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Aggregation Properties of Heavy Atom Substituted Squaraine Dyes: Evidence for the Formation of J-Type Dimer Aggregates in Aprotic Solvents

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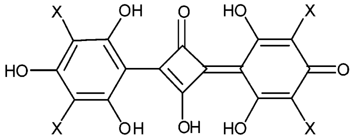
The squaraine dye bis(2,4,6-trihydroxyphenyl)squaraine (SqH) was earlier reported to form J-type dimer aggregates in acetonitrile solutions at higher concentrations. Subsequent studies have suggested that concentration-dependent changes in the absorption spectrum of SqH in acetonitrile could be attributed to shifts in the acid−base equilibrium due to the presence of water as an impurity. In this work, we describe our studies on the effect of varying acid and dye concentration on the absorption spectra of the bromo and iodo substituted dyes, bis(3,5-dibromo-2,4,6-trihydroxyphenyl)squaraine (SqBr) and bis(3,5-diiodo-2,4,6-trihydroxyphenyl)squaraine (SqI). Analysis of the changes in the absorption spectra as a function of dye concentration and the nature of the solvent composition confirmed the formation of J-type dimer aggregates in aprotic solvents in this class of dyes. Further confirmation for the formation of the J-type dimer aggregates could be obtained by comparing the differences in the triplet excited state properties of the neutral and aggregated forms of the dyes using time-resolved spectroscopy.

1. Introduction

Squaraine dyes possess strong and intense absorption in the visible and near-infrared regions, which makes them suitable for various applications such as in optical recording,[1−3] in solar cells,[4−7] in electrophotographic devices,[1,7] in development of sensors,[8−12] and in nonlinear optics.[13−15] The general tendency of dyes to form aggregates in the solid state and within heterogeneous environments present in most of the above-mentioned applications results in drastic changes in their absorption and photophysical properties.[16−19] In view of this, there have been several efforts to study the nature of the squaraine dye aggregates as well as the driving forces involved in their aggregation processes.[20−33]

Squaraine dyes of the type bis(2,4,6-trihydroxyphenyl)-squaraine (SqH; Chart 1) are of considerable importance due to their potential application in biological systems. These dyes have been shown to have good potential for application as photosensitizers in photodynamic therapy.[34−37] The presence of the hydroxyl groups, which are easily deprotonated, makes the absorption spectra of this class of dyes largely dependent on the pH of the medium. The absorption spectrum of SqH in neutral acetonitrile consists of two bands, a broad band with a maximum at 480 nm and a narrow band with a maximum at 563 nm. We had earlier proposed that the band at the lower wavelength could be assigned to that of the monomer while the band at longer wavelength, which was observed only at higher concentration of the dye, could be attributed to the formation of J-type dimer aggregates.[20] Griffiths and Mama,[38] have shown that in protic solvents the broad band with a maximum at 510 nm was due to the monoanion of the dye, and the long-wavelength band with a maximum at 562 nm which was observed in weakly acidic solutions was attributable to the neutral species. Scott and Tran have suggested that the formation of the two bands observed in acetonitrile[20] could be attributed to the formation of the monoanionic and neutral species, due to the presence of water as an impurity, in view of the difficulties associated with completely drying a solvent such as acetonitrile, and not due to the formation of aggregates.[39] In solvents such as acetone and dichloromethane, which could be obtained in the anhydrous form more easily, they observed only the long-wavelength band.[38,39] A recent study by Lopes et al. based on resonance Raman spectra of SqH also suggests that the species assigned earlier as aggregates should be assigned as the neutral species.[40] This study was however carried out in methanol in which SqH does not form aggregates.[20] Since the pK_a of the dye was 7.0, the dye could readily lose a proton in the presence of trace amounts of water in the solvent at neutral pH to form the monoanionic species. Also sub-micromolar quantities of acid were sufficient to convert the dye to its neutral form, which has an absorption spectrum, closely matching that suggested for the aggregate at higher concentrations in acetonitrile. In view of these facts it was difficult to unambiguously prove that the species formed at higher concentrations was indeed due to aggregation of the dye and not due to the presence of trace amounts of acid. To investigate whether the dyes in this class do indeed form aggregates, we have now carried out a detailed study on the acid and dye concentration dependent changes in the ground-state absorption spectra and triplet excited state properties of two heavy atom substituted squaraines, bis(3,5-dibromo-2,4,6-trihydroxyphenyl)squaraine (SqBr) and bis(3,5-

CHART 1: Chemical Structures of the Squaraines



SqH, X = H
SqBr, X = Br
SqI, X = I

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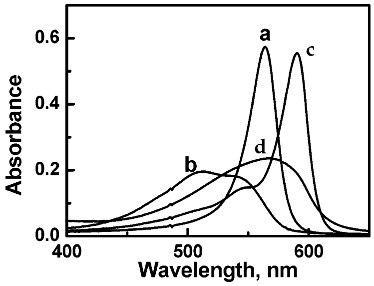
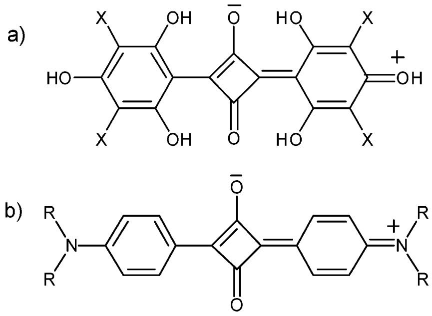


Figure 1. Absorption spectra of SqH (1.6 μM) in (a) methanol containing 0.29 μM HCl, (b) neutral methanol, (c) methanol containing 1.1 μM KOH, and (d) methanol containing 62 mM KOH.

CHART 2: Zwitterionic Structures of Squaraines



diiodo-2,4,6-trihydroxyphenyl)squaraine (SqI) (Chart 1). These dyes have been reported to form H-aggregates with face-to-face geometry in protic solvents.[41] Due to the presence of electron-withdrawing bromo and iodo substituents, these dyes are more acidic and hence less susceptible to shifts in their acid−base equilibrium in the presence of trace amounts of acid or water.

2. Experimental Methods

The bis(2,4,6-trihydroxyphenyl)squaraine dyes SqH, SqBr, and SqI were synthesized and purified by reported procedures.[34,42] Solutions were prepared in spectroscopic grade toluene or acetonitrile, which was dried by standard procedures.[43] Absorption spectra were recorded on a Shimadzu UV-3101 PC UV−vis−near-IR scanning spectrophotometer. Nanosecond laser flash photolysis experiments were carried out in an Applied Photophysics Model LKS-20 laser kinetic spectrometer using a second harmonic (532 nm, 130 mJ/pulse) of a Quanta Ray GCR-12 series pulsed Nd:YAG laser with a pulse duration of 10 ns. All solutions were deaerated by bubbling argon for 15 min. Aggregate solutions of SqBr and SqI were stabilized for 12 h before carrying out laser flash photolysis experiments. All experiments were carried out in 1 cm cells, unless specified.

3. Results

3.1. Absorption Properties. The absorption spectra of SqH in methanol containing acid and varying amounts of KOH in methanol are shown in Figure 1. The spectra are very similar to those reported earlier.[28,38] The dye has a sharp absorption at 564 nm in methanol containing trace amounts of hydrochloric acid (spectrum a, Figure 1). In neutral methanol, the dye possesses a broad band with its maximum centered at 510 nm (spectrum b, Figure 1). With increasing concentrations of base, a strong, sharp and bathochromically shifted absorption spectrum with a maximum centered at 591 nm is observed (spectrum c, Figure 1). On further increase in concentration of the base, a broad band centered on 570 nm (spectrum d, Figure 1) was observed. In earlier studies we had assumed the broad peak around 510 nm (spectrum b) observed in neutral methanol to be that of the neutral form, while the peak centered at 564 nm (spectrum a) observed in the presence of acid was attributed to the protonated form.[28] The neutral form of the dye can be drawn as shown in Chart 2a. In such a zwitterionic structure, the chromophore is neutral and electronically symmetrical, with the positive charge shared equally by the terminal hydroxyl groups.

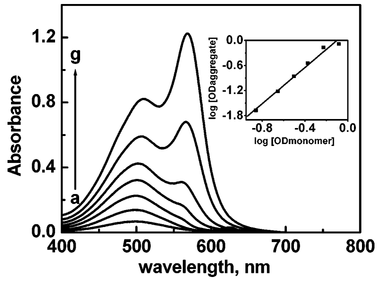


Figure 2. Absorption spectra of SqI in acetonitrile at different concentrations recorded in a 0.5 cm cell. [SqI]: (a) 3, (b) 8, (c) 12, (d) 22, (e) 28, (f) 38, and (g) 56 μM. Inset shows plot of log[$\mathrm{OD_{aggregate}}$] versus log[$\mathrm{OD_{monomer}}$] for OD measured at 507 and 569 nm for the monomer and aggregate, respectively.

Griffiths and Mama have suggested that the band with a maximum centered on 564 nm may be attributed to the neutral form of the dye (Chart 2a), since the sharp absorption band is indicative of a symmetrical structure with minimal geometry changes between the ground and excited states. Moreover the structure is similar to that observed for the bis-dialkylaminophenyl squaraine derivatives shown in Chart 2b. The presence of the positive charge on the oxygen atom can also result in deprotonation taking place very easily, accounting for its high pK_a value. On the basis of these arguments and the nature of the spectral changes caused by the addition of base, Griffiths and Mama have correctly attributed the species with absorption maxima at 564, 510, 591, and 570 nm shown in Figure 1 to the neutral, monoanionic, dianionic, and trianionic species, respectively.[38]

As described in the earlier studies, neutral solutions of SqH showed an additional species absorbing around 563 nm at high concentrations in aprotic solvents.[20] This spectrum was very similar to the absorption spectrum of the neutral species (Figure 1, spectrum a). Since nearly the same absorption band was formed on both the addition of trace amounts of acid and an increase in concentration of the dye, it was difficult to distinguish whether the species formed under the two conditions were indeed different from each other.

In view of this we have carried out similar investigations using the halogenated derivatives SqI and SqBr, since in these molecules the presence of electron-withdrawing bromo and iodo substituents makes them more acidic and hence their absorption properties less susceptible to changes due to the presence of trace amounts of acidic impurities. The absorption spectra of SqI in dry acetonitrile recorded at different dye concentrations are shown in Figure 2. At lower concentrations (<8 μM), SqI exhibited a broad band centered on 505 nm. The absorbance of this band followed the Beer−Lambert law at low dye concentrations. At higher concentrations however a new sharp band centered on 568 nm was observed. The relative intensity of this band increased with respect to the short-wavelength band with increasing dye concentration, suggesting that the long-wavelength band may be attributed to the aggregated form of the dye.

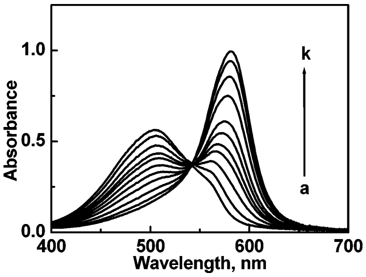


Figure 3. Effect of TFA on absorption spectra of SqI (7.2 μM) in acetonitrile. [TFA]: (a) 0, (b) 0.18, (c) 1.61, (d) 3.24, (e) 4.45, (f) 6.51, (g) 10.56, (h) 32.56, (i) 40.70, (j) 48.84, and (k) 56.98 mM.

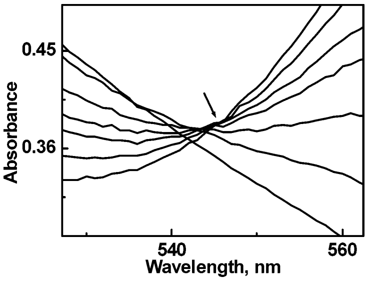


Figure 4. Closer view of the isosbestic point of the spectra obtained on addition of TFA to SqI (7.2 μM) in acetonitrile.

The effect of trifluoroacetic acid on the absorption spectra of SqI in acetonitrile is shown in Figure 3. It can be observed from the figure that an increase in acid concentration resulted in the formation of a new band with a peak centered at 582 nm and a decrease in the peak centered at 505 nm. These changes were marked by the presence of an isosbestic point at 543 nm. Although trifluoroacetic acid (TFA) is a much stronger acid than the dye, a substantially higher concentration of TFA is required to bring about the protonation of the dye in an aprotic solvent such as acetonitrile. In a protic solvent such as methanol, however, only micromolar quantities of TFA are required to bring about similar spectral changes (see Figure S1 in the Supporting Information).

By comparison with the parent dye, the peak at 505 nm can be assigned to that of the monoanionic form of the dye and the peak around 582 nm formed on addition of acid can be assigned to that of the neutral form of the dye. High concentrations of TFA ($\geq$10 mM) were required to obtain substantial amounts of the neutral form. Thus, the peak formed at 568 nm at higher concentrations of the dye in the absence of acid can clearly be attributed to a species different from the neutral species, and its formation at higher concentrations and strong red shift compared to the monomer spectrum suggests the formation of aggregates.[44,45]

Closer examination of the isosbestic point of the spectra obtained on addition of acid (Figure 4) revealed an initial deviation from the true isosbestic point, clearly indicating the involvement of more than two species. Thus, on addition of acid, protonation of the monoanion can result initially in the breakup of the aggregate, following which the acid−base equilibrium is completely established.

The dependence of the absorption spectra of SqBr on dye concentration and the addition of TFA were very similar to that observed for SqI (see Figure S2 and Figure S3 in the Supporting Information). At lower concentrations of SqBr, the main peak observed around 497 nm, attributable to the anionic form of the dye, obeyed the Beer−Lambert law. With increasing concentration, an additional band was observed with a peak centered at 572 nm, suggesting the formation of an aggregated species. The neutral form of SqBr which was formed on addition of acid has a peak centered at 578 nm, which is 6 nm red-shifted compared to the peak observed at higher concentrations. The observed shift in absorption maximum due to the changes in dielectric properties of the solvent mixture in the presence of acid can be ruled out since the species observed at higher concentrations is found to be different from that observed for the neutral form. On the basis of the detailed analysis, we assign the species formed under these conditions as being due to the formation of aggregates. For the spectra obtained with changing dye concentration, a plot of log[$\mathrm{OD_{aggregate}}$] vs log[$\mathrm{OD_{monomer}}$] for the two dyes (insets of Figure 2 and in Figure S2 in the Supporting Information) was linear with a slope of 2, confirming that the dye aggregation involved formation of a dimer unit.

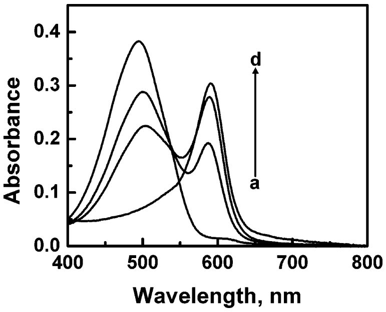


Figure 5. Absorption spectra of SqBr (13.6 μM) in acetonitrile containing different proportions of toluene in a 0.5 cm cell: (a) 0, (b) 70, (c) 80, and (d) 90%.

Addition of trace amounts of hydrogen bond donating or accepting solvents such as methanol or acetone to the acetonitrile solutions containing dye aggregates of SqI or SqBr resulted in a breakup of the aggregate and the formation of the anionic monomer. The equilibrium between the monomer and aggregate of SqI and SqBr could, however, be shifted in favor of the aggregate by addition of nonpolar solvents such as toluene. Figure 5 shows the effect of toluene on acetonitrile solutions containing SqBr. The enhancement in the formation of aggregate in nonpolar solvents suggests that hydrophobic interactions between the dye molecules play an important role in the formation of the aggregates. The absorption maximum of the aggregated species formed in the solvent mixture containing mainly toluene was 590 nm, which is red-shifted, compared to that observed in pure acetonitrile. This may be attributed to stabilization of the aggregate in toluene.

3.2. Triplet Excited State Properties. Nanosecond laser flash photolysis experiments were carried out on solutions of SqI and SqBr, in order to study the triplet excited state properties of the anionic dye aggregates and compare them with those of the anionic and neutral monomers. The intersystem crossing efficiencies of squaraine dyes are generally very low.[46] In SqI and SqBr, however, the presence of heavy atom has been reported to substantially increase the intersystem crossing efficiency of these dyes.[34]

These dyes have sufficient absorption around 532 nm, making it possible to excite them directly with the second harmonic of the Nd:YAG laser. Excitation of acetonitrile solution of SqBr at concentrations less than 10 μM, where the dye exists mainly as the monomer anion, using 532 nm laser pulses led to the formation of a transient spectrum with absorption in the 300−450 nm region and a bleach in the region corresponding to the ground-state absorption spectra (450−580 nm). Figure 6 shows the transient absorption spectra of SqBr recorded immediately after the laser pulse.

The transient absorption, which was formed within the laser pulse, decayed by a first-order process. The rate constant for

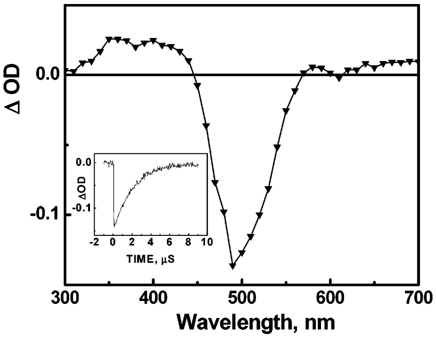


Figure 6. Transient absorption spectrum of the monomeric form of SqBr (8.5 μM) in acetonitrile, recorded immediately after the 532 nm laser pulse. The inset shows the transient monitored at 490 nm after the 532 nm laser pulse.

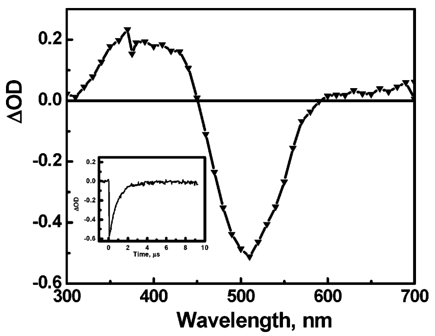


Figure 7. Transient absorption spectrum of the monomeric form of SqI (7.6 μM) in acetonitrile, recorded immediately after the 532 nm laser pulse. The inset shows the transient monitored at 510 nm after the 532 nm laser pulse.

the decay of the transient absorption matched that of the recovery of the ground-state absorption. Complete recovery of the ground-state absorption indicated negligible formation of any permanent products (inset in Figure 6). The transient formed which was readily quenched by oxygen could be attributed to its triplet state, on the basis of its similarity with the triplet spectrum of the dyes in methanol reported earlier.[34] Similar results were observed in the case of the SqI monomer anion (Figure 7). The triplet lifetimes of the monomer anions SqBr and SqI in acetonitrile were found to be 1.7 and 1.75 μs, respectively.

Efforts to study the excited state of the dimer aggregate in acetonitrile were not successful since even at the highest concentrations studied a considerable amount of the monomeric species existed in the solution. However, as described above (Figure 5), the dye existed mainly in its aggregated form in 90% toluene/acetonitrile mixtures. Figure 8 shows the transient absorption spectrum of SqI in an acetonitrile/toluene (1:9) mixture recorded immediately after the 532 nm laser pulse. A bleach was observed above 500 nm, with the peak centered at 570 nm. The decay rate of the positive band was identical to that of the recovery of the ground-state absorption (τ = 3.1 μs), indicating that one form was converting to the other. In the transient absorption spectrum, both the positive band and the bleach were quenched by oxygen, supporting the view that the transient species was a triplet state. This was also confirmed by energy transfer to β-carotene. Since the intersystem crossing efficiency in β-carotene is negligible, formation of its triplet via direct excitation is not possible.[34] The formation of the β-carotene triplet in this case clearly indicates that it arises from triplet energy transfer from the transient species.

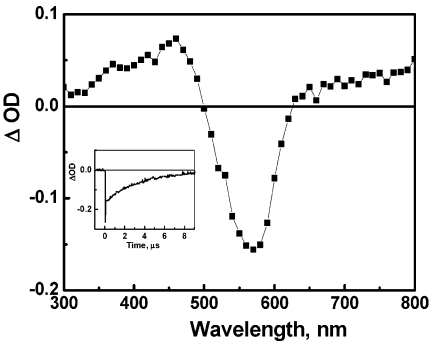


Figure 8. Transient absorption spectrum of SqI (12 μM) in the acetonitrile/toluene (1:9) mixture, recorded immediately after the 532 nm laser pulse. The inset shows the transient monitored at 570 nm.

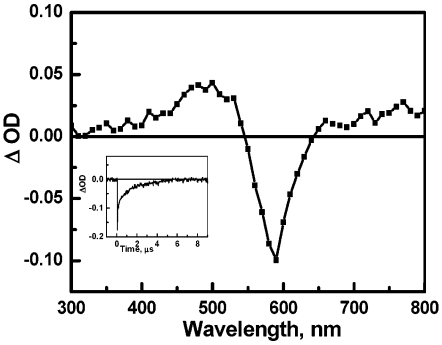


Figure 9. Transient absorption spectrum of SqI (12 μM) in the acetonitrile/toluene (1:9) mixture in the presence of TFA (56 mM), recorded immediately after the 532 nm laser pulse. The inset shows the transient monitored at 590 nm.

Addition of 56 mM of TFA to the solution of the acetonitrile/toluene (1:9) mixture resulted in the formation of the neutral species with an absorption peak centered at 580 nm. Figure 9 shows the transient absorption spectrum of SqI in the acetonitrile/toluene (1:9) mixture in presence of TFA recorded immediately after the 532 nm laser pulse. A bleach in the transient spectrum could be observed with a peak centered at 590 nm. The triplet lifetime of the protonated form of SqI in the acetonitrile/toluene (1:9) mixture was estimated as 1.53 μs. The triplet maxima for the aggregate (460 nm) and the protonated (500 nm) forms were also significantly different.

4. Discussion

Our study indicates that for the halogenated bis(2,4,6-trihydroxyphenyl)squaraine dyes, the long-wavelength absorbing species formed at high dye concentration is clearly different from the neutral species formed on addition of acid. A substantial amount of TFA ($\geq$10 mM) has to be added to acetonitrile solutions of these dyes in order to generate their neutral species. The species formed by increasing the concentrations of the dyes in neutral acetonitrile or by addition of toluene can therefore not be explained on the basis of the presence of spurious amounts of acid or water in the solution and may be attributed to the formation of aggregates. Analyses of the spectral changes as a function of dye concentration are indicative of a dimeric structure for the aggregates. Interaction between the chromophores in their ground state has been fairly well explained by McRae and Kasha in terms of exciton coupling theory, in which the excited state of the aggregates splits into two energy levels (Davydov splitting). The transition to the upper state is allowed in the case of H-type dimers with parallel stacking characterized by a hypsochromically shifted absorption band, while that to the lower state is allowed for the head-to-tail or J-type dimers, resulting in a bathochromically shifted

SCHEME 1

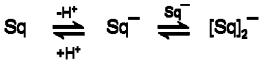
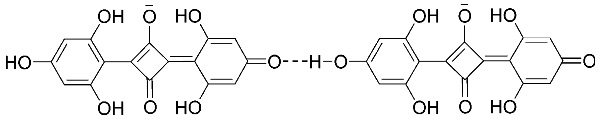


CHART 3: Proposed Structure of the Squaraine Dimer



absorption band compared to the isolated monomer.[44,45] The spectral changes observed with increasing dye concentration can therefore be attributed to the formation of the head-to-tail stacked J-type dimers. Since the aggregate formation is disrupted on addition of protic solvents, a plausible mode of the dimer formation could be via intermolecular hydrogen bonding. The similarity of the structure of the parent dye, and the dependence of the ground absorption spectra, dye concentration, and the presence of acid with those of the halogenated dyes reported here, strongly supports the view that J-type dimers are formed in concentrated solutions of the dye in acetonitrile as indicated in the previous studies.[20,30]

On the basis of the dependence of the ground-state absorption spectra and excited triplet properties of SqI and SqBr on acid, dye concentration, and presence of hydrophobic solvents, the dimer form of the dye can be described to exist in equilibrium with the anionic and neutral forms, as shown in Scheme 1. Under neutral conditions the dyes exist mainly in the monoanionic form. At higher concentrations, the monomer anions can aggregate, resulting in the formation of the dimer. Addition of acid will result in a shift of the equilibrium in favor of the neutral species as indicated in Scheme 1 and consequently to the breakup of the dimer. A proposed structure of the dimer is shown in Chart 3.

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Supporting Information Available: Absorption spectra of SqI in methanol in the presence of different concentrations of TFA, SqBr in acetonitrile at different concentrations, and effect of TFA on absorption spectra of SqBr in acetonitrile. This material is available free of charge via the Internet at http://pubs.acs.org.

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