Optodynamers: expression of color and fluorescence at the interface between two films of different dynamic polymers†

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Color and fluorescence changes were expressed at the interface between two different polyhydrazone polymer films, induced by hydrazone bond exchange and component recombination through the interface, resulting in an extension of conjugation.

Dynamic polymers, dynamers,[1] are supramolecular[2,3] or molecular[1,4,5] polymers based on monomeric components linked respectively by non-covalent interactions and by reversible covalent bonds. They possess in principle the ability to exchange, incorporate, eliminate or recombine components and thus give access to a range of novel properties.

In particular, covalent dynamers, based for instance on reversible hydrazone bonds,[4,5] are unique materials displaying unusual features due to their ability to undergo bond rearrangement and constitutional change.[5–9] Indeed, they have been shown to be amenable to marked modifications in mechanical properties,[8] as well as to respond to chemical and physical effectors.[9] The induction of optical properties would be of special interest, as it could both demonstrate the occurrence of constitutional dynamics[10] in a system and implement dynamics to confer novel physical features.

We here describe some results of our studies on the modulation of optical properties in a system of two films of hydrazone-based dynamic polymers, demonstrating i) the expression of novel optical features, ii) that reveals the occurrence of bond reorganization and component diffusion through the interface of the two films, and iii) allows the generation of optical patterns.

The process relies on the modification of conjugation on bond recombination, leading to changes in absorption and emission properties due to the generation of moieties presenting a more extended conjugation pathway.

Polymeric or supramolecularly assembled materials possessing conjugated moieties have attracted considerable attention for implementation in systems such as sensors or molecular electronic devices, because they have an inherent potential to change their conjugation and optical properties by recombination or reconfiguration in response to external stimuli.[11]

In order to obtain information on the color and fluorescence of bis-hydrazone containing moieties presenting different extents of conjugation, UV–visible and emission spectroscopic measurements were first performed on the model compounds **1–3** (Fig. 1), obtained by condensation of the corresponding hydrazine and aldehyde parent molecules.

The absorption area of the bis-hydrazone compound **1** showed λ_{max} = 384 nm and extended to around 430 nm, conferring a light yellow color in $CHCl_3$ solution (Fig. 2). Compound **1** is expected to present a certain degree of conjugation through two hydrazone bonds and a thiophene moiety (Fig. 1).

Introduction of a phenyl group instead of benzyl on the hydrazone moieties was effective in expanding the degree of conjugation in **2** with respect to **1**. Indeed the absorption band of the bis-hydrazone compound **2** shifted to λ_{max} = 421 nm and extended to around 480 nm, yielding a vivid yellow color in $CHCl_3$ solution. Furthermore, compound **2** exhibited notable fluorescence around 450–550 nm under excitation at 421 nm. The distinct yellow–green fluorescence was also observed visually for the neat powder under 365 nm excitation. Furthermore, compound **4** containing a single phenyl hydrazone unit on one thiophene moiety displayed much less effective conjugation and compound **5** derived from an aliphatic aldehyde presented a much more blue shifted absorption (Fig. 2).

In view of these results, two polyhydrazone polymers **P1** and **P2** (Fig. 3) were selected as initial materials to demonstrate color and fluorescence changes induced by bond exchanges and component migration through the interface of these two polymer films. Polycondensation between the corresponding bis-hydrazine and dialdehyde monomers in $CHCl_3$ or in $CHCl_3$–THF mixture in the presence of acid catalyst‡ gave respectively an almost colorless, slightly turbid film for the polymer **P1** and a light yellow film for the polymer **P2**. A *tert*-butyl group was introduced in the polymer **P2** to increase solubility and facilitate the polycondensation reaction. The polymer **P3** was prepared as a reference material in the same manner, giving a dark orange film. These films were soft, slightly stretchy and easily cut with scissors. Gel permeation chromatography gave a molecular weight M_n = 38400 and a distribution M_w/M_n = 2.9 for the polymer **P1**, M_n = 13900 and

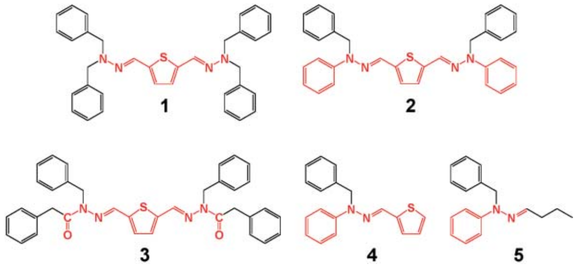

Fig. 1 Structures of hydrazone compounds. The conjugation domain is represented in red.

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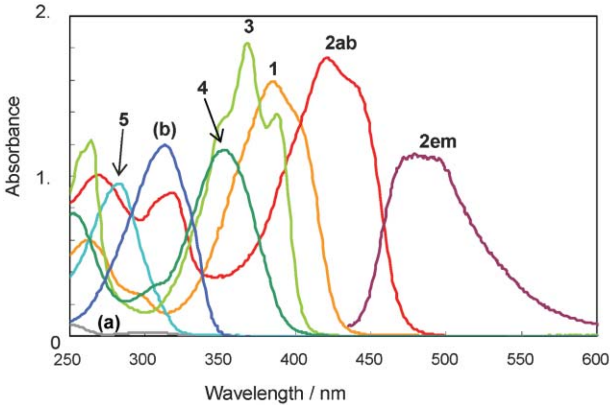

Fig. 2 UV–visible absorption spectra of the hydrazone compounds **1**–**5**, (a) *N*,*N*-dibenzylhydrazine and (b) thiophene-2,5-dicarboxaldehyde in $CHCl_3$ (0.05 mM on the basis of hydrazone, hydrazine or aldehyde) and fluorescence emission spectrum of bis-hydrazone compound **2** in $CHCl_3$ (0.02 mM) under excitation at 412 nm.

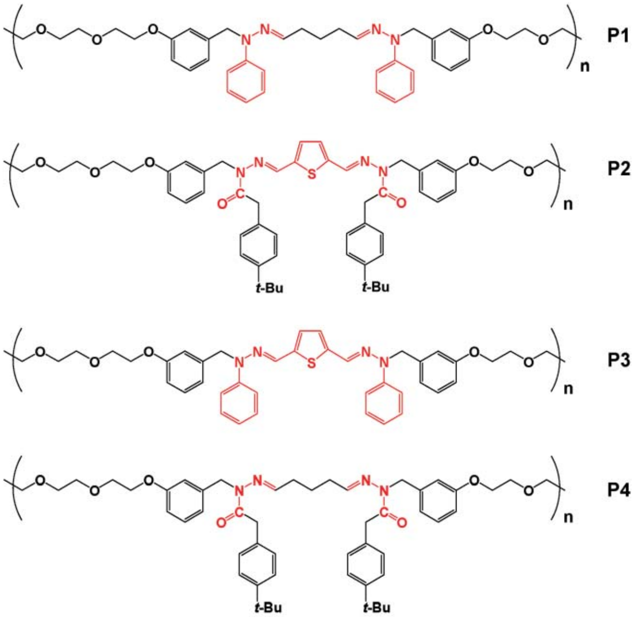

Fig. 3 Structures of polyhydrazone dynamers **P1–P4**. The conjugation pathway is shown in red.

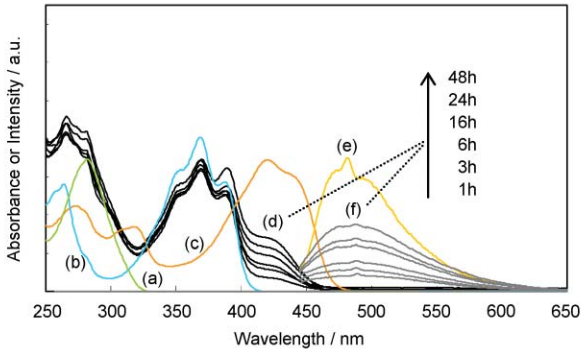

Fig. 4 UV–visible absorption spectra in $CHCl_3$ of the hydrazone polymers (a) **P1**, (b) **P2** and (c) **P3**, and (d) heating time dependence of polymer blend **P1** and **P2**; fluorescence emission spectra in $CHCl_3$ of (e) the hydrazone polymer **P3** and (f) heating time dependence of the fluorescence of polymer blend **P1** and **P2** under excitation at 425 nm.

M_w/M_n = 3.1 for the polymer **P2**, M_n = 34500 and M_w/M_n = 2.7 for the polymer **P3** (with polystyrene calibration).

Changes in UV–visible absorption and fluorescence induced by bond exchange and crossover component recombination were demonstrated firstly by means of a polymer blend film, prepared by just mixing solutions of the two homopolymers **P1** and **P2** in presence of added acid. The visual color of the blend polymer film obtained, initially light yellow, changed progressively to vivid yellow on heating at 120 °C. The UV–visible absorption around 400–450 nm in $CHCl_3$ evolved toward that of polymer **P3** as a function of heating time (Fig. 4). In a similar way, a fluorescence band appeared around 450–600 nm and its intensity increased toward that of polymer **P3**. These results indicate that the change of color and the emergence of fluorescence resulted from bond exchange and crossover component recombination between the dynamic polymers **P1** and **P2**, generating the functional fragment characteristic of polymer **P3**. The fourth combination that results from combination of the monomer of **P1** and **P2** yields the bis-hydrazone moieties shown in polymer **P4**. It would not be expected to present notable absorption or emission features in view of the presence of the isolating trimethylene chain between the two hydrazone groups.[12]

Color and fluorescence expressions may be expected to emerge even at the interface of two different dynamer films. Indeed, superimposing films of the dynamers **P1** and **P2** and applying bond exchange conditions should lead to the appearance of the absorption and emission features characteristic of dynamer **P3** in the overlapping region of the two films (Fig. 5, top). A simple demonstration was performed (Fig. 5, bottom) with two polymer films **P1** and **P2** (54 μm and 64 μm thickness, respectively). Two films cut by scissors were superimposed on a glass plate and heated at around 160–170 °C with a heat gun for 5 min. Only the domain where the two films were superimposed changed to vivid yellow and produced a yellow–green fluorescence observable visually under 365 nm excitation, thus generating a distinctive pattern. On the other hand, the colors of the rest of the films remained almost the same as the original ones and no fluorescence was observed.

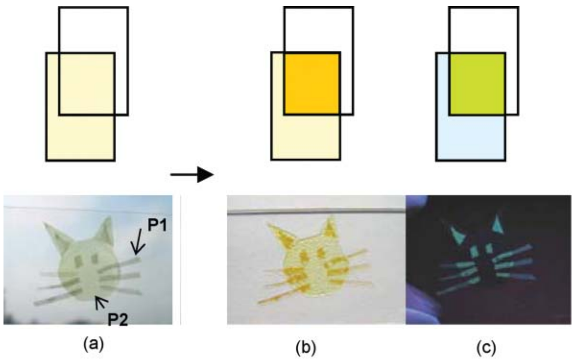

Fig. 5 Visual color change and fluorescence emergence by heating of superimposed polymer films **P1** and **P2**. (Top) Schematic representation; (bottom) an illustrative example: (a) color before heating under sunlight, (b) color after heating, (c) fluorescence after heating under excitation at 365 nm.

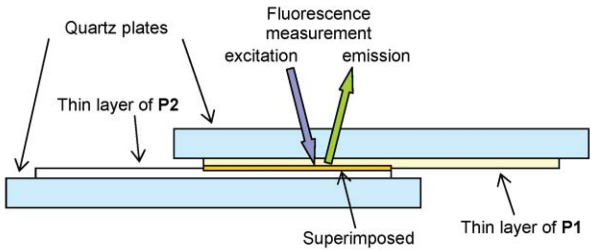

Fig. 6 Cross-sectional schematic representation of the superimposition of two hydrazone polymer layers.

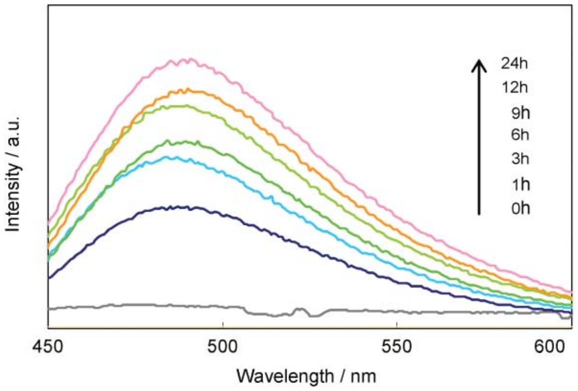

Fig. 7 Fluorescence emission spectra of the overlapping domain of neat hydrazone polymer films **P1** and **P2** under excitation at 425 nm as a function of heating time.

A detailed study on the emergence of fluorescence at the interface was performed with two thin layers (average thickness of about 0.15–0.2 μm, determined by a stylus method) of dynamers **P1** and **P2** coated on a quartz plate§, which were superimposed face-to-face (Fig. 6) and heated to 120 °C in an oven under a stream of argon. The fluorescence intensity of the overlapping part around 450–600 nm, measured on the layers, increased with heating time in a manner similar to the case of the polymer blend (Fig. 7). The result indicates that hydrazone bond exchange and component migration occurred by heating through the interface of the polymer layers **P1** and **P2**, leading to expression of fluorescence along with conjugation extension between the hydrazone moieties.

In conclusion, the present results show that color and fluorescence of polyhydrazone dynamers can be modified by hydrazone bond exchange and component recombination. They also demonstrate that such processes can occur even at the interface of two different polymer films, resulting in chemical interconnection of the films. This feature has promising potential for implementation in optical materials for systems such as molecular sensing or photoactive devices. It gives access to smart and adaptive dynamic materials[1,10,13] controlled by and responding to external stimuli, and may extend over the modulation of other properties such as electronic (redox modifications, conductivity), magnetic, and mechanical. The dynamic polymers are illustrative of the potential offered by the application of the principles of constitutional dynamic chemistry[1,4,10] to materials science.

Notes and references

‡ Equimolar amounts of the corresponding bis-hydrazine (compounds L and P, ESI†) and the dialdehyde monomers at concentrations around 0.04 M each were dissolved in the mixture of $CHCl_3$ and THF (8 : 2 in volume ratio; for the polymer **P1**) or $CHCl_3$ (for the polymers **P2**, **P3**), followed by addition of pentadecafluorooctanoic acid in 0.1 molar ratio with respect to the resulting total hydrazone bonds. The solution was heated at 60 °C for 12 h, then poured into a petri dish of 50 mm diameter made of fluoroplastic, followed by evaporation at 60 °C at normal pressure until most of the solvent had disappeared and then kept at 60 °C *in vacuo* for 12 h. About 200 mg of the total amounts of monomers were used to obtain polymer film of around 0.04–0.06 mm thickness.

§ Polymer thin layers were prepared using a 2 wt% THF solution of the polymer by spin-coating onto 5 cm square quartz plates, which were rinsed with acetone prior to use. The spin-speed and the period were 500 rpm and 60 s, respectively. These layers were subsequently dried *in vacuo* at 60 °C for 12 h.

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