



# Synthesis, optical, and electrochemical properties of 2,3-diphenyl-10*H*-indeno[1,2-*g*]quinoxaline, 15*H*-dibenzo[*a,c*]indeno[1,2-*i*]phenazine, and 15*H*-indeno[1,2-*i*]phenanthro[4,5-*abc*]phenazine derivatives



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## ABSTRACT

A series of 2,3-diphenyl-10*H*-indeno[1,2-*g*]quinoxaline, 15*H*-dibenzo[*a,c*]indeno[1,2-*i*]phenazine, and 15*H*-indeno[1,2-*i*]phenanthro[4,5-*abc*]phenazine derivatives containing different terminal aromatic units such as phenyl, phenylethynyl, naphthyl, anthryl, pyrenyl, or 4-(diphenylamino)phenyl have been synthesized by employing palladium-catalyzed C–C cross-coupling reactions in good yields. All of the target compounds were characterized using <sup>1</sup>H NMR, <sup>13</sup>C NMR, high resolution MS, optical absorption, and emission spectra. Even though the electronic absorption spectra of the compounds were influenced by the nature of the peripheral arenes, the emission spectra indicated close similarity for the excited states in the 15*H*-indeno[1,2-*i*]phenanthro[4,5-*abc*]phenazine series compounds. Most compounds possess a medium fluorescence-emitting ability with  $\phi_{FL}$  values in the region of 0.40–0.71 and displayed blue, green, yellow, or red emission depending on the nature of the whole molecule. Structure–optical behavior characteristics and further details of the electronic properties from cyclic voltammetry measurements and theoretical calculations were discussed.

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## 1. Introduction

Conjugated materials, which are one of the most investigated classes of advanced materials, have attracted much attention in recent years because of their potential applications in electronics, photonics, and optoelectronics [1–3]. Enormous efforts have been made toward the development of new high-performance materials with desirable properties [4–21]. Due to their rigid planarized oligophenyl unit within the backbone as well as the possibility of facile functionalization at the methylene bridge, fluorene-based derivatives, including polymers and oligomers, exhibit unique photoluminescent properties and have been widely used as luminescent materials [22–24], as well as carrier transport materials for FETs [25–28]. However, small-molecule fluorene derivatives with good thermal stability and high photoluminescence (PL) efficiency have been little reported [29–31]. Until now, there

have only been a few linear fused-ring compounds with the introduction of the fluorene substructure, which may be due to the lack of efficient synthetic strategies [32–34]. Fluorescent heterocyclic compounds are of interest in many areas such as emitters for electroluminescence devices, molecular probes for biochemical research, in traditional textile and polymer fields, fluorescent whitening agents and photoconducting materials. Diazines which belong to the most important heterocycles containing nitrogen are six-membered aromatics with two nitrogen atoms. Among which, pyrazine and quinoxaline derivatives have been intensively studied not only for their medicinal uses, but also for their technical applications as dyes, electroluminescent materials, organic semiconductors and as suitable ligands in coordination chemistry [35–38]. Fluorescent characteristics rely largely on molecular structure and molecular assembly. Changes in the substitutional groups and substitution pattern, conjugation, and molecular electronic structure can bring about very different optical and physical properties such as absorption, emission, and thermal stability for such materials. There is presently great interest to increase the structural or spatial dimensions of  $\pi$ -conjugated molecules in order to tune and acquire more favorable physical properties.

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We recently presented detailed structure–property relationship investigations into new fluorene derivatives based on 3,9-dioctyl-9,9-dioctylfluoreno[3,2-*d*]imidazole (DOFI) and 10,10-dioctyl-3,6-dihydrofluoreno[2,3-*d*:6,7-*d'*]diimidazoles (DOFDIs) [39,40]. As an expanded continuation of our studies related to the synthesis and optical properties of heterocycle-based chromophores, in this paper, we present the initial synthesis and characterization of a series of asymmetrically substituted 2,3-diphenyl-10*H*-indeno[1,2-*g*]quinoxaline derivatives **3a–g**, 15*H*-dibenzo[*a,c*]indeno[1,2-*i*]phenazine derivatives **4a–g**, and 15*H*-indeno[1,2-*i*]phenanthro[4,5-*abc*]phenazine derivatives **5a–g** (Fig. 1), in which a fluorene unit is fused with 2,3-diphenylpyrazine, dibenzo[*f,h*]quinoxaline or phenanthro[4,5-*fg*]quinoxaline, respectively. Extended conjugation is believed to result in intermolecular stacking interactions which are detrimental to the emission characteristics. Therefore, two octyl groups were introduced to the C-9 position of the fluorene moiety to increase solubility as well as to release intermolecular  $\pi$ – $\pi$  stacking. And we focused our attention on different terminal aromatic units such as phenyl, phenylethynyl, naphthyl, anthryl, pyrenyl, or 4-(diphenylamino)phenyl to investigate their optical and electrochemical properties.

## 2. Experimental

### 2.1. Reagents and instruments

Commercially available reagents were purchased and were used without further purification unless otherwise mentioned.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance (500 MHz) spectrometer in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ , unless otherwise noted. Chemical shifts are reported in parts per million (ppm) and coupling constants (*J*) are reported in Hertz (Hz). Coupling patterns are described by abbreviations: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad). Chemical shifts were reported in the scale relative to  $\text{CHCl}_3$  (7.26 ppm) or  $\text{DMSO-}d_6$  (2.50 ppm) for  $^1\text{H}$  NMR, and to  $\text{CDCl}_3$  (77.16 ppm) or  $\text{DMSO-}d_6$  (39.70 ppm) for  $^{13}\text{C}$  NMR, as internal references. The center line of the multiplets of  $\text{DMSO-}d_6$  was defined as 2.50 for  $^1\text{H}$  NMR. Silica gel plate GF254 was used for thin layer chromatography (TLC) and silica gel 300–400 mesh was used for flash column chromatography. Melting points were measured on a digital melting point apparatus without correction. Yields are shown in terms of those isolated pure materials. The absorption and fluorescence spectra were recorded using a UV-2501Pc spectrophotometer and an RF-5301 fluorescence spectrophotometer. HR-MS were recorded on a Bruker Daltonics, Inc. APEXIII7.0 TESLA FTMS instrument. The redox potentials of the

compounds were determined with cyclic voltammetry (CV) using a Base 2000 CV system. HOMO values were recalculated from reported literature values as  $\text{HOMO} = [E_{\text{onset}}]_{\text{red/ox}} (\text{vs SCE}) + 4.6$ ,  $E_g = 1240/\text{UV}(\text{onset})$ . Density functional theory (DFT) calculations have also been applied to characterize the three-dimensional geometries and the frontier molecular orbital energy levels of the representative compounds at the B3LYP/6-31G\* level by using the Gaussian 03 program.

### 2.2. Synthesis

#### 2.2.1. 2-Bromo-7-nitro-9*H*-fluorene (**1b**)

To a stirred solution of 2-nitrofluorene [41] (**1a**, 5 g, 23.67 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) was added  $\text{Br}_2$  (47.34 mmol) slowly. The mixture was stirred for 5–6 h. The yellow precipitate was filtered off and washed with 5%  $\text{NaHSO}_3$ . The crude yellowish product was purified by recrystallization from DMF to afford **1b** (5.5 g, 80% yield) as light yellow powder. Mp 235–237 °C  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ ):  $\delta$  ppm 8.46 (s, 1H), 8.28 (m, 1H), 8.16 (m, 1H), 8.03 (m, 1H), 7.90 (s, 1H), 7.66 (m, 1H), 4.10 (s, 2H).

#### 2.2.2. 2-Bromo-7-nitro-9,9-dioctyl-9*H*-fluorene (**1c**)

To a solution of compound **1b** (5.5 g, 18.96 mmol) in DMSO (30 mL) were added KOH (4.25 g, 75.8 mmol) and the mixture was stirred at room temperature. After stirring for 30 min,  $n\text{-C}_8\text{H}_{17}\text{Br}$  (11 g, 56.87 mmol) was added slowly with the help of syringe. The resulting mixture was stirred continually for an additional 5 h. The reaction mixture was then extracted with ethyl acetate (30 mL  $\times$  3), and the organic layer was washed with saturated brine and dried over  $\text{Na}_2\text{SO}_4(\text{s})$ . After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate–hexane (1:30) as eluent to afford **1c** (9 g, 92% yield) as a yellow-white powder. Mp 60–62 °C  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  ppm 8.27–8.24 (dd,  $J_1 = 7.0$  Hz,  $J_2 = 2.0$  Hz, 1H), 8.18 (d,  $J = 1.9$  Hz, 1H), 7.76 (d,  $J = 6.9$  Hz, 1H), 7.65–7.62 (m, 1H), 7.54–7.51 (m, 2H), 2.06–1.93 (m, 4H), 7.65–7.62 (m, 1H), 1.23–1.02 (m, 20H), 0.81 (t,  $J = 7.1$  Hz, 6H), 0.61–0.51 (m, 4H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  ppm 154.39, 151.62, 147.39, 146.45, 137.71, 130.72, 126.57, 123.69, 123.43, 122.48, 119.96, 118.29, 56.00, 39.94, 31.71, 29.76, 29.12, 23.69, 22.56, 14.03.

#### 2.2.3. 7-Bromo-9,9-dioctyl-9*H*-fluorene-2-amine (**1d**)

To a stirred solution of compound **1c** (9 g, 16.5 mmol) in MeOH (30 mL) were added ferric chloride hexahydrate (0.45 g, 1.65 mmol) and activated carbon (1.8 g). The mixture was heated to reflux with stirring under nitrogen atmosphere. After refluxed for 10 min,

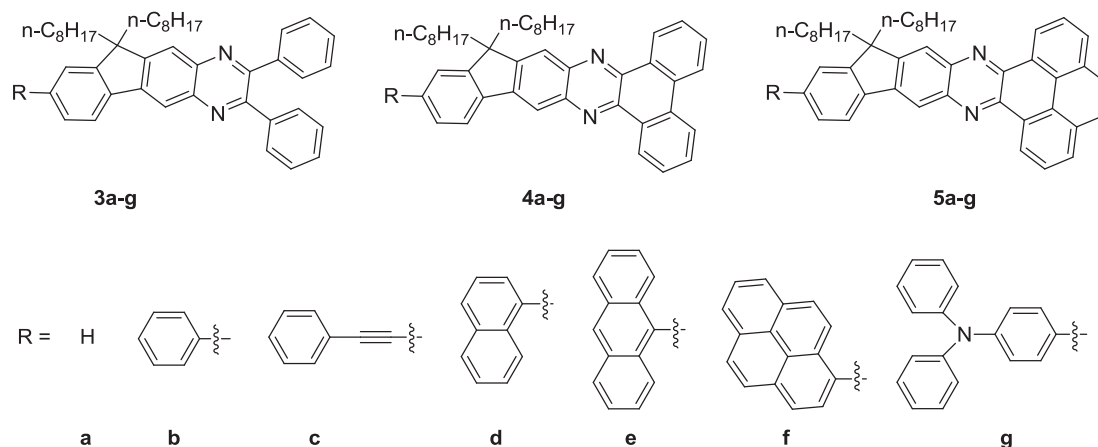


Fig. 1. The molecular structures of the studied chromophores.

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