Highly Soluble and Green Indigo Dyes: 4,4′,7,7′-Tetraalkoxy-5,5′-diaminoindigotins

by **Gundula Voss**[a])*, **Michael Gradzielski**[b]), **Jürgen Heinze**[c]), **Helmut Reinke**[d]), and **Carlo Unverzagt**[a])

[a]) Department of Bioorganic Chemistry, University of Bayreuth, D-95440 Bayreuth
[b]) Department of Physical Chemistry II, University of Bayreuth, D-95440 Bayreuth
[c]) Department of Physical Chemistry, University of Freiburg, D-79104 Freiburg
[d]) Department of Inorganic Chemistry, University of Rostock, D-18051 Rostock

Dedicated to the 70th birthday of Prof. Dr. emeritus *Hans Gerlach*

Two new types of 4,4′,7,7′-tetraalkoxyindigotins, **1a–f** and **2a–f** along with the new *N*-substituted indigotins **4e–f**, were synthesized from dinitrobenzaldehydes **5a–f**, which were prepared from 2-hydroxy-5-methoxybenzaldehyde (**7**) *via* dialkoxybenzaldehydes **6a–f** (*Scheme*). The new dialkoxyindigotin **3g** was obtained from dialkoxybenzaldehyde **6g** *via* nitrobenzaldehyde **8g**. The 1,4-dialkoxy-2,3-dinitrobenzenes **9** were isolated as by-products. The 4,4′,7,7′-tetraalkoxy-5,5′-diaminoindigotins **1** are soluble in organic solvents, and their solutions are green, which is highly uncommon for indigotins and is primarily caused by electronic effects of substituents, steric effects playing a minor role. The indigotins **1** produce a strong red shift of the longest-wavelength absorption and negative solvatochromism indicating the predominance of polar resonance structures in the ground state. Tautomeric structures were excluded. These indigotins are valuable compounds for technical applications, for synthetic purposes, and for analytical studies. SANS (Small-angle neutron scattering) experiments showed that certain 4,4′,7,7′-tetraalkoxy-5,5′-diaminoindigotins **1** form rod-like aggregates in solution. The similarly substituted 4,4′,7,7′-tetraalkoxy-5,5′-dinitroindigotins **2** are far less soluble. They produce red monoanions (preferably dimers) and bluish-purple dianions in organic solvents.

1. Introduction. – Indigotin (= 2-(1,3-dihydro-3-oxo-2*H*-indol-2-ylidene)-1,2-dihydro-2*H*-indol-3-one) is the oldest known natural dye and has been used for more than 5000 years. In the last century, many derivatives have been synthesized and technically evaluated as dyes. Today the utilization of dyestuffs is not limited to textile applications, dyes have gained importance in completely new industries [1]. Indigo dyes have some valuable, unique properties. However, potential applications are rather restricted by their low solubility. The indigo chromophore limits the absorption range of VIS light to *ca.* 570–645 nm [2a,b]. Thus, indigo dyes are associated with poor solubility and blue color. These investigations probably will challenge both assumptions.
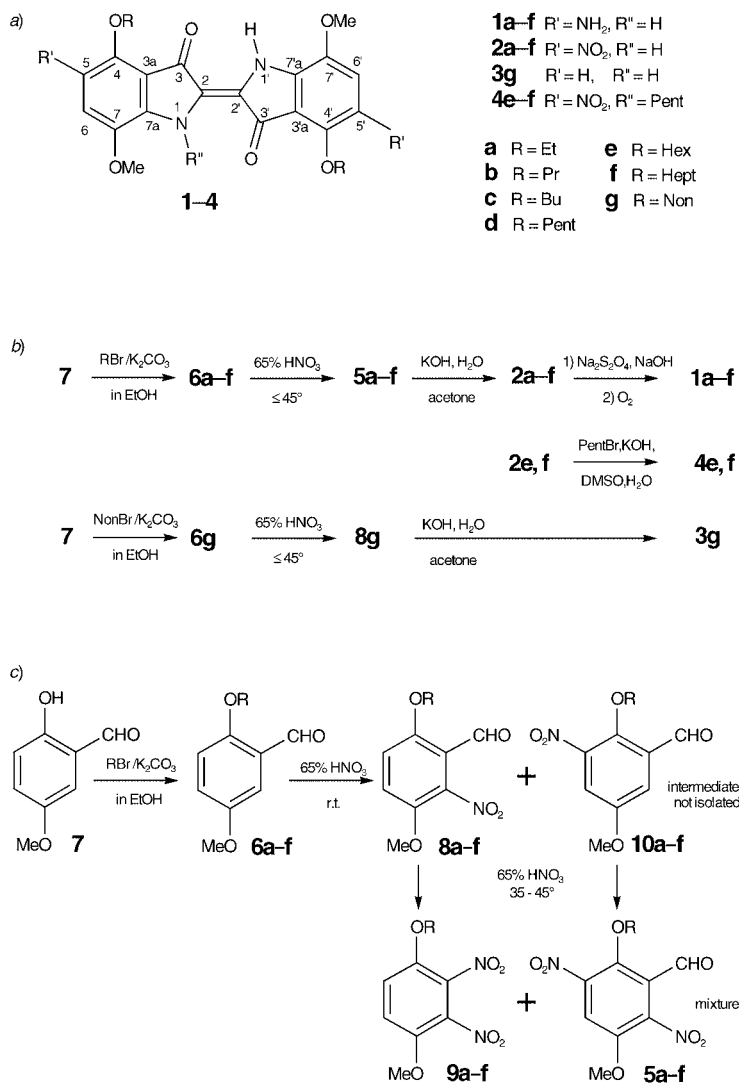
We present a new group of 4,4′,7,7′-tetraalkoxy-5,5′-diaminoindigotins **1** (*Scheme*, *a*) that are highly soluble in organic solvents and of green color in solution. Previous attempts to increase the solubility of indigotins took advantage of steric effects by bulky substituents [3a,b]. In contrast, the solubility of indigotins **1** is preferentially enhanced by electronic effects of the substituents in the 5,5′- and 7,7′-positions. Steric effects of the alkoxy groups in the 4,4′- and 7,7′-positions (as would be expected) contribute only little to the increased solubility. The uncommon properties of **1** draw parallels to those of 5,5′-bis(dimethylamino)indigotin [4], which is described as well-soluble in CHCl$_3$, acetone, benzene, nitrobenzene, and AcOEt with a green color.

The high solubility of the indigotins **1** allows the utilization of valuable indigo-inherent properties. For example, oxidation to yellow isatines was used for sensitive and selective detection of ozone in gaseous mixtures [5]. Similarly to natural *N*-glycosylated 5,5′-dichloroindigotins (akashines A, B, and C) [6], derivatives of **1** are active against human-tumor cell lines [7]. Further research is in progress to obtain H_2O-soluble indigotins. Uncommon for indigotins, spectroscopic investigations even in nonpolar solvents could be performed. Differently colored anions recommend 5,5′-dinitroindigotins **2** as indicator dyes in dipolar aprotic solvents. The 1,4-dialkoxy-2,3-dinitrobenzenes **9**, obtained as by-products, have been used in preparing liquid-crystal mixtures [8a,b]. Compounds of type **1**, **2**, and **4** have not been described previously. Only 4,4′,7,7′-tetramethoxyindigotin [9][10] and 4,4′,7,7′-tetrabutoxyindigotin [10] of type **3** have been reported.

2. Results and Discussion. – 2.1. *Syntheses.* The 5,5′-diaminoindigotins **1a**–**f** were prepared by reaction of 5,5′-dinitroindigotins **2a**–**f** with sodium dithionite [11] (*Scheme, b*). The primarily formed *leuco* compounds of the dinitroindigotins **2a**–**f** are not stable [12]. They were transformed immediately into the *leuco* forms of diaminoindigotins **1a**–**f** (pale gray precipitates), which were converted into indigotins **1a**–**f** by exposure to air oxygen. The 5,5′-dinitroindigotins **2a**–**f** and indigotin **3g** were synthesized from 3,6-dinitrobenzaldehydes **5a**–**f** and 2-nitrobenzaldehyde **8g**, respectively, by reaction with KOH in acetone/H_2O [13a,b]. The nitrobenzaldehydes **5a**–**f** and **8g** were accessible from dialkoxybenzaldehydes **6a**–**g** by nitration with 65% HNO_3 solution at elevated temperatures [14]. As by-products, 1,4-dialkoxy-2,3-dinitrobenzenes **9** were formed. Above an optimum temperature of 35–45°, the yield of dinitrobenzaldehydes **5** decreased in favor of these deformylated compounds **9**. Generally, reaction at lower temperatures gives rise to mononitration yielding nitrobenzaldehydes of type **8** [9][15]. However, increasing length of the 2-alkoxychain of **6** favored products of type **8** even at elevated temperatures. Thus, nitration of 2-(nonyloxy)benzaldehyde **6g** at 45° gave 2-nitro-6-(nonyloxy)benzaldehyde **8g**. The dialkoxybenzaldehydes **6a**–**g** were prepared by alkylation of 2-hydroxy-5-methoxybenzaldehyde (**7**) [16] which was accessible by formylation of commercially available 4-methoxyphenol [17]. Traces of 4,4′,7,7′-tetraalkoxy-5-nitroindigotins, 4,4′,7,7′-tetraalkoxy-5-aminoindigotins, and of substituted indirubins were isolated in the reactions leading to **2** and **1**, respectively.

Both 2-nitrobenzaldehydes **8** and 3-nitrobenzaldehydes **10** are primary nitration products of dialkoxybenzaldehydes **6** [9][15]. Surprisingly, not the 2-nitrobenzaldehydes **8** (main products), but the 3-nitrobenzaldehydes **10** (minor products) are precursors of the dinitrobenzaldehydes **5** (*Scheme, c*). This was concluded from reactions reported: nitration of 2,5-dimethoxy-3-nitrobenzaldehyde (type **10**) yielded 2,5-dimethoxy-3,6-dinitrobenzaldehyde (type **5**) [18], whereas further nitration of 3,6-dimethoxy-2-nitrobenzaldehyde (type **8**) gave 2,3-dinitro-1,4-dimethoxybenzene (type **9**) [19]. The structure of 2,5-dialkoxy-3,6-dinitrobenzaldehydes **5a**–**f** was established by an X-ray crystal-structure determination of the 2-(heptyloxy) derivative **5f** (*Fig. 1*). The 5,5′-positions of the amino groups in indigotins **1** were verified by H,C HMBC (heteronuclear multiple-bond correlation) experiments of the 4,4′-bis(hexyloxy) derivative **1e**.

Scheme

a)

1a–f R' = NH₂, R" = H
2a–f R' = NO₂, R" = H
3g   R' = H,   R" = H
4e–f R' = NO₂, R" = Pent

a R = Et   **e** R = Hex
b R = Pr   **f** R = Hept
c R = Bu   **g** R = Non
d R = Pent

b)

c)

a) *New indigotins* **1**–**4**. b) *Synthesis of indigotins* **1**–**4**. c) *Synthesis of 3,6-dinitrobenzaldehydes* **5** *and of 2-nitrobenzaldehydes* **8** (precursors of **2** and **3**).

The reaction sequence **6** → **10** (not **8**) → **5** → **2** explains *a)* the absence of any isomeric 4,4′,7,7′-tetraalkoxy-6,6′-dinitroindigotins and *b)* the low yield of **2** with respect to **6** (7–15%, two steps). The reactions can be scaled up without problems because column chromatography was avoided. Probably, the synthesis of **2** could be improved by use of independently synthesized 2,5-dialkoxy-3-nitrobenzaldehydes **10**.
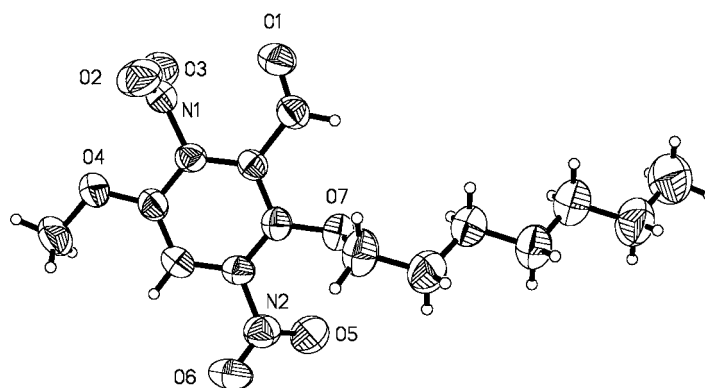
Fig. 1. *ORTEP Representation of 2-(heptyloxy)-5-methoxy-3,6-dinitrobenzaldehyde* (**5f**)

Compounds **10** should be accessible from **7** in two steps analogously to 2,5-dimethoxy-3-nitrobenzaldehyde [18].

The 4,4',7,7'-tetraalkoxy-5,5'-dinitro-1-pentylindigotins **4e,f** were prepared by alkylation of dinitroindigotins **2e,f** with 1-bromopentane in DMSO in the presence of KOH/H₂O. They were isolated as mixtures with some starting material **2e,f**. The reactions were not optimized; their objective was preferentially the characterization of the anions of **2**. No traces of *N,N'*-dialkylated 4,4',7,7'-tetraalkoxy-5,5'-dinitroindigotins were found. *Kuhn* and *Trischmann* have described the *N,N'*-dimethylation of indigotin in DMF/H₂O with BaO as base [20]. Both *N*-monoalkylation and *N,N'*-dialkylation are reported for pyrrol-indigotin [21a,b].

2.2. *Properties of Indigotins* **1 – 4**. *Solubility and Color.* The 4,4',7,7'-tetraalkoxy-5,5-diaminoindigotins **1a – f** display highly unusual properties for indigo dyes. They are well soluble in organic solvents such as CHCl₃ (*Fig. 2*), acetone, DMF, and DMSO, yielding green solutions. The indigotins **1** dye cotton green by means of these solutions, no reduced form (*leuco* form) is required for dyeing. As solids, they are dark blue (λ_{max} 745 nm, KBr). The solubility of **1a – c**[1] (*ca.* 30 mg/ml CHCl₃) surpasses the solubility of indigo derivatives described (see [3a,b] for examples) and of dinitroindigotins **2a – f** by far. The steric effects of the alkoxy substituents in the 4,4',7,7'-positions contribute to the enhanced solubility only to a minor degree, as established by direct comparison with the similarly substituted 4,4',7,7'-tetraalkoxy-5,5'-dinitroindigotins **2a – f**.

Surprisingly, the green color provides the key to understanding the increased solubility of indigotins **1** and of 5,5'-bis(dimethylamino)indigotin. All of them carry strong electron-donating groups in the 5,5'-positions, and **1** additionally in the 7,7'-positions. These substituents polarize the π-electron system to such a degree that polar resonance structures dominate in the ground-state (*Fig. 3*) and less-polar resonance structures in the first exited state. The polar structure of **1** causes the strong red shift of the longest-wavelength absorption (λ_{max} 736 nm in CHCl₃, see *Fig. 4*) and negative

---

[1]   The indigations **1d – f** with longer 4,4'-dialkoxy chains are still more soluble due to formation of rod-like aggregates; uncertainties of measured values are possible due to increased viscosity of some solutions.
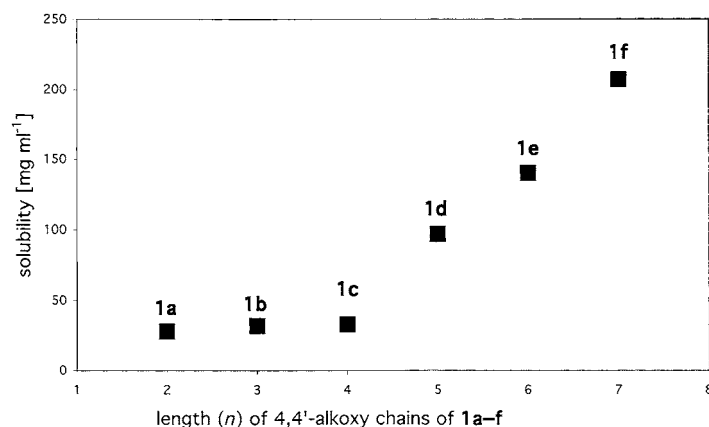
Fig. 2. *Solubility of 5,5′-diaminoindigotins* **1a**–**f** *in CHCl₃ (20°)*

solvatochromism (λ_{max} 715 nm in MeOH; 703 nm in acetone). It lowers the indigo-typical intermolecular interactions resulting in enhanced solubility and decreased melting points. Protonation of **1** results in blue salts in which the indigo chromophore is re-established (**1e**, hydrochloride: λ_{max} 648 nm in MeOH). Blue salts are reported for 5,5′-bis(dimethylamino)indigotin too [4].
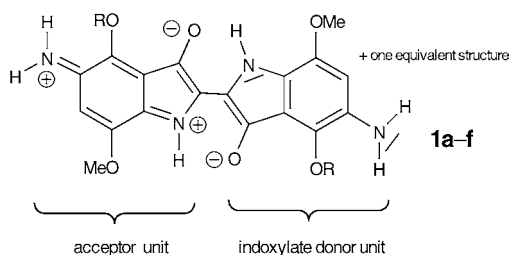

Fig. 3. *Representation of the polar ground state of 5,5′-diaminoindigotins* **1**

The green color is rare among indigo dyes. The anions of indigotin [21b][22], the anions of indigo-5,5′-disulfonic acid [21b][22][23], and anionic metal complexes of substituted indigotins [22][24a,b] exhibit green solutions ($\lambda_{max} \geq 700$ nm); the anions of 5,5′-dinitroindigotins **2** absorb light of similar frequencies. The bathochromic absorption of these compounds was explained by an increased electron-donating ability of the deprotonated N-atom of the anions and by an increased electron-donating ability of the negatively charged indoxylate (=1*H*-indol-3-olate) unit of the anionic metal complexes, respectively [21b][22]. Obviously, strong electron-donating substituents in the 5,5′- and 7,7′-positions of indigotin have a similar effect. Other reasons for the red shift of the longest-wavelenth absorption[2]) of diaminoindigotins **1** could be excluded. Both

---

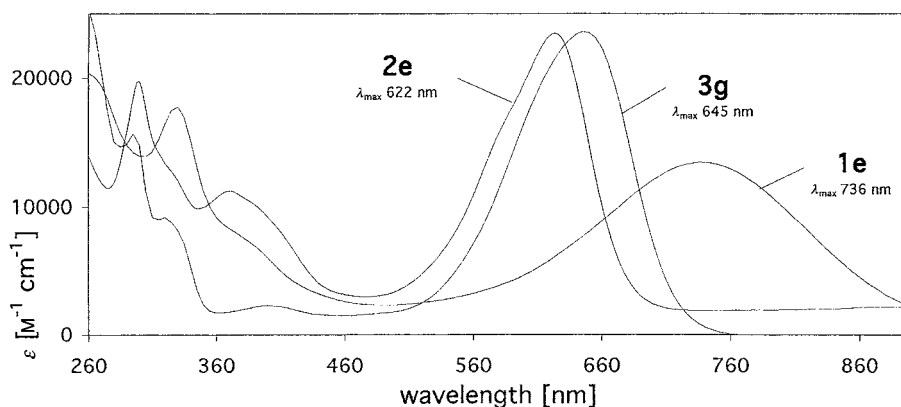[2]) For instance, lacking planarity [25][26], intermolecular H-bonding [27][28], or formation of dimers [29].

Fig. 4. *UV/VIS spectra of indigotins* **1e**, **2e**, *and* **3g** *in CHCl₃*

lacking planarity and intermolecular H-bonding could be ruled out by the structural similarity of **1** with the 4,4′,7,7′-tetraalkoxy-5,5′-dinitroindigotins **2**, which show properties typical for indigotins. *Lambert – Beer*'s law was found to be obeyed for **1** in a concentration range of $5 \cdot 10^{-4}$ to $5 \cdot 10^{-7}$ M (in CHCl₃), excluding absorption changes by aggregation.

The 4,4′,7,7′-tetraalkoxy-5,5′-dinitroindigotins **2a – f** and 4,4′,7,7′-tetraalkoxyindigotin **3g** are blue as solids and in solvents such as chlorinated hydrocarbons, alkanols, and acetone. Compounds **2a – f** show a strong bathochromic shift of the longest-wavelength absorption (λ_{max} 622 nm in CHCl₃) in comparison to red 5,5′-dinitroindigotin [25]. This indicates a considerable contribution of ionic structures to the resonance system[3]. The solubility of 4,4′,7,7′-tetraalkoxyindigotins **2a – f** (≤ 2 mg/ml of CHCl₃) is enhanced as expected by steric effects of the alkoxy groups in the 4,4′- and 7,7′-positions. The bathochromic absorption of tetraalkoxyindigotin **3g** (λ_{max} 645 nm in CHCl₃) is preferentially due to the electron-donating effect of the MeO groups in the 7,7′-positions. The solubility of **3g** is remarkably high (*ca.* 40 mg/ml of CHCl₃).

The N-monoalkylated indigotins **4e,f** are well-soluble in CHCl₃ and less-soluble in DMSO and DMF. As a representative for *N*-pentylindigotins **4e,f**, the bis(heptyloxy) derivative **4f** was characterized spectroscopically. The electronic spectrum of **4f** shows a red shift of the longest-wavelength absorption as expected [26].

NMR Spectra. The number of ¹H-NMR signals of indigotins **1 – 3** and of ¹³C-NMR signals of **1** and **3** is reduced by half caused by their symmetric structure. The ¹H-NMR spectra of **1** display significantly broadened NH resonances. Tautomeric structures of **1** were excluded by a distinct ¹H,¹⁵N-coupling. Compounds **2a – f** and **3g** show sharper NH signals. The ¹⁵N-NMR resonance of **3g** appears at -210 ppm, the ¹H,¹⁵N-coupling is similar to that of **1e** ($J = 102.0 \pm 0.5$ Hz). The ¹H-NMR spectrum of **4f** exhibits the entire number of expected signals.

IR Spectra. The alkoxy substituents in the 4,4′- and 7,7′-positions of indigotins **1 – 4** prevent intermolecular H-bonding as confirmed by the high-wavenumber NH

---

[3]) For effects of substituents on color of indigotins, see [30].

absorption ($\tilde{v}$ (NH) ≥ 3400 cm^{-1}). Under this assumption, the carbonyl absorption allows conclusions regarding the electronic effects of the substituents in the 5,5'-positions. A low-wavenumber absorption ($\tilde{v}$ (CO) 1620–1630 cm^{-1}) verifies the presence of polarized mesomeric structures with partial C−O single bonds (**1** and **2**). The indigotins **3g**, **4f**, and the hydrochloride of **1e** exhibit CO absorptions at *ca.* 1640 cm^{-1} [25][31]. For the 5,5'-diaminoindigotins **1,** two additional N−H absorptions must be taken into consideration ($\tilde{v}_s$ (NH$_2$) and $\tilde{v}_{as}$ (NH$_2$)). Highly uncommon for indigotins, the IR spectra of **1** could be measured in CCl$_4$ solutions. As expected, they show three weak but distinct bands in the range of 3375 to 3460 cm^{-1}.

Mass Spectra. All new compounds were characterized by low-resolution MS. The molecular compositions were confirmed by high-resolution MS of the molecular-ion peaks M^+. Representative for diaminoindigotins **1a–f** and dinitroindigotins **2a–f**, typical fragment ions of the propoxy derivatives **1b** and **2b** were analyzed by high-resolution MS (see *Exper. Part*).

Anions of Dinitroindigotins **2**. The blue color of solutions of 5,5'-dinitroindigotins **2** in common organic solvents changes to red by addition of bases (*e.g.*, KOH/H$_2$O or NaOMe/MeOH); deprotonation yields red monoanions. However, dissolving of **2** in dipolar aprotic solvents such as DMSO or DMF also results in red 'solutions', but in the absence of classical bases. Color and electronic spectra of these 'solutions' are similar to those of the monoanions of **2** created by classical bases in other solvents (λ_{max} *ca.* 785 nm), *i.e.*, dipolar aprotic solvents are able by themselves to abstract an NH proton of dinitroindigos **2**.

The red monoanions of **2** preferably exist as dimers: the electronic spectrum of the anion of **2c** develops a new maximum at 710 nm in addition to the original absorption at 785 nm upon dilution up to concentrations of $< 10^{-6}$ M (in DMSO). Since the spectral evolution shows isosbestic points, it is likely a conversion of dimers to monomers (*Fig. 5*). The UV spectrum of pure monomer **2c**$^-$ could be taken of a diluted sample only after several hours. Obviously, additional processes play a role in the process of de-aggregation (*e.g.*, kinetic effects or solvatation).

The addition of strong bases (KOH/H$_2$O or NaH) to the red monoanions of 5,5'-dinitroindigotins **2** in dipolar aprotic solvents changes the color again, now to bluish-purple (dianions of **2**, λ_{max} *ca.* 810 nm). Both color changes are reversible. The bluish-purple solutions of the dianions turn red again by addition of protic acids. An excess of acid gives turquoise-blue solutions, *i.e.*, the color of neutral indigotins **2** in acidified dipolar aprotic solvents (see *Fig. 6* and *Fig. 7,a* and *b*)[4]).

The anions of **2** were characterized by ^{1}H-NMR spectra[5]) as saturated solutions in (D$_6$)DMSO. The monoanion of the 4,4'-dipropoxyindigotin **2b** shows the whole number of sharp signals and only one proton attached to an N-atom (*Fig. 8,a*). However, the monoanions of the higher homologues **2c–f** exhibit only half the number of broader signals. It could be shown that the signal reduction is caused by aggregation:

---

[4])   For 4,4',7,7'-tetramethoxy-5,5'-dinitroindigotin (simplified equivalent of **2**), absorption maxima were predicted by PPP calculations in vacuum (λ, strength of oscillation): 4,4',7,7'-tetramethoxy-5,5'-dinitroindigotin, 449 nm (0.68); 4,4',7,7'-tetramethoxy-5,5'-dinitroindigotin monoanion, 559 (0.66) and 403 nm (0.27); 4,4',7,7'-tetramethoxy-5,5'-dinitroindigotin dianion, 479 (1.18) and 409 nm (0.42).

[5])   The solubilities of **2a**$^-$, **2a**$^{2-}$, and **2b**$^{2-}$ were too low for measuring ^{1}H-NMR spectra.
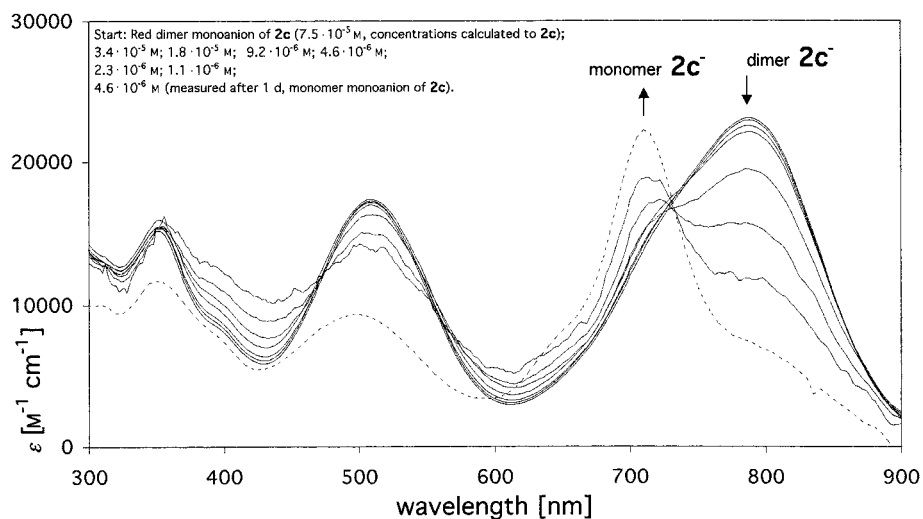
Fig. 5. *UV/VIS Spectra in DMSO: dissociation of dimer* **2c⁻** *into monomer* **2c⁻** *by dilution.* Arrows indicate associated spectral changes.

Fig. 6. *Colors of* **2c** (blue in CHCl₃), *of* **2c⁻** (red dimer in DMSO), *and of* **2c²⁻** (bluish-purple in DMSO/H₂O/KOH)

At *ca.* 100-fold dilution, the monoanion of 4,4′-dibutoxyindigotin **2c** exhibits a spectrum similar to that of **2b⁻** with the whole number of expected signals (*Fig. 8,b*). This confirms the result of dilution experiments of the monoanion of **2c** (dimer → monomer, in DMSO) which were followed by electronic spectra (see *Fig. 5*). ¹H-NMR Spectra of the dianions of **2c–f** exhibit the expected reduction of signals.
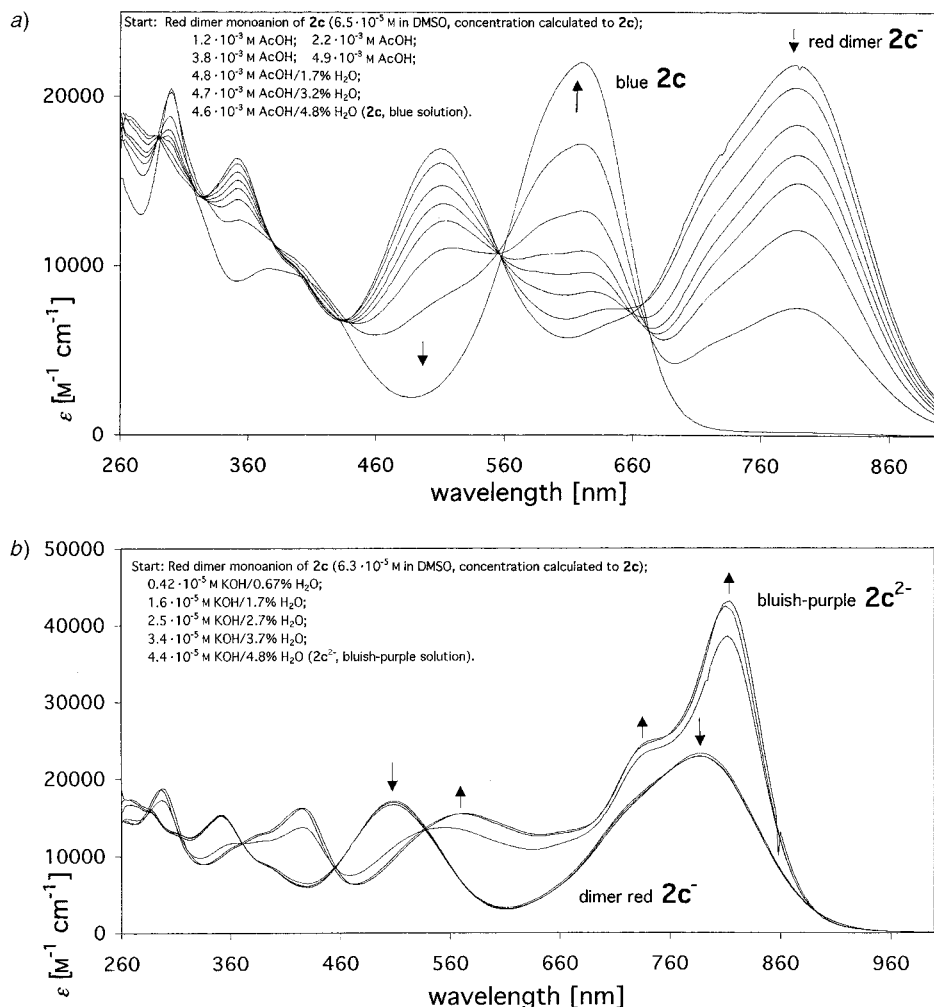
a)

b)

Fig. 7. *UV/VIS spectra of* **2c⁻** (red dimer in DMSO): a) *Gradual addition of AcOH/H₂O gives neutral blue* **2c** (arrows indicate change of spectra with increasing acidity); b) *gradual addition of KOH/H₂O gives bluish-purple* **2c²⁻** (arrows indicate change of spectra with decreasing acidity).

The monoanions of **2** are comparatively stable in DMF or DMSO (as dimers). Highly diluted solutions ($\leq 10^{-5}$ M) show changes of the electronic spectra due to dissociation after several hours (see *Fig. 5*). The solutions of the dianions of **2** are less stable, they exhibit color change to yellow.

It is reported that dipolar aprotic solvents may dissociate protons [32a–c], they solvate preferentially large planar anions [32a,b]. These properties explain the ability of DMSO or DMF to abstract an NH proton of 5,5'-dinitroindigotins **2**. Other examples are 'neutral' haloform reactions in DMSO or DMF [33], and the
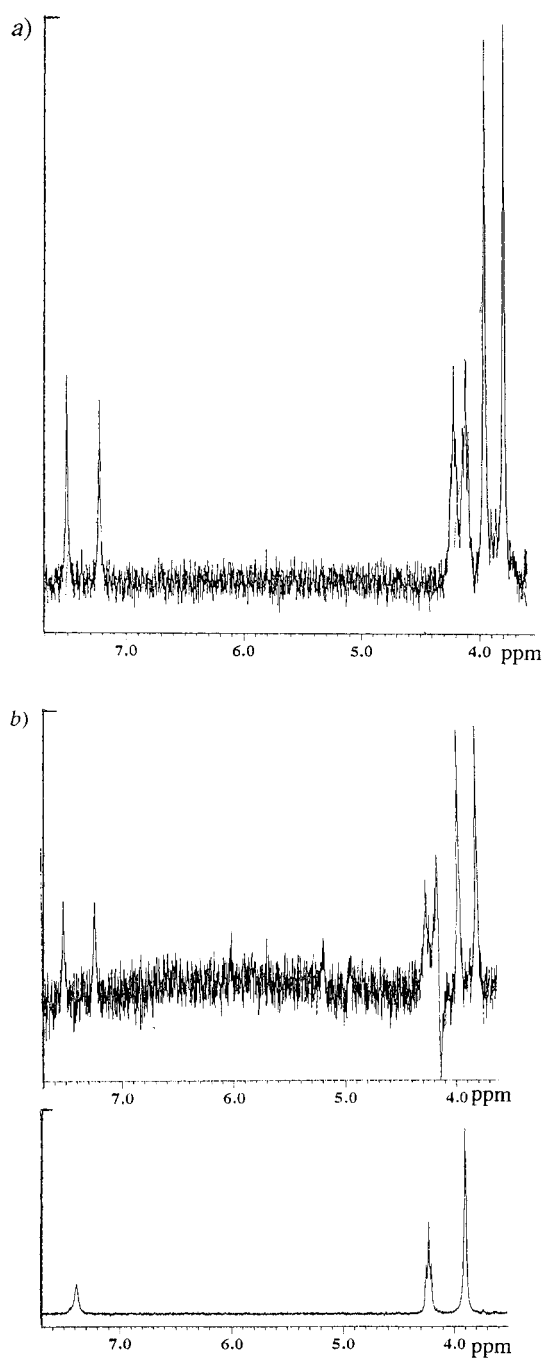
Fig. 8. *1H-NMR Spectrum of* a) *monomer* **2b⁻** *in (D₆)DMSO and* b) *of monomer* **2c⁻** (top) *and of dimer* **2c⁻**
(bottom) *in (D₆)DMSO*

deprotonation of *Methylene azure B* (protonated trimethylthionine) by HMPA[6] [34a,b]. Similarly to the indigotins **2**, indigo-5,5′-disulfonic acid disodium salt (*Indigo Carmine*) shows a color change at pH 11–13 due to deprotonation [23]. *Indigo Carmine* is commercially used as acid-base indicator dye in aqueous solutions.

2.3. *Electrochemistry of Indigotins* **2**. The electrochemistry of indigotin and its derivatives is not well-understood. The only certainty is that unsubstituted indigo undergoes a one-electron reduction forming a radical anion. However, already the next tip is unclear. Voltammetric data reveal that a dianion is formed [35]. But the height of the second reduction wave is considerably smaller than that of the first redox step, indicating some reversible follow-up process such as aggregation after the first charge transfer.

The electrochemistry of the newly synthesized indigotins **2** resembles that of indigo. Thus, **2c** can be reduced in CH_2Cl_2 (blue solution) at a potential of -0.625 V to its radical anion. The process is chemically reversible (*Fig. 9*). A second reductive electron-transfer step occurs at a potential of -1.12 V, showing the formation of a dianionic species, and a third redox step is observed in the reverse sweep at a potential of -0.8 V. The decreasing heights of the reduction waves during the successive reduction steps give evidence that, between these different redox states, reversible dimerization or aggregation must take place. Cyclic voltammetry also shows that the indigotins can be oxidized to their monocations at potentials of *ca.* 1.2 V. Again, these redox reactions are chemically reversible.

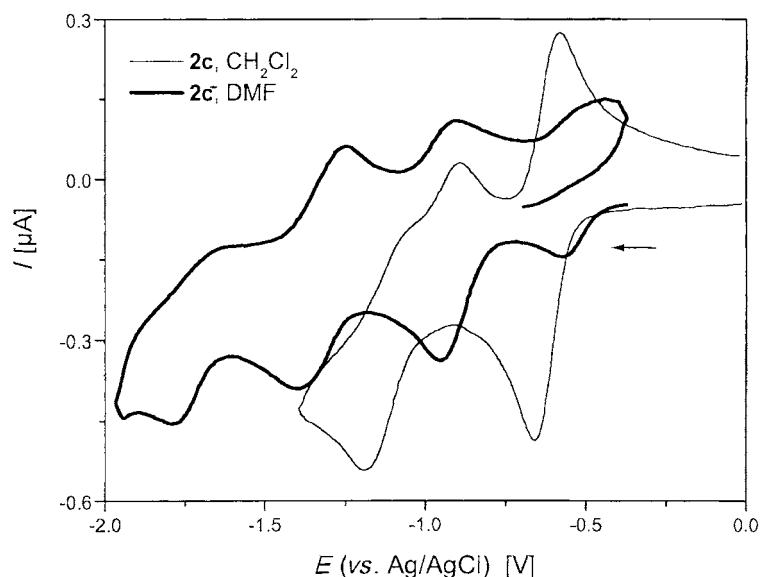Fig. 9. *Cyclic voltammograms of* **2c** *in* CH_2Cl_2 *and of* **2c⁻** *in DMF* (containing 0.1M $(Bu_4N)PF_6$)

---

[6]   The blue dye *Methylene azure B* instantaneously turns pink when treated with HMPA (hexamethylphosphoric triamide), *i.e.*, to the color of the free base; the pink solution changes to blue again by addition of an acid.

A drastic change of the cyclic voltammetric response occurs when the electro-chemical experiments are carried out in DMF (red solution, $2c^-$). The first small wave at a peak potential of -0.540 V indicates a chemical reaction preceding the first redox step (*Fig. 9*). Subsequently, the system can be reduced within three additional redox steps to a tetraanion ($E_2^0 = -0.950$ V, $E_3^0 = -1.3$ V, $E_4^0 = -1.750$ V). This very complex behavior will be analyzed in the future.

2.4. *Small Angle Neutron Scattering (*SANS*) Experiments of Indigotins* **1**. To obtain further information regarding the solution structure of the indigo derivatives, small-angle neutron-scattering (SANS) experiments were performed. SANS Spectra were taken at 25° from saturated solutions in (D_6)acetone of **1d**–**f**. The obtained SANS spectra are shown in *Fig. 10*, where the scattering intensity is given as a function of the magnitude q of the scattering vector.
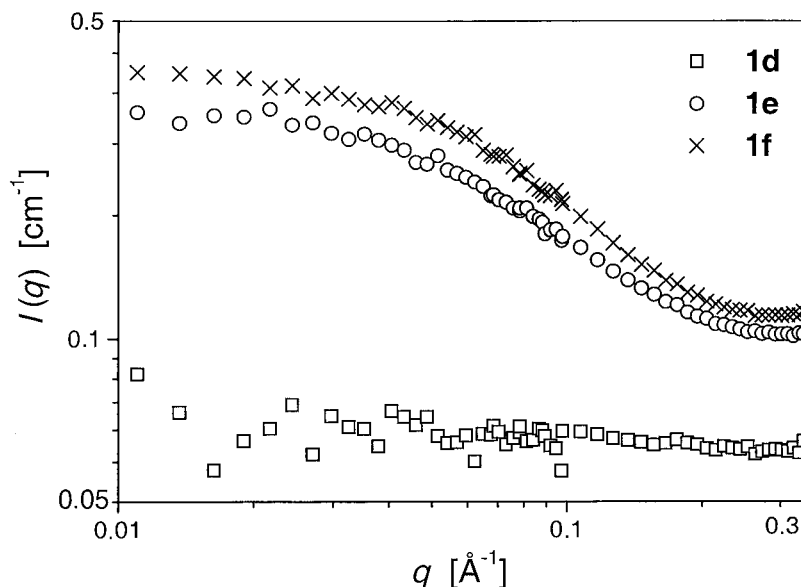

Fig. 10. *SANS Spectra of indigotins* **1d**–**f** *in (D₆)acetone*

For the compounds with short alkyl chains, basically flat SANS spectra are observed, indicating that here only an unstructured molecular solution is present. However, the scattering pattern changes significantly for the compounds with longer alkoxy chains, which also possess a much higher solubility. Here, a marked increase in scattering intensity is observed for the lower q-range, which indicates that, in these solutions, larger particles must be present.

The shape of the increase of the scattering curves can be well-described by rod-like aggregates. Fitting a model of rods to the solutions of compound **1e** and **1f** in acetone yields a radius of 12.7 and 13.6 Å, respectively. These values are in good agreement with the molecular dimension of the compounds, *i.e.*, they correspond to half the longest dimension of the molecules. Therefore, the analysis of the scattering pattern indicates that, in these solutions, rod-like aggregates are present where the individual

molecules are stacked on top of each other, and where the diameter of these rod-like aggregates is simply given by the length of the molecule.

A more-detailed description of the present particles may be obtained if one assumes an isodesmic model for the aggregation of the dye molecules, *i.e.*, a model where the equilibrium constants K_n for the association process are equal (as it is to be expected for such an aggregation process of dye molecules; $K = x_n/(x_1 x_{n-1})$). Here x_n and x_1 are the mole fractions of the *n*-mer and the monomer, respectively. With such a model, one obtains the number distribution $N_l = (K x_1)^{l/L-1}$ for the length of aggregates, where L is the effective thickness of one dye molecule in the aggregate, *i.e.*, its effective extension along the rod axis. With such a model, the absolute intensities are well accounted for, and they yield a good fit to the experimental data with the same radii of 12.7 and 13.6 Å mentioned above.

In conclusion, one can state that the SANS experiments rationalize the increase of solubility with increasing length of the alkyl chain. Evidently, for the longer-chain compounds, aggregation in solvents such as (D_6)acetone takes place. This aggregate formation is responsible for a significant increase in solubility to a much higher value than the monomer solubility. In an analogous way, micelle formation increases the solubility of amphiphiles [36]. Presumably, the driving force for aggregation is the ability of the longer alkyl chains to interact more favorably with the solvent. There is less interaction in the solid state of the pure compound. At the same time, alkoxy chains present a steric hindrance for edge-to-edge association. Therefore, only aggregates of stacked single dye molecules are observed.

3. Conclusions. – The new 4,4′,7,7′-tetraalkoxy-5,5′-diaminoindigotins **1** are highly soluble in organic solvents, and their solutions are green – a combination of properties remarkable for indigotins. Both properties are primarily caused by the electron-donating groups in the 5,5′- and 7,7′-positions; steric effects of the substituents in the 4,4′- and 7,7′-positions play a minor role. A strong red shift of the longest-wavelength absorption and negative solvatochromism indicate a predominance of polar resonance structures in the ground state; tautomeric structures were excluded. SANS Experiments showed that homologues with long alkoxy chains in the 4,4′-positions form rod-like aggregates of molecular diameter in (D_6)acetone. The high solubility of **1** is important for technical applications, for spectroscopic investigations in solution, and for synthetic purposes (*e.g.*, for the preparation of biologically active substances). The 5,5′-diaminoindigotins **1** were compared to similarly substituted 5,5′-dinitroindigotins **2** which are blue and by far less soluble. They form red monoanions and bluish-purple dianions in some organic solvents. Alkylation yields *N*-monosubstituted indigotins **4**.

Experimental Part

General. All solvents were distilled before use. Column filtration: *Merck* silica gel *60* (0.04–0.063 mm). TLC: *Merck* silica gel *60 F$_{254}$* (precoated silica gel plates). Solubility: determined by evaporation of sat. solns. at 20°. M.p.: *Büchi 510*, uncorrected. Differential scanning calorimetry (DSC): *Netzsch DSC 200*, heating rate 10°/min (in parentheses temp. of phase change). GC: *Carlo-Erba Fractovap 41060* with FID, *CS-FS-OV-1-CB-0.5* column (0.32 mm × 25 m), 120–250°, 5°/min, carrier gas H$_2$, 0.3 kg/cm²; t_R in min.

UV/VIS: λ_{max} in nm, ε in M^{-1} cm^{-1}; *Specord 200 (Analytik Jena AG)*; $1 \cdot 10^{-5}$ M to $5 \cdot 10^{-5}$ M solns. if not mentioned otherwise; calc. electronic spectra by semi-empirical PM3 calculations in vacuum (Hyper-Chem 5.01, *HyperCube*). IR Spectra: in cm^{-1}; *Perkin-Elmer Paragon 1000 FT*. NMR Spectra: δ in ppm, *J* in Hz; *Jeol. JNM-EX 270* (¹H 270 MHz, ¹³C 67.9 MHz), *Bruker AM 360* (¹H 360 MHz, ¹³C 90.6 MHz), *Bruker DRX 500* (¹H 500 MHz, ¹⁵N 50.7 MHz); $\delta(H)$ and $\delta(C)$ rel. to SiMe$_4$ and $\delta(N)$ rel. to MeNO$_2$; for (non-systematic) atom numbering, see *Scheme 1,a*. EI-MS: in *m/z* (rel. %); *Varian MAT 312* at 70 eV. SANS Spectra: *Paxe* instrument, *Laboratoire Léon Brillouin,* Saclay, France; at 25° with sat. solns. in (D$_6$)acetone; the wavelength λ chosen was 6 Å, and the sample-detector distances were 1.07 m and 3.87 m, respectively, thereby covering an effective *q* range of 0.011 to 0.34 Å^{-1}, where *q* is the magnitude of the scattering vector *q*, as defined by $q = 4 \pi \lambda^{-1} \sin\theta/2$ (λ: wavelength; θ: scattering angle).

General Procedure A (GP A). Under vigorous stiring, *ca.* 1.8 equiv. of 1-bromoalkane (or 1-iodoalkane) was added within 10 min at r.t. to a suspension of 1.0 equiv. of **7** [17] and 1.8 equiv. of K$_2$CO$_3$ in EtOH (*ca.* 1.2 ml/mmol of **7**). The mixture was heated to reflux for 16 h. After cooling, the mixture was filtered and the solid carefully washed with EtOH. The filtrate was evaporated and the residue dissolved in toluene/Et$_2$O 1:4 and extracted twice with 1M KOH. The aq. phases were re-extracted with toluene/Et$_2$O 1:4. The combined org. phase was dried (Na$_2$SO$_4$) and evaporated, and the crude product was purified by destillation *in vacuo: **6a–g*** (75–86%).

General Procedure B (GP B). Under vigorous stirring, **6a–g** was added dropwise without external cooling to 65% HNO$_3$ soln. ($d = 1.41$; *ca.* 2.7 ml/mmol of **6**) within ca. 1.5 h at 35–45°. After stirring for additional 4 h at r.t., the mixture was poured into ice water (*ca.* 20 g/mmol of **6**). The resulting yellow precipitate was filtered off, washed with H$_2$O until neutral, and then dissolved in toluene/Et$_2$O 1:4. The soln. was extracted with H$_2$O until neutral, dried (Na$_2$SO$_4$), and evaporated. The residue was filtered over a *ca.* 40-fold amount of silica gel with toluene/AcOEt 19:1 to give **5a–f** or **8g** (impure; < 48% yield), which was used in the next step without further purification. For analysis, a sample was purified by crystallization. Compounds **9** were isolated from polar fractions and purified by crystallization.

General Procedure C (GP C). A soln. of **5a–f** or **8g** (from **6a–g**) in acetone at r.t. (*ca.* 15 ml/g of impure **5** or **8**) was cooled to $-10°$, and 0.2M KOH (*ca.* 2 ml/g of **5** or **8**) was added dropwise within 10 min under vigorous stirring. After 15 min, 0.4M KOH (ca. 15 ml/g of crude **5** or **8**) was added at 5° within 20 min under stirring. The resulting dark-colored suspension was stirred at r.t. for additional 16 h and then centrifuged (30 min; 10000 rpm). The precipitate was washed several times with H$_2$O (until neutral and almost colorless), EtOH, and Et$_2$O, and air-dried: 7–15% (rel. to **6a–f**) of **2a–f**; 24% (rel. to **6g**) of **3g**.

Monoanions of **2**. Dissolution of **2** in DMF or DMSO gave red solns. of monoanions, preferentially dimers. Monoanions **2b⁻** and **2c⁻** were also characterized as monomers (¹H-NMR in (D$_6$)DMSO) and **2c⁻** (UV/VIS in DMSO).

Dianions of **2**. Addition of 2M KOH (*ca.*1% (*w/w*) to solns. of monoanions of **2** in DMF or DMSO gave bluish-purple solns. of dianions.

General Procedure D (GP D). To a stirred suspension of powdered **2** in 1M NaOH (*ca.* 40 ml/mmol of **2**), Na$_2$S$_2$O$_4$ (85%; $\leq$10 mmol/mmol of **2**) was added at 50°. The mixture was heated, and suddenly the dark blue solid was converted into a gray precipitate (at *ca.* 80°). After 10 min stirring, the hot suspension was filtrated; on contact with air, the color of the precipitate changed to blue. After careful washing (H$_2$O and some EtOH), the solid was dissolved in CHCl$_3$, the soln. filtered through a pad of silica gel rinsing with CHCl$_3$, and the filtrate evaporated: dark-colored **1** (79%–88%[7]).

General Procedure E (GP E). To a soln. of *ca.* 1–2 mg of **2** in 1.0 ml of DMSO containing two drops of 2N KOH, two drops of 1-bromopentane were added (color change from bluish-purple to green). After *ca.* 4 h, the resulting dark-colored precipitate of **4** (1-2 mg, containing some **2**) was filtered off, washed with EtOH, and air-dried. The reaction was not optimized.

---

[7]   The yield of **1a** (11%) is not representative.

2-Ethoxy-5-methoxybenzaldehyde (**6a**). According to *GP A*, with **7** (26.05 g, 171 mmol), iodoethane (24.6 ml, 48.0 g, 308 mmol), K_2CO_3 (42.5 g, 308 mmol), and EtOH (180 ml): 23.2 g (75%) of **6a**. Yellow oil, which solidified to pale yellow crystals. B.p. 76–81°/0.05 Torr ([35]: 50°/0.05 Torr). M.p. 47.6–49.5° ([37]: 54°). R_f (toluene/AcOEt 19:1) 0.46. GC: t_R 9.8. IR (CCl$_4$): 3077, 3046, 3001, 2985, 2941, 2908, 2865, 2760, 1687 (CO), 1613, 1587, 1495, 1476, 1423, 1390, 1277, 1220, 1160, 1047. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 1.36 (t, $^3J = 7.0$, *Me*CH$_2$O); 3.75 (s, MeO); 4.13 (t, $^3J = 6.9$, MeCH$_2$O); 7.16 (d, $^4J = 3.1$, H–C(6)); 7.18 (d, $^3J = 8.2$, H–C(3)); 7.25 (dd, $^3J = 8.2$ Hz, $^4J = 3.1$, H–C(4)); 10.35 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 15.0 (q, *Me*CH$_2$O); 56.0 (q, MeO); 65.2 (t, MeCH$_2$O); 110.5 (d, C(3)); 116.0 (d, C(6)); 123.6 (d, C(4)); 125.1 (s, C(1)); 153.6 (s, C(2)); 156.1 (s, C(5)); 189.4 (d, CHO). EI-MS: 180 (95, M^+), 152 (79, $[M - C_2H_4]^+$), 151 (75, $[M - C_2H_5]^+$), 137 (100). HR-MS: 180.0786 (M^+, $C_{10}H_{12}O_3^+$; calc. 180.0786).

5-Methoxy-2-propoxybenzaldehyde (**6b**). According to *GP A*, with **7** (24.0 g, 158 mmol), 1-bromopropane (26.4 ml, 35.7 g, 290 mmol), K_2CO_3 (40.2 g, 291 mmol), and EtOH (176 ml): 25.1 g (82%) of **6b**. Pale yellow oil. B.p. 86–90°/0.05 Torr. R_f (toluene/AcOEt 19:1) 0.49. GC: t_R 12.2. IR (CCl$_4$): 3077, 3047, 3005, 2968, 2940, 2878, 2758, 1687 (CO), 1613, 1588, 1494, 1467, 1423, 1388, 1277, 1220, 1159, 1042. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 1.00 (t, $^3J = 7.0$, *Me*CH$_2$CH$_2$O); 1.77 (*sext.*, $^3J = 7.0$, MeCH$_2$CH$_2$O); 3.75 (s, MeO); 4.04 (t, $^3J = 6.5$, MeCH$_2$CH$_2$O); 7.16 (d, $^4J = 3.0$, H–C(6)); 7.18 (d, $^3J = 9.0$, H–C(3)); 7.25 (dd, $^3J = 9.0$, $^4J = 3.0$, H–C(4)); 10.37 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 10.7 (q, Me(3′)); 22.6 (t, C(2′)); 55.8 (q, MeO); 70.7 (t, C(1′)); 110.4 (d, C(3)); 115.4 (d, C(6)); 123.3 (d, C(4)); 125.1 (s, C(1)); 153.6 (s, C(2)); 156.2 (s, C(5)); 189.0 (d, CHO). EI-MS: 194 (78, M^+), 152 (100, $[M - C_3H_6]^+$), 137 (78). HR-MS: 194.0941 (M^+, $C_{11}H_{14}O_3^+$; calc. 194.0942).

2-Butoxy-5-methoxybenzaldehyde (**6c**). According to *GP A*, with **7** (23.4 g, 153 mmol), 1-bromobutane (27.9 ml, 35.6 g, 260 mmol), and K_2CO_3 (35.9 g, 260 mmol), and EtOH (185 ml): 27.1 g (86%) of **6c**. Pale yellow oil. B.p. 92–98°/0.03 Torr. R_f (toluene/AcOEt 19:1) 0.50. GC: t_R 14.6. IR (CCl$_4$): 3078, 3042, 3002, 2962, 2937, 2914, 2874, 2758, 1686 (CO), 1614, 1588, 1495, 1466, 1423, 1388, 1276, 1219, 1160, 1043. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.93 (t, $^3J = 7.0$, Me(4′)); 1.45 (*sext.*, $^3J = 7.0$, CH$_2$(3′)); 1.74 (*quint.*, $^3J = 7.0$, CH$_2$(2′)); 3.75 (s, MeO); 4.08 (t, $^3J = 6.5$, CH$_2$(1′)); 7.16 (d, $^4J = 3.0$, H–C(6)); 7.18 (d, $^3J = 9.0$, H–C(3)); 7.25 (dd, $^3J = 9.0$, $^4J = 3.0$, H–C(4)); 10.35 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.1 (q, Me(4′)); 19.3 (t, C(3′)); 31.2 (t, C(2′)); 56.0 (q, MeO); 69.1 (t, C(3′)); 110.5 (d, C(3)); 115.9 (d, C(6)); 123.6 (d, C(4)); 125.1 (s, C(1)); 153.6 (s, C(2)); 156.2 (s, C(5)); 189.2 (d, CHO). EI-MS: 208 (20, M^+), 152 (100, $[M - C_4H_8]^+$), 137 (22). HR-MS: 208.1099 (M^+, $C_{12}H_{16}O_3^+$; calc. 208.1099).

5-Methoxy-2-(pentyloxy)benzaldehyde (**6d**). According to *GP A*, with **7** (19.1 g, 126 mmol), 1-bromopentane (28.1 ml, 34.2 g, 226 mmol), K_2CO_3 (31.2 g, 226 mmol), and EtOH (159 ml): 21.2 g (76%) of **6d**. Pale yellow oil. B.p. 114–117°/0.05 Torr. R_f (toluene/AcOEt 19:1) 0.51. GC: t_R 17.1. IR (CCl$_4$): 3080, 3048, 3003, 2959, 2938, 2863, 2758, 1687 (CO), 1613, 1588, 1495, 1467, 1423, 1388, 1276, 1220, 1160, 1042. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.85 (t, $^3J = 7.0$, Me(5′)); 1.22–1.46 (CH$_2$(3′), CH$_2$(4′)); 1.70 (*quint.*, $^3J = 6.5$, CH$_2$(2′)); 3.72 (s, MeO); 3.99 (t, $^3J = 6.5$, CH$_2$(1′)); 7.12 (d, $^3J = 9.0$, H–C(3)); 7.13 (d, $^4J = 3.0$, H–C(6)); 7.18 (dd, $^3J = 9.0$, $^4J = 3.0$, H–C(4)); 10.33 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.3 (q, Me(5′)); 22.4 (t, C(4′)); 28.2 (t, C(3′)); 28.9 (t, C(2′)); 55.9 (q, MeO); 69.3 (t, C(1′)); 110.4 (d, C(3)); 115.7 (d, C(6)); 123.5 (d, C(4)); 125.0 (s, C(1)); 153.6 (s, C(2)); 156.3 (s, C(5)); 189.1 (d, CHO). EI-MS: 222 (52, M^+), 152 (100, $[M - C_5H_{10}]^+$), 137 (58). HR-MS: 222.1254 (M^+, $C_{13}H_{18}O_3^+$; calc. 222.1255).

2-(Hexyloxy)-5-methoxybenzaldehyde (**6e**). According to *GP A*, with **7** (16.3 g, 107 mmol), 1-bromohexane (27.8 ml, 32.7 g, 198 mmol), K_2CO_3 (27.3 g, 198 mmol), and EtOH (136 ml): 21.7 g (86%) of **6e**. Yellow oil which solidified to a pale yellow solid. B.p. 123–125°/0.04 Torr. M.p. 25.5–26.6°. R_f (toluene/AcOEt 19:1) 0.52. GC: t_R 19.4. IR (CCl$_4$): 3077, 3051, 3004, 2958, 2935, 2862, 2758, 1686 (CO), 1614, 1588, 1495, 1467, 1423, 1388, 1276, 1219, 1160, 1043. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.86 (t, $^3J = 6.8$, Me(6′)); 1.22–1.48 (CH$_2$(3′), CH$_2$(4′), CH$_2$(5′)); 1.74 (*quint.*, $^3J = 6.5$, CH$_2$(2′)); 3.72 (s, MeO); 4.06 (t, $^3J = 6.5$, CH$_2$(1′)); 7.15 (d, $^4J = 3.0$, H–C(6)); 7.17 (d, $^3J = 9.0$, H–C(3)); 7.23 (dd, $^3J = 9.0$, $^4J = 3.0$, H–C(4)); 10.34 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.3 (q, Me(6′)); 22.6 (t, C(5′)); 25.7 (t, C(4′)); 29.1 (t, C(3′)); 31.5 (t, C(2′)); 56.0 (q, MeO), 69.4 (t, C(1′)); 110.4 (d, C(3)); 115.8 (d, C(6)); 123.6 (d, C(4)); 125.0 (s, C(1)); 153.6 (s, C(2)); 156.3 (s, C(5)); 189.2 (d, CHO). EI-MS: 236 (26, M^+), 152 (100, $[M - C_6H_{12}]^+$), 137 (29). HR-MS: 236.1410 (M^+, $C_{14}H_{20}O_3^+$; calc. 236.1411).

2-(Heptyloxy)-5-methoxybenzaldehyde (**6f**). According to *GP A*, with **7** (23.0 g, 151 mmol), 1-bromoheptane (45.0 ml, 51.3 g, 287 mmol), K_2CO_3 (39.6 g, 287 mmol), and EtOH (200 ml): 30.95 g (82%) of **6f**. Pale yellow oil. B.p. 148–152°/0.05 Torr. R_f (toluene/AcOEt 19:1) 0.54. GC: t_R 21.6. IR (CCl$_4$): 3077, 3041, 3004, 2959, 2937, 2862, 2758, 1687 (CO), 1612, 1588, 1495, 1467, 1423, 1388, 1276, 1220, 1160, 1042. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.86 (t, $^3J = 6.5$, Me(7′)); 1.20–1.50 (CH$_2$(3′), CH$_2$(4′), CH$_2$(5′), CH$_2$(6′)); 1.74 (*quint.*, $^3J = 6.5$,

$CH_2(2')$); 3.75 (s, MeO); 4.06 (t, $^3J = 6.5$, $CH_2(1')$); 7.16 (d, $^4J = 3.0$, H−C(6)); 7.17 (d, $^3J = 9.0$, H−C(3)); 7.23 (dd, $^3J = 9.0$, $^4J = 3.0$, H−C(4)); 10.35 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.3 (q, Me(7')), 22.6 (t, C(6')), 26.0 (t, C(5')); 29.0 (t, C(4')), 29.2 (t, C(3')), 31.9 (t, C(2')), 55.9 (q, MeO), 69.3 (t, C(1')); 110.4 (d, C(3)); 115.6 (d, C(6)); 123.5 (d, C(4)); 125.0 (s, C(1)); 153.6 (s, C(2)); 156.3 (s, C(5)); 189.0 (d, CHO). EI-MS: 250 (14, M^+), 152 (100, $[M − C_7H_{14}]^+$), 137 (58). HR-MS: 250.1567 (M^+, $C_{15}H_{22}O_3^+$; calc. 250.1568).

5-Methoxy-2-(nonyloxy)benzaldehyde (**6g**). According to *GP A*, with **7** (28.2 g, 185 mmol), 1-bromono-nane (55.4 ml, 60.1 g, 290 mmol), K_2CO_3 (40.1 g, 290 mmol), and EtOH (230 ml): 38.9 g (75%) of **6g**. Pale yellow oil. B.p. 170−175°/0.002 Torr. M.p. 30.9−35.9°. R_f (toluene/AcOEt 19:1) 0.55. GC: t_R 25.8. IR (CCl$_4$): 3074, 3047, 3002, 2956, 2930, 2858, 2758, 1687 (CO), 1613, 1588, 1508, 1495, 1467, 1422, 1388, 1276, 1220, 1160, 1043. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.83 (t, $^3J = 6.5$, Me(9')), 1.15−1.50 (12 H, $CH_2(3')$ to $CH_2(8')$), 1.72 (*quint.*, $^3J = 6.5$, $CH_2(2')$); 3.73 (s, MeO); 4.03 (t, $^3J = 6.5$, $CH_2(1')$); 7.14 (d, $^4J = 3.0$, H−C(6)); 7.21 (dd, $^3J = 9.0$, $^4J = 3.0$, H−C(4)); 10.34 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.5 (q, Me(9')); 22.7 (t, C(8')); 26.1 (t, C(7')); 29.18 (t, C(6')); 29.34 (t, C(5')); 29.4 (t, C(4')); 29.5 (t, C(3')); 31.9 (t, C(2')); 56.0 (q, MeO); 69.4 (t, C(1')); 110.4 (d, C(3)); 115.7 (d, C(6)); 123.6 (d, C(4)); 125.1 (s, C(1)); 153.6 (s, C(2)); 156.3 (s, C(5)); 189.1 (d, CHO). EI-MS: 279 (5, M^+), 278 (18, M^+), 152 (100, $[M − C_9H_{18}]^+$), 137 (19). HR-MS: 278.1880 (M^+, $C_{17}H_{26}O_3^+$; calc. 278.1881).

2-Ethoxy-5-methoxy-3,6-dinitrobenzaldehyde (**5a**) and *1-Ethoxy-4-methoxy-2,3-dinitrobenzene* (**9a**). According to *GP B*, with **6a** (18.66 g, 104 mmol) and 65% HNO$_3$ soln. (286 ml) ($T \leq 53°$): 8.55 g of **5a** (impure, < 29%). A sample was recrystallized from cyclohexane/toluene 1:3. Pale yellow solid. M.p. 133.3−133.9°. R_f (toluene/AcOEt 19:1) 0.50. GC: t_R 19.4. IR (CCl$_4$): 3039, 2956, 2936, 2874, 2774, 1714 (CO), 1561, 1546, 1495, 1468, 1438, 1420, 1386, 1362, 1310, 1275, 1241, 954, 860. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 1.34 (t, $^3J = 7.0$, $MeCH_2O$); 3.97 (s, MeO); 4.20 (q, $^3J = 6.9$, $MeCH_2O$); 8.30 (s, H−C(4)); 10.16 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 15.5 (q, $MeCH_2O$); 58.6 (q, MeO); 76.0 (t, $MeCH_2$); 116.5 (d, C(4)); 123.0 (s, C(1)); 139.4, 146.0, 146.8, 147.5 (4s, C(2), C(3), C(5), C(6)); 186.1 (d, CHO). EI-MS: 270 (38, M^+), 242 (10, $[M − C_2H_4]^+$), 224 (100), 194 (22), 179 (35), 164 (39), 136 (35). HR-MS: 270.0488 (M^+, $C_{10}H_{10}N_2O_7^+$; calc. 270.0488).

From polar fractions, a sample was recrystallized from cyclohexane/AcOEt (1:1): **9a**. Yellow crystals. M.p. 155−161°. R_f (toluene/AcOEt 19:1) 0.30. GC: t_R 19.0. IR (KBr): 3025, 2989, 2952, 2889, 2849, 1550, 1494, 1366, 1279, 1051, 810. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 1.30 (t, $^3J = 7.0$, $MeCH_2O$); 3.95 (s, MeO); 4.25 (q, $^3J = 6.9$, $MeCH_2O$); 7.67, 7.70 (2d, $^3J = 9.5$, H−C(5), H−C(6)). ^{13}C-NMR ((D$_6$) DMSO): 14.8 (q, $MeCH_2O$); 58.4 (q, MeO); 67.1 (t, $MeCH_2$); 119.6, 120.7 (2d, C(5), C(6)); 133.2, 133.7 (2s, C(2), C(3)); 144.6, 145.4 (2s, C(1), C(4)). EI-MS: 242 (42, M^+), 214 (100, $[M − C_2H_4]^+$), 184 (14), 136 (18). HR-MS: 242.0538 (M^+, $C_9H_{10}N_2O_6^+$; calc. 242.0538).

5-Methoxy-3,6-dinitro-2-propoxybenzaldehyde (**5b**) and *4-Methoxy-2,3-dinitro-1-propoxybenzene* (**9b**). According to *GP B*, with **6b** (20.0 g, 103 mmol) and 65% HNO$_3$ soln. (280 ml) ($T \leq 45°$): 11.4 g of **5b** (impure, < 38%). A sample was recrystallized from cyclohexane/AcOEt 9:1. Pale yellow crystals. M.p. 146.2−147.1°. R_f (toluene/AcOEt 19:1) 0.53. GC: t_R 22.0. IR (KBr): 3023, 2961, 2944, 2877, 1712 (CO), 1558, 1480, 1467, 1438, 1420, 1365, 1310, 1274, 1243, 1101, 1023. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.95 ($t,^3J = 7.5$, $MeCH_2CH_2O$); 1.75 (*sext.*, $^3J = 7.5$, $MeCH_2CH_2O$); 3.98 (s, MeO); 4.08 (t, $^3J = 6.5$, $MeCH_2CH_2O$), 8.31 (s, H−C(4)); 10.14 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 10.3 (q, $MeCH_2CH_2O$); 23.1 (t, $MeCH_2CH_2O$); 58.5 (q, MeO); 81.4 (t, $MeCH_2CH_2O$); 116.4 (d, C(4)); 123.0 (s, C(1)); 139.4, 146.0, 146.8, 147.5 (4s, C(2), C(3), C(5), C(6)); 185.9 (d, CHO). EI-MS: 284 (10, M^+), 242 (30, $[M − C_3H_6]^+$), 224 (75), 194 (23), 43 (100, $C_3H_7^+$). HR-MS: 284.0643 (M^+, $C_{11}H_{12}N_2O_7^+$; calc. 284.0644).

From polar fractions, a sample was recrystallized from cyclohexane: **9b**. Yellow platelets. M.p. 107.4−108.5. R_f (toluene/AcOEt 19:1) 0.34. GC: t_R 20.8. IR (KBr): 3016, 2976, 2950, 2884, 2848, 1543, 1495, 1352, 1277, 1061, 811. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.92 (t, $^3J = 7.3$, $MeCH_2CH_2O$); 1.68 (m, $MeCH_2CH_2O$); 3.94 (s, MeO); 4.14 (t, $^3J = 6.5$, $MeCH_2CH_2O$), 7.63, 7.69 (2d, $^3J = 9.6$, H−C(5)), H−C(6)). ^{13}C-NMR ((D6)DMSO): 10.5 (q, $MeCH_2CH_2$); 22.3 (t, $MeCH_2CH_2$); 58.3 (q, MeO); 72.5 (t, $MeCH_2CH_2O$); 119.5, 120.5 (2d, C(5), C(6)); 133.2, 133.7 (2s, C(2), C(3)); 144.7, 145.4 (2s, C(1), C(4)). EI-MS: 256 (15, M^+), 214 (100, $[M − C_3H_6]^+$), 184 (5), 151 (8), 136 (8). HR-MS: 56.0695 (M^+, $C_{10}H_{12}N_2O_6^+$; calc. 256.0695).

2-Butoxy-5-methoxy-3,6-dinitrobenzaldehyde (**5c**) and *1-Butoxy-4-methoxy-2,3-dinitrobenzene* (**9c**). According to *GP B*, with **6c** (19.1 g, 91.8 mmol) and 65% HNO$_3$ soln. (250 ml) ($T \leq 42°$): 10.6 g of **5c** (impure, < 38%). A sample was recrystallized from cyclohexane/AcOEt 9:1. Pale yellow crystals. M.p. 123.8−124.7°. R_f (toluene/AcOEt 19:1) 0.55. GC: t_R 24.6. IR (CCl$_4$): 3023, 2964, 2936, 2877, 2760, 1714 (CO), 1561, 1546, 1479, 1467, 438, 1419, 1380, 1358, 1310, 1241, 1101, 1026. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.91 (t, $^3J = 7.3$, Me(4')); 1.40 (*sext.*, $^3J = 7.3$, $CH_2(3')$); 1.72 (*quint.*, $^3J = 6.5$, $CH_2(2')$); 3.97 (s, MeO); 4.14 (t, $^3J = 6.4$, $CH_2(1')$); 8.30 (s, C(4)); 10.14 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.1 (q, Me(4')); 18.9 (t, C(3')); 31.8 (t, C(2')); 58.6

(q, MeO); 79.8 (t, C(1′)); 116.5 (d, C(4)); 123.0 (s, C(1)); 139.2, 146.1, 146.8, 147.4 (4s, C(2), C(3), C(5), C(6)); 186.0 (d, CHO). EI-MS: 298 (11, M^+), 242 (36, [$M - C_4H_8$]$^+$), 224 (100), 194 (28), 57 (86, C$_4$H$_9^+$). HR-MS: 298.0801 (M^+, C$_{12}$H$_{14}$N$_2$O$_7^+$; calc. 298.0801).

From polar fractions, a sample was recrystallized from cyclohexane/AcOEt 9:1: **9c** [8a,b]. Yellow needles. M.p. 119.5 – 120.8°. R_f (toluene/AcOEt 19:1) 0.35. GC: t_R 22.8. IR (KBr): 3039, 2967, 2949, 2880, 2849, 1546, 1498, 1361, 1280, 1057, 809. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.90 (t, $^3J = 7.5$, Me(4′)); 1.38 (*sext.*, $^3J = 7.5$, CH$_2$(3′)); 1.67 (*quint.*, $^3J = 7.5$, CH$_2$(2′)); 3.94 (s, MeO); 4.19 (t, $^3J = 6.1$, CH$_2$(1′)); 7.68, 7.70 (2d, $^3J = 9.9$, H–C(5), H–C(6)). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.0 (q, Me(4′)); 19.0 (t, C(3′)); 30.9 (t, C(2′)); 58.4 (q, MeO); 70.8 (t, C(1′)); 119.6, 120.6 (2d, C(5), C(6)); 133.2, 133.7 (2s, C(2), C(3)); 144.7, 145.4 (2s, C(1), C(4)). EI-MS: 270 (8, M^+), 214 (100, [$M - C_4H_8$]$^+$), 197 (5), 179 (8), 149 (10). HR-MS: 270.0852 (M^+, C$_{11}$H$_{14}$N$_2$O$_6^+$; calc. 270.0852).

5-Methoxy-3,6-dinitro-2-(pentyloxy)benzaldehyde (**5d**) *and 4-Methoxy-2,3-dinitro-1-(pentyloxy)benzene* (**9d**). According to *GP B*, with **6d** (16.3 g, 73.4 mmol) and 65% HNO$_3$ soln. (200 ml) ($T \leq 40°$): 11.1 g of **5d** (impure, < 48%). A sample was recrystallized from cyclohexane/AcOEt 9:1. Pale yellow crystals. M.p. 79.2 – 80.4°. R_f (toluene/AcOEt 19:1) 0.58. GC: t_R 26.6. IR (CCl$_4$): 3026, 2961, 2938, 2876, 2758, 1712 (CO), 1559, 1526, 1480, 1467, 1438, 1420, 1387, 1365, 1310, 1275, 1242, 1101, 1024. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.89 (m, Me(5′)); 1.20 – 1.42 (CH$_2$(3′), CH$_2$(4′)); 1.71 (*quint.*, $^3J = 6.5$, CH$_2$(2′)); 3.98 (s, MeO); 4.14 (t, $^3J = 6.5$, CH$_2$(1′)); 8.31 (s, H–C(4)); 10.14 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.1 (q, Me(5′)); 22.3 (t, C(4′)); 27.0 (t, C(3′)); 29.5 (t, C(2′)); 58.2 (q, MeO); 80.2 (t, C(1′)); 116.4 (d, C(4)); 122.9 (s, C(1)); 139.2, 146.2, 146.8, 147.7 (4s, C(2), C(3), C(5), C(6)); 185.9 (d, CHO). EI-MS: 312 (8, M^+), 242 (14, [$M - C_5H_{10}$]$^+$), 224 (12), 194 (5), 70 (84, C$_5$H$_{10}^+$), 43 (100, C$_3$H$_7^+$). HR-MS: 312.0956 (M^+, C$_{13}$H$_{16}$N$_2$O$_7^+$; calc. 312.0957).

From polar fractions, a sample was recrystallized from cyclohexane: **9d**. Yellow platelets. M.p. 93.2 – 94.1°. R_f (toluene/AcOEt 19:1) 0.36. GC: t_R 24.8. IR (KBr): 3016, 2965, 2934, 2862, 2848, 1550, 1495, 1352, 1276, 1059, 814. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.86 (t, $^3J = 7.4$, Me(5′)); 1.20 – 1.40 (CH$_2$(3′), CH$_2$(4′)); 1.67 (m, CH$_2$(2′)); 3.93 (s, MeO); 4.16 (t, $^3J = 6.5$, CH$_2$(1′)); 7.63, 7.69 (2d, $^3J = 9.6$, H–C(5), H–C(6)). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.2 (q, Me(5′)); 22.2 (t, C(4′)); 27.8 (t, C(3′)); 28.5 (t, C(2′)); 58.3 (q, MeO); 71.1 (t, C(1′)); 119.4, 120.4 (2d, C(5), C(6)); 133.3, 133.7 (2s, C(2), C(3)); 144.7, 145.4 (2s, C(1), C(4)). EI-MS: 284 (10, M^+), 214 (100, [$M - C_5H_{10}$]$^+$), 184 (5), 151 (5), 136 (5). HR-MS: 284.1008 (M^+, C$_{12}$H$_{16}$N$_2$O$_6^+$; calc. 284.1008).

2-(Hexyloxy)-5-methoxy-3,6-dinitrobenzaldehyde (**5e**) *and 1-(Hexyloxy)-4-methoxy-2,3-dinitrobenzene* (**9e**). According to *GP B*, with **6e** (21.5 g, 91.1 mmol) and 65% HNO$_3$ soln. (240 ml) ($T \leq 39°$): 11.8 g of **5e** (impure, < 39%). A sample was recrystallized from cyclohexane/AcOEt 19:1. Pale yellow crystals. M.p. 79.0 – 80.1°. R_f (toluene/AcOEt 19:1) 0.60. GC: t_R 28.4 min. IR (CCl$_4$): 3022, 2959, 2933, 2874, 2762, 1713 (CO), 1561, 1546, 1479, 1467, 1438, 1419, 1380, 1360, 1310, 1241, 1101, 1023, 954. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.89 (m, Me(6′)); 1.20 – 1.42 (CH$_2$(3′), CH$_2$(4′), CH$_3$(5′)); 1.69 (*quint.*, $^3J = 7.0$, CH$_2$(2′)); 3.96 (s, MeO); 4.20 (t, $^3J = 6.5$, CH$_2$(1′)); 8.32 (s, H–C(4)); 10.15 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.4 (q, Me(6′)); 22.5 (t, C(5′)); 25.5 (t, C(4′)); 29.7 (t, C(3′)); 31.4 (t, C(2′)); 58.6 (q, MeO); 80.1 (t, C(1′)); 116.4 (d, C(4)); 122.9 (s, C(1)); 139.1, 146.1, 146.8, 147.4 (4s, C(2), C(3), C(5), C(6)); 186.0 (d, CHO). EI-MS: 326 (9, M^+), 242 (18, [$M - C_6H_{12}$]$^+$), 224 (60), 194 (14), 84 (100, C$_6$H$_{12}^+$), 43 (92, C$_3$H$_7^+$). HR-MS: 326.1114 (M^+, C$_{14}$H$_{18}$N$_2$O$_7^+$; calc. 326.1114).

From polar fractions, a sample was recrystallized from cyclohexane: **9e**. Pale yellow solid. M.p. 76.2 – 77.9°. R_f (toluene/AcOEt 19:1) 0.40. GC: t_R 26.8. IR (KBr): 3016, 2958, 2935, 2862, 1542, 1494, 1361, 1282, 1060, 813. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.86 (m, Me(6′)), 1.10 – 1.50 (CH$_2$(3′), CH$_2$(4′), CH$_2$(5′)); 1.66 (m, CH$_2$(2′)); 3.95 (s, MeO); 4.18 (t, $^3J = 6.5$, CH$_2$(1′)), 7.63, 7.69 (2d,$^3J = 9.6$, H–C(5), H–C(6)). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.2 (q, Me(6′)); 22.5 (t, C(5′)); 25.3 (t, C(4′)); 28.8 (t, C(3′)); 31.3 (t, C(2′)); 58.3 (q, MeO); 71.1 (t, C(1′)); 119.4, 120.5 (2d, C(5), C(6)); 133.3, 133.7 (2s, C(2), C(3)); 144.7, 145.4 (2s, C(1), C(4)). EI-MS: 298 (8, M^+), 214 (100, [$M - C_6H_{12}$]$^+$), 197 (12), 179 (6), 149 (7). HR-MS: 298.1165 (M^+, C$_{13}$H$_{18}$N$_2$O$_6^+$; calc. 298.1165).

2-(Heptyloxy)-5-methoxy-3,6-dinitrobenzaldehyde (**5f**) and *1-(Heptyloxy)-4-methoxy-2,3-dinitrobenzene* (**9f**). According to *GP B*, with **6f** (29.1 g, 85.9 mmol) and 65% HNO$_3$ soln. (230 ml) ($T \leq 48°$): 12.3 g of **5f** (impure, < 41%). A sample was recrystallized from cyclohexane/toluene 19:1). Pale yellow solid. M.p. 74.0 – 75.9°. R_f (toluene/AcOEt 19:1) 0.64. GC: t_R 30.4. IR (CCl$_4$): 3025, 2950, 2931, 2874, 2760, 1712 (CO), 1545, 1539, 1479, 1467, 1438, 1419, 1380, 1363, 1310, 1277, 1241, 1101, 1023, 954. ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 0.86 (m, Me(7′)); 1.20 – 1.42 (CH$_2$(3′), CH$_2$(4′), CH$_2$(5′), CH$_2$(6′)); 1.73 (*quint.*, $^3J = 6.8$, CH$_2$(2′)); 3.96 (s, MeO); 4.13 (t, $^3J = 6.5$, CH$_2$(1′)); 8.30 (s, H–C(4)); 10.14 (s, CHO). ^{13}C-NMR (67.9 MHz, (D$_6$)DMSO): 14.4 (q, Me(7′)); 22.6 (t, C(6′)); 25.5 (t, C(5′)); 28.9 (t, C(4′)); 29.7 (t, C(3′)); 31.7 (t, C(2′)); 58.6 (q, MeO); 80.1 (t, C(1′)); 116.4 (d, C(4)); 123.0 (s, C(1)); 139.4, 146.1, 146.8, 147.4 (4s, C(2), C(3), C(5), C(6)); 186.0 (d, CHO). EI-MS: 340 (2, M^+), 242 (5, [$M - C_7H_{14}$]$^+$), 224 (10), 194 (5), 98 (62, C$_7$H$_{14}^+$), 57 (100, C$_4$H$_9^+$). HR-MS: 340.1270 (M^+, C$_{15}$H$_{20}$N$_2$O$_7^+$; calc. 340.1269).

From the polar fractions, **9f** was isolated. Yellow solid. R_f (toluene/AcOEt 19:1) 0.50.

Crystal-Structure Determination of **5f**[8]). A crystal of **5f** was selected and mounted onto a needle, and a rotational photo was taken to check the crystal quality prior to the data collection. From the photo, 13 reflections were chosen to determine a reasonable cell to start with. Then the reduced cell was determined with the automatic routine of the *Bruker* xscans software. The data collection was done on a *Bruker-P4*-four-circle diffractometer with graphite monochromator in routine ω-scan. The structure was solved by direct methods (*Bruker* SHELXTL) and refined by the full-matrix least-squares methods of SHELXL-97 [38]. All non-H-atoms were refined anisotropically while the H-atoms were put into theoretical positions and refined according to the riding model. The nitro groups in the 3- and 6-positions are tilted against the aromatic ring at angles of 39.35 and 87.40°, resp. Data in the *Table*.

Table. *Crystallographic Data of* **5f**

Crystallized from	EtOH
Empirical formula	$C_{15}H_{20}N_2O_7$
M_r	340.33
Crystal color, habit	pale yellow, plate
Crystal dimensions [mm]	$0.66 \times 0.52 \times 0.12$
Temp. [K]	293
Crystal system	monoclinic
Space group	$P2_1/n$
Z	4
Unit cell dimensions:	
a [Å]	8.886 (1)
b [Å]	7.467 (1)
c [Å]	26.202 (4)
β [°]	93.71 (1)
V [Å³]	1734.9 (4)
D_x [Mg m⁻³]	1.303
$\mu(MoK_\alpha)$ [mm⁻¹]	0.104
Scan type	ω-scan
Θ range	2.38 – 22.49
Total reflections measured	3285
Symmetry-independent reflections	2269
Reflections used [$I > 2\sigma(I)$]	1315
Parameters refined	217
R_1	0.497 (obs.), 0.959 (all)
wR_2	0.1175 (obs.), 0.1426 (all)
Goodness-of-fit	1.022
Δ/ρ (max; min) [e Å⁻³]	0.139; 0.150

3-Methoxy-2-nitro-6-(nonyloxy)benzaldehyde (**8g**). According to *GP B*, with **6g** (13.9 g, 50.0 mmol) and 65% HNO_3 soln. (130 ml) ($T \leq 45°$): 8.83 g of **8g** (impure, < 49%). For analysis, a sample was recrystallized from cyclohexane. Pale yellow solid. M.p. 81.0 – 82.1°. R_f (toluene/AcOEt 19:1) 0.45. GC: t_R 32.8. IR (CCl₄): 3018, 2957, 2928, 2856, 2745, 1703 (CO), 1553, 1490, 1469, 1440, 1368, 1287, 1270, 1310, 1188 1092, 954. ¹H-NMR (270 MHz, (D₆)DMSO): 0.83 (t, ³J = 6.5, Me(9′)); 1.15 – 1.50 (12 H, CH₂(3′) to CH₂(8′)); 1.74 (*quint.*, ³J = 6.5, CH₂(2′)); 3.84 (*s*, MeO); 4.13 (t, ³J = 6.5, CH₂(1′)); 7.44, 7.65 (2d, ³J = 9.2, H–C(4), H–C(5)); 10.26 (*s*, CHO). ¹³C-NMR (67.9 MHz, (D₆)DMSO): 14.5 (q, Me(9′)); 22.6 (t, C(8′)); 25.90 (t, C(7′)); 28.93 (t, C(6′)); 29.18 (t, C(5′)); 29.25 (t, C(4′)); 29.45 (t, C(3′)); 31.8 (t, C(2′)); 57.8 (q, MeO); 70.4 (t, C(1′)); 115.7 (*s*, C(1)); 117.6, 122.3

---

8) Crystallographic data for structure **5f** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-189589. Copies of the data can be obtained, free of charge, *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

(2*d*, C(4), C(5)), 137.7, 144.2, 155.2 (3*s*, C(2), C(3), C(6)); 187.2 (*d*, CHO). EI-MS: 323 (62, *M*⁺), 197 (100, [*M* − C₉H₁₈]⁺), 179 (78), 149 (60), 121 (76). HR-MS: 323.1733 (*M*⁺, C₁₇H₂₅NO₅⁺; calc. 323.1733).

4,4′-Diethoxy-7,7′-dimethoxy-5,5′-dinitroindigotin (= *4-Ethoxy-2-(4-ethoxy-1,3-dihydro-7-methoxy-5-nitro-3-oxo-2*H-*indol-2-ylidene)-1,2-dihydro-7-methoxy-5-nitro-3*H-*indol-3-one*; **2a**). According to *GP C*, with impure **5a** (8.25 g, < 30.5 mmol; from 104 mmol of **6a**), acetone (165 ml) and KOH (16 ml of 0.2ᴍ; 120 ml of 0.4ᴍ): 1.85 g (7% rel. to **6a**) of **2a**. Dark blue solid. Dec.p. (241°) 335°(DSC). R_f (cylohexane/AcOEt 4 : 1) 0.18. UV/VIS (CHCl₃): 622 (19212), 368 (8484), 300 (16277). IR (KBr): 3417 (NH), 2984, 1624 (CO), 1588, 1535, 1490, 1474, 1449, 1414, 1340, 1274, 1201, 1154, 1112, 1079, 1156, 1004. ¹H-NMR (270 MHz, CDCl₃): 1.05 (*t*, ³*J* = 7.0, 2 *Me*CH₂O); 3.97 (*s*, 2 MeO); 4.38 (*t*, ³*J* = 7.0, 2 MeC*H*₂O); 7.59 (*s*, 2 arom. H); 9.30 (2 NH). EI-MS: 501 (18, *M*⁺), 500 (100, *M*⁺), 456 (30), 439 (32), 411 (38), 395 (90). HR-MS: 500.1179 (*M*⁺, C₂₂H₂₀N₄O₁₀; calc. 500.1179).

7,7′-Dimethoxy-5,5′-dinitro-4,4′-dipropoxyindigotin (= *2-(1,3-Dihydro-7-methoxy-5-nitro-4-propoxy-3-oxo-2*H-*indol-2-ylidene)-1,2-dihydro-7-methoxy-5-nitro-4-propoxy-3*H-*indol-3-one*; **2b**). According to *GP C*, with impure **5b** (11.2 g, < 39.4 mmol; from 103 mmol of **6b**), acetone (170 ml) and KOH (20 ml of 0.2ᴍ; 170 ml of 0.4ᴍ): 2.97 g (11% rel. to **6b**) of **2b**. Dec.p. (199°) 296° (DSC). R_f (cylohexane/AcOEt 4 : 1) 0.26. UV/VIS (CHCl₃): 622 (21090), 372 (12479), 298 (18073). IR (KBr): 3433 (NH), 2963, 2938, 2878, 2839, 1615 (CO), 1588, 1532, 1501, 1406, 1260, 1250, 1206, 1077, 1057, 976, 915. ¹H-NMR (270 MHz, CDCl₃): 1.06 (*t*, ³*J* = 7.3, 2 *Me*CH₂CH₂O); 1.60 (*m*, 2 MeC*H*₂CH₂); 4.00 (*s*, 2 MeO); 4.30 (*t*, ³*J* = 6.6, 2 MeCH₂C*H*₂O); 7.60 (*s*, 2 arom. H); 9.31 (2 NH). EI-MS: 529 (20, *M*⁺), 528 (100, *M*⁺), 483 (12), 470 (42), 444 (32), 428 (35), 411 (55), 395 (30). HR-MS: 528.1492 (*M*⁺, C₂₄H₂₄N₄O₁₀⁺; calc. 528.1492); 483.1642 (C₂₄H₂₅N₃O₈⁺; calc. 483.1642); 470.1074 (C₂₁H₁₈N₄O₉⁺; calc. 470.1074); 444.0553 (C₁₈H₁₂N₄O₁₀⁺; calc. 444.0553); 428.0604 (C₁₈H₁₂N₄O₉⁺; calc. 428.0604); 411.0577 (C₁₈H₁₁N₄O₈⁺; calc. 411.0577); 395.0627 (C₁₈H₁₁N₄O₇⁺; calc. 395.0627).

Monoanion of **2b** (monomer). ¹H-NMR (270 MHz, sat. soln. in (D₆)DMSO): 0.95 – 1.00 (2 *Me*CH₂CH₂O); 1.65 – 1.85 (2 MeC*H*₂CH₂O); 3.82, 3.98 (2*s*, 2 MeO); 4.14, 4.32 (2*t*, ³*J* = 6.5, 2 MeCH₂C*H*₂O); 7.24, 7.52 (2*s*, 2 arom. H); 10.15 (1 NH).

Monoanion of **2b** (dimer). UV/VIS (DMF)⁹): 784 (21335), 506 (16049), 350 (14210). UV/VIS (DMSO)⁹): 786 (21877), 512 (16809), 350 (16327).

Dianion of **2b**. UV/VIS (DMF/2ᴍ KOH): 808 (38554), 742 (sh, 19157), 560 (14824), 414 (15877), 390 (15234).

4,4′-Dibutoxy-7,7′-dimethoxy-5,5′-dinitroindigotin (= *4-Butoxy-2-(4-butoxy-1,3-dihydro-7-methoxy-5-nitro-3-oxo-2*H-*indol-2-ylidene)-1,2-dihydro-7-methoxy-5-nitro-3*H-*indol-3-one*; **2c**). According to *GP C*, with impure **5c** (10.4 g, < 34.9 mmol; from 91.8 mmol of **6c**), acetone (150 ml) and KOH (20 ml of 0.2ᴍ; 160 ml of 0.4ᴍ): 3.73 g (15% rel. to **6c**) of **2c**. Dark blue solid. Dec.p. (243°) 300°(DSC). R_f (cylohexane/AcOEt 4 : 1) 0.32. UV/VIS (CHCl₃): 622 (22631), 370 (9568), 298 (18474). IR (KBr): 3409 (NH), 2959, 2918, 2870, 1627 (CO), 1585, 1527, 1506, 1465, 1443, 1386,1318, 1258, 1239, 1204, 1171, 1143, 1070, 1050, 1003, 904. ¹H-NMR (270 MHz, CDCl₃): 1.01 (*t*, ³*J* = 7.3, 2 Me(4′)); 1.50 (*m*, 2 CH₂(3′)); 1.86 (*quint.*, ³*J* = 7.3, 2 CH₂(2′)); 3.97 (*s*, 2 MeO), 4.33 (*t*, ³*J* = 6.5, 2 CH₂(1′)); 7.59 (*s*, 2 arom. H); 9.30 (2 NH). EI-MS: 557 (26, *M*⁺), 556 (100, *M*⁺), 511 (16), 484 (26), 467 (55), 444 (52), 428 (34), 411 (48), 395 (29). HR-MS: 556.1805 (*M*⁺, C₂₆H₂₈N₄O₁₀⁺; calc. 556.1805).

Monoanion of **2c** (monomer). UV/VIS (≤10⁻⁶ ᴍ in DMSO): 710. ¹H-NMR (270 MHz, ≤10⁻⁶ ᴍ in (D₆)DMSO): 0.92 – 0.96 (2 Me(4′)); 1.40 – 1.45 (2 CH₂(3′)); 1.71 – 1.76 (2 CH₂(2′)); 3.81, 3.98 (2*s*, 2 MeO); 4.17, 4.29 (2*m*, 2 CH₂(1′)); 7.24, 7.52 (2*s*, 2 arom. H); 10.23 (1 NH).

Monoanion of **2c** (dimer). UV/VIS (DMF)⁹): 784 (20663), 506 (15936), 350 (15155). ¹H-NMR (270 MHz, (D₆)DMSO): 2 × [0.91 (*t*, ³*J* = 7.5, 2 Me(4′)); 1.43 (sext., ³*J* = 7.5, 2 CH₂(3′)); 1.72 (*quint.*, ³*J* = 7.5, 2 CH₂(2′)); 3.89 (*s*, 2 MeO); 4.22 (*t*, ³*J* = 6.5, 2 CH₂(1′)); 7.37 (*s*, 2 arom. H); 10.0 (1 NH)].

Dianion of **2c**. UV/VIS (DMF/2ᴍ KOH): 808 (43016), 742 (sh, 21592), 562 (16360), 416 (17127), 392 (17001). ¹H-NMR (270 MHz, (D₆)DMSO/KOD/D₂O): 0.91 (*t*, ³*J* = 7.5, 2 Me(4′)); 1.43 (sext., ³*J* = 7.3, 2 CH₂(3′)); 1.71 (*quint.*, ³*J* = 7.3, 2 CH₂(2′)); 3.80 (*s*, 2 MeO); 4.16 (*t*, ³*J* = 6.5, 2 CH₂(1′)); 7.07 (*s*, 2 arom. H).

7,7′-Dimethoxy-5,5′-dinitro-4,4′-bis(pentyloxy)indigotin (= *2-[1,3-Dihydro-7-methoxy-5-nitro-3-oxo-4-(pentyloxy)-2*H-*indol-2-ylidene]-1,2-dihydro-methoxy-5-nitro-4-(pentyloxy)-3*H-*indol-3-one*; **2d**). According to *GP C*, with impure **5d** (11.0 g, < 35.2 mmol; from 73.4 mmol of **6d**), acetone (150 ml) and KOH (22 ml of 0.2ᴍ; 15 ml of 0.4ᴍ): 2.72 g (13% rel. to **6d**) of **2d**. Dark blue solid. Dec.p. (175°) 297° (DSC). R_f (cylohexane/AcOEt 4 : 1) 0.36. UV/VIS (CHCl₃): 622 (21208), 370 (11483), 298 (19578). IR (KBr): 3408 (NH), 2954, 2950, 2870, 1627 (CO), 1584, 1532, 1505, 1406, 1320, 1261, 1240, 1169, 1143, 1070, 1052, 1004, 905. ¹H-NMR (270 MHz,

---

⁹)   Concentration calculated to **2**.

CDCl$_3$): 0.93 (*t*, $^3J = 7.3$, 2 Me(5′)); 1.25 – 1.55 (2 CH$_2$(3′), 2 CH$_2$(4′)); 1.89 (*quint.*, $^3J = 7.3$, 2 CH$_2$(2′)); 3.97 (*s*, 2 MeO), 4.33 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)), 7.56 (*s*, 2 arom. H); 9.27 (2 NH). EI-MS: 585 (23, M^+), 584 (100, M^+), 498 (92), 444 (72), 428 (74), 411 (63), 395 (22). HR-MS: 584.2118 (M^+, C$_{28}$H$_{32}$N$_4$O$_{10}^+$; calc. 584.2118).

Monoanion of **2d** (dimer). UV/VIS (DMF)^9): 784 (20921), 506 (16195), 350 (15576). ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 2 × [0.90 (*t*, $^3J = 7.5$, 2 Me(5′)); 1.20 – 1.50 (2 CH$_2$(3′), 2 CH$_2$(4′)); 1.72 (*quint.*, $^3J = 7.3$, 2 CH$_2$(2′)); 3.90 (*s*, 2 MeO); 4.22 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.38 (*s*, 2 arom. H); 10.18 (1 NH)].

Dianion of **2d**. UV/VIS (DMF/2M KOH): 808 (41015), 742 (sh, 20531), 562 (15840), 410 (17850), 390 (18253). ^{1}H-NMR (270 MHz, (D$_6$)DMSO/KOD/D$_2$O): 0.87 (*t*, $^3J = 7.5$, 2 Me(5′)); 1.25 – 1.45 (2 CH$_2$(3′), 2 CH$_2$(4′)); 1.71 (*quint.*, $^3J = 7.2$, 2 CH$_2$(2′)); 3.78 (*s*, 2 MeO); 4.14 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.06 (*s*, 2 arom. H).

4,4′-Bis(hexyloxy)-7,7′-dimethoxy-5,5′-dinitroindigotin (=*4-(Hexyloxy)-2-[4-(hexyloxy)-1,4-dihydro-7-methoxy-5-nitro-3-oxo-2H-indol-2-ylidene]-1,2-dihydro-7-methoxy-5-nitro-3H-indol-3-one*; **2e**). According to *GP C*, with impure **5e** (116.6 g, < 35.6 mmol; from 91.1 mmol of **6e**); acetone (165 ml) and KOH (32 ml of 0.2M; 160 ml of 0.4M): 4.22 g (15% rel. to **6e**) of **2e**. Dark blue solid. Dec.p. (195°) 301°(DSC). R_f (cylohexane/AcOEt 4 : 1) 0.39. UV/VIS (CHCl$_3$): 622 (22948), 368 (10878), 298 (19919). IR (KBr): 3408 (NH), 2928, 2932, 2857, 1628 (CO), 1585, 1528, 1505, 1466, 1443, 1385, 1317, 1260, 1240, 1207, 1170, 1142, 1070, 1051, 1003, 976, 904. ^{1}H-NMR (270 MHz, CDCl$_3$): 0.89 (*t*, $^3J = 7.3$, 2 MeO(6′)); 1.25 – 1.55 (2 CH$_2$(3′), 2 CH$_2$(4′, 2 CH$_2$(5′)); 1.90 (*quint.*, $^3J = 7.3$, 2 CH$_2$(2′)); 3.96 (*s*, 2 MeO); 4.33 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.59 (*s*, 2 arom. H); 9.28 (2 NH). EI-MS: 613 (20, M^+), 612 (100, M^+), 567 (96), 512 (82), 467 (55), 444 (85), 428 (55), 411 (50), 395 (22). HR-MS: 612.2433 (M^+, C$_{30}$H$_{36}$N$_4$O$_{10}^+$; calc. 612.2432).

Monoanion of **2e** (dimer). UV/VIS (DMF)^9): 784 (21219), 506 (16099), 350 (14986). ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 2 × [0.88 (*t*, $^3J = 7.3$, 2 Me(6′)); 1.25 – 1.55 (2 CH$_2$(3′), 2 CH$_2$(4′), 2 CH$_2$(5′)); 1.73 (*quint.*, $^3J = 7.3$, 2 CH$_2$(2′)); 3.98 (*s*, 2 MeO), 4.22 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.38 (*s*, 2 arom. H); 10.20 (1 NH)].

Dianion of **2e**. UV/VIS (DMF/2M KOH): 808 (40549), 742 (sh, 20245), 560 (15413), 412 (17025), 392 (17294). ^{1}H-NMR (270 MHz, (D$_6$)DMSO/KOD/D$_2$O): 0.86 (*t*, $^3J = 7.5$, 2 Me(6′)); 1.20 – 1.50 (2 CH$_2$(3′), 2 CH$_2$(4′), 2 CH$_2$(5′)); 1.71 (*quint.*, $^3J = 7.3$, 2 CH$_2$(2′)); 3.79 (*s*, 2 MeO); 4.15 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.07 (*s*, 2 arom. H).

4,4′-Bis(heptyloxy)-7,7′-dimethoxy-5,5′-dinitroindigotin (=*4-(Heptyloxy)-2-[4-heptyloxy-1,3-dihydro-7-methoxy-5-nitro-3-oxo-2H-indol-2-ylidene]-1,2-dihydro-7-methoxy-5-nitroindol-3-one*; **2f**). According to *GP C*, reaction of impure **5f** (12.1 g, < 35.5 mmol; from 85.9 mmol of **6f**), acetone (150 ml) and KOH (26 ml of 0.2M; 150 ml of 0.4M): 3.71 g (14% rel. to **6f**) of **2f**. Dark blue solid. Dec.p. (191°) 305°(DSC). R_f (cylohexane/AcOEt 4 : 1) 0.44. UV/VIS (CHCl$_3$): 622 (22579), 372 (11478), 298 (19714). IR (KBr): 3382 (NH), 2950, 2927, 2855, 1616 (CO), 1583, 1534, 1506, 1458, 1443, 1394, 1317, 1268, 1241, 1207, 1175, 1143, 1066, 1050, 901. ^{1}H-NMR (270 MHz, CDCl$_3$): 0.89 (*t*, $^3J = 7.3$, 2 Me(7′)); 1.25 – 1.55 (16 H, 2 CH$_2$(3′) to 2 CH$_2$(6′)); 1.89 (*quint.*, $^3J = 7.5$, 2 CH$_2$(2′)); 3.94 (*s*, 2 MeO); 4.33 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.59 (*s*, 2 arom. H); 9.29 (2 NH). EI-MS: 641 (18, M^+), 640 (48, M^+), 595 (38), 526 (45), 435 (63), 444 (40), 428 (38), 411 (30), 395 (20). HR-MS: 640.2744 (M^+, C$_{32}$H$_{40}$N$_4$O$_{10}^+$; calc. 640.2744).

Monoanion of **2f** (dimer). UV/VIS (DMF)^9): 782 (21179), 502 (15110), 350 (14830). ^{1}H-NMR (270 MHz, (D$_6$)DMSO): 2 × [0.87 (*t*, $^3J = 7.3$, 2 Me(7′)); 1.20 – 1.50 (16 H, 2 CH$_2$(3′) to 2 CH$_2$(6′)); 1.73 (*quint.*, $^3J = 7.5$, 2 CH$_2$(2′)); 3.91 (*s*, 2 MeO); 4.21 (*t*, $^3J = 6.5$, 2 CH$_2$(1′)); 7.40 (*s*, 2 arom. H); 10.17 (1 NH)].

Dianion of **2f**. UV/VIS (DMF/2M KOH): 808 (35226), 742 (sh, 17654), 558 (14163), 414 (17464), 392 (17355). ^{1}H-NMR (270 MHz, (D$_6$)DMSO/KOD/D$_2$O): 0.84 (*t*, $^3J = 7.5$, 2 Me(7′)); 1.15 – 1.45 (16 H, 2 CH$_2$(3′) to 2 CH$_2$(6′)); 1.73 (*quint.*, $^3J = 7.2$, 2 CH$_2$(2′)); 3.78 (*s*, 2 MeO); 4.15 (*t*, $^3J = 6.1$, 2 CH$_2$(1′)); 7.05 (*s*, 2 arom. H).

7,7′-Dimethoxy-4,4-bis(nonyloxy)indigotin (=*2-1,3-Dihydro[7-methoxy-4-nonyloxy-3-oxo-2H-indol-2-ylidene]-1,2-dihydro-7-methoxy-4-(nonyloxy)-3H-indol-3-one*; **3g**). According to *GP C*, with impure **8g** (8.81 g, < 24.8 mmol; from 50.0 mmol of **6g**), acetone (115 ml) and KOH (11 ml of 0.2M; 120 ml of 0.4M): 3.56 g (24% rel. to **6g**) of **3g**. A sample was recrystallized from CHCl$_3$. Dark blue solid with an intensive coppery luster. R_f (cylohexane/AcOEt 4 : 1) 0.32. M.p. (127°) 246° (DSC). Solubility: 42 mg/ml of CHCl$_3$. UV/VIS (CHCl$_3$): 645 (23560), 396 (2900), 318 (9903), 292 (16220). IR (KBr): 3420 (NH), 3008, 2922, 2851, 1642 (CO), 1627, 1597, 1514, 1471, 1455, 1403, 1343, 1293, 1270, 1242, 1204, 1148, 1102, 1074, 1042, 934. ^{1}H-NMR (270 MHz, CDCl$_3$): 0.86 (*t*, $^3J = 6.8$, 2 Me(9′)); 1.20 – 1.35 (10 H, 2 CH$_2$(4′) to 2 CH$_2$(8′)); 1.52 (*m*, 2 CH$_2$(3′)); 1.87 (*quint.*, $^3J = 6.8$, 2 CH$_2$(2′)); 3.85 (*s*, 2 MeO); 4.05 (*t*, $^3J = 6.7$, 2 CH$_2$(1′)); 6.24, 6.86 (2*d*, $^3J = 8.1$, 4 arom. H); 8.98 (2 NH). ^{1}H-NMR (500 MHz, CDCl$_3$): 8.98 (*d*, ^1J (N,H) = 102.0 ± 0.5, NH). ^{13}C-NMR (67.9 MHz, CDCl$_3$): 14.1 (*q*, Me(9′)); 22.7 (*t*, C(8′)), 25.9, 25.1, 29.3, 29.4, 29.5 (5*t*, C(3′), C(4′), C(5′), C(6′), C(7′)); 31.9 (*t*, C(2′)); 56.3 (*q*, 2 MeO); 68.9 (*t*, C(1′)); 102.5 (*s*, arom. C(5,5′)); 110.1 (*s*, arom. C(3a,3′a)); 118.3 (*d*, arom. C(6,6′)); 121.6 (*s*, arom. C(2,2′)); 139.6, 142.9 (2*s*, arom. C(7,7′), arom. C(7a,7a′)); 152.2 (*s*, arom. C(4,4′)); 186.2 (*s*, arom. C(3,3′)). ^{15}N-NMR (50.7 MHz,

CDCl$_3$): – 210. EI-MS: 607 (12, M^+), 606 (100, M^+), 480 (12), 479 (20). HR-MS: 606.3667 (M^+, C$_{36}$H$_{50}$N$_2$O$_6^+$; calc. 606.3668).

7,7′-Dimethoxy-5,5′-dinitro-1-pentyl-4,4′-bis(pentyloxy)indigotin (= *2-[1,3-Didydro-7-methoxy-5-nitro-3-oxo-4-(pentyloxy)-2*H-*indol-2-ylidene]-1,2-dihydro-7-methoxy-5-nitro-1-pentyl-4-(pentyloxy)-3*H-*indol-3-one*; **4d**). According to *GP E* with **2d**: **4d** containing **2d**. Dark-colored solid. R_f (cylohexane/AcOEt 4 : 1) 0.50. EI-MS: 655 (40, M^+), 654 (100, M^+). HR-MS: 654.2901 (M^+, C$_{33}$H$_{42}$N$_4$O$_{10}^+$; calc. 654.2901).

4,4′-Bis(hexyloxy)-7,7′-dimethoxy-5,5′-dinitro-1-pentylindigotin (= *4-(Hexyloxy)-2-[4-(hexyloxy)-1,3-dihydro-7-methoxy-5-nitro-3-oxo-2*H-*indol-2-ylidene]-1,2-dihydro-7-methoxy-5-nitro-1-pentyl-3*H-*indol-3-one*; **4e**). According to *GP E* with **2e**: **4e** containing **2e**. Dark-colored solid. R_f (cylohexane/AcOEt 4 : 1) 0.53. EI-MS: 683 (40, M^+), 682 (100, M^+). HR-MS: 682.3214 (M^+, C$_{35}$H$_{46}$N$_4$O$_{10}^+$; calc. 682.3214).

4,4′-Bis(heptyloxy)-7,7′-dimethoxy-5,5′-dinitro-1-pentylindigotin (= *4-(Heptyloxy)-2-[4-(heptyloxy)-1,3-dihydro-7-methoxy-5-nitro-3-oxo-2*H-*indol-2-ylidene]-1,2-dihydro-7-methoxy-5-nitro-1-pentyl-3*H-*indol-3-one*; **4f**). According to *GP E* with **2f**: **4f** containing **2f**. Dark-colored solid. R_f (cylohexane/AcOEt 4 : 1) 0.57. UV/VIS (CHCl$_3$): 635, 370, 295. IR (CHCl$_3$): 3402 (NH), 2931, 2858, 1651 (CO), 1586, 1531, 1412, 1330, 1272, 1076, 1053. ^{1}H-NMR (270 MHz, CDCl$_3$): 0.78 – 0.92 (2 Me(7′), *Me*(CH$_2$)$_4$N); 1.20 – 1.60 (2 CH$_2$(3′), 2 CH$_2$(4′), 2 CH$_2$(5′), 2 CH$_2$(6′), Me*CH$_2$CH$_2$*(CH$_2$)$_2$N); 1.85 – 1.95 (2 CH$_2$(2′), Me(CH$_2$)$_2$*CH$_2$*CH$_2$N); 3.97, 3.98 (2*s*, 2 MeO); 4.23, 4.26 (2*t*, ^3J = 7.0, 2 CH$_2$(1′)), 4.73 (*t*, ^3J = 7.5, Me(CH$_2$)$_3$*CH$_2$*N); 7.58, 7.60 (2*s*, 2 arom. H); 11.08 (1 NH). EI-MS: among others 711 (34, M^+), 710 (100, M^+). HR-MS: 710.3527 (M^+, C$_{37}$H$_{50}$N$_4$O$_{10}^+$; calc. 710.3527).

5,5′-Diamino-4,4′-diethoxy-7,7′-dimethoxyindigotin (= *5-Amino-2-(5-amino-4-ethoxy-1,3-dihydro-7-methoxy-3-oxo-2*H-*indol-2-ylidene)-4-ethoxy-1,2-dihydro-7-methoxy-3*H-*indol-3-one*; **1a**). According to *GP D*, with **2a** (1.21 g, 2.42 mmol), Na$_2$S$_2$O$_4$ (5.5 g, 27 mmol), and 1M NaOH (100 ml)): 0.12 g (11%) of **1a**. A sample was recrystallized from CHCl$_3$. Dark blue solid. M.p. 257° (dec., DSC). R_f (cylohexane/AcOEt 1 : 1) 0.14. Solubility: 28 mg/ml of CHCl$_3$. UV/VIS (CHCl$_3$): 732 (13580), 375 (sh, 8090), 330 (21670). IR (CHCl$_3$): 3416 (NH, NH$_2$), 2986, 2938, 2846, 1619 (CO), 1467, 1398, 1344, 1270, 1120, 1055, 933. ^{1}H-NMR (360 MHz, CDCl$_3$): 1.42 (*t*, ^3J = 8.1, 2 *Me*CH$_2$O); 3.6 (2 NH$_2$); 3.83 (*s*, 2 MeO); 4.29 (*q*, ^3J = 7.0, 2 Me*CH$_2$*O); 6.51 (*s*, 2 arom. H); 8.7 (2 NH). ^{13}C-NMR (90.5 MHz, CDCl$_3$): 15.8 (*q*, *Me*CH$_2$O); 56.0 (*q*, MeO), 76.7 (*t*, Me*CH$_2$*O); 107.2 (*d*, arom. C(6,6′)); 113.5 (*s*, arom. C(3a,3′a)); 122.1 (*s*, arom. C(2,2′)); 132.8 (*s*, arom. C(5,5′)); 135.1 (*s*, arom. C(7a,7′a)); 136.7 (*s*, arom. C(4,4′)); 141.4 (*s*, arom. C(7,7′)); 186.2 (*s*, arom. C(3,3′)). EI-MS: 441 (21, M^+), 440 (100, M^+) 425 (10), 412 (15), 411 (92), 383 (12), 382 (10), 368 (10), 367 (15), 192 (10), 191 (8). HR-MS: 440.1696 (M^+, C$_{22}$H$_{24}$N$_4$O$_6^+$; calc. 440.1696).

5,5′-Diamino-7,7′-dimethoxy-4,4′-dipropoxyindigotin (= *5-Amino-2-(5-amino-1,3-dihydro-7-methoxy-4-propoxy-3-oxo-2*H-*indol-2-ylidene)-1,2-dihydro-7-methoxy-4-propoxyindol-3-one;* **1b**). According to *GP D*, with **2b** (2.10 g, 4.0 mmol), Na$_2$S$_2$O$_4$ (8.6 g, 42 mmol), and 1M NaOH (160 ml): 1.66 g (88%) of **1b**. A sample was recrystallized from CHCl$_3$. Dark blue fine crystals. M.p. (63°) 268° (dec., DSC). R_f (cyclohexane/AcOEt 1 : 1) 0.26. Solubility: 32 mg/ml of CHCl$_3$. UV/VIS (CHCl$_3$): 735 (11570), 375 (sh, 8640), 330 (20220). IR (CCl$_4$): 3458, 3421, 3375 (NH, NH$_2$), 2967, 2926, 2880, 2854, 1622 (CO), 1508, 1447, 1399, 1340, 1264, 1200, 1120, 930. ^{1}H-NMR (360 MHz, CDCl$_3$): 1.06 (*t*, ^3J = 7.5, 2 *Me*CH$_2$CH$_2$O); 1.83 (*m*, 2 MeC*H$_2$*CH$_2$O); 3.2 (4 H, (2 NH$_2$)); 3.83 (*s*, 2 MeO); 4.18 (*t*, ^3J = 7.0, 2 CH(1′)); 6.49 (*s*, 2 arom. H); 8.76 (2 NH). ^{13}C-NMR (90.5 MHz, CDCl$_3$): 10.5 (*q*, *Me*CH$_2$CH$_2$); 23.5 (*t*, Me*CH$_2$*CH$_2$O); 55.9 (*q*, MeO); 75.9 (*t*, MeCH$_2$*CH$_2$*); 107.1 (*d*, arom. C(6,6′)); 113.0 (*s*, arom. C(3a,3′a)); 122.1 (*s*, arom. C(2,2′)); 132.6 (*s*, arom C(5,5′)); 135.0 (*s*, arom. C(7a,7′a)); 136.9 (*s*, arom. C(4,4′)); 141.3 (*s*, arom. C(7,7′)); 186.1 (*s*, arom. C(3,3′)). EI-MS: 469 (20, M^+), 468 (100, M^+), 425 (85, [M – C$_3$H$_7$]$^+$), 383 (48), 368 (18), 353 (16), 192 (22). HR-MS: 468.2009 (M^+, C$_{24}$H$_{28}$N$_4$O$_6^+$; calc. 468.2009); 425.1461 (C$_{24}$H$_{21}$N$_4$O$_6^+$; calc. 425.1461); 383.0992 (C$_{18}$H$_{15}$N$_4$O$_6^+$; calc. 383.0992); 368.0757 (C$_{17}$H$_{12}$N$_4$O$_6^+$; calc. 368.0757); 353.0522 (C$_{16}$H$_9$N$_4$O$_6^+$; calc. 353.0522); 192.0535 (C$_9$H$_8$N$_2$O$_3^+$; calc. 192.0535).

5,5′-Diamino-4,4′-dibutoxy-7,7′-dimethoxyindigotin (= *5-Amino-2-(5-amino-4-butoxy-1,3-dihydro-7-methoxy-3-oxo-2*H-*indol-2-ylidene)-4-butoxy-1,2-dihydro-7-methoxy-3*H-*indol-3-one*; **1c**). According to *GP D*, with **2c** (4.80 g, 8.63 mmol), Na$_2$S$_2$O$_4$ (19.2 g, 94 mmol), and 1M NaOH (250 ml): 3.62 g (85%) of **1c**. A sample was recrystallized from CHCl$_3$. Dark blue needles. M.p. (167°) 262° (dec., DSC). R_f (cyclohexane/AcOEt 1 : 1) 0.33. Solubility: 33 mg/ml of CHCl$_3$. UV/VIS (CHCl$_3$): 735 (13480), 375 (sh, 8090), 328 (21567). IR (CCl$_4$): 3459, 3424, 3375 (NH, NH$_2$), 2960, 2932, 2874, 1622 (CO), 1510, 1447, 1398, 1341, 1272, 1200, 1120, 1057, 931. ^{1}H-NMR (360 MHz, CDCl$_3$): 0.98 (*t*, ^3J = 7.3, 2 Me(4′)); 1.52 (*m*, 2 CH$_2$(3′)); 1.79 (*m*, 2 CH$_2$(2′)); 3.5 (4 H, (2 NH$_2$)); 3.83 (*s*, 2 MeO); 4.20 (*t*, ^3J = 6.6, 2 CH$_2$(1′)); 6.50 (*s*, 2 arom. H); 8.76 (2 NH). ^{13}C-NMR (90.5 MHz, CDCl$_3$): 14.0 (*q*, Me(4′)); 19.3 (*t*, C(3′)); 32.5 (*t*, C(2′)); 56.0 (*q*, MeO); 74.3 (*t*, C(1′)); 107.2 (*d*, arom. C(6,6′)); 113.6 (*s*, arom. C(3a,3′a)); 122.1 (*s*, arom. C(2,2′)); 132.6 (*s*, arom. C(5,5′)); 135.0 (*s*, arom. C(7a,7′a)); 137.0 (*s*, arom. C(4,4′)); 141.3 (*s*, arom. C(7,7′)); 186.1 (*s*, arom. C(3,3′)). EI-MS: 497 (20, M^+), 496 (100, M^+), 439 (80, [M – C$_4$H$_9$]$^+$), 383 (55), 368 (18), 353 (14), 192 (15). HR-MS: 496.2320 (M^+, C$_{26}$H$_{32}$N$_4$O$_6^+$; calc. 496.2321).

5,5′-Diamino-7,7′-dimethoxy-4,4′-bis(pentyloxy)indigotin (= *5-Amino-2-[5-amino-1.3-dihydro-4-methoxy-3-oxo-4-(pentyloxy)-2*H-*indol-2-ylidene]-1,2-dihydro-7-methoxy-4-(pentyloxy)-3*H-*indol-3-one*; **1d**). According to *GP D* with **2d** (2.41 g, 4.1 mmol), $Na_2S_2O_4$ (8.80 g, 43 mmol), and 1M NaOH (180 ml): 1.69 g (79%) of **1d**. A sample was recrystallized from $CHCl_3$. Dark blue fine crystals. M.p. (84°) 236° (dec., DSC). R_f (cyclohexane/AcOEt 1:1) 0.40. Solubility: 97 mg/ml of $CHCl_3$. UV/VIS ($CHCl_3$): 736 (13430), 374 (sh, 8510), 330 (2075). IR (CCl_4): 3449, 3421, 3371 (NH, NH_2), 2960, 2955, 2874, 1622 (CO), 1500, 1446, 1398, 1340, 1265, 1200, 1120, 1056, 932. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.94 (*t*, $^3J = 7.1$, 2 Me(5′)); 1.3–1.5 (2 CH_2(3′), 2 CH_2(4′)); 1.81 (*m*, 2 CH_2(2′)); 3.3 (2 NH_2); 3.82 (*s*, 2 MeO); 4.20 (*t*, $^3J = 6.6$, 2 CH_2(1′)); 6.47 (*s*, 2 arom H); 8.75 (2 NH). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 14.0 (*q*, Me(5′)); 22.6 (*t*, C(4′)); 28.2, 29.9 (2*t*, C(2′), C(3′)); 55.9 (*t*, MeO); 74.5 (*t*, C(1′)); 107.2 (*d*, arom. C(6,6′)); 113.6 (*s*, arom. C(3a,3′a)); 122.0 (*s*, arom. C(2,2′)); 132.6 (*s*, arom. C(5,5′)); 134.9 (*s*, arom. C(7a,7′a)); 137.0 (*s*, arom. C(4,4′)); 141.2 (*s*, arom. C(7,7′)); 186.0 (*s*, arom. C(3,3′)). EI-MS: 525 (19, M^+), 524 (100, M^+), 453 (65, $[M – C_5H_{11}]^+$), 383 (25), 368 (12), 353 (8), 192 (15). HR-MS: 524.2634 (M^+, $C_{28}H_{36}N_4O_6^+$; calc. 524.2633).

5,5′-Diamino-4,4′-bis(hexyloxy)-7,7′-dimethoxyindigotin (= *5-Amino-2-[5-amino-4-(hexyloxy)-1,3-dihydro-7-methoxy-3-oxo-2*H-*indol-2-ylidene]-4-(hexyloxy)-1,2-dihydro-7-methoxy-3*H-*indol-3-one*; **1e**). According to *GP D* with **2e** (4.01 g, 6.5 mmol), $Na_2S_2O_4$ (14.1 g, 69 mmol), and 1M NaOH (250 ml): 3.10 g (86%) of **1e**. A sample was recrystallized from $CHCl_3$. Dark blue solid. M.p. (105°) 221° (dec., DSC). R_f (cyclohexane/AcOEt 1:1) 0.46. Solubility: 140 mg/ml of $CHCl_3$. UV/VIS ($CHCl_3$): 736 (13430), 374 (sh, 8510), 328 (20750). IR (CCl_4): 3442, 3424, 3374 (NH, NH_2), 2958, 2935, 2861, 1622 (CO), 1508, 1446, 1398, 1339, 1270, 1199, 1120, 1058, 955, 933. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.89 (*t*, $^3J = 7.0$, 2 Me(6′)); 1.2–1.5 (2 CH_2(3′), 2 CH_2(4′), 2 CH_2(5′)); 1.80 (*m*, 2 CH_2(2′)); 3.5 (2 NH_2); 3.81 (*s*, 2 MeO); 4.20 (*t*, $^3J = 6.6$, 2 CH_2(1′)); 6.47 (*s*, 2 arom. H); 8.74 (2 NH). ^{1}H-NMR (500 MHz, $CDCl_3$): 8.74 (*d*, ^1J (N,H) $= 103.0 ± 0.5$, 2 NH). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 14.0 (*q*, Me(6′)); 22.6 (*t*, C(5′)); 25.7, 30.3, 31.7 (3*t*, C(2′), C(3′), C(4′)); 55.9 (*q*, MeO)); 74.5 (*t*, C(1′)); 107.1 (*d*, arom. C(6′)); 113.3 (*s*, arom. C(3a,3′a)); 122.0 (*s*, arom. C(2,2′)); 132.6 (*s*, arom. C(5,5′)); 134.9 (*s*, arom. C(7a,7′a)); 136.9 (*s*, arom. C(4,4′)); 141.2 (*s*, arom. C(7,7′)); 186.0 (*s*, arom. C(3,3′)). EI-MS: 553 (45, M^+), 552 (100, M^+), 467 (52, $[M – C_6H_{13}]^+$), 383 (37), 368 (28), 353 (16), 192 (22). HR-MS: 552.2947 (M^+, $C_{30}H_{40}N_4O_6^+$; calc. 552.2946).

Hydrochloride of **1e**. Indigotin **1e** was dissolved in a sat. HCl soln. in MeOH. After 1 d at r.t., the solvent was evaporated: hydrochloride of **1e**. Dark blue solid. UV/VIS (MeOH, sat. soln.): 648, 310, 296. IR (KBr): 3415 (NH), 2930, 2858, 2585 (NH_3^+), 1654, 1648, 1637 (CO), 1598, 1498, 1405, 1278, 1209, 1117, 1050, 923.

5,5′-Diamino-4,4′-bis(heptyloxy)-7,7′-dimethoxyindigotin (= *5-Amino-2-[5-amino-4-(heptyloxy)-1,3-dihydro-7-methoxy-3-oxo-2*H-*indol-2-ylidene]-4-heptyloxy-1,2-dihydro-7-methoxy-3*H-*indol-3-one*; **1f**). According to *GP D* with **2f** (3.27 g, 5.1 mmol), $Na_2S_2O_4$ (11.2 g, 55 mmol) and 1M NaOH (250 ml): 2.38 g (80%) of **1f**. A sample was recrystallized from $CHCl_3$. Dark blue solid. M.p. (118°) 196° (dec., DSC). R_f (cyclohexane/AcOEt 1:1) 0.51. Solubility: 207 mg/ml of $CHCl_3$. UV/VIS ($CHCl_3$): 736 (11250), 376 (sh, 9150), 328 (1780). IR (CCl_4): 3442, 3419, 3372 (NH, NH_2), 2957, 2931, 2858, 1622 (CO), 1508, 1466, 1447, 1398, 1340, 1271, 1234, 1200, 1120, 1056, 931. ^{1}H-NMR (360 MHz, $CDCl_3$): 0.89 (*t*, $^3J = 7.0$, 2 Me(7′)); 1.2–1.5 (16 H, 2 CH_2(3′) to 2 CH_2(6′)); 1.80 (*m*, 2 CH_2(2′)); 3.1 (2 NH_2); 3.82 (*s*, 2 MeO), 4.29 (*t*, $^3J = 6.6$, 2 CH_2(1′)); 6.47 (*s*, 2 arom. H,); 8.76 (2 NH). ^{13}C-NMR (90.5 MHz, $CDCl_3$): 14.1 (*q*, Me(7′)); 22.6 (*t*, C(6′)); 26.0, 29.2, 30.4, 31.8 (4*t*, C(2′), C(3′), C(4′), C(5′)); 55.9 (*q*, 2 MeO), 74.5 (*t*, C(1′)); 107.1 (*d*, arom. C(6,6′)); 113.3 (*s*, arom. C(3a,3′a)); 122.0 (*s*, arom. C(2,2′)); 132.6 (*s*, arom. C(5,5′)); 134.9 (*s*, arom. C(7a,7′a)); 136.9 (*s*, arom. C(4,4′)); 141.2 (*s*, arom. C(7,7′)); 186.0 (*s*, arom. C(3,3′)). EI-MS: 581 (38, M^+), 580 (100, M^+), 481 [(72, $M – C_7H_{15}]^+$), 383 (85), 368 (60), 353 (58), 192 (45). HR-MS: 580.3259 (M^+, $C_{32}H_{44}N_4O_6^+$; calc. 580.3260).

REFERENCES

[1] 'Colorants For Non-textile Applications', Eds. H. S. Freeman and A. T. Peters, Elsevier, Amsterdam, 2000.
[2] a) M. Klessinger, W. Luettke, *Tetrahedron* **1963**, *19* (Suppl. 2), 315; b) L. Serrano-Andres, B. O. Roos, *Chem.–Eur. J.* **1997**, *3*, 717.
[3] a) S. J. Holt, P. W. Sadler, *Proc. R. Soc. London B* **1958**, *148*, 495; b) H. Meier, W. Luettke, *Liebigs Ann. Chem.* **1981**, 1303.
[4] M. Freund, A. Wirsing, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 204.
[5] J. Heinze, G. Voss, unpublished results.
[6] R. P. Maskey, I. Gruen-Wollny, H. H. Fiebig, H. Laatsch, *Angew. Chem.* **2002**, *114*, 623; *Angew. Chem., Int. Ed.* **2002**, *41*, 597.
[7] G. Voss, C. Unverzagt, unpublished results.

[8] a) A. V. Ivashenko, P. Yu. Adomenas, V. L. Baraboshkin, M. I. Barnik, S. V. Belyaev, L. M. Blinov, B. M. Bolotin, Yu. P. Bobylev, M. F. Grebenkin, *et al.*, WO 8200654, 1982 (*Chem. Abstr.* **1982**, *97*, P 82797e); b) A. V. Ivashenko, M. I. Barnik, P. Yu. Adomenas, B. M. Bolotin, V. L. Baraboshkin, S. V. Belyaev, L. M. Blinov, Yu. P. Bobylev, M. F. Grebenkin, *et al.*, FR Pat. 2503703, 1982 (*Chem. Abstr.* **1983**, *99*, P 97257u).

[9] L. Rubenstein, *J. Chem. Soc.* **1925**, *127*, 1998.

[10] S. Kawai, S. Fujiki, S. Baba, *Nippon Kagaku Zasshi* **1959**, *80*, 795 (*Chem. Abstr.* **1961**, *55*, 3555c).

[11] G. Voss, W. Schramm, *Helv. Chim. Acta* **2000**, *83*, 2884.

[12] A. von Baeyer, *Ber. Dtsch. Chem. Ges.* **1879**, *12*, 1309.

[13] a) A. von Baeyer, V. Drewsen, *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 2856; b) L. Gindraux, *Helv. Chim. Acta* **1929**, *12*, 921.

[14] C. A. Fetscher, *Org. Synth.* **1963**, Coll. Vol. *4,* 735.

[15] M. Del Mar Blanco, C. Avendano, N. Cabezas, J. C. Menendez, *Synth. Commun.* **1993**, *23*, 1351.

[16] S. Kobayashi, *Scient. Papers Inst. Physical. Chem. Res.* **1927**, *6*, 149; *Chem. Zentralbl. I* **1928**, 1026.

[17] H. B. Gillespie, *Biochem. Prep.* **1953**, *3*, 79.

[18] G. Malesani, F. Marcolin, G. Rodighiero, P. Benetti, *Chim. Ther.* **1970**, *5*, 255.

[19] P. Cotelle, J. P. Catteau, *Synth. Commun.* **1996**, *26*, 4105.

[20] R. Kuhn, H. Trischmann, Chem. Ber. **1961**, *94*, 2258.

[21] a) G. Pfeiffer, H. Bauer, *Liebigs Ann. Chem.* **1980**, 564; b) H. Bauer, G. Pfeiffer, *Chemiker-Ztg.* **1976**, *100*, 373.

[22] A. Lenz, Ch. Schmidt, A. Lehmann, B. Wagner, W. Beck, *Z. Naturforsch., B* **1997**, *52*, 474.

[23] P. W. Preisler, E. S. Hill, R. G. Loeffel, P. A. Shaffer, *J. Am. Chem. Soc.* **1959**, *81*, 1991.

[24] a) W. Beck, Ch. Schmidt, R. Wienold, M. Steinmann, B.Wagner, *Angew. Chem.* **1989**, *101*, 1532; *Angew. Chem., Int. Ed.* **1989**, *28*, 1529; b) Ch. Schmidt, H.-U. Wagner, W. Beck, *Chem. Ber.* **1992**, *125*, 2347.

[25] P. W. Sadler, *Spectrochim. Acta* **1960**, *16*, 1094.

[26] G. Miehe, P. Suesse, V. Kupcik, E. Egert, M. Nieger, G. Kunz, B. Gerke, B. Knieriem, M. Niemeyer, W. Luettke, *Angew. Chem.* **1991**, *103*, 1008; *Angew. Chem., Int. Ed.* **1991**, *30*, 964.

[27] J. Weinstein, G. M. Wyman, *J. Am. Chem. Soc.* **1956**, *78*, 2387.

[28] R. J. H. Clark, C. J. Cooksey, *New J. Chem.* **1999**, 323.

[29] C. Miliani, A. Romani, G. Favaro, *Spectrochim. Acta, Part A* **1998**, *54*, 581.

[30] P. F. Gordon, P. Gregory, 'Organic Chemistry in Colour', Springer-Verlag, Berlin, 1987, p. 213.

[31] P. W. Sadler, *J. Org. Chem.* **1956**, *21,* 316.

[32] a) D. Martin, A. Weise, H.-J. Niclas, *Angew. Chem.* **1967**, *9*, 340; *Angew. Chem., Int. Ed.* **1967**, *6*, 318; b) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, A. J. Parker, *J. Am. Chem. Soc.* **1966**, *88*, 1911; c) D. Laria, R. Kapral, D. Estrin, G. Ciccotti, *J. Chem. Phys.* **1996**, *104*, 6560.

[33] R. S. Freedlander, T. A. Bryson, R. B. Dunlap, E. M. Schulman, C. A. Lewis Jr., *J. Org. Chem.* **1981**, *46*, 3519.

[34] a) S. K. Sengupta, *Indian J. Chem., Sect. A* **1985**, *24*, 54; b) K. Bergmann, C. T. O'Konski, *J. Phys. Chem.* **1963**, *67*, 2169.

[35] A. M. Bond, F. Marken, E. Hill, R. G. Compton, H. Hügel, *J. Chem. Soc., Perkin Trans 2* **1997** 1735.

[36] C. Tanford, 'The Hydrophobic Effect: Formation of Micelles and Biological Membranes', 2nd edn., John Wiley&Sons, New York, 1980, p. 42.

[37] G. Malesani, G. Chiarelotto, *Gazz. Chim. Ital.* **1975**, *105*, 293.

[38] G. M. Sheldrick, 'SHELX-97, Programs for Crystal Structure Determinations', University of Cambridge, 1997.