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Supplementary Information

Solvatochromic Properties of Schiff Bases Derived from 5-Aminobarbituric Acid: Chromophores with Hydrogen Bonding Pattern as Components for Coupled Structures

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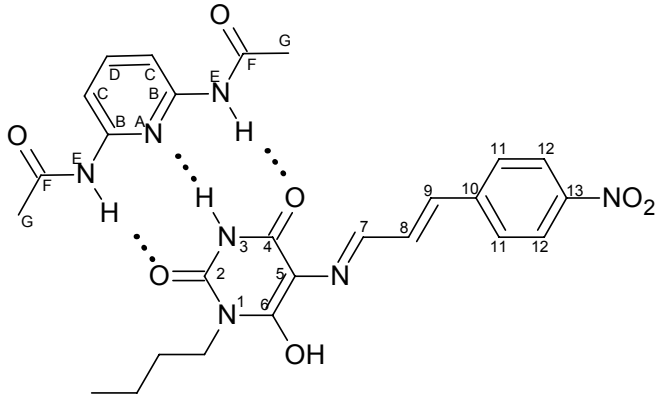
Table of contents

Synthesis and characterization of the complex 1b+DAC

General. Unless otherwise noted, all materials were used as received from a commercial supplier without further purification. All reaction solvents were redistilled over appropriate drying agents prior to use. The Schiff base 1-butyl-5-[(1*E*,2*E*)-3-(4-nitrophenyl)prop-2-enyliden]aminobarbituric acid **1b** was synthesized as described in the previous work.[S1] The model base 2,6-diacetamidopyridine **DAC** was prepared as described.[S2]
Calorimetric melting profiles were determined in the temperature range from 25°C to 400°C (scan rate of 10°C min^{-1}) in a stream of nitrogen using a Mettler DSC 30. Elemental analysis was recorded on a Vario EL (Elementar Analysensysteme GmbH Hanau). The FTIR spectrum was measured with a BIO-RAD FTS 165 spectrometer in diffuse reflection with KBr as reference. The intensity is indicated as follows: s (strong), m (medium), w (weak) and b (broad). The ^{1}H NMR spectrum was obtained on a Varian Gemini-300 spectrometer. Chemical shifts were reported as δ-values in parts per million (ppm) relative to $Si(CH_3)_4$ as relative reference (δ = 0 ppm) and to the solvent d_6-DMSO as internal reference. Peak multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), se (sextet), m (multiplet) and b (broad). High resolution liquid-state ^{13}C NMR spectroscopy was not suitable due to the poor solubility.

Synthesis of the complex 1b+DAC. 0.2 mmol of **1b** were dissolved in 20 ml dried ethanol (EtOH) and added with 0.2 mmol **DAC**. The mixture is refluxed for 1h and after cooling at 22°C the complex was crystallized. The precipitate was filtered off, washed with a few amount of EtOH and dried in vacuo. **1+DAC** was obtained as a red, fine crystalline solid.



Yield: 78%; **m.p.**: 196 °C, 211 °C, 215 °C (decomp.); **Anal.** calculated for $C_{26}H_{29}N_7O_7$ (found): C 56.62 (56.42), H 5.30 (5.10), N 17.78 (17.63); **IR (cm^{-1})**: 3300 – 3162 (w), 3071, (w), 3025 (w), 2960 (m), 2875 (w), 1690 (s), 1660 (m), 1609 (m), 1594 (s), 1575 (w), 1517 (m), 1486 (m), 1451 (s), 1420 (m), 1339 (s), 1227 (m), 1108 (m), 1038 (m), 865 (m), 810 (m), 764 (m), 583 (m); **^{1}H NMR**: δ 0.90 (t, 3H, CH_3) 1.28 (se, 2H, CH_2), 1.50 (quin, 2H, CH_2), 2.10 (s, 6H, G), 3.74 (t, 2H, N-CH_2), 7.53 – 7.87 (m, 7H, 9, C, D, 11, 8), 8.29 (d, 2H, 12), 9.53 (d, 1H, 7), 10.05 (s, 2H, E), 10.7 (s, 1H, 3), 13.11 (bs, 1H, 6).

Quantitative determination of the association constant K_A

The quantitative determination of the association constant K_A is based on the absorbance variation of the host (H) in the presence of the guest (G) with certain concentration.[S3]

$$H + G \rightleftharpoons C$$

In the simplest case, where one binding site exists per host molecule, only a 1:1 supramolecular complex (C) can form, which has a K_A, according to eqn (4):

$$K_A = \frac{[C]}{[H][G]} = \frac{[C]}{([H_0] - [C])([G]_0 - [C])} \qquad (4)$$

The absorbance A, measured at a certain wavelength is expressed as:

$$A = d\,([H]\,\varepsilon_H + [G]\,\varepsilon_G + [C]\,\varepsilon_C)$$

where ε_H, ε_G and ε_C are the molar extinction coefficients of H, G, and C, respectivly, and d is the width of the absorption cell.
The absorbance in the reference cell A_R is expressed as:

$$A_R = d\,[H]_0\,\varepsilon_{H_0}$$

where $[H_0]$ is the total concentration of the host in the absence of the guest.
Therefore, the difference in the absorbance ΔA is expressd as:

$$\Delta A = A - A_R = d\,([C]\,(\varepsilon_C - \varepsilon_H - \varepsilon_G) + [G]_0\,\varepsilon_G) \qquad (5)$$

Combination of eqn (4) with (5) gives eqn (6) with $\Delta\varepsilon = \varepsilon_C - \varepsilon_H - \varepsilon_G$ and $[H] = [H]_0 / (1 + K_A\,[G])$.

$$\Delta A = K_A\,\Delta\varepsilon\,d\,[H]\,[G] \qquad (6)$$

The binding isotherm (eqn 7) and its x-reciprocal form (eqn 8) represent the relationship between the observed absorbance change per centimeter and the system variables and parameters.

$$\frac{\Delta A}{d} = \frac{[H]_0\,K_A\,\Delta\varepsilon\,[G]}{1 + K_A\,[G]} \qquad (7)$$

$$\frac{\Delta A}{d\,[G]} = -\frac{K_A\,\Delta A}{d} + [H]_0\,K_A\,\Delta\varepsilon \qquad (8)$$

A plot of ΔA versus ΔA / [G] yields a straight line whose slope is $-K_A$. This plot was apparently first discribed by Foster in the context of spectroscopy;[S4] in supramolecular binding complexes, this curve is called Scatchard plot.[S5]

Table S1. UV/Vis absorption maxima ($\tilde{\nu}_{max}$) of the Schiff bases **1a**, **1b**, **2a** and **2b** in various solvents, the empirical Kamlet-Taft parameters[S6–S9] α, β, π^* and the extend of the solvatochromic absorption shift.

solvent	α	β	π^*	$\tilde{\nu}_{max}$ [10^{-3} cm^{-1}]			
				1a	**1b**	**2a**	**2b**
2,2,2-trifluoroethanol	1.49	0	0.73	22.6	22.7	20.1	20.1
1,1,1,3,3,3-hexafluoro-2-propanol	1.96	0	0.65	**22.8**[c]	**22.9**[c]	**19.8**[b]	**19.8**[b]
benzene	0	0.10	0.59	21.0	–[a]	-[e]	-[e]
p-xylene	0	0.12	0.43	21.0	–[a]	-[e]	-[e]
dichloromethane	0.13	0.10	0.82	20.4[d]	–[a]	19.9	19.9
tetrachloromethane	0	0	0.28	21.6	21.2	-[e]	-[e]
tetrachloroethane	0	0	0.95	21.2	21.4	-[e]	-[e]
methanol	0.98	0.66	0.60	22.5	22.6[d]	-[e]	-[e]
ethanol	0.54	0.75	0.86	22.1	22.9[d]	-[e]	-[e]
2-propanol	0.76	0.84	0.48	21.8	21.9	-[e]	-[e]
1-butanol	0.84	0.84	0.47	21.6	21.8	-[e]	20.4
anisole	0	0.22	0.73	20.8	21.2	-[e]	-[e]
tetrahydrofurane	0	0.55	0.58	20.4[d]	20.3	**20.5**[c]	**20.5**[c]
acetone	0.08	0.48	0.71	21.3	21.8[d]	-[e]	-[e]
ethyl acetate	0	0.45	0.55	21.3	20.7	-[e]	-[e]
γ-butyrolactone	0	0.49	0.87	21.3	21.4	-[e]	-[e]
nitromethane	0.22	0.06	0.85	21.5	21.6	-[e]	-[e]
triethylamine	0	0.71	0.14	–[a]	20.8	-[e]	-[e]
pyridine	0	0.64	0.87	20.0[d]	20.0[d]	-[e]	-[e]
tetramethyl urea	0	0.80	0.83	21.1	20.3	-[e]	-[e]
formamide	0.71	0.48	0.96	21.3	21.6	-[e]	-[e]
N-methylformamide	0.62	0.80	0.90	21.1	21.2	-[e]	-[e]
N, *N*-dimethylformamide	0	0.69	0.88	20.1[d]	**20.0**[b]	20.4	20.4
dimethyl sulfoxide	0	0.76	1.00	**20.6**[b]	20.3	20.3	20.4
$\Delta\lambda$ [nm]				46	64	18	18
$\Delta\nu$ [cm^{-1}]				2160	2923	732	732

[a]compound insoluble, [b]highest bathochromic shift, [c]highest hypsochromic shift, [d]excluded for correlation, [e]solvent not tested

Table S2. The solvent-independent correlation coefficients of the solvatochromic compounds **1a** and **1b** using the Kamlet–Taft linear solvation energy relationship.[S6–S9]

compound	$\tilde{\nu}_{max(0)}$	a	b	s	r	sd	F	n
1a	21.64685	1.04914	-0.23435	-0.95578	0.86090	0.39816	<0.0001	24
	20.88552	1.07350	———	———	0.80398	0.44371	<0.0001	24
	21.60638	1.05267	———	-1.04315	0.85412	0.39557	<0.0001	24
	21.55615	0.89303	———	-0.67775	0.90722	0.26149	<0.0001	20
	21.58331	0.89314	-0.17087	-0.61376	0.91180	0.26311	<0.0001	20
	21.10793	0.89041	———	———	0.87368	0.29381	<0.0001	20
	21.59998	———	-0.26308	———	0.14495	0.59773	0.5	20
	21.92500	———	———	-0.6522	0.23490	0.58721	0.3	20
	21.21733	0.89098	-0.26907	———	0.88626	0.28794	<0.0001	20
	21.95188	———	-0.16884	-0.58897	0.25163	0.60162	0.6	20
1b	21.53407	1.20649	-0.57771	-0.51235	0.83122	0.53909	<0.0001	22
	21.15858	1.22223	-0.56714	———	0.82169	0.53789	<0.0001	22
	21.2625	1.02086	-0.84350	———	0.89872	0.37196	<0.0001	18
	21.34478	1.02147	-0.84163	-0.11611	0.89938	0.38382	<0.0001	18
	20.84275	1.13600	———	———	0.83589	0.45079	<0.0001	18
	21.85006	———	-1.30567	———	0.52755	0.69769	0.02	18
	21.35201	———	———	-0.11864	0.03521	0.82076	0.9	18
	20.94227	1.13621	———	-0.13897	0.83107	0.48053	0.0003	18
	21.53407	1.20649	-0.57771	-0.51235	0.83122	0.53909	<0.0001	22

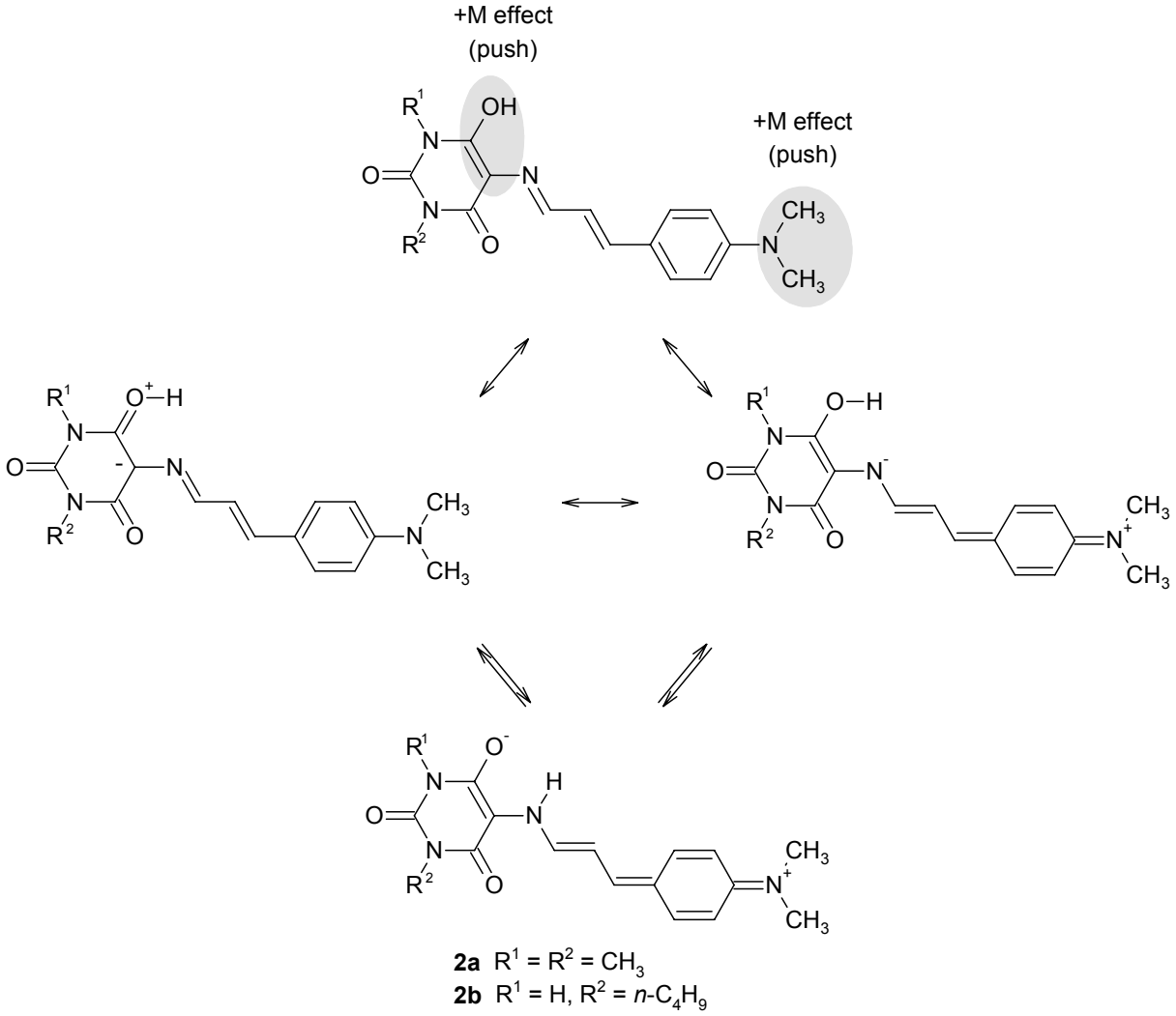


Figure S1. Push-push character of the *N*,*N*-dimethylamino-substituted barbituric acids **2a** and **2b**.

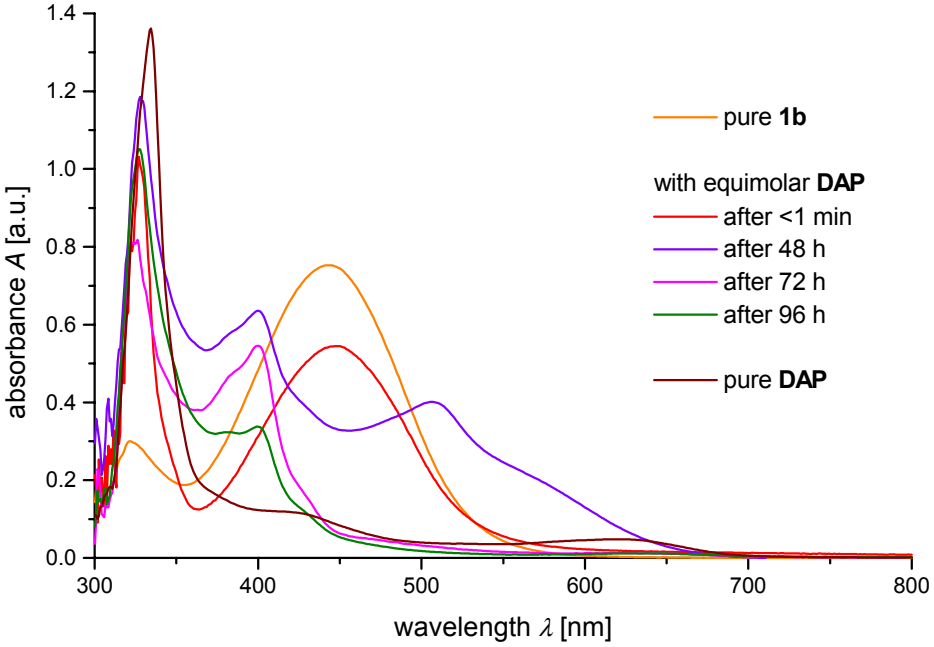


Figure S2. UV/Vis spectra of the decomposition of the Schiff base **1b** in the presence of equimolar 2,6-diaminopyridine **DAP** in methanol.[S10]

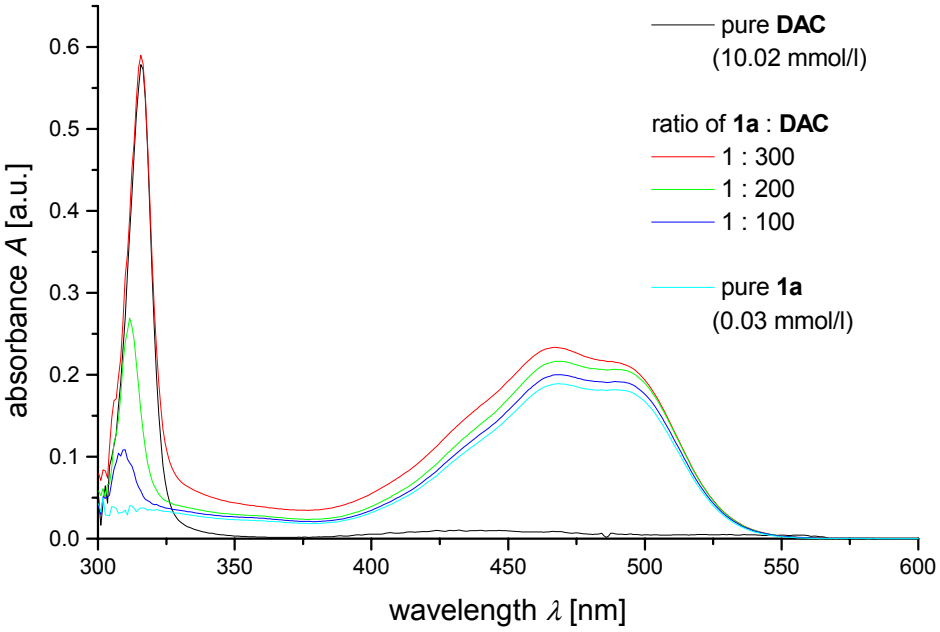
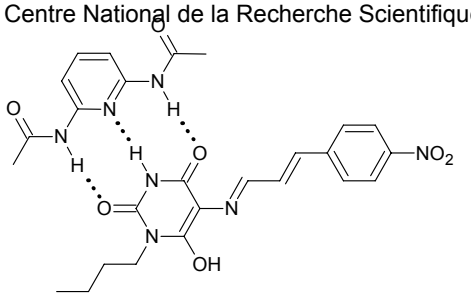


Figure S3. UV/Vis study using the dye **1a** (0.03 mmol/l) and 2,6-diacetamidopyridine **DAC** in dichloromethane.



molar ratio of **1b** : **DAC**	δ[ppm] OH-**1b**	NH-**1b**	
1 : 50	13.117	10.690	10.046
1 : 1	13.114	10.689	10.045
1 : 0	13.088	10.642	-

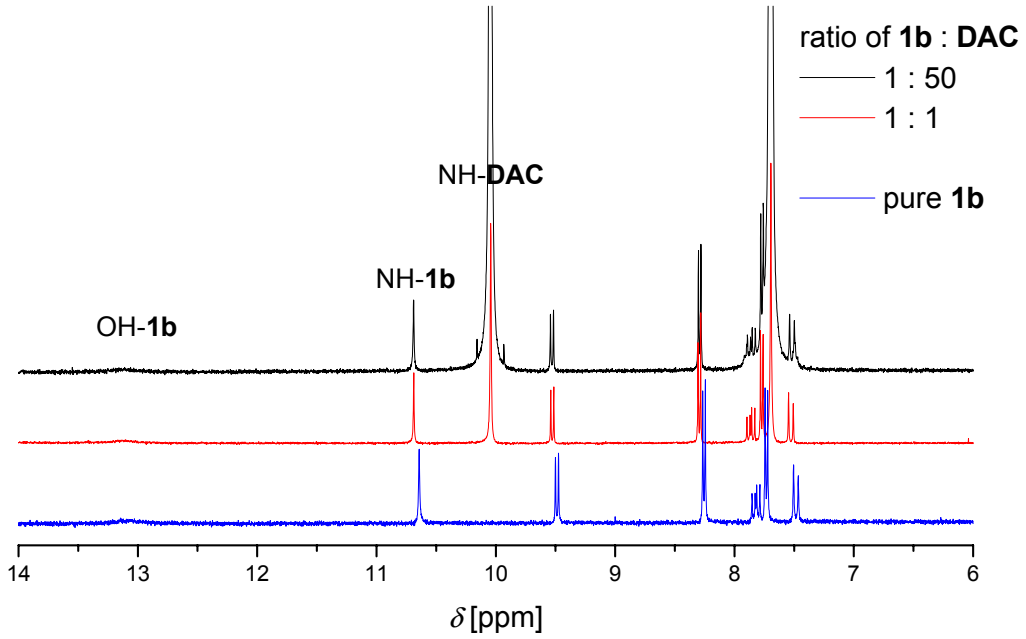


Figure S4. ^{1}H NMR spectra of **1b** (5.58 mmol/l) with different molar ratio of **DAC** in d_6-DMSO.

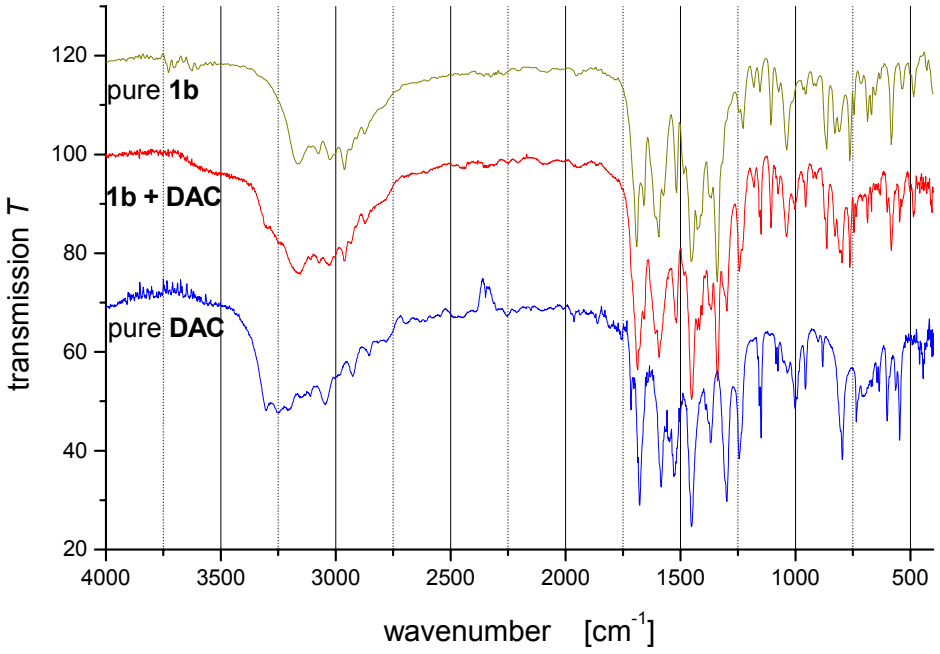


Figure S5. Comparision of the IR spectra of the complex **1b+DAC** with its starting compounds in diffuse reflection. Due to band overlaping and relatively low sensitivity of the vibration frequencies of O-H, N-H, and related bands the determination of the association constant K_A is not useful.[S3]

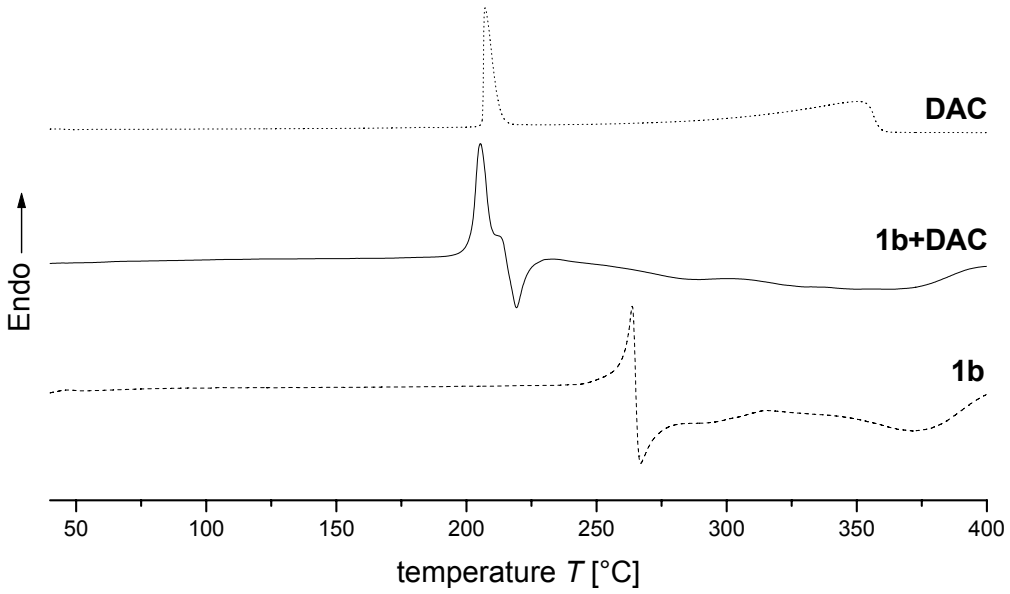


Figure S6. Comparison of the DSC traces of the complex **1b+DAC** with its starting compounds. The endothermic transition at 196 °C is attributed to the melting of the complex affected by a small amount of unbound **DAC** at approximately 211 °C. The exothermic transition at 215 °C reflects the decomposition.

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