Supporting Information for

Solvatochromism and Acidochromism of Azobenzene-Functionalized Poly(vinyl amines)

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Table S1: Crystallographic data and collection parameters for **5M**.

empirical formula	$C_{15}H_{14}N_6O_6$
formula weight	374.32
colour	red
wavelength (Å)	1.54184
temperature (K)	100
crystal system	monoclinic
space group	*C2*
a [Å]	13.8296(5)
b [Å]	6.6323(2)
c [Å]	35.6388(12)
α [°]	90
β [°]	90.160(3)
γ [°]	90
volume ($Å^3$)	3268.85(19)
Z	8
calcd. density (g^*cm^{-3})	1.521
absorption coefficient (mm^{-1})	1.033
F(000)	1552
crystal size (mm^3)	0.40 x 0.06 x 0.04
Θ range for data collection(°)	3.27–62.49
index ranges	$-15 \leq h \leq 15, -7 \leq k \leq 6, -41 \leq l \leq 41$
reflections collected	10647
independent reflections	3970
R_{int}	0.0268
data/restraints/parameter	3970/1/495
refinement method	full-matrix least-squares on F^2
goodness-of-fit on F^2	0.995
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0283, *w*R2 = 0.0673
R indices all data	R1 = 0.0325, *w*R2 = 0.0683
absolute structure parameter	0.34(13)
largest diff. peak and hole ($e^* Å^{-3}$)	0.158, −0.204

Some difficulties have been encountered in the determination of the crystal system and space group for **5M**. In particular, the question was raised whether **5M** crystallized in an ortho-rhombic or monoclinic lattice. While the beta angle significantly deviated from 90 °, the comparison of symmetry equivalent reflections suggested the Laue symmetry *mmm*. Space

group determination after integration in an orthorhombic lattice resulted in centrosymmetric *Cmca* or non-centrosymmetric *Aba*2 due to the systematic absence of reflections. In *Cmca* no reasonable solution was found. In contrast, using *Aba*2 a solution was obtained with one molecule **5M** in the asymmetric unit statistically disordered (ratio 0.51:0.49) on two positions (parallel orientation). However, the resulting structural parameters: R_1 0.2195, wR_2 0.5128, GOF 2.91, residual electron density 0.57 and –1.22, absolute structure parameter 0.2(9) indicate that *Aba*2 is the wrong space group and hence orthorhombic is the wrong lattice. It is commonly observed that a monoclinic lattice with beta angle of approximately 90 ° may emulate orthorhombic. Space group determination in a monoclinic lattice revealed *C*2, *C*2/*c* and *Cm* as possible space groups. Only in case of *C*2 a reasonable solution was found.

Table S2. Bond lengths /Å for **5M**.

C(1)-N(1)	1.473(2)	C(16)-N(7)	1.466(3)
C(1)-C(3)	1.513(3)	C(16)-C(18)	1.518(3)
C(1)-C(2)	1.518(3)	C(16)-C(17)	1.519(3)
C(1)-H(1)	0.9800	C(16)-H(16)	0.9800
C(2)-H(2A)	0.9600	C(17)-H(17A)	0.9600
C(2)-H(2B)	0.9600	C(17)-H(17B)	0.9600
C(2)-H(2C)	0.9600	C(17)-H(17C)	0.9600
C(3)-H(3A)	0.9600	C(18)-H(17A)	0.9600
C(3)-H(3B)	0.9600	C(18)-H(17B)	0.9600
C(3)-H(3C)	0.9600	C(18)-H(17C)	0.9600
C(4)-N(1)	1.337(2)	C(19)-N(7)	1.330(3)
C(4)-C(9)	1.428(3)	C(19)-C(20)	1.434(3)
C(4)-C(5)	1.441(2)	C(19)-C(24)	1.44182)
C(5)-C(6)	1.385(2)	C(20)-C(21)	1.386(3)
C(5)-N(2)	1.445(2)	C(20)-N(8)	1.454(2)
C(6)-C(7)	1.381(3)	C(21)-C(22)	1.388(2)
C(6)-H(6)	0.9300	C(21)-H(21)	0.9300
C(7)-N(3)	1.404(2)	C(22)-N(9)	1.397(2)
C(7)-C(8)	1.417(2)	C(22)-C(23)	1.415(3)
C(8)-C(9)	1.362(2)	C(23)-C(24)	1.358(3)
C(8)-H(8)	0.9300	C(23)-H(23)	0.9300
C(9)-H(9)	0.9300	C(24)-H(24)	0.9300
C(10)-C(15)	1.389(2)	C(25)-C(30)	1.398(2)
C(10)-C(11)	1.401(2)	C(25)-C(26)	1.399(3)
C(10)-N(4)	1.427(2)	C(25)-N(10)	1.418(2)
C(11)-C(12)	1.382(3)	C(26)-C(27)	1.378(3)
C(11)-H(11)	0.9300	C(26)-H(26)	0.93000
C(12)-C(13)	1.388(3)	C(27)-C(28)	1.397(2)
C(12)-H(12)	0.9300	C(27)-H(27)	0.9300
C(13)-C(14)	1.385(2)	C(28)-C(29)	1.378(3)
C(13)-N(5)	1.471(2)	C(28)-N(11)	1.470(2)
C(14)-C(15)	1.383(3)	C(29)-C(30)	1.376(3)
C(14)-H(14)	0.9300	C(29)-H(29)	0.9300
C(15)-N(6)	1.473(2)	C(30)-N12)	1.474(2)
N(1)-H(1N)	0.80(3)	N(7)-H(7N)	0.80(2)
N(2)-O(2)	1.234(2)	N(8)-O(8)	1.228(2)
N(2)-O(1)	1.238(2)	N(8)-O(7)	1.236(2)
N(3)-N(4)	1.258(2)	N(9)-N(10)	1.267(2)
N(5)-O(4)	1.217(2)	N(11)-O(10)	1.222(2)
N(5)-O(3)	1.226(2)	N(11)-O(9)	1.224(2)
N(6)-O(5)	1.210(2)	N(12)-O(12)	1.213(3)
N(6)-O(6)	1.223(2)	N(12)-O(11)	1.221(3)

Table S3. Bond angles /deg for **5M**.

N(1)-C(1)-C(3)	110.11(17)	N(7)-C(16)-C(18)	110.16(17)
N(1)-C(1)-C(2)	108.16(16)	N(7)-C(16)-C(17)	108.10(16)
C(3)-C(1)-C(2)	112.83(17)	C(18)-C(16)-C(17)	112.92(17
N(1)-C(1)-H(1)	108.5	N(7)-C(16)-H(16)	108.5
C(3)-C(1)-H(1)	108.5	C(18)-C(16)-H(16)	108.5
C(2)-C(1)-H(1)	108.5	C(17)-C(16)-H(16)	108.5
C(1)-C(2)-H(2A)	109.5	C(16)-C(17)-H(17A)	109.5
C(1)-C(2)-H(2B)	109.5	C(16)-C(17)-H(17B)	109.5
H(2A)-C(2)-H(2B)	109.5	H(17A)-C(17)-H(17B)	109.5
C(1)-C(2)-H(2C)	109.5	C(16)-C(17)-H(17A)	109.5
H(2A)-C(2)-H(2C)	109.5	H(17A)-C(17)-H(17C)	109.5
H(2B)-C(2)-H(2C)	109.5	H(17B)-C(17)-H(17C)	109.5
C(1)-C(3)-H(3A)	109.5	C(16)-C(18)-H(18A)	109.5
C(1)-C(3)-H(3B)	109.5	C(16)-C(18)-H(18B)	109.5
H(3A)-C(3)-H(3B)	109.5	H(18A)-C(18)-H(18B)	109.5
C(1)-C(3)-H(3C)	109.5	C(16)-C(18)-H(18C)	109.5
H(3A)-C(3)-H(3C)	109.5	H(18A)-C(18)-H(18C)	109.5
H(3B)-C(3)-H(3C)	109.5	H(18B)-C(18)-H(18C)	109.5
N(1)-C(4)-C(9)	120.98(16)	N(7)-C(19)-C(20)	123.83(16)
N(1)-C(4)-C(5)	123.65(16)	N(7)-C(19)-C(24)	120.96(16)
C(9)-C(4)-C(5)	115.36(15)	C(20)-C(19)-C(24)	115.19(16)
C(6)-C(5)-C(4)	121.45(15)	C(21)-C(20)-C(19)	121.67(15)
C(6)-C(5)-N(2)	116.42(14)	C(21)-C(20)-N(8)	116.23(15)
C(4)-C(5)-N(2)	122.13(15)	C(19)-C(20)-N(8)	122.10(15)
C(7)-C(6)-C(5)	121.20(15)	C(20)-C(21)-C(22)	121.10(16)
C(7)-C(6)-H(6)	119.4	C(20)-C(21)-H(21)	119.4
C(5)-C(6)-H(6)	119.4	C(22)-C(21)-H(21)	119.4
C(6)-C(7)-N(3)	115.30(15)	C(21)-C(22)-N(9)	115.39(15)
C(6)-C(7)-C(8)	118.80(15)	C(21)-C(22)-C(23)	118.74(16)
N(3)-C(7)-C(8)	125.89(15)	N(9)-C(22)-C(23)	125.87(15)
C(9)-C(8)-C(7)	120.68(16)	C(24)-C(23)-C(22)	120.80(16)
C(9)-C(8)-H(8)	119.7	C(24)-C(23)-H(23)	119.6
C(7)-C(8)-H(8)	119.7	C(22)-C(23)-H(23)	119.6
C(8)-C(9)-C(4)	122.48(16)	C(23)-C(24)-C(19)	122.47(16)
C(8)-C(9)-H(9)	118.8	C(23)-C(24)-H(24)	118.8
C(4)-C(9)-H(9)	118.8	C(19)-C(24)-H(24)	118.8
C(15)-C(10)-C(11)	118.30(15)	C(30)-C(25)-C(26)	117.99(16)
C(15)-C(10)-N(4)	116.58(14)	C(30)-C(25)-N(10)	116.83(15)
C(11)-C(10)-N(4)	125.07(16)	C(26)-C(25)-N(10)	125.12(15)
C(12)-C(11)-C(10)	119.93(16)	C(27)-C(26)-C(25)	120.04(15)
C(12)-C(11)-H(11)	120.0	C(27)-C(26)-H(26)	120.0
C(10)-C(11)-H(11)	120.0	C(25)-C(26)-H(26)	120.0
C(11)-C(12)-C(13)	119.56(15)	C(26)-C(27)-C(28)	119.39(16)
C(11)-C(12)-H(12)	120.2	C(26)-C(27)-H(27)	120.3
C(13)-C(12)-H(12)	120.2	C(28)-C(27)-H(27)	120.3
C(14)-C(13)-C(12)	122.35(15)	C(29)-C(28)-C(27)	122.48(16)
C(14)-C(13)-N(5)	118.13(15)	C(29)-C(28)-N(11)	118.13(15)
C(12)-C(13)-N(5)	119.52(15)	C(27)-C(28)-N(11)	119.39(15)
C(15)-C(14)-C(13)	116.65(16)	C(30)-C(29)-C(28)	116.60(16)
C(15)-C(14)-H(14)	121.7	C(30)-C(29)-H(29)	121.7
C(13)-C(14)-H(14)	121.7	C(28)-C(29)-H(29)	121.7
C(14)-C(15)-C(10)	123.18(15)	C(29)-C(30)-C(25)	123.47(16)
C(14)-C(15)-N(6)	117.29(15)	C(29)-C(30)-N(12)	117.32(15)
C(10)-C(15)-N(6)	119.53(14)	C(25)-C(30)-N(12)	119.22(15)
C(4)-N(1)-C(1)	125.72(16)	C(19)-N(7)-C(16)	125.74(15)
C(4)-N(1)-H(1N)	116.0(15)	C(19)-N(7)-H(7N)	118.9(17)
C(1)-N(1)-H(1N)	118.1(14)	C(16)-N(7)-H(7N)	115.3(17)
O(2)-N(2)-O(1)	122.07(15)	O(8)-N(8)-O(7)	121.96(14)

O(2)-N(2)-C(5)	118.62(14)	O(8)-N(8)-C(20)	118.73(15)
O(1)-N(2)-C(5)	119.31(14)	O(7)-N(8)-C(20)	119.31(15)
N(4)-N(3)-C(7)	114.52(14)	N(10)-N(9)-C(22)	114.82(14)
N(3)-N(4)-C(10)	112.17(14)	N(9)-N(10)-C(25)	112.42(14)
O(4)-N(5)-O(3)	124.01(14)	O(10)-N(11)-O(9)	124.17(15)
O(4)-N(5)-C(13)	118.14(14)	O(10)-N(11)-C(28)	118.13(15)
O(3)-N(5)-C(13)	117.85(15)	O(9)-N(11)-C(28)	117.70(14)
O(5)-N(6)-O(6)	124.60(15)	O(12)-N(12)-O(11)	124.75(15)
O(5)-N(6)-C(15)	118.13(17)	O(12)-N(12)-C(30)	117.92(17)
O(6)-N(6)-C(15)	117.26(16)	O(11)-N(12)-C(30)	117.30(17)

Table S4. Torsion angles /deg for **5M**

|			
N(1)-C(4)-C(5)-C(6)	177.5(2)	N(7)-C(19)-C(20)-C(21)	-177.4(2)
C(9)-C(4)-C(5)-C(6)	-1.4(3)	C(24)-C(19)-C(20)-C(21)	1.3(3)
N(1)-C(4)-C(5)-N(2)	-2.7(3)	N(7)-C(19)-C(20)-N(8)	3.1(3)
C(9)-C(4)-C(5)-N(2)	178.4(2)	C(24)-C(19)-C(20)-N(8)	-178.25(19)
C(4)-C(5)-C(6)-C(7)	0.0(3)	C(19)-C(20)-C(21)-C(22)	0.3(3)
N(2)-C(5)-C(6)-C(7)	-179.90(19)	N(8)-C(20)-C(21)-C(22)	179.81(18)
C(5)-C(6)-C(7)-N(3)	-179.55(19)	C(20)-C(21)-C(22)-N(9)	179.58(19)
C(5)-C(6)-C(7)-C(8)	0.9(3)	C(20)-C(21)-C(22)-C(23)	-1.1(3)
C(6)-C(7)-C(8)-C(9)	-0.2(3)	C(21)-C(22)-C(23)-C(24)	0.4(3)
N(3)-C(7)-C(8)-C(9)	-179.7(2)	N(9)-C(22)-C(23)-C(24)	179.6(2)
C(7)-C(8)-C(9)-C(4)	-1.3(3)	C(22)-C(23)-C(24)-C(19)	1.2(3)
N(1)-C(4)-C(9)-C(8)	-176.8(2)	N(7)-C(19)-C(24)-C(23)	176.7(2)
C(5)-C(4)-C(9)-C(8)	2.1(3)	C(20)-C(19)-C(24)-C(23)	-2.0(3)
C(15)-C(10)-C(11)-C(12)	0.4(3)	C(30)-C(25)-C(26)-C(27)	-0.4(3)
N(4)-C(10)-C(11)-C(12)	177.7(2)	N(10)-C(25)-C(26)-C(27)	-177.6(2)
C(10)-C(11)-C(12)-C(13) -	1.4(3)	C(25)-C(26)-C(27)-C(28)	1.3(3)
C(11)-C(12)-C(13)-C(14)	0.8(3)	C(26)-C(27)-C(28)-C(29) -	0.6(3)
C(11)-C(12)-C(13)-N(5)	-178.80(19)	C(26)-C(27)-C(28)-N(11)	178.75(19)
C(12)-C(13)-C(14)-C(15)	0.8(3)	C(27)-C(28)-C(29)-C(30)	-0.9(3)
N(5)-C(13)-C(14)-C(15)	-179.60(19)	N(11)-C(28)-C(29)-C(30)	179.69(19)
C(13)-C(14)-C(15)-C(10)	-1.8(3)	C(28)-C(29)-C(30)-C(25)	1.9(3)
C(13)-C(14)-C(15)-N(6)	177.77(17)	C(28)-C(29)-C(30)-N(12)	-177.73(18)
C(11)-C(10)-C(15)-C(14)	1.3(3)	C(26)-C(25)-C(30)-C(29)	-1.3(3)
N(4)-C(10)-C(15)-C(14)	-176.23(19)	N(10)-C(25)-C(30)-C(29)	176.2(2)
C(11)-C(10)-C(15)-N(6)	-178.34(18)	C(26)-C(25)-C(30)-N(12)	178.31(19)
N(4)-C(10)-C(15)-N(6)	4.2(3)	N(10)-C(25)-C(30)-N(12)	-4.2(3)
C(9)-C(4)-N(1)-C(1)	-3.3(3)	C(20)-C(19)-N(7)-C(16)	-177.9(2)
C(5)-C(4)-N(1)-C(1)	177.9(2)	C(24)-C(19)-N(7)-C(16)	3.5(3)
C(3)-C(1)-N(1)-C(4)	-83.4(2)	C(18)-C(16)-N(7)-C(19)	83.0(2)
C(2)-C(1)-N(1)-C(4)	152.9(2)	C(17)-C(16)-N(7)-C(19)	-153.2(2)
C(6)-C(5)-N(2)-O(2)	1.5(3)	C(21)-C(20)-N(8)-O(8)	-1.2(3)
C(4)-C(5)-N(2)-O(2)	-178.37(19)	C(19)-C(20)-N(8)-O(8)	178.4(2)
C(6)-C(5)-N(2)-O(1)	-179.01(18)	C(21)-C(20)-N(8)-O(7)	178.99(18)
C(4)-C(5)-N(2)-O(1)	1.1(3)	C(19)-C(20)-N(8)-O(7)	-1.5(3)
C(6)-C(7)-N(3)-N(4)	177.17(19)	C(21)-C(22)-N(9)-N(10)	-176.89(19)
C(8)-C(7)-N(3)-N(4)	-3.3(3)	C(23)-C(22)-N(9)-N(10)	3.9(3)
C(7)-N(3)-N(4)-C(10)	-178.57(17)	C(22)-N(9)-N(10)-C(25)	178.51(17)
C(15)-C(10)-N(4)-N(3)	-177.34(19)	C(30)-C(25)-N(10)-N(9)	177.07(18)
C(11)-C(10)-N(4)-N(3)	5.4(3)	C(26)-C(25)-N(10)-N(9)	-5.7(3)
C(14)-C(13)-N(5)-O(4)	-0.1(3)	C(29)-C(28)-N(11)-O(10)	0.0(3)
C(12)-C(13)-N(5)-O(4)	179.5(2)	C(27)-C(28)-N(11)-O(10)	-179.46(19)
C(14)-C(13)-N(5)-O(3)	-179.9(2)	C(29)-C(28)-N(11)-O(9)	179.8(2)
C(12)-C(13)-N(5)-O(3)	-0.3(3)	C(27)-C(28)-N(11)-O(9)	0.4(3)
C(14)-C(15)-N(6)-O(5)	-115.9(2)	C(29)-C(30)-N(12)-O(12)	115.6(2)
C(10)-C(15)-N(6)-O(5)	63.7(3)	C(25)-C(30)-N(12)-O(12)	-64.0(3)
C(14)-C(15)-N(6)-O(6)	62.8(2)	C(29)-C(30)-N(12)-O(11)	-62.5(3)
C(10)-C(15)-N(6)-O(6)	-117.6(2)	C(25)-C(30)-N(12)-O(11)	117.8(2)
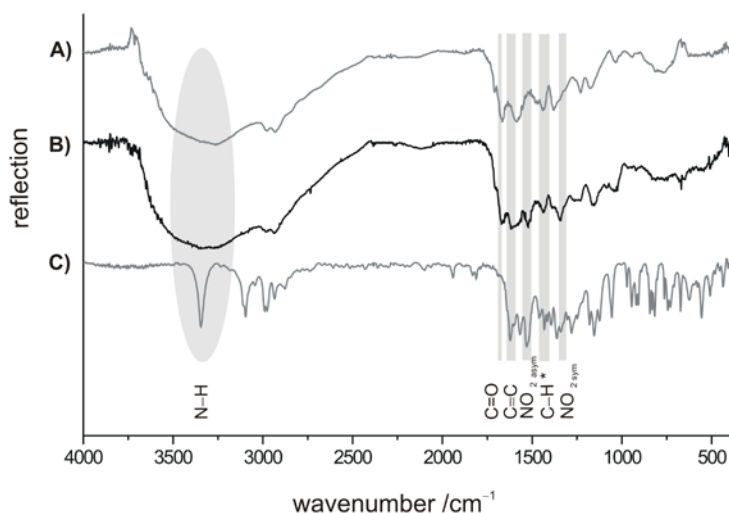
Figure S1 FTIR spectra of A) pure PVAm, B) **5P** (10 mol%) and C) **5M** in diffuse reflections diluted with KBr. The asterisk (*) indicates deformation vibrations.

Table S5: Glass transition temperatures T_g, weight loss of the azobenzene-functionalized PVAms and decomposition temperatures T_d of the model compounds (mc).

functionalized PVAm	n_F:n_{PVAm} /Mol%	T_g /°C via DSC	weight loss /% via TGA		T_d /°C (mc)[a] via TGA
			100-170 °C	200-400 °C	
2P	1	73	0	62.5	
	5	76	6.6	55.3	316
	10	97	4.1	59.3	
3P	1	105	7.5	47.9	
	5	106	4.8	58.6	285
	10	105	3.5	60.8	
4P	1	95	4.5	60.3	
	5	77	9.0	49.7	321
	10	91	13.7	39.6	
5P	1	104	4.5	62.2	
	5	96	4.2	56.4	310
	10	111	4.5	46.9	

[a] T_d (mc) = decomposition temperature where there is > 95 wt loss under helium.

Table S6: Kamlet−Taft- und Catalán parameter sets.

solvent	Kamlet−Taft parameter set[S1,2]			Catalán parameter set[S3–S5]				
	α	β	π^*	SA	SB	SPP	SP	SdP
gas phase	0	0	−1.26	0	0	0	0	0
n-hexane	0.00	0.00	−0.04	0.000	0.056	0.519	0.616	0
triethylamine	0.00	0.71	0.14	0.000	0.885	0.617	0.660	0.108
diethyl ether	0.00	0.47	0.27	0.000	0.562	0.694	0.617	0.385
tetrachlormethane	0.00	0.10	0.28	0.000	0.044	0.632	0.768	0
p-xylene	0.00	0.12	0.43	0.000	0.160	0.617	0.778	0.175
toluene	0.00	0.11	0.54	0.000	0.128	0.655	0.782	0.284
1,4-dioxane	0.00	0.37	0.55	0.000	0.444	0.701	0.737	0.312
ethyl acetate	0.00	0.45	0.55	0.000	0.542	0.795	0.656	0.603
tetrahydrofuran	0.00	0.55	0.58	0.000	0.591	0.838	0.714	0.634
benzene	0.00	0.10	0.59	0.000	0.124	0.667	0.793	0.270
anisole	0.00	0.32	0.73	0.084	0.299	0.823	0.820	0.543
1,2-dichloroethane	0.00	0.10	0.81	0.030	0.126	0.890	0.771	0.742
tetramethylurea	0.00	0.80	0.83	0.000	0.624	0.952	0,778	0.878
pyridine	0.00	0.64	0.87	0.033	0.581	0.922	0.841	0.761
HMPA[a]	0.00	1.05	0.87	0.000	0.813	0.932	0.774	1.100
N,N-dimethylformamide	0.00	0.69	0.88	0.031	0.613	0.939	0.759	0.977
N,N-dimethylacetamide	0.00	0.76	0.88	0.028	0.650	0.930	0.763	0.987
benzonitrile	0.00	0.37	0.90	0.047	0.281	0.960	0.851	0.852
1,1,2,2-tetrachlorethane	0.00	0.00	0.95	0.043	0.017	0.887	0.845	0.792
dimethyl sulfoxid	0.00	0.76	1.00	0.072	0.647	1.000	0.830	1.000
acetone	0.08	0.43	0.71	0.000	0.475	0.881	0.651	0.907
dichloromethane	0.13	0.10	0.82	0.040	0.178	0.876	0.761	0.769
acetonitrile	0.19	0.40	0.75	0.044	0.286	0.895	0.645	0.974
chloroform	0.20	0.10	0.53	0.047	0.071	0.786	0.783	0.614
nitromethane	0.22	0.06	0.85	0.078	0.236	0.907	0.710	0.954
1-decanol	0.70	0.82	0.45	0.259	0.912	0.765	0.722	0.383
formamide	0.71	0.48	0.97	0.549	0.414	0.833	0.814	1.006
2-propanol	0.76	0.84	0.48	0.283	0.830	0.848	0.633	0.808
1-butanol	0.84	0.84	0.47	0.341	0.809	0.837	0.674	0.655
1-propanol	0.84	0.90	0.52	0.367	0.782	0.847	0.658	0.748
ethanol	0.86	0.75	0.54	0.400	0.658	0.853	0.633	0.783
1,2-ethanediol	0.90	0.52	0.92	0.717	0.534	0.932	0.771	0.910
methanol	0.98	0.66	0.60	0.605	0.545	0.857	0.608	0.904
water	1.17	0.47	1.09	1.062	0.025	0.962	0.681	0.997
2,2,2-trifluoroethanol	1.51	0.00	0.73	0.893	0.107	0.908	0.543	0.922
HFIP[b]	1.96	0.00	0.65	1.011	0.014	1.007	-[c]	-[c]

[a] hexamethylphosphoramide, [b] 1,1,1,3,3,3-hexafluoro-2-propanol, [c] value was not determined.

Table S7. UV/vis absorption maxima of **2M–5M** and of **2P–5P** measured in 34 solvents of different polarity and hydrogen bond ability.

solvent	$\tilde{\nu}_{max}$ /10^3 cm^{-1}							
	2M	**3M**	**4M**	**5M**	**2P**	**3P**	**4P**	**5P**
n-hexane	23.31	27.47	25.13	23.40	$-^f$	$-^f$	$-^f$	$-^f$
triethylamine	22.03	27.25	25.00	23.47	$-^f$	$-^f$	24.10	$-^f$
diethyl ether	22.22	27.25	24.94	23.64	$-^f$	$-^f$	$-^f$	$-^f$
tetrachloromethane	22.77	27.03	24.69	23.15	$-^f$	25.45	$-^f$	$-^f$
p-xylene	22.47	26.74	24.45	22.99	$-^f$	$-^f$	$-^f$	$-^f$
toluene	22.42	26.67	24.39	22.99	$-^f$	$-^f$	$-^f$	$-^f$
1,4-dioxane	22.12	26.67	24.51	23.20	$-^f$	26.25	$-^f$	23.47
ethyl acetate	21.79	26.88	24.63	23.64	$-^f$	$-^f$	$-^f$	$-^f$
tetrahydrofuran	21.32	26.60	24.39	23.26	$-^f$	$-^f$	24.69	$-^f$
benzene	22.37	26.60	24.39	22.99	$-^f$	$-^f$	$-^f$	$-^f$
anisole	21.74	26.39	24.15	22.88	$-^f$	$-^f$	$-^f$	$-^f$
1,2-dichloroethane	21.74	26.67	24.27	23.20	$-^f$	$-^f$	$-^f$	$-^f$
tetramethylurea	20.33	26.32	24.10	23.20	$-^f$	$-^f$	23.42	23.31
pyridine	20.37	26.25	23.92	22.99	$-^f$	$-^f$	$-^f$	$-^f$
HMPA^a	19.76	26.17	24.04	23.20	$-^f$	25.38	23.47	$-^f$
DMF	20.41	26.32	24.15	23.26	21.88	25.38	24.39	23.94
DMAA^b	20.28	26.32	24.15	23.26	21.88	25.45	24.39	23.20
benzonitrile	20.79	26.32	24.04	22.88	$-^f$	$-^f$	$-^f$	$-^f$
TCE^c	21.46	26.67	24.10	22.88	$-^f$	$-^f$	$-^f$	$-^f$
DMSO	19.96	26.11	23.92	23.20	21.51	25.32	24.21	22.99
acetone	21.36	26.74	24.51	23.64	$-^f$	$-^f$	$-^f$	$-^f$
dichloromethane	21.88	26.67	24.27	23.20	$-^f$	$-^f$	$-^f$	$-^f$
acetonitrile	21.55	26.67	24.63	23.64	$-^f$	25.84	$-^f$	$-^f$
chloroform	22.03	26.81	24.33	23.20	$-^f$	$-^f$	$-^f$	$-^f$
nitromethane	21.28	26.18	24.33	23.31	$-^f$	$-^f$	$-^f$	$-^f$
1-decanol	20.79	26.88	24.51	23.26	$-^f$	$-^f$	$-^f$	$-^f$
formamide	20.33	26.46	$-^f$	23.20	22.03	25.45	24.75	23.26
2-propanol	20.88	27.25	24.63	23.64	22.32	$-^f$	$-^f$	
1-butanol	20.75	26.95	24.63	23.58		$-^f$	$-^f$	23.47
1-propanol	20.62	26.95	24.63	23.53	22.27	25.38	24.51	23.70
ethanol	20.92	27.03	24.75	23.70	22.22	25.77	24.69	23.64
1,2-ethandiol	$-^f$	26.32	$-^f$	23.56	$-^f$	$-^f$	$-^f$	$-^f$
methanol	21.14	26.95	24.69	23.70	22.37	26.25	24.81	23.75
water	$-^f$	$-^f$	$-^f$	$-^f$	22.17	27.03	24.69	23.04
TFE^d	20.92	26.95	24.88	23.75	22.83	26.53	$-^f$	24.03
HFIP^e	20.12	26.91	24.69	23.47	$-^f$	27.03	25.97	24.45
$\Delta \tilde{\nu}_{max}$ (10^3 cm^{-1})	3550	1363	1200	870	1320	1650	2550	1460

^{a} Hexamethylphosphoramide. ^{b} Dimethyl acetamide. ^{c} 1,1,2,2-Tetrachloroethane. ^{d} 2,2,2-Trifluoroethanol. ^{e} 1,1,1,3,3,3-Hexafluoro-2-propanol. ^{f} not soluble,

Table S8. Solvent-independent correlation coefficients a, b and c of the Catalán parameters *SA*, *SB* and *SPP*, solute property of the reference system $\tilde{v}_{max,0}$ (gas phase), number of solvents (n), correlation coefficient (r), standard deviation (sd), and significance (f) of the calculated solvatochromism of the model compounds **2M–5M**

Comp.	$\tilde{v}_{max,0}$ /10^3 cm^{-1}	a	b	c	n	r	sd	f
2M	26.244	−0.373	−1.298	−5.210	33	0.951	0.268	< 0.0001
3M	28.483	0.543	0	−2.265	34	0.735	0.238	< 0.0001
4M	25.949	0.797	0	−1.950	32	0.804	0.184	< 0.0001
5M	23.613	0.849	0.357	−0.742	30	0.765	0.175	< 0.0001

Table S9. Solvent-independent correlation coefficients a, b and d of the Catalán parameters *SA*, *SB* and *SP*, solute property of the reference system $\tilde{v}_{max,0}$ (gas phase), number of solvents (n), correlation coefficient (r), standard deviation (sd), and significance (f) of the calculated solvatochromism of the model compounds **2M–5M**

Comp.	$\tilde{v}_{max,0}$ /10^3 cm^{-1}	a	b	d	n	r	sd	f
2M	26.739	−1.998	−2.110	−5.812	33	0.798	0.523	< 0.0001
3M	29.320	−0.206	−0.214	−3.442	34	0.700	0.251	< 0.0001
4M	27.382	−0.291	−0.217	−3.885	32	0.865	0.158	< 0.0001
5M	25.580	0.182	0	−3.148	33	0.944	0.086	< 0.0001

Table S10. Solvent-independent correlation coefficients a, b and c of the Catalán parameters *SA*, *SB* and *SPP*, solute property of the reference system $\tilde{v}_{max,0}$ (gas phase), number of solvents (n), correlation coefficient (r), standard deviation (sd), and significance (f) of the calculated solvatochromism of the model compounds **2P–5P**

Comp.	$\tilde{v}_{max,0}$ /10^3 cm^{-1}	a	b	c	n	r	sd	f
2P	26.552	0	−1.032	−6.182	9	0.922	0.145	< 0.0014
3P	28.311	0.516	−1.127	−2.318	11	0.933	0.156	< 0.0005
4P	24.635	0.922	−0.838	0	13	0.896	0332	< 0.0002
5P	24.045	1.173	0	−1.010	12	0.920	0.175	< 0.0002

UV/vis absorption spectra measured as powders

Generally, the UV/vis absorption bands are non-symmetric and show several absorption maxima. As depicted in Figure S3 (B, **5M** and **5P**), the half-width of the UV/vis absorption bands of the polymers **3P–5P** are broader than the half-width of the UV/vis absorption bands of the model compounds. The amino groups of the PVAm generate an internal basic surrounding and therefore a bathochromic shift is observed. In contrast, **2P** shows a smaller UV/vis absorption band and a hypsochromic shift compared to **2M**. These results are in

agreement with the pH-depending UV-vis absorption measurements in aqueous solutions and reflect the strong influence of the amino groups of the polymer chains on the UV/vis spectroscopic behavior of the azobenzene-functionalized PVAms.
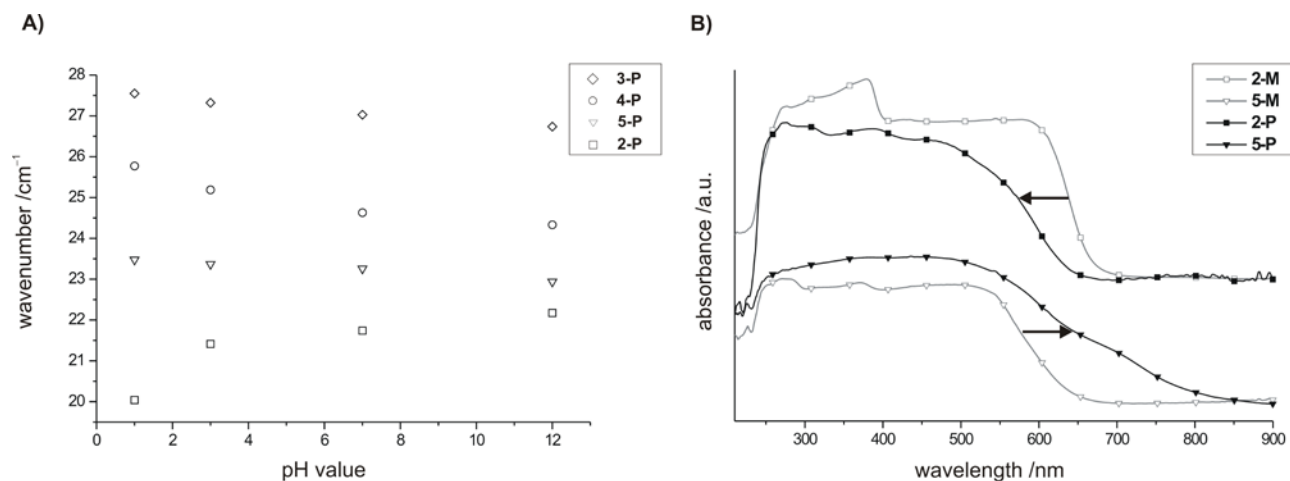

Figure S2 A) Positions of the UV/vis absorption maxima in water with different pH values of **2P–5P** (5 Mol%), and B) UV/vis absorption spectra of the model compounds **2M** and **5M**, and the polymers **2P** and **5P** (5Mol%), resp., as powders.
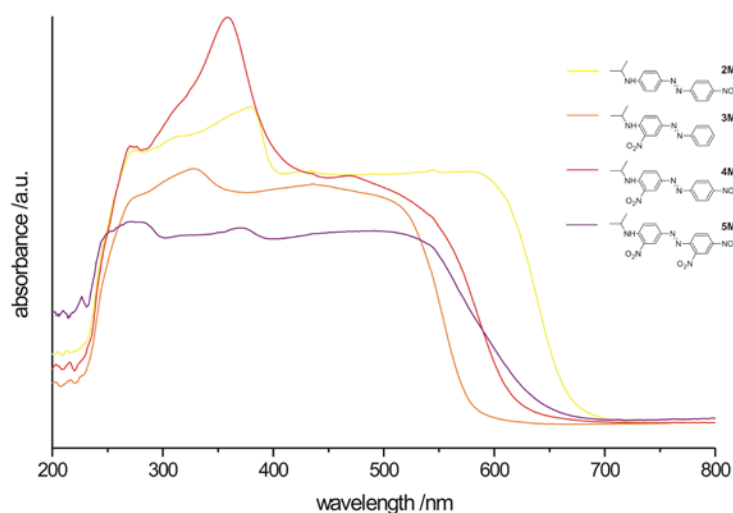

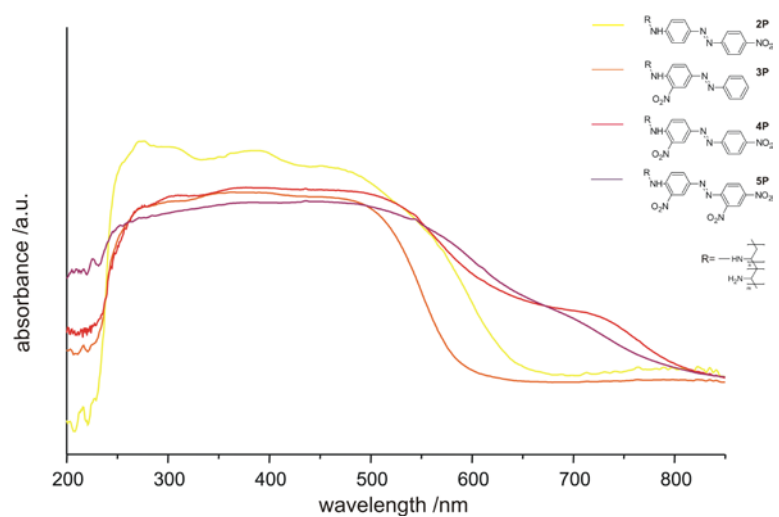**Figure S3** UV-vis absorption spectra of **2M–5M** as powders.

Figure S4 UV-vis absorption spectra of **2P–5P** as powders.

References

S1. Reichardt, C. In Solvents and Solvent Effects in Organic Chemistry, 2nd edn.; VCH, Weinheim, 1988, and references therein.

S2. Marcus, Y. Chem. Soc. Rev. 1993, 22, 409–416.

S3 J. Catalán, In Handbook of Solvents, Chem.Tech Publishing Toronto, 2001, Chaper9.3, p 583.

S4. J. Catalán, H. Hopf, *Eur. J. Org. Chem.*, **2004**, 4694–4702.

S5. J. Catalán, *J. Phys Chem. B*, **2009**, *113*, 5951–5960.