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Amphiphilic [tpy-M^{II}-tpy] metallotriangles: synthesis, characterisation and hierarchical ordering

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ABSTRACT

Long chain (C_{16}) alkylated metallocycles are synthesised and characterised. Their ordered aggregation was studied via TEM to gauge to the effects of molecular topology, solvent, counterion and metal centre(s) on morphology and nanoscale structure. The results indicate that their amphiphilicity significantly enhanced their self-ordering characteristics relative to controls and enabled the formation of nanoscale structures. Similar ordering was observed for both labile and non-labile analogues with SAXD showing comparable d-spacing values, suggesting the presence of intramolecular π - π stacking. Effect of counterion and solvent was studied with the non-labile system. Nanotubular, ribbon, or sheet-like structures were afforded depending upon conditions.

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Self-assembly; hierarchical ordering; terpyridine; directional bonding; aggregation; nanotube





Introduction

Biomolecular systems employ a variety of non-covalent, inter- and intra-molecular interactions including van der Waals, H-bonding, π - π stacking and electrostatic, as well as metal-ligand coordination to achieve macromolecular structures and to instill specific utilitarian functionality (1, 2). Use of these forces to construct synthetic macromolecular assemblies is known as supramolecular chemistry (3). Metal-ligand self-assembly with *N*-heteroaromatic ligands, specifically [2,2':6',2"]terpyridine (tpy) using the directional bonding approach (4), has expanded the field of metallosupramolecular chemistry (5) and created a collection of new 2D (6–10) and 3D structures (6, 11, 12).

Various strategies have been utilised to incorporate these well-defined supramolecular structures into larger, macroscopic compositions or materials, including the synthesis of nanoscale and macromolecular structures (5), functionalisation of nanoparticles (13, 14) and attachment to diverse surfaces (15). There is also an increasing interest in using non-covalent forces in the second order, self-assembly of nanostructures (16, 17). Whereas metallosupramolecular chemistry (6) allows for precise placement and concentration of [tpy-M^{II}-tpy] moieties or functionality within a macromolecular architecture, it can also be utilised for positioning directors of intermolecular recognition/self-organisation at the material scale (17). In crystal engineering, such moieties have been termed supramolecular synthons (18) and their location and orientation have been shown to affect self-ordering behaviour (19, 20), a key component in the creation of precise nanostructures (21, 22). The use of non-covalent forces in bottom-up fabrication of nanomaterials is projected to offer potential advantages including economic assembly, self-healing, stimuli responsiveness and recyclability (23).

Nature provides examples of self-assembly of metal complexes into nanostructures, namely, the self-ordering of chlorophyll b (BChl) into rolls of light-adsorbing arrays by photosynthetic bacteria (18). BChl is a macrocyclic metal complex [porphyrin (Mg^{II})] with alkyl chains, ranging in size from C_{16} to C_{20} (24). Thus, BChl is amphiphilic possessing both a hydrophilic, ionic metal complex region and a hydrophobic chain. Synthetic amphiphiles including surfactants and amphiphilic block copolymers have also been used to create ordered structures (17) and the field of supra-amphiphiles has been pioneered by the Zhang group (25, 26). Studies of hierarchical ordering of amphiphilic metallocycles are limited to those using pyridine (15), bipyridine ligands (27), phthalocyanine (28) and porphyrins (29). Investigation into self-ordering of [tpy-M^{II}tpy]-based supramolecular structures using non-covalent intermolecular interactions has been generally focused on using ion pairing (9, 10, 14) to enhance intermolecular stacking. Previous studies looking into hierarchical ordering of [tpy–M^{II}–tpy]-based amphiphiles (9, 14) only used non-labile complexes and did not use controls to gauge the effect of amphiphilicity in the observed ordering. This study includes such comparisons in order to provide a foundation for future investigations with [tpy-M^{II}-tpy] systems and their hierarchial ordering into nanostructures (scheme 1).

Given the limited information concerning self-ordering of amphiphilic, terpyridine-based metallosuprastructures, unanswered questions include (1) how does the introduction of hydrophobic/hydrophilic-type interactions impact ordering? (2) Does lability of the [tpy–M^{II}–tpy] complex affect ordering? (3) Does counterion type affect ordering? (4) How does the solvent system affect ordering? To address these questions, we synthesise, characterise and evaluate self-ordering of a simple series of metallotriangles



Scheme 1. (Colour online) Self-assembly of bis-C₁₆ functionalised bisterpyridine with M^{II} forming amphiphilic triangles, which are subsequently ordered into lamella and rod-like structures. Graphics adapted with permission from Lee and coworkers, *Acc. Chem. Res.*, 2011, 44, 72–82. Copyright 2011 American Chemical Society.

that include alkylated (C_{16}) and non-alkylated controls that are self-assembled with both labile (Zn^{II}) and non-labile (Fe^{II}) metals. We also probe how the counterion type and solvent system affect morphology of the non-labile system.

Experimental

Chemicals were commercially purchased and used without further purification. Thin layer chromatography was conducted on flexible sheets (Baker-flex) precoated with Al₂O₃ (IB-F) or SiO₂ (IB2-F) and visualised by UV light. Column chromatography was conducted using basic Al₂O₃ (60-325 mesh, Brockman Activity I) or SiO₂ (60-200 mesh, Fisher Scientific). ¹H NMR spectra were recorded on a Varian 500 MHz spectrometer. Electrospray ionisation (ESI) mass spectra (MS) were obtained on a Synapt High Definition Mass Spectrometry (HDMS) quadrupole/time-of-flight (Q/ ToF) mass spectrometer (Waters Corp., Milford, MA). For the transmission electron microscopy (TEM) studies, solutions were prepared with 0.1 μ M in 5/1 MeCN/CHCl₃ or 2/1 CHCl₃/MeOH and cast onto carbon-coated copper grids (300 mesh) using a JOEL JEM-1230 transmission electron microscope. AFM height and phase images were obtained on a Nanoscope III multimode microscope from Digital Instruments operating in the tapping mode with aluminium-coated AFM probe from (Nanosensors PPP-NCHR, length 125 mm, width 30 mm, thickness 4 mm, 330 kHz frequency).

1,2-Bis(hexadecyloxy)benzene (1): To a solution of catechol (721 mg, 6.55 mmol) and 1-bromohexadecane (5.00 g, 16.4 mmol) in MeCN (200 mL), K₂CO₃ (4.32 g, 26.2 mmol) was added, then the mixture was refluxed for 2 days. After cooling to 25 °C, the mixture was filtered, dried in vacuo to give a solid that was dissolved in CHCl₂ and extracted (2X) with water, then washed with a brine solution. After drying (MgSO₄), the organic solution was filtered and concentrated in vacuo to give a white solid, which was washed with hexane and dried to give 1, as a white solid: 3.08 g (84%), mp 51–52 °C (lit (30) mp 53–54 °C); ¹H NMR (500 MHz, CDCl₃): δ 6.90 (s, 4H, ArH), 3.92 (t, J = 7 Hz, 4H, OCH₂), 1.82 (m, 4H), 1.48 (br m, 8H), 1.33 (br m, 44 H), 0.89 (t, J = 7 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 14.12, 22.69, 26.06, 29.36, 29.37, 29.45, 29.65, 29.66, 29.67, 29.71, 29.72, 31.93, 69.25, 114.14, 120.99, 149.25; MALDI-ToF MS (m/z): Found: 559.5. Calcd (C₃₈H₇₀O₂ + H)⁺; 559.5; Found: 581.5. Calcd $(C_{38}H_{70}O_2 + Na)^+$: 581.5.

1,2-Dibromo-4,5-bis(hexadecyloxy)benzene (2): 1,2-Bis(hexadecyloxy)benzene (2.00 g, 4.0 mmol) was dissolved in CH_2CI_2 (150 mL) and cooled to 0 °C; then bromine (1.43 g, 8.96 mmol) in CH_2CI_2 (12 mL) was added dropwise over *ca*. 2 h. The stirred mixture was warmed to 25 °C over 12 h, then quenched with sodium metabisulfate, dried (MgSO₄), filtered and concentrated *in vacuo* to give **2**, as a white solid: 2.58 g (89%), mp 57–58 °C (lit (*31*) mp 59.5 °C); ¹H NMR (300 MHz, CDCl₃): δ 7.07 (s, 2H, Ar-H), 3.95 (t, J = 7 Hz, 4H, OCH₂), 1.80 (m, 4H), 1.46 (br m, 8H), 1.29 (br m, 44H), 0.89 (br m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ 14.12, 22.69, 25.93, 29.05, 29.34, 29.37, 29.59, 29.61, 29.67, 29.69, 29.71, 31.93, 69.62, 114.66, 118.04, 149.04; MALDI-ToF MS (*m/z*): Found: 739.4. Calcd (C₃₈H₆₈Br₂O₂ + Na)⁺: 739.3.

4;4""-(4;5'-Bis(hexadecyloxy)[1,1':2;1"-terphenyl]-4,4"-diyl)-di[2,2':6',2"-terpyridine] (3): A mixture of toluene (150 mL), water (150 mL) and EtOH (50 mL) in a round bottom flask was deaerated with argon for 30 min. Then 2 (1.69 g, 2.36 mmol), 4-(2,2':6',2"-terpyridin-4'-yl)phenylboronic acid (32) (2.50 g, 7.09 mmol), and Na₂CO₃ (3.75 g, 35.4 mmol) were added. The stirred mixture was then evacuated in vacuo and backfilled with argon (5X). Pd(PPh₃)₂Cl₂ (334 mg, 472 µmol) was added and the mixture was refluxed for 48 h. After cooling to 25 °C, the organic layer was removed in vacuo. The aqueous layer was extracted with CH₂Cl₂ (2X, 150 mLs each); the organic layers were combined, dried (MgSO₄) and filtered. The resultant pinkish solution was concentrated in vacuo, dried, and the resultant solid was recrystallised from EtOAc and hexane to give 3, as a white solid: 1.7 g (62%), mp 98 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.75 (s, 4H, tpyH^{3',5'}), 8.69 (d, J = 5 Hz, 4H, tpyH^{6,6"}), 8.65 (d, J = 8 Hz, 4H, tpy $H^{3,3"}$), 7.86 (t, J = 8 Hz, 4H, tpy $H^{4,4"}$), 7.82 (d, J = 9 Hz, 4H, ArH), 7.32 (m, 8H, ArH, tpyH^{5,5"}), 7.04 (s, 2H), 4.13 (t, J = 7 Hz, 4H, OCH₂), 1.90 (m, 4H), 1.53 (m, 4H), 1.36 (m, 48H), 0.88 (t, J = 6 Hz, 6H); ¹³C NMR [125 MHz, CDCl₃]: δ 13.86, 22.40, 25.83, 29.11, 29.21, 29.41, 29.43, 29.47, 29.48, 31.67, 69.32, 76.49, 76.75, 76.95, 77.00, 115.94, 118.50, 121.03, 123.43, 126.71, 130.22, 132.32, 135.96, 136.50, 142.07, 148.46, 148.82, 149.54, 155.60, 156.07; MALDI-ToF MS (m/z): Found: 1173.8029. Calcd ($C_{s0}H_{96}N_6O_2 + H$)⁺: 1173.7595.

(3) ${}_{3}Fe_{3}^{+6}[6PF_{6}^{-}]$ (4) or [6Cl⁻] (4a): To a stirred solution of 3 (181.7 mg, 0.155 µmol) dissolved in CH₂Cl₂ (250 mL), MeOH (50 mL) was gradually added. A solution of FeCl₂(4H₂O) (3.23 mg, 0.163 µmol) in MeOH (20 mL) was added dropwise. The reaction mixture was stirred at 25 °C for 12 h., then concentrated and dried in vacuo to give a solid that was chromatographed (SiO₂) eluting with CH₂Cl₂:MeOH (9:1) to give 4a, as a purple solid: 71 mg (35%). Conversion to PF₆ counterion was achieved by dissolving this solid in CHCl₃/MeOH (4:1) and precipitating with NH₄PF₆ affording the desired **4**: mp > 300 °C; ¹H NMR (500 MHz, CD₃CN/ CDCl₃ 5:1): δ 9.16 (s, 12H, tpy $H^{3',5'}$), 8.59 (d, J = 8 Hz, 12H, tpyH^{3,3}"), 8.23 (d, J = 8 Hz, 12H, ArH), 7.80 (t, J = 8 Hz, 12H, tpyH^{4,4}"), 7.64 (d, J = 8 Hz, 12H, ArH), 7.27 (s, 6H, ArH), 7.15 (d, J = 6 Hz, 12H, tpy $H^{6,6"}$), 7.03 (dd, $J_1 = 8$ Hz, $J_2 = 6$ Hz, 12H, tpy $H^{5,5"}$), 4.13 (t, J = 6 Hz, 12H, OC H_{2}), 1.90 (m, 12H), 1.59 (m, 12H), 1.46 (m, 132H), 1.28 (m, 12H), 0.88 (m, 18H); ¹³C NMR [125 MHz, CD₃CN/CDCl₃ (5:1)]: δ 13.80, 22.56, 26.11, 29.26, 29.38, 29.42, 29.56, 29.59, 29.61, 29.63, 29.65, 31.83, 69.83, 104.99, 116.23, 121.39, 124.20, 127.60, 131.32, 132.49, 134.11, 138.79, 144.01, 149.23, 150.87, 152.44, 157.89, 159.99; ESI **4a** (*m*/*z*): 1264.7118 [M-3Cl]³⁺ (Calcd *m*/*z* = 1263.6633), 939.7875 [M-4Cl]⁴⁺ (Calcd *m*/*z* = 939.0053), 744.6249 [M-5Cl]⁵⁺ (Calcd *m*/*z* = 744.2104), and 614.6895 [M-6Cl]⁶⁺ (Calcd *m*/*z* = 614.3472); ESI **4** (*m*/*z*): 1374.1188 [M-3PF₆]³⁺ (Calcd *m*/*z* = 1373.6586), 994.3414 [M-4PF₆]⁴⁺ (Calcd *m*/*z* = 994.0029), 766.4863 [M-5PF₆]⁵⁺ (Calcd *m*/*z* = 766.2095) and 614.5782 [M-6PF₆]⁶⁺ (Calcd *m*/*z* = 614.3472).

(3), Zn, +6[6PF,] (5): To a stirred mixture of 3 (10 mg, 8.5 µmol) in CH₂Cl₂:MeOH (4:1, 12.5 mL), a solution of Zn(NO₃)₂(6 H₂O) (2.53 mg, 8.52 μmol) in MeOH (536 μL) was added. The solution turned yellow and was stirred for 30 min. Then NH₄PF₆ (80 mg) was added. After stirring for an additional 15 min., MeOH (2.5 mL) was added. A light yellow solid was filtered, washed sequentially with MeOH, water and MeOH; the solid was dried in vacuo to give **5**: 11 mg (84%), mp > 300 °C; ¹H NMR [500 MHz, $CD_{2}CN/CDCI_{2}(5:1)$]: δ 8.94 (s, 12H, tpy $H^{3',5'}$), 8.69 (d, J = 8 Hz, 12H, tpyH^{3,3"}), 8.04 - 8.14 (m, 24H, tpyH^{4,4"}, ArH), 7.81 (d, J = 5 Hz, 12H, tpy $H^{6,6"}$), 7.58 (d, J = 8 Hz, 12H, ArH), 7.35 (dd, J₁8 Hz, J₂5 Hz, 12H, tpyH^{5,5}"), 7.20 (s, 6H, ArH), 4.19 (t, J = 6 Hz, 12H, OCH₂), 1.84 - 1.92 (m, 12H), 1.57 (m, 12H), 1.41 - 1.49 (m, 12H), 1.19 - 1.41 (m, 132H), 0.84 - 0.92 (m, 18H); ¹³C NMR [125 MHz, CD₃CN/CDCl₃ (5:1)]: δ 14.93, 23.89, 27.41, 30.58, 30.64, 30.67, 30.86, 30.87, 30.92, 30.93, 30.94, 33.15, 70.83, 106.44, 122.72, 124.69, 129.01, 129.18, 132.75, 133.46, 135.57, 142.66, 145.87, 149.29, 149.39, 150.72, 151.21, 157.28; ESI (m/z): 1383.7075 $[M-3PF_6]^{3+}$ (Calcd m/z = 1382.7237), 1001.5275 $[M-4PF_6]^{4+}$ (Calcd *m*/*z* = 1000.8017), and 772.2182 [M-5PF₆]⁵⁺ (Calcd m/z = 771.6485).

3,4-Bis(4'-terpyridyl-p-phenyl)-o-dimethoxybenzene (6) and $(6)_3 Zn_3^{+6}[6PF_6]$ (7) were prepared as previously described (10).

(6)₃Fe₃⁺⁶[6PF₆] (8) was prepared as described: (33).

Results and discussion

Synthesis

Ligand **3** was synthesised in three steps (Figure 1): alkylation of catechol with 1-bromohexadecane, followed by bromination and then Suzuki–Miyaura coupling (*34*) to generate the desired *bis*-C₁₆ functionalised, 60°-directed, *bis*terpyridine monomer in an overall yield of 46%.

The 60°-directed monomer **3** was subsequently selfassembled (Figure 2) using Fe^{II} to generate the non-labile, amphiphilic triangle **4**, which was purified by column chromatography. The corresponding labile Zn^{II} triangle **5** was isolated in 84% yield without further purification.



Scheme 2. (Colour online) Molecular models and topology of 4, 5, 7 and 8.





Figure 2. (Colour online) Self-assembly of 3 at 1:1 ratio with M^{II} to form the amphiphilic triangles 4 (Fe^{II}) and 5 (Zn^{II}) and of 6 to form non-amphiphilic 'control' triangles 7 (Zn^{II}) and 8 (Fe^{II}).



Figure 3. (Colour online) ¹H NMR (500 MHz) spectra of ligand 3 in CDCl₂ and alkylated triangles 4 and 5 in CD₃CN/CDCl₃ (5:1) (*-CHCl₃).



Figure 4. (Colour online) ESI-TOF-MS of the self-assembled triangle Fe/C_{16} (4) with chloride counterion. Isotope patterns are for the 6+ charge state. $R = C_{16}$.



Figure 5. (Colour online) Comparisons in TEM study.

Self-assembly using ligand **6** (Figure 2) gave the nonamphiphilic, 'control' triangles **7** and **8**, which were compared with **4** and **5** to gauge the effect of alkylation on self-assembly and resultant morphology.

This series of related compounds will allow us to gauge the effect of molecular topology on the self-ordering of [tpy $-M^{II}$ -tpy]-based structures. The differences between the structures are modelled and represented in Scheme 2.

NMR and mass spectrometry

The ¹H NMR spectra of **4** and **5** each reveal a single set of terpyridine proton signals consistent with the macrocyclic structures (Figure 3). Compared to the initial ligand **3**, the upfield shift of the 6,6"-tpy*H* signals [8.69 to 7.15 (**4**) and 7.81 (**5**) ppm] indicates *bis*terpyridine complex formation; no uncomplexed terpyridine termini were observed in



Figure 6. (Colour online) TEM images. Aggregates of Zn^{\parallel} based triangles. Top – 7 (control). Bottom – 5, (C₁₆ functionalised). Cast from MeCN/CHCl₃ (5:1, v:v).



Figure 7. (Colour online) TEM images. Aggregates of Fe^{II}-based triangles. Top 8 (control), Bottom 4 (C₁₆ functionalised). Cast from 5/1 MeCN/CHCl₃ (5:1, v:v).

either case. The relative shifts between Fe and Zn complexes, such as the less pronounced 6,6"-tpyH shift for Zn complexes and the highly deshielded 3',5'-tpyH for the Fe complexes, match well with previously reported systems (*35*). Both **4** and **5** show a single triplet corresponding to the OCH₂ protons at 4.13 and 4.19 ppm, respectively. COSY NMR spectra support the proton assignments (Figure S5–6 in the ESI†). The ¹H NMR shifts for controls **7** and **8** also matched well with previous values.

4, **5**, **7** and **8** were each characterised by ESI-MS. See Figure S7–8 in ESI† for spectra of **4** and **5**. Spectra for **7** and **8** were reported previously (*10*, *33*). The spectrum of **4** with Cl⁻ counterions is shown in Figure 4. The series of peaks matches charge states 3+ through 6+ corresponding to three ligands, three Fe^{II} atoms, and the corresponding number of Cl⁻ anions.

Microscopy

Using TEM, 0.1 μ M solutions were cast onto copper grids and viewed in order to evaluate the presence of added amphiphilicity and metal type upon the morphology; these comparisons are represented in Figure 5. Figure 6 shows representative pictures of the Zn/OC_{16} (5) vs. control Zn/OMe (7). Aggregates of 7 are coarse and amorphous; however, those formed by the more amphiphilic 5 comprised extended, rod-like structures with diameters of *ca*. 40 nm. The sharp, uniform edges were likely formed at an interface during the ordering process. Lamellar features are observed, suggesting the presence of greater surface area during the formation of the amphiphile-based aggregates. The aspect ratio of the resultant structures is consistent with 1D propagation process seen where π - π stacking can occur (*17*).

Figure 7 shows a similar comparison for the macrocycles that self-assemble when using the non-labile metal Fe^{II}. Again, the Fe/OMe (**8**) forms coarse, granular structures with no clear nanoscale order. Conversely, aggregation of Fe/OC₁₆ (**4**) shows a combination of highly directional, anisotropic rod-like structures and lamellar regions. Concentration effects upon supramolecular structure and stoichiometry with labile [tpy–M^{II}–tpy] systems have been demonstrated (*36, 37*) and could potentially affect ordering/morphology under these conditions. However, when comparing Zn/OC₁₆ (**5**) to Fe/OC₁₆ (**4**), it is clear that



Figure 8. (Colour online) TEM of Zn^{II} metallotriangle 5 lamellar regions with SAXD pattern and a proposed packing model, based upon two d-spacing values. The triangular plane in each molecule is highlighted in green to aid in visualisation. The lower right corner is a cutaway showing stacks of complexes indicated by the model.



Figure 9. (Colour online) Ordering of non-labile alkylated Fe^{II} triangles 4 (Cl⁻) from CHCl₃/MeOH (2:1, v:v). Top-left shows a tube-like structure with overall diameter of *ca*. 40 nm with an outer edge/wall thickness of *ca*. 8 nm.

both form extended structures relative to their respective controls, Zn/OMe (**7**) and Fe/OMe (**8**). No major differences between the labile and non-labile based metal systems were conclusively noted. Possible mechanisms for creation of these rod-like structures include formation of anisotropic lamellae, which subsequently roll, curl or stack into rod-like structures upon concentration, precipitation and drying that can occur after casting. Formation of micelles, which aggregate to form cylindrical vesicles, is an alternate possibility (*16*). Constable, Housecroft et al. (*38–41*) recently studied the effects of alkylation (C_8 vs. Me) on

ordering/crystallisation of metal complexes formed using divergent isomeric terpyridines (*e.g.* 4,2':6',4"-connectivity). They reported that the longer alkyl chains promoted enhanced 2D sheet formation as well as interpenetration; this was preliminarily attributed to enhanced solubility. Improved solubility could be contributing to enhanced ordering here as well.

TEM diffraction was conducted on **4** and **5** to gain insight into molecular packing. Figure 8 includes a diffraction pattern for **5**. The notable streaked pattern is due to defects and disordered regions within the ribbon-like



Figure 10. Ordering of non-labile alkylated Fe^{II} triangles 4 (Cl⁻) from CHCl₃/MeOH (2:1, v:v) into tube-like structures.

organisation and is commonly observed in stacked, liquid crystalline phases (14, 42). From these diffraction patterns, the estimated d-spacing values of 8.9 and 46 Å were ascertained. A proposed 2D packing model, based on these values, is shown in Figure 8. Modelling studies indicate that to achieve spacing of 8.9 Å, very close intermolecular packing of these triangles is necessary and that intermolecular π - π stacking of the [tpy-M^{II}-tpy] would be present; the stacking corresponds to the longitudinal direction of the structures. Such π - π stacking has been reported, both intra- (43, 44) and inter-molecularly (45, 46), in [tpy-M^{II}-tpy]-based molecules and materials. Diffraction of the Fe^{II} structures gave similar d-spacing values of 8.9 and 48 Å (Supplemental S9). The almost identical dspacing values, observed with the labile (5) and non-labile (4) systems, suggest that the labile structures remain as triangles during the ordering process. Previously reported (7) fibres of the non-alkylated Zn^{\parallel} triangle (7) using a single hexacarboxylate counterion for each triangle showed similar spacing values of 8.4 and 40 Å and also exhibited a stacking directionality corresponding to the longitudinal course of the fibre. That report did not make note that a spacing value of 8.4 Å would likely require intermolecular π - π stacking. The higher spacing values observed here (i.e. 48 Å vs. 40 Å) can be explained by the presence of the bulky aliphatic chains. The different counterions could also be a factor. These results support the proposition that [tpy–M^{II}–tpy] moieties, due to their ionic and π – π stacking interactions, constitute a crystal engineering motif or synthon (45). Also, the coalescence promoted by the hydrophobic/hydrophilic interactions facilitates and propagates molecular information sharing and recognition between the molecules/synthons to thus enable formation of more uniform and extended nanostructures.

The counterion has been shown to impact morphology of self-assembled, amphiphilic nanostructures (47). To gauge the effect of counterions and solvent on morphology with this system, **4** (Cl⁻) was cast utilising a solvent mixture of MeCN/CHCl₃ (5/1). Disordered lamellae but no rods were observed (S10); however, the TEMs of **4** (Cl⁻) cast from CHCl₃/MeOH (2:1) are shown in Figures 9 and 10. Rod-like structures are present with lengths approaching a micron and transverse dimensions of <50 nm. There are also examples of intact rods as well as others in varying states of unrolling, twisting and/or separating. These observations are consistent with lamellar or sheet-like structures, which have rolled up, a mechanism that has been described in the formation of nanotubes (*21, 48*).

Structures formed by **4** were also evaluated by AFM. A 0.1 μ M solution of **4** was cast onto a glass slide and allowed to dry in a controlled saturated MeCN atmosphere. Height and phase images are shown in Figure S11 (Supplemental Information) and confirm their 3D, rod-like structural characteristics, which were bundled and entangled. Diametres of the base structures ranged from *ca*. 30 to 90 nm.

Conclusions

In this study, we designed, synthesised, and characterised (1D and 2D NMR, ESI-MS) a series of [tpy–M^{II}–tpy] metallotriangles in order to study the effect of amphiphilic character upon hierarchical ordering as well as to understand the effects of lipophilic appendages in the preparation of complex macromolecules. Aggregate morphology was examined using TEM and AFM. We observed that the introduction of amphiphilic character, via the incorporation of long alkyl chains into the initial ligands, enhanced the initial solubility of the reagents leading to improved structural ordering when compared to non-amphiphilic controls. Whereas, the non-amphiphilic analogues formed coarse, granular structures with aspect ratios of <10, the amphiphilic metallotriangles formed highly directional

lamellar and rod-like structures with sharp, uniform edges. This was observed with both the labile (Zn^{II}) and non-labile (Fe^{II}) systems. Molecular modelling, based on *d*-spacing values derived using electron diffraction (SAXD) studies, indicated eclipsed, longitudinal stacking of the amphiphilic metallotriangles and the presence of intermolecular π - π stacking. The similarity in *d*-spacing values between the labile and non-labile systems indicates that the labile structures remained as triangles during the hierarchical ordering process. Therefore, with this ligand, metal type (labile vs. non-labile) did not have an observed impact on ordering. Counterion type (Cl-vs. PF₆) was studied with the non-labile system and did impact aggregate morphology giving either disordered lamellae or nanotubes depending upon solvent conditions. Incorporation of amphiphilic character into the metallocycles, and the resultant hydrophobic/hydrophilic interactions, facilitates cooperative molecular information sharing during hierarchical self-assembly, thus enabling the formation of nanoscale structures. Finally, enhancing the solubility of the initial ligands combined with a directional bonding approach to metal-ligand supramolecular assemblies affords a path towards materials with ordered arrays of [tpy-M^{II}-tpy] metal centres via hierarchical self-assembly.

Supplemental material

Supplemental data for this article can be accessed online here: http://dx.doi.org/10.1080/10610278.2016.1174243

Disclosure statement

No potential conflict of interest was reported by the authors.

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