Probing Surface Polarity of Inorganic Oxides using Merocyanine-type Dyes derived from Barbituric Acid

Susan Seifert[a], Andreas Seifert[a], Gunther Brunklaus[b], Katja Hofmann[a], Tobias Rüffer[c], Heinrich Lang[c], and Stefan Spange*[a]

[a]Department of Polymer Chemistry, Chemnitz Technical University, Strasse der Nationen 62, 09107 Chemnitz, Germany. [b]Department of Physical Chemistry, University of Muenster, Corrensstrasse 28/30, 48149 Muenster, Germany, [c]Department of Inorganic Chemistry, Chemnitz Technical University, Strasse der Nationen 62, 09107 Chemnitz, Germany.

Supporting Information file

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Crystal data was collected on an Oxford Gemini Diffractometer at low temperature (105 K) using Cu-K_α-radiation (λ = 1.54 Å). The structure was solved by direct methods using SHELXS-97[S1]. The structure was refined by full-matrix least squares procedures on F^2, using SHELXL-97[S2]. All non hydrogen atoms were refined anisotropically. All hydrogen atoms were added on calculated positions, except of OH and NH which were found in difference fourier synthesis.

Table S1 Crystallographic data and collection parameters of **4**.

empirical formula	$C_{15}H_{15}N_3O_3$
formular weight [g·mol^{-1}]	285.30
color	dark violet
wavelength [Å]	1.54184
temperature [K]	105
crystal system	monocline
space group	P2(1)/n
a [Å]	4.5663(2)
b [Å]	9.6254(5)
c [Å]	30.3857(14)
α [°]	90
β [°]	91.668(5)
γ [°]	90
volume [Å^3]	1334.96(11)
Z	4
crystal size [mm^3]	0.3 x 0.2 x 0.1
calculated density [g·cm^{-3}]	1.420
F(000)	600
absorption coeffizient [mm^{-1}]	0.836
Θ range for data collection [°]	4.82 – 65.53
index range	$-5 \le 5, -10 \le 11, -35 \le 23$
reflections collected	8822
independent reflections	2277
R_{int}	0.0500
data	2277
restraints	0
refinement method	full-matrix least-squares on F^2
parameter	198
goodness-of-fit on F^2	0.958
final *R* indicates [$I \ge 2\sigma(I)$]	R1 = 0.0565, *w*R2 = 0.1460
R indicates all data	R1 = 0.0694, *w*R2 = 0.1530
largest diff. peak and hole [e Å^{-3}]	0.269, –0.316

Table S2 Bond length [Å] and angles [°] of **4**.

C(1)-N(1)	1.443(3)	C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600	C(1)-H(1C)	0.9600
C(2)-N(1)	1.463(3)	C(2)-H(2A)	0.9600
C(2)-H(2B)	0.9600	C(2)-H(2C)	0.9600
C(3)-N(1)	1.357(3)	C(3)-C(8)	1.412(3)
C(3)-C(4)	1.423(3)	C(4)-C(5)	1.372(3)
C(4)-H(4)	0.9300	C(5)-C(6)	1.404(3)
C(5)-H(5)	0.9300	C(6)-C(7)	1.409(3)
C(6)-C(9)	1.432(3)	C(7)-C(8)	1.373(3)
C(7)-H(7)	0.9300	C(8)-H(8)	0.9300
C(9)-C(10)	1.368(3)	C(9)-H(9)	0.9300
C(10)-C(11)	1.407(3)	C(10)-H(10)	0.9300
C(11)-C(12)	1.371(3)	C(11)-H(11)	0.9300
C(12)-C(15)	1.460(3)	C(12)-C(13)	1.465(3)
C(13)-O(1)	1.230(3)	C(13)-N(2)	1.383(3)
C(14)-O(2)	1.223(2)	C(14)-N(2)	1.366(3)
C(14)-N(3)	1.372(3)	C(15)-O(3)	1.225(2)
C(15)-N(3)	1.387(3)	N(2)-H(2N)	0.79(3)
N(3)-H(3N)	0.87(3)		

N(1)-C(1)-H(1A)	109.5	N(1)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5	N(1)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5	H(1B)-C(1)-H(1C)	109.5
N(1)-C(2)-H(2A)	109.5	N(1)-C(2)-H(2B)	109.5
H(2A)-C(2)-H(2B)	109.5	N(1)-C(2)-H(2C)	109.5
H(2A)-C(2)-H(2C)	109.5	H(2B)-C(2)-H(2C)	109.5
N(1)-C(3)-C(8)	121.75(19)	N(1)-C(3)-C(4)	120.9(2)
C(8)-C(3)-C(4)	117.33(18)	C(5)-C(4)-C(3)	121.0(2)
C(5)-C(4)-H(4)	119.5	C(3)-C(4)-H(4)	119.5
C(4)-C(5)-C(6)	121.7(2)	C(4)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1	C(5)-C(6)-C(7)	116.84(19)
C(5)-C(6)-C(9)	123.6(2)	C(7)-C(6)-C(9)	119.5(2)
C(8)-C(7)-C(6)	122.4(2)	C(8)-C(7)-H(7)	118.8
C(6)-C(7)-H(7)	118.8	C(7)-C(8)-C(3)	120.4(2)
C(7)-C(8)-H(8)	119.8	C(3)-C(8)-H(8)	119.8
C(10)-C(9)-C(6)	128.1(2)	C(10)-C(9)-H(9)	116.0
C(6)-C(9)-H(9)	116.0	C(9)-C(10)-C(11)	121.3(2)
C(9)-C(10)-H(10)	119.3	C(11)-C(10)-H(10)	119.3
C(12)-C(11)-C(10)	129.5(2)	C(12)-C(11)-H(11)	115.3
C(10)-C(11)-H(11)	115.3	C(11)-C(12)-C(15)	122.40(19)
C(11)-C(12)-C(13)	118.4(2)	C(15)-C(12)-C(13)	118.98(18)
O(1)-C(13)-N(2)	119.92(18)	O(1)-C(13)-C(12)	123.92(19)
N(2)-C(13)-C(12)	116.15(19)	O(2)-C(14)-N(2)	122.49(18)
O(2)-C(14)-N(3)	121.9(2)	N(2)-C(14)-N(3)	115.56(18)
O(3)-C(15)-N(3)	118.9(2)	O(3)-C(15)-C(12)	125.15(19)
N(3)-C(15)-C(12)	115.95(18)	C(3)-N(1)-C(1)	121.43(19)
C(3)-N(1)-C(2)	120.27(19)	C(1)-N(1)-C(2)	118.25(17)
C(14)-N(2)-C(13)	126.22(18)	C(14)-N(2)-H(2N)	119.9(18)
C(13)-N(2)-H(2N)	113.8(18)	C(14)-N(3)-C(15)	126.2(2)
C(14)-N(3)-H(3N)	119.7(15)	C(15)-N(3)-H(3N)	114.0(15)

Table S3 Torsions angle [°] of **4**.

C(4) C(3) N(1) C(1)	0.54	C(4) C(3) N(1) C(2)	177.83
C(8) C(3) N(1) C(1)	-178.87	C(8) C(3) N(1) C(2)	-1.58
N(1) C(3) C(4) C(5)	-175.77	C(8) C(3) C(4) C(5)	3.66
N(1) C(3) C(8) C(7)	175.84	C(4) C(3) C(8) C(7)	-3.59
C(3) C(4) C(5) C(6)	-0.51	C(4) C(5) C(6) C(7)	-2.69
C(4) C(5) C(6) C(9)	174.77	C(5) C(6) C(7) C(8)	2.76
C(9) C(6) C(7) C(8)	-174.81	C(5) C(6) C(9) C(10)	-5.04
C(7) C(6) C(9) C(10)	172.35	C(6) C(7) C(8) C(3)	0.41
C(6) C(9) C(10) C(11)	-177.36	C(9) C(10) C(11) C(12)	170.79
C(10) C(11) C(12) C(13)	-175.44	C(10) C(11) C(12) C(15)	-0.43
C(11) C(12) C(13) O(1)	-11.84	C(11) C(12) C(13) N(2)	166.98
C(15) C(12) C(13) O(1)	172.98	C(15) C(12) C(13) N(2)	-8.20
C(11) C(12) C(15) O(3)	11.37	C(11) C(12) C(15) N(3)	-167.56
C(13) C(12) C(15) O(3)	-173.65	C(13) C(12) C(15) N(3)	7.42
O(1) C(13) N(2) C(14)	179.75	C(12) C(13) N(2) C(14)	0.88
O(2) C(14) N(2) C(13)	-173.86	N(3) C(14) N(2) C(13)	6.89
O(2) C(14) N(3) C(15)	172.93	N(2) C(14) N(3) C(15)	-7.81
O(3) C(15) N(3) C(14)	-178.21	C(12) C(15) N(3) C(14)	0.78
H(1A) C(1) N(1) C(2)	3	H(1A) C(1) N(1) C(3)	-179
H(1B) C(1) N(1) C(2)	-117	H(1B) C(1) N(1) C(3)	61
H(1C) C(1) N(1) C(2)	123	H(1C) C(1) N(1) C(3)	-59
H(2A) C(2) N(1) C(1)	-3	H(2A) C(2) N(1) C(3)	180
H(2B) C(2) N(1) C(1)	-123	H(2B) C(2) N(1) C(3)	60
H(2C) C(2) N(1) C(1)	117	H(2C) C(2) N(1) C(3)	-60
N(1) C(3) C(4) H(4)	4	C(8) C(3) C(4) H(4)	-176
N(1) C(3) C(8) H(8)	-4	C(4) C(3) C(8) H(8)	176
C(3) C(4) C(5) H(5)	179	H(4) C(4) C(5) C(6)	179
H(4) C(4) C(5) H(5)	-1	H(5) C(5) C(6) C(7)	177
H(5) C(5) C(6) C(9)	-5	C(5) C(6) C(7) H(7)	-177
C(9) C(6) C(7) H(7)	5	C(5) C(6) C(9) H(9)	175
C(7) C(6) C(9) H(9)	-8	C(6) C(7) C(8) H(8)	-180
H(7) C(7) C(8) C(3)	-180	H(7) C(7) C(8) H(8)	0
C(6) C(9) C(10) H(10)	3	H(9) C(9) C(10) C(11)	3
H(9) C(9) C(10) H(10)	-177	C(9) C(10) C(11) H(11)	-9
H(10) C(10) C(11) C(12)	-9	H(10) C(10) C(11) H(11)	171
H(11) C(11) C(12) C(13)	5	H(11) C(11) C(12) C(15)	180
O(1) C(13) N(2) H(2N)	3	C(12) C(13) N(2) H(2N)	-176
O(2) C(14) N(2) H(2N)	3	N(3) C(14) N(2) H(2N)	-176
O(2) C(14) N(3) H(3N)	-5	N(2) C(14) N(3) H(3N)	174

Details of the single-crystal X-ray structure of 4

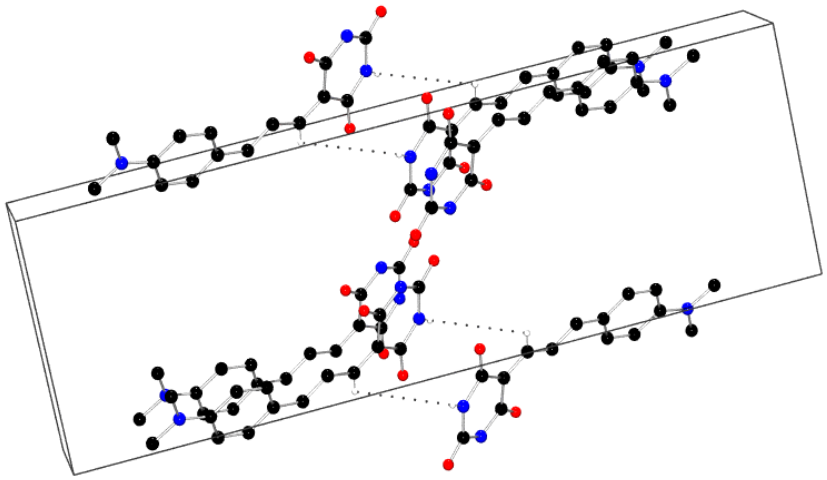

Fig. S1 Single-crystal X-ray structure of **4.** Contact between *N2H* and *CH11* with a distance of about 4.10 Å.

^{1}H–^{1}H 2D DQ MAS, ^{1}H MAS and liquid ^{1}H NMR spectra of 6

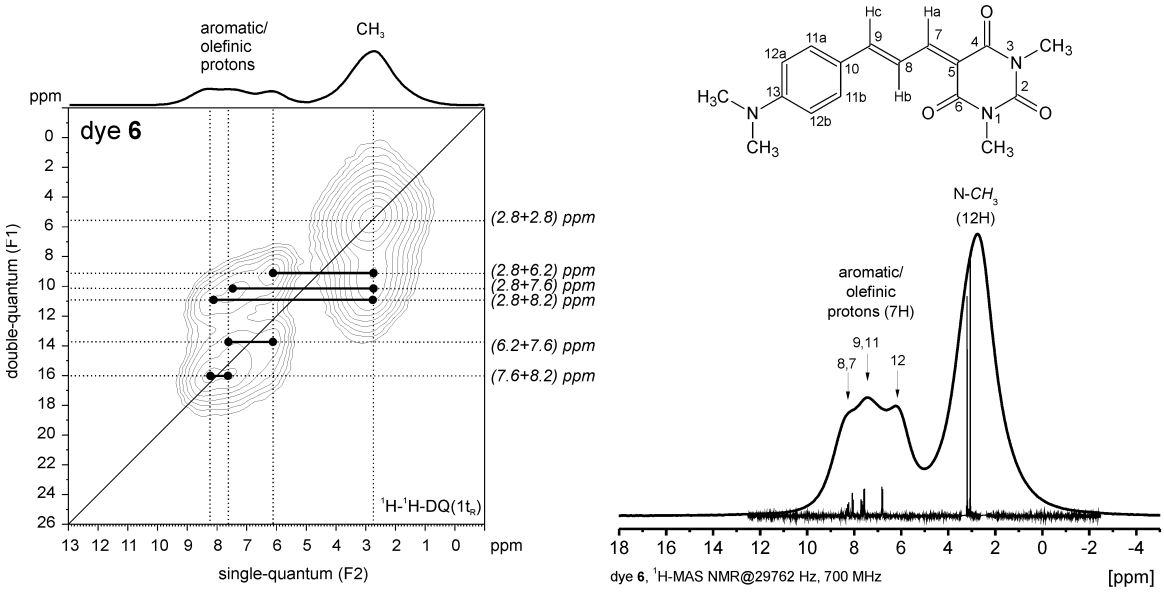

Fig. S2 ^{1}H–^{1}H 2D DQ MAS NMR spectrum of compound **6** at 700 MHz and 29762 Hz MAS, acquired under the following experimental conditions: 120 t_1 increments at steps of 33.6 μs, relaxation delay 5 s, 32 transients per increment. The F2 projection is shown on the top. The ^{1}H MAS NMR and liquid ^{1}H NMR spectra of compound **6** are compared at the right side.

Table S4 Measured UV/vis absorption maxima $\tilde{\nu}_{max}$(dye) of dyes **4**–**7** dissolved in various solvents and accordingly solvents polarity parameters in terms of Kamlet-Taft.

solvents	$\tilde{\nu}_{max}$(**4**)* / 10^3 cm^{-1}	$\tilde{\nu}_{max}$(**5**)* / 10^3 cm^{-1}	$\tilde{\nu}_{max}$(**6**)* / 10^3 cm^{-1}	$\tilde{\nu}_{max}$(**7**)* / 10^3 cm^{-1}	α[S3]	β[S3]	π^*[S3]
acetic acid	17.98	18.22	18.54	17.08	1.12	0.45	0.64
acetone	19.59	19.51	19.47	18.03	0.08	0.43	0.71
acetonitrile	19.17	19.28	19.36	17.75	0.19	0.40	0.75
acetophenone	18.76	18.76	18.78	17.39	0.04	0.49	0.90
aniline	17.82	17.85	17.93	16.71	0.26	0.50	0.73
anisol	18.98	19.11	19.27	17.67	0.00	0.32	0.73
benzene	19.01	19.30	19.54	17.91	0.00	0.37	0.90
benzonitrile	18.55	18.62	18.73	17.27	0.00	0.37	0.90
1-butanol	18.75	18.72	18.65	17.51	0.84	0.84	0.47
tert-butanol	18.98	18.83	18.69	[a]	0.42	0.93	0.41
γ-butyrolacton	18.90	18.94	19.05	17.45	0.00	0.49	0.87
chloroform	18.30	18.48	18.73	17.24	0.20	0.10	0.58
1-decanol	19.05	19.01	18.94	17.79	0.70	0.82	0.45
1,2-dichlorethane	18.48	18.69	18.98	17.30	0.00	0.10	0.81
dichloromethane	18.41	18.61	18.87	17.26	0.13	0.10	0.82
diethylether	20.32	20.34	20.07	18.74	0.00	0.47	0.27
N,N-dimethylacetamid	19.38	19.23	19.05	17.89	0.00	0.76	0.88
1,4-dioxane	20.20	20.12	20.12	18.59	0.00	0.37	0.55
dimethyl formamide	19.24	19.15	19.01	17.66	0.00	0.69	0.88
dimethyl sulfoxide	18.98	18.89	18.69	17.70	0.00	0.76	1.00
ethanol	18.84	18.80	18.76	17.63	0.86	0.75	0.54
ethyl acetate	19.90	19.87	19.84	18.34	0.00	0.45	0.55
1,2-ethanediol	17.86	17.92	17.98	16.79	0.90	0.52	0.92
formamide	17.83	17.86	17.95	16.72	0.71	0.48	0.97
HFIP[b]	17.08	17.05	17.09	16.31	1.96	0.00	0.65
HMPA[c]	19.88	19.08	18.55	18.21	0.00	1.05	0.87
methanol	18.73	18.73	18.76	17.48	0.98	0.66	0.60
N-methylformamide	18.73	18.73	18.69	17.42	0.62	0.80	0.90
nitromethane	18.59	18.76	19.05	17.27	0.22	0.06	0.85
piperidine	20.86	20.52	19.59	20.33	0.00	1.04	0.30
pyridine	19.27	19.12	18.90	17.67	0.00	0.64	0.87
1-propanol	18.45	18.42	18.35	17.33	0.84	0.90	0.52
2-propanol	18.93	18.83	18.69	17.64	0.76	0.76	0.48
tetrachloroethane	17.99	18.18	18.38	16.89	0.00	0.00	0.95
tetrachloromethane	[a]	19.49	19.72	[a]	0.00	0.10	0.28
tetrahydrofuran	20.15	19.87	19.71	18.41	0.00	0.55	0.58
tetramethylurea	19.49	19.27	19.16	17.92	0.00	0.80	0.83
toluene	19.42	19.46	19.66	17.97	0.00	0.11	0.54
trichloroacetic acid	26.11	26.11	26.32	24.57	--	--	--
N,N,N-triethylamine	21.14	20.79	20.12	19.34	0.00	0.71	0.14
trifluoroacetic acid	26.80	26.91	26.98	25.24	--	--	--
2,2,2-trifluoroethanol	17.48	17.52	17.62	16.54	1.51	0.00	0.73
p-xylole	19.12	19.62	19.82	17.84	0.00	0.12	0.43
$\Delta\lambda$ [nm]	113	106	88	96			
$\Delta\tilde{\nu}$ [cm^{-1}]	4060	3740	3030	3030			

*this work, [a]The dye is insoluble in this solvent.[b]1,1,1,3,3,3-hexafluoroisopropanol, [c]hexamethylphosphoramide

Interactions with tetra-*n*-butyl ammonium fluoride (TBAF)

The UV/vis spectra of **4** and **6** are shown in Figure S3. An irreversible decrease of the intensity of the UV/vis absorption band was observed after TBAF addition to **6** dissolved in dichloromethane. Furthermore, signals of *N,N*-dimethylamino cinnamonaldehyde and *N,N*-dimethylaminobenzaldehyde were measured in the ^{1}H NMR spectra (Figure S4-a) confirming the degradation of dye **6**.

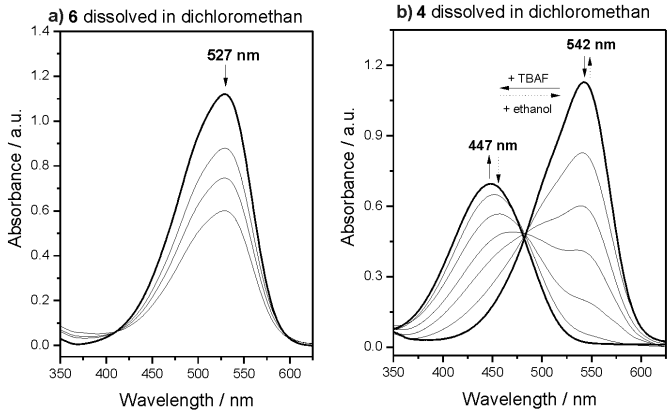

Fig. S3 a) Time-dependent (within 20 min) UV/vis absorption spectra of **6** after singular addition of TBAF*(left) and b) UV/vis titration of **4** with TBAF*(right) (*1 M solution in tetrahydrofuran).

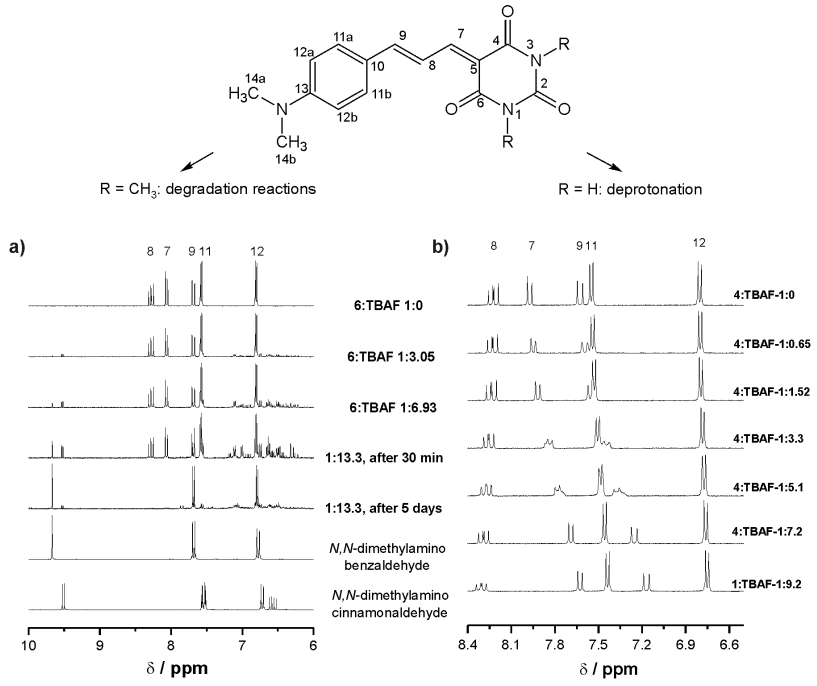

Fig. S3 a) ^{1}H NMR spectra of dye **6**, *N,N*-dimethylamino benzaldehyde, and *N,N*-dimethylamino cinnamonaldehyde dissolved in DMSO-d_6 with TBAF addition. b) ^{1}H NMR titration of dye **4** dissolved in DMSO-d_6 with TBAF.

In contrast, the UV/vis absorption band of **4** in dichloromethane show a hypo- and hypsochromic shift with addition of TBAF. The UV/vis absorption spectra intersect in an isosbestic point at 483 nm. The reaction is reversible with addition of traces of water, for example, using undried ethanol. The ^{1}H NMR-titration of **4** with TBAF in DMSO-d_6 indicates a deprotonation reaction of the barbituric acid moiety.

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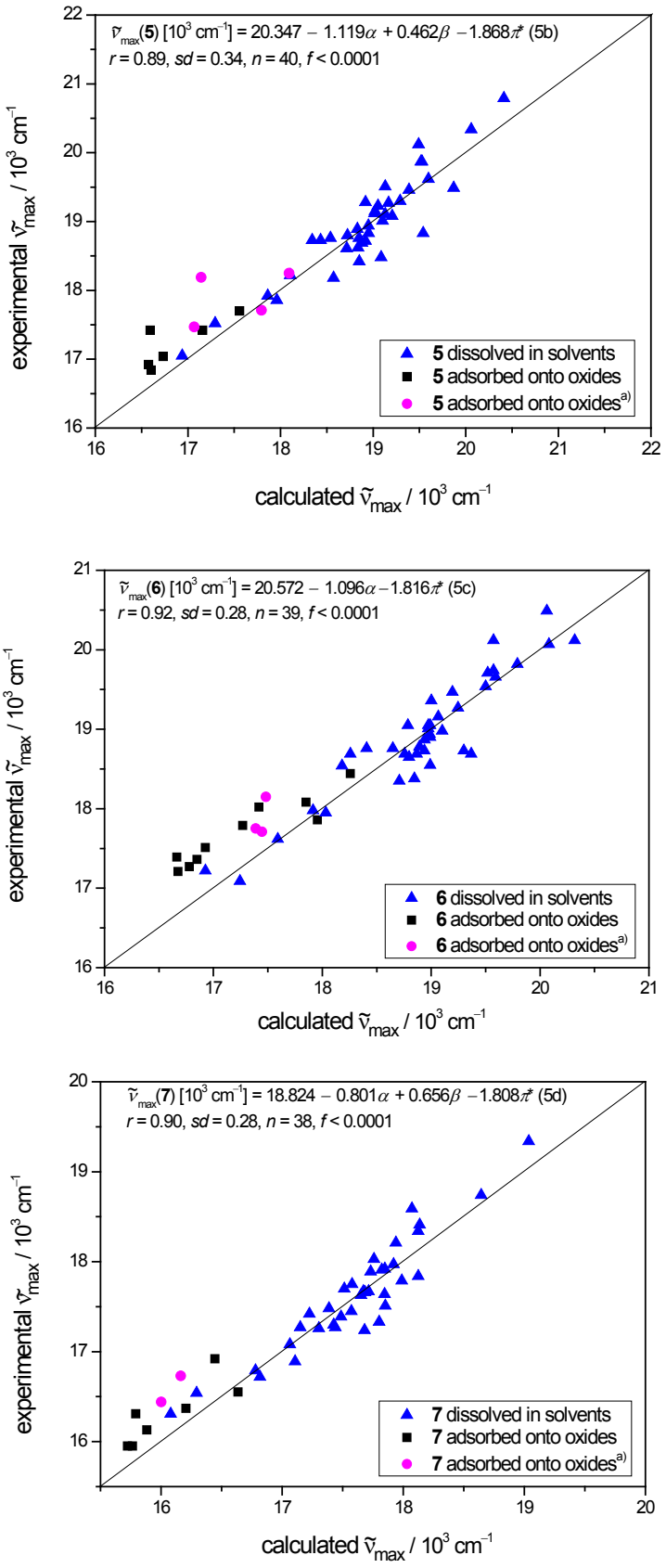

Fig. S5 Correlation of experimental found and calculated wavenumbers of dye **5**–**7** dissolved in different solvents (▲) and adsorbed onto oxidic surfaces (■) ([a)]longest wavelength UV/vis maximum after multipeak fitting (●)), obtained using equation 5b (dye **5**), 5c (dye **6**), 5d (dye **7**) and the polarity parameters of Tables 6 and S4, respectively.

UV/vis absorption spectra of iron(III) oxide and tungsten(VI) oxide

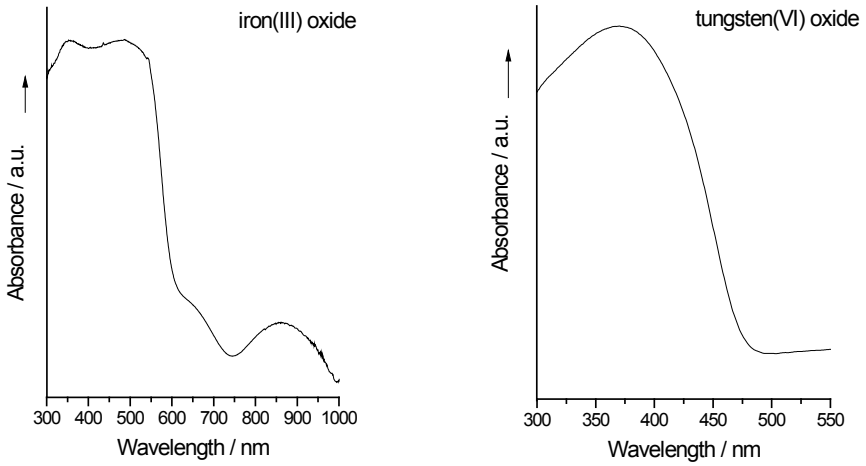

Fig. S6 UV/vis absorption spectra of iron(III) oxide and tungsten(VI) oxide.

Used metals and metal oxides, BET, and source

Table S5 Used metals and metal oxides, BET and source.

	BET / $m^2\ g^{-1}$	purity / %	source
ZnO	5	99.99	Alfa Aesar
Al_2O_3	100	--	Degussa
Al_2O_3	339	--	Merck
Siral 1.5	240	--	Condea
Siral 15	357	--	Condea
Siral 30	351	--	Condea
Siral 60	356	--	Condea
Siral 80	227	--	Condea
Fe_2O_3	8	99.80	Alfa Aesar
KG 60	423	--	Merck
MgO	7	99.95	Alfa Aesar
$CaCO_3$	6	--	Fluka
TiO_2 (rutile)	7	97	Alfa Aesar
TiO_2 (anatas)	229	99	Alfa Aesar
WO_3	3	99.8	Alfa Aesar
Zinc	2	99.90	Alfa Aesar
Aluminium	2	99.97	Alfa Aesar

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[S2] Sheldrick, G. M. SEHLXL-97, *Programm for Crystal Structure Refinement*, 1997, University of Göttingen.

[S3] Y. Marcus, *Chem. Soc. Rev.*, 1993, 409.