Supporting Information

Hybrid dimers based on metal-substituted Keggin polyoxometalates (metal = Ti, Ln) for cyanosilylation catalysis

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I. Supplementary Structure Figs



Fig. S1 (a) Polyhedral representation of the coordination mode of Ce(1) cation in compound **1**. (b) Polyhedral representation of the coordination mode of Ce(2) cation in compound **1**.



Fig. S2 EDS analysis of compound 1 shows a nearly 5:1:1 ratio of W: Ti: Ce.



Fig. S3 EDS analysis of compound 2 shows a nearly 5:1:1 ratio of W: Ti: Nd.



Fig. S4 EDS analysis of compound 3 shows a nearly 5:1:1 ratio of W: Ti: Sm.



Fig. S5 Image highlighting the pure single crystal of compound 1.



Fig. S6 (a) Polyhedral representation of the coordination mode of La(1) cation in **4**. (b) Polyhedral representation of the coordination mode of La(2) cation in **4**.









Fig. S7 (a) IR spectrum for compound 1. (b) IR spectrum for compound 2. (c) IR spectrum for compound 3. (d) IR spectrum for compound 4. (e) IR spectrum for compound 5. (f) IR spectrum for compound 6.







Fig. S8 (a) TG curve for compound **1**. (b) TG curve for compound **2**. (c) TG curve for compound **3**. (d) TG curve for compound **4**. (e) TG curve for compound **5**. (f) TG curve for compound **6**.







Fig. S9 (a) The calculated and experimental PXRD patterns for compound **1**. (b) The calculated and experimental PXRD patterns for compound **2**. (c) The calculated and experimental PXRD patterns for compound **3**. (d) The calculated and experimental PXRD patterns for compound **4**. (e) The calculated and experimental PXRD patterns for compound **5**. (f) The calculated and experimental PXRD patterns for compound **6**.



Fig. S10 UV-vis spectra for compounds 2 and 6.





Fig. S11 (a) Plots of cyanohydrin yield vs. time for the cyanosilylation reaction of benzaldehyde with TMSCN with compounds **1–3**. (b) Plots of cyanohydrin yield vs. time for the cyanosilylation reaction of benzaldehyde with TMSCN with compounds **4–6**.



Fig. S12 IR spectra for (a) as-synthesized compound 1 and (b) recovered catalyst after catalysis reaction.



Fig. S13 IR spectra for (a) as-synthesized compound **5** and (b) recovered catalyst after catalysis reaction.



Fig. S14 (a) IR spectra of **1** (bottom), benzaldehyde (top), and **1** obtained after the absorption of benzaldehyde (middle). (b) IR spectra of **5** (bottom), benzaldehyde (top), and **5** obtained after the absorption of benzaldehyde (middle).

III. Supplementary Tables

Table S1 Study on recycling of catalysts 1 and 5 for the heterogeneouscyanosilylation of benzaldehyde under the same condition.

Compound	Entry	Efficiency(%)
1	1	99.2
	2	98.6
	3	97.1
5	1	70.4
	2	69.4
	3	68.2