Response to reviewers for the manuscript “Formation characteristics of aerosol triplet state and coupling effect between the separated components with different polarity” (acp-2021-842)

We appreciate the comments from the editor and reviewer. According to the reviewer's comments, we have revised this paper. The details are as follows. *The blue italics are comments of reviewer. The red italics are improvements and original text of manuscript.* The black font are responses.

Response to Anonymous Referee #1

Attention to detail is part of the scientific endeavour, and unfortunately this manuscript is missing important data to adequately assess the results. As it stands this manuscript is not fit for publication. Insufficient detail was provided, and other scientists cannot build upon the work, then the endeavour is fruitless. I encourage the authors to pay thorough attention to the details of their methods and results to clearly communicate to other scientists what was done and how to reproduce the data to subsequently build upon it. These steps include:

1. Build on existing literature. The introduction has little information on what has been done in this field so far. And key words and examples are missing, leaving the reviewer wondering why this research was done in the first place.

Many thanks to the reviewers for their suggestions. For the research progress in this field so far, the research method and formation process of triplet are introduced in the preface. The study of triplet states in complex systems starts from aqueous systems, so there are few references for aerosols that can be used for reference. The novelty of this paper also makes up for the lack of related research in aerosol systems. If photochemical reactivity and different polar components can be linked, it will be helpful to further study photochemical reactions and control air pollution. The introduction part of the preface is more about the methods and ideas of studying triplet state. The photochemical properties of water-soluble components in aerosols have been published previously by our group. This paper is an extension of previous research. Therefore, the description of the research background has been added as follow.

We have added “*In previous studies, it was confirmed that water-soluble components in aerosols can generate triplet states, and is related to season and source.*” in introduction in the improved paper.

- Chen, Q. C., Mu, Z., Xu, Li.: Triplet-state organic matter in atmospheric aerosols: Formation characteristics and potential effects on aerosol aging, *Atmos. Environ.*, 252, 118343, https://doi.org/10.1016/j.atmosenv.2021.118343, 2021.

We have deleted “*The environmental organic matter components are composed of complex compounds with different polarities, which are expected to have different optical properties and photochemical reactivity.*” in introduction in the improved paper.

We have corrected “*because the atmospheric chromophore is not a single substance, but a complex organic mixture, this also increases the difficulty of studying the generation mechanism of 3C* in* *actual atmospheric environment.*" to "*the environmental organic matter are complex, and we cannot study a certain substance alone, which may ignore the mutual influence that the system will have.*"

We have corrected "*Due to the large differences in the sources and chemical processes of organic matter in the atmospheric environment and the water environment, the research conclusions on the 3C* generation characteristics of water bodies may not be suitable for atmospheric aerosols.*" to "*Different from the water environment, the source and chemical reaction of organic matter in aerosol is more complex, and the generation characteristics of 3C* will be different.*"

2.Communicate the mechanisms correctly. Lines 39-40 incorrectly describe how triplet state organic matter forms from the intersystem crossing of singlet state organic matter. (The reader is left concerned after reading this section.)

We have corrected "*After absorbing solar radiation, some organics will transition from the ground state to the excited singlet state (1C*), and then rapidly transition to 3C* through the intersystem.*" to "*The ground-states of some organic matters (C) can be excited to the singlet states (1C*) under solar irradiation. And a part of 1C* can transit rapidly into 3C* by intersystem crossing (ISC)"* in introduction in the improved paper.

3. Tell a story – why were PM and lab-generates filters made? What was the purpose of the comparison? Which hypotheses were being tested?

(1) In winter, burning biomass and coal is the main heating method in northern China, especially in the rural areas. Coal burning is also the main source of energy in China. At the same time, previous studies have shown that the photochemical properties of aerosols from different sources are different. Therefore, we selected some lab-generates samples that are expected to share photochemical and optical properties with the PM samples.
(2) We have added "*because burning biomass and coal is the main heating method in northern China* " in section 2.2 in the improved paper.

- Li, J., Chen, Q., Hua, X., et al.: Occurrence and sources of chromophoric organic carbon in fine particulate matter over Xi'an, China. *Science of the Total Environment*, 2020, 725, 138290, https://doi.org/10.1016/j.scitotenv.2020.138290.

4. Purify chemicals used, particularly the probes. (Line 107 explicitly states that all chemicals were used as is, and it is common practice in the community to distill furfuryl alcohol since it can easily dimerize and oxidize. Most papers in the field state that FFA is purified by distillation.)

Thanks to the reviewers for the questions and suggestions. As the reviewer said attention to detail is important part of the scientific endeavor, we also take into account the purity of the drug product when planning the experiment. Section 2.1 of the text shows the purity and manufacturer information of FFA, and this purity sets the stage for a successful experiment. At the same time, there are literatures supporting that the chemical under this purity can be tested without purification. References are as follows:

- Bodhipaksha, L. C., Sharpless, C. M., Chin, Y. P.: Triplet photochemistry of effluent and natural organic matter in whole water and isolates from effluentreceiving rivers, *Environ. Sci. Technol.*, 2015, 49, 3453-3463, https://doi.org/10.1021/es505081w.

- Dalrymple, R. M., Carfagno, R. K., Sharpless, R. M.: Correlations between dissolved organic matter optical properties and quantum yields of singlet oxygen and hydrogen peroxide, *Environ. Sci. Technol.*, 2010, 44, 5824-5829, https://doi.org/10.1021/es101005u.
- Glover, C. M., Rosario-Ortiz, F. L.: Impact of halides on the photoproduction of reactive intermediates from organic matter, *Environ. Sci. Technol.*, 2013, 47, 13949-13956, https://doi.org/10.1021/es4026886.
- Mostafa, S., Rosario-Ortiz, F. L.: Singlet oxygen formation from wastewater organic matter, *Environ. Sci. Technol.*, 2013, 47, 8179-8186., https://doi.org/10.1021/es401814s.
- Vione, D., Minella, M., Maurino, V., et al.: Indirect photochemistry in sunlit surface waters: Photoinduced production of reactive transient species, *Chem. Eur. J.*, 2014, 20, 10590-10606, https://doi.org/10.1002/chem.201400413.

5. Describe all blanks in detail and show all the results. What were the field blanks, which controls were done? Line 158 is simply not good enough. Showing all the data of adequate background samples.

(1) Thanks to the reviewer for the suggestion. The experimental description here is not clear. “field blanks” means “background sample”. We have elaborated the background sample preparation process in the improved paper.

(2) we have removed *Line 158* of original paper, and added “*Three background sample and three parallel samples were used for the experiments. The background sample is a sample that simulates the entire process from sampling to extraction with a blank membrane to deduct possible anthropogenic contamination. The parallel sample is to select one of the 10 aerosol $PM_{2.5}$ samples, trim and extract three identical samples to verify the repeatability of the experiment. Each part of the experiment presents information about the background sample.*” in section 2.2 in the improved paper.

6. Use the most up-to-date rate constants. For example, FFA decay was revised back in 2017 by (Appiani et al., 2017) to be $1.00´10^{8}$ M^{-1} s^{-1}.

(1) We have performed calculations with new rate constants. After the change, it will slightly affect the original value and will not change the existing results and laws of this article.

(2) We have corrected the Table 1. in the improved paper.

Table 1. Formation rate constant (k_{TMP}), quantum yield coefficient (f_{TMP}) and singlet oxygen quantum yield ($\Phi_{^1O_2}$) of $^3C^*$ in the different polar components of each sample.

Sample number	**HP-WSM**			**HULIS**			**MSM**		
	k_{TMP} (min^{-1})	f_{TMP} (M^{-1})	Φ_{1O2} (%)	k_{TMP} (min^{-1})	f_{TMP} (M^{-1})	Φ_{1O2} (%)	k_{TMP} (min^{-1})	f_{TMP} (M^{-1})	Φ_{1O2} (%)
2019/12/21	0.005	51.9	7.956	0.020	89.9	5.484	0.007	0.007	8.916
2019/12/25	0.006	56.9	6.936	0.025	158.3	9.12	0.014	0.014	14.292
2020/1/3	0.005	32.0	3.336	0.013	35.6	4.116	0.018	0.018	6.48
2020/1/9	0.006	71.5	11.076	0.021	82.7	7.74	0.033	0.033	17.244
2020/1/13	0.001	5.2	6.18	0.037	167.6	5.616	0.032	0.032	8.496
2020/1/16	0.002	24.5	7.836	0.025	140.9	8.184	0.022	0.022	10.128
2020/1/18	0.006	60.4	5.268	0.013	75.8	5.52	0.007	0.007	8.112
2020/1/23	0.008	91.8	14.304	0.010	43.7	4.284	0.015	0.015	8.436
2020/1/25	0.002	39.5	4.308	0.018	102.9	7.056	0.011	0.011	7.704
2020/2/1	0.002	22.6	8.148	0.009	40.3	6.444	0.028	0.028	9.948
Wheat-straw1	0.000	0.00	3.972	0.000	4.6	2.04	0.000	0.000	5.868
Wheat-straw2	0.000	0.00	2.616	0.000	5.4	1.788	0.000	0.000	7.608
Rice-straw1	0.000	0.00	7.164	0.001	0.0	3.708	0.005	0.005	8.52
Rice-straw2	0.000	0.00	4.392	0.001	0.0	5.592	0.004	0.004	5.7
Wood1	0.001	16.3	2.94	0.000	2.0	2.34	0.001	0.001	10.56
Wood2	0.001	10.3	2.88	0.000	1.5	3.624	0.003	0.003	9.132
Coal 1	0.000	3.2	1.788	0.047	270.8	46.62	0.050	0.050	31.104
Coal 2	0.000	0.0	1.764	0.054	417.2	41.016	0.062	0.062	58.524
Ambient samples	0.004	45.64	7.536	0.02	93.78	6.36	0.019	0.019	9.972
(mean±SD)	±0.002	±24.54	±2.56	±0.01	±45.97	±1.31	±0.009	±0.009	±2.61
Primary samples	0-0.001	0-16.3	1.8-7.2	0-0.05	0-417	1.8-46.6	0-0.06	0-0.06	5.7-58.5
(range(mean))	(0.0002)	(3.7)	(3.48)	(0.01)	(88)	(13.32)	(0.02)	(0.02)	(17.16)

7. Caption all figures with thorough details. What do the colour wheels represent in Figure 1 and 2? The figure captions in the supporting information section contain so little data that figures are not understandable. (Striking examples include: Table S1 where all units are missing, copyright infringement for Figure S3, column with data not matching headings in Table S3 and in Table S4, poor resolution of Figure S10, no details in caption of Figure S12, no details of any of the 60 (!!) graphs in Figure S14.

Thanks to the reviewers for their suggestions. We have added relevant explanations or changes to the charts involved, which makes our articles better quality.

(1) The color wheel in Figure 1 represents the average relative content of organic carbon in different polar components, which is the percentage of the organic carbon content in the solution sample to the organic carbon content in the film sample.

(2) The color wheel in Figure 2 represents the proportion of k_{TMP} value of different polar components. We assume that the initial triplet reaction rate of the sample has only two parts, WSM and MSM. WSM is divided into HPWSM and HULIS. If the triplet state generation process between the

components is independent, then the sum should be the same as that of WSM, otherwise there is a more complicated reaction mechanism.

(3) We have supplemented Table S1 with units.

We have modified Figure S3.

We have modified the heading of Table S3 to "*Information of sample selection, trimming, and volume of post-extraction solutions*".

We have modified the heading of Table S4 to "*Sample concentrations used for absorbance and fluorescence experiments of different polar components of the sample*".

We have reprocessed the Figure S10.

We have added a detailed description of Figure S12, "*The picture shows the results of carbon analysis of the samples using the OC/EC analyzer. Including four organic carbon components (OC1-OC4) and six elemental carbons (EC1-EC6), the red dotted line represents the optical pyrolyzed carbon produced during the analysis*".

We have added a detailed description of Figure S14, "*The picture shows the results of the fluorescence experiments using the samples with the concentrations listed in Table S4. The legend on the right shows the unit fluorescence intensity*".

8. Rewrite the abstract to describe what was done: specific which aerosols were analysed and why, and what methods were used to study the processes.

We have added "*The experimental samples were selected from winter atmospheric* $PM_{2.5}$ *samples. At the same time, due to the influence of the northern heating season in winter, and in order to highlight the generality of results, simulated combustion samples were also used in the experiment. Experiments using carbon analysis, probe method and electron paramagnetic resonance method to study the photochemical properties of different samples.*" in abstract in the improved paper.

9. It is inaccurate to draw regressions through clusters of data as in Fig. 6.

Thank you for your comment, but I don't understand what you mean of this comment. The purpose of our correlation analysis using the data in Figure 6 is to establish the relationship between the photochemical and optical properties of the samples. The results obtained so far can be interpreted with a certain degree of reliability.

10. Use acronyms consistent with the literature. (MSM and HP-SWM are not acronyms used by the community and are confusing, WSM in the community should be WSOC), use the word "probe" instead of capture agent.

(1) Reviewers have extensive experience with research in this area. As the reviewer said, the abbreviations used in this article are slightly different from those in the references, because the WSM in this article refers to direct water solvent extraction without the process of desalination, which contains non-organic substances such as inorganic salts. This is also the key for this study to verify the coupling effect between inorganic salts and organic carbon. Therefore, the use of abbreviations such as WSOC may cause ambiguity.

(2) As suggested by the reviewer, we have replaced "*capture agent*" with "*probe*" in the full text.

11. Rewrite the environmental implications. As it stands that section reads as a summary. However, the implications section should extrapolate the findings to their impact on the environment and future work.

According to the comment, we have rewrote the environmental implications as following: “$^{3}C^*$ *plays an important role in the formation and aging process of atmospheric aerosols. On the one hand,* $^{3}C^*$ *itself is reactive and can directly react with other substances. On the other hand, it can produce* $^{1}O_2$ *and ·OH and other ROS substances, which indirectly participate in the generation reaction of aerosol components. This study demonstrated that the 3C* generation characteristics of different polar components in atmospheric particulate matter samples are different. Low polar components appear to play an important role in photochemical properties. Previous studies have suggested that water-soluble organic matter may play an important role in the generation of triplet states, but at present, water-insoluble substances or hydrophobic substances may contribute more to the generation of triplet states. This has certain implications for future research directions.*
The results of this paper show that the heterogeneous aerosol reaction can enhance the triplet photochemical reaction. The obtained results also proved that there is a coupling effect of photochemical reaction between HP-WSM and HULIS. What is the specific coupling effect between substances, and what is the coupling mechanism that is necessary to explore this aspect in the future.”

12. The concentrations used by the authors of 100 mgC/L is very high. How did the authors obtain such high concentrations from aerosol filters (about a factor 10-100 more than typically found on PM filters in polluted environments)

The samples used in this paper are concentrated. After the extraction is obtained according to the normal extraction steps, the concentration at this time is not enough for triplet experiments, so the solution is evaporated by rotary evaporation and nitrogen blowing, and then quantitatively dissolved in a solvent to obtain the sample solution we used. The following figure shows the *concentration flow chart*. We have added this schematic to the supplementary material.

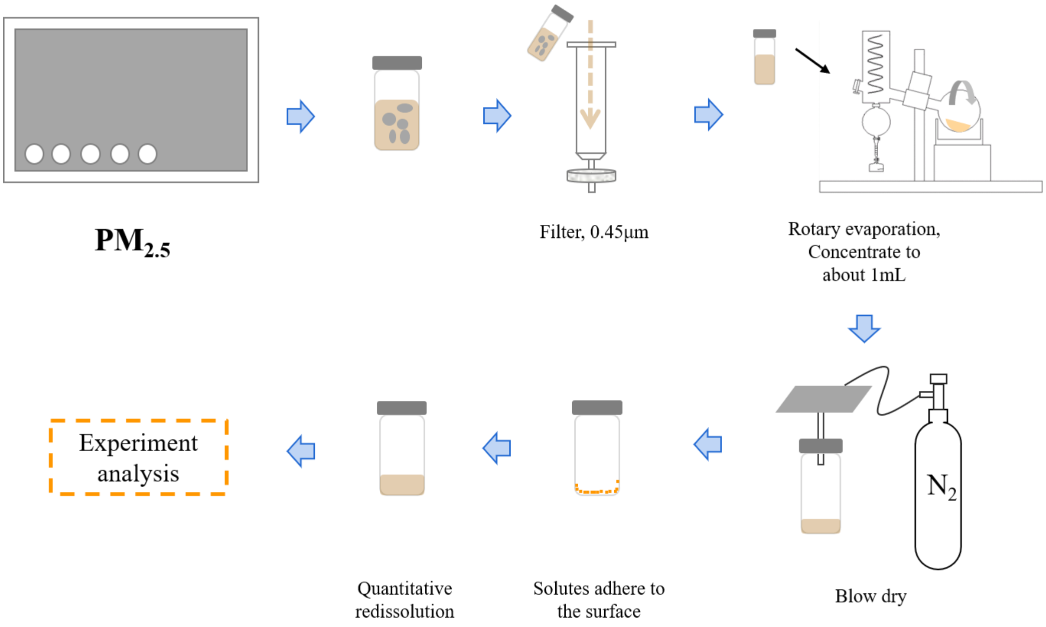


Fig.S4. Schematic diagram of solution sample concentration process.

13. How were the percentages in the first paragraph of the results calculated?

We have added "*Relative content is determined by the ratio of the OC value in the sample solution and the total OC value in the original film sample. The unit has been uniformly converted to the equivalent atmospheric mass concentration.*" in the description of Figure 1.

14. The authors must compare their results with the literature (ex. Line 213-214, "moderate level" compared to what?)

Since the content of HULIS fluctuates greatly according to different seasons and regions, it is impossible to generalize its content level, so this sentence in the improved paper has been deleted.

We have deleted "*In this study, HULIS accounts for 26% of WSOC, which is at a moderate level.*"

15. The EPR results are promising, but how do these measurements compare with quantitative methods?

EPR is the most direct and effective technical means to detect the generation of free radicals. Probe methods are somewhat non-specific and can lead to overestimate results. The EPR method can aid in the illustration. In this study, we did not use EPR to quantitatively study free radical production. We used it to directly verify free radical production and relative comparison.

16. Show the blanks/controls in Fig. 5

In order to remove the artificial interference during the experiment, the data curve results have been processed to subtract the value of the background sample. In Figure 5, the purpose is to verify whether there is a coupling effect between HPWSM and HULIS. The figure below is a comparison chart with the background signal. We have added the Figure S22 in the SI.

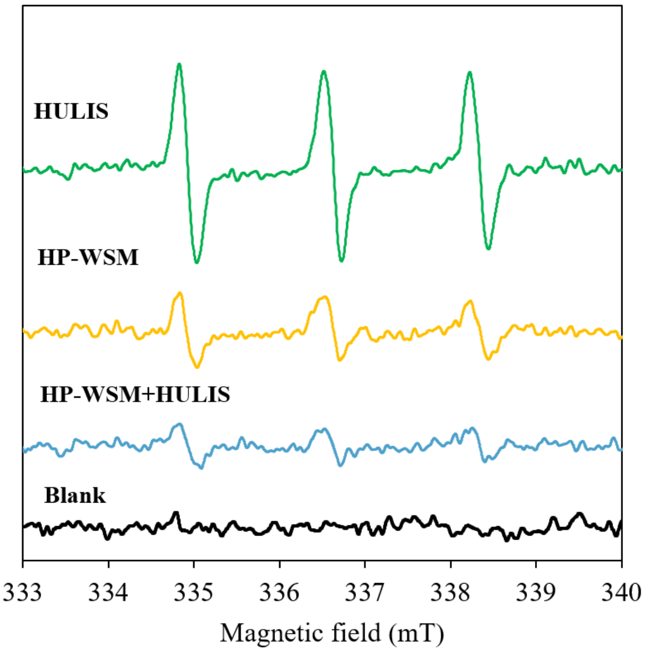


Fig.S22. EPR diagrams of different polar components and their interactions for produces $^1O_2$.

Response to Anonymous Referee #2

The authors examine the photogeneration of triplet excited states ($^3C^*$) in extracts of fine particles collected from the atmosphere and from several emissions sources (e.g., wood burning). The novel aspect of the work is examining triplet generation in three different polarity fractions of the PM: high-polar water soluble material (HP-WSM), water-soluble humic-like substances (HULIS), and lower polarity methanol soluble material (MSM). They also measure the formation of singlet molecular oxygen ($^1O_2^*$) and hydroxyl radical (OH) in some of their samples. The broad idea of examining the photoreactivity of chromophores as a function of polarity is interesting. There are also some interesting results in the manuscript. But it's not clear that the results can be trusted since there are several important experimental errors, described below. The manuscript also suffers from a frustrating lack of care in the writing, which makes the work very difficult to read and understand. Based on these important and widespread problems, I recommend that the manuscript be rejected.

We appreciate the comments from reviewer. We appreciate the positive evaluation of this work and very professional suggestions for improvement. According to the reviewer's comments, we have revised this paper. The details are as follows. *The blue italics are comments of reviews. The red italics are improvements and original text of reviews.* The black font are responses.

1. Quenching. The quenching experiments used to distinguish between high and low energy triplets (Section 3.3) are problematic. The authors examine the difference in 1O2 formation with and without 1 mM sorbic alcohol (SA), which they believe will quench the high energy triplet states. But this concentration of SA is not high enough to completely prevent high-energy triplet states from reacting with dissolved O2 to make 1O2*. This leads to an incorrect assessment of high and low energy triplets. The authors need to use the kinetics of the 3C* + SA and 3C* + O2(aq) reactions, along with the SA and dissolved O2 concentrations, to understand what fraction of high-energy triplet states were actually quenched. They can then use this information to revise their estimate of high- and low-energy triplets. Worse, the quenching experiments used to determine the contribution of triplets to OH generation (Section 3.4) are unusable. Sorbic alcohol, which they use as a triplet quencher, also reacts rapidly with OH to suppress its concentration. Thus examining the decline in OH with SA does not indicate the contribution of triplets to OH generation, as the authors believe, but shows the direct scavenging of OH. This is why the authors find an unreasonably high contribution of triplet states to the generation of OH. The authors should calculate the expected decrease in OH signal based on the competition of OH between the EPR probe DMPO and SA. This likely explains most of the reduction in OH observed, indicating these results are unusable. Also in Section 3.4, the authors need to dig deeper into their 1O2* results with the triplet quencher sorbic alcohol. Of course "...3C* is an important precursor for the photochemical generation of 1O2". This is well known. The more interesting question is why doesn't sorbic alcohol completely quench 1O2* generation? The authors should examine the competition kinetics of 3C* reacting with sorbic acid and O2 to see if their results make sense based on the concentrations of the two reactants.*

(1) In this study, sorbic alcohol was selected as the quencher to quench the high-energy triplet state. Its concentration was obtained according to the reference (Zhou, H. X., et al., 2019). Secondly, we also used 2mM sorbic alcohol as a comparison, and verified that the concentration of 1mM can

completely quench high-energy triplet state, adding "*1 mM, enough to quench*" in the section 2.6 in the improved paper.

- Zhou, H. X., Yan, S. W., Lian, L. S., Song, W. H.: Triplet-state photochemistry of dissolved organic matter: triplet-state energy distribution and surface electric charge conditions, Environ. Sci. Technol., 53, 2482-2490, http://dx.doi.org/10.1021/acs.est.8b06574, 2019.

(2) The picture below shows the same sample quenched by 1mM and 2mM SA, respectively (the MSM of the simulated coal-burning samples is selected because it has the strongest triplet ability).

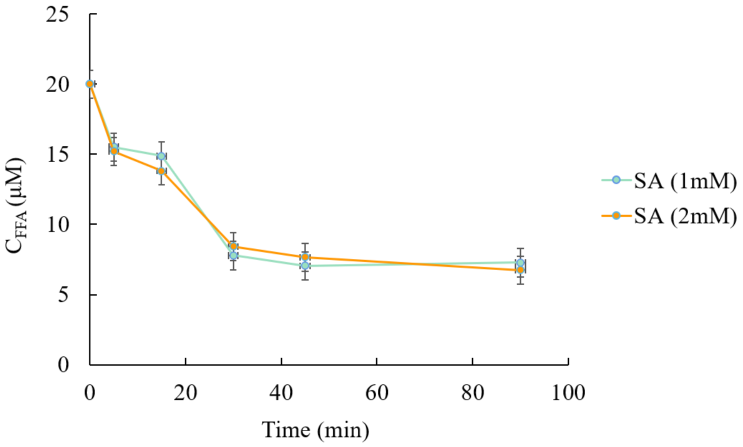


Fig.S10. Quenching effect of different concentrations of quencher on samples.

(3) The reviewers' concerns are understandable and do explain the findings of this paper. Many previous studies used sorbic acid to quench the triplet state, and later studies reported that Sorbic alcohol is a quencher with stronger specificity and more stable properties than sorbic acid (Zhou, H. X., et al., 2017a), so this paper selects Sorbic alcohol as the quencher. And the ·OH signal is indeed weakened after quenching with sorbic acid in the previous article published by our research group (Chen, Q. C., et al., 2021). Therefore, we believe that the triplet state contributes to the generation of hydroxyl groups, and it remains to be verified how much the contribution is.

(4) The generation and quenching of triplet states is a dynamic process. They reach a dynamic equilibrium at a certain stage of the reaction, and the appearance is that the triplet is no longer generated and is reacted away. When O_2 intervenes, a new balance will be reached, so each will not disappear. This is the amount of dynamic balance.

- Zhou, H. X., Yan, S. W., Ma, J. Z., Lian, L. S., Song, W. H.: Development of novel chemical probes for examining triplet natural organic matter under solar illumination, *Environ. Sci. Technol.*, 51, http://dx.doi.org/10.1021/acs.est.7b02828, 11066-11074, 2017a.
- Chen, Q. C., Mu, Z., Xu, Li.: Triplet-state organic matter in atmospheric aerosols: Formation characteristics and potential effects on aerosol aging, *Atmos. Environ.*, 252, 118343, https://doi.org/10.1016/j.atmosenv.2021.118343, 2021.

2. TMP as a Measure of Triplets. The authors have ignored the potential inhibition of TMP decay by sample constituents, especially phenols and dissolved copper (Canonica, Photochem. Photobiol. Sci. 2008; Pan, ES&T, 2018). This inhibition slows the apparent decay of TMP, leading to an *underestimate of triplet concentrations (or, here, k(TMP) and f(TMP)). Since both phenols and copper will be most enriched in the HP-WSM fraction, the slow TMP loss seen in this fraction could be a result of inhibition (which is an artifact) and not the result of low triplet concentrations. The authors should measure inhibition factors of TMP loss in different fractions. This inhibition of TMP loss is a more likely explanation of their HP-WSM results than is the theory presented on page 12. TMP inhibition is probably also a major contributor to the apparent lack of TMP loss in the BB samples (Fig. 2). Previous work has shown that biomass burning PM generate high levels of triplets (e.g., Kaur, ACP, 2019), including the authors' own recent work showing that BB emissions had the highest triplet reactivity (Chen, Atm Env, 2021). I suspect that part/most of this "missing reactivity" is due to inhibition of the TMP probe, which has been seen previously at DOC concentrations of 20 mg-C/L. Essentially, the oxidized TMP probe is reduced back to TMP by phenols in the BB extracts, reducing the apparent loss of TMP. See work by Canonica and others for a description of the inhibition. If this is the reason for the Fig. 2A BB results (which seems likely), it means that they're incorrect and that triplets are generated. Also, the authors appear to believe that oxidant probes are perfectly specific, i.e., only react with the oxidant of interest, but this is not true. For example, TMP reacts with OH and 1O2* as well as triplets. These interferences have often been minor in past studies, but this is not always the case. The authors should quantify OH and 1O2* in some samples to see if they make significant contributions to TMP loss. Finally, for triplets the authors report k(TMP), the pseudo-first-order rate constant for TMP loss, and f(TMP), the quantum yield coefficient for 3C*. While these quantities are useful for comparing with past work, they're limited in value otherwise. It would be much better to estimate and report 3C* production rates and quantum yields, which are more useful. The authors should think about how they could estimate these quantities based on their data.*

(1) Thanks to the reviewers for their valuable comments. It is undeniable that there are indeed some metal ions (eg, dissolved copper) that inhibit triplet formation. However, As mentioned in the article of Pan et al., when the copper ion reaches 50μM, it will have an inhibitory effect on the triplet state. But the content of copper in the actual aerosol is very low, even if the concentration is increased several times in this experiment, the content of dissolved copper in the sample is still at the nM level. So, this content of copper ion is not enough to have a fundamental impact on the experimental results.

We have added "*It is worth noting that although HP-WSM contains a lot of inorganic salts, its concentration is still very low and will not have a negative effect on the experiment.*" in section 3.2.

(2) It cannot be denied that the low triplet activity exhibited by the biomass samples in this paper is inconsistent with previous studies. It is even inconsistent with the results of previous articles of this research group. Through a comprehensive comparison from sample preparation to measurement process, it is found that the problem may be generated in the preparation of the combustion samples. About 2 g of raw material was weighed in the preparation of the simulated combustion samples in this study, which was several times higher in previous studies. Since there are more raw materials, there are more combustion products, which may cause more molecular species to polymerize to form macromolecular species during the collection process. As a result, the physicochemical properties of the sample itself have been changed.

We have add "*Weigh a certain mass of raw material samples for combustion (about 2 g), and collect spawns through a self-built combustion-gathering device.*" in the section 2.2.

(3) The probe method to study triplet states is a simple and widely used method. And TMP is the most commonly used triplet probe. As the reviewer said, although it cannot be said that TMP is completely specific to the triplet state, it is generally recognized that it has strong stability and anti-interference. The references cited in this paper all use TMP as a triplet probe. At the same time, except for triplet, the content of other oxidizing substances (hydroxyl, singlet oxygen) contained in the sample is very small, which has little effect on the loss of TMP.

- Bodhipaksha, L. C., Sharpless, C. M., Chin, Y. P.: Triplet photochemistry of effluent and natural organic matter in whole water and isolates from effluentreceiving rivers, *Environ. Sci. Technol.*, 49, 3453-3463, https://doi.org/10.1021/es505081w, 2015.
- Halladja, S., Ter-Halle, A., Aguer, J. P.: Inhibition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol: Evidence for reactivity of the phenol with humic triplet excited states, *Environ. Sci. Technol.*, 41, 6066-6073, https://doi.org/10.1021/es070656t, 2007.
- Kaur, R., Anastasio, C.: First measurements of organic triplet excited states in atmospheric waters. *Environ, Sci. Technol.*, 52, 5218-5226, https://doi.org/10.1021/acs.est.7b06699, 2018.

(4) Very much agree with the reviewer's comments. The quantum yield is the most direct and effective method to evaluate the triplet generation ability. However, f_{TMP} is also widely used as an evaluation index for triplet generation, which is also scientific and objective. Compared to quantum yield, f_{TMP} requires less experimental measurement.

3. The Writing. The manuscript is often difficult to read, sometimes because there are multiple ideas strung together without a logical flow or transitions, and sometimes because the text doesn't make sense. Examples of the latter include:
line 80, "The cause of the formation of 3C is directly related to the chromophore."*

We have corrected "*The cause of the formation of 3C* is directly related to the chromophore.*" to "*Since the chromophore is the direct reason of triplet generation.*" in the improved paper.

lines 170-172, "The sorbic alcohol (1 mM) is used as a high-energy quencher to quench high-energy 3C (Zhou et al., 2017a), and combine the Φ(1O2) to quantify the energy distribution of different 3C*."*

We have corrected "*The sorbic alcohol (1 mM) is used as a high-energy quencher to quench high-energy* $^3C^*$ *(Zhou et al., 2017a), and combine the* Φ_{1O2} *to quantify the energy distribution of different* $^3C^*$." to "*Dissolved oxygen can be converted into singlet oxygen by energy transfer due to triplet state. Therefore,* Φ_{1O2} *can be used to evaluate the energy distribution of the triplet state. The sorbic alcohol (1 mM) is used as a quencher to quench high-energy* $^3C^*$ *(Zhou et al., 2017a).*" in the improved paper.

line 371: "For the organic component HULIS, the production of ·OH is mainly the effect of organic matter."

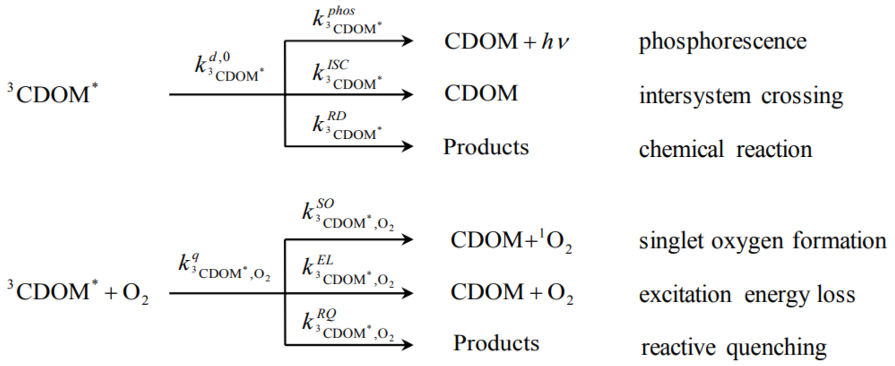
We have corrected "*For the organic component HULIS, the production of ·OH is mainly the effect of organic matter.*" to "*For HULIS components, the generation of ·OH are only possible from organics.*" in the improved paper.

In addition, portions of the text are incorrect. For example, lines 122-123: "Note that the MSM [methanol-soluble material] here does not actually contain water-soluble substances, thus it represents water-insoluble organic matter." This is almost certainly not true: a significant portion of the compounds in the particles will be soluble in both water and methanol. Another example is lines 264-265: "At the same time, these small molecules are also easy to quench the triplet state." The evidence I have seen – that small molecules do not quench triplet states – contradicts the authors' claim.

(1) The MSM here is obtained by water solvent extraction followed by methanol solvent extraction. At this time, most of the extracted substances are not easily soluble in water. In order to study from the perspective of polarity, they are called water-insoluble substances here.

(2) The expression "*lines 264-265*" means that energy can be released through physical processes without chemical reactions. The figure below shows a possible reaction pathway for the triplet state stated in the study by Rosario-Ortiz et al., which verify 3C* to lose energy through physical processes.

We have corrected "*At the same time, these small molecules are also easy to quench the triplet state.*" to "*3C* release energy by physical means*" in the improved paper.



Deactivation pathways for 3CDOM* in the presence and absence of oxygen
(Rosario-Ortiz & Canonica, 2016)

- Rosario-Ortiz, F.L., Canonica, S., Probe Compounds to assess the photochemical activity of dissolved organic matter, *Environ. Sci. Technol.*, 50, 12532-12547. http://doi.org/10.1021/acs.est.6b02776, 2016.

Another writing issue is that the authors were not very careful, with numerous instances of typographic errors, incorrect capitalization, noun-verb disagreement, and other issues. The manuscript needs significant attention from a scientific English editor, but it also needs a reworking so that the authors clearly state what they mean. There are also multiple instances of incorrect citations, suggesting little care was taken in citing references. For example, on line 237, the Ervens et al. citation does not discuss any of the issues of the accompanying sentence. Finally, in terms of writing, much of the discussion about the results is speculative and ignores or glosses over inconsistencies, either within the results or compared to past results. For example, the BB results (no triplet formation) directly contradicts past results showing high triplet reactivity in BB-influenced samples. In addition, it doesn't make any sense that the HULIS + HP-WSM mixture increases 3C levels but significantly decreases 1O2*. I wonder if the mixture makes more OH, which reacts with TMP to make it appear as if more 3C* is formed.*

The typography and writing issues of the article have been rechecked and corrected. Thanks to the reviewers for their careful review and valuable suggestions as below.

We have corrected “the formation characteristics of ^{3}C* in the aerosol components with different *polarity* were investigated…” to “the formation characteristics of ^{3}C* in the aerosol components with different *polarities* were investigated...” in the abstract.

We have corrected “including highly polar water-soluble matter (HP-WSM), humic-like substances (HULIS) *and* methanol-soluble matter (MSM)…” to “including highly polar water-soluble matter (HP-WSM), humic-like substances (HULIS)*, and* methanol-soluble matter (MSM)...” in the abstract.

We have corrected “The results show that the ^{3}C* generation characteristics *is* strongly dependent on the polarity of these components.” to “The results show that the ^{3}C* generation characteristics *are* strongly dependent on the polarity of these components.” in the abstract.

We have corrected “…and the MSM *contribute* the most to the total generation of ^{3}C*…” to “…and the MSM *contributes* the most to the total generation of ^{3}C*…”in the abstract.

We have checked the full text, see modified version for other revisions.

4. Other Experimental Issues.

There is no discussion of pH, which is an important variable. Were the pH values of the extracts controlled with a buffer? pH values (at least of aqueous extracts) should be listed in the paper. It seems likely that the different polarity extracts had different acidities, which could affect reactivity. This issue should be discussed.

PH does have an important influence on atmospheric chemical reactions. However, the pH of the aerosols in the region tends to be stable and will not change significantly. Urban aerosols are generally weakly acidic (around 5), as explained in the study by Ding J et al. In particular, the samples used in this study are low-concentration solutions. Therefore, it will not change its pH in aerosol-related research, preventing the physical and chemical properties of the sample from being changed. The HULIS component is also weakly acidic. The study by Sengupta D et al. also involved the extraction of components with different polarities. The method is the same as this paper, without changing the pH of the sample.

We have added “*And pH is not expected to affect the results of this study because the diluted sample solution*.” in the section 2.2.

- ➢ Ding, J., Zhao, P. S., Dong, Q., Du, X., Zhang, Y. F.: Aerosol pH and its driving factors in Beijing, *Atmos. Chem. Phys.*, 19, 7939–7954, https://doi.org/10.5194/acp-19-7939-201, 2019.
- ➢ Sengupta, D., Samburova, V., Bhattarai, C., Kirillova, E., Mazzoleni, L., Iaukea-Lum, M., Watts, A., Moosmüller, H., Khlystov, A..: Light absorption by polar and non-polar aerosol compounds from laboratory biomass combustion, *Atmos. Chem. Phys.*, 18, 10849–10867, https://doi.org/10.5194/acp-18-10849-2018, 2018.

There are no reported daily actinometry (i.e., photon flux) measurements, which make it impossible to extrapolate oxidant rates of formation to ambient conditions. Fig. S5 shows that the experimental light has a much higher photon flux at short wavelengths than actual sunlight, which might affect the chemistry. This should be shown in more detail. I assume that the two curves in this figure are *adjusted to have the same peak magnitude, but this should be indicated. Actinometry is needed to relate the two curves.*

The photon flux of sunlight in the figure is a standard value for reference. The photon flux varies from region to region. The actual intensity of the light source simulated by the device is similar to the local one after filtering out the unwanted light.

Minor Issues

The authors should report k(TMP) in each polarity fraction of the extracts of the field blanks (that were taken through the entire sample procedure) and compare these to sample values. Also, additional information is needed about how blank corrections were done and the magnitude of these blank corrections.

There are three sets of backgrounds in this study. We increased the TMP background depletion for each polar component. It can be seen that the background hardly consumes TMP, that is to say, the contamination of the experimental process is small and can be ignored. Furthermore, since the TMP of the background sample is almost not depleted, the decay of TMP does not conform to first-order reaction kinetics, i.e. no *k* value can be derived.

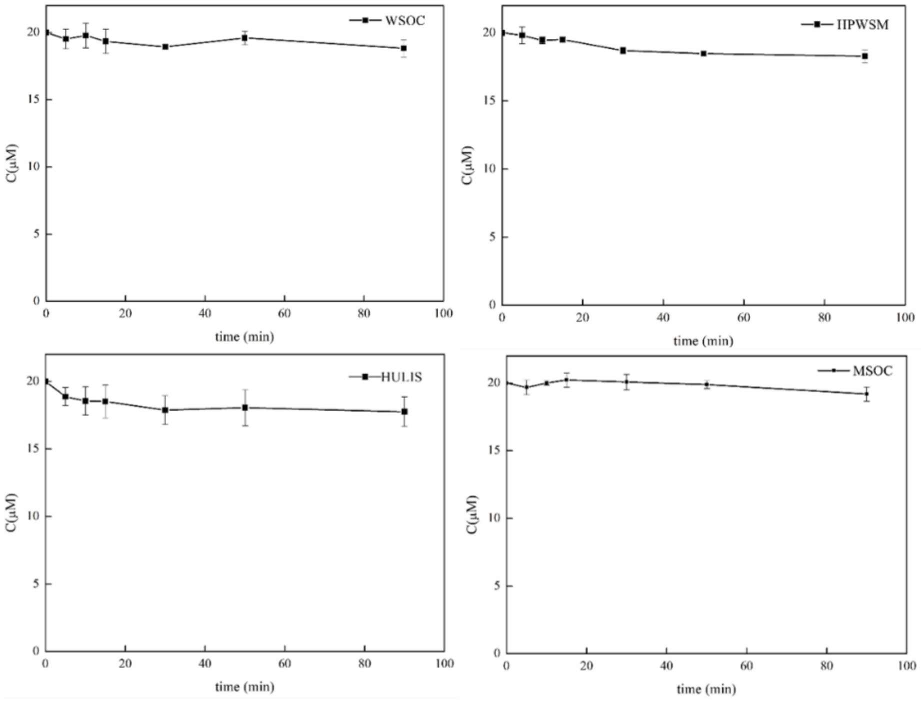


Fig.S19. Loss of TMP in different polar components of background samples. The figure shows the consumption of TMP in the triplet test of the extraction solution of the background sample. The data fluctuates at different time points, indicating the absence of a specific response. In addition, the difference between the initial concentration and the lowest point is 5% of the sample solution, that is, it can be said that the background influence is controlled within 5%.

The authors use the terms "probe" and "quencher" interchangeably, which is confusing. A probe is generally added at a low concentration to measure (but not perturb) the oxidant steady-state concentration, while a quencher is typically added at a high concentration to greatly suppress the oxidant concentration.

We have replaced “*capture agent*” with “*probe*” in the full text.

Information about the absorbance by each extract needs to be reported, e.g., MAE at 300 nm, Angstrom absorption exponent, and calculated rate of light absorption.

We have added graphs of the optical properties of each polar component of the sample in SI. To visualize the results, we averaged the samples.

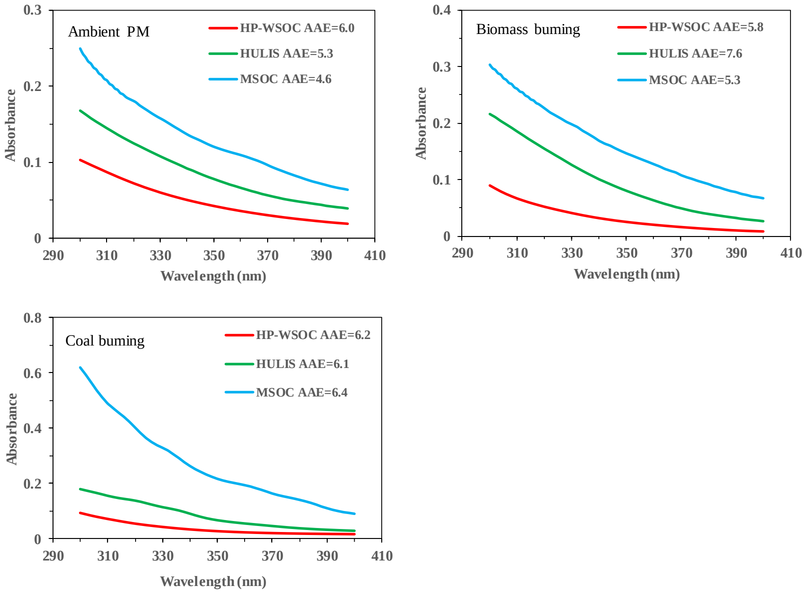


Figure S15. Absorption spectra of different polar components in ambient aerosol, biomass burning, and coal burning samples.

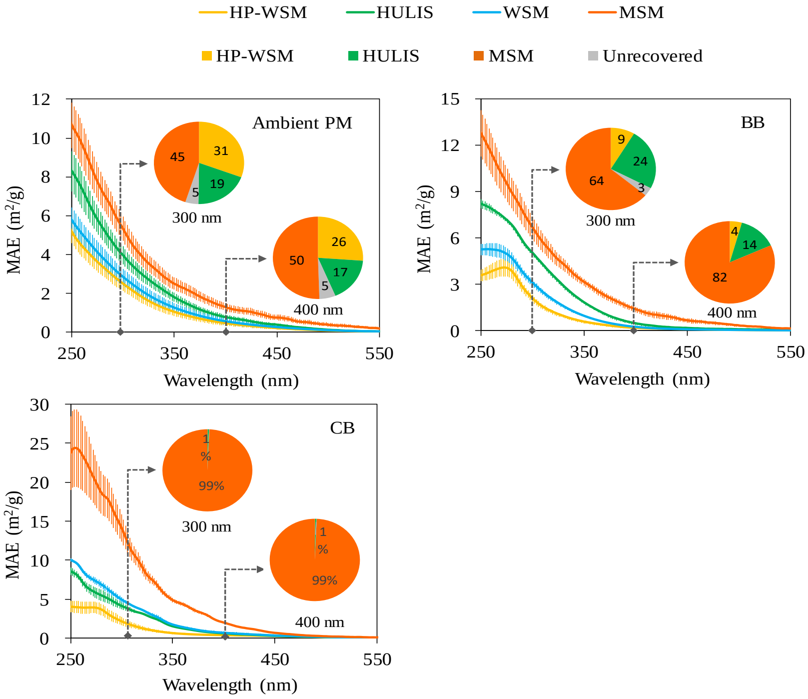


Fig.S16. The relationship between MAE and wavelength of different polar components in ambient aerosol, biomass burning, coal burning samples, and the relative contribution of different polar components to the light absorption at 300 nm and 400 nm

The word "ambient" is usually misspelled in the manuscript (e.g., in figures).

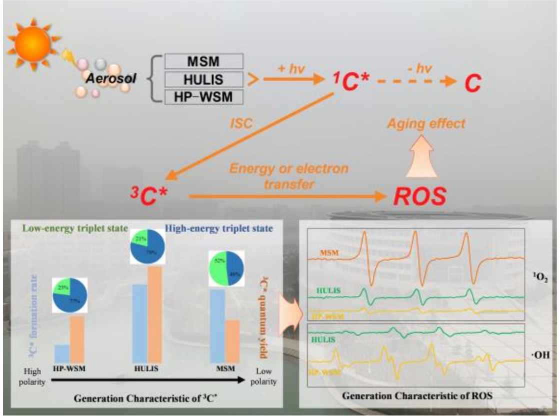
We have corrected to correct spelling *in the Figure 1 and Figure 2*.

The title is confusing ("Formation characteristics of aerosol triplet state and coupling effect between the separated components with different polarity").

According to the comment, we have revised the title as "Characterization of aerosol triplet state in the separated components with different polarity".

The abstract TOC art shows "Aging" converting ROS to C, but this process seems very unlikely. I recommend they remove this arrow unless there's good evidence this occurs.

According to the comment, we have revised the abstract TOC.



line 32. This text is wrong: "Part of the photochemical reaction of aerosol is direct photolysis, and in most cases, it is driven by photochemically generated reactive intermediates…" This is incorrect: in direct photolysis, reactions are initiated directly by light, not by reactive intermediates.

We have corrected "*Part of the photochemical reaction of aerosol is direct photolysis, and in most cases, it is driven by photochemically generated reactive intermediates….*" to "*Aerosols can undergo direct photolysis reactions under light radiation, and can also undergo secondary reactions with reactive intermediates, including triplet organics (3C*) and reactive oxygen species (ROS)"* in the improved paper.

l. 112. What was the flow rate of the sampler?

We have added sampled traffic information "*with a sampling flow rate of 1000 L/min*"

l. 128. What was the maximum storage time in the refrigerator?

Generally, the samples used for the next experiment (1-3 days) will be stored at -4 ℃, and the temporarily unused samples will be stored frozen (-20 ℃).

Section 2.3. This OC/EC analysis section is confusing. By "original sample" do the authors mean the sampled filter? Is the "6 mm diameter filter membrane" a 6-mm punch taken out of the sampled filter and analyzed for OC/EC?

Yes, in order to analyze the OC content of the original sample, we use the filter sample for analysis.

l.172. k(TMP) is a rate constant, not a rate.

We have corrected in the improved paper.

l. 187. The rate of light absorption (eq. 3) was determined for a wavelength range of 320 to 600 nm. But there is significant light absorption, and some photons from the solar simulator, at shorter wavelengths, so the lower wavelength range should be extended to 280 nm or shorter. Values of R(a) should be reported in the supplement.

In this study, to better simulate the solar spectrum, we used a UV filter, which has almost filtered out the light below 320nm. In fact, the ultraviolet rays below 320 nm that sunlight irradiates on the ground are already very little and can be ignored.

l. 224-226. Fig. S11 doesn't seem to be correct figure for this point. The fact that the OC from combustion samples is higher than ambient samples is only a result of dilution. This last sentence doesn't add anything to the manuscript and should be deleted.

According to the comment, we have removed useless information.

Fig. 1 (and other figures). (a) It would be helpful to have an explanation of how to read the nested pie (and bar) charts in the caption. (b) In bottom plot of Fig. 1, why isn't the OC bar equal to 100% on the Relative Content axis? Is it because EC or inorganic carbon included in the C budget? Why are the errors so large on the OC bars? The relative standard deviations are much larger here than on the absolute OC mass concentration bars in the panel above. (c) There is essentially no OC in the HULIS fraction of coal burning PM (Fig. 1), so how can this lead to significant TMP consumption (Fig. 2)? Is this caused by contamination?

(1) We have added "*Bottom legend applies to column and pie charts.*" in the title of Figure 1.

(2) Yes, the C budget included EC and OC. The uneven distribution of particles on the filter membrane may be the result of large errors.

(3) The content of HULIS in coal is very small, so we make it reach the experimental conditions by the method of concentration.

Fig. 2. (a) In part A, how did the authors determine an "average" attenuation curve of TMP consumption across the samples? Or are the curves shown in Fig. 2 from the median reactivity sample? (b) Also in part A, the TMP decay order for ambient PM is HULIS > WSOC ~ MSOC. But the corresponding values for k(TMP) are MSOC ~ HULIS > WSOC. Why is this? Are k(TMP) values determined based on C/Co vs. t or ln(C/Co) vs t? It appears that the authors used the former method, but the latter gives more robust results. (c) In Fig. 2B, there are large error bars for several of the extract conditions, which I assume reflects the intersample variability, but this should be explained. (d) To better show the difference between the measured and calculated HP+HULIS conditions, the authors should make a supplemental figure that shows the ratio of (measured/calculated) for each sample and the overall average; this would reduce the impact of the large differences in absolute reactivity between samples. (e) Examining the interactions of metals with HULIS components, and how it affects triplet concentrations, is interesting. But the description of the process followed is very difficult to understand. (f) For Figure 2C, it's not clear how the "Other" category was calculated and why it is all attributed to WSOC. This should be explained in the text.

(1) The data in the figure was obtained by calculating the average of all individual sample data.

We have added “*n: number of samples, n=10 for Ambienr PM; n= 6 for BB; n=2 for CB.*” in the caption of the figure 2.

(2) (A) is the averaged decay curve for all samples; while (B) shows the average of the decay constants for all samples. Thus presenting seemingly different results.

We have added “We have added “*The k_{TMP} value is the average of the sums of all individual sample k_{TMP} values.*” in the caption of the figure 2.

(3) The source and chemical composition of particulate matter in ambient samples vary, so it is normal to have large variability. In addition, the *k* value of biomass burning samples in this study is small and seems to be highly variable, which has a great relationship with the combustion conditions, and the combustion in this study is relatively sufficient.

(4) We have supplemented *the k value information for each sample into the supporting information*.

Components **Sample number**	**WSM**	**MSM**	**HP-WSM**	**HULIS**	**HP-WSM + HULIS**
2019/12/21	0.016	0.007	0.005	0.020	0.016
2019/12/25	0.009	0.014	0.006	0.025	0.018
2020/1/3	0.011	0.013	0.003	0.010	0.013
2020/1/9	0.011	0.033	0.006	0.021	0.027
2020/1/13	0.02	0.032	0.001	0.037	0.013
2020/1/16	0.009	0.022	0.002	0.025	0.011
2020/1/18	0.012	0.007	0.006	0.013	0.011
2020/1/23	0.009	0.015	0.008	0.010	0.009
2020/1/25	0.015	0.011	0.002	0.018	0.016
2020/2/1	0.017	0.028	0.002	0.009	0.009
Ave	0.013	0.018	0.004	0.019	0.014
SD	0.004	0.009	0.002	0.008	0.005
Wheat-straw1	0.002	0.000	0.000	0.000	0.000
Wheat-straw2	0.001	0.000	0.000	0.000	0.000
Rice-straw1	0.001	0.005	0.000	0.001	0.001
Rice-straw2	0.002	0.004	0.000	0.001	0.001
Wood1	0.001	0.001	0.001	0.000	0.001
Wood2	0.001	0.003	0.001	0.000	0.000
Ave	0.001	0.002	0.000	0.000	0.000
SD	0.000	0.002	0.000	0.000	0.000
coal 1	0.031	0.050	0.000	0.047	0.033
coal 2	0.01	0.062	0.000	0.054	0.018
Ave	0.020	0.056	0.000	0.051	0.025
SD	0.015	0.008	0.000	0.004	0.011

(5) This suggestion is very good, but not the focus of this study. We have also recently focused on the changes in optical properties caused by the interaction of metallic elements with HULIS, which will be reported in a separate study.

(6) WSM is a mixture of HULIS and HP-WSM, and there is a coupling effect of TMP depletion between them. HULIS and HP-WSM alone cannot explain the TMP depletion of WSM partly due to the coupling effect.

We have added “We have added “*‘Other’ represents the change in k_{TMP} value due to coupling*” in the caption of the figure 2.

l. 301. The addition of nitrate should lead to additional TMP consumption, since nitrate photolysis is a source of OH, which will react with TMP. What nitrate concentration was tested? How does it compare to the maximum ambient sample value?

Confirmatory experiments used 0.1M sodium nitrate. As a result, TMP was not consumed, indicating that there was no strong specific reaction between TMP and hydroxyl.

Figure 4. What sample is this? (The sample ID(s) should be indicated for all figures.)

Figure 4 uses an ambient aerosol sample, and it is a mixed sample (mix the samples in equal volumes to form the ambient samples)

Table.S8. Sample list for the samples used in Figure 4.

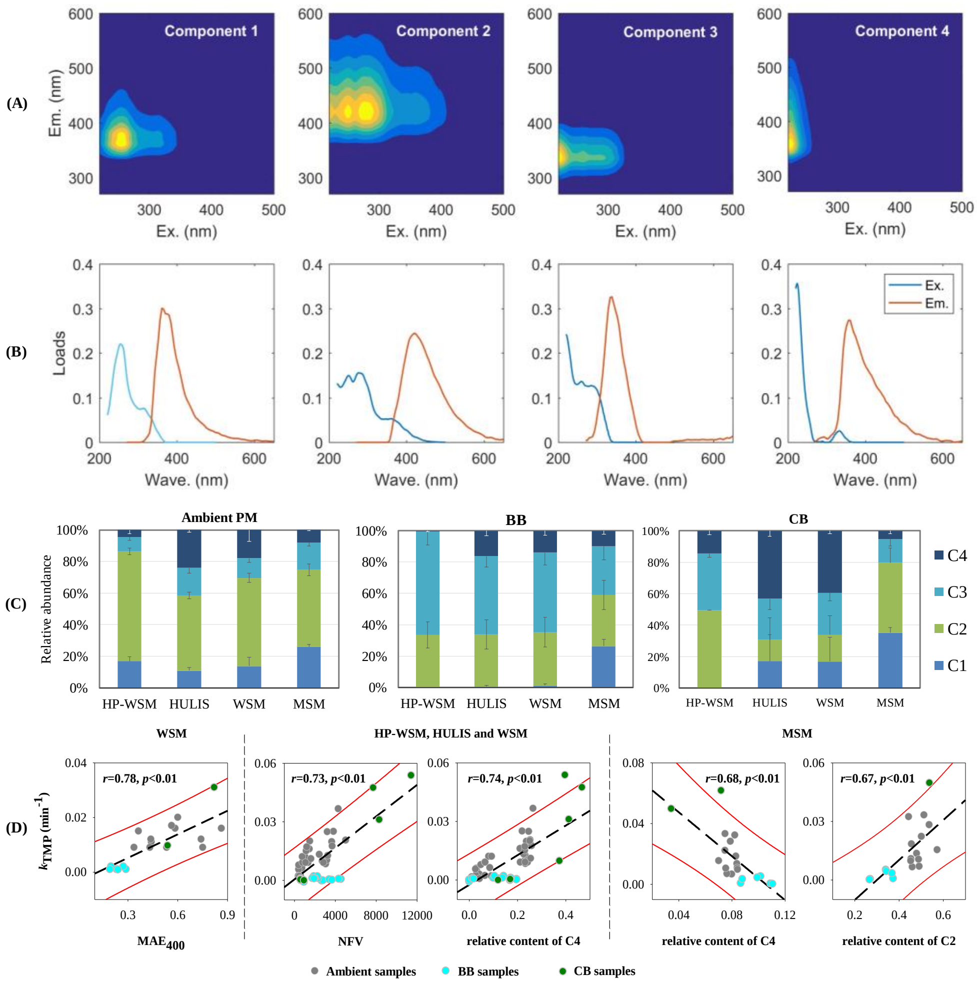
Combined sample	Original sample
S1	2019/12/21 2019/12/25 2020/01/03
S2	2020/01/13 2020/01/16 2020/01/18
S3	2020/01/23 2020/01/25 2020/02/01

Fig. 5. The last sentence of the caption should be deleted since it only repeats information from earlier in the caption.

We have removed the last sentence of the caption in the improved paper.

Fig. 6. (a) What samples are included in these regressions? Is it only the ambient PM extracts or does it also include the primary emission sources? If the latter, the points should be marked (e.g., with different symbols or colors) to show the different particle types (ambient, BB, CB). (b) The correlation of k(TMP) is strongest with light absorption at 400 nm. This plot is labeled WSM, but these “whole extract” experiments were not discussed previously - was TMP loss measured in whole water extracts of the PM? Why not show the HULIS and HP-WSM results on this plot also? And what about the MSM results?

(1) We have modified the figure 6 in the improved paper, as follow.



(2) Only the most significant data results are listed in the main text. The rest of the data are placed in supporting information. Please see the table

l.429. f(TMP) is not a quantum yield.

We have corrected "*quantum yield*" to "*quantum yield coefficient"* in the improved paper.

page 20. This discussion of the correlations does not add much to the manuscript and would be better shortened, without the speculative text about energy and electron transfer.

we have removed "*The correlation between the different polar components k_{TMP} and the composition of chromophores were explored (Fig.6), and the correlation analysis between the quantum yield coefficient f_{TMP} and different types of chromophores was also carried out, and the results were similar to k_{TMP} Trend (Fig.S18).*" in the improved paper.

Section 4. Environmental Implications. This section, which is too long, is mostly just a summary of the results. It should be significantly shortened to focus on the implications.

We have rewrote the last part, "*$^{3}C^{*}$ plays an important role in the formation and aging process of atmospheric aerosols. On the one hand, $^{3}C^{*}$ itself is reactive and can directly react with other substances. On the other hand, it can produce $^{1}O_2$ and ·OH and other ROS substances, which indirectly participate in the generation reaction of aerosol components. This study demonstrated* *that the $^3C*$ generation characteristics of different polar components in atmospheric particulate matter samples are different. Low polar components appear to play an important role in photochemical properties. Previous studies have suggested that water-soluble organic matter may play an important role in the generation of triplet states, but at present, water-insoluble substances or hydrophobic substances may contribute more to the generation of triplet states. This has certain implications for future research directions.*

The results of this paper show that the heterogeneous aerosol reaction can enhance the triplet photochemical reaction. The obtained results also proved that there is a coupling effect of photochemical reaction between HP-WSM and HULIS. What is the specific coupling effect between substances, and what is the coupling mechanism that is necessary to explore this aspect in the future."

Supporting Information

The supporting information has some useful components, but it is also filled with errors and text that is difficult to understand. For example:

(a) Table S1–are values averages over the sampling period? If so, give statistics (e.g., mean, standard deviation, range). What are the units for each quantity?

The information in Table S1 comes from the information released by the local weather station, not from the experiment. The purpose is to show the degree of air quality on the day of sampling. The units of each indicator have been added in the improved supporting information.

(b) Table S3 - It's not clear what most of the column headings mean, e.g., what is "Number of membranes" or "solvent amount"? All of these need to be explained in footnotes.

We have added footnote information in the improved supporting information, " *'number of membranes' refers to 'the number of filter membranes cut out in the experiment'; 'membrane diameter' refers to 'the diameter of the film cut in the experiment'; 'volume of solvent' refers to 'the volume of solvent used for ultrasonic extraction of membranes in the experiment'; 'volume after separation' refers to 'the volume of HULIS and HP-WSM after separation by C18 solid phase extraction column in the experiment'* "

(c) Page S8 – the description of the triplet and singlet oxygen experiments doesn't make sense. Part of the confusion is describing the oxidant probe as "quenching" the oxidant (e.g., TMP for 3C). But the probe doesn't quench the oxidant - it is added at a low concentration so as not to perturb the oxidant steady state concentration. Also, the probe concentrations listed here are twice as high as those stated in main text. Which is correct?*

We have revised some text description, changing *"quenching" to "reaction" and "quencher" to "probe".*

The concentration here is the same as in the main text, but the concentration here is the concentration before mixing, and the concentration in the main text is the concentration after mixing.

(d) Page S9 - Why make a standard curve for the oxidant probes? Their loss is first order, so the initial concentration doesn't matter: a plot of (Area)t/(Area)0 vs. t will give a line with a slope equal to the negative of the pseudo-first order rate constant for probe loss, e.g., k(TMP).

The analysis was performed using HPLC, and the consumption of the probe was directly reflected by the change in the peak shape area. Here the area and concentration are linked, the effect is the same, but it is easier to express.

(e) Page S10 - In Equation 1, "a" needs to be defined. The definition of quantum yield uses the term "quantum" sometimes to refer to "photon", which is confusing.

"a" is a constant, here is 1.

We have corrected the confusing description.

(f) Page S11 – need references for rate constants.

References have been added, "*references 7,8*".

- Mostafa, S., Rosario-Ortiz, F. L.: Singlet oxygen formation from wastewater organic matter, *Environ. Sci. Technol.*, 47, 8179-8186., https://doi.org/10.1021/es401814s, 2013.
- Dalrymple, R. M., Carfagno, R. K., Sharpless, R. M.: Correlations between dissolved organic matter optical properties and quantum yields of singlet oxygen and hydrogen peroxide, *Environ. Sci. Technol.*, 44, 5824-5829, https://doi.org/10.1021/es101005u, 2010.

(g) Table S4 could be deleted and replaced with a few sentence description.

We have added "*Different concentration requirements are required when performing optical experiments on samples. The following table shows the concentrations used in the measurement of absorbance and fluorescence for the different components of each sample.*" In the improved supporting information

(h) Table S5 only repeats data from Table 1 in the main text and should be deleted. (i) Fig. S12 – Describe what the dashed red boxes represent in the caption.

We have deleted table S5, and added "*the red dotted line represents the optical pyrolyzed carbon produced during the analysis.*" in the Figure S12.

(j) Fig. S16 – Purple symbols should be yellow.

we have modified in the improved paper.

(k) Fig. S18 – What do the two middle plots represent? What samples are shown in this figure? All? If so, use different symbols to represent different sample types.

(l) The 54 regressions shown in Figures S18 and S19 form the basis of some statistically sketchy work. The authors seem unaware that if you examine dozens of correlations you will get some significant relationships just by chance. Also, they seem unconcerned about the many cases where the correlations are driven by just one or two outliers. They need to deal with these issues in a rigorous statistical way.

we have deleted the Figure.S18 and Figure.S19 in the improved paper.

For better expression, we have added Table S6 and Table S7.

Table.S6. *Correlation between k_{TMP}, f_{TMP} and MAE_{400}, NFV, C1-C4 chromophores (Note: the C1-C4 chromophore data is its relative content).*

Factor / Sample	MAE_{400} with k_{TMP}		MAE_{400} with f_{TMP}	
HP-WSM	r=0.49	p>0.01	r=0.30	p>0.01
HULIS	r=0.23	p>0.01	r=0.06	p>0.01
MSM	r=0.60	p<0.01*	r=0.53	p>0.01
	NFV with k_{TMP}		NFV with f_{TMP}	
HP-WSM	r=0.47	p>0.01	r=0.52	p>0.01
HULIS	r=0.76	p<0.01*	r=0.85	p<0.01*
MSM	r=0.72	p<0.01*	r=0.75	p<0.01*
	C1 with k_{TMP}		C1 with f_{TMP}	
HP-WSM	r=0.71	p<0.01*	r=0.56	p>0.01
HULIS	r=0.56	p>0.01	r=0.39	p>0.01
MSM	r=0.66	p<0.01*	r=0.74	p<0.01*
	C2 with k_{TMP}		C2 with f_{TMP}	
HP-WSM	r=0.67	p<0.01*	r=0.62	p<0.01*
HULIS	r=0.28	p>0.01	r=0.51	p>0.01
MSM	r=0.37	p>0.01	r=0.23	p>0.01
	C3 with k_{TMP}		C3 with f_{TMP}	
HP-WSM	r=0.68	p<0.01*	r=0.64	p<0.01*
HULIS	r=0.50	p>0.01	r=0.35	p>0.01
MSM	r=0.61	p<0.01*	r=0.50	p>0.01
	C4 with k_{TMP}		C4 with f_{TMP}	
HP-WSM	r=0.04	p>0.01	r=0.13	p>0.01
HULIS	r=0.88	p<0.01*	r=0.85	p>0.01
MSM	r=0.70	p<0.01*	r=0.60	p<0.01*

*Indicates a significant correlation at the 0.01 level (two-tailed).

***Table.S7.** Correlation between $^3C^*$ energy and C1-C4 chromophore content (Note: the C1-C4 chromophore data is its relative content).*

Sample	**Factor**	**Correlation (two-tailed)**		
HP-WSM and HULIS	High energy 3C*	C1	r=0.42	p>0.01
		C2	r=0.24	p>0.01
		C3	r=0.09	p>0.01
		C4	r=0.58	p>0.01
HP-WSM and HULIS	Low energy 3C*	C1	r=0.17	p>0.01
		C2	r=0.10	p>0.01
		C3	r=0.16	p>0.01
		C4	r=0.17	p>0.01
MSM	High energy 3C*	C1	r=0.79	p<0.01*
		C2	r=0.24	p>0.01
		C3	r=0.17	p>0.01
		C4	r=0.36	p>0.01
MSM	Low energy 3C*	C1	r=0.85	p<0.01*
		C2	r=0.24	p>0.01
		C3	r=0.19	p>0.01
		C4	r=0.53	p>0.01

*Indicates a significant correlation at the 0.01 level (two-tailed).