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Preparation and optical properties of amorphous silica doped with porphins, TCPP

Motohiro Uo ^a, Mitsuharu Yamana ^b, Kohei Soga ^c, Hiroyuki Inoue ^c and Akio Makishima ^c

^a Department of Dental Materials and Engineering, School of Dentistry, Hokkaido University
North13 West7, Kita-ku, Sapporo 060, JAPAN

^b ULSI Device Development Laboratories, NEC Corporation
1120 Shimokuzawa, Sagamihara, Kanagawa 229, JAPAN

^c Department of Materials Science, Faculty of Engineering, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, JAPAN

ABSTRACT

Tetrakis(4-carboxyphenyl)porphine (TCPP), which is well known as a photochemical hole burning (PHB) dye, was incorporated in amorphous silica materials ($a\text{-SiO}_2$) by a sol-gel process with using tetramethoxysilane (TMOS) and aminopropyltriethoxysilane (APTES). With using APTES as precursor of silica gel, TCPP was cross-linked to $a\text{-SiO}_2$ matrix through aminopropyl group of APTES. The cross-linkage of TCPP and APTES was confirmed by the FT-IR measurement. The TCPP incorporated in $a\text{-SiO}_2$ matrices showed activity in PHB. In the TCPP cross-linked $a\text{-SiO}_2$, properties of photochemical hole, such as hole width, quantum efficiency and irreversible broadening under cycle annealing experiment, were improved. A burnt hole at 3.6K was observed after cycle annealing experiment up to 80K in the TCPP cross-linked $a\text{-SiO}_2$.

Keywords: TCPP, sol-gel process, photochemical hole burning (PHB), aminopropyltriethoxysilane (APTES), FT-IR, cross-link, hole width, quantum efficiency, irreversible broadening

1. INTRODUCTION

Amorphous silica matrices usually have the advantages of transparency, thermal, chemical and mechanical stability compared with organic matrices and these properties are desirable as the matrices for organic dye dispersion. The sol-gel process makes possible to disperse organic dyes into amorphous silica matrices in low temperature. A variety of organic dyes have been incorporated in silica gel matrices with sol-gel process, and their optical properties have been investigated ¹⁻¹⁸. The authors also reported the preparation of organic dye/ $a\text{-SiO}_2$ systems using sol-gel process and their properties, such as PHB, photo-conductivity and laser emission ^{9-13,16-18}. Photochemical hole burning (PHB) has been attracting attention in recent years because of its scientific interest and the possibility of the application to high density optical data storage ¹²⁻²⁶. It is expected that the frequency domain recording by PHB improve the information storage density of optical media. Furthermore, PHB is the useful method to estimate the local structure around the organic dyes. The porphyrins are well-known PHB dyes. The authors have been prepared various porphyrin derivatives dispersed silica gels with sol-gel process, and their PHB properties have been studied. In these systems, photochemical holes are stable at extremely low temperature around liquid helium temperature, and irreversible broadening of holes were inevitable under higher temperature. In order to apply the PHB to high density optical media, improvement of thermal stability of photochemical hole is necessary.

Sakoda et al. prepared porphin-cross-linked polymers and reported that the cross-linkage between porphin and polymer is effective to suppress spectral diffusion ^{25,26}. With usual sol-gel process using silicon tetra alkoxide, such cross-linkage between porphins and silica gels were not formed. Aminopropyltriethoxysilane (APTES) is well known silanization reagent and that covalently bonds to the organic compound which has carboxyl group with amide

bond. In this paper, the authors reported about preparation and PHB properties of porphin, TCPP cross-linked silica gels by sol-gel process with APTES.

2. EXPERIMENTAL PROCEDURE

The reagent grade chemicals of TCPP, TMOS, TEOS, APTES, poly-vinylalcohol(PVA), aminopropane(AP), ethanol and sodium hydrate(NaOH) were used. All organic chemicals were obtained by Tokyo Kasei Kogyo Company. Compositions and synthesis conditions of samples were shown in Table 1.

Table 1 Compositions of samples (molar ratio)

	TMOS	TEOS	APTES	PVA	AP	NaOH	ethanol	H ₂ O	TCPP	Drying
APTES40	1		0.5				6	6	10 ⁻⁴	40°C
APTES240	1		0.5				6	6	10 ⁻⁴	240°C
TMOS40	1					0.01	6	6	10 ⁻⁴	40°C
AP/a-SiO ₂	1	0.375			0.5		6	6	10 ⁻⁴	40°C
APTES/PVA			0.5	2			6	30	10 ⁻⁴	40°C

APTES40 and APTES240 were containing aminopropyl-triethoxysilane(APTES) in sol solution, therefore, cross-link between TCPP and gel matrix is expected. TMOS40 was prepared by usual sol-gel method using TMOS as the reference. AP/a-SiO₂ and APTES/PVA systems were prepared in order to estimate the effect of cross-link. In these systems, TCPP is able to link with AP and APTES, however, the cross-linkage between AP and a-SiO₂ matrix or APTES and PVA matrix are not formed.

Starting solutions were prepared by mixing TMOS, distilled water ethanol and TCPP. TCPP was dissolved in ethanol before mixing. A catalyst (NaOH) was added to this mixture if necessary. In addition of APTES, Aqueous solution of APTES is highly basic, therefore, pure APTES addition to the starting solution occurs sudden gelation. Thus, APTES was diluted by ethanol and added to starting solution. In the same reason, AP was added by the same way as APTES addition. The hydrolysis for gelling and drying was carried out at 40 for several weeks. This schime is shown in Fig.1.

In order to estimate chemical bonding state between TCPP and a-SiO₂ matrix, FT-IR measurements were carried. TCPP concentrations in gel samples tabulated in Table 1 were extremely low (10⁻⁴ mol/molTMOS) for FT-IR analysis. Therefore, the samples which include high concentration of TCPP were prepared. TMOS, APTES, distilled water, ethanol and TCPP were mixed to be 1:0.5:9*10³:9*10³:0.1 in molar ratio. The mixtures were dried at 40 and powdery samples were prepared. In some cases, powdery samples were dried between 100 and 300 under vacuum. After drying, powdery samples were mixed with KBr to be 1wt% of sample concentration, and measured IR spectra on JASCO FT-IR300. For hole-burning experiments, the samples were placed in a He gas-flow cryostat (Oxford, CF1204) at temperature between 3.6K, and 80K. Photochemical hole was burnt at 3.6K by tunable dye laser (Coherent, 699-01) with 1mW/cm² laser power at the absorption peek of lowest Q_x(0,0) band. The hole was detected by the change of transmittance with a 1m monochromator (Jasco, CT100C).

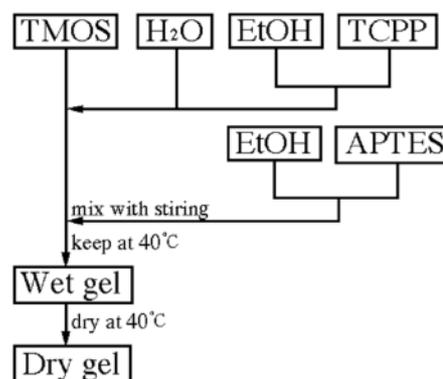


Fig.1 Schematic representation of the sol-gel process with TMOS and APTES

3. RESULTS AND DISCUSSION

3.1 Cross-link estimation by FT-IR measurement.

FT-IR spectra of TCPP and mixture of TCPP, TMOS and APTES in Fig.2. In the spectrum of TCPP, absorption bands due to carboxyl groups at 1715cm^{-1} (C=O), $1400\text{-}1440\text{cm}^{-1}$ (C-O-H) and 1280cm^{-1} (C-O) were observed. However, in the spectrum of TCPP, TMOS and APTES mixture, absorption bands due to carboxyl groups were disappeared and absorption bands centered at 1400cm^{-1} and 1600cm^{-1} were observed. These absorption bands were assigned to C-O symmetric and asymmetric stretching vibration of carboxylic ions in TCPP. An absorption band centered at 1540cm^{-1} assigned to N-H deformation vibration of ionic amino groups in APTES. After drying at 200°C of the mixture, absorptions due to C-O symmetric and asymmetric stretching vibration of carboxylic ions were decreased, and an absorption band centered at 1640cm^{-1} was appeared. This band was assigned as C=O stretching and N-H deformation vibration of amide. Absorption bands centered at 1600cm^{-1} due to C=C stretching in TCPP were observed in all spectra shown in Fig.2 in similar absorbance. From these results, the states of TCPP and APTES in samples are presumed as Fig.3. In the sample dried at 40°C , carboxyl groups of TCPP and amino groups in APTES were also ionized (Fig.3(b)). In this situation, ionic interaction between TCPP and APTES was expected.

By drying at 200°C under vacuum, TCPP and APTES were cross-linked by amide bonds as Fig.3(c).

Fig.4 shows change in IR spectra by drying temperature. The absorption bands assigned to C-O symmetric and asymmetric stretching vibration of carboxylic ions were decreased and the absorption bands assigned to C=O stretching and N-H deformation vibration of amide were increased by increasing the drying temperature up to 240°C . The spectra were not changed by drying temperature higher than 240°C . Thus, TCPP and APTES were sufficiently cross-linked with amide bonds by drying at 240°C .

3.2 Photochemical hole burning(PHB)

Fig.5 shows hole spectra of TCPP incorporated gels burnt for 15second at 3.6K . The hole width in APTES40 was narrower than those of TCPP incorporated in a-SiO_2 by conventional sol-gel process (TMOS40) and in AP/a-SiO_2 . The typical change in hole spectra of TCPP incorporated in AP/a-SiO_2 complex are shown in Fig.6.

The initial hole width under lowest burning fluence, G_{HOLE} , and apparent quantum efficiency, F , should be estimated by dependence of hole width on laser fluence time as Table 2. F is calculated by using the following equation ²¹

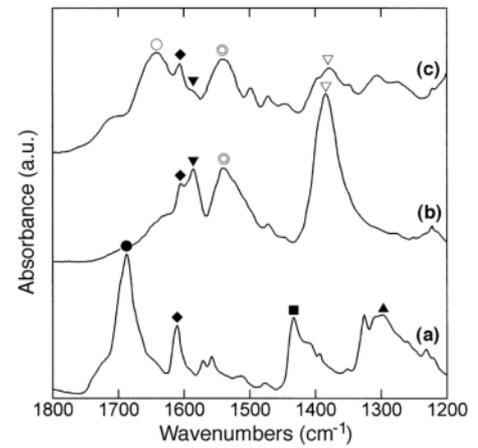


Fig.2 FT-IR spectra of TCPP(a) and TCPP/APTES mixtures((b):dried at 40°C , (c):dried at 200°C)

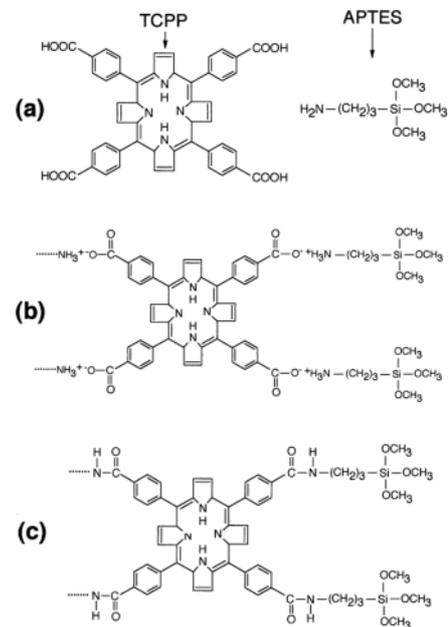


Fig.3 Schematic representation of the interaction between TCPP and APTES

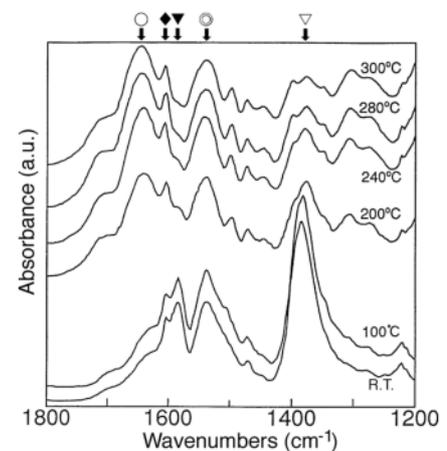


Fig.4 Change in FT-IR spectra of TCPP/APTES mixtures by drying temperature

●:C=O in COOH ▼:C=O asymmetric ○:N-H
◆:C=C in TCPP ▽:C=O symmetric

$$F = [d(A/A_0)/dt]_{t=0} A_0 (Dw_h/Dw_i) [10^3 I_0 (1-10^{-A_0}) e] (1)$$

where, A is time-varying absorbance, A_0 is the absorbance before irradiation, $[d(A/A_0)/dt]_{t=0}$ is the initial slope of the irradiation time dependence of hole depth, I_0 is the incident laser intensity, e is the molar extinction coefficient for inhomogeneous line profile at the hole burning wavelength and temperature. The homogeneous line width Dw_h , is estimated from the initial hole width at each temperature.

Table 2 Characteristics of hole spectra

	APTES40	APTES240	TMOS40	AP/a-SiO ₂	APTES/PVA
$\Gamma_{\text{HOLE}} (\text{cm}^{-1})$	0.7	0.7	1.6	2.0	0.7
Φ	7×10^{-4}	6×10^{-4}	3.6×10^{-4}		1×10^{-3}

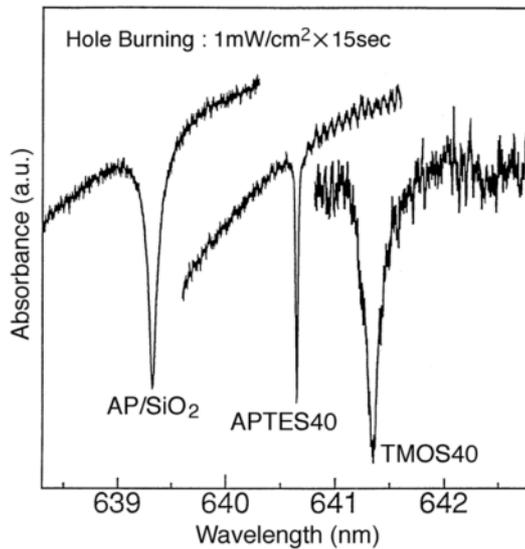


Fig.5 Hole spectra of TCP in various gels

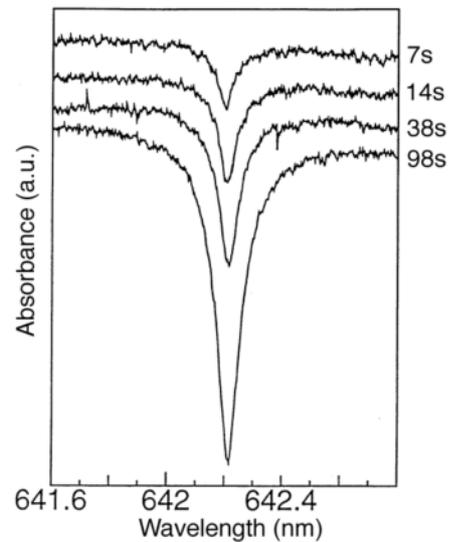


Fig.6 Hole formation of TCP in AP/SiO₂

The hole width, G_{HOLE} , of TCP cross-linked a-SiO₂ (APTES40, APTES240) were narrower than that of incorporated in other a-SiO₂ matrices (TMOS40, AP/a-SiO₂), and these values were same as that of APTES/PVA and other porphyrin/polymer systems^{22,23}. We considered about this difference of hole width within the samples prepared with sol-gel process, as follows. Generally silica gels prepared with sol-gel process, are porous without heat treatment. The TCP incorporated in TMOS40 is adsorbed on the surface of pore, therefore, it is easily affected from silanol groups, residual methoxy groups and sodium ions with adsorbed solvents on pore surface. In AP/a-SiO₂, TCP was linked to the AP, however, not linked with a-SiO₂ matrix. Therefore, the TCP is also adsorbed on pore surface as the TCP/AP complex. Thus, it is expected that the broadness of hole width in TMOS and AP/a-SiO₂ are responsible for the influence from pore surface. On the other hand, in the APTES40 and APTES240, the TCP was ionically or covalently bonded to a-SiO₂ matrix through the APTES. Thus, it is expected that the influence from gels is weaker than that of TCP adsorbed on pores.

For the apparent quantum efficiency, η , the values for TCP in APTES40 and APTES240 are comparable to that of APTES/PVA and other porphyrin/polymer systems^{22,23}. And the TCP in APTES40 and APTES240 showed higher efficiency value compared to that of TMOS40. During the gelation process, the organic dyes are dissolved in interstitial liquid phase. Thus, there is a possibility of dimerization or aggregation of dye molecules. In the APTES containing samples, it is expected that the TCP is linked to APTES in the initial stage of gelation process, therefore, dimerization or aggregation is inhibited.

Thermal stability of a hole burnt at low temperature have been studied with cycle annealing experiment. Cycle

annealing experiments were carried as follows. First, a hole was burnt at low temperature (3.6K) and measured in the profile, and then temperature of the sample was elevated and annealed, then, the hole profile was measured. Next the sample was cooled down to the previous temperature, and the profile was measured again. One of the typical results of spectrum for cycle annealing is shown in Fig.7. The hole area is decreased and hole width is increasing with increasing the annealing temperature. For the irreversible broadening of holes, the dependence of increase of hole width on cycle annealing temperature is shown in Fig.8. TMOS40 showed the laegest irreversible broadening and the hole was disappeared after cycle annealing at 80K. In AP/a-SiO₂, the broadening was slightly suppressed, but the hole was also disappeared after cycle annealing at 80K. In the APTES containing samples, the irreversible broadening is suppressed especially in low temperature range (<40K) and the holes were remained after annealing at 80K. The hole broadening of APTES40 and APTES240 were slightly lower than that of APTES/PVA after annealing at 80K. It is considered that the irreversible broadening of photochemical hole by annealing is caused by the structural change of organic dyes and amorphous matrices. In APTES40 and APTES240, the dye TCPP was ionically or covalently bonded to a-SiO₂ matrix, thus the suppression of structural change is expected. There is no significant defference between APTES40 and APTES240. It is explained that the porphyrin ring which contribute to PHB, is apart from the bonding part, therefore, PHB properties are not affected by the varaiety of bonds. In AP/a-SiO₂, it is considered that TCPP is not linked to matrix, but, TCPP is bonded to AP and this bonding is effective to suppress structural change.

The relationship between normalized hole area and annealing temperatures in cycle annealing experiment is shown in Fig.9. Open marks show the hole area measured at annealing temperatures and solid marks show hole area measured at 3.6K. The decrease of hole areas measured at 3.6K after cycle annealing (open marks) is caused by the irreversible broadening of holes due to the structural change of TCPP. Further decrease of hole areas at respective annealing temperatures (solid marks) is reversible change caused by the change in Debye-Waller factor by temperature. In Fig.8, the reversible changes, which are shown in the gaps between open and solid mark, is varied with the samples. This suggests the temperature dependence of Debye-Waller factor is defferent in each samples

The Debye-Waller factor represents a fraction of a zero-phonon line in the integrated molecular absorption. Temperature dependence of Debye-Waller factor reflects low energy excitation mode coupling with PHB dyes in amorphous matrix. According to Horie et al., the energy difference between a zero-phonon hole and a pseudo phonon side hole, E_s, reflects the energy of a phonon mode coupling with dyes in polymer systems, and E_s does not

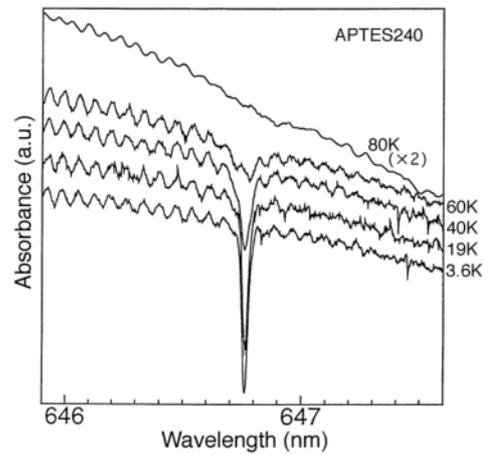


Fig.7 Change in hole spectra during cycle annealing experiment

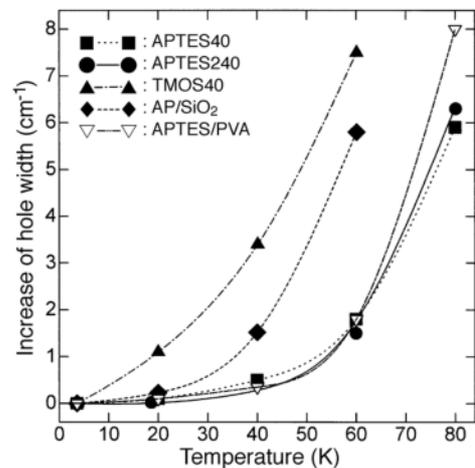


Fig.8 Irreversible hole broadening during cycle annealing experiment

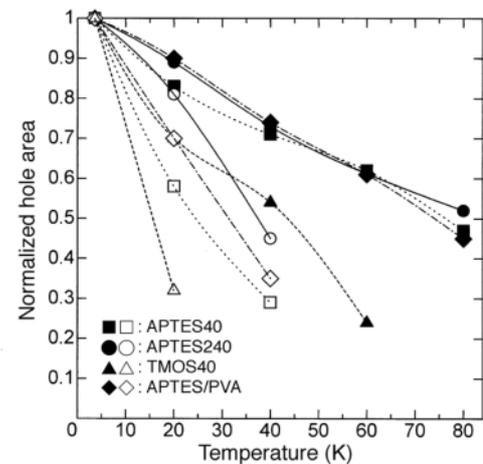


Fig.9 Temperature dependence of normalized hole area during cycle annealing experiments

depend on the nature of the guest molecules, but is specific to the host matrices^{21,22}. Fig.10 shows the spectra of zero-phonon hole and a pseudo phonon side hole in studied samples and E_s in these systems are shown in Table 3. The values of E_s are between 25 to 30 cm^{-1} and no significant difference is observed among the studied samples. Thus, the temperature dependence of Debye-Waller factor in TCPP/a-SiO₂ system is not explained by single phonon mode of E_s , and effects of other phonon mode are considered.

Table 3 The energy difference between a zero-phonon hole and a pseudo phonon side hole, E_s

	APTES40	APTES240	TMOS40	APTES/PVA
E_s (cm^{-1})	30	26	30	25

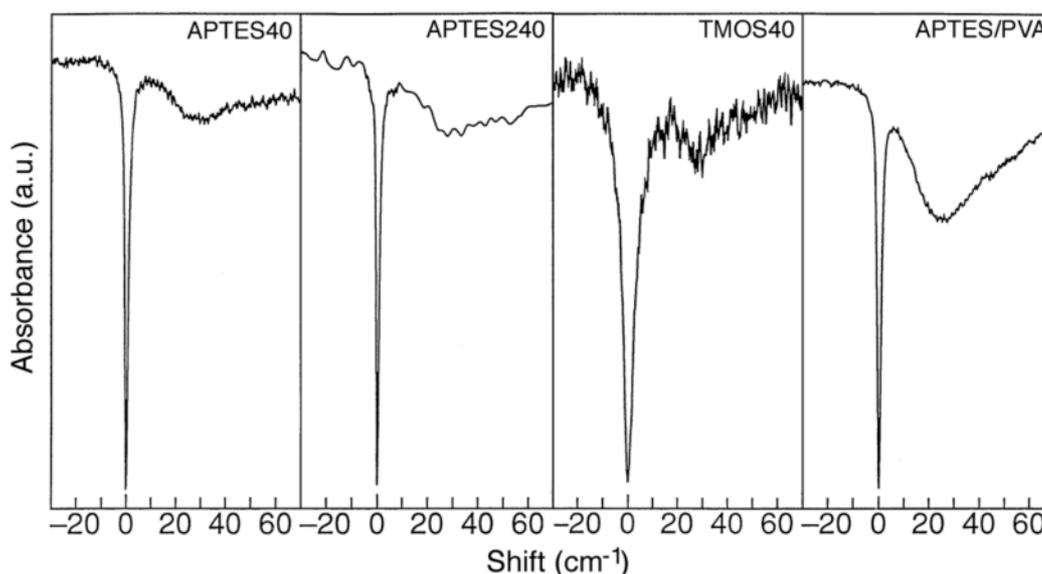


Fig.10 Zero phonon hole and pseudo-phonon side hole spectra of various systems

4. CONCLUSION

The authors synthesized TCPP cross-linked silica gels with using APTES containing starting solutions. The cross-linkage formation was confirmed with FT-IR measurement. At first, TCPP and APTES were ionically interacted in a sample dried at 40, and covalent bonds (amide bonds) were formed by vacuum drying higher than 240. In PHB measurement, the TCPP cross-linked silica gels showed narrow photochemical hole width and high quantum efficiency, and these values were close to that of porphin/polymer systems. By observing the irreversible broadening of photochemical hole under cycle annealing experiment, the cross-linkage between TCPP and APTES suppressed the structural change.

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