Fast pH Optodes for use in pH eddy covariance

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Introduction

pH eddy covariance is considered as a precise method to indirectly measure natural and artificially induced pH and CO_2 fluxes[1]. The basic idea of the method is that vertical pH flux can be presented as a covariance of the vertical flow velocity and the concentration of H^+ ions. This technique poses challenging requirements for pH sensor performance, such as a high sensor resolution (<0.003 pH units), a fast response time (t_{90} < 3 s and preferably < 1 s) and high sensitivity around the typical pH of seawater (~pH 8). Such performance can only be achieved by a drastic enhancement of sensor material properties and a dedicated setup, which is optimized seamlessly over all sensor components.

Measurement principle

Optical pH sensors are based on dyes which change their fluorescence properties upon protonation or deprotonation. Our sensor materials are based on aza-BODIPY dyes, which exhibit excellent photophysical properties.[2,3] They are highly fluorescent when protonated and quenched by a photoinduced electron transfer (PET) mechanism when deprotonated.

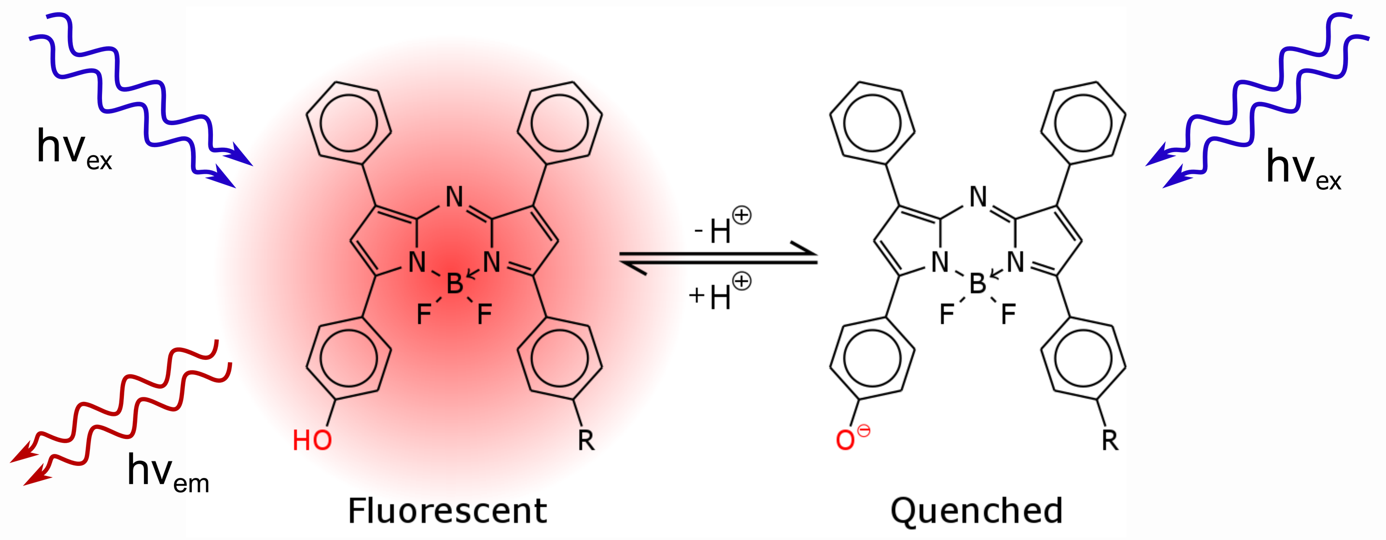

Figure 1: Measurement principle of optical pH sensors based on aza-BODPIY dyes (see also Figure 1 of poster P57)

Covalent immobilization

A combination of the pH indicator dye "OH butoxy aza-BODIPY" covalently linked to the sensor matrix poly(acryloylmorpholine-co-hydroxyethylacrylamide) PAMcoHEAA proved to be the most suited for application in pH eddy covariance An optimized procedure for the covalent attachment of the indicator dye to the polymer led to an increased concentration of the dye in the polymer and therefore a decreased thickness of the sensing layer. More information on covalent immobilization and subsequent crosslinking step can be found on poster P57.

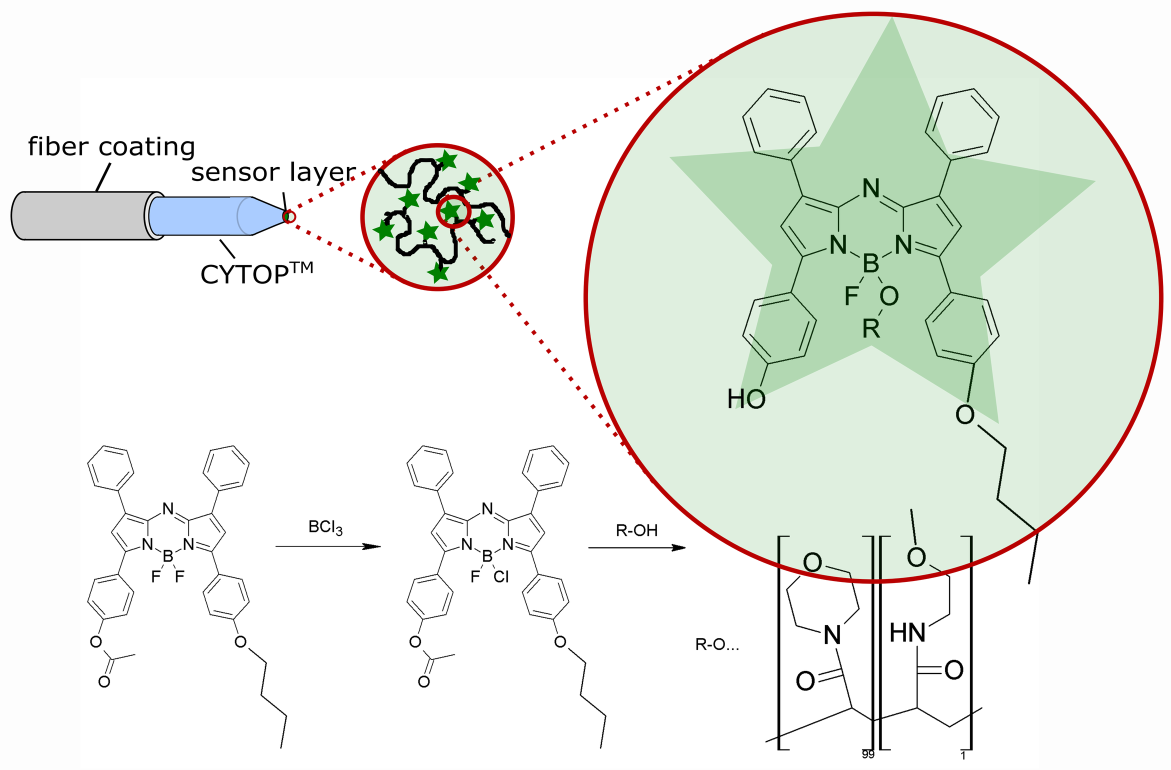

Figure 2: Principle of covalently immobilized indicator dyes at the distal end of an optical fiber (upper part) and reaction scheme for the covalent attachment of the indicator to the sensor matrix PAMcoHEAA (lower part).

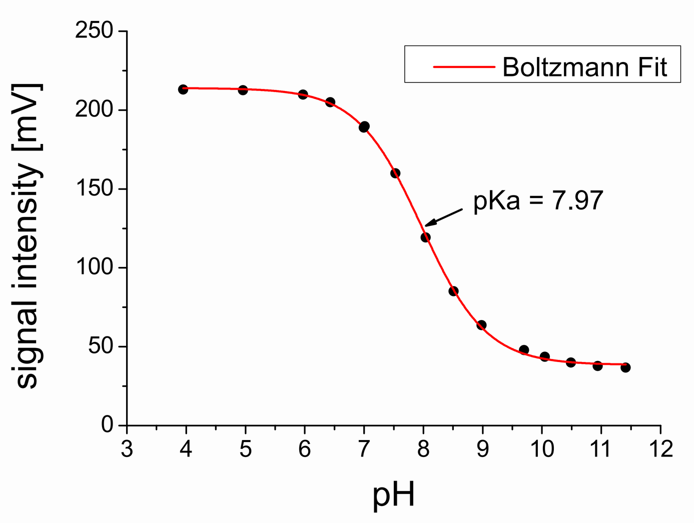

Figure 3: Calibration of OH butoxy aza BODIPY covalently linked to PAMcoHEAA. pH sensors exhibited a pK_a of 7.97 at an ionic strength of 700 mM. With a dynamic range of pK_a ± 1.5 pH unit this makes them ideally suited for application in seawater (pH 7.5 - 8.4)

Fiber geometry

An optical microsensor setup was chosen for realization of fast pH optodes. Tapering the distal end of a 400 µm fiber led to an improved sensor performance on the one hand by maximizing the amount of light guided to and from the "sensing chemistry" (improved S/N ratio) and on the other hand by optimizing diffusion conditions at the sensor tip (improved response times).

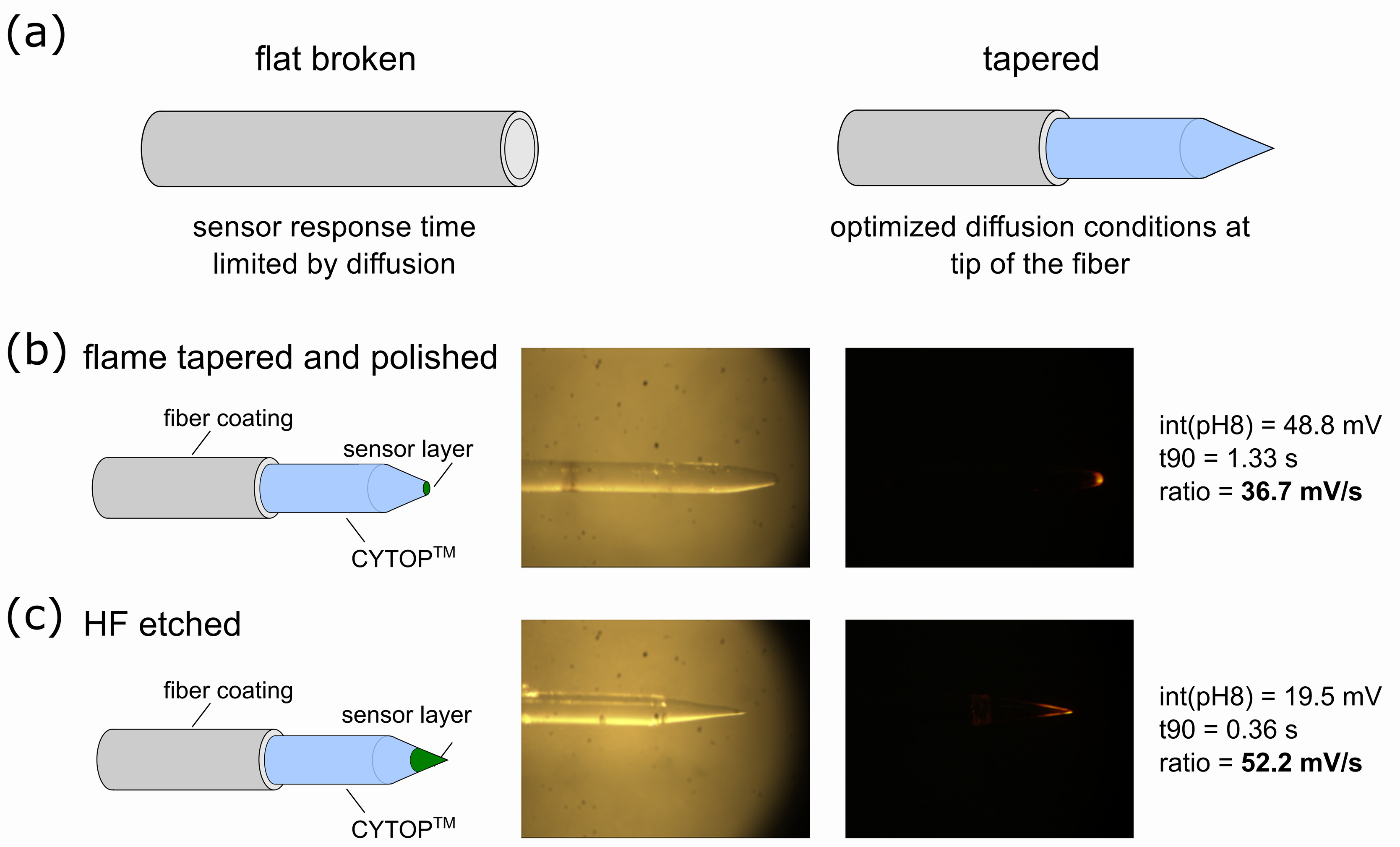

Figure 4: (a) General comparison of different fiber geometries, **(b)** and **(c)** fiber geometries for optimized performance. **(b)** flame tapered and polished and **(c)** HF-etched fibers.

Characterisation of fast pH optodes

pH optodes were evaluated for their applicability in pH eddy covariance. Results are presented in Figures 5 and 6.

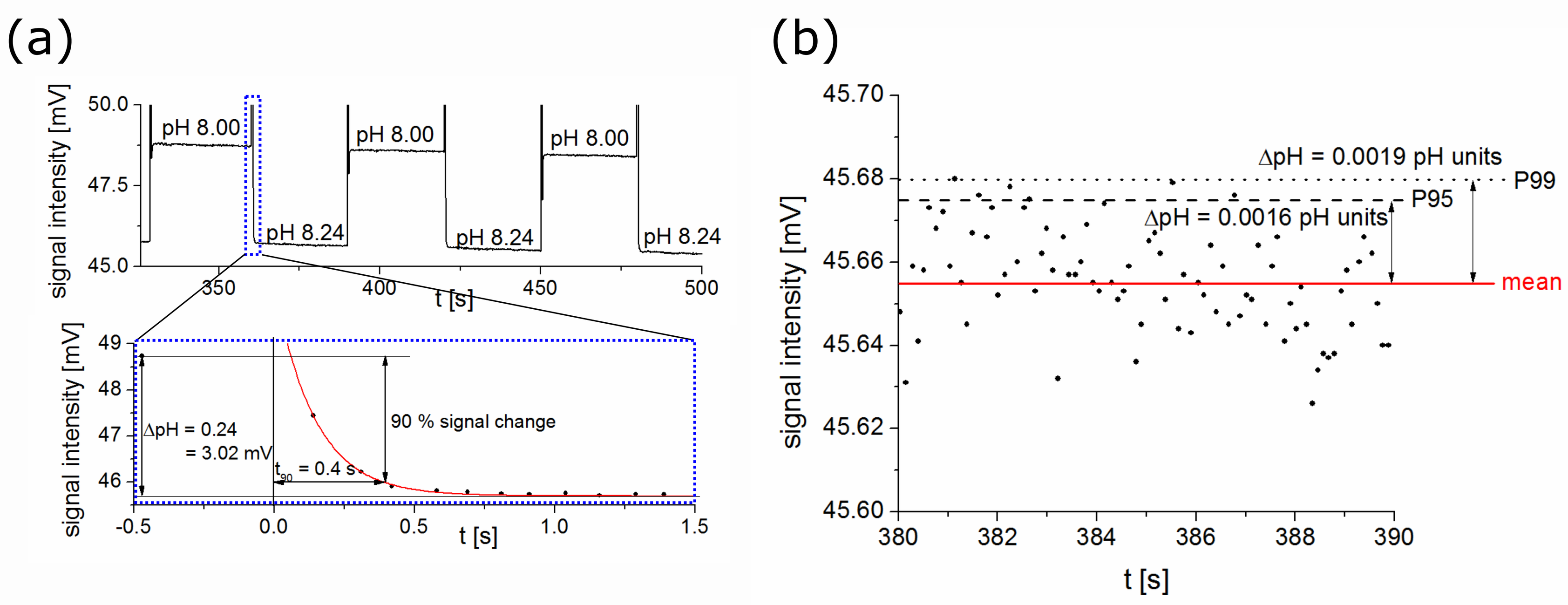

Figure 5: Characteristics of the pH optode prototype. **(a)** The prototype pH optode response time t_{90} is 0.4 s, and **(b)** 95 % of the noise lies within 0.0016 pH units.

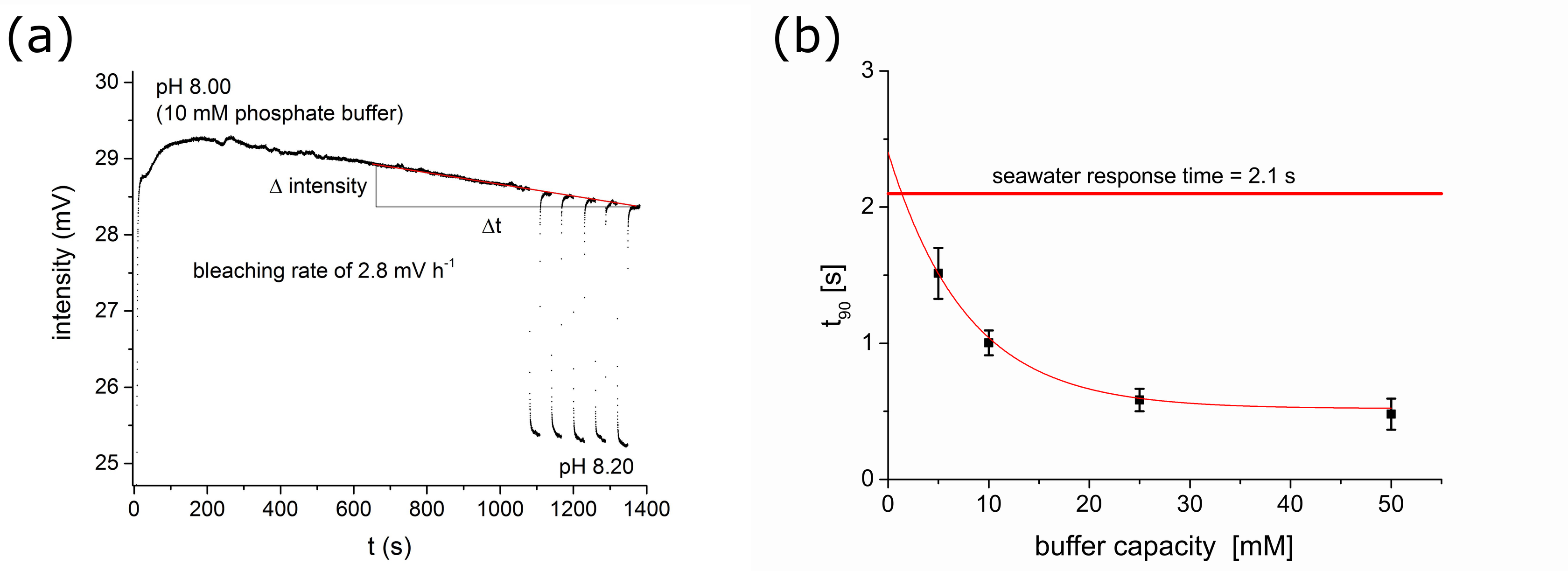

Figure 6: (a) pH optodes exhibited a minor signal drift due to photobleaching and **(b)** a response time dependency from buffer capacity.

Conclusion

pH optodes feature an improved sensing performance with a high sensitivity around the typical pH of seawater, a response time t_{90} below 1 s and a resolution better than 0.002 pH units. These features are adequate to capture most of the turbulent flux and therefore, pH optodes represent a promising tool to be used in pH eddy covariance.

References

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