



Special Feature: Nanostructured Materials

Research Report

Visible-light Emission from Dye-doped Mesostructured Organosilica Hybrid Films

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■ABSTRACT■ Highly fluorescent organosilica mesostructured films were prepared by surfactant-directed self-assembly of organosilane precursors with oligo(phenylenevinylene) (OPV) or tetraphenylpyrene (TPPy) bridging moieties. Co-condensation of the bridged organosilane precursors with appropriate amounts of tetraethyl orthosilicate was required to form well-defined periodic mesostructures in the films. The OPV- and TPPy-based mesostructured films exhibited strong blue fluorescence with quantum yields of 0.25–0.66 and 0.70–0.79, respectively. Doping of the mesostructured films with fluorescent dyes resulted in efficient fluorescence emission over a wide range of the visible spectrum. Upon excitation of the framework chromophores of the dye-doped OPV–silica and TPPy–silica films, non-radiative Förster resonance energy transfer from the organosilica framework to guest dyes in the mesopores occurred, which enabled flexible tuning of the fluorescence emission intensities of the framework organics and the doped dyes. The emission colors were tuned from blue to green and yellow, including white. The transparent and highly fluorescent organosilica hybrids with mesostructures have significant potential for various luminescence applications including light-emitting diodes and fluorescence sensors.

■KEYWORDS■ Self-assembly, Energy Transfer, Fluorescence, Hybrid Materials, Mesostructures, Thin Films

1. Introduction

Periodic mesostructured and mesoporous organosilica materials prepared by surfactant-directed polycondensation of organic-bridged alkoxy silane precursors ($R[Si(OR')_3]_n$; $n \geq 2$, R: organic bridging groups, R': methyl, ethyl, etc.) have attracted much attention due to their potential applications as adsorbents, solid supports, catalysts, and optical materials.⁽¹⁻³⁾ Various organic bridges (R), such as π -conjugates, heteroaromatics, and metal complexes, have been incorporated into pore walls of the mesostructured materials by molecular design of the precursors.⁽¹⁻⁹⁾ In these organosilica hybrids with well-defined mesostructures, both organosilica frameworks and the inner parts of the mesochannels are available for functional design, which has broadened potential applications of periodic mesostructured organosilicas to solid photocatalysts, sensing systems, and electronic devices.⁽¹⁰⁻¹⁴⁾

Organosilica hybrids with periodic mesostructures are, in particular, advantageous for luminescence applications due to the following properties: (i) organic

bridging groups can be densely embedded within pore walls, realizing efficient absorption of excitation light; (ii) different chromophores can be incorporated into two spatially separated regions, i.e., into both the framework and mesopores; (iii) dye-doped mesostructured organosilicas have been found to exhibit light-harvesting antenna properties, i.e., efficient and non-radiative energy funneling from the organosilica framework to the guest dye in the mesopores occurs,⁽¹⁵⁻¹⁷⁾ which enables flexible tuning of the fluorescence emission intensities of the framework organics and doped dyes; and (iv) organosilica hybrids can be obtained as transparent films, which are favorable for optical materials, by acidic sol–gel polycondensation of precursors in the presence of evaporable organic solvents.

Here we report on efficient visible-light emission from dye-doped mesostructured organosilica films. **Figure 1** shows a scheme for the preparation of these fluorescent mesostructured materials. Mesostructured organosilica films are obtained by acidic sol–gel polycondensation of fluorescent organosilane precursors and tetraethyl orthosilicate (TEOS) in the

presence of a template surfactant P123, accompanied by dye-doping and evaporation of organic solvents (tetrahydrofuran (THF) and ethanol). The excitation light (near UV to visible light) is efficiently absorbed by the high density of framework chromophores. When an appropriate amount of dye molecules (e.g. 1–2 mol%) are confined in the mesopores, a part of the excitation energy is transferred from the organosilica framework to the dye dopant by Förster resonance energy transfer (FRET), which leads to fluorescence emission from the guest dye. Therefore, the emission colors can be altered by selection of the doped dyes and their concentrations. In order to construct highly fluorescent organosilica frameworks, mesostructured organosilica films were developed that contained oligo(phenylenevinylene) (OPV) and tetraphenylpyrene (TPPy) bridging groups (**Fig. 2**),^(18,19) which are typical blue-fluorescent chromophores. Co-condensation of the fluorescent precursors with TEOS resulted in highly fluorescent and mesostructured films. Incorporation of fluorescent dyes into the mesostructured films led to color-tunable fluorescence emission over a wide range of the visible spectrum.^(19,20)

2. Results and Discussion

2.1 Fluorescent Mesostructured Films Based on OPV

Three OPV-derived precursors with different lateral substituents, **OPV-H**, **OPV-C6**, and **OPV-EH**, were designed for the preparation of fluorescent films to examine the steric effects of the substituents (**Fig. 2**).

The organosilane precursors with OPV moieties were synthesized by Rh-catalyzed silylation of the corresponding aromatic iodides.⁽¹⁸⁾

Mesostructured organosilica films containing OPV bridging groups (**OPV-H-Fn**, **OPV-C6-Fn**, and **OPV-EH-Fn**) were prepared by acidic sol-gel polycondensation via an evaporation-induced self-assembly process. **Table 1** gives the compositions of the sol mixtures and the meso-scale periodicities determined by X-ray diffraction (XRD) measurements. While no mesostructured films were obtained from the sol mixtures containing 100% OPV precursors as silica sources, addition of TEOS to the sol mixtures resulted in the formation of mesostructures with *d*-spacings of 8.6–11.6 nm. **Figure 3** shows an XRD pattern and a transmission electron microscopy (TEM) image of the **OPV-C6**-bridged organosilica film (**OPV-C6-F4**). The intense diffraction peak at *d* = 11.2 nm indicates the formation of a periodic mesostructure. Disordered arrays of mesochannels with a periodicity of approximately 10 nm are evident in the TEM image of the organosilica film. As shown in **Table 1**, addition of twofold or more weight ratio of TEOS was required to form periodic mesostructures in the **OPV-C6-Fn** and **OPV-EH-Fn** films, while mesostructured **OPV-H-Fn** films could be obtained from a 1:1 mixture of **OPV-H** and TEOS. Introduction of lateral alkoxy substituents into the OPV moieties increases the hydrophobicity of the precursors, which requires the addition of excess TEOS to balance the hydrophilic and hydrophobic properties between the silica sources and the template surfactant.

The UV-vis absorption and fluorescence properties

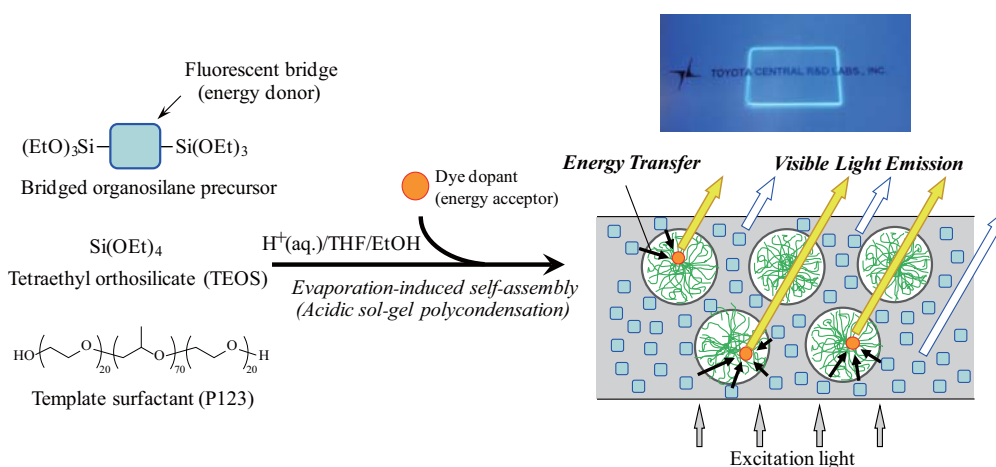


Fig. 1 Preparation of periodic mesostructured organosilica films with fluorescent organic bridges and dye dopants.

of the OPV–silica films are shown in **Fig. 4** and Table 1. **OPV-H-F_n** has a maximum absorption wavelength (λ_{abs}) at 348–349 nm, while λ_{abs} for a dilute solution of **OPV-H** in THF is 363 nm. The blue shift of λ_{abs} for the films indicates the side-by-side aggregation of OPV moieties in the **OPV-H**-based organosilica films. The fluorescence emission wavelength (λ_{em}) of the **OPV-H**-bridged films was observed at 438–444 nm. The fluorescence quantum yields (QYs) were 0.25–0.34, which are much lower than that for a dilute

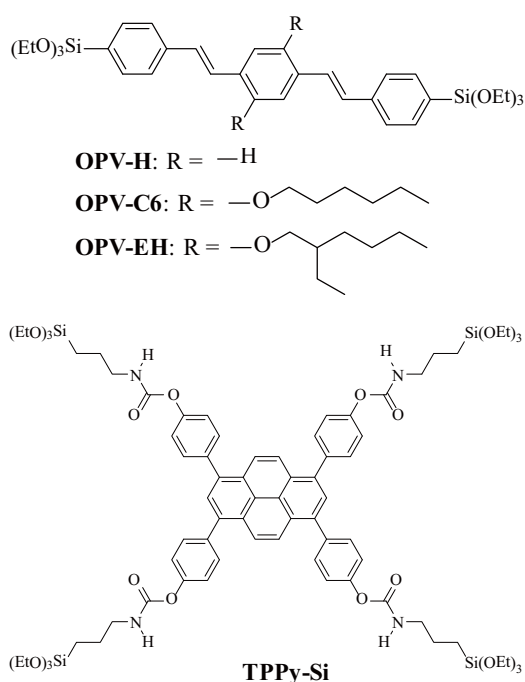


Fig. 2 Chemical structures of organosilane precursors with blue-fluorescent chromophores.

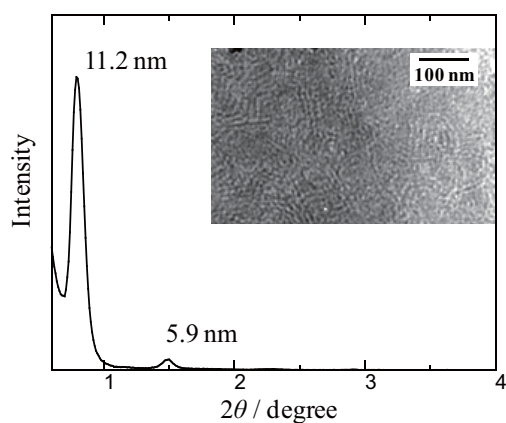


Fig. 3 XRD pattern and TEM image of **OPV-C6-F4**.

solution of **OPV-H** in 2-propanol (0.87). The side-by-side aggregation of **OPV-H** bridging groups results in strong fluorescence quenching, probably due to the formation of non-emissive dimer or excimer sites. On the other hand, the **OPV-C6-F_n** and **OPV-EH-F_n** films exhibited strong blue fluorescence (λ_{em} = 485–486 nm) with high QYs of 0.48–0.61 and 0.63–

Table 1 Structural and optical properties of the OPV–silica hybrid films.

Sample	P123/OPV/TEOS (weight ratio)	Meso-scale periodicity ^a (nm)	λ_{abs} (nm)	λ_{em} ^b (nm)
OPV-H (in THF)	—	—	363	422 (0.87) ^c
OPV-H-F1	16/5/0	—	349	443 (0.28)
OPV-H-F2	16/5/5	10.3	349	439 (0.25)
OPV-H-F3	12/5/0	—	349	444 (0.34)
OPV-H-F4	12/5/5	10.9	348	442 (0.30)
OPV-H-F5	6/5/10	9.7	348	438 (0.27)
OPV-C6 (in THF)	—	—	397	451 (0.77) ^c
OPV-C6-F1	12/5/0	—	396	486 (0.48)
OPV-C6-F2	12/5/5	—	396	485 (0.56)
OPV-C6-F3	12/5/10	9.0, 8.6	396	485 (0.58)
OPV-C6-F4	12/5/20	11.2	396	485 (0.61)
OPV-EH (in THF)	—	—	400	454 (0.81) ^c
OPV-EH-F1	12/5/0	—	399	486 (0.63)
OPV-EH-F2	12/5/5	—	398	486 (0.66)
OPV-EH-F3	12/5/10	10.6	399	485 (0.66)
OPV-EH-F4	12/5/20	11.6	399	485 (0.66)

^a Main *d*-spacing values obtained by XRD measurements.

^b Fluorescence quantum yields are in parenthesis.

^c Quantum yields were measured in 2-propanol solution.

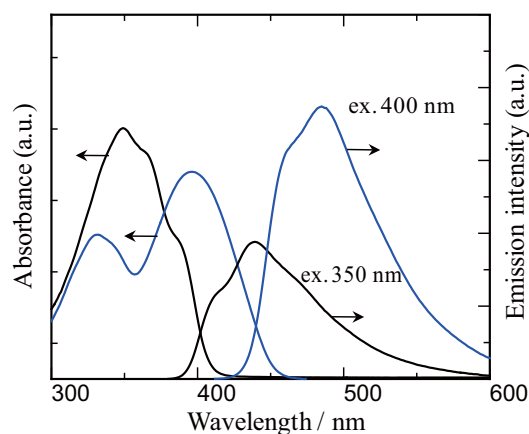


Fig. 4 UV-vis absorption and fluorescence spectra for **OPV-H-F2** (black) and **OPV-C6-F4** (blue).

0.66, respectively. In comparison with **OPV-H-Fn**, the introduction of alkoxy substituents into the OPV moiety led to a red shift of absorption and fluorescence spectra (Fig. 4). Moreover, no blue shift of λ_{abs} between the precursor solutions and films was observed for the **OPV-C6** and **OPV-EH** films, which suggests that side-by-side aggregation of OPV moieties is suppressed by the bulky alkoxy substituents. The QYs also increase with increasing amounts of TEOS (Table 1). These results indicate that the introduction of bulky alkoxy lateral substituents into the OPV core and dilution of the chromophore with TEOS effectively suppress the aggregation of OPVs, which diminishes quenching processes in the organosilica frameworks.

2.2 Fluorescent Mesostructured Films Based on TPPy

A TPPy-derived precursor **TPPy-Si** (Fig. 2) with four silyl groups was synthesized by the reaction of 1,3,6,8-tetrakis(4-hydroxyphenyl)pyrene with 3-triethoxysilylpropyl isocyanate.⁽¹⁹⁾

Mesostructured organosilica films with a TPPy bridging group were prepared by an evaporation-induced self-assembly process similar to that used for the OPV-based films. **Table 2** gives the compositions of the sol mixtures and the meso-scale periodicities determined by XRD measurements. All the TPPy-

silica films (**TPPy-Si-Fn**) possess periodic mesostructures with $d = 8.7\text{--}10.5$ nm. **Figure 5** shows XRD patterns for **TPPy-Si-F4** and **TPPy-Si-F8** with a TEM image of **TPPy-Si-F8**. The XRD peaks become conspicuous with increased amounts of TEOS and the d -spacing of the periodic mesostructure tends to increase with increased amounts of TEOS and P123 (Table 2). It is worth noting that large amounts of the hydrophobic and bulky TPPy units were successfully embedded within the mesostructured framework. The four-armed molecular design of **TPPy-Si** seems to aid the interaction between the hydrolyzed precursor molecules and hydrophilic surface of the micellar aggregates of P123.

The TPPy-bridged mesostructured films had λ_{abs} of 386–387 nm and exhibited strong blue fluorescence (**Fig. 6**). The fluorescence properties of **TPPy-Si-Fn** are given in Table 2. λ_{em} for the TPPy-bridged films appeared at 443–458 nm. The QYs were 0.70–0.79, while a dilute solution of **TPPy-Si** in 2-propanol had a QY of 0.92. It is remarkable that high QYs are realized in the mesostructured organosilica films with a high density of TPPy units. With increased amounts of TEOS and P123, λ_{em} and the QYs tend to be shorter and higher, respectively, due to dilution of the TPPy units.

2.3 Dye-doped Mesostructured Films

Doping of the blue-light-emitting OPV-silica and TPPy-silica films with fluorescent dyes enabled

Table 2 Structural and optical properties of the TPPy-silica hybrid films.

Sample	P123/TPPy-Si/TEOS (weight ratio)	Meso-scale periodicity ^a (nm)	λ_{abs} (nm)	λ_{em} ^b (nm)
TPPy-Si (in 2-propanol)	—	—	384	423 (0.92)
TPPy-Si-F1	2/3/0	8.8 (broad)	387	458 (0.70)
TPPy-Si-F2	3/3/0	9.1 (broad)	387	458 (0.71)
TPPy-Si-F3	4/3/0	9.7 (broad)	387	458 (0.71)
TPPy-Si-F4	4/3/3	8.7	386	457 (0.75)
TPPy-Si-F5	6/3/3	10.0	387	457 (0.74)
TPPy-Si-F6	8/3/3	10.5	387	457 (0.74)
TPPy-Si-F7	6/3/6	9.0	387	445 (0.76)
TPPy-Si-F8	10/3/12	10.0	386	443 (0.79)

^a Main d -spacing values obtained by XRD measurements.

^b Fluorescence quantum yields are in parenthesis.

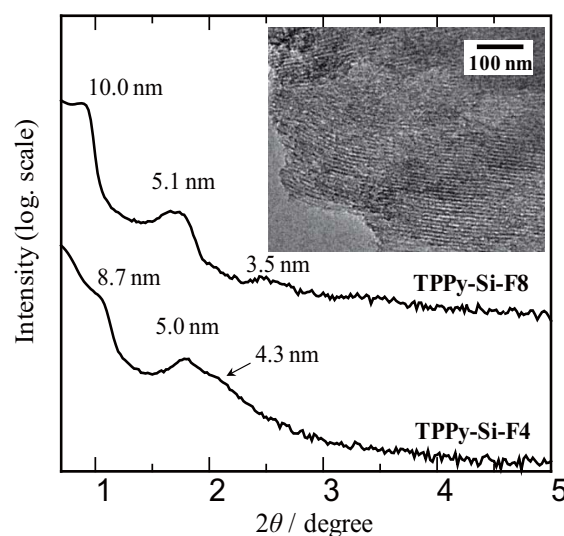


Fig. 5 XRD patterns for **TPPy-Si-F4** and **TPPy-Si-F8** and TEM image of **TPPy-Si-F8** after extraction of P123.

flexible tuning of the fluorescence emission colors over a wide range of the visible spectrum.^(19,20) Here we selected **OPV-C6-F4** and **TPPy-Si-F4** as host mesostructured films due to their significant optical properties and the formation of well-defined mesostructures. Three fluorescent dyes, yellow-light-emitting **Rub** (QY = 0.75 in hexane) and **Rhd6G** (QY = 0.95 in 2-propanol), and green-light-emitting **Bodipy** (QY = 0.89 in 2-propanol), were incorporated into the mesopores of the organosilica films at concentrations of 0–10 mol% to the framework chromophores (**Fig. 7**).

Figure 8 shows fluorescence spectra of **OPV-C6-F4** doped with **Rub** upon excitation at $\lambda = 400$ nm. For

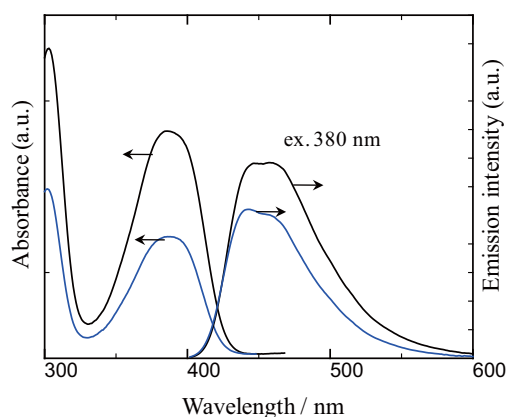


Fig. 6 UV-vis absorption and fluorescence spectra for **TPPy-Si-F4** (black) and **TPPy-Si-F8** (blue).

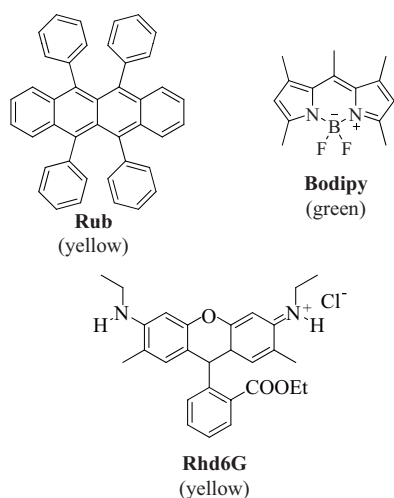


Fig. 7 Chemical structures of fluorescent dye dopants employed.

the non-doped film, a blue fluorescence emission of **OPV-C6-F4** at $\lambda = 485$ nm was observed. An emission band attributed to the fluorescence of **Rub** appeared around $\lambda = 560$ nm when the concentration of **Rub** was increased, with subsequent quenching of the blue fluorescence of **OPV-C6-F4**. The fluorescence emission from the dye dopant, which has no absorption band at $\lambda = 400$ nm, is caused by FRET from the framework OPV chromophores within the pore walls. In the **OPV-C6-F4/Rub** films, a doping concentration of more than 5 mol% **Rub** to the OPV units is required to achieve complete energy transfer. Mesostructured biphenyl–silica hybrids doped with a coumarin dye are reported to exhibit 100% energy transfer at 0.80 mol% dye doping for a powder sample with a pore diameter of 3.5 nm, or 1.8 mol% dye doping for a film with a periodicity of $d = 9.4$ nm.⁽¹⁵⁾ The lower efficiency of energy transfer in the **OPV-C6-F4/Rub** film is presumably due to the larger pore size, dilution of the OPV unit by TEOS addition, and the low affinity of hydrophobic **Rub** for the hydrophilic pore walls containing OPV energy donors.

The colors of the emissions from dye-doped OPV–silica and **TPPy**–silica films were plotted in the Commission Internationale de l’Eclairage (CIE) 1931 chromaticity diagram (**Fig. 9**). The emission colors of the **OPV-C6-F4/Rub** films changed from blue with CIE coordinates of (0.18, 0.35) to yellow (0.46, 0.49). The film containing 0.6 mol% of **Rub** exhibited pseudo white-light emission with CIE coordinates of (0.31, 0.41) and a QY of 0.67. The emission colors of the **TPPy-Si-F4/Bodipy** films changed from blue with CIE coordinates of (0.15, 0.13) to green (0.22, 0.59).

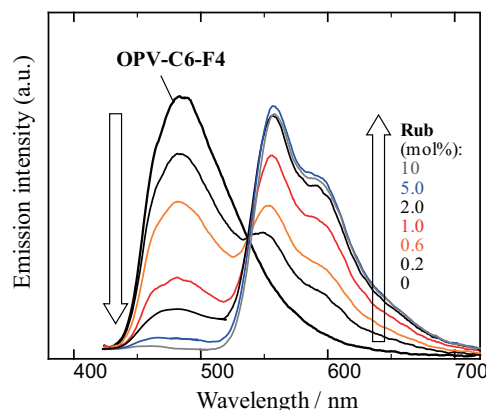


Fig. 8 Fluorescence spectra for **OPV-C6-F4** doped with **Rub** (0–10 mol% ratio to the OPV unit) upon excitation at 400 nm.

The **TPPy-Si-F4/Rhd6G** films exhibited fluorescence emissions between (0.15, 0.13) and (0.41, 0.38). The **TPPy-Si-F4/Rhd6G** film containing 1.0 mol% of **Rhd6G** exhibited a white light emission with CIE coordinates of (0.32, 0.34) and a QY of 0.43. **Figure 10** shows some examples of the fluorescent films with different emission colors. These color-tunable and transparent fluorescent films are applicable to various optical devices including light-emitting diodes.⁽¹⁹⁾

3. Conclusions

Fluorescent mesostructured films with QYs of over 0.6 were obtained by surfactant-directed polycondensation of chromophore-bridged alkoxy silane precursors. Doping of the mesostructured films with fluorescent dyes enabled color-tunable photoluminescence over a wide range of the visible spectrum, including a white light emission. The transparent and highly fluorescent organosilica hybrid films with mesostructures have significant potential for various luminescence applications including light-emitting diodes and fluorescence sensors.

4. Experimental

4.1 Characterization

X-ray diffraction (XRD) measurements were performed using Cu-K α radiation (Rigaku RINT-TTR,

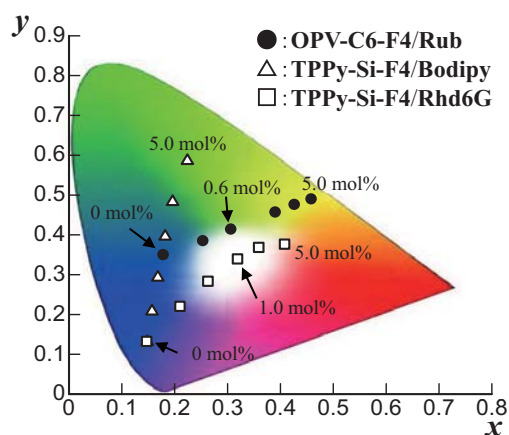


Fig. 9 Tuning of fluorescence emission colors (CIE 1931 chromaticity diagram) by doping of blue-light-emitting mesostructured organosilica films **OPV-C6-F4** and **TPPy-Si-F4** with fluorescent dyes.

50 kV, 300 mA). Transmission electron microscopy (TEM) of the organosilica hybrid films was performed using a Jeol JEM 2100F with an accelerating voltage of 200 kV. UV-vis absorption spectra were measured using a Jasco V-670 spectrometer. Fluorescence spectra were obtained with a Jasco FP-6500 spectrometer. Fluorescence quantum yields (within an error margin of $\pm 3\%$) were determined using a photoluminescence quantum yield measurement system equipped with a calibrated integrating sphere (Hamamatsu Photonics, C9920-02). The CIE 1931 chromaticity coordinates were calculated using U6039 software (Hamamatsu Photonics).

4.2 Preparation of Dye-doped Mesostructured Films

Organosilane precursors, TEOS, and P123 with the compositions given in Tables 1 and 2 were dissolved in a 1:1 mixture of THF and ethanol (w/w). After the addition of hydrochloric acid, the sol mixture was stirred at room temperature for 24 h. For the sol solution, appropriate amounts of dyes were added. Dye-doped mesostructured films were prepared by spin-coating of the sol solutions onto quartz substrates (4000 rpm, 30 s) and drying under reduced pressure at room temperature.

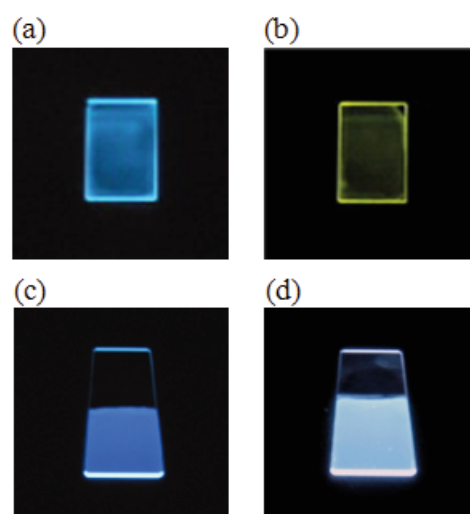


Fig. 10 Photographs of (a) **OPV-C6-F4**, (b) **OPV-C6-F4/Rub** (5.0 mol%), (c) **TPPy-Si-F4**, and (d) **TPPy-Si-F4/Rhd6G** (1.0 mol%) under UV irradiation at 365 nm.

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