

Supporting Information

Core-shell structured phosphorescent nanoparticles for detection of exogenous and endogenous hypochlorite in live cells via ratiometric imaging and photoluminescence lifetime imaging microscopy

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General Experimental Information

All solvents were of analytical grade and purified according to standard procedures.¹ All buffer components were of biological grade and used as received. ¹H NMR spectra were recorded on a Bruker ACF400 (400 MHz) spectrometer at 298 K using deuterated solvents. Chemical shifts (δ , ppm) were reported relative to tetramethylsilane (TMS). Mass spectra were recorded on a Bruker autoflex matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer (MS3). Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2100 transmission electron microscope at an acceleration voltage of 150 kV. Average particle size was measured via dynamic light scattering (DLS) on Zetasizer Nanoseries (Nano ZS90). Zeta-potential was measured by a Zeta-plus zeta potential analyzer. Nitrogen adsorption–desorption measurements were carried out on a 3H-2000PS2 surface area analyzer at 77 K using the volumetric method and samples were degassed at 150 °C for 4 h under vacuum before measurements. Brunauer–Emmett–Teller (BET) specific surface areas were calculated by using adsorption data at $P/P_0 = 0.05$ – 0.25 (five points collected). Pore size distributions were estimated from adsorption branches of the isotherms by using the Barrett–Joyner–Halenda (BJH) method. Powder small-angle X-ray diffraction (XRD) measurements were carried out on a Bruker Smart APEX CCD diffractometer at 40 kV and 20 mA using Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$). UV-Vis absorption spectra were recorded on a UV-1700 Shimadzu UV-Vis spectrophotometer. Photoluminescence (PL) spectra and emission lifetimes were measured on an Edinburgh FL 920 spectrophotometer. Photographs of the solution samples were taken with a Cannon EOC 400D digital camera under a hand-held UV lamp. ROS and RNS are prepared and quantified according to the literature.^{2–6}

Confocal luminescence imaging was carried out on an Olympus IX81 laser scanning confocal microscope. The FLIM setup is integrated with the same Olympus IX81 laser scanning confocal microscope. The lifetime values were calculated with professional software provided by PicoQuant Company.

Synthesis:

Complex **1** was prepared according to the literature procedure.⁷

The preparation of the bis(pyridylbenzaldehyde) precursor complex $[\text{Ir}(\text{pba})_2(\text{bqu})](\text{PF}_6)$ (Hpba = pyridylbenzaldehyde, bqu = 2,2'-biquinoline) was similar to the reported procedure.⁸ A mixture of the dichloro-bridged dimer (118 mg, 0.10 mmol) and 2,2'-biquinoline (51 mg, 0.20 mmol) in methanol/dichloromethane (30 mL; 1:1 v/v) was heated under reflux for 4 h in the dark under nitrogen (Scheme S1). The orange solution was then cooled to room temperature. Metathesis with KPF_6 and subsequent recrystallization from dichloromethane/diethyl ether gave the product complex as orange crystals. Yield: 168 mg (88%); $^1\text{H NMR}$ (400 MHz, $(\text{CD}_3)_2\text{SO}$, 298 K, TMS): δ 9.68 (s, 2H), 9.00 (d, $J = 8.9$ Hz, 2H), 8.93 (d, $J = 8.7$ Hz, 2H), 8.35 (d, $J = 8.0$ Hz, 2H), 8.11 – 8.01 (m, 8H), 7.68 (d, $J = 8.9$ Hz, 2H), 7.57 (t, $J = 7.5$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.23 (t, $J = 6.6$ Hz, 2H), 7.16 (t, $J = 7.9$ Hz, 2H), 6.63 (s, 2H); IR (KBr): $\bar{\nu}$ 1688 cm^{-1} (CHO), 842 cm^{-1} (PF_6); MALDI-TOF-MS m/z : 813 $[\text{M} - \text{PF}_6^-]^+$.

The preparation of complex **2** was similar to the reported procedure.⁶ A mixture of $[\text{Ir}(\text{pba})_2(\text{bqu})](\text{PF}_6)$ (77 mg, 0.08 mmol), hydroxylamine hydrochloride (22 mg, 0.32 mmol), and triethylamine (67 μL , 0.48 mmol) in methanol/dichloromethane (30 mL; 1:2 v/v) was heated under reflux for 16 h in the dark under nitrogen (Scheme S1). The orange solution was then cooled to room temperature and the solvent was removed under

reduced pressure. The residue was dissolved in dichloromethane (15 mL) and was washed with water (5 mL × 3), dried over anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by column chromatography on silica gel. The desired product was eluted with dichloromethane/methanol (20:1). Subsequent recrystallization of the complex from a dichloromethane/diethyl ether mixture afforded complex **2** as orange-red crystals (56 mg, 71%); ¹H NMR (400 MHz, (CD₃)₂SO, 298 K, TMS): δ 11.14 (s, 2H), 9.00 (d, *J* = 7.6 Hz, 2H), 8.94 (d, *J* = 7.8 Hz, 2H), 8.18 – 8.12 (m, 4H), 7.92 – 7.84 (m, 10H), 7.58 (t, *J* = 7.5 Hz, 2H), 7.19 – 7.09 (m, 6H), 6.48 (s, 2H); IR (KBr): $\bar{\nu}$ 3568 cm⁻¹ (O–H), 1621 cm⁻¹ (C=N), 958 (N–O), 847 cm⁻¹ (PF₆); MALDI-TOF-MS *m/z*: 843 [M – PF₆⁻]⁺.

References:

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Scheme S1 Synthetic procedure of complex **2**.

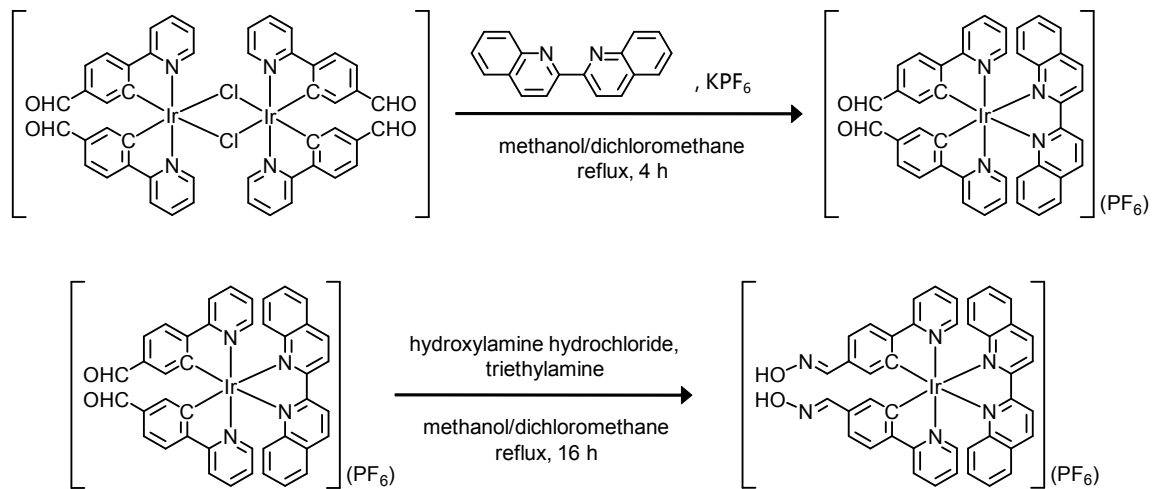


Fig. S1 FT-IR spectrum of SiO₂-1@mSiO₂-2.

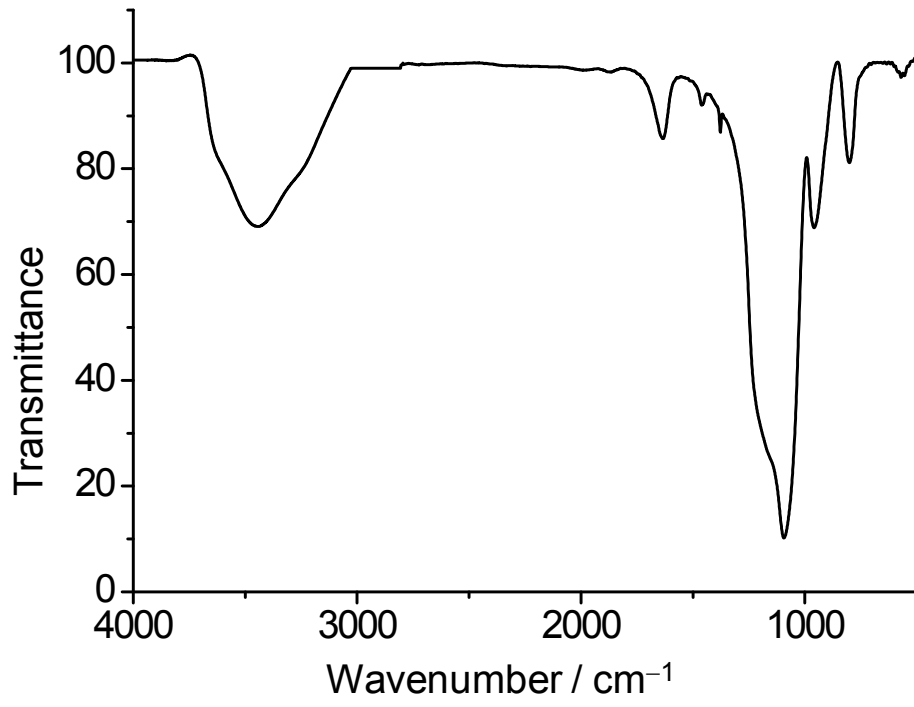


Fig. S2 Absorption spectra of complexes **1** (green) and **2** (red) and nanoparticles SiO₂-**1**@mSiO₂ (blue) and SiO₂-**1**@mSiO₂-**2** (black).

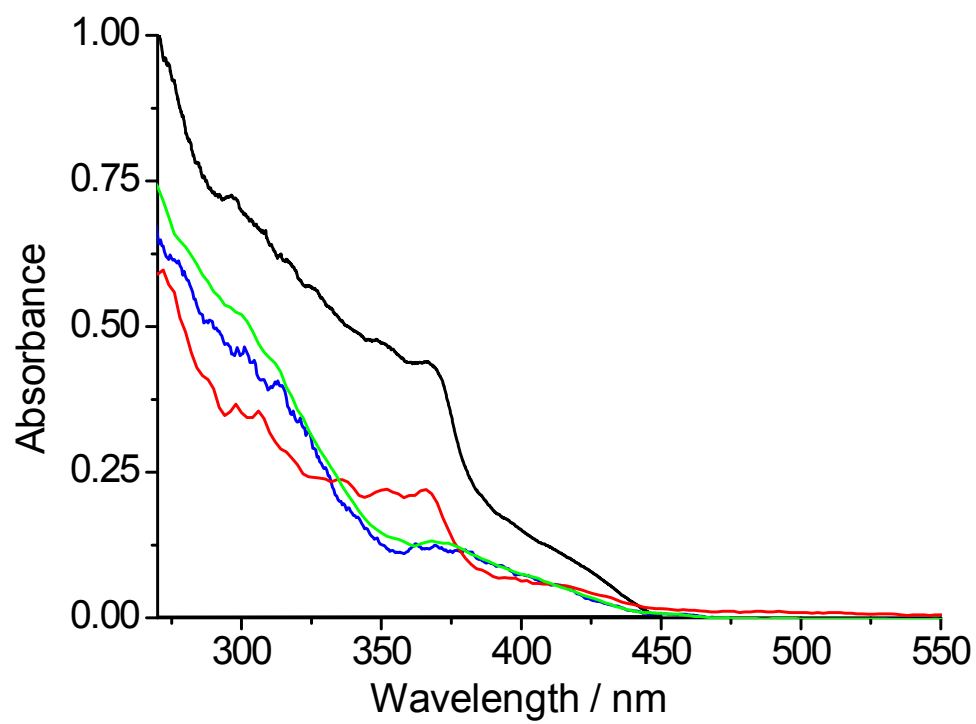


Fig.S3 Luminescence images of RAW 264.7 cells treated with SiO₂-1@mSiO₂-2 followed by incubation with NaClO (50 μM) for 1 h.

