How to cite: *Angew. Chem. Int. Ed.* **2024**, *63*, e202411003
doi.org/10.1002/anie.202411003

Energy Transfer

# Optimizing Upconversion Quantum Yield via Structural Tuning of Dipyrrolonaphthyridinedione Annihilators

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**Abstract:** Triplet-triplet annihilation upconversion (TTA-UC) is a photophysical process in which two low-energy photons are converted into one higher-energy photon. This type of upconversion requires two species: a sensitizer that absorbs low-energy light and transfers its energy to an annihilator, which emits higher-energy light after TTA. In spite of the multitude of applications of TTA-UC, few families of annihilators have been explored. In this work, we show dipyrrolonaphthyridinediones (DPNDs) can act as annihilators in TTA-UC. We found that structural changes to DPND dramatically increase its upconversion quantum yield (UCQY). Our optimized DPND annihilator demonstrates a high maximum internal UCQY of 9.4 %, outperforming the UCQY of commonly used near-infrared-to-visible annihilator rubrene by almost double.

Photon upconversion, the transformation of low energy photons into higher energy photons, is noted for its extensive potential applications.[1,2] These range from increasing the efficiency of photovoltaics,[3–5] to low-energy photocatalysis,[6,7] to biological imaging,[8,9] among many others.[10–14] Unlike lanthanide-doped nanocrystal upconversion or two-photon absorption, triplet-triplet annihilation upconversion (TTA-UC) proceeds even at incoherent subsolar flux,[15] expanding its application scope.[16,17] Two separate species are needed in TTA-UC, a sensitizer and an annihilator. The sensitizer is a strongly light-absorbing compound which efficiently undergoes intersystem crossing (ISC). The annihilator is a highly emissive chromophore able to undergo triplet-triplet annihilation (TTA).[18,19] The sensitizer absorbs a low-energy photon, upon which its first excited singlet state ($^1$[Sen]*) is populated. This compound then undergoes ISC, populating the first excited triplet state ($^3$[Sen]*) of the sensitizer. Next, energy is transferred from the sensitizer to an annihilator via Dexter type triplet energy transfer. This results in the first excited triplet state of the annihilator ($^3$[An]*) being populated. Two annihilators in the excited triplet state can then undergo TTA, during which the energy of the two excited states is combined. This yields one annihilator in its first excited singlet state ($^1$[An]*) while another annihilator relaxes to the ground state. The annihilator in its first excited singlet state ($^1$[An]*) can then decay to the ground state via fluorescence, emitting a photon that is higher in energy than the ones initially absorbed by the sensitizer. These steps are summarized in Figure 1. For TTA-UC to occur, certain energetic conditions must be satisfied. First, the excited triplet state of the sensitizer must be roughly equal to or higher than the excited triplet state of the annihilator ($^3[\mathrm{Sen}]^* \geq {}^3[\mathrm{An}]^*$). This allows the sensitizer to transfer energy to the annihilator. Second, the excited singlet state of the annihilator needs to be less than or equal to twice the energy of its excited triplet state ($^1[\mathrm{An}]^* \leq 2\times{}^3[\mathrm{An}]^*$) (Figure 1). This enables $^1$[An]* to be populated upon TTA.

Given the wide span of potential applications of TTA-UC, it is crucial to expand the range of available sensitizers and annihilators. Ideally, we could fine-tune the physical and electronic properties of the components of an upconverting system to fit the needs of any desired application. Currently, most research efforts are focused on discovering innovative sensitizers. This has unveiled numerous new molecules and materials that display efficient TTA upconversion in conjunction with known annihilators.[20–28] While much research has focused on derivatives of established upconversion annihilators,[29–34] there has been little focus on creating entirely new families of upconversion annihilators (Scheme 1). However, it was recently shown that new

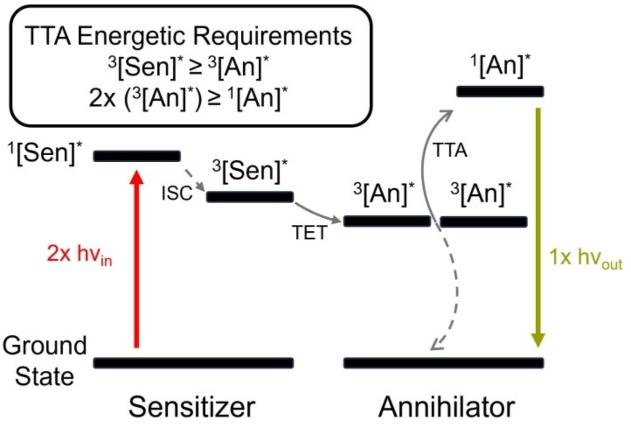

***Figure 1.*** Schematic of the TTA-UC process, showing intersystem crossing (ISC), triplet energy transfer (TET), and triplet-triplet annihilation (TTA). Sensitizer and annihilator species denoted by [Sen] and [An], respectively. Spin-state singlets and triplets denoted with superscript 1 and 3, respectively. Star denotes first excited state.

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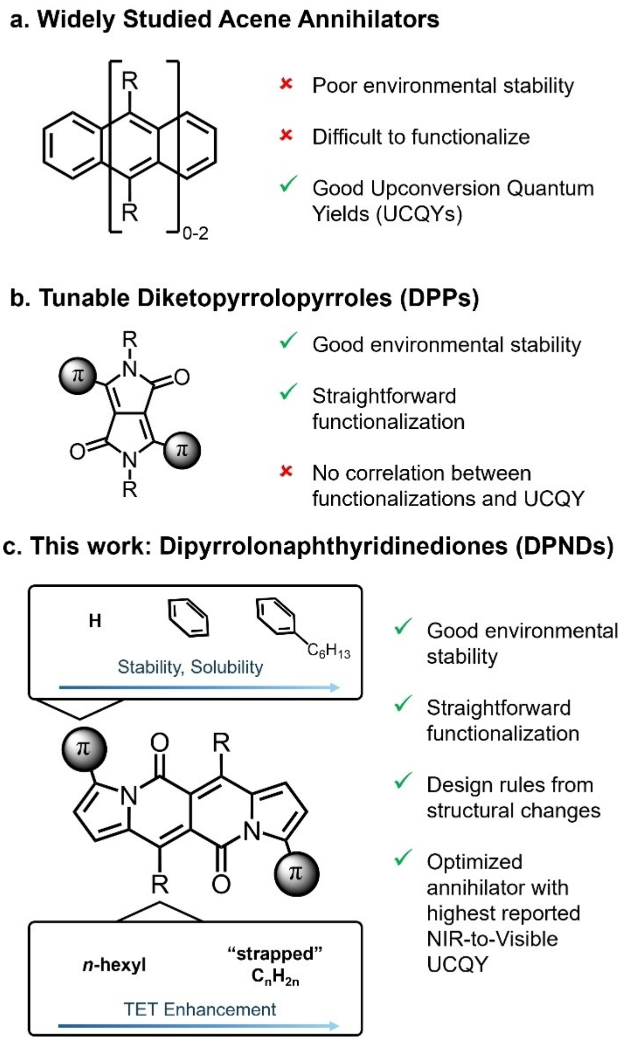

***Scheme 1.*** Triplet-triplet annihilation upconversion annihilators.

families of annihilators could be developed, as long as the energetic requirements of TTA-UC (Figure 1) were met.[35]

One such family of compounds that we were interested in exploring as an annihilator is dipyrrolonaphthyridinedione (DPND) (Scheme 1c). DPND in its simplest form has a first excited triplet state ($T_1$) energy of ~1.2 eV, with a first excited singlet state ($S_1$) energy of ~2.4 eV,[36] therefore meeting the energetic requirements of a TTA-UC annihilator. While thin films of DPND have been shown to undergo singlet fission, solutions of DPND exhibited high photoluminescence quantum yields,[37,38] suggesting they could serve as annihilators in TTA-UC. In addition, DPNDs exhibit other desirable qualities such as stability in ambient conditions, evidenced by minimal changes in absorption to a thin film of DPND over 50 days that was exposed to air and light.[36] Furthermore, it has been shown that DPND can be readily derivatized.[39] These synthetic adaptions are far more straight-forward than those of the commonly used near-infrared (NIR) -to-visible annihilator rubrene, whose derivatization has been hindered by synthetic difficulties.[41] Besides tuning the emission wavelength of the upconverting system, the structural changes to the annihilator have a significant impact on the upconversion quantum yield (UCQY).

Herein, we demonstrate that DPND can act as an annihilator in NIR-to-visible TTA-UC. Via synthesis of various DPND derivatives, we uncover structure–property relationships in our DPND annihilators. Finally, by applying these design rules, we synthesize an optimized DPND derivative, which has a high maximum UCQY (9.4 %) outperforming rubrene (5.7 %), the most-commonly used NIR-to-visible TTA-UC annihilator.

To investigate how structural changes impact the efficiency of upconversion, we synthesized a series of DPND derivatives (Figure 2a). The stability and tunability of DPND enabled the swift and varied synthesis of the molecules described herein. As previously reported, DPNDs can readily be obtained via two-step synthesis from commercially available starting materials.[37] DPND was initially synthesized with n-hexyl solubilizing chains (Compound **1**), or with a strapped alkyl chain forming a cyclophane (Compound **2**).[40] This strapped derivative was synthesized as it was previously shown that strapped alkyl chains enhance UCQY in other annihilators.[41] These parent DPNDs were further functionalized via direct arylation (See Supporting Information Section S2).[42] The steady-state absorption spectra (Figure 2b) of the synthesized derivatives show a gradually decreasing first excited state singlet energy ($^1[\mathrm{An}]^*$) compared to **1**. Accordingly, the same red-shift is seen in the steady-state photoluminescence (PL) spectra of the DPND derivatives (Figure 2c). Concurrently, the $T_1$ energy of DPND (~1.2 eV) is not expected to change significantly upon derivatization, as the triplet is localized on the DPND core which is not being modified. This is supported by density functional theory (DFT) calculations performed on compounds **1–6** (See Supporting Information Section S11, Table S6). These calculations show that while the $S_1$ energy of compounds **1–6** fluctuates by 0.4 eV (0.3 eV experimentally), the $T_1$ energy of compounds **1–6** only fluctuates by 0.1 eV. This phenomenon, of a tunable $S_1$ energy with a relatively stationary $T_1$ energy, has been reported previously in other chromophores, such as acenes and diketopyrrolopyrroles.[35,43,44]

Therefore, all the synthesized compounds fulfill the energetic requirements for TTA, as they all have a singlet energy $<2.4$ eV, smaller than or equal to twice the first excited triplet state ($^1[\mathrm{An}]^* \leq 2\times{}^3[\mathrm{An}]^*$). The ability of these derivatives to undergo TTA-UC was demonstrated by combining them with a suitable sensitizer in toluene, where it was seen that compounds **1–6** could successfully serve as TTA-UC annihilators (Figure 3). The annihilator concentrations in the reported mixtures were chosen after optimization to maximize upconverted photoluminescence. PdPc-$(OBu)_8$ was chosen as a sensitizer due to its triplet energy of ~1.24 eV, suitable for triplet energy transfer to the DPNDs via a Dexter type mechanism.[45] The results indicate that DPNDs can be used as annihilators in TTA-UC, provided that the energetic criteria for upconversion are met.

Next, we evaluated the external UCQYs ($\Phi_{UC}$) of our different upconversion solutions (See Supporting Informa-

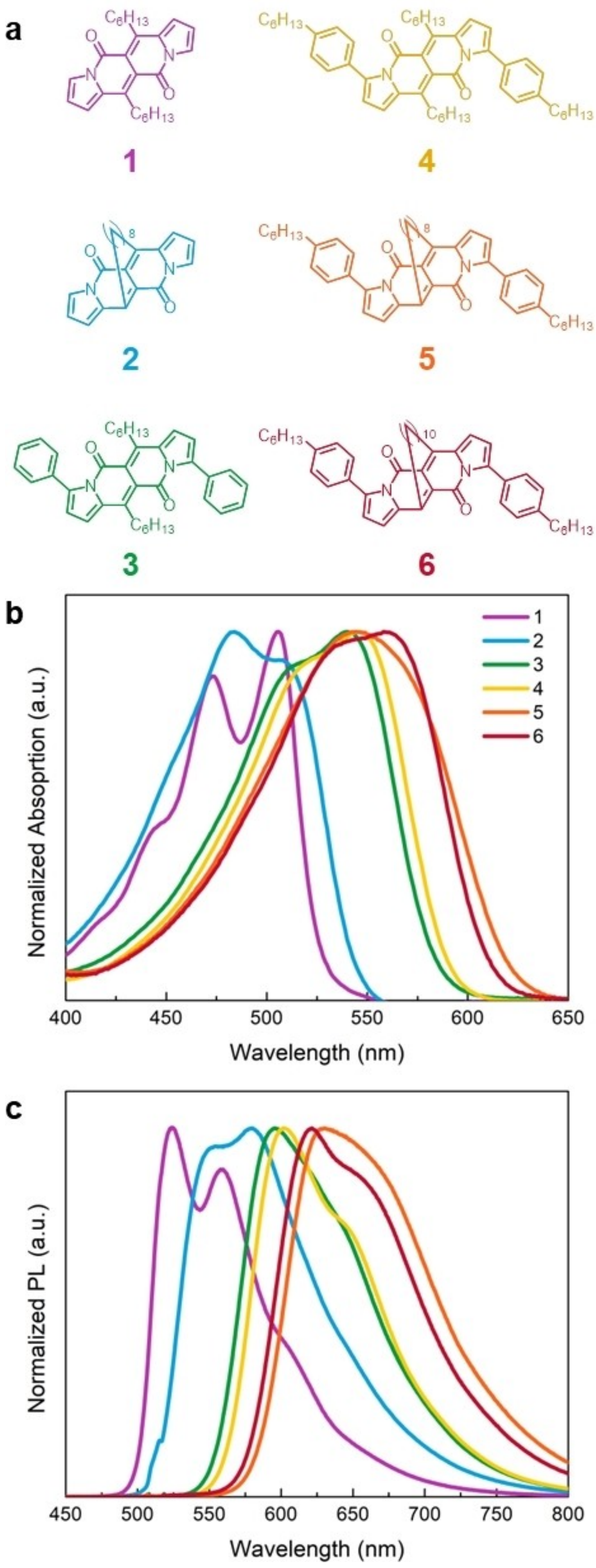

**Figure 2.** a) Structures of **1** (purple), **2** (cyan) **3** (green), **4** (yellow) **5** (orange) and **6** (red). b) Steady-state absorption and c) steady-state photoluminescence (PL) of **1** (purple), **2** (cyan) **3** (green), **4** (yellow) **5** (orange) and **6** (red) ($10^{-5}$ M) in toluene.

tion Section S4),[46] which guided our synthetic design of our DPNDs. $\Phi_{UC}$ is equal to the number of emitted photons detected per absorbed photon. We note that because one photon is emitted per two photons absorbed, $\Phi_{UC}$ has a maximum value of 50 %.[47] The results of these measurements are presented in Table 1. The simplest DPND, compound **1**, exhibited a relatively low $\Phi_{UC}$ of 0.29 %. To improve upon this, we explored compounds with a strapped alkyl chain. Previous work has shown annihilators with strapped alkyl chains have higher UCQYs than those with unstrapped alkyl chains.[41] This is likely because the strapped alkyl chain leaves one face of the DPND exposed, making it easier for these compounds to approach one another by reducing steric interactions which leads to enhanced TTA efficiency. The exposed DPND core also leads to enhanced triplet energy transfer (TET) from sensitizer to annihilator. The rate of TET ($k_{TET}$) was experimentally determined with Stern–Volmer measurements (See Supporting Information Section S5, Table S2). This data revealed that strapped DPNDs do in fact show higher $k_{TET}$ values than their unstrapped counterparts. As hoped, this modification led to a large increase in $\Phi_{UC}$, with a simple strapped DPND (Compound **2**) already exhibiting a $\Phi_{UC}$ of 1.68 %.

Next, we sought to improve our annihilators by functionalizing DPND. It is known that organic compounds can adopt a biradical form when in the triplet state.[48,49] By drawing a resonance structure which maximizes double bonds on six membered rings following Clar's sextet rule, we can find the most likely location of the two radicals in the biradical form of an organic radical.[50] When this is done with DPND, we see that the radicals should be localized on the 3 and 9 positions of DPND (See Figure S7). This was further confirmed with calculations which predict a high triplet spin density at the 3 and 9 positions (See Figure S8). It has been shown that introducing bulky groups can stabilize organic radicals via steric protection,[51] therefore we sought to add bulky groups to the 3 and 9 positions of our DPNDs. Substitution of unstrapped DPND with phenyl groups led to compounds **3** and **4** which had $\Phi_{UC}$ values of 1.79 % and 1.45 % respectively. We were also able to synthesize a DPND with phenyl groups at the 2 and 8

***Table 1:*** Upconversion quantum yields and threshold intensities of DPNDs.

| Compound | $\Phi_{UC}$[a] (%) | $\Phi_{UC,g}$[b] (%) | $\Phi^{\infty}_{UC,g}$[c] (%) | $I_{th}$[d] (mW/cm$^2$) |
|---|---|---|---|---|
| **1** | 0.29 | 0.52 | 0.94 | 80 |
| **2** | 1.68 | 2.32 | 5.72 | 200 |
| **3** | 1.79 | 2.57 | 5.74 | 133 |
| **4** | 1.45 | 1.76 | 3.02 | 43 |
| **5** | 1.66 | 2.75 | 4.62 | 57 |
| **6** | 2.41 | 3.97 | 9.36 | 167 |

[a] External upconversion quantum yield. [b] Internal upconversion quantum yield. [c] Maximum internal upconversion quantum yield. [d] Threshold intensities for annihilators studied. Measured for toluene solutions with sensitizer concentration of $10^{-5}$ M, and annihilator concentrations of 25, 15, 10, 5, 1, and 2.5 mM for compounds **1**–**6**, respectively.

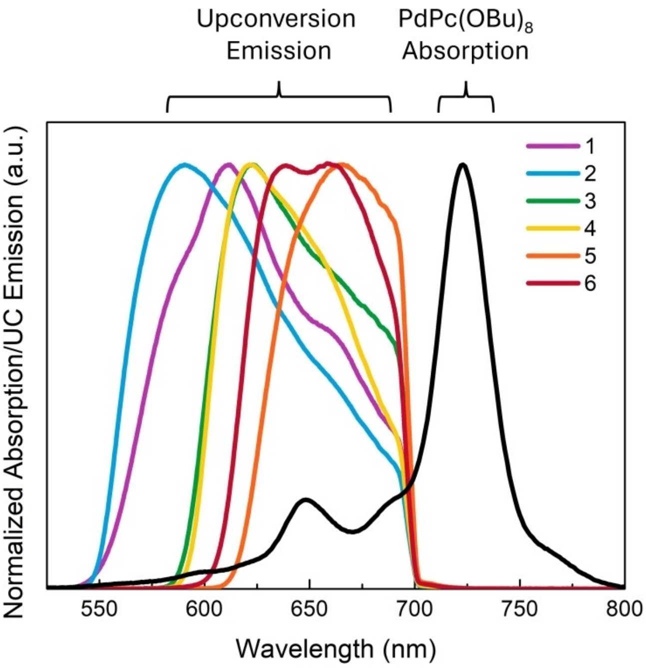

*Figure 3.* Normalized UC emission of **1** (purple), **2** (cyan) **3** (green), **4** (yellow) **5** (orange) and **6** (red) with PdPc(OBu)$_8$ in toluene. Sensitizer concentration is $10^{-5}$ M, with annihilator concentration of 25, 15, 10, 5, 1, and 2.5 mM for compounds **1–6**, respectively. Solutions were excited with a 730 nm laser diode, with a 700 nm short-pass filter utilized. Normalized steady-state absorption of $10^{-5}$ M PdPc(OBu)$_8$ in toluene shown in black.

positions of our DPND (Compound **9**, see SI). This compound exhibited lower UC photoluminescence compared to the analogous compound **3** with 3,9 phenyl substitution (See Figure S9), further confirming that the radicals are localized at the 3 and 9 positions of DPND in the biradical triplet state.

We then combined our strategies of using strapped alkyl chains and bulky phenyl groups to maximize $\Phi_{UC}$. However, compound **5** exhibited a $\Phi_{UC}$ of 1.66 %, with no improvement to previous DPNDs. We measured photoluminescence quantum yields (PLQYs) for all of our compounds (see Table S1) and observed that compound **5** has a lower PLQY than our other derivatives, leading to lower than predicted $\Phi_{UC}$. This low PLQY is likely due to the strapped alkyl chain being too short, leading to ring strain.[40] Therefore, we synthesized compound **6**, with a longer strapped alkyl chain. This compound has a PLQY of 46 %, and a measured $\Phi_{UC}$ of 2.41 %, confirming the benefits of both the strapped alkyl chain and the bulky groups that protect the biradical.

Threshold intensity ($I_{th}$) is another important figure of merit for TTA-UC systems. This is the power at which TTA-UC reaches 38.2 % of its maximum UCQY, an important parameter given the power dependence of TTA-UC.[52] A low $I_{th}$ value means a TTA-UC system can operate efficiently at low excitation power, greatly expanding the possible applications of the system. $I_{th}$ values for our DPNDs were experimentally measured (details in Supporting Information Section S8) up to 200 mW/cm$^2$ (Table 1). Lower $I_{th}$ values, down to 3.2 mW/cm$^2$,[15] have been reported for NIR-to-visible TTA-UC, but these UC systems use nanocrystals as sensitizers. Previous reports of TTA-UC using rubrene with a similar PdPc macrocycle as a sensitizer gave a minimum $I_{th}$ of 1.9 W/cm$^2$, nearly 10 times higher than our highest values.[53] The best $I_{th}$ values for NIR-to-visible UC systems with metal macrocycle sensitizers are similar to those reported for our DPNDs.[1] Together, this shows DPNDs have suitable $I_{th}$ values to compete with existing annihilators.

To further compare our DPNDs to other reported annihilators, we determined the internal, or generated, UCQY ($\Phi_{UC,g}$). This is done by taking into account absorption losses in the $\Phi_{UC}$ measurement, primarily due to annihilator self-reabsorption as well as the presence of a 700 nm short pass filter in our measurements (See Supporting Information Section S7). This absorption correction has been previously reported by various groups.[33,53,54] We then determined the relation between $\Phi_{UC,g}$ and excitation power density ($I_{ex}$). By fitting this data, we could determine the maximum UCQY ($\Phi^{\infty}_{UC,g}$) (See Supporting Information section S8).[55,56] We believe the maximum UCQY values are useful as they allow for direct comparison of the performance of a UC system between different groups, even if they are using excitation sources with different optical output power. These values for our compounds are shown in Table 1. Notably, compound **6** has a $\Phi^{\infty}_{UC,g}$ value of 9.4 %, higher than the 5.7 % reported for rubrene, the most commonly used NIR-to-visible TTA annihilator.[53] This previous report also uses the same sensitizer as we do, PdPc(OBu)$_8$. To the best of our knowledge, $\Phi^{\infty}_{UC,g} = 9.4$ % with DPND is the highest reported UCQY (out of a maximum 50 %) for NIR-to-visible upconversion.[1] Our value exceeds the previous record of 7.1 % for metal macrocycle sensitization of perylene and 8.4 % for nanocrystal sensitization of rubrene.[7,57]

In this work, we have developed DPNDs as a new class of efficient NIR-to-visible annihilators in TTA-UC. The versatile chemistry of DPND allows for straight-forward synthesis and derivatization, allowing us to obtain an optimized annihilator after uncovering structure-function relations from earlier DPND designs. This yields an annihilator with a higher maximum $\Phi^{\infty}_{UC,g}$ than rubrene, the benchmark and most commonly used NIR-to-visible TTA-UC annihilator. We believe these design rules are general and will guide the synthesis of further optimized TTA-UC annihilators, further expanding the already growing application space of TTA-UC.

## Supporting Information

The authors have cited additional references within the Supporting Information.[58–66]

## Acknowledgements

This work was supported by start-up funds provided by the University of California San Diego. The authors acknowledge the use of facilities and instrumentation supported by NSF through the UC San Diego Materials Research Science and Engineering Center (UCSD MRSEC), grant # DMR-2011924. The authors acknowledge the Keck Foundation for providing computational resources.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Annihilators · Energy Transfer · Organic Electronics · Photochemistry · Upconversion

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Manuscript received: June 11, 2024
Accepted manuscript online: July 19, 2024
Version of record online: September 12, 2024