

# Supporting Information

## Multistate Electrically Controlled Photoluminescence Switching

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## Part S1 Chemicals and Instrumentation

### Chemicals

Sodium citrate dihydrate, cadmium perchlorate hexahydrate, thioacetamide and *N,N*-dimethylselenourea were purchased from Alfa Aesar. Polyethyleneimine and (3-aminopropyl)trimethoxysilane were purchased from Sigma-Aldrich. Other chemicals are commercially available with the highest purity, and Milli-Q-deionized water was used for all the experiments.

### Methods

UV-vis spectra were collected using a U-4100 UV/vis spectrophotometer (HITACHI). Luminescence measurements were carried out on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc., France) with excitation and emission slit widths of 5 nm. Electroswitched luminescence experiments were performed with CHI860 electrochemical workstation (Shanghai Chenhua Instrument Corporation, China) and a Fluoromax-4 spectrometer using ITO working electrode (with a geometric area of  $\sim 1 \times 5$  cm) coated with CdSe@CdS QDs/POM thin film, an Ag/AgCl reference electrode (saturated KCl) and a Pt wire counter electrode.

## Part S2: Synthesis and the property of $P_8W_{48}$ POMs and citrate-stabilized CdSe@CdS QDs

**Synthesis of citrate-stabilized CdSe@CdS QDs.** Different-sized citrate-capped CdSe@CdS QDs were synthesized according to reference.<sup>S1</sup> 0.1 g of sodium citrate dihydrate (Aldrich) and 4 mL of  $4 \times 10^{-2}$  M cadmium perchlorate hexahydrate were added to 90 mL water, and the pH was adjusted to 9.0 with 0.5 M NaOH. After the solution had been bubbled with nitrogen for 10 min, 4 mL of  $1 \times 10^{-2}$  M *N, N*-dimethylselenourea was added, and the mixture was heated in a conventional 900 W (Sharp) microwave oven for 50 s. 4 mL thioacetamide solution ( $4 \times 10^{-2}$  M) was added into prepared CdSe NPs solution to synthesize CdSe@CdS core-shell NPs. The mixture was then heated in a sealed round-bottom flask inside a silicon oil bath to 70 °C for 24 h.

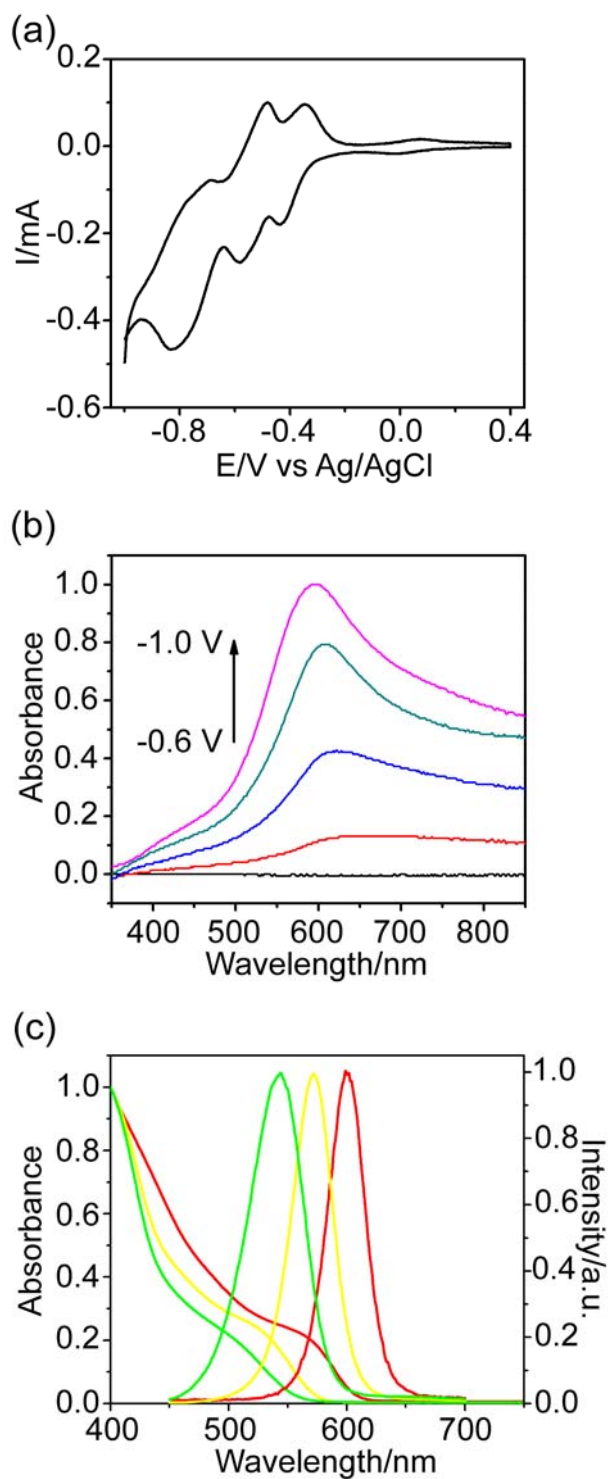
The CdSe@CdS QD solution had a rather strong emission at 600 nm, 571 nm and 546 nm, respectively. The diameters of these three QDs were estimated to be 5.51 nm (red QDs), 5.17 nm (yellow QDs) and 4.70 nm (green QDs) upon statistical measurement of NPs by their TEM images.

**Synthesis of  $P_8W_{48}$  POM.**  $K_{28}Li_5H_7P_8W_{48}O_{184} \cdot 92H_2O$  was synthesized according to literature procedures.<sup>S2</sup> The preparation of  $P_8W_{48}$  POMs followed a classic three-step pathway including assembly, partial disassembly and reassembly.

a) **Synthesis of  $K_{12}H_2[\alpha-P_2W_{12}O_{48}] \cdot 24H_2O$ .**  $K_{12}H_2[\alpha-P_2W_{12}O_{48}] \cdot 24H_2O$  was synthesized according to the literature method.<sup>S3</sup>  $(NH_4)_6[\alpha-P_2W_{18}O_{62}] \cdot 11H_2O$  (20.22 g, 4.33 mmol) and tris(hydroxymethyl)aminomethane (12.1 g, 0.1 mol) were

dissolved in 75 mL and 50 mL H<sub>2</sub>O, respectively. Two solutions were mixed and stirred for 40 minutes. NH<sub>4</sub>Cl (14.35 g, 0.27 mol) was then added and stirring continued for a further 5 minutes before addition of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (9.59 g, 0.1 mol in 50 mL H<sub>2</sub>O). A white precipitate began to form after ~ 15 minutes stirring. The precipitate was filtered and dried overnight in a dessicator.

b) **Synthesis of K<sub>28</sub>Li<sub>5</sub>H<sub>7</sub>P<sub>8</sub>W<sub>48</sub>O<sub>184</sub>·92H<sub>2</sub>O.** K<sub>12</sub>H<sub>2</sub>[P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>]·24H<sub>2</sub>O (28 g, 7.1 mmol) was dissolved in 1 L of a mixture of lithium chloride (0.5 mol), lithium acetate (0.5 mol), and acetic acid (0.5 mol) in water. After 5 minutes stirring, the solution was left to crystallize. After 1 day fine white radiating needles appeared, and crystallization continued for several days. The products were collected and dried overnight in a dessicator.

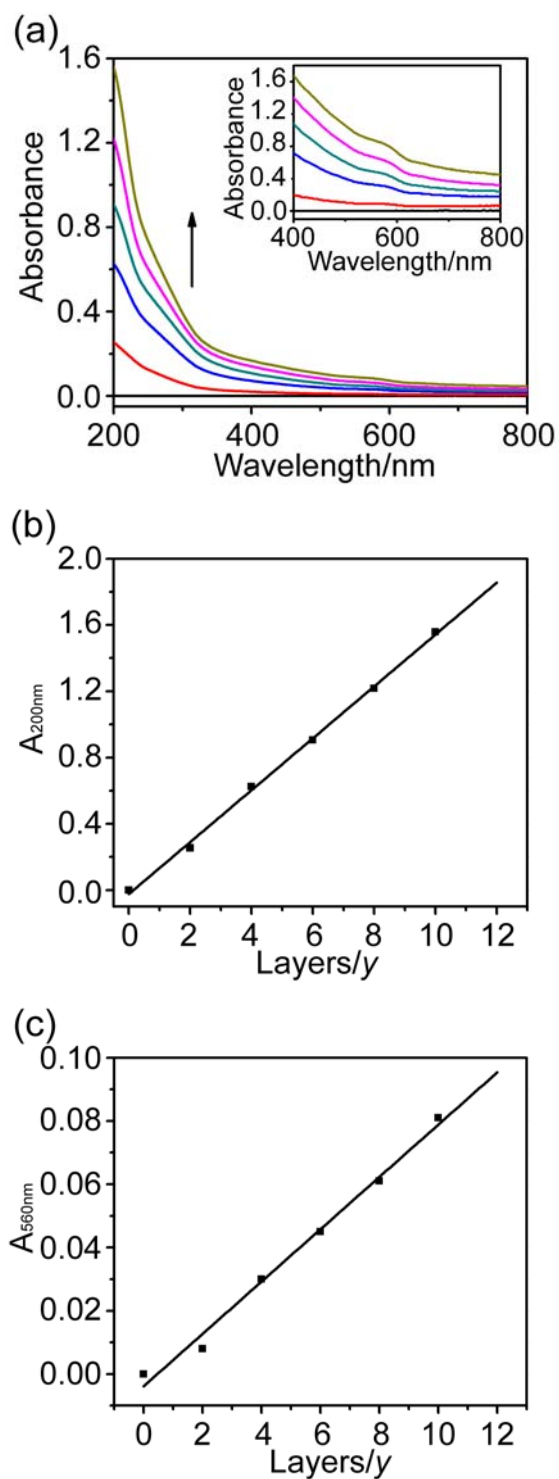


**Fig. S1** (a) CVs of 1 mM  $P_8W_{48}$  POMs in 0.10 M PBS (pH 7.4) at the ITO electrode. Scan rate:  $10 \text{ mV s}^{-1}$ . (b) UV-Vis spectra of 1 mM  $P_8W_{48}$  POMs at different potential. (c) UV-Vis spectra and photoluminescence spectra of different-sized citrate-stabilized CdSe@CdS QDs. The emission maxima of CdSe@CdS QDs are 600 nm (red curve),

571 nm (yellow curve) and 546 nm (green curve), and their average particle sizes are estimated to be 5.51 nm, 5.17 nm and 4.70 nm, respectively.

**Part S3. Fabrication of the hybridized nanostructured films of [(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>x</sub>/PEI/CdSe@CdS]<sub>y</sub>**

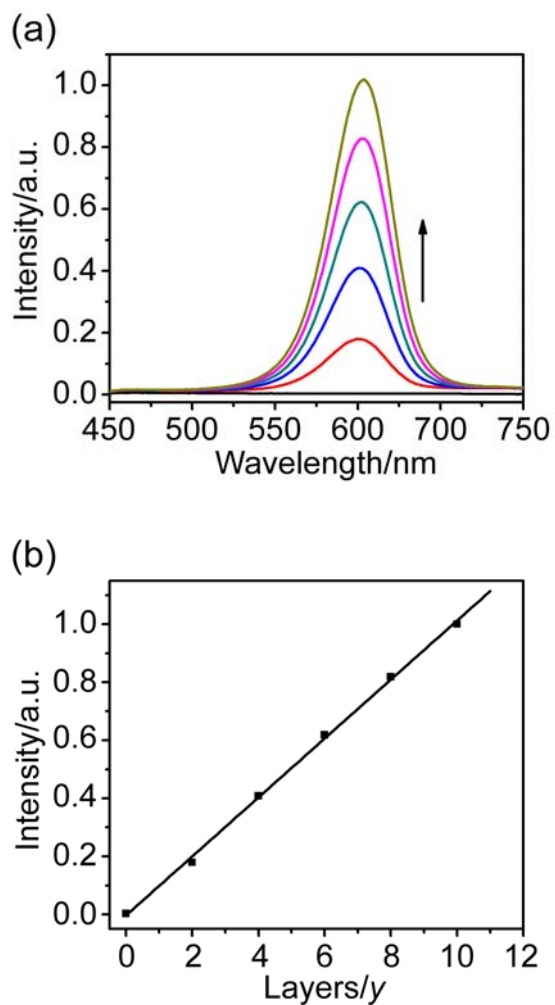
ITO-coated glass (on one side, about 30 Ω, 10 × 50 mm<sup>2</sup>) substrates were cleaned according to a literature procedure.<sup>S4, S5</sup> Before assembly, the cleaned ITO-coated glass electrodes were functionalized with (3-aminopropyl)trimethoxysilane to yield an amine-functionalized surface. Other substrates (glass or silicon) were immersed into the mixed solution (H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub> =1:3) at the temperature 70 °C. After 30 min, the substrates were picked and washed by deionized water and dried under N<sub>2</sub> flow. The [(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>x</sub>/PEI/CdSe@CdS]<sub>y</sub> films were alternatively deposited from 1 mg/mL PEI (Mw 50 000, Aldrich) solution, 1 mg/mL aqueous solution of P<sub>8</sub>W<sub>48</sub>, and 3.0 × 10<sup>-6</sup> M CdSe@CdS, using an immersion time of 5 min, and then rinsed with pure water and dried under N<sub>2</sub> flow.



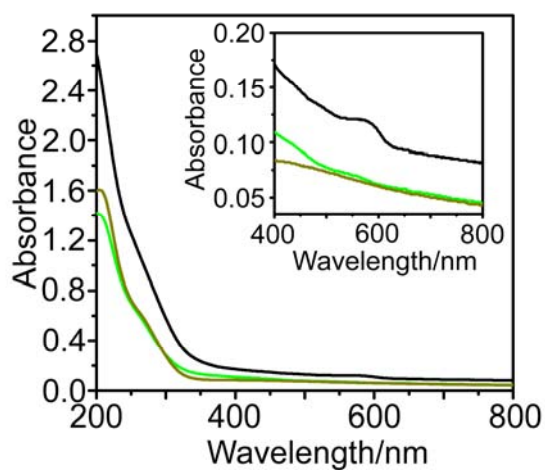
**Fig. S2** (a) UV-Vis absorption spectra of  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@\text{CdS}_{600}]_y$  multilayers as a function of the number of layers,  $y$ . (b) Relationship of the absorbance at 200 nm as a function of the number of layers,  $y$ . (c) Relationship of the



absorbance at 560 nm as a function of the number of layers,  $y$ , confirming linear and uniform thin-film growth.

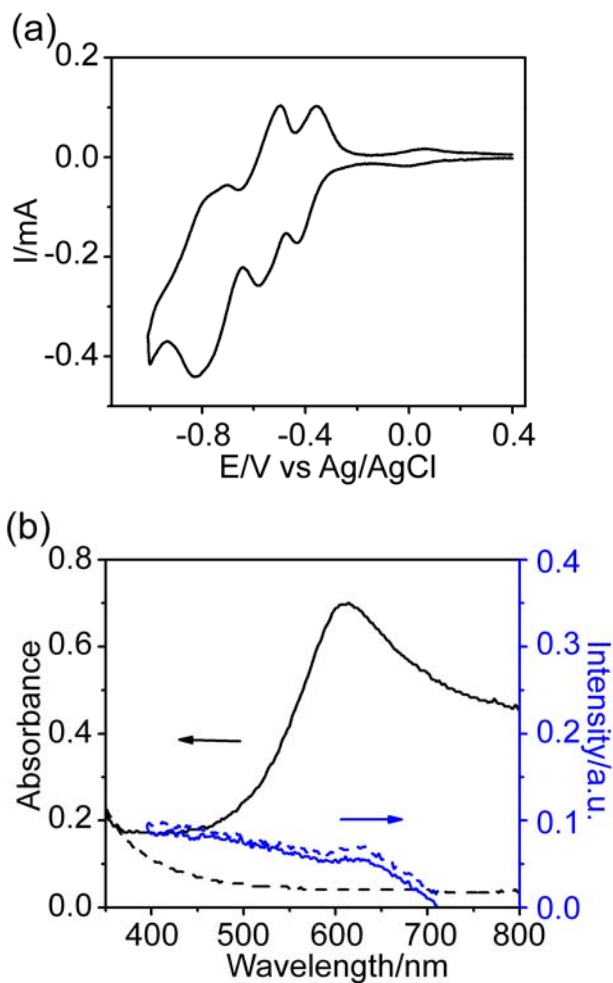


**Fig. S3** (a) Photoluminescence spectra of  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@\text{CdS}_{600}]_y$  multilayers as a function of the number of layers,  $y$ . (b) The relationship of the photoluminescence intensity at 600 nm as a function of the number of layers,  $y$ .

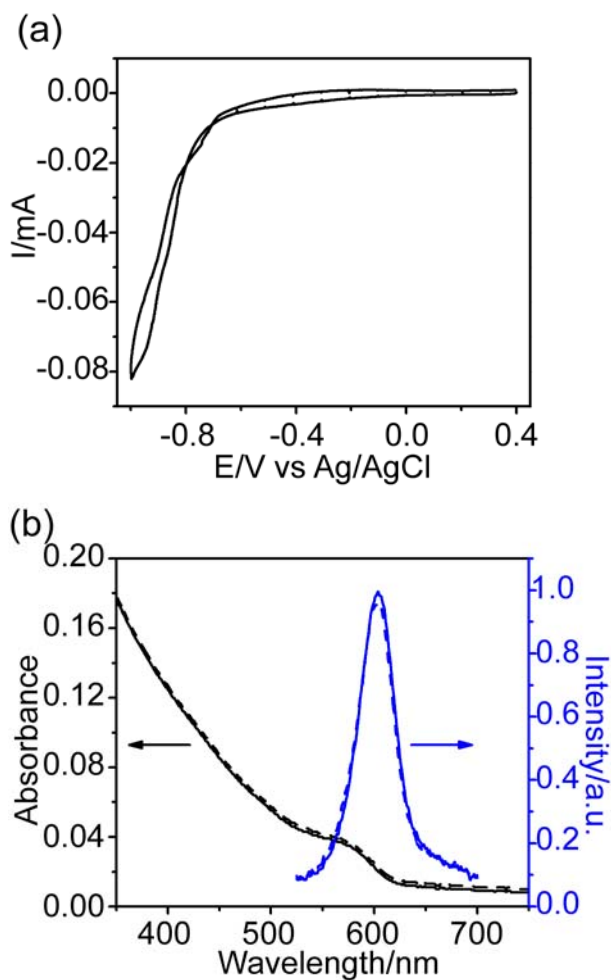


**Fig. S4** UV-Vis absorption spectra of  $[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe@CdS}_{571}]_{10}$  multilayers (dark yellow line),  $[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe@CdS}_{546}]_{10}$  multilayers (green line) and  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe@CdS}_{546}]_4/[(\text{PEI}/\text{P}_8\text{W}_{48})_2/[(\text{PEI}/\text{P}_8\text{W}_{48})_4/\text{PEI}/\text{CdSe@CdS}_{571}]_4/[(\text{PEI}/\text{P}_8\text{W}_{48})_3/[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe@CdS}_{600}]_4]$  multilayers (black line).

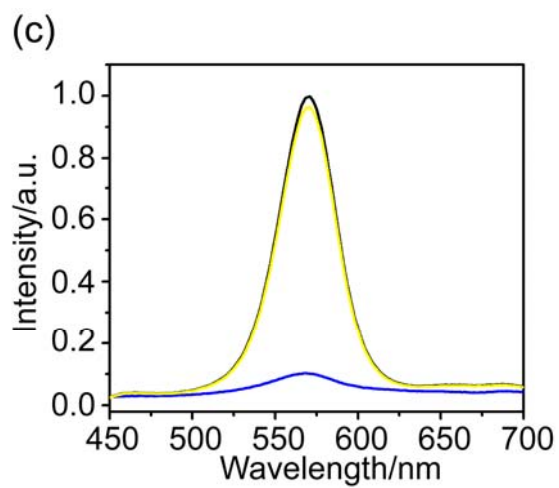
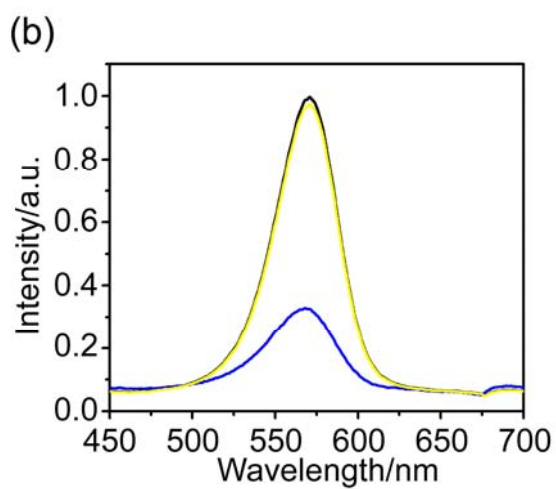
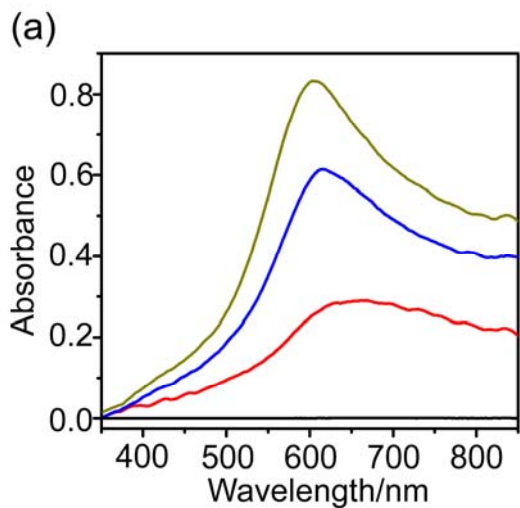
### Part S4. Photoluminescence switching properties of the $P_8W_{48}$ POM/CdSe@CdS QD multilayers

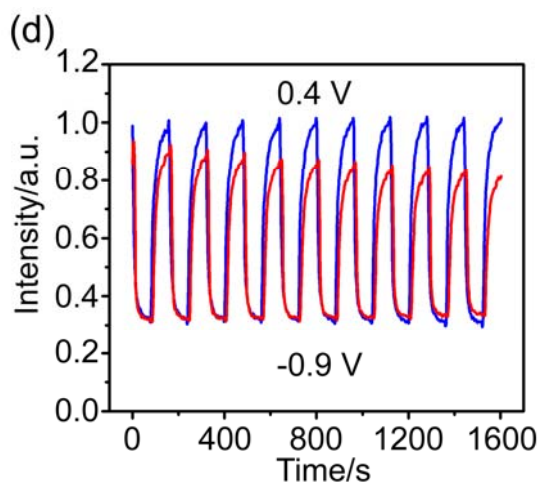


**Fig. S5** (a) CVs of ITO electrode coated with  $(PEI/P_8W_{48})_{10}$  multilayer in 0.10 M PBS (pH 7.4). Scan rate:  $10 \text{ mV s}^{-1}$ . (b) Absorption spectra (black curves) and photoluminescence spectra (blue curves) of ITO electrode coated with  $(PEI/P_8W_{48})_{10}$  multilayer before (dashed curves, 0 V versus Ag/AgCl) and after reduction (solid curves, -0.90 V versus Ag/AgCl).

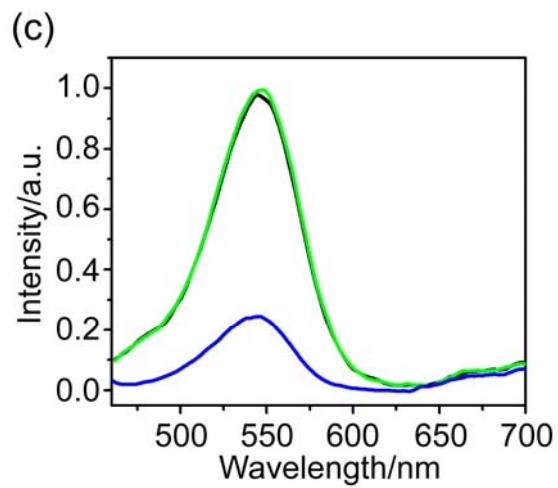
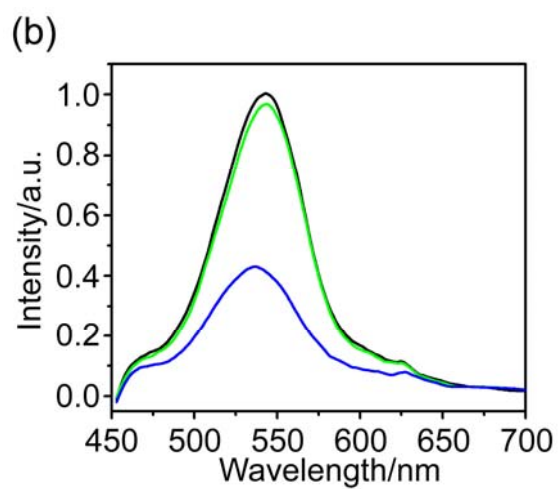
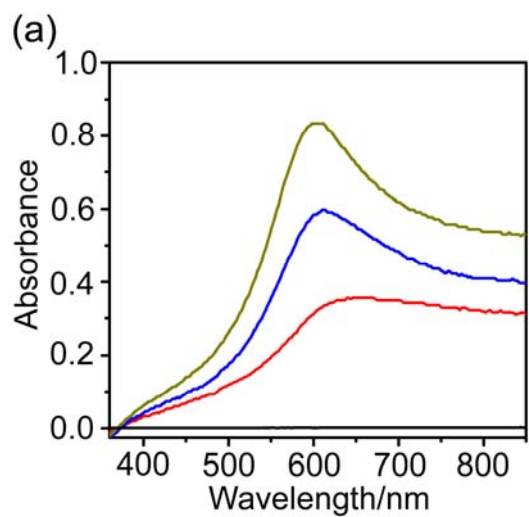


**Fig. S6** (a) CVs of ITO electrode coated with (PEI/CdSe@CdS QD<sub>600</sub>)<sub>10</sub> multilayer in 0.10 M PBS (pH 7.4). Scan rate: 10 mV s<sup>-1</sup>. (b) Absorption spectra (black curves) and photoluminescence spectra (blue curves) of ITO electrode coated with (PEI/CdSe@CdS QD<sub>600</sub>)<sub>10</sub> multilayer before (dashed curves, 0 V versus Ag/AgCl) and after reduction (solid curves, -0.90 V versus Ag/AgCl).

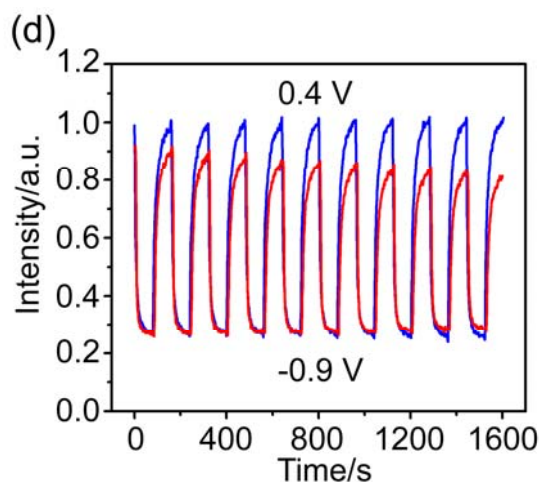




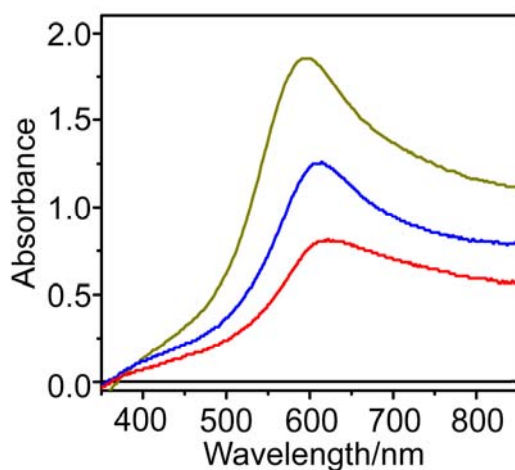
**Fig. S7** (a) Absorption of  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@/\text{CdS}_{571}]_{10}$  at 0.4 V (black curves), -0.6 V (red curves), -0.8 V (blue curves), -0.9 V (dark yellow curves), respectively. Each spectrum is obtained after the potential is held for 4 min. Reversible photoluminescence switching of (b)  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@/\text{CdS}_{571}]_{10}$  and (c)  $[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe}@/\text{CdS}_{571}]_{10}$  multilayers at open circuit (black curve), to a potential of -0.90 V (blue curve), to a potential of 0.40 V (yellow curve) in 0.10 M PBS (pH 7.4). (d) Photoluminescence switching response of ITO electrode coated with  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@/\text{CdS}_{571}]_{10}$  multilayer monitored at 571 nm under applied step potential of -0.90 to 0.40 V with a step duration time for 80s. Blue and red curves stand for 1st and 200th cycles, respectively. The response time for “luminescence on” and “luminescence off” is 41s and 17 s, respectively.







**Fig. S8** (a) Absorption of  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@/\text{CdS}_{546}]_{10}$  at 0.4 V (black curves), -0.6 V (red curves), -0.8 V (blue curves), -0.9 V (dark yellow curves), respectively. Each spectrum is obtained after the potential is held for 4 min. Reversible photoluminescence switching of (b)  $[(\text{PEI}/\text{P}_8\text{W}_{48})_3/\text{PEI}/\text{CdSe}@/\text{CdS}_{546}]_{10}$  and (c)  $[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe}@/\text{CdS}_{546}]_{10}$  multilayers at open circuit (black curve), to a potential of -0.90 V (blue curve), to a potential of 0.40 V (green curve) in 0.10 M PBS (pH 7.4). (d) Photoluminescence switching response of ITO electrode coated with  $[(\text{PEI}/\text{P}_8\text{W}_{48})_6/\text{PEI}/\text{CdSe}@/\text{CdS}_{546}]_{10}$  multilayer monitored at 546 nm under applied step potential of -0.90 to 0.40 V with a step duration time for 80s. Blue and red curves stand for 1st and 200th cycles, respectively. The response time for “luminescence on” and “luminescence off” is 41s and 22 s, respectively.



**Fig. S9** Absorption of [(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>3</sub>/PEI/CdSe@CdS<sub>546</sub>]<sub>4</sub>/(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>2</sub>/[(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>4</sub>/PEI/CdSe@CdS<sub>571</sub>]<sub>4</sub>/(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>3</sub>/[(PEI/P<sub>8</sub>W<sub>48</sub>)<sub>6</sub>/PEI/CdSe@CdS<sub>600</sub>]<sub>4</sub> at 0.4 V (black curves), -0.6 V (red curves), -0.8 V (blue curves), -0.8 V (dark yellow) respectively. Each spectrum is obtained after the potential is held for 4 min.

**Table S1** Switching parameters of some photoswitching or electrofluorescent systems.

<i>Active components</i>	<i>External Stimuli</i>	<i>Max. on/off contrast</i>	<i>Response time</i>	<i>Stability</i>	<i>Year/reference</i>
<b>Photoswitching systems</b>					
9,10-anthracenedinaphthalene and benzothiazole diarylethene as the FL dye and the PC compound	Visible light $\lambda \geq 500$ nm (on) 340 nm UV light (off)	90%	90s (on) 90s (off)	less than 5% decrease of FL intensity change after 10 cycles	2005[S6]
bisthienylethene-bridged naphthalimide dimer	Visible light $\lambda \geq 510$ nm (on) 365 nm UV light (off)	85:1	5min (on) 5min (off)	the film could keep a relatively high contrast (>35:1) during 1h of continuous reading	2005[S7]
FL benzofurazan and PC spiropyran	562 nm Visible light (on) 341 nm UV light (off)	15%	830s (on) 360s (off)		2005[S8]
the supramolecular assembly between 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]cyclopentene (BTEPy) and 3,4,5-tris(dodecyloxy)benzoic acid	Visible light (on) 365 nm UV light (off)	~90%	160min (on) 160min (off)	The PL maxima decreased by 30% after 6 cycles	2007[S9]
(1,3)-di(N,N-dimethyl-4-benzamino)-(2,4)-di(2-benzoxazolyl)-cyclobutane in PMMA film	393nm UV light (on) 254 nm UV light (off)	3:1	10min (on) 2 min (off)	There is little attenuation in FL intensity after 16 cycles	2008[S10]
PC diarylethene/up-conversion LaF <sub>3</sub> :Yb,Ho nanophosphors-loaded PMMA film	Visible light $\lambda \geq 450$ nm (on) 365 nm UV light (off)	~96%	1800s (on) 1800s (off)	the luminescent switch had good reversibility for many cycles	2008[S11]
composite films from [Eu(SiW <sub>10</sub> MoO <sub>39</sub> ) <sub>2</sub> ] and	70 °C in O <sub>2</sub> (on) UV light $\lambda < 365$ nm (off)	100%	15min (on) 120s (off)	The PL maxima decreased by 12% after	2009[S12]

agarose				7 cycles	
multilayers of	Visible light (on)	90%	1h (on)	The PL maxima	2010[S13]
$K_{14}[Na(H_2O)P_5W_{30}O_{110}]$ and	UV light (off)		30s (off)	decreased by 20% after	
CdSe@CdS nanoparticle				10 cycles	
<i>Electrofluorescent systems</i>					
the tetrazine polymer film	2V (on)	3:1	2s (on)	The PL maxima	2006[S14]
	-2V (off)		2s (off)	decreased by 10% after	
				35 cycles	
Copolymer of s-triazine and	-1.5V (on)	~2:1	10s (on)	The PL maxima	2008[S15]
p-phenylene vinylene	1.5V (off)		10s (off)	decreased by 13.8%	
				after 50 cycles	
the tetrazine polymer film	2V (on)	4:1	10s (on)	The PL maxima	2009[S16]
	-2V (off)		10s (off)	decreased by 18% after	
				22 cycles	
multilayer of	0.7V (on)	3	60s (on)	the changes of the FL	2010[S17]
$[Eu(GeW_{11}O_{39})(H_2O)_2]^{10-}$	-0.7V (off)		60s (off)	intensities are less than	
and $P_2W_{18}$				4% in 7 cycles	
methylene anthracene	-2V (on)	3.86	4s (on)	The electrochemical FL	2010[S18]
polymer film	2V (off)		4s (off)	switching was longer	
				than 1,000 cycles	
composite material	Open circuit (on)	3000	15min (on)	The PL maxima	2011[S19]
containing europium (III)	2.2V (off)		5s (off)	decreased by 22% after	
complex and diheptyl				4 cycles	
viologen					
multilayer of	0.9V (on)	4.4	120s (on)	The changes of the FL	2011[S20]
tris(2,2'-bipyridine)	-0.9V (off)		120s (off)	intensities are less than	
ruthenium and $P_2W_{18}O_{62}^{6-}$				2% after 9 cycles	
hybrid film of CdTe QDs	-0.4V (on)	2.5	60s (on)	Noticeable changes	2011[S21]
and poly(methylene blue)	0V (off)		60s (off)	were observed	
				in 20 cycle	
A patternable	1.8V (on)	2.5	10s (on)	a cyclability longer	2011[S22]
poly(1,3,4-oxadiazole) thin	-1.8V (off)		10s (off)	than 1000 cycles	
film			with contrast		
			ratio 1.2		
$Eu(hfa)_3(TPPO)_2, HV^{2+}$ and	1.4V (on)	100%	10s (on)	The emission intensity	2012[S23]

Prussian blue	0.8V (off)		10s (off)	was nearly completely maintained after 250 cycles	
hybrid film of poly (3,4-ethylenedioxythiophene), PMo <sub>12</sub> O <sub>40</sub> <sup>3-</sup> and Pyronin Y-doped silica nanoparticles	0.6V (on)	3:1	60s (on)	The PL maxima decreased by 5% after 20 cycles	2012[S24]
multilayer of Au nanocluster and Prussian blue	0V (on)	3:1	60s (on)	The PL maxima decreased by 5% after 15 cycles	2013[S25]
multilayer of CdSe@CdS QDs and P <sub>8</sub> W <sub>48</sub>	0.4V (on)	Quenching 91%	38s (on)	The PL maxima decreased by 19% after 200 cycles	This manuscript
	-0.6V (off)		60s (off)		
	0.5V (off)		60s (off)		
	-0.9V (off)		17s (off)		

**Abbreviation:** PL: fluorescence; PC: photochromic; PMMA, poly(methyl methacrylate)

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