A Low Band Gap Iron Sulfide Hybrid Semiconductor with Unique 2D [Fe₁₆S₂₀]⁸⁻ Layer and Reduced Thermal Conductivity

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Supporting Information

S1. Sample Preparation

Fe(III)(en)₃Cl₃ compound for X-ray absorption analysis was prepared by adding slowly and stirring anhydrous Fe(III)Cl₃(1.0 mmol, anhydrous, 98%, Stream) dissolved in 6.0 ml absolute ethanol, followed by 1ml ethylenediamine (8.0 ml, 99%, Acros Organics) in a teflon autoclave. The reaction was heated at 50°C in furnace for 6 hours and the pale green-colored solids was filtered, washed with ether, and dried under Ar protection. The dry solids are stable for weeks in glove-box under N₂.

S2. Structure Characterization, Optical Absorption and Thermogravimetric (TG) Analysis

Single crystal X-ray diffraction was carried out on a Bruker-AXS smart APEX CCD diffractometer with graphite-monochromated MoK α Radiation ($\lambda = 0.71073$ Å). All calculations were performed using the SHELXL-97 crystallographic software package. The data were collected at a temperature 100(2) K to a maximum θ value of 23.35°. Of a total of 39073 reflections collected, 8318 were independent (Rint = 0.2169). The structure was solved by direct methods and expanded using Fourier techniques. The final cycle of full matrix least-squares refinement on F^2 was based on 8318 observed reflections as well as 596 variable parameters and converged at R1 = 0.0690. The unit cell parameters, along with data collection and refinement details, are listed in Table S1. Atomic coordinates and equivalent isotropic temperature factors are listed in Tables S2.

The phase purity of each powder sample was analyzed by powder X-ray diffraction using a Rigaku D/M-2200T automated diffraction system (Ultima+). The measurements

were made with a 2 θ range between 3 and 70° at the operation power of 40 KV/40 mA. A PXRD pattern of as-made sample of [Fe(en)₃]₂·[Fe₁₆S₂₀]·enH₂ is given in Figure S1.



Figure S1. Powder X-ray patterns of as-made sample (red) and post-TGA sample (blue, after heating at 160°C for an hour).

The band gap of samples was assessed by optical diffuse reflectance experiments at room temperature. All measurements were made on a Shimadzu UV-3101PC double beam, double monochromated spectrophotometer in the range of 200-2000 nm. Thermogravimetric analysis (TGA) was carried out on a TA Instrument Q50 Thermogravimetric analyzer under nitrogen. The TG profile of a powder sample of $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$ is shown in Figure S2. The PXRD pattern of the same sample after TGA (RT-160°C) is also shown in Figure S1. Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2010



Figure S2. TGA profile for a powder sample of $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$ (RT-160°C and kept at 160°C for about an hour. The small weight loss was due to the solvent on the sample surface.



Figure S3. Powder X-ray pattern of a post-TGA sample of $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$ (after heating to 500°C (black lines: Fe_9S_{10}).

S3. X-ray Absorption Analysis (XAS)

The Fe-*K* X-ray absorption analysis (XAS) measurements were performed in the fluorescence mode on crystal samples on beamline X19A (Upton, New York USA) at the Brookhaven National Synchrotron Light Source. A double crystal Si (111)

monochromator was used. The incident and transmitted beam intensities were measured with ionization chambers and the fluorescence intensities with Canberra PIPS detectors. The absolute energy calibration was set to the elemental Fe-*K* edge (first inflection point) 7.112 KeV. The simultaneous standard technique was used in which a standard sample (FeO in this case) is placed after the second ionization chamber and a simultaneous fluorescence spectrum is collected for the standard. This allows a relative energy calibration between spectra of better than 0.05 eV.

S4. Heat Capacity, Thermal Diffusivity, and Thermal Conductivity

Specific Heat Measurement

Specific heat measurements were made in the temperature range 25°C to 95° using Netzsch DSC 204 F1 Phoenix. The sample (12 mg) was cooled to 9°C, held at 9°C for 6 minutes and then heated up to 95°C. From the ratio of the heat flow to the sample to the heat flow to a standard sapphire sample (of known specific heat) taken through the same temperature program, the specific heat of the sample is determined. Figure S3 shows the specific heat of the sample.

Thermal Conductivity

Thermal conductivity κ of the samples is measured indirectly by measuring the thermal diffusivity α , specific heat C_P and density ρ of the samples and using the relation:

$$\kappa = \rho \alpha C_{P}$$

The diffusivity and specific heat measurements are made in the temperature range 25°C to 90°C. Thermal diffusivity measurements were made on circular pellets of diameter 10

mm and thickness 0.7-1.0 mm. The pellets were made by cold-pressing the sample powders under 2500 atm pressure and annealing in vacuum at 70°C for 5-6 hours. The thermal diffusivity is measured by using the laser flash method using the Netzsch LFA 457 instrument, where the bottom face of the sample receives a pulse of radiant energy coming from a laser. The thermal diffusivity value is computed from the resulting temperature response on the opposite (top) face of the sample. The specific heat capacity C_P and thermal diffusivity α of a [Fe(en)₃]₂·[Fe₁₆S₂₀]·enH₂ pellet sample are plotted in Figure S4 and S5, respectively.



Figure S4. Specific heat capacity of a hybrid $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$ pellet sample.



Figure S5. Thermal diffusivity of the hybrid $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$ sample.

Identification code	JR1-14D			
Empirical formula	C14 H58 Fe18 N14 S20	C14 H58 Fe18 N14 S20		
Formula weight	2069.24			
Temperature	100(2) K			
Wavelength	0.71073 Å			
Crystal system	Monoclinic			
Space group	P2(1)/c			
Unit cell dimensions	a = 8.3836(15) Å	α= 90°.		
	b = 33.209(6) Å	$\beta = 90.314(4)^{\circ}.$		
	c = 20.450(4) Å	$\gamma = 90^{\circ}$.		
Volume	5693.5(17) Å ³			
Z	4			
Density (calculated)	2.414 Mg/m ³	2.414 Mg/m ³		
Absorption coefficient	5.194 mm ⁻¹	5.194 mm ⁻¹		
F(000)	4112	4112		
Crystal size	.31 x .04 x .005 mm ³	.31 x .04 x .005 mm ³		
Theta range for data collection	2.08 to 23.34°.	2.08 to 23.34°.		
Index ranges	-9<=h<=9, -36<=k<=37	-9<=h<=9, -36<=k<=37, -20<=l<=22		
Reflections collected	19953	19953		
Independent reflections	7844 [R(int) = 0.0946]	7844 [R(int) = 0.0946]		
Completeness to theta = 23.34°	94.7 %	94.7 %		
Absorption correction	Semi-empirical from eq	Semi-empirical from equivalents		
Max. and min. transmission	0.427 and 0.338	0.427 and 0.338		
Refinement method	Full-matrix least-square	Full-matrix least-squares on F ²		
Data / restraints / parameters	7844 / 923 / 596	7844 / 923 / 596		
Goodness-of-fit on F ²	1.060	1.060		
Final R indices [I>2sigma(I)]	R1 = 0.1089, wR2 = 0.1	R1 = 0.1089, w $R2 = 0.1936$		
R indices (all data)	R1 = 0.1861, wR2 = 0.2	R1 = 0.1861, $wR2 = 0.2279$		
Largest diff. peak and hole	1.52 and -1.99 e.Å ⁻³	1.52 and -1.99 e.Å ⁻³		

Table S1. Crystal and structure refinement data for $[Fe(en)_3]_2 \cdot [Fe_{16}S_{20}] \cdot enH_2$.

	X	у	Z	U(eq)
Fe(1)	-1570(5)	2428(1)	-256(2)	13(1)
Fe(2)	-4653(5)	2089(1)	-248(2)	12(1)
Fe(3)	-5332(5)	2898(1)	-70(2)	10(1)
Fe(4)	-303(5)	1667(1)	-236(2)	9(1)
Fe(5)	1568(5)	2569(1)	-85(2)	11(1)
Fe(6)	-6525(5)	1182(1)	-45(2)	11(1)
Fe(7)	-5322(5)	404(1)	26(2)	10(1)
Fe(8)	325(5)	3341(1)	-47(2)	13(1)
Fe(9)	-8423(5)	85(1)	75(2)	12(1)
Fe(10)	327(5)	858(1)	-8(2)	10(1)
Fe(11)	-6596(5)	3664(1)	-14(2)	10(1)
Fe(12)	-3361(5)	1328(1)	-209(2)	10(1)
Fe(13)	-3448(5)	3831(1)	-150(2)	10(1)
Fe(14)	-378(5)	4153(1)	-118(2)	10(1)
Fe(15)	-4652(5)	4595(1)	-94(2)	9(1)
Fe(16)	-1575(5)	4912(1)	-63(2)	11(1)
S(1)	-3691(8)	2616(2)	-853(3)	13(1)
S(2)	-2470(9)	1890(2)	357(3)	10(1)
S(3)	-6332(8)	2364(2)	517(3)	12(1)
S(4)	-506(8)	2802(2)	546(3)	14(1)
S(5)	1336(9)	1404(2)	543(3)	12(1)
S(6)	527(8)	2186(2)	-883(3)	11(1)
S(7)	-7451(9)	3132(2)	-646(3)	11(1)
S(8)	-7488(8)	612(2)	-578(3)	10(1)
S(9)	-5417(8)	1547(2)	-854(3)	12(1)
S(10)	-4476(8)	954(2)	589(3)	12(1)
S(11)	-3643(9)	81(2)	-702(3)	14(1)
S(12)	-10552(8)	359(2)	652(3)	11(1)
S(13)	-4540(8)	3411(2)	585(3)	12(1)
S(14)	-1258(8)	1122(2)	-809(3)	11(1)
S(15)	-1339(8)	3651(2)	-775(3)	12(1)

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å²x 10³) for [Fe(en)₃]₂·[Fe₁₆S₂₀]·enH₂. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

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S(16)	-8682(8)	3836(2)	615(3)	9(1)
S(17)	-2521(8)	4355(2)	504(3)	11(1)
S(18)	-5497(8)	4092(2)	-757(3)	8(1)
S(19)	505(8)	4688(2)	-712(3)	10(1)
S(20)	-6356(8)	4875(2)	652(3)	11(1)
Fe(17)	3414(5)	3301(1)	-2570(2)	10(1)
N(1)	1720(30)	3620(6)	-1920(9)	13(2)
N(2)	3160(30)	3896(6)	-3048(9)	12(2)
C(1)	1020(30)	3962(7)	-2273(12)	13(3)
C(2)	2350(30)	4182(8)	-2632(12)	13(2)
N(3)	5390(20)	3173(6)	-3236(9)	13(2)
N(4)	5550(20)	3420(6)	-1924(10)	14(2)
C(3)	6880(30)	3365(8)	-3007(11)	14(2)
C(4)	6970(30)	3266(8)	-2277(11)	14(2)
N(5)	3260(30)	2683(6)	-2143(9)	12(2)
N(6)	1550(20)	3016(6)	-3158(9)	10(2)
C(5)	2180(30)	2441(7)	-2555(12)	11(2)
C(6)	910(30)	2667(7)	-2828(12)	10(2)
Fe(18)	1659(5)	451(1)	-2475(2)	9(1)
N(7)	3410(30)	121(6)	-1837(9)	13(2)
N(8)	1820(30)	-157(6)	-2952(10)	14(2)
C(7)	3980(30)	-216(8)	-2181(12)	14(3)
C(8)	2600(30)	-428(8)	-2509(12)	15(2)
N(9)	3540(30)	737(6)	-3070(9)	11(2)
N(10)	1790(30)	1069(6)	-2044(9)	11(2)
C(9)	4140(30)	1107(7)	-2745(12)	11(2)
C(10)	2800(30)	1341(7)	-2470(12)	11(2)
N(11)	-460(30)	309(7)	-1840(10)	16(2)
N(12)	-200(20)	591(7)	-3150(10)	16(2)
C(11)	-1910(30)	380(8)	-2203(12)	18(3)
C(12)	-1750(30)	435(8)	-2902(12)	19(2)
N(13)	8230(40)	1498(10)	-3031(16)	70(6)
N(14)	6510(40)	2290(9)	-3154(14)	56(6)
C(13)	8330(50)	1687(12)	-2440(20)	68(6)
C(14)	6900(50)	2044(11)	-2586(18)	59(6)