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Chemical Stabilities of the Lowest Triplet State in Aryl Sulfones and Aryl Phosphine Oxides Relevant to OLED Applications

Huifang Li,^{a,b} Minki Hong,^{a,b} Annabelle Scarpaci,^a Xuyang He,^a Chad Risko,^{a,c} John S. Sears,^a Stephen Barlow,^a Paul Winget,^a Seth R. Marder,^{*,a} Dongwook Kim,^{*,d,b} and Jean-Luc Brédas^{*,a,b}

^a School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, USA

^b Laboratory for Computational and Theoretical Chemistry of Advanced Materials, Physical Science and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

^c Department of Chemistry and Center for Applied Energy Research (CAER), University of Kentucky, Lexington, Kentucky, 40506, USA

^d Department of Chemistry, Kyonggi University, 154-42 Gwanggyosan-Ro, Yeongtong-Gu, Suwon, 16227 Korea

*Emails: seth.marder@chemistry.gatech.edu; dongwook-kim@kyonggi.ac.kr; jean-luc.bredas@chemistry.gatech.edu

This work is dedicated to Dr. Guy Laurent at the occasion of his retirement from Solvay and to the memory of Dr. Ardeshir Momtaz and Dr. Roland Martin.

Abstract

Aryl sulfones and phosphine oxides are widely used as molecular building blocks for host materials in the emissive layers of organic light-emitting diodes. In this context, the chemical stability of such molecules in the triplet state is of paramount concern to long-term device performance. Here, we explore the triplet excited-state (T_1) chemical stabilities of aryl sulfonyl and aryl phosphoryl molecules by means of UV absorption spectroscopy and density functional theory calculations. Both the sulfur–carbon bonds of the aryl sulfonyl molecules and the phosphorus–carbon bonds of aryl phosphoryl derivatives are significantly more vulnerable to dissociation in the T_1 state when compared to the ground (S_0) state. Although the vertical $S_0 \rightarrow T_1$ transitions correspond to non-bonding $\rightarrow \pi$ -orbital transitions, geometry relaxations in the T_1 state lead to σ - σ^* character over the respective sulfur–carbon or phosphorus–carbon bond, a result of significant electronic state mixing, which facilitates bond dissociation. Both the activation energy for bond dissociation and the bond dissociation energy in the T_1 state are found to vary linearly with the adiabatic T_1 -state energy. Specifically as T_1 becomes more energetically stable, the activation energy becomes larger, and dissociation becomes less likely, *i.e.*, more endothermic or less exothermic. While substitutions of electron-donating or accepting units onto the aryl sulfones and aryl phosphine oxides have only marginal influence on the dissociation reactions, extension of the π -conjugation of the aryl groups leads to a significant reduction in the triplet energy and a considerable enhancement in the T_1 -state chemical stabilities.

I. Introduction

Since the groundbreaking work of Tang and Van Slyke in 1987,¹ organic light-emitting diodes (OLEDs) have triggered a significant academic and industrial interest. First-generation OLEDs were based on fluorescent emitters, limiting their inherent quantum efficiencies. Significant changes in chemistry and device design, however, have resulted in remarkable improvements over the past two decades.² In particular, second-generation OLEDs that incorporate phosphorescent metal-organic coordination complexes overcome the quantum efficiency limitations, allowing device internal quantum efficiencies (IQE) to reach unity;³⁻⁶ with further device optimization, external quantum efficiencies (EQE) of nearly 30% have been reported.⁷ Third-generation OLEDs based on the concept of thermally activated delayed fluorescence (TADF) have garnered recent attention, as the purely organic TADF emitters can potentially replace the expensive heavy-metal containing phosphorescent emitters without undermining device performance, also allowing demonstration of IQE values approaching 100%.⁸⁻¹² Although there remains considerable room for improvement, OLED display and lighting technologies are surpassing more traditional and inorganic LED technologies in a number of commercial applications.

A key concern for OLED materials is operational lifetime, which is related to molecular chemical stability in the presence of impurities (such as ambient oxygen and/or water) and under electronic or optical excitation.¹³⁻¹⁵ Adverse water vapor and oxygen degradation¹⁶ can be mitigated via device encapsulation.¹⁷ Chemical degradation due to either electronic or optical processes that take place during device operation,^{18,19} however, remain a key impediment to wide commercialization, in particular for high-energy, blue-emitting devices based upon phosphorescent emitters.²⁰⁻²² In spite of their importance, studies on the stabilities

of such materials are rather limited,²²⁻²⁴ although the insight they can provide needs to be considered in the initial materials design paradigm.

Aryl sulfone (SO₂)²⁵⁻²⁷ and aryl phosphine oxide (PO)^{5,28-33} derivatives have attracted interest as OLED components. Both the sulfonyl and phosphoryl groups have strong inductive electron-withdrawing character, and can energetically stabilize the lowest unoccupied molecular orbital (LUMO) of the π -conjugated molecular cores to afford electron-transport materials.³³ Combined with their high triplet energies, aryl SO₂ and aryl PO derivatives have been used in the development of host materials that inhibit self-quenching of the light-emitting guests in both blue phosphorescent³⁴⁻⁴⁰ and TADF OLEDs.⁴¹⁻⁴³ In addition, such aryl SO₂ and aryl PO based host materials exhibit good thermal stabilities.⁴⁴⁻⁴⁶ Unfortunately, however, some of these materials under UV irradiation or in electrically stressed devices exhibit decomposition, which limits material lifetime. For example, diphenylsulfone (DPSO) has long been known to decompose under UV irradiation via cleavage of the S–C bond.^{19,47-51} Ponterini and Momicchioli presented a detailed study of the triplet decay mechanism for the photodissociation in DPSO using laser flash photolysis,⁵¹ providing a dissociation mechanism of the S–C bond that involves two triplet excited states: a lower energy phenyl-localized $^3\pi\pi^*$ state and a higher lying C–S $^3\sigma\sigma^*$ state. Excitation to the lowest phenyl $^3\pi\pi^*$ state can be followed by conversion into the $^3\sigma\sigma^*$ state with a potential energy barrier of *ca.* 0.37 eV; once this barrier is overcome, the S–C bond undergoes fast homolytic dissociation following the repulsive $^3\sigma\sigma^*$ potential energy curve. UV instabilities of other aryl SO₂ and aryl PO OLED materials have also been reported.^{18,19} For example, 5,5'-(5-(9*H*-carbazol-9-yl)-1,3-phenylene)bis(benzo[*b*]phosphindole 5-oxide) (CzPO2), a typical host material for OLEDs, exhibits high triplet energy, good thermal stability, and solution processibility, but suffers from the dissociation of the P–C bond under UV irradiation.¹⁸ In order to enhance the operational

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2
3 stabilities of aryl SO₂ and aryl PO derivatives for OLED, it remains important to gain a more
4
5 thorough understanding of the excited-state chemical instabilities.
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8 Here, we explore the decomposition of aryl SO₂ and aryl PO molecules, with particular focus
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10 on bond dissociation processes in the low-lying triplet (T₁) state. We combine experimental
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12 studies on the photostability of three aryl sulfonyl molecules – diphenylsulfone (DPSO), 4,4'-
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14 bis(*m*-tolylsulfonyl)-1,1'-biphenyl (TTBSO), and 2,2',6,6'-tetramethyl-4,4'-bis(phenylsulfonyl)-
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16 1,1'-biphenyl (PPTSO) – with results from density functional theory (DFT) calculations to
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18 explore the T₁ bond dissociation of DPSO; we also analyze the T₁ bond dissociation of
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20 triphenyl phosphine oxide (TPPO). We then seek to broaden our chemical understanding by
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22 exploring the impact of electron-donating and electron-withdrawing substituents on bond
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24 dissociation in the aryl SO₂ and aryl PO families, as well as the impact of extending the π -
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26 conjugation lengths of the aryl substituents. The totality of these results allows us to draw
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28 meaningful conclusions regarding the design of aryl SO₂ and aryl PO derivatives in order to
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30 limit their photoinduced chemical decomposition.
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40 **II. Experimental and Computational Methods**

41 **2.1. Experimental details**

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46 DPSO was used as purchased. TTBSO and PPTSO were synthesized by *meta*-
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48 chloroperoxybenzoic acid (mCPBA) oxidation of the corresponding bis(arylthio)biphenyl
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50 derivatives, which in turn were obtained from the appropriate arylthiol and 4,4'-
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52 dibromobiphenyl derivative (vide infra for details). TTBSO and PPTSO were purified by
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54 sublimation and were deoxygenated by bubbling with argon prior to photochemical stability
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56 studies. Acetonitrile (MeCN) was HPLC grade and used without further purification. UV-Vis
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spectra were measured in MeCN in 1 cm quartz cells using a Varian Cary 5E spectrometer. The UV irradiation was carried out in a Rayonet Photochemical Reactor using 16 photochemical lamps (RPR = 2537 Å).

4,4'-Bis(*m*-tolylthio)biphenyl. K₂CO₃ (18 g, 128 mmol, 8 eq.) and 3-methylbenzenethiol (4.8 mL, 64 mmol, 4 eq.) were added to a stirred solution of 4,4'-dibromobiphenyl (5 g, 16 mmol, 1 eq.) in DMF (140 mL) under nitrogen. The reaction mixture was heated at 160 °C overnight. Water was then added to the mixture, which was then extracted 3 times with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried over MgSO₄, filtered, and evaporated under reduced pressure. The product was purified on silica gel using hexanes as eluent (4.41 g, 70%). ¹H NMR (300 MHz, CDCl₃): δ 7.50 (dt, *J* = 8.7, 2.1 Hz, 4H), 7.37 (dt, *J* = 8.7, 2.1 Hz, 4H), 7.39-7.34 (m, 6H), 7.11-7.08 (m, 2H), 2.33 (s, 6H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 139.1, 138.7, 135.6, 134.8, 132.1, 130.9, 129.1, 128.6, 128.2, 127.5, 21.3. HRMS-EI (*m/z*): calcd for C₂₆H₂₂S₂ (M⁺), 398.1163; found, 398.1150. Anal. Calcd for C₂₆H₂₂S₂: C, 78.35; H, 5.56; S, 16.09. Found C, 78.35; H, 5.55; S, 16.08.

(2,2',6,6'-Tetramethylbiphenyl-4,4'-diyl)bis(phenylsulfane). Thiophenol (1 mL, 10 mmol, 4 eq.) was added to a stirred solution of 4,4'-dibromo-2,2',6,6'-tetramethylbiphenyl⁵² (940 mg, 2.5 mmol, 1 eq.) and K₂CO₃ (2.8 g, 20 mmol, 8 eq.) in DMF (33 mL) under nitrogen. The reaction mixture was heated at 160 °C overnight. Water was then added to the mixture, which was then extracted 3 times with ethyl acetate. The product was purified on silica gel using hexanes as eluent (765 mg, 70%). ¹H NMR (300 MHz, CDCl₃): δ 7.40–7.20 (m, 10H), 7.13 (s, 4H), 1.86 (s, 12H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 138.9, 138.0, 135.4, 134.4, 131.6, 129.8, 127.7, 126.1, 19.9. HRMS-EI (*m/z*): calcd for C₂₈H₂₆S₂ (M⁺), 426.1476; found, 426.1472. Anal. Calcd for C₂₈H₂₆S₂: C, 78.83; H, 6.14; S, 15.03. Found C, 78.56; H, 6.11; S, 15.08.

4,4'-Bis(*m*-tolylsulfonyl)biphenyl (TTBSO). A solution of mCPBA (70 wt%, 16.3 g, 66.4 mmol, 6 eq.) in dichloromethane (410 mL) was added to a solution of 4,4'-bis(*m*-tolylthio)biphenyl (4.4 g, 11 mmol, 1 eq.) in dichloromethane (635 mL). The reaction mixture was stirred for 24 h; a 10% aqueous solution of K₂CO₃ was added and the mixture was stirred for a further 5 min. The layers were separated and the aqueous layer was further extracted. The crude product was purified by chromatography on silica gel using ethyl acetate / hexanes (7:3) (2.15 g, 42%). ¹H NMR (300 MHz, CDCl₃): δ 8.02 (dt, *J* = 8.1, 1.8 Hz, 4H), 7.80-7.76 (m, 4H), 7.67 (dt, *J* = 8.1, 1.8 Hz, 4H), 7.44-7.37 (m, 4H), 2.40 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.9, 141.6, 141.1, 139.7, 134.2, 129.2, 128.3, 128.2, 128.0, 124.9, 213. HRMS-EI (*m/z*): calcd for C₂₈H₂₆S₂O₄ (M⁺), 462.0960; found, 462.0962. Anal. Calcd for C₂₆H₂₂S₂O₄: C, 67.51; H, 4.79; S, 13.86. Found C, 67.47; H, 4.74; S, 13.82.

2,2',6,6'-Tetramethyl-4,4'-bis(phenylsulfonyl)biphenyl (PPTSO). A solution of mCPBA (70 wt%, 2.9 g, 17.5 mmol, 6 eq.) in dichloromethane (350 mL) was added to a solution of 2,2',6,6'-tetramethylbiphenyl-4,4'-diylbis(phenylsulfane) (1.5 g, 2.8 mmol, 1 eq.) in dichloromethane (600 mL). The reaction mixture was stirred for 24 h; a 10% aqueous solution of K₂CO₃ was added and the mixture was stirred for a further 5 min. The layers were separated and the aqueous layer was further extracted. The crude product was purified by chromatography on silica gel using ethyl acetate / hexanes (7:3) (600 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.4 Hz, 4H), 7.70 (s, 4H), 7.62-7.52 (m, 6H), 1.87 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 143.7, 141.6, 140.7, 136.9, 133.2, 129.3, 127.8, 126.8, 19.9. HRMS-EI (*m/z*): calcd for C₂₈H₂₆S₂O₄ (M⁺), 490.1273; found, 490.1263. Anal. Calcd for C₂₈H₂₆S₂O₄: C, 68.54; H, 5.34; O, 13.04; S, 13.07. Found C, 68.14; H, 5.29; O, 12.89; S, 13.43.

2.2. Computational approach

Density functional theory (DFT) calculations were carried out using the long-range corrected ω B97X-D functional⁵³ and the 6-31G(d,p) basis set.^{54,55} Optimized geometries were obtained using either spin-restricted Kohn-Sham orbitals for molecules in their ground state (S_0) or spin-unrestricted orbitals for the molecules in their lowest triplet excited (T_1) state and the radical products of their bond dissociation. Vibrational frequencies of all species were calculated and zero-point vibrational energies (ZPVE) were considered in the energetic evaluations. The transition states for the bond cleavage of DPSO and TPPO derivatives along the T_1 -state potential curve were located and confirmed by both vibrational frequency calculations and subsequent intrinsic reaction coordinate (IRC)^{56,57} calculations. To clarify the nature of the triplet excited states, time-dependent DFT (TDDFT)^{58,59} calculations followed by natural transition orbital (NTO)⁶⁰ analyses were performed. Natural bond orbital (NBO)⁶¹ and natural population analyses (NPA) were also conducted to provide additional information on the bond dissociation reactions. We also simulated absorption spectra of the experimentally measured molecules, i.e., DPSO, TTBSO, PPTSO, and their possible dissociation radical products, with the full widths at half maximum value being 4000 cm^{-1} using SWizard program.⁶² All calculations were carried out with the Gaussian09 Rev. D.01 suite⁶³ of programs.

III. Results and Discussion

3.1. Photostability of sulfone-based molecules: DPSO, TTBSO and PPTSO

The chemical structures of diphenyl sulfone (DPSO), 4,4'-bis(*m*-tolylsulfonyl)-1,1'-biphenyl (TTBSO), and 2,2',6,6'-tetramethyl-4,4'-bis(phenylsulfonyl)-1,1'-biphenyl (PPTSO) are shown in Figure 1. The photostabilities of these aryl SO_2 -based molecules were monitored by UV-Vis

spectral and thin-layer chromatographic (TLC) analyses. In this photostability study, DPSO served as a model compound for comparison. The remaining sulfones of interest incorporate two DPSO-like units. The biphenyl bridges in TTBSO and PPTSO are expected to be twisted to varying degrees depending on the molecular chemistry (*vide infra*).

The absorption spectra of DPSO, TTBSO, and PPTSO in acetonitrile (MeCN) were obtained both before and after irradiation at 254 nm for 5 minutes, as shown in Figure 2; we see a fair agreement between the experimental and theoretical spectra. DPSO displays a complete change in the absorption spectra, indicating photoinduced decomposition, consistent with previous reports,⁵¹ which suggest that this photodecomposition occurs through intersystem crossing and subsequent S–C cleavage from the T_1 state. The absorption spectra for PPTSO also clearly shows a change after irradiation. Interestingly, however, only very little spectral difference for TTBSO was observed, demonstrating that it remains intact even after UV irradiation in acetonitrile. TLC results for these sulfone derivatives, before and after irradiation, also indicate that DPSO and PPTSO are completely transformed to new species with different retention factors, while TTBSO appears unchanged; see Figure S1 in the Supporting Information.

Figure 1. Chemical structures of three aryl sulfonyl based molecules examined experimentally: diphenyl sulfone (DPSO) (a), 4,4'-bis(*m*-tolylsulfonyl)-1,1'-biphenyl (TTBSO) (b) and 2,2',6,6'-tetramethyl-4,4'-bis(phenylsulfonyl)-1,1'-biphenyl (PPTSO) (c).

Figure 2. Experimental (left) and simulated (right) absorption spectra of (top) DPSO, (middle) TTBSO, and (bottom) PPTSO in acetonitrile before and after irradiation at 254 nm.

3.2. DFT exploration of the photodecomposition mechanisms of aryl SO₂ and aryl PO molecules

Given the experimental results, it is of interest to understand why DPSO and PPTSO appear to undergo photodegradation, though TTBSO does not, in as much as the main chemical features of these molecules are so similar. Hence, we undertook a series of DFT calculations to explore the potential energy surfaces (PES) of the S₀ and T₁ states.

a) Photodecomposition of DPSO

DPSO comprises one of the simplest building blocks for elucidating the photophysical properties of aryl SO₂-based host materials.^{26,27,40} Moreover, gas-phase electron-diffraction experiments by Rozsondai and co-workers⁶⁴ provide relevant information pertaining to the gas-phase geometry of DPSO, allowing direct comparison to DFT-based isolated molecule studies. Relevant bond lengths from experiment and ω B97X-D/6-31G(d,p) calculations for the ground (S₀) and the lowest triplet (T₁) states of DPSO are depicted in Figure 3. The ω B97X-D/6-31G(d,p) bond lengths of DPSO are in very good agreement with experiment, generally differing by only 0.01-0.02 Å.⁶⁴ We also note good agreement between the calculated and experimentally measured bond angles, see Table S1 in the Supporting Information. For the purpose of the work presented here, the ω B97X-D/6-31G(d,p) geometries appear to provide for a reliable description of DPSO.

Figure 3. Representative bond lengths (Å) of DPSO at the ω B97X-D/6-31G(d,p) level for the S_0 (in black) and T_1 (in red) states. The corresponding experimental data for the S_0 -state geometry were taken from Ref [64] and put in parentheses.

The structure of DPSO in the S_0 state corresponds to C_{2v} point group, making its two phenyl rings equivalent. The C_{2v} symmetry of DPSO, however, is lifted upon excitation and subsequent relaxation within the lowest triplet excited (T_1) state. Here, one of the phenyl rings undergoes a marked structural deformation, while the other retains a geometry similar to that for S_0 . The bonds between the C_S and C_α atoms (Figure 3) become *ca.* 0.08 Å longer than in the S_0 state (1.47 vs 1.39 Å, respectively), while those between the C_α and C_β atoms shorten from 1.39 to 1.36 Å. These changes in bond lengths are in accord with previous investigations⁶⁵ and indicate that the triplet state resides largely on a single phenyl ring. The most intriguing deformation in the T_1 state is, however, associated with the planarity of the phenyl rings. Although the S– C_S bond of DPSO is elongated only by 0.02 Å, for example, the S– C_S bond is no longer in the plane formed by C_S , $C_{\alpha'}$, and $C_{\alpha''}$, and the ring itself is “hinged” along the C_α – $C_{\alpha'}$ axis. These two effects leading to a decrease of the $\angle SC_S C_\gamma$ angle from 180° to *ca.* 120°, while the same angle in the other phenyl moiety remains 180°; the calculated potential energy

surfaces (PES) in the S_0 and T_1 states as a function of the $\angle SC_5C_7$ angle confirm this difference (see Figure S2 in the Supporting Information).

Another description of the T_1 evolution can be obtained via natural transition orbital (NTO) analysis based on TDDFT calculations; the hole-electron wavefunctions for the T_1 state of DPSO at both the S_0 - and T_1 -state geometries are depicted in Figure 4. We first note that the S_0 - T_1 vertical transition essentially corresponds to a HOMO $\rightarrow$ LUMO excitation (Figure S3); i.e., the hole and electron NTO largely correspond with these molecular orbitals, allowing us to rely on the HOMO and LUMO energies to assess the T_1 -state stability. The LUMO at the T_1 geometry is significantly lower in energy than that at the S_0 -state geometry (*ca.* -0.88 vs 0.43 eV), while the HOMO energy substantially increases (from *ca.* -9.15 to -8.24 eV). As a result, the HOMO-LUMO energy gap significantly reduces, which is a factor that explains why the T_1 state is more stable at this geometry. Given that a triplet state favors a more contracted exciton wavefunction, a feature that maximizes the exchange energy,⁶⁶⁻⁶⁹ such a structural relaxation over a single phenyl moiety also contributes to stabilize the T_1 state.

We now turn to a discussion of the PES in both the S_0 and T_1 states along the internal reaction coordinates (IRCs) for the S-C₅ bond dissociations. Table 1 provides the adiabatic triplet energy (E_T), the energy barrier to the S-C₅ bond dissociation in the T_1 state (E_a), and the S-C₅ bond dissociation energy in the S_0 state (E_d) for DPSO. The DFT energies are in very good agreement with those reported from experimental laser flash photolysis measurements,⁶⁴ although the activation energy (E_a) for the homolytic bond dissociation is somewhat underestimated (*ca.* 0.25 eV calc. vs. 0.37 eV exp.), suggesting that the ω B97X-D/6-31G(d,p) computed PES provide valuable insights into these systems. Given the generally good agreement among the DFT and experimental energies for DPSO, we now discuss the dissociation processes solely in the context of the DFT results.

Figure 4. Predominant hole-electron natural transition orbitals (NTOs) for the T_1 state of DPSO using the S_0 -state (a) and T_1 -state (b) geometries as determined at the ω B97X-D/6-31G(d,p) level of theory; the NTOs are given for both side (left) and oblique (right) viewpoints. The contribution from a given NTO pair is denoted on the bottom; lesser contributing NTO pairs in the S_0 -state geometry can be found in Figure S4.

Table 1. Experimental and theoretical energy values (in eV) for the homolytic S–C_S and P–C_P bond dissociations of DPSO and TPPO, respectively.

	DPSO		TPPO
	Theo. ^a	Exp. ^b	Theo. ^{a,c}
E_T	3.43	3.43	3.51
E_a	0.25	0.37	0.70
ΔE_0	3.30	3.17	4.02

^a Calculated at the ω B97X-D/6-31G(d,p) level of theory; zero-point vibration energies (ZPVE) were considered. ^b Ref [51]. ^c To the best of our knowledge, the corresponding experimental data for TPPO are not available.

Following the S–C_S bond dissociation, the IRC for DPSO (Figure 5) reveals a monotonous increase in the potential energy of the S₀ state. At 3.0 Å, where the S–C_S bond can be viewed as broken, the potential energy is *ca.* 3.30 eV, demonstrating a significant energy barrier to the bond dissociation in the S₀ state. In the T₁ state, on the other hand, as the S–C_S bond elongates, the potential energy slightly increases until a bond length of *ca.* 2.19 Å, where a saddle point forms, then monotonously decreases to the point corresponding to the appearance of a fully cleaved phenyl ring. The potential energy barrier for bond cleavage in the T₁ state is only *ca.* 0.25 eV, which is thus much smaller than in the S₀ state. This is consistent with the experimental observation that aryl SO₂ derivatives are much more vulnerable to S–Cs bond breakage in the T₁ state than in the ground state.⁵¹

Figure 5. Calculated PES as a function of S–C_S bond length of DPSO in the S₀ and the T₁ excited states as determined at the ωB97X-D/6-31G(d,p) level of theory.

The inherently high T_1 energy might be expected to facilitate the S–C_S bond cleavage of DPSO; however, the relationship between a high T_1 energy and a modest energy barrier to dissociation is not straightforward. To shed more light on the chemical instability of DPSO in the T_1 state, we explored the evolution of the nature of the T_1 -state in the course of the geometric deformation. As shown in Figure 4, the T_1 -state NTOs correspond mainly to a π - π^* (HOMO-to-LUMO) transition, with these orbitals being localized on one or both of the phenyl rings, at both S_0 - and T_1 -state geometries. However, since the photoexcited chemical instability of DPSO is associated with the S–C_S bond cleavage, it is important to focus on the characteristics of the T_1 -state NTOs around this bond. In the initial excitation to the T_1 state at the S_0 -state geometry, the hole wavefunction presents a nonbonding character between S and C_S atoms, while the electron (particle) wavefunction has π -bonding character. Thus, the T_1 state at the S_0 geometry corresponds to a transition from non-bonding to somewhat π -bonding orbitals between the S and C_S atoms. Importantly, the structural relaxation in the T_1 state and in particular the bending deformations impart σ^* character on the electron wavefunction for the T_1 state; likewise, the initial non-bonding character on the S–C_S bond in the T_1 -state hole wavefunction evolves to a σ -like character in the course of the geometric relaxation, see Figure 4(b). Hence, the relaxation in the T_1 state leads to a mixing of a non-bonding-to- π -bonding transition with a $\sigma\sigma^*$ transition. Additionally, as the reaction proceeds, both the hole and electron wavefunctions shift increasingly from the phenyl ring to the S-C_S bond, magnifying the $\sigma\sigma^*$ character, as seen in Figure 5 at the S–C_S bond dissociation limit. Therefore, the substantial reduction in the energy barrier to bond breaking in DPSO stems from the significant $\sigma\sigma^*$ character appearing in the T_1 state, as illustrated in Figure 6. We note that DFT-based analyses of the reduced and oxidized forms of DPSO reveal interesting trends: S-C_S bond dissociation can proceed in reduced DPSO, while such bond dissociation is much more difficult

in oxidized DPSO. These results can be understood from the bonding/anti-bonding character of the wavefunction for the respective states at the elongated S–C_s bond (Figure S5); when stretched, the S–C_s bond in reduced DPSO has a clear σ -anti-bonding character, while that in oxidized DPSO has a σ -bonding character. As a result, the final dissociation products of reduced DPSO, *i.e.*, phenyl sulfone anion and phenyl radical, are only 1.17 eV higher in energy than reduced DPSO itself. This dissociation energy is far smaller than in oxidized and neutral DPSO, which have ΔE_0 values of 2.48 and 3.30 eV, respectively.

Figure 6. Illustration of the S–C_s bond dissociation of DPSO in both S_0 and T_1 states as determined at the ω B97X-D/6-31G(d,p) level of theory.

b) Relative photostabilities of TPPO and DPSO

We now turn from the aryl SO₂ based molecules to the aryl PO based analogs, which have also been widely used to develop high-efficiency blue-emitting host materials.³⁴⁻³⁹ In the case of TPPO, the initial photodegradation step under UV irradiation has been shown to correspond to the homolytic dissociation of the relatively weak P-C_p bond.^{18,19} Optimized bond lengths for the S₀ and the T₁ states of TPPO are depicted in Figure 7. Geometric parameters from X-ray diffraction studies for the crystal structure of TPPO are included for comparison.^{70,71} There is good agreement between the computed and experimental geometric parameters of TPPO, with deviations ranging from 0.01-0.02 Å, see Table S1 in the Supporting Information for further comparison.

Upon excitation to the T₁ state, one of the phenyl rings in TPPO, as with DPSO, relaxes into a hinge-like structure (Figure S6), and such a contorted phenyl ring significantly facilitates the bond dissociation in DPSO and TPPO (Figure S7). Again, the $\sigma\sigma^*$ character of the P-C_p bond suggests much easier dissociation in the T₁ state, as depicted in Figure S8. However, there are marked differences between DPSO and TPPO in terms of the relevant energies for S-C_s/P-C_p bond dissociation, as listed in Table 1. Since both reactions share a common dissociation product (*i.e.*, a phenyl radical), the differences in the ΔE_T and E_a values can be attributed to the relative stabilities of the diphenyl phosphoryl and phenyl sulfonyl radicals. Natural population analyses (NPA) indicate that the unpaired electron in the phenyl sulfonyl radical has a 0.37 |e| population on the S atom, while that on the P atom of the diphenyl phosphoryl radical is 0.53 |e|. This points to a greater delocalization and thus stabilization of the unpaired electron in the former system. Thereby, unlike DPSO, the P-C_p T₁-state bond dissociation in TPPO is computed to be endothermic; see Figure 8.

Figure 7. Geometries of TPPO determined at the ω B97X-D/6-31G(d,p) level for the S₀ (in black) and T₁ (in red) states. Experimental data (X-ray crystal structure, given in parentheses) are taken from Ref. [70].

Due to this endothermicity, the transition state is expected to resemble products more for TPPO than DPSO, leading to a more repulsive PES of the former. Indeed, the transition states are located at P-C_P and S-C_S distance of *ca.* 2.34 Å and 2.19 Å for TPPO and DPSO, respectively (the bond lengths are similar (*ca.* 1.81 Å) at their respective T₁ minima, Figures 5 and S6). Therefore, the energy barrier for TPPO ($E_a = 0.70$ eV) is significantly larger than that for DPSO ($E_a = 0.25$ eV). This suggests that the photostability of TPPO is greater than that of DPSO.

For the sake of comparison, we also calculated the C(O)-C bond photodissociation in a carbonyl analog, benzophenone (BP), see Figure S9. The calculated triplet energy E_T for BP is 2.85 eV, a lower value than in DPSO (3.43 eV) and TPPO (3.51 eV), which is attributed to the more delocalized character of the hole-electron wavefunctions in BP, see Figure S10. In addition, the phenyl ring of BP in the T₁ state is not contorted in the same way as was observed for the sulfones and phosphine oxides. As a result, the energy barrier for the C(O)-C bond

dissociation of BP in the triplet state is 1.44 eV, which is much higher than those for the S-C_S (DPSO) and P-C_P (TPPO) dissociation reactions. Furthermore, the computed C(O)-C bond dissociation energy of BP is about 4.23 eV, a value larger than those of S-C_S (DPSO) and P-C_P (TPPO) bonds by 0.93 eV and 0.21 eV, respectively. Therefore, the C(O)-C bond dissociation process is far more endothermic with ΔE_T being 1.14 eV, while such values for DPSO and TPPO are -0.13 and 0.51 eV, respectively. These results point out that the CO moiety provides the best photostability.

In order to gain more practical insight, we also carried out further calculations for the S-C_S, P-C_P, and C(O)-C bond dissociations, respectively, in a typical SO-containing host material, 4,4'-di(9H-carbazol-9-yl)-diphenylsulfone (CzSF), a PO-containing host material, 9-(3,5-bis(diphenylphosphoryl)phenyl)-9H-carbazole (CzPO2), and a CO-containing host material bis(9,9'-spirobifluorene-2-yl)ketone (SBFK), which have been investigated experimentally.¹⁹ The chemical structures and reaction pathways are given in Figures S11 and S12, respectively. Again, the C(O)-C bond in SBFK shows the highest energy barrier to dissociation (1.22 eV), while the S-C_S and P-C_P bonds in CzSF and CzPO2 exhibit much lower energy barriers (0.34 eV and 0.71 eV, respectively). These values are consistent with the experimental data reported earlier,¹⁹ and the results we discussed above for the model compounds.

Figure 8. IRC for the bond dissociation reaction in the T_1 state of DPSO (top) and TPPO (bottom) as determined at the ω B97X-D/6-31G(d,p) level.

c) Substituent effects on the bond dissociation in DPSO and TPPO derivatives

We now turn to the effect that substituents can have on the electronic structures of DPSO and TPPO and on their photochemical stabilities. The chemical structures of the aryl SO₂ and aryl PO derivatives investigated here are depicted in Figure 9 and were chosen to examine the impact of both *para*- and *meta*-substitutions on one aryl group. In this case, two dissociation pathways can occur, *i.e.*, one where an unsubstituted phenyl moiety is released (Path 1) and one where the substituted phenyl moiety is released (Path 2); relevant energies are provided in Tables 2 and 3.

Figure 9. Chemical structure of the DPSO and TPPO derivatives and illustration of possible products of their bond dissociation reaction. Different substituents are considered: 1: X=H; 2: X=CH₃; 3: X=OH; 4: X=OCH₃; 5: X=NH₂; 6: X=F; 7: X=Cl; 8: X=CF₃; 9: X=CCl₃; 10: X=CN. The ring that is bent upon relaxation in the triplet state is highlighted in red.

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3 It is useful to first discuss the conclusions we find among triplet energy E_T , energy barrier E_a ,
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5 and reaction energy ΔE_T of the various derivatives, see Figure 10. The overall linear inverse
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7 correlation between the reaction barrier E_a and the triplet energy E_T (Figure 10a and b) points
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9 to a similar energy of the transition state in all sulfonyl derivatives, at about 3.6 eV, and in all
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11 phosphoryl derivatives, at about 4.2 eV. Likewise, a linear inverse correlation between E_T and
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13 the energy of the dissociated state ΔE_T (Figure 10c and d) is found and the latter remains even
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15 more constant; the ΔE_T values for all derivatives of the sulfonyl and phosphoryl derivatives are
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17 around 3.2 and 4.0 eV, respectively. As discussed earlier, these energies are reasonable because
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19 the bond-breaking process is associated with the $\sigma\sigma^*$ character localized on the bond that
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21 dissociates and this character becomes even more intensified as the reaction proceeds (Figure
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23 5 and S6). The rather constant transition-state energies underline that higher triplet-state
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25 energies result in more facile dissociation pathways. In addition, for an equivalent triplet-state
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27 energy, the phosphoryl derivatives appear as much less prone to dissociation than their sulfonyl
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29 counterparts.
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36 Regarding the pathway giving rise to the unsubstituted phenyl radical (Path 1 in Figure 9), both
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38 E_T and E_a in the triplet state remain almost constant, varying by *ca.* 10 and 40 meV, respectively,
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40 demonstrating that the excited-state wavefunctions for the triplets and the corresponding
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42 transition states are predominantly localized on the unsubstituted phenyl groups (Figure S13).
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44 Thus the substituents have negligible effect on the energetics of this reaction pathway.
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Figure 10. Plots for the correlations of E_T vs. E_a (a for DPSO derivatives and b for TPPO derivatives), E_T vs. ΔE_T (c for DPSO derivatives and d for TPPO derivatives), and E_a vs. ΔE_T for all the sulfonyl and phosphoryl derivatives (e). The numbers (1) and (2) refer to the two pathways displayed in Figure 9. Relevant energies for DPSO, TPPO, TTBSO, and PPTSO are highlighted with red: These molecules are investigated only for the pathway yielding radical products with an intact biphenyl group; see Figure 11. All data are obtained at the ω B97X-D/6-31G(d,p) level of theory.

Table 2. Adiabatic triplet transition energies of the triplet state (E_T), energy barriers (E_a), and the S–C_S bond dissociation energy in the T₁ (ΔE_T) and S₀ (ΔE_0) states associated with each pathway of the mono-substituted DPSO derivatives as determined at the ω B97X-D/6-31G(d,p) level of theory. All energies are in eV.

	<i>para</i> -DPSO (pathway 1)				<i>para</i> -DPSO (pathway 2)			
	E_T	E_a^a	ΔE_T	ΔE_0	E_T	E_a^a	ΔE_T	ΔE_0
-H	3.43	0.25 (3.68)	-0.13	3.30				
-NH₂	3.43	0.26 (3.69)	-0.14	3.29	3.27	0.31 (3.58)	0.17	3.45
-OH	3.43	0.26 (3.69)	-0.13	3.30	3.36	0.30 (3.66)	0.03	3.39
-OCH₃	3.42	0.26 (3.68)	-0.13	3.29	3.33	0.29 (3.62)	0.05	3.34
-F	3.43	0.25 (3.68)	-0.12	3.31	3.42	0.27 (3.69)	-0.08	3.34
-Cl	3.43	0.25 (3.68)	-0.11	3.32	3.35	0.30 (3.65)	-0.05	3.30
-CH₃	3.44	0.25 (3.69)	-0.15	3.29	3.36	0.27 (3.63)	-0.02	3.34
-CN	3.42	0.24 (3.66)	-0.08	3.34	3.24	0.33 (3.57)	-0.01	3.23
-CF₃	3.42	0.24 (3.66)	-0.09	3.33	3.37	0.24 (3.61)	-0.11	3.26
-CCl₃	3.43	0.22 (3.67)	-0.11	3.32	3.28	0.30 (3.58)	-0.02	3.26
	<i>meta</i> -DPSO (pathway 1)				<i>meta</i> -DPSO (pathway 2)			
	E_T	E_a^a	ΔE_T	ΔE_0	E_T	E_a^a	ΔE_T	ΔE_0
-NH₂	3.43	0.25 (3.68)	-0.15	3.28	3.06	0.56 (3.62)	0.25	3.31
-OH	3.43	0.25 (3.68)	-0.14	3.29	3.33	0.29 (3.62)	-0.05	3.28
-OCH₃	3.43	0.25 (3.68)	-0.14	3.29	3.44	0.21 (3.65)	-0.16	3.28
-F	3.42	0.25 (3.67)	-0.11	3.31	3.40	0.26 (3.66)	-0.14	3.26
-Cl	3.42	0.25 (3.67)	-0.09	3.33	3.39	0.26 (3.65)	-0.13	3.26
-CH₃	3.43	0.25 (3.68)	-0.14	3.29	3.37	0.25 (3.62)	-0.07	3.30
-CN	3.42	0.24 (3.66)	-0.07	3.35	3.42	0.24 (3.66)	-0.17	3.25
-CF₃	3.41	0.23 (3.64)	-0.08	3.33	3.40	0.24 (3.64)	-0.13	3.27
-CCl₃	3.39	0.23 (3.62)	-0.05	3.34	3.34	0.29 (3.63)	-0.07	3.27

^a The values in parentheses correspond to the ones with reference to the S₀ state.

Table 3. Adiabatic triplet transition energies of the triplet state (E_T), energy barriers (E_a), and the P-C_p bond dissociation energy in the T_1 (ΔE_T) and S_0 (ΔE_0) states associated with each pathway of the mono-substituted TPPO derivatives as determined at the ω B97X-D/6-31G(d,p) level of theory. All energies are in eV.

	<i>para</i> -TPPO (pathway 1)				<i>para</i> -TPPO (pathway 2)			
	E_T	E_a^a	ΔE_T	ΔE_0	E_T	E_a^a	ΔE_T	ΔE_0
-H	3.51	0.70(4.21)	0.51	4.02				
-NH ₂	3.50	0.71(4.21)	0.50	4.00	3.34	0.87(4.21)	0.79	4.13
-OH	3.50	0.71(4.21)	0.52	4.02	3.45	0.80(4.25)	0.66	4.11
-OCH ₃	3.50	0.71(4.21)	0.51	4.01	3.42	0.76(4.18)	0.68	4.10
-F	3.50	0.72(4.22)	0.52	4.02	3.51	0.74(4.25)	0.56	4.07
-Cl	3.51	0.70(4.21)	0.52	4.03	3.42	0.78(4.20)	0.62	4.04
-CH ₃	3.51	0.70(4.21)	0.51	4.02	3.46	0.71(4.17)	0.59	4.05
-CN	3.50	0.71(4.21)	0.53	4.03	3.20	0.90(4.10)	0.80	4.00
-CF ₃	3.51	0.70(4.21)	0.53	4.04	3.43	0.70(4.13)	0.58	4.01
-CCl ₃	3.50	0.71(4.21)	0.54	4.04	3.32	0.77(4.09)	0.70	4.02
	<i>meta</i> -TPPO (pathway 1)				<i>meta</i> -TPPO (pathway 2)			
	E_T	E_a^a	ΔE_T	ΔE_0	E_T	E_a^a	ΔE_T	ΔE_0
-NH ₂	3.50	0.70(4.20)	0.50	4.00	3.15	1.05(4.20)	0.88	4.03
-OH	3.50	0.71(4.21)	0.50	4.00	3.38	0.78(4.16)	0.61	3.99
-OCH ₃	3.50	0.70(4.20)	0.50	4.00	3.54	0.59(4.13)	0.45	3.99
-F	3.50	0.71(4.21)	0.52	4.02	3.50	0.68(4.18)	0.50	4.00
-Cl	3.49	0.72(4.21)	0.53	4.02	3.47	0.69(4.16)	0.53	4.00
-CH ₃	3.51	0.70(4.21)	0.50	4.01	3.46	0.70(4.16)	0.56	4.02
-CN	3.50	0.72(4.22)	0.54	4.04	3.50	0.66(4.16)	0.50	4.00
-CF ₃	3.51	0.71(4.22)	0.52	4.03	3.47	0.63(4.10)	0.55	4.02
-CCl ₃	3.50	0.71(4.21)	0.53	4.03	3.40	0.69(4.09)	0.61	4.01

^a The values in parentheses correspond to the ones with reference to the S_0 state.

Turning to the dissociation of the substituted phenyl groups (Path 2 in Figure 9), the excited-state wavefunctions for the triplet transition states are predominantly localized on the substituted phenyl group (Figure S14) and the triplet energies vary as a function of the substituent, ranging between 3.24 and 3.42 eV. The transition states are 0.24 to 0.33 eV higher in energy with reference to the respective triplet-state minimum. The 0.09 eV variation for the

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3 reaction barrier, when compared to the 0.18 eV difference in triplet energies, suggest that the
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5 transition states are somewhat less sensitive to the substituents. As noted, it is presumably
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7 related to the fact that the hole-electron wavefunctions for the transition state of DPSO shift
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9 more towards the S–C_S bond away from the phenyl ring compared to those for the triplet state
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11 minimum, and thus the substitution effect on the phenyl ring should decrease in the transition
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13 state, see Figure 6.
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17 As pointed out above, a more stable triplet state is likely to correlate with a larger E_a . For
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19 example, the more strongly electron-donating -NH₂ gives rise to a more stable triplet state than
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21 the -CH₃ group (3.27 eV vs 3.36 eV of E_T) and hence the larger E_a (0.31 eV vs 0.27 eV,
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23 respectively). Likewise, in the case of electron-withdrawing groups, the relative lower triplet-
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25 state energy for -CN group (3.24 eV) compared to that of the -CF₃ group (3.37 eV) corresponds
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27 to a larger energy barrier, E_a (0.33 for the former vs 0.24 eV for the latter). Substitution at the
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29 *meta* position has similar impact, despite the delicate difference in E_T and E_a modulation; see
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31 Supporting Information for more details.
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36 However, we note that such modulations in E_T and E_a are rather marginal and are unlikely to
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38 be sufficiently effective to prevent aryl SO₂ and aryl PO derivatives from undergoing
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40 photoinduced degradation; the increase in the E_a values are all approximately 0.1 eV, with the
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42 exception of NH₂-substitution at the *meta* position (*ca.* 0.31 eV increase for the Path 2). Such
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44 consistency concerning substituent effects on the geometries and energies the DPSO T₁ state
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46 likely lies with the regular hinge-like phenyl rings across all structures. Further, considering
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48 that E_T for pure blue emitters is around 3.0 eV, this strongly suggests that there remains room
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50 for further reduction in E_T .
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d) **T₁ decay in TTBSO, PPTSO and other DPSO derivatives with extended π -conjugation**

We now return to a discussion of the photostability of three aryl sulfonyl based molecules, DPSO, TTBSO, and PPTSO, examined experimentally. To be systematic, we also investigated 4-(*m*-tolylsulfonyl)-1,1'-biphenyl (TBSO) and 2,2',6,6'-tetramethyl-4-(phenylsulfonyl)-1,1'-biphenyl (PTSO), which have only one sulfonyl group and hence can be more directly compared to DPSO, see Figure 11.

Figure 11. Chemical structures of aryl sulfone derivatives and their possible homolytic dissociation products: (a) 4,4'-bis(*m*-tolylsulfonyl)-1,1'-biphenyl (TTBSO) (b) 2,2',6,6'-tetramethyl-4,4'-bis(phenylsulfonyl)-1,1'-biphenyl (PPTSO), (c) 4-(*m*-tolylsulfonyl)-1,1'-biphenyl (TBSO), and (d) 2,2',6,6'-tetramethyl-4-(phenylsulfonyl)-1,1'-biphenyl (PTSO). The phenyl rings in red undergo structural deformation and bond-dissociation in the triplet state.

The calculated E_T , E_a , and ΔE_T values for these molecules are listed and compared to those for DPSO in Table 4. Again, the transition states are similar and the radical product states are nearly constant; see the values in parentheses in Table 4. The variation in E_T has a range of 0.43 eV, while the transition state (0.27 eV) and dissociated product state (0.04 eV) energies fall within smaller ranges. Consequently, in the dissociation from the T_1 state, TTBSO and TBSO exhibit the largest energy barrier for the dissociation (*ca.* 0.51 and 0.50 eV, respectively) and the largest endothermicity (with ΔE_T being *ca.* 0.30 and 0.27 eV, respectively) with reference to their respective T_1 -state minima, since they have the smallest E_T (*ca.* 3.00 and 3.04 eV, respectively), a feature consistent with experiment.⁷² On the other hand, PPTSO and PTSO have moderately reduced E_T (*ca.* 3.26 and 3.27 eV, respectively) and thus show much less significant E_a (*ca.* 0.32 eV for both) and little endothermicity (*ca.* 0.07 eV for both), which combines to present a rather facile photoinduced dissociation.⁷³ Hence, both DPSO and PPTSO undergo a photoinduced decomposition, while TTBSO appears unchanged after irradiation. These results are easily understood given that the biphenyl groups of PPTSO and PTSO have mutually conflicting methyl groups, forcing them to be twisted even in the T_1 state, leading to larger E_T , a result supported by the NTO presented in Figure 12. The hole-electron wavefunctions for TTBSO and TBSO are delocalized over the biphenyl group, which is in line with their small E_T . On the other hand, those of PPTSO and PTSO remain localized on a single phenyl unit, similar to those of DPSO. These results strongly suggest that elongation of the π -conjugation pathway represents a more effective strategy to reduce the E_T of the aryl SO_2 derivatives and provide photochemical stability, as opposed to chemical substitutions on the aryl rings. The energetic values associated with the S-C_S bond dissociation in the lowest triplet state of TTBSO and TBSO were explored as a function of the torsional angle between the phenyl rings of the biphenyl group (ranging from 0° to 80°), see Figure S17. A robust inverse

linear relationship between E_T and E_a is found again; more importantly, these results clearly show that the decrease in torsional angle leads to smaller E_T and hence larger E_a , demonstrating that the photostability should be improved with increased π -conjugation in the molecules. On the other hand, it is of course important to retain a sufficiently high value of E_T for efficient energy transfer to phosphorescent or TADF guest emitters and the value for TTBSO may be unsuitable for pure blue emitters.

Table 4. Computed T_1 -state energies (E_T), the activation energy (E_a) and the S–C_S bond dissociation energy in the T_1 (ΔE_T) and S_0 (ΔE_0) states of DPSO and its derivatives with the extended π -conjugation as determined at the ω B97X-D/6-31G(d,p) level of theory. All energies are in eV. (Photodissociation pathway and corresponding optimized T_1 states of TTBSO are shown in Figure S15 and S16).

	E_T	E_a^a	ΔE_T	ΔE_0
DPSO	3.43	0.25(3.68)	-0.13	3.30
TTBSO^b	3.00	0.51(3.51)	0.30	3.30
PPTSO^b	3.26	0.32(3.58)	0.07	3.33
TBSO^b	3.04	0.50(3.54)	0.27	3.31
PTSO^b	3.27	0.32(3.59)	0.07	3.34

^a The values in and out of parentheses correspond to the ones with reference to the S_0 and the T_1 states, respectively. ^b The data correspond to the pathways producing biphenyl-radical derivatives.

Figure 12. Predominant natural transition orbital (NTO) pairs of aryl sulfonyl derivatives with biphenyl groups for the lowest triplet excited (T_1) state at their respective T_1 geometries: (a) 4,4'-bis(*m*-tolylsulfonyl)-1,1'-biphenyl (TTBSO) (b) 2,2',6,6'-tetramethyl-4,4'-bis(phenylsulfonyl)-1,1'-biphenyl (PPTSO), (c) 4-(*m*-tolylsulfonyl)-1,1'-biphenyl (TBSO), and (d) 2,2',6,6'-tetramethyl-4-(phenylsulfonyl)-1,1'-biphenyl (PTSO). The contribution from a given NTO pair is denoted on the bottom.

IV. Synopsis

We investigated the chemical stabilities of aryl SO₂ and aryl PO derivatives in their T₁ states to explore their utility as host materials for OLED emitters. Unlike in the S₀ state, the S–C_S bond of DPSO in T₁ dissociates readily, with the activation energy being *ca.* 0.25 eV. The dissociation pathway stems from considerable geometry relaxation in the T₁ state that imparts a $\sigma\sigma^*$ character in the relaxed T₁ geometry to the non-bonding-to- π transition at S₀ geometry. The elongation of the S–C_S bond to the dissociation limit further magnifies such a $\sigma\sigma^*$ character. Likewise, TPPO also exhibits $\sigma\sigma^*$ character in its P–C_P bond in the T₁ state. However, the TPPO radical products are less stable than those for DPSO, with the P–C_P bond dissociation of TPPO being endothermic and its activation energy even higher than in its sulfonyl counterpart, constraints that portend a higher photochemical stability.

The localized $\sigma\sigma^*$ character in the dissociating bond and its enhancement in the course of the dissociation process lead to rather constant energies of the transition state and dissociation limit within the same molecular scaffold. Therefore, as the T₁ state gets more stable (while maintaining a sufficiently high energy for relevant applications), E_a tends to be larger, and the reaction is more likely endothermic, meaning that the bond dissociation becomes less likely from both kinetic and thermodynamic standpoints. In other words, the modulation of the E_T energy is the key factor in controlling the photostability of such molecules.

Despite their small modulations of E_T, the introduction of various electron-donating or withdrawing groups on the phenyl groups is an ineffective way to prevent photoinduced degradation. Rather, extension of the π -conjugation in one of the subgroups can significantly stabilize the T₁ state and effectively inhibit the photoinduced bond dissociation.

The results presented here demonstrate that either use of molecular skeletons that destabilize their dissociation products (sulfonyl *vs.* phosphoryl) or extension of π -conjugation within the same molecular framework, which stabilizes their reactant T_1 state (PPTSO *vs.* TTBSO), effectively enhances the chemical stabilities of potential host materials in the T_1 state. Given that the organic compounds present in the active layers of organic electronic devices, such as solar cells or light-emitting diodes, inevitably undergo electronic excitations (either photoexcitation followed by ISC or hole-electron recombination) and are more subject to chemical breakdown in the excited states, we believe that our findings are useful to design and develop more stable functional materials.

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Supporting Information Available: Table S1 collects the geometry parameters of isolated DPSO and TPPO. The frontier orbital energies and corresponding energy gaps for singly substituted DPSO/TPPO are listed in Table S2. The experimental TLC tests for DPSO, TTBSO, and PPTSO are shown in Figure S1. The PES as a function of $\angle SC_5C_7$ angle in DPSO is illustrated in Figure S2. Figure S3 shows the HOMO-LUMO energy gaps and the $S_0 \rightarrow T_1$ excitation energies obtained for optimized DPSO in the S_0 and T_1 states. Figure S4 displays

some lesser contributing NTO pairs in the T_1 state of DPSO at the S_0 geometry. PES as a function of S–C_S bond length of DPSO in the reduced and oxidized states is shown in Figure S5. Geometry-optimized DPSO and TPPO in the S_0 and T_1 states are displayed in Figure S6. Figure S7 shows the PES as a function of S–C_S bond length of DPSO and P–C_P bond length of TPPO with fixed nonbended phenyl rings and bended phenyl rings. The PES as a function of P–C_P bond length of TPPO is displayed in Figure S8. Optimized BP in the S_0 and T_1 states are shown in Figure S9. NTO pairs in the T_1 state of BP at the S_0 geometry are shown in Figure S10. Chemical structures of CzSF, CzPO2 and SBFK as well as there bond dissociation pathways are shown in Figure S11 and S12. The hole-electron wavefunction pairs of NTO for substituted DPSO are given in Figures S13 and S14. The confirmation of the photodissociation pathways and the corresponding optimized T_1 states of TTBSO are illustrated in Figures S15 and S16. Plots for the correlations of torsional angle between phenyl rings *vs.* E_T , E_T *vs.* E_a , torsional angle *vs.* E_a for TTBSO and TBSO are shown in Figure S17.

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73. We note that another reaction pathway can be initiated from the triplet state localizing on the terminal aryl group. As the data of Table 4 demonstrate, however, the reaction proceeds less likely along this pathway; in the case of PPTSO, for example, such a reaction corresponds to ca. 0.17 eV higher triplet state and more importantly ca. 0.1 eV higher transition state.

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