# Supporting Information

### Organic and Biomolecular Chemistry

### A fluorescent combinatorial logic gate with Na<sup>+</sup>/H<sup>+</sup>- enabled OR and H<sup>+</sup>-driven low-medium-high ternary logic functions

Jasmine M. A. Spiteri, Carl J. Mallia, Glenn J. Scerri and David C. Magri\*

Department of Chemistry, Faculty of Science University of Malta, Msida Malta, MSD 2080 email: david.magri@um.edu.mt Phone: (+356) 2340 227

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#### **Experimental**

#### Chemicals

Anhydrous magnesium sulfate (99.5%, Alfa Aesar), chloroform (99.99%, Fisher), chloroform-d (99.8 atom % D, Sigma-Aldrich), 1,2-dichloroethane (99.8%, Lab Scan), dichloromethane (99.99%, Fisher), N,N-dimethylformamide (DMF) (99.97%, Fisher), glacial acetic acid (Analar grade, Carlo-erba), methanesulfonic acid (≥99.5%, Sigma-Aldrich), methanol (99.9%, Aldrich), *n*-heptane (99.9%, Lab-scan), (*N*-methyl)aminomethylanthracene (99.0%, Sigma-Aldrich), phosphorus oxychloride (99.0%, Sigma-Aldrich), potassium carbonate (99.0%, Hopkins & Williams), octan-1-ol (98%, Fisher Scientific), (sodium methanesulfonate (98%, Aldrich Chemical Co. Ltd.), tetrabutylammonium hydroxide solution (purum, 25% in water, Fluka Analytical) were used as provided. Sodium triacetoxyborohydride (95.0%, Sigma-Aldrich) was stored in a desiccator. Molecular sieves (4Å cylindrical, Roth) were activated in a furnace at 350 °C for 96 hours and stored afterwards in a desiccator. Silica gel (particle size 0.063-0.20 mm, 70-230 mesh ASTM) and alumina (activated, neutral, 150 µm, 150 mesh, Brockmann I) were used without prior activation for column chromatography and silica on TLC aluminum foils plates (silica gel matrix on aluminum foil with fluorescence indicator 254 nm) (Fluka Analytical) were used as provided. All chemicals were used without further purification unless otherwise stated.

#### Instrumentation

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD NMR spectrometer with an Ascend 500 11.75 Tesla superconducting magnet and a multinuclear 5 mm PABBO probe at 298 K operating at 500.13 MHz and 125.76 MHz for <sup>1</sup>H and <sup>13</sup>C NMR, respectively. <sup>13</sup>C NMR DEPT experiments were performed to determine the number of protons attached to each carbon atom. They are labelled as either upright ( $\uparrow$ ), inverted ( $\downarrow$ ) or no peak (–). These symbols correspond to carbon atoms with one or three protons attached ( $\downarrow$ ), a carbon atom with two protons attached ( $\downarrow$ ), or a carbon atom with no protons attached (–), respectively.

Samples of 5-10 mg were dissolved in 0.8 mL of chloroform-*d* containing 0.03% v/v TMS (99.8% D, Aldrich Chemical Co. Ltd.) for <sup>1</sup>H NMR and 30 mg for <sup>13</sup>C NMR. Chemical shifts are reported in parts per million (ppm) downfield from TMS set to 0.00 ppm for both <sup>1</sup>H and <sup>13</sup>C

experiments. The infrared spectra were recorded on a Shimadzu IRAffinity-1 spectrophotometer, calibrated using 1601 cm<sup>-1</sup> polystyrene absorption peak. Liquid samples were analysed as thin films on polished sodium chloride windows, while solid samples were analysed using KBr disks. Melting points were recorded using a Griffin melting point apparatus and Fisherbrand UK thermometer (-10 to 160°C) and measurements are uncorrected.

UV-visible absorption and fluorescence spectra were recorded on a Jasco V-650 spectrophotometer and Jasco FP-8300 spectrofluorimeter, respectively. The excitation wavelength was 365 nm. The scan window was typically 380-550 nm with excitation and emission slit widths at 2.5 nm. Data was acquired at 0.5 nm increments at a scan speed of 500 nm min<sup>-1</sup> and medium sensitivity.

A Schimadzu GC-17A gas chromatography with flame ionization detector (FID) was used to check the purity of products. A silica capillary column (30 m × 0.25 mm) coated with CP-sil CB (dimethylpolysiloxane) (OPTIMA<sup>®</sup> - 1 - 0.25  $\mu$ m) and nitrogen as the carrier gas were used. The temperature programme consisted of an initial temperature of 65 °C for 3 minutes and an end temperature of 300 C at a rate of 15 C/min with a holding time of 8 minutes. Data was acquired using XCalibur Version 1.3 software. Electron impact (EI) settings were used in the mass spectrometer. HRMS were obtained from Medac Ltd. UK.

#### **Synthesis**

Compounds **3-5** were synthesised according to a literature procedure using reduced quantities according to H. He, M.A. Mortellaro, M. J. P. Leiner, S. T. Young, R. J. Fraatz and J. K. Tusa, *Anal. Chem.*, 2003, **75**, 549 (Scheme S1). Compounds **3-5** were obtained as oils in 88%, 20% and 30% respectively, and gave <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis consistent with reported literature. The synthesis and characterisation of **3-5** were recently reported by B. J. Müller, T. Rappitsch, C. Staudinger, C. Rüschitz, S. M. Borisov, and I. Klimant, *Anal. Chem.* 2017, 89, 7195.



Scheme S1. Synthesis of molecular logic gate 1.



**Fig. S1** UV-visible absorption spectra of 6  $\mu$ M **1** in 1:1 ( $\nu/\nu$ ) MeOH/H<sub>2</sub>O as a function of pH (in the presence of Na<sup>+</sup>).



**Fig. S2**: <sup>1</sup>H NMR spectrum of **1** in CDCl<sub>3</sub> at 500 MHz.



Fig. S3: <sup>13</sup>C NMR spectrum of 1 in CDCl<sub>3</sub> at 500 MHz.



Fig. S4: <sup>13</sup>C DEPT NMR spectrum of 1 in CDCl<sub>3</sub> at 500 MHz.



Fig. S5: IR spectrum of 1 on a NaCl plate as a thin film from chloroform–*d*.



Fig. S6: High resolution mass spectrum of 1 by time-of-flight (TOF).

**Elemental Composition Report** 

Single Mass Analysis Tolerance = 10.0 PPM / DBE: min = -1.5, max = 80.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions 455 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass) Elements Used: C: 34-34 H: 0-150 N: 0-10 O: 0-20 Na: 0-1 Minimum: -1.5 10.0 80.0 Maximum: 5.0 PPM Mass DBE Calc. Mass mDa i-FIT i-FIT (Norm) Formula 581.2991 14.5 C34 H42 N2 O5 Na 581.2994 0.3 0.5 111.5 0.0