Supplementary Material (ESI) for Chemical Communications

Supporting information (experimental details and crystal-structure determination) belonging to the publication:

Structural characterization of porphyrin-carborane organometallic assemblies based on 1, 2-dicarba-*closo*-dodecaborane (12) ligands

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General Considerations. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents, THF, hexane were dried over sodium benzophenone ketyl and freshly distilled prior to use. $CHCl_3$ were refluxed over CaH_2 for several days and distilled immediately prior to use. All chemicals were purchased from either Aldrich or Sinopharm. Co. and used as received unless otherwise noted. $Cp^*Ir[S_2C_2(B_{10}H_{10})]_2$ were prepared according to the reported procedures.[5] Infrared spectra were recorded on a Nicolet AVATAR-360IR spectrometer, whereas $^1H\{500MHz\}$, $^{11}B(160MHz)$ - NMR spectra were obtained on a Bruker DMX-500 spectrophotometer in $CDCl_3$, respectively. Elemental analyses were performed on Elementar vario EI Analyzer. TGA were carried out on a Perkin Elemer TGA-7 analyser. UV/vis spectra were obtained on a HP 8453 spectrophotometer in $CDCl_3$ and fluorescence spectra were performed on a Varian Cary Eclipse spectrophotometer.

Synthesis for **2**: Stirring a mixture of **1** (0.4mmol, 213 mg) and Zn-TpyP(0.1 mmol, 68 mg) in THF at room temperature for 36h. The solvent was removed under reduced pressure, produced deep red solid. After extracted with toluene, the residue solids were recrystallized from THF / hexane to give red crystals of **2**(225 mg, 76%). Elemental analysis calcd 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, $CDCl_3$): 1.83 (s, Cp*, 60H), 1.75, 3.73 (m, THF, 8H), 8.21 (d, 3, 5-pyridyl, 8H), 9.01 (d, 2, 6-pyridyl, 8H), 8.85 (m, pyrrole, 8H); ^{11}B NMR (160 MHz, $CDCl_3$): -6.5, -8.2, -9.0, -10.5. IR (KBr disk): $\nu = 2572cm^{-1}(\nu_{B-H})$, 1595, 1408, 995, $793cm^{-1}$. UV-vis($CHCl_3$): 308, 418, 562, 605nm.

Synthesis for **3**: Stirring a mixture of **1** (0.4mmol, 213 mg) and Cu-TPyP(0.1 mmol, 68 mg) in THF at room temperature for 36h. The solvent was removed under reduced pressure, produced deep red solid. After extracted with toluene, the residue solids were recrystallized from THF / hexane to give red crystals of **3**(245 mg, 83%). Elemental analysis calcd 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, $CDCl_3$): 1.81 (s, Cp*, 60H), 1.72, 3.69 (br, THF, 8H), 8.50 (br, pyridyl, 16H), 8.79 (br, pyrrole, 8H); ^{11}B NMR (160 MHz, $CDCl_3$): -5.9, -8.1, -9.6, -112. IR (KBr disk): ν = 2565cm^{-1}(ν_{B-H}), 1588, 1421, 989, 798cm^{-1}.

Synthesis for **4**: Stirring a mixture of **1** (0.2mmol, 106 mg) and Zn-TPyP(0.1 mmol, 68 mg) in $CHCl_3$ at room temperature for 48h. The solvent was removed under reduced pressure, produced deep red solid. After extracted with toluene, the residue solids were recrystallized from $CHCl_3$ / hexane to give red crystals of **3** (153 mg, 62%). Elemental analysis calcd 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, $CDCl_3$): 1.83 (s, Cp*, 15H), 1.75 (s, Cp*, 15H), 1,43 (br, 3,5-pyridyl, 4H, Zn), 3.74 (d, 2,6-pyridyl, 4H, Zn), 2.35 (d, 3, 5-pyridyl, 4H, Ir), 5.01 (br, 2,6-pyridyl, 4H, Ir), 6.97 (m, pyrrole, 8H) ^{11}B NMR (160 MHz, $CDCl_3$): -6.6, -8.2, -9.2, -10.3. IR (KBr disk): ν = 2582, 2563 cm^{-1}(ν_{B-H}), 1589, 1402, 995, 788cm^{-1}. UV-vis($CHCl_3$): 319, 420, 555, 595nm.

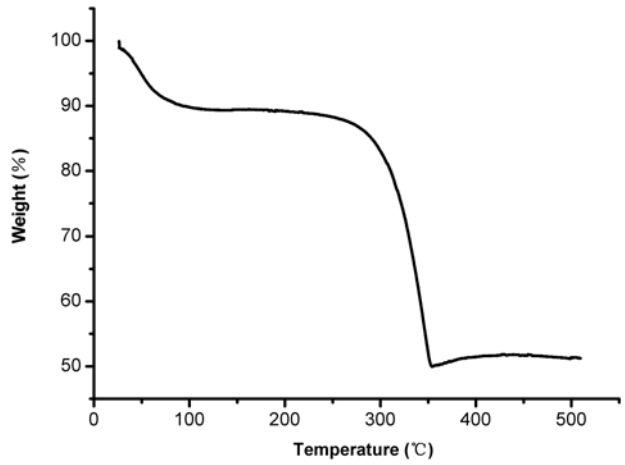


Figure **S1**. Thermal gravimetric analyses (TGA) spectra of compound **4**

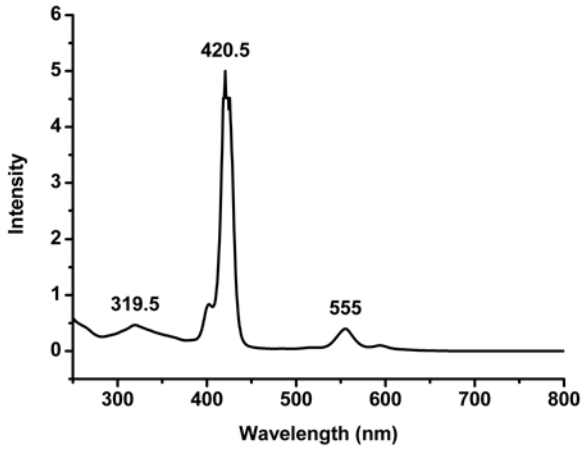
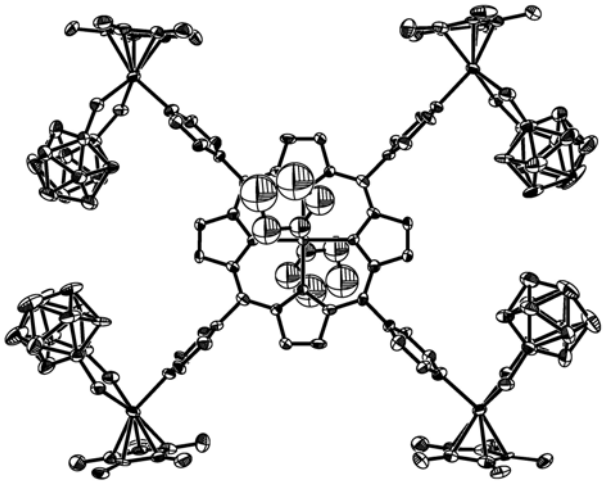


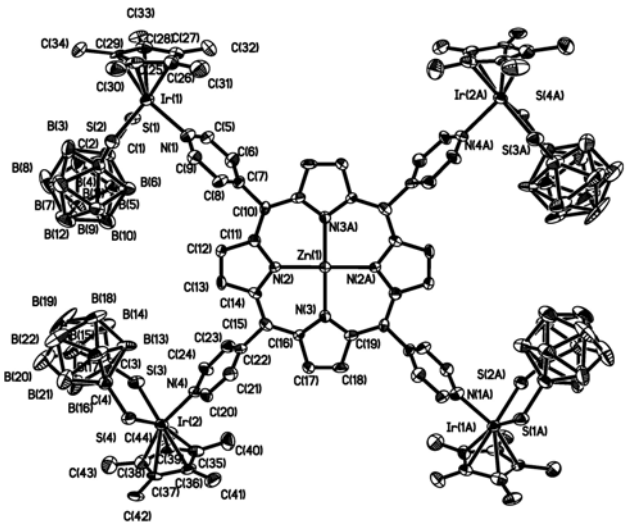
Figure **S2**. UV/ vis spectra of compound **4**

Crystal Structure Determination of **2**, **3**, **4**

Crystallographic data for **2, 3** and **4** are summarized in Table S1-S3. Each crystal was mounted on glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated MoKα radiation (λ = 0.71073Å) at 293K. Empirical absorption corrections were applied using the program SADABS. The structures were solved by directed methods (SHELXS-97, G. M. Sheldrick, SHELXL-97, Universität Göttingen 1997) and refined on F^2 by full-matrix least squares (SHELX-97, G. M. Sheldrick, SHELXL-97, Universität Göttingen 1997) using all unique data. All non-hydrogen atoms were refined anisotropically, expect for the THF molecule in 2, and $CHCl_3$ molecule in 4. The hydrogen atoms were included in the calculated positions. Using the PLATON program (A. L. Spek, 1990) program we estimate overall free voids are 42.9% of the cell volume.



(a)



(b)

Figure S3. (a) An ORTEP representation of **2** with labeling scheme and 30% probability. All hydrogen atoms are omitted for clarity. (b) An ORTEP representation of **2** with labeling scheme and 30% probability. THF molecular and all hydrogen atoms are omitted for clarity.

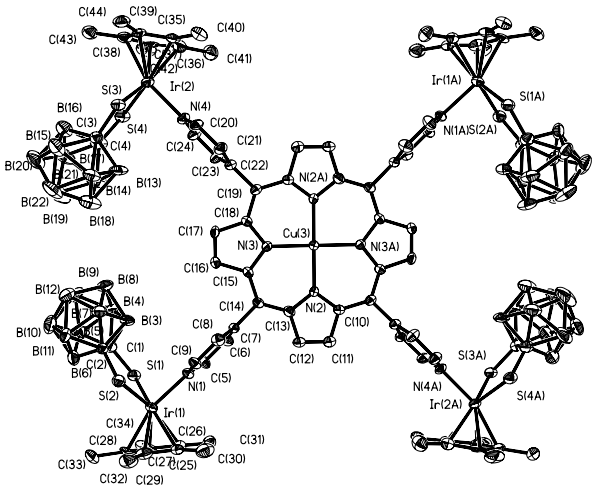


Figure S4. An ORTEP representation of **3** with labeling scheme and 30% probability. THF molecular and all hydrogen atoms are omitted for clarity.

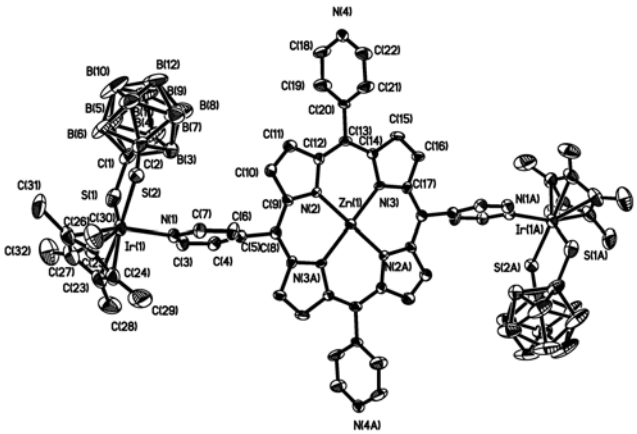


Figure S5. An ORTEP representation of a section of the polymeric **4** with labeling scheme and 30% probability. All hydrogen atoms are omitted for clarity.