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Supporting Information

Silica-supported dual-dye nanoprobes for ratiometric hypoxia sensing

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Contents

1. General information

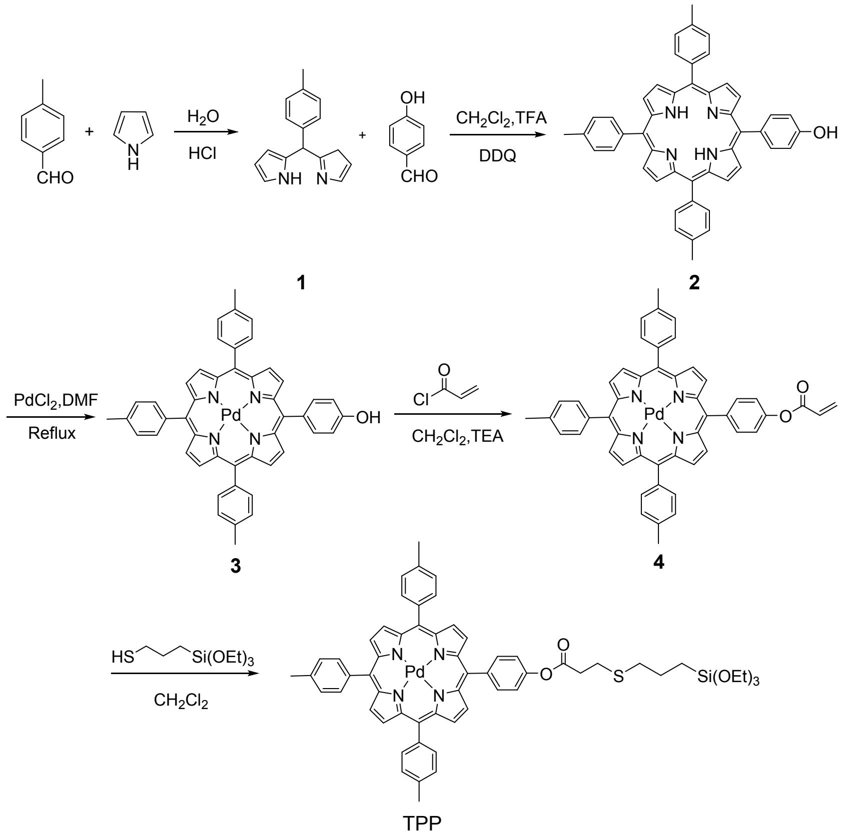
All reagents and solvents were used as received without any further purification. Triethylamine (TEA), 7-(diethylamino) coumarin-3-carboxylic acid (DEAC), (3-aminopropyl) triethoxysilane (APTES), tetraethyl orthosilicate (TEOS), chlorotrimethylsilane (TMSCl), 4-hydroxybenzaldehyde, pyrrole, 4-tolualdehyde, trifluoroacetic acid (TFA), acryloyl chloride, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), 9, 10-diphenylanthracene (DPA), tris(2,2'-bipyridyl)ruthenium (II) chloride ([Ru(bpy)$_3$]Cl$_2$), (3-mercaptopropyl)triethoxysilane, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI) were purchased from TCI. 1-Hydroxybenzotriazole (HOBt) was purchased from J&K. PdCl$_2$ was purchased from Acros. F-127 was purchased from Sigma-Aldrich. Concentrated hydrochloric acid, N,N-dimethylformamide (DMF), Na_2SO_4, $NaHCO_3$, NaCl, acetic acid, dichloromethane, petroleum ether, ammonia, ethyl acetate were purchased from Beijing Chemical Works.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance 400 spectrophotometer and are referenced to solvent signals. High-resolution mass spectra (HRMS) were obtained on Bruker Apex IV Fourier Transform Mass Spectrometer. Absorption spectra were determined on a Hitachi U-3900 UV–visible spectrophotometer. Emission spectra were determined on a Hitachi 4500 spectrophotometer. Phosphorescence decays were measured by time-correlated single photon counting (Edinburgh instruments FLS-920). Excitation was provided by using a microsecond flash lamp. Quartz cuvettes with optical path length of 1 cm were used. The values of lifetime were calculated by exponential function fitting with luminescence spectrometer software F900. DLS investigations were carried out on a Wyatt Dynapro NanoStar (Wyatt Technology) with a gallium-arsenide diode laser of 658 nm emission. Hydrodynamic diameters of the nanoparticles were determined by DLS at least 3 times for each sample. TEM images were obtained using a JEOL-2100 microscope with an accelerating voltage of 200 kV. TEM samples were prepared by placing a few drops of the water dispersion of the nanoparticles onto a carbon-coated copper grid. EPR spectra were recorded with a Bruker E-500 spectrometer operating in the X-band at room temperature. The modulation amplitude is 9.8 GHz, and the sweep width is 100 GHz. TEMP (3 μL) and the nanoprobe in air-saturated water (100 μL, 4 μM) were injected into a specially made quartz capillary for EPR analysis and illuminated by Hg lamp light (100 mW). Blank experiment was carried out under the same condition by adding TEMP (3 μL) and water (100 μL) into the quartz capillary. CCK-8 analysis was performed on a microplate reader (EnSpire®, PerkinElmer) using the absorbance at 450 nm. Confocal fluorescence imaging was performed with Nikon A1R Eclipse Ti confocal laser scanning microscope (CLSM) with a 60× water-immersion objective lens and a TDKAI HIT live cell imaging system. The luminescence was excited at 405 nm with a Si laser.

To access the oxygen sensitivity, the silica nanoparaticles in aqueous solution was placed in screw-capped quartz cuvettes and the respective gas mixtures were bubbled through the cuvette for 15 min. Calibration mixtures were produced by mixing nitrogen (99.9999%, Huanyujinghui Gas, Beijing) and O_2 (99.999%, Jumingcheng Gas) using a electronic gas mixing device (XMG Zhinengliuliangyi)

2. Synthesis of silanized dyes

Silanized coumarin derivative CM was prepared according to the reported method.[1] Silanized porphyrin derivative TPP (Scheme S1) was synthesized by Michael addition reaction of the alkene substituted Pd (II) porphyrin complexes and sulfydryl siloxane [$HS(CH_2)_3Si(OEt)_3$] at room temperature in about 50% yield.



Scheme S1. Synthetic route to TPP.

Synthesis of compound **1**

Concentrated hydrochloric acid (1 mL) and deionized water (200 mL) were added into a 500 mL round-bottom flask equipped with a stir bar. Then, pyrrole (8 mL, 115.31 mmol) was added into the acid solution and the mixture was kept under stirring for half an hour. After that, 4-tolualdehyde (2.5 mL, 21.12 mmol) was added into the mixture and kept stirring for 2 h at room temperature. Ammonia (4 mL) was added to stop the reaction. The crude product was collected by filtration and washed with deionized water and petroleum ether and subsequently dried overnight under vacuum at 60 ℃. Further purification was carried out by silica gel column chromatography with dichloromethane/petroleum ether (2:1, v/v) to afford 3.86 g yellow solid as product. Yield: 77%. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 2H), 7.12 (m, 4H), 6.69 (dd, 2H, J = 4.4 Hz, 2.8 Hz), 6.16 (dd, 2H, J = 5.6 Hz, 2.8 Hz), 5.93 (dd, 2H, J =5.6 Hz, 4.4 Hz), 5.45 (s, 1H), 2.34 (s, 3H).

Synthesis of compound **2**

Compound **1** (3.65 g, 15.45 mmol), 4-hydroxybenzaldehyde (1.89 g, 15.45 mmol), trifluoroacetic acid (TFA, 1.15 mL, 15.45 mmol) and CH_2Cl_2 (600 mL) were added into a 1 L round-bottom flask under nitrogen atmosphere. The flask was covered with a piece of aluminum foil to protect the reaction system from light and kept stirring at room temperature for 6 h. Then, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 4.21 g, 18.53 mmol) was added to the resulted solution and kept stirring overnight at room temperature. The resulting mixture was extracted with deionized water and saturated aqueous $NaHCO_3$. The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography with dichloromethane/ethyl acetate (20:1, v/v) to afford 520 mg purple solid as product. Yield: 15%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 2.0 Hz, 8H), 8.06 (dd, J = 8.2, 8.2 Hz, 8H), 7.50 (d, J = 7.7 Hz, 6H), 7.21 (d, J = 8.3 Hz, 2H), 5.06 (s, 1H), 2.71 (s, 9H), -2.77 (s, 2H). [2]

Synthesis of compound **3**

Compound **2** (200 mg, 0.30 mmol), $PdCl_2$ (320 mg, 1.80 mmol) and DMF (5 mL) were added into a 50 mL round-bottom flask equipped with a stir bar and covered with a piece of aluminum foil to protect the reaction system from light. After being kept refluxing and stirring for 15 minutes at 150 °C, the resulting mixture was cooled back to room temperature by an ice bath and poured into deionized water (20 mL). The crude product was collected by filtration and washed with deionized water. The residue was dried under vacuum at 60 °C. The further purification was carried out by silica gel column chromatography with CH_2Cl_2 to afford 185 mg brick-red solid as product. Yield: 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 2.8 Hz, 8H), 8.03 (dd, J = 8.1, 8.1 Hz, 8H), 7.54 (d, J = 7.7 Hz, 6H), 7.19 (d, J = 8.4 Hz, 2H), 5.01 (s, 1H), 2.70 (s, 9H). HRMS (MALDI): *m/z* calculated for $C_{47}H_{34}N_4OPd$ $[M]^+$ 776.1767, found 776.1790.

Synthesis of compound **4**

Under nitrogen atmosphere, compound **3** (160 mg, 0.21 mmol), triethylamine (TEA, 100 μL, 0.72 mmol) and anhydrous CH_2Cl_2 (50 mL) were added into a 100 mL round-bottom flask equipped with a stir bar and covered with a piece of aluminum foil to protect the reaction system from light. Acryloyl chloride (60 μL, 0.74 mmol) was added dropwisely to the system in an ice bath. The resulting mixture was then kept stirring for 5 h at room temperature. After the reaction was completed, the resulting mixture was extracted with deionized water. The organic layer was collected and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was further purified by silica gel column chromatography with dichloromethane/petroleum ether (1:1, v/v) to afford 160 mg orange-red solid as product. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86–8.79 (m, 8H), 8.18 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.3 Hz, 6H), 7.54 (dd, J = 7.8, 4.9 Hz, 8H), 6.78 (d, J = 17.3 Hz, 1H), 6.51 (dd, J = 17.3, 10.4 Hz, 1H), 6.15 (d, J = 10.4 Hz, 1H), 2.70 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 150.6, 141.94, 141.87, 141.6, 139.00, 138.97, 137.6, 137.5, 135.0, 134.2, 133.0, 131.3, 131.2, 131.1, 130.9, 128.2, 127.6, 122.1, 122.0, 120.5, 119.9, 21.7. HRMS (MALDI): *m/z* calculated for $C_{50}H_{36}N_4O_2Pd$ $[M]^+$ 830.1873, found 830.1888.

Synthesis of compound TPP

Compound **4** (160 mg, 0.19 mmol), TEA (200 μL, 1.44 mmol), (3-mercaptopropyl)triethoxysilane (100 μL, 0.41 mmol) and CH_2Cl_2 (40 mL) were added to a 100 mL round-bottom flask covered with a piece of aluminum foil under nitrogen atmosphere. The resulting mixture was kept stirring overnight at room temperature. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) to afford 98 mg orange-red solid as product. Yield: 48%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86–8.78 (m, 8H), 8.17 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 7.8 Hz, 6H), 7.54 (d, J = 7.6 Hz, 6H), 7.49 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 17.3 Hz, 1H), 6.51 (dd, J = 17.3, 10.4 Hz, 1H), 6.15 (d, J = 10.4 Hz, 1H), 3.86 (q, J = 7.0 Hz, 6H), 3.09–3.00 (m, 4H), 2.75–2.66 (m, 11H), 1.89–1.76 (m, 2H), 1.26 (t, J = 7.0 Hz, 9H), 0.91–0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 150.6, 141.94, 141.86, 141.6, 139.7, 138.98, 138.96, 137.5, 137.4, 135.0, 134.2, 131.3, 131.2, 131.1, 131.0, 130.8, 127.6, 122.1, 122.0, 120.4, 119.9, 58.6, 35.45, 35.40, 27.1, 23.4, 21.6, 18.5, 10.1. HRMS (MALDI): *m/z* calculated for $C_{59}H_{58}N_4O_5PdSSi$ $[M]^+$ 1068.2932, found 1068.2910.

3. Preparation of silica nanoprobe

Preparation of the oxygen nanoprobe is presented in scheme 1 and follows the general procedures: Pluronic F-127 (100 mg) and desired amount of silanized dyes (Table S1) dissolved in dichloromethane (1-2 mL) were added to a 20 mL round-bottom flask under dark. After stirring by 30 min, the solvent was removed by means of a general nitrogen flow, and the resulting mixture was dried under vacuum at 30 °C. Then, NaCl (68 mg) was added into the solid and the mixture was dissolved with acetic acid (1M, 1.56 mL). After being kept stirring for 3 h at 25 °C, TEOS (180 μL) was added into the system and stirred by another 3 h at 25 °C. Then the terminating agent (TMSCl, 10 μL) was added into the resulting homogeneous aqueous solution. The resulting mixture was kept under stirring for 48 h at 25 °C and then diluted with 6 mL deionized water. The dialysis treatments were carried out versus deionized water at room temperature under general stirring with dialysis tube (Solarbio, mol wt. cut off: 8000~14000 Da).

Table S1. The preparation conditions of hypoxia silica nanoprobe.

Sample	CM mg	TPP mg	TEOS^a μL	n(CM)/n(TEOS) molar ratio	n(TPP)/n(TEOS) molar ratio
$CM_{0.25}@SiO_2$	0.93	0	180	0.25:100	/
$TPP_{0.25}@SiO_2$	0	2.14	180	/	0.25:100
$CM_{0.25}TPP_{0.25}@SiO_2$	0.93	2.14	180	0.25:100	0.25:100
$CM_{0.25}TPP_{0.5}@SiO_2$	0.93	4.28	180	0.25:100	0.5:100
$CM_{0.5}TPP_{0.25}@SiO_2$	1.86	2.14	180	0.5:100	0.25:100
$CM_{0.5}TPP_{0.5}@SiO_2$	1.86	4.28	180	0.5:100	0.5:100

a. n(TEOS)=0.8 mmol

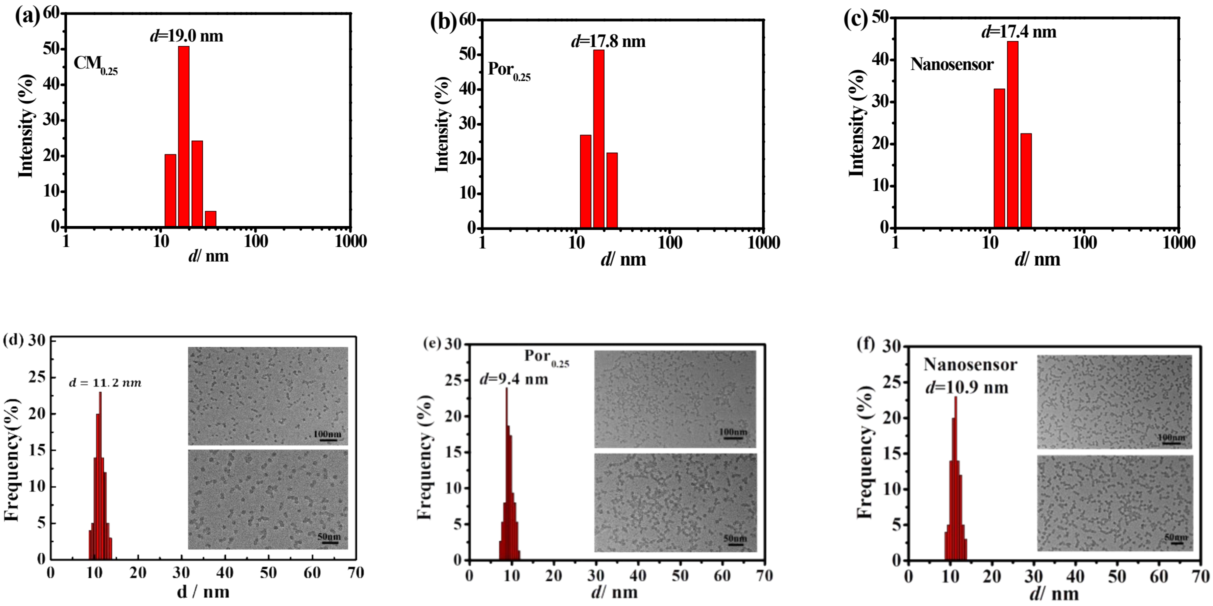


Figure S1. The diameter distribution of silica nanoparticles measured by DLS (a~c) and TEM (d~f).

4. Photophysical properties of CM and TPP in different media

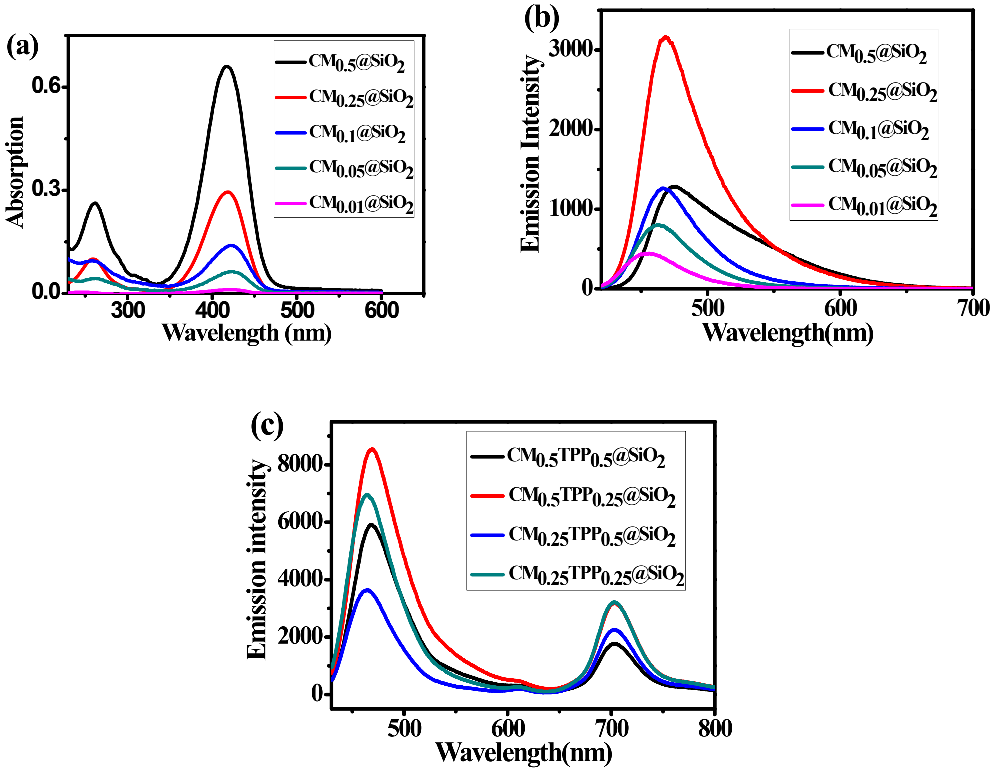


Figure S2. (a) Absorption and (b) emission of CM covalently-bonded silica nanoparticles at different loading levels in N_2-saturated water, and (c) emission spectra of CM and TPP dual-dye covalently-bonded silica nanoparticles at different loading levels in N_2-saturated water (The concentration of silica nanoparticles is 1.4×10^{-7} M, λ_{ex}=410 nm).

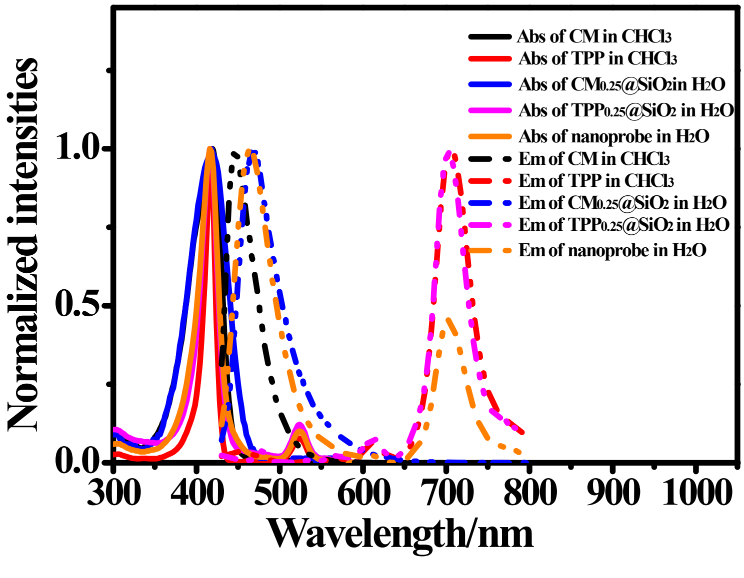


Figure S3. Absorption and emission spectra of monomer CM and TPP in $CHCl_3$, $CM_{0.25}$@SiO_2, $TPP_{0.25}$@SiO_2, and nanoprobe in N_2-saturated water (The concentration of nanoprobe is 1.4×10^{-7} M, λ_{ex}=410 nm). [3]

5. Luminescence quantum yields of CM and TPP

Quantum yields (ϕ) were measured by the relative standard method, and were calculated according to the following equation:

$$\phi u = \phi s \times \frac{K_u}{K_s} \times (\eta_u^2/\eta_s^2) \tag{1s}$$

Where ϕ stands for quantum yield, K is the slope of the plot of integrated fluorescence intensity *vs* absorbance at the excitation wavelength, η is the refractive index of the solvent, and the subscripts *u* and *s* refer to sample and standard respectively.

In this article, we took 9, 10-diphenylanthracene (DPA, ϕ=0.90 in cyclohexane[4]) as a standard for $CM_{0.25}@SiO_2$ and compound CM, and tris(2,2'-bipyridyl)ruthenium (II) chloride hexahydrate (ϕ=0.094 in acetonitrile[5]) as a standard for $TPP_{0.25}@SiO_2$, nanoprobe and compound TPP.

The calculation of Stern-Volmer constant and quenching efficiency by oxygen

$$\frac{R_{N_2}}{R} = 1 + K_{SV}\,pO_2 \tag{2s}$$

Where R is defined as the ratio of phosphorescence intensity at 704 nm to that of the fluorescence intensity at 465 nm ($R=I_P/I_F$), R_{N_2} is the emission intensity ratio in fully deoxygenated solution, pO_2 is the oxygen partial pressure, and K_{SV} is the Stern-Volmer constant.

$$Q = \frac{R_{N_2} - R_{O_2}}{R_{N_2}} \times 100\% \tag{3s}$$

6. Energy transfer calculations

The Föster radius was estimated according to the following equation[6]:

$$R_0(\text{Å}) = 0.211 \times (J\phi\kappa^2\eta^{-4})^{1/6} \tag{4s}$$

Where J refers to the spectral overlap integration between donor's emission spectrum and acceptor's absorption spectrum, ϕ stands for donor's luminescence quantum yield, κ^2 is the dipole orientation factor which assumed to be 2/3, and η is the refractive index of the solvent.

The spectral overlap integration J was calculated according to the following equation:

$$J = \frac{\int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \tag{5s}$$

Where λ is the wavelength of light (nm), $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor at that wavelength ($M^{-1}\cdot cm^{-1}$), and $F_D(\lambda)$ is the donor emission intensity at that wavelength.

The overlap integral was estimated to be 3.851×10^{14} $M^{-1}cm^{-1}nm^4$ between donor CM and acceptor TPP, and 1.228×10^{14} $M^{-1}cm^{-1}nm^4$ between two donors. The luminescence quantum yield of donor is 0.927, and the refractive index of $CHCl_3$ is 1.447. Thus, the Föster radius was calculated to be 4.1 nm for transfer between donor and acceptor, and 3.4 nm for transfer between two donors.

The energy transfer efficiency (η_{ET}) was calculated according to the data from Fig. S4 by using the following equation[7]:

$$\eta_{\mathrm{ET}} = 1 - \frac{I_{\mathrm{DA}}}{I_{\mathrm{D}}} \qquad (6s)$$

where I_{D} and I_{DA} are the emission intensities of donor in the absence and presence of the acceptor, respectively. The energy transfer efficiency of nanoprobe was estimated to be 91.9%.

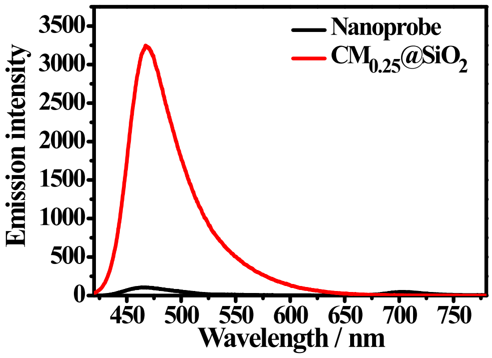


Figure S4. Emission spectra of $CM_{0.25}@SiO_2$ and nanoprobe in H_2O. ($c=7\times10^{-7}$ M, λ_{ex}=410 nm)

7. Phosphorescence decays of TPP and $TPP_{0.25}@SiO_2$

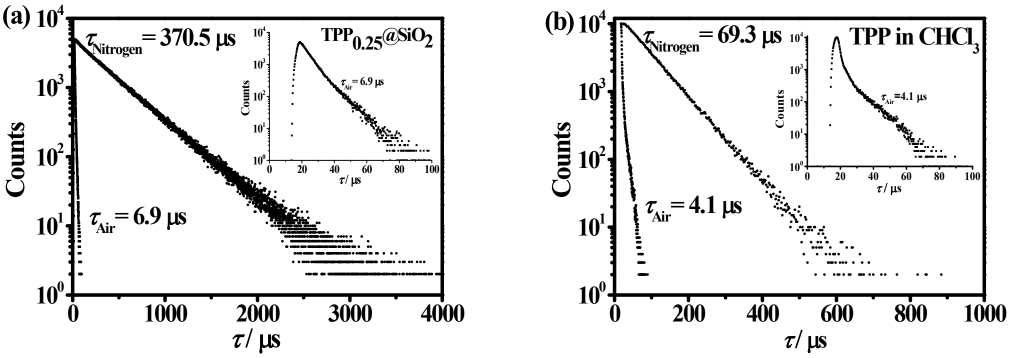


Figure S5. (a) Phosphorescence decays at 704 nm of TPP in chloroform saturated with N_2 and air respectively. (The concentration of TPP is 1.0×10^{-6} M, λ_{ex}=405 nm). (b) Phosphorescence decays at 704 nm of $TPP_{0.25}@SiO_2$ in aqueous solution saturated with N_2 and air respectively. (The concentration of NPs is 1.4×10^{-7} M, λ_{ex}=405 nm).

8. Comparison of various silica oxygen sensors

Table S2. Various silica oxygen sensor, their excitation/emission wavelengths (in nm) and sensitivity. [8]

Dye/matrix	$\lambda_{\mathrm{ex}}/\lambda_{\mathrm{em}}$	Sensitivity	Reference
Perylenedibutyrate on silica	468/514	I_0/I_{100} = 1.67; I_0/I_{21} = 1.19	[9]
Erythrosine B on amino-modified silica	547/695	$I_0/I_{0.05\%} \sim 4.2$	[10]
Fluorescent Yellow on silica gel	466/519	$I_0/I_{21} \sim 3$	[11]
$Ru(dpp)_3Cl_2$ on SiO_2 in PDMS	470/>550	I_0/I_{21} = 1.4	[12]

$Ru(bpy)(DMCH)_2(PF_6)_2$ on SiO_2	528/736	$I_0/I_{air} = 1.45$	[13]
$Ru(bpy)_3$ on SiO_2 spheres	360/600	$I_0/I_{100} \sim 2.1$	[14]
PtTFPP-doped silica nanoparticles in sol-gel matrix	405/650	$I_0/I_{100} = 106$	[15]
PdTFPP in silica gel beads in silicone	405/680	$I_0/I_{1000Pa} = 5$	[16]
PtOEP in TEOS sol–gel	586/645	$I_0/I_{100} = 41$	[17]
PtTPTBP in silica nanoparticle	650/769	$I_0/I_{100} = 10.6$	[18]
$Ru(dpp)_3Cl_2$ in upconversion silica nanoparticle	477/613	$I_0/I_{100} = 2.6$	[19]
PtTFMPP in silicone rubber	395/646	$I_0/I_{100} = 42$	[20]
Our nanoprobe	**410/704**	$\boldsymbol{I_0/I_{100} = 153;\ I_0/I_{21} = 57}$	**This work**

9. EPR spectra of TEMP in water without nanoprobe

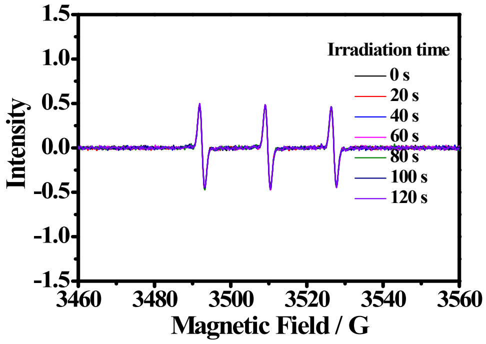


Figure S6. EPR spectra of the air-saturated aqueous solution of TEMP (3 μL TEMP in 100 μL water) in the absence of nanoprobe upon irradiation by a Hg lamp (100 mW).

10. Singlet oxygen quantum yield of oxygen nanoprobe

Singlet oxygen quantum yield (ϕ_Δ) was detected by monitoring the oxidation of 9, 10-anthracenediyl-bi(methylene)dimalonic acid (ABDA). An air-saturated aqueous solution of ABDA (OD $\approx$ 1 at 378 nm) containing low concentrations photosensitizers (OD $\approx$ 0.1 at the irradiation wavelength) was prepared in dark and irradiated with a 532 nm laser at a power of 50 mW/cm^2 in an interval of 1 min[21]. Upon irradiation by the light source, $^1O_2$ would be generated owing to the energy transfer process between the excited triplet state of the photosensitizers and the ground state of molecular oxygen ($^3O_2$). The generated $^1O_2$ reacts with ABDA and produces an endoperoxide with decrease conjugation compared to the parent molecule, which leads to a decrease of ABDA absorbance[22].

The absorbance of ABDA at 378 nm was obtained by UV-visible spectrophotometer. The value of ϕ_Δ was estimated by the relative method using Rose Bengal (RB, $\phi_\Delta = 0.75$ in H_2O[23]) as the standard and calculated according to the following equations:

$$\phi_{\Delta(x)} = \phi_{\Delta(RB)} \times \frac{S_{(x)}}{S_{(RB)}} \times \frac{F_{(RB)}}{F_{(x)}} \tag{7s}$$

Where ϕ_Δ refers to the singlet oxygen quantum yield, subscripts x and RB stand for nanoprobe and RB respectively, S stands for the slope of plot of the natural logarithm of the optical density of ABDA (at 378 nm) vs irradiation time, and F is the absorption correction factor, which is calculated by $F = 1 - 10^{-OD}$(OD is the optical density of the photosensitizers at 532 nm).

To ensure the decrease of optical density at 378 nm was induced by the oxidation of ABDA instead of photodegradation, the photostability of ABDA, nanoprobe and RB in aqueous solution was also measured (Figure S7c) respectively. It turned out that no significant absorption changes were observed when ABDA, nanoprobe and RB were exposed to the 532 nm laser at a power of 50 mW /cm^2.

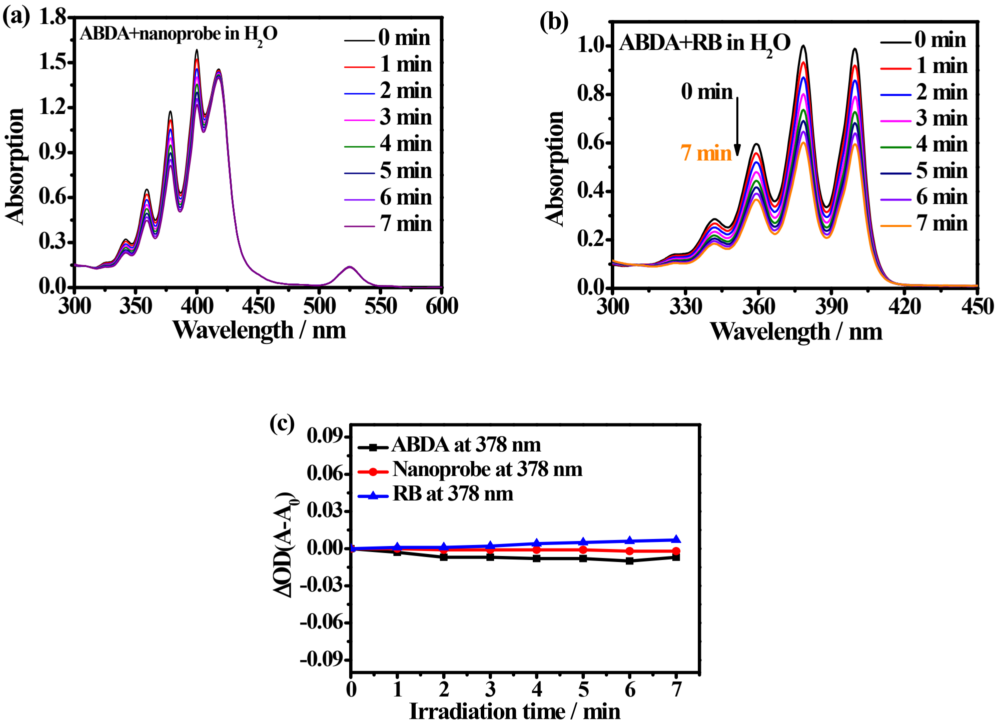
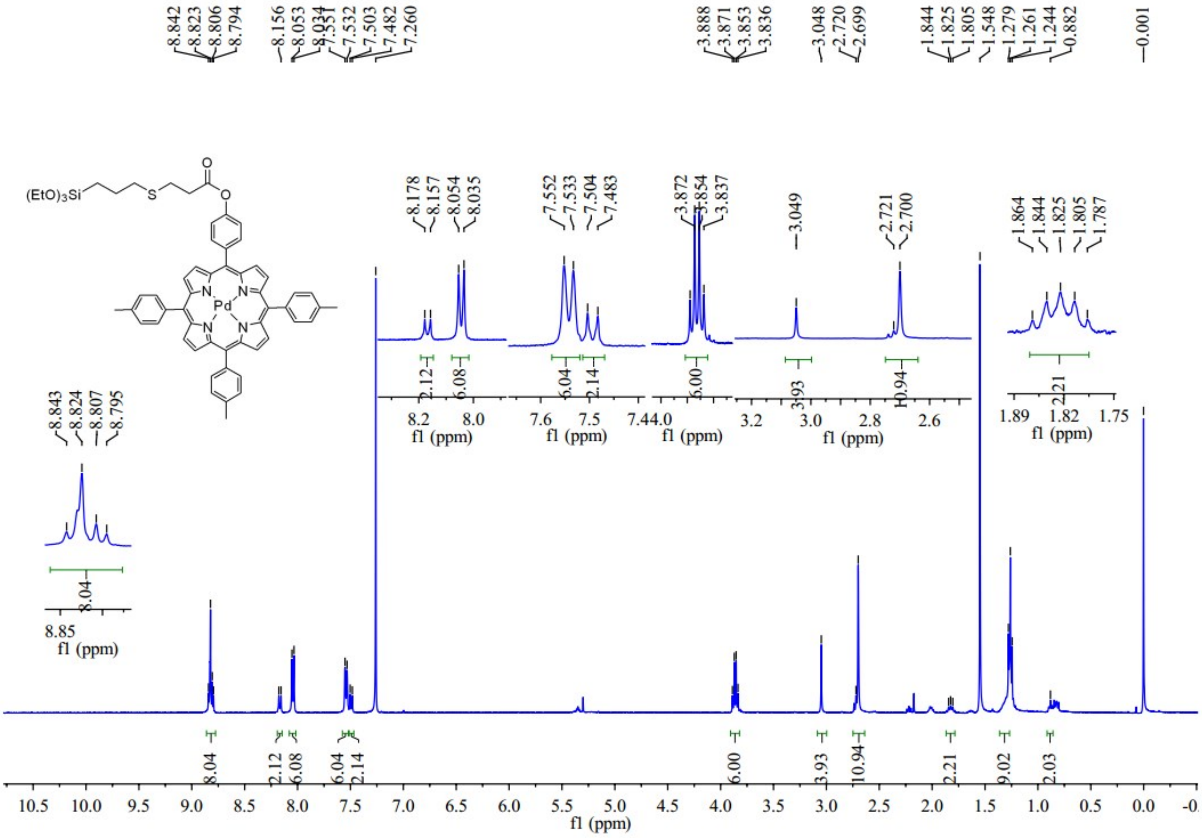


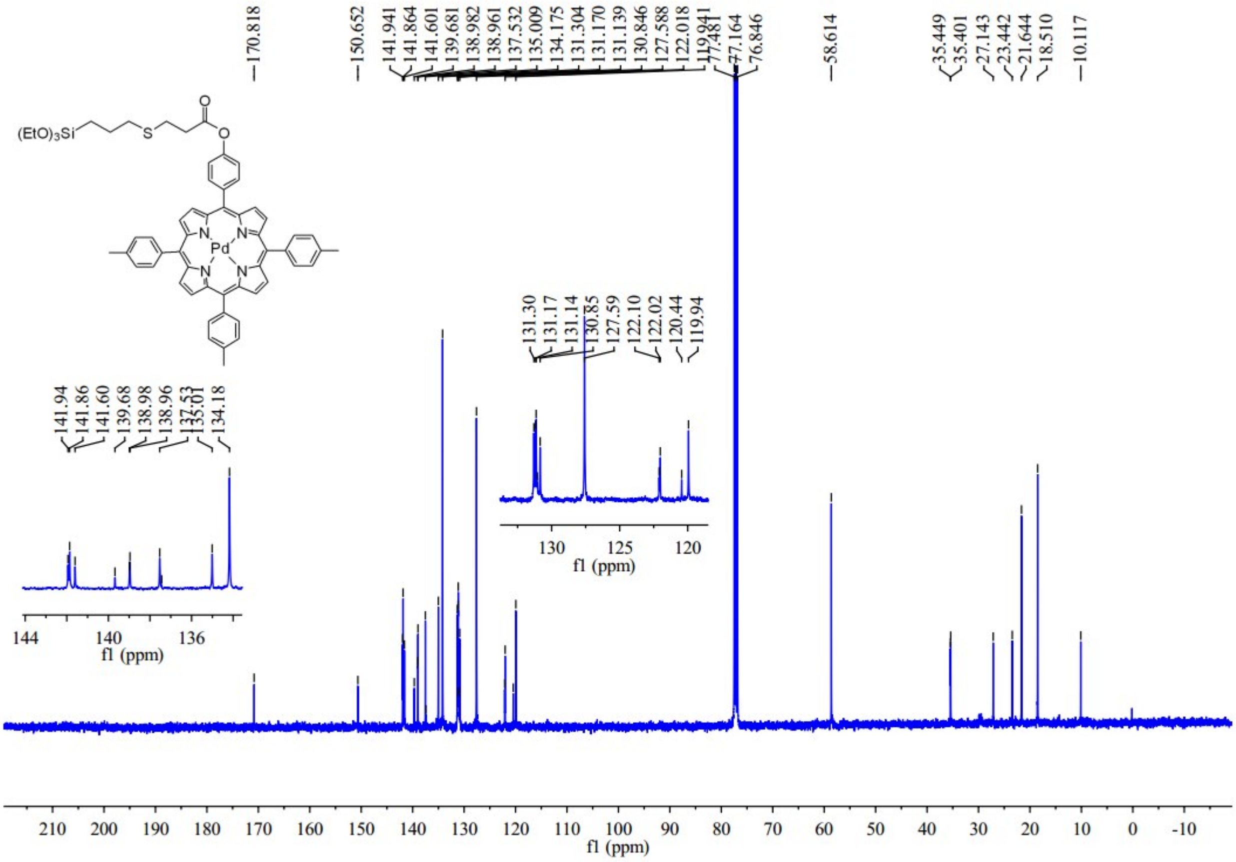
Figure S7. Changes in absorption spectra of ABDA upon irradiation in the presence of nanoprobe (a) and RB (b) for 0-7 min (recorded at 1 min intervals) in water, λ_{ex}=532 nm. (c) Changes in optical density of ABDA (black line), nanoprobe (red line) and RB (blue line) at 378 nm upon irradiation by a 532 nm laser at a power of 50 mW.

11. Cytotoxicity assay

Cell culture: HeLa cells were cultured in Dulbecco's Modified Eagle's Medium (DMEM), supplemented with 10% fetal bovine serum, penicillin (100 units mL^{-1}), and streptomycin (100 mg mL^{-1}) at 37 °C in a humidified atmosphere of 5% CO_2 for 24 h. The dark cytotoxicity and photocytotoxicity of nanoprobes were evaluated in HeLa cells using the standard CCK-8 assay. Particularly, the nanoprobe stock solutions were diluted by fresh medium (DMEM) into different concentrations (0, 0.25, 1, 2.5, 10, 25 μM). Cells were seeded in a 96-well plate (5×10^3 cells per well) and cultured overnight. The cells medium was then changed with different concentrations of nanoprobe solutions. After being incubated at 37 °C in 5% CO_2 for 3 h, the cells were washed with fresh medium to remove free NPs twice before being irradiated by a 532 nm laser at a power of 5.0 mW/cm^2 for 20 min. After being incubated for another 20 h at 37 °C in 5% CO_2, the medium was removed carefully, followed by the addition of 100 μL of fresh medium with 10 μL CCK-8 reagent to each well. Then the plates was incubated for 3 h at 37 °C in 5% CO_2 before recording the absorbance intensity at 450 nm using an EnSpire Multimode Plate Reader (PerkinElmer). The absorbance measured for an untreated cell population under the same experimental conditions was used as the reference point to establish 100% cell viability.

12. ^{1}H NMR, ^{13}C NMR and HRMS of TPP

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131.139
130.846
127.588
122.018
119.941
77.481
77.164
76.846
58.614
35.449
35.401
27.143
23.442
21.644
18.510
10.117
(EtO)3Si
S
O
O
N
Pd
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141.86
141.60
139.68
138.98
138.96
137.53
135.01
134.18
144
140
136
f1 (ppm)
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131.17
131.14
130.85
127.59
122.10
122.02
120.44
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180
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160
150
140
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120
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10
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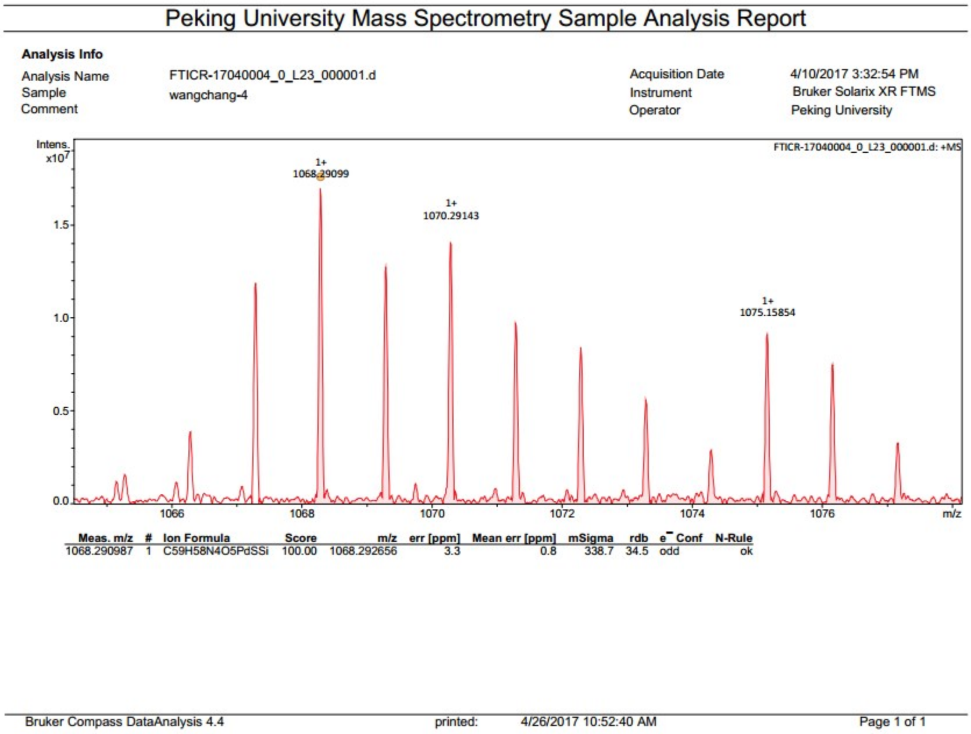
-10
f1 (ppm)



Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	FTICR-17040004_0_L23_000001.d	Acquisition Date	4/10/2017 3:32:54 PM
Sample	wangchang-4	Instrument	Bruker Solarix XR FTMS
Comment		Operator	Peking University

Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
1068.290987	1	C59H58N4O5PdSSi	100.00	1068.292656	3.3	0.8	338.7	34.5	odd	ok

Bruker Compass DataAnalysis 4.4 printed: 4/26/2017 10:52:40 AM Page 1 of 1

13. References

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