Probing surface acidity, basicity, and dipolarity/polarizability of 12-tungstophosphoric acid by means of solvatochromic dyes

Yvonne Zimmermann and Stefan Spange*

Department of Polymer Chemistry, Institute of Chemistry, University of Technology Chemnitz, Straße der Nationen 62, 09111, Chemnitz, Germany

Empirical surface polarity parameters α, β, and π^* in terms of the Kamlet–Taft scale as well as Gutmann's acceptor number (AN) of 12-tungstophosphoric acid (H_3PW), pre-treated at various temperatures, have been estimated using solvatochromic dyes as probes. α (hydrogen-bond donating acidity) or AN and π^* (dipolarity/polarizability), respectively, have been investigated by means of $Fe(phen)_2(CN)_2$ [*cis*-dicyanobis(1,10-phenanthroline)iron(II)] (1) and Michler's ketone [4,4′-bis(dimethylamino)benzophenone] (2) as solvatochromic surface polarity indicators. Apparent β (hydrogen-bond accepting ability) parameters have been evaluated by means of an aminobenzodifuranone dye. Also, coumarin 153 has been checked to analyse the surface polarity of H_3PW. The outstanding surface properties of H_3PW when pre-treated at 250 °C are supported by UV/vis spectroscopic results of triphenylmethylium/H_3PW adducts. The chemical interpretation of the polarity parameters and nature of interactions which they reflect are discussed.

Introduction

Heteropolyacids have been widely used in homogeneous and heterogeneous catalytic systems as well as photocatalysts.[1–17] They and related compounds have attracted increasing interest in catalysis owing to their ability to catalyze both acidic and redox processes.[18–22]

The acidic strength of heteropolyacids in solution has been studied by conductivity,[23] UV/vis spectroscopy of Hammett (H_0) indicators,[24] NMR spectroscopy,[25] and ^{13}C NMR chemical shift of mesityl oxide as a probe.[8] IR spectroscopy of adsorbed bases (*e.g.* NH_3, pyridine),[5,26,27] TPD (temperature programmed desorption) of NH_3 or pyridine,[5,28] and microcalorimetry of adsorbed ammonia[29] have been used to investigate the acidity of these solid catalysts.

The calorimetric titration of 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, H_3PW) with a series of bases in CH_3CN gives equilibrium constants and enthalpies for three deprotonation steps.[1] These results indicate that the three protons are not of equal strength as proposed from gas–solid calorimetry measurements.[1] Only one strong acidic proton per molecule of the solid acid is furnished for stoichiometric or catalytic reactions in any solvent of basicity equal to or less than that of CH_3CN. According to the literature claims of superacidity, the enthalpies of H_3PW with pyridine in acetonitrile show that H_3PW is comparable to triflic acid, and it is stronger than sulfuric acid and *p*-toluenesulfonic acid.[1]

The objective of this work is the classification of the surface acidity and dipolarity of a heteropolyacid in terms of empirical polarity parameters relating to established scales from the literature.

For this exemplary study, the heteropoly compound 12-tungstophosphoric acid, $H_3PW_{12}O_{40} \cdot xH_2O$, has been used. H_3PW is the most stable and strongest acid in the Keggin series.[30] Since it has an acid strength of $H_0 < -13.16$, it is a superacid.[24,31]

The catalytic activity of heteropolyacids like H_3PW is significantly dependent on the pre-treatment temperature.[13–15,20b,32] Therefore, the main objective of this work is focussed on the determination of Kamlet–Taft surface polarity parameters (see below) as well as Gutmann's acceptor number (AN) for H_3PW as a function of the pre-treatment temperature. As a model reaction to study independently the surface acidity of H_3PW, we make use of triphenylmethyl compounds which undergo chemisorption on solid acids as indicated by the characteristic triphenylmethylium UV/vis absorption maxima at $\lambda = 410$ and 435 nm.[33,34]

For classification of the surface polarity of various solid acids, the Kamlet–Taft solvent parameters α (hydrogen-bond donating acidity), β (hydrogen-bond accepting ability), and π^* (dipolarity/polarizability)[35] have been recommended by several authors as a reference system.[36–38] For instance, α and π^* values of various solid materials[36–38] have been determined by means of LSE (linear solvation energy) relationships[39–41] using the Kamlet–Taft solvent parameters as a reference system. For these purposes, solvatochromic dyes have been found suitable since the LSE relationships derived from solution processes can be applied to the surface effects. This presumption is not always accomplished and has to be proven for each materials system under study, because the mechanism of solvation of a dye in solution is often different from the mechanism of adsorption due to the nature of interaction between the dye molecules and the surface which varies as a function of the surface.[37d]

The simplified Kamlet–Taft equation applied to solvatochromic shifts of adsorbed indicators [XYZ = ν_{max}(indicator)] (indicator)] is given in eqn. (1).[35a,39–41]

$$XYZ = (XYZ)_0 + a\alpha + + b\beta + s(\pi^* + d\delta) \qquad (1)$$

$(XYZ)_0$ is the value of a solvent reference system, either a nonpolar medium or the gas phase, the origin α describes the HBD (hydrogen-bond donating) acidity, β the HBA (hydrogen-bond accepting) ability, and π^* the dipolarity/polarizability of the solvents. δ is a polarizability correction term that is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents; a, b, s, and d are solvent-independent coefficients.[35]

In previous papers we reported on the determination of Kamlet–Taft parameters α and π^* of various moderately strong solid acids (silicas, aluminas, aluminosilicates)[37] by means of the indicators 1 {Fe(phen)$_2$(CN)$_2$, cis-dicyano-bis(1,10-phenanthroline)iron(II)}[38,42] and 2 {Michler's ketone, [4,4'-bis(dimethylamino)benzophenone]}.[37a,38] However, both dyes are moderately weak bases.[41,43] With these genuine solvatochromic dyes one can distinguish very small differences in the polarity of solvents,[40] macromolecules,[44] surfaces of organically functionalised silica particles,[37b] and various inorganic solid acids.[37a]

The solid acids used in previous studies were different in structure and composition, and they have both Brønsted and Lewis acid sites on the surface.[37a] The acidity of silica to aluminosilicate ranges between $1 \leqslant \alpha \leqslant 1.8$ in terms of the Kamlet–Taft solvent parameter scale. These Kamlet–Taft parameters α or Gutman's acceptor numbers AN calculated for a series of silicas, aluminas, and aluminosilicates correlate well with the catalytic activity of these solid acids.[45]

Till now, there has been a lack of suitable solvatochromic indicators for determining the basicity of strong solid acids.[18] In this paper we will check a special aminobenzodifuranone,[46] dye 3, for probing the surface basicity (β value) of the heteropolyacid.

A sensitive solvatochromic indicator for analysing the dipolarity/polarizability of acidic surfaces is 4 (coumarin 153).[47] This probe molecule has been used for determining π^* values of polysaccharides.[47b]

The formulas of the solvatochromic probes used in this paper are shown in Scheme 1.

Experimental

Chemicals

H$_3$PW was obtained from Fluka. It was used as-received and after pre-treatment at various temperatures (70, 150, 250, 400, and 500 °C, respectively) for 12 hours, and allowed to cool to room temperature under inert atmosphere.

Dichloromethane (Merck, analytical grade) was freshly distilled over CaH$_2$ and stored under dried argon.

Fe(phen)$_2$(CN)$_2$ was prepared and purified according to Schilt.[48] Michler's ketone was purchased from Merck, re-crystallized twice from ethanol and carefully dried before

use. Coumarin 153 was purchased from Radiant Dyes Laser Accessories GmbH. The aminobenzodifuranone was kindly provided by the BASF Aktiengesellschaft, Manchester, UK.

Chlorotriphenylmethane, triphenylmethanol, and triphenylmethane are commercially available products. They were recrystallized from toluene and carefully dried before use.[45]

UV/vis spectroscopy

The UV/vis spectra of the probe dyes 1, 2, 3 and 4, when adsorbed on H$_3$PW, were recorded using a diode array spectrometer with glass fibre optics.

The pre-treated acid was placed in the measuring cell and immediately suspended in dichloromethane. Then a solution of the probe dye in dichloromethane (usually 10^{-5} mol l^{-1}) or the triphenylmethylium precursor dissolved in dichloromethane was added to this slurry.

The UV/vis spectra of the non-transparent slurries of 12-tungstophosphoric acid were recorded by a special reflectance technique.[37a] A quartz plate was used as the bottom of the closed cell containing the solid sample in the organic liquid. The sensor head for measuring the reflectance spectra was located at this quartz plate and the UV/vis spectrum of the adsorbed dye was monitored after the particles were deposited.

Thermal gravimetric analysis

The thermal gravimetric analysis was carried out with the analyser TGA 7 (Perkin Elmer) in a temperature range between 30 and 600 °C. The heating rate was 10 K min^{-1} in helium flowing at 30 ml min^{-1}.

Calculation of the polarity parameters

α and π^* values were calculated by a correlation analysis of the measured UV/vis absorption maxima v_{max} (in cm^{-1}) of the dyes 1 and 2, using the corresponding multiple correlations of α or $\pi^* = f[v_{max}(\mathbf{1})$ and $v_{max}(\mathbf{2})]$ with the Kamlet–Taft solvent parameters as the reference system.[37,47b] This procedure is described in detail in ref. 38(b). The following multiple correlation equations (2) and (3) were used to separate the respective property α or π^* from the unit of measurement of v_{max}(indicator) 1 and 2 (r: correlation coefficient, sd: standard deviation, n: number of solvents, F: significance)

$$\alpha = -7.90 + 0.45 \; v_{max}(\mathbf{1}) \times 10^{-3} + 0.02 \; v_{max}(\mathbf{2}) \times 10^{-3}$$
$$r = 0.95, \; sd = 0.17, \; n = 34, \; F < 0.0001 \qquad (2)$$

$$\pi^* = 13.89 - 0.25 \; v_{max}(\mathbf{1}) \times 10^{-3} - 0.32 \; v_{max}(\mathbf{2}) \times 10^{-3}$$
$$r = 0.57, \; sd = 0.15, \; n = 36, \; F < 0.0001 \qquad (3)$$

Despite the low correlation coefficient of eqn. (3) the significance is high and eqn. (3) has been established for determining reliable π^* values.[37a,44]

The multiple correlation [eqn. (4)] was used in order to separate the quantity β from the unit of measurement of $v_{max}(\mathbf{3})$.[44]

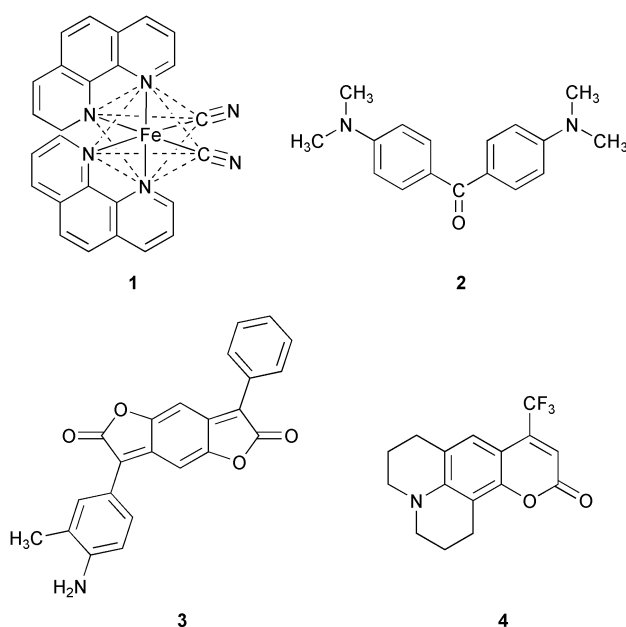$$\beta = 3.06 + 0.17 \; v_{max}(\mathbf{1}) \times 10^{-3} - 0.33 \; v_{max}(\mathbf{3}) \times 10^{-3}$$
$$r = 0.95, \; sd = 0.10, \; n = 21, \; F < 0.0001 \qquad (4)$$

For calculating eqn. (4), an extended set of $v_{max}(\mathbf{3})$ in various solvents was used.[44b]

According to refs. 38a and 49, Gutmann's AN can be simply calculated from $v_{max}(\mathbf{1})$ (eqn. (5)).

$$AN = \{v_{max}(\mathbf{1}) \times 10^{-3} - 15.17\}/0.073$$
$$r = 0.98, \; sd = 1.12, \; n = 27 \qquad (5)$$

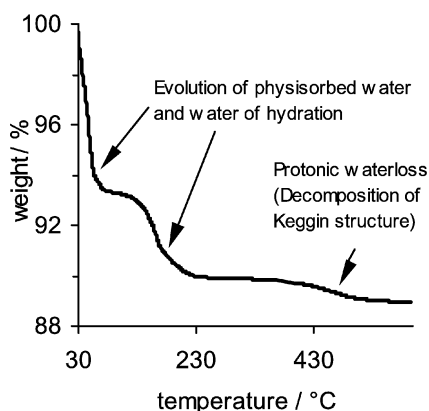**Scheme 1** Formulas of the probe dyes used.

Fig. 1 Thermal gravimetric analysis of H_3PW (temperature: 30–600 °C, heating rate: 10 K min^{-1}, helium flow: 30 ml min^{-1}).

Results and discussion

H_3PW is a commercially available product which contains hydration water.

Water molecules of the hydration shell desorb at first during the thermal gravimetric analysis (see Fig. 1), and the anhydrous Keggin structure with associated protons is produced.[32]

From the first two fractions of lost mass, 14 mol physisorbed and hydration water per mol H_3PW was calculated. In the range between 400 and 500 °C, a third fractional loss in mass (−0.99%) is detectable. In this temperature interval, the decomposition of the Keggin structure begins and the anhydride of the acid is formed. To survey surface polarity as function of pre-treatment temperature, H_3PW samples from the same batch were investigated using pre-treatment temperatures of 70, 150, 250, 400, and 500 °C, respectively.

The UV/vis spectra of the polarity indicators **1**, **2**, and **3**, when adsorbed on H_3PW pre-treated at various temperatures, were immediately recorded after the components were mixed (see Fig. 2).

Immediately after adsorption of **1** on H_3PW in dichloromethane, the slurry shows an orange colour, but it changes to yellow very fast (few seconds). When **2** is adsorbed on H_3PW, it shows an intense yellow colour. **3**, when adsorbed on H_3PW, shows also a yellow colour. But the colour of **3** was red when adsorbed on the H_3PW pre-treated at 250 °C, indicating an increase of either the HBA capacity or donor strength. No utilizable UV/vis absorption bands of the probe on H_3PW were obtained when the coumarin dye **4** was used. The supernatant solution with the dissolved dye **4** loses its fluorescence and decolourisation takes place after few seconds if thermally pre-treated H_3PW samples are used. In contrast, the colour and fluorescence of **4** remain stable in the supernatant solution in the presence of the unpretreated H_3PW acid. These results indicate that **4** becomes protonated at the nitrogen atom by H_3PW. Therefore, **4** is not suitable as a surface dipolarity/polarizability indicator for H_3PW, because the solvatochromism of **4** expressed by a LSE relationship according to eqn. (1) does not consider protonation attacks upon the nitrogen atom.[47b]

The π^* values observed with **2** are quite ambiguous, because some of them have a negative sign. The LSE relationship eqn. (3) is only valid for **2** since protonation at one of the nitrogen atoms does not take place.[38,50] Because **2** can be protonated at different sites (the carbonyl oxygen [high π^*] or the lone electron pair of the dimethylamino groups [low π^*]),[37a,50] some of the π^* values seem questionable. Thus, the π^* values are not reasonable for the samples pre-treated at 150 or 250 °C. The other data are apparent values. This result agrees with that observed with **4** as a polarity indicator. As a consequence, the
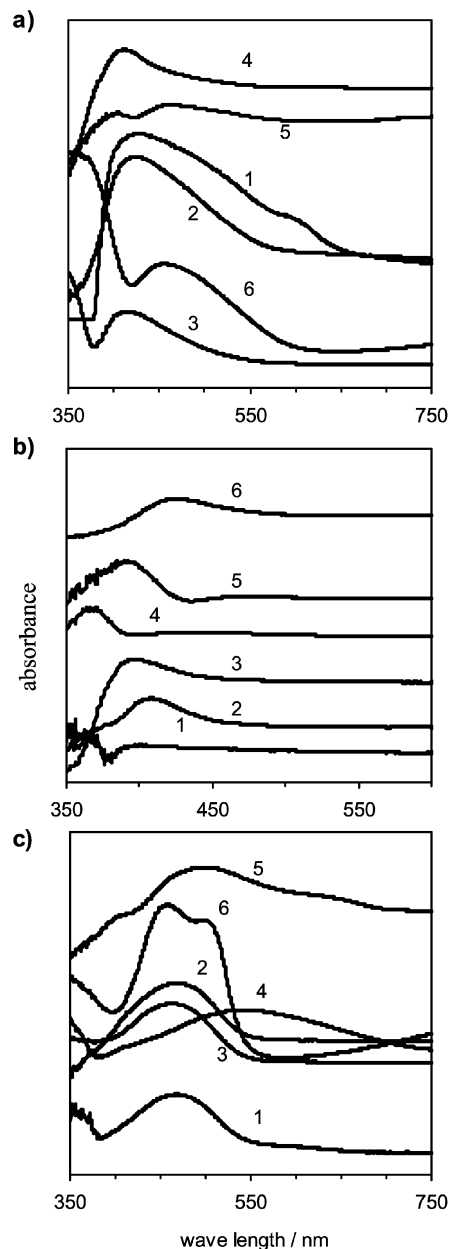

Fig. 2 UV/vis spectra of the solvatochromic probe dyes **1** (a), **2** (b), and **3** (c), respectively, when adsorbed on H_3PW without any pre-treatment (1) and pre-treated at 70 (2), 150 (3), 250 (4), 400 (5), and 500 °C (6).

α values calculated must also be handled with caution, because $v_{max}(\mathbf{2})$ is used in eqn. (2) for separation the contribution of π^* from $v_{max}(\mathbf{1})$. However, it makes no difference whether AN or α is used for the discussion (see also Fig. 3 below), because the contribution of $v_{max}(\mathbf{2})$ to α is not of importance. The solvent independent correlation coefficient of $v_{max}(\mathbf{2})$ from eqn. (2) contributes to about 4% to α.

The probe dye indicator **3** shows outstanding UV/vis spectroscopic behaviour when adsorbed on H_3PW pre-treated at 250 °C. When **3** is adsorbed on H_3PW pre-treated at 70, 150, or 400 °C, its UV/vis spectrum is similar to those on silica or an aluminosilicate.[51]

Two UV/vis absorption bands are observed when **3** is adsorbed on H_3PW pre-treated at 500 °C (see Fig. 2c) indicating two different acidic and/or basic sites. Both maxima were utilized (see Table 1). This effect is probably caused by a minor decomposition of the Keggin structure which is also indicated by a second weak intense absorption band in the UV/vis

Table 1 UV/vis absorption maxima of the probe dyes **1**, **2**, and **3** when adsorbed on H₃PW pre-treated at various temperatures, and the apparent polarity parameters α, β, π*, and AN calculated

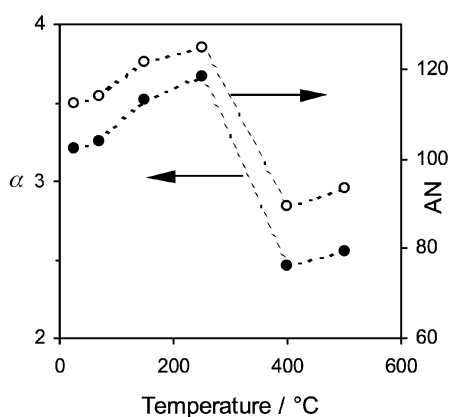| Pre-treatment	$v_{max}(\mathbf{1})/10^{-3}$ cm^{-1}	$v_{max}(\mathbf{2})/10^{-3}$ cm^{-1}	$v_{max}(\mathbf{3})/10^{-3}$ cm^{-1}	AN	α	π*	β
without	23.4	25.1	21.4	112.3	3.21	−0.02	0.04
70 °C	23.5	24.5	21.4	113.8	3.25	0.15	0.06
150 °C	24.0	25.2	21.6	121.5	3.52	−0.21	0.08
250 °C	24.3	27.2	18.5	124.7	3.67	−0.90	1.18
400 °C	21.7	25.5	20.1	89.4	2.46	0.28	0.17
500 °C	22.0	23.5	20.1/21.9	93.3	2.55	0.84	−0.36/0.24

Fig. 3 Influence of pre-treatment temperature on the related acidity parameters (α and AN) of H₃PW.

spectrum of **3** at about $\lambda \approx 400$ nm when adsorbed on the H₃PW sample pre-treated at 400 °C.

The measured UV/vis absorption maxima of the probe dyes **1**, **2**, **3** adsorbed, and the surface polarity parameters α, β, and π* as well as the acceptor numbers AN determined are listed in Table 1.

However, the α value found for the non-thermally pre-treated H₃PW is also unprecedentedly large indicating a strongly acidic fraction of mobile protons in the hydration shell.[1b]

The large value of the acidity parameter of H₃PW is in good agreement with its strong catalytic activity. Altogether, the α values for H₃PW are fairly large. They range between α = 2.46 (pre-treated at 400 °C) and α = 3.67 (pre-treated at 250 °C). Compared to other solid acid catalysts, HBD solvents, and ionic solutes,[52] H₃PW shows one of the largest α values reported so far. α parameters of different solutes, related solid acids, and solvents from literature are compiled in Table 2.

In the solid acid form, heteropolyacids have a low surface area and no explicit pore structure.[4] In this case non-polar molecules such as hydrocarbons are adsorbed only on its external surface (surface area is less than 10 m² g⁻¹) and react on these surface sites (surface type reactions). However, polar compounds like alcohols, water, pyridines, and esters are able to penetrate into the bulk structure forming a so-called "pseudo-liquid" phase.[20,53] This behaviour is due to the flexible nature of the secondary structure of the solid heteropolyacid. Thus, ammonia, pyridine, and methanol react with protons on the external surface of H₃PW and likewise with those in the internal frame of the solid. Hence, in these cases the overall acidity of the catalyst (bulk and external surface) is determined by all interactions with these probe molecules. Therefore, often no correlations between the acidity measured by these techniques and the catalytic activity for surface type reactions have been found.

When non-polar molecules are not adsorbed within the frame of heteropolyacids, reactions of those molecules can therefore be used to probe the surface acidity of heteropoly compounds.[5] That means, non-polar solvent molecules like

dichloromethane are unable to penetrate into the bulk structure. Reagents dissolved in this solvent (our probe dyes) should preferentially interact only on the external surface acid sites (surface-type reactions).[4]

The surface acidity (α value or AN) of H₃PW is strongly dependent on the pre-treatment temperature of H₃PW (see Fig. 3).

The unpretreated acid has a large water content, 14 mol water per mol H₃PW. Acid sites of the surface are covered with hydration water. Thus, the UV/vis absorption intensity which corresponds to the adsorbed amount of the indicator is quite low. This shows that the acidic sites are not completely able to interact with the solvatochromic indicator used.

Chlorotriphenylmethane undergoes no chemisorption to (C₆H₅)₃C⁺ using the unpretreated H₃PW despite its large α value (see Fig. 4). The reason for this result seems likely because physisorbed water molecules react with the triphenylmethylium ion. When chlorotriphenylmethane is adsorbed on thermally pre-treated H₃PW, then the characteristic triphenylmethylium ion UV/vis absorption band at $\lambda_{max} \approx 438$ nm can be always monitored (Fig. 4).[33,34,54–58] This carbenium ion is also formed by adsorption of triphenylmethane on the strong acidic form pre-treated at 250 °C (Fig. 5), whereas moderately strong solid acids like silica or alumina do not ionize (C₆H₅)₃CH.[45] This indicates that a redox process is associated with the chemisorption of (C₆H₅)₃CH on H₃PW. However, the fate of the hydride ion could not be determined.[34]

Usually, the triphenylmethylium UV/vis absorption shows a double band with two maxima at $\lambda_{max} = 410$ nm and 435 nm, the positions of which are independent of the environment used.[45,54–58] It should be emphasized that when (C₆H₅)₃C⁺ is adsorbed on H₃PW two effects in the UV/vis spectrum are observed which are different to its behaviour with other solid acids or Lewis acids in solution.[45,54–58] The main UV/vis absorption band evidently undergoes a bathochromic shift of about $\Delta\lambda \approx 10$ nm, and secondly an additional UV/vis absorption band at $\lambda_{max} = 500$ nm appears as a shoulder. Both effects occur independently of the counter ion X (Cl, OH, or H) of (C₆H₅)₃CX used (see Table 3). The new UV/vis band is probably caused by a charge-transfer (CT) transition from the

Table 2 Comparison of α and π* values of several organic solvents, solid acids, and ionic solutes from the literature

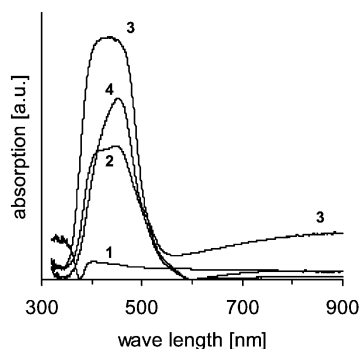| Species	α	π*	Reference
Methanol	0.98	0.6	52
Silica	1.0	1.0	37b
Formic acid	1.23	0.65	52
Cellulose (crystalline part)	1.4	0.35	44
2,2,2-Trifluoroethanol	1.51	0.73	52
Aluminosilicate	1.7	0.6	37a
1,1,1,3,3,3-Hexafluoro-2-propanol	1.96	0.65	52
Li⁺	2.07	—	52
H₃PW	3.5 ± 0.2	—	this work
Zn²⁺	3.67	—	52
Ba²⁺	5.15	—	52

Fig. 4 UV/vis absorption spectra of the triphenylmethylium ion when chemisorbed on H$_3$PW pre-treated at various temperatures. 1: unpretreated, 1.0852 g H$_3$PW; 2: pre-treated at 150 °C, 1.1990 g H$_3$PW; 3: pre-treated at 250 °C, 1.1179 g H$_3$PW; 4: pre-treated at 400 °C, 0.9818 g H$_3$PW; in each case: 5 ml dichloromethane, 357 µmol (C$_6$H$_5$)$_3$CCl.

Table 3 UV/vis absorption maxima of the triphenylmethylium ion when (C$_6$H$_5$)$_3$CX has been adsorbed on H$_3$PW pre-treated at various temperatures

Pre-treatment	λ/nm		
	X = Cl	X = OH	X = H
without	438	438	[a]
150 °C	444	444	[a]
250 °C	444/501	444/501	444/501
400 °C	451	451	[a]

[a] Not measured.

negatively charged framework of H$_3$PW as the donor to the triphenylmethylium as the acceptor.[59] This suggestion is supported by the fact that the UV/vis band at λ_{max} = 500 nm preferably appears when triphenylmethylium is adsorbed on a H$_3$PW sample which has been pre-treated at 250 °C. Maybe the large β value obtained for this H$_3$PW sample indicates an electron excess which is in accordance with the electron donor property of the H$_3$PW framework. However, the electron donor strength and HBA ability of a compound are related properties.[40a,60] Accordingly, the large β value corresponds to the unexpected UV/vis spectroscopic results of the triphenylmethylium/H$_3$PW adduct. Assuming a CT transition and using the linear correlation of v_{max}(CT) with the ionisation energy (I_P) from ref. 59(b), the electron donor strength of this site of H$_3$PW would correspond to an I_P of about 8.4 ± 0.2 eV.[59b] This value is comparable to the I_P of durene as a moderately strong π donor.[59]

The bathochromic shift of the main UV/vis absorption band of triphenylmethylium when adsorbed on H$_3$PW increases with increasing pre-treatment temperature, but is also independent of the counter ion used. (Table 3)

We think the bathochromic shift is caused by electron donor sites of H$_3$PW which are formed at higher pre-treatment temperatures. These sites are responsible for single electron transfer processes to acceptor molecules such as **3** and triphenylmethylium, respectively. However, since these processes occur then the original definition of the β value is not completely accomplished.[39,60]

The apparent Kamlet–Taft β values are quite low for H$_3$PW when pre-treated at temperatures of 70, 150, 400, and 500 °C.

It is still not clear on the basis of available data which structural feature is the reason for the unprecedentedly high β value for a H$_3$PW catalyst pre-treated at 250 °C.

We think that residual water traces influence significantly the electron donor ability of H$_3$PW, which can be likely detected with suitable acceptor molecules as the probe.

The high sensitivity of the probe **3** especially for observing small differences in the surface polarity of H$_3$PW is striking in this context. We think that the use of **3** as a versatile β and donor site indicator promises also for other solid acid catalysts more detailed information in the future.

Conclusion

The surface acidity of H$_3$PW can be estimated with genuine solvatochromic dyes like Fe(phen)$_2$(CN)$_2$. However, it seems the LSE concept approaches its limit for the strong acid H$_3$PW.

Thermal pre-treatment of H$_3$PW significantly influences both surface acidity and dipolarity/polarizability. Using 250 °C as pre-treatment temperature, H$_3$PW exhibits both the largest α as well as a quite large β value. In particular, the aminobenzodifuranone **3** has been found suitable for investigating the surface polarity of H$_3$PW. These qualitative UV/vis results are indications for the outstanding surface properties of H$_3$PW. Coumarin 153 (**4**) becomes completely and Michler's ketone (**2**) partly protonated by H$_3$PW when thermally pre-treated. Therefore, these probes are not suitable for determining reasonable π^* values of H$_3$PW.
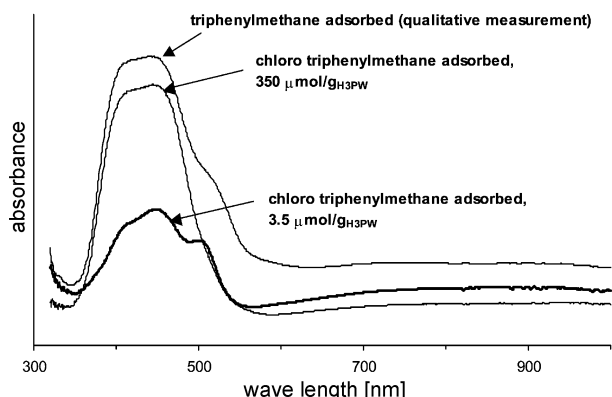
Fig. 5 UV/vis absorption spectra of triphenylmethylium when chemisorbed on H$_3$PW pre-treated at 250 °C using triphenylmethane (qualitative measurements) and chlorotriphenylmethane (two different concentrations) as carbenium precursors, respectively.

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