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Spectral Characterization of Thiophene Acylhydrazides

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Abstract The spectroscopic properties of a series of new thiophene acylhydrazides were examined. Extremely low fluorescence quantum yields were observed for all these compounds including the hydrazide parent compound and their acylhydrazide homologous polymers. The heteroatoms concomitant with the thiophene sulfurs were responsible for decreasing the singlet-triplet energy level resulting in increased intersystem crossing and low fluorescence emission for the studied compounds. Intramolecular triplet self-quenching from the acylhydrazide bond ultimately deactivates the triplet state by non-emissive means.

Keywords Thiopheno acylhydrazides · Fluorescence · Quantum yields · Triplet state · Intersystem crossing

Introduction

The complex photophysics [1] and photochemistry of energy transfer of light harvesting materials are decipherable by studying interchromophore distance-dependencies and structure-dependent energy transfer relationships through the use of model compounds [2]. Such studies provide important insight into the intricate mechanisms of efficient light harvesting leading to the eventual design of materials for artificial systems such as solar cells [3–5], biomimetic photosynthesis [6], and other energy transducers [7]. Even though such studies are extremely useful, the synthesis of the compounds required for deconvoluting structure-dependent energy transfer efficiency is problematic. The synthesis of suitable models usually involves complicated multi-step synthesis with low chemical yields and difficult purification. The resulting compounds also suffer from low energy transfer efficiencies [8–10]. The challenging synthesis limits thorough examination of important parameters and their influence upon efficient energy transfer such as chromophore rigidity, interchromophore distances, effect of various chromophores and donor-acceptor pairs, to name but a few. We recently used a simple method to synthesize energy transfer cassettes via imine linkages to satisfy the need for easily synthesized photoactive compounds [11, 12]. These modular units, consisting of a donor and an acceptor chromophore separated by a thiophene unit, undergo high energy transfer efficiencies. The simplified synthesis in part addressed the need of easily synthesized compounds to examine the structure-property relationship of efficient energy transfer.

Owing to our previous success in the synthesis and photophysical study of imine containing energy transfer cassettes and other conjugated materials [13–19], we investigated whether acylhydrazides (–C(O)NHN=CH–) could be used as alternative coupling methods to covalently link chromophores via a thiophene central unit. This condensation approach would have the advantage of relative ease with which the new compounds are obtained and would facilitate the study of the structure-property relationship of energy transfer. Moreover, the hydrazide group is amenable to other functionalities that would allow for easy incorporation of various chromophores while satisfying the requirement of easily synthesized photoactive compounds. Since little is known about the spectroscopic properties of hydrazides and their corresponding acylhydrazides [20, 21], the fluorescence and excited state characterization of these compounds were examined. The

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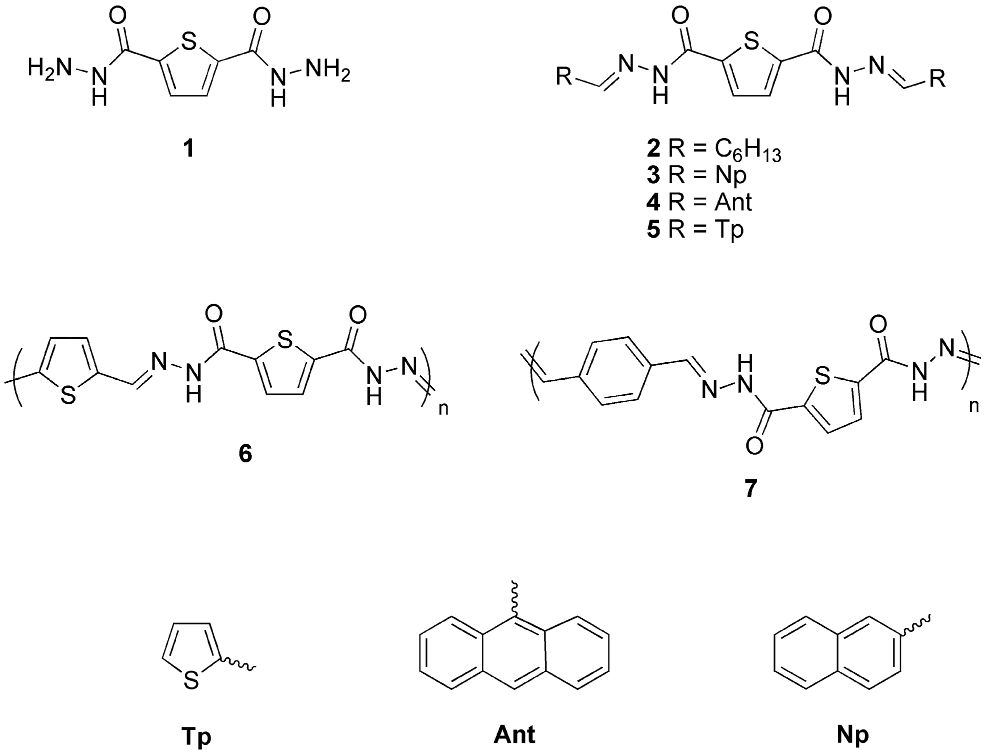
Fig. 1 Structures of compounds examined



synthesis and spectroscopic characterization of naphthalene and anthracene chromophores linked via acylhydrazide units and their polymeric analogues reported in Fig. 1 are presented.

Experimental

All reagents were commercially available from Aldrich and were used as received. ^{1}H-NMR spectra of the polymers were obtained on a Bruker 300 spectrometer in [D]DMSO. Absorption measurements were done on a Varian Cary-500 UV-Visible spectrometer and the solvent absorption spectra were subtracted from the analyzed samples. Emission studies were done with an Edinburgh Instruments FLS920 combined steady-state and time resolved fluorimeter after deaerating the samples thoroughly with nitrogen for 20 min in anhydrous solvents. The fluorescence spectra were measured in 10 mm cuvettes exciting at the corresponding absorption maximum while the samples were prepared with absorptions below 0.08 at the excitation wavelength. The fluorescence lifetimes were measured according to standard TCSPC methods with the FLS-920 and they were recorded by exciting the specific compound at its maximum absorption wavelength. All fluorescence decays were unimolecular and the lifetimes were obtained by fitting with a monoexponential decay function with 99.9% confidence and the calculated values contain approximately a 10% experimental error. The fluorescence spectra were smoothed in origin 7.5 according to the 5 point adjacent smoothing option. Naphthalene and anthracene were recrystallized twice from absolute ethanol and used as actinometers. The low temperature measurements were done using a Cary Eclipse using a 4:1 ethanol/methanol glass matrix at 77 K exciting at the compound's absorption maximum. Laser flash photolysis was done using a Luzchem mini-LFP unit using the forth harmonic of a Continuum Surelite Nd:YAG laser as the excitation source at 266 nm firing 10 ns pulse widths with 50 mJ of power. The LFP probe lamp source was a 175 W Xenon lamp using standard cut-off filters controlled by the software. The kinetic traces used to determine the rate constants for generating the transient absorption spectra were based upon an average of 15 shots per wavelength. Samples for laser flash photolysis were prepared in DMSO with absorbances ca. 0.3 at 266 nm in 10 mm cuvettes. These were thoroughly deaerated with nitrogen prior to use. An Anthracene sample was prepared in the same fashion to which was added known amounts of a 10.2 mM stock solution of **1** in DMSO. The change in rate constants with the addition of **1** was monitored at 430 nm. The same procedure was used to quench the anthracene triplet with **2**–**4**. Intra-chromophore distances were semi-empirically calculated using AM1 geometry optimization with Spartan '06 by Wavefunction.

The general synthetic procedure for compounds **2**–**7** involved combining **1** with the corresponding aldehyde in 100 ml absolute ethanol followed by refluxing for 18 h. The resulting precipitate was filtered, washed with cold ethanol, and then dried under reduced pressure. Unless otherwise stated, the yields of the products were quantitative.

Thiophene-2,5-dicarboxylic acid dimethyl ester Thiophene-2,5-dicarboxylic acid (221 mg, 1.28 mmol) was dissolved in 100 ml methanol followed by two drops of concentrated sulfuric acid and then refluxed for 12 h. The solvent was removed under reduced pressure and the solid was dissolved in ethylacetate then extracted with aqueous sodium bicarbonate until the aqueous layer was alkaline. The product was obtained as a white solid to yield (114 mg, 40%) upon solvent removal. M.p. 49–51°C. ^{1}H-NMR (200 MHz, [D] chloroform): δ=7.73 (s, 2 H), 3.91 (s, 6 H). ^{13}C-NMR (50 MHz, [D] chloroform): δ=190.62, 138.90, 133.13, 52.65. EI-MS: m/z 200.1 ([M]+, 40%), 169.1 ($[M–OCH_3]^+$, 100%). Anal. calc. for $C_8H_8O_4S$ (200.2): C 47.99, H 4.03, O 31.96, S 16.02 found: C 47.29, H 3.79, S 16.24.

Thiophene-2,5-dicarboxylic acid dihydrazide (1) Thiophene-2,5-dicarboxylic acid dimethyl ester (114 mg, 0.52 mmol) was dissolved in 100 ml of absolute ethanol to which hydrazine monohydrate (500 ml, 7.8 mmol) was added. The solution was stirred at room temperature for 2 h then heated for 12 h under nitrogen. The resulting white precipitate (84 mg, 81%) was filtered under vacuum, washed with chilled water and absolute ethanol followed by drying under reduced pressure. M.p.>210°C. ^{1}H-NMR (200 MHz, [D] DMSO): δ=9.86 (s, 2 H), 4.50 (br, s, 4). FAB-MS: m/z 201.1 ([M]+, 100%).

Thiophene-2,5-dicarboxylic acid hexanlidene-hydrazide (2) **1** (13.9 mg, 0.07 mmol) and hexanal (100 ml, 0.84 mmol). ^{1}H-NMR (200 MHz, [D] DMSO): δ=11.46 (s, 2 H), 8.28 (s, 2 H), 7.76 (s, 2 H), 1.25 (m, 16 H), 0.84 (t, 6 H).

Thiophene-2,5-dicarboxylic acid naphthalen-2-ylmethylene-hydrazide (3) **1** (103 mg, 0.52 mmol) and 2-naphthaldehyde (162 mg, 1.03 mmol). ^{1}H-NMR (200 MHz, [D] DMSO): δ=12.15 (s, 2 H), 8.64 (s, 1 H), 8.36 (s, 1 H), 8.11 (d, 4 H), 8.01 (m, 8 H), 7,6 (d, 4 H).

Thiophene-2,5-dicarboxylic acid anthracen-9-ylmethylene-hydrazide (4) **1** (108 mg, 0.54 mmol) and 9-anthraldehyde (223 mg, 1.08 mmol). ^{1}H-NMR (200 MHz, [D] DMSO): δ=11.6 (s, 2 H), 9.07 (s, 2 H), 9.03 (s, 4 H), 8.23 (d, 6 H), 7.68 (m, 10 H).

Thiophene-2,4-dicarboxylic acid thiophen-2-ylmethylene-hydrazide (5) **1** (10.3 mg, 0.05 mmol) and 2-thiophene carboxaldehyde (190 ml, 0.2 mmol) to give 5.3 mg of product (73%). ^{1}H-NMR (400 MHz, [D] DMSO): δ=12.00 (s, 2 H), 8.67 (d, 1 H), 8.31 (s, 1 H), 8.02 (d, 1 H), 7.88 (s, 1 H), 7.68 (d, 2 H), 7.51 (s, 2 H), 7.13 (d, 2 H).

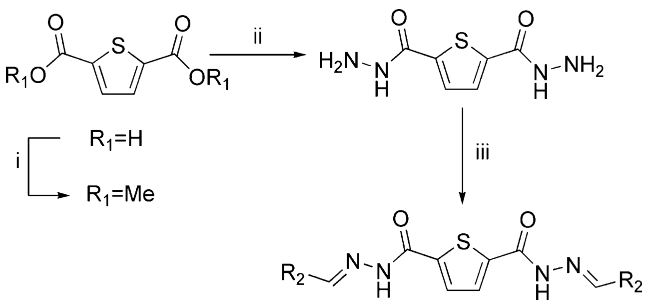
Polyacylhydrazone thiophene (6) **1** (82.1 mg, 0.41 mmol) and 2,5-thiophene dicarboxaldehyde (38.2 mg, 0.41 mmol) to yield 80 mg of product (76%). ^{1}H-NMR (400 MHz, [D] DMSO): δ=11.54 (s, 1 H), 11.07 (s, 1 H), 7.13 (br, s, 6 H). Degree of polymerization (DP)=25, $\overline{M_n}$=5 913 g/mol.

Polyacylhydrazone phenylthiophene (7) **1** (34.4 mg, 0.17 mmol) and terephthalic dicarboxaldehyde (24.6 mg, 0.17 mmol) to give 58.1 mg (79%) of product. ^{1}H-NMR (400 MHz, [D] DMSO): δ=12.14 (s, 1H), 9.89 (s, 1H), 7.89 (br, s, 6H). Degree of polymerization (DP)=12. $\overline{M_n}$= 6.744 g/mol.

Results and discussion

Synthesis of the target compounds and their precursors were achieved in three steps using inexpensive commercially available materials according to Scheme 1. Once formed, the products required little purification. The ideal precursors required are obtained by methyl esterification of the corresponding dicarboxylic acid, followed by dihydrazide formation. This can be done either in neat hydrazine hydrate or with a tenfold excess of hydrazine hydrate and then purified by filtering and washing. The robust acylhydrazide formation occurs quantitatively by condensing the hydrazide with its complementary aldehyde. This is typically done with an excess of aldehyde at room temperature in anhydrous ethanol along with a catalytic amount of trifluoroacetic acid. The desired products precipitate from the reaction medium making their isolation easy requiring no subsequent purification. Further washing with standard organic solvents or cold ethanol provides the desired clean products in quantitative yields.

Since little is known about the spectroscopic properties of acylhydrazides, they were examined using anthracene



Scheme 1 *i* Catalytic H_2SO_4 methanol, reflux; *ii* hydrazine–hydrate, ethanol, RT; *iii* R_2CHO, cat. TFA, ethanol, RT

and naphthalene as terminal units. These chromophores were chosen since their photophysical properties are well characterized [22] and would allow examination the acylhydrazide bond effect on their spectroscopic properties. Furthermore, the absorption and emission overlap of anthracene and naphthalene, respectively, would eventually make them suitable candidates to examine Förster energy transfer similar to our imine studies. The compounds synthesized for studying the spectral properties are reported in Fig. 1. Owing to our previous success with thiophene aryl units [11, 12], this unit was used as a core. Not only does it increase solubility, it also ensures a correct distance and orientation between the two chromophores when combined with the rigid acylhydrazide bond. In conjunction with the acylhydrazide bond, the thiophene core locks the chromophores in a semi-rigid motif in which the chromophores are roughly the same plane of orientation. This ensures the two chromophore end units are kept more than 12 Å apart.[1] By doing so, any π-face or edge-to-face contact is prevented, which are known to promote excimer formation and unwanted energy dissipation [22]. The rigid thiophene aromatic core also acts as a communication block that is responsible for disrupting the conjugation. This effectively limits the conjugation of the two chromophores allowing examination of the acylhydrazide effect on the spectroscopic properties.

From the absorption and emission spectra shown in Figs. 2 and 3, respectively, the lack of extended conjugation between the two chromophores and the thiophene unit is apparent. This is illustrated by the absence of any pronounced bathochromic π,π^*-absorption shifts in the visible spectrum. Only a slight bathochromic shift of 25 nm relative to the pristine naphthalene and anthracene chromophores is observed, along with a lack of structured absorption and emission spectra. These suggest that there is only a weak conjugation arising from the imine (–N=CH–) type linkage of the acylhydrazide bond connecting the chromophore to the thiophene core. The slight conjugation increase is a result of delocalization through the nitrogen lone electron pairs. However, the conjugation does not span the entire molecule such as with imines and therefore the chromophores remain independent. The lack of conjugation is further supported by the absence of pronounced bathochromic shift in the absorption spectrum in addition to the lack of highly colored compounds formed. Conversely, such a colored behavior is apparent with its highly conjugated imine analogues, which exhibit a 110 nm bathochromic shift relative to **5** [11–13, 15–19].

Photoexcitation studies revealed the photophysical properties listed in Table 1. It can be seen that all these compounds fluoresce weakly when excited in the UV region and they exhibit unimolecular fluorescence rate constants. This includes compounds **3** and **4** whose measured fluorescence yields were unexpectedly 12 times smaller than their unsubstituted analogues [11, 23, 24]. The observed low fluorescence yields do not arise from self-quenching processes since similar fluorescence yields and lifetimes were observed regardless of the concentration. This is further supported by the measured mono-exponential deactivation rate constants. Furthermore, similar mono-exponential decays and fast nonradiative (k_{nr}) decay kinetics were found for all the compounds implying a common deactivation mode.

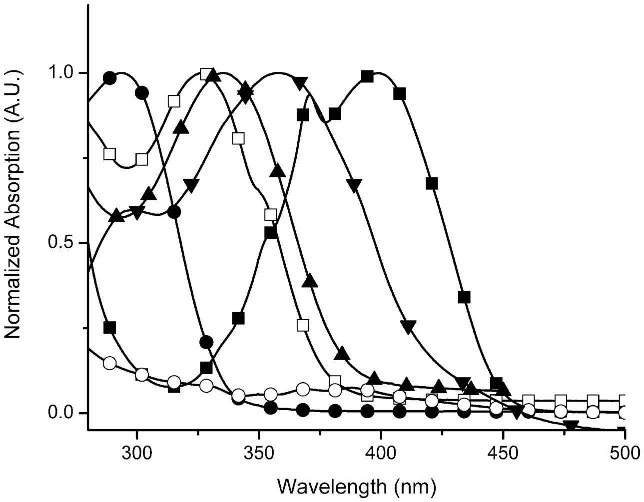


Fig. 2 Normalized ground state absorption spectra of **1** (*filled circle*), **2** (*open circle*), **3** (*open square*), **4** (*filled square*), and **5** (*filled triangle*) and **7** (*filled inverted triangle*) measured in acetonitrile at 25°

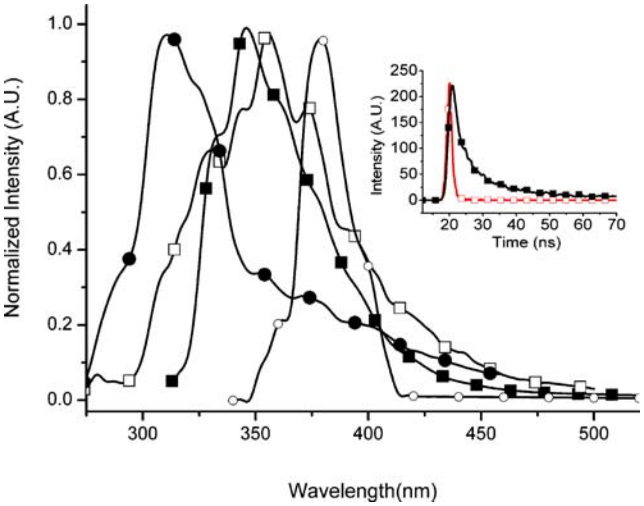


Fig. 3 Normalized fluorescence spectra of compounds in acetonitrile at 25°C: **2** (*open square*), **4** (*filled circle*), **5** (*open circle*), and **6** (*filled square*). *Inset* Fluorescence lifetime decay of **6** (*filled square*) and the instrument response frequency (*open square*)

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[1] The ground state geometry was optimized by conformational analyses using semi-empirical AM1 calculations.

Table 1 Photophysical properties measured at 25°C in acetonitrile

Compound	λ_{max}(abs)[a]	λ(fl)[a]	τ (ns)	Φ_{fl}[b] (10^{-2})	k_r (10^6 s^{-1})[c]	k_{nr} (10^8 s^{-1})[d]
1	255	311	11.3	0.2	0.2	0.9
2	295	356	5.2	0.1	0.2	1.9
3	327	368	3.8	2.4	6.3	2.6
4	400	489	5.0	3.8	7.6	1.9
5	335	382	12.4	0.2	0.2	0.8
6	328	346	34.3	0.6	1.8	0.3
7	358	346	33.4	2.0	5.8	0.3

[a] nm

[b] Based on Φ_{fl}=0.3 for anthracene [24, 29, 30]

[c] Rate constant for radiative decay (k_r=Φ_{fl}/τ)

[d] Rate constant for nonradiative decay k_{nr}=k_r•$(1-\Phi_{fl})/\Phi_{fl}$.

Evidence for the unexpected weak fluorescence is provided by the nonradiative (k_{nr}) and radiative (k_r) rates constants that are calculated from the fluorescence lifetimes and quantum yields. The measured slow radiative rate constants concomitant with the fast nonradiative decay rate constants imply the predominant singlet excited state deactivation is by intersystem crossing (ISC) to the triplet state. This is not surprising since thiophenes are known to readily undergo ISC to efficiently populate their triplet state, regardless of their degree of conjugation [22, 25, 26]. The net result is the observed weak fluorescence yields of ca. 10^{-2}, which are consistent with other oligothiophenes. This is supported by both the observed lower quantum yield and the nonradiative rate constant for **5** that undergoes a higher degree of ISC owing to its three thiophene units. The slight increase in the degree of conjugation observed with the compounds, evidenced by the 25 nm bathochromic shift, also contribute to increasing the amount of ISC. This decreases the singlet-triplet energy gap which is further supported by the high k_{nr} value [27]. Even though non radiative modes such as internal conversion (IC) are potential deactivation modes for acylhydrazides, this is not possible since no enhanced emission at 77 K was observed. At such an extremely low temperature, the activation barrier for normal nonradiative deactivation such as bond rotations cannot be overcome resulting in increased fluorescence. The preferred deactivation of the singlet excited state by nonradiative means is further supported by the k_{nr} values that are substantially higher than their corresponding k_r values. Further evidence of the non-emissive deactivation mode is derived from the k_{nr} values that are an order of magnitude smaller than their oligothiophene analogues whose fluorescence quantum yields are ten times greater [26, 27].

Compound **1** serves as a model compound since it contains only the hydrazide group and one thiophene. It was therefore expected to undergo ISC to produce the triplet state in high yields owing to the enhanced ISC associated with the thiophenes. Enhanced triplet state formation was also expected for polymers **6** and **7** since they posses a high number of thiophene repeating units. The observed low fluorescence quantum yields for these compounds was not surprising owing to the high degree of ISC. Laser flash photolysis was used to visualize and to quantify the thiophene triplet according to its characteristic triplet–triplet absorption maximum ca. 340 nm [23, 28]. Interestingly, no transient was detected for these compounds as seen in Fig. 4. Only a strong ground state bleaching was observed at 330 nm for all the compounds reported in Scheme 1 evidenced by the negative signal seen in the inset of Fig. 4. The absence of any positive signal in the transient absorption spectra implies the triplet states of all the compounds are quenched faster than the time resolution of the laser flash photolysis system. This suggests the hydrazide bond acts a triplet quencher that

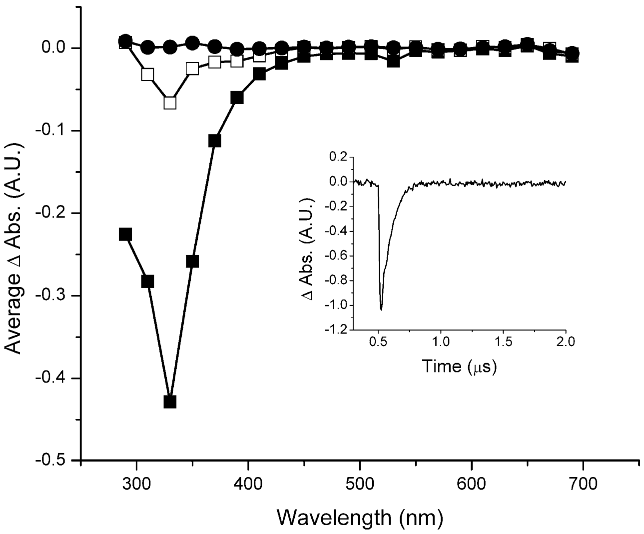

Fig. 4 Transient absorption spectra of **1** in DMSO recorded 0.07 (*filled square*), 0.2 (*open square*), and 0.6 μs (*filled circle*) after the laser pulse at 266 nm. *Inset* Ground state recovery monitored at 330 nm

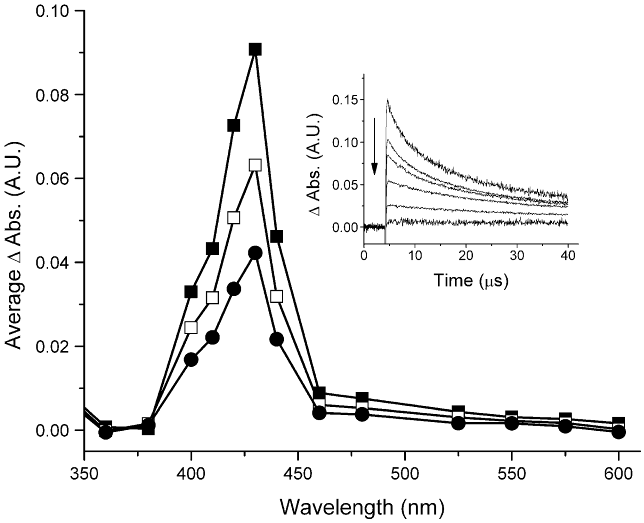

Fig. 5 Transient absorption spectra of anthracene in DMSO recorded 2.5 (*filled square*), 8.4 (*open square*), and 19.5 μs (*filled circle*) after the laser pulse at 266 nm. *Inset* Quenching of anthracene triplet with **1** (0 to 1.6×10^{-5} M) monitored at 430 nm

deactivates the triplet state by a Dexter nonradiative energy transfer mechanism [22]. To confirm the triplet quenching effect of the acylhydrazide bond, quenching of the anthracene triplet was examined with **1**. Anthracene was examined as an analogue to 9-anthraldehyde since it produces a highly visible triplet by laser flash photolysis at 430 nm [23, 28] as seen in Fig. 5. Even though 9-anthraldehyde is a better candidate to probe the quenching effects, it unfortunately reacts spontaneously at room temperature with **1** to afford **4**, which would complicate the transient analyses. This notwithstanding, the addition of **1** to the anthracene sample quenches the triplet signal as seen in the inset of Fig. 5. The same anthracene triplet quenching effect was also observed with **2**–**4**. The observed decrease in the signal results from triplet quenching by energy transfer to the acylhydrazide, which acts as a triplet acceptor. The available quencher amount that can participate in an intramolecular quenching process is understood to be 1 M while the amount of transient actually produced upon photoexcitation is micromolar [23]. Therefore, the acylhydrazide quencher concentration is approximately is six orders of magnitude greater than the excited chromophore when it is directly tethered to the chromophore as with **2**–**7** [22]. The large concentration difference leads to rapid and efficient intramolecular energy transfer quenching of the triplet by the acylhydrazide triplet acceptor. Given the fastest lifetime that can be resolved by the LFP system is ~100 ns combined with the approximate intramolecular quenching concentration ([Q]) of 1 M, the intramolecular rate constant (k_q) for triplet quenching by the acylhydrazide bond can be estimated at 1×10^{7} M^{-1} s^{-1} according to $k_{obs}=k_o+k_q[Q]$, where k_o is the triplet kinetic in the absence of quencher. The calculated rate constant is slower than diffusion controlled (10^{10} M^{-1} s^{-1}) [29] implying the energy transfer quenching process is endothermic, however the large concentration of the acylhydrazide quencher assures efficient quenching. The slow quenching rate constant implies the triplet state of **1** is higher than that of anthracene, which is not surprising given the higher degree of conjugation of anthracene relative to **1**. Photoexcitation of the acylhydrazide compounds therefore undergoes intersystem crossing concomitant with efficient triplet state deactivation by nonradiative energy transfer, which are responsible for the observed weak fluorescence.

Conclusion

The simple condensation of aldehydes with a thiopheno dihydrazide leads to robust covalent acylhydrazides bonds. The resulting thiophene compounds have rigid configurations in which the chromophores are locked in a semi-planar arrangement, yet are soluble in acetonitrile. The slight increase in conjugation arising from the acylhydrazide bond concomitant with the heteroatoms and thiophene units increase the amount of excited state energy dissipation by intersystem crossing. The resulting triplet is rapidly quenched via intramolecular energy transfer by the acylhydrazide. The manifold shift results in a drastically reduced fluorescence quantum yield whereby limiting these linkages for use in energy transfer cassettes.

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