Photomodulable Materials. Synthesis and Properties of Photochromic 3*H*-Naphtho[2,1-*b*]pyrans Linked to Thiophene Units *via* an Acetylenic Junction

by **Michel Frigoli**, **Corinne Moustrou***, **André Samat**, and **Robert Guglielmetti**

LCMOM, ESA CNRS 6114, Université de la Méditerranée, Faculté des Sciences de Luminy, F-13288 Marseille
Cedex 9 (Fax: 33.4.91.82.93.01; e-mail: moustrou@luminy.univ-mrs.fr)

The synthesis of 3*H*-naphtho[2,1-*b*]pyrans linked to mono-, di-, or terthiophene *via* an acetylenic junction is described (*Schemes 2* and *3*). The synthetic approaches involve successive *Sonogashira* coupling reactions. The photochromic properties in solution of these novel materials were investigated under continuous irradiation.

Introduction. – The design and the development of molecular systems for which a given physical property may be controlled or modified by external stimulation is presently a major focus of research in organic chemistry, due to their potential applications in electro-optic devices. Photochromic compounds that reversibly change their physical and chemical properties upon light irradiation [1] can be used to achieve this goal. Until now, a great number of photochromic molecular systems or devices have been proposed, involving various photochromic families such as spiropyrans [2], spirooxazines [3], azobenzenes [4], fulgides [5], and diarylethenes [6].

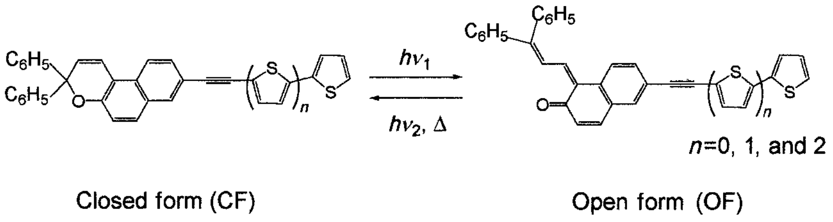
In the context, in previous publications, we described the synthesis of spiropyrans, spirooxazines [7], and chromenes [8] containing a thiophene moiety. The introduction of this heterocycle allows subsequent elaboration of polythiophene with photomodulable optoelectronic properties by electrochemical polymerization [9]. However, the applications of polythiophene are limited due to its poor solubility, processability, and mechanical properties [10]. Moreover, the regulation of the chain lengths during the polymerization and the structural characterization of the polymer are difficult [11].

Recently, it was discovered that the oligomer materials containing up to six thiophene units inherently possess the basic or much improved electronic, optical, and electrochemical properties of polythiophenes while maintaining excellent processability [12].

In this paper, we report the synthesis of 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans linked to a thiophene oligomer. The diphenyl-substituted naphthopyran skeleton is considered a good basis for building new molecules due to its quite satisfying photochromic behavior [13].

The photochromic properties of such 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyrans are based on a reversible color change observed upon UV irradiation [1]. The initial colorless or closed form (CF) absorbs UV light and gives different stereoisomers of the opened colored form (OF), for which we represent the most stable one (*Scheme 1*). The reaction is thermally or photochemically (VIS light) reversible. The two isomers differ not only in the absorption spectra but also regarding dipole-moment, dielectric constant, oxidation/reduction potential, and geometric structure. The rapid modification of physical properties of these materials upon photoirradiation are promising for their use in various electro-optic devices such as photo-optical switches. The thiophene units were linked to the photochromic entity through an acetylenic junction insuring the rigidity of the system and the extension of the π-system. The position 8 of the naphthopyran was chosen for the linkage to have the best orbital overlap between the two entities.

Scheme 1



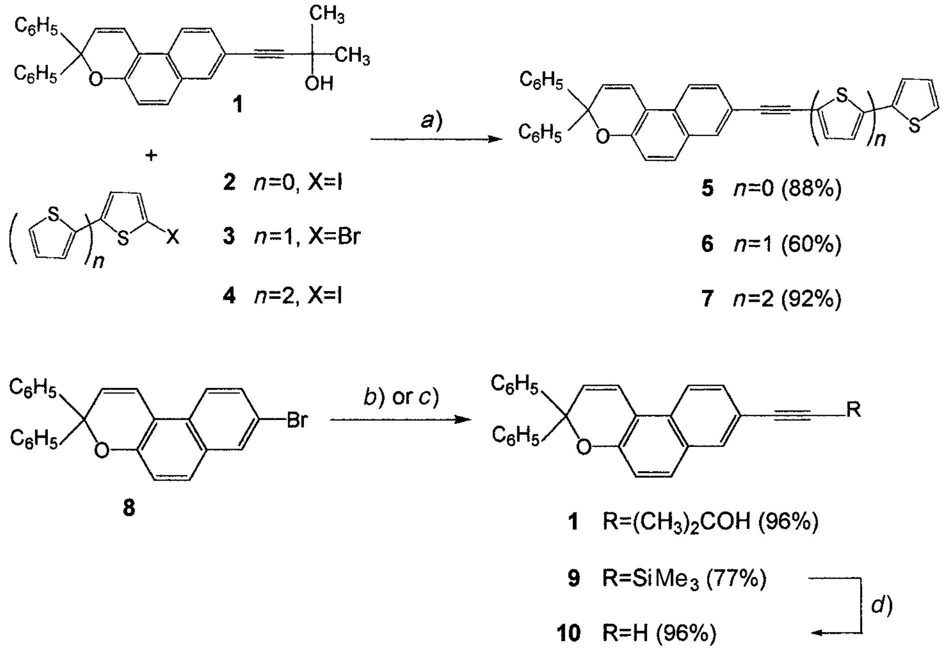
Results and Discussion. – *Synthesis.* Among the various methods for introducing alkynyl groups at aromatic nuclei, the most powerful and useful is the Pd-catalyzed cross-coupling reaction of halogenoarenes with terminal alkynes, which was reported for the first time by *Sonogashira-Hagihara* [14] and *Cassar* [15] in 1975. Usually, this cross-coupling reaction proceeds in the presence of catalytic amounts of Pd-complexes such as $[Pd(PPh_3)_4]$ or $[PdCl_2(PPh_3)_2]$ and a catalytic amount of copper(I) iodide, in an amine as solvent. A variation of this synthetic procedure involves the use of protecting groups [16]. Coupling of halogenoarenes with the commercially available ethynyl trimethylsilane or with 2-methylbut-3-yn-2-ol provides (2-arylethynyl)trimethylsilane [17] and 3-arylalkynol [18] respectively. These compounds generate a terminal arylacetylene moiety by removal of the protecting group, which can be involved in an other *Sonogashira* coupling to afford diarylalkynes [19]. Recently, many extensive applications of this coupling methodology have been reported for the preparation of functionalized compounds and polymers towards development of a new generation of materials [20].

Herein, we report, on the one hand, the synthesis of (thiophenylethynyl)chromenes **5**–**7** (*Scheme 2*), which were obtained by successive *Sonogashira* coupling reactions; on the other hand, this approach was extended to the preparation of bichromophoric compounds.

The synthesis of **1**, precursor of chromenes **5**–**7**, required the preliminary preparation of 8-bromo-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**8**) (*Scheme 2*). This latter was obtained in 80% yield by condensing 1,1-diphenylpropyn-1-ol with 6-bromonaphthalen-2-ol in CH_2Cl_2 under acid catalysis (TsOH) [21] at room temperature for 3 days.

It is well-known that this 'one-pot' procedure for the synthesis of photochromic compounds proceeds *via* a *Claisen* rearrangement of alkynyl aryl ethers resulting from naphthalenol '*O*-alkylation', followed by an H-shift and electrocyclic ring closure [22]. In the presence of a catalytic amount of $[PdCl_2(PPh_3)_2]$ and CuI, the classic

Scheme 2



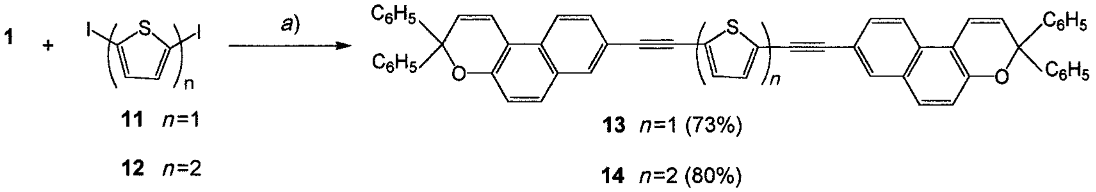
a) [Pd(PPh$_3$)$_4$, CuI, benzene, aq. 5.5N NaOH, PhCH$_2$NEt$_3$$^+Cl^-$. *b*) [PdCl$_2$(PPh$_3$)$_2$], CuI, Et$_2$NH, r.t., CH≡CC(CH$_3$)$_2$OH. *c*) [PdCl$_2$(PPh$_3$)$_2$, CuI, Et$_3$N, r.t., CH≡CSiMe$_3$. *d*) KOH, MeOH/CH$_2Cl_2$.

Sonogashira reaction of **8** with the commercially available 2-methylbut-3-yn-2-ol [18] in Et$_2$NH (room temperature, 16 h) afforded **1** in nearly quantitative yield (*Scheme 2*). To establish a correlation between the structure and the spectrokinetic properties, compound **10** was also prepared. Our attempts to deprotect **1** by modifying the reaction temperature and solvent (toluene, CH$_2$Cl$_2$) were unsuccessful, probably due to the decomposition of the desired product. Another alternative preparation of **10** *via* **9** was finally chosen. A *Sonogashira* coupling of **8** with excess ethynyltrimethylsilane [17] in Et$_3$N at 70° for 24 h gave the coupled alkyne **9** in 77% yield. Deprotection of the trimethylsilyl group was accomplished under mild conditions by treatment of **9** with KOH in MeOH/CH$_2$Cl$_2$ to afford **10** in 96% yield.

A modified version of the *Sonogashira* coupling, carried out under phase-transfer conditions [23], allowed the synthesis of compounds **5**–**7** (*Scheme 2*). Reaction of **1** with the appropriate halogenothiophene **2**–**4** at 70° for 24–72 h, in the presence of benzyltriethylammonium chloride as phase-transfer agent, aqueous 5.5N NaOH as base, benzene as solvent, and a mixture of [Pd(PPh$_3$)$_4$] and CuI as catalysts, gave **5**, **6**, and **7** in 88, 60 and 92% yield, respectively. It is noteworthy that the mechanism of the condensation in the basic aqueous medium in which it was carried out is most likely the '*retro*' version of the '*Favorskii-Babayau* carboxy-ethynylation', generating **10** *in situ*. The latter then reacted with the halogenothiophene to afford the desired product.

The modified version of the *Sonogashira* coupling allowed also the preparation of bichromophoric systems such as **13** and **14** from a dihalogenothiophene (*Scheme 3*).

Scheme 3



a) [Pd(PPh_3)$_4$], CuI, benzene, aq. 5.5N NaOH, $PhCH_2NEt_3^+Cl^-$.

Thus, **13** and **14** were prepared in 73 and 80% yield, respectively, from 2,5-diodothiophene (**11**) and 5,5′-diodo-2,2′-bithiophene (**12**) and 2.1 equiv. of **1** (70°, 48–72 h).

Photochromic Properties. The photochromic behavior of the new naphthopyrans **5**–**7** or bisnaphthopyrans **13** and **14** was evaluated under continuous UV irradiation (for conditions, see *Exper. Part*). The data are summarized in the *Table* and compared to those obtained with the unsubstituted parent compound, the 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran (**CHR**), and with naphthopyrans **1**, **9**, and **10**, used as intermediates during the synthesis and bearing an ethynyl substituent at the 8-position.

Table. *Fading Rates* (k_Δ), *Absorption Wavelengths* (λ_{max}), *and 'Colorability'* (absorbance at the photostationary state; A_∞) *of Naphtho[2,1-*b*]pyrans, Measured under Continuous Irradiation in Toluene at 20°* ($2.5 \cdot 10^{-5}$M)

	CHR	**1**	**9**	**10**	**5**	**6**	**7**	**13**	**14**
λ_{max}[nm]	432	457	454	454	471	485	[b])	474	[b])
A_∞	0.21	0.10	0.11	0.10	0.23	0.29		0.20	
k_Δ[s^{-1}]	0.06	0.11	0.13	0.13	0.15	0.14		0.14	
(Amplitude%)[a])	(73)	(94)	(94)	(95)	(90)	(89)		(91)	

[a]) The second rate constant, corresponding to the kinetics of lower amplitude (5–27%), is *ca.* 10^{-3} to 10^{-4} s^{-1}.
[b]) No photochromic properties.

Three main parameters were considered for the characterization of the colored form: the absorption wavelength in the VIS range (λ_{max}), the thermal fading rate (k_Δ), and the coloration ability (or 'colorability') measured as the absorbance (A_∞) at λ_{max} when the photostationary state is reached. In a first approximation, at low concentration, A_∞ is proportional to both the quantum yield of photocoloration and the molar absorptivity of the colored form, but inversely proportional to the fading-rate constant [24]. Examples of the variation of the absorbance at λ_{max} during irradiation experiments are given in *Figs. 1* and *2* for a toluene solution of **6**.

Among the new compounds, **7** and **14** do not show photochromic properties. It seems that a too-large extension of the π-system inhibits the photoreactivity of the naphthopyran unit (C–O bond breaking) and favors the luminescence (fluorescence is qualitatively observed). Experiments are in progress to confirm this assumption.

From a general point of view, two phases of the fading-rate kinetics are observed, which probably correspond to different isomers of the open form. Taking into account the results of a recent NMR study performed on the 3,3-bis(4-fluorophenyl)-3*H*-

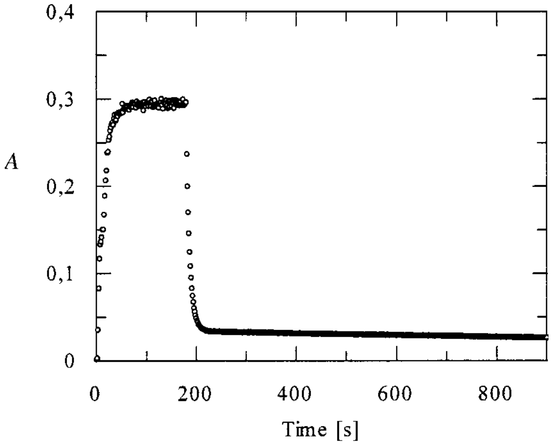


Fig. 1. *Variation of the absorbance at* λ_{max} *of a toluene solution* ($2.5 \cdot 10^{-5}$ M) *of* **6** *under irradiation by the Xe lamp* (180 s) *or without irradiation* (20°)

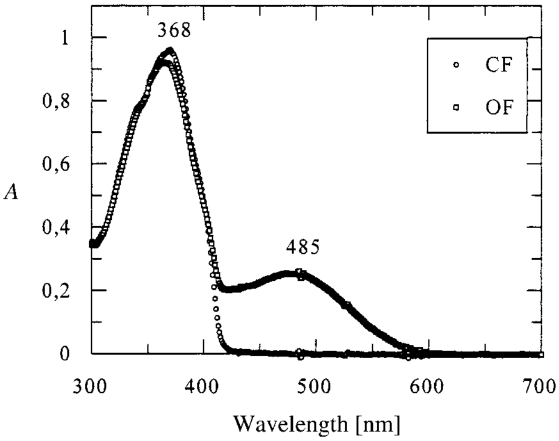
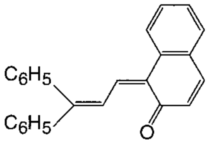
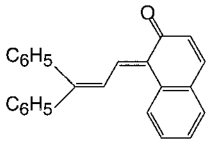


Fig. 2. *UV/VIS Absorption spectra of a toluene solution* ($2.5 \cdot 10^{-5}$ M) of **6** *without irradiation* (○) *and at the photostationary state under continuous irradiation* (□) (Xe lamp, 20°)



A ***trans,cis***



B ***trans,trans***

naphtho[2,1-*b*]pyran [25], these isomers could differ only in the configuration at the C=C bond attached to the naphthalene ring (see **A** and **B**).

The higher rate constant (from 0.06 s^{-1} for the reference compound **CHR**, to 0.15 s^{-1} for **5**) is related to the kinetics of higher amplitude (73–95%). The presence of an ethynyl group at the 8-position increases by about two times the fading rate, independently of the substitution of the ethyne moiety. Regarding the electronic absorption of the colored form, the introduction of the ethynyl group (**1**, **9**, and **10**) induces a bathochromic shift of +22 to +25 nm due to the extension of the π-system. This shift is *ca.* +40 nm (see **5** and **13**) when one thiophene unit is linked to the ethyne moiety, and +53 nm with a bithiophene (see **6**). In parallel, there is an increase of the colorability on adding one (see **5** and **13**) or two thiophene rings (see **6**), A_∞ being three times higher in this last case (compare **6** *vs.* **10**). One can suppose that this enhancement of the colorability is mainly due to an increase of the molar absorptivity of the colored forms, thiophene rings being strong chromophoric groups. On the other hand, the colorability of compounds incorporating thiophene units (**5**, **6**, and **13**) is of the same order of magnitude as that of the parent compound **CHR** despite a faster fading rate. The decrease of the absorbance at the photostationary state, normally expected with an increase of the rate, is balanced for these compounds by the high molar absorptivity of the colored forms.

Conclusion. – A series of new photochromic 8-ethynyl-3*H*-naphtho[2,1-*b*]pyrans and [3*H*]-naphtho[2,1-*b*]pyrans linked to thiophene units by an acetylenic spacer was prepared under mild conditions by the *Sonogashira-Hagihara* coupling reaction from the 8-bromo-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran as starting material (**8**). The initial aim of developing such structures was focused on the photomodulation of the semiconducting properties of oligothiophenes linked to the photochromic chromene moiety. Nevertheless, the interesting spectrokinetic behavior of the photochromic compounds prepared, compared to the 8-unsubstituted reference compound 3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran, constitutes an attractive property indicating their potential as classical variable optical transmission materials [26].

Experimental Part

General. Et_3N, Et_2NH, DMF, $CHCl_3$, and benzene were purchased from *Aldrich*. The reactions were conducted in oven-dried (120°) glassware under Ar. All solvents for Pd-catalyzed coupling reactions were degassed and saturated with Ar before use. The commercially available $[PdCl_2(PPh_3)_2]$ and $[Pd(PPh_3)_4]$ (*Aldrich* and *Strem*, resp.) were used as received. The following compounds were prepared according to literature procedures: 2,2′-bithiophene [27], 2,2′:5′,2″-terthiophene [28], 5-bromo-2,2′-bithiophene [29], 5,5′-diodo-2,2′-bithiophene [30] and 5-iodo-2,2′:5′,2″-terthiophene [31]. Column chromatography (CC): silica gel *60* (*Merck 7734*). M.p.: in capillary tubes; *Büchi-510* apparatus, uncorrected. *Fourier*-transform IR spectra: *Matson-Polaris* spectrophotometer; KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AC 250* (250 MHz) or *AMX 400* (400 MHz); δ in ppm, referenced internally to the residual proton resonance of $CDCl_3$ (=7.24 ppm) or to $SiMe_4$ (=0.00 ppm) for ^1H and to $CDCl_3$ (=77.0 ppm for centerline) for ^{13}C; coupling constants *J* in Hz). FAB-MS: positive mode; in *m/z*.

Photochromic Measurements. These were performed in toluene solns. of spectrometric grade (*UCB*) at 20° (±0.2°). The analysis cell (optical path length, 10 mm) was placed in a thermostated copper block inside the sample chamber of a *Beckman-DU-7500*-diode-array spectrophotometer. Solns. were stirred continuously during experiments. An *Oriel-150-W*-high-pressure Xe lamp equipped with a diaphragm and aq. soln. (IR filter) was used for irradiation.

*8-Bromo-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran* (**8**). Under Ar, a soln. of 3 g (14.4 mmol) of 1,1-diphenylprop-2-yn-1-ol, 3.53 g (1.58 mmol) of 6-bromonaphthalen-2-ol and cat. TsOH in dry CH_2Cl_2 (30 ml) was stirred at r.t. for 3 days (TLC monitoring (pentane/Et_2O 4 : 1): no alkynol left). The mixture was evaporated and the crude product purified by CC (silica gel, pentane/Et_2O 100 : 0 → 70 : 30): 4.76 g (80%) of **8**. White solid. M.p. 149.5° ([32]: 148°). IR: 3433, 3084, 3055, 3024, 1634, 1582, 1499, 1446, 1244, 1213, 1092, 1000, 878, 809, 771, 763, 752, 733, 700. ^{1}H-NMR (250 MHz): 6.19 (*d*, $J = 10.0$, 1 H); 7.05 – 7.50 (*m*, 14 H); 7.71 (*d*, $J = 9.1$, 1 H); 7.75 (*d*, $J = 2.0$, 1 H). ^{13}C-NMR (62.5 MHz): 82.88 (C); 114.29 (C); 117.46 (C); 119.24 (CH); 119.59 (CH, C); 123.32 (CH); 127.15 (4 CH); 127.81 (2 CH); 128.32 (4 CH); 128.42 (CH); 129.01 (CH); 129.92 (CH); 130.52 (CH); 130.63 (CH); 144.79 (2 C); 150.91 (C). Anal. calc. for $C_{25}H_{17}BrO$ (413.306): C 72.64, H 4.14; found: C 72.60, H 4.13.

*8-(3-Hydroxy-3-methylbut-1-ynyl)-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran* (**1**). $[PdCl_2(PPh_3)_2]$ (0.203 g, 0.29 mmol) and CuI (30 mg, 0.145 mmol) were added successively to **8** (600 mg, 1.45 mmol) and 2-methylbut-3-yn-2-ol (366 mg, 4.35 mmol) in Et_2NH (15 ml) under Ar at r.t. After stirring for 16 h at r.t., Et_2NH was removed *in vacuo*, the residue diluted with benzene (30 ml), the soln. filtered through *Celite*, the latter washed carefully with benzene, the combined filtrate evaporated, and the residue purified by CC (silica gel, pentane/acetone 100 : 0 → 50 : 50): **1** (580 mg, 96%). Light yellow solid. Recrystallization from pentane/CH_2Cl_2 gave crystalline material. M.p. 75 – 76°. IR: 3700 – 3100, 3058, 3027, 2979, 2929, 2866, 2212, 1633, 1587, 1492, 1467, 1447, 1380, 1356, 1263, 1245, 1222, 1158, 1093, 1055, 1008, 943, 889, 822, 809, 759, 744, 732, 699. ^{1}H-NMR (250 MHz): 1.64 (*s*, 6 H); 2.09 (*s*, 1 H); 6.27 (*d*, $J = 10.0$, 1 H); 7.15 – 7.52 (*m*, 13 H); 7.59 (*d*, $J = 8.8$, 1 H); 7.80 (br. *s*, 1 H); 7.86 (*d*, $J = 8.8$, 1 H). ^{13}C-NMR (62.5 MHz): 31.66 (2 Me); 67.78 (C); 82.50 (C); 82.83 (C); 93.80 (C); 114.00 (C); 117.80 (C); 119.05 (C); 119.23 (CH); 121.50 (CH); 127.07 (4 CH); 127.71 (2 CH); 128.02 (CH); 128.24 (4 CH); 128.91 (C); 129.27 (C); 129.32 (CH); 129.77 (CH); 132.18 (CH); 144.80 (2 C); 151.31 (C). Anal. calc. for $C_{30}H_{24}O_2$ (416.510): C 86.50, H 5.81; found: C 86.40, H 5.76. FAB-MS: 416.18 (M^+).

*3,3-Diphenyl-8-[(trimethylsilyl)ethynyl]-3*H*-naphtho[2,1-*b*]pyran* (**9**). A mixture of **8** (1.5 g, 3.63 mmol), ethynyltrimethylsilane (713 mg, 7.26 mmol), $[PdCl_2(PPh_3)_2]$ (510 mg, 0.726 mmol), CuI (69 mg, 0.363 mmol), and anh. Et_3N (20 ml) was stirred at 70° for 24 h. The mixture was allowed to cool to r.t., and the Et_3N was evaporated. The residue was diluted with benzene (30 ml), the mixture filtered through *Celite*, the filtrate evaporated, and the residue purified by CC (silica gel, pentane/Et_2O 100 : 0 → 80 : 20): 1.20 g (77%) of **9**. White solid. Recrystallization from hexane/CH_2Cl_2 gave crystalline material. M.p. 177°. IR: 3062, 3030, 2957, 2897, 2151, 1633, 1580, 1491, 1466, 1447, 1382, 1249, 1224, 1181, 1091, 1008, 954, 947, 856, 841, 810, 760, 732, 703, 690. ^{1}H-NMR (250 MHz, (D_6)benzene): 0.24 (*s*, 9 H); 5.87 (*d*, $J = 10.0$, 1 H); 6.76 (*d*, $J = 10.0$, 1 H); 6.88 – 7.54 (*m*, 14 H); 7.73 (br. *s*, 1 H). ^{13}C-NMR (62.5 MHz): 0.01 (3 Me); 82.71 (2 C); 93.91 (C); 105.42 (C); 113.83 (C); 118.02 (C); 118.89 (CH); 119.06 (CH); 121.28 (CH); 126.92 (4 CH); 127.55 (2 CH); 127.83 (CH); 128.08 (4 CH); 128.70 (C); 129.31 (CH); 129.69 (CH); 132.54 (CH); 144.66 (2 C); 151.28 (C). FAB-MS: 430.12 (M^+). Anal. calc. for $C_{30}H_{26}OSi$ (430.612): C 83.67, H 6.09; found: C 83.79, H 6.11.

*8-Ethynyl-3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran* (**10**). To a soln. of **9** (839 mg, 1.95 mmol) in CH_2Cl_2 (15 ml), a soln. of KOH (327 mg, 5.85 mmol) in MeOH (10 ml) was added dropwise. The mixture was stirred for 3 h at r.t. After evaporation, the residue was diluted with Et_2O (30 ml), the soln. washed with H_2O (2 × 20 ml) and brine (2 × 20 ml), dried ($MgSO_4$), and evaporated, and the residue purified by CC (silica gel): **10** (670 mg, 96%). White solid. A sample of **10** was recrystallized from hexane/CH_2Cl_2. M.p. 143°. IR: 3278, 3058, 3040, 2151, 1631, 1580, 1490, 1464, 1446, 1379, 1242, 1217, 1092, 1007, 952, 887, 821, 805, 769, 755, 740, 713, 700, 615. ^{1}H-NMR (250 MHz, (D_6)benzene): 2.71 (*s*, 1 H); 5.85 (*d*, $J = 10.0$, 1 H); 6.74 (*d*, $J = 10.0$, 1 H); 6.80 – 7.50 (*m*, 14 H); 7.63 (*s*, 1 H). ^{13}C-NMR (62.5 MHz): 77.08 (CH); 82.84 (C); 84.04 (C); 114.01 (C); 117.08 (C); 119.13 (CH); 119.16 (CH); 121.55 (CH); 127.02 (4 CH); 127.67 (2 CH); 128.07 (CH); 128.19 (4 CH); 128.76 (C); 129.38 (CH); 129.53 (C); 129.78 (CH); 132.89 (CH); 144.71 (2 C); 151.48 (C). FAB-MS: 358.13 (M^+). Anal. calc. for $C_{27}H_{18}O$ (358.431): C 90.47, H 5.06; found: C 90.52, H 5.10.

5-Bromo-2,2′-bithiophene (**3**). In the absence of light, a soln. of *N*-bromosuccinimide (5.35 g, 0.03 mol) in DMF (20 ml) was added slowly and dropwise to an ice-cooled soln. of 2,2′-bithiophene (5 g, 0.03 mol) in DMF (80 ml) with stirring. The mixture was allowed to warm to r.t. and stirred for 6 h. The resulting mixture was poured into ice-water (200 ml) and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. extract was washed with brine (4 × 40 ml), dried ($MgSO_4$), and evaporated and the residue purified by CC (silica gel, pentane): 4.80 g (65.3%) of **3**. Light green solid. M.p. 33° ([29]: 33 – 34°). IR: 3085, 3040, 2852, 2736, 1789, 1738, 1641, 1586, 1504, 1442, 1417, 1352, 1323, 1301, 1239, 1219, 1200, 1177, 1080, 1054, 967, 881, 840, 789, 690, 647, 582, 514, 458. ^{1}H-NMR (250 MHz): 6.99 (*AB*, $J_{AB} = 3.8$, $\Delta\upsilon = 13.2$, 2 H); 7.06 (*dd*, $J = 3.6$, 5.1, 1 H); 7.16 (*dd*, $J = 1.0$, 3.6, 1 H); 7.28 (*dd*, $J = 1.0$, 5.1, 1 H). ^{13}C-NMR (62.5 MHz): 110.86 (C); 123.80 (CH); 124.01 (CH); 124.78 (CH); 127.83 (CH); 130.55 (CH); 136.36 (C); 138.86 (C).

5-Iodo-2,2′:5′,2″-terthiophene (**4**). To a soln. of 2,2′:5′,2″-terthiophene (1 g, 4 mmol) in dry $CHCl_3$ (50 ml) under Ar, I_2 (1.19 g, 4.68 mmol) and HgO (0.72 g, 3.32 mmol, yellow crystal), were added at 0° in small portions within 3 h. The mixture was allowed to warm to r.t. and stirred for 12 h. The HgI_2 was filtered through *Celite*, the filtrate washed with 10% aq. sodium thiosulfate soln. (100 ml), dried ($MgSO_4$), and evaporated, and the brown residue, purified by CC (silica gel, pentane): 700 mg (46.7%) of **4**. Orange solid. M.p. 134–135° ([31]: 138–139°). IR: 3077, 3064, 3042, 2921, 2850, 1496, 1457, 1418, 1229, 1196, 1067, 1196, 1067, 1047, 862, 835, 830, 793, 702, 688, 455. ^{1}H-NMR (250 MHz, (D_6)DMSO): 6.88 (*d*, *J* = 3.8, 1 H); 6.92 (*dd*, *J* = 3.7, 5.0, 1 H); 7.00–7.20 (*m*, 4 H); 7.36 (*dd*, *J* = 1.1, 5.0, 1 H). ^{13}C-NMR (100 MHz, (D_5)pyridine): 76.76 (C); 135.77 (C); 137.40 (C); 137.53 (C); 138.73 (CH); 125.10 (CH); 125.53 (CH); 125.94 (CH); 126.13 (CH); 126.37 (CH); 129.09 (CH).

5,5′-Diiodo-2,2′-bithiophene (**12**). To a soln. of 2,2′-bithiophene (1.46 g, 8.8 mmol) in benzene (10 ml), at 0°, I_2 (4.52 g, 17.8 mmol) and HgO (3.86 g, 17.9 mmol, yellow crystal) were added alternatively, in small portions. The mixture was then allowed to be stirred at r.t. for 14 h. An additional portion of I_2 (0.51 g, 2.01 mmol) was added at r.t. and the mixture stirred at r.t. for 24 h. The mixture was dissolved in $CHCl_3$ (100 ml), the soln. washed with aq. sat. KI and $Na_2S_2O_3$ solutions, dried ($MgSO_4$), and evaporated, and the residue recrystallized from $CHCl_3$/EtOH 95 : 5: 2.90 g (79%) of **12**. Light yellow solid. M.p. 164° ([30]: 165–166°). IR: 3085, 3061, 3026, 1495, 1411, 1195, 1058, 945, 866, 795, 788, 455. ^{1}H-NMR (250 MHz): 6.79 (*d*, *J* = 3.8, 2 H); 7.15 (*d*, *J* = 3.8, 2 H). ^{13}C-NMR (62.5 MHz, (D_6)DMSO): 76.00 (2 C); 126.42 (2 CH); 138.02 (2 CH); 141.06 (2 C).

Thienylethynyl Derivatives **5**–**7**: *General Procedure.* To a deaerated soln. of **1** (300 mg, 0.721 mmol) and the appropriate halogenothiophene (0.865 mmol) in benzene (15 ml), CuI (6 mg, $3.24 \cdot 10^{-5}$ mol), $[Pd(PPh_3)_4]$ (37 mg, $3.24 \cdot 10^{-5}$ mol), and $(PhCH_2NEt_3)Cl$ (5 mg, $2.3 \cdot 10^{-5}$ mol) were added successively. Deareated aq. 5.5N NaOH (15 ml) was then added and the mixture stirred for 24–72 h at 70° (TLC monitoring (pentane/CH_2Cl_2 80 : 20): disappearance of **1**. After cooling to r.t., the mixture was filtered through *Celite*, the latter washed with benzene, the filtrate decanted, the aq. layer extracted with benzene (2 × 10 ml), the combined org. phase washed with H_2O (3 × 20 ml), dried ($MgSO_4$), and evaporated, and the residue purified by CC (silica gel, pentane/CH_2Cl_2 100 : 0 → 70 : 30) to afford the thienylethynyl derivative. Recrystallization from hexane/CH_2Cl_2 gave crystalline material.

*3,3-Diphenyl-8-[(2-thienyl)ethynyl]-3*H-*naphtho[2,1-*b*]pyran* (**5**): Yield 88%. M.p. 220–221° (beige solid). IR: 3097, 3069, 3048, 3023, 1628, 1587, 1580, 1493, 1486, 1466, 1449, 1381, 1250, 1219, 1184, 1161, 1093, 1082, 1055, 1008, 962, 906, 883, 850, 811, 767, 748, 728, 703. ^{1}H-NMR (250 MHz, (D_6)benzene): 5.90 (*d*, *J* = 10.0, 1 H); 6.52 (*dd*, *J* = 3.6, 5.1, 1 H); 6.63 (*dd*, *J* = 1.1, 5.1, 1 H); 6.80 (*d*, *J* = 10.0, 1 H); 6.90–7.12 (*m*, 7 H); 7.15 (*dd*, *J* = 1.1, 3.6, 1 H); 7.40–7.50 (*m*, 7 H); 7.65 (br. *s*, 1 H). ^{13}C-NMR (100 MHz, (D_5)pyridine): 83.64 (C); 83.88 (C); 94.65 (C); 115.18 (C); 118.70 (C); 120.04 (2 CH, C); 122.96 (CH); 127.77 (4 CH); 128.41 (CH); 128.47 (2 CH); 128.86 (CH); 129.10 (4 CH); 129.30 (CH); 129.68 (CH); 129.88 (C); 130.24 (C); 130.80 (CH); 132.85 (CH); 133.15 (CH); 145.87 (2 C); 152.34 (C). FAB-MS: 440.12 (M^+). Anal. calc. for $C_{31}H_{20}OS$ (440.556): C 84.51, H 4.58, S 7.27; found: C 84.32, H 4.62, S 7.20.

*8-([2,2′-Bithiophen]-5-ylethynyl)-3,3-diphenyl-3*H-*naphtho[2,1-*b*]pyran* (**6**): Yield 60%. M.p. 185°. IR: 3104, 3069, 3022, 2200, 1628, 1579, 1490, 1469, 1446, 1425, 1378, 1354, 1265, 1247, 1221, 1181, 1157, 1110, 1081, 1051, 1005, 953, 888, 840, 817, 793, 778, 764, 701. ^{1}H-NMR (250 MHz): 6.24 (*d*, *J* = 10.0, 1 H); 6.98 (*dd*, *J* = 3.7, 5.1, 1 H); 7.03 (*d*, *J* = 3.8, 1 H); 7.10–7.35 (*m*, 15 H); 7.49 (*dd*, *J* = 1.4, 8.9, 1 H); 7.58 (*d*, *J* = 8.9, 1 H); 7.80–7.90 (*m*, 2 H). ^{13}C-NMR (62.5 MHz): 82.69 (C); 82.87(C); 94.64 (C); 114.08 (C); 117.85 (C); 119.11 (CH); 119.16 (CH); 121.65 (CH); 122.19 (C); 123.65 (CH); 124.27 (CH); 125.02 (CH); 127.05 (4 CH); 127.70 (2 CH); 128.02 (CH); 128.09 (CH); 128.22 (4 CH); 128.89 (CH); 128.96 (C); 129.36 (C); 129.87 (CH); 131.96 (CH); 132.73 (CH); 136.86 (C); 138.84 (C); 144.76 (2 × C); 151.49 (C). FAB-MS: 522.20 (M^+). Anal. calc. for $C_{35}H_{22}OS_2$ (522.681): C 80.42, H 4.24, S 12.27; found: C 80.21, H 4.36, S 12.10.

*8-([2,2′:5′,2″-Terthiophen]-5-ylethynyl)-3,3-diphenyl-3*H-*naphtho[2,1-*b*]pyran* (**7**): Yield 92%. M.p. 234–235° (orange solid). IR: 3094, 3068, 3015, 2925, 1628, 1580, 1490, 1470, 1447, 1378, 1264, 1246, 1216, 1184, 1159, 1088, 1053, 1007, 956, 892, 793, 757, 729, 669. ^{1}H-NMR (400 MHz, (D_5)pyridine): 6.54 (*d*, *J* = 10.0, 1 H); 7.08 (*dd*, *J* = 3.6, 5.0, 1 H); 7.22 (*d*, *J* = 4.0, 1 H); 7.24 (*d*, *J* = 3.9, 1 H); 7.25–7.31 (*m*, 3 H); 7.34 (br. *d*, *J* = 3.5, 1 H); 7.35–7.41 (*m*, 5 H); 7.42 (br. *d*, *J* = 5.1, 1 H); 7.43 (*d*, *J* = 3.8, 1 H); 7.50 (*d*, *J* = 10.0, 1 H); 7.65–7.71 (*m*, 5 H); 7.73 (*d*, *J* = 8.9, 1 H); 8.01 (*d*, *J* = 1.0, 1 H); 8.10 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR (100 MHz, (D_5)pyridine): 83.64 (C); 83.81 (C); 96.18 (C); 115.21 (C); 118.54 (C); 120.04 (2 CH); 122.88 (C); 123.00 (CH); 124.96 (CH); 125.24 (CH); 125.66 (CH); 126.27 (CH); 126.33 (CH); 127.76 (4 CH); 128.43 (2 CH); 129.11 (5 CH); 129.32 (CH); 129.64 (CH); 129.87 (C); 130.29 (–); 130.85 (CH); 132.92 (CH); 134.31 (CH); 135.97 (C); 137.48 (C); 137.83 (C); 139.32 (C); 145.86 (2 C); 152.41 (C). FAB-MS: 604.10 (M^+). Anal. calc. for $C_{39}H_{24}OS_3$ (604.805): C 77.45, H 4.00, S 15.90; found: C 77.69, H 4.21, S 15.80.

Thiophenediethyndiyl Derivatives **13** *and* **14**: *General Procedure.* To a deaerated soln. of **1** (400 mg, 0.961 mmol) and the appropriate dihalogenothiophene (0.457 mmol) in benzene (20 ml), CuI (9 mg, $4.6 \cdot 10^{-5}$ mol), [Pd(PPh$_3$)$_4$] (52 mg, $4.6 \cdot 10^{-5}$ mol), and ($PhCH_2NEt_3$)Cl (11 mg, $4.6 \cdot 10^{-5}$ mol) were rapidely added. Deaerated aq. 5.5N NaOH (20 ml) was then added, and the mixture was stirred for 48–72 h at 70°. (TLC monitoring (pentane/CH_2Cl_2 80:20)): disappearance of **1**. The biphasic mixture was allowed to cool and filtered through *Celite*, the latter washed carefully with benzene, the aq. layer of the filtrate extracted with benzene (2×20 ml), the combined org. layer washed with H_2O (3×25 ml) and brine (3×25 ml), dried ($MgSO_4$), and evaporated, and the residue purified by CC (silica gel, pentane/CH_2Cl_2 100:0 → 50:50) to give the thiophenediethynyl derivative. Recrystallization from benzene gave crystalline material.

*8,8'-(Thiophene-2,5-diyldiethyne-2,1-diyl)bis[3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran]* (**13**): Yield 73%. M.p. 137° (yellow solid). IR: 3058, 3026, 2195, 1631, 1581, 1493, 1464, 1447, 1380, 1355, 1267, 1246, 1217, 1091, 1081, 1054, 1006, 893, 822, 805, 756, 732, 699. ^{1}H-NMR (400 MHz, (D$_5$)pyridine): 6.53 (*d*, $J = 10.0$, 2 H); 7.24–7.40 (*m*, 12 H); 7.43 (*d*, $J = 9.0$, 2 H); 7.45 (*s*, 2 H); 7.49 (*d*, $J = 10.0$, 2 H); 7.64–7.70 (*m*, 10 H); 7.72 (*d*, $J = 9.0$, 2 H); 8.00 (br. *s*, 2 H); 8.09 (*d*, $J = 8.9$, 2 H). ^{13}C-NMR (100 MHz, (D$_5$)pyridine): 83.40 (2 C); 83.66 (2 C); 96.03 (2 C); 115.20 (2 C); 118.24 (2 C); 120.01 (2 CH); 120.09 (2 CH); 123.01 (2 CH); 125.59 (2 C); 127.77 (8 CH); 128.48 (4 CH); 129.11 (8 CH); 129.33 (2 CH); 129.63 (2 CH); 129.82 (2 C); 130.38 (2 C); 130.88 (2 CH); 133.16 (2 CH); 133.45 (2 CH); 145.85 (4 C); 152.48 (2 C). FAB-MS: 796.30 (M^+). Anal. calc. for $C_{58}H_{36}O_2S$ (796.971): C 87.40, H 4.55, S 4.02; found: C 87.15, H 4.70, S 4.10.

*8,8'-([2,2'-Dithiophene]-5,5'-diyldiethyne-2,1-diyl)bis[3,3-diphenyl-3*H*-naphtho[2,1-*b*]pyran]* (**14**): Yield 80%. M.p. >270° (orange solid). IR: 3057, 3024, 2923, 2852, 2194, 1632, 1582, 1492, 1466, 1446, 1380, 1246, 1222, 1180, 1161, 1091, 1083, 1054, 1007, 953, 892, 819, 793, 762, 733, 699. ^{1}H-NMR (400 MHz, (D$_5$)pyridine): 6.54 (*d*, $J = 10.0$, 2 H); 7.26 (*d*, $J = 3.9$, 2 H); 7.28 (*t*, $J = 7.6$, 4 H); 7.34–7.41 (*m*, 8 H); 7.42 (*d*, $J = 3.9$, 2 H); 7.43 (*d*, $J = 8.7$, 2 H); 7.50 (*d*, $J = 10.0$, 2 H); 7.69 (*d*, $J = 7.6$, 8 H); 7.71 (*d*, $J = 8.9$, 2 H); 7.74 (*d*, $J = 8.7$, 2 H); 8.03 (br. *s*, 2 H); 8.12 (*d*, $J = 8.9$, 2 H). ^{13}C-NMR (100 MHz, (D$_5$)pyridine): 83.69 (4 C); 96.42 (2 C); 115.22 (2 C); 118.47 (2 C); 120.03 (2 CH); 120.09 (2 CH); 123.03 (2 CH); 123.56 (2 C); 125.63 (2 CH); 127.78 (8 CH); 128.49 (4 CH); 129.11 (8 CH); 129.34 (2 CH); 129.63 (2 CH); 129.89 (2 C); 130.35 (2 C); 130.87 (2 CH); 133.00 (2 CH); 134.31 (2 CH); 138.75 (2 C); 145.87 (4 C); 152.46 (2 C). FAB-MS: 878.30 (M^+). Anal. calc. for $C_{62}H_{38}O_2S_2$ (879.096): C 84.70, H 4.36; S 7.29; found: C 83.54, H 4.15, S 7.00.

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