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Synthesis and optical properties of organic–inorganic hybrid gels containing fluorescent molecules

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ABSTRACT

Organic–inorganic hybrid gels containing fluorescent molecules, pyrene, anthracene, pelyrene, 9,10-diphenylanthracene, were synthesized from multi-functional cyclic siloxane, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS), or cubic silsesquioxane, 1,3,5,7,9,11,13,15-octakis(dimethylsilyloxy)pentacyclo-[9,5,1,1,1,1]octasilsesquioxane (POSS), as crosslinking reagents with α,ω-nonconjugated dienes, 1,5-hexadiene (HD) or 1,9-decadiene (DD), as spacer monomers, using a photo hydrosilylation reaction with a bis(acetylacetonato) platinum catalyst in toluene. The gels containing pyrene showed higher emission intensity than the toluene solution of pyrene. The emission intensity of pyrene increased as proceeding of the network formation in the gel. The gels composed of long spacer monomer of DD or cubic cross-linking reagent of POSS showed higher intensity of the emission than the gels synthesized by HD or TMCTS. Only a slight increase of the emission intensity was observed in the gels containing anthracene, pelyrene, 9,10-diphenylanthracene.

1. Introduction

Organic–inorganic hybrid polymers having network structures have been developed due to their characteristic properties, high transparency, high thermal stability, good mechanical strength, excellent solvent resistance, low dielectric constant, and so on. The organic–inorganic hybrid polymers are prepared with some effective methods [1]. Hydrosilylation reaction of multi-functionalized corss-linking reagents containing Si–H or vinyl group is one of the effective methods to yield organic–inorganic network polymers. We reported synthesis of organic–inorganic hybrid gels using hydrosilylation reaction of cyclic siloxane or cubic silsesquioxane and α,ω-nonconjugated dienes with a highly active Pt catalyst, Karstedt's catalyst. Network structure of the resulting gels was characterized by a characteristic analytical method, namely scanning microscopic light scattering (SMILS) system [2]. The characterization cleared that the network structure in the gels formed extremely narrow distribution of mesh size [3]. The mesh size of the gels quantitatively corresponded with the length of the α,ω-nonconjugated dienes used. The mesh size of the organic–inorganic hybrid gel was precisely controllable by means of co-gelation [4]. These gels also could be synthesized with photo hydrosilylation reaction using bis(acetylacetonato) platinum (Pt(acac)$_2$) catalyst under UV-irradiation [5].

Theses gels include organic solvent, such as toluene, and the mesh of the gel should be usable as a separated space. We came up with an idea of dispersing fluorescent small molecules in the meshes to develop the organic–inorganic hybrid gel with luminescent property. Solution of fluorescent molecules was applied for electrogenerated chemiluminescent (ECL) cell of the light-emitting devices. The solution of fluorescent molecules, not only small molecules but also polymers, were developed as solution electrogenerated chemiluminescent (SECL) or solution light-emitting device (SLED) [6–16]. The SECL or SLED consists of only a solution of fluorescent molecule sandwiched between two electrodes, and has advantage in process-ability of the light-emiting device (LED). Furthermore, gel light-emitting devices (GLED), which are composed of organic solvent and conjugated polymer (physical gel) [17] or crosslinked polymer with fluorescent molecule (chemical gel) [18,19] sandwiched between two electrodes, were also developed to improve the production process of the LED.

The mesh size of the developed organic–inorganic hybrid gels was about 1.5–2 nm, which should be suitable to incorporate fluorescent small molecules in their mesh. Synthesis of the organic–inorganic hybrid gel in the presence of fluorescent molecule should be applicable to the GLED. This paper reports synthesis of organic–inorganic hybrid gels from multiple Si–H functional cross-linking reagents, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) or 1,3,5,7,9,11,13,15-octakis(dimethylsilyloxy)pentacyclo-[9,5,1,1,1,1]

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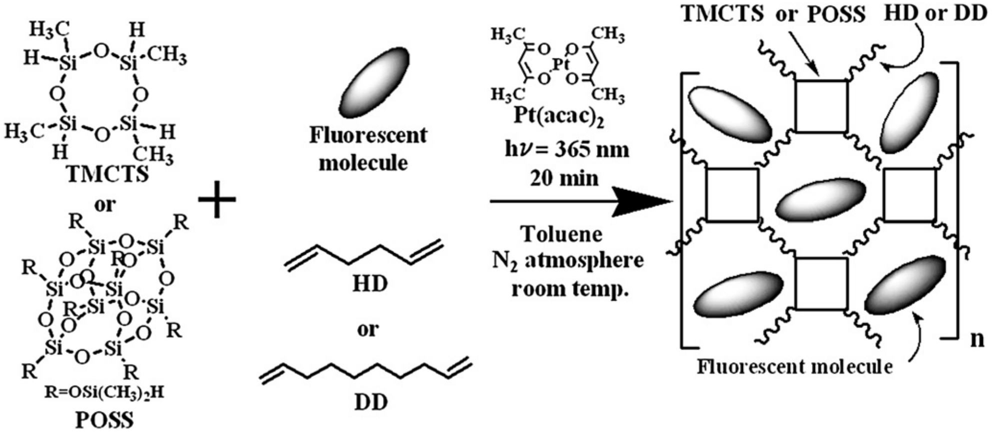


Scheme 1. Synthesis of organic–inorganic hybrid gels containing fluorescent molecules.

octasilsesquioxane (POSS), and α,ω-nonconjugated dienes (HD, DD) as spacer monomers by means of a photo hydrosilylation reaction with $Pt(acac)_2$ catalyst in the presence of fluorescent molecules, pyrene, antracene, pelyrene, and 9,10-diphenylanthracene, as shown in Schemes 1 and 2. Optical properties of the resulting gels were investigated with UV–vis absorption spectroscopy and emission spectroscopy, and the fluorescent molecules, especially pyrene, showed higher emission intensity in the gels than that in the solutions.

2. Experimental section

2.1. Materials

HD and DD (Tokyo Kasei Kogyo Co.) were distilled over calcium hydride under nitrogen atmosphere. TMCTS (Chisso Co. Ltd.) and POSS (Aldrich Chemical Co. Ltd.), illustrated in Scheme 1, were used without further purification. Pyrene (Kanto Chemical Co. Ltd.), anthracene (Wako Pure Chemical Industries), pelyrene (Tokyo Kasei Kogyo Co.), 9,10-diphenylanthracene (Tokyo Kasei Kogyo Co.) and $Pt(acac)_2$ (Wako Pure Chemical Industries) were commercially obtained, and used as received. Toluene was dried over calcium hydride under refluxing for 6 h and distilled before use. The mole ratio of vinyl group in diene to Si–H group in cross-linking reagent was adjusted to 1.0. The molar ratio of vinyl group (or Si–H group) to the Pt catalyst was 1000 in the reaction system. Samples were prepared by the following procedures with special care for getting rid of dust and measured in as-prepared state at 25 °C.

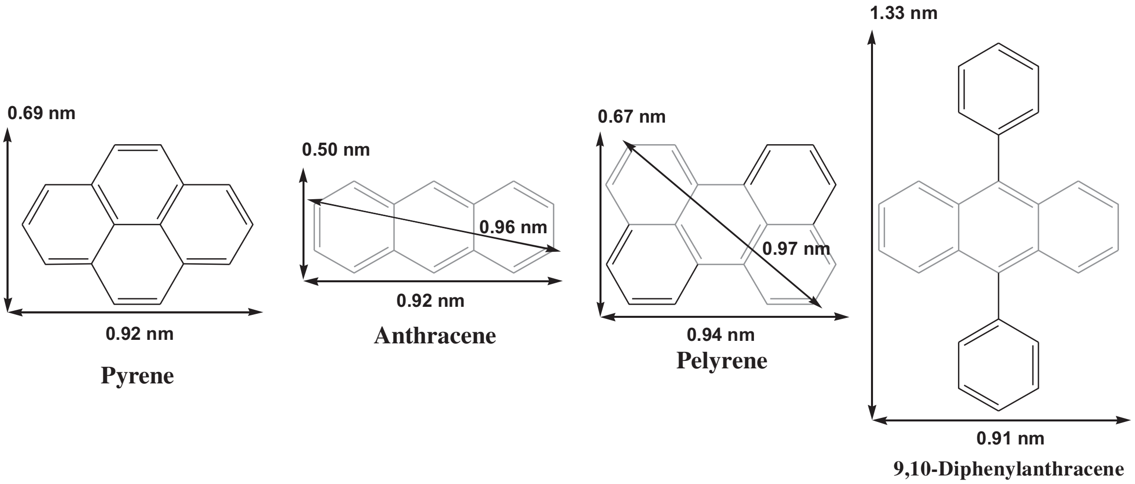
2.2. Synthesis of organic–inorganic hybrid gels containing pyrene by means of a photo hydrosilylation reaction

2.2.1. Photo hydrosilylation of TMCTS with HD in the presence of 0.1 mM of pyrene (P_M1)

0.1 mg (0.25 μmol) of $Pt(acac)_2$, 21.4 mg (0.26 mmol) of HD, 31.3 mg (0.13 mmol) of TMCTS, and 0.1 mM toluene solution of pyrene (244 μL) were added to a sample tube of 4 mm diameter under the nitrogen atmosphere, and the catalyst was dissolved with shaking to yield a homogeneous solution. After the sample tube was sealed by burning off, UV of 365 nm, 1220 $\mu W/cm^2$ was irradiated for 20 min. It was placed without stirring in the dark. The colorless and clear gel was generated. The gels containing 10.0 mM of pyrene, other fluorescent molecules, or with DD were prepared with the same procedure.

2.2.2. Photo hydrosilylation of POSS with HD in the presence of 0.1 mM of pyrene (P_M3)

0.1 mg (0.25 μmol) of $Pt(acac)_2$, 10.5 mg (0.128 mmol) of HD, 32.6 mg (0.032 mmol) of POSS, and 0.1 mM toluene solution of pyrene (199 μL) were added to a sample tube of 4 mm diameter



Scheme 2. Structure and molecular size (calculated by MM2) of fluorescent molecules.

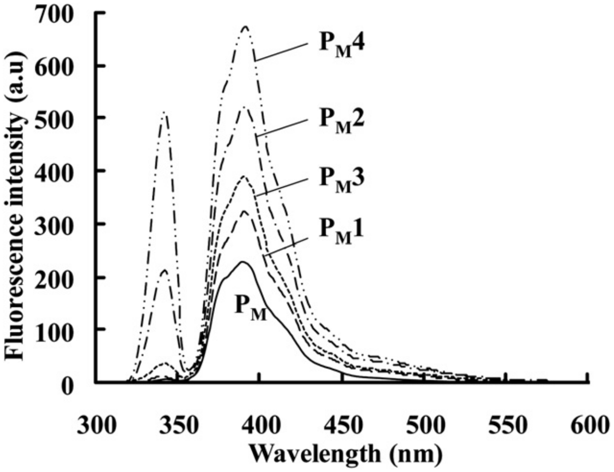


Fig. 1. Emission spectra of TMCTS-HD (P_M1),TMCTS-DD (P_M2), POSS-HD (P_M3), POSS-DD (P_M4) gels containing 0.1 mM of pyrene, and 0.1 mM of pyrene solution (P_M), excitation wavelength = 338 nm.

under the nitrogen atmosphere, and the catalyst was dissolved with shaking to yield a homogeneous solution. After the sample tube was sealed by burning off, UV of 365 nm, 1220 μW/cm^2 was irradiated for 20 min. It was placed without stirring in the dark. The colorless and clear gel was generated. The gels containing 10.0 mM of pyrene, other fluorescent molecules, or with DD were prepared with the same procedure.

2.3. Analytical procedures

The samples for the photophysical studies were prepared in an optical quartz cell of 0.7 mL volume equipped a seal cap according to the synthetic methods described above. UV–vis absorption spectroscopy was conducted with a SHIMADZU UV-1600PC. A slit of 2 nm was applied, and the absorption was recorded by 0.1 nm at a scan rate of 550 nm/min. Emission spectroscopy was investigated with a SHIMADZU RF-1500 or RF-5300PC equipped a 150 W xenon lamp. A slit of 5 nm was applied, and the absorption was recorded by 1 nm at a scan rate of 600 nm/min. Quantitative determination of minute mesh size of the gels was performed with the scanning microscopic light scattering (SMILS) system [2]. The radius of mesh ξ (mesh size) was calculated from the relaxation time in SMILS analysis with Einstein–Stokes formula,

$$\xi = \frac{16\pi n^2 \tau_R K_B \sin^2\frac{\theta}{2}}{3\eta\lambda^2}$$

where n, τ_R, K_B, θ, η, and λ are refractive index of toluene, Ensemble-averaged relaxation time (s), Boltzmann constant (1.38×10^{-23} J K^{-1}), scattering angle (90°), viscosity coefficient of toluene at 298 K (5.6×10^{-4} Nm^2 s^{-1}), wavelength of incident ray (4.42×10^{-7} m), respectively.

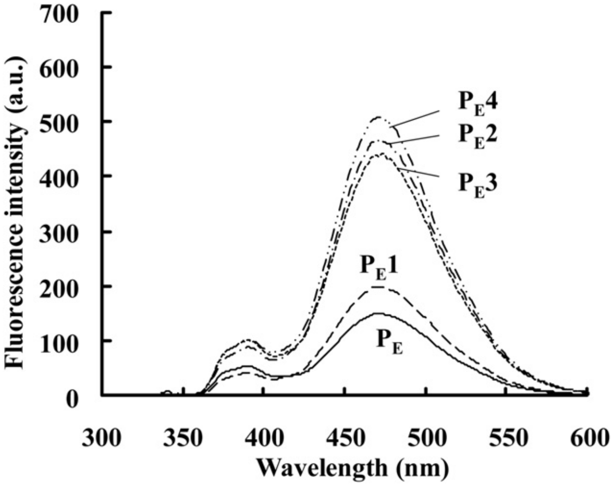


Fig. 2. Emission spectra of TMCTS-HD (P_E1), TMCTS-DD (P_E2), POSS-HD (P_E3), POSS-DD(P_E4) gels containing 10 mM of pyrene, and 10 mM of pyrene solution (P_E), excitation wavelength = 338 nm.

3. Results and discussion

The photo hydrosilylation reaction of TMCTS or POSS with HD or DD was investigated in the presence of pyrene. The TMCTS-HD, TMCTS-DD, POSS-HD, and POSS-DD gels were prepared under the monomer concentrations (wt% of cross-linking reagent and spacer monomer in the gel) of 20.0 wt%, 9.1 wt%, 20.0 wt%, and 7.4 wt%, respectively. These monomer concentrations are termed “optimal gelation concentration”, which produces the gels with the minimum mesh size and a narrow mesh size distribution in each gel, as previously reported [5]. Mesh sizes (radius of mesh) of the gels obtained under the optimal gelation concentration were about 1.4–1.6 nm. The mesh sizes and mesh size distributions of the gels containing pyrene were almost the same with those of the corresponding gels without pyrene. These results indicate that the presence of pyrene does not inhibit the formation of homogeneous network structure of the gels. In the measurement of UV–vis spectroscopy, all the gels showed absorbance peaks at 307, 322, and 388 nm, which were also observed in toluene solution of pyrene [20]. Fig. 1 shows emission spectra of the gels containing 0.1 mM of pyrene. The spectra showed monomer emission of pyrene at $\lambda_{max} = 390$ nm. All the gels containing pyrene showed increase of relative intensity of the emission peak in comparison with that of the toluene solution of pyrene. The emission intensity of the gels with DD was much higher than that of the gels with HD. The gels containing 10 mM of pyrene, which showed excimer emission, were also prepared in the same way. The emission spectra of the gels containing 10 mM of pyrene are shown in Fig. 2. Remarkable increase of the relative intensity of the excimer emission peak at $\lambda_{max} = 470$ nm was observed in the gels of TMCTS-DD, POSS-HD or DD in comparison with that of the pyrene solution. Whereas, only

Table 1
Emission properties of the organic–inorganic hybrid gels containing pyrene.

Sample	monomer	wt.%	$Pt(acac)_2$ g/L	pyrene mM	I_M[a] a.u.	I_E[a] a.u.	R[b]	Φ_f[c]
P_M[d]				0.1	228			0.52
P_M1	TMCTS-HD	20.0	0.15	0.1	404			0.76
P_M2	TMCTS-DD	9.1	0.22	0.1	522			0.81
P_M3	POSS-HD	20.0	0.16	0.1	320			0.53
P_M4	POSS-DD	7.4	0.19	0.1	675			0.92
P_E[d]				10	54	149	0.36	0.05
P_E1	TMCTS-HD	20.0	0.15	10	42	198	0.21	0.09
P_E2	TMCTS-DD	9.1	0.22	10	89	469	0.19	0.15
P_E3	POSS-HD	20.0	0.16	10	102	443	0.23	0.14
P_E4	POSS-DD	7.4	0.19	10	105	510	0.21	0.18

[a] Emission intensity at 390 nm (monomer emission; I_M) or at 471 nm (eximer emission; I_E).

[b] $R = I_M/I_E$.

[c] Photo luminance quantum yields were relatively calculated using quinine sulfate in 1 N H_2SO_4 aqueous solution as a standard reference (10^{-5} mol/L, $\Phi_f = 0.55$, excited at 328 nm) [27].

[d] Toluene solution of pyrene for reference.

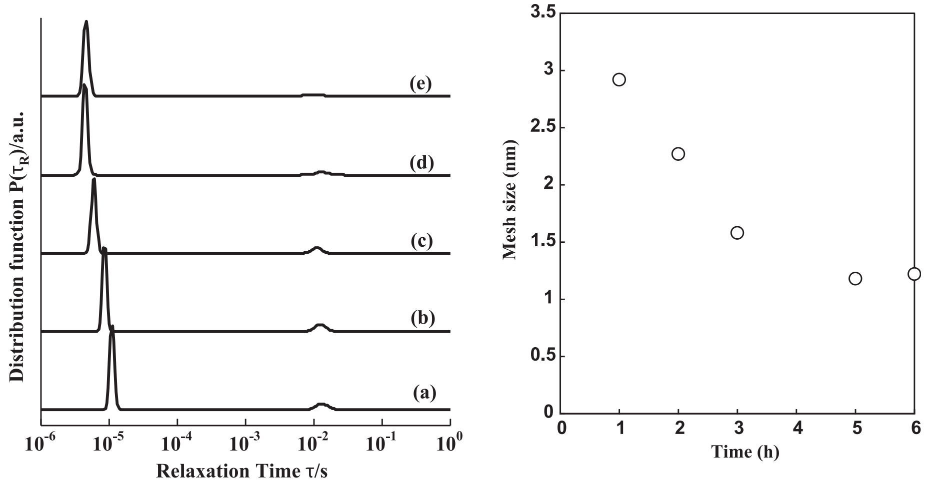


Fig. 3. Time evolution of relaxation peak (left) acquired by SMILS and mesh size (right) of TMCTS-DD gel containing 0.1 mM of pyrene at (a) 1 h, (b) 2 h, (c) 3 h, (d) 5 h, (e) 6 h after irradiation period for 20 min.

a slight increase of the peak intensity was observed in the TMCTS-HD gel.

There is a point which needs to be clarified: Do monomers and/or Pt(acac)$_2$ catalyst enhance the relative intensity of emission peak of pyrene? We confirmed that the addition of monomers (TMCTS, POSS, HD, DD) to toluene solution of pyrene did not affect the emission intensity [21]. In addition, the emission intensity of toluene solution of pyrene decreased in the presence of the catalyst [22]. Effect of catalyst concentration on emission intensity was investigated in the TMCTS-HD gels containing 0.1 mM of pyrene, and increase of the catalyst concentration decreased the emission intensity [23]. These results make it clear that Pt(acac)$_2$ not encourages but extinguishes the emission of pyrene.

Increase of monomer emission intensity of pyrene was previously reported in a polymerization system of *s*-triazine dimethacrylic monomer and ethylene glycol phenyl ether acrylate due to the increase of the viscosity around the pyrene molecules [24]. In that case, the ratio of the fluorescence intensities for monomer emission against excimer emission ($R = I_M/I_E$) of pyrene was linearly dependent on the viscosity of medium as the following equation [25].

$$R = I_M/I_E = A\eta[Py]^{-1} \tag{1}$$

where η is the viscosity coefficient, [Py] is the concentration of pyrene, and A is a constant. If the viscosity around the pyrene molecules would cause increase of the pyrene monomer emission intensity, the increase of R value should also increase with increasing of the emission intensity.

The emission intensity and R value of the resulting gels containing 10 mM of pyrene are summarized in Table 1. The intensity of the excimer emission of pyrene in the gels were higher than those of the corresponding toluene solutions of pyrene, as described above. On the other hand, the R values of the gels were lower than those in the toluene solution containing 10 mM of pyrene. If the increase of the emission intensity in the gels would derive from the increase of the viscosity around the pyrene molecules, the R values in the gels should become higher than that in the toluene solution, according to the equation (1). Additionally, no clear relationship was observed between the emission intensities and the R values of the gels.

Network structure and emission intensity were traced during the formation of TMCTS-DD gel containing 0.1 mM of pyrene to clear the relationship between gel formation process and the emission intensity. Time evolutions of relaxation peak in SMILS analysis and mesh size are shown in Fig. 3. The relaxation peaks

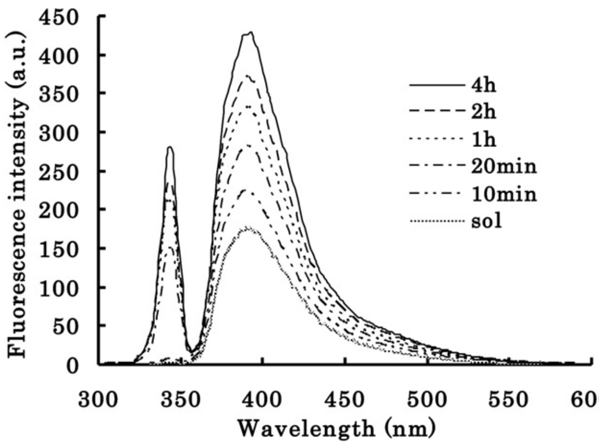


Fig. 4. Time evolution of emission spectra of TMCTS-DD gel containing 0.1 mM of pyrene, excitation wavelength = 338 nm, sol = reaction solution before UV irradiation.

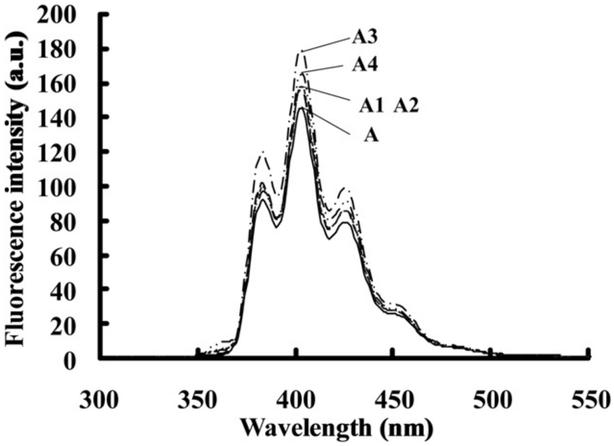


Fig. 5. Emission spectra of TMCTS-HD (A1), TMCTS-DD (A2), POSS-HD (A3), POSS-DD (A4) gels containing 10 mM of anthracene solution (A), excitation wavelength = 359 nm.

Table 2
Fluorescence intensities ratio of the fluorescent molecules in the gels against in the toluene solution.

Network	Pyrene		Anthracene	Pelyrene	Diphenylanthracene
	0.1 mM[a]	10 mM[b]	10 mM	1 mM	10 mM
TMCTS-HD	2.4	1.3	1.1	1.2	1.2
TMCTS-DD	3.5	3.1	1.1	1.1	1.2
POSS-HD	2.1	3.4	1.2	1.2	1.2
POSS-DD	4.5	4.3	1.2	1.2	1.2

[a] Monomer emission at 390 nm.
[b] Excimer emission peak at 470 nm.

detected at $< 10^{-5}$ s were corresponding to the mesh size of 1.2 nm derived from the mesh of TMCTS-DD network. The mesh size decreased with progressing of the reaction as summarized in right side of Fig. 3 due to the formation of dense and fine mesh, as previously reported [5].

Fig. 4 shows the time evolution of emission spectrum of the TMCTS-DD gel containing 0.1 mM of pyrene. The gel was generated at 20 min after the UV irradiation. The intensity of the emission increased with the increase of the reaction time. The result clears that formation of TMCTS-DD mesh should enhance the emission of pyrene. It seems reasonable to suppose that incorporation of pyrene in the present organic–inorganic hybrid gels would induce the enhancement of fluorescent intensity due to the effective dispersion and/or isolation of pyrene in the mesh of the organic–inorganic hybrid gels

The gels containing other fluorescent molecules, anthracene (10 mM), pelyrene (1 mM), and 9,10-diphenylanthracene (10 mM), were also prepared to investigate the emission intensity in the gels. Fig. 5 shows emission spectra of the gels containing 10 mM of anthracene, and that of a toluene solution for a reference. Only a slight increase of the emission intensity of anthracene was observed in the gels in comparison with that in the toluene solution. Pelyrene and 9,10-diphenylanthracene also showed a slight increase of the emission intensity in the gels [26]. The ratio of the fluorescence intensities of the fluorescent molecules in each gel against in the toluene solution is summarized in Table 2. The degrees of increase in the emission intensity of these molecules were much lower than that of pyrene.

These results may account for enhancement of the emission intensity of pyrene in the gels. One explanation for the enhancement of the emission intensity of pyrene may be that a part of pyrene molecules in the gels should be separately incorporated in the mesh of the gels. This incorporation of pyrene in the mesh would raise the emission efficiency. The photo luminance quantum yields of monomer emission and excimer emission of pyrene in the gels was relatively calculated using quinine sulfate in 1 N H_2SO_4 aqueous solution as a standard reference [27]. The quantum yields (Φ_f) were summarized in Table 1. The quantum yields of pyrene in the gels were larger than those in the toluene solution in both the cases of monomer emission and excimer emission. These results clear that the increase of the emission intensity of pyrene in the gels is derived from the increase of the quantum yield. We name this phenomenon as ‘framed effect’. The degree of ‘framed effect’ may be concerned with the size of spacer monomer and the structure of cross-linking reagent. Calculated molecular size by MM2 calculation was applied to explain the degree of ‘framed effect’ qualitatively. The calculated molecular size at the extended structure of DD (1.1 nm) is larger than that of HD (0.64 nm). In addition, the calculated molecular size of pyrene (0.92 nm) is larger than that of HD, but smaller than that of DD. Although, the calculated molecular sizes are not enough to discuss in quantitative, it seems reasonable to suppose that the degree of framed effect is in relation to the molecular sizes of pyrene and spacer molecules. The incorporation of pyrene in the mesh of gels formed by DD would be more effective than that of the gels formed by HD, especially in the case of low concentration of pyrene which shows monomer emission, as summarized in Table 2. In the case of the high concentration of pyrene which shows excimer emission, pyrene dimer would be hard to be incorporated in the mesh of TMCTD-HD, and caused only a slight increase of the emission intensity. Structure of the cross-linking reagent also affects degree of the ‘framed effect’. The gels with POSS showed higher intensity of emission peaks than those with TMCTS. POSS has three dimensional cubic structure, whereas TMCTS has two dimensional in plane molecular structure. Three dimensional formation of mesh with POSS would incorporate pyrene more effectively than the two dimensional formation of mesh with TMCTS.

Other fluorescent molecules, anthracene, pelyrene, and 9,10-diphenylanthracene showed only a slight increase of the emission intensity in the gels. One explanation for the results is that these fluorescent molecules should not be framed in the mesh of the gels due to their molecular size and/or structure of anthracene unit, containing three phenyl units in the molecules.

The present organic–inorganic hybrid gels containing fluorescent molecules should be useful for GLED. Application of the gels for GLED is now proceeding, and the results will be reported elsewhere.

Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.09.005.

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