Molecularly Controlled Blending of Metals and Organic Metals with Polyolefins for the Preparation of Materials with Modulated Optical Properties

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Summary: In this paper, after revisiting previous data on terthiophene molecules, several attempts are described to use metal containing species such as nanoclusters and molecular complexes as dispersed chromophores in the same ethylene polymer matrix in order to extend an approach to new classes of molecules and improve some specific optical responses including fluorescence dichroism and behaviour as linear optical polarizers is evaluated. Comparison with typical linear polarizers from the same polymer and terthiophenes of innovative gold clusters is discussed as well as transition metal complexes.

Keywords: chromophores; copper complexes; gold nanoclusters; nickel complexes; polarizers; polyolefins

Introduction

Polymer film for linear polarizers application can be produced by dispersing into oriented polymers, light absorbing low molecular weight species such as highly conjugated organic molecules (organic metals) or metal clusters and complexes.[1]

In previous papers we reported about the use of terthiophene (TT) derivatives and their dispersion in ethylene polymers.[2] Different attempts aimed to optimize the chromophore structure in terms of dispersion and electronic properties allowed to obtain polymer films showing interestingly dichroic ratios in relation to the stretching degree of the film.[3]

The modulation of the molecular structure of the chromophore hss allowed to optimize both dispersion in the polyethylene matrix and performances of the derived linear polarizers. Indeed

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the variation of the chromophoric moiety and the compatibilizing effect by linear and branched alkyl groups attached to the chromophore has allowed to obtain very high dichroic ratio and good device performances.

The same approach and concepts are now used to develop field responsive materials combining the excellent thermomechanical properties of polymers from 1-alkenes with the electro-optical properties of metals nanoclusters and complexes. In the former case gold particles are dispersed in the polyethylene matrix after deposition on their surface of a molecular organic layer which includes organic chromophores capable of energy transfer to the metal. In the latter case molecular complexes of Nickel and Copper with ligands providing the molecule with a permanent dipole moment where prepared and then dispersed in the polyethylene matrix thanks to the substantially hydrophobic shell around the metal atom(s) provided by the ligands selected geometry.

The results are discussed in terms of the effect of the molecular structure of the chromophores on their dispersion and on self-induced and/or stress induced orientation.

Experimental

Apparatus and Methods

FT-IR spectra were recorded by a Perkin-Elmer Spectrum One spectrophotometer on dispersions in KBr. The melting points were accomplished by a Reichert Polyvar optical microscope with crossed polarizers, equipped with a programmable Mettler FP 52 hot stage. Elementary analyses were made by microanalysis laboratories at the Faculty of Pharmacy, University of Pisa. Differential scanning calorimetry (DSC) analyses were performed by a Perkin-Elmer DSC7 calorimeter equipped with a CCA7 cooling device. The calibration was carried out by using Mercury (m.p. = -38.4°C) and Indium (m.p. = 156.2°C) standards. Heating and cooling thermograms were carried out at standard rate of 10°C/min. The Scanning Electron Microscopy (SEM) analysis was performed with a Jeol 5600-LV microscope, equipped with Oxford X-rays EDS microprobe, instrument at the Chemical Engineering Department of Pisa University. Optical absorption studies were carried out in heptane or xylene ($5\cdot10^{-5}$ M) solutions with a Jasco 7850 UV-Vis spectrophotometer or on polymer films in polarized light with the same instrument, fitted with Sterling Optics UV linear polarizer, or with a Perkin-

Elmer Lambda 900, fitted with Glan-Thomson polarizers, instrument of the Federal Polytechnic of the University of Zurich (Switzerland) ETHZ. The films roughness was diminished, using ultra-pure silicon oil (Poly(methylphenylsiloxane), 710® fluid, Aldrich) to reduce surface scattering between the polymeric films and the quartz slides used to keep them planar. In the analysis of the absorption and emission data, the scattering contribution was corrected by the use of appropriate baselines. The fitting procedure was performed by using Origin 6.1, software by Microcal Origin®.

Materials

1-hexylamine and 1-octadecylamine (Aldrich) were used as received. Gold nanoparticles was synthesized as described in a previous work according to literature procedures.[4] Ultra High Molecular Weight Polyethylene (UHMWPE), $\overline{M}_w = 3.6 \cdot 10^6$, $\delta = 0.928$ g/cm^3 (Stamylan UH210, DSM, The Netherlands) was used as polymer matrix.

Ni, Cu Complexes Preparation

Nickel and Copper bis(salicylaldiminate) complexes (**I**) were prepared according to a general method reported in a previous work.[5] In a typical procedure for the preparation of **I1** complexes, 3.5 mmol of the relative salicylaldehydato complex was added in small portions to 4 mL of 1-hexylamine and the solution heated for 30 min. The amine was successively distilled off, and the residue was recrystallized from n-heptane.

Bis(1-hexylsalicylaldiminate)Nickel(II) (**I1a**) was obtained as green crystals. m.p.= 123-125°C. FT-IR (KBr): 1613 cm^{-1} ($\nu_{C=N}$). UV-VIS (heptane): $\lambda_{max} = 420$ nm; $\varepsilon = 9{,}000$ Lmol^{-1}cm^{-1}. Anal. Calc. $C_{26}H_{36}N_2O_2Ni$: C, 66.83%; H, 7.77%; N, 6.00%. Found: C, 66.99%; H, 7.61%; N, 5.88%.

Bis(1-hexylsalicylaldiminate)Copper(II) (**I1b**) was obtained as olive-green crystals. m.p.= 85-87°C. FT-IR (KBr): 1613 cm^{-1} ($\nu_{C=N}$). $\lambda_{max} = 368$ nm; $\varepsilon = 11{,}000$ Lmol^{-1}cm^{-1}. Anal. Calc $C_{26}H_{36}N_2O_2Cu$: C, 66.14%; H, 7.69%; N, 5.93%. Found: C, 66.31; H, 7.76%; N, 5.89%.

In a typical procedure for the preparation of **I2** complexes, 11 mmol of 1-octadecylamine was heated at 70°C and 2 mmol of the relative salicylaldehydato complex was added in small portions. The solution was heated for 30 min, cooled, and recrystallized twice from n-heptane.

Bis(1-octadecylsalicylaldiminate)Nickel(II) (**I2a**) was obtained as green crystals.

m.p.= 78-79°C. FT-IR (KBr): 1622 cm^{-1} ($\nu_{C=N}$). λ_{max} = 368 nm; ε = 7,000 $Lmol^{-1}cm^{-1}$. Anal. Calc. $C_{50}H_{84}N_2O_2Ni$: C, 74.70%; H, 10.53%; N, 3.48%. Found: C, 76.89%; H, 10.61%; N, 3.34%.

Bis(1-octadecylsalicylaldiminate)Copper(II) (**I2b**) was obtained as olive-green crystals. m.p.= 71-74°C. FT-IR (KBr): 1621 cm^{-1} ($\nu_{C=N}$). λ_{max} = 368 nm; ε = 9,700 $Lmol^{-1}cm^{-1}$. Anal. Calc. $C_{50}H_{84}N_2O_2Cu$: C, 74.25%; H, 10.47%; N, 3.46%. Found: C, 74.37%; H, 10.56%; N, 3.50%.

Film Preparation by Solution Casting

0.5 g of UHMWPE and the appropriate amount of chromophore were dissolved in 75 ml of *p*-xylene at 125°C and stirred until complete dissolution occurred; the solution was then cast on a glass and slowly evaporated at room temperature.

Table 1. Polymer blend films prepared in this work.

Blend	Metal complex	
	Type	Concentration (wt.%)
UHI1a3	I1a	3
UHI1b3	I1b	3
UHI2a12	I2a	12
UHI2b5	I2b	5
UHI2b12	I2b	12

Polymer Orientation

Solid state drawings of the host-guest films were performed on thermostatically controlled hot stages at 125°C. The draw ratio was determined by measuring the displacement of ink-marks printed onto the films before stretching.

Results and Discussion

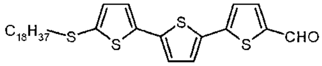
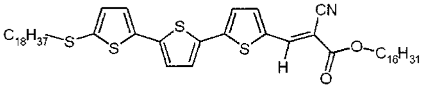
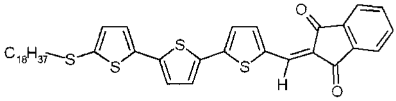
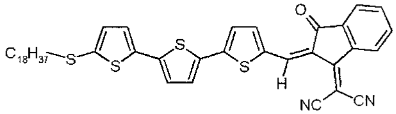
Noble metal nanoparticles incorporated in polymeric matrices have been the object of considerable scientific efforts due to their potential properties as nanostructured materials. Gold and silver colloids, for instance, exhibit interesting optical properties due to the bright colours of their dispersions, the possibility to absorb different ranges of visible light and very low scattering characteristics depending on the particle size, shape and aggregations.[6,7]

On the other hand, it has long been recognized that incorporation of metals and metal complexes into synthetic polymers may also lead to desirable properties. Examples include data storage materials, superconductors and catalysts.[8]

Also, the optical response of metal nanoparticles is enhanced by the introduction of photoactive organic molecules into or onto the particles. Indeed, the interaction between a metal and a metal-bound chromophore can modify the excited state of the latter leading to an energy transfer to the surface plasmon resonance of the metal.[9] In this connection, we have recently studied the optical properties of oriented UHMWPE films containing the gold nanoparticles bound to terthiophene chromophores.[10]

These last when dispersed into oriented UHMWPE, show high dichroism and can be used as absorption polarizers and as fluorescence polarizers (Table 2).[2a]

Table 2. Polarizer performances on varying chromophore load and drawing ratio (DR).[2a]

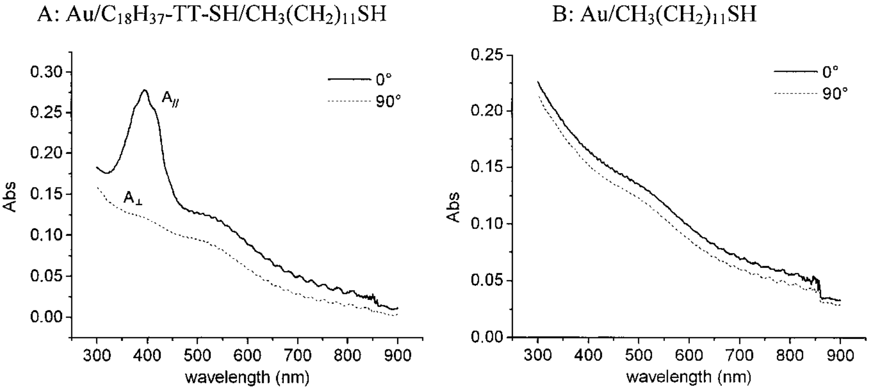
Dye	**Conc. (wt.%)**	**DR**	**R***	**R_e***
	1.0	20	21	13
	2.0	40	39	2
	1.6	20	24	3
	3.0	40	30	29

*$R=A_{//}/A_{\perp}$: dichroic ratio[2]; $R_e=E_{//}/E_{\perp}$: emission dichroic ratio.[2]

The highly anisotropic behaviour, both in absorption and emission, and degree of orientation of the terthiophenes (TT) based dyes into oriented polyethylene films achieved thanks to their highly linear and delocalized electronic structure, suggested us to couple a similar terthiophene structure bearing a free thiol group ($C_{18}H_{37}S$-TT-SH) with gold nanoparticles.[10] The optical properties of terthiophene coated gold nanoparticles (A: Au (70 wt.%)/ $C_{18}H_{37}S$-TT-SH (15 wt.%)/ $CH_3(CH_2)_{11}SH$ (15 wt.%)) dispersed in oriented UHMWPE in small concentration

(4 wt.%) was evaluated and compared to those prepared by using just an aliphatic thiol as coating layer (B: Au (70 wt.%)/$CH_3(CH_2)_{11}SH$ (30 wt.%)).

As reported in figure 1 the gold absorption (around 550 nm) was characterized by poor dichroism in both cases: the high thiol content of both nanoparticles not only reduced the intensity of the plasmon resonance, but also limited the particle aggregation and helped in keeping a centrosymmetric (non-dichroic) structure.[11]High dichroism (R = 30 at 400 nm, DR = 30) was on the contrary recorded for the terthiophene band (around 400 nm) of A nanoparticles, showing the chromophores to be sensitive to mechanical orientation also when complexed with gold.



A: Au/$C_{18}H_{37}$-TT-SH/$CH_3(CH_2)_{11}SH$

B: Au/$CH_3(CH_2)_{11}SH$

Fig. 1. UV-Vis spectroscopy in polarized light of A (left) and B (right) oriented nanoparticles in UHMWPE (4 wt.%, DR=30) as a function of the light polarization direction.

The emission behaviour (irradiation at 288 nm) of the UHMWPE nanocomposites based on gold nanoparticles doped with terthiophene thiol (A) showed an interestingly increased response with respect to B nanoparticles in the same spectral region and with a max at about 435 nm (Figure 2).

This enhancement is not attributable to the free terthiophene chromophores dispersed in the polymer matrix. Indeed this chromophore with excitation at 390 nm showed very high fluorescence with emission maximum at 470 nm. On the contrary the irradiation at the same wavelength of PE film containing the nanoparticles A did not show any appreciable fluorescence (Figure 3), suggesting the absence of uncomplexed terthiophene molecules.

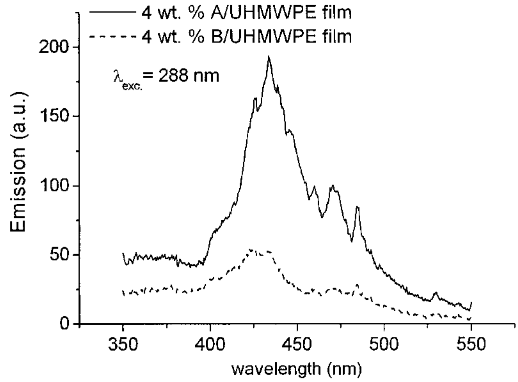


Fig. 2. Fluorescence spectroscopy of A and B nanoparticles in oriented PE ($\lambda_{exc.}$ 288 nm).

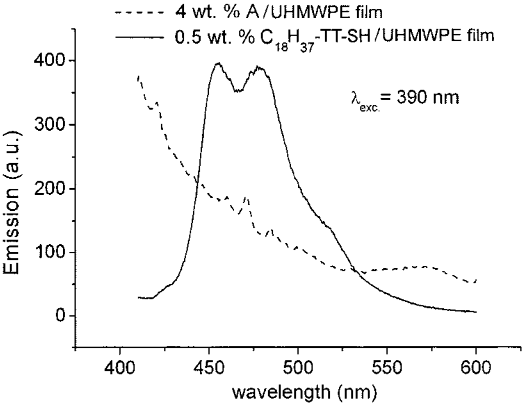


Fig. 3. Fluorescence spectroscopy of A and the terthiophene based thiol (right) in oriented PE at different excitation wavelength ($\lambda_{exc.}$ 390nm).

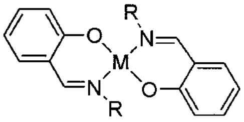
Both A and B nanocomposite films gave after orientation emission dichroism but A colloids showed significant strongly enhanced response as a function of the drawing ratio with respect to B particles (Table 3).

The enhancement of the gold fluorescence response, the loss of the terthiophene emission in gold nanoparticles and the drawing dependence of the gold dichroism suggest electronic interactions between the terthiophene chromophores and gold nanoparticles in A system. In particular, the "antenna" behaviour of terthiophene derivative and its high orientability make the gold oriented UHMWPE nanocomposites an example of effective device for application as emission linear polarizer.

Table 3. Anisotropic behaviour of the gold emission band (λ_{exc} = 288nm; λ_{em} = 435nm) in oriented gold UHMWPE nanocomposites.

Sample	**DR**	**R_e**
A/UHMWPE film	20	8
	40	23
B/UHMWPE film	20	6
	40	9

The effective enhancement of dispersibility of terthiophene alkyl derivatives in UHMWPE observed when varying the nature of the alkyl lateral functionalization (R),[3] suggested the preparation of different metal complexes from ligands bearing alkyl chains with different length, in order to provide the metal with a hydrophobic shell thus allowing a better dispersion into polyethylene matrix. Metal complexes such as Bis(salicylaldiminate)metal(II) complexes have been widely investigated since the second half of the last century, due to the easy preparation and modulation of their structural and electronic characteristics by changing the nature of the substituents on the imino and aromatic moieties, respectively.[12] Nickel(II) and Copper(II) complexes with linear alkyl groups attached to the N-atoms (**I**) were prepared and dispersed at various concentrations (Table 1) in UHMWPE.



I

R = 1-hexyl (1)
1-octadecyl (2)

M = Ni (a)
Cu (b)

Scanning electron microscopy investigations revealed a good dispersion of the (**I**) complexes in polyethylene films containing 3 wt.% of I1a and I1b (Figure 4).

DSC measurements showed a small endothermic peak at about 80°C of the first heating run of the film containing 3 wt.% of the Cu complex I1b attributable to the melting of complex crystals that segregate partially from the semicrystalline polymer matrix (Figure 5).

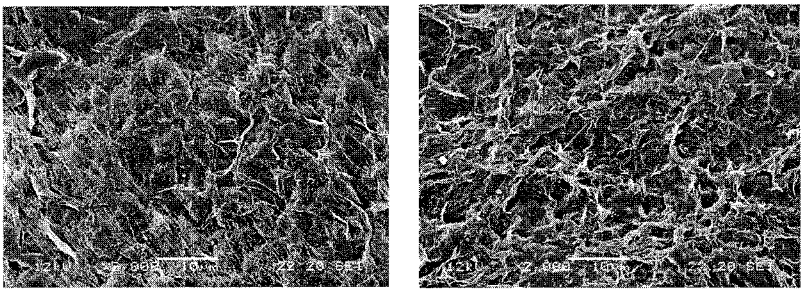


Fig. 4. SEM micrographs of UHI1a3 (left) and UHI1b3 (right) films.

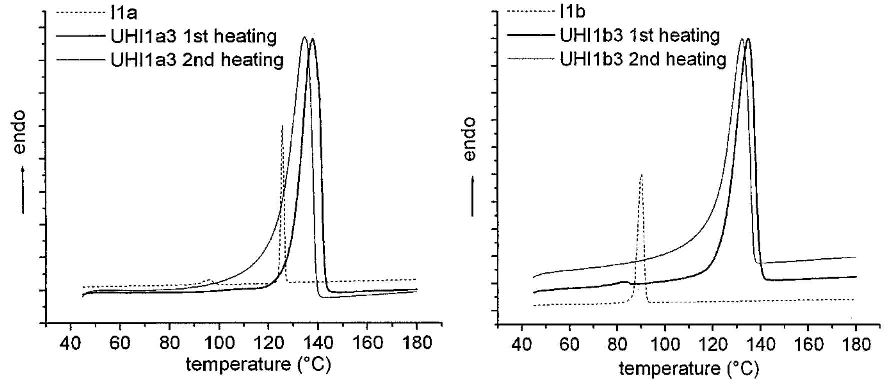


Fig. 5. DSC thermograms of I1a3 and UHI1a3 (left) and I1b and UHI1b3 (right) films respectively.

On the contrary, no Nickel complex melting transition is recordable from the first and the second heating scans of the similar film UHI1a3 containing 3 wt.% of the complex I1a.

A more efficient dispersion of the Copper complexes in UHMWPE matrix was obtained by mixing the polymer with the bis(octadecyl salicylaldiminate) derivative, I2b, probably due to a more effective hydrophobic interaction with PE due to the longer octadecyl substituents instead of hexyl (Figure 6).

UHMWPE films with higher complex concentration (12 wt.%) were also prepared in order to analyse the influence of the chromophore amount on the final properties. SEM analyses performed on these last films revealed an high degree of phase separation (Figure 7 left).

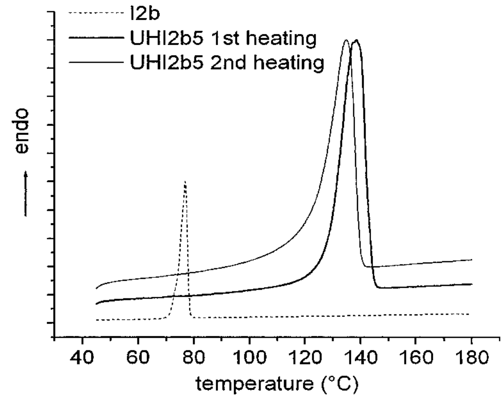


Fig. 6. DSC scans of I2b and UHI2b5 film.

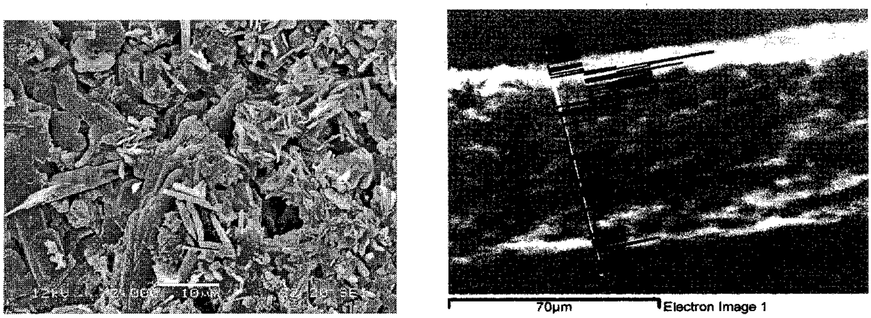


Fig. 7. SEM micrograph of UHI2b12 (left) and Copper concentration profile of a section of the same film (right).

In addition, the SEM microanalysis (Figure 7 right) performed on a section of the prepared films evidenced a preferred metal distribution near to the surface exposed to air, similar to what previously observed for terthiophene chromophores dispersed by solution casting in PE blends.[2a,3b] The phase segregation of complexes (**I**) in UHMWPE films prepared by using high concentration of metal is also confirmed by DSC scans showing the melting point of the free complexes deriving from the segregation in the composite of crystals derived from the metal complexes. The UHMWPE films containing the **I** metal complexes showed absorption spectra with maxima in the visible wavelength range connected to the π-π* and n-π* electronic transition (Figure 9). The dichroic performances of oriented metal complex/UHMWPE films were evaluated by UV-Vis spectroscopy in polarized light in order to study the anisotropic behaviour of Nickel and Copper Bis(salicylaldiminate) complexes (**I**) (Figure 8).

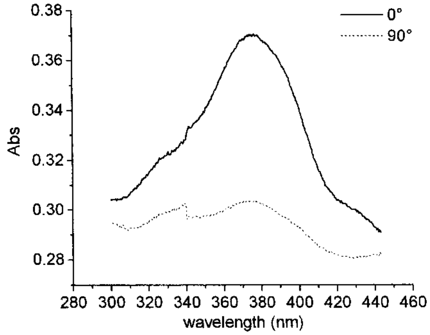


Fig. 8. UV-Vis spectra in polarized light of a UHI2a12 film, submitted to a drawing ratio DR=30 (polarization direction parallel (0°) and perpendicular (90°) to the drawing axis).

As expected, concerning the non linear structure of the complexes **I**, very low dichroic ratios from 1 to 4 were observed. The most favourable case is that of the complex I2 that at DR = 30 shows R = 4.0 at 373 nm (Figure 8).

The poor influence of the angle between the polarization direction of the exciting radiation and the drawing axis on the absorption could be probably attributed to the low directionality of the complexes transition dipole moment and to the almost centrosymmetric structure of Bis(salicylaldiminate)metal(II) molecules that confer them very low orientations also at high drawing ratio. This behaviour is slightly improved for complexes functionalized by the C_{18} alkyl chains, especially for Ni derivatives, suggesting higher anisotropic performances with films characterized by better phase dispersion of the components.

These results are in perfect agreement on what demonstrated in our previous works about the relationship between chromophore structure and film morphology and the optical performances of polyethylene based linear polarizers.[3]

Conclusions

The results reported in the present work provide a nice confirmation of the high potentiality of the blending approach for producing in a simple way films with innovative optical properties based on the concept of macromolecular metal complexes.

The excellent mechanical features of polyethylene make it ideal as the polymer matrix; however these good properties are flanked by a scarce compatibility with polar organic or organometallic chromophores. This problem has been solved in the present work by designing chromophores bearing a significant amount of aliphatic functionalities. The methodology is shown to be rather general and valid for organic conjugated molecules, metal particles and transition metal complexes.

Parallel to the chromophore molecular structure, the obtained dispersion provided by the mentioned aliphatic groups plays a significant role in determining the dichroic ratio in oriented films which is taken as a primary selection step for material suitability in producing optical devices.

The basic data reported here provide also an excellent starting basis for the optimization of the composite systems in terms of optical performances.

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