JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

A Photo-driven Polyoxometalate Complex Shuttle and Its Homogeneous Catalysis and Heterogeneous Separation

Yang Yang, Bin Zhang, Yizhan Wang, Liang Yue, Wen Li,* and Lixin Wu*

State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China

Supporting Information

ABSTRACT: A "smart" core−shell complex is designed to combine a catalytic reaction and automatic separation through remote light control. Here, we present the induced amphiphilic behavior of a surfactant-encapsulated polyoxometalate complex with photoresponsive azobenzene units on the periphery. The reversible phase transfer of the complex shuttle between two incompatible phase termini, driven by a photoisomerization-induced polarity change, further facilitates the separation and recycle of the catalyst.

Homogeneous catalysis has higher activity and selectivity than heterogeneous catalysis, but it is often inconvenient for industrial purposes.[1] In contrast, heterogeneous catalysis is easier to run and separate, yielding a sustainable catalytic process even if sophisticated post-treatment becomes necessary. Consequently, automatic heterogenization of homogeneous catalysts is of interest. If the catalytic reaction is controllable through the catalyst's response to environmental stimuli such as pH, magnetism, temperature, light, external chemicals, and so on,[2] the catalysis becomes "smart" and valuable. Polyoxometalates (POMs) are discrete nano-sized metal oxide clusters with abundant compositions and structures, and versatile properties leading to potential applications in the fields of medicine, photochromic materials, solar energy, and so forth.[3−6] Because of their specific redox properties, POMs have also been widely used as effective catalysts for oxidations of various compounds such as alkenes, alcohols, sulfides, and even water.[7−11] To improve the high lattice energy, the low mass transfer, and the low compatibility with organic solvents, the surfaces of POMs are often modified to increase their ability to adapt to different chemical environments.[12−17] Among the reported strategies, a simple and frequently used approach is to replace the counterions of POMs with cationic amphiphiles, generating surfactant-encapsulated POM (SEP) complexes.[18] When the complexes are applied for homogeneous catalysis, they show superior efficiency and selectivity compared to POM-based heterogeneous catalysts.[19] However, the separation and recycle of POM catalysts from reaction systems remain a key challenge. Many efforts have been made to realize both high reaction efficiency and quick separation of POM complexes: nanofiltration,[20] addition of poor solvent,[21] magnetic field,[22] temperature-controlled phase separation,[23] and reaction-controlled phase separation[24,19] methods have been developed to separate POM-based homogeneous catalysts. But these recovery routes also involve a post-treatment filtration procedure, which restrains their possible use in microfluidic systems and trace utilizations.[25] Therefore, more convenient approaches that can separate POM catalysts from the reactions automatically through a remote control are needed.

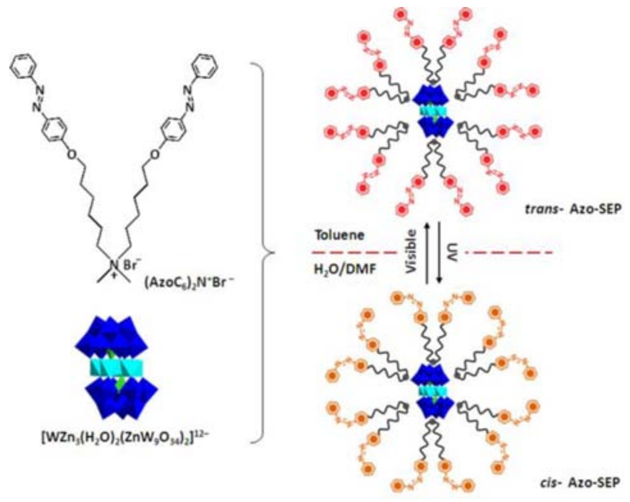
Light is an excellent trigger because of its noninvasive character and the easy mediation of wavelength, intensity, illuminated area, and duration. Wang et al. demonstrated the recycle of a homogeneous ruthenium−carbene catalyst via the light-controlled reversible transition of a nitrobenzospiropyran unit.[25] Azobenzene (Azo) derivatives possess a photosensitive group and undergo a reversible isomerization upon light irradiation.[26,27] In the *trans* state, the Azo group is in its linear structure and its polarity is small due to the axial symmetry, while in the *cis* state, the bent structure leads to an increased dipolar moment due to its non-axial symmetry. This configuration change provides a favorable feature for controlling both spatial alignment and polarity of Azo-containing compounds, because the former can be utilized for reversible transformation of self-assembled structures and the latter can be applied for assembly and disassembly of complexes.[28,29] Therefore, it can be predicted that, by selecting incompatible solvents, the Azo-group-containing POM complexes can be applied to controllable phase separation systems, with performance superior to that of most known phase-transfer methods for nanoparticles.[30−35] To realize an agile recovery of POM-based catalysts, we design and prepare a photoresponsive SEP complex in which the surface of the POM is electrostatically modified with cationic surfactants bearing Azo groups at the hydrophobic ends (Scheme 1). By alternating irradiations with UV and visible lights, we successfully create a deft method to recycle the homogeneous catalyst using this POM complex as a reversible phase-transfer shuttle.

A POM with zinc-sandwiched structure possessing catalytic activity, $Na_{12}[WZn_3(H_2O)_2(ZnW_9O_{34})_2]$[36] (its polyanion is abbreviated as $Zn_5W_{19}O_{68}$), is selected as the polyanionic core, and an Azo-ended cationic surfactant (its cation is abbreviated as $(AzoC_6)_2N$)[29] is employed as the responsive shell. By mixing the inorganic cluster aqueous solution and organic surfactant chloroform solution, a photoresponsive complex, Azo-SEP, was prepared through an ion-exchange reaction.[37] Due to the electrostatic interaction, the counterions of POM clusters were easily replaced by hydrophobic cations. Unlike the $Zn_5W_{19}O_{68}$ cluster that is soluble in water, the obtained Azo-SEP complex was immiscible in water but readily dissolved in common

Received: June 10, 2013
Published: September 16, 2013

dx.doi.org/10.1021/ja4057882 | *J. Am. Chem. Soc.* 2013, 135, 14500−14503

Scheme 1. Chemical Structures of Cationic Surfactant $(AzoC_6)_2N^+Br^-$ and a POM Cluster and Preparation of an Azo-SEP Complex, as Well as Reversible Phase Transfer of the Complex between Toluene and H_2O/DMF Mixed Solution



organic solvents, e.g., toluene, dimethylformamide (DMF), tetrahydrofuran, and chloroform. The solubility change indicates successful encapsulation, and the obtained complex has an average chemical formula of $[(AzoC_6)_2N]_9Na_3[Zn_5W_{19}O_{68}]$ (MW = 10 474.25), which is identified by FT-IR, ^{1}H NMR, elemental analysis, thermogravimetric analysis, and MALDI-TOF measurements. A 53.5% (in w/w) mass loss before 700 °C (Figure S2, Supporting Information) matches well with the theoretical value of 53.2%, estimated from the above chemical formula by assuming that the organic component decomposes completely and the POM transforms into its corresponding oxides. In the NMR spectra taken in both $CDCl_3$ and D_2O/DMF-d_7 mixed solvents (Figures S3 and S4), obvious proton peak shifting and broadening are observed for the $(AzoC_6)_2N$ component in Azo-SEP. Compared with the signals of free surfactant, these changes confirm the strong electrostatic interaction between the cationic head and the anionic POM in both solutions. The absorption bands of W−O and W−O−W vibrations (Table S1) in FT-IR spectra of the complex (Figure S5) indicate the well-kept frame structure of POM and support the strong electrostatic interaction between surfactant and POM. The MALDI-TOF result (Figure S6) around 10 475 confirms the predicted chemical formula.

It has been reported that the hydrophobicity change resulting from isomerization of the Azo group triggers opposite assembling behaviors of Azo-SEP in strongly polar and weakly polar solvents.[29] Similarly, in the present study, the turbid solution and bigger size of aggregates imply poorer solubility, while the transparent solution and good dispersion reflect good solubility (Figures S8 and S9). Typically, Azo-SEP in its *trans* state dissolves well in the weakly polar solvent toluene but poorly in the strongly polar solvent H_2O/DMF (1:1 vol/vol). In contrast, Azo-SEP in its *cis* state displays the opposite behavior in the two solvents. Importantly, because the two solvents are often used in chemical reactions and are immiscible with each other, we select them as phase termini for the photosensitive phase-transfer study of the POM complex shuttle. Upon 365-nm light irradiation, the Azo group isomerizes from *trans* to *cis* form, while under visible light irradiation around 450 nm, the reverse change from *cis* to *trans* form takes places.[26,27] UV−vis spectral characterization (Figure S10) verifies the reversible isomerization of Azo groups in both toluene and H_2O/DMF solutions. No obvious degradation is found even after 10 cycles of photoisomerizations. For both cases, the photostationary state can be reached in less than 2 min, though the transformation from *trans* to *cis* is faster than the reverse process (Figures S11 and S12). The rapid isomerization is further characterized by ^{1}H NMR spectra (Figure S13), and the result shows that over 94% of the initial Azo groups are in the *trans* form in polar solvent. After UV light irradiation, 98% of the Azo groups isomerize into the *cis* form. With subsequent visible light irradiation of the solution, only 70% of the *cis*-form Azo groups return to the *trans* form. This non-equivalent back-transformation further indicates the polar character of the complex with its Azo groups in *cis* state and the non-polar character of the complex with its Azo groups in *trans* state.

When the two immiscible solvents are mixed in one glass vessel, as expected, the photomediated reversible phase transfer of Azo-SEP is observed upon alternate UV and visible light irradiations, as shown in Figure 1. At the initial state or upon visible light irradiation, the upper toluene phase is transparent and yellow in color, while the bottom H_2O/DMF phase is colorless, indicative of the complex mainly existing in toluene. Upon UV light irradiation, the upper toluene phase turns to colorless, while concurrently the bottom phase becomes yellow, indicating the phase transfer of the complex. It is known that the polarity of Azo-SEP bearing *cis*-Azo groups is much higher than that of it bearing *trans*-Azo groups.[27] So, at the initial state and/or upon visible light irradiation, the *trans*-state Azo-SEP complex with smaller polarity prefers to stay in the toluene phase. After UV light irradiation, the Azo groups isomerize into the *cis* form, the polarity becomes larger, and the complex is no longer compatible with toluene. The increased polarity propels the complex to depart from toluene and enter into the polar solvent of H_2O/DMF. Upon visible light irradiation, the formation of *trans*-Azo groups makes the polarity decrease, which drives the complex to transfer back into the toluene phase. Therefore, it is the photoisomerization-induced polarity change of Azo groups that triggers the photoresponsive phase transfer of Azo-SEP between toluene and H_2O/DMF phases. According to the UV−vis spectra (Figure 2), the phase-transfer efficiency of the Azo-SEP complex can reach 98−99% when the volume ratio of H_2O/DMF is increased to 2:1, while the value is ca. 96−98% when the volume ratio remains at 1:1 (Figure S14), and the values remain similar even after 10 transfer cycles. The incomplete phase transfer of Azo-SEP is probably caused by trace amounts of DMF in the toluene phase and toluene in

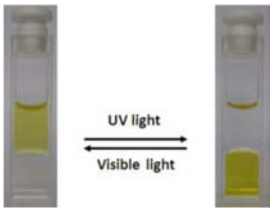


Figure 1. Digital photographs of reversible phase transfer of Azo-SEP complex between toluene and H_2O/DMF (1:1 vol/vol) mixed solution upon UV and visible light irradiations.

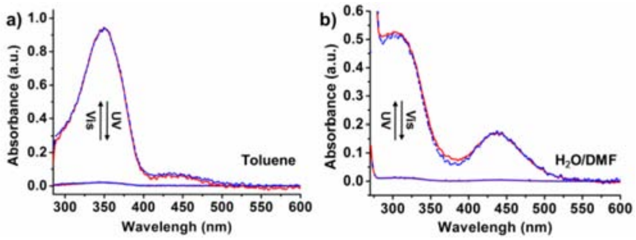


Figure 2. UV−vis spectra of Azo-SEP before and after phase transfer in (a) toluene and (b) H_2O/DMF (2:1 vol/vol) mixed solution upon UV and visible light irradiations: red, after one cycle; blue, after 10 cycles of UV and visible light irradiations.

the H_2O/DMF phase. The higher water content reduces the amounts of DMF in the toluene phase (Figures S15−S17) and toluene in the H_2O/DMF phase (Figures S18−S20). However, further increasing the water content leads to poor phase transfer due to the decreased solubility of the complex.

Next we demonstrate the use of photoresponsive phase transfer and shuttle recycle of the $Zn_5W_{19}O_{68}$ complex with high activity for the oxidation of sulfides to sulfones.[7,36] Phenothiazine (PH), a useful intermediate in organic synthesis, is selected as the substrate to carry out the homogeneous catalysis. Due to its hydrophobicity, PH was oxidized in toluene at 30 °C with cumyl hydroperoxide (CHP) as the homogeneous oxidizing agent. The UV−vis spectral change of the reaction mixture as a function of reaction time clearly reveals the oxidation process (Figure 3 and Figure S21). The absorption band at 319 nm, deriving from the initial PH, decreases as the reaction proceeds and finally disappears, while the intensities of the bands at 306 and 339 nm corresponding to the oxidized product apparently increase. At the same time, the color of the reaction solution becomes a bit darker after the oxidation (Figure 4). Due to the homogeneous catalytic reaction, the reaction is quick and finishes when the spectrum is no longer changing. According to the NMR result (Figure S22), the substrate PH has been completely oxidized into its product *S,S*-dioxide (PHDO) in 4 h. After addition of the same volume of H_2O/DMF mixed solvent as that of toluene followed by UV light irradiation, the Azo-SEP catalyst transfers to the water phase automatically due to the increased polarity of *cis*-Azo-SEP, while the light pink product and residual oxidant remain in the toluene phase (Figures S18 and S23). Through a simple phase separation operation, the homogeneous catalyst can be easily removed from the reaction phase. Furthermore, after addition of the substrate solution, Azo-SEP catalyst can be conveniently transferred back to the toluene phase through a simple visible light irradiation, and the catalytic oxidation takes place again. After several recycles, the catalyst is confirmed to be quite stable, and no obvious decomposition is found (Figures S24 and S25). Using the same extraction solvent in the subsequent recycles, after five recycles the recovered complex catalyst is still at ca. 88.6−94.1% of its initial amount in the case of the 2:1 volume ratio of H_2O/DMF mixed solvent (Figure S26).[38] Because of partial loss of the catalyst, the product selectivity becomes low (Figure S27), but it can be recovered by prolonging the reaction time or supplementing the catalyst.

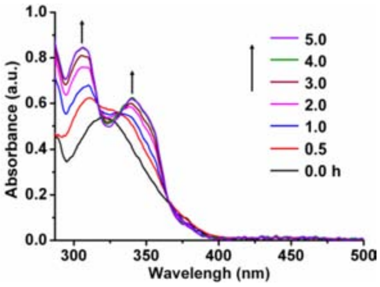


Figure 3. UV−vis spectra of PH oxidation reaction in toluene solution versus reaction time under the catalysis of Azo-SEP. The reaction solution has been diluted 40-fold.

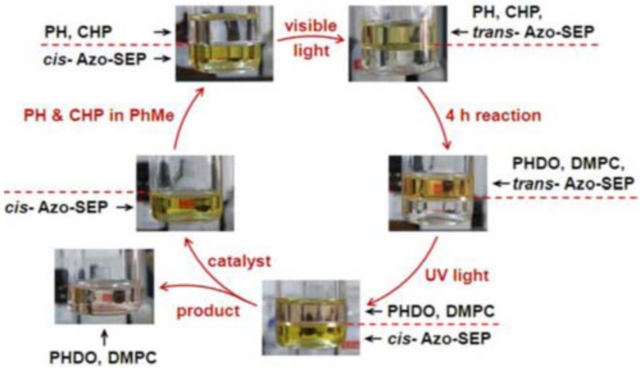


Figure 4. Schematic catalytic and phase-transfer recycle of photoresponsive catalyst Azo-SEP, driven by alternate UV and visible light irradiations (reduced oxidant DMPC = dimethylphenylcarbinol).

To confirm the universality of such a concept, we utilize Azo-ended surfactants to encapsulate POMs with different charges and topological shapes, Keplerate-type $(NH_4)_{72}\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}\{Mo_2O_4(SO_4)\}_{30}$ (Mo_{132}) and disk-like $K_{12.5}Na_{1.5}[NaP_5W_{30}O_{110}]$ (P_5W_{30}),[39] to prepare two new complexes. As expected, upon UV and visible light irradiations, reversible phase transfers of these two complexes between two phases were also observed, as can be seen in Figure S28. We also employed the (P_5W_{30}) complex as the homogeneous catalyst for the oxidation of PH (Figure S29) and successfully recycled it through light-mediated reversible phase transfer.

In summary, we have demonstrated a "smart" photoresponsive catalyst based on a POM hybrid complex, which combines the advantages of both a homogeneous catalyst and heterogeneous separation. The POM hybrid complex shows high catalytic activity and can be easily recycled through a simple photomediated phase transfer. The polarity change of the complex induced by the photoisomerization of Azo groups on the periphery is distinct enough to trigger the reversible transfer of the complex shuttle between two immiscible solvents. The present method provides a general strategy for recycle of POM-based homogeneous catalysts and similar systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and characterization details, and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

wenli@jlu.edu.cn
wulx@jlu.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the National Basic Research Program (2013CB834503), NSFC (91227110, 21221063), Ministry of Education of China (20120061110047), 111-Project (B06009) for the collaboration with WVU, and Open Project of SKL of Polymer Physics & Chemistry, CAS.

■ REFERENCES

(1) Cornils, B.; Herrmann, W. A. *J. Catal.* **2003**, *216*, 23.
(2) Bergbreiter, D. E. *Catal. Catal.* **2000**, *42*, 321.
(3) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.
(4) Long, D.-L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105.
(5) Special issue on "Polyoxometalates". *Chem. Rev.* **1998**, *98*, 1−390.
(6) Special issue on "Polyoxometalates cluster science". *Chem. Soc. Rev.* **2012**, *41*, 7325−7648.
(7) Vasylyev, M. V.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 884.
(8) Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.; Hikichi, S.; Mizuno, N. *Science* **2003**, *300*, 964.
(9) Lü, H.; Gao, J.; Jiang, Z.; Jing, F.; Yang, Y.; Wang, G.; Li, C. *J. Catal.* **2006**, *239*, 369.
(10) Carraro, M.; Sartorel, A.; Toma, F.; Puntoriero, F.; Scandola, F.; Campagna, S.; Prato, M.; Bonchio, M. *Top. Curr. Chem.* **2011**, *303*, 121.
(11) Hill, C. L. *J. Mol. Catal. A: Chem.* **2007**, *262*, 2.
(12) Nlate, S.; Astruc, D.; Neumann, R. *Adv. Synth. Catal.* **2004**, *346*, 1445.
(13) Qi, W.; Wang, Y.; Li, W.; Wu, L. *Chem.—Eur. J.* **2010**, *16*, 1068.
(14) Liu, S. Q.; Kurth, D. G.; Bredenkötter, B.; Volkmer, D. *J. Am. Chem. Soc.* **2002**, *124*, 12279.
(15) Wang, Z. L.; Ma, Y.; Zhang, R.; Peng, A.; Liao, Q.; Cao, Z.; Fu, H. B.; Yao, J. N. *Adv. Mater.* **2009**, *21*, 1737.
(16) Du, Y.; Rheingold, A. L.; Maatta, E. A. *J. Am. Chem. Soc.* **1992**, *114*, 345.
(17) Li, D.; Song, J.; Yin, P.; Simotwo, S.; Bassler, A. J.; Aung, Y.; Roberts, J. E.; Hardcastle, K. I.; Hill, C. L.; Liu, T. *J. Am. Chem. Soc.* **2011**, *133*, 14010.
(18) Kurth, D. G.; Lehmann, P.; Volkmer, D.; Cölfen, H.; Koop, M. J.; Müller, A.; Du Chesne, A. *Chem.—Eur. J.* **2000**, *6*, 385.
(19) Xi, Z.; Zhou, N.; Sun, Y.; Li, K. *Science* **2001**, *292*, 1139.
(20) Witte, P. T.; Chowdhury, S. R.; ten Elshof, J. E.; Sloboda-Rozner, D.; Neumann, R.; Alsters, P. L. *Chem. Commun.* **2005**, 1206.
(21) Boglio, C.; Lemière, G.; Hasenknopf, B.; Thorimbert, S.; Lacôte, E.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3324.
(22) Nisar, A.; Lu, Y.; Zhuang, J.; Wang, X. *Angew. Chem., Int. Ed.* **2011**, *50*, 3187.
(23) Ding, Y.; Zhao, W. *J. Mol. Catal. A: Chem.* **2011**, *337*, 45.
(24) Leng, Y.; Wang, J.; Zhu, D.; Ren, X.; Ge, H.; Shen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 168.
(25) Liu, G.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 4425.
(26) Kumar, G. S.; Neckers, D. C. *Chem. Rev.* **1989**, *89*, 1915.
(27) Han, M. R.; Hirayama, Y.; Hara, M. *Chem. Mater.* **2006**, *18*, 2784.
(28) Yan, Y.; Wang, H.; Li, B.; Hou, G.; Yin, Z.; Wu, L.; Yam, V. W. W. *Angew. Chem., Int. Ed.* **2010**, *49*, 9233.
(29) Yang, Y.; Yue, L.; Li, H.; Maher, E.; Li, Y.; Wang, Y.; Wu, L.; Yam, V. W.-W. *Small* **2012**, *8*, 3105.
(30) Dong, A.; Ye, X.; Chen, J.; Kang, Y.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. *J. Am. Chem. Soc.* **2010**, *133*, 998.
(31) Yuan, X.; Luo, Z.; Zhang, Q.; Zhang, X.; Zheng, Y.; Lee, J. Y.; Xie, J. *ACS Nano* **2011**, *5*, 8800.
(32) Dorokhin, D.; Tomczak, N.; Han, M.; Reinhoudt, D. N.; Velders, A. H.; Vancso, G. J. *ACS Nano* **2009**, *3*, 661.
(33) Qin, B.; Zhao, Z.; Song, R.; Shanbhag, S.; Tang, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 9875.
(34) Cheng, L.; Liu, A.; Peng, S.; Duan, H. *ACS Nano* **2010**, *4*, 6098.
(35) Cioran, A. M.; Musteti, A. D.; Teixidor, F.; Krpetić, Ž.; Prior, I. A.; He, Q.; Kiely, C. J.; Brust, M.; Viñas, C. *J. Am. Chem. Soc.* **2011**, *134*, 212.
(36) Haimov, A.; Cohen, H.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 11762.
(37) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673.
(38) The first recycle loses 1−2% twice from toluene to water and back. After this cycle, there is no additional weight loss in the further recycles of catalyst from H_2O/DMF to toluene phase. Therefore, each of the following recycles loses only 1−2% of catalyst in the transfer process from toluene to water.
(39) As the complex composed of $(AzoC_6)_2N$ and (P_5W_{30}) is not soluble in toluene, we changed the surfactant $(AzoC_6)_2N$ to another Azo-ended surfactant, $(AzoC_6)(C_4)N$. The corresponding synthesis and characterization are shown in the Supporting Information.