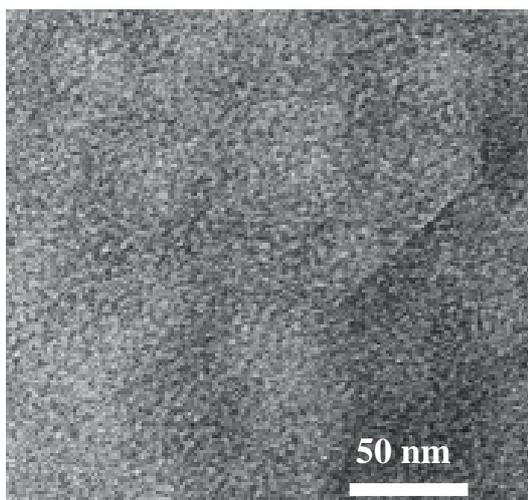
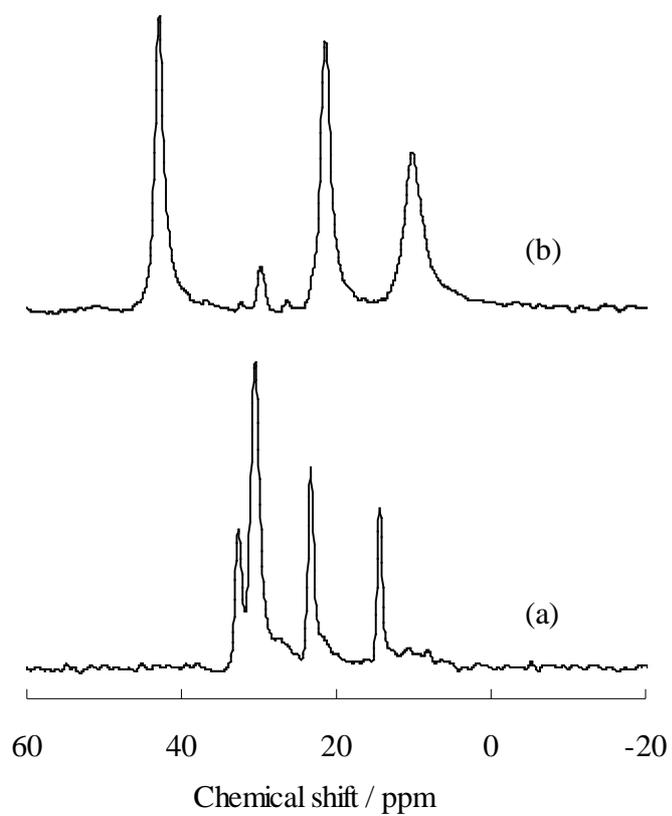


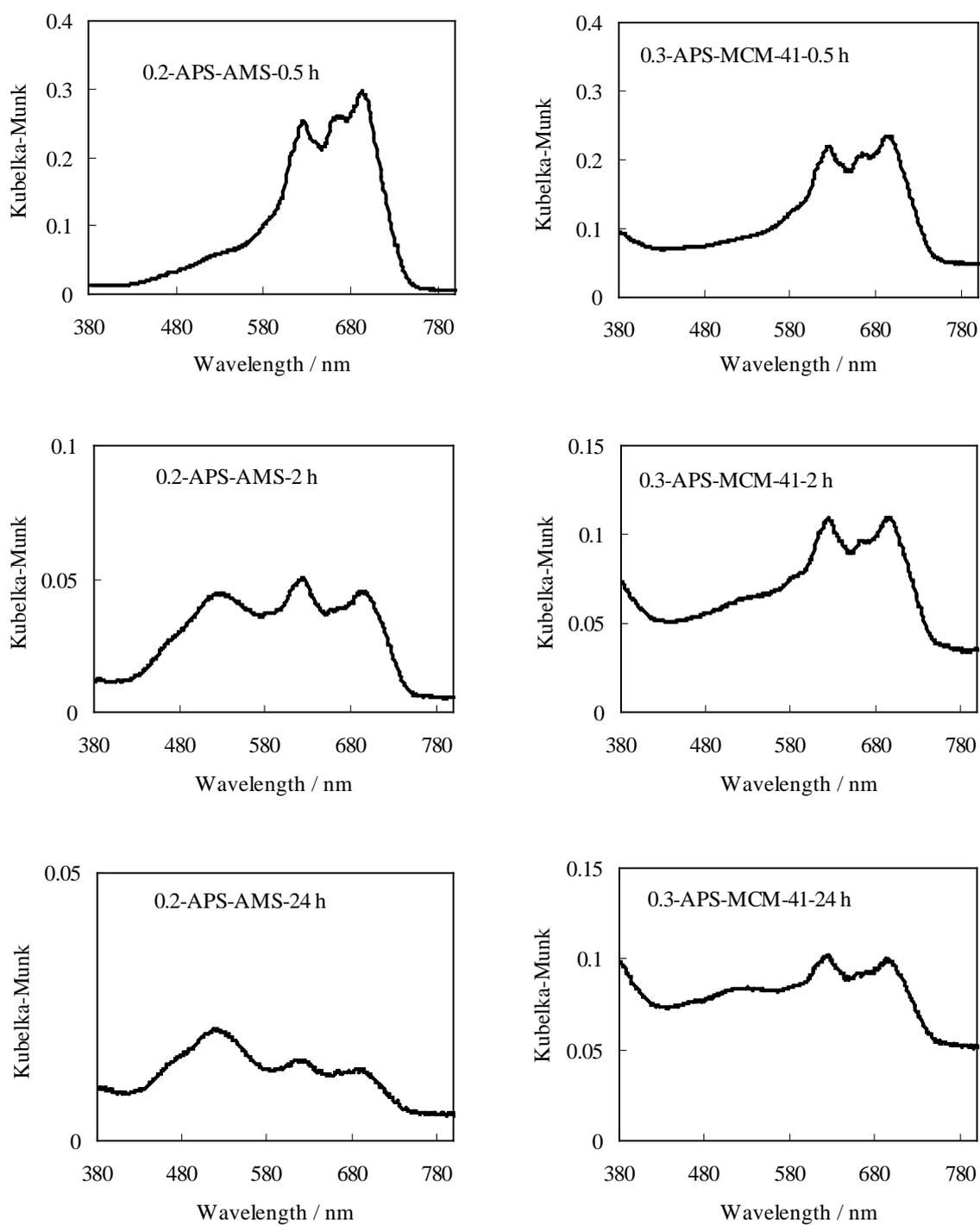
**Figure S1** XRD patterns of surfactant-extracted x-APS-MCM-41, where x is the proportion of APS in the silica sources<sup>20</sup>.



**Figure S2** TEM image of the surfactant-extracted 0.4-APS-AMS.



**Figure S3**  $^{13}\text{C}$  CP-MAS NMR spectra of (a) as-synthesized and (b) surfactant-extracted 0.4-APS-AMS.



**Figure S4** The time-course of the visible spectra of the Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 samples.

**Figure S4** The time-course of the visible spectra of the Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 samples.

The Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 samples were dried and allowed to stand in contact with air while their visible spectra were monitored in order to investigate the state of the Co-amine complexes. Figure S4 shows the time-course of the visible spectra of the Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 samples. The colors of the Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 after the drying followed by allowing to stand in air for 0.5 h were blue and light blue, respectively. The three peaks at 630, 670 and 700 nm observed in both visible spectra of the Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 after the drying followed by allowing to stand in air for 0.5 h are approximately similar to those observed in the typical spectrum of a blue  $[\text{CoCl}_4]^{2-}$  with a tetrahedral structure. The plausible structure of the tethered complex might be a tetrahedral  $[\text{Co}(-\text{NH}_2)_3\text{Cl}]\text{Cl}$ . However, this tetrahedral structure might not directly reflect the complex structure before the drying because the drying would promote the removal of the ligand molecules such as *i*-PrOH and  $\text{H}_2\text{O}$ , causing a structural transition. The pink color of the tethered complex before drying supports this supposition. We can assume that the octahedral  $\text{Co}^{2+}$ -amine complex before the drying is  $[\text{Co}(-\text{NH}_2)_4\text{X}_2]$  or  $[\text{Co}(-\text{NH}_2)_4\text{XY}]\text{X}$ , where X and Y are Cl and *i*-PrO, respectively, on the basis of the molar ratio of N / Co.

It is interestingly noted that the difference in behavior on the color change between the dried Co/0.2-APS-AMS and Co/0.3-APS-MCM-41 samples were observed with an increase in time. When the dried Co/0.2-APS-AMS at 373 K was allowed to stand in air, the color and the visible spectra of the material changed with time. The blue color of the dried Co/0.2-APS-AMS sample was lightened to light blue after allowing to stand in air for 2 h, and finally changed to light purple after 24 h. In the spectra of the AMS sample, a peak at around 530 nm newly appeared with an increase in time. In the case of the dried Co/0.3-APS-MCM-41, however, the drastic color change was not observed; the light blue color

still remained after allowing to stand in air for 24 h. The visible spectra did not change appreciably unlike the AMS sample.

A  $\text{Co}^{2+}$ -amine complex can be oxidized to the corresponding  $\text{Co}^{3+}$  amine complex by oxygen in air accompanied by the ligand exchange reaction of  $\text{Cl}^-$  ions with  $\equiv\text{SiO}^-$  or  $\text{H}_2\text{O}$  molecules, causing a structural transition, and such oxidized  $\text{Co}^{3+}$ -amine complex are stabilized by amino groups<sup>27</sup>. The change of the visible spectra of the Co/0.2-APS-AMS after the drying followed by allowing to stand in air for 24 h are probably attributed to the presence an octahedral  $\text{Co}^{3+}$ -amine complex with ligands of  $\text{H}_2\text{O}$  and  $\equiv\text{SiO}^-$  as well as  $-\text{NH}_2$ ; the plausible structure of the Co/0.2APS-AMS after the drying followed by allowing to stand in air for 24 h is an octahedral  $[\text{Co}(-\text{NH}_2)_4(\equiv\text{SiO})(\text{H}_2\text{O})]^{2+}$ . It is indicated that the oxidation and stabilization of the  $\text{Co}^{2+}$  complex on the AMS sample easily occurred; on the other hand, the MCM-41 sample was not easily oxidized likely due to the lower surface density of the amino groups.