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# Picosecond Electron Transfer from Quantum Dots Enables a General and Efficient Aerobic Oxidation of Boronic Acids

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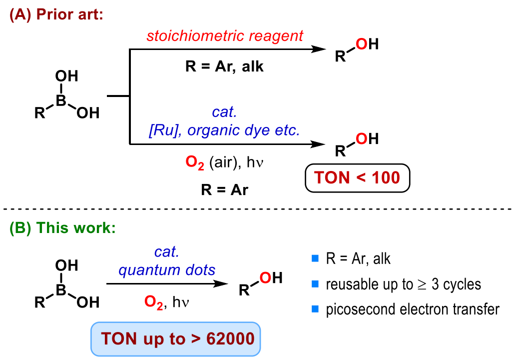
*Supporting Information Placeholder*

**ABSTRACT:** A general visible light-mediated aerobic oxidation of boronic acids is unveiled using CdSe nanocrystal quantum dots (QDs) as the photoredox catalyst. This protocol requires mild reaction conditions, low catalyst loading (down to 10 ppm) and tolerates various functional groups. The resulting phenols and aliphatic alcohols are produced in good to excellent yields with outstanding turnover numbers (up to >62000). The reaction mechanism is probed using ultrafast transient absorption and luminescence spectroscopy. The existence of a rapid 350 ps initial electron transfer followed by a hole transfer is demonstrated.
**KEYWORDS:** quantum dots, photoredox catalysis, boronic acid, aerobic oxidation, cadmium selenide, phenols, alcohols

Semiconductor nanocrystals, also known as quantum dots (QDs), have recently attracted attention as photosensitizers that can dictate outcome of organic reactions.[1] Unlike conventional photoredox agents, nanocrystals offer improved stability and larger surface area, which in turn allows higher photon penetration and consequently better catalyst turnover.[2] It is further possible to engineer redox activity of nanocrystals, thereby optimizing them towards either selectivity or generality. Here we demonstrate the ability of CdSe nanocrystals to sensitize the visible light mediated aerobic oxidation of aliphatic and aromatic boronic acids for the synthesis of aliphatic alcohols and phenols.

**Scheme 1. Oxidative Hydroxylation of Boronic Acids: (A) Previous Reports and (B) Present Work**



The ubiquitous nature of phenols and aliphatic alcohols in natural products and various synthetic intermediates[3] has made their efficient and economic synthesis essential. Among various methods known,[4] oxidative hydroxylation of boronic acids is arguably the most attractive and versatile route to phenols and alcohols. The reliability of this route makes this conversion particularly attractive for late-stage applications in complex syntheses. While a variety of oxidants have been reported,[5] molecular oxygen remains the most economical and sustainable oxidant.[6] In 2012, Xiao, Jørgensen and co-workers reported an aerobic oxidative hydroxylation of boronic acids under visible light photoredox catalysis using $Ru(bpy)_3Cl_2$ as the catalyst (Scheme 1A).[7] Despite high efficiency, the scope of this protocol is restricted only to aryl boronic acids.

In this article we show that the QD catalyzed oxidation is amenable to aliphatic boronic acids as well (Scheme 1B). Consistent with the enhanced substrate scope, our ultrafast studies confirm that this QD catalyzed reaction proceeds through a somewhat different reaction sequence. We further find the efficacy of the reaction to be a strong function of QD band gap and architecture, with wide band gap materials being significantly more efficient at driving the reaction. A turnover number (TON) in excess of 62000 is observed under optimized reaction conditions.

Figure 1a shows a typical absorption (red) and emission spectrum (green) of CdSe QDs. Transmission electron micrographs (TEM) and high resolution transmission electron micrographs (HRTEM) images further exemplify the narrow size distribution of the QDs employed in this work (Figure 1b-c).

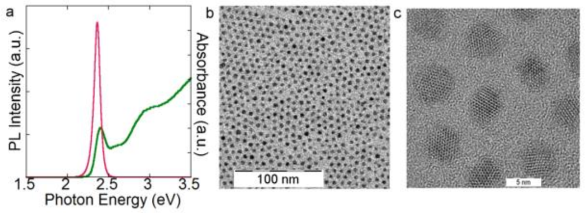
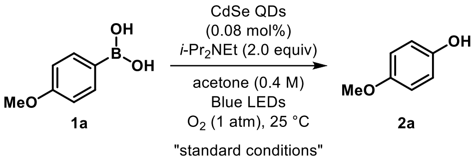


**Figure 1.** (a) Absorption and emission spectra of CdSe with band gap of 2.35 eV. (b) TEM and (c) HRTEM images of the same sample.

To evaluate the suitability of these QDs as photoredox catalyst for the aerobic oxidation of boronic acids, we designed a model reaction with 4-methoxyphenylboronic acid (**1a**) as the substrate (Table 1). In a typical reaction, 0.08 mol% CdSe and 2.0 equiv of *i*-$Pr_2NEt$ were dispersed in an acetone medium. It is observed that under these conditions, QDs form a turbid dispersion. When the reaction flask was irradiated with a blue LED of 450 nm wavelength in air at ambient temperature, we were pleased to note the formation of 4-methoxy phenol (**2a**) in 56% yield within 48 h (entry 1). Despite rather modest yield, this experiment clearly validated our hypothesis. The use of molecular oxygen instead of air led to significant improvement in yield (entry 2). While the reaction was found to take place under the irradiation of white LED (100W), **2a** was formed with somewhat reduced yield (entry 3). We undertook further optimization of reaction conditions in order to improve the chemical yield of the product. While increasing the amount of *i*-$Pr_2NEt$ did not improve the yield, lowering the same reduced the yield considerably (entries 4-5). Further attempts to improve the yield by increasing the surface area of QDs using silica coated CdSe also proved to be abortive (entry 6). No product formation was observed when the reaction was carried out in dark or in the absence of any one of the reaction components (CdSe, base, $O_2$) under otherwise standard conditions (entries 7-10), thereby highlighting the essentiality of each of these components. In addition, heating a mixture of **1a**, *i*-$Pr_2NEt$ and CdSe under oxygen in the absence of blue LED failed to furnish any product (entry 11). These results unambiguously eliminate the involvement of any thermal oxidation and support the photoredox pathway.

**Table 1. Optimization of Reaction Conditions**[a]



| entry | change from "standard conditions" | time (h) | yield (%)[b] |
|---|---|---|---|
| 1 | air instead of $O_2$ | 48 | 56 |
| 2 | none | 48 | 85 |
| 3 | 100W white LED instead of blue LED | 60 | 69 |
| 4 | 4.0 equiv of *i*-$Pr_2NEt$ | 48 | 81 |
| 5 | 1.0 equiv of *i*-$Pr_2NEt$ | 48 | 52 |
| 6 | silica coated QD | 48 | 40 |
| 7 | no light | 48 | <5[c] |
| 8 | no CdSe | 48 | <5[c] |
| 9 | no *i*-$Pr_2NEt$ | 48 | <5[c] |
| 10 | argon instead of $O_2$ | 48 | <5[c] |
| 11 | no light at 40 °C | 48 | <5[c] |

[a]Reactions were carried out on a 0.2 mmol scale. [b]Yields correspond to the isolated yield, unless stated otherwise. [c]Conversion as determined by $^1H$ NMR spectroscopy.

The reaction was also conducted with differently sized QDs in order to arrive at the most optimal QD band gap for driving the reaction.[8] We employed QDs with band gaps of 2.3, 2.14, 2.03 and 1.91 eV. The lamp spectrum is shown in the supporting information (Figure S1).[9] We observed that under these conditions, reaction yields increase with increasing QD band gap (Figure 2). In particular, we observed that the yield increases exponentially from 40 to 85%, with a maximum yield over a 48 h reaction cycle being observed for QDs with an S exciton position of 2.3 eV (540 nm). We further found that yields drop to 20% for core shell quantum dots CdSe/CdS (1 ML). Details of this experiment are provided in the supporting information Figure S2.[9] This trend is consistent with an activation energy barrier for electron transfer.[10] It is nevertheless clear that the optimal results are observed in the case of QDs with a band gap of 2.3 eV. CdSe QDs with still narrower band gaps are unstable in the reaction medium.

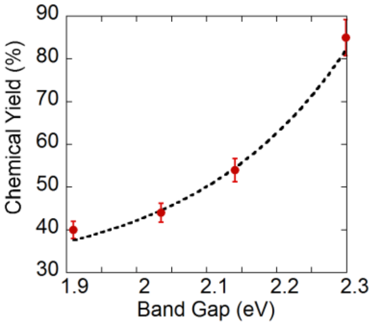
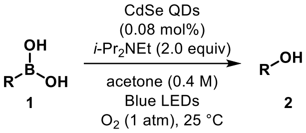


**Figure 2.** Chemical yield of the reaction as a function of the band gap (1S exciton position) of CdSe quantum dots.

Having optimized the reaction conditions (Table 1, entry 2), the generality of this QD-catalyzed aerobic oxidation protocol was evaluated. As shown in Table 2, a range of aryl boronic acids furnished the corresponding phenols in good to excellent yields within reasonable time scales. Both electron-donating as well as electron-withdrawing substituents at various positions of the aryl ring were well tolerated (entries 1-9). It must be noted that the formyl group, which is generally susceptible to oxidation conditions, not only survived, but afforded *para*-salicylaldehyde **2i** in high yields within 16 h (entry 9). Inspired by this result, other oxidizable functional groups (amine and acetamide) on the aryl ring (**1j-k**) were also tested. While our reaction conditions tolerated these functional groups, the corresponding phenols (**2j-k**) were formed in low to moderate yields (entries 10-11). In addition, both naphthols can also be obtained with good yields, albeit after prolonged stirring (entries 12-13).

**Table 2. Scope of Boronic Acids**[a]



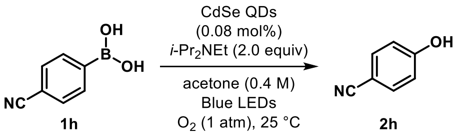
| entry | R (**2**) | time (h) | yield (%)[b] | TON[c] |
|---|---|---|---|---|
| 1 | 4-$OMeC_6H_4$ (**2a**) | 48 | 85 | 1063 |
| 2 | Ph (**2b**) | 24 | 74 | 925 |
| 3 | 2-$MeC_6H_4$ (**2c**) | 48 | 79 | 988 |
| 4 | 3-$MeC_6H_4$ (**2d**) | 40 | 79 | 988 |
| 5 | 4-(*t*-Bu)$C_6H_4$ (**2e**) | 40 | 73 | 913 |
| 6 | 3-$NO_2C_6H_4$ (**2f**) | 72 | 86 | 1075 |
| 7 | 4-$CF_3C_6H_4$ (**2g**) | 16 | 77 | 963 |
| 8 | 4-(CN)$C_6H_4$ (**2h**) | 28 | 88 | 1100 |
| 9 | 4-(CHO)$C_6H_4$ (**2i**) | 16 | 82 | 1025 |
| 10 | 3-($NH_2$)$C_6H_4$ (**2j**) | 65 | 32 | 400 |
| 11 | 3-(NHAc)$C_6H_4$ (**2k**) | 38 | 59 | 738 |
| 12 | 1-naphth (**2l**) | 96 | 66 | 825 |
| 13 | 2-naphth (**2m**) | 96 | 71 | 888 |
| 14 | *n*-$C_8H_{17}$ (**2n**) | 28 | 81 | 1013 |
| 15 | *c*-pent (**2o**) | 7 | 65[d] | 813 |

[a]Reactions were carried out on a 0.2 mmol scale. [b]Yields correspond to the isolated yield after column chromatography. [c]TON = Turnover number. [d]NMR yield.

Our protocol is not restricted to aryl boronic acids and can be applied to the oxidation of aliphatic boronic acids as well. For example, both long chain and alicyclic boronic acids were smoothly converted to the corresponding alcohols in good to high yields within reasonable reaction time (entries 14-15). Boronic esters can also be used as substrates, albeit with a considerably slower reaction rate.[9]

A noteworthy feature of our protocol is the high turnover number (TON) obtained for all the substrates, irrespective of their steric and electronic nature.

### Table 3. One-Pot Catalyst Recycling Experiment[a]

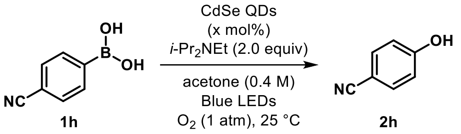


| cycle | time (h) | overall yield (%)[b] | TON |
|---|---|---|---|
| 1st | 24 | | |
| 2nd | 30 | | |
| 3rd | 96 | 62 | 2325 |

[a]Each batch of reaction was carried out on a 0.2 mmol scale. [b]Yield corresponds to the isolated yield.

The practicality of our protocol was tested by performing a one-pot recyclability experiment using 4-cyanophenylboronic acid (**1h**) as substrate (Table 3). Here, new batches of **1h** were added after consumption of the previous batch (monitored by TLC). Each reaction cycle was carried out with 0.2 mmol of **1h**. At the end of third cycle, the product **2h** was isolated in 62% yield while the overall TON was found to be 2325. Decrease in overall yield and reaction rate for the subsequent batches are possibly due to gradual decrease in effective catalyst loading.

### Table 4. Reaction with Lower Catalyst Loading[a]



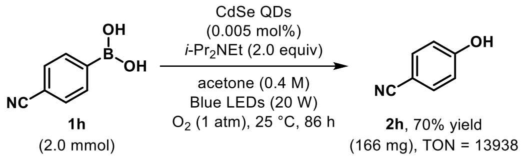
| entry | x (mol %) | time (h) | yield (%)[b] | TON |
|---|---|---|---|---|
| 1 | 0.001 | 72 | 63 | 62972 |
| 2 | 0.0001 | 96 | 8 | 83963 |

[a]Reactions were carried out on a 0.4 mmol scale using 20W blue LED source. [b]Yield corresponds to the isolated yield.

High catalytic activity and photostability of the CdSe QDs as displayed by high TON allowed us to reduce the loading of QDs. As shown in Table 4, in the presence of as low as 0.001 mol% (10 ppm) of CdSe, the product was obtained in 63% yield with a TON close to 63000 (entry 1). Further lowering of catalyst loading (to 1 ppm) compromised the reaction rate drastically. Nonetheless, extraordinarily high TON is maintained. Such turnover numbers are outstanding, even in the domain of photoredox catalysis[1d] and are not the consequence of a chain process since such a possibility has been eliminated through control experiments.[9]

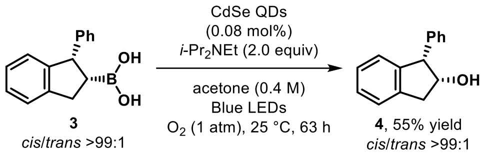
The scalability of this reaction is established by carrying out the oxidation of **1h** on a 2.0 mmol scale – 10 times that used for demonstrating the scope of the reaction, using only 50 ppm of CdSe (Scheme 2). We were pleased to find that 4-cyanophenol **2h** was formed in 70% yield with excellent TON.

### Scheme 2. Oxidative Hydroxylation Reaction on a Larger Scale



In order to gain insights on the stereochemical aspects of this reaction, we subjected *cis*-1-phenyl-2-indanylboronic acid **3** to our standard reaction conditions (Scheme 3). We were delighted to find that the reaction proceeded with complete stereospecificity to furnish *cis*-1-phenyl-2-indanol **4** in 55% yield. This observation clearly points to a concerted oxidation pathway.

### Scheme 3. Stereospecificity of the Oxidative Hydroxylation Reaction



The remarkably high turnover numbers as well as the broad substrate scope prompted us to study the reaction mechanism in greater detail.

We first examined the effects of treatment of QDs with the boronic acid. In general, it is observed that addition of boronic acid to QDs in hexane strongly enhances their luminescence. In the example shown in Figure 3a, the luminescence quantum yield (QY) of the QDs increases from 8.4% (green curve) to 14.3% (blue curve) upon addition of 20 µL of phenyl boronic acid to 2 mL of 0.04 mM QDs in hexane. This increase is not associated with a shift in the QD spectrum, and is consequently consistent with improved passivation of the QDs upon exposure to the boronic acid.[11] This interpretation is supported by the lengthening of the QD emission lifetime in time correlated single photon counting (TCSPC) experiments. For example, Figure 3b shows the emission lifetimes of CdSe QDs (green, 17 ns) as well as a solution of CdSe QDs treated with phenyl boronic acid (blue, 23 ns). In each case we report the averaged lifetime described by the expression shown in the supporting information.[9]

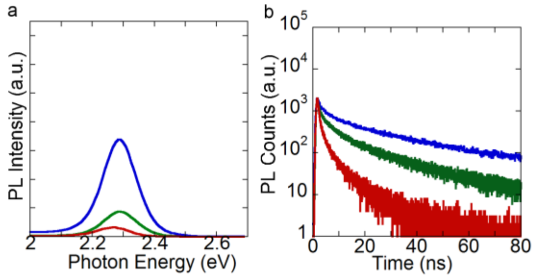


**Figure 3.** (a) Emission spectra of the CdSe (green), CdSe with 20 µL phenyl boronic acid (blue) and CdSe with 20 µL phenyl boronic acid and 20 µL Hunig's base (red) with QYs of 8.4, 14.3 and 2.5% where excitation energy of 3.1eV. (b) Emission kinetics of the same sample.

Further treatment of these boronic acid treated QDs with Hünig's base leads to a drop in quantum yield from 14.3% (blue curve, Figure 3a) to 2.5% (red curve, Figure 3a). We found that this drop in QY is again correlated with a change in the luminescence lifetimes as measured through TCSPC. As shown in Figure 3b, the addition of both base and boronic acid to QDs lowers the lifetime to 9.3 ns. This decrease could be caused either by a change in surface passivation or due to the initiation of the chemical reaction. In order to distinguish between these possibilities, we further studied the electron and hole residence times in these QDs through ultrafast spectroscopy.[11,12] Electron residence times were determined through ultrafast transient absorption (TA). In a typical experiment, QDs dispersed in hexane were pumped with frequency doubled pulses of a 100 fs Coherent Libra laser. The band edge dynamics was probed using a broadband white light probe. Figure 4a shows the dynamics observed when QDs are pumped by a 400 nm pulse that generates 0.6 excitons per QD. As shown in Figure 4a, the electron dwell times of QDs may be fit to biexponentials with time constants of 12 ps (34%) and 8.3 ns (66%) (green circle). Treatment with acid alone slows down this dynamic, and we observe electron dwell times of 17 ps (38%) and 10.1 ns (62%) (blue circle). This slowing down of the electron decay dynamic most likey arises from improved surface passivation of the QDs. Once both acid and base are present in the medium, the electron population decays significantly faster, with time constants of 6.4 ps (34%) and 357 ps (66%) (red circle) corresponding to an average lifetime of 353 ps. Our results are therefore consistent with an electron transfer from the QDs on a 300 ps timescale only if both reacting species are present. We further verified this electron transfer criterion by checking the dynamics in presence of base alone. This is highlighted in Figure 4b that compares the dynamics of QDs treated with base alone (red hollow symbols) with the dynamics of untreated QDs (green solid symbols). As evident from the figure, both samples show identical dynamics. Since faster TA transients corresponding to electron transfer are only observed when both acid and base are present, we infer that the presence of both species is essential to trigger the electron transfer sub-step of the photochemical reaction.[13]

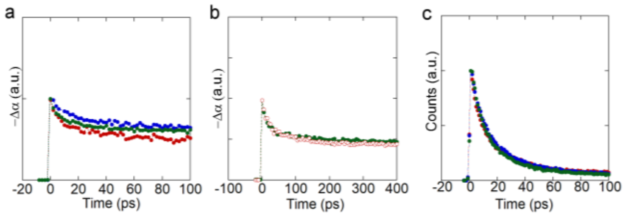
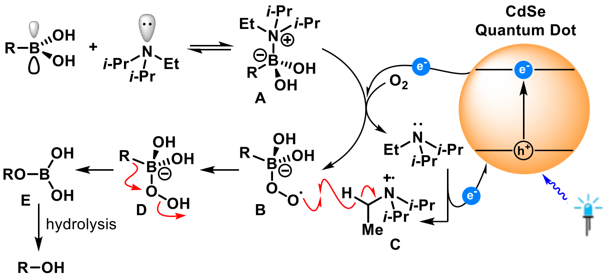


**Figure 4.** (a) Transient bleach decay of CdSe (green), CdSe with 20 µL phenyl boronic acid (blue) and CdSe with 20 µL phenyl boronic acid and 20 µL Hunig's base (red). (b)Transient bleach decay of CdSe (green), CdSe with 20 µL Hunig's base (red) of the same sample. (c) Luminescence upconversion decay of the CdSe (green), CdSe with 20 µL phenyl boronic acid (blue) and CdSe with 20 µL phenyl boronic acid and 20 µL Hunig's base (red).

While TA spectroscopy provides insights into electron dynamics, a full understanding of the mechanism also requires inferring the dynamics of the hole. We note that a consistent trend in lifetimes is observed in luminescence upconversion measurements that allow us to resolve the early parts of the excitonic dynamics. These experiments (Figure 4c) were performed on a Halcyone-Femtosecond Fluorescence Spectrometer from Ultrafast Systems. Samples were illuminated with a 100 fs 400 nm pump pulse. An 800 nm pulse was employed as the gate. We observe that in case of UPL, all samples show identical early-time luminescence dynamics. We note that the interpretation of UPL measurements is somewhat complicated by the fact that these only interrogate the emissive members of the ensemble, and further, the early time dynamic is dominated by non-radiative decay that is intrinsic to CdSe QDs. Nevertheless, our inability to detect the emergence of a new transient significantly shorter than 350 ps in the acid and base treated QDs is consistent with the occurrence of the hole transfer step after the electron transfer.[13b] To summarize these results, for the QD catalyzed reaction, the electron transfer from the QDs occurs as the first step, while hole transfer occurs at a later, unresolved timescale.[14] This is illustrated in Scheme 4. The requirement of both the boronic acid and the Lewis base (tertiary amine) to accomplish the first electron transfer further suggests the formation of a Lewis acid-base adduct **A** that acts as the electron acceptor. In the presence of molecular oxygen, the adduct **A** collapses to furnish the boronic acid-superoxide radical anion adduct **B** with concomitant release of the tertiary amine base. The exact mechanism for this single-electron transfer (SET) step requires further study. However, involvement of such Lewis acid-base adducts in light-driven SET has been demonstrated by Van der Eycken, Ley and co-workers.[15] Another SET from tertiary amine to the QD valence band restores the QDs to their neutral ground state, and produces tertiary ammonium radical cation **C**. A hydrogen atom abstraction from **C** by **B** generates the peroxyboronate intermediate **D**, which upon rearrangement and hydrolysis produces alcohols/phenols. The stereospecificity of the oxidation as depicted in Scheme 3 supports the intermediacy of **D** and the subsequent steps.

**Scheme 4. Mechanistic Proposal for the Aerobic Oxidation of Boronic Acids**



In conclusion, we have demonstrated the ability of CdSe nanocrystals to sensitize the visible light mediated aerobic oxidation of boronic acids. This general and mild protocol allows for the efficient oxidation of both aromatic as well as aliphatic boronic acids for the synthesis of phenols and aliphatic alcohols in good to excellent yields. Requirement of low catalyst loading (down to 10 ppm) combined with excellent photostability of the QDs helped us achieving outstanding turnover numbers (>62000) even in the domain of photoredox catalysis. We further show that this reaction occurs via an initial rapid (~350 ps) electron transfer from the photoexcited QDs, followed by the later abstraction of the hole. Considering the mildness and functional group tolerance, we expect our protocol to be applicable for the late-stage hydroxylation in complex syntheses. In addition, QDs as photoredox catalyst will no doubt make its mark in other visible light mediated bond constructions, bond cleavages and rearrangements in the near future.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interests.

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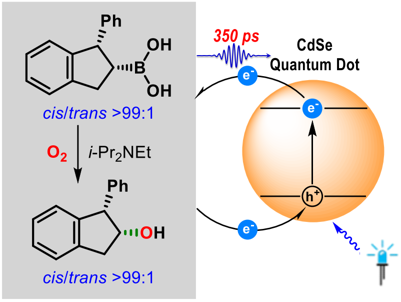
## TOC Graphic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Quantum Dot
e⁻
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h⁺
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