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Synthesis, electrochemical and photochromic behaviour of a series of (1,4-dithiafulven-6-yl)substituted 3*H*-naphtho[2,1-*b*]pyran derivatives

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Abstract—The synthesis and electrochemical and photochromic properties of new 3,3-diphenyl-8-(1,4-dithiafulven-6-yl)-[3*H*]-naphtho[2,1-*b*]pyran derivatives containing differently substituted dithiafulvenyl units are described. An example of electrochemical dimerization is shown which gives access to electroactive bichromophoric systems. Such systems could allow the study of the interplay of photochromic and electrochemical properties.

1. Introduction

Tetrathiafulvalene (TTF) and naphthopyrans have been widely investigated during the three last decades for the generation of superconductive charge-transfer salts[1] and photochromic materials,[2] respectively.

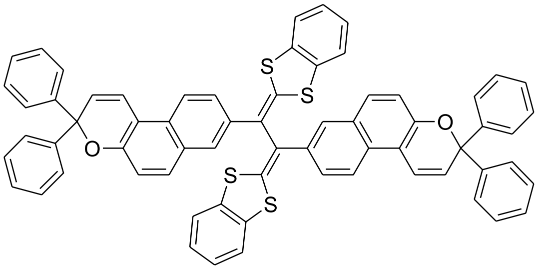
Naphthopyrans belong to an important class of organic photochromic compounds which exhibit reversible changes between colorless and colored isomers. The colored isomer is obtained by UV irradiation while the reverse reaction is thermally controlled. To obtain the bistability of the two different forms with the possibility of a binary on/off control of the interconversion, most of the investigations have focused on naphthopyrans bearing different pendant groups.[3]

In this context, we have designed a new molecule (**1c**) including naphthopyran and TTF vinylogue units, that possess both electrochromic and photochromic properties (Chart 1).

Indeed, the TTF vinylogue unit can be reversibly oxidized to the dication. Then, it was anticipated that such system could represent a new class of molecular switches in which a reversible redox change could alter the photochromic response of the naphthopyran unit (Scheme 1).

In this work, the synthesis and the characterizations of new organic photochromic compounds (**2a–d**) which combine 3,3-diphenylnaphthopyrans and substituted 1,4-dithiafulvenes units are presented (Chart 2).

The synthesis of **1c** by the electrochemical dimerization of **2c** was investigated and the preliminary photochromic results presented.



1c

Chart 1.

Keywords: Tetrathiafulvalene; Naphthopyran.

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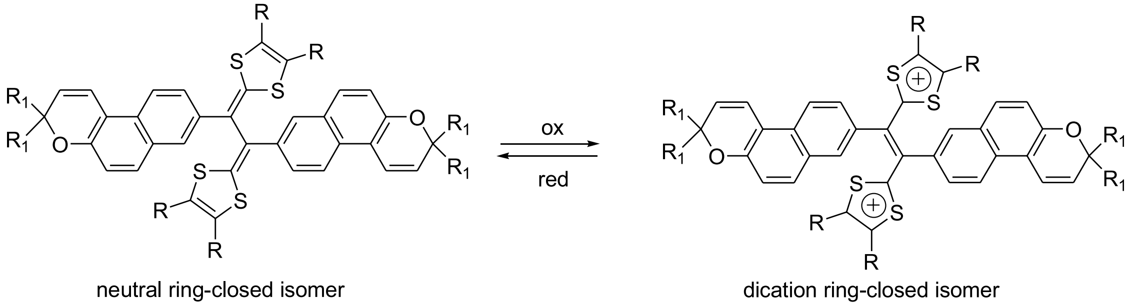


Scheme 1.

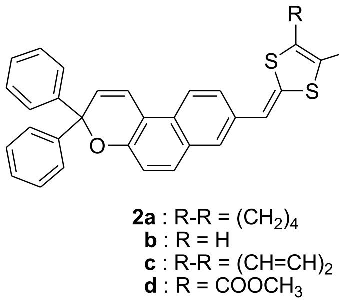


Chart 2.

2. Results and discussion

2.1. Synthesis of compounds 2a–d

The synthesis of compounds **2a–d** is depicted in Scheme 2.

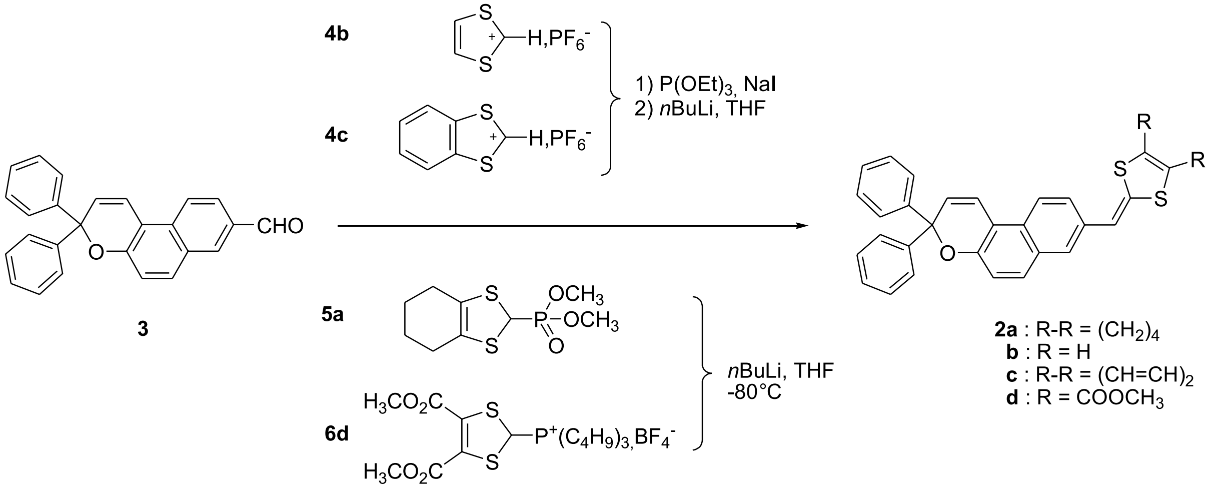
The target compounds **2a–d** were then obtained in 45–50% yield from the Wittig–Horner olefination of 3,3-diphenyl-8-formyl-[3*H*]-naphtho[2,1-*b*]pyran **3** prepared as described in the literature[4] using an appropriately substituted dithiolium salts **4b**,**c** or phosphonate anion **5a** or phosphonium salt **6d**.

2.2. Electrochemistry of compounds 2a–d and electrosynthesis of 1

Electrochemical studies of compounds **2a–d** were performed by cyclic voltammetry with a platinum disk electrode ($A=2\ \mathrm{mm}^2$) in a 10^{-3} M acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte and an Ag/AgCl reference electrode. The electrochemical data are collected in Table 1.

In all cases the cyclic voltammograms (CV) of compounds **2a–d** exhibit one irreversible oxidation wave (Fig. 1).

As expected the replacement of the electron-withdrawing methylcarboxylate group in **2d** by an electron-donating group, such as the cyclohexyl substituent, leads to a 0.34 V



Scheme 2.

Table 1. Electrochemical data for compounds **2a–d** vs Ag/AgCl at 25 °C. Ferrocene used as internal standard

Compound	R	E_{pa}/V	E_{pa}new/V	E_{pc}new/V
2a	$(CH_2)_4$	0.61	0.38	0.34
2b	H	0.68	0.44	0.39
2c	$(CH{=}CH)_2$	0.82	0.64	0.60
2d	$COOCH_3$	0.95	0.80	0.71

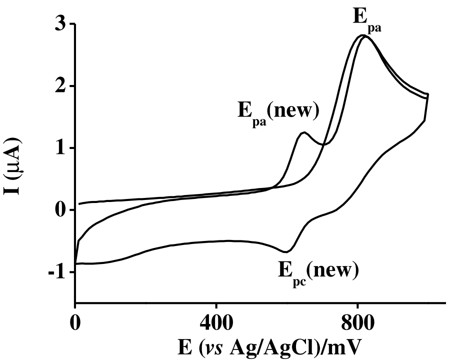


Figure 1. Cyclic voltammogram of **2c** in $CH_3CN/n\text{-}Bu_4NPF_6$ 0.1 M at a scan rate of 100 mV s^{-1}.

negative shift of E_{pa}. In all cases the appearance of a new reversible redox system at lower potentials, is observed after the first scan (Fig. 1). Previous works on phenyl substituted 1,4-dithiafulvenes which can be reversibility oxidized in cation radical have shown that these compounds lead to the formation of tetrathiafulvalene vinylogues by electrochemical dimerization.[5]

By analogy the new redox system can be attributed to the dimer formation in the solution. In order to confirm this hypothesis the electrosynthesis of the dimer of **2c**, **1c**, was performed on a preparative scale using a reticulated vitreous carbon working electrode and 2 mol of electron per mol of substrate as described in the literature. After reduction the target dimer was purified classically by chromatography on silica gel column. The CV of **1c** was recorded under the same experimental conditions as those used for compound **2c** and displayed a reversible two-electron oxidation wave with an anodic peak at 0.63 V and the corresponding cathodic wave at 0.60 V (Fig. 2) in good accordance with the electrochemical response observed for TTF vinylogue substituted derivatives on the vinylogue bonds by phenyl groups.

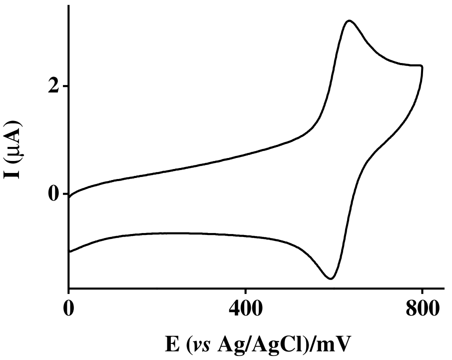


Figure 2. Cyclic voltammogram of **1c** in $CH_3CN/n\text{-}Bu_4NPF_6$ 0.1 M at a scan rate of 100 mV s^{-1}.

2.3. Optical properties

Upon UV irradiation, the compounds **2a–d** were shown to undergo a thermally reversible color change due to an electrocyclic rearrangement of the pyrane moiety. The photochromic behaviour of these new TTF naphthopyrans have been evaluated under continuous irradiation with a xenon lamp at room temperature using toluene as solvent (Fig. 3).

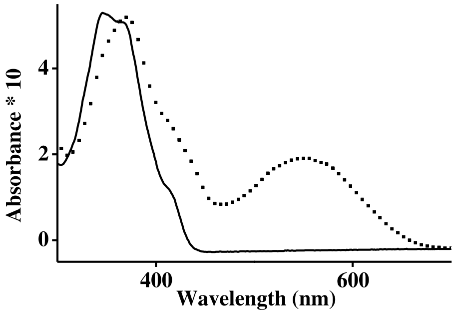


Figure 3. Electronic absorption spectra of the closed (solid line) and opened (dotted line) forms of compound **2c** (toluene, $c=10^{-3}$ mol L^{-1}, 20 °C).

Spectrokinetic data are summarized in Table 2 and compared with those obtained with the unsubstituted naphthopyran taken as a reference. Three parameters were considered in order to characterize the colored form: the maximum wavelength of absorption; the thermal decoloration rate (k_Δ) and the colorability ($A\infty$), e.g. the absorbance measured under steady-state irradiation.

When compared to the unsubstituted naphthopyran the absorption maxima wavelength of the closed form (λ_{max}CF) shift bathochromically in the case of **2a** and hypsochromically for **2b–d** in accordance with the electro-donating and the electron-withdrawing groups. This behaviour is again more pronounced in the opened form. Thus, the absorption maxima wavelength of the colored opened forms (λ_{max}OF) of **2a–c** undergo important bathochromic shifts, from 92 to 117 nm when compared to the unsubstituted naphthopyran. These results reveal that the effect of substituted 1,4-dithiafulvenes groups on the naphthopyran core is more important in the opened forms. Moreover, compounds **2a–c** display the same colorability $A\infty$ as that of the unsubstituted chromene and present a faster thermal decoloration. The thermal decoloration rate for **2a–c** increase from 0.038 to 0.051 s^{-1} in accordance with the electron-withdrawing effect of the substituent grafting on the 1,4-dithiafulvenes moiety. On other hand compound **2d** was observed not to display any photochromic properties under our conditions due to the very strong electron-withdrawing effect of the ester groups.

The dimer compound, **1c**, was observed to display a weak photochromic behaviour (Fig. 4).

Very little absorbance was observed for the opened form of compound **1c** which indicate a quasi disappearance of the photochromic properties due to a very stable closed form or a faster thermally reverse reaction. On the basis of the literature the neutral compound **1c** is probably non planar.[5] In this context the stability of the closed or/and opened forms could be altered by steric hindrances. Moreover, the absorption maximum wavelength of the closed and opened

Table 2. Photochromic parameters obtained under continuous irradiation in toluene solutions (150 W xenon lamp, 25 °C) for compounds **2a–d**

Compound	R	λ_{max}CF	λ_{max}OF	$A\infty$	K_{Δ} (s^{-1})
Naphthopyran	—	345	432	0.17	0.060
2a	$(CH_2)_4$	369	549	0.17	0.038
2b	H	342	532	0.17	0.042
2c	$(CH{=}CH)_2$	336	524	0.17	0.051
2d	$COOCH_3$	327	—	—	—

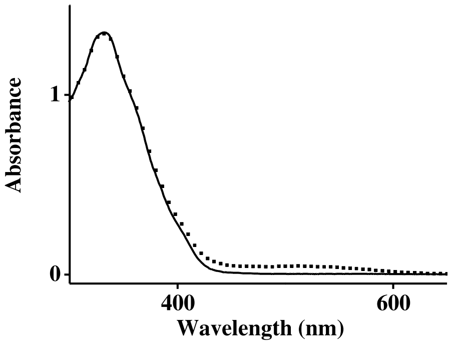


Figure 4. Electronic absorption spectra of the closed (solid line) and opened (dotted line) forms of compound **1c** (tetrahydrofurane, $c = 10^{-5}$ mol L^{-1}, 20 °C).

forms were recorded at 333 and about 511 nm, respectively, corresponding to hypsochromic shifts relative to the naphthopyran precursor **2c**. More detailed investigations are currently underway especially to determine the influence of the TTF vinylogue moiety redox state on the photochromic properties of **1c**.

3. Conclusion

The synthesis of new substituted 3,3-diphenyl-8-(1,4-dithiafulven-6-yl)-[3*H*]-naphtho[2,1-*b*]pyrans has been performed. These compounds display interesting photochromic properties. The spectroscopic data show that the shift of the absorption maximum and the thermal decoloration rate correlate with the electro-donating or electron-withdrawing effect of the substituent groups. Future work is directed of the improvement of the photochromic properties of naphthopyran derivatives incorporating a TTF vinylogue unit and the investigation of synergistical coupling between optical and electrochemical properties.

4. Experimental

4.1. General

Materials. Cyclohexane, methylenechloride, diethylether, tetrahydrofurane (THF), chloroform, hexane, ethylacetate were purchased from CarloErba. Anhydrous acetonitrile (analytical grade) was purchased from CarloErba and used as received. Tetrabutylammonium hexafluorophosphate was purchased from Fluka. Silica gel (240–400 mesh) from Merck. Triethylphosphite, butyllithium in hexane, were purchased from Sigma-Aldrich.

Instrumentation. Melting points are uncorrected and were obtained from an Electrothermal 9100 apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC 250 at, respectively, 250 MHz and 62.5 MHz. UV spectra were obtained on Varian Cary 50. FAB mass spectra were obtained with a JEOL FX 102 Mass spectrometer (Laboratoire de Mesures Physiques, USTL, Montpellier, France). The bulk electrolysis and the cyclic voltammetry (CV) were performed with computer-based Bioanalytical instrument (BAS 100) electrochemical workstation. The bulk electrolysis was made in a divided cell with reticulated vitreous carbon working electrode, platinium counter electrode and reference electrode, Ag/AgCl. The CV data were acquired using a with 1.6 mm diameter platinium working electrode; platinium counter electrode; reference electrode, Ag/AgCl.

For compounds **2a–d** the photochromic measurements were performed in toluene solutions of spectrometric grade at 20 °C (0.2°), at a concentration of 5×10^{-3} mol L^{-1}. For compound **1c** the photochromic measurements were performed in tetrahydrofurane solution of spectrometric grade at 20 °C (0.2°), at a concentration of 5×10^{-5} mol L^{-1}. The irradiation flux in each case was 4 W m^{-2}. The analysis cell (optical pathlength 10 mm) was placed in a thermostated copper block inside the sample chamber of a Varian Cary 50 spectrometer. An Oriel 150 W high pressure Xe lamp was used for irradiation.

4.1.1. 8-(4,5-Cyclohexeno-1,3-benzodithiol-2-ylidene)-3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrane 2a. Into a flask of 50 mL, 181 mg (0.68 mmol) of phosphonate **5a** prepared as describe in literature,[6] and 7 mL of anhydrous THF were cooling to −78 °C under argon. 0.27 mL (0.68 mmol) of *n*BuLi (solution 2.5 M in hexane) are added drop by drop and 120 mg (0.45 mmol) of chromene carbaldehyde **3** was added. The mixture is let return at ambient temperature. Water was added and the mixture is extracted with methylene chloride. The combined organic phases were washed with water, dried ($MgSO_4$), and evaporated in vacuo. The crude product was purified on a silica gel column and eluting with ethyl acetate–cyclohexane mixture (5/95). The desired fractions were pooled and concentrated to afford 0.10 g (44%) of pale yellow solid: Mp 192–194 °C; ^{1}H NMR (400 MHz, pyridine-d_5) δ: 1.74–1.82 (m, 4H); 2.22–2.32 (m, 4H); 6.24 (d, $J=9.9$ Hz, 1H); 6.54 (s, 1H); 7.16 (d, $J=8.8$ Hz, 1H); 7.20–7.33 (m, 7H); 7.36 (dd, $J=1.7$, 8.9 Hz, 1H); 7.44–7.50 (m, 4H); 7.55 (br s, 1H); 7.62 (d, $J=8.8$ Hz, 1H); 7.86 (d, $J=8.9$ Hz, 1H). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 82.64 (C); 22.63 ($-CH_2-$); 22.67 ($-CH_2-$); 25.06 ($-CH_2-$); 25.68 ($-CH_2-$); 112.08 ($-CH{=}$); 114.09 (C); 118.67 ($-CH{=}$); 119.63 ($-CH{=}$); 121.44 ($-CH{=}$); 123.98 (C); 124.30 (C); 125.08 ($-CH{=}$);

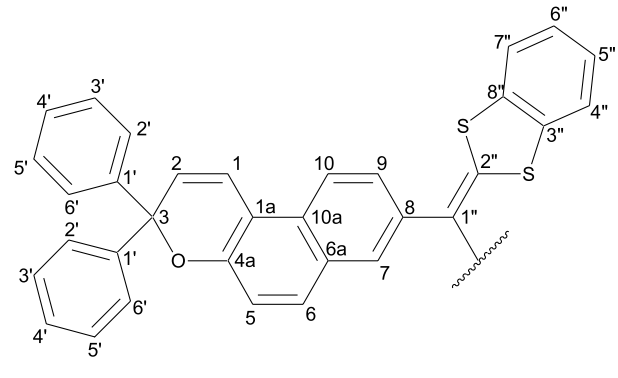
126.85 (–CH=); 127.11 (4×–CH=); 127.60 (2×–CH=); 127.87 (–CH=); 128.18 (4×–CH= and C); 129.63 (C); 129.85 (–CH=); 132.72 (C); 134.32 (C); 144.97 (2×C); 150.40 (C). IR (KBr) 3059, 3019, 2935, 2925, 2857, 1634, 1587, 1579, 1543, 1492, 1469, 1447, 1372, 1246, 1210, 1094, 1083, 1010, 954, 857, 837, 806, 764, 729, 701, 636, 606. MS (EI) 502 (M^+, 5), 307 (30); HRMS for $C_{33}H_{26}OS_2$ calcd 502.1425, found 502.1432.

4.1.2. 8-(Bis(1,3-dithiol-2-ylidene)-3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrane 2b. In a round-bottomed flask equipped with a dropping funnel and argon inlet were introduced dithiolium salt **4b**[7] (0.20 g, 0.8 mmol), triethyl phosphite (0.14 mL, 0.8 mmol) and NaI (0.12 g, 0.8 mmol) in 4 mL of acetonitrile. After 2 h stirring at room temp., evaporation of the solvent and excess of triethyl phosphite left the phosphonate as an oil. Dry THF (4 mL) and chromene carbaldehyde **3** (0.29 g, 0.8 mmol) were then added and the mixture cooled to 0 °C. *n*-Butyllithium (0.5 mL, 0.8 mmol) (1.6 M in hexanes) was added dropwise, and the mixture stirred for 2 h at room temp. Upon addition of methanol a red precipitate and was formed which is filtered, washed with methanol–diethyl ether and dried. Yield 0.19 g (54%): Mp ^{1}H NMR (400 MHz, pyridine-d_5) δ: 6.26 (dd, J=1.2, 6.7 Hz, 1H); 6.35 (d, J=6.7 Hz, 1H); 6.63 (br s, 1H); 7.18 (d, J=8.8 Hz, 1H); 7.22–7.34 (m, 6H); 7.26 (superimposed d, J=9.9 Hz, 1H); 7.37 (dd, J=1.8, 8.8 Hz, 1H); 7.44–7.50 (m, 4H); 7.57 (d, J=1.8 Hz, 1H); 7.63 (d, J=8.8 Hz, 1H); 7.89 (d, J=8.8 Hz, 1H). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 82.65 (C); 112.73 (–CH=); 114.09 (C); 117.42 (–CH=); 117.50 (–CH=); 118.76 (–CH=); 119.56 (–CH=); 121.54 (–CH=); 124.99 (–CH=); 126.61 (–CH=); 127.09 (4×–CH=); 127.61 (2×–CH=); 127.78 (C); 127.92 (–CH=); 128.18 (4×–CH=); 129.54 (C); 129.85 (–CH=); 132.46 (C); 136.01 (–C=); 144.92 (2×C); 150 50 (C). IR (neat) 3062, 3027, 1688, 1633, 1600, 1566, 1508, 1493, 1447, 1264, 1245, 1222, 1160, 1092, 1007, 879, 809, 762, 737, 700, 646.

4.1.3. 8-(1,3-benzodithiol-2-ylidene)-3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrane 2c. Into a flask of 50 mL, 302 mg (1 mmol) of 4,5,6,7-tetrahydro-benzo[1,3]dithiol-1-ylium hexafluorophosphate **4c**[8] 0.171 mg (1 mmol) of triethyl-phosphite, 149 mg (1 mmol) of sodium iodide and 3 mL of acetonitrile are successively introduced. The reaction carried out under inert argon. After 2 h of agitation at ambient temperature the solvent were remove under vaccuo. The resulting oil is taken again with 3 mL of anhydrous THF and the reactional mixture is brought to 0 °C under argon. 362 mg (1 mmol) of carboxaldehyde chromene **3** and 0.625 mL (1 mmol) of *n*BuLi (solution 1.6 M in hexane) are added drop by drop without the temperature exceeding 5 °C. The mixture is let return at ambient temperature. The reaction is controlled by CCM with a pentane/diethylic mixture (50:50). The addition of methanol leads to the precipitation of the compound **2c**. After filtration, 408 mg (0.441 mmol, 44%) of product are obtained in the form of a yellow powder: Mp 227–228 °C; ^{1}H NMR (400 MHz, pyridine-d_5) δ: 6.30 (d, J=9.9, 1H); 6.67 (s, 1H); 7.09–7.20 (m, 2H); 7.23 (d, J=8.8 Hz, 1H); 7.25–7.40 (m; 9H); 7.47 (br s, J=8.7 Hz, 1H); 7.52 (d, J=7.6 Hz, 4H); 7.68 (br s, 1H); 7.69 (d, J=8.8 Hz, 1H); 7.95 (d, J=8.7 Hz, 1H). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 82.70 (C); 114.08 (C); 114, 65 (–CH=); 118.84 (–CH=); 119.49 (–CH=); 121.01 (–CH=); 121.61 (–CH=); 121.78 (–CH=); 125.66 (–CH=); 125.95 (–CH=); 126.02 (–CH=); 126.69 (–CH=); 127.08 (4×–CH=); 127.60 (2×–CH=); 127.95 (–CH=); 128.10 (C); 128.17 (4×–CH=); 129.47 (C); 129.93 (–CH=); 132.17 (2×C); 134.87 (C); 136.41 (C); 144.90 (2×C); 150.71 (C). UV (toluene) (log ε): 346 (4.33); 369 (4.30);415 (3.64). IR (KBr) 3059, 3032, 2925, 2852, 1632, 1587, 1572, 1556, 1510, 1491, 1460, 1448, 1381, 1245, 1221, 1091, 1009, 841, 809, 765, 753, 743, 734, 699, 614. MS (EI) 498 ($M^{\cdot +}$, 22), 421 (12), 347 (8); HRMS for $C_{33}H_{22}OS_2$ calcd 498.1112, found 498.1152.

4.1.4. 8-(4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene)-3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyrane 2d. Into a flask of 50 mL, 421 mg (0.8 mmol) of [4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-yl]tributyl-phosphonium tetrafluoroborate **6d**[9] are introduced in 5 mL of THF. The reactional mixture is brought to 0 °C under argon. 200 mg (0.55 mmol) of carboxaldehyde chromene **3** and 0.38 mL (0.61 mmol) of *n*BuLi (solution 1.6 M in hexane) are added drop by drop without the temperature exceeding 5 °C. The addition of methanol leads to the precipitation of the compound **2d**. After filtration, 204 mg (66%) of product are obtained in the form of a orange solid: Mp 196–197 °C; ^{1}H NMR (400 MHz, pyridine-d_5) δ: 3.87 (s, 3H); 3.89 (s, 3H); 6.31 (d, J=9.9 Hz, 1H); 6.56 (br s, 1H); 7.23 (d, J=8.8 Hz, 1H); 7.25–7.40 (m, 8H); 7.51 (d, J=7.5 Hz, 4H); 7.53 (br s, 1H); 7.67 (d, J=8.9 Hz, 1H); 7.93 (d, J=8.8 Hz, 1H). ^{13}C NMR (100 MHz, pyridine-d_5) δ: 53.30 (CH_3–); 53.46 (CH_3–); 82.76 (C); 114.09 (C); 115.68 (–CH=); 119.01 (–CH=); 119.37 (–CH=); 121.81 (–CH=); 125.95 (–CH=); 126.31 (–CH=); 127.06 (4×–CH=); 127.64 (2×–CH=); 128.06 (–CH=); 128.18 (4×–CH=); 128.31 (C); 129.32 (2×C); 129.68 (C); 129.97 (–CH=); 131.30 (C); 131.49 (C); 144.75 (2×C); 150.94 (C); 159.91 (OC=O); 160.35 (OC=O). IR (KBr) 3060, 3028, 2949, 2928, 1741, 1732, 1701, 1631, 1584, 1553, 1491, 1470, 1448, 1431, 1376, 1247, 1093, 1086, 1054, 1010, 868, 836, 807, 769, 756, 738, 700, 637. HRMS for $C_{33}H_{26}OS_2$ calcd 564.1065, found 564.1057.

4.1.5. 3,3-diphenyl-8-8-[Benzo[1,3]dithiol-2-ylidene-methyl]-[3*H*]-naphto-[2,1-*b*]pyrane 1c. 68.3 mg (0.14 mmol) of **2c** was dissolved in 75 mL of acetonitrile containing 19.35 g (50 mmol) of tetrabutylammonium hexafluorophosphate The solution is then oxidized under controlled potential (0.80 V vs Ag/AgCl). The colored solution is reduced at −0.2 V vs Ag/AgCl without any treatment (1 mol of electron per mol of substrate). The solvent was removed under reduce pressure and diethyl-ether was added to the residue. Tetrabutylammonium hexafluorophosphate precipitated and was filtered off. The solvent was evaporated in vacuo and the crude product was purified on a silica gel column and eluting with methylene chloride–cyclohexane mixture (1/1). Concentration under reduced pressure affords 57 mg (0.06 mmol, 83%) of yellow powder corresponding to title compound: Mp 304–305 °C.



^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.23 (d, $J=9.9$ Hz, 2H, H_2), 7.05 (m, 2H, $H_{6''}$), 7.08 (m, 2H, $H_{5''}$), 7.15 (d, $J=8.9$ Hz, 2H, H_5), 7.16 (m, 2H, $H_{4''}$), 7.21 (m, 2H, $H_{7''}$), 7.23 (d, $J=9.9$ Hz, 2H, H_1), 7.23 (m, 4H, $H_{4'}$), 7.30 (m, 8H, $H_{3'}$, $H_{5'}$), 7.46 (m, 8H, $H_{2'}$, $H_{6'}$), 7.61 (d, $J=8.9$ Hz, 2H, H_6), 7.63 (dd, $J=8.9$;1.8 Hz, 2H, H_9), 7.86 (d, $J=9.0$ Hz, 2H, H_{10}), 7.91 (d, $J=1.6$ Hz, 2H, H_7), ^{13}C NMR (270 MHz, $CDCl_3$) δ: 82.65 (C_3), 114.16 (C_{1a}), 118.70 (C_5), 119.60 (C_1), 121.39 ($C_{4''}$), 121.63 ($C_{7''}$), 121.87 (C_{10}), 125.50 ($C_{1''}$), 125.57 ($C_{5''}$), 125.75 ($C_{6''}$), 125.93 (C_9), 126.77 (C_7), 127.08 ($C_{2'}$), 127.60 ($C_{4'}$), 127.92 (C_2), 128.17 ($C_{3'}$), 128.79 (C_{10a}), 129.41 (C_{6a}), 130.12 (C_6), 133.35 (C_8), 136.33 ($C_{2''}$), 136.47 ($C_{3''}$), 136.56 ($C_{8''}$), 144.85 ($C_{1'}$), 150.88 (C_{4a}); UV–Vis (CH_2Cl_2) λ_{max} nm (log ε); MS (EI) 994 ($M^{\cdot+}$, 100), 55 (15), 22 (31); HRMS for $C_{66}H_{42}O_2S_4$ calcd 994.2068, found 994.2060.

References and notes

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