Enhanced Photoluminescence of Sulfur-Bridged Organic Chromophores

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S Supporting Information

ABSTRACT: A general approach to enhancing the emission quantum yield of several widely studied organic chromophores is presented. The luminescence properties of a series of symmetrical sulfur-bridged chromophores are reported as a function of the oxidation state of the bridging sulfur atom. The photoluminescence quantum yield is significantly enhanced by successively oxidizing the sulfur bridge from sulfide (S), to sulfoxide (SO), to sulfone (SO_2).

Figure 1. (A) Bar graph showing the successive increase in Φ_f as the bridging sulfur is oxidized for bridged bithiophene (T_2), terthiophene (T_3), naphthalene (**Nap**), and pyrene (**Pyr**) species along with the respective parent arenes in CH_2Cl_2. (B) Relative absorption-corrected photoluminescence spectra for $2SO_n$ and T_3 showing the increase in intensity as the sulfur bridge is oxidized.

Highly emissive organic molecules continue to receive a great deal of attention for their use in organic light emitting devices (OLEDs).[1] Solution processing of organic molecules under ambient conditions may enable low cost, high throughput manufacturing of devices utilizing these materials on a wide range of substrates.[2] For over two decades conjugated oligomers and polymers have been targeted as emissive materials for OLEDs.[3] While luminescent polymers are often better suited for solution processing, the performance of small molecule OLEDs is typically superior.[4] The photoluminescence (PL) of conjugated oligomers in solution can be enhanced by increasing oligomer length;[5] for example, the PL quantum yield (Φ_f) increases from ~0.06 for terthiophene (T_3) to 0.34 for sexithiophene (T_6).[6] A disadvantage of larger aromatic molecules, however, is their generally poor solubility and the introduction of nonradiative decay pathways in close-packed solid state morphologies.[7] Alkyl substituents are often used to improve the solubility of these molecules[8] and to inhibit intermolecular quenching.[9] A wide variety of functionalized thiophene,[10] naphthalene,[11] and pyrene[12] derivatives have been synthesized both to improve solubility and to minimize nonradiative decay related to packing of molecules; however, it is challenging to optimize these parameters without also hindering intermolecular charge transfer, essential for efficient OLED operation.[13]

Here, we present a new approach for enhancing the solution and solid-state light emitting properties of a series of organic chromophores, where each chromophore is bridged symmetrically about a sulfur atom. Successive oxidation of the bridging sulfur from sulfide (S), to sulfoxide (SO), to sulfone (SO_2) results in a systematic increase in Φ_f. In most cases the sulfoxide (SO), and in all examples the sulfone (SO_2) bridged chromophores exhibit photoluminescence quantum yields greater than the parent arenes (Figure 1). Previously studied systems, notably, asymmetric sulfoxides and sulfones exhibit
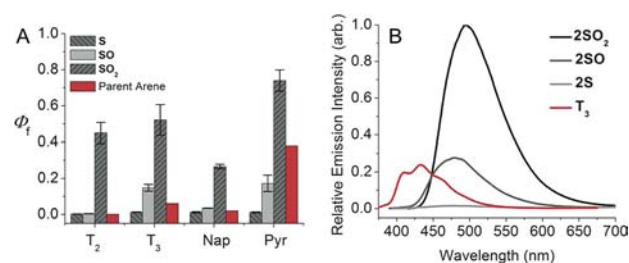
different photophysical behavior.[14,15] In some cases,[14a,b] the sulfoxides are less emissive than both the corresponding sulfones and parent arenes, attributed to nonradiative pathways including α-cleavage/recombination and/or pyramidal inversion at sulfur. In other cases,[14c,15] the sulfones are less emissive. Enhanced photoluminescence of symmetrically bridged bis-aryl sulfoxides (Ar−SO−Ar) is unprecedented and differs significantly from the behavior of asymmetric aryl sulfoxides (Ar−SO−R) where R is an alkyl[14] or aryl group.[15] Here, the enhanced quantum efficiency with sulfur-bridged chromophores is achieved without diminishing the solubility of these molecules in common organic solvents, and the lack of bulky substituents is anticipated to allow for efficient charge transfer in OLED applications. Furthermore, sulfone-bridged arenes are also well-known for their high mechanical and thermal stability[16] which is also important for robust OLED operation.[13]
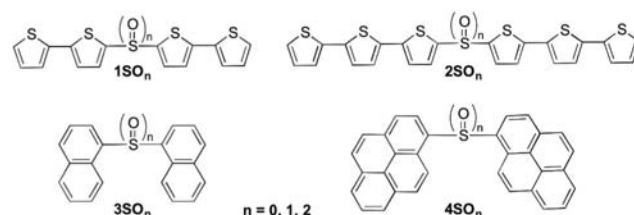
Bithiophene, terthiophene, naphthalene, and pyrene were bridged symmetrically about a sulfur atom in good yields

(synthetic details in Supporting Information). Photophysical properties of the sulfur-bridged chromophores were examined as a function of the oxidation state of the bridging sulfur atom (Table 1). The PL quantum yields (Φ_f) were calculated using

Table 1. Photophysical Data for Compounds in CH$_2$Cl$_2$ Solutions ($c \approx 10^{-6}$ M)

compound	absorption		emission	
	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_f (nm)	Φ_f (298 K)
bithiophene	305	1.3×10^4	365	0.001
1S	334	3.4×10^4	383	0.002 ± 0.001
1SO	325	2.9×10^4	447	0.003 ± 0.001
1SO$_2$	349	3.2×10^4	430	0.45 ± 0.06
terthiophene	349	2.5×10^4	432	0.06
2S	374	5.8×10^4	473	0.012 ± 0.001
2SO	371	5.3×10^4	479	0.15 ± 0.02
2SO$_2$	398	4.3×10^4	495	0.52 ± 0.09
napthalene	277	7.7×10^3	355	0.02
3S	302	1.3×10^4	368	0.012 ± 0.003
3SO	296	1.3×10^4	368	0.035 ± 0.001
3SO$_2$	298	1.0×10^4	368	0.27 ± 0.01
pyrene	337	9.7×10^3	372	0.38
4S	362	4.9×10^4	401	0.011 ± 0.002
4SO	351	4.6×10^4	449	0.17 ± 0.05
4SO$_2$	353	4.3×10^4	432	0.74 ± 0.06

9-cyanoanthracene as a standard. The emission from all chromophores is short-lived (on the order of nanoseconds) and attributed to decay from singlet states. The emission spectra are identical in intensity and appearance when collected under air or when the solutions are purged with argon. As the bridging sulfur is oxidized from sulfide (S), to sulfoxide (SO), to sulfone (SO$_2$), Φ_f increases with the level of oxidation in all cases (Figure 1). An enhancement as high as 0.01 to 0.74 is observed for the series of sulfur-bridged pyrene compounds.

The electronic absorption spectra for all the sulfur-bridged compounds are red-shifted relative to the spectra of the parent arenes. The DFT calculated highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for **1SO$_n$** (Figure S1) and **2SO$_n$** (Figure 2) are
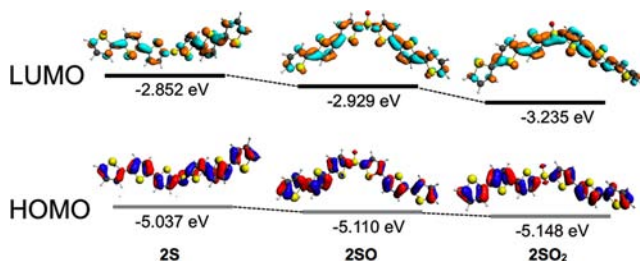

Figure 2. Frontier molecular orbitals (FMOs) for **2S**, **2SO**, and **2SO$_2$**. Geometry optimized structures calculated in C_2 symmetry for **2S** and **2SO$_2$** and C_s for **2SO**.

delocalized over both aryl groups. The absorption maxima of **1S**, **1SO**, and **1SO$_2$** are consistent with two weakly coupled bithiophene units (λ_{max} = 305 nm) rather than a longer thiophene oligomer (i.e., tetrathiophene, λ_{max} = 377 nm)[5,6,17,18] which would be expected if the sulfur bridge allowed a strong interaction between the thiophene units. The same comparison can be drawn between bridged terthiophene compounds (**2SO$_n$**), where λ_{max} is between that of terthiophene (λ_{max} =

349 nm) and sexithiophene (λ_{max} = 432 nm).[6,19] The extinction coefficients (ε) for the sulfur-bridged compounds are roughly twice those of the parent arenes, except for the pyrene compounds (**4SO$_n$**) where ε is nearly five times as large as that of pyrene.

Excited state calculations for **2S**, **2SO**, and **2SO$_2$** show small geometry differences from calculated ground state geometries (see Supporting Information), with increased planarization of the thiophene rings and decreases in the interannular C−C bonds seen in all cases. Thiophene oligomers containing S-oxides and S,S-dioxide rings have been previously found to maintain planar, or quasiplanar, conformations yielding red-shifted electronic absorption spectra and enhanced solid-state emission.[20] The C−S−C angle of the bridging sulfur atom decreases by 0.6° in **2S** and by 0.01° in **2SO** in the excited state; however in **2SO$_2$** this angle increases by 1.8° in the excited state. Thus, as the oxidation state of the bridging sulfur is increased, the geometry in the excited state prefers a slightly more linear configuration.

In the sulfoxide and sulfone derivatives, the presence of the electron deficient bridging sulfur group[21] results in the possibility of intramolecular charge transfer (ICT) playing a role in the photophysical behavior of these molecules. Fluorene substituted dibenzothiophene-S,S-dioxides have been previously shown to have localized excited (LE) states that dominate in nonpolar solvents, while ICT states are activated in more polar solvents due to stabilization of the induced excited state dipole moment.[22] To assess the relative ICT character between sulfide, sulfoxide, and sulfone bridging units, the absorption and emission energies for **2SO$_n$** were plotted (Figure S3) against the Lippert−Mataga solvent polarizability Δf.[23] For compounds **2SO** and **2SO$_2$** a linear increase in the Stokes shift was observed with increasing polarity, while the Stokes shift in compound **2S** shows no trend. In low to moderately polar solvents (cyclohexane, CHx → dichloromethane, DCM) little or no broadening in the emission profile is observed; however, in more polar solvents (DCM → acetonitrile, ACN) a sharp, nearly linear increase in the full width at half-maximum (fwhm) is observed for **2S**, **2SO**, and **2SO$_2$** (Figure S5). The increasing fwhm and Stokes shift in response to polar media strongly supports[22b,24] the conclusion that ICT is occurring in **2SO** and **2SO$_2$** and furthermore that ICT is strongest with the SO$_2$ bridge.

The photoluminescence quantum yields were determined in solvent mixtures with Δf between 0.0 and 0.3 (Figure 3). In the least polar solvent (CHx), **2S**, **2SO**, and **2SO$_2$** all have $\Phi_f \approx 0.1$, the same as that measured for terthiophene (T$_3$) in CHx. For terthiophene, the low Φ_f has been attributed to intersystem crossing (ISC) promoted by the presence of sulfur.[5] In nonpolar solvents it is reasonable that for **2S**, **2SO**, and **2SO$_2$** a more localized excited (LE) state on the terthiophene moiety exists and is deactivated via ISC similarly to terthiophene. Compound **2S** shows a linear decrease in Φ_f as the solvent polarity is increased, while Φ_f values for **2SO** and **2SO$_2$** increase with solvent polarity reaching a maximum in DCM. Excited state DFT calculations show that a small degree of charge transfer occurs upon excitation, with the bridging sulfur becoming more positive in **2S**, and less positive in **2SO** and **2SO$_2$**. Our data show that with increased contribution from ICT **2SO** and **2SO$_2$** are more emissive than in nonpolar solvents where the LE state is dominant. This is further evidenced by comparing the solvent dependence of the series **2S**, **2SO**, and **2SO$_2$** to T$_3$, where only a small variation in Φ_f is
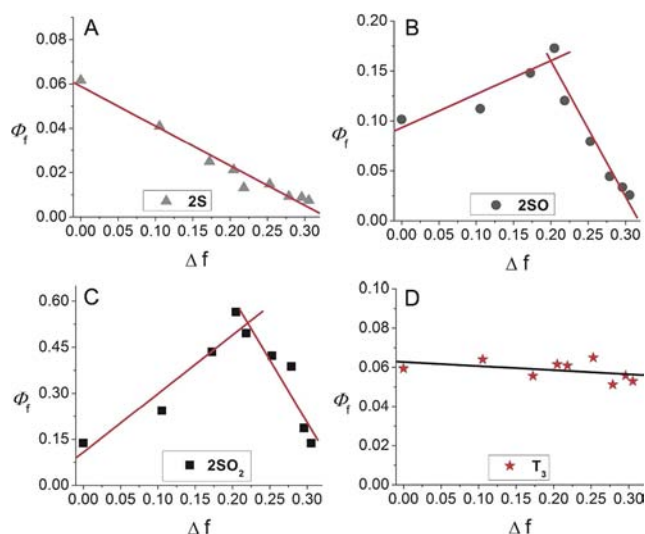
Figure 3. Photoluminescence quantum yield (Φ_f) for **2S** (A), **2SO** (B), **2SO$_2$** (C), and **T$_3$** (D) as a function of the solvent polarizability (Δf).

Figure 4. Thin film solid-state emission using glass substrates for **1S**, **1SO**, and **1SO$_2$** compared to bithiophene (A) and **2S**, **2SO**, **2SO$_2$** compared to terthiophene (B) obtained using an integrating sphere. Relative emission intensities for **1S**, **1SO**, and **1SO$_2$** (C) and **2S**, **2SO**, and **2SO$_2$** (D) on alumina. Also shown are the parent arenes **T$_2$** and **T$_3$** on alumina as well as the background spectra (BKG).

observed (Figure 3D). It is also possible that a decrease in ISC due to reduction in the number of lone pairs on the bridging sulfur with oxidation, i.e. $^1(\pi,\pi^*) \rightarrow {}^3(n,\pi^*)$, plays a role in enhancing Φ_f.

In more polar solvents ($\Delta f > 0.22$) a decrease in Φ_f is observed for both **2SO** and **2SO$_2$**. Previous studies have shown that two different nonradiative pathways, one more prominent in polar solvents, (related to a twisted intramolecular charge transfer (TICT) state), and the other more prominent in nonpolar solvents (attributed to a LE state), were observed in aminostyryl donor−acceptor dyes.[24] Evidence for a TICT state has also been shown in SO$_2$-bridged aryl molecules.[25]

Interestingly, the Φ_f values for **1SO$_2$** (0.45) and **2SO$_2$** (0.52) exceed those of tetrathiophene, **T$_4$** (0.18−0.20), and sexithophene, **T$_6$** (0.34−0.40).[5,6,19] The increase in Φ_f between **T$_4$** and **T$_6$** has been attributed to a decrease in k_{ISC} with increasing oligomer length. In the sulfone and sulfoxide bridged oligomers, the influence of ICT is greater than the effect of ISC on Φ_f with increasing oligomer length.[5]

Solid-state photoluminescence measurements were performed on the bithiophene (**1SO$_n$**) and terthiophene (**2SO$_n$**) series (Figure 4A and B). Thin films were prepared by dropcasting suspensions (∼1 mg/mL in hexanes) onto precleaned glass substrates, and quantum yields were determined using an integrating sphere (Table S7). The relative solid-state emission intensity was observed to be **1SO** < **T$_2$** < **1S** < **1SO$_2$** in the bithiophene series and **2S** < **2SO$_2$** < **1SO** < **T$_3$** in the terthiophene series. While the trend in emission is different than that in solution, a large enhancement is observed for **1SO$_2$** compared to the parent arene **T$_2$**. Further solid-state photoluminescence data were collected using a modified literature procedure.[26] Alumina thin-layer chromatography (TLC) plates were cut into 1 cm^2 pieces and developed slowly in 50 μL aliquots of the analyte (∼1 mg/mL, CHCl$_3$) to achieve uniform coverage. The plates were dried under ambient conditions and were subsequently subjected to photoluminescence measurements. On alumina substrates both **1SO$_2$** and **2SO$_2$** are significantly more emissive than their parent arenes (Figure 4C and D) under these conditions.
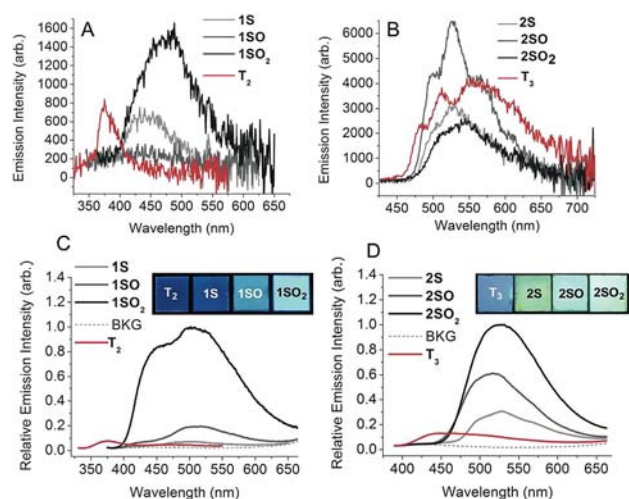
In summary, we have identified a general method to improve the photoluminescence quantum yield for a series of symmetrical sulfur-bridged chromophores, by oxidation of the bridging sulfur. Solvatochromism and band broadening of the emission spectra in high polarity solvents indicate charge transfer is more prevalent in the sulfoxide (SO) and sulfone (SO$_2$) bridged chromophores. It is proposed that CT states resulting from oxidized sulfur bridges allow for enhanced emission. The enhanced photoluminescence combined with the processability of these soluble compounds is anticipated to be useful in the fabrication of OLED devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details and characterization data (NMR, IR, and mass spectrometry), absorption and emission spectra, and details and summary of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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