# Laser Welding of Polymers using Unsymmetrical Squaraine Dyes

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**ABSTRACT**: Transmission laser welding of plastic is typically achieved by incorporating a laser absorbing dye into one of the two pieces of plastic one wishes to weld together and mediating the welding process using a laser emitting light at a suitable wavelength. Desirable properties of laser absorbing dyes include: (1) the dye is colorless in the visible region but absorbs strongly in the region at the wavelength where the laser emits, (2) the dye has a good conversion of the energy from the laser to heat, (3) the dye is stable enough to be incorporated into the molten plastic, (4) the dye is soluble in the plastic of choice to give an even distribution in the plastic, and (5) the dye is nontoxic. Here, we explore an alternative approach to achieve laser welding of colorless plastics using a laser dye that is colored, but that can be bleached after the welding process. Nonsymmetrical squaraine dyes were prepared by condensation of squaric acid and two equivalents of various 3,5-dimethoxy-*N*,*N*-dialkylanilines. After the incorporation into polyethylene and laser welding, the plastic was bleached either by heat treatment or by irradiation with a high pressure Xe-lamp giving colorless polyethylene. © 2018 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2018**, *56*, 2245–2254

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**INTRODUCTION** The interdiffusion of polymer layers across their boundaries due to the influence of a heat source is of immense importance for the processing of polymers and is more commonly referred to as welding of polymers.<sup>1</sup> Insight into the chemical and physical processes that are occurring when the melts interact and mix into the interdiffusion zone or "welding zone" has been the subject of many reports and has been investigated with a wide variety of techniques such as neutron scattering and microscopy techniques.<sup>2-22</sup> Energy has to be transferred from a source to the polymer layers in order to cause the change of phase from solid to liquid for the interdiffusion or welding process to take place. The heat sources could be something as simple as heated metal that transfers heat to the polymer upon contact or more sophisticated techniques such as ultrasound, where an ultrasound horn is placed in direct mechanical contact with the polymer part.<sup>23</sup> Heat is then transferred upon bringing the horn to vibrate with a frequency in the ultrasound region and heat is then generated due to friction. A novel technique is to induce heat by conversion of light<sup>8,11,17:</sup> One of the polymer parts contains an absorbent with absorption properties that are optimized for the wavelength of the laser used in the process. By traversing the laser in the pattern for the desired weld, heat is generated as a result of a photophysical process thus melting the polymers. Conversion of the incident laser light into heat is in part explained by the Stokes shift: The Stokes

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shift is the difference between the energy of the absorbed and emitted photon, which is converted into vibrational energy thus heat.<sup>24</sup> If the fluorescence quantum yield is smaller than one, then additional photophysical processes can take place such as intersystem crossing. Decay from the excited state back to the ground state through release of vibrational energy is also possible and for the efficiency of a laser absorber for welding more desirable. To a first approximation, it is desirable for the laser absorber to have large Stoke's shift and a small fluorescence and triplet quantum yield.

The coupling between the absorption and fluorescence spectra and the phonons involved can be identified with a Franck-Condon/Huang-Rhys analysis<sup>24,25</sup> in order to determine some of the phonons that are active in the generation of heat. There are several references, mainly in commercial literature, detailing which semicrystalline polymers are suitable for welding with a laser absorbing dye.<sup>26-34</sup> As an example, polyethylene is normally not considered suitable to be welded with this technique, whereas it can readily be welded with other techniques such as ultrasonic welding, which leads to the speculation that the transfer of energy from the absorbing dye to polyethylene is not very efficient. Another reason could be the dispersibility or solubility of the dye in the polymer. In the case of poor heat transfer, this reflects back to the active phonons available for generating heat both in the laser absorber





**FIGURE 1** Schematic illustration of the laser welding process. The red arrow illustrates the laser that is used to weld together the two items of polymer parts. The lower polymer part contains a laser absorber that is responsible for the photophysical process, where light is converted into heat. [Color figure can be viewed at wileyonlinelibrary.com]

itself and in the polymers—due to the "chemical simplicity" of polyethylene there are relatively few vibrational modes when comparing to, for example, polycarbonate, which is considered very compatible with, for example, perylene bisimides as the laser absorbing dyes. Perylene bisimides have limited solubility in almost every solvent unless long alkyl substituents are placed on the dye which makes the argument of heat transfer the more likely for determining the compatibility of this class of dyes in a polymer for welding purposes.

A recent report<sup>20</sup> has detailed the importance of light scattering in laser welding, where having light scattering particles such as  $TiO_2$  present can decrease the amount of energy needed for achieving a sufficient melting and subsequent interdiffusion. Having this finding in mind, it becomes important to choose the right substitution pattern on a novel dye for laser welding applications in order to make it disperse sufficiently but also make sure that the dye is not dissolved in the polymer.

Here, we report the synthesis of a type of laser-absorbing dye molecule based on a squaric acid motif that is suitable for joining two polymer parts. Characterization of this dye is carried out with the purpose of understanding the interplay of physical-chemical properties with the polymer in which the dye is dispersed.

#### **EXPERIMENTAL**

#### **General Data**

Nuclear magnetic resonance (NMR) spectra were measured with a 500 MHz CryoProbe instrument from Bruker. All chemical shift values in the <sup>1</sup>H and <sup>13</sup>C NMR spectra are referenced to the solvent ( $\delta$ H = 7.26 ppm;  $\delta$ C = 77.00 ppm). Thin-layer chromatography was carried out on commercially available precoated plates (silica 60) with fluorescence indicator. Melting points were measured with a Büchi B-140 melting point apparatus and are uncorrected. Elemental analyses were performed with a Thermo Scientific Flash 2000 Organic Elemental Analyzer. matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Bruker Autoflex spectrometer in the positive ion mode using

dithranol as the matrix. Column chromatography was performed on Merck Kieselgel 60 (0.015–0.040 mm) by using the DCVC technique or on Merck Kieselgel 60 (0.040–0.063 mm) for flash chromatography. Ultraviolet/visible (UV/Vis) spectra were recorded on a CARY 5E UV–VIS–near-infrared region (NIR) spectrophotometer. Fourier transform infrared spectra were recorded on a Bio-Rad Excalibur series instrument. The electrochemical experiments were recorded using a CH Instruments electrochemical workstation. Fluorescence spectra were recorded on a Perkin Elmer LS50B fluorimeter with a Hamamatsu 928 PMT. GC–MS data were collected on a Agilent 6890N/5793 system. Temperature-dependent UV/Vis was recorded in a custom made apparatus inserted into a CARY 5E UV/Vis/NIR spectrophotometer.<sup>35</sup>

#### **Synthesis**

#### N,N-dimethyl-3,5-dimethoxyaniline (1a)

Under a nitrogen atmosphere, 1-chloro-3,5-dimethoxybenzene (27.7 g, 0.16 mol) was dissolved in dry THF (170 ml) at 0 °C. A solution of dimethyl amine (100 ml 2 M, 0.2 mol) was added. Butyl lithium (2.5 M, 80 ml, 0.2 mol) was added gradually. The reaction was stirred over night at room temperature. Water (150 ml) was added and THF was evaporated in vacuo. The water was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 x 150 ml). The organic phases were combined and the solvent was removed in vacuo. The isolated crude product was recrystallized from ethanol. Yield: 16.44 g, (90 mmol) 57% as pale yellow crystals; mp 100-101 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.84 (s, 3H), 3.71 (s, 6H), 2.85 (s, 6H); <sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>) δ 161.57, 152.47, 91.85, 88.74, 55.20, 40.63. HRMS (MALDI-TOF) m/z 182.1194 [M + H] + (Calcd for  $C_{10}H_{16}NO_2^+$  m/z 182.1176); Anal. Calcd for C<sub>10</sub>H<sub>15</sub>NO<sub>2</sub>: C, 66.27, H 8.34, N 7.73; Found: C, 66.33; H, 8.45; N, 7.56.

#### N,N-diisobutyl-3,5-dimethoxyaniline (1b)

Diisobutylamine (4.1 g, 31 mmol) and 1-chloro-3,5 dimethoxybenzene (5.2 g 30.3 mmol) were dissolved in dry THF (150 ml) at 0 °C under a dry nitrogen atmosphere. n-Butyl lithium (14 ml 2.5 M in ether, 35 mmol) was added dropwise. After 2 h, all 1-chloro-3,5-dimethoxy-benzene had reacted, as seen with GC-MS. Water (50 ml) was added to the reaction mixture and THF was removed in vacuo. The remaining water phase was extracted with  $CH_2Cl_2$  (4 × 50 ml). The solvent was removed in vacuo from the combined organic phases leaving a crude product which was recrystallized from ethanol. Yield 5.46 g (20 mmol) 68% as yellow crystals; mp 62–65  $^{\circ}$ C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) & 5.76 (m, 3H), 3.70 (s, 6H), 3.04 (d, 4H, J = 7.2 Hz), 2.10-1.96 (m, 2H), 0.81 (d, 12H, J = 6.7 Hz);  $^{13}\text{C-NMR}$  (126 MHz, CDCl3)  $\delta$  161.51, 150.03, 91.93, 86.96, 60.52, 55.09, 26.54, 20.43; HRMS (MALDI-TOF) m/z 266.2114  $[M + H]^+$  (Calcd for  $C_{16}H_{28}NO_2^+$  m/z 266.2115); Anal. Calcd for C<sub>16</sub>H<sub>28</sub>NO<sub>2</sub>: C, 72.41; H, 10.25; N, 5.28; Found: C, 72.24; H, 10.48: N. 5.13.

#### N,N-bis-decyl-3,5-dimethoxyaniline (1c)

Bis-decyl amine (25.0 g 84 mmol) and 1-chloro-3,-5-dimethoxybenzene (13.2 g 76 mmol) were dissolved in dry THF (100 ml) at 0  $^{\circ}$ C under a dry nitrogen atmosphere. *n*- Butyl lithium (52 ml 1.6 M, 83 mmol) was added dropwise. After 1 h, the reaction mixture still contained 5-chloro-1,-3-dimethoxybenzene (as determined by GC-MS) and additional *n*-butyl lithium was added (15 ml 1.6 M, 24 mmol). Water (70 ml) was added to the mixture and THF was removed in vacuo. The aqueous phase was extracted with  $CH_2Cl_2$  (4 × 80 ml) and the organic phases were combined. Celite was added and the solvents were removed in vacuo. The crude product was purified by dry column vacuum chromatography (column  $\emptyset$  = 10 cm, fractions 100 ml) with CH<sub>2</sub>Cl<sub>2</sub> in *n*-heptane with 5% increments. Yield 22.38 g (51 mmol) 68% as a yellow oil. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 5.82-5.73 (m, 3H), 3.70 (s, 6H), 3.18-3.09 (m, 4H), 1.56-1.45 (m, 4H), 1.29–1.10 (m, 28H), 0.81 (t, 6H, J = 6.8 Hz); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 161.69, 150.00, 91.11, 87.12, 55.09, 51.22, 31.91, 29.68, 29.59, 29.55, 29.33, 27.35, 27.20, 22.69, 14.13; HRMS (MALDI-TOF) m/z 434.3995  $[M + H]^+$  (Calcd for C<sub>28</sub>H<sub>52</sub>NO<sub>2</sub><sup>+</sup> m/z 434.3993).

# N,N-bis(2-ethylhexyl)-3,5-dimethoxyaniline (1d)

Bis(2-ethylhexyl)amine (1.13 g, 6.1 mmol) and 1-chloro-3,-5-dimethoxybenzene (0.73 g, 4.2 mmol) were dissolved in dry THF (40 ml) under a dry nitrogen atmosphere and stirred at 0 °C. n-Butyl lithium (1.8 ml 2.5 M, 4.5 mmol) was added gradually. After 30 min all 5-chloro-1,3- dimethoxybenzene had reacted, as seen by GC-MS. Water (75 ml) was added to the mixture and the THF was removed in vacuo. The remaining water phase was extracted with  $CH_2Cl_2$  (4 × 50 ml) and the organic phases were combined. Celite was then added and the solvents removed in vacuo. The crude product was subsequently purified by dry column vacuum chromatography (column  $\emptyset$  = 5 cm, fractions 50 ml), CH<sub>2</sub>Cl<sub>2</sub> in *n*-heptane with 3% increments. Yield 1.14 g (3.0 mmol) 72% as a yellow oil. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 5.78 (d, 2H, J = 2.1 Hz), 5.75 (t, 1H, I = 2.1 Hz, 3.69 (s, 6H), 3.20–3.02 (m, 4H), 1.74 (h, 2H, I = 6.1 Hz, 1.34–1.10 (m, 16H), 0.88–0.76 (m, 12H); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 161.43, 150.12, 91.85, 87.47, 56.58, 55.06, 36.96, 30.75, 28.78, 23.98, 23.25, 14.10, 10.75; HRMS (MALDI-TOF) m/z 378.3367  $[M + H]^+$  (Calcd for  $C_{24}H_{44}NO_2^+$  m/z 378.3367).

# Methyl Trimethoxy Hydroxy Squaraine Dye (2a)

N,N-Dimethyl-3,5-dimethoxy aniline (15.0 g, 83 mmol) and squaric acid (4.3 g, 37 mmol) were dissolved in n-butanol (100 ml) and toluene (300 ml). The reaction mixture was heated to reflux with removal of water by azeotropic distillation over night. Celite was added to the reaction mixture and the solvents were removed in vacuo. The resulting crude product was purified by dry column chromatography on silica (column  $\emptyset$  = 12 cm, fractions 200 ml). First with heptane:ethyl acetate with 10% increments, followed by ethyl acetate:methanol with 1% increments. The product was recrystallized from 96% ethanol. Yield: 100 mg (0.23 mmol) 6% as blue crystals; mp (decomp) 257 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 15.88 (s, 1H), 5.79 (s, 2H), 5.77 (d, 1H, J = 2.3 Hz), 5.57 (d, 1H, J = 2.3 Hz), 3.93 (s, 3H), 3.91 (s, 6H), 3.17 (s, 6H), 3.09 (s, 6H); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 189.83, 185.13, 176.85, 174.10, 168.96, 164.71, 161.74, 160.32, 155.35, 107.19, 100.35, 94.16, 88.40, 87.68, 55.97, 55.57, 40.56, 40.39; HRMS (MALDI-TOF) m/z 427.1862  $[M + H]^+$  (Calcd for  $C_{23}H_{27}N_2O_6^+$ : m/z 427.1864). Anal. Calcd for  $C_{23}H_{26}N_2O_6$ : C, 64.78; H, 6.15; N, 6.57; Found: C, 64.14; H, 6.10; N, 6.30.

# Isobutyl Trimethoxy Hydroxy Squaraine Dye (2b)

N,N-diisobutyl-3,5-dimethoxy aniline (35 g, 132 mmol) and squaric acid (8.6 g, 75 mmol) were dissolved in n-butanol (100 ml) and toluene (300 ml). The reaction mixture was heated to with removal of water by azeotropic distillation overnight. Celite was added to the reaction mixture and the solvents were removed in vacuo. The resulting crude product was purified by dry column chromatography on silica (column  $\emptyset$  = 12 cm, fractions 200 ml). First with heptane:ethyl acetate with 10% increments, followed by ethyl acetate:methanol 1% increments. The product was recrystallized from ethanol. Yield: 1.49 g (2.5 mmol) 4% as blue/green crystals; mp (decomp): 160 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 15.78 (s, 1H), 5.79 (s, 2H), 5.77 (d, 1H, J = 2.3 Hz), 5.59 (d, 1H, J = 2.3 Hz), 3.91 (s, 3H), 3.88 (s, 6H), 3.27 (d, 4H, J = 7.4 Hz), 3.23 (d, 4H, J = 7.2 Hz), 2.20–2.07 (m, 4H), 0.93 (t, 24H, J = 6.7 Hz); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 188.84, 185.12, 177.01, 173.98, 168.72, 164.36, 161.71, 158.99, 153.71, 106.81, 100.08, 94.75, 89.15, 88.47, 60.40, 55.81, 55.43, 27.79, 27.18, 20.43, 20.29; HRMS (MALDI-TOF) m/z 595.3736  $[M + H]^+$  (Calcd for  $C_{35}H_{51}N_2O_6^+ m/z 595.3742$ ).

# Decyl Trimethoxy Hydroxy Squaraine Dye (2c)

N,N-bis-decyl-3,5-dimethoxy aniline (19.3 g, 44 mmol) and squaric acid (2.3 g, 20 mmol) were dissolved in n-butanol (100 ml) and toluene (300 ml). The reaction mixture was heated to reflux with removal of water by azeotropic distillation over night. Celite was added to the reaction mixture and the solvents were removed in vacuo. The resulting crude product was purified with dry column chromatography (column  $\phi$  = 10 cm, fractions 150 ml), with heptane:ethyl acetate with 10% increments, on two consecutive columns with the same gradient increments. A blue semisolid was isolated. Yield: 900 mg (4%); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 15.85 (s, 1H), 5.79 (s, 2H), 5.77 (d, 1H, J = 2.2 Hz), 5.58 (d, 1H, J = 2.2 Hz), 3.93 (s, 3H), 3.91 (s, 6H), 3.46-3.31 (m, 8H), 1.75-1.60 (m, 8H), 1.43-1.21 (m, 56H), 0.98-0.83 (m, 12H); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ 188.61, 185.11, 176.98, 173.62, 168.86, 164.62, 161.89, 158.61, 153.41, 106.83, 100.01, 93.98, 88.36, 87.75, 55.88, 55.47, 51.71, 51.42, 31.90, 31.88, 29.60, 29.56, 29.52, 29.45, 29.37, 29.30, 29.29, 27.97, 27.53, 27.12, 27.02, 22.68, 14.12; HRMS (MALDI-TOF) m/z 931.7467  $[M + H]^+$  (Calcd for  $C_{35}H_{51}N_2O_6^+$  m/z 931.7498).

# 2-Ethyl Hexyl Trimethoxy Hydroxy Squaraine Dye (2d)

*N,N*-Bis(2-ethylhexyl)-3,5-dimethoxy aniline (45.1 g, 129 mmol) and squaric acid (6.3 g, 55 mmol) were dissolved in *n*-butanol (100 ml) and toluene (300 ml). The reaction mixture was heated to reflux with removal of water by azeotropic distillation over night. Celite was added to the reaction mixture and the solvents were removed *in vacuo*. The resulting crude product was purified with dry column chromatography (column  $\emptyset$  = 12 cm, fractions 200 ml), with heptane:ethyl



acetate with 10% increments. The isolated product was further purified with another chromatography step with heptane: ethyl acetate in 5% increments. A blue semisolid was isolated. Yield 1.45 g (3.4%); <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  15.74 (s, 1H), 5.80 (s, 2H), 5.78 (d, 1H, J = 3 Hz), 5.61 (t, 1H, J = 3 Hz), 3.91 (s, 3H), 3.87 (s, 6H), 3.41–3.20 (m, 8H), 1.89–1.75 (m, 4H), 1.42–1.13 (m, 32H), 0.96–0.78 (m, 24H); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  188.65, 185.22, 177.13, 174.00, 168.61, 164.28, 161.63, 159.00, 153.41, 106.81, 99.98, 94.93, 89.31, 88.70, 56.93, 56.84, 55.82, 55.47, 38.31, 37.70, 30.97, 30.93, 30.63, 28.98, 28.65, 23.13, 23.07, 14.04, 10.95, 10.92, 10.74; HRMS (MALDI-TOF) m/z 819.6236 [M + H]<sup>+</sup> (Calcd for C<sub>47</sub>H<sub>74</sub>N<sub>2</sub>O<sub>6</sub><sup>+</sup> m/z 819.6246).

# Voltammetry

In the square wave voltammetric experiments, a threeelectrode setup was employed with a freshly polished glassy carbon electrode (o.d. = 1 mm) serving as the working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. All experiments were performed at a 1 mM concentration of dye in a 100 mM solution of tetrabutylammonium hexafluorophosphate in CH<sub>2</sub>Cl<sub>2</sub>. All potentials are referenced to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) redox couple, by measurement of said redox couple immediately after collection of data. All experiments utilized the instrumental option of correcting for the ohmic drop of the system as incorporated in the CHI electrochemical workstation.

# **Computational Details**

Geometry optimizations for determining the molecular structures in the present work were performed at the B3LYP/6-31G(d) level using the Gaussian 09 suite of programs.<sup>37</sup> Vibrational frequency calculations were carried out on the optimized structures in order to verify that the structures represent minima on the potential energy surface. These geometry optimizations and frequency calculations were performed for the molecules in isolation.

# **RESULTS AND DISCUSSION**

#### Synthesis

Squarine absorbers have been reported in other contexts, where electronic properties have been achieved by carefully selecting the substituents on the squaric acid motif.<sup>38–41</sup> The use of 3,5-dimethoxy-*N*,*N*-dialkylanilines (**1**) has been chosen in the present work as a convenient way of introducing various alkyl-substituents and the methodology of condensing 3,5-dimethoxy-*N*,*N*-dialkylaniline with squaric acid has not previously been described. The ability to introduce various alkyl substituents in a convenient way comes in the present work at the price of not having absorption properties in the NIR but rather in the visible region. The aniline is isolated in a distillation process. A convenient method to prepare 3,5-dimethoxy-*N*,*N*-dialkylanilines in high yields via a reaction between 3,5-dimethoxy-chlorobenzene and a secondary amine has been developed (see Scheme 1).

The condensation reactions were performed in a mixture of toluene and n-butanol with removal of water using a Dean–Stark setup. Although the yields are not high, the procedure is reproducible and consistently affords the trimethoxy-mono-hydroxy-4-(N,N-dialkylamino)-phenyl]-squarines (**2a-d**). Methods to prepare nonsymmetrical squarine absorbers are scarce, and normally require several synthetic steps. Synthetic protocols for unsymmetrically substituted squarine dyes (two different anilines) have been described via a condensation of the acid chloride of squaric acid and an N,N-dialkylaniline followed by hydrolysis and another condensation reaction with a different N,N-dialkylaniline. This is the first nonsymmetrical squarine absorber to be prepared in a one-step procedure.

# UV-Vis and Fluorescence Spectroscopy Solvent Effects

The coupling between absorption of light and the distribution of heat into the embedding polyethylene is suggested above to occur through vibrational redistribution of energy. As such, it is important to look in more details into the absorption and fluorescence properties of the squaric absorbers. Squarine dyes of the type shown in Scheme 1 have absorption bands in the region 623–670 nm depending on the substitution pattern on the squarine motif. The exact position of the band is strongly solvent dependent and varies from 613 nm in hexane to 640 nm in NMP for **2b** (Fig. 2).

Chromophores with significant intramolecular charge transfer (CT) have UV–VIS spectra that strongly depend on the polarity of the solvent which is ascribed to how well the solvent stabilizes the ground and exited states. Squaraine dyes show a negative solvatochromism (Fig. 3, top), where a redshift of the absorption maximum is observed with increasing polarity of the solvent: The  $E_T(30)$  values are used as the measure of solvent polarity and for hexane the  $E_T(30)$  value 31 kcal mol<sup>-1</sup>, 40.7 kcal mol<sup>-1</sup> for dichloromethane and 42.2 kcal mol<sup>-1</sup> for NMP.

The solvent effects of the absorption properties of the squaranine absorbers shows that the extinction coefficients are also



R = a: Me, b: *iso*-Bu, c:  $C_{10}H_{21}$ , d: ethyl-hexyl

**SCHEME 1** Synthesis of trimethoxy-mono-hydroxy-4-(N,N-dialkylamino-phenyl)-squarines. (a) THF, n-BuLi, HNR<sub>2</sub>, 80–90%, (b) toluene, n-BuOH.



**FIGURE 2** Absorption spectra of **2b** in hexane, dichloromethane and *N*-methyl-pyrolidene. [Color figure can be viewed at wileyonlinelibrary.com]

dependent of the polarity of the solvent—and to a quite significant extent. Figure 3 (bottom) shows the extinction coefficients as a function of the  $E_T(30)$  for a series of solvents. A maximum seems to be observed at a value of ~40 kcal mol<sup>-1</sup> which corresponds to an apolar solvent (hexane) and thus mimics rather well the polarity of a polyolefin such as polyethylene. Previously, it has been reported that for CT dyes, the strongest absorbance occurs in solvents with polarity corresponding to an equal distribution between a polar and apolar resonance form.<sup>42</sup> Suitable resonance forms that displays polar and apolar charge distributions can be drawn for squaraine absorbers (Fig. 4).

A linear dependence between the Stokes shift and the  $E_T(30)$  values of a series of solvent is expected.<sup>24</sup> Chemical interactions can be inferred from the  $E_T(30)$  plots: If for example, there was a linear dependence of the Stokes shift on the  $E_T(30)$  values for alcohols with a different slope than for similar plots including a wide variety of solvents with different chemical functionalities, there is most likely hydrogen bonding between the alcohols and the solute. The dependence of the Stokes shifts on the  $E_T(30)$  values for the range of solvents displays a single linear dependence and thus there are no apparent outliers or groups of solvents that shows a separate trend than the rest. In particular, hydrogen-bonding

solvents (alcohols) fall on the same line as the rest of the solvents, thereby strongly suggesting that despite the presence of OH-functionalities on the squaric acid motif there are no hydrogen bonding to an H-donor.

#### **Electronic Structure**

To gain further insights to the electronic structure of the squaraine dyes, calculations were carried out at the B3LYP/6-31G(d) level of theory. A geometry optimization was performed out and the geometry was confirmed by calculating the frequencies.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots support the theory that there is CT occurring during an electronic transition (assuming that the HOMO–LUMO transition dominates the electronic transition) inasmuch as there seems to be a change in charge located at the central oxygen atoms when comparing the HOMO and LUMO orbitals (Fig. 5).

#### Electrochemistry

Redox potentials of the squaraine dye have been obtained in 0.1 mM  $CH_2Cl_2$  with 0.1 M  $Bu_4NPF_6$  as the carrier electrolyte, a freshly mirror-polished platinum disc electrode, platinum wire as the counter electrode. A Ag/AgCl electrode was used as a reference electrode. Ferrocene was used as a reference to determine the oxidation potential. Similar to previously reports on electrochemical data for squaraine dyes, where two oxidation potentials obtained. The first oxidation is partially reversible while the second oxidation is reversible (Fig. 6).<sup>38</sup>

The first two oxidation potentials for 2b were determined to be 0.16 and 0.68 V.

#### Generation of Heat after Excitation

The release of heat after excitation to a higher excited electronic state is described as nonradiative processes, where vibrational modes in the molecule and surroundings are activated. A typical Jablonski diagram showing the different pathways after excitation is shown in Figure 7.

Excitation can occur to, for example, a  $S_2$  state but emission almost always occurs from the  $S_1$  state as rapid relaxation



FIGURE 3 Top: Stokes shift as a function of ET(30) values for 2b. Bottom: Solvent polarity as a function of ET(30) values for 2b





**FIGURE 4** More polar and less polar resonance forms of the charge-transfer squaraine dye.

occurs. Indeed, Kasha's rule states that most photochemical processes occur from either the  $S_1$  or the  $T_1$  state.<sup>24</sup> Thus, excitation from  $S_0$  to a higher singlet state usually results in nonradiative decay to the  $S_1$  state—in the nonradiative process heat is generated as the vibrational levels are activated. Intersystem crossing to the triplet manifold can also occur and from here other radiative and nonradiative processes can also occur. Usually, emission of a photon from the  $S_1$  results in fluorescence.

A recent study has quantified the triplet quantum yield of a series of squaraine dyes.43 Low quantum yields were observed in both air and N<sub>2</sub> saturated toluene indicating that intersystem crossing from the singlet to the triplet manifold is not a significant pathway. Another interesting finding from this study is also that a linear dependence between the fluorescence lifetime and the fluorescence quantum yield was observed for the different compounds, indicating that the radiative rate of decay is independent of the substitution pattern of the squaraine compounds studied. The fluorescence quantum yields of the series of compounds studies were in many cases very low (<0.1) but in some cases significant quantum yields were observed.<sup>43</sup> In the present study, there was no detected fluorescence from the squaraine embedded in the polymer matrix indicating that radiative relaxation from S<sub>1</sub> to S<sub>0</sub> does not occur. As it is also not likely that the triplet manifold is populated based on the findings,43 it appears most likely that nonradiative decay from  $S_1$  to  $S_0$  takes place.

The rate at which the nonradiative decay from  $S_1$  to  $S_0$  occurs can be described with time-dependent perturbation theory

$$k_{\rm nr} = \frac{2\pi}{\hbar} |\langle \psi_{\rm i} | \hat{\nu} | \psi_{\rm f} \rangle|^2 \rho({\rm E}),$$

where  $k_{nr}$  is the rate constant for the nonradiative decay,  $\psi_i$  and  $\psi_f$  are the wave functions for the initial (S<sub>0</sub>-state) and final state (S<sub>1</sub>-state), respectively,  $\hat{v}$  is the kinetic energy operator and  $\rho(E)$  is the density of states, at the energy E. By invoking the Born–Oppenheimer approximation, the wave functions can be factored into electronic ( $\psi_i^e$  and  $\psi_f^e$ ) and nuclear ( $\psi_i^n$  and  $\psi_f^n$ ) wave functions, which results in the following:

$$\begin{aligned} k_{nr} &= \frac{2\pi}{\hbar} \left| \left\langle \psi_i^e | \hat{v} | \psi_f^e \right\rangle \right|^2 \left| \left\langle \psi_i^n | \hat{v} | \psi_f^n \right\rangle \right|^2 \rho(E) = \frac{2\pi}{\hbar} \left| \left\langle \psi_i^e | \hat{v} | \psi_f^e \right\rangle \right|^2 \\ & \text{FC}_{i \to f} \rho(E) \end{aligned}$$

where FC is the Franck–Condon factor between the two states. The Franck–Condon factors can be found the absorption spectrum and is further related to the Huang–Rhys factor (S)





**FIGURE 5** LUMO (top) and HOMO (bottom) of **2a** calculated at the B3LYP/6-31G(d) level of theory. [Color figure can be viewed at wileyonlinelibrary.com]

$$FC_{0\to f} = \frac{e^{-S}S^n}{n!}$$

where the initial state is set as the ground state.

The vibrational mode that is active in the absorption of light by a squarine dye can be identified by employing a Franck– Condon analysis of the absorption spectrum using the expression. Including a more general treatment of the Franck– Condon analysis than that described above results in the following expression for analyzing electronic transitions,

$$I(\omega) \propto \sum_{n_i} \prod_i \frac{S_i^{n_i} \exp(-S_i)}{n_i!} \exp\left(-\frac{(\omega - \omega_0 \pm \sum_i n_i \omega_{p,i})^2}{2\sigma^2}\right),$$

where  $\omega$  is the frequency,  $\omega_0$  is electronic origin frequency,  $\omega_p$  is the phonon frequency,  $S_i$  is the Huang–Rhys factor, *i* is a normal mode in the final state with frequency  $\omega_p$ ,  $\sigma$  is the width of the broadened line at half height for the electronic transition at  $\omega_0$ , and  $n_i$  is the progression of the *i*th normal mode in the Poisson distribution. The "+" sign is used for analyzing absorption spectra and the "–" sign for emission spectra. The Franck–Condon analysis is carried out for compound 6b but only for *i* = 1. The resulting fitted curves along with experimental data are shown in Figure 8.

There is a very good agreement with the experimental data and the fitted Franck–Condon models. The parameters used in the data modeling are presented in Table 1.



**FIGURE 6** Cyclic voltammogram of 2b (R = isobutyl) recorded at 0.1 mM  $CH_2CI_2$  using  $PF_6Bu_4N$  as the carrier electrolyte.



FIGURE 7 Jablonski diagram showing excitation from the S<sub>0</sub> state to a higher vibrational state of the electronic S<sub>2</sub> state. Subsequent internal conversion leads to the population of the S<sub>1</sub> state after activation of vibrational modes ("curved arrow"). From the S<sub>1</sub>-state, several pathways can result in either population of vibrational modes or radiative decay.

The analysis reveals that there is a vibration at  $\sim$ 1442–1594 cm<sup>-1</sup>, depending on the solvent, that is coupled to the absorption of a photon.

A similar analysis was carried out for the commercial laser dyes Lumogen 788 and 765 and the results are presented in Table 1.

For molecules where the fluorescence and triplet quantum yields are negligible, it is apparent that the nonradiative decay is dependent on the transition elements between the two electronic states and the Franck–Condon factor. When, for example, compound 6b is embedded in a polymer matrix there is no fluorescence observed. Lumogen 765 and Lumogen 788 are commercially available pigments specifically for laser welding and they are chemically most likely rylenes, which means they have very high extinction coefficients (>100.000 M<sup>-1</sup>·cm<sup>-1</sup>) and broad spectral features. When comparing compound 6b with these two commercial dyes it is evident that the Lumogens should perform better than, for example, compound 2b as they have higher extinction coefficients and higher Franck–Condon factors.

TABLE 1 Pa	arameters	from	the	Franck-	Condon	anal	ysis
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	hexane	NMP	$CH_2CI_2$		
	2a	2a	2a	Lumogen 765	Lumogen 788
S	0.21	0.24	0.18	0.49	0.45
σ	0.066	0.068	0.066	0.052	0.054
ω <sub>0</sub> /eV	2.02	1.94	1.96	1.62	1.59
ω <sub>p</sub> /eV	0.20	0.18	0.18	0.16	0.17
ω <sub>p</sub> /cm <sup>-1</sup>	1594	1442	1490		

# Thermal Stability

When incorporating the laser absorbing dye into plastic for use in the laser welding experiments, the plastic is typically heated to a temperature where it is soft or melted. Then, the dye is added and the plastic is mixed and the soft plastic injection molded and cooled to give the laser absorbing plastic product. It is important that the dye does not decompose to any significant degree during this treatment.

The simplest method to quantify the stability of a dye is by exposing it to heat at one temperature, and then follow the degradation process by UV–Vis spectroscopy. To this end, the dye was heated in a thermostated cell in a UV–Vis spectrophotometer in a dodecane solution and the disappearance of the main absorbance was monitored. In a parallel experiment, this was done in a degassed dodecane solution. Dodecane was chosen to mimic polyethylene (Fig. 9). It is apparent that oxygen does not play a major role in the decomposition.

The decomposition rate is strongly solvent dependent. In an aromatic solvent like chlorobenzene no decomposition is observed after 10 h at 90 °C. At reflux in chlorobenzene (132 °C), the dye is less than 90% decomposed after 5 h, but in dodecane, the same dye is more than 90% decomposed after 3 h at 115 °C, which could reflect different solubilities of oxygen in the various solvents.

The stability to light exposure was examined in a chlorobenzene solution and after incorporated into polyethylene. The stability to light is important to estimate stability of the dye against both laser light and to gauge the stability at storage. The solution is exposed to light from a Xe-lamp in a cuvette



FIGURE 8 Franck–Condon model fitted to experimental data for different solvents (2b).





FIGURE 9 Decomposition of dye 2b in 90 °C dodecane, under ambient atmosphere and with a nitrogen atmosphere.

with stirring, the concentration is determined via UV–Vis absorbance measurements. Under oxygen-free conditions in a degassed solution the degradation rate is about 25% lower than in the presence of  $O_2$ , which also lend support to differences in stability when the dye is solubilized in either chlorobenzene or dodecane when exposed to light.

Another useful technique to characterize thermal stability is to examine the neat material in a thin film. We have built an oven insert for a UV-Vis spectrophotometer that allows us to monitor the absorbance as a function of temperature of thin films. We monitored the disappearance of the main absorbance band of the laser absorber as a function of increasing temperatures. Absorbance spectra are shown in Figure 9. The dye decomposes gradually. At 150 °C, 50% of the dye had decomposed.

#### **Decomposition Products**

To our satisfaction, we observed that the squarine dyes decomposed to colorless products. This is significant for the future use of this type of dye in plastic. To investigate the composition of the decomposition products obtained after thermal decomposition, we heated a solid sample to 150  $^{\circ}$ C for 30 min and analyzed the resulting mixture using LC-MS analysis. Law et al. have analyzed the mass spectra from



**FIGURE 10** Decomposition of dye **2b** by exposure to light from a Xenon lamp. Degradation is about 25% slower in a degassed solution. Solvent chlorobenzene. The decomposition process is first order, approaching zero order at high concentrations. [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 11** Transmission spectrum of PE with **2b**. [Color figure can be viewed at wileyonlinelibrary.com]

electro spray of squaraine dyes and they observed alkyl transfer from nitrogen to oxygen in the squaric acid ring. It is not clear exactly what the decomposition products are, but the majority of products appear to result from a decomposition of the squaric acid ring.

#### Laser Welding

Laser absorbing dyes can be incorporated in polymers by distribution on polymer pellets followed by compounding—a loading of 0.1 wt% of **2b** in a linear low density PE matrix (Flexirene MS 20 A from Versalis) was used. This was done at



**FIGURE 12** Decomposition of the isobutyl trimethoxy hydroxyl dye (**2b**) in PE by exposure to light from a Xenon lamp. The dye clearly decomposes to yield the PE as a colorless material. The last picture shows the PE exposed to light for 1 h (bottom part). [Color figure can be viewed at wileyonlinelibrary.com]





**FIGURE 13** Top: laser welding setup. Bottom: picture of laser welding zone when using the drop casting method to apply the dye (**2b**). [Color figure can be viewed at wileyonlinelibrary.com]

140 °C and the plastic is extruded (twin screw extruder) and divided into pellets. In the compounding process, the polymer was melted and admixture with the dye was obtained. After the compounding process, the polymer can be molded in different shapes. After these processes, polymers with laser absorbing dyes can be welded to laser transparent polymers. The successful incorporation was verified by recording simple transmission spectra (Fig. 11) that showed the absorbance in the region where the dye absorbs. Visually, it is also apparent that the dye is incorporated in the PE.

The typical available wavelength used for laser welding is 808 nm, but high energy lasers with various wavelength are now readily available—presently, lasers with wavelength lower than 700 nm are less commonly used due to costs.

The polymers can be bleached after incorporation/welding using a Xenon lamp (450 W), in Figure 12, a polymer containing a squaraine dye incorporated with gradual decomposition and bleaching as a function of light exposure. It is significant that the dye bleaches completely into colorless products leaving the PE colorless.

Laser welding experiments were performed using a home build setup as shown in Figure 13. The welding process can be performed using PE with the dye incorporated or with the dye applied to the surface of the PE by simple drop casting.

The laser welding was performed using 1.7 W optical effect with a 650 nm diode laser. This is equivalent to a current of 1.4 A or a voltage of 6.25 V. The spot size was estimated to be  $2 \times 2$  mm, which gives an output per area of ~0.4 W mm<sup>-2</sup>. The laser was traversed a rate of 40 mm s<sup>-1</sup>. To our satisfaction, the strength of the welding zone as evaluated by tensile strength (each end of the specimen is fastened into clamps and the force required to move the clamps away from each other is recorded and noted upon breaking the specimen) and the strength of the welding zone was comparable to that of the plastic itself.

#### CONCLUSIONS

A series of squaraine compounds have been synthesized and characterized. It is also discussed how to describe potential new laser welding absorbers with respect to efficiency and it suggested that such an analysis can be carried out by applying a Huang–Rhys/Franck–Condon analysis and deriving the Huang–Rhys factors. This value together with the extinction coefficient can be used as a guideline for the characterizing the efficiency of laser dyes. However, if the potential laser dye intersystem crosses to a significant extent to the triplet manifold and/or fluorescence, these pathways must also be taken into account, making the analysis more subtle.

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