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Supplementary Information

Convenient Solvatochromic Probes for the Determination of Solvent Properties: β-Carotene and 2-Chloro-7-nitro-9*H*-fluorene

Omar A. El Seoud,* Paulo A. R. Pires, Carina Loffredo, Muhammad Imran, Paolo D. Pulcini, Michelle F. Corrêa and Rizwana Mustafa

Institute of Chemistry, University of São Paulo, CP 26077, 05513-970 São Paulo-SP, Brazil

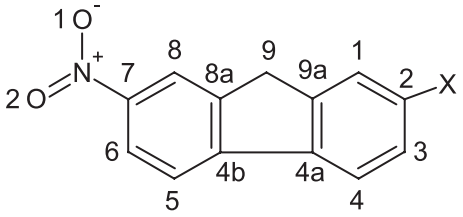

Figure S1. Numbering of the heavy atoms of the nitrofluorene halo-compounds. X = F or Cl.

Table S1. Frequencies of the absorption maximum of the longest wavelength transitions, $\tilde{\nu}_{max}$ of FNF, ClNF and DMANF, and the corresponding solvent dipolarity/polarizability (SDP)

No.	Solvent	$\tilde{\nu}_{max;FNF;Exp}$ / cm^{-1} [a,b]	$\tilde{\nu}_{max;ClNF;Exp}$ / cm^{-1} [c]	$\tilde{\nu}_{max;DMANF;Exp}$ / cm^{-1} [a,b]	$(SDP)_{FNF}$ [a,b]	$(SDP)_{ClNF}$ [c]
	gas	32923	32522	28231	0	0
	Aliphatic and alicyclic hydrocarbons					
1	1-pentane	31056	30901	25290	0.507	0.513
2	1-hexane	30984	30839	25191	0.519	0.528
3	1-heptane	30931	30784	25125	0.526	0.532
4	1-octane	30888	30735	25047	0.542	0.543
5	1-nonane	30840	30712	24978	0.552	0.561
6	1-decane	30807	30685	24925	0.562	0.571
7	1-dodecane	30764	30641	24863	0.571	0.578
8	1-pentadecane	30708	30605	24792	0.578	0.592
9	1-hexadecane	30731	30621	24814	0.578	0.590
10	2,2,4-trimethylpentane	30984	30905	25163	0.533	0.564
11	cyclohexane	30764	30629	24891	0.557	0.563
	Halogenated compounds					
12	dichloromethane	29812	29786	23263	0.876	0.868
13	chloroform	29763	29743	23405	0.786	0.796
14	tetrachloromethane	30544	30398	24513	0.632	0.620
15	1,2-dichloroethane	29836	29772	23258	0.89	0.865
16	2,2,2-trifluoroethanol	29441	29451	22824	0.908	0.909
17	1-chlorobutane	30449	30364	23984	0.837	0.813
18	1-bromoethane	–	30088	23716[e]	–	0.810
19	1-bromobutane	–	30107	23807[e]	–	0.781
20	1-bromohexane	–	30184	23929[e]	–	0.764
21	1-bromooctane	–	30257	23989[e]	–	0.769
22	1-bromodecane	–	30449	24023[e]	–	0.830
23	1-bromododecane	–	30880	24119[c]	–	0.961

*e-mail: elseoud@iq.usp.br

Table S1. continuation

No.	Solvent	$\tilde{\nu}_{max;FNF;Exp}$ / cm^{-1} [a,b]	$\tilde{\nu}_{max;ClNF;Exp}$ / cm^{-1} [c]	$\tilde{\nu}_{max;DMANF;Exp}$ / cm^{-1} [a,b]	$(SDP)_{FNF}$ [a,b]	$(SDP)_{ClNF}$ [c]
			Aromatic compounds			
24	benzene	30019	29953	23913	0.667	0.680
25	toluene	30028	29988	23947	0.655	0.681
26	xylenes	30120	30065	24123	0.616	0.642
27	anisole	29775	29768	23339	0.823	0.832
28	tetralin	29944	29908	23836	0.668	0.693
29	chlorobenzene	29726	29701	23288	0.824	0.825
30	nitrobenzene	29290	29280	22463	1.008	0.982
			Nitriles			
31	acetonitrile	30091	30104	23502	0.895	0.899
32	benzonitrile	29417	29398	22693	0.959	0.939
			Aliphatic and cyclic ethers			
33	1,4-dioxane	30296	30219	24118	0.701	0.704
34	THF	30181	30164	23712	0.838	0.841
35	diethyl ether	30751	30646	24589	0.694	0.687
36	di(1-butyl) ether	30733	30615	24659	0.652	0.648
37	1-butyl methyl ether	30669	30579	24504	0.695	0.694
38	bis (2-methoxyethyl) ether	30051	30029	23547	0.855	0.852
			Carboxylic acid amides			
39	DMF	29652	29645	22939	0.954	0.939
40	DMAC	29651	29673	22902	0.97	0.965
			DMSO and pyridine			
41	DMSO	29368	29419	22557	1.000	1.000
42	pyridine	29528	29518	22883	0.922	0.912
			Alcohols			
43	methanol	30302	30282	23795	0.857	0.854
44	ethanol	30365	30318	23865	0.853	0.841
45	1-propanol	30290	30235	23802	0.847	0.833
46	1-butanol	30338	30253	23873	0.837	0.813
47	1-pentanol	30342	30265	23918	0.817	0.800
48	1-hexanol	30333	30241	23923	0.81	0.788
49	1-octanol	30366	30274	24009	0.785	0.768
50	2-propanol	30315	30304	23825	0.848	0.851
51	2- butanol	30357	30295	23880	0.842	0.826
52	2-methylpropan-2-ol	30403	30369	23955	0.829	0.826
53	3-methylbutan-1-ol	30387	30335	23970	0.814	0.807
54	2-pentanol	30344	30267	23984	0.787	0.775
55	2-hexanol	30402	30368	23916	0.847	0.841
56	2-octanol	30383	30291	24025	0.786	0.768
57	cyclopentanol	30048	30035	23522	0.865	0.864
58	cyclohexanol	30139	30069	23652	0.847	0.827
59	ethylene glycol	29626	29612	22959	0.932	0.919
60	allyl alcohol	29972	29945	23426	0.875	0.867
			Miscellaneous compounds			
61	hexamethylphospho-triamide	29481	29446	22815	0.932	0.910
62	triethylamine	30823	30750	24824	0.617	0.636
63	acetic acid	30298	30258	23950	0.781	0.785
64	2-butanone	30106	30025	23548	0.881	0.850

Table S1. continuation

No.	Solvent	$\tilde{\nu}_{max;FNF;Exp}$ / cm^{-1} [a,b]	$\tilde{\nu}_{max;ClNF;Exp}$ / cm^{-1} [c]	$\tilde{\nu}_{max;DMANF;Exp}$ / cm^{-1} [a,b]	$(SDP)_{FNF}$ [a,b]	$(SDP)_{ClNF}$ [c]
			Carboxylic acid esters			
65	methyl acetate	30400	30292	24044	0.785	0.761
66	1-propyl acetate	30396	30291	24047	0.782	0.760
67	1-butyl acetate	30420	30302	24067	0.784	0.756
68	2-propyl acetate	–	30197	23867	–	0.793
69	di(1-butyl) phthalte	–	29955	23316	–	0.913
70	propylene carbonate	29721	29665	23059	0.930	0.900
71	methyl formate	30323	30198	23927	0.804	0.770
72	ethyl acetate	30423	30376	24047	0.795	0.793
73	ethyl propionate	30396	30328	24064[d]	0.774	0.767
74	ethyl butyrate	–	30395	24140[d]	–	0.764
75	ethyl pentanoate	–	30375	24170[d]	–	0.744
76	ethyl hexanoate	–	30362	24187[d]	–	0.733
77	ethyl decanoate	–	30329	24209[d]	–	0.711
78	ethyl dodecanoate	–	30297	24263[d]	–	0.678
			2-Alkoxyethanols			
79	2-methyloxyethanol	–	29919	23368[d]	–	0.879
80	2-ethyloxyethanol	–	30054	23522[d]	–	0.872
81	2-(1-propyloxy)ethanol	–	30075	23572[d]	–	0.860
82	2-(1-butyloxy)ethanol	–	30109	23635[d]	–	0.849
83	2-(1-pentyloxy)ethanol	–	30086	23655[d]	–	0.832
84	2-(1-hexyloxy)ethanol	–	30149	23756[d]	–	0.817
85	2-(1-octyloxy)ethanol	–	30214	23930[d]	–	0.775
86	2-(1-decyloxy)ethanol	–	30288	24050[d]	–	0.757
87	2-(1-tetradecyloxy)ethanol	–	30305	24248[d]	–	0.687
			Carboxylic acid anhydrides			
88	acetic anhydride	30025	29985	23384[d]	0.897	0.880
89	propionic anhydride	–	30045	23555[d]	–	0.871
90	butanoic anhydride	–	30001	23527[d]	–	0.849
91	pentanoic anhydride	–	29927	23597[d]	–	0.793
92	hexanoic anhydride	–	29181	23618[d]	–	0.495
			Ionic liquids[e]			
93	AlMeImCl	–	29030	22230[c]	–	0.976
94	AlBuImCl	–	29080	22398[c]	–	0.930
95	AlHxImCl	–	29109	22552[d]	–	0.881
96	AlHpImCl	–	29130	22589[d]	–	0.875
97	AlOcImCl	–	29147	22658[d]	–	0.855
98	AlDcImCl	–	29178	22813[d]	–	0.807

[a]Data taken from literature.[2] [b]Data taken from literature.[3] [c]Present work. [d]Data taken from literature.[4] [e]The acronyms of ionic liquids stand for 1-allyl-3-(1-alkyl)imidazolium chlorides, where Me, Bu, Hx, Hp, Oc, and Dc stand for methyl, 1-butyl, 1-hexyl, 1-heptyl, 1-octyl and 1-decyl, respectively.

Table S2. Theoretically calculated Gibbs free energy of solvation, $\Delta G_{Solvation}$, and values of the frequency of maximum absorption, $\tilde{\nu}_{max}$, for FNF and ClNF

entry	Solvent	FNF			ClNF		
		$\Delta G_{Solvation}$ / (kcal mol^{-1})	$\tilde{\nu}_{max}$ / cm^{-1}	$\Delta\tilde{\nu}_{max}$ / %	$\Delta G_{Solvation}$ / (kcal mol^{-1})	$\tilde{\nu}_{max}$ / cm^{-1}	$\Delta\tilde{\nu}_{max}$ / %
1	methanol	–7.83	26377	12.95	–8.64	26190	13.51
2	ethanol	–8.57	26503	12.72	–9.41	26315	13.20
3	1-propanol	–8.45	26500	12.51	–9.30	26311	13.06
4	1-butanol	–8.22	26512	12.61	–9.08	26322	12.99
5	1-hexanol	–7.96	26564	12.43	–8.84	26371	12.73
6	1-octanol	–7.61	26621	12.33	–8.50	26424	12.72
7	1-decanol	–7.11	26714	–	–8.00	26511	–
8	nitromethane	–10.12	27228	8.73	–10.86	27031	–
9	cyanomethane	–10.83	27254	9.43	–11.59	27056	10.13
10	1-cyanopropane	–11.51	27343	9.07	–12.30	27141	–
11	1-cyanobutane	–11.74	27378	–	–12.55	27175	–
12	1,4-dioxane	–6.75	28142	7.11	–7.69	27857	7.82
13	THF	–10.57	27555	8.70	–11.42	27333	9.39
14	acetone	–11.12	27343	9.28	–11.94	27139	–
15	DMSO	–8.05	27300	7.04	–8.82	27103	7.87
16	DMF	–9.78	27299	7.94	–10.60	27101	8.58
17	heptane	–10.08	28299	8.51	–11.06	27999	9.05
18	cyclohexane	–12.01	27608	10.26	–12.88	27380	10.61
19	CH_2Cl_2	–12.33	27314	8.38	–13.21	27105	9.00
20	$CHCl_3$	–11.44	27420	7.87	–12.39	27194	8.57
21	CCl_4	–11.38	28099	8.00	–12.41	27816	8.49
22	$ClCH_2$-CH_2Cl	–11.37	27262	8.63	–12.23	27056	9.12
23	benzene	–10.95	28047	6.57	–12.01	27768	7.30
Gas phase							
24		–	29630	10.00	–	29216	10.34

For each probe $\Delta\tilde{\nu}_{max} = 100\dfrac{\tilde{\nu}_{max;Exp} - \tilde{\nu}_{max;Theo}}{\tilde{\nu}_{max;Exp}}$, where Exp. and Theo are experimental and theoretical values, respectively. Values of $\tilde{\nu}_{max;Exp}$ are listed in Table S1 in the SI section.

Table S3. Optimized bond lengths, angles and dihedrals of 2-fluoro-7-nitrofluorene (FNF) and 2-chloro-7-nitrofluorene (ClNF), calculated by DFT using B3LYP/6-311G(d,p) followed by B3LYP/CC-pVDZ and X-ray experimental data of fluorene (see heavy atom numbering in Figure S1). For the three molecules, the ring structure is planar

Bond	Bond / cm		
	FNF	ClNF	Fluorene[a]
C1–C2	1.395	1.399	1.388
C2–C3	1.397	1.401	1.383
C3–C4	1.396	1.396	1.391
C4–C4a	1.400	1.400	1.391
C4a–C4b	1.467	1.467	1.491
C4b–C5	1.401	1.401	1.391
C5–C6	1.395	1.395	1.391
C6–C7	1.399	1.399	1.383
C7–C8	1.400	1.400	1.388
C8–C8a	1.388	1.388	1.397
C8a–C9	1.514	1.514	1.504
C9–C9a	1.513	1.514	1.505
C9a–C1	1.392	1.392	1.397
C2–X	1.349	1.758	–
C7–N	1.475	1.476	–
N–O1	1.227	1.227	–
N–O2	1.227	1.226	–
Bond	Angle / degree		
C1–C2–C3	122.8	121.9	122.0
C2–C3–C4	119.2	119.7	121.3
C3–C4–C4a	119.2	119.2	117.0
C4–C4a–C4b	131.0	131.1	130.1
C4a–C4b–C5	131.0	131.0	130.1
C4b–C5–C6	119.1	119.1	117.0
C5–C6–C7	119.3	119.3	121.3
C6–C7–C8	122.6	122.7	122.0
C7–C8–C8a	117.7	117.7	117.4
C8–C8a–C9	129.2	129.2	128.9
C8a–C9–C9a	102.7	102.7	102.7
C9–C9a–C1	129.1	129.0	128.9
C9a–C1–C2	117.6	118.1	117.4
C1–C2–X	118.6	119.0	–
C3–C2–X	118.6	119.1	–
C6–C7–N	118.8	118.7	–
C8–C7–N	118.6	118.6	–
C7–N–O1	117.5	117.5	–
C7–N–O2	117.7	117.7	–
O1–N–O2	124.8	124.8	–
Bond	Dihedral / degree		
C8–C7–N–O1	0.001	–0.005	–
C6–C7–N–O2	–0.001	–0.001	–
C8–C7–N–O1	0.001	–0.005	–

[a]Data taken from literature.[1]

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