

Low-Power Upconversion in Poly(Mannitol-Sebacate) Networks with Tethered Diphenylanthracene and Palladium Porphyrin

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Abstract Efforts to fabricate low-power upconverting solid-state systems have rapidly increased in the past decade because of their possible application in several fields such as bio-imaging, drug delivery, solar harvesting or displays. The synthesis of upconverting cross-linked polyester rubbers with covalently tethered chromophores is presented here. Cross-linked films were prepared by reacting a poly(mannitol-sebacate) pre-polymer with 9,10-bis(4-hydroxymethylphenyl) anthracene (DPA-(CH₂OH)₂) and palladium mesoporphyrin IX. These chromophores served as emitters and sensitizers, respectively, and through a cascade of photophysical events, resulted in an anti-Stokes shifted emission. Indeed, blue emission (~440 nm) of these solid materials was detected upon excitation at 543 nm with a green laser and the power dependence of integrated up-converted intensity versus excitation was examined. The new materials display upconversion at power densities as low as 32 mW/cm², and do not display phase de-mixing, which has been identified as an obstacle in rubbery blends comprising untethered chromophores.

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1 Introduction

Light upconversion, i.e., the conversion of incident photons of a given wavelength into photons of a higher energy, has garnered considerable attention due to its potential use in bio-imaging, drug delivery, solar harvesting or optical displays [1–5]. Upconverting schemes such as two-photon absorption and second or third harmonic generation usually involve excitation with monochromatic high-power lasers [2, 6–12]. However, for a number of the aforementioned applications, it is required to operate at low power densities (below 100 mW/cm²) and with non-coherent excitation. Discovered over fifty years ago, upconversion via triplet–triplet annihilation (TTA-UC) meets these requirements. This process relies on a sequence of photophysical events between a pair of dyes: a sensitizer and an emitter. These sequential events include absorption by the sensitizer, intersystem crossing to populate the triplet level of the sensitizer, triplet–triplet energy transfer to the emitter, triplet–triplet annihilation of two emitters in their triplet excited state and, finally, delayed fluorescence from the singlet excited state of one of the emitters [13–15].

For decades only known to occur in solution, the TTA-UC process was recently transposed into solid-state materials [16]. The first examples of TTA-UC in the solid state were demonstrated in rubbery materials, such as poly(ethylene oxide-*co*-epichlorohydrin) (EO-EPI) copolymers and polyurethanes and small amounts of suitable sensitizer/emitter pairs [17]. It was hypothesized, and experimentally verified that the dye molecules display sufficient mobility at

temperatures exceeding the glass transition temperature (T_g) to facilitate the necessary energy transfers processes, even at low dye content [18, 19]. To circumvent de-mixing, various strategies were explored to incorporate TTA-UC dye pairs into glassy materials, including kinetically trapping high concentrations of the chromophores, in a thermodynamically unstable molecularly dispersed state, by fast cooling of polymer blends [20]. Another interesting strategy to evade de-mixing is covalent tethering of both the sensitizer and the emitter to a host polymer. First demonstrated by Balushev et al. [21, 22] on oligomeric polyarenes, this approach was recently extended to oligo(vinyl diphenylanthracene) by Boutin et al. [23]. However, there has been, to the best of our knowledge, no reported attempt to incorporate an upconverting chromophore pair into rubbery materials by way of covalent attachment.

Thus, the covalent attachment of DPA and palladium porphyrin into a poly(mannitol-sebacate) (PMS) matrix is reported here. These low- T_g polyesters represent a family of bio-sourced rubbery polymers that have been used in a variety of systems such as soft tissue engineering, nerve-guidance, drug delivery, and tissue adhesive [24–26]. Sonseca et al. [27] reported the reinforcement of PMS with cellulose nanocrystals, which act as both a stiff nanofiller and a chemical crosslinker. PMS polymers contain many residual alcohol groups, and are thus ideal scaffolds for the covalent tethering of an appropriately functionalized upconverting dye pair. We showed here that palladium meso-porphyrin IX (PdmP) and dihydroxymethyl-diphenylanthracene (DPA(CH_2OH)₂), can be readily reacted with a PMS pre-polymer to afford elastomeric cross-linked polyesters (Fig. 1) which display green to blue upconversion at power densities as low as 32 mW/cm². Therefore, this work aimed to attain a new kind of bio-based upconverting rubbery systems with covalently tethered chromophores.

2 Experimental Details

2.1 Materials and Sample Preparation

Sebacic acid (99 % purity), D-mannitol (99 % purity) and 9,10-dibromoanthracene were all purchased from Sigma Aldrich. Palladium mesoporphyrin IX (PdmP) was purchased from Frontier Scientific. A poly(mannitol-sebacate) pre-polymer was prepared following a previously described procedure with slight modification of mannitol:sebacic acid ratio to achieve a feed-ratio of 1:2 (Supplementary Fig. S1) [27]. Anthracene-9,10-diylbis(4,1-phenylene)dimethanol was synthesized in one step from 9,10-dibromoanthracene using a procedure adapted from literature [28]. MALDI-TOF Bruker ultrafleXtreme was used for routine mass analysis of chemicals. Nuclear magnetic resonance (NMR)

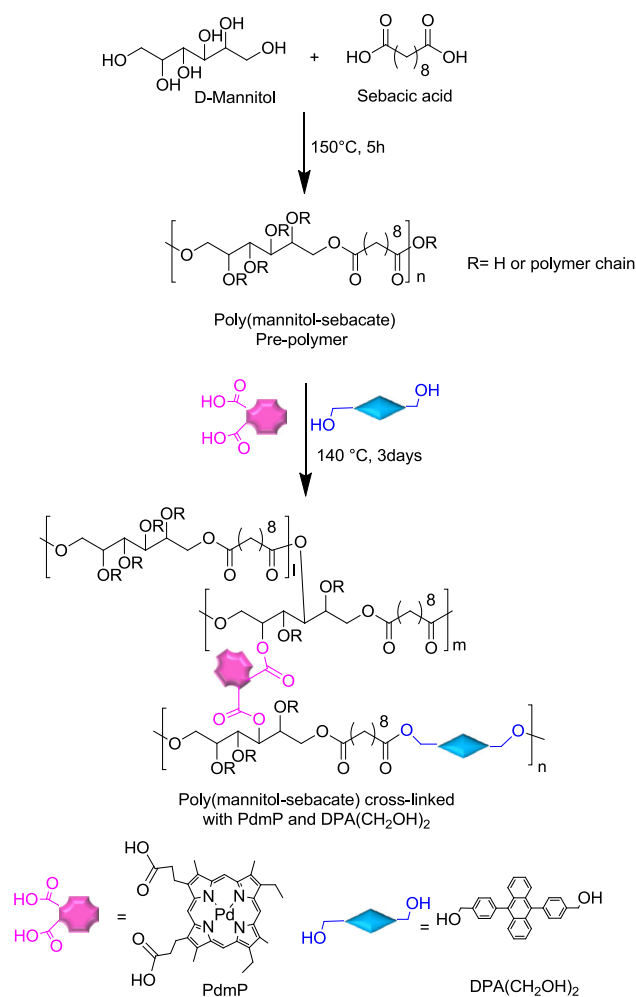


Fig. 1 Synthesis of pre-polymer via condensation reaction of D-mannitol and sebacic acid and subsequent polycondensation and incorporation of PdmP and DPA(CH_2OH)₂

spectra were obtained with a Bruker analytik GmbH DPX360 MHz spectrometer at 300 K. Chemical shifts were given in parts per million (δ) and were referenced to DMSO- d_6 . All NMR data were reported and analyzed using MestReNova 2D software.

2.1.1 Anthracene-9,10-diylbis(4,1-Phenylene)Dimethanol (DPA(CH_2OH)₂)

In a 25 mL microwave tube, 9,10-dibromoanthracene (500 mg, 1.5 mmol, 1 eq.), 4-(hydroxymethyl) phenylboronic acid (500 mg, 3.12 mmol, 2.1 eq.) and K_2CO_3 (69, mg, 0.5 mmol, 0.3 eq.) were dissolved in a mixture of dimethylformamide (DMF) (10 mL) and water (5 mL). $\text{Pd}(\text{PPh}_3)_4$ (34.4 mg, 29.5 μmol , 0.02 eq.) was then quickly added to the mixture. The reaction mixture was bubbled with argon for 15 min before sealing the vessel. The sealed vessel was then heated to 150 °C for 15 min at 3–4 bar in the

microwave synthesizer (Biotage[®] Initiator). After the microwave reaction, the solution mixture was concentrated, then re-dissolved in DMF (1 mL) to be purified by precipitation in dichloromethane (DCM, 10 mL). Anthracene-9,10-diylbis(4,1-phenylene)dimethanol was finally obtained as white powder by filtration through a fritted glass with porosity 3, washed 3 times with DCM (3 × 20 mL). Yield = 45 %. ¹H NMR (360 MHz, DMSO-d₆, δ): 7.24–7.73 ppm (m, 16H, Ar), 4.68 (s, 4H, CH₂), 4.48 (s, 2H, OH); ¹³C NMR (75.5 MHz, DMSO-d₆, δ): 142.1 ppm, 136.6, 136.4, 130.7, 129.3, 126.7, 126.5, 125.4, 62.5; MALDI-MS (*m/z*): 390.16 (calculated: 390.16); m.p.: 132 °C.

2.1.2 Preparation of Cross-Linked Poly(Mannitol-Sebacate) with PdmP and DPA(CH₂OH)₂

In a Teflon[®] Petri dish (diameter = 2 cm), DPA(CH₂OH)₂ (50 mg, 0.26 mmol), PdmP (0.06 mg, 0.28 μmol), and 80 mg of pre-polymer poly(mannitol-sebacate) were dissolved with DMF (0.5 mL) at 70 °C. After complete dissolution, the solution mixture was placed in an oven and heated at 140 °C overnight, then at the same temperature under vacuum for 2 days. A dark red cross-linked elastomeric solid was obtained. A thickness of 890 μm was measured using Caliper Pro-Max.

2.1.3 Determination of Covalent Attachment

A piece of the upconverting PMS film (24.86 mg) was placed in a vial with 6 mL of DMF for 24 h. A UV–Vis absorbance spectrum of the supernatant solution was measured and the amounts of unreacted DPA(CH₂OH)₂ and PdmP were calculated based on the extinction coefficient of the chromophores at their respective absorption maxima at 373 nm ($\epsilon = 14,000 \text{ L mol}^{-1} \text{ cm}^{-1}$), and at 545 nm ($\epsilon = 55,500 \text{ L mol}^{-1} \text{ cm}^{-1}$) respectively.

2.2 Thermal Stability of Derived Emitter

DPA(CH₂OH)₂ (5 mg) was dissolved in DMF (6 mL) after heated in an oven at 140 °C for 1 day, before vacuum was applied at the same temperature for 2 days. An absorption spectrum and a fluorescence emission spectrum of the residual solid were measured and compared to those of original material (Supplementary Fig. S7).

2.3 Thermal Characterization

Thermogravimetric analysis (TGA) of the upconverting PMS was conducted on a Mettler-Toledo TGA STAR instrument by heating from 25 to 500 °C under nitrogen (N₂) at 10 °C/min. The thermal behavior of the elastomer

was studied by differential scanning calorimetry (DSC) experiments which were performed on Mettler-Toledo STAR DSC instrument by heating the samples from 25 to 200 °C, cooling from 200 to –80 °C, and heating again to 200 °C under N₂ atmosphere, at 10 °C/min (Supplementary Figs. S3 and S4).

2.4 Optical Experiments

The optical absorption spectra of PdmP and DPA in solution were recorded with a Shimadzu UV-2401PC UV–Vis spectrophotometer. The fluorescence spectra were measured by excitation at 370 nm with an arc lamp A-1010B and an 814 photoluminescence detector from Photon Technology International.

Upconverted fluorescence emission of upconverting elastomer film excited at 543 nm with a green HeNe laser (2.0 mW, 320 mW/cm²) from Thorlabs, was measured with the detector described above. The upconverting film was placed in a solid state sample holder at a 40° angle from the excitation and detection was recorded at 90° from the incident light. A laser line filter at 543 nm from Thorlabs was placed on the excitation side to ensure monochromatic excitation of the laser at 543 nm. The power dependence of the upconverted fluorescence versus excitation intensity was explored by varying the excitation density from 32 to 320 mW/cm² (measured with a power meter PM 100USB from Thorlabs) using a series neutral density filters to attenuate the irradiation from the HeNe laser.

3 Results and Discussion

3.1 Selection of Chromophores for Upconverting PMS

Palladium mesoporphyrin IX, a well-known phosphorescent heme analog [29], was selected as a sensitizer taking an account of its suitable photophysical properties and the presence of two pendant carboxylic acid groups, which enable its incorporation into a polyester matrix (Fig. 1). The absorption spectra of PdmP in DMF exhibits a Soret band at 375 nm and two Q-bands at 513 and 543 nm. Upon irradiation at its Q₁-band (543 nm), PdmP shows phosphorescence with maximum emission at 665 nm, (<700 nm, energy in triplet state of DPA), which suitably positions its triplet excited state with the corresponding DPA derivative's energy levels for low-power upconversion. DPA(CH₂OH)₂ has the maximum absorbance at 375 nm and the fluorescence at 440 nm (Fig. 2) on luminescence spectra which match to the photoluminescence properties of the neat DPA. Furthermore upconverted delayed fluorescence was observed in the DMF solution containing PdmP and

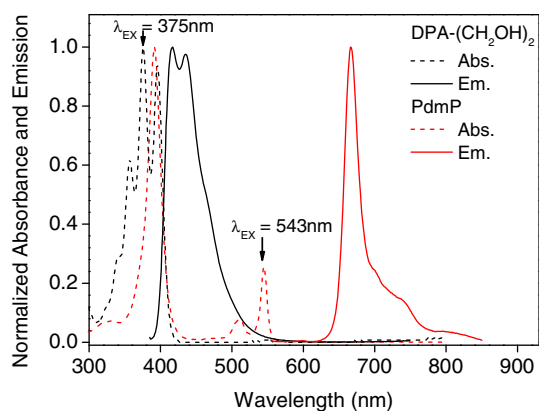


Fig. 2 Normalized absorption (dotted line) and emission (solid line) spectra of PdmP (10^{-5} M) and DPA(CH₂OH)₂ (2×10^{-3} M) in DMF solution upon excitation at 543 nm with a 2 mW diode laser (green solid line with laser line filter at 543 nm)

DPA(CH₂OH)₂ (after having purged with argon to reduce oxygen quenching of triplet molecules) upon excitation at 543 nm with a laser, this result demonstrated that the end groups of PdmP and DPA(CH₂OH)₂ do not interfere in green to blue upconversion process (Supplementary Fig. S2).

3.2 Fabrication of TTA-UC PMS Film

An oligo(mannitol-sebacate) pre-polymer was synthesized by a condensation reaction of sebacic acid with mannitol affording a low molecular weight pre-polymer (in the early stage of polymerization mostly with linear structure, $M_w = 7,500$ g/mol) [30], in which predominantly the primary hydroxyl groups of the mannitol have reacted with carboxyl groups of the sebacic acid at 150 °C for 5 h with a molar ratio of 2:1 (Fig. 1 and Supplementary Fig. S1). This pre-polymer was further reacted with PdmP (0.05 wt%) and DPA(CH₂OH)₂ (34 wt%) to result upconverting PMS film with covalently attached sensitizer and emitter. The content of sensitizer and emitter were chosen based on the optimal upconversion concentrations determined for previously reported glassy poly(methyl methacrylate)s [31]. The reaction was performed at 140 °C for 3 days under vacuum to promote cross-linking, removal of the solvent, and drive the condensation reaction to the product side. An 890 μ m-thick, dark red elastomeric film was thus obtained (Fig. 3a). The cross-linked nature of the film and the high dye content precluded direct measurement of the quantity of attached dyes in the film. Therefore, the extent of covalent attachment was determined indirectly by extraction of the cross-linked film in DMF and measuring of the dye contents in the supernatant by way of UV-Vis absorption spectroscopy (Supplementary Fig. S3). This analysis revealed that 1.5 and 25 % of the originally introduced DPA(CH₂OH)₂ and PdmP were not covalently

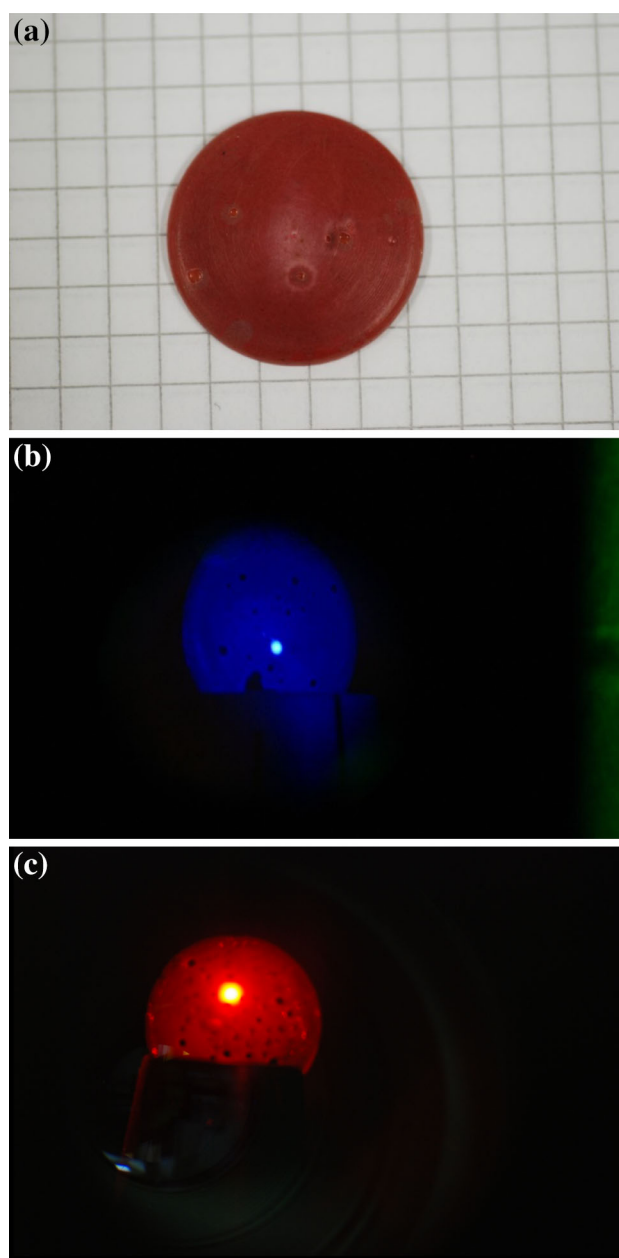


Fig. 3 **a** Optical photograph of UC PMS film, containing 34 wt% DPA(CH₂OH)₂ and 0.05 wt% PdmP. **b** Upconversion of film excited at 543 nm viewed through a 500 nm short pass filter. **c** Phosphorescence of film excited at 543 nm viewed through a 600 nm long pass filter

tethered. Given the rather small amounts of unreacted dyes, the films were used as synthesized, i.e., the residual of unreacted dyes were not removed.

3.3 Phosphorescence of Upconverting PMS Film

As previously reported, the crosslinkage of pre-polymers highly depended on the ratio of mannitol and sebacic acid, and their crosslinking temperature. The thermal properties

of the material were therefore evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA thermogram showed a 2 % onset of decomposition at 188 °C and a char yield of 18 % (Supplementary Fig. S4), while the DSC trace showed T_g at -1 °C (Supplementary Fig. S5). Consequently, all optical measurements were performed at room temperature, i.e. well above T_g .

The TTA-UC effect was examined qualitatively by irradiating the rubbery film at 543 nm with a green HeNe laser using a laser-line filter at a power density of 320 mW/cm² (Supplementary Fig. S6). Blue upconverted fluorescence was observed through a 500 nm short pass filter (Fig. 3b). Additionally, intense red phosphorescence was visible through a 600 nm long-pass filter (Fig. 3c). Despite the significant excess of emitter relative to the sensitizer (molar ratio of DPA(CH₂OH)₂ and PdmP = 1,000 to 1) The phosphorescence intensity is relatively higher compared to the upconverted fluorescence (Supplementary Fig. S6) [11, 15, 32]. Regardless the supposed flexibility of the matrix and covalent attachment of dyes to polymer while preventing unfavorable phase separation, we presumed that triplet energy transfer from the sensitizer to the emitter was limited. Similar high phosphorescence was reported in solution-cast rubber upconverting films based on EO-EPI [17, 33]. Therefore, in order to elucidate the cause of this apparent increase of phosphorescence, DPA(CH₂OH)₂ was heated as a powder for 3 days at 140 °C to reproduce the synthesis conditions and evaluate the potential for oxidation. The fluorescence spectra before and after heat treatment were recorded solutions in DMF (2.6 mM) by exciting at 370 nm as well as their absorption spectra was determined (Supplementary Fig. S7). The data showed only a mild decrease in fluorescence intensity, which indicates a limited degradation.

3.4 Delayed Fluorescence of TTA-UC PMS Film

Upconversion was recorded by measuring blue-shifted light between 400 and 500 nm upon excitation at 543 nm with a 2 mW HeNe laser. The resulting upconverted emission spectrum of rubbery film overlapped with the fluorescence spectrum of neat DPA(CH₂OH)₂ in DMF (Figs. 2, 4a). The upconversion emission intensities of the film were then recorded with varying incident power densities from 32 to 320 mW/cm² (Fig. 4). For each incident power, the upconversion emission was integrated and the data was plotted in a double logarithmic plot (Fig. 4b). A linear fit of the data with a power law function resulted in an exponent of 1.5. This pseudo-linear regime of upconversion with varying excitation power density suggests that once the triplet manifold of the emitter is populated, relatively efficient annihilation step has occurred. The film

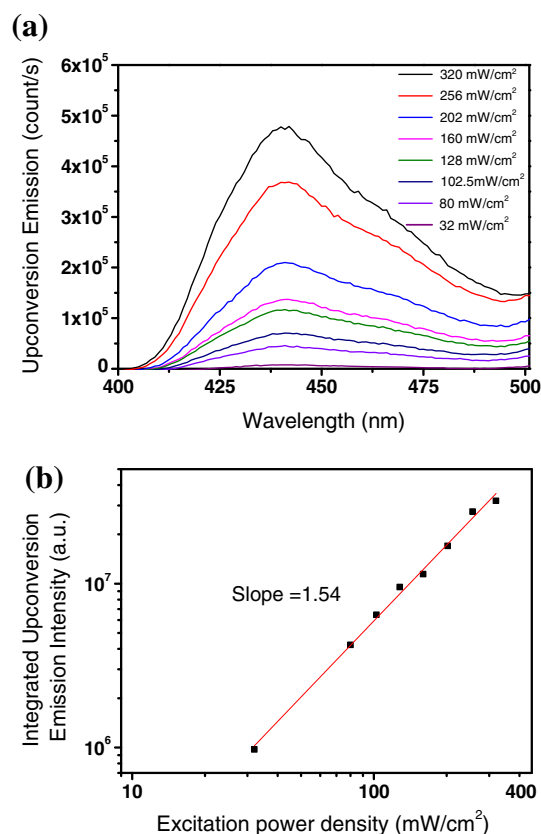


Fig. 4 **a** Upconverted emission spectra of cross-linked PMS with 0.05 wt% of PdmP and 34 wt% DPA of upon excitation with a HeNe laser at 543 nm at different excitation power densities as indicated in the graph. **b** Double logarithmic plots of the data shown in **a**, and a least square fit of the data (slope = 1.54)

fabrication method allowed inclusion of high emitter content (34 wt%) in the polymer which is required for efficient energy transfer between upconverting dyes in solid state, while preventing undesirable phase separation.

4 Summary

The present paper shows the covalent attachment of upconverting pair, PdmP and DPA(CH₂OH)₂, into a poly(mannitol-sebacate) cross-linked elastomer. The resulting films displayed blue fluorescence emission upon excitation with green light even at relatively low power density (32 mW/cm²). This system represents, to the best of our knowledge, the first rubbery material, wherein the upconverting pair has been covalently incorporated to the network of the polymer matrix. The biocompatibility of the matrix together with the simple scale-up procedure opens up new prospects of such materials in a variety of applications where covalent attachment of the dyes is necessary. However we observed a limited degradation of DPA during the film fabrication

process due to the high reaction temperature (140 °C) and its relatively long reaction time (3 days). It is thus necessary to develop this system in other types of polyester such as polyurethane or polybutylene succinate which can be prepared in a mild condition such as lower reaction temperature.

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