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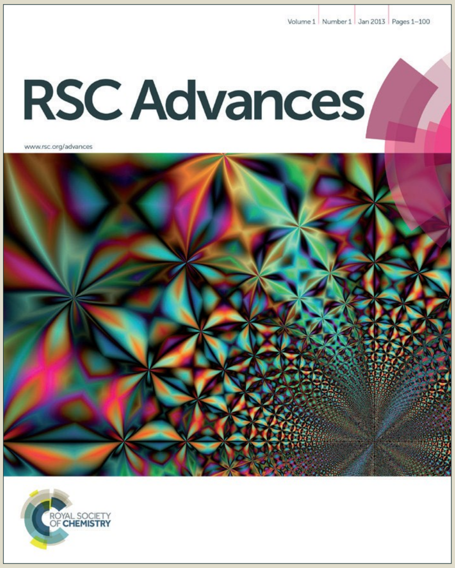

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Exploration on charge transfer and absorption spectra of porphyrin-polyoxometalate hybrids for searching high performance sensitizers

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Based on porphyrin derivative (system **1**), Lindqvist-, Keggin-, Anderson-type polyoxometalates (POMs) organic-inorganic hybrids (systems **2-4**) were designed aiming to investigate the charge transfer characters and screen the high performance p-type sensitizers. The electronic structures and absorption spectra of systems **1-4** were systematically investigated by means of density functional theory (DFT) and time-dependent DFT (TD-DFT) methods. The results indicate that Lindqvist- and Keggin-type POMs affect the lowest unoccupied molecular orbital (LUMO) energy levels, while the Anderson-type POM does not contribute to the frontier molecular orbitals (FMOs). Furthermore, the absorption spectrum of Lindqvist-type POM porphyrin derivative (system **2**) exhibits strong and broad absorption in the visible region and is red shifted about 100 nm in comparison with system **1**. Further studies point out that system **2** can balance the photovoltaic parameters, *LHE*, *HJE*, *CSE* and *DRE*, indicating that it will be a promising high performance dye sensitizer in p-type dye-sensitized solar cell (DSSC).

Introduction

The frequent occurrence of fog and haze in Asian countries attribute to the burning of fossil fuel, and energy crisis also make the environmental pollution problem more and more serious. Therefore, we are in urgent need of searching clean and safe energy resources and technologies.[1] As a promising renewable energy device to solve the energy crisis, dye-sensitized solar cells (DSSCs) have attracted tremendous attentions recently due to their flexibility, cost effective, easy production processes and environmental-friendly fabrication.[2-6] Since the seminal work on the sensitization of n-type semiconductor TiO_2 reported by O'Regan and Grätzel in 1991, enormous efforts have been devoted to DSSCs.[7-8] At current stage, the highest reported efficiency of n-DSSC is up to 15%.[9] In 1999, Lindqvist and co-workers first reported the performance and characterization of p-type DSSC based on a porous nickel oxide (NiO) electrode sensitized by a freebase porphyrin or by erythrosine B.[10] Although many efforts have been paid, the efficiencies of p-DSSCs are so far relatively very low.[11] While a potential utility of p-DSSCs is leading to the fabrication of tandem DSSCs (pn-DSSCs), which the overall efficiencies could be higher than those of n-DSSCs.[12] Thus, developing efficient p-DSSCs are of great significant for pn-DSSCs to further enhance the overall efficiencies. There are many paths improving the efficiencies of p-DSSCs, such as expanding the range of absorption spectra of dyes in the solar spectra and maintaining the charge separation, etc. The dye with donor-π linker-acceptor (D-π-A) structural motif exhibits high molar extinction coefficient and can facilitate the photo-induced charge separation, therefore we adopt this pattern of dyes.[13-16]

Polyoxometalates (POMs), as one kind of significant anionic metal–oxide clusters, have widely potential applications in catalysis, photochemical, biology and medicine because of their structural diversity, unique physical and chemical properties.[17-19] POMs have become a subject of general interest not only for their excellent electronic properties and strong electron-withdrawing ability, but also for extensively employed as inorganic building blocks for the construction of organic-inorganic hybrid materials. Recently, the covalent organic modifications of POMs draw much attention due to their synergistic properties between POMs and organic groups.[20-22] Up to now, a great deal of Lindqvist-, Keggin-, Dawson- and Anderson-type POMs organic hybrids have been synthesized.[23-26] POM-based hybrid materials perform great potential in DSSCs as their favorable absorption properties. In our previous work, the Lindqvist-type POM-based organic-inorganic hybrids were studied by density functional theory (DFT) methods.[21,22,27-30] It turns out that this kind of POM-

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based hybrids present high stability and intense absorption in the visible region, and can be promising photovoltaic materials in DSSCs.

Porphyrins, the attractive components in materials, are widely used in material chemistry and biochemistry because of their fascinating chemical properties, such as long-lived excited states and tunability by chemical derivatization.[31] Herein, POM-based organic-inorganic hybrids by covalently linked with porphyrin were designed for searching high efficient dyes for DSSCs.

To further investigate the properties of POM-based hybrids, the quantum chemical calculations as reliable and suitable avenues are crucial to explore the relationship between structures and properties. In past several years, the stability, redox, optical and nonlinear optical properties of Lindqvist-, Keggin- and Anderson-type POMs hybrids were systematically investigated.[21,32-37] Obviously, DFT and time-dependent DFT (TDDFT) can shed light on the electronic and optical properties of POM-based complexes.[38] Herein, a series of POM-based organic-inorganic hybrids were constructed in which the porphyrin derivative was covalently linked with three kinds of POMs, Lindqvist-, Keggin- and Anderson-type POMs, respectively. DFT and TDDFT calculations on their structural and electronic structures, absorption spectra and transition nature were performed in order to screen out the high efficient dyes for DSSCs. Furthermore, the results are expected to provide theoretical guidance and prediction for experimental synthesis of POM-based organic-inorganic hybrids.

Methods

Theoretical background

Based on the working principle of p-type DSSCs, the energy conversion efficiency is closely connected to light harvesting efficiency (*LHE*), holes injecting efficiency (*HJE*), dye regeneration efficiency (*DRE*) and charge recombination efficiency (*CRE*).

LHE is an important parameter to assess the performance of DSSCs, which is under the influence of oscillator strength (*f*) of the dye corresponding to the maximum absorption λ_{max}. *LHE* is expressed as following:[39]

$$LHE = 1 - 10^{-f} \tag{1}$$

HJE is affected by the free enthalpy ΔG_{inj}, which is related to the hole injection from the excited states of dye into the valance band (VB) of NiO. It can be determined by:[40-41]

$$\Delta G_{inj} = -\left[E_{00}(S^*) - E(S/S^-)\right] - E_{VB} \tag{2}$$

where E_{VB} is the VB edge of NiO (-4.96 eV),[29] $E_{00}(S^*)$ is the energy of excited state sensitizer, and $E(S/S^-)$ is the reduction potential of dye.

DRE can be measured by ΔG_{reg}, which is determined by the following equation:

$$\Delta G_{reg} = E\left(I_2/I_3^-\right) - E\left(S/S^-\right) \tag{3}$$

where $E(I_2/I_3^-)$ is the reduction potential of the redox mediator (-4.80eV).[29]

The free energy of *CRE* is ΔG_{CR}, which can be expressed as follows:

$$\Delta G_{CR} = E(S/S^-) - E_{VB} \tag{4}$$

The four equations indicate that reducing ΔG_{inj}, ΔG_{reg} and increasing ΔG_{CR} as well as *LHE* might be effective ways to achieve higher efficiency dyes.

Computation details

All calculations were carried out by using Gaussian 09 A02 program package.[42] The geometrical structures were optimized by B3LYP functional with 6-31G* for non-metal atoms and LanL2DZ basis set for Mo and Sn atoms.[43] As a range-separated hybrid functional, CAM-B3LYP functional can wonderfully describe the charge transfer situation of excited states. Therefore, the absorption spectra and transition characteristics were analyzed by TDDFT calculations at CAM-B3LYP/6-31G* level, and LanL2DZ basis set for Mo and Sn atoms. And the numbers of excited states we calculated via TDDFT method are 20, 50, 50 and 80 for systems **1-4**, respectively. The solvent effect was taken into account during the geometry optimization and TDDFT calculations in solvent N,N-Dimethyl Formamide (DMF) by means of the polarizable continuum model (PCM).[44]

Results and discussion

Molecular structures

In this work, the 10-ethynyl-5,15-biphenyl-porphyrin that benzoic acid is linked by the ethynyl group is named as system **1**. And the carboxyl is added as the anchoring group to bond to the semiconductor surface. In 2007, Wei et al. synthesized the hexamolybdate derivative, $[Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)]^{2-}$ in which the naphthylamine was linked with hexamolybdate through Mo≡N.[45] It is found that the introduction of hexamolybdate (Lindqvist-type POM) into naphthylamine can red shift UV-Vis spectrum. The theoretical study indicates that the hexamolybdate acts as an electron acceptor and the organic group as an electron donor.[27] Therefore, this phenomenon brings up an interesting question: whether the other type POMs, such as Keggin- and Anderson-type POMs in POM-porphyrin hybrids have the same charge transfer character and red shift the absorption spectra. With the purpose for searching the high-performance dyes, the systems **2**, **3** and **4** were designed by introducing system **1** to $[Mo_6O_{18}N]^{2-}$, $[PSnMo_{11}O_{39}]^{3-}$ (Keggin-type POM) and $[MnMo_6O_{24}[C(CH_2)_3]CH_3]^{3-}$

(Anderson-type POM), respectively. The molecular structures of systems **1-4** are shown in Fig. 1.

Electronic structures

It is known that the energy levels and distributions of frontier molecular orbitals (FMOs) affect on the electronic transition characters of dyes. The distributions of the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) for systems **1-4** are displayed in Fig. 2. It should be noted that system **4** has an unpaired electron, its multiplicity and charge are 5 and -3, respectively. So the FMOs are discussed by α and β spin states. In system **1**, the HOMO is delocalized over the whole molecule, and LUMO is mainly localized on the porphyrin ring and extended to the anchoring group. As can be seen, the FMO distributions of systems **2** and **3** are very similar, which the HOMO is mainly delocalized over the organic segment and also has some distribution from the Mo$\equiv$N part for system **2**, while the LUMO is localized on POM clusters, indicating that the Lindqvist- and Keggin-type POMs play a vital role for the LUMO distributions. There is an excellent synergistic effect between organic segment and POM cluster in system **2** and **3**, and the intramolecular charge transfer is predicted to be better than that of system **1**. As for system **4**, the distributions of electron density on FMO are almost the same as that of system **1**. It is clearly seen that the Lindqvist- and Keggin-type POMs contribute to the FMOs of studied POM-based porphyrin hybrids, while the Anderson-type POM almost has no effect on the FMO distributions. With the purpose of accelerating hole injection from the excited state of dye into the VB of NiO, the HOMO distribution of the dye should significantly extend to the anchoring group and overlap with the VB of NiO, which is beneficial for the strong electron coupling with the semiconductor. Furthermore, the LUMO of dye should predominantly locate far away from the surface of NiO, which can reduce the combination of electron and hole, and promote the dye regeneration. From the distributions of FMOs, it reasonably infers that the electron transitions of Lindqvist- and Keggin-type POMs porphyrin derivatives are mainly from organic groups to POM clusters, which are in favor of the efficient hole injection and facilitating the regeneration of reduced dyes.

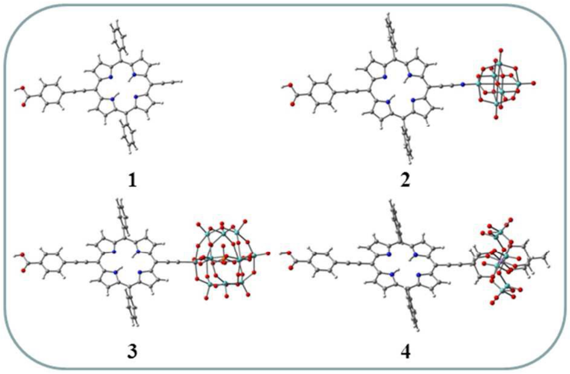


Fig. 1. Molecular structures of systems **1-4**.

The energy levels of FMOs and HOMO-LUMO gaps are computed and shown in Table 1. Comparing with system **1**, the HOMO levels of systems **2-4** are slightly up-shifted, while the LUMOs of systems **2** and **3** are down-shifted, and the LUMO energy level of system **4** is slightly changed. In order to explain the phenomenon, the compositions of the LUMOs for systems **1-4** are further analyzed and the results are listed in Table S1. The LUMOs of systems **2** and **3** mainly consist of d orbitals from Mo atoms (63% for system **2**, 69% for system **3**) and have some contributions from p orbitals of O atoms (33% for system **2**, 19% for system **3**), while the LUMOs are both composed of 86% p orbitals from C atoms for systems **1** and **4**. For studied clusters in this work, the LUMOs are localized on Lindqvist- and Keggin-type POM clusters for systems **2** and **3**, respectively. While the LUMO of system **4** is located on the porphyrin ring, and Anderson-type POM does not contribute to LUMO. Thus, the LUMO energy levels of systems **2** (-3.45eV) and **3** (-3.58eV) are determined by LUMO energies of Lindqvist- (-3.49eV) and Keggin-type (-3.29eV) POMs, which were computed at B3LYP/6-31G* (LanL2DZ) level (Fig. S1), while the LUMO energy of system **4** (-2.87eV) is determined by that of porphyrin (-2.97eV). Therefore, it can conclude that Lindqvist- and Keggin-type POMs affect the FMO energies of POM-based porphyrin hybrids, while the Anderson-type POM has slight influence, which are well consistent with the distributions of FMOs. The HOMO-LUMO energy gaps of Lindqvist- and Keggin-type

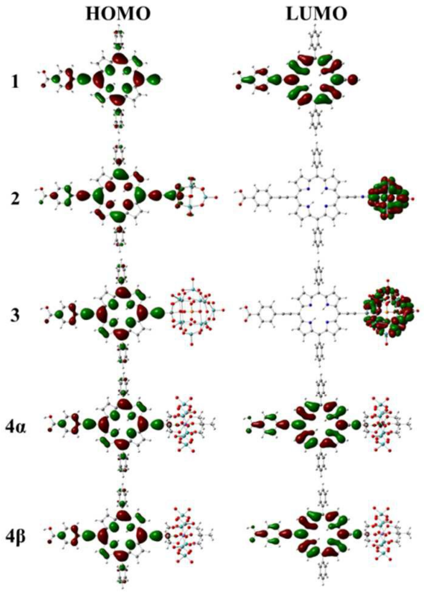


Fig. 2. Frontier molecular orbital profiles of systems **1-4**.

POMs porphyrin derivatives decrease, predicting that their absorption spectra may red shift in comparison with that of system **1**. It is worth mentioning that the HOMO energies of Lindqvist- and Keggin-type POMs porphyrin derivatives are lower than the VB of NiO and LUMO energy levels are higher than I^-/I_3^- redox level, which are beneficial to high hole injection quantum yield and dye regeneration.

Table 1 Frontier molecular orbital energies and energy gaps of systems **1-4** (eV).

System	1	2	3	4
LUMO	-2.97	-3.45	-3.58	-2.87
HOMO	-5.26	-5.21	-5.12	-5.13
H-L$_{gap}$	2.29	1.76	1.54	2.26

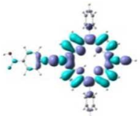
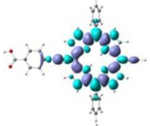
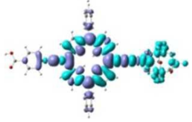
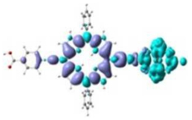
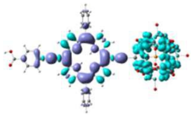
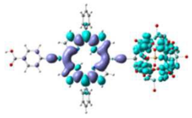
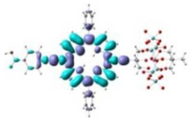
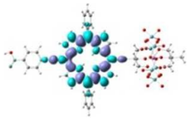
Note: H=HOMO, L=LUMO.

Absorption spectra

As we all know, the dye with excellent performance in p-type DSSC should have wide absorption, which is in good agreement with the solar spectra. To investigate the effect of different types of POM moieties on the optical properties, we perform TD-DFT calculations on systems **1-4** to simulate the ultraviolet-visible (UV-vis) absorption spectra in DMF solution. The excitation energies (E_v), maximum absorption wavelengths (λ_{max}), oscillator strengths (f) and dominant transition configurations for studied systems are listed in Table 2, and the UV-Vis spectra of systems **1-4** are presented in Fig. 3. It is clearly seen that the simulated spectra of all systems are divided into two distinct absorption ranges: the first intense peak locates in the 300-500 nm region and the other one is in the range of 500-800 nm. The spectrum of system **1** consists of two peaks at 399 and 633 nm with relevant oscillator strength of 2.01 and 0.23, respectively. It is worthy to mention that the band **2** in system **2** not only red shift from 633nm (system **1**) to 730 nm (system **2**) but also become broader. The result certifies that Lindqvist-type POM is a strong electron acceptor, which plays a vital role to red-shift and reinforce the UV-Vis spectra. The maximum absorption wavelengths for systems **3** and **4** are similar to that of system **1**, while the corresponding oscillator strengths (f) slightly increase. It can be found that the introduction of Keggin- and Anderson-type POMs has negligible influence on λ_{max}. As a consequence, different kinds of POMs produce different effects on the spectra. For studied systems, the spectrum of Lindqvist-type POM porphyrin derivative overlaps well with the solar spectra. Therefore, based on the absorption spectra, we infer that Lindqvist-type POM porphyrin derivative may be a promising candidate for DSSC.

To give an intuitional impression on the origin of absorption spectra, the electron density difference maps (EDDMs) in Table 2 characterize the dominant electron transitions for systems **1-4**. For system **1**, both band **1**

Table 2 Excitation energies (E_v), maximum absorption wavelengths (λ_{max}), dominant transition configurations, oscillator strengths (f), and the electron density difference maps (EDDMs) of systems **1-4**.

System	E_v (eV)	λ_{max} (nm)	Major assignment	f	EDDMs
1	1.96	633	H→L(51%) H→L+1(17%) H-1→L(16%) H-1→L+1(14%)	0.23	
	3.11	399	H-1→L+1(45%) H-1→L(20%) H→L+1(17%) H→L(14%)	2.01	
2	1.70	730	H→L(82%)	1.40	
	3.02	411	H-1→L+6(28%) H-1→L+7(28%) H→L(10%)	2.47	
3	1.94	640	H→L+2(39%) H→L+3(16%) H→L+8(15%) H-1→L+8(14%)	0.38	
	3.09	401	H-1→L+8(43%) H→L+8(17%) H→L+3(14%) H-1→L+2(14%)	2.06	
4	1.94	637	H(α)→L(α) (28%) H(β)→L(β) (27%)	0.33	
	3.10	401	H-1(α)→L+1(α)(22%) H-1(β)→L+1(β)(22%) H-1(α)→L(α) (11%) H-1(β)→L(β) (11%)	2.12	

Note: The charge transfer is from purple area to blue area.

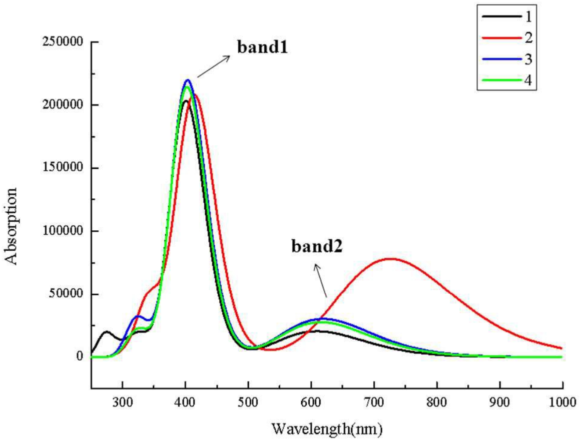


Fig. 3. Simulated absorption spectra of systems **1-4** in DMF.

and band **2** are mainly assigned to the electron promotion from HOMO to LUMO/LUMO+1, and mix with some transition from HOMO-1 to LUMO/LUMO+1. The charge transfer of system **1** is within porphyrin ring, which is assigned to π→π* transition. With regard to systems **2** and **3**, it is clear that the two systems have similar charge transfer characters, that is, the major transition originates from the porphyrin segment to POM cluster through $C\equiv C$ and minor one is π → π* transition within the porphyrin ring, which is well agreement with the electronic structure analysis discussed above. While for system **4**, the charge transfer character is almost the same as that of system **1**, indicating that the Anderson-type POM does not participate in the charge transfer process. Considering the analysis on electronic structure and absorption spectra, the introduction of Lindqvist- and Keggin-type POMs would be favorable for the hole injection to the VB of NiO, while the Anderson-type POM fails to promote the above process.

Photovoltaic performance

As discussed above, the high efficient dye requires high *LHE*. In the meantime, we should also take *HJE*, *DRE* and *CRE* into consideration for fully evaluating the performance of dye. In order to give an intuitional impression whether these systems can serve as dyes, we calculated *LHE*, ΔG_{inj}, ΔG_{reg} and ΔG_{CR}, which are listed in Table 3. It is found that the *LHE* of Keggin- and Anderson-type POMs porphyrin derivatives are relative very low. Furthermore, ΔG_{inj} of Anderson-type POM porphyrin derivative is positive, which hinders the hole injection. While the *LHE* of Lindqvist-type POM porphyrin derivative is 0.96 and higher than those of other dyes reported in literatures[21,22], indicating that the covalent linking porphyrin with Lindqvist-type POM improves the light harvesting ability. Because of the negative ΔG_{inj} and ΔG_{reg}, Lindqvist-type POM porphyrin derivative (system **2**) has sufficient driving force to insure efficient electron injection and dye regeneration. The ΔG_{CR} is positive, which means the charge recombination process is not spontaneous. As a consequence of the above results, system **2** meets the requirements of dye. Therefore, we expect Lindqvist-type POM porphyrin derivative can be a promising candidate for p-type DSSC.

Table 3 Excitation Energy E_v, $E(S/S-)$, ΔG_{inj}, ΔG_{reg}, ΔG_{CR} (eV) and *LHE* for systems **2-4**.

System	E_v	$E(S/S-)$	ΔG_{inj}	ΔG_{reg}	ΔG_{CR}	*LHE*
2	1.70	-3.68	-0.42	-1.12	1.28	0.96
3	1.94	-3.73	-0.71	-1.07	1.23	0.58
4	1.94	-3.01	0.01	-1.79	1.95	0.53

Conclusions

In order to shed light on the influence of different type POMs on the charge transfer of POM-based organic-inorganic hybrids as well as searching high efficient p-type dyes, the Lindqvist-, Keggin-, Anderson-type POMs porphyrin hybrids were designed. The geometries, electronic structures and absorption spectra of systems **1-4** were systematically investigated by means of DFT and TD-DFT methods. Comparing with porphyrin derivative (system **1**), the LUMO energy levels for Lindqvist- and Keggin-type POMs porphyrin derivatives decrease due to the introduction of Lindqvist- and Keggin-type POMs. Meanwhile, the LUMO distributions for Lindqvist- and Keggin-type POMs porphyrin derivatives mainly locate on POM clusters, while the Anderson-type POM does not contribute to the FMOs. The absorption spectrum of system **2** is red shifted about 100 nm in comparison with system **1**. Therefore, Lindqvist-type POM porphyrin derivative exhibits strong and broad absorption in the visible region, which well overlaps with solar spectra. As for systems **3** and **4**, the absorption spectra are not improved by introduction of Keggin- and Anderson-type POMs. The analysis on charge transfer shows that the Lindqvist-type POM is a strong electron acceptor. The performance of system **2** as dye was further verified, showing that Lindqvist-type POM porphyrin derivative possesses high *LHE,* large *HJE*, *DRE* and retarded charge recombination, and matches the requirements of p-type DSSCs. Thus, introducing Lindqvist-type POM is an effective way to improve the property of dye. As a consequence, Lindqvist-type POM porphyrin derivative is a potential candidate among these designed POM-based complexes. It is expected that our studies can be helpful for the future designing and screening out new efficient porphyrin-POM dyes to enhance the performance of p-type DSSCs.

Acknowledgements

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