

jz-2024-001702.R1

Name: Peer Review Information for "Sub-50-fs Formation of Charge Transfer States Rules the Fate of Photoexcitations in Eumelanin-Like Materials"

#### First Round of Reviewer Comments

Reviewer: 1

##### Comments to the Author

A nice work elucidating photoexcitations phenomena in eumelanin-like materials is presented. The results are clearly reported and commented. I have just a couple of minor notes for the Authors.

- 1) The structure of the manuscript is rather unusual, but maybe this is requested by the journal, being it a "Letter".
- 2) A more comprehensive introduction to the biomedical applications of melanin-like nanomaterials would be beneficial (see, for example, 10.1016/j.nantod.2024.102151).

Reviewer: 2

##### Comments to the Author

This manuscript reports the use of sub-30-fs time-resolved optical pump-probe spectroscopy to investigate the ultrafast photophysical dynamics of polydopamine, a eumelanin-like material. The study provides convincing evidence for the formation of photoprotecting charge-transfer (CT) states on the sub-20-fs timescale. On the other hand, the competing interpretation of the ultrafast dynamics in the literature, involving exciton localization and internal conversion, is not supported by the experimental data. The study addresses an important problem in UV photoprotection. At the same time, the conclusion of is supported by high-quality data and the manuscript is well-written. I recommend publication of the manuscript more or less in the current form. One suggestion that I would make is for the authors to merge Fig. S3 in the SI with Fig. 1 of the main text. That way, the readers can see the chemical structures of the compounds used in the study and also more easily visualize the transitions that appear in the UV-visible absorption spectrum.

Reviewer: 3

## Comments to the Author

The manuscript by Montalti, Maiuri, Cerullo and coworkers is a very interesting piece of work. It is aimed to shine light on the photophysical properties of a large class of species, with important effects on several biological behavior.

The paper is very well organized, the experiments are of top level, and the discussion is solidly-based on the experimental results.

The conclusions and the data reported can largely contribute to enhance the knowledge and stimulate further work on a topical area of research. I am in favor of publication of this nice article in its present form.

## Author's Response to Peer Review Comments:

Dear Editor,

thank you for your swift handling of our manuscript and for providing us with the reviewers' report. We are happy to read that all three reviewers recommend publication of our manuscript with only minor or no modifications. In the revised version, we have performed all the requested scientific and non-scientific changes (see attached file for details). We hope that the current version of the manuscript is suitable for publication in the Journal of Physical Chemistry Letters.

Best regards

Giulio Cerullo (on behalf of all co-authors)

## Referee: 1

A nice work elucidating photoexcitations phenomena in eumelanin-like materials is presented. The results are clearly reported and commented. I have just a couple of minor notes for the Authors.

- 1) The structure of the manuscript is rather unusual, but maybe this is requested by the journal, being it a "Letter".
- 2) A more comprehensive introduction to the biomedical applications of melanin-like nanomaterials would be beneficial (see, for example, 10.1016/j.nantod.2024.102151).

**Authors' Reply:** We extend thank the Reviewer for carefully evaluating our manuscript and providing a positive assessment and valuable feedback. Concerning the organisation of the manuscript, we are indeed constrained in length and structure by the Letter format. While comprehensive reviews on the photophysics and potential applications of eumelanin-like materials are available in the literature cited

in our paper, we recognize the importance of offering additional context concerning the applications of eumelanin-like materials for a broader readership. In response to the suggestion, we have included references to relevant reviews that delve into the applications of synthetic and natural eumelanin materials.

**Action taken;** Original Text: “Mammalian eumelanin, in particular, plays a key role as photoprotection agent.<sup>4</sup>”

Revised Text: “Specifically, mammalian eumelanin, present in skin, hair, and eyes, plays a key role as photo-protection agent.<sup>4</sup> Hence, inspired by Nature, eumelanin-like materials have emerged as versatile platforms with profound implications in areas of significant social and economic impact, such as in human health preservation<sup>5,6</sup>, clean energy production<sup>7,8</sup>, and environmental remediation<sup>8</sup>”

The additional references (5-8) can be seen below:

- (5) Cheng, W.; Zeng, X.; Chen, H.; Li, Z.; Zeng, W.; Mei, L.; Zhao, Y. Versatile Polydopamine Platforms: Synthesis and Promising Applications for Surface Modification and Advanced Nanomedicine. *ACS Nano* **2019**, *13* (8), 8537–8565.
- (6) Battaglini, M.; Emanet, M.; Carmignani, A.; Ciofani, G. Polydopamine-Based Nanostructures: A New Generation of Versatile, Multi-Tasking, and Smart Theranostic Tools. *Nano Today* **2024**, *55*, 102151.
- (7) Zhao, X.; Huang, C.; Xiao, D.; Wang, P.; Luo, X.; Liu, W.; Liu, S.; Li, J.; Li, S.; Chen, Z. Melanin-Inspired Design: Preparing Sustainable Photothermal Materials from Lignin for Energy Generation. *ACS Appl. Mater. Interfaces* **2021**, *13* (6), 7600–7607.
- (8) Galeb, H. A.; Wilkinson, E. L.; Stowell, A. F.; Lin, H.; Murphy, S. T.; Martin-Hirsch, P. L.; Mort, R. L.; Taylor, A. M.; Hardy, J. G. Melanins as Sustainable Resources for Advanced Biotechnological Applications. *Global Challenges* **2021**, *5* (2), 2000102.

## Referee: 2

This manuscript reports the use of sub-30-fs time-resolved optical pump-probe spectroscopy to investigate the ultrafast photophysical dynamics of polydopamine, a eumelanin-like material. The study provides convincing evidence for the formation of photoprotecting charge-transfer (CT) states on the sub-20-fs timescale. On the other hand, the competing interpretation of the ultrafast dynamics in the literature, involving exciton localization and internal conversion, is not supported by the experimental data. The study addresses an important problem in UV photoprotection. At the same time, the conclusion of is supported by high-quality data and the manuscript is well-written. I recommend publication of the manuscript more or less in the current form.

**Authors' Reply:** We sincerely thank the Reviewer for reading our paper, for the positive comments and the recommendation to publish the paper pending minor revisions.

One suggestion that I would make is for the authors to merge Fig. S3 in the SI with Fig. 1 of the main text. That way, the readers can see the chemical structures of the compounds used in the study and also more easily visualize the transitions that appear in the UV-visible absorption spectrum.

**Authors' Reply:** We thank the Reviewer for this suggestion, which gives us the opportunity to improve the clarity of our manuscript. Consequently, we have integrated Fig. S3 in the Supplementary Information with Fig. 1 in the main text, as illustrated in the revised Figure 1 (shown as Figure R2 below).

**Action taken:** Original Figure 1 of the main text (Figure R1):

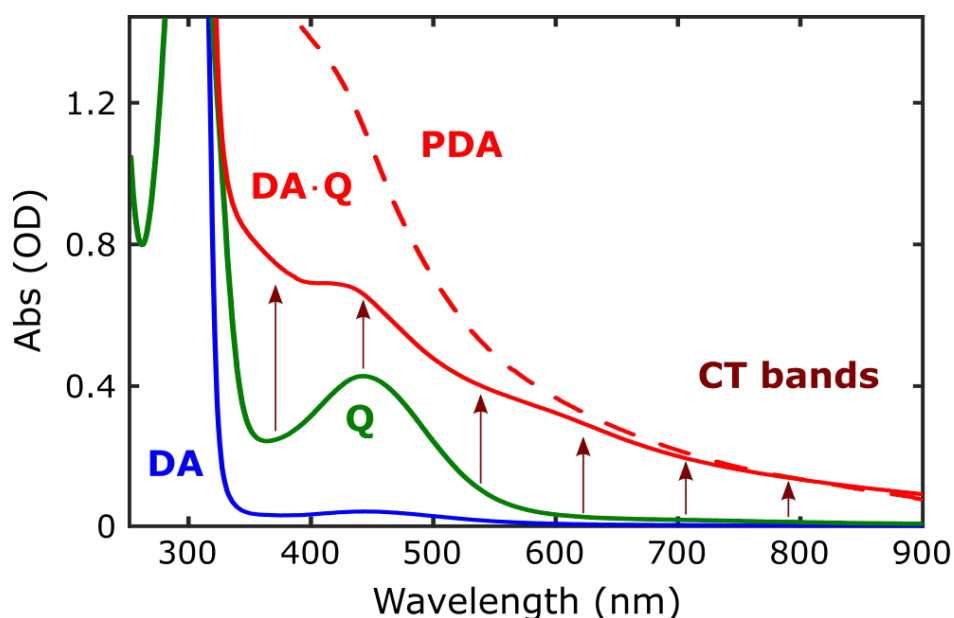


Figure R1: Absorption spectrum of DA (0.7 mM) in the absence of oxygen (blue line). In the presence of atmospheric oxygen, DA is oxidized to form Q (0.7 mM) with absorption spectrum given by the green line. Q solution was hence de-oxygenated and 7 mM DA was added. The resulting absorption spectrum (solid red line) is very different from the sum of the spectra of Q and DA, revealing the formation of a DA·Q adduct with new CT bands (brown arrows) clearly detectable in the 600-900 nm region. The spectrum of the adduct is compared with the one of PDA (dashed red line).

Revised Figure 1 of the main text:

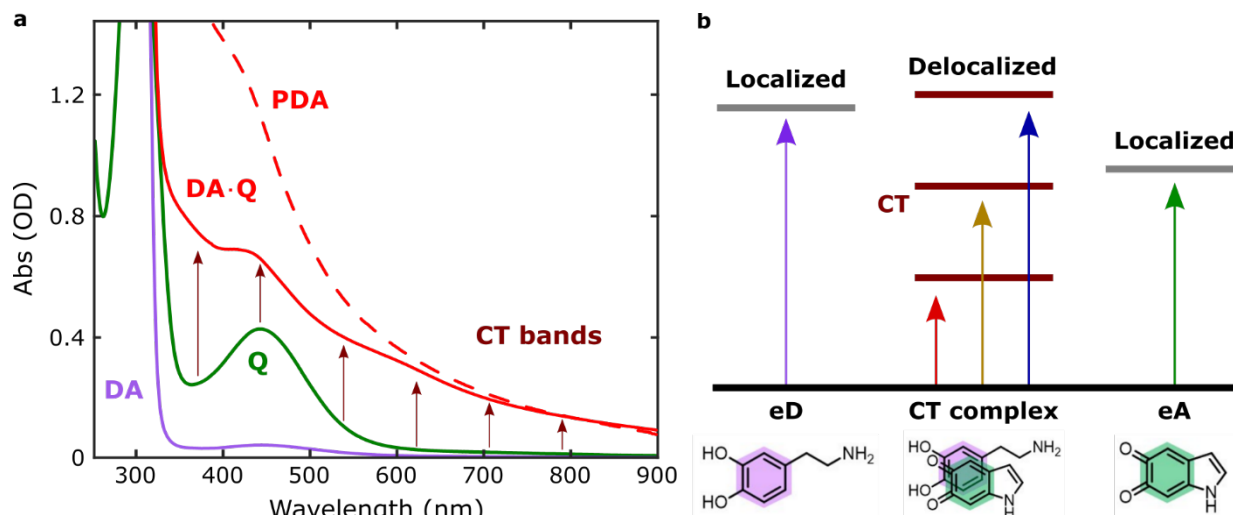


Figure R2: (a) Absorption spectrum of DA (0.7 mM) in the absence of oxygen (violet line). In the presence of atmospheric oxygen, DA is oxidized to form Q (0.7 mM) with absorption spectrum given by the green line. Q solution was hence de-oxygenated and 7 mM DA was added. The resulting absorption spectrum (solid red line) is very different from the sum of the spectra of Q and DA, revealing the formation of a DA·Q adduct with new CT bands (brown arrows) clearly detectable in the 600-900 nm region. The spectrum of the adduct is compared with the one of PDA (dashed red line). (b) A simplified scheme that illustrates the electronic states and transitions involved when mixing the PDA precursor, DA, and its oxidized quinonic unit Q in a solution. In this scheme, DA acts as the eD moiety, and Q serves as the eA. The resulting supramolecular adduct exhibits broad CT bands that enhance absorption in the UV, visible, and NIR regions.

## Referee: 3

The manuscript by Montalti, Maiuri, Cerullo and coworkers is a very interesting piece of work. It is aimed to shine light on the photophysical properties of a large class of species, with important effects on several biological behavior.

The paper is very well organized, the experiments are of top level, and the discussion is solidlybased on the experimental results.

The conclusions and the data reported can largely contribute to enhance the knowledge and stimulate further work on a topical area of research. I am in favor of publication as this nice article in its present form.

**Authors' Reply:** We sincerely thank the Reviewer for appreciating our work and for the very positive comments, recommending its publication in the present form.

## Editor

Please also make the following non-scientific changes:

1) References: In both the main file and the supporting information, fix the style of all references to use JPCL formatting (check all references carefully). \*\*\*JPC Letters reference formatting requires that journal references should contain: () around numbers; author names; article title (titles entirely in title case or entirely in lower case); abbreviated journal title (italicized); year (bolded); volume (italicized); and pages (first-last). Book references should contain author names; book title (in the same pattern); publisher; city; and year. Websites must include date of access.

2) Supporting Information: Please number SI pages in the following format: "S1, S2..."

**Authors' Reply:** In addition to the scientific changes, we have also made all the requested nonscientific changes, highlighted in yellow.