Supplementary Information

Click Chemistry–Driven Heteromolecular Integration into Layered Zeolite Frameworks for Photochemical Upconversion Applications

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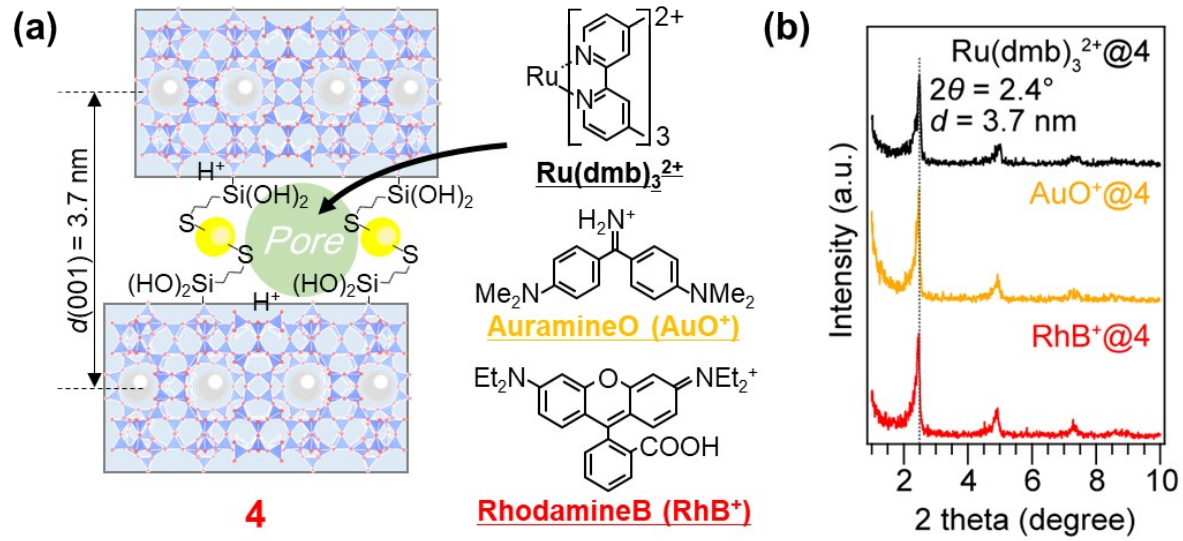
Table S1. CHN elemental analysis results

Sample	C wt%	H wt%	N wt%	Ash wt%
ERB-1P	4.10	1.76	0.99	93.15
Structure 1	11.37	2.85	1.01	84.77
Structure 2	8.18	2.28	0.62	88.92
Structure 3	11.56	2.30	0.78	85.36
Structure 4	11.73	2.37	0.29	85.61
4 + $Ru(dmb)_3^{2+}$	12.23	2.27	0.39	85.11
4 + AuO^+	11.17	2.12	0.41	86.31
4 + RhB^+	11.33	2.14	0.38	86.15

Figure S1. (a) Schematic illustration of the introduction of cationic luminescent species. (b) XRD patterns after the incorporation of luminescent molecules.



Experimental section

1. Synthesis of MWW-zeolitic layered precursor

ERB-1P: The seed-assisted synthesis method was employed to obtain high-quality crystals. Precursor gel with a molar ratio of SiO_2:0.33B_2O_3:0.2Na_2O:11H_2O:PI (piperidine) was prepared using Aerosil200 as SiO_2, H_3BO_4 as B source and NaOH as Na source. Seed crystals corresponding to 1 wt% of the silica content were added to the precursor mixture. Then, the mixed precursor gel was sealed in a Teflon-lined autoclave and heated at 175 °C for 9 days. The solid product was collected by filtration and ubsequently dried at 60 °C to obtain ERB-1P.

MCM-22P: Precursor gel with a molar ratio of 2.7Na_2O:Al_2O_3:30SiO_2:1347H_2O:15HMI (hexamethyleneimine) was prepared using Aerosil200 as SiO_2, $NaAlO_2$ as Al source and NaOH. Then, the mixed precursor gel was sealed in a Teflon-lined autoclave and heated at 150 °C for 7 days while being rotated at approximately 40 rpm. The solid product was collected by filtration and subsequently dried at 60 °C to obtain MCM-22P.

ITQ-1P: The synthesis was carried out using 1-adamantyltrimethylammonium hydroxide (TMAdaOH) as a structure-directing agent. Precursor gel with a molar ratio of SiO_2:0.25TMAdaOH:44H_2O:0.31HMI (hexamethyleneimine) was prepared using Aerosil200 as SiO_2. Then, the mixed precursor gel was sealed in a Teflon-lined autoclave and heated at 150 °C for 5 days while being rotated at approximately 40 rpm. The solid product was collected by filtration and subsequently dried at 60 °C to obtain ITQ-1P.

2. Synthesis of 9,10- bis[p-styryl]anthracene

A mixture of 3 mmol of dibromoanthracene, 9 mmol of 4-vinylphenylboronic acid, 18 mmol of potassium carbonate, and a catalytic amount of $Pd_2(dba)_3$ (dba = dibenzylideneacetone) and $Pd(P^tBu_3)_2$ was added to 50 mL of anhydrous toluene and heated at 110 °C for 48 h under a nitrogen atmosphere. After the reaction, the Pd catalysts were removed by filtration, and the filtrate was evaporated to afford an oily product. The obtained product was dissolved in a CH_2Cl_2/H_2O mixture, and the organic layer was separated using a separatory funnel. After evaporation of the solvent and subsequent drying, yellow crystalline solids were obtained. The obtained crystals were identified as 9,10-bis(p-styryl)anthracene by ^{1}H NMR spectroscopy in $CDCl_3$.

3. DPA-unit pillar formation in MWW-zeolitic layered precursor

Interlayer Expansion: One gram of the MWW-type precursor was dispersed in a mixed solution containing 5.7 g of cetyltrimethylammonium bromide (CTAB), 2.5 g of

tetrapropylammonium hydroxide (TPAOH), and 17.75 g of H_2O. The mixture was stirred at room temperature for 16 h, and the resulting solid was collected by filtration. The resultant material was structure 1 in Figure 1.

Thiol Functionalization: Structure 1 (200 mg) was dispersed in 20 mL of toluene, purged with argon, and then heated to 100 °C. To the dispersion, 10 mmol of 3-mercaptopropyltrimethoxysilane (MPTMS) was added, and the mixture was refluxed for 2 days. The solid product was recovered by centrifugation. The obtained material corresponds to Structure 2 shown in Figure 1.

Click Reaction: Structure 2 (150 mg) was dispersed in 15 mL of toluene containing 75 mg of 9,10-bis(p-styryl)anthracene and 65 mg of azobisisobutyronitrile (AIBN). The mixture was purged with argon and heated at 80 °C under stirring for 2 days. The solid product was collected by centrifugation. The obtained material corresponds to Structure 3 shown in Figure 1.

Acid Treatment: Structure 3 (150 mg) was dispersed in 15 mL of 0.05 M H_2SO_4/ethanol solution and heated at 70 °C for 1 h. The solid product was collected by centrifugation and subsequently dispersed in 15 mL of 0.15 M HCl/ethanol solution. The mixture was then heated at 90 °C for 16 h. After centrifugation and drying, the resulting material was structure 4 in Figure1.

3. Introduction of chromophore molecules or sensitizers

Luminescent Cations: Structure 4 (100 mg) was dispersed in 10 mL of an ethanol solution of Rhodamine B (1 mM), $Ru(dmb)_3^{2+}$ (0.1 mM), or Auramine O (1 mM), and the mixture was stirred at room temperature for 24 h. The resulting solid was collected by centrifugation.

Pt(OEP): Structure 4 (100 mg) was dispersed in 20 mL of chloroform, followed by the addition of 0.52 mL of a 0.192 mmol L^{-1} chloroform solution of Pt(OEP). The mixture was heated at 100 °C for 4 h. After the reaction, the solvent was evaporated, and the resulting powder was collected. To remove Pt(OEP) molecules that were not incorporated into the pores, the sample was washed sequentially with ethanol and acetone.

4. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultima IV diffractometer using Cu Kα radiation. Raman spectra were measured with a JASCO RMP-510 spectrometer equipped with a 532 nm laser excitation source. Elemental (CHN) analysis was performed using a CE-440 analyzer (Exeter Analytical). Nitrogen adsorption–desorption measurements were carried out with an Autosorb-iQ2-MP instrument (Anton Paar). Prior to the measurements, the samples were calcined in air using a

muffle furnace, in which the temperature was gradually increased from ambient temperature to 300 °C over 24 h. Fluorescence excitation and emission spectra were recorded using a FP-8500 fluorescence spectrophotometer (JASCO). The samples were packed in quartz-windowed cells and excited using a 150 W Xe lamp monochromated by diffraction gratings. Photoluminescence quantum yields were determined with a Hitachi F-7000 fluorescence spectrometer equipped with a Hitachi integrating sphere system calibrated for absolute measurements. Luminescence decay curves were obtained using a Quantaurus-Tau C11367-01 time-resolved emission spectrometer (Hamamatsu Photonics). UV–vis absorption and diffuse reflectance spectra were recorded with a V-670 spectrophotometer (JASCO) equipped with a diffuse reflectance attachment