

【助成 39-14】

有機合成に頼らない有機 EL 材料開発：
アントラセン発光体分子のナノ空間閉じ込めによる発光色変調

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〔研究の概要〕

The development of light-emitting materials that exhibit a variety of luminescent colors is being vigorously studied for a broad range of applications such as solar energy utilization. This project demonstrated that photoluminescence of the unsubstituted anthracene confined in zeolites was drastically affected by the zeolite topology, Si/Al ratio of the host zeolite, and the acidity of the solvent used for the anthracene introduction, resulting in ultrapure blue and white emission from 2DA confined in MOR and FAU zeolites, respectively.

〔研究経過および成果〕

The development of pure-blue and single-white light emitters is considered very significant for the development of full-color light-emitting devices. Various polycyclic aromatic hydrocarbons (PAHs), mainly anthracene and pyrene rings, have been reported as pure-blue emitters. However, because the methods used to synthesize these PAHs are very complex, alternative green methods are needed from a green chemistry perspective. Indeed, white light-emitting devices can be obtained by mixing the

respective light-emitting molecules that emit the three primary colors of light, but it is further difficult to create ideal conditions due to phase separation and cohesive quenching.

Strong confinement of luminescent molecules or metal clusters into angstrom-sized nanospace is an alternative strategy for controlling luminescence behavior without complex organic synthesis. The confinement of small molecular PAHs in micropores such as zeolites can be proposed as a promising method for highly obtaining color-rendering

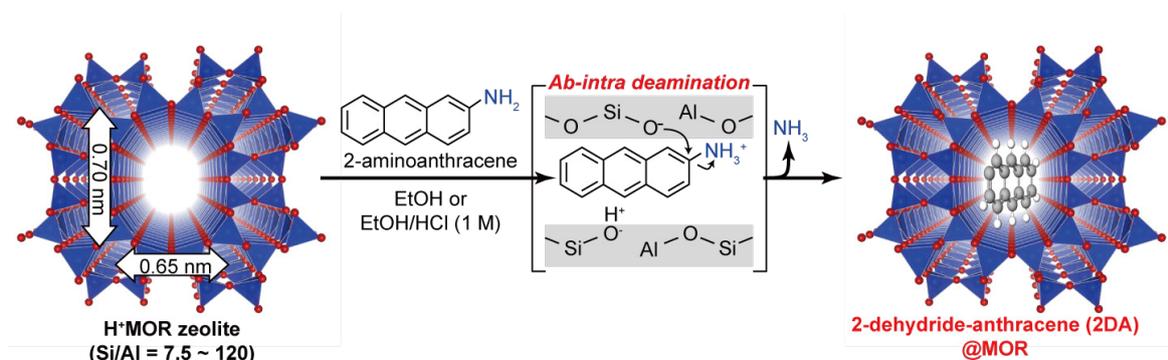


Fig. 1. Scheme of 2-dehydride-anthracene incorporation in MOR zeolite (2DA@MOR) synthesis via deamination of 2AA already introduced in the microcavity.

luminescent materials without complex organic synthesis.

In this paper, we have integrated unsubstituted anthracene molecules in the nanocavity of Al-rich zeolites via *ab-intra* zeolite catalyzed deamination of anthrylammonium cation already introduced in the zeolite cavity, which is an application of our previously reported introduction technique of unsubstituted anthracene into layered clay minerals. Figure 1 shows the schematic image of the liquid-phase introduction of unsubstituted anthracene into the microcavity of proton-type mordenite (H⁺MOR) zeolite using 2-aminoanthracene (2AA) as a precursor. The introduced 2AA was protonated by the protons in the zeolite cavity to form a 2-anthrylammonium cation. Subsequently, acidic sites of zeolite induce catalytic deamination for cleaving the C–N bond of intercalated 2-anthrylammonium to generate 2-dehydride-anthracene (2DA) in the zeolite cavity. The addition of mineral acid such as hydrochloric acid in the solution of 2AA introduction induces the formation of extra-framework aluminum (EFAL) species in the cavity to some extent simultaneously occurring with the confinement of the 2DA. Photoluminescence of the 2DA was drastically affected by the zeolite topology, Si/Al ratio of the host zeolite, and the acidity of the solvent used for 2AA introduction, resulting in ultrapure blue and white emission from 2DA confined in MOR (Fig. 2) and FAU zeolites (Fig. 3), respectively.

[発表論文]

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2. F. Kishimoto, K. Hisano, K. Iyoki, T. Wakihara, T. Okubo, Stable ultrapure blue and white emission from unsubstituted anthracene confined in zeolites, *under evaluation*.

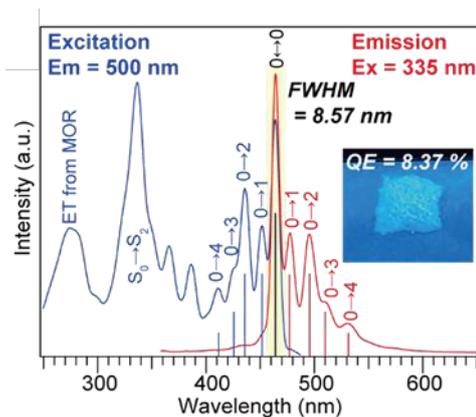


Fig. 2. Emission and excitation spectra of 2DA@MOR (Si/Al = 7.9) synthesized in EtOH/HCl mixed solvent. Inset shows the photograph of the particulate sample under 365 nm light irradiation.

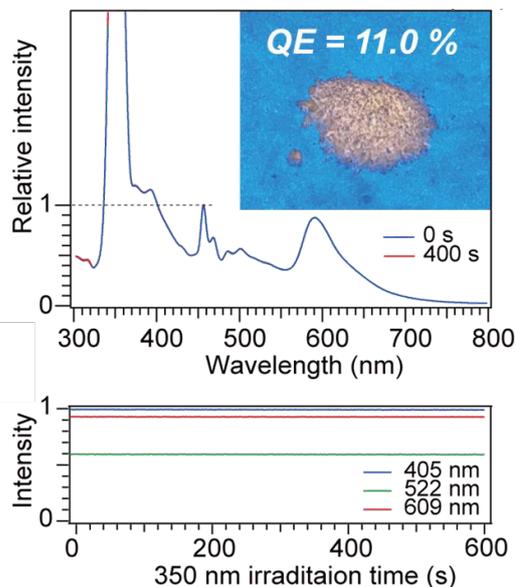


Fig. 3. Emission spectrum and a lifetime of 2DA@FAU (Si/Al = 250) synthesized in EtOH/HCl mixed solvent. Inset shows the photograph of the particulate sample under 365 nm light irradiation.