

Supporting Information

The precise termination of nanoscaled Keplerate-type polyoxometalates with NH₂-groups via alkoxy silane: reactive sites, mechanisms and dye conjugations

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EXPERIMENTAL SECTION

Materials and Analysis

All chemicals were analytical grade, obtained from Sigma Aldrich and used as received. The methanol was freshly distilled. The elemental analysis was performed with an iCAP 6500 Duo atomic emission spectrometer (Thermo Scientific). The samples for elemental analysis were dissolved in water with the addition of concentrated nitric acid and measured until fresh. The IR spectra were collected in ATR mode by means of a Nicolet 6700 FT-IR spectrometer (Thermo Scientific). The obtained IR spectra were corrected with OMNIC software to level the dependency of the IR absorbance on the wavelength. The Raman spectra were measured using an Alpha 300 AR confocal Raman microscope (WiTec GmbH) at the low power of the laser beam (633 nm) in order to prevent the destruction of the samples. X-ray photoelectron spectroscopy (XPS) measurements were performed using a K-Alpha + electron spectrometer (Thermo Fisher Scientific, USA) with monochromatic Al K α radiation (1486 eV). The charge compensation system was applied, and the vacuum was maintained at 10⁻⁷ mbar. The internal Au- standard (Au 4f, 84 eV) was used for spectrometer calibration. The spectrum scale was corrected with a C 1s signal (284.8 eV). The samples were placed on a double-stick carbon tape. The X-ray beam was focused on the 300 μ m spot, and the spectrum was collected at a suitable analyzer pass energy: 200 eV for the survey spectrum and 50 eV for the narrow spectral range. Scanning electron microscopy (SEM) was carried out by means of AURIGA CrossBeam (Carl Zeiss NTS) equipped with an EDX accessory (Oxford Instruments). The EDX's X-ray beam was focused on the 1 μ m spot. The UV-Vis spectra were registered with a UV-1800 spectrometer (Shimadzu). The photoluminescence and photoluminescence excitation spectra were measured with RF-6000 (Shimadzu) Fluoromax 4 (Horiba, Kyoto, Japan) spectrometers. The time-resolved fluorescence measurements were carried out with a Horiba FluoroMax 4 (Kyoto, Japan), equipped with a nanosecond light-emitting diode (LED) (370 nm) using time-correlated single-photon counting (TC-SPC). The optical density of the solutions did not exceed 0.1. Two LSP01-1A (LongerPump) syringe pumps were used to add the desired solution stepwise into the reaction mixture. ¹H NMR was recorded with an AVANCE 500 (Bruker BioSpin).

Synthesis

The $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{72}\text{Fe}_{30}\}$ crystals were produced via standard protocol.^{1,2} Their structures were confirmed by IR and Raman spectroscopy and comparison with the literature.³

The molar ratios of $\{\text{Mo}_{132}\}$, APTMS, HCl and TEAB are recorded in Table 1. The common synthetic procedure of the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ consists of the following: 0.019 g of $\{\text{Mo}_{132}\}$ was dissolved in 5 ml of MeOH with 10 min of ultrasound and stored under an argon flow; then 1 ml of the methanol solution with desired APTMS concentration was inserted either immediately (samples #1, #2) or dropwise together with 1 ml methanol solution containing desired HCl amount (samples #5 – #8). The dropwise insertion was realized by using two syringe pumps with insertion rate 1ml/h. TEAB was added after POM dissolution when required (samples 9# – #12). Next, the reaction mixture was left overnight at room temperature with stirring and under an argon blanket.

For samples #3 and #4, the same amount of $\{\text{Mo}_{132}\}$ was suspended in toluene for 10 min of ultrasound and stored under an argon flow. Then 1ml of toluene solution with the desired concentration of APTMS and an equimolar amount of methanol (for sample #4 only) were added immediately. Next, the reaction mixture was left overnight at room temperature with stirring and under an argon blanket.

When the reactions were finished, the crude product was purified of the undesired admixtures of free siloxanes: 5 ml of toluene was added to the reaction mixture, shaken for 1 min and transferred into a 15-ml falcon tube for centrifugation. After centrifugation at 6000 rpm for 10 min, the product was separated from the liquid phase, washed with 7 ml of toluene in a vortex (2700 rpm) for 10 min and centrifuged at 6000 rpm for 10 min. The obtained brown sample was stored under a layer of toluene (2ml) at 4°C. The $\{\text{Mo}_{72}\text{Fe}_{30}\}(\text{SiPrNH}_2)_{29\pm 1}$ sample was produced and purified in the same way as the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$.

In order to conjugate the fluorescein onto $\{\text{Mo}_{132}\}$, we prepared two $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ samples through the aforementioned procedure with a 10-fold and 20-fold molar excess of APTMS in the reaction mixture. The produced samples were dried in air, weighed and dissolved in acetonitrile. Then fluorescein NHS-ester (20 or 40-fold molar excess, respectively) and trimethylamine (TEA, 40 or 80-fold molar excess, respectively) were added to the acetonitrile solution. The obtained mixture was left overnight at room temperature with stirring and an argon blanket. The product was precipitated with acetone and centrifuged (6000 rpm for 10 min). Next, the product was washed with 5ml of acetone which was followed by centrifugation (6000 rpm for 10 min). This procedure was repeated three times. This procedure was repeated with 1 ml of DMSO instead of acetone. The purified product was dissolved into DMSO and used while fresh.

The fluorescein NHS-ester was synthesized as described elsewhere.⁴ The produced NHS-ester was purified with column flash-chromatography, as described here.⁴ The purification was controlled via TLC. The structure was studied with NMR (¹H) spectroscopy: ¹H NMR (500 MHz, DMSO) δ 8.13 (d, $J = 7.9$ Hz, 1H), 7.80 (t, $J = 7.5$ Hz, 1H), 7.71 (dd, $J = 7.9, 7.5$ Hz, 2H), 7.41 (d, $J = 7.5$ Hz, 1H), 6.57 (d, $J = 9.2$ Hz, 2H), 6.26 (dd, $J = 9.3, 1.8$ Hz, 2H), 6.22 (d, $J = 1.7$ Hz, 2H), 3.17 (s, 4H).

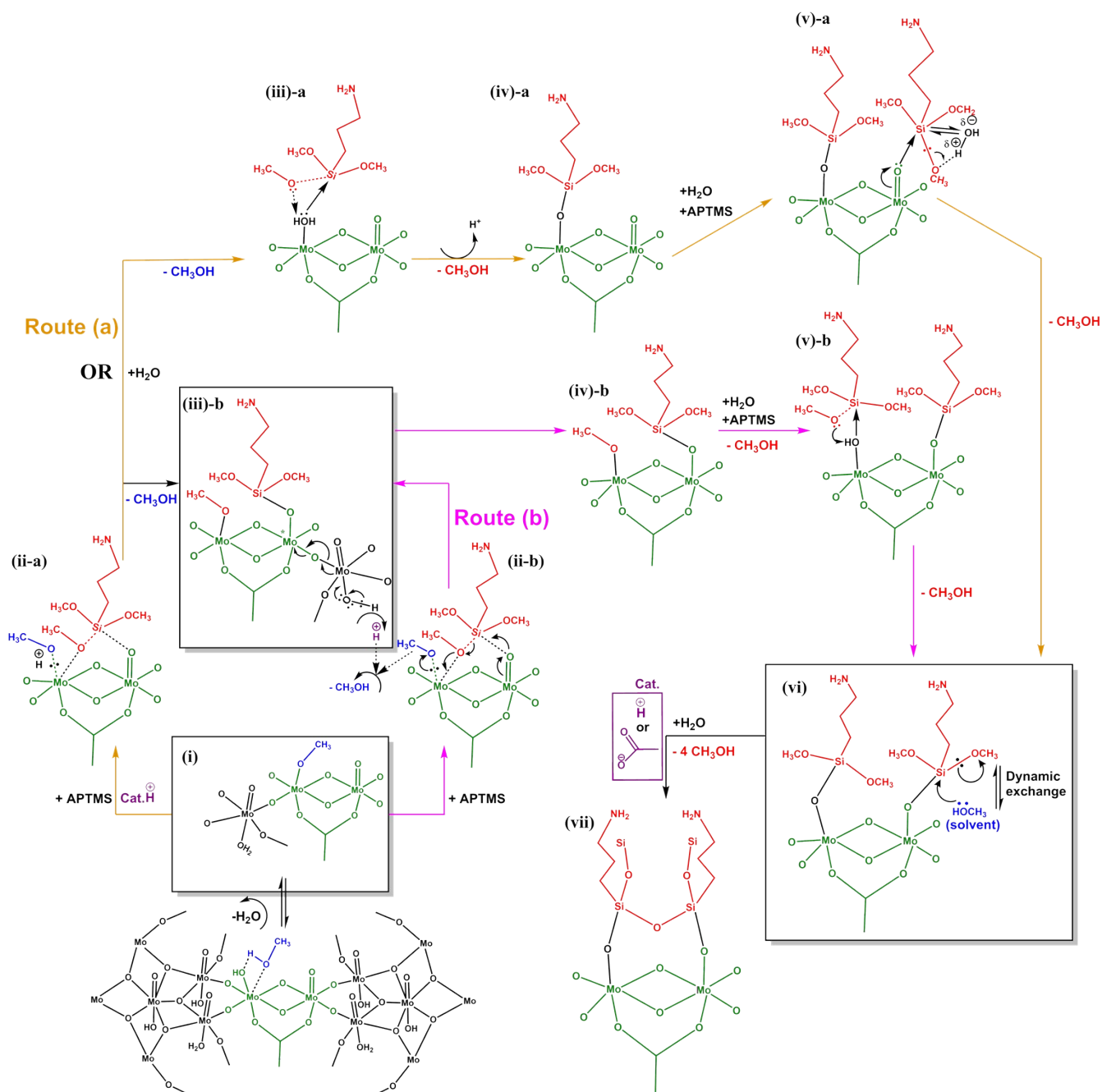


Figure S1. The ligand exchange (LE) process, with methanol molecules assisting APTMS (red) hydrolysis on the {Mo₂} bridged unit (green), which connects the two {Mo₆} fragments (black).

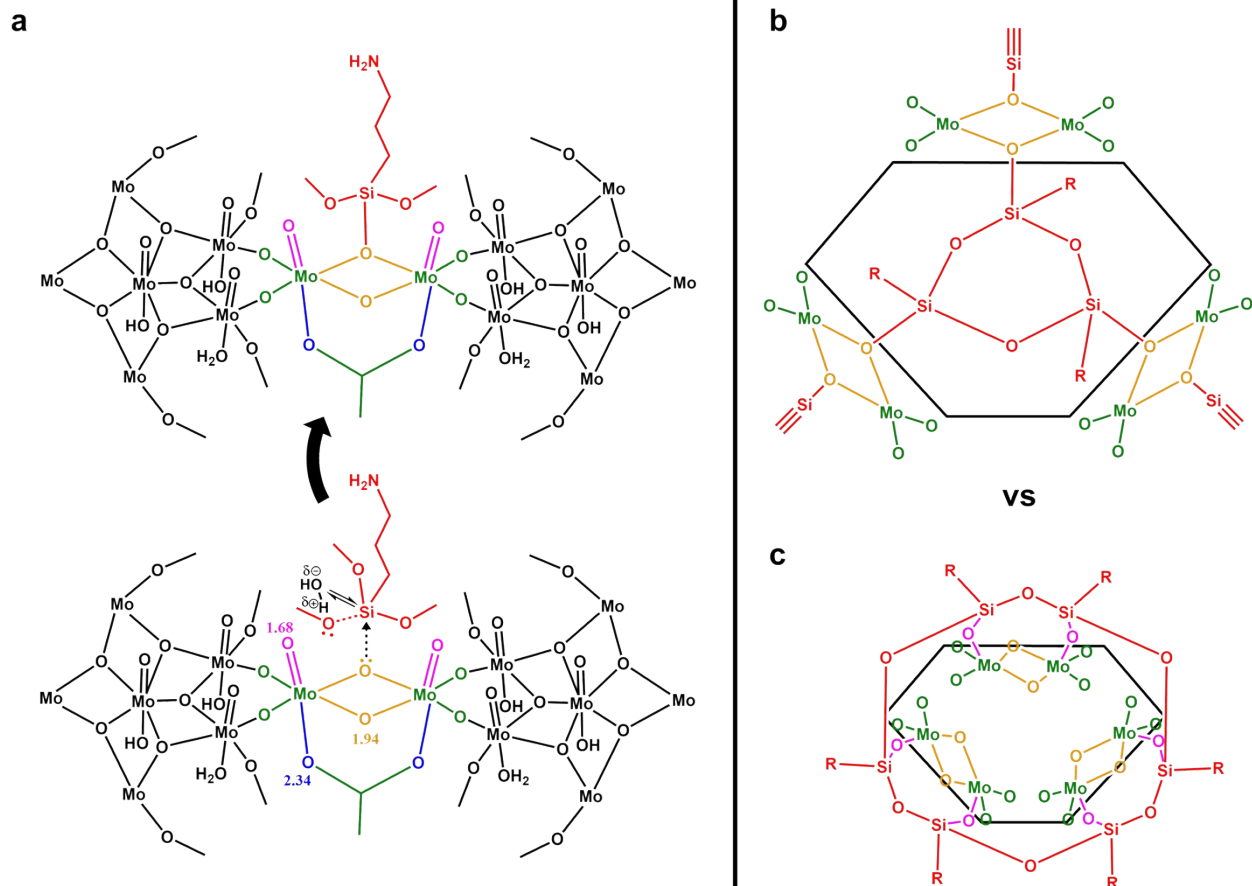


Figure S2. **a** – the scheme of APTMS grafting via μ_2 -O oxygen in $\{\text{Mo}_2\}$ unit accompanied with hydrolyses by Keprate incorporated water. The pink, blue and orange numbers correspond to bond length (\AA) in Mo-O pairs with similar color code; **b, c** – the comparison of arrangement of APTMS molecules inside the hexagonal pore due to participation of different reactive sites, bridging (**b**) or terminal (**c**) oxygens. R is n-aminopropyl.

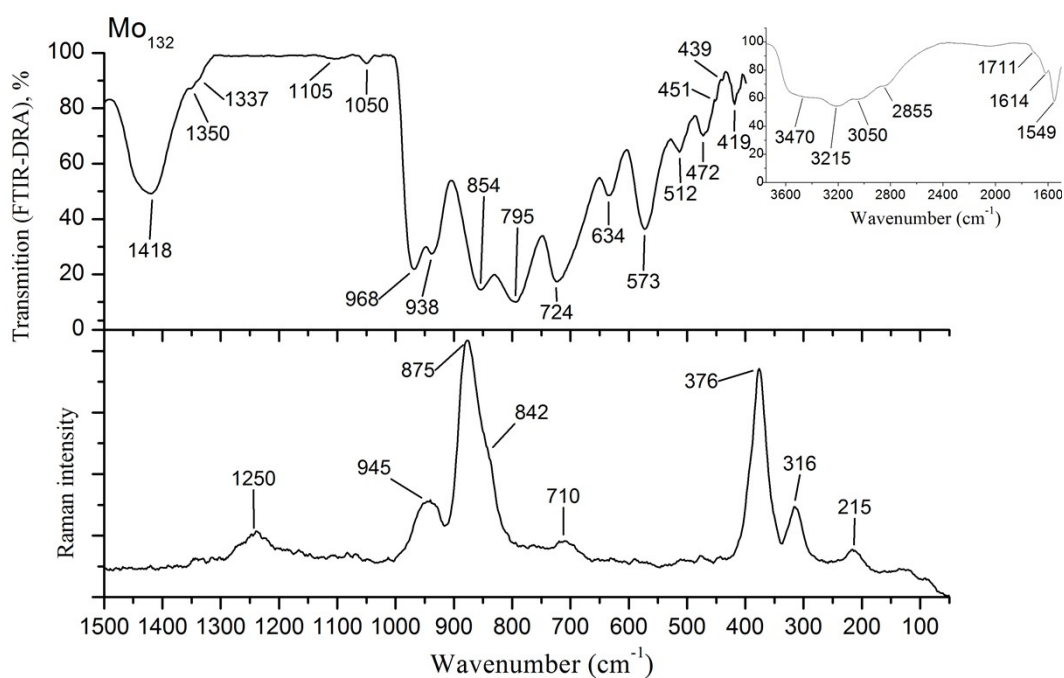


Figure S3. The IR spectrum in ATR mode (top: the high-frequency part is an insert) and Raman spectrum acquired with a 633-nm He-Ne laser (bottom) of a solid state sample of Mo₁₃₂.

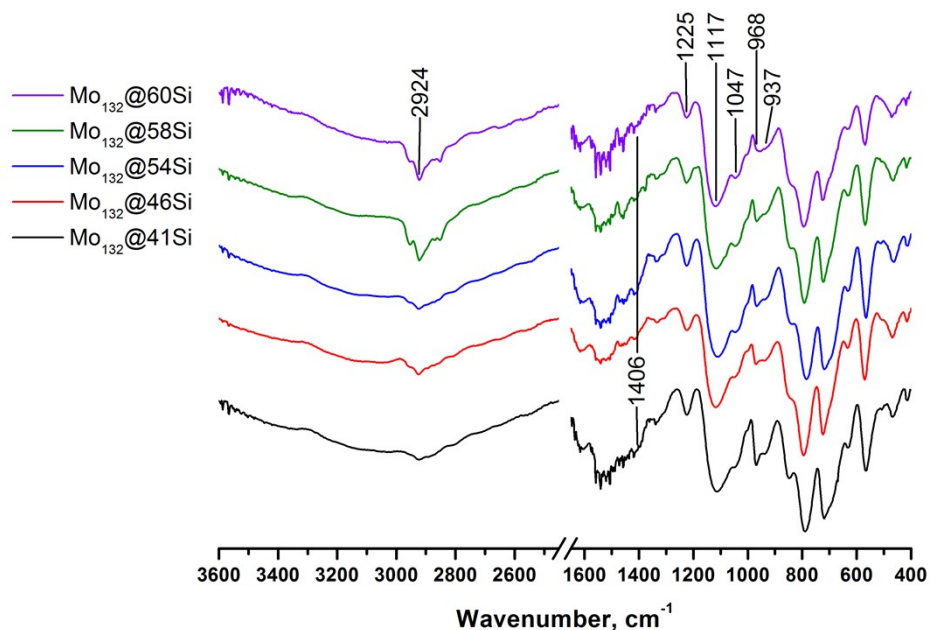


Figure S4. The IR spectra in ATR mode of the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ with different conjugation degrees produced in methanol. @The number in the legend corresponds to the number of APTMS molecules grafted onto the POM (according to elemental analysis).

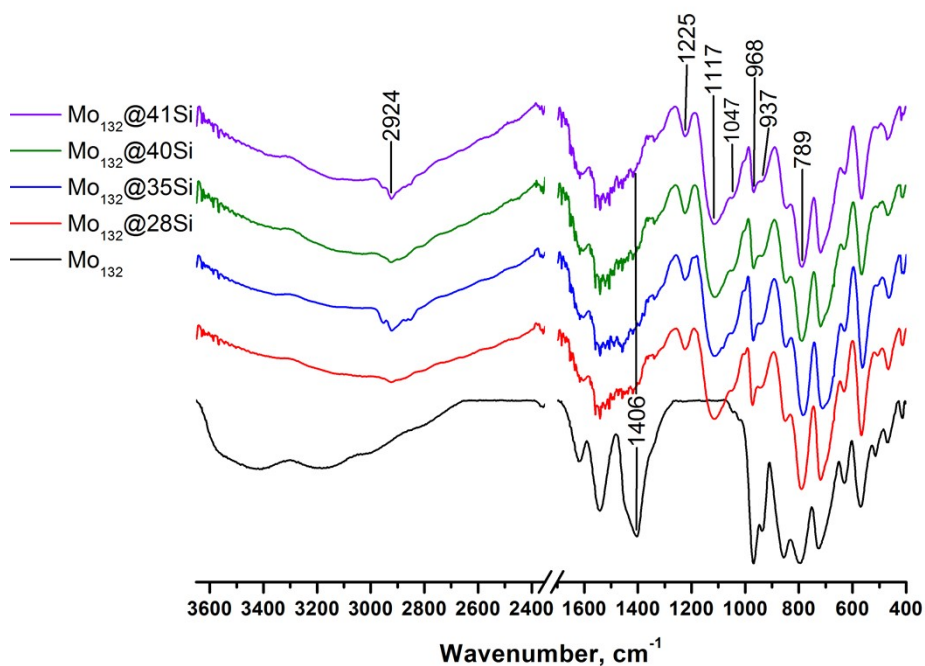


Figure S5. The IR spectra in ATR mode of the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ with different conjugation degrees produced in methanol. @ The number in the legend corresponds to the number of APTMS molecules grafted onto the POM (according to elemental analysis).

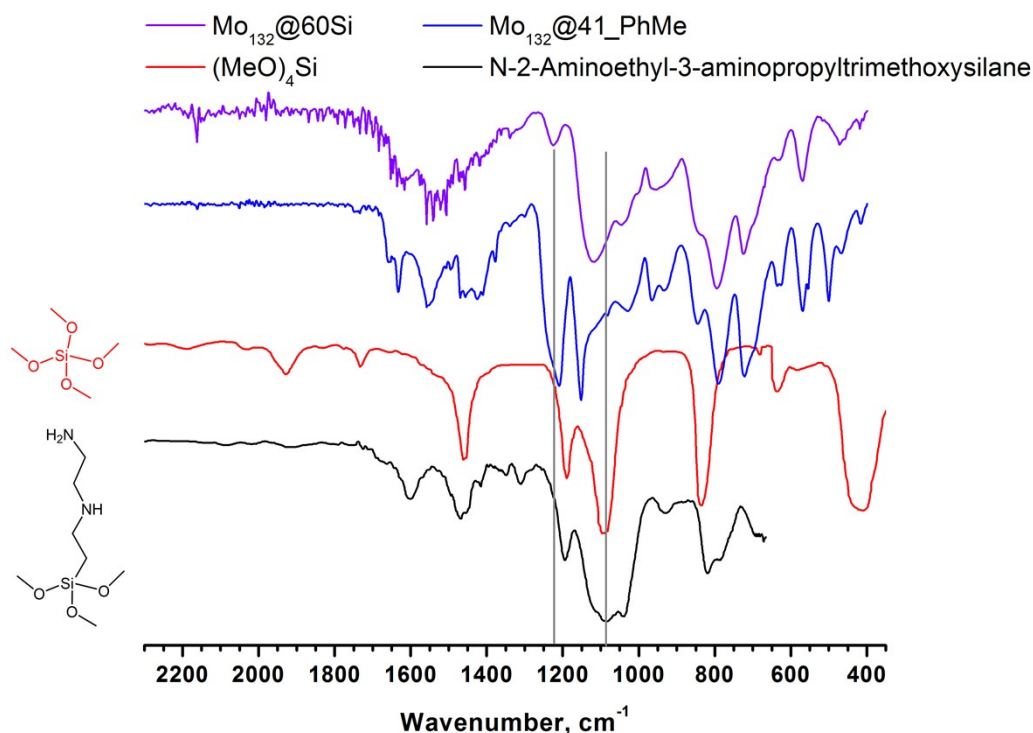


Figure S6. The comparison of IR spectra for the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ produced in acidified methanol or in toluene (samples #7 and #3 from Table 1, respectively, see manuscript) with the standard spectra of tetramethoxysilane (red) and alkylamino derivative (black). The vertical lines correspond to the stretching of the Si-O-PrNH₂ bond at 1225 cm⁻¹ and the Si-O-CH₃ bond at 1151 cm⁻¹, respectively. The spectra were obtained from the NIST Chemistry WebBook, NIST Standard Reference Database Number 69, Eds. P.J. Linstrom and W.G. Mallard.

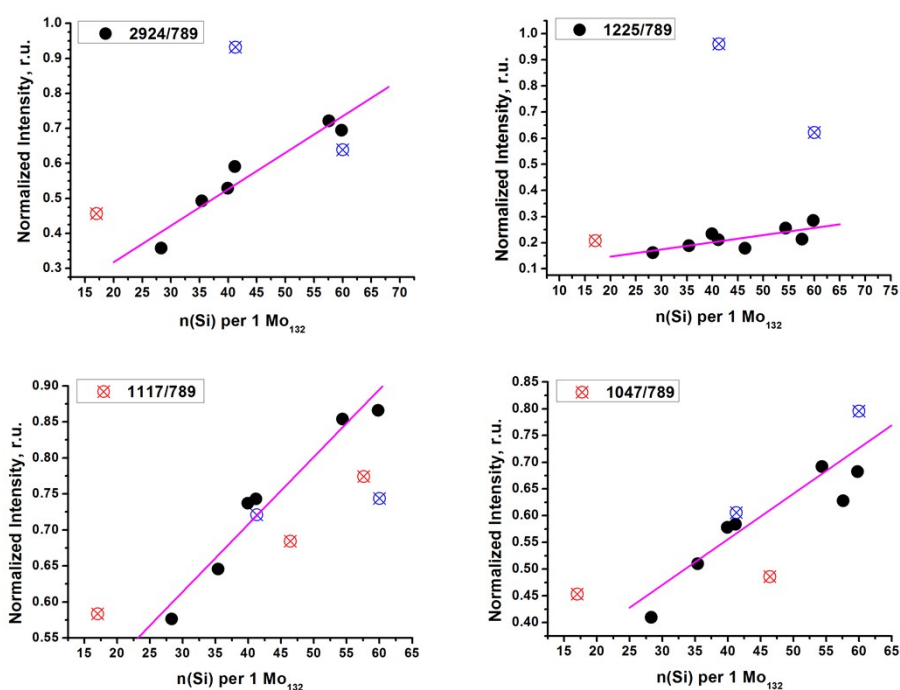


Figure S7. The dependency of IR band intensity (see legends), normalized in terms of a band intensity at 789 cm⁻¹, the conjugation degree in $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ and the linear fitting of data. Black spots – samples produced in methanol; blue spots – samples produced in toluene or a toluene/methanol mixture; red spots – unfitted data.

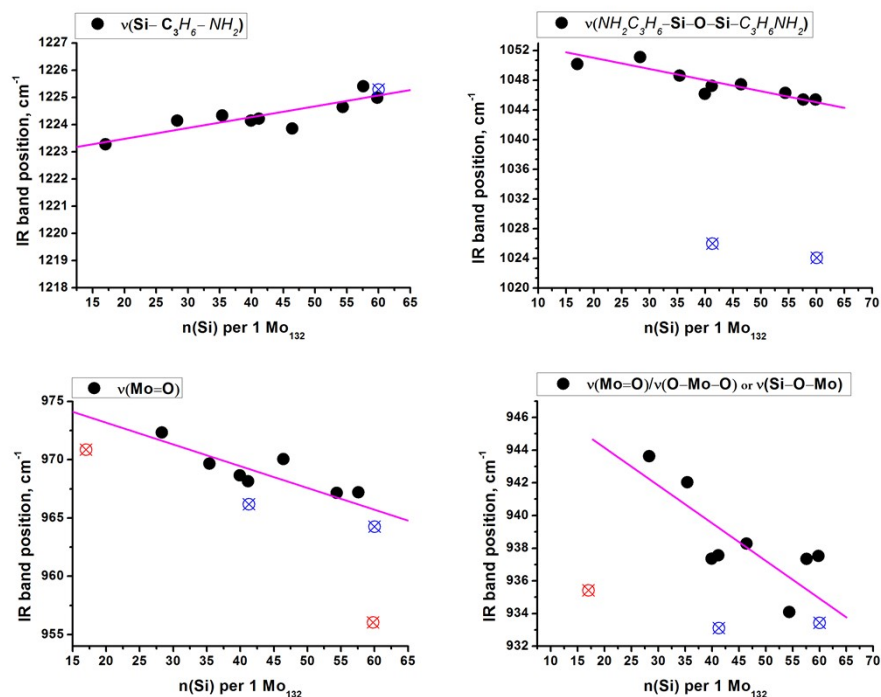


Figure S8. The dependency of IR band position on $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n$ conjugation degree and the linear fitting of data. Black spots – samples produced in methanol; blue spots – samples produced in toluene or the toluene/methanol mixture (in the top-left plot, the second blue spot is out of range); red spots – unfitted data. The type of vibrations is in the legend.

Table S1. XPS data analysis.

Sample	Atomic shell	Peak number	Peak position, eV	Area	FWHM, eV	GL, %	Mo-signal area sum	Fraction of signals	Atomic fraction
Mo₁₃₂									
Mo1	Mo3d5/2	1	232.16	24542.86	1.99	2	40904.77	0.33	43
	Mo3d3/2	2	235.31	16361.91	2.066	2			
Mo2	Mo3d5/2	3	233.287	39888.77	2.19	2	66481.28	0.53	70
	Mo3d3/2	4	236.437	26592.51	2.192	2			
Mo3	Mo3d5/2	5	234.663	10575.68	2.362	2	17626.133	0.14	19
	Mo3d3/2	6	237.813	7050.453	2.4	2			
Total area							125012.18		
							3		
Mo₁₃₂:Si=1:6									
Mo1	Mo3d5/2	1	231.184	30251.28	1.515	2	50418.8	0.36	47
	Mo3d3/2	2	234.334	20167.52	1.624	2			
Mo2	Mo3d5/2	3	232.295	44590.38	1.41	2	74317.3	0.53	70
	Mo3d3/2	4	235.445	29726.92	1.448	2			
Mo3	Mo3d5/2	5	233.719	9331.404	2.141	2	15552.34	0.11	15
	Mo3d3/2	6	236.869	6220.936	2.2	2			
Total area							140288.44		
Si1	2p	1	101.907	9191.034	1.597	7			
Si2	2p	2	103.979	967.132	2.2	8			

Mo1	Mo3d5/2	1	231.428	35082.83	1.448	2	58471.38	0.39	52
	Mo3d3/2	2	234.578	23388.55	1.448	2			
Mo2	Mo3d5/2	3	232.589	46679.82	1.718	2	77799.7	0.52	69
	Mo3d3/2	4	235.739	31119.88	1.68	2			
Mo3	Mo3d5/2	5	234.247	7909.17	1.921	2	13181.95	0.09	12
	Mo3d3/2	6	237.397	5272.78	1.742	2			
Total area							149453.03		
Si1	2p	1	102.03	4385.186	1.547	0			
Si2	2p	2	103.674	926.738	2.2	0			

Mo ₁₃₂ -Si=1:45									
Mo1	Mo3d5/2	1	231.43	22120.91	1.941	0	36868.18	0.44	58
	Mo3d3/2	2	234.58	14747.27	1.991	0			
Mo2	Mo3d5/2	3	232.598	15850.94	2.053	0	26418.24	0.32	42
	Mo3d3/2	4	235.748	10567.3	2	0			
Mo3	Mo3d5/2	5	233.83	12217.95	2.2	4	20363.247	0.24	32
	Mo3d3/2	6	236.98	8145.297	2.197	4			
Total area							83649.667		
Si1	2p	1	102.139	7809.862	1.906	8			
Si2	2p	2	103.948	4780.886	2.049	23			

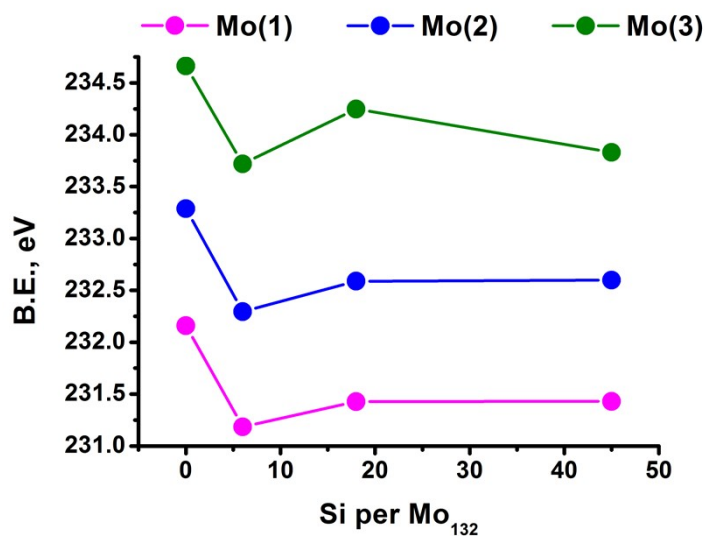


Figure S9. The dependence of the position of Mo3d_{5/2} signals position on {Mo₁₃₂}(SiPrNH₂)_n conjugation degree.

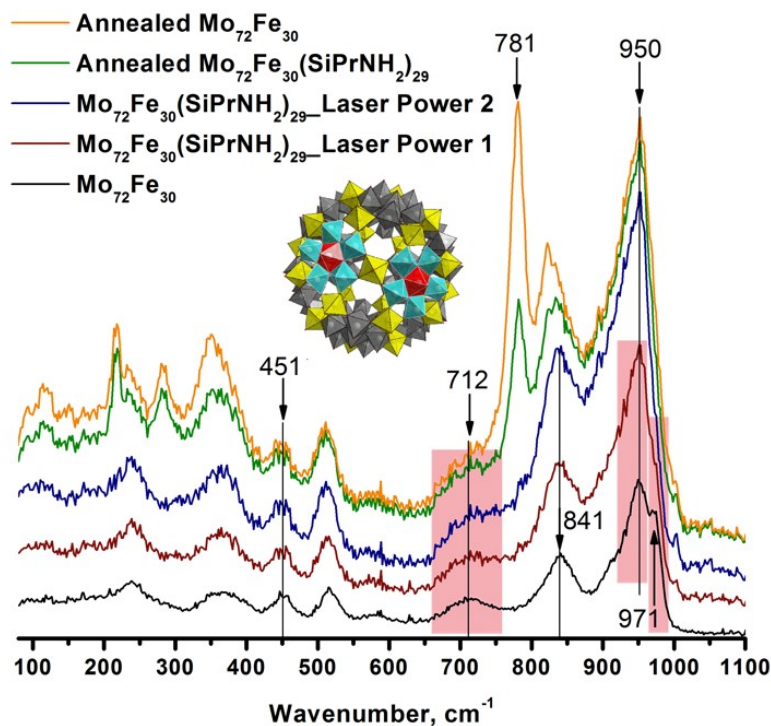


Figure S10. Raman spectra acquired with a 633 nm He-Ne laser for: pure $\{\text{Mo}_{72}\text{Fe}_{30}\}$ (black), its destruction product (a mixture of $\text{Fe}_2(\text{MoO}_4)_3$ and MoO_3 , orange), the conjugate $\{\text{Mo}_{72}\text{Fe}_{30}\}(\text{SiPrNH}_2)_{29}$ at different laser powers (red and blue), and the destruction product of the conjugate (green).

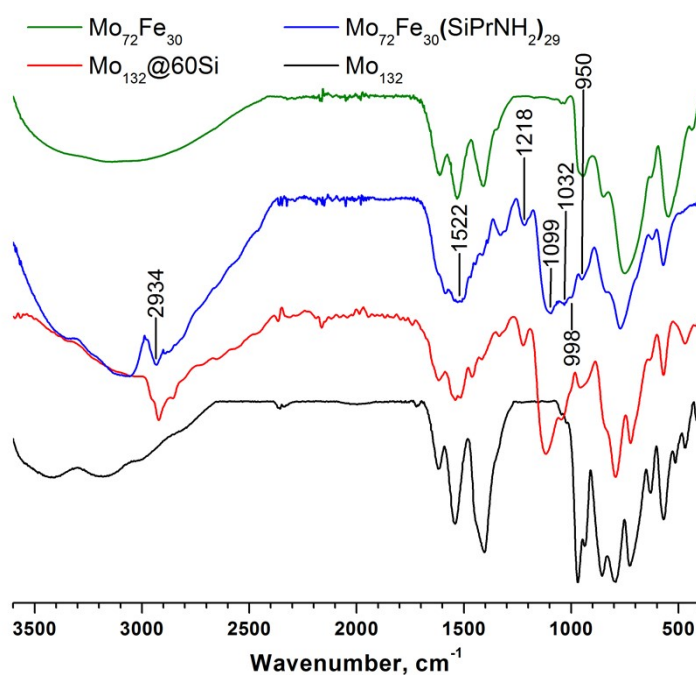


Figure S11. The IR spectra in ATR mode of pure $\{\text{Mo}_{72}\text{Fe}_{30}\}$ and $\{\text{Mo}_{132}\}$ (green and black, respectively) and the conjugates $\{\text{Mo}_{72}\text{Fe}_{30}\}(\text{SiPrNH}_2)_{29}$ and $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_{60}$ produced in methanol (blue and red, respectively).

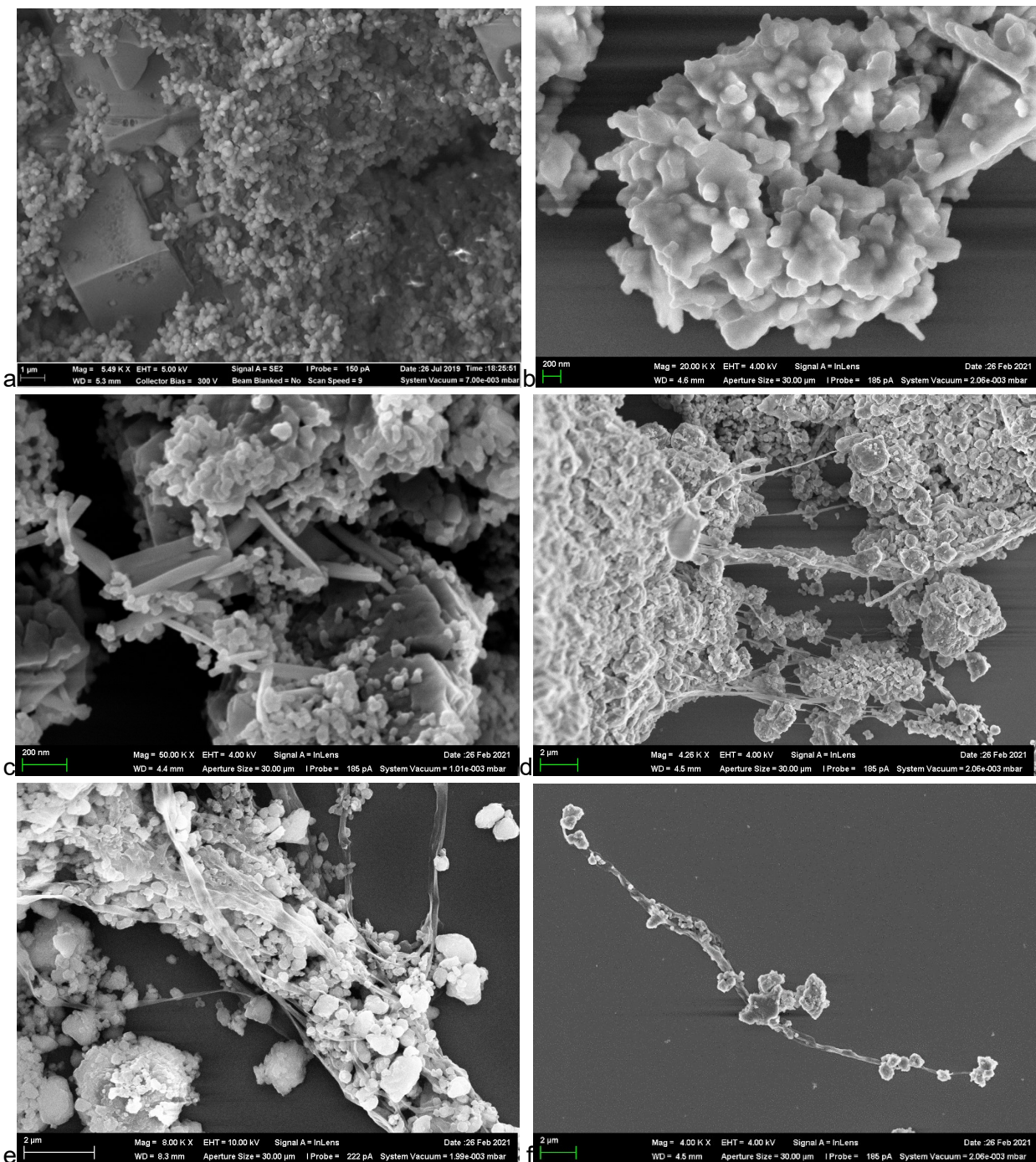


Figure S12. SEM images of pure Mo_{132} treated with MeOH for 8 h (a); sample #9 (b); sample #1 (c); and sample #4 (d-f) precipitated in a toluene suspension on a monocrystal silicon substrate (for details, see Table 1 in manuscript).

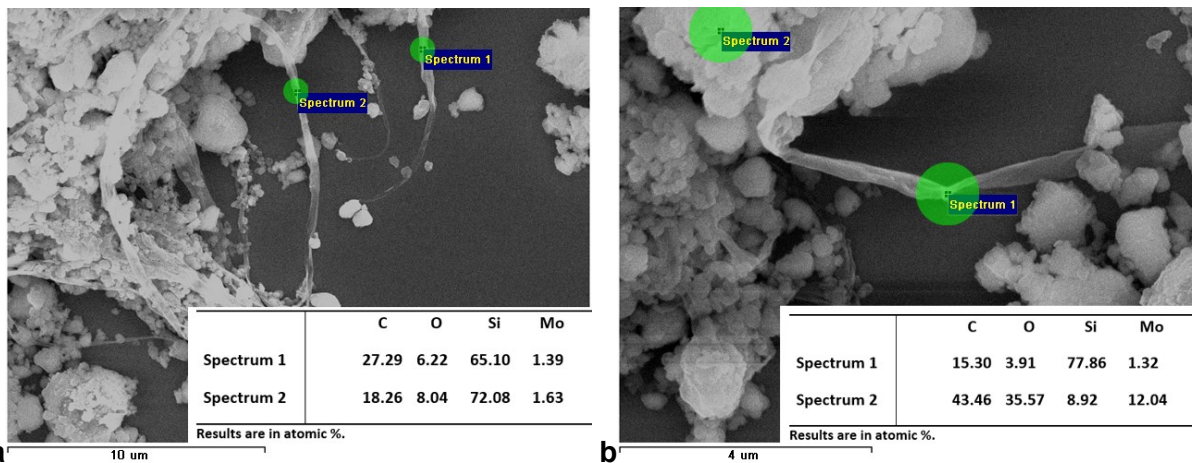


Figure S13. SEM images and the results of EDX elemental analysis (the analyzed area is marked with green) for sample #4 (for details, see Table 1 in Manuscript) precipitated in a toluene suspension on a monocrystal silicon substrate.

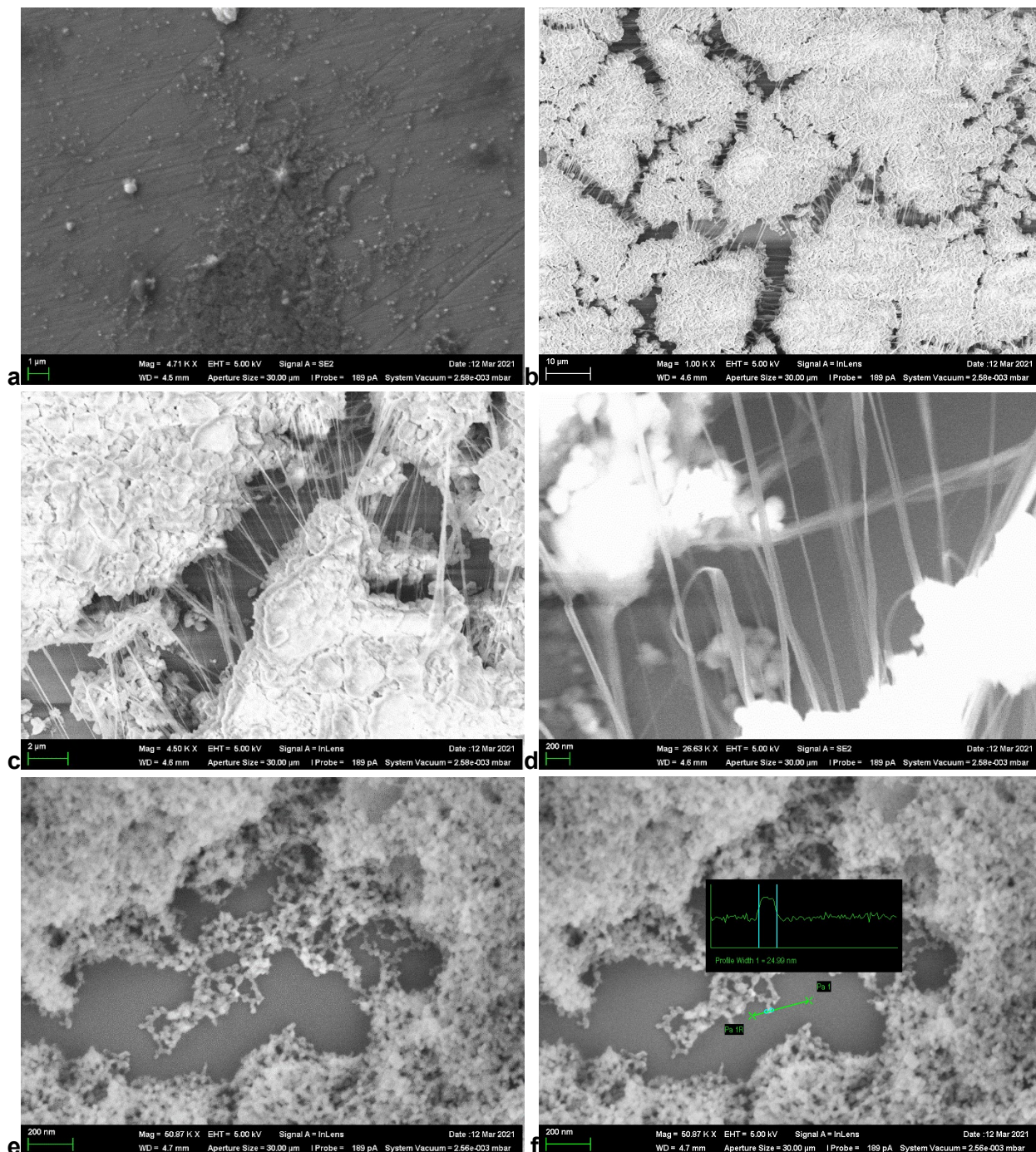


Figure S14. SEM images of sample #4 (for details, see Table 1 in manuscript) produced after the evaporation of the methanol solution centrifuged at 2000 rpm for 2 min (a) and precipitated from the methanol suspension before centrifugation (b-d). The SEM image (e) of the conjugate $\{\text{Mo}_{72}\text{Fe}_{30}\}(\text{SiPrNH}_2)_{29\pm 1}$ precipitated from a methanol suspension and the size profile of the produced spherical nanoparticles (f).

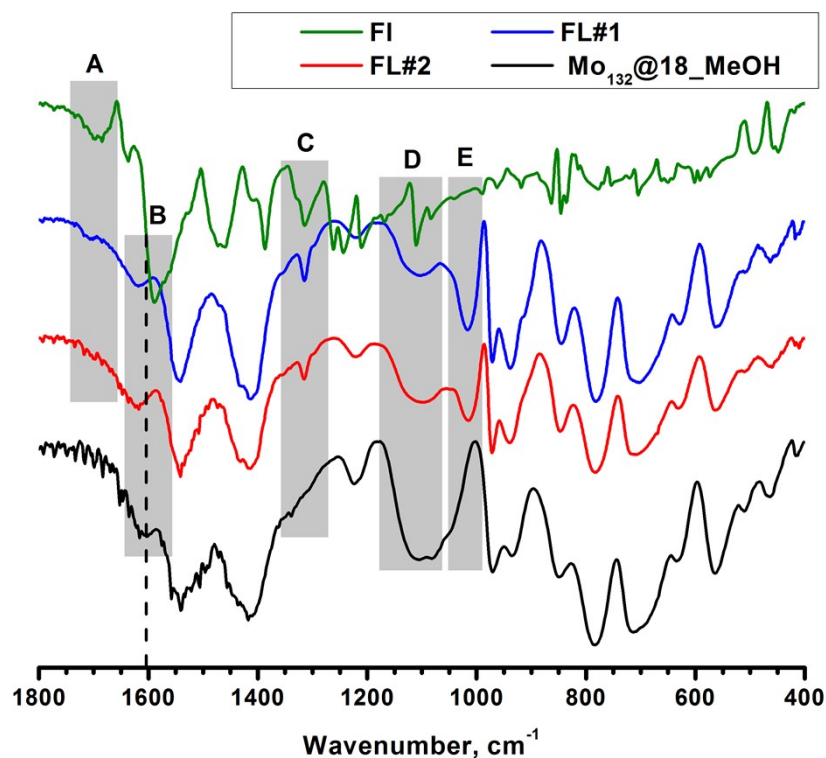


Figure S15. IR spectra registered in ATR mode of the conjugate $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_{18}$ (black) and the conjugates $\{\text{Mo}_{132}\}(\text{SiPrNH}_2)_n\text{FL}_m$ – FL#1 and FL#2 (blue and red, respectively) – and pure fluorescein (green). The IR regions (grey), which are significantly different for the mentioned samples, are marked with the letters A-E.

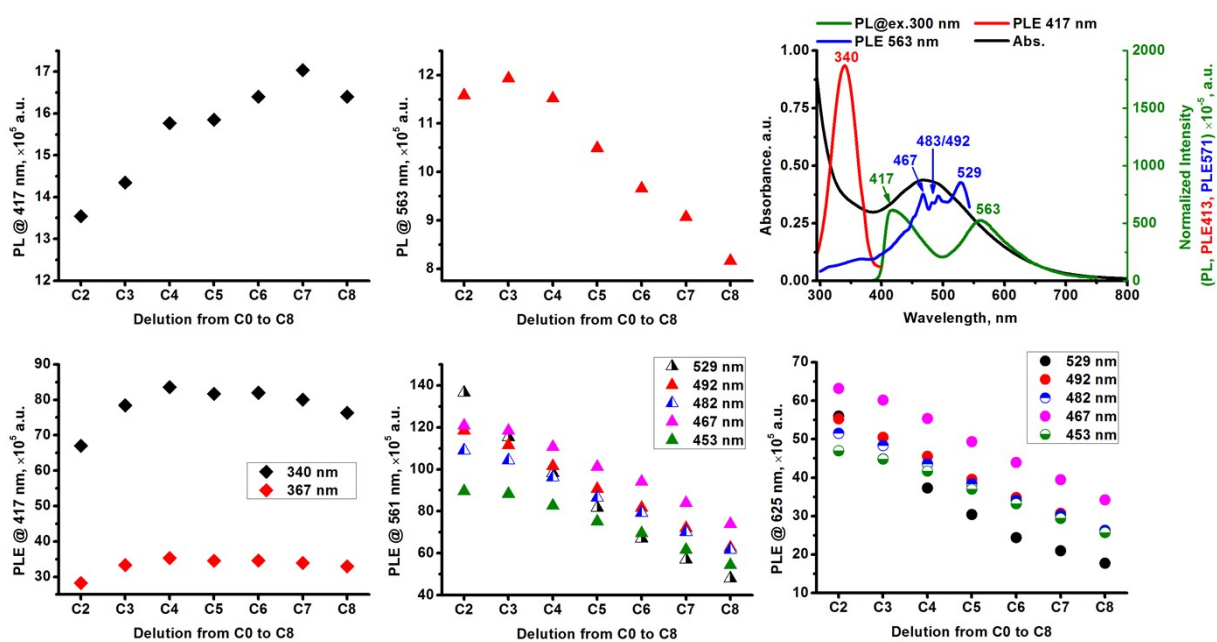


Figure S16. The dependence of the photophysical parameters (maximum intensity of the PL and PLE spectra) of the conjugate FL#1 on the dilution of the initial DMSO solution. The UV-Vis, PL and PLE spectra (right top) correspond to C2 dilution.

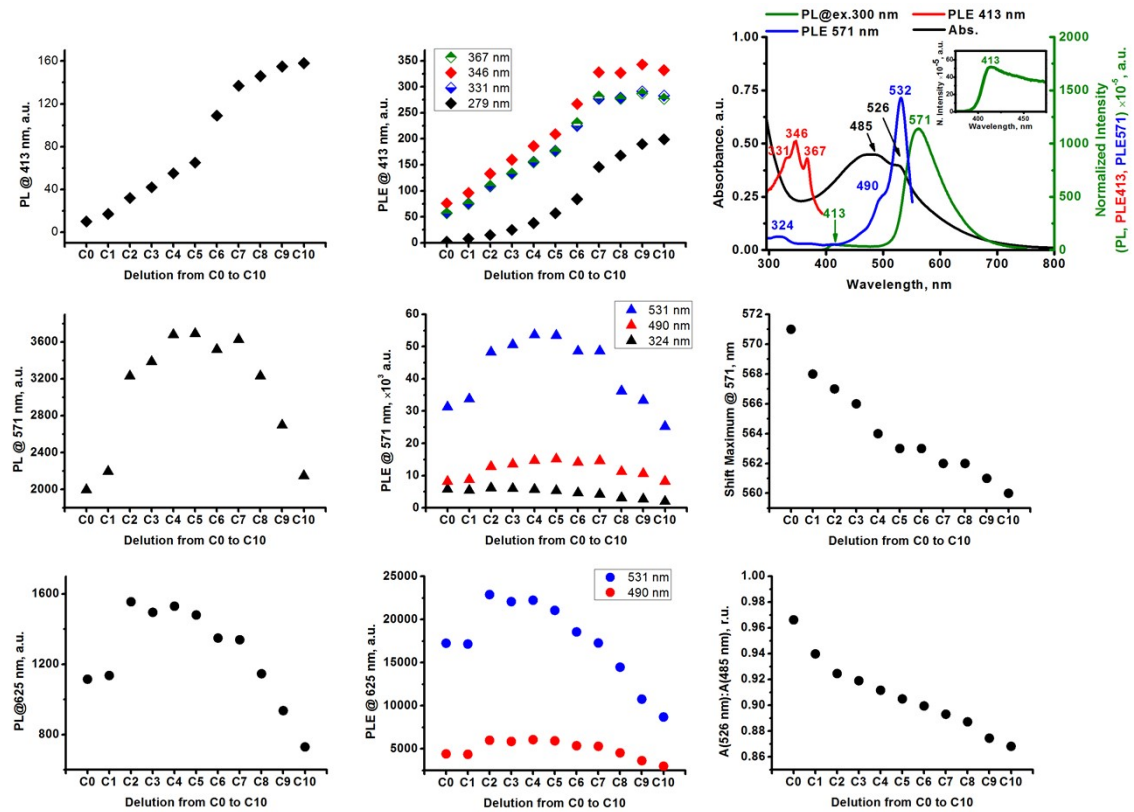
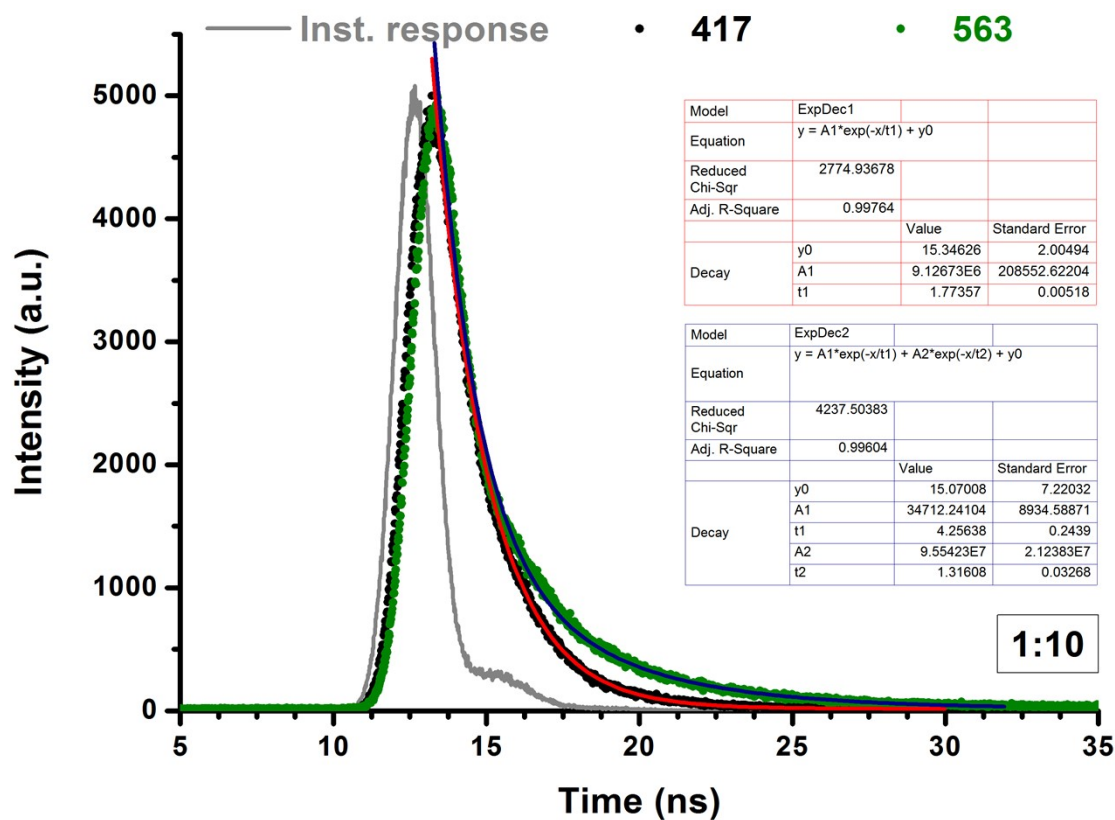
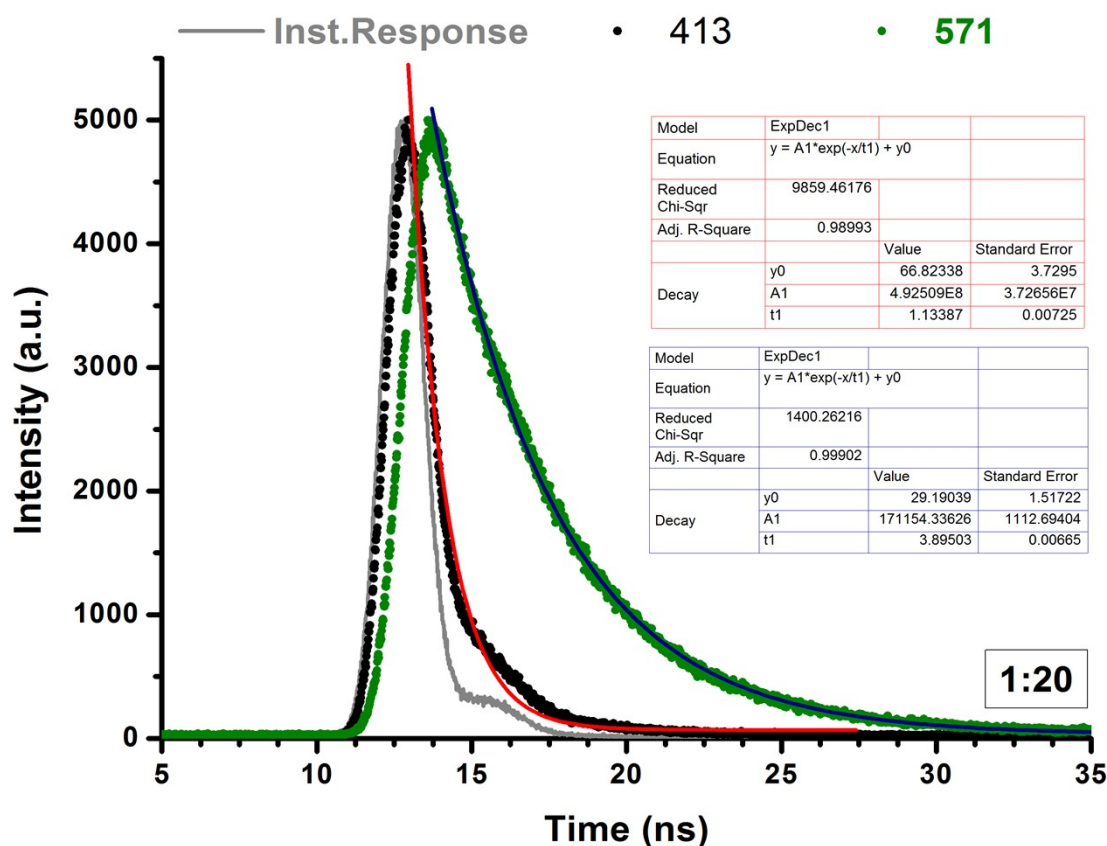


Figure S17. The dependence of photophysical parameters (maximum intensity of the PL and PLE spectra, the UV-Vis band ratio and the wavelength shift) of the conjugate FL#2 on dilution of the initial DMSO solution. The UV-Vis, PL and PLE spectra (top right) correspond to C8 dilution.



a



b

Figure S18. The PL decay curves (TC-SPC) of samples FL#1 (a) and FL#2 (b) at different emission wavelengths. The instrument response is the grey spectrum. The fitting data are in the inserted tables (t1 and t2 are the lifetimes of fluorescence). In plot (b), the poor fitting (even with triexponential function) of the signal with the emission at 413 nm (black) is caused by very low emission intensity, as seen in Figure S13.

References

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