Magnetically remote-controlled, optical sensor spheres for monitoring oxygen or pH

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1. Spectra and structures of the dyes

Chemical structures, emission and excitation spectra of Iridium(III)((benzothiazol-2-yl)-7-(diethylamino)-coumarin)₂(acetylacetonate) (Ir(C₅H₇(acac)), 1-hydroxypyrene-3,6,8-tris-(2-ethylhexyl)sulfonamide (HPTS(DHA)₃) and platinum(II)-tetrphenyltetraphenoporphyrin (PtTPTBP).

Fig. S1. Chemical structures and spectral properties of the oxygen sensitive dyes PtTPTBP and Ir(C₅H₇(acac)), and the pH-indicator HPTS(DHA)₃.

Fig. S2. (a) Normalized absorption spectra of the acidic and basic form of the pH-indicator, the reference dye (Ir(C₅H₇(acac)) and the emission spectrum of the excitation light, a blue LED. (b) Normalized luminescence emission spectra of the pH-indicator (acidic and basic form) and the reference dye plotted together with the transmission spectrum of the OG550 filter. Only the basic form of HPTS(DHA)₃ and the reference dye are efficiently excited and detected by the system, while the acidic form does not contribute to the resulting signal. Therefore, the ratio between acidic and basic form can be detected by the combined apparent phase shift of HPTS(DHA)₃ (fluorescent, φ = 0) and Ir(C₅H₇(acac)) (phosphorescent, φ ≠ 0).
2. Spray-coating of sensor spheres

During the spray-coating procedure, the spheres are continuously shaken to avoid the sticking of the spheres to the dish or to each other.

![Diagram of spray-coating process]

Fig. S3. The coating of the steel spheres was carried out with a conventional airbrush. During the coating, the spheres were vigorously shaken.

The luminescence image of MagSeMacs coated with PS and Ir(C$_5$)$_2$(acac) shows some inhomogeneities (Figure S4a). The surface structure of the layers differs depending on the cocktail composition (Figure S4c-d).

![Luminescence images and SEM surface images]

Fig. S4. (a) Luminescence image of oxygen sensitive MagSeMacs. SEM surface images of an uncoated sphere (b), a PS-coated, oxygen-sensitive sphere (c) and a hydrogel-coated, pH-sensitive sphere (d). The scale bars in all electron micrographs are 100 µm.

3. Modes of operation

A MagSeMac can either be directly mounted to an optical fiber tip, or its position can be remote-controlled through a transparent wall of e.g. a reaction vessel. The remote-controlling of a MagSeMac allows the continuous readout of the analyte concentration at multiple positions with a single sensor. In contrary, a MagSeMac fixed to an optical fiber dip-probe can be moved to any position which is accessible to the fiber and the separator. Separators with barriers to avoid an accidental sweeping of the MagSeMac from the separator are shown in Figure S5a-d. These separators protect the MagSeMac and ensure fast analyte exchange close to the MagSeMac.

4. Magnetic fixation of sensors for dip-probes

![Magnetic separators and sensor patches]

Fig. S5. Magnetic separators for fixing a MagSeMac in front of an optical fiber tip. In (b-d) a separator for a MagSeMac is shown with its barriers protecting the spherical sensor. Figures (e-f) show a conventional sensor patch glued to an iron ring which can then be magnetically fixed to magnetic rings to form a dip-probe. Finally, it is possible to use a plain sensor patch with the magnetic cap shown in Figures (g-i). Here, the circular sensor foil is clamped between magnetic rings around the fiber and a steel cap.
5. Applications

Potential applications of MagSeMacs are depicted in Figure S6. The mobility of the magnetic spheres allows monitoring of analyte gradients in stirred flasks (a) or plug-flow reactors (c). Due to the strong magnetic retention of the sphere, it is also possible to follow analyte levels in shaking (d) or rotating flasks (b) (Movie ac02393u_u002.avi). In case of a dip-probe, the MagSeMac is magnetically fixed at the optical fiber tip with a modified magnetic separator (Figure S5b-d). The probe is applied as conventional dip-probe (f). After usage, the MagSeMac can be replaced by a new sphere.

Even the application in magnetically stirred solutions was possible. The difference in magnetic field strength between the separator and the magnetic stirring bar was high enough to allow trapping of the sphere separately from the stirring bar. In case the MagSeMac stuck to the stirring bar, shortly increasing the steering speed disrupted the weak attraction between the bar and the sphere. However, this happened rarely.

Finally, we modified a SensorDish-Reader for 24-well culture plates with magnets in order to capture the magnetic sphere in front of the optical readout-unit. The thin layer of magnets focused the magnetic spheres reliably in front of the optical read-out unit. In this experiment, the MagSeMacs performed similarly to the other tested systems. However, they were the most convenient sensors to work with. A dosing device for MagSeMacs can be seen as a schematic drawing (Figure S7) and in a short movie (Movie ac02393u_u003.avi). After the measurement, the spheres were either magnetically retained in the plate for a washing step or withdrawn from the medium by a magnet. A dosing device for sensor spheres can be seen in Figure S7 and in the Movie ac02393u_u003.avi.

Fig. S7. Schematic representation of a dosing device for MagSeMacs. Each time the button is pushed, a sphere from the reservoir is ejected.