Photo-writing self-erasable phosphorescent images using poly(*N*-vinyl-2-pyrrolidone) as a photochemically deoxygenating matrix

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Materials. All reagents and solvents were used as received unless otherwise indicated. Platinum(II) octaethylporphyrin (Pt(OEP)) and platinum(II) *meso*-tetraphenyl tetrabenzoporphyrin (Pt(TPBP)) were purchased from Frontier Scientific Inc.. Compound **Au2** was prepared according to literature procedures.[1] Poly(*N*-vinyl-2-pyrrolidone) polymers with a variety of viscosity average molecular weight and with commercial names of K15, K17, K23–27, K30, K29–32 were purchased from Tokyo Chemical Industry Co. Ltd., Alfa Aesar Chemicals Co. Ltd., Aladdin Industrial Co. Ltd., Aladdin Industrial Co. Ltd. and Tokyo Chemical Industry Co. Ltd., respectively. Dimethyl sulfoxide (DMSO), *N*-methyl pyrrolidone (NMP) and dichloromethane (CH_2Cl_2) in spectroscopic grade were purchased from J&K Scientific Ltd.. Analytical grade methanol (CH_3OH) were purchased from Shanghai Lingfeng Chemical Research Co. Ltd..

Spectroscopic characterization. UV-vis absorption spectra were recorded on a Thermo Scientific Evolution 201 UV-visible spectrophotometer. Photo-emission, excitation spectra and lifetimes for solutions were recorded on Edinburg spectrometer FLS-980 equipped with a Xe-light source, an MCP-PMT detector in a cooled housing (–20 ^{o}C) which covers a range of 200–870 nm, and an NIR-PMT detector in a cooled housing (–80 ^{o}C, cooled by liquid nitrogen) which covers a range from 600–1700 nm. Upon the measurements of NIR emission of singlet oxygen, an 850 nm long-pass filter was inserted in-between the sample and the detector to avoid many high-order diffraction from the visible emission. Lifetime data were analyzed with F980 software package. Lifetimes for PVP gel were recorded on Edinburg spectrometer LP-920 with ICCD and PMT detectors and were analyzed with LP-920 software package. All the measurements have been performed at room temperature (RT).

Using Xe-lamp light as excitation source, emission traces of Pt(OEP) in aerated NMP solutions and PVP gels were recorded on Edinburg FLS-980 by using the *multiple scan* mode and the shutter was set as always open. Emission intensity at fixed wavelength versus time elapsed were recorded on Edinburg FLS-980 by using the *kinetic scan* mode and the shutter was set as always open. For each of the measurements, the optical power density (OPD) of excitation in the Edinburg FLS-980 spectrometer was checked with a CEL-NP2000 optical power meter (Beijing CeauLight Sci. & Technol. Ltd.). The excitation power densities of the Edinburg FLS-980 spectrometer at a variety of wavelengths were stable.

A 365 nm UV torch was used as the light sources for the fast photo-activation processes and photo-written phosphorescent images. For each of the measurements under photo-irradiation, the optical power density (OPD) of the 365 nm UV torch was checked with the

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(1) S. G. Wan and W. Lu, *Angew. Chem. Int. Ed.*, 2017, **56**, 1784.

CEL-NP2000 optical power meter to minimize the errors. The optical power densities of the 365 nm UV torch was 40 mW cm^{-2} (the OPDs were measured at the distance of 3.0 cm from the light bulbs) upon fully charged and decreased to about 27 mW cm^{-2} after 30 min long-term irradiation experiments. For short-term irradiation experiments (for example, photo-writing in a gel sample usually took 5−10 s for the PVP/CH_2Cl_2 gel, 60 s for the PVP/CH_3OH gel, and 180 s for the PVP/H_2O gel), the variations in OPD of the 365 nm UV torch could be ignored.

Rheometric measurements. The gel formation was confirmed by Rheometer HAAKE MARS III and the rheology experiments were carried out at 25 °C. The frequency and pressure of the measurements were setted at 1 Hz and 10 Pa, respectively.

Scanning electron microscopy (SEM) measurements. The SEM micrographs were taken on a ZEISS Merlin scanning electron microscope operating at 2–5 kV. SEM samples were prepared by drop-casting the gels onto silicon wafers. The excess solvent was evaporated in air before measurements.

Differential air pressure (ΔP) measurements: The variations in the air pressure (ΔP) were recorded with a Smart Sensor AS510 digital differential pressure manometer. Two glass NMR tubes containing NMP solution (0.5 mL) of PtOEP (concentration $\sim 5\times10^{-6}$ mol dm^{-3}) and pure NMP solvent (0.5 mL) respectively were connected with hoses to the pressure sensing probes of the differential manometer. The two NMR tubes were irradiated by a 365 nm UV torch and the relative pressure variations were recorded against the irradiation time (30 min). The measurements were repeated for at least three times to obtain the consistent results with error of ±5 Pa. For each of the measurement duration, the optical power density (OPD) of the 365 nm UV torch was checked with the CEL-NP2000 optical power meter.

Preparation of PVP/CH_2Cl_2 gels containing Pt(OEP). The powder of PVP (6 g) was added to a CH_2Cl_2 solution (10 ml) of Pt(OEP) (concentration $\sim 5\times10^{-6}$ mol dm^{-3}) and the mixture was stirred vigorously and sonicated until a clear viscous fluid was obtained. The fluid was poured into a petri dish with a diameter of 5 cm and was evaporated for 12 h in dark under air. The weights of the as-prepared transparent PVP/CH_2Cl_2 gels conatined in the petri dish were measured constantly to ensure that the weights of the residual CH_2Cl_2 in the gels were controlled to be 4.0±0.5 g.

Preparation of PVP/CH_3OH gels containing Au2. The powder of PVP (6 g) was added to a CH_3OH solution (10 ml) of **Au2** (concentration $\sim 1\times10^{-5}$ mol dm^{-3}) and the mixture was stirred vigorously and sonicated until a clear viscous fluid was obtained. The fluid was poured into a petri dish with a diameter of 5 cm and was evaporated for 72 h in dark under air. The as-prepared transparent PVP/CH_3OH gel contained residual CH_3OH (2.0 g).

Preparation of PVP/H_2O gels containing Au2. The powder of PVP (6 g) was added to a H_2O solution (10 ml) of **Au2** (concentration ~1×10^{-5} mol dm^{-3}) and the mixture was stirred vigorously and sonicated until a clear viscous fluid was obtained. The fluid was poured into a petri dish with a diameter of 5 cm and was evaporated for one week in dark under air. The as-prepared transparent PVP/H_2O gel contained residual H_2O (1.5 g).

Procedure of photo-writing and self-erasing of the phosphorescent images in the PVP gels. For each of the photo-writing processes, the optical power density (OPD) of the 365 nm UV torch was checked with the CEL-NP2000 optical power meter. A petri dish containing PVP/CH_2Cl_2/Pt(OEP) gels with a diameter of 5 cm was placed upside down and then a stencil with pierced patterns was putted on the surface of the petri dish. The red emission from gel could be observed in 5−10 s upon irradiated by using a 365 nm UV torch from a distance of around 3 cm in dark. Then the stencil was removed from the surface of petri dish and the brightly red-emissive pattern was visualized using a portable 365 nm UV lamp from at a distance larger than 20 cm (optical power density less than 0.4 mW cm^{-2}). Also included in Supporting Information are the videos depicting the writing processes. The emissive images remained in the gel for up to 140 min and the exact time duration for self-erasing by diffusional oxygen quenching depended on the viscosity average molecular weight of PVP (Fig. S8 and Fig. S9). A second pattern can be written into the gel immediately after the phosphorescent images in the gel became invisible to the naked eyes under the portable 365 nm UV lamp. We repeated the photo-writing, self-erasing and photo-rewriting cycles for over ten times in a single piece of PVP/CH_2Cl_2 gel. The procedure of photo-writing and self-erasing of the phosphorescent images in the PVP/CH_3OH/**Au2** gels and PVP/H_2O/**Au2** gels were the same as in the PVP/CH_2Cl_2 gels, except that the time for photo-writing was 1 min and 3 min, respectively. The optical power densities of UV torch and the UV lamp were checked with the CEL-NP2000 optical power meter before each of the photo-writing and visualizing processes.

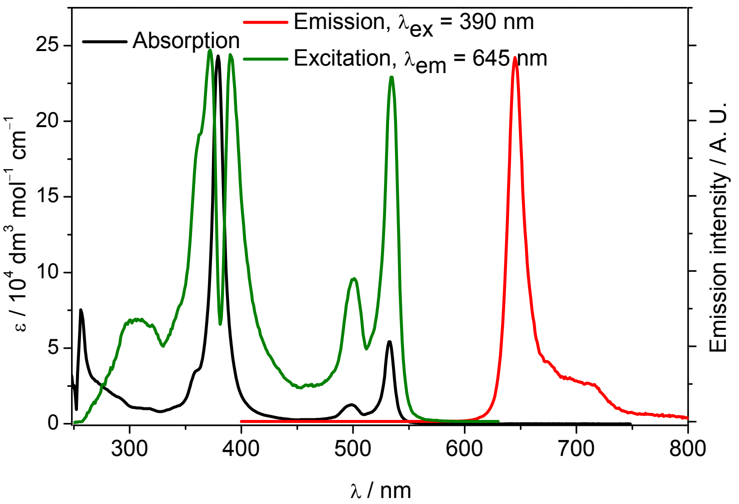


Fig. S1 Absorption, emission and excitation spectrum of a nitrogen-bubbled NMP solution of Pt(OEP) (concentration ~1.0×10^{-5} mol dm^{-3}) at 298 K.

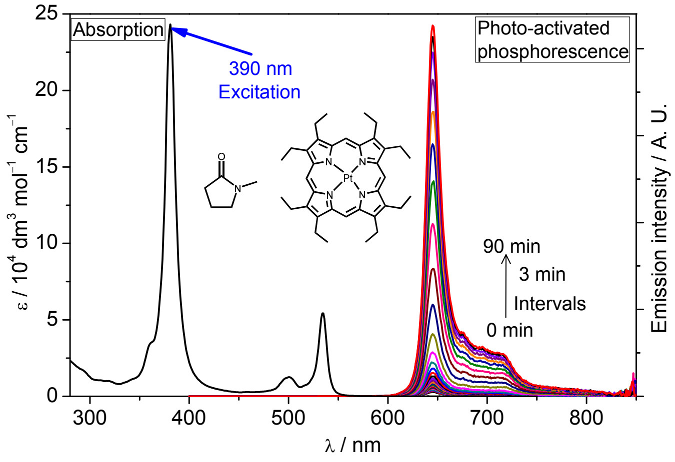


Fig. S2 Absorption spectrum and emission traces of an *aerated* NMP solution of Pt(OEP) (concentration ~ 1.0×10^{-5} mol dm^{-3}) upon continuous excitation at 390 nm at 298 K.

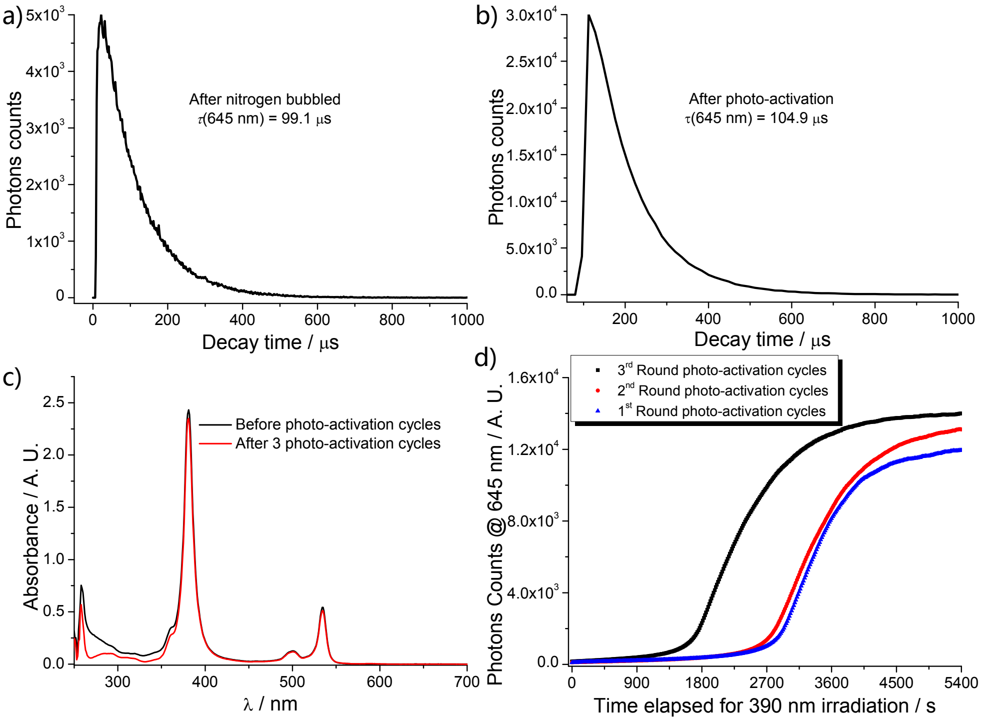


Fig. S3 Emission decay curves of Pt(OEP) recorded at 645 nm in NMP solutions (concentration ~ 1.0×10^{-5} mol dm^{-3}) deoxygenated by nitrogen-bubbled (a) and by photo-activation (b); (c) Absorption spectra of Pt(OEP) in an aerated NMP solution before and after photo-activation cycles; (d) Plots of photon counts at 645 nm against time elapsed for an aerated NMP solution containing Pt(OEP) (~1.0×10^{-5} mol dm^{-3}) upon 390 nm excitation in three photo-activation cycles.

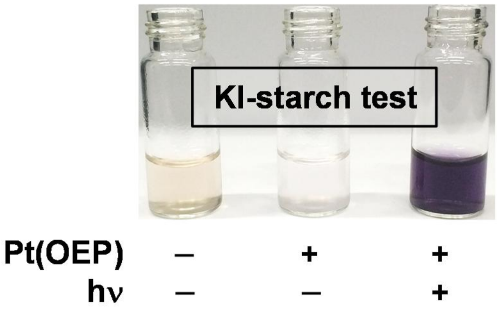


Fig. S4 KI-Starch test for qualitative analysis of the oxidized products in NMP solutions of Pt(OEP) after 365 nm photo-irradiation under air: NMP (0.1 mL), Pt(OEP) (1.0×10^{-5} mol dm^{-3}), saturated aqueous solution of starch (1.4 mL), and KI (0.1 mol dm^{-3}), where applicable. hν means that the solution was irradiated with 365 nm UV torch and then exposed to air for ten cycles. This result revealed that the mechanism of photochemical deoxygenation in NMP is likely peroxides.

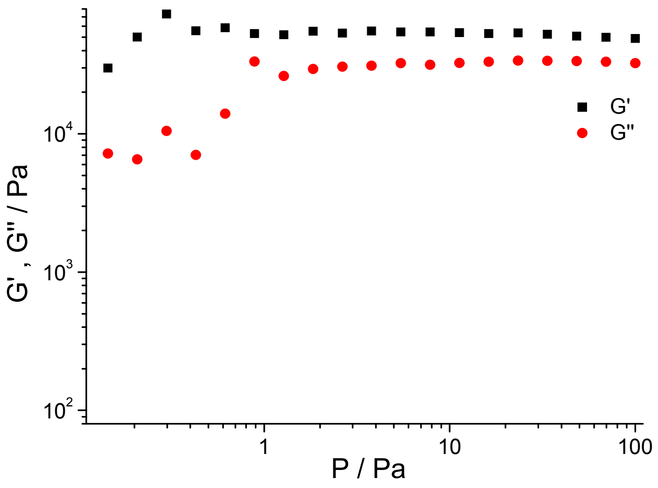


Fig. S5 Plots of storage modulus (G′) and loss modulus (G″) against applied shear stress on the PVP/CH_2Cl_2 gel. The measurement shear frequency was fixed at 1 Hz.

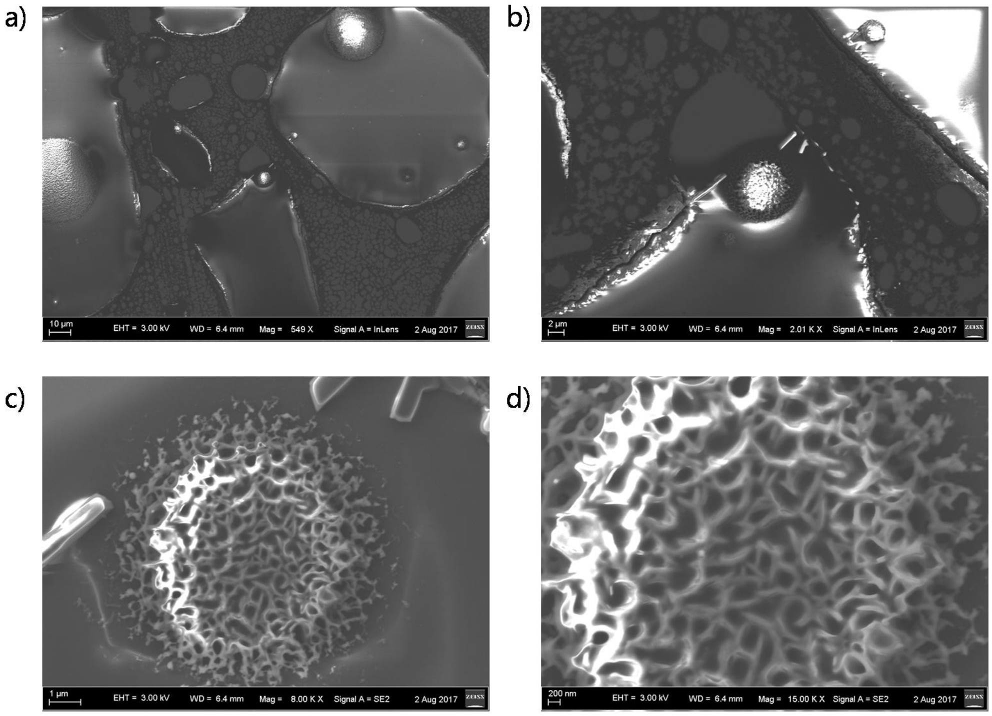


Fig. S6 SEM micrographs of a dried film of the PVP/CH_2Cl_2 gel in length scales of (a)10 μm; (b) 2 μm; (c) 1 μm and (d) 200 nm.

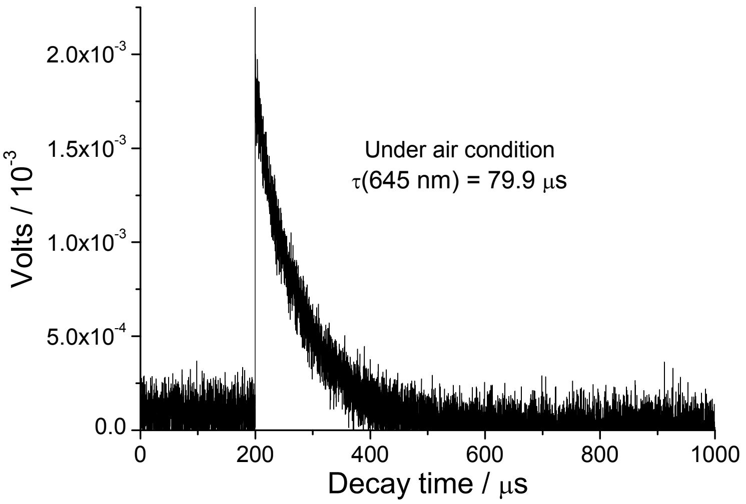


Fig. S7 Emission decay curves of Pt(OEP) recorded at 645 nm in PVP/CH_2Cl_2 (concentration ~ 1.0×10^{-5} mol dm^{-3}) under air and after photo-activation.

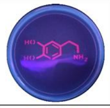
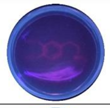
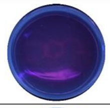
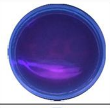
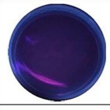
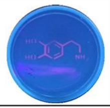
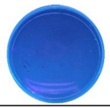
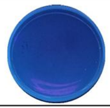
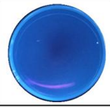
Viscosity average molecular weight of PVP	Time elapsed for self-erasing photo-written phosphorescent images / min							
	0	20	40	60	80	100	120	140
58 kDa (K29-32)								
40 kDa (K30)								
24 kDa (K23-27)								
10 kDa (K15)								
0.8 kDa (K17)								

Fig. S8 Time needed for self-erasing a photo-written phosphorescent image in the PVP/CH_2Cl_2 was largely proportional to the viscosity average molecular weight of the PVP used for gel preparation. Note that the concentration of Pt(OEP) was fixed at concentration ~1.0×10^{-5} mol dm^{-3}.

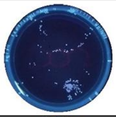
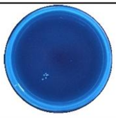
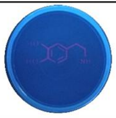
Viscosity average molecular weight of PVP	Time elapsed for self-erasing photo-written phosphorescent images / min			
	0	20	40	60
58 kDa (K29-32)				
40 kDa (K30)				
24 kDa (K23-27)				
10 kDa (K15)				
0.8 kDa (K17)				

Fig. S9 Time needed for self-erasing a photo-written phosphorescent image in the PVP/CH_2Cl_2 was largely proportional to the viscosity average molecular weight of the PVP used for gel preparation. Note that the concentration of Pt(OEP) was fixed at concentration ~5.0×10^{-6} mol dm^{-3}.

Fig. S10 The photo-writing, self-erasing, and photo-rewriting on a single piece of PVP(K17)/CH_2Cl_2 gel containing Pt(OEP) (concentration ~1.0×10^{-5} mol dm^{-3}) for 12 times (self-erasing time intervals for each of the imaging process was about 1 h).

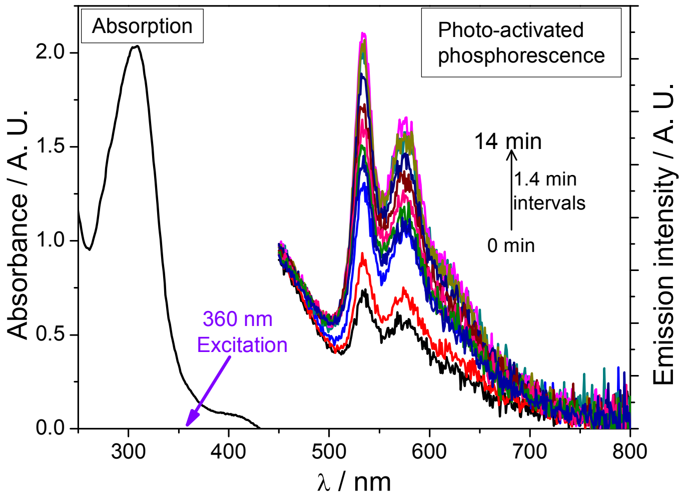


Fig. S11 Absorption spectrum and emission traces of an aerated PVP/H_2O gel of **Au2** (concentration ~1.0×10^{-4} mol dm^{-3}) upon continuous excitation at 360 nm.

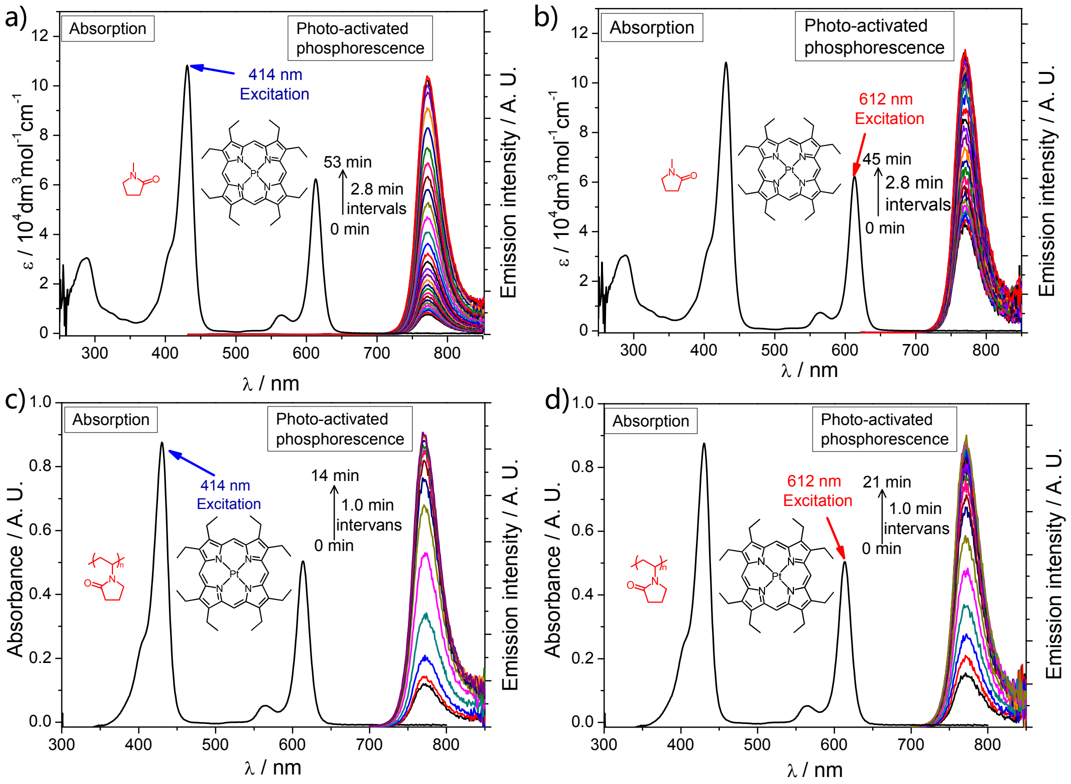


Fig. S12 Absorption spectra and emission traces of aerated NMP solutions of Pt(TPBP) (concentration ~1.0×10^{-5} mol dm^{-3}) upon continuous excitation (a) at 414 nm and (b) at 612 nm; Absorption spectrum and emission traces of a PVP/CH_2Cl_2 gel containing Pt(TPBP) (concentration ~1.0×10^{-5} mol dm^{-3}) under air upon continuous excitation (c) at 414 nm and (d) at 612 nm.