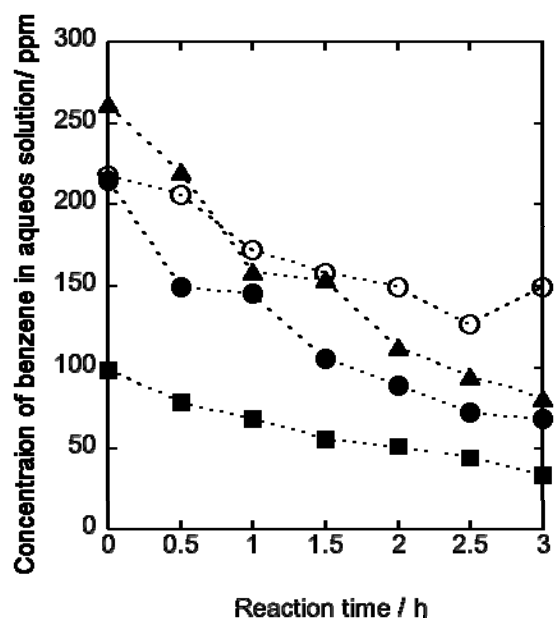


ESI 1. X-ray diffraction patterns of saponite (a), PIC-clay (b), PIC-caly@TiO₂ (c), clay@TiO₂ (d) and clay@TiO₂(external PIC) (e).

In the patterns (c), (d) and (e), the low weight fraction of the clay in the dye-clay-hybrids (lower than 2.5%, calculated based on the added amount) made it difficult to show the diffraction attributed to 001 of clay.



ESI 2. Visible-light-induced catalytic decomposition of benzene in aqueous solution with PIC-clay@TiO₂ (filled circle and filled triangle), PIC-clay@TiO₂ after 3h irradiation (filled square) and clay@TiO₂(external PIC) (open circle), respectively.

ESI 3.

Synthesis procedure:

An aliquot (50 mL) of 2-propanol suspension of saponite (0.5 g; Synthetic saponite, Sumecton SA, Kunimine Ind. Co., Cation Exchange Capacity (CEC) is 71 meq (100 g of clay)⁻¹) was mixed with an 2-propanol solution (50 mL) of 1,1'-diethyl-2,2'-cyanine (pseudocyanine; abbreviated as PIC, Hayashibara Biochemical Laboratories, Inc., the molecular structure is shown in scheme 2) and magnetically stirred for more than 1 hour. The amount of PIC cation in the mixtures was 3.5 % of CEC of saponite. The mixture (3 mL) was added to deionized water (9.56 g), and the aqueous mixture was magnetically stirred at room temperature for 30 min. Then, 2-propanol solution (37.5 mL) of titanium tetraisopropoxide (TTIP, 2.33 g, Kanto Chemical Co., Inc.) was added with vigorous stir by magnetic stirrer, and the mixture was allowed to react for 30 min. at room temperature. The addition of TTIP 2-propanol solution immediately made the mixture white as a result of the hydrolytic polycondensation of TTIP. Ethylene glycol (1.19 g) was further added in order to suppress the oxidative decomposition of the dyes during the hydrothermal treatment. The crystallization of titania was conducted by hydrothermal reaction at 150 °C for 1 day, using Teflon-lined autoclaves (volume; 80 mL) rotating at 20 rpm. The product (designated as PIC-clay@TiO₂) was washed with 2-propanol and dried under a reduced pressure. To avoid the condensation of TTIP, 2-propanol for preparing TTIP 2-propanol solution was dehydrated by the immersion with dried zeolite 4A.

Photocatalytic reaction

The photocatalysts (50 mg) were added to benzene aqueous solutions (500 ppm, 100 mL) in 200 mL glass bottles. After the adsorption of the benzene from aqueous solutions onto the catalysts had reached an equilibrium (3 h), the irradiation was started. The suspensions were irradiated by Hamamatsu photonics 150 W Xe lamp equipped with HOYA L-42 filter to cut UV light. Samples for HPLC analysis were removed from the reactor with a syringe at regular intervals (30 min.) and filtered (Whatman 0.2-mm PVDF syringe filters) to remove the catalyst particles. Above experiments were conducted under magnetic stirring.

HPLC (Shimadzu SCL-10Avp equipped with a UV detector) was used for the evaluation of benzene concentration. A reverse-phase C-18 column (YMC-Pack ODS-A) and water-acetonitrile eluant (25:75) were used. Absorbance at 254 nm was used to evaluate the concentrations of benzene.

Photodecomposition of Ru polypyridine complex containing hybrids

The photocatalysts ([Ru(bpy)₃]²⁺-clay@TiO₂ or Ru470@P25, 16.7 mg) were dispersed in deionized water (10 mL). The suspension were irradiated by visible light using a solar simulator San-Ei Electronic XES-502S and the decomposition of dyes was evaluated by the naked eye observations.

Measurement procedure for diffuse reflectance UV-Vis spectra:

The samples after the visible light irradiation were collected by centrifugation and dried under reduced pressure. The powder samples (25 mg) before and after visible light irradiation were mixed with MgO (50 mg) respectively, and the mixture was loaded evenly onto sample holder for reflectance measurement. Thus, it is valid to evaluate the degradation of the dye quantitatively.