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Peer Review File

Integrating Molecular Photoswitch Memory with Nanoscale Optoelectronics for Neuromorphic Computing

Corresponding Author: Professor Anders Mikkelsen

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Version 0:

Decision Letter:

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Dear Professor Mikkelsen,

Thank you for submitting your manuscript, "Integrating Molecular Photoswitch Memory with Nanoscale Optoelectronics for Neuromorphic Computing", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that while they find your work of interest, some important points are raised. We are interested in the possibility of publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

In particular, the reviewers ask about the advantages, such as the synaptic device in this work compared to optoelectronic synapses, and for integration. They also ask to clarify important points such as why the absorbance spectra of this work doesn't match a previous report, and about the dye switch speed and whether this has an impact for applications.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

-A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

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Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Dr Jet-Sing Lee
Associate Editor
Communications Materials
orcid.org/0000-0002-6740-8700

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

In the manuscript entitled "Integrating molecular photoswitch memory with nanoscale optoelectronics for neuromorphic computing" (COMMSMAT-24-0455-T), the authors report a neuromorphic computing device based on the light-controlled linear-cyclic isomerization of donor-acceptor Stenhouse adducts (DASA). DASA exhibits negative photochromism and switches from colored to colorless after visible light irradiation. The gradually decreased absorbance of DASA in visible light region supplies a synaptic-like response to light, where the photocurrent is increased with the proceeding of irradiation. This work is with a clear design, although other photoswitches such as azobenzene, spiropyran and diarylethene have been reported before to dynamically control the current of optoelectronic devices, this is the first report on neuromorphic computing with the help of DASA. However, the structure of the device is not with high novelty, the function and property of the device is predicable after knowing the photoisomerization of DASA. The insect navigation part is interesting. All in all, this is a solid work with clear design and excellent performance, some points need to be taken care during the revision.
(1) What does DPS mean in the manuscript? There is no description.
(2) Figure 1, the chemical structure is wrong, it should be a C-O bond rather than C-H bond on the triene bridge. The same problem exists in Figure 2.
(3) The DASA structure used in this work is reported by Read de Alaniz's group in 2018 (J. Am. Chem. Soc., 2018, 140,

10425-10429.), but the absorbance spectra between these two works are not well-matched. In this work, there is a clear shoulder pear, which is much more obvious than the previous report. Could the authors explain this?
(4) Why use PAMS as the polymer matrix for the DASA, how about the dynamics of photoisomerization of DASA in PAMS?
(5) From the spectra (Figure 2C), it seems like there is obvious intermolecular aggregation between DASA in the polymer films. How does the aggregation affect the photoisomerization of DASA?
(6) Figure 4 (b), for each pulse of light irradiation, the wave is not typical square wave, why?

Reviewer #2 (Remarks to the Author):

The manuscript demonstrates a novel device combining organic dye with III-V semiconductor optoelectronic devices. The device holds versatile functions, suitable for bio-inspired optical neural networks. The key point is an on-chip weight memory unit via reversible switching of dyes embedded in a polymer. I recommend it for publication if the paper can be further improved from the following aspects:

1. The authors state that this work achieves the light communication between the dye and the solid-state optoelectronics. Compared to other optoelectronic synapses, what are the advantages of the synaptic device in this work? What's the uniqueness?
2. Please give the full name of the dye molecules and the related abbreviation. Otherwise, readers will not know what DPS is. Furthermore, DPS and DASA are both used in the text and figures. I guess DPS and DASA represent the same molecules in this work. Please clarify it.
3. The paper mentions that STP can be implemented in devices, but no figure in the main text confirms this point.
4. In Figure 5, the noise tolerance in the photoswitch model (exponential) is better than that in the original model (linear). The authors said that it is not related to the exponential properties of the DPS. The authors should explain the reason clearly in the main text or SI.

Reviewer #3 (Remarks to the Author):

The manuscript by Alcer et al describes a photoswitch memory based on a donor acceptor dye that can be switched controllably with light. The concept is interesting and the paper reads well. I only have a few minor comments:

1. Introduction: "information transfer will be inherently fast."

This true for light, but generally dye's photoswitching is slow. How fast can the dye switch? And is this an issue for the applications envisioned?

2. "Several important features must characterise a potential connection weight solution"

I would argue that weight programming also needs to be predictable (linear/symmetric) allowing for blind updates in ANN training. Is this possible with the current material?

3. "As no electrical connections is needed to the dyes, they exclusively communicate optically with the nano-optoelectronics"

I understand the advantages of fully optical systems, but would the integration of the nano-optoelectronics not also need highly integrated electronics? One needs to be able to turn on the light with specific characteristics at a specific location (i.e. weight), right? With a dense network of weights how can you program each weight individually? Can the authors elaborate on this point of integration advantages?

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Version 1:

Decision Letter:

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Dear Professor Mikkelsen,

Your manuscript titled "Integrating Molecular Photoswitch Memory with Nanoscale Optoelectronics for Neuromorphic Computing" has now been seen again by our referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials.

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if the process may take longer.

Best regards,

Dr Jet-Sing Lee
Senior Editor
Communications Materials
orcid.org/0000-0002-6740-8700

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

In the revised manuscript entitled "Integrating Molecular Photoswitch Memory with Nanoscale Optoelectronics for Neuromorphic Computing" (COMMSMAT-24-0455A), the authors have addressed all the reviewers' comments. The revised version clearly states the novelty of the design, and improves the structure and logic of the manuscript. Therefore, I suggest this work to be published on Communications Materials.

Reviewer #2 (Remarks to the Author):

The authors have addressed my concerns. I suggest the publication of this work.

Reviewer #3 (Remarks to the Author):

The authors have successfully addressed all my comments and I believe the manuscript can be accepted for publication.

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Reviewer 1 (R1):

In the manuscript entitled "Integrating molecular photoswitch memory with nanoscale optoelectronics for neuromorphic computing" (COMMSMAT-24-0455-T), the authors report a neuromorphic computing device based on the light-controlled linear-cyclic isomerization of donor-acceptor Stenhouse adducts (DASA). DASA exhibits negative photochromism and switches from colored to colorless after visible light irradiation. The gradually decreased absorbance of DASA in visible light region supplies a synaptic-like response to light, where the photocurrent is increased with the proceeding of irradiation. This work is with a clear design, although other photoswitches such as azobenzene, spiropyran and diarylethene have been reported before to dynamically control the current of optoelectronic devices, this is the first report on neuromorphic computing with the help of DASA. However, the structure of the device is not with high novelty, the function and property of the device is predicable after knowing the photoisomerization of DASA. The insect navigation part is interesting. All in all, this is a solid work with clear design and excellent performance, some points need to be taken care during the revision.

Answer:

We thank the reviewer for the encouraging words on performance and the insect navigation model and we have addressed all the reviewer's comments below which has helped us improve the manuscript. For the novelty of our concept compared to previous work using organic dyes (e.g. in our completely light driven synapse with an opto-electronic neuron) we have now elaborated on that in the introduction of the paper as well as in the comments below.

(r1) **What does DPS mean in the manuscript? There is no description.**

Answer:

"DPS" is an abbreviation of "DASA PhotoSwitch", i.e. "Donor-Acceptor Stenhouse Adduct PhotoSwitch" in full. In both cases, the abbreviation refers to the same DASA dye molecule species, namely the one called "D1A3" in [1]. To avoid confusion, we have revised the manuscript and figures to consistently use only "DASA" as the preferred abbreviation throughout and removed any use of DPS.

(r1) **Figure 1, the chemical structure is wrong, it should be a C-O bond rather than C-H bond on the triene bridge. The same problem exists in Figure 2.**

Answer:

We thank the reviewer for seeing this error in our depiction of the chemical structures presented in Figures 1 and 2. We recognize that the bond on the triene bridge was indeed incorrectly depicted as a C-H bond instead of the correct C-O bond. We have revised both figures accordingly to accurately represent the chemical structures.

(r1) **The DASA structure used in this work is reported by Read de Alaniz's group in 2018 (J. Am. Chem. Soc., 2018, 140, 10425-10429.), but the absorbance spectra between these two works are not well-matched. In this work, there is a clear shoulder pear, which is much more obvious than the previous report. Could the authors explain this?**

Answer:

In the article mentioned by the reviewer (noted as [2] in the list of references at the end of this answer), the main results report on absorbance with the DASA molecule in dichloromethane (DCM), while the absorption spectrum we show was measured with the DASA molecule in toluene. In the Supporting Information of [2], absorption spectra from several different solvents for the relevant DASA species (DASA-7-S7 in [2]) are reported. It can be observed that while the two peaks of the absorption spectra are generally visible the ratio can vary significantly. Differences in solvent polarity can have these effects on the absorbance spectra [1,2,3] (solvatochromic shift). The absorbance spectrum of DASA-7-S7 in toluene in the SI of [2] is in good agreement with the spectrum as reported in our manuscript, with a more distinct shoulder than in e.g. DCM.

We acknowledge that the effect of the solvent in which the absorbance spectrum was measured should be discussed, and have added the following sentence to the manuscript to rectify this:

"We note that the absorbance spectrum may show slight variations depending on the solvent used [32,47,51]"

where we reference the three articles referenced in this answer that includes the one mentioned by the reviewer. Furthermore, we have added a note in the main text specifying the solvent used (this was previously only noted in the caption of Figure 1). As a final side note, a small hump/shoulder between 480-550 nm is an artifact that arises from the detector of the spectrometer we use that could be misinterpreted as a shoulder band. In the figure it is covered by a dashed region.

***(r1)* Why use PAMS as the polymer matrix for the DASA, how about the dynamics of photoisomerization of DASA in PAMS?**

Answer:

From literature (e.g. the review of [3]), it has been observed that both the spectral properties and the dynamics of DASA photoswitches are affected by the polarity of the medium, be it a solvent or a polymer matrix. In our previous work [1], the thin film performance of several DASA species as a function of polymer type, in terms both of polymer polarity (polar/nonpolar) and the polymer glass transition temperature have been investigated. Polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(alpha-methylstyrene) (PAMS), and PS-co-PAMS were tested together with various DASAs [1]. Of these, PMMA is relatively polar while the rest are relatively nonpolar. It was found (Figure 5 in [1]) that in polar (PMMA) polymer matrix, the DASA absorbance spectrum was blue-shifted, and that the back-reaction rate was markedly reduced. In contrast, the nonpolar polymers did not shift the DASA absorbance spectrum, and all allowed for a faster back-reaction rate, even though their glass transition temperatures differed [1]. Based on these results, PAMS was chosen for the polymer matrix in this work, as the back-reaction timescales available using this polymer were well-aligned with the envisioned neuromorphic application (insect navigation). We note that besides the choice of polymer, the preparation of the dye polymer film on the surface will influence the dynamic and optical properties of the dye which gives another parameter for controlling it.

***(r1)* From the spectra (Figure 2C), it seems like there is obvious intermolecular aggregation between DASA in the polymer films. How does the aggregation affect the photoisomerization of DASA?**

Answer:

Generally, organic chromophore aggregation has been addressed in several studies. At these high DASA concentrations, intermolecular interactions can affect the DASA kinetics through different mechanisms. Referring to e.g. section 2.3.5 of [3], both the photoinduced forward reaction and the thermally activated back reaction have been found to be inhibited at high DASA concentrations in polymer. This could partly be caused by long range dipolar interactions, as well as "stacking" of the open-form (aggregation). Aggregation of DASA leads to a broadening of the absorbance spectrum and a change in the vibronic pattern of the absorbance as compared to a monomeric solution [1,3]. For example, distinct band broadening and enhancement of vibronic features at high concentrations in polystyrene has been found previously [14]. Hence, that we observe similar effects with DASA in a nonpolar polymer (PAMS) is in line with these previous studies. Aggregation can lead to slower kinetics and thus a slower photo switching rate of the DASA. As aggregation also lead to a non-homogeneous dispersion of DASA this potentially results in multiexponential decay/recovery rates in the polymer matrix as compared to the monomeric/homogenous solution [1,3]. While we do see indications of slower behavior upon strong aggregation, multiexponential behavior has not been observed.

Various molecular properties such as the dipole moment and the open isomer planarity can be tuned to minimize the prevalence of aggregation if so desired [3]. An example of this is already incorporated in the specific DASA species used in the current work ("D1A3" of [1]), as it features a 2-methyl indoline group which counteracts stacking of the open isomer. Another potential avenue is changing the way the DASA is incorporated into the polymer matrix; e.g. by attaching the DASA to the polymer via covalent conjugation and/or by encapsulating the single DPS molecules using metal-organic frameworks [23], thereby inhibiting from aggregation.

We acknowledge the aggregation as a relevant phenomenon to consider, and have added the following lines including the two above mentioned references to the manuscript:
"The spectral shapes in Fig. 2C indicate the presence of some aggregation of DASA molecules in the PAMS matrix [51], which can lead to slower kinetics as compared to a monomeric solution as well as multiexponential decay rates [32]. However, decay processes reported here are well-described by single exponentials, and the achieved kinetics are well-suited for biologically relevant tasks (see below)."

***(r1)* Figure 4 (b), for each pulse of light irradiation, the wave is not typical square wave, why?**

Answer:

We thank the reviewer for the observation regarding Figure 4(b). From the comment, we recognize that the data presentation will benefit from further clarification. Square wave pulses of light *were* employed in the experiment, but they were not explicitly shown in the figure instead the device photocurrent due to the light is shown.

To elaborate, Figure 4(b) shows the photocurrent detected by the DASA-covered nanowire array in response to the light pulses. The light intensity per square pulse is large compared to the DASA

concentration, meaning that each pulse decolorizes a significant portion of the DASA molecules. Hence, the photocurrent rises logarithmically for a given pulse-set (e.g. the green curve), as the steady-state of de-colorization vs recovery of color is approached after ~20 such square light pulses. In contrast, the intensity of the square light pulses used in Figure 4(a) is small compared to the DASA concentration. Hence, the Figure 4(a) cyan curve shows a linear increase of photocurrent for each consecutive light pulse.

To clarify this point, we have for Figure 4(b) added an inset showing the nominal square pulse shape employed for this experiment, as well as a note in the Figure caption explaining the inset.

Reviewer 2 (R2)

The manuscript demonstrates a novel device combining organic dye with III-V semiconductor optoelectronic devices. The device holds versatile functions, suitable for bio-inspired optical neural networks. The key point is an on-chip weight memory unit via reversible switching of dyes embedded in a polymer. I recommend it for publication if the paper can be further improved from the following aspects:

Answer:

We thank the reviewer for the positive assessment and the comments which were really helpful, and we have followed them to improve the manuscript.

(r2) **Please give the full name of the dye molecules and the related abbreviation. Otherwise, readers will not know what DPS is. Furthermore, DPS and DASA are both used in the text and figures. I guess DPS and DASA represent the same molecules in this work. Please clarify it.**

Answer:

We acknowledge that the use of abbreviations as well as their explanation in the manuscript was not as good as it should have been for the reader to follow the work. "DPS" is an abbreviation of "DASA PhotoSwitch", i.e. "Donor-Acceptor Stenhouse Adduct PhotoSwitch" in full. In both cases, the abbreviation refers to the same DASA dye molecule species, namely the one called "D1A3" in [1] . To avoid confusion, we have revised the manuscript and figures to consistently use "DASA" as the preferred abbreviation throughout.

In addition, and to further clarify which DASA molecule we have used, we have added the sentence:

"The chemical structure of the specific DASA used here is depicted in Fig. 1B (further characterization given in [32])."

to the manuscript, where [32] refers to the article denoted [1] in the reference list to this answer.

(r2) **The authors state that this work achieves the light communication between the dye and the**

solid-state optoelectronics. Compared to other optoelectronic synapses, what are the advantages of the synaptic device in this work? What's the uniqueness?

Answer:

This is a relevant question which we have given quite some thought to - although we gave it limited attention in the paper. There are several points to this that we will try and convey here and which we have also included in the paper to improve on this point.

First, in most optoelectronic solutions for artificial synapses the fundamental concept is different from ours as they use a combination of electrical and optical signals in contrast to our pure optical synapse solution. In the standard concept the photo-responsive material controls an electrical current between electrodes in the synaptic device. So, the electrical response of the synapse is changed via optical stimuli [4-9]. The synapse itself becomes an optoelectronic device that needs electrical connections to function. In those cases, the optical signal is then typically used to transmit input from the outside into a layer of synapses upon which the further computation happens electrically.

In our case, the synaptic effect exclusively depends on responding to and controlling the light passing through the DASA dye. So only the actual neural node (that received input from the synapses) is an optoelectronic device that needs external electrical power – not each synapse. This is a significant difference: For each neural node there can be thousands of synaptic connections, thus it is a significant disadvantage if all the synapses need electrical power connections. As a result, our optical synapses can be used throughout an optical network as the synapse "workhorse" and not only for the initial input part. A single other fully optical synapses that work in the same spirit as in our dye case is phase change memories (PCMs) [10], however here the memory is set via heat, do not have the wavelength flexibility of the dyes and needs significant physical space to function.
As a sidenote, in the previous standard solutions the memory response is often driven by light induced charge trap states or movement of ions and as a result the functional response can be unpredictable as it relies on defects in the material. The DASA dyes function via a highly predictable (reversible) structural change in the molecule, thus making it simpler to control the quantitative function of the system in a reliable fashion.

Second, a unique advantage of our solution is in the excellent *combination* of properties of the DASAs, which has resulted in a large interest in them in recent years [1,2,3,12]. They are a unique class of state-of-the-art visible-light responsive reversible photoswitches exhibiting a range of desirable material properties such as negative photochromism (photoinduced decolorization and thermal/photo coloration), visible-light absorption, polarity switching, high fatigue resistance and a straightforward synthesis. These are all useful properties for neuromorphic nanophotonics. Additionally, wavelength variation is useful as it will allow memory that operates with light signals of different colours (allowing multiplexing). The highly variable (but controllable) memory dynamics possible with memory retention times across several orders of magnitude is important as also biological systems have memories that act on several timescales. Further, they can have multiple stages in their switching which allows for both setting the memory and controlling its dynamics via light[16]. Finally, as they can be combined with standard polymers they can be integrated easily with semiconductors as we demonstrate. While other materials systems may have some of these properties, the combination is unique.

Third, the presented combined dye and optoelectronics ability to mimic the insect brain's central complex (CX) neural network in a circuit, particularly its path integration (PI) function, demonstrates its practical applicability in real-world bio-inspired tasks that have not been addressed before with photonic solutions. The DASA dyes embedded in a polymer act as effective on-chip weight memory units, capable of reversible switching and long-term reproducibility, which are crucial for neuromorphic computing. Here the memory lifetimes and response times are very well suited for the timescales found for navigation in the natural world.

(r2) **The paper mentions that STP can be implemented in devices, but no figure in the main text confirms this point.**

Answer:

It is correct that no figure in the main text clearly displayed the STP behavior (as was presented in the schematic of Fig1) and we discussed it only very briefly in the text. We have improved the manuscript and figures as well as added new experimental data for a better discussion and illustration of the STP effect in our concept.

To reiterate, short term plasticity (STP) refers to a situation where a memory state can change significantly without direct outside stimuli during the computation cycle [26,27]. This can be a set memory that reverses over time with a time constant much shorter than the computation time. This can result in a variety of different functionalities [28] depending on how fast the change is compared to the task being computed and the signals transmitted between neural nodes as well as received from the outside.

Since the dyes we presently use can be made to provide memory decay times that are much shorter than the time of computing (e.g. down to the timestep 0.1-1s for the biological navigation system explored in the paper) STP is fundamentally possible [1,3]. But we should also consider how we observe it:

A basic illustration of STP that we observe in our data (although it was not clearly described) is the case of the spike signals as in Fig 4a. Most basic, if the time between spikes is much longer than the memory decay time, the dye absorption will not be changed after the spike input. However, if the time between spikes is shorter than the memory decay, the dye absorption will decrease resulting in building up a stronger signal transmission (we now show this case in Fig 1). Or to put it in a more quantitative way, for a long-term memory, the memory build-up will be directly linear proportional to the rate of spikes, while for short term memory the memory build-up will depend non-linearly on the spike rate.

With this in mind, STP behavior can be seen in Fig 4A in the following way: During the scan we decreased the spike rate by a factor of 2 (after a third of the scan). If we were in a LTP scenario the change in the linear slope of photocurrent increase should be exactly 2, but the slope of photocurrent increase between spikes instead decreased by a factor of 2.7. So memory response is no longer direct proportional to the spike rate showing STP behavior.

To further illustrate the STP scenario we have added new experimental data to the SI as Fig S4. The spiking pattern is the same as in Fig 4a, but we have altered the dye memory decay rate to make it faster. As seen, we now come into a situation where the fast spike rate (in the beginning of the scan) results in a

build-up up a higher photocurrent (due to de-colorization of the dye), however the slower spike rate (later in the scan) is not able to keep up with the memory decay and a decrease in the photocurrent is in fact observed. Thus, only a sufficiently fast spike rate will lead to a memory build-up as is the consequence of a STP scenario.

Dynamic STP response between pulses is also as illustrated in the SI information Fig S6, in a different way. Here we show that by changing the sample temperature (which increases the memory decay rate) we can also go from a situation of very little change in the memory between pulses to a complete decay of the memory between pulses.

We finally note that the memory decay times found in with the specific DASA dye used in our paper are relevant for the Insect navigation circuit simulated in the paper. This dye also best matched the capabilities of our measurement systems, so we chose to use this dye with a long memory decay time. If we wanted to increase the speed of the memory decay, to address other STP scenarios, this could be done by choosing a "faster" dye which is available [1].

We have extended the discussion of STP, to better explain how we see that STP can be achieved as well as added the new SI figure S4. To better also illustrate the STP situation of Fig 4 and Fig S6 in the schematic of Fig 1, we modified that in Fig 1. In the original version it is a rather extreme STP where input and decay time constants are more or less equal, which is possible, but a more normal case where decays is slower than input rise is now shown.

(r2) **In Figure 5, the noise tolerance in the photoswitch model (exponential) is better than that in the original model (linear). The authors said that it is not related to the exponential properties of the DPS. The authors should explain the reason clearly in the main text or SI.**

Answer:

The models compared in Figure 5 and discussed in related text are very information dense and we recognize that there is room for clarifications of the conclusions drawn from that comparison. The sentence "verifying that the photoswitch model breaks at lower noise level (20%) than the original model (30%; see SI Fig. S14)" was meant to convey that the noise tolerance of the exponential model is worse (max 20% noise) than that of the linear (original) model (max 30% noise). We note that the exponential model nevertheless tolerates very significant noise levels, with 20% noise being sufficient for applications as demonstrated in the modeling.

The explanation we offer of the difference is as follows: In the original model, the in-neuron memory can be both actively stored and erased. In contrast, the in-neuron memory for the photoswitch case can only be actively stored, while the erasing of memory occurs passively through the thermally activated back-reaction of the photoswitch dye. This limitation gives rise to the lower noise tolerance of the photoswitch model.

We have updated the manuscript with the following explanation to clarify this to the reader:

NEW:
"We run the same simulation varying the response noise from 0% to 40%: the original model breaks at a 30% noise level, while the photoswitch model is less tolerant to noise, and breaks at a 20% noise level (see SI Fig. S14). The difference is not related to the exponential properties of the DASA, instead it occurs because light can only increase the memory stored in each neuron (transmittance of the DASA).

This is not the case in the original model, where the in-neuron memory can be both actively stored and actively erased. In contrast, the in-neuron memory for the DASA case can only be actively stored, while the erasing of memory occurs passively through the thermally activated back-reaction of the DASA. This limitation gives rise to the lower noise tolerance of the photoswitch (DASA) model. A multiwavelength signal that allows differential increase or decrease of the photoswitch transmittance (like in [41]) could resolve this by introducing a light induced back-reaction. We note however, that the current noise tolerance level still is considerable, and sufficient for realistic use-cases."

OLD:
"We run the same simulation varying the response noise from 0% to 40%, verifying that the photoswitch model breaks at lower noise level (20%) than the original model (30%; see SI Fig. S14). This effect is not related to the exponential properties of the DASA, instead it occurs because light can only increase the memory stored in each neuron (transmittance of the photoswitch), which is not the case in the original model. A multiwavelength signal that allows differential increase or decrease of the photoswitch transmittance (like in [41]) could resolve this."

Reviewer 3 (R3):

The manuscript by Alcer et al describes a photoswitch memory based on a donor acceptor dye that can be switched controllably with light. The concept is interesting and the paper reads well. I only have a few minor comments:

Answer:

We thank the reviewer for the appreciation of the manuscript, and for the very valuable comments and questions which have helped us further clarify the manuscript and elaborate on the advantages and properties of the memory system presented in the manuscript.

(r3) **Introduction: "information transfer will be inherently fast."**
This true for light, but generally dye's photoswitching is slow. How fast can the dye switch? And is this an issue for the applications envisioned?

Answer:

We thank the reviewer for raising this relevant point regarding information transfer versus switching of the dyes. We are in the current work more emphasizing the potential of energy efficiency and flexibility of the system for navigation and not so much the speed. However, we do mention that the transmission of light signals is inherently fast in the introduction and should have additionally emphasized and discussed that the switching of the molecules is slower (we will come back to the actual speed below).

In a light driven system with dyes as memory components this would mean that the system can respond extremely fast if the dye weights have already been set (then limited by the ps response time of the optoelectronic nanocomponents in the neurons). However, a learning process would be slower as that would correspond to the time it takes the dyes to react to light and turn colorless. While the photo absorption step itself occurs within 2 ps [3,12], the complete structural change of the molecule takes longer time and depends on the surrounding material, temperature and structure of the molecule. This is

not fully understood but the complete time will be in the order of ns or more [3,12] depending on the surrounding material, which would set an ultimate limit. Then the rate of photo switching observed will depend also on the intensity of the light and the probability of absorption.

For navigation assignments as we explore in the current case, the memory needs to be updated with relation to the speed of the insect and then 1s to 100ms is needed. This timescale is well achievable with the DASAs in general [3], as well as with the dyes that are available to us as synthesized dyes in [1]. Orders of magnitude further improvement of response times have been found with further development of molecules [24,25], thus μs photoswitching should be achievable with new dyes. The ultimate limit is presumably ns for dyes where a structural re-arrangement occurs. To go even faster, other types of dye signal storage (such as in a charged state) may be relevant, but then the memory retention times would go down also.

In the manuscript we have rewritten the introduction to further elaborate on these points.

(r3) **"Several important features must characterise a potential connection weight solution". I would argue that weight programming also needs to be predictable (linear/symmetric) allowing for blind updates in ANN training. Is this possible with the current material?**

Answer:

Several options exist for dynamic programming of the dye weights in a predictable fashion. For the present application of navigation, the decrease in absorption of the dye (and thus increase in weight of the light passing through that channel) is predictable but it is not linear instead it follows a logarithmic behavior. We note that many natural/analog systems will have such a nonlinear behavior. However, as seen in Fig 2A: The range of 0% to ~60% change in the observed photocurrent (due to optical changes of the dye) can be well approximated by a linear function. Further, in Fig 4a it is seen that spikes gives a linear change in absorption as a function of number of spikes again showing that predictable and linear behavior is possible with a usable variable range of the dye.

For the DASA dye used in the present work the only way to reduce the transmission weight is by heating the sample, which we use to reset the memory. However, other dyes can be found [15] where one light wavelength can switch the dye to a new absorbing wavelength and then light at this new wavelength can switch it back. Thus, by using two different wavelengths (which is achievable over the complete visible spectrum with III-V semiconductors) predictable and approximately symmetric and linear behavior of dyes for both increasing and decreasing the signal can be accomplished. Interestingly, further properties of the DASA dyes can add relevant functionality for controlling the reduction of the weights. As was shown recently, a multi-stage photoswitching system can be designed [16]. This allows one wavelength of light to be used for setting the memory of the dye, but another wavelength can be used to increase the speed at which the dye reaches its final colorless state or reverses back to the original state. This can be used to further manipulate the function of the memory locally and induce both decrease of the weights or different dynamics behavior. Mixing such light pulses would be an interesting future research project presented by the dyes. As described in the next section, the memory function on different places on the chip can also be modified.

We have added a discussion of this in the end of manuscript, since it is an interesting point

(r3) **"As no electrical connections is needed to the dyes, they exclusively communicate optically with the nano-optoelectronics"**
I understand the advantages of fully optical systems, but would the integration of the nano-optoelectronics not also need highly integrated electronics? One needs to be able to turn on the light with specific characteristics at a specific location (i.e. weight), right? With a dense network of weights how can you program each weight individually? Can the authors elaborate on this point of integration advantages?

Answer:

This is a relevant point that we have given some consideration, although we did not put it in the original paper. Besides the comments below we have added a brief discussion on this at the end of the paper.

First, in the simplest implementation of the dye where it is evenly distributed between nano-optoelectronic components that emit and receive light between them (as in the network for insect navigation) local weight tuning of the dye will inherently occur as areas where much light communication occur the dye will become more transparent, while in areas with little communication the dye will remain absorbing. For maximum compression of the network system in physical space the components need to be nanoscale as can be done with III-V nanowires discussed in the manuscript and in [17]. How dense a network that can then be produced will depend on the ability to focus light locally to affect the polymer in specific regions, which can be sub-wavelength using either plasmonic effects or dielectrics [17,18]. Further, the possible network density depends on how long a distance the light must travel in the polymer medium to experience significant absorption due to the dye (e.g. transmission reduction >20%). Here we are helped by the DASAs having a high molar absorption coefficient (Table S1 and ref [3]). From some of our experiments on dye absorption as a function of polymer thickness (Fig S1) we can see that thickness down to 1micron is already available for our experiments, while further decrease in the thickness (where the DASA still functions [3]) down to ~200nm should be possible. In the end, optical systems can never be as compact as pure electrical systems (and that must not be the point when using light for connectivity in a design), but using the dye and a broadcasting strategy [17] components can be packed to distances at least 2 orders of magnitude denser than what is possible with present optical solutions that are already demonstrated as potentially useful for neuromorphic computing [19]. Here it can be noted that combining optical and electrical driven circuits together is an interesting further potential avenue.

Second, local permanent modification of the absorption properties of the dyes is possible using strong light signals that can lead to permanent de-colorization of a percentage of the DASA molecules (dependent on intensity and duration of the light). As a result, optical lithography can be used to pattern areas where the dyes absorb light more and areas where they absorb less with the precision of lithography as used for microelectronics fabrication. This will then introduce areas of different memory weight capabilities.

Third, printing patterns in the polymers using lithographic tools is also available [20] which can allow variation of absorption. Here also different dyes can be combined in lithographic patterns [21] by printing polymer areas with different dyes. As the dyes can operate at different wavelengths mixing of dyes in the same area could potentially also be used for multiplexed memories in the same regions of space. Finally it

can be noted that dyes can be infused into e.g. a polymer also after initial deposition opening up for patterning with several different dyes in the same region[22].

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