Molecular Engineering of Benzo[*b*]pyrylium Salts by Indirect Electrophilic Substitution☆

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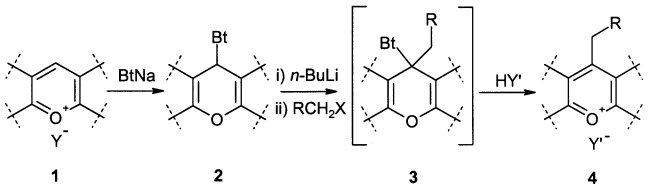
Benzotriazole-mediated indirect electrophilic substitution in the position *para* to the oxygen atom of benzo[*b*]pyrylium salts has been used for the synthesis of long-chain and bifunctional benzo[*b*]pyrylium species. The methodology has potential for application in high technology and the pharmaceutical industries, for the molecular engineering of new functionalized derivatives.

O-Heterocyclic salts of the pyrylium, benzo[*b*]pyrylium, and xanthylium type are important as absorption/fluorescent probes with high quantum yields, for use in ion detection[1], as laser dyes[2] and as potential photochemotherapeutic agents[3]. They also occur widely in nature[4]. It is of considerable importance to be able to incorporate these highly conjugated moieties easily into various chemical systems. Of particular significance are: i) stabilization of the pyrylium nucleus against nucleophilic attack; ii) solubilization of the parent pyrylium species; iii) labeling of synthetic and natural polymers[1], and iv) coupling these long-wave absorbing, highly fluorescent chromophores with substituents of complementary physicochemical properties, i.e. UV absorbing, fluorescent species or bichromophoric systems[5][6]. The introduction of new methodologies which allow easy derivatization of π-electron-deficient oxygen heterocycles is important for the molecular tailoring of molecules containing a pyrylium nucleus. Derivatization of compounds **1** with non-π-conjugating residues, to give derivatives **4**, should not significantly affect their photophysical properties. Of particular importance are analogs of compound **5** (Scheme 2). For example **5b** itself has a fluorescence quantum yield of one, independent of the solvent polarity[7], but the low solubility of **5b** in non-polar solvents and the possibility of nucleophilic attack at its 4-position has limited its potential for application.

O-Heterocycles **1** are well known to react easily with nucleophiles, but rarely undergo direct or stepwise reactions with electrophiles[8][9][10]. We have recently introduced a new methodology for a two-step, indirect electrophilic substitution in the position *para* to the oxygen atom of these heterocycles[11], which utilizes the properties of benzotriazole as an efficient synthetic auxiliary[12]. Initial investigations[11a] demonstrated that sterically hindered pyrylium salts of type **1** (Scheme 1) undergo nucleophilic addition of benzotriazole at the position *para* to the oxygen atom, without giving rise to *ortho* addition products. Intermediates **2** could be readily deprotonated and treated with electrophiles, and subsequent treatment with mineral acids gave the *para*-electrophile-substituted derivatives **4**. Furthermore, analogous thiopyrylium and pyrylium cations can undergo similar transformations[11b].

Scheme 1



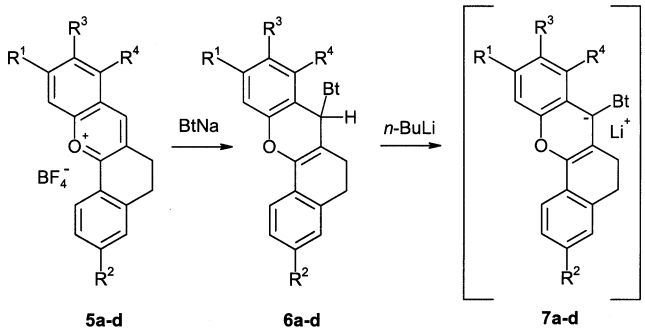
In the present work, we investigated the regiospecificity of the addition of benzotriazole to the sterically non-hindered 2-aryl-substituted benzo[*b*]pyrylium (flavylium) systems without a 3,2′ bridge, and demonstrate that we can also derivatize these compounds by electrophilic substitution.

We further extend the methodology shown in Scheme 1 in several directions, to synthesize: i) long-chain aliphatic derivatives; ii) ω-aryl-substituted alkyl derivatives; iii) unsymmetrical bifunctional molecules connected by an aliphatic chain, and iv) symmetrical bifunctional systems connected by an aliphatic chain. Symmetrical bispyrylium salts connected through the 3-position by an aliphatic or aromatic chain have previously been accessed by the reaction of open-chain pentene-1,5-dione enolate intermediates with the appropriate bifunctional electrophiles, followed by mineral acid catalyzed ring closure[13].

The selective *para* addition of sodium benzotriazolate to bridged benzo[*b*]pyrylium species **5a**−**c** gives chromenes of type **6a**−**c**. These are readily deprotonated by *n*-butyllithium at low temperature to form the anions **7a**−**c** as de-

  1434−193X/98/1111−2623 $ 17.50+.50/0

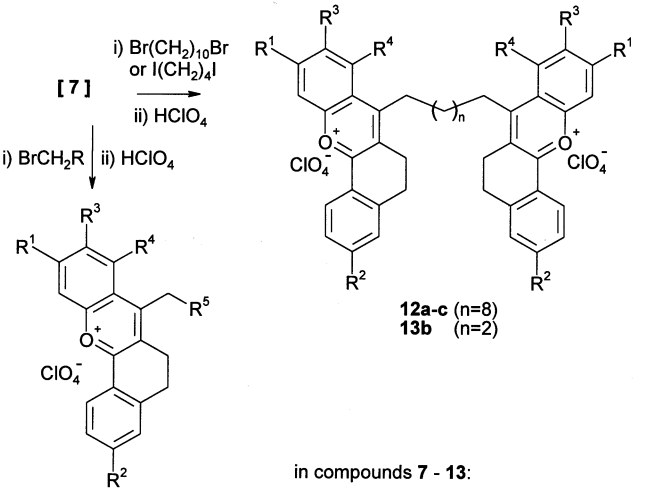
Scheme 2



a: $R^1 = R^2 = R^3 = R^4 = H$;
b: $R^1 = R^3 = R^4 = H$; $R^2 = OCH_3$;
c: $R^1 = N(C_2H_5)_2$; $R^2 = OCH_3$; $R^3 = R_4 = H$;
d: $R^1 = R^2 = H$; $R^3,R^4 = (CH=CH)_2$

scribed[11]. Subsequent reaction of the heterocyclic carbanions with electrophiles, followed by acid-promoted debenzotriazolylation generates the derivatized benzo[*b*]- and naphtho[2,1-*b*]pyrylium salts[11]. We have now carried out further reactions of **7a**–**c** and of the new analog **7d** with other electrophiles as shown in Scheme 3.

Scheme 3



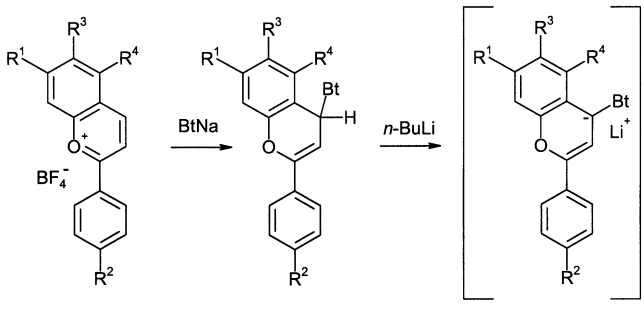
8b,d ($R^5 = n\text{-}C_{21}H_{43}$)
9b ($R^5 = CH_2Ph$)
10b ($R^5 = (CH_2)_2Ph$)
11b ($R^5 = (CH_2)_3Cl$)

in compounds **7** - **13**:
a: $R^1 = R^2 = R^3 = R^4 = H$;
b: $R^1 = R^3 = R^4 = H$; $R^2 = OCH_3$;
c: $R^1 = N(C_2H_5)_2$; $R^2 = OCH_3$; $R^3 = R_4 = H$;
d: $R^1 = R^2 = H$; $R^3,R^4 = (CH=CH)_2$

The synthesis of long-alkyl-chain pyrylium cations is of contemporary interest for Langmuir-Blodgett films and membrane probes due to their amphiphilic nature[1], and had previously been achieved in yields of ca. 25% using classical methodology[14]. We have already reported[11] the synthesis of a variety of medium- and long-chain-derivatized pyrylium, benzo[*b*]pyrylium and xanthylium salts by our simple, high-yielding, and general synthetic method. We previously employed benzyl bromide as the electrophile, and now show that the use of longer ω-aryl-substituted alkyl bromides (ω-bromoethylbenzene and 1-bromo-3-phenylpropane) is also successful (Scheme 3, compounds **9b** and **10b**; Scheme 5, compound **18b**). We have further extended the method to alkyl chains of 22 carbon atoms (Scheme 3, compound **8b**,**d**; Scheme 5, compound **21f**), by utilizing $C_{22}H_{45}Br$ which is amongst the longest carbon-chain electrophiles commercially available. The method is regioselective for the *para* position of the oxygen heterocycle, and the two-step process is essentially quantitative. Products **8b**,**d** and **21f** are crystalline materials, isolated simply by recrystallization of the crude reaction mixtures.

Most of the naturally occurring and synthetically available benzo[*b*]pyrylium compounds are of the non-bridged variety. It was therefore of interest to investigate the addition of benzotriazole to such non-bridged systems, to be able to extend the application of our indirect electrophilic substitution methodology. Indeed, upon treating 2-aryl-substituted benzo[*b*]pyrylium (flavylium) salts **14b**,**c**,**e**–**g** with sodium benzotriazolate, regiospecific *para* substitution was observed, to give **15b**,**c**,**e**–**g** in almost quantitative yield (Scheme 4). Thus, the regioselective nucleophilic addition of benzotriazole to salts **5a**–**d** is now demonstrated not to require the steric hindrance and higher stability of the tetra-substituted pyrylium ring.

Scheme 4

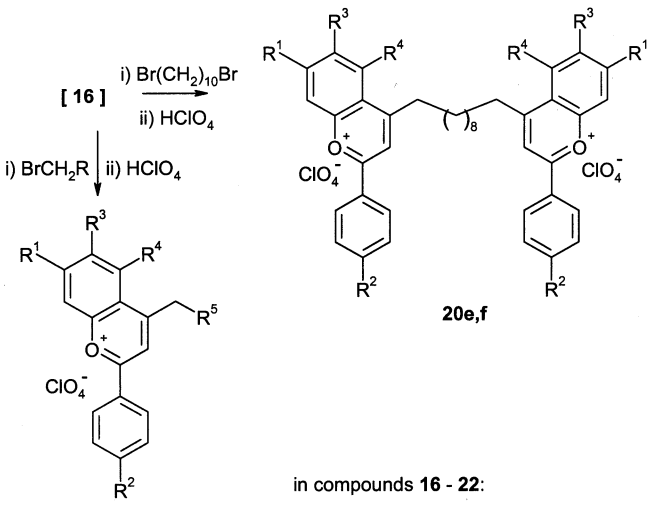


b: $R^1 = R^3 = R^4 = H$; $R^2 = OCH_3$;
c: $R^1 = N(C_2H_5)_2$; $R^2 = OCH_3$; $R^3 = R_4 = H$;
e: $R^1 = R^3 = R^4 = H$; $R^2 = CH_3$;
f: $R^1 = H$; $R^2 = CH_3$; $R^3,R^4 = (CH=CH)_2$;
g: $R^1 = H$; $R^2 = OCH_3$; $R^3,R^4 = (CH=CH)_2$

In the formation of **15b**,**c**,**e**–**g**, no *ortho* addition or ring-opened by-products were observed, which is in contrast to the well-documented nucleophilic addition of other nitrogen or oxygen nucleophiles[8][15]. In the case of compounds **15e** and **15f**, the 1-benzotriazolyl isomer was isolated as the main product, and could be easily purified by one recrystallization from ethanol. Compounds **15b**,**c** and **15g** were obtained as mixtures of the 1- and 2-benzotriazolyl isomers which were used without separation. Subsequent deprotonation of **15b**,**c**,**e**–**g**, reaction with electrophiles, and debenzotriazolylation of the intermediates **16b**,**c**,**e**–**g** gave, after recrystallization, the 3,2′-non-bridged products **17**–**22**

in yields comparable to those achieved for compounds **8**−**13** from the bridged pyrylium carbanions of type **7**.

Scheme 5



17e-g ($R^5 = C_{11}H_{23}$)
18b ($R^5 = (CH_2)_2Ph$)
19c,e-g ($R^5 = (CH_2)_3Cl$)
21f ($R^5 = C_{21}H_{43}$)
22g ($R^5 = (CH_2)_2Cl$)

in compounds **16** - **22**:

b: $R^1 = R^3 = R^4 = H$; $R^2 = OCH_3$;
c: $R^1 = N(C_2H_5)_2$; $R^2 = OCH_3$; $R^3 = R_4 = H$;
e: $R^1 = R^3 = R^4 = H$; $R^2 = CH_3$;
f: $R^1 = H$; $R^2 = CH_3$; $R^3,R^4 = (CH{=}CH)_2$;
g: $R^1 = H$; $R^2 = OCH_3$; $R^3,R^4 = (CH{=}CH)_2$

Reactions of the benzo[*b*]pyranyl anions **7a**−**c** and **16e**,**f** with bifunctional electrophiles such as α,ω-dihalogenoalkanes are also successful. When the ratio of electrophile (1,4-diiodobutane or 1,10-dibromodecane) to anion is one to two, the α,ω-bisbenzo[*b*]pyrylium derivatives **12a**−**c**, **13b** and **20e**,**f** were conveniently prepared in high yield (Schemes 3 and 5).

By using an excess of 1,10-dibromodecane as electrophile the mono addition products were prepared, but in considerably lower yield, along with the previously described bis derivatives **12a**−**c** and **20e**,**f** as by-products. The synthesis of mono addition products could be facilitated by using differently doubly halogenated electrophiles. Thus, the reaction of the in situ generated anions **7b** and **16c**,**e**−**g** with one equivalent of 1-bromo-3-chloropropane or 1-bromo-4-chlorobutane gives the mono addition products **11b**, **19c**,**e**−**g** and **22g** selectively, and in high yield. These compounds have potential for further derivatization, and could be used for the synthesis of unsymmetrical bifunctional derivatives (e.g. bichromophores[5]).

We have herein extended our indirect electrophilic substitution of π-deficient O-heterocycles to incorporate the synthesis of longer chain aliphatic derivatives **8**, **17** or **21**, ω-aryl-substituted aliphatic-chain derivatives **9**, **10** or **18**, bifunctional aliphatically linked systems derived from α,ω-dihalogenated aliphatic chains **12**, **13** or **20** and potential unsymmetrical aliphatically connected bifunctional molecules **11**, **19** or **22**. The methodology has been applied to sterically hindered-3,2′-bridged **7**, and for the first time to 3,2′-non-bridged 2-aryl-substituted benzo[*b*]pyrylium (flavylium) systems **16**. The physicochemical properties and potential applications of these new fluorescent dyes will be investigated.

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Table 1. UV/Vis and fluorescence data

Compound	Molecular mass	λ_a	ε	λ_f	ϕ_f
8b	671.36	463	52900	494	1.00
8d	691.39	464	44900	505	0.87
9b	466.92	468	46100	494	1.00
10b	480.94	464	52500	495	0.93
11b	453.32	465	51000	495	1.00
12a	803.73	421	−	456	0.31
12b	863.79	459	94800	497	0.89
12c	1006.03	556	80200	598	0.33
13b	779.62	462	−	489	0.88
17e	489.15	416	41600	443	0.57
17f	539.11	456	42500	493	0.78
17g	555.11	477	55800	508	0.91
18b	454.91	452	45100	494	0.78
19c	498.40	543	34700	592	0.33
19e	411.28	418	33200	447	0.59
19f	461.53	459	39100	497	0.80
19g	477.34	479	54000	511	0.90
20e	778.23	413	71500	444	0.52
20f	879.83	452	78100	495	0.65
21f	679.38	459	−	493	0.75
22g	463.31	481	55700	514	0.84

Experimental Section

General: Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H-and ^{13}C-NMR spectra were recorded at 300 MHz and 75 MHz respectively with a Varian XL 300 spectrometer in $CDCl_3$, or a mixture of $CDCl_3/CF_3CO_2D$ = 5:1; referenced to TMS for the proton spectra and the solvent for the carbon spectra. Elemental (C, H, N) analyses were performed with a Carlo Erba 1106 elemental analyzer and high-resolution mass spectrometry (HRMS) with a Finnigan MAT 95Q mass spectrometer. UV/Vis absorption spectra were recorded with a Perkin-Elmer Lambda 16 spectrophotometer. Corrected fluorescence and fluorescence excitation spectra of solutions with an absorbance around 0.05 were measured with a Perkin-Elmer LS 50B spectralfluorometer. Fluorescence quantum yields were obtained using rhodamine 6G in ethanol as a standard (ϕ_f = 0.95). Refractive index corrections were made to adjust for the different solvents used. THF was distilled under nitrogen from sodium/benzophenone immediately before use. All reactions with water-sensitive compounds were carried out under dry nitrogen. 5,6-Dihydro(naphtho[1,2-*b*]benzo[*e*]pyrylium) tetrafluoroborates **5** and 4*H*-(1*H*-benzotriazol-1-yl)benzo[*b*]pyrans **6a**−**c** were prepared according to literature procedures[11][16].

General Procedure for the Preparation of the 2-Arylbenzo[b]pyrylium Tetrafluoroborates **14b**,**e**−**g**: The corresponding 2-hydroxybenzaldehyde (20 mmol) and aryl methyl ketone (20 mmol) were dissolved in acetic acid (25 ml) and HBF_4 (5 ml, 48−50%) while stirring. Acetic anhydride (ca. 25 ml) was added dropwise to maintain the temperature of the reaction mixture at 60°C until no more exothermic reaction was observed. After stirring at room temp. for about 12 h and the addition of ethyl acetate (50 ml), the precipitate was filtered off and recrystallized from glacial acetic acid.

2-(4-Methoxyphenyl)benzo[b]pyrylium Tetrafluoroborate (**14b**): Sparkling green needles, yield 3.11 g (48%), m.p. 191−191.5°C. −

^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 4.03 (s, 3 H), 7.23 (d, *J* = 8.9 Hz, 2 H), 7.88 (t, *J* = 7.4 Hz, 1 H), 8,10−8.24 (m, 3 H), 8.44−8.54 (m, 3 H), 9.14 (d, *J* = 9.1 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 56.5, 116.8, 116.9, 118.8, 120.3, 123.5, 130.3, 130.6, 134.1, 139.0, 154.7, 155.5, 169.5, 174.8. − $C_{16}H_{13}BF_4O_2$ (324.1): calcd. C 59.30, H 4.04; found C 59.20, H 3.96.

2-(4-Methylphenyl)benzo[b]pyrylium Tetrafluoroborate (**14e**): Green/yellow microcrystals, yield 2.84 g (46%), m.p. 196.2−197.5°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.55 (s, 3 H), 7.56 (d, *J* = 8.2 Hz, 2 H), 7.95 (t, *J* = 8.1 Hz, 1 H), 8.24−8.32 (m, 3 H), 8.39 (d, *J* = 8.3 Hz, 2 H), 8.64 (d, *J* = 9.0 Hz, 1 H), 9.39 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.4, 117.4, 119.1, 124.3, 125.5, 130.8, 130.9, 131.0, 131.7, 140.0, 152.1, 156.2, 157.2, 175.9. − $C_{16}H_{13}BF_4O$ (308.1): calcd. C 62.38, H 4.25; found C 62.47, H 3.96.

2-(4-Methylphenyl)naphtho[2,1-b]pyrylium Tetrafluoroborate (**14f**): Yellow powder crystals, yield 4.23 g (59%), m.p. 210.5−211.5°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.54 (s, 3 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.92 (t, *J* = 7.4 Hz, 1 H), 8.02 (t, *J* = 7.2 Hz, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 8.18 (d, *J* = 6.6 Hz, 1 H), 8.34 (d, *J* = 8.4 Hz, 2 H), 8.70 (t, *J* = 8.5 Hz, 2 H), 8.77 (d, *J* = 8.3 Hz, 1 H), 9.99 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.1, 116.4, 116.8, 123.0, 123.4, 125.3, 127.7, 129.8, 130.4, 130.8, 131.6, 131.7, 131.8, 143.8, 150.5, 150.8, 158.5, 172.8. − HRMS-FAB ($C_{20}H_{15}O$): calcd. 271.1123; found 271.1119; Δ = 0.4 mmU.

2-(4-Methoxyphenyl)naphtho[2,1-b]pyrylium Tetrafluoroborate (**14g**): Orange microcrystals, yield 2.99 g (40%), m.p. 255°C (dec.). − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 3.99 (s, 3 H), 7.19 (d, *J* = 9.1 Hz, 2 H), 7.86 (t, *J* = 7.4 Hz, 1 H), 7.96 (t, *J* = 7.2 Hz, 1 H), 8.07 (d, *J* = 9.1 Hz, 1 H), 8.11 (d, *J* = 7.9 Hz, 1 H), 8.42 (d, *J* = 9.0 Hz, 2 H), 8.56 (d, *J* = 9.3 Hz, 1 H), 8.58 (d, *J* = 9.1 Hz, 1 H), 8.68 (d, *J* = 8.4 Hz, 1 H), 9.78 (d, *J* = 9.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 56.3, 116.3, 116.4, 116.6, 120.2, 121.8, 123.2, 127.7, 130.2, 130.3, 131.4, 131.6, 132.9, 142.5, 149.0, 157.5, 168.4, 172.1. − $C_{20}H_{15}BF_4O_2$ (374.1): calcd. C 64.21, H 4.04; found C 63.84, H 3.86.

Preparation of the 7-Diethylamino-2-(4-methoxyphenyl)benzo[b]pyrylium Tetrafluoroborate (**14c**): 4-Diethylamino-2-hydroxybenzaldehyde (10 mmol, 1.93 g) and 4-methoxyacetophenone (10 mmol, 1.50 g) were dissolved in acetic acid (30 ml) and refluxed in the presence of HBF_4 (48−50%, 2 ml) for 30 min. The precipitate formed on cooling was collected by filteration and recrystallized from glacial acetic acid to give the product (2.29 g, 58%), deep red crystals, m.p. 198°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.34 (t, *J* = 7.1 Hz, 6 H), 3.74 (q, *J* = 7.1 Hz, 4 H), 3.99 (s, 3 H), 7.16 (d, *J* = 9.1 Hz, 2 H), 7.38 (s, 1 H), 7.45 (dd, *J* = 1.8 Hz, *J* = 9.1 Hz, 1 H), 7.85 (d, *J* = 8.3 Hz, 1 H), 7.97 (d, *J* = 9.3 Hz, 1 H), 8.27 (d, *J* = 8.9 Hz, 2 H), 8.60 (d, *J* = 8.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 11.6, 48.5, 56.1, 110.5, 116.1, 119.2, 119.7, 121.2, 131.6, 132.7, 149.4, 153.4, 153.5, 158.4, 166.9, 169.7. − HRMS-FAB ($C_{20}H_{22}NO_2$): calcd. 308.1651; found 308.1651; Δ = 0.0 mmU.

General Procedure for the Preparation of the 2-Aryl-4H-(1H-benzotriazol-1-yl)benzo[b]pyrans **6d**, **15b**,**c**,**e**−**g**: To a solution of benzotriazole (1.19 g, 10 mmol) in dry THF (50 ml) was added NaH (0.40 g of 60% in mineral oil, 10 mmol). The reaction mixture was stirred at room temp. for 20 min before adding the corresponding 2-arylbenzo[*b*]pyrylium tetrafluoroborate **14b**,**c**,**e** or the corresponding 2-arylnaphtho[2,1-*b*]pyrylium tetrafluoroborate **5d** or **14f**,**g** (10 mmol) portionwise. The reaction mixture was left stirring for 20 min before the precipitated inorganic by-product was filtered off. After evaporation of the solvent, the crude product was purified by recrystallization from ethanol, and isolated as colourless microcrystals.

7H-(1H-Benzotriazol-1-yl)-5,6-dihydro(dinaphtho[1,2-b;1,2-e]pyran) (**6d**): Yield 2.97 g (74%), m.p. 228°C. − ^{1}H NMR ($CDCl_3$): δ = 2.05−2.15 (m, 1 H), 2.55−2.65 (m, 2 H), 2.83−2.93 (m, 1 H), 7.01−7.05 (m, 1 H), 7.09−7.18 (m, 3 H), 7.26 (t, *J* = 6.8 Hz, 1 H), 7.35 (t, *J* = 7.4 Hz, 2 H), 7.42−7.57 (m, 3 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.85−7.96 (m, 3 H), 8.19 (d, *J* = 8.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 23.8, 27.5, 55.9, 104.6, 108.2, 110.0, 117.4, 118.4, 120.0, 122.1, 122.8, 123.7, 124.9, 126.6, 127.1, 127.6, 127.8, 128.5, 128.7, 128.9, 130.8, 131.3, 131.5, 136.4, 145.1, 146.7, 149.8. − $C_{27}H_{19}N_3O$ (401.5): calcd. C 80.78, H 4.77, N 10.47; found C 80.82, H 4.87, N 10.16.

4H-(1H-Benzotriazol-1-yl)-2-(4-methylphenyl)benzo[b]pyran (**15e**): Yield 3.01 g (91%), m.p. 119°C. − ^{1}H NMR ($CDCl_3$): δ = 2.39 (s, 3 H), 5.77 (d, *J* = 4.2 Hz, 1 H), 7.03 (t, *J* = 7.2 Hz, 1 H), 7.14−7.40 (m, 9 H), 7.67 (d, *J* = 7.8 Hz, 2 H), 8.02 (d, *J* = 7.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 21.3, 54.0, 93.5, 110.5, 116.8, 117.2, 118.4, 120.0, 123.8, 124.6, 125.2, 127.1, 129.0, 129.3, 130.1, 131.5, 140.0, 147.0, 151.1, 152.2. − $C_{22}H_{17}N_3O$ (339.4): calcd. C 77.86, H 5.05, N 12.38; found C 78.12, H 5.12, N 12.52.

4H-(1H-Benzotriazol-1-yl)-2-(4-methylphenyl)naphtho[2,1-b]pyran (**15f**): Yield 2.24 g (66%), m.p. 194.3−195.0°C. − ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 3 H), 5.91 (d, *J* = 5.2 Hz, 1 H), 7.03 (d, *J* = 7.2 Hz, 1 H), 7.09−7.17 (m, 2 H), 7.22 (d, *J* = 7.7 Hz, 2 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.50 (d, *J* = 8.9 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 5.7 Hz, 2 H), 7.86 (d, *J* = 9.1 Hz, 1 H), 7.93 (d, *J* = 7.2 Hz, 1 H), 8.16 (d, *J* = 8.3 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 21.3, 52.2, 94.3, 108.3, 110.1, 117.4, 120.0, 122.8, 123.6, 125.1, 125.2, 127.1, 127.8, 128.5, 129.3, 129.7, 130.9, 131.3, 139.9, 146.8, 150.0, 151.9. − $C_{26}H_{19}N_3O$ (389.5): calcd. C 80.19, H 4.92, N 10.79; found C 80.46, H 5.06, N 10.52.

In the case of compound **15b**,**c** and **15g** we used the crude product without characterization for further reactions.

General Procedure for the Preparation of the Benzo[b]pyrylium Perchlorates **8**−**11**, **17**−**19**, **21** *and* **22**: To a solution of the corresponding 2-aryl-4*H*-(1*H*-benzotriazol-1-yl)benzo[*b*]pyran **6b** and **15b**,**c**,**e** or the corresponding 2-aryl-4*H*-(1*H*-benzotriazol-1-yl)-naphtho[2,1-*b*]pyran **6d** and **15f**,**g** (1.25 mmol) in dry THF (30 ml), at −78°C, was added *n*BuLi (0.78 ml, 1.25 mmol, 1.6 M in hexane). The solution was stirred at −78°C for 30 min, before adding the electrophile (1.25 mmol) as a solution in dry THF (10 ml). The reaction mixture was stirred overnight and allowed to warm up to room temp., before being quenched with saturated aqueous NH_4Cl solution (40 ml), and extracted with diethyl ether (2 × 30 ml). The combined organic extracts were washed with brine and water then dried with $MgSO_4$. The solvent was removed in vacuo and the resulting oil dissolved in acetic acid (20 ml) and $HClO_4$ (0.4 ml, 70%). The precipitate formed after the addition of water (50 ml) was collected by filtration and recrystallized from glacial acetic acid.

5,6-Dihydro-7-docosyl-3-methoxy(naphtho[1,2-b]benzo[e]pyrylium) Perchlorate (**8b**): Yellow powder crystals, yield 0.83 g (100%), m.p. 119°C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.5 Hz, 3 H), 1.15−1.40 (m, 36 H), 1.52−1.60 (m, 2 H), 1.65−1.75 (m, 2 H), 3.25−3.38 (m, 6 H), 3.98 (s, 3 H), 6.98 (d, *J* = 1.9 Hz, 1 H), 7.05 (dd, *J* = 2.0 Hz, *J* = 8.9 Hz, 1 H), 7.80 (t, *J* = 7.4 Hz, 1 H), 8.03 (t, *J* = 7.2 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 8.17 (d, *J* = 8.3 Hz, 1 H), 8.44 (d, *J* = 8.9 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.6, 23.6, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 30.1, 30.2, 30.3,

31.9, 56.5, 114.1, 116.4, 118.4, 119.5, 123.5, 126.0, 127.2, 129.3, 132.2, 136.7, 149.3, 153.4, 167.6, 168.4, 169.4. − $C_{40}H_{59}ClO_6$ (671.4): calcd. C 71.56, H 8.86; found C 71.76, H 9.10.

5,6-Dihydro-7-docosyl(dinaphtho[1,2-b;1,2-e]pyrylium) Perchlorate (**8d**): Yellow powder crystals, yield 0.63 g (73%), m.p. 129°C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, *J* = 6.4 Hz, 3 H), 1.13−1.50 (m, 36 H), 1.61−1.70 (m, 2 H), 1.90−2.00 (m, 2 H), 3.29 (t, *J* = 7.7 Hz, 2 H), 3.45 (t, *J* = 7.7 Hz, 2 H), 3.62−3.72 (m, 2 H), 7.40 (d, *J* = 7.7 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.79 (t, *J* = 7.4, 1 H), 7.88 (t, *J* = 7.3, 1 H), 8.03 (d, *J* = 9.1 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 8.36 (d, *J* = 8.0 Hz, 1 H), 8.41 (d, *J* = 9.1 Hz, 1 H), 8.66 (d, *J* = 8.5 Hz, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 24.0, 26.6, 27.8, 29.1, 29.3, 29.5, 29.6, 29.7, 30.0, 31.9, 34.5, 117.7, 123.4, 125.4, 127.1, 127.8, 128.0, 128.6, 128.9, 129.3, 130.1, 130.3, 131.1, 132.7 136.4, 141.9, 143.4, 157.4, 165.0, 171.6. − $C_{43}H_{59}ClO_5$ (691.4): calcd. C 74.70, H 8.60; found C 74.95, H 8.86.

5,6-Dihydro-3-methoxy-7-(2-phenylethyl)(naphtho[1,2-b]benzo-[e]pyrylium) Perchlorate (**9b**): Fine yellow/orange needles, yield 0.54 g (92%), m.p. 112°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.90−2.98 (m, 4 H), 3.14 (t, *J* = 7.4 Hz, 2 H), 3.63 (t, *J* = 7.3 Hz, 2 H), 4.00 (s, 3 H), 6.91 (d, *J* = 1.7 Hz, 1 H), 7.06−7.12 (m, 3 H), 7.20−7.29 (m, 3 H), 7.79−7.85 (m, 1 H), 8.04−8.09 (m, 2 H), 8.16 (d, *J* = 8.5 Hz, 1 H), 8.39 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.6, 26.8, 31.9, 35.9, 56.4, 114.2, 116.6, 118.3, 119.3, 123.3, 126.0, 127.3, 127.9, 128.5, 128.9, 129.6, 132.1, 137.0, 138.5, 149.4, 153.4, 165.6, 169.0, 169.6. − $C_{26}H_{23}ClO_6$ (466.9): calcd. C 66.88, H 4.97; found C 66.72, H 5.05.

5,6-Dihydro-3-methoxy-7-(2-phenylpropyl)(naphtho[1,2-b]-benzo[e]pyrylium) Perchlorate (**10b**): Yellow/orange powder crystals, yield 0.56 g (93%), m.p. 171°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.02−2.10 (m, 2H), 2.92 (t, *J* = 6.8 Hz, 2 H), 3.15 (s, 4 H), 3.27 (t, *J* = 8.2 Hz, 2 H), 4.02 (s, 3 H), 6.98 (d, *J* = 1.7 Hz, 1 H), 7.11 (dd, *J* = 2.1 Hz, *J* = 9.0 Hz, 1 H), 7.22−7.38 (m, 5 H), 7.72−7.78 (m, 1 H), 8.90 (d, *J* = 8.3 Hz, 1 H), 8.02−8.09 (m, 2 H), 8.38 (d, *J* = 9.0 Hz, 1H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.3, 27.0, 29.1, 31.5, 35.8, 56.4, 114.4, 116.6, 118.4, 119.3, 123.4, 126.0, 126.9, 127.0, 128.7, 128.9, 129.7, 132.0, 137.1, 140.2, 149.2, 153.6, 167.2, 169.0, 169.7. − $C_{27}H_{25}ClO_6$ (480.94): calcd. C 67.43, H 5.24; found C 67.28, H 5.29.

7-(4-Chlorobutyl)-5,6-dihydro-3-methoxy(naphtho[1,2-b]benzo-[e]pyrylium) Perchlorate (**11b**): Deep yellow powder crystals, yield 0.40 g (71%), m.p. 168°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.90−1.98 (m, 2 H), 2.03−2.12 (m, 2 H), 3.22−3.28 (m, 2 H), 3.29−3.38 (m, 4 H), 3.68 (t, *J* = 6.0 Hz, 2 H), 4.02 (s, 3 H), 6.99 (d, *J* = 2.0 Hz, 1 H), 7.12 (dd, *J* = 2.3 Hz, *J* = 9.0 Hz, 1 H), 7.83−7−89 (m, 1 H), 8.05−8.10 (m, 2 H), 8.23 (d, *J* = 8.2 Hz, 1 H), 8.41 (d, *J* = 9.0 Hz, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.5, 26.8, 27.0, 29.0, 32.0, 43.9, 56.4, 114.3, 116.7, 118.3, 119.3, 123.3, 126.0, 127.2 129.8, 132.0, 137.1, 149.4, 153.6, 166.6, 169.0, 169.8. − HRMS (70 eV) ($C_{22}H_{21}ClO_2$): calcd. 352.1230; found 352.1159; Δ = 7.1 mmU. − $C_{22}H_{22}Cl_2O_6$ (453.3): calcd. C 58.29, H 4.89; found C 58.41, H 4.88.

4-Dodecyl-2-(4-methylphenyl)benzo[b]pyrylium Perchlorate (**17e**): Yellow/green powder crystals, yield 0.40 g (65%), m.p. 128−129°C. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, *J* = 6.3 Hz, 3 H), 1.23−1.35 (m, 16 H), 1.45−1.58 (m, 2 H), 1.70−1.95 (m, 2 H), 2.44 (s, 3 H), 3.48 (t, *J* = 7.8 Hz, 2 H), 7.45 (d, *J* = 7.8 Hz, 2 H), 7.94 (t, *J* = 7.5 Hz, 1 H), 8.22 (t, *J* = 7.1 Hz, 1 H), 8.32 (t, *J* = 7.8 Hz, 2 H), 8.46 (d, *J* = 8.1 Hz, 2 H), 8.66 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 22.3, 22.6, 29.2, 29.3, 29.4, 29.5, 29.8, 30.9, 31.8, 34.4, 117.5, 120.2, 123.7, 125.5, 126.4, 130.3, 130.9, 131.3, 139.1, 150.2, 155.2, 173.3, 175.8. − $C_{28}H_{39}ClO_5$ (489.1): calcd. C 68.82, H 7.64; found C 68.92, H 7.77.

4-Dodecyl-2-(4-methylphenyl)naphtho[2,1-b]pyrylium Perchlorate (**17f**): Yellow rhombic crystals, yield 0.37 g (55%), m.p. 164−165.5°C. − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, *J* = 6.3 Hz, 3 H), 1.15−1.50 (m, 16 H), 1.60−1.72 (m, 2 H), 1.95−2.08 (m, 2 H), 2.24 (s, 3 H), 3.78 (t, *J* = 7.8 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 7.82 (t, *J* = 7.4 Hz, 1 H), 7.94 (t, *J* = 8.0 Hz, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 8.22 (d, *J* = 9.1 Hz, 1 H), 8.36 (d, *J* = 8.1 Hz, 2 H), 8.58 (d, *J* = 9.0 Hz, 1 H), 8.64 (d, *J* = 7.2 Hz, 1 H), 8.65 (s, 1 H). − ^{13}C NMR ($CDCl_3$): δ = 14.0, 21.9, 22.6, 29.1, 29.3, 29.4, 29.5, 29.8, 31.8, 39.4, 118.2, 119.4, 122.1, 124.8, 127.0, 127.8, 129.5, 129.8, 130.9, 131.0, 131.2, 132.5, 143.0, 148.6, 158.8, 168.4, 174.3. − $C_{32}H_{39}ClO_5$ (539.1): calcd. C 71.29, H 7.29; found C 71.36, H 7.46.

4-Dodecyl-2-(4-methoxyphenyl)naphtho[2,1-b]pyrylium Perchlorate (**17g**): Fine orange needles, yield 0.40 g (57%), m.p. 200°C. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.3 Hz, 3 H), 1.15−1.50 (m, 16 H), 1.60−1.75 (m, 2 H), 1.92−2.05 (m, 2 H), 3.65−3.76 (m, 5 H), 6.97 (d, *J* = 9.0 Hz, 2 H), 7.82 (t, *J* = 7.4 Hz, 1 H), 7.92 (t, *J* = 8.0 Hz, 1 H), 8.12 (d, *J* = 7.7 Hz, 1 H), 8.20 (d, *J* = 9.1 Hz, 1 H), 8.47 (d, *J* = 9.0 Hz, 2 H), 8.50 (d, *J* = 9.0 Hz, 1 H), 8.56 (s, 1 H), 8.63 (d, *J* = 8.6 Hz, 1 H). -^{13}C NMR ($CDCl_3$): δ = 14.1, 22.6, 29.1, 29.3, 29.5, 29.6, 29.8, 31.9, 39.3, 56.0, 116.0, 118.2, 119.0, 119.6, 121.2, 126.8, 127.9, 129.1, 130.6, 131.1, 132.4, 132.9, 142.0, 158.1, 166.9, 168.3, 172.6. − $C_{32}H_{39}ClO_6$ (555.1): calcd. C 69.24, H 7.08; found C 69.13, H 7.11.

4-Docosyl-2-(4-methylphenyl)naphtho[2,1-b]pyrylium Perchlorate (**21f**): Yellow powder crystals, yield 0.32 g (38%), m.p. 145°C. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, *J* = 6.3 Hz, 3 H), 1.17−1.42 (m, 36 H), 1.60−1.72 (m. 2 H), 1.98−2.02 (m, 2 H), 2.24 (s, 3 H), 3.78 (t, *J* = 7.8 Hz, 2 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.83 (t, *J* = 7.5 Hz, 1 H), 7.94 (t, *J* = 7.8 Hz, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 8.22 (d, *J* = 9.0 Hz, 1 H), 8.35 (d, *J* = 8.4 Hz, 2 H), 8.56 (d, *J* = 9.0 Hz, 1 H), 8.62−8.68 (m, 2 H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.0, 22.6, 29.1, 29.3, 29.4, 29.5, 29.7, 29.8, 31.9, 39.5, 118.2, 119.5, 122.2, 124.9, 127.1, 127.9, 129.5, 129.8, 130.9, 131.0, 131.2, 132.5, 142.9, 148.6, 158.9, 168.5, 174.3. − $C_{42}H_{59}ClO_5$ (679.4): calcd. C 74.25, H 8.75; found C 74.47, H 8.99.

2-(4-Methoxyphenyl)-4-(3-phenylpropyl)benzo[b]pyrylium Perchlorate (**18b**): Dark yellow fine needles, yield 0.27 g (48%), m.p. 159−160.5°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.18−2.25 (m, 2 H), 2.87 (t, *J* = 7.2 Hz, 2 H), 3.37 (t, *J* = 7.8 Hz, 2 H), 4.01 (s, 3 H), 7.15−7.29 (m, 7 H), 7.77−7.83 (m, 1 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 8.05−8.15 (m, 2 H), 8.28 (s, 1 H), 8.44 (d, *J* = 9.0 Hz, 2 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 31.6, 33.5, 35.5, 56.4, 116.4, 116.6, 119.6, 120.2, 123.1, 126.1, 126.5, 128.6, 128.7, 129.8, 133.7, 138.3, 140.4, 154.8, 168.6, 172.5, 172.7. − $C_{25}H_{23}ClO_6$ (454.9): calcd. C 66.01, H 5.10; found C 65.73, H 5.09.

4-(4-Chlorobutyl)-2-(4-methylphenyl)benzo[b]pyrylium Perchlorate (**19e**): Green/yellow fine needles, yield 0.36 g (70%), m.p. 116°C. − ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.98−2.12 (m, 4 H), 2.44 (s, 3 H), 3.45−3.55 (m, 2 H), 3.56−3.70 (m, 2 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.92 (t, *J* = 7.4 Hz, 1 H), 8.17−8.27 (m, 2 H), 8.35−8.45 (m, 3 H), 8.68 (s, 1 H). − ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.3, 27.6, 32.0, 33.3, 44.5, 117.5, 120.0, 123.7, 125.4, 126.6, 130.4, 130.9, 131.3, 139.1, 150.4, 155.2, 173.4, 175.0. − $C_{20}H_{20}Cl_2O_5$ (411.3): calcd. C 58.41, H 4.90; found C 58.60, H 4.99.

4-(4-Chlorobutyl)-7-diethylamino-2-(4-methoxyphenyl)-benzo[b]pyrylium Perchlorate (**19c**): Sparkling green/blue needles,

yield 0.31 g (50%), m.p. 229°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D) : δ = 1.33 (t, *J* = 7.1 Hz, 6 H), 1.98–2.06 (m, 4 H), 3.21–3.29 (m, 2 H), 3.65 (t, *J* = 5.2 Hz, 2 H), 3.76 (q, *J* = 7.1 Hz, 4 H), 4.0 (s, 3 H), 7.18 (d, *J* = 9.0 Hz, 2 H), 7.53–7.61 (m, 2 H), 7.85 (s, 1 H), 8.19 (d, *J* = 9.9 Hz, 1 H), 8.32 (d, *J* = 9.0 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 11.5, 27.1, 31.8, 32.5, 44.1, 49.5, 56.2, 112.1, 112.2, 112.3, 116.2, 119.6, 120.8, 128.7, 132.0, 132.2, 151.5 157.5, 167.2, 167.3. – $C_{24}H_{29}Cl_2NO_6$ (498.4): calcd. C 57.84, H 5.86, N 2.81; found C 57.89, H 5.98, N 2.84.

4-(3-Chloropropyl)-2-(4-methoxyphenyl)naphtho[2,1-b]pyrylium Perchlorate (**22g**): Sparkling dark orange needles, yield 0.34 g (59%), m.p. 230°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.48–2.60 (m, 2 H), 3.84–4.00 (m, 7 H), 7.16 (d, *J* = 8.1 Hz, 2 H), 7.89 (t, *J* = 7.5 Hz, 1 H), 7.99 (t, *J* = 7.8 Hz, 1 H), 8.09 (d, *J* = 9.0 Hz, 1 H), 8.17 (d, *J* = 8.1 Hz, 1 H), 8.42 (d, *J* = 8.4 Hz, 2 H), 8.48 (s, 1 H), 8.57 (d, *J* = 9.0 Hz, 1 H), 8.85 (d, *J* = 8.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 30.9, 36.7, 44.3, 56.2, 112.5, 116.2, 116.4, 117.4, 118.8, 119.7, 121.6, 127.1, 127.9, 129.6, 131.2, 132.5, 142.5, 158.5, 167.6, 168.8, 170.7. – $C_{23}H_{20}Cl_2O_6$ (463.3): calcd. C 59.63, H 4.35; found C 59.49, H 4.28.

4-(4-Chlorobutyl)-2-(4-methylphenyl)naphtho[2,1-b]pyrylium Perchlorate (**19f**): Dark yellow fine needles, yield 0.36 g (62%), m.p. 157°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.14–2.32 (m, 4 H), 2.48 (s, 3 H), 3.72 (t, *J* = 6.0 Hz, 2 H), 3.85 (t, *J* = 7.8 Hz, 2 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.91 (t, *J* = 7.4 Hz, 1 H), 8.02 (t, *J* = 7.2 Hz, 1 H), 8.14 (d, *J* = 9.0 Hz, 1 H), 8.19 (d, *J* = 7.5 Hz, 1 H), 8.32 (d, *J* = 8.3 Hz, 2 H), 8.55 (s, 1 H), 8.62 (d, *J* = 9.1 Hz, 1 H), 8.75 (d, *J* = 8.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.1, 25.9, 32.0, 38.5, 44.2, 117.5, 118.8, 122.5, 124.9, 127.2, 127.9, 129.5, 129.9, 131.3, 131.4, 131.5, 132.6, 143.4, 149.6, 159.2, 169.2, 173.2. – HRMS (70 eV) ($C_{24}H_{21}ClO$): calcd. 360.1281; found 360.1275; Δ = 0.6 mmU.

4-(4-Chlorobutyl)-2-(4-methoxyphenyl)naphtho[2,1-b]pyrylium Perchlorate (**19g**): Orange microcrystals, yield 0.36 g (61%), m.p. 219°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.10–2.30 (m, 4 H), 3.71 (t, *J* = 5.7 Hz, 2 H), 3.80 (t, *J* = 7.2 Hz, 2 H), 3.96 (s, 3 H), 7.18 (d, *J* = 8.7 Hz, 2 H), 7.89 (t, *J* = 7.6 Hz, 1 H), 8.00 (t, *J* = 7.4 Hz, 1 H), 8.09 (d, *J* = 9.1 Hz, 1 H), 8.18 (d, *J* = 7.9 Hz, 1 H), 8.42 (d, *J* = 8.2 Hz, 2 H), 8.44 (s, 1 H), 8.57 (d, *J* = 9.0 Hz, 1 H), 8.73 (d, *J* = 8.4 Hz, 1 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 25.9, 32.0, 38.4, 44.2, 56.2, 116.4, 117.4, 118.3, 119.7, 121.6, 126.9, 128.1, 129.6, 131.3, 132.4, 132.6, 142.5, 158.5, 167.6, 168.9, 171.6. – $C_{24}H_{22}Cl_2O_6$ (477.3): calcd. C 60.39, H 4.65; found C 60.19, H 4.59.

General Procedure for the Preparation of the Bisbenzo[b]pyrylium Bisperchlorates **12**,**13** *and* **20**: The procedure used was the same as for the benzo[*b*]pyrylium salts described above, except that half one equivalent of electrophile was used (0.63 mmol). The products were recrystallized from glacial acetic acid/nitromethane (10:1, v/v).

1,4-Bis{5,6-dihydro-3-methoxy(naphtho[1,2-b]benzo[e]pyrylium-7-yl)}butane Bisperchlorate (**13b**): Yellow powder crystals, yield 0.27 g (55%), m.p. 323°C (decomposed). – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 2.04–2.16 (m, 4 H), 3.20–3.50 (m, 12 H), 4.03 (s, 6 H), 7.00 (d, *J* = 1.9 Hz, 2 H), 7.11 (dd, *J* = 2.2 Hz, *J* = 9.0 Hz, 2 H), 7.88 (t, *J* = 6.6 Hz, 2 H), 8.01–811 (m, 4 H), 8.32 (d, *J* = 8.3 Hz, 2 H), 8.37 (d, *J* = 9.1 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.6, 27.0, 29.7, 30.0, 56.3, 114.1, 116.9, 118.5, 119.0, 123.5, 126.4, 127.7, 130.0, 131.8, 137.1, 149.9, 153.7, 166.2, 169.0, 170.0. – HRMS-FAB ($C_{40}H_{36}O_4$): calcd. 580.2614; found 580.2643; Δ = 2.9 mmU. – $C_{40}H_{36}Cl_2O_{12}$ (779.6): calcd. C 61.62, H 4.65; found C 61.13, H 4.70.

1,10-Bis{5,6-dihydro(naphtho[1,2-b]benzo[e]pyrylium-7-yl)}decane Bisperchlorate (**12a**): Pale yellow powder crystals, yield 0.35 g (71%), m.p. 268°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.28–1.45 (m, 8 H), 1.58–1.68 (m, 4 H), 1.72–1.83 (m, 4 H), 3.25–3.32 (m, 4 H), 3.38–3.49 (m, 8 H), 7.52 (d, *J* = 7.5 Hz, 2 H), 7.61 (t, *J* = 7.6 Hz, 2 H), 7.80 (t, *J* = 7.4 Hz, 2 H), 7.93–7.99 (m, 2 H), 8.17–8.24 (m, 4 H), 8.34 (d, *J* = 8.5 Hz, 2 H), 8.42 (d, *J* = 8.0 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.5, 26.4, 29.1, 29.2, 30.2, 30.5, 30.8, 119.7, 124.3, 125.6, 126.5, 128.4, 128.7, 129.2, 129.6, 130.6, 138.6, 145.2, 154.4, 170.3, 172.0. – HRMS (70 eV) ($C_{44}H_{42}O_2$): calcd. 602.3185; found 602.3162; Δ = 2.3 mmU. – $C_{44}H_{44}Cl_2O_{10}$ (803.7): calcd. C 65.75, H 552; found C 65.45, H 5.50.

1,10-Bis{3-methoxy-5,6-dihydro(naphtho[1,2-b]benzo[e]pyrylium-7-yl)}decane Bisperchlorate (**12b**): Deep yellow powder crystals, yield 0.50 g (93%), m.p. 263°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.25–1.40 (m, 8 H), 1.55–1.62 (m, 4 H), 1.70–1.78 (m, 4 H), 3.20–3.35 (m, 12 H), 4.02 (s, 6 H), 7.00 (s, 2 H), 7.11 (dd, *J* = 2.2 Hz, *J* = 9.0 Hz, 2 H), 7.80–7.89 (m, 2 H), 8.03–8.12 (m, 4 H), 8.21 (d, *J* = 8.3 Hz, 2 H), 8.38 (d, *J* = 8.9 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 23.5, 27.0, 29.1, 29.2, 30.1, 30.2, 30.3, 56.4, 114.2, 116.7, 118.4, 119.2, 123.4, 126.2, 127.0, 129.7, 131.8, 137.1, 149.3, 153.6, 167.7, 168.9, 169.6. – $C_{46}H_{48}Cl_2O_{12}$ (863.8): calcd. C 63.96, H 5.60; found C 63.52, H 5.63.

1,10-Bis{7-diethylamino-5,6-dihydro-3-methoxy(naphtho[1,2-b]benzo[e]pyrylium-7-yl)}decane Bisperchlorate (**12c**): Violet/purple powder crystals, yield 0.47 g (74%), m.p. 283°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.31 (t, *J* = 7.1 Hz, 12 H), 1.35–1.49 (m, 8 H), 1.61–1.69 (m, 4 H), 1.72–1.82 (m, 4 H), 3.25–3.40 (m, 12 H), 3.90 (q, *J* = 7.1 Hz, 8 H), 4.09 (s, 6 H), 7.05 (d, *J* = 1.7 Hz, 2 H), 7.18 (dd, *J* = 2.0 Hz, *J* = 9.0 Hz, 2 H), 7.99 (dd, *J* = 1.8 Hz, *J* = 8.9 Hz, 2 H), 8.33 (d, *J* = 1.7 Hz, 2 H), 8.47 (d, *J* = 9.1 Hz, 2 H), 8.51 (d, *J* = 9.1 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 10.0, 10.2, 23.8, 27.0, 29.3, 29.4, 30.4, 30.5, 55.3, 56.6, 115.0, 117.4, 118.3, 122.2, 124.3, 128.9, 129.0, 129.9, 133.6, 143.2, 151.0, 153.6, 165.4, 171.0, 171.1. – HRMS-FAB ($C_{54}H_{66}N_2O_4$): calcd. 806.5023; found 806.4953; Δ = 7.0 mmU. – $C_{54}H_{66}Cl_2N_2O_{12}$ (1006.0): calcd. C 64.47, H 6.61, N 2.78; found C 64.27, H 6.64, N 2.85.

1,10-Bis{2-(4-methylphenyl)benzo[b]pyrylium-4-yl)}decane Bisperchlorate (**20e**): Pale yellow/green powder crystals, yield 0.16 g (33%), m.p. 208°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.24–1.48 (m, 8 H), 1.50–1.62 (m, 4 H), 1.86–1.98 (m, 4 H), 2.52 (s, 6 H), 4.44 (t, *J* = 7.5 Hz, 4 H), 7.52 (d, *J* = 8.1 Hz, 4 H), 7.92–7.98 (m, 2 H), 8.18–8.28 (m, 4 H), 8.34 (d, *J* = 6.0 Hz, 2 H), 8.37 (d, *J* = 7.9 Hz, 4 H), 8.46 (s, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.2, 28.7, 28.8, 29.6, 30.4, 34.5, 116.8, 119.8, 123.8, 125.4, 126.5, 130.4, 130.5, 131.4, 139.3, 150.9, 155.4, 173.6, 175.7. – $C_{42}H_{44}Cl_2O_{10}$ (778.2): calcd. C 64.76, H 5.70; found C 64.48, H 5.70.

1,10-Bis{2-(4-methylphenyl)naphtho[2,1-b]pyrylium-4-yl)}decane Bisperchlorate (**20f**): Dark yellow powder crystals, yield 0.48 g (87%), m.p. 231°C. – ^{1}H NMR ($CDCl_3$/CF_3CO_2D): δ = 1.35–1.52 (m, 8 H), 1.60–1.75 (m, 4 H), 1.98–2.12 (m, 4 H), 2.43 (s, 6 H), 3.76 (t, *J* = 7.8 Hz, 4 H), 7.46 (d, *J* = 8.2 Hz, 4 H), 7.86 (t, *J* = 7.5 Hz, 2 H), 7.99 (t, *J* = 7.5 Hz, 2 H), 8.12 (d, *J* = 8.7 Hz, 2 H), 8.15 (d, *J* = 6.1 Hz, 2 H), 8.32 (d, *J* = 8.1 Hz, 4 H), 8.52 (s, 2 H), 8.58 (d, *J* = 9.0 Hz, 2 H), 8.69 (d, *J* = 8.4 Hz, 2 H). – ^{13}C NMR ($CDCl_3$/CF_3CO_2D): δ = 22.0, 28.7, 28.8, 29.5, 39.5, 117.6, 118.8, 122.3, 124.8, 127.1, 127.9, 129.5, 129.7, 131.2, 131.3,

132.5, 143.2, 149.2, 159.0, 168.8, 174.2. – $C_{50}H_{48}Cl_2O_{10}$ (879.8): calcd. C 68.26, H 5.50; found C 67.98, H 5.45.

☆ Dedicated to Professor *H. Hartmann* (Merseburg) on the occasion of his 60th birthday.

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