

## Photodecaging from 9-substituted 2,7-dihydroxy and dimethoxyfluorenes: competition between heterolytic and homolytic pathways

Aron Roxin, Alex Chase, Elizabeth Jeffers and Matthew Lukeman\*

Received 19th November 2010, Accepted 6th January 2011

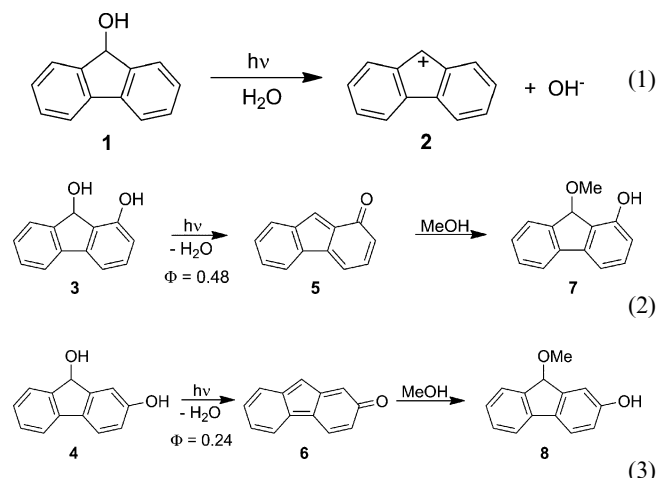
DOI: 10.1039/c0pp00351d

2,7-Dihydroxy-9-fluoreno1 (**9**), 2,7-dimethoxy-9-fluoreno1 (**10**), and 2,7-dimethoxy-9-acetoxyfluorene (**11**) were prepared and their photochemistry was studied in methanol and aqueous methanol solution in the hopes of observing efficient expulsion of the substituents positioned at the 9-position. For all three compounds, the primary photoproducts were 2,7-disubstituted-9-fluorenes and 2,7-disubstituted-9-methoxyfluorenes. A mechanism of reaction is proposed for production of these products, and involves competing homolytic and heterolytic pathways that produce radical and carbocation intermediates. Reaction quantum yields (for substrate disappearance) ranged between 0.21 and 0.31.

### Introduction

The photochemistry of 9-fluoreno1 (**1**) and its derivatives has received much attention since the initial discovery by Wan and coworkers that when aqueous solutions of **1** are irradiated, heterolytic cleavage of the C–O bond takes place to expel hydroxide ion and generate the 9-fluorenyl cation **2** (eqn (1)).<sup>1</sup> This cation is of significant theoretical interest, since the central five-membered ring of this cation contains  $4n$   $\pi$ -electrons and is thus formally anti-aromatic according to the Hückel rule. Since this discovery, the photochemistry of several derivatives of **1** has been explored, most differing from **1** only in the nature of the substituents at the 9-position.<sup>2,3</sup> We were particularly interested in one report on the photochemistry of 1- and 2-hydroxy-9-fluoreno1s **3** and **4**.<sup>3</sup> These compounds undergo photodehydration in aqueous methanol to give quinone methides **5** and **6**, which are subsequently trapped by nucleophilic attack of the 9-position by methanol to give ethers **7** and **8** (eqn (2) and (3)). The reaction quantum yields for the photomethanolysis of **3** and **4** are 0.48 and 0.24, respectively, which are higher than the quantum yield of 0.15 for the photoreaction of **1** in eqn (1).<sup>1</sup> The proposed reaction mechanism involved an initial excited state proton transfer (ESPT) from the phenolic OH to solvent to yield the excited state phenolate, which then expels hydroxide from the 9-position, a process which is facilitated by the strongly electron-donating phenolate. For the *ortho* derivative **3**, direct excited state intramolecular proton transfer (ESIPT) from the phenolic OH to the departing hydroxyl group is also possible, an additional mechanism that may account for the higher quantum yield of **3** relative to **4**. Regardless of the operative mechanism, the addition of the hydroxyl group to the 1- or 2-position of the 9-

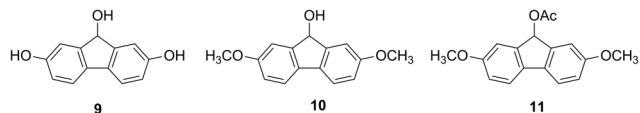
fluoreno1 skeleton greatly facilitates heterolytic departure of the functional group at the 9-position on photolysis.



Our interest in the photochemistry of **3** and **4** (and **1**) stems from our interest in the development of new photoremovable protecting groups (PPGs). Compounds **3** and **4** show many attributes that would be desirable in a PPG – the photochemistry is clean and efficient (at least for release of water), and the release kinetics are estimated to be sub-nanosecond.<sup>3</sup> Although **3** reacts with double the efficiency of **4**, we considered it unsuitable for PPG applications since it produces the long-lived quinone methide **5** ( $\tau = 5\text{--}10$  s) that could interfere by absorbing incoming light and/or alkylating biological molecules. The *meta* isomer (**4**) was deemed a superior choice because the *m*-quinone methide generated (**6**) has a very short lifetime in aqueous solution, likely because nucleophilic attack at the 9-position regenerates two aromatic rings, whereas only one is regenerated for **5**. As a result of its short lifetime, **6** will not compete for incoming light, and its most likely fate is capture by nearby solvent water molecules. While **4** (with leaving groups

Department of Chemistry, 6 University Ave., Acadia University, Wolfville, NS, B4P 2R6, Canada. E-mail: mlukeman@acadiau.ca; Fax: +1 (902) 585-1114; Tel: +1 (902) 585-1009

such as carboxylates substituted at the 9-position) shows a number of qualities suitable for PPG applications, we envisioned that PPGs based on 2,7-dihydroxy-9-fluorenol (**9**) might be superior for a number of reasons: (1) the additional OH group may lead to further increases in reaction quantum yield; (2) the additional OH group may increase water solubility; (3) the additional OH group was expected to red-shift the absorption, enabling the use of less damaging excitation sources; and (4) the increased symmetry of **9** relative to **4** renders the 9-position achiral, avoiding complications associated with diastereomeric mixtures when releasing chiral molecules.<sup>4</sup> For these reasons, we prepared and investigated the photochemistry of **9** in aqueous solution, as well as related derivatives **10–11**.



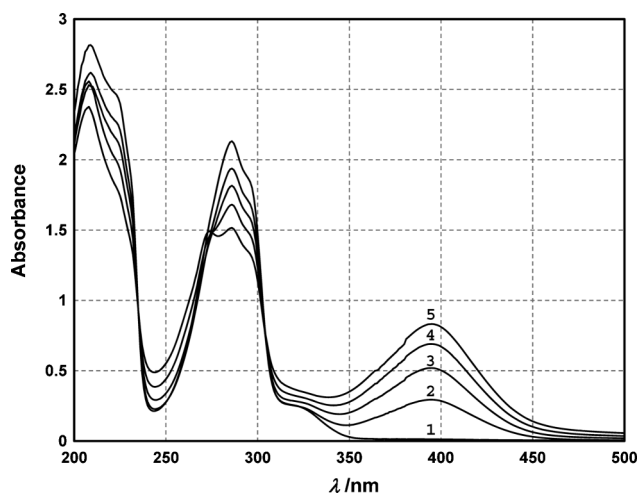
## Results and discussion

### Synthesis

The desired derivatives **9–11** were all made from the common synthetic intermediate 2,7-dihydroxy-9-fluorenone (**12**) (Scheme 1), which we prepared according to a modification of the procedures reported by the groups of Andrews<sup>5</sup> and Agrawal.<sup>6</sup> **9** was obtained by borohydride reduction of **12**. Treatment of **12** with methyl iodide in basic DMSO gave the diether **13**, which gave **10** on reduction with NaBH<sub>4</sub>. **11** was obtained by acetylation of **10** with acetic anhydride in pyridine.

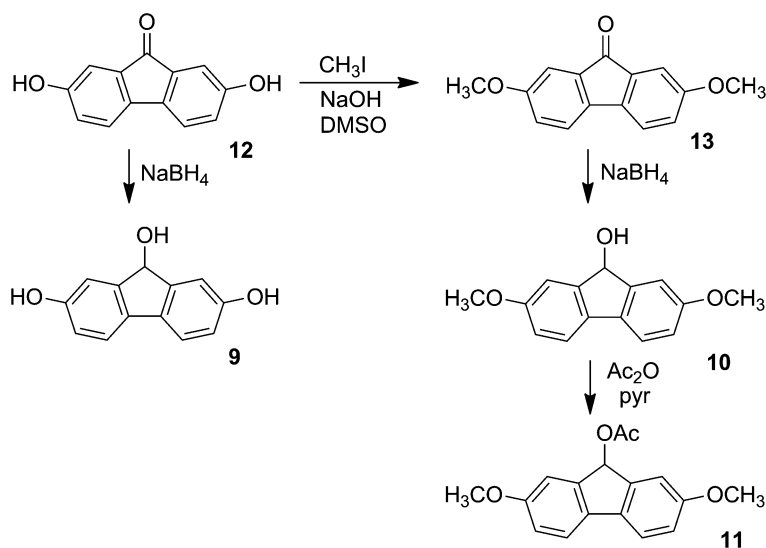
### UV-Vis spectroscopy

The UV-Vis spectrum of a solution of **9** (in oxygenated 1:1 H<sub>2</sub>O–CH<sub>3</sub>CN) has the longest wavelength absorption band with a maximum at ~320 nm that tails off just above 350 nm (Fig. 1, trace 1). Irradiation of this solution led to marked changes in the absorption profile, with the most obvious change being the growth of a new absorption band with a maximum at 393 nm.

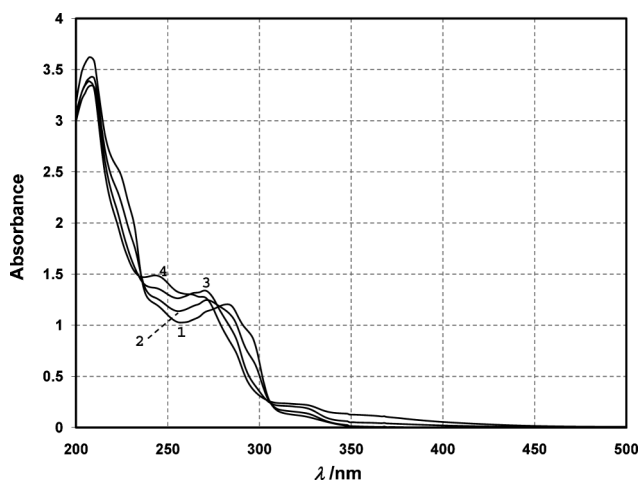


**Fig. 1** UV-Vis spectra of a solution of **9** (in 1:1 CH<sub>3</sub>CN–H<sub>2</sub>O, oxygen purged) before (trace 1) and after 30 s (trace 2), 60 s (trace 3), 90 s (trace 4), and 120 s (trace 5) of irradiation in a LuzChem LZC photoreactor equipped with 10 lamps with maximum output at 300 nm.

Along with this new peak, the existing peaks at 207 nm and 284 nm decreased in intensity, and isosbestic points were observed at 235 nm and 304 nm. A third isosbestic point is present close to 265 nm for the earliest spectra obtained, however, later spectra do not pass through this point, indicating that more than one product is likely being formed. Addition of a few drops of a sodium thiosulfate solution to the irradiated solution led to the complete and immediate disappearance of the 393 nm peak, suggesting that the species giving rise to this absorption is easily reduced. Our first suspicion was that irradiation of **9** was giving rise to a quinone product such as **14** or **15**. Our suspicion was supported by the fact that the closely related quinone from 4,4'-bisphenol (**16**) has an absorption maximum at 408 nm and has an absorption profile that is similar in appearance to that observed on irradiation of **9**.<sup>7</sup> Spectra similar to those in Fig. 1 were also obtained when **9** was irradiated in oxygenated water and 1:1 water–methanol solutions. Irradiation of argon-bubbled solutions

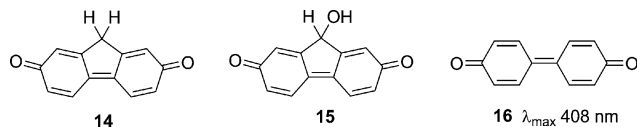


**Scheme 1**



**Fig. 2** UV-Vis spectra of a solution of **9** (in 1 : 1 CH<sub>3</sub>OH–H<sub>2</sub>O, argon purged) before (trace 1) and after 2 min (trace 2), 4 min (trace 3), and 10 min (trace 4) of irradiation in a LuzChem LZC photoreactor equipped with 10 lamps with maximum output at 300 nm.

of **9** in 1 : 1 water–methanol led to UV-Vis changes that are less dramatic (Fig. 2). Most notable is the absence of the 393 nm band that is tentatively assigned to a quinone such as **14** or **15** under deoxygenated conditions, suggesting that the 393 nm absorbing species is a product of oxidation by O<sub>2</sub>. Isosbestic points are not clearly defined, indicating that more than one product is forming under these conditions as well.

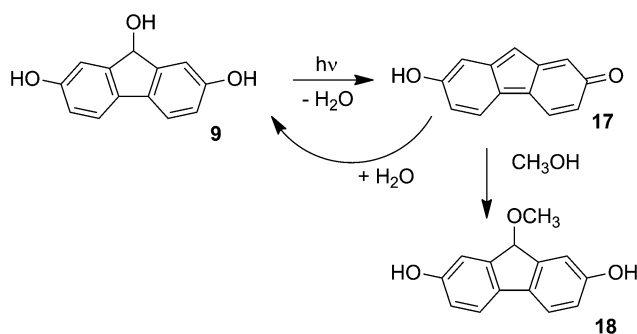


Irradiation of **10** or **11** was not expected to give quinone products (similar to **14** and **15**) since the conversion of the phenolic OH groups to methoxy groups removes this possibility. Irradiation of solutions of **10** or **11** (argon or oxygen purged, 1 : 1 CH<sub>3</sub>OH–H<sub>2</sub>O or 1 : 1 CH<sub>3</sub>CN–H<sub>2</sub>O) did lead to observable changes in their absorption spectra, and as expected, a strong band near 400 nm was not present in either case. Neither solutions of **10** nor **11** gave clearly defined isosbestic points during irradiation, indicating that multiple products are formed in each case.

### Product studies

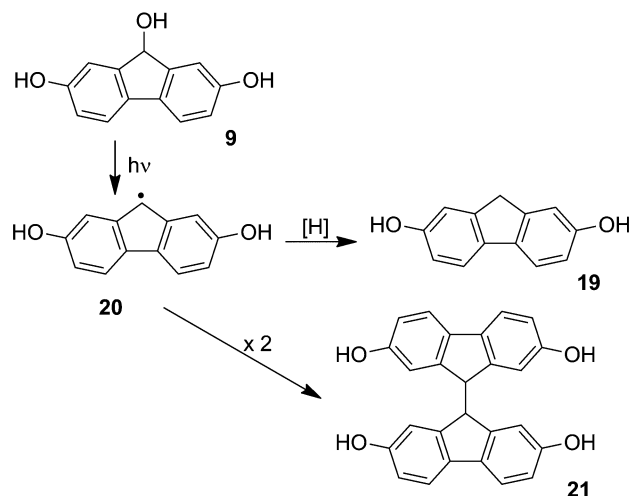
Product studies were carried out for **9–11** by irradiating them in solutions of aqueous acetonitrile, aqueous methanol, or neat methanol, and analyzing the resultant products by <sup>1</sup>H NMR and GCMS (after removal of solvent). The identity of each photoproduct was determined by MS and NMR characterization after isolation from the photolysate and by comparison with standards obtained *via* independent synthesis.

Photolysis of **9** was first carried out in aqueous methanol. Methanol was chosen as a co-solvent in the photolysis of **9** to trap the expected quinone methide intermediate **17** that would be formed *via* a photodehydration reaction analogous to those of **3** and **4** (eqn (2) and (3)), which would give methyl ether **18** as the expected major product (Scheme 2). Irradiation of **9** in aqueous acetonitrile (λ<sub>ex</sub> = 300 nm, argon purged, 30 min) caused the solution to turn from colourless to deep brown, and



**Scheme 2**

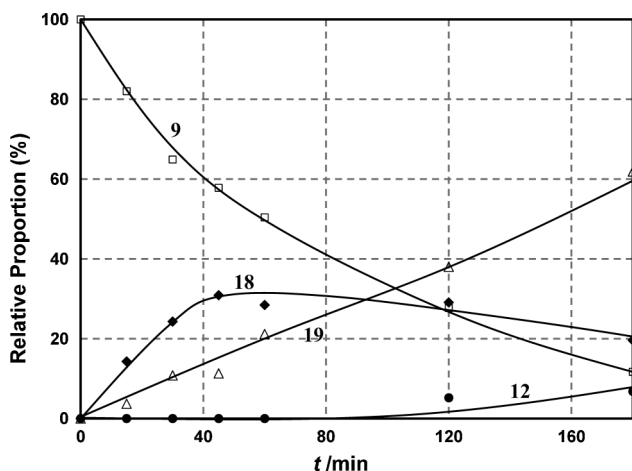
GCMS and <sup>1</sup>H NMR analysis indicated that two products were formed: the expected methyl ether **18** (Scheme 2), as well as 2,7-dihydroxyfluorene **19** (Scheme 3). Neither of these products was expected to absorb at 400 nm, and no evidence was obtained by <sup>1</sup>H NMR spectroscopy or GCMS analysis for the presence of additional products such as quinones **14** or **15** that might be responsible for the brown color. It is possible that either or both of these quinones are present in very small amounts precluding their detection by NMR or GCMS, but are observable by UV-Vis owing to large extinction coefficients. It is also possible that the visible light absorbing products are reduced during the workup and therefore not detected by GCMS or NMR analysis. The formation of the photoreduced dihydroxyfluorene **19** is most likely the result of homolytic cleavage of the C–O bond at the 9-position to give the 2,7-dihydroxy-9-fluorenyl radical **20** (Scheme 3). Fluorene products have been previously observed on irradiation of 9-fluorenyl compounds, and radical pathways are generally invoked.<sup>2,3</sup> Hydrogen abstraction by **20** from a hydrogen donor (such as methanol) would give **19** directly. We anticipated that this radical might also produce **21** *via* dimerization, although we were unable to detect this product, possibly because the concentrations of **20** were never sufficient for the dimerization pathway to compete with hydrogen abstraction. It is worth noting that a variety of phenolic compounds are well known to be excellent antioxidants, and operate by donating hydrogen atoms to carbon-centered radicals with very fast rates.<sup>8</sup> The plethora of phenolic OH groups



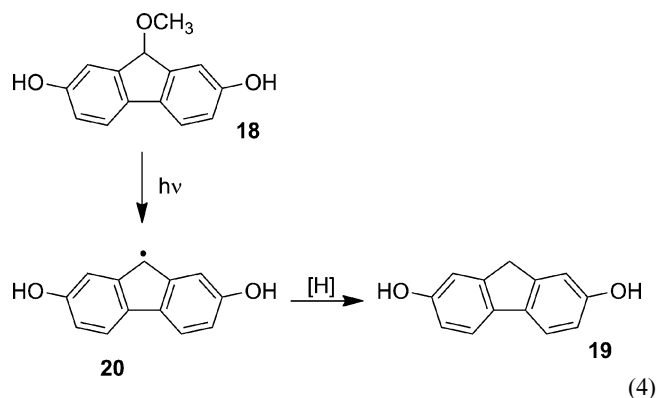
**Scheme 3**

present in solution might lead to rapid reduction of radical **20** to fluorene **19**, preventing the dimerization reaction from taking place.

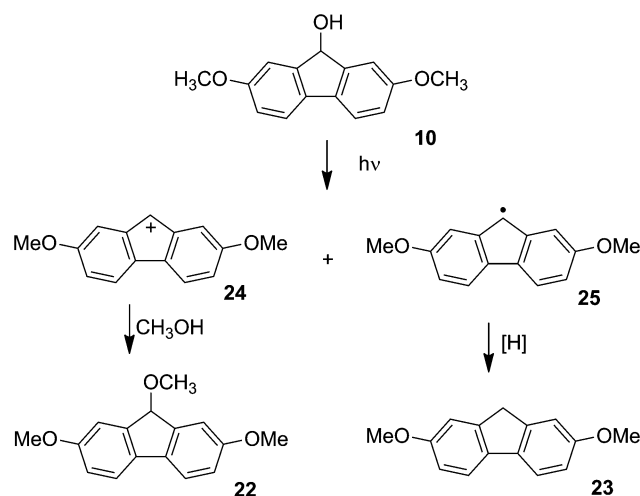
Solutions of **9** in methanol were irradiated ( $\lambda_{\text{ex}}$  300 nm, argon purged) at varying time intervals up to 180 min, and the relative proportions of starting material (**9**), and the two primary photoproducts **18** and **19** (as measured by  $^1\text{H}$  NMR) were plotted as a function of time (Fig. 3). The disappearance of **9** roughly follows an exponential decay, as would be expected due to increasing competition for incoming light as the photoproducts form. Formation of the methyl ether **18** is initially more efficient than formation of the fluorene **19**, indicating that quinone methide formation is the dominant reaction. The yield of methyl ether **18** reaches a maximum at 45 min, after which time, its relative concentration begins to drop. In contrast, the yield of the fluorene increases steadily throughout the photolysis period. The most likely explanation for this behavior is that **18**, once formed, undergoes secondary photolysis to give the 9-fluorenyl radical **20**, which ultimately gives the fluorene **19** after hydrogen abstraction (eqn (4)). This view is supported by the fact that between 120 and 180 min, the rate of formation of fluorene **19** is greater than the rate of loss of starting material **9**, demonstrating that **9** cannot be the only source of **19**. To confirm this possibility, an authentic sample of **18** was prepared by refluxing **9** in acidic methanol, and this sample was independently irradiated in methanol, giving **19** as the only product. At long photolysis times ( $\geq 2$  h), an additional photoproduct was observed and identified as fluorenone **12** based on its  $^1\text{H}$  NMR spectrum and MS. This product was expected to result from oxidation of radical **20** with oxygen. Although we deoxygenated our solutions prior to irradiation by bubbling with argon, we did not maintain an absolute seal, and it is likely that small amounts of oxygen slowly entered the flask over the long photolysis times. When the photolysis of **9** was saturated with oxygen prior to irradiation, the yield of **12** obtained after 180 min was nearly double what was obtained in this experiment, providing further evidence that fluorenone **12** results from reaction with oxygen.



**Fig. 3** Plot of relative product distributions of **9** (squares), **18** (diamonds), **19** (triangles), and **12** (circles) following irradiation of solutions of **9** in methanol ( $\lambda_{\text{ex}}$  300 nm, argon purged) for various periods of time, as determined by  $^1\text{H}$  NMR spectroscopy. Lines were added as a guide and are not the result of a fitting procedure. Errors are estimated to be  $\pm 5\%$ .



Photolysis of **10** in argon-purged methanol gave only two products: the methyl ether **22** and the fluorene **23** (Scheme 4). Heterolysis of the 9-hydroxyl group to give cation **24** and hydroxide ion, followed by reaction of **24** with solvent would give methyl ether **22**, whereas homolysis of the C–O bond at the 9-position would give radical **25**, which would give the observed fluorene **23** following hydrogen abstraction. The evolution of the product distribution with photolysis time is given in Fig. 4. Methyl ether **22** grows in moderately more efficiently than fluorene **23** initially, but after  $\sim 100$  min of irradiation time, the yield of **22** begins to drop, while the yield of **23** continues to rise. This is likely because the methyl ether **22** undergoes secondary photolysis to give the 9-fluorenyl radical **25** which gives **23** following hydrogen abstraction, similar to the case observed for **9**.



**Scheme 4**

Irradiation of methanol solutions of **11** gave results similar to those observed for **10** – the only products observed were methyl ether **22** and fluorene **23**. Unlike the case of **10**, where the major product was the one resulting from heterolytic cleavage (**22**), the major product observed on irradiation of **11** was the fluorene **23** (Fig. 5).

The photolyses of **9–11** were repeated in aqueous methanol in which the solvent composition was varied incrementally from 80 : 20  $\text{H}_2\text{O} - \text{CH}_3\text{OH}$  to neat methanol. The product distributions after 60 min of irradiation time were found to be strongly impacted by the composition of the solvent. The changes were most obvious for the 2,7-dimethoxy substituted compounds **10** and **11**, where



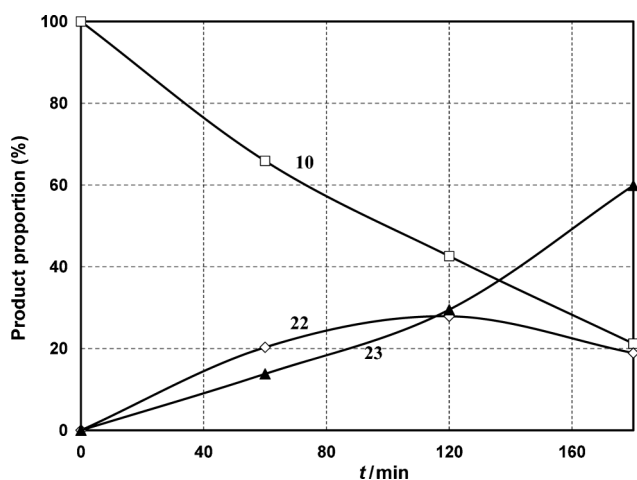


Fig. 4 Plot of relative product distributions of **10** (squares), **22** (diamonds), and **23** (triangles) following irradiation of solutions of **10** in methanol ( $\lambda_{\text{ex}}$  300 nm, argon purged) for various periods of time, as determined by  $^1\text{H}$  NMR spectroscopy. Lines were added as a guide and are not the result of a fitting procedure. Errors are estimated to be  $\pm 5\%$ .

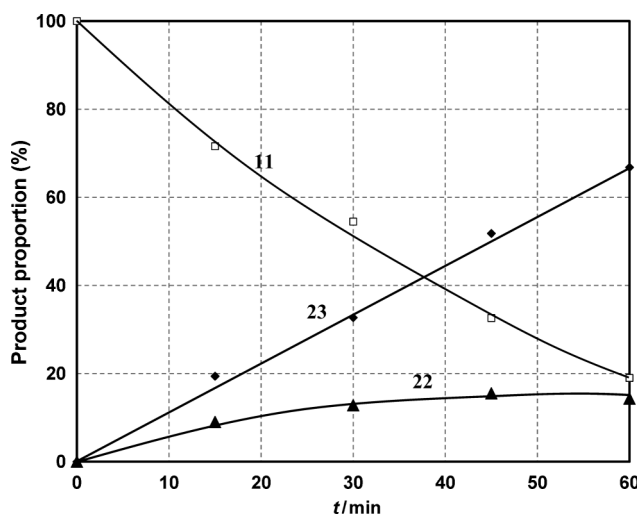


Fig. 5 Plot of relative product distributions of **11** (squares), **22** (triangles), and **23** (diamonds) following irradiation of solutions of **11** in methanol ( $\lambda_{\text{ex}}$  300 nm, argon purged) for various periods of time, as determined by  $^1\text{H}$  NMR spectroscopy. Lines were added as a guide and are not the result of a fitting procedure. Errors are estimated to be  $\pm 5\%$ .

moving from neat methanol to 80:20 water-methanol changed the ether/fluorene product ratio from 0.33 to 1.32 (for **10**) and from 0.26 to 1.12 (for **11**). These changes can be rationalized by considering the increasing polarity of the solvent system as the water content is increased. A more polar solvent system would be expected to stabilize the formation of charged intermediates relative to radical intermediates, and thus result in an increased methyl ether to fluorene ratio. The changes in product distributions on changing solvent composition were much less dramatic for **9** than for **10** and **11**, perhaps because the quinone methide formed from **9** does not carry a formal charge, and thus would not experience the same degree of solvent stabilization as would be expected for cation **24**.

Reaction quantum yields for the disappearance of substrate were measured for **9–11** in 1:1  $\text{CH}_3\text{OH-H}_2\text{O}$  solution (argon

Table 1 Photophysical and photochemical parameters for **9–11**

Compound	$\lambda_{\text{max}}$ (em)/nm <sup>a</sup>	$\Phi_{\text{F}}$ <sup>a</sup>	$\tau_{\text{r}}$ /ns <sup>a</sup>	$\Phi_{\text{R}}$ <sup>b</sup>
<b>9</b>	400	0.006	2.9	0.21
<b>10</b>	399	—	3.2	0.31
<b>11</b>	399	—	4.3	0.21

<sup>a</sup> In anhydrous  $\text{CH}_3\text{CN}$ . <sup>b</sup> In 1:1  $\text{CH}_3\text{OH-H}_2\text{O}$ .

purged), using the related reaction of 9-fluoreneol in the same solvent as a reference standard.<sup>1</sup> The values obtained for **9–11** were  $\Phi_{\text{R}} = 0.21, 0.31,$  and  $0.21,$  respectively (Table 1). These values are all close to the reaction quantum yield reported for 2-hydroxy-9-fluoreneol (**4**) ( $\Phi_{\text{R}} = 0.24$ ), indicating that two electron-donating substituents on the ring do not function cooperatively in this system. It is also interesting to note that the methoxy-substituted compound **10** has a somewhat higher quantum yield than the phenolic analogue **9**, suggesting that the additional ES IPT pathway that is potentially available to **9**, but not to **10**, does not lead to enhanced reaction efficiency. The quantum yields of the primary photochemical step (ES IPT, heterolysis, or homolysis), are higher than the values reported here, since radical or ion pairs that recombine will regenerate starting material and thus not lead to product formation.

### Quenching studies

In an effort to delineate the multiplicity of the reactive excited state for **9–11**, quenching studies were performed in which solutions of **9–11** in 1:1  $\text{H}_2\text{O-CH}_3\text{OH}$  containing either no quencher, 10 mM potassium sorbate, or 10 mM sorbic acid were irradiated simultaneously, and the product distribution was determined by  $^1\text{H}$  NMR spectroscopy. Sorbic acid and the sorbate ion are water-soluble 1,3-diene derivatives with  $E_{\text{T}} \sim 50\text{--}55 \text{ kcal mol}^{-1}$ .<sup>9</sup> We expected both to be good quenchers of the triplet excited-states of **9–11** since substituted fluorenes have significantly higher triplet energies (in the  $65\text{--}68 \text{ kcal mol}^{-1}$  range).<sup>9</sup> We used both sorbic acid and its potassium salt separately in these runs to ensure that any changes to the product distributions observed were not a consequence of acid or base catalysis enabled by the added quencher. For all of **9** to **11**, the presence of sorbic acid or potassium sorbate did not lead to significant decreases in product yields or distributions, indicating that the reaction most likely proceeds from the singlet excited state for all derivatives. Singlet photochemistry is common for phenolic compounds, particularly for ESPT and ES IPT processes. Nevertheless, based on our results we cannot rule out reactivity from a very short-lived triplet state.

### Fluorescence spectroscopy

Excitation of a solution of **9** in neat acetonitrile results in a single broad fluorescence emission band at 400 nm (Fig. 6). Changing the solvent composition to 10% water (v/v) in acetonitrile causes the quenching of this band by more than 50%. Fluorescence quenching by relatively small amounts of water is consistent with an ES IPT process that is mediated by water, and has been previously observed for other phenols that exhibit ES IPT.<sup>10</sup> Inclusion of more water in the solvent system beyond 10% leads to further quenching of this band, although the first 10% increment of water added had the largest quenching effect. On moving to neat

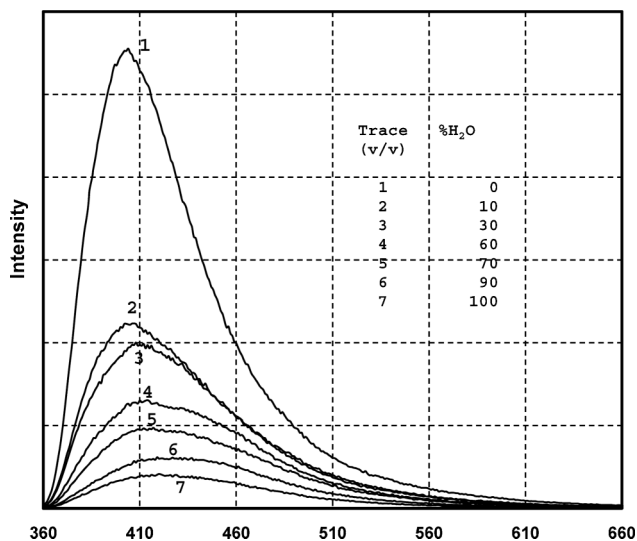


Fig. 6 Fluorescence emission spectra of **9** in acetonitrile containing varying amounts of water ranging from neat acetonitrile (trace 1) to neat water (trace 7). The amount of water (percent by volume) present in the solvent system is indicated for each trace in the legend.

water, the fluorescence emission has been quenched by almost 95%, and the emission band appears to have red-shifted. The red shift is likely the result of ESPT of **9** to solvent to give the excited phenolate ( $9^*$ ), whose emission overlaps with that from the phenol, giving a total spectrum with an apparently longer maximum wavelength. To isolate the fluorescence emission from  $9^*$ , the fluorescence spectrum of **9** in 10% water in acetonitrile was scaled down by a factor of 9 and subtracted from the fluorescence spectrum of **9** in 100% water. The resulting difference spectrum, shown in Fig. 7, has a single emission band with  $\lambda_{\text{max}} = 440$  nm. The observation of phenolate emission confirms that ESPT takes place for **9**, and that the process is adiabatic, producing the phenolate in its excited state.

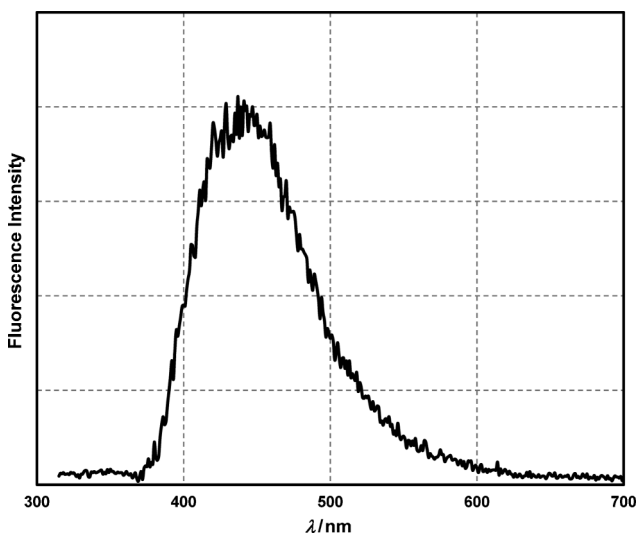


Fig. 7 Fluorescence spectrum of **9** in neat water after subtraction of scaled fluorescence spectrum of **9** in 10%  $\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  (scale factor = 9). The resulting difference spectrum is emission from the phenolate  $9^*$ .

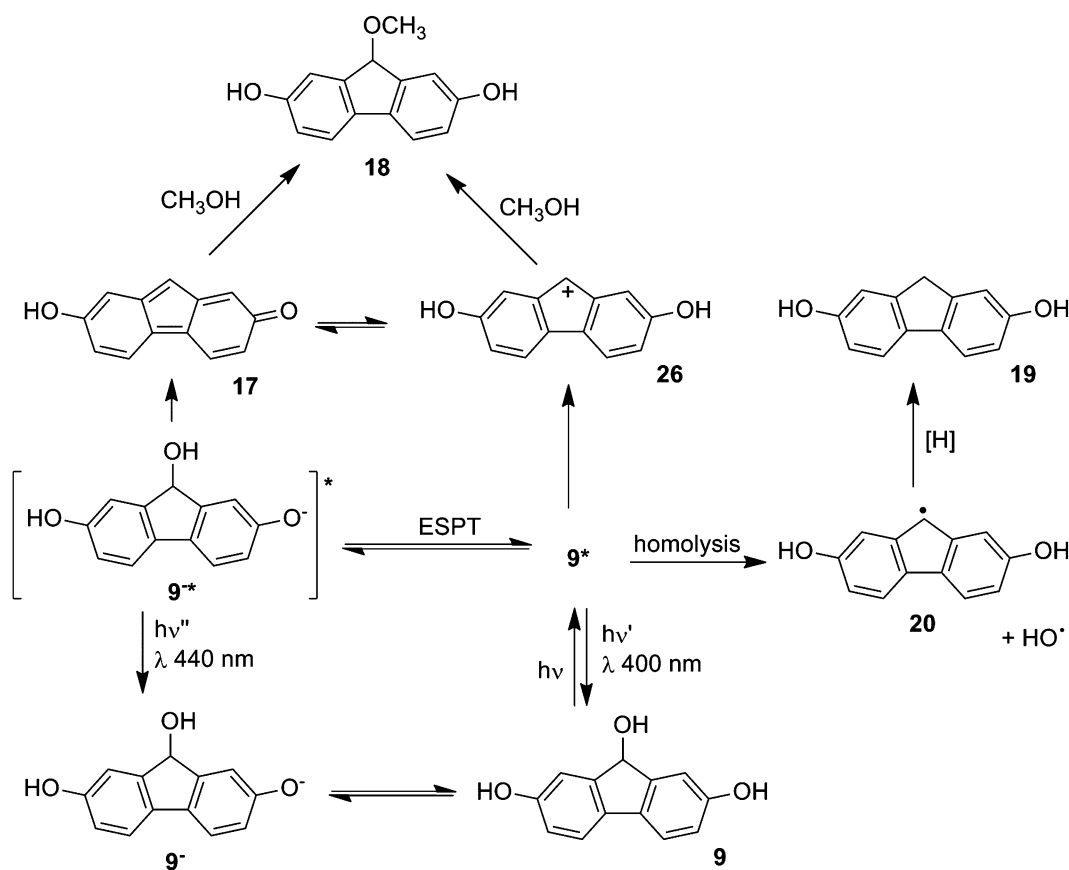
The fluorescence quantum yield of **9** was measured in anhydrous acetonitrile using tryptophan ( $\Phi_F = 0.13$  in water)<sup>11</sup> as a reference standard, and was determined to be 0.006 (Table 1). This value is in the typical range for 9-substituted fluorenyl compounds, and is much less fluorescent than unsubstituted fluorene, whose intense fluorescence gives the chromophore its name.

Fluorescence spectroscopy was also employed to investigate the photophysics of **10** and **11**. These compounds both emit with  $\lambda_{\text{max}} = 399$  nm in neat acetonitrile solution. Adjustment of the solvent composition to 10% (v/v) water in acetonitrile leads to some quenching of the fluorescence emission, but the dramatic  $>50\%$  quenching that was observed for **9** is not observed for **10** and **11**. This is again consistent with the initial quenching of **9** resulting from the addition of small amounts of water which enables an ESPT process from the singlet state that competes with fluorescence. The lack of strong quenching on addition of 10% water for **10** and **11** is due to the fact that these compounds do not possess phenolic OH groups and thus cannot participate in an ESPT reaction like **9** can. Addition of greater amounts of water to the solvent system leads to additional fluorescence quenching for **10** and **11**, which is likely a bulk solvent effect; as the solution becomes more polar, heterolytic dissociation becomes more favourable and is better able to compete with the fluorescence pathway. We were unable to measure fluorescence quantum yields for **10** and **11** due to the presence of an additional fluorescence band with  $\lambda_{\text{max}} \sim 350$  nm that overlapped with the emission of **10** and **11**, that might be a result of small amounts of dimethoxyfluorene **23** that would be produced on irradiation. For both **10** and **11**, the fluorescence quantum yields were very low, and likely within a similar range as **9**.

The fluorescence lifetimes of **9–11** (in neat acetonitrile) were also measured and appear in Table 1.

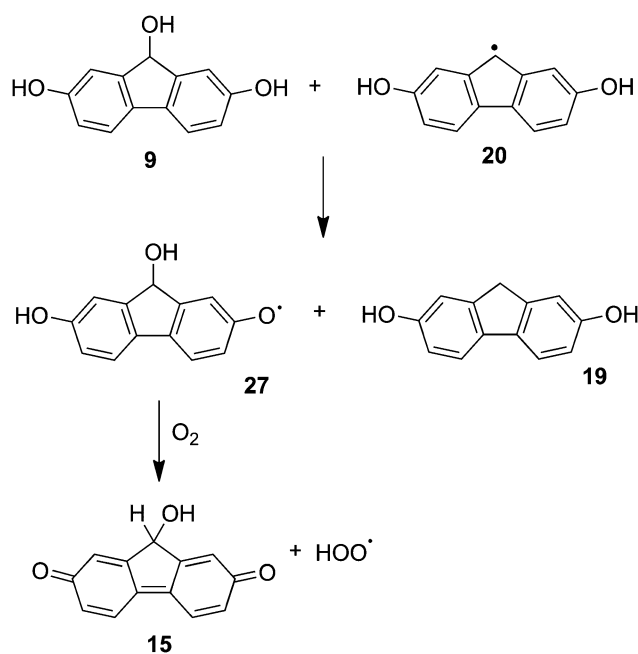
## Mechanism

The proposed mechanism of reaction for **9** is shown in Scheme 5. Excitation of **9** and relaxation to the first singlet excited state ( $9^*$ ) is followed by adiabatic deprotonation of one of the phenolic OH groups to give the excited phenolate ( $9^*$ ). Evidence for this process was provided by fluorescence experiments, in which the phenolate emission was observed. Phenols are well known to become significantly more acidic in the excited state, and ESPT and ESPT reactions are commonly observed.<sup>12</sup> Proton transfers are rapid processes and entirely reversible. Homolysis of the 9-OH substituent (as the hydroxyl radical) from  $9^*$  furnishes the 9-fluorenyl radical **20**, whereas heterolysis from  $9^*$  ejects the hydroxide ion and gives the 9-fluorenyl cation **26**. Heterolysis may also take place from  $9^*$ , giving quinone methide **17**. Nucleophilic attack by water can take place at the 9-position of **17** or **26**, either case returning the intermediate back to starting material. Alternatively, nucleophilic attack by methanol gives the methyl ether **18**. Radical **20** can undergo reduction (by H abstraction) to give fluorene **19**. While the source of hydrogen atoms has not been determined in this work, phenolic OH groups are well known to be good hydrogen donors. Donation of hydrogen atoms would produce phenoxy radicals, which could undergo several reactions, including dimerization, disproportionation, and reduction. No evidence was obtained in the product studies for dimer formation, so it is unlikely that this would be a primary pathway. The methyl

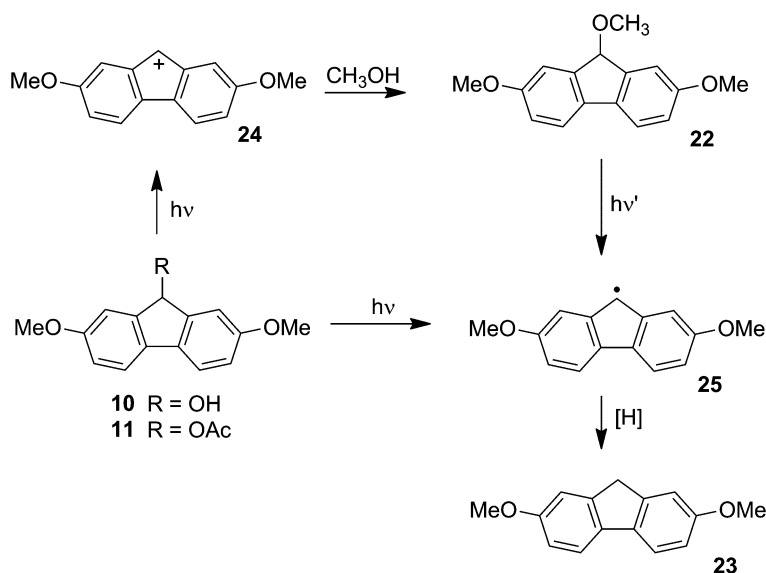


ether **18** can itself undergo secondary photochemistry to produce radical **20**, whose eventual fate is reaction to give fluorene **19**. In addition to these pathways, a minor pathway is available that leads to formation of one or more products that absorb visible light and are tentatively assigned to a quinone such as **14** or **15**. Quinone **14** can be formed directly from quinone methide **17** via tautomerization, although the UV-Vis studies indicated that the formation of the quinones was accelerated in the presence of oxygen. A related quinone methide to quinone tautomerization has been recently reported.<sup>13</sup> A proposed pathway which accounts for the effects of oxygen is shown in Scheme 6. A molecule of **9** can donate a hydrogen atom to the previously photogenerated radical **20**, producing the fluorene **19**, and a phenoxy radical (**27**). Reaction of the phenoxy radical with a molecule of oxygen would give quinone **15**. The assignment of the coloured product as a quinone is supported by its spectral similarity to known related quinones, its sensitivity to reducing agents, and the fact that it is not observed for the dimethoxy derivatives **10** and **11**.

The proposed reaction mechanism for **10** and **11** is shown in Scheme 7 and is simpler than for **9**, since conversion of the phenolic OH groups to their methyl ethers reduces the number of reaction possibilities. Irradiation of **10** or **11** leads to direct homolysis or heterolysis of the 9-substituent, producing either radical **25** or cation **24**, respectively. Radical **25** can be reduced by H-abstraction to give the fluorene **23**, and cation **24** can react with the nucleophilic solvent to give methyl ether **22**. Secondary photolysis of the methyl ether **22** generates radical **25**, which produces fluorene **23**, which can be thought of as the final 'sink'



which is produced in high yield after long periods of irradiation. In the case of the hydrogen abstraction reaction converting radical **25** to the fluorene **23**, the most reasonably hydrogen source in this system is methanol.



Scheme 7

The reactivities of **9–11** are similar to that of the mono-hydroxy derivatives **3** and **4**, although in the cases of **3** and **4**, radical formation was reportedly only observed as a result of secondary photochemistry from the initial photoproducts, whereas our product evolution plots (Fig. 3–5) indicate that homolysis occurs directly from **9–11**, and is not solely the result of secondary photolysis. It is surprising that addition of the second hydroxyl group (to make **9**) did not lead to further enhancement in heterolysis yields, and actually reduced the heterolysis to homolysis ratio. This might be a consequence of reduced polarization of the chromophore in the excited state, since the addition of the second hydroxyl group effectively creates a ‘push-push’ system.

An additional consideration in this work is whether the ‘apparent’ heterolysis products (ethers **18** and **22**) result from direct heterolysis of the 9-substituent, or whether ion formation is preceded by a homolysis reaction which then gives the ionic intermediates following an electron transfer reaction. The homolysis-electron transfer mechanism has been proposed by Pincock *et al.* to be an important source of the ion-derived products in resulting from the photohydrolysis of benzylacetates,<sup>14</sup> which are structurally related to **9–11**. Peters *et al.* have investigated the photosolvolysis of a variety of benzyl compounds, and have observed the formation of ion pairs from radical pairs directly using picosecond and femtosecond time-resolved techniques.<sup>15</sup> In the absence of ultrafast time-resolved data, the extent of the contribution of initial homolysis to the yield of ionic products is difficult to assess for **9–11**. By comparison to other benzylic systems, however, at least some ion formation *via* this mechanism can be expected.

While compounds **9–11** do show suitable absorption properties for application as PPG chromophores and release leaving groups from the 9-position with good efficiency, the formation of radical intermediates on irradiation will limit their ultimate usefulness. Further modification of these compounds may allow their properties to be tuned such that the heterolysis pathway outcompetes the homolysis pathway. For example, arylation of the 9-position of **9–11** with phenyl or alkoxyphenyl groups might enhance the

heterolysis yield (as it does for **1**, **3**, and **4**).<sup>1–3</sup> Further, the formation of byproducts that absorb in the visible region of the spectrum on irradiation of **9** represents an additional disadvantage to using 2,7-dihydroxyfluorene-based compounds, although this limitation is not present for the 2,7-dimethoxy derivatives.

## Experimental

### General

Solvents were purchased from Caledon and used as received and fine chemicals were purchased from Sigma–Aldrich Canada and used as received. NMR solvents were purchased from Norell Inc. and used as received. NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. UV-Vis spectra were recorded on a Cary Bio 100 spectrometer. Fluorescence spectra were recorded on a PTI LPS 220B Fluorescence Spectrometer. GCMS experiments were carried out on a Varian 450-GC equipped with a Varian 240-MS.

### Synthesis

**9H-Fluorene-2,7-disulfonic acid dipotassium salt.** 800 g of concentrated H<sub>2</sub>SO<sub>4</sub> (434.8 ml) was heated in a 2 L beaker on a hot plate to 100 °C, and 200 g (1.2 moles) of fluorene was added in small portions, causing the mixture to turn dark purple and evolve gas. During the addition of the fluorene and for five minutes afterwards, the mixture was stirred vigorously, and then removed from the heat and allowed to cool to 40 °C. Ice was added to bring the total volume of the mixture to 2 L, and the mixture was allowed to stand for 24 h, after which the solution was filtered to remove small amounts of undissolved solid. The filtrate was divided into two equal portions and each was heated to 100 °C. To each solution was added 200 g of KCl which was allowed to dissolve. The solutions were allowed to cool to room temperature, resulting in precipitation of a greyish-brown solid which was removed by suction filtration, leaving a blue filtrate. The



filtrates were further divided into a total of four portions and each portion was diluted with 1.75 L of H<sub>2</sub>O and heated to 100 °C. 175 g of K<sub>2</sub>CO<sub>3</sub> was slowly added to each solution with stirring. When the addition was complete, and the gas evolution had stopped, the mixtures were allowed to cool to room temperature and stand for 24 h, resulting in the precipitation 9*H*-fluorene-2,7-disulfonic acid dipotassium salt as a white solid, which was collected by filtration. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz): δ 7.8–7.9 (4H, m), 7.68 (2H, d, *J* = 6.6 Hz), 3.96 (2H, s, CH<sub>2</sub>). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 146.86, 143.62, 141.35, 124.94, 122.86, 119.94, 36.87. FTIR (KBr Pellet) 3554 cm<sup>-1</sup> (s), 3467 cm<sup>-1</sup> (s), 3060 cm<sup>-1</sup> (m), 2920 cm<sup>-1</sup> (m), 1643.7 cm<sup>-1</sup> (s), 1409 cm<sup>-1</sup> (s), 1200 cm<sup>-1</sup> (s), 1099 cm<sup>-1</sup> (s), 1034 cm<sup>-1</sup> (s), 1002 cm<sup>-1</sup> (s), 829 cm<sup>-1</sup> (s), 703 cm<sup>-1</sup> (s), 623 cm<sup>-1</sup> (s).

**9-Oxo-9*H*-fluorene-2,7-disulfonic acid dipotassium salt.** The 9*H*-fluorene-2,7-disulfonic acid dipotassium salt from the previous step was divided into four portions, and to each was added 440 mL of H<sub>2</sub>O and heated to dissolve the salt. Four solutions were prepared, each containing 52 g of KMnO<sub>4</sub> dissolved in 875 ml of H<sub>2</sub>O, and were heated to 80 °C. Each hot potassium permanganate solution was then slowly added to one of the 9*H*-fluorene-2,7-disulfonic acid dipotassium salt (**56**) solutions over 1 h, resulting in the precipitation of a brown solid (MnO<sub>2</sub>). The mixtures were suction filtered to remove MnO<sub>2</sub>, and the filtrates were heated to reduce the volume to 1.125 L each. Any further MnO<sub>2</sub> was removed by filtration, and the filtrate was cooled to ~4 °C for 20 h. 9-Oxo-9*H*-fluorene-2,7-disulfonic acid dipotassium salt was collected as a bright yellow solid and was collected by suction filtration. A second crop of this compound was obtained by reducing the volume of each portion to 375 ml by boiling off excess water, followed by cooling. After combining three crops of the collected product from the four solutions, a total of 160 g of 9-oxo-9*H*-fluorene-2,7-disulfonic acid dipotassium salt was collected (32% from fluorene). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz): δ 7.84 (2H, d, *J* = 7.5 Hz, Ar–H), 7.77 (2H, d, *J* = 7.5 Hz, Ar–H), 7.76 (2H, s, Ar–H).

<sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 150.33, 143.83, 133.88, 132.75, 121.34. FTIR (KBr Pellet) 3425 cm<sup>-1</sup> (br w), 3054 cm<sup>-1</sup> (w), 1715 cm<sup>-1</sup> (s), 1617 cm<sup>-1</sup> (m), 1604 cm<sup>-1</sup> (m), 1234 cm<sup>-1</sup> (s), 1185 cm<sup>-1</sup> (s), 1088 cm<sup>-1</sup> (s), 1035 cm<sup>-1</sup> (s), 729 cm<sup>-1</sup> (s), 617 cm<sup>-1</sup> (s).

**4,4'-Dihydroxybiphenyl-2-carboxylic acid.** 210 g of NaOH pellets were placed in a stainless steel beaker and heated with a Bunsen burner for several minutes and stirred until the NaOH was completely molten. 105 g of 9-oxo-9*H*-fluorene-2,7-disulfonic acid dipotassium salt was slowly added to the molten NaOH and was carefully stirred with a glass rod. When the addition was complete, the reaction mixture was cooled yielding a pink-brown solid. The solid was dissolved in 1.5 L H<sub>2</sub>O, heated to near boiling, and hot-filtered to remove a brown insoluble solid. The filtrate was acidified by addition of 500 mL of conc. HCl, precipitating 4,4'-dihydroxybiphenyl-2-carboxylic acid as an off-white solid with a yield of 52.6 g (91% yield). Mp 266–269 °C (lit. 281–282 °C).<sup>6</sup> <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz): δ 12.64 (1H, s, COOH), 9.77 (1H, s, ArO–H), 9.44 (1H, s, ArO–H), 7.15 (1H, d, *J* = 7.0 Hz, Ar–H), 7.08 (2H, d, *J* = 7.2 Hz, Ar–H), 7.07 (1H, s, Ar–H), 6.93 (1H, d, *J* = 7.0 Hz, Ar–H), 6.77 (2H, d, *J* = 7.2 Hz, Ar–H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 170.38, 156.72, 156.31, 133.57, 132.09, 131.95, 131.9, 129.74, 118.03, 115.77, 115.32. FTIR (KBr

Pellet) 3169 cm<sup>-1</sup> (br s), 1697 cm<sup>-1</sup> (s), 1491 cm<sup>-1</sup> (s), 1399 cm<sup>-1</sup> (m), 1244 cm<sup>-1</sup> (s), 1203 cm<sup>-1</sup> (s), 818 cm<sup>-1</sup> (m).

**2,7-Dihydroxy-9-fluorenone (12).** 10 g of anhydrous and freshly fused ZnCl<sub>2(s)</sub> was ground up with 5.0 g of 4,4-dihydroxybiphenyl-2-carboxylic acid with a mortar and pestle. This solid mixture was then placed in a 200 ml beaker and heated to 210 °C. The mixture was stirred until water vapour evolved and a purple solid formed. The mixture was maintained at ~210 °C for 10 min, and then allowed to cool to ~50 °C. The mixture was added to 50 mL of H<sub>2</sub>O to dissolve the zinc salt, and **12** was collected by suction filtration as a deep red solid. The crude solid was recrystallized from 95% ethanol, yielding 4.17 g (90%) of **12** as deep red crystals. Mp 326–329 °C (lit. 338 °C).<sup>6</sup> <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): δ 8.78 (2H, s, ArO–H), 7.40 (2H, d, *J* = 7.9 Hz, Ar–H), 7.02 (2H, 2, *J* = 2.2 Hz, Ar–H), 6.96 (2H, dd, *J* = 7.9, 2.2 Hz, Ar–H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 193.84, 158.01, 136.15, 135.62, 121.50, 121.42, 111.53. FTIR (KBr Pellet) 3391 (s), 1702 cm<sup>-1</sup> (s), 1601 cm<sup>-1</sup> (m), 1478 cm<sup>-1</sup> (s), 1408 cm<sup>-1</sup> (s), 1295 cm<sup>-1</sup> (s), 1236 cm<sup>-1</sup> (s), 793 cm<sup>-1</sup> (s).

**2,7-Dihydroxy-9-fluorenol (9).** To solution composed of 5 mL CH<sub>3</sub>CN, 5 mL H<sub>2</sub>O, and **12** (0.30 g, 1.4 mmol) was added 10 equiv. of NaBH<sub>4</sub>. The mixture was stirred at room temperature for 3 h, and quenched by the addition of 30 ml of 10% HCl. The mixture was diluted with 30 mL of water and extracted with 3 × 20 ml of diethyl ether. The combined organics were dried with MgSO<sub>4</sub> and filtered. The ether was removed under reduced pressure yielding **9** (0.176 g, 58% yield). Mp 213–217 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): δ 9.33 (2H, s, ArO–H), 7.37 (2H, d, *J* = 7.8 Hz, Ar–H), 6.94 (2H, s, Ar–H), 6.70 (2H, d, *J* = 7.8 Hz, Ar–H), 5.67 (1H, br s, O–H), 5.27 (1H, s, C–H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 156.68, 148.61, 131.52, 119.78, 115.33, 112.8, 73.84. EIMS: 214 (100), 213 (35), 198 (15), 197 (74), 168 (17), 157 (17), 141 (13), 128 (14). FTIR (KBr Pellet) 3221 cm<sup>-1</sup> (br s), 1613 cm<sup>-1</sup> (m), 1457 cm<sup>-1</sup> (s), 1242 cm<sup>-1</sup> (s), 813 cm<sup>-1</sup> (m).

**2,7-Dimethoxy-9-fluorenone (13).** 1.0 g of NaOH pellets were crushed with a mortar and pestle and added to 15 ml of DMSO in a round-bottom flask. To this was added **12** (2.00 g, 9.4 mmol), generating a dark purple solution. To this was added 4 equiv. of iodomethane (5.3 g, 37.3 mmol) dropwise. The reaction vessel was sealed with a rubber septum and the solution was stirred for 3 h. The reaction was quenched by the addition of 50 mL of 10% HCl, which precipitated a deep orange product, which was collected by suction filtration. The product was then washed with 0.1 M NaOH to remove traces of the starting material and mono-substituted by-product, and then washed with water. **13** was obtained in 65% yield (1.1 g). Mp 115–118 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 300 MHz): δ 7.58 (2H, d, *J* = 7.7 Hz, Ar–H), 7.11 (2H, s, Ar–H), 7.09 (2H, d, *J* = 7.8 Hz, Ar–H), 3.82 (6H, s, OC–H<sub>3</sub>). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>SO, 75.5 MHz): δ 193.28, 160.18, 137.29, 135.62, 121.94, 120.77, 110.08, 56.14. FTIR (KBr Pellet) 2963 cm<sup>-1</sup> (w), 2931 cm<sup>-1</sup> (w), 2851 cm<sup>-1</sup> (w), 1712 cm<sup>-1</sup> (m), 1577 cm<sup>-1</sup> (s), 1475 cm<sup>-1</sup> (s), 1435 cm<sup>-1</sup> (m), 1289 cm<sup>-1</sup> (m), 1224 cm<sup>-1</sup> (m), 1043 cm<sup>-1</sup> (m), 785 cm<sup>-1</sup> (m).

**2,7-Dimethoxy-9-fluorenol (10).** To a 250 mL round bottomed flask was added CH<sub>3</sub>CN (5 mL), H<sub>2</sub>O (5 mL), **13** (1.0 g, 4.2 mmol), and NaBH<sub>4</sub> (1.6 g), and the mixture was stirred at room temperature for 3 h. The reaction was quenched by addition

of 30 ml of 10% HCl and diluted with 30 mL of water. The resulting mixture was extracted with 3 × 20 ml of diethyl ether, and the combined organics were dried with MgSO<sub>4</sub> and filtered. The ether was removed under reduced pressure yielding **10** as a brown powder with a mass of 0.97 g (96% yield). Mp 136–138 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): δ 7.57 (2H, d, *J* = 8.0 Hz, Ar–H), 7.13 (2H, s, Ar–H), 5.84 (1H, d, *J* = 7.1 Hz, O–H), 6.91 (2H, d, *J* = 8.2 Hz, Ar–H), 5.39 (1H, d, *J* = 7.1 Hz, C–H), 3.80 (6H, s, OC–H<sub>3</sub>). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 75.5 MHz): δ 55.76, 73.97, 111.23, 114.45, 120.32, 132.68, 148.84, 159.05. EIMS: 242 (M<sup>+</sup>, 100), 277 (30), 225 (24), 211 (33), 210 (10), 199 (18), 171 (20), 139 (18), 128 (12). FTIR (KBr Pellet) 3396 cm<sup>-1</sup> (br m), 3007 cm<sup>-1</sup> (w), 2938 cm<sup>-1</sup> (w), 2834 cm<sup>-1</sup> (w), 1611 cm<sup>-1</sup> (m), 1474 cm<sup>-1</sup> (s), 1236 cm<sup>-1</sup> (s), 1043 cm<sup>-1</sup> (s), 1019 cm<sup>-1</sup> (m), 810 cm<sup>-1</sup> (m).

**9-Acetoxy-2,7-dimethoxyfluorene (11).** A sample of 2,7-dimethoxy-9-fluorenol (1.2 g, 5.0 mmol) was dissolved in 20 ml of acetic anhydride containing pyridine (4 g) and refluxed for 4.5 h. 50 mL of water was added to the mixture and extracted with 3 × 30 mL of diethyl ether. The combined ethers were washed with 20 ml of 2% HCl and dried over MgSO<sub>4</sub>. The ether was removed by rotary evaporation and 30 mL of water was added. Acetonitrile was added until the solid dissolved and the solution was then left to stir overnight at room temperature. The product was extracted with 3 × 30 ml of diethyl ether and the ether was washed with 6 × 25 ml of 0.1 M NaOH to remove the remaining acetic acid. The ether was then dried with MgSO<sub>4</sub>, filtered and the solvent was removed by rotary evaporation to obtain the final product. This gave 0.76 g (54% yield) of **11** as a brown solid. Mp 64–67 °C. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): 7.63 (2H, d, *J* = 8.3 Hz, Ar–H), 7.10 (2H, s, Ar–H), δ 6.98 (2H, d, *J* = 8.3 Hz, Ar–H), 3.79 (6H, s, OC–H<sub>3</sub>), 2.17 (1H, s, C–H<sub>3</sub>), 6.61 (1H, s, C–H). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 75.5 MHz): δ 171.65, 159.2, 143.70, 133.65, 120.77, 115.41, 112.25, 74.65, 55.88, 21.38. EIMS: 284 (100), 242 (85), 241 (17), 225 (37), 211 (35), 210 (26), 199 (20), 182 (33), 167 (27), 139 (40). FTIR (KBr Pellet) 2987 cm<sup>-1</sup> (w), 2962 cm<sup>-1</sup> (w), 2937 cm<sup>-1</sup> (w), 2832 cm<sup>-1</sup> (w), 1734 cm<sup>-1</sup> (m), 1612 cm<sup>-1</sup> (m), 1473 cm<sup>-1</sup> (s), 1245 cm<sup>-1</sup> (s), 1027 cm<sup>-1</sup> (m), 853 cm<sup>-1</sup> (m), 821 cm<sup>-1</sup> (m).

**2,7-Dihydroxy-9-methoxyfluorene (18).** A sample of **9** (0.13 g) was dissolved in 20 ml of methanol. Conc. H<sub>2</sub>SO<sub>4</sub> (2 mL) was added and the mixture was refluxed for 22 h. The reaction mixture was diluted with 100 ml of water and extracted with diethyl ether (30 mL × 3). The combined organics were then dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give 120 mg of **18** as a dark red-brown powder. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): δ 8.34 (2H, s, ArOH), 7.45 (2H, d, *J* = 8.3 Hz, Ar–H), 7.04 (2H, d, *J* = 2.2 Hz, Ar–H). 6.86 (2H, dd, *J* = 8.3, 2.2 Hz, Ar–H), 5.40 (1H, s, CH), 3.07 (3H, s, OCH<sub>3</sub>). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 75.5 MHz): δ 156.92, 144.62, 133.36, 119.97, 116.01, 113.01, 81.35, 52.05. EIMS: 228 (100), 213 (86), 211 (26), 197 (83), 168 (27), 139 (36), 81 (25), 69 (30), 67 (25), 55 (28). FTIR (KBr Pellet) 3334 (s), 3213 cm<sup>-1</sup> (s), 3028 cm<sup>-1</sup> (m), 2993 cm<sup>-1</sup> (m), 2955 cm<sup>-1</sup> (m), 1595 cm<sup>-1</sup> (s), 1469 cm<sup>-1</sup> (s), 1358 cm<sup>-1</sup> (s), 1241 cm<sup>-1</sup> (s), 1109 cm<sup>-1</sup> (s), 1050 cm<sup>-1</sup> (s), 811 cm<sup>-1</sup> (s).

**2,7,9-Trimethoxyfluorene (22).** A sample of **10** (0.12 g) was dissolved in 20 ml of methanol. Conc. H<sub>2</sub>SO<sub>4</sub> (2 mL) was added and the mixture was refluxed for 22 h. The reaction mixture was diluted with 100 ml of water and extracted with diethyl ether

(30 mL × 3). The combined organics were then dried with MgSO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure to give **22** 20 mg (16% yield) of 2,7,9-trimethoxyfluorene (**22**), which was a reddish powder. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 300 MHz): δ 7.62 (2H, d, 8.2 Hz, Ar–H), 7.12 (2H, s, Ar–H), 6.96 (2H, d, 8.1 Hz, Ar–H), 5.48 (1H, s, C–H), 3.82 (6H, s, OC–H<sub>3</sub>), 3.08 (3H, s, OC–H<sub>3</sub>). <sup>13</sup>C NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 75.5 MHz): δ 159.13, 144.45, 133.62, 120.62, 115.07, 111.61, 81.12, 55.84, 53.19. EIMS: 256 (100), 226 (17), 225 (95), 241 (30), 183 (14), 182 (10), 139 (35).

## Product studies

Product studies were carried out by preparing a solution of the compound of interest in the desired solvent and transferring the solution to a quartz vessel. The solution was then purged by bubbling oxygen or argon through the solution for 5 min, after which time the vessel was sealed either with a rubber stopper or Parafilm. The solution within the vessel was then irradiated in a LuzChem ORG photochemical reactor fitted with 10 low pressure mercury lamps with maximum output of either 254 or 300 nm. After irradiation, the solutions were directly injected into the GCMS if the solvent was purely organic, after which the remainder of the photolysate was concentrated by rotary evaporation, and analyzed by NMR. If the solvent system contained water, the photolysate was first diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub> or ether, the organics were separated, dried over MgSO<sub>4</sub>, and analyzed by GCMS. Solvent was then removed *via* rotary evaporation and the resulting residue was analyzed by NMR.

**2,7-Dimethoxyfluorene (23).** A sample of **11** (98 mg) was dissolved in 100 mL of methanol, transferred to a quartz flask in which the solution was purged with nitrogen for 5 min and sealed. The flask was irradiated in a Luzchem-ORG photochemical reactor equipped with 10 UVC lamps (max output at 254 nm) for a period of 10 h. When the photolysis was complete, the solvent was removed under reduced pressure, and the resulting solid was analyzed by NMR and GCMS. GCMS analysis indicated that the majority of the photolysate (>90%) was 2,7-dimethoxyfluorene. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 7.59 (2H, d, *J* = 7.8 Hz), 7.09 (2H, s), 6.94 (2H, d, *J* = 7.8 Hz), 3.88 (6H, s), 3.68 (2H, s). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 158.83, 144.85, 135.12, 119.99, 113.09, 111.08, 55.90, 37.45. EIMS: 226 (100), 212 (11), 211 (75), 183 (17), 139 (17).

**2,7-Dihydroxyfluorene (19).** A sample of **9** (97 mg) was dissolved in 100 mL of methanol, transferred to a quartz flask in which the solution was purged with nitrogen for 5 min and sealed. The flask was irradiated in a Luzchem-ORG photochemical reactor equipped with 10 UVC lamps (max output at 254 nm) for a period of 10 h. When the photolysis was complete, the solvent was removed under reduced pressure, and the resulting solid was analyzed by NMR and GCMS. GCMS analysis indicated that the majority of the photolysate (>80%) was 2,7-dimethoxyfluorene. NMR data matched that of a previous report,<sup>16</sup> and MS data matched that of a second report.<sup>17</sup>

## UV-Vis and fluorescence spectroscopy

Solutions for UV-Vis and fluorescence spectroscopy were prepared by first making a stock solution of the compound of interest (~30 mg) in 3 mL of CH<sub>3</sub>CN. The UV-Vis or fluorescence cuvettes

were then filled with the solvent of interest, and 1–10  $\mu\text{L}$  of the stock was injected. Solutions were then bubbled with a slow stream of oxygen, argon, or nitrogen gas for 4 min. Fluorescence solutions were prepared so that the longest wavelength absorption band had a maximum absorbance of 0.1.

## Acknowledgements

We wish to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding of this work through the Discovery program. We also acknowledge the Canadian Foundation for Innovation (CFI) and the Nova Scotia Research and Innovation Trust (NSRIT) for infrastructure funding. AR thanks Acadia University for an Acadia Graduate Award (AGA) and EJ and AC thank Acadia University for partial funding through the Acadia Research Fund (25.55).

## References

- 1 P. Wan and E. Krogh, *J. Chem. Soc., Chem. Commun.*, 1985, 1027; P. Wan and E. Krogh, Contrasting photosolvolytic reactivities of 9-fluorenol vs. 5-suberenol derivatives. Enhanced rate of formation of cyclically conjugated four  $\pi$  carbocations in the excited state, *J. Am. Chem. Soc.*, 1989, **111**, 4887.
- 2 F. L. Cozens, N. Mathivanan, R. A. McClelland and S. Steenken, Reactivities of 9-arylfluoren-9-yl and 1-(4-dimethylaminophenyl)ethyl cations in water and trifluoroethanol studied by laser flash photolysis, *J. Chem. Soc., Perkin Trans. 2*, 1992, 2083–2090; L. J. Johnston, P. Kwong, A. Shelemay and E. Lee-Ruff, Electron-deficient carbocations. Direct observation of  $\alpha$ -carbonylmethyl cations by laser flash photolysis, *J. Am. Chem. Soc.*, 1993, **115**, 1664–1669; C. S. Q. Lew, R. A. McClelland, L. J. Johnston and N. P. Schepp, Photochemical generation of the 9-(trimethylsilylmethyl)fluoren-9-yl cation. Flash photolysis observation of a  $\beta$ -silyl-substituted carbenium ion, *J. Chem. Soc., Perkin Trans. 2*, 1994, 395–397; A. D. Allen, J. D. Colomvakos, O. S. Tee and T. T. Tidwell, 9-(Trifluoromethyl)fluorenyl cation: A new doubly destabilized carbocation, *J. Org. Chem.*, 1994, **59**, 7185–7187; C. S. Q. Lew, B. D. Wagner, M. P. Angelini, E. Lee-Ruff, J. Luszyk and L. J. Johnston, Detection and characterization of a transient zwitterion, the 9-carboxylate-9-fluorenyl cation, and its conjugate acid, *J. Am. Chem. Soc.*, 1996, **118**, 12066–12073; C. S. Q. Lew, D. F. Wong, L. J. Johnston, M. Bertrone, A. C. Hopkinson and E. Lee-Ruff, Characterization and reactivity of the [*N,N*-dimethyl(thioformamidyl)]-9-fluorenyl cation, *J. Org. Chem.*, 1996, **61**, 6805–6808; X. Creary and A. Wolf, Effect of oxime substituents on 9-fluorenyl carbocations, *J. Phys. Org. Chem.*, 2000, **13**, 337–343; M. A. O'Neill, F. L. Cozens and N. P. Schepp, Generation and direct observation of the 9-fluorenyl cation in non-acidic zeolites, *Tetrahedron*, 2000, **56**, 6969–6977; G. Mladenova, L. Chen, C. F. Rodriguez, K. W. M. Siu, L. J. Johnston, A. C. Hopkinson and E. Lee-Ruff, Studies of 9-fluorenyl carbocations. Intramolecular hydride migration in a substituted 9-fluorenyl carbocation, *J. Org. Chem.*, 2001, **66**, 1109–1114; S. Ward, T. Messier and M. Lukeman, Electrophilicity of a 9-aryl-9-fluorenyl cation in water—Kinetic evidence for antiaromaticity, *Can. J. Chem.*, 2010, **88**, 493–499.
- 3 M. Fischer, Y. Shi, B. Zhao, V. Snieckus and P. Wan, Contrasting behavior in the photosolvolytic of 1- and 2-hydroxy-9-fluorenols in aqueous solution, *Can. J. Chem.*, 1999, **77**, 868–874.
- 4 For an example of a situation where diastereomeric PPGs show very different photochemistry, see: A. Soldevilla and A. G. Griesbeck, Chiral photocages based on phthalimide photochemistry, *J. Am. Chem. Soc.*, 2006, **128**, 16472–16473.
- 5 E. R. Andrews, R. W. Fleming, J. M. Grisar, J. C. Kihm, D. L. Wenstrup and G. D. Mayer, Bis-basic-substituted polycyclic aromatic compounds. A new class of antiviral agents. 2. Tilorone and related bis-basic ethers of fluorenone, fluorenol, and fluorene, *J. Med. Chem.*, 1974, **17**, 882–886.
- 6 K. C. Agrawal, Fluorene derivatives for antitumor activity, *J. Med. Chem.*, 1967, **10**, 99–101.
- 7 T. N. Das, Absorption spectra,  $pK_a$ , and reduction potential of phenoxyl radical from 4,4'-biphenol in aqueous medium, *J. Phys. Chem. A*, 2001, **105**, 5954–5959.
- 8 G. W. Burton and K. U. Ingold, Autoxidation of biological molecules. 1. Antioxidant activity of vitamin E and related chain-breaking phenolic antioxidants in vitro, *J. Am. Chem. Soc.*, 1981, **103**, 6472–6477.
- 9 S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, 2nd edn, Marcel Dekker, Inc., New York, 1993.
- 10 For example, see: M. Lukeman, D. Veale, P. Wan, V. R. N. Munasinghe and J. E. T. Corrie, Photogeneration of 1,5-naphthoquinone methides via excited-state (formal) intramolecular proton transfer (ESIPT) and photodehydration of 1-naphthol derivatives in aqueous solution, *Can. J. Chem.*, 2004, **82**, 240–253; D. W. Brousmiche, M. Xu, M. Lukeman and P. Wan, Photohydration and photosolvolytic of biphenyl alkenes and alcohols via biphenyl quinone methide-type intermediates and diarylmethyl carbocations, *J. Am. Chem. Soc.*, 2003, **125**, 12961–12970; M. Flegel, M. Lukeman, L. Huck and P. Wan, Photoaddition of water and alcohols to the anthracene moiety of 9-(2'-hydroxyphenyl)anthracene via formal excited state intramolecular proton transfer, *J. Am. Chem. Soc.*, 2004, **126**, 7890–7897.
- 11 J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 2nd edn, Kluwer Academic/Plenum Publishers, New York, London, Moscow, Dordrecht, 1999.
- 12 M. Lukeman, in *Quinone Methides*, ed. S. E. Rokita, Wiley, Hoboken, New Jersey, 2009, ch. 1, pp. 1–25.
- 13 A. P. Kostikov and V. V. Popik, 2,5-Dihydroxybenzyl and (1,4-dihydroxy-2-naphthyl)methyl, novel reductively armed photocages for the hydroxyl moiety, *J. Org. Chem.*, 2007, **72**, 9190–9194.
- 14 J. A. Pincock, Photochemistry of arylmethyl esters in nucleophilic solvents: radical pair and ion pair intermediates, *Acc. Chem. Res.*, 1997, **30**, 43–49; D. P. DeCosta and J. A. Pincock, Photochemistry of substituted 1-naphthylmethyl esters of phenylacetic and 3-phenylpropionic acid—radical pairs, ion-pairs, and Marcus electron-transfer, *J. Am. Chem. Soc.*, 1993, **115**, 2180–2190; J. W. Hilborn, E. MacKnight, J. A. Pincock and P. J. Wedge, Photochemistry of substituted benzyl acetates and benzyl pivalates—a reinvestigation of substituent effects, *J. Am. Chem. Soc.*, 1994, **116**, 3337–3346; J. A. Pincock and P. J. Wedge, The photochemistry of methoxy-substituted benzyl acetates and benzyl pivalates—homolytic vs. heterolytic cleavage, *J. Org. Chem.*, 1994, **59**, 5587–5595.
- 15 K. S. Peters, Nature of dynamic processes associated with the  $S_N1$  reaction mechanism, *Chem. Rev.*, 2007, **107**, 859–873; K. S. Peters, Dynamic processes leading to covalent bond formation for  $S_N1$  reactions, *Acc. Chem. Res.*, 2007, **40**, 1–7; L. R. Heeb and K. S. Peters, Picosecond kinetic study of the photoinduced homolysis of benzhydryl acetates: The nature of the conversion of radical pairs into ion pairs, *J. Am. Chem. Soc.*, 2008, **130**, 1711–1717.
- 16 A. Mathieu, J. C. Milano and J. Douris, Étude par resonance magnétique en série fluorénique. VI.—Fluorènes substituées en position 2 ou 2,7, *Bull. Soc. Chim. Fr.*, 1974, 299–304.
- 17 Z. I. Finkelstein, B. P. Baskunov, E. L. Golovlev, J. Vervoort, I. M. C. M. Rietjens, M. A. Baboshin and L. A. Golovleva, Fluorene transformation by bacteria of the genus *Rhodococcus*, *Microbiology*, 2003, **72**, 746–751.