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# Radiation sensitive hybrid polymer based on Mn-Anderson polyoxometalate cluster and a UV active organic monomer: synergistic effects lead to improved photocurrent in a photoresponse device

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Vishwanath Kalyani,[a] V. S. V. Satyanarayana,[a] Abdus Salam Sarkar,[a] Ashwani Kumar,[a] Suman K. Pal,[a] Subrata Ghosh,[a] Kenneth E. Gonsalves,*[a] Chullikkattil P. Pradeep*[a]

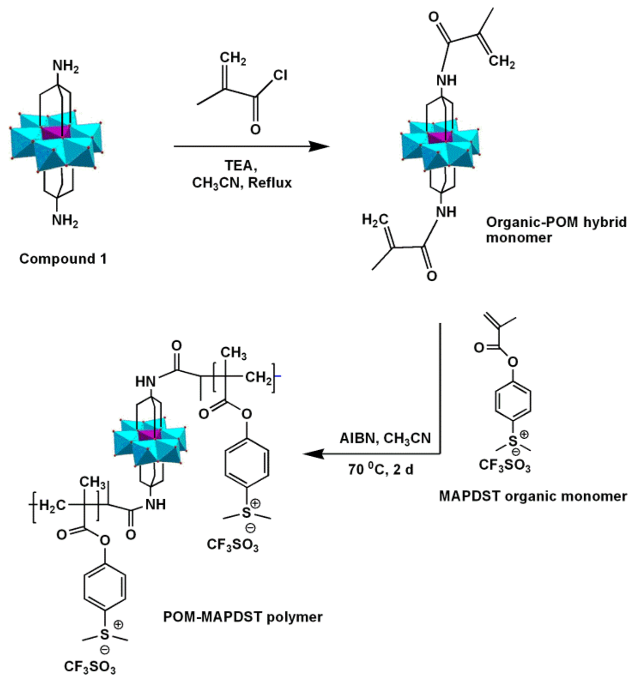
**A new radiation sensitive polyoxometalate/polymer hybrid, POM-MAPDST, has been synthesized from Mn-Anderson cluster based hybrid and a UV active organic monomer and tested for its photo-response properties by fabricating an ITO/POM-MAPDST/Al device. This device showed improved I-V characteristics under illumination possibly due to the synergistic interactions between polyoxometalate cluster and organic components of the hybrid polymer.**

Polymers are among the most widely used materials having applications in diverse areas. The properties as well as the applicability of organic polymers can be enhanced by incorporating inorganic components into the base polymer framework.[1-4] Polyoxometalates (POMs) are an important group of inorganic components used in the development of inorganic-organic hybrid polymers. POMs are a class of discrete, soluble metal oxide clusters of early transition metals like W, Mo, V, Nb, Ta etc. capable of exhibiting versatile structural features and properties.[5] The incorporation of POMs into a polymer framework can be achieved by using a variety of techniques including physical blending, electrostatic attraction and covalent binding.[6] Among these, the covalent binding approach is known to produce stable POM-polymer hybrids and hence is widely used in the development of hybrid polymers containing diverse cluster types such as Wells-Dawson,[7-8] Lindqvist,[9-10] Anderson[11] and Keggin[12-13] derivatives.

Polyoxometalate are known to act as electron banks as they can accept and release a number of electrons without cluster disintegration.[5] Moreover, POMs display multi-step reduction processes in a narrow potential range making them attractive candidates for the design of multi-level charge-storage materials.[14] Photoredox properties of POMs are comparable to that of semi-conductor (SC) nanoparticles.[15-16] Absorption of suitable radiation leads to O→M ligand-to-metal charge transfer (LMCT) in POM clusters corresponding to the promotion of an electron from ligand bonding orbital (HOMO) to an empty antibonding orbital of the metal (LUMO) resulting in the generation of a hole center ($O^-$) and a trapped electron center (generally $M^{5+}$, where M = W, Mo). The energy for this charge transfer are qualitatively analogous to the band gap of solid semiconductor metal oxides that also generates electron-hole pair under irradiation.[17] The semiconductor-like behaviour of POM clusters has been widely explored towards the development of POM based devices for a variety of applications. For example, Cronin group have recently shown that core-shell POM molecules can act as candidate storage nodes for metal-oxide-semiconductor flash memory.[18] Makarona *et al.* have reported the charge transport phenomena in metal-insulator-semiconductor devices containing self-assembled monolayers (SAMs) of tungsten polyoxometalates in order to assess the potential of POM-SAMs as electron storage media.[19] Electron transfer properties of a functionalized Keggin-type POM cluster covalently anchored onto a glassy carbon electrode have been reported by Rinfray *et al*.[20] Joo *et al.* have explored organosilyl/-germyl polyoxotungstate covalently grafted onto n-type silicon wafer towards the realization of POM-based multilevel memory devices.[21] Hybrid organic–inorganic films, fabricated *via* the layer-by-layer (LBL) self-assembly method, have also been evaluated as molecular materials for electronic devices.[22] The transport properties of molecular materials prepared by embedding tungsten polyoxometalates into polymer matrices have been investigated by Glezos *et al*. towards their electronic device applications.[23]

Meanwhile, research on photo-response materials and devices have attracted much attention in recent decades because of their importance in optoelectronics and energy crises.[24] Among the various photo-response materials, organic-inorganic hybrids are of particular importance as they can take advantage of both organic and inorganic moieties leading to improved performances. Various inorganic semiconducting nanoparticles, for example, Ge nanocrystals, have been successfully employed in hybrid composites to develop photoresponse materials.[25]

Anderson type POM cluster based hybrids have been well studied over the past few decades because of their relevance in a variety of materials applications.[26] Polymers containing Mn-Anderson cluster have also attracted attention as photo-response materials, gels etc.[27] A recent study has also shown the usefulness of a Mn-Anderson cluster based polymer synthesized by copolymerizing $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNHCO(CH_3)C=CH_2\}_2]$ with methylmethacrylate (MMA) monomer in the development of devices for high density data storage application. In this polymer, the multi-redox property of the POM component is exploited towards the memory application of the polymer.[28] In the present study, we have developed a radiation sensitive hybrid polymer (POM-MAPDST) by co-polymerizing an Anderson type POM cluster hybrid with a photoresponsive organic monomer (methacryloyloxy)phenyldimethylsulfoniumtriflate (MAPDST)[29-30] and explored its photo-conducting properties by fabricating a device. In comparison to the control devices, POM-MAPDST hybrid polymer based device exhibited much improved photo conducting behaviour at lower voltages possibly because of the synergistic effects between the POM cluster and the photo responsive organic polymer moiety.



**Scheme 1**. Schematic representation of the synthesis of organic-POM hybrid monomer and its polymerization with MAPDST monomer.

The synthetic scheme for the POM-MAPDST hybrid polymer is shown in Scheme 1, see ESI for experimental details. Organic-POM hybrid monomer $(TBA)_3[MnMo_6O_{18}\{(OCH_2)_3CNH\}_2(CO(CH_3)C=CH_2)_2]$, (**2**), where TBA = tetrabutylammonium, was co-polymerized with MAPDST organic monomer in presence of AIBN as the radical initiator. After completion of the polymerization reaction, the viscous reaction mixture was added drop-wise into excess of diethyl ether under vigorous stirring to give the product as a light orange coloured solid in good yields (69 %). The formation of POM-MAPDST hybrid polymer was confirmed by $^1$H NMR and IR spectroscopic techniques along with gel-permeation chromatography (GPC) and thermal (TGA/DSC) analyses. The $^1$H NMR spectrum of the POM-MAPDST hybrid polymer is presented in Figure 1. A broad peak appearing at 1.0-1.7 ppm range can be assigned to the methyl protons of the MAPDST moiety, while the methylene proton signals of the polymeric chain are located at 1.8-2.8 ppm range. The sharp peak observed at 3.23 ppm can be assigned to the methyl protons attached to the sulphonium group of the MAPDST unit. The aromatic peaks of MAPDST moiety were observed at 7.43 and 8.04 ppm. The absence of tetrabutylammonium counter ion signals in the $^1$H NMR spectrum of the POM-MAPDST hybrid polymer could be due to the limited number of POM clusters in the polymer. Similar cases have been reported earlier in the case of Mn-Anderson and $[P_2V_3W_{15}O_{62}]^{9-}$ cluster based hybrid polymers.[7a,28] $^{19}$F NMR analysis of POM-MAPDST hybrid polymer shows a peak at −77.6 ppm, see Figure S2(b) of ESI, which confirms the presence of $CF_3SO_3^-$ unit in it as expected.

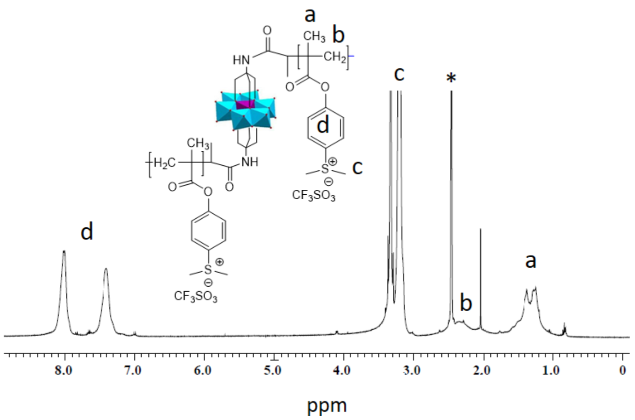


**Figure 1.** $^1$H NMR spectrum of POM-MAPDST hybrid polymer (* the peak of DMSO-$d_6$).

The IR spectrum of POM-MAPDST hybrid polymer shows a sharp and intense band appearing at 1754 cm$^{-1}$, which can be assigned to the carbonyl (C=O) stretching vibrations of the MAPDST moiety. The IR bands observed at 948 & 927 cm$^{-1}$ can be assigned to the Mo=O groups and peaks observed at 807 & 636 cm$^{-1}$ can be assigned to the Mo-O-Mo stretching vibrations (see Figure S1, ESI).

Further, the influence of Mn-Anderson cluster on the thermal properties of POM-MAPDST hybrid polymer was studied by using thermogravimetric analyses (TGA) (Figure S2(a), ESI) under $N_2$ atmosphere. TGA studies revealed that the POM-MAPDST hybrid polymer starts to decompose at 249 °C leading to ~5 % weight loss. This shows that the thermal stability of hybrid polymer has improved significantly as compared to pure MAPDST homopolymer, which is known to start decomposition at 226 °C.[29] This observed improvement in the thermal property of POM-MAPDST hybrid polymer could probably be due to the inclusion of inorganic cluster in the polymer framework. The thermo gravimetric analysis showed a residual mass of 5.9 % at 800 °C, mostly due to the molybdenum and manganese oxides, which indicates the attachment of ~0.3 cluster units per polymer chain considering the molecular weight of the polymer calculated through GPC analyses, *vide infra*. The glass transition temperature ($T_g$) of the POM-MAPDST hybrid polymer is found to be 135 °C. Transmission electron microscopy (TEM) analysis of POM-MAPDST revealed the formation of spherical agglomerates having size in the range ~300-400 nm as shown in Figure S4, ESI. The small dark spots observed on the surface of the agglomerates could be due to the electron dense POM clusters. Energy-dispersive X-ray (EDX) analysis on POM-MAPDST hybrid polymer shows signals due to molybdenum, manganese, carbon, nitrogen, oxygen and sulfur elements. The observed weight percentage of Mo:Mn in EDX analysis is close to the theoretically calculated value (Figure S5, ESI), confirming the existence of Mn-Anderson clusters in the polymer.

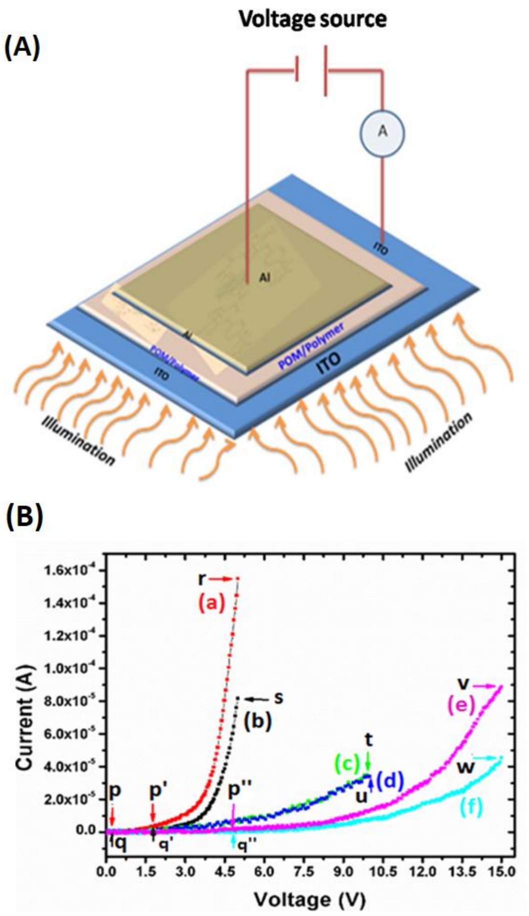


**Figure 2.** (A) Representation of ITO/POM-MAPDST/Al device structure and (B) I-V characteristics of : (a) & (b) – ITO/POM-MAPDST/Al device; (c) & (d) – ITO/POM-MMA/Al device; (e) & (f) – ITO/MAPDST/Al device. The first curve in each group (curves (a), (c) and (e)) is under photo-illumination while the 2nd curve (curves (b), (d) and (f)) is under dark condition.

The as synthesized POM-MAPDST hybrid polymer is soluble in acetonitrile, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvents at room temperature. The molecular weight as well as the polydispersity index (PDI) of POM-MAPDST hybrid polymer were determined by gel-permeation chromatography (GPC) analysis using different PEO and PEG standards (Figure S3, ESI). The weight average molecular weight of the POM-MAPDST hybrid polymer is 6312 $g/mol^{-1}$ with a PDI of 1.53.

The Mn-Anderson based POM/polymer hybrids are known to exhibit interesting redox properties, whose effective carriers can be controlled electrically. Because of this reason, such systems are explored in the design of multilevel memory materials.[28] In the present study, we decided to combine the redox property of Mn-Anderson cluster with the photo-response property of an organic polymer to study their combined effects towards the development of a photo-response device. In order to measure the I-V characteristics of the POM-MAPDST hybrid polymer under dark and illuminated conditions, we fabricated a device by spin coating the polymeric material onto an ITO glass substrate followed by depositing a layer of Al as the top electrode. The thickness of the polymer film was measured to be ~70 nm with a roughness of ~10.5 nm. A schematic representation of the fabricated device is shown in Figure 2 (A). This device was then subjected to I-V measurements under dark and illuminated conditions separately.

Figure 2(B) curves (a) and (b) shows the I-Vcharacteristics of ITO/POM-MAPDST/Al device in the forward bias under 100 $mW/cm^2$ illuminated and dark conditions respectively. Here, the I-V characteristics under illumination and dark vary from p to p' and q to q' corresponding to the current values $3.0\times10^{-6}$ and $1.0\times10^{-6}$ A respectively at lower voltages (upto 1.7 V). Although the current values are low, the photoinduced current enhancement is obvious from above values even under such low applied voltages. On increasing the voltage further, the current under illumination varies from p' to r (curve (a)) while that under dark conditions vary from q' to s (curve (b)). It can be observed that the current increases along with the increase in voltage both under dark and illuminated conditions. Under the experimental conditions, the maximum current observed under illumination (corresponding to the point r on curve (a)) was $1.5 \times 10^{-4}$ A, while the maximum current observed under dark (at the point s on curve (b)) was $8.0 \times 10^{-5}$ A. On an average, 100 % improvement in the photocurrent was observed at higher operating voltages. However, the photocurrent did not reach to its saturation value under the measurement conditions employed here.

In order to understand the roles of both the POM cluster and the MAPDST polymer units in the observed photo-conducting nature of ITO/POM-MAPDST/Al device, we fabricated two control devices: i) ITO/MAPDST/Al and ii) ITO/POM-MMA/Al (where MMA = methylmethacrylate polymer) and studied their I-V characteristics in comparison to that of ITO/POM-MAPDST/Al device under identical experimental conditions. In the first control device, we used MAPDST homopolymer[29] instead of POM-MAPDST hybrid polymer, thus removing the effect of POM cluster on the I-V properties of this device. The I-V characteristics of the ITO/MAPDST/Al device under illuminated and dark conditions are given in Figure 2(B), curves (e) and (f) respectively. These curves clearly show that pure MAPDST hybrid polymer requires much higher voltages to achieve the higher current values exhibited by POM-MAPDST polymer based device. The current observed at the point marked as p'' (on curve (e) at 4.7 V) under illumination was 2.1 × $10^{-6}$ A, whereas at the same voltage under dark conditions (marked as q'' on curve (f)), the current observed was 1.0 × $10^{-6}$ A. This shows a considerable increase in the current under illumination at this particular voltage. This trend continues at higher voltages as well, as shown in Figure 2 (B) curves (e) and (f). The maximum current observed for MAPDST homopolymer based device under illumination was 8.8 × $10^{-5}$ A at 15 V, whereas the current observed at the same voltage under dark conditions was 4.5 × $10^{-5}$ A.

In the second control device, ITO/POM-MMA/Al, we used MMA polymer moiety instead of MAPDST in combination with Mn-Anderson cluster, thus removing the effect of MAPDST polymer from the device material while retaining the same POM cluster. The I-V characteristics of the ITO/POM-MMA/Al device under illuminated and dark conditions are given in Figure 2 (B) curves (c) and (d) respectively. It can be noted from these curves that the maximum current observed under illumination (the point marked as t on the curve (c)) is same as that observed under dark (marked as u on the curve (d)) for POM-MMA hybrid system at 10 V . These curves clearly show that there is no effect of illumination in the case of POM-MMA based device; the observed increase in current is mainly a function of increasing potential.

From the above results, the following observations can be made: a) In the case of ITO/MAPDST/Al device, there is a clear increase in the current under illumination indicating the generation of photocurrent b) in the case of ITO/POM-MMA/Al device, the current raises as a function of voltage and there was no effect of illumination on the observed current values and c) in the case of ITO/POM-MAPDST/Al device, the current was much higher both under dark and under illumination compared to the control devices. The voltage required to generate a particular current (say 3.0 × $10^{-6}$ A) in ITO/POM-MAPDST/Al device was very low compared to the control devices indicating a low turn-on voltage. Therefore, illumination is definitely playing a crucial role for POM-MAPDST in the observed current enhancement.

The I-V characteristics exhibited by the three devices may be explained in terms of the changes in the effective charge carrier densities of the device materials under electric potential and/or under illumination. On increasing the applied potential, the Mn centres of the Mn-Anderson clusters undergo a valence shift from Mn(III) to Mn(IV), thereby changing the charge state of the polyoxometalate clusters resulting in the release of some TBA counter-ions associated with the clusters. These changes could lead to changes in the effective carrier density of the material leading to an increase in the conductivity of the device as shown in Figure 2.[28] Cyclic voltammetric analysis on POM-MAPDST hybrid polymer showed that Mn(III) to Mn(IV) oxidation occurs at 1.2 V, Figure S6, ESI. From Figure 2 (B), it is obvious that the POM containing devices (ITO/POM-MAPDST/Al and ITO/POM-MMA/Al) show observable increase in current only after ~1.2 V, probably because of this reason. The possibility of triflate counter ions associated with the MAPDST polymer moiety contributing to the increased current in the case of ITO/POM-MAPDST/Al device can be ruled out at these low voltages; because pure MAPDST polymer based control device ITO/MAPDST/Al showed observable increase in current only at a much higher potential, ~3.5 V. In the case of ITO/MAPDST/Al control device, the MAPDST polymer itself is in a charge separated ionic state, see Scheme 1. On reaching a sufficiently high potential, (3.5 V or above, see Figure 2 (B) curves (e) and (f)) more and more of the triflate counter ions could be contributing to the conductivity as observed by an increase in the current as a function of increasing voltage even under dark conditions.

The observed enhancement of current under illumination for MAPDST containing devices (ITO/POM-MAPDST/Al and ITO/MAPDST/Al) in comparison to their corresponding current values under dark, can be explained based on the photo-degradation of alkyl(aryl)sulfonium triflates on exposure to 365 nm UV radiation, which is well documented in the literature.[31-34] Cleavage of $S^+$–C bond is reported to occur in such compounds on irradiation with 365 nm, that could lead to the generation of additional ions in the medium. Therefore, we believe that the significant increase in the photocurrent of MAPDST based devices under illumination (ITO/POM-MAPDST/Al and ITO/MAPDST/Al) may be attributed to the generation of higher numbers of free charge carrier ions or *e-h* pairs due to the MAPDST polymer moiety on irradiation. The two separate effects viz. redox property of Mn-Anderson cluster as well as the photo-generation of ions by MAPDST moiety on illumination could be contributing in a synergistic manner to the observed enhancement of current in the case of ITO/POM-MAPDST/Al device. This synergistic effect is reflected in the low turn-on voltage of the POM-MAPDST based device in which the highest current under experimental conditions was achieved below 4.5 V, where as in control devices, the highest current were achieved at much higher potential (9.5 V for ITO/POM-MMA/Al device and 15 V for pure ITO/MAPDST/Al device). The low turn-on voltage of ITO/POM-MAPDST/Al device in comparison to the control devices could be attributed to the efficient injection of charge carriers due to proper matching of the work-function of electrodes with highest occupied and lowest unoccupied molecular orbitals of the hybrid. Studies conducted to explore the reversible nature of the conductivity enhancement on ITO/POM-MAPDST/Al device did not yield good results, probably because of the irreversible nature of the photo-generation of ions by MAPDST moiety.

## Conclusions

We have developed a new radiation sensitive POM/polymer hybrid, POM-MAPDST, based on Anderson-type polyoxometalate cluster hybrid and a UV active organic monomer through radical initiated co-polymerization procedure. An ITO/POM-MAPDST/Al device fabricated based on POM-MAPDST hybrid polymer showed good conductivity features under dark and illuminated conditions in comparison to the control devices fabricated by using POM-MMA hybrid polymer and MAPDST homopolymer separately. We believe that the redox property of the Mn-Anderson cluster as well as the photogeneration of ions by MAPDST polymer on irradiation may be contributing to the observed photoconductivity behaviour of POM-MAPDST hybrid polymer device in a synergistic manner. To the best of our knowledge, there are not many reports in the literature on photoconducting POM/polymer hybrids. Such materials are expected to have potential applications in electrophotography and/or photovoltaics.[35] We believe therefore that the present study may generate much research interests in this direction in future.

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## Notes and references

[a] School of Basic Sciences, Indian Institute of Technology Mandi, Mandi 175001, Himachal Pradesh, India. Fax: +91 1905 267 009; Tel: +91 1905 267 045; E-mail: pradeep@iitmandi.ac.in (CPP), kenneth@iitmandi.ac.in (KEG).

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