Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Optical Sensor for Discriminating Chemical Composition and Size of Plastic Particles in Water Based on Water-Soluble Networks Consist of Polyhedral Oligomeric Silsesquioxane Presenting Dual Luminescent Colors

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General. Octa-substituted ammonium POSS (Amino-POSS), 7-diethylaminocoumarin-3-carboxylate (coumarin D-1421),[1] silica particles (SPs)[2–4] and surface modified SPs[5] were prepared according to the previous reports. Polystyrene, poly(lactic acid) and poly(methyl methacrylate) particles (PSPs, PLAPs, PMMAPs, respectively) were purchased from micromod Partikeltechnologie GmbH (micromer®) and used as received. The sizes of SPs were determined by TEM observation and others were based on nominal diameter from suppliers. Triethylamine (Et_3N), hydrochloric acid (HCl), dimethyl sulfoxide (DMSO) and methanol were obtained from Wako Pure Chemical Industries, Ltd. Succinic acid, methoxytrimethylsilane and 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) was obtained from Tokyo Chemical Industry co., Ltd., DMSO-d_6 was obtained from Euriso-Top. Deionized water was purified with an Autopure WEX3 system from Yamato Scientific Co., Ltd.

Measurements. ^{1}H, ^{13}C and ^{29}Si NMR spectra were measured with a JEOL EX-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 80 MHz for ^{29}Si) spectrometer or a JEOL JNM-AL400 spectrometer. Coupling constants (J value) are reported in Hertz. The chemical shifts are expressed in ppm downfield from tetramethylsilane, using residual dimethyl sulfoxide ($\delta = 2.50$ in ^{1}H NMR, $\delta = 39.5$ in ^{13}C NMR) as an internal standard. UV–vis absorption spectra were recorded with a SHIMADZU UV–vis–NIR Spectrometer UV-3600 at 25 °C. Emission spectra from the samples were monitored using a HORIBA FluoroMax-4P at 25 °C using 1 cm path length cell. The dynamic light scattering (DLS) measurements were carried out at 90° scattering angle and 20 ± 0.2 °C using a FPAR-1000 particle analyzer with a He-Ne laser as a light source. The CONTIN program was used for data analysis to extract information on the average hydrodynamic size. MASS spectra were obtained on a JEOL JMS-SX102A.

Synthetic procedures and characterization

Preparation of Coumarin-POSS (C-POSS). Coumarin D-1421 (500 mg, 1.9 mmol) was dissolved in DMSO (25 mL) in a flask. DMT-MM (1.1 g, 4.0 mmol) was added to the solution, and the mixture was stirred at room temperature for 1 h, followed by addition of Amino-POSS (1.2 g, 1.0 mmol) and triethylamine (430 μL, 3.1 mmol). The mixture was stirred at room temperature for 20 h and dropped into acetonitrile (250 mL) containing 0.1 wt% HCl to form precipitation. The product was collected by filtration, washed with acetonitrile and dried *in vacuo*. The yellow powder of C-POSS was then obtained (1.2 g, 0.76 mmol, 74%). ^{1}H NMR (Chart S1, 400 MHz, DMSO-d_6, 25 °C): δ 8.69−8.51 (m, 3.2H), 8.20−8.14 (br, 18H), 7.72−7.54 (m, 1.6H), 6.83−6.74 (m, 1.6H), 6.61−6.46 (m, 1.6H), 3.90−3.77 (m, 2H), 2.79 (br, 5.9H), 1.72−1.62 (br, 16H), 1.16−1.09 (m, 9.6H), 0.74 (br, 16H) ppm.^{13}C NMR (Chart S3, 100 MHz, DMSO-d_6, 25 °C): δ 161.7, 157.0, 152.3, 147.4, 131.4, 117.7, 110.0, 109.4, 107.5, 95.7, 44.2, 40.9, 22.4, 20.5, 12.2, 8.3 ppm. ^{29}Si NMR (Chart S4, 80 MHz, DMSO-d_6, 25 °C): δ −65.8, −66.3, −66.4 ppm. The substitution rate of coumarin D-1421 (R_2 in scheme 1) was estimated from the integration ratios of the ^{1}H NMR peaks at the propyl moiety in POSS as shown in Chart S2.

Preparation of Coumarin-POSS networks (CPN). A typical procedure is shown here. Succinic acid (22 mg, 0.19 mmol) was dissolved in DMSO (5 mL) in a Schlenk flask. DMT-MM (120 mg, 0.44 mmol) was added to the solution, and the mixture was stirred at room temperature for 1 h, followed by addition of C-POSS (100 mg, 0.062 mmol) and triethylamine (62 μL, 0.44 mmol). The mixture was additionally stirred at room temperature for 24 h and dropped into acetonitrile (35 mL) containing 0.1 wt% HCl. The precipitation was collected by centrifugation and washed with acetonitrile twice to eliminate impurities and dried *in vacuo*. The solid was suspended with deionized water and filtered with a 0.45 μm PTFE syringe filter for removing insoluble to give CPN. CPN was preserved as stock solutions until the tests of optical properties. ^{1}H NMR (Chart S5, 400 MHz, DMSO-d_6, 25 °C): δ 10.54 (br, 0.3H), 8.64 (br, 1.4H), 7.81 (br, 8.6H), 7.67−7.60 (m, 0.9H), 6.80−6.75 (m, 0.8H), 6.61−6.52 (m, 0.9H), 3.80 (br, 0.8H), 3.00 (m, 6.9H), 2.78 (br, 3.4H), 2.42 (br, 2.8H), 2.30 (br, 7.2H), 1.60 (br, 7.9H), 1.43 (br, 8.9H), 1.18−1.12 (m, 5.9H), 0.60 (br, 16H) ppm. ^{13}C NMR (Chart S7, 100 MHz, DMSO-d_6, 25 °C): δ 202.3, 173.8, 171.1, 149.9, 112.3, 107.7, 105.2, 102.9, 97.8, 45.4, 44.2, 40.9, 40.4, 30.0, 29.2, 22.5, 20.6, 12.3, 8.4 ppm. ^{29}Si NMR (Chart S8, DMSO-d_6, 25 °C): δ −65.9 ppm. The substitution rate of coumarin D-1421 (R_2 in Figure

1 and Scheme S1), succinic acid (R_4 in Figure 1 and Scheme S1), and succinic acid linking (R_3 in Figure 1 and Scheme S1) were estimated from the integration ratios of the ^{1}H NMR peaks basically at the propyl moiety in POSS as shown in Chart S6.

Preparation of C, 7-(diethylamino)-2-oxo-N-propyl-2H-chromene-3-carboxamide. Coumarin D-1421 (500 mg, 1.9 mmol) was dissolved in 25 mL of DMSO in a flask. DMT-MM (1.1 g, 4.0 mmol) was added to the solution, and the mixture was stirred at room temperature for 1 h, followed by addition of propylamine (120 mg, 2.0 mmol) and triethylamine (570 μL, 4.1 mmol). The mixture was additionally stirred at room temperature for 24 h and dropped into 250 mL of 0.5 M $NaHCO_3$*aq*. and the products were precipitated. The precipitation was collected by filtration and washed with water and dried *in vacuo*. Recrystallization from hot EtOH/water afforded **C** as a yellow crystal (0.50 g, 1.6 mmol, 80%). ^{1}H NMR (Chart S9, DMSO-d_6, 25 °C): δ 8.65−8.63 (m, 2H), 7.68 (d, *J* = 4.0 Hz, 1H), 6.81 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 3.48 (q, *J* = 7.2 Hz, 4H), 3.26 (q, *J* = 6.6 Hz, 2H), 1.52 (sext, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (Chart S10, 100 MHz, DMSO-d_6, 25 °C): δ 162.0, 161.7, 157.1, 152.3, 147.5, 131.5, 110.1, 109.5, 107.6, 95.8, 44.2, 40.5, 22.3, 12.2, 11.3 ppm. ESIMS $[M+H]^+$ calcd. 303.1703, found 303.1699.

Measurement of fluorescent properties. CPN was adjusted from the stock solution to 10 μM as the coumarin unit with deionized water for optical measurements. C-POSS was also adjusted to 10 μM for the tests through two protocols. One was solving the powder with deionized water directly to obtain desired concentrations, and another was dissolving to 1 mM, storing at room temperature for more than 1 d and then diluting 100 times. Samples containing either C-POSS or CPN and various particles were prepared by mixing the same volumes of these stock samples. Final concentrations of C-POSS and CPN were 5.0 μM as the coumarin unit, and particles were adjusted based on surface areas (29 cm^2/mL). The series of measurements were performed 10 min after mixing. The raw spectra data of the mixture was subtracted with the spectra of particles as a blank.

Separation of particles from mixtures by centrifugation. The mixture samples were centrifuged at 25,000 *g* for 60 min. The supernatants were directly served to optical measurements. The precipitations were suspended with deionized water and re-centrifuged. Finally, the precipitation was suspended with the same volume of water as before centrifugation followed by optical measurements.

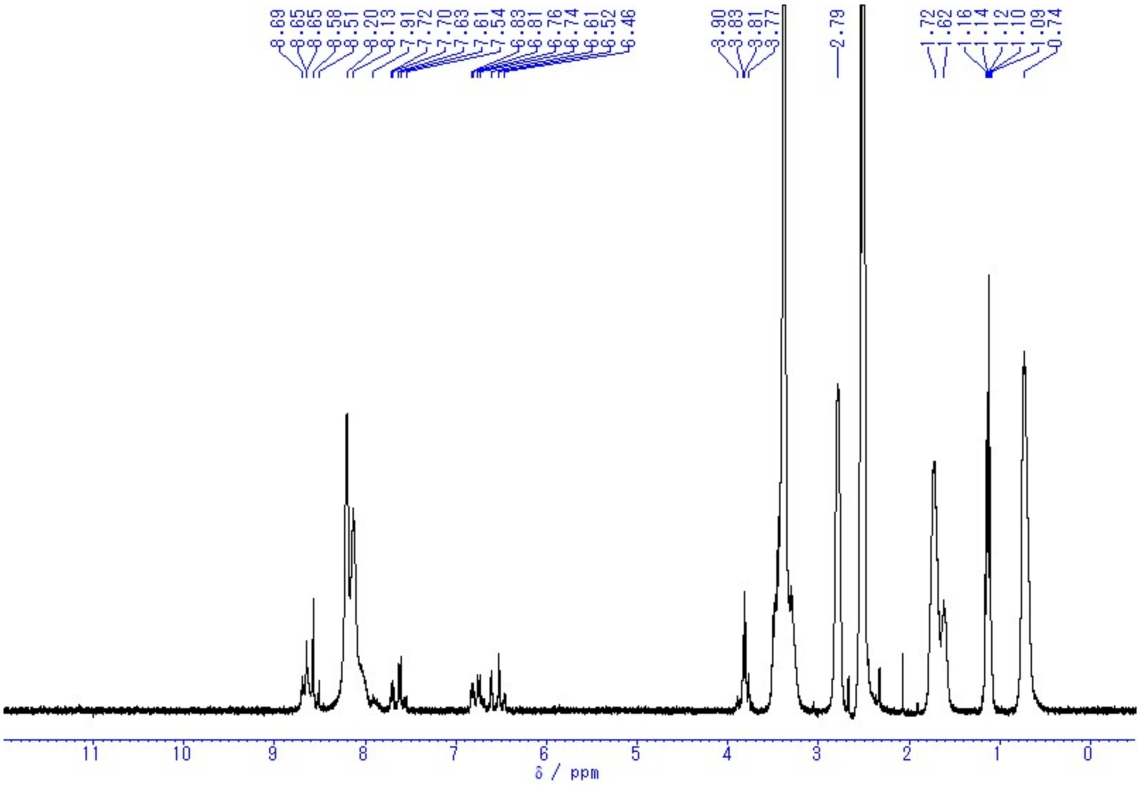
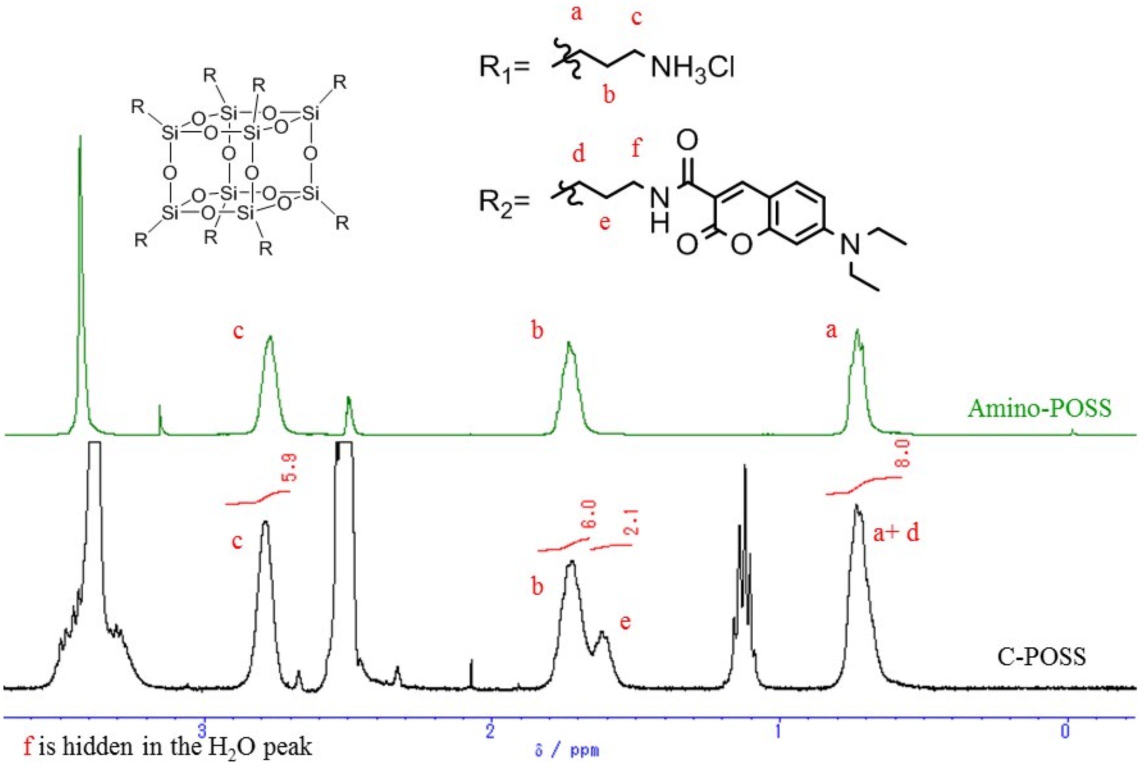


Chart S1. ^{1}H NMR spectrum of the **C-POSS** in DMSO-d_6 at 25 °C (400 MHz)



f is hidden in the H$_2$O peak

Chart S2. ^{1}H NMR spectra of the propyl moiety in **C-POSS** in DMSO-d_6 (400 MHz)

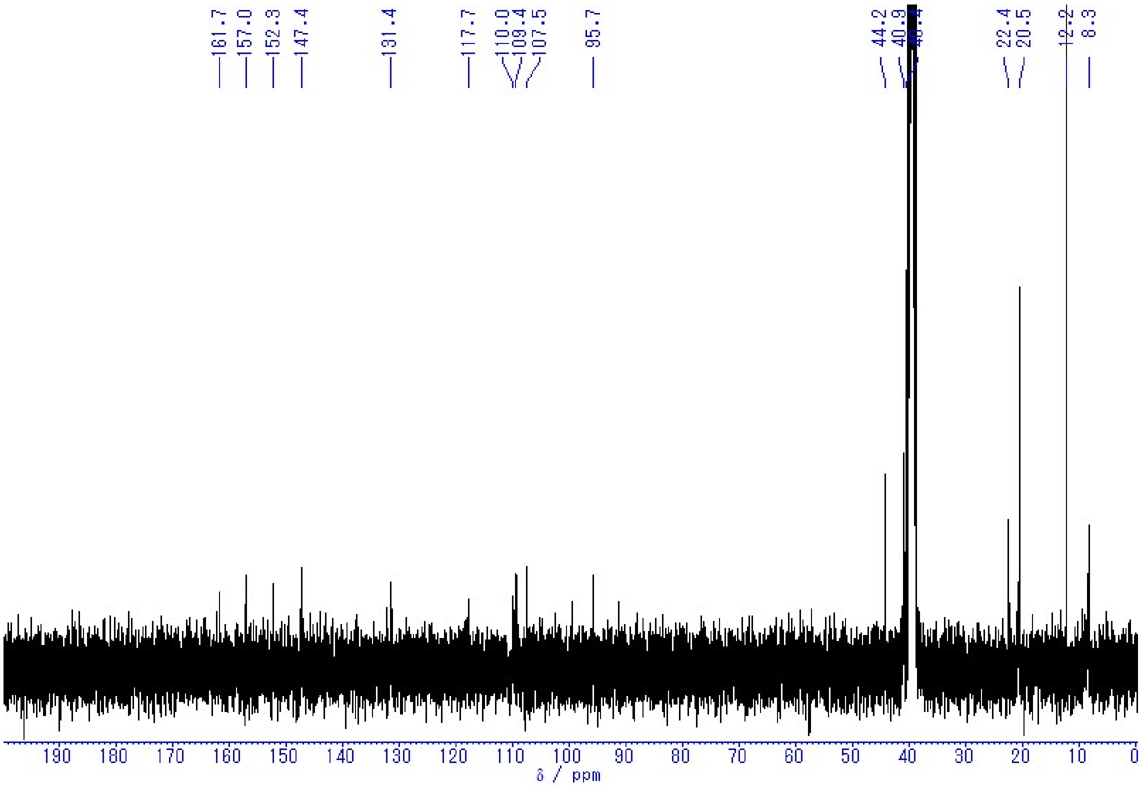


Chart S3. ^{13}C NMR spectrum of the **C-POSS** in DMSO-d_6 at 25 °C (100 MHz)

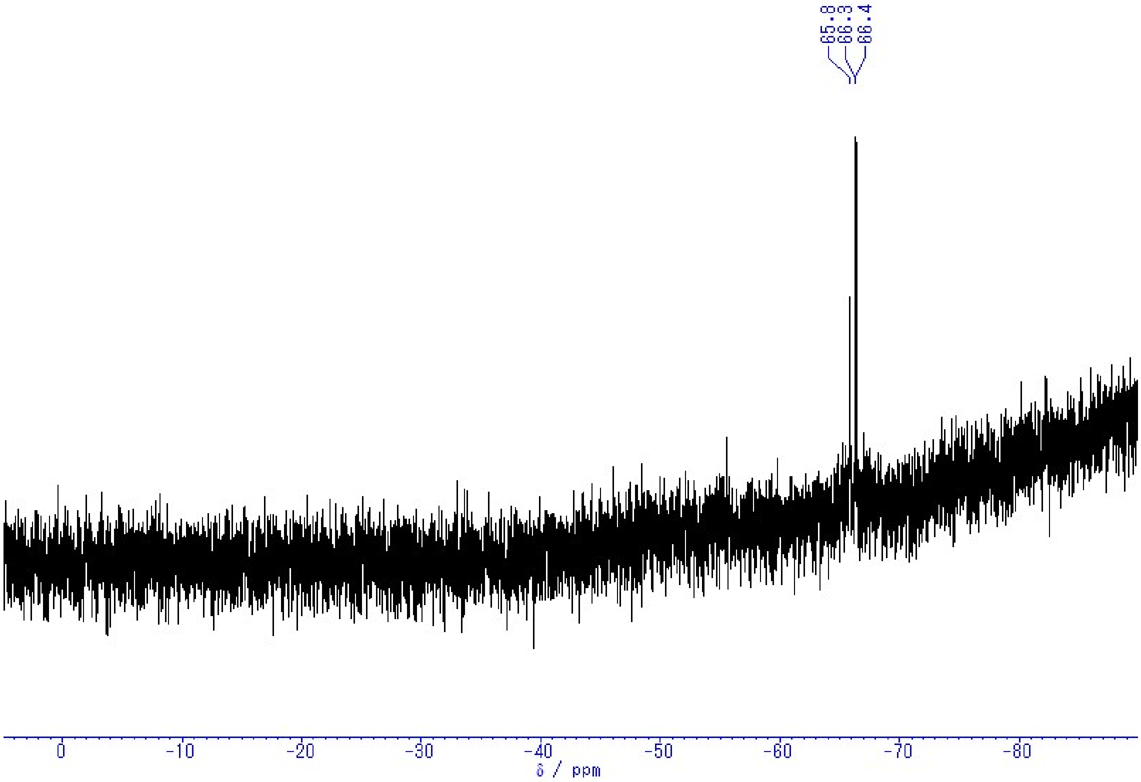


Chart S4. ^{29}Si NMR spectrum of the **C-POSS** in DMSO-d_6 at 25 °C (80 MHz)

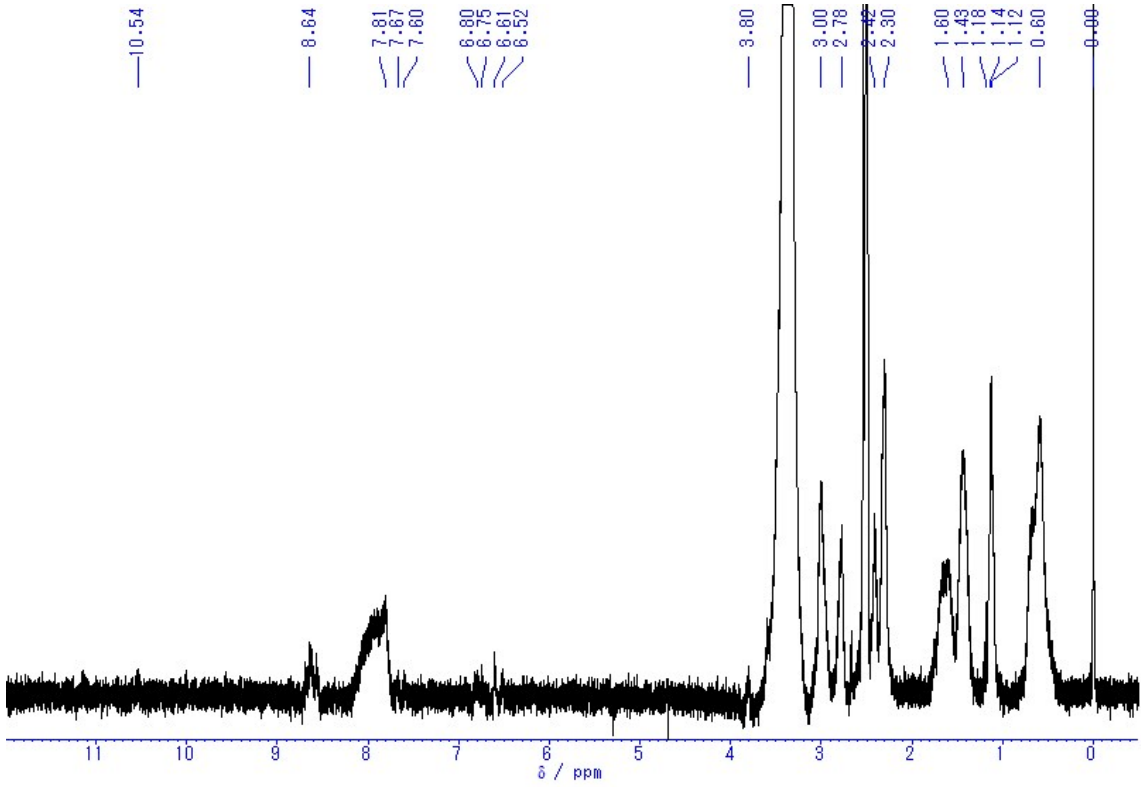
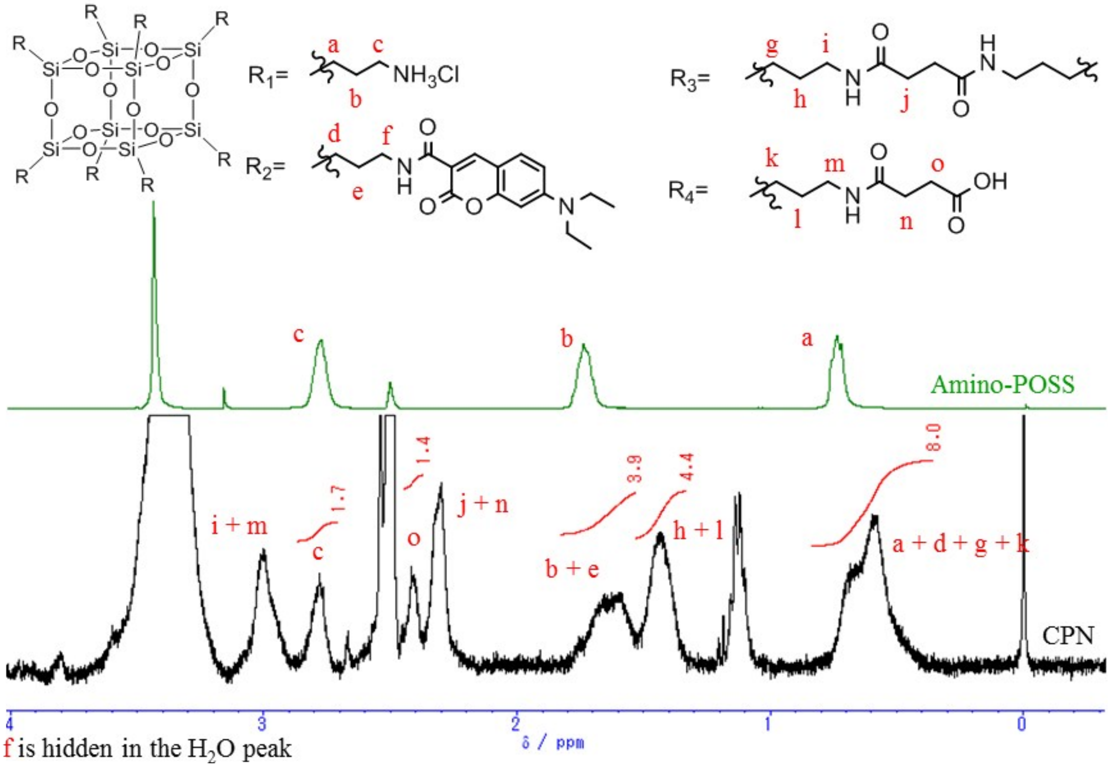


Chart S5. ^{1}H NMR spectrum of the **CPN** in DMSO-d_6 at 25 °C (400 MHz)



f is hidden in the H_2O peak

Chart S6. ^{1}H NMR spectra of the propyl and succinic acid moiety in **CPN** in DMSO-d_6

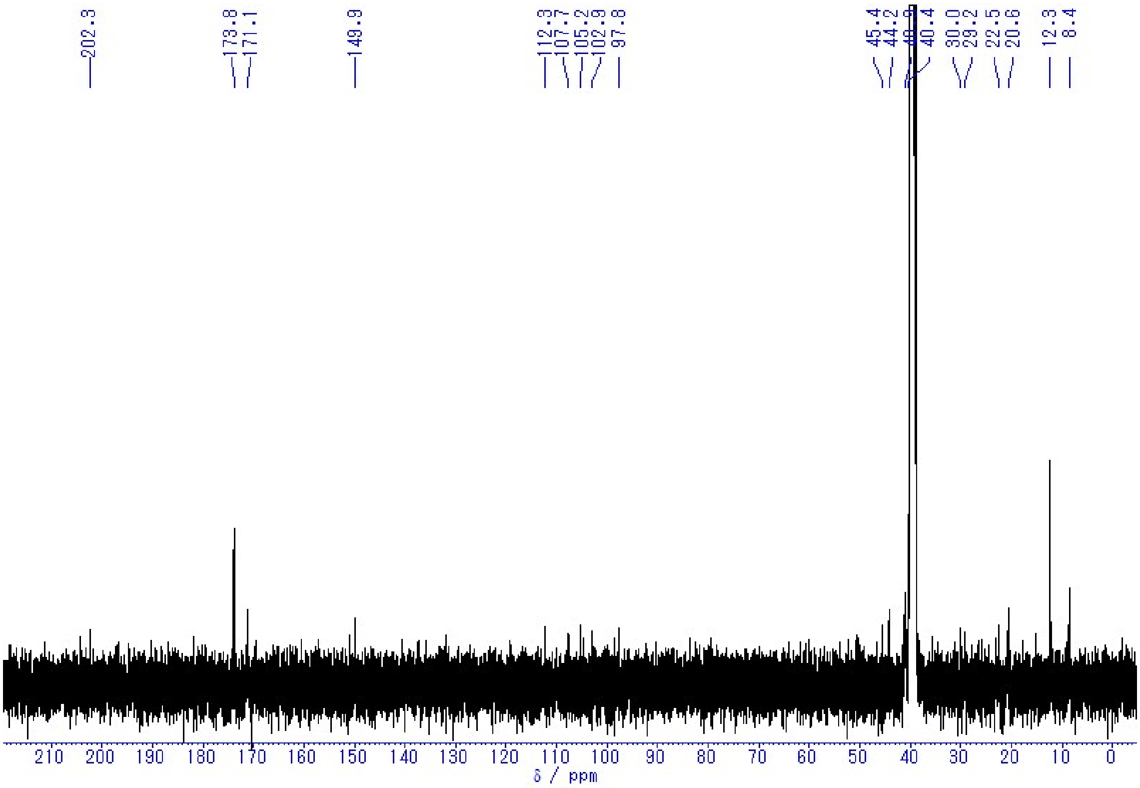


Chart S7. ^{13}C NMR spectrum of the **CPN** in DMSO-d_6 at 25 °C (100 MHz)

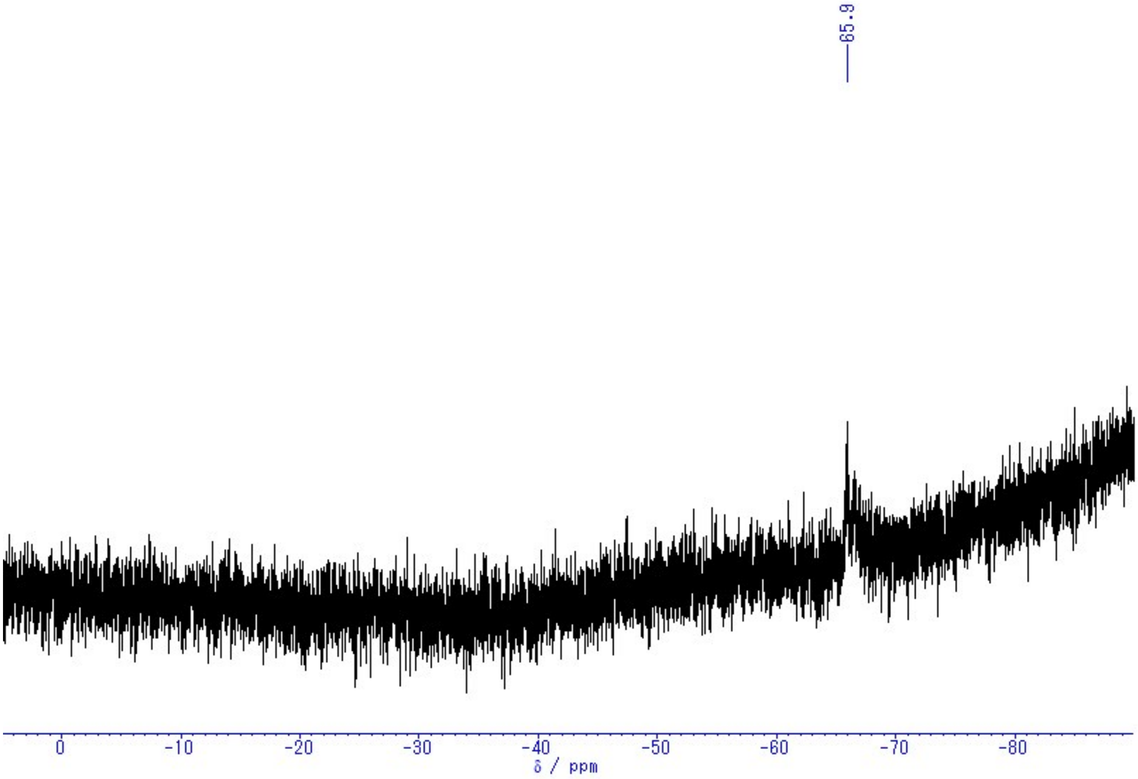


Chart S8. ^{29}Si NMR spectrum of the **CPN** in DMSO-d_6 at 25 °C (80 MHz)

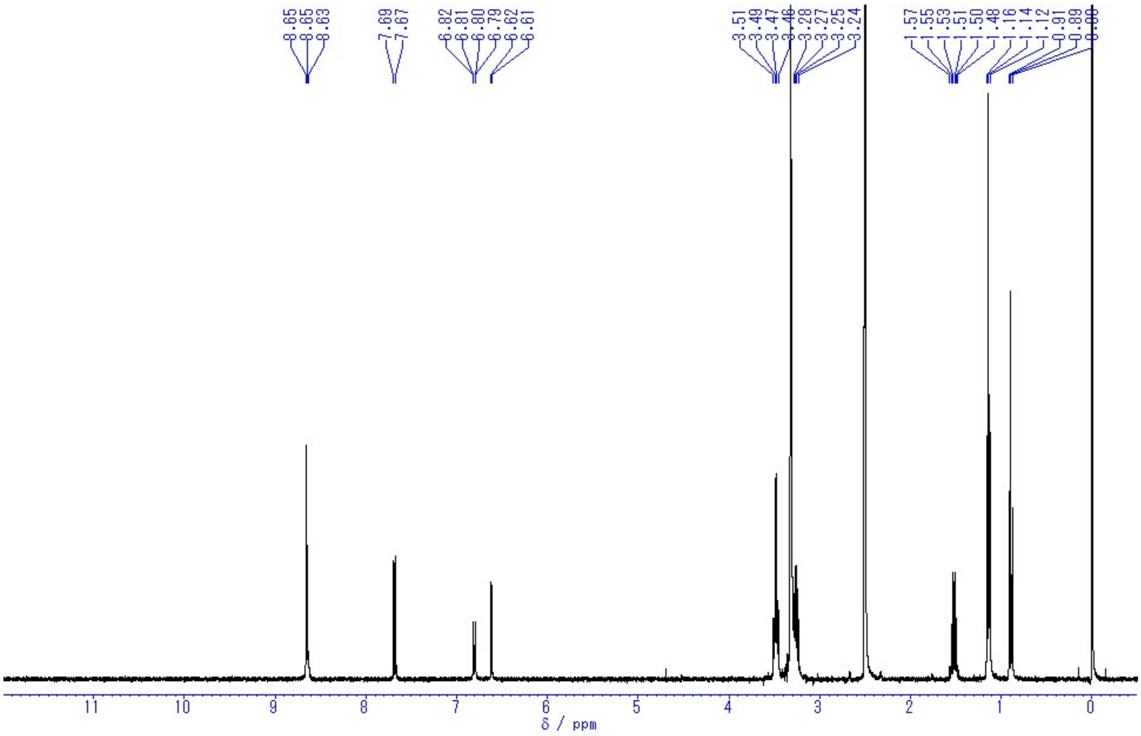


Chart S9. ^{1}H NMR spectrum of **C** in DMSO-d_6 at 25 °C (400 MHz)

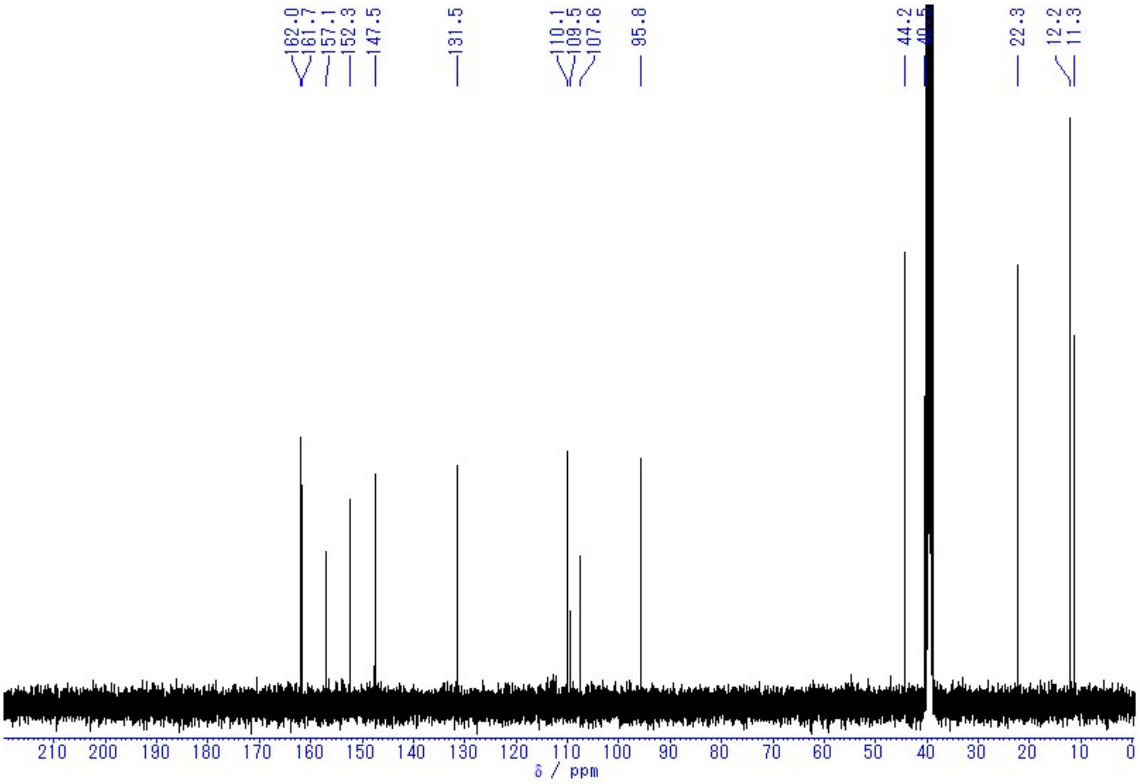
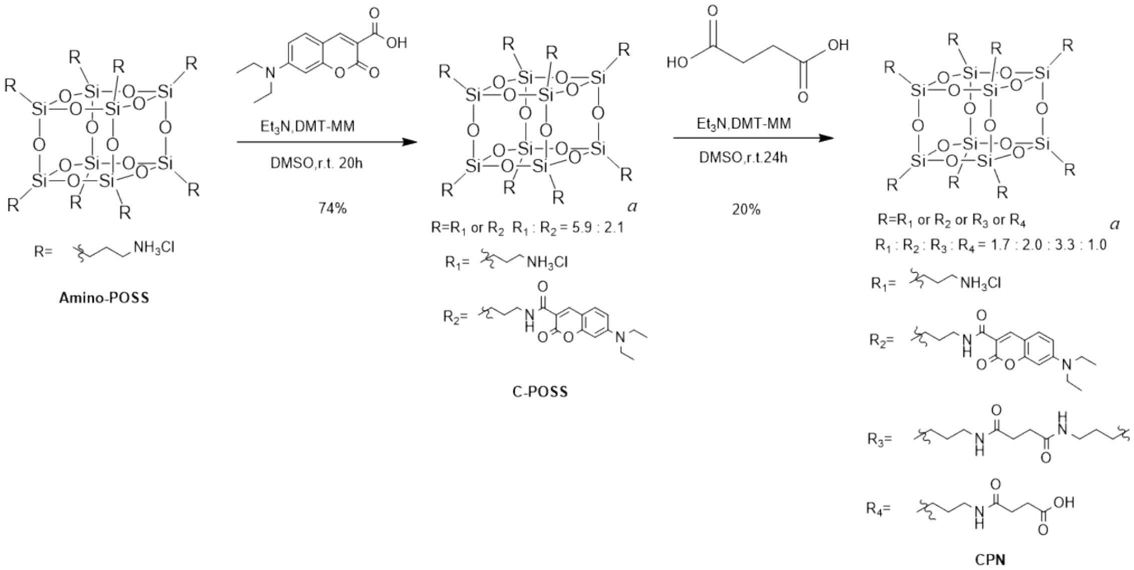


Chart S10. ^{13}C NMR spectrum of **C** in DMSO-d_6 at 25 °C (100 MHz)

Scheme S1. Synthesis of the POSS networks



[a] Estimated from the ^{1}H NMR spectra.

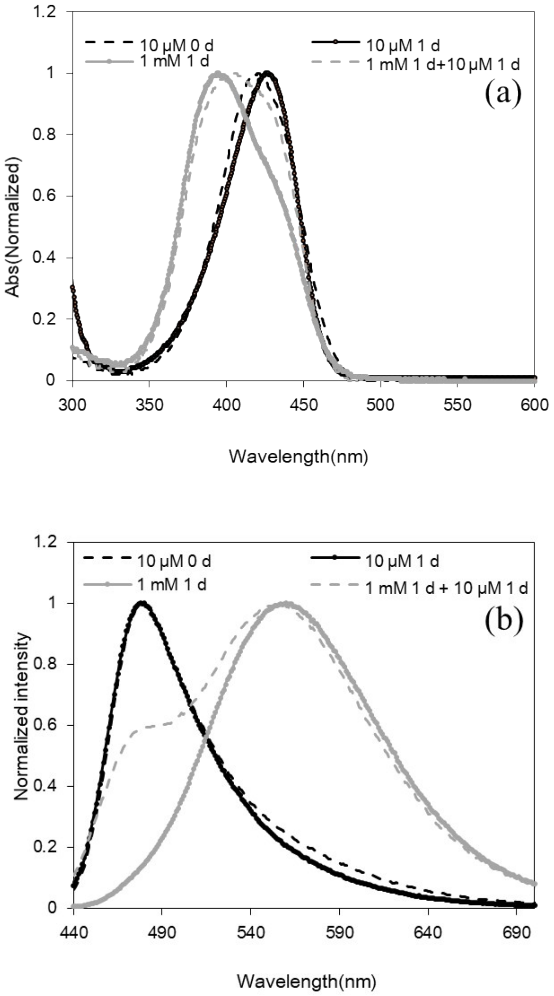


Figure S1. (a) UV–vis absorption and (b) PL spectra of C-POSS with the excitation light at 427 nm in water at either 10 μM or 1 mM with variable incubation times. The concentration was based on the coumarin D-1421 unit. The agglomeration of C-POSS strongly occurred in water (1 mM) and that showed only yellow emission. The agglomeration was partially dissociated by 100 times dilution and blue emissive components were generated (10 μM).

Table S1. Hydrodynamic radii (r_H) of C-POSS in various concentrations

Preincubation [a]	Concentration	Time	r_H (nm)
No	1 mM	0.5 h	N.D.
		1 h	14.6±6.2
		3 h	24.6±5.6
		5 h	26.2±5.9
		3 d	28.4±8.2
Yes	10 μM	0.5 h	105.2±61.2
		1 h	160.2±106.6
No	10 μM	0.5 h	N.D.
		1 h	N.D.

[a] Storing C-POSS solutions at 1 mM for more than 1 day

Table S2. Amounts of particles in the samples

particle	Diameter (nm)	Surface area (cm^2)	Weight (μg)	Number of particles ($\times 10^8$)
PSP	50	29	25	3,700
	100		50	920
	200		100	230
	500		250	36
	1,000		500	9
SP	40	29	38	5,800
	460		438	44
	950		905	10

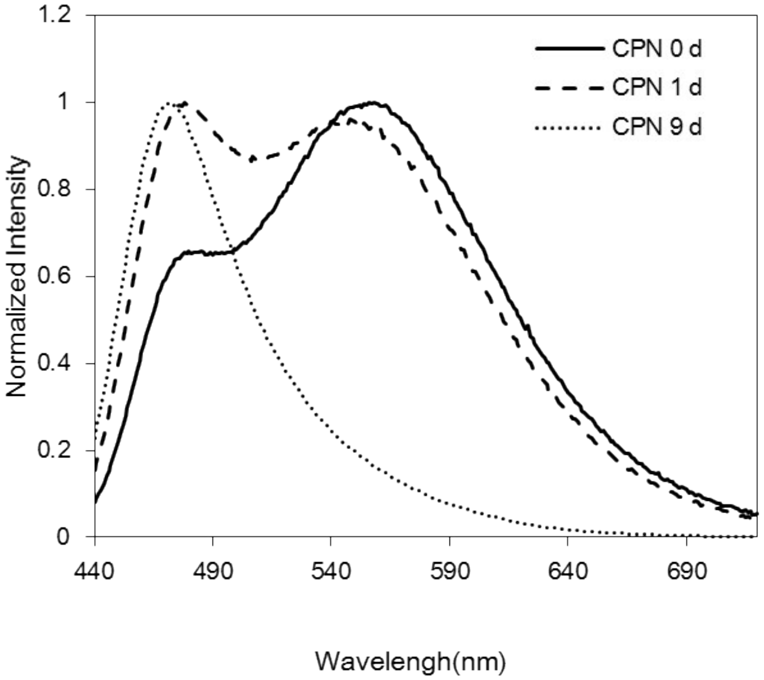


Figure S2. PL spectra of CPN in water at various incubation times after dilution of the stock solution from 1 mM to 10 μM. The concentration was based on the coumarin unit. The excitation wavelength was at 427 nm.

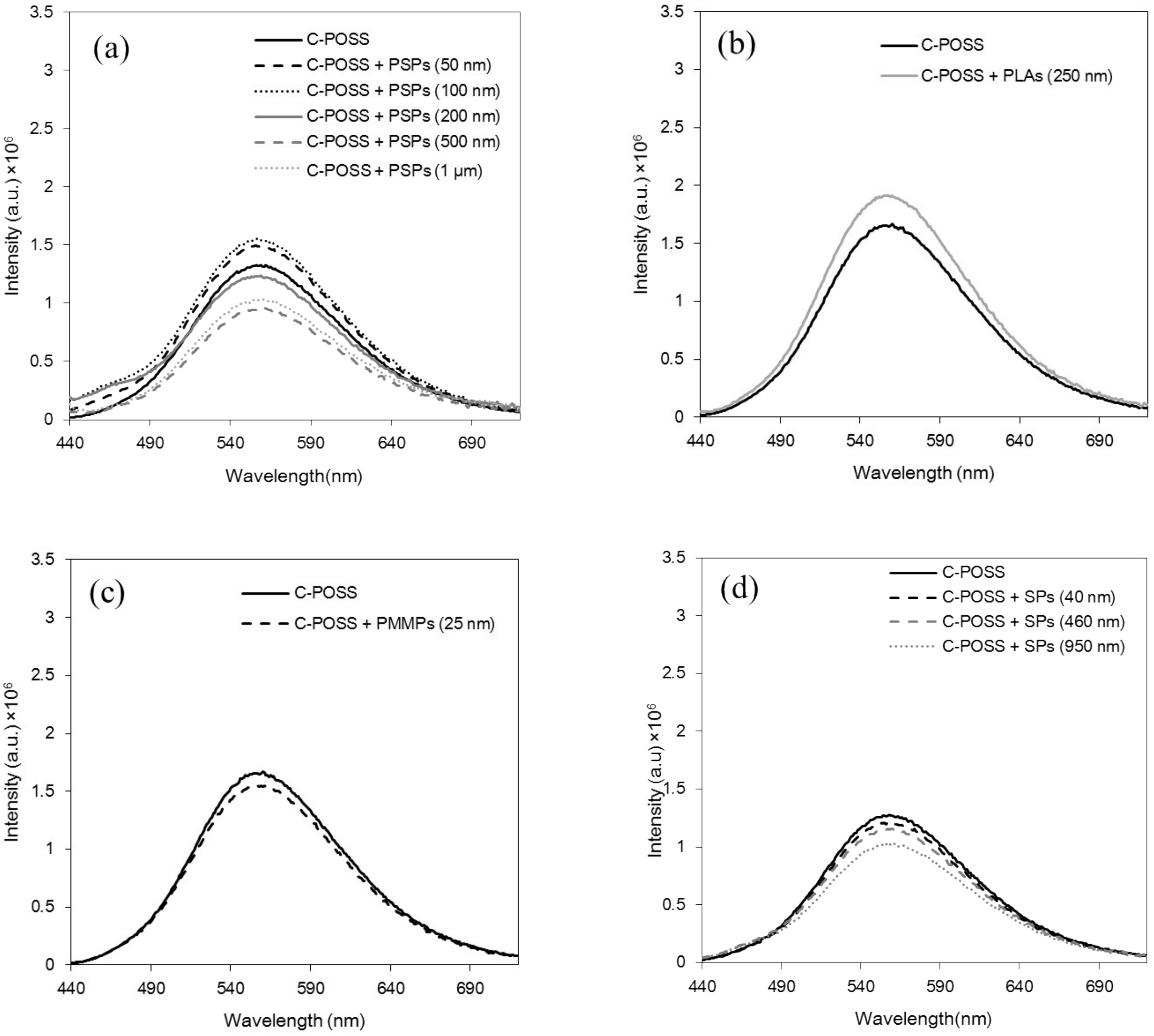


Figure S3. PL spectra of C-POSS with (a) PSPs, (b) PLAPs, (c) PMMAPs and (d) SPs.

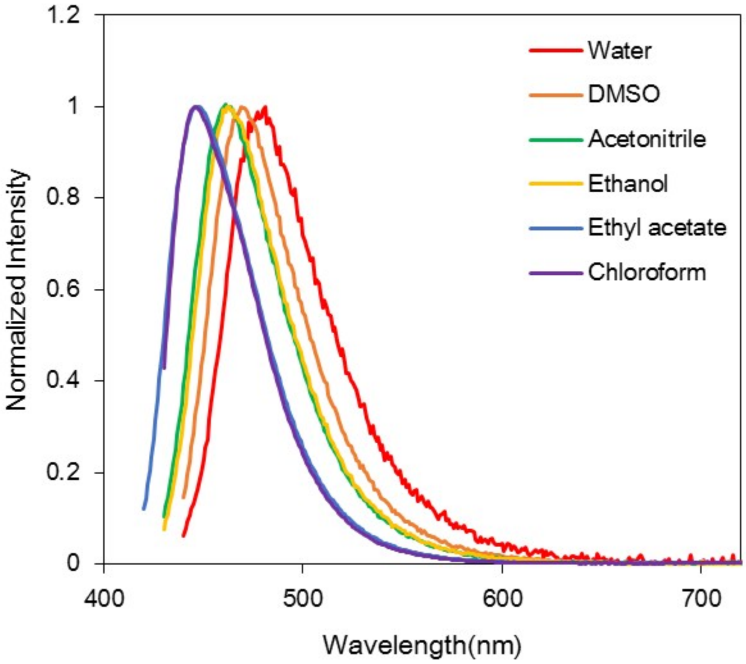


Figure S4. PL spectra of **C** in various solvents. The concentration was preliminary adjusted to 1mM with DMSO followed by dilution with arbitrary solvents to 10 μM.

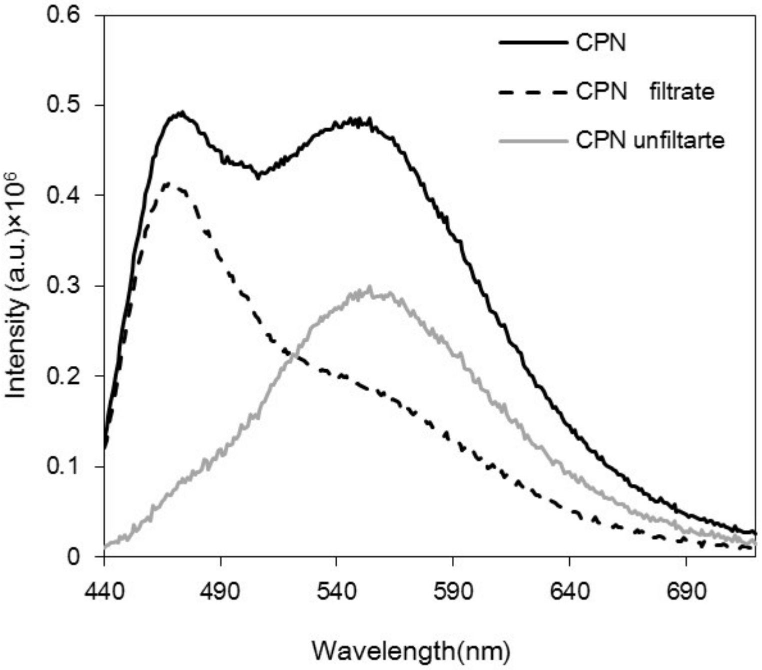


Figure S5. Change of PL spectra of CPN by filtration. The aqueous solution of CPN was filtered with a 0.20 μm PTFE syringe filter. The excitation light at 427 nm. The spectrum of the CPN unfiltrate was calculated by subtracting 'CPN filtrate' from 'CPN'.

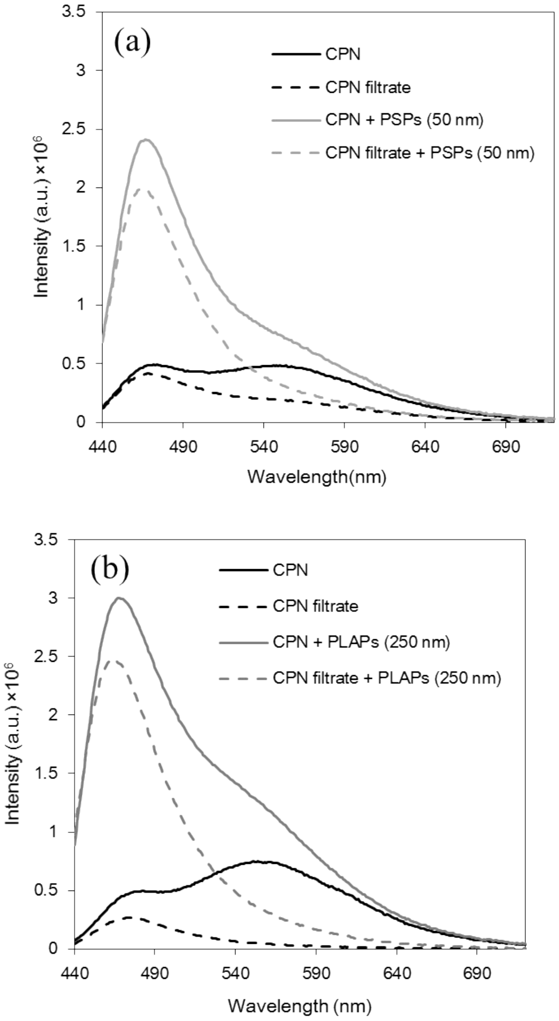


Figure S6. Effects of filtration on the interaction of CPN with (a) PSPs (50 nm), (b) PLAPs (250 nm). 5.0 μM of CPN as final concentration was filtrated by 0.20 μm PTFE syringe filter.

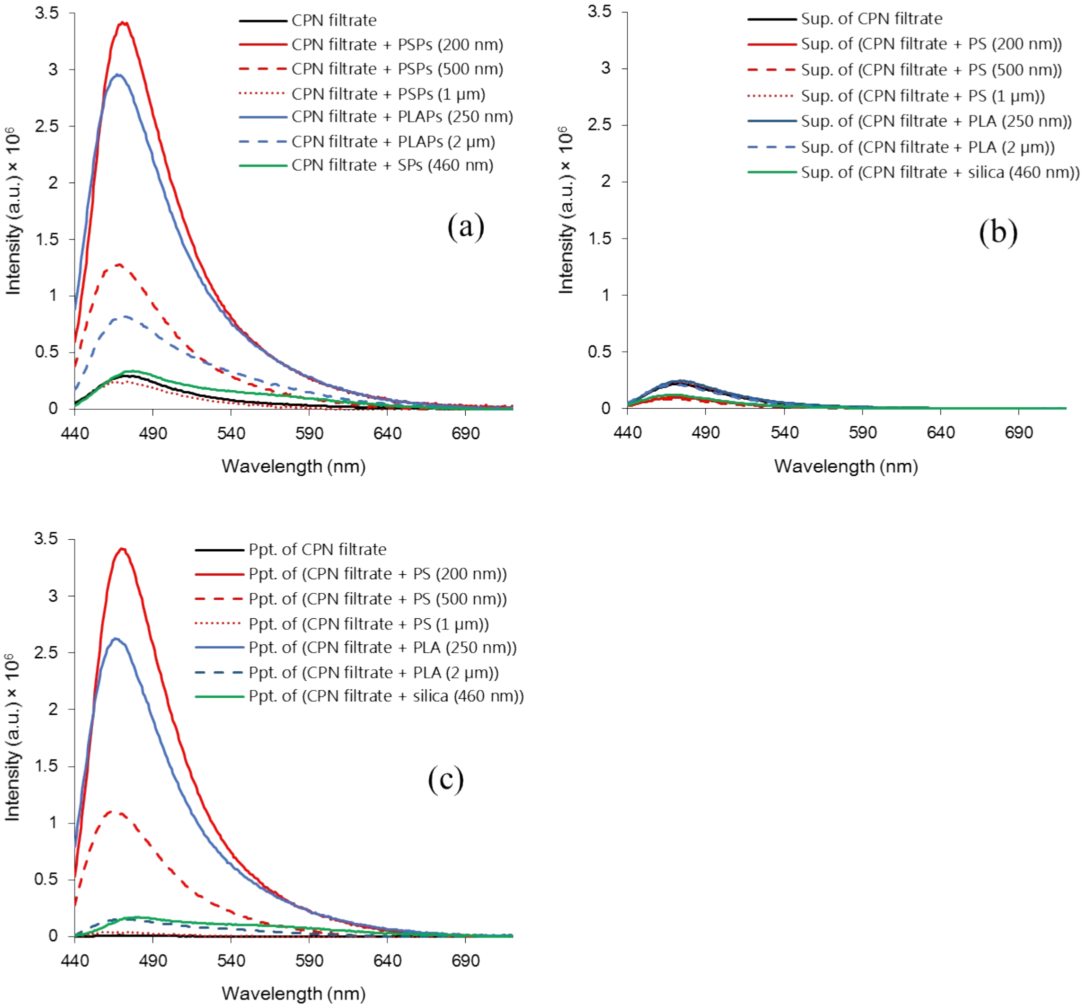


Figure S7. Distribution of CPN-BE in coexisting of various particles. CPN was filtrated by 0.20 *μ*m PTFE syringe filter to get BE-type species. (a) Before centrifugation, (b) supernatant (sup.) and (c) precipitate (ppt.) after centrifugation. Precipitation was diluted with the same volume of water as before centrifugation.

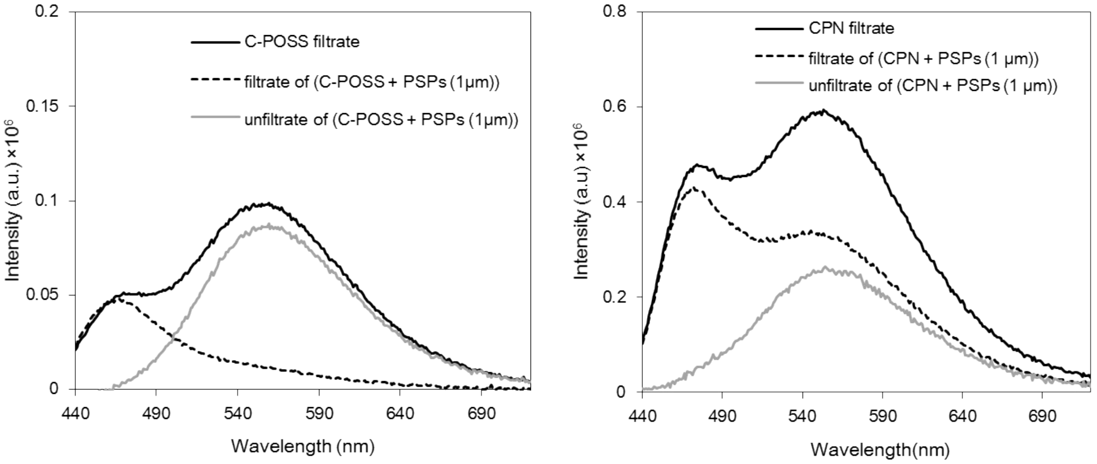


Figure S8. PL spectra of C-POSS-YE and CPN-YE in the presence of PSPs (1 μm). Filtration was executed with a 0.45 μm PTFE syringe filter to get rid of PSPs. The spectra of the unfiltrate are calculated value by subtracting filtrate of the mixture from those of C-POSS or CPN.

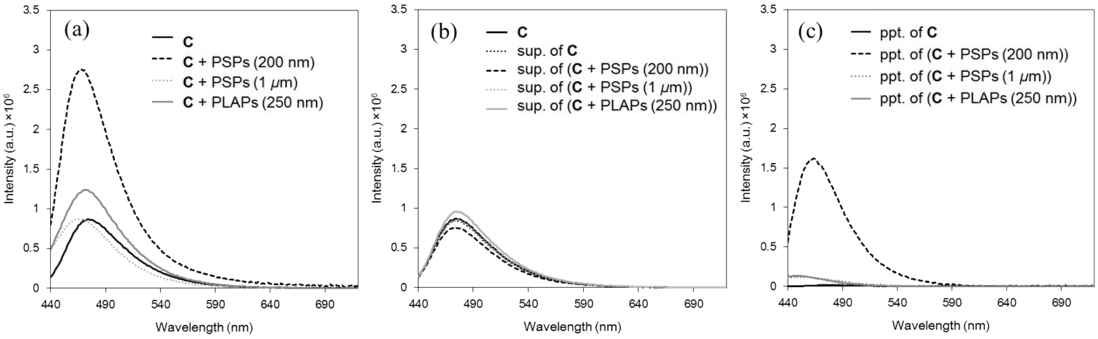


Figure S9. Interactions of **C** with a variety of particles in PL spectra and distribution of **C**. (a) Before centrifugation, (b) supernatant (sup.) and (c) precipitate (ppt.) after centrifugation. The samples represented as ppt. was diluted with the same volume of water as before centrifugation. Final concentrations of **C** were 2.5 μM.

Table S3. Shifts of peak wavelength in photoluminescence spectra of CPN by attaching to particles

		$\lambda_{\mathrm{em}}^{\mathrm{Max}}$ (nm)
CPN (2) filtrate	(CPN (2)-BE)[a]	475
	with PSPs (200 nm)[b]	470
	with PLAPs (250 nm)[b]	466
C		475
	with PSPs (200 nm)[b]	464

[a] Filtration by 0.20 μm PTFE syringe filter.

[b] Precipitaion by centrifugation.

Table S4. Fluorescence lifetime of CPN and **C** in the presence of PSPs (50 nm)

		τ (ns)
CPN-BE		3.7 (87%), 3.0 (13%)
	with PSPs (50 nm)	3.8 (81%), 2.5 (19%)
C		3.7
	with PSPs (50 nm)	3.3

Table S5. List of water contact angles at the surfaces of the materials tested in this study

material	Water contact angle
Polystyrene	81-91[6,7]
Poly (lactic acid)	76-80[8,9]
Poly (methyl methacryrate)	66-67[10,11]
Silica	0-42 (particle)[12], 28-32 (quartz)[13]

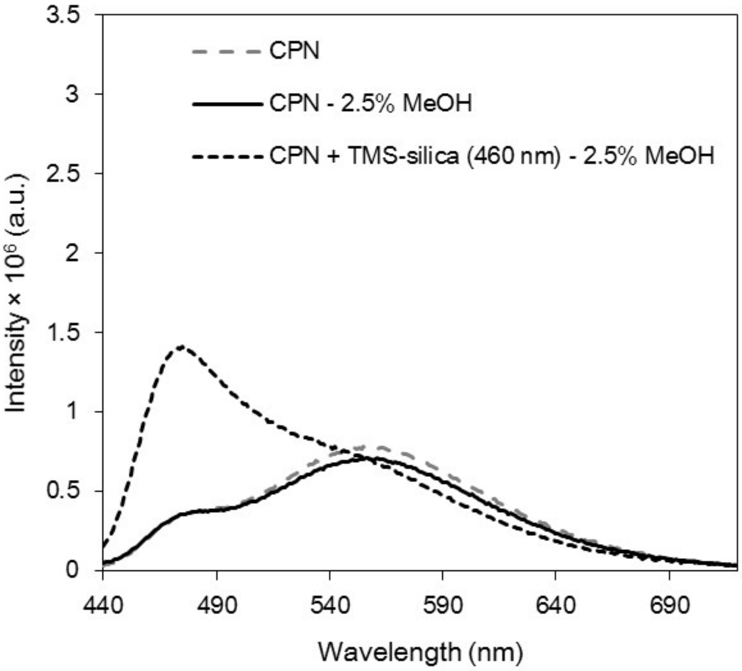


Figure S10. Interactions of CPN with TMS-SPs (460 nm) in PL spectra with the excitation light at 427 nm. Due to poor dispersibility of TMS-SPs in water, TMS-SPs were once dispersed in methanol, then diluted 20 times with water.

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