

Supporting information

A ratiometric luminescent oxygen sensor based on a chemically functionalized quantum dot

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1. Materials and Methods

Chemicals. Cadmium oxide (CdO, 99.99%), 1-hexadecylamine (98%, HDA), trioctylphosphine oxide (TOPO, 99%), 1-n-octadecene (ODE, tech. 90%), dioctylamine (98%) and oleic acid (OA, tech. 90%) were purchased from Aldrich; elemental selenium (99.999%, 200 mesh), stearic acid (SA, 99%), elemental sulphur (325 mesh, 99.5%), Zinc oxide (ZnO, 99.999%) and tributylphosphine (97%) were from Alfa Aesar. Chloroform, methanol and hexane of HPLC grade were purchased from Aldrich., 1-n-octadecene (ODE, tech. 90%) were purchased from Aldrich. Imidazole was purchased from Lancaster and other organic reactants were purchased from Aldrich and used as received. Acetonitrile and dichloromethane were distilled from calcium hydride just before use.

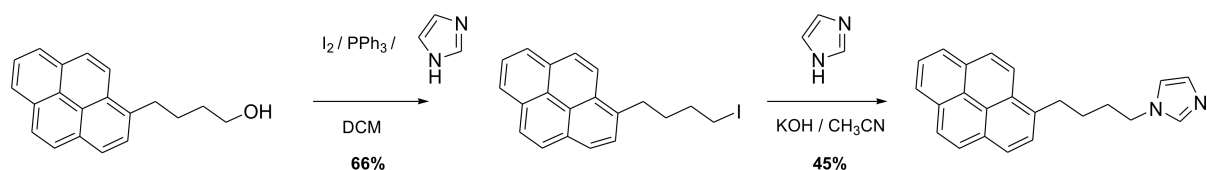
Synthesis of CdSe NCs. The synthesis of plain CdSe core NCs has been achieved accordingly with established procedures^{1,2} with slight modifications. Briefly, 0.20 mmol of CdO and 0.80 mmol of stearic acid were heated at 170 °C in a three-neck flask under stirring and argon flow till the reaction was completed (the solution turns from reddish to clear). After cooling the mixture at room temperature, 0.5 g of TOPO, 1.5 g of HDA and 2.0 g of ODE were added into the flask. The mixture was heated up again to 250 °C. At this temperature it was swiftly injected a Se stock solution (2.0 mmol Se, 0.65 g of TBP and 1.5 g of dioctylamine). The temperature was set at 220 °C immediately after the injection where the nanocrystal growth occurred. After cooling to room temperature the NC were purified by 3 extraction cycles with a 1:1 methanol/hexane mixture.

Synthesis of CdSe/ZnS NCs. The shell synthesis was performed following an established SILAR procedure.³ Typically, 4×10^{-5} mmol of CdSe ($d=5.8$ nm, determined by the excitonic peak position⁴) dispersed in hexane, 1.0 g of oleic acid and 5.0 g of ODE were loaded in a three necked flask. The mixture was initially placed under vacuum for the removal of hexane, oxygen and water from the core solution. At 70 °C argon was inserted into the reaction vessel and the temperature was gradually raised at 230 °C where calculated amounts of 0.04 M Zn (ZnO:OA 1:8 in ODE) and S (S:OA 1:8 in ODE) stock solutions were alternatively inserted into the flask. Each half layer was left to grow for 20 minutes. Three full layers of ZnS were deposited on top of the core NCs. The shell thickness for a full monolayer of ZnS was assumed to be 0.35 nm, so the NC diameter increased of 2.1 nm after the deposition of the three monolayers with a final total size of 7.9 nm.

Synthesis of PYI ligand.

Synthesis was carried out according to the scheme below.

¹H and ¹³C-NMR experiments were performed at 295 K on a Brüker Avance DPX 300 or a Brüker AC-D50 spectrometer. Chemical shifts are reported in ppm (δ) and are referenced to the NMR solvent residual peaks. Abbreviations used are s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were performed by the CESAMO on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is required with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 4500 V and operated at room temperature. Samples were introduced by injection through a 10 μ L sample loop into a 200 μ L/min flow of methanol from the LC pump.



Synthesis of 1-(4-iodobutyl)pyrene (adapted from ref [5]). Iodine (0.254 g, 1 mmol) was added to a solution of PPh₃ (0.262 g, 1 mmol) and imidazole (0.068 g, 1 mmol) in 10 mL of dichloromethane at 0°C. After 20 minutes of stirring, 1-pyrenebutanol (0.2 g, 0.73 mmol) dissolved in dichloromethane (3 mL) was added. The resulting solution is stirred for 3 h at room temperature, diluted with water, washed successively with 1N aqueous Na₂S₂O₃ solution and brine, and then dried with MgSO₄. The solvent was removed in vacuo, and the crude material was subjected to column chromatography on silica gel, eluting with pentane / ethyl acetate (8:2; v/v) to give 0.186 g of 1-(4-iodobutyl)pyrene (yield = 66%).

¹H NMR (CDCl₃, 300 MHz) δ = 8.28 (d, J = 9.3 Hz, 1H), 8.18 (d, J = 7.5 Hz, 2H), 8.16 (d, J = 7.8 Hz, 2H), 8.04 (s, 2H), 8.00 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 3.37 (t, J = 7.2 Hz, 2H), 3.26 (t, J = 6.6 Hz, 2H), 2.00 (m, 4H).

¹³C NMR (CDCl₃, 75 MHz) δ = 136.3, 131.7, 131.2, 130.2, 128.9, 127.8, 127.6, 127.5, 127.0, 126.1, 125.4, 125.3, 125.2, 125.1, 125.0, 123.5, 33.6, 32.8, 32.7, 6.9.

MS (HR-ESI) m/z calcd for (M-Ag⁺) C₂₀H₁₇AgI: 490.9420; found: 490.9401.

Synthesis of 1-(4-(pyren-1-yl)butyl)imidazole. Potassium hydroxide (0.056 g, 1 mmol) and 1-(4-iodobutyl)pyrene (0.186 g, 0.48 mmol) were added to a solution of imidazole (0.033 g, 0.48 mmol) in 10 mL of acetonitrile. The resulting solution was refluxed for 4 h. After cooling to room temperature, the solvent was removed in vacuo. The crude material was purified via column chromatography on silica gel, eluting with ethyl acetate / methanol (96:4; v/v) to give 70 mg of the final product (yield = 45%).

¹H NMR (CDCl₃, 300 MHz): δ = 8.8-8.2 (m, 3H), 8.08 (d, J = 8.5 Hz, 2H), 8.01 (s, 2H), 7.98 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.4 Hz, 1H), 7.41 (s, 1H), 7.05 (s, 1H), 6.83 (s, 1H), 3.84 (t, J = 6.7 Hz, 2H), 3.29 (t, J = 6.9 Hz, 2H), 1.82 (m, 4H).

¹³C NMR (CDCl₃, 75 MHz): δ = 137.1, 135.8, 131.50, 130.9, 130.0, 129.5, 128.6, 127.6, 127.5, 127.3, 126.9, 126.0, 125.2, 125.1, 125.1, 124.9, 123.1, 118.8, 46.9, 32.9, 31.0, 28.6.

MS (HR-ESI) m/z calcd for (M-H⁺): C₂₃H₂₁N₂, 325.1699; found: 325.1702.

Synthesis of PYI-coated NCs. Typically, 5 mL of a 12.2 μ M solution of TOPO-coated NCs in chloroform were mixed with 5 mL of 5.6 mM solution of PYI in MeCN. This mixture was first let (under stirring and bubbling argon continuously) at about 65 °C for 24 hours, and then under stirring at room temperature for an additional two days. The flask was filled with argon and refilled from time to time. The final product was precipitated with methanol in order to remove the unreacted (or partially reacted) quantum dots. The solution was placed under rotary evaporator. Moreover, because of the difference in solubility it was possible to wash the product with MeCN in order to get rid of the free PYI ligand. The powder was washed three times with acetonitrile in order to remove unreacted ligand molecules. During the last washing the solution was gently heated at about 40 °C. The solutions discarded were spectrophotometrically checked and while the first shows strong absorption/emission features arising from the pyrene moieties, the latter two were almost optically inactive, consistent with a successfully purification procedure.

Photophysical measurements. Absorption spectra were recorded with a Perkin Elmer Lambda 45 spectrophotometer in air equilibrated solutions. Luminescence spectra were recorded with a Perkin-Elmer LS50B spectrofluorimeter equipped with a Hamamatsu R928 phototube. Photoluminescence quantum yields were determined with the optically dilute method using cresyl violet (ϕ_F =0.54, air-equilibrated) in methanol as standard.⁶ Luminescence lifetimes were determined with an Edinburgh Instruments FLS920 spectrofluorimeter, exciting the sample at 280 nm (PYI) and 405 nm (NCS) with a diode and a laser, respectively.

The experimental errors are ± 1 nm for the wavelengths and $\pm 10\%$ for the luminescence intensities, quantum yields and lifetimes.

Experiments at different oxygen pressures have been carried out by saturating the QD-PYI solution in CHCl_3 with argon (research grade, >99.9997%) and oxygen (technical grade, >99.0%).

TEM experiments. A Philips CM 100 transmission electron microscope operating at 80 kV was used. For TEM investigations a 400 mesh copper coated with formvar support grid was dried up under vacuum after deposition of a drop of nanoparticles solution diluted with hexane.

2. Morphology of CdSe and CdSe/ZnS NCs

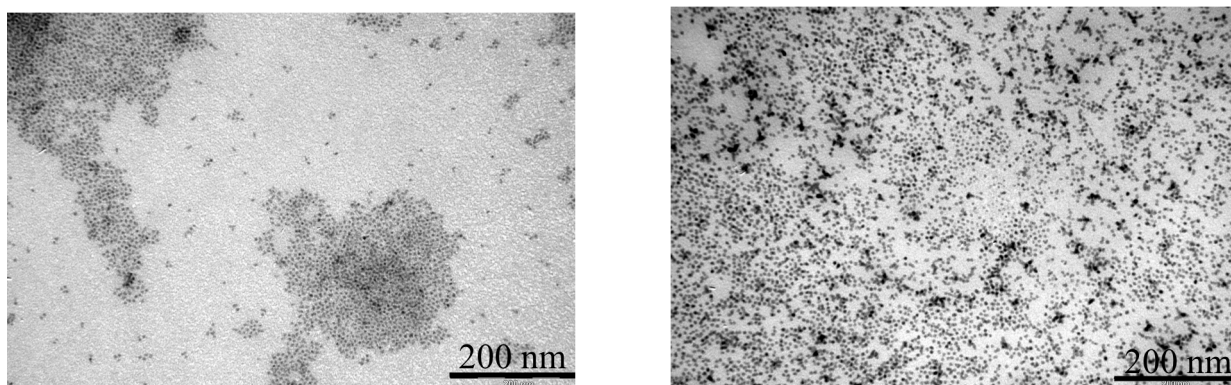


Figure S1. TEM pictures of CdSe NCs (left) and CdSe/ZnS NCs (right).

3. Absorption spectrum of the nanoconjugate NCs

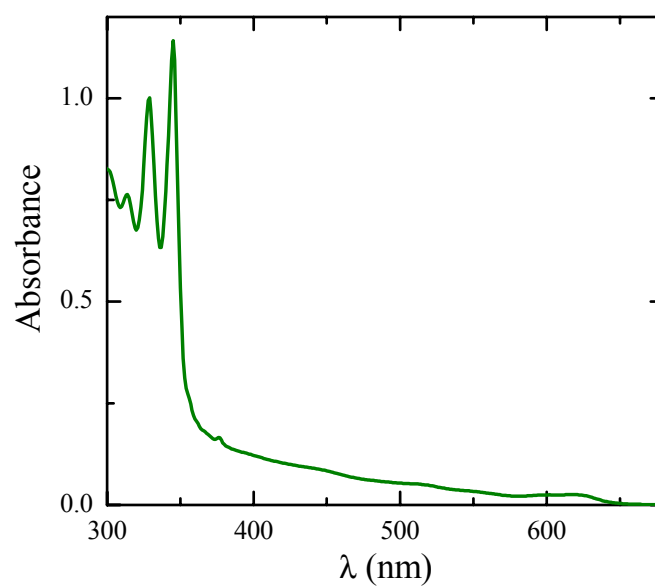


Figure S2. Absorption spectrum of PYI coated CdSe/ZnS quantum dots in CHCl_3 at RT.

4. Decay-times of the nanoconjugates at different O₂ pressures

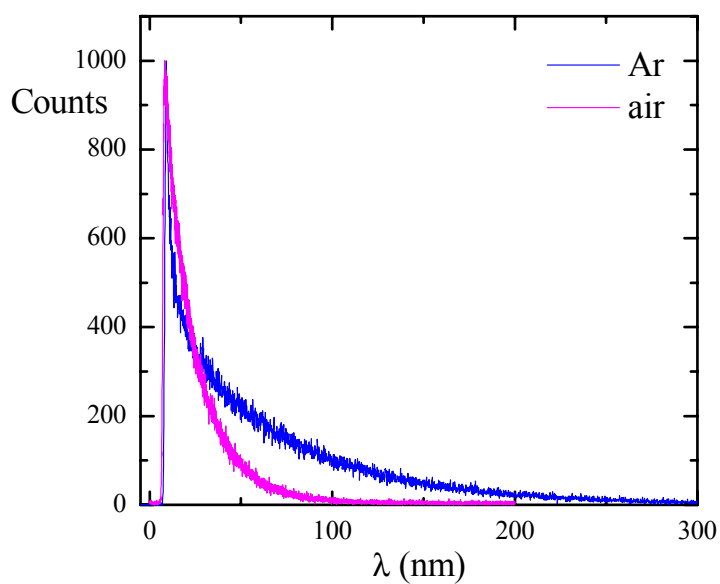


Figure S3. Decay-times of PYI in the nanoconjugate at different oxygen pressures. Experimental conditions: $\lambda_{\text{exc}}=280$ nm; $\lambda_{\text{em}}=400$ nm (CUTOFF=305 nm); chloroform at RT.

Table S1. Decay-time values of PYI at different oxygen pressures.

p_{O_2} (bar)	τ_1 (ns)	τ_2 (ns)	τ_{avg} (ns)
0	63.7 (95%)	3.6 (5%)	60.4
0.213	18.6 (94%)	6.2 (6%)	17.8

5. Stern-Volmer plots

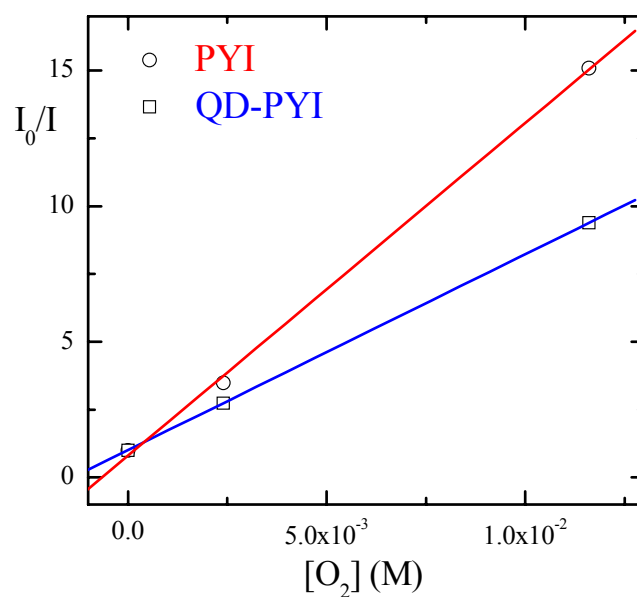


Figure S4. Stern Volmer plots of pyrene moieties in PYI and in QD-PYI nanoconjugates in $CHCl_3$ at RT.

Table S2. Quenching constant by O_2 of PYI and QD PYI.

Compound	$K_{SV} (M^{-1})$	$\tau_0 (ns)$	$kq (M^{-1} s^{-1})$
PYI	1230	73.1 ^a	1.7×10^{10}
QD-PYI	720	63.7 ^b	1.1×10^{10}

a Monoexponential

b Dominant component of a biexponential decay (see Table S1).

6. Evaluation of pyrene molecules per quantum dot

From the absorption spectrum of the bare QD-TOPO, we determined the ratio R between the absorbance at the excitonic peak (623 nm) and that at the wavelength of the pyrene absorption maximum (345 nm), $R = A_{623}/A_{345}$. We then evaluated the concentration of the QD-PYI nanocrystals in solution from the absorption spectrum, using the equation reported in ref. 4 to determine the molar absorption coefficient of the excitonic peak (e.g. [QD-PYI] = 4.4×10^{-8} M in Fig. S2). The QD contribution to the total QD-PYI absorbance at the wavelength of the PYI absorption maximum (345 nm) was calculated using the above discussed ratio (R): $A_{345(\text{QD})} = A_{623}/R$. The PYI contribution to the total QD-PYI absorbance was evaluated by subtracting the QD contribution to the overall QD-PYI absorbance: $A_{345(\text{PYI})} = A_{345} - A_{345(\text{QD})}$. The total concentration of PYI in solution is, thus, calculated (e.g. [PYI] = 2.4×10^{-6} M in Fig. S2). The ratio between the PYI and QD-PYI concentrations yields the average number of PYI ligands per QD; in our case the calculation shows that there are approximately 55 pyrene molecules per quantum dot.

It should be noted that these calculations assume that the absorption spectrum of QD-PYI is a linear combination of the absorption spectra of TOPO-QD and PYI, i.e., that the spectra are additive. Such an assumption, which corresponds to say that the ground-state interactions between the inorganic nanocrystal and the surface-attached pyrene moieties are negligible, seems reasonable because the QD and PYI absorption bands in the nanohybrid (Fig. S3) occur at very similar wavelengths compared to the separated components (Fig. 2 in the main text).

References

- 1) Z.A. Peng, X. Peng, *J. Am. Chem. Soc.* **2002**, *124*, 3343-3353.
- 2) C. R. Bullen, P. Mulvaney, *Nano Lett.* **2004**, *4*, 2303-2307.
- 3) J. J. Li, Y. A. Wang, W. Z. Guo, J. K. Keay, T. D. Mishima, M. B. Johnson, X. Peng, *J. Am. Chem. Soc.* **2003**, *125*, 12567-12575.
- 4) W. W. Yu, L. Qu, W. Guo, X. Peng, *Chem. Mater.* **2003**, *15*, 2854-2860.
- 5) D. Stien, S. Gastaldi, *J. Org. Chem.* **2004**, *69*, 4464-4470.
- 6) M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi, *Handbook of photochemistry* (third ed.), CRC Press, Boca Raton, **2006**.