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Chiral imides as potential chiroptical switches: synthesis and optical properties

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Abstract—A series of chiral aromatic imides and diimides were synthesized and their electrochemical, absorption, fluorescent, and chiroptical properties were examined for their potential application as molecular chiroptical switches. These compounds exhibit strong UV–vis absorptions, and can be electrochemically reduced to radical anions that absorb in the near infrared (NIR) region. Further reduction to the dianionic states results in new absorptions in the visible region. The changes in circular dichroism upon redox switching were apparent in the UV–vis region but were absent in the NIR region.

There has been considerable interest in recent years in the development of a new class of molecular switch based on changes in the optical properties of a compound.[1–4] To be useful as a molecular switch, such a molecule must possess bistability, meaning that two different forms of the molecule can be interconverted by application of external stimuli. The major methods used to stimulate molecular switching are by chemical, electrochemical and photochemical means. Electrochemical switches are based on the changes in optical, electrical, chemical, and/or physical properties of a molecule upon application of electric fields to the switching cell or device.[5–7] Electrochromic compounds are able to change colors when they undergo redox reactions, which can readily be monitored using standard spectroscopic techniques. By introducing chiral elements into an electrochromic molecule, a chiroptical switch can be attained in which its chiroptical property changes upon application of a bias to the electrochemical cell. To be an effective chiroptical switch, reduction or oxidation of the chromophore must occur rapidly and reversibly and the chiroptical properties of the two states must be sufficiently different.

Aromatic imides are known to be electrochromic with intense UV–vis absorptions in their neutral states.[8–13] These imides exhibit bathochromic shifts to a longer wavelength toward the near infrared (NIR) region when they undergo one-electron reductions. Accordingly, the introduction of chiral centers into aromatic imides would allow for the detection and analysis of these chromophores using techniques dependent upon their optical activity, such as circular dichroism (CD). There are a few reports on the synthesis and spectroscopic characterizations of chiral imides.[14–18] Circular dichroism was used to study exciton coupling in chiral imides, which allowed for identification of the conformers that were present in these chromophores. It was also shown that large Cotton effects resulted from exciton interactions in naphthalene and perylene chromophores. However, there have been no studies to examine the effects of electrochemical reactions on the chiroptical properties of chiral imides and to evaluate the possibility of using chiral imides as molecular chiroptical switches. Thus, chiral imides (**1**–**3**) were synthesized via imidization reactions of commercially available anhydride and

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dianhydrides with *R*- and *S*-α-methylbenzylamine, respectively.[†] A keto-anhydride was first obtained according to literature procedures,[19,20] and reacted with *R*- and *S*-α-methylbenzylamine, respectively, to yield chiral imides **4**.[‡] These different chiral imides are to be investigated as model chiroptical switches that can be modulated by an electrochemical means (Fig. 1).

Cyclic voltammetry was utilized to examine the electrochemical properties of these chiral imides. While these compounds possess intense visible absorptions in their neutral states, one-electron reduction led to intense NIR absorptions, attributed to π*–π* (SOMO → LUMO) transitions of the radical anions of these imides.[3] It was found that the imide group in **1** undergoes a reversible one-electron reduction, while compounds **2**–**4** each undergo two reversible one-electron reduction steps. The first reductions correspond to the formation of radical anions, while the second reductions correspond to the formation of dianions (Scheme 1). Formation of the radical anion of imide **1** occurred at $E_{1/2} = -1.22$ V, while the other three imides were reduced at much less negative potentials. For diimides **2** and **3**, the first one-electron reductions occurred at $E_{1/2} = -0.49$ and -0.46 V, respectively, and the dianions were formed at $E_{1/2} = -1.02$ and -0.74 V. The fact that diimides **2** and **3** are more easily reduced than imide **1** suggests that the odd electrons in these diimides are delocalized throughout these systems. Compound **4** was also reduced in two separate steps, with $E_{1/2}$ values of -0.79 and -1.10 V.

Spectroelectrochemistry of the imides and diimides was performed in order to examine their spectral changes upon reduction. It was found that the radical anions exhibited NIR absorptions with maxima at 833, 770, 958, and 944 nm, respectively, for compounds **1**–**4**, respectively. When compounds **2**–**4** were further reduced, these NIR absorptions disappeared and new peaks appeared in the visible region. The NIR absorption for compound **4** was quite broad covering from 600 to 1180 nm. Figure 2 shows the spectra obtained for diimide **2** in its neutral, radical anion and dianion states.

The fluorescence of naphthalene- and perylene-based diimides has been studied, and it has been shown that the former systems are more fluorescent with high quantum yields than the latter.[21–23] It has also been reported that the intensity of fluorescence emission decreases when perylene-containing polyimides are electrochemically reduced to their radical anion states and that there is no signal for the dianionic states.[11] The fluorescent properties of these chiral chromophores were measured in acetonitrile solutions. Excitation of the naphthalene imides **1** and diimides **2** at 300 nm produced fluorescence emissions at 418 and 549 nm, respectively. The perylene diimides **3** were irradiated at 490 and 526 nm, corresponding to the intense peaks in their absorption spectra. Excitation at 490 nm produced an intense peak at 531 nm, as well as an emission at 570 nm, while excitation at 526 nm also resulted in an emission at 570 nm. Compound **4** emits at 366 nm when excited at 330 nm.

The chiroptical properties of these chiral imides were also examined by CD measurements. The *R*- and *S*-enantiomers displayed opposite spectra, in which the CD bands appeared in similar locations as those found in the corresponding UV–vis spectra. The molar ellipticities for compounds **1**–**3** were between approximately $-75{,}000$ and $75{,}000$ deg cm^2/dmol. However, the *R*- and *S*-enantiomers of **4** possessed molar ellipticities between $-15{,}000$ and $15{,}000$ deg cm^2/dmol, which is consistent with the fact that the optical rotations for

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[†] Imides **1**–**3** were obtained by condensation of (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine (0.58 mL, 4.5 mmol) with 1,8-naphthalic anhydride (0.79 g, 4 mmol), 1,4,5,8-naphthalenetetracarboxylic dianhydride (0.54 g, 2 mmol) or 3,4,9,10-perylenetetracarboxylic dianhydride (0.78 g, 2 mmol) in 5 mL of *m*-cresol containing three drops of isoquinoline. The solutions were stirred at 180–200 °C for 4 h or until no anhydride was detected by IR. The solutions were poured into water or water/methanol solutions and the resulting precipitates were collected in crucibles, washed with water and dried under reduced pressure. The imides were isolated in 78–93% yields.
Compound **1***R*, mp = 165–166 °C, $[\alpha]_D$ +212 (*c* 1.40, $CHCl_3$); **1***S*: mp = 165–167 °C, $[\alpha]_D$ −214 (*c* 1.41, $CHCl_3$).
Compound **1**: (^1H NMR, $CDCl_3$): $\delta = 1.99$ (d, 3H, $J = 7.1$ Hz, CH_3), 6.55 (q, 1H, $J = 7.1$ Hz, CH), 7.22 (t, 1H, $J = 7.3$ Hz, Ar), 7.32 (t, 2H, $J = 7.5$ Hz, Ar), 7.51 (d, 2H, $J = 7.3$ Hz, Ar), 7.72 (t, 2H, $J = 7.8$ Hz, Ar), 8.18 (d, 2H, $J = 7.6$ Hz, Ar), 8.56 (d, 2H, $J = 7.3$ Hz, Ar). (^{13}C NMR, $CDCl_3$): $\delta = 16.3$ (CH_3), 50.1 (CH), 123.1 (Ar–C), 126.9, 126.9, 127.1, 128.1 (Ar–CH), 128.3 (Ar–C), 131.3 (Ar–CH), 131.5 (Ar–C), 133.8 (Ar–CH), 140.9 (Ar–C), 164.2 (CO). IR (NaCl): 1695, 1662 cm^{-1}.
Compound **2***R*, mp = 238–242 °C, $[\alpha]_D$ +273 (*c* 1.40, $CHCl_3$); **2***S*, mp = 237–238 °C, $[\alpha]_D$ −276 (*c* 1.43, $CHCl_3$).
Compound **2**: (^1H NMR, $CDCl_3$): $\delta = 2.00$ (d, 6H, $J = 7.1$ Hz, CH_3), 6.52 (q, 2H, $J = 7.1$ Hz, CH), 7.27 (t, 2H, $J = 7.3$ Hz, Ar), 7.33 (t, 4H, $J = 7.5$ Hz, Ar), 7.49 (d, 4H, $J = 7.7$ Hz, Ar), 8.69 (s, 4H, Ar). (^{13}C NMR, $CDCl_3$): $\delta = 16.3$ (CH_3), 50.8 (CH), 126.7, 126.8 (Ar–C), 127.3, 127.3, 128.3, 131.1 (Ar–CH), 140.0 (Ar–C), 162.9 (CO). IR (NaCl): 1701, 1665 cm^{-1}.
Compound **3***R*, mp = 345 °C (DSC); **3***S*, mp = 346 °C (DSC).
Compound **3**: (^1H NMR, $CDCl_3$): $\delta = 2.07$ (d, 6H, $J = 7.1$ Hz, CH_3), 6.53 (q, 2H, $J = 7.1$ Hz, CH), 7.31 (t, 2H, $J = 7.3$ Hz, Ar), 7.40 (t, 4H, $J = 7.6$ Hz, Ar), 7.64 (d, 4H, $J = 7.6$ Hz, Ar), 7.73 (d, 4H, $J = 7.1$ Hz, Ar), 8.16 (d, 4H, $J = 7.6$ Hz, Ar). (^{13}C NMR, $CDCl_3$): $\delta = 16.3$ (CH_3), 50.6 (CH), 123.1 (Ar–C), 126.9, 126.9, 127.1, 128.1 (Ar–CH), 128.3 (Ar–C), 131.3 (Ar–CH), 131.5 (Ar–C), 133.8 (Ar–CH), 140.9 (Ar–C), 164.2 (CO). IR (NaCl): 1696, 1665 cm^{-1}.

[‡] (*R*)-(+)- or (*S*)-(−)-α-methylbenzylamine (0.2 g, 1.6 mmol) was dissolved in 20 mL DMF, and the corresponding anhydride (0.46 g, 1.6 mmol) was added. The reagents were stirred at room temperature for about 1 h and then heated to reflux for about 16 h. The solution was poured into water, filtered, washed with water, and dried in air. The crude product was purified by flash chromatography, eluting with CH_2Cl_2. After drying in a vacuum oven, a light green product was obtained in 70% yield.
Compound **4***R*, mp = 231–232 °C, $[\alpha]_D$ +38 (*c* 0.254, $CHCl_3$) (C, H, N) (Exp. C, 75.51; H, 3.96; N, 3.65); **4***S*, mp = 236–238 °C, $[\alpha]_D$ −41 (*c* 0.246, $CHCl_3$) (Exp. C, 75.47; H, 4.05; N, 3.67).
Compound **4**: (^1H NMR, $CDCl_3$): $\delta = 1.98$ (d, 3H, $J = 7.3$ Hz, CH_3), 5.64 (q, $J = 7.3$ Hz, 1H, CH), 7.29 (t, 1H, $J = 7.4$ Hz, Ar), 7.35 (t, 2H, $J = 7.3$ Hz, Ar), 7.54 (d, 2H, $J = 7.3$ Hz, Ar), 7.87 (dd, 2H, $J = 5.8$ Hz, Ar), 8.35(dd, 2H, $J = 5.8$ Hz, Ar), 8.73 (s, 2H, Ar). (^{13}C NMR, $CDCl_3$): $\delta = 17.4$ (CH_3), 50.4 (CH), 122.5, 127.6, 127.7, 128.0, 128.6 (Ar–CH), 133.0 (Ar–C), 134.9 (Ar–CH), 135.7, 138.0, 139.6 (Ar–C), 166.3, 181.5 (CO). IR (KBr): 1773, 1717, 1682 cm^{-1}.

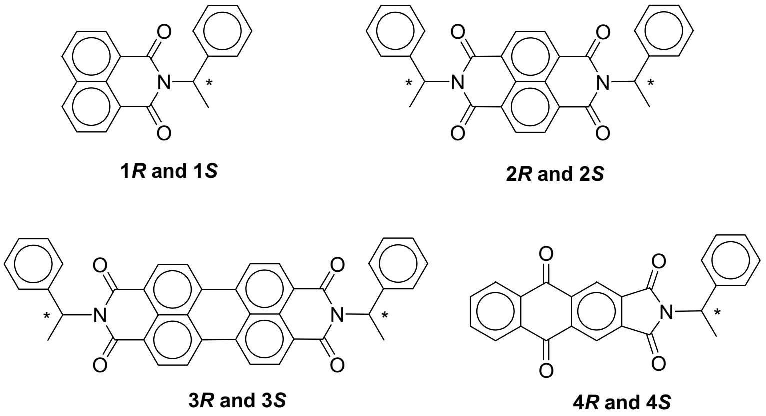
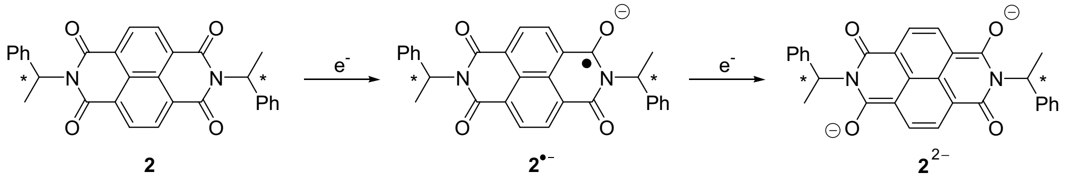


Figure 1. Chiral imides and diimides **1**–**4**.



Scheme 1.

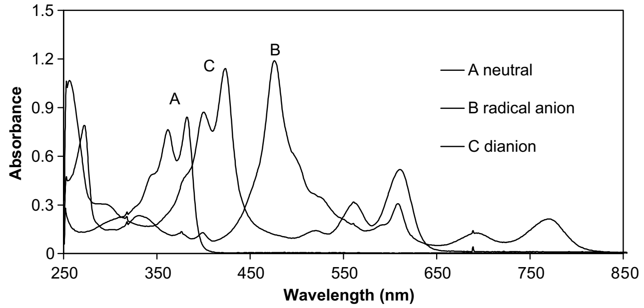


Figure 2. UV/vis-NIR absorption spectra of diimide **2** (10^{-3} M containing 0.1 M TBAP) and its electrochemically generated radical anion and dianion in DMF.

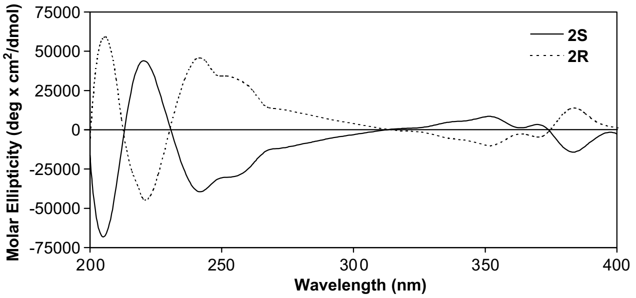


Figure 3. CD spectra of **2***S* and **2***R* in CH_3CN (10^{-3} M).

imides **4** were much lower than those of compounds **1**–**3**. For example, specific optical rotations of **2***S* and **4***S* were −276 and −41, respectively. The CD spectra of **2***S* and **2***R* are shown in Figure 3. It has been reported that the perylene diimides (**3***R* and **3***S*) form aggregates in solution and that their spectra can only be obtained in dilute lipid solutions at 300 K.[10] However, in this study, the absorption and CD spectra of **3***R* and **3***S* were readily obtained in acetonitrile and DMF solutions. In addition, the absorption spectra in acetonitrile showed two sharp peaks at 490 and 526 nm, whereas the spectra previously reported in lipid vesicles were broad and undefined.

Considering the above three optical properties that these chiral imides possess, their chiroptical properties would provide a unique means to modulate this type of molecular switch, as chiroptical (CD) signals would appear at two separate and distinct regions (e.g., at visible and NIR wavelengths) for the two bistable states (e.g., neutral and radical anion). An electrochemical setup was attached to the CD cell used to monitor the changes in chiroptical properties upon redox switching. An acetonitrile solution of the imides containing tetrabutylammonium perchlorate (TBAP) was subjected to electrolysis at progressively more negative potentials. Color changes were observed in the solutions as the imides were reduced to their radical and dianionic states. Changes in the CD signal intensities were apparent in the visible region upon reduction, although there were no new CD bands for the reduced states of chromophores **1**–**4**. Figure 4 shows the CD spectra of diimide **2***S* in its neutral state and reduced states. These results indicate that it is possible to modulate this switching system by applying a bias between 0 and −1.5 V and monitoring the two CD signals at 384 nm, between one intense signal (−15,500 deg cm^2/dmol) and one measuring nearly zero.

In summary, a series of chiral aromatic imides and diimides were synthesized and their optical properties were examined using absorption and fluorescence

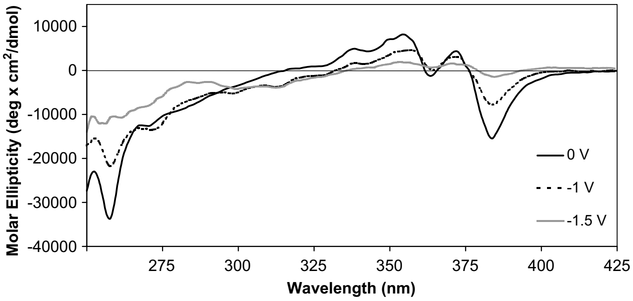


Figure 4. CD spectra of 10^{-3} M **2***S* containing 0.1 M TBAP upon electrochemical reduction.

spectroscopic means, as well as by circular dichroism. Chromophores in their reduced states exhibited significantly different absorption spectra than their neutral analogs, while circular dichroism could detect a reasonably large change in the molar ellipticities of these chiral imides in their neutral and reduced states. Further structural modification can be envisioned by moving the chiral centers closer to the chromophore system, in order to enhance the chiroptical activity and thus increase the chiroptical change upon switching.

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