

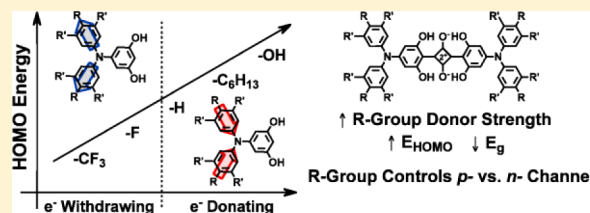
Effect of Substituents on Optical Properties and Charge-Carrier Polarity of Squaraine Dyes

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S Supporting Information

ABSTRACT: A series of squaraine dyes was synthesized with electron-donating (OH, C₆H₁₃) and electron-withdrawing (F, CF₃) groups allowing for tuning of the optical and electrochemical properties of the dyes. The squaraines exhibited strong absorbance ($\epsilon = 10^4$ – 10^5 M⁻¹ cm⁻¹) at long wavelengths ($\lambda_{\text{max}} = 660$ – 690 nm), attributed to an intramolecular charge transfer (ICT). As the electron-donating character of the dyes increases, the absorbance of the dyes red shifts and the band gap decreases. Interestingly, the ICT band seemed to be strongly dependent on the nature of the solvent, providing insights into the importance of hydrogen-bonding-induced coplanarity in these molecules. The squaraines were investigated for their charge-carrier mobility in FET configuration. Dyes with fluorine functional groups were found to exhibit either ambipolar (–F) or n-type (–CF₃) charge-carrier characteristics, although the molecules themselves are made of traditionally *p*-type triarylaminines.



INTRODUCTION

The ability to form stable radical cations has made triarylaminines popular in several applications.¹ At the molecular level, this feature has resulted in the use of triarylamine-based molecules for intervalence charge-transfer studies^{2,3} and organic magnetic materials.^{4–7} From a materials perspective, there has been great interest in utilizing triarylaminines as hole transporters⁸ in photorefractives,^{9,10} xerography,¹¹ and organic light-emitting diodes.^{12,13} The stability of triarylamine radical cations has also resulted in the exploration of these molecules as donor components in donor– π –acceptor (D– π –A) systems for applications such as second-order nonlinear optical materials^{14,15} and photovoltaics.^{16–18} Among the D– π –A systems explored for photovoltaics, triarylamine squaraine-based materials have attracted particular attention.^{19–22} These squaraines, exemplified by structure 1 (Figure 1), are of interest as they provide a dramatically reduced optical band gap and high molar absorptivities (10^4 – 10^5 M⁻¹ cm⁻¹)^{23,24} by means of a strong ICT absorption process. This feature, along with convenient synthetic accessibility, also makes these molecules attractive targets for small-molecule-based photovoltaics—an area that has recently caught considerable attention.^{25,26}

Triarylaminines are considered to be relatively weak donors due to the delocalization of electron density throughout the three aryl rings, and thus, the triarylamine-based squaraines can be considered to be a “weak donor–strong acceptor–weak donor” dye molecule, a feature that is considered to be advantageous for many optoelectronic applications because of the low-lying HOMO associated with these molecules.^{27,28} Considering these, we became interested in systematically altering the frontier molecular orbital energy levels of the triarylamine squaraines. A convenient method of manipulating

the frontier orbital energy levels involves systematic introduction of electron-donating and electron-withdrawing functional groups in the molecules. In fact, such a strategy has been taken with triarylamine-based hole transporters to systematically tune its redox potential, i.e., the frontier orbital energy level.^{29–31} However, the weak donor–strong acceptor combination in the triarylamine-based squaraines provides an interesting twist. Squaraine-based D–A–D molecules are thought to have three canonical structures—the two cyanine-like structures that are identical in both structure and energy and a third structure that is fully aromatic with a zwitterionic core (Figure 1). Contributions from the two cyanine-like structures will be dependent on the extent of donor–acceptor coupling in the molecule. We were interested in testing the effect of introducing electron-donating and electron-withdrawing substituents on this coupling. Through this systematic investigation we show that (i) the HOMO energy levels can be tuned in these molecules over a larger range, compared to the effect of these substituents on the LUMO energy level, (ii) solvents can greatly influence the optical properties of these molecules and the extent of this influence is directly dependent on how strongly the donor and acceptor components are coupled in the molecule, and (iii) the substituents have a surprising effect on the polarity of the charge carried through the molecule in an organic field effect transistor (OFET).

RESULTS AND DISCUSSION

Considering the target of systematically tuning the frontier orbital energy levels, we designed triarylamine-based squaraine

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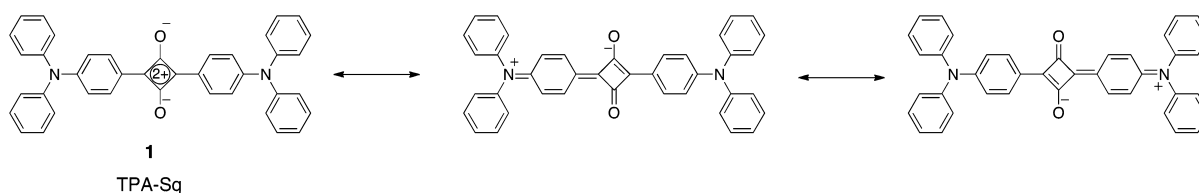
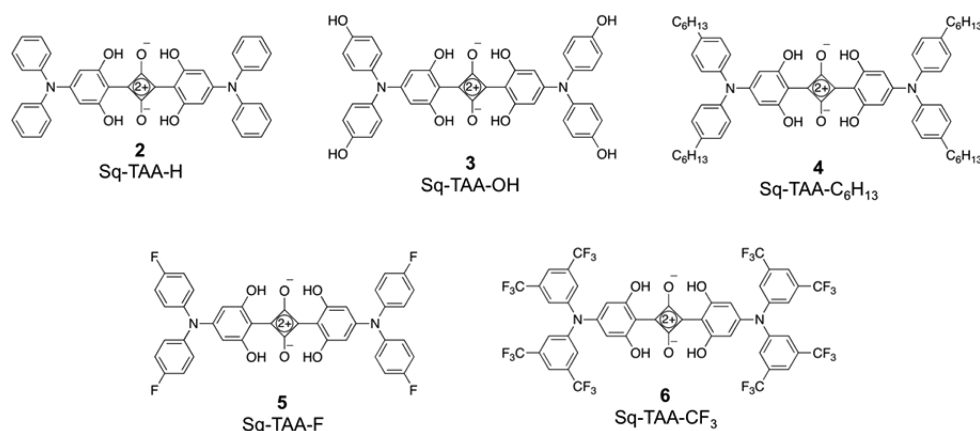


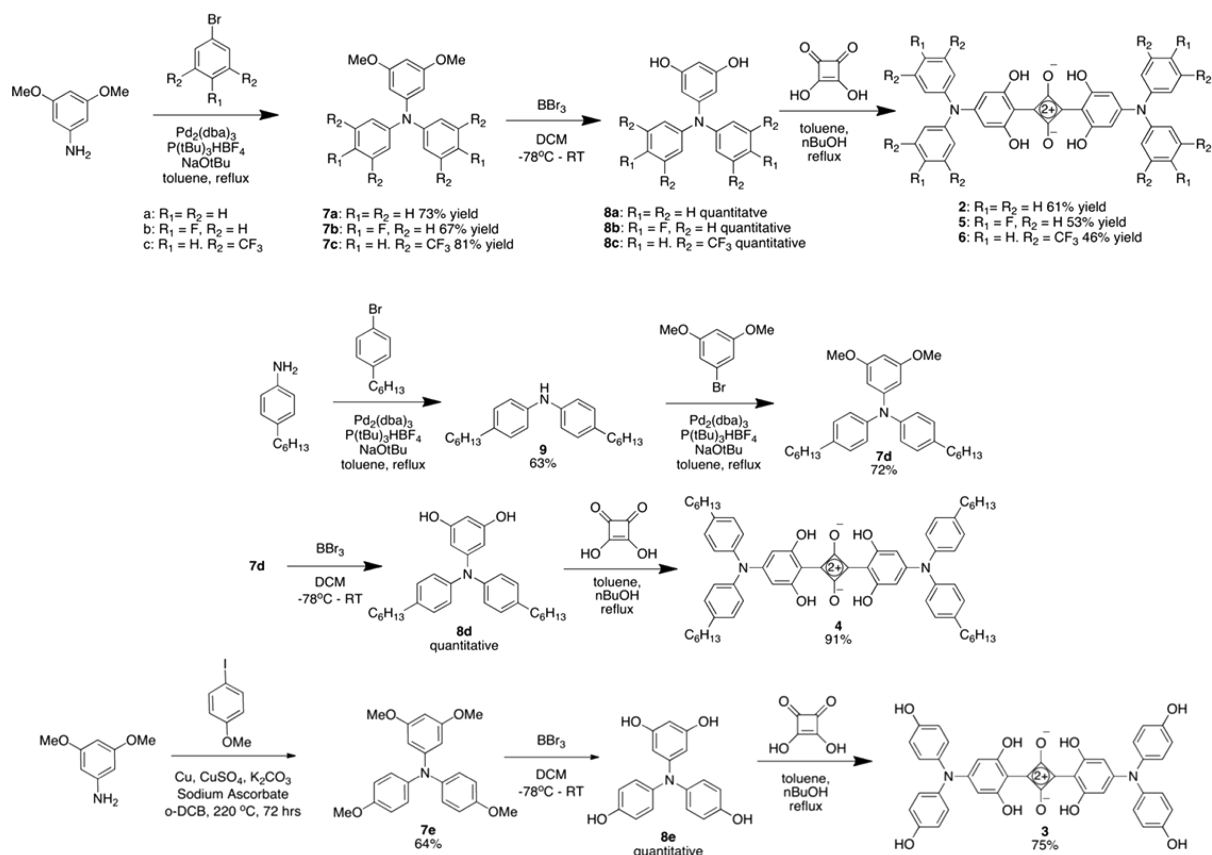
Figure 1. Resonance structures of a squaraine dye. Structure on the left is an all-aromatic structure with a cyclobutadienyldication-based zwitterion at the core. Structure in the middle and on the right are the structurally identical cyanine-type canonical structures.

Chart 1. Molecular Design of Squaraine Dyes with Tunable Band Gaps and HOMO Energy Levels^a



^aSq-TAA-H offers a control molecule for reference. Sq-TAA-C₆H₁₃ and Sq-TAA-OH are squaraine dyes with increasing electron-donor strength. Sq-TAA-F and Sq-TAA-CF₃ are squaraine dyes with increasing electron-withdrawing strength.

Scheme 1. Synthetic Approaches for the Squaraine Dyes^a



^aAll squaraine dyes are synthesized by either Buchwald or Ullmann coupling followed by demethylation with BBr₃ and condensation with squaric acid.

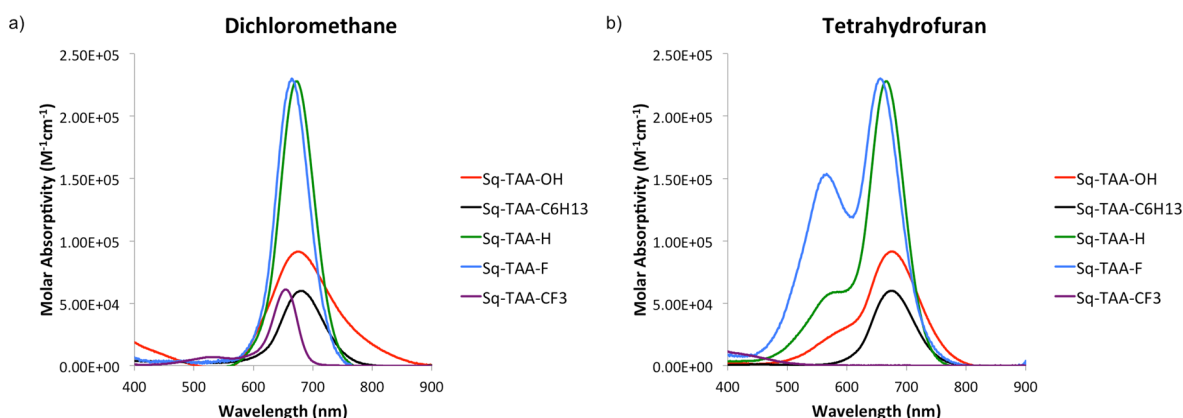


Figure 2. Absorbance spectra of the squaraine dyes in (a) DCM and (b) THF.

molecules 2–6. The structures of the molecules are shown in Chart 1. While molecule 2 serves as the control without any substituent, the other four molecules were each functionalized with strong electron-donating (*para*-phenolic moieties), weak electron-donating (*para*-alkyl), weak electron-withdrawing (*para*-fluoro), or strong electron-withdrawing (*meta*,*meta*-trifluoromethyl) functional groups. Note that in all these structures two hydroxyl groups are introduced in the bridging aryl ring to fulfill the requirement that these hydroxyl groups are necessary for the coplanarity between the bridging aryl ring and the four-membered squaraine ring.^{19,32}

The targeted triarylamine were synthesized by first assembling the triarylamine moiety and then assembling the Sq-TAA molecule in the final steps of the synthesis. In all these triarylamine the two peripheral aryl rings are identical and the bridging aryl ring contains two hydroxyl moieties. Therefore, we started the syntheses of 2, 5, and 6 with 3,5-dimethoxyaniline, as shown in Scheme 1. Treatment of this molecule with an excess of the corresponding bromoarene, under the palladium-catalyzed Hartwig–Buchwald coupling conditions, provided the respective substituted triarylamine in one step in 67–81% yield. Compound 4 was synthesized in two steps: first, a Hartwig–Buchwald coupling of 4-hexylaniline and 1-(4-bromophenyl)hexane in 63% yield, followed by a subsequent Hartwig–Buchwald coupling with 1-bromo-3,5-dimethoxybenzene in 72% yield. The methoxy moiety in the triarylamine was then deprotected to liberate the resorcinol moiety using boron tribromide in quantitative yield. These triarylamine were then condensed with squaric acid to afford the targeted triarylamine–squaraine dye molecules in 46–91% yield, as shown in Scheme 1. For targeting 3, the 3,5-dimethoxyaniline molecule was coupled with *p*-iodoanisole under Ullmann coupling conditions, which afforded four methoxy moieties in the triarylamine in 64% yield. All four methoxy moieties were converted to the corresponding hydroxyl moieties during the boron tribromide reaction with quantitative yield. We were gratified to note however that condensation with squaric acid proceeded at the resorcinol ring to afford 3 in 75% yield. Detailed synthetic procedures for synthesis of all squaraine dyes can be found in the Supporting Information.

Optical and Electrochemical Properties. Absorbance spectra of the dyes are shown in Figure 2. All spectra were recorded in dichloromethane, Figure 2a, in order to determine the effect of structural modifications on the dyes' absorbance properties. Table 1 summarizes the optical properties of the dyes in dichloromethane (DCM). All of the squaraine dyes

Table 1. Summary of the Absorbance Properties of the Squaraine Dyes in DCM

compound	λ_{\max}^a (nm)	ϵ (10^4 M ⁻¹ cm ⁻¹)	λ_{onset} (nm)	$E_g^{\text{opt } b}$ (eV)
Sq-TAA-OH	684	9.12	883	1.40
Sq-TAA-C ₆ H ₁₃	688	6.02	792	1.57
Sq-TAA-H	670	22.8	764	1.62
Sq-TAA-F	667	23.0	753	1.65
Sq-TAA-CF ₃	663	6.14	713	1.74

^aSolvent: DCM. ^bCalculated from λ_{onset} using the equation $E_g^{\text{opt}} = 1240/\lambda_{\text{onset}}$.

show absorption maxima around 660–690 nm, which are attributed to an ICT absorption process. The ICT absorbance onset is used as an estimate of the HOMO–LUMO energy gap and reported in Table 1 as E_g^{opt} . The absorbance onsets red shift as the electron-donating character of the dye increases, which we hypothesize is a reflection of HOMO destabilization. This effect is minimal for 4 (weakly donating) and 5 (weakly withdrawing), but significantly more pronounced for 3 (strongly donating) and 6 (strongly withdrawing).

The hydroxyl groups on the triarylamine play an essential role in the squaraine dye; we believe that the hydroxyl groups are hydrogen bonded with the enolate-type oxygen in the central ring, resulting in planarization of the molecule. In order to determine the effect that hydrogen bonding has on the absorbance properties of the molecule, we tested solvents that are known to exhibit predictably different capabilities for hydrogen bonding. This provides us with information regarding the intramolecular hydrogen-bonding strength as a function of the component TAA's electron-donating/withdrawing character. When the dyes are dissolved in tetrahydrofuran (THF), which competes effectively with the intramolecular hydrogen bonding at the squarylium core, the emergence of a high-energy peak with concurrent decrease in the low-energy peak can be seen in the absorption spectra of the dyes (Figure 2b). We hypothesize that this is due to squarylium–triarylamine out-of-plane twisting, which breaks the D–A–D conjugation and thereby increases the excitation energy. This is most pronounced in 6, the dye with the most electron-withdrawing TAA module in this study, where the low-energy peak is completely replaced by a significantly blue-shifted peak corresponding to the absorbance of TAA itself, i.e., a triarylamine without any acceptor. Absorbance spectra of all squaraine dyes were also recorded in chloroform (CHCl₃), toluene (non-hydrogen-bond-accepting solvents), dimethyl

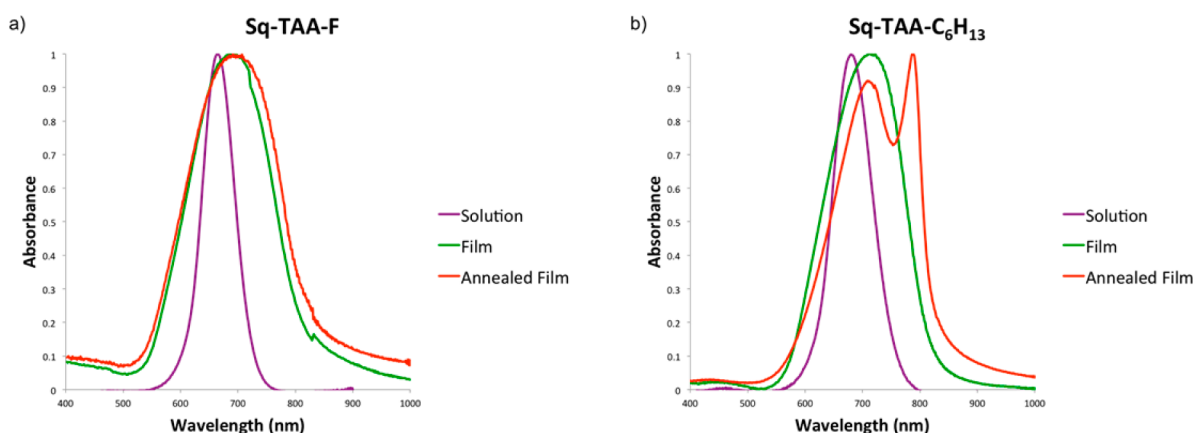


Figure 3. Comparison of the solution (DCM) and thin film absorbance of (a) 5 and (b) 4.

sulfoxide (DMSO), and acetonitrile (MeCN) (hydrogen-bond-accepting solvents). All spectra consistently showed that the hydrogen-bonding capability of the solvent has an effect on the spectral features of these molecules, with the dyes containing the most electron-withdrawing TAA modules having the most easily disrupted hydrogen-bonding core (see Supporting Information). Absorbance spectra in CHCl_3 and toluene show a single low-energy peak, similar to that seen in DCM. Similar to the spectra recorded in THF, spectra in DMSO and MeCN also show the emergence of a high-energy band. In fact, when a mixture of solvents was used, a systematic emergence of the high-energy band with concurrent reduction in the low-energy band was observed (see Supporting Information for details). Briefly, in the dye with the most extreme electron-withdrawing TAA, TAA- CF_3 (6), the core hydrogen bonding is completely disrupted with as little as 40% DMSO/ CHCl_3 , in contrast with the other dyes which require at least 60% DMSO/ CHCl_3 to reach low/high-energy peak intensity equivalency (see Supporting Information for titration curves). This seems to suggest that squaraine dyes constructed from extremely electron-withdrawing TAA modules have core hydrogen bonding that is significantly easier to disrupt.

The thin film absorbance of these molecules is red shifted and broadened when compared to the solution absorbance, suggesting significant aggregation in the film. Solution and thin film absorbance of 5 and 4, as a representative comparison, are shown in Figure 3a and 3b, respectively. All of the other thin film absorbance spectra can be found in the Supporting Information. Annealing the films shows the emergence of a low-energy peak for 4 but no change in the other dyes. This suggests a greater degree of ordering in the 4 film upon annealing, most likely due to the reorientation of the alkyl groups allowing for better packing.

The HOMO and LUMO energy levels as well as the electrochemical band gap, E_g^{elec} , were determined by thin film cyclic voltammetry (CV) and are summarized in Table 2. The HOMO energy level of 6 could not be determined electrochemically, most likely due to *N*-para dimerization by route of triarylamine oxidation to the radical cation followed by deprotonation, a process accelerated by electron-withdrawing groups such as $-\text{CF}_3$.³³ Therefore, the HOMO energy level of 6 was calculated from the optical band gap and the electrochemically determined LUMO energy level. Electron-donating groups resulted in destabilization of the HOMO energy level, while electron-withdrawing groups resulted in HOMO level stabilization in accord with our hypothesis.

Table 2. Summary of the Electrochemical Properties of the Squaraines

compound	HOMO ^a (eV)	LUMO ^b (eV)	E_g^{elec} (eV)
Sq-TAA-OH	−4.97	−4.18	0.79
Sq-TAA- C_6H_{13}	−5.30	−4.16	1.14
Sq-TAA-H	−5.48	−4.08	1.40
Sq-TAA-F	−5.80	−4.00	1.80
Sq-TAA- CF_3	−5.94 ^c	−4.17	

^aEstimated from thin film CV vs Fc/Fc^+ . $\text{HOMO} = -(4.8 + E_{\text{ox}}^{\text{onset}})$.

^bEstimated from thin film CV vs Fc/Fc^+ . $\text{LUMO} = -(4.8 + E_{\text{red}}^{\text{onset}})$.

^cHOMO energy level determined by the optical band gap.

LUMO energy levels were not significantly affected by triarylamine functionalization, which was also expected due to the fact that the squarylium electron-accepting module was kept constant. Thin film CV for oxidation of 2 and 3 can be seen in Figure 4a and 4b, respectively. It can be seen that oxidation of 3 is more reversible, as a result of the stabilization due to the electron-donating groups. The reversibility of the oxidation process becomes poorer with more electron-withdrawing substituents, but the reduction becomes better (See Supporting Information for details).

Charge-Transport Properties. Squaraine dyes were investigated for their charge-transport properties using bottom contact field effect transistors. Output and transfer characteristics of each squaraine dye can be found in the Supporting Information. All dyes were investigated for both hole and electron mobility, both before and after annealing at various channel lengths. The channel length with the highest mobility for each dye is reported in Table 3. Compounds 3, 4, and 2 are all exclusively hole-transporting materials. Neither 3 nor 2 shows any improvement in mobility upon annealing; however, 4 shows significant improvement upon annealing. These data, in combination with the observed change in the absorption spectrum between the thin film of molecule 4 before and after annealing, suggest that there is significant reorganization upon annealing in 4 but little in the other films.

Fluorinated derivatives show an interesting trend in that 5 is ambipolar and 6 is strictly electron transporting. To the best of our knowledge, this is the first report of ambipolar or electron-transporting squaraine dyes as well as the first reported n-type triarylamine. It has been often demonstrated in the literature that installing fluorine atoms into a hole-transporting molecule results in a change in the charge-carrier polarity.^{34–39} One suggested explanation for this change is that installing fluorine

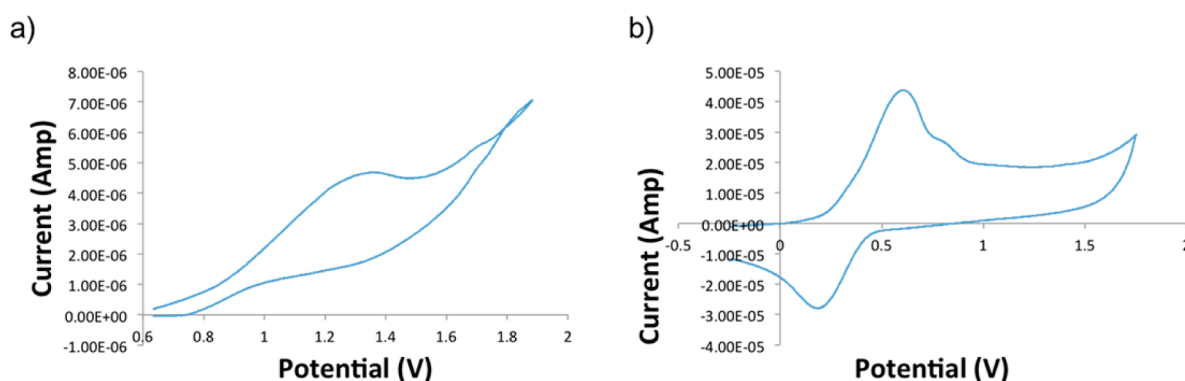


Figure 4. Thin film CV for oxidation of 2 and 3.

Table 3. Summary of the TFT Characteristics of the Squaraines

compound	charge carrier	as is μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	annealed ^a μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
Sq-TAA-OH	hole	$1.90 \times 10^{-5} \pm 7.40 \times 10^{-6}$	$1.91 \times 10^{-5} \pm 6.60 \times 10^{-6}$
Sq-TAA-C ₆ H ₁₃	hole	$4.17 \times 10^{-6} \pm 6.50 \times 10^{-8}$	$2.54 \times 10^{-3} \pm 8.25 \times 10^{-4}$
Sq-TAA-H	hole	$9.63 \times 10^{-4} \pm 1.99 \times 10^{-4}$	$5.71 \times 10^{-4} \pm 2.25 \times 10^{-5}$
Sq-TAA-F	hole	$2.22 \times 10^{-6} \pm 2.30 \times 10^{-7}$	$5.18 \times 10^{-6} \pm 6.20 \times 10^{-7}$
Sq-TAA-CF ₃	electron	$1.06 \times 10^{-6} \pm 8.10 \times 10^{-8}$	$9.57 \times 10^{-6} \pm 1.94 \times 10^{-6}$
	electron	$6.11 \times 10^{-6} \pm 1.13 \times 10^{-6}$	$7.29 \times 10^{-6} \pm 5.55 \times 10^{-7}$

^aAnnealed at 80 °C for 30 min.

atoms lowers the LUMO energy level, resulting in easier reduction and opening of the electron transport channel. However, it has been shown that this phenomenon also occurs when the LUMO energy level is unaffected by functionalization with fluorine atoms,³⁷ as in the case of the fluorinated squaraine dyes reported here. Despite the several reported molecules that exhibit this change, the cause is still unknown.

In order to gain further insight into the change in charge-carrier polarity, DFT calculations were performed using Gaussian 09⁴⁰ at the B3LYP level of theory with structural optimization and electronic property evaluation using the 6-311g(d, p) basis set. HOMO and LUMO surfaces calculated from the optimized structure are shown in the Supporting Information. There are no significant differences in the surfaces of the HOMO and LUMO energy levels of the molecules, although it might be expected that the polarity of the charge carrier would result from a change in the LUMO distribution of the fluorinated dyes. Further investigation into the cause of this change is underway.

CONCLUSIONS

We systematically varied the substituents in the triarylamine part of triarylamine-squaraine based D–A–D molecules. We found that (i) functionalization of squaraine dyes with electron-donating or electron-withdrawing groups onto the triarylamine donor moiety can be utilized to systematically tune the dye's HOMO energy level and (ii) all of these molecules exhibit a low-energy ICT absorption band centered around 660–690 nm with large extinction coefficients and that their absorbance onset is red shifted as the electron-donating capability of the substituent increases. This observation is consistent with increasing HOMO and has little effect on the LUMO, thereby decreasing the overall HOMO–LUMO gap in the molecule. (iii) The low-energy band is very sensitive to the hydrogen-bonding nature of the solvents, i.e., the band reduces in intensity as the hydrogen-bonding capability of a solvent

increases, which is attributed to interruption of the hydrogen-bonding-based planarization of the D–A–D system. (iv) The low-energy absorption band is significantly broadened and red shifted in thin film, compared to solution spectra, which has been attributed to the likely enhancement in π – π interactions in the solid state. (v) The hexyl chains in these squaraine dyes can afford additional ordering in the solid state upon annealing, as observed from the change in the spectral characteristics and the charge-transport ability of molecule 4. (vi) Although triarylamine-based squaraine dyes are typically hole transporters, installing fluorine atoms onto the triarylamines results in ambipolar transport for 5 and electron transport for 6. The reasons for the switch in polarity of charge transport in these molecules are currently under investigation.

ASSOCIATED CONTENT

Supporting Information

Detailed synthetic and experimental procedures, selected solution and film UV, CV, FET, and DFT-calculated HOMO and LUMO distributions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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