Photochemistry

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Oxidation-State-Dependent Photochemistry of Sulfur-Bridged Anthracenes[**]

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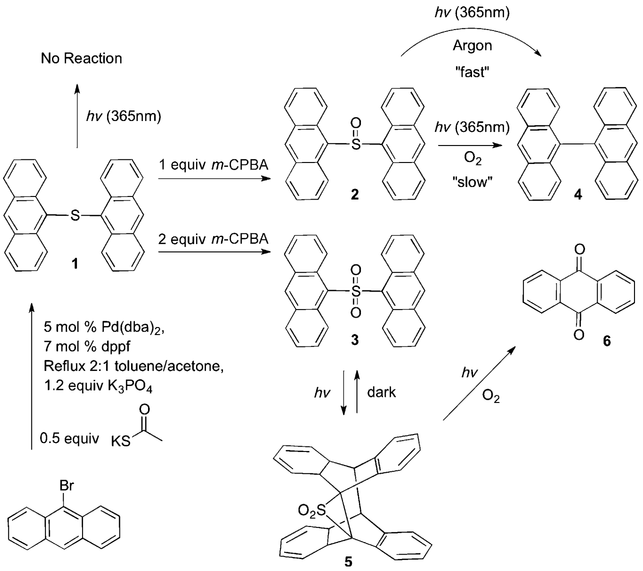
In chemical synthesis, functional group tolerance often determines the utility of a reaction. Where one functional group may inhibit reactivity, another may accelerate the rate ten-fold.[1] In photochemical reactions, slight modifications in functional groups can also have dramatic consequences, with electronic and conformational configurations determining how molecules behave in the presence of light.[2] In order to better predict the outcomes and rationally design photochemical syntheses, a broader understanding of functional group behavior is needed. Organic sulfides, sulfoxides, and sulfones are common functional groups relevant to pharmaceutical,[3] agrochemical,[4] and light-emitting compounds.[5] The photochemistry of various alkyl and aryl sulfoxides has been examined by Lee and Jenks with a focus on the mechanism of pyramidal inversion at sulfur.[6] There are very few reports, however, where the photochemistry of sulfur-containing molecules is studied as a function of the oxidation state at sulfur. We recently reported enhanced photoluminescence (PL) of several soluble sulfur-bridged aromatic molecules, whereby successive oxidation of the sulfur bridge results in a systematic increase in the PL quantum yield (Φ_{PL}).[7] During the course of this study, we found that analogous sulfur-bridged compounds, in which the aromatic substituent is anthracene, exhibit comparatively low Φ_{PL} in all oxidation states. This unusual behavior stands in contrast to the other aromatic groups that were examined and led us to study the photophysics and photochemistry of sulfide, sulfoxide, and sulfone-bridged anthracenes in more detail.

Sulfide **1** was synthesized using palladium-catalyzed cross-coupling[8] of 9-bromoanthracene and potassium thioacetate (Scheme 1). Attempts to use Cu^{I}[9] or Pd^{0}[10] catalysts to couple 9-anthracenethiol and 9-bromoanthracene were unsuccessful, possibly because of catalyst poisoning with the electron-rich thiol. The corresponding sulfoxide **2** and sulfone **3** were obtained by oxidation of **1** with one or two equivalents, respectively, of *meta*-chloroperoxybenzoic acid (*m*-CPBA; details are found in the Supporting Information).

Sulfide **1** exhibits relatively weak photoluminescence and dilute solutions are stable to irradiation at 365 nm for several hours. Irradiation of sulfoxide **2** under the same conditions results in rapid (seconds) loss of the bridging SO and formation of a new carbon–carbon bond yielding 9,9′-bianthryl **4** in >99% isolated yields. On the other hand, irradiation of sulfone **3** using the same light source yields a new anthracene dimer **5** containing a three-membered episulfone ring. Extended (overnight) irradiation of **3** or **5** in the presence of oxygen results in the formation of anthraquinone (**6**). Under the same extended irradiation conditions, no anthraquinone is formed from **4**. In the dark, the bridged compound **5** reverts thermally back to **3**.



Scheme 1. Synthesis and photochemical products of sulfur-bridged anthracenes (*m*-CPBA = *meta*-chloroperoxybenzoic acid, dba = dibenzylideneacetone, and dppf = 1,1′-bis(diphenylphosphanyl)ferrocene).

Single crystals of compounds **1**–**3**, and **5** were obtained and the structures were determined using X-ray diffraction.[11] Crystallographic data for 9,9′-bianthryl (**4**) were previously reported.[12] The molecular structures of the series of sulfur-bridged anthracenes **1**–**3** are qualitatively similar with only minor differences observed in the solid-state geometries. The intramolecular anthracene–anthracene centroid (An-An) distance remains relatively constant throughout the series (**1** = 5.100 Å, **2** = 4.984 Å, **3** = 5.019 Å), and the through space distance between the bridge-head carbons are all about 2.9 Å. One noteworthy point is that the closest intermolecular An-An contacts decrease as the oxidation state of the bridging sulfur increases (**1** = 5.748 Å, **2** = 4.478 Å, **3** = 3.941 Å; see Figure S1 in the Supporting Information). This behavior is consistent with that of anthracene derivatives possessing electron-withdrawing groups (i.e. perfluoroanthracenes)

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which are known to exhibit contracted intermolecular packing compared to unsubstituted anthracene.[13]

The structure of the bridged dimer **5** contains a three-membered episulfone ring with bond angles of about 60° at each vertex. Bridged anthracene dimers are well-known; the [4+4] cycloaddition of anthracene, first observed in 1867 by Fritzsche,[14] has been reviewed several times.[15] Strained carbon–sulfur bonds have been synthetic targets for several decades as precursors for introducing unsaturated bonds into organic compounds,[16] yet this is, to our knowledge, the first photochemical preparation of an episulfone.

^{1}H NMR spectroscopy was employed to monitor the conversion of **2** to **4**, and of **3** to the bridged species **5** (Figure S2). Notably, the singlet at $\delta = 8.68$ ppm in the spectrum of **3**, which corresponds to the aromatic proton directly opposite to the sulfur bridge, is shifted upfield at $\delta = 4.64$ ppm in the bridged species **5**, typical of anthracene photodimers.[15b] Under the same irradiation conditions no change was observed in the ^{1}H NMR spectrum of **1**. The formation of **5** was also monitored with $\{^1H\}$-^{13}C HSQC to correlate the change in the aromatic singlet to the change in the carbon atom at this position (Figure S3).

The solid-state photoreactivity of **2** and **3** was probed by monitoring the powder X-ray diffraction (PXRD) patterns of the two solids before and after irradiation with the same 365 nm lamp used in the solution experiments (Figure S4). Even with overnight irradiation no change was observed in the PXRD patterns of the two solids. Solution ^{1}H NMR spectra taken before and after irradiation of the solid samples also show no evidence for the formation of photoproducts **4** and **5** in the solid state.

The UV/Vis absorption spectra of compounds **1**–**3** show the structured "fingerprint" profiles common of anthracenes (Figure S5). While the spectra for **1**–**3** are all structured, they are red-shifted, and have less well-defined vibronic structure than other tethered anthracenes. The presence of pronounced vibronic structure in electronic absorption profiles indicates minimal π–π overlap between anthracenes in the ground state.[17] Upon irradiation, the absorption spectrum of **2** exhibits loss of the band centered at 410 nm and an increase in the vibronic structure between 315 and 385 nm as bianthryl (**4**) is formed (Figure 1), indicating that significantly more π–π orbital overlap is present in **2** than in **4**. Photoconversion of **3** to **5** results in a decrease in the structured absorbance between 325–425 nm (Figure S6) attributed to the introduction of new sp^3 carbons.

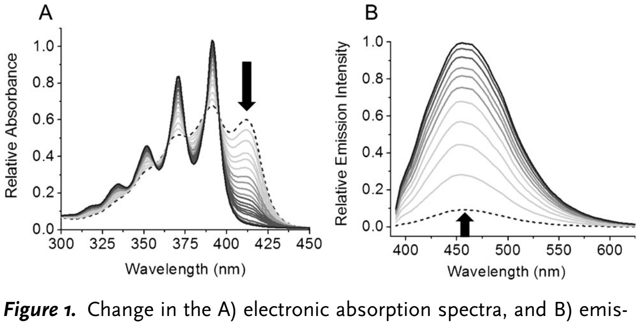


Figure 1. Change in the A) electronic absorption spectra, and B) emission spectra with photoconversion of 2 [– – –] to 4 [——] in CH_2Cl_2.

The PL spectra for compounds **1**–**3** were obtained in nonpolar cyclohexane (CHx), dichloromethane (Ch_2Cl_2), and polar acetonitrile (MeCN). In Ch_2Cl_2, the photoluminescence of **2** is broad, unstructured, and centered around 455 nm (Figure 1 B). Upon conversion to bianthryl (**4**) the overall shape and maximum wavelength are the same as for **2**, however, there is a significant increase in the PL intensity.

Twisted intramolecular charge-transfer (TICT) states can occur in tethered anthracenes when orbital overlap is minimal (i.e. orthogonal anthracene units). For example, a TICT state is observed in 9,9′-bianthryl, where the anthracene units adopt a minimally overlapped, antiplanar orientation relative to one another.[18] In more polar solvents the dipolar charge-separated excited state in 9,9′-bianthryl is stabilized, and red-shifted, structureless emission is observed. A pronounced red-shift in the PL spectrum of **2** is observed as the solvent polarity is increased from CHx to MeCN indicating that emission from this SO-bridged anthracene is likely occurring from a TICT state (Figure 2 A).

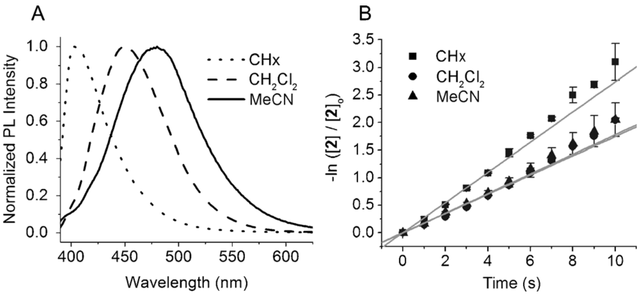


Figure 2. A) PL spectra of **2** taken in CHx (•••••), CH_2Cl_2 (-----), MeCN (——), and B) solvent-dependent kinetics $-\ln([\mathbf{2}]/[\mathbf{2}]_o)$ for the conversion of **2** to **4**. $[\mathbf{2}]_o = 1 \times 10^{-5}$ M

The PL spectra of compounds **1** and **3** display complex, solvent-dependent profiles. In CHx a combination of structured PL between 390–450 nm is present along with broad, unstructured emission at wavelengths larger than 450 nm (Figure 3). Moreover, the broad long-wavelength emission is most prominent in nonpolar solvents. Previous studies have shown that anthracenes tethered together with alkyl linkers can exhibit broad emission resulting from a combination of excimer (Ex), and charge-transfer (CT) excited states,

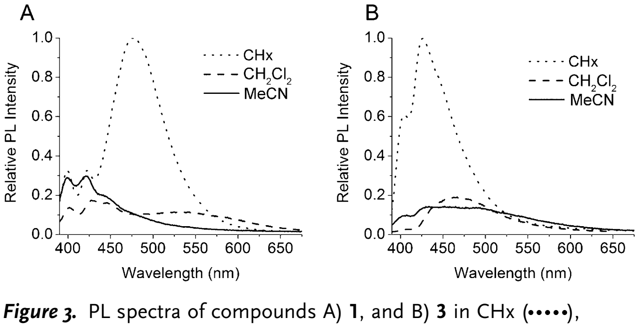


Figure 3. PL spectra of compounds A) **1**, and B) **3** in CHx (•••••), CH_2Cl_2 (– – –), and MeCN (——).

whereas structured, shorter-wavelength emission results from delocalized inter-anthracene excited states.[17] For compounds **1** and **3**, the observation that broad emission is most prominent in nonpolar media indicates that this emission results from Ex states, rather than CT states.

The kinetics of the formation of **4** from **2** were followed by monitoring the changes in absorbance as a function of irradiation time in different solvents (Figure 2B). The loss of **2** was fit to a single exponential decay function yielding pseudo first-order rates of reaction in dilute solution. It was found that a slight increase in the rate of formation of **4** occurs in nonpolar solvent (CHx) whereas in dichloromethane and MeCN the rates are identical. This indicates that formation of **4** likely involves both Ex and CT states.

The increase in emission intensity $I_f = F/F_{\mathbf{max}}$ (F = area under photoluminescence spectrum) also exhibits single exponential kinetics, directly proportional to the loss of **2**, suggesting the formation of **4** occurs in an intramolecular fashion (Figure 4A). To provide further evidence for intramolecular conversion of **2** to **4**, a dimethyl-substituted analogue of **2** (**2Me$_2$**) was irradiated in the presence of **2**, and the reaction products were characterized (Scheme S1). If the cross-product 10-methyl-9,9′-bianthryl were to form, this would indicate that the conversion of **2** to **4** occurs through a diffusional, intermolecular process. Analysis of the reaction products shows only the two homo-coupled products **4**, and 10,10′-dimethyl-9,9′-bianthryl (**4Me$_2$**) which strongly suggests intramolecular reactivity.

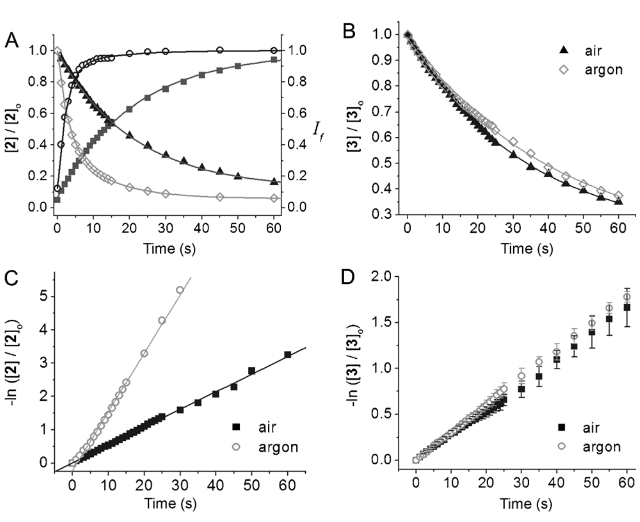


Figure 4. Conversion of A) **2** to **4**, and B) **3** to **5** in CH_2Cl_2. The plots show the change in concentration of **2** ([**2**]/[**2**]$_o$), and **3** ([**3**]/[**3**]$_o$) in the presence of oxygen (▲) and purged with argon (◇) as well as emission intensity (I_f) in the presence of oxygen (■) and purged with argon (○) as a function of the irradiation time (t) in seconds. C) Plot of $-\ln$([**2**]/[**2**]$_o$), and D) $-\ln$([**3**]/[**3**]$_o$) for the conversion of **2** to **4**, and **3** to **5** in the presence of air (■), and purged with argon (○).

Kinetic data for the conversion of **3** to **5** was collected by monitoring the loss in long-wavelength absorbance at 415 nm as a function of time (Figure 4B). The rate of formation for **5** was found to exhibit single exponential kinetics slower than that of the conversion of **2** to **4**.

The rate of formation of **4** also depends significantly on the presence of oxygen (Figure 4C). Argon-purged samples of **2** in CH_2Cl_2 exhibit rates of conversion nearly five times faster than in the presence of oxygen (Tables S2 and S3) suggesting that the transformation of **2** to **4** involves a triplet state.[19] In contrast, the formation of **5** shows no dependence on the presence of oxygen (Figure 4D), suggesting that the rate-limiting step in this reaction does not involve a triplet state. It has previously been shown that the photodimerization of anthracene proceeds through an excited singlet state.[15]

The room-temperature photoluminescence lifetimes (τ_{PL}) of compounds **1**–**3** were found to be dependent on the oxidation state of the bridging sulfur. All of the compounds exhibit prompt (≤ 1 ns) τ_{PL} while compounds **2** and **3** have multiexponential lifetimes with a substantially longer (about 30 ns) component (Table 1). The longest lived component was found to increase as the oxidation state of the bridging sulfur increases, τ_{PL}: **1** < **2** < **3** both in the presence of air, and when the solution is purged with argon. Previous studies[17] have correlated longer-lived bi-exponential τ_{PL} in tethered anthracenes to the rate of deactivation of eximer states (longer τ_{PL} indicates longer lived excimer states). The longer τ_{PL} of compounds **2** and **3** suggests that long-lived excited-state species may be responsible for the observed reactivity. While the excited state of **1** is deactivated rapidly through either nonradiative intersystem crossing or through photoluminescence, **2** and **3** can undergo larger structural rearrangements in the excited state.

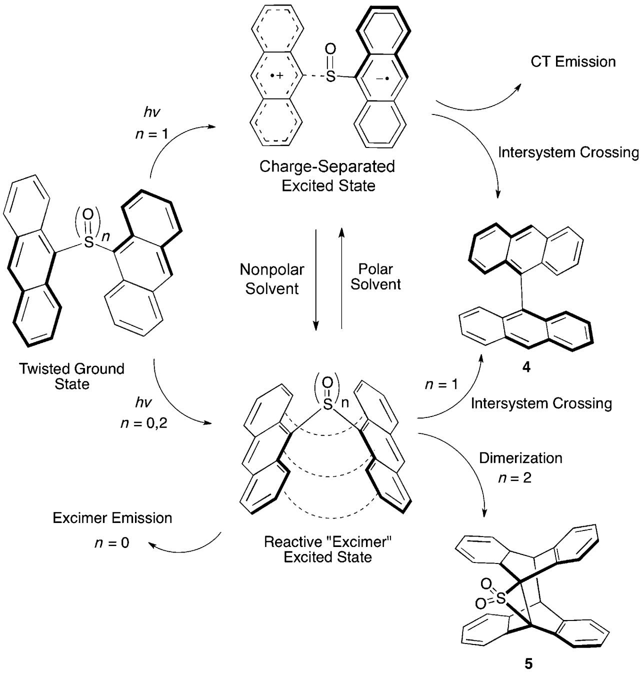
Table 1: Room-temperature photoluminescence lifetimes for compounds **1**–**4** collected in argon atmosphere.

	1	2[b]	3[c]	4
τ_1 [ns][a]	≤1	≤1	≤1	≤1
τ_2 [ns]	–	27.0(1)	29.2(1)	27.6(1)

[a] In all cases τ_1 was shorter than the measurable minimum. [b] Errors shown are standard deviations. [c] τ_3 not shown, see Tables S2, and S3 for details.

The relatively short photoluminescence lifetimes observed for all compounds (nanoseconds) are consistent with emission from singlet states, however, the slower photochemical conversion of **2** to **4** in the presence of oxygen suggests that a nonemissive triplet state may be playing a role in this reaction. To probe the possible involvement of a triplet state in the formation of **4** from **2**, the effect of adding a triplet sensitizer, $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) on the rate of the photochemical reaction was tested. Ruthenium polypyridyl complexes are excellent triplet sensitizers and have found several applications as photocatalysts in organic chemistry.[20]

Ruthenium polypyridyl dyes are particularly useful for sensitizing organic reactions involving triplet states since intersystem crossing is very fast in these compounds resulting in high quantum yields of long-lived (microseconds) triplet states.[21] In addition, the metal-to-ligand charge-transfer (MLCT) states most commonly involved in rapid triplet formation occur at low energies, typically in the visible portion of the spectrum.[21] Following work by Islangulov and Castellano,[22] wherein the photodimerization of anthracene was sensitized by a ruthenium dye, the conversion of **2** to **4** was measured in the presence of $[Ru(bpy)_3]^{2+}$. This species is suitable as a triplet photosensitizer for monitoring the conversion of **2** to **4** because the MLCT band has a maximum around 450 nm and absorption is present to about 500 nm, allowing for selective excitation of the $[Ru(bpy)_3]^{2+}$ in the presence of **2.** Dilute solutions of **2** were irradiated at 475 nm in the presence and absence of $[Ru(bpy)_3]Cl_2$ (Figure S9) using a pulsed nanosecond laser as the light source (details in the Supporting Information). There is a substantial enhancement in the rate at which **2** is lost in the presence of the dye, providing strong evidence for the involvement of a triplet state in the formation of **4**.



Scheme 2. Proposed mechanism for the observed oxidation-state-dependent photochemistry of sulfur-bridged anthracenes.

Different excited-state deactivation pathways can explain the disparity in photochemical reactivity observed for **1**–**3** (Scheme 2). We propose that initially, direct excitation (DE) of anthracene occurs, as evidenced by the structured UV/Vis absorption profiles. After this DE, one or more excited states (CT and Ex), involving both of the bridged anthracenes, result, evidenced by the solvent dependence of the PL spectra.

The excited-state deactivation depends heavily on the oxidation state of the bridging sulfur. For S-bridged anthracene **1**, the excited state may be deactivated either through short-lived excimer fluorescence, or through other nonradiative pathways, most likely including a large degree of intersystem crossing. For SO-bridged anthracene **2**, the excited state likely involves a combination of CT and Ex states as evidenced by PL and measured rates of conversion to **4** in various solvents. Second, the conversion of **2** to **4** likely involves intersystem crossing to a reactive triplet state. SO_2-bridged anthracene **3** appears to possess the largest amount of Ex character in the excited state as evidenced by its long-lived PL, and the geometry of the resulting photochemical product (**5**).

Previous studies involving the extrusion of SO from sulfoxides have proposed both triplet radical,[23] and singlet homolytic[24] cleavage mechanisms. While no cross-products are formed when **2Me₂** is irradiated in the presence of **2** this does not allow for the unambiguous distinction between radical and homolytic cleavage of the carbon–sulfur bond.

In summary, novel photochemistry of sulfur-bridged anthracenes is presented. The excited-state reactivity was found to depend on the oxidation state of the bridging sulfur atom. Sulfide (S) bridged anthracene does not react in the excited state, and the sulfoxide (SO) and sulfone (SO_2) analogs react rapidly to form different products. Sulfoxide-bridged anthracene was found to liberate SO and form bianthryl in an intramolecular fashion. The formation of an episulfone-bridged compound is observed when SO_2-bridged anthracene is subjected to photoirradiation. The photoreactivity of SO and SO_2-bridged anthracenes is believed to result from longer-lived excited states, notably through the formation of reactive triplet states, as confirmed for compound **2** by triplet sensitization. The role of excimer formation in the excited-state is also believed to play a large role in the formation of both **4** and **5**. This chemistry, with optimization of the synthetic conditions, is expected to be useful for the synthesis of longer aromatic oligomers and polymers.

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