Electronic Supplementary Information for:

Fluorescence Studies on Phenylene Moieties Embedded in a Framework of Periodic Mesoporous Organosilica

Tadashi Okada,[a] *Ken-ichi Yamanaka,*[b,c] *Yoshiharu Hirose,*[b] *Yasutomo Goto,*[b,c] *Takao Tani,*[b,c] *and Shinji Inagaki*[b,c]

Toyota Physical & Chemical Research Institute, Nagakute, Aichi 480-1192, Japan; Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan; and Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan.

CONTENTS

1. Details of the sample suspension

2. Fractions of uncondensed silanol groups

3. Emission spectra at 77 K

4. Fluorescence decay curves of Ph-PMOs at 77K

5. Emission spectra of crystal-like Bp-PMO and BTEBp at 77 K

1. Details of the sample suspension

A very dilute suspension of Ph-PMO powder was prepared for the measurements to avoid re-absorption of the fluorescence.

Typically, 0.76 mg of Ph-PMO powder was dispersed in a mixed solvent of methanol (Nacalai, Spectrograde: 5 mL) and ethanol (Aldrich, Spectrograde: 5 mL). The initial suspension was placed for 2 h in order to remove large Ph-PMO primary particles and their aggregates from the supernatant by sedimentation. The average particle diameter in the decanted supernatant (sample suspension) was determined as 170 nm (Fig. S1) by dynamic light scattering (Microtrac, UPA-250EX). The suspension was stable and showed no change in the fluorescence intensity after 3.5 h (Fig. S2).

The amount of the powder in the suspension was estimated by weighing the sediment after drying and obtained as less than 10% (2, 3 and 6% for three samples) of the added powder. The result indicates that the powder concentration in the suspension is < 7.6 mg/L which correspond to the Ph moiety concentration of $< 4.2 \times 10^{-5}$ M (180.27 g/mol for $O_{1.5}Si-C_6H_4-SiO_{1.5}$). From the molar extinction coefficients of the Ph moiety (450 $M^{-1} cm^{-1}$ at 280 nm and 80 $M^{-1} cm^{-1}$ at 290 nm), the absorbance of the suspension is calculated as < 0.02 (280 nm) and < 0.003 (290 nm) for a 1-cm cell, which are small enough to ignore re-absorption effect for the analysis. Actually, the fluorescence intensity of the suspension at shorter wavelengths is stronger than that of the Ph-PMO powder sample (Fig. S3) possibly due to almost no re-absorption effect for the suspension.
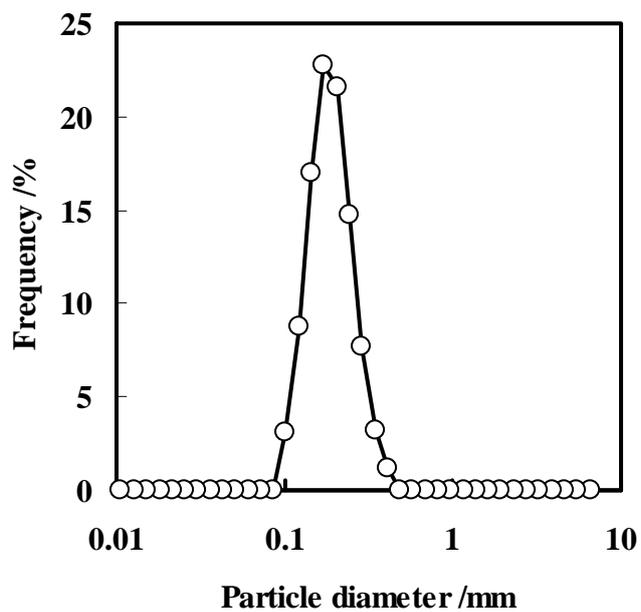
Fig. S1 Size distribution of Ph-PMO particles in the decanted supernatant.
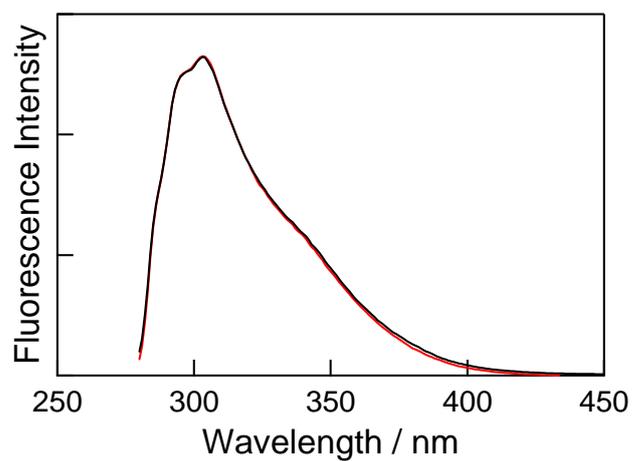

Fig. S2 Fluorescence spectra of the Ph-PMO suspension just after decantation (black) and after 3.5 h (red) upon excitation at 266 nm at 200 K.
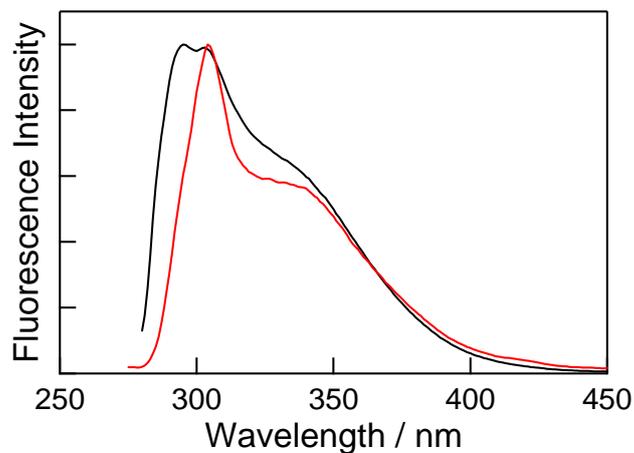
Fig. S3 Normalized fluorescence spectra for the Ph-PMO suspension (black) and the Ph-PMO powder sample (red) upon excitation at 266 nm.

2. Fractions of uncondensed silanol groups

^{29}Si MAS NMR measurements (Bruker ADVANCE 400) were carried for crystal-like and amorphous Ph-PMO powders. The T^1: T^2: T^3 ratios (T^n: R-Si(OSi)$_n$(OH)$_{3-n}$) were calculated as 4.9: 39.7: 55.4 and 13.6, 55.9: 30.5 for crystal-like and amorphous Ph-PMOs, respectively, from integral intensities of the corresponding peaks. From the ratios, the fractions of uncondensed silanol groups to the Si-O bonds were obtained as 16.5% and 27.7% for crystal-like and amorphous Ph-PMOs, respectively.
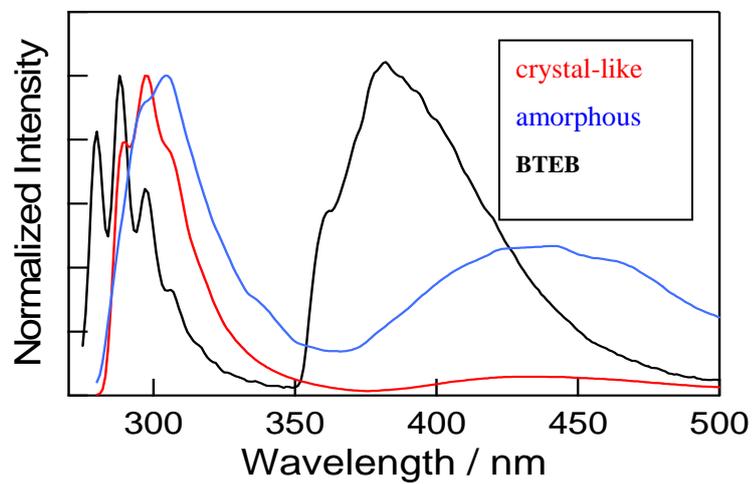
3. Emission spectra at 77 K

Fig. S4 Fluorescence and phosphorescence spectra of crystal-like and amorphous Ph-PMOs dispersed in MeOH/EtOH and BTEB 4.4 x 10^{-4}M in MeOH/EtOH observed at 77K.
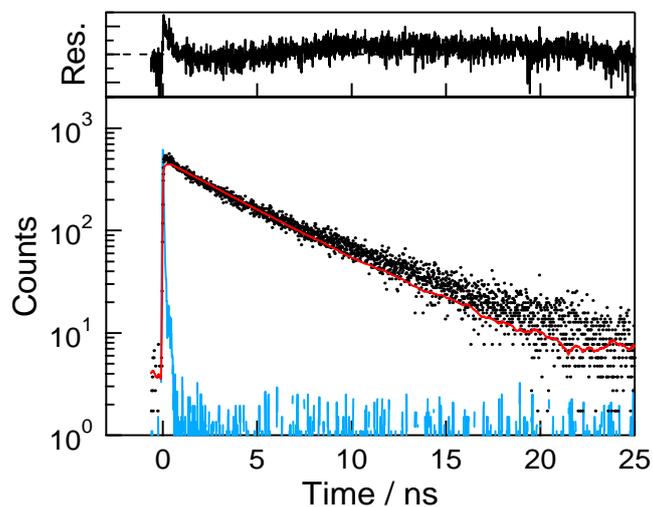
4. Fluorescence decay curves of Ph-PMOs at 77K

Fig. S5 Fluorescence decay curve at 290 nm for crystal-like Ph-PMO dispersed in 2-methyl-THF at 77K.

USERFUNC=A(1)*EXP(-X/A(2)-A(3)*((X/A(2))**0.5))

**** CURVE FITTING RESULTS ****

17 ITERATIONS

A(1) =   0.10253E+00   STD. DEV. = 0.98926E-03

A(2) =   0.37330E+03 ch = 4.558 ns   STD. DEV. = 0.40345E+01 ch

A(3) =   0.98762E-01 ch$^{-1/2}$ = 28245.36 s$^{-1/2}$ STD. DEV. = 0.22249E-01 ch$^{-1/2}$

SHIFT =   -0.15785E+01   STD. DEV. = 0.26447E-01

50 ns / 4095 ch ;   1ch = 12.21 ps ;   1 ch$^{-1/2}$ = 2.86 x 10^5 s$^{-1/2}$

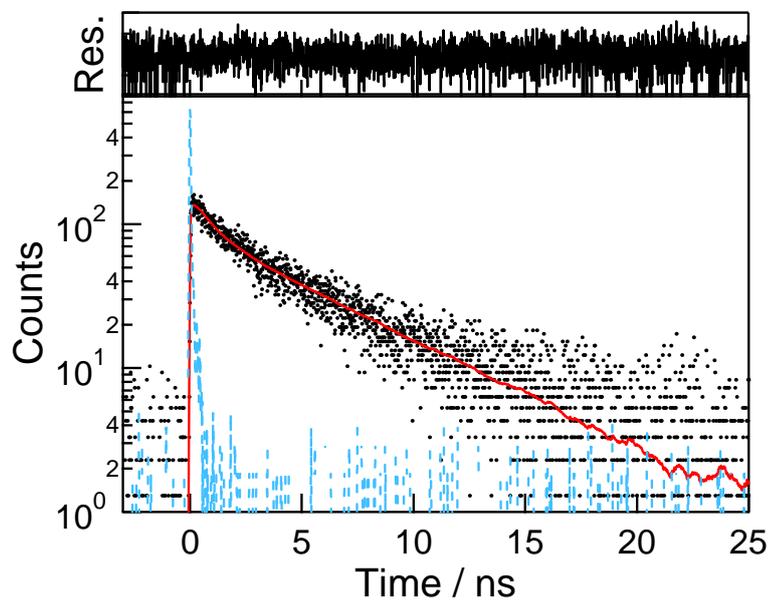$$I_F^{crystal}(t) = I_F^0 \exp\{-t/4.6\text{ns}-(1.5\times10^2 \text{ s}^{-1/2})t^{0.5}\}$$

Fig. S6 Fluorescence decay curve at 290 nm for amorphous Ph-PMO dispersed in 2-methyl-THF at 77K.

$I_F^{amorphous}(t) = 0.45\exp(-t/0.84\text{ ns}) + 0.55\exp(-t/5.5\text{ ns})$

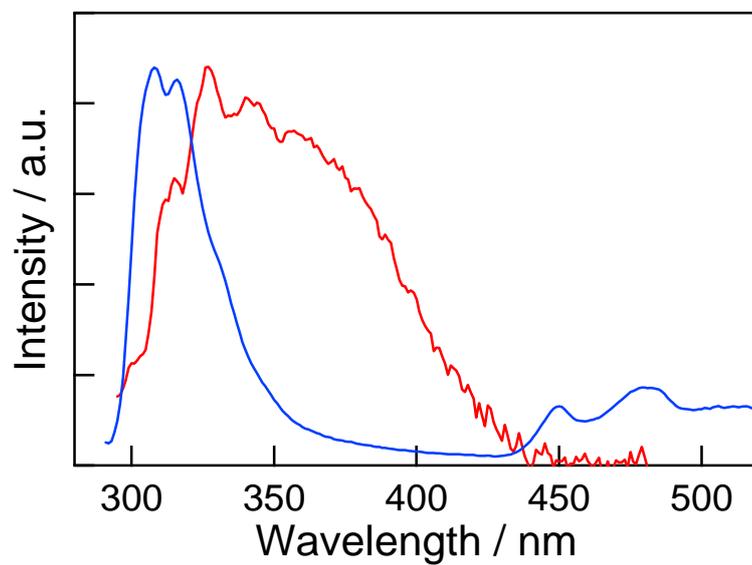**5. Emission spectra of crystal-like Bp-PMO and BTEBp at 77 K**

Fig. S7 Fluorescence spectrum of crystal-like Bp-PMO dispersed in 2-methyl-tertrahydrofuran at 77K (red line). Fluorescence and phosphorescence spectrum of BTEBp in 2-propanol at 77K (blue line).