Synthesis and Properties of 1-(4-Aminophenyl)-2,4-dicyano-3-diethylamino-9,9-diethylfluorenes: Potential Fluorescent Material

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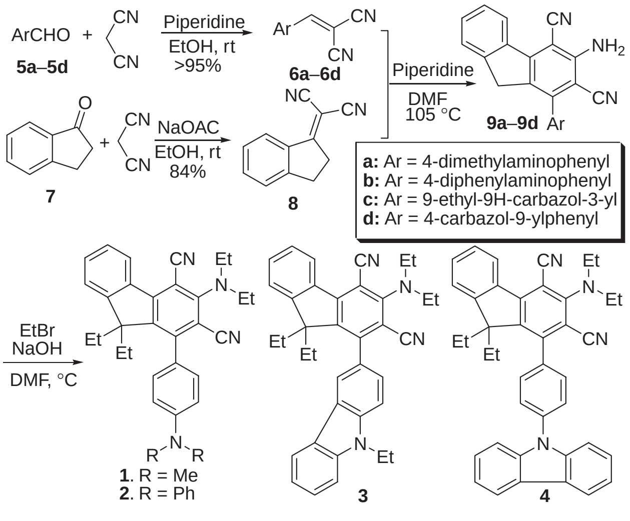
(Received January 31, 2008; CL-080116; E-mail: orgwyg@zju.edu.cn)

Four new fluorenes bearing two electron donors and two electron acceptors were synthesized and found to emit blue fluorescence in both solution and solid states.

Donor–acceptor (D–A) molecules have gained much attention due to their potential application in electronic devices such as light-emitting diodes[1] and field-effect transistors.[2] 2,6-Dicyanoanilines are typical A–D–A systems which have been found to exhibit strong fluorescence in our previous studies.[3] There are several publications involving the synthesis of this class of compounds, but most of them did not reported their optical properties.[4] We herein report the synthesis and properties of a new class of 2,6-dicyanoaniline derivatives with a fluorene moiety: 1-(4-aminophenyl)-2,4-dicyano-3-diethylamino-9,9-diethylfluorenes **1**–**4** (Scheme 1). These multifunctional molecules contain two amino groups as the electron donors (D) and two cyano groups as the electron acceptors (A).

Synthesis of compounds **1**–**4** is outlined in Scheme 1. Aryl aldehydes **5** reacted with malononitrile by the Knoevenagel condensation in the presence of piperidine to afford 2-arylidenemalononitriles **6** in excellent yields. 2-(Indan-1-ylidene)malononitrile (**8**) was prepared by the condensation of indan-1-one (**7**) and malononitrile according to the published procedure.[5] **6** reacted with **8** in the presence of piperidine (1.3 equiv) to afford **9** in moderate yields (41–62%). Ethylation of **9** with ethyl bromide in the presence of sodium hydroxide gave **1**–**4** in good yields (82–85%).[6]

As next step, we investigated the physical properties of compounds **1**–**4** and results were summarized in Table 1. The glass-transition temperatures (T_g) of **1**–**4** ranged from 70 °C to 110 °C. Compounds **3** and **4** presented higher T_g than that of **1** and **2**. T_gs of compounds **3** and **4** were rather higher than the commonly used hole-transport materials, such as 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (NPB, $T_g = 95$ °C) and *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD, $T_g = 65$ °C).[7] Compounds **2** and **3** have the decomposed temperature (T_d) higher than 300 °C while that of compound **1** is too low.



Scheme 1. Synthesis of compounds **1**–**4**.

Table 1. Physical property data of compounds **1**–**4**

Compd.	**1**	**2**	**3**	**4**
$T_g/T_m/T_d{}^a$/°C	70/220/ 275	82/179/ 323	110/239/ 324	107/261/ 355
$\lambda_{abs.}$/nm Hexane/Film	266, 308, 320, 387/ 264, 309, 321,	307, 317, 385/309, 320, 389	265, 293, 320, 385/ 265, 296, 323,395	293, 322, 392/295, 324, 387
ε^b/dm^3 cm^{-1} mol^{-1}	16520 (387 nm)	14631 (385 nm)	9859 (385 nm)	9643 (392 nm)
$\lambda_{em}{}^c$/nm Hexane/DCM /MeOH/ Powder/Film	425/514/ 568/467/ 500	427/517/ 561/458/ 469	423/447/ 457/446/ 449, 464	427/450/ 461/451/ 450, 462
$\Phi_f{}^d$ DCM/MeOH	0.18/0.11	0.24/0.16	0.11/0.08	0.16/0.14
$E_{onset}{}^{oxe}$/V	0.89	0.88	0.94	0.95
HOMO/ LUMO/ $E_g{}^f$/eV	5.29/2.41 /2.88 (5.35/1.94 /3.41)^g	5.28/2.40 /2.88 (5.12/1.93 3.19)^g	5.34/2.46/ 2.88	5.35/2.47/ 2.88

^{a}Obtained from DSC and TGA measurements under N_2. ^{b}Measured in hexane. ^{c}Excited at 313 nm. ^{d}Using quinine sulfate monohydrate ($\Phi_{313} = 0.48$) as a standard. ^{e}Two platinum electrodes used as the counter and working electrodes, respectively, and one Ag/AgCl electrode used as the reference electrode. ^{f}HOMO level values computed from the $E_{onset}{}^{ox}$ plus 4.4 eV. E_g values are calculated from the lowest energy absorption edge of UV–vis absorption spectra. ^{g}Values are computed by Gaussian 98.

Cyclic voltammograms (CVs) of the four compounds in dichloromethane (DCM) are shown in Figure 1. One reversible oxidation wave was observed for **1**–**4**. The onset potentials ($E_{ox}{}^{onset}$ vs. Ag/AgCl, Table 1) of **1**–**4** are 0.89, 0.88, 0.94,

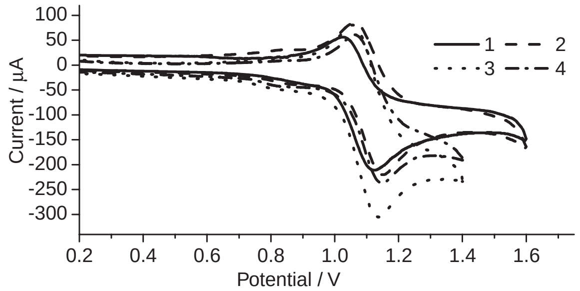


Figure 1. Cyclic voltammograms of compounds **1**–**4**.

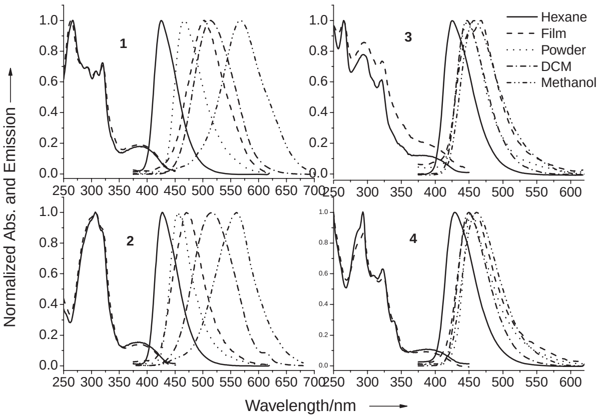


Figure 2. Normalized UV–vis absorption and PL emission of **1**–**4**.

and 0.95 V, respectively. Then, the estimated HOMO levels (HOMO = $E_{ox}^{onset} + 4.4$ eV) for **1**–**4** are 5.29, 5.28, 5.34, and 5.35 eV, respectively. E_g and LUMO values are listed in Table 1. All compounds have same E_g of 2.88 eV, which is suitable to serve as blue light emitting material. No obvious change was found when compound **4** was scanned for three cycles, so this compound is electrochemically stable.

UV–vis absorption spectra of **1**–**4** were measured in dilute hexane and film (Figure 2 and Table 1). There are three absorption bands in all of the four compounds. A same lowest weak energy absorption was found ranging from 360–420 nm, which can be assigned to the intermolecular charge-transfer characteristic from aminophenyl moiety to fluorene skeleton containing with 2,4-dicyano groups. The second absorption at 310–330 nm can be attributed to the delocalized π–π^* transition. The highest energy absorption band at 255–275 nm for **1** and **3** and 275–310 nm for **2** and **4** is associated with the absorption of fluorene moiety. The UV–vis absorption spectra in solid film are similar to that in dilute hexane.

PL emission spectra were recorded in hexane, DCM, and methanol solution as well as powder and film state at excitation wavelength of 313 nm (Table 1 and Figure 2). All compounds emitted blue light with the maximum emission wavelengths ranged from 423–427 nm in hexane. Much larger positive solvatochromism was observed in the PL emission spectra of **1** and **2** than **3** and **4**, this can be explained by the much stronger electron donating ability of aminophenyl than the carbazolyl substituent. Solid-state PL emission spectra of these compounds are red-shifted comparing to that in hexane solution. The quantum yields of **1**–**4** ranged from 0.11 to 0.24 measured in DCM (Table 1).

Molecular orbital calculations for **1** and **2** at the B3LYP/6-31G* level showed that the HOMO and LUMO orbital are located at different part of the molecule (Figure 3), this is coincidence to the solvatochromism observed in PL emission. HOMO and LUMO levels calculated by Gassian 98[8] are very close to that of experiment (Table 1). The computed reorganization energies λ_- (anionic) and λ_+ (cationic) of **2** and several compounds are listed on Table 2. The lower λ_+ proved **2** is suitable to be used as hole-transport material by the theoretical calculation level. But the λ_- is not low enough for electron transport although there are two cyano groups in the molecule.

In conclusion, we synthesized four new 1-(4-aminophenyl)-2,4-dicyano-3-diethylamino-9,9-diethylfluorene derivatives and investigated their photophysical, electrochemical, and thermo properties. These molecules exhibited medium fluorescent quantum yields with blue-light emission and high thermostability. The preliminary calculation suggested that the new molecules have good hole mobility. Further solid-state studies and single layer device test are underway.

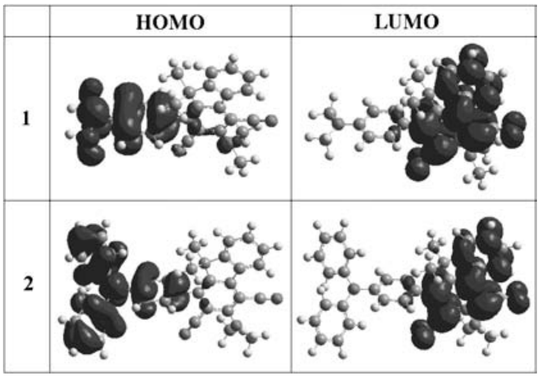


Figure 3. Computed HOMO and LUMO orbital surfaces of **1** and **2**.

Table 2. The computed reorganization energies of some compounds

Molecule	λ_-	λ_+
Benzene	0.41	0.30
Anthracene	0.20	0.14
NPB	0.19	0.29
2	0.29	0.12

We thank the Natural Science Foundation of Zhejiang Province (no. R404109), and the Specialized Research Fund for Doctoral Program of Higher Education (no. 20050335101).

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