

# Colorful surface architectures with three different types of dynamic covalent bonds: integration of anthocyanins, tritylium ions and flavins

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## Supporting Information

### 1. Material and methods

As in ref. S1, Supporting Information. Briefly, cyanidin chloride, mavidin chloride, pyrocatechol violet (PV), and riboflavin were purchased from Sigma-Aldrich. Indium tin-oxide (ITO) coated glass substrates were obtained from Präzisions Glas & Optik GmbH (Iserlohn, Germany). Unless stated otherwise, UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller and are reported as maximal absorption wavelength in nm. Photocurrents were measured using a 150 W solar simulator (Newport) and an Electrochemical Analyzer (CH Instruments 660C). The irradiation power was measured using a radiant power energy meter (Newport model 70260).

**Abbreviations.** AcOH: Acetic acid; DIPEA: *N,N*-Diisopropylethylamine; DMSO: Dimethylsulfoxide; EtOH: Ethanol; HEPES: 4-(2-Hydroxyethyl)-1-piperazineeth

anesulfonic acid; ITO: Indium tin oxide; MeOH: Methanol; NDI: 1,4,5,8-Naphthalenediimide; rt: Room temperature; SOSIP: Self-organizing surface-initiated polymerization; TEOA: Triethanolamine; TSA: Templated stack addition; TSE: Templated stack exchange.

## 2. Templated stack exchange with hydrazones

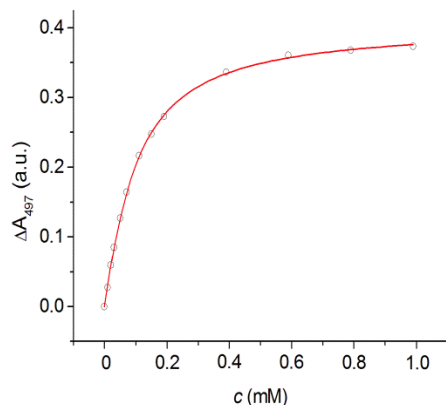
**S1H2**.<sup>S1</sup> ITO electrodes **S1H1**<sup>S2</sup> were placed in an aqueous solution of NH<sub>2</sub>OH·HCl (2.0 mL, 1.0 M, pH 3.0) at 40 °C. After 1 day the hydrazone-oxime exchange was completed.<sup>S1,S2</sup> Coated ITO electrodes after NH<sub>2</sub>OH treatment **S1H1** were placed in DMSO solution of 2-fluoro-4-formylphenylboronic acid **H2** (50 mM) and AcOH (4% v/v) for 10 h at room temperature. The resulting electrodes were rinsed with MeOH and dried under flow of air.

## 3. Boronic esters in solution

**\*H2B5**. Based on UV-Vis experiments (Figure 6a), the dissociation constants ( $K_D$ ) of **\*H2B5** in MeOH/H<sub>2</sub>O 3:1 (100 mM HEPES, pH 7.4) was determined to be  $70.0 \pm 1.3 \mu\text{M}$ . To determine dissociation constants ( $K_D$ ) from titration experiments,  $K_D$ 's were deduced from equation (S1) for 1:1 binding motif.<sup>S3</sup>

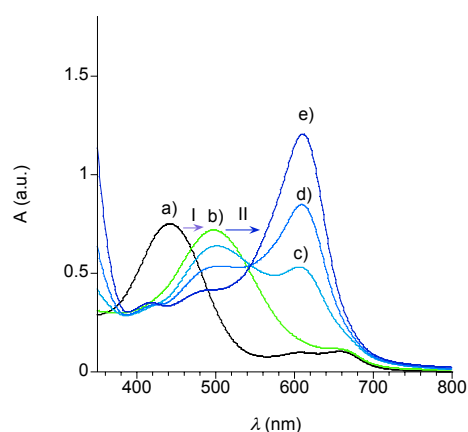
$$\Delta A = (\Delta A_{\max} / [B]_0) \times (0.5 \times [H] + 0.5 \times ([B]_0 + K_D) - (0.5 \times (([H]^2) + (2 \times ([H]) \times (K_D - [B]_0)) + (K_D + [B]_0)^2)^{0.5})) \quad (\text{S1})$$

where  $\Delta A = A - A_0$ ,  $[H]$  = concentration of **B5**, and  $[B]$  = concentration of **\*H2**.



**Fig. S1.** Changes in absorption  $\Delta A$  at 497 nm of **B5** (50  $\mu\text{M}$ ) in MeOH/H<sub>2</sub>O 3:1 (100 mM HEPES, pH 7.4) as a function of the concentration of **\*H2**, with fit to equation (S1).

**\*H2B6.** In MeOH/H<sub>2</sub>O 3:1 (100 mM HEPES, pH 7.4), the absorption at long wavelength for dimer **\*H2B6** was detectable only with excess **\*H2** (Figure S2).



**Fig. S2.** UV-Vis spectra of **B5** (50  $\mu\text{M}$ ) in MeOH/H<sub>2</sub>O 3:1 (100 mM HEPES, pH 7.4) in the presence of increasing concentrations of **\*H2**: a) 0 mM, b) 1.0 mM (**\*H2B5**), c) 7.7 mM, d) 23.2 mM, and e) 59.4 mM (**\*H2B6**).

To determine TSE yields  $\eta$ , the following extinction coefficients  $\epsilon$  were determined in solution (MeOH/H<sub>2</sub>O 3:1 (100 mM HEPES, pH 7.4)):

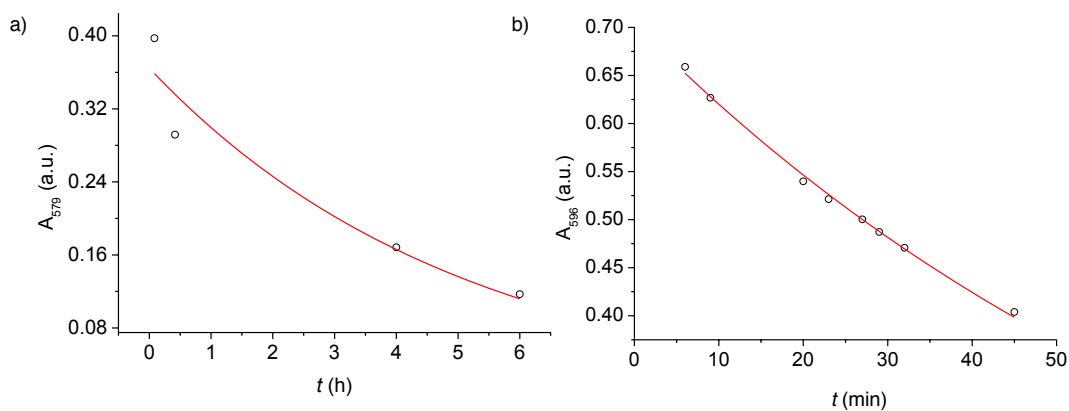
<b>S1</b> (unsubstituted NDIs) <sup>S1</sup>	$\epsilon_{381} = 14.5 \text{ mM}^{-1} \text{ cm}^{-1}$
* <b>H2B1</b> (cyanidin)	$\epsilon_{389} = 36 \text{ mM}^{-1} \text{ cm}^{-1}$
* <b>H2B5</b> (PV)	$\epsilon_{497} = 15.3 \text{ mM}^{-1} \text{ cm}^{-1}$
* <b>H2B6</b> (PV)	$\epsilon_{497} = 27.3 \text{ mM}^{-1} \text{ cm}^{-1}$
<b>B7</b> (riboflavin)	$\epsilon_{448} = 12.6 \text{ mM}^{-1} \text{ cm}^{-1}$

#### 4. Templated stack addition with boronic esters

**S1H2B1, S1H2B2, S1H2B7.** ITO electrodes **S1H2** were placed solutions of cyanidin chloride **B1**, malvidin chloride **B2** or riboflavin **B7** in DMSO (concentrations varied, Figure 3), for 24 h, at room temperature. The resulting electrodes were quickly rinsed with DMSO and then CH<sub>2</sub>Cl<sub>2</sub>, and dried under flow of air (Figures 2, 3, 8).

**S1H2B6.** ITO electrodes **S1H2** were placed in solutions of PV **B5** in DMSO/H<sub>2</sub>O 8:2 (100 mM HEPES, pH 7.4) for 6 h at room temperature. The resulting electrodes were quickly rinsed with water and EtOH, and dried under flow of air (Figure 6b).

## 5. The stability of the cyanidin boronic esters in basic conditions



**Fig. S3.** a) Change in absorption  $A_{579}$  (right) of ITO electrode **S1H2B1** as a function of the time of incubation in DMSO (2% v/v DIPEA) at rt,  $t_{50} = 3.5 \pm 0.5$  h (Figure 4c). b) Change in absorption  $A_{596}$  as a function of time after the addition of 2% DIPEA to a solution of **B1** (50  $\mu$ M) and **\*H2** (14 mM) at rt,  $t_{50} = 55 \pm 5$  min (Figure 4d).

## 6. Photocurrent measurements

As described:<sup>S2</sup> The final architectures were used as working electrode with a Pt wire as a counter electrode and Ag/AgCl as a reference electrode. The electrodes were immersed in a deaerated (by bubbling Ar gas) aqueous solution of TEOA (50 mM) and  $\text{Na}_2\text{SO}_4$  (0.1 M) and irradiated with a solar simulator (area of irradiation:  $a \sim 0.5 \text{ cm}^2$ ). Changes in current upon on-off switching of irradiation were measured at 0 V vs Ag/AgCl. The power of irradiation was  $88 \text{ mWcm}^{-2}$  (Figure 9).

## 7. Supporting references

- S1 K.-D. Zhang and S. Matile, *Angew. Chem. Int. Ed.*, 2015, **54**, 000.
- S2 N. Sakai and S. Matile, *J. Am. Chem.Soc.*, 2011, **133**, 18542-18544.
- S3 W. Li, D. L. Jiang, Y. Suna and T. Aida, *J. Am. Chem.Soc.*, 2005, **127**, 7700-7702.