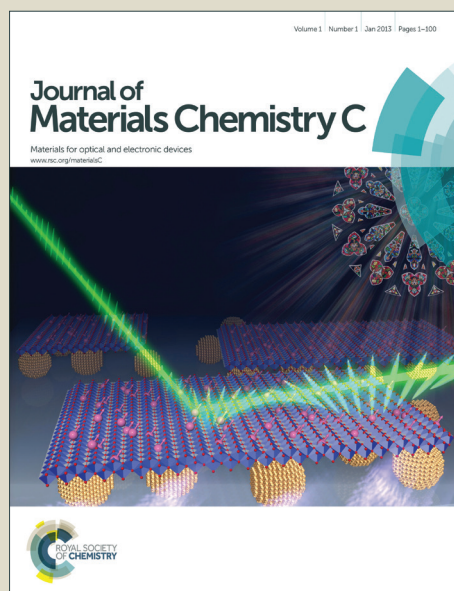


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ARTICLE

Reversible Photodimerization of Coumarin-Modified Wells-Dawson Anions

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Wei Chen,^a UnSong Tong,^a Tao Zeng,^a Carsten Streb^{*b} and Yu-Fei Song^{*a}Received 00th January 2012,
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Organo-modified photo-sensitive polyoxometalates (POMs) are a unique class of functional molecular materials. Here we show how the light-driven dimerization in organo-functionalized POMs can be achieved. To this end, the vanadium-substituted Wells-Dawson cluster $[P_2V_3W_{15}O_{62}]^{9-}$ was modified with a coumarin-based derivative to give the new organic-inorganic hybrid $(nBu_4N)_4H_2[C_{12}H_9O_4NHC(CH_2O)_3P_2W_{15}V_3O_{59}]$. Upon photo-irradiation, the compound undergoes photodimerization which was characterized using various spectroscopic methods including FT-IR, UV-Vis, DLS (dynamic light scattering), 1H NMR, COSY NMR and ESI-MS. These results are in good agreement with the formation of dimer species. In addition, XPS and EPR analyses of the photo-irradiation product indicate that V^{5+} is partially reduced to V^{4+} , while W^{6+} is not affected, suggesting that the coupled photo-dimerization and selective redox-switching might become possible.

Introduction

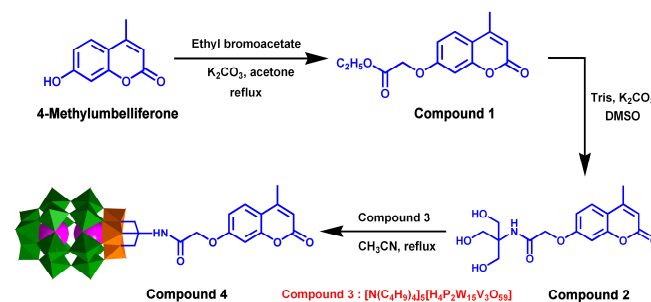
Polyoxometalates (POMs) are anionic molecular metal oxides typically based on early transition metals (e.g. V, Mo, W). Due to their architectural and chemical variability, POMs have been widely applied in energy conversion, catalysis, medicine and molecular nanoscience.¹⁻⁵ In recent years, it has been recognized that covalent functionalization of POMs gives unique access to tailor-made POM-containing organic-inorganic hybrids which allow the bottom-up design of multifunctional materials.⁵⁻⁶ In terms of construction of novel POMs-based hybrid materials, careful selection and design of the organic and inorganic building units as well as the control of synergistic interactions between the counterparts is critical.^{2,7}

A prime example for this approach is the organo-functionalization of the Wells-Dawson anion $[P_2V_3W_{15}O_{62}]^{9-}$. Functionalization of the “ $\{V_3\}$ ” cap of the anion (Fig. 1) with organic tri-alcohols such as tris (= tris(hydroxymethyl)-aminomethane) has given access to valuable building blocks for tailor-made organic-inorganic hybrid materials through hydrogen bonding, π - π interactions and covalent functionalization.^{8,9}

In our own research we have focused on the organo-functionalization of the smaller Anderson anion $[MnMo_6O_{24}]^{9-}$ where tris functionalization is also possible. Following this general route, we have recently shown that functionalization of the Anderson cluster with coumarin gives access to reactive hybrid materials which undergo spontaneous photopolymerization upon irradiation with UV light.¹⁰ Coumarin was chosen as an easily accessible model compound with

well-known photoreactivity. Its linkage to POM anions also shows that POMs can be functionalized with natural products, potentially offering access to bio-active hybrid materials.

Here, our research focus is to broaden our understanding of the photochemical reactivity of coumarin-functionalized POMs. To this end, we opted to covalently attach a suitable coumarin-derivative to the Wells-Dawson anion $(nBu_4N)_5H_4[P_2V_3W_{15}O_{62}]$ (**3**) using the tris-functionalization route described earlier. In the following step, we were then interested in examining the behavior of the compound under irradiation.



Scheme 1. The synthetic procedure for compound **4** with the molecular formula of $(nBu_4N)_4H_2[C_{12}H_9O_4NHC(CH_2O)_3P_2V_3W_{15}O_{59}]$.

Experimental

All chemicals were purchased from Alfa Aesar and used without further purification except for CH_3CN , which was dried by distillation in the presence of CaH_2 prior to use. 1H

NMR spectra were recorded on a AV400 NMR spectrometer with DMSO-*d*₆ and CD₃CN solvent.

Electrospray ionization mass spectra (ESI-MS) of compound **1** and **2** were recorded on a Xevo G2 QT mass spectrometer using methanol as solvent, while the ESI-MS spectrum of compound **4** was recorded on a Bruker APEX IV FTMS in negative ion mode using CH₃CN as solvent. Fourier transform infrared (FT-IR) spectra were carried out on a Bruker Vector 22 infrared spectrometer using KBr pellets; intensities are given as vs = very strong, s = strong, m = medium, w = weak, and vw = very weak. UV-Vis absorption spectra were recorded on a TU-1901 Double-beam ultraviolet-visible spectrophotometer. Elemental analyses were performed on a VarioEL cube from Elementar Analysensysteme GmbH.

Ethyl 2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy) acetate¹¹ (Compound **1**), N-(1,3-dihydroxy-2-(hydroxymethyl)propan-2-yl)-2-((4-methyl-2-oxo-2*H*-chromen-7-yl)oxy)acetamide¹¹ (Compound **2**, denoted as Coumarin-Tris), and (*n*Bu₄N)₅H₄[P₂V₃W₁₅O₆₂]^{6a,6b} (compound **3**) were prepared according to literature methods.

Synthesis of (*n*Bu₄N)₄H₂[C₁₂H₉O₄NHC(CH₂O)₃P₂W₁₅O₅₉] (Compound **4**)

Compound **3** (3.0 g, 0.6 mmol) was dissolved in 60 mL of acetonitrile. Compound **2** (0.2 g, 0.6 mmol) was added and the solution was refluxed in the dark under N₂ atmosphere for 6 days. The resulting solution was added drop wise to an excess of diethyl ether under vigorous stirring, and the resulting solid was collected. The solid was dried under vacuum, dissolved in acetonitrile (10 mL), re-precipitated using an excess of dry diethyl ether, and finally dried overnight in vacuum. The greenish-yellow precipitate was then dissolved in acetone (20 mL) and re-crystallized by diethyl ether diffusion into acetone solution of compound **4**. Yield 2.50 g (83 %, based on (*n*Bu₄N)₅[H₄P₂W₁₅V₃O₆₂]). ¹H NMR (400 MHz, CD₃CN-*d*₃, ppm) δ = 7.71 (m, 1H), 7.09 (m, 2H), 6.67 (m, 1H), 6.19 (m, 1H), 5.78 (m, 6H), 4.57 (m, 2H), 3.17 (m, 32H), 2.43 (m, 3H), 1.67 (s, 32H), 1.43 (d, *J* = 6.39 Hz, 32H), 1.02 (t, *J* = 6.62 Hz, 48H); ³¹P NMR (162 MHz, CD₃CN-*d*₃, ppm) δ = -7.61 (s, 1P), -13.71 (s, 1P). FT-IR (KBr, cm⁻¹): ν = 2960 (m), 2930 (m), 2871 (m), 2361 (vw), 1710 (w), 1654 (vw), 1616 (w), 1483 (m), 1383 (w), 1088 (s), 1021 (vw), 956 (s), 910 (s), 817 (vs), 733 (s), 598 (w), 527 (w), 475 (w). Elemental analysis calcd. (%) for C₈₀H₁₆₂N₅O₆₆P₂V₃W₁₅: C 18.40, H 3.13, N 1.34, Found: C 20.99, H 3.77, N 1.65.

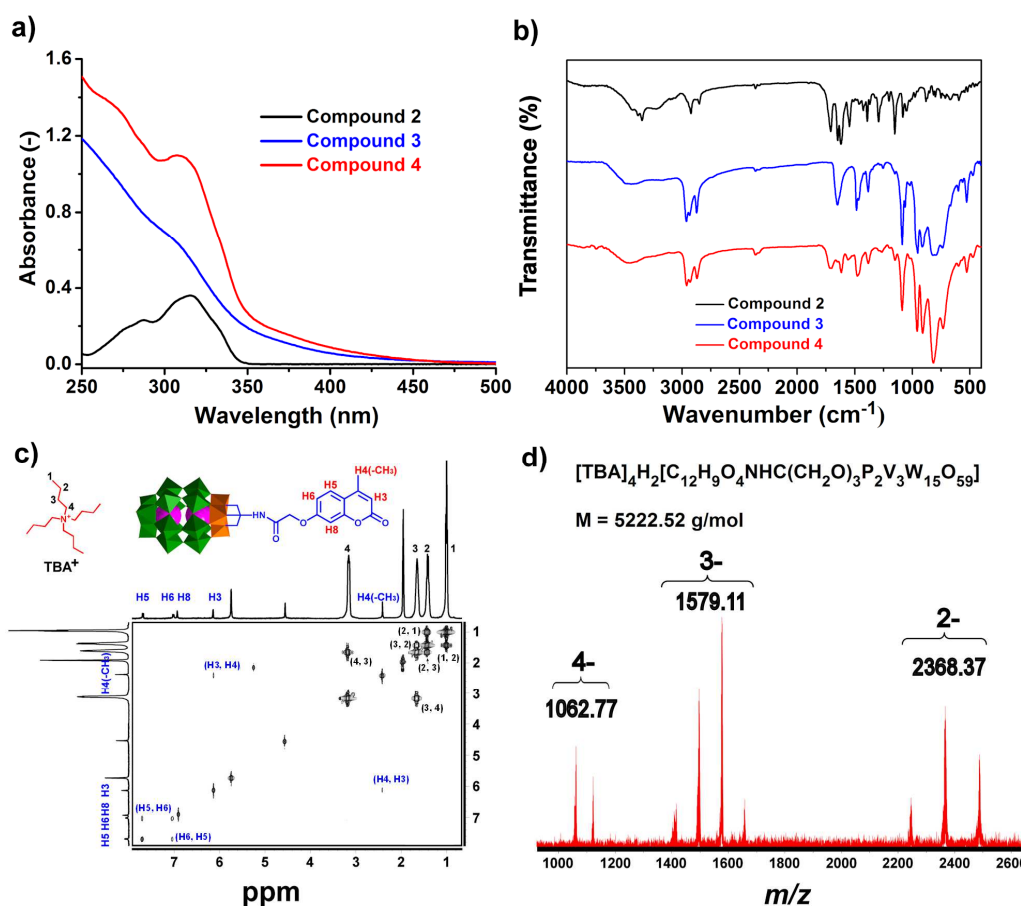


Figure 1. (a) UV-Vis and (b) FT-IR spectroscopy studies of compounds **2**, **3** and **4**; (c) 2D NMR and (d) ESI-MS spectrum of compound **4**.

ARTICLE

Results and discussion

Although the coumarin photochemistry has been studied extensively, most studies have so far been focused on purely organic derivatives and polymers.¹²⁻¹⁷ In contrast, only few examples of coumarin-functionalized POMs have so far been reported and their photo-reactivity is little understood.¹⁰ In this work, we present the successful covalent attachment of the coumarin-derivative **2** (Coumarin-tris) to the Wells-Dawson anion **3** ($(n\text{Bu}_4\text{N})_5\text{H}_4[\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{62}]$) by reaction of both compounds in MeCN for 6 days (Scheme 1). Compound **4**, $(n\text{Bu}_4\text{N})_4\text{H}_2[\text{C}_{12}\text{H}_9\text{O}_4\text{NHC}(\text{CH}_2\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]$, was isolated in yields of 85%, and was fully characterized by ^1H NMR, FT-IR, UV-Vis, 2D COSY NMR and ESI-MS spectroscopy.

Fig 1a shows the UV-vis spectra of **2**, **3** and **4**. The organic coumarin-tris derivative **2** features a characteristic transition at 308 nm; in contrast, the inorganic Wells-Dawson anion **3** only features non-characteristic LMCT transitions tailing into the visible up to ca. 450 nm. The coumarin-functionalized Wells-Dawson anion **4** in essence combines the absorption features of both precursors and still features the tailing LMCT transitions as well as the characteristic, coumarin-based absorption peak at 307 nm. In Fig 1b, the FT-IR spectrum of **2** shows the stretching bands of N-H and C=O at 3347 and 1708 cm^{-1} , respectively. Compound **3** exhibits C-H vibrations at 2962, 2873, 1485 and 1383 cm^{-1} , and P-O vibration at 1654 and 1087 cm^{-1} ; the stretching bands at 952, 914, 1020 and 822 cm^{-1} correspond to W=O, W-O-W, V=O and V-O-V, respectively. The hybrid compound **4**, features stretches associated with the organic and the inorganic precursors: C-H absorption at 2960, 2930, 2871, 1483, 1383 cm^{-1} ; C=O absorption at 1710 cm^{-1} ; P-O at 1654 and 1088 cm^{-1} ; and W-O and V-O at 1021, 956, 910, 817 cm^{-1} . These results are consistent with the molecular structures of **2-4**.

The 2D COSY NMR spectroscopy provides further support for the formation of **4** (see Fig. 1c). The results show the correlation between H5 and H6, as well as H3 and H4 ($-\text{CH}_3$) in the coumarin moiety, and/or the protons of $n\text{Bu}_4\text{N}^+$ in compound **4**. ESI-MS spectroscopy of **4** in negative ion mode (Fig 1d) shows signals associated with the complete cluster anion at $m/z = 2368.37$, 1579.11 and 1062.77; these are assigned to $\{[n\text{Bu}_4\text{N}]_2\text{H}_2[\text{C}_{12}\text{H}_9\text{O}_4\text{NHC}(\text{CH}_2\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]\}^{2-}$, $\{[n\text{Bu}_4\text{N}]\text{H}[\text{C}_{12}\text{H}_9\text{O}_4\text{NHC}(\text{CH}_2\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]\}^{3-}$ and $\{\text{H}_2[\text{C}_{12}\text{H}_9\text{O}_4\text{NHC}(\text{CH}_2\text{O})_3\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}]\}^{4-}$, respectively. The above results demonstrate that the coumarin-tris moiety has been successfully grafted onto the Well-Dawson cluster.

As the photo-reactivity, and in particular the photo-dimerization of coumarin is well-established, we were

interested to determine whether photo-dimerization is also possible for the hybrid compound **4**. To this end, **4** was irradiated with UV light at 365 nm and 254 nm in MeCN solution, respectively. The UV-Vis spectral changes were followed spectroscopically as a function of time. Upon irradiation at 365 nm, a decrease of the coumarin-based transition at 307 nm was observed (Fig 2a), which is consistent with a photo-induced dimerization of **4** (Fig 2b). This process is reversible upon irradiation of the dimerization species at 254 nm. Initial studies suggested second-order kinetics; thus, the concentration changes of **4** were plotted as $(1/C_t - 1/C_0)$ against irradiation time t (Fig 2b; C_0 = initial concentration of **4**; C_t concentration of **4** at irradiation time t). The linear fit of the kinetic data reveals pseudo-second-order reaction kinetics with $R^2 = 0.9920$. The rate constant k of the dimerization reaction is determined to be $0.0189 \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ on the basis of equation (1) and (2). Based on the UV-Vis spectroscopy, the reaction reaches a plateau after ca. 15 min.

$$-\frac{dC_t}{dt} = kC_t^2 \dots\dots\dots (1)$$

$$\frac{1}{C_t} - \frac{1}{C_0} = kt \dots\dots\dots (2)$$

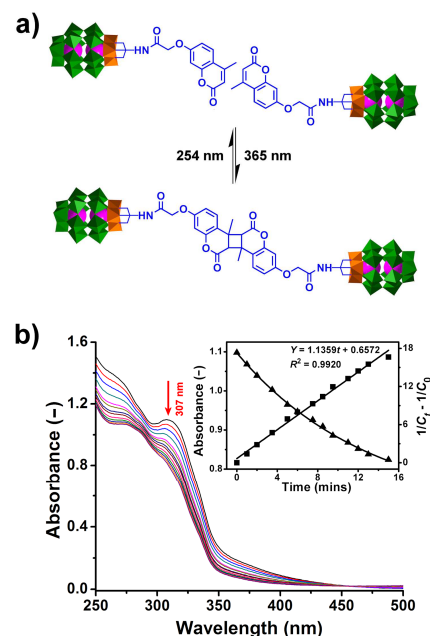


Figure 2. a) Schematic representation of the photo-induced dimerization process, b) UV-Vis spectroscopy change upon photo-irradiation at 365 nm ($2 \times 10^{-5} \text{ mol/L}$ CH_3CN solution) with the time increase.

The photoreaction can also be followed by $^1\text{H-NMR}$ spectroscopy: before irradiation, **4**, features signals at $\delta = 6.2$ (H3) and 2.4 (H4) ppm, respectively; after irradiation for 15 min, these signals shift to $\delta = 3.2$ (H3) and 1.5 (H4) ppm, respectively, see Fig.3a. This observation is consistent with the photo-dimerization of the coumarin groups in **4**, leading to the formation of a cyclobutane-type bridge (Fig. 3).

The photo-controlled dimerization of **4** was further characterized by 2D COSY NMR spectroscopy. Before irradiation of **4**, the signals for H3(-CH) and H4(-CH₃) appear at 6.2 ppm and 2.4 ppm, which shift to 3.3 ppm and 1.9 ppm upon irradiation, respectively. It should be noted that (1) after irradiation, there is no correlation between H_d3(-CH) and H_d4(-CH₃); (2) Upon photo-irradiation, as shown in Fig 3b, the H₅, H₆ and H₈ in coumarin moiety of compound **4** have shifted from 7.71, 7.03 and 6.94 to 7.58 (H_d5), 6.86 (H_d6) and 6.75 (H_d8) ppm, respectively. The correlation between H5 and H6 still exist. Moreover, the conjugate system of the coumarin moiety is destroyed due to the formation of the cyclobutane-bridged photo-dimer after irradiation, leading to the above-mentioned chemical shifts.

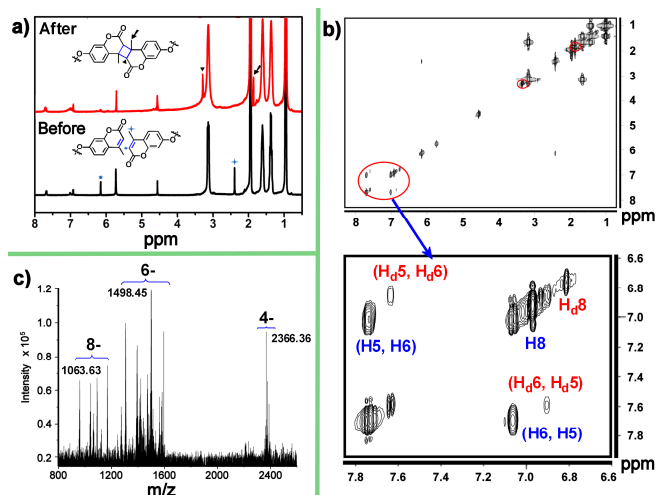


Figure 3. $^1\text{H-NMR}$ (a) and ESI-MS (c) of photo-irradiation of compound **4**; (b) 2D NMR spectroscopy after irradiation of compound **4** under UV light of 365 nm.

As shown in Figure 3c, the ESI-MS spectrum after 15 min photo-irradiation of **4** exhibits three different groups of peaks at 1063.63, 2366.36 and 1498.45 m/z, respectively; these correspond to the dimeric units $[(n\text{Bu}_4\text{N})_4\{\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNHC}_{12}\text{H}_9\text{O}_4\}_2]^{8-}$, $[(n\text{Bu}_4\text{N})_6\{\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNH-C}_{12}\text{H}_9\text{O}_4\}_2]^{6-}$ and $[(n\text{Bu}_4\text{N})_8\{\text{P}_2\text{V}_3\text{W}_{15}\text{O}_{59}(\text{OCH}_2)_3\text{CNH-C}_{12}\text{H}_9\text{O}_4\}_2]^{4-}$, respectively. ESI-MS analysis therefore provides further evidence of the dimer formation.

To examine the dimerization of **4** in solution, dynamic light scattering (DLS) analysis was utilized to provide information of the particle size changes upon irradiation. As shown in Fig. 4, before photo-irradiation, an average particle size for **4** of ~ 2 nm

was observed in MeCN solution. After irradiation under standard conditions, larger particles with an average particle size of ~ 55 nm were observed. This aggregation cannot only be associated with the dimerization process but suggests that the dimers undergo an additional aggregation step, which might be associated with the increased molecular charge of the dimer species; the presence of these aggregates was further observed by transmission electron microscopy (TEM) where particles in the 40-70 nm size range were observed (see ESI); however, further studies on the solution aggregation of the dimer are required to fully understand the aggregation behaviour. Contrast experiments using the non-functionalized Wells-Dawson anion **3** as a model show no changes in particle size upon photo-irradiation. Interestingly, both compounds **3** and **4** show pronounced colour changes upon irradiation; for **3**, a colour change from yellow to light green is observed; for **4**, the colour changes from light yellow to deep brown. Both colour changes are associated with the photo-induced reduction of the metal centres within the cluster shell.¹⁸

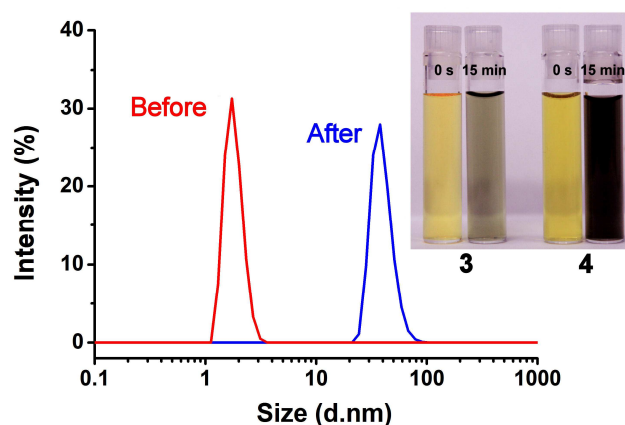


Figure 4. Size distribution of compound **4** by DLS at a concentration of 400 μM before and after photo-irradiation at $\lambda = 365$ nm; Inset: the colour change before and after photo-irradiation of compound **3** (left) and compound **4** (right).

To probe the photo-induced redox process within the metal oxide cluster shell, X-ray photoelectron spectroscopy (XPS) was used to gain insight into the metal oxidation states of **4** before and after irradiation (Fig. 5). Using the XPS curve fitting procedure of Doniach and Sunjic,¹⁹ As shown in Figure 5, before photo-irradiation, XPS analyses of **4** show the $\text{W}4\text{f}_{5/2}$ and $\text{W}4\text{f}_{7/2}$ at 37.8 eV and 35.6 eV, and the $\text{V}2\text{p}_{3/2}$ at 516.79 eV, which are in good agreement with the expected signals for W^{6+} and V^{5+} ions, respectively.

After photo-irradiation of **4** at 365 nm, two signals for $\text{V}2\text{p}_{3/2}$ are observed at 516.34 eV and 515.46 eV, respectively, indicating the reduction of one or several V^{5+} ions to V^{4+} . It is important to notice that photo-dimerization of the coumarin and photo-reduction of the vanadium centres are two distinct and independent processes which are chemically not linked. They might however be combined to give multi-functional materials where redox-switching and dimerization can be simultaneously triggered by a single input signal. The XPS deconvolution shows four different W-based peaks ($\text{W}4\text{f}_{5/2}$ and $\text{W}4\text{f}_{7/2}$),

suggesting the presence of two types of W centres. This might be due to the different chemical environments of the W^{6+} ions (i.e. purely W-O-W vs mixed W-O-W and W-O-V bridges). Alternatively, the observed signals might be due to beam damage during the XPS measurement, resulting in partial W^{6+} reduction on the sample surface. However, from, UV-Vis and EPR spectroscopy (see below), W^{6+} reduction during the photoirradiation is not observed.

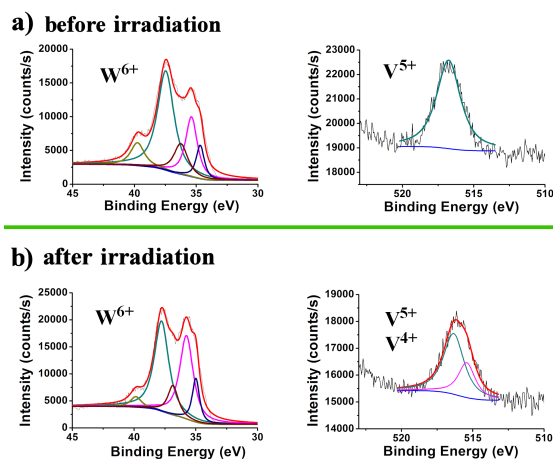


Figure 5. XPS analyses of the oxidation state of W and V (a) before and (b) after irradiation of compound **4**.

To provide further support that the V^{5+} ions in **4** are partially reduced upon irradiation, X-band EPR analyses were carried out in MeCN at room temperature (Fig 6). Before photo-irradiation, the EPR spectrum of **4** is EPR silent, which is in line with the diamagnetic nature of **4**. After photo-irradiation of **4** at 365 nm, the spectrum exhibits an characteristic V^{4+} signal closely matching previous literature reports.²⁰ The observed hyperfine coupling is due to the 7/2 nuclear spin of the ^{51}V and suggests that the unpaired electron is localized on a vanadium centre.²⁰ Thus, EPR spectroscopy provides further evidence for the photo-induced vanadium reduction in **4**. EPR gives no indication for the presence of W^{5+} .

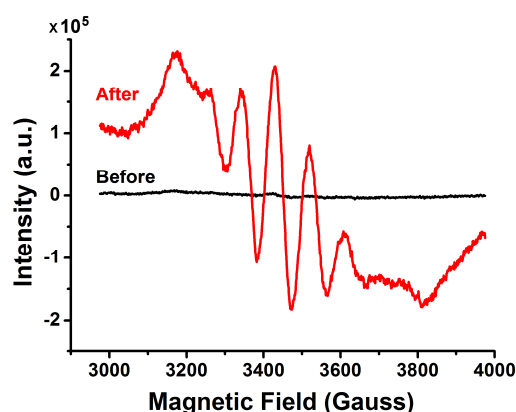


Figure 6. EPR spectroscopy of compound **4** in MeCN before and after irradiation at room temperature.

Conclusion

In summary, a photosensitive coumarin-functionalized POM has been accessed by reaction of a vanadium-functionalized Wells-Dawson anion with a triol-substituted coumarin-derivative. The resulting hybrid of compound **4** is fully characterized and shows photo-controlled reversible dimerization behaviour upon alternating photo-irradiation at 365 nm and 254 nm. Evidence for the dimer formation is observed by UV-Vis, 1D and 2D- 1H -NMR spectroscopy and ESI-MS analysis. Upon irradiation, a second photochemical process is observed namely the reduction of V^{5+} species to V^{4+} within the cluster shell; this is confirmed by XPS and EPR analyses. In contrast, the W^{6+} is not affected by the photo-irradiation. The photo-sensitive material based on coumarin modified Wells-Dawson cluster provides an excellent example for the rational design and well-controlled development of light-responsive, reversibly switchable materials. Future work will target the development of systems where the responsiveness to external stimuli can be tuned by modification of the organic and inorganic moieties.

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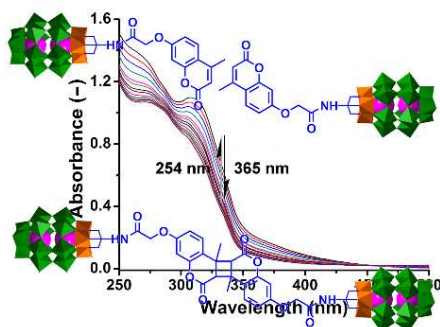
Notes and references

- ^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China. E-mail: songyufei@hotmail.com, songyuf@mail.buct.edu.cn; Fax: (+86) 10-64431832;
^b Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany. Email: carsten.streb@uni-ulm.de.

† Electronic Supplementary Information (ESI) available: Analytical, spectroscopic and microscopic details are given. See DOI: 10.1039/b000000x/

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The light-driven reversible dimerization of a coumarin-functionalized organic-inorganic hybrid polyoxometalate anion and the resulting changes in their aggregation and redox-behaviour are reported.