

Supporting Information

**Room-Temperature-Phosphorescence-Based Dissolved Oxygen
Detection by Core-Shell Polymer Nanoparticles Containing Metal-Free
Organic Phosphors**

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Supporting Information

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Scheme 1

Figure S1.

Figure S2.

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Experimental Procedures

1. Methods

1.1. Chemicals

Styrene (Aldrich, >99 %) and methyl methacrylate (Aldrich, >99%) were passed through a neutral alumina column, dried over calcium hydride (CaH₂), distilled under reduced pressure, and degassed by three freeze-pump-thaw cycles. 2,2'-azoisobutyronitrile (AIBN, Junsei, 96%) was recrystallized twice from methanol. 2-methyl-2-oxazoline (MeOx, TCI, >98.0 %), acetonitrile (AcN, Aldrich, >99%), *N,N*-dimethylformamide (DMF, Aldrich, 98.0%) were dried over CaH₂, distilled under reduced pressure, and degassed by three freeze-pump-thaw cycles. Other reagents were used as received without further purification. 4-bromo-2,5-bis(hexyloxy)benzaldehyde (Br6A) and 2-cyano-5-hydroxypentan-2-yl dodecyl carbonotrithioate (CDP) were synthesized as described elsewhere.^[1,2] C1 was synthesized according to the procedures shown in Scheme S1.

1.2. Synthetic details

The progress of reaction was checked on TLC plates (Merck 5554 Kiesel gel 60 F254), and the spots were visualized under 254 nm (and/or 365 nm) UV light and/or charring after dipping the TLC plate into vanillin solution (9.0 g of vanillin and 1.5 mL of concentrated sulfuric acid in 300 mL of MeOH) or KMnO₄ solution (3 g of KMnO₄, 20 g of K₂CO₃, and 5 mL of 5% NaOH solution in 300 mL of water). Column chromatography was performed on silica gel (Merck 9385 Kiesel gel 60). Unless otherwise specified, all reactions were conducted under a slight positive pressure of dry nitrogen. The usual work-up refers to washing the quenched reaction mixture with brine, drying the combined organic extracts over anhydrous MgSO₄ and evaporating under reduced pressure using a rotary evaporator.

1.3. Preparation of Br6A-doped and C1-crosslinked PMMA for photophysical measurements at RT

Preparation of Br6A-doped PMMA: 1 wt% phosphor doped PMMA was dissolved in CHCl₃. The mixed solutions were drop-cast on a pre-cleaned glass substrate and kept at RT for 10 mins. The resulting drop-cast films were thermally annealed at 120 °C for 20 mins and kept in a vacuum chamber for 30 minutes to completely remove residual solvents and oxygen. The resulting polymer films were packaged by attaching a glass lid to the polymer films using an epoxy seal (EPOXY TECHNOLOGY 305) around the perimeter and kept at RT for 24 hrs. All processes from drop-casting to packaging were done in a nitrogen filled glove box.

Preparation of C1-crosslinked PMMA films:

The preparation of phosphor C1-crosslinked PMMA was carried out as follows: 0.045g of C1 and 0.045g of AIBN were dissolved in 5ml of anisole and 0.5 ml of MMA mixture. The reaction mixture was purged with nitrogen for 30 min, and then stirred at 70°C for 24h. After the polymerization, the resulting product was diluted with THF and precipitated in excess of methanol. The polymer was dried in a vacuum oven at 50°C for 24h.

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1.4. Characterization of synthesized molecules, polymers, and polymeric nanoparticles

Newly synthesized small molecules were characterized by ¹H-NMR, ¹³C-NMR, and mass spectrometry. ¹H-NMR spectrum was recorded on a Varian, MR 400 (400 MHz) in CDCl₃ or DMSO-d₆ solution. ¹³C-NMR spectrum was recorded on a Varian, MR400 (400 MHz) in CDCl₃ solution. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard, and coupling constants in Hertz. Mass spectra were recorded on an Agilent Q-TOF 6520 system using electrospray ionization in positive ion detection (ESI+) mode. Significant fragments are reported in the following fashion: *m/z* (relative intensity).

The molecular weights (MWs) and MW distribution of polymers synthesized were determined by gel permeation chromatography (GPC, Water 1515, Isocratic HPLC pump) coupled with a refractive index (RI) detector (Waters 2414, RI detector) and three columns (Styragel HR 2, Styragel HR 3, Styragel HR 4, Waters). Chloroform was used as the eluent at 25°C at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibration. The polymer composition was determined using a ¹H-NMR spectrometer (Varian, MR 400 (400 MHz)) with CDCl₃ or DMSO-d₆ as the solvent.

The size and shape of core-shell NPs were observed using scanning electron microscopy (SEM, FEI Helios 650 Nanolab SEM/FIB) after applying a Pt coating. The number-average diameter (D_n) of the core-shell NPs, the coefficient of variation (CV) of particle diameter and particle size distribution (PSD) were calculated after measuring core-shell NPs from SEM images. Dynamic light scattering analysis (DLS) was also additionally conducted for the 320nm NPs to double check the size and size distribution. To determine the hydrodynamic size (diameter, nm) and polydispersity index (PDI) of the core-shell NPs, samples were suspended in

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water and measured from three repeated experiments by DLS (Malvern Zetasizer Nano ZSP, Model number: ZEN5600) in disposable cuvettes (ZEN0040). All measurements were conducted at a backscattering angle of 173° (NIBS default) at 25 °C.

1.5. Measurements of photophysical properties of solutions and films

UV-visible absorption spectra were measured on a Varian Cary50 UV/Vis spectrophotometer. Photoluminescence and absolute phosphorescence quantum yield (Φ_P) were obtained using a Photon Technologies International (PTI) QuantaMaster spectrofluorometer equipped with an integrating sphere. Absorption and emission inside the sphere were determined by comparison to a blank sample (glass only). A neutral density filter was used to allow for maximization of the emission signal without saturating the photomultiplier tube detector with excitation light. Each sample type was run in quadruplicate with each quantum yield measurement coming from a freshly prepared sample that was sealed with epoxy resin under nitrogen atmosphere (detailed procedures for thin film preparation and sealing are described above). Measurements proved highly repeatable, and errors are given as ± 1 standard deviation.

1.6. Preparation of the planar optode

60 mg of the green-emitting 320nm NPs and 60 mg of polyurethane hydrogel D4 (HydroMed™, AdvanSource Biomaterials) were dispersed/dissolved in a mixture of 550 mg of EtOH and 100 mg of water. The “cocktail” was blade-coated onto a transparent poly(ethelene terephthalate) support Melinex 505 (Pütz, Germany) and the solvents were let to evaporate under ambient conditions. Photographic images of the sensor foil were obtained with a Canon 5D digital camera under illumination of the foil with 365 nm line of a laboratory UV lamp.

1.7. Measurements of oxygen sensing properties

The steady state and time resolved phosphorescence spectra were acquired on Fluorolog 3 spectrometer from Horiba. For the steady state spectra Xenon lamp was used for the excitation whereas SpectraLED ($\lambda = 390 \pm 10$ nm) from Horiba was used to acquire the time-resolved spectrum (delay 2 ms). Oxygen dependency of the decay time for the phosphor NPs was measured using a two-phase lock-in amplifier (SR830, Stanford Research Inc., USA) equipped with a photomultiplier tube (H5701-02, Hamamatsu, Japan). The excitation was performed with the light of a 375-nm LED (Roithner Lasertechnik, Austria) filtered through a BG-12 filter from Schott (Germany). The excitation light was sinusoidally modulated at a modulation frequency of 49 Hz. A bifurcated fiber bundle was used to guide the excitation light to the sensor material and the emission light back to the detector. The emission was filtered using a combination of a glass OG-530 filter (Schott) and medium yellow plastic filter from Lee filters. Average decay times τ were calculated as $\tau = \tan(\phi)/2\pi f$, where ϕ is the luminescence phase shift and f is the modulation frequency.

To access the oxygen sensitivity, the aqueous dispersion of the particles was placed in screw-capped quartz precision cuvettes from Hellma Analytics and the respective gas mixtures were bubbled through the cuvette for 10 min. Calibration mixtures were produced by mixing nitrogen (5.0, Linde Gas, Austria) and compressed air or nitrogen and test gas (2% O₂ in nitrogen, Linde Gas) using a computer-controlled gas mixing device (Red-y smart series, Vögtlin Instruments). Generally, the response of optical oxygen sensors is determined by the oxygen partial pressure and not the concentration, therefore partial pressure scale is preferable and used. The pO₂ values in the gas phase are determined by the setting of the gas mixing device and the gases used but also by the total pressure during the experiment which was measured independently. For measurements in water the additional correction considering the water partial pressure at a given temperature is required.

Temperature was adjusted with a Cary SPV-1X0 Single Cell Peltier Accessory Peltier element from Varian in combination with a refrigerated/heating circulator (ThermoHaake DC50, Thermo Fisher Scientific Inc).

2. Synthesis

2.1. Synthesis of tosyl-functionalized RAFT agent (4-cyano-4-(dodecylthiocarbonothioylthio)pentyl-4-methylbenzenesulfonate (CDPS))

CDP (3g, 7.69 mmol) was dissolved in 30 mL of anhydrous MC and cooled in an ice bath. *p*-Toluenesulfonyl chloride (2.2 g, 11.5 mmol) in 20 mL of dichloromethane (anhydrous, Aldrich, >99.8%) was added dropwise to this solution. Pyridine (0.9 mL, 11.5 mmol) was then added to the solution and stirred for 24 h. Subsequently, the reaction mixture was washed 3 times with water and brine. The organic phase was dried over MgSO₄. The solvent was then removed under reduced pressure and the crude product (viscous orange color oil) was purified by column chromatography using hexane/ethyl acetate (9:1 v/v) to afford an orange-colored viscous oil. (yield = 65.4%). ¹H NMR (CDCl₃) δ = 7.73 (d, 2H), 7.32 (d, 2H), 4.02 (t, 2H), 3.38 (t, 2H), 2.44 (t, 3H), 1.98-2.32 (m, 2H), 1.89 (s, 3H), 1.68 (m, 2H), 1.28 (br, 18H), 0.89 (t, 3H).

2.2. Synthesis and characterization of phosphor cross-linkers (Scheme S1)

4-bromo-2,5-bis(2-hydroxyethoxy)benzaldehyde: 4-bromo-2,5-dihydroxybenzaldehyde (0.4g, 1.8mmol), ^[3] K₂CO₃ (0.76g, 5.5mmol) and small amount of potassium iodine were dissolved in 10ml of DMF. And 2-bromoethanol (0.39 ml, 5.5mmol) was added slowly and stirred at 80 °C overnight. The reaction mixture was then cooled and filtered. The product is purified by silica column

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chromatography with EA:hexanes (3:7)(Yield=77.5%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ = 10.17 (s, 1H), 7.22 (s, 1H), 7.13 (s, 1H), 4.32(t, 4H), 3.78 (t, 4H).

((2-bromo-5-formyl-1,4-phenylene)bis(oxy))bis(ethane-2,1-diyl) bis(2-methylacrylate) (C1): 4-bromo-2,5-bis(2-hydroxyethoxy)benzaldehyde (0.25g, 0.8mmol) and triethylamine (0.38ml, 2.7mmol) were dissolved in 20ml of anhydrous tetrahydrofuran and flask was placed into an ice bath. Methacryloyl chloride was slowly added into the reaction flask and stirred for 24 hours at ambient temperature. After desired time, a salt was removed by filtration and organic solution was concentrated to provide the crude product. The crude product was diluted with ethyl acetate, washed with saturated aqueous NaHCO_3 and brine, and dried with MgSO_4 . Organic layer was concentrated and purified by recrystallization from methanol (Yield=81.5%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ = 10.24 (s, 1H), 7.24 (s, 1H), 7.13 (s, 1H), 6.13 (s, 2H), 5.67 (s, 2H), 4.62 (t, 4H), 4.51 (t, 4H), 1.93 (s, 6H).

2.3. Synthesis of poly(2-methyl-2-oxazoline)(PMeOx) with CDPS

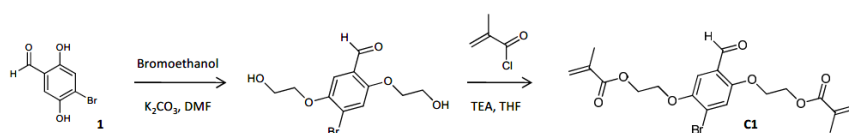
The synthesis of PMeOx was performed at a feed ratio of $[\text{MeOx}]_0/[\text{CDPS}]_0 = 100/1$ at 80 °C. MeOx (3 mL, 35.3 mmol) and CDPS (0.1891 g, 0.353 mmol) were dissolved in 3 mL of DMF and stirred at 80 °C for 24h. The polymerization reaction was quenched by small portion of water and the mixture was precipitated with diethylether, and dried under vacuum at 60 °C. The conversion of polymerization was determined by gravimetric analysis. The molecular weight and PDI were measured by gel permeation chromatography.

2.4. Synthesis of PMeOx-*b*-PAAm for macro-initiator

The polymerization of PMeOx-*b*-PAAm was conducted at the feed ratio of $[\text{AAM}]_0/[\text{PMeOx}]_0/[\text{AIBN}]_0 = 20/1/0.2$. AAM (0.2 mL, 2.9 mmol), and PMeOx (0.540 g, 0.15 mmol) were dissolved in 0.7 mL of DMF and stirred at 60 °C for 24h. The reaction mixture was then precipitated with diethylether and dried under vacuum at 60°C. The composition of block copolymer was determined by $^1\text{H NMR}$ ($\text{DMSO}-d_6$, ppm) δ = 3.07~3.55 (b, 4H, methylene of PMeOx), 1.86~1.95 (b, 2H, methyl of PMeOx), 1.98~2.27 (b, H, methine of PAAm), 1.28~1.72 (b, 2H, methylene of PAAm).

2.5. Dispersion polymerization of PS NPs with phosphor cross-linker

The dispersion polymerization of PS NPs with PMeOx-*b*-PAAm block copolymer as a macro-initiator was performed as follows: 0.091g of PMeOx-*b*-PAAm (20 wt% of monomer) was dissolved in 5ml of water/EtOH (4:1 by volume ratio). The 0.045g of phosphor cross-linker (C1) and 0.9mg of AIBN were dissolved in 0.5 ml of styrene and transferred into PMeOx-*b*-PAAm solution. The reaction mixture was purged with nitrogen for 30 min, and then stirred at 200 rpm at 70°C for 24h. After the polymerization, the product was diluted with methanol and purified by centrifugation 3 times to remove the residual PMeOx-*b*-PAAm block copolymer and unreacted styrene. The product was dried in a vacuum oven. The particle size was determined by SEM and the average particle size was calculated. Well-defined 320 nm NPs were obtained from this ~ 10 wt% macro-initiator receipt. When twice larger amount (20 wt%) of macroinitiator was used 180 nm NPs were obtained (Figure S1).



Scheme S1. The synthetic route of C1. Detailed synthetic procedures and characterizations are described in the section 2.2.

2.6. Photostability of optical sensor system

Photostability is an important property of an optical sensor. Oxidation of the chromophore with photosynthesized singlet oxygen is one of the potential mechanisms of photodegradation. To investigate the limits and byproduct formation through photooxidation, the optode continuously irradiated by a light of 375 nm LED light source, measuring the luminescence intensity and phase shift (see Figure S5). Under these harsh conditions, a significant decrease of the luminescence intensity is observed, and the photobleaching rate appears to decrease in time. Evidently, the chromophore is completely photooxidized; however, without formation of other luminescent species since the luminescence phase shift remains almost constant (see Figure S5). Importantly, photobleaching slowed down considerably when the light dose was reduced (by 15-fold). In fact, the luminescence intensity decreases by only a few per cent after 100 min of measurement and the luminescence phase shift is not affected at all. It should be stressed at this point here that acquisition times of 20-50 ms are fully sufficient for the sensor read-out, thus the lifetime of the sensor can be further greatly extended (20-50 fold). Noteworthy, photooxidation can be safely excluded for most practical applications, particularly if lifetime read-out is used.

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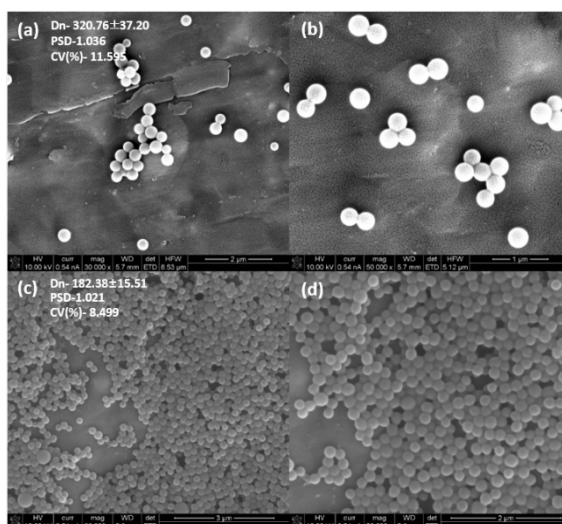


Figure S1. SEM images of C1 cross-linked core-shell PS NPs with 10 (a,b) and 20 wt% (c,d) of PMeOx-*b*-PAAm block copolymer as a macroinitiator.

Results

	Size (d.nm):	% Intensity:	St Dev (d.nm):
Z-Average (d.nm): 330.4	Peak 1: 347.5	100.0	95.50
Pdi: 0.148	Peak 2: 0.000	0.0	0.000
Intercept: 0.927	Peak 3: 0.000	0.0	0.000
Result quality: Good			

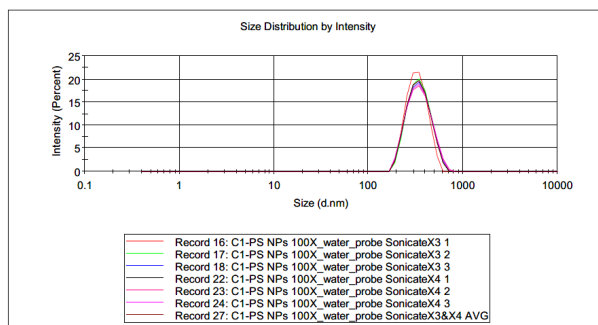


Figure S2. DLS result of 320 nm C1 cross-linked core-shell NPs

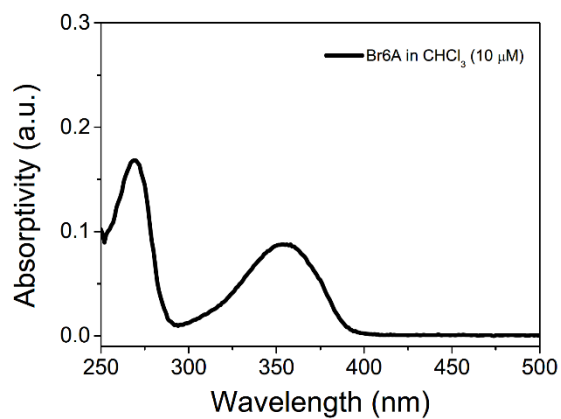


Figure S3. UV/Vis spectrum of Br6A having the same core unit of C1 in CHCl_3 solution.

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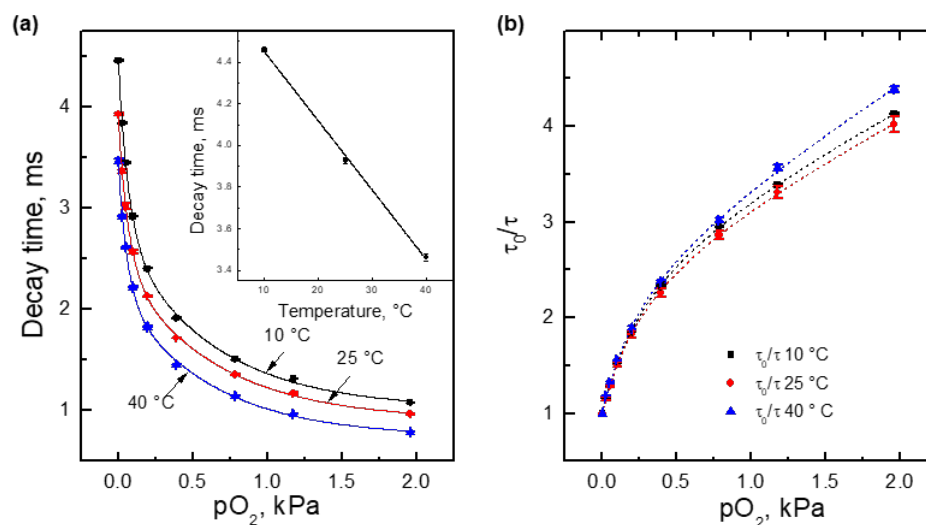


Figure S4. (a) Decay time plots and temperature dependency of τ_0 (inset) and (b) Stern-Volmer plots of dry 320 nm C1 cross-linked core-shell NPs exposure to oxygen in gaseous phase.

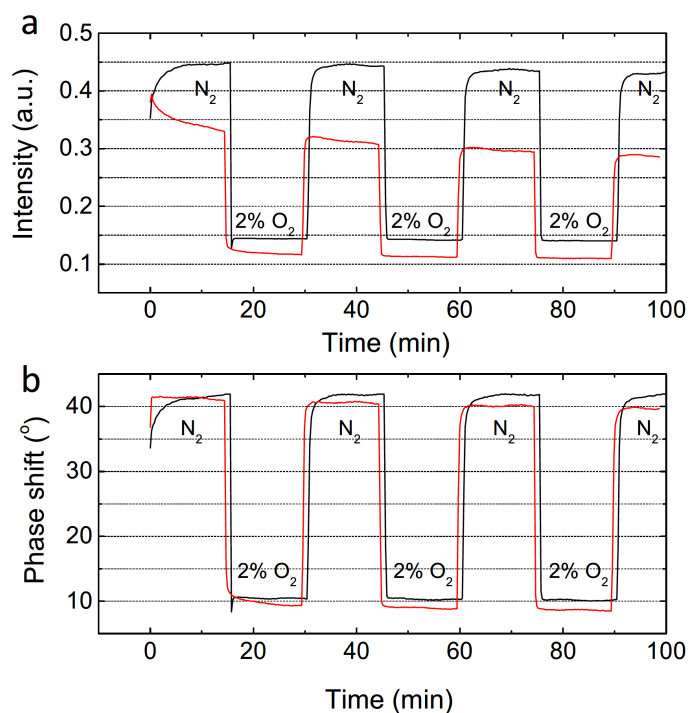


Figure S5. Photostability of the sensor based on 320 nm NPs dispersed in hydrogel D4 upon continuous illumination with a 375 nm LED (red lines) and a 1s illumination by the same LED each 15 s (black lines). The phosphorescence was collected at $\lambda > 530$ nm. Phosphorescence intensity (a) and phase shift (b) read-out.

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