nature portfolio

Peer Review File

Melanin-like nanofibers with highly ordered structures achieve ultrahigh specific electromagnetic interference shielding efficiency

Corresponding Author: Professor Yiwen Li

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

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)
Chen et al. reported that highly ordered melanoidin-like nanofibers were constructed by modulating intramolecular π-π stacking, and the material was ultimately transformed into a carbon aerogel, which exhibited very excellent microwave absorption properties. In addition, this work extends the electromagnetic response of melanoidin polymers to the microwave frequency range for the first time, advancing their potential applications in electromagnetic shielding and stealth technology. The material has excellent properties and the data in the article are detailed and complete. However, the pyrolytic treatment of carbon materials and their wave-absorbing properties are well established and the existing studies are highly repetitive. Nature Communications should publish more innovative work. Therefore, the authors are advised to submit the article to other journals.

Reviewer #2

(Remarks to the Author)
This paper presented an interesting breakthrough in the field of melanin-like polymers. Although a small number of works have reported melanin materials with oriented nano-morphologies, they do not show a truly ordered structure and brand-new structures and properties. This work started from disassembling and cutting into the origin of the disordered structure of melanin and chooses the strategy of using structural analogs in the supramolecular assembly path to strengthen the oriented π - π interaction therein. This is undoubtedly a very ingenious method because different structural inductions can form completely different melanin materials in the biomimetic synthesis of melanin. Surprisingly, the ordered melanin nanofibers reported in the manuscript also show functions that have not been seen before, which is a significant expansion for the melanin field. Therefore, I suggest that this manuscript can be published. Moreover, if these details can be further integrated, perhaps to give the reader a greater inspiration.
1. This new type of melanin had excellent electromagnetic shielding performance. In Figure 4, I noticed that its reflection coefficient is very low, and it was an electromagnetic shielding material with low - reflection behavior. At present, most high-performance electromagnetic shielding materials obtained excellent performance based on the high-reflection behavior of impedance mismatch. Why can the ordered melanin material exhibit such excellent high-performance and low-reflection shielding performance? Compared with traditional materials, what are the uniqueness or corresponding structures of the ordered melanin material?
2. Figure 1l showed a very strong G-peak signal, and the author attributed to the tetramer structure. This was a reasonable explanation but not sufficient. Please provide the calculated spectrum of this structure to confirm their consistency.
3. The visible spectral absorption of ordered melanin was very different from that of conventional melanin. Does the relatively pure spectrum mean that there may be other energy conversion behaviors? Like fluorescent phosphorescence?
4. Why does the ordered structure on Raman spectra and XRD disappear after sintering? Please discuss the relevant issues in the manuscript.

The following are some format details, please check and modify the author.

5. The data accuracy of the spacing between layers in Figure 1 and Figure 4 was inconsistent, please check.
6. The font size of the legend in Figure 4 is inconsistent, please correct it.
7. The embedded illustration in Figure 2H is too small, so it is recommended to delete it.
8. The comparison diagram in Figure 3E contains more references than the data shown in the figure, please check.
9. The horizontal coordinates of figure 3D are all frequency, please check.

Reviewer #3

(Remarks to the Author)
Referee Report for Manuscript # NCOMMS-25-14141-T

This manuscript presents an experimental approach for developing melanin-like nanofibers for electromagnetic interference shielding. The critical component seems to be enhancing the pi-pi interactions between the DHI tetramers, which leads to the formation of the nanofibers. The resulting nanofibers were transformed into carbon aerogels with an outstanding EMI shielding effectiveness of 47909.9 dB cm2/g in the X-band, which is superior to other organic materials. The work is well-structured, with very strong experimental validation and presents an interesting new experimental pathway for achieving highly ordered microstructures of melanin-like polymers. It also includes computer simulations to characterize the self-assembly process. Therefore, it could be of interest to the wide readership of Nature Communications. However, a revision is required to provide further clarification and additional data in certain sections (see below).

Comments:

1. Lines 141-142: I may be mistaken but Fig. S9 shows a dimer of 5-hydroxyindole as M1, coupled DHI and 5-hydroxyindole as M2, which is in contrast to what the text (141-142) says. Related to the molecular structures: In Fig. S8B there are only 4 peaks visible in contrast to the proposed 5 structures in Fig. S9. I assume there are two peaks hidden in the peak of M3 ([M3+H++Na+] and [M3+2H+]) at about 300?

2. The details regarding the simulation results should be expanded. The structures (1-4) in Fig. 1G are very interesting, however there is almost no information written about them. Is the structure 1 the prefferable one for nanofiber formation? How were other structures obtained: by performing an ensemble of simulations or do these structures dynamically transform into one another? The information on the temperature, the pressure, the timestep is also missing. Although the intent of the simulations was to validate self-assembly process, it would be interesting, although I do not insist on it, to simulate a larger system than just 11 molecules of the tetramer.

3. Fig. 1D: Is this an image of a single nanofiber and the stacking of the molecules within the nanofiber? If so, then it would be useful to add an arrow or a line representing the direction of the nanofiber.

4. Line 145: Is the ratio 11:10 correct. In line 487 it is mentioned that the ratio is 11:1, or are these two different ratios?

5. Line 197: the text says (t = 0, 20, 50, 100 ns), in contrast to the figure labels (0, 20, 50, 1000 ns). 1000 ns is also mentioned on line 148.

6. Line 149: What is meant by ”key structural analysis”?

7. Equation (6): The definitions for SER, SEA, SEM seem to be missing.

8. Are there any challenges of scaling up the material for real-world applications compared to the existing electromagnetic shielding materials?

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.

Reviewer #5

(Remarks to the Author)

This study obtained intriguing structures through the pre-regulation of biomass-derived melanin and developed lightweight high-performance electromagnetic shielding materials. The regulation of biomass materials is typically highly challenging due to the complex interactions and formation mechanisms involved. By utilizing structural analogs to guide the assembly process, this work provides a novel approach for biomass structure regulation. Therefore, I recommend this article for publication.
At the same time, some concerns need to be further supplemented.
(1) Why does the traditional melanin appear black while the ordered melanin appears yellow?
(2) Since the precursor of melanin is dopamine rather than indole, why is indole considered as a structural analog for induction?
(3) I noticed that the Raman spectrum in Figure 1 shows a very ideal G-peak signal, does it match the structure inferred in this paper?
(4) What materials do the electron microscope images in Figure 2B-D correspond to? The text does not appear to have been accurately marked.
(5) How does the excellent porous structure of the material shown in Figure 2 contribute to the performance? Can it also provide a good basis for other applications of this material?
(6) The thickness of the material in your electromagnetic shielding test is 2mm, which doesn't seem to be a very outstanding thickness in the field.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
Thank the authors for answering the reviewers' questions well, and the revised manuscript has been greatly improved. The authors' proposal of electromagnetic interference shielding materials based on pyrolytic processing of intrinsically conjugated materials has excellent properties and processability, which is of significance to the field of electromagnetic interference shielding. The authors are requested to carefully check the writing of the full text, e.g., the correctness of the symbols, and the following issues. The paper may be accepted after minor revisions.

On page 11, please modify the analysis of Raman spectra, e.g. “Additionally, the G peak widened after pyrolysis, which was due to the random destruction and reconstruction of different sites of the structure during pyrolysis. Meanwhile, the proportion of sp^2 carbon in the NFAG samples increased with rising pyrolysis temperatures, which is favorable for electron transport.” is stated first and then “This trend was further validated by Raman spectroscopy (Figure 2F)…..”, this description logic is not very common. In addition, the description of ID/IG values is usually not in XXX%, so please correct this.
On page 14, the discussion about microwave absorption. Firstly, please use only “microwave absorption” or “Electromagnetic absorption”, and the former is suggested. Secondly, on line 14, the authors mentioned “shielding ability”. Even though absorption is part of SET, the authors are suggested to modify it.
About the discussion on “Impedance matching”, displayed in Figure 3f, please refer to DOI: 10.1016/j.carbon.2024.119923.
On page 15, the statement “Moreover, Figure 3G illustrates the EAB range of NFAG-900 at various thicknesses, showing that complete coverage of the 2–18 GHz frequency range was achieved with a thickness below 5 mm.” is not appropriate. It’s easy to achieve MA coverage of 2-18 GHz by changing the thickness, and what’s important is the coverage of a single thickness, just like the marks the authors made in Figure 3c.
On page 18, the authors mentioned “conduction loss” and “polarization loss”, which could be calculated to further enhancing the statement in this manuscript. Please refer to DOI: 10.1021/acsami.5c03124.

Reviewer #2

(Remarks to the Author)
The authors have answered all the questions well. Therefore, I suggested that this work be published in the journal without any revision.

Reviewer #3

(Remarks to the Author)
Thank you for the clarifications and the additional details provided in the revised manuscript.
I have two follow-up comments regarding the simulation section:

While the discussion of the simulation results has been expanded, the self-assembly process, which remains central to understanding fiber formation, would benefit from further elaboration. In particular, plotting the cluster length as a function of time could provide valuable insight into the characteristic timescales of cluster formation.

Although temperature and time-step information have been added, the pressure value still appears to be missing and should be specified for completeness.

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.

Reviewer #5

(Remarks to the Author)
In this revised version, the authors have taken into consideration the reviewers' comments and made the suitable modification in the manuscript and supporting information. Now the questions have been well addressed, I would like to recommend its publication on the journal.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this revised version, the authors have taken into consideration the reviewers' comments and made the suitable modification in the manuscript and supporting information. Now the questions have been well addressed, I would like to recommend its publication on the journal.

Reviewer #3

(Remarks to the Author)
I have reviewed the revised manuscript and the authors' responses to the previous comments. I am satisfied that both of the raised concerns have been addressed adequately. The authors have made the necessary clarifications and revisions to improve the quality and rigor of the work. I therefore recommend the manuscript for publication in its current form.

Reviewer #1: *Chen et al. reported that highly ordered melanoidin-like nanofibers were constructed by modulating intramolecular π-π stacking, and the material was ultimately transformed into a carbon aerogel, which exhibited very excellent microwave absorption properties. In addition, this work extends the electromagnetic response of melanoidin polymers to the microwave frequency range for the first time, advancing their potential applications in electromagnetic shielding and stealth technology. The material has excellent properties and the data in the article are detailed and complete. However, the pyrolytic treatment of carbon materials and their wave-absorbing properties are well established and the existing studies are highly repetitive. Nature Communications should publish more innovative work. Therefore, the authors are advised to submit the article to other journals.*

Reply: Thanks for your positive comments on our work. Sorry for not accurately conveying the innovative significance of our work. we have made corresponding changes to the document to avoid such a situation. As you said, there has been a lot of work in the field of the thermal decomposition of carbon materials for wave absorption, but the traditional strategy is limited to finding organic matter with a variety of different structures, and the intrinsic properties of precursors greatly limit its performance and further optimization. Therefore, this work proposed the pre-regulation of organic matter to construct ordered structures, which greatly optimized the performance improvement in the pyrolysis of organic matter and achieved extremely high electromagnetic shielding and microwave absorption properties. We believe that this is different from a lot of repetitive work on "finding organic-pyrolytic-property characterization" and can provide a new rational design idea in this field.

Page 1, Line 19-25

Lightweight, high-performance electromagnetic shielding materials are crucial for protection and detection, relying heavily on the precise design of electromagnetic response structures. Conventional shielding materials often involve complex fabrication of conjugated composites or graphitization of organic materials, facing challenges in balancing their performance and processability. As such, seeking and designing intrinsically conjugated materials with superior processability is crucial. Natural

melanin and melanin-like polymers have garnered considerable attention as emerging promising energy-dissipating substances with a wide range from ionizing radiation to infrared light. In this work, we have engineered those bioinspired polymers with highly ordered microstructures as a new class of promising high-performance and lightweight electromagnetic shielding materials for the first time.

Page 2, Line 20-Page 3, Line 2

An Alternative strategy is to graphitize natural or organic materials to obtain a high degree of conjugated structures, However, the inherent defects would be present in the graphitized products, which is difficult to regulate accurately. The resulting electromagnetic shielding materials often exhibited limited performance. Therefore, the key to breaking through the lightweight and high-performance electromagnetic shielding materials is to develop a new class of intrinsic conjugated organic materials with well-regulated structures and functions.

Reviewer #2: This paper presented an interesting breakthrough in the field of melanin-like polymers. Although a small number of works have reported melanin materials with oriented nano-morphologies, they do not show a truly ordered structure and brand-new structures and properties. This work started from disassembling and cutting into the origin of the disordered structure of melanin and chooses the strategy of using structural analogs in the supramolecular assembly path to strengthen the oriented π - π interaction therein. This is undoubtedly a very ingenious method because different structural inductions can form completely different melanin materials in the biomimetic synthesis of melanin. Surprisingly, the ordered melanin nanofibers reported in the manuscript also show functions that have not been seen before, which is a significant expansion for the melanin field. Therefore, I suggest that this manuscript can be published. Moreover, if these details can be further integrated, perhaps to give the reader a greater inspiration.

Reply: Thanks for your kind comments and sharing on the field of melanin. Based on your valuable suggestions, we addressed each of your concerns and revised the manuscript accordingly. By solving these problems, the quality of our work has improved significantly. We believe that after the revision, the manuscript will be more in line with the requirements of the journal.

COMMENT 1. *This new type of melanin had excellent electromagnetic shielding performance. In Figure 4, I noticed that its reflection coefficient is very low, and it was an electromagnetic shielding material with low - reflection behavior. At present, most high-performance electromagnetic shielding materials obtained excellent performance based on the high-reflection behavior of impedance mismatch. Why can the ordered melanin material exhibit such excellent high-performance and low-reflection shielding performance? Compared with traditional materials, what are the uniqueness or corresponding structures of the ordered melanin material?*

Reply: Thank you very much for your important discovery and sharing, which will be of great help to the importance of our work. Traditional electromagnetic shielding materials rely on the reflection caused by high impedance mismatch to achieve high efficiency shielding. The ordered melanin

material has excellent impedance adaptation through the π-π-stacking ordered skeleton, showing the absorption type electromagnetic loss. The essential difference with traditional materials lies in the difference of conjugation structure, the traditional covalent conjugation has a high degree of free delocalization of π electrons, and the transmission process is almost no loss, while the π-π electron conduction between the aromatic ring layers needs to pass through complex polarization field and path, resulting in loss. We think this is an emerging material that is very suitable for microwave absorption applications and added the corresponding discussion hope to enlighten the reader as follows. Finally, thank you again for your important discovery.

Page 19, Line 3-12

The shielding performance of NFAGs with π-π stacking framework is primarily dominated by absorption, in contrast to traditional conjugated materials, which often suffer from poor impedance matching. The essential difference with traditional materials lies in the difference of conjugation structure, the traditional covalent conjugation has a high degree of free delocalization of π electrons, and the transmission process is almost no loss, while the π-π electron conduction between the aromatic ring layers needs to pass through complex polarization field and path, resulting in loss.[40] The higher degree of graphitization and the increased number of polarization centers, resulting from higher heat treatment temperatures, were crucial factors contributing to the enhanced absorption.

Reference

1. A. Liu, H. Qiu, X. H. Lu, H. Guo, J. W. Hu, C. B. Liang, M. K. He, Z. Yu, Y. L. Zhang, J. Kong and J. W. Gu, Advanced Materials, 2025, **37**.

COMMENT 2. *Figure 1I showed a very strong G-peak signal, and the author attributed to the tetramer structure. This was a reasonable explanation but not sufficient. Please provide the calculated spectrum of this structure to confirm their consistency.*

Reply: Thanks for your professional advice. As suggested, we first simulated the stacking structure of four tetramers by Gaussian, which was highly consistent with the simulated structure in the paper.

According to this structure, we calculated the Raman spectrum, which corresponded to the peak of the experimental spectrum. Through magnification observation, it is found that similar peak patterns are displayed in the D-peak region, which has a high degree of structural matching.

Page 9, Line 16-18

Upon magnifying the Raman spectrum, a very small signal in the D-peak region was detected. Although this peak was visually masked, its area accounts for only 1.61% of the G-peak area. Further, we compare it with the computed Raman spectra obtained by Gaussian optimized Structure 1, and obtain a high consistency (Figure S10 and S11). This result was consistent with the XRD findings, reaffirming the highly ordered structures within the PDA nanofibers.

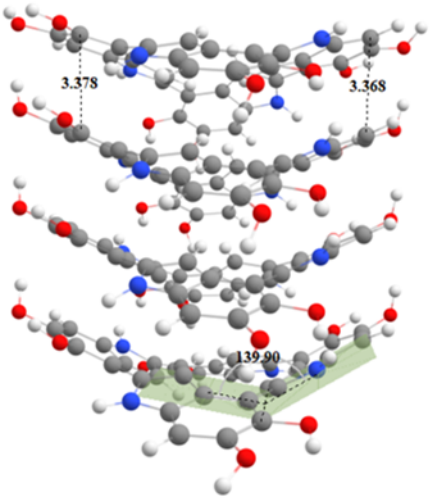

Figure S10. Tetramer structure optimized by Gaussian.

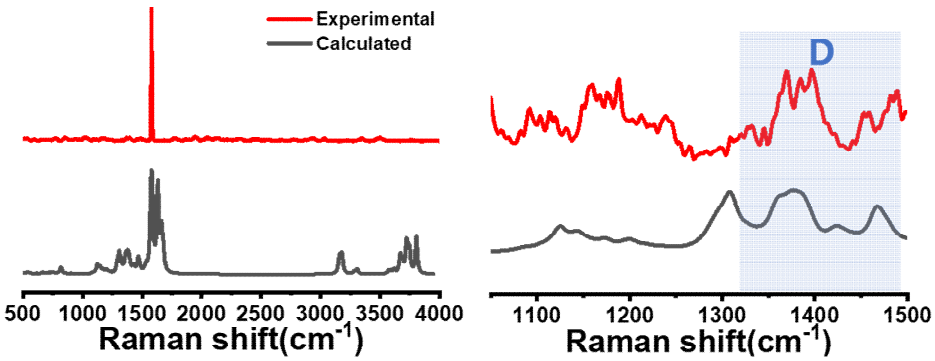

Figure S11. The calculated and experimental Raman spectra of PDA nanofibers.

COMMENT 3. *The visible spectral absorption of ordered melanin was very different from that of conventional melanin. Does the relatively pure spectrum mean that there may be other energy conversion behaviors? Like fluorescent phosphorescence?*

Reply: Thank you so much for your keen and professional insights. According to your suggestion, we found that it really has fluorescence characteristics, which will provide us with the possibility to further explore its application.

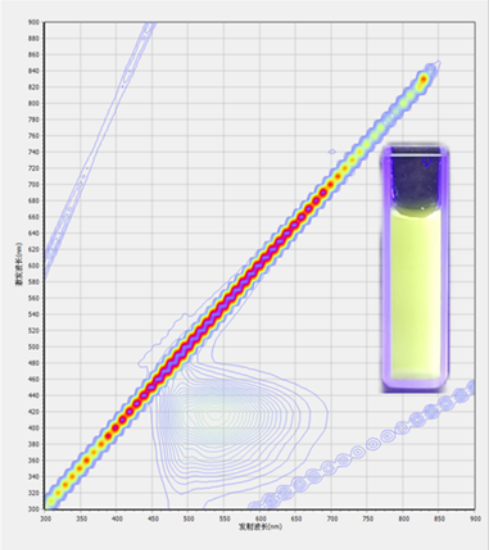

Figure. The Fluorescence spectrum and photograph of PDA nanofibers.

COMMENT 4. *Why does the ordered structure on Raman spectra and XRD disappear after sintering? Please discuss the relevant issues in the manuscript.*

Reply: Thanks for your concerns. The pyrolysis process degraded the structure to varying degrees, so the sharp G-peak is widened. In fact, even MOFs, COFs and other materials will appear after pyrolysis.

Page 11, Line 15-18

Additionally, the G peak widened after pyrolysis, which was due to the random destruction and reconstruction of different sites of the structure during pyrolysis. Meanwhile, the proportion of sp^2 carbon in the NFAG samples increased with rising pyrolysis temperatures, which is favorable for electron transport.

Reference

H. L. Lv, Z. H. Yang, H. G. Pan and R. B. Wu, *Progress in Materials Science*, 2022, 127, 52-64.

COMMENT 5. *The data accuracy of the spacing between layers in Figure 1 and Figure 4 was inconsistent, please check.*

Reply: Thanks for your careful comments. We have unified the two accuracies.

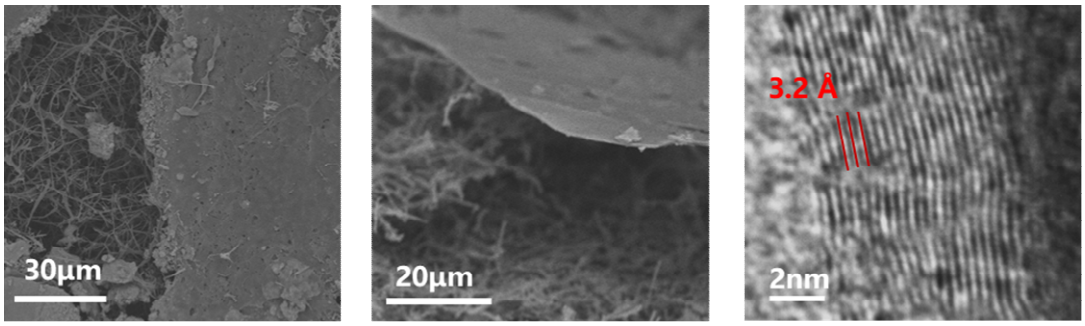

Figure 4. Electromagnetic shielding performance of NFAGs in X band. (I) SEM and TEM images of multi-scale skin core structure.

COMMENT 6. *The font size of the legend in Figure 4 is inconsistent, please correct it.*

Reply: Thanks for your careful comments. We have unified the font size of the legend.

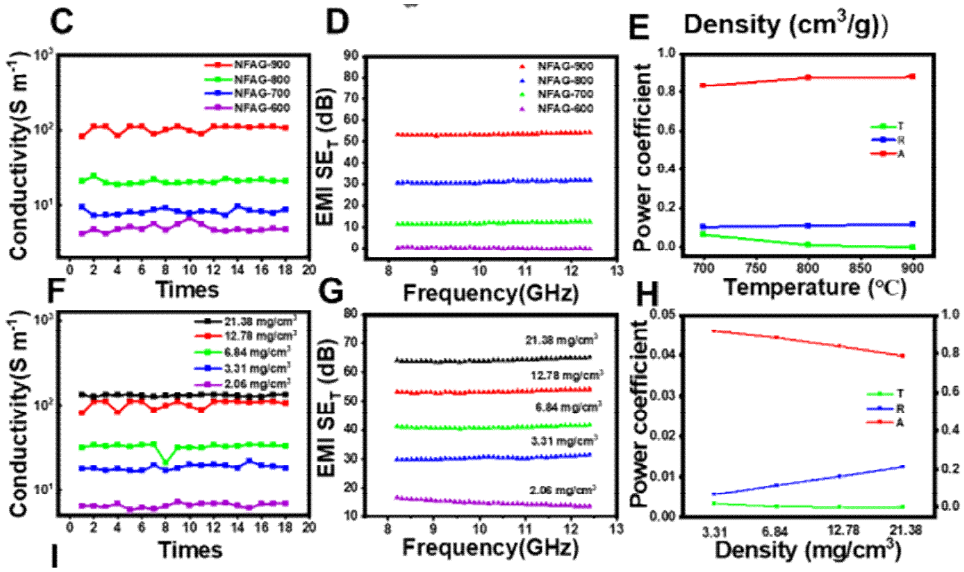

Figure 4. Electromagnetic shielding performance of NFAGs in X band.

(A) Schematic illustration of the EMI mechanism of the skin-core structure. (B) Comparison of SSE/t of typical reported carbon aerogels as a function of density. [36, 41-56] (C)–(E) C) Conductivity, D) EMI

shielding efficiency, E) EMI shielding parameter of NFAGs at different heat treatment temperatures. (F)–(H) F) Conductivity, G) EMI shielding efficiency, H) EMI shielding parameter of NFAGs in different concentrations. (I) SEM and TEM images of multi-scale skin core structure.

COMMENT 7. *The embedded illustration in Figure 2H is too small, so it is recommended to delete it.*

Reply: Thanks for your practical advice. We have completed the corresponding adjustment according to your suggestion.

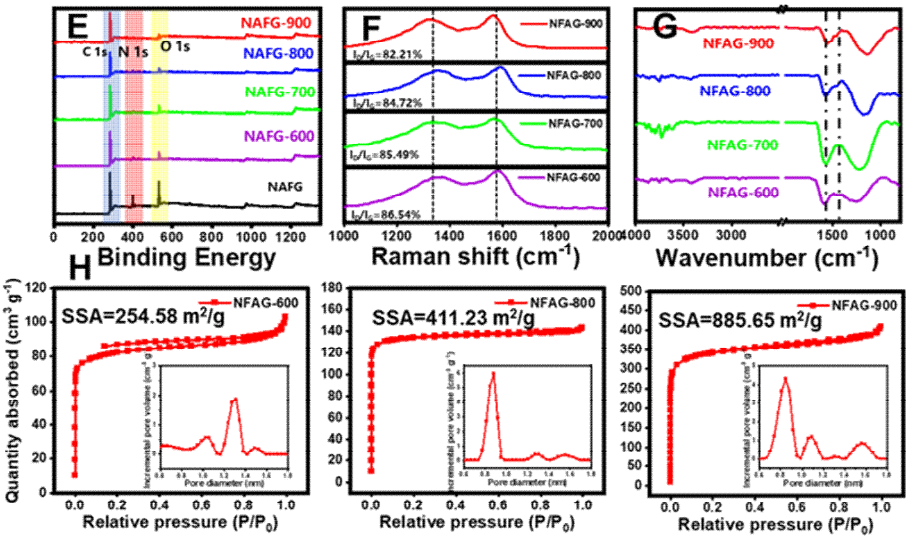

Figure 2. Fabrication and characterization of PDA carbon aerogels. (E) XPS survey, (F) Raman spectra, and (G) FTIR spectra of NFAGs. (H) Nitrogen adsorption-desorption isotherms and pore width distributions of NFAGs.

COMMENT 8. *The comparison diagram in Figure 3E contains more references than the data shown in the figure, please check.*

Reply: Thank you for your kind reminder. In order to ensure the presentation of the text chart, we selected the more representative work to show. In fact, we conducted a larger range of comparison work, and correspondingly, we showed the complete data in Figures S18 and S19.

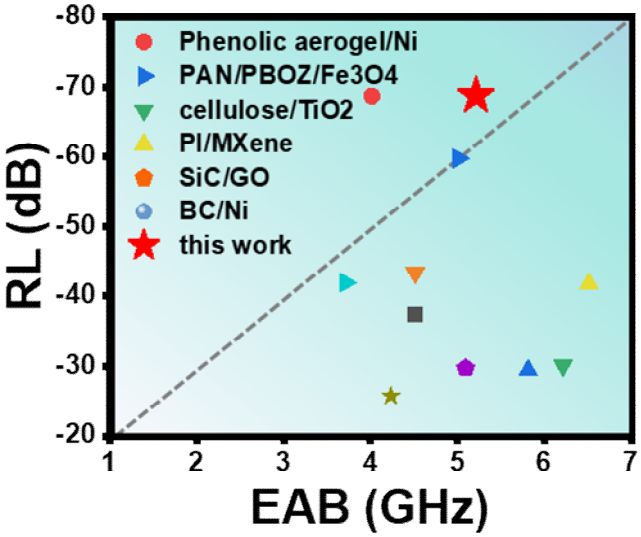

Figure 3. (E) Comparison of RL and EAB of typical reported carbon aerogels. [23-35]

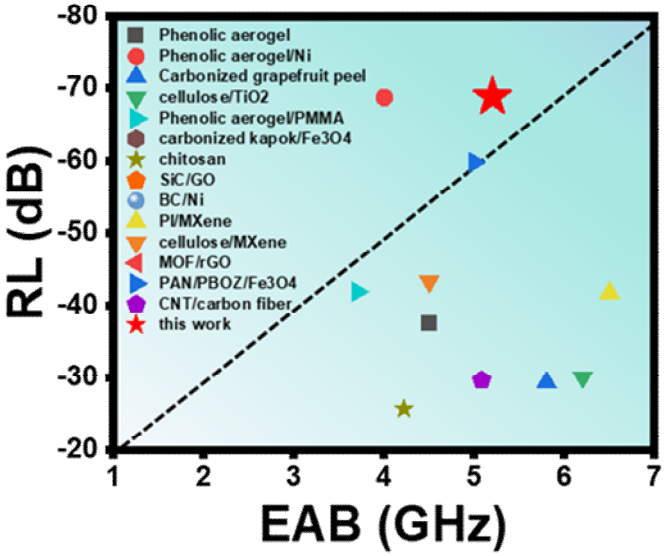

Figure S18. Comparison of RL and EAB of typical reported carbon aerogels for more related work.

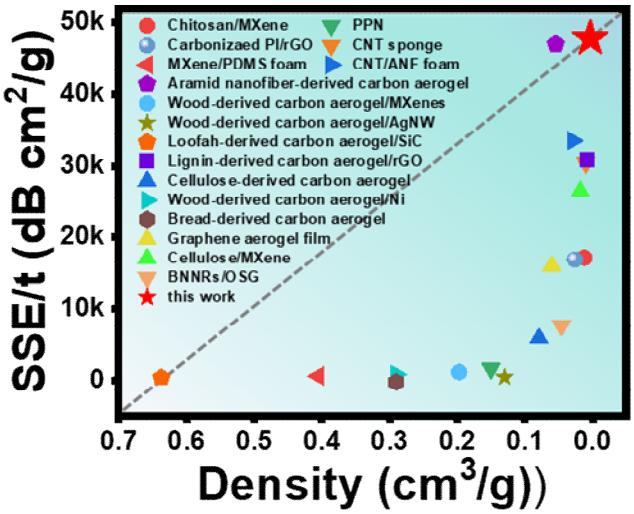

Figure S19. Comparison of SSE/t of typical reported carbon aerogels as a function of density for more related work.

COMMENT 9. *The horizontal coordinates of figure 3D are all frequency, please check.*

Reply: Thank you very much for your careful reminding, we have corrected this.

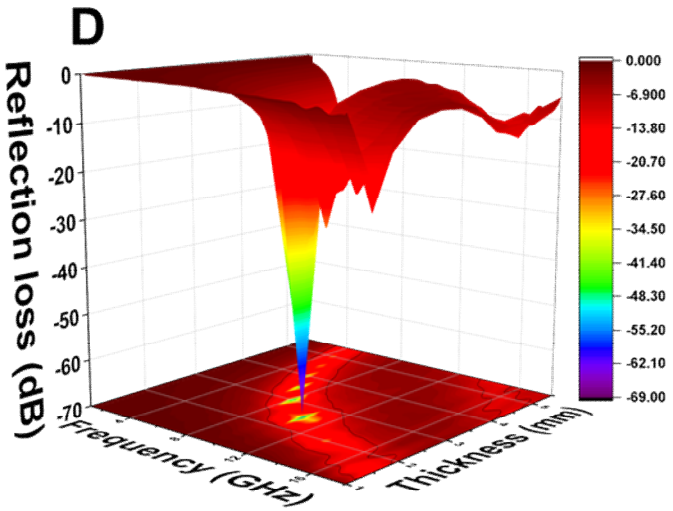

Figure 3. (D) Three-dimensional representations and two-dimensional projection images of RL value of NFAG-900.

Reviewer #3: *This manuscript presents an experimental approach for developing melanin-like nanofibers for electromagnetic interference shielding. The critical component seems to be enhancing the pi-pi interactions between the DHI tetramers, which leads to the formation of the nanofibers. The resulting nanofibers were transformed into carbon aerogels with an outstanding EMI shielding effectiveness of 47909.9 dB cm^2/g in the X-band, which is superior to other organic materials. The work is well-structured, with very strong experimental validation and presents an interesting new experimental pathway for achieving highly ordered microstructures of melanin-like polymers. It also includes computer simulations to characterize the self-assembly process. Therefore, it could be of interest to the wide readership of Nature Communications. However, a revision is required to provide further clarification and additional data in certain sections (see below).*

Reply: Thank you very much for your comments. Based on your valuable suggestions, we addressed each of your concerns and revised the manuscript accordingly. By solving these problems, the quality of our work has improved significantly. We believe that after the revision, the manuscript will be more in line with the requirements of the journal.

COMMENT 1. *Lines 141-142: I may be mistaken but Fig. S9 shows a dimer of 5-hydroxyindole as M1, coupled DHI and 5-hydroxyindole as M2, which is in contrast to what the text (141-142) says. Related to the molecular structures: In Fig. S8B there are only 4 peaks visible in contrast to the proposed 5 structures in Fig. S9. I assume there are two peaks hidden in the peak of M3 ([M3+H++Na+] and [M3+2H+]) at about 300?*

Reply: Thank you for your important and careful reminder. We have corrected and unified this as follows: the coupled molecules of DHI and 5-hydroxyindole (M1), the dimer of 5-hydroxyindole (M2), and the ring tetramer of DHI (M3). On the other hand, Figure S9 also contained the peaks in Figure 1F in the text. We apologize for the misunderstanding caused by the incorrect description of the title of our chart.

Page 7, Line 5-8

Electrospray ionization mass spectrometry (ESI-MS) analysis of the disassembled PDA nanofibers in

methanol solution revealed prominent peaks that closely matched the coupled molecules of DHI and 5-hydroxyindole (M1), the dimer of 5-hydroxyindole (M2), and the ring tetramer of DHI (M3) (Figures S8 and S9).

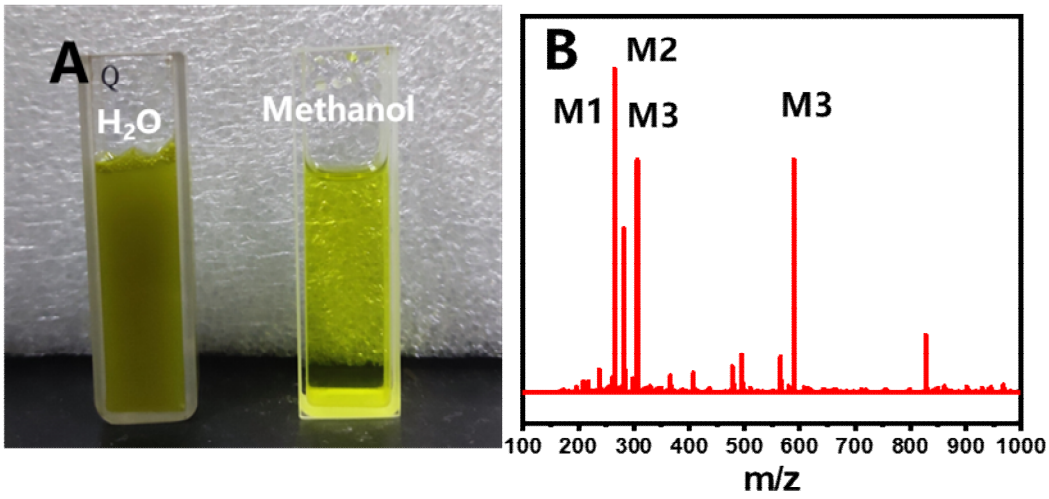

Figure S8. (A) Optical photograph of PDA nanofibers in methanol solution and water solution. (B) Electrospray Ionization Mass Spectrometry of nanofibers methanol solution.

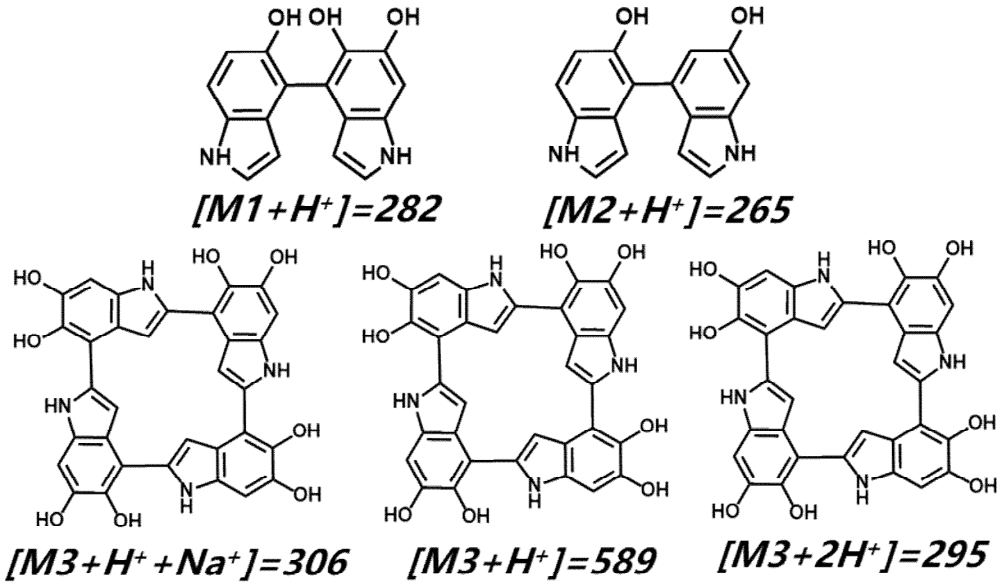

Figure S9. Proposed intermediate molecular structures assigned to main peaks in Fig. S8 and Figure 1F.

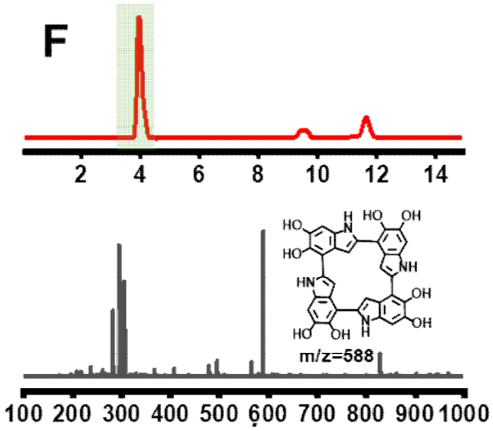

Figure 1. (F) UPLC-MS spectra of PDA nanofibers.

COMMENT 2. *The details regarding the simulation results should be expanded. The structures(1-4) in Fig. 1G are very interesting, however there is almost no information written about them. Is the structure 1 the prefferable one for nanofiber formation? How were other structures obtained: by performing an ensemble of simulations or do these structures dynamically transform into one another? The information on the temperature, the pressure, the timestep is also missing. Although the intent of the simulations was to validate self-assembly process, it would be interesting, although I do not insist on it, to simulate a larger system than just 11 molecules of the tetramer.*

Reply: Thanks for the much-needed reminder. The structures shown were those that occurred frequently during the analysis of still frames during the simulation by performing a comprehensive simulation of the entire system. The whole system tended to be stable after 100ns, maintaining a relatively stable structure with Structure1-4. Parameters such as temperature and step size are added in the characterization section, and corresponding discussions are also added in the manuscript. Among them, structure 1 is considered to be crucial, so we simulated the tetramer packing structure by Gaussian, showing a high consistency. According to this structure, we calculated the Raman spectrum, which corresponded to the peak of the experimental spectrum. Through magnification observation, it is found that similar peak patterns are displayed in the D-peak region, which has a high degree of structural matching.

Page 7, Line 15-19

The whole system is arranged and stacked autonomously, driven by its interaction force. Over a simulation time of 100 ns, the molecules exhibited a general tendency to form fibrous assemblies. Through the analysis of the still frames at different times, a series of frequent structures are found by performing a dynamic simulation of the entire system, which were preserved in the final stable structure.

Page 28, Line 20- Page 29, Line 16

For random insertion of molecules, the GROMACS insert-molecules tool was used. The amber14sb force field parameters were used for both molecules, and the system was solvated using the TIP3P model. The system containing a total of 1800 water molecules,800 molecules of ethanol, which is consistent with the reaction environment, 11 molecules of structure 1 and 1 molecule of structure 2 was used for the simulation. The steepest descent method was used to minimize the energy of the system and NPT ensemble was performed with 100ps. The production of the simulation was run for 100 ns using a 2 fs time step. The V-rescale method was used for temperature coupling and the Parrinello-Rahman method was used for pressure coupling. The Particle Mesh Ewald (PME) method was used for long-range electrostatic interactions. 14 Å cut-off was employed for van der waals force (VdW) and short-range coulombic interaction. MD calculations were performed with the GROMACS molecular dynamic simulation package. Pymol was used for all molecular visualizations. The Antechamber program was used to generate complex force field parameters, and the team (Amber 18.0 Module) was used to generate the molecular topology. The HF/6-31G* method and basis set were used to calculate the electrostatic potential (ESP) and then the result was employed to calculate the restricted ESP(RESP)2 charge.

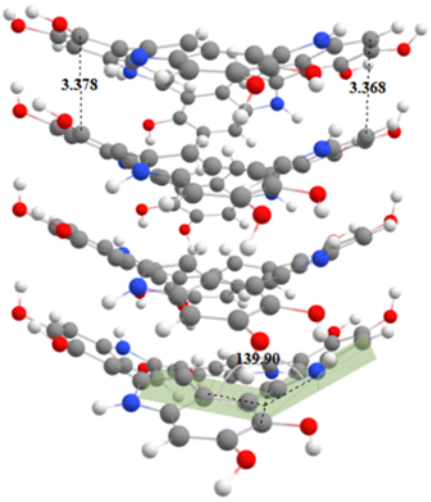

Figure S10. Tetramer structure optimized by Gaussian.

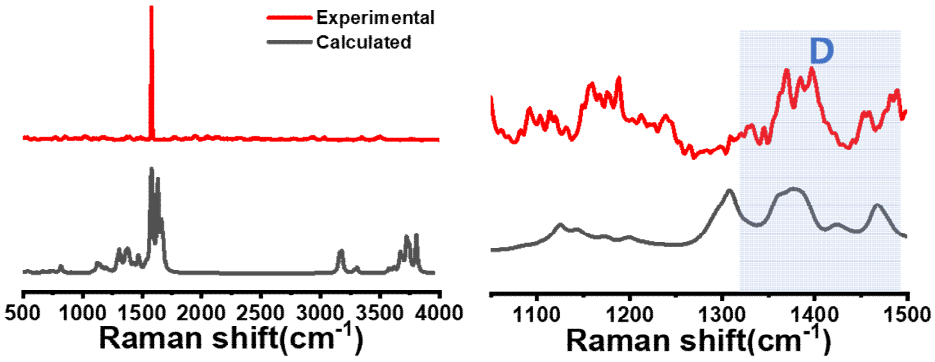

Figure S11. The calculated and experimental Raman spectra of PDA nanofibers.

COMMENT 3. *Fig. 1D: Is this an image of a single nanofiber and the stacking of the molecules within the nanofiber? If so, then it would be useful to add an arrow or a line representing the direction of the nanofiber.*

Reply: Thanks for your very useful advice, we have also revised the illustration to clarify its meaning.

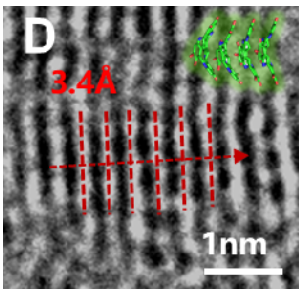

Figure 1. (D) HRTEM image and stacking structure of PDA nanofibers. The red line shows the π-π

stacking spacing.

COMMENT 4. *Line 145: Is the ratio 11:10 correct. In line 487 it is mentioned that the ratio is 11:1, or are these two different ratios?*

Reply: Thank you very much for your important reminder. This is a mistake in our writing, the correct ratio is 11:10.

Page 28, Line 19

Molecular Simulation: The molecular ratio was calculated as DA tetramer (structure 1): Bimolecular conjugate (structure 1)= 11:10, according to the proportion of elements obtained by EA, which was used to simulate molecular stacking in GROMACS.

COMMENT 5. *Line 197: the text says (t = 0, 20, 50, 100 ns), in contrast to the figure labels (0, 20, 50, 1000 ns). 1000 ns is also mentioned on line 148.*

Reply: Thanks very much for your vital errata. The correct time is 1000ns. We are sorry for the trouble caused to you by our mistake.

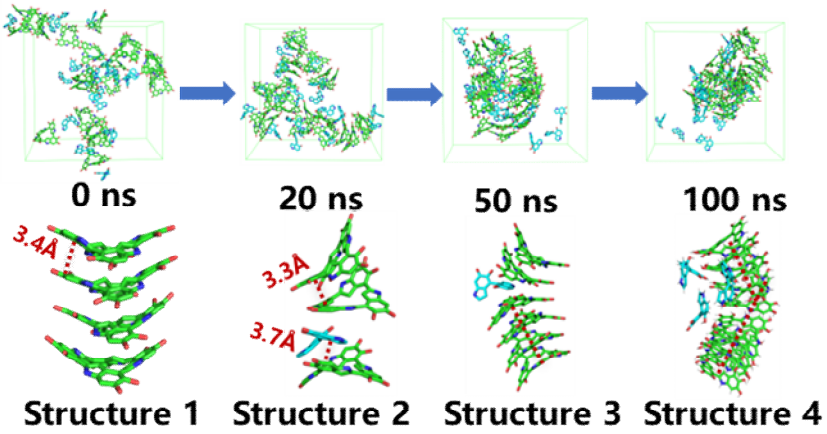

Figure 1. (G) Graphical result of molecular stacking at time t (t=0, 20, 50, 100 ns) in GROMACS and specific characteristic structures and corresponding interlayer spacing

COMMENT 6. *Line 149: What is meant by "key structural analysis"?*

Reply: Thanks for asking. The "key structures" were those that occurred frequently during the analysis of still frames during the simulation by performing a comprehensive simulation of the entire system. The whole system tended to be stable after 100ns, maintaining a relatively stable structure with Structure1-4. Therefore, we have carried out corresponding analysis on the itinerary of these structures, and we have described this part of the discussion in detail in the paper, hoping to avoid ambiguity.

Page 7, Line 15-19

The whole system is arranged and stacked autonomously, driven by its interaction force. Over a simulation time of 100 ns, the molecules exhibited a general tendency to form fibrous assemblies. Through the analysis of the still frames at different times, a series of frequent structures are found by performing a dynamic simulation of the entire system, which were preserved in the final stable structure.

COMMENT 7. *Equation (6): The definitions for SER, SEA, SEM seem to be missing.*

Reply: Thank you for your careful reminder, we have made the corresponding supplements as follows:

Additionally, The EMI SE of shielding materials can be defined as the logarithmic ratio of the incident power (PI) to transmitted power (PT) of an EM wave, and can be expressed in the following equation:

Page 30, Line 8-10

$$SE_T = 10\log\left(\frac{P_I}{P_T}\right) = SE_R + SE_A + SE_M \qquad (6)$$

Where SE_T, SE_R and SE_A represent the overall shielding effectiveness, reflection and absorption effectiveness (dB).

COMMENT 8. *Are there any challenges of scaling up the material for real-world applications compared to the existing electromagnetic shielding materials?*

Reply: Thank you for your question. We think there are two main challenges: the first is that to scale

up production need to consider its performance retention, and the second is its cost, so we are also trying to expand it into high-performance areas such as aerospace.

Reviewer #4: *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.*

Reply: Thanks very much for your help in our work. Your joint participation has helped us to improve the quality of the manuscript, and we hope that our response will address your concerns.

Reviewer #5: *This study obtained intriguing structures through the pre-regulation of biomass-derived melanin and developed lightweight high-performance electromagnetic shielding materials. The regulation of biomass materials is typically highly challenging due to the complex interactions and formation mechanisms involved. By utilizing structural analogs to guide the assembly process, this work provides a novel approach for biomass structure regulation. Therefore, I recommend this article for publication.*

Reply: Thanks for your kind comments about our work. Based on your valuable suggestions, we addressed each of your concerns and revised the manuscript accordingly. By solving these problems, the quality of our work has improved significantly. We believe that after the revision, the manuscript will be more in line with the requirements of the journal.

COMMENT 1. *Why does the traditional melanin appear black while the ordered melanin appears yellow?*

Reply: Thank you for your question. Traditional melanin involves a complex formation process and structure, which makes it not have the characteristic absorption of a specific band, but a broad spectrum absorption. Ordered melanin, on the other hand, has a relatively pure yellow color due to its relatively uniform structure.

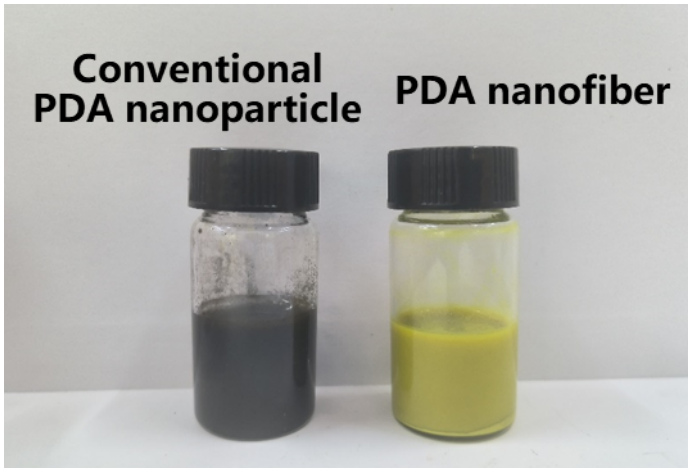

Figure S1. Optical photographs of PDA nanoparticles and nanofibers.

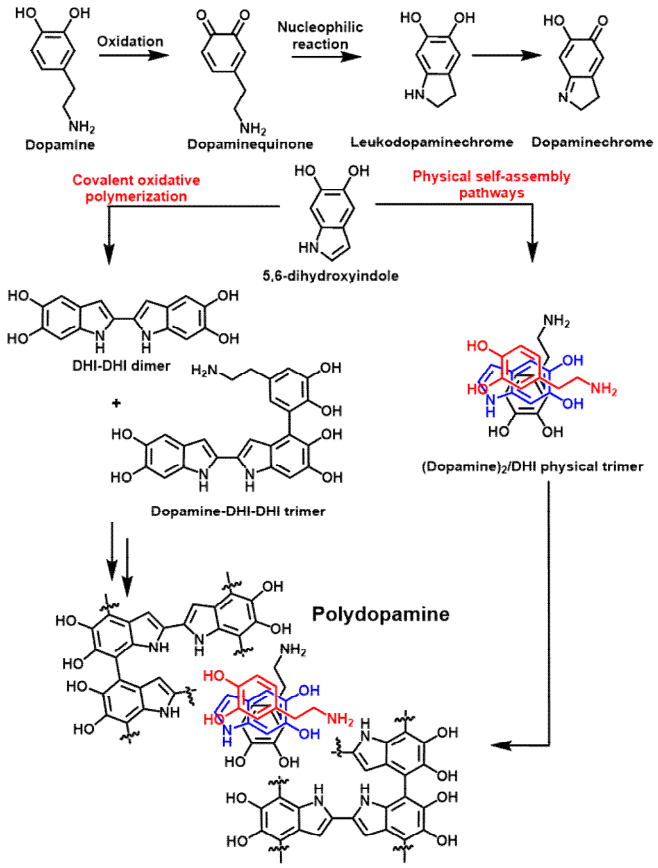

Figure The mechanism of PDA generation through chemical crosslinking and physical self-assembly

COMMENT 2. *Since the precursor of melanin is dopamine rather than indole, why is indole considered as a structural analog for induction?*

Reply: Thanks for your very professional question. In fact, the synthesis of melanin is very complex, as shown in the figure below. One of the key steps is the cyclization of dopamine to form DHI, which leads to the rapid subsequent covalent non-covalent assembly of the active species.

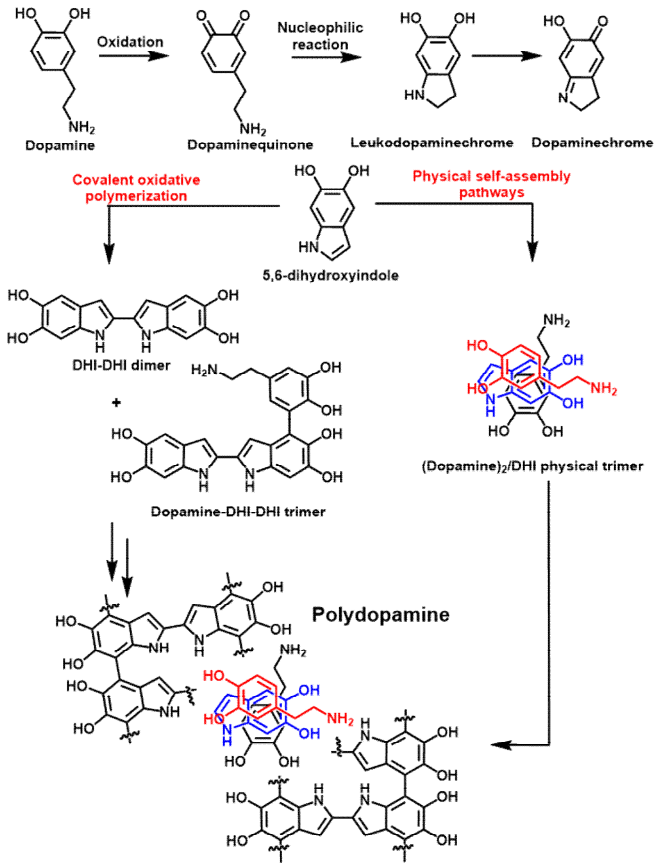

Figure The mechanism of PDA generation through chemical crosslinking and physical self-assembly

Reference

1. **Y. L. Liu, K. L. Ai and L. H. Lu, *Chemical Reviews*, 2014, 114, 5057-5115.**

COMMENT 3. *I noticed that the Raman spectrum in Figure 1 shows a very ideal G-peak signal, does it match the structure inferred in this paper?*

Reply: Thanks for your very professional question. As suggested, we first simulated the stacking structure of four tetramers by Gaussian, which was highly consistent with the simulated structure in the paper. According to this structure, we calculated the Raman spectrum, which corresponded to the peak of the experimental spectrum. Through magnification observation, it is found that similar peak patterns are displayed in the D-peak region, which has a high degree of structural matching.

Page 9, Line 16-18

Upon magnifying the Raman spectrum, a very small signal in the D-peak region was detected.

Although this peak was visually masked, its area accounts for only 1.61% of the G-peak area. Further, we compare it with the computed Raman spectra obtained by Gaussian optimized Structure 1, and obtain a high consistency (Figure S10 and S11). This result was consistent with the XRD findings, reaffirming the highly ordered structures within the PDA nanofibers.

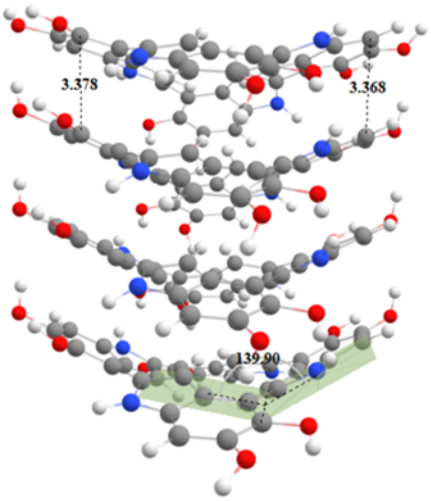

Figure S10. Tetramer structure optimized by Gaussian.

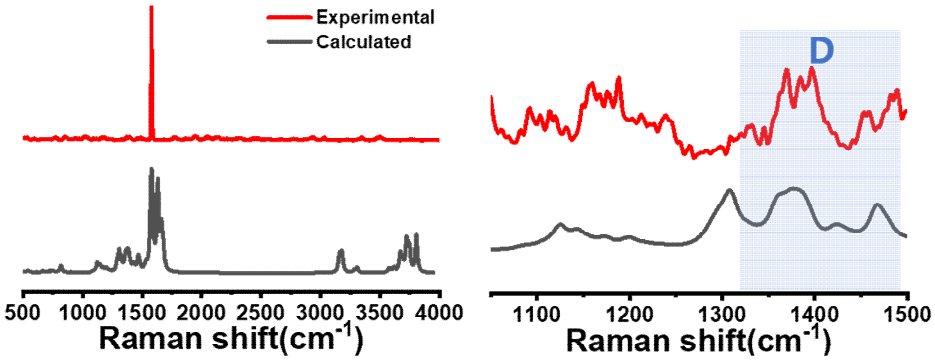

Figure S11. The calculated and experimental Raman spectra of PDA nanofibers.

COMMENT 4. *What materials do the electron microscope images in Figure 2B-D correspond to? The text does not appear to have been accurately marked.*

Reply: Thanks for your kind reminder. Figures B-D is NFAG-700, NFAG-800 and NFAG-900, respectively. We also annotated in the manuscript.

\

Page 11, Line 9-11

SEM imaging in Figure 2B-D(NFAG-700, 800, 900) confirmed that the carbonized aerogels still retained their long fibrous morphologies, indicating structural stability during carbonization.

[editorial note: panel redacted]

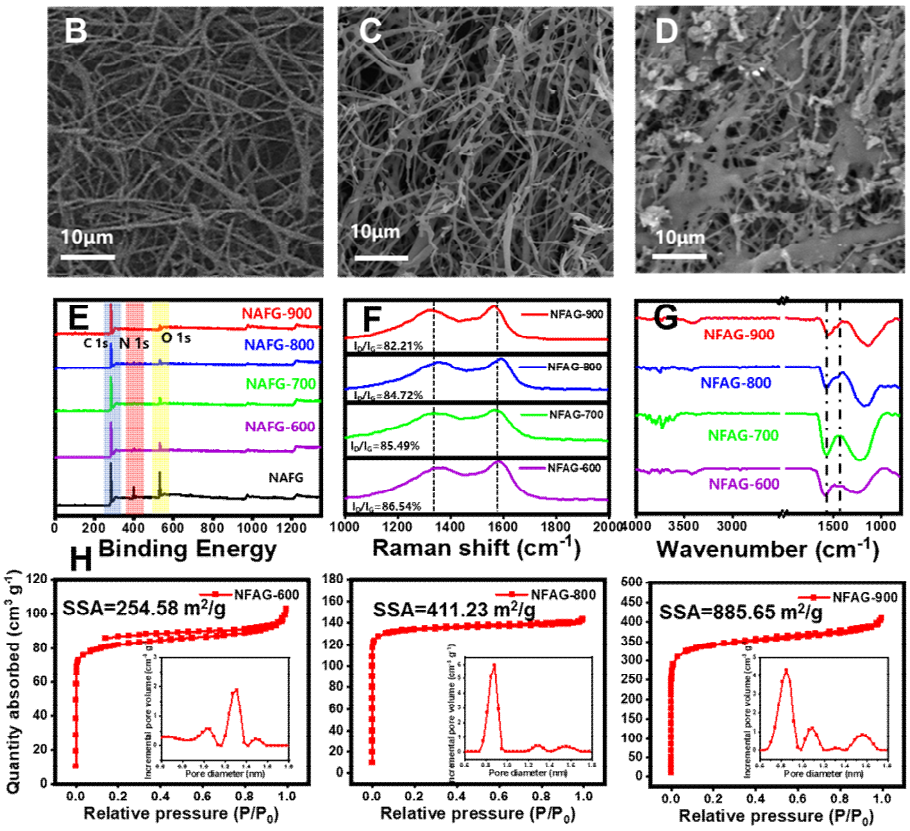

Figure 2. Fabrication and characterization of PDA carbon aerogels. (A) Schematic illustration of the NFAGs. (B)-(D) SEM image of NFAG-i (i=700(B), 800(C), 900(D)). (E) XPS survey, (F) Raman spectra, and (G) FTIR spectra of NFAGs. (H) Nitrogen adsorption-desorption isotherms and pore width distributions of NFAGs.

COMMENT 5. *How does the excellent porous structure of the material shown in Figure 2 contribute to the performance? Can it also provide a good basis for other applications of this material?*

Reply: Thanks for your asking. We see the main contribution as twofold. First, a large number of air phase structures are provided which facilitate impedance matching. Secondly, it provides a large number of heterogeneous interfaces and defects, which is conducive to electromagnetic loss. Such excellent pore structure may be conducive to the application of the material in electrochemical energy storage.

Page 12, Line 13-16

The predominant micropores (<2 nm) play a crucial role in facilitating ion transport, improving electrical applications, optimizing impedance matching and enabling the construction of abundant gas-solid heterostructures.

COMMENT 6. *The thickness of the material in your electromagnetic shielding test is 2mm, which doesn't seem to be a very outstanding thickness in the field.*

Reply: Thank you for your very professional question. Traditional electromagnetic shielding materials rely on the reflection caused by high impedance mismatch to achieve high-efficiency shielding, While the ordered melanin material relies on excellent impedance matching to achieve electromagnetic wave loss by absorption. Microwave absorbing materials need to have a certain thickness to meet the skin depth of electromagnetic waves. In fact, the thickness of NFAG in absorbing materials is relatively excellent, and we also made corresponding comparisons in the manuscript.

Table S1. Comparison of RL and EAB of typical reported carbon aerogels.

Materials	RL (dB)	EAB (GHz)	Reference
Phenolic aerogel	**-37.5**	4.5	1
Phenolic aerogel/Ni	-68.8	4	2
Carbonized grapefruit peel	-29.5	5.8	3
cellulose/TiO_2	-30.2	6.2	4
Phenolic aerogel/PMMA	-42	3.7	5
carbonized kapok/Fe_3O_4	-17.3	2.1	6
chitosan	-25.8	4.22	7
SiC/GO	−47.3	4.7	8

BC/Ni	−55.5	5.35	9
PI/MXene	-41.8	6.5	10
cellulose/MXene	-43.4	4.5	11
MOF/rGO	− 58.1	6.48	12
PAN/PBOZ/Fe_3O_4	-59.85	5	13
CNT/carbon fiber	29.8	5.08	14
This work	**-68.9**	**5.25**	

Response to Referees

Reviewer #1: *Thank the authors for answering the reviewers' questions well, and the revised manuscript has been greatly improved. The authors' proposal of electromagnetic interference shielding materials based on pyrolytic processing of intrinsically conjugated materials has excellent properties and processability, which is of significance to the field of electromagnetic interference shielding. The authors are requested to carefully check the writing of the full text, e.g., the correctness of the symbols, and the following issues. The paper may be accepted after minor revisions.*

Reply: Thanks for your kind comments and sharing on the field of melanin. Based on your valuable suggestions, we addressed each of your concerns and revised the manuscript accordingly. By solving these problems, the quality of our work has improved significantly. We believe that after the revision, the manuscript will be more in line with the requirements of the journal.

COMMENT 1. *On page 11, please modify the analysis of Raman spectra, e.g. "Additionally, the G peak widened after pyrolysis, which was due to the random destruction and reconstruction of different sites of the structure during pyrolysis. Meanwhile, the proportion of sp^2 carbon in the NFAG samples increased with rising pyrolysis temperatures, which is favorable for electron transport." is stated first and then "This trend was further validated by Raman spectroscopy (Figure 2F)⋯..", this description logic is not very common. In addition, the description of ID/IG values is usually not in XXX%, so please correct this.*

Reply: Thank you very much for your detailed suggestions. We are very sorry that our writing has caused you confusion. According to your reminder, we have made the corresponding revisions as follows:

Page 11, Line 15-20.

These defects act as polarization centers, significantly enhancing the dielectric properties of the

material (Figure 2E). Figure 2F showed the Raman spectra of NFAGs, where the D band (centered at ~1350 cm^{-1}) and G band (centered at ~1590 cm^{-1}) intensities were analyzed. The D/G ratio (ID/IG), indicative of the relative proportions of disordered and graphitic carbon, showed a gradual increase in the graphite phase with rising temperatures, reaching an I_D/I_G value of 0.8221 for NFAG-900, which is favorable for electron transport. FTIR spectra (Figure 2G) further corroborated these findings, showing a significant reduction or complete disappearance of organic C=O and C–N peaks, consistent with the XPS results.

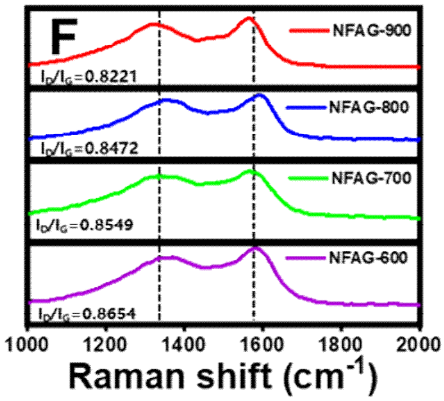

Figure 2F. Raman spectra of NFAGs.

COMMENT 2. *On page 14, the discussion about microwave absorption. Firstly, please use only "microwave absorption" or "Electromagnetic absorption", and the former is suggested. Secondly, on line 14, the authors mentioned "shielding ability". Even though absorption is part of SET, the authors are suggested to modify it.*

Reply: Thanks for your very detailed and professional reminder. We have made corresponding adjustments to the relevant parts in the manuscript.

Page 14, Line 7-14.

Next, the microwave absorption capacity of NFAGs (NFAG-600, NFAG-700, NFAG-800, NFAG-900) was evaluated, respectively. Generally, an RL value below −10 dB is considered the threshold for

effective absorption, indicating that more than 90% of incident microwaves are absorbed [1]. The corresponding microwave frequency range is referred to as the effective absorption bandwidth (EAB), a critical parameter for assessing the broadband performance of microwave-absorbing (MA) materials. The RL values of NFAGs were calculated using Equations 4 and 5, with the results presented in Figure 3C-D and Figure S15. The data revealed that the absorption efficiency of NFAGs improved with increasing pyrolysis temperature.

COMMENT 3. *About the discussion on "Impedance matching", displayed in Figure 3f, please refer to DOI: 10.1016/j.carbon.2024.119923.*

Reply: Thank you for your professional suggestions. We have refined our discussion based on your reference.

Page 15, Line 8-14.

Impedance matching ($Z = |Z_{in}/Z_0|$) is employed to assess the alignment between the material and free space, with optimal matching achieved when the Z_{in}/Z_0 ratio approaches 1. As shown in Figure 3F, NFAG-900 displayed excellent impedance matching over a wide frequency range, where the position of the maximum absorption corresponded to the optimal impedance-matching position. This facilitated the penetration of significant electromagnetic waves into the material.[22] Furthermore, when comparing the attenuation constant, NFAG-900 exhibited high values, confirming its effective ability to dissipate electromagnetic waves (Figure S17).

Reference

22. Y. Li, S. R. Guo, L. L. Zhao, S. Y. Chen, Y. D. Li, X. L. Yang, P. Wang, W. Feng, Z. H. Mou, H. N. Jiang, H. J. Wei and G. Cerullo, Carbon, 2025, 233, 119923.

COMMENT 4. *On page 15, the statement "Moreover, Figure 3G illustrates the EAB range of NFAG-900 at various thicknesses, showing that complete coverage of the 2–18 GHz frequency range was achieved with a thickness below 5 mm." is not appropriate. It's easy to achieve MA coverage of 2-18*

GHz by changing the thickness, and what's important is the coverage of a single thickness, just like the marks the authors made in Figure 3c.

Reply: Thank you for your professional suggestions. We have revised this part of the discussion based on the suggestions as follows:

Page 15, Line 16-19.

According to the λ/4 theory, NFAGs with different thicknesses correspondingly exhibited different adaptive frequency bands. As the thickness increases, the adaptive frequency bands showed a trend of moving towards low frequencies(Figure 3G).[22]

Reference

22. Y. Li, S. R. Guo, L. L. Zhao, S. Y. Chen, Y. D. Li, X. L. Yang, P. Wang, W. Feng, Z. H. Mou, H. N. Jiang, H. J. Wei and G. Cerullo, Carbon, 2025, 233, 119923.

COMMENT 5. *On page 18, the authors mentioned "conduction loss" and "polarization loss", which could be calculated to further enhancing the statement in this manuscript. Please refer to DOI: 10.1021/acsami.5c03124.*

Reply: Thank you for your suggestion. Based on your suggestion and reference, we conducted a further analysis of the contribution to the microwave absorption performance in this work.

Page 16, Line 9-12.

As shown in Figure 3G, the curve displayed two distinct sections with varying characteristics. In the low-frequency region, the Cole-Cole plot exhibited an approximately linear relationship, primarily attributed to dielectric loss due to interface polarization, while in the high-frequency region, the classical Cole–Cole semicircle revealed significant Debye relaxation polarization. [4] This phenomenon is understandable, as interface polarization occurs at heterogeneous interfaces and requires charge accumulation or complete dipole migration, which necessitates a longer response time. In contrast, Debye relaxation polarization involves directional dipole polarization of lower intensity. Upon removal of the external field relaxation, the dipole loses its orientation under thermal motion, leading

to a significantly shorter response time compared to interface polarization. By fitting with a nonlinear square fitting model, the contributions from polarization losses and conduction losses can be determined separately. As shown in Figure S18, polarization loss made a major contribution to dielectric loss. [23]

Reference

23. Y. Li, L. L. Zhao, W. Feng, S. Y. Chen, S. R. Guo, X. L. Yang, P. Wang, K. Li, N. K. Taieh, G. Cerullo and H. J. Wei, ACS Applied Materials & Interfaces, 2025, DOI: 10.1021/acsami.1025c03124.

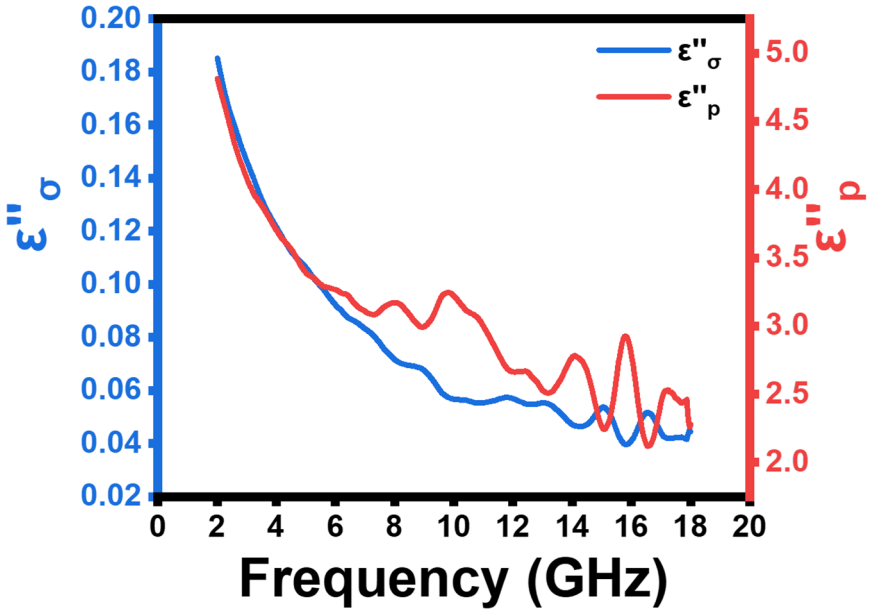

Figure S18. Fitted electromagnetic parameters of NFAG-900.

Reviewer #3: Thank you for the clarifications and the additional details provided in the revised manuscript. I have two follow-up comments regarding the simulation section: While the discussion of the simulation results has been expanded, the self-assembly process, which remains central to understanding fiber formation, would benefit from further elaboration. In particular, plotting the cluster length as a function of time could provide valuable insight into the characteristic timescales of cluster formation. Although temperature and time-step information have been added, the pressure value still appears to be missing and should be specified for completeness.

Reply: Thanks for your further suggestions. Firstly, regarding the cluster length you mentioned, we actually also wanted to conduct quantitative statistics on it. However, in the actual operation process, the molecules applied were in a state of continuous dynamic change. It is difficult to define what distance or arrangement could be regarded as a unified "cluster" to evaluate its length. It is not until a certain period of time that the system approaches stability. However, this process is not a controllable and orderly growth process, but rather a relatively stable arrangement is obtained through repeated random movements. Indeed, when using GROMACS for self-assembly simulation analysis, many similar works adopted a similar approach to infer its assembly behavior, making it difficult to measure the length of aggregates. So we employed the qualitative analysis to explain its tendency to form clusters in this work as usual and have also further provided corresponding supplementary explanations in the simulation part of the manuscript.

1. C. Wu, Y. Duan, L. Yu, Y. Hu, C. Zhao, C. Ji, X. Guo, S. Zhang, X. Dai, P. Ma, Q. Wang, S. Ling, X. Yang and Q. Dai, *Nature Communications*, 2024, **15**, 4643.

2. Z. Álvarez, A. N. Kolberg-Edelbrock, I. R. Sasselli, J. A. Ortega, R. Qiu, Z. Syrgiannis, P. A. Mirau, F. Chen, S. M. Chin, S. Weigand, E. Kiskinis and S. I. Stupp, *Science*, 2021, **374**, 848-856.

3. Y. Wu, S. Chen, J. Wu, F. Liu, C. Chen, B. Ding, X. Zhou and H. Deng, *Science Advances*, 2024, **10**, eadn8662.

Page 29, Line 17-20

The Antechamber program was used to generate complex force field parameters, and the team (Amber 18.0 Module) was used to generate the molecular topology. The HF/6-31G* method and basis set were used to calculate the electrostatic potential (ESP) and then the result was employed to calculate the restricted ESP(RESP)2 charge. During the running time, the molecules within the system would spontaneously move and arrange based on their interaction forces. The applied molecules were in a constantly dynamic changing state to achieve an energy stable state.

Additionally, we are sorry that in the last round of revision, we overlooked this important information about pressure. This process was completed under one standard atmosphere, and we have also made corresponding supplements in the manuscript.

Page 29, Line 6.

Molecular Simulation: The molecular ratio was calculated as DA tetramer (structure 1): Bimolecular conjugate (structure 1)= 11:10 according to the proportion of elements obtained by EA, which was used to simulate molecular stacking in GROMACS. For random insertion of molecules, the GROMACS insert-molecules tool was used. The amber14sb force field parameters were used for both molecules, and the system was solvated using the TIP3P model. The system containing a total of 1800 water molecules,800 molecules of ethanol, which is consistent with the reaction environment, 11 molecules of structure 1 and 1 molecule of structure 2 was used for the simulation. The steepest descent method was used to minimize the energy of the system and NPT ensemble was performed with 100ps. The production of the simulation was run for 100 ns using a 2 fs time step under standard atmospheric pressure. The V-rescale method was used for temperature coupling and the Parrinello-Rahman method was used for pressure coupling.