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Supporting Information

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Redox-Active Monolayers as a Versatile Platform for Integrating Boolean Logic Gates**

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Experimental Section

Materials and Methods. The Ru^{2+}- and Os^{2+}-based monolayers were produced as previously described on silicon, quartz and glass substrates.[s1,s2] $Ce(SO_4)_2 \cdot 4H_2O$ was purchased from BDH Chemicals Ltd. Anhydrous $FeCl_3$ and $FeCl_2$ were purchased from Merck and Aldrich, respectively. All other metal salts were purchased from BDH or Merck. Solvents (AR grade) were purchased from Bio-Lab (Jerusalem), Frutarom (Haifa), or Mallinckrodt Baker (Phillipsburg, NJ). Pentane and toluene were dried and purified using an M. Braun (Garching, Germany) solvent purification system. Dichloromethane (DCM) was purified with H_2SO_4 and distilled under N_2 over P_2O_5. DCM was degassed and stored in a M. Braun glovebox with O_2 and H_2O levels < 2 ppm over activated 4 Å molecular sieves with exclusion of light. Soda-lime glass (Chase Scientific Glass) was cleaned by immersion in a "piranha" solution (7:3 (v/v) H_2SO_4/30% H_2O_2) for 1 h. *Caution: piranha solution is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection.* Subsequently, the substrates were rinsed with deionized (DI) water followed by the RCA cleaning protocol: 1:5:1 (v/v) $NH_3 \cdot H_2O/H_2O/30\%$ H_2O_2 at room temperature for 45 min. The substrates were washed with an ample amount of DI water and were dried under an N_2 stream. All substrates were then dried in an oven for 2 h at 130°C. The monolayer formation and characterization were carried out under an inert atmosphere using either standard Schlenk/cannula techniques or a glovebox using previously reported procedures.[S1-S2] All the glassware was silanized with octadecyltrichlorosilane or phenyltrichlorosilane and oven dried to reduce background noise due to the presence of traces of water. UV/vis spectroscopy was carried out using a Cary 100 spectrophotometer. All measurements were carried out at 298 K. All redox experiments were repeated at least 7 times.

Boolean operation with $Os^{2+/3+}$-based monolayers. The Os^{2+}-based monolayers were oxidized in <1 min using 100 ppm of any of the following analytes: Ce^{4+} (in water or MeCN), Cr^{6+} (in acidified water, pH<3), Fe^{3+} (in water or MeCN), NO^{+} (in MeCN or DCM), Ag^{+} (in DCM), NO_2 (in air), and Os^{3+}-based monolayer were reduced in <1 min using 100 ppm of water (in MeCN or DCM), cobaltocene (in MeCN). The combination of any one, two, or three of these oxidizing and reducing agents yields outputs consistent with the output of various logic gates and circuits.

AND and NAND Gate. To use Os^{2+}-based monolayers as a molecular AND and/or NAND logic gate, one input is defined as $AgBF_4$, and the other input is dichlomethane (DCM). In a particular set of experiments, an Os^{2+}-based monolayer was placed in a glass vial and 1 ml of 1000 ppm $AgBF_4$ (in MeCN) was added as input (IN1). Subsequently, 9 mL dichloromethane was added as another input (IN2). The solution was stirred for <1 min. Next, the Os^{2+}-based monolayer was removed from the solution, washed with dry DCM and carefully wiped with task paper before recording the UV/vis spectra. Oxidation of the monolayer makes the molecule reach a peak at λ = 317 nm with a simultaneous decrease of the peak at λ = 516 nm. With neither input on, the absorption intensity at λ = 317 nm is below a threshold level (0.02), and the AND gate remains off. With the addition of $AgBF_4$ in another solvent such as MeCN, acetone, or THF, the absorption is triggered, resulting in the output of a very weak peak that is below the threshold value. Only DCM does not affect the spectrum. Thus, the molecule meets the criteria for an AND gate at λ = 317 nm. In contrast, the AND gate the NAND gate were generated simultaneously using the same input but at λ = 516 nm.

OR and NOR Gates. To use Os^{3+}-based monolayers as a molecular OR and/or NOR logic gates, one input that is used is 100 ppm of cobaltocene in dry MeCN and the other input used is double distilled H_2O. Os^{3+}-based monolayer is easily reduced using cobaltocene (in MeCN) and/or H_2O as separate inputs or together. Either one of them or both inputs brings the peak to λ = 516 nm, with the peak simultaneously vanishing at λ = 317 nm. Therefore, the same inputs (cobaltocene and water) at λ = 516 nm yield an OR gate whereas at λ = 317 nm they yield a NOR gate.

XOR and XNOR Gates. To use Os^{2+}-based monolayers as XOR and/or XNOR logic gates, one input used is 100 ppm of Cr^{6+} in acidic water (pH =3) and the other input used is 100 ppm of $NOBF_4$ in basic MeCN (with 10 μL of triethyl amine). Os^{2+}-based monolayers yield a signal at λ = 516 nm as output when neither of the two inputs are added. However, if 10 mL of one of the above two is added independently after 1 min, the absorption at λ = 516 nm vanishes, due to oxidation of Os^{2+}-based monolayers with Cr^{6+} in acidic water or with NO^+ in basic MeCN solvent. After both inputs are added simultaneously (5 mL + 5 mL), Cr^{6+} and NO^+ become inactive. However, this does not affect the output signal of Os^{2+}-based monolayers. The Cr^{6+} in neutral media becomes inactive whereas NO^+ is very reactive to water and become inactive. Thus, a logic gate incorporating a truth table constitutes the XNOR logic gate at λ = 516 nm. Whereas, an XOR logic gate is simultaneously generated at λ = 317 nm.

INH and IMP systems. To demonstrate INH and IMP logic gate behavior with Os^{2+}-based monolayers, one input is defined as NO^+ in acetonitrile/DCM and the other input used is double distilled H_2O. With only water as an input does the original spectrum of Os^{2+}-based monolayers not change, whereas 100 ppm of NO^+ in organic solvent (MeCN or CH_2Cl_2) generates a band at λ = 317 nm after a reaction time of 1 min. When we use both NO^+ and H_2O together, then no bans were observed at λ = 317 nm because NO^+ reacts with H_2O before interacting with the monolayer. Thus, the logic circuit incorporating truth tables constitutes the INHIBIT gate at λ = 317 nm while the output at λ = 516 nm matches with the output of an IMP system.

NOT gate. The NOT gate was implemented using double distilled H_2O as an input and it governs an absorption band at λ = 317 nm of an Os^{3+}-based monolayer. When we add H_2O, it reduces the system and the band at λ = 317 nm disappears.

Boolean operations with $Ru^{2+/3+}$-based monolayers. The Ru^{2+}-based monolayers were oxidized in <1 min using 100 ppm of Ce^{4+} (in acidic water), and Ru^{3+}-based monolayers were reduced in <1 min using 100 ppm of H_2O (in MeCN or DCM), Fe^{2+} (in MeCN or DCM). The combination of these inputs yields various logic gates. For instance, an OR and NOR logic gate has been achieved with two inputs: IN1 = $FeCl_2$ in dry MeCN and IN2 = H_2O. For example, a Ru^{3+}-based monolayer was placed in a glass vial and 5 mL of 100 ppm $FeCl_2$ solution (in dry MeCN) was added (IN1). Subsequently, 5 mL of 100 ppm H_2O (in MeCN) was added (IN2). The solution was stirred for <1 min. Next, the Ru^{3+}-based monolayer was removed from the solution, washed with dry MeCN, and carefully wiped with task paper before recording the UV/vis spectra. Reduction of the monolayer affords a band at λ = 463 nm with a

simultaneous decrease of the band at λ = 317 nm. The addition of 10 mL of 100 ppm $FeCl_2$ reduces the Ru^{3+}-based monolayer as a band is observable at λ = 463 nm. Treatment of the monolayer with H_2O also results in a band at λ = 463 nm. Thus, the monolayer meets the criteria for an OR gate at λ = 463 nm. The NOR gates were generated simultaneously using the same input but with optical read-out at λ = 317 nm, which follows De Morgan's Law. Likewise other logic gates and circuits with two and three inputs were generated.

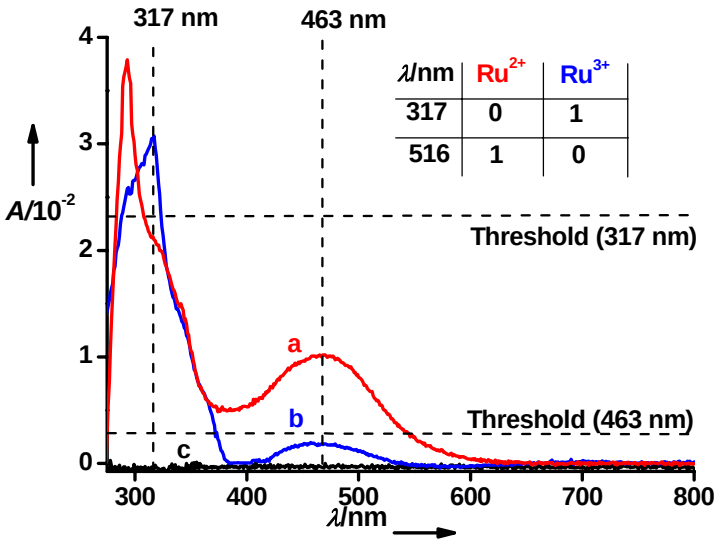
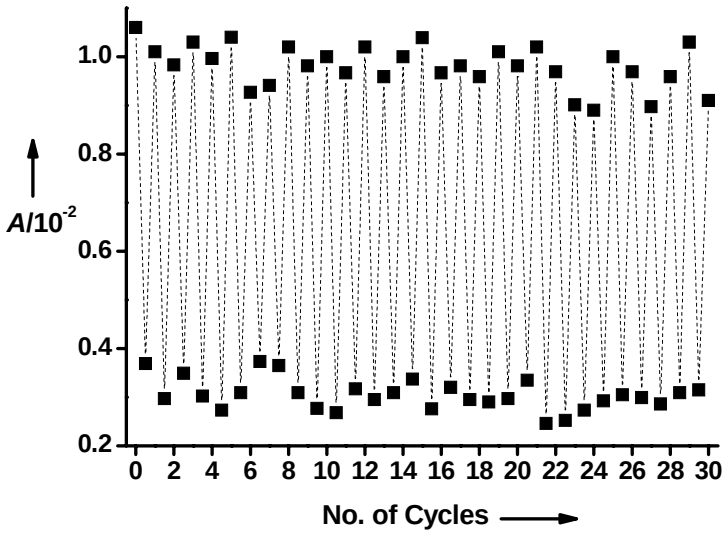


Figure S1. Representative absorption spectra of $Ru^{2+/3+}$-based monolayers. (a) Ru^{2+}, red line; (b) Ru^{3+}, blue line; (c) baseline, black line. The absorption intensities at λ = 317 and λ = 463 nm were used as output (0 or 1). Inset: Truth table for the Boolean Logic of a function of a wavelength and a metal oxidation state.

A)



B)

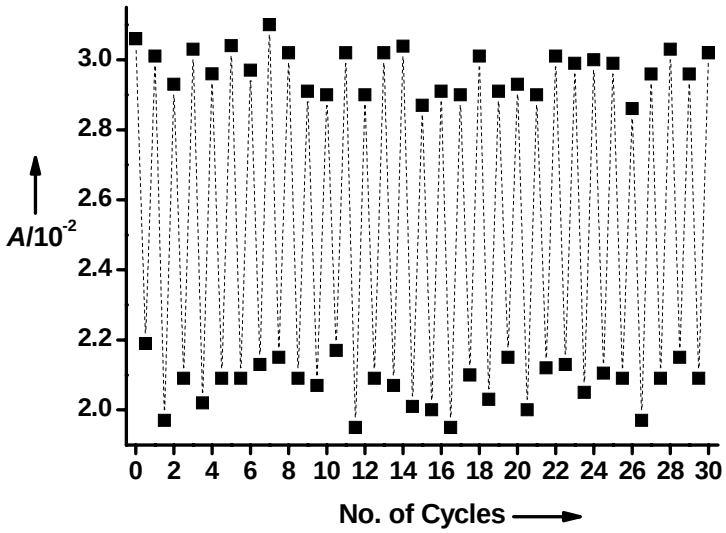


Figure S2. A) Representative chemical on/off switching of the ^{1}MLCT bands at λ = 516 nm. A vs the number of $Os^{2+/3+}$ redox cycles. Oxidation was carried out in a CH_2Cl_2/MeCN (1:0.1 v/v) solution of $AgBF_4$ (0.5 mM) while reduction was carried out with water (3 min each). B) Representative chemical on/off switching of the band at λ = 317 nm. A vs the number of $Os^{2+/3+}$ redox cycles. Oxidation was carried out in a CH_2Cl_2/MeCN (1:0.1 v/v) solution of $AgBF_4$ (0.5 mM) while reduction was carried out with water (3 min each).

Table S1. Truth table and aborption data ($\times 10^{-4}$) for the Boolean Logic functions of the Os-based monolayer operating with two chemical inputs.

Inputs		Output, λ = 317 nm			Output, λ = 516 nm		
IN1	IN2	AND[a,b]	NOR[c]	XOR[d]	NAND[a,b]	OR[c]	XNOR[d]
0	0	0 (215 ± 10)	1 (301 ± 10)	0 (214 ± 10)	1 (104 ± 05)	0 (028 ± 02)	1 (102 ± 05)
0	1	0 (217 ± 12)	0 (210 ± 09)	1 (295 ± 09)	1 (106 ± 08)	1 (105 ± 08)	0 (032 ± 02)
1	0	0 (213 ± 16)	0 (214 ± 11)	1 (302 ± 12)	1 (092 ± 07)	1 (109 ± 06)	0 (035 ± 02)
1	1	1 (305 ± 18)	0 (218 ± 07)	0 (217 ± 11)	0 (026 ± 02)	1 (110 ± 08)	1 (087 ± 06)

[a][IN1 = Ag^+, IN2 = DCM]; [b][IN1 = Cr^{6+}, IN2 = H^+]; [c][IN1 = $CoCp_2$, IN2 = H_2O]; [d][IN1 = Cr^{6+} (pH = 3), IN2 = NO^+]

Three chemical inputs. The Os^{2+}-based monolayer have been treated with two sets of three chemical inputs: set 1: $NOBF_4$ in MeCN (100 ppm) (IN1), double distilled H_2O (IN2) and $Ce(SO_4)_2.4H_2O$ in MeCN (100 ppm) (IN3) and set 2: $Ce(SO_4)_2.4H_2O$ in MeCN (100 ppm) (IN1), double distilled H_2O (IN2) and NO_2 in air (1000 ppm) (IN3). In particular set of experiments, the Os^{2+}-based monolayer was placed in a glass vial with a Teflon sample holder and 10 mL of the abovementioned NO^+ solution was added as an input (IN1), the solution was stirred for 3 min. Next, the monolayer was removed from the solution, washed with dry MeCN, and carefully wiped with task paper before recording the UV/vis spectra. Generation of a Os^{3+} monolayer by oxidation with NO^+ resulted in the disappearance of the characteristic MCLT band at λ = 516 nm (output = 0). Eight combinations of experiments were performed with the two set of abovementioned inputs in a similar manner using the same monolayer. The total amount of volume for a combination of inputs is always 10 mL.The obtained data is presented in Table 2 and the logic circuit diagrams are shown in Figure 4.

Gate-to-gate communication. The Os^{2+} and the Ru^{3+}-based monolayers (surface areas 18.7 cm^2 and 4.7 cm^2, respectively) were placed in one vial using a Telfon sample holder. The systems was operated under stirring with three chemical inputs: Fe^{3+} in MeCN (100 ppm) (IN1), double distilled H_2O (IN2) and $Ce(SO_4)_2.4H_2O$ in acidic water (pH = 3, 100 ppm) (IN3). For instance, 10 mL of abovementioned Fe^{3+} solution was added as an input (IN1), the solution was stirred for 3 min. Subsequently, the Ru^{3+}-based monolayer was removed from the solution, washed with dry MeCN, and carefully wiped with task paper before recording the UV/vis spectra. Reduction of the Ru^{3+}-based monolayer with the *in-situ* generated Fe^{2+} (by the

reaction of Os^{2+}-based monolayer and Fe^{3+}) resulted in the appearance of the signal at λ = 463 nm (output **1**). Eight combinations of experiments were performed with the set of abovementioned inputs in a similar manner using the same set-up. The total amount of volume for a combination of inputs is always 10 mL. The obtained data is presented in Table 3. Figure 6A shows the experimental set-up and the logic circuit diagram.

References

S1. T. Gupta, M. Altman, A. D. Shukla, D. Freeman, G. Leitus, M. E. van der Boom, *Chem. Mater*. **2006**, *18*, 1379.

S2. T. Gupta, M. E. van der Boom, *Angew. Chem. Int. Ed.* **2008**, *47*, 2260.