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Novel indoline dye tetrabutylammonium carboxylates attached with a methyl group on the cyclopentane ring for dye-sensitized solar cells

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ABSTRACT

(2*R*,3a*R*,8b*R*)- and (2*S*,3a*S*,8b*S*)-2-Methyl indoline dye tetrabutylammonium carboxylates exhibited the highest conversion efficiency among four *regio* and stereo isomers. These indoline dyes also showed higher conversion efficiency than **DN350**.

1. Introduction

Significant effort has been directed toward the development of efficient organic sensitizers for dye-sensitized solar cells (DSSCs). Most efficient sensitizers such as porphyrines [1–7] and carbazole dyes [8–12] possess long alkyl chains to prevent H-aggregate formation and improve the short-circuit photocurrent (J_{sc}) [13–15]. The alkyl group(s) can also inhibit approaching the reduction species of the electrolyte to improve the open-circuit photovoltage (V_{oc}) [16,17]. Thus, the introduction of alkyl group(s) into highly efficient sensitizers can further improve the cell performance. Indoline dyes are also highly efficient organic sensitizers [18–24]. A single X-ray crystallography of **D149** ethyl ester, a well-known indoline dye, indicated that the planar π-chromophore is surrounded by the cyclopentane ring, phenylene moiety, and a phenyl group to prevent aggregate formation [25]. We reported that the substitution of 4-(2,2-diphenylethenyl)phenylene moiety with 2-(9,9-dimethylfluorenyl) group could improve the cell performance due to less H-aggregate formation [20]. Therefore, **DN350** (Scheme 1) exhibits the best conversion efficiency (η) among the indoline dyes. We consider that when an alkyl group is introduced onto the cyclopentane ring, the steric hindrance increases, thereby further preventing aggregate formation of indoline dyes. We report here the synthesis, identification, and performance of novel indoline dye tetrabutylammonium carboxylates substituted with a methyl group on the cyclopentane ring.

2. Results and discussion

2.1. Synthesis

New indoline dyes **9A**, **9B**, **9C**, and **9D** were prepared as shown in Scheme 1. 3-Methylcyclopentanone (**1**) was allowed to react with phenylhydrazine (**2**) to give a mixture of 1- and 2-methylindoles **3** with a 30% yield. This reaction has been reported to afford both 1- and 2-methyl *regio* isomers **3** [26]. The product

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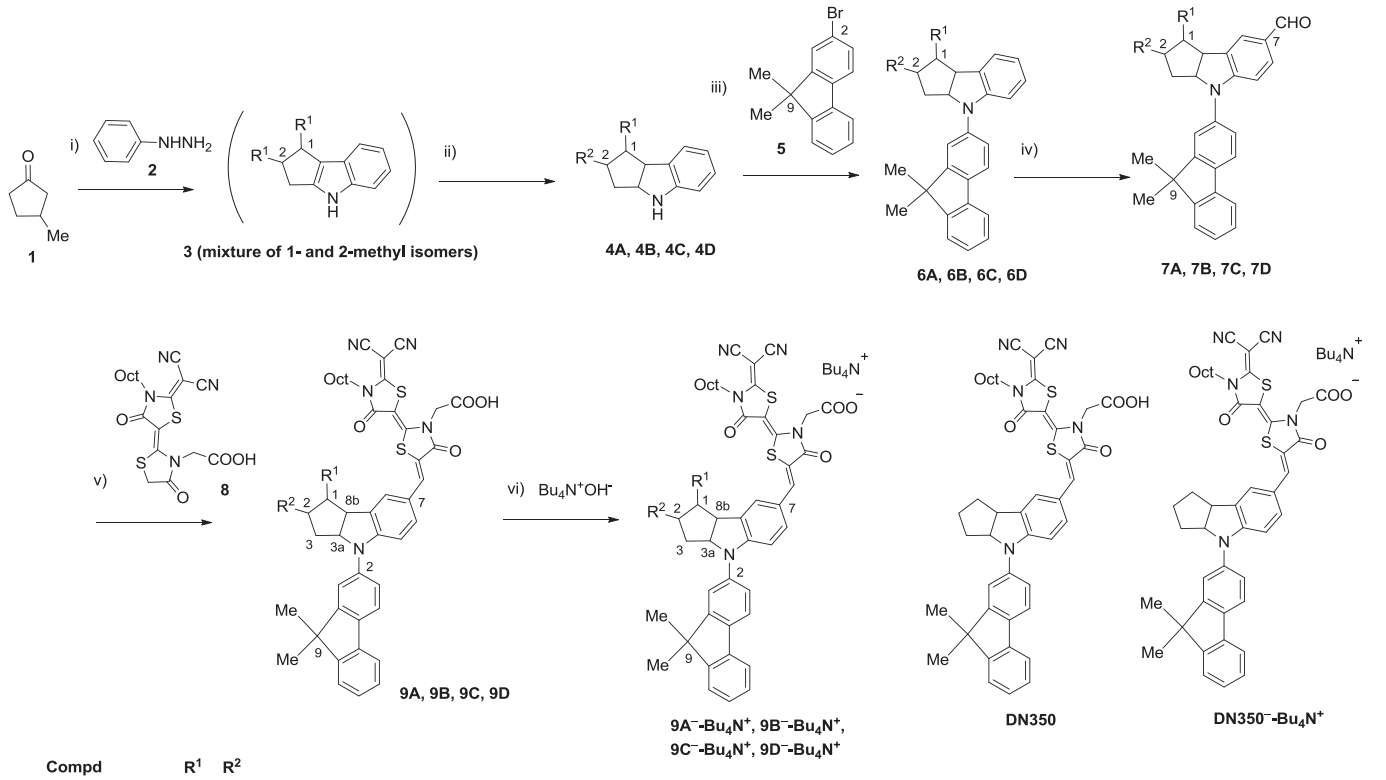

Compd	R^1	R^2	
4A, 6A, 7A, 9A	Me	H	(1*R*, 3a*R*,8b*R*), (1*S*, 3a*S*,8b*S*)
4B, 6B, 7B, 9B	H	Me	(2*R*, 3a*S*,8b*S*), (2*S*, 3a*R*,8b*R*)
4C, 6C, 7C, 9C	Me	H	(1*R*, 3a*S*,8b*S*), (1*S*, 3a*R*,8b*R*)
4D, 6D, 7D, 9D	H	Me	(2*R*, 3a*R*,8b*R*), (2*S*, 3a*S*,8b*S*)
DN350	H	H	

Scheme 1. Reagents and conditions: i) **1** (1.0 equiv.), **2** (1.0 equiv.), conc. H_2SO_4, 100 °C, 6 h reflux, ii) Pd/C, H_2, CH_2Cl_2, room temperature, overnight, separation by medium pressure liquid chromatography, iii) **4** (1.0 equiv.), **5** (1.1 equiv.), *t*-BuOK (2.5 equiv.), $Pd(OAc)_2$ (2 mol%), X-Phos (1.0 equiv.), toluene, reflux, overnight, iv) **6** (1.0 equiv.), $POCl_3$ (18 equiv.), DMF, room temperature, 24 h, v) **7** (1.0 equiv.), **8** (1.2 equiv.), AcOH, $AcONH_4$, reflux, 2 h, vi) **9** (1.0 equiv.) $Bu_4N^+OH^-$ (1.0 equiv.), MeOH–$CHCl_3$, stirring at room temperature (30 min) then sonication (30 min).

distribution between the 1- and 2-methyl isomers was calculated to be *ca.* 1–2 by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The mixture was treated with hydrogen gas in the presence of Pd/C to produce 1- and 2-methylindolines **4**. Then, the products were separated using medium pressure liquid chromatography (SiO_2, hexane:ethyl acetate = 100:1). Three asymmetric centers, 1- or 2-, 3a- and 8b-positions, are present in **4**. Since the hydrogenation reaction proceeds *via syn* addition at the double bond from both the *Re* and *Si* faces of indoles **3**, a pair of diastereomers with a pair of enantiomers are produced for the 1- and 2-methyl *regio* isomers, respectively. When the pair of enantiomers are not separated, two diastereomers are isolated from 1- and 2-methylindolines **4**. Fortunately, four *regio* and stereo isomers **4A**, **4B**, **4C**, and **4D** were successfully isolated in 11, 6, 13, and 42% yields, respectively.

Fig. 1 shows the H–H correlation spectroscopy (COSY) spectrum of **4A**. The doublet methyl proton peak at 0.99 ppm correlates with the multiplet H1 peak in the range of 2.14–2.26 ppm, which in turn correlates with the *vicinal* doublet–doublet H^{8b} peak at 3.69 ppm. Therefore, compound **4A** is identified as the 1-methylindoline derivative. The coupling constants of the doublet–doublet H^{8b} peak are observed to be 9.2 and 9.2 Hz. Two sets of diastereomers are considerable for **4A**: the racemate of (1R, 3a*R*, 8bR)- and (1*S*, 3a*S*, 8b*S*)-1-methylindoline, in which the H1 and H^{8b} protons are located at the *anti*-position, and the racemate of (1R, 3a*S*, 8b*S*)- and (1*S*, 3a*R*, 8bR)-1-methylindoline, in which the H1 and H^{8b} protons at the *syn*-position. The optimized structures of these isomers by the DFT calculations (B3LYP/3-21G) are shown in Scheme S1. The H1–C1–C^{8b}–H^{8b} torsion angles of the *anti*- and *syn*-H1 and H^{8b} protons are calculated to be 162.2° and 33.10°, respectively. According to the Karplus rule, the coupling constant of *anti*-protons is larger than that of the *syn*-protons. As describe later, compound **4C** is also 1-methylindoline derivative. The doublet H1-H^{8b} coupling constant of **4A** (9.2 Hz) is larger than that of **4C** (5.5 Hz) (Fig. 3), the H1 and H^{8b} protons being located at *anti*-position. Therefore, compound **4A** is identified as the racemate of (1R, 3a*R*, 8bR)- and (1*S*, 3a*S*, 8b*S*)-1-methylindoline, which are the diastereomers of (1R, 3a*S*, 8b*S*)- and (1*S*, 3a*R*, 8bR)-1-methylindoline **4C**.

Fig. 2 presents the heteronuclear multiple-bond correlation (HMBC) spectrum of **4B**. The doublet methyl proton peak at 0.99 ppm correlates with the C1 and C3 peaks at 43.65 and 47.63 ppm, respectively. Furthermore, the C2 peak at 32.44 ppm correlates with the H^{8b} and H^{3a} peaks at 3.83 and 4.38 ppm, respectively. No correlation between the methyl proton and C^{8b} peaks is observed. Therefore, compound **4B** is identified as 2-methylindoline derivative.

Fig. 3 shows the H–H COSY spectrum of **4C**. The methyl proton peak at 1.15 ppm correlates with the *germinal* multiplet H1 peak in the range of 2.01–2.13 ppm, which correlates with the *vicinal* H^{8b} peak at 3.19 ppm. This result indicates that compound **4C** is the 1-methyl derivative. The coupling constants of doublet-doublet H^{8b} peak are observed to be 9.2 and 5.5 Hz. The H^{8b}–H1 coupling