1B), we can see that the singlet state decays rapidly into the ground state with a time constant of 26.4 ps. Notably, no triplet state signal was observed in the evolution process of the singlet state, which is consistent with the uphill thermodynamic driving force (1.33 kcal/mol). The discussion has been added to the revised manuscript (see page 12) and Figure 1 has been added to the revised manuscript as Figure 6.

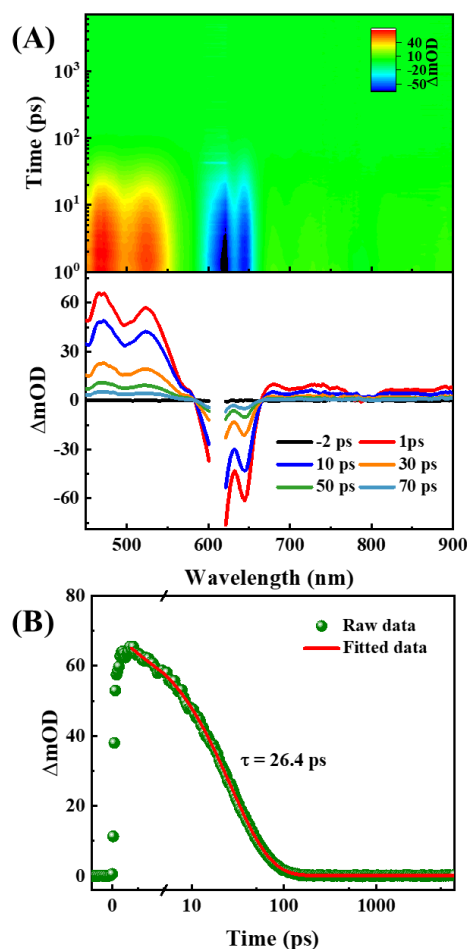


Figure 1. (A) fs-TA 2D spectra and time-resolved spectra of compound **1** in degassed DCM ($\lambda_{\text{ex}} = 610$ nm). (B) Single-wavelength dynamics probed at 470 nm.

Reviewer 3

Comments:

In this paper, Zhang et al. reported the synthesis and isolation of a peri-hexacene derivative. The structure of peri-hexacene is confirmed via single-crystal analysis, and its electronic and magnetic properties are fully characterized using means of techniques. Additionally, the ACID and NICS analyses also revealed the aromaticity of the target molecule. While this is a well-executed study, this reviewer feels that the paper lacks the importance and novelty to be published in Nature Communication by considering the following points. Synthetic strategy: The synthetic route employed in this work is largely an extension of strategies previously developed for peri-tetracene and peri-heptacene by Feng and Wu. The difference here lies in the use of perylene units instead of biphenyl on the outer edges. The authors should comment on and provide insights into this strategy, particularly whether other larger periacenes could also be synthesized by changing the related building blocks. Properties: The characterization of peri-hexacene here follows standard techniques used for other reported [n,m]periacenes, including UV-Vis spectroscopy, CV, EPR, and SQUIDS. While the addition of this new member

to the *periacene* family is commendable, the authors are encouraged to introduce new measurements (i.e. pulsed EPR) to demonstrate the unique aspects of stable *periacene* diradicaloids in comparison to other reported diradicaloids.

Response: Thank you very much for taking the time to review this paper and providing constructive comments, which have undoubtedly helped us enhance the quality of our manuscript. The novelty and significance of this work have also been well received by the other two reviewers. We have carefully responded to your concerns and revised our paper accordingly. Please see our point-by-point response below.

- (1) After we have carefully read the comments from you, we realize that the major merits of our work were not fully identified or recognized by you. Here we would emphasize that the most notable merits of our manuscript include: Open-shell graphene fragments (GFs) with controlled singlet-triplet energy gap have promising applications for spintronics and quantum information processing. Among diverse potential structures, zigzag-edged *peri*-acenes have demonstrated tunable open-shell diradical character and singlet-triplet energy gap from *peri*-tetracene onwards. However, the synthesis of *peri*-acenes with larger sizes becomes increasingly difficult due to the significant rise in their diradical character. So far, solution-phase synthesis of stable crystalline lateral π -extended *peri*-acenes larger than *peri*-tetracene has never been achieved. Our work successfully accomplishes the challenging synthesis of a stable *peri*-hexacene derivative in crystalline form. It should be mentioned that *peri*-hexacene is a star molecule and a long-awaited graphene fragment with open-shell diradical character in organic synthetic and material community. Its structure was unequivocally confirmed by X-ray crystallographic analysis and its electronic properties were systematically studied by both experimental methods and theoretical calculations. On the other hand, the obtained *peri*-hexacene derivative shows reasonable stability ($t_{1/2} = 24$ h under ambient conditions) due to the kinetic blocking although possessing a very large diradical character ($y_0 = 94.5\%$). Most importantly, its successful realization is also crucial for elucidating the structure-property relationship of the *peri*-acene family from both fundamental and applied perspectives. In other words, this work not only reveal the fundamental change of electronic structures and aromaticity of *peri*-acenes upon lateral extension, but also provide some insights into the synthesis of larger size *peri*-acene molecules or other zigzag-edged graphene-like molecules with significant diradical character. I believe that this work will attract broad interests of organic chemists, physical organic chemists and material scientists working on π -conjugated systems.
- (2) Yes, we chose the CP-perylene building block to synthesized the target *peri*-hexacene based on the following several reasons: (a) as you knows, the intrinsic electron-rich character of the *N*-annulated perylene (NP) unit renders the larger conjugated molecules being have high-lying HOMO energy level, and thus they are unstable in air, but a cyclopenta (CP) ring-fused perylene (CP) building block where an sp^3 carbon

substituted by two aryl groups is annulated to the bay region of the perylene unit, which can not only solve the aggregation and stability problems but also reduce HOMO energy level compared to NP; (b) the bay regions of the *peri*-hexacene was protected by CP units to avoid the Diels-Alder reaction in the final oxidation step, further improving stability. On the other hand, it is interesting that we found copper bromide in the presence of base could achieve one-pot reaction of benzannulation and intramolecular oxidative cyclodehydrogenation (from 6 to 7, Scheme 1 in the revised manuscript), which could provide another effective strategy to build other open-shell graphene fragments. In fact, our group is currently working on synthesizing [9]*peri*-acene derivative using a similar approach. Consequently, it is feasible to create larger *peri*-acenes by modifying the relevant building blocks in line with the expansion of these strategies. Although their synthesis remains challenging, we believe the larger [n]*peri*-acenes molecule will be achieved in the near future.

- (3) According to the reviewer's suggestion, we conducted pulsed EPR measurements. Rabi cycles at 70 K by an echo-detected nutation experiment of compound **1** were conducted (see Figure 2a below), and a stable tris(2,4,6-trichlorophenyl)methyl (TTM, $S = 1/2$) radical is employed as an external standard. The results show that the slope of the linear dependence of Rabi frequency on the B_1 magnetic field is approximately $\sqrt{2}$ times that of a doublet species ($S = 1/2$), indicating the triplet species derived by thermal excitation (see Figure 2b below).⁵⁰⁻⁵¹ The spin-lattice relaxation time (T_1) and spin coherence time (T_m) of **1** were obtained using the inversion recovery method and Hahn-echo sequences (see Figures 3 and 4 below). The spin-echo decay curves of **1** were fitted with an exponential decay to extract T_1 of 16.7 ms and T_m of 0.85 μ s at 70 K, demonstrating its potential for quantum information processing and two-qubit systems. The discussion has been added to the revised manuscript (see pages 9-10) and Figure 2 has been added to the revised manuscript as Figure 4, Figures 3 and 4 have been added to the revised SI as Figures S4 and S5.

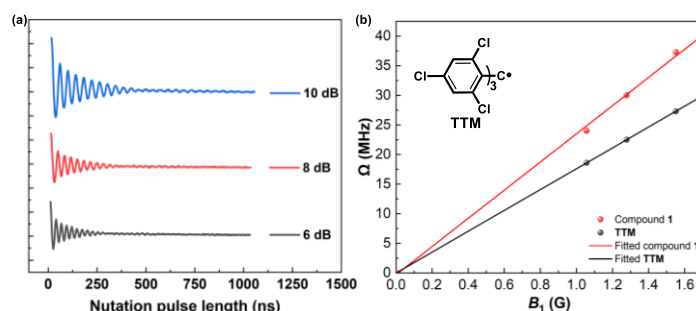


Figure 2. (a) Dependence of the Rabi oscillations of **1** on the microwave power attenuation. (b) Corresponding dependence of the Rabi frequency (Ω) on the B_1 field. Key: standard radical TTM (black line; the molecular structure of TTM is shown in Figure 3d), **1** (red line).

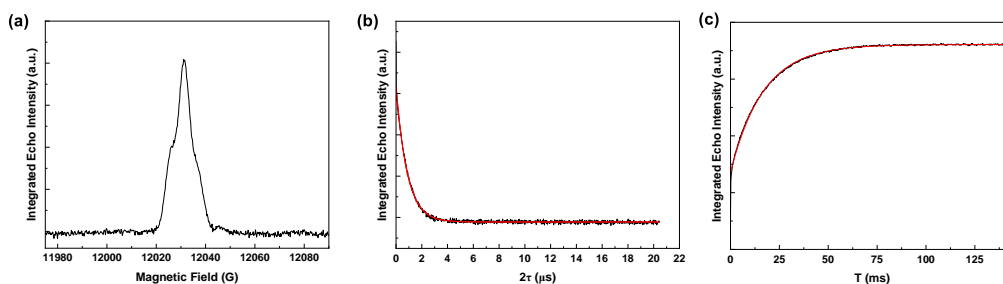


Figure 3. (a) Echo-detected field-swept spectrum (EDFS) for **1** indicated that the applied field of 12031 G with a microwave frequency of 33.720742 GHz gave the largest intensity spin echo. (b) Integrated echo intensity as a function of delay time (2τ) for **1** at 70 K with graphical depiction of Hahn-echo pulse sequence. The red line is a best fit to a stretched exponential decay with $T_m = 0.85 \mu\text{s}$. (c) Integrated echo intensity as a function of delay time (T) for **1** at 70 K with graphical depiction of Hahn-echo pulse sequence. The red line is a best fit to a stretched exponential decay with $T_1 = 16.7 \text{ ms}$.

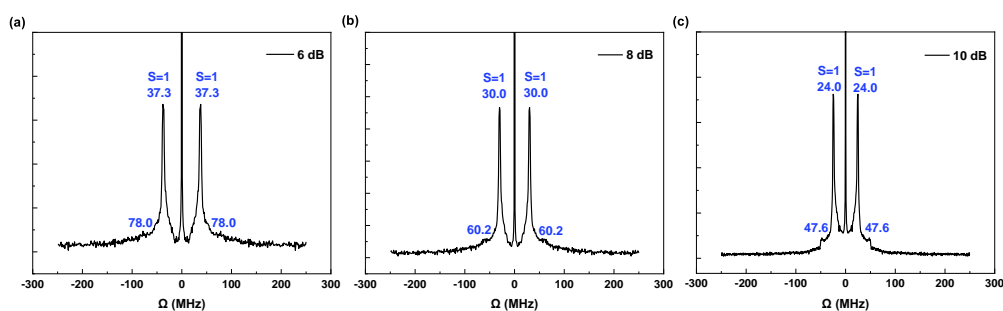


Figure 4. The nutation pulses were applied in three distinctive microwave powers (6 (a), 8 (b), and 10 (c) dB) at 70 K so as to vary the B_1 field, which are assigned to the triplet state of **1** and a small amount of doublet impurity, respectively.

we also investigated the excited state behavior of **1** by using ultra-fast absorption spectroscopy. To reveal the excited-state dynamics of compound **1**, its femtosecond transient absorption (fs-TA) spectra have been recorded in degassed DCM (see Figure 5 below). As shown in Figure 5A, upon photoexcitation, two photo-induced bleaching (PIB) bands centered at ~ 600 and $\sim 644 \text{ nm}$ were observed for fs-TA spectra of **1**. The proximity of these two bands to the position of the ground-state absorption peak suggests they are originated from ground-state bleaching (GSB). Furthermore, two excited-state absorption (ESA) bands centered at ~ 470 and $\sim 520 \text{ nm}$ at blue region, as well as a broad band after 660 nm at the red region were observed, which should be originated from its singlet state. With the delay of the time, the TA signal recovered into the ground state without no further spectral evolution, suggesting that no new excited state was formed. From the fitting result of the single-wavelength dynamics of 470 nm (see Figure 5B below), we can see that the singlet state decays rapidly into the ground state with a time constant of 26.4 ps . Notably, no triplet state signal was observed in the evolution process of the singlet state, which is consistent with the uphill thermodynamic driving force (1.33 kcal/mol). The discussion has been added to the revised manuscript (see page 12) and Figure 1 has been added to the revised manuscript as Figure 6.

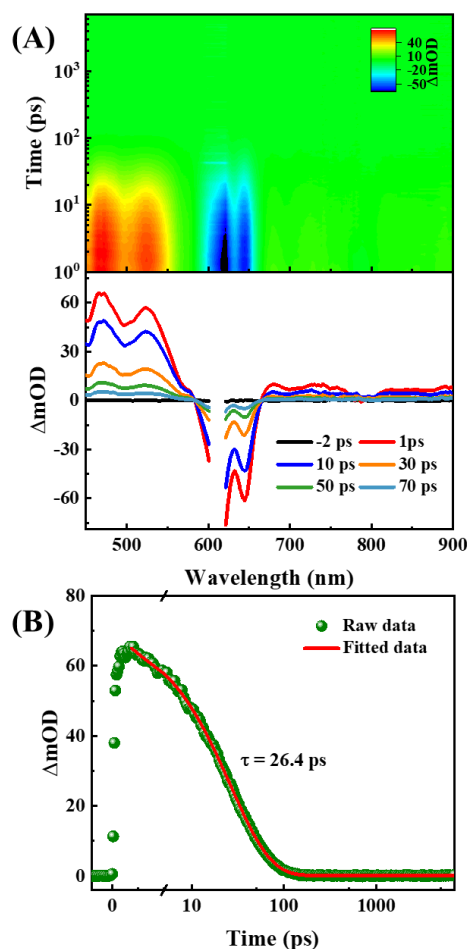


Figure 5. (A) fs-TA 2D spectra and time-resolved spectra of compound **1** in degassed DCM ($\lambda_{\text{ex}} = 610$ nm). (B) Single-wavelength dynamics probed at 470 nm.

Other comments:

(1) The EPR signal for the target molecule in the solid state is very broad, it will be helpful to include the simulated EPR data and also provide the VT EPR in the solution phase;

Response: According to the reviewer's suggestion, we conducted VT EPR measurements in both solid and solution phase (see Figure 6 below). **1** in toluene showed a three-line EPR signal (see Figure 6a below), which can be well-simulated based on the calculated spin density distribution and hyperfine coupling constants. The EPR intensity decreased with the lowering of temperature, and fitting of the data in both solid and frozen solution by using Bleaney-Bowers equation gave a singlet-triplet energy gap (ΔE_{S-T}) of -1.41 kcal/mol and -1.74 kcal/mol, respectively (see Figures 6c and 6e below), in consistence with SQUID experiments (ΔE_{S-T}) = -1.33 kcal/mol). In the solid states, we could observe the weak axially symmetric triplet state EPR signals corresponding to the $\Delta M_s = \pm 1$ transition (see Figures 2-4 above), and the spectral simulation showed the spin-Hamiltonian parameters of $S = 1$, $g = 2.0022$, $|D/hc| = 0.00825$ cm^{-1} , and $|E/hc| = 0.00191$ cm^{-1} . Accordingly, the spin distance was determined to be 6.9 Å, which close to distance of the two zigzag

edges of hexacene (7.06 Å) in the crystals. The discussion has been added to the revised manuscript (see pages 9-10) and Figures 6a-c have been added to the revised manuscript as Figures 4a-c, Figures 6d,e have been added to the revised SI as Figures S6a,b.

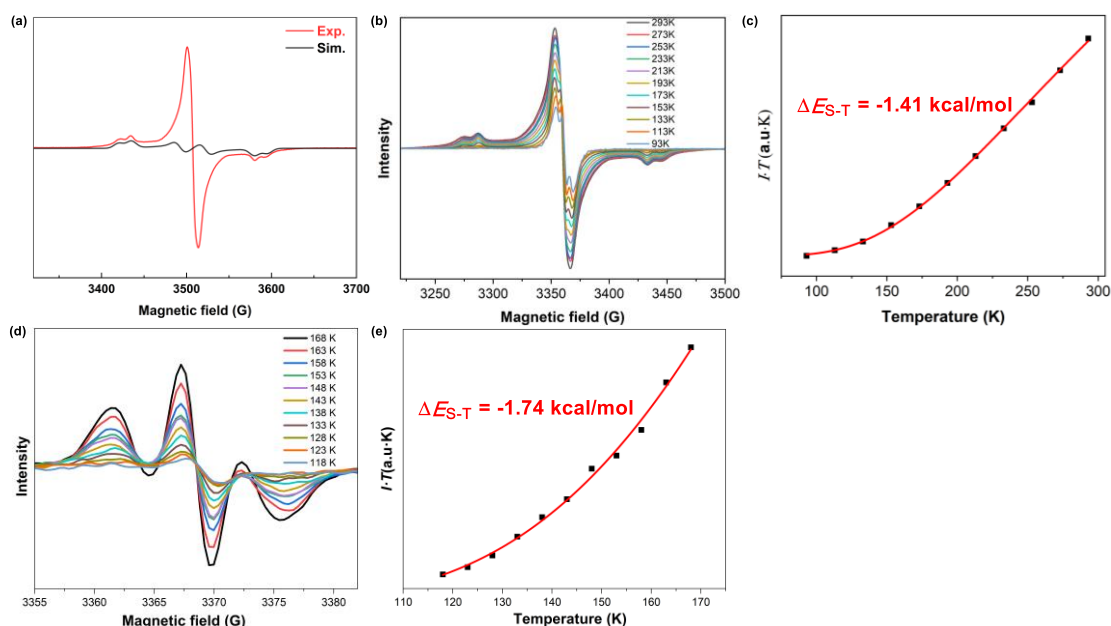


Figure 6. (a) X-band cw EPR spectra of compound **1** in toluene at 293 K (red line: experiment; black line: simulation). VT EPR spectra of **1** in solid state (b) and frozen solution (d). (c,e) The fitted $I \times T - T$ curve by using Bleaney-Bowers equation.

(2) Regarding the oxidized species, the authors claimed that “All absorption spectra are in agreement with the time-dependent (TD) DFT calculations (see SI)”. However, this is not accurate, as the simulated spectra differ significantly from the experimental results, such as in Figure S7;

Response: TD-DFT for open-shell singlet diradicaloid systems is known to be inaccurate and can only be referenced to a limited extent. This remains a well-recognized challenge for computational scientists. Therefore, attempting to strictly match computational results with experimental spectra may not be meaningful. However, the reviewer rightly points out that the simulated spectra differ significantly from the experimental results. In response, we recalculated the TDDFT of the oxidized using long-range corrected functionals, specifically CAM-B3LYP and ω B97XD, in both restricted and unrestricted forms. The experimental spectrum shows good agreement when considering a combination of the results from both forms and functionals (see Figures 7-9 below). These Figures have been added to the revised SI.

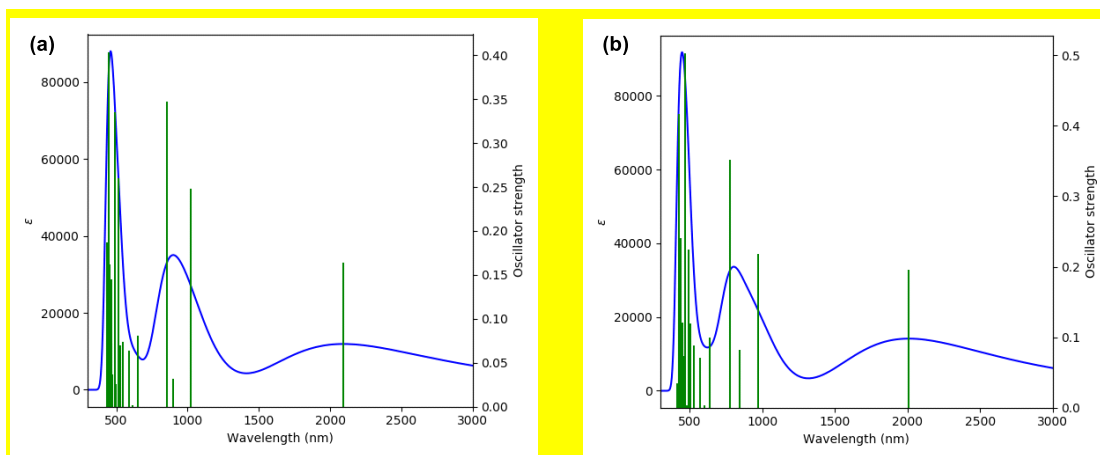


Figure 7. TDDFT calculation of radical cation under **unrestricted** a) CAM-b3lyp/6-31G(d,p) and b) ωb97xd/6-31G(d,p).

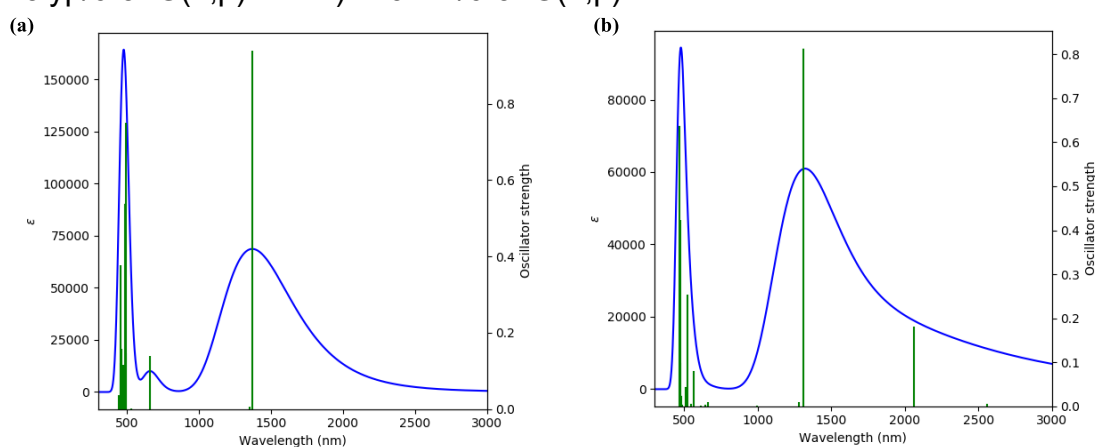


Figure 8. TDDFT calculation of target compound under a) restricted and b) unrestricted CAM-b3lyp/6-31G(d,p).

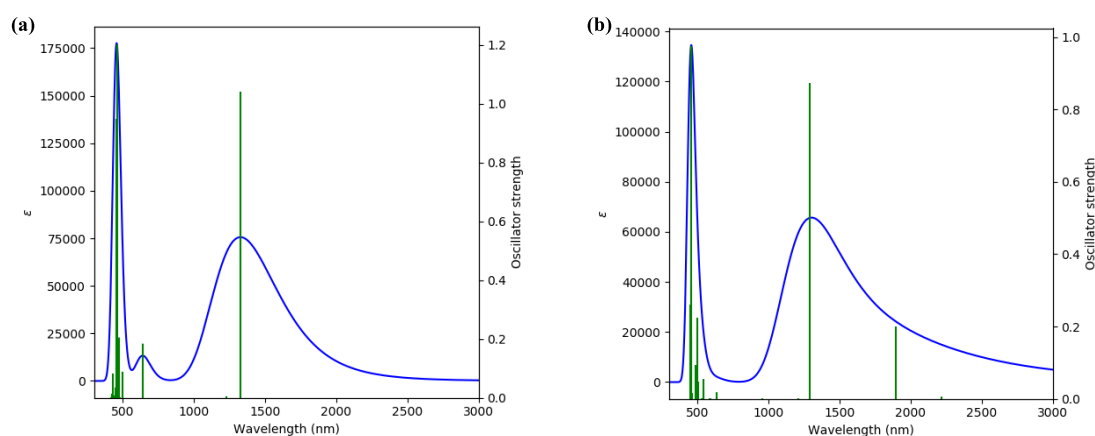


Figure 9. TDDFT calculation of target compound under a) restricted and b) unrestricted ωb97xd/6-31G(d,p).

(3) To improve clarity, the authors should consider adding resonance structures "Form B" and "Form C" of peri-hexacene to Figure 1d;

Response: The correction has been done in the revised manuscript.

(4) Some typos in the paper, i.e. “(UB3LYP/6-31G(d,p) ” “procedre ” “monobrom ” . A thorough proofreading is recommended.

Response: The correction has been done accordingly in the revised manuscript.

Reviewer 4

Comments:

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response: Thank you very much for taking the time to co-review this paper. Your valuable comments and suggestions have significantly enhanced the quality of our paper.

Point-by-point response to the reviewers' comments

We would like to express our sincere appreciation to the referees for taking the time to review this paper and providing helpful comments which have improved the quality of the paper. We have revised the manuscript in accordance with their suggestions.

Reviewer 2

Comments:

The authors have addressed my concerns in an acceptable way and thus I recommend its publication.

Response: We sincerely appreciate your recognition and recommendation.

Reviewer 3

Comments:

This reviewer appreciates the author's efforts to address the previously raised concerns. However, some issues remain unresolved.

Response: Thank you very much for taking the time to review this paper and providing constructive comments, which have undoubtedly helped us enhance the quality of our manuscript. We have carefully responded to your concerns and revised our paper accordingly. Please see our point-by-point response below.

*(1) As noted in previous comments, the synthetic strategy employed in this study lacks innovation, a point also raised by another reviewer. In the rebuttal, the authors referred to the unique nature of "peri-hexacene as a star molecule," highlighted the "reasonable stability of the peri-hexacene derivative ($t_{1/2} = 24$ h under ambient conditions)," and defended "the selection of the CP-Perylene building block". However, these points do not adequately address the novelty of the synthetic approach. A recent publication in *J. Am. Chem. Soc.* 2024, 146, 27293–27298, reported the synthesis of both peri-pentacene and peri-hexacene derivatives using a similar method. Although this reported work did not employ bay position protection for target diradicaloids, it achieved better stability with a $t_{1/2}$ of 72 hours. The authors are encouraged to discuss this reference in relation to their studies.*

Response: In our molecular design aimed at achieving the synthesis of [6]PA with adequate stability and solubility, we strategically introduced four bulky and electron-withdrawing 2,6-dichlorophenyl groups at the most reactive sites along the two zigzag edges. Additionally, two 3,5-di-*tert*-butylphenyl-substituted C(sp^3)-bridged cyclopenta (CP) rings were fused at the bay regions of [6]PA. The incorporation of CP rings in these bay regions not only enhances solubility but also restrains the Diels-Alder reaction in these areas, a phenomenon observed in the previous report concerning the synthesis of *peri*-tetracene

derivative (see *J. Am. Chem. Soc.* **2018**, 140, 6240-6244). As anticipated, this modification conferred good stability to the *peri*-hexacene derivative **1**, which can be attributed to a kinetic protection mechanism.

In our synthetic approach, we developed a novel method to construct the main skeleton. The key intermediate **7** was synthesized by treating **6** with CuBr₂ in the presence of K₃PO₄ through a one-pot process (see Scheme 1 in the revised manuscript). This method differs from the stepwise syntheses typically reported for *peri*-acene derivatives. Our one-pot strategy not only streamlines the procedure but also enhances overall efficiency, thereby providing an alternative pathway for the construction of other graphene fragments.

During the submission of our work, Wu et al. reported the synthesis of both *peri*-pentacene and *peri*-hexacene derivatives utilizing a similar synthetic strategy (see *J. Am. Chem. Soc.* 2024, 146, 27293–27298). Their studies indicated that the *peri*-hexacene derivative exhibited remarkable stability, with its absorbance at the maximum decreasing by only 1% after 72 hours of exposure to ambient air and light, which surpassed the stability of our *peri*-hexacene derivative **1** under similar conditions. The exceptional stabilities observed in their work can be ascribed to the protection of the zigzag edges with bulky groups through a synergistic captodative effect, wherein the electron donor and acceptor collaboratively stabilize the radicals by forming a zwitterionic radical structure. In contrast to the stabilization strategy based on kinetic blocking combined with a synergistic captodative effect, our design employed kinetic protection of both zigzag edges and bay regions by bulky groups with similar electronic characteristics, resulting in reasonable stability. These findings offer valuable insights for the synthesis of a broader range of unprecedented graphene fragments with zigzag edges in the future.

The above discussion has been added to the revised manuscript and this reference has been cited in the revised manuscript as ref. 42.

(2) Following the above comment, this reviewer would suggest that the authors focus more closely on the physical and magnetic properties of this peri-hexacene derivative. While the addition of TA and pulsed EPR data is appreciated, essential details regarding the measurements are missing. For instance, what is the device information? was the pulsed EPR measured in solution or in the solid state of the sample? What solvent and concentration were used? Did the authors conduct temperature-dependent measurements? Additionally, how do the spin properties compare with other reported radicaloids?

Response: Thanks for your comments. The details of measurement conditions for TA and Pulsed ESR have been added to the revised SI (see page S2-S3).

(1) The Transient absorption (TA) spectra were recorded using a femtosecond pump-probe detection system. The laser source was an ultrafast laser amplifier (Coherent) with a central wavelength of 800 nm, a repetition rate of 1 kHz, a pulse width of 100 fs, and a pulse energy of 6 mJ. The output laser beam was divided into two paths using a beam splitter. The reflected beam was directed into a pump optical parametric amplifier (OPA, Spectra-Physics, TOPAS) to generate pump beams with tunable wavelengths ranging from 250 to 2500 nm. A chopper reduced the pump beam's frequency to 500 Hz for sample excitation, and its intensity was adjusted using a continuously variable

neutral density filter wheel. The transmitted beam was used to generate a continuous white light (350–800 nm) via a CaF₂ crystal, serving as the probe beam. After passing through the sample, the probe beam was collected by a fiber-coupled spectrometer. An optical delay line controlled the delay between the pump and probe beams. For the fs-TA experiment, the excitation wavelength was set at 610 nm. The sample concentration was 0.1 mM, and the solvent used was DCM.

(2) CW-EPR spectra were recorded using a Bruker Elexsys E580 spectrometer equipped with a Superhigh sensitivity probehead ($\omega = 9.8$ GHz). Pulsed EPR measurements were conducted on a SuperQ-FT spectrometer ($\omega = 33.7$ GHz). The zero field splitting parameters were determined by fitting with the EasySpin package in Matlab. The pulsed-EPR experiment signals were acquired through the integration of the Hahn echo sequence ($\pi/2$ - τ - π - τ -echo) with τ set to 400 ns. The T_1 value was assessed using the inversion recovery method (π - τ - $\pi/2$ - τ - π - τ -echo) and a four-step phase cycling protocol. The T_m value was derived by incrementing the τ value in the Hahn echo sequence with a 16-step phase cycling method. The durations of the $\pi/2$ and π pulses for T_1 and T_m measurements were 12 and 24 ns, respectively. Furthermore, the linearity of the oscillation frequency response to the B_1 field across various fields was quantified, verifying the detectability of Rabi cycles. The Rabi frequency (Ω) for the transition $M_s \rightarrow (M_s + 1)$ of spin S adheres to the established formula:

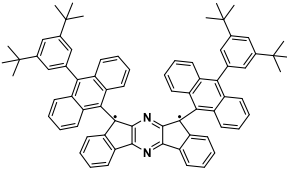
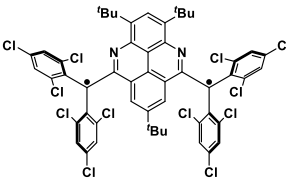
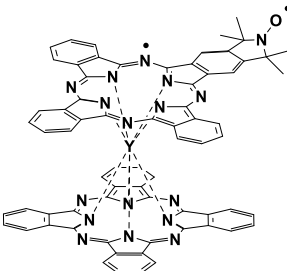
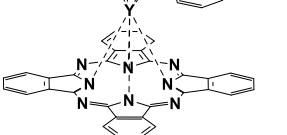
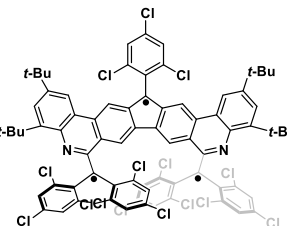
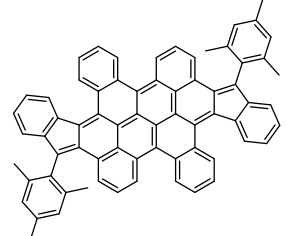
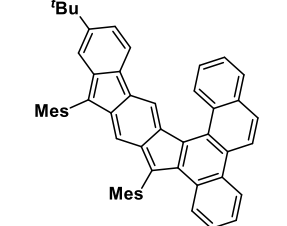
$$\Omega_R^{M_s \leftrightarrow M_s + 1} = g\mu_R B_1 \sqrt{S(S + 1) - M_s(M_s + 1)}, (M_s = -S, \dots, S-1)$$

where g is the g-factor, μ_R is the Bohr magneton, and B_1 is the magnetic field amplitude of the microwave pulse. During this study, the value of $g\mu_R B_1$ was standardized against a stable tris(2,4,6-trichlorophenyl)methyl radical (TTM, $S = 1/2$). The Rabi frequency is expected to show a linear relationship with the B_1 field, and assuming constant g values, the slope for an $S = 1$ species would be $\sqrt{2}$ times greater than that for an $S = 1/2$ species.

CW-EPR measurements were conducted on the sample in both solid and liquid states, with toluene serving as the solvent at a concentration of 80 $\mu\text{mol/L}$ in the liquid state, and temperature dependence was assessed. For pulsed EPR, the sample was measured in its liquid state, again with toluene as the solvent, but at a higher concentration of 160 $\mu\text{mol/L}$, without performing temperature dependence tests.

(3) Compared to most reported radicaloids (see Table 1 below), *perihexacene 1* exhibits a longer spin-lattice relaxation time ($T_1 = 16.7$ ms) and a comparable spin coherence time ($T_m = 0.85$ μs), with T_m significantly exceeding the duration of spin manipulation pulses (on the order of 10 ns) by nearly two orders of magnitude. These characteristics highlight its potential applications in quantum information processing and two-qubit systems. This has been added to the revised manuscript (see page 10).

Table 1. The structure, spin-lattice relaxation time (T_1) and spin coherence time (T_m) of the radicaloids.

Radical structure	T (K)	T_1	T_m	References
This work	70 K	16.7 ms	0.85 μ s	-
	100 K	4.3 ms	3.0 μ s	<i>Angew. Chem. Int. Ed.</i> 2021 , 60, 4594-4598.
	50 K	1.47 ms	0.75 μ s	<i>Angew. Chem. Int. Ed.</i> 2023 , 62, e202314900.
	20 K	12.7 ms	14.0 μ s	
	90 K	0.4 ms	6.8 μ s	<i>Chem. Eur. J.</i> 2024 , 30, e202400420.
	50 K	1.76 ms	1.78 μ s	<i>J. Am. Chem. Soc.</i> 2024 , 146, 21752-21761.
		T_1 up to around 100 ms in solution (both in d-toluene and CS ₂) at 5 K, T_m up to 290 μ s in CS ₂ at 90 K.		<i>Science</i> , 2019 , 366, 1107-1110.
		T_1 up to 1 ms in solid d ₁₄ OTP matrix at room temperature, T_m up to 38 μ s in solid d ₁₄ OTP matrix at 200 K.		<i>Chem</i> , 2021 , 7, 1363-1378.

Point-by-point response to the reviewers' comments

We would like to express our sincere appreciation to the referees for taking the time to review this paper and providing helpful comments which have improved the quality of the paper. We have revised the manuscript in accordance with their suggestions.

Reviewer 3

Comments:

The manuscript appears acceptable for publication since the authors have now clarified the synthetic approach employed in this study and properly addressed my previous comments. One additional point is that some relevant references in the table comparing spin coherence times are missing, such as Chem. Commun., 2022, 58, 3019; J. Am. Chem. Soc. 2023, 145, 14064, etc.

Response: We sincerely appreciate your recognition and recommendation. Thank you very much for taking the time to review this paper and providing constructive comments, which have undoubtedly helped us enhance the quality of our manuscript. According to the reviewer's suggestion, we have added relevant references in the spin coherence times. and these references have been cited in the revised manuscript as ref.59. and ref. 60.