SUPPLEMENTARY INFORMATION

An Integrated Electrochromic Nanoplasmonic Optical Switch

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Figure S1. Secondary electron microscope (SEM) image of a sample consisting of a sputtered Au film on a glass substrate (Au thickness: 250nm), incorporating two focused-ion-beam milled slits of width ≈ 50 nm. The individual slit dimensions are identical to those used in the optical switching experiments described in the main text. The image is acquired after 51 cycles of deposition of Prussian Blue onto the sample surface. Preferential deposition of Prussian Blue nanocrystals on the side walls of the slits is apparent, with a slit fill fraction ≈ 25 %.

Figure S2. Auger electron microscope image of a sample consisting of a sputtered Au film on a glass substrate (Au thickness: 250nm), incorporating two focused-ion-beam milled slits of width ≈ 50 nm. The individual slit dimensions are identical to those used in the optical switching experiments described in the main text. Auger electron spectra (insets) are acquired after 5 cycles of deposition of Prussian Blue onto the sample surface. Elemental maps indicate preferential deposition of Prussian Blue inside the nanoslits, as evidenced by detection of Fe and N only in those regions.

Figure S3. X-ray diffraction pattern of a sample consisting of a 50nm-thick Au film on glass (semi-transparent reference Sample B) after 300 cycles of Prussian Blue deposition. The diffraction pattern is collected using a powder diffractometer and Cu K-alpha x-rays (0.154 nm).

FDTD Simulations:

Figure S4. Sample and illumination geometry used for two-dimensional finite difference time domain (FDTD) simulations of transmission through a nanoslit filled with Prussian Blue nanocrystals, as they are switched between PB and PW states. I_0 and $I_{PW(PB)}$ represent, respectively, the light intensity of the incident plane wave and the transmitted light intensity into the far field on the exit side of the device. E , H , k : electric field polarization, magnetic field polarization and propagation wave vector of the incident plane wave ($\lambda_0=633\text{nm}$).

Prussian Blue Deposition Rate:

The deposition rate can be quantified by integrating the PB/PW reduction current from voltammograms similar to those shown in Fig. 2(a, b). Only the current associated with the sharp reduction peak at -0.4 V is integrated; ferricyanide reduction to ferrocyanide is considered background current and is subtracted from the PB/PW current. A typical charge density – cycle # plot is shown below.

The slope of a linear fit of the data yields a charge density per cycle ($Q_{PB/cyc}$) of $4.0 \mu C/(cm^2 \cdot cycle)$. This can be converted to moles of PB per cycle ($N_{PB/cyc}$) using Faraday's law,

$$N_{PB/cyc} = \frac{Q_{PB/cyc}}{nF}$$

where n is the number of electrons passed per mole of PB reduced and F is Faraday's constant (96500 C/mol). It is assumed that PB reduction is described by the following electrochemical reaction (eqn. #2 in the paper),

which defines n as 1.0. This yields a value for $N_{PB/cyc}$ of $4 \times 10^{-11} \text{ mol/cm}^2$ of $KFeFe(CN)_6$ per cycle. The coverage calculation (in monolayers) assumes a cubic unit cell with $10.13 \text{ \AA}$ lattice parameter and that each unit cell contains $3KFe^{III}Fe^{II}(CN)_6$. This yields a $KFeFe(CN)_6$ coverage of approximately 0.1 monolayers per cycle. Based on this growth rate, 200 cycles would produce a film approximately 20 nm thick, assuming uniform deposition.