Supporting Information

Controlled Morphology and Photoreduction Characteristics of Polyoxometalate(POM)/Lipid Complexes and the Effect of Hydrogen Bonding at Molecular Interfaces

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Scheme 1. Synthetic route for lipids 1-3.



Figure S1. TEM-EDX spectrum of nanofibrous assemblies prepared from the CHCl₃ solution of $[SiMo_{12}O_{40}](1)_4$ (1 μ M). The co-existence of Mo, Si, N elements is confirmed, consistent with the complex structure.



Figure S2. Structural transformation of helical ribbons $[SiMo_{12}O_{40}](2)_4$ into nanotubes and their bundles.



Figure S3. FT-IR spectra of air-dried gel prepared from the CHCl₃ gel (4 mM) of $[SiMo_{12}O_{40}](1-3)_4$ and the powdery sample of $[SiMo_{12}O_{40}](DODA)_4$.



Figure S4. Dependence of IVCT absorption maxima on the photoirradiation time.



Figure S5. Schematic illustration of photoreduction and formation of a charge-transfer complex.



Figure S6. Vis-NIR spectrum of $[SiMo_{12}O_{40}](DODA)_4$ in CHCl₃ (4 mM, 1 mm cell). After photoillumination for 120 min.



Figure S7. XPS spectra of $[SiMo_{12}O_{40}](1)_4$ and $[SiMo_{12}O_{40}](2)_4$ before (a,c) and after (b,d) photoirradiation for 120 min, respectively. From the spectral area of the Mo(V) and Mo(VI) peaks, percentages of Mo(V) were determined as 21% for $[SiMo_{12}O_{40}](1)_4$ and 29% for $[SiMo_{12}O_{40}](2)_4$.



Figure S8. (a) Chemical structure of $[SiMo_{12}O_{40}](4)_4$. (b,c) Photoreduction behavior of $[SiMo_{12}O_{40}](4)_4$ in CHCl₃ (b) and in CHCl₃/MeOH (1:1 v/v) (c). (d) Comparison of absorption intensity increase for $[SiMo_{12}O_{40}](4)_4$ in CHCl₃ and in CHCl₃/MeOH (1:1 v/v). (e) Comparison of ¹H NMR spectra for $[SiMo_{12}O_{40}](4)_4$ in CDCl₃ and in CDCl₃/CD₃OD (1:1 v/v).

To confirm that the photoreduction property of POMs is not impaired by self-assembly, we prepared a new POM-lipid complex $[SiMo_{12}O_{40}](4)_4$ (Figure S8a). The amphiphile 4 contains ether linkages in the alkyl chain moiety, which show better dispersibility in organic solvents. $[SiMo_{12}O_{40}](4)_4$ was dispersed in CHCl₃ or in the 1:1 (v/v) mixture of CHCl₃/MeOH.

When $[SiMo_{12}O_{40}](4)_4$ is dispersed in chloroform, ordered self-assemblies are formed as indicated by the broadening of ¹H-NMR spectrum. On the other hand, $[SiMo_{12}O_{40}](4)_4$ does not form aggregates when methanol is added to chloroform at 1:1 (v/v) ratio, as shown by the sharp ¹H-NMR spectrum (Figure S8e).

Upon photoillumination of $[SiMo_{12}O_{40}](4)_4$, blue-colored solutions were obtained with broad absorption bands at 726 nm, indicative of intervalence charge-transfer (IVCT, $Mo^V \rightarrow Mo^{VI}$) bands for reduced $SiMo_{12}O_{40}$ clusters (Figure S8b,c). Although methanol is known to serve as sacrificial electron donor in the photoreduction of POMs, it is noticeable that photoreduction of POMs-lipid complexes proceeded more effectively in CHCl₃, in the ordered nano-assemblies (Figure S8d). These results clearly demonstrate that the redox properties of POMs are well maintained in the self-assembly.