Supplementary Material (ESI) for Chemical Communications

Supplementary information for

Formation of an unusual charge-transfer network from an ionic liquid

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1. Procedure for crystallization of DMDP:$EV^{\cdot}(Tf_2N)_2$.

The ionic liquid N-butyl-N-methylpyrrolidinium bistrifylamide ($[C_4mpy][Tf_2N]$) was synthesized by reacting N-butyl-N-methylpyrrolidinium bromide with one equivalent of lithium bistrifylamide in water. The resulting ionic liquid forms a separate layer, which is extracted with dichloromethane, washed several time with water, and dried under vacuum at 60°C. Equimolar molar amounts of dimethyldihyrdophenazine (DMDP) and diethylviologen bistrifylamide ($EV[Tf_2N]_2$) were dissolved in hot (200°C) $[C_4mpy][Tf_2N]$, and the solution was allowed to cool to room temperature, yielding green crystalline material. In acetone, the DMDP and $EV[Tf_2N]_2$ were dissolved in hot acetone, and the solution was allowed to cool and solvent volume reduced, resulting in green crystals.

2. Crystal coordinates for DMDP:$EV^{\cdot}(Tf_2N)_2$.

Table 1. Crystal data and structure refinement for DMDP:$EV(Tf_2N)_2$.

Identification code	DMDP:$EV(Tf_2N)_2$	
Empirical formula	$C_{32}\ H_{32}\ F_{12}\ N_6\ O_8\ S_4$	
Formula weight	984.88	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.490(5) Å	α= 71.643(6)°.
	b = 12.820(5) Å	β= 72.240(7)°.
	c = 13.993(6) Å	γ = 82.390(8)°.
Volume	2023.5(14) $Å^3$	
Z	2	
Density (calculated)	1.616 Mg/m^3	
Absorption coefficient	0.347 mm^{-1}	
F(000)	1004	
Crystal size	0.44 x 0.32 x 0.10 mm^3	
Theta range for data collection	1.60 to 25.39°.	
Index ranges	-14<=h<=15, -15<=k<=15, -16<=l<=16	
Reflections collected	12935	
Independent reflections	6768 [R(int) = 0.0200]	
Max. and min. transmission	0.9661 and 0.8623	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6768 / 0 / 559	
Goodness-of-fit on F^2	1.650	
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1568	
R indices (all data)	R1 = 0.0730, wR2 = 0.1609	
Largest diff. peak and hole	0.676 and -0.564 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for DMDP:EV(Tf_2N)$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7865(1)	7840(1)	2879(1)	42(1)
S(2)	9580(1)	6201(1)	2838(1)	41(1)
S(3)	4935(1)	2103(1)	626(1)	43(1)
S(4)	4259(1)	2718(1)	2477(1)	38(1)
F(1)	7486(2)	7879(2)	4815(2)	58(1)
F(2)	6006(2)	7748(3)	4386(2)	82(1)
F(3)	7132(2)	6346(2)	4681(2)	64(1)
F(4)	9878(3)	6991(3)	813(2)	89(1)
F(5)	11271(2)	7178(3)	1313(2)	89(1)
F(6)	10941(3)	5591(3)	1275(3)	101(1)
F(7)	6999(2)	1335(2)	558(2)	66(1)
F(8)	5745(2)	472(2)	1915(2)	64(1)
F(9)	5933(2)	244(2)	411(2)	77(1)
F(10)	2490(2)	3509(3)	1824(2)	84(1)
F(11)	3585(3)	4736(2)	1653(2)	89(1)
F(12)	2535(2)	3930(2)	3163(2)	79(1)
O(1)	7866(2)	9008(2)	2616(2)	57(1)
O(2)	7311(2)	7356(2)	2386(2)	59(1)
O(3)	8792(2)	5455(2)	2901(2)	56(1)
O(4)	10356(3)	5809(2)	3444(2)	60(1)
O(5)	3894(2)	1575(3)	922(2)	56(1)
O(6)	5402(3)	2685(3)	-452(2)	69(1)
O(7)	4857(2)	3104(2)	3011(2)	53(1)
O(8)	3664(2)	1730(2)	3018(2)	45(1)
N(1)	8952(2)	2343(2)	4589(2)	31(1)
N(2)	7221(2)	1223(2)	4611(2)	34(1)
N(3)	9091(3)	7381(2)	2916(2)	42(1)
N(4)	5028(3)	2816(2)	1329(2)	46(1)
N(5)	1105(3)	224(3)	2311(2)	45(1)
N(6)	6124(2)	5162(2)	2331(2)	35(1)
C(1)	9902(3)	2885(3)	4596(3)	38(1)
C(2)	6361(3)	547(3)	4631(3)	43(1)
C(3)	8009(3)	2146(2)	5486(2)	29(1)
C(4)	7952(3)	2463(3)	6365(3)	37(1)
C(5)	7059(3)	2165(3)	7270(3)	43(1)
C(6)	6202(3)	1588(3)	7292(3)	45(1)
C(7)	6224(3)	1295(3)	6400(3)	38(1)
C(8)	7123(3)	1558(2)	5500(2)	31(1)
C(9)	7877(3)	1844(2)	3634(3)	32(1)
C(10)	7701(3)	1887(3)	2688(3)	39(1)
C(11)	8416(3)	2462(3)	1740(3)	46(1)
C(12)	9288(3)	3021(3)	1723(3)	44(1)
C(13)	9459(3)	3011(3)	2665(3)	36(1)
C(14)	8777(3)	2425(2)	3620(2)	30(1)
C(15)	5245(3)	5038(2)	4435(2)	31(1)
C(16)	6200(3)	4437(3)	4081(3)	40(1)
C(17)	6627(3)	4508(3)	3037(3)	41(1)
C(19)	5211(3)	5772(3)	2648(3)	49(1)
C(20)	4759(3)	5722(3)	3676(3)	51(1)
C(21)	6585(3)	5186(3)	1208(3)	46(1)
C(22)	7617(4)	5837(4)	698(3)	68(1)

C(23)	231(3)	61(2)	4430(2)	28(1)
C(24)	-368(3)	-257(3)	3876(3)	35(1)
C(25)	84(3)	-171(3)	2837(3)	42(1)
C(27)	1694(3)	577(3)	2803(3)	38(1)
C(28)	1278(3)	504(3)	3843(2)	32(1)
C(29)	1631(4)	242(5)	1194(3)	80(2)
C(30)	1081(8)	762(10)	514(4)	257(8)
C(31)	7073(3)	7424(3)	4271(3)	47(1)
C(32)	10477(4)	6512(4)	1493(3)	58(1)
C(33)	5969(3)	976(3)	895(3)	46(1)
C(34)	3158(4)	3787(3)	2263(3)	51(1)

Table 3. Bond lengths [Å] and angles [°] for DMDP:EV(Tf_2N)$_2$.

S(1)-O(2)	1.420(3)
S(1)-O(1)	1.426(3)
S(1)-N(3)	1.576(3)
S(1)-C(31)	1.835(4)
S(2)-O(4)	1.421(3)
S(2)-O(3)	1.426(3)
S(2)-N(3)	1.578(3)
S(2)-C(32)	1.821(4)
S(3)-O(6)	1.429(3)
S(3)-O(5)	1.431(3)
S(3)-N(4)	1.576(3)
S(3)-C(33)	1.832(4)
S(4)-O(8)	1.425(3)
S(4)-O(7)	1.427(3)
S(4)-N(4)	1.576(3)
S(4)-C(34)	1.830(4)
F(1)-C(31)	1.335(4)
F(2)-C(31)	1.319(4)
F(3)-C(31)	1.321(4)
F(4)-C(32)	1.336(5)
F(5)-C(32)	1.309(5)
F(6)-C(32)	1.326(5)
F(7)-C(33)	1.319(5)
F(8)-C(33)	1.326(4)
F(9)-C(33)	1.330(4)
F(10)-C(34)	1.315(5)
F(11)-C(34)	1.317(5)
F(12)-C(34)	1.317(5)
N(1)-C(14)	1.407(4)
N(1)-C(3)	1.416(4)
N(1)-C(1)	1.455(4)
N(2)-C(9)	1.406(4)
N(2)-C(8)	1.406(4)
N(2)-C(2)	1.455(4)
N(5)-C(25)	1.337(5)
N(5)-C(27)	1.346(4)
N(5)-C(29)	1.494(5)
N(6)-C(19)	1.334(4)
N(6)-C(17)	1.338(4)
N(6)-C(21)	1.491(4)
C(3)-C(4)	1.392(5)
C(3)-C(8)	1.412(4)
C(4)-C(5)	1.393(5)
C(5)-C(6)	1.367(5)
C(6)-C(7)	1.404(5)
C(7)-C(8)	1.389(5)
C(9)-C(10)	1.391(5)
C(9)-C(14)	1.421(4)

C(10)-C(11)	1.392(5)
C(11)-C(12)	1.372(5)
C(12)-C(13)	1.394(5)
C(13)-C(14)	1.385(5)
C(15)-C(16)	1.378(5)
C(15)-C(20)	1.389(5)
C(15)-C(15)#1	1.489(6)
C(16)-C(17)	1.371(5)
C(19)-C(20)	1.359(5)
C(21)-C(22)	1.489(6)
C(23)-C(28)	1.397(5)
C(23)-C(24)	1.401(4)
C(23)-C(23)#2	1.486(6)
C(24)-C(25)	1.363(5)
C(27)-C(28)	1.365(5)
C(29)-C(30)	1.304(8)

O(2)-S(1)-O(1)	119.30(17)
O(2)-S(1)-N(3)	117.06(16)
O(1)-S(1)-N(3)	107.45(17)
O(2)-S(1)-C(31)	104.85(18)
O(1)-S(1)-C(31)	103.68(17)
N(3)-S(1)-C(31)	102.12(17)
O(4)-S(2)-O(3)	118.13(17)
O(4)-S(2)-N(3)	109.83(16)
O(3)-S(2)-N(3)	116.30(17)
O(4)-S(2)-C(32)	103.3(2)
O(3)-S(2)-C(32)	104.97(19)
N(3)-S(2)-C(32)	101.84(18)
O(6)-S(3)-O(5)	118.65(18)
O(6)-S(3)-N(4)	108.92(19)
O(5)-S(3)-N(4)	116.24(16)
O(6)-S(3)-C(33)	103.92(18)
O(5)-S(3)-C(33)	104.74(19)
N(4)-S(3)-C(33)	102.09(17)
O(8)-S(4)-O(7)	118.36(16)
O(8)-S(4)-N(4)	116.70(15)
O(7)-S(4)-N(4)	108.46(18)
O(8)-S(4)-C(34)	104.40(18)
O(7)-S(4)-C(34)	104.02(18)
N(4)-S(4)-C(34)	102.74(17)
C(14)-N(1)-C(3)	117.7(3)
C(14)-N(1)-C(1)	118.9(3)
C(3)-N(1)-C(1)	118.5(3)
C(9)-N(2)-C(8)	118.3(3)
C(9)-N(2)-C(2)	118.7(3)
C(8)-N(2)-C(2)	119.1(3)
S(1)-N(3)-S(2)	124.75(19)
S(4)-N(4)-S(3)	125.0(2)
C(25)-N(5)-C(27)	119.8(3)
C(25)-N(5)-C(29)	121.3(3)
C(27)-N(5)-C(29)	118.9(3)
C(19)-N(6)-C(17)	119.3(3)
C(19)-N(6)-C(21)	121.2(3)
C(17)-N(6)-C(21)	119.4(3)
C(4)-C(3)-C(8)	119.3(3)
C(4)-C(3)-N(1)	122.5(3)
C(8)-C(3)-N(1)	118.2(3)
C(3)-C(4)-C(5)	120.8(3)
C(6)-C(5)-C(4)	120.1(3)
C(5)-C(6)-C(7)	119.9(3)
C(8)-C(7)-C(6)	120.9(3)
C(7)-C(8)-N(2)	123.1(3)
C(7)-C(8)-C(3)	118.9(3)
N(2)-C(8)-C(3)	117.9(3)

C(10)-C(9)-N(2)	122.9(3)
C(10)-C(9)-C(14)	119.0(3)
N(2)-C(9)-C(14)	118.1(3)
C(9)-C(10)-C(11)	120.6(3)
C(12)-C(11)-C(10)	120.6(3)
C(11)-C(12)-C(13)	119.6(3)
C(14)-C(13)-C(12)	121.1(3)
C(13)-C(14)-N(1)	123.2(3)
C(13)-C(14)-C(9)	119.1(3)
N(1)-C(14)-C(9)	117.7(3)
C(16)-C(15)-C(20)	116.3(3)
C(16)-C(15)-C(15)#1	122.1(3)
C(20)-C(15)-C(15)#1	121.6(4)
C(17)-C(16)-C(15)	121.1(3)
N(6)-C(17)-C(16)	120.8(3)
N(6)-C(19)-C(20)	121.6(3)
C(19)-C(20)-C(15)	120.8(3)
C(22)-C(21)-N(6)	111.0(3)
C(28)-C(23)-C(24)	115.9(3)
C(28)-C(23)-C(23)#2	122.6(4)
C(24)-C(23)-C(23)#2	121.5(4)
C(25)-C(24)-C(23)	120.8(3)
N(5)-C(25)-C(24)	121.5(3)
N(5)-C(27)-C(28)	120.8(3)
C(27)-C(28)-C(23)	121.2(3)
C(30)-C(29)-N(5)	117.8(5)
F(2)-C(31)-F(3)	108.6(3)
F(2)-C(31)-F(1)	108.3(3)
F(3)-C(31)-F(1)	107.8(3)
F(2)-C(31)-S(1)	110.3(3)
F(3)-C(31)-S(1)	111.4(2)
F(1)-C(31)-S(1)	110.5(3)
F(5)-C(32)-F(6)	109.2(4)
F(5)-C(32)-F(4)	107.2(4)
F(6)-C(32)-F(4)	106.7(4)
F(5)-C(32)-S(2)	112.4(3)
F(6)-C(32)-S(2)	110.2(3)
F(4)-C(32)-S(2)	110.9(3)
F(7)-C(33)-F(8)	108.4(3)
F(7)-C(33)-F(9)	108.3(3)
F(8)-C(33)-F(9)	108.3(3)
F(7)-C(33)-S(3)	111.4(3)
F(8)-C(33)-S(3)	110.7(3)
F(9)-C(33)-S(3)	109.6(3)
F(10)-C(34)-F(11)	108.0(3)
F(10)-C(34)-F(12)	107.6(4)
F(11)-C(34)-F(12)	108.1(4)
F(10)-C(34)-S(4)	110.9(3)
F(11)-C(34)-S(4)	111.7(3)
F(12)-C(34)-S(4)	110.4(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y,-z+1