Dyes and Pigments 123 (2015) 257-266

Contents lists available at ScienceDirect

## Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

# High quantum yield both in solution and solid state based on cyclohexyl modified triphenylamine derivatives for picric acid detection

Yuyang Zhang <sup>a</sup>, Jianting Pan <sup>a</sup>, Chenyang Zhang <sup>a</sup>, Haowei Wang <sup>a</sup>, Gaobin Zhang <sup>a</sup>, Lin Kong <sup>a</sup>, Yupeng Tian <sup>a</sup>, Jiaxiang Yang <sup>a, b, \*</sup>

<sup>a</sup> Department of Chemistry, Anhui University and Key Laboratory of Functional Inorganic Materials of Chemistry of Anhui Province, Hefei 230039, PR China <sup>b</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

## ARTICLE INFO

Article history: Received 25 June 2015 Received in revised form 6 August 2015 Accepted 9 August 2015 Available online 18 August 2015

Keywords: Triphenylanime Cyclohexyl Solvent-free reaction Solvatochromic effect High quantum yields Picric acid detection

#### 1. Introduction

## ABSTRACT

Five triphenylamine derivatives containing cyclohexyl have been designed and synthesized with a solvent-free green procedure. The compounds possess high quantum yields both in solution and solid state. Our investigation shows that the steric effects of the chair conformation cyclohexyl and strong intramolecular hydrogen bond play a key role for the high emission. Moreover, a conjugated triphe-nylamine core and strong polar groups (pyridinyl and hydroxy) and their location in the molecule formed a typical non-planar push–pull electronic structure. This special chemical structure endows the molecules with solvatochromic effect and exhibit interesting fluorescent behavior in binary solvent systems of THF-H<sub>2</sub>O due to the strong intramolecular charge transfer (ICT), which has been confirmed by DFT calculation, absorption and fluorescence spectra of the compounds in different polar solvents. In addition, their high emission characters, both in solution and solid state are utilized for picric acid (PA) detection.

© 2015 Elsevier Ltd. All rights reserved.

Highly efficient  $\pi$ -conjugated organic luminescent materials have received considerable attention due to their potential applications in organic light-emitting diodes (OLEDs), organic fluorescent chemosensors, photoconductor, switching devices, organic field-effect transistors (OFETs) and solid-state dye laser [1]. However, in most cases, organic luminescent materials become weakly emissive or no fluorescence in the aggregate or solid state [2]. This kind of materials is known as the notorious aggregation-caused quenching (ACQ) effect due to strong  $\pi - \pi$  stacking interactions, which restricted the scope of the application fields [3]. To alleviate the ACQ effect, various chemical and physical methods have been developed [4]. Recently, the aggregation-induced emission (AIE) or aggregation-induced emission enhancement (AIEE) materials have been applied to overcome ACQ effect [5]. They are faintly or weekly emissive in solutions, but were strongly luminescent upon aggregations. Although AIEE materials emit both in solution and in solid-

E-mail address: jxyang@ahu.edu.cn (J. Yang).

state, their fluorescence quantum yields are usually relatively lower in diluted solution than that in the solid state [6]. There is still few blue or deep-blue emissions of organic molecules in both solution and solid states were reported. Thus, it is an attractive topic that design and synthesis molecules emitting efficiently both in solution and in the solid-state. Recently, some luminophors emit efficiently in dilute solution and aggregates have been reported [7]. However, materials with high quantum yield both in solution and solid state have rarely been reported in the literature to date.

Triphenylamine (TPA) is excellent blue luminescent material and usually employed to construct organic photoelectric functional materials with electron donor–acceptor structure [8]. Meanwhile, the three-dimensional propeller structure of TPA can improve the fluorescence quantum yields by avoiding intermolecular  $\pi$ – $\pi$ stacking. In addition, there is another strategy that introducing bulky groups to prevent molecular aggregation [9]. Many researchers attempt to modify the triphenylamine *via* introducing a conjugate moiety to achieve different fluorescence emission and high quantum yield [10]. Nevertheless, the intricate synthesis process, poor solubility and film-forming ability of extensive conjugate molecule hind their applications [11]. Thus, developing high emission triphenylamine fluorogen with a simple method is a fascinating work.







<sup>\*</sup> Corresponding author. Department of Chemistry, Anhui University and Key Laboratory of Functional Inorganic Materials of Chemistry of Anhui Province, Hefei 230039, PR China. Tel.: +86 551 63861279.

Recently, there is a critical need for detection of picric acid (PA), which is a powerful explosive and easily contaminates soil and groundwater [12]. Various techniques are employed for the detection of PA [13]. Among these, the fluorescence probe is regarded as the ideal method for PA detection because of its cost-effectiveness and inherent sensitivity [14]. Even though organic  $\pi$ -conjugated polymers, nanoparticles and metal-organic architectures have been used to detect PA [15]. However, most of the fluorogen for PA detection is only working in single system due to they could not emit efficiently both in solution and solid state. Developing florescence sensors with high quantum yield both in solution and solid state for detection of PA in dual system is still a challenge.

Herein, our work is to introduce a cyclohexyl structure with a chair conformation into triphenylamine group to gain functional triphenylamine derivatives with high emission. The flexible cyclohexyl could increase the intermolecular steric hindrance and filmforming ability of the title compounds. In addition, in order to obtain bond site for PA, we modify the cyclohexyl with two pyridine groups. The strong polar hydroxyls and carbonyl appending in cyclohexyl could form a strong intramolecular hydrogen bond, which could stabilize the chair structure decrease the molecular vibration. The other subsidiary groups, such as p-methylphenyl, phenyl, thienyl, p-fluorophenyl, p-methoxylphenyl, were introduced to adjust the photophysics properties and intermolecular interaction. For the purpose of gaining these TPA derivatives with high emission both in solution and solid state, we adopted a facile and highly efficient method by aldol condensation and solvent-free Michael addition reactions. The X-ray crystal structure, optical properties, electrochemical properties, thermal properties and picric acid (PA) detection were systematically investigated.

## 2. Experimental

## 2.1. Materials and instruments

All chemicals were obtained from commercial suppliers. The solvents were purified by conventional methods before used. FT-IR spectra were obtained on a Nicolet NEXUS 870 spectrometer (400–4000 cm<sup>-1</sup>, KBr pellets). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance 400 (400 MHz) spectrometer, using CDCl<sub>3</sub>, DMSO-d<sub>6</sub> or CD<sub>3</sub>COCD<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. Melting points were determined on a MELTTLER Toledo type FP62. Identification and quantification of compounds were carried out using a Agilent 6410 LC-MS/MS system (USA) consisted of a Agilent 1200 liquid chromatographic system with the volume injection set to 5  $\mu$ L. And the triple quadrupole mass spectrometer equipped with an electrospray ion source (ESI). The data were obtained by Mass Hunter software. Column chromatography was carried out on silica gel. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were obtained on Hitachi FL-7000 (Hitachi high technologies corporation, Tokyo, Japan). The absolute photoluminescence quantum yield of solid state was measured on HORIBA FluoroMax-4 spectrofluorometer using an integrating sphere (HORIBA Scientific, F-3092 integrating sphere). Cyclic voltammetry were carried on a CHI660D instrument. Electrochemical analyzer with three-electrode cell glassy carbon was used as working electrode and Platinum wire as counter electrode, and Ag/ AgCl as reference electrode at room temperature.

## 2.2. Synthesis

## 2.2.1. Synthesis of 4-acetyltriphenylamine (1)

To a stirring of triphenylamine 0.50 g (2.04 mmol) in anhydrous methylene dichloride (15 mL) was added immediately anhydrous

AlCl<sub>3</sub> 0.55 g (4.12 mmol), yielding a black suspension. The mixture was cooled to 0 °C under ice bath. Acetic anhydride 1.20 mL (1.20 g, 20.00 mmol) dissolved methylene dichloride (10 mL) was slowly added dropwise via syringe under vigorous stirring. On completion of the addition, the ice bath was removed, and the dark green slurry solution was warm to room temperature with stirring about 5 h. The mixture was poured into a mixture of ice and concentrated HCl. extracted three times with CH<sub>2</sub>Cl<sub>2</sub>, washed with 1.0 M Na<sub>2</sub>CO<sub>3</sub> solutions and saturated brine consequently, and the extracts was separated, dried over MgSO<sub>4</sub>. After removing solvents under reduced pressure, the residue was purified by flash chromatography on silica gel using petroleum/ethyl acetate (5:1) as elution, and got yellow solid 4-acetyltriphenylamine. Yield: 0.47 g, 80%. FT-IR (KBr, cm<sup>-1</sup>): 3036, 3005, 1944, 1673, 1584, 1488, 1417, 1357, 1332, 1269, 1173, 1150, 1074, 1029, 953, 843, 821, 755, 699, 675, 621, 588 and 525. <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 400 MHz) δ: 2.49 (s, 3H), 6.95 (d, 2H, J = 8.8 Hz), 7.19 (m, 6H), 7.39 (t, 4H, J = 7.9 Hz), 7.85 (d, 2H, I = 8.8 Hz).

## 2.2.2. Synthesis of compounds 3a–3e

To a stirred solution of substituted aldehyde (1.74 mmol) in ethanol (50 mL) was added NaOH 0.10 g (2.50 mmol) and 14 mL H<sub>2</sub>O and the reaction mixture was room temperature for overnight. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was cooled to room temperature and the precipitate was filtered, washed with water and recrystallized with ethanol, and then dried to give products **3**. The compounds **3a**–**3e** were obtained in 64–85% yields, respectively.

Compound **3a**: yellow solid, yield 78%; mp: 153.5 °C. FT–IR (KBr, cm<sup>-1</sup>): 3037, 2920, 1655, 1586, 1508, 1490, 1419, 1384, 1337, 1284, 1225, 1175, 1024, 811, 755 and 697. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 2.35 (s, 3H), 6.91 (d, 2H, J = 8.9 Hz), 7.20 (m, 6H), 7.26 (d, 2H, J = 8.0 Hz), 7.41 (t, 4H, J = 7.9 Hz), 7.66 (d, 1H, J = 15.5 Hz), 7.74 (d, 2H, J = 8.0 Hz), 7.83 (d, 1H, J = 15.5 Hz), 8.04 (d, 2H, J = 8.9 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 21.53, 119.16, 121.46, 125.51, 126.47, 129.17, 129.99, 130.39, 130.82, 132.63, 140.82, 143.28, 146.34, 152.06, 187.23.

Compound **3b**: yellow solid, yield 77%. FT–IR (KBr, cm<sup>-1</sup>): 1656, 1585, 1490, 1337, 1285, 1271, 1223, 1714, 763 and 697. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 6.91 (d, 2H, J = 8.8 Hz), 7.20 (m, 6H), 7.42 (m, 7H), 7.71 (d, 1H, J = 15.6 Hz), 7.85 (m, 2H), 7.89 (d, 1H, J = 15.6 Hz), 8.05 (d, 2H, J = 8.8 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 119.12, 122.54, 123.93, 125.55, 126.50, 129.14, 129.36, 129.90, 130.40, 130.89, 143.22, 146.31, 147.79, 152.14, 187.24.

Compound **3c**: yellow solid, yield 82%; mp: 183.4 °C. FT–IR (KBr, cm<sup>-1</sup>): 1650, 1588, 1489, 1368, 1334, 1280, 1241, 1170, 1026, 820, 753, 722 and 699. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 6.90 (d, 2H, J = 8.8 Hz), 7.20 (m, 7H), 7.41 (t, 4H, J = 7.8 Hz), 7.51 (d, 1H, J = 15.3 Hz), 7.64 (d, 1H, J = 3.4 Hz), 7.75 (d, 1H, J = 5.0 Hz), 7.86 (d, 1H, J = 15.3 Hz), 7.98 (d, 2H, J = 8.8 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 119.09, 120.79, 125.58, 126.53, 129.14, 130.07, 130.43, 130.45, 130.76, 132.94, 136.05, 140.41, 146.28, 152.09, 186.65.

Compound **3d**: yellow solid, yield 85%. FT–IR (KBr, cm<sup>-1</sup>): 3068, 2919, 1942, 1656, 1586, 1487, 1419, 1343, 1314, 1279, 1219, 1179, 1156, 1025, 976, 821, 748 and 696. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 6.91 (d, 2H, *J* = 8.9 Hz), 7.20 (m, 6H), 7.29 (t, 2H, *J* = 8.9 Hz), 7.41 (t, 4H, *J* = 7.9 Hz), 7.70 (d, 1H, *J* = 15.6 Hz), 7.85 (d, 1H, *J* = 15.6 Hz), 7.93 (m, 2H), 8.05 (d, 2H, *J* = 8.9 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 116.35 (d, *J* = 21 Hz), 119.10, 122.44 (d, *J* = 2 Hz), 125.55, 126.50, 130.23, 130.40, 130.89, 131.45 (d, *J* = 9 Hz), 132.03 (d, *J* = 3 Hz), 141.97, 146.30, 152.14, 163.72 (d, *J* = 247 Hz), 187.16.

Compound **3e**: yellow solid, yield 64%; mp: 150.5 °C. FT–IR (KBr, cm<sup>-1</sup>): 1649, 1591, 1507, 1490, 1418, 1339, 1285, 1256, 1221, 1170, 1032, 980, 819, 750 and 695. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 3.82 (s, 3H), 6.91 (d, 2H, J = 8.8 Hz), 7.01 (d, 2H, J = 8.8 Hz), 7.19 (m, 6H), 7.41 (t, 4H, J = 7.9 Hz), 7.67 (d, 1H, J = 15.5 Hz), 7.75 (d, 1H, J = 15.5 Hz), 7.81 (d, 2H, J = 8.8 Hz), 8.03 (d, 2H, J = 8.8 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 55.82, 114.85, 119.26, 120.00, 125.44, 126.42, 127.98, 130.38, 130.60, 130.73, 130.99, 143.21, 146.38, 151.94, 161.62, 187.18.

## 2.2.3. Synthesis of compounds 4a–4e

Compound **3** (1.29 mmol) and 2-acetylpyridine 0.51 g (0.47 mL, 4.21 mmol) and power NaOH 0.28 g were crashed together with a pestle and mortar at room temperature for 0.5 h, the mixture was put overnight. The resulting mixture was purified by flash chromatography with petroleum/ethyl acetate (V:V = 2:1) as elution, and gave the compounds **4**. The compounds **4a**–**4e** were obtained in 42–63% yields, respectively.

Compound 4a: yellow solid, yield 55%; mp: 124.7 °C. FT-IR (KBr, cm<sup>-1</sup>): 3741, 3443, 2918, 1640, 1583, 1495, 1277, 1224, 1178, 756 and 696. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.74 (d, 1H, J = 14.3 Hz), 1.90 (d, 1H, J = 13.0 Hz), 2.16 (s, 3H), 2.61 (t, 1H, *J* = 13.0 Hz), 3.18 (d, 1H, *J* = 14.3 Hz), 3.94 (t, 1H, *J* = 12.1 Hz), 4.61 (d, 1H, J = 12.1 Hz), 6.04 (s, 1H), 6.31 (s, 1H), 6.50 (d, 2H, *I* = 8.8 Hz), 6.94 (t, 6H, *I* = 8.9 Hz), 7.12 (m, 3H), 7.25 (m, 5H), 7.35 (t, 5H, I = 7.9 Hz), 7.53 (t, 1H, I = 7.3 Hz), 7.72 (d, 1H, I = 8.0 Hz),7.81 (t, 1H, J = 7.7 Hz), 8.40 (d, 1H, J = 4.2 Hz), 8.54 (d, 1H, J = 4.2 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 20.48, 38.18, 45.24, 46.16, 54.96, 75.91, 78.32, 118.96, 119.26, 119.68, 121.70, 121.95, 124.35, 125.04, 127.75, 128.69, 129.51, 129.70, 131.23, 134.91, 136.24, 136.85, 140.77, 146.05, 147.94, 148.08, 150.35, 163.55, 165.83, 199.60. MS (ESI+, 4.5 kV, 200 °C): m/z = 632.1 ([M+H]<sup>+</sup>), calcd for  $C_{42}H_{37}N_3O_3^+ = 631.3$  ([M]<sup>+</sup>). MS (MALDI-TOF): 632.290  $([M+H]^+)$ , calcd for: 631.283.

Compound 4b: yellow solid, yield 63%; mp: 200.1 °C. FT-IR (KBr, cm<sup>-1</sup>): 3742, 3453, 3279, 2923, 2857, 1638, 1581, 1488, 1350, 1275, 1221, 1173, 753 and 693. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 1.76 (d, 1H, J = 14.3 Hz), 1.94 (d, 1H, J = 13.2 Hz), 2.66 (t, 1H, J = 13.2 Hz), 3.21 (d, 1H, J = 14.3 Hz), 4.01 (t, 1H, J = 12.0 Hz), 4.66 (d, 1H, J = 12.0 Hz), 6.07 (s, 1H), 6.36 (s, 1H), 6.49 (d, 2H, 2H)J = 8.8 Hz), 6.93 (d, 4H, J = 7.8 Hz), 7.10 (m, 6H), 7.26 (t, 3H, J = 7.8 Hz), 7.35 (m, 7H), 7.52 (t, 1H, J = 8.4 Hz), 7.72 (d, 1H, J = 7.9 Hz), 7.81 (t, 1H, J = 8.7 Hz), 8.41 (d, 1H, J = 4.4 Hz), 8.55 (d, 1H, J = 4.4 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 38.68, 45.23, 46.19, 54.82, 75.89, 78.35, 118.97, 119.21, 119.69, 121.72, 121.95, 124.35, 125.08, 126.07, 127.89, 128.12, 129.52, 129.70, 131.18, 136.23, 136.83, 143.82, 146.03, 147.96, 148.10, 150.40, 163.57, 165.82, 199.63. MS (ESI+, 4.5 kV, 200 °C): m/z = 618.3 ([M+H]<sup>+</sup>), calcd for  $C_{41}H_{35}N_3O_3^+ = 617.3$  ([M]<sup>+</sup>). MS (MALDI-TOF): 618.264 ([M+H]<sup>+</sup>), calcd for: 618.276.

Compound **4c**: yellow solid, yield 49%; mp: 191.7 °C. FT–IR (KBr, cm<sup>-1</sup>): 3742, 3472, 3344, 3052, 2916, 1633, 1580, 1491, 1278, 1223, 1174, 837,755 and 693. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.74 (d, 1H, J = 14.3 Hz), 2.12 (d, 1H, J = 13.1 Hz), 2.65 (t, 1H, J = 13.1 Hz), 3.16 (d, 1H, J = 14.3 Hz), 4.32 (t, 1H, J = 12.0 Hz), 4.52 (d, 1H, J = 12.0 Hz), 6.00 (s, 1H), 6.38 (s, 1H), 6.52 (d, 2H, J = 8.7 Hz), 6.79 (t, 1H, J = 4.0 Hz), 6.94 (m, 5H), 7.14 (m, 3H), 7.19 (d, 1H, J = 4.9 Hz), 7.32 (m, 8H), 7.52 (t, 1H, J = 7.7 Hz), 7.72 (d, 1H, J = 7.9 Hz), 7.82 (t, 1H, J = 7.3 Hz), 8.41 (d, 1H, J = 4.2 Hz), 8.55 (d, 1H, J = 4.2 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 33.78, 46.08, 46.18, 56.48, 75.78, 78.16, 118.95, 119.12, 119.65, 121.74, 122.04, 123.20, 124.34, 124.41, 125.15, 126.61, 129.52, 129.72, 130.99, 136.25, 136.91, 146.00, 147.52, 148.02, 148.16, 150.44, 163.27,

165.56, 198.79. MS (ESI+, 4.5 kV, 200 °C): m/z = 624.3 ([M+H]<sup>+</sup>), calcd for C<sub>39</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>S<sup>+</sup> = 623.2 ([M]<sup>+</sup>). MS (MALDI-TOF): 624.223 [M+H]<sup>+</sup>, calcd for: 624.232.

Compound **4d**: yellow solid, yield 63%. FT–IR (KBr, cm<sup>-1</sup>): 3742, 3449, 3303, 3050, 2922, 2858, 1729, 1638, 1582, 1500, 1224, 1174, 1077, 835, 755 and 693. <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$ : 1.75 (d, 1H, *J* = 14.3 Hz), 1.91 (d, 1H, *J* = 13.2 Hz), 2.66 (t, 1H, *J* = 13.2 Hz), 3.17 (d, 1H, *J* = 14.3 Hz), 3.99 (t, 1H, *J* = 12.0 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 6.09 (s, 1H), 6.30 (s, 1H), 6.51 (d, 2H, *J* = 8.8 Hz), 6.95 (m, 6H), 7.12 (m, 3H), 7.27 (m, 3H), 7.37 (m, 7H), 7.54 (t, 1H, *J* = 7.7 Hz), 7.72 (d, 1H, *J* = 8.0 Hz), 7.81 (t, 1H, *J* = 7.7 Hz), 8.40 (d, 1H, *J* = 4.2 Hz), 8.54 (d, 1H, *J* = 4.2 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 38.59, 45.51, 46.66, 54.46, 76.38, 78.89, 115.25 (d, *J* = 20 Hz), 119.48, 119.69, 120.20, 122.27, 122.48, 124.89, 125.60, 130.07, 130.22, 130.29, 131.59, 136.78, 137.35, 140.35 (d, *J* = 2 Hz), 146.50, 148.46, 148.60, 150.96, 161.04 (d, *J* = 240 Hz), 164.05, 166.26, 200.33. MS (MALDI-TOF): 636.258 ([M+H]<sup>+</sup>), calcd for: 636.266.

Compound 4e: yellow solid, yield 42%; mp: 95.7 °C. FT-IR (KBr, cm<sup>-1</sup>): 3743, 3319, 1652, 1588, 1498, 1335, 1280, 1222, 1172, 1029, 819, 751 and 695. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 1.73 (d, 1H, *J* = 14.3 Hz), 1.90 (d, 1H, *J* = 13.2 Hz), 2.63 (t, 1H, *J* = 13.2 Hz), 3.17 (d, 1H, J = 14.3 Hz), 3.63 (s, 3H), 3.92 (t, 1H, J = 12.0 Hz), 4.60(d, 1H, J = 12.0 Hz), 6.08 (s, 1H), 6.31 (s, 1H), 6.50 (d, 2H, J = 8.7 Hz), 6.70 (d, 2H, J = 8.6 Hz), 6.93 (d, 4H, J = 7.8 Hz), 7.11 (m, 3H), 7.26 (m, 5H), 7.37 (m, 5H), 7.53 (t, 1H, J = 7.3 Hz), 7.73 (d, 1H, J = 7.9 Hz), 7.81 (t, 1H, J = 7.2 Hz), 8.40 (d, 1H, J = 4.2 Hz),8.55 (d, 1H, I = 4.2 Hz). <sup>13</sup>C NMR (DMSO- $d_6$ , 100 MHz)  $\delta$ : 37.89, 45.27, 46.15, 54.80, 55.07, 75.91, 78.41, 113.45, 118.97, 119.16, 119.66, 121.72, 121.93, 124.38, 125.10, 128.86, 129.55, 129.64, 129.71, 131.17, 135.56, 136.85, 146.03, 147.94, 148.07, 150.41, 157.45, 163.62, 165.85, 200.05. MS (ESI+, 4.5 kV, 200 °C): m/z = 648.3 ([M+H]<sup>+</sup>), calcd for C<sub>42</sub>H<sub>37</sub>N<sub>3</sub>O<sub>4</sub><sup>+</sup> = 647.3 ([M]<sup>+</sup>). MS (MALDI-TOF): 648.286 ([M+H]<sup>+</sup>), calcd for: 648.286.

### 3. Results and discussion

#### 3.1. Synthesis

The synthetic routes of the proposed compounds 3 and 4 are outlined in Scheme 1. The chalcone **3a**–**3e** can be easily prepared by Claisen–Schmidt condensation by 4-acetyltriphenylamine (1) and aromatic aldehyde 2a-2e with adjusting water and the proportion of ethanol. These compounds can also be prepared by the reaction in ethanol, but obtained in lower yields. After optimizing the reaction conditions, we further explored the next step reaction. According to the literature, the highly useful C–C bond formation through Michael addition of 2-acetylpyridine to  $\alpha$ ,  $\beta$ -unsaturated ketones always forms the diketone using 2.4 equivalents of the 2-acetylpyridine. Instead of the diketone, the compounds 4a-4e were obtained in 42-63% yields by a mild, efficient, and solventfree green procedure by Michael addition, when 2-acetylpyridine was used in excess. The structures of the products 3a-3e and 4a-4e were characterized by the analyses of their spectral data, including <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and MS comparing with X-ray diffraction analysis.

#### 3.2. X-ray crystallography analysis

Suitable single crystals of **4c** for X-ray structural analysis were obtained by slow evaporation of a dichloromethane solution of **4c** at room temperature for several days. The spatial structures of compound **4c** were determined by using X-ray diffraction analysis. A summary of crystallographic data collection parameters and refinement parameters for **4c** are compiled in Tables S1–S3. The



Scheme 1. The synthetic routes of compounds 4a-4e. Reagents and conditions: (I) NaOH, EtOH/H<sub>2</sub>O, 25 °C; (II) 2-acetylpyridine, NaOH, grind.

single crystal structure and atomic number chosen for **4c** were shown in Fig. 1. The structure of compound **4c** was crystallized in monoclinic space group P2(1)/c.

The triphenylamine group and cyclohexyl in **4c** was propeller structure and chair conformation, being consistent with our estimates. The crystal packing was stabilized by intermolecular interactions such as C(phenyl)–H···O(hydroxyl) and three kind different C(11, 23, 37)–H··· $\pi$  bonds. The hydrogen bond distance (Å) is 2.432 and the C(11, 23, 37)–H··· $\pi$  bond distances are 3.238, 3.597, 3.069, respectively. In addition, the cyclohexyl structure was almost perpendicular the thienyl group and two pyridine moiety, which are 72.25°, 88.83° and 83.60°, respectively.

## 3.3. Photophysical properties

The UV–vis spectra of the compounds **4a**–**4e** in different solvents are shown in Fig. 2 and Fig. S1. The normalized absorption spectra of compounds **4a**–**4e** in thin film was shown in Fig. S2. The optical characteristics were summarized in Table 1. Compounds **4a**–**4e** exhibited similar absorption spectra with two peaks. The 290 nm absorption bands were due to  $\pi$ – $\pi$ \* transition and the 360–375 nm absorption regions were attributed to intramolecular charge transfer (ICT) [16]. The absorbance of compounds **4a**–**4e** were different depending on various substitutions. For example, the molar absorption coefficients ( $\varepsilon_{max}$ ) of **4c** are the highest and **4d** 



**Fig. 1.** (A) Crystal structure of compound **4c**, (B) intermolecular interactions (C) show  $C-H\cdots O$  and  $C-H\cdots \pi$  bonds along the *a*-axis (Hydrogen atoms except H2A and H3B are omitted for the sake of clarity).



Fig. 2. The UV-vis spectra and fluorescence spectra of 4a in solvents with different polar (3.0  $\mu$ M).

Table 1	
Photophysical properties of compounds 4a-4e in different polar solv	/ents

Compound	Solvents	$\lambda_{max}^{a}$	$\lambda_{max}^{\ b}$	$\epsilon$ (×10 <sup>4</sup> ) <sup>c</sup>	$\Phi^{d}$	Δν <sup>e</sup>	$\Phi_{s}^{f}$
4a	Benzene	370	466	2.9695	0.97	5568	0.43
	Dichloromethane	372	516	3.1752	0.27	7502	
	THF	366	495	2.8933	0.54	7120	
	Ethanol	366	511	2.8648	0.01	7753	
	Ethyl acetate	366	496	2.9143	0.44	7161	
	Acetonitrile	364	525	2.9771	0.02	8425	
	DMF	360	523	2.7724	0.03	8657	
4b	benzene	372	468	3.0387	0.93	5514	0.32
	Dichloromethane	372	516	2.8857	0.25	7502	
	THF	368	496	2.8143	0.48	7013	
	Ethanol	368	511	2.6553	0.01	7604	
	Ethyl acetate	366	499	2.7867	0.40	7282	
	Acetonitrile	364	523	2.7190	0.02	8352	
	DMF	358	524	2.4943	0.03	8849	
4c	Benzene	372	471	3.1724	0.90	5650	0.19
	Dichloromethane	374	520	3.4724	0.22	7507	
	THF	370	501	3.1362	0.24	7107	
	Ethanol	368	515	3.0857	0.01	7756	
	Ethyl acetate	366	497	3.1943	0.35	7202	
	Acetonitrile	364	526	3.2695	0.01	8461	
	DMF	358	523	2.8810	0.02	8813	
4d	Benzene	376	485	2.3748	0.74	5977	0.49
	Dichloromethane	374	518	2.3724	0.21	7433	
	THF	370	502	2.3467	0.40	7107	
	Ethanol	368	515	2.3390	0.01	7756	
	Ethyl acetate	366	502	2.2524	0.34	7402	
	Acetonitrile	364	523	2.4162	0.02	8352	
	DMF	364	524	2.1695	0.02	8389	
4e	Benzene	370	468	2.5286	0.93	5660	0.23
	Dichloromethane	370	513	2.6419	0.26	7534	
	THF	366	495	2.4524	0.50	7120	
	Ethanol	366	504	2.4695	0.01	7481	
	Ethyl acetate	366	495	2.6029	0.42	7120	
	Acetonitrile	366	522	2.5914	0.02	8165	
	DMF	358	521	2.3333	0.03	8739	

<sup>a</sup> Peak position of the longest absorption band.

<sup>b</sup> Peak position of SPEF, excited at the absorption maximum.

<sup>c</sup> Molar absorptivity (L/cm/mol).

<sup>d</sup> Quantum yields determined by using quinine sulfate as standard.

<sup>e</sup> Stokes' shift in cm<sup>-1</sup>.

<sup>f</sup> Quantum yields in solid.

are the lowest than other compounds in the same solvents. It indicated that the subsidiary groups had an influence on their photophysics properties.

The emission spectra of compounds **4a–4e** in different solvents were shown in Fig. 2 and Fig. S1. The detailed data were summarized in Table 1. The normalized fluorescence spectra of compounds **4a–4e** in thin film were shown in Fig. S2. It can be found that the

fluorescence intensity differed from each other both in solution and solid state, which illustrated that the different substituent groups had an influence on the emission. On the other hand, the compounds exhibited an evident solvatochromic effect. The emission wavelength of the compounds were red-shifted companied with the decreased of quantum yields with the increasing of solvent polarity (Fig. 2 and Table 1). This phenomenon was commonly observed in the molecules with ICT. The molecular polarity was significant increased when it transferred from ground state to excited state. This would induce the strong dipole—dipole interaction between solute and solvent. The interaction forced the solvent molecules around the excited solute molecule occurred realignment resulting the emission from a relaxation state. Thus, the fluorescence wavelength was bathochromic [17].

To better understand the photophysical processes, molecular orbitals were investigated by hybrid density functional theory (B3LYP) with 6-31G\* basis set employing the Gaussian 09 program package [18]. The frontier molecular orbital electron cloud distributions of **4a**–**4e** were similar. The electron cloud of highest occupied molecular orbital (HOMO) was localized on the triphenylamine unit and carbonyl. While, the lowest unoccupied molecular orbital (LUMO) was localized on the cyclohexyl and carbonyl. The compounds exhibited the obviously charge separation of the HOMO and the LUMO (Table S6). It indicated a typical ICT effect. Moreover, the calculated band gaps of **4a**–**4e** had little difference which was consistent with our experimental results that the absorbance spectra of them were similar.

The quantum yields in solid state of compounds **4a**–**4e** had been determined and analyzed (Table 1). The steric hindered effect of the chair conformation cyclohexyl impeded the intermolecular  $\pi - \pi$ stacking in aggregation state. In addition, the formation of intramolecular hydrogen bond between the hydroxyls and carbonyl improved the electronic conjugation and coupling by both throughbond and through-space interactions [19]. Thus, the solid **4a–4e** could emit stronger fluorescence and had a high quantum vield in solid state than the precursor of TPA. For the different substituent groups, the quantum yields of 4a-4e in solid state were in the range of 0.19-0.49. However, the quantum yield of TPA in solid state was just 0.08. Obviously, the solid quantum yields of TPA derivatives were increased about 2.5-6.1 fold after functioned with the cyclohexyl. The reasons of different  $\Phi_s$  of **4a**–**4e** were caused by the influence of different subsidiary groups of cyclohexyl structure. According to the single crystal structure analysis of compound **4c**, we could find that the thienyl group influence the stacking of TPA by C (thienyl, 37)-H $\cdots \pi$  bonds of intermolecular. The substitutions of six-membered affected the arrangement of TPA derivatives 4a-4e in solid state; therefore, the quantum yields were different with each other.

These compounds were good soluble in organic solvent such as THF, whereas insoluble in water. To further study the optical properties in aggregation state, we added deionized water to THF in order to cause molecules formation of aggregates. The concentration of 4a-4e was kept at 10 µM in THF-water mixtures. The UV-vis absorption and PL emission spectra of compounds 4a-4e in THFwater with different water volume fraction  $(f_w)$  were displayed in Fig. 3, Figs. S3 and S4. The compound 4c was analyzed carefully as a representative of the material. When the water fractions increased from 0 to 70%, the absorption band almost remained at the same position of 370 nm and the molar absorbance ( $\varepsilon_{max}$ ) not showing obvious change. This indicates that most of the molecules were still free. When reach up to 80%, it worth that the lifted level-off tail when the water volume fraction was 80%-99% in the absorption spectra, which were attributed to Mie scattering caused by nanosized particles [20]. It showed that the molecular start aggregating. Moreover, the absorption peak of compounds 4a-4e red shifted about 7 nm, 22 nm, 11 nm, 13 nm, and 12 nm, respectively. This phenomenon suggests that the molecules were J-type aggregation that arranged in a head-to-tail direction indicating a better conjugation when the compounds become nanosized particles [21].

The emission spectra of **4a**–**4e** in different water contents were investigated (show in Fig. 4). **4a**–**4e** had an analogous change process of fluorescence. They exhibited strong fluorescence



Fig. 3. The UV-vis spectra of compound 4c in different water fractions.

emission in pure THF. However, with an increasing content of water from 0 to 5%, the emission intensity of compounds was decrease swiftly and remains faint emission intensity until the water content was increased to 80%. When  $f_{\rm W}$  was further increased to 80%, the molecule aggregates formed, accompanied by the emission of 4a-4e drastically increased, which demonstrated that 4a-4e emitted both in solution and solid state. Interestingly, the profiles of the  $f_w$  dependent fluorescence spectra of **4a–4e** were different from the traditional AIEEgens. When  $f_{\rm W}$  was less than 80%, the aggregates were not formed. The strong polar groups possessed the ability to form hydrogen bond interactions with themselves, as well as with the polar solvents [22]. The polarity of the mixed solution was increased with the addition of water in the binary solvent systems of THF-H<sub>2</sub>O. Thus, the emission of the compounds was gradually decreased due to the solvatochromic effects. Meanwhile, the emission wavelengths of compound 4c were blue-shift about 28 nm between 60%  $\leq f_{\rm W} \leq$  99%. We noted that the film emission of compound 4c was hypochromatic about 10 nm compare to its pure THF solution. The reason of blue-shift might be attributed to the formation of crystalline aggregates in high water fraction as the previous literature [23].

## 3.4. Thermal properties

The compounds were heated at 10 °C/min under a nitrogen atmosphere to detect the decomposition temperatures ( $T_d$ ) by thermogravimetric analysis (TGA). The detailed data were listed in Table S4. The compounds **4a**–**4e** exhibited high thermal stabilities and the decomposition temperature at 236.6, 231.4, 238.4, 234.5 and 230.5 °C, respectively. The high decomposition temperatures revealed that the compounds were stable.

## 3.5. Electrochemical properties

The electrochemical properties of compounds **4a–4e** were analyzed by cyclic voltammetry (CV) in  $CH_2Cl_2$  in the presence of  $Bu_4NClO_4$  (0.10 mol  $L^{-1}$ ) as supporting electrolyte. All CV measurements were recorded at room temperature with a conventional three-electrode configuration consisting of a glass carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode under argon. The subsidiary groups had a slight effect on their electrochemical behavior. As shown in Fig. S6, all of **4a–4e** showed better redox reversibility that there was an oxidation peaks about 0.9 V and a reduction peaks about 1.1 V. The



Fig. 4. Fluorescence spectra of compound 4c in different water fractions (up left); effect of water fraction on the maximum fluorescence intensity and emission wavelength (up right); optical photographs recorded under 365 nm UV irradiation with various fractions of water (down).

HOMO energy values of them were calculated by using the expressions: HOMO =  $[-(E_{onset}^{OX} + 4.38)] eV(E_{onset}^{OX}$  is the first oxidation onset potential) [9a,24], displayed in Table S5. The onset oxidation potentials of the compounds **4a**–**4e** were, 0.98, 0.95, 0.94, 0.97, and 1.08, respectively, nearly equal to one another. The calculated HOMO energy values were -5.36, -5.33, -5.32, -5.35 and -5.46, respectively, which were consisted with the values, -5.04, -5.14, -5.28, -5.19 and -5.07, respectively, obtained from DFT calculation.

## 3.6. Explosive detection

Firstly, the recognition behaviors of the compounds **4a**–**4e** toward the selected explosive compounds (NACs) were investigated by UV–vis and fluorescence spectra in dilute solution, as shown in Fig. 5 and Fig. S7. For compounds **4a**–**4e**, the concentration was kept at 10  $\mu$ M in THF and the NACs were kept at 5 mM in acetonitrile. Among the various nitro derivatives, all of the compounds **4a**–**4e** exhibited selectivity toward PA (Fig. S8). In Fig. 5,

a new band at 425 nm of UV-vis spectra was formed with the titration of PA, suggesting an interaction between the compounds 4a–4e and PA occurred [25]. Almost 63% quenching of fluorescence intensity happened when ten equivalents of PA were titrated. For other NACs, however, no more than 18% when keeping the same equivalents, indicated that compound **4c** can be as a sensor for PA. As shown in Fig. S9, Stern–Volmer plots of compounds 4a–4e are similar to each other. The detection limits of these compounds **4a–4e** were calculated to be 6.0  $\times$  10<sup>-7</sup>, 1.8  $\times$  10<sup>-6</sup>, 1.5  $\times$  10<sup>-6</sup>,  $1.0 \times 10^{-6}$ ,  $7.5 \times 10^{-7}$  mol L<sup>-1</sup> for PA, respectively. The fluorescence quenching mechanism of compound 4c for PA could be explained by fluorescence resonance energy transfer (FRET) [15c,26]. As shown in Fig. S11, there was a clearly spectral overlap of the absorption spectrum of PA and the emission spectrum of 4c in the range of 400–480 nm in THF solution. For other compounds. the similar phenomena were observed in THF solution, it indicated that the fluorescence quenching mechanism was the same to 4c.

Based on the high emission of **4a–4e** in solid state, to employ the detection in a feasible method, test strips were prepared that



Fig. 5. Changes in UV-vis and fluorescence spectra of compound 4c (10 µM) upon titration with picric acid (0-15 equiv.) in THF.



**Fig. 6.** Photographs of fluorescence quenching of compounds **4a–4e** for detecting different concentrations of PA (I) Blank, (II)  $10^{-6}$  M, (III)  $10^{-5}$  M, (IV)  $10^{-4}$  M, (V)  $10^{-3}$  M, under 365 nm UV light.

put the Whatman filter into the solution of **4a**–**4e** for 10 min, and then dried under vacuum. As shown in Fig. 6, with the increase of PA, there was an obviously different of quenching degree. With the concentration of PA reaches to 1.0 mM, the fluorescence was quenched completely. Besides, the response times of **4a**–**4e** in solutions were evaluated. As shown in Fig. S10, the fluorescence of the compounds were quenched immediately after adding PA. The compounds are efficient fluorescence sensors for convenient detecting PA.

Caution! PA, TNT and other nitroaromatics should be used with extreme care using the best safety precautions owing to their highly explosive character. They should be handled only in small quantities.

## 4. Conclusions

A series of innovative high efficient deep-blue luminescent materials (**4a**–**4e**) based on triphenylamine derivatives were synthesized by a solvent-free Michael addition reaction. The compounds can emit highly efficient deep-blue luminescence, possessing high quantum yields, both in solution and solid state. The molecules exhibit solvatochromic effect and interesting fluorescent behavior in binary solvent systems of THF-H<sub>2</sub>O due to the strong intramolecular charge transfer (ICT) caused by the unique push–pull electronic structure. The synergistic effect of strong intramolecular hydrogen bond and the steric hindrance of cyclohexyl are the reason for burst emission both in solution and solid state. The high emission characters are utilized for picric acid (PA) detection both in solution and solid state.

## Acknowledgments

This work was supported by the Educational Commission of Anhui Province of China (KJ2014ZD02) and the National Natural Science Foundation of China (51432001).

## Appendix A. Supplementary material

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.08.013.

## References

[1] (a) Zhang ZH, Jiang W, Ban XX, Yang M, Ye SH, Huang B, et al. Solution-processed efficient deep-blue fluorescent organic light-emitting diodes based on novel 9,10-diphenyl-anthracene derivatives. RSC Adv 2015;5:29708–17.

(b) Wu TL, Chou HH, Huang PY, Cheng CH, Liu RS. 3,6,9,12-tetrasubstituted chrysenes: synthesis, photophysical properties, and application as blue fluorescent OLED. J Org Chem 2014;79:267–74.

(c) Chen B, Yu G, Li X, Ding YB, Wang C, Liu ZW, et al. Full-colour luminescent compounds based on anthracene and 2,2'-dipyridylamine. J Mater Chem C 2013;1:7409–17.

(d) Thirion D, Romain M, Berthelot JR, Poriel C. Intramolecular excimer emission as a blue light source in fluorescent organic light emitting diodes: a promising molecular design. J Mater Chem 2012;22:7149–57.

(e) Jou JH, Kumar S, Agrawal A, Li TH, Sahoo S. Approaches for fabricating high efficiency organic light emitting diodes. J Mater Chem C 2015;3:2974–3002. (f) Feng XJ, Tian PZ, Xu Z, Chen SF, Wong MS. Fluorescence-enhanced chemosensor for metal cation detection based on pyridine and carbazole. J Org Chem 2013;78:11318–25.

(g) Yang MD, Zhang Y, Zhu WJ, Wang HZ, Huang J, Cheng LH, et al. Difunctional chemosensor for Cu(II) and Zn(II) based on Schiff base modified anthryl derivative with aggregation-induced emission enhancement and piezochromic characteristics. J Mater Chem C 2015;3:1994–2002.

(h) Cao XQ, Bai SM, Wu YS, Liao Q, Shi Q, Fu HB, et al. Self-assembly of twisted tetrachloroperylenediimide chromophores into two dimensional brick-stone aggregates: exciton dynamics and photoconductivity. Chem Commun 2012;48:6402–4.

(i) Ortiz RP, Herrera H, Blanco R, Huang H, Facchetti A, Marks TJ, et al. Organic n-channel field-effect transistors based on arylenediimide-thiophene derivatives. J Am Chem Soc 2010;132:8440–52.

(j) Wang H, Li F, Ravia I, Gao BR, Li YP, Medvedev V, et al. Cyano-substituted oligo(*p*-phenylene vinylene) single crystals: a promising laser material. Adv Funct Mater 2011;21:3770–7.

(k) Wang YQ, Xu L, Wei XD, Li X, Agren H, Wu WJ, et al. 2-Diphenylaminothiophene as the donor of porphyrin sensitizers for dyesensitized solar cells. New J Chem 2014;38:3227–35.

(I) Ding YB, Tang YY, Zhu WH, Xie YS. Fluorescent and colorimetric ion probes based on conjugated oligopyrroles. Chem Soc Rev 2015;44:1101–12.

(m) Wang YQ, Chen B, Wu WJ, Li X, Zhu WH, Tian H, et al. Efficient solar cells sensitized by porphyrins with an extended conjugation framework and a carbazole donor: from molecular design to cosensitization. Angew Chem Int Ed 2014;53:10779–83.

(n) Xie YS, Wei PC, Li X, Hong T, Zhang K, Furuta H. Macrocycle contraction and expansion of a dihydrosapphyrin isomer. J Am Chem Soc 2013;135: 19119–22.

[2] (a) Ning ZJ, Chen Z, Zhang Q, Yan YL, Qian SX, Cao Y, et al. Aggregationinduced emission (AIE)-active starburst triarylamine fluorophores as potential non-doped red emitter for organic light-emitting diodes and Cl<sub>2</sub> gas chemodosimeter. Adv Funct Mater 2007;17:3799–807.

(b) Kubota Y, Kasatani K, Takai H, Funabiki K, Matsui M. Strategy to enhance solid-state fluorescence and aggregation-induced emission enhancement effect in pyrimidine boron complexes. Dalton Trans 2015;44:3326–41.

- (a) Hong YN, Lam JWY, Tang BZ. Aggregation-induced emission: phenomenon, mechanism and applications. Chem Commun 2009:4332–53.
   (b) Thomas S, Joly GD, Swager TM. Chemical sensors based on amplifying
- fluorescent conjugated polymers. Chem Rev 2007;107:1339–86. [4] (a) Yang JS, Yan JL. Central-ring functionalization and application of the rigid,
- aromatic, and H-shaped pentiptycene scaffold. Chem Commun 2008: 1501–12.

(b) Wang J, Zhao YF, Dou CD, Sun H, Xu P, Ye KQ, et al. Alkyl and dendron substituted quinacridones: synthesis, structures, and luminescent properties. J Phys Chem B 2007;111:5082–9.

(c) Gaylord BS, Wang SJ, Heeger AJ, Bazan GC. Water-soluble conjugated oligomers: effect of chain length and aggregation on photoluminescencequenching efficiencies. J Am Chem Soc 2001;123:6417–8.

(d) Lee SH, Jang BB, Kafafi ZH. Highly fluorescent solid-state asymmetric spirosilabifluorene derivatives. J Am Chem Soc 2005;127:9071-8.

(e) Chiang CL, Tseng SM, Chen CT, Hsu CP, Shu CF. Influence of molecular dipoles on the photoluminescence and electroluminescence of dipolar spirobifluorenes. Adv Funct Mater 2008;18:248–57.

[5] (a) Luo JD, Xie ZL, Lam JWY, Cheng L, Chen HY, Qiu CF, et al. Aggregationinduced emission of 1-methyl-1,2,3,4,5-pentaphenylsilole. Chem Commun 2001:1740–1.

(b) Tang BZ, Zhan XW, Yu G, Lee PPS, Liu YQ, Zhu DB. Efficient blue emission from siloles. J Mater Chem 2001;11:2974–8.

(c) Zheng Z, Yu ZP, Yang MD, Jin F, Zhang Q, Zhou HP, et al. Substituent group variations directing the molecular packing, electronic structure, and aggregation-induced emission property of isophorone derivatives. J Org Chem

2013;78:3222-34.

(d) Wu WB, Ye SH, Huang LJ, Xiao L, Fu YJ, Huang Q, et al. A conjugated hyperbranched polymer constructed from carbazole and tetraphenylethylene moieties: convenient synthesis through one-pot "A<sub>2</sub> + B<sub>4</sub>" Suzuki polymerization, aggregation-induced enhanced emission, and application as explosive chemosensors and PLEDs. J Mater Chem 2012;22:6374–82.

(e) Shi CX, Guo ZQ, Yan YL, Zhu SQ, Xie YS, Zhao YS, et al. Self-assembly solidstate enhanced red emission of quinolinemalononitrile: optical waveguides and stimuli response. ACS Appl Mater Interfaces 2013;5:192–8.

(f) Jia WB, Wang HW, Yang LM, Lu HB, Kong L, Tian YP, et al. Synthesis of two novel indolo[3,2-*b*]carbazole derivatives with aggregation-enhanced emission property. J Mater Chem C 2013;1:7092–101.

(g) Ån BK, Kwon SK, Jung SD, Park SY. Enhanced emission and its switching in fluorescent organic nanoparticles. J Am Chem Soc 2002;124:14410–5.

[6] (a) Zhang Y, Wang JH, Zheng J, Li D. A Br-substituted phenanthroimidazole derivative with aggregation induced emission from intermolecular halogen--hydrogen interactions. Chem Commun 2015;51:6350–3.

(b) Shen XY, Wang YJ, Zhao EG, Yuan WZ, Liu Y, Lu P, et al. Effects of substitution with donor–acceptor groups on the properties of tetraphenylethene trimer: aggregation-induced emission, solvatochromism, and mechanochromism. J Phys Chem C 2013;117:7334–47.

(c) Rananaware A, Bhosale RS, Ohkubo K, Patil HL, Jones A, Jackson SL, et al. Tetraphenylethene-based star shaped porphyrins: synthesis, self-assembly, and optical and photophysical study. J Org Chem 2015;80:3832–40.

[7] (a) Zhu XL, Liu R, Li YH, Huang H, Wang Q, Wang DF, et al. An AIE-active boron-difluoride complex: multi-stimuli-responsive fluorescence and application in data security protection. Chem Commun 2014;50:12951–4.
 (b) Lai CT, Hong IL Influence of molecular weight on the aggregation-induced

emission enhancement and spectral stability of vinyl polymers containing the fluorescent 2,4,6-triphenylpyridine pendant groups. J Mater Chem 2012;22: 9546–55.

(c) Qin W, Ding D, Liu JZ, Yuan WZ, Hu Y, Liu B, et al. Biocompatible nanoparticles with aggregation-induced emission characteristics as far-red/nearinfrared fluorescent bioprobes for in vitro and in vivo imaging applications. Adv Funct Mater 2012;22:771–9.

(d) Yang CJ, Trinh QT, Wang XC, Tang YX, Wang K, Huang S, et al. Crystallization-induced red emission of a facilely synthesized biodegradable indigo derivative. Chem Commun 2015;51:3375–8.

[8] (a) Shang YL, Wen YQ, Li SL, Du SX, He XB, Cai L, et al. A triphenylaminecontaining donor-acceptor molecule for stable, reversible, ultrahigh density data storage. J Am Chem Soc 2007;129:11674–5.

(b) Tang XL, Liu WM, Wu JS, Lee CS, You JJ, Wang PF. Synthesis, crystal structures, and photophysical properties of triphenylamine-based multicyano derivatives. J Org Chem 2010;75:7273–8.

(c) Cias P, Slugovc C, Gescheidt G. Hole transport in triphenylamine based OLED devices: from theoretical modeling to properties prediction. J Phys Chem A 2011;115:14519–25.

(d) Huang XM, Fang Y, Li X, Xie YS, Zhu WH. Novel dyes based on naphthalimide moiety as electron acceptor for efficient dye-sensitized solar cells. Dyes Pigments 2011;90:297–303.

(e) Jiang X, Karlsson KM, Gabrielsson E, Johansson EMJ, Quintana M, Karlsson M, et al. Highly efficient solid-state dye-sensitized solar cells based on triphenylamine dyes. Adv Funct Mater 2011;21:2944–52.

(f) Yang SQ, Liu JY, Liu JY, Zhou PW, Han KL, He GZ. Photo-induced intramolecular charge transfer from antenna to anchor groups in phenoxazine dyes. Chem Phys Lett 2011;512:66–9.

(g) Lee KH, Kim SO, Yook KS, Jeon SO, Lee JY, Yoon SS. Highly efficient blue light-emitting diodes containing spirofluorene derivatives end-capped with triphenylamine/phenylcarbazole. Synth Met 2011;161:2024–30.

[9] (a) Wang HW, Chen Y, Ye WB, Xu JK, Liu DF, Yang JX, et al. A facile and highly efficient green synthesis of carbazole derivatives containing a six-membered ring. Dyes Pigments 2013;96:738–47.

(b) Qi QK, Zhang JB, Xu B, Li B, Zhang SXA, Tian WJ. Mechanochromism and polymorphism-dependent emission of tetrakis(4-(dimethylamino)phenyl) ethylene. J Phys Chem C 2013;117:24997–5003.

(c) Zhang XQ, Chi ZG, Zhou X, Liu SW, Zhang Y, Xu JR. Influence of carbazolyl groups on properties of piezofluorochromic aggregation-enhanced emission compounds containing distyrylanthracene. J Phys Chem C 2012;116: 23629–38.

(d) Dai Q, Liu WM, Zeng LT, Lee CS, Wu JS, Wang PF. Aggregation-induced emission enhancement materials with large red shifts and their self-assembled crystal microstructures. CrystEngComm 2011;13:4617–24.

[10] (a) Omer KM, Ku SY, Cheng JZ, Chou SH, Wong KT, Bard AJ. Electrochemistry and electrogenerated chemiluminescence of a spirobifluorene-based donor (triphenylamine)-acceptor (2,1,3-benzothiadiazole) molecule and its organic nanoparticles. J Am Chem Soc 2011;133:5492–9.

(b) Misra R, Maragani R, Patel KR, Sharma GD. Synthesis, optical and electrochemical properties of new ferrocenyl substituted triphenylamine based donor-acceptor dyes for dye sensitized solar cells. RSC Adv 2014;4:34904–11. (c) Zhao X, Xue PC, Wang K, Chen P, Zhang P, Lu R. Aggregation-induced emission of triphenylamine substituted cyanostyrene derivatives. New J Chem 2014;38:1045–51.

(d) Tang S, Li WJ, Shen FZ, Liu DD, Yang B, Ma YG. Highly efficient deep-blue electroluminescence based on the triphenylamine-cored and peripheral blue emitters with segregative HOMO-LUMO characteristics. J Mater Chem

2012;22:4401-8.

(e) Quinton C, Rizzo VA, Verdes CD, Miomandre F, Clavier G, Audebert P. Redox- and protonation-induced fluorescence switch in a new triphenylamine with six stable active or non-active forms. Chem A Eur J 2015;21: 2230–40.

(f) Pina J, Melo JSSD. Triphenylamine-benzimidazole derivatives: synthesis, excited-state characterization, and DFT studies. J Org Chem 2013;78: 11389–95.

(g) Tao SL, Zhou YC, Lee CS, Lee ST, Huang D, Zhang XH. Highly efficient nondoped blue organic light-emitting diodes based on anthracene-triphenylamine derivatives. J Phys Chem C 2008;112:14603–6.

[11] (a) Chien CH, Kung LR, Wu CH, Shu CF, Chang SY, Chi Y. A solution-processable bipolar molecular glass as a host material for white electrophosphorescent devices. J Mater Chem 2008;18:3461–6.
(b) Wu XF, Li HB, Xu YX, Xu BW, Tong H, Wang LX. Thin film fabricated from solution-dispersible porous hyperbranched conjugated polymer nanoparticles without surfactants. Nanoscale 2014;6:2375–80.
(c) Huang CY, Lee WH, Lee RH. Solution processable star-shaped molecules with a triazine core and branching thienylenevinylenes for bulk hetero-

junction solar cells. RSC Adv 2014;4:48150–62. [12] (a) Sivaraman G, Vidya B, Chellappa D. Rhodamine based selective turn-on sensing of picric acid. RSC Adv 2014;4:30828–31.

(b) Xu YQ, Li BH, Li WW, Zhao J, Sun SG, Pang Y. "ICT-not-quenching" near infrared ratiometric fluorescent detection of picric acid in aqueous media. Chem Commun 2013;49:4764–6.

- (a) Acharyya K, Mukherjee PS. A fluorescent organic cage for picric acid detection. Chemical Communications 2014;50:15788–91.
   Bhalla V, Gupta A, Kumar M, Rao DSS, Prasad SK. Self-assembled pentacenequinone derivative for trace detection of picric acid. ACS Appl Mater Interfaces 2013;5:672–9.
- [14] (a) Vishnoi P, Walawalkar MG, Sen S, Datta A, Patwari GN, Murugavel R. Selective fluorescence sensing of polynitroaromatic explosives using triaminophenylbenzene scaffolds. Phys Chem Chem Phys 2014;16:10651–8. (b) Ding AX, Yang LM, Zhang YY, Zhang GB, Kong L, Zhang XJ, et al. Complexformation-enhanced fluorescence quenching effect for efficient detection of picric acid. Chem A Eur J 2014;20:12215–22.

[15] (a) Roy B, Bar AK, Gole B, Mukherjee S. Fluorescent tris-imidazolium sensors for picric acid explosive. J Org Chem 2013;78:1306–10.
(b) Toal SJ, Trogler WC. Polymer sensors for nitroaromatic explosives detection. J Mater Chem 2006;16:2871–83.
(c) Li DD, Liu JZ, Kwok RTK, Liang ZQ, Tang BZ, Yu JH. Supersensitive detection of explosives by recyclable AIE luminogen-functionalized mesoporous materials. Chem Commun 2012;48:7167–9.

(d) An ZF, Zheng C, Chen RF, Yin J, Xiao JJ, Shi HF, et al. Exceptional blueshifted and enhanced aggregation-induced emission of conjugated asymmetric triazines and their applications in superamplified detection of explosives. Chem A Eur J 2012;18:15655–61.

(e) Vajpayee V, Kim H, Mishra A, Mukherjee PS, Stang PJ, Lee MH, et al. Self-assembled molecular squares containing metal-based donor: synthesis and application in the sensing of nitro-aromatics. Dalton Trans 2011;40: 3112–5.

- [16] Grabowski ZR, Rotkiewicz K. Structural changes accompanying intramolecular electron transfer: focus on twisted intramolecular charge-transfer states and structures. Chem Rev 2003;103:3899–4031.
- [17] (a) Wang J, Mei J, Hu RR, Sun JZ, Qin AJ, Tang BZ. Click synthesis, aggregationinduced emission, E/Z isomerization, self-organization, and multiple chromisms of pure stereoisomers of a tetraphenylethene-cored luminogen. J Am Chem Soc 2012;134:9956–66.
  (b) Galer P, Korosec RC, Vidmar M, Sket B. Crystal structures and emission properties of the BF<sub>2</sub> complex 1-phenyl-3-(3,5-dimethaxyphenyl)-propane-

1,3-dione: multiple chromisms, aggregation- or crystallization-induced emission, and the self-assembly. J Am Chem Soc 2014;136:7383–94.

[18] (a) Tsipis AC. DFT/TDDFT insights into the chemistry, biochemistry and photophysics of copper coordination compounds. RSC Adv 2014;4:32504–29. (b) Cramer CJ, Truhlar DG. Density functional theory for transition metals and transition metal chemistry. Phys Chem Chem Phys 2009;11:10757–816.

[19] (a) Gong YY, Zhao LF, Peng Q, Fan D, Yuan WZ, Zhang YM, et al. Crystallizationinduced dual emission from metal-and heavy atom-free aromatic acids and eaters. Chem Sci 2015;6:4438–44.
(b) Zhu QH, Zhang YL, Nie H, Zhao ZJ, Liu SW, Wong KS, et al. Insight into the strong aggregation-induced emission of low-conjugated racemic C6unsubstituted tetrahydropyrimidines through crystal-structure—property relationship of polymorphs. Chem Sci 2015;6:4690–7.

- [20] (a) Auweter H, Haberkorn H, Heckmann W, Horn D, Luddecke E, Rieger J, et al. Supramolecular structure of precipitated nanosize β-carotene particle. Angew Chem Int Ed 1999;38:2188–91.
  (b) Zhang XQ, Chi ZG, Xu BJ, Jiang L, Zhou X, Zhang Y, et al. Multifunctional organic fluorescent materials derived from 9,10-distyrylanthracene with alkoxyl endgroups of various lengths. Chem Commun 2012;48:10895–7.
- [21] (a) Ilharco LM, Barros RB. Aggregation of pseudoisocyanine iodide in cellulose acetate films: structural characterization by FTIR. Langmuir 200;16: 9331-7.

(b) Kabe R, Nakanotani H, Sakanoue T, Yahiro M, Adachi C. Effect of molecular morphology on amplified spontaneous emission of bis-styrylbenzene derivatives. Adv Mater 2009;21:4034–8.

- [22] Liu YW, Zhang Y, Wu XH, Lan Q, Chen CS, Liu SW, et al. Deep-blue luminescent compound that emits efficiently both in solution and solid state with considerable blue-shift upon aggregation. J Mater Chem C 2014;2:1068–75.
- [23] (a) Zhu LN, Yang CL, Qin JG. An aggregation-induced blue shift of emission and the self-assembly of nanoparticles from a novel amphiphilic oligofluorene. Chem Commun 2008:6303–5.

(b) Wu QY, Zhang T, Peng Q, Wang D, Shuai ZG. Aggregation induced blueshifted emission – the molecular picture from a QM/MM study. Phys Chem Chem Phys 2014;16:5545–52.

(c) Kong L, Tian YP, Chen QY, Zhang Q, Wang H, Tan DQ, et al. Self-assembly of metal ion induced highly emissive fluorophore-triphenylamine nanostructures: enhanced two-photon action cross-section for bioimaging applications. J Mater Chem C 2015;3:570–81.

[24] Jia WB, Yang P, Li JJ, Yin ZM, Kong L, Lu HB, et al. Synthesis and characterization of a novel cyanostilbene derivative and its initiated polymers: aggregation-induced emission enhancement behaviors and light-emitting diode applications. Polym Chem 2014;5:2282–92.

- [25] Li WF, Ma HC, Lei ZQ, Self-assembled triphenylamine derivative for trace detection of picric acid. RSC Adv 2014;4:39351–8.
- [26] (a) Wang J, Mei J, Yuan WZ, Lu P, Qin AJ, Sun JZ, et al. Hyperbranched poly-triazoles with high molecular compressibility: aggregation-induced emission and superamplified explosive detection. J Mater Chem 2011;21:4056–9.
  (b) Xiong JF, Li JX, Mo GZ, Huo JP, Liu JY, Chen XY, et al. Benzimidazole derivatives: selective fluorescent chemosensors for the picogram detection of picric acid. J Org Chem 2014;79:11619–30.
  (c) Bhalla V, Gupta A, Kumar M. Fluorescent nanoaggregates of pentacene-

quinone derivative for selective sensing of picric acid in aqueous media. Org Lett 2012;14:3112–5.