

5,10,15,20-Tetrakis[4'-(terpyridinyl)phenyl]porphyrin and its Ru^{II} complexes: Synthesis, photovoltaic properties, and self-assembled morphology†

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A novel tetrakis(terpyridinyl)porphyrin derivative and its Ru^{II} complexes were efficiently synthesized using microwave enhanced synthesis and shown to possess photovoltaic properties. Transmission electron microscopy and selected area electron diffraction were used to investigate its nanowire self-assembly.

Porphyrin-based polypyridinyl systems have been widely studied due to their attractive photophysical properties.¹ Elegant work by Sauvage and coworkers² has resulted in the synthesis of diad and triad terpyridinyl porphyrin metal complexes. More recently, Elliott *et al.*,³ reported the synthesis of a tetrakisbipyridinylporphyrin and its Ru complex for use as a catalyst in electrochemical olefin epoxidation. These works provided the inspiration to design and synthesize a four-directional tetrakis(terpyridinyl)porphyrin, which has the potential to be a suitable core for construction of porphyrin containing metallodendritic motifs possessing unique photovoltaic properties. Herein, we report the efficient, microwave-assisted synthesis of a tetrakis(terpyridinyl)porphyrin and its heteroleptic Ru^{II} complexes and their photovoltaic properties.

4'-(*p*-Formylphenyl)terpyridine (**1**) was prepared according to the literature procedure.^{2a} The Adler method⁴ of refluxing aldehyde **1** with 1 equiv. of pyrrole in propionic acid was employed to synthesize the tetrakis(terpyridinyl)porphyrin (**2**, Scheme 1), which was isolated in 3% yield after purification using column chromatography (Al₂O₃, CHCl₃). The structure of **2** was confirmed (¹H NMR) by singlets observed at −2.64 ppm assigned to the porphyrin internal amine protons, 9.00 ppm for the outer pyrrole protons, and 9.10 ppm representing the 3',5'-tpyHs (terpyridine = tpy, these signals integrated as expected in a 4 : 4 : 1 ratio), along with a mass peak (ESI-MS) at *m/z* 1539.2 [M + H]⁺. Alternatively, the microwave enhanced synthesis⁵ (400 W, 10 min.) of porphyrin **2** gave rise to an improved, albeit still low, overall yield (12%) and decreased reaction time. The UV/Vis spectrum of **2** showed typical absorption peaks expected for a

porphyrin derivative including the Soret band at 423 nm and 4 Q-bands at 519, 554, 593, and 652 nm.

The tetrakisRu^{II} complex **3** (Scheme 1) was synthesized by combining porphyrin **2** with 4 equiv. of the paramagnetic [4'-tolylterpyridine]Ru^{III} adduct⁶ **5** in the presence of a catalytic amount of *N*-ethylmorpholine in ethylene glycol; the suspension was subjected to microwave irradiation (450 W, 20 min.). The crude product was purified using column chromatography (silica, H₂O : sat. aq. KNO₃ : MeCN = 1 : 1 : 10) and subsequently treated with methanolic NH₄PF₆ to convert the counterions to PF₆[−] to aid in solubility. Structural support (¹H NMR) for complex **3** included resonances attributed to the 3',5'-tpyHs of inner terpyridine [9.49 ppm (8H)] and outer terpyridine [9.08 ppm (8H)] moieties. Resonances assigned to the pyrrole and amines of the porphyrin ring were observed as expected at 9.24 (8H) and −2.54 ppm (2H), respectively. The methyl group on the outer terpyridine appeared as a singlet [2.59 ppm (12H)] while the ESI-mass spectrum for **3** displayed molecular ion peaks at *m/z* = 954.5 [M − 4PF₆]⁺, *z* = 4, (calcd. 954.4), 734.6 [M − 5PF₆]⁺, *z* = 5, (calcd. 734.5), 588.1 [M − 6PF₆]⁺, *z* = 6, (calcd. 587.9), 483.2 [M − 7PF₆]⁺, *z* = 7, (calcd. 483.2), 404.5 [M − 8PF₆]⁺, *z* = 8, (calcd. 404.7).

Zinc metallation⁷ of the porphyrin complex **3** (Cl[−] counterions) was achieved by refluxing with 1 equiv. of Zn(OAc)₂ in MeOH for 3 h to give complex **4** (72%). The ¹H NMR of **4** (PF₆[−] counterions) exhibited a similar resonance pattern to that of **3** with the expected disappearance of the internal amine proton peak. Molecular ion peaks (ESI-MS) were observed at *m/z* = 970.6 [M − 4PF₆]⁺, *z* = 4, (calcd. 970.4), 747.5 [M − 5PF₆]⁺, *z* = 5, (calcd. 747.3), 598.6 [M − 6PF₆]⁺, *z* = 6, (calcd. 598.6), 492.3 [M − 7PF₆]⁺, *z* = 7, (calcd. 492.3), 412.8 [M − 8PF₆]⁺, *z* = 8, (calcd. 412.7).

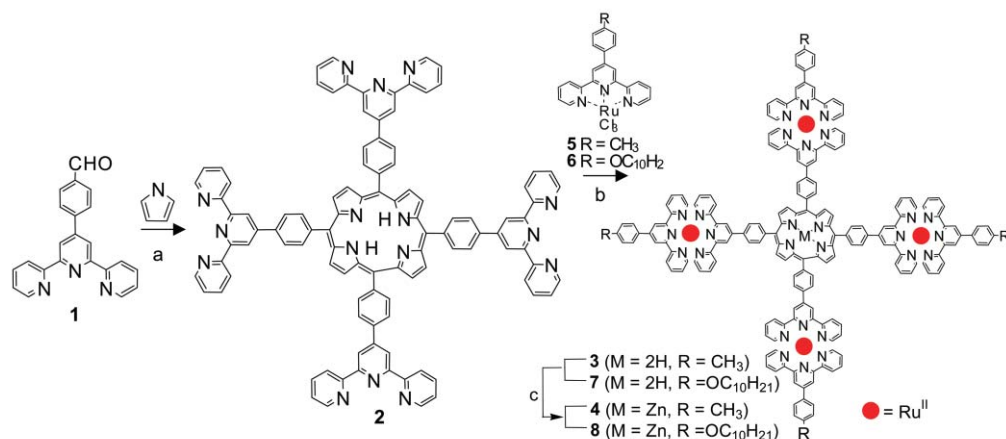
A peripherally modified complex employing 4'-(*p*-decyloxyphenyl)terpyridine to enhance solubility was prepared by a modified procedure of Constable *et al.*⁸ This terpyridine was then treated with 1 equiv. of RuCl₃ in refluxing EtOH to give (90%) the paramagnetic [4'-(*p*-decyloxyphenyl)terpyridine]Ru^{III} adduct **6**. Tailored tetrakisRu^{II} complexes **7** and **8** (Scheme 1) were synthesized using the same procedures for **3** and **4**, respectively (**7**: 36%, **8**: 81% yield). Structural support (¹H NMR) for complex **7** included resonances for the 3',5'-tpyHs of inner terpyridine [9.39 ppm (8H)] and outer terpyridine [9.02 ppm (8H)] moieties. Resonances attributed to the outer pyrrole and the inner amine protons were observed at 9.23 (8H) and −2.53 ppm (2H), respectively. The alkyl methyl and −OCH₂−R groups on the

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Scheme 1 Synthesis of the porphyrin–Ru-complex: a: propionic acid, 400 W, 10 min. microwave reactor, b: ethylene glycol, 450 W microwave reactor, 20 min., c: Zn(OAc)₂, MeOH, reflux, 3 h, followed by NH₄PF₆.

decyloxy chain appeared as two triplets [0.92 ppm (12H)] and [4.19 ppm (8H)], respectively. The ESI-mass spectrum for **7** displayed molecular ion peaks at $m/z = 1096.0$ [$\text{M} - 4\text{PF}_6^+$, $z = 4$, (calcd. 1096.7), 848.6 [$\text{M} - 5\text{PF}_6^+$, $z = 5$, (calcd. 848.6), 682.8 [$\text{M} - 6\text{PF}_6^+$, $z = 6$, (calcd. 682.8), 564.8 [$\text{M} - 7\text{PF}_6^+$, $z = 7$, (calcd. 564.6), 476.0 [$\text{M} - 8\text{PF}_6^+$, $z = 8$, (calcd. 475.9). The ¹H NMR of the Zn-metallated porphyrin complex **8** showed a similar absorption pattern to that of **7** except for the disappearance of the internal amine proton peak. Molecular ion peaks were observed at $m/z = 1111.6$ [$\text{M} - 4\text{PF}_6^+$, $z = 4$, (calcd. 1112.2), 861.1 [$\text{M} - 5\text{PF}_6^+$, $z = 5$, (calcd. 860.8), 693.3 [$\text{M} - 6\text{PF}_6^+$, $z = 6$, (calcd. 693.2), 573.7 [$\text{M} - 7\text{PF}_6^+$, $z = 7$, (calcd. 573.4), 483.6 [$\text{M} - 8\text{PF}_6^+$, $z = 8$, (calcd. 483.6).

Cyclic voltammograms (CVs) for **8**, **4**, **7** and **3** revealed reversible redox peaks attributed to Ru^{III}|Ru^{II} couple around 1.0 V vs. Fc⁺|Fc (S1; S1).⁹ Also, porphyrin-containing Ru^{II} complexes revealed another two waves at −1.47 V and −1.60 V, respectively, corresponding to redox processes of the terpyridine moieties. Additional electrochemical data are discussed in the ESI†.

Construction of dye-sensitized solar cells (DSSC) started with nanocrystalline TiO₂ electrodes that were prepared by electrophoretic deposition; experimental details have been reported elsewhere.¹⁰ Action spectra obtained for Zn^{II}-porphyrins showed significant photocurrents at ca. 450–600 nm (Fig. 1). This behavior

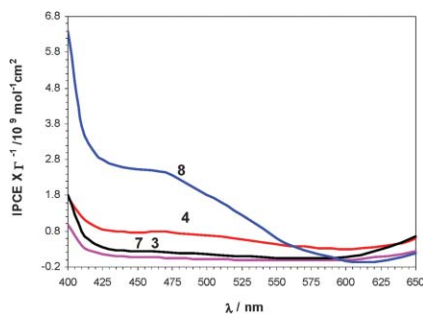


Fig. 1 Normalized action spectra obtained for the dye-sensitized solar cell (DSSC) assembled with modified TiO₂ with **8** (blue line), **4** (red line), **7** (black line), and **3** (pink line).

is associated to the excitation of the Zn^{II}-porphyrin and <tpy–Ru^{II}–tpy> complexes around 425 nm and 495 nm, respectively.¹⁰ The photoelectrochemical response (Fig. 1) for the Zn^{II}-porphyrin having the long hydrocarbon chain (**8**) is larger than that possessing only the methyl group (**4**) by a factor of ~3 (at 425 nm). In the following stage, we obtained *j*-*E* plots (ESI; S3†) in order to calculate their photovoltaic performance. Thus, Table 1 shows that the global photoconversion efficiency (η) for TiO₂/**8** system is almost 10 times larger than for TiO₂/**4**. The photovoltaic results (Table 1) suggest that the peripheral aliphatic groups promote a decrease in recombination of the photogenerated electrons.¹¹

Estimation of electron lifetimes (τ_n) for DSSC constructed with dyes **8** and **4** was calculated from electrochemical impedance spectroscopy experiments under polychromatic illumination (2.2 mW cm^{−2}) according to the methodology previously reported by Bisquert *et al.*^{12a} and Grätzel *et al.*^{12b} Experimental spectra were fitted to the corresponding equivalent circuit^{12a} (Table 1 and ESI; S7†) revealing that τ_n for TiO₂/**8** and TiO₂/**4** systems were 5.14 ms and 0.13 ms, respectively. This suggests that electron recombination for TiO₂/**8** system is almost 40 times slower than for TiO₂/**4**.

Photoelectrochemical evaluation of the free-base porphyrin–<tpy–Ru^{II}–tpy> complexes (**3** and **7**) was also conducted. First, the surface coverage (Table 1) for each dye was investigated and showed similar values to those of the Zn-porphyrin–<tpy–Ru^{II}–tpy> complexes. According to the action spectra (Fig. 1) in the presence of Zn^{II}, complexes **4** and **8** could inject electrons on the TiO₂ semiconductor film. However, when Zn^{II} was absent (*e.g.*, **3** and **7**), the results of photocurrent action spectra indicated that

Table 1 Surface coverage of the dyes and photovoltaic performance of the DSSC

Dye	^a <i>I</i> /10 ^{−11} mol cm ^{−2}	<i>E</i> _{oc} /mV	<i>j</i> /μA cm ^{−2}	^b <i>ff</i>	^c η (%)	τ_n /ms
8	4.10	330	729.93	0.262	2.85	5.14
4	6.55	170	143.18	0.279	0.30	0.13
7	4.60	NA	NA	NA	NA	NA
3	6.87	NA	NA	NA	NA	NA

^a Dye coverage. ^b Fill factor *ff* = $P_{\text{max}}/(E_{\text{oc}} \times j)$ where P_{max} denotes maximum power cell. ^c Global photoconversion efficiency η (%) = $(ff \times E_{\text{oc}} \times j) \times 100/P_{\text{input}}$ where $P_{\text{input}} = 2.2 \text{ mW cm}^{-2}$.

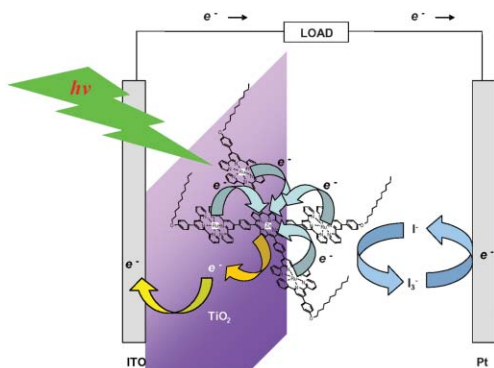


Fig. 2 The proposed charge transfer through a DSSC by using sensitized TiO_2 electrodes with Zn-porphyrin- $\langle\text{tpy-Ru}^{\text{II}}\text{-tpy}\rangle$ complexes.

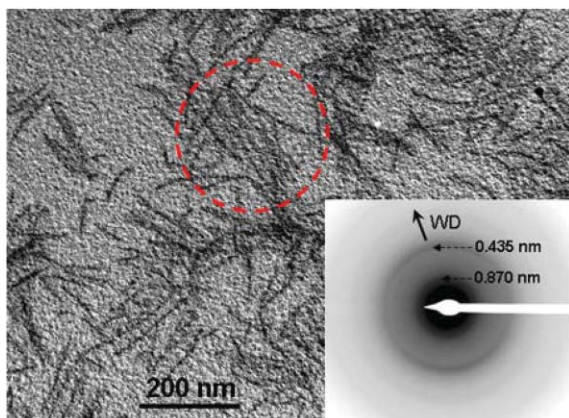


Fig. 3 TEM image of the self-assembled nanowires constructed using the discotic porphyrin complex **7**. The inset image is the SAED of the bundle of nanowires taken in the circled region of Fig. 3. Here, WD indicates the wires long direction.

this process was interrupted.¹³ From this observation, we propose an electron transfer mechanism, which assumes that electrons introduced into the $\langle\text{tpy-Ru}^{\text{II}}\text{-tpy}\rangle$ moiety can be transferred to the TiO_2 through the Zn-porphyrins.¹⁴ This porphyrin-containing transition metal polypyridinyl device (Fig. 2) is a potential “switch” for controlling charge transfer between “electron containers” ($\langle\text{tpy-Ru}^{\text{II}}\text{-tpy}\rangle$) and “electron acceptors” (TiO_2 films).

Fig. 3 shows a TEM image of the self-assembled nanowires with a width of ca. 7 nm, which is comparable to the diameter of porphyrin complex **7**, and 0.3–0.5 μm in length. In order to know the detailed molecular packing inside these nanowires, selected area electron diffraction (SAED) was conducted in the region shown in the inset of Fig. 3. Based on the morphological observation and its SAED, the wires long direction is in the meridian direction of the SAED pattern. Calibration of the SAED

spacing was conducted using the standard evaporated thallos chloride, which has a largest first-order spacing diffraction of 0.384 nm. SAED pattern showed that a strong diffraction appeared on the meridian at 0.870 nm with a second order diffraction at 0.435 nm. The d -spacing of 0.870 nm is close to the thickness of the porphyrin complex **7** (about 0.86 nm).

Therefore, we can conclude that the normal direction of the self-assembled porphyrin complex is parallel to the wires long direction and nanowires generated from the single column of porphyrin complex (disc-shape) building block. Diffused diffractions at the meridian and quadrants (0.212 and 0.286 nm, respectively) are likely from the alkyl chains at the end of complex **7**.¹⁵

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