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Supramolecular complex in the aluminum phthalocyanine chloride–β-cyclodextrin system: formation, spectral properties and stabilization mechanisms

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Experimental Details and Instrument Parameters

Materials.

Chloro(29H,31H-phthalocyaninato)aluminum AlClPc with chloride extraligand was obtained from Acros Organics (Belgium). N,N-dimethylformamide (DMF) was purchased from Reakhim (Russia) and purified by double distillation. Crystalline purity of AlClPc was verified using MALDI-TOF mass spectrometry (Thermo DSQ II device, USA). β-cyclodextrin (β-CD) was obtained from Sigma-Aldrich (USA) and used as received. Deionized water was prepared using standard laboratory distillation equipment.

Titration Protocol.

A stock solution of AlClPc was prepared by dissolving a dry sample (weight of 0.0025 g) in 10 mL of double-distilled DMF at ambient temperature. This was followed by a 200-fold dilution (10 μL of the stock in 2 mL of DMF) to prepare the base solution for further spectral measurements. Aqueous solutions of β-CD ($C = 2.71\times10^{-4}$ mol/L) were pre-heated at 80 °C for 60 min under continuous stirring to ensure full de-aggregation and precise solubilization. The host–guest complexation was driven by systematic incremental titration: 0.1 mL aliquots of the aqueous β-CD solution were sequentially introduced into 2 mL of the base AlClPc solution in DMF within a standard 10 mm quartz optical cuvette (K10) for a total of 20 additions. Each full titration routine was performed in triplicate to guarantee statistical reliability and data reproducibility.

Spectroscopic Measurements.

- UV-Vis Spectroscopy: Electronic absorption profiles were mapped across the 200–900 nm range on a TU-1901 dual-beam UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). Spectral processing was evaluated via baseline Gaussian deconvolution of the absorption bands.
- Fluorescence Spectroscopy: Emission spectra were collected using a Fluorat-02 Panorama spectrofluorometer (Lumex, Russia) within the 400–860 nm range using a fixed excitation wavelength (λ_{ex} = 650 nm) at room temperature.
- Attenuated Total Reflectance Infrared Spectroscopy (ATR IR): Vibrational modes (520–4000 cm^{-1}) were measured on a Simex Analytical Equipment FT-803 IR Fourier spectrometer equipped with a Single-Reflection ATR (Attenuated Total Reflectance) module. This method excludes the influence of the shape and size of droplets on the resulting spectrum under experimental parameters. The analytical specimens were prepared in the form of drops of a 20 μL solution applied directly to a horizontal diamond substrate, completely overlapping it. Before each measurement of the sample, a baseline calibration was performed using a pure pristine diamond substrate. The reliability and accuracy of the configuration were validated against reference measurements of pure ethanol.

Mathematical Equations and Corrections

To compensate for the dilution during titration, the raw experimental optical density values (A_0) were normalized using the following relationship:

$$A_i = \frac{A_0}{\frac{V_1}{(V_1+V_2)}}$$

where A_i and A_0 — corrected and experimental optical density of the solution; V_1 = 2 mL — the initial volume of the AlClPc–DMF solution; V_2 — the volume of β-CD–water solution added to the cuvette (from 0.1 to 1 mL).

The binding constants (K_b) and system configurations were modeled using the classic Benesi–Hildebrand linear expression for 1:1 host–guest interactions:

$$lg\frac{A_i - A_0}{A_f - A_0} = lg[C] + lgK_b$$

where A_0, A_i and A_f denote the absorbance values of the solution in the absence of the host, at intermediate concentrations, and at the saturation point, respectively; [C] represents the equilibrium concentration of the added β-CD; K_b — the binding constant.

The fluorescence quenching parameters were evaluated using the linear Stern–Volmer relationship:

$$\frac{I_0}{I_i} = 1 + [C] \cdot K_{SV}$$

Where I_0 and Ii are the fluorescence intensities before and after the addition of the titrant; [C] — the equilibrium concentration of the added β-CD; K_{SV} — the Stern–Volmer constant.

Supplementary Spectral Data and Plots

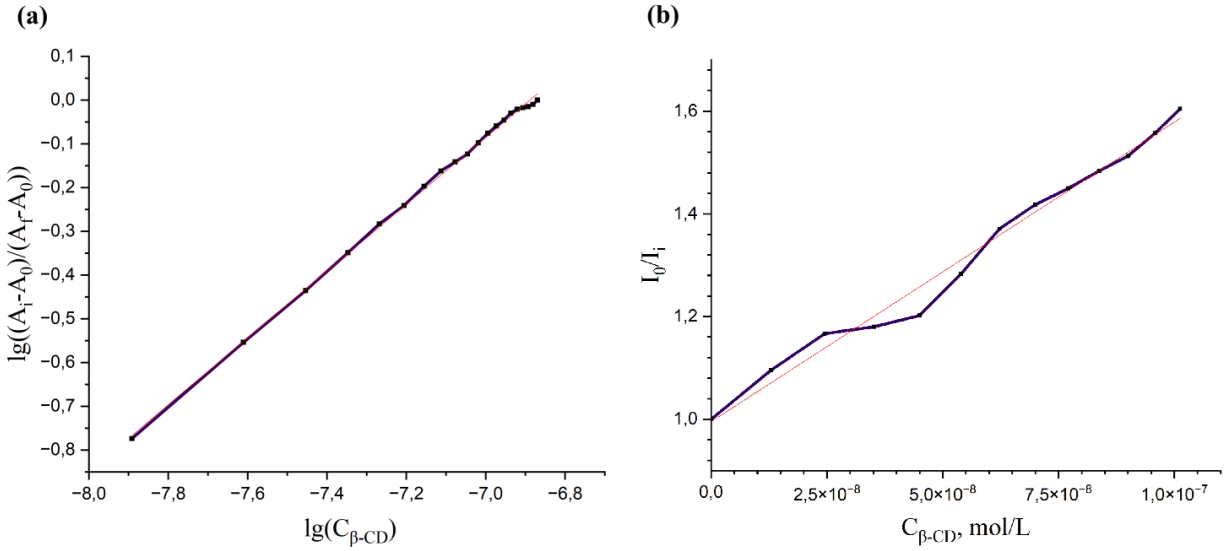


Figure S1. (a) Graph for calculating the binding constant in Benesi-Hildebrand coordinates (0.764x + 5.26, R^2_{adj} = 0.999) and (b) graph for calculating Stern-Volmer constant (5.86×10^6x + 0.993, R^2_{adj} = 0.983).

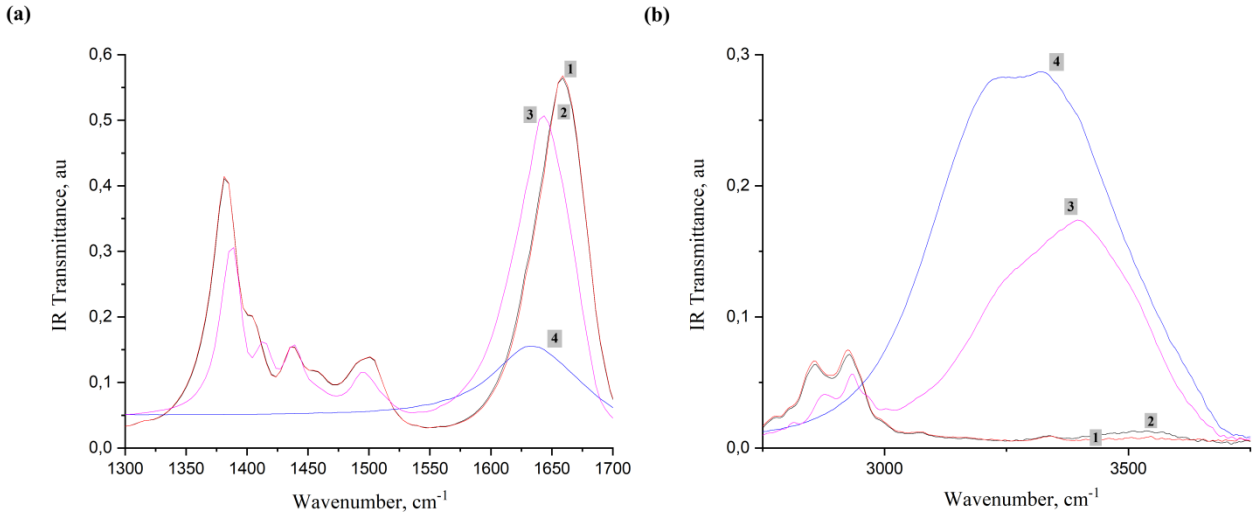


Figure S2. IR spectra of (1) pure DMF, (2) AlClPc in DMF, (3) the AlClPc–β-CD complex, and (4) β-CD in water in the spectral regions of (a) 1300–1700 cm^{-1} and (b) 2700–3800 cm^{-1}.