Anthraquinone-Imide-Based Dimers: Synthesis, Piezochromism, Liquid Crystalline, and Near-Infrared Electrochromic Properties

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A series of anthraquinone-imide-based dimers, C5\textsubscript{-AQI-Si2}, C5\textsubscript{-AQI-Si3}, C5\textsubscript{-AQI-Si4}, and C5\textsubscript{-AQI-Si8}, have been prepared by the hydrosilylation of \(N\)-(hex-5-enyl)-6-(4'-((S)-2-methylbutoxy)phenyl)anthraquinone-2,3-dicarboxylic imide and hydride-terminated siloxanes with different lengths. Their liquid crystalline behaviors, and piezochromic and near-infrared electrochromic properties have been characterized by DSC, wide-angle X-ray diffraction, cyclic voltammetry, and UV–vis–NIR spectroscopy. Although anthraquinone imide is not liquid crystalline by itself, all the dimers formed a smectic A mesophase. Under moderate pressure, the color of the dimers changed from light yellow to deep red. Upon reduction to a radical anionic state, the dimers exhibited an intense NIR absorption at 844 nm. These anthraquinone-imide-based dimers are probably the first multifunctional molecules with combined liquid crystalline, mechanochromic, and NIR electrochromic properties.

Introduction

Organic materials that respond to external stimuli such as heat, light, pH, and electric fields have attracted extensive attention as a result of their academic importance and practical applications.\textsuperscript{[1–10]} External pressure responsive materials, i.e., piezochromic materials that present coloration reversibly or irreversibly in solid specimens or solution samples under pressure, can find significant potential applications as pressure-sensitive paints and shock detectors, for instance.\textsuperscript{[2]} Since the early studies on piezochromic phenomena,\textsuperscript{[11,12]} the reported piezochromic materials so far mainly include polymers such as poly(di-n-alkylsilanes)\textsuperscript{[13–15]} and poly(3-alkylthiophene),\textsuperscript{[16–21]} inorganic metal complexes,\textsuperscript{[22,23]} and some organic dyes.\textsuperscript{[24–27]} The reported piezochromic properties are mainly presented under high pressure, for example, above one GPa, but relatively low applied pressure is preferred for many applications in our daily life.

Electrochromic (EC) materials are another chromic species that can reversibly change optical properties upon electrochemical oxidation or reduction and have been of interest for several decades.\textsuperscript{[8]} Besides their applications in switchable display devices,\textsuperscript{[28–31]} smart windows in buildings,\textsuperscript{[32–34]} and antiglare car rear-view mirrors\textsuperscript{[35]} in the UV-visible region, those showing optical activity in the near-infrared (NIR) region (typically, 780–2,000 nm) have
attracted growing attention owing to their unique electrical/optical properties and potential applications in photonics, telecommunications, and tissue and biological studies. Although both physical and chemical external stimuli may cause chromic phenomena, it is rare to observe more than one kind of chromism in the same material. We have been focusing on NIR EC materials.

A novel kind of NIR EC anthraquinone imide (AQI) bearing functional groups at the 6-position on the anthraquinone moiety were found to absorb intensely in the NIR region of 700–1 100 nm upon one-electron electrochemical reduction to the radical anionic state. AQI was also used as side groups of helical polyacetylenes to build chiroptical switches. Molecular assemblies with ordered structures always give rise to additional functionalities that are different from those of their individual molecules for example, Kato et al. reported the incorporation of terthiophene mesogens and terminal imidazolium groups into layered liquid crystalline (LC) structures with two-dimensional (2D) alternating pathways for electronic charges and ionic species and as a result, a distinct reversible EC response was achieved without additional electrolyte solution. As such, herein we report utilizing AQI as a building block to construct a series of LC dimers, which show either piezochromicity under moderate pressure or NIR electrochromicity upon reduction. Such functional materials with ordered LC structures, piezochromic and NIR EC properties have not been previously reported.

**Experimental Section**

**Materials**

1.1,3,3-Tetramethyldisiloxane (97%, Acros), 1.1,3,3,5,5-hexamethyldisiloxane (97%, Acros), 1.1,3,3,5,7,7-octamethyldisiloxane (95%, Fluorochem), hydride-terminated silicone oil (with an average Mn of ≈580, or with an average eight siloxane units, Aldrich) and Karstedt’s catalyst (platinum(0)-divinyltetramethylsiloxane complex in xylene, 2 wt.-% Pt, Pt(dvs), Aldrich) were used as purchased. 6-Bromo anthraquinone-2,3-dicarboxylic anhydride was synthesized following the procedure reported previously. 6-Aminohex-1-ene was synthesized according to the literature method. 4-(5’-2’-Methylbutyloxy)phenylboronic acid and tetraakis(triphenylphosphine)palladium(0) ([PPh3]4Pt0) were synthesized in our laboratory. Toluene used in the hydrosilylation method.

**Synthesis**

N-(Hex-5-yl)-6-bromo-anthraquinone-2,3-dicarboxylic imide (6Br-AQI-C4-ene)

6-Bromo anthraquinone-2,3-dicarboxylic anhydride (3.10 g, 8.7 mmol) was placed in a 50 mL three-necked round bottom flask. Under nitrogen atmosphere, a solution of 6-aminohex-1-ene (0.88 g, 10 mmol) in dry N,N-dimethylformamide (DMF, 15 mL) was added into the flask. After stirring for 1 h at room temperature, the mixture was heated to reflux for 6 h. The mixture was then allowed to cool to room temperature, and poured into a dilute hydrochloric acid solution (100 mL). The solids thus precipitated were filtered off and washed with methanol. After drying, the crude product was purified by silica gel column chromatography (with CH2Cl2 as eluent) to afford the target compound (2.20 g) as a yellow solid in 86% yield. 1H NMR (400 MHz, CDCl3, δ): 8.78 (s, 2H, J = 2.8 Hz), 8.50 (d, 1H, J = 2.0 Hz), 8.24 (d, 1H, J = 8.3 Hz), 8.02 (q, 2H, J = 8.4 Hz), 5.82 (m, 1H), 5.04 (m, 2H), 3.80 (t, 2H, J = 8.3 Hz), 2.14 (m, 2H), 1.76 (m, 2H), 1.50 (m, 2H). 13C NMR
(100 MHz, CDCl₃, δ): 180.85, 180.56, 166.44, 138.06, 137.98, 137.83, 137.64, 136.19, 136.08, 134.03, 131.6, 130.72, 129.42, 122.63, 122.60, 115.07, 38.60, 33.17, 27.86, 26.08. Anal. calc. for C₂₂H₁₄BrNO₄: C 69.62, H 3.71, N 1.91; found: C 69.64, H 3.77, N 1.94.

**N-(Hex-5-eny)-6-[(4′-((5′-2-methylbutoxy)phenyl)-anthraquinone-2,3-dicarboxylic imide (C₅′-AQUI-C₄-ene)**

To a 250 mL three-necked round bottom flask fitted with a magnetic stirring bar and a condenser was added 1.50 g (3.4 mmol) of 6Br-AQUI-C₄-ene, 0.75 g (3.6 mmol) of 4-((5′-2-methylbutoxy)phenylboronic acid, 1.5 g (8 mmol) of NaHCO₃, and 20 mg (0.018 mmol) of (PPp₃)₂PdCl₂. After degassing and reacting with nitrogen three times, 90 mL of benzene, 15 mL of ethanol, and 30 mL of distilled water were added under a nitrogen atmosphere. The mixture was then heated to reflux for 4 h. After cooling, the reaction mixture was separated into two phases. The organic layer was isolated and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layer was washed successively with water and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (with CH₂Cl₂ as eluent) to give 1.32 g of C₅′-AQUI-C₄-ene in 96% yield. ¹H NMR (400 MHz, CDCl₃, δ): 8.74 (d, 2H, J = 3.6 Hz), 8.47 (s, 1H), 8.34 (d, 1H, J = 8.1 Hz), 8.01 (d, 1H, J = 8.1 Hz), 7.66 (d, 2H, J = 8.5 Hz), 7.02 (d, 2H, J = 8.5 Hz), 5.82 (m, 1H), 5.04 (m, 2H), 3.91 (m, 4H), 2.15 (m, 2H), 1.93 (m, 1H), 1.78 (m, 2H), 1.51 (m, 2H), 1.34 (m, 2H), 1.05 (d, 3H), 0.98 (t, 3H). ¹³C NMR (100 MHz, CDCl₃, δ): 181.68, 181.03, 166.56, 160.49, 147.14, 138.16, 138.07, 138.00, 135.82, 135.67, 133.34, 132.14, 130.85, 130.23, 128.48, 124.94, 120.10, 121.51, 115.21, 73.05, 38.48, 34.70, 33.15, 27.85, 26.12, 26.07, 16.51, 11.31. Anal. calc. for C₁₅H₁₁NO₅: C 75.99, H 5.99, N 2.69; found: C 75.95, H 5.98, N 2.61.

**AQI Dimers**

The AQI dimers containing different siloxane linkages, namely, 1,3-bis(N-hexyl-6-[(4′-((5′-2-methylbutoxy)phenyl)-anthraquinone-2,3-dicarboxylic imide]-1,1,3,3-tetramethyldisiloxane (C₅′-AQUI-Si₂), 1,5-bis(N-hexyl-6-[(4′-((5′-2-methylbutoxy)phenyl)-anthraquinone-2,3-dicarboxylic imide]-1,3,3,5,5-hexamethytrisiloxane (C₅′-AQUI-Si₃), 1,7-bis(N-hexyl-6-[(4′-((5′-2-methylbutoxy)phenyl)-anthraquinone-2,3-dicarboxylic imide]-1,3,3,5,5,7-octamethyltetrasiloxane (C₅′-AQUI-Si₄), and N-hexyl-6-[(4′-((5′-2-methylbutoxy)phenyl)-anthraquinone-2,3-dicarboxylic imide-terminated silicone oil (C₅′-AQUI-Si₈) were synthesized under standard hydrosilylation conditions with a general yield of about 85%. As a typical experiment, the synthesis of dimer C₅′-AQUI-Si₈ is described as follows. C₅′-AQUI-C₄-ene (0.220 g, 0.422 mmol) was placed into a 50 mL Schlenk tube. The tube was degassed and refilled with nitrogen three times. Toluene (3.0 mL) was added to the tube, followed by 50 μL of 1,3,3,5,5-hexamethytrisiloxane (0.197 mmol) and 15 μL of Pt(dvs) after all the solids were dissolved. The pale yellow solution became red after the catalyst was added, and the mixture was stirred at 120 °C for 2 d. Triphenylphosphine (PPh₃, ~5 mg) was added to deactivate the Karstedt’s catalyst. After stirring for another 2 h, the mixture was allowed to cool to room temperature. Toluene was then evaporated under vacuum. The crude product was purified by silica gel column chromatography with dichloromethane/petroleum ether (4:1, v/v) and then with dichloromethane/petroleum ether (4:1, v/v).

**Results and Discussion**

**Synthesis**

The synthetic route of AQI and its dimers is shown in Scheme 1. 6-Bromo anthraquinone anhydride was first converted into AQI with an olefinic end group and then...
Suzuki coupling between the bromo-substituted imide and phenylboronic acid with a solubility enhancing alkoxy group was carried out to obtain the AQI (C₅^−-AQI-C₄-ene) with high yield, which was linked to 1,1,3,3-tetramethyl-disiloxane (Si₂-H), 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (Si₄-H), and disiloxane (Si₂-H), 1,1,3,3,5,5-hexamethyltrisiloxane (Si₃-H), and hydride-terminated silicone oil (average Mₙ ≈ 580) using Karstedt’s catalyst at 120 °C. An excess of AQI was used to ensure completion of the hydrosilylation reaction. The progress of the reaction was followed by FT-IR spectroscopy. The complete disappearance of the Si–H stretching at 2134 cm⁻¹ indicated the complete reaction of the oligosiloxane. FT-IR spectra of Si₃, C₅^−-AQI-C₄-ene and the corresponding product C₅^−-AQI-Si₃ are shown in Figure 1. After the completion of the hydrosilylation, a few crystals of PPh₃ were added to deactivate the catalyst.[52] The final products were purified by silica column chromatography as pale yellow solids with good yield.

The ¹H NMR spectrum of dimer C₅^−-AQI-Si₈, as shown in Figure 2, shows all the expected features with well resolved resonances for the dimer. The pseudo-triplet (Si-CH₂) at about 0.5 ppm and the complete absence of signals at 2.0–2.5 ppm are indicative within the limit of detection of complete a-addition (the linear Si—CH₂—CH₂—R isomer) of the Si—H bond to the alkene. ¹³C NMR spectroscopy also showed the disappearance of the chemical shift of the terminal alkene at 138.07 and 115.21 ppm, respectively.

MALDI-TOF results allowed further confirmation of the correct product showing a singlet at 1273.5 ([M + Na]⁺). The dimers show similar characteristics except for the product of the hydride-terminated silicone oil (average Mₙ ≈ 580). Fine splitting of the low field AQI moiety signals in the ¹H NMR spectrum become broad and the molecular weight of C₅^−-AQI-Si₈ has a distribution which is proved by MALDI-TOF (m/z: 1495.6, 1569.6, 1643.6, and 1717.7 corresponding to [C₅^-AQI-Si₆ + Na]⁺, [C₅^-AQI-Si⁷ + Na]⁺, [C₅^-AQI-Si₈ + Na]⁺, and [C₅^-AQI-Si₉ + Na]⁺, respectively) indicating the product is a mixture with 6, 7, 8, and 9 siloxane units. For the sake of clarity, it is still marked as C₅^−-AQI-Si₈. For the four dimers, the solubility in common organic solvents, e.g., CH₂Cl₂, is enhanced with the increase of siloxane units.

**Thermal Properties**

DSC thermograms of AQI and the dimers recorded during the first cooling and subsequent heating cycles at a scanning rate of 10 °C·min⁻¹ are shown in Figure 3. The phase transition temperatures are summarized in Table 1. The AQI has only one endothermic peak during the heating process and one exothermic peak during the cooling process. Phase transitions of C₅^−-AQI-Si₂, C₅^−-AQI-Si₃, C₅^−-AQI-Si₄, and C₅^−-AQI-Si₈ are similar to each other. Only one isotropic transition and a melting transition can be observed during the heating process, while upon cooling, two exothermic peaks appear. When cooled or heated to the temperature range between these peaks, the samples become birefringent and fluid under cross-polarizing microscopy. Therefore, the phase between the transition temperatures corresponds to a LC phase. From Table 1, two trends are observed with increasing siloxane unit number: one is that the isotropic–LC transition temperature upon cooling decreases and the other is that the temperature range of the LC phase decreases. These phenomena may be attributed to the increased separation of the main chain with increasing number of siloxane units.
The molar enthalpy at each transition is also summarized in Table 1. $\Delta H$ (in kJ mol$^{-1}$) of the dimers during the isotropic–LC transition is in the range of 2 to 7 kJ mol$^{-1}$.

Thermotropic LC Behavior

The textures observed by optical microscopy for mesophases of the dimers are shown in Figure 4. During the heating process of the samples from room temperature under cross-polarized microscopy, they turned intensely birefringent, and fan-shaped textures were observed when the temperature was beyond the melting temperatures; they turned black again above the clearing temperatures. While cooling, the opposite phenomena were observed. The clear fan-shaped texture was assigned to a smectic LC phase. In order to identify the smectic structure, 1D-WAXD measurements were performed.

Figure 5 shows the WAXD patterns of C5*-AQI-Si8 during heating in the small-angle and wide-angle regions. As shown in Figure 5, at temperatures lower than the crystal–liquid crystal transition temperature (e.g., 100 °C), intense crystal diffraction peaks are observed. When heated near to the transition temperature, the crystal diffraction peaks weaken, and when heated into the LC range, another two intensive diffraction peaks appear in the small-angle region, and the ratio of the two corresponding layer spacings is approximately 2, while in the wide-angle region only an amorphous peak appears, indicating a well-layered structure. After heating to the isotropic state, the intense peak is replaced by an amorphous peak. Together with the $\Delta H$ and fan-shaped textures, the mesophase is assigned to be a smectic A phase. The WAXD patterns of the other dimers give the same results. The layer spacings from the XRD measurements are calculated and summarized in Table 1.

Considering the construction of the dimers, there are three different parts: an AQI moiety bearing alkyl chain,
methylene, and siloxane units. The extended molecular configurations and calculated molecular length of C$_5$/C$_3$-AQI-Si$_2$ and C$_5$/C$_3$-AQI-Si$_3$ are illustrated in Figure 6a. Considering the relationship between the calculated molecular length ($l$) and layer spacing ($d$) given by WAXD patterns, the ratio $d/l$ is approximately 0.5. For smectic A liquid crystals with $d/l = 0.5$, there are two possible molecular arrangements: intercalated structures and horseshoe-like structures.$^{[53]}$

However, for symmetric dimers, there exists an empirical rule that for dimers containing terminal alkyl chains to exhibit smectic properties the terminal chain length must be greater than half the spacer length,$^{[54]}$ which is the opposite in the present case. Therefore, we concluded a horseshoe-like structure and a schematic illustration is shown in Figure 6b. However, the exact arrangement of the spacer linkages in the structure is unknown yet.

**Piezochromic Properties**

The dimers synthesized here also show piezochromic properties as shown in Figure 7. The original powders of the dimers which were obtained by rotary evaporation from a CH$_2$Cl$_2$ solution were light yellow. However, the color changed to red after manual grinding. To study the pressure needed to introduce piezochromic properties, tablets of a dimer/KBr mixture were pressed at different pressures, and the results are presented in Figure 7a. The original C$_5$-AQI-Si$_8$/KBr tablet was yellow. However, after pressing at 369 MPa for 2 min, it turned red from yellow (Figure 7a, right). Even at a low pressure, such as 36.9 MPa, parts of the tablet exhibited a color change (Figure 7a, left). The yellow powders could be reestablished by dissolving the red powders in organic solvents such as CH$_2$Cl$_2$ and drying by rotary evaporation. Because of the enhanced film forming property, the spectra of the solution and films before and after pressure of C$_5$-AQI-Si$_8$ are illuminated in Figure 7b. In

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**Table 1. Thermotropic properties (°C) and layer spacings (Å) of the dimers.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transition temperature$^a$</th>
<th>$d$$^b$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>[°C] ($\Delta H$ [kJ mol$^{-1}$])</td>
<td>[Å]</td>
</tr>
<tr>
<td>C$_5$-AQI-C$_4$-ene</td>
<td>Cr 255 (33.6) Iso/Iso 242 (34.9) Cr</td>
<td>—</td>
</tr>
<tr>
<td>C$_5$-AQI-Si$_2$</td>
<td>Cr 261 (40.1) SmA 278 (1.6) Iso/Iso 266 (7.1) SmA 243 (43.8) Cr</td>
<td>30.59</td>
</tr>
<tr>
<td>C$_5$-AQI-Si$_3$</td>
<td>Cr 252 (42.7) SmA 274 (8.8) Iso/Iso 268 (5.4) SmA 235 (42.7) Cr</td>
<td>31.45</td>
</tr>
<tr>
<td>C$_5$-AQI-Si$_4$</td>
<td>Cr 256 (57.6) SmA 273 (0.2) Iso/Iso 253 (1.8) SmA 234 (57.5) Cr</td>
<td>33.24</td>
</tr>
<tr>
<td>C$_5$-AQI-Si$_8$</td>
<td>Cr 220 (45.8) SmA 239 (3.2) Iso/Iso 229 (3.8) SmA 208 (28.5) Cr</td>
<td>38.86</td>
</tr>
</tbody>
</table>

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(a) C$_5$-AQI-Si$_2$ at 255°C; (b) C$_5$-AQI-Si$_3$ at 260°C; (c) C$_5$-AQI-Si$_8$ at 220°C; (d) C$_5$-AQI-Si$_4$ at 250°C

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**Figure 4.** POM images of the dimers in a mesogenic state taken during the cooling process.

**Figure 5.** Powder WAXD patterns of C$_5$-AQI-Si$_8$ at different temperatures.
solution, there are two major absorption peaks at 310.5 and 421 nm. When drop-coated onto a glass slide, a weak and poorly defined peak at 423.5 nm with a 2.5 nm red-shift compared to the solution appeared. After manual grinding of the film, the weak peak is enhanced and continuously red-shifts to 428.5 nm. This red-shift can also be reversed by solvent. However, at temperatures below the melting point this shift remains for much longer, for instance, two days.

It has been reported that the face-to-face distances between polythiophene planes of poly(3-octylthiophene) decrease under high pressure, and therefore the intermolecular electronic interaction increases, which further results in an absorption shift to a longer wavelength.\[20,55,56\] The same reason was applied in two more recent papers about polyanthraquinone\[57\] and a series of conjugated polymers consisting of isothianaphthene and dialkoxy-p-phenylene units.\[58\] For the dimers reported in this paper, a proposed explanation for the piezochromic property is that external pressure is expected to decrease the torsion angle between the benzene ring and the AQI core, which enables a more compressed stacking and also probably an enhanced charge transfer to cause piezochromism. To verify the proposed reason for the piezochromic property of the dimers, the pressure-induced coloration experiments of the anthraquinone imide, C5'-AQI-C4-ene, was carried out. The result revealed that a slightly higher pressure, i.e., 450 MPa, could also induce a color change from yellow to red for the C5'-AQI-C4-ene/KBr mixture tablet, indicating that the piezochromism of the dimers results from the AQI group. The exact mechanism of the piezochromism needs further investigation, which is under way.

**EC Studies**

The redox properties of the dimers were investigated by CV in CH2Cl2 with TBAP as an electrolyte. Reduction potentials were measured relative to the internal standard, ferrocene/ferricenium (Fc/Fc'). As demonstrated in Figure 8, the imide group undergoes two reversible one-electron reductions, corresponding to the formation of a radical anion and dianion, respectively. The potentials are summarized in Table 2.

Comparing the reduction and oxidation potentials of different AQI derivatives as shown in Table 2, it is clear that substituents at the anthraquinone moiety have a strong influence on the redox properties of the derivatives. The one described in ref.\[42\] showed more negative reduction potentials, while AQI and the dimers synthesized here all showed much less negative reduction potentials. However, among the AQI and the dimers, the reduction potentials are almost the same, which indicates the oligosiloxane has little influence on the redox properties of the AQI moiety.

To investigate the NIR EC properties of the dimers, spectroelectrochemical measurements were carried out using an OTTLE cell. The applied voltage was chosen according to cyclic voltammetric results. The UV-Vis-NIR spectra of \(C5^ {-} \text{AQI-Si3}\) is shown in Figure 9. In its neutral state, \(C5^ {-} \text{AQI-Si3}\) shows an absorption at 416 nm. Upon one-electron reduction, intensive NIR absorption of the corresponding radical anion appeared around 600–
1200 nm centered at 844 nm. The absorption is realized as the π⁻–π⁺ (SOMO→LUMO) transition of the radical anion of the imide. Upon further reduction, the NIR absorption disappeared and a new band at 590 nm appeared. The UV-Vis-NIR spectra of other dimers were similar to the one shown in Figure 9.

**Conclusion**

We have reported the synthesis of a series of AQI based dimers with different siloxane linkages by hydrosilylation reactions. Thermal analyses, powder WAXD patterns, and
POM measurements revealed a smectic A structure. Although the AQI is non-liquid crystalline, the dimers are able to display a horseshoe-like ordered structure. External pressure and electric dual response characteristics of the dimers were demonstrated. When a moderate pressure is applied, the powders of the dimers turn to red from yellow and the absorption of the dimer films presents a red shift, a process that can be reversed by solvent. Upon one-electron reduction, the dimers are converted into radical anions and give out an intense NIR absorption centered at 844 nm. As far as we know, this is the first report on functional materials with combined LC structures, piezochromism, and NIR electrochromic properties, which may find applications in fields such as nanostructured electronic/optical materials.

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