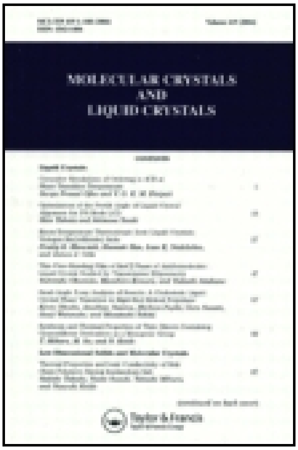

# Molecular Crystals and Liquid Crystals

# Dyads and Triads Based on Dithienyletheneand Indolino[2,1-b]Oxazolidine

Jiaan Gan [a] , Lionel Sanguinet [a] & Jean-Luc Pozzo [a]
[a] Photochemistry for Nanoscience, CNRS UMR 5802, University Bordeaux 1, Talence, France

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# Dyads and Triads Based on Dithienylethene and Indolino[2,1-b]Oxazolidine

**Jiaan Gan**
**Lionel Sanguinet**
**Jean-Luc Pozzo**
Photochemistry for Nanoscience, CNRS UMR 5802, University Bordeaux 1, Talence, France

*Photochromic and acidochromic properties of dithienylethene-indolino[2,1-b]oxazolidine dyads and triads along with their reduced forms were investigated. Upon protonation the π-conjugated system is greatly increased. The resulting acidoinduced indoleninium species deeply influence the maxima absorption of the dithienylethene subunits whose maxima for the closed forms is red-shifted to the infrared region. These examples constitute a promising approach towards multiaddressable molecular switches based on diarylethenes.*

**Keywords:** acidochromism, dithienylethene, indolino[2,1-b]oxazolidine, photochromism

## INTRODUCTION

Diarylethene derivatives are still attracting extensive attention for the development of photonic devices and molecular switches [1,2] because of their promising thermal irreversible and high fatigue resistant photochromic performance [3,4]. Indolino[2,1-b]oxazolidines are stable in their closed forms and give colorless solutions. Ring opening of the oxazolidine derivatives can be achieved upon protonation and results in a strong visible absorption band [5]. The closed forms and open forms of indolino[2,1-b]oxazolidine subunits as well as those of the diarylethene moieties can be considered as “0” and “1” of a digital binary code. Covalently linked dithienylethene-oxazolidine dyads

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Address correspondence to Jean-Luc Pozzo, Photochemistry for Nanoscience, CNRS UMR 5802, University Bordeaux 1, Talence, France. E-mail: jl.pozzo@lcoo.u-bordeaux1.fr

and triads were designed and synthesized to build protons and light driven logic gate using absorbance as output across entire Visible region and Near InfraRed region at a single molecular level [6].

When different substituents were connected at para-positions of the phenyl groups of bis(2,4-dimethyl-5-phenylthiophene-3-yl)perfluorocyclopentenes, photochromic properties such as cylization and ring-opening quantum yields, and absorption coefficients of the closed form of these derivatives were strongly affected. Electron-donating substituents were found to be effective to increase the absorption coefficient and to decrease the ring-opening quantum yield [7]. In this study, we use the dithienylethene-oxazolidine dyads and triads and their reduced forms as model compounds to obtain acido-and photoaddressable diarylethenes.

## EXPERIMENTAL

$^{1}$H NMR, $^{13}$C NMR characterizations were performed on a Bruker AC250, Bruker Avance 300 or PPX 400 instrument. $^{19}$F NMR spectra were recorded on a PPX 200 instrument. The residual protons from solvent are taken as an internal reference and chemical shift are reported in parts per million relative to tetramethylsilane. UV-vis measurements were performed using a Hitachi U-3300 spectrophotometer. MALDI-MS spectra were recorded in the positive mode by using 2,5-dihydroxy-benzoic acid in dioxane as the matrix. Melting points were uncorrected.

## Materials

All commercially available materials were used without further purification unless otherwise stated. Solvents used for spectroscopic measurements were all spectrograde. Column chromatography was performed using silica gel Si 60 (40–63 μm) from Merck. The synthesis of **SU** and **DU** will be published elsewhere.

To a solution of **SU** (135 mg, 0.2 mmol) in 20 mL ice-cooled methanol, $NaBH_4$ (15 mg, 0.4 mmol) was added. The mixture was stirred for 2 h, ice water was then added to quench the reaction and the product was extracted with dichloromethane and dried over $Na_2SO_4$. Removal of the solvent gave a light red crude product which was subsequently purified by flash column chromatography with 20:1 dichloro methane/methanol as eluent to afford 98 mg of **SR** in 75% yield as a white powder. **SR**: 82–83 mp°C; $^{1}$H NMR ($CDCl_3$, 300 MHz) $\delta$ 7.17 (d, J = 7.14, 1H), 7.11 (t, J = 7.53, 1H), 6.95 (s, 1H), 6.88 (s, 1H), 6.74 (t, J = 7.16, 1H), 6.63 (d, J = 15.81 Hz, 1H), 6.53 (d, J = 7.92 Hz, 1H), 5.83 (dd, J = 9.42 Hz, 1H), 4.75 (s, 2H), 3.91 (d, J = 9.42 Hz, 1H), 3.75 (t, J = 5.46 Hz, 2H), 3.27 (m, 2H), 1.93 (s, 3H), 1.86 (s, 3H), 1.85–1.26 (m, 10H); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 150.0, 142.3, 142.1, 140.9, 139.6, 137.8, 127.7, 127.6, 126.0, 125.3, 125.1, 124.8, 124.4, 123.3, 117.9, 106.6, 60.5, 59.9, 48.4, 48.0, 36.8, 31.4, 25.7, 22.8, 22.4, 14.6 (2 C); $^{19}$F NMR ($CDCl_3$, 188 MHz) $\delta$ −110.1, −110.3, −132.0; MS (MALDI) $m/z$ 654.0 [M + H$^+$].

The synthesis route for **DR** is the same as **SR**. DR (yield 65%): mp 114°C (decom.); $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 7.17 (d, J = 7.32, 2H), 7.10 (d, J = 7.62, 2H), 6.90 (s, 2H), 6.74 (t, J = 7.15, 2H), 6.64 (d, J = 15.68 Hz, 2H), 6.53 (d, J = 7.63 Hz, 2H), 5.83 (dd, J = 9.45 Hz, 2H), 3.92 (d, J = 9.45 Hz, 2H), 3.76 (t, J = 5.5 Hz, 4H), 3.26 (m, 4H), 1.89 (s, 6H), 1.85–1.20 (m, 20H); $^{13}$C NMR ($CDCl_3$, 50 MHz) $\delta$ 149.9, 140.9, 139.7, 137.8, 127.7, 127.6, 126.1, 125.3, 125.1, 123.3, 117.9, 106.6, 60.4, 48.3, 48.0, 36.8, 31.4, 25.7, 22.8, 22.4, 14.7; $^{19}$F NMR ($CDCl_3$, 188 MHz) $\delta$ −110.2, −131.9; MS (MALDI) $m/z$ 879.3 [M + H$^+$].

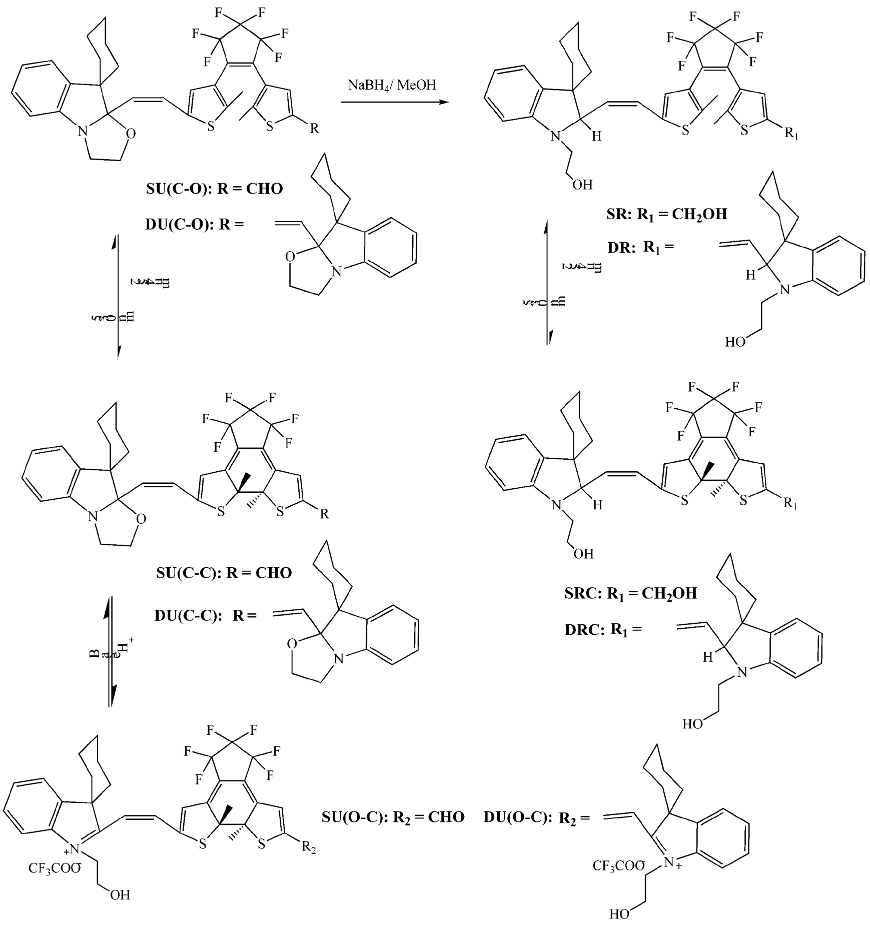
## RESULTS AND DISCUSSION

### Photochromic Properties

The interconversion using external stimuli such as light, acidity and chemical between the different isomers of the model compounds is depicted in Scheme 1. The absorption spectra for all the compounds were shown in Figure 1 and the absorption data were listed in Table 1.

A colorless solution of dyad **SU(C-O)** in acetonitrile turned blue upon irradiation with 254 nm light. The absorption band at 220–320 nm decreased and an immediate increase in the absorption intensity in the visible spectral region due to the appearance of the absorption bands for the "closed-closed" isomer **SU(C-C)** was observed. Photoisomerization of **DU(C-O)** at the same irradiation condition afforded **DU(C-C)** with a typical absorption maximum at 586 nm for the closed form. Irradiation of the "closed-closed" isomers **SU(C-C)** and **DU(C-C)** at wavelengths greater than 500 nm resulted in the rapid dithienylethene ring opening photo-cycloreversion and photo-regeneration of the original absorption spectrum corresponding to **SU(C-O)** and **DU(C-O)** respectively, indicating that the indolino-[2,1-b]-oxazolidine unit is photostable upon irradiation with 254 nm light.

**SU(O-C)** was obtained upon protonation of the blue solution of **SU(C-C)** in acetonitrile with trifluoroacetic acid and the solution turned green. A new strong absorption band centered at 423 nm was observed. The absorption band of the dithienylethene unit was shifted to 520–820 nm, the maximum at 605 nm for **SU(C-C)** becoming



**SCHEME 1** Interconversion of the model compounds

centred at 678 nm. This huge variation is also accompanied by a significant increase of the molar extinction coefficient. Using light and acidic stimuli, the absorption bands extend to the Near Infrared region. Protonation of **DU(C-C)** with CF$_3$COOH in acetonitrile afforded **DU(O-C)**. The same absorption maximum at 423 nm was observed. The "push-pull" analogue for **SU(C-C),** in which the formyl group is the electron-withdrawing group and the amino group of indolino[2,1-b]oxazolidine represent an electron donor, changes to a "pull-pull" analogue **SU(O-C)** upon protonation. The "push-push" analogue for **DU(C-C)** changed to a "pull-pull" analogue **DU(O-C)** upon

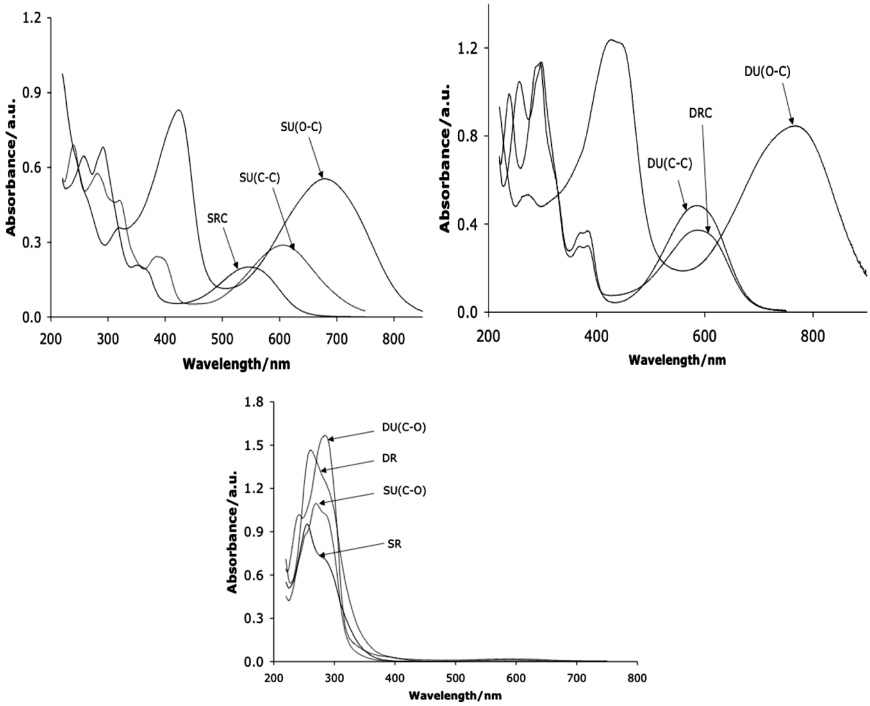


**FIGURE 1** Absorption spectral changes of model compounds in acetonitrile ($3.6 \times 10^{-5}$ M). Photostationary states were obtained under irradiation with 254-nm light as described in Table 1.

protonation. These changes were attributed to the long $\pi$-conjugation between the indolino[2,1-b]oxazolidine unit and the dithienylethene unit induced by the ring opening of oxazolidine. In the triad **DU(O-C)**, longer $\pi$-conjugation along the two oxazolidine units and one dithienylethene further shifted the absorption maximum to 769 nm. The "closed-closed" forms **SU(C-C)** and **DU(C-C)** could be regenerated from the "open-closed" isomers **SU(O-C)** and **DU(O-C)** by the addition of triethylamine.

When **DU(C-O)** was reduced with $NaBH_4$ in Methanol, **DR** was obtained. Photoisomerization of **DR** in acetonitrile with 254 nm UV light afforded **DRC**. The absorption maximum of the closed form **DRC** did not change in comparison with that of **DU(C-C)**, because that the $\pi$-conjugation for the dithienylethene unit did not change. The reduction resulted in the decrease of the absorption coefficent because the electron-donating substitution combined with the oxygen atom was removed. However when **SU(C-O)** was reduced to **SR,** the

**TABLE 1** UV-vis data of the model compounds[a]

| Compound | $\lambda_{max}$/nm ($\varepsilon \times 10^{-4}$L mol$^{-1}$cm$^{-1}$) |
|---|---|
| **SR** | 252 (2.59) 290[b] (1.88) |
| **SRC** | 252 (1.74) 285 (1.81) 355 (2.78) 545 (0.56) |
| **SU(C-O)** | 265 (2.94) 282[b] (2.86) |
| **SU(C-C)** | 235 (1.83) 274 (1.53) 318 (1.29) 383 (0.67) 605 (0.8) |
| **SU(O-C)** | 312 (0.95)[b] 423 (2.78) 678 (1.54) |
| **DR** | 257 (4.00) |
| **DRC** | 253 (2.82) 294 (3.06) 359 (0.75)[b] 379 (0.82)[b] 586 (1.03) |
| **DU(C-O)** | 235 (2.36) 278 (3.67) |
| **DU(C-C)** | 238 (2.75) 295 (3.15) 364 (0.95)[b] 382 (1.03)[b] 586 (1.34) |
| **DU(O-C)** | 268 (1.47) 423 (3.42) 769 (2.35) |

[a] UV/vis spectroscopic data were obtained at ambient temperature. The photostationary state were obtained by irradiation of the solution of the open form with a hand-held 254-nm UV (470 μW/cm$^2$) lamp. [b] shoulder.

strong electron-withdrawing formyl group on 5-position was transformed to a weak electron-donating hydroxymethyl group and the electron-donating substitution comined with the oxygen atom linking on the other side of the dithienylethene unit was removed. The "push-pull" analogue for **SU(C-C)** changed to a "push-push" analogue **SR** upon reduction. The absorption maximum of the closed form **SRC** was blue-shifted as much as 60 nm and the absorption coefficient decreased in comparison with those of **SU(C-C)**. No absorption spectral change was observed when the reduced closed forms **SRC** and **DRC** were protonated by $CF_3COOH$ in acetonitrile. This suggested that only the substituents linking directly on the $\pi$-conjugation system of the dithienylethenes would affect the absorption spectrum of the closed forms.

## CONCLUSION

Protonation and Reduction of dithienylethene-oxazolidine dyad and triad resulted in oxazolidine ring opening. All the model compounds studied in this report showed typical absorption spectral changes of P-type photochromic diarylethene derivatives. Prolongation of the $\pi$-conjugation between the dithienylethene units and the oxazolidine units resulted in red-shift of the absorption spectrum for the closed forms of dithienylethenes. Only the substituents incorporated directly on the $\pi$-conjugation system of the dithienylethenes would be effective to change the absorption spectrum of the closed forms.

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