Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic supplementary information

A three-valued photoelectrochemical logic device realising *accept anything* and *consensus* operations

M. Warzecha,[a] M. Oszajca,[b] K. Pilarczyk[c,d,*] and K. Szaciłowski[d,e,*]

[a] Strathclyde Institute of Pharmacy and Biomedical Sciences, University of Strathclyde, 161 Cathedral Street, Glasgow, United Kingdom

[b] Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zurich, Switzerland

[c] AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. A. Mickiewicza 30, 30-059 Kraków, Poland; e-mail: kacper.pilarczyk@fis.agh.edu.pl

[d] AGH University of Science and Technology, Academic Centre for Materials and Nanotechnology, al. A. Mickiewicza 30, 30-059 Kraków, Poland

[e] AGH University of Science and Technology, Faculty of Non-Ferrous Metals, al. A. Mickiewicza 30, 30-059 Kraków, Poland; E-mail: szacilow@agh.edu.pl

Experimental

1. Materials

Synthesis of the tetraethylammonium hexacyano-3,4-diazahexadienediide

Salt of the $HCDAH^{2-}$ was prepared from the reaction of TCNE with hydrazine. Solution of 2.5 ml of hydrazine hydrate in 25 ml of water was mixed rapidly with cooling with 3.2 g (25 mmol) of powdered tetracyanoethylene. 5.25 g of tetraethylammonium bromide (25 mmol) was added and the mixture was stirred. The orange-brown precipitate that formed was collected on a filter, washed with water and recrystallized from ethyl alcohol. There was obtained 2.03 g (33% yield) of orange tetraethylammonium 1,1,2,6,6-hexacyano-3,4- diazahexadienediide. Anal. Calcd. for $C_{26}N_{10}H_{40}$: C 63.38, H 8.18, N 28.43. Found: C 63.13, H 8.05, N 28.45

Synthesis of the hexacyanobuta-1,3-diene (HCBD)

Hexacyanobutadiene was obtained by three-stage reaction. The first stage was to reduce tetracyanoethylene to tetracyanoethane. The second step was the conversion of disodium tetracyanoethanediide to disodium hexacyanobutenediide in solution of 1,2-dimethoxyethane and in the presence of monosodium salt of tetracyanoethane. The last step was to oxidize the $HCBD^{2-}$ to HCBD.

Tetracyanoethane. A solution of 3.2 g (25 mmol) of tetracyanoethylene in 20 ml of acetone was cooled above liquid nitrogen, and 6 ml of mercaptoacetic acid was added with stirring. The solution was cooled to 0°C, and 25 ml of cold water was added. The white needles which separated were collected on a filter and washed with water. After drying in a vacuum desiccator there was obtained 2.56 g (80% yield) of tetracyanoethane in the form of long white needles.

Sodium 1,1,2,3,4,4-hexacyanobutenediide (Na_2HCBD). A suspension of 1.6 g (37 mmol) of sodium hydride-mineral oil dispersion (60% NaH) in 12 ml of glyme (1,2-dimethoxyethane) was cooled in ice bath under nitrogen and stirred vigorously. A solution of 2.45 g (18 mmol) of 1,1,2,2-tetracyanoethane in 10 ml of glyme was added in a slow stream over a period of 30 minutes. The white suspension of sodium tetracyanoethanediide was then refluxed (about 80°C) for 1 h. The color of the mixture changed to deep orange, and oil separated. The mixture was cooled down to room temperature, and the top layer containing glyme and mineral oil was decanted and discarded. The remaining suspension was shaken with 20 ml of acetonitrile and was filtered. Sodium cyanide remained on the filter. The orange filtrate was concentrated to dryness, and the residue was refluxed for 2 hr in 20 ml of acetonitrile. The mixture was cooled to room temperature, and crude *trans-* Na2HCBD (3.30 g 70% yield) was collected on a filter. Anal. Calcd. for $Na_2C_{10}N_6$: C 48.02, H 0.00 N 33.60, Na 18.38 Found: C 45.72, H 0.51, N 31.77, Na 22.00

Hexacyanobutadiene HCBD: For preparing small amounts of HCBD, it was found convenient to use nitric acid as the oxidant. Concentrated nitric acid 2.5 ml, was added in one portion to an ice-cold solution of 0.30 g (0.1 mmol) of Na_2HCBD in 1.5 ml of water. HCBD (20 mg, 8.2% yield) was collected on a filter, was washed with water, and dried. Hexacyanobutadiene is a colorless, crystalline solid.

The preparation of the TiO_2 modified with TCNE derivatives was based on mixing a suspension of TiO_2 (P-25, Evonik) in CH_3CN with appropriate solutions of the cyanocarbons in CH_3CN. The resulting material was centrifuged, decanted, washed 4 times with CH_3CN and dried. The materials are relatively photostable, their properties are not affected by 10 hours of illumination. Longer photostability tests have not been performed.

2. Instrumentation

The diffuse reflectance spectra were recorded on Lambda 950 (Perkin Elmer, USA) spectrophotometer equipped with 150 mm integration sphere. The sample was dispersed in spectrally pure $BaSO_4$ in 1:50 weight ratio, pressed $BaSO_4$ pellet was used as a reference. Photoelectrochemical characterization was performed using a photoelectric spectrometer (Instytut Fotonowy, Poland) composed of stabilized 150 W xenon arc lamp, monochromator and coupled with the SP-300 potentiostat. The working electrode was prepared by deposition of neat or modified TiO_2 onto indium-tin oxide (ITO) coated polyethylene terephthalate foil. All measurements were performed in air-equilibrated 0.1 M KNO_3 solution as a supporting electrolyte, with Pt wire as a counter electrode and Ag/AgCl (sat. KCl) reference.

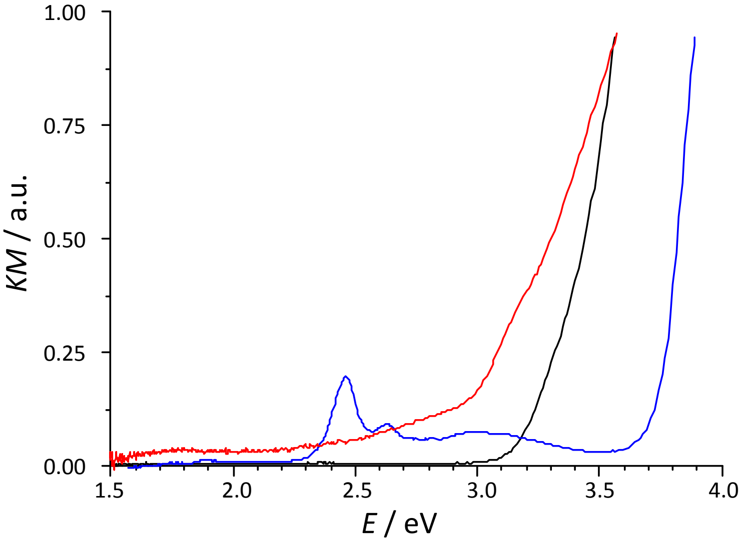


Figure S1. Comparison of diffuse reflectance spectrum of TiO_2 (black), **1**@TiO_2 (red) and absorption spectrum of **1** in chloroform (blue)

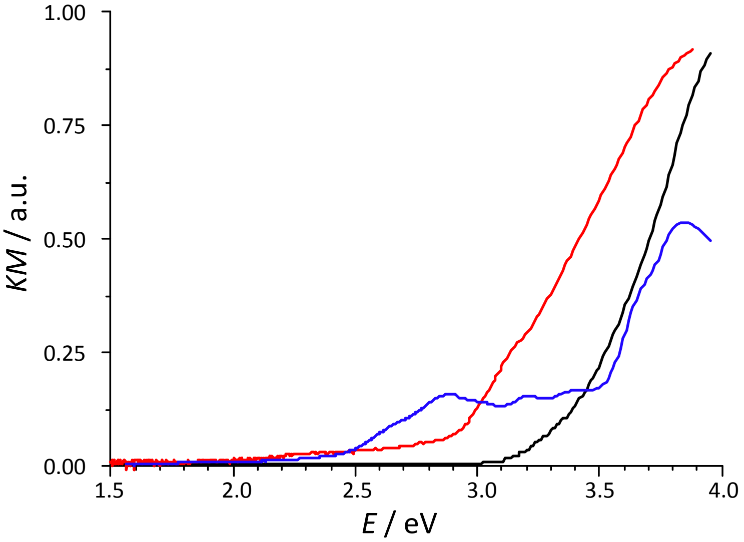


Figure S2. Comparison of diffuse reflectance spectrum of TiO_2 (black), **2**@TiO_2 (red) and absorption spectrum of **2** in chloroform (blue)

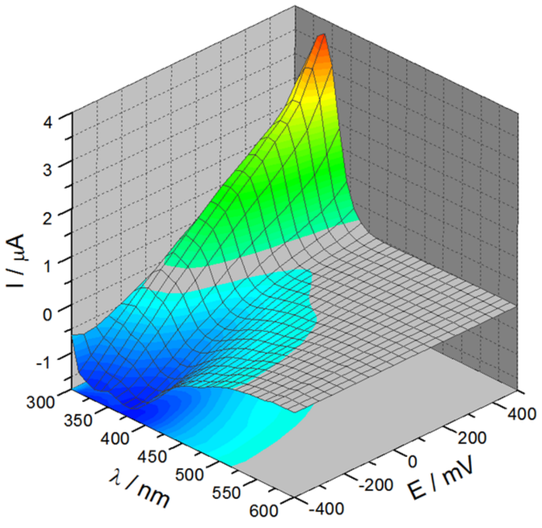
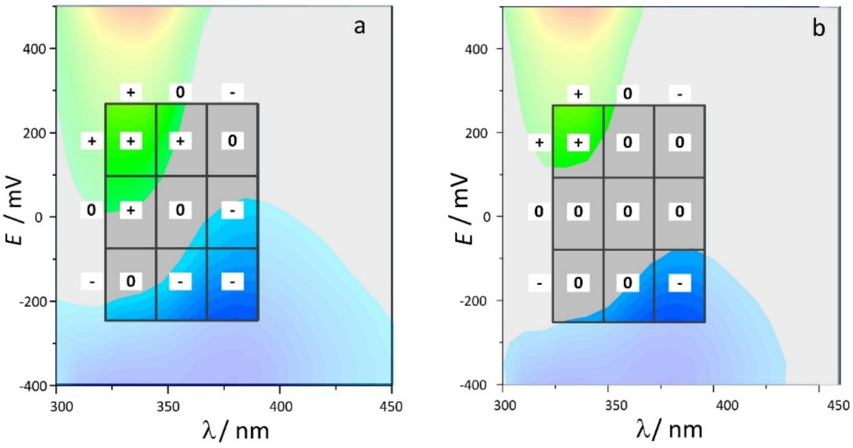


Figure S3. The photocurrent action spectra recorded for TiO_2 modified with **2** in the presence of oxygen in 0.1 M KNO_3.



	+	0	-
+	+	+	0
0	+	0	-
-	0	-	-

	+	0	-
+	+	0	0
0	0	0	0
-	0	0	-

Figure S4. A fragment of a photocurrent action map of **2**-modified TiO_2 with the three-valued truth table corresponding to the *accept anything* operation (a). The *consensus* operation can be realized by neglecting the photocurrents with lowest intensities (b). It can be seen, however, that assignment of logic values is much better in the case of compound **1**.