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Altering the Emission Behavior with the Turn of a Thiophene Ring: The Photophysics of Condensed Ring Systems of Alternating Benzenes and Thiophenes

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Six aromatic compounds with embedded thiophenes differing in the number of rings (2−5) and thiophene orientation along the long axis of the molecule (syn, anti) were investigated. Photophysical properties, steady-state absorption, fluorescence, phosphorescence, lifetimes, quantum yields, and a comprehensive time-resolved spectroscopic analysis (femtosecond and nanosecond transient absorption spectroscopy) have been studied as a function of molecular structure.

1. Introduction

Ladder-type, sulfur-containing ring compounds are an important source of materials for optoelectronic device applications, such as organic light-emitting diodes, organic field-effect transistors, and solar cells.[1−5] Fused, ladder-type materials have inherent advantages such as extended pi-frameworks, favorable stacking behavior in the solid state, conductivity, and high field-effect mobility.[6−11] While the rich excited-state properties of thiophene, oligo- and polymeric derivatives, have been extensively studied,[12−16] condensed S-containing aromatic systems have rarely been investigated systematically.[17−20] In particular, efforts to characterize the rich excited-state properties of these aromatic systems in the (sub)nanosecond time domain are scarce.[21−23] In this context, we have synthesized a series of well-defined, isomer−pure fused ring systems[11,24,25] and report herein the singlet- and triplet-state photophysical properties of a series of compounds composed of well-defined alternating benzene and thiophene moieties, Figure 1. We used steady-state absorption, fluorescence, and phosphorescence spectroscopy, as well as femto- and nanosecond time-resolved spectroscopy.

Compounds **3** and **4** contain one thiophene ring more than benzothiophene (**1**) in anti and syn orientation, respectively. Compounds **5** and **6** are derived from compound **2** with two additional thiophene moieties in the anti and syn orientation, respectively. We believe this to be the first report of the femtosecond (fs) transient absorption signals for this complete series of compounds **1**−**6**.

2. Experimental Section

2.1. Materials. Benzothiophene (**1**) was distilled prior to use. Dibenzothiophene (**2**, sublimed, 99%) was used as received. Benzo[1,2-*b*:4,5-*b*′]dithiophenes (**3**),[9] benzo[1,2-*b*:5,4-*b*′]dithiophenes (**4**),[26] thieno[2,3-*f*:5,4-*f* ′]bis[1]benzothiophene (**5**),[24] and thieno[3,2-*f*:4,5-*f* ′]bis[1]benzothiophene (**6**)[25] were synthesized according to the detailed procedures published elsewhere.

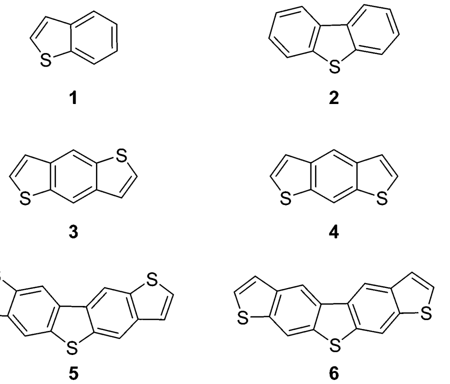

Figure 1. Fused thiophene compounds: [1]Benzothiophene (**1**), dibenzothiophene (**2**), benzo[1,2-*b*:4,5-*b*′]dithiophene (**3**), benzo[1,2-*b*:5,4-*b*′]dithiophene (**4**), thieno[2,3-*f*:5,4-*f* ′]bis[1]benzothiophene (**5**), and thieno[3,2-*f*:4,5-*f* ′]bis[1]benzothiophene (**6**).

2.2. Steady-State Spectroscopic Measurements. UV−vis absorption spectra were acquired on a Shimadzu UV−visible spectrophotometer (UV-2401 PC and Multispec-1501). Fluorescence spectra were acquired in ethanol and in methylcyclohexane (MCH) on a SPEX Fluorolog3-11 using a 450 W xenon short arc and sample detection in a 90° geometry. Fluorescence lifetimes were determined using time-correlated single-photon counting (TCSPC) in MCH under ambient conditions as previously described.[27] Phosphorescence spectra were acquired using a SPEX 1934D3 phosphorimeter on a Fluorolog 3 spectrometer utilizing a UV xenon flash lamp (450 W Xe lamp, R928 Hamamatsu single-photon counting photomultiplier tube (PMT) detector). Emission detection in phosphorescence mode with a delay time ≥ 50 μs was carried out in a 90° geometry. Emission spectra were acquired in a matrix of diethyl ether, isopentane, ethyl alcohol (EPA, 5/5/2) using quartz NMR tubes (o.d. = 5 mm) immersed in liquid nitrogen in a quartz dewar flask. Phosphorescence quantum yields were determined using biphenyl [$\Phi p = 0.24$] as standard,[28] and phosphorescence lifetimes were determined using decay by delay method.

2.3. Transient absorption spectroscopy was carried out with sample solutions of 0.5−1.0 OD in MCH at the excitation wavelength. The solutions were filtered (PTFE filter, 0.45 μm) and checked for decomposition before and after laser excitation using UV−vis spectrometry. A detailed description of the

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TABLE 1: Collection of Spectroscopic and Photophysical Properties of 1−6[a]

	unit	**1**	**2**	**3**	**4**	**5**	**6**
$\lambda_{\max}(S_0 \rightarrow S_n)$ [b]	nm	*227*, 298	*233*, 326	*258*, 336	*248*, 328	*261*, 378	*263*, 363
$\lambda_{F,\max}$(MCH)	nm	298, 309, 320 (sh)	327, 342, 357 (sh)	336, 353, 370 (sh)	328, 336, 344, 362 (sh)	381, 401, 425 (sh)	365, 386, 405 (sh)
$E(S_1)$ [c]	eV	4.17 [21]	3.80 [38]	3.72	3.78	3.27	3.41
Φ_F(EtOH)		0.019 [21]	0.08 [39] (CH)	0.014 [d]	0.009 [d]	0.14 [e]	0.012 [e]
τ_F(MCH)	ns	0.28 [21]	0.9 [40]	<1 [f]	∼1.12 [f]	4.6	<1 [f]
k_F [g]	10^7 s^{-1}	12.8	5.6	>1.4	∼0.8	3.04	>1.2
k_{NR} [g]	10^8 s^{-1}	34.5	10	>9.86	∼8.85	1.87	>9.88
$\lambda s_{,\max}$	nm	525-625	630	400, 500	460, 600−725	460, >750	425, 575, 780
τ_s [h]	ns	0.35	0.9	0.25	>1.0 [i]	>1.0 [i]	0.57
$\lambda_{P,\max}$(EPA)	nm	414, 423, 431, 442, 452, 461, 473, 484	409, 424, 437, 447, 455, 470, 480, 489	496 (sh), 506, 526, 540, 550.	474 (sh), 484, 498, 512, 522.	509, 523, 542, 556, 569.	453 (sh), 471, 487, 497, 510.
$E(T_1)$ [j]	eV	3.02	3.06	2.59	2.67	2.51	2.77
Φ_p(77K,EPA)		0.42 [19]	0.47 [19]	0.02	0.1	0.04	0.56
τ_p(77K,EPA)	s	0.32 [19,41]	1.3 [42]	0.11	0.27	0.21	0.38
$\lambda_{\max,T}$(MCH)	nm	430	390 [22]	490	410, 500	520	390, 520
τ_T(MCH) [k]	μs	17.3	47.9	21.8	5	128	13.6
Laser power	μJ/pulse	500	100	100	200	30	500
$k_q(O_2$,MCH)	10^9 (Ms)$^{-1}$	6.78	1.57	2.1	3.3	0.97	3.98

[a] Abbreviations: EPA = diethyl ether, isopentane, ethyl alcohol (5/5/2); MCH = methylcyclohexane; sh = shoulder; EtOH = ethanol; CH = cyclohexane. [b] Value in italics is the absorption maximum; the second number is the longest wavelength absorption band. [c] $E(S_1)$ was obtained from the crossing point of normalized absorption and fluorescence spectra. [d] Standard: Φ_F(2-aminopyridine) = 0.6 in 0.1 N H_2SO_4 and Φ_F(anthracene) = 0.27; values ±15%. [e] Standard: Φ_F(9-bromoanthracene) = 0.02 and Φ_F(anthracene) = 0.27 in ethanol; values ±5%. [f] Lifetime faster than instrument resolution. [g] $k_F = \Phi_F/\tau_F$; $k_{NR} = [1 - \Phi_F]/\tau_F$. [h] Value determined by femtosecond transient absorption spectroscopy. [i] Lifetime longer than instrument resolution. [j] $E(T_1)$ value was obtained from the onset of the phosphorescence band. [k] Data acquired after thorough purging with Ar (30 min). As the lifetime is strongly dependent on purging, only the longest determined lifetimes are reported.

apparatus for femtosecond time-resolved experiments is described elsewhere.[29] In brief, the fourth harmonic of a Spectra-Physics Hurricane femtosecond laser served as excitation source (267 nm) and a white light continuum probe was generated in a CaF_2 plate. A temporal delay of ∼2.67 ps is experienced until the red region of the probe pulse is registered. The samples were pumped through a CaF_2 cell with an optical path of 0.8 mm, connected to a solution reservoir and a pump system (Micropump Corp.) to avoid interference from long-lived species generated in an earlier excitation pulse.

Nanosecond UV−vis time-resolved absorption spectroscopy was carried out as reported elsewhere.[30] In all experiments, the fourth harmonic of a Continuum Surelite Q-switched Nd:YAG laser (267 nm) at a 5 Hz repetition rate was used as the excitation source. The energy per pulse is reported in Table 1; the pulse duration was ca. 7 ns. Sample solutions were purged with argon for at least 30 min prior to and kept under argon during photolysis.[31] Transient UV−vis absorption spectra were acquired at a step-size of 10 nm in the spectral region of 330−800 nm. Quenching constants for oxygen were determined by Stern−Volmer analysis by assuming that unimolecular decay and bimolecular quenching by oxygen are the only processes by which the triplet excited molecules deactivate. Lifetimes of the triplet state were determined in solutions purged with argon, air (equilibrated, $c[O_2] = 2.6 \times 10^{-3}$ mol/L)[28] and oxygen ($c[O_2] = 12.5 \times 10^{-3}$ mol/L).[28]

3. Results and Discussion

3.1. Steady-State Photophysical Properties. Absorption spectra of **1**−**6**[9,26,32−35] were obtained in MCH and are summarized in Table 1. The fusion of one thiophene ring on the *f*-bond of benzothiophene (**1**) results in a 38 (30) nm bathochromic shift of the longest wavelength absorption band of **3** (**4**). Two thiophene rings fused on the terminal bonds of dibenzothiophene (**2**) affect a 52 (37) nm bathochromic shift for **5** (**6**). Overall, a molecule in the anti orientation shows a greater bathochromic shift than that in a syn orientation, indicating a more effective conjugation in the anti geometry compared to the syn isomer.

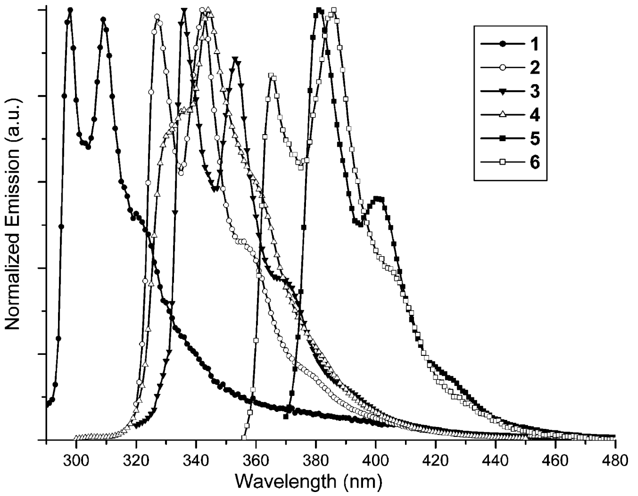

Figure 2. Fluorescence spectra of **1**−**6** in methylcyclohexane.

Fluorescence Properties. A bathochromic shift of emission of 38 nm for anti (**3**) and 30 nm for syn (**4**) is observed upon extending the ring system by one thiophene ring, Figure 2. Similarly, two thiophene rings result in a shift in the fluorescence of 54 and 38 nm respectively for anti and syn compounds **5** and **6**. Compounds **1**, **3**, and **4** thus show a negligible Stokes shift, and **2**, **5**, and **6** exhibit a Stokes shift of 1−2 nm. These small shifts are characteristic for rigid, polycyclic aromatic systems. Marginal fluorescence quantum yields (1%) are generally observed though **2** and **5** fluoresce with 8 and 14% yields, respectively. Such low quantum yields are indicative of the effective competition of radiationless processes such as the $S_1 \rightarrow T_1$ intersystem crossing and fast internal conversion ($S_1 \rightarrow S_0$). A remarkably long fluorescence lifetime of 4.6 ns was observed for **5**, while the lifetimes of **3**, **4**, and **6** were estimated at or below 1 ns (Table 1). The rate constants for radiative decay of S_1 (k_F) range from 8×10^6 to 1.3×10^8 s^{-1}, and the

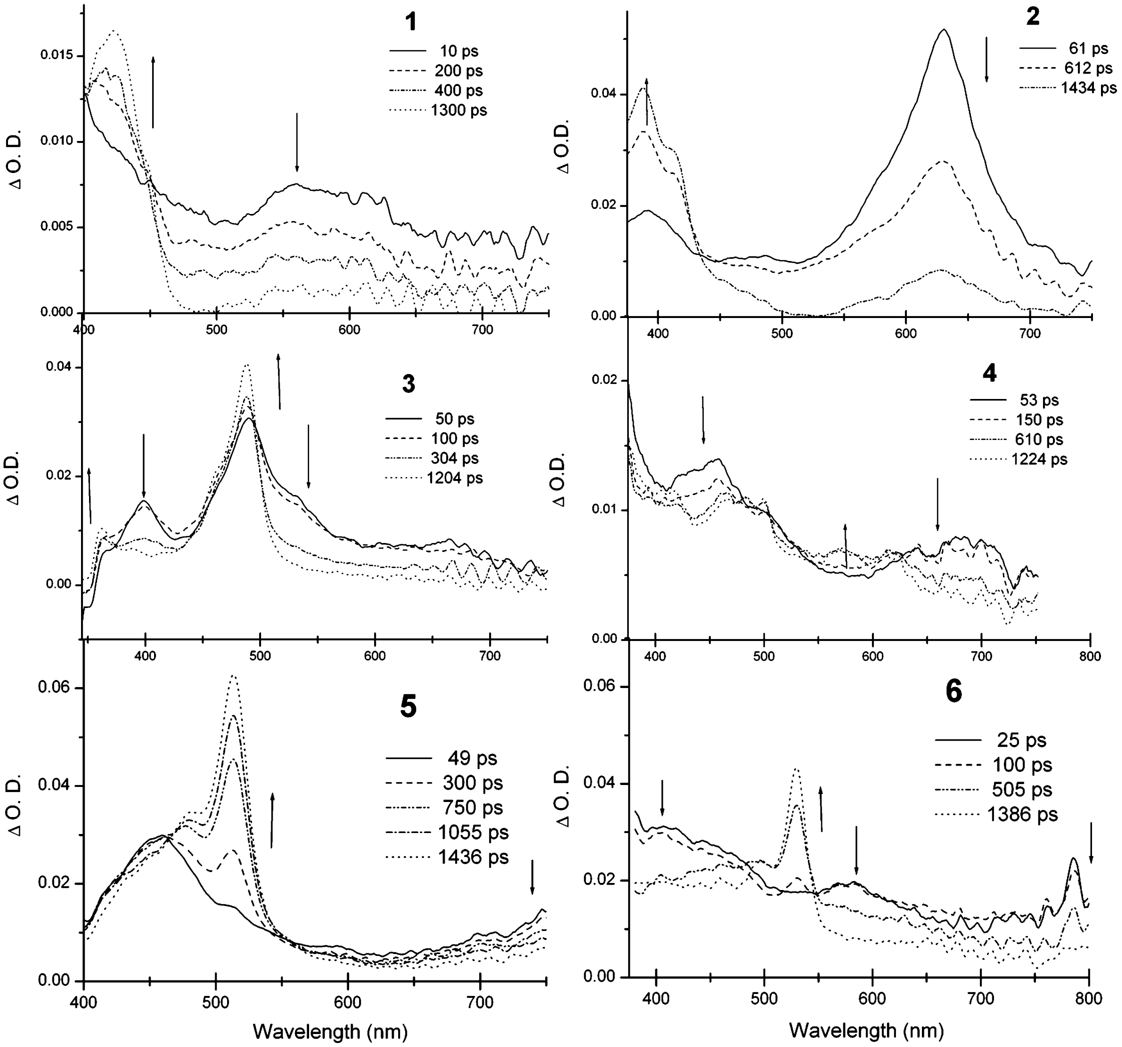

Figure 3. Femtosecond time-resolved absorption spectra of **1**−**6** in methylcyclohexane at various times after laser excitation (10−1435 ps).

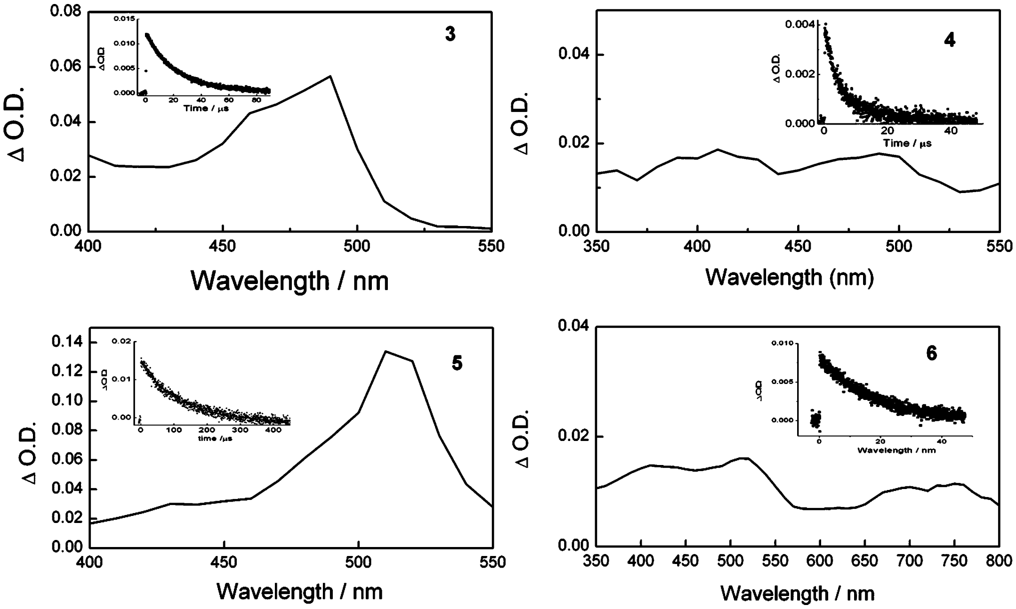

Figure 4. Transient absorption spectra of **3**−**6** ∼0.4 μs after laser excitation in MCH. Inserts: Absorption−time profiles observed at 490 (**3**), 490 (**4**), 520 (**5**), and 500 nm (**6**). The spectrum of **6** was smoothed for clarity.

nonradiative decay rate constants (k_{NR}) range from 1.9×10^8 to 3.5×10^9 s^{-1}. The nonradiative deactivation pathway is thus 6 times faster than the radiative one for compound **5** (anti) and about 110 times faster for compound **4** (syn).

Phosphorescence.[36] The phosphorescence properties of **1**−**6**, summarized in Table 1, indicate emission spectra of compounds **3**−**6** are less structured than those of **1** and **2** and show few vibronic progressions with energy spacing of 350 to 850 cm^{-1}.

A comparison of the anti isomers **3**, **5** with the syn isomers **4**, **6** indicates the opposite behavior. The onset of emission of **5** was weakly red-shifted compared to **3**, yet the onset of emission of **6** was blue-shifted relative to **4**. Specifically, the emission of **3** is red-shifted by 82 nm compared to the emission of **1,** but the emission is only 60 nm red-shifted for **4**. Extension of the ring system by two thiophene moieties in anti orientation, i.e., **2** to **5**, results in a 100 nm bathochromic shift, as opposed to a 44 nm bathochromic shift for the syn orientation, i.e., from **2** to **6**. The phosphorescence quantum yields and lifetimes vary substantially among the two isomer groups in that the phosphorescence lifetimes were ∼2-fold longer in the syn isomers compared to the anti isomers. Embedded, polycyclic thiophene containing compounds are expected to have high phosphorescence quantum yields,[17−19] yet only a negligible phosphorescence quantum yield of below 5% was observed for anti compounds **3** and **5** in a glass matrix at 77 K. Higher phosphorescence quantum yields are observed only for the syn compounds, i.e., **4** ($\Phi = 0.10$) and **6** ($\Phi = 0.57$). For **1**, **2**, and **6** more than 40% of the excited molecules decay via phosphorescence. The fusion of one (two) thiophene ring(s) onto parent **1** (**2**) effectively shortens the phosphorescence lifetime more for an anti fusion than for a syn fusion. A singlet−triplet splitting ($\Delta E(S_1-T_1)$) of ∼1.1 eV was calculated for compounds **1**, **3**, and **4**, while the values for **2** and **5** were ∼0.7 eV.[37] Compound **6** had a lower singlet−triplet energy splitting of only 0.6 eV. These values are smaller than the typical values for π,π^* S_1-T_1 splitting for aromatic systems of 1.3−1.73 eV.[37]

3.2. Time-Resolved Photophysical Properties. Femtosecond laser excitation of benzothiophene (**1**) resulted in one broad absorption band with $\lambda_{max} = 550$ nm. With time, this band decreased, while a new band grew in at 430 nm. The signals are connected by two clear isosbestic points at 400 and 450 nm. At 1.3 ns, the differential absorption spectrum with a maximum at $\lambda_{max} = 430$ nm resembled that of the $T_1 \rightarrow T_n$ spectrum of **1**.[21] The absorption signal at 550 nm was fitted to a lifetime of ∼0.35 ns, a value close to the reported fluorescence lifetime of 0.28 ns.[21] It was therefore assigned to the decay of the $S_1 \rightarrow S_n$ absorption of **1**. An equally clear spectrum was observed upon laser excitation of dibenzothiophene (**2**). Immediately after excitation, a strong absorption band at 630 nm, which decayed with a lifetime of 0.9 ns was detected coinciding with the fluorescence decay time reported by Berlman.[40] The signal was connected to the rising signal at 390 nm, with an isosbestic point at $\lambda = 435$ nm and assigned to the triplet state of **2** (vide supra).[22] The signals of **3**−**6** were assigned accordingly, Table 1. All spectra are depicted in Figure 3. The structured spectra of **3**, **5**, and **6** show a predominant absorption band growing in at a later time after the laser excitation pulse connected by clear isosbestic points. Specifically, **3** exhibited several absorption bands. The decay signal of the negative transient absorption signal at 350 nm and the decay at 400 nm each had a time constant of 260 ps. This value is in the range of the fluorescence lifetime estimated by TCSPC. The kinetic trace at 400 nm also exhibited fast components. Because excitation with a laser light of 267 nm leads to a population of higher order excited states such as S_2 or above, the fast decaying signals observed during the early picosecond times of data acquisition can be ascribed to internal conversions from these higher order singlet states to the lowest energy excited state of S_1.

Transient absorptions for **4** were detected at 460 and >690 nm, yet no clear absorption profile for a rising triplet-state absorption was detected in the spectral window. Consistently only weak absorptions were observed for both fs and ns (vide infra) transient absorption spectra for **4**. The decaying trace at 755 nm was composed of two components 26 and ∼1020 ps. The longer component was assigned to the decay of the singlet excited state, a value consistent with ∼1.12 ns estimated by TCSPC. For compound **5**, the slow rise and decay profiles as observed at 513 and 780 nm could not be fitted due to the long time constants expected from the long fluorescence lifetime. For compound **6**, the decay of the singlet-state and the rise of the triplet-state population were observed with time constants of 0.57 ns.

Triplet states in the series were detected using transient absorption spectroscopy in the nanosecond time regime. The spectra of **1** and **2** were previously reported,[22,23] while the transient absorption spectra and decay profiles of **4**−**6** are shown in Figure 4. At high laser power, second-order decay of the absorption time profiles is observed, pointing toward triplet−triplet annihilation. Lowering the laser intensity leads effectively to the observation of first-order decay profiles in all cases. The laser powers used are indicated in Table 1. As demonstrated by Jabbarzadeh and co-workers,[31] the lifetime of the triplet state is highly dependent on the presence of oxygen. The lifetimes reported in Table 1 were determined after purging the samples with argon for 30 min. In general, compounds with anti-constitution have a longer triplet-state lifetime than the syn-compounds. Interestingly, **5** showed the longest lifetime with 128 μs. The anti **3** and **5** exhibit pronounced absorption bands at 490 and 520 nm, respectively. For **4** and **6** we could only detect broad differential absorption bands (vide supra). The absorption bands for all compounds observed on a nanosecond time scale were readily quenched by the addition of *cis*,*cis*-1,3-cyclooctadiene or oxygen, confirming that these bands correspond to the triplet excited state. Rate constants of quenching of the lowest energy triplet excited states by oxygen were determined as 0.97×10^9 to 6.78×10^9 (Ms)$^{-1}$. These values are typical for polycylic aromatic hydrocarbons.[43]

4. Conclusions

We report steady-state and time-resolved investigations of a series of ladder-type S-containing compounds. Excited-state properties reveal a strong dependence of the emission properties on molecular structure. Materials with S-atoms oriented toward the same side of the molecule in general have longer phosphorescence lifetimes and higher phosphorescence quantum yields. Interestingly, despite the presence of three S-atoms in the molecule, compound **5** carries a high fluorescence quantum yield of 14%, constituting an effective switch in predominant emission behavior from phosphorescence to fluorescence.

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Supporting Information Available: Absorption spectra of **1**−**6** and phosphorescence spectra of **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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