

Organic hydrophilic dye for water-based dye-sensitized solar cells

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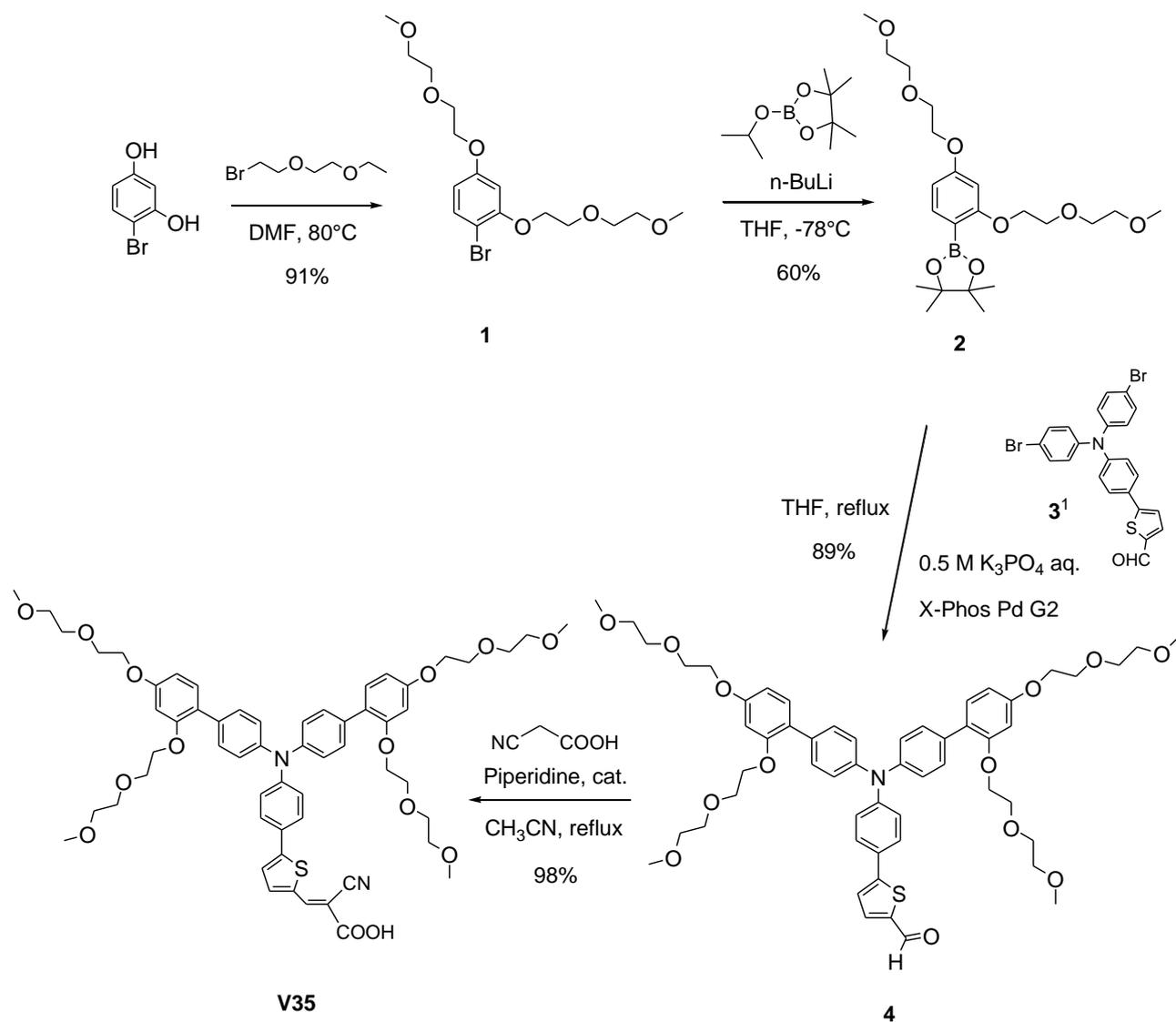
Synthesis and characterization: general methods.

NMR spectra were recorded on an instrument operating at 500.13 (^1H) and 125.77 MHz (^{13}C) using the residual signals $\delta = 7.26$ ppm and 77.1 ppm from CDCl_3 and $\delta = 2.05$, 29.84, and 206.26 ppm from acetone- d_6 , as internal references for ^1H and ^{13}C respectively. Coupling constants are given in Hz. HRMS measurements were performed using a Bruker micrOTOF (ESI-TOF MS) mass spectrometer. Flash chromatography was performed with silica gel 60 Å (35–63 μm). Chemicals used in the synthesis were purchased from Sigma-Aldrich unless otherwise specified. Tetrahydrofuran (THF) was dried by passing through a solvent column composed of activated alumina. Commercially available reactants were used without further purification unless otherwise noted. Reactions under nitrogen were performed in oven-dried glassware and monitored by thin layer chromatography using UV light (254 and 365 nm) as a visualizing agent. Extracts were dried with anhydrous MgSO_4 and filtered before removal of the solvent by evaporation.

Synthesis of V35.

The synthetic route of V35 is shown in Scheme S1.

Scheme S1. Synthetic route for dye V35.



Note: Intermediate **3** was prepared according to literature procedure.¹

1. D. P. Hagberg, X. Jiang, E. Gabrielsson, M. Linder, T. Marinado, T. Brinck, A. Hagfeldt, and L. Sun, *J. Mater. Chem.*, 2009, **19**, 7232.

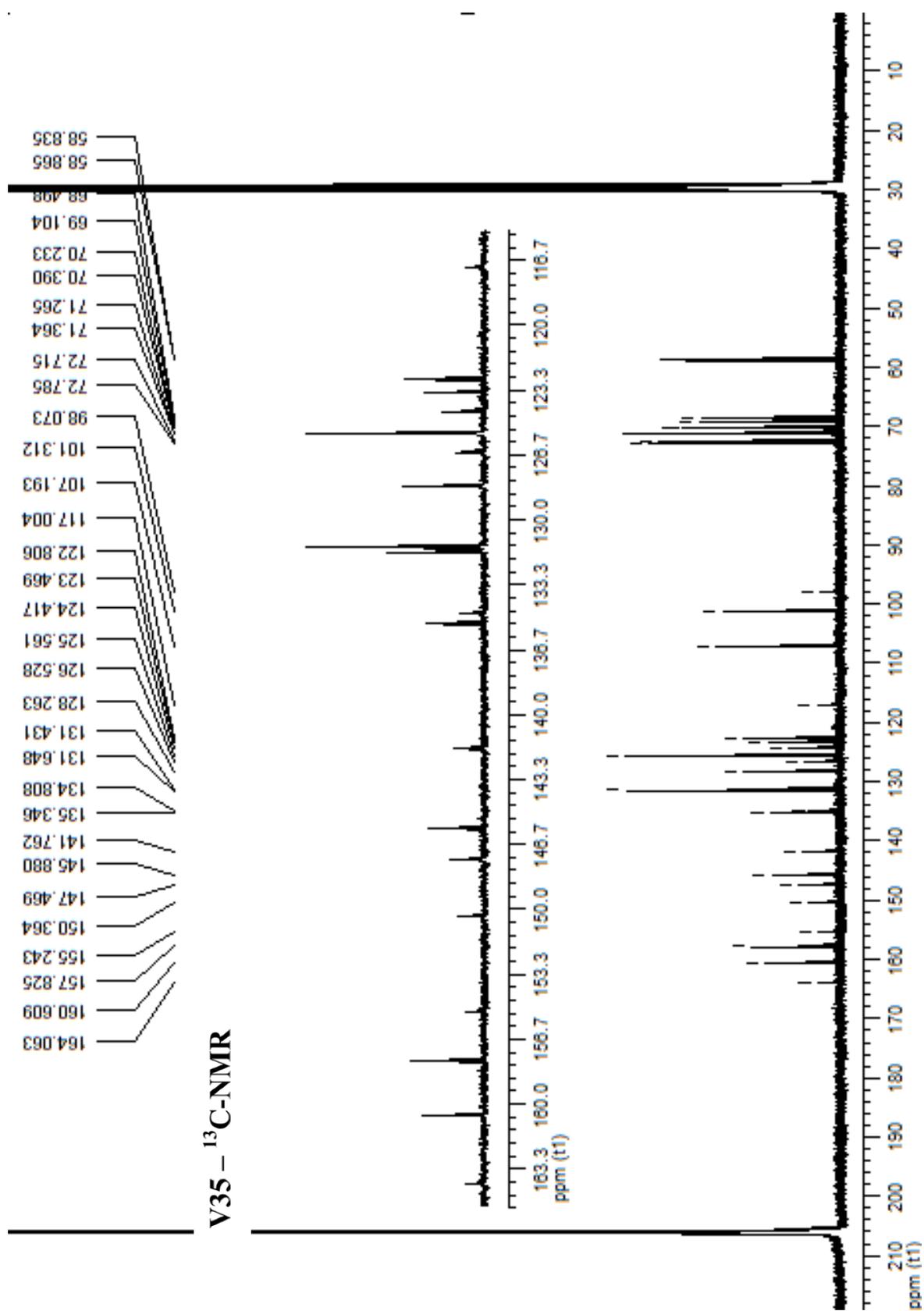
1-bromo-2,4-bis(2-(2-methoxyethoxy)ethoxy)benzene (1). To a solution of 4-Bromoresorcinol (2.03 g, 10.74 mmol) in dry DMF (30 mL), 1-bromo-2-(2-methoxyethoxy)ethane (7.86 g, 42.96 mmol) and K_2CO_3 (5.94 g, 42.96 mmol) were added at room temperature. After being stirred at 80°C for 6 h, the mixture was cooled down to room temperature and petroleum ether was added. The mixture was filtered to remove K_2CO_3 in excess, petroleum ether was evaporated under reduced pressure and the resulting solution was distilled. The residual oil was poured in H_2O (100 mL) and extracted with Et_2O (2 x 150 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo to give the desired product as a colorless oil (3.84 g, 9.77 mmol, 91%). 1H -NMR ($CDCl_3$) δ 7.35 (d, $J = 8.7$ Hz, 1H), 6.51 (d, $^4J = 2.6$ Hz, 1H), 6.38 (dd, $J = 8.7$, $^4J = 2.6$ Hz, 1H), 4.12 (t, $J = 4.8$, 2H), 4.08 (t, $J = 4.6$, 2H), 3.88 (t, $J = 5.0$ Hz, 2H), 3.82 (t, $J = 4.9$ Hz, 2H), 3.78-3.76 (m, 2H), 3.69-3.67 (m, 2H), 3.56-3.54 (m, 4H), 3.37 (s, 3H), 3.36 (s, 3H). ^{13}C -NMR ($CDCl_3$) δ 159.27, 155.85, 133.09, 107.18, 103.16, 101.86, 72.03, 71.93, 71.07, 70.76, 69.66, 69.44, 69.04, 67.72, 59.09, 59.07. ESI-HRMS: calcd for $[M + Na]^+$ $C_{16}H_{25}BrNaO_6$ 415.0730, found 415.0727.

2-(2,4-bis(2-(2-methoxyethoxy)ethoxy)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (2). Under nitrogen atmosphere, a solution of 1-bromo-2,4-bis(2-(2-methoxyethoxy)ethoxy)benzene **1** (1.23 g, 3.12 mmol) in anhydrous THF (30 mL) was cooled to -78°C (dry ice-acetone bath). To this, was added chilled n-BuLi (2.5 mL, 6.20 mmol, 2.5 M solution in hexanes) dropwise from a syringe, and the reaction mixture was stirred at -78 °C for 2.5 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.82 mL, 9.35 mmol) was added to the mixture that was kept at -78°C for 1.5 h, and then allowed to reach room temperature. After 4 h the reaction was poured into H_2O and extracted with Et_2O (3 x 150 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo, affording the crude compound (0.824 g, 1.87 mmol, 60% estimated from NMR), used for the following step without further purification. 1H -NMR ($CDCl_3$) δ 7.57 (d, $J = 8.2$ Hz, 1H), 6.45 (dd, $J = 8.2$, $^4J = 1.8$ Hz, 1H), 6.40 (d, $^4J = 1.8$ Hz, 1H), 4.13-4.07 (m, 4H), 3.88-3.86 (m, 2H), 3.82-3.80 (m, 2H), 3.70-3.67 (m, 4H), 3.56-3.54 (m, 4H), 3.36 (s, 6H), 1.29 (s, 12H). ESI-HRMS: calcd for $[M + Na]^+$ $C_{22}H_{37}BNaO_8$ 463.2478, found 463.2480.

5-(4-(bis(2',4'-bis(2-(2-methoxyethoxy)ethoxy)biphenyl-4-yl)amino)phenyl)thiophene-2-carbaldehyde (4). X-Phos aminobiphenyl palladium chloride precatalyst (19 mg, 0.024 mmol), compound **2** (0.550 g, 1.25 mmol) and dibromo intermediate **3**, (0.246 g, 0.480 mmol) were dissolved in THF (30 mL). After stirring for 10 minutes, a solution 0.5 M of K_3PO_4 in H_2O (3.84 mL, 1.92 mmol) was added to the reaction. The resulting mixture was refluxed for 4 h. After being cooled to room temperature, the reaction mixture was poured into water, filtered on celite and

extracted with ethyl acetate (3 x 120 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. Flash chromatography purification with gradient elution (ethyl acetate/Ethanol, 4/1) gave the product as a yellow solid (0.418 g, 0.427 mmol) in 89% yield. ¹H-NMR (Acetone-d₆) δ 9.90 (s, 1H), 7.91 (d, *J* = 3.9 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.5, 4H), 7.53 (d, *J* = 3.9, 1H), 7.29 (d, *J* = 8.4, 2H), 7.17 (d, *J* = 8.5 Hz, 4H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.70 (d, ⁴*J* = 2.0 Hz, 2H), 6.62 (dd, *J* = 8.4, ⁴*J* = 2.0 Hz, 2H), 4.20-4.15 (m, 8H), 3.84-3.77 (m, 8H), 3.67-3.63 (m, 4H), 3.61-3.57 (m, 4H), 3.53-3.50 (m, 4H), 3.46-3.42 (m, 4H), 3.30 (s, 6H), 3.19 (s, 6H). ¹³C-NMR (Acetone-d₆) δ 183.54, 160.57, 157.80, 154.38, 150.12, 145.50, 142.50, 139.36, 135.17, 131.67, 131.41, 128.14, 126.88, 125.42, 124.29, 123.47, 123.02, 107.15, 101.31, 72.78, 72.72, 71.36, 71.27, 70.40, 70.23, 69.07, 68.49, 58.86. ESI-HRMS: calcd for [M + Na]⁺ C₅₅H₆₅NNaO₁₃S 1002.4069, found 1002.4037.

(E)-3-(5-(4-(bis(2',4'-bis(2-(2-methoxyethoxy)ethoxy)biphenyl-4-yl)amino)phenyl)thiophen-2-yl)-2 cyanoacrylic acid (V35). To a solution of **4** (0.250 g, 0.255 mmol) in CH₃CN (12 mL), cyanoacetic acid (0.217, 2.55 mmol) and a catalytic amount of piperidine were added. The reaction was refluxed for 24 h, poured into HCl 10% (100 mL) and stirred overnight at rt. After evaporation of CH₃CN, a dark precipitate was formed. Isolation of the precipitate by vacuum filtration afforded pure product as highly hygroscopic dark-red solid (0.260 g, 0.250 mmol) in quantitative yield. ¹H-NMR (Acetone-d₆) δ 8.43 (s, 1H), 7.97 (d, *J* = 4.0 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.66-7.61 (m, 5H), 7.32 (d, *J* = 8.4, 2H), 7.21 (d, *J* = 8.5, 4H), 7.16 (d, *J* = 8.7 Hz, 2H), 6.71 (d, ⁴*J* = 2.1 Hz, 2H), 6.64 (dd, *J* = 8.4, ⁴*J* = 2.1 Hz, 2H), 4.21-4.17 (m, 8H), 3.84-3.78 (m, 8H), 3.68-3.65 (m, 4H), 3.62-3.59 (m, 4H), 3.53-3.50 (m, 4H), 3.47-3.43 (m, 4H), 3.31 (s, 6H), 3.21 (s, 6H). ¹³C-NMR (Acetone-d₆) δ 164.06, 160.61, 157.82, 155.24, 150.36, 147.47, 145.88, 141.76, 135.35, 134.81, 131.65, 131.43, 128.26, 126.53, 125.56, 124.42, 123.47, 122.81, 117.00, 107.19, 101.31, 98.07, 72.78, 72.71, 71.36, 71.27, 70.39, 70.23, 69.10, 68.50, 58.86, 58.83. ESI-HRMS: calcd for [M + Na]⁺ C₅₈H₆₆N₂NaO₁₄S 1069.4127, found 1069.410



Electrochemical characterization.

Dye **V35** was submitted to electrochemical characterization. The chromophore was dissolved (20 mM) in a 0.1 M solution of LiClO₄ (Aldrich, 99.9%) in CH₃CN (Aldrich) as the supporting electrolyte. Cyclic voltammeteries (CV) were carried out at a scan rate of 1 mVs⁻¹ using a Mini-autolab potentiostat in a one-chamber three-electrode electrochemical cell. The working, counter, and pseudo-reference electrodes were a Pt wire, graphite rod (3 mm diameter), and a silver wire, respectively. The Ag/AgNO₃ pseudo-reference electrode was calibrated by adding ferrocene to the test solution.

The current potential profile is shown in Figure S1. The oxidative wave is reversible.

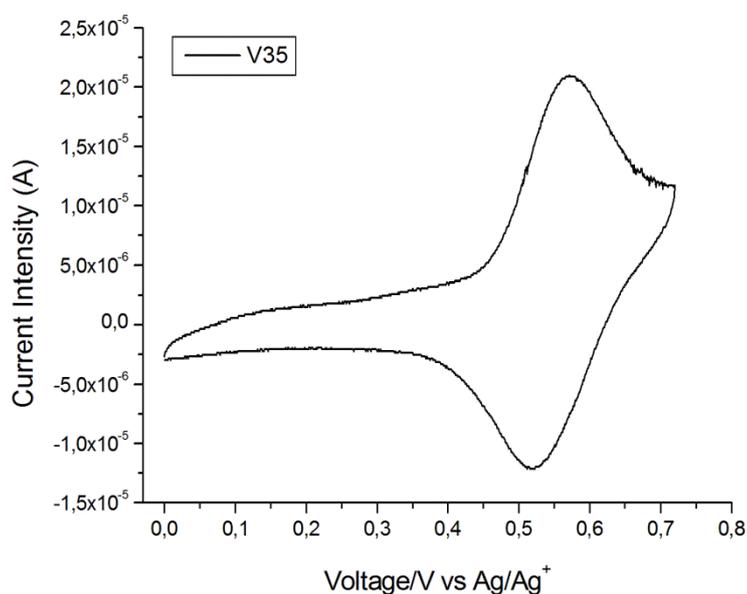


Figure S1. Cyclic voltammetry of V35.

UV-Vis desorption spectra of V35

To test the tendency of V35 to desorb from the surface, transparent working electrodes (active layer around 2.0-2.5 μm thick) were sensitized with V35 and placed into 5 mL of distilled water, and a buffer solution of distilled water at pH 4.0. The absorption spectra recorded show negligible desorption at acidic pH and reduced intensity of the absorption peak in neutral conditions (Figure S2).

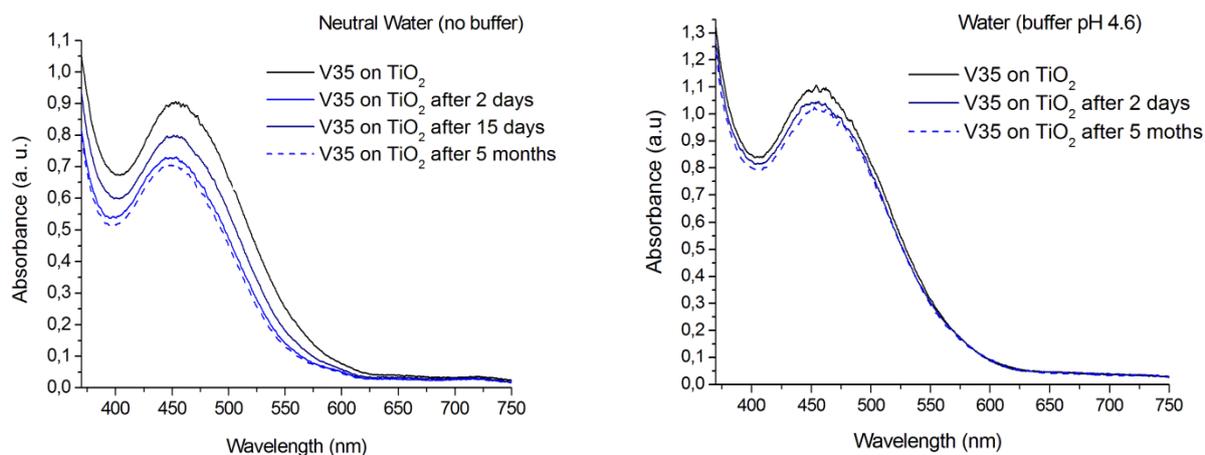


Figure S2. Desorption spectra of V35 in distilled water (a) and in a distilled water buffer solution at pH 4.6 (b).

In both conditions the equilibrium is reached after 2 weeks, since there is no significant desorption after this period. It must be pointed out that the volume of water is enormously bigger compared to the one injected in the devices, therefore the equilibrium is completely shifted in favour of desorption. No desorption in neutral water occurred inside the assembled devices. In addition, test performed on the complete devices at basic pH buffer show very good and stable data for cells until pH 9.0. To our knowledge, this results to be the most limited desorption recorded for dyes able to perform strong interaction with water.