

Supporting Information for

“Potential and Ion Switched Molecular Photonic Logic Gate”

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Synthesis

All reagents were of highest purity commercially available and were used without further purification. ¹H NMR spectra were recorded on a Varian Gemini 300 (300 MHz) spectrometer at 25°. All chemical shifts are referenced to residual solvent signals previously referenced to tetramethylsilane (TMS) and splitting patterns are designated as s (singlet) and d (doublet). UV/Visible absorption and emission spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer and a SPEX Fluoromax-2 spectrofluorometer, respectively. All IR spectra were measured on a Bruker IFS 88S FT-IR spectrometer.

cis-Bis(cyano) ruthenium(II)-bis-2,2'-bipyridine-4,4'-dicarboxylate, sodium salt, Na₄[Ru(dcbpy)₂Cl₂], (**I**) was prepared and characterized as previously described.¹ In a typical preparation, a suspension of 0.13 g of [Ru(dcbpy)₂Cl₂] in 10 mL of water was prepared. A stoichiometric amount of concentrated NaOH was added and the pH was adjusted to 7. Addition of 200 mL of acetone resulted in the formation of a deep orange powder, Na₄[Ru(dcbpy)₂Cl₂]. 0.15 g of this product and 0.2 g of NaCN were refluxed in 20 mL of methanol for 3 h. The methanol was removed with a rotary evaporator. The solid

was redissolved in water, and HCl was added drop wise until precipitation of an orange-red solid was complete (at pH 2.5). The solid was filtered, redissolved in methanol, loaded on a 5 x 1.5 cm silica gel column, and eluted with methanol. The first orange-red fraction was collected. A red-brown fraction, probably cyano-bridged polynuclear complexes based on the (dcbpy)₂Ru²⁺ unit was retained by the column.² The orange-red fraction containing [Ru(dcbpy)₂(CN)₂] was evaporated to dryness and converted to the anionic form (**I**), as described elsewhere.¹ ¹H NMR (**D**₂**O**): δ = 9.37 ppm (d, 2 H, 6), 8.64 (s, 2 H, 3), 8.55 (s, 2H, 3'), 7.83 (d, 2 H, 5), 7.53 (d, 2 H, 6'), 7.38 (d, 2 H, 5'). **IR**: CN stretching (ν) = 2073 and 2059 cm⁻¹. **Elemental Analysis**: Calculated for Na₄[Ru(dcbpy)₂(CN)₂].2H₂O (RuC₂₆H₁₆N₆O₁₀ Na₄): C, 40, 80; H, 2.11; N, 10.98. Found: C, 40.46; H, 2.14; N, 10.90.

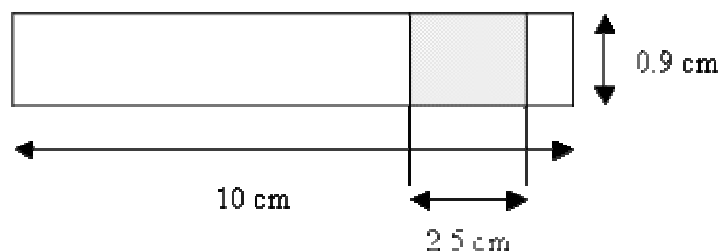
Preparation of Nanostructured TiO₂ Thin Films

Transparent nanostructured TiO₂ (anatase) films were prepared on fluorine-doped tin oxide (FTO) glass substrates (10 Ω/cm², 0.5 μm, Glatron). Briefly, a colloidal TiO₂ dispersion was prepared by hydrolysis of 50 ml of titanium tetra(isopropoxide) (Fluka) in order to obtain a concentration of 150 - 170 g/L.³ The solution was autoclaved at 200 °C for 12 hours to yield a dispersion of 10 nm diameter particles. Addition of Carbowax 20000 (Aldrich) (60 g/L) was made to give a viscous white sol. Conducting glass substrates were masked by Scotch™ tape and the paste evenly spread using a glass rod. Following drying in air for 30 minutes, the film was fired in air at 450 °C for 2 h. The resulting film was 5 μm thick with a surface area geometric enhancement factor of *ca.* 1000.

Adsorption of (**I**) on TiO₂ films

Complex **I** was adsorbed onto nanostructured TiO₂ (anatase) thin films on FTO glass from a 10⁻⁴ M methanol solution over 24 hours. On adsorption of **I** onto TiO₂, the Ru^{II} based MLCT absorption band centred at 456 nm in aqueous solution (pH 7) shifts to 467 nm. Also on adsorption, the emission band

centred at 650 nm in aqueous solution shifts to 668 nm. The **I**-functionalized TiO₂ thin films were then cut into finger electrodes of 0.9 x 10 cm in order to perform spectroelectrochemical experiments. The exposed surface area covered by TiO₂ for spectroelectrochemical experiments was 2.5 x 0.9 cm; see Scheme S1.



Scheme S1: Schematic of exposed surface area of the **I** functionalized TiO₂ thin film monitored during spectroelectrochemical experiments.

Spectroelectrochemical Characterisation

All spectroelectrochemical characterization was performed in SPEX Fluoromax-2 spectrofluorometer using an AMEL model 552 potentiostat controlled by an AMEL model 568 programmable function generator. The **I**-functionalized TiO₂ thin films on FTO (**I**-TiO₂) formed the working electrode of an open three electrode single compartment cell, with a Pt counter electrode and a Ag/AgCl reference electrode. The CH₃CN electrolyte (4 mL total volume) contained 0.1 M LiClO₄. Luminescence spectra were recorded as a function of both applied potential (vs. Ag/AgCl) and Cu²⁺ ion concentration.

Emission Behaviour of **I**-TiO₂ Versus Cu²⁺ Concentration

The effect of Cu²⁺ concentration on the luminescence of the **I**-TiO₂ thin films was measured using the experimental set-up described above. Fig. S1 shows the effect of added Cu²⁺ on the luminescence spectra of a **I**-TiO₂ thin film (for $V_{app} \geq V_{fb}$). A marked decrease in the emission band centred at 668 nm (467 nm excitation) is observed after addition of 0.5 mL of 10⁻³ M Cu(ClO₄)₂ in CH₃CN (dotted line) to

the spectroelectrochemical cell ($V_{\text{app}} = -0.5 \text{ V vs. Ag/AgCl}$). The luminescence is almost completely quenched after adding a total of 1 mL of a $10^{-3} \text{ M Cu}^{2+}$ solution (dashed line).

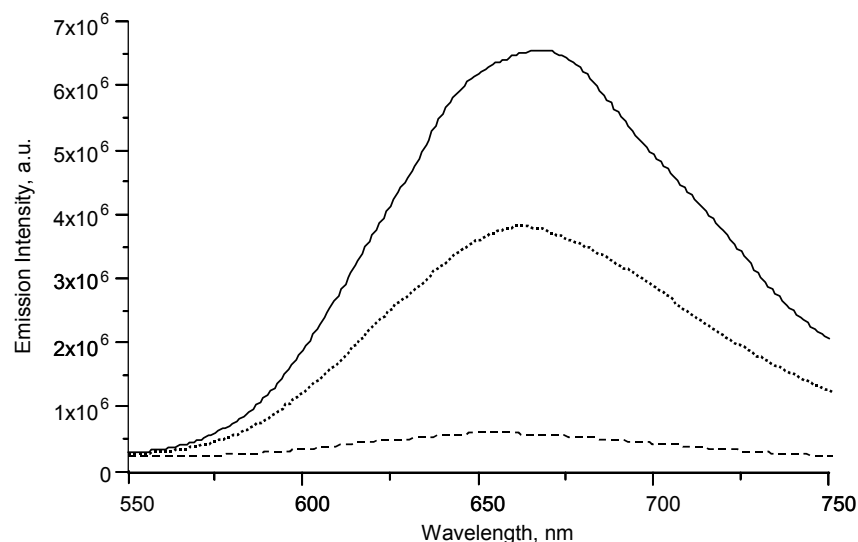


Fig. S1: Effect of Cu^{2+} concentration on the luminescence spectrum of a **I**- TiO_2 film. Emission spectra recorded before (solid line) and after the addition of 0.5 mL (dotted) and 1.0 mL (dashed) of $10^{-3} \text{ M Cu}(\text{ClO}_4)_2$ are shown. The **I**- TiO_2 working electrode was maintained at a potential of $V_{\text{app}} = -0.5 \text{ V vs. Ag/AgCl}$ throughout.

References (Supporting Information)

1. T. A. Heimer, C. A. Bignozzi and G. J. Meyer, *J. Phys. Chem.*, 1993, **97**, 11987- 11994.
2. C. A. Bignozzi, S. Roffia, C. Chiorboli, J. Davila, M. T. Indelli and F. Scandola, *Inorg. Chem.*, 1989, **28**, 4350-4358.
3. B. O'Regan and M. Grätzel, *Nature*, **1991**, 353, 737-740.