8.1 INTRODUCTION

N-Phenylphthalimide and its derivatives possess beneficial pharmacological properties that include anticonvulsant (Abdel et al. 2004) and anti-inflammatory activities (Bailleux et al. 1994; Sano et al. 2004), and some imide derivatives are also used in tuberculosis therapy, as well as a growth stimulant for plants (Hargreaves et al. 1970; Shibata et al. 1996). Phthalimide derivatives are also widely used in polymer and synthetic chemistry (Jayakumar et al. 2000; Lima et al. 2002). Hence, such imide derivatives are significant, especially with respect to industrial and pharmaceutical applications. A screening of phthalimide derivatives for anticonvulsant activity test in mice by Vamecq and co-workers (2000) led to the selection of compounds of the type 3i (Scheme 8.2) as shown in figure 1 for oral MES evaluation in rats.

![Figure 8.1: Compound 3i: 2-(2,6-dimethylphenyl)isoindoline-1,3-dione](image)

N-Phenylphthalimide derivatives have been synthesized by many methods, including condensation of an anhydride with an amine in acetic anhydride medium catalyzed by acids (Hurd et al. 1959), N-alkylation of phthaloyl dichloride with azide in the presence of triphenylphosphine (Aubert et al. 1991), and N-alkylation of imides in alcohol media (Walker et al. 1995). However, these methods have obvious
disadvantages, like longer reaction times, use of acids, volatile organic solvents and toxic catalysts at stoichiometric levels, and recovery in small quantities.

Apart from conventional methods, phthalimide synthesis has also been reported in ionic liquids like [bmim][PF$_6$] (Zhou et al. 2003) and [bmim][BF$_4$] (Dabiria et al. 2007) or nonionic green solvents like polyethylene glycol (Liang et al. 2009). Although these methods showed improved yields, they still hold some limitations like longer reaction times, use of organic solvents during work-up, difficulty in recovery of reaction media or higher reaction temperatures. In addition, ionic liquids especially based on imidazole with fluorinated anions suffer from the demerits of being non-bio-degradable, toxic, commercially expensive and their production is also related to the use of large amounts of unsafe and volatile organic solvents (Zhao et al. 2007).

Therefore, it is essential to develop a cost-effective and environmentally benign catalytic system which is of utmost importance in contemporary organic synthesis. Owing to this, we planned the synthesis of $N$-aryl phthalimide derivatives in efficient, bio-degradable and economically viable solvent system such as deep eutectic solvents and glycerol. Deep eutectic solvents include simple eutectics made from a combination of quaternary ammonium salts, like choline chloride, with either hydrogen bond donors like urea and glycerol, or with Lewis acids like zinc chloride. Such eutectic mixtures possess many significant properties (Abbott et al. 2003) similar to conventional ionic liquids, such as low vapor pressure, and low flammability. Their cost-effectiveness is owing to the large scale commercial
production of choline chloride as a chicken feed additive. In addition, the manufacture of choline chloride is done through a simple and efficient gas phase reaction between trimethylamine, ethylene oxide and HCl. The Roger Sheldon E factor (Sheldon et al. 1992) for this salt is close to zero because almost no waste products are formed during this reaction. The same can also be applicable for preparation of deep eutectic solvent since no by-products are generated during its formation.

The ability of deep eutectic solvents to act as catalysts or solvents, has not been explored adequately in the field of synthetic organic chemistry, except for some reactions like Fischer indole synthesis (Mehnert et al. 2002), acetylation of carbohydrates and cellulose (Abbott et al. 2005), selective N-alkylation (Singh et al. 2011) and Knoevenagel condensation (Sonawane et al. 2010).

Glycerol is a polar, non-toxic, biodegradable, recyclable, highly inert and stable solvent manufactured on a large scale from renewable sources. It has been utilized as an alternative for organic solvents in several reactions like asymmetric reductions of prochiral ketones catalyzed by baker's yeast (Wolfson et al. 2006), hydrogenation, C-C coupling, and kinetic resolution of racemates (Wolfson et al. 2006a). A review relating to the use of glycerol as a solvent has been published recently (Gu et al. 2010). Also, a recent paper shows the effectiveness of eutectic solvents of choline chloride and glycerol in esterification reaction (Abbott et al. 2011).

Herein, we present N-aryl phthalimide synthesis in glycerol and two different deep eutectic solvents prepared from choline chloride and malonic acid/urea.

*Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis*
8.2 RESULTS AND DISCUSSION

8.2.1 Synthesis of Deep eutectic solvents

In this study, deep eutectic solvents (DES) were synthesized according to the procedures reported in the literature (Abbott et al. 2003). Choline chloride (1 eq) and urea (2 eq) were mixed together and heated at 74 °C to obtain a clear transparent solution. In a similar way, another deep eutectic solvent was prepared using choline chloride and malonic acid in 1:2 ratio.

Scheme 8.1: Preparation of Deep Eutectic Mixture

8.2.2 Synthesis of N-aryl phthalimide in different media

In order to compare the efficiency of our method with conventional routes, we conducted N-phenylphthamide synthesis (scheme 8.2) in different organic solvents and bio-degradable media like glycerol and deep eutectic solvents, as summarized in Table 8.1.
Scheme 8.2: Synthesis of N-phenylphthalimide derivatives from phthalic anhydride and primary aromatic amines using glycerol or deep eutectic solvents

8.2.3 Optimisation of solvent/ biodegradable media

It is interesting to observe that the reaction gave poor yields in organic solvents. However, deep eutectic solvent (choline chloride: urea) gave best yields when used as a reaction media at 80 °C that could be owing to lesser viscosity of DES or greater solubility of phthalic anhydride at higher temperatures. On the contrary, the deep eutectic solvent of choline chloride and malonic acid gave best yields when used in catalytic amounts. It is also observed that the deep eutectic of choline chloride and glycerol gave poorer yields under all conditions.
**Table 8.1:** Effect of different catalysts and reaction media on the synthesis of N-phenyl phthalimide from phthalic anhydride and aniline

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Solvents(^a)</th>
<th>Catalyst</th>
<th>Reaction temperature (in °C)</th>
<th>Yield (%)(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>-</td>
<td>65</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Dichloromethane</td>
<td>-</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Toluene</td>
<td>-</td>
<td>80</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>-</td>
<td>80</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>Glycerol</td>
<td>-</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>6</td>
<td>DES(^b) (choline chloride:glycerol)</td>
<td>-</td>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>DES(^b) (choline chloride:urea)</td>
<td>-</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>8</td>
<td>DES(^b) (choline chloride: malonic acid)</td>
<td>-</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>9</td>
<td>Glycerol</td>
<td>-</td>
<td>65</td>
<td>56</td>
</tr>
<tr>
<td>10</td>
<td>DES(^b) (choline chloride:glycerol)</td>
<td>-</td>
<td>65</td>
<td>40</td>
</tr>
<tr>
<td>11</td>
<td>DES(^b) (choline chloride:urea)</td>
<td>-</td>
<td>65</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>DES(^b) (choline chloride: malonic acid)</td>
<td>-</td>
<td>65</td>
<td>62</td>
</tr>
<tr>
<td>13</td>
<td>Methanol(^c)</td>
<td>Glycerol</td>
<td>65</td>
<td>52</td>
</tr>
<tr>
<td>14</td>
<td>Methanol(^c)</td>
<td>DES(^b) (choline chloride: glycerol)</td>
<td>65</td>
<td>45</td>
</tr>
<tr>
<td>15</td>
<td>Methanol(^c)</td>
<td>DES(^b) (choline chloride: urea)</td>
<td>65</td>
<td>69</td>
</tr>
<tr>
<td>16</td>
<td>Methanol(^c)</td>
<td>DES(^b) (choline chloride: malonic acid)</td>
<td>65</td>
<td>84</td>
</tr>
</tbody>
</table>

\(^a\) Reaction media: \(^b\) DES (deep eutectic solvent) made of choline chloride and the corresponding acid; \(^c\) Reaction conditions: \(c\) catalytic amount
Chapter 8: Deep Eutectic Solvents and Glycerol: A Simple, Environmentally Benign and Efficient Catalyst/Reaction Media for Synthesis of N-aryl phthalimide derivatives

<table>
<thead>
<tr>
<th></th>
<th>Methanol$^d$</th>
<th>Malonic acid</th>
<th>65</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>Glycerol</td>
<td>-</td>
<td>Room temperature</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>DES$^b$ (choline chloride: urea)</td>
<td>-</td>
<td>Room temperature</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: phthalic anhydride (1.0 g, 7 mmol), aniline (0.6 ml, 7 mmol), reaction media (10 vol), Reaction time - 2.5 hrs.

$^b$ DES: Deep eutectic solvent

$^c$ Reaction conditions: phthalic anhydride (1.0 g, 7 mmol), aniline (0.6 ml, 7 mmol), Catalyst (30% v/v), reaction media (10 vol), Reaction time - 2.5 hrs.

$^d$ Reaction conditions: phthalic anhydride (1.0 g, 7 mmol), aniline (0.6 ml, 7 mmol), Catalyst (40% w/w of malonic acid), reaction media (10 vol), Reaction time - 2.5 hrs.

$^e$ Isolated yields

The $^1$H NMR spectra of the DES (Choline chloride: malonic acid) without and with (30% v/v) dilution using deuterated methanol confirmed that the DES remains in its original form even on dilution. The fact that the reaction did not proceed with malonic acid as catalyst in methanol (Table 8.1, entry 17) suggests that the reaction occurs because of deep eutectic solvent and not due to its individual components.

After screening different methods for synthesis of N-phenylphthalimide, three best and efficient systems were chosen for further studies that included reactions of functionalized aniline derivatives as shown in Scheme 8.2. As summarized in Table 8.2, the reaction gave good results by all the three different methods for a variety of functional groups that include both electron-donating as well as electron-withdrawing groups. The reaction was faster in the presence of electron-donating...
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substituents (Table 8.2, entries 2b-2f), with relatively better yields. The reaction offered moderate to good yields even in the case of electron-withdrawing aromatic amines (Table 8.2, entry 2h) and ortho-substituted amines (Table 8.2, entry 3i). The reaction times were comparatively shorter than many reported methods in the literature.

Table 8.2: Synthesis of N-arylphthalimides in glycerol and deep eutectic solvents ChCl: urea) as reaction media and deep eutectic solvent (ChCl: malonic acid) as catalyst at 80°C and 65°C respectively.

<table>
<thead>
<tr>
<th>Entry</th>
<th>-Ar</th>
<th>Time (h)</th>
<th>Reaction yields (%) a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Glycerolb</td>
<td>Choline Chloride :Urea b</td>
<td>Choline Chloride: Malonic acid c</td>
</tr>
<tr>
<td>3a.</td>
<td>-C₆H₅</td>
<td>2.5</td>
<td>65</td>
</tr>
<tr>
<td>3b.</td>
<td>p-MeOC₆H₅</td>
<td>2</td>
<td>71</td>
</tr>
<tr>
<td>3c.</td>
<td>m-MeOC₆H₅</td>
<td>2.5</td>
<td>70</td>
</tr>
<tr>
<td>3d.</td>
<td>p-MeC₆H₅</td>
<td>2.5</td>
<td>72</td>
</tr>
<tr>
<td>3e.</td>
<td>m-MeC₆H₅</td>
<td>2.5</td>
<td>70</td>
</tr>
<tr>
<td>3f.</td>
<td>o-MeC₆H₅</td>
<td>2.5</td>
<td>68</td>
</tr>
<tr>
<td>3g.</td>
<td>p-ClC₆H₅</td>
<td>3.5</td>
<td>70</td>
</tr>
<tr>
<td>3h.</td>
<td>p-NO₂C₆H₅</td>
<td>4.5</td>
<td>63</td>
</tr>
<tr>
<td>3i.</td>
<td>2,6-diMeC₆H₅</td>
<td>3.5</td>
<td>61</td>
</tr>
</tbody>
</table>
Chapter 8: Deep Eutectic Solvents and Glycerol: A Simple, Environmentally Benign and Efficient Catalyst/Reaction Media for Synthesis of N-aryl phthalimide derivatives

[a] Isolated yields
[b] Reaction conditions: phthalic anhydride (1.0 g, 7mmol), aromatic amine (7mmol), reaction media (10 vol); reaction temperature = 80 °C
[c] Reaction conditions: phthalic anhydride (1.0 g, 7mmol), aniline (7mmol), Catalyst (30% v/v), methanol (10 vol); reaction temperature = 65 °C

The synthesis of N-aryl phthalimide derivatives from phthalic anhydride and primary aromatic amines in imidazolium ionic liquids has been reported earlier in the literature (Zhou et al. 2003). In these studies, the ionic liquid was recycled by heating with ethanol to extract the ionic liquid. In the present method, glycerol/deep eutectic solvent (ChCl: urea) was recovered by simply evaporating water (added during work-up) from the reaction mass after filtration of the solid product. In case of the other deep eutectic solvent (ChCl: malonic acid), the filtrate, obtained after separation of solid product, was subjected to removal of methanol by distillation under vacuum. We tried the reaction of phthalic anhydride with aniline in fresh media/catalyst, as well as in those recovered from the successive runs as summarized in Figure 8.2. The yields did not show much decrease in activity, even after five successive runs. Thus, these methods employing glycerol and deep eutectic solvents are environmentally-benign, both with respect to synthesis and work-up, since it prevented much use of organic solvents especially due to the simplification of procedure. Moreover, the catalyst/media are biodegradable and non-toxic.
Figure 8.2: Recycling of glycerol and deep eutectic solvents in the synthesis of N-phenylphthalimide from phthalic anhydride and aniline
8.3 EXPERIMENTAL

8.3.1 General Methods

The progress of the reaction was monitored by TLC on silica gel plates. All compounds were characterized by Mass spectrometry, FT-IR, UV, $^1$H NMR and $^{13}$C NMR spectroscopy. The compounds were also checked for their melting points which were in well accordance with the literature values (Table 8.2). Also, the $^1$H NMR and $^{13}$C NMR for DES (Choline chloride: Urea) along with the $^1$H NMR spectra of the DES (Choline chloride: Malonic acid) in its actual and diluted forms is recorded. FT-IR spectra were recorded on a Bomem Hartmann and Braun MB-Series FT-IR spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on Varian 300 MHz mercury plus spectrometer and mass spectral data were obtained with a micromass-Q-TOF (YA105) spectrometer. Common reagent grade chemicals were procured from S.D. Fine Chemical Ltd. India, Sigma Aldrich, Loba chemicals and were used without further purification.

8.3.2 Preparation of Deep eutectic solvent

In this study, two deep eutectic solvents were prepared by combining choline chloride with urea/ malonic acid (Scheme 8.1) according to the procedures reported in the literature (Abbott et al. 2003). Choline chloride (100 g, 714 mmol) and urea (86 g, 1.43mol) were placed and heated at 74 °C, until a clear solution began to form. The deep eutectic solvent (a) thus formed (186 g, 100%) was cooled and used in reactions without further purification. The other deep eutectic solvent (b) was prepared similarly by mixing choline chloride (100 g, 714 mmol) and malonic acid (75 g, 714 mmol) at 100°C.
The atom efficiency for both the above reaction is 100% since all the atoms present in the starting materials were incorporated in the products.

8.3.3 General Procedure for synthesis of N-arylphthalimides in bio-degradable media including glycerol/Deep eutectic solvent (ChCl: urea)

In a 50 mL round bottomed flask, a mixture of phthalic anhydride 1 (1.0 g, 7.0 mmol) and reaction media (glycerol/Deep eutectic solvent) (10 ml, 10vol) were taken to which Primary aromatic amine 2 (7.0 mmol) was added to the above mixture in two equal portions with a time interval of 10 minutes. The reaction mixture was stirred at 80 ºC for an appropriate time as indicated in Table 8.2. The product formation was monitored by thin layer chromatography (TLC). After cooling, the reaction mixture was poured in water (10 ml) and the solid product 3 obtained was filtered off, washed with water (3-6 ml), dried in air and further purified by silica gel column chromatography using toluene as an eluent. The mother liquor obtained from filtration was subjected to evaporation of water under vacuum to recover reaction media.

8.3.4 General Procedure for synthesis of N-arylphthalimides using catalytic amounts of Deep eutectic solvent (ChCl: malonic acid)

In a 50 mL round bottomed flask, a solution of phthalic anhydride 1 (1.0 g, 7.0 mmol) in methanol (10 ml, 10vol) was added to which the catalyst (deep eutectic solvent of ChCl: malonic acid) was added in 30%v/v quantity with respect to methanol. Then primary aromatic amine 2 (7.0 mmol) was added in two equal portions with a time interval of 10 minutes and the reaction mixture was stirred at 65 ºC for an appropriate time as indicated in Table 8.2. The product formation was
monitored by thin layer chromatography (TLC). After cooling, the reaction mixture was distilled under vaccum partially to remove excess of methanol and then filtered off to separate the solid product 3 which was further separately washed with water, dried in air and purified by silica gel column chromatography using toluene as an eluent. The mother liquor was subjected to evaporation of methanol under vacuum to recover the catalyst.

This reaction was also scaled up to 50 g of phthalic anhydride with aniline thus producing \( N \)-phenylphthalimide with a yield of 67% in glycerol, yield of 80% in deep eutectic solvent (choline chloride: urea) and 85% in deep eutectic solvent (choline chloride: malonic acid). The recovered bio-degradable media was used for recycling studies.
8.4 CONCLUSION

This paper offers a prospective alternative to conventional catalysts and solvents in the synthesis of $N$-arylphthalimide derivatives by use of glycerol and deep eutectic solvents of choline chloride with urea/malonic acid. These methods showed some important advantages over previously reported procedures like lesser reaction times (within 2-4 hours), easy availability/preparation of catalyst/solvent especially owing to the fact that choline chloride is inexpensive and easily available. Moreover, the deep eutectic solvents are eco-friendly in nature and method using them requires simple work-up method. In addition, the non-tedious recovery, efficient recyclability and cost-effectiveness of glycerol and deep eutectic solvents open a wide scope for industrial applicability of these methods.
8.5 Spectroscopic data for compounds

2-Phenylisoindoline-1,3-dione 3a
m.p. 202 °C (205°C Lit. (23)); λmax (methanol)/nm 214 and 292; IR (KBr); ν max (in cm⁻¹) = 3071, 1736, 1707, 1593, 1495, 1358 and 1261; ¹H NMR (δ in ppm, CDCl₃): δ = 7.25-7.96 (9H, m, aromatic CH); ¹³C NMR (δ in ppm, CDCl₃): δ = 123.8, 126.6, 128.1, 129.1, 131.8, 134.4, 167.3; m/z (EI) 224.0 (M+1); C₁₄H₉NO₂ calculated m/z: 223.0

2-(4-Methoxyphenyl) isoindoline-1,3-dione 3b
m.p. 154 °C (162°C Lit. (23)); λmax (methanol)/nm 228 and 267; IR (KBr); ν max (in cm⁻¹) = 3082, 1740, 1708, 1514, 1463, 1256, 1175; ¹H NMR (δ in ppm, CDCl₃): δ = 7.25-7.96 (8H, m, aromatic CH), 3.85 (3H, s, OCH₃); ¹³C NMR (δ in ppm, CDCl₃): δ = 55.58, 114.55, 123.73, 124.36, 128.01, 131.91, 134.36, 159.34, 167.63; m/z (EI) 254.1 (M+1); C₁₅H₁₁NO₃ calculated m/z: 253.1

2-(3-Methoxyphenyl) isoindoline-1,3-dione 3c
m.p. 122°C (128°C Lit. (24)); λmax (methanol)/nm 226 and 228; IR (KBr); ν max (in cm⁻¹) = 2843, 1781, 1720, 1608, 1497, 1463, 1379, 1225; ¹H NMR (δ in ppm, CDCl₃): δ = 6.98-7.96 (8H, m, aromatic CH), 3.84 (3H, s, OCH₃); ¹³C NMR (δ in ppm, CDCl₃): δ = 55.51, 112.45, 114.19, 118.95, 123.82, 129.86, 131.83, 132.76, 134.46, 160.13, 167.27; m/z (EI) 254.1 (M+1); C₁₅H₁₁NO₃ calculated m/z: 253.1

2-(4-Methylphenyl) isoindoline-1,3-dione 3d
m.p. 200 °C (204°C Lit. (23)); λmax (methanol)/nm 235 and 292; IR (KBr); ν max (in cm⁻¹) = 3040, 2916, 2864, 1747, 1714, 1514, 1464, 1383, 1219; ¹H NMR (δ in ppm, CDCl₃): δ = 7.31-7.95 (8H, m, aromatic CH), 2.41 (3H, s, CH₃); ¹³C NMR (δ in ppm, CDCl₃):
2-(3-Methylphenyl) isoindoline-1,3-dione 3e
mp 176 °C (176°C Lit. (23)); $\lambda_{\text{max}}$ (methanol)/nm 236 and 292; IR (KBr); $\nu_{\text{max}}$ (in cm$^{-1}$) = 2923, 1771, 1709, 1606, 1489, 1465, 1369, 1238; $^1$H NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 7.23-7.94 (8H, m, aromatic CH), 2.42 (3H, s, CH$_3$); $^{13}$C NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 21.40, 123.68, 127.28, 128.93, 129.02, 131.56, 131.80, 134.34, 139.10, 167.35; m/z (EI) 238.0 (M+1);C$_{15}$H$_{11}$NO$_2$ calculated m/z: 237.0

2-(2-Methylphenyl) isoindoline-1,3-dione 3f
m.p. 180 °C (182 °C Lit. (23)); $\lambda_{\text{max}}$ (methanol)/nm 234 and 294; IR (KBr); $\nu_{\text{max}}$ (in cm$^{-1}$) = 3090, 2924, 2851, 1745, 1712, 1496, 1463, 1379, 1225; $^1$H NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 7.21-7.96 (8H, m, aromatic CH), 2.21 (3H, s, CH$_3$); $^{13}$C NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 17.97, 123.66, 126.79, 128.70, 129.34, 130.60, 131.06, 131.94, 134.27, 136.47, 167.25; m/z (EI) 238.0 (M+1);C$_{15}$H$_{11}$NO$_2$ calculated m/z: 237.0

2-(4-Chlorophenyl) isoindoline-1,3-dione 3g
m.p. 194 °C (192°C In a 50 mL round bottomed flask, Lit. (25)); $\lambda_{\text{max}}$ (methanol)/nm 218 and 292; IR (KBr); $\nu_{\text{max}}$ (in cm$^{-1}$) = 3061, 1742, 1715, 1496, 1389, 1121; $^1$H NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 7.26-7.96 (8H, m, aromatic CH); $^{13}$C NMR ($\delta$ in ppm, CDCl$_3$): $\delta$ = 123.89, 127.71, 129.34, 130.28, 131.67, 133.84, 134.60, 167.01; m/z (EI) 258.0 (M+1);C$_{14}$H$_{8}$ClNO$_2$ calculated m/z: 257.0

2-(4-Nitrophenyl)isoindoline-1,3-dione 3h
M.p. 268 °C (267 °C Lit. (23)); $\lambda_{\text{max}}$ (methanol)/nm 225, 270 and 345; IR (KBr); $\nu_{\text{max}}$ (in cm$^{-1}$) = 3118, 1782, 1728, 1517, 1342, 1596, 1494, 1377, 1224; $^1$H NMR ($\delta$...
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Synthesis of novel colorants for dye-sensitized solar cells and use of greener protocols for heterocyclic synthesis

δ = 7.26-8.40 (8H, m, aromatic CH); $^{13}$C NMR (δ in ppm, CDCl$_3$): δ = 29.78, 124.27, 124.52, 126.43, 131.47, 135.09, 166.50; m/z (El) 269.0 (M+1); C$_{14}$H$_8$N$_2$O$_4$ calculated m/z: 268.0

2-(2,6-Dimethylphenyl)isoindoline-1,3-dione 3i
m.p. 202 °C; $\lambda_{max}$ (methanol)/nm 230 and 291; IR (KBr); $\nu_{max}$ (in cm$^{-1}$) = 3070, 2933, 2862, 1778, 1706, 1595, 1468, 1375, 1260; $^1$H NMR (δ in ppm, CDCl$_3$): δ = 7.2-7.97 (7H, m, aromatic CH), 2.16 (6H, s, CH$_3$); $^{13}$C NMR (δ in ppm, CDCl$_3$): δ = 18.06, 123.75, 128.46, 129.42, 129.85, 131.98, 134.34, 136.85, 167.20; m/z (El) 261.1 (M+1); C$_{15}$H$_{11}$NO$_2$ calculated m/z: 251.1

DES (ChCl:urea)
$^1$H NMR (δ in ppm, CDCl$_3$): δ = 3.187 (9H, s, CH$_3$), 3.505 (2H, m, CH$_2$), 3.95 (2H, m, CH$_2$), 4.424 (1H, OH), 6.095 (8H, NH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$), δ= 161.9, 67.8, 55.9, 54.0.

DES (ChCl:malonic acid)
$^1$H NMR (δ in ppm, DMSO): δ = 4.5 (1H, OH), 3.9 (2H, m, CH$_2$), 3.5 (2H, m, CH$_2$), 3.2 (9H, s, CH$_3$), 1.9 (2H, s, CH$_2$); $^{13}$C NMR (75 MHz, CDCl$_3$), δ= 161.9, 67.8, 55.9, 54.0.

DES (ChCl:malonic acid) (30 % v/v in Deuterated methanol)
$^1$H NMR (δ in ppm, Deuterated MeOH): δ = 5.2 (2H, s, COOH), 4.6 (1H, OH), 4.0 (2H, m, CH$_2$), 3.6 (2H, m, CH$_2$), 3.3 (9H, s, CH$_3$), 2.0 (2H, s, CH$_2$).
2-phenylisoindoline-1,3-dione (3a)
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2-(4-methoxyphenyl) isoindoline-1,3-dione (3b)
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2-(3-methoxyphenyl) isoindoline-1,3-dione (3c)
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2-m-tolyisoindoline-1,3-dione (3e)
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2-o-tolyisoindoline-1,3-dione (3f)
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2-(4-chlorophenyl)isoindoline-1,3-dione (3g)
2-(4-nitrophenyl) isoindoline-1,3-dione (3h)
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2-(2,6-dimethylphenyl)isoindoline-1,3-dione (3i)
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$^1$H-NMR spectra of DES (ChCl: Malonic acid)
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$^1$H-NMR spectra of DES (ChCl:Malonic acid) [(30% v/v) diluted with deuterated methanol]
13C NMR Spectra

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FT-IR spectra

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