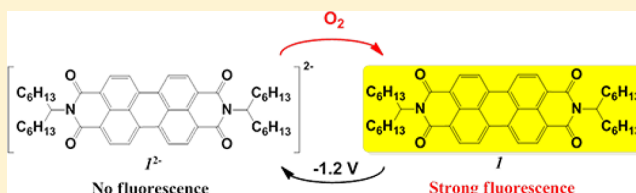


Efficient Fluorescence “Turn-On” Sensing of Dissolved Oxygen by Electrochemical Switching

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Supporting Information

ABSTRACT: We report on a novel method for sensing oxygen that is based on the use of a perylene diimide dye (**1**) which is electrochemically reduced to its nonfluorescent dianion form (**1**²⁻). In the presence of oxygen, the dianion is oxidized to its initial form via an electron-transfer reaction with oxygen upon which fluorescence is recovered. As a result, the fluorescence intensity of the dianion solution increases upon the addition of oxygen gas. Results demonstrate that high sensitivity is obtained, and the emission intensity shows a linear correlation with oxygen content (0.0–4.0% v/v) at ambient barometric pressure. In addition, using electrochemical reduction, oxygen determination becomes regenerative, and no significant degradation is observed over several turnovers. The limit of detection is 0.4% oxygen in argon gas.



Molecular oxygen is considered to be one of the most important chemical species in our environment as it is found as either a reactant or a product in a large number of chemical and biochemical reactions. Determination of the amount of dissolved oxygen in a solution is necessary in the medical, food processing, waste management, and petrochemical industries. Considerable efforts have been devoted to the development of sensing methods for the quantitation of oxygen.¹ The Clark electrode and its modified forms have been widely used with great success.² Optical methods such as fiber optic sensors³ or planar sensors,⁴ sometimes based on the measurement of fluorescence decay time,⁵ offer attractive alternatives to conventional Clark electrodes due to their insensitivity to electromagnetic interference, their fast response time, and the possibility to use them in dangerous environments.^{6,7} Among the many optical methods employed for oxygen sensing, photoluminescence has attracted special attention because it is highly sensitive⁸ and noninvasive,⁹ it has low toxicity,¹⁰ it provides a very fast response,¹¹ it is potentially reversible,¹² and it has versatile spatial resolution.¹³ Most photoluminescent methods exploit a decrease in luminescence intensity on quenching the excited state of a dye by an energy-transfer mechanism with an oxygen molecule. This phenomenon is described by the Stern–Volmer relationship. The optical sensors based on this quenching approach have achieved extremely sensitive monitoring of dissolved oxygen.

Herein, we present a fluorescence “turn-on” method for determination of dissolved oxygen. This is based on the reduced form of a latent probe that generates fluorescence emission upon exposure to an oxygen molecule. In this approach, as schematically shown in Scheme 1, the latent probe

(compound **1**) consisting of a lipophilic perylene diimide first undergoes reduction under an electrochemical potential. Compound **1**, originally possessing strong red fluorescence, turns nonfluorescent as the reduction process occurs. When the reduced solution is subsequently exposed to oxygen gas, it rapidly returns to its initial fluorescent state, even though the reduction potential is still being applied. A significant enhancement in fluorescence emission is observed on exposure to oxygen. This enhancement is owing to the big difference in the level of emission between the latent probe itself and its nonfluorescent reduced form. The reversibility of this switching behavior indicates that the same probe solution can be repeatedly reused for oxygen sensing.

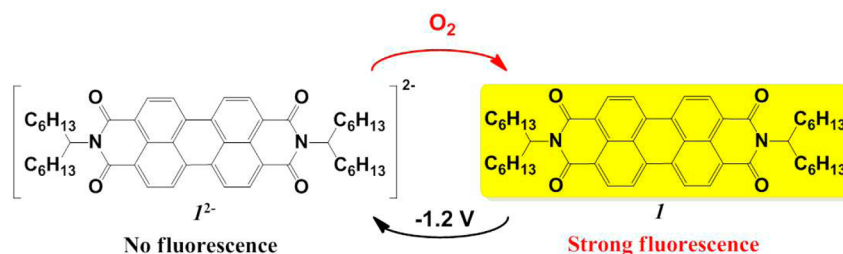
We employed a nonfluorescent reduced form of a lipophilic perylene tetracarboxylic diimide (PTCD) as the oxygen-sensitive probe. PTCD-based molecules have been widely studied in various optoelectronic devices, including thin-film transistors,¹⁴ photovoltaics,¹⁵ liquid crystals,¹⁶ and light-emitting diodes,¹⁷ owing to their high thermal, electrochemical, and photophysical stability. PTCDs have also attracted much interest for the fabrication of single-molecule devices, such as fluorescence switches,¹⁸ sensors,¹⁹ molecular wires,²⁰ and transistors.²¹ When compared to other common organic semiconductors, PTCDs have a number of unique features. They form a class of n-type semiconductor in contrast to the more common p-type counterpart in organic semiconductors.¹⁴ The extended π -conjugation system of PTCDs provides significant aromatic stabilization of the dianion intermediate.

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Scheme 1. Brief Explanation for Fluorescence Turn-On Sensing of Dissolved Oxygen



Therefore, the reduced aromatic dianion of PTCD²⁻ is extremely stable when in solution and can even be stored for months in deoxygenated water.²² This unique stability provides the possibility for reversible conversion between PTCD/PTCD²⁻ and an electrocatalytic reduction reaction between PTCD²⁻ and other chemical species. The latent probe (**1**) displays reversible electrochemical conversion to **1**²⁻, which is extremely sensitive to oxygen exposure, resulting in a significant enhancement of the fluorescence. As our method utilizes a fluorescence enhancing sensitizer, we expect that it would offer a sensitive measurement technique for very low content of oxygen.

EXPERIMENTAL SECTION

Materials. All reagents used in the chemical synthesis protocol were purchased from either Sigma-Aldrich (Sigma-Aldrich Corp.; www.sigmaaldrich.com) or TCI (Tokyo Chemical Industry; www.tci-asiapacific.com) and were used without any further purification. Deuterated solvents were acquired from Cambridge Isotope Laboratories (www.isotope.com). Acetonitrile (MeCN, >99.5%) was purchased from Merck, Germany. Tetrahydrofuran (THF, >99.6%) and dichloromethane (DCM, 99.99%) were obtained from Acros Organic (www.acros.be). DCM (dichloromethane) and triethylamine (TEA) were purified by distillation from CaH₂ prior to use. Tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, electrochemical grade, ≥99%) and silver nitrate (ACS reagent, ≥99%) were purchased from Sigma-Aldrich. Argon gas and synthetic air were acquired from Linde (www.linde.de).

Instrumentation. ¹H and ¹³C NMR spectra were recorded using a Bruker AVANCE DPX-300 (www.bruker.com). Chemical shifts are given in parts per million using the residual resonances of deuterated solvents (δ in CDCl₃) as internal references. ESI-MS data were obtained using a QUATTRO LC triple quadrupole tandem mass spectrometer (Waters Corp.; www.waters.com), and they are reported in units of mass to charge (m/z). High-resolution mass spectrometry (MALDI-TOF) was performed on a Voyager-DE STR Biospectrometry Workstation (Applied Biosystems; www.appliedbiosystems.com). Analytical thin layer chromatography was performed using silica gel plates (product 60F-254; Merck; www.merck.de). Column chromatography was carried out on Merck silica gel 60 and aluminum oxide 60 (70–230 mesh; Merck). UV–vis spectra were measured with a Scinco 2100 spectrophotometer (www.scinco.com), and photoluminescence (PL) spectra were obtained with a Jasco FP-7500 spectrofluorometer (www.jascoinc.com).

All electrochemical experiments were carried out with a potentiostat (model 650A, CH Instruments; www.chinstruments.com). A homemade Ag/Ag⁺ reference electrode

(0.1 M AgNO₃ in acetonitrile with NBu₄PF₆), a platinum wire counter electrode, and a BASi SEC-C platinum gauze working electrode (www.basinc.com) were used. All electrochemical potentials are referred to the Ag/Ag⁺ electrode. Photoluminescence was recorded with an Ocean Optics USB 2000+ spectrometer and an Ocean Optics HL-2000 continuous halogen excitation light source (www.oceanoptics.com). Mass flow controllers (MKS Instruments; www.mksinst.com) were used to prepare the gas mixtures.

Synthesis. Synthesis of *N,N'*-di(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic acid diimide (**1**). The polyaromatic compound, **1**, was synthesized by following the standard condensation method developed by Langhals.²³ Details are reported in the Supporting Information.

Electrochemical Measurements. Cyclic voltammetry (CV) measurements were taken for the individual solutions in order to investigate the electrochemical oxidative and reductive behavior. The solutions were prepared in a drybox incorporating a N₂ atmosphere and then sealed in an airtight cell. A Pt disk working electrode (2 mm diameter) and Pt gauze counter electrode were used for the CV experiments, which were carried out in a DCM solution (0.1 M NBu₄PF₆ was used as a supporting electrolyte). The electrochemical solutions were freshly prepared for each experiment, and the Pt working electrode was polished with 0.05 M alumina (Buehler; www.buehler.com) on a felt pad following sonication in a 1:1 mixed solution of deionized water and absolute ethanol for 5 min. The Pt mesh electrode was treated in piranha solution (3:1 mixture of concentrated H₂SO₄ and 30% H₂O₂) for 3 min, followed by rinsing with deionized water several times (*Caution: piranha solution is an extremely strong oxidant and is potentially explosive, so it should be handled with extreme caution.*) The electrodes were dried with a stream of nitrogen. A separate solution was used for each experiment and then discarded after data had been collected.

Detection of Spectroelectrochemical Fluorescence. A schematic of the setup for studying the effect of oxygen is shown in the Supporting Information. It consists of a spectrometer with a continuous halogen lamp as a light source. There was no need for an excitation filter or emission filter because no scattered light was detectable. All experiments were carried out in a 1 × 1 × 3 cm glass cuvette, and the fluorescence was detected at an angle of 90°. The reference electrode, counter electrode, working electrode, and a hollow needle were immersed into the sample solution such that no excitation light was reflected toward the spectrometer. The hollow needle was connected to a gas mixing system. The gas supply was used to (a) remove oxygen by bubbling the solutions with argon and (b) saturate the solutions with defined quantities of oxygen by bubbling the solutions with appropriate argon–oxygen gas mixtures (0–20% oxygen). The sample volume was 2 mL. The

electrolyte (NBu_4PF_6) was added to obtain a 0.1 M concentration in THF. The gas was first bubbled through a 50 mL round-bottom flask filled with THF to minimize the evaporation rate of THF, and then the whole cell was sealed with Parafilm. A slow but constant flow of argon was passed above the solution at a rate of $50 \text{ mL}\cdot\text{min}^{-1}$.

A static potential of -1.25 V was first applied to the unstirred solution for 30 min in order to complete the electrochemical reduction of **1**. After each reduction, the sample solution was bubbled with argon gas containing various fractions (0–20%) of oxygen at a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$ for 2 s. Oxygen fractions in the range of 0.4–2.4% were adjusted by mixing synthetic air with argon. Fluorescence intensity was recorded at 575 nm in all experiments. The reversibility of the system was studied in the following manner: **1** was first completely electrochemically reduced at -1.25 V . The argon–oxygen mixture was then bubbled through the solution for 2 s. Finally, **1** was electrochemically reduced again by applying the negative potential for 3 min. These steps were repeated several times.

RESULTS AND DISCUSSION

Several derivatives of PTCd were synthesized, including two heptyl, hexylheptyl, or nonyldecyl side chains. Compound **1** was obtained in good yield, in crystalline form with high purity, and was highly soluble in most organic solvents, including THF. This level of solubility or miscibility with polymer blends is critical for further manipulation such as surface immobilization or solidification. The alkyl branches were used to confer solubility on the polyaromatic compound and had no effect on the photophysical and thermodynamic properties, meaning that all of the photochemical characteristics came from the heterocyclic core. The branched structure of long alkyl chains could also be substituted with other derivatives. Polyethylene glycol, for example, could be used in order to render the compound soluble in aqueous solution.

Compound **1** forms a red solution in organic solvents with an intense yellow fluorescence. A typical UV/vis spectrum of **1** is given in Figure 1a, which shows three pronounced peaks between 450–525 nm and a shoulder at around 425 nm. The fluorescence spectrum depicts a similar peak structure mirroring the absorption with the emission maxima at 535 and 575 nm. Since the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the chromophore have nodes at the nitrogen atoms,^{23–25} substitution of the side chain with different moieties does not change the electronic structure of the molecule, and thus, **1** can be used as an optical probe that has the same photophysical properties independent of the side chain used. The extraordinarily high photophysical, thermal, and chemical stabilities of PTCds are additional advantages for optical applications. PTCds are known to have an even higher photostability than that of rhodamine 6G,²⁶ one of the most stable laser dyes currently known. In addition, they are not easily decomposed under chemically and thermally harsh conditions such as contact with concentrated sulfuric acid or temperatures up to $550 \text{ }^\circ\text{C}$.²³ PTCds are also strongly fluorescent, with the quantum yield approaching unity for the majority of derivatives.³

Recently, Shirman et al. reported that the dianion of a PTCd derivative, produced by chemical reduction, exhibited remarkable stability in solution due to efficient charge delocalization through its aromatic system.^{22,27} It even underwent reversible electrochemical reduction in water. In fact, most other organic

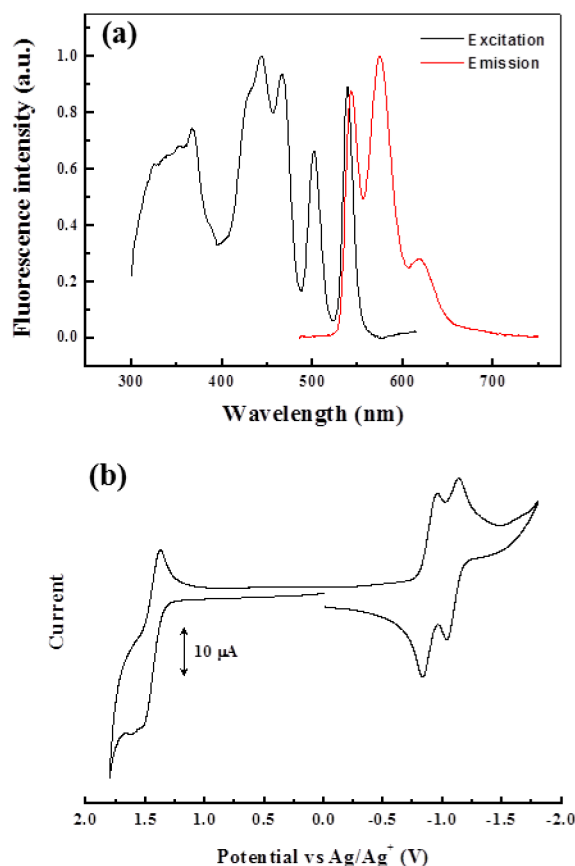


Figure 1. (a) Absorption spectrum (black; left) and emission spectrum (red; right) of **1** in THF solution; (b) cyclic voltammogram of a 2 mM solution of **1** in DCM solution (0.1 M NBu_4PF_6 as the supporting electrolyte) at a scan rate of 0.2 V/s.

compounds with planar aromatic rings are readily decomposed in their redox states, so that it is difficult to obtain stable anion or cation intermediates. In the CV study (Figure 1b), compound **1** underwent (a) partly irreversible oxidation at E_{ox}^0 of 1.44 V (the peak-to-peak-separation, $\Delta E_{\text{pp}} = 0.15 \text{ V}$) and (b) two quasi-reversible reductions (E_{red}^0 at -0.89 and -1.08 V (with $\Delta E_{\text{pp}} = 0.12$ and 0.10 V , respectively), which means that the electron transfer between **1**, 1^- , and 1^{2-} occurs quickly without significant thermodynamic barriers, and all of them are electrochemically quite stable and reversibly transformed to each other at the given scan rate.²²

The absorption bands of **1** also undergo a change upon electrochemical reduction (Figure S2, Supporting Information). A solution of **1** in DCM (or MeCN) turned a deep blue–magenta color from red (Figure S3, Supporting Information) after a static potential of -1.20 V (which is slightly more negative than that of the secondary reduction peak) was applied to the working electrode. Once the color had changed, it did not recover its original color in the N_2 atmosphere because the dianion intermediate is extremely inert. Once the DCM solution of 1^{2-} was exposed to air, however, it rapidly recovered its original color and showed no further change under air exposure even if the negative potential was applied again. A similar tendency was obtained for fluorescence emission.

The THF solution of **1** also loses its fluorescence if reduced by the application of a negative potential of -1.25 V (Figure 2a). However, a reduced form of **1** quickly recovers

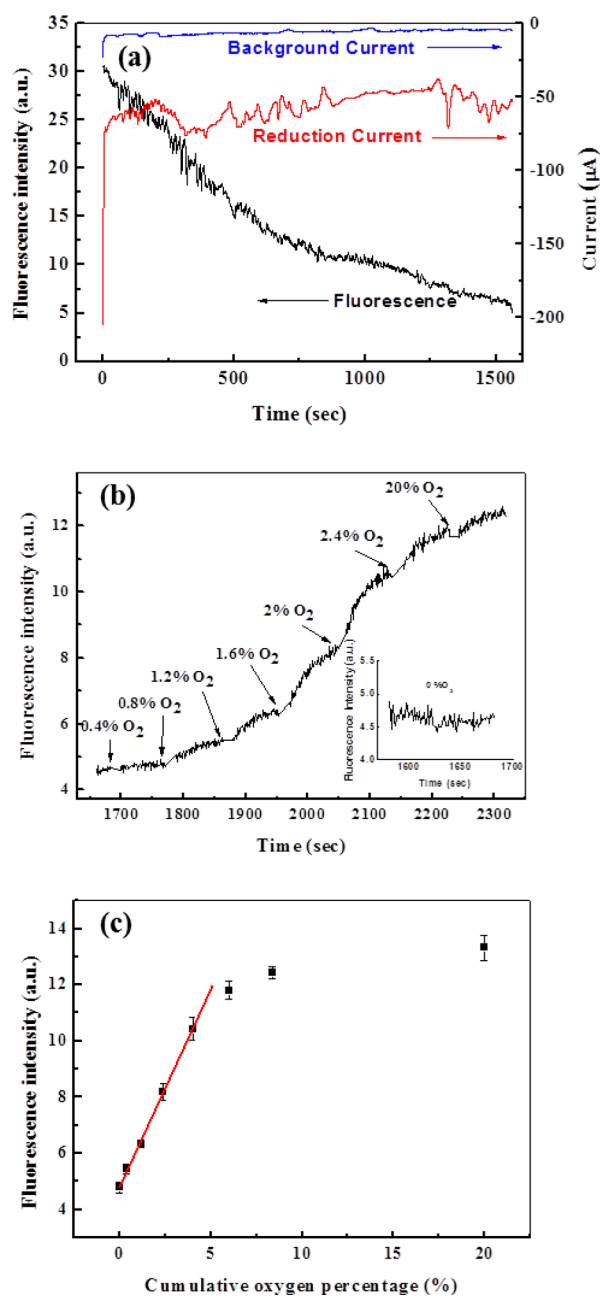


Figure 2. (a) Change in fluorescence at 575 nm while electrochemically reducing **1** (1 mM in THF) and its current profile (dimensions of the electrode: 7×5 mm with 40 wires per centimeter and a diameter of 0.1 mm). (b) Changes in the fluorescence intensity upon the addition of increasing fraction of oxygen in a mixed argon–oxygen gas to 1 mM $\mathbf{1}^{2-}$ in THF. Each arrow marks the time at which bubbling with the respective gas mixture was started (for 2 s); inset: fluorescence intensity for 0% of oxygen added. (c) A plot of the average fluorescence intensity as a function of cumulative oxygen content in the applied gas.

fluorescence after its exposure to air. The dianion form of $\mathbf{1}^{2-}$ is chemically inert and stable but highly energetic to certain chemical species that have a reduction potential of less negative than -1.08 V. Therefore, when $\mathbf{1}^{2-}$ meets the chemical species, it can donate electrons to the counterpart, and thus, it can be subsequently oxidized. Upon air exposure, $\mathbf{1}^{2-}$ undergoes reoxidation to the neutral form via electron transfer with dissolved oxygen ($E_{\text{red}}^0(\text{O}_2/\text{O}_2^{2-}) = -0.82$ V vs SCE). The

dianion form of $\mathbf{1}^{2-}$ can be used to measure O_2 concentration by observation of color or emission changes under electrochemical manipulation.

In order to examine the potential of this probe for use in oxygen sensing, it was fully reduced to $\mathbf{1}^{2-}$ at -1.25 V and then subjected to controlled gas mixtures of argon and oxygen (0–20% of oxygen) using a spectroelectrochemical cell that was built in-house. The fluorescence of **1**, as mentioned above, gradually decreased as the electrochemical reduction took place. In Figure 2a, the changes in emission intensity can be seen to correlate with the profile of the current passing through the solution. When the argon–oxygen gas was gradually added, the fluorescence intensity at 575 nm recovered as shown in Figure 2b due to a redox reaction with the dissolved oxygen. A solution of $\mathbf{1}^{2-}$ in THF is extremely sensitive to oxygen exposure, resulting in an initial rapid increase in fluorescence and almost complete saturation at an oxygen fraction of 2.4%. A plot of the average fluorescence intensity as a function of cumulative oxygen percentage in the applied gas is displayed in Figure 2c. The limit of detection (three times the standard deviation of the baseline) is estimated to be 0.4% of oxygen in the mixed gas (signal/noise ratio = 3, $n = 5$), and the response to oxygen shows a linear correlation in the range from 0.0 to 4.0% of cumulated oxygen at ambient barometric pressure when the concentration of **1** is constant at 1 mM ($R^2 = 0.998$, $y = 1.41x + 4.79$).

In order to generate $\mathbf{1}^{2-}$ dianion in THF, we applied -1.25 V to the probe **1**. This potential value is, however, slightly beyond the secondary reduction peak ($E_{\text{red}}^0 = -1.08$ V) and is not sufficiently negative to complete the direct 2-electron reduction of **1**. The anion intermediate of $\mathbf{1}^-$ can be presumably produced during the electrolysis too. Interestingly, this reduction intermediate, $\mathbf{1}^-$, can readily undergo disproportionation reaction itself producing $\mathbf{1}^{2-}$ and **1** spontaneously ($2 \mathbf{1}^- \rightarrow \mathbf{1}^{2-} + \mathbf{1}$). The overall potential of the proportionation can be calculated as $\Delta E^0 = E^0(\mathbf{1}^-/\mathbf{1}^{2-}) - E^0(\mathbf{1}/\mathbf{1}^-) = -0.19 - (-0.89) = 0.70$, which is highly exothermic. Therefore, it is likely that the regeneration of **1** can cause the entire reduction process to be incomplete. In Figure 2a, a considerable amount of reduction current ($\sim 20\%$ of its initial value) is still observed even after a 30 min electrolysis of 2 mL sample while almost no fluorescence was detected at the same time. It seems that $\sim 20\%$ of molecules have been reoxidized even after the reduction process completed. We assume this observation is partly due to the disproportionation reaction of $\mathbf{1}^-$ which results in **1** and $\mathbf{1}^{2-}$ after the reduction process. Although a significant amount of **1** would be continuously regenerated, the fluorescence intensity gradually decreased and finally diminished after a 30 min electrolysis because of inner filter effect; in our experiment, we employed 1 mM of probe **1** in THF which is excessive enough to cause self-absorption. In Figure 3a, the presence of an inner filter effect clearly appeared where the high energy emission peak is severely attenuated and the emission in the presence of the $\mathbf{1}^{2-}$ bears little resemblance to the emission in its absence.

Therefore, the electrochemical reduction of **1** produces the mixture of $\mathbf{1}^{2-}$ and $\mathbf{1}^-$, and the former is eventually degraded to $\mathbf{1}^{2-}$ and **1**.



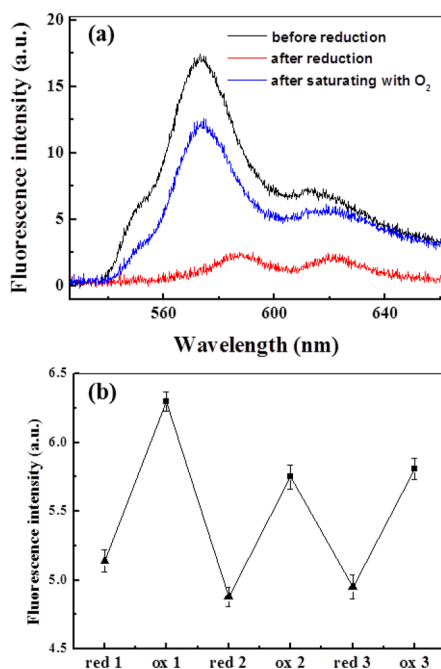


Figure 3. (a) Change in fluorescence of 1 mM **1** in THF before and after reduction and after bubbling with oxygen, and (b) decrease in the intensity of the fluorescence of **1** after each oxidation and reduction.

The oxygen sensing phenomenon is mainly caused by the reversible electron transfer between energetic I^{2-} and O_2 molecule.

Fluorescence is almost completely recovered on exposure to oxygen. As shown in Figure 3a, two major peaks (located at 625 and 575 nm) appear in the emission spectra, and their ratio (referred to as I_{625}/I_{575}) correlates with the redox state of **1**. The value of I_{625}/I_{575} was measured as 0.37 before the electrochemical reduction, 1.69 after the reduction, and 0.43 after treatment with oxygen. This finding additionally suggests that ratiometric sensing for oxygen could also be possible.

The fluorescence intensity at 575 nm was repeatedly monitored during the several successive applications of electrochemical reduction and oxygen exposure and recorded along with the reduction current (Figure 3b). This demonstrates that reoxidation on oxygen exposure did not lead to full recovery but underwent a 26% decrease after the first turnover. However, there was only a 2% further decrease after the second turnover, and the signal became fairly stable after four cycles.

CONCLUSION

In conclusion, we report on a proof-of-principle for a fluorescence “turn-on” method for the detection and quantitation of dissolved oxygen. It has the potential of forming an alternative to the classical sensing schemes based on the use of a Clark electrode or on quenchemetric methods. Its merits include a simple optoelectronic system and easily accessible and very stable reagents that display uncommon photochemical and electrochemical properties. Further studies are needed to modify the scheme so that it works in a solid-state matrix and to demonstrate its practical applicability for oxygen sensing.

ASSOCIATED CONTENT

Supporting Information

Synthesis of *N,N'*-di(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic acid diimide. Scheme of the setup for the detection of the spectroelectrochemical fluorescence. 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 interest.

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