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New irreversible thermochromic polydiacetylenes

Laurent Rougeau [a], Dominique Picq [a,*], Marie Rastello [b], Yves Frantz [b]

[a] *Laboratoire des Matériaux Organiques à Propriétés Spécifiques, UMR 5041 CNRS—Université de Savoie, chemin du canal, 69360 Solaise, France*
[b] *Société EURACLI, 284 Chemin des Roues, 38670 Chasse-sur-Rhône, France*

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ABSTRACT

New diacetylenic compounds are described. These compounds are unfunctionalised, monoalcohols, diols or monoesters and present irreversible thermochromic behaviour. When heated, these diynes change colour from blue to red in temperature ranging between −50 and +75 °C depending on chain lengths. A relationship between the number of atoms and the thermochromism temperature has been highlighted. Moreover, a mechanism of this thermochromic phenomenon is demonstrated based on Raman spectroscopy, ESR and solid NMR.

1. Introduction

Since the 1970s, thermochromic compounds have attracted scientists' attention. Among the large choice of existing products, a special family has been studied: the diacetylenes. Eight years ago, Barentsen[1] showed the advantage of these compounds because it is possible to obtain a great number of various structures. The first studied compounds were the urethanes,[2] which improved the solubility of polymers obtained from diynes; this property facilitated their study. Other functions were more or less well studied thereafter[3,4] but generally colour changes were reversible: from blue to red or red to yellow when heated, followed by a return to the initial colour when temperature decreased. We report here new diacetylenic compounds turning from blue to red in an irreversible way when heated.

We were in fact interested by the creation of an 'intelligent' label that indicates, by a colour change, whether the product it is stuck on has been exposed to a temperature higher than a predetermined one, or not. This is the reason why we were looking for irreversible colour change.

As these labels have an industrial application, they had to comply with specifications, such as raw materials at low prices and syntheses must be industrially applicable at low cost and should be easily reproducible.

2. Results and discussion

2.1. Syntheses and thermochromic behaviour

The diacetylenic compounds are synthesised in 1 step or 2 steps for monoesters. A coupling reaction was used according to the procedure described by Hay[5] (Scheme 1). At the end of the reaction, when two different alkynes were used (Scheme 2), three diynes are recovered: the two symmetrical and the unsymmetrical compound **C**. These three diynes are then separated by column chromatography with a suitable eluent.

The Hay coupling has been preferred to the Cadiot–Chodkievicz coupling,[6] which only gives the unsymmetrical compound according to the literature. During our tries between a bromoalkyne and an alkyne according to Cho,[7] we observed an intermolecular transbromination. This phenomenon led to a mixture of three diynes. So, 50% was the maximum yield for the attempted unsymmetrical diyne. This result is in agreement with the yields reported in the literature;[8] the authors did not explain their results and did not give the structure of the other products.

In this case, the second step is a classical esterification of the alcohol function with an aliphatic alkyl chloride with a chain length varying from 7 to 16 carbon atoms. We thus obtain a great number of diacetylenic compounds with various chain lengths **D** (Scheme 2). After purification by column chromatography, the compounds are irradiated under UV (topochemical polymerisation described in the literature[9]) using DPC (Differential PhotoCalorimetry), which is traditional DSC (Differential Scanning Calorimetry) coupled to a UV radiation source. This equipment allowed us to precisely know the colour changing temperature. It is noteworthy that compounds must be irradiated in the solid state. Generally, irradiation occurs at

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* Corresponding author. Tel.: +33 478022269; fax: +33 478027738.
E-mail address: picq@lmops.cnrs.fr (D. Picq).

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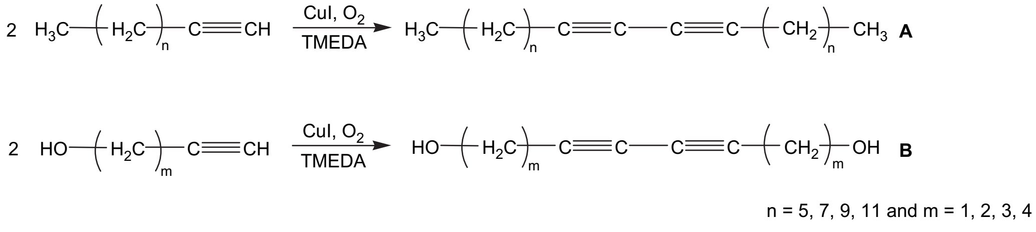
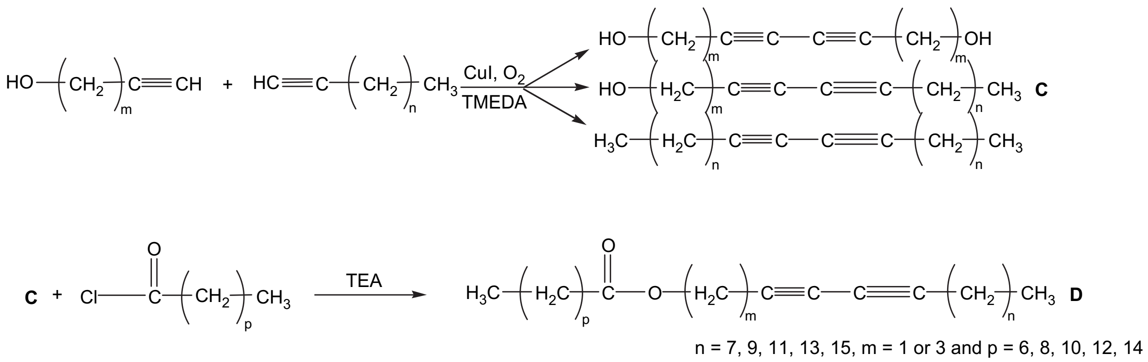


Scheme 1. Hay coupling of alkyne **A** and alkyn-1-ol **B**.



Scheme 2. Hay coupling of an alkyne with an alkyn-1-ol **C** and esterification reaction **D**.

20 °C but in some cases, when diynes are liquid at room temperature, they are irradiated at lower temperature (up to −70 °C). During this step, the compounds turn blue. They are then heated and we noticed that all these diynes turned red at temperature depending on their structure and in an irreversible way. By comparing the various obtained results (Tables 1 and 2), we can propose a relationship between the overall diynes chain lengths and the thermochromism temperature. The total value $m+n+p$ (cf. Schemes 1 and 2) is an influent parameter, not each term taken separately. The results are shown in Figure 1. Moreover we have noticed a relationship between the thermochromism temperature and the melting point of the starting diacetylenic ester. This is very important and will be discussed later in this paper. Concerning the propargylic alcohol function, it seems that the hydroxyl group close to the triple bond dramatically increases thermochromism temperature (cf. Table 2 and Fig. 1).

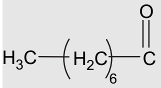
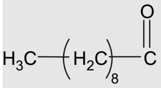
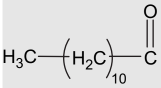
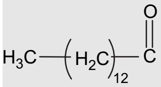
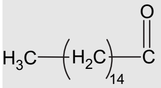
2.2. Compound characterisation

During the diacetylenic compounds' characterisation, we had to face with various problems. First, the red compounds were insoluble in the classical organic solvents. Thus, only solid analytical techniques were possible (NMR, Raman spectroscopy, ESR…). Then, we also had to face with the low stability of the blue compounds. Indeed, these compounds are also solvatochromic (they turn red in the presence of a solvent) and mechanochromic (they turn red if

Table 1
The different diynes and diyne-diols and their thermochromic temperatures after UV irradiation

Compound	Thermochromic temperature
$H_3C\text{—}(H_2C)_5\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_5\text{—}CH_3$	−50
$H_3C\text{—}(H_2C)_7\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_7\text{—}CH_3$	−3
$H_3C\text{—}(H_2C)_9\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_9\text{—}CH_3$	14
$H_3C\text{—}(H_2C)_{11}\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_{11}\text{—}CH_3$	35
$HO\text{—}H_2C\text{—}\equiv\text{—}\equiv\text{—}CH_2\text{—}OH$	No phenomenon
$HO\text{—}(H_2C)_2\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_2\text{—}OH$	26
$HO\text{—}(H_2C)_3\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_3\text{—}OH$	34
$HO\text{—}(H_2C)_4\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_4\text{—}OH$	43

Table 2
The different monoester diynes and their thermochromic temperatures after UV irradiation (— not synthesised, P only photochrome)

R	$R\text{—}O\text{—}(H_2C)_x\text{—}\equiv\text{—}\equiv\text{—}(CH_2)_y\text{—}CH_3$							
	$(x;y)$							
	(1;7)	(1;9)	(1;11)	(1;13)	(1;15)	(3;7)	(3;11)	(3;15)
H	35	50	55	65	75	6	45	P
 $H_3C\text{—}(H_2C)_6\text{—}\overset{O}{\overset{\|}{C}}$	−7	10	20	31	38	7	28	40
 $H_3C\text{—}(H_2C)_8\text{—}\overset{O}{\overset{\|}{C}}$	4	—	—	—	—	16	—	—
 $H_3C\text{—}(H_2C)_{10}\text{—}\overset{O}{\overset{\|}{C}}$	15	—	—	—	—	25	—	—
 $H_3C\text{—}(H_2C)_{12}\text{—}\overset{O}{\overset{\|}{C}}$	26	—	—	—	—	34	—	—
 $H_3C\text{—}(H_2C)_{14}\text{—}\overset{O}{\overset{\|}{C}}$	37	—	—	50	58	43	—	—

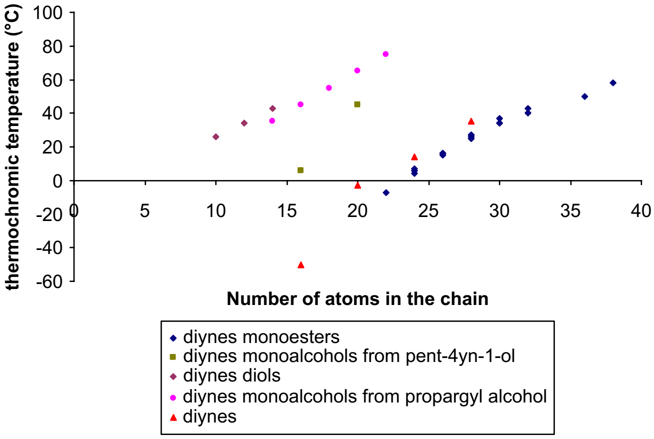


Figure 1. Relationship between overall chain length and thermochromic temperature of diynes.

crushed). Recently, we found that the rate of irradiation was low. We noticed that the three solid NMR spectra of the blue compound, the white one and the red one are the same. Further studies show that the irradiation rate was only 1%; it explains why the melting point of the white compound is the same as the thermochromic temperature of the blue one, because of the solvatochromic effect.

Moreover, we thought that the low stability of the bluish intermediate can be due to radicals. Bloor[9c] had proposed four structures (Fig. 2) for the intermediate but without going further. Only one of these four structures will give a response in ESR: the (**A**) intermediate. Neither the carbenes (**B**) and (**D**), nor compound (**C**) will give a signal in ESR. We then tried to confirm existence of the (**A**) structure using ESR spectroscopy (for the radicals) and Raman spectroscopy (to show the presence of the butatriene function).

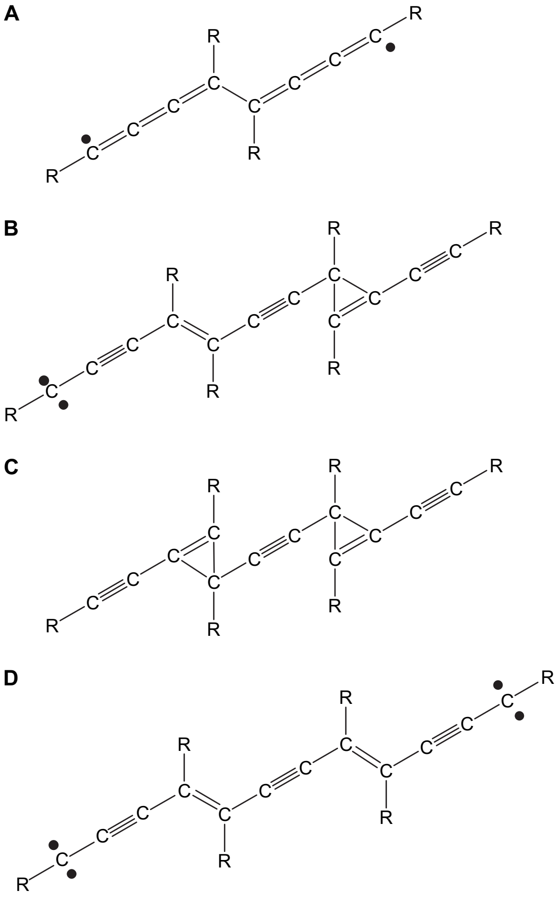


Figure 2. Different structures for the blue intermediate from Bloor.[9c]

For the further analysis, we had to prepare 'high' quantity of pure red compound, because, as we have shown before, the irradiation rate is only 1% so the analysis would show a mixed result of either white/blue or white/red compounds. To get pure red, we have to make several cycles of irradiation, heating, solving and filtrate (because red compound is not soluble) until we get enough products for the analysis.

2.3. ESR study

We have recorded different ESR spectra. Figures 3 and 5 show that the white and red compounds did not respond and Figure 4 that the blue one gives an answer corresponding to a radical. This proves that the blue compound contains radicals.

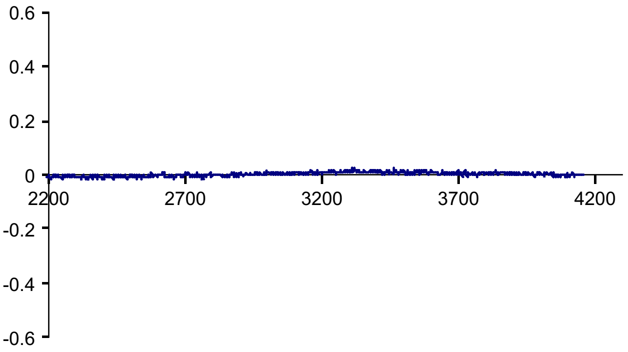


Figure 3. ESR spectrum of pentadeca-4,6-diynyl hexadecanoate.

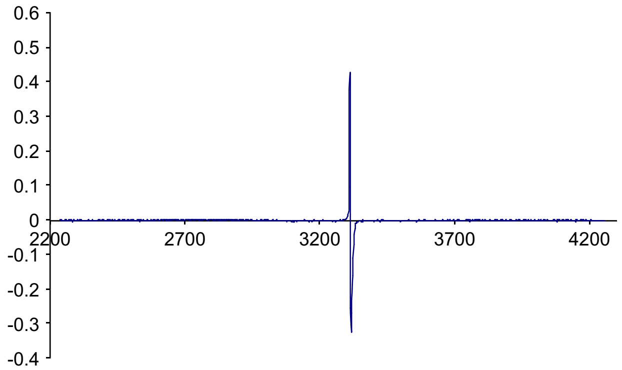


Figure 4. ESR spectrum of the blue derivative.

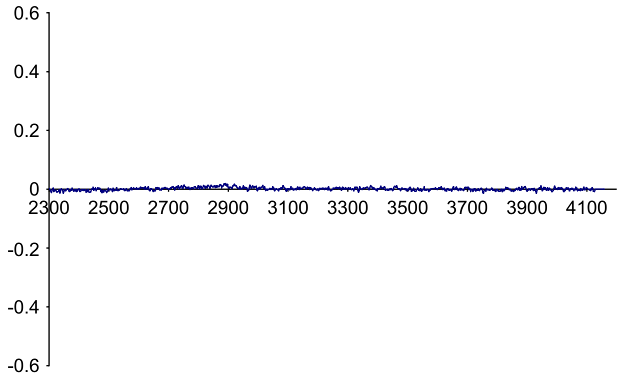


Figure 5. ESR spectrum of the red derivative.

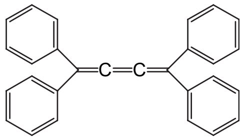


Figure 6. Structure of the tetraphenylbutatriene.

2.4. Raman spectroscopy study

To help us in the comprehension of the spectra, we have used the only cumulene commercially available for comparison (Fig. 6).

Spectrum of tetraphenylbutatriene (Fig. 7a) compared with spectrum of tetraphenylethylene (Fig. 7b) shows an additional band at 2029 cm^{-1}, which can be attributed to the cumulene. Spectra of white diyne (Fig. 8) and blue derivative (Fig. 9) have been recorded, and we can observe this band only for the blue one. During transformation of the blue form into the red one (Figs. 10 and 11), this band has disappeared and two new bands corresponding to conjugated double (at 1517 cm^{-1}) and triple (at 2114 cm^{-1}) bonds have appeared.

These results hardly confirm the proposed butatrienic structure of the blue compound.

2.5. NMR study

Last confirmation came from ^{13}C solid NMR. Spectra of white, blue and red compounds are strictly the same (Fig. 12) due to the mixture 99/1 of white and blue (or red) compounds. As explained before, we have made many cycles of irradiation, heating, solving and filtration to get enough insoluble red products for the analysis. Spectrum of the pure red polymer (Fig. 13) is very different and shows two signals corresponding to an enyne structure.

2.6. Conclusion

These three analytical studies proved that the blue intermediate has a radical structure (one of those proposed by Bloor[9c]) and the red one a conjugated enyne unit. So we can propose the following mechanism (Fig. 14).

3. Conclusion

New irreversible thermochromic diyne families are described from a simple and quick way. We can notice a relationship between the chain lengths and the thermochromic temperature: when the carbon atom number increases by two units, the temperature rises

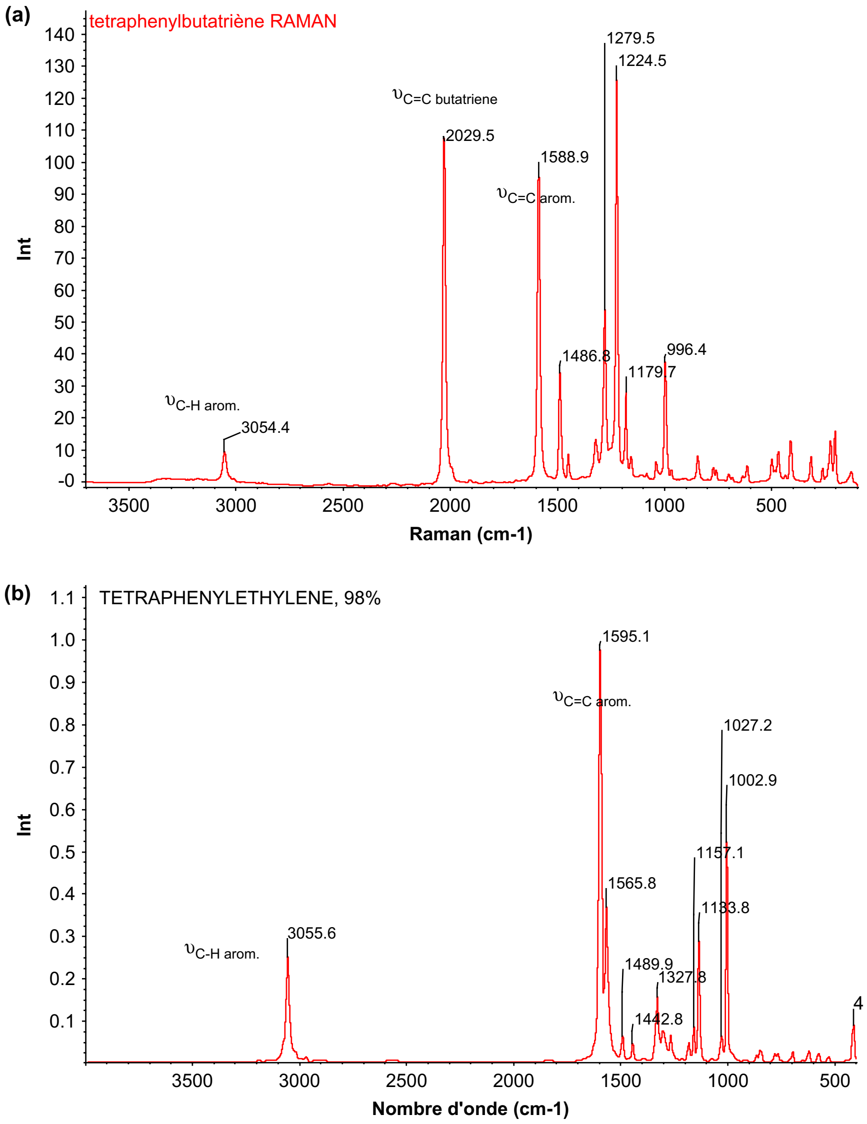


Figure 7. (a) Raman spectrum of tetraphenylbutatriene, (b) Raman spectrum of tetraphenylethylene.

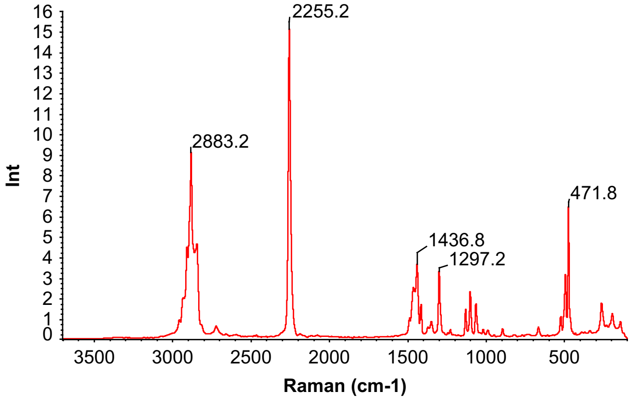


Figure 8. Raman spectrum of a white compound.

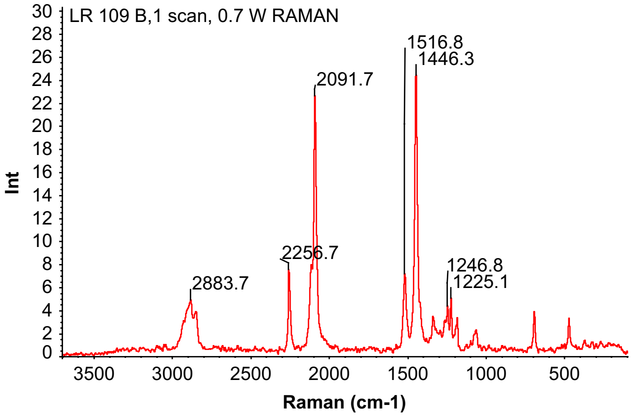


Figure 9. Raman spectrum of a blue compound.

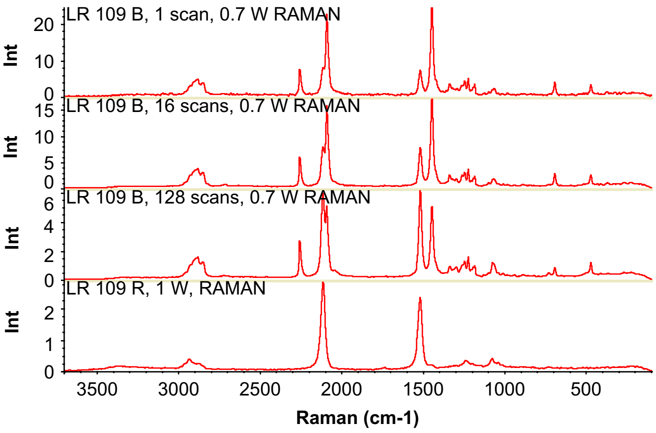


Figure 10. Raman spectra of the blue compound turning to the red one.

around 10 °C. Moreover the determination of compound structure at each step leads us to propose a mechanism for the transformation. The blue intermediate obtained after UV irradiation is a radical with cumulene units, which turn into a red polyenyne when heated.

4. Experimental section

4.1. General procedure for the synthesis of symmetric diynes A

In a 100 mL three-necked flask, 20 mmol of the alkyne, 2 mmol of tetramethylethylenediamine (TMEDA), 1 mmol of copper iodide (CuI) and 30 mL of dimethoxyethane (DME) are introduced. The mixture is then subjected to oxygen bubbling and stirred at 55 °C overnight. The solution is then filtered on Celite® and DME is stripped off using a rotary evaporator. The obtained mixture is then treated with 30 mL of dichloromethane (CH_2Cl_2) and 50 mL of aqueous HCl 0.1 N in a separating funnel and then washed with distilled water until pH 7. The organic phase is then dried on sodium sulfate, filtered and finally the solvent is evaporated with a rotary evaporator to give generally a white powder or liquid with

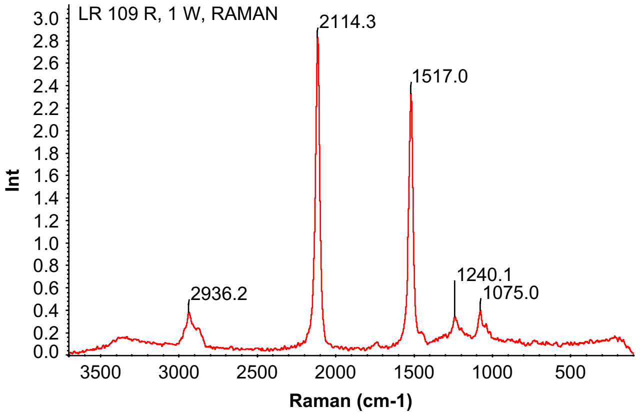
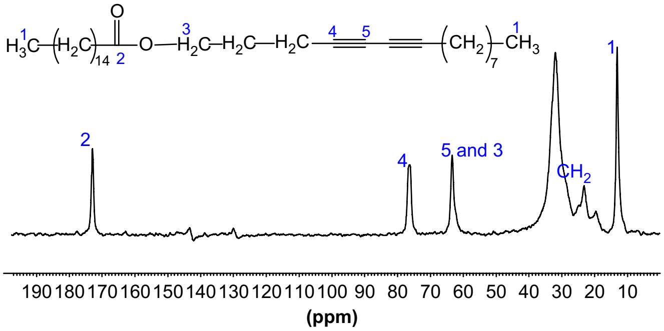
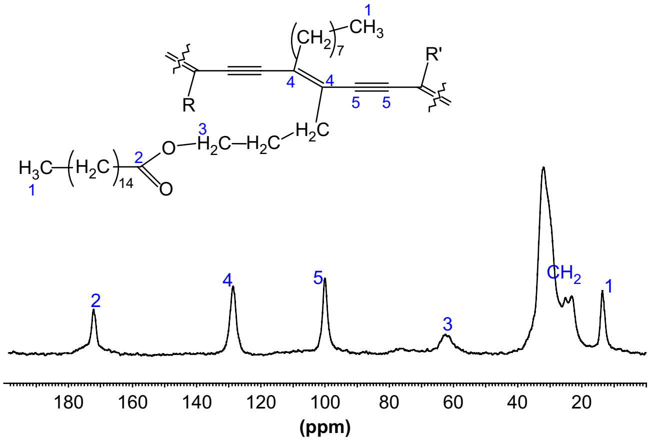


Figure 11. Raman spectrum of a red compound.



^{13}C NMR (solid): 172.9 (C2), 76.2 (C4), 63.3 (C5 and C3), 31.9 - 23.1 (CH_2), 13.1 (C1)

Figure 12. ^{13}C solid NMR spectrum of pentadeca-4,6-diynyl hexadecanoate.



^{13}C NMR (solid): 172.1 (C2), 128.6 (C4), 100.0 (C5), 62.5 (C3), 31.9 - 23.1 (CH_2), 13.1 (C1)

Figure 13. ^{13}C solid NMR spectrum of pure red polymer.

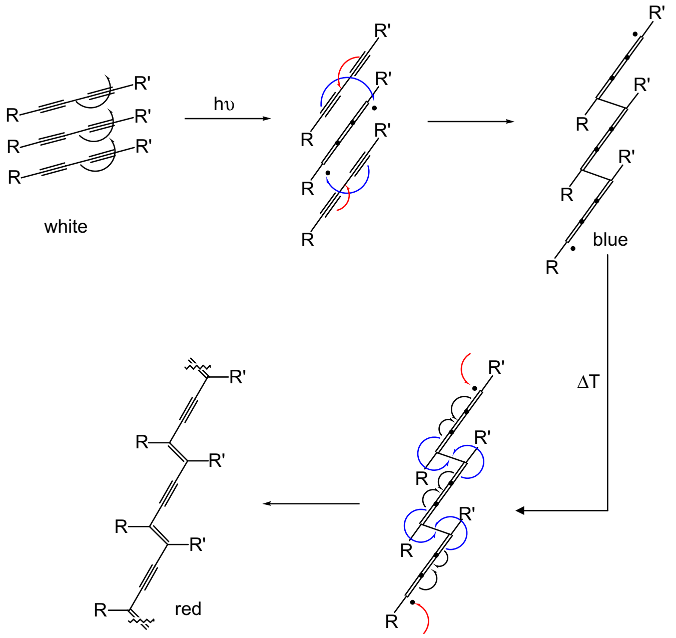


Figure 14. Mechanism of the irreversible thermochromism phenomenon.

more than 90% yield. Further purification of the crude product by column chromatography with a suitable eluent leads to the pure compound. All NMR spectra are quite the same and one example is given below.

4.1.1. Eicosa-9,11-diyne (n=7)

^{1}H NMR ($CDCl_3$): δ=2.24 (4H, t, ^3J=7 Hz, 2≡CCH_2), 1.50 (4H, quint, 2CH_2), 1.26 (20H, m, 10CH_2), 0.88 (6H, t, ^3J=7 Hz, 2CH_3).

^{13}C NMR ($CDCl_3$): δ=77.5 (2Cq), 65.3 (2Cq), 32–25 (10CH_2), 22.7 (2CH_2), 19.3 (2≡CCH_2), 14.1 (2CH_3).

4.2. General procedure for the synthesis of symmetric diyne-diols B

In a 100 mL three-necked flask, 20 mmol of the alkynol, 2 mmol of tetramethylethylenediamine (TMEDA), 1 mmol of copper iodide (CuI) and 30 mL of dimethoxyethane (DME) are introduced. The mixture is then subjected to oxygen bubbling and stirred at 55 °C overnight. The solution is then filtered on Celite® and DME is stripped off using a rotary evaporator. The obtained mixture is then treated with 30 mL of ethyl acetate and washed with brine. The organic phase is then dried on sodium sulfate, filtered and finally the solvent is evaporated with a rotary evaporator to give a solid with more than 90% yield. Further purification of the crude product by column chromatography with a suitable eluent leads to the pure compound. As for **A** compounds, all NMR spectra are quite the same and one example is given below.

4.2.1. Deca-4,6-diyn-1,10-diol (m=3)

^{1}H NMR (DMSO-d_6): δ=3.74 (4H, t, ^3J=6.2 Hz, 2CH_2OH), 2.39 (4H, t, ^3J=7 Hz, 2≡CCH_2), 1.80 (4H, quint, CH_2), 1.74 (2H, s, OH).

^{13}C NMR (DMSO-d_6): δ=80.8 (2Cq), 65.6 (2Cq), 60.1 (2CH_2OH), 31.3 (2CH_2), 15.6 (2≡CCH_2).

4.3. General procedure for the synthesis of diynols C

In a 100 mL three-necked flask, 10 mmol of each alkyne, 2 mmol of tetramethylethylenediamine (TMEDA), 1 mmol of copper iodide (CuI) and 30 mL of dimethoxyethane (DME) are introduced. The mixture is then subjected to oxygen bubbling and stirred at 55 °C overnight. The solution is then filtered on Celite® and DME is stripped off using a rotary evaporator. The obtained mixture is then treated with 30 mL of dichloromethane (CH_2Cl_2) and 50 mL of aqueous HCl 0.1 N in a separating funnel and then washed with distilled water until pH 7. The organic phase is then dried on sodium sulfate, filtered and finally the solvent is evaporated with a rotary evaporator to give generally a yellow mixture with more than 90% yield.

During the coupling reaction three products are formed. The separation step is easily realised by column chromatography with CH_2Cl_2 as eluent. The mixed diynes are obtained pure with yield higher than 40% and their structures have been confirmed by ^{1}H and ^{13}C NMR. Two examples are reported, one for synthesis of diynes starting from propargyl alcohol (*m*=1) and one starting from pent-4-yn-1-ol (*m*=3).

4.3.1. Trideca-2,4-diyn-1-ol (m=1, n=7)

^{1}H NMR (DMSO-d_6): δ=5.35 (1H, s, OH), 4.09 (2H, s, OCH_2), 2.13 (2H, t, ^3J=7 Hz, ≡CCH_2), 1.54 (2H, quint, CH_2), 1.35 (10H, m, 5CH_2), 0.88 (3H, t, ^3J=7 Hz, CH_3).

^{13}C NMR (DMSO-d_6): δ=81.9 (Cq), 75.9 (Cq), 68.8 (Cq), 64.7 (Cq), 49.8 (OCH_2), 31–22 (6CH_2), 19.4 (≡CCH_2), 13.9 (CH_3).

4.3.2. Pentadeca-4,6-diyn-1-ol (m=3, n=7)

^{1}H NMR (DMSO-d_6): δ=4.44 (1H, s, OH), 3.46 (2H, t, ^3J=6.4 Hz, OCH_2), 2.26 (2H, t, ^3J=7.1 Hz, ≡CCH_2), 2.22 (2H, t, ^3J=7 Hz, ≡CCH_2), 1.66 (2H, quint, CH_2), 1.50 (2H, quint, CH_2), 1.32 (10H, m, 5CH_2), 0.87 (3H, t, ^3J=7 Hz, CH_3).

^{13}C NMR (DMSO-d_6): δ=81.3 (Cq), 80.8 (Cq), 65.5 (Cq), 64.4 (Cq), 60.1 (OCH_2), 31–22 (8CH_2), 19.2 (≡CCH_2), 13.9 (CH_3).

4.4. General procedure for the synthesis of diynesters D

In a 100 mL three-necked flask, 10 mmol of alcohol, 12 mmol of triethylamine and 20 mL of CH_2Cl_2 are introduced. Alkyl chloride (11 mmol) in CH_2Cl_2 (10 mL) is added dropwise. The solution is stirred for 1 h and washed with distilled water until pH 7. The organic phase is then dried on sodium sulfate, filtered, and the solvent is evaporated with a rotary evaporator to give a white or yellow product with yield higher than 90%. The diacetylenic compounds are purified, when necessary, on a silica column with CH_2Cl_2 as eluent. The structure of diynes has been confirmed by ^{1}H and ^{13}C NMR. Two examples are reported, one starting from propargyl alcohol (*m*=1) and one starting from pent-4-yn-1-ol (*m*=3).

4.4.1. Octanoyl trideca-2,4-diyn-1-oate (m=1, n=7, p=6)

^{1}H NMR ($CDCl_3$): δ=4.71 (2H, s, OCH_2), 2.30 (2H, t, ^3J=7.2 Hz, O=CCH_2), 2.24 (2H, t, ^3J=7 Hz, ≡CCH_2), 1.60 (2H, quint, CH_2), 1.48 (2H, quint, CH_2), 1.26 (18H, m, 9CH_2), 0.88 (6H, t, 2CH_3).

^{13}C NMR ($CDCl_3$): δ=174.7 (CO), 83 (Cq), 75.4 (Cq), 72.9 (Cq), 63.4 (Cq), 52.8 (OCH_2), 33.9 (O=CCH_2), 32–22 (11CH_2), 19.2 (≡CCH_2), 14.1 (2CH_3).

4.4.2. Octanoyl pentadeca-4,6-diyn-1-oate (m=3, n=7, p=6)

^{1}H NMR ($CDCl_3$): δ=4.15 (2H, t, ^3J=6.2 Hz, OCH_2), 2.27 (2H, t, ^3J=7.1 Hz, O=CCH_2), 2.24 (2H, t, ^3J=7 Hz, ≡CCH_2), 2.20 (2H, t, ^3J=7.1 Hz, ≡CCH_2), 1.84 (2H, quint, CH_2), 1.54 (2H, quint, CH_2), 1.47 (2H, quint, CH_2), 1.25 (18H, m, 9CH_2), 0.88 (6H, t, 2CH_3).

^{13}C NMR ($CDCl_3$): δ=175.9 (CO), 78.4 (2Cq), 66.8 (2Cq), 66.3 (OCH_2), 34 (O=CCH_2), 32-22 (11CH_2), 19.3 (≡CCH_2), 14.9 (≡CCH_2), 14.1 (2CH_3).

4.5. ^{13}C solid NMR studies

All ^{13}C solid NMR spectra were carried out on a Brüker ARX300 spectrometer or a Brüker AVANCE 300, equipped with a probe CP/MAS (Cross Polarization/Magic Angle Spinning) whose frequency is 75.5 MHz. Samples are placed in a zirconium oxide bucket of 4 mm diameter, the rotation speed applied to samples was 4, 5 or 6 kHz, with a contact time of 1 ms and an interval of 3 s between each pulse. The method used, TOSS (TOtal Sideband Suppression), allows the removal of sidebands. The chemicals shifts are listed in parts per million (ppm) using glycine as calibration.

4.6. ESR spectroscopy

The ESR spectra were obtained with a Varian line E-101 spectrometer and analyses were made at X-band at a frequency of about 9.4 GHz with a magnetic field varying from 0 to 1.2 T. The reference used was DPPH (diphenylpicrylhydrazide). Spectra are recorded after a sweep from 2200 to 4200 Gauss.

4.7. Raman spectrometry

Raman spectra were obtained with a Raman Module from NICOLET (near IR). The exciter is an Nd:YAG (neodyme, yttrium/aluminium/garnet) laser with a wavelength of 1064 nm and a power on the sample ranging from 0.6 to 1.2 W. The spectrometer is equipped with a separating CaF_2 and an InGaAs detector (indium/gallium/arsenic) with a resolution of 8 cm^{-1}.

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