Supporting Information for

Fluorosolvatochromism of furanyl- and thiophenyl-substituted acetophenones

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Content.

Table S1. Theoretically calculated HOMO-LUMO energy differences and experimentally measured UV/Vis absorption maxima of acetophenone derivatives.

R	HOMO-LUMO gap [eV][a]	$\tilde{\nu}_{\text{max, exp.}}$ [10^3 cm^{-1}][b]
H	5.212	41.49
OMe	5.007	37.31
thiophene	4.146	31.45
furan	4.045	31.45
2-cyanofuran	4.010	31.95
2-methoxyfuran	3.737	28.65

[a] Calculated at the B3LYP/def2TZVPP level of theory.
[b] Measured in dichloromethane.

Table S2. CATALÁN parameter set[S1–S3]

solvent	SA	SB	SP	SdP
gas phase	0	0	0	0
n-hexane	0	0.056	0.616	0
diethyl ether	0	0.562	0.617	0.385
tetrachloromethane	0	0.044	0.768	0
p-xylene	0	0.160	0.778	0.175
toluene	0	0.128	0.782	0.284
1,4-dioxane	0	0.444	0.737	0.312
ethyl acetate	0	0.542	0.656	0.603
tetrahydrofuran	0	0.591	0.714	0.634
acetone	0	0.475	0.651	0.907
hexamethylphosphoramide	0	0.813	0.744	1.100
N,*N*-dimethylacetamide	0.028	0.650	0.763	0.987
N,*N*-dimethylformamide	0.031	0.613	0.759	0.977
pyridine	0.033	0.581	0.842	0.761
dichloromethane	0.040	0.178	0.761	0.769
acetonitrile	0.044	0.286	0.645	0.974
trichloromethane	0.047	0.071	0.783	0.614
butyrolactone	0.057	0.399	0.775	0.945
dimethyl sulfoxide	0.072	0.647	0.830	1.000
anisole	0.084	0.299	0.820	0.543
1-decanol	0.259	0.912	0.722	0.383
2-propanol	0.283	0.830	0.633	0.808
1-butanol	0.341	0.809	0.674	0.655
1-propanol	0.367	0.782	0.658	0.748
ethanol	0.400	0.658	0.633	0.783
2,3-butanediol	0.461	0.652	0.714	0.877
1,2-propanediol	0.475	0.598	0.731	0.888
methanol	0.605	0.545	0.608	0.904
acetic acid	0.689	0.390	0.651	0.676
1,2-etanediol	0.717	0.534	0.777	0.910
2,2,2-trifluoroethanol	0.893	0.107	0.543	0.922
1,1,1,3,3,3-hexafluoro-2-propanol	1.011	0.014	–	–
water	1.062	0.025	0.681	0.997

Table S3. UV/Vis absorption and emission maxima, STOKES shift $\Delta\tilde{\nu}$ of **O1**, **O2**, **O3** and **S1** measured in 26 solvents of different polarity and hydrogen bond abilitiy.

solvent	**O1**			**O2**			**O3**			**S1**		
	10^3 cm^{-1}											
	$\nu_{max, abs}$	$\tilde{\nu}_{max, em}$	$\Delta\tilde{\nu}$	$\nu_{max, abs}$	$\tilde{\nu}_{max, em}$	$\Delta\tilde{\nu}$	$\nu_{max, abs}$	$\tilde{\nu}_{max, em}$	$\Delta\tilde{\nu}$	$\nu_{max, abs}$	$\tilde{\nu}_{max, em}$	$\Delta\tilde{\nu}$
n-hexane	32.26	–	–	29.67	24.63	5.04	32.47	22.78	9.69	32.26	23.53	8.73
Et_2O	32.15	23.87	8.28	29.33	24.04	5.29	32.36	22.68	9.68	32.15	23.09	9.06
tetra[a]	31.75	23.53	8.22	28.90	25.13	3.77	32.05	23.87	8.18	31.75	22.88	8.87
p-xylene	31.75	23.31	8.44	29.07	23.92	5.15	31.95	23.20	8.75	31.65	22.57	9.08
toluene	31.75	23.98	7.77	28.90	24.15	4.75	31.85	23.31	8.54	31.65	23.04	8.61
dioxane	31.95	23.20	8.75	29.15	23.75	5.40	32.05	23.31	8.74	31.85	22.88	8.97
EtOAc	31.95	23.58	8.37	29.15	23.31	5.84	32.26	23.87	8.39	31.95	22.78	9.17
THF[b]	31.85	23.64	8.21	28.90	23.53	5.37	31.85	22.32	9.53	31.75	22.62	9.13
acetone	30.12	21.97	8.15	28.99	22.73	6.26	30.30	23.04	7.26	30.21	22.27	7.94
HMPA[c]	29.15	24.04[j]	5.11	28.41	22.62	5.79	30.12	23.04	7.08	30.96	27.78[j]	3.18
DMAc[d]	31.35	22.94	8.41	28.74	22.22	6.52	31.95	22.83	9.12	31.45	21.83	9.62
DMF[e]	31.55	21.41	10.14	28.65	21.88	6.77	31.95	22.78	9.17	31.45	21.74	9.71
pyridine	31.35	–	–	28.41	22.68	5.73	31.75	22.99	8.76	31.06	23.58[j]	7.48
DCM[f]	31.45	23.09	8.36	28.65	22.94	5.71	31.95	23.36	8.59	31.45	22.17	9.28
acetonitrile	31.85	22.73	9.12	29.07	22.27	6.80	32.26	22.99	9.27	31.85	21.88	9.97
trichloro-methane	31.25	21.69	9.56	28.41	23.09	5.32	30.12 27.62	23.36	–	31.35	22.03	9.32
butyrolactone	31.45	21.41	10.04	28.74	22.17	6.57	31.95	22.88	9.07	31.65	21.65	10.00
DMSO[g]	31.25	22.37	8.88	28.57	21.79	6.78	31.75	22.37	9.38	31.25	21.46	9.79
anisole	31.45	22.52	8.93	28.65	23.09	5.56	31.75	23.20	8.55	31.35	22.52	8.83
2-propanol	31.35	24.69	6.66	28.41	21.51	6.90	32.47	22.27	10.20	31.55	24.39	7.16
1-butanol	31.25	24.45	6.80	28.33	21.37	6.96	32.36	21.98	10.38	31.45	24.21	7.24
1-propanol	31.45	24.15	7.30	28.33	21.28	7.05	32.26	21.88	10.38	31.45	23.98	7.47
ethanol	31.25	23.87	7.38	28.65	21.19	7.46	32.36	21.69	10.67	31.35	23.92	7.43
methanol	31.85	23.47	8.38	28.65	20.87	7.78	32.36	21.28	11.08	31.65	23.75	7.90
TFE[h]	31.15	22.99	8.16	28.41	21.05	7.36	32.15	20.70	11.45	31.35	23.36	7.99
water	30.86	22.47	8.39	38.17 28.65	22.42[j]	–	34.01	23.75[j]	10.26	31.35	22.83	8.52
1-decanol	–	–	–	–	–	–	30.21	22.73	7.48	–	–	–
1,2-ethane-diol	–	–	–	–	–	–	29.76	20.88	8.88	–	–	–
1,2-propane-diol	–	–	–	–	–	–	30.03	21.46	8.57	–	–	–
2,3-butane-diol	–	–	–	–	–	–	30.21	21.93	8.28	–	–	–
acetic acid	–	–	–	–	–	–	29.94	21.65	8.29	–	–	–
HFIP[i]	–	–	–	–	–	–	29.76	20.33	9.43	–	–	–

[a] tetrachloromethane, [b] tetrahydrofuran, [c] hexamethylphosphoramide, [d] *N*,*N*-dimethylacetamide, [e] *N*,*N*-dimethylformamide, [f] dichloromethane, [g] dimethyl sulfoxide, [h] 2,2,2-trifluoroethanol, [i] 1,1,1,3,3,3-hexafluoro-2-propanol, [j] was not included in LSER by CATALÁN. The last-mentioned solvents were only used for the LSER calculation of the compound **O3**.

Table S4. UV/Vis absorption and emission maxima, STOKES shift $\Delta\tilde{\nu}$ of **O1**, **O2**, **O3** and **S1** measured as powder.

compound	$\tilde{\nu}_{max, abs}$ (10^3 cm^{-1})	$\tilde{\nu}_{max, em}$ (10^3 cm^{-1})	$\Delta\tilde{\nu}$ (10^3 cm^{-1})
O1	28.90	–[a]	–
O2	28.41	19.08	9.33
O3	29.33 (25.25)[b]	20.58	8.75 (4.67)[b]
S1	28.82	21.50	7.32

[a] solid-state fluorescence was not observed.
[b] double band

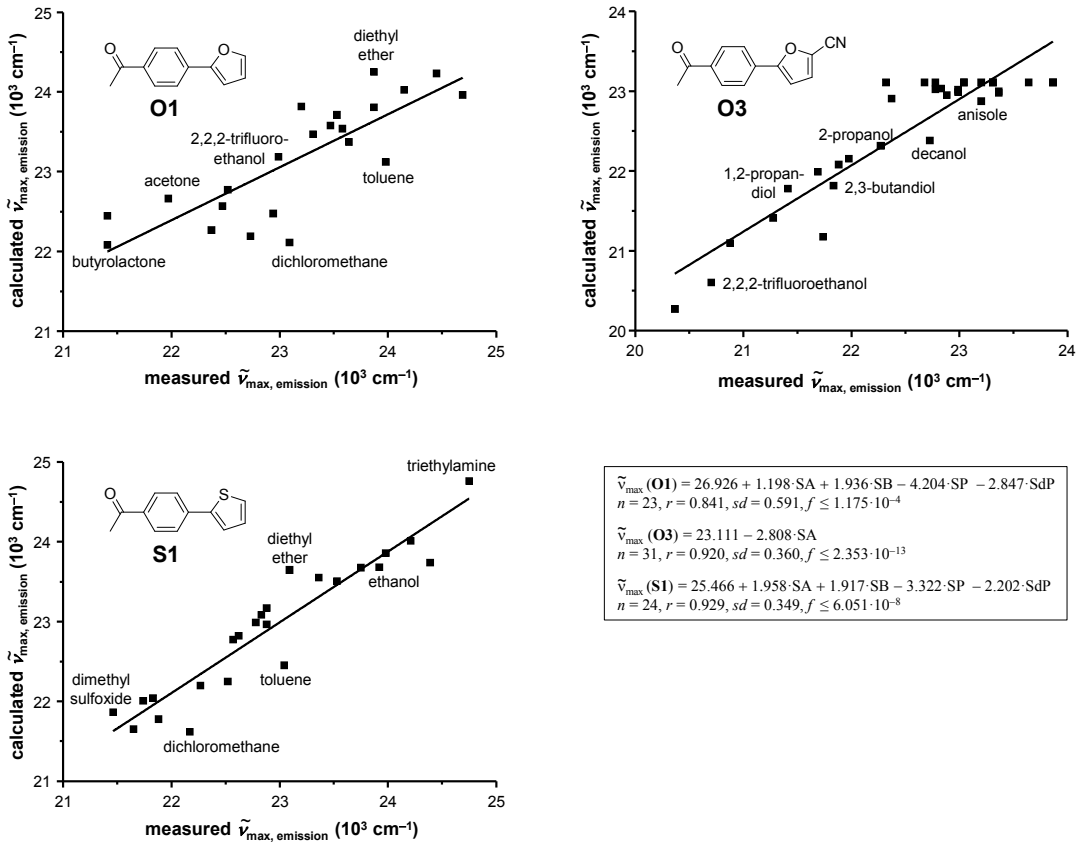

Figure S1. Linear solvation energy relationships for the emission of **O1**, **O3** and **S1** in various solvents. Plots of measured vs. calculated emission maxima, according to the CATALÁN equation, are shown.

References

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[S3] J. Catalán, C. Díaz, V. López, P. Pérez, J.-L. G. de Paz, J. G. Rodríguez, *Liebigs Ann.* **1996**, 1785–1794.