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# Design, synthesis and photoelectrochemical properties of hexagonal metallomacrocycles based on triphenylamine: $[M_6(4,4'\text{-bis}(2,2':6',2''\text{-terpyridinyl})\text{triphenylamine})_6(X)_{12}]$ ; $[M = \text{Fe(II)}, \text{PF}_6^- \text{ and } \text{Zn(II)}, \text{BF}_4^-]$

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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 metallomacrocyclic family,  $[\text{Fe}_6(\mathbf{2})_6(\text{PF}_6)_{12}]$  and  $[\text{Zn}_6(\mathbf{2})_6(\text{BF}_4)_{12}]$ , utilizing terpyridine-metal(II)-terpyridine connectivity. The crystal structure of the novel ligand shows that the angle between the two terpyridinyl moieties is  $119.69^\circ$ , 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  $[\text{Fe(II)}$  or  $\text{Zn(II)}]$  in a one-pot reaction, the resultant structures were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, UV/Vis and mass spectroscopies. The expected metal-to-ligand charge transfer (MLCT;  $\lambda_{\text{max}} = 582 \text{ nm}$ ) and emission ( $\lambda_{\text{em}} = 575 \text{ nm}$ ) characteristics were exhibited by both  $[\text{Fe}_6(\mathbf{2})_6(\text{PF}_6)_{12}]$  and  $[\text{Zn}_6(\mathbf{2})_6(\text{BF}_4)_{12}]$ . 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.<sup>1,2</sup> Elegant work in the area of self-assembly by Stang and coworkers,<sup>3–5</sup> Lehn and coworkers,<sup>6–8</sup> Constable *et al.*,<sup>9–14</sup> and many others<sup>15–19</sup> 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,<sup>20</sup> squares,<sup>21–26</sup> pentagons,<sup>27</sup> and hexagons.<sup>28–30</sup>

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  $120^\circ$  angle with respect to the two ligating moieties 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”<sup>31</sup> 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 optoelectronics<sup>32–35</sup> in both

photoreceptor devices<sup>36</sup> and organic light-emitting diodes.<sup>37,38</sup> Here, we describe a new type of bis(terpyridine) ligand that can form the desired hexagonal metallomacrocyclic, 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

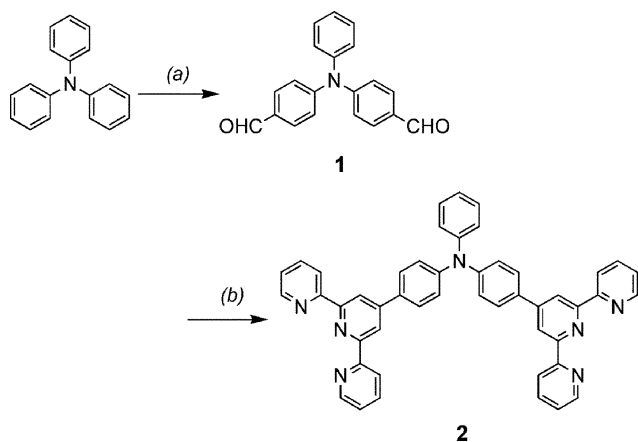
Treatment of triphenylamine with excess of DMF and  $\text{POCl}_3$ , the well-known Vilsmeier reagent, gave the desired dialdehyde **1** in 52% yield (Scheme 1), which was supported by the appearance of the characteristic absorption ( $^{13}\text{C}$  NMR) at 191.72 ppm assigned to the  $\text{Ar-CHO}$  and mass peak (ESI-MS) at  $m/z$  323.8  $[\text{M} + \text{Na}]^+$ . Reaction of dialdehyde **1** with 4.4 equiv. of 2-acetylpyridine under basic conditions at  $25^\circ\text{C}$  for 24 h, followed by addition of excess  $\text{NH}_4\text{OAc}$  in  $\text{AcOH}$  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 ( $^1\text{H}$  NMR) at 8.73 (m, 6,6''-tpyH, 3',5'-tpyH), 8.67 (d, 3,3''-tpyH) and 7.35 ppm (dd, 5,5''-tpyH) attributed to the terpyridinyl moieties and the presence of the definitive number and position of the peaks in the  $^{13}\text{C}$  NMR; a mass peak (ESI-MS) at  $m/z$  816.3  $[\text{M} + \text{Ag}]^+$  further confirmed the structure.

Vapor diffusion of hexane into a  $\text{CHCl}_3$  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

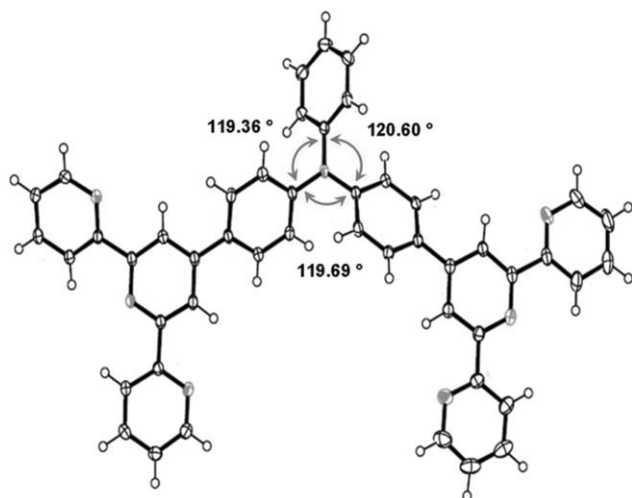
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**Scheme 1** Reagents and conditions: (a) POCl<sub>3</sub>, DMF, dichloroethane; (b) (i) 4.4 equiv. 2-acetylpyridine, NaOH; (ii) NH<sub>4</sub>OAc, AcOH, reflux.

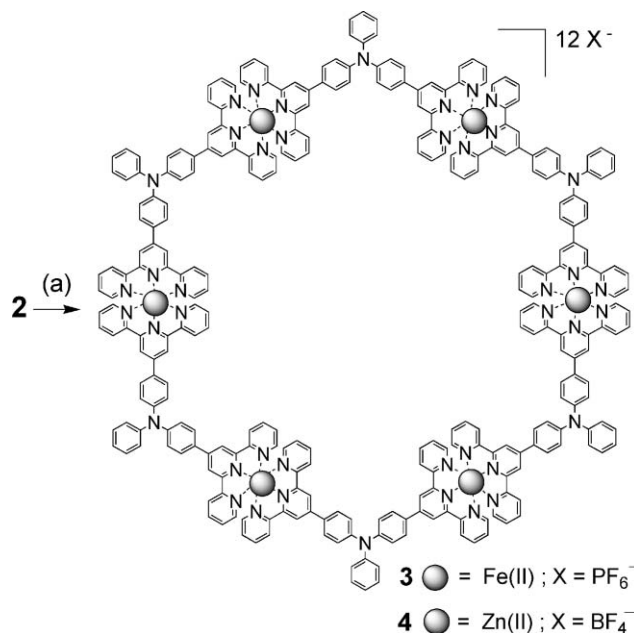


**Fig. 1** ORTEP drawing of bis(terpyridine) ligand **2**. The probability chosen for the ellipsoids was 50%.

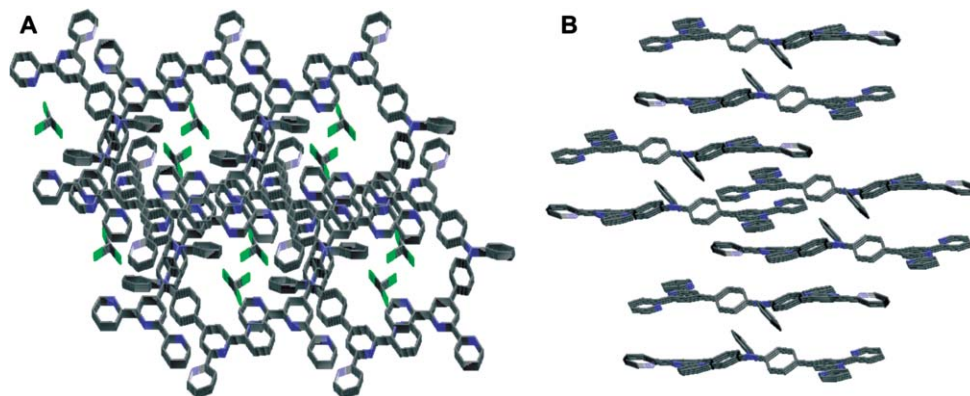
they possessed the desired angle (119.69°) juxtaposition necessary for hexamer formation. The pyridine rings of the terpyridinyl moieties adopted the *anti*-conformation with N–C–C–N torsion angles in the range 159.63(15)–176.25(17)°, typical of all such structures. The crystal packing architecture of 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**, [Fe<sub>6</sub>(**2**)<sub>6</sub>(PF<sub>6</sub>)<sub>12</sub>], was readily prepared by self-assembly of ligand **2** by treatment with one equivalent of FeCl<sub>2</sub>·4H<sub>2</sub>O in MeOH for 12 h (Scheme 2). The <sup>1</sup>H NMR spectrum of **3** revealed a sharp singlet at 9.20 ppm (3',5'-tpyH), 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.<sup>29</sup> The Fe(II) metallomacrocyclic was confirmed by the observed upfield shift for the doublet at 7.24 ppm (6,6''-tpyHs; Δδ = −1.49) and a downfield shift for the singlet at 9.20 ppm (3',5'-tpyHs; Δδ = 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) FeCl<sub>2</sub>·4H<sub>2</sub>O, MeOH or Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O, MeCN, reflux; (ii) for **3**, NH<sub>4</sub>PF<sub>6</sub>/MeOH.

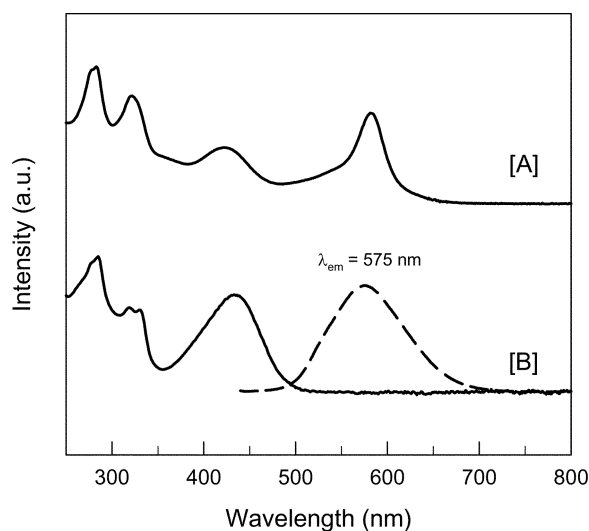


**Fig. 2** Crystal packing of ligand **2**: (A) top view of packing morphology indicating solvent (CHCl<sub>3</sub>) encapsulation channel, (B) side view of the asymmetric units packing.

definitive signals for multiple-charged entities ranging from a +8 to +11 charge state derived from the loss of PF<sub>5</sub> and PF<sub>6</sub><sup>−</sup>, either separately or together.

The related yellow semicrystalline [Zn<sub>6</sub>(2)<sub>6</sub>(BF<sub>4</sub>)<sub>12</sub>] was generated (55%) by the treatment of a 1 : 1 mixture of ligand **2** with Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O in MeCN for 24 h at 80 °C. The absence (<sup>1</sup>H 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''-tpyHs; Δδ = −0.86) and the singlet at 8.99 ppm (3',5'-tpyHs; Δδ = 0.26) along with definitive ESI-MS data (*m/z* 544.4 [M − 9BF<sub>4</sub>]<sup>9+</sup>, 624.5 [M − 8BF<sub>4</sub>]<sup>8+</sup>, 725.1 [M − 7BF<sub>4</sub>]<sup>7+</sup>, 860.3 [M − 6BF<sub>4</sub>]<sup>6+</sup>, 1049.6 [M − 5BF<sub>4</sub>]<sup>5+</sup>, 1333.6 [M − 4BF<sub>4</sub>]<sup>4+</sup>, 1807.8 [M − 3BF<sub>4</sub>]<sup>3+</sup>), 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\* orbitals<sup>37</sup> appeared at 582 nm. In the case of the Zn(II) hexamer **4**, absorption bands at λ<sub>max</sub> = 285, 319, 330, 433 nm originating from intraligand charge transfer (<sup>1</sup>ILCT) were observed without MLCT peaks; the MLCT of the Zn(II) terpyridine complex can be excluded.<sup>38</sup> 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 TiO<sub>2</sub> electrodes (prepared by dipping the semiconductor substrate into a 0.2 mM MeCN solution of each hexamer) properly fitted in a solar cell device,<sup>27</sup> were conducted using an AM 1.5 (100 mW cm<sup>−2</sup>) incident light source and an electrolyte containing 0.3 M KI + 0.015 M I<sub>2</sub> dissolved in a 4 : 1 ratio of propylene and ethylene carbonate. Discharge experiments conducted with

**Table 1** Photovoltaic performances of dye-sensitized solar cell device (ITO:TiO<sub>2</sub>|hexamer:KI–I<sub>2</sub> electrolyte|graphite) under 100 mW cm<sup>−2</sup> light source

Complex	<i>J</i> <sub>sc</sub> <sup>a</sup> /μA cm <sup>−2</sup>	<i>V</i> <sub>oc</sub> <sup>b</sup> /mV	<i>ff</i> <sup>c</sup> (%)	<i>η</i> <sup>d</sup> (%)
<b>3</b>	160	255	26.9	0.032
<b>4</b>	230	391	68.1	0.180

<sup>a</sup> Short-circuit photocurrent density. <sup>b</sup> Open-circuit photovoltage. <sup>c</sup> Fill factor. <sup>d</sup> 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*<sub>sc</sub>), as well as the open circuit photopotential (*V*<sub>oc</sub>) for the Zn(II) metallomacrocyclic, showed superior results over the Fe(II) metallomacrocyclic. 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) metallomacrocyclic **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, self-assembled, hexagonal metallomacrocyclics. The structures of the ligand and the corresponding metallomacrocyclics were confirmed by means of <sup>1</sup>H and <sup>13</sup>C 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<sub>2</sub>O<sub>3</sub> (IB–F) or SiO<sub>2</sub> (IB<sub>2</sub>–F) and visualized by UV light. Column chromatography was conducted using basic Al<sub>2</sub>O<sub>3</sub>, Brockman Activity I (60–325 mesh) or SiO<sub>2</sub> (60–200 mesh) from Fisher Scientific. The melting points were determined on an Electrothermal 9100 heater. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl<sub>3</sub>, 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<sub>2</sub>Cl<sub>2</sub>. The extract was washed with sat. brine solution and the solvent was evaporated *in vacuo*. The residue was

purified by column chromatography (SiO<sub>2</sub>) eluting with a hexane–EtOAc (3 : 1, v/v) mixture to afford **1** (52%) as a light-yellow solid: mp 143 °C; <sup>1</sup>H 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); <sup>13</sup>C 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]<sup>+</sup> (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 Na<sub>2</sub>CO<sub>3</sub>. The crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub> and column chromatographed (Al<sub>2</sub>O<sub>3</sub>) eluting with a hexane–EtOAc (1 : 2, v/v) mixture to afford **2** (34%) as a yellow solid: mp 290–291 °C (decomp.); <sup>1</sup>H 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-ArH, 2,5-Ar'H, 3,5-Ar''H, 7H), 7.14 (t, *J* = 4.8 Hz, 4-Ar'H, 1H); <sup>13</sup>C 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]<sup>+</sup> (calc. *m/z* 816.2).

#### [Fe<sub>6</sub>(2)<sub>6</sub>(PF<sub>6</sub>)<sub>12</sub>] (**3**)

A MeOH solution of one equivalent of FeCl<sub>2</sub>·4H<sub>2</sub>O (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 (SiO<sub>2</sub>) eluting with a H<sub>2</sub>O–CH<sub>3</sub>CN–sat. aq. KNO<sub>3</sub> (1 : 7 : 1, v/v/v) mixture to afford **3** (>50%) as a purple solid: mp >400 °C (decomp.); <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 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 Hz, 5,5''-tpyH, 4H); <sup>13</sup>C NMR (CD<sub>3</sub>CN): δ 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): λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>) 224 (3.06 × 10<sup>5</sup>), 283 (4.37 × 10<sup>5</sup>), 321 (3.43 × 10<sup>5</sup>), 423 (1.77 × 10<sup>5</sup>), 582 nm (2.88 × 10<sup>5</sup>); ESI-MS: *m/z* 428.9 [M – 11PF<sub>6</sub>]<sup>−11+</sup> (calc. *m/z* = 429.8), 494.2 [M – 6PF<sub>6</sub> – 4PF<sub>5</sub>]<sup>10+</sup> (calc. *m/z* 494.8), 558.1 [M – 9PF<sub>6</sub>]<sup>9+</sup> (calc. *m/z* 557.5), 657.2 [M – 3PF<sub>6</sub> – 5PF<sub>5</sub>]<sup>8+</sup> (calc. *m/z* 657.1).

#### [Zn<sub>6</sub>(2)<sub>6</sub>(BF<sub>4</sub>)<sub>12</sub>] (**4**)

Zn(BF<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O (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 Et<sub>2</sub>O (150 mL) was added to precipitate the complex, which was filtrated to afford **4** (>55%) as an orange solid: mp >400 °C (decomp.); <sup>1</sup>H NMR (CD<sub>3</sub>CN): 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); <sup>13</sup>C NMR (CD<sub>3</sub>CN): 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): λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>−1</sup> cm<sup>−1</sup>) 285 (5.97 × 10<sup>5</sup>), 319 (3.72 × 10<sup>5</sup>), 330 (3.62 × 10<sup>5</sup>), 433 nm (4.29 × 10<sup>5</sup>); ESI-MS: *m/z* 544.4 [M – 9BF<sub>4</sub>]<sup>9+</sup> (calc. *m/z* = 544.4), 624.5 [M – 8BF<sub>4</sub>]<sup>8+</sup> (calc. *m/z* 623.3), 725.1 [M – 7BF<sub>4</sub>]<sup>7+</sup> (calc. *m/z* 724.8), 860.3 [M – 6BF<sub>4</sub>]<sup>6+</sup> (calc. *m/z* 860.1), 1049.6 [M – 5BF<sub>4</sub>]<sup>5+</sup> (calc. *m/z* 1049.4), 1333.6 [M – 4 BF<sub>4</sub>]<sup>4+</sup> (calc. *m/z* 1333.5), 1807.8 [M – 3BF<sub>4</sub>]<sup>3+</sup> (calc. *m/z* 1806.9).

#### Crystal data for **2**

C<sub>48</sub>H<sub>33</sub>N<sub>7</sub>·CHCl<sub>3</sub>, *M* = 827.18, triclinic, space group *P* $\bar{1}$ , *a* = 12.9078(10), *b* = 13.573(2), *c* = 13.602 (2) Å, *α* = 90.432(6), *β* = 109.097(7), *γ* = 115.196(6)°, *V* = 2007.4(4) Å<sup>3</sup>, *T* = 110 K, *Z* = 2, μ(Mo-Kα) = 0.275 mm<sup>−1</sup>, 13328 independent reflections, *R*<sub>int</sub> = 0.037, *R*<sub>1</sub> = 0.057, *wR*<sub>2</sub> = 0.154 (for all data).

CCDC reference number 601362.

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

#### Fabrication of the photovoltaic cell device

Nanocrystalline TiO<sub>2</sub> electrodes were prepared by applying a 4 V potential difference<sup>39</sup> between a steel sheet and an ITO conducting glass substrate immersed in a 10 mL [0.5 g TiO<sub>2</sub> (P25, Degussar AG, Germany, a mixture of *ca.* 30% rutile and 70% anatase, BET surface area 55 m<sup>2</sup> g<sup>−1</sup>) in 5% 2-propanol in water (v/v)] colloidal suspension for 40 s. Following previous reports in the literature,<sup>40</sup> 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 profilometry). From the characterization results, it was found that the electrode thus prepared consisted of nanoparticulate TiO<sub>2</sub> in the anatase phase, with roughness factors of 540, an average thickness of ~2 μm and a flat band potential, *E*<sub>FB</sub>, of −0.2 V vs. NHE. This value agrees well with previous reports,<sup>41,42</sup> 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 reported<sup>41</sup> recently, is associated with an increase of Ti<sup>3+</sup> dopant surface sites that result from hydrogen adsorption during the electrophoretic deposition process. Hexamers, as the dye, were coated onto the TiO<sub>2</sub> layer by dipping the electrode for 12 h in a MeCN solution (*ca.* 0.2 mmol L<sup>−1</sup>). The assembled devices for photovoltaic measurements consisted of a dye-coated TiO<sub>2</sub> 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<sub>2</sub> aqueous solution,<sup>43</sup> and Teflon tape that was used to maintain a 0.5 mm gap between the two electrodes.

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