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Anchoring pyrazolines on a 2,2′:6′,2″-terpyridine backbone

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ABSTRACT

Introducing pyrazoline derivatives into the classical 2,2′:6′,2″-terpyridine (2,2′:6′,2″-tpy) backbone leads to the synthesis of a new class of compounds, 4′-pyrazolinyl-2,2′:6′,2″-tpys. Six such derivatives bearing differently substituted pyrazolines have been synthesized with a facile two-step procedure using simple chalcone compounds and 4′-hydrazino-2,2′:6′,2″-tpy as starting materials, and they were fully characterized by IR, NMR, MS and elemental analysis. Two representative crystal structures have been determined by single crystal X-ray diffraction analysis. The solid state structures reveal the presence of two enantiomers as a racemate in each of these compounds and the arrangement between aromatic rings in both tpy and pyrazoline domains can be affected by the substituents. The intermolecular packing is mainly driven by the π-stacking interactions between aromatic regions. The solution electronic absorption and emission behaviors of the new compounds were also investigated.

1. Introduction

Pyrazolines are well known in organic chemistry and represent a class of important *N*-heterocyclic compounds [1]. A large number of pyrazoline derivatives have been found to display considerable biological activities [2]. In the past decades, extensive research has been conducted to establish the prominent biological effects of pryazolines, such as antimicrobial, antimycobacterial, antifungal, antiamoebic, anti-inflammatory, analgesic, antidepressant and anticancer activities [3–10]. As a result, the synthesis and modification of pyrazolines with various substituents on the 5-membered ring have become a focus of research. In addition, aryl-substituted pyrazolines are highly blue fluorescent materials and have been used as whitening or brightening reagents [11,12]. Some functionalized pyrazolines have also found extended applications in electro- and photo-luminescence materials and chemosensors [13–16].

2,2′:6′,2″-tpy is a classical ligand with a convergent N coordination site [17]. The derivatives of 2,2′:6′,2″-tpy have played an important role as strong chelating agents for transition metals thanks to their ability to form structurally defined metal complexes displaying interesting photo/electrochemical and catalytic properties [18–25]. Therefore, the functionalization of 2,2′:6′,2″-tpy on different positions of its three aromatic rings has been extensively explored in the past decades [26–34]. Due to its easiness of synthesis, introducing an additional functional group in the 4′-position of 2,2′:6′,2″-tpy is a popular way while pursuing specific catalytic and materials properties, which resulted in the synthesis of a tremendous amount of interesting supramolecular compounds containing 2,2′:6′,2″-tpy moieties [35]. Despite of the extensive efforts on the functionalization of 2,2′:6′,2″-tpy, the direct anchoring of a pyrazoline unit on the 2,2′:6′,2″-tpy backbone is, surprisingly, unknown.

Herein, we report for the first time the synthesis of a series of 4′-pyrazolinyl-2,2′:6′,2″-tpy derivatives. The spectroscopic, photophysical and structural characterization of the new pyrazoline-tpy compounds are described. These new class of compounds are anticipated to show intriguing coordination chemistry and fluorescence sensing properties upon complexation with transition metal ions, as well as potential biological activities. Prior to a thorough investigation on their metal coordination chemistry, herein we present our results on the synthesis and characterization of the free ligands.

2. Experimental

2.1. General

Solvents and reagents were purchased from Fisher Scientific or Sigma-Aldrich in the US. All reactions were performed under ambient conditions (under air). ^{1}H, ^{13}C and 2D NMR spectrum was

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obtained at room temperature on a Bruker III 500 MHz spectrometer with TMS as an internal standard. Electrospray mass spectra were recorded using a Finnigan MAT LCQ mass spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8400 S spectrophotometer with solid samples on a Golden Gate diamond ATR accessory. Solution electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu F-4500 spectrophotometer. Chalcones **1**–**6** and 4′-hydrazino-2,2′:6′,2″-terpyridine were synthesized according to the literature method [36,37].

2.2. Synthesis of **7**

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **1** (20.8 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 3.5 h, after which the resulting mixture was cooled slowly to room temperature. White solid of **7** was collected by filtration under vacuum, washed with cold ethanol (2 × 2 mL) and dried in vacuo over P_2O_5. Yield: 30.0 mg (66%). Singe crystals were grown by slow evaporation of a CH_2Cl_2/MeOH solution of **7**. M.p.: 264–265 °C. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF), 279 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 46.7), 355 (2.20), 377sh (1.02). FT-IR (solid, cm^{-1}): 3057 w, 3026 w, 1599 m, 1580 s, 1562 s, 1545 m, 1466 s, 1445 m, 1410 m, 1346 m, 1304 w, 1256 w, 1236 m, 1132 m, 1115 m, 1074 w, 1030 m, 1009 m, 984 m, 895 w, 872 m, 856 m, 791 m, 766 m, 756 m, 732 m, 689s, 671 s, 621 m. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, J = 4.7 Hz, 2H, H^{A6}), 8.52 (d, J = 7.9 Hz, 2H, H^{A3}), 8.09 (s, 2H, H^{B3}), 7.82 (d, J = 7.1 Hz, 2H, H^{D2}), 7.77 (td, J = 1.6, 7.8 Hz, 2H, H^{A4}), 7.40 (t, J = 7.2 Hz, 2H, H^{D3}), 7.37 (m, 1H, H^{D4}), 7.33 (d, J = 7.2 Hz, 2H, H^{E2}), 7.30 (overlapping, m, 2H, H^{E3}), 7.26 (overlapping, m, 2H, H^{A5}), 7.20 (t, J = 7.2 Hz, 1H, H^{E4}), 5.65 (dd, J = 4.8, 12.1 Hz, 1H, H^{C5}), 3.91 (dd, J = 12.1, 17.0 Hz, 1H, H^{C4}), 3.23 (dd, J = 4.9, 17.1 Hz, 1H, $H^{C4'}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 157.1 (C^{A2}), 156.2 (C^{B2}), 151.3 (C^{B4}), 149.8 (C^{C3}), 149.2 (C^{A6}), 141.5 (C^{E1}), 136.8 (C^{A4}), 132.3 (C^{D1}), 129.56 (C^{D4}), 129.42 (C^{E3}), 128.8 (C^{D3}), 128.1 (C^{E4}), 126.6 (C^{D2}), 126.0 (C^{E2}), 123.6 (C^{A5}), 121.5 (C^{A3}), 105.4 (C^{B3}), 63.0 (C^{C5}), 43.6 (C^{C4}). ESI-MS (CH_2Cl_2/MeOH) m/z 454.6 [M + H$^+$] (calc. 454.6), 476.3 [M + Na$^+$] (base peak, calc. 476.2), 929.7 [2 M + Na$^+$] (calc. 929.4). Anal. Calc. for $C_{30}H_{23}N_5 \cdot 1/3H_2O$, C 78.41, H 5.19, N 15.24%; Found C 78.56, H 5.20, N 15.46%.

2.3. Synthesis of ***8***

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **2** (22.2 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 6 h, after which the resulting mixture was cooled to room temperature. The solution was then concentrated to 2.0 mL and Et_2O (2.0 cm^{-3}) was added. The solution was further cooled to −18 °C overnight to give yellow precipitate, which was collected by filtration under vacuum, washed with Et_2O (2 × 1 mL) and dried in vacuo over P_2O_5. Yield: 20.5 mg (44%). M.p.: 209–210 °C. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF): 279 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 41.4), 354 (2.00), 375sh (1.18). FT-IR (solid, cm^{-1}): 3013 w, 1597 m, 1578 s, 1560 s, 1543 m, 1466 s, 1445 s, 1410 s, 1348 m, 1302 w, 1254 w, 1234 m, 1178 w, 1132 m, 1109 m, 1092 m, 1032 m, 1011 m, 982 m, 874 m, 858 m, 814 s, 791 s, 758 s, 735 s, 687 s, 671 s, 658 s, 621 s. ^{1}H NMR (500 MHz, $CDCl_3$) δ /ppm 8.66 (d, J = 4.4 Hz, 2H, H^{A6}), 8.52 (d, J = 7.9 Hz, 2H, H^{A3}), 8.09 (s, 2H, H^{B3}), 7.82 (d, J = 7.3 Hz, 2H, H^{D2}), 7.77 (td, J = 1.4, 7.8 Hz, 2H, H^{A4}), 7.40 (t, J = 7.3 Hz, 2H, H^{D3}), 7.35 (t, J = 7.1 Hz, 1H, H^{D4}), 7.26 (overlapping, m, 2H, H^{A5}), 7.21 (d, J = 8.0 Hz, 2H, H^{E2}), 7.08 (d, J = 8.0 Hz, 2H, H^{E3}), 5.62 (dd, J = 4.8, 12.0 Hz, 1H, H^{C5}), 3.88 (dd, J = 12.0, 17.0 Hz, 1H, H^{C4}), 3.20 (dd, J = 4.8, 17.0 Hz, 1H, $H^{C4'}$), 2.24 (s, 3H, H^{CH3}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 157.1 (C^{A2}), 156.1 (C^{B2}), 151.3 (C^{B4}), 149.8 (C^{C3}), 149.2 (C^{A6}), 138.6 (C^{E1}), 137.7 (C^{E4}), 136.8 (C^{A4}), 132.4 (C^{D1}), 130.1 (C^{E3}), 129.5 (C^{D4}), 128.8 (C^{D3}), 126.6 (C^{D2}), 125.9 (C^{E2}), 123.6 (C^{A5}), 121.6 (C^{A3}), 105.4 (C^{B3}), 62.7 (C^{C5}), 43.7 (C^{C4}), 21.3 (C^{CH3}). ESI-MS (CH_2Cl_2/MeOH) m/z 468.3 [M + H$^+$] (base peak, calc. 468.2), 490.1 [M + Na$^+$] (calc. 490.2). Anal. Calc. for $C_{31}H_{25}N_5 \cdot 1.75H_2O$, C 74.60, H 5.23, N 14.15%; Found C 74.30, H 5.23 N 14.15%.

2.4. Synthesis of ***9***

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **3** (23.8 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 4 h, after which the resulting mixture was cooled slowly to room temperature. White solid of **9** was collected by filtration under vacuum, washed with cold ethanol (2 × 1 mL) and dried in vacuo over P_2O_5. Yield: 32.0 mg (66%). M.p.: 215–216 °C. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF): 280 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1}, 42.4), 359 (2.04), 380sh (0.634). FT-IR (solid, cm^{-1}): 3055 w, 2833s 1599 m, 1580 s, 1562 s, 1543 m, 1510 m, 1462 s, 1447 m, 1408 m, 1348 m, 1302 w, 1246 s, 1177 m, 1105 m, 1099 m, 1032 m, 1018 m, 984, 891 w, 868 w, 827 m, 793 s, 758 s, 744 s, 735 m, 687 s, 671 s, 621 m. ^{1}H NMR (500 MHz, $CDCl_3$) δ /ppm 8.66 (d, J = 4.6 Hz, 2H, H^{A6}), 8.52 (d, J = 7.9 Hz, 2H, H^{A3}), 8.09 (s, 2H, H^{B3}), 7.82 (d, J = 7.2 Hz, 2H, H^{D2}), 7.78 (td, J = 1.6, 7.7 Hz, 2H, H^{A4}), 7.40 (t, J = 7.3 Hz, 2H, H^{D3}), 7.36 (t, J = 7.2 Hz, 1H, H^{D4}), 7.26 (overlapping, m, 2H, H^{A5}), 7.24 (overlapping, 2H, H^{E2}), 6.80 (d, J = 8.7 Hz, 2H, H^{E3}), 5.61 (dd, J = 4.7, 12.0 Hz, 1H, H^{C5}), 3.87 (dd, J = 12.0, 17.0 Hz, 1H, H^{C4}), 3.69 (s, 3H, H^{CH3}), 3.20 (dd, J = 4.8, 17.0 Hz, 1H, $H^{C4'}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 159.3 (C^{E4}), 157.1 (C^{A2}), 156.1 (C^{B2}), 151.3 (C^{B4}), 149.8 (C^{C3}), 149.2 (C^{A6}), 136.8 (C^{A4}), 133.6 (C^{E1}), 132.4 (C^{D1}), 129.5 (C^{D4}), 128.8 (C^{D3}), 127.2 (C^{E2}), 126.6 (C^{D2}), 123.6 (C^{A5}), 121.6 (C^{A3}), 114.7 (C^{E3}), 105.4 (C^{B3}), 62.5 (C^{C5}), 55.4 (C^{CH3}), 43.7 (C^{C4}). ESI-MS (CH_2Cl_2/MeOH) m/z 484.6 [M + H$^+$] (calc. 484.2), 506.3 [M + Na$^+$] (base peak, calc. 506.2), 989.7 [2 M + Na$^+$] (calc. 989.4). Anal. Calc. for $C_{31}H_{25}N_5O \cdot 0.5H_2O$, C 75.59, H 5.32, N 14.22%; Found, C 75.13, H 5.17, N 14.03%.

2.5. Synthesis of ***10***

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **4** (25.1 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 4 h, after which the resulting mixture was cooled slowly to room temperature. White solid of **10** was collected by filtration under vacuum, washed with cold ethanol (2 × 1 mL) and dried in vacuo over P_2O_5. Yield: 18.0 mg (36%). M.p.: 243–244 °C. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF): 278 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 44.0), 360 (2.06), 378sh (1.20). FT-IR (solid, cm^{-1}): 3051 w, 2887 w, 1597 m, 1580 s, 1562 s, 1543 m, 1518 m, 1468 s, 1445 m, 1408 m, 1346 m, 1254 w, 1234 w, 1188 w, 1165 w, 1113 s, 1092 w, 1032 w, 984 w, 943 w, 895 m, 874w, 852 m, 814 s, 189 s, 756 s, 744 s, 735 m, 688 s, 671 s, 621 m. ^{1}H NMR (500 MHz, $CDCl_3$) δ /ppm 8.66 (d, J = 4.1 Hz, 2H, H^{A6}), 8.51 (d, J = 7.9 Hz, 2H, H^{A3}), 8.11 (s, 2H, H^{B3}), 7.82 (d, J = 7.2 Hz, 2H, H^{D2}), 7.77 (td, J = 1.7, 7.8 Hz, 2H, H^{A4}), 7.40 (t, J = 7.3 Hz, 2H, H^{D3}), 7.35 (t, J = 7.2 Hz, 1H, H^{D4}), 7.26 (overlapping, m, 2H, H^{A5}), 7.18 (d, J = 8.7 Hz, 2H, H^{E2}), 6.62 (d, J = 8.8 Hz, 2H, H^{E3}), 5.58 (dd, J = 4.6, 11.9 Hz, 1H, H^{C5}), 3.84 (dd, J = 11.9, 17.0 Hz, 1H, H^{C4}),

3.20 (dd, J = 4.7, 17.0 Hz, 1H, $H^{C4'}$), 2.85 (s, 6H, H^{CH3}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 157.2 (C^{A2}), 156.1 (C^{B2}), 151.4 (C^{B4}), 150.2 (C^{E4}), 149.9 (C^{C3}), 149.2 (C^{A6}), 136.8 (C^{A4}), 132.6 (C^{D1}), 129.4 (C^{D4}), 129.2 (C^{E1}), 128.7 (C^{D3}), 126.9 (C^{E2}), 126.6 (C^{D2}), 123.5 (C^{A5}), 121.6 (C^{A3}), 113.1 (C^{E3}), 105.4 (C^{B3}), 62.6 (C^{C5}), 43.7 (C^{C4}), 40.7 (C^{CH3}). ESI-MS (CH_2Cl_2/MeOH) m/z 497.1 [M + H^+] (base peak and the only peak, calc. 497.3). Anal. Calc. for $C_{32}H_{28}N_6$, C 77.39, H 5.68, N 16.92%; Found C 76.89, H 5.79, N 16.72%.

2.6. Synthesis of **11**

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **5** (23.8 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 4.5 h, after which the resulting mixture was cooled slowly to room temperature. White solid of **11** was collected by filtration under vacuum, washed with cold ethanol (2 × 1 mL) and dried in vacuo over P_2O_5. Yield: 30.0 mg (66%). M.p.: 238–239 °C. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF): 279 ($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 41.5), 353 (2.76), 380sh (0.784). FT-IR (solid, cm^{-1}): 3040 w, 1599 s, 1578 s, 1562 s, 1543 m, 1516 w, 1466 s, 1408 m, 1346 w, 1306 w, 1248 s, 1175 m, 1111 m, 1034 m, 982 m, 856 m, 829 s, 795 s, 773 m, 743 m, 702 m, 675 s, 658 s, 636 m, 621 m. ^1H NMR (500 MHz, $CDCl_3$) δ /ppm 8.64 (d, J = 4.5 Hz, 2H, H^{A6}), 8.51 (d, J = 7.9 Hz, 2H, H^{A3}), 8.06 (s, 2H, H^{B3}), 7.77 (overlapping, 4H, H^{A4+D2}), 7.33 (t, J = 7.7 Hz, 2H, H^{E2}), 7.29 (overlapping, 2H, H^{E3}), 7.26 (overlapping, m, 2H, H^{A5}), 7.20 (t, J = 7.0 Hz, 1H, H^{E4}), 6.92 (d, J = 8.5 Hz, 2H, H^{D3}), 5.62 (dd, J = 8.3 Hz, 1H, H^{C5}), 3.88 (dd, J = 12.1, 17.0 Hz, 1H, H^{C4}), 3.83 (s, 3H, H^{CH3}), 3.19 (dd, J = 4.7, 17.0 Hz, 1H, $H^{C4'}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 160.9 (C^{D4}), 157.1 (C^{A2}), 156.0 (C^{B2}), 151.3 (C^{B4}), 149.1 (C^{A6}), 141.7 (C^{E1}), 136.8 (C^{A4}), 129.4 (C^{E3}), 128.1 (C^{D2}), 128.0 (C^{E4}), 126.0 (C^{E2}), 125.0 (C^{D1}), 123.6 (C^{A5}), 121.6 (C^{A3}), 114.2 (C^{D3}), 105.4 (C^{B3}), 62.8 (C^{C5}), 55.6 (C^{CH3}), 43.8 (C^{C4}), C^{C3} not observed. ESI-MS (CH_2Cl_2/MeOH) m/z 484.7 [M + H^+] (calc. 484.2), 506.3 [M + Na^+] (base peak, calc. 506.2), 989.7 [2 M + Na^+] (calc. 989.4). Anal. Calc. for $C_{31}H_{25}N_5O \cdot H_2O$, C 74.23, H 5.43, N 13.96%; Found C 74.52, H 5.19, N 14.00%.

2.7. Synthesis of **12**

4′-Hydrazino-2,2′:6′,2″-terpyridine (29.0 mg, 0.11 mmol) and chalcone **6** (30.8 mg, 0.10 mmol) were dissolved in ethanol (5 mL) under N_2 in a 25 mL round-bottom flask equipped with a magnetic bar and condenser, to which K_2CO_3 (13.8 mg, 0.010 mmol) was added. The solution was heated to reflux under rigorous stirring for 16 h, after which the resulting mixture was cooled slowly to room temperature. White solid of **12** was collected by filtration under vacuum, washed with cold ethanol (2 × 1 mL) and dried in vacuo over P_2O_5. Yield: 20.0 mg (36%). M.p.: 276–277 °C. Single crystals were grown by slow evaporation of a solution of **12** in $CDCl_3$. UV–vis λ_{max}/nm (5.0×10^{-6} mol dm^{-3}, THF), 258($\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} 28.8): 279 (43.3), 357 (2.70), 372sh (2.32), 394sh (0.200). FT-IR (solid, cm^{-1}): 3049 w, 2953 m, 1597 m, 1578 s, 1560 s, 1545 s, 1462 s, 1445 s, 1408 s, 1346 m, 1312 w, 1159 w, 1113 m, 1092 m, 1059 m, 1038 s, 984 m, 953 m, 879 m, 860 s, 833 m, 789 s, 727 s, 687 s, 671 s, 642 m, 615 m. ^1H NMR (500 MHz, $CDCl_3$) δ /ppm 8.72 (d, J = 9.0 Hz, 1H, H^{E1}), 8.44 (s, 1H, H^{E10}), 8.37 (d, J = 3.6 Hz, 2H, H^{A6}), 8.27 (d, J = 7.9 Hz, 2H, H^{A3}), 8.11 (d, J = 8.5 Hz, 1H, H^{E4}), 8.04 (d, J = 8.7 Hz, 1H, H^{E8}), 7.99 (overlapping, 2H, H^{D2}), 7.93 (overlapping, 1H, H^{E5}), 7.75 (m, 1H, H^{E2}), 7.63 (overlapping, 2H, H^{A4}), 7.61 (overlapping, 1H, H^{E3}), 7.46 (t, J = 7.3 Hz, 2H, H^{D3}), 7.42 (t, J = 7.2 Hz, 1H, H^{D4}), 7.32 (overlapping, 1H, H^{E6}), 7.29 (overlapping, 1H, H^{E7}), 7.12 (dd, J = 5.1, 6.6 Hz, 2H, H^{A5}), 6.90 (dd, J = 10.4, 13.2 Hz, 1H, H^{C5}), 4.09 (dd, J = 13.5, 17.5 Hz, 1H, H^{C4}), 3.68 (dd, J = 10.3, 17.6 Hz, 1H, $H^{C4'}$). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ ppm 156.8 (C^{A2}), 156.0 (C^{B2}), 151.9 (C^{B4}), 149.9 (C^{C3}), 148.9 (C^{A6}), 136.5 (C^{A4}), 132.3 (C^{E4a}), 132.2 (C^{D1}), 131.6 (C^{E9}), 130.8 (C^{E1a}), 130.3 (C^{E5}), 130.1 (C^{E4}), 130.0 (C^{E5a}), 129.7 (C^{E8a}), 129.5 (C^{E10}), 129.3 (C^{D4}), 128.9 (C^{D3}), 127.4 (C^{E2}), 126.9 (C^{E7}), 126.7 (C^{D2}), 125.2 (C^{E6}), 125.0 (C^{E3}), 123.8 (C^{E8}), 123.3 (C^{A5}), 122.7 (C^{E1}), 121.1 (C^{A3}), 105.8 (C^{B3}), 59.3 (C^{C5}), 42.4 (C^{C4}). ESI-MS (CH_2Cl_2/MeOH) m/z 554.6 [M + H^+] (calc. 554.2), 576.3 [M + Na^+] (base peak, calc. 576.2), 1129.7 [2 M + Na^+] (calc. 1129.4). Anal. Calc. for $C_{38}H_{27}N_5 \cdot 0.5H_2O$, C 81.12, H 5.02, N 12.45%; Found C 81.57, H 4.74, N 12.62%.

2.8. X-ray structural determinations

Suitable crystals of **7** and **12** were mounted on a Cryoloop with oil at 123 K. Data were collected on a Bruker APEXII diffractometer and CRYSTALS were used for the data reduction, solution and refinement. Structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2 and all hydrogen atoms were placed in calculated positions with appropriate riding parameters. Due to the decay of diffused $CHCl_3$ solvents in the crystal of **12** during data collection, the structure was refined at a relatively high R_f level. Crystal structures and packing figures were drawn with the program Mercury v. 2.4 [38]. The crystallographic refinement data are listed below.

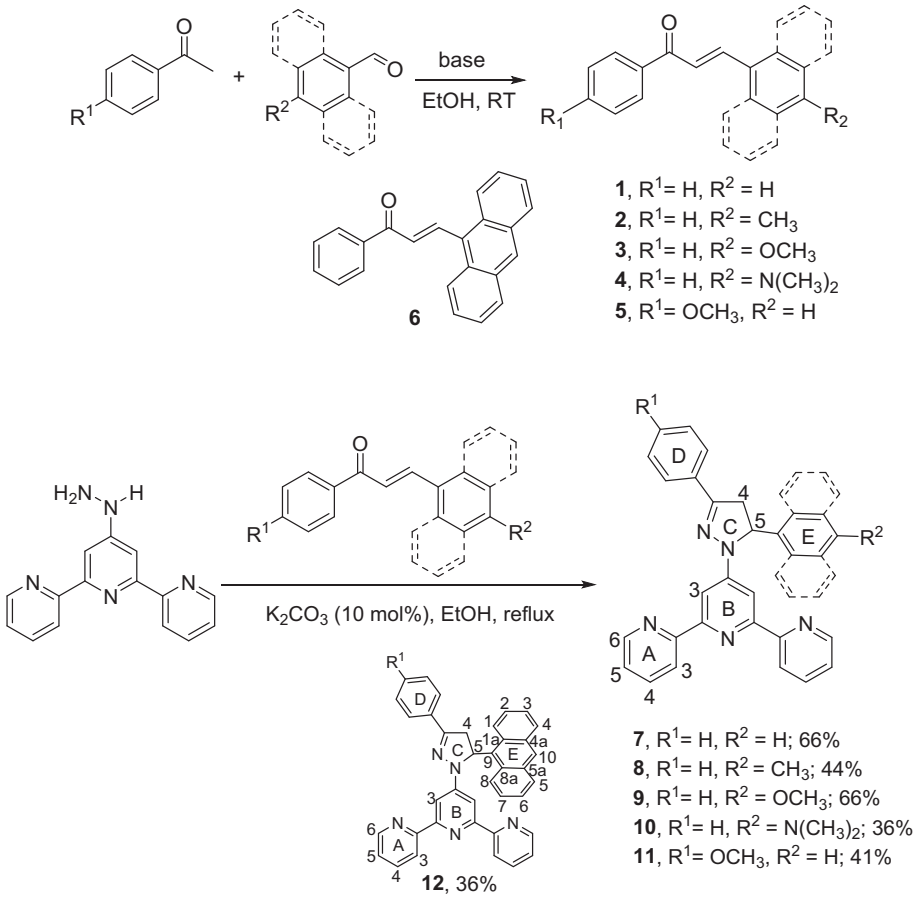
7: $C_{30}H_{23}N_5$, M = 453.55, colorless needle, monoclinic, space group $P21/n$, a = 18.2004 (8), b = 5.5954(3), c = 22.8030(9) Å, β = 100.818(2), U = 2280.95 (18) Å^3, Z = 4, D_c = 1.321 mg m^{-3}, μ(Mo-Kα) = 0.080 mm^{-1}, T = 123 K. Total 57269 reflections, 4459 unique. Refinement of 8203 reflections (316 parameters) with $I > 2\sigma$ (I) converged at final R_1 = 0.0320 (R_1 all data = 0.0382), wR_2 = 0.0520 (wR_2 all data = 0.0754), GOF = 1.1153.

12·3(CHCl$_3$): $C_{41}H_{30}Cl_9N_5$, M = 911.80, colorless block, monoclinic, space group $P2_1/c$, a = 14.9087(13), b = 9.7891(8), c = 27.404(2) Å, β = 96.628 (5), U = 3972.7(6) Å^3, Z = 4, D_c = 1.524 mg m^{-3}, μ(Mo-Kα) = 0.674 mm^{-1}, T = 123 K. Total 54941 reflections, 6911 unique. Refinement of 11001 reflections (496 parameters) with $I > 2\sigma$ (I) converged at final R_1 = 0.1017 (R_1 all data = 0.1253), wR_2 = 0.1079 (wR_2 all data = 0.1569), GOF = 0.9751.

3. Results and discussion

3.1. Synthesis and characterization

The functionalization in the 4′-position of 2,2′:6′,2″-tpy utilizes mainly two intermediates up to now, 4′-chloro-2,2′:6′,2″-tpy and its precursor 2,6-bis-(pyrid-2-yl)-4-pyridone [28,30]. In contrast, there were numerous reports on the nucleophilic aromatic substitution of the chlorine-function in 4′-chloro-2,2′:6′,2″-tpy, readily leading to 4′-R-alkoxy-2,2′:6′,2″-tpys [28]. Likewise, the same type of reaction also afforded 4′-hydrazino-2,2′:6′,2″-tpy when hydrazine was used as a nucleophile. Accordingly, the facile condensation of 4′-hydrazino-2,2′:6′,2″-tpy with aromatic aldehydes led to a variety of 4′-hydrazone-2,2′:6′,2″-tpys, whose properties and coordination chemistry have been revealed earlier [39–41]. Alternatively, we envisaged that it would be equally straightforward to prepare pyrazoline-containing 2,2′:6′,2″-tpys through the conventional pyrazoline condensation between 4′-hydrazino-2,2′:6′,2″-tpy and chalcones under basic conditions. Therefore, our synthesis began with the preparation of several substituted aromatic chalcones **1**–**6** as shown in Scheme 1. The synthesis of **1**–**6** was achieved in high yields under basic conditions by using the method reported in the literature [36]. In the next step, the stoichiometric reaction was conducted by using the resultant chalcones **1**–**6** and 1.0 equiv. of 4′-hydrazino-2,2′:6′,2″-tpy in the presence of K_2CO_3



Scheme 1. The synthesis of chalcones **1**–**6** and pyrazoline-tpy **7**–**12** with atom-labeling for NMR assignments.

(10 mol%), respectively. Consequently, the desired pyrazoline-tpy products **7**–**12** were harvested in 36–66% yields when the reactions were carried out in ethanol upon refluxing for 3.5–16 h (Scheme 1). The products are well soluble in $CHCl_3$, CH_2Cl_2, DMF or DMSO, but poorly soluble in acetone, methanol or acetonitrile.

Compounds **7**–**12** were fully characterized by UV–vis, FT-IR, ^1H and ^{13}C NMR spectroscopy, ESI-MS spectrometer and elemental analysis. The mass spectra of all compounds show peak envelops matched with those calculated. The ^1H and ^{13}C NMR spectra of these new compounds in $CDCl_3$ were assigned by 2D techniques and were in complete agreement with the molecular structures shown in Scheme 1. It is worth noting that a new stereogenic center was generated on C^{C5} atom upon the formation of pyrazolinyl moiety and the diastereotopic protons on C^{C4} sense the presence of this stereogenic center in ^1H NMR spectra for all compounds. For instance, the diastereotopic protons in **7** appear as two *dd* signals at

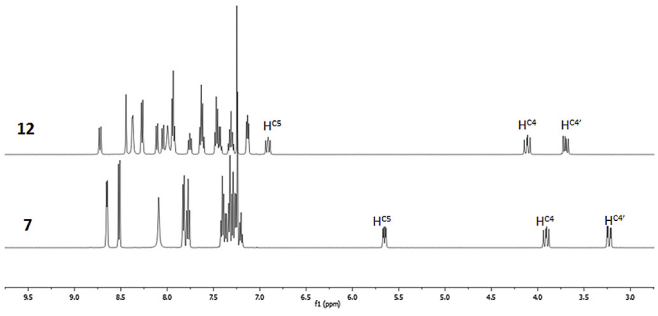


Fig. 1. The ^1H NMR spectra of **7** and **12**.

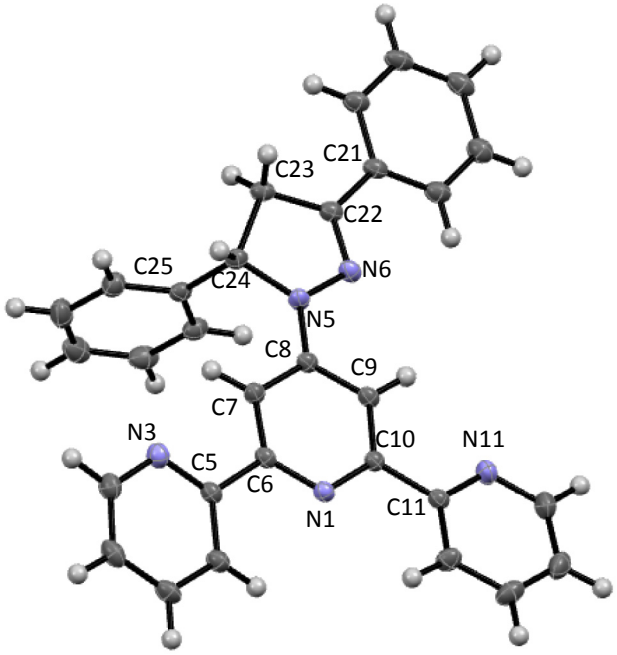


Fig. 2. An ORTEP presentation of the X-ray structure of **7** with thermal ellipsoids plotted at the 50% probability level. Selected bond parameters: N5–N6 = 1.3782(14), N5–C24 = 1.4707(16), N6–C22 = 1.2920(15), C21–C22 = 1.4637(16), C22–C23 = 1.5064(18), C23–C24 = 1.5516(16), C24–C25 = 1.5164(16) Å; Dihedral angle: N1–C10–C11–N11 = 7.19, N3–C5–C6–N1 = 13.23, N6–N5–C8–C9 = 4.19°.

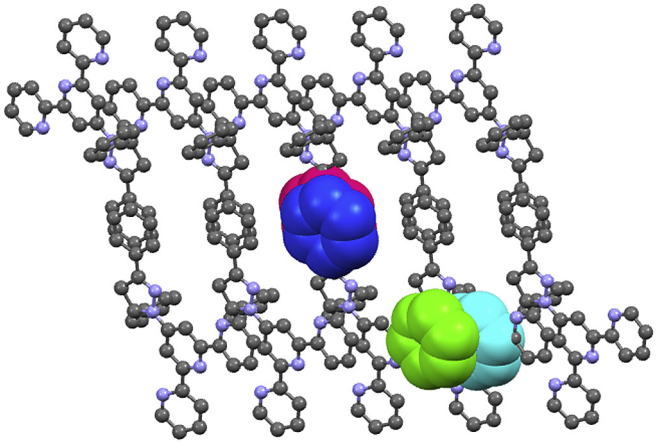


Fig. 3. The molecular packing in **7** along the crystallographic *b* axis, highlighting two types of π-stacking interactions with space-filling representation.

3.91 and 3.23 ppm with different coupling constants, respectively. In **7**–**11**, the chemical shifts for H^{C4} vary slightly between 3.91 and 3.88 ppm for one proton and 3.23–3.19 for another one. However, in compound **12** containing an anthryl group at C^{C5} the two H^{C4} protons shift downfield to 4.09 and 3.68 ppm, respectively. In addition, H^{C5} for compound **12** is notably downfield shifted to 6.90 ppm, while it remains constantly in the range of 5.65–5.58 ppm for **7**–**11.** Fig. 1 shows a comparison of the ^{1}H NMR spectra for these protons in **7** and **12**.

3.2. Crystal structures of **7** and **12**

To further confirm the molecular structures of the new pyrazoline-tpy compounds, crystals of **7** and **12** were grown and the structures were determined by single-crystal X-ray diffraction analysis. Colorless needles of **7** were obtained by slow evaporation of a CH_2Cl_2/MeOH solution of the compound over three days. X-ray structural analysis unambiguously confirmed its structure as illustrated in Scheme. 1. The ORTEP representation of the crystal structure of **7** is shown in Fig. 2 and relevant bond parameters are listed in the caption. **7** crystallizes in the monoclinic space group *P*21/n and the asymmetric unit includes one molecule of **7**. The bond lengths and angles of the terpyridine domain are unexceptional and close to those of known 2,2′:6′,2″-tpy derivatives. The X-ray structure shows that the tpy domain is close to being planar and adopts the expected *trans*, *trans*-conformation as found in most tpy derivatives [39–41]. Two side pyridine rings deviate slightly from the plane of central pyridine and the dihedral angles between side and central pyridines are 7.19 and 13.23°, respectively. The pyrazolinyl ring is almost coplanar with the central pyridine, as well as the phenyl ring containing C21, and the torsional angles between these rings are 4.19 and 2.28°, respectively. In addition, the phenyl ring on the tetrahedral C24 atom is twisted away from the plane (<N5–C24–C25 = 68.07(2)°) as expected, minimizing the steric interactions. The stereogenic C24 adopts an *S*-configuration (Fig. 2) and the *R*-enantiomer of **7** is also observed in the unit cell. Intermolecular packing is dominated by π…π interactions along the crystallographic *b* axis as shown in Fig. 3. The π…π interactions involve packing between the pyrazoline-phenyl groups as well as the tpy domains and the shortest inter-atomic distances for the π-

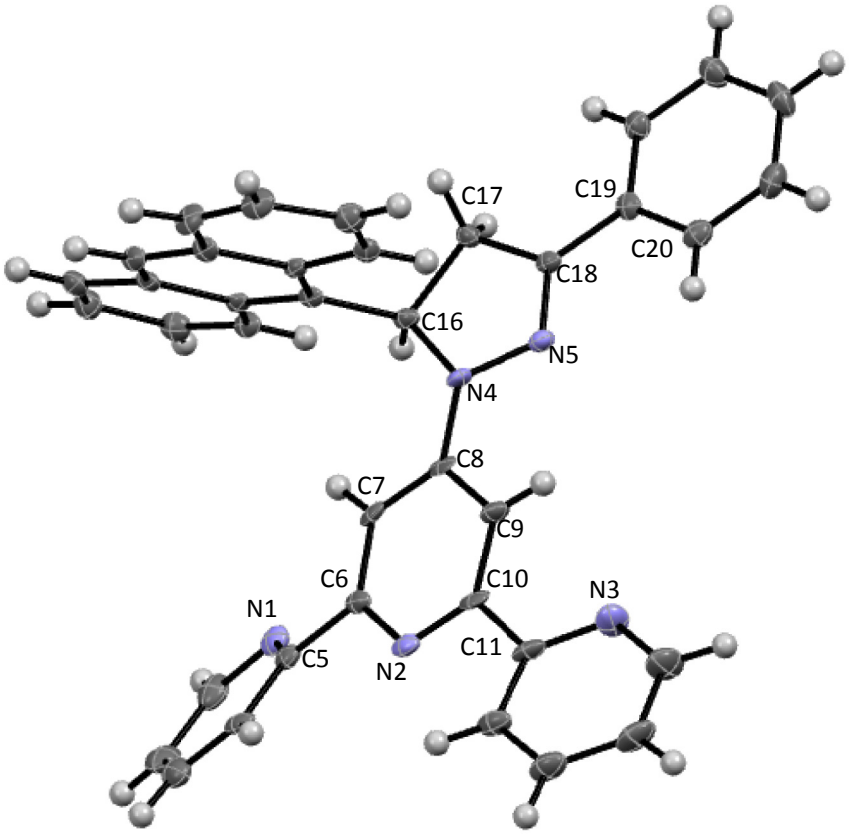


Fig. 4. An ORTEP structure of **12** with thermal ellipsoids plotted at the 50% probability level. Three $CHCl_3$ molecules are omitted for clarity. Selected bond parameters: N4–N5 = 1.381(6), N5–C18 = 1.294(6), C18–C17 = 1.504(7), C17–C16 = 1.535(7), N4–C16 = 1.486(6) Å; Dihedral angle: N1–C5–C6–C7 = 34.43, N3–C11–C10–C9 = 25.85°.

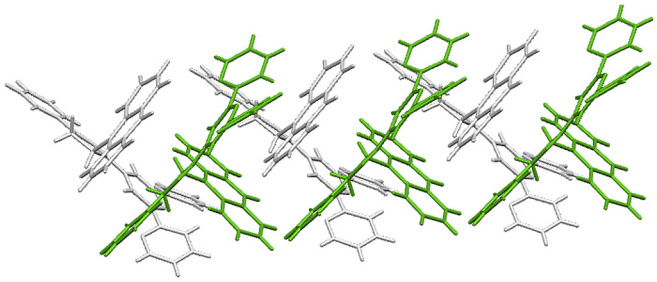


Fig. 5. The molecular packing mode in **12** along the crystallographic *b* axis.

stacking were found to be approximately 3.664 and 3.535 Å, respectively (see Fig. 3).

Single crystals of **12·3CHCl$_3$** were grown by slow evaporation of a $CHCl_3$ solution. Despite of the decay of crystals due to the loss of interstitial $CHCl_3$ molecules during the data collection which resulted in relatively poor quality of data, the main structure of **12** was clearly established. **12·3CHCl$_3$** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit includes one molecule of **12** (Fig. 4). Like **7**, the tpy domain adopts the *trans*, *trans*-conformation and two enantiomers of **12** are also observed in the unit cell. Due to the presence of an anthryl group on the pyrazolinyl unit, the planes of three pyridyl rings are severely distorted, while all bond lengths remain very close to those in **7**. The dihedral angles between the central pyridine and side pyridines are 34.43 and 25.85°, respectively. In the molecular packing mode, the anthryl group is mainly responsible for intermolecular π-stacking interactions (Fig. 5). The π…π interactions occur between the anthryl group and pyrazolinyl or pyridyl rings of adjacent molecules and the shortest interatomic distances are around 3.295 and 3.586 Å, respectively. In addition, non-classical C—H…π hydrogen bonds are also found between the anthracene moieties. The solvent $CHCl_3$ molecules reside in cavities formed by the packing of **12**, hydrogen bonded to the side-arm pyridine N atoms (H···N 2.464 Å, C···N 3.139(3) Å, C—H···N 125°).

3.3. UV–vis and fluorescence

The new compounds **7**–**12** were further characterized by UV–vis and fluorescence spectra. The THF solution of these at room temperature all display intense, high energy absorption centered at 280 nm from ligand-centered $\pi^* \leftarrow \pi$ transition, except that compound **12** also shows a higher energy band at 258 nm. Less intense $\pi^* \leftarrow \pi$ transition bands also appear as broad peaks at between 320 and 390 nm. Compared to the absorption of tpy moiety [42], the obvious red shift upon the introduction of the aromatic rings pendant pyrazoline substituents corresponds to a lowering in energy of the ligand π^* orbitals. In addition, the characteristic fine peaks for anthracene are observed in the absorption of **12**, while the peaks are slightly red shifted. (see Fig. 6)

The fluorescent emission spectra of these compounds were also recorded in THF solution with the same concentration as for UV–vis measurements (Fig. 7). Compounds **7**–**9** displayed very similarly blue fluorescence centered at 400 and 419 nm, while excited at 355 nm. Compound **10** shows fluorescence with two similar peaks, yet with decreased intensity. In contrast, the emission band of **11** features a single peak band and shifted to 442 nm, with the intensity being close to that of **10**. This indicates that the electronic substituents on the pyrazoline unit have a significant impact on the emission spectra of the compounds, although their UV–vis spectra were very close. Surprisingly, compound **12** is non-emissive under the same conditions, which is presumably attributed to the excited state energy transfer between the tpy-pyrazoline and anthrance chromophores. Preliminary studies on the fluorescence properties of **12** upon complexation with metal ions show that the emission could be intrigued by the introduction of zinc ions in the solution. Details on the influence of metal ions in the emission of these compounds will be reported in due course.

4. Conclusion

In conclusion, we herein report the synthesis and characterization of six new 2,2′:6′,2″-tpy derivatives by anchoring aromatic substituted pyrazolines on the 4′-position. The facile pyrazoline condensation between 4′-hydrazino-2,2′:6′,2″-tpy and simple chalcones allows for the synthesis of such compounds containing multiple chromophores with high purity and in moderate to good yields. This represents the first example of synthesis of pyrazoline-tpy derivatives. The aromatic substituents on the pyrzaoline moiety were found to play a role in affecting both the solid state molecular structure and emission properties. The fluorescence properties

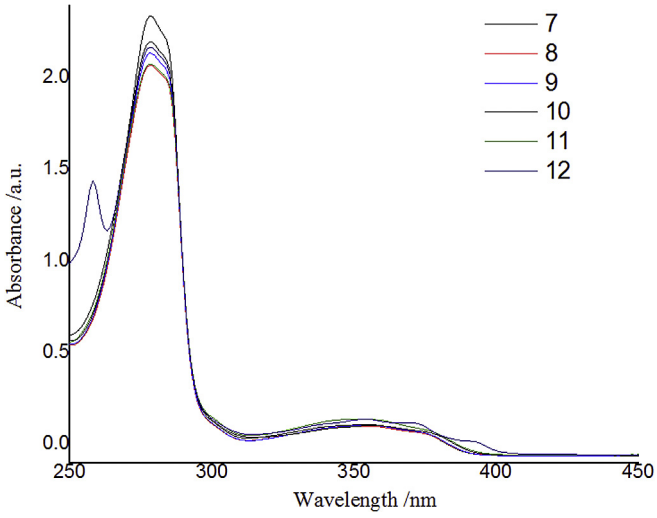


Fig. 6. UV–vis spectra of compounds **7**–**12** in THF (c = 5 × 10^{-6} M) at room temperature.

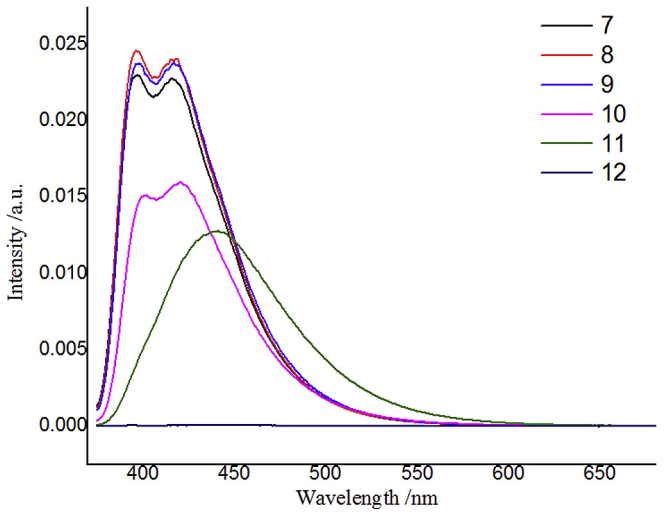


Fig. 7. The fluorescence spectra of compounds **7**–**12** in THF (c = 5 × 10^{-6} M) at room temperature. Excitation wavelengh = 355 nm.

corresponding to metal sensing behavior might be worth further investigating, whereas studies on the coordination chemistry of these compounds are currently in progress.

Acknowledgements

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Appendix A. Supplementary data

CCDC Nos. 1553719–1553720 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.xx.xxxx.

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