

## Encapsulation of Organic Dyes in Layered Minerals by Host-Guest Reactions

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In order to develop intercalation reactions as encapsulation methods of organic dyes, dyes containing the azobenzene groups were incorporated into inorganic layered materials. As host materials, montmorillonite and magadiite were used, and different synthetic strategies were attempted. Homoionic montmorillonite-*p*-aminoazobenzene intercalation compounds were prepared by solid-state reactions. When interlayer cations were metallic ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Ni}^{2+}$ ), IR spectroscopy revealed that the amino groups interacted with interlayer cations, indicating the intercalation of *p*-aminoazobenzene. The adsorption maxima of *p*-aminoazobenzene shifted considerably from that of *p*-aminoazobenzene in solvents, and the color of the products depended on the interlayer cations. When n-dodecylammonium (DA) -montmorillonite was used as a host, the basal spacing increased by the reaction with *p*-aminoazobenzene, indicating the intercalation of *p*-aminoazobenzene. The color and adsorption maximum were consistent with those of *p*-aminoazobenzene. The irradiation of UV light led to reversible cis-trans photoisomerization in the interlayer space of montmorillonite. For magadiite, the grafting reaction was attempted to immobilize the azobenzene group covalently on the interlayer surface. Sodium ions in the interlayer space of magadiite were exchanged with dodecyltrimethylammonium (DTMA) ions to form DTMA-magadiite. Then aminopropyltriethoxysilane was reacted with DTMA-magadiite. IR and solid-state NMR spectroscopy revealed that the aminopropylsilyl (APS) groups were present in the interlayer space of magadiite and DTMA ions were released, suggesting successful silylation. When 4-phenylazobenzoyl chloride was reacted with APS-magadiite, the basal spacing slightly decreased, and the absorption due to the azobenzene groups were observed in the UV-Vis spectrum of the product, implying the possible immobilization of azobenzene groups by amido-formation in the interlayer space of magadiite.