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Investigation of the effect of ferroelectric polarization on the spin state of spin crossover complexes embedded in a piezopolymer matrix

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ABSTRACT

Recent experiments indicate that the spin state of molecules adjacent to ferroelectric layers depends on the magnitude and direction of the polarization. Since similar effects could arise in nanocomposites, we synthesized samples with spin crossover particles embedded in a ferroelectric polymer. The spin transition phenomenon in the poled and non-poled composites was investigated by hot-stage optical microscopy and calorimetry, but no sizeable effect of the poling on the spin-state equilibrium was detected. On the other hand, subtle matrix effects on the spin crossover properties and a rather unusual sensitivity of the spin transition on thermal annealing was detected.

1. Introduction

The molecular spin crossover (SCO) phenomenon between the high spin (HS) and low spin (LS) states of certain (pseudo)-octahedral $3d^4$ - $3d^7$ complexes [1–3] can be conveniently induced by temperature [4], pressure [5] or light irradiation [6]. Numerous SCO complexes respond also to chemical stimuli (e.g. adsorption of guest molecules) [7]. A very intense magnetic field can also alter the spin state of the molecules [8]. On the other hand, the possible influence of electric fields remains elusive, despite the obvious technological interest of electric field control of molecular spin states.

The rationale behind a possible electric field effect is that the dielectric permittivity of the material in the LS and HS states is different [9] and therefore the spin state equilibrium will be altered in the presence of an intense electrical field. In other words, the interaction energy between the electric field and the electric dipolar moment (permanent or induced) of the molecules depends on the spin state of the latter, leading to a shift of the transition temperature. However, one can expect a significant shift of the spin-state equilibrium and, in general, one can achieve an electrostatic contribution to the free energy comparable with typical reaction enthalpies only for very high fields [10]. Indeed, a rough estimation gives a change of energy of ~ 20 kJ/mol when a molecule with a dipole component of 1 D, oriented along the field direction, is subjected to a field of 1 GV/m [11]. In practice, such extreme fields can

be achieved only locally, at specifically designed interfaces. For instance, Climent et al. [12] theoretically predicted a large modification of the spin state equilibrium temperature (up to 40–50 K) of selected SCO molecules placed in plasmonic nanocavities and argued that this effect is linked to the strong coupling between the (spin state dependent) dipole moment of the molecule and the intense local electromagnetic field of the plasmonic cavity.

From an experimental point of view, at the single-molecule level, several research teams have demonstrated spin state switching by applying a voltage bias through SCO molecules by means of the tip of a scanning tunneling microscope [13–15]. On a macroscopic level, the application of high external fields ($>MV/m$) revealed some interesting effects [16], but the use of such high fields remains complicated due to the potential breakdown of the material. Furthermore, in the past decade, a considerable effect of local electrical fields on the spin state of molecules near the interface of polarized ferroelectric polymeric substrates was indicated [17–20]. Notably, Hao et al. [18] reported that both polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) and croconic acid layers adjacent to the SCO complex $[Fe\{H_2B(pz)_2\}_2(bipy)]$ ($H_2B(pz)_2$ = bis(hydrido)-bis-(1H-pyrazol-1-yl)borate, bipy = 2,2'-bipyridine) appear to lock to a large extent either the HS or the LS state of the molecule, depending on the direction of the ferroelectric polarization. Further experiments by Mosey et al. [19] showed that such effects are even perceptible in relatively thick (65 nm) SCO films.

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Fig. 1. Photographs of the neat P(VDF₈₀-TrFE₂₀) film (from left to right): blade-casted, annealed at 120 °C and hot pressed.

Although the phenomenon remain debated [21] and the mechanisms largely uncertain, these findings suggest that intense local electric fields, generated at interfaces, could alter the spin state equilibrium.

In this context, a series of interesting samples were obtained recently by embedding SCO particles into piezoelectric polymers, such as P(VDF-TrFE) (poly(vinylidene fluoride-co-trifluoro-ethylene) [22–24] and PVDF (poly(vinylidene fluoride) [25]. These composites revealed remarkable electromechanical couplings, such as current discharge at the spin transition and spin-state dependent ferroelectric properties. Incidentally, Rat et al. [22] observed also a small downshift of the transition temperature in the polarized composites (vs. the nonpolarized sample). An analogy between these SCO@piezopolymer samples and the ferroelectric/SCO multilayers appears thus, which motivated us to design dedicated experiments aiming to answer the question whether the ferroelectric polarization in the composite had an effect on the spin transition properties of the embedded particles. The results of these experiments are reported below.

2. Materials and methods

All chemicals and solvents were obtained from Sigma Aldrich and used without any further purification. P(VDF₈₀-TrFE₂₀) with a ratio of vinylidene/trifluoroethylene of 80/20 was provided by Piezotech. SCO nanoparticles of ca. 60 nm mean size and formulae [Fe(Htrz)₂(trz)](BF₄)·0.7H₂O (1) and [Fe(Htrz)_{2.1}(NH₂trz)_{0.1}(trz)_{0.8}](BF₄)·0.8H₂O (2) were synthesized and characterized as described by Piedrahita et al. [26]. For the synthesis of SCO@P(VDF-TrFE) composite films, we prepared two suspensions of 80 mg of each SCO compound in 1.6 ml of butanone, in which we dissolved 240 mg of P(VDF₈₀-TrFE₂₀). This mixture was then blade casted on a heated (35 °C) glass substrate at 1.50 mm blade height. After drying, the resulting membranes had a thickness around 100 μm and a particle concentration of ca. 25 wt%. The membranes were then hot pressed at 145 °C at a pressure of 0.2 bar for 30 s. The samples were finally polarized using a low frequency (200 mHz) AC voltage of 3.6 kV in amplitude, corresponding typically (depending on the sample thickness) to an electrical field of 1 MV/cm. During the poling process, the composite films were placed between two disk-shaped copper electrodes in an aluminium crucible, filled with Castor oil. The piezoelectric charge coefficient d_{33} of the poled samples was measured by means of a Piezotest PM200 instrument using the Berlincourt method at 110 Hz and 0.25 N applied force. Variable temperature (white light) optical reflectance measurements on the films

were conducted using a Motic SMZ168 stereomicroscope equipped with a color camera (MotiCam 2) and a heating stage (Linkam Scientific THMS600). DSC thermograms were acquired using a Netzsch DSC 3500 Sirius instrument with a heating/cooling ramp of ±10 °C/min and a nitrogen gas purge of 20 mL/min. Temperature and enthalpy were calibrated using the melting transition of indium.

3. Results and discussion

In contrast to our previous works, wherein the SCO@P(VDF-TrFE) composites were made using polymers with 70–30 or 75–25 mol% monomer ratio [22–24], in the present work we opted for the copolymer with 80–20 mol%. This choice was motivated by the relatively high Curie temperature of this copolymer ($T_{Curie} = 135$ °C) in comparison with the previous ones. The Curie point denotes the temperature at which the ferroelectric phase is transformed into a paraelectric one, destroying thus the ferroelectric polarization. Since the SCO samples we used must be heated to relatively high temperatures (ca. 100 °C) to ensure a complete spin transition, it is important to use a copolymer with a high T_{Curie} . However, reducing the TrFE content of the copolymer involves an adverse effect, which is the reduced piezoelectric performance. To mitigate this issue, in the present work we employed a hot press (following blade casting of the composite film), which affords for an improved recrystallization of the sample, ensuring a high concentration of the polar β phase, which displays the highest piezoelectric performance [27,28].

Fig. 1 presents the visual differences observed in pure P(VDF₈₀-TrFE₂₀) samples subjected to different treatments, highlighting the relationship between opacity and β phase concentration. The casted sample appears transparent, indicating a minimal presence of the β phase and suggesting that the polymer chains are in a less ordered state. In contrast, the sample annealed at 120 °C is translucent, reflecting a partial increase of the concentration of the β phase in the polymer. The hot-pressed sample is opaque, signifying the highest concentration of the β phase in the polymer chain structure. This increase in opacity correlates with an enhanced piezoelectric response, which permits the achievement of the higher polarization yield.

For a more quantitative analysis, the hot pressed composite samples were analyzed using differential scanning calorimetry (DSC) to observe the peaks associated with the Curie and the melting transitions. More importantly, the area under these peaks, which is proportional to the amount of the crystalline β -phase, was measured. The DSC

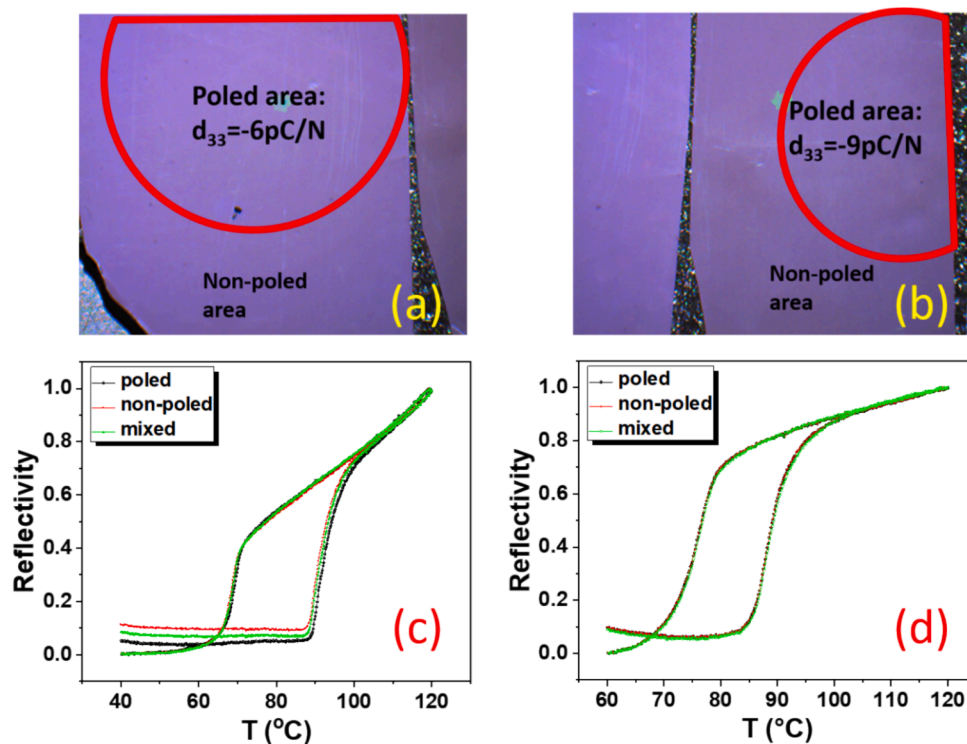


Fig. 2. (a and b) Selected room temperature optical images of the composites (a) 1@P(VDF₈₀-TrFE₂₀) and (b) 2@P(VDF₈₀-TrFE₂₀) showing the polarized regions by a red line. Note that the color recorded by the camera differs from that perceptible by the naked eye due to the color balance settings. (c and d) Variable temperature optical reflectivity (normalized to the highest temperature) of the composites (c) 1@P(VDF₈₀-TrFE₂₀) and (d) 2@P(VDF₈₀-TrFE₂₀) integrated for the poled (black) and non-poled (red) regions, as well as for the entire image (green).

measurements in the heating mode revealed the expected peaks related to the Curie transition in the P(VDF₈₀-TrFE₂₀) copolymer at 135 °C and another peak at 155 °C that represents the melting point of the polymer. In cooling, the solidification occurs around 126 °C and the Curie transition near 80 °C. In the first heating cycle the integrated area of the Curie and melting peaks was 50 J/g, from which a crystallinity of ca. 48 % can be inferred, using the approach reported in Ref. [27]. Note that the temperature we chosen for the hot pressing (145 °C) falls just in between the Curie and melting temperatures, which was shown in previous works as the optimum temperature to ensure the highest possible β phase content (see for example Ref. [28]).

In the next step, the composites 1@P(VDF₈₀-TrFE₂₀) and 2@P(VDF₈₀-TrFE₂₀) (both 25 wt%) were poled in an AC field resulting in d_{33} piezoelectric coefficients of -6 pC/N and -9 pC/N , respectively. Not surprisingly, these values are inferior to what we could obtain for the pure P(VDF₈₀-TrFE₂₀) copolymer processed in the same conditions (ca. -20 pC/N), but remain very substantial for such high particle loads [22–24], confirming thus the efficiency of our sample processing protocol. The poled films were attached via a thermally conductive tape to a thin silicon substrate to ensure a homogeneous temperature distribution and were submitted to a heating–cooling cycle around the spin transition region at a rate of 1 °C/min. Importantly, sample heating was limited to 120 °C to reach completeness of the spin transition, while avoiding the depolarization of the polymer that occurs around 136 °C. During the thermal cycle color photographs of the films were acquired covering both polarized and non-polarized regions of the samples (see Fig. 2a and b). The key experimental observation is the fact that in none of the images (before, after and during the spin transition) we could observe a color contrast between the poled and non-poled regions, indicating comparable SCO behaviors. This finding is visualized in Fig. 2c and d showing that the thermal SCO curves recorded simultaneously for the polarized and non-polarized areas are virtually identical for both samples. In other words, the ferroelectric polarization does not

lead to any appreciable change of the spin state equilibrium in these composite samples. (N.B. A shift of the baseline is discernible in Fig. 2c, which we attribute to thermal drift of the sample, but this does not affect the observation of the abrupt spin transition.)

At this stage, we shall discuss the link between the directions of the ferroelectric polarization (perpendicular to the sample plane) and that of the dipole moments of the SCO complexes in our samples. Indeed, we have purposefully used in these experiments small (ca. 60 nm) isomorphous SCO particles, which afford for isotropic composites with a random particle distribution – contrary to high aspect ratio particles, which tend to give rise to specific particle orientations [29]. Obviously, using randomly oriented particles does not allow us to maximize the interaction with the ferroelectric polarization, but most importantly it ensures that a significant proportion of the particles is oriented such a way that the local dipole moments are aligned with the polarization direction in any case. Besides the particle orientation, the particle size, the polarization of the matrix and the change of dielectric permittivity at the spin transition are also important parameters. The compounds we used show an important variation of the dielectric permittivity in comparison with other SCO complexes [30], and also a fairly high degree of matrix polarization, which are favorable assets. As for the particle size, it remains an open question, which certainly needs to be investigated. It may be also worth to note that despite the simple physical mixing we used, there is a good adhesion between the particles and the matrix, which can be inferred from previously published mechanical and electromechanical tests on similar composites [22,23,29].

To further analyze the potential effects of the ferroelectric polarization on the spin-state equilibrium, we performed a series of DSC analysis on the composite 1@P(VDF₈₀-TrFE₂₀). For this experiment we used two samples, one from the previous optical reflectivity experiment (denoted 1A) and another one, which could be poled to reach a d_{33} value of -9 pC/N (denoted 1B). In comparison with the optical reflectivity measurements, the disadvantage of calorimetry is that the poled and

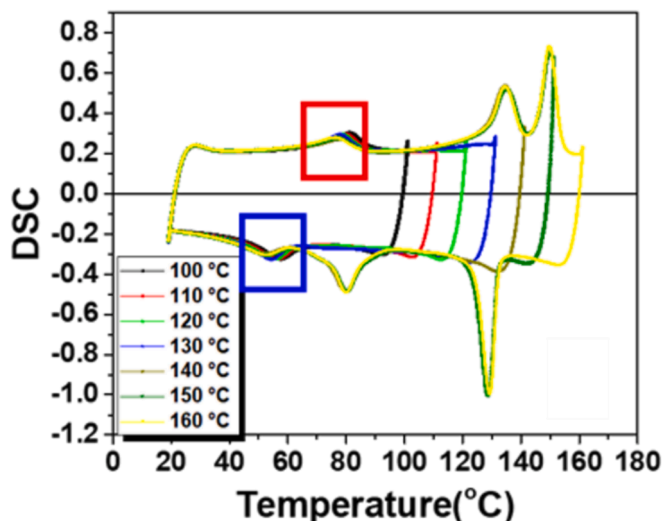


Fig. 3. DSC measurements on sample $1A^{\text{poled}}$ through multiple thermal cycles, with identical starting temperatures ($20\text{ }^{\circ}\text{C}$) and increasing end temperatures (from 100 to $160\text{ }^{\circ}\text{C}$).

non-poled sample regions cannot be analyzed simultaneously. For this reason, altogether four samples were investigated: $1A$ and $1B$, both poled and non-poled. On the other hand, the DSC technique provides also several advantages, notably, it allows us to control in-situ if the Curie transition is reached (partially or totally) during the thermal cycles. To better explore this aspect, we measured in our DSC multiple

temperature cycles, each starting at $20\text{ }^{\circ}\text{C}$ and ending at different temperatures (see Fig. 3 for an example). In the first cycle, the final temperature was set to $100\text{ }^{\circ}\text{C}$ and then it was increased by steps of $10\text{ }^{\circ}\text{C}$ to reach $160\text{ }^{\circ}\text{C}$ (i.e. above the melting point of the matrix). Each cycle was repeated twice and the data reported below corresponds to the second run.

Fig. 4 summarizes the DSC data obtained for the different composite samples. Surprisingly, we observed that the spin transition temperature of each sample decreases when heated to higher temperatures. This phenomenon is, however, an intrinsic property of the neat SCO particles, which display a similar behavior when analyzed in the same experimental conditions (see Fig. 5). This decrease of the spin transition temperature is reversible: when the sample is left in ambient air for a month and re-analyzed subsequently by DSC, a very similar curve is obtained, which signifies that the sample recovered to a large extent its initial SCO properties upon storage. Based on this observation we can suggest that heating of the particles leads to a progressive loss of their water content and, as a result, to a progressive change of their SCO behavior. Then, in ambient conditions the sample reabsorbs water molecules and regains (roughly) its initial SCO properties. Although this phenomenon complicates the analysis of the DSC data obtained for the composite samples, we can extract several interesting information. The poled and non-poled samples display slightly different transition temperatures, although the differences remain small ($<5\text{ }^{\circ}\text{C}$), in particular for sample $1B$, which displays higher polarization. However, if the differences were the result of the polarization of the polymer, we expect they disappear after heating above $140\text{ }^{\circ}\text{C}$, because the Curie temperature will be surpassed and the polarization of the polymer will be destroyed. This is clearly not the case in our experiments, wherein the transition temperatures change in a similar (parallel) manner both

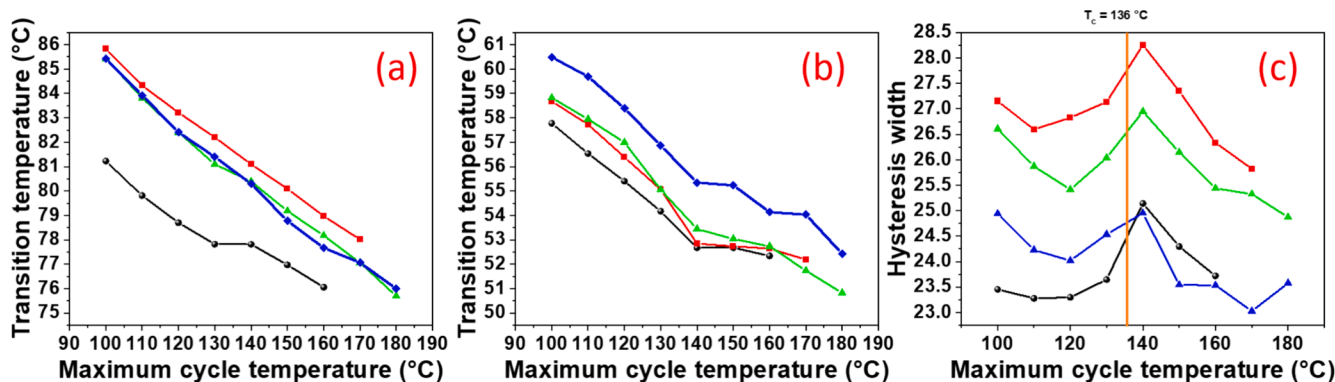


Fig. 4. Spin transition temperatures in the heating (a) and cooling (b) modes as well as the associated width of the hysteresis (c) as a function of the 'highest heating temperature' for samples $1A^{\text{poled}}$ (black), $1A^{\text{non-poled}}$ (red), $1B^{\text{poled}}$ (green) and $1B^{\text{non-poled}}$ (blue).

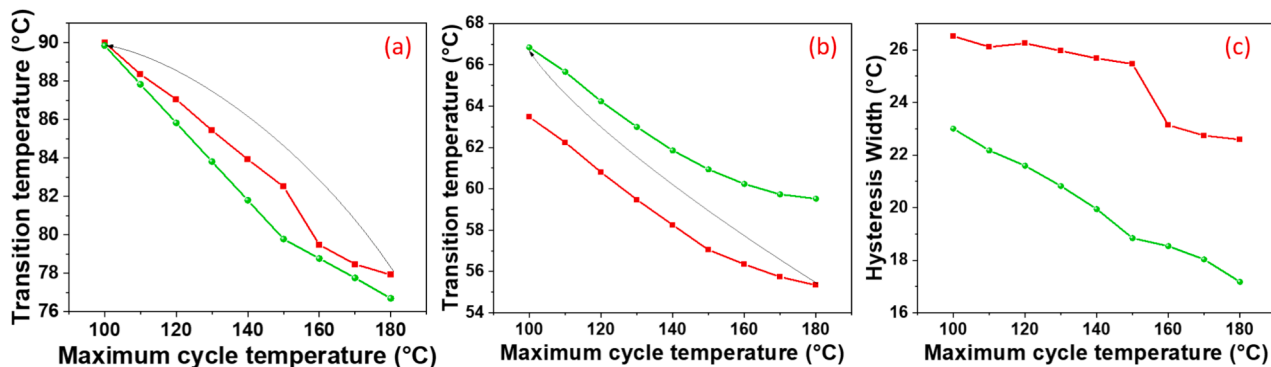


Fig. 5. Spin transition temperatures in the heating (a) and cooling (b) modes as well as the associated width of the hysteresis (c) as a function of the 'highest heating temperature' for the neat powder sample 1. Two series of experiments are shown: a first experiment (in red) and a second experiment (in green) conducted on the same DSC sample pan following one month storage in ambient air.

below and above the Curie temperature. In agreement with the optical microscopy observations, we can conclude therefore that the ferroelectric polarization has no considerable impact on the spin transition behavior of the samples.

Another interesting observation is the occurrence of a maximum of the hysteresis width when the samples are annealed at 140 °C (Fig. 4c). This finding is not related to the polarization of the polymer matrix, since we observe it also in the non-polarized samples, neither to the intrinsic properties of the bulk material, since we do not observe it in the neat powder sample (Fig. 5c). We can thus suggest that this phenomenon is related to a partial recrystallization of the P(VDF₈₀-TrFE₂₀) polymer into its β phase, which is the most efficient at this temperature. This subtle influence of the degree of crystallinity on the SCO phenomenon might be linked to different mechanical and/or interfacial properties.

4. Conclusions

No sizeable effect of the ferroelectric polarization of the P(VDF₈₀-TrFE₂₀) matrix on the spin crossover properties of embedded Fe(II)-triazole particles could be observed, despite a relatively high degree of polarization, attested by a piezoelectric charge coefficient of -9 pC/N. On the other hand, the experiments revealed a small, but distinct influence of the degree of crystallinity of the polymer on the width of the hysteresis associated with the thermal spin transition. Incidentally, a considerable sensitivity of the spin transition on the thermal annealing conditions was also uncovered and, tentatively, linked to the dehydration of the samples. Further work is anticipated to address the effect of strong local electric fields on the spin-state equilibrium using on-purpose designed nanostructures, such as plasmonic nanocavities.

CRediT authorship contribution statement

Ion Soroceanu: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Onkar Kulkarni:** Methodology, Investigation. **Eric Dantras:** Supervision, Funding acquisition. **Aurelian Rotaru:** Supervision, Funding acquisition, Data curation, Conceptualization. **Lionel Salmon:** Supervision, Methodology, Funding acquisition, Formal analysis. **Gábor Molnár:** Writing – review & editing, Supervision, Methodology, Formal analysis, Conceptualization. **Azzedine Bousseksou:** Writing – review & editing, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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