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Author contact	steven.defeyter@kuleuven.be + 32 (0)16 327921
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Reversible Anion-Driven Switching of an Organic 2D Crystal at a Solid-Liquid Interface

Kang Cui, Kunal S. Mali, Dongqing Wu, Xinliang Feng, Klaus Müllen, Michael Walter, Steven DeFeyter,* and Stijn F. L. Mertens*

Ionic self-assembly of charged molecular building blocks relies on the interplay between long-range electrostatic forces and short-range, often cooperative, supramolecular interactions, yet has been seldom studied in two dimensions at the solid–liquid interface. Here, we demonstrate anion-driven switching of 2D crystal structure at the Au(111)/octanoic acid interface. Using scanning tunneling microscopy (STM), three organic salts with identical polyaromatic cation (PQPC₆⁺) but different anions (perchlorate, anthraquinonedisulfonate, benzenesulfonate) are shown to form distinct, highly ordered self-assembled structures. Reversible switching of the supramolecular arrangement is demonstrated by *in situ* exchange of the anion on the pre-formed adlayer, by changing the concentration ratio between the incoming and outgoing anion. Density functional theory calculations reveal that perchlorate is highly mobile in the adlayer, and corroborate why this anion is only resolved transiently in STM. Surprisingly, the templating effect of the anion persists even where it does not become part of the adlayer 2D fabric, which we ascribe to differences in stabilization of cation conformations by the anion. Our results provide important insight into the structuring of mixed anion–cation adlayers. This is essential in the design of tectons for ionic self-assembled superstructures and biomimetic adaptive materials and valuable also to understand adsorbate–adsorbate interactions in heterogeneous catalysis.

1. Introduction

Supramolecular chemistry, at the origin of most processes from which life itself has emerged, provides a fascinating toolbox for structure formation that has been explored systematically only since a few decades. Self-assembly comprising ionic species is particularly powerful.^[1,2] Indeed, the structure and function of many molecular machines in Nature rely on the interaction between ions and suitable receptors,^[3] including the opening and closing of ion channels,^[4,5] and lead to diseases where these are defective.^[6,7] Inspired by so much ingenuity, there have been incessant efforts to construct charged supramolecular building blocks that lead to functional units of ever-increasing complexity.^[8,9] These include capsules that form around charged guest molecules and 1-dimensional aggregates relevant for artificial photosynthesis.^[10,11]

The structure-inducing effect of counterions has been demonstrated repeatedly in 3-dimensional structure formation.^[10–12] Somewhat surprisingly, therefore, these principles have been scarcely explored

in two dimensions,^[13] even though 2D structures can be efficiently studied in submolecular detail with scanning probe techniques.^[14] A few reports for purely inorganic systems exist, where simple 2D co-crystallization of spherical anions and cations was investigated.^[15] By using organic charged tectons, true supramolecular chemistry, in the sense of combining van der Waals and electrostatic interactions with shape complementarity and steric effects, is expected to give access to much higher levels of complexity.

The class of compounds we investigate here consists of a large polyaromatic discoid cation (PQPC₆⁺) and a range of anions (perchlorate ClO₄[−]; anthraquinonedisulfonate AQDSA^{2−}, and benzenesulfonate BS[−]), **Figure 1**.^[10,11] These anions differ in their affinity for the substrate, size, and total net charge. In a previous report on PQPs,^[16] bias-dependent structural transformations of the adlayer were demonstrated. In two further reports,^[17,18] both under electrochemical conditions, the observed self-assembled structures were dominated by the cation and the externally applied interfacial potential. The lesser role of the anions under electrochemical conditions

Dr. K. Cui, Dr. K. S. Mali, Prof. S. De Feyter, Dr. S. F. L. Mertens
Department of Chemistry
KU Leuven
Celestijnenlaan 200F, 3001 Leuven, Belgium
E-mail: steven.defeyter@kuleuven.be; stmerten@gmail.com

Dr. D. Wu, Prof. X. Feng, Prof. K. Müllen
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz, Germany
Dr. M. Walter
University of Freiburg
Institute of Physics and FIT – Freiburg Center for Interactive Materials
and Bioinspired Technologies
Georges-Köhler-Allee 105, 79110 Freiburg, Germany

Dr. S. F. L. Mertens
Institut für Angewandte Physik
TU Wien
Wiedner Hauptstraße 8–10/E134, 1040 Wien, Austria

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Figure 1. Molecular structure of the organic salts used in this study: (A) cation 9-hexyl-2-phenylbenzo[8,9]quinolino-[4,5,6,7-fed]phenanthridinium PQPC₆⁺ and anions (B) perchlorate ClO₄⁻; (C) 2,6-anthraquinonedisulfonate AQDSA²⁻; (D) benzenesulfonate BS⁻.

can be understood as in aqueous environment, both ions are strongly solvated by a solvent with high permittivity and therefore relatively independent. Accordingly, we did not directly observe the anions in the STM images, and potential-dependent electrocompression was identified as the key driving force to switch between structures with varying packing and concomitant charge densities. Because of negligible overall solubility of the PQP salts in the aqueous electrolyte, thin films had to be prepared by dropcasting from a volatile solvent (e.g. ethanol). This, in turn, limits the degrees of freedom of the ions at the electrode–electrolyte interface.

An electrochemical environment can provide fine control over supramolecular self-assembly,^[19] which we demonstrated for PQPs switching between open porous, auto-host–guest and bilayer structures.^[18] However, a comprehensive understanding of electrostatics-driven self-assembly must also include conditions without external potential control, by tuning for instance size and structure of the anion in mixed cation–anion adlayers.

Here, we report STM results of PQPs at the Au(111)/octanoic acid interface. Compared to the previously discussed electrochemical experiments,^[17,18] this choice of solvent imposes three important constraints on the system: first, the target molecules are soluble in octanoic acid, providing a more straightforward deposition than through dropcasting. Secondly, the static dielectric constant of octanoic acid is lower by a factor 30 than that of water (2.5 versus 80.3 at 20 °C).^[20] This low permittivity results in dissolution of the PQP salts as poorly solvated anion–cation pairs. The enforced close proximity within these ion pairs may lead to increased templating effects among oppositely charged ions. Thirdly, the organic solvent does not introduce other ions, which is hard to achieve under electrochemical conditions.

This paper is organized as follows. First, we report the self-assembled structures observed for each of the pure PQPC₆⁺ salts at the Au(111)/octanoic acid interface. Density functional theory (DFT) calculations are used to substantiate why the perchlorate ions in PQPC₆ClO₄ are only fleetingly resolved in STM, and to explain why templating by the anion may differ also in cases where it does not become incorporated in the 2D adlayer. Finally, we describe *in situ* anion exchange experiments to determine under which conditions anion-induced switching between supramolecular patterns can be observed.

2. Results and Discussion

2.1. PQPC₆⁺ Salts

2.1.1. Perchlorate [PQPC₆ClO₄]

Figure 2A shows a representative high-resolution STM image acquired at the interface between a saturated solution of PQPC₆ClO₄ in octanoic acid and Au(111). A highly ordered structure consisting of parallel double lines is observed. These are separated by darker trenches and reveal a zipper-like pattern of T-shaped repeat units. For this PQP salt, no polymorphism was found. The submolecular resolution achieved in the image, and comparison with the molecular structure in Figure 1, suggest the model shown in Figure 2B: each PQPC₆⁺ cation is visualized as a T-shape with the aromatic rings imaging bright. Within each double row of PQPC₆⁺ cations in antiparallel arrangement, the lone phenyl ring of neighboring molecules interdigitates. The *n*-hexylchains, which typically exhibit low contrast in STM images, are accommodated in the trenches between the double rows. The van der Waals dimensions of the cationic tectons allow assuming adsorption of the entire tecton, and there is no evidence for desorption of the alkyl chain. The calculated packing density of this supramolecular structure is 0.51 PQPC₆⁺ cations per nm². This value is comparable to that under electrochemical conditions and may reflect a similar total energy content for the molecular packing.^[17]

In our electrochemical investigations of PQPs,^[17,18] all attempts to resolve the perchlorate anions directly in the STM images were unsuccessful. In the present case, we managed to transiently visualize the perchlorate counter ions. For electroneutrality reasons, these must occupy positions close to the stably visualized cationic part of the adlayer. Figure 3A,B shows two high-resolution STM images displaying the PQPC₆⁺ cations as discussed previously. In addition to the cation lattice, which is imaged in a stable manner, occasional bright features can be seen, indicated by arrows. The additional features appear limited to one per cation, are much smaller than the cations and in many cases have an elongated or even streaky appearance in the fast STM scan direction (that is, from left to right in the images), suggesting high mobility. Zoom-ins of individual PQPC₆⁺ cation snapshots with a superimposed bright feature are presented in Figure 3C, together with tentative models that show ClO₄⁻ in its approximate position for each image.

In order to rationalize why ClO₄⁻ is highly mobile in the PQPClO₄ adlayer, we performed DFT calculations of the PQPClO₄ salt. For this calculation, the PQP⁺ cations were arranged on the Au(111) substrate as experimentally observed, Figure 4A (see Supporting Information for details). To reduce the size of the system, and because the presence of the *n*-hexyl chain is not expected to affect the charge distribution in the molecule significantly, the alkyl chain was omitted. Per unit cell, which consists of two PQPClO₄ units, one of the perchlorate ions was forced to move along a diagonal path as outlined in Figure 4B, and the total energy as a function of the position is plotted in Figure 4C. While the position of the perchlorate near the center of the PQPC₆⁺ cation is energetically the most

Figure 2. (A) High-resolution STM image of PQPC₆ClO₄ monolayer at the Au(111)/octanoic acid interface. For large-scale images, see Figure S1 (Supporting Information). $U_b = -0.2$ V, $I_t = 0.8$ nA. The unit cell parameters are $a = 2.6 \pm 0.2$ nm, $b = 1.5 \pm 0.2$ nm and $\alpha = 86 \pm 2^\circ$. (B) Tentative model.

favorable, the energy landscape experienced by the perchlorate ion is very shallow as long as its position lies within the perimeter of the PQP⁺ cation. This result corroborates that ClO₄[−] is highly mobile within the PQPC₆ClO₄ adlayer and can be easily moved by the STM tip during scanning.

2.1.2. 2,6-Anthraquinonedisulfonate [(PQPC₆)₂AQDSA]

The anthraquinone-based salt (PQPC₆)₂AQDSA (Figure 1B) was investigated previously under electrochemical conditions, in the presence of 0.1 M HClO₄ as an electrolyte.^[17]

Figure 3. (A, B) Transient observation of ClO₄[−] in high-resolution STM images of PQPC₆ClO₄ at the Au(111)/octanoic acid interface. $U_b = -0.2$ V, $I_t = 0.8$ nA. Perceived positions of ClO₄[−] (bright) on the PQPC₆⁺ lattice are highlighted with colored arrows (center, red; lone phenyl ring, green; sides, yellow). (C) Magnified snapshots (upper panels) of individual PQPC₆ClO₄ molecules with visualized perchlorate (bright). Tentative models (lower panels) showing ClO₄[−] anions in their likely positions on top of T-shaped PQPC₆⁺ cations. C sky blue, H white, N dark blue, Cl green, O red.

Figure 4. Simulation of perchlorate mobility in a PQPClO₄ adlayer. (A) Initial arrangement of ion pairs on the Au(111) substrate (Au yellow, C gray, H white, Cl green, O red, N blue). The unit cell containing two PQPClO₄ molecules is indicated. (B) Diagonal path (green) along which movement of ClO₄[−] is considered. (C) Total energy of PQPC₆ClO₄ as function of ClO₄[−] position along the path shown in panel B with $\rho = \sqrt{x^2 + y^2}$ defined as the horizontal distance from the N-position.

The electrochemical signature of the AQDSA^{2−} dianion was observed in cyclic voltammetry, but the anion was not visualized in EC-STM. At the Au(111)/octanoic acid interface, by contrast, two polymorphs were observed, each consisting of a regular pattern of two differently shaped building blocks. The first pattern, **Figure 5A**, in addition to the T-shaped PQPC₆⁺

cations, also comprises rectangular features, which are assigned to the AQDSA^{2−} dianion. The rectangular shape of adsorbed AQDSA^{2−} in STM was confirmed independently by imaging its sodium salt on Au(111) (see Figure S5, SI).

In the mixed adlayer structure, the ratio between PQPC₆⁺ monocations and AQDSA^{2−} dianions is 1:2, as required for

Figure 5. Polymorphism in (PQPC₆)₂AQDSA at the Au(111)/octanoic acid interface: First polymorph: (A) High-resolution STM image with unit cell parameters $a = 3.9 \pm 0.2$ nm, $b = 1.7 \pm 0.2$ nm and $\alpha = 42 \pm 3^\circ$. (B) Tentative model. Second polymorph: (C) High-resolution STM image with unit cell parameters $a = 3.4 \pm 0.2$ nm, $b = 1.4 \pm 0.2$ nm and $\alpha = 89 \pm 3^\circ$. (D) Tentative model. $U_b = -0.2$ V, $I_t = 0.8$ nA. For large-scale STM images, see Figures S2, S3 (Supporting Information).

electroneutrality. Each sulfonate group of AQDSA²⁻ points at the bay region of a neighboring PQP⁺, which results in one dianion alternating with two monocations in both main directions of the adlattice. Since the alkyl chains are not visible in the STM image, and the unit cell parameters cannot account for adsorption of the alkyl chains on the Au(111) surface, all the alkyl chains of the cations must be desorbed and free to move in solution, yielding an entropic energy gain. The model in Figure 5B does not include the alkyl chains, yet provides good agreement with the experimental data.

A second structural polymorph exists for the (PQPC₆)₂AQDSA monolayer, Figure 5C, where four PQPC₆⁺ cations surround one AQDSA²⁻ dianion in a rectangular arrangement. The adlayer consists of regular molecular rows of both T-shaped cations and rectangular anions, aligned along the “a” and “b” vector directions which are perpendicular to each other. Figure 5D provides a tentative model. In the second polymorph, the *n*-hexyl substituent on the PQPC₆⁺ cation can be seen in the dark rhombus-shaped spaces that separate two molecular rows, and can be accounted for in the model. This leads to a 10% lower molecular packing density in polymorph 2 (at 0.21 (PQPC₆)₂AQDSA units per nm²) compared to polymorph 1 (which has 0.23 (PQPC₆)₂AQDSA units per nm²).

The modulation of brightness visible in Figure 5 is due to the thermal reconstruction of Au(111), which is not lifted by the adsorption events. A certain degree of directional templating by the reconstruction lines can be seen in Figure 5A, even though this does not disrupt the overall adlayer direction or cause domain formation, as is visible from larger-scale images (Figures S2, S3, Supporting Information).

2.1.3. Benzenesulfonate [PQPC₆BS]

Benzenesulfonate (BS⁻), an anion with intermediate size, furnishes a rather complex supramolecular pattern, Figure 6A. Lamellae can be identified that each consists of three molecular rows in which individual PQPC₆⁺ units can be recognized.

Within each lamella, the PQPC₆⁺ tectons assume a square arrangement, and their orientation within each molecular row changes in a periodic manner. Mutually, the lamellae are offset by about half the size of a PQP core. As for ClO₄⁻, the BS⁻ anions are not visualized, suggesting similar mobility in both cases. However, clearly distinct supramolecular patterns for the (identical) PQPC₆⁺ cations in the two cases are observed, indicating that the interaction of the anion with the (visualized) cations must be different. A key difference between the two supramolecular patterns is that in the perchlorate structure (Figure 2), the *n*-hexylchain of PQPC₆⁺ is adsorbed on the Au(111) substrate, whereas it is desorbed in the benzenesulfonate structure (Figure 6). An adsorbed tail gains van der Waals interactions with gold and an enthalpic benefit, while a desorbed tail, with higher conformational freedom, is entropically favorable. The resulting Gibbs free energy difference can be small, as is also suggested by coexistence of domains with ad- and desorbed C₆ tails for (PQPC₆)₂AQDSA (see previous section). Our DFT investigations indeed show that for the perchlorate salt, the flat conformation of PQPC₆⁺ is more stable by 0.30 eV compared to an upright tail. By contrast, the BS⁻ anion is able to stabilize the upright conformation so that it is less favorable by 0.17 eV only (see Supporting Information for details). This small energetic preference can explain why PQPC₆BS self-organizes differently from PQPC₆ClO₄, even though both anions are highly mobile, and lends further proof to our hypothesis that the anion steers the packing. As in all three cases saturated solutions in octanoic acid were studied, we confirmed that small differences in solubility are not at the basis of the differences in supramolecular structure: indeed, for each of the three PQPC₆⁺ salts, dilutions of up to a factor 10 yielded the same patterns in STM.

As an intermediate conclusion, we have demonstrated that in organic mixed PQP anion–cation adlayers, the anion templates the supramolecular pattern. For this templating effect, the anion does not have to be part of the actual 2D fabric of the adlayer, as follows from comparing PQPC₆ClO₄ and PQPC₆BS: in both cases, the anion is not visualized as static part of the monolayer, yet distinct patterns are formed.

Figure 6. (A) High-resolution STM image of PQPC₆BS monolayer at the Au(111)/octanoic acid interface. $U_b = -0.2$ V, $I_t = 0.8$ nA. The unit cell parameters are $a = 4.34 \pm 0.2$ nm, $b = 2.67 \pm 0.2$ nm and $\alpha = 68 \pm 2^\circ$. (B) Tentative model.

Figure 7. STM image of $(\text{PQPC}_6)_2\text{AQDSA}$ monolayer at the Au(111)/octanoic acid interface (A) before and (B) after addition of NaClO_4 solution to the supernatant. $U_b = -0.2$ V, $I_t = 0.8$ nA.

2.2. Anion-driven Structural Switching

For three PQP-based salts with identical cations yet different anions, three distinct supramolecular structures were found at a Au(111)/octanoic acid interface. To provide ultimate evidence for the templating nature of the anion, and to demonstrate the dynamic nature of the adlayer structure, we performed anion post-assembly exchange experiments, by adding the sodium salt of the alternative anion to the supernatant.

2.2.1. Forward Transformation: $(\text{PQPC}_6)_2\text{AQDSA}$ into $\text{PQPC}_6\text{ClO}_4$

Following successful imaging of $(\text{PQPC}_6)_2\text{AQDSA}$, most of the supernatant was removed from the surface using filter paper, taking care that no actual drying took place. Immediately afterwards, 10 μL of a 1.4×10^{-4} M solution of NaClO_4 in octanoic acid was placed on the Au(111) sample carrying the $(\text{PQPC}_6)_2\text{AQDSA}$ adlayer and imaging was resumed. For solubility reasons, a few percent ethanol was added to the octanoic acid as a co-solvent to prepare the NaClO_4 solution. In a separate control experiment, we confirmed that the presence of ethanol alone did not trigger any changes in the adlayer structure.

Figure 7A shows the adlayer structure before and **Figure 7B** immediately after addition of sodium perchlorate, that is, as soon as molecular resolution was achieved again (ca. 30 min). In

Figure 7A, the characteristic structure of the $(\text{PQPC}_6)_2\text{AQDSA}$ adlayer (polymorph 1, compare with **Figure 5A**) is found.

After the addition of NaClO_4 , **Figure 7B**, only the adlayer structure typical for $\text{PQPC}_6\text{ClO}_4$ is observed, confirming that interfacial exchange of the anion has taken place, and that this exchange is sufficient to switch to the corresponding adlayer structure. From the dimensions of the Au(111) sample, the concentration and volume of the perchlorate solution and the footprint of $(\text{PQPC}_6)_2\text{AQDSA}$ in the adlayer, we can estimate a molar ratio between ClO_4^- and AQDSA^{2-} of maximum 120:1, assuming complete removal of $(\text{PQPC}_6)_2\text{AQDSA}$ from the supernatant before addition of perchlorate. The 2 orders of magnitude difference in chemical potential between the anions is therefore sufficient to induce the anion exchange and trigger the supramolecular rearrangement.

2.2.2. Backward Transformation: $\text{PQPC}_6\text{ClO}_4$ into $(\text{PQPC}_6)_2\text{AQDSA}$

To demonstrate the reversibility of the supramolecular switching, the inverse experiment was also carried out: after assembly and imaging of pure $\text{PQPC}_6\text{ClO}_4$ and removal of the supernatant, **Figure 8A**, 10 μL of 8.0×10^{-5} M Na_2AQDSA in octanoic acid was added. In this case, it took several hours for ordered domains to emerge. In **Figure 8B**, the striped structure

Figure 8. STM image of $\text{PQPC}_6\text{ClO}_4$ monolayer at the Au(111)/octanoic acid interface (A) before and (B) after addition of Na_2AQDSA . $U_b = -0.2$ V, $I_t = 0.8$ nA.

of Figure 5A is again clearly identified in which both cations and anions are adsorbed on Au(111) and self-organize into ordered close-packed arrays. In this exchange experiment, only the higher-density polymorph 1 (see section 1) was observed. This may indicate that this denser polymorph represents a thermodynamic minimum, and that the ion exchange, as it requires extensive mobility within the adlayer, has an annealing effect. The generation of ordered motifs at the solid–liquid interface follows from interplay of complex interactions between the anolyte molecules, the solvent molecules, and the substrate.^[21] On the one hand, 1-octanoic acid does not compete efficiently with the PQP molecules for physisorption on the Au(111) surface. On the other hand, its apolar nature favors the formation of ion pairs, and therefore, increases structural templating by the anion. The anion exchange experiments reflect the dynamics and reversible nature of the system. While we cannot claim that the self-assembly and anion exchange processes occur under thermodynamic control, it is clear that increasing the concentration of a counterion in the supernatant promotes the exchange. The experiments described here prove structural templating by the anion, but do not reveal details about the mechanism of the exchange, which can occur on the surface, in the supernatant or a combination thereof.

3. Conclusions and Outlook

Using STM, we have investigated templating effects in the self-organization of charged PQPs with the same cation (PQPC₆⁺) and different anions (AQDSA²⁻, ClO₄⁻ and BS⁻) at the Au(111)/octanoic acid interface. The low-permittivity solvent dissolves the salts as confined ion pairs and increases structural templating effects, leading to distinct supramolecular arrangements under otherwise identical experimental conditions. Reversible anion-driven switching between supramolecular patterns is demonstrated by on-surface anion exchange, by visualization of characteristic patterns when AQDSA²⁻ is exchanged by perchlorate and vice versa. These observations prove the structure-templating effect of the anions, even though in two out of three cases, these are not visualized in STM as static part of the adlayer. The principles demonstrated here are important for designing biomimetic adaptive materials, which change properties depending on the chemical environment. Also, as composition–structure–reactivity relationships are essential to understand the performance and selectivity of many catalytic processes, our results provide an entry to steering adsorbate–adsorbate and adsorbate–substrate interactions in supramolecular catalysis.

4. Experimental Section

All experiments were performed at room temperature (20–24 °C) using a PicoLE (Agilent) system operating in constant-current mode with the tip immersed in the supernatant liquid. STM tips were prepared by mechanical cutting of Pt/Ir wire (80%/20%, 0.25 mm diameter). Au(111) films on mica (Georg Albert PVD) were used as substrates. The substrates were annealed in a butane flame followed by cooling under a stream of argon. Reconstruction lines of Au(111) were not always present after sample annealing. Octanoic acid (Sigma-Aldrich, 99%) was

used as a solvent without further purification. For each measurement a 10 µL drop of the desired solution was applied directly to the flame-annealed substrate and STM imaging commenced immediately. Syntheses of PQPC₆ClO₄, (PQPC₆)₂AQDSA and PQPC₆BS are reported elsewhere.^[10,11] Sodium perchlorate (NaClO₄, Sigma-Aldrich, 99%) and disodium 9,10-anthraquinone-2,6-disulfonate (Na₂AQDSA, Sigma-Aldrich, 99%) were used without further purification. STM images were analysed using SPIP (Image Metrology, version 5.1.4) software and the molecular models were built using Hyperchem 7.0 program.

DFT calculations were performed within the PAW formalism,^[22] where the smooth Kohn–Sham wave functions and the electron density were represented on real space grids^[23,24] with a grid spacing of 0.2 Å for the wave functions. The density functional was approximated in the generalized gradient approximation and van der Waals corrections were applied.^[25,26] Further details are given in Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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