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Backbone effects on the charge transport in poly-imidazole membranes: a theoretical study

Giuseppe Felice Mangiatordi, Damien Laage and Carlo Adamo

SUPPLEMENTARY INFORMATION

Contents

1. Force Field calibration

According to its orbital hybridization and bonding connectivity, the General Amber Force Field (GAFF)[1,2] assigns an type to each atom. The tables S1 and S2 report the obtained atom numbers, atom types and relatives RESP[3,4] partial charges for the considered molecular systems: 3mer (table S1) and 15mer (table S2). As in the previous investigation on P4VI[5], all the intramolecular interaction parameters for imidazole reported by Voth and coworkers[6] have been included. Furthermore, in analogy with the previous work, the GAFF has been calibrated on the DFT data obtained for the trimeric model. Notably, in order to accurately reproduce them, different scaling factors with respect to the GAFF default values have been applied to the 1-4 non bonded interactions (Table S3). Figure S1 shows the resulting energetic profile provided using the modified GAFF version (MM single point calculations on the relaxed DFT structures) and the DFT protocol: the MM energy profile obtained has a close shape of that calculated at DFT level.

2. Details on Molecular Dynamics simulations on 15mer

In order to minimize spurious effects arising from the consideration of a single polymer chain (i.e coiling during MD simulations) and simulate locally linear rearrangement as in the real system, all the molecular dynamics simulations have been performed keeping fix the carbons of the backbone to the optimized B3LYP/6-31G(d) structure.

Data were sampled every 500 fs and a time-step of 1fs has been used. An equilibration of 0.5 ns has been carried out before 80 ns of MD trajectory performed at 393 and 453 K. All simulations have been performed in the canonical ensemble. In all umbrella sampling calculations[7] carried out for the calculation of the free energy profiles reported in figure 8, dynamics have been run for 2 ns and a force constant for the harmonic bias potential of k = 120 kcal/mol/rad^2 has been used. Windows of 10 degrees have been considered along the reaction coordinates represented by a torsion angle of the investigated system. To determinate the potentials of mean force (PMF) the results have been processed using the weighted histogram analysis method (WHAM).[8,9] The bin dimension applied in the WHAM equation has been equal to 2 degrees.

References

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Table S1: Atom numbers, GAFF atom types and relative RESP partial charges computed for 3mer.

atom number	GAFF atom type	q (e^-)
1	c3	0.060
2	hc	0.033
3	hc	0.033
4	c3	-0.473
5	hc	0.131
6	c3	0.060
7	hc	0.033
8	hc	0.033
9	c3	-0.108
10	hc	0.098
11	cd	-0.428
12	cc	0.162
13	cd	0.649
14	cd	0.445
15	na	-0.365
16	nc	-0.633
17	c3	-0.308
18	hc	0.092
19	hc	0.092
20	Hc	0.092
21	c3	-0.108
22	hc	0.098
23	c3	-0.308
24	hc	0.092
25	hc	0.092
26	hc	0.092
27	cd	-0.457
28	cd	0.445
29	na	-0.189
30	na	-0.189
31	nc	-0.656
32	nc	-0.633
33	cd	-0.457
34	cc	0.145
35	cc	0.162
36	hn	0.330
37	hn	0.428
38	hn	0.330
39	h4	0.247
40	h4	0.113
41	h4	0.250
42	h4	0.115
43	h4	0.247
44	h4	0.113

Table S2: Atom numbers, GAFF atom types and relative RESP partial charges computed for 15mer

atom number	GAFF atom type	q (e^-)
1	c3	-0.010
2	hc	0.026
3	hc	0.026
4	c3	-0.232
5	hc	0.088
6	c3	0.025
7	hc	0.043
8	hc	0.043
9	c3	-0.34
10	hc	0.112
11	cd	-0.375
12	cc	-0.0149
13	cd	0.425
14	cd	0.406
15	nc	-0.453
16	c3	0.153
17	hc	0.002
18	hc	0.002
19	c3	-0.008
20	hc	0.039
21	c3	-0.092
22	hc	0.021
23	hc	0.021
24	hc	0.021
25	cd	0.009
26	cd	0.385
27	nc	-0.479
28	cd	-0.314
29	cd	-0.312
30	na	-0.200
31	na	-0.155
32	nc	-0.546
33	na	-0.222
34	cc	0.0548
35	hn	0.299
36	hn	0.298
37	hn	0.271
38	c3	-0.198
39	c3	0.222

40	hc	0.117
41	cd	0.326
42	hc	-0.042
43	hc	-0.042
44	c3	-0.305
45	nc	-0.538
46	na	-0.084
47	hc	0.094
48	c3	0.073
49	cd	0.420
50	cc	0.076
51	cd	-0.380
52	hn	0.215
53	hc	0.033
54	hc	0.033
55	c3	-0.091
56	na	-0.206
57	nc	-0.467
58	hc	0.089
59	cd	0.315
60	cd	-0.318
61	hn	0.288
62	cc	-0.015
63	nc	-0.585
64	na	0.021
65	cc	0.130
66	cd	-0.469
67	hn	0.188
68	c3	-0.174
69	c3	-0.158
70	hc	0.087
71	hc	0.087
72	c3	0.260
73	hc	0.098
74	cd	0.278
75	hc	-0.034
76	hc	-0.034
77	c3	-0.537
78	nc	-0.471
79	na	-0.152
80	hc	0.140

81	c3	0.260
82	cd	0.472
83	cc	0.007
84	cd	-0.281
85	hn	0.286
86	hc	-0.034
87	hc	-0.034
88	c3	-0.158
89	na	-0.189
90	nc	-0.534
91	hc	0.098
92	cd	0.278
93	c3	-0.174
94	cd	-0.319
95	hn	0.288
96	cc	0.013
97	nc	-0.471
98	na	-0.152
99	hc	0.087
100	hc	0.087
101	cc	0.007
102	cd	-0.281
103	hn	0.286
104	c3	-0.091
105	c3	0.073
106	hc	0.089
107	cd	0.315
108	hc	0.033
109	hc	0.033
110	c3	-0.305
111	nc	-0.585
112	na	0.021
113	hc	0.094
114	c3	0.222
115	cd	0.420
116	cc	0.130
117	cd	-0.469
118	hn	0.188
119	hc	-0.042
120	hc	-0.042
121	c3	-0.198

122	na	-0.206
123	nc	-0.467
124	hc	0.117
125	cd	0.326
126	c3	0.153
127	cd	-0.318
128	hn	0.288
129	cc	-0.015
130	nc	-0.538
131	na	-0.084
132	hc	0.002
133	hc	0.002
134	cc	0.076
135	cd	-0.380
136	hn	0.215
137	c3	-0.337
138	c3	0.025
139	hc	0.112
140	cd	0.406
141	hc	0.043
142	hc	0.043
143	c3	-0.232
144	nc	-0.453
145	na	-0.200
146	hc	0.089
147	c3	-0.010
148	cd	0.425
149	cc	-0.015
150	cd	-0.314
151	hn	0.299
152	hc	0.026
153	hc	0.026
154	c3	-0.008
155	na	-0.155
156	nc	-0.546
157	cd	0.385
158	cd	-0.375
159	hn	0.271
160	cc	0.055
161	nc	-0.479
162	na	-0.222

163	cc	0.009
164	cd	-0.313
165	hn	0.298
166	hc	0.039
167	c3	-0.092
168	hc	0.021
169	hc	0.021
170	hc	0.021
171	h4	0.211
172	h4	0.134
173	h4	0.229
174	h4	0.125
175	h4	0.215
176	h4	0.138
177	h4	0.227
178	h4	0.116
179	h4	0.220
180	h4	0.140
181	h4	0.246
182	h4	0.113
183	h4	0.188
184	h4	0.136
185	h4	0.216
186	h4	0.138
187	h4	0.188
188	h4	0.136
189	h4	0.246
190	h4	0.113
191	h4	0.220
192	h4	0.140
193	h4	0.227
194	h4	0.116
195	h4	0.215
196	h4	0.138
197	h4	0.229
198	h4	0.125
199	h4	0.211
200	h4	0.134

Table S3: Default and modified scaling factors for 1-4 electrostatic and 1-4 van der Waals interactions.

Interaction	scaling factors	
	default	modified
1-4 electrostatic	0.833	0.667
1-4 van der Waals	0.500	0.100

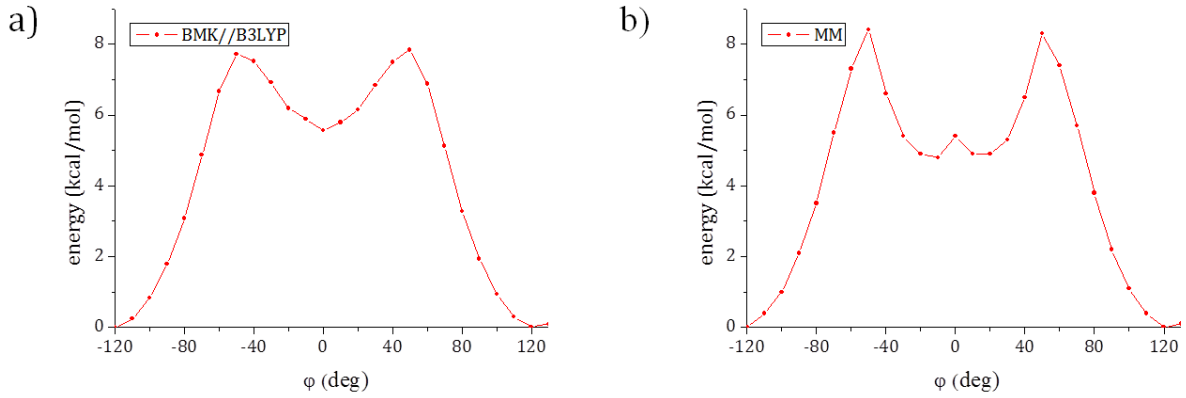

Figure S1. DFT (left) and MM (right) potential energy profile for the torsion around the dihedral angle φ_2. MM values have been obtained with the modified GAFF.

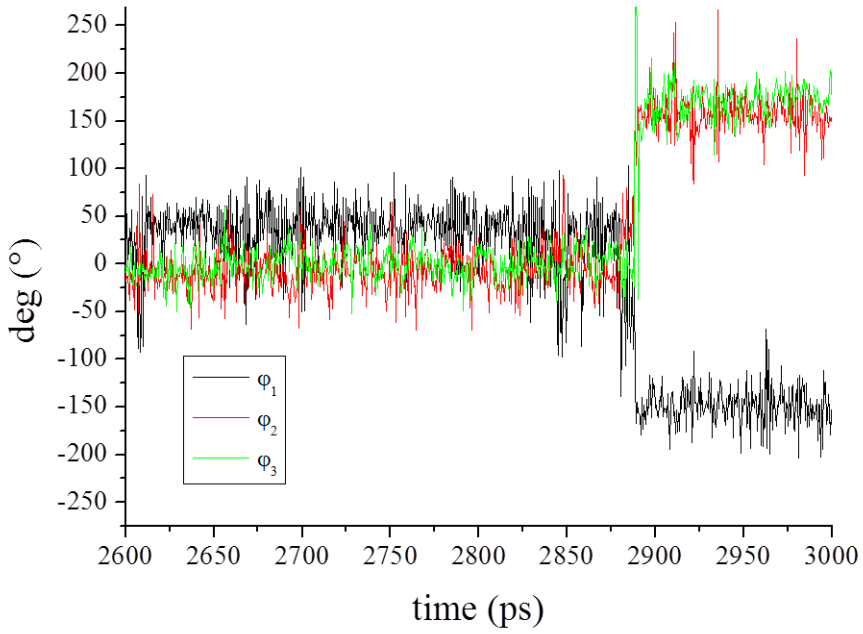

Figure S2. Time-dependent fluctuations of dihedral φ_1 φ_2 and φ_3 extracted from the 80-ns trajectory obtained for the 15*mer* at 453K.

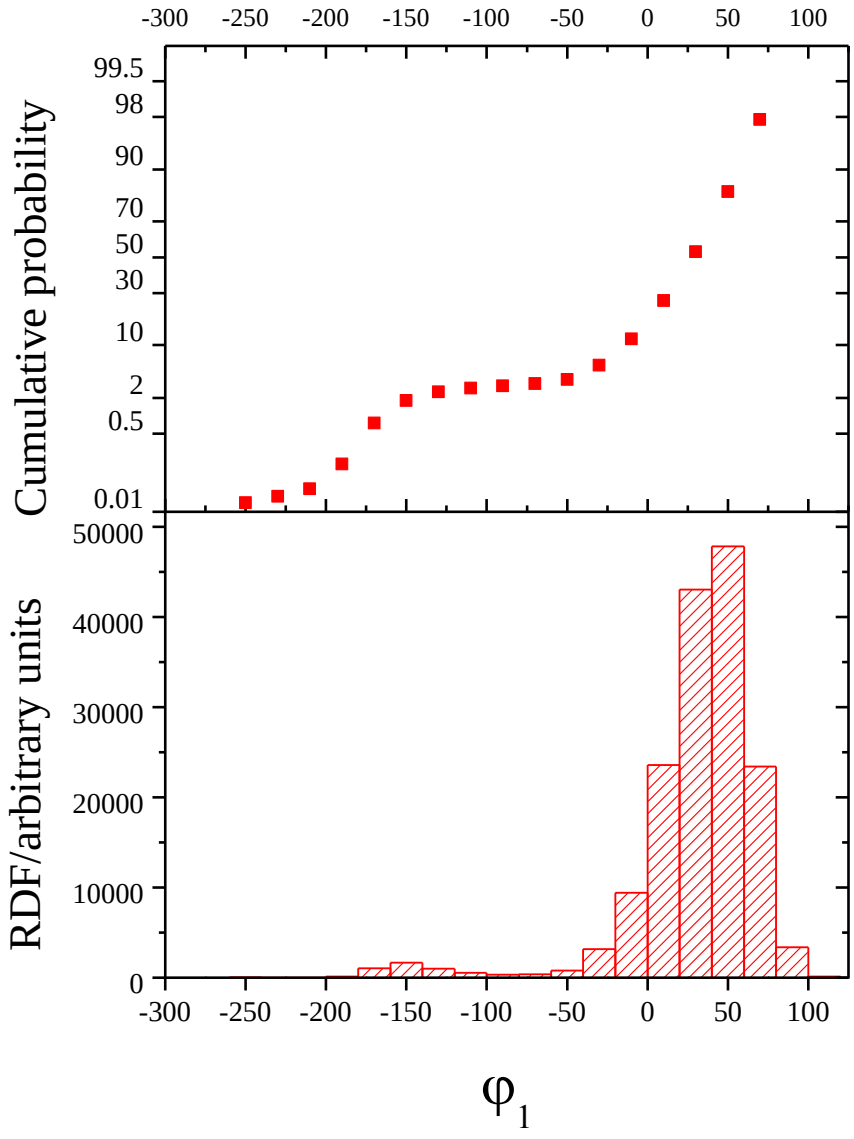

Figure S3. Distribution function and cumulative probability of φ_1 computed for the 80 ns trajectory. All the values are normalized so that the DFT optimized value is referred as φ_1=0.

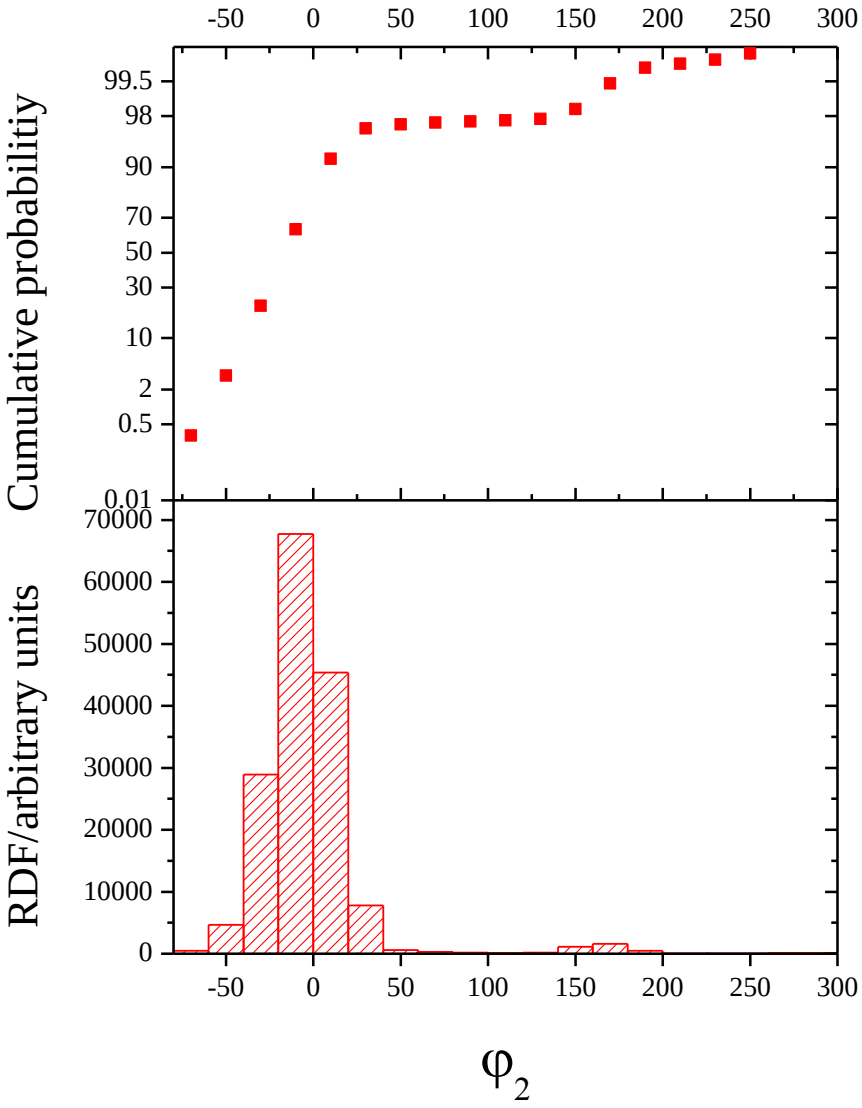

Figure S5. Distribution function and cumulative probability of φ_2 computed for the 80 ns trajectory. All the values are normalized so that the DFT optimized value is referred as φ_2=0.

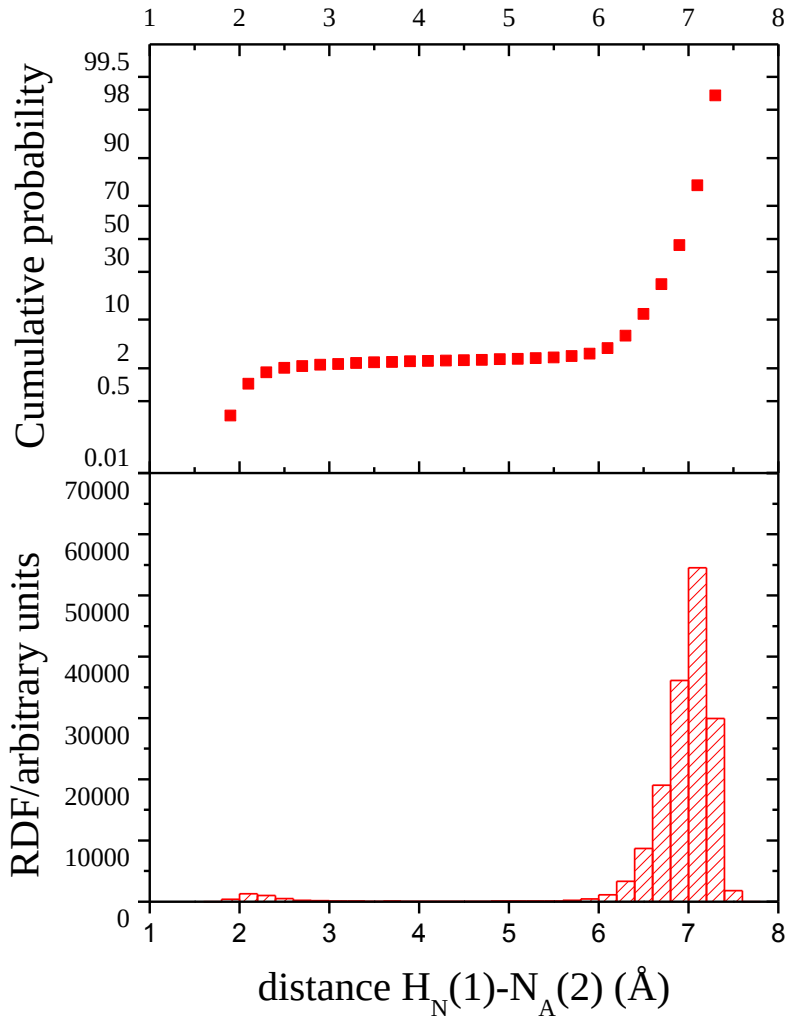

Figure 11. Distribution function and cumulative probability of the distance between the hydrogen bonded to the nitrogen atom of Im_1 ($H_N(1)$) and the acceptor nitrogen atom of Im_2 ($N_A(2)$) computed for the 80 ns trajectory.