Supplementary Information

Anionic Chromogenic Chemosensors Highly Selective for Fluoride or Cyanide Based on 4-(4-Nitrobenzylideneamine)phenol

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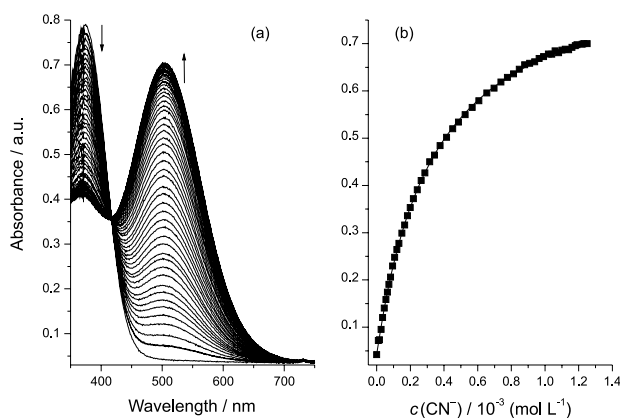An anionic chromogenic chemosensor based on an acid-base strategy

Figure S1. (a) Influence of the addition of increasing amounts of CN^- on the UV-Vis spectra of **2a** (5.0×10^{-5} mol L^{-1}) in acetonitrile with 1.4% (v/v) of water at 25 °C. The final concentration of CN^- was 1.22×10^{-3} mol L^{-1}; (b) curve of the variation in the absorbance at 504.0 nm of **2a** with the addition of increasing amounts of CN^-.
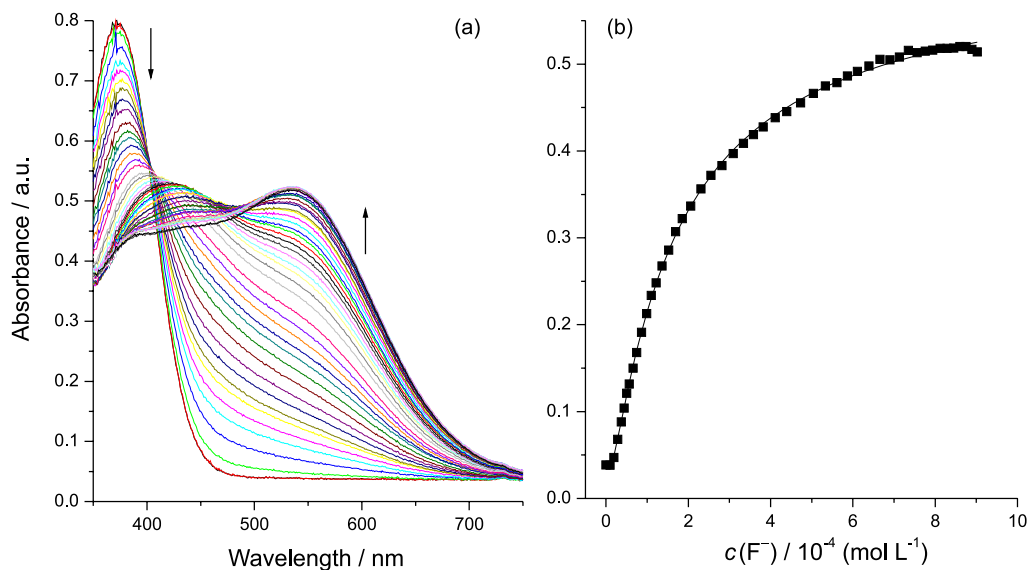

Figure S2. (a) Influence of the addition of increasing amounts of F^- on the UV-Vis set spectra of **2a** (5.0×10^{-5} mol L^{-1}) in acetonitrile at 25 °C. The final concentration of F^- was 9.02×10^{-4} mol L^{-1}; (b) curve of the variation in the absorbance at 547.0 nm of **2a** with the addition of increasing amounts of F^-.

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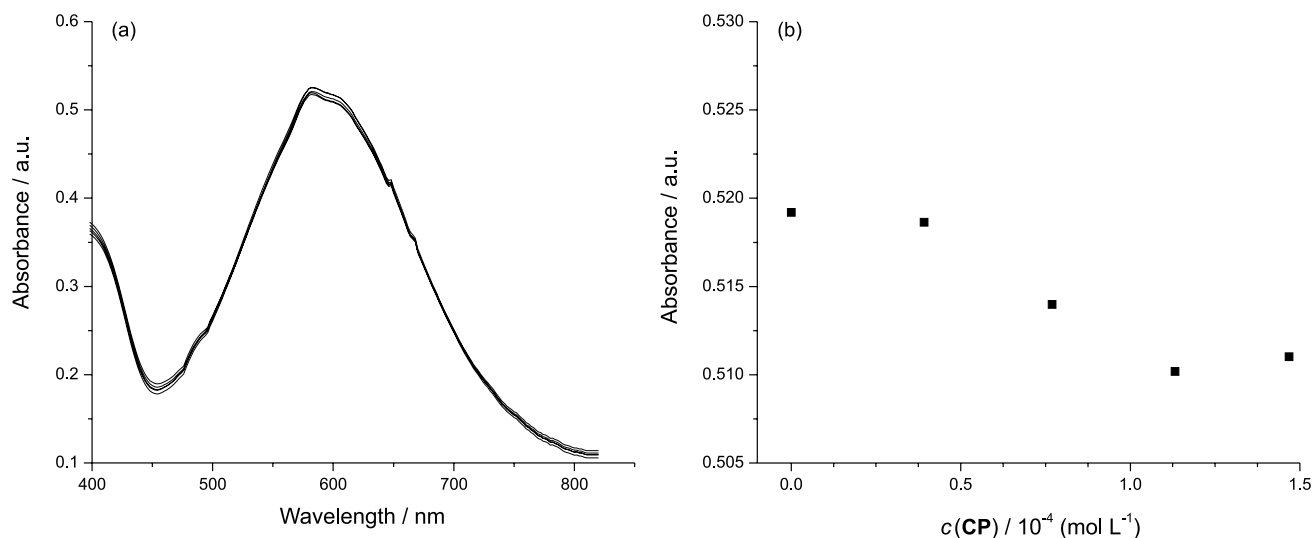An anionic chromogenic chemosensor based on a displacement assay

Figure S3. (a) UV-Vis spectra of **1b** (4.0×10^{-5} mol L^{-1}) in acetonitrile at 25 °C after addition of increasing amounts of **CP**. The final concentration of **CP** was 1.5×10^{-4} mol L^{-1}; (b) changes in the absorbance values at 582.0 nm as a function of the concentration of **CP**.

Determination of binding constant by displacement titration

The binding constant between **CP** and F$^-$ was estimated using the following equation[1–3] by plotting S_t/P as a function of Q:

$$c(F^-)_t/P = QK_I/K_{11} + 1,$$

where:

$$Q = (A - A_{CP-2b})/(A_I - A),$$
$$P = c(CP)_t - [1/QK_I] - [c(2b)_t/(Q + 1)],$$

K_I is the binding constant between **CP** and **2b** and K_{11} is the binding constant between **CP** and F$^-$

Table S1. Spectrophotometric study based on a displacement assay of **CP-2b**-F$^-$ System

$c(F^-)$ / 10^{-4} (mol L^{-1})	A_{obs}	Q	P / 10^{-4}	$c(F^-)_t$ / P
0.447	0.56	0.39	0.833	0.54
0.788	0.62	0.68	1.34	0.59
0.985	0.67	0.93	1.53	0.65
1.18	0.70	1.22	1.64	0.72
1.36	0.75	1.69	1.73	0.79
1.55	0.78	2.29	1.79	0.87
1.72	0.80	2.77	1.81	0.95
1.89	0.82	3.35	1.83	1.03
2.10	0.83	3.76	1.84	1.14

$A_{CP-2b} = 0.40$, $K_I = 1.85 \times 10^4$ L mol^{-1}
$A_I = 0.95$ $c(2b)_t = 4.0 \times 10^{-5}$ mol L^{-1}
$c(CP)_t = 1.90 \times 10^{-4}$ mol L^{-1}
$c(F^-)_t/P = (K_I/K_{11})*Q + 1$
$c(2b)_t$ = total concentration of **2b**
$Q = (A - A_{CP-2b})/(A_I - A)$
$c(F^-)_t$ = total concentration of F$^-$

A_I = absorbance of free **2b**
$c(CP)_t$ = total concentration of **CP**
A_{CP-2b} = absorbance of **CP-2b**
A = absorbance at given wavelength
K_{CP-2b} = binding constant of **CP-2b**
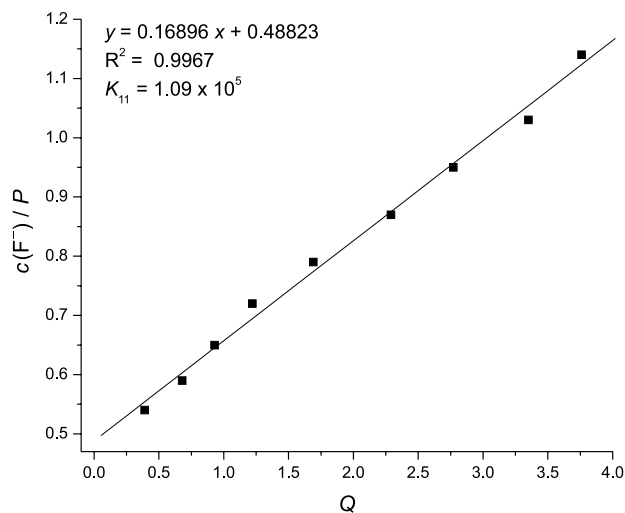K_{11} = binding constant of **CP**-F$^-$

Figure S4. Plot of $c(F^-)/P$ as a function of Q, used to estimate the K_{11} value for **CP**-F^- complex.
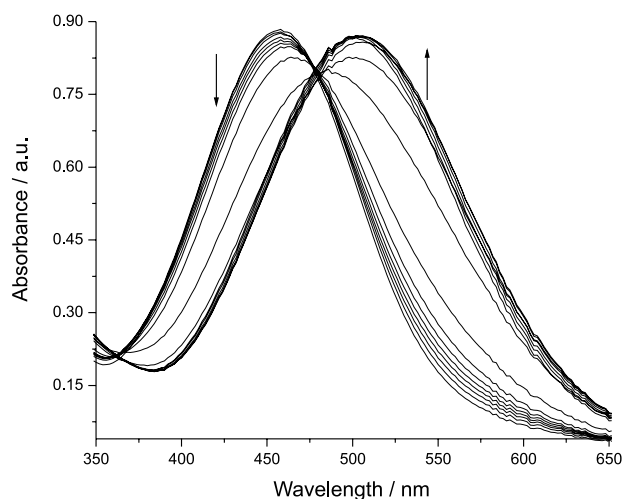

Figure S5. UV-Vis spectra of **CP**-**2b** in acetonitrile at 25 °C after addition of increasing amounts of water.
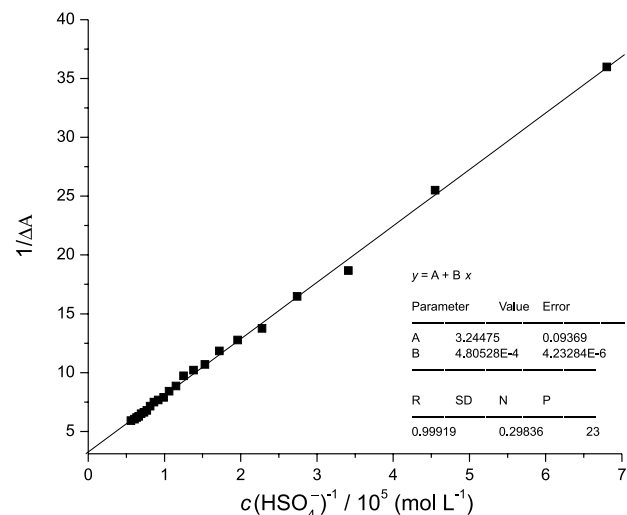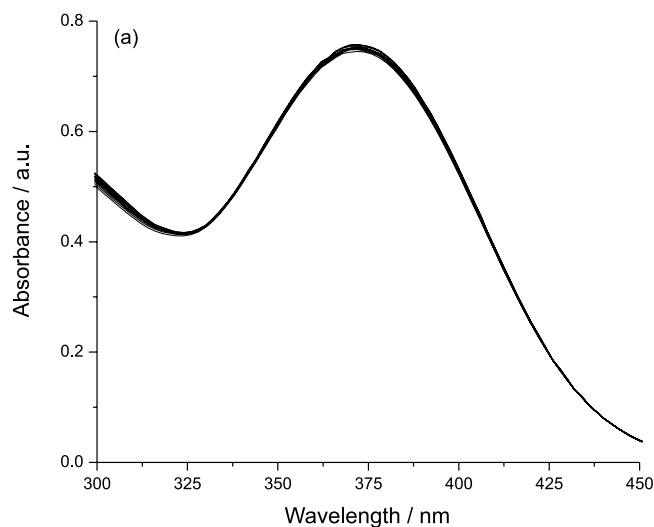

Figure S6. Titration of **2b** and HSO_4^- in acetonitrile at 25 °C. Absorbance values were collected at 456.0 nm and Benesi-Hildebrand treatment for the experimental data, fitted using equation 2.

Studies on the stability of **2a** in solution

Figure S7 shows UV-Vis spectra for **2a** and **2b** in acetonitrile at 50 °C over a period of 2 h. A significant change in the spectrum of the compound was not observed, indicating that the compound exhibits thermal stability. Figure S8 shows the influence of ambient light on the UV-Vis spectrum of **2a** (a) and **2b** (b) in acetonitrile at 25 °C. The spectra were recorded at 24 h intervals over a period of seven days and the data show that the deprotonated compound is more sensitive to the influence of light than **2a**: considering their maximum at the wavelength a reduction in the absorbance of only 5.1% occurred over a period of seven days for **2a**, while for **2b**, a reduction of 20.2% in the absorbance value was recorded.
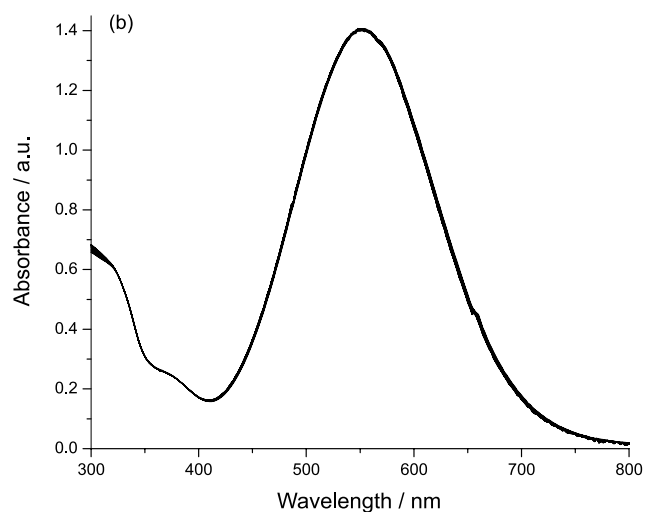

Figure S7. UV-Vis spectra of **2a** (a) and **2b** (b) in acetonitrile at 50 °C. The spectra were recorded at 10 min intervals over a period of 2 h.
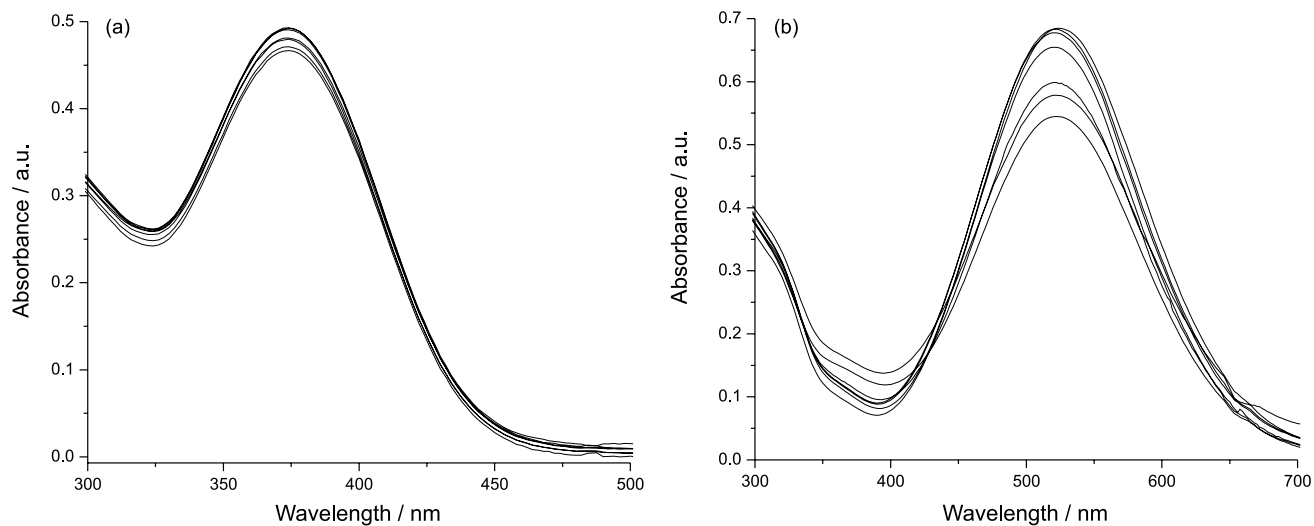
Figure S8. Study on the influence of ambient light on the stability of **2a** (a) and **2b** (b) in acetonitrile at 25 °C. The spectra were recorded at 24 h intervals over a period of seven days.

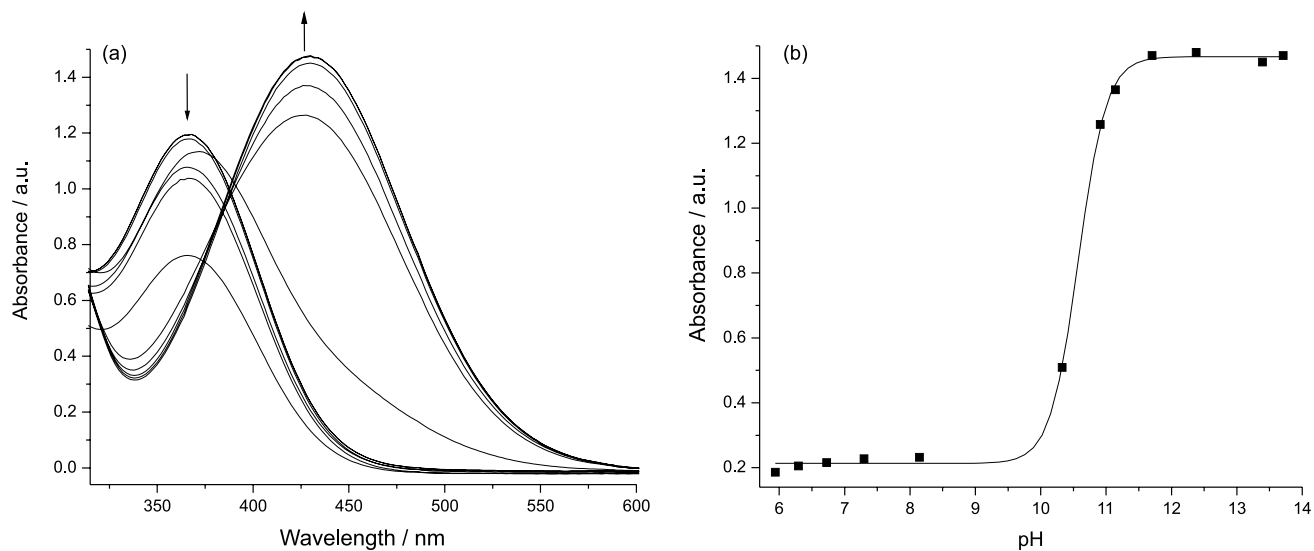## pKa value for **2a** in aqueous solution

Figure S9. (a) UV-Vis spectra of **2a** at increasing pH values and (b) absorbance values for **2a** at 430.0 nm as a function of pH. Data were fitted using a sigmoid equation to give a pKa value of 10.57 ± 0.01 (SD = 2.99×10^{-4} and $r^2 = 0.999$).

Relationship between pKa values in water and acetonitrile and in DMSO and acetonitrile

In order to verify whether the acidity of **2a** in acetonitrile matches the basicity of the anions responsible for its deprotonation, a study was carried out to estimate the pKa values for the species. The pKa values of various phenols in water and in acetonitrile were experimentally determined and compiled by Coleman and Murray[4] and Jover *et al.*[5] (Table S2). These data were used to obtain a plot of pKa values in acetonitrile as a function of pKa values in water (Figure S10) and a linear correlation was observed ($r^2 > 0.99$). The equation obtained (pKa (CH_3CN) = 1.68 pKa (water) + 9.80) was used to estimate (employing the pKa determined experimentally in water) the pKa value for **2a** in acetonitrile, which is equal to 27.6.

Considering the experimental problems that hinder the determination of pKa values of HCN and HF in
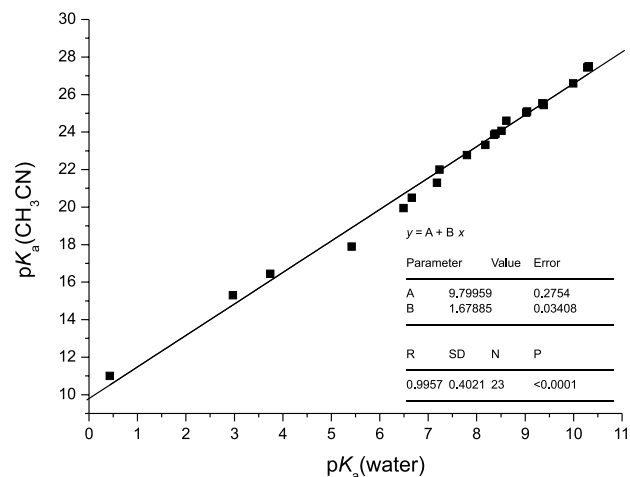

Figure S10. Correlation between the pKa values reported in the literature for phenols in acetonitrile and in water.

acetonitrile,[6,7] it was also tried to estimate the pKa values for these species using pKa values for different substances (inorganic acids and phenols) in acetonitrile and in DMSO (Table S3).[4,8,9] These data were used to construct a plot of the pKa values in DMSO as a function of pKa (CH_3CN), which is shown in Figure S11. The data could be correlated linearly ($r^2 > 0.96$) and were used to estimate the pKa values for HCN and HF through the following equation: pKa (CH_3CN) = 1.014 pKa (DMSO) + 10.017. The pKa values for HF and HCN in DMSO are 15.0 and 12.9,[6] respectively, while the estimated pKa value for HF in acetonitrile is 25.2 and for HCN is 23.1.

Table S2. pKa values for phenols in acetonitrile and water[a]

Compound	pKa (CH_3CN)	pKa (water)
2,4,6-Trinitrophenol	11.0	0.43
4-Chloro-2,6-dinitrophenol	15.3	2.97
2,6-Dinitrophenol	16.45	3.74
3,4-Dinitrophenol	17.90	5.42
3-Chloro-4-nitrophenol	19.95	6.49
3,5-Dinitrophenol	20.50	6.66
4-Nitrophenol	21.3	7.18
2-Nitrophenol	22.00	7.23
4-Cyanophenol	22.77	7.80
3,5-Dichlorophenol	23.31	8.18
3-Nitrophenol	23.85	8.36
2-Bromophenol	23.92	8.39
3,4-Dichlorophenol	24.06	8.51
3-Cyanophenol	24.6	8.61
3-Chlorophenol	25.04	9.02
3-Trifluoromethylphenol	25.1	9.04
4-Chlorophenol	25.44	9.38
4-Bromophenol	25.53	9.36
Phenol	26.6	9.99
4-Methylphenol	27.45	10.28
4-*Tert*-butylphenol	27.48	10.31
2-Methylphenol	27.50	10.31

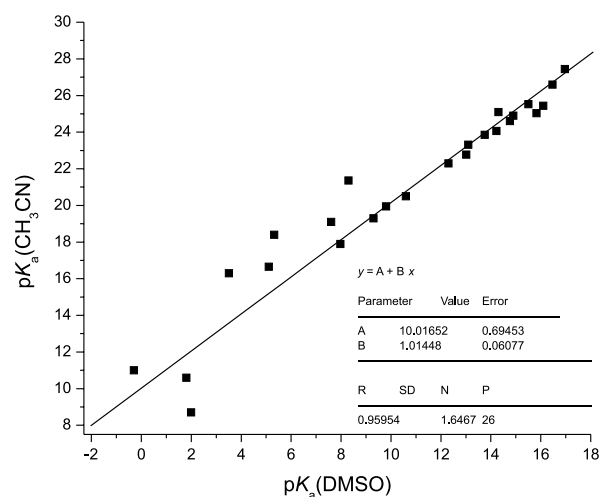[a]All values were obtained from references 4 and 5.

Figure S11. Correlation between the pKa values reported in the literature for some compounds in acetonitrile and in DMSO.

Table S3. pKa values for some compounds in acetonitrile and DMSO[a]

Compound	pKa (CH₃CN)	pKa (DMSO)
Hydrogen bromide	6.6	0.9
Sulfuric acid	8.7	1.99
Hydrogen chloride	10.6	1.8
2,4,6-Trinitrophenol	11	–0.3
4-Chloro-2,6-dinitrophenol	16.30	3.51
2,4-Dinitrophenol	16.66	5.1
3,4-Dinitrophenol	17.90	7.97
2,4-Dinitrophenol	18.4	5.32
2,6-Di-*tert*-butyl-4-nitrophenol	19.1	7.60
3-Trifluoromethyl-4-nitrophenol	19.30	9.30
3-Chloro-4-nitrophenol	19.95	9.80
3,5-Dinitrophenol	20.50	10.60
9-Cyanofluorene	21.36	8.3
Acetic acid	22.30	12.3
4-Cyanophenol	22.77	13.01
3,5-Dichlorophenol	23.31	13.09
3-Nitrophenol	23.85	13.75
3,4-Dichlorophenol	24.06	14.22
3-Cyanophenol	24.6	14.76
2-Chloro-4-phenylphenol	24.90	14.90
3-Chlorophenol	25.04	15.83
3-Trifluoromethylphenol	25.1	14.30
4-Chlorophenol	25.44	16.10
4-Bromophenol	25.53	15.5
Phenol	26.6	16.47
4-Methylphenol	27.45	16.96

[a]All values were obtained from references 8 and 9.

References

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