Electronic Supplementary Information for

A switchable electrochromism and electrochemiluminescence bifunctional sensor based on the electro-triggered isomerization of spiropyrane/layered double hydroxides

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Contents:

Experimental Section:

Reagents and materials: Poly (tert-butyl acrylate-co-ethyl acrylate-co-methacrylic acid) $[CH_2CH[CO_2C(CH_3)_3]_3]_x[CH_2CH(CO_2C_2H_5)]_y[CH_2C(CH_3)(CO_2H)]_z$ (PTBEM), and poly dimethyldiallylammonium chloride (PDDA, Mw=100000−200000) were purchased from Sigma-aldrich development Co. Ltd. 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran ($C_{20}H_{20}N_2O_4$, SP), Tetrabutylammonium perchlorate, 4-Benzylamine-7-nitrobenzofurazan (NBD) were purchased from J&K Chemical Reagents. Analytical grade $Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, acetonitrile and ethylene glycol monobutyl ether ($CH_3(CH_2)_3OCH_2CH_2OH$) were purchased from Beijing Chemical Co. Ltd. All other chemicals were analytical grade and used as received without further purification. Deionized water was used throughout the experimental process.

Synthesis of CoAl-NO_3-LDH nanoparticles: The synthesis of CoAl-LDHs colloidal suspension was prepared according to the separate nucleation and aging steps (SNAS) method reported by our group.[1-3]

Preparation of SP@PTBEM micelle: The SP@PTBEM micelle was synthesized by a liquid synthesis method. The SP was dissolved in ethylene glycol monobutyl ether (GME) solvent to give a solution (1 mg/mL); 2 mL of SP in GME solution was added dropwise into a 38 mL of PTBEM micelle solution (0.368 mg/mL, pH=7.0, adjusted by 0.1 M NaOH solution) with ultrasonic treatment, keeping the pH value of the final SP@PTBEM micelle at 7.0.

Preparation of (SP@PTBEM/CoAl-LDHs)$_n$ UTF electrode: The ITO glass substrate was first cleaned in ethyl alcohol for 30 min and then washed with pure water. The cleaned substrate was dipped into a PDDA solution (1.0 g/L) for 20 min, then thoroughly rinsed with

water and dried in air, so as to obtain a positively-charged surface. The pretreated substrate was immersed into the negatively-charged SP@PTBEM micelle for 10 min followed by washing and then treated with CoAl-NO_3-LDH nanoplatelets for another 10 min and washed thoroughly. The multilayer $(SP@PTBEM/CoAl\text{-}LDHs)_n$ UTFs were fabricated by the alternate deposition of SP@PTBEM micelle and LDHs nanoplatelets for *n* cycles.

For the enhancement of ECL, NBD (5 mM) and tetrabutyl perchlorate (0.1 M) were dissolved in acetonitrile as electrolyte.

For the Zn^{2+} detection, $Zn(NO_3)_2$ was dissolved in deionized water with the concentration of 10 μM, which was then dropped into acetonitrile with 0.1 M tetrabutyl perchlorate as electrolyte. The final concentration of Zn^{2+} was maintained at 1 μM.

Sample characterization: The fluorescence spectra were performed on a RF-5301PC fluorospectrophotometer. A Zeiss Supra 55 scanning electron microscope (the accelerating voltage applied was 20 kV) and NanoScopeIIIa atomic force microscope (AFM)were used to investigate the surface morphology of UTFs. X-ray diffraction (XRD) patterns of the films were recorded using a Rigaku 2500VB2+PC diffractometer using the Cu Kα radiation (λ= 1.541844 Å) at 40 kV and 50 mA with the step-scanned mode in 0.04° (2θ) per step and count time of 10 s/step in the range from 3 to 70°.The Zeta potential was performed on aMalvern ZEH-3600. A conventional three-electrode system was used, including amodified ITO glass as the working electrode, a platinum foil as the auxiliary electrode and a saturated Ag/AgCl electrode(0.799 V) as the reference electrode. The ECL signals were recordedby a MPI-B multifunctional chemiluminescence analytical system (Remax Electronic Co. Ltd, Xi'an, China) with the voltage of thephotomultiplier tube (PMT) set to 800 V.

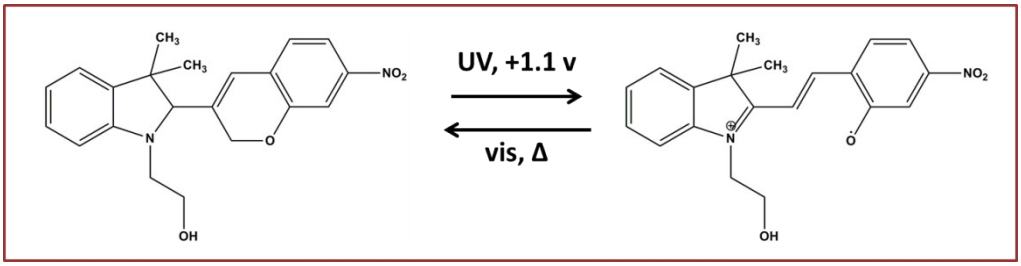

Figure S1. Schematic diagram of SP and MC induced by UV, 1.1 V and visible light/thermal treatment.

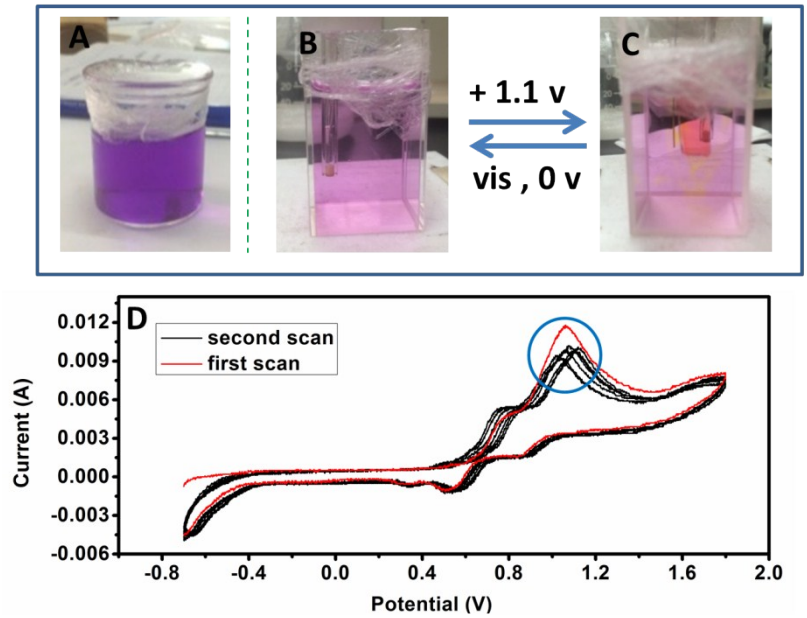

Figure S2. (A) A fresh SP solution and (B) after 120 sexposure to visible light; (C) SP solution in electrochemical cell during applied potential 1.1 V to the ITO electrode; (D) cyclic voltammograms curves of SP solution.

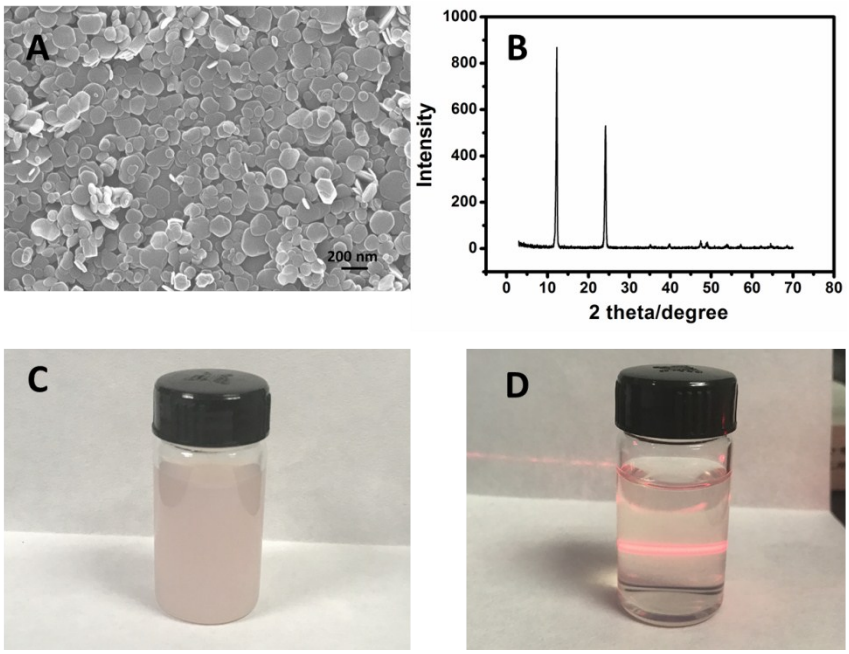

Figure S3. (A) SEM and (B) XRD of CoAl-LDHs nanoplatelets. Photographs of (C) initial and (D) dilute CoAl-LDHs nanoplatelets suspension.

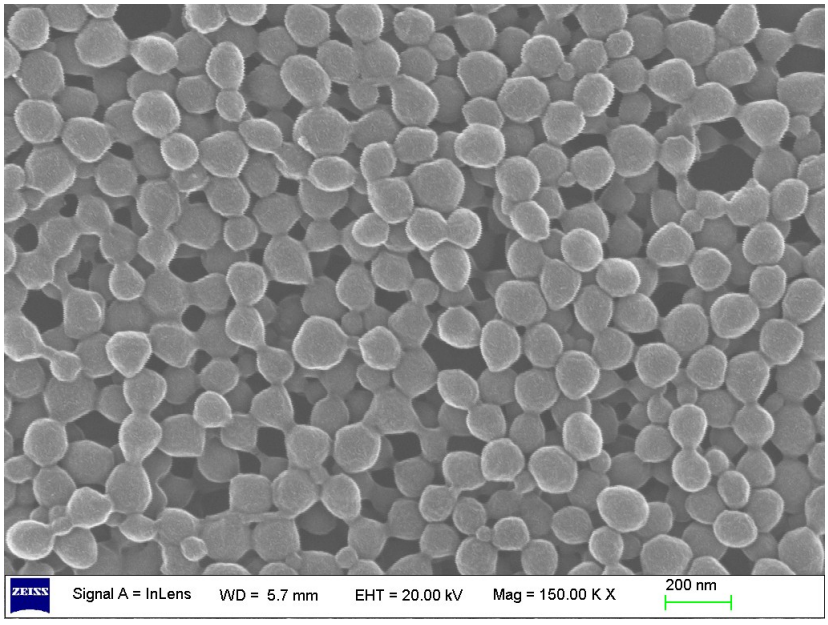

Figure S4. SEM image of SP@PTBEM micelles.

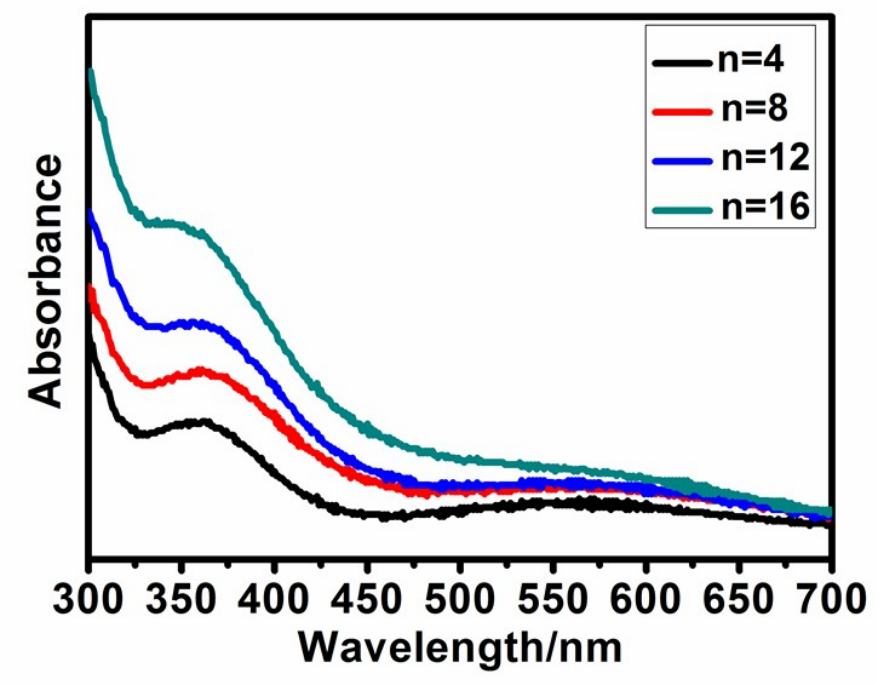

Figure S5. UV-vis absorption spectra of $(SP@PTBEM/CoAl\text{-}LDHs)_n$ UTF.

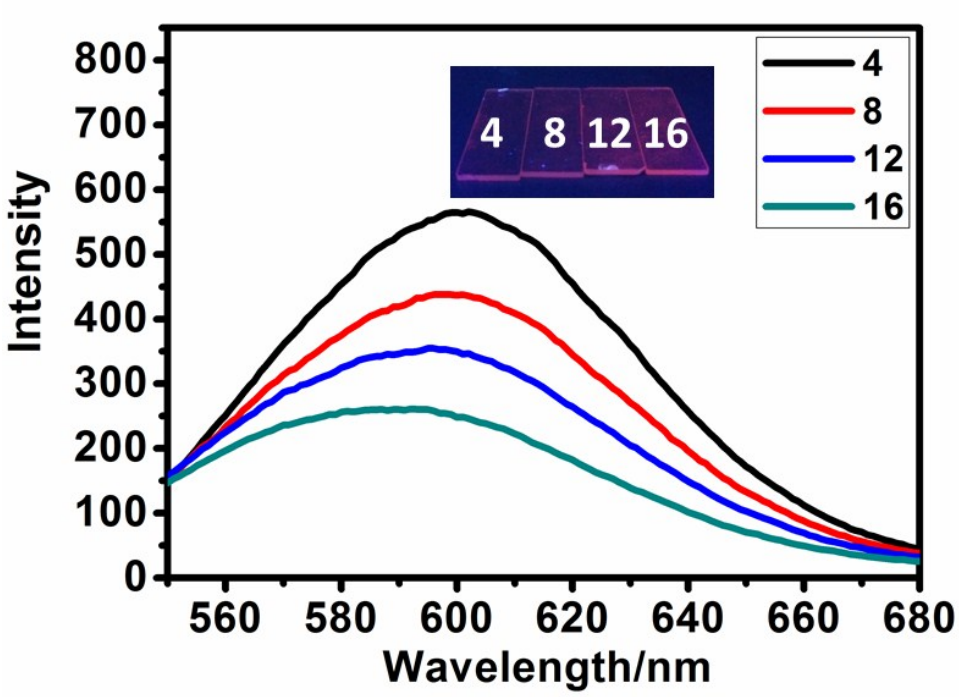

Figure S6. Fluorescent spectra of $(SP@PTBEM/CoAl\text{-}LDHs)_n$ UTF.

Table S1 Comparison of responsive time between SP/LDHs UTF in this work and previously reported systems

References	This work	*J. Am. Chem. Soc.* 2011, 133, 5453–5462	*Chem. Commun.* 2006, 28, 3016–3018	*Adv. Funct. Mater.* 2012, 22, 2425–2431	*J. Am. Chem. Soc.* 2012, 134, 16929−16932	*Chem. Commun.* 2008, 43, 5580–5582
Responsive time (s)	20	50	150	50	10	40

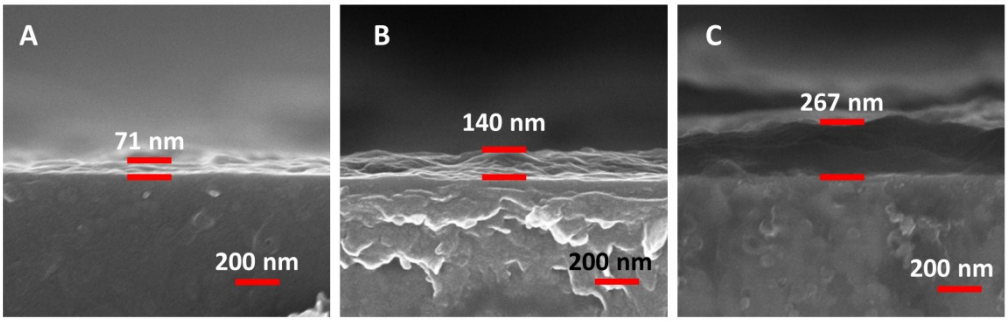

Figure S7. Side-view of SEM images for: (A) $(SP@PTBEM/CoAl\text{-}LDHs)_4$, (B) $(SP@PTBEM/CoAl\text{-}LDHs)_8$, (C) $(SP@PTBEM/CoAl\text{-}LDHs)_{16}$ UTF.

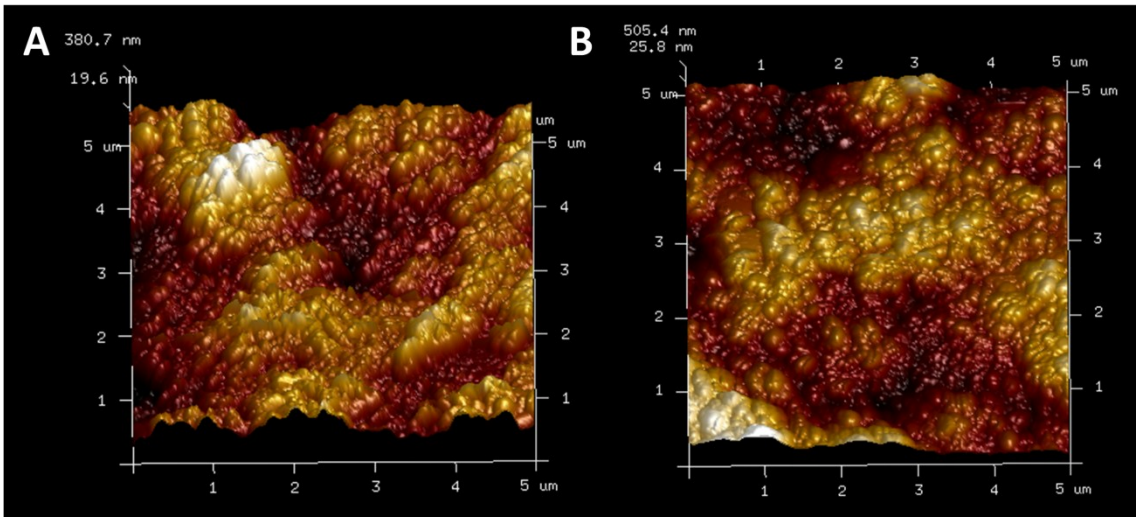

Figure S8. Tapping-mode AFM images of (A) electrochemistry-triggered $(SP@PTBEM/CoAl\text{-}LDHs)_{16}$ UTF and (B) after a further visible light irradiation.

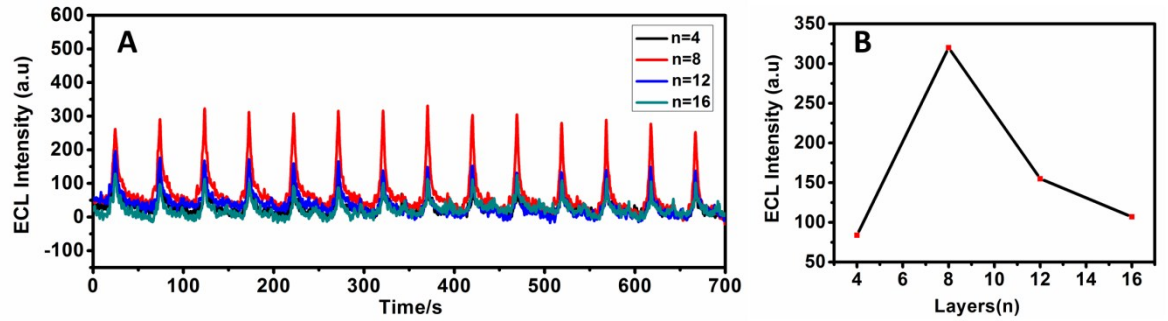

Figure S9. (A) ECL intensity of $(SP@PTBEM/CoAl\text{-}LDHs)_n$ UTFs (n=4, 8, 12, 16) in acetonitrile with 0.1 M tetrabutyl perchlorate as electrolyte; (B) ECL intensity as a function of bilayer number.

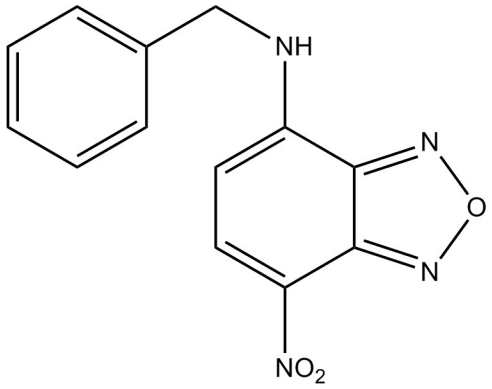

Figure S10. Molecular structure of NBD.

References:

1. Y. Zhao, F. Li, R. Zhang, D. G. Evans and X. Duan, *Chem. Mater.*, 2002, **14**, 4286-4291.

2. R. P. Bontchev, S. Liu, J. L. Krumhansl, J. Voigt and T. M. Nenoff, *Chem. Mater.*, 2003, **15**, 3669-3675.

3. Y. Zhou, D. Yan and M. Wei, *J. Mater. Chem. C*, 2015, **3**, 10099-10106.