Supplementary Material (ESI) for Chemical Communications

Supporting information

(experimental details, crystal-structure determination)

belonging to the publication

Route to Multicluster Containing Ancillary *ortho*-Carborane-1,2-Dithiolato Ligands

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General Considerations. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents, hexane, benzene and ethyl ether were dried over sodium benzophenone ketyl and freshly distilled prior to use. CH_2Cl_2, 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.[1] 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. UV/vis spectra were obtained on a HP 8453 spectrophotometer in $CDCl_3$ and fluorescence spectra were performed on a Varian Cary Eclipse spectrophotometer.

Crystal Structure Determinations of 2, 3, 5

Crystallographic data for 2, 3 and 5 are summarized in Table S1, S2, S3. Each crystal was mounted on glass fiber or sealed in glass tube. Crystallographic measurements were made on a Bruker Smart Apex 1000 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. The hydrogen atoms were included in the calculated positions.

Table S1. Crystal data and structure refinement for **2**

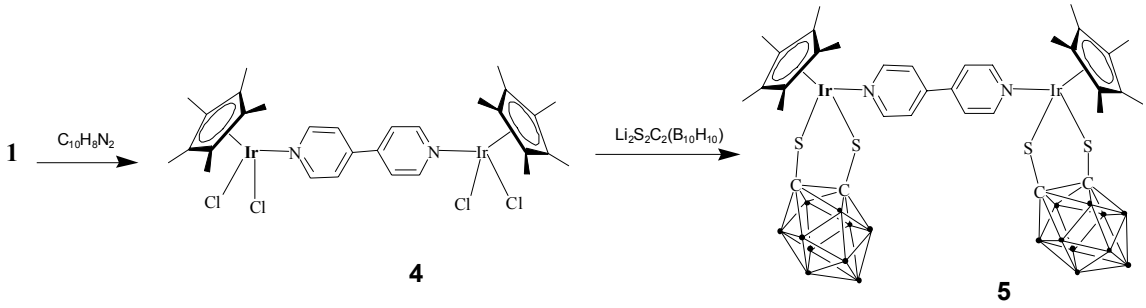
Empirical formula	$C_{48}H_{57}Cl_6Ir_3N_6$
Formula weight	1507.30
Crystal system	Trigonal
space group	R3m
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 24.096(7)Å α= 90º b = 24.096(7)Å β= 90º c = 7.479(3) Å γ = 120 º
Volume	3761(2) Å ^{3}
Z	3
Calculated density	1.997 Mg/m^3
Absorption coefficient	8.302 mm^{-1}
F(000)	2160
Crystal size	0.10 × 0.05 × 0.05 mm
Theta range for data collection	1.69 to 25.01 º
Limiting indices	-28<=h<=28, -24<=k<=28, -8<=l<=8
Reflections collected / unique	5271 / 1572 [R(int) = 0.1157]
Completeness to theta = 25.01	100.0 %
Absorption correction	Multi-scan
Max. and min. transmission	0.6816 and 0.4907
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1572 / 25/ 106
Goodness-of-fit on F^2	0.900
Final R indices [I>2sigma(I)]	R1 = 0.0535, wR2 = 0.0975
R indices (all data)	R1 = 0.0866, wR2 = 0.1041
Largest diff. peak and hole	1.914 and -0.899e·A^{-3}

Table S2. Crystal data and structure refinement for **3**

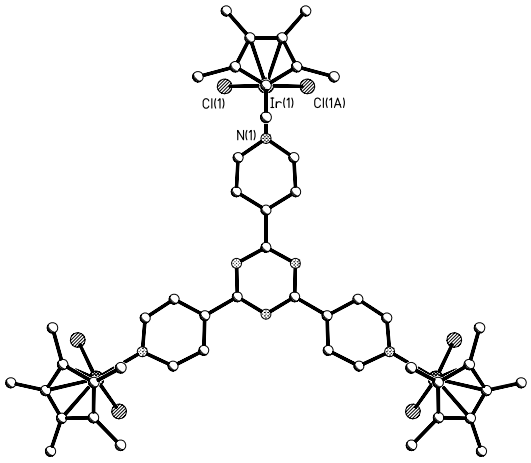
Empirical formula	$C_{54}H_{87}B_{30}Ir_3N_6S_6$
Formula weight	1913.56
Crystal system	Tetragonal
space group	P4(2)/ncm
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 35.258(6) Å α = 90 º b = 35.258(6) Å β = 90 º c = 16.150(4) Å γ = 90 º
Volume	20076(6) $Å^3$
Z	8
Calculated density	1.266 Mg/m^3
Absorption coefficient	4.124 mm^{-1}
F(000)	7440
Crystal size	0.20 × 0.10 × 0.08 mm
Theta range for data collection	0.82 to 25.01 º
Limiting indices	-41<=h<=41, -41<=k<=41, -15<=l<=19
Reflections collected / unique	81696 / 9083 [R(int) = 0.1202]
Completeness to theta = 25.01	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7338 and 0.4926
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9083 / 18 / 474
Goodness-of-fit on F^2	1.151
Final R indices [I>2sigma(I)]	R1 = 0.0704, wR_2 = 0.1930
R indices (all data)	R1 = 0.1090, wR_2 = 0.2177
Largest diff. peak and hole	1.267 and -0.851 $e·Å^{-3}$

Table S1. Crystal data and structure refinement for **5**

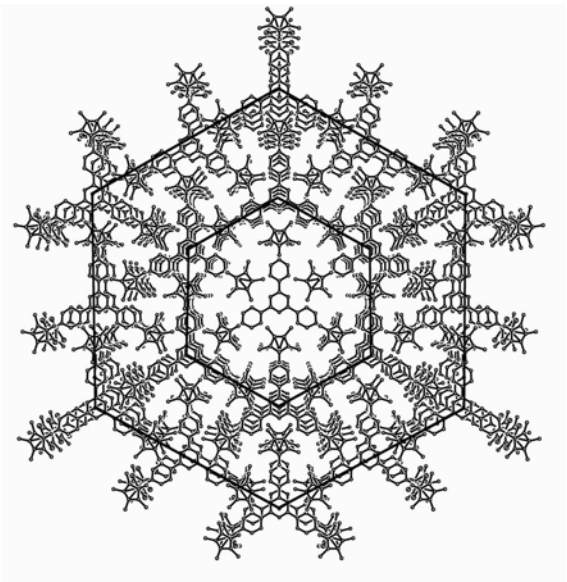
Empirical formula	$C_{36}H_{62}B_{20}Cl_4Ir_2N_2S_4$
Formula weight	1393.52
Crystal system	Triclinic
space group	P-1
Temperature	293(2) K
Wavelength	0.71073 Å
Unit cell dimensions	a = 10.223(2) Å α = 101.052(2)º b = 11.336(2) Å β = 109.107(3)º c = 13.688(3) Å γ = 94.826(3) º
Volume	1452.6(5) $Å^3$
Z	1
Calculated density	1.593 Mg/m^3
Absorption coefficient	4.933 mm^{-1}
F(000)	678
Crystal size	0.50 × 0.20 × 0.10 mm
Theta range for data collection	1.62 to 25.01 º
Limiting indices	-9<=h<=12, -13<=k<=13, -16<=l<=16
Reflections collected / unique	6144 / 5042 [R(int) = 0.0154]
Completeness to theta = 25.01	98.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6382 and 0.1917
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5042 / 18 / 317
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0904
R indices (all data)	R1 = 0.0346, wR2 = 0.0920
Largest diff. peak and hole	1.480 and -1.329 $e·Å^{-3}$



Scheme S1 Prepare of **4**, **5**



(a)



(b)

Fig. S1 (a) Molecular structure of **2**. (b) Crystal packing representation of **2**

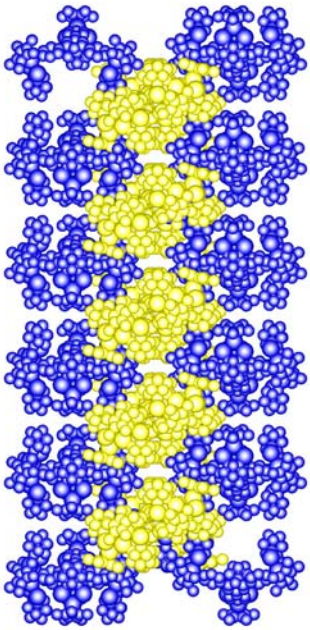


Fig. S2 Crystal structures of **3**. viewed along the *c* axis.

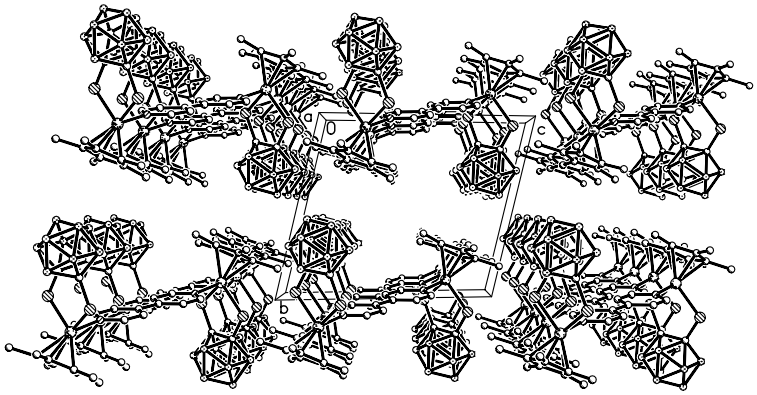
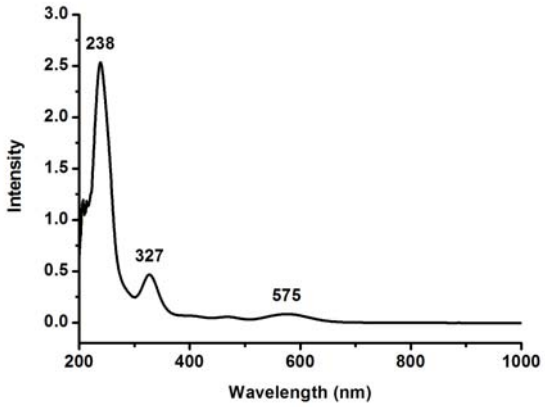
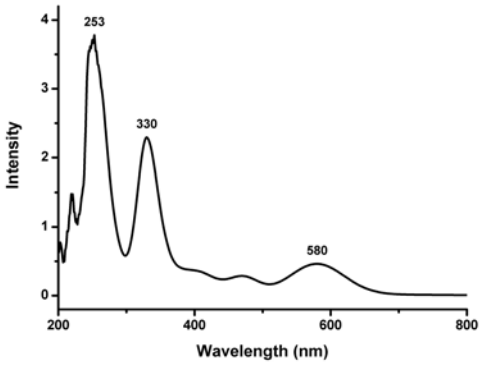


Fig. S3 Crystal packing representation of **5.**



(a)



(b)

Fig. S5 (a) Absorption spectra of **3** in CH_2Cl_2 (1.0×10^{-3} mmol), (b) absorption spectra of **5** in CH_2Cl_2 (1.5×10^{-3} mmol)

Reference

1 (a) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *J. Organomet. Chem,*, 1999, **587**, 252; (b) M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, *Eur. J. Inorg. Chem.*, 1999, 873; (c) X.-F. Hou, X.-C. Wang; J.-Q. Wang; G.-X. Jin, *J. Organomet .Chem.*, 2004, **689**, 2228; (d) Q. Kong, G.-X. Jin, S.-Y. Cai, L.-H. Weng, *Chin. Sci. Bull.*, 2003, **48**, 1733.