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Synthesis and Optical Properties of $(A)_n\text{-}\pi\text{-(Ph)}_3\text{N}$ Type Dyes

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Two new $(A)_n\text{-}\pi\text{-(Ph)}_3\text{N}$ type dyes were designed, synthesized and characterized. The optical properties and structures of them were studied, including UV-visible spectroscopy, photo-luminescence spectroscopy. The geometric structures of them were calculated theoretically based on the DFT level using BLYP/GGA basis set, the HOMO/LUMO levels were also measured and calculated.

Keywords: geometric structures; HOMO/LUMO; optical properties; synthesize

INTRODUCTION

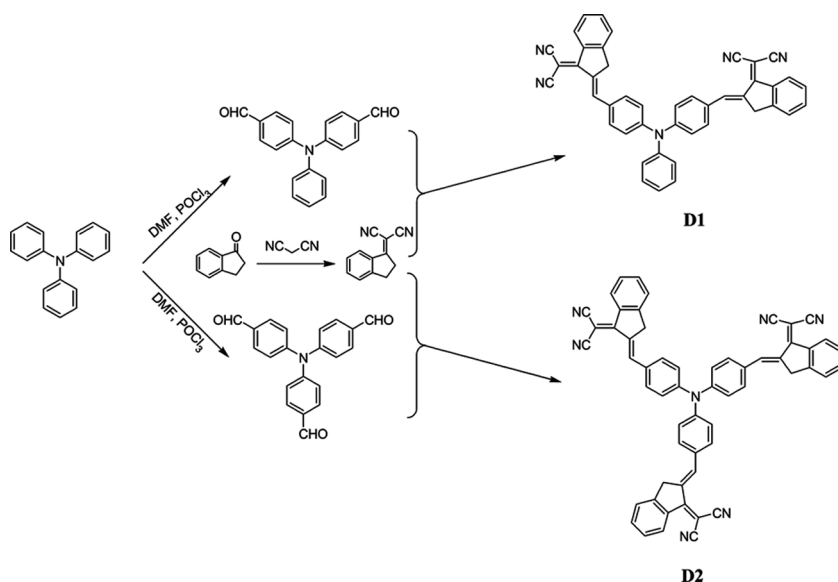
Small organic functional molecules have attracted more and more attention as active materials in organic solar cells (OSCs) [1,2] and organic light-emitting diodes (OLEDs) [3] due to their high purity and good reproducible optoelectronic properties. Recently considerable research efforts have led to major progress in the design and synthesis

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of new small organic functional molecules [4–7]. The properties of the devices, such as power conversion efficiency, photostability, electron mobility, and so on, are closely related to the chemical structure of the molecules used as the active layer of the device. Thus, it is vital to understand the relationship between the structure design and properties of small organic functional molecules which plays key roles for obtaining higher efficiency.

Herein, we report two new cap-shaped or half cap-shaped organic molecules (as shown in Scheme 1) with (A)_n-π-D structured branches based on triphenylamine (TPA) as core and donor units (D), 1-dicyanovinylindane as acceptor units, and the ethylene double bonds as π-connections between them. The design of the molecule structure was from the following considerations: (1) the TPA-based cap-shaped molecules possess three-dimensional spatial structure with good solution processibility and have been used in electroluminescence and photovoltaics [8,9]; (2) the D-π-A structure is in the molecule to reduce the bandgap of the material and make its absorption spectrum reach to the solar spectrum; (3) TPA core are for improving its solubility and enhancing its hole mobility because TPA is a typical hole transporting group [10].



SCHEME 1 Synthetic routes for **D1** and **D2**.

EXPERIMENTAL

Materials

Solvents used in photochemical measurements were spectroscopic grade and were purified by distillation before use. ^1H -NMR spectra were recorded on a NMR spectrometer JEOL-AL400 operating at 400 MHz. Chemical shifts were referenced to internal Me_4Si (TMS). Mass spectra were measured with a mass spectrometer LC-MS (Waters QToF). Absorption spectra measured with Agilent 8453 spectrophotometer. Fluorescence spectra measured on a SHMADZU RF-5301PC Fluorescence spectrophotometer.

Electrochemical Measurements

Cyclic-voltammetric measurements were carried out in a conventional three-electrode cell using a Pt button working electrode of 2 mm diameter, a platinum-wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled VersaStat 3 model V3 at room temperature. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF_6) was used as supporting electrolyte and the scan rate was set to 100 mV/s. The energy levels were calculated using the ferrocene (E_{FOC}) value of -4.8 eV as the standard. In this report, we use the ionization potential converted from oxidation potentials for comparison of the energies of the highest occupied molecular orbital (HOMO).

Preparation and Characterization

As presented in scheme 1, the two target compounds were synthesized by conventional condensation. 1-dicyanovinlyindane was synthesized by literature method [11].

Dye 1 (D1)

261 mg (1.45 mmol) 1-dicyanovinlyindane and 199 mg (0.66 mmol) 4,4'-diformyltriphenylamine were dissolved in 15 mL toluene. Several drops of piperidine were added. The mixture was heated to reflux for 12 h. Then the mixture was cooled and the solvent was evaporated in vacuum. The residue was purified by column chromatography (dichloromethane) to give pure **D1** 210 mg (51%).

^1H NMR (CDCl_3): 8.61 (d, 2H); 8.29 (s, 1H); 7.61-7.42 (m, 14H); 7.22-7.17 (m, 5H); 4.03 (s, 4H). MS m/z : 625 (M^+). Anal. Calcd. for $\text{C}_{44}\text{H}_{27}\text{N}_5$: C, 84.46; H, 4.35; N, 11.19; Found: C, 84.50; H, 4.39; N, 11.15.

Dye 2 (D2)

216 mg (1.20 mmol) 1-dicyanovinlyindane and 120 mg (0.36 mmol) tris-(4-formylphenyl)amine were dissolved in 15 mL toluene. Several drops of piperidine were added. The mixture was heated to reflux for 24 h (the reaction time was not optimized). Then the mixture was cooled and the solvent was evaporated in vacuum. The residue was purified by column chromatography (dichloromethane) to give pure **D2** 130 mg (44%).

¹H NMR (CDCl₃): 8.62 (d, 3H); 8.30 (s, 3H); 7.61-7.46 (m, 16H); 7.31-7.23 (m, 5H); 4.06 (s, 6H). MS *m/z*: 815 (M⁺). Anal. Calcd. for C₅₇H₃₃N₇: C, 83.91; H, 4.08; N, 12.02; Found: C, 83.87; H, 4.11; N, 12.19.

RESULTS AND DISCUSSION

Both **D1** and **D2** are soluble in common organic solvents, such as dichloromethane, toluene, THF and so on. The absorption spectrum of **D1** and **D2** solution in several typical organic solvents, as shown in Figure 1, displays two peaks in the UV-visible region. The absorption spectrum of **D1** solution in dichloromethane displays two peaks in the UV-visible region. The UV absorption band with a maximum at 310 nm corresponds to the π-π* absorption of the molecule, and the visible absorption band with a peak at 540 nm could be assigned to the intramolecular charge transfer (ICT) transition between the tri-phenylamine (TPA) moiety and 1-dicyanovinlyindane unit. The **D2** solution in dichloromethane shows UV absorption with a maximum at 320 nm and a shoulder at 360 nm, and the ICT band peak at 540 nm. Similar results were also found in other organic solvents.

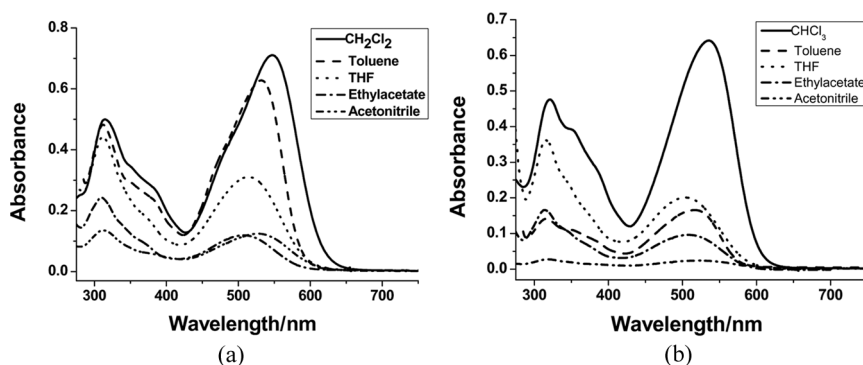


FIGURE 1 Absorption spectra of **D1** (a) and **D2** (b) in different solvents with 1×10^{-5} M.

Obviously, the ICT band of **D1** and **D2** is red-shifted 40 nm with the decreasing of polarity of the solvent (Fig. 1).

The emission spectra of **D1** and **D2** were measured in several different solvents. The two compounds display a strong emission solvatochromism that is reflected by a large bathochromic shift of their fluorescence emission maxima with increasing solvent polarity. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds presenting an internal charge transfer upon excitation and has been fully documented for numerous fluorophores containing donor-acceptor units. All the two dyes exhibited positive solvatochromism with the increasing solvent polarity, Figure 2. The emission spectrum of **D1** was observed with a peak around 405 nm in CH_2Cl_2 , which was excited at 315 nm. A broad and red-shifted emission (110 nm) of **D1** was observed ($\lambda_{\text{max}} = 515 \text{ nm}$) in CH_3CN . In case of **D2**, 55 nm red-shift was found, which is smaller than that of **D1**. These results demonstrate that the three-branched star-burst compound **D2** has smaller push-pull effect than that of the V-shaped molecule **D1**. These results further indicate that the push-pull effect was also influenced by the shape of molecules.

According to previous theoretical results [12,13], ICT is the major mechanism responsible for the solvent-reliant emission properties. However, the emissions of **D1** and **D2** at the ICT band are very weak. The relatively strong emissions of **D1** and **D2** are measured on irradiation at 315 nm which obtained by corresponding excitation spectra. Interestingly, the two compounds having the same kind of acceptor-spacer-donor units, display large solvent-reliant properties. Compared with **D2**, **D1** has much longer emissions, much larger Stokes shifts, and much broader emission bands, which indicate more effective ICT processes. Photo-excitation of a "push-pull" π electron system will generate an electric field with the positive pole at the position of the electron donor and the negative pole at the position of the electron acceptor [14]. In **D1** or **D2**, their positive poles are located at the triphenylamine nitrogen atom, but their negative poles are affected greatly by geometric structure and solvents.

In order to determine the HOMO and LUMO energy levels of **D1** and **D2**, electrochemical cyclic voltammetry was carried out on Pt button electrode. Figure 3 shows the cyclic voltammetry. It can be seen that there are reversible oxidation peaks in the positive potential region with the onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) at 0.68 V (**D1**) and 0.29 V (**D2**) *vs.* Ag/Ag^+ , and an irreversible reduction peak in the negative potential region with peak reduction potential ($E_{\text{onset}}^{\text{red}}$) at -0.80 V (**D1**) and -0.86 V (**D2**) *vs.* Ag/Ag^+ . The HOMO and LUMO

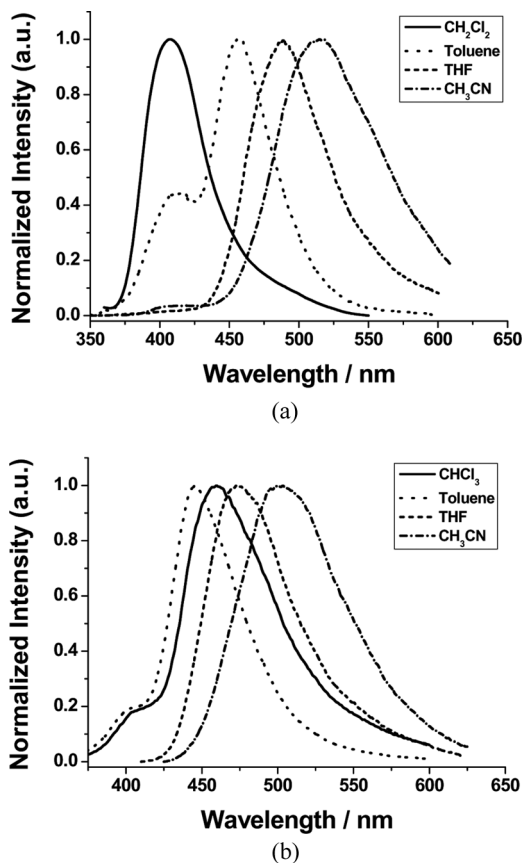


FIGURE 2 Emission spectra of **D1** (a) and **D2** (b) excited at 315 nm in different solvents with 1×10^{-5} M. The quantum yield were estimated to be 0.05 (CH₂Cl₂), 0.10 (toluene), 0.30 (THF), 0.26 (CH₃CN) for **D1** and 0.003 (CH₂Cl₂), 0.25 (toluene), 0.27 (THF), 0.16 (CH₃CN) for **D2** with quinesulfate ($\Phi=0.55$ in 50 mM H₂SO₄ solution) as a standard.

levels were calculated to be -5.39 eV and -3.91 eV respectively for **D1**, and -5.00 eV and -3.85 eV respectively for **D2**. It showed the LUMO values of **D1** and **D2** were considerably lower than the most popular electron-transport material Alq₃ (-3.0 eV) [15].

The geometry and electronic properties of **D1** and **D2** were investigated by means of theoretical calculation with the Material Studio program package at hybrid density functional theory (DFT) level. Becke's gradient corrected functional (BLYP) with a GGA basis was used for full geometry optimization. Figure 4 presents the

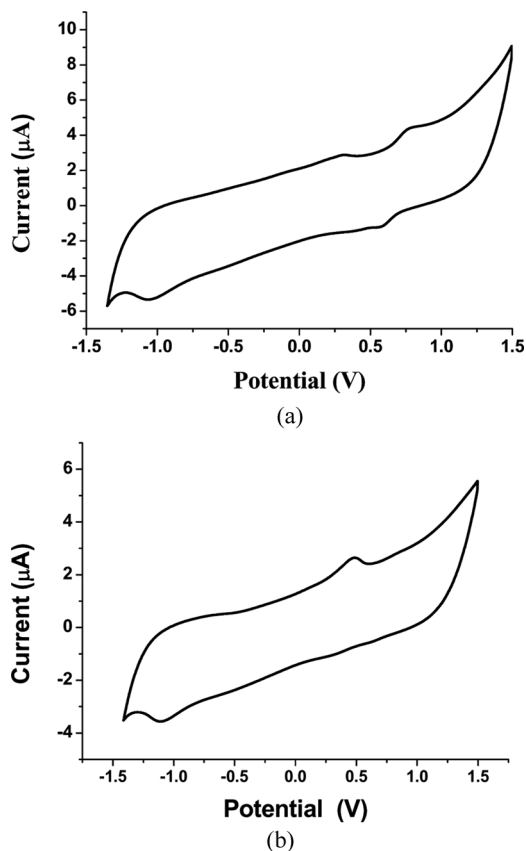


FIGURE 3 Cyclic voltammograms of **D1** and **D2** measured in CH_2Cl_2 solution containing 0.1 M TBPAF₆ at 20°C.

geometric structure of **D1** and **D2**. For the geometry observed for **D1** and **D2**, steric hindrance between the (A- π -core) arms grafted on the central nitrogen atom generated the propeller shape of molecule. This geometry could be beneficial for good solution process-ability and to forming amorphous films. The HOMO of **D1** is mainly distributed on the central **TPA** moiety with some extending to the 1-dicyanovinylindane moieties (Fig. 5). The LUMO is localized mainly on one of 1-dicyanovinylindane electron-withdrawing groups. The orbital contribution of **D2** is the same as that of **D1**. According to the orbital level analysis, the band gaps were calculated to be 1.52 eV for **D1** and 1.22 eV for **D2**, which agrees well with that obtained from CV and absorption edges.

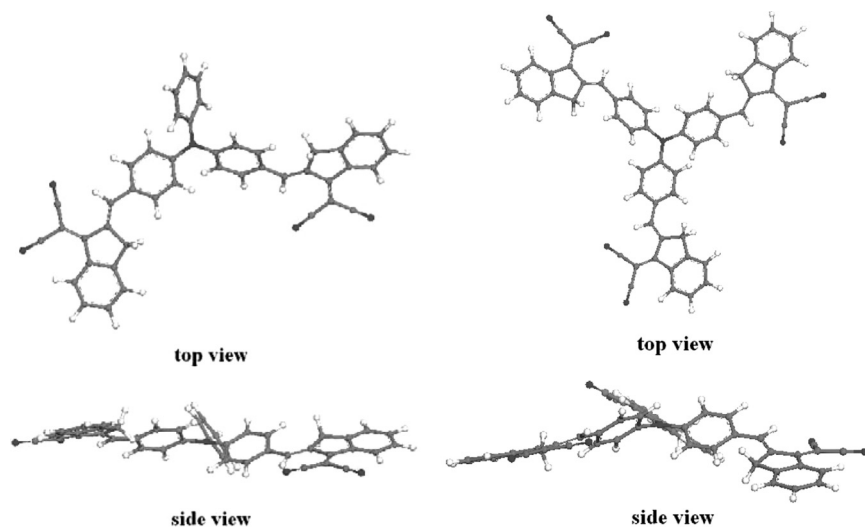


FIGURE 4 Optimized structure of **D1** (left) and **D2** (right).

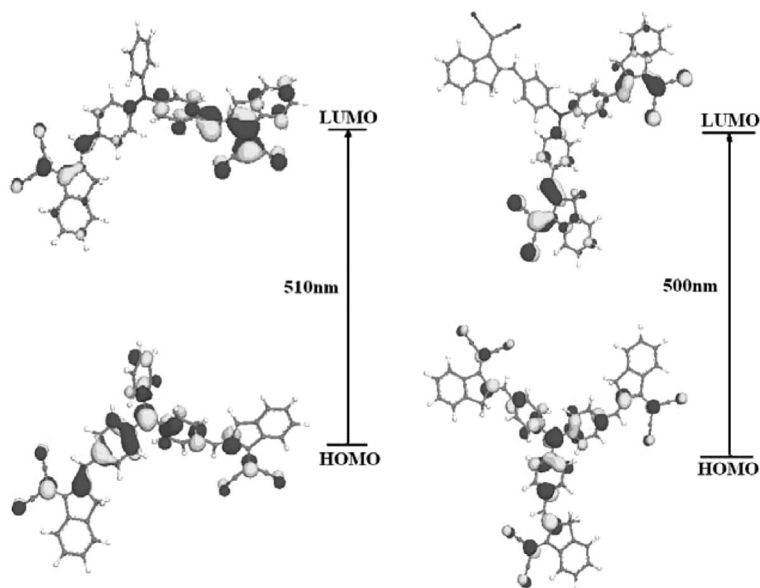


FIGURE 5 The HOMO and LUMO of **D1** (left) and **D2** (right) that are involved in the lowest-energy transition.

CONCLUSIONS

We designed and synthesized V-shaped and star-shaped molecules with $(A)_n-\pi-(Ph)_3N$ structure. The two compounds exhibit good stability and solubility in common organic solvents. Both **D1** and **D2** show broader and stronger absorption in the visible region covering the region of 400–600 nm. A positive solvatochromism in the emission spectra of **D1** and **D2** was observed. These properties qualify them as multifunctional fluorophores that can be employed in light-emitting or sensing applications.

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