



## Julolidine fluorescent molecular rotors as vapour sensing probes in polystyrene films



Giulio Martini<sup>a</sup>, Elisa Martinelli<sup>a, b</sup>, Giacomo Ruggeri<sup>a, b</sup>, Giancarlo Galli<sup>a, b</sup>,  
Andrea Pucci<sup>a, b, \*</sup>

<sup>a</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Pisa, Italy

<sup>b</sup> INSTM, UdR Pisa, Italy

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### ABSTRACT

We introduce a new sensing polymer system for detection of volatile organic compounds (VOCs) based on the optical response of polystyrene (PS) films doped with julolidine fluorescent molecular rotors (FMRs). The julolidine FMRs exhibited viscosity-dependent changes in the fluorescence intensity, that was enhanced when glycerol was added to ethanol solutions and when they were dispersed in PS films. Thus, reduction in medium mobility slowed down internal motions and allowed for a major radiative decay pathway. The FMR/PS films were exposed to several VOCs, and showed a significant decrease in fluorescence emission when exposed to chloroform, whereas a negligible variation in their emission occurred when methanol was utilized. This vapour sensing behaviour was much more evident when a perfluorodecyl chain was linked to the julolidine core being the molecule segregated at the film surface. This responsive behaviour was affected by solvent composition and its reproducible response was easily determined by luminescence experiments.

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### 1. Introduction

Luminescent materials have been actively pursued recently, owing to their various promising applications in diverse fields, ranging from solar energy conversion [1], to optoelectronic devices [2] and chromogenic materials [3–6]. Chromogenic systems are capable to respond to various stimuli (e.g. light, heat, mechanical stress and chemical stimuli) through a macroscopic optical output [4,7,8]. The energy of the stimulus is properly transduced into optical variations (i.e., absorption, emission, refractive index) as a function of external interference.

Recently, luminescent materials which display reversible colour changes upon exposure to vapours of volatile organic compounds (VOCs), have also rapidly evolved due to their potential application for chemical vapour detection [9–11]. The detection of VOCs can often occur by the naked eye, thus suggesting such systems as promising tools for environmental monitoring and safety systems at workplaces.

The optical response to vapours is often associated with changes in the weak metal–metal interactions of coordination complexes as a result of analyte vapour sorption [9]. As an alternative, solvatochromic fluorescent organic species are used for the detection of organic vapours, since their wavelength emission depends on the polarity of VOCs [12,13]. In the last years, organic luminophors such as tetraphenylethene derivatives [14–17], have been proposed as compounds with effective vapour sensitivity. They display aggregation induced luminescent properties [10,18] and the vapour uptake caused changes in their intermolecular interactions thus affecting molecular packing and emission [19].

For practical applications, those molecules are fabricated into thin solid films or incorporated in polymer matrices. The success of vapour sensing polymer films is largely due to the ability of volatile compounds to spread rapidly inside the polymer matrix and interact with the sensor molecule giving a fast and reliable response [20,21]. The use of visible-light transparent polymer matrices with good film-forming capacity allows also the preparation of large area devices at ambient conditions by low-cost fabrication techniques.

Fluorescent molecular rotors (FMRs) are fluorescent molecules composed by an electron donor unit in conjugation with an electron acceptor moiety and are reported to undergo non-radiative relaxation from the fluorescent excited state [22–24]. More

\* Corresponding author. Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35, 56126 Pisa, Italy. Tel.: +39 050 2219270; fax: +39 050 2219260.

E-mail address: [andrea.pucci@unipi.it](mailto:andrea.pucci@unipi.it) (A. Pucci).

specifically, in the ground state the FMR is almost planar and highly conjugated as well as its locally excited (LE) state. Nevertheless, solvent relaxation and rapid internal torsional motion occur, thus resulting in a twisted intramolecular charge transfer (TICT) excited state, which rapidly decays in a non-radiative way through internal rotation [22,25–27]. Moreover, non-radiative deactivation of the first excited state is controlled by rapid internal torsional motion, which is substantially restricted in viscous media [28,29] When this internal rotation is hindered, e.g. due to an increase in viscosity or steric constraints, the radiative decay of LE state is favoured, and an increase in quantum yield is obtained [27].

The apparent sensitivity to fluid motion of FMRs like julolidine derivatives is also found to be an indirect effect of a photoisomerization reaction [30].

FMRs have received popularity in the last 5–10 years thanks to their easy applicability as non-mechanical viscosity sensors, tools for protein characterization and local microviscosity imaging [31–34]. Moreover, the high sensitivity towards viscosity changes has reached a precision comparable to commercial mechanical rheometers with shorter measurement time [35].

While the application of julolidine FMRs as viscosity sensors is widespread, their behaviour within polymer matrices is still under debate. A few examples have been reported for the determination of the molecular weight dependence of viscosity in polymer melts [36] and for sensing free volume and plasticity in thermoplastic polymers [37,38].

Herein, we report on the emission properties of different julolidine FMRs dispersed (~0.05 wt.%) within a transparent and amorphous PS matrix as a function of the exposure to different VOCs and the results are discussed in terms of sensitivity and reproducibility of the fluorescence response of the systems. Different julolidine FMRs were utilized, i.e. DCVJ, 9-(2-carboxy-2-cyanovinyl)julolidine (CCVJ) and 9-(2-(1H,1H,2H,2H-perfluorodecyloxycarbonyl)-2-cyanovinyl)julolidine (F8CVJ), in order to identify best suited molecular rotors for sensor performance. The perfluorodecyl chain was selected to favour fluorophore segregation near the film–air interface as to be more responsive to VOC exposure.

## 2. Experimental part

### 2.1. Materials and methods

Julolidine, *N,N'*-dicyclohexylcarbodiimide (DCC), phosphorous oxychloride, 9-(2,2-dicyanovinyl)julolidine, 9-(2-carboxy-2-cyanovinyl)julolidine were purchased from Aldrich and used as received. Cyanoacetic acid (Aldrich) was recrystallized from a mixture of toluene/acetone 2:3 v/v. *N,N*-dimethylformamide and dichloromethane (Aldrich) were refluxed over CaH<sub>2</sub> for 2 h and distilled under nitrogen. Tetrahydrofuran (Aldrich) was refluxed over Na/K alloy for 3 h and distilled under nitrogen. Triethylamine (Aldrich) was refluxed over KOH for 3 h and distilled under nitrogen. 1H,1H,2H,2H-perfluorodecyl alcohol (Fluorochem) was used as received. Atactic polystyrene (PS, Repsol, *M<sub>w</sub>* = 86,000 g/mol) was used as received. Spectroscopy grade solvents (Carlo Erba or Aldrich) were utilized without further purification.

### 2.2. Synthesis of 9-formyljulolidine (1)

The synthesis of 9-formyljulolidine (1) was carried out modifying a reported procedure [33]. In brief, phosphorous oxychloride (0.29 mL, 3.17 mmol) was added dropwise to a solution of julolidine (0.5 g, 2.88 mmol) and *N,N*-dimethylformamide (0.27 mL, 3.45 mmol) in anhydrous dichloromethane (5 mL) and the mixture was stirred for 8 h at 25 °C. The reaction was treated with an

aqueous solution of sodium hydroxide (2 M) and the mixture was stirred at 0 °C for 4 h. The organic layer was extracted with diethyl ether, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (230–400 mesh) using diethyl ether/*n*-hexane (3/7 v/v) as eluent mixture (*R<sub>f</sub>* = 0.37) (60% yield).

FT-IR (KBr, cm<sup>-1</sup>): 2950, 2895, 1662, 1600, 1320, 900, 720.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 9.6 (s, 1H, CHO), 7.3 (s, 2H, aromatic), 3.3 (t, 4H NCH<sub>2</sub>), 2.7 (t, 4H NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.9 (m, 4H NCH<sub>2</sub>CH<sub>2</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 191.3 (CHO), 149.1 (=C–N aromatic), 128.5 to 122.0 (aromatic), 49.3 (NCH<sub>2</sub>), 28.1 to 20.4 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

EI-MS *m/z* (%): 201 (100, M<sup>+</sup>).

The spectral properties of this compound are in agreement with those previously reported [33].

### 2.3. Synthesis of 1H,1H,2H,2H-perfluorodecyl cyanoacetate (2)

A solution of 1.03 g (5 mmol) of DCC in 5 mL of anhydrous dichloromethane was added dropwise to a solution of cyanoacetic acid (0.43 g, 5 mmol) and 1H,1H,2H,2H-perfluorodecyl alcohol (2.32 g, 5 mmol) in anhydrous dichloromethane (10 mL). The mixture was kept under stirring for 24 h at 25 °C. Then, it was diluted with dichloromethane (10 mL) and the precipitate formed during the reaction was filtered off. The filtrate was dried under vacuum and the residue was purified by column chromatography on silica gel (230–400 mesh) using dichloromethane as eluent (*R<sub>f</sub>* = 0.91) (41% yield).

FT-IR (KBr, cm<sup>-1</sup>): 2980, 2960, 2188, 1756, 1355–1055, 660.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 4.6 (t, 2H, CH<sub>2</sub>CH<sub>2</sub>CF<sub>2</sub>), 3.5 (s, 2H, CNCH<sub>2</sub>COO), 2.6 (m, 2H CH<sub>2</sub>CF<sub>2</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 164.2 (COO), 114.6 (CN), 123 to 107 (CF), 56.3 (OCH<sub>2</sub>), 31.8 (OCH<sub>2</sub>CH<sub>2</sub>), 26.0 (CH<sub>2</sub>CN).

Anal. Calcd for C<sub>13</sub>H<sub>6</sub>F<sub>17</sub>NO<sub>2</sub>: C, 29.40; H, 1.14. Found: C, 30.0; H, 1.0.

### 2.4. Synthesis of 9-(2-(1H,1H,2H,2H-perfluorodecyloxycarbonyl)-2-cyanovinyl)julolidine (F8CVJ)

Triethylamine (0.3 mL, 2.14 mmol) was added to a solution of 2 (0.83 g, 1.56 mmol) and 1 (0.21 g, 1.06 mmol) in tetrahydrofuran (8 mL) and the mixture was stirred at 50 °C for 10 h. The solvent was then evaporated and the residue was purified in a first step by column chromatography on silica gel using dichloromethane/*n*-hexane (4/6 v/v) as mobile phase. The obtained product was further purified by elution on preparative TLC plates using ethyl acetate/*n*-hexane (4/6 v/v) as eluent mixture (*R<sub>f</sub>* = 0.59) (20% yield).

FT-IR (KBr, cm<sup>-1</sup>): 2925, 2855, 2215, 1720, 1615–1525, 1450, 1322–1130, 660.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm): 7.9 (s, 1H, CNCCH), 7.5 (s, 2H, aromatic), 4.5 (t, 2H, COOCH<sub>2</sub>), 3.3 (t, 4H, NCH<sub>2</sub>), 2.7 (t, 4H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.6 (m, 4H, CH<sub>2</sub>CF<sub>2</sub>), 1.9 (m, 4H, NCH<sub>2</sub>CH<sub>2</sub>).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) (ppm): 164.4 (COO), 154.8 (PhCH = ), 147.8 (=C–N aromatic), 128.2 to 121.0 (aromatic), 117.6 (CN), 123–107 (CF), 57.3 (OCH<sub>2</sub>), 50.2 (NCH<sub>2</sub>), 27.2–21.0 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

<sup>19</sup>F NMR (CDCl<sub>3</sub>/CF<sub>3</sub>COOH) (ppm): –6 (CF<sub>3</sub>), –38 (2F, CH<sub>2</sub>CF<sub>2</sub>), –49 to –47 (10F, CF<sub>2</sub>), –52 (2F, CF<sub>2</sub>CF<sub>3</sub>).

EI-MS *m/z* (%): 95 (48), 186 (15), 251 (15), 267 (16), 463 (8).

### 2.5. Preparation of polymeric films

Films of julolidine derivative/PS mixtures were prepared by dissolving 1 g of PS and the desired amount of dye (0.005–0.1 wt.%) in 150 mL of CHCl<sub>3</sub>. After solvent evaporation, the polymer mixture was melt-pressed between two Teflon foils in a Carver 3851-0 press at 150 °C and 4 tons of pressure for 5 min. After removal from the

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