Design, self-assembly, and photophysical properties of pentameric metallomacrocycles: $[M_5(N\text{-hexyl}[1,2\text{-bis}(2,2':6',2''\text{-terpyridin-4-yl})]\text{carbazole})_5][M = Fe(II), Ru(II), and Zn(II)]$†

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Received (in Columbia, MO, USA) 7th July 2005, Accepted 26th July 2005
First published as an Advance Article on the web 23rd August 2005
DOI: 10.1039/b509662f

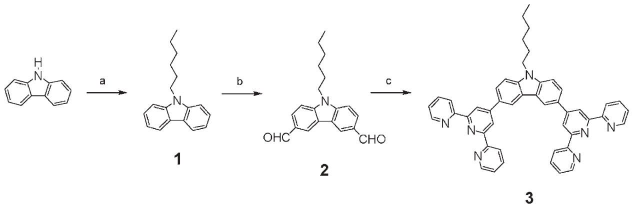
A novel family of metallopentacycles was constructed by the facile self-assembly of a bis(terpyridine)–carbazole monomer utilizing terpyridine–metal(II)–terpyridine connectivity; its photophysical properties were investigated.

The design of highly ordered supramolecular structures has attracted considerable interest in that the self-assembly of specifically tailored building blocks, possessing appropriate directionality of binding loci underpin the generation of novel, utilitarian supramolecular complexes with two- and three-dimensional nano- and macro-structures.[1–3] Owing to their electronic and steric versatility, aromatic *N*-heterocycles continue to play a prominent role as classical ligands in coordination compounds,[4,5] bridging ligands in binuclear derivatives,[6–8] and as building blocks for supramacromolecular assemblies. In addition to the ability of these polyheteroaromatics to be connected by metal centers, they provide the opportunity of π-back-bonding and thereby may affect the delocalization and transport of electrons as well as the capture of photons for light-energy conversion.[9,10]

So far, many successful strategies have been developed for the construction of metallomacrocyclic structures with trigonal,[11,12] square,[13–19] hexagonal,[20–22] heptagonal,[23] and octagonal[24] shapes; the pentagonal shape has been reported[25,26] albeit to a limited extent relative to its homologous counterparts.

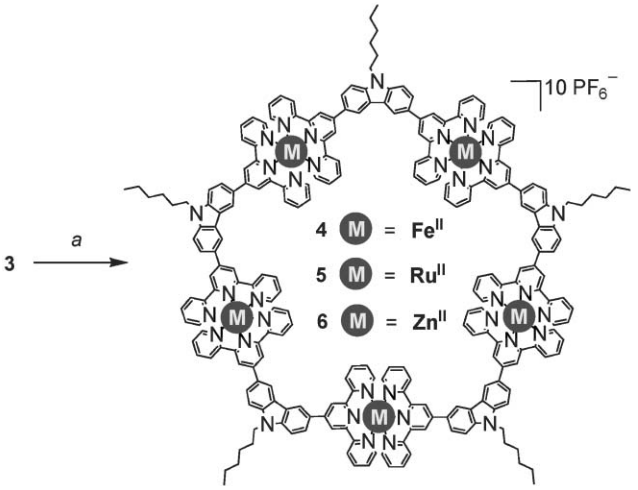
We herein report the assembly and photophysical properties (luminescence and photovoltaics) of a related family of metallomacrocycles based on a carbazole unit connecting two, rigidly held, and appropriately directed (*ca.* 105°) terpyridine ligands. This bis-ligand was then self-assembled to give metallopentacycles utilizing terpyridine–metal(II)–terpyridine connectivity.

Chemically, carbazole has been shown to be easily functionalized at its 3-, 6- or 9-positions.[27] Therefore, synthesis of the key building block **3** (Scheme 1) began with commercially available 9*H*-carbazole, which was *N*-alkylated with 1-bromohexane using KOH to give **1** (71%) that was subsequently treated with 3 equiv. of DMF and $POCl_3$ (Vilsmeier reagent) to form the desired dialdehyde **2** (52%). This transformation was supported (^1H and ^{13}C NMR) by the appearance of peaks at 10.15 (–C*H*O) and 191.72 (–*C*HO) ppm, respectively, and the 3,6-substitution pattern was confirmed by the aromatic coupling constants. Dialdehyde **2** was treated with 3 equiv. of 2-acetylpyridine under basic conditions for 24 h at 25 °C, followed by the addition of excess NH_4OAc in AcOH. After refluxing for 12 h, the desired angular building block **3** (34%) was isolated and structurally confirmed (^1H NMR) by the peaks at 4.38 ppm (t) for NCH_2, 8.11 ppm (d) for 3-Ar*H*, and 7.90 ppm (dd) for 4,4″-tpy*H* (these signals integrated in the expected 1 : 1 : 2 ratio). Also, a mass peak (ESI-MS) at *m*/*z* 715.2 $[M + H]^+$ was recorded.



Scheme 1 *Reagents and conditions*: (a) 1-bromohexane, KOH, DMF, reflux; (b) DMF, $POCl_3$; (c) *(i)* 4.4 equiv. 2-acetylpyridine, NaOH, *(ii)* NH_4OAc, AcOH, reflux.

Treatment of **3** with one equiv. of $FeCl_2 \cdot 4H_2O$ in MeOH for 12 h at 25 °C (Scheme 2) gave the self-assembled pentameric



Scheme 2 *Reagents and conditions*: (a) *(i)* M^{2+}, reflux; *(ii)* NH_4PF_6–MeOH.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures with analytical data and solar cell device fabrication procedure. See http://dx.doi.org/10.1039/b509662f

complex [$Fe_5(\mathbf{3})_5(PF_6)_{10}$] (**4**). The ^{1}H NMR spectrum of **4** revealed two sharp doublets at 8.56 (3-Ar*H*) and 8.08 (2-Ar*H*) ppm. These sharp peaks imply the presence of a single homogenous environment for all such groups; this is in contrast to the broadened or multiple signals expected for linear oligomers. The observed upfield shift for the doublet at 7.31 ppm (6,6″-tpy*H*s; $\Delta\delta = -1.49$ ppm) and downfield shift for the singlet at 9.39 ppm (3′,5′-tpy*H*s; $\Delta\delta = 0.46$ ppm) when compared to the absorptions for the uncomplexed starting material, confirm the symmetry associated with macrocyclization. Lastly, the pentagonal motif was established (ESI-MS) by the definitive signals for multiply-charged entities ranging from the +5 to the +10 charge states derived from the loss[28] of both PF_5^- and PF_6^-.

The self-assembled Ru(II) counterpart, [$Ru_5(\mathbf{3})_5(PF_6)_{10}$] (**5**), was prepared by treatment of a MeOH solution of monomer **3** with one equiv. of [$Ru(DMSO)_4(Cl)_2$] over 36 h at 50 °C. This method gave the desired pentameric complex possessing chloride counterions, which, after chromatography and counterion exchange (Cl^- to PF_6^-), afforded the pure macrocycle **5** (overall *ca.* 35%). The ^{1}H NMR spectrum of **5** exhibited a similar pattern to that of **4**, including the diagnostic shifts for the doublet at 7.54 ppm (6,6″-tpy*H*s; $\Delta\delta = -1.26$ ppm), and the singlet at 9.24 ppm (3′,5′-tpy*H*s; $\Delta\delta = 0.31$ ppm) in accord with ring-formation. The ESI-MS of **5** gave signals for the multiply-charged entities ranging from the +5 to the +8 charge states.

The [$Zn_5(\mathbf{3})_5(PF_6)_{10}$] complex (**6**) was generated by the reaction of a 1 : 1 mixture of ligand **3** with $Zn(BF_4)_2 \cdot 8H_2O$ in MeCN for 24 h at 80 °C affording a light yellow solid (35%). The absence of extraneous peaks in the ^{1}H NMR spectrum excluded the presence of starting materials, intermediates, and oligomeric materials. The diagnostic shifts of the doublets at 7.93 ppm (6,6″-tpy*H*s; $\Delta\delta = -0.87$ ppm), and the singlet at 9.17 ppm (3′,5′-tpy*H*s; $\Delta\delta = 0.24$ ppm) along with definitive ESI-MS data all support the structural assignment. COSY and HETCOR spectra of the bis(terpyridine)s and the corresponding self-assembled metallomacrocycles verified the peak assignments as well as the coupling patterns.

To elucidate and support the composition of the metallopentacycles, their UV-vis absorption spectra were measured (MeCN). From the absorption spectra of **4** and **5** in Fig. 1, each showed the lowest energy ligand-centered π–π^* transitions of the terpyridine moieties at ~310 and ~390 (shoulder) nm. While the metal–ligand charge-transfer (MLCT) transitions, which are derived from the promotion of an electron from the metal [Fe(II) or Ru(II)]-centered d-orbitals to unfilled ligand-centered π^* orbitals,[29] appeared at 573 and 504 nm respectively. In the case of the Zn(II) metallopentacycle **6**, the absorption bands at $\lambda_{max} = 240, 285, 316, 398$ nm originating from intra-ligand charge transfer (^{1}ILCT) are observed without MLCT peaks; the MLCT of Zn(II) to terpyridine can be excluded.[30]

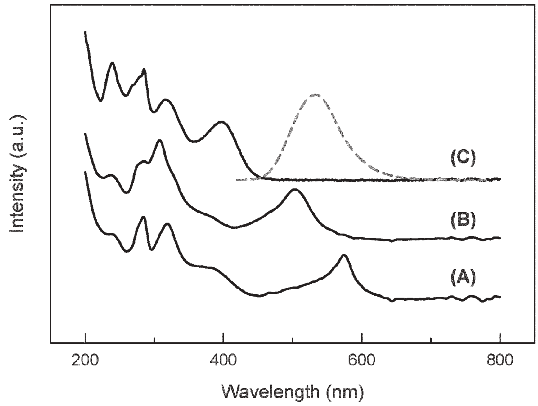

Fig. 1 UV-vis absorption (solid line) and emission (dashed line) spectra for metallopentacycles **4** (A); **5** (B); **6** (C).

Although the Ru(II) complexes of bipyridinyl ligands exhibit characteristic red luminescence from the ^{3}MLCT state, in the case of the Ru(II) complex with terpyridinyl ligands, this state is quenched by a low-lying ^{3}MC state and room temperature emission is not observed.[31] Whereas the Ru(II) metallopentacycle employing the carbazole moiety, which is a well known material for fluorescence, does not show fluorescence at 25 °C, the Zn(II) pentameric metallomacrocycle does show a strong yellow emission when excited with UV light (400 nm). The fluorescence of the Zn(II) pentamers in MeCN solution is shown in Fig. 1(C).

The electrochemical responses of the metallopentacycles were characterized by cyclic voltammetry (CV) experiments using 0.2 mM solutions of the relevant compound dissolved in DMF with 0.1 M Bu_4NBF_4 at 25 °C. Whereas pentamers **4** and **5** showed metal related redox waves for Fe(III)|Fe(II) and Ru(III)|Ru(II) pentamers at 0.49 and 0.57 V *vs.* Fc^+|Fc respectively, the electrochemical response of the Zn(III)|Zn(II) couple in pentamer **6** was not observed due to the completely filled d-shell of the Zn(II) complex.[32]

Cathodic scans of the pentamers **4**–**6** however, exhibited a set of reversible reduction waves that were followed by large current reduction peaks at more negative potentials, reflecting complex processes probably associated with decomposition. The first two reduction processes for **4** (Table 1) are related to metal reduction events,[22] and the only distinguishable peak in **5** is related to the monoelectronic reduction of one of the coordinated terpyridine ligands.[22] In the case of **6**, two closely positioned reversible waves are observed before current induced irreversible events take place. Based on the half-wave potential difference associated with these signals, terpyridine and metal-related processes are suggested as an explanation of the CV response,[21,22] instead of sequential terpyridine associated events.

From the CV responses at different scan rates (20–100 mV s^{-1}), values of the diffusion coefficients (*D*) of **4**–**6** were obtained (Table 1) using the Randles–Sevcik equation.[33] These values are nearly equal, further supporting the proposed structure of the three metallopentacycles.

Due to their light absorption properties, these materials were also studied as sensitizer materials for solar cell devices. Photovoltaic performance experiments using dye-covered nanocrystalline TiO_2 electrodes (prepared by dipping the semiconductor

Table 1 Electrochemical data of metallopentacycles, **4**–**6**, (0.2 mM) obtained in 0.1 M Bu_4NBF_4 in DMF at 25 °C using a glassy carbon working electrode; scan rate = 100 mV s^{-1}

	$E_{1/2}$(*vs.* Fc^+|Fc)/V				
Complex	L|L$^-$	M(I)|M(0)	M(II)|M(I)	M(III)|M(II)	$D/10^{-8}cm^2\ s^{-1}$
4	—	−1.837	−1.733	0.492	2.83
5	−1.843	—	—	0.574	2.1
6	−1.791	—	−1.929	—	3.1

Table 2 Photovoltaic performances and surface coverage values of ITO/TiO_2/pentamer/KI–I_2 electrolyte/graphite dye-sensitized cells measured using a polychromatic 1.5 mW cm^{-2} light source

Complex	$j_{sc}{}^{a}$/μA cm^{-2}	$V_{oc}{}^{b}$/mV	ff^{c} (%)	η^{d} (%)	$\Gamma/10^{-11e}$/mol cm^{-2}
4	90.4	250	32.6	0.49	3.03
5	300.4	290	26.3	1.53	5.49
6	137.6	269	29.5	0.73	6.22

[a] Short-circuit photocurrent density. [b] Open-circuit photovoltage. [c] Fill factor. [d] Photoconversion efficiency of the cell. [e] Surface coverage.

substrate in a 0.2 mM MeCN solution of each one of the metallopentacycles) properly fitted in a solar cell device,[34] were conducted using a polychromatic (1.5 mW cm^{-2}) incident light source and an electrolyte containing 0.3 M KI + 0.015 M I_2 dissolved in a 4 to 1 ratio of propylene and ethylene carbonate. The surface coverage (Γ) of each metallopentacycle on the TiO_2 electrode was calculated using UV-vis spectroscopy experiments as reported by Grätzel *et al.*[35] Notably, the values obtained (Table 2) are fairly close to each other, thus supporting the similar structure and dimensions of compounds **4–6**. Discharge experiments conducted with these devices also allowed the calculation of some of the values in Table 2.[34] Whereas the fill factor (*ff*) of the three electrodes studied here remains similar, the Ru(II) metallopentacycle showed the best results for the short circuit photocurrent (j_{sc}) as well as the open circuit photopotential (V_{oc}). Also, total photoconversion efficiency of the cell (η) using electromagnetic radiation spanning the visible region of the spectrum exhibited the highest value in the case of the Ru(II) pentamer **5**.

In summary, we have demonstrated the formation and characterization of a series of unique, self-assembled, metallopentacycles. Employing terpyridine–metal(II)–terpyridine connectivity, these complexes are stable and irreversible under the reaction conditions. The structures of these pentagonal architectures were characterized by means of ^{1}H and ^{13}C NMR, UV-vis spectroscopy, and mass spectroscopy. Preliminary studies of photoelectrochemical performance for the metallopentacycles demonstrated their potential for solar cell development. Further experiments are currently ongoing to investigate the electroluminescence behavior using LED devices.

The authors gratefully thank the National Science Foundation (DMR-041780, INT-0405242), the Air Force Office of Scientific Research (F49620-02-1-0428,02), the Ohio Board of Regents and the Mexican Council for Science and Technology (CONACyT), for financial support.

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