Four-Step Route to Novel Bisflavylium Dications – First Synthesis of Phloroglucinol-Type Derivatives

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Received: 09.05.2012; Accepted after revision: 08.06.2012

Abstract: Various bisflavylium dications have been prepared in an efficient four-step manner utilizing the acid-mediated condensation between bis(arylethynylketones) and activated phenols as the key step. Of special note is that phloroglucinol-type bisflavylium salts have been obtained for the first time thanks to this procedure.

Key words: chromophores, condensation, flavylium, phenols, polycations

The flavylium skeleton **1** is an organic chromophore of particular relevance because of the characteristic of anthocyanins, the most widespread class of natural pigments after chlorophylls (Figure 1).[1] Natural flavylium-containing pigments are indeed responsible for a wide range of colors (from shades of red to blue) of flowers, fruits and man-made red wine.[2] Their aptitude for imprinting colors of almost the whole visible spectrum is related to diverse parameters such as pH, complexation with either metal ions (metalloanthocyanins) or aromatic compounds (copigmentation), as well as the structure of the pigments themselves (i.e., the nature and the position of the functional groups attached to **1**).[1,3] In addition, flavylium-based pigments **1** possess an inherent chemical reactivity that pushes these native cationic structures into a well-established network of chemical equilibria giving birth to mixtures of structurally and thus color-modified species.[3d,4] The position of the resulting and reversible multistate/multifunctional system is of course governed by previously mentioned parameters (i.e., pH, complexation, and pigments' structure).[3d]

Profiting from this palette of attractive physico-chemical properties, research on flavylium-based pigments has undergone great advances in the last 30 years.[1,3d] Thus, natural and synthetic derivatives have been suggested as food colorants,[5] hair[6] and laser[7] dyes, sensitizers for solar cells,[8] water/humidity sensors,[9] molecular-level optical memories and logic gates.[10] Interestingly, flavylium salts are also attracting keen interest due to their potent beneficial effects on human health, various flavylium salts having been identified as authentic bioactive species[11] and more recently as in vitro precursors of bioactive species.[12]

Being involved in flavylium chemistry,[1m,2d,12,13] we were aware of the possibility of designing novel flavylium-containing compounds that could further improve their properties. We thus became interested in non-natural biflavylium dications that are surprisingly scarce in the literature (Figure 1). Indeed, only a handful of reports deal with such dicationic species despite their attractiveness both in terms of structures and applications.

To date, various bisflavylium ions connected via their C4 positions, in a direct manner (i.e., compound **2**) or via a

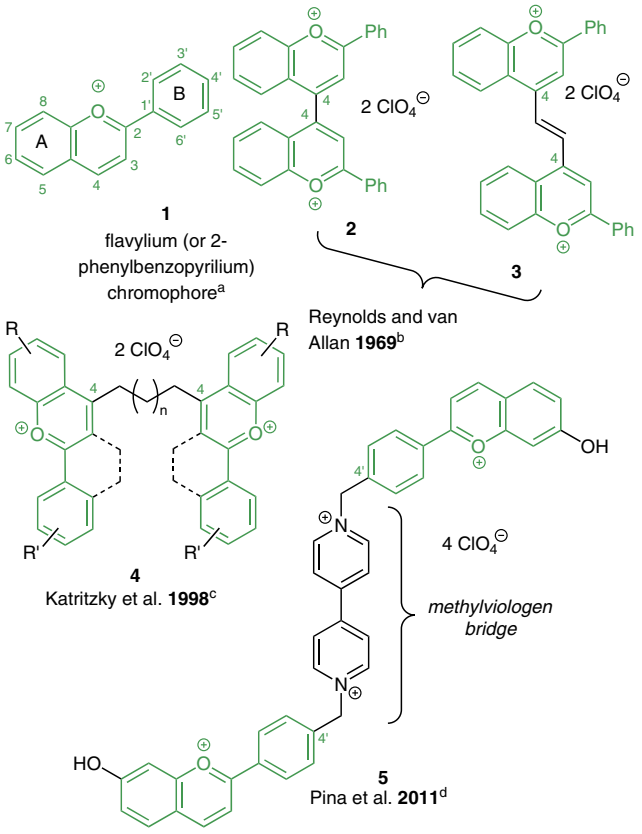
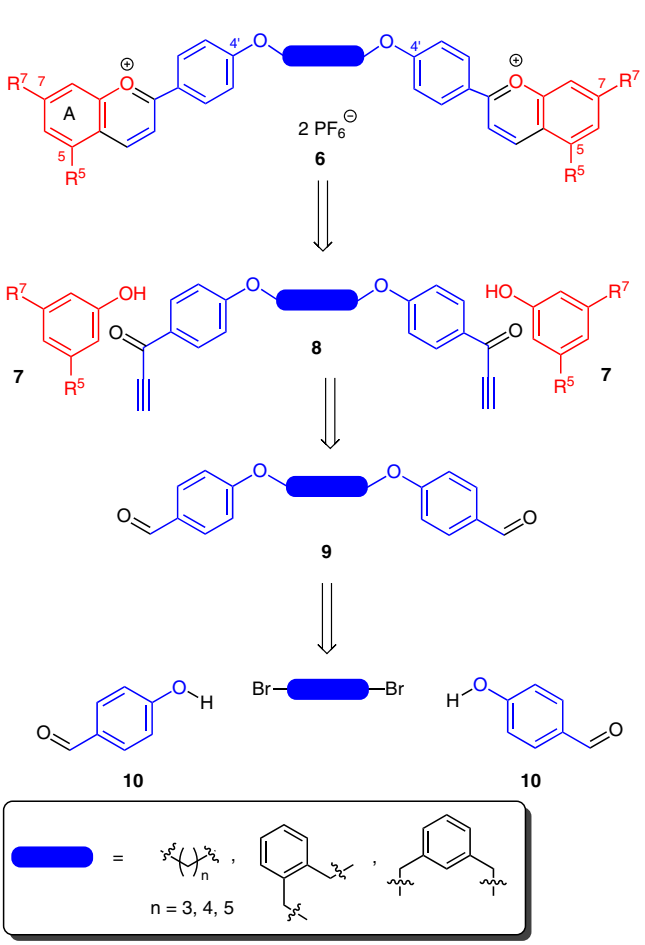


Figure 1 Structure of the flavylium chromophore **1** and summary of the bisflavylium skeletons **2**–**5** reported so far in the literature. [a] The numbering is indicated according to flavonoid nomenclature; [b] see ref. 14; [c] see ref. 15; [d] see ref. 16.

SYNLETT 2012, 23, 2053–2058
Advanced online publication: 08.08.2012
DOI: 10.1055/s-0032-1316681; Art ID: ST-2012-D0402-L

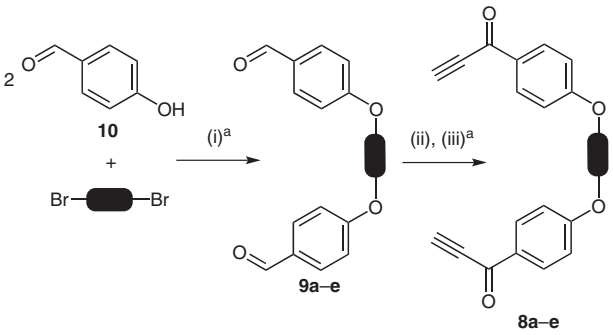
carbon chain unit (i.e., compounds **3** and **4**), have been reported in the literature and proved to exhibit promising UV/Vis absorption/fluorescence features.[14,15] From a synthetic point of view, the preparation of dications **2**–**4** relies on a common approach, that is, the functionalization/dimerization of a precursor already featuring the C6–C3–C6 structure peculiar to flavonoids. Very recently, Pina et al. described the synthesis of the symmetric bisflavylium **5** linked via their C4′ positions by a methyl viologen bridge.[16] The authors succeeded in the synthesis of this unique tetracationic framework through standard acid-catalyzed Robinson condensation.[17] Interestingly enough, the multistate/multifunctional behavior of **5** was investigated and proved to be influenced by a cooperative effect of the two covalently linked photochromic systems. Of particular note is that all reported methods are generally low-to-modest yielding and display a restricted substrate scope regarding the A-ring substitution, especially in the case of phloroglucinol-type A-ring which is the most frequent motif encountered in natural flavylium-based pigments.

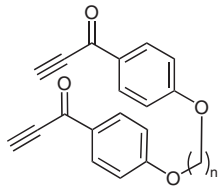
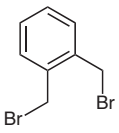
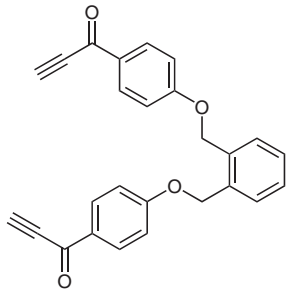
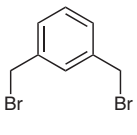
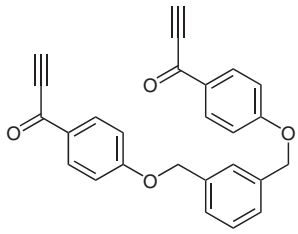
In this letter, we describe the synthesis of a series of novel bisflavylium dications **6** linked via their C4′ positions by more or less flexible aliphatic/aromatic spacers (Scheme 1). In order to construct such dicationic species, we planned to evaluate for the first time the potential of the acid-catalyzed condensation between phenolic derivatives **7** and bis(arylethynylketones) **8**, a well-known method for preparing monocationic flavylium salts recently revisited by us.[13a,b] Worth mentioning here is that we also concentrated on phloroglucinol-type bisflavylium salts whose synthesis and physicochemical properties have never been reported so far in the literature (Scheme 1, with $R^5 = R^7 = OH$).



Scheme 1 Retrosynthetic analysis

Table 1 Preparation of Bis(arylethynylketones) **8a–e**



Entry	Br—⬭—Br	Product **8**	Overall isolated yield (%)[b]
1 2 3	Br—(CH2)n—Br	 **8a** n = 3 **8b** n = 4 **8c** n = 5	**8a** 74 **8b** 81 **8c** 82
4		 **8d**	91
5		 **8e**	81

[a] Reaction conditions: (i) **10** (2.4 equiv), K_2CO_3 (3.0 equiv), DMF, 100 °C, 12 h (84–97% yield); (ii) ≡–MgBr (2.6 equiv), THF, 0 °C to r.t. (84–99% yield); (iii) IBX (4.0 equiv), EtOAc, 80 °C, 12 h (85–99% yield).

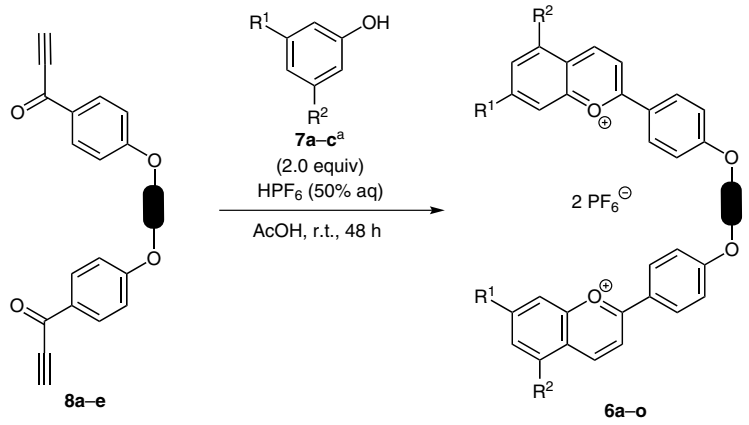
[b] See Supporting Information for the characterization data of all compounds.

Starting from commercially available *p*-hydroxybenzaldehyde (**10**, Scheme 1), we first prepared via a three-step sequence a series of five bis(arylethynylketones) **8a–e** featuring spacers of diverse length and nature (Table 1). The sequence began with a known procedure consisting in coupling two equivalents of **10** with diverse dibrominated alkylating agents.[18] This coupling step via O-alkylation of **10** allowed the efficient formation of bis(benzaldehydes) **9a–e** in which native phenolic moieties are separated by 3-, 4-, and 5-carbon aliphatic units (**9a–c**) as well as 4- and 5-carbon units possessing an aromatic residue (**9d**,**e**). Bis(benzaldehydes) **9a–e** were then submitted to a nucleophilic addition–oxidation sequence to furnish the expected bis(arylethynylketones) **8a–e**. The nucleophilic addition of ethynylmagnesium bromide to both aldehydic functions of **9a–e** resulted in bis(prop-2-yn-1-ol) intermediates which were smoothly oxidized by IBX to the corresponding bis(ynones) **8a–e**.[19] Noteworthy is that this three-step sequence enabled the access to the desired bis(arylethynylketones) in a straightforward and efficient manner, **8a–e** being obtained in good to excellent overall yields (i.e., from a 74% yield for **8a** to 91% for **8d**).

With these five bis(arylethynylketone) building blocks **8a–e** in hand, we then investigated the key condensation step proposed to furnish the targeted bisflavylium cations. To this end, we considered three phenolic derivatives **7a–c** as condensation partners [i.e., resorcinol (**7a**), 3,5-dimethoxyphenol (**7b**), and phloroglucinol (**7c**)] and submitted all **7**/**8** combinations to the condensation conditions we reported recently (acetic acid as solvent in the presence of aqueous hexafluorophosphoric acid, Table 2).[13a,b] After 48 hours stirring at room temperature, each of the 15 possible bisflavylium salts **6a–o** precipitated out in the medium and were obtained in almost quantitative yields, no trace of product resulting from a monocondensation event being detected in the crude material.

Interestingly enough, all pigments **6a–o** were only washed with a little volume of diethyl ether, thus meeting most criteria of a 'click chemistry' reaction.[20] Furthermore, the biscondensation of resorcinol (**7a**) with each of the ketonic partners **8a–e** occurred in a highly regioselective manner (Table 2, entries 1–3, 10, and 13). Under these conditions, the only dicationic regioisomer to be formed exhibited two 7-hydroxyflavylium moieties, with no trace of a 5-hydroxyflavylium moiety being detected by NMR spectroscopic analysis of the crude products. This regiochemical outcome is in full agreement with our recent monocondensation experiments.[13a]

Table 2 Synthesis of Bisflavylium Dications via the Acid-Mediated Condensation of Bis(arylethynylketones) **8a–e** and Activated Phenols **7a–c**



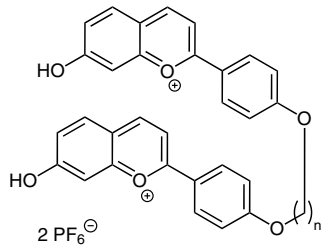
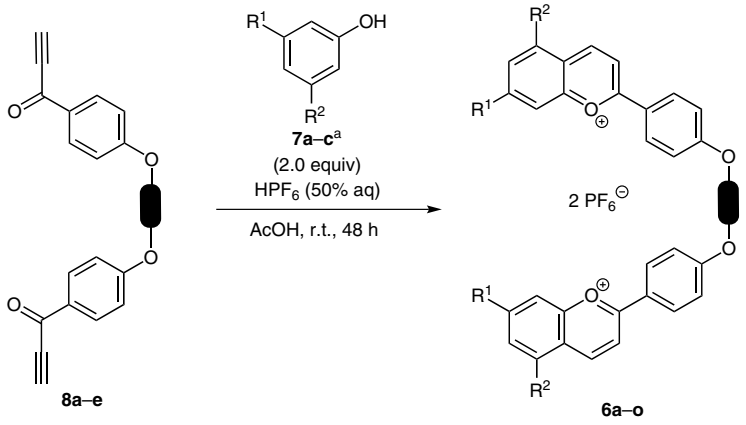
Entry	Phenol **7**	Product **6**	Isolated yield (%)[b]
1–3	**7a**	 **6a** n = 3 **6b** n = 4 **6c** n = 5	**6a** 95 **6b** 99 **6c** 99

Table 2 Synthesis of Bisflavylium Dications via the Acid-Mediated Condensation of Bis(arylethynylketones) **8a–e** and Activated Phenols **7a–c** (continued)



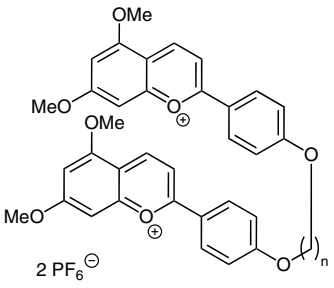
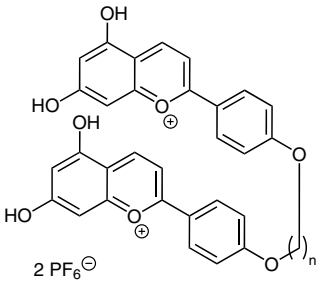
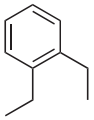
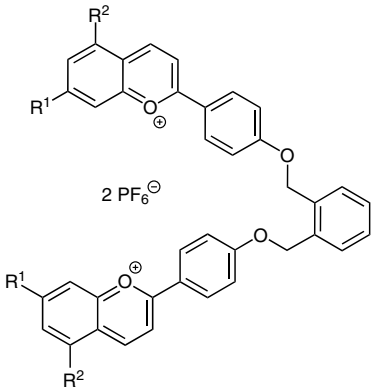
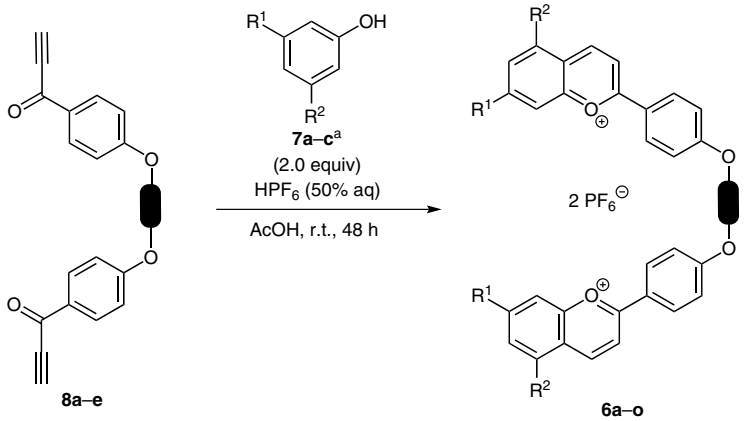
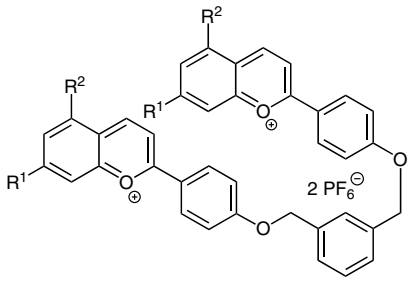
Entry	Phenol **7**		Product **6**	Isolated yield (%)[b]
4–6	**7b**		 **6d** n = 3 **6e** n = 4 **6f** n = 5	**6d** 95 **6e** 98 **6f** 94
7–9	**7c**		 **6g** n = 3 **6h** n = 4 **6i** n = 5	**6g** 95 **6h** 99 **6i** 99
10–12	**7a–c**		 **6j** R^1 = OH; R^2 = H **6k** R^1 = R^2 = OMe **6l** R^1 = R^2 = OH	**6j** 95 **6k** 98 **6l** 99

Table 2 Synthesis of Bisflavylium Dications via the Acid-Mediated Condensation of Bis(arylethynylketones) **8a–e** and Activated Phenols **7a–c** (continued)



Entry	Phenol **7**	Product **6**	Isolated yield (%)[b]
13–15	**7a–c**		**6m** 94 **6n** 99 **6o** 92

6m R^1 = OH; R^2 = H
6n R^1 = R^2 = OMe
6o R^1 = R^2 = OH

[a] Compound **7a**: R^1 = OH, R^2 = H; compound **7b**: R^1 = R^2 = OMe; compound **7b**: R^1 = R^2 = OH.
[b] See Supporting Information for the characterization data of all dications, spectroscopic data for **6a**,**g** are being given in ref.[21,22] as illustrative examples.

In conclusion, we have developed an expeditious and highly efficient procedure (i.e., overall yields of 70–90%) for the synthesis of bisflavylium skeletons. The key final step of the sequence consists in the facile acid-mediated biscondensation of activated phenols and easy-to-prepare bis(arylethynylketones), thus expanding the scope of this 'click chemistry'-like protocol. Of particular interest is that this procedure allowed the successful access for the first time to bisflavylium pigments composed of two phloroglucinol-type (i.e., 5,7-dihydroxylated) flavylium moieties. This four-step route is thus alternative but, above all, complementary to the routes reported so far in the literature for accessing to such dicationic patterns.[14–16] These dicationic pigments represent novel and attractive bichromophoric materials whose physicochemical properties and potential applications are currently explored.

While the present work only focused on B-ring 4′,4′-linked bisflavylium dications, one can easily conceive the application of the sequence for preparing a wider range of derivatives, going from regioisomeric B-ring linked bisflavylium to triflavylium or even oligoflavylium cations. Further work is now under way in those respects and will be published in due time.

Typical Procedure for the Acid-Mediated Condensation of Phenolic Derivatives with Bis(arylethynylketones)
To a solution of phenol **7** (1.0 mmol, 2.0 equiv) and bis(arylethynylketone) **8** (0.5 mmol, 1.0 equiv) in AcOH (2 mL) was added aqueous HPF_6 (0.5 mL, 50% in H_2O). The solution, becoming immediately dark red, was stirred at r.t. for 48 h. The resulting mixture was then poured into Et_2O (20 mL) when the bisflavylium dihexafluorophosphate precipitated. The orange to red solid was recovered by filtration, washed with Et_2O, and finally dried under vacuum to give the required dicationic species **6** in pure form. Recrystallization from AcOH was performed when necessary.

Acknowledgment

The authors thank the CNRS and the French Ministry of Research for financial supports.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

References and Notes

(1) (a) Timberlake, C. F.; Bridle, P. In *The Flavonoids*; Harborne, J. B.; Mabry, T. J.; Mabry, H., Eds.; Chapman and Hall: London, **1975**, 21. (b) Brouillard, R. *Phytochemistry*

1977, *22*, 1311. (c) Hrazdina, G. In *The Flavonoids: Advances in Research*; Harborne, J. B.; Mabry, T. J., Eds.; Chapman and Hall: London, **1982**, 135. (d) Harborne, J. B.; Grayer, R. J. In *The Flavonoids: Advances in Research since 1980*; Harborne, J. B., Ed.; Chapman and Hall: London, **1988**. (e) Strack, D.; Wray, V. In *The Flavonoids: Advances in Research since 1986*; Harborne, J. B., Ed.; Chapman and Hall: London, **1994**, 1. (f) Harborne, J. B.; Williams, C. A. *Nat. Prod. Rep.* **1998**, *15*, 631. (g) Harborne, J. B.; Williams, C. A. *Nat. Prod. Rep.* **2001**, *18*, 310. (h) Williams, C. A.; Grayer, R. J. *Nat. Prod. Rep.* **2004**, *21*, 539. (i) Andersen, O. M.; Jordheim, M. In *Flavonoids: Chemistry, Biochemistry and Applications*; Andersen, O. M.; Markham, K. R., Eds.; CRC Press: Boca Raton, **2006**, 471. (j) Andersen, O. M. In *Recent Advances in Polyphenol Research*, Vol. 1; Daayf, F.; Lattanzio, V., Eds.; Wiley-Blackwell: Chichester, **2008**, 167. (k) *Anthocyanins – Biosynthesis, Functions, and Applications*; Gould, K.; Davies, K.; Winefield, C., Eds.; Springer: New York, **2009**. (l) Yoshida, K.; Mori, M.; Kondo, T. *Nat. Prod. Rep.* **2009**, *26*, 884. (m) Brouillard, R.; Chassaing, S.; Isorez, G.; Kueny-Stotz, M.; Figueiredo, P. In *Recent Advances in Polyphenol Research*, Vol. 2; Santos-Buelga, C.; Escribano-Bailon, M. T.; Lattanzio, V., Eds.; Wiley-Blackwell: Chichester, **2010**, 1.

(2) (a) Somers, T. C. *Phytochemistry* **1971**, *10*, 2175. (b) Liao, H.; Cai, Y.; Haslam, E. *J. Sci. Food Agric.* **1992**, *59*, 299. (c) Rivas-Gonzalo, J. C.; Santos-Buelga, C. In *Polyphenols, Wine and Health*; Chèze, C.; Vercauteren, J.; Verpoorte, R., Eds.; Kluwer: Dordrecht, **2001**, 99. (d) Brouillard, R.; Chassaing, S.; Fougerousse, A. *Phytochemistry* **2003**, *64*, 1179. (e) Quideau, S.; Jourdes, M.; Lefeuvre, D.; Montaudon, D.; Saucier, C.; Glories, Y.; Pardon, P.; Teissedre, P.-L. *Chem. Eur. J.* **2005**, *11*, 6503. (f) de Freitas, V. A. P.; Mateus, N. In *Recent Advances in Polyphenol Research*, Vol. 2; Santos-Buelga, C.; Escribano-Bailon, M. T.; Lattanzio, V., Eds.; Wiley-Blackwell: Chichester, **2010**, 59. (g) Chassaing, S.; Lefeuvre, D.; Jacquet, R.; Jourdes, M.; Ducasse, L.; Galland, S.; Grelard, A.; Saucier, C.; Teissedre, P.-L.; Dangles, O.; Quideau, S. *Eur. J. Org. Chem.* **2010**, 55.

(3) (a) Brouillard, R. In *The Flavonoids: Advances in Research since 1980*; Harborne, J. B., Ed.; Chapman and Hall: London, **1988**, 525. (b) Goto, T.; Kondo, T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 17. (c) Boulton, R. *Am. J. Enol. Vitic.* **2001**, *52*, 67. (d) Pina, F.; Melo, M. J.; Laia, C. A. T.; Parola, A. J.; Lima, J. C. *Chem. Soc. Rev.* **2012**, *41*, 869.

(4) (a) Brouillard, R.; Dubois, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 1359. (b) Brouillard, R.; Delaporte, B. *J. Am. Chem. Soc.* **1977**, *99*, 8461.

(5) (a) *Anthocyanins as Food Colors*; Markakis, P., Ed.; Academic Press: London, **1982**. (b) Iacobucci, G. A.; Sweeny, J. G. *Tetrahedron* **1983**, *39*, 3005. (c) Francis, F. J. *Trends Food Sci. Tech.* **1992**, *3*, 27.

(6) (a) Darmenton, P.; Philippe, M. FR 2757383, **1996**; *Chem. Abstr.* **1998**, *129*, 140458n (b) Sauter, G.; Braun, H.-J.; Brouillard, R.; Fougerousse, A.; Roehri-Stoeckel, C. WO 03000214 A1, **2003**.

(7) Czerney, P.; Graness, G.; Birckner, E.; Vollmer, F.; Rettig, W. *J. Photochem. Photobiol. A* **1995**, *89*, 31.

(8) (a) Cherepy, N. J.; Smestad, G. P.; Grätzel, M.; Zhang, J. Z. *J. Phys. Chem. B* **1997**, *101*, 9342. (b) Sirimanne, P. M.; Senevirathna, M. K. I.; Premalal, P. K. D.; Pitigala, P. K. D. D. P. *Semicond. Sci. Technol.* **2006**, *21*, 818. (c) Sirimanne, P. M.; Senevirathna, M. K. I.; Pitigala, P. K. D. D. P.; Sivakumar, V.; Tennakone, K. *J. Photochem. Photobiol. A* **2006**, *177*, 324.

(9) Galindo, F.; Lima, J. C.; Luis, S. V.; Melo, M. J.; Parola, A. J.; Pina, F. *J. Mater. Chem.* **2005**, *15*, 2840.

(10) (a) Pina, F.; Maestri, M.; Balzani, V. *Chem. Commun.* **1999**, 107. (b) Maestri, M.; Pina, F.; Balzani, V. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, **2001**, 309. (c) Pina, F.; Maestri, M.; Balzani, V. In *Handbook of Photochemistry and Photobiology*; Nalwa, H. S., Ed.; American Scientific Publishers: Valencia, USA, **2003**, 411. (d) Pina, F.; Parola, A. J.; Gomes, R.; Maestri, M.; Balzani, V. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, **2012**, 181. (e) Pina, F.; Petrov, V.; Laia, C. A. T. *Dyes Pigments* **2012**, *92*, 877.

(11) Kong, J.; Chia, L.; Goh, N.; Chia, T.; Brouillard, R. *Phytochemistry* **2003**, *64*, 923.

(12) (a) Kueny-Stotz, M.; Chassaing, S.; Brouillard, R.; Nielsen, M.; Goeldner, M. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 4864. (b) Jiang, R.; Miyamoto, A.; Martz, A.; Specht, A.; Ishibashi, H.; Kueny-Stotz, M.; Chassaing, S.; Brouillard, R.; de Carvalho, L. P.; Goeldner, M.; Nakebura, J.; Nielsen, M.; Grutter, T. *Brit. J. Pharmacol.* **2011**, *162*, 1326.

(13) (a) Chassaing, S.; Kueny-Stotz, M.; Isorez, G.; Brouillard, R. *Eur. J. Org. Chem.* **2007**, 2438. (b) Kueny-Stotz, M.; Isorez, G.; Chassaing, S.; Brouillard, R. *Synlett* **2007**, 1067. (c) Chassaing, S.; Isorez, G.; Kueny-Stotz, M.; Brouillard, R. *Tetrahedron Lett.* **2008**, *49*, 6999.

(14) For bisflavylium ions **2** and **3**, see: Reynolds, G. A.; van Allan, J. A. *J. Heterocycl. Chem.* **1969**, *6*, 623.

(15) For biflavylium **4**, see: Katritzky, A. R.; Czerney, P.; Level, J. R.; Du, W. *Eur. J. Org. Chem.* **1998**, 2623.

(16) Diniz, A. M.; Pinheiro, C.; Petrov, V.; Parola, A. J.; Pina, F. *Chem. Eur. J.* **2011**, *17*, 6359.

(17) (a) Robinson, R.; Pratt, D. D. *J. Chem. Soc.* **1922**, 1577. (b) Kuhnert, N.; Clifford, M. N.; Radenac, A.-G. *Tetrahedron Lett.* **2001**, *42*, 9261. (c) Mas, T. *Synthesis* **2003**, 1878.

(18) Zhou, Z.; Schuster, D. I.; Wilson, S. R. *J. Org. Chem.* **2006**, *71*, 1545.

(19) More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001.

(20) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

(21) **Resorcinol-Type Dication 6a**
Yellow powder; yield 95%. IR (KBr): 3380 (OH), 1635 (C=O), 855 (PF) cm^{-1}. UV/Vis (MeCN–10% 1 N HCl): λ_{max} (ε) = 262 (15700), 466 (38600 M^{-1} cm^{-1}) nm. ^1H NMR (500 MHz, CD_3CN–1% TFA-d_1): δ = 2.37 (quin, *J* = 5.9 Hz, 2 H), 4.40 (t, *J* = 5.9 Hz, 4 H), 7.23 (m, 4 H), 7.40 (dd, *J* = 8.8, 2.2 Hz, 2 H), 7.47 (dd, *J* = 2.2, 0.7 Hz, 2 H), 8.06 (d, *J* = 8.8 Hz, 2 H), 8.15 (d, *J* = 8.8 Hz, 2 H), 8.38 (m, 4 H), 8.95 (dd, *J* = 8.8, 0.7 Hz, 2 H). ^{13}C NMR (125 MHz, CD_3CN–1% TFA-d_1): δ = 29.9, 66.9, 104.3, 114.2, 117.9, 120.7, 122.6, 122.8, 133.9, 134.2, 155.4, 160.5, 168.2, 169.5, 174.0. ESI-MS (positive mode): *m/z* (%) = 259 (100) [M^{2+}]. ESI-HRMS: *m/z* calcd for $C_{33}H_{26}O_6$ [M^{2+}]: 259.0859; found: 259.0847.

(22) **Phloroglucinol-Type Dication 6g**
Orange powder; yield 95%. IR (KBr): 3400 (OH), 1635 (C=O), 835 (PF) cm^{-1}. UV/Vis (45% EtOH–45% MeCN–10% 1 N HCl): λ_{max} (ε) = 278 (14500), 326 (6200), 416 (sh), 476 (20800 M^{-1} cm^{-1}) nm. ^1H NMR (500 MHz, CD_3CN–1% TFA-d_1): δ = 2.35 (quin, *J* = 6.2 Hz, 2 H), 4.38 (t, *J* = 6.2 Hz, 4 H), 6.72 (d, *J* = 2.2 Hz, 2 H), 6.96 (dd, *J* = 2.2, 0.7 Hz, 2 H), 7.19 (m, 4 H), 7.94 (d, *J* = 8.8 Hz, 2 H), 8.29 (m, 4 H), 9.04 (dd, *J* = 8.8, 0.7 Hz, 2 H). ^{13}C NMR (125 MHz, CD_3CN–1% TFA-d_1): δ = 29.9, 66.7, 96.9, 104.0, 111.5, 114.2, 117.7, 122.6, 133.2, 150.4, 159.6, 160.1, 167.7, 171.5, 173.2. ESI-MS (positive mode): *m/z* (%) = 275 (100) [M^{2+}]. ESI-HRMS: *m/z* calcd for $C_{33}H_{26}O_8$ [M^{2+}]: 275.0808; found: 275.0798.

