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Synthesis, photophysical and iron-sensing properties of terpyridyl-based triphenylamine derivatives

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1. Introduction

ABSTRACT

A series of new terpyridyl phenyl/styryl triphenylamine chromophores were designed and synthesized. The branching number and the rigid/flexible bridge structures had a remarkable effect on the photophysical, selectivity and sensitivity for Fe(II) ion properties of these chromophores. The fluorescence lifetimes of the rigid terpyridyl phenyl triphenylamine chromophores are longer than that of the flexible terpyridyl styryl triphenylamine derivatives. The terpyridyl phenyl/styryl triphenylamine chromophores present an increasing fluorescence lifetime with the increase in the number of branches from 1 to 3. The terpyridyl flexible styryl triphenylamine derivatives have a higher sensitivity than that of the terpyridyl rigid phenyl triphenylamine derivatives for Fe(II) ion in neutral aqueous solution amongst other divalent metal ions such as Cu^{2+} , Co^{2+} , Ni^{2+} , Mg^{2+} , Pb^{2+} , Zn^{2+} .

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Ir(III) dyad that exhibits high charge-separation efficiency [15]. Lin et al., reported a series of *p*-conjugated bis-terpyridyl ligands having donor-acceptor units and their corresponding Ru(II)-containing main-chain metallo-polymers for solar cell applications [16]. The properties were significantly influenced by the position of the 4'-terpyridyl substituent which affected the photophysics of the terpyridyl-Pt(II) complexes [17]. In particular, a large aryl substituent (such as pyrenyl) in the 4'-position of the terpyridyl ligand led to alteration of the lowest excited state [18].

Terpyridine ligands have generally not been used for sensors and the reason is attributed to their strong ability to coordinate with metal ions (i.e., the binding constant is extremely high). The terpyridyl derivatives self-assembled with ferrous ions showing a band in the visible region of the absorption spectrum. In preliminary studies, we found that the properties of terpyridyl derivatives self-assembled withe Fe(II) ion could be controlled by using the rigid phenyl triphenylamine and flexible styryl striphenylamine groups. This feature is crucial to the binding of ferrous ions because iron plays crucial roles in the transport and storage of oxygen and also in electron transport in diverse metalloenzymes [19–22]. Obviously, because iron is

Triphenylamine derivatives have been widely used as twophoton absorption (TPA) materials [1,2], in memory devices [3] and hole transporting materials [4–10]; these applications make use of the fact that triphenylamine derivatives exhibit multifunctional properties. On the other hand, the multifunctional 4'-terpyridyl unit, which is capable of chelation, can be assembled with metal ions to furnish materials that possess useful properties, as exemplified by the bis-terpyridyl-stilbene derivatives of Ru(II) and Ir(III), which have been examined for two-photon luminescence [11]. A terpyridyl-Pt(II) complex is used for label- and immobilization-free detection of the lysozyme, thrombin [12] and generation of hydrogen from water [13]. To date, research has been devoted to the synthesis of terpyridyl-type of ligands in order to understand fundamental chemical properties [14]. For example, Flamigni et al., have reported a triphenylamine/bis(terpyridine)

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present is living systems, the tracking of its homeostasis is of significance [23,24].

2. Experimental section

2.1. Synthesis

2.1.1. Synthesis of components

2.1.1.1. Synthesis of 1-[3-oxo-3-(2-pyridyl)propen-1-yl]-4-bromobenzene (compd 1). To a methanol (100 mL) solution of 4bromobenzaldehyde (2.0 g, 10.8 mmol) was added 2acetylpridine (1.30 g, 10.8 mmol) and 2% aqueous NaOH (0.44 g, 22 mL), and the mixture was stirred for 2 h at room temperature (Scheme 1). The white precipitate formed was collected by filtration, and washed sequentially with H₂O, methanol for three times, respectively. The off-white solid was dried *in vacuo* to give product 1.75 g, 56.3%. m.p. 118–119 °C. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 7.44 (t, 1H, *J* = 6.0 Hz, pyridyl-H), 7.48 (d, 2H, *J* = 8.0 Hz, benzene –H), 7.53 (d, 2H, *J* = 8.0 Hz, benzene –H), 7.78–7.84 (m, 2H, pyridyl-H), 8.13 (d, 1H, *J* = 8.0 Hz, CH–H), 8.24 (d, 1H, *J* = 12.0 Hz, CH–H), 8.68 (d, 1H, *J* = 4.0 Hz, pyridyl-H).

2.1.1.2. Synthesis of pyridinium iodide salt (compd **2**). Under the anhydrous and oxygen-free conditions, I₂ (5.06 g, 20 mmol) was dissolved in pyridine (30 mL) and the mixture was stirred and heated to 70 °C for 0.5 h. Then 2-acetylpridine (2.42 g, 20.0 mmol) was added to the solution and the mixture was stirred and heated to 80 °C for 4 h. After the mixture cooled, the solution was filtered and washed with ethanol for five times. The yellow-green solid was then dried *in vacuo* to give product 4.38 g, 67.2%. m.p. 227–228 °C. ¹H NMR(CDCl₃, 400 MHz, TMS): δ 6.89 (s, 2H, CH₂–H), 7.58 (t, 1H, J = 6.0 Hz, pyridyl-H), 8.08 (t, 2H, J = 8.0 Hz, pyridyl-H), 8.02 (d, 1H, J = 8.0 Hz, pyridyl-H), 8.72 (d, 1H, J = 8.0 Hz, pyridyl-H), 9.12 (d, 2H, J = 4.0 Hz, pyridyl-H).

2.1.1.3. Synthesis of 4'-(4-bromophenyl)-2,2':6',2"-terpyridine (compd 3). A methanol (100 mL) solution of 1-[3-oxo-3-(2-pyridyl) propen-1-yl]-4-bromobenzene (1.75 g, 6.07 mmol) was added pyridinium iodide salt (1.98 g, 6.07 mmol) and ammonium acetate (11.01 g, 142.8 mmol) at room temperature, and the mixture was stirred and refluxed (70 °C) for overnight. The white precipitate formed was collected by filtration, and washed sequentially with H₂O and methanol for three times, respectively. The white solid was then dried in vacuo to give product 0.84 g, yielding 35.6%. m.p 134–136 °C. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 7.29–7.32 (m, 2H, pyridyl-H), 7.58 (d, 2H, J = 8.0 Hz, benzene-H), 7.72 (d, 2H, *J* = 8.0 Hz, benzene-H), 7.81–7.85 (m, 2H, pyridyl-H), 8.61 (d, 2H, I = 4.0 Hz, pyridyl-H), 8.64 (s, 2H, pyridyl-H), 8.67 (d, 2H, I = 8.0 Hz, pyridyl-H).

2.1.1.4. Synthesis of 4-(4,4,5,5-tertramethyl-[1,3,2]dioxaborolane) phenyl-N,N-diphenylamine (compd **4**). n-Butyl lithium in hexane (1.6 M, 1.25 mL, 2.0 mmol) was added to a stirred solution of 4-bromotriphenylamine (0.64 g, 2.0 mmol) in dry tetrahydrofuran (THF) (50 mL) at -78 °C under nitrogen atmosphere. After stirring for 30 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.37 g, 2.0 mmol) was added to the reaction mixture. The ensuing mixture was warmed to room temperature and then quenched with water (10 mL). The mixture was extracted with chloroform. Next, the organic phases were dried with magnesium sulfate and the solution was concentrated *in vacuo*. The crude product was purified by column chromatography on SiO₂ using hexane as the eluent and 0.50 g product was obtained as white solid in 68. 1% yield. m.p 103–104 °C. ¹H NMR (400 MHz, CDCl₃,

TMS): δ 1.32 (s, 12H, -CH₃), 7.04 (t, 4 H, *J* = 8.0 Hz, benzene-H), 7.11 (d, 4 H, *J* = 8.0 Hz, benzene-H), 7.26 (t, 4 H, *J* = 8.0 Hz, benzene-H), 7.66 (d, 2 H, *J* = 8.0 Hz, benzene-H).

2.1.1.5. Synthesis of 4,4'-bis(4,4,5,5-tertramethyl-[1,3,2]dioxaborolane)phenyl-N-phenylamine (compd 5). n-Butyl lithium in hexane (1.6 M. 2.50 mL. 4.0 mmol) was added to a stirred solution of 4,4'-bisbromotriphenylamine (0.81 g, 2.0 mmol) in dry THF (50 mL) at -78 °C under nitrogen atmosphere. After stirring for 30 min, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.74 g, 4.0 mmol) was added to the reaction mixture. The ensuing mixture was warmed to room temperature and then quenched with water (10 mL). The mixture was extracted with chloroform. Next, the organic phases were dried with magnesium sulfate and the solution was concentrated in vacuo. The crude product was purified by column chromatography on SiO₂ using hexane as the eluent and 0.52 g product obtained as white solid in 52.7% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.32 (s, 24H, -CH₃), 6.96-7.08 (m, 9H, benzene-H), 7.61-7.68 (m, 4H, benzene-H).

2.1.1.6. Synthesis of 4,4',4''-tri(4,4,5,5-tertramethyl-[1,3,2]dioxaborolane)phenylamine (compd **6**). To a solution of 4,4',4''-tri(4-bromophenyl)amine (2.41 g, 5.0 mmol) in dry THF (50 mL) at -78 °C was added n-butyllithium (1.6 M in hexane, 8.85 mL, 15 mmol). After stirring at -78 °C for 30 min, 2-isopropoxy-4,4,5,5-tetramethethyl-dioxaborolane (3.07 g, 16.5 mmol) was added to the resulting suspension and stirring was continued for another 2 h at this temperature. The solution was allowed to warm up to room temperature and quenched by the addition of water. The solid product was purified by column chromatography on silica using petroleum ether as the eluant to give light green solid 1.10 g, in 34.8% yeild. m.p > 300 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 1.34 (s, 36H, -CH₃), 7.07 (d, 6H, J = 8.0 Hz, benzene-H), 7.68 (d, 6H, J = 8.0 Hz, benzene-H).

2.1.1.7. Synthesis of 4- vinylphenyl-N,N-diphenylamine (compd **7**). 4-(Diphenylamino) benzaldehyde (3.05 g, 11.16 mmol) and methyl triphenylphosphonium iodide [25] (10.64 g, 26.30 mmol) were dissolved in dry 1,4-dioxane (50 mL). To this solution was added sodium ethoxide (2.0 g, 29.40 mmol) as strong base at room temperature. The mixture was refluxed for 6 h under the nitrogen atmosphere and then poured into excess distilled water. The precipitate was purified by column chromatography on silica using petroleum ether as the eluant to give white solid 1.72 g, 6.35 mmol, in 56.9% yield. m.p 75–76 °C. ¹H NMR (400 MHz, CDCl₃, TMS): δ 5.16 (d, 1H, *J* = 10.8 Hz, =CH), 5.64 (d, 1H, *J* = 17.6 Hz, =CH), 6.62–6.70 (m, 1H, -CH =), 7.01 (d, 2H, *J* = 8.0 Hz, benzene-H), 7.168–7.362 (m, 10H, benzene-H), 7.68 (d, 2H, *J* = 8.0 Hz, benzene-H).

2.1.1.8. Synthesis of 4,4'-bisvinylphenyl-N-phenylamine (compd **8**). 4,4'-Bisformylphenyl-N-phenylamine (1.0 g, 3.3 mmol) and methyl triphenylphosphonium iodide (5.92 g, 14.65 mmol) were dissolved in 50 mL of dry1,4-dioxane. To this solution was added sodium ethoxide (1.2 g, 17.6 mmol) as strong base at room temperature. The mixture was refluxed for 6 h under the nitrogen atmosphere and then poured into excess distilled water. The precipitate was purified by column chromatography on silica using petroleum ether as the eluant to give yellow liquid 0.49 g, in 49.9% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 5.15 (d, 2H, =CH₂), 5.63 (d, 2H, =CH₂), 6.61–6.68 (m, 2H, -CH =), 7.02 (d, 5H, benzene-H), 7.08 (d, 2H, J = 8.0 Hz, benzene-H), 7.21–7.28 (m, 6H, benzene-H).

2.1.1.9. Synthesis of 4,4',4''-trivinylphenylamine (compd **9**). 4,4'4''-Triformylphenylamine (0.6 g, 1.8 mmol) and methyl



Scheme 1. The synthetic routes for chromophores I–VI.

triphenylphosphonium iodide (6.25 g, 18.3 mmol) were dissolved in dry 1,4-dioxane (50 mL). To this solution was added sodium ethoxide (0.3 g, 4.4 mmol) as strong base at room temperature. The mixture was refluxed for 6 h under the nitrogen atmosphere and then poured into excess distilled water. The precipitate was purified by column chromatography on silica using petroleum ether as the eluant to give yellow liquid 0.27 g, in 46.4% yield. ¹H NMR (400 MHz, CDCl₃, TMS): δ 4.99 (d, 3H, J = 8.0 Hz, =CH), 5.64 (d, 3H, J = 16.0 Hz, =CH), 5.84–5.88 (m, 3H, -CH =), 6.62, 6.69 (m, 6H, benzene-H), 7.47–7.60 (m, 6H, benzene-H).

2.1.2. Synthesis of chromophores

2.1.2.1. 4-[4-(2,2':6',2''-terpyridinyl)]phenyltriphenylamine (chromophore 4-(4,4,5,5-tertramethyl-[1,3,2]dioxaborolane) I). Using phenyl-N,N-diphenylamine (compd 4) (0.37 g, 1.0 mmol) with 4'-(4-bromophenyl)-2, 2':6', 2"-terpyridine (compd 3) (0.39 g, 1.0 mmol), tetrakis (triphenylphosphine)palladium (0) [Pd(PPh₃)₄ ed. Note: caution: irritant; air sensitive; light sensitive; incompatible with oxidants] (0.10 g) and Na₂CO₃ (6.40 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) were heated at 70 °C for 15 h (Scheme 1). The crude product was distillated in vacuo and purified by column chromatography on SiO₂ using hexane and THF as the eluent. Then, 0.40 g of chromophore I was obtained as a white solid in 72.5% yield. MS (m/e): 552.45; m.p 251–252 °C; Anal. Calcd for C₃₉H₂₈N₄ (%): C, 84.76; H, 5.11; N, 10.14. Found C, 84.80; H, 5.08; N, 10.12; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.17 (t, 4H, J = 6.0 Hz, benzene-H), 7.23–7.30 (m, 4H, benzene-H), 7.36 (t, 2H, J = 8.0 Hz, benzene-H), 7.56 (d, 2H, J = 8.0 Hz, benzene-H), 7.65 (t, 2H, J = 8.0 Hz, benzene-H), 7.72 (d, 2H, J = 8.0 Hz, benzene-H), 7.89 (t, 2H, J = 8.0 Hz, pyridyl-H), 7.99 (d, 2H, J = 8.0 Hz, benzene-H), 8.68 (t, 4H, J = 8.0 Hz, pyridyl-H), 8.73 (t, 2H, J = 8.0 Hz, pyridyl-H), 8.79 (s, 2H, pyridyl-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.64, 121.40, 121.79, 123.07, 123.37, 123.81, 123.96, 124.54, 124.99, 127.04, 127.71, 127.77, 128.92, 129.33, 132.12, 135.85, 136.90, 149.16, 149.82, 156.32.

2.1.2.2. 4,4'-bis[4-(2,2':6',2''-terpyridinyl)]phenyltriphenylamine

(*chromophore* **II**). Chromophore **II** was synthesized by an analogous method to that used for chromophore **I** by using compd **3** (0.79 g, 2.0 mmol), compd **5** (0.50 g, 1.0 mmol), tetrakis (triphenylphosphine) palladium (0) (0.10 g), Na₂CO₃ (6.40 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) and obtained yellow solid 0.45 g, in 28.9% yield. MS m/e: 860.17; m.p 181–182 °C; Anal. Calcd for C₆₀H₄₁N₇ (%): C, 83.79; H, 4.81; N, 11.40. Found C, 83.80; H, 4.78; N, 11.42; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.22–7.26 (m, 9H, benzene-H, pyridyl-H), 7.35–7.38 (m, 4H, benzene-H), 7.50–7.55 (m, 4H, benzene-H), 7.58–7.61 (m, 4H, benzene-H), 7.67–7.50 (m, 4H, benzene-H), 8.00 (d, 4H, *J* = 8.0 Hz, pyridyl-H), 8.79 (s, 4H, pyridyl-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.66, 121.39, 123.77, 124.21, 125.49, 127.71, 128.42, 129.15, 131.41, 136.85, 149.14, 155.98, 156.36.

2.1.2.3. 4,4',4''-tri[4-(2,2':6',2''-terpyridinyl)]phenyltriphenylamine

(chromophore **III**). Chromophore **III** was synthesized by an analogous method to that used for chromophore **I** by using compd **3** (0.58 g, 1.5 mmol), compd **6** (0.31 g, 0.5 mmol), tetrakis (triphenylphosphine)palladium (0) (0.10 g), Na₂CO₃ (6.40 g, 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) and obtained yellow solid 0.44 g, in 75.6% yield. MS m/e: 1165; m.p 274–275 °C; Anal. Calcd for C₈₁H₅₄N₁₀ (%): C, 83.34; H, 4.66; N, 12.00. Found C, 83.40; H, 4.65; N, 11.98; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.31 (d, 6H, *J* = 6.0 Hz, benzene-H), 7.36 (t, 6H, benzene-H), 7.54–7.63 (m, 6H, benzene-H), 8.00 (t, 6H, *J* = 6.0 Hz, pyridyl-H), 8.87 (d, 6H, *J* = 8.0 Hz, pyridyl-H), 8.75 (d, 6H, *J* = 4.0 Hz, pyridyl-H), 8.80 (d, 6H, *J* = 4.0 Hz, pyridyl-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.67, 121.41, 123.83, 124.21, 124.87, 127.76, 127.88, 127.99, 128.46, 129.44, 132.16, 134.94, 136.88, 141.26, 149.16, 149.80, 155.99, 156.34.

2.1.2.4. 4-[4-(2,2':6',2''-terpyridinyl)] styryl triphenylamine (chromophore **IV**). Under anhydrous and oxygen-free conditions compd. **7** (0.81 g, 3.0 mmol), compd **3** (1.16 g, 3.0 mmol), a small amount of triphenylphosphine (0.16 g) and palladium acetate (0.045 g) in refined acetonitrile (20 mL) and refined triethylamine (30 mL) mixture solvent were stirred and refluxed in a flask at 85 °C for 48 h under an argon atmosphere (Scheme 1). The crude product solvent was removed by evaporation, and the slurry was purified through a chromographic column on silica gel by using pure chloroform and THF as the eluent. Yellow powders (0.93 g) were obtained in 53.7% yield. MS m/e: 578.47; m.p 135–136 °C; Anal. Calcd for C₄₁H₃₀N₄ (%): C, 85.09; H, 5.23; N, 9.68. Found C, 85.04; H, 5.28; N, 9.62; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.36 (t, 4H, *J* = 8.0 Hz, benzene-H), 7.63 (d, 4H, *J* = 8.0 Hz, benzene-H), 7.77 (d, 4H, *J* = 8.0 Hz, benzene-H), 7.89 (t, 4H, *J* = 8.0 Hz, pyridyl-H), 8.66–8.75 (m, 14H, benzene-H, pyridyl-H, -CH =); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.57, 121.40, 123.96, 128.91, 132.12, 136.94, 149.15, 156.09.

2.1.2.5. 4,4'-bis[4-(2,2':6',2''-terpyridinyl)] styryl triphenylamine (chromophore **V**). Chromophore **V** was synthesized by an analogous method to that used for chromophore **IV** by using compd. **8** (0.50 g, 1.68 mmol), compd **3** (1.31 g, 3.36 mmol), triphenylphosphine (0.08 g), palladium acetate (0.023 g) and obtained yellow solid 1.08 g, in 70.4% yield. MS m/e: 912.17; m.p 128–129 °C; Anal. Calcd for C₆₄H₄₅N₇ (%): C, 84.28; H, 4.97; N, 10.75. Found C, 84.30; H, 5.01; N, 10.72; ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.37 (t, 6H, *J* = 8.0 Hz, benzene-H), 7.64 (d, 6H, *J* = 8.0 Hz, benzene-H), 7.78 (d, 6H, *J* = 8.0 Hz, benzene-H), 7.89 (t, 6H, *J* = 8.0 Hz, pyridyl-H), 8.66–8.74 (m, 21H, benzene-H, pyridyl-H, -CH =); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.59, 121.41, 123.50, 123.98, 127.15, 127.60, 128.58, 128.92, 132.12, 136.96, 137.43, 149.15, 156.05, 156.10.

2.1.2.6. 4,4',4''-tri[4-(2,2':6',2''-terpyridinyl)] styryl triphenylamine (chromophore **VI**). Chromophore **VI** was synthesized by an analogous method to that used for chromophore **IV** by using compd. **9** (0.25 g, 0.77 mmol), compd **3** (0.90 g, 2.31 mmol), a small amount of triphenylphosphine (0.08 g) and palladium acetate (0.023 g) and obtained yellow solid 0.55 g, in 57.4% yield. m.p 158–159 °C; Anal. Calcd for C₈₇H₆₀N₁₀ (%): C, 83.90; H, 4.86; N, 11.25. Found C, 83.91; H, 4.88; N, 11.22; ¹H NMR (400 MHz, CDCl₃, TMS): 7.36–7.42 (m, 9H, benzene-H), 7.63 (d, 8H, *J* = 8.0 Hz, benzene-H), 7.78 (d, 8H, *J* = 8.0 Hz, benzene-H), 7.86–7.90 (m, 9H, pyridyl-H), 8.66–8.75 (m, 26 H, benzene-H, pyridyl-H, -CH =); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 118.56, 121.34, 123.43, 123.87, 127.50, 128.86, 132.07, 137.43, 149.10, 156.08.

2.2. Measurements

All chemicals were purchased from Aldrich or Acros Chemical Co. and were used without any further purification. Electron impact (mode laser) mass spectra and EI mass spectra were obtained on a 4700 Proteome Analyzer (MALDI-TOF-TOF, ABI Company) and HP 5989 mass spectra instrument, respectively. Melting points (m.p.) were recorded on an X-5 melting point measurement instrument (Gongyi City Yuhua Instrument Co., Ltd). Elemental analyses were determined with a PE CHN 2400 analyzer. ¹H NMR of the chromophores was performed on a INOVA-400 spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. X-ray diffraction data crystals were collected on a Bruker SMART APEX diffractometer.

UV-vis absorption spectra were measured on a Hitachi U-3500 recording spectro-photometer from quartz curettes of 1 cm path. Fluorescence measurements were carried out with a PTI (Photo Technology International) fluorescence spectrometer. All the fluorescence spectra were recorded on a FluoroMax[®] 3 Fluorometer (HORIBA). The fluorescence quantum yields (Φ) were measured by using a standard method under the same experimental conditions for all compounds. Fluorescein dissolved in methanol ($\Phi = 0.93$) [26], at the same concentration as the other sample, was used as the standard. Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime Spectrometer (Photo Technology International) with 375 nm laser pulses from a nitrogen laser fiber-

 Table 1

 Crystal data collection and structure refinement of chromophore I.

Formula	$C_{39}H_{28}N_4$
Formula weight	552.65
Temperature	296 (2)
Crystal system	Orthorhombic
Space group	P2 (1) 2 (1) 2 (1)
a (Å)	11.2141 (8)
b (Å)	14.8037 (11)
c (Å)	35.007 (3)
α(0)	90.00
β (0)	90.00
$\gamma(0)$	90.00
Volume (Å ³)	5811.4 (7)
Density (calcd.) (g/cm ³)	1.263
Ζ	8
Goodness-of-fit on F^2	1.013
Final R indices $[I/2\sigma(I)]$ R1	0.0691
wR2	0.1365
R indices (all data) R1	0.1825
wR2	0.2259

coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufactures web site, http://www.pti-nj.com. The fitting results were judged by their values of "reduced chisquared". All measurements were carried out in air at room temperature. The band gaps were obtained from the absorption spectra (absorption edge) of the chromophores, and the LUMO level was calculated from the values of band gap and the HOMO [27].

3. Results and discussion

3.1. Crystal structure of chromophore I

The crystal of chromophore **I**, suitable for X-ray analysis, was obtained from the slow evaporation CH_2Cl_2 /ethanol at room temperature (Table 1). The ORTEP drawing is shown in Fig. 1 and its packing diagram is shown in Fig. 2. As shown in Fig. 1, there are two independent molecules (molecules **I** and **II**) in the unit cell.

In both molecules, the biphenyl ring system is twisted about the biphenyl bond, the dihedral angle being 41.8 (2)° in one molecule, and 37.6 (2)° in the other. For the 4'-terpyridyl substituent, the N-atoms of the flanking pyridine rings are oriented away from the N-atom of the central pyridine ring. If these had pointed towards inwards, the substituent would have been planar owing to less crowding. In fact, only one of the two flanking rings is severely twisted, as noted by the dihedral angles of 1.5 (3) and 32.2 (2)° in the first molecule, and 7.7 (3) and 28.3 (2)° in the second. This nonplanar feature differs from other reported examples [28]. At the diphenylamino end, the central nitrogen exists in a trigonal plane, with the sum of the three C–N–C angles being almost 360°. The three benzene rings connected to this atom are arranged in



Fig. 1. ORTEP drawings of chromophore I, showing 35% probability displacement ellipsoids: (A) molecule I and (B) molecule II.



Fig. 2. A packing diagram of chromophore I along the *a* direction.

a propeller-like fashion. Further details of the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC834975 for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html(or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK [fax: +44 1223 336033; e-mail:deposit@ccdc.cam.ac.uk]).

3.2. UV-vis absorption spectroscopy

The UV–vis absorption spectra of chromophores **I**–VI in tetrahydrofuran (THF) ($C = 1.0 \times 10^{-5}$ mol/L) exhibit two absorption bands at around 290–302 nm and 352–410 nm (Fig. 3). The first absorption band at around 290–302 nm contributes to the triphenylamine [29,30] and the conjugated terpyridine. The second absorption band at around 352–410 nm contributes to π – π^* intramolecular charge transfer (CT) between triphenylamine benzene



Fig. 3. Absorption spectrum of chromophores I-VI in THF solution ($C = 1.0 \times 10^{-5}$ mol/L). The inset presents the normalized UV–vis spectra of chromophores **VI**, **V**, **VI** in films.

ring and adjacent benzene rings for chromophores **I**–**III** or between triphenylamine benzene ring and adjacent vinylbenzene rings for chromophores **IV–VI**. The results show that the molar extinction coefficient ratios of the second/first absorption bands of chromophore **I–III** are larger than that of chromophores **IV–VI**. This clearly suggests that the π – π * intra-molecular transition energy level in the triphenylamine benzene ring and adjacent rigid benzene rings for chromophores **I–III** are higher than that of the flexible styryl system for chromophores **IV–VI**

For the similar containing phenyl or styryl chromophores, the molar extinction coefficient of chromophores in the first band at around 290–302 nm increase with a corresponding increasing the number of terpyridine multibranches from 1 to 3. For chromophores **I**–**VI**, the molar extinction coefficient is in the order of chromophore **III** > **I** and chromophore **VI** > **V** > **IV**. On the other hand, the absorption peak is shifted to the red with the corresponding branching increased in the second band around 352–410 nm. Compared with chromophore **I**, the chromophores **II** and **III** have red shifted maxima by about 20 nm and the absorption peaks of chromophores **V** and **VI** have a red shift of about 15 nm in comparison with chromophore **IV**.

In order to investigate the UV–vis properties in the solid state the chromophores were processed as a film in quartz glass [31], which show similar absorption properties as compared to that in THF solution. In the second absorption band the chromophores **II**, **III** have a red shift compared to chromophore I and chromophores **V**, **VI** have a red shift compared to chromophore **IV**, respectively. The second maximum absorption peaks of π – π * intra-molecular charge transfer (ICT) in triphenylamine adjacent vinylbenzene rings for chromophores **IV**, **V**, **VI** films increases with the branch numbers (see Fig. 3 inset). This property is different from that in THF solution due to the fact that in the solid film there is restricted torsion of the flexible molecular structure [30].

It is obvious that in the second absorption band, maximum absorption intensities for chromophores **I**–**III** are higher than that of chromophores **IV–VI** whether in THF solution or in a solid film due to the effect of the rigid phenyl versus flexible styryl ring structure. On the other hand, the absorption peaks of multibranches (chromophores **II**, **III**, **VI**, **V**) are red shifted, relative to those of monobranched chromophores (chromophores **I**, **IV**) due to the monobranching effect.

In order to further investigate the optical properties of chromophores I-VI by means of molecular orbital calculations at the B3LYP/ 6–31G level of density functional theory (DFT) were used [32]. Seen the HOMO is a π orbital concentrated on the central triphenylamine moiety; LUMO is of π^* character distributed on the terpyridyl ring (Fig. 4) for chromophores I, II and V, VI. The LUMO mainly accumulates in the two arms of terpyridyl ring moiety which is similar to other multi-branched systems [32]. The DFT results indicate that the features of the frontier molecular orbital do not change significantly with phenyl or styryl groups. The calculated HOMO-LUMO gaps for chromophores I-VI follow the order: chromophore I (339.34 kJ/ mol) > chromophore II (336.24 kJ/mol) > chromophore III (333.87 kJ/mol) > chromophore IV (305.10 kJ/mol) > chromophore**V** (290.60 kJ/mol) > chromophore **VI** (284.27 kJ/mol). It was shown that the phenyl/stryryl groups effectively determine the properties of the HOMOs. The trend is expected because the terpyridyl phenyl triphenylamine chromophores tend to stabilize the HOMO significantly, giving the energy gap larger than that of terpyridyl styryl triphenylamine chromophores.

3.3. Luminescence spectroscopy

On excitation at the respective maximum absorption wavelength, the chromophores **I**–**VI** emit strong fluorescence, as shown



Fig. 4. Calculated spatial distributions of the HOMO and LUMO levels of chromophores I-VI.



Fig. 5. The fluorescence emission spectral of chromophores in different solvents at $C = 1.0 \times 10^{-5} \text{ mol/L}$: (A) for chromophore I and (B) for chromophore IV.

in the Fig. 5. It is found that the fluorescence intensities of the multibranching chromophores are stronger than those of the monobranched chromophores in dichloromethane $(1 \times 10^{-5} \text{ M})$. The six fluorescence spectra incline to red shift as the solvent dielectric constant increase (see Table 2), as for chromophore I, from 408 nm (hexane, k, 1.89) to 464 nm (ethyl acetate, k, 6.02), to 469 nm (tetrahydrofuran, k, 7.58), to 486 nm (dichloromethane, k, 9.1), to 507 nm (actone, k, 20.7), to 540 nm (methanol, k, 31.2) [33]. The fluorescence intensity decreased with the increased solvent dielectric constant for chromophore I, this can be explained by the "twisted intra-molecular charge transfer" (TICT) model in which the solvent with the larger dielectric constant solvates the TICT state more efficiently so that the chromophore gives very low fluorescence intensity in such solvent [34]. A similar trend was observed for the other chromophores.

Here, the dipole moment of dye in the excited state is also greater than that in the ground state, which can be certified by the Lipperte-Mataga equation [35,36][Fig. 6].

$$\hbar c (v_{\rm abs} - v_{\rm em}) = \frac{1}{4\pi\varepsilon_o} \frac{2}{\alpha^3} \mu_e (\mu_e - \mu_g) \Delta f + \text{const}$$
(1)

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\left(n^2 - 1\right)}{2n^2 + 1} \tag{2}$$

Table 2

The absorption spectra and fluorescence spectra of chromophores $I{-VI}$ in different solvents at $1\,\times\,10^{-5}$ M.

Chromo	Solvent	Hexane	Ethyl acetate	Tetrahydro- furan	Dichloro- methane	Actone	Methanol
I	Abs ^a	352	353	356	358	354	356
	Em	408	464	469	486	507	540
п	Abs	367	370	373	372	374	369
	Em	418	469	476	487	509	536
III	Abs	375	373	375	376	373	376
	Em	422	467	470	471	502	489
IV	Abs	382	386	389	389	387	387
	Em	430	495	496	516	529	563
v	Abs	383	390	393	394	389	391
	Em	485	495	498	520	537	558
VI	Abs	390	393	393	396	395	392
	Em	440	495	506	514	543	556

^a Abs and Em are absorption and fluorescence emission maxima of chromophores in different solvent, respectively.

where, μ_e and μ_g are the dipole moments in the excited and ground states, respectively. $(v_{abs}-v_{em})$ is Stokes shift. The symbols α and care the molecular size and the speed of light in a vacuum, respectively. The symbol h is Plank constant. Orientation polarizability of solvent (Δf) is defined by Eq. (2), wherein ε is the dielectric constant and *n* is the optical refractive index. One can see that the slopes are all larger than zero. As a result, the fluorescence spectra of the chromophores are red shifted with the increase of dielectric constant (k). The slope (k) is proportional to the value of $\mu_e/\mu_{ge}/\alpha^3$. Since the molecular dimension (α) becomes larger with the branch number, the fact that slopes (k) in the order of chromophore I > chromophores II/III and chromorphore IV > chromophores V/VI implies the same sequence of dipole moment change $(\Delta \mu_{ge} = \mu_e - \mu_g)$, that is, the excited state (μ_e) is larger than that in the ground state (μ_g). The fluorescence emission spectra maximum value of the chromophores increased with the polarity of the solvent, and is consistent with the other triphenylamine derived chromophores [37].

Time-resolved decay curves for all chromophores in dichloromethane are shown in Fig. 7 and the corresponding lifetime (τ) data are presented in Table 3. It is obvious that the fluorescence lifetime of triphenylamine in the rigid benzyl unit chromophores **I–III** (lifetime 2.94–3.16 ns) are longer than that of flexible styryl unit chromophores **IV–VI** (lifetime 2.11–2.48 ns). As can be seen for



Fig. 6. The Lippert-Mataga plots for chromophores I-VI.



Fig. 7. The fluorescence lifetime of chromophores in CH₂Cl₂ ($C = 1.0 \times 10^{-5}$ mol/L): (A) for chromophore I and (B) for chromophore IV.

structurally similar chromophores (containing phenyl or styryl unit), the fluorescence lifetime (τ) values in dichloromethane are increasing with the increase of molecular branch from 1 to 3, in the order of chromophore **III** > **I** and chromophore **VI** > **V** > **IV**.

3.4. Colorimetric sensor for detecting ions (II)

Table 3

The chromophore **IV** was based on a donor- π -acceptor system that could display a strong color development as well as intense absorbance; such properties are useful for the development of colorimetric sensors. The selective and sensitive signal response ability of the chormohore **IV** for Fe²⁺ ion was studied through UV–vis spectra in aqueous solution around pH 7.0

Fluorescence, electrochemical and thermogravimetric analysis properties of chromophores I–VI.

Chromophores	Φ	τ (ns)	HOMO/LUMO (ev)	Eg	$T_{\rm d}$ (°C)
I	0.54	2.94	-5.79/-2.93	2.86	481
II	0.42	2.99	-5.77/-3.11	2.66	487
III	0.80	3.16	-5.78/-3.03	2.75	549
IV	0.88	2.11	-5.78/-2.90	2.88	334
V	0.81	2.29	-5.77/-3.15	2.62	344
VI	0.74	2.48	-5.69/-3.06	2.63	340



Fig. 8. The normalized UV–vis absorption spectra of chromophore **IV** in water obtained upon addition of different divalent metal ions (1 equivalent). The inset presents the changes in absorption spectral of (10^{-5} M in water) on the addition of Fe²⁺ in aqueous solution.

 $(C = 1.0 \times 10^{-5} \text{ mol/L})$. As shown in Fig. 8 inset, it is of interest to note that following addition of Fe^{2+} ion to chromophore IV a strong metal-to-ligand-charge transfer (MLCT) [38,39] band originates centered at 567 nm with the evolution of a bright violet color. With the increasing of Fe²⁺ ion, the sharp new peak gradually intensified until the mole ratio (chromophore IV/Fe^{2+}) of 1:1 was reached. It was of interest to assess the colorimetric sensing ability of the chromophores towards different cationic guests. In order to do so, a series of coloring experiments were performed in water. The addition of other metal ions, such as Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Mg^{2+} , Ni²⁺, Pb²⁺, Zn²⁺, did not show significant changes in absorption between 450 and 700 nm for aqueous solution, compared with the addition of Fe²⁺ ion [see Fig. 8]. The observed distinct changes in absorption suggest that chromophore IV has strong binding affinity for Fe²⁺ with high selectivity for identifying the colour changes by eye [see Fig. 8]. The new MLCT band centered at 567 nm in the case of Fe²⁺ ion over the other metal ions suggests that the chromophore IV can act as an effective chemosensor towards the detection of Fe²⁺ ion in solution.



Fig. 9. Comparison of UV–vis absorption spectra of different chromophores in water ($C = 1.0 \times 10^{-5}$ mol/L) with addition of 1 equivalent of Fe²⁺.

Similar to chromophore IV, chromophores I, II, III, V, VI were examined in water upon addition of Fe^{2+} ion. As shown in Fig. 9, an absorbance band centered at 567 nm increased with the addition of Fe^{2+} ion until the $[Fe^{2+}]/[terpyridyl]$ of chromophores \bm{V} and $\bm{V}\bm{I}$ reaches 1:1, the aqueous solution showing a magenta color which can be seen by eve. No color change was observed by eve for chromophers I. II. III (see Fig. 9 and inset) when the same amount of Fe^{2+} ion was added under the same conditions. From the above, the conclusion can be drawn that the chromophers with flexible styryl unit have high selectivity and sensitivity for Fe^{2+} ion in neutral aqueous solution among the divalent metal ions such as Cd^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Fe^{2+} , Mg^{2+} , Ni^{2+} , Pb^{2+} , Zn^{2+} , while the chromophores with a rigid phenyl terpyridyl unit do not display these colour development properties due to the rigid phenyl unit influencing the activity characteristics of the linked terpyridyl unit. These characteristic can be confirmed from the calculated HOMO-LUMO gaps for chromophores I-VI because of chromophores I–III giving the energy gap larger 20% than that of chromophores **IV–VI**. The higher energy gaps of rigid phenyl triphenylamine derivatives result in more stable chromophores than those containing flexible styryl units. That is, the chromophores I–III cannot form stable metal-to-ligand-charge transfer (MLCT) with Fe^{2+} ion at room temperature, in comparison with the chromophores IV-VI.

4. Conclusion

In conclusion, six new multi-branched 4'-terpyridyl rigid phenyl and flexible styryl triphenylamine derivatives were synthesized and their optical and selective iron(II) properties were investigated in detail. It has been demonstrated that the molar extinction coefficient of chromophores containing the rigid phenyl unit are higher than that of chromophores containing the flexible styryl unit. The fluorescence lifetime of the rigid structure chromophores are longer than that of the flexible triphenylamine derivatives in dichoromethane solution and the fluorescence lifetime increases with the increase of molecular terpyridyl branches from 1 to 3. The flexible triphenylamine derivatives have a higher sensitivity than the rigid triphenylamine derivatives for Fe²⁺ ion in neutral aqueous solution in the presence of the other divalent metal ions such as Cu²⁺, Co²⁺, Ni^{$\overline{2}+$}, Hg²⁺, Mg²⁺, Pb²⁺, Zn²⁺. These results will contribute to understanding of the 4'-terpyridyl rigid phenyl and flexible styryl triphenylamine derivatives on the performance for further potential applications.

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