Electronic Supplementary Information for

A highly sensitive and fast-responding optical oxygen sensor based on POSS-contained hybrid copolymer film

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Experimental Section

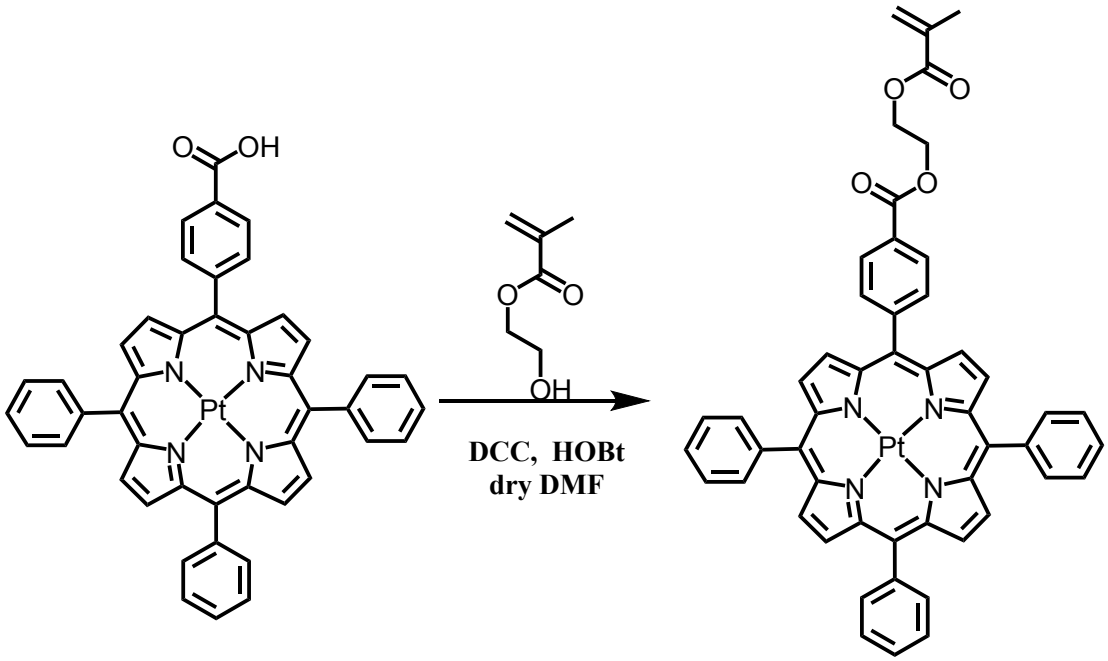
Synthesis of the PtTPP, TPMA-PtTPP, TPMA-PtTPP-POSS and PtTPP-POSS hybrid copolymers

PtTPP-pendant monomer (PtTPP) 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 °C with $K_2[PtCl_4]$ in a mixture of benzonitrile 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 1).[1]

Copolymer was synthesized by free radical polymerization of PtTPP, TPMA and POSS initiated by AIBN in 10 mL tetrahydrofuran (THF) by following a typical procedure for the synthesis of the copolymers. TPMA, PtTPP, POSS, AIBN and THF (10 mL) were added to a flask. The solution was degassed four times through a standard freeze-thaw process and then added to the reaction system under the protection of nitrogen. The polymerization was performed at 70 °C for 24 h. Then, the reaction mixture was precipitated into a large amount of cool cyclohexane. The products were then purified by four dissolution/precipitation cycles from acetone into cyclohexane and dried in vacuum overnight at 50 °C. The copolymers formulations with various TPMA and POSS were listed in Table S1. The hybrid copolymers were dissolved in acetone and a solution of 4 mg/mL were prepared. The polymer solutions were used to prepare the sensing films on the glass plate.

Table S1. The formulations of the copolymers

Sampes	THF (mL)	TPMA (mol/10^5)	PtTPP (mol/10^5)	POSS (mol/10^5)	POSS (wt %)
TPMA-PtTPP	10	100	0.034	0	0 %
TPMA-PtTPP-POSS-11%	10	97	0.034	3	10.52 %
TPMA-PtTPP-POSS-30%	10	90	0.034	10	29.70 %
TPMA-PtTPP-POSS-62%	10	70	0.034	30	61.97%
TPMA-PtTPP-POSS-79%	10	50	0.034	50	79.18 %
PtTPP-POSS	10	0	0.034	10	100 %



Scheme S1 Synthesis of PtTPP-pendant monomer

Characterization of the copolymer films and oxygen detection

The ^{1}H NMR spectra were recorded on a Bruker AVANCE AV 400 spectrometer in $CDCl_3$ with tetramethlsilane as the internal standard. A HORIBA Fluoromax-4 spectrofluorophotometer was used for fluorescence measurements. The roughness of membrane was determined by using an atomic force microscopy (AFM) (Bruker, Dimension Icon). The roughness parameters of the membrane surface were assessed by software Nanoscope Analysis. The surface roughness parameters were reflected in terms of the average roughness (R_a). 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.

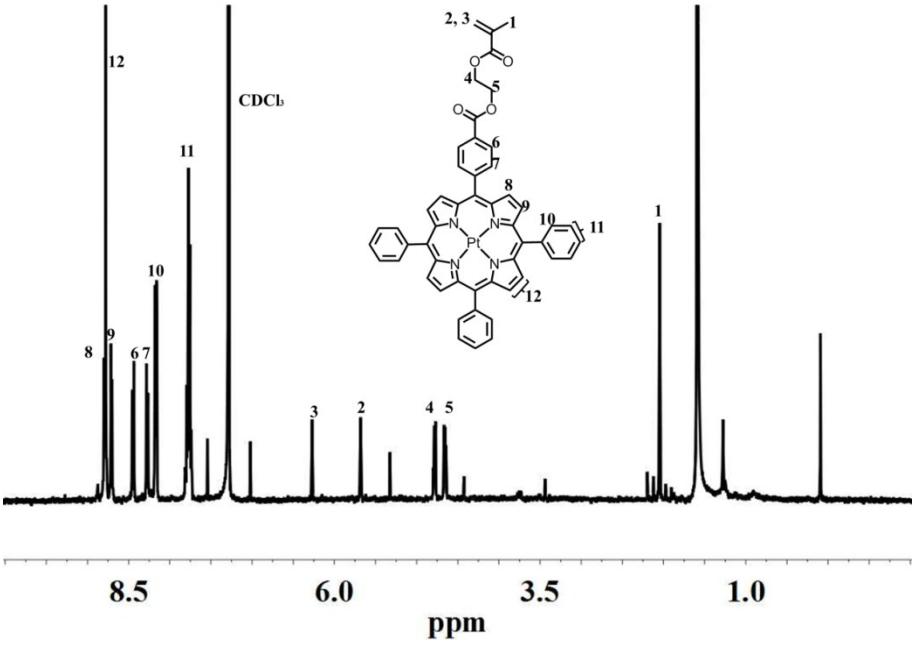


Fig. S1 ^{1}HNMR spectrum of PtTPP-pendant monomer

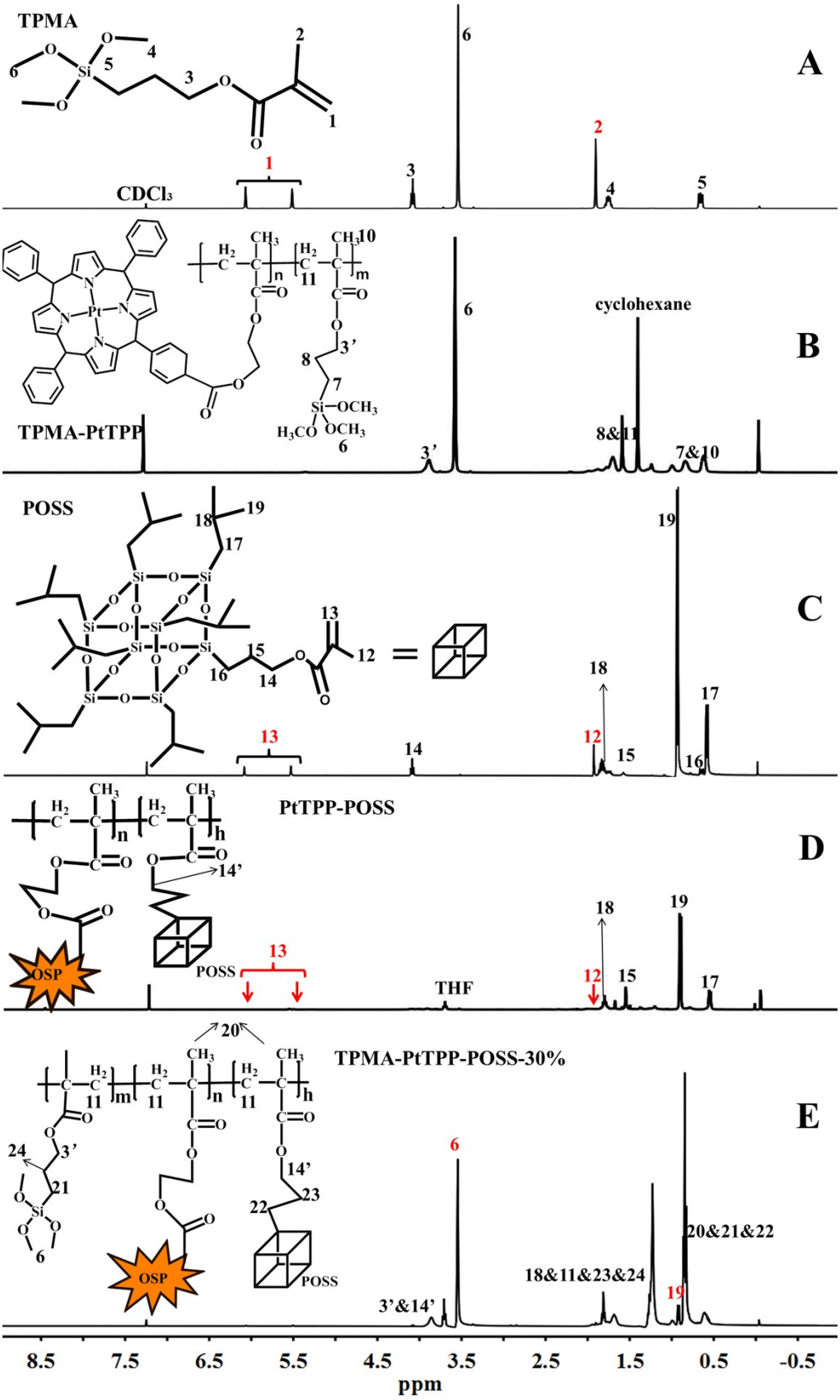


Fig. S2 [1]HNMR spectra of TPMA (A), TPMA-PtTPP (B), POSS (C), PtTPP-POSS (D) and TPMA-PtTPP-POSS (E). (OSP = Tetraphenylporphyrin-Pt(II))

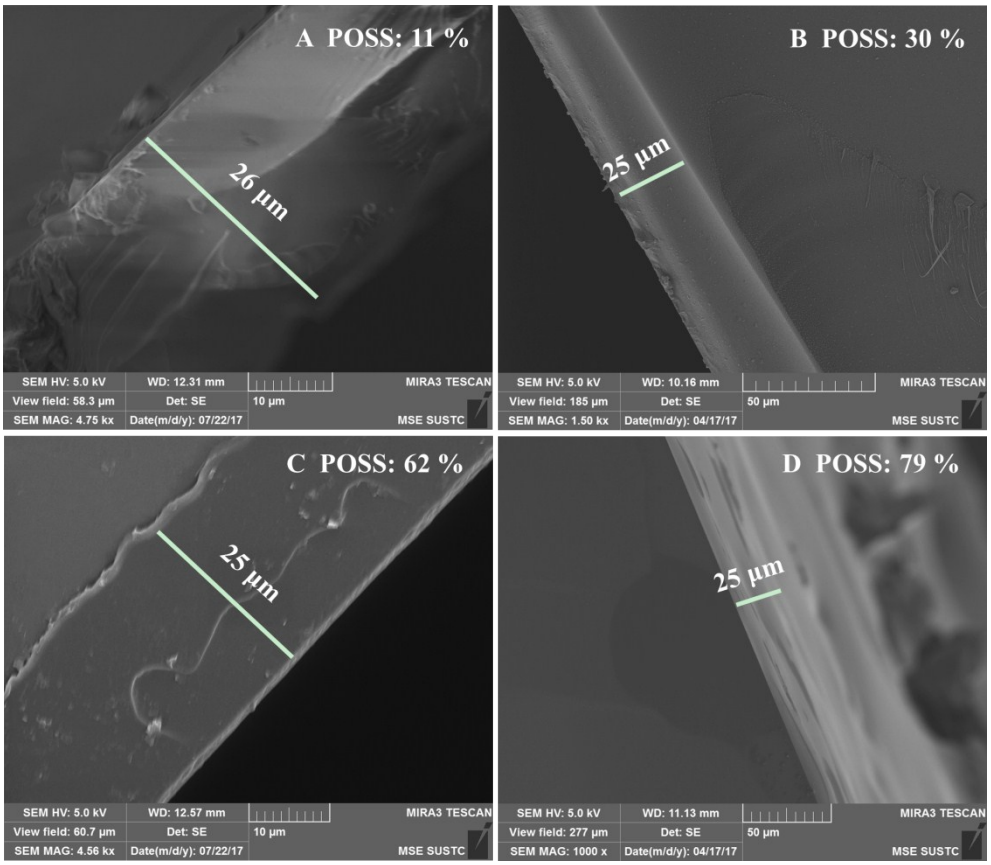


Fig. S3 Cross-sectional morphologies of the POSS-contained sensing films (TPMA-PtTPP-POSS-11%, 30%, 62% and 79%).

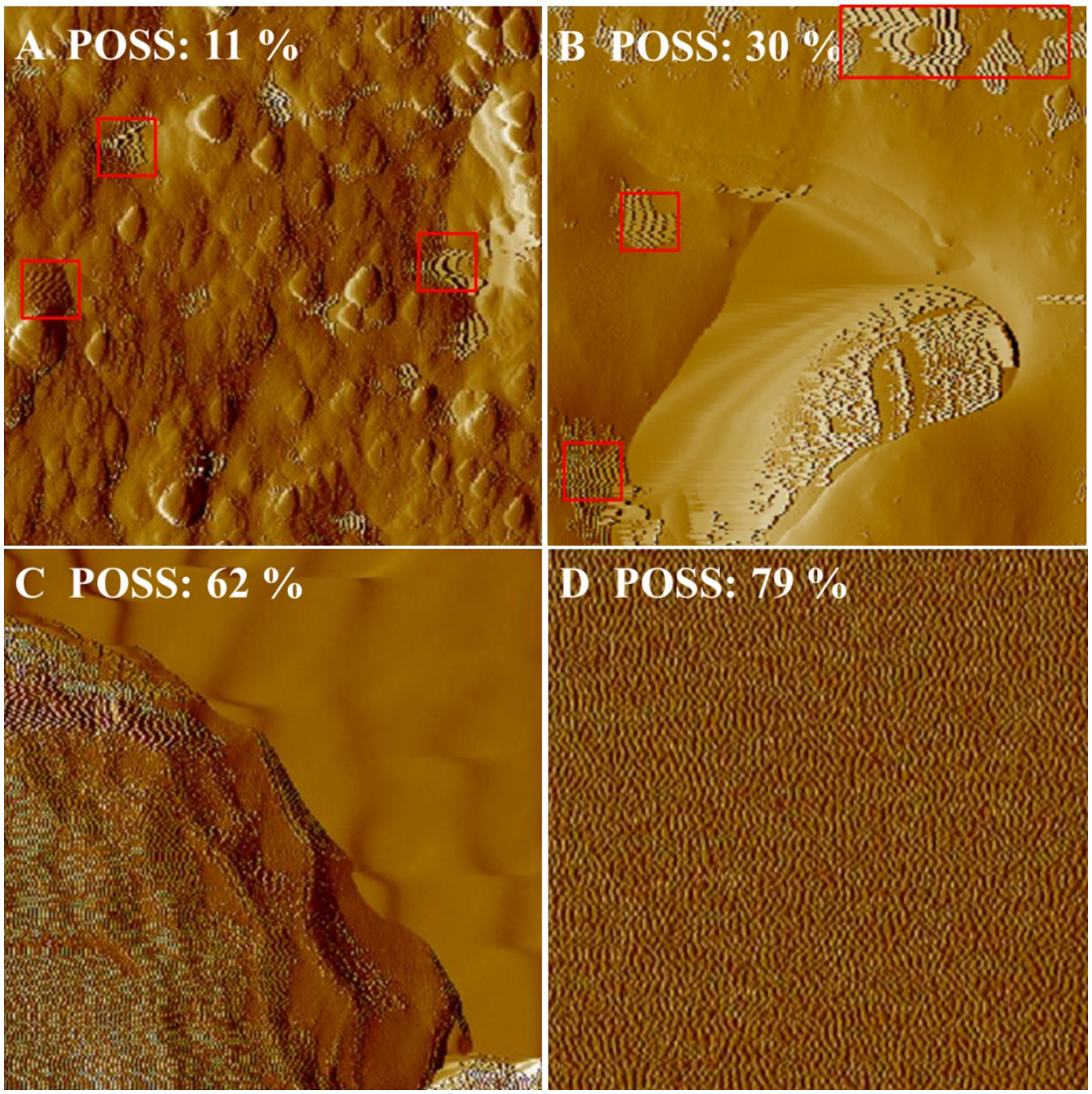


Fig. S4 AFM images of POSS-contained copolymer sensing film: (A) TPMA-PtTPP-POSS-11%; (B) TPMA-PtTPP-POSS-30%; (C) TPMA-PtTPP-POSS-62%; (D) TPMA-PtTPP-POSS-79%; (scale: 5μm*5μm).

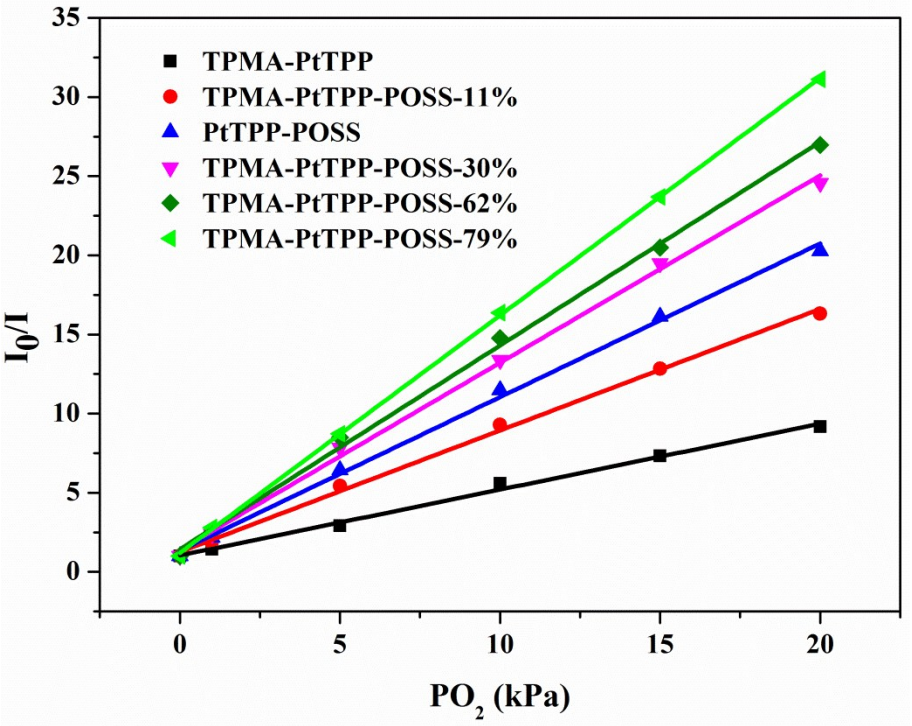


Fig. S5 Stern-Volmer plots for different copolymer sensing films at 25 °C with linear fit (pO_2: 0-21 kPa).

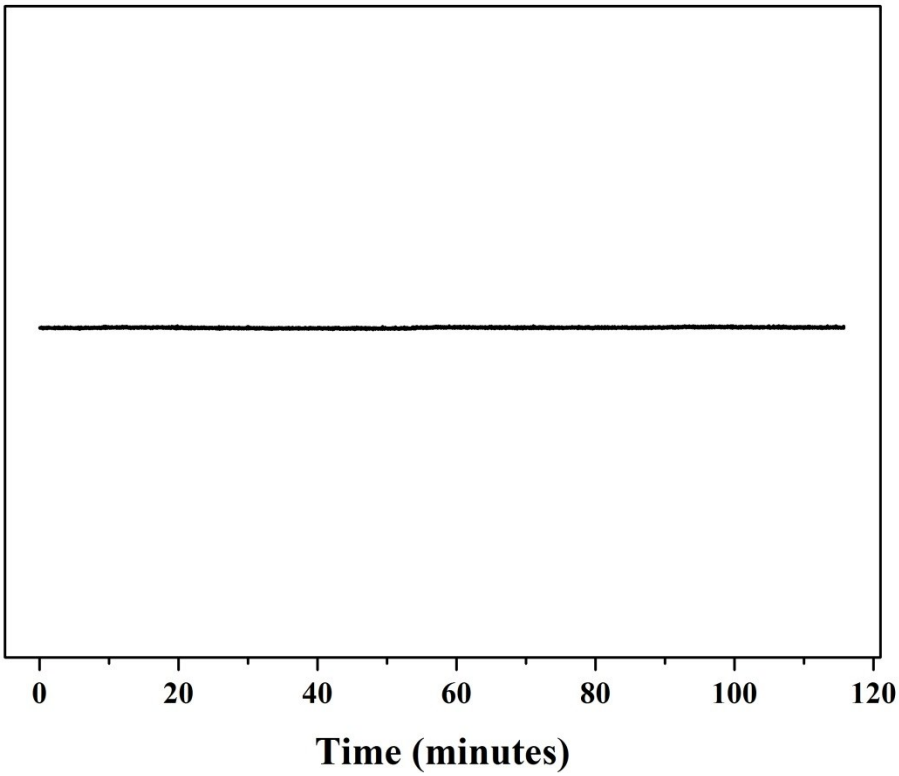


Fig. S6 Photostabilities of sensor film in air atmosphere with 2 h of exposure to the LED lamp (λ_{ex}=405 nm, λ_{em}=660 nm, T=25 ^{o}C).

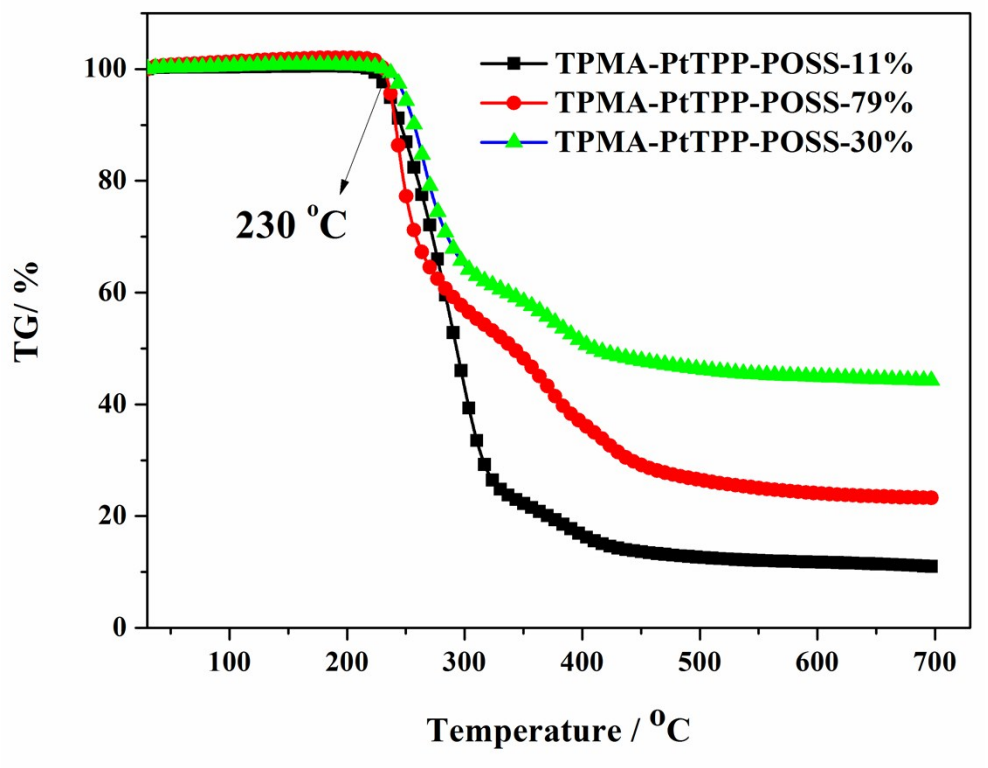


Fig. S7 TGA curves of POSS-contained copolymer sensing films.

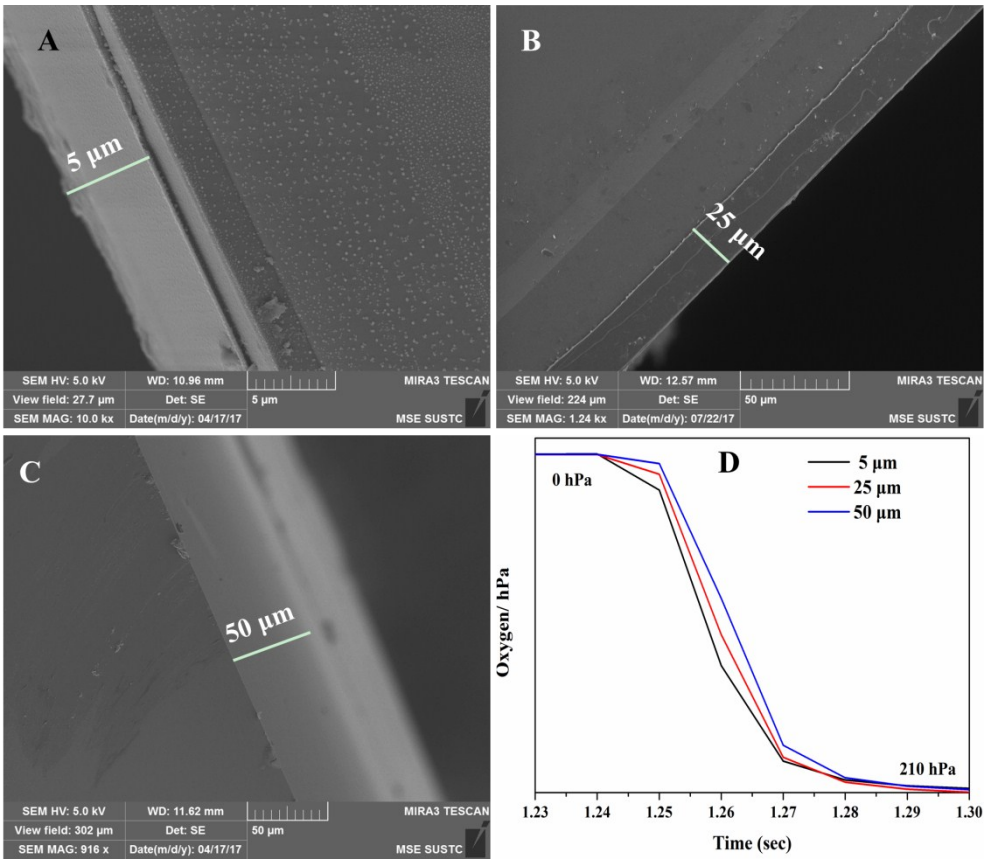


Fig. S8 SEM images of films with different thickness (A) 5 µm, (B) 25 µm, (C) 50 µm; (D) Influence of the sensor thickness on the response time in the same conditions (TPMA-PtTPP-POSS-62%).

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.