

Microwave-assisted One-pot Synthesis of Luminescent Organic–Inorganic Hybrids via Simultaneous Process of Sol–Gel and Suzuki–Miyaura Coupling Reactions

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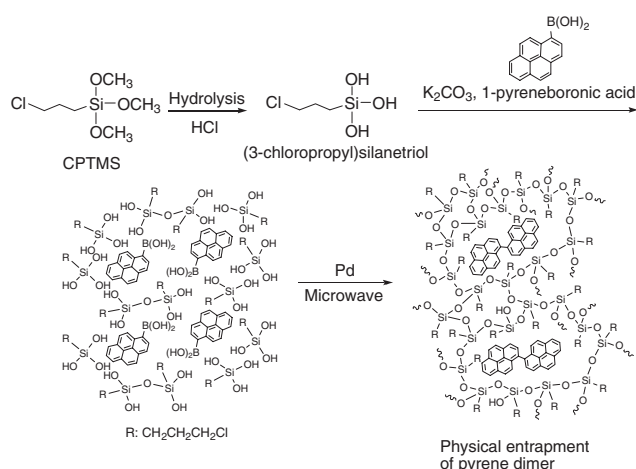
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In order to disperse luminescent compounds with low solubility or high crystallinity into silica matrices, we demonstrate here facile one-pot synthesis of organic–inorganic luminescent hybrids via simultaneous process of sol–gel reaction of 3-(chloropropyl)trimethoxysilane (CPTMS) and the Suzuki–Miyaura homocoupling of 1-pyreneboronic acid under microwave irradiation. Highly luminescent hybrid without aggregates of the pyrene dimer, which was efficiently generated in situ, was obtained by microwave irradiation due to rapid formation of silica matrices, whereas huge aggregates were observed in the hybrid prepared under conventional heating.

The Suzuki–Miyaura coupling has emerged as an extremely powerful carbon–carbon bond-forming protocol available to practitioners of π -conjugated architectures. Numerous interests have been devoted to synthesis of conjugated biaryl compounds that are applicable as organic light-emitting diodes (OLEDs),¹ polymer LEDs,² and nonlinear optical materials.³ Simple scaffolds of the conjugated compounds, i.e., nonsubstituted biaryl compounds, usually lead to low solubility and high crystallinity originating from the intermolecular π – π stacking interaction. Therefore, the introduction of long alkyl chains into the conjugated compounds is required to increase the solubility of them. Recently, the utility of microwave irradiation for the Suzuki coupling has been widely reported. In particular, Leadbeater et al. have demonstrated that the microwave-assisted Suzuki–Miyaura coupling can be performed using low levels of ligandless palladium salts as the catalyst and water/ethanol mixtures as the solvent, and the coupling reaction can proceed efficiently in either sealed or open vessels.^{4–7} Furthermore, microwave irradiation has been applied to the preparation of some organic–inorganic polymer hybrids, in which sol–gel reaction of alkoxy silanes is highly accelerated.^{8–10} In this paper, we demonstrate a facile one-pot synthesis of luminescent hybrids via the simultaneous Suzuki–Miyaura coupling reaction and sol–gel process under microwave irradiation. Two conceivable advantages of one-pot synthesis of the hybrids under microwave irradiation are as follows; (1) the objective emissive compounds can be facilely prepared without individually multistage reaction and (2) it is possible to share both dispersion and incorporation of the molecules with low solubility and high crystallinity, which were generated by the Suzuki–Miyaura coupling in situ, into sol–gel matrices, providing the enhancement of photoproperties such as fluorescence quantum yield. Herein, 3-(chloropropyl)trimethoxysilane (CPTMS) and 1-pyreneboronic acid were used as an alkoxy silane and a substrate of Suzuki–Miyaura homocoupling, respectively.

Generally, the Suzuki–Miyaura coupling is carried out using bases such as sodium carbonate or potassium carbonate. Therefore, the sol–gel reaction must be conducted under basic conditions to perform the Suzuki–Miyaura homocoupling of 1-pyreneboronic acid together. Prior to preparation of luminescent hybrid, we examined hybridization of CPTMS without 1-pyreneboronic acid in the absence of palladium catalyst under microwave irradiation and basic conditions. However, the obtained hybrids formed viscous gel due to poor condensation of CPTMS. To improve the condensation of CPTMS, CPTMS was hybridized under acidic conditions to provide the complete formation of (3-chloropropyl)silanetriol, and then added aqueous potassium carbonate solution. Further, the mixture was exposed to microwave. Accordingly, the obtained hybrid showed high transparency, implying the possibility for one-pot processing of the Suzuki–Miyaura homocoupling and sol–gel reaction. Although the role of the chloropropyl groups has not been cleared yet, they may affect the film formability of silica matrices. Next, optimization of the Suzuki–Miyaura homocoupling was carried out using several palladium catalysts such as palladium acetate (Pd(OAc)₂), tetrakis(triphenylphosphine)palladium(0) [Pd(PPh₃)₄], and acid-stabilized palladium stock solution. Consequently, it was found that a palladium hydrochloric acid solution was the most efficient catalyst for the homocoupling. As shown in Scheme 1,¹¹ transparent and homogeneous luminescent hybrids were obtained under microwave irradiation (200 W 10 min, 500 W 10 min, and 800 W 10 min, sequentially). The yield of the in situ Suzuki–Miyaura homocoupling of 1-pyreneboronic acid was estimated by



Scheme 1. Reaction scheme of the Suzuki–Miyaura homocoupling and sol–gel reaction.

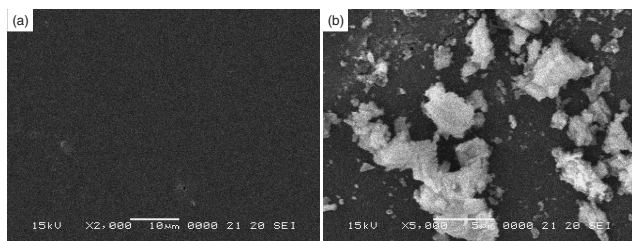


Figure 1. SEM images of the surface of the hybrids prepared under (a) microwave irradiation and (b) conventional heating.

extracting the product with chloroform just before the sol–gel reaction proceeded completely. When 5 mol % of palladium was added, the isolated yield of the pyrene dimer was sufficiently high (90%), and the structure of the dimer was confirmed by ^1H NMR and mass spectrometry.^{11,12} It was found that the Suzuki–Miyaura homocoupling of 1-pyreneboronic acid proceeded efficiently in the sol–gel solution.

The obtained hybrid prepared under microwave irradiation possesses high transparency, and visually emitted blue light under UV lamp (365 nm) irradiation. In the SEM image (Figure 1a), no aggregate of pyrene dimer was observed. On the other hand, some huge aggregates of pyrene dimer existed on the surface of the hybrid prepared under conventional heating, as shown in Figure 1b. In the case that microwave irradiation was employed, sol–gel reaction of CPTMS proceeded rapidly before the aggregation or crystallization of pyrene dimer. In contrast, under conventional heating, sol–gel reaction of CPTMS was slower in comparison with generation of the aggregation of pyrene dimer. In this experiment, the first microwave condition was set at low output power (200 W) to investigate the yield of the homocoupling. Higher output power of the microwave condition allows for more ease and rapid preparation of transparently luminescent hybrid without the aggregation of pyrene dimer, e.g., 500 W for 20 min.

The optical properties of the obtained hybrids and pyrene dimer in solid state were investigated by UV–vis absorbance and photoluminescence (PL) spectroscopies. A broad absorption peak of the hybrid prepared under microwave irradiation was observed at around 320–340 nm, and almost the same absorption peak was observed in the hybrid prepared under conventional heating. Figure 2 shows the PL spectra of the hybrids prepared under both methods and pyrene dimer in solid state. The hybrid prepared under microwave irradiation showed emission maxima at around 418 nm (excited at 338 nm) which corresponds to the emission peak from pyrene dimer, whereas excimer emission peak of pyrene dimer in solid state was observed at 467 nm. This finding indicates that the pyrene dimer was successfully generated in situ without aggregation. In contrast, lower emission intensity of pyrene dimer was observed in the hybrid prepared under conventional heating than microwave irradiation. The fluorescence quantum yields, measured by integrating sphere, of the hybrids prepared under microwave irradiation and conventional heating were 29%, and 16%, respectively. Microwave acceleration should be responsible for the higher luminescent properties of the hybrid; i.e., aggregation derived from π – π stacking between pyrene dimers, which lead to serious self-quenching, was suppressed by rapid formation of silica matrices.

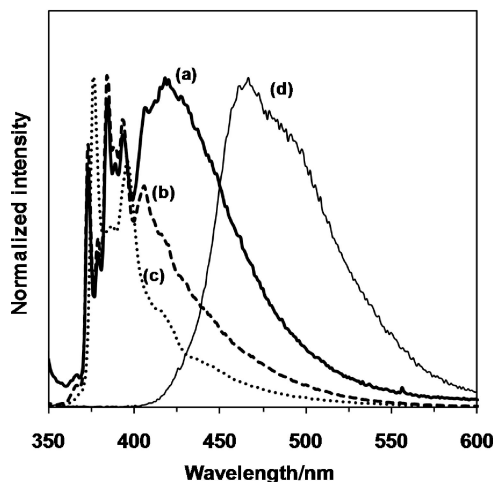


Figure 2. Photoluminescent spectra of hybrids prepared under (a) microwave irradiation, Pd 5 mol %, (b) conventional heating, Pd 5 mol %, (c) 1-pyreneboronic acid in chloroform (1.0×10^{-5} mol L $^{-1}$) and (d) pyrene dimer in solid state. Excitation wavelength: 338 nm.

In conclusion, we successfully prepared transparent and highly luminescent organic–inorganic hybrids by conducting sol–gel reaction of CPTMS and the Suzuki–Miyaura reaction of 1-pyreneboronic acid simultaneously under microwave irradiation. Microwave-accelerated sol–gel reaction led to the inhibition of aggregation of the pyrene dimer generated in situ, so that higher luminescent properties of the hybrid were achieved as compared to conventional heating. To the best of our knowledge, this is the first example of one-pot process involving sol–gel and coupling reactions. We believe that this method can incorporate various kinds of conjugated compounds into silica matrices.

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