## **Supporting Information**

Reversible Photo-Chem-Electrotriggered Three-State Luminescence



Switching Based on Core-Shell Nanostructures

Fig. S1 IR absorption spectrum of Na-POM powder in KBr pellet.



**Fig. S2** CVs of ITO/PAH/Na-POMs@PYDS/PDDA electrode at different scan rates (from inner to outer): 0.01, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 v/s in 0.1 M HAc-NaAc buffer solution (pH = 4.5). Inset: plot of peak current (Ip) vs. scan rate.



**Fig. S3** Cyclic voltammograms of ITO/PAH/PYDS/PDDA electrode at 100 mVs<sup>-1</sup> in 0.1 M HAc-NaAc buffer solution (pH = 4.5).



**Fig. S4** 100 consecutive CV cycles of ITO/PAH/Na-POMs@PYDS/PDDA electrode at 100 mVs<sup>-1</sup> in 0.1 M HAc-NaAc buffer solution (pH = 4.5).



Fig. S5 Fluorescence switching of ITO/PAH/Na-POMs@PYDS/PDDA (A),

ITO/(PAH/Na-POMs@PYDS)<sub>3</sub>/PDDA (B), and ITO/(PAH/Na-POMs@PYDS)<sub>5</sub>/ PDDA (C) electrodes under alternating applied potential with 0 V (black lines) and -0.6 V (red lines). The experiments were performed in a 0.1 M HAc-NaAc buffer solution (pH = 4.5).



**Fig. S6** Luminescence spectra of the Na-POMs@PYDS film at applied different potential (from top to bottom: 0, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6 and -0.7 V).



Fig. S7 Absorption spectra of Na-POMs on ITO electrode at applied potential of -0.6 V and 0 V in 0.1 M HAc-NaAc buffer solution (pH = 4.5).



**Fig. S8** Luminescence spectra of the Na-POMs@PYDS film at applied potential of -0.6 V (red curve) and 0 V (black curve) for different duration.



**Fig. S9** I-t curves of the Na-POMs@PYDS film at applied potential of -0.6 V for different duration times.



**Fig. S10** Normalized fluorescence intensity against time for ITO/PAH/Na-POMs@ PYDS/PDDA electrode on application of -0.6 V (OFF state) and 0 V (ON state).