JOC The Journal of Organic Chemistry

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Fluoride-Triggered Ring-Opening of Photochromic Diarylpyrans into Merocyanine Dyes: Naked-Eye Sensing in Subppm Levels

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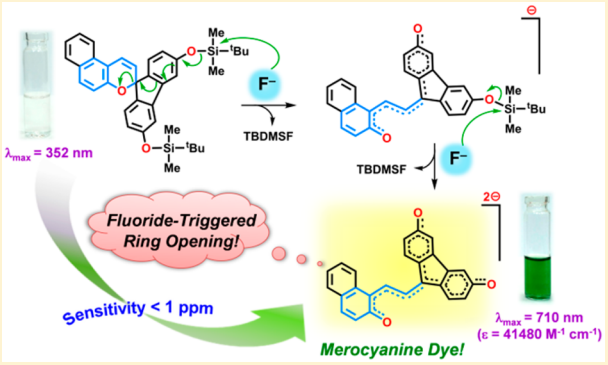
Supporting Information

ABSTRACT: The fluoride-mediated desilylation reaction has been exploited, for the first time, to trigger ring-opening of photochromic diarylbenzo-/naphthopyrans into highly colored anionic merocyanine dyes with high molar absorptivities to permit naked-eye sensing. The absorption spectral shifts, i.e., differences in the absorption maxima of colorless and colored forms, observed for a rationally designed set of silyloxy-substituted diarylpyrans subsequent to fluoride-induced ring opening are remarkably high (330−480 nm), and are unknown for any colorimetric probe. In particular, the disilyloxy-substituted diphenylnaphthopyran and its analog, in which the diphenyl groups are fused in the form of fluorene, allows "naked-eye" detection of fluoride in subppm levels (<1.0 ppm) in THF as well as in DMSO-H_2O. The sensing is specific for fluoride among various other anions. This approach for colorimetric sensing of fluoride by ring-opening of the otherwise photochromic benzo-/naphthopyrans is heretofore unprecedented.



INTRODUCTION

Development of optical receptors for selective recognition of anions is of paramount significance, as the anions are known to play diverse roles in a variety of chemical and biological processes.[1] In particular, selective recognition and sensing of fluoride—an anion with smallest ionic radius, highest charge density, and hard Lewis basic character—has elicited a lot of interest due to its involvement as a contaminant in drinking water, its role in the refinement of uranium used in nuclear weapons, and its presence as a common ingredient in hypnotics, psychiatric drugs, pesticides, military nerve gases, etc.[2] Furthermore, excessive consumption of fluoride is known to manifest in severe consequences, such as collagen breakdown, bone disorders, and thyroid activity leading to depression, immune system disruption, etc.[2] Therefore, molecular probes for naked-eye detection of fluoride are indispensable.[3] In general, some of the strategies employed for sensing of fluoride rely primarily on strong forces such as the ones taking place between fluoride and Lewis-acidic boron,[2a,4] hydrogen bonding/deprotonation,[1a,5] anion-π interaction,[6] etc. In particular, fluoride-mediated Si−O bond cleavage reaction has been exploited as one of the most attractive ways to develop selective optical sensors and chemodosimeters due to the rapid formation of Si−F bond almost irreversibly at the expense of the cleavage of the Si−O bond.[7]

We have been concerned with the phenomenon of photochromism[8] exhibited by the class of 2,2-diarylbenzopyrans, popularly known as chromenes,[9] and modulation of spectrokinetic properties of their photogenerated colored transient intermediates.[10] Diarylbenzo-/naphthopyrans undergo C(sp^3)−O bond heterolysis in the presence of UV-light to give rise to colored open-forms, termed as *o*-quinonoid intermediates, which revert to the initial colorless closed-forms by either visible light or heat (Scheme 1).[9,10] In the course of our investigations, we wished to explore if the colorless diarylbenzo-/naphthopyrans could be opened up by a chemical trigger to generate highly colored merocyanine dyes, whereby naked-eye sensing of the chemical trigger should be feasible. We surmised that the silyloxy-substituted benzo- and naphthopyrans could be desilylated with fluoride as a trigger to generate phenoxide anions, which may induce benzo-/naphthopyran C−O bond cleavage, leading to highly colored anionic merocyanine dyes, cf. Scheme 1.

Herein we report that fluoride indeed triggers the ring opening of *tert*-butyldimethylsilyloxy-substituted benzopyrans (**BPs**) and naphthopyrans (**NPs**) in Figure 1, leading to their corresponding colored anionic merocyanine species to permit its highly selective naked-eye sensing among all other anions. The spectral shifts ($\Delta\lambda_{max}$s), i.e., the differences in the absorption maxima of the colorless and colored forms, are by 330−480 nm, and are unprecedented for sensing by any colorimetric probe to date. The high molar absorptivities of the colored forms permit the fluoride ion to be detected in subppm levels.

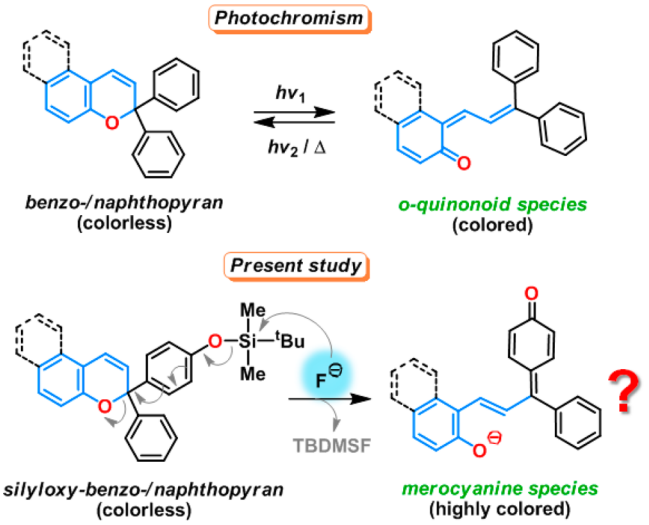
RESULTS AND DISCUSSION

Synthesis of Silyloxy-Substituted Pyrans and X-ray Crystal Structure Determinations. The syntheses of all the

Received: June 14, 2016
Published: July 22, 2016

DOI: 10.1021/acs.joc.6b01361
J. Org. Chem. 2016, 81, 7741−7750

Scheme 1. Photochromism of Benzo-/naphthopyrans and the Premise Envisaged for Ring Opening by a Chemical Trigger



BPs and NPs were accomplished according to the routes shown in Scheme 2. To begin with, silyloxy-substituted diarylpropargyl alcohols (**PA1**−**PA5**) were prepared by the reaction of sodium acetylide with the precursor carbonyl compounds **1**−**5** in THF. Cyclocondensation reactions of appropriate propargyl alcohols with phenol and β-naphthol in the presence of *p*-toluenesulfonic acid (PTSA) as catalyst furnished the silyloxy-substituted BPs and NPs in good isolated yields.

Single crystals of suitable quality were successfully grown for some of the pyrans, namely, **BP-P1**, **BP-P2**, **NP-F1**, and **NP-P2**, by slow evaporation of their solutions in $CHCl_3$/CH_2Cl_2 at rt and were subjected to X-ray structure determinations (Supporting Information). In Figure 2 are shown perspective drawings of their molecular structures, which reveal considerable twisting of the pyran moiety with respect to the benzene ring.

Influence of Fluoride on Silyloxy-Substituted Pyrans as Followed by UV−vis Absorption Spectral Changes. To investigate the influence of fluoride ion on the silyloxy-substituted BPs and NPs, titration of the dilute solution of each of the pyrans (50 μM in THF) against tetrabutylammomium fluoride (TBAF) was carried out at rt, as monitored by UV−vis absorption spectroscopy. Addition of TBAF to the colorless solutions of all BPs and NPs, with the exception of **BP-P1**, led to instant naked-eye visible colorations with the formation of broad band(s) in the visible and near-infrared region that extend up to ca. 1000 nm, cf. Figure 3 and Supporting Information.

In contrast, treatment of the solution of **BP-P1** with increasing concentrations of TBAF led to a broad absorption peaking at ca. 415 nm, cf. Supporting Information. The absorptions due to the colored species were found to increase progressively for addition of fluoride up to ca. 1 (for **NP-P1** and **NP-F1**), 2 (for **NP-P2** and **NP-F2**), and 10 mol equiv (for **BP-P2**), and subsequently saturate. In Table 1 are collected the data for observed changes in the absorption properties of all the BPs and NPs before and after treatment with fluoride.

Accordingly, **NP-P1** gives rise to light green coloration (λ_{max} = 705 nm; ε = 8100 M^{-1} cm^{-1}) for addition of 1 equiv of TBAF with a $\Delta\lambda_{max}$ of 357 nm, cf. Supporting Information. On the other hand, treatment of the fluorenyl derivative **NP-F1** with 1 equiv of TBAF led to brownish coloration with a considerably red-shifted absorption band of much higher intensity in the near-IR region (λ_{max} = 834 nm; ε = 14660 M^{-1} cm^{-1}); the $\Delta\lambda_{max}$ in this instance is as high as 482 nm, cf. Supporting Information. A similar treatment of the solutions of disilyloxy-substituted pyrans **BP-P2**, **NP-P2**, and **NP-F2** with TBAF led to colored species of relatively much higher intensity. The observed spectral changes with increasing amounts of TBAF are shown in Figure 3. The solution of **BP-P2** in THF turns bluish with a broad spectral feature that spans a range of 500−800 nm with maximum at 645 nm (ε = 8260 M^{-1} cm^{-1}) and a spectral shift of ca. 345 nm. The absorption was found to saturate for addition of TBAF in excess of 10 equiv (Supporting Information). In the same manner, addition of 2 equiv of TBAF to the solution of **NP-P2** led to deep blue coloration with absorption peaking at ca. 685 nm (ε = 27760 M^{-1} cm^{-1}); the $\Delta\lambda_{max}$ in this case was found to be ca. 337 nm. A similar exercise with **NP-F2** led to the observation of dark green color (λ_{max} = 710 nm; ε = 41480 M^{-1} cm^{-1}) with a $\Delta\lambda_{max}$ of ca. 358 nm, cf. Figure 3.

Mechanistic Studies of Fluoride-Triggered Ring-Opening of Diarylpyrans into Merocyanine Dyes. The fact that the fluoride ion attacks silyl group to bring about desilylation and formation of phenoxide anion is well-known. The phenoxide ions generally exhibit absorptions below 450 nm.[11] Thus, the observed absorption with a $\Delta\lambda_{max}$ of 115 nm and maximum at 415 nm for treatment of **BP-P1** with ca. 10 equiv of TBAF should be readily attributed to the desilylated phenoxide anion. As mentioned earlier, all other BPs and NPs in Figure 1 show, upon treatment with TBAF

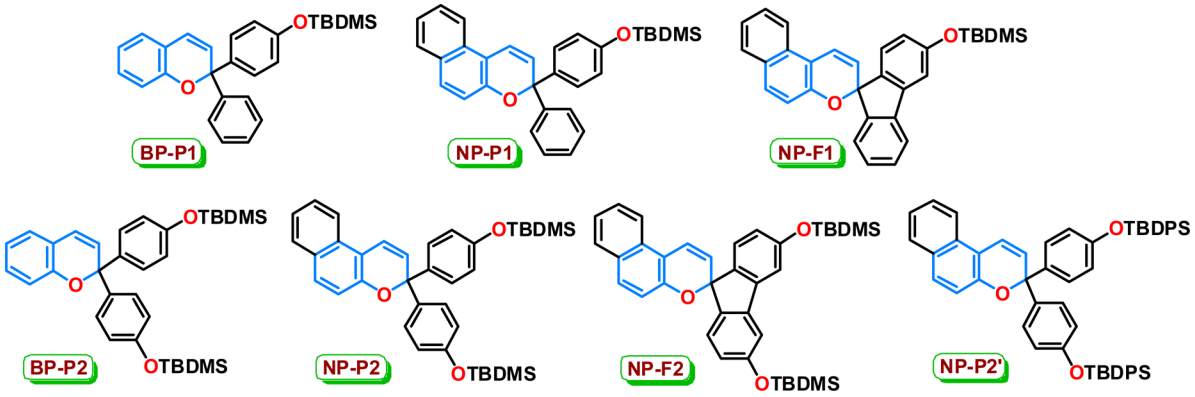


Figure 1. Structures of the silyloxy-substituted benzo- (BPs) and naphthopyrans (NPs).

DOI: 10.1021/acs.joc.6b01361
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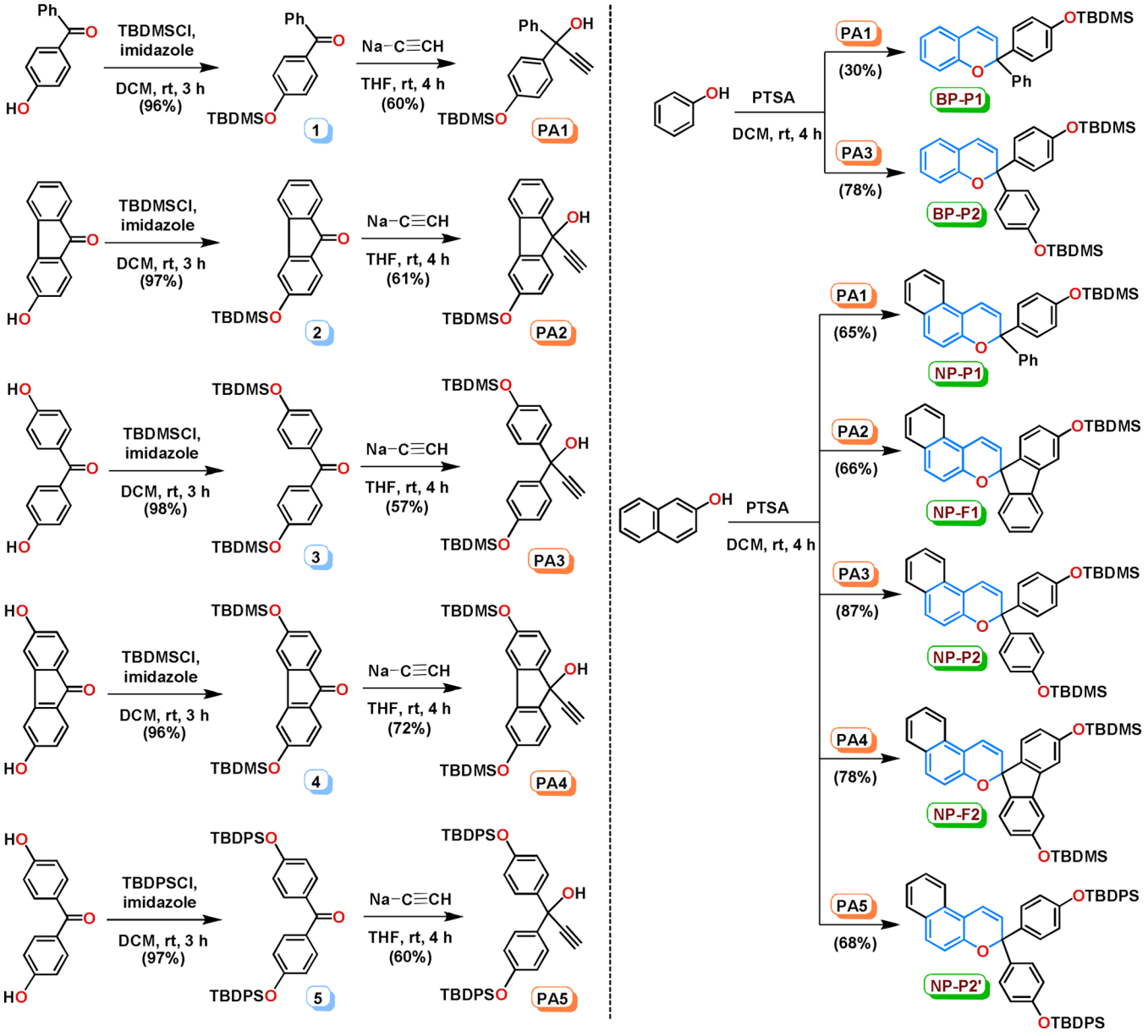
Scheme 2. Synthesis of BPs and NPs



under similar conditions, drastically different intense colored absorptions, attesting to the formation of highly delocalized desilylated species. We attribute the colored species in these cases—as envisaged at the outset—to the pyran ring-opened anionic forms of the merocyanine dyes with extensive delocalization of the charge(s) as shown in Scheme 3; NMR and IR spectral analyses do indeed offer evidence in favor of the formation of such species, vide infra.

A more careful analysis of the UV−vis titration experiments in the case of disilyoxy-pyrans with TBAF is quite revealing. While a broad spectral feature is observed for **BP-P2** with increasing equivalents of TBAF, one observes notable differences for the case of **NP-F2**, cf. Figure 3. For addition up to 1 mol equiv of the fluoride ion, the long wavelength absorption increases at ca. 820 nm. For further addition of TBAF, another absorption band (λ_{max} = 710 nm) with a higher absorptivity that is shifted hypsochromically by 110 nm develops and saturates for addition of TBAF beyond 2 equiv, while the absorbance at 820 nm corresponding to the first band remains almost intact. The initial long wavelength absorption maximum at 820 nm for addition up to 1 mol equiv of TBAF should be reconciled as corresponding to the ring-opened monodesilylated species. As one should expect, didesilylation should render the system more electron rich, whereby hypsochromic shift should be expected, as is observed. The observed spectral features are in agreement with sequential desilylation, although the didesilylated species contributes marginally to the overall absorption spectra even at 1 mol equiv of TBAF, as is evident from the appearance of two bands, as for example in **NP-F2**. A similar trend is observed in a subtle manner without any well-defined maxima for the case of **NP-P2** as well, cf. Figure 3. In this instance, while the absorption is found to saturate with 2 equiv of TBAF, one observes that the initial absorption maximum shifts progressively from 705 nm by ca. 20 to 685 nm.

We have monitored the reaction of **NP-P2** with increasing amounts of TBAF by ^{1}H and ^{13}C NMR spectroscopy, cf. Figure 4 and Supporting Information. The latter show that for addition up to less than 1 mol equiv of TBAF, one observes

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J. Org. Chem. 2016, 81, 7741−7750

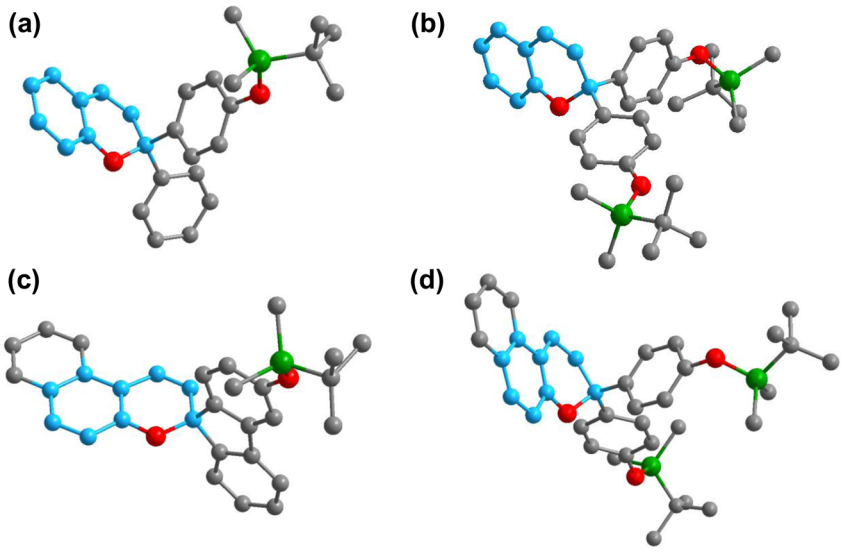

Figure 2. Perspective drawings of the X-ray determined molecular structures of **BP-P1** (a), **BP-P2** (b), **NP-F1** (c), and **NP-P2** (d).

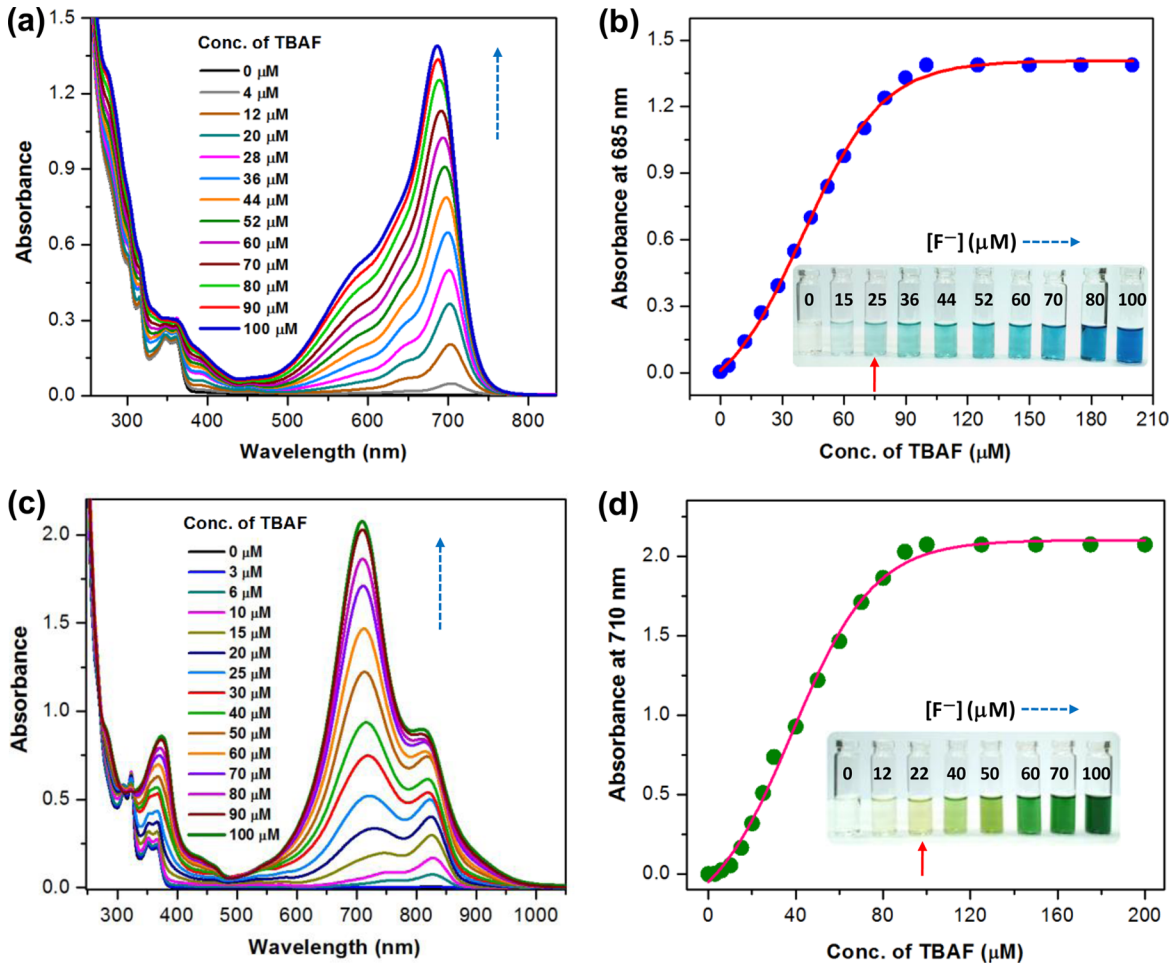

Figure 3. UV−vis absorption spectra of 50 μM solutions of **NP-P2** (a) and **NP-F2** (c) in THF with the addition of increasing concentrations of TBAF. Increase in the absorbances of the colored species of **NP-P2** (b) and **NP-F2** (d) at the absorption maxima with increasing concentrations of fluoride. The naked-eye visible color changes are shown in insets. The lowest concentration of fluoride at which the sensing is reckoned as being discernible to the naked eye is shown with a vertical arrow in red in each case.

complex signals corresponding to monodesilylated species, while simple spectra emerge for addition of TBAF beyond 2 mol equiv. Although the signal due to the carbonyl is not observed in ^{13}C NMR, IR spectrum reveals evidence for contribution from the quinonoid structure, cf. Supporting Information.

The fact that the desilylated species from **BP-P1** remains intact and does not undergo ring-opening to yield colored

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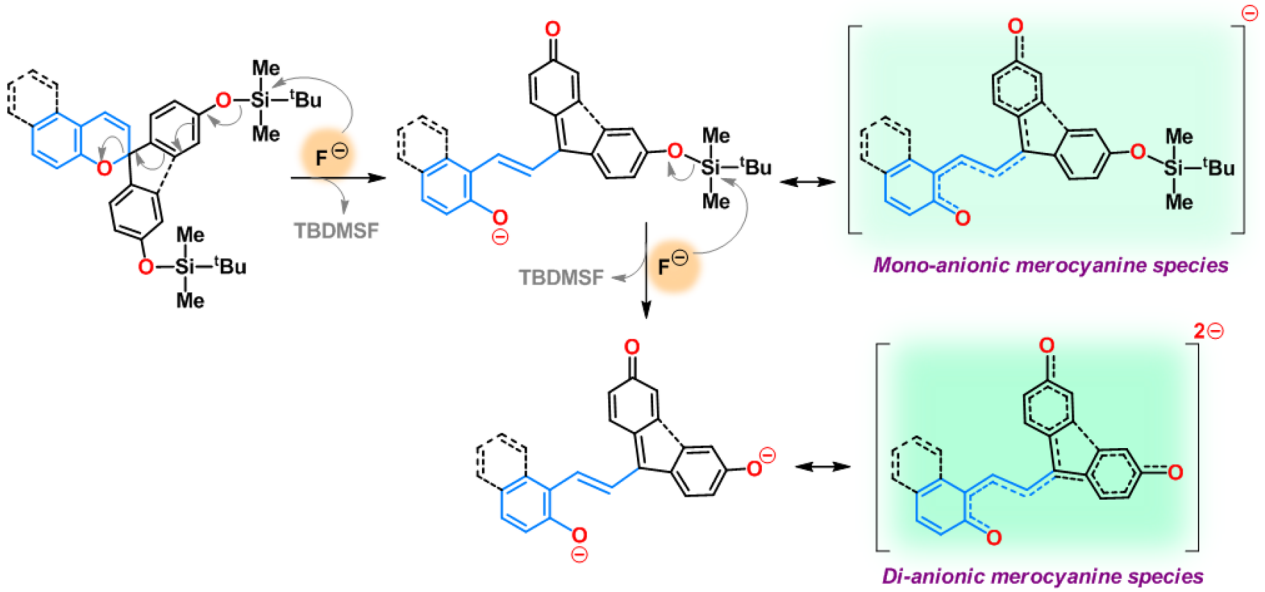
Table 1. Absorption Properties of BPs and NPs, and those of the Colored Species Derived from them upon Treatment with TBAF

	absorption properties[a,b]					"naked-eye" visible changes[a]		
	without fluoride		with fluoride				detection limit[e]	
pyran	λ_{max}(nm)	ε (M^{-1} cm^{-1})	λ_{max}(nm)	ε (M^{-1} cm^{-1})[d]	spectral shift $\Delta\lambda_{max}$ (nm)[c]	observed color	in μM	in ppm[f]
BP-P1	300 (sh)	5020	415	[g]	115	colorless	[g]	[g]
NP-P1	348	4940	705	8100	357	light green	30	0.57
NP-F1	352	5840	834	14660	482	brownish	27	0.51
BP-P2	300 (sh)	5260	645 (br)	8260	345	light blue	370	7.03
NP-P2	348	4540	685	27760	337	deep blue	25	0.47
NP-F2	352	4800	710	41480	358	dark green	22	0.42

[a]For THF solutions of 50 μM concentration at 298 K. [b]sh = shoulder and br = broad. [c]Spectral shift refers to the difference in the absorption maxima of the solutions before and after treatment with large excess of TBAF (ca. 10 mol equiv). [d]Calculated at the λ_{max} for a 50 μM solution of the pyrans treated with large excess of TBAF (ca. 10 mol equiv). [e]Determined from naked-eye perception of the color changes of the solutions as shown in the insets of Figure 3. [f]The ppm (i.e., mg/L) values are calculated as follows: x (in ppm) = y (in μM) × 0.019; see ref 12. [g]Not determined, see text.

Scheme 3. Ring Opening of BPs and NPs Triggered by Fluoride-mediated Desilylation



merocyanine species is intriguing. Seemingly, the ring-opened species does not enjoy the stability that is comparable to those of the analogous monosilyloxy-pyrans, namely, **NP-P1** and **NP-F1**, such that the C(sp^3)-O bond dissociation energy is higher. In other words, the phenoxide ion formed subsequent to treatment of **BP-P1** with TBAF is apparently not effective enough to induce heterolytic C(sp^3)-O cleavage and hence ring opening, leading to the colored merocyanine species. However, the diphenoxide species of **BP-P2** is evidently strong and forceful to induce such a C−O bond heterolysis, leading to intense coloration upon treatment of **BP-P2** with TBAF.

Selectivity of Silyloxy-Substituted Pyrans Toward Fluoride. To assess the selectivity of silyloxy-pyrans to detect fluoride, the influence of other anions was investigated with **NP-P2** and **NP-F2** as representative probe systems. As shown in Figure 5, treatment of these pyrans (50 μM) with a large excess (1 mM) of diverse anions, such as Cl^-, Br^-, I^-, CH_3COO^-, NO_3^-, ClO_4^-, PF_6^-, HSO_4^-, and $H_2PO_4^-$, in the form of their tetrabutylammonium salts led to no discernible changes in the UV−vis absorption spectra. In contrast, development of intense blue and dark green colors were observed for **NP-P2** and **NP-F2**, respectively, in the presence of 100 μM TBAF. This clearly attests to remarkable selectivity of the silyloxy-substituted pyrans toward fluoride over all other anions.

Detection Limits for Naked-Eye Sensing in Organic and Aqueous Media. To gauge the sensitivity limits for response of **BP**s and **NP**s toward fluoride as discerned by naked-eye, titration experiments with increasing amounts of TBAF were carried out. The minimum concentration of fluoride at which the visible color could be made out was followed for each of the **BP**s and **NP**s as shown in the insets of Figure 3 and Supporting Information. Accordingly, one observes that the limiting (lowest) levels of fluoride that can be detected with various **BP**s and **NP**s by naked eye follow the order: **NP-F2** (22 μM, i.e., 0.42 ppm) < **NP-P2** (25 μM, i.e., 0.47 ppm) < **NP-F1** (27 μM, i.e., 0.51 ppm) < **NP-P1** (30 μM, i.e., 0.57 ppm) < **BP-P2** (370 μM, i.e., 7.03 ppm). Clearly, the disilyloxy-substituted naphthopyrans, i.e., **NP-P2** and **NP-F2**, exhibit superior detection limits toward fluoride when compared to those of the monosilyloxy-substituted analogs, i.e., **NP-P1** and **NP-F1**. This is due to the fact that the dianionic species display very high molar absorptivities (εs), cf. Table 1.

We were motivated by the observed dramatic $\Delta\lambda_{max}$s, high sensitivity, and remarkable selectivity of **BP**s and **NP**s toward

DOI: 10.1021/acs.joc.6b01361
J. Org. Chem. 2016, 81, 7741−7750

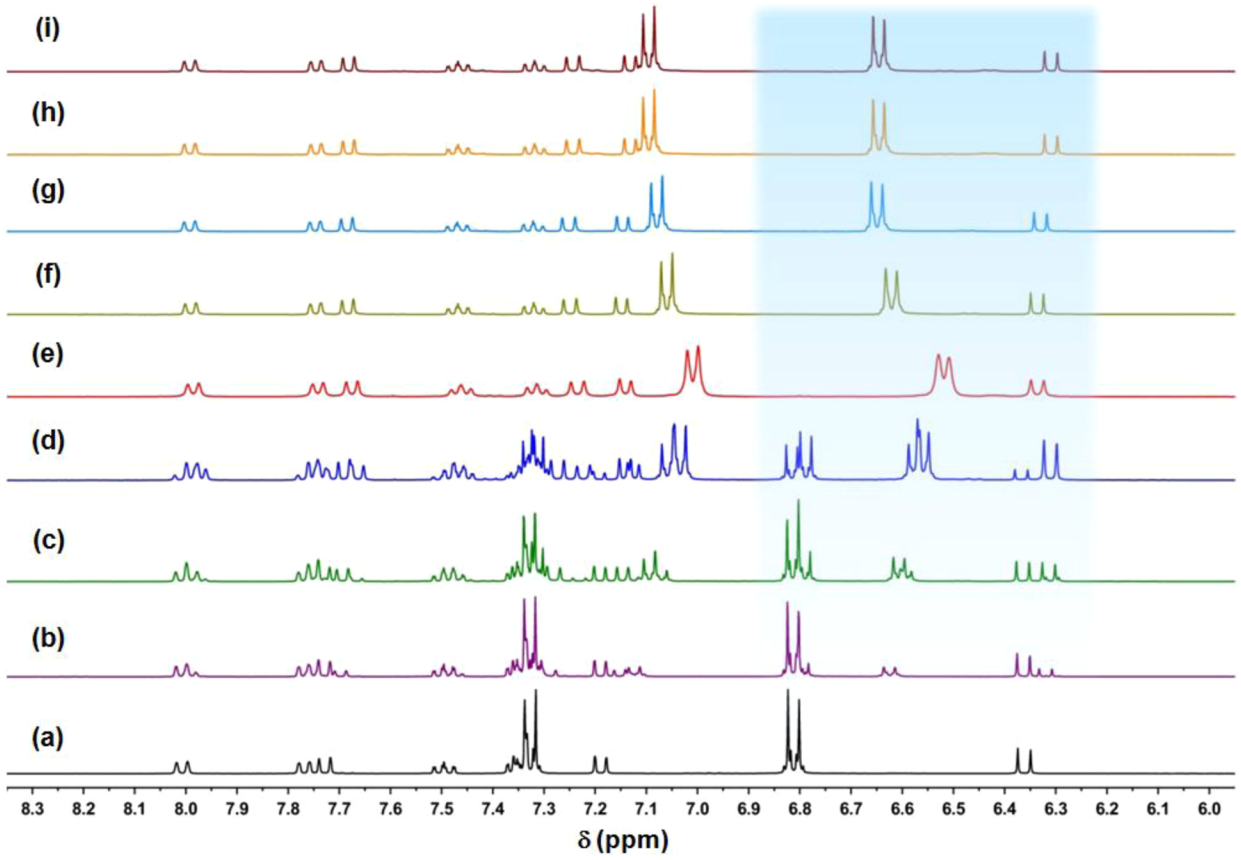


Figure 4. ^{1}H NMR (400 MHz) spectra of **NP-P2** (0.03 M in CD_3CN) in the presence of 0 (a), 0.15 (b), 0.3 (c), 0.6 (d), 1 (e), 1.3 (f), 1.6 (g), 2.0 (h), and 10 (i) molar equivalents of TBAF.

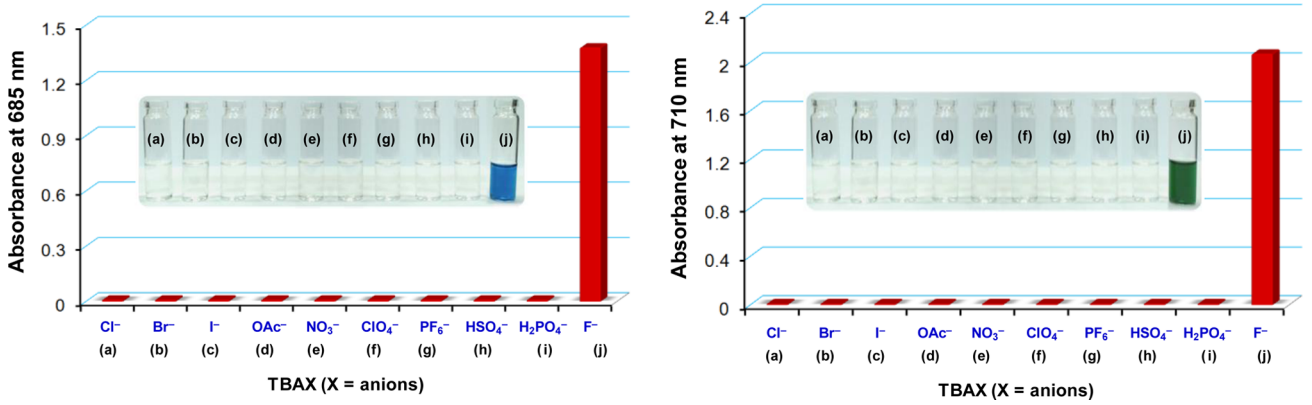


Figure 5. Response of the solutions (50 μM in THF) of **NP-P2** (left) and **NP-F2** (right) toward tetrabutylammonium salts of various anions (1 mM) and fluoride (100 μM). Insets: Photographs of the solutions of pyrans in the presence of various anions.

fluoride ion to investigate sensing of inorganic fluoride in aqueous medium. Therefore, UV−vis titrations were carried out with dilute solutions (50 μM) of **NP-P2** and **NP-F2** as representative cases against NaF in DMSO-H_2O (95:5, *v*/*v*), cf. Supporting Information. As observed for TBAF in THF, the treatment of **NP-P2** and **NP-F2** with NaF also led to intense absorption bands with their maxima at ca. 687 and 712 nm, respectively. The $\Delta\lambda_{max}$s were found to be 341 and 362 nm for **NP-P2** and **NP-F2**, respectively, in DMSO-H_2O (95:5, *v*/*v*) system, and these are almost similar to those observed with TBAF in THF. Otherwise, we note that the coloration is observed at marginally higher concentrations of NaF in DMSO-H_2O as compared to TBAF in THF. This is a result of hydration of fluoride anion in aqueous medium, which decreases its reactivity toward desilylation. Thus, the detection limits for naked-eye sensing of NaF by **NP-P2** (38 μM, i.e., 0.72 ppm) and **NP-F2** (35 μM, i.e., 0.66 ppm) in DMSO-H_2O solvent system are somewhat higher when compared to those achieved for TBAF in THF, cf. Table 1 and Supporting Information. Be this as it may, the naked-eye sensing limits are exceptionally lower and allow sensing of fluoride in either of the forms within the permissible limit advocated by the WHO, which is 1.0 ppm.[13]

Furthermore, to perform sensing experiments in a medium containing higher water content, a modified **NP-P2**, i.e., **NP-P2′**, with the TBDMS groups replaced by bulkier TBDPS groups was synthesized; it should be noted that the TBDPS groups are

DOI: 10.1021/acs.joc.6b01361
J. Org. Chem. 2016, 81, 7741−7750

known to hinder the accessibility of water to the silicon.[7c] The sensing experiments with **NP-P2′** were carried out in DMSO-H_2O (90:10, *v/v*) with its dilute solution (50 μM) against NaF cf. Supporting Information. Although similar blue coloration was observed, a higher concentration of NaF was found to be necessary when compared to that for **NP-P2** in DMSO-H_2O (95:5, *v/v*). The coloration was found to saturate (λ_{max} = 688 nm, ε = 26400 M^{-1} cm^{-1}) at ca. 2.2 mol equiv of NaF. Thus, the limit for naked-eye detection for **NP-P2′** was found to be 42 μM, which translates into 0.80 ppm, cf. Supporting Information. It is noteworthy that for **NP-P2** in DMSO-H_2O (90:10, *v/v*), no coloration was observed even at high concentrations of the fluoride. Although literature survey reveals two instances of sensing by fluoride-mediated ring-opening of spirolactone and spirolactam in fluorescein-[14a] and rhodamine-based molecular systems,[14b] the spectral shifts are unremarkable and the sensing limits are significantly lower in both of these cases.

CONCLUSIONS

Fluoride-mediated desilylation has been exploited to trigger ring-opening of a rationally designed set of silyloxy-substituted diarylbenzo-/naphthopyrans, which are renowned for their photochromism, leading to the formation of highly colored anionic forms of the merocyanine dyes to permit naked-eye sensing of fluoride. The observed spectral shifts, i.e., differences in the absorption maxima of colorless and colored forms, are remarkably high (ca. 330−480 nm), and are unprecedented to the best of our knowledge for any colorimetric sensor. Competition experiments show that the silyloxy-substituted benzo- and naphthopyrans are specific for fluoride anion among various other anions. The sensitivity limits for naked-eye sensing of fluoride are very high with the latter being sensed in subppm levels in both THF as well as DMSO-H_2O. Besides the fact that the chemically triggered opening of the otherwise photochromic benzo-/naphthopyrans is heretofore unknown, the fluoride ion sensing by this approach involving ring-opening of photochromic benzopyrans by a chemical trigger is unprecedented.

The detection of fluoride by this approach is superior to traditional analytical methods involving such techniques as ion chromatography, ion-selective electrolysis, etc. The latter are time-consuming, require access to costly instruments, and preclude in vivo sensing in biological systems.[15] Although many fluorescent probes are known that exhibit high selectivity, high sensitivity as well as quick response to detect fluoride,[15] the diarylpyran-based colorimetric sensors reported herein should be advantageous in permitting ready naked-eye detection and obviating the use of sophisticated instruments.

EXPERIMENTAL SECTION

General Aspects. Anhydrous tetrahydrofuran (THF) was prepared by freshly distilling the solvent over sodium prior to use. All the solvents were distilled prior to use. Column-chromatography was conducted on silica gel (60−120 mesh). NMR spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ and CD_3CN as solvents. IR spectra were recorded on an FT-IR spectrophotometer. The ESI mass spectra were recorded on an ESI-Q^{TOF} machine.

Synthesis of Silyloxy-Substituted Carbonyl Compounds (1−5). The silyloxy-substituted carbonyl compounds **1**−**5** were synthesized by silylation of the precursor phenolic compounds in the presence of imidazole. A representative procedure is described below.

*(4-(tert-Butyldimethylsilyloxy)phenyl) (phenyl)methanone (**1**).*[16] To a solution of *tert*-butyldimethylchlorosilane (4.95 g, 32.80 mmol) in dry DCM (80 mL) was added imidazole (2.18 g, 32.80 mmol), and the solution stirred for 10 min at rt under N_2 gas atmosphere. Solid 4-hydroxybenzophenone[16] (5.0 g, 25.22 mmol) was then added to the reaction mixture and it was stirred at rt for 3 h. After completion of the reaction, the reaction mixture was quenched with distilled water and the organic matter was extracted with DCM. The combined organic extract was dried over anhyd Na_2SO_4, filtered, and concentrated to dryness under reduced pressure. The crude material was purified by column chromatography to obtain (4-(*tert*-butyldimethylsilyloxy)-phenyl) (phenyl)methanone (**1**) as a colorless liquid in 96% yield (5.79 g);^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 6H), 1.00 (s, 9H), 6.89−6.92 (m, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.53−7.58 (m, 1H), 7.74−7.78 (m, 4H).

*3-(tert-Butyldimethylsilyloxy)-9H-fluoren-9-one (**2**).* The reaction of 3-hydroxy-9*H*-fluoren-9-one[17] (5.0 g, 25.48 mmol) with *tert*-butyldimethylchlorosilane (4.99 g, 33.12 mmol) and imidazole (2.25 g, 33.12 mmol) in dry DCM (80 mL) at rt for 3 h according to the above procedure gave rise to 3-(*tert*-butyldimethylsilyloxy)-9*H*-fluoren-9-one (**2**) as a pale yellow solid in 97% yield (7.67 g). mp. 66−68 °C; IR (KBr) cm^{-1} 3051, 2927, 2855, 1702, 1609, 1448, 1275, 1099; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 6H), 1.02 (s, 9H), 6.69 (dd, J_1 = 8.2 Hz, J_2 = 1.8 Hz, 1H), 6.95 (d, J = 2.3 Hz, 1H), 7.27−7.31 (m, 1H), 7.45−7.48 (m, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.3, 18.2, 25.6, 112.5, 119.6, 120.6, 123.8, 126.1, 127.6, 129.1, 134.1, 135.1, 143.5, 147.0, 162.0, 192.6; ESI-MS$^+$ *m/z* Calcd for $C_{19}H_{23}O_2Si$ 311.1467 $[M+H]^+$, found 311.1467.

*Bis(4-(tert-butyldimethylsilyloxy)phenyl)methanone (**3**).*[18] Reaction of 4,4′-dihydroxybenzophenone (5.0 g, 23.36 mmol) with *tert*-butyldimethylchlorosilane (10.56 g, 70.28 mmol) and imidazole (4.77 g, 70.28 mmol) in dry DCM (80 mL) according to the above procedure, led to bis(4-(*tert*-butyldimethylsilyloxy)phenyl)methanone (**3**) as a colorless liquid in 98% yield (10.13 g).^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 12H), 1.00 (s, 18H), 6.89 (d, J = 8.7 Hz, 4H), 7.72 (d, J = 8.7 Hz, 4H).

*3,6-Bis(tert-butyldimethylsilyloxy)-9H-fluoren-9-one (**4**).* The reaction of 3,6-dihydroxy-9*H*-fluoren-9-one[19] (5.0 g, 23.58 mmol) with *tert*-butyldimethylchlorosilane (10.66 g, 70.74 mmol) and imidazole (4.81 g, 70.74 mmol) in dry DCM (80 mL) under similar conditions yielded 3,6-bis(*tert*-butyldimethylsilyloxy)-9*H*-fluoren-9-one (**4**) as a pale yellow solid in 96% yield (10.29 g). mp. 68−70 °C; IR (KBr) cm^{-1} 2954, 2885, 1703, 1608, 1487, 1301, 1237, 1179; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (s, 12H), 1.00 (s, 18H), 6.67 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 2H), 6.89 (d, J = 1.8 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.3, 18.2, 25.6, 112.5, 119.4, 125.5, 128.6, 145.9, 161.6, 191.4; ESI-MS$^+$ *m/z* Calcd for $C_{25}H_{37}O_3Si_2$ 441.2281 $[M+H]^+$, found 441.2286.

*Bis(4-(tert-butyldiphenylsilyloxy)phenyl)methanone (**5**).* Reaction of 4,4′-dihydroxybenzophenone (5.0 g, 23.36 mmol) with *tert*-butyldiphenylchlorosilane (19.26 g, 70.08 mmol) and imidazole (4.77 g, 70.08 mmol) in dry DCM (80 mL) according to the above procedure, led to bis(4-(*tert*-butyldiphenylsilyloxy)phenyl)methanone (**5**) as a colorless liquid in 97% yield (15.64 g). IR (KBr) cm^{-1} 3070, 2929, 2857, 1653, 1597, 1471, 1265, 1163; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 18H), 6.78 (dd, J_1 = 8.7 Hz, J_2 = 1.0 Hz, 4H), 7.35−7.40 (m, 8H), 7.41−7.47 (m, 4H), 7.52−7.57 (m, 4H), 7.69−7.74 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 26.4, 119.3, 127.9, 130.1, 130.9, 131.9, 132.2, 135.4, 159.2, 194.6; ESI-MS$^+$ *m/z* Calcd for $C_{45}H_{47}O_3Si_2$ 691.3064 $[M+H]^+$, found 691.3063.

Synthesis of Silyloxy-Substituted Propargyl Alcohols (PA1−PA5). The silyloxy-substituted propargyl alcohols were synthesized by the reaction of sodium acetylide with the precursor carbonyl compounds in THF. A representative procedure is described below.

*1-(4-(tert-Butyldimethylsilyloxy)phenyl)-1-phenylprop-2-yn-1-ol (**PA1**).* To a solution of (4-(*tert*-butyldimethylsilyloxy)phenyl) (phenyl)methanone (2.6 g, 8.32 mmol) in dry THF (50 mL) contained in a two-necked round-bottom flask was added sodium acetylide (18% slurry in xylene; 4.44 g, 16.64 mmol) dropwise at 0 °C under N_2 gas atmosphere. The resulting reaction mixture was stirred at rt for further 4 h. Subsequently, it was quenched with water and extracted

DOI: 10.1021/acs.joc.6b01361
J. Org. Chem. 2016, 81, 7741−7750

with EtOAc. The organic layer was dried over anhyd Na_2SO_4, filtered, concentrated under reduced pressure and the residue obtained was purified by column chromatography to get hold of 1-(4-(*tert*-butyldimethylsilyloxy)phenyl)-1-phenylprop-2-yn-1-ol (**PA1**) as a colorless solid in 60% yield (1.19 g). mp. 62−64 °C; IR (KBr) cm^{-1} 3425, 3069, 2955, 2886, 1579, 1447, 1254, 1087; ^1H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 6H), 0.98 (s, 9H), 2.78 (s, 1H), 2.87 (s, 1H), 6.79 (d, J = 9.2 Hz, 2H), 7.26−7.30 (m, 1H), 7.32−7.37 (m, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.59 (d, J = 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.1, 25.6, 74.0, 75.2, 86.6, 119.5, 119.6, 125.8, 125.9, 127.3, 127.4, 127.6, 127.7, 128.1, 128.2, 137.1, 144.5, 155.3; ESI-MS^+ m/z Calcd for $C_{21}H_{25}OSi$ $[M+H-H_2O]^+$ 321.1674, found 321.1679.

*3-(tert-Butyldimethylsilyloxy)-9-ethynyl-9H-fluoren-9-ol (**PA2**).* Reaction of 3-(*tert*-butyldimethylsilyloxy)-9*H*-fluoren-9-one (4.5 g, 14.49 mmol) and sodium acetylide (18% slurry in xylene; 7.73 g, 28.98 mmol) in dry THF (80 mL) according to the above-mentioned procedure led to 3-(*tert*-butyldimethylsilyloxy)-9-ethynyl-9*H*-fluoren-9-ol (**PA2**) as a off-white solid in 61% yield (2.97 g).Mp. 88−90 °C; IR (KBr) cm^{-1} 3431, 2931, 2859, 1609, 1585, 1481, 1262, 1204; ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 6H), 1.01 (s, 9H), 2.50 (s, 1H), 2.53 (s, 1H), 6.79 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 1H), 7.05 (d, J = 2.3 Hz, 1H), 7.23−7.42 (m, 2H), 7.54−7.58 (m, 2H), 7.69 (d, J = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.3, 18.2, 25.7, 71.0, 74.0, 84.0, 111.9, 120.1, 124.1, 125.0, 128.6, 129.7, 138.9, 139.3, 140.7, 147.4, 157.4; ESI-MS^+ m/z Calcd for $C_{21}H_{24}O_2SiNa$ 359.1443 $[M+Na]^+$, found 359.1447.

*1,1-Bis(4-(tert-butyldimethylsilyloxy)phenyl)prop-2-yn-1-ol (**PA3**).* Synthesis of 1,1-bis(4-(*tert*-butyldimethylsilyloxy)phenyl)prop-2-yn-1-ol (**PA3**) was accomplished with the reaction of bis(4-(*tert*-butyldimethylsilyloxy)phenyl)methanone (1.2 g, 2.71 mmol) and sodium acetylide (18% slurry in xylene; 1.44 g, 5.42 mmol) in dry THF (30 mL) by adopting the procedure as described above. The pure compound was obtained as a colorless solid in 57% yield (0.72 g). mp. 102−105 °C; IR (KBr) cm^{-1} 3308, 3038, 2956, 2886, 2858, 1605, 1581, 1472, 1263; ^1H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 12H), 0.98 (s, 18H), 2.74 (s, 1H), 2.84 (s, 1H), 6.79 (d, J = 9.1 Hz, 4H), 7.43 (d, J = 8.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.1, 25.6, 73.7, 75.0, 86.9, 119.6, 127.3, 137.3, 155.2; ESI-MS^+ m/z Calcd for $C_{27}H_{39}O_2Si_2$ $[M+H-H_2O]^+$ 451.2488, found 451.2487.

*3,6-Bis(tert-butyldimethylsilyloxy)-9-ethynyl-9H-fluoren-9-ol (**PA4**).* The reaction of 3,6-bis(*tert*-butyldimethylsilyloxy)-9*H*-fluoren-9-one (1.2 g, 2.72 mmol) and sodium acetylide (18% slurry in xylene; 1.44 g, 5.44 mmol) in dry THF (30 mL) under similar conditions gave rise to 3,6-bis(*tert*-butyldimethylsilyloxy)-9-ethynyl-9*H*-fluoren-9-ol (**PA4**) as a off-white solid in 72% yield (0.91 g). mp. 68−70 °C; IR (KBr) cm^{-1} 3310, 2956, 2858, 1610, 1584, 1446, 1295, 1174; ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 12H), 1.01 (s, 18H), 2.46(s, 1H), 2.59 (s, 1H), 6.78 (dd, J_1 = 9.9 Hz, J_2 = 2.3 Hz, 2H), 6.97 (d, J = 2.2 Hz, 2H), 7.51 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.2, 25.6, 70.7, 73.5, 84.3, 111.9, 120.0, 124.9, 140.3, 140.5, 157.3; ESI-MS^+ m/z Calcd for $C_{27}H_{37}O_2Si_2$ $[M+H-H_2O]^+$ 449.2332, found 449.2330.

*1,1-Bis(4-(tert-butyldiphenylsilyloxy)phenyl)prop-2-yn-1-ol (**PA5**).* Synthesis of 1,1-bis(4-(*tert*-butyldiphenylsilyloxy)phenyl)prop-2-yn-1-ol (**PA5**) was accomplished with the reaction of bis(4-(*tert*-butyldiphenylsilyloxy)phenyl)methanone (1.3 g, 1.88 mmol) and sodium acetylide (18% slurry in xylene; 1.00 g, 3.76 mmol) in dry THF (30 mL) by adopting the procedure as mentioned earlier. The pure compound was obtained as a colorless liquid in 60% yield (0.81 g). IR (KBr) cm^{-1} 3427, 3071, 3050, 2958, 2858, 1604, 1505, 1472, 1391; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 18H), 2.60 (s, 1H), 2.75 (s, 1H), 6.68 (d, J = 8.7 Hz, 4H), 7.23 (d, J = 8.7 Hz, 4H), 7.32−7.38 (m, 8H), 7.39−7.44 (m, 4H), 7.69 (d, J = 8.7 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 26.5, 73.6, 74.8, 86.8, 119.2, 127.1, 127.7, 129.8, 132.7, 135.5, 137.0, 155.1; ESI-MS^+ m/z Calcd for $C_{47}H_{47}O_2Si_2$ $[M+H-H_2O]^+$ 699.3115, found 699.3117.

Synthesis of Silyloxy-Substituted Pyrans. As mentioned earlier, all the **BP**s and **NP**s were prepared by acid-catalyzed cyclocondensation reactions of appropriate phenolic compounds and suitably substituted propargyl alcohols (**PA**s). A representative procedure for the synthesis of the pyrans is described below.

*tert-Butyldimethyl(4-(2-phenyl-2H-chromen-2-yl)phenoxy)silane (**BP-P1**).* A 50 mL two-necked round-bottom flask was charged with phenol (0.53 g, 5.64 mmol), 1-(4-(*tert*-butyldimethylsilyloxy)phenyl)-1-phenylprop-2-yn-1-ol, i.e., **PA1** (2.30 g, 6.76 mmol), a catalytic amount of PTSA (0.11 g, 0.56 mmol), and dry DCM (20 mL). The resulting solution was stirred at rt for 4 h under nitrogen gas atmosphere. After this period, the reaction mixture was washed with saturated Na_2CO_3 solution, and the organic contents were extracted with DCM (20 mL × 3). The combined extract was dried over anhyd Na_2SO_4, filtered and concentrated to dryness under reduced pressure. Purification of the crude material by silica gel column chromatography using 1% ethyl acetate in hexane, afforded pure **BP-P1** as a colorless crystalline solid in 30% yield (0.70 g). mp. 70−72 °C; IR (KBr) cm^{-1} 3055, 2935, 2859, 1634, 1607, 1463, 1362, 1216; ^1H NMR (400 MHz, $CDCl_3$,) δ 0.20 (s, 6H), 0.99 (s, 9H), 6.14 (d, J = 10.1 Hz, 1H), 6.60 (d, J = 10.1 Hz, 1H), 6.79 (d, J = 8.7 Hz, 2H), 6.82−6.86 (m, 1H), 6.92 (d, J = 8.2 Hz, 1H), 7.00 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.11−7.15 (m, 1H), 7.23−7.36 (m, 5H), 7.43−7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.1, 25.6, 82.4, 116.4, 119.4, 121.0, 123.6, 126.5, 126.9, 127.3, 128.0, 128.4, 129.0, 129.4, 137.6, 145.1, 152.5, 155.0; ESI-MS^+ m/z Calcd for $C_{27}H_{31}O_2Si$ 415.2093 $[M+H]^+$, found 415.2093.

*tert-Butyldimethyl(4-(3-phenyl-3H-benzo[f]chromen-3-yl)-phenoxy)silane (**NP-P1**).* Similarly, the cyclocondensation reaction of β-naphthol (0.53 g, 3.67 mmol) with **PA1** (1.49 g, 4.41 mmol) in the presence of catalytic amount of PTSA (0.069 g, 0.44 mmol) in dry DCM (20 mL) led to **NP-P1** as a crude material. Silica gel column chromatography of the latter using 1% ethyl acetate in hexane furnished the pure product as a colorless solid in 65% yield (1.11 g). mp. 82−84 °C; IR (KBr) cm^{-1} 3056, 2931, 2858, 1631, 1607, 1507, 1462, 1216; ^1H NMR (400 MHz, $CDCl_3$) δ 0.20 (s, 6H), 0.98 (s, 9H), 6.26 (d, J = 10.1 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 10.1 Hz, 1H), 7.24−7.37 (m, 7H), 7.46−7.54 (m, 3H), 7.67 (d, J = 9.1 Hz, 1H), 7.73 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.1, 25.6, 82.4, 113.9, 118.4, 119.2, 119.4, 121.3, 123.5, 126.5, 126.9, 127.4, 127.9, 128.0, 128.4, 128.5, 129.3, 129.7, 129.8, 137.5, 145.0, 150.5, 155.0; ESI-MS^+ m/z Calcd for $C_{31}H_{33}O_2Si$ 465.2249 $[M+H]^+$, found 465.2242.

*tert-Butyldimethyl(spiro[benzo[f]chromene-3,9′-fluorene]-3′-yloxy)silane (**NP-F1**).* The cyclocondensation reaction of β-naphthol (0.53 g, 3.66 mmol) with 3-(*tert*-butyldimethylsilyloxy)-9-ethynyl-9*H*-fluoren-9-ol, i.e., **PA2** (1.47 g, 4.39 mmol), under similar conditions in the presence of catalytic amount of PTSA (0.69 g, 0.36 mmol) in dry DCM (20 mL) yielded **NP-F1** as a crude solid. Silica gel column chromatography of the latter using 1% ethyl acetate in hexane, afforded the pure product as a colorless crystalline solid in 66% yield (1.15 g). mp. 118−120 °C; IR (KBr) cm^{-1} 3056, 2952, 2885, 1644, 1611, 1585, 1386, 1242; ^1H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 6H), 1.01 (s, 9H), 5.71 (d, J = 10.1 Hz, 1H), 6.68 (dd, J_1 = 8.2 Hz, J_2 = 2.3 Hz, 1H), 7.05 (d, J = 10.1 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H), 7.21−7.26 (m, 1H), 7.30−7.45 (m, 4H), 7.52−7.57 (m, 2H), 7.61 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H), 8.08 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.3, 18.2, 25.7, 85.0, 111.8, 113.0, 118.4, 119.8, 120.0, 121.1, 123.6, 125.1, 126.0, 126.7, 128.4, 128.6, 129.3, 129.8, 138.8, 140.4, 140.7, 148.2, 152.1, 157.5; ESI-MS^+ m/z Calcd for $C_{31}H_{31}O_2Si$ 463.2093 $[M+H]^+$, found 463.2096.

*4,4′-(2H-Chromene-2,2-diyl)bis(4,1-phenylene))bis(oxy)bis(tert-butyldimethylsilane) (**BP-P2**).* Cyclocondensation reaction of phenol (0.50 g, 5.31 mmol) with 1,1-bis(4-(*tert*-butyldimethylsilyloxy)-phenyl)prop-2-yn-1-ol, i.e., **PA3** (4.98 g, 10.62 mmol), under similar conditions in the presence of catalytic amount of PTSA (0.05 g, 0.28 mmol) in dry DCM (20 mL) gave rise to **BP-P2** as a crude solid. Silica gel column chromatography of the latter using 1% ethyl acetate in hexane, furnished the pure product as a colorless crystalline solid in 78% yield (2.26 g). mp. 78−80 °C; IR (KBr) cm^{-1} 3038, 2955, 2858, 1636, 1607, 1579, 1472, 1259; ^1H NMR (400 MHz, $CDCl_3$,) δ 0.18 (s, 12H), 0.96 (s, 18H), 6.07 (d, J = 10.0 Hz, 1H), 6.54 (d, J = 9.6 Hz, 1H),

DOI: 10.1021/acs.joc.6b01361
J. Org. Chem. 2016, 81, 7741−7750

6.75 (d, J = 8.7 Hz, 5H), 6.80−6.84 (m, 1H), 6.86 (d, J = 7.7 Hz, 1H), 6.98 (dd, J_1 = 7.7 Hz, J_2 = 1.4 Hz, 1H), 7.08−7.12 (m, 1H), 7.24 (d, J = 8.7 Hz, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.6, 18.1, 25.6, 82.3, 116.4, 119.4, 120.9, 121.0, 122.7, 126.4, 128.3, 129.3, 129.4, 137.9, 152.6, 154.9;ESI-MS$^+$ m/z Calcd for $C_{33}H_{45}O_3Si_2$ 545.2907 $[M+H]^+$, found 545.2905.

*(4,4′-(3H-Benzo[f]chromene-3,3-diyl)bis(4,1-phenylene))bis(oxy)-bis(tert-butyldimethylsilane) (**NP-P2**).* Cyclocondensation reaction of β-naphthol (0.50 g, 3.47 mmol) with **PA3** (2.11 g, 4.50 mmol) in the presence of a catalytic amount of PTSA (0.065 g, 0.34 mmol) in dry DCM (20 mL) gave rise to **NP-P2** as a crude solid. Purification of the latter by silica gel column chromatography using 1% ethyl acetate in hexane, afforded thepure product as a colorless crystalline solid in 87% yield (1.79 g). mp. 102−104 °C; IR (KBr) cm^{-1} 3060, 2956, 2858, 1634, 1606, 1471, 1389, 1265; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.17 (s, 12H), 0.96 (s, 18H), 6.19 (d, J = 10.0 Hz, 1H), 6.77 (d, J = 8.7 Hz, 4H), 7.17 (d, J = 10.0 Hz, 1H), 7.25−7.34 (m, 6H), 7.46 (t, J = 7.8 Hz, 1H), 7.65 (d, J = 9.2 Hz, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.1, 25.6, 82.3, 113.8, 118.4, 118.8, 119.3, 121.3, 123.4, 126.5, 128.1, 128.3, 128.5, 129.2, 129.6, 129.8, 137.7, 150.6, 154.9; ESI-MS$^+$ m/z Calcd for $C_{37}H_{47}O_3Si_2$ 595.3064 $[M+H]^+$, found 595.3063.

*3′,6′-Bis(tert-butyldimethylsilyloxy)spiro[benzo[f]chromene-3,9′-fluorene] (**NP-F2**).* Similar cyclocondensation reaction of β-naphthol (0.50 g, 3.47 mmol) with 3,6-bis(*tert*-butyldimethylsilyloxy)-9-ethynyl-9*H*-fluoren-9-ol, i.e., **PA4** (2.10 g, 4.50 mmol), in the presence of catalytic amount of PTSA (0.064 g, 0.34 mmol) in dry DCM (20 mL) led to **NP-F2** as a crude solid. Purification of the latter by silica gel column chromatography using 1% ethyl acetate in hexane afforded to the pure product as a colorless solid in 78% yield (0.496 g). mp. 148−150 °C; IR (KBr) cm^{-1} 3042, 2952, 2884, 1636, 1582, 1470, 1272, 1176; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 12H), 1.02 (s, 18H), 5.70 (d, J = 9.6 Hz, 1H), 6.67 (dd, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 2H), 7.04 (d, J = 2.3 Hz, 1H), 7.06 (d, J = 9.1 Hz, 1H), 7.35−7.42 (m, 4H), 7.51−7.55 (m, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.3, 18.2, 25.7, 84.5, 111.8, 113.0, 118.4, 119.7, 119.8, 121.1, 123.5, 125.4, 125.8, 126.6, 128.6, 129.2, 129.3, 129.8, 140.5, 141.2, 152.2, 157.4; ESI-MS$^+$ m/z Calcd for $C_{37}H_{45}O_3Si_2$ 593.2907 $[M+H]^+$, found 593.2912.

*(4,4′-(3H-Benzo[f]chromene-3,3-diyl)bis(4,1-phenylene))bis(oxy)-bis(tert-butyldiphenylsilane) (**NP-P2′**).* Cyclocondensation reaction of β-naphthol (0.50 g, 3.47 mmol) with 1,1-bis(4-(*tert*-butyldiphenylsilyloxy)-phenyl)prop-2-yn-1-ol, i.e., **PA5** (3.73 g, 5.20 mmol), in the presence of catalytic amount of PTSA (0.065 g, 0.34 mmol) in dry DCM (20 mL) gave rise to **NP-P2′** as a crude solid. Purification of the latter by silica gel column chromatography using 1% ethyl acetate in hexane furnished the pure product as a colorless solid in 68% yield (1.79 g). mp. 68−70 °C; IR (KBr) cm^{-1} 3070, 2957, 1930, 2857, 1604, 1506, 1428, 1361, 1257; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (s, 18H), 6.07 (d, J = 9.6 Hz, 1H), 6.65 (d, J = 8.7 Hz, 4H), 7.05−7.11 (m, 5H), 7.17 (d, J = 10.0 Hz, 1H), 7.26−7.33 (m, 9H), 7.35−7.46 (m, 5H), 7.50 (d, J = 8.7 Hz, 1H), 7.60−7.71 (m, 9H), 7.90 (d, J = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 26.5, 82.2, 113.8, 118.4, 118.7, 119.0, 121.2, 123.4, 126.4, 127.7, 128.0, 128.4, 129.2, 129.5, 129.8, 132.8, 135.5, 137.4, 150.5, 154.8; ESI-MS$^+$ m/z Calcd for $C_{57}H_{55}O_3Si_2$ 843.3690 $[M+H]^+$, found 843.3698.

X-ray Crystal Structure Determinations. The X-ray diffraction intensity data collection for the crystals of the pyrans were carried out with an APEX-II CCD detector system with Mo-sealed Siemens ceramic diffraction tube (λ = 0.7107 Å) and a highly oriented graphite monochromator operating at 50 kV and 30 mA. Subsequently, the data were collected in a hemisphere mode and processed with Bruker SAINT. Empirical absorption correction was made using Bruker SADABS. The structure was solved in each case by direct methods using SHELXL package and refined by full matrix least-squares method based on F^2 using SHELX-2014 program (Sheldrick 2014). The hydrogens were fixed geometrically, treated as riding on their nonhydrogens, and refined isotropically, while all nonhydrogens were subjected to anisotropic refinement. CCDC-1451550 (**BP-P1**), 1451551 (**BP-P2**), 1451552 (**NP-F1**), and 1451553 (**NP-P2**) contain the supplementary X-ray crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Fluoride Sensing Experiments. The fluoride sensing experiments were carried out by performing UV−vis titrations with the dilute solution of each of the pyrans (50 μM in THF) against standard tetrabutylammomium fluoride solution in THF at 298 K. After each addition of TBAF to the pyran solutions, the reaction mixtures—contained in a 3.5 mL quartz cuvette—were allowed for an equilibration time of ca. 30 s prior to spectral acquisition throughout the titration experiments. In the case of sensing investigations with inorganic fluoride, similar titrations were performed by gradual addition of standard NaF solution (prepared in DMSO-H_2O; 95:5, v/v) to the dilute solutions (50 μM) of **NP-P2** and **NP-F2** in DMSO-H_2O (95:5, v/v). For **NP-P2′**, however, the titration with NaF was carried out in DMSO-H_2O; 90:10, v/v. The naked-eye detection limits were calculated at the lowest level of fluoride for which distinct color changes were observed.

For ^{1}H NMR titrations, the solutions (0.5 mL) of the pyrans in CD_3CN (0.03 M) were treated with increasing equivalents of TBAF and the ^{1}H NMR spectra of the solutions were recorded at rt. After addition of TBAF to the pyran solutions each time, the reaction mixtures contained in the NMR tubes were allowed for an equilibration time of ca. 1 min prior to spectral acquisition throughout the titration experiments.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01361.

Single crystal X-ray data, fluoride sensing experiments, NMR titration and ^{1}H and ^{13}C NMR spectra of all the compounds (PDF)

X-ray crystallographic data for **BP-P1**, **BP-P2**, **NP-F1**, and **NP-P2** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.N.M. is thankful to the Science and Engineering Research Board (SERB), New Delhi, for financial support through J. C. Bose fellowship. A.M. and V.K.M. gratefully acknowledge Council of Scientific and Industrial Research (CSIR), New Delhi for senior and junior research fellowships, respectively. We thank Dr. Savitha Govardhan for her help with refinement of some of the X-ray structures. Mr. Debanjan Bhattacharjee is thanked for his help during the initial stages of the project.

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DOI: 10.1021/acs.joc.6b01361
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