

# Supplementary Material (ESI) for Chemical Communications  
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## **Controlling the Directions of Photocurrents by Means of CdS Nanoparticles and Cytochrome c-Mediated Biocatalytic Cascades**

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### **Supplementary information**

#### ***Chemicals and Materials***

Cytochrome c (Cyt c, from bovine heart), cytochrome-dependent L-lactate dehydrogenase (LDH, from baker's yeast, type IV-SS, EC 1.1.1.27), cytochrome-dependent nitrate reductase (NR, from *E. coli*, EC 1.9.6.1), 1,4-dithiolbenzene, 4-mercaptopyridine and all other chemicals were purchased from Sigma or Aldrich and used without further purification. The reduced form of Cyt c was generated by the reaction with sodium ascorbate (0.05 M, in 0.1 M phosphate buffer, pH 8.0) and purified on a Sephadex G-15 column. Semiconductive CdS nanoparticles (NPs) (ca. 5.5 nm) were prepared in water using polyphosphate as a capping agent. Ultrapure water from NANOpure Diamond<sup>TM</sup> (Barnstead) source was used throughout all the experiments.

#### ***Chemical modification of electrodes***

A Au-coated (50 nm gold layer) glass plate (Analytical- $\mu$ System, Germany) was used as a working electrode. The electrode surface was modified with a monolayer of 1,4-dithiobenzene upon reaction with the ethanolic solution of the dithiol (10 mM) for 10 hours, followed by rinsing of the electrode with ethanol and water. CdS NPs (ca.  $1 \times 10^{-6}$  M in 0.1 M phosphate buffer, pH 7.0) were deposited onto the dithiol-functionalized electrode overnight, and then the electrode surface was rinsed with water. The CdS-functionalized electrode was further reacted overnight with 4-mercaptopyridine (10 mM in 0.1 M phosphate buffer, pH 7.0) to yield the pyridine-capped CdS NPs on the electrode surface.

***Photoelectrochemical and microgravimetric measurements***

The photocurrent action spectra were recorded without application of an external potential on the photoactive electrode using a home-made system that is based on the a lock-in amplifier and provides an amplified alternative photocurrent. The direct photocurrent measurements were performed at  $\lambda = 420$  nm upon application of 0 V (vs. SCE) on the photoelectrode using an electrochemical analyzer (model 6310, EG&G) connected to a personal computer with EG&G 270/250 software). The measurements were carried out at ambient temperature ( $25 \pm 2^\circ\text{C}$ ) in a conventional electrochemical cell consisting of a modified Au working electrode ( $0.3\text{ cm}^2$  area exposed to the solution) assembled at the bottom of the electrochemical cell, a glassy carbon auxiliary electrode and a saturated calomel electrode (SCE) connected to the working volume with a Luggin capillary. Phosphate buffer (0.1 M, pH 7.0) was used as an aqueous background electrolyte. The irradiation of the photoactive electrode was performed from the bottom of the electrochemical cell through the semi-transparent electrode. Argon bubbling was used to remove oxygen from the solutions in the electrochemical cell. The cell was placed in a grounded Faraday cage. The photoelectrochemical measurements were performed in the presence of Cyt c (oxidized or reduced)  $5 \times 10^{-5}$  M. The cytochrome-dependent enzymes (LDH or NR) were used with concentrations  $1\text{ mg mL}^{-1}$  in the presence of the variable concentrations of the respective substrates (lactate or nitrate).

A QCM analyzer (Fluke 164T multifunction counter, 1.3 GHz, TCXO) and quartz crystals (AT-cut, 9 MHz, Seiko) sandwiched between two Au electrodes (area  $0.196\text{ cm}^2$ , roughness factor ca. 3.2) were employed for the microgravimetric analyses in air.