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2012

Gao, J., Liu, X., Liu, Y., Yu, L., Feng, Y., Chen, H., et al. (2012). Experimental and theoretical studies on pyrene-grafted polyoxometalate hybrid. Dalton Transactions, 41, 12185-12191.

<https://hdl.handle.net/10356/96764>

<https://doi.org/10.1039/C2DT31474F>

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Experimental and theoretical studies on pyrene-grafted polyoxometalate hybrid $\ddagger$ Junkuo Gao,^a Xinfeng Liu,^b Yi Liu,^a Lingling Yu,^a Yuhua Feng,^b Hongyu Chen,^b Yongxin Li,^b Ganguly Rakesh,^b Cheng Hon Alfred Huan,^b Tze Chien Sum,^b Yang Zhao^a and Qichun Zhang^{*a}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A novel pyrene covalently-attached polyoxometalate (POM) hybrid has been synthesized and fully characterized. The attractive electronic and photophysical properties of pyrene derivatives make the hybrid promising for studying and understanding electron transfer mechanisms in organic-functionalized POMs. The hybrid has an electronic absorption at 450 nm, indicating that there is a strong electronic interaction between the organic pyreneimido group and inorganic hexamolybdate cluster. The electron transfer mechanism of the as-prepared hybrid is illuminated *via* the combined studies of theoretical calculations and transient absorption spectroscopy. Time-dependent density functional theory studies revealed that the strong electronic absorption at the visible region mainly comes from the optically allowed π – π^* transitions of the pyreneimido component (S_0 to S_2 transition). The electron transfer process from the excited pyreneimido moiety to the inorganic POM cluster is at the time scale of ~ 700 fs, which could be ascribed to the internal conversion of singlet excited states from S_2 state to S_1 state. This study provided a clear understanding of the mechanism governing the electron transfer process in organoimido derivatives of POMs. This result might offer a new route for the design of new charge transfer hybrid clusters of organic functionalized POMs and crucial guidance for their applications in optical and electrical devices.

Introduction

Polyoxometalates (POMs), a rich family of early transition metal–oxygen anion clusters, show various applications in materials science, catalysis, biology, and medicine chemistry due to their nanosized geometry, unique optical, electronic and magnetic properties as well as excellent chemical reactivity.^{1–3} In the last two decades, organic functionalized POMs, especially organoimido derivatives of lindqvist type POMs have attracted considerable attention.^{4–7} The organic components in arylimido derivatives of POMs could extend their π -electron conjugation to the inorganic clusters, which not only modulates the electronic structure, reactivity and physical properties of hybrid clusters, but also displays novel synergistic effects from organic components and inorganic POMs. In addition, recent efforts to fabricate the ordered semiconductor nanostructures, metal nanoparticles, and carbon nanotubes pave the way to employ

organoimido functionalized POMs as building blocks for super-molecular assemblies, nano-materials, polymer-inorganic hybrids and chiral metallamacrocycles.^{8–10} More and more studies focus on organic-grafted POM hybrids because their tunable band edge could offer new opportunities to harvest light energy in the entire visible region of solar light.

Hybrid complexes (especially organic covalently bonded POMs), involving electron-transfer from organic donors to POMs acceptors, showed promising applications in functional devices for the photoconversion of light into energy such as photovoltaic cells and artificial photosynthetic devices.^{11–14} The organic dyes play a key role in light harvesting and transfer the excited electrons to POMs, since POMs themselves are only photoactive in the UV region. In fact, many arylimido derivatives of POMs emerged in the last decade might display possible electron transfer processes from the organoimido ligands to the lindqvists.^{15,16} However, to our best knowledge, arylimido–POM hybrids that could shift the absorption to the visible region are still rare. The maximum absorptions of most reported arylimido derivatives of POMs are in the UV region.^{17,18} In addition, the mechanism and process of electron transfer from organic dyes to POM clusters have not been studied *via* ultrafast spectroscopy and theoretical studies. This gap in knowledge strongly encourages us to carry on these researches.

In this report, we are interested in pyrene-attached POMs for two reasons: (1) to the best of our knowledge, there are no pyreneimido derivatives of POMs reported till now, and (2)

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$\ddagger$ In memory of Professor Ma Jan.

$\dagger$ Electronic supplementary information (ESI) available: Crystallographic data for **MoAP**, the photophysical properties of **IAP** in acetonitrile and the energy diagrams for the molecular orbitals of **MoAP**, **IAP** and **Mo₆O₁₉**. CCDC 879741. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31474f

pyrene and its derivatives have quite long fluorescent lifetimes, large quantum yield, high sensitivity of vibronic fine structure to environment and propensity to form excimers *via* π - π interactions.^{19,20} Clearly, the large quantum yield of fluorescence as well as long life excited states make pyrene and its derivatives promising candidates for studying and understanding the electron transfer mechanism in organic-functionalized POMs. Although several pyrene-grafted POMs have already shown some novel optical properties and potential applications in sensors and catalysts,^{21–23} the linkers between pyrene and POMs in these hybrid materials are not efficient for electron “communication” of the two parts. In order to enhance the “communication” efficiency, it is necessary to directly attach organic donors into POMs through a short rigid bond. In our research, we believe that the imido group could enhance the interactions between the highly delocalized π - π electrons of the pyrene ring and the d orbital of the POM skeleton, generating novel photo-physical properties and providing opportunity to study the electron transfer mechanism of organic functionalized POM hybrid materials.

Here we reported a new pyreneimido derivative of hexamolybdate (named **MoAP**) *via* the DCC coupling protocol²⁴ and studied the photophysical properties of this hybrid cluster using both experimental and theoretical methods. The UV-Vis absorption of the organoimido hybrid cluster was successfully extended to the visible region. The electron transfer states from organic chromophore components to inorganic polyanion clusters were observed and confirmed for the first time in organic covalently functionalized POM-based hybrid materials *via* fs transient absorption spectra and theoretical calculations. In addition, the corresponding mechanism was also studied.

Results and discussion

Synthesis and characterization of hybrid cluster MoAP

Pioneering work to attach organoimido to POMs was done by Maatta *et al.*; later on, an extensive series of mono- and multi-functionalized organoimido derivatives of POMs were prepared with various imido-releasing reagents.^{25–27} In order to avoid the tedious work on the synthesis of imido-releasing reagents, Peng *et al.* developed a novel method, namely DCC coupling, which can dramatically facilitate the reaction between lindqvist type POMs and aromatic amines under mild conditions and in high yields.²⁴ Following his method, we successfully synthesized **MoAP** through reacting α -[TBA]₄[Mo₈O₂₆] with 1-aminopyrene (**1AP**) hydrochloride salt and DCC in anhydrous acetonitrile under refluxing conditions, where DCC acted as the dehydrating and coupling agent from the reaction of the Mo₈ cluster to the organic functionalized Mo₆ cluster. The **MoAP** crystals suitable for single crystal X-ray diffraction analysis were prepared by the slow diffusion of ether into acetonitrile solution.

Structural analysis shows that **MoAP** crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 12.35$ Å, $b = 12.89$ Å, $c = 19.69$ Å, $\alpha = 78.36^\circ$, $\beta = 78.47^\circ$, $\gamma = 72.72^\circ$, and $V = 2900.4(2)$ Å³. The ORTEP representation of the **MoAP** anion is displayed in Fig. 1(a). The structure shows that the pyrene component is covalently attached to the hexamolybdate skeleton *via* the imido group. The charge of the **MoAP** cluster is -2 ,

Fig. 1 (a) Molecular structure of the hybrid cluster anion **MoAP** shown in combined ball-and-stick representation. (b) The dimer structure of hybrid cluster anion **MoAP**.

which is balanced by two tetrabutylammonium cations. The short Mo–N bond length (1.747(7) Å) and the angle between the N and its neighbor Mo and C atoms (173.2(7)°) indicate the typical characteristic of the Mo≡N triple bond.²⁸ Also, the distance of the Mo–O band between the central oxygen atom and the Mo atom bearing imido group is significantly shortened compared to other Mo–O bond distances in the cluster, which is quite consistent with the structures of organoimido derivatives of hexamolybdate.²⁹ Due to the strong π - π stacking ability of pyrene component, the dimerization of the hybrid cluster is observed in the crystal structure, as shown in Fig. 1(b). The parallel alignment of pyrene part between two neighbor cluster anions and the short vertical aromatic ring distance (3.04 Å) demonstrates the existence of supermolecular π - π interactions in **MoAP** crystals.

The FTIR spectra of **MoAP**, **1AP** and (TBA)₂[Mo₆O₁₉] (**Mo₆O₁₉**) are displayed in Fig. 2. The band-pattern characteristic for the lindqvist structure was described in the low wavenumber region of the spectra (below 1000 cm⁻¹). The $\nu(\text{Mo}-\text{O}_t)$ and $\nu(\text{Mo}-\text{O}_b)$ of **Mo₆O₁₉** are located at 957 cm⁻¹ and 799 cm⁻¹, which are similar to a previous report.³⁰ In the spectrum of **MoAP**, the peak near 957 cm⁻¹ is split into two bands as commonly observed in arylimido derivatives of hexamolybdates.³¹ The peaks at 975 cm⁻¹ and 953 cm⁻¹ can be assigned to $\nu(\text{Mo}-\text{N})$ and $\nu(\text{Mo}-\text{O}_t)$, confirming the formation of arylimido groups. The peak (785 cm⁻¹) of $\nu(\text{Mo}-\text{O}_b)$ in **MoAP** is red shifted compared to that of **Mo₆O₁₉**, which indicates that the Mo–O bonds are much weaker after grafting of arylimido groups.³²

Electronic and electrochemical properties

The UV-Vis absorptions of **MoAP**, **1AP** and (TBA)₂[Mo₆O₁₉] (**Mo₆O₁₉**) were measured in acetonitrile solution (Fig. 3). The lowest energy electronic transition absorption at 325 nm of

Fig. 2 FT-IR spectra of 1AP, Mo_6O_{19} and **MoAP**.

Fig. 3 UV-Vis absorption spectra of compound **1AP**, Mo_6O_{19} and **MoAP** in acetonitrile at the concentration of 2.5×10^{-5} M.

Mo_6O_{19} could be assigned to the charge-transfer transitions from the π -type HOMO orbital of oxygen to the π -type LUMO orbital of molybdenum.³³ In **1AP**, the lowest energy electronic transition band is at 400 nm with regular vibrational fine structure of pyrene derivatives, which is primarily described as the transition from HOMO to LUMO.³⁴ **MoAP** displays a shoulder near 456 nm and an intense absorption peak at 435 nm with quite high molar absorption coefficients, which belongs to the allowed π - π^* transitions of this complex and the characteristic vibronic structure of substituted pyrene. Compared with those of Mo_6O_{19} and **1AP**, the lowest energy electronic transition absorption of **MoAP** shows an obvious red shift, which not only indicates that the formation of $\text{Mo}\equiv\text{N}$ triple bonds leads to increased delocalization of the aromatic π -electrons to the inorganic cluster, but also implies that the strong electron-withdrawing nature of $[\text{Mo}_6\text{O}_{19}]^{2-}$ affects the molecular orbitals of pyrene component more than the electron-donating amino group does. In addition, both **MoAP** and Mo_6O_{19} show an absorption band at 254 nm, which could be assigned as the transition from π -type nonbonding orbitals of oxygen to the π -type LUMO orbital of molybdenum, indicating the existence of hexamolybdate skeleton in **MoAP**.³¹

Fig. 4 Cyclic voltammograms of **1AP**, Mo_6O_{19} and **MoAP** in acetonitrile.

The luminescence spectra of **1AP** and **MoAP** were also studied in acetonitrile. **1AP** displays a strong and broadened emission centered at 424 nm with a lifetime of 4.7 ns (Fig. S1†), while the emission of the pyrene group in **MoAP**, is totally quenched, which could confirm the intramolecular electron transfer from the excited pyreneimido group to the POMs.

The electrochemical properties of **1AP**, Mo_6O_{19} and **MoAP** were studied in degassed acetonitrile. The cyclic voltammograms are shown in Fig. 4. All the three compounds show a quasi-one electron reversible reduction wave. Their $E_{1/2}$ values are 0.364 V, 0.939 V and 0.816 V for Mo_6O_{19} , **1AP** and **MoAP**, respectively. Compared to that of Mo_6O_{19} , the negative shift (0.452 eV) of the $E_{1/2}$ value of **MoAP** implies that the POM cluster in **MoAP** is more difficult to reduce, which indicates the strong π -donor ability of the pyreneimido ligand.³⁵

Theoretical calculations

In relation to the above experimental observations, the electronic structures of the product **MoAP** were also theoretically investigated. The low-lying vertical excitation energies were calculated *via* time-dependent DFT (TD-DFT).³⁶ The geometry of **1AP** was optimized at the B3LYP/6-31G* level.^{37,38} For **MoAP** anion, the atomic coordinates obtained from the crystal structure were used as the initial estimated structure and optimized fully by the DFT in the gas phase. Recently, TD-DFT was widely used to investigate the electronic structures and nonlinear optical properties of diverse POMs, showing both good accuracy and efficiency.^{39–41}

The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) orbitals of **1AP** in the ground state are shown in Fig. 5. The HOMO and LUMO orbitals of **1AP** show characteristics of pyrene derivatives. The electronic density on the nitrogen atom in the LUMO orbital is efficiently reduced compared to the HOMO orbital, indicating the existence of charge transfer from amino group to pyrene component.⁴² The diagrams for frontier molecular orbitals of **MoAP** in the ground states are displayed in Fig. 6, while the energy diagrams of the molecular orbitals are shown in Fig. S2.† In the HOMO orbital of **MoAP**, the π -electrons of the

Fig. 5 The HOMO and LUMO orbitals of compound **1AP**.

Fig. 6 Frontier orbitals of **MoAP** anion.

pyrene component extend over the pyreneimido segment to the neighbouring Mo atom through the bonding N atom. The delocalized π -bond consists of a d-p π -bond from the p_z orbital of the N atom and the d_{xz} orbital on the Mo atom (linked to the N atom) and the π -bond of the pyrene part, implying strong electronic interaction between pyreneimido units and hexamolybdate components. For most arylimido derivatives of hexamolybdate studied in the literature, the LUMO orbitals showed similar characteristics to the LUMO orbital of $[\text{Mo}_6\text{O}_{19}]^{2-}$ and were totally localized on the inorganic cluster. The main compositions are Mo d-orbitals with some antibonding participation from the O p-orbitals, illuminating that the attachment of the arylimido group has no influence on the character of the LUMO orbital compared to $[\text{Mo}_6\text{O}_{19}]^{2-}$.⁴³ For the new pyreneimido derivative **MoAP**, the LUMO orbital is now mainly composed of the delocalized π -antibond of the pyreneimido group. Only the d-orbitals of the Mo atom that are attached to the N atom in the inorganic cluster, significantly contribute to the LUMO orbital. Excluding

Table 1 The selected vertical excitations of compound **1AP** and **MoAP**

Compound	λ_{max} (nm)	f (oscillator strength)	Assignment
1AP	363.9 ($S_0 \rightarrow S_1$)	0.2772	HOMO $\rightarrow$ LUMO
	340.2 ($S_0 \rightarrow S_2$)	0.0318	HOMO $\rightarrow$ LUMO + 1
MoAP	478.7 ($S_0 \rightarrow S_1$)	0.0007	HOMO $\rightarrow$ LUMO + 1 (64%)
	454.5 ($S_0 \rightarrow S_2$)	0.8448	HOMO $\rightarrow$ LUMO + 3 (36%)
	431.9 ($S_0 \rightarrow S_3$)	0.0029	HOMO $\rightarrow$ LUMO
			HOMO $\rightarrow$ LUMO + 3

the HOMO and LUMO orbitals, all the HOMO - 1, LUMO + 1, LUMO + 2 and LUMO + 3 orbitals are constituted by the inorganic hexamolybdate cluster. Compared to other arylimido derivatives, the novel electronic structures of pyreneimido POMs are reported for the first time, making a potential route for understanding the charge-transfer mechanism in organoimido POMs.

The low-lying electronic excited states of **1AP** and **MoAP** were calculated using the TD-DFT approach. The transition energies, oscillator strengths, and contributions from the molecular orbitals for the most relevant singlet excited states are summarized in Table 1. The lowest energy transition for compound **1AP** corresponds to the excitation from the HOMO to LUMO orbitals with large oscillator strength ($f = 0.2772$).⁴⁴ In compound **MoAP**, the HOMO to LUMO electronic transition contributes to the $S_0 \rightarrow S_2$ excitation with an excitation energy of 454.5 nm (2.73 eV) and oscillator strength of 0.8448, which shows quite good agreement with the experimental value and leads to the optical absorption in the visible region for light harvesting. The $S_0 \rightarrow S_1$ excitation band of **MoAP** is almost optically forbidden and mainly results from the HOMO $\rightarrow$ LUMO + 1 (64%) and HOMO $\rightarrow$ LUMO + 3 (36%) transition with a very small oscillator strength (0.0007), where the excited electron is mainly localized on the hexamolybdate cluster as shown in the electronic structures of LUMO + 1 and LUMO + 3 orbitals. The electronic excitation structures of **MoAP** is quite similar to the electronic excitation structures of pyrene where the $S_0 \rightarrow S_2$ excitation with strong absorption strength is primarily described by a HOMO $\rightarrow$ LUMO transition while the weakly optically allowed $S_0 \rightarrow S_1$ excitation has almost equal contributions of HOMO $\rightarrow$ LUMO + 1 and HOMO - 1 $\rightarrow$ LUMO as reported in the literature.^{20,44} The negligible oscillator strength of $S_0 \rightarrow S_1$ excitation of **MoAP** indicates that the direct charge transfer from the pyreneimido component (HOMO) to inorganic cluster is not obvious. But, the lowest electronic transition energy of S_1 and characteristic electronic structure of POMs can offer a potential approach for the organic to inorganic charge transfer through other excited states with higher energies (S_2). The charge transfer process was well studied and confirmed *via* the femtosecond transient absorption spectroscopy, and will be discussed in detail as below.

Femtosecond transient absorption

The fs transient absorption spectroscopy is a convenient way to probe the charge transfer process that even occurs on a sub-pico-second time scale. The TA spectra of **MoAP** recorded at different time delays after 400 nm excitation in acetonitrile are displayed

Fig. 7 (a) TA spectra of **MoAP** at various delay times in acetonitrile; (b) the time evolution of the photoinduced electrons probed at 550 nm with excitation at 400 nm, inset shows the results of a best fit for the trace (black and red solid line).

in Fig. 7(a). The spectrum shows a broad absorption peak at ~ 550 nm and the negative signal can be ascribed to the pump induced excited states absorption (ESA) from both the optically allowed S_1 to S_n states and S_2 to S_n states. The kinetic trace of the ESA dynamics at 550 nm is shown in the Fig. 7(b). The decay dynamics were best fitted with a tri-exponential function with an extremely short sub-ps lifetime component ($A_1 \sim 49\%$), an intermediate lifetime component with tens of ps ($A_2 \sim 29.5\%$) and a very long lifetime component of few ns ($A_3 \sim 21.3\%$). This “decay” is in fact a recovery of the ESA signals to the equilibrium brought about by depopulation of the carriers at the excited states. For comparison, the TA spectra of **1AP** at 550 nm were also collected and fitted. This ESA signal originates only from the S_1 to S_n excited states absorption as reported in the literature,⁴⁵ where three lifetime components can be deconvoluted. The dominant long-lived component of **1AP** agrees satisfactorily with the value obtained from the fluorescence lifetime deduced from time resolved fluorescent measurements, indicating that the decay of the excited S_1 state mainly occurred *via* the radiative transition to the ground state. The near correspondence of the pre-exponential factors and lifetimes of the **1AP** and **MoAP** samples for the intermediate lifetime component suggests that they originate from the same spectra dynamics and could be ascribed to the solvation dynamics of the corresponding S_1 state as reported for some amino- and nitro-polyaromatic hydrocarbons in polar solvents

Scheme 1 Schematic representation of the charge transfer pathways in **MoAP**.

and ionic liquids.^{46–48} From these measurements, one can infer that the long ns lifetime and the intermediate lifetime in the **MoAP** sample originate from the depopulation of the S_1 state (*via* non-radiative relaxation process). The sub-ps lifetime (with a very large pre-exponential contribution) could be assigned to the internal conversion from the excited S_2 to the S_1 state, where the charge transfer process occurs from the excited pyreneimido component to the inorganic POM cluster. Thus, a general charge transfer pathway in **MoAP** is shown in Scheme 1. When absorbing light, the electron is excited from the ground state to the optically allowed excited state S_2 that is mainly localized on the pyreneimido part, then the electron is transferred from the excited pyrene chromophore to the S_1 state consisting of the POM cluster *via* internal conversion at a time scale of ~ 700 fs. Then the electron in the charge separated S_1 state decays to the ground state *via* the non-radiative relaxation process at the time scale of 1.9 ns. This is the first observation of detailed charge transfer process and exploration of charge transfer mechanism in organoimido derivatives of POMs through ultrafast spectroscopy. The understanding of the charge transfer mechanism is crucial for designing new charge transfer hybrids for use in functional devices.

Conclusion

In summary, a new organic–inorganic hybrid, where pyrene is covalently attached to POM *via* the imido group, was prepared and fully characterized. The electronic absorption peak of this hybrid was successfully extended beyond 450 nm, indicating strong electronic interactions between the organic pyreneimido group and inorganic cluster. The result of fs transient absorption spectroscopy indicated that the electron transfer process from the excited pyreneimido moiety to the inorganic POM cluster was on a time scale of ~ 700 fs. The electronic structures of the pyreneimido–POM hybrid were also calculated *via* the TD-DFT method, confirming the electron transfer mechanism that the excited electron was transferred from the excited S_2 state to the S_1 state *via* the internal conversion process. The present study provided a clear understanding of the mechanism governing the charge transfer process in organoimido derivatives of POMs and offered a new route for the design of new organic–POM electron transfer hybrids.

Experimental section

Materials

All chemicals (except acetonitrile) were purchased from Alfa Aesar, TCI Chemicals and Aldrich and used without further purification. Acetonitrile was distilled over drying agents before use. 1-Aminopyrene hydrochloride, $[TBA]_2[Mo_6O_{19}]$ and $\alpha-[TBA]_4[Mo_8O_{26}]$ were synthesized according to the literature.^{49,50}

Characterization

1H NMR and ^{13}C NMR spectra were taken on a Bruker Avance DMX300 spectrometer using tetramethylsilane (TMS) as an internal standard. UV-vis absorption spectra were obtained using a Shimadzu UV-2450 spectrophotometer. Steady-state fluorescence was measured on a Shimadzu RF-5301pc spectrofluorophotometer. FTIR spectra were recorded from KBr pellets by using a Perkin Elmer FTIR SpectrumGX spectrometer. Cyclic voltammetry was performed with a CHI750A electrochemical working station in moisture-free and oxygen-free acetonitrile with a scan rate of 200 mV s^{-1} . Elemental analyses were obtained from a EuroVector Euro EA elemental analyzer. High resolution mass spectrometry was obtained from the Waters Q-TOF Premier Mass Spectrometer.

Synthesis of MoAP

$\alpha-[TBA]_4[Mo_8O_{26}]$ (2.14 g, 1.0 mmol), 1-aminopyrene hydrochloride (0.39 g, 1.5 mmol) and DCC (0.52 g, 2.5 mmol) were mixed in 10 ml of anhydrous acetonitrile and refluxed for 12 h. During the reaction, the color of the solution changed from yellow to dark red, and some precipitate was formed. After the reaction, the mixture was cooled to room temperature and the resulting precipitate was filtrated out. Then, the precipitate was washed with 80 mL of acetonitrile and the resulting solution was evaporated under reduced pressure. The as-obtained product was obtained as a dark yellow powder. Yield: 56% (based on Mo). 1H NMR (400 MHz, $DMSO-d_6$, δ ppm) 0.92 (t, 24H, CH_3), 1.29 (m, 16H, CH_2), 1.55 (s, 16H, CH_2), 3.15 (t, 16H, CH_2), 7.94 (d, 1H, ArH), 8.16–8.22 (m, 3H, ArH), 8.30–8.42 (m, 4H, ArH), 8.87 (d, 1H, ArH). ^{13}C NMR (125 MHz, $DMSO-d_6$, ppm): δ = 148.05, 130.50, 130.45, 130.41, 129.75, 128.88, 128.73, 126.81, 126.68, 126.43, 124.94, 124.68, 123.52, 123.18, 122.04, 113.1, 57.41, 22.95, 19.12, 13.38. Anal. Calcd (%) for $Mo_6O_{18}C_{48}H_{81}N_3$: C, 36.86; H, 5.22; N, 2.69. Found: C, 37.11; H, 5.29; N, 2.48. MALDI/TOF HRMS: [M] calcd for $Mo_6O_{18}C_{48}H_{81}N_3$, 1565.0009; found, 1564.9948.

Crystallographic measurements

Dark yellow crystals of MoAP were grown through diffusing ether into acetonitrile solution at room temperature. Data collection was carried out on Bruker APEX II CCD diffractometer equipped with a graphite-monochromatized $MoK\alpha$ radiation source ($\lambda = 0.71073\text{ \AA}$) at 103 K. Empirical absorption was performed, and the structure was solved by direct methods and refined with the aid of a SHELXTL program package. All

hydrogen atoms were calculated and refined using a riding model. CCDC number for compound **MoAP** is 879741.

Transient absorption measurements.

The laser system comprises a 1 kHz Coherent LegendTM regenerative amplifier seeded by a 80 MHz Coherent VitesseTM oscillator. The 800 nm output pulses from the regenerative amplifier were frequency doubled to 400 nm using a BBO crystal. Time resolved photoluminescence (TRPL) measurements were performed in a conventional backscattering geometry where the PL emission was collected using an Optronis OptoscopeTM streak camera system that has an ultimate system temporal resolution of 10 ps. For the transient absorption (TA) measurements, 400 nm pulses were focused onto a 200 micrometer spot and overlapped with white-light continuum probe pulses generated with a thin sapphire plate. Pump-induced changes were monitored using a monochromator/PMT configuration coupled to a lock-in amplifier. The pump beam was chopped at 83 Hz and used as the reference frequency for the lock-in. The details of the TRPL and TA setup are described elsewhere.⁵¹

Computational approach

All theoretical calculations were performed with the Gaussian 03 program.⁵² The ground state geometry optimization of **1AP** and **MoAP** anion cluster at the gas phase was calculated using the density functional theory (DFT) method with the hybrid exchange-correlation functional B3LYP. The polarized double-zeta basis set 6-31G(d) was used to describe the C, N, O and H atoms while the relativistic effective frozen-core LANL2DZ basis set was used for Mo atoms. The vertical electronic excitation energies were calculated using the time-dependant DFT theory based on the optimized molecular geometries at the same level of calculation. At least 20 excited states were calculated for the compounds.

Acknowledgements

The work is supported by the Singapore National Research Foundation through the Competitive Research Programme under Project No. NRF-CRP5-2009-04 (J.G., X.L, T.C.S., and Y.Z.). Q.Z. acknowledges the financial support from start-up grant (Nanyang Technological University), AcRF Tier 1 (RG 18/09) from MOE, CREATE program (Nanomaterials for Energy and Water Management) from NRF, and New Initiative Fund from NTU, Singapore. C. H. A. H. acknowledges the financial support from the NTU New Initiatives Grant (M4080554.110).

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