Electronic Supplementary Information for

Platinum porphyrin/3-(trimethoxysily)propylmethacrylate functionalized flexible PDMS micropillar arrays as optical oxygen sensors

Yongyun Mao[a,b], Qian Zhao[b], Tingting Pan[a,b], Jiayan Shi[b], Shimei Jiang[c], Meiwan Chen[d], Bingpu Zhou[a※], Yanqing Tian[b※]

[a]Institute of Applied Physics and Materials Engineering, University of Macau, Avenida da Universidade, Taipa, Macau, China. E-mail: bpzhou@umac.mo

[b]Department of Materials Science and Engineering, South University of Science and Technology of China, No. 1088, Xueyuan Rd., Xili, Nanshan District, Shenzhen, Guangdong, 518055, China. E-mail: tianyq@sustc.edu.cn

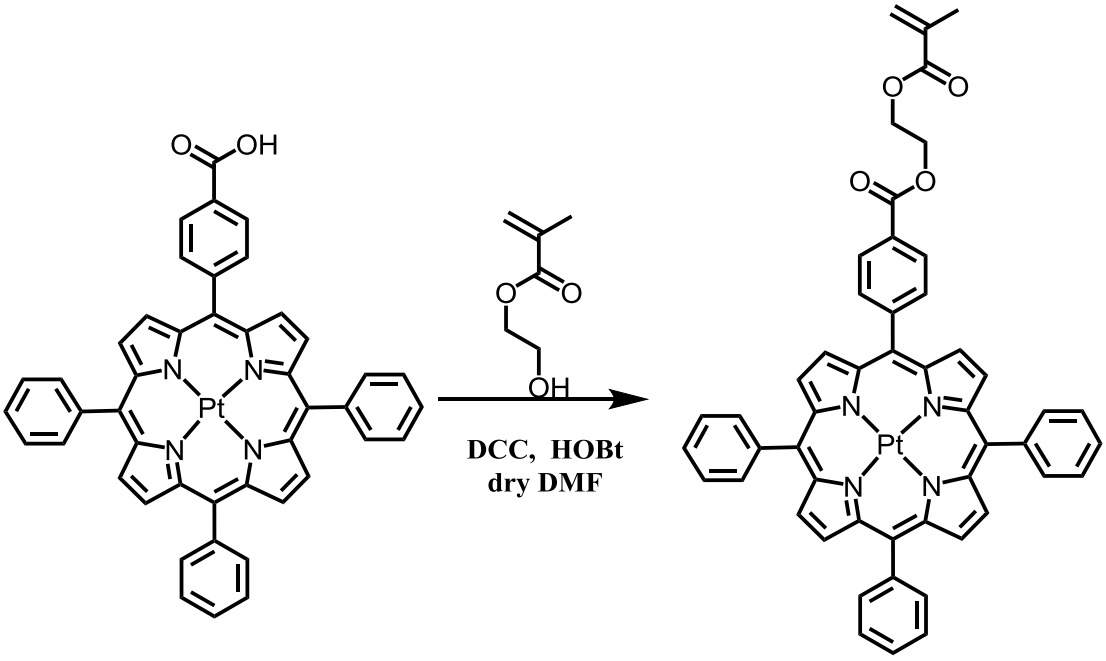
[c]Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun 130012, PR China

[d]State Key Laboratory of Quality Research in Chinese Medicine, Institute of Chinese Medical Sciences, University of Macau, Avenida da Universidade, Taipa, Macau, China

Experimental Section

Synthesis of the PtTPP and PtTPP/TPMA copolymer

PtTPP-pendant monomer was synthesized by Obata et al.'s method.[1] Platinum(Ⅱ) ion was inserted into 5-(4-methoxycarbonylphenyl)-10,15,20- tetraphenylporphyrin via heating at 180 ℃ with $K_2[PtCl_4]$ in a mixture of AcONa and AcOH to give 5-(4-methoxycarbonylphenyl)-10,15,20-triphenylporphinato platinum(II) as a deep red. After saponification of the methyl ester, the esterification of 5-(4-carboxylphenyl)-10,15,20-triphenylporphinato platinum(II) with 2-hydroxyethyl methacrylate (HEMA) was carried out with dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole as condensing reagents (Scheme S1). The crude product was purified by silica gel column chromatography, followed by recrystallization from CH_2Cl_2-MeOH, to afford PtTPP-pendant monomer as a deep red powder. The structure of compound PtTPP-pendant monomer was confirmed by ^{1}HNMR (Fig S 2).[1] Poly (PtTPP-co-TPMA) copolymer was synthesized by free radical polymerization of PtTPP (0.65 mg) and TPMA (650 mg) initiated by AIBN (10 mg) in 10 mL tetrahydrofuran (THF). Polymerization was carried out in absolute THF at 70 ℃ for 24 h under nitrogen atmosphere. The products were then purified by four dissolution/precipitation cycles from acetone into hexane and dried in vacuum overnight at 50 ℃.



Scheme S1 Synthesis of PtTPP-pendant monomer

Characterization of the PtTPP/TPMA-PDMS-MPAs film and oxygen detection

Fourier-transform infrared (FTIR) spectra were collected on a Nicolet spectrophotometer using KBr pellets. The ^{1}HNMR spectra were recorded on a Bruker AVANCE AV 400 spectrometer in $CDCl_3$ with tetramethysilane as the internal standard. The apparent morphology of the 3D PtTPP/TPMA-PDMS-MPAs film was characterized by scanning electron microscope (SEM). A HORIBA Fluoromax-4 spectrofluorophotometer was used for fluorescence measurements. The samples were excited at 405 nm with slit width of 3 nm and emission slit width of 3 nm for entrance and exit slit. Oxygen and nitrogen were mixed at different concentration using gas flow meters. All measurements were performed at room temperature.

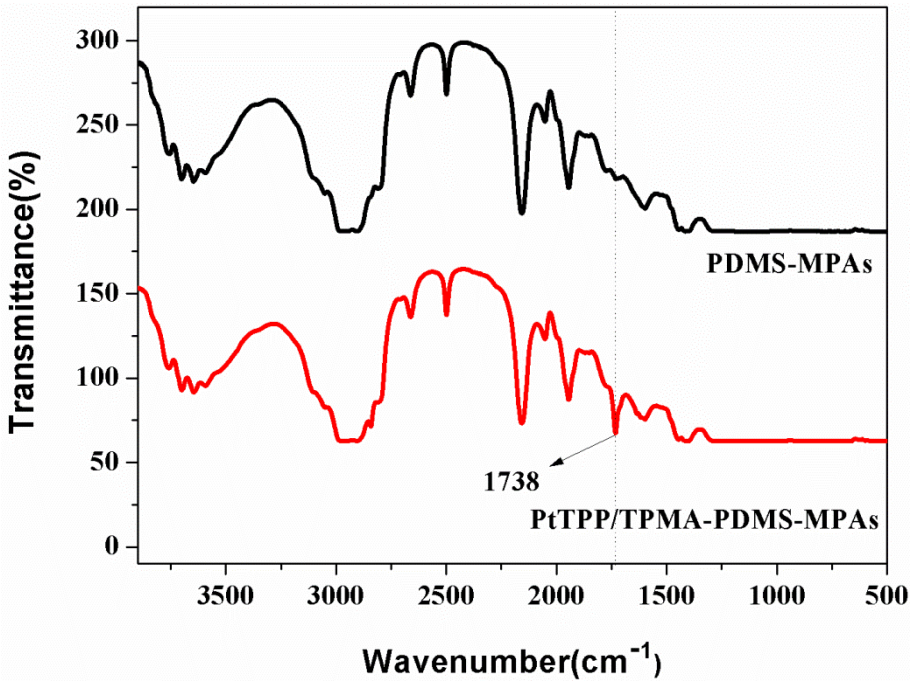


Fig. S1 FTIR spectra of PDMS-MPAs and the functionalized PtTPP/TPMA-PDMS-MPAs.

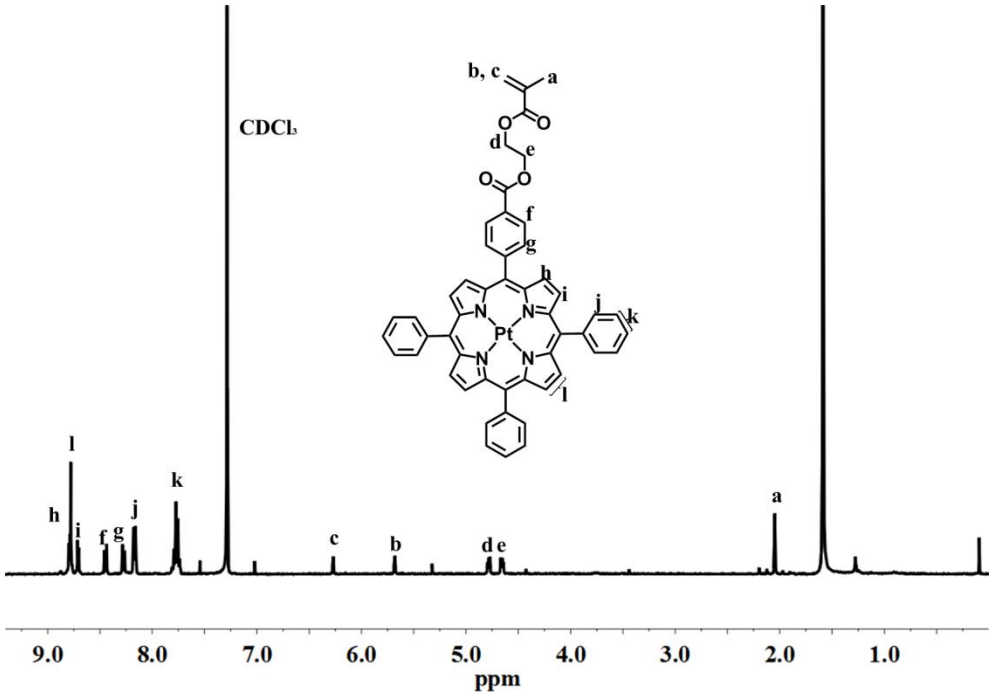


Fig. S2 ^{1}HNMR spectrum of PtTPP-pendant monomer

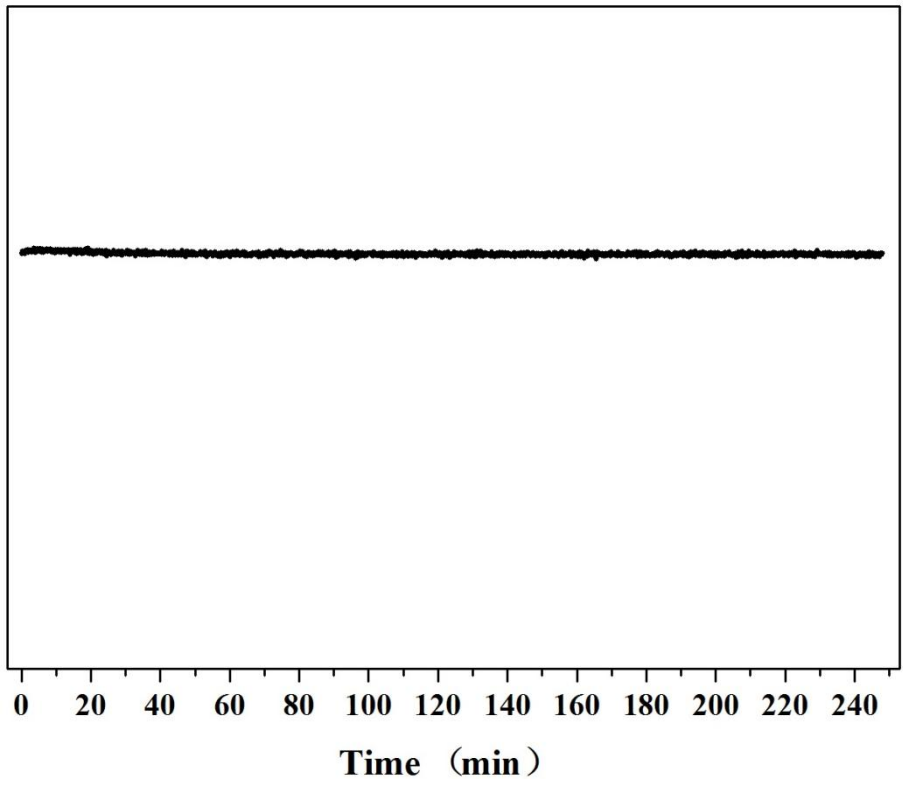


Fig. S3 Photostabilities of PtTPP/TPMA-PDMS-MPAs film in air atmosphere with 4 h of exposure to the LED lamp (λ_{ex}=405 nm, λ_{em}=660 nm, T=25 ^{o}C).

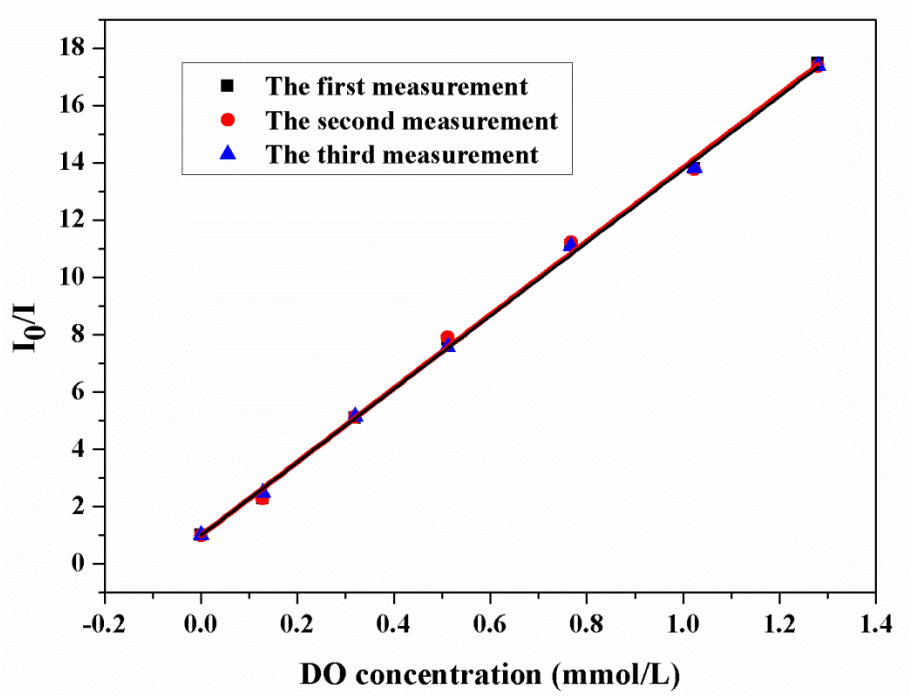


Fig. S4 The Stern-Volmer plot of the PtTPP/TPMA-PDMS-MPAs film in solutions.

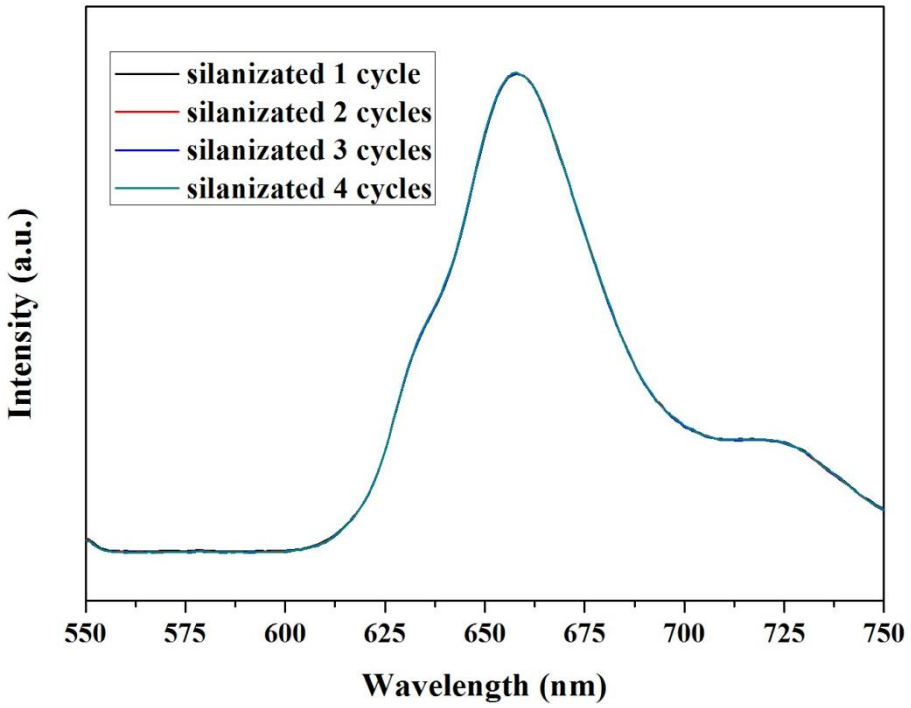


Fig. S5 The fluorescence intensity of the PtTPP/TPMA-PDMS-MPAs film in atmospheric conditions (silanizated 1 cycle, 2 cycles, 3cycles and 4 cycles).

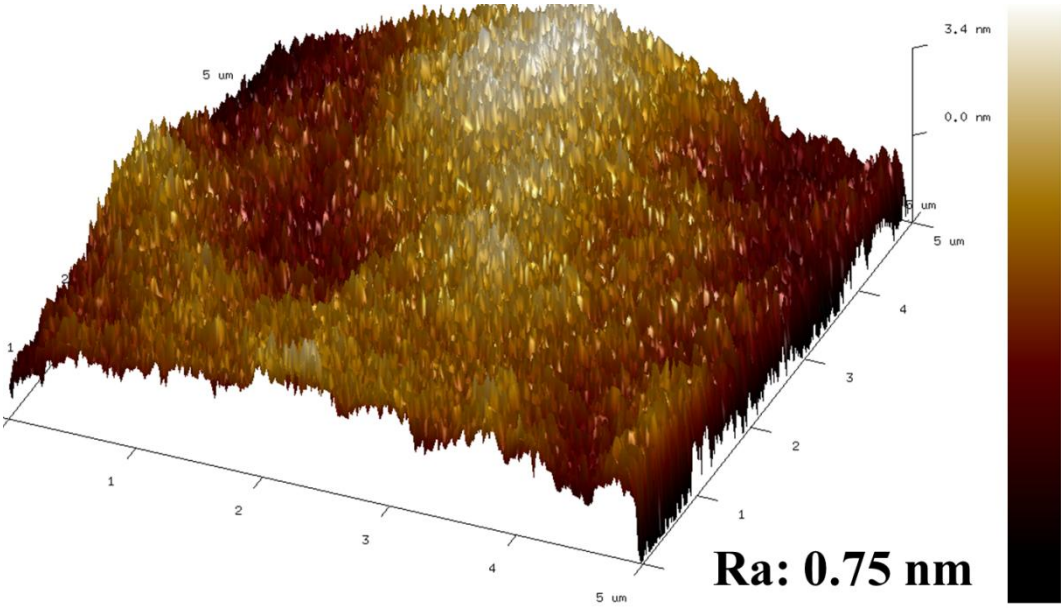


Fig. S6 AFM image of OSP film on PDMS-MPAs surface.

References

1. M. Obata, Y. Tanaka, N. Araki, S. Hirohara, S. Yano, K. Mitsuo, K. Asai, M. Harada, T. Kakuchi and C. Ohtsuki, *J. Poly.Sci. Poly. Chem.* 2005, **43**, 2997-3006.