Electronic Supplementary Material for CrystEngComm

Electronic Supplementary Information

Synthesis, Crystal Structure, and Characterization of Charge-transfer Salt: $(BEDT\text{-}TTF)_5[Fe(C_2O_4)_3]\cdot(H_2O)_2\cdot CH_2Cl_2$ (BEDT-TTF = bis (ethylenedithio)tetrathiafulvalene)

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Table S1 Selected bond lengths at 180K

Fe(1)–O(2)	1.990(3)	Fe(1)–O(10)	1.998(3)	Fe(1)–O(6)	2.009(3)
Fe(1)–O(5)	2.009(2)	Fe(1)–O(9)	2.010(3)	Fe(1)–O(1)	2.014(3)
S(1)–C(1)	1.736(4)	S(1)– (3)	1.745(4)	S(2)–C(4)	1.739(4)
S(2)–C(1)	1.742(4)	S(3)– (2)	1.733(4)	S(3)–C(5)	1.749(4)
S(4)–C(2)	1.732(4)	S(4)–C(6)	1.753(4)	S(5)–C(3)	1.736(4)
S(5)–C(7)	1.816(4)	S(6)–C(4)	1.744(4)	S(6)–C(8)	1.803(4)
S(7)–C(5)	1.734(4)	S(7)–C(9)	1.813(4)	S(8)–C(6)	1.740(4)
S(8)–C(10)	1.804(4)	C(1)–C(2)	1.362(5)	C(3)–C(4)	1.352(5)
C(5)–C(6)	1.357(5)	C(7)–C(8)	1.520(5)	C(9)–C(10)	1.497(5)
S(9)–C(11)	1.739(4)	S(9)–C(13)	1.745(4)	S(10)–C(11)	1.743(4)
S(10)–C(14)	1.748(4)	S(11)–C(12)	1.730(4)	S(11)–C(15)	1.745(4)
S(12)–C(12)	1.731(4)	S(12)–C(16)	1.739(4)	S(13)–C(13)	1.733(4)
S(13)–C(17)	1.805(4)	S(14)–C(14)	1.746(4)	S(14)–C(18)	1.806(4)
S(15)–C(15)	1.747(4)	S(15)–C(19)	1.805(4)	S(16)–C(16)	1.746(4)
S(16)–C(20)	1.799(4)	C(11)–C(12)	1.362(5)	C(13)–C(14)	1.355(5)
C(15)– C(16)	1.356(5)	C(17)–C(18)	1.517(5)	C(19)–C(20)	1.507(5)
S(17)–C(21)	1.732(4)	S(17)–C(22)	1.750(4)	S(18)–C(21)	1.716(4)
S(18)–C(23)	1.732(4)	S(19)–C(22)	1.732(4)	S(19)–C(24)	1.801(4)
S(20)–C(23)	1.743(4)	S(20)–C(25)	1.802(4)	C(21)–C(21A)	1.382(7)
C(22)–C(23)	1.362(5)	C(24)–C(25)	1.508(5)		
S(21)–C(26)	1.741(4)	S(21)–C(27)	1.749(4)	S(22)–C(26)	1.744(4)
S(22)–C(28)	1.761(4)	S(23)–C(27)	1.751(4)	S(23)–C(29)	1.794(3)
S(24)–C(28)	1.738(4)	S(24)–C(30)	1.807(4)	C(26)–C(26B)	1.359(7)
C(27)–C(28)	1.352(5)	C(29)–C(30)	1.515(5)		
S(25)–C(31)	1.731(4)	S(25)–C(33)	1.744(4)	S(26)–C(31)	1.729(4)
S(26)–C(34)	1.753(4)	S(27)–C(35)	1.739(4)	S(27)–C(32)	1.747(4)
S(28)–C(32)	1.734(4)	S(28)–C(36)	1.742(4)	S(29)–C(33)	1.743(4)
S(29)–C(37)	1.798(4)	S(30)–C(34)	1.735(4)	S(30)–C(38)	1.796(4)
S(31)–C(35)	1.736(4)	S(31)–C(39)	1.804(4)	S(32)–C(36)	1.755(4)
S(32)–C(40)	1.802(4)	C(31)–C(32)	1.362(5)	C(33)–C(34)	1.349(5)
C(35)–C(36)	1.350(5)	C(37)–C(38)	1.489(5)	C(39)–C(40)	1.529(5)
S(33)–C(41)	1.721(4)	S(33)–C(43)	1.751(4)	S(34)–C(41)	1.733(4)
S(34)–C(44)	1.745(4)	S(35)–C(42)	1.731(4)	S(35)–C(45)	1.740(4)

S(36)–C(42)	1.738(4)	S(36)–C(46)	1.743(4)	S(37)–C(43)	1.731(4)
S(37)–C(47)	1.768(5)	S(38)–C(44)	1.742(4)	S(38)–C(48)	1.803(4)
S(39)–C(45)	1.736(4)	S(39)–C(49)	1.797(4)	S(40)– (46)	1.731(4)
S(40)–C(50)	1.784(4)	C(41)–C(42)	1.371(5)	C(43)–C(44)	1.354(5)
C(45)–C(46)	1.355(5)	C(47)–C(48)	1.447(6)	C(49)– (50)	1.494(5)

Symmetry Code: A –X, 1-Y, 1-Z; B –X, 1-Y, -Z

Table S2 Short contacts and hydrogen bonds in **1**

Short contacts between donors (Å)

S(4)···S(14)_$1 3.568(2), S(4)···S(20)_$1 3.423(1), S(5)···S(15)_$2 3.526(1)
S(5)···S(18)_$4 3.457(2), S(5)···S(20)_$4 3.553(2), S(6)···S(17)_$3 3.531(1)
S(6)···S(19)_$3 3.487(1), S(7)···S(13)_$2 3.465(1), S(8)···S(14)_$1 3.581(2)
S(8)···S(20)_$1 3.328(1), S(14)···S(16)_$1 3.327(1), S(21)···S(40)_$ 3.555(1)
S(22)···S(39)_$5 3.399(1), S(23)···S(40)_$6 3.401(1), S(24)···S(39)_$5 3.326(1)
S(24)···S(34)_$7 3.371(1), S(24)···S(38)_$7 3.503(1), S(25)···S(31)_$8 3.469(2)
S(25)···S(39)_$8 3.588(1), S(40)···S(26)_$7 3.365(2), S(26)···S(40)_$7 3.365(2),
S(27)···S(27)_$8 3.600(2), S(32)···S(38)_$7 3.522(2), S(30)···C(56)_$7 3.492(4)
S(35)···S(36)_$10 3.589(2), S(25)···C(39)_$8 3.470(4), S(32)···C(46) 3.461(4),
S(38)…C(40)_$7 3.467(4)

Short contact between donors and solvent molecules(Å)

S(7)···Cl(2)_$2a 3.399(4) O(4)···S(15)_$2 2.950(3) O(8)··· S(19)_$3 3.233(3)
O(7)···S(23)_$3 3.285(3) O(11)···S(38)_$7 3.258(3)

Hydrogen bonds between donors in a donor layer (Å/°)

C(17)-H(17B)···S(5)_$2 3.68/165, C(20)-H(20A) ...S(19)_$13 3.76/159
C(24)-H(24B)···S(13) 3.78/153, C(25)-H(25B)···S(15)_$13 3.82/161
C(29)-H(29A)···S(31)_$8 3.62/163, C(39)-H(39A)···S(39) 3.70/155
C(40)-H(40A)···S(24)_$8 3.73/156

Hydrogen bonds between donors and anions (Å/°)

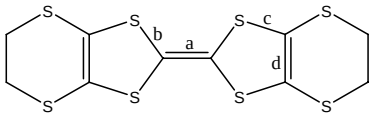
C(8)–H(8A)···O(6)_$2 3.23/159, C(9)-H(9B)···O(12)_$14 3.06/125
C(19)-H(19B)···O(4)_$2 3.05 /123, C(19)-H(19B)···O(14)_$2 3.25/135
C(20)-H(20B)···O(10)_$12 3.27/135, C(24)-H(24A)···O(8) _$6 3.11/133
C(25)-H(25A)···O(13) 3.46/177, C(29)-H(29B)···O(7)_$6 3.05/136
C(40)-H(40B)···O(11)_$8 3.21/139 , C(49)-H(49A)···O(1) _$8 3.23/138
C(49)-H(49B)···O(9) _$8 3.23/125, C(50)-H(50A)···O(5) _$8 3.24/174
C(17)-H(17A)···Cl(2) 3.53 /141, C(39)-H(39B)···Cl(1)_$8 3.64/153
C(29)-H(29B)···Cl(1) 3.45/124

Symmetry Code:

#1 1-x, -y, 1-z; #2 1-x, 1-y, 1-z; #3 1+x, -1+y, z; #4 1+x, y, z;
#5 -1+x, y, z; #6 -1+x,1+y,z; #7 1-x,-y,-z; #8 1-x,1-y,-z;
#9 -x,-y, -z; #10 2-x, -y, -z; #11 x, -1+y, z; #12 1-x, -y, 1-z;
#13 -x,1-y,1-z; #14 x,1+y,z.

Table S3 Bond Lengths of the TTF Core on the BEDT-TTF molecule

(a –d were defined as follows)



$\delta = (b + c) – (a + d)$

$Q = 6.347 – 7.463$

C atom of donor	a	b	c	d	δ	Q	Formal charge
C1-C10	1.367	1.739, 1.735 1.733, 1.727	1.739, 1.735 1.733, 1.727	1.337 1.344	0.772	0.68	~ +0.5
C11-C20	1.356	1.744, 1.743 1.731, 1.725	1.736,1.743 1.745,1.740	1.351 1.345	0.773	0.67	~ +0.5
C21-C25	1.384	1.724, 1.718	1.747, 1.741	1.351	0.73	0.99	~ +1.0
C26-C30	1.384	1.724, 1.718	1.747, 1.741	1.351	0.73	0.99	~ +1.0
C31-C40	1.364	1.733, 1.743 1.733, 1.728	1.736, 1.743 1.744, 1.746	1.352 1.340	0.766	0.72	~ +0.5
C41-C50	1.355	1.735, 1.748 1.722, 1.735	1.730, 1.734 1.738, 1.758	1.354 1.333	0.7766	0.64	~ +0.5