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Spectral studies of multi-branched fluorescence dyes based on triphenylpyridine core

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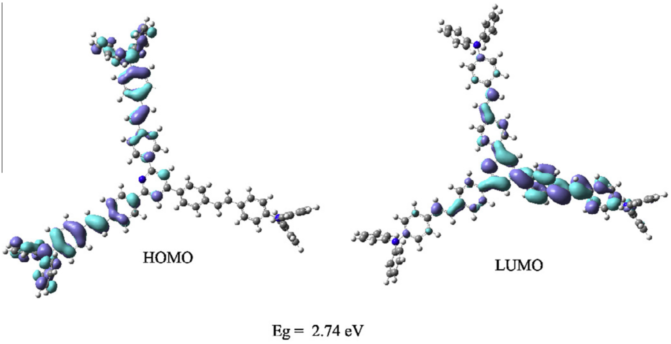
HIGHLIGHTS

- New fluorescence dyes based on triphenylpyridine were synthesized.
- Compounds exhibited efficient emission from blue to green with high quantum yields.
- HOMO/LUMO energy levels were obtained by CV and theoretical calculation.
- The effects of solvents on the fluorescence characteristics were investigated.
- All of the compounds possess of suited HOMO ranges (−5.56 to −5.70 eV).

GRAPHICAL ABSTRACT

New framework triphenylpyridine derivatives containing triphenylamine groups were synthesized and the relationship of photoluminescence property and structure were investigated. Quantum chemical calculations were used to obtain optimized ground-state geometry, spatial distributions of the HOMO, LUMO levels of the compounds.



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ABSTRACT

A series of novel triphenylpyridine-containing triphenylamine derivatives have been carefully designed and prepared in good yields using the stepwise route reactions. The relationship of photoluminescence property and structure of compounds **9–13** was systematically investigated via UV–vis, fluorescence, thermogravimetric and electrochemical analyzer. The highest occupied molecular orbital and the lowest unoccupied molecular orbital distributions of compounds **9–13** were calculated by density functional theory method. The high fluorescence quantum yields, desirable the highest occupied molecular orbital levels and high thermal stability of compounds **9–13** indicate that the linkage of triphenylpyridine and triphenylamine is an efficient means to enhance hole-transporting ability and fluorescent quantum yield.

Introduction

Organic fluorescent compounds have been extensively investigated for a myriad of potential applications in the biological labels, photovoltaic cells, light emitting diodes, and optical sensors etc.

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[1–12]. Fluorescent characteristic relies largely on molecular structure and assembly. Therefore, it is important to clarify the structure–property relationship of fluorescence because it enable us to design and employ more useful fluorescent reagents in the fields of analytical, biological chemistry and OLEDs in the future.

Triphenylamine molecular possesses a propeller-shaped structure with highly rich electron and it can maintain uninterrupted conjugation between central nitrogen lone pair electrons and the arms. In recent years, it has been widely employed in organic light emitting diodes, organic solar cells or organic field-effect transistors as electron-donating moieties [13–33]. Pyridine has been a key building block in constructing functional materials in view of its outstanding mechanical and dielectric properties [34–39].

Therefore, to afford suitable fluorescent materials [40,41] with higher hole-transporting ability and fluorescent quantum yield for analytical and biological chemistry, herein we introduced triphenylamine units into the 2,4,6-triphenylpyridine framework. As expected, the fluorescence emission color of products can be easily tuned from blue to green by changing the number of triphenylamine moieties and these compounds **9**–**13** possess higher fluorescence quantum yields (0.30–0.45) except compound **12**. Particularly, these compounds exhibit good the highest occupied molecular orbital (HOMO) levels (−5.56 to −5.70 eV), which is lower than that of the widely-used, hole-transporting material, 4,4-bis(1-naphthylphenylamino)biphenyl (NBP) (−5.50 eV), it might be beneficial for the hole-transport capacity. As a result, these compounds lead to promising applications in functional materials.

Experimental

Chemicals and instruments

All solvents were carefully dried and freshly distilled. All reactants were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and were uncorrected. ^{1}H and spectra were recorded at 295 K on a Bruker Avance DPX-400 MHz spectrometer using $CDCl_3$ or d_6-DMSO as solvent and TMS as internal standard. UV–vis absorption spectra were recorded on a Shimadzu UV-2501PC spectrometer. Fluorescence spectra were obtained on a Hitachi FL-4500 spectrofluorometer. HRMS data were measured using microTOF-Q(ESI) instrument. Thermal properties was performed under nitrogen on a SDT 2960 (heating rate of 20 °C min^{-1}). Cyclic voltammetry was carried on a Chi 1200 A electrochemical analyzer with three-electrode cell (Platinum was used as working electrode and as counter electrode, and SCE (saturated calomel electrode) as reference electrode) in CH_2Cl_2 solution in the presence of TBAHFP (tetrabutylammonium hexafluorophosphate) (0.10 mol L^{-1}) as supporting electrolyte.

*4-(Diphenylamino)benzaldehyde (**2a**)*

Phosphorus oxychloride (1.6 mL, 16.8 mmol) was added dropwise to DMF (1.3 mL, 19.5 mmol) at 0 °C, and the mixture was stirred at 0 °C for 1 h. Triphenylamine (3.3 g, 13.3 mmol) was added and the reaction mixture was stirred at 100 °C for 6 h. Then, the mixture was cooled to room temperature, poured into ice water and carefully neutralized to pH 7 with 5% NaOH aqueous solution. The solution was extracted with dichloromethane (3 × 150 mL). Then, the organic phase was washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane, 3/1, v/v) to produce white solid.

Compound **2a**: yield 82%, white ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (s, 1H), 7.69 (d, J = 8.8 Hz, 2H), 7.34 (t, J = 8.0 Hz, 4H), 7.17–7.19 (m, 6H), 7.03 (d, J = 8.8 Hz, 2H).

*4,4′-Diformyl triphenylamine (**2b**)*

Phosphorus oxychloride (9.23 mL, 0.1 mol) was added dropwise to a stirred (7.74 mL, 0.1 mol) of DMF at 0 °C. The mixture was stirred at 0 °C for 1 h and then stirred at room temperature for another 1 h. After the loading of (10.0 g, 0.04 mol) of triphenylamine dissolved in chloroform, the mixture was stirred at 100 °C for 48 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with 5% NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at vacuum. The residue was chromatographed on a silica gel column (silica gel, hexane/dichloromethane, 3/1, v/v) to produce of yellowish solid.

Compound **2b**: yield 70%, yellow ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 2H), 7.84 (d, J = 8.4 Hz, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 6.8 Hz, 1H), 7.18–7.20 (m, 6H).

*Tris-(4-formyl-phenyl)amine (**2c**)*

Phosphorus oxychloride (9.23 mL, 0.1 mol) was added dropwise to a stirred (7.74 mL, 1.0 mol) of DMF at 0 °C. The mixture was stirred at 0 °C for 1 h and additionally stirred at room temperature for 1 h. After the addition of (6.0 g, 0.02 mol) of **2b** in chloroform, the mixture was stirred at 100 °C for 48 h. After cooling, the solution was poured into water. The resulting mixture was neutralized to pH 7 with 5% NaOH aqueous solution and extracted with dichloromethane. The extract was washed with plenty of brine and the solvent was removed at vacuum. The residue was chromatographed on a silica gel column (silica gel, hexane/dichloromethane, 2/1, v/v) to produce yellowish solid.

Compound **2c**: yield 20%, yellow ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.95 (s, 3H), 7.86 (d, J = 8.7 Hz, 6H), 7.27 (d, J = 8.1 Hz, 6H).

*1,3,5-Trip-tolylpentane-1,5-dione (**5**)*

A mixture of *p*-tolualdehyde **3** (1.8 g, 15 mmol), 4-methylacetophenone **4** (4.3 g, 32 mmol) and powder NaOH (2.4 g, 60 mmol) were crashed together with a pestle and mortar for 2 h and then recrystallized with ethanol to give white needle crystal. Yield: 4.73 g, 85%.

*2,6-Diphenyl-4-p-tolyl-pyridine (**6d**)*

1,3,5-trip-tolylpentane-1,5-dione (**5d**) (3.7 g, 10 mmol) was added to a stirred solution of ammonium acetate (8 g, excess) in ethanol (100 mL). The reaction mixture was heated at refluxing for 10 h. Upon cooling to room temperature; a precipitate was filtered, washed with water three times and dried to afford the product. It was purified by flash column chromatography on silica. Elution with petroleum/ethyl acetate (8:1) gave a white solid **6d**. Yield: 2.8 g, 75%. Mp: 181–183 °C.IR (cm^{-1}): 3027, 2962, 2919, 2858, 1600, 1543, 1389, 1184, 1114, 1018, and 809. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ 8.09 (d, J = 7.9 Hz, 2H), 7.81 (s, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.30 (d, 6H), 2.42 (s, 9H).

*Phosphonium salt (**8**)*

Phosphonium salt **8** prepared via free radical bromination of (**6a–c**) with NBS (Fig. 1) and was reacted with triethylphosphite to yield phosphoniumsalt **8a–c** (without isolation for further reaction).