



# Study of an indoline–phenothiazine based organic dye for Dye-Sensitized Solar Cells. Theoretical calculations and experimental data



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## ABSTRACT

A new donor– $\pi$ -acceptor organic dye based on an indoline–phenothiazine combination (denoted, **VG12**) was synthesized and studied as sensitizer of nanoparticulate titania in standard Dye-Sensitized Solar Cells. Theoretical calculations gave the profile of the dye, which was verified by spectrometric measurements. The energy levels of the dye are located at  $-3.5$  eV and  $-5.5$  eV for its LUMO and HOMO levels, respectively. The efficiency of solar cells constructed with this new dye was measured in comparison with equivalent constructions based on the standard ruthenium dye **N719**. The obtained efficiency was 7.2% in the case of **VG12** and 9.3% in the case of **N719**. The reported data also show the very important effect that the additive chenodeoxycholic acid has on the performance of the solar cell.

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## 1. Introduction

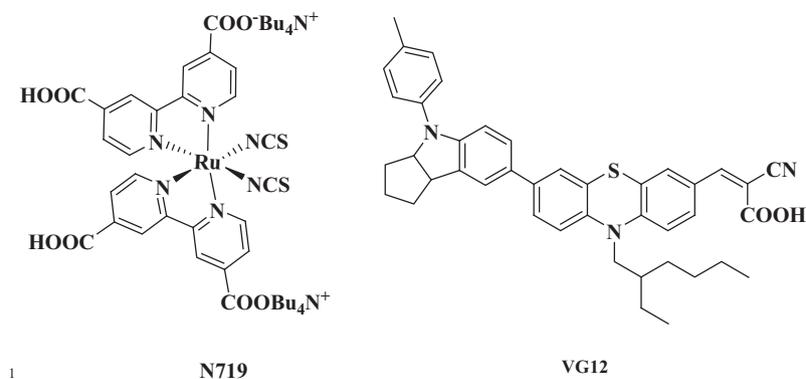
Sensitized mesoscopic solar cells make one of the most popular fields of research. The main component of sensitized solar cells is a nanostructured oxide semiconductor, typically nanoparticulate titania (np-TiO<sub>2</sub>), which is combined with a molecular or a semiconductor sensitizer. The sensitizer absorbs visible light and injects the photogenerated excited electron into the conduction band of the semiconductor. This is the first and principal step of electron-hole separation and transformation of light into electricity. Most extensively studied molecular sensitizers are organometallic complexes of Ru and among them the most popular are bis(tetrabutylammonium)-*cis*-di(thiocyanato)-N,N'-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) (**N719** dye, see *Scheme 1*) [1] and tri thiocyanato 4,4'-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (**Black Dye**) [2], which produced solar-to-electricity conversion efficiencies ( $\eta$ ) up to 10.2% under 100 mW cm<sup>-2</sup> AM 1.5 simulated solar radiation. Novel

Ruthenium dyes have been able to raise the efficiency up to 11.3% by increasing the response into the red region of the solar spectrum while maintaining high molecular absorption extinction coefficient [3]. Finally, by moving beyond the bipyridine ligand-based complexes into porphyrin dyes and utilizing cobalt-based electrolytes, efficiency has been recently raised to the record high of 13% [4].

Despite their high efficiencies, the above dye sensitizers are rather expensive to produce and they are charged of toxicity because of their metal component. Metal-free organic donor- $\pi$  bridge-acceptor (D- $\pi$ -A) dyes can be prepared rather inexpensively by following established design strategies. The major advantages of these metal-free dyes are their tuneable absorption and electrochemical properties through suitable molecular design [5]. Recently, numerous organic dyes leading to the construction of Dye-Sensitized Solar Cells (DSSCs) with high efficiency have been reported. Such organic dyes generally consist of electron donor moieties like triarylamine [6], carbazole [6] and indoline [7],  $\pi$ -conjugated groups like thiophenes, benzene, benzothiadiazole as spacer and electron withdrawing units like cyano acetic acid, rhodanine acetic acid, malonic acid and pyridine as acceptors [8]. Many different organic dyes with conversion efficiencies in the range of 6–8% have been reported in the last years but only a

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**Scheme 1.** Molecular structures of dyes **VG12** and **N719**.

few examples have overcome efficiencies of 10% [9–12]. Recently D-A- $\pi$ -A and D-D- $\pi$ -A type organic dyes have been shown to facilitate electron aggregation and improve photo stability [13–15].

In this work, we synthesized a new organic dye (denoted, **VG12**) based on an indoline-phenothiazine unit with cyano acetic acid as acceptor (Scheme 1). Indoline group is introduced as an electron donor while the ethylhexyl alkyl chain on the phenothiazine group is introduced to prevent aggregation. The indoline group with good electron donating and transporting ability is attached on the electron rich phenothiazine unit, which provides satisfactory relay for electron migration from indoline to cyano acrylate acceptor. The addition of indoline moiety to phenothiazine gave a satisfactory solar cell efficiency, which reached 7.20% not much lower than the corresponding cells made with N719, which gave an efficiency of 9.3%. The design of **VG12** was supported by Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) theoretical calculations.

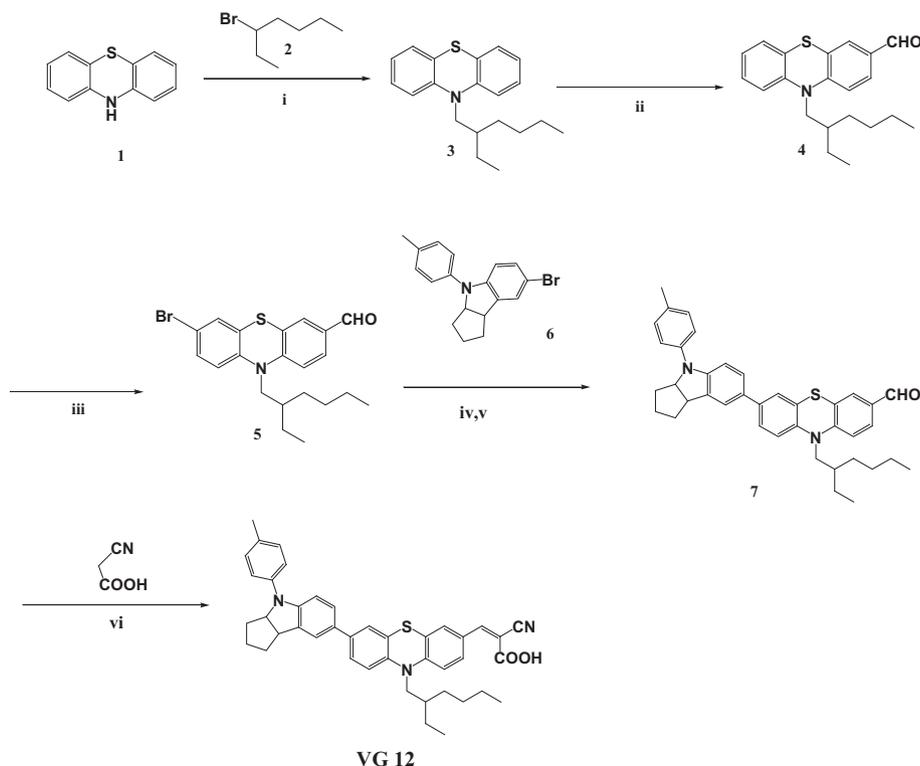
## 2. Experimental

### 2.1. Materials

N,N-dimethylformamide (DMF), phosphorylchloride, 1,2 dichloromethane, chloroform, piperidine and THF were distilled before use. Pd(PPh<sub>3</sub>)<sub>4</sub>, N-bromosuccinimide (NBS), potassium carbonate, Sodium *tert*-butoxide cyanoacetic acid, chenodeoxycholic acid, 4-*tert*-butylpyridine (TBP) and *n*-butyllithium (2.0 M in hexane) were purchased from Sigma–Aldrich.

### 2.2. Synthesis and characterization

The structure of **VG12** is shown in Scheme 1 and the synthetic route is depicted in Scheme 2. 1,7-bromo-1,2,3,3a,4,8b-hexahydro-4-(4-methylphenyl)-cyclopent[b]indole(6) was synthesized as per the earlier reported procedure [16]. Ethyl hexyl



**Scheme 2.** Synthetic route of **VG12**. (Reaction conditions): (i) sodium *tert*-butoxide, dry THF, reflux 12 h. (ii) DMF, POCl<sub>3</sub>, 1,2 dichloroethane. (iii) NBS, CHCl<sub>3</sub>, room temperature. (iv) *n*-BuLi, THF, B(OCH<sub>3</sub>)<sub>3</sub>, –78 °C; (v) Pd(PPh<sub>3</sub>)<sub>4</sub>, 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution, THF, 6 h, 80 °C; (vi) piperidine, CHCl<sub>3</sub>, reflux 12 h.

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