Anion– π interaction of naphthalenediimide (NDI) at the solid/water interfaces

Masaaki Akamatsu^{1,2*}, Ayumi Kimura¹, Koji Yamanaga¹, Kenichi Sakai^{1,2}, Hideki Sakai^{1,2*}

1) Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan

2) Research Institute for Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba, 278-8510, Japan

Corresponding Authors' e-mail addresses: makamatsu@rs.tus.ac.jp, hisakai@rs.tus.ac.jp

Supplementary Information

1. Materials

Solvents and reagents were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan) and FUJIFILM Wako Pure Chemical Co. (Osaka, Japan) and used without further purification. All reaction mixtures and fractions eluted by column chromatography were monitored using thin layer chromatography (TLC) plates (Merck, Kieselgel 60 F254). The TLC plates were observed under UV light at 254 and 365 nm. Flash column chromatography over silica gel (Wakosil C-200, 64–201 μ m) was used for separation. Methoxytriethylene glycol amine as an intermediate was prepared according to the literature¹.

2. Synthesis of TEG-NDI-TES.

Scheme S1. Synthesis of TEG-NDI-TES.



In a 100mL flask, a mixture of naphthalene-1,4,5,8-tetracarboxylic dianhydride (NDA) (1.60 g, 6.00 mmol), methoxytriethylene glycol amine (0.9965 g, 6.105 mmol) in dehydrated ethanol (50 mL) was stirred at 83 °C for 12 h. Then, 3-Aminopropyltriethoxysilane (1.35 g, 6.09 mmol) was added and stirred at 83 °C for 12h. The solvent was removed under reduced pressure. The crude product was subjected to silica gel column chromatography (dichloromethane/methanol = 50:1, v/v). After removal of the solvent, the product was dried in a vacuum oven at 70 °C. The yield was 24 % (0.89 g). ¹H-NMR (300 MHz, CDCl₃): δ = 8.75 (s, 4H), 4.47 (t, *J* = 5.8 Hz, 2H), 4.20 (t, *J* = 7.6 Hz, 2H), 3.79–3.88 (m, 8H), 3.72 (t, *J* = 4.5 Hz, 2H), 3.63–3.57 (m, 4H), 3.46 (dd, *J* = 5.4, 3.6 Hz, 2H), 3.32 (s, 3H), 1.87 (t, *J* = 8.0 Hz, 2H), 1.22 (t, *J* = 6.9 Hz, 9H), 0.76 (t, *J* = 8.5 Hz, 2H) ppm. ¹³C-NMR: (75 MHz, CDCl₃): δ = 162.8, 162.7, 130.9, 130.8, 126.6, 126.4, 71.8, 70.5, 70.4, 70.0, 67.7, 58.9, 58.4, 43.2, 39.5, 21.5, 18.2, 7.9 ppm. ESI-MS (+ve) calcd. for C₃₀H₄₀N₂O₁₀Si: 639.2, found: 639.2. Elemental analysis: calcd for C₃₀H₄₀N₂O₁₀Si: %C: 58.43, %H: 6.54, %N: 4.54, found %C: 57.19, %H: 6.52, %N: 4.31.



Fig. S2 ¹³C-NMR spectrum of TEG-NDI-TES in CDCl₃

3. Preparation of NDI@silica.

For AFM measurements, flat silica plates were prepared from silicon wafers (Nilaco) by chemical oxidation with a following procedure². A silicon wafer was immersed in a mixed solution of $H_2O:NH_3:H_2O_2 = 5:1:1$ (in volume) for 15 min at 80 °C, followed by a copious rinsing with deionized water to give a hydroxylated silica surface. A fresh piece of silica was used for each experiment and then discarded. For QCM-D measurements, a silica sensor was cleaned with an UV/ozone ProCleaner. Those silica substrates were used for immobilization of **TEG-NDI-TES**.

The silica substrates were immersed in a dichloromethane solution of **TEG-NDI-TES** (1.0 mM) at ambient temperature for 15 h, and then were rinsed exhaustively with ultrapure water/ and dichloromethane. Finally, these substrates were heated at 100 °C for 1 h.

4. Atomic force microscopy (AFM)

AFM measurements were performed using a Hitachi High-Tech Science AFM 5200S/5000II. The measurements were carried out with triangular silicon nitride cantilevers (Olympus OMCLTR800PSA) and the nominal spring constant (0.08 N m⁻¹) was used with calibration. The cantilevers were immersed in ethanol for 10 min and then cleaned by UV irradiation using a Bioforce Nanosciences UV/ozone ProCleaner to remove organic contaminants. All the experiments were conducted 10 min after the immersion of the silica plate in solution at room temperature. For acquiring all the data, plural cantilevers were used and individual differences of these cantilevers were averaged in the histogram analysis. The force curves were corrected from 100 points, which were randomly selected within a square of 507.3 nm × 507.3 nm. The cantilever was approached and retracted for the distance of 240 nm in 5 s, which means that loading/pulling speed is 48 nm/s.

The force curve of van der Waals (vdW) interaction between a general organic film and cantilever is assumed with the following equation.

$$F = -\frac{AR}{6D^2}$$
(Eq. S1)

where *F* is the detected force [nN], *A* is the Hamaker constant [J], *R* is the nominal radius of cantilever tip [nm] (R = 15 nm) and *D* is distance between two surfaces [nm].

Here, A is expressed by the equation.

$$A = \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 + n_3^2)^{1/2}(n_2^2 + n_3^2)^{1/2} \{(n_1^2 + n_3^2)^{1/2} + (n_2^2 + n_3^2)^{1/2}\}}$$
(Eq. S2)

where k is the Boltzmann constant [J/K] (1.38×10^{-23} J/K), T is temperature [K] (298 K), h is the Planck constant [J·s] (6.63×10^{-34} J·s), v_e is the main electronic absorption

frequency in the ultraviolet light (UV) $[s^{-1}]$ ($v_e = \sim 3.0 \times 10^{15} s^{-1}$), ε_n and n_n are the dielectric permittivity [F/m] and the refractive index of the medium, as listed in Table S2.

Table S2. Dielectric permittivity (ε_n), refractive index (n_n), and Hamaker constant (A) of the medium.

Medium	ε_n [F/m]	<i>n</i> _n [-]	Hamaker constant (A) [J]
Silicon nitride (medium 1)	8.0	1.98	
Polystyrene (medium 2)	2.55	1.50	2.84×10^{-20}
Water (medium 3)	80.1	1.33	

5. QCM-D

A Biplon Scientific Q-Sense Explorer was used to evaluate amounts of anion adsorption. The adsorption mass (Δm) was calculated from a change in the third overtone of the resonance frequency (F_n , n is the overtone number of 3 in this case). A Q-Sense QCM-D sensor with a silica coating (QSX303) was used after throughout cleaning. Water and sample solutions were injected into the fluid cell at a fixed flow rate of 0.1 cm³ min⁻¹ until equilibration. The QCM-D measurements were performed at a constant temperature of 25 °C.

6. Additional figures and table



Fig. S3 Images of water droplet on the silica substrates before and after modification of **TEG-NDI-TES** and the contact angle.



Fig. S4 (a) AFM phase images of **NDI@silica** and bare SiO₂ substrate. (b) Variations in UV/Vis absorption spectra of **NDI@silica** in THF with additions of TBAF.



Fig. S5 Variation in the frequency ($\Delta F_3/3$) as a function of the time when a series of anion species in water was injected (a: (TBA)₂SO₄, b: TBA(NO₃), c: TBACl, d: TBABr, e: TBAI). The salt concentration was fixed at 1.0×10^{-5} M. (f) After injection of the aqueous (TBA)₂SO₄ solution, the solution was replaced with.



Fig. S6 Histograms of the observed forces on **NDI@silica** in aqueous solutions of TBACl. The TBACl concentrations were set at 100, 10, and 0.1 mM (a–c).

References

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