Supplementary Material for PCCP

Solid and liquid charge-transfer complex formation between 1-methylnaphthalene and 1-alkyl-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide ionic liquids

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Electronic Supplementary Information

Table S1. Intramolecular distance constraints used to define the basic structure of the 1-methyl-4-cyanopyridinium cation.

Table S2. Intramolecular distance constraints used to define the basic structure of the bis{(trifluoromethyl)sulfonyl}imide anion.

Table S3. Intramolecular distance constraints used to define the basic structure of the 1-methylnaphthalene molecule.

Figure S1 Local structure around a central cation in the crystal structures of the 1:1 complex of 1-methyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (*top*) and 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide (*middle*) with 1-methylnaphthalene, and pure 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide with disordered anion (*bottom*). All contacts shown are less than the sum of the van der Waals radii except those connecting cations in the 1-ethyl-4-cyanopyridinium bis{(trifluoromethyl)sulfonyl}imide/1-methylnaphthalene structure which are less than the sum of the van der Waals radii plus 0.3 Å.

Figure S2 Distributions of $CF_3 \cdots CF_3$ distances from EPSR analysis of the pure ionic liquid (black line) and the 1:1 complex with 1-methylnaphthalene (red line), and simulated data for the 1:1 complex (red dashed line).

Figure S3 Cumulative probabilities of aromatic-aromatic plane-plane angles for the tiny pre-shoulder (red, $0 < r < 4.7$ Å) in the MD aromatic-aromatic RDF, the bulk of the main peak (green, $4.7 < r < 7.1$ Å) and another apparent shoulder (blue, $7.1 < r < 9.8$ Å).

Table S1. Intramolecular distance constraints used to define the basic structure of the 1-methyl-4-cyanopyridinium cation.

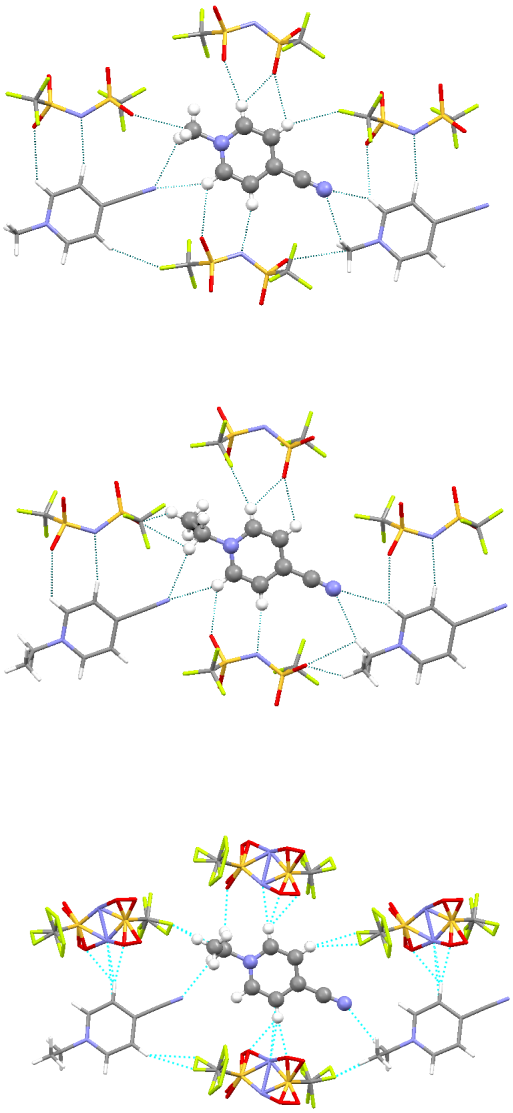
d / Å	$N(R)_1$	$C(R)_2$	$C(R)_3$	$C(R)_4$	$C(R)_5$	$C(R)_6$	$C(N)_7$	$N(N)_8$	$C(M)_9$	$H(R)_{10}$	$H(R)_{11}$	$H(R)_{12}$	$H(R)_{13}$	$H(M)_{14}$	$H(M)_{15}$	$H(M)_{16}$
$N(R)_1$		1.37	2.40	2.78	2.40	1.37	4.22	5.37	1.46	2.14	3.38	3.38	2.13	2.14	2.12	2.12
$C(R)_2$			1.40	2.41	2.77	2.37	3.73	4.84	2.46	1.08	2.15	3.86	3.36	2.57	3.18	3.18
$C(R)_3$				1.40	2.41	2.77	2.46	3.51	3.75	2.14	1.08	3.40	3.86	3.97	4.38	4.38
$C(R)_4$					1.40	2.41	1.44	2.60	4.24	3.39	2.16	2.16	3.39	4.78	4.73	4.73
$C(R)_5$						1.40	2.46	3.51	3.73	3.86	3.40	1.08	2.14	4.54	4.07	4.07
$C(R)_6$							3.73	4.84	2.44	3.36	3.86	2.15	1.08	3.38	2.75	2.75
$C(N)_7$								1.16	5.68	4.60	2.69	2.69	4.60	6.19	6.14	6.14
$N(N)_8$									6.84	5.65	3.51	3.51	5.65	7.33	7.29	7.29
$C(M)_9$										2.68	4.61	4.59	2.65	1.11	1.11	1.11
$H(R)_{10}$											2.46	4.94	4.26	2.32	3.45	3.45
$H(R)_{11}$												4.31	4.94	4.63	5.27	5.27
$H(R)_{12}$													2.46	5.49	4.80	4.80
$H(R)_{13}$														3.73	2.68	2.68
$H(M)_{14}$															1.80	1.80
$H(M)_{15}$																1.81
$H(M)_{16}$																

Table S2. Intramolecular distance constraints used to define the basic structure of the bis{(trifluoromethyl)sulfonyl}imide anion.

d / Å	N(A)	S(A)	O(A)	O(A)	C(A)	F(A)	F(A)	F(A)	S(A)	O(A)	O(A)	C(A)	F(A)	F(A)	F(A)
N(A)		1.77	2.63	2.65	3.06	4.22	3.40	3.42	1.76	2.77	2.75	2.95	3.28	3.27	4.14
S(A)			1.55	1.55	1.83	2.63	2.63	2.63							
O(A)				2.41	2.81	3.17	3.20	3.97							
O(A)					2.83	3.19	3.98	3.24							
C(A)						1.38	1.38	1.38							
F(A)							2.26	2.26							
F(A)								2.26							
F(A)															
S(A)										1.72	1.72	1.81	2.62	2.62	2.62
O(A)											2.75	2.97	3.31	4.14	3.33
O(A)												2.95	4.13	3.28	3.31
C(A)													1.38	1.38	1.38
F(A)														2.26	2.26
F(A)															2.26
F(A)															

Table S3. Intramolecular distance constraints used to define the basic structure of the 1-methylnaphthalene molecule.

	C(Ar)$_1$	C(Ar)$_2$	C(Ar)$_3$	C(Ar)$_4$	C(Ar)$_5$	C(Ar)$_6$	C(Ar)$_7$	C(Ar)$_8$	C(Ar)$_9$	C(Ar)$_{10}$	C(Ar)$_{11}$	H(Ar)$_1$	H(Ar)$_2$	H(Ar)$_3$	H(Ar)$_5$	H(Ar)$_6$	H(Ar)$_7$	H(Ar)$_8$	H(Ar)$_{11a}$	H(Ar)$_{11b}$	H(Ar)$_{11c}$
C(Ar)$_1$		1.38	2.43	2.82	3.76	4.25	3.75	2.49	1.43	2.46	1.48	4.00	2.16					2.14		2.14	2.14
C(Ar)$_2$			1.41	2.42	4.23	5.05	4.86	3.74	2.42	2.8	2.49		1.08	2.17							
C(Ar)$_3$				1.37	3.72	4.85	5.05	4.23	2.81	2.42	3.79		2.17	1.08							
C(Ar)$_4$					2.42	3.73	4.23	3.74	2.42	1.4	4.3	1.08		2.15							
C(Ar)$_5$						1.37	2.42	2.8	2.46	1.42	4.98				1.08	2.15			4.00		
C(Ar)$_6$							1.42	2.42	2.62	2.42	5.16				2.16	1.08	2.17				
C(Ar)$_7$								1.37	2.43	2.8	4.3					2.17	1.08		2.15		
C(Ar)$_8$									1.42	2.44	2.92				4.00		2.15		1.08		
C(Ar)$_9$											2.52			4.00		4.00			2.18		
C(Ar)$_{10}$											3.81	2.18	4.00		2.18		4.00				
C(Ar)$_{11}$																		1.12		1.12	1.12
H(Ar)$_1$																					
H(Ar)$_2$																					
H(Ar)$_3$																					
H(Ar)$_5$																					
H(Ar)$_6$																					
H(Ar)$_7$																					
H(Ar)$_8$																				1.76	1.76
H(Ar)$_{11a}$																					
H(Ar)$_{11b}$																					1.76
H(Ar)$_{11c}$																					



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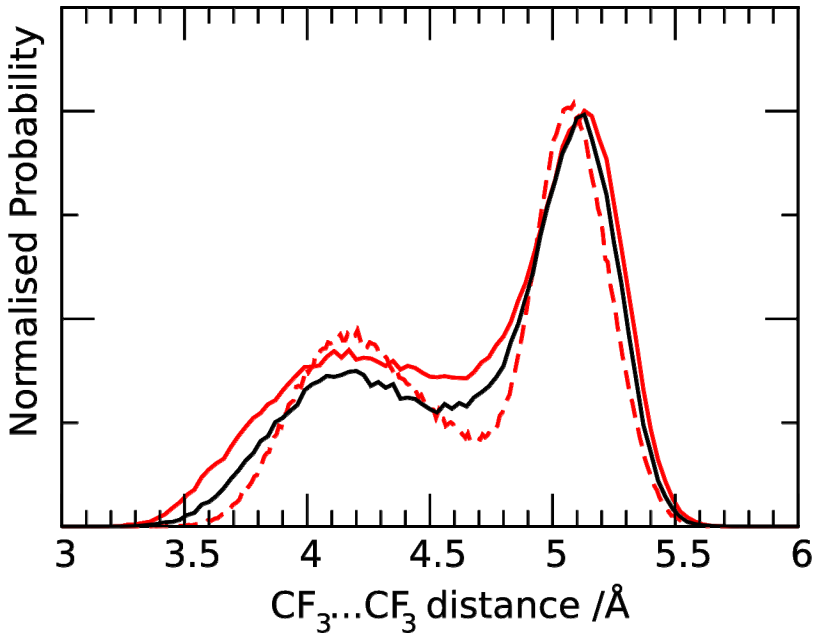

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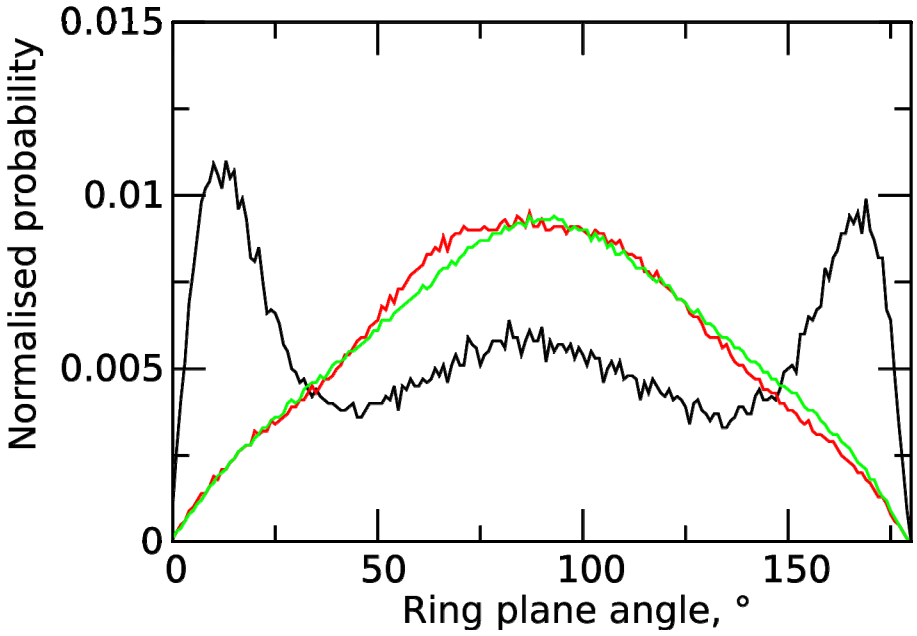

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