Electronic Supplementary Information

Computational Study of DPAP Rotor in Various Environments: From Force Field Development to Molecular Dynamics Simulations and Spectroscopic Calculations

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1 Mean square displacement and Autocorrelation Function equations

Mean square displacement (*MSD*) has been calculated as:

$$MSD(t) = \lim_{t\to\infty} \langle [r(t_0 + t) - r(t_0)]^2 \rangle \tag{1}$$

where r has been considered as the position of the molecular center of mass at a particular time t.

ACF of a vector p has been computed as:

$$C_p(t) = \langle P_2(p(t_0) \cdot p(t_0 + t)) \rangle \tag{2}$$

where P_2 is the second order Legendre polynomial.

$$P_2(x) = \frac{1}{2}(3cos^2 x - 1) \tag{3}$$

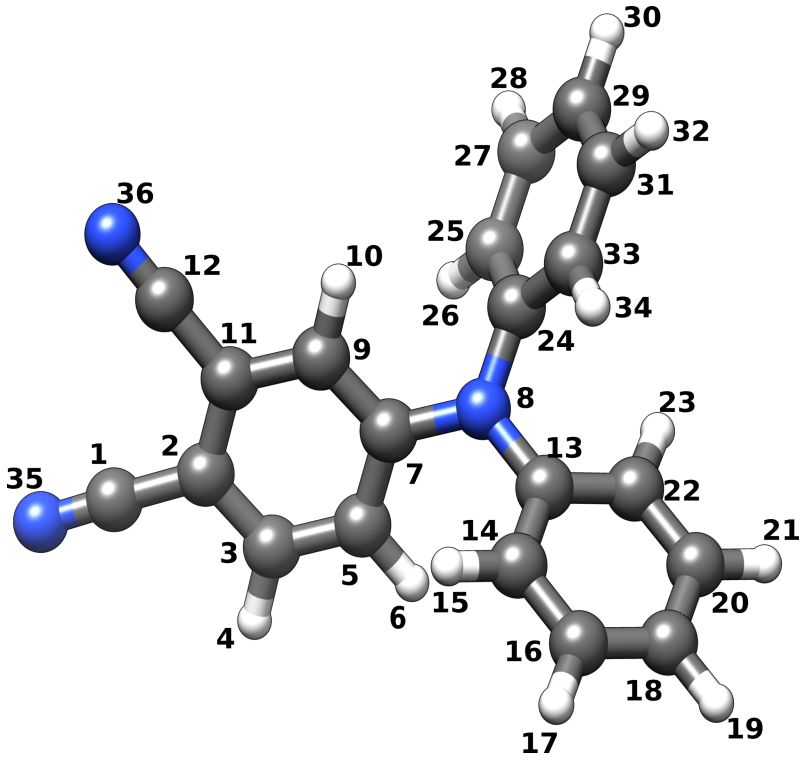

Figure S1: DPAP atom labeling used in Table S1 to Table S6.

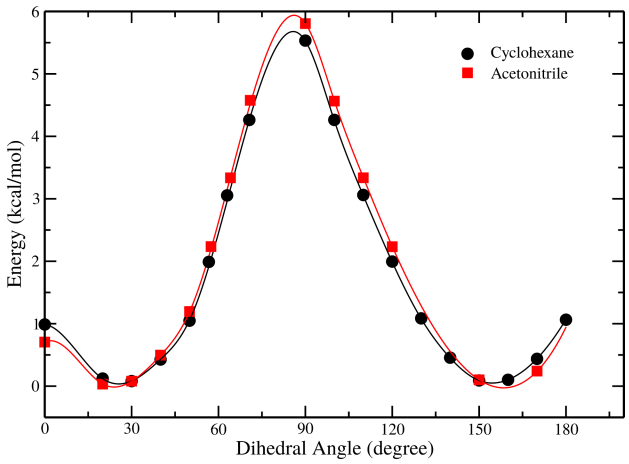

Figure S2: QM torsional profile for dihedral angle **1** in acetonitrile (red square dots and line) and in cyclohexane (black dots and line). Environment effects have been modeled by means of C-PCM.

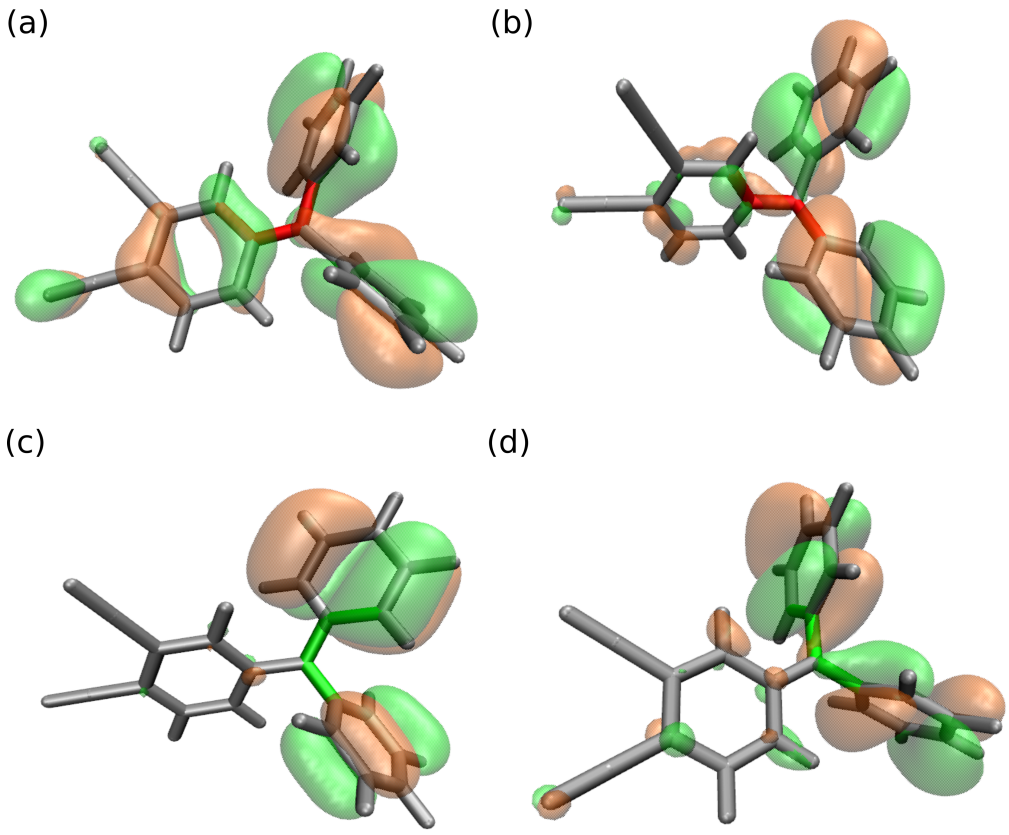

Figure S3: Representation of nitrogen aminic LP_1 orbital obtained from Natural Bond Orbital (NBO) analysis performed on four conformers: (a) dihedral angle **1** (colored in red) equal to 0°; (b) dihedral angle **1** equal to 90°; (c) dihedral angle **3** (colored in green) equal to 0°; (d) dihedral angle **3** equal to 90°.

Table S1: DPAP force field non-bonded parameters.

Non-bonded Parameters			
atom	σ (nm)	ϵ (kJ/mol)	charge
1	3.65000e-01	6.27600e-01	0.194079
2	3.55000e-01	2.92880e-01	0.001146
3	3.55000e-01	2.92880e-01	-0.063950
4	2.42000e-01	1.25520e-01	0.129524
5	3.55000e-01	2.92880e-01	-0.082391
6	2.42000e-01	1.25520e-01	0.120872
7	3.55000e-01	2.92880e-01	0.137370
8	3.30000e-01	7.11280e-01	-0.295163
9	3.55000e-01	2.92880e-01	-0.074139
10	2.42000e-01	1.25520e-01	0.123468
11	3.55000e-01	2.92880e-01	0.022105
12	3.65000e-01	6.27600e-01	0.207369
13	3.55000e-01	2.92880e-01	0.099989
14	3.55000e-01	2.92880e-01	-0.094065
15	2.42000e-01	1.25520e-01	0.114456
16	3.55000e-01	2.92880e-01	-0.096189
17	2.42000e-01	1.25520e-01	0.111658
18	3.55000e-01	2.92880e-01	-0.101147
19	2.42000e-01	1.25520e-01	0.109806
20	3.55000e-01	2.92880e-01	-0.096189
21	2.42000e-01	1.25520e-01	0.111658
22	3.55000e-01	2.92880e-01	-0.094065
23	2.42000e-01	1.25520e-01	0.114456
24	3.55000e-01	2.92880e-01	0.099678
25	3.55000e-01	2.92880e-01	-0.093872
26	2.42000e-01	1.25520e-01	0.114647
27	3.55000e-01	2.92880e-01	-0.095871
28	2.42000e-01	1.25520e-01	0.111831
29	3.55000e-01	2.92880e-01	-0.100695
30	2.42000e-01	1.25520e-01	0.110007
31	3.55000e-01	2.92880e-01	-0.095871
32	2.42000e-01	1.25520e-01	0.111831
33	3.55000e-01	2.92880e-01	-0.093872
34	2.42000e-01	1.25520e-01	0.114647
35	3.20000e-01	7.11280e-01	-0.400313
36	3.20000e-01	7.11280e-01	-0.382804

Table S2: DPAP force field stretching parameters.

Bonds			
ai	aj	r_{eq}(nm)	k^s (kJ/mol nm^2)
1	2	0.1424	325609.235
2	3	0.1403	317335.500
3	4	0.1085	334783.052
3	5	0.1384	327121.563
5	6	0.1083	334783.052
5	7	0.1413	281475.110
7	8	0.1388	265578.413
7	9	0.1411	281475.110
9	10	0.1083	334783.052
2	11	0.1415	230073.749
9	11	0.1391	317335.500
11	12	0.1433	325609.235
8	13	0.1434	265578.413
13	14	0.1400	281475.110
14	15	0.1086	334783.052
14	16	0.1394	327121.563
16	17	0.1086	334783.052
16	18	0.1397	327121.563
18	19	0.1086	334783.052
18	20	0.1396	327121.563
20	21	0.1086	334783.052
13	22	0.1399	281475.110
20	22	0.1395	327121.563
22	23	0.1086	334783.052
8	24	0.1434	265578.413
24	25	0.1400	281475.110
25	26	0.1086	334783.052
25	27	0.1394	327121.563
27	28	0.1086	334783.052
27	29	0.1397	327121.563
29	30	0.1086	334783.052
29	31	0.1397	327121.563
31	32	0.1086	334783.052
24	33	0.1399	281475.110
31	33	0.1395	327121.563
33	34	0.1086	334783.052
1	35	0.1164	1119383.487
12	36	0.1161	1119383.487

Table S3: DPAP force field bending parameters.

Angles				
ai	aj	ak	θ_{eq}(degr)	k$^{\theta}$(kJ/mol rad^2)
1	2	3	120.53	826.0873
1	2	11	121.41	392.6911
2	1	35	179.60	242.1940
2	3	4	119.28	357.5271
2	3	5	121.17	306.8322
3	2	11	118.07	490.1432
4	3	5	119.55	323.8368
3	5	6	119.08	323.8368
3	5	7	121.15	716.7162
6	5	7	119.76	286.0881
5	7	8	121.35	608.1875
5	7	9	117.91	425.4345
8	7	9	120.75	608.1875
7	8	13	121.13	338.8713
7	8	24	121.20	338.8713
7	9	10	120.15	286.0881
7	9	11	120.82	478.0010
10	9	11	119.03	357.5271
2	11	9	120.88	490.1432
2	11	12	120.29	392.6911
9	11	12	118.82	826.0873
11	12	36	179.93	242.1940
8	13	14	120.38	608.1875
8	13	22	119.83	608.1875
13	8	24	117.67	338.8713
13	14	15	119.72	286.0881
13	14	16	119.97	716.7162
14	13	22	119.78	425.4345
15	14	16	120.31	323.8368
14	16	17	119.50	323.8368
14	16	18	120.33	603.0479
17	16	18	120.17	323.8368
16	18	19	120.18	323.8368
16	18	20	119.62	603.0479
19	18	20	120.20	323.8368
18	20	21	120.15	323.8368
18	20	22	120.33	603.0479
21	20	22	119.51	323.8368
13	22	20	119.97	716.7162
13	22	23	119.65	286.0881
20	22	23	120.38	323.8368
8	24	25	120.36	608.1875
8	24	33	119.84	608.1875
24	25	26	119.72	286.0881
24	25	27	119.96	716.7162
25	24	33	119.79	425.4345

26	25	27	120.32	323.8368
25	27	28	119.50	323.8368
25	27	29	120.32	603.0479
28	27	29	120.17	323.8368
27	29	30	120.18	323.8368
27	29	31	119.63	603.0479
30	29	31	120.19	323.8368
29	31	32	120.15	323.8368
29	31	33	120.33	603.0479
32	31	33	119.51	323.8368
24	33	31	119.96	716.7162
24	33	34	119.65	286.0881
31	33	34	120.39	323.8368

Table S4: DPAP force field stiff torsional parameters.

Stiff Dihedrals					
ai	aj	ak	al	ξ_{eq}	k^{ξ}(kJ/mol)
11	2	3	4	-179.3	79.017
11	2	3	5	-0.1	88.959
35	1	2	3	1.8	0.001
1	2	11	12	0.7	105.609
2	3	5	6	-179.3	32.981
3	2	11	9	0.0	97.751
4	3	5	7	179.2	61.357
3	5	7	9	0.1	35.342
6	5	7	9	179.5	67.394
5	7	9	11	-0.2	60.572
8	7	9	10	-0.8	31.209
7	9	11	2	0.2	22.464
10	9	11	2	-179.2	79.017
9	11	12	36	13.8	0.001
8	13	14	16	-179.3	179.055
8	13	22	20	178.6	179.055
13	14	16	17	179.9	61.357
22	13	14	16	-0.7	35.342
14	13	22	23	-179.9	67.394
15	14	16	18	-179.0	87.040
14	16	18	20	-0.2	73.958
17	16	18	19	0.4	30.534
16	18	20	21	-179.9	87.040
19	18	20	22	179.8	87.040
18	20	22	13	0.5	48.999
21	20	22	23	-0.1	30.534
33	24	25	26	179.0	67.394
8	24	33	34	-1.2	31.209
24	25	27	28	179.9	61.357
8	24	25	27	-179.3	179.055
25	24	33	31	0.1	35.342
26	25	27	29	-178.9	87.040
25	27	29	30	179.6	87.040
28	27	29	31	-179.4	87.040
27	29	31	33	-0.4	73.958
30	29	31	32	0.3	30.534
29	31	33	24	0.5	48.999
32	31	33	34	-0.1	30.534

Table S5: DPAP force field improper dihedral angles parameters.

Improper Dihedrals					
ai	aj	ak	al	ξ_{eq}	k^{ξ}(kJ/mol)
2	1	3	11	-0.0	52.740
5	2	4	3	0.5	275.811
7	3	6	5	0.4	268.761
9	5	8	7	-0.1	541.118
8	7	13	24	0.0	28.016
11	7	10	9	-0.4	210.894
12	2	9	11	-0.4	22.646
13	8	14	22	0.8	541.118
16	13	15	14	-0.1	253.992
18	14	17	16	-0.5	245.364
20	16	19	18	-0.1	245.364
22	18	21	20	0.3	245.364
23	13	20	22	-0.0	345.666
24	8	25	33	0.8	541.118
27	24	26	25	-0.2	253.992
29	25	28	27	-0.5	245.364
31	27	30	29	-0.1	245.364
33	29	32	31	0.3	245.364
34	24	31	33	-0.0	345.666

Table S6: DPAP force field flexible torsional parameters.

Flexible Dihedrals						
ai	aj	ak	al	γ	k^{ϕ}(kJ/mol)	n
5	7	8	13	0.00	0.324	3
5	7	8	13	0.00	-4.632	2
5	7	8	13	0.00	2.880	4
9	7	8	24	0.00	0.324	3
9	7	8	24	0.00	-4.632	2
9	7	8	24	0.00	2.880	4
13	8	24	25	0.00	3.642	2
13	8	24	25	0.00	2.707	4
13	8	24	25	0.00	-0.015	3
7	8	24	33	0.00	3.642	2
7	8	24	33	0.00	2.707	4
7	8	24	33	0.00	-0.015	3
7	8	13	22	0.00	3.642	2
7	8	13	22	0.00	2.707	4
7	8	13	22	0.00	-0.015	3
24	8	13	14	0.00	3.642	2
24	8	13	14	0.00	2.707	4
24	8	13	14	0.00	-0.015	3

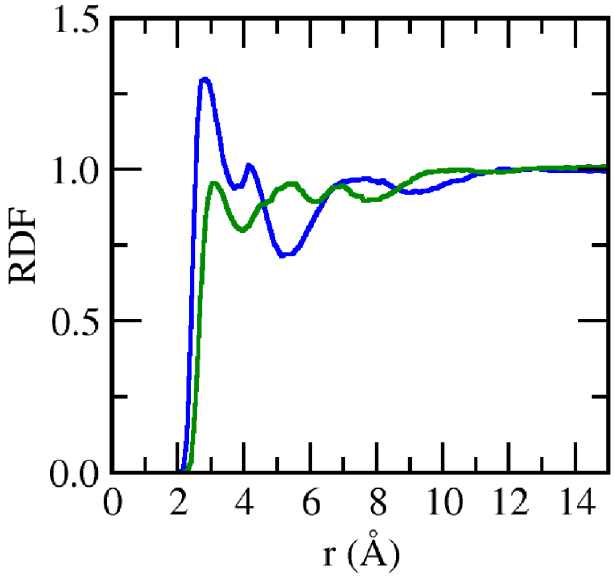

Figure S4: Radial distribution functions between DPAP (cyano) N and acetonitrile H atoms (blue) or cyclohexane H atoms (green).

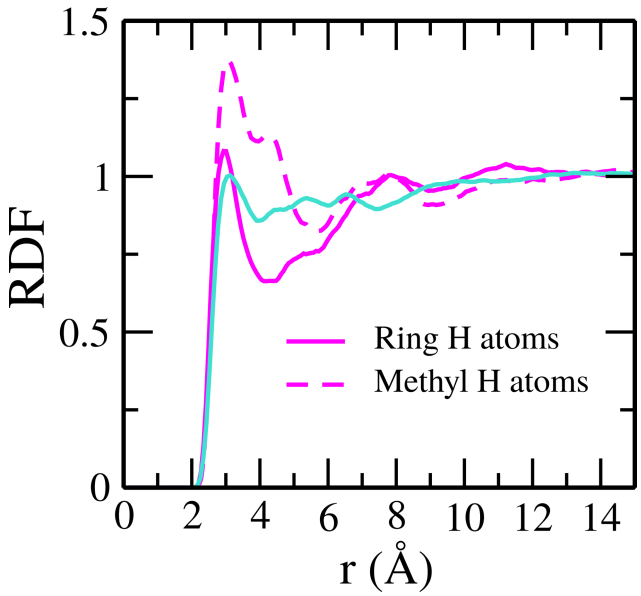

Figure S5: Radial distribution functions between DPAP (cyano) N and tetrahydrofuran H atoms (cyan) or *o*-xylene H atoms (magenta). For *o*-xylene H atoms are divided in ring H atoms (solid magenta line) and methyl H atoms (dashed magenta line).

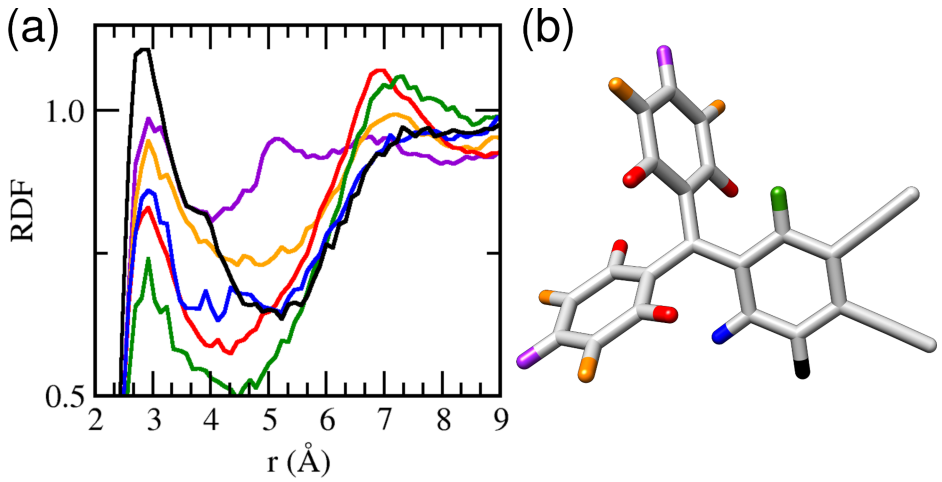

Figure S6: (**a**) Radial distribution functions computed between different H atoms on DPAP and N atom on acetonitrile. Each H atom, and corresponding distribution, is highlighted following the color scheme depicted in (**b**).

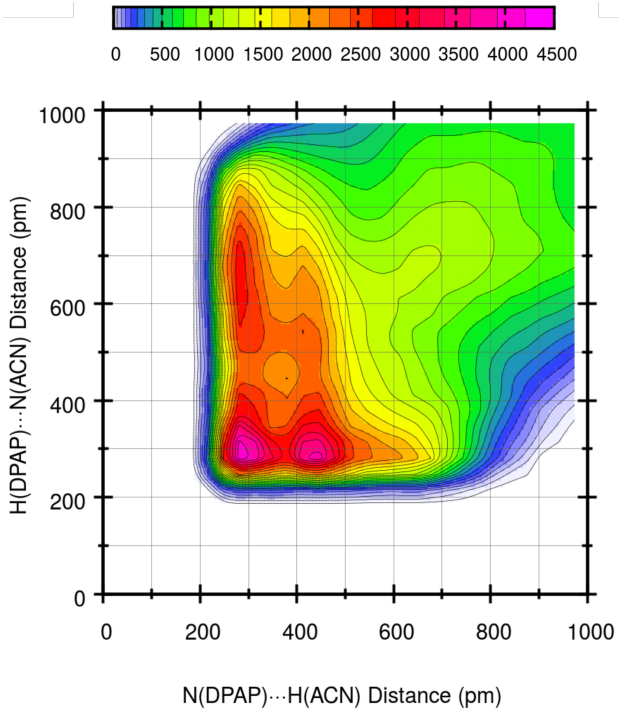

Figure S7: Combined distribution function between the rdf N(DPAP)$\cdots$H(ACN) (N(DPAP) are the nitrogen atoms of the two cyano substituents) and H(DPAP)$\cdots$N(ACN) (the H(DPAP) is colored in black in Figure S6).

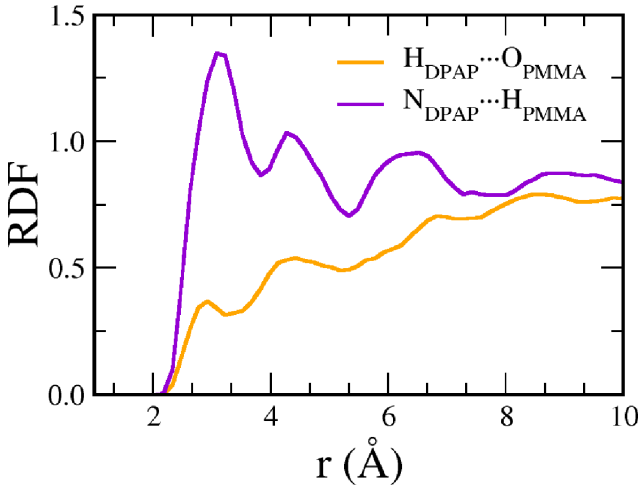

Figure S8: Radial distribution functions computed between DPAP H atoms and PMMA (carbonyl) O atoms (orange) and DPAP (cyano) N and PMMA (methyl) H atoms (violet).

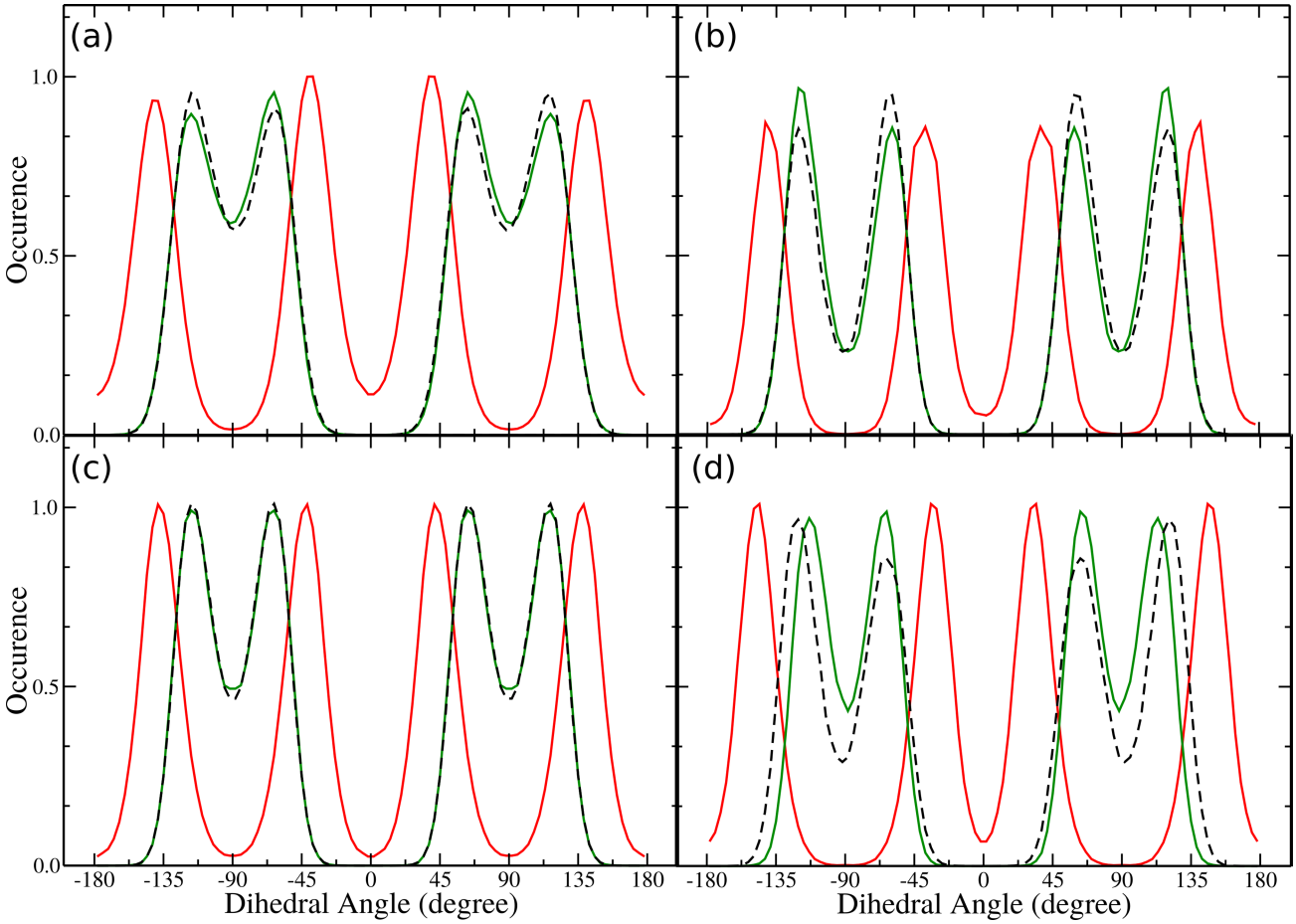

Figure S9: Dihedral distribution function of the three dihedral angles: in solid red line dihedral angle **1**, in black dashed line dihedral angle **2** and in solid green line dihedral angle **3** in the four environments. **(a)** ACN. **(b)** Cyclohexane. **(c)** Hydrated 1,2-dioleoyl-*sn*- glycero-3-phosphocholine (DOPC) lipid bilayer. **(d)** Poly(methyl methacrylate) polymeric matrix. (Note that the distributions have been symmetrized for the sake of comparison). In Figure Figure S10 the not symmetrized distribution fon DPAP in ACN is shown.

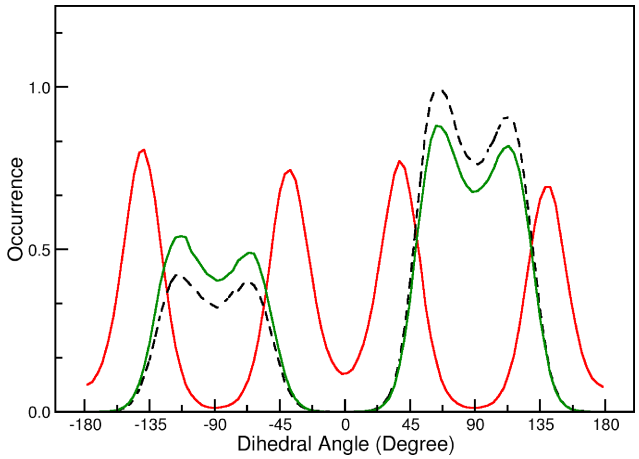

Figure S10: Dihedral distribution function of the three dihedral angles: in solid red line dihedral angle **1**, in black dashed line dihedral angle **2** and in solid green line dihedral angle **3** in ACN. Distribution not symmetrized.

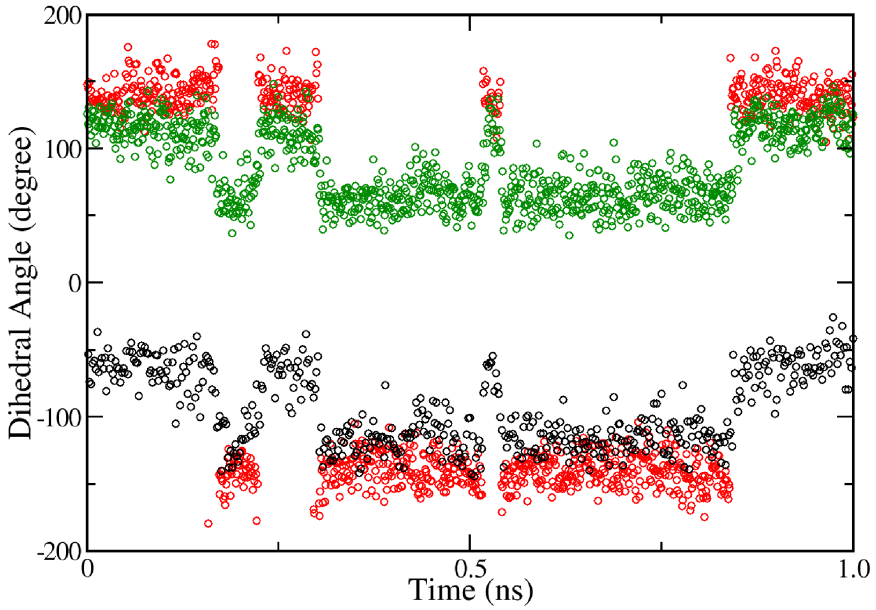

Figure S11: Time dependent dihedral angle distribution function in cyclohexane (in red results for dihedral angle **1**, in black for dihedral angle **2** and in green for dihedral angle **3**). The first ns of simulation is reported.

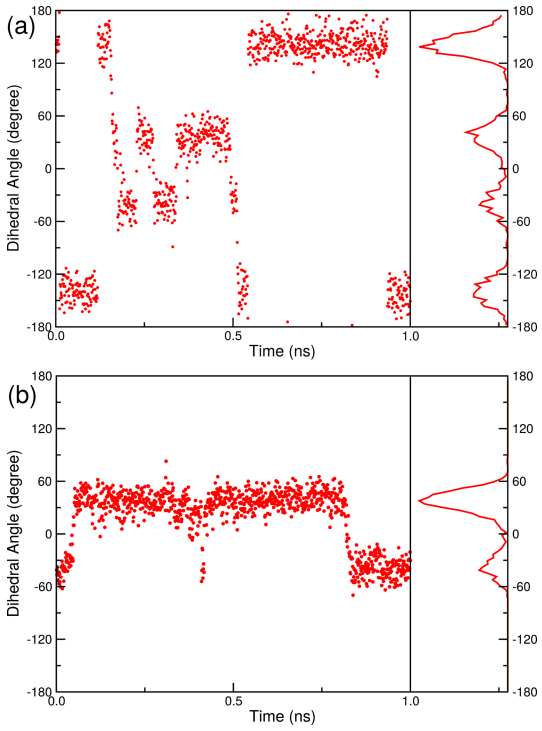

Figure S12: Time dependent dihedral distribution function for dihedral angle **1** for the first ns of simulation in tetrahydrofuran **(a)** and *o*-xylene **(b)**.

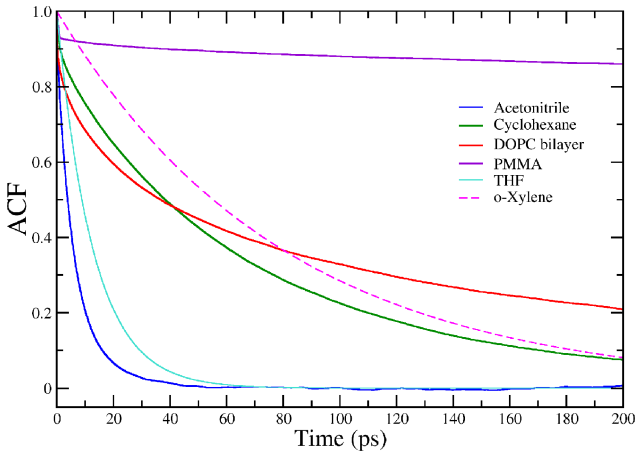

Figure S13: Autocorrelation function calculated considering a vector perpendicular to the ring 1 (Figure 2).

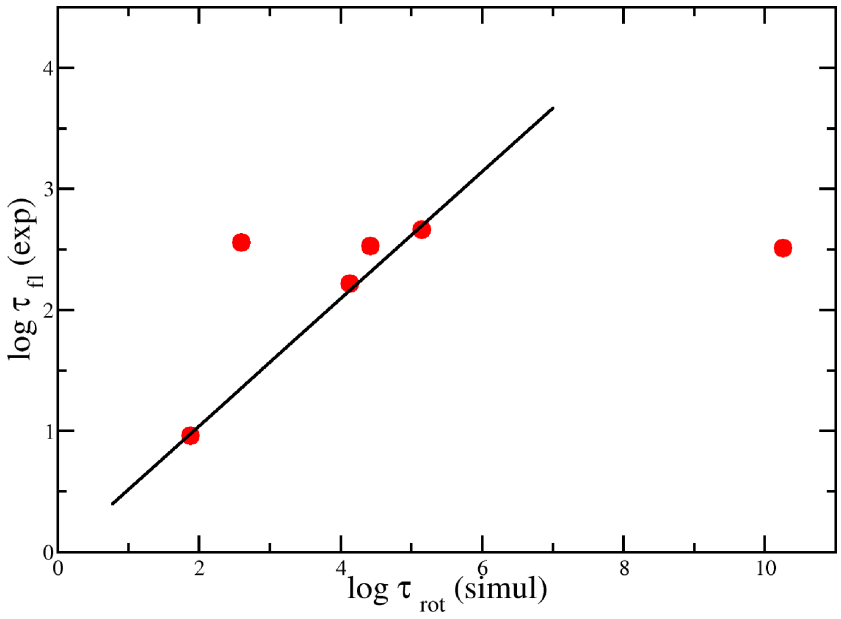

Figure S14: Correlation between DPAP rotational correlation time (ps) and fluorescence lifetimes (ns) in the four considered environments.

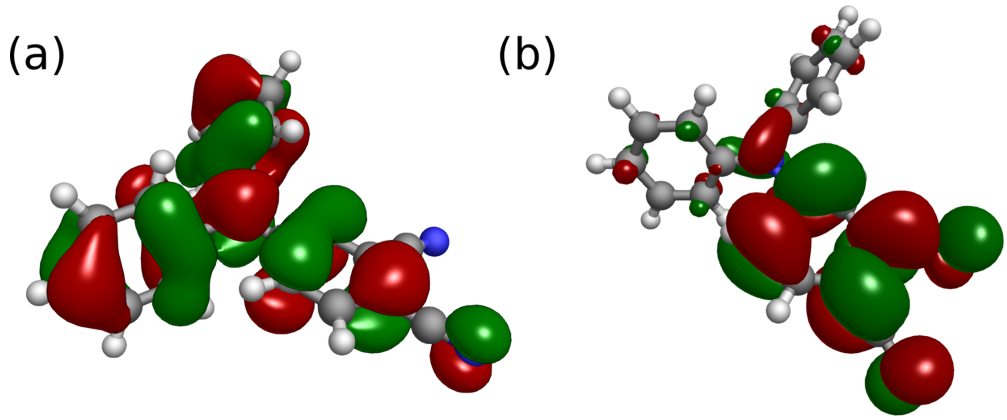

Figure S15: Isodensity surface (0.02 a.u.) plots of key molecular orbital of DPAP involved in the electronic excitations. (a) HOMO; (b) LUMO.

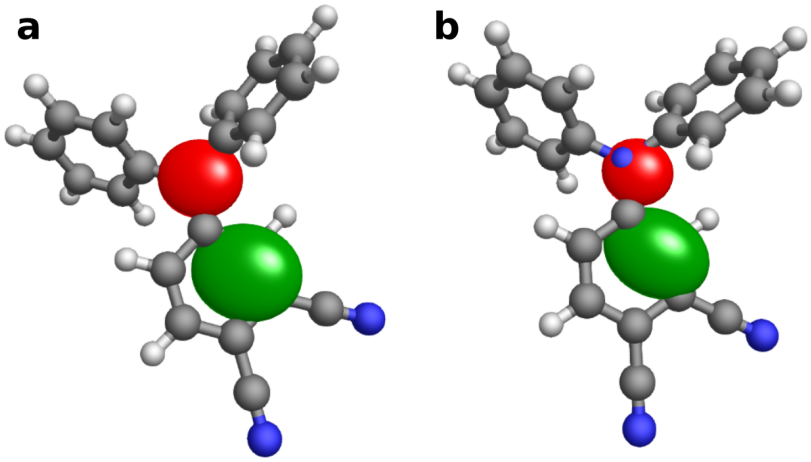

Figure S16: Graphical representation of centroids of charge (green: positive, red: negative) for DPAP in acetonitrile **(a)** and in cyclohexane **(b)**.

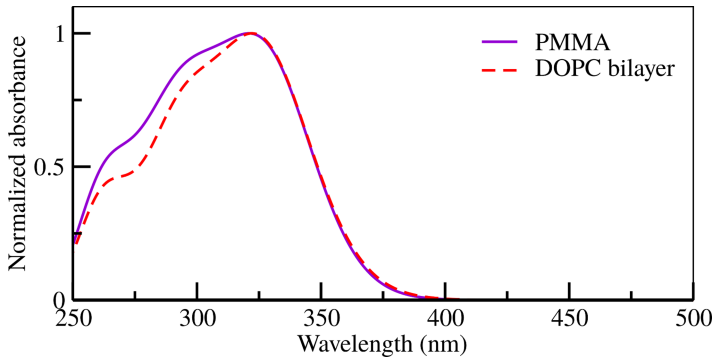

Figure S17: Absorption spectra of DPAP in membrane (red) and in PMMA (violet line) using PCM as environment model.