

Molecular association between flavin derivatives and dendritic polymers at the water|1,2-dichloroethane interface

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Supplementary material

Molecular association between flavin derivatives and dendritic polymers at the water|1,2-dichloroethane interface

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S1. Electrochemical data measured for dendritic polymers at the water|DCE interface

Cyclic voltammograms (CVs) measured for the fourth generation (G4) PAMAM dendrimer and hyperbranched bis-MPA polyester-64-hydroxyl (HBP) are shown in **Fig. S1a**. The voltammetric responses at $0.2 \text{ V} < \Delta_o^w \phi$ in the presence of the dendrimer are correlated to the ion transfer and adsorption responses of positively charged dendrimers accompanied by the facilitated transfer of the organic electrolyte anion [1]. On the other hand, CVs for HBP coinciding with the base electrolyte system indicated no charge transfer within the potential window. The capacitance curves in **Fig. S1b** exhibited significant adsorption of the positively charged dendrimer and neutral HBP in the positive and negative potential regions, respectively [2].

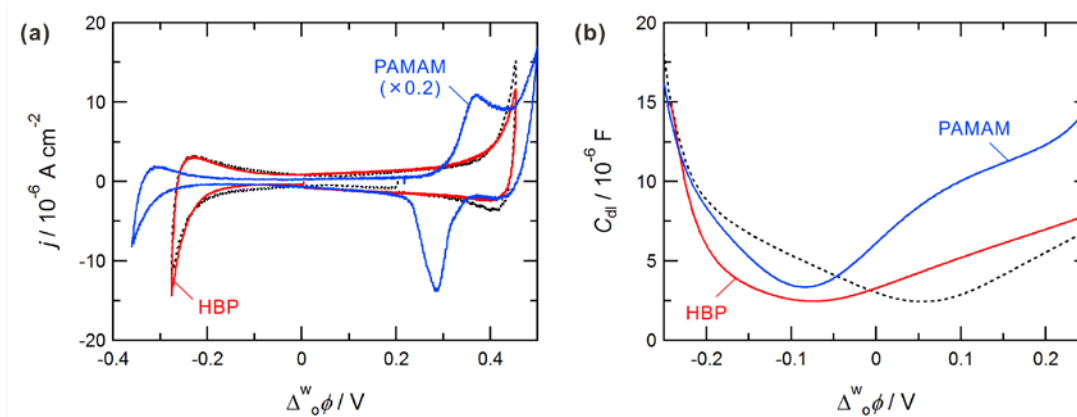


Fig. S1 (a) CVs and **(b)** capacitance curves measured for the G4 PAMAM dendrimer (pH 7.3) and HBP (pH 7.1) at the water|DCE interface. The potential sweep rates were **(a)** 50 mV s^{-1} and **(b)** 5 mV s^{-1} , respectively. The dotted lines refer to the base electrolyte system at pH 7.1. The concentration of dendritic polymers was $1.0 \times 10^{-5} \text{ mol dm}^{-3}$.

S2. Potential-modulated fluorescence (PMF) spectroscopy [3, 4]

S2-1. PMF for a quasi-reversible ion transfer process

The PMF signal associated with a quasi-reversible ion transfer (ΔF_t) is correlated with the faradic ac current ($i_{f,ac}$). Considering that the ion transfer occurs from the water to the organic phase, ΔF_t with total internal reflection excitation is described as

$$\Delta F_t = \frac{4.606 \varepsilon \Phi_f I_0}{j \omega z F S \cos \psi} i_{f,ac} \quad (\text{S1})$$

where ε is the molar absorption coefficient, Φ_f is the fluorescence quantum yield, I_0 is the

intensity of excitation light, j is the imaginary number, ω is the angular frequency, z is the charge number, S is the interfacial area, and ψ is the angle of incidence. Then, the real and imaginary components of PMF for the ion transfer process can be expressed by

$$\Delta F_{t, \text{re}} = \frac{4.606 \varepsilon \Phi_f I_0}{zFS \cos \psi} \left[\frac{\Delta_o^w \phi_{ac} \sigma \omega^{-3/2}}{\left(R_{ct} + \sigma \omega^{-1/2} \right)^2 + \left(\sigma \omega^{-1/2} \right)^2} \right] \quad (\text{S2})$$

$$\Delta F_{t, \text{im}} = -\frac{4.606 \varepsilon \Phi_f I_0}{zFS \cos \psi} \left[\frac{\Delta_o^w \phi_{ac} \left(R_{ct} + \sigma \omega^{-1/2} \right) \omega^{-1}}{\left(R_{ct} + \sigma \omega^{-1/2} \right)^2 + \left(\sigma \omega^{-1/2} \right)^2} \right] \quad (\text{S3})$$

where $\Delta_o^w \phi_{ac}$ is the amplitude of the potential modulation, R_{ct} is the charge transfer resistance, and σ is the Warburg term.

S2-2. PMF for an adsorption process

The PMF signal associated with the adsorption (ΔF_a) from the aqueous phase to the interface is expressed as a function of the ac surface coverage (θ_{ac}).

$$\Delta F_a = 2.303 \varepsilon \Phi_f I_0 \Gamma_s \theta_{ac} \quad (\text{S4})$$

$$\theta_{ac} = \frac{bzF \Delta_o^w \phi_{ac}}{RT} \left[\frac{k_{a,dc} \alpha c_i (1 - \theta_{dc}) - k_{d,dc} (\alpha - 1) \theta_{dc}}{k_{a,dc} c_i + k_{d,dc} + j\omega} \right] \quad (\text{S5})$$

where Γ_s is the saturated interfacial concentration, b is the portion of applied potential employed for adsorption process, α is the overall transfer coefficient for adsorption process (~ 0.5), θ_{dc} is the dc surface coverage, c_i is the bulk concentration, $k_{a,dc}$ and $k_{d,dc}$ are the dc components of adsorption and desorption rate constants at given potentials. The real and imaginary components of ΔF_a are described as

$$\Delta F_{a, \text{re}}^w = \frac{2.303 \varepsilon \Phi_f I_0 \Gamma_s SbzF}{RT} \left[\frac{\Delta_o^w \phi_{ac} \left(k_{a,dc} \alpha c_i (1 - \theta_{dc}) - k_{d,dc} (\alpha - 1) \theta_{dc} \right) \left(k_{a,dc} c_i + k_{d,dc} \right)}{\left(k_{a,dc} c_i + k_{d,dc} \right)^2 + \omega^2} \right] \quad (\text{S6})$$

$$\Delta F_{a, \text{im}}^w = -\frac{2.303 \varepsilon \Phi_f I_0 \Gamma_s SbzF}{RT} \left[\frac{\Delta_o^w \phi_{ac} \left(k_{a,dc} \alpha c_i (1 - \theta_{dc}) - k_{d,dc} (\alpha - 1) \theta_{dc} \right) \omega}{\left(k_{a,dc} c_i + k_{d,dc} \right)^2 + \omega^2} \right] \quad (\text{S7})$$

The appropriate reverse sign is applied for the adsorption process from the organic phase because of an opposite potential dependence of the surface concentration.

S3. Interaction between PAMAM dendrimer and lumichrome in aqueous solution

Fig. S2 shows typical absorption and fluorescence spectra of lumichrome (LC) in the presence and absence of the G4 PAMAM dendrimer at pH 7.1–7.3. The fluorescence intensity of LC was increased by the addition of the dendrimer. It has been reported that monoanionic LC species (LC^-) electrostatically interact with the human serum albumin and, as a result, the fluorescence intensity of LC increases [5]. Taking into account the acidity constant of LC ($\text{p}K_{\text{a,LC}} = 8.2\text{--}8.28$) [6, 7], the spectral changes under neutral pH conditions could be arisen from the electrostatic interaction between LC^- and the positively charged dendrimer.

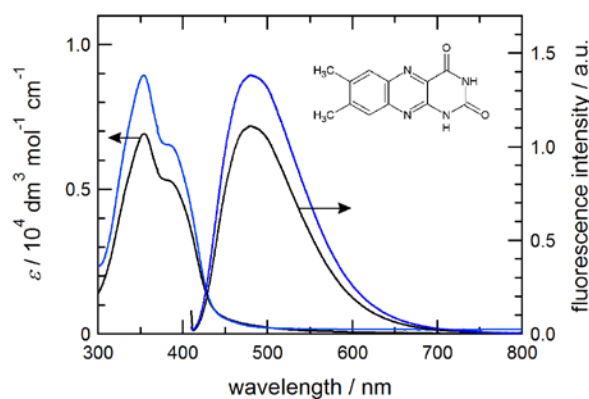


Fig. S2 (a) Absorption and **(b)** fluorescence spectra of LC in the aqueous solution at pH 7.1–7.3. The black and blue lines depict the spectra in the absence and presence of the G4 PAMAM dendrimer, respectively. The concentration of LC and the dendrimer was $1.0 \times 10^{-5} \text{ mol dm}^{-3}$. The fluorescence spectra were measured at an excitation wavelength of 404 nm.

S4. Spectroelectrochemical analysis of lumichrome at the water|DCE interface

Fig. S3 shows CVs and capacitance curves measured for LC in the presence and absence of the dendrimer under the neutral conditions. In the LC system, CVs and capacitance curves were almost identical to the base electrolyte system because of no charge transfer and adsorption at the interface. In the presence of the G4 PAMAM dendrimer, electrochemical responses of the flavin derivatives were buried in the ion transfer and adsorption responses of the dendrimer (cf. **Fig. S1**) [1]. In contrast to the electrochemical measurements, the potential dependences of the PMF responses associated with the adsorption of LC species at either side of the interface were

observed in the positive and negative potential regions (**Fig. S4**, black lines). In the presence of the positively charged PAMAM dendrimer, the PMF signals were measured as positive real ($\Delta F_{\text{re}} > 0$) and negative imaginary components ($\Delta F_{\text{im}} < 0$) at 0.34 V and $\Delta F_{\text{re}} < 0$ and $\Delta F_{\text{im}} > 0$ at 0.38 V, respectively (**Fig. S4**, blue lines). These PMF responses were attributed to the ion transfer and adsorption of the dendrimer-bound fluorescent LC species at the organic side of the interface [1, 8]. The slight enhancement of the fluorescence intensity confirmed the interaction between LC and the dendrimer as indicated from fluorescence spectra in aqueous solutions (**Fig. S2**).

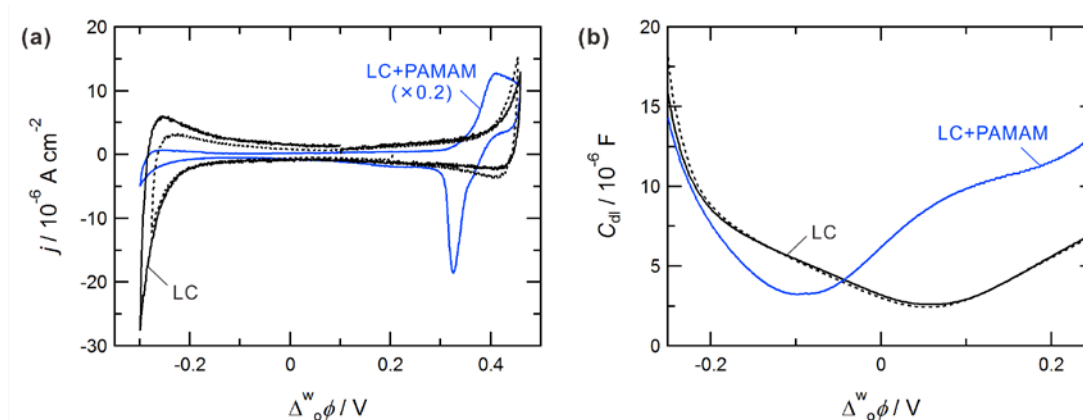


Fig. S3 (a) CVs and (b) capacitance curves measured for LC in the presence and absence of the G4 PAMAM dendrimer at the water|DCE interface. The potential sweep rates were (a) 50 mV s^{-1} and (b) 5 mV s^{-1} , respectively. The dotted lines refer to the base electrolyte system at pH 7.1. The concentration of LC and the dendrimer was $1.0 \times 10^{-5} \text{ mol dm}^{-3}$.

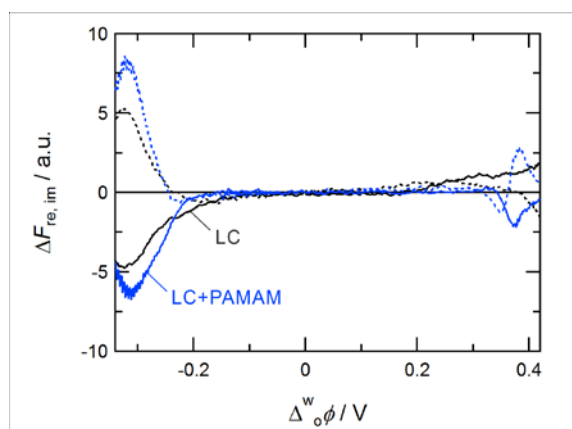


Fig. S4 Potential dependences of the PMF responses for LC in the presence and absence of the G4 PAMAM dendrimer at pH 7.1–7.3. The solid and dotted lines depict the real and imaginary components, respectively. The concentration of LC and the dendrimer was $1.0 \times 10^{-5} \text{ mol dm}^{-3}$. The excitation and detection wavelengths were 404 nm and 457 nm, respectively.

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