Porphyrin–carborane organometallic assemblies based on 1, 2-dicarba-*closo*-dodecaborane (12) ligands†

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Received (in Cambridge, UK) 2nd September 2005, Accepted 25th October 2005
First published as an Advance Article on the web 18th November 2005
DOI: 10.1039/b512416f

The assembly of soluble, air-stable, supramolecular structures {(Zn-TPyP)[Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_4$(THF)$_2$}‡ (2), {(Cu-TPyP)-[Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_4$(THF)$_2$} (3) and {(Zn-TPyP)[Cp*Ir-{$S_2C_2(B_{10}H_{10})$}]$_2$·6(CHCl$_3$)}$_n$ (4), based on metal-containing moieties [Cp*Ir{$S_2C_2(B_{10}H_{10})$}] (1) bridged by nitrogen-based organic spacers, are described.

Carboranyl-containing porphyrins are promising delivery drugs in Boron Neutron Capture Therapy (BNCT) for cancer due to their demonstrated remarkable chemical ability to localize in tumors and their high boron content.[1] Moreover, porphyrins have the capability of complexing with various metals such as Zn, Ni, Cu, *etc.*,[2] and this provides an opportunity to determine the microdistribution of such boronated porphyrins using their stable chelates with radioactive metals.[3] Porphyrin–carborane compounds containing up to four or eight carboron clusters attached to the porphyrin macrocycle have been synthesized.[4] Some of them have been evaluated in cellular and animal studies. The results from these investigations showed that this type of compound can selectively deliver therapeutic concentrations of boron to tumor cells with low toxicity.[5]

Ourselves and Ko *et al.* have already reported on the synthesis of the 16 electron "pseudo-aromatic" half-sandwich complexes [Cp*M{$E_2C_2(B_{10}H_{10})$}] (M = Co, Rh, Ir; E = S, Se).[6] In recent publications from our laboratory, we have suggested that these species may be promising for further transformations, owing to their electron deficiency at the metal center.[7] This has allowed the construction of polycarborane molecular architectures that take advantage of this attribute, such as addition reactions at the metal center.[6] For example, we have employed the Cp*Ir[$S_2C_2(B_{10}H_{10})$] organometallic cluster as a unit in star shaped species.[8] Our general interest in such kinds of clusters prompted an investigation of whether these units were capable of acting as building blocks in some porphyrin–carborane structures.

Herein, we describe the assembly of soluble, air-stable, supramolecular structures based on the metal-containing moieties [Cp*Ir{$S_2C_2(B_{10}H_{10})$}] (1), bridged by nitrogen-based organic spacers.

Treatment of Zn tetra(4-pyridyl)porphyrin (Zn-TPyP) with four equivalents of **1** in THF yields the complex {(Zn-TPyP)[Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_4$(THF)$_2$} (**2**) in 76% yield.§ As shown in Fig. 1,¶ **2** consists of four [Cp*Ir{$S_2C_2(B_{10}H_{10})$}] units which bond to the nitrogen atoms of Zn-TPyP. The dihedral angle along the S···S vector in the iridadithiolate metallocycle (IrS$_2$C$_2$) is about 175°, compared to 180° in **1**.[6e] An interesting feature of this solid state structure is that the [Cp*Ir{$S_2C_2(B_{10}H_{10})$}] units adopt a tail-to-tail contact mode, not a head-to-tail mode, in spite of the large steric repulsion between the two carborane ligands. Two THF units form weak coordinative interactions through the oxygen atoms to the Zn atom at the center of the complex (Zn–O = 2.436(19) Å). Pairs of these weak interactions result in the formation of centrosymmeterically-related tetramers.

The analogous reaction of Cu tetra(4-pyridyl)porphyrin (Cu-TPyP) with four equivalents of **1** in THF afforded the compound {(Cu-TPyP)[Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_4$(THF)$_2$} (**3**), which was crystallized and its structure determined (Fig. 2). Much weaker interactions exist between the O and Cu atoms (Cu–O = 2.81(3) Å). The molecular structure of **3** is similar to **2**, this being the first definitive crystallographic investigation of Cu–porphyrin–carborane molecules.

Following the successful generation of **2**, the reaction of Zn-TPyP with two equivalents of **1** in CHCl$_3$ at room temperature afforded polymeric{(Zn-TPyP)[Cp*Ir{$S_2C_2(B_{10}H_{10})$}]$_2$·6(CHCl$_3$)}$_n$ (**4**) in 62% yield. This compound is readily soluble in CHCl$_3$, THF and other common polar organic solvents. X-ray crystallographic analyses were performed, and the results reveal that there are layered structures with similar building blocks of the same packing sequence. The coordination geometry around each zinc ion is

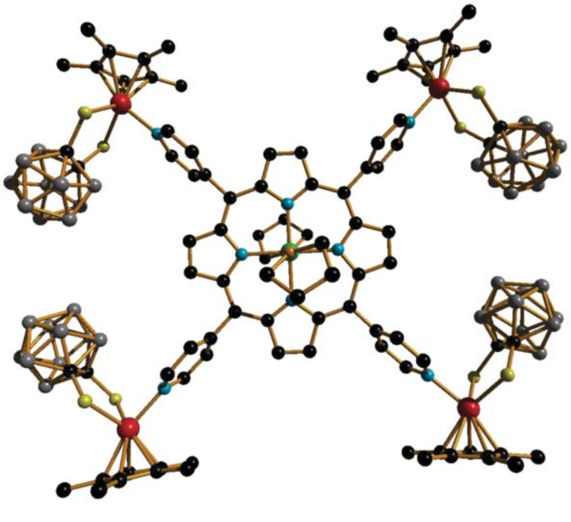

Fig. 1 Molecular structure of **2**. Ir, Zn, S, N, C, B and O atoms are represented by red, green, yellow, blue, black, grey and brown spheres, respectively. H atoms have been omitted for clarity.

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† Electronic Supplementary Information (ESI) available: Experimental details and crystal structure determination. See DOI: 10.1039/b512416f

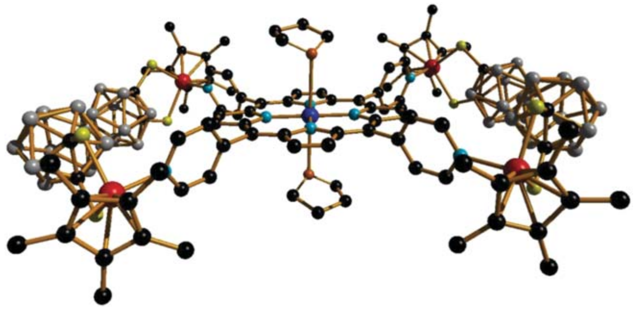
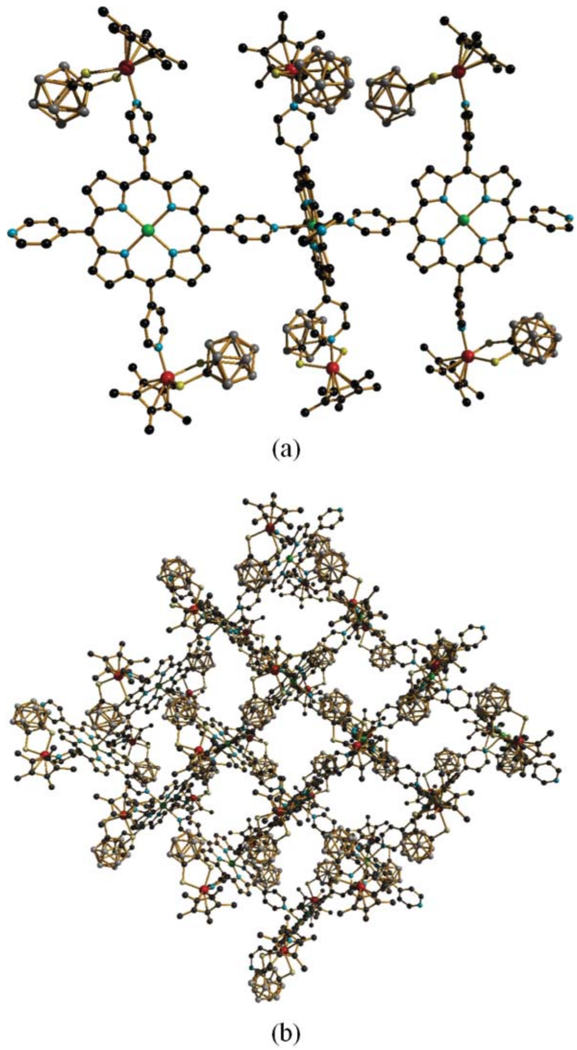


Fig. 2 Molecular structure of **3**. Ir, Cu, S, N, C, B and O atoms are represented by red, blue, yellow, blue, black, grey and brown spheres, respectively. H atoms have been omitted for clarity.



(a)

(b)

Fig. 3 View of the structure of **4**. (a) Inter-porphyrin four-fold coordination in directions parallel and roughly perpendicular to the porphyrin plane. (b) Stereoview of the interlinked polymeric patterns of **4**. Ir, Zn, S, N, C and B atoms are represented by red, green, yellow, blue, black and grey spheres, respectively. $CHCl_3$ molecules and H atoms have been omitted for clarity

octahedral (Fig. 3a). The equatorial positions located in the porphyrin plane are occupied by four N donor atoms from four pyrrole moieties of the porphine ligand (Zn–N = 2.048(7)–2.062(7) Å). The axial positions are occupied by two nitrogen atoms of pyridines from the two adjacent porphine molecules with identical Zn–N bond lengths of 2.489(9) Å. In the same layer, all the zinc atoms are located in the same plane and form a tessellated geometry with square edge dimensions of 10.2 × 10.2 Å. All neighboring porphyrins are mutually perpendicular to each other. Such an arrangement gives rise to a two-dimensional paddle-wheel-like pattern with a "paddle" depth of 19.6 Å (Ir···Ir). Two $[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]$ organometallic clusters are located at the end of the "paddle". As illustrated in Fig. 3b, there are channels running along the a-axis. Overall, the free voids form 42.9% of the cell volume, omitting solvent molecules and hydrogen atoms.[9] Most of this solvent appears to be lost when the sample is exposed to the atmosphere. Thermal gravimetric analysis (TGA) reveals a weight of loss of 10.6% in the range 25–100 °C. No further weight loss is observed upon heating up to approximately 260 °C, and at this point the compound starts to decompose.

Compared with normal porphyrin framework solids,[10] the introduction of carborane ligands provides a more abundant set of structural and functional properties. The UV-vis spectrum of **4** shows four absorption bands in its optical spectrum. As with its Zn–porphyrin precursors, **4** has the Soret band at 420 nm. Photochemical and photophysical investigations of **2** and **4** reveal that the strong luminescence of the zinc porphyrin is completely quenched, which may due to an intramolecular electron transfer between the porphyrin site and the binding cluster **1** in the photoexcited singlet state.[11]

In conclusion, the present work represents an example where three unprecedented porphyrin–carborane organometallic assemblies are based on a combination of **1**, 2-dicarba-*closo*-dodecaborane (12) and porphyrin ligands. The design strategies reported here lead to multi-chormophoric arrays of defined rigidity, dimensionality and selectivity. Our further work will explore the behavior of **2**, **3** and **4**, as well as investigate the coordination chemistry of **1** with other metalloporphyrins.

Financial support by the National Science Foundation of China for Distinguished Young Scholars (20421303, 20531020, 20441003) and by the Doctoral Fund of the Education Ministry of China (no. 20020246011) is gratefully acknowledged.

Notes and references

‡ Abbreviation: Zn-TPyP = Zn tetra(4-pyridyl)porphyrin.

§ All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were purified by standard methods prior to use. $Cp^*IrS_2[C_2(B_{10}H_{10})]$ was prepared according to reported procedures.[6b] *Synthesis of* **2**: A mixture of **1** (0.4 mmol, 213 mg) and Zn-TPyP (0.1 mmol, 68 mg) in THF was stirred at room temperature for 36 h. The solvent was removed under reduced pressure, producing a deep red solid. After extraction with toluene, the residue solids were recrystallized from THF/hexane to give red crystals of **2** (225 mg, 76%). Elemental analysis calc. for $C_{96}H_{132}B_{40}N_8O_2S_8Ir_4Zn$: C, 39.04; H, 4.51; N, 3.79. Found: C, 38.87; H, 4.38; N, 3.69%. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 1.75$ and 3.73 (m, THF, 8 H), 1.83 (s, Cp*, 60 H), 8.21 (d, 3,5-pyridyl, 8 H), 8.85 (m, pyrrole, 8 H) and 9.01 (d, 2,6-pyridyl, 8 H). ^{11}B NMR (160 MHz, $CDCl_3$): −10.5, −9.0, −8.2 and −6.5. IR (KBr disk): $v = 2572$ ($v_{B\text{–}H}$), 1595, 1408, 995 and 793 cm^{-1}. UV-vis ($CHCl_3$): 605, 562, 418 and 308 nm. *Synthesis of* **3**: The procedure is similar to **2**. A mixture of **1** (0.4 mmol, 213 mg) and Cu-TPyP (0.1 mmol, 67 mg) in THF was stirred at room temperature for 36 h. The solvent was removed under reduced pressure, producing a deep red solid. After extraction with toluene, the residue solids were recrystallized from THF/hexane to give red crystals of **3** (245 mg, 83%). Elemental analysis calc. for $C_{96}H_{132}B_{40}N_8O_2S_8Ir_4Cu$: C, 39.07; H, 4.51; N, 3.80. Found: C, 39.01; H, 4.51; N, 3.72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.72 and 3.77 (br, THF, 8 H), 1.81 (s, Cp*, 60 H), 8.50 (br, pyridyl, 16 H) and 8.79 (br, pyrrole, 8 H). ^{11}B NMR (160 MHz, $CDCl_3$): −112, −9.6, −8.1 and −5.9. IR (KBr disk): v = 2565 (v_{B-H}), 1588, 1421, 989 and 798 cm^{-1}. *Synthesis of* **4**: A mixture of **1** (0.2 mmol, 106 mg) and Zn-TPyP (0.1 mmol, 68 mg) in $CHCl_3$ was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, producing a deep red solid. After extraction with toluene, the residue solids were recrystallized from $CHCl_3$/hexane to give red crystals of **4** (153 mg, 62%). Elemental analysis calc. for $C_{64}H_{74}B_{20}N_8S_4Ir_2Zn\cdot 6CHCl_3$: C, 34.10; H, 3.27; N, 4.54. Found: C, 33.87; H, 3.18; N, 4.39%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (br, 3,5-pyridyl, 4 H, Zn), 1.75 (s, Cp*, 15 H), 1.83 (s, Cp*, 15 H), 2.35 (d, 3,5-pyridyl, 4 H, Ir), 3.74 (d, 2,6-pyridyl, 4 H, Zn), 5.01 (br, 2,6-pyridyl, 4 H, Ir) and 6.97 (m, pyrrole, 8 H). ^{11}B NMR (160 MHz, $CDCl_3$): −10.3, −9.2, −8.2 and −6.6. IR (KBr disk): v = 2582, 2563 (v_{B-H}), 1589, 1402, 995 and 788 cm^{-1}. UV-vis ($CHCl_3$): 595, 555, 420 and 319 nm.

¶ *Crystal data for* **2**: [Zn-TPyP($Cp^*IrS_2C_2B_{10}H_{10})_4(THF)_2$], $C_{88}H_{124}B_{40}Ir_4N_8O_2S_8Zn\cdot 2C_4H_8O$, M = 2961.21, monoclinic, space group $P2_1/c$, a = 13.785(6), b = 27.191(13), c = 20.552(10) Å, β = 104.947(7)°, V = 7443(6) Å^3, Z = 2, D_{calc} = 1.318 g cm^{-3}. The final R factor was 0.0863 for 6830 reflections with $I_o > 2\sigma(I_o)$, Rw = 0.2535 for all data, 13112 reflections, GOF = 1.025, largest differential peak and hole were 2.511 and −3.063 e Å^{-3}, respectively. *Crystal data for* **3**: [Cu-TPyP($Cp^*IrS_2C_2B_{10}H_{10})_4(THF)_2$], $C_{88}H_{124}B_{40}Ir_4N_8O_2S_8Cu\cdot 2C_4H_8O$, M = 2959.38, monoclinic, space group $P2_1/c$, a = 13.822(5), b = 27.187(9), c = 20.635(7) Å, β = 105.145(5)°, V = 7485(4) Å^3, Z = 2, D_{calc} = 1.310 g cm^{-3}. The final R factor was 0.0799 for 6830 reflections with $I_o > 2\sigma(I_o)$, Rw = 0.2256 for all data, 13194 reflections, GOF = 1.193, largest differential peak and hole were 2.585 and −2.401 e Å^{-3}, respectively. *Crystal data for* **4**: $\{(Zn\text{-}TPyP)[Cp^*Ir\{S_2C_2(B_{10}H_{10})\}]_2(CHCl_3)_5\}_n$, $C_{64}H_{74}B_{20}N_8S_4Ir_2Zn\cdot 5CHCl_3$, M = 2346.36, monoclinic, $P2_1/c$, a = 24.852(8), b = 13.702(5), c = 15.216(5) Å, β = 103.958(5)°, V = 5029(3) Å^3, Z = 2, D_{calc} = 1.550 g cm^{-3}. The final R factor was 0.0709 for 5403 reflections with $I_o > 2\sigma(I_o)$, Rw = 0.2016 for all data, 8866 reflections, GOF = 1.045, largest differential peak and hole were 3.047 and −1.238 e Å^{-3}, respectively. All data were measured at 293 K on a Bruker SMART APEX CCD diffractometer ($\lambda_{Mo\text{-}K\alpha}$ = 0.71073 Å) using a graphite monochromator. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program.[12] The THF and $CHCl_3$ molecules in **2** and **4** were refined with isotropic temperature factors and restrained to give a reasonable geometry. CCDC 282857 (**2**), 282858 (**3**) and 282859 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512416f

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