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Synthesis and Photochromism of Novel Phenylene-Linked Photochromic Bispyrans

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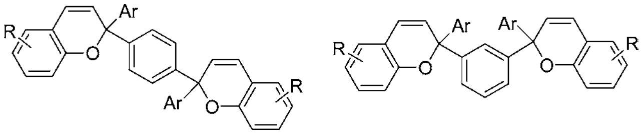
ABSTRACT



Phenylene-linked bisnaphthopyrans were synthesized in good yields via the one-pot reaction of bis-propargyl alcohols with naphthols. Temperature-dependent photochromism in 1,4-phenylene-linked bispyrans leads to up to 60 nm bathochromic shift between the colored species formed at room temperature and at –20 °C. Better fatigue resistance and higher colorability was observed in 1,4-phenylene-linked bis-[2*H*]-naphtho[1,2-*b*]pyrans by comparison to the 1,3-phenylene linked bis-[2*H*]-naphtho[1,2-*b*]pyrans.

The successful commercialization of ophthalmic lenses and glasses using organic photochromic dyes have attracted great interest in the design and synthesis of photochromic compounds with improved properties.[1,2] There has been recent particular interest in the design, synthesis, and study of novel bisphotochromophores.[3−7] Recently, we reported oligothiophene-linked bispyrans exhibiting unprecedented sequential or temperature-dependent photochromism.[6] Terthiophene- and quaterthiophene-linked bispyrans have also been reported by Guglielmetti et al.[7] However, fundamental questions persist regarding the role of oligothiophenes as indispensable subunits for the observation of sequential or temperature-dependent photochromic behavior of such bispyrans; moreover, there is relatively little data that permits evaluation of linker effects on the photochromic properties of these systems. Additionally, truly general strategies for the production of novel bispyrans are lacking. The reported synthesis of bispyrans generally adopt either Pd-catalyzed Stille coupling reactions of distannyl bithiophene with bromothienyl pyrans or Cu-promoted homocoupling reaction of thiophene-substituted pyrans.[6,7] The use of organotin compounds in the former method detract from their utility, and in the latter case, the prescribed use of strong base limits the extent to which the method is tolerant of various functionalities. Herein, we report efficient synthesis and photochromic properties of novel phenylene-linked bisnaphthopyrans utilizing a new and general synthetic pathway,

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(1) Crano, J. C.; Guglielmetti, R. *Organic Photochromic and Thermochromic Compounds*; Plenum Press: New York, 1999.

(2) (a) Willner, I. *Acc. Chem. Res.* **1997**, *30*, 347−356. (b) Feringa B. L. *Molecular Switches*; Wiley-VCH: Weinheim, 2001. (c) Dürr, H.; Bouas-laurent, H. *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, 2003.

(3) For diarylethene, see: (a) Higashiguchi, K.; Matsuda, K.; Irie, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3537−3540. (b) Kobatake, S.; Irie, M. *Tetrahedron* **2003**, *59*, 8359−8364. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896−9897. (d) Chen, B.; Wang, M.; Luo, Q.; Tian, H. *Synth. Met.* **2003**, *137*, 985−987. (e) Luo, Q.; Chen, B.; Wang, M.; Tian, H. *Adv. Funct. Mater.* **2003**, *13*, 233−239. (f) Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922−8923.

(4) For benzodihydropyrene, see: (a) Mitchell, R. H.; Bandyopadhyay, S. *Org. Lett.* **2004**, *6*, 1729−1732. (b) Mitchell, R. H.; Ward, T. R.; Chen, Y.; Wang, Y.; Weerawarna, S. A.; Dibble, P. W.; Marsellam M. J.; Almutair, A.; Wang, Z. *J. Am. Chem. Soc.* **2003**, *125*, 2974−2988. (c) Mitchell. R. H.; Ward, T. R.; Wang. Y.; Dibble, P. W. *J. Am. Chem. Soc.* **1999**, *121*, 2601−2602.

(5) For dihydroindolizines, see: Bleisinger, H.; Scheidhauer, P.; Dürr, H.; Wintgens, V.; Valat, P.; Kossanyi, J. *J. Org. Chem.* **1998**, *63*, 990−1000.

(6) (a) Zhao, W.; Carreira, E. M. *J. Am. Chem. Soc.* **2002**, *124*, 1582−1583. (b) Zhao, W.; Carreira, E. M. *J. Am. Chem. Soc.* Submitted for publication.

(7) (a) Yassar, A.; Galy, N. R.; Frigoli, M.; Moustrou, C.; Samat, A.; Guglielmetti, R.; Jaafari, A. *Synth. Met.* **2001**, *124*, 23−27. (b) Yassar, A.; Jaafari, H.; Galy, N. R.; Frigoli, M.; Moustrou, C.; Samat, A.; Guglielmetti, R. *Eur. Phys. J. Appl. Phys.* **2002**, *18*, 3−8.

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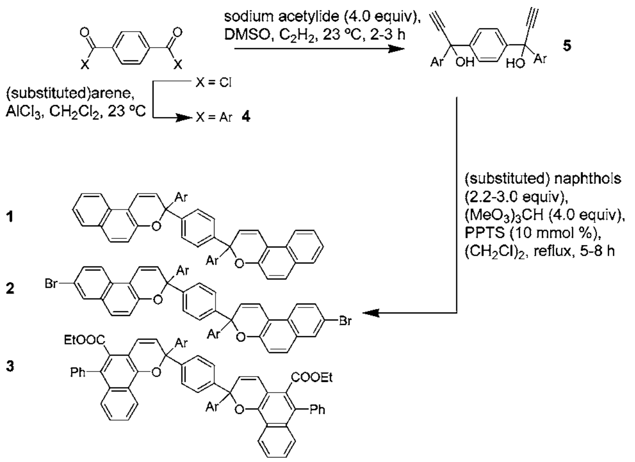
which permits the preparation of both phenylene-linked bis-[3*H*]-naphtho[2,1-*b*]pyrans and bis-[2*H*]-naphtho[1,2-*b*]-pyrans.

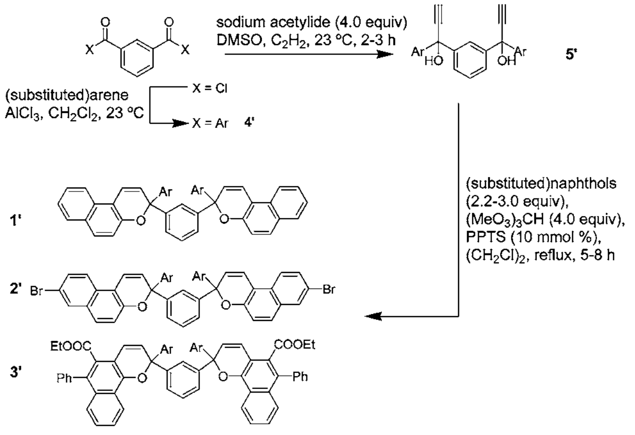
The starting point of our synthesis was the commercially available terphthaloyl or isophthaloyl chlorides. Friedel−Crafts acylation afforded the required bisketones (**4a**−**c** and **4′a**/**4′b**) in good to excellent yields (Scheme 1).[8] The next step in the sequence requires the generation of bispropargyl alcohols.

Scheme 1. Synthesis of the Phenylene-Linked Compounds



a: Ar = Ph; **b**: Ar = *p*-F-Ph; **c**: Ar = *p*-MeO-Ph

	4	**5**	**1**	**2**	**3**
a	89%	73%	82%	94%	71%
b	96%	52%	84%	78%	69%
c	86%	49%	88%	93%	84%



a: Ar = Ph; **b**: Ar = *p*-F-Ph

	4’	**5’**	**1’**	**2’**	**3’**
a	99%	48%	74%	81%	69%
b	98%	64%	73%	86%	72%

A general problem that we encountered in the preparation of the requisite propargyl alcohols is that significant amounts of side products (2-butyne-1,4-diol derivatives) result from double addition of acetylene to the ketone.[9] Through the use of modified conditions, wherein sodium acetylide with excess acetylene gas in DMSO was used, the amount of such side products could be reduced significantly, allowing for the isolation of bispropargyl alcohols (**5a**−**c** and **5′a**/**5′b**) in preparatively useful yields. Following this step, we prepared the bispyrans under acid-catalyzed conditions, which we have previously documented.[10,11] Good to excellent yields of phenylene-linked bispyrans (**1a**−**c**/**2a**−**c**/**3a**−**c**, **1′a**/**1′b**/**2′a**/**2′b**/**3′a**/**3′b**) were obtained (Scheme 1). The synthesis strategy delineated herein represents its first general application to the preparation of bispyrans linked through sp^3-hybridized centers and complements strategies involving Pd- and Cu-mediated couplings.[6,7]

With the targeted compounds in hand, we focused our efforts on the study of the photophysical properties of the bis-[3*H*]-naphtho[2,1-*b*]pyrans **1a**−**c** and **1′a**/**1′b**. The spectrum of **1a** has four absorption bands in the region of 300−400 nm at 304, 317, 347, and 361 nm and the same absorption maxima as 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]-pyran (**6**),[12] which was chosen as a standard for comparison, but with higher extinction coefficient (e.g., 9000 versus 4900 dm^3·mol^{-1}·cm^{-1} at 361 nm**)**. This indicates that the two photochromic units in **1a** are well insulated and the absence of any interaction between the two pyran units in its closed forms.

Compound **1a** exhibits temperature-dependent photochromism, whereas 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran **6** lacks this feature. The absorption spectra of compound **1a** prior to and after UV irradiation at room temperature and 5 and −20 °C are shown in Figure 1. At room temperature, the colorless solution of **1a** in toluene displays rapid yellow coloration **(**$\lambda_{\max} = 434$ nm) under UV irradiation, similar to 3,3-diphenyl-[3*H*]-naphtho[2,1-*b*]pyran **6 (**$\lambda_{\max} = 432$ nm). In contrast, at −20 °C under UV irradiation, **1a** displays red coloration **(**$\lambda_{\max} = 494$ nm) while 3,3-diphenyl-[3*H*]-naphtho-[2,1-*b*]pyran **6** remains yellow. The latter (**6**) displayed increased intensity at −20 °C compared to that observed at room temperature. This likely results from the fact that the second photochromic unit in the bispyrans undergoes opening when the thermal fading of the first opened pyran unit becomes slow at low temperature. It is surprising that the simple phenylene linker could afford as much as 60 nm bathochromic shift between the colored species formed at

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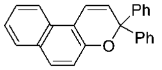
[8] Gilb, W.; Grötsch, G.; Schubert, H. U.S. Patent 5,300,693, 1994.

[9] Coelho, P. J.; Salvador, M. A.; Oliveira, M. M.; Carvalho, L. M. *Tetrahedron* **2004**, *60*, 2593−2599.

[10] Zhao, W.; Carreira, E. M. *Org. Lett.* **2003**, *5*, 4153−4154.

[11] The method for pyran preparation from a propargyl alcohol and a naphthol in the presence of an acid catalyst is known to generate naphthopyran in moderate yields in most cases [e.g., 55−63% for compound **6**. See: (a) Tanaka, K.; Aoki, H.; Hosomi, H.; Ohba, S. *Org. Lett.* **2000**, *2*, 2133. (b) Heller, H. G.; Levell, J. R. U.S. Patent 5,955,520, 1999. (c) Harie, G.; Samat, A.; Guglielmetti, R. *Tetrahedron Lett.* **1997**, *38*, 3075. However, for the generation of bispyrans wherein each pyran is fused onto a common naphthalene moiety only low yields have been reported (12−17%). See: (d) Tanaka, K.; Aoki, H.; Hosomi, H.; Ohba, S. *Org. Lett.* **2000**, *2*, 2133. (e) Knowles, D. B.; Von Gemert, B. U.S. Patent 5,464,567, 1995].

[12] The structures of the reference compounds (**6** and **7**) used in this study are:



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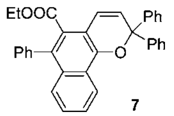

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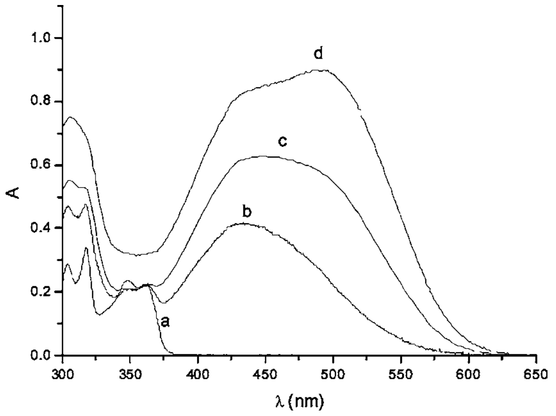
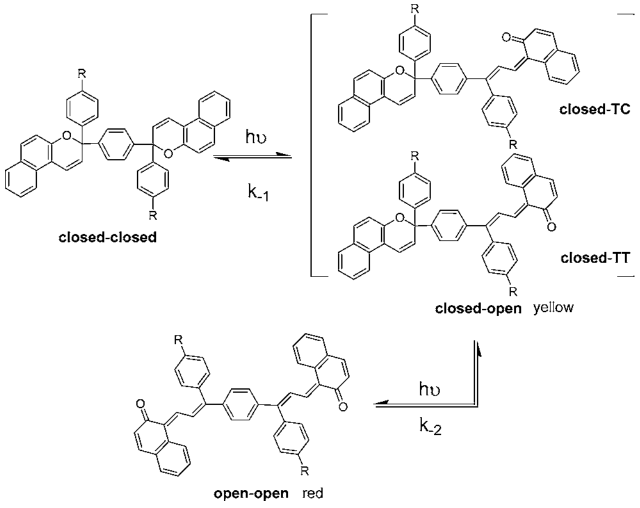


Figure 1. UV-vis spectra of compound **1a** (2.5×10^{-5} mol/L in toluene) prior to and after UV (366 nm) irradiation for 4 min at various temperature. (a) prior to UV irradiation; (b) UV (366 nm) irradiation for 4 min at ambient temperature; (c) UV irradiation for 4 min at 5 °C; (d) UV irradiation for 4 min at −20 °C.

room temperature and at −20 °C. Temperature-dependent photochromism was also observed for the other dimers (**1**−**3** and **1′**−**3′**); however, such effect is less pronounced for those bispyrans with fast fading rates. The photochromic transformations of **1** are shown in Scheme 2. The original state of **1** is the closed-closed form (closed-closed); upon UV irradiation, one pyran unit opens to generate closed-open forms (closed-open) which constitute the fast fading closed-trans-cis isomer (closed-TC) and closed-trans-trans isomer (closed-TT), which display yellow color. Under UV irradiation at low temperature, the second pyran units undergo opening to generate open-open forms (open-open, only one isomer is shown), which display red color.

Scheme 2. Photochromic Reaction of Compounds **1a**−**c**



Using low-temperature chromatography, we could obtain the pure monocolored closed-TC and closed-TT forms in **1b** with extinction coefficients of 21300 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for closed-TC and 18300 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for closed-TT. The photocoloration quantum yield for the generation of closed-TC in dichloromethane was then measured to be 0.72 by the standard procedure using potassium ferrioxalate as actinometer (see Supporting Information for details).[13]

The 1,3-linked bispyran **1′b** has identical quantum yield as 1,4-linked bispyran **1b**. However, the colorability[14] (A_0, the absorbance at photostationary state under white light irradiation), thermal fading rate (k_{-1}, the bleaching rate of the colored form in the dark), and fatigue resistance ($T_{1/2}$, time required to decrease to the half of the colorability) of **1′a**/**1′b** are quite different from those of **1a**/**1b** (see Table 1).

Table 1. Colorability (A_0), Absorption Maxima, Thermal Bleaching Rate (k_{-1}), and Fatigue Resistance ($T_{1/2}$) of Bispyran at Room Temperature in Toluene

entry	compd	A_0/λ_{max} (nm)	k_{-1} (s^{-1})	$T_{1/2}$ (min)
1	**1a**	0.411/434	0.087	90
2	**1b**	0.353/433	0.135	93
3	**1c**	0.310/465	0.199	266[b]
4	**1′a**	0.377/432	0.103	16
5	**1′b**	0.355/430	0.158	20
6	**2a**	0.232/454	0.187	76
7	**2b**	0.252/452	0.288	108
8	**2c**	0.221/477	0.422	396[b]
9	**2′a**	0.277/450	0.197	40
10	**2′b**	0.232/446	0.275	53
11	**6**[a]	0.294/432	0.101	117

[a] 3,3-Diphenyl-[3*H*]-naphtho[2,1-*b*]pyran. [b] Estimated from 1 h result.

As shown in Table 1 the colorability of **1a** is much higher than that of reference compound 3,3-diphenly-[3*H*]-naphtho-[2,1-*b*]pyran **6** (compare entry 1 to entry 11); however, the thermal fading rate and fatigue resistance of **1a** are slightly lower than that of the reference. *para*-Fluoro substitution on the 3-phenyl group (**1b**) has little effect on the absorption maxima of the colored form (closed-open); however, it induces increased thermal fading rate (compare entry 2 to entry 1). *para*-Methoxy substitution results in much faster thermal fading rate and much improved fatigue resistance, albeit lower colorability (compare entry 3 to entry 1). Bromo substitution on the naphthalene subunit inevitably leads to much faster thermal fading rate and improved lifetime in most cases (compare entry 6 to entry 1, entry 7 to entry 2, and entry 8 to entry 3). Increased thermal fading could also

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[13] Murov, S. L.; Carmichael, L.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993; pp 298−305.

[14] Colorability (A_0) is defined as the absorbance at the photostationary state under conditions of the experiment. The photochromic behavior of compounds was studied in 1 cm light path quartz cells as 2.5×10^{-5} mol/L toluene solutions (2.5 mL) at 25 °C under continuous irradiation with white light (320−700 nm) from an 150 W ozone-free Xe lamp (the light was passed through a water circulated heat trap and a C3C26 optical filter to eliminate heat, infrared light, and UV light less than 320 nm. The output of the white light was measured to be 1940 W/m^{-2} with an EPM-1000 power meter).

be realized by changing linking sites from 1,4 to 1,3 (**1** versus **1′** and **2** versus **2′**); however, at the unexpected expense of fatigue resistance. The improved photostability observed for methoxy-substituted bispyrans is attributed to the low equilibrium intensity of the colored forms. *meta*-Phenylene-linked bispyrans displayed increased fading rate and thus a lower colorability presumably due to the steric congestion in the open forms. The unexpected observation of lower fatigue resistance in this case is presumably attributed to the unwanted interaction of the radical products generated in the degradation process on the pyran fragment within the same structure.[15]

We then turned our attention to the identification of a bispyran with higher colorability and improved fatigue resistance. This could be accomplished by changing the pyran portion from [3*H*]-naphtho-[2,1-*b*]pyran (as in **1a**−**c**, **2a**−**c**, **1′a**−**b**, and **2′a**−**b**) to [2*H*]-naphtho-[1,2-*b*]pyran (**3a**−**c** and **3′a**−**b**) as shown in Scheme 1.[16] For **3a**−**c** and **3′a**−**b** the photochromic properties are collected in Table 2, and 2,2-diphenyl-5-ethoxycarbonyl-6-phenyl-[2*H*]-naphtho [1,2-*b*]pyran (**7**) was used as the reference for comparison.[12]

From Table 2, it could be concluded that the colorabilty of the bispyrans is higher than reference **7**. The most notable features for bispyrans **3a**−**c** are that they display higher colorability and better fatigue resistance than the reference **7** (compare entries 1−3 to entry 6), and 1,4-linked bispyran **3a**/**3b** are more fatigue-resistant than 1,3-linked species **3′a**/**3′b** (compare entries 1 and 2 to entries 4 and 5). Bispyrans **3a**−**c** (Table 2, entries 1−3) also display significantly improved fatigue resistance over bispyrans **1a**−**c** and **2a**−**c** (Table 1, entries 1−3 and entries 6−8).

Table 2. Colorability (A_0), Absorption Maxima, Thermal Bleaching Rate (k_{-1}), and Fatigue Resistance ($T_{1/2}$) of Bispyrans **3a**−**c** and **3′a**/**3′b** at Room Temperature in Toluene

entry	compd	$A_0/\lambda_{\max}$ (nm)	k_{-1} (s^{-1})	$T_{1/2}$ (min)
1	**3a**	0.808/487	0.0062	379[b]
2	**3b**	0.759/487	0.0103	486[b]
3	**3c**	0.710/499	0.0260	860[b]
4	**3′a**	0.768/480	0.0152	215[b]
5	**3′b**	0.656/479	0.0190	192
6	**7**[a]	0.516/476	0.0106	332[b]

[a] 2,2-Diphenyl-5-ethoxycarbonyl-6-phenyl-[2*H*]-naphtho [1,2-*b*]pyran. [b] Estimated from 1 h measurement.

From Table 2, it could also be concluded that *para*-fluoro substitutions on the 3-phenyl subunit induce increased thermal fading rate (compare entry 2 to entry 1, and entry 5 to entry 4). *para*-Methoxy-substituted bispyran **3c** displays much faster thermal fading rate and much improved fatigue resistance over **3a** lacking substitution (compare entry 3 to entry 1). These observations are similar to the cases for bispyrans **1a**−**c** and **2a**−**c** in Table 1.

In conclusion, we have synthesized novel phenylene-linked photochromic bispyrans displaying temperature-dependent photochromism. Up to 60 nm bathochromic shift between the colored species formed at room temperature and was observed at low temperature of −20 °C. The high colorability and excellent fatigue resistance of bispyrans **3a**−**c** provide new avenues for the design of the next generation of longer-lasting, fatigue-resistant photochromic compounds.

Acknowledgment. We thank the ETH-Z for support.

Supporting Information Available: Detailed synthesis and characterization data for bispyrans and their precusors. Isolation of the colored forms of the photochromic bispyrans, kinetics of photocoloration and thermal fading, and measurements for the fatigue resistance of photochromic compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Strokach, Y.; Alfimov, M.; Barachevsky, V.; Arsenov, V.; Gorelik, A. *Mol. Cryst. Liq. Cryst.* **1997**, *298*, 97−103. (b) Malatesta, V. *Photodegradation of Organic Photochromes*. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R., Eds.; Plenum Press: New York, 1999; Vol. 2.

(16) (a) The fatigue resistance of photochromic compounds can be dramatically affected by substituents: Coelho, P. J.; Carvalho, L. M.; Abrantes, S.; Oliveira, M. M.; Oliveira-Campos, A. M. F.; Samat, A.; Guglielmetti, R. *Tetrahedron* **2002**, *58*, 9505−9511. (b) It is known that unsubstituted [2*H*]-naphtho-[1,2-*b*]pyrans have much lower fatigue resistance than the [3*H*]-naphtho-[2,1-*b*]pyran due to the high abundance of the colored forms for the former under irradiation. However, an alkoxycarbonyl substituent at the 5-position of [2*H*]-naphtho-[1,2-*b*]pyrans is known to result in much improved fatigue resistance while still providing sufficient colorability. Such alkoxycarbonyl-substituted pyrans are commercially used in plastic ophthalmic lenses: (c) Lin, J. WO 01/51483, 2001. (d) Van Gemert, B.; Kish, D. G. U.S. Patent 5,753,146, 1998.