Design, synthesis and photoelectrochemical properties of hexagonal metallomacrocycles based on triphenylamine: $[M_6(4,4'-bis(2,2':6',2''-terpyridinyl)triphenylamine)_6(X)_{12}]; [M = Fe(II), PF_6^- and Zn(II), BF_4^-]$

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Synthesis of a novel bis(terpyridine) ligand, 4,4'-bis(2,2':6',2"-terpyridinyl)triphenylamine, utilizing triphenylamine, as a specific angle controller, has led to the self-assembly of a unique hexagonal metallomacrocycle family, $[Fe_6(2)_6(PF_6)_{12}]$ and $[Zn_6(2)_6(BF_4)_{12}]$, utilizing terpyridine–metal(II)–terpyridine connectivity. The crystal structure of the novel ligand shows that the angle between the two terpyridinyl moieties is 119.69°, which enabled the formation of the hexagonal-shaped macrocycles. The crystal packing architectures of this starting ligand revealed channels induced by solvent encapsulation. Following complexation of this ligand with transition metals [Fe(II) or Zn(II)] in a one-pot reaction, the resultant structures were characterized by ¹H and ¹³C NMR, UV/Vis and mass spectroscopies. The expected metal-to-ligand charge transfer (MLCT; $\lambda_{max} = 582 \text{ nm}$) and emission ($\lambda_{em} = 575 \text{ nm}$) characteristics were exhibited by both [Fe₆(2)₆(PF₆)₁₂] and [Zn₆(2)₆(BF₄)₁₂]. The photoelectrochemical characteristics of these hexagonal metallomacrocycles demonstrate that they can be used as sensitizers in dye-sensitized solar cells.

Introduction

The design and construction of supramolecular macrocyclic architectures have been the subject of considerable attention by many research groups over the past decade.^{1,2} Elegant work in the area of self-assembly by Stang and coworkers,³⁻⁵ Lehn and coworkers,⁶⁻⁸ Constable *et al.*,⁹⁻¹⁴ and many others¹⁵⁻¹⁹ has offered a better understanding of (macro)molecular systems. This has led to many successful strategies aimed at the construction of metallomacrocyclic structures with motifs such as, triangles,²⁰ squares,²¹⁻²⁶ pentagons,²⁷ and hexagons.²⁸⁻³⁰

The combination of various substitution patterns can result in a plethora of predetermined internal bond angles within molecular superstructures. So far, our strategy has been based on *m*-bis(terpyridinyl)arenes possessing the specific 120° angle with respect to the two ligating moleties for the construction of hexagonal metallomacrocycles. This angle facilitates the assembly of six programmed building blocks with six connecting transition metals in the ubiquitous benzenoid shape, which is envisioned to be the basis of a "modular building block set"³¹ capable of being used to access "higher order" (fractal) architectures.

Owing to their relatively simple synthetic accessibility and stability to oxidation, triarylamines have been widely used as hole-transport components in optoelectronics³²⁻³⁵ in both

photoreceptor devices³⁶ and organic light-emitting diodes.^{37,38} Here, we describe a new type of bis(terpyridine) ligand that can form the desired hexagonal metallomacrocycle, possessing the disubstituted triphenylamine unit, as an angle-control element as well as potentially offering an opportunity to improve selected photophysical properties. We expect that the incorporation of this triphenylamine moiety into structurally rigid metallomacrocyclic assemblies will start to expand the understanding of the optoelectronic characteristics in specific supramolecular macroconstructs.

Results and discussion

Treatment of triphenylamine with excess of DMF and POCl₃, the well-known Vilsmeier reagent, gave the desired dialdehyde **1** in 52% yield (Scheme 1), which was supported by the appearance of the characteristic absorption (¹³C NMR) at 191.72 ppm assigned to the Ar–CHO and mass peak (ESI-MS) at m/z 323.8 [M + Na]⁺. Reaction of dialdehyde **1** with 4.4 equiv. of 2-acetylpyridine under basic conditions at 25 °C for 24 h, followed by addition of excess NH₄OAc in AcOH and then refluxing for 12 h gave the angular building block **2** in 34% yield (Scheme 1). The successful generation of **2** was evidenced by the appearance of the expected new signals (¹H NMR) at 8.73 (m, 6,6"-tpy*H*, 3',5'-tpy*H*), 8.67 (d, 3,3"-tpy*H*) and 7.35 ppm (dd, 5,5"-tpy*H*) attributed to the terpyridinyl moieties and the presence of the definitive number and position of the peaks in the ¹³C NMR; a mass peak (ESI-MS) at m/z 816.3 [M + Ag]⁺ further confirmed the structure.

Vapor diffusion of hexane into a CHCl₃ solution of **2** afforded a single crystal for X-ray analysis (Fig. 1). The crystal structure data revealed the terpyridines to be approximately coplanar and that

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Scheme 1 *Reagents and conditions*: (a) POCl₃, DMF, dichloroethane; (b) (i) 4.4 equiv. 2-acetylpyridine, NaOH; (ii) NH₄OAc, AcOH, reflux.



Fig. 1 ORTEP drawing of bis(terpyridine) ligand **2**. The probability chosen for the ellipsoids was 50%.

they possessed the desired angle (119.69°) juxtaposition necessary for hexamer formation. The pyridine rings of the terpyridinyl moieties adopted the *anti*-conformation with N–C–C–N torsion angles in the range 159.63(15)–176.25(17)°, typical of all such structures. The crystal packing architecture of ligand **2** revealed channels created by solvent encapsulation (Fig. 2(A)) while the side view (Fig. 2(B)) of the crystal packing exhibits a layered stacking with an average separation of *ca.* 4.4 Å. Inspection of the unit cell reveals (see supporting information; CIF file) two antiparallel terpyridine ligands.

The diamagnetic, hexameric Fe(II) complex **3**, [Fe₆(**2**)₆(PF₆)₁₂], was readily prepared by self-assembly of ligand **2** by treatment with one equivalent of FeCl₂·4H₂O in MeOH for 12 h (Scheme 2). The ¹H NMR spectrum of **3** revealed a sharp singlet at 9.20 ppm (3',5'-tpy*H*), indicating the presence of a single homogenous environment; this is in contrast to the broadened or multiple signals realized for either linear or polymeric oligomers, as demonstrated in related systems.²⁹ The Fe(II) metallomacrocycle was confirmed by the observed upfield shift for the doublet at 7.24 ppm (6,6"-tpy*H*s; $\Delta \delta = -1.49$) and a downfield shift for the singlet at 9.20 ppm (3',5'-tpy*H*s; $\Delta \delta = 0.47$) when compared to the absorptions for the uncomplexed starting material. The hexagonal cyclic motif was further established (ESI-MS) by the



Scheme 2 Reagents and conditions: (a) (i) FeCl₂·4H₂O, MeOH or $Zn(BF_4)_2$ ·8H₂O, MeCN, reflux; (ii) for 3, NH₄PF₆/MeOH.



Fig. 2 Crystal packing of ligand 2: (A) top view of packing morphology indicating solvent (CHCl₃) encapsulation channel, (B) side view of the asymmetric units packing.

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definitive signals for multiple-charged entities ranging from a +8 to +11 charge state derived from the loss of PF_5 and PF_6^- , either separately or together.

The related yellow semicrystalline $[Zn_6(2)_6(BF_4)_{12}]$ was generated (55%) by the treatment of a 1 : 1 mixture of ligand **2** with $Zn(BF_4)_2 \cdot 8H_2O$ in MeCN for 24 h at 80 °C. The absence (¹H NMR) of extraneous peaks excluded the presence of starting materials, intermediates and linear oligomers. The diagnostic shifts of the doublets at 7.87 ppm (6,6″-tpy*H*s; $\Delta \delta = -0.86$) and the singlet at 8.99 ppm (3',5'-tpy*H*s; $\Delta \delta = 0.26$) along with definitive ESI-MS data (*m*/*z* 544.4 [M - 9BF₄-]⁹⁺, 624.5 [M - 8BF₄-]⁸⁺, 725.1 [M -7BF₄-]⁷⁺, 860.3 [M - 6BF₄-]⁶⁺, 1049.6 [M - 5BF₄-]⁵⁺, 1333.6 [M - 4BF₄-]⁴⁺, 1807.8 [M - 3BF₄-]³⁺), all support the structural assignment.

The UV/Vis spectra of **3** and **4** were measured (MeCN) and are shown in Fig. 3. The Fe(II) hexamer showed the lowest energy ligand-centered π - π * transitions of the terpyridine moieties at 423 nm. While the metal-to-ligand charge-transfer (MLCT) transitions derived from the promotion of an electron from the Fe(II) d-orbitals to unfilled ligand π * orbitals³⁷ appeared at 582 nm. In the case of the Zn(II) hexamer **4**, absorption bands at λ_{max} = 285, 319, 330, 433 nm originating from intraligand charge transfer (¹ILCT) were observed without MLCT peaks; the MLCT of the Zn(II) terpyridine complex can be excluded.³⁸ The Zn(II) hexamer shows a strong yellow emission at 575 nm when excited with UV light (400 nm). The fluorescence of the Zn(II) hexamer in MeCN solution is shown in Fig. 3(B); whereas, the Fe(II) hexamer did not show an emission peak.



Fig. 3 UV/Vis absorption (solid line) and emission (dashed line) spectra for metallomacrocycles 3 (A) and 4 (B).

Due to their light absorption properties, constructs **3** and **4** were also studied as sensitizer materials for solar cell devices. Photovoltaic experiments using dye-covered nanocrystalline TiO₂ electrodes (prepared by dipping the semiconductor substrate into a 0.2 mM MeCN solution of each hexamer) properly fitted in a solar cell device,²⁷ were conducted using an AM 1.5 (100 mW cm⁻²) incident light source and an electrolyte containing 0.3 M KI + 0.015 M I₂ dissolved in a 4 : 1 ratio of propylene and ethylene carbonate. Discharge experiments conducted with

Complex	$J_{\rm sc}{}^a/\mu{\rm A~cm^{-2}}$	$V_{\rm oc}{}^{b}/{ m mV}$	ff ^c (%)	η^{d} (%)
3	160	255	26.9	0.032
4	230	391	68.1	0.180

^{*a*} Short-circuit photocurrent density. ^{*b*} Open-circuit photovoltage. ^{*c*} Fill factor. ^{*d*} Photoconversion efficiency of the solar cell.

these devices allowed the calculation of the values shown in Table 1. The fill factor (*ff*), the short circuit photocurrent (J_{sc}), as well as the open circuit photopotential (V_{oc}) for the Zn(II) metallomacrocycle, showed superior results over the Fe(II) metallomacrocycle. Further, the total photoconversion efficiency of the cell (η) using electromagnetic radiation spanning the visible region of the spectrum exhibited better values than in the case of the Zn(II) metallomacrocycle **4**.

Conclusion

A new ditopic triphenylamine-based bis(terpyridine) ligand possessing a critical 119.69° angle relative to each coordination site has been crafted and demonstrated to form of a series of unique, selfassembled, hexagonal metallomacrocycles. The structures of the ligand and the corresponding metallomacrocycles were confirmed by means of ¹H and ¹³C NMR, UV-Vis spectroscopy and mass spectrometry. Preliminary results of the photoelectrochemical performances for these materials show their potential for application in dye-sensitized solar cells.

Experimental

Chemicals were purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets precoated with Al_2O_3 (IB–F) or SiO₂ (IB₂–F) and visualized by UV light. Column chromatography was conducted using basic Al_2O_3 , Brockman Activity I (60–325 mesh) or SiO₂ (60–200 mesh) from Fisher Scientific. The melting points were determined on an Electrothermal 9100 heater. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl₃, except where noted. Mass spectra were obtained on a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS). UV/Vis absorption spectra were obtained on Hewlett-Packard UV/Vis spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer.

4,4'-Diformyltriphenylamine (1)

Phosphorus oxychloride (37.3 mL, 400 mmol) was added dropwise to stirred DMF (62 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h and then stirred at 25 °C for another 1 h. After the addition of triphenylamine (8.0 g, 32.6 mmol) dissolved in dichloroethane, the mixture was stirred at 80 °C for 48 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with aq. NaOH solution and extracted with CH_2Cl_2 . The extract was washed with sat. brine solution and the solvent was evaporated *in vacuo*. The residue was

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purified by column chromatography (SiO₂) eluting with a hexane– EtOAc (3 : 1, v/v) mixture to afford **1** (52%) as a light-yellow solid: mp 143 °C; ¹H NMR: δ 9.90 (s, CHO, 2H), 7.78 (d, J = 8.4 Hz, 3,5-ArH, 3,5-Ar'H, 4H), 7.41 (t, J = 7.5 Hz, 3,5-Ar"H, 2H), 7.27 (t, J = 7.2 Hz, 4-Ar"H, 1H), 7.21–7.17 (m, 2,6-ArH, 2,6-Ar'H, 3,5-Ar"H, 6H); ¹³C NMR: δ 122.98, 124.75, 126.47, 127.28, 130.36, 131.52, 145.72, 152.23, 190.71; ESI-MS: m/z 323.8 [M + Na]⁺ (calc. m/z 324.1).

4,4'-Bis(2,2':6',2"-terpyridinyl)triphenylamine (2)

The dialdehyde 1 (4.8 g, 15.9 mmol) was dissolved in EtOH (100 mL) then 2-acetylpyridine (8.49 g, 70.1 mmol) was added, followed after 2 min by NaOH powder (2.8 g, 70.0 mmol). After the dark pink solution had been stirred at 25 °C for 24 h, the solvent was evaporated in vacuo to yield a dark brown solid, as the intermediate. Ammonium acetate (26 g, excess) and glacial AcOH (100 mL) were added and the mixture was refluxed for 12 h. The dark brown solution was cooled and neutralized with aqueous Na₂CO₃. The crude product was extracted with CH₂Cl₂ and column chromatographed (Al₂O₃) eluting with a hexane-EtOAc (1 : 2, v/v) mixture to afford 2 (34%) as a yellow solid: mp 290–291 °C (decomp.); ¹H NMR: δ 8.73 (m, 6,6"-tpyH, 3',5'tpyH, 8H), 8.67 (d, J = 7.8 Hz, 3,3''-tpyH, 4H), 7.90–7.83 (m, 4,4"-tpyH, 2,6-ArH, 6H), 7.35 (dd, J = 4.8, 7.2 Hz, 5,5"-tpyH, 4H), 7.27–7.21 (m, 3,5-Ar*H*, 2,5-Ar*H*, 3,5-Ar*H*, 7H), 7.14 (t, *J* = 4.8 Hz, 4-Ar'H, 1H); ¹³C NMR: δ 156.58, 156.12, 149.89, 149.53, 148.52, 147.27, 137.04, 132.86, 129.77, 128.52, 125.47, 124.16, 124.12, 123.97, 121.55, 118.60; ESI-MS: m/z 816.3 [M + Ag]⁺ (calc. m/z 816.2).

[Fe₆(2)₆(PF₆)₁₂] (3)

A MeOH solution of one equivalent of FeCl₂·4H₂O (54 mg, 270 µmol) was added to a suspension of ligand 2 (190 mg, 270 µmol) in MeOH (40 mL). The mixture was stirred at 25 °C for 24 h. The resultant deep purple solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was purified by column chromatography (SiO₂) eluting with a H_2O-CH_3CN -sat. aq. KNO₃ (1 : 7 : 1, v/v/v) mixture to afford 3 (>50%) as a purple solid: mp >400 °C (decomp.); ¹H NMR $(CD_3CN): \delta 9.20 (s, 3', 5'-tpyH, 4H), 8.64 (d, J = 7.8 Hz, 3, 3''-tpyH),$ 4H), 8.37 (d, J = 8.4 Hz, 3,5-ArH, 4H), 7.93 (dd, J = 7.2, 7.2 Hz, 4,4''-tpyH,4H), 7.58 (d, J = 6.9 Hz, 2,6-ArH, 2,6-Ar'H,4H), 7.45– 7.37 (m, 3,4,5-Ar'H, 3H), 7.24 (d, J = 5.4 Hz, 6,6"-tpyH, 4H), 7.11 $(dd, J = 6.6, 6.0 \text{ Hz}, 5, 5'' \text{-tpy}H, 4\text{H}); {}^{13}\text{C} \text{ NMR} (\text{CD}_3\text{CN}): \delta 161.36,$ 159.26, 154.20, 150.68, 150.60, 147.60, 139.79, 131.61, 131.35, 130.19, 128.36, 127.95, 126.90, 124.91, 121.86, 119.19; UV/vis (MeCN): $\lambda_{max}/nm (\epsilon/dm^3 mol^{-1} cm^{-1}) 224 (3.06 \times 10^5)$, 283 (4.37 × 10^{5}), 321 (3.43 × 10^{5}), 423 (1.77 × 10^{5}), 582 nm (2.88 × 10^{5}); ESI-MS: m/z 428.9 [M - 11PF₆⁻]¹¹⁺ (calc. m/z = 429.8), 494.2 [M - $6PF_6^- - 4PF_5^{10+}$ (calc. m/z 494.8), 558.1 [M - $9PF_6^-$]⁹⁺ (calc. m/z 557.5), 657.2 [M - 3PF₆⁻ - 5PF₅]⁸⁺ (calc. m/z 657.1).

$[Zn_6(2)_6(BF_4)_{12}]$ (4)

 $Zn(BF_4)_2 \cdot 8H_2O$ (77 mg, 200 µmol) was added to a solution of **2** (143 mg, 200 µmol) in MeCN and the mixture was refluxed for 48 h. After the mixture had cooled to 25 °C, the resultant solution

was filtered through Celite, then Et₂O (150 mL) was added to precipitate the complex, which was filtrated to afford 4 (>55%) as a orange solid: mp >400 °C (decomp.); ¹H NMR (CD₃CN): δ 8.99 (s, 3', 5'-tpyH, 4H), 8.76 (d, J = 8.1 Hz, 3, 3''-tpyH, 4H), 8.25 (d, J = 8.4 Hz, 3,5-ArH, 4H), 8.19 (dd, J = 8.1, 6.9 Hz, 4,4"-tpyH, 4H), 7.87 (d, J = 4.5 Hz, 6,6"-tpyH, 4H), 7.56 (dd, J = 8.4, 6.9 Hz, 3,5-Ar'H, 2H), 7.49 (d, J = 8.4 Hz, 2,6-ArH, 4H), 7.45–7.39 (m, 4-Ar'H, 5,5"-tpyH, 5H); ¹³C NMR (CD₃CN): δ 156.36, 151.00, 150.89, 149.13, 149.07, 147.28, 142.31, 131.36, 130.89, 130.45, 128.55, 128.12, 124.65, 124.26, 121.59, 119.23; UV/vis (MeCN): $\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm dm^3~mol^{-1}~cm^{-1}})$ 285 (5.97 × 10⁵), 319 (3.72 × 10⁵), $330 (3.62 \times 10^5), 433 \text{ nm} (4.29 \times 10^5); \text{ESI-MS: } m/z 544.4 \text{ [M} - 10^5)$ $9BF_4^{-}]^{9+}$ (calc. m/z = 544.4), 624.5 [M - $8BF_4^{-}]^{8+}$ (calc. m/z623.3), 725.1 $[M - 7BF_4^{-}]^{7+}$ (calc. m/z 724.8), 860.3 $[M - 6BF_4^{-}]^{6+}$ (calc. m/z 860.1), 1049.6 [M - 5BF₄⁻]⁵⁺ (calc. m/z 1049.4), 1333.6 $[M - 4 BF_4^{-}]^{4+}$ (calc. m/z 1333.5), 1807.8 $[M - 3BF_4^{-}]^{3+}$ (calc. *m*/*z* 1806.9).

Crystal data for 2

C₄₈H₃₃N₇·CHCl₃, M = 827.18, triclinic, space group $P\overline{1}$, a = 12.9078(10), b = 13.573(2), c = 13.602 (2) Å, a = 90.432(6), $\beta = 109.097(7)$, $\gamma = 115.196(6)^{\circ}$, V = 2007.4(4) Å³, T = 110 K, Z = 2, μ (Mo-K α) = 0.275 mm⁻¹, 13328 independent reflections, $R_{int} = 0.037$, $R_1 = 0.057$, $wR_2 = 0.154$ (for all data).

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603691k

Fabrication of the photovoltaic cell device

Nanocrystalline TiO₂ electrodes were prepared by applying a 4 V potential difference³⁹ between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL [0.5 g TiO₂ (P25, Degussar AG, Germany, a mixture of ca. 30% rutile and 70% anatase, BET surface area 55 m² g⁻¹) in 5% 2-propanol in water (v/v)] colloidal suspension for 40 s. Following previous reports in the literature,⁴⁰ the electrodes were then taken out of the electrophoretic apparatus, sintered at 450 °C in air for 30 min and characterized by general tools (AFM, XRD, Raman spectroscopy, cyclic voltammetry and perfilometry). From the characterization results, it was found that the electrode thus prepared consisted of nanoparticulate TiO₂ in the anatase phase, with roughness factors of 540, an average thickness of $\sim 2 \ \mu m$ and a flat band potential, $E_{\rm FB}$, of -0.2 V vs. NHE. This value agrees well with previous reports,41,42 and is substantially more positive than that reported for nanocrystalline electrodes prepared using the typical spin coating protocol (-0.5 V vs. NHE). This effect, which has been reported⁴¹ recently, is associated with an increase of Ti³⁺ dopant surface sites that result from hydrogen adsorption during the electrophoretic deposition process. Hexamers, as the dye, were coated onto the TiO₂ layer by dipping the electrode for 12 h in a MeCN solution (ca. 0.2 mmol L⁻¹). The assembled devices for photovoltaic measurements consisted of a dye-coated TiO₂ electrode, Ti substrate covered with a film of colloidal graphite as a counter electrode, the electrolyte containing a deoxygenated 0.3 M of KI + 0.015 M of I_2 aqueous solution,⁴³ and Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.

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