Dear professor Chiara Giorio,

Thank you for your decision to allow us to revise our manuscript for publication in ***Atmospheric Chemistry and Physics***. Below is a point by point response to the comments of reviewers.

Editor:

The manuscript by Yang and co-workers investigates the role of organic carbon complexed with metals as a potentially important pathway for sulfate transformation. The study employs a broad range of analytical and computational techniques to characterize the investigated systems. Overall, the conclusions are generally supported by the presented data, and I therefore believe that publication may be warranted after revision. My main concern is that several of the analytical techniques are not sufficiently discussed in terms of their limitations and interpretation. As a result, some conclusions appear to rely more on correlations than on direct evidence of causation. For example, changes in absorption spectra are attributed to the formation or absence of metal−ligand complexes, yet alternative explanations, such as contributions from contaminant metals or other matrix effects, do not appear to have been adequately evaluated. I believe the manuscript would benefit from a more detailed discussion of the analytical capabilities, limitations, and quality assurance aspects of each technique used. In addition, the following points should be addressed:

Re: Thanks very much for allowing us to revise this manuscript. We have carefully modified our manuscript according to your comments and suggestions. The limitations of the analytical techniques have been discussed, and the interpretation of results has been revised accordingly. The UV-vis absorbance changes were measured as supporting spectroscopic evidence for OC and TMI interactions. To assess the contribution of contaminant metals, the background concentrations of Fe, Mn and Cu in OC were measured by ICP-MS, and they varied in the range of 1.23−7.70 μg L^{-1}. This accounted for only 0.0045%−0.0276% of TMI concentrations used for OC@TMI. Thus, the contribution of intrinsic Fe, Mn and Cu to the observed TMI dependent spectral changes was considered to be very limited. The related ICP-MS method and discussion have been added in lines 83−85 and 252−256 of the revised manuscript and Text S2 of the Supplement. We added more detailed descriptions of the analytical limitations, quality

assurance and quality control procedures in Text S1, S2 and S7 of the Supplement. The details of the DFT calculations were also clarified in Section 2.3.7 of the revised manuscript and Text S10 of the Supplement. Detailed responses to each specific comment are provided below.

1. Can the authors provide more context regarding the distinction between "weak" and "strong" complexation? Ideally, this should be related to stability constants (log K values) and placed into a broader chemical complexation context.

Re: Thank you. In the coordination chemistry, complexation strength is commonly described by stability constants, which are usually expressed as log K values. Larger log K values mean more stable metal ligand complexes. The OC used in this study was a heterogeneous mixture with multiple potential binding sites. The log K values may not be exactly determined. Weak and strong complexation described here was relative sense, according to UV-vis differential absorbance, fluorescence quenching and complexation energy. This clarification has been given in lines 306−310 of the revised manuscript.

2. It is not entirely clear what is meant by the terms "OC@Me" and "OC+Me". These terms are used frequently throughout the manuscript, but the distinction between them is not adequately explained.

Re: Thank you. Me denotes the corresponding metal ion. OC@Me refers to the actual sample prepared by introducing a specific metal ion into OC. OC+Me is defined as a reference sample, where the interaction between OC and Me is assumed to be nonoccurrence. The property of OC+Me represent the arithmetic sum of that measured separately for OC and metal ion. Thus, OC+Me was used as a reference to evaluate synergistic or antagonistic effects of OC and Me. The definitions of OC@Me and OC+Me have been clarified in lines 93−98 of the revised manuscript, and figure captions have been updated to describe the specific parameter shown for OC+Me.

3. The samples appear to be prepared under relatively simple laboratory conditions. How representative are these systems of real atmospheric environments? Under which atmospheric conditions and in which environments would such complexes realistically form?

Re: Thank you. The OC samples were collected from smoke aerosols generated during coal combustion. The TMIs concentrations selected here were atmospherically relevant soluble metal levels. These systems may roughly represent the coexistence of OC and TMIs for atmospheric aerosols in polluted regions affected by coal combustion emissions. High humidity and acidic conditions may promote metal dissolution and facilitate the complexation between soluble metal ions and OC. The related discussion has been clarified in lines 405−410 of the revised manuscript.

4. The ROS experiments and the subsequent analyses appear to have been conducted on different subsamples. Could this introduce variability that affects the interpretation of the results? Please discuss the implications for data consistency and reproducibility.

Re: Thank you. For ROS, electrochemical and XPS analyses, a single sample could not be used sequentially for all measurements in the current experimental setup. However, all analyses were performed using subsamples from the same initial batch of OC@TMIs to minimize potential variability. This clarification has been added in lines 103–105 of the revised manuscript. As shown in Fig. 1a–c and Fig 2b of the revised manuscript, the consistent SO_2 uptake and sulfate formation among replicate subsamples suggest that sample variation is limited.

5. The DFT calculations are interesting and potentially valuable. However, it is not entirely clear whether the computational models adequately represent the real systems studied experimentally. Consequently, the reported correlations may not necessarily support the processes occurring in atmospheric environments. Furthermore, the methodological description of the DFT calculations is too brief to properly assess the quality and reliability of the computational work.

Re: Thank you. The selection of the molecular models was based on the functional groups identified in OC by FT-IR analysis. PH and BA represented hydroxyl- and carboxyl-containing aromatic structures, respectively. MS contained adjacent hydroxyl and carboxyl groups on a π-conjugated aromatic backbone to represent multifunctional chelating sites. These models covered single-site coordination and multidentate chelation between OC and TMIs. Although they cannot capture the full molecular heterogeneity of OC, the consistency between the

calculated results and experimental trends helped to understand the complexation effects of OC with TMIs. The related description has been given in lines 297–300 and 304–306 of the revised manuscript and in Text S11 of the Supplement. Additional details of the DFT methodology have been added in Section 2.3.7 of the revised manuscript and in Text S10 of the Supplement.

6. A more comprehensive discussion of quality assurance and quality control (QA/QC) procedures is needed for most, if not all, analytical techniques. For example, what were the detection limits of the ion chromatography (IC) measurements, and how close were these limits to the lowest concentrations reported in the study?

Re: Thank you. For IC analysis, the detection and quantification limits for sulfate were 0.0005 and 0.001 mg L^{-1}, respectively. The lowest sulfate concentration reported in this study was 0.00579 mg L^{-1}, which was above the quantification limit. Thus, these reported sulfate concentrations were within the reliable quantification range. The related description has been added in Text S7 of the Supplement. In addition, the detection limits for TOC and ICP-MS have been added in Texts S1 and S2 of the Supplement.

7. I am concerned that insufficient attention has been paid to potential artifacts arising from sample preparation, storage, and analytical procedures. For example:

a. For the Cu measurements obtained by XPS, how can the authors exclude changes induced during sample storage?

Re: Thank you. Before the XPS analysis, the samples were stored in a vacuum environment to minimize the changes in the Cu valence state. The related description has been added in lines 166−168 of the revised manuscript.

b. Were possible beam-induced effects assessed during XPS analysis?

Re: Thank you. Beam-induced effects were assessed by collecting consecutive C 1s spectra at the same sample position. The peak positions and spectral shapes remained consistent, indicating that beam-induced effects were negligible under the measurement conditions. The related description has been added in lines 172−175 of the revised manuscript.

c. The UV-Vis measurements were performed offline. Why were in situ measurements not considered, for example using a fiber-optic probe? Please discuss how sample handling may have affected the observed results and provide evidence that the reported trends are not analytical artifacts.

Re: Thank you. In situ fiber optic UV-vis measurements were not available in the current experimental setup. Offline UV-vis analysis was carefully performed under identical testing conditions to minimize handling-related variations, which has been added in lines 127−128 of the revised manuscript. As shown in Figure S9d of the supplement, the differential absorbance was also calculated to better compare the changes in optical property. The consistency among UV-vis, EEM-PARAFAC and DFT results suggests that the spectral changes are unlikely to be caused by analytical artifacts.

8. The Conclusions and Atmospheric Implications sections appear somewhat simplistic given the complexity of the studied system. The associated uncertainties and limitations should be acknowledged more explicitly. Inclusion of uncertainty estimates, error propagation, and sensitivity analyses would substantially strengthen the atmospheric relevance of the findings and provide a more realistic assessment of the robustness of the conclusions.

Re: Thank you. The single parameter value was used in the original calculations of SO_2 lifetime (τ_{SO_2}) and sulfate formation rate (R), including the aerosol surface area concentration, organic aerosol mass fraction and $PM_{2.5}$ mass concentration. This didn't represent their variability under atmospheric conditions. These parameter have been reused with the reported ranges to provide more realistic bounds for the atmospheric estimation. Based on these revised parameter ranges, the resulting τ_{SO_2} and R values were 1.8−379 days and 0.07−5.95 μg m^{-3} h^{-1}, respectively. The revisions have been made in lines 414−416, 417−419 and 428−430 of the revised manuscript.

The derived linear relationship between •OH intensity and sulfate formation was established using fresh OC from coal combustion and different TMIs at the same concentration. OC in aerosols generally stems from diverse sources and undergoes the atmospheric aging processes, which would significantly modify the compositions and structures of OC. TMIs types and concentrations also display temporal and spatial variations. These may alter the complexation between OC and TMIs and consequently affect •OH generation and sulfate

formation. Thus, there may be some uncertainties for the applicability of this linear relationship under ambient conditions. The related discussion has been given in lines 447−454 of the revised manuscript.

Reviewer #1:

This study investigated the effects of interactions between OC and TMIs on the heterogeneous photooxidation of SO_2 to sulfates. Spectroscopic analyses and DFT calculations consistently confirmed the complexation between OC and TMIs. Variation in the complexation strength modulated the generation of reactive species, especially •OH as the key oxidant. This manuscript is well organized with ample data and clear figures and tables. It can be published in *Atmospheric Chemistry and Physics* after minor revisions.

Re: Thanks. We have carefully modified our manuscript according to your comments and suggestions.

1. Fe^{3+}, Cu^{2+} and Mn^{2+} were selected as representative transition metal ions. However, the reasons for choosing these specific metal ions were not clearly stated. It is suggested to provide a brief explanation.

Re: Thank you. Fe, Cu and Mn are the most abundant transition metals in atmospheric aerosols and cloud water (Singh et al., *Chemosphere,* 2017, 181, 725−737). Their soluble ionic forms, including Fe^{3+}, Cu^{2+} and Mn^{2+}, can catalyze or regulate SO_2 oxidation and sulfate formation in atmospheric processes (Liu et al., *npj Clim. Atmos. Sci.,* 2025, 8, 57). Therefore, Fe^{3+}, Cu^{2+} and Mn^{2+} were chosen as representative TMIs in this study. The related description has been added in lines 63−66 of the revised manuscript.

2. In Section 3.1, NaCl was used as a control to examine the effect of chloride ions on SO_2 uptake. The specific NaCl concentration was not provided, and the chloride ions content differed among divalent and trivalent salts. Authors should clarify the NaCl concentration and discuss whether these differences could affect the results.

Re: Thank you. The NaCl concentration for the OC@NaCl control experiment was set to 1.5 mM. This Cl^- concentration was the same as that in 0.5 mM $FeCl_3$ and higher than that in 0.5

mM $CuCl_2$ or $MnCl_2$. The related description has been added in lines 98−99 of the revised manuscript. As shown in Fig. S6, the changes in SO_2 concentration on OC@NaCl was the same as that on OC. This suggests no measurable effect of Cl^- on SO_2 uptake. The related clarification has been given in lines 192−194 of the revised manuscript.

3. Different SO_2 concentrations were employed in the uptake, ATR-IR and IC experiments. The reasons for different SO_2 concentrations should be briefly explained.

Re: Thank you. The SO_2 concentration was set at 40 ppb in the uptake experiments to represent atmospherically relevant SO_2 level (Liu et al., *Atmos. Chem. Phys.,* 2022, 22, 7071−7085). A SO_2 concentration of 2 ppm was used in the ATR-IR experiments to improve spectral signals. For IC analysis, the SO_2 concentration set at 200 ppb ensured that sulfates formed in the experiments were above the IC detection limit. The related description has been given in Texts S4, S6 and S7 of the Supplement.

4. In previous studies, gas-phase sulfuric acid formation was observed. It is unclear whether gas-phase sulfuric acid was generated in the current experiments (Section 3.2).

Re: Thank you. Both surface sulfate and gaseous sulfuric acid trapped at the reactor outlet were measured in the experiments. The sulfates reported in this manuscript referred to the total mass of sulfate and gaseous sulfuric acid. The related description has been revised in Text S7 of the Supplement.

5. In lines 236−237, the phrase “can served” is grammatically incorrect and should be revised to “can serve.” Authors should ensure grammatical consistency throughout the manuscript.

Re: Thank you. This has been modified in line 259 of the revised manuscript. In addition, we have carefully checked the manuscript for similar grammatical errors.

6. In lines 238−240, ΔAbs was mentioned when comparing OC@TMIs and OC+TMIs, but the specific meaning or calculation method of ΔAbs was not clearly defined.

Re: Thank you. Differential absorbance (ΔAbs) is obtained by subtracting the absorbance of OC@TMIs from that of OC+TMIs. It was calculated as ΔAbs = Abs(OC+TMIs) −

Abs(OC@TMIs), where TMIs refer to Fe^{3+}, Cu^{2+} or Mn^{2+}. The related description has been added in lines 262−264 of the revised manuscript.

7. It was confirmed that TMIs modulated photochemical reactive species and then influenced sulfate formation under irradiation. However, it remains unclear whether Fe^{3+}, Cu^{2+} and Mn^{2+} could affect sulfate formation in the absence of light. The dark control experiments can be conducted for OC@TMIs to evaluate their non-photochemical contribution.

Re: Thank you. Dark control experiments were conducted for OC and OC@TMIs under identical conditions. The SO_2 uptake and sulfate formation on OC@TMIs under dark conditions were slightly different from those on OC. Thus, the contribution of Fe^{3+}, Cu^{2+} and Mn^{2+} to SO_2 uptake and sulfate formation on OC@TMIs was limited under dark conditions. These results have been provided in Fig. S7 and Fig. S8 of the Supplement. The related descriptions have been added in lines 200−202 and 232−234 of the revised manuscript.

Reviewer #2:

Organic carbon usually coexists with transition metal ions in atmospheric aerosols. This study demonstrated that the heterogeneous conversion of SO_2 to sulfates was strongly modulated through the complexation interactions between OC and TMIs. The complexation strength adjusted the generation of •OH, which can dominate the sulfate formation. This manuscript is well designed and clearly written. It can be accepted to publish in *Atmospheric Chemistry and Physics* after minor revisions.

Re: Thanks. We have carefully modified our manuscript according to your comments and suggestions.

Major Concerns:

1. Whether sulfates in fresh samples were subtracted in IC measurements? This should be considered to ensure the accuracy of sulfate production.

Re: Thank you. The background sulfate concentration in the fresh OC samples was 0.0620 ± 0.0058 mg L^{-1}. This has been subtracted from the sulfate concentrations measured after the reaction. The corrected results have been updated in Fig. 2b, Fig. 6b, Fig. S8 and Fig. S21.

2. In lines 226−240, the decrease in absorbance of OC@TMIs compared to OC+TMIs is attributed to complexation between OC and TMIs. This interpretation is insufficiently supported. A mechanistic relationship between the decrease in the absorbance and OC–TMI complexation is necessary to better understand this phenomenon.

Re: Thank you. The complexation of TMIs with electron-donating groups in OC, such as hydroxyl, carboxyl and carbonyl groups, can perturb the electronic structure of OC chromophores. This perturbation can affect π-π* or n-π* electronic transitions and induce a hypochromic effect in the UV-vis spectra. Therefore, the lower absorbance of OC@TMIs compared with OC+TMIs was interpreted as supporting evidence for interactions between OC and TMIs. The related description has been added in lines 260−262 of the revised manuscript.

3. In EPR measurements, the data under irradiation are reported. Whether any reactive species may be generated under dark conditions. The experiments can be carried out to determine the formation of reactive species in the absence of light.

Re: Thank you. EPR measurements under dark conditions were carried out. No obvious EPR signals of BMPO-•OH or DMPO-$HO_2^{\bullet}$/$\bullet O_2^-$ adducts were observed in the absence of light, indicating that the generation of reactive species was mainly driven by irradiation. The EPR spectra in the dark have been provided in Fig. S16 and S19 of the Supplement.

4. In lines 352–356, O_2 activation on MS@Cu^{2+} is discussed according to O_2 adsorption energy and O−O bond length. The O−O bond length increases slightly from 1.20 Å for MS to 1.21 Å for MS@Cu^{2+}. This should be refined to avoid overemphasizing the O_2 activation ability of Cu^{2+}.

Re: Thank you. The O_2 adsorption energy suggested an enhanced O_2 adsorption on MS@Cu^{2+}, while the O−O bond length increased slightly from 1.20 to 1.21 Å. This indicates that Cu^{2+} may facilitate O_2 adsorption, but its effect on O−O bond activation is limited compared with Mn^{2+}. Accordingly, the statement about O_2 activation by Cu^{2+} has been softened in lines 386−387 of the revised manuscript.

5. In lines 406−422, an extended discussion about the effects of different OC@TMIs on SO_2 photooxidation to sulfates is given. However, environmental concentrations of these metal ions vary in aerosols. A discussion limitation may be considered.

Re: Thank you. The linear relationship between •OH intensity and sulfate formation was established using different TMIs at the same concentration. The effects of OC@TMIs on sulfate formation depend not only on the types of TMIs but also on their abundance. Variations in TMI concentrations may alter the complexation between OC and TMIs and thus affect •OH generation and sulfate formation. Thus, there may be some uncertainties for the applicability of this linear relationship under ambient conditions. This limitation has been added in lines 447−454 of the revised manuscript.

6. In line 415 and Figure 6b, the reported linear relationship had a relative large error of approximately 70% and appears to assume a zero intercept. Forcing the regression through the origin may affect the reliability of the slope. A linear fitting without forcing the intercept to zero should be provided.

Re: Thank you. The relationship between •OH intensity and sulfate mass was refitted by linear regression without forcing the intercept to zero. The revised equation is $M_{sulfates} = (1.68 \pm 0.11) \times 10^{-2} \times I - (0.43 \pm 0.08) \times 10^{-2}$, which has been updated in Fig. 6b and lines 446−447 of the revised manuscript.

Minor Concerns:

1. OC+TMIs was defined multiple times throughout the text. Authors should provide a clear definition at the first occurrence and avoid repeating it unnecessarily.

Re: Thank you. OC+TMIs has been clearly defined in lines 95−98 of the revised manuscript. The figure captions have been revised to describe the specific parameter for OC+TMIs.

2. In ATR-IR measurements, potential interference from ZnSe could affect the detection of sulfates or other functional groups and should be described.

Re: Thank you. The ATR-IR spectra in the control experiments were obtained by exposing the blank ZnSe plate to 2 ppm SO_2 under irradiation (Yang et al., *J. Environ. Sci.*, 2025, 156,

539−548). The IR signals were minimal, indicating that interference from the ZnSe plate was negligible under comparable conditions. This has been described in Text S6 of the Supplement.

3. Why were samples extracted with formaldehyde aqueous solution in Text S6? The rationale should be explained.

Re: Thank you. Formaldehyde solution was used as a sulfite oxidation inhibitor, as reported in previous studies (Li et al., *Environ. Sci.: Nano*., 2021, 8, 698−710). This has been added in Text S7 of the Supplement.

4. In lines 249−250, the manuscript draws a key conclusion regarding the complexation between OC and TMIs. However, no literature references are provided to support this conclusion.

Re: Thank you. The references have been cited in lines 276−277 of the revised manuscript.

Reviewer #3:

Major Comments:

1. It would interesting know the formation of reactive species under dark conditions.

Re: Thank you. EPR measurements under dark conditions were carried out. No obvious EPR signals of BMPO-•OH or DMPO-$HO_2^{\bullet}$/$\bullet O_2^-$ adducts were observed in the absence of light, indicating that the generation of reactive species was mainly driven by irradiation. The EPR spectra in the dark have been provided in Fig. S16 and S19 of the Supplement.

2. For how were the sampling done for each trials? Did the author measure or corrected sampling artifacts of OC? If yes, then it should be mentioned in the manuscript. If no, the authors must mention that too.

Re: Thank you. Three independent sampling trials were conducted under controllable conditions. OC sampling artifacts were not quantified or corrected in this study. The OC contents in the three independent sampling trials were 765.4, 871.4 and 810.5 μg C mL^{-1}, respectively. This suggests a good reproducibility among the sampling trials. Thus, possible sampling artifacts were expected to be similar among samples. This description has been added

in Text S1 of the Supplement.

3. The authors are suggested to explain why only Fe, Cu and Mn were selected as TMIs for this study.

Re: Thank you. Fe, Cu and Mn are the most abundant transition metals in atmospheric aerosols and cloud water (Singh et al., *Chemosphere,* 2017, 181, 725−737). Their soluble ionic forms, including Fe^{3+}, Cu^{2+} and Mn^{2+}, can catalyze or regulate SO_2 oxidation and sulfate formation in atmospheric processes (Liu et al., *npj Clim. Atmos. Sci.,* 2025, 8, 57). Therefore, Fe^{3+}, Cu^{2+} and Mn^{2+} were chosen as representative TMIs in this study. The related description has been added in lines 63−66 of the revised manuscript.

4. Line 238: ΔAbs has not been defined earlier.

Re: Thank you. Differential absorbance (ΔAbs) is obtained by subtracting the absorbance of OC@TMIs from that of OC+TMIs. It was calculated as ΔAbs = Abs(OC+TMIs) − Abs(OC@TMIs), where TMIs refer to Fe^{3+}, Cu^{2+} or Mn^{2+}. The related description has been added in lines 262−264 of the revised manuscript.

5. The conclusion introduces to new equations, figures and discussions. The authors are suggested to discuss those results in a section before the conclusion. Then keep conclusion section exclusively for concluding the discussion, and not start another discussion.

Re: Thank you. The Conclusions and Atmospheric implications section has been divided into separate Discussion and Conclusion sections in the revised manuscript.

Thank you very much for your help.

Sincerely yours,

Chong Han

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