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Solvent-dependent steady-state fluorescence spectroscopy for searching ESPT-dyes: solvatochromism of HPTS revisited

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Received 23rd September 2008, Accepted 18th December 2008
First published as an Advance Article on the web 3rd February 2009
DOI: 10.1039/b816695a

Published on 03 February 2009 on http://pubs.rsc.org | doi:10.1039/B816695A
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We reinvestigated the solvatochromism of 8-hydroxypyrene-1,3,6-trisulfonate (pyranine) in conjunction with that of 8-methoxypyrene-1,3,6-trisulfonate and of 1-hydroxypyrene (pyrenol) by use of 25 different solvents. Conclusions for the prediction of ESPT behaviour of synthetic dyes were drawn by comparison with the solvatochromism of *p*-hydroxystyryl Bodipy dyes. Solvents were chosen according to their Kamlet–Taft parameters α and β for elucidating the acidicity of the dyes and the basicity of their conjugated bases in the ground and excited state. Comparison of the spectra of pyranine and pyrenol in solvents with varying β-values revealed that the acidity of both dyes is similar therein. The well-known ESPT behaviour of pyranine in water is assigned to a change of the electronic state at α-values $\sim$0.7 to 0.8. The high acidity of this excited state also appears in the vanishing solvatochromism of the photoproduct fluorescence. However, prediction of an ESPT tendency of synthetic dyes might fail when only fluorescence emission data are considered. We propose to refer instead to the energetic difference of the 0–0 transition *in absorption* together with the solvatochromism of the acidic form in aprotic solvents of similar polarity.

1. Introduction

Excited state proton transfer (ESPT) of 8-hydroxypyrene-1,3,6-trisulfonate (HPTS; pyranine) to water was first described by Förster[1,2] more than 50 years ago and is still the focus of scientific research.[3] This photochemical reaction exemplifies the more general case of various aromatic alcohols which undergo an increase of their acidity upon excitation (for reviews, see ref. 4–6). Naphthol and pyrene derivatives were especially thoroughly investigated in the past, but ESPT reactions were also detected in stilbene derivatives, fluorescent dyes and proteins.[7–11] ESPT is not limited to water as final acceptor but protonation of other solvents can be observed in super-photoacids.[5,12,13] One reason for the ongoing interest is that proton transfer reactions are the most basic chemical reactions with an overwhelming importance in many areas of chemistry. Especially helpful are ESPT systems where both substrate and product are fluorescent. Thus, triggering of these reactions with short excitation pulses allows for studies of the underlying photophysical mechanisms which precede the protolysis with time-resolved fluorescence spectroscopy.[3,10–18] Additionally, the fluorescent product states are long-living ($\sim$ns), and the kinetics of diffusion-controlled recombination processes also can be monitored by the same techniques.[6,18–20]

In most of the cited systems, excitation has to be performed in the UV or near-UV range. Ubiquitously excited background fluorescence, enhanced Raman scattering and the energy content of the absorbed photons make an observation of ESPT in ultrasensitive spectroscopy challenging. Even in cases, where ESPT could be initiated by near UV light, photodestruction and photoconversion counteract these experiments.[21,22] This deficiency of known molecules provokes our search for dye molecules which exhibit ESPT and strong visible fluorescence in both states. Though, straightforward and systematic synthetic work relies on a tool with which the synthetic direction can be confined and, finally, the ability of ESPT can be predicted. Steady-state fluorescence and UV-Vis spectroscopic signatures are most convenient in this approach as they can be applied to screening techniques.

The increase of acidity of a dye upon excitation can roughly be estimated by thermodynamics applied to optical spectroscopy. A red-shift in the lowest electronic transition of the conjugate base compared to the acidic form results in a change of the acidity constant pK_A according to

$$\Delta \mathrm{p}K_A \approx \frac{(h\nu_A - h\nu_B)}{kT \ln 10} \quad (1)$$

where ν_A and ν_B are the frequencies of 0–0 optical transitions of the acid and the base, respectively.[5,6] Time constants for proton transfer to solvent ought to be faster than the radiation emission, otherwise ESPT remains hidden. Therefore, kinetic parameters have to be converted to spectroscopic data to be useful in screening applications.

Such a more-kinetic approach is based on the analysis of spectroscopic data of aromatic alcohols, recorded in different solvents with varying hydrogen-bonding capability.[23–26] Most often, the Kamlet–Taft parameters α and β are used to describe the ability of a solvent to donate (α) or accept (β) a hydrogen-bond (HB).[24–29] Solvatochromism of a solute, *i.e.* the difference of the transition frequency ν_i to a reference transition frequency ν_{i0} in dependence of the solvent, then

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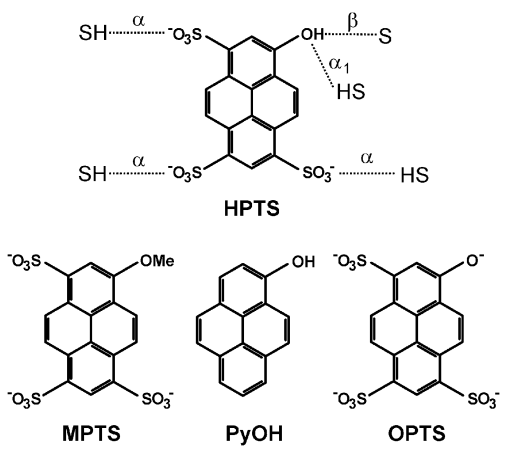
provides a tool to quantify the stabilization of the excited state with respect to the ground state. The index i describes whether properties of the ground state (i = exc) or the excited state (i = em) of the probe molecule are investigated.[6] This classification results from the different time scales of the instantaneous absorption/emission process and the subsequent rearrangement of nuclei. Eqn (2) comprehends solvatochromism in a mathematical way with π* as a measure of the dipolarity of the solvent.

$$\nu_i = \nu_{i0} + p_i\pi^* + b_i\beta + a_i\alpha \qquad (2)$$

a_i, b_i and p_i are parameters of the molecule under investigation. The latter value is related to the change of charge distribution within the molecule whereas the first two parameters characterize therein the acidity (a_i) and basicity (b_i) in the considered electronic state. Applied to HPTS, specific interactions like the HBs depicted in Scheme 1 can be probed in the respective electronic state if reference molecules like 1-hydroxypyrene (pyrenol, PyOH) and the methoxy-derivative of HPTS, 8-methoxypyrene-1,3,6-trisulfonate (MPTS), are at disposal.

Nonspecific dipolar solvation, which contributes to the Stokes-shift in systems with a considerable change of the static dipole moment, can be eliminated by comparison of the spectra of hydroxyl-arenes and their methoxy-derivatives (“differential solvatochromism”).[6,26,27] Only a few ESPT systems were investigated so far, but the known examples share a dependence of solvatochromic shifts on the solvents’ β-values. These shifts are more pronounced in fluorescence than in absorption and are explained by a stronger HB from the solute to the solvent in the excited state. This is not unexpected because proton release occurs along this coordinate.

ESPT can also be investigated from the product side, *i.e.* by inspecting solvatochromism of the conjugated base. All studied examples of naphtholate bases show that the excitation spectra are more affected by the solvent acidity than the emission spectra.[6] Again, this is reasonable as the basicity of the ESPT products is reduced compared to the ground state since the acidity of the photoacid is increased in the excited state.



Scheme 1 Structure of HPTS, its anionic form OPTS and the reference dyes MPTS and PyOH. HB between protic solvents (HS) and basic solvents (S) are probed by varying α- and β-values of the solvent. The effect of HB at the donor and the sulfonate-groups differs as indicated by the subscript.

The contribution of HB-donating, protic solvents to the stabilization of the excited state before ESPT is ambiguous.[24,26] In HPTS, a strong dependence of the red-shift in fluorescence on parameter α is observed, whereas in naphthol and its derivatives, only the spectral position of the excitation maximum is sensitive to α.[6] A recently accepted explanation resolves this discrepancy by ascribing the impact of α to charge stabilization at the sulfonate groups of HPTS in protic solvents.[24] Recent experiments with derivatives of HPTS show that strongly withdrawing substituents are necessary to enable charge transfer in the excited state.[13,14] As a consequence, HBs directly from solvent to the hydroxyl-moiety (α_1 in Scheme 1) therefore appear less important or even detrimental for the initial stages of ESPT. In conclusion, solvatochromism of fluorescent acids in solvents of varying β-values as well as solvatochromism of the conjugated base in solvents of varying α-values is promising in search of new ESPT dyes.

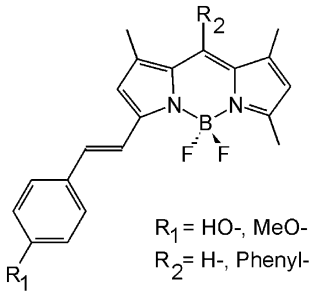
In our contribution, we reinvestigate the solvent dependence of spectra of paradigmatic HPTS and compare it to solvatochromism of its sulfonato-deficient derivative PyOH and its methoxy-derivative MPTS. To date, solvent variation of MPTS and HPTS was mainly performed with polar and protic solvents, of which the H-bond donating capability exerted a stronger effect on spectroscopic band position and shape of the solute than their HB accepting power.[16,23,30,31] Multiparameter fitting according to eqn (2) was used to extract the values of a_i and b_i.[24] However, when the assumed linearity in the energetics is no longer maintained, such analyses are misleading. Our strategy separates both contributions: in the first part, we focus on the dependence of fluorescence excitation and emission spectra on the Kamlet–Taft parameter β of the solvent which aims at finding reliable values for b_i. Next, we analyse the influence of solvents on the spectra of MPTS. The reduced basicity of the photoproduct 8-oxypyrene-1,3,6-trisulfonate (OPTS) is characterized by the impact of HB-donating solvents on its spectra. Solubility problems are overcome by the usage of crown ether. The presented results are discussed with respect to our ongoing synthetic work of borondipyrromethene (Bodipy, BDP)-dyes.[22,32]

2. Experimental

Materials and synthesis

HPTS (Aldrich, 97%), MPTS (Fluka, 98%), Pyrenol (Aldrich, 98%) and 18-Crown-6 (Aldrich, 99%) were used without further purification. The solvents used in this study were of highest available purity (Spectranal, Chromasolv, Uvasol or HPLC-grade) and—if not—tested for fluorescent impurities. All solvents were used as received.

The *p*-hydroxystyryl- and *p*-methoxystyryl–Bodipy dyes (HO-BDP, MeO-BDP; Scheme 2) were synthesized by Knoevenagel condensation in boiling toluene of methylated, green fluorescent Bodipy dyes[22,32–34] and *p*-hydroxybenzaldehyde (Aldrich, 98%) or *p*-methoxybenzaldehyde (Aldrich, 98%), respectively.[35] The raw product was purified twice by column



Scheme 2 Structures of the synthesized Bodipy dyes. HO-BDP (R_1 = HO–) and MeO-BDP (R_1 = HO–) were carrying a phenyl-group in the *meso*-position (R_2 = phenyl–). Only for the measurements of the spectra of O-BDP (Fig. 5a) we used a better soluble and more fluorescent HO-BDP (R_1 = HO–. R_2 = H–).

chromatography to finally yield the desired product. Details will be described elsewhere. The solubilities of HO-BDP and MeO-BDP were high enough to record spectra in all solvents; however, due to the vanishingly small fluorescence quantum yield of deprotonated HO-BDP (O-BDP), we synthesized for these measurement HO-BDP lacking the phenyl moiety in the *meso*-position.[33,34]

Sample preparation—spectra of acidic forms in apolar solvents

PyOH, MPTS and HPTS were dissolved in methanol (MeOH) or ethanol (EtOH), and an aliquot was taken for each sample, which ensured that the optical density in the final experiments was low enough in each case to avoid spectral distortion due to innerfilter effects and emission reabsorption. After complete evaporation of EtOH, the final solvent was added. Visual inspection of the fluorescence by means of blacklight illumination showed us whether enough dye was dissolved for recording reliable fluorescence and excitation spectra. In the cases where no fluorescence could be detected, 10–25 mg of crown ether was added in order to improve the solubility of the multiply charged dye anions by complexation of sodium counter ions. The final concentration of the crown ether (<20 mM) resulted in an ionic strength far below those which were reported to influence the spectra of HPTS.[36] Please note also, that the actual concentration of sodium ions is still considerably smaller than millimolarity as the only source of these counter ions was the dye. However, we cross-checked our procedure with solvents where fluorescence was sufficient without addition of the helper molecule (Table 1).

Only in a few cases (chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2) and bromobenzene (BrB)), saturated solutions of the crown ether were able to dissolve some amount of the charged dyes. We were not able to record fluorescence excitation or emission spectra of HPTS and MPTS in cyclohexane, toluene, acetophenone, ethyltrichloroacetate or of HPTS in BrB.

Sample preparation—spectra of 8-oxypyrene-1,3,6-trisulfonate (OPTS)

An aliquot of HPTS was taken as described above, and the organic solvent was added after complete drying. Except from water, the solutions showed typical blue fluorescence of HPTS. Therefore, 10–25 mg crown ether and additional, solid NaOH ($\sim$5–10 mg) was added. Greenish fluorescence indicated successful deprotonation. Spectra of OPTS could be detected only in a few, highly polar solvents, in which HPTS itself was already analysed. The solubility in protic solvents was higher;

Table 1 Used solvents in this study and their physical (refractive index n_0, dielectric constant ε_{rel}) and solvatochromic parameters (α, β, π^*)[24,28,43]

#	Solvent	α	β	π^*	ε_{rel}	n_0	PyOH	HPTS	MPTS	OPTS
1	Acetone	0.08	0.48	0.71	20.56	1.359	—	—	+	—
2	Acetonitrile	0.19	0.31	0.75	35.94	1.344	—	—	+	0
3	Benzonitrile	0	0.41	0.90	25.20	1.528	—	+	+	—
4	Bromobenzene	0	0.07	0.71	5.40	1.557	+	—	—	—
5	Butyrolactone	0	0.49	0.87	40.96	1.437	+	+	+	—
6	Chloroform	0.44	0	0.58	4.81	1.446	—	—	0	—
7	Cyclohexane	0	0	0	2.02	1.426	+	—	—	—
8	Dichloromethane	0.30	0	0.82	8.93	1.424	—	—	0	—
9	Dimethyl formamide	0	0.69	0.88	36.71	1.431	+	+	+	0
10	Dimethyl sulfoxide	0	0.76	1.00	46.45	1.479	+	+	+	+
11	Dioxane	0	0.37	0.55	2.21	1.422	+	+	+	—
12	Ethanol	0.83	0.77	0.54	24.55	1.361	—	—	+	+
13	Ethyl acetate	0	0.45	0.55	6.02	1.372	+	0	0	—
14	Ethylene glycol	0.90	0.52	0.92	37.7	1.432	—	—	+	+
15	Formamide	0.71	0.48	0.97	111.0	1.448	—	—	+	+
16	Hexafluoro-2-propanol	1.96	0	0.65	16.70	1.275	—	—	+	0
17	Hexamethyl-phosphoric triamide	0	1.05	0.87	29.6	1.459	+	+	+	0
18	Methanol	0.93	0.62	0.60	32.66	1.328	—	—	+	+
19	2-Propanol	0.76	0.95	0.48	19.92	1.377	—	—	+	+
20	Propylene carbonate	0	0.40	0.83	64.92	1.422	+	+	+	+
21	Tetrahydrofuran	0	0.55	0.58	7.58	1.407	+	+	+	—
22	Tetramethylurea	0	0.80	0.83	23.60	1.449	+	+	+	0
23	Toluene	0	0.11	0.54	2.38	1.497	+	—	—	—
24	Trifluoroethanol	1.51	0	0.73	26.53	1.30	—	—	+	+
25	Water	1.17	0.47	1.09	78.30	1.333	—	—	+	+

Definition of symbols: +: good spectra; 0: noisy spectra or spectra under extreme conditions recorded; —: no spectra obtained; −: no spectra recorded.

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only in HFiP, no reliable excitation spectra and a very weak fluorescence spectrum of OPTS was detectable.

Fluorimetry

Depicted fluorescence excitation and emission spectra of the blue-green emitting dyes were recorded with a fluorescence spectrophotometer (Fluoromax-3, Jobin-Yvon and FP 6500, Jasco) with 1 nm resolution. Afterwards, spectra were converted to the wavenumber range with the necessary corrections.[37] As far as comparison to reported values is possible, the evaluated maxima of our study lie within <100 cm^{-1} of ref. 24. Slight deviations (<200 cm^{-1}) from the fluorescence values of ref. 30 are noticed.

3. Results and discussion

3.1 Correlation of spectroscopic maxima and β-values of the solvents

All solvents used in this section share the property that they are aprotic, *i.e.* $\alpha = 0$. Excitation and emission spectra of PyOH and HPTS in several solvents with similar polarity, *i.e.* similar values of Kamlet–Taft parameter π^*, are displayed in Fig. 1 and 2, respectively. Table 2 summarizes the found spectroscopic maxima. Both dyes exhibit red-shifts of the maxima upon increasing β values of the solvents. These dependencies are displayed in Fig. 1c and 2c. The regression lines represent single parameter fits according to eqn (2), of which the slope is b_i and the intercept at the ordinate is an extrapolation to the transition energy ν_{i0} of a non-interacting solvent. b_i is a property of the solute's electronic state and describes its tendency to release the proton. The results of these one-parameter fits are summarized in Table 4.

Solvents with similar π^* values are evenly distributed around the regression lines. PyOH was reported to exhibit only a small change of its static dipole moment.[24] MPTS, which is taken as analogue to HPTS, does not show a clear dependence in a Lippert–Ooshika–Mataga plot (data not shown). This is compatible with a minor change of the static dipole moment upon excitation, which is predicted by theoretical calculations.[30] It is therefore justified to neglect the dependency of the energy gap on π^* while applying eqn (2) to solvatochromism of HPTS and PyOH.

The obtained b_i values are close for HPTS and PyOH (-320 cm^{-1} *vs.* -390 cm^{-1} for b_{exc}; -560 cm^{-1} *vs.* -530 cm^{-1} for b_{em}). The hydroxyl-moieties are more strongly interacting with the solvent in the excited than in the ground state as indicated by $|b_{em}| > |b_{exc}|$. This is in agreement with a higher acidity in the excited state and resembles the behaviour of naphthol derivatives.[6,26]

For comparison, we also investigated the solvatochromism of MPTS. The b_i-values for MPTS are close to 0 within their error limits (Fig. 2d). This is expected due to lack of an acidic proton. The data also verify that other acidic hydrogen atoms in the core structure are missing.

Specific and reliable assignment of spectroscopic changes to an altered local environment can be found out by differential solvatochromism.[6,26] Here, the frequency values ν_i of HPTS are subtracted from those of MPTS and, subsequently, the spectroscopic differences can be traced back to HB differences among different solvents. It is assumed that other solvent–solute interactions are cancelled. Taking the differences between the excitation and emission maxima yields $b'_{exc} = -360$ (± 90) cm^{-1} and $b'_{em} = -630$ (± 170) cm^{-1}, and thus, similar values as above are obtained within the error limits (Table 4). Bathochromic shifts in HPTS with increasing HB-accepting power of the solvent, therefore, reflect solely the increased HB-strength in the excited state of the solute compared to its ground state.

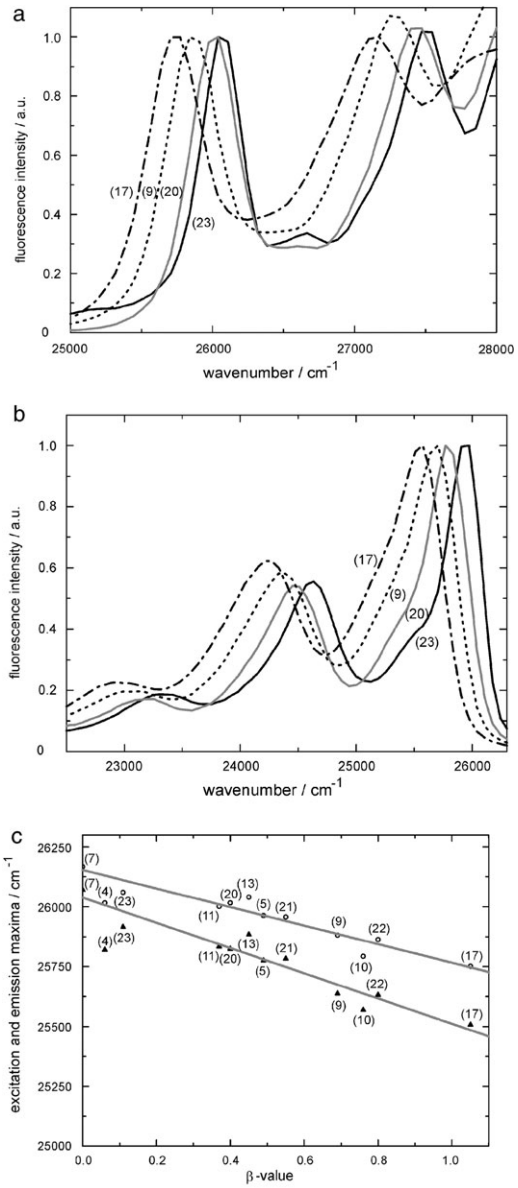

Fig. 1 Solvatochromism of PyOH in solvents with varying β-values ($\alpha = 0$). Depicted numbers correspond to the solvent numbers in Table 1. (a) Fluorescence excitation spectra (λ_{det} = 380–420 nm). (b) Fluorescence emission spectra (λ_{exc} = 365–375 nm). (c) Plot of all spectroscopic maxima *versus* the solvent's β-value. The grey lines represent linear fits to the excitation maxima (open circles) and emission maxima (filled triangles), respectively. For PyOH, $b_{exc} = -390$ (± 40) cm^{-1} and $b_{em} = -530$ (± 50) cm^{-1}. The data of bromobenzene (4) were not considered for the fit.

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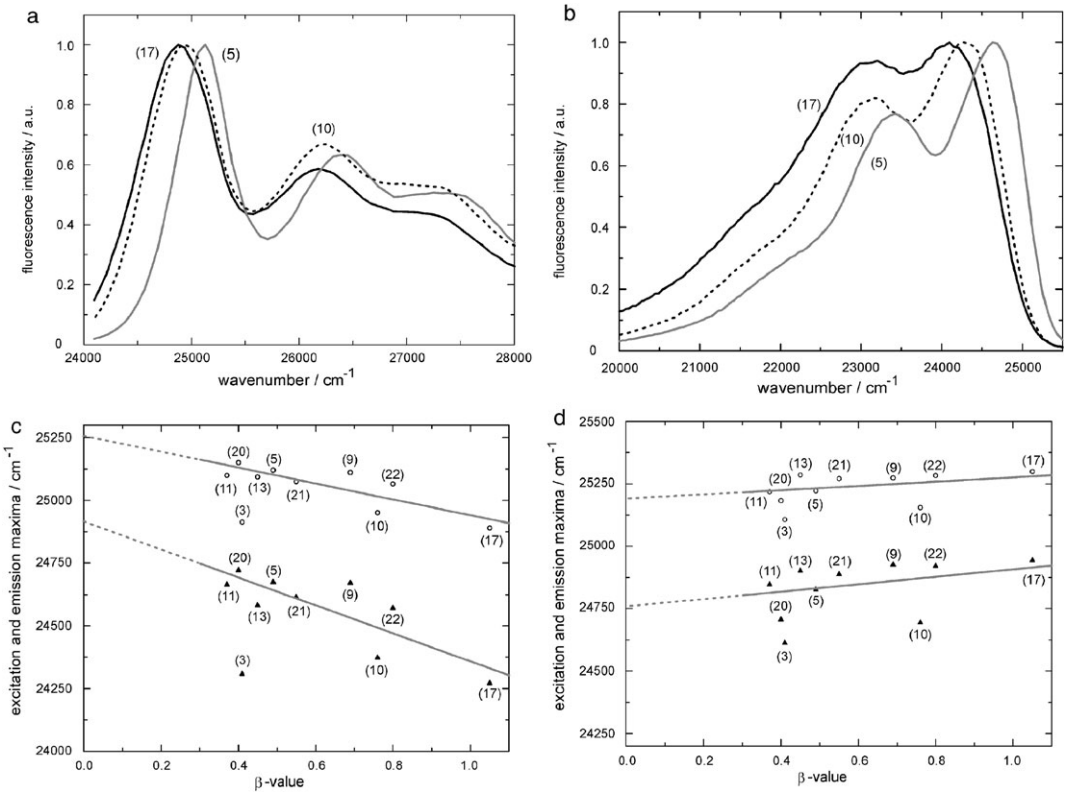

Fig. 2 Solvatochromism of HPTS in solvents with varying β-values ($\alpha = 0$). Depicted numbers correspond to the solvent numbers in Table 1. (a) Fluorescence excitation spectra (λ_{det} = 400–450 nm). (b) Fluorescence emission spectra (λ_{exc} = 380–390 nm). (c) Plot of all spectroscopic maxima *versus* the solvent's β-value. The grey lines represent linear fits to the excitation maxima (open circles) and emission maxima (filled triangles), respectively. For HPTS, $b_{exc} = -320\ (\pm 80)\ cm^{-1}$ and $b_{em} = -560\ (\pm 140)\ cm^{-1}$. The data of benzonitrile (3) were not considered for the fit. Differential solvatochromism verifies these values. (d) For comparison: Plot of the excitation and emission maxima of MPTS *vs.* the solvent's β-value. The slopes are close to 0 within the error margins.

Table 2 Fluorescence excitation and emission maxima of PyOH, HPTS and MPTS in β-solvents ($\alpha = 0$) ($\pm 30\ cm^{-1}$)

		Excitation maximum/cm^{-1}			Emission maximum/cm^{-1}		
#	Solvent	PyOH	HPTS	MPTS	PyOH	HPTS	MPTS
3	Benzonitrile	—	24 913	25 106	—	24 308	24 613
4	Bromobenzene	26 010	—	—	25 820	—	—
5	Butyrolactone	25 963	25 120	25 222	25 775	24 675	24 827
7	Cyclohexane	26 167	—	—	26 071	—	—
9	Dimethylformamide	25 881	25 111	25 274	25 638	24 671	24 926
10	Dimethyl sulfoxide	25 793	24 951	25 155	25 569	24 373	24 694
11	Dioxane	26 001	25 099	25 218	25 834	24 665	24 848
13	Ethyl acetate	26 040	25 093	25 285	25 884	24 581	24 902
17	Hexamethylphosphoric triamide	25 751	24 890	25 299	25 507	24 271	24 943
20	Propylene carbonate	26 016	25 150	25 182	25 824	24 722	24 706
21	Tetrahydrofuran	25 957	25 075	25 271	25 783	24 615	24 888
22	Tetramethylurea	25 863	25 066	25 283	25 632	24 570	24 921
23	Toluene	26 060	—	—	25 916	—	—

We conclude that the acidity of HPTS upon excitation is rather similar to the increased acidity of PyOH. However, even a small discrepancy might not explain the differences in the ESPT behaviour: HPTS easily releases a proton to water whereas PyOH requires "catalysis" by hydrogenphosphate.[31]

3.2 Influence of HB-donating solvents on the spectra of MPTS

The missing differences of spectroscopic behaviour between PyOH and HPTS encouraged us to investigate the influence of increasing α-values of the solvent. Previously, HPTS was examined in a variety of solvents, and multiparameter fitting of the spectroscopic maxima was performed.[24] While b_{exc} reported in this reference is close to our value, b_{em} deviates strongly. As redoing the same measurements presumably would not lead to different results, we performed fluorescence spectroscopy of MPTS in different solvents (Fig. 3 and Table 3). MPTS can substitute HPTS due its spectroscopic, chemical and electronic similarity.[16,30] The extrapolated values

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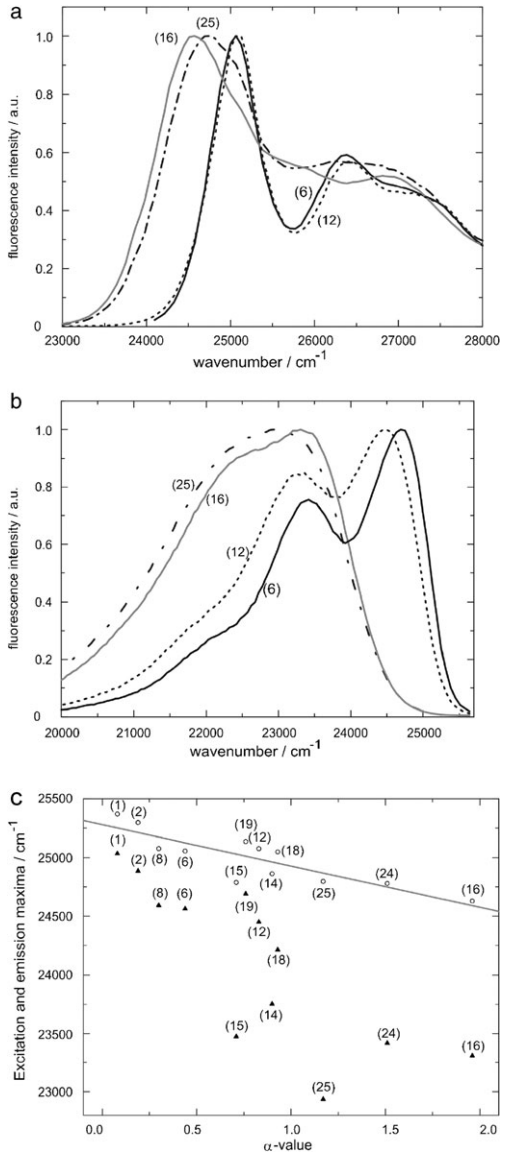

Fig. 3 Solvatochromism of MPTS in solvents with varying α-values. Depicted numbers correspond to the solvent numbers in Table 1. (a) Fluorescence excitation spectra (λ_{det} = 450 nm). (b) Fluorescence emission spectra (λ_{exc} = 380–390 nm). (c) Plot of all fitted spectroscopic maxima *versus* the solvent's α-value. The grey line represents a linear fit to the excitation maxima (open circles) and yields for MPTS, $a_{exc} = -350\ (\pm 70)\ cm^{-1}$. The value of a_{em} was not determined by a fit to the emission maxima (filled triangles), see text for further details.

of ν_{i0} in Fig. 2c and d coincide within the error limits (Table 4) and, thus, verify this similarity. MPTS, however, is convenient as it does not exhibit a spectroscopic dependence on the HB-accepting power of the solvent. As shown in section 3.1, p_i and b_i of MPTS are approximately 0. Hence, solvatochromism can be analysed on the basis of varying α-values independent of the solvent's β-value and multiparameter fits can be avoided. This is helpful in screening applications where elaborate computations should be avoided. Fig. 3a shows the excitation and Fig. 3b the emission spectra of MPTS in several solvents with differing α-values. Increasing α-values are accompanied by bathochromic shifts both in excitation and

Table 3 Fluorescence excitation and emission maxima of MPTS and OPTS in α-solvents (±30 cm^{-1})

		Excitation maximum/cm^{-1}		Emission maximum/cm^{-1}	
#	Solvent	MPTS	OPTS	MPTS	OPTS
1	Acetone	25 370	—	25 035	—
2	Acetonitrile	25 297	20 619	24 886	19 493
6	Chloroform	25 056	—	24 563	—
8	Dichloromethane	25 076	—	24 592	—
12	Ethanol	25 076	21 459	24 450	19 608
14	Ethylene glycol	24 862	21 645	23 753	19 531
15	Formamide	24 788	21 142	23 474	19 268
16	Hexafluoro-2-propanol	24 629	—	23 310	19 763
18	Methanol	25 049	21 838	24 213	19 646
19	2-Propanol	25 136	21 097	24 691	19 569
24	Trifluoroethanol	24 779	23 095	23 419	19 685
25	Water	24 797	21 692	22 936	19 569

emission. This behaviour is different to what has been described for naphthol-derivatives and PyOH.[24,26] A blue-shift of the electronic spectra, which corresponds to positive a_i values, is explained by a HB between the oxygen atoms of the aromatic alcohols and the solvent (*e.g.* α_1 in Scheme 1) which is weakened upon excitation. In terms of the molecular electronics of the probe molecule, electron density is transferred from the donor to the aromatic core upon excitation.

A plot of the spectroscopic maxima against α can return a_{exc} and a_{em} of MPTS after fitting, which is a measure of the HB-accepting character of the respective electronic state (Fig. 3c). The extracted value for a_{exc}, −350 (±70) cm^{-1}, is of the same order as the value given by ref. 24 for HPTS. A negative value (in HPTS) was traced back to the increasing electron withdrawing power of sulfonate groups in conjunction with the donor ability of a hydroxyl-group. The sulfonamide derivative of HPTS, in which the electron-withdrawing strength of the substituents is further enhanced, also exhibits red-shifted spectra compared to HPTS.[13,15] The same argumentation also holds for MPTS. It is worth mentioning that the observed red-shift is reduced most likely as a result of the blue-shift due to HB directly at the methoxy-position.

The influence of α on the fluorescence maxima is more complex. While at low HB-donating ability, the fluorescence is (more or less linearly) bathochromically shifted by a higher solvent acidity. The observed Stokes-shifts ($\nu_{exc} - \nu_{em}$) are in the range of the extrapolated values of HPTS and MPTS in the β-dependence plot (Fig. 2c and d; $\nu_{exc,0} - \nu_{em,0}$). In contrast, the fluorescence emission maxima are nearly constant at high α values. A change of behaviour appears around an α-value of 0.7–0.8. Both sections are separated by a step of ~1000 cm^{-1}. Also the line shape changes.[38] In HPTS under highly acidic conditions, this change of behaviour was attributed to charge redistribution, but was explicitly excluded for MPTS.[14] We, however, argue by means of a rough estimate that, indeed, MPTS and HPTS are identical in the occurrence of the charge transfer state: ν_{em} of MPTS in water is ~22 900 cm^{-1} which is larger by ~300 cm^{-1} than the value of ν_{em} of HPTS.[24] If we add the bathochromic shift due to HB between the base H_2O and the photoacid HPTS, then we further reduced the transition energy by $b_{em}*\beta$ (the β-value of H_2O is ~0.5) which is in the range of the missing 300 cm^{-1}. The mentioned change

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Table 4 Fitting results of solvatochromism experiments. All data are obtained using linear fits according to eqn (2). *R* denotes the correlation coefficient

Spectra: solvent dependence		Fig.	Ordinate intercept/cm^{-1}	Slope a_i, b_i/cm^{-1}	*R*
Exc.	PyOH: β	1a,c	ν_{exc0}: 26 150 (±20)	b_{exc}: −390 (±40)	0.96
	HPTS: β	2a,c	ν_{exc0}: 25 260 (±50)	b_{exc}: −320 (±80)	0.84
	MPTS: β	2d	ν_{exc0}: 25 190 (±50)	b_{exc}: +90 (±80)	0.38
	Diff. solvato-chrom. HPTS	—	30 (±60)	b'_{exc}: −360 (±90)	0.82
	HO-BDP	5b,d	ν_{exc0}: 17 635 (±40)	b_{exc}: −350 (±70)	0.87
	MeO-BDP	5e	ν_{exc0}: 17 620 (±50)	b_{exc}: −160 (±80)	0.58
	Diff. solvato-chrom. HO-BDP		10 (±20)	b'_{exc}: −190 (±30)	0.91
	MPTS: α	3a	ν_{exc0}: 25 280 (±60)	a_{exc}: −350 (±70)	0.86
	OPTS: α	4a	ν_{exc0}: 20 830 (±160)	a_{exc}: +780 (±210)	0.75
	O-BDP: α	5a	ν_{exc0}: 17 190 (±80)	a_{exc}: +190 (±80)	0.74
Em.	PyOH: β	1b,c	ν_{em0}: 26 040 (±30)	b_{em}: −530 (±50)	0.96
	HPTS: β	2b,c	ν_{em0}: 24 920 (±90)	b_{em}: −560 (±140)	0.83
	MPTS: β	2d	ν_{em0}: 24 760 (±100)	b_{em}: +150 (±150)	0.36
	Diff. solvato-chrom. HPTS	—	100 (±110)	b'_{em}: −630 (±170)	0.80
	HO-BDP	5c,d	ν_{em0}: 17 340 (±50)	b_{em}: −525 (±90)	0.91
	MeO-BDP	5f	ν_{em0}: 17 320 (±50)	b_{em}: −310 (±80)	0.81
	Diff. solvato-chrom. HO-BDP	—	10 (±30)	b'_{em}: −220 (±40)	0.87
	MPTS: α	3b	Not determined	Not determined	—
	OPTS: α	5	ν_{em0}: 19330 (±50)	a_{em}: +240 (±60)	0.75
	O-BDP: α	5a	Not determined	Not determined	—

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of spectroscopic behaviour, although not further quantified, has impact on previous solvatochromic investigations: it indicates that multiparameter fitting procedures are misleading when a linear dependence is not given. This might especially be important in the investigation of chemical reactions.

3.3 Influence of HB-donating solvents on the spectra of OPTS

The deprotonated OPTS is the photoproduct after ESPT of HPTS. The idea behind the investigation of its solvatochromism in α-solvents is that we now explore ESPT dyes from the photoproduct side. We would like to find out whether this approach is appropriate to find target structures. First of all, the response of the OPTS-spectra to stronger HB from the solvent allows verification of whether the basicity of the excited state is reduced compared to the ground state. For very strong photoacids, $|a_{em}| < |a_{exc}|$ was found in agreement with a higher excited state acidity and opposite to the effect of HB-donating solvents at the reactant side. The values are positive indicating spectral blueshifts with increasing solvent acidity (Fig. 4a). For the search of ESPT dyes, the a_{em} values, which are specific for the properties of the excited state, are more important.

Fluorescence emission spectra of OPTS in different solvents are depicted in Fig. 4b, and the spectral maxima positions *versus* the solvents' α-value are shown in Fig. 4c. The spectra in highly protic solvents are broader than in aprotic solvents; however the centre is hardly affected by the α-value: a_{em}, obtained as +240 (±60) cm^{-1} from the linear fit in Fig. 4c, indeed is comparably small with respect to other deprotonated ESPT dyes.[6] The peak positions of fluorescence in purely aprotic solvents (α = 0) cover a spectral range which is as large as the whole energetic variation due to HB. Thus, these non-HB interactions are equally important for the spectral position, and might be the reason for the low correlation value of a_{em} and a_{exc} (R = 0.75) in our one-parameter correlation. However, a correlation with polarity (π* or the dielectric constant ε_{rel}) was not found. In contrast to the excited state, the ground state is more sensitive to HB as expected for a base (a_{exc} = +780 (±210) cm^{-1}). The acidity of HFiP (pK_A = 9.3), which shifts the equilibrium to HPTS, might therefore be the reason, why only rather poor spectra of OPTS could be obtained in this solvent.

It is interesting to compare the effect of solvents with high α-values on the emission spectra of MPTS, which is similar to HPTS shortly before ESPT, and OPTS, which is HPTS after the ESPT. Although the HB at the electron-donor moiety (methoxy group *vs.* oxy-group) is different in both species, the HB at the sulfonate-groups is nearly identical. a_{em} of MPTS, although not further determined (Fig. 3c), and a_{em} of OPTS are in a similar range. This comparison shows that, once charge redistribution occurred at a α-value of ~0.8, excited HPTS becomes more acidic than before and only then the proton can be transferred to the solvent without the need of catalysts. This is also reflected by the equilibrium constant of HPTS + H_2O/OPTS + H_3O^+ which is shifted to the neutral chromophore state on a time scale before charge redistribution occurs.[18] It is not possible to discuss whether $^1L_a/^1L_b$ state reversal or not occurs along the ESPT-coordinate on the basis of our experiments.[16,24,38] Nevertheless, we adhere to the mentioned acidity change in the excited state of HPTS as the difference to PyOH.

3.4 Discussion of solvent effects with respect to HO-BDP

According to the revisited solvatochromism of HPTS, the wealth of available dyes can be narrowed down during the search of ESPT-dyes by the investigation of solvatochromism.

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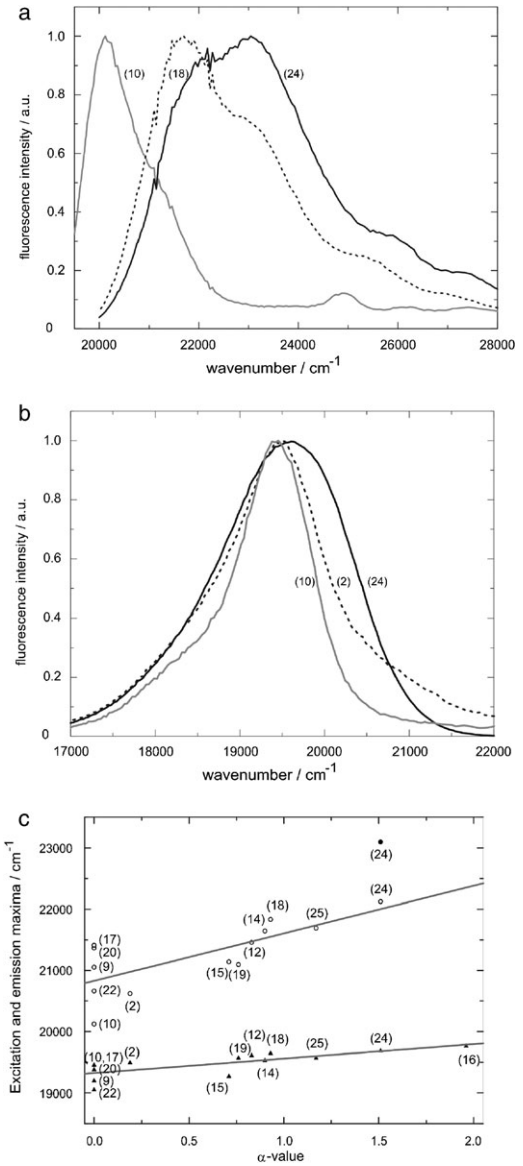

Fig. 4 Solvatochromism of OPTS in solvents with varying α-values. Depicted numbers correspond to the solvent numbers in Table 1. (a) Fluorescence excitation spectra (λ_{det} = 530 nm). (b) Fluorescence emission spectra (λ_{exc} = 420–460 nm). (c) Plot of all fitted spectroscopic maxima *versus* the solvent's α-value. The grey lines represent linear fits to the excitation maxima (open circles) and emission maxima (filled triangles), respectively. For OPTS, a_{exc} = +780 (±210) cm^{-1} and a_{em} = +240 (±60) cm^{-1}. For the fit of the excitation maxima, not the maximum in trifluoroethanol (24), but the shoulder at λ = 452 nm (see a) was used. An excitation maximum in hexafluoro-2-propanol (16) was not found.

In this last section, we would like to discuss the example where an acidity increase of an aromatic alcohol is not observed although fluorescence emission data misled us to assume its ESPT-capability. This is the case of HO-BDP (Scheme 2).

We applied the solvatochromic method to HO-BDP in order to find out whether this compound might be a target structure for an ESPT-dye in the visible range. Bodipy dyes exhibit high fluorescence quantum yields, are superior to fluorescein dyes in terms of photostability and are therefore appropriate for our long-term goal of ESPT-dyes in the visible range.[22,32–34] The dye in the focus of this section has in its neutral form λ_{exc} = 569 nm, λ_{em} = 581 nm and in its anionic form λ_{exc} = 573 nm, λ_{em} ~ 710 nm (Fig. 5a). According to eqn (1), one calculates ΔpK_a = 0.25 on the basis of the excitation data and ΔpK_a = 6.55 on the basis of the emission data. Even if we take the average, as suggested by ref. 5, then a distinct increase of the acidity by more than 3 orders of magnitude could be expected.

Other dyes with styryl-moieties were shown to exhibit ESPT.[7] However, we were led by the spectroscopic similarity of ammonium-groups and hydroxyl-groups and their deprotonated counterparts, *i.e.* amino-groups and oxy-substituents. The comparability is *e.g.* manifested in substituted xanthene dyes, *i.e.* rhodamine *vs.* fluoresceine dyes. With respect to ESPT, the similarity was already noticed by Förster[1,2] and, quite recently, by time-resolved spectroscopy.[14] Differences between isoelectronic NH_3^+ and OH-groups concern the pK_a values of the considered dyes.

The synthesis and spectroscopic properties of *p*-dimethylaminostyryl Bodipy dyes (NMe_2-BDP) were published in the last years,[35,39] and recently, we performed theoretical calculations to elucidate its ESPT-behaviour.[40] Whereas the protonated dye exhibits only small Stokes-shifts upon excitation, the neutral chromophore undergoes charge-transfer with a large change of the static dipole moment. The reported spectroscopic values of excitation and emission maxima for NMe_2-BDP and its conjugated acid NMe_2H^+-BDP are close to our values of the pair HO-BDP/O-BDP. We therefore assume that all conclusions drawn for NMe_2-BDP/NMe_2H^+-BDP pair also hold for HO-BDP/O-BDP although we did not perform such elaborate solvatochromic studies as in ref. 39. We summarize that if ESPT occurs then charge-transfer as the thermodynamic driving force would act only *after* ESPT.

We studied the solvatochromism of HO-BDP in β-solvents (Fig. 5b–d). We renounced the aromatic solvents benzonitrile (3), bromobenzene (4) and toluene (23) which showed systematic deviations in the spectra of PyOH and HPTS. We assign this to putative π–π interactions between the solvent and the aromatic solute. The b_i-values, b_{exc} and b_{em}, are close to the values of PyOH and HPTS (Table 4). However, the uncritical interpretation as an increased acidity in the excited state like in the case of PyOH and HPTS fails: the β-dependence of the spectra of the methoxy-derivative MeO-BDP as well as differential solvatochromism provide evidence that the acidity of the OH-group is not substantially raised and that some other slightly acidic proton exists within the molecule (Table 4). Very acidic solvents like hexafluoro-2-propanol shift both excitation and emission spectra of MeO-BDP in equal measure to the blue (Fig. 5e and f). The blue-shift is in agreement with a reduction of the donor properties of the methoxy-moiety; the likewise blue-shift in the ground state as well as in the excited state imply, however, that a_{exc} ~ a_{em} and that no additional electron density is shifted from the electron donor toward the aromatic system in the excited state.

We also performed excitation and emission spectra of O-BDP, the conjugated base of HO-BDP, in dependence of

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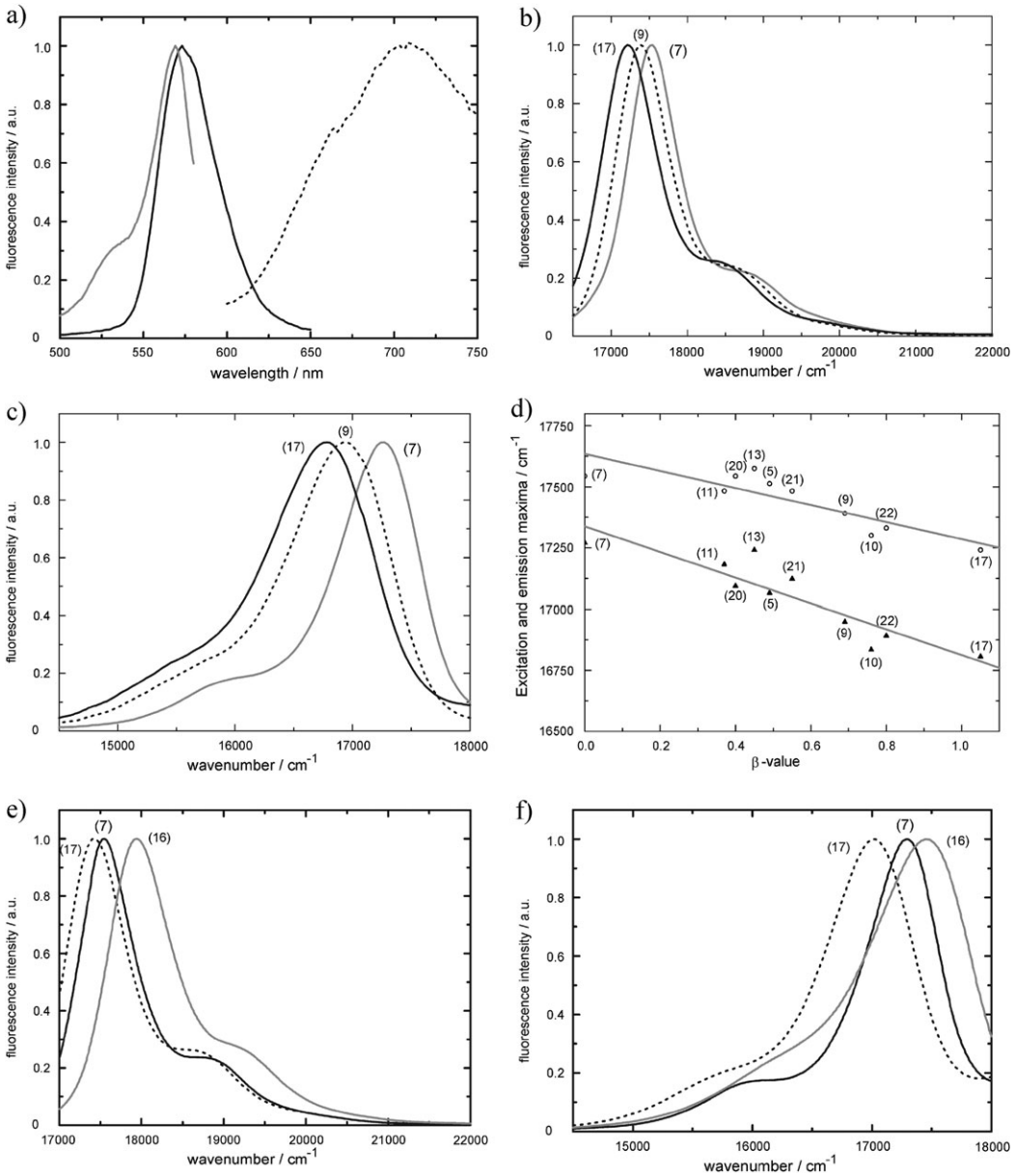

Fig. 5 Solvatochromism of Bodipy dyes. Depicted numbers correspond to the solvent numbers in Table 1. (a) Fluorescence excitation (full lines) of HO-BDP (grey, λ_{det} = 590 nm) and its conjugated base O-BDP (black, λ_{det} = 710 nm) and fluorescence emission spectrum of O-BDP (black-dotted, λ_{exc} = 585 nm) in water. The large Stokes-shift of the anionic form was considered as an indication of ESPT. Note also the very uncommon line shape of the excitation spectrum of O-BDP. (b) Fluorescence excitation spectra (λ_{det} = 600–635 nm) of HO-BDP in solvent with varying β-values. (c) Fluorescence emission spectra (λ_{exc} = 520–550 nm) of HO-BDP in solvent with varying β-values. (d) Plot of all spectroscopic maxima of HO-BDP *versus* the solvent's β-value. The grey lines represent linear fits to the excitation maxima (open circles) and emission maxima (filled triangles), respectively. For HO-BDP, b_{exc} = −350 (±70) cm^{-1} and b_{em} = −525 (±90) cm^{-1}. However, differential solvatochromism yields b'_{exc} = −190 (±30) cm^{-1} and b'_{em} = −220 (±40) cm^{-1}. (e) Fluorescence excitation spectra (λ_{det} = 600–615 nm) of MeO-BDP in different solvents. Note the spectral shifts of MeO-BDP in highly basic solvent (17). (f) Fluorescence emission spectra (λ_{exc} = 525–550 nm) of MeO-BDP in solvent with varying β-values. Note the spectral shifts of MeO-BDP in highly basic solvent (17).

the α-value of some protic solvents (solvents 12, 14, 15, 18, 19, 24, 25; Fig. 5a). They share as common property a similar Lippert solvation parameters $\Delta f \sim 0.3$

$$\Delta f = \frac{\varepsilon_{rel} - 1}{2\varepsilon_{rel} + 1} - \frac{n^2 - 1}{2n^2 + 1} \qquad (3)$$

where ε_{rel} is the dimensionless dielectric constant and n the refractive index of the solvent. This should ensure that the contribution of unspecific dipolar solvation is cancelled. A slight blue-shift of the excitation spectra was found for O-BDP, a_{exc} = +190 cm^{-1}, which is unexpectedly small for a base on the basis of naphtholate or OPTS data.[6] One has to consider the noticed solvatochromism of MeO-BDP in the sense that here also the β-values of the solvents have an impact on the spectral position. For a_{em}, however, we could not find a clear dependence. All fluorescence maxima lie within a range

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of 705 to 710 nm. The fact that all recorded emission data are broad in combination with very weak fluorescence aggravates here the analysis and a proper assignment of the emission maxima is hardly achievable. Moreover, it is questionable whether one-parameter fitting can fully describe the solvatochromism of a charge-transfer dye, even if solvents with similar Δf-values but differing α-values are used. Nevertheless, our data are in good agreement with the behaviour of NMe_2-BDP where vanishingly small a_{exc} and a_{em} were found by multiparameter fitting.[39]

In summary, the situations for HPTS (at early times), PyOH and HO-BDP are not so different: whenever a suitable proton acceptor is so close that proton transfer can occur, this will happen in the excited state.[31,41] For example, ultrafast ESPT to acetate was observed for HPTS on a time scale before charge redistributation occurs.[36] However, differences among the investigated dyes concern the time scales of proton transfer. The rate constants for proton transfer are related to the free energy release ΔG during the reaction.[42] This is also exemplified in the protonation kinetics of pyrene-1-carboxylate by various acids.[20] While the acidity increase of HPTS (at early times) and PyOH, which is probed by the variation of the solvent β-value, consequently enables proton transfer during the excited state lifetime, ESPT is rather unlikely to proceed in HO-BDP. If, however, ESPT accidentally occurs in HO-BDP, then the energy release due to solvation in the anionic state would lock the thermodynamics.

We therefore conclude that the spectroscopic signature which points to the ESPT propensity is likely the difference of the excitation maxima of acid and conjugated base, *i.e.* the transition energy difference $\Delta\nu_{exc0}$ before solvent relaxation occurs. $\Delta\nu_{exc0}$ be regarded as a measure for the gradient of ESPT although subtleties of the potential energy surface are ignored. In the case of HO-BDP, $\Delta\nu_{exc0}$ is 100–150 cm^{-1} which is in contrast to a roughly ten-times-larger value of PyOH.[31]

4. Conclusion

In our contribution, we investigated the solvatochromism of several dyes with the aim to predict the ESPT behaviour of freshly synthesized dyes. The dyes HPTS, PyOH and HO-BDP are all aromatic alcohols but decreasingly tend to undergo ESPT. The strong photoacidity of HPTS presumably results from charge redistribution in succession of solvent rearrangement, *i.e.* the formation of strong electron withdrawing substituents by HB from solvent to HPTS.[14,24] PyOH, HO-BDP and many naphtholes have in common that acidic solvents do not accelerate ESPT. We therefore propose the following criteria to distinguish potential ESPT dyes like PyOH from slower reacting dyes like HO-BDP. Firstly, differences in $\Delta\nu_{exc0}$ are related to the thermodynamics and should hint at the overall ESPT driving force. The best procedure would be to compare the spectra in a solvent of low polarity; solubility problems can be overcome by use of crown ether. Secondly, spectra of the acid in solvents with varying β-values should explore their kinetic tendency of ESPT. Differential solvatochromism ensures to assign observed effects to a certain proton. In the case where methoxy-derivatives are not available, solvents of similar polarity are preferential. A set of 5 solvents (butyrolactone, dimethylformamide, hexamethylphosphoric triamide, propylene carbonate and tetramethylurea) covers a large range of β-values and should already provide an insight into the ESPT behaviour. Finally, we do not recommend judging the ESPT tendency on the basis of a_{em} since dipolar relaxation might mask subtle effects of the solvent acidity.

Acknowledgements

The authors thank M. Wild for assistance in the synthetic work and I. Bernhardt for generous support. The work was supported by the German Science Foundation (DFG JU650/1).

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