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meso-Indolo[3,2-*b*]carbazolyl-Substituted Porphyrinoids: Synthesis, Characterization and Effect of the Number of Indolocarbazole Moieties on the Photophysical Properties

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meso-Indolocarbazolylporphyrins endowed with a different number of indolocarbazole units have been synthesized via condensation of an appropriately substituted monoformylated 5,11-dihydroindolo[3,2-*b*]carbazole precursor and mesityldipyrromethane. Under specific conditions, analogous *meso*-indolocarbazolylcorroles could also be prepared. The photophysical features of the novel luminescent free-base and Zn-porphyrin derivatives were investigated. The introduction of indolocarbazole substituents results in progressive bathochromic shifts of the porphyrin absorbance and fluorescence bands due to the rising energy of the a_{2u} orbital. The excitation energy is efficiently transferred from the *meso*-indolocarbazole units to the porphyrin macrocycle. An increased number of indolocarbazole moieties does not lead to porphyrin fluorescence quenching; on the contrary, a small increase of the fluorescence quantum yield is observed. The main route for excitation energy deactivation of all the studied porphyrins is intersystem $S_1 \rightarrow T_1$ crossing, with the intersystem crossing quantum yield, as determined by the photosensitized formation of singlet molecular oxygen, being as high as about 70 % for the free-bases and more than 80 % for the Zn complexes. The intersystem crossing quantum yield seems to be barely affected by *meso*-indolocarbazole substitution. A noticeable part of the excitation energy was found to deactivate through radiationless internal $S_1 \rightarrow S_0$ conversion.

Introduction

Indolocarbazoles, indole-carbazole ring-fused heterocycles, have attracted considerable attention in recent years. Among the five isomeric indolocarbazole ring systems, differentiated by the position and orientation of the ring fusion, indolo[3,2-*b*]carbazoles are actively being investigated, both for their biological significance as well as their distinct electrical and optical features.[1] Monomeric and (co)polymeric indolo[3,2-*b*]carbazole derivatives, electron-rich extended π structures related to well-established oligo(*p*-aniline) (e.g., triarylamines, carbazoles) and pentacene components, have been applied as a new subclass of active (charge-transport) materials for the construction of (opto)electronic devices such as organic light-emitting diodes (LEDs),[2,3] thin-film field-effect transistors (FETs),[3–5] and photovoltaic cells (PCs).[5,6] The high current interest in indolocarbazoles as promising materials for high-performance organic electronics can also be judged from the appreciable amount of recent patents dealing with applications of these molecules.[7]

From a synthetic point of view, several pathways towards indolo[3,2-*b*]carbazoles (ICZs) have been developed over the years. Most of the reported methods, however, involve multiple steps affording only slightly soluble, mostly symmetrical derivatives in rather low overall yields, hampering straightforward elaboration to readily functionalized ICZs.[1] Within one of our groups, alternative protocols that allow a facile and rather general synthesis of various 6-monosubstituted and asymmetrically 6,12-disubstituted 5,11-dihydroindolo[3,2-*b*]carbazoles in moderate to good yields (20–50 %) have recently been established.[8] The enhanced solubility and stability towards oxidative degradation of the newly prepared ICZs enabled easy further structural modification of the indolocarbazole skeleton by numerous pathways, e.g., *N*-alkylation and *N*-arylation,

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Ullmann coupling, regioselective bromination, formylation and *tert*-butylation, azo-coupling and Suzuki cross-coupling.

Since both indolo[3,2-*b*]carbazoles and porphyrins are compounds with attractive properties for the design of electro-optical materials, novel systems combining both planar aromatic chromophores into one single molecule are evidently appealing targets.[9] In previous work, the Leuven group has prepared porphyrins with appended hole-transporting (oligo)carbazole dendrons and their photophysical and redox behaviour were explored.[10] This study has now been extended to the (indolocarbazole)–porphyrin congeners. In this manuscript, we report the first synthetic protocols towards both porphyrins and corroles with indolocarbazolyl moieties at the periphery in fair-to-good yields by exploring different monoformylated ICZ starting products. As a first step towards potential application of these novel materials, their spectroscopic properties have been investigated, with emphasis on the porphyrin moiety, to elucidate how functionalization with ICZ fragments affects the photophysical properties of the porphyrin macrocycle.

Results and Discussion

Synthetic Exploration

The synthesis of (indolocarbazole)–porphyrin conjugates remains a challenging and to date unresolved task. To synthesize porphyrins equipped with *meso*-indolo[3,2-*b*]-carbazolyl moieties, suitable ICZ building blocks are required and effective macrocyclization conditions should be pursued. Straightforward access to variously functionalized ICZ derivatives has only recently been disclosed.[1c,8] Based on previous work, 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**1**) was chosen as the parent ICZ substrate of preference for its high-yielding three-stage, one-pot synthesis (47%), good solubility in common organic solvents and simple conversion to the monoformylated ICZ derivative **2** (Figure 1). Indeed, 6-formyl-ICZ **2** was readily synthesized by regioselective C-formylation of **1** under standard Vilsmeier conditions ($POCl_3$, DMF; 50% yield).[8a,8c]

The first attempt towards *meso*-indolocarbazolyl-substituted porphyrins involved a [2+2]-condensation of 6-formyl-ICZ **2** and 5-mesityldipyrromethane (**5**),[11] in an equimolar ratio, under Lindsey conditions using boron trifluoride–diethyl ether (0.5 equiv.) as a Lewis acid catalyst and subsequent oxidation of the porphyrinogen with *p*-chloranil.[12] Unfortunately, the targeted *trans*-A_2B_2-porphyrin could not be obtained under these macrocyclization conditions (as analyzed by TLC and ESI-MS). Surprisingly, when the crude reaction mixture, containing a considerable amount of unreacted aldehyde **2**, was left standing on the bench for a rather long time (ca. two months) open at the air, the formation of AB_2-corrole **6** was observed (by TLC and ESI-MS), which was chromatographically purified and isolated in a modest 3% yield (Scheme 1). The formation of the contracted porphyrin analogue, *meso*-indolocarbazolylcorrole **6**, rather than the expected A_2B_2-porphyrin

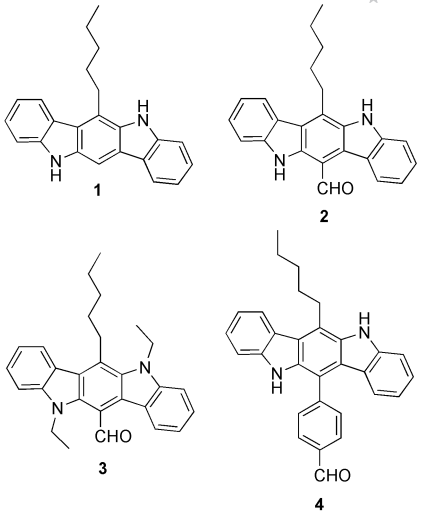
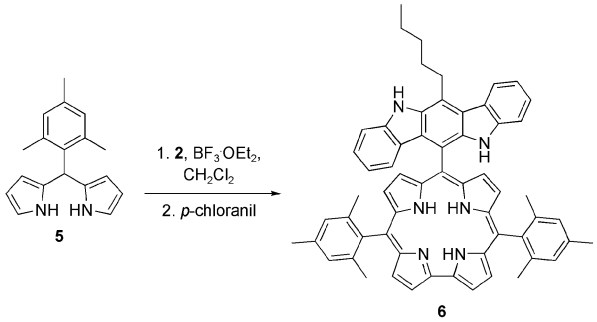


Figure 1. Indolo[3,2-*b*]carbazole precursors **1**–**4**.

may possibly be attributed to the limited solubility of ICZ **2** in dichloromethane. Even though a highly diluted solution was used (5.6 mM), part of the aldehyde **2** still did not dissolve. As a result, the ICZ-carbaldehyde was not equimolar to the dipyrromethane (DPM) in solution, favouring the tetrapyrrane [2+1]-condensation product, which upon oxidation furnished AB_2-corrole **6**. The reason for the very slow conversion of the tetrapyrrolic precursor to the corresponding corrole remains unclear at this stage.[13]



Scheme 1. Synthesis of ICZ-corrole conjugate **6**.

To verify our solubility hypothesis, a more soluble ICZ derivative, 5,11-diethyl-6-formyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**3**), was prepared by formylation of the *N*,*N*-diethyl precursor, in turn easily accessible from **1** by *N*-alkylation with bromoethane (NaH, DMF, 70 °C; 83% yield), under similar Vilsmeier conditions in 71% yield.[8a,8c] The synthesis of an ICZ-porphyrin conjugate based on this novel aldehyde **3** was pursued under the aforementioned conditions, but again no porphyrinic material was obtained. In like fashion, a small amount of corrole (ca. 3%) could be isolated when the crude reaction mixture was allowed to stand open at the air for more than a month.

At this stage, we argued that the reactivity of 6-formyl-ICZs towards reaction with a dipyrromethane might simply be too low (for electronical and, in particular, steric reasons), impeding efficient (cyclo)condensation. Porphyrin

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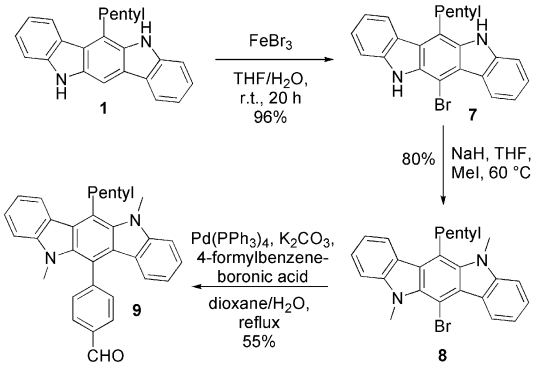
syntheses starting from analogous sterically bulky aromatic aldehydes, e.g., 9-anthrylaldehyde, are known to afford only very low yields of porphyrin macrocycles under classical Adler or Lindsey conditions.[14] Insertion of a phenyl ring between the formyl group and the ICZ chromophore might provide a solution to this problem. Hence, 6-(*p*-formylphenyl)-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**4**)[8a,8c] (Figure 1) and its *N*,*N*-dimethylated analogue **9**, both highly soluble in dichloromethane, were prepared. *N*,*N*-Dimethyl-ICZ **9** was synthesized via monobromination of **1** with anhydrous $FeBr_3$, followed by *N*-methylation and subsequent Suzuki cross-coupling with 4-formylbenzeneboronic acid (Scheme 2).[8c]



Scheme 2. Synthesis of 6-(*p*-formylphenyl)-substituted ICZ **9**.

Using the novel *N*-methylated ICZ-carbaldehyde **9**, the synthesis of ICZ-porphyrin conjugates finally succeeded through cyclocondensation with 5-mesityldipyrromethane (**5**), catalyzed by $BF_3{\cdot}OEt_2$ (0.85 equiv.), and subsequent oxidation with *p*-chloranil. However, not only the expected *trans*-A_2B_2-porphyrin **11a**, but a mixture of 4 different porphyrins **10a**–**13a** was observed (Figure 2). After column chromatographic separation (silica), AB_3-porphyrin **10a** (A = ICZ, B = mesityl) was obtained in 2.5% yield, a mixture of both A_2B_2-porphyrin isomers **11a**,**12a** (*trans* and *cis*, respectively) was obtained in 17% yield, and A_3B-porphyrin **13a** was isolated in 7% yield. Traces of the symmetrical B_4-porphyrin (tetramesitylporphyrin TMP) were also observed, while no A_4-porphyrin was detected.

This mixture of ICZ-porphyrins can only be formed if the oligopyrrolic nonaromatic porphyrin precursors are undergoing (dynamic) fragmentation and recombination, a phenomenon referred to as *scrambling*.[15] The scrambling observed for the combination of mesityldipyrromethane and ICZ **9** might be due to the rather low reactivity of the aldehyde and the high amount of borontrifluoride catalyst. When a smaller amount of $BF_3{\cdot}OEt_2$ (0.425 equiv.) was used, scrambling was still observed, but the ICZ-porphyrins could be obtained in higher yields (6.5% AB_3 **10a**, 29% *trans*-A_2B_2 or ABAB **11a**, 6% *cis*-A_2B_2 or AABB **12a**, 13% A_3B **13a**), the overall yield of porphyrinic material exceeding 50%. Separation of both A_2B_2-porphyrin isomers **11a** and **12a** is not trivial, but could be realized by repeated and careful column chromatography. Direct condensation with pyrrole under Lindsey conditions did not result in any

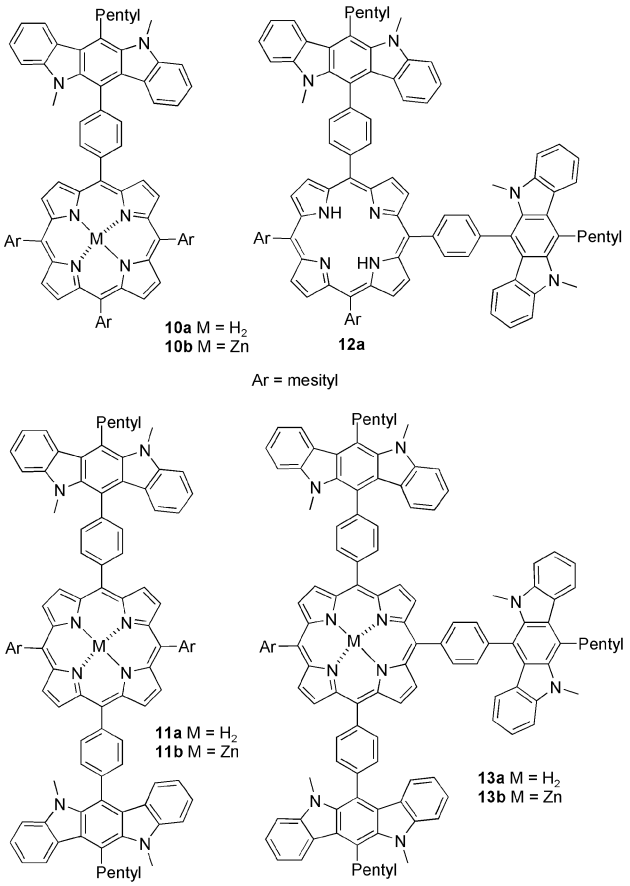


Figure 2. *meso*-Indolo[3,2-*b*]carbazolyl-substituted porphyrins **10a/b**–**13a/b**.

A_4-porphyrin, neither for ICZ precursors **4** or **9**. On metallation of the free-base porphyrins **10a**–**13a** with zinc(II) {using $Zn(OAc)_2$ in chloroform}, Zn-porphyrins **10b**–**13b** were nearly quantitatively obtained (Figure 2).[17]

Since corroles, contracted porphyrin congeners lacking one *meso*-carbon, are currently receiving steadily growing interest due to their particular (catalytical, photophysical and medicinal) properties,[18] a more usable, selective synthetic pathway towards *meso*-indolocarbazolylcorroles was pursued, based on the conditions previously optimized for *meso*-pyrimidinylcorroles.[19] In a first attempt, 6-formyl-ICZ **2** and 5-mesityldipyrromethane (**5**) (2 equiv.) were condensed with a highly reduced amount of $BF_3{\cdot}OEt_2$ (0.086 equiv., 4.5 h at room temp.), favouring corrole formation,[19] followed by oxidation with *p*-chloranil. Unfortunately, no AB_2-corrole could be obtained from this approach. A similar reaction with 6-(*p*-formylphenyl)-ICZ **4** (1 equiv. DPM, 1 equiv. $BF_3{\cdot}OEt_2$, 4 h at room temp.) provided only trace amounts of corrole and A_2B_2-porphyrin (as observed by ESI-MS). On the other hand, dropwise addition of ICZ-carbaldehyde **9**, activated by 0.043 equiv. $BF_3{\cdot}OEt_2$, to a solution of mesityldipyrromethane (**5**) (3 equiv.) in dichloromethane overnight, followed by further reaction for another 12 h and oxidation with *p*-chloranil, afforded the desired AB_2-corrole **14**, albeit in only 1.5%

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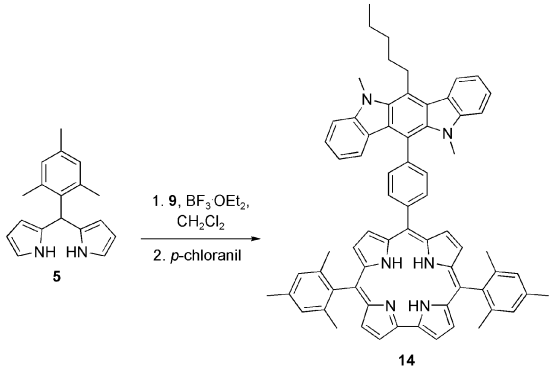
yield (Scheme 3). On applying 6 equiv. of dipyrromethane **5** and flash column chromatographic purification of the corrole, limiting oxidative degradation, the yield could be improved to (a still modest) 5%.



Scheme 3. Synthesis of *meso*-indolo[3,2-*b*]carbazolyl-substituted AB_2-corrole **14**.

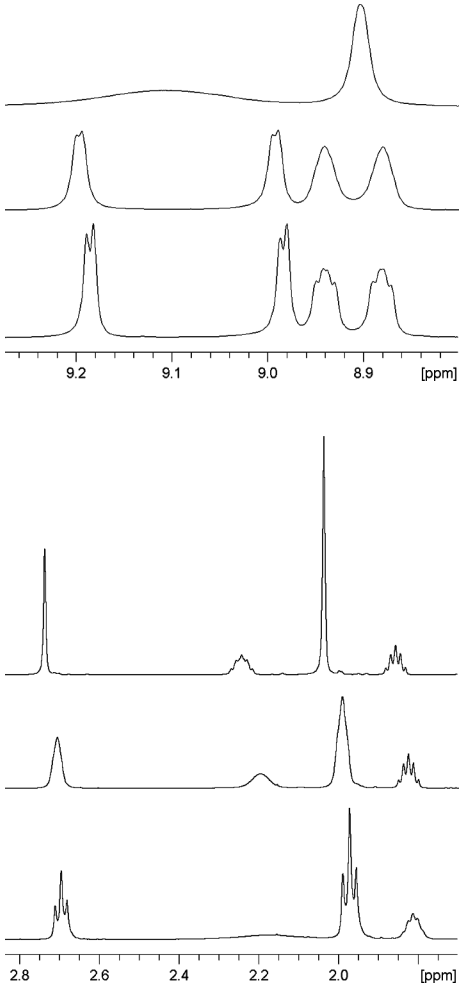


Figure 3. Detailed regions (β-pyrrolic protons at the top, methyl groups of mesityl substituents at the bottom) of the ^{1}H NMR spectrum (600 MHz) of *trans*-A_2B_2-porphyrin **11a** in [D_2]tetrachloroethane, obtained at different temperatures (298 K *down*, 323 K *middle*, 373 K *up*).[20]

Characterization

All novel indolo[3,2-*b*]carbazoles and porphyrinoids were fully characterized by ^{1}H and ^{13}C NMR spectroscopy,[20] mass spectrometry (CI/ESI) and UV/Vis spectroscopy. Due to hindered rotation, the *meso*-indolocarbazolyl moieties may adopt different orientations with respect to the porphyrin plane and the other *meso*-substituents, and hence different porphyrin (atrop)isomers may be formed depending on the number of ICZ units, which is reflected in their respective ^{1}H NMR spectra. For example, in the ^{1}H NMR spectrum of free-base *trans*-A_2B_2-porphyrin **11a**, for which 2 isomers can be distinguished, several doublets (not all well-resolved) were observed in the β-pyrrolic proton region (δ = 9.3–8.8 ppm), and multiple signals were observed for the methyl groups of the *meso*-mesityl moieties (at $\delta \approx 2.7$ and 2.0 ppm) (Figure 3). Variable-temperature NMR studies allowed observation of the rotational barriers. Coalescence of the *o*- and *p*-methyl signals was observed at 50 °C, with a gradual sharpening of these signals at higher temperatures (and a concurrent sharpening of the pentyl signals), indicating facilitated rotation, while the multiply coupled pattern for the β-pyrrolic protons simplified into two broad signals, both corresponding to 4 protons, at 100 °C (Figure 3). The NH resonance gradually shifted to higher field upon raising the temperature (total shift ca. 0.4 ppm in the range 278–373 K).[20]

Absorption and Fluorescence Spectra

The UV/Vis absorption spectra of the ICZ-porphyrin conjugates are composed of porphyrin bands, the intense Soret band in the UV region and less intense Q-bands in the visible range, and ICZ centered bands in the UV region, the $S_0 \rightarrow S_2$ transition (vibronic progression) in the region 320–350 nm and the $S_0 \rightarrow S_1$ transition at higher wavelength (ca. 400 nm) overlapped by the porphyrin Soret band (see example in Figure 4).[21,22] The ground state interaction of the porphyrin core and the ICZ substituents seems to be rather weak.

When the excitation wavelength was chosen in the UV range, where the ICZ moiety absorbs, no/hardly detectable indolocarbazole emission signals, but strong porphyrin emission was observed (see example in Figure 5). The emission of the porphyrin moiety upon UV excitation indicates that light energy absorbed by the indolocarbazole units is efficiently transferred to the porphyrin core. The fluorescence spectra of all the studied porphyrin–indolo[3,2-*b*]-carbazole conjugates show the expected double porphyrin $S_1 \rightarrow S_0$ emission bands, centered around 650 and 725 nm for the free-base derivatives and around 600 and 650 nm for the Zn complexes. Thus, the indolo[3,2-*b*]carbazole units act as light-harvesting antennae for the porphyrin core.

A more detailed photophysical study of the *meso*-indolo[3,2-*b*]carbazolylporphyrins was then undertaken, with emphasis on the porphyrin chromophore, since the excitation energy deactivation proceeds majorly via the porphyrin moiety. The progressive substitution with ICZ frag-

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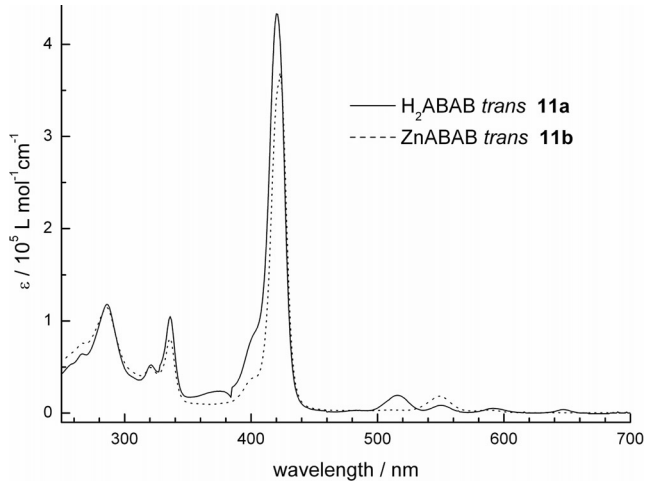

Figure 4. UV/Vis absorption spectra for ICZ-porphyrin conjugates **11a**,**b** in CH_2Cl_2.

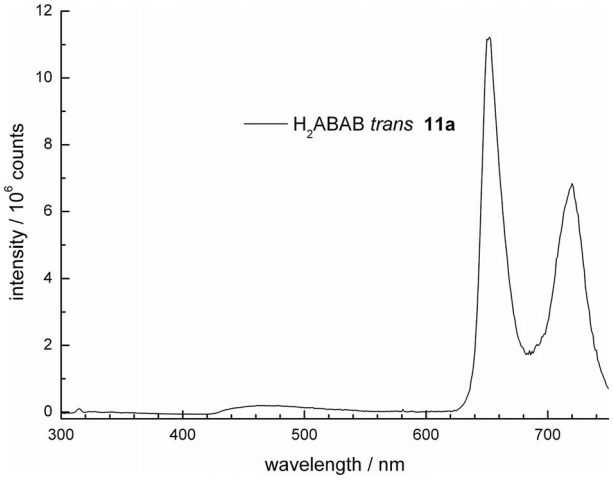

Figure 5. Emission spectrum of ICZ-porphyrin conjugate **11a** measured upon excitation at 286 nm.

ments at the *meso*-positions of the porphyrin macrocycle leads to relatively small, but well detectable changes in the porphyrin absorption and fluorescence spectra (Figure 6 and Figure 7). The data obtained for both free-base and Zn complexes in toluene are listed in Table 1. Toluene has been used as a (noncoordinating) solvent to avoid any possible complications due to axial ligation.

The data in Table 1 show that the introduction of ICZ substituents results in progressive subtle bathochromic changes of the absorbance and fluorescence bands (see Figures 6 and 7). The energy difference between the absorption and fluorescence maxima remains practically the same (about 10 nm and 5.5–6.5 nm for the Zn and free-base derivatives, respectively), indicating that there are no structural rearrangements (perturbations) in the excited singlet state upon increase in the number of ICZ units. There are also no specific solute-solvent interactions since essentially the same values have been measured for these compounds in dichloromethane (data are not shown).

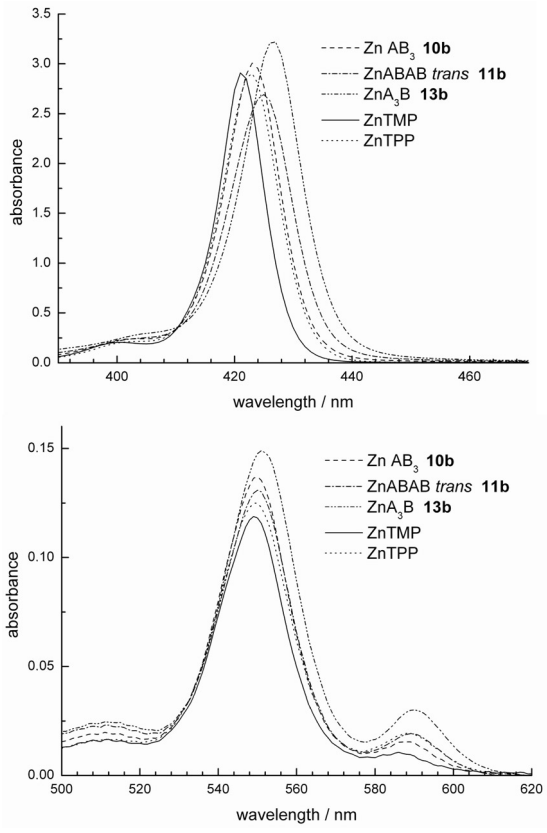

Figure 6. Absorption spectra of Zn-porphyrin complexes in toluene: Soret region (top) and visible region (bottom).

The fact to be stressed here is the change in the ratio of the intensities of the pure electronic band and the vibronic one in both absorption ($A_{0,0}/A_{1,0}$) and fluorescence ($F_{0,0}/F_{0,1}$) spectra. The $A_{0,0}/A_{1,0}$ ratio is directly proportional to the ratio of the transition dipole moments of these transitions. It is known that this ratio is proportional to the square of the energy difference between the two one-electron configurations for the porphyrin macrocycle: $A_{0,0}/A_{1,0} \approx [^1E(a_{2u},e_g) - {}^1E(a_{1u},e_g)]^2$,[23] and it is often used as a measure for the energy mismatch between the highest occupied molecular orbitals (HOMOs) a_{2u} and a_{1u} (orbital notations are given for the D_{4h} point symmetry group). It is well established that addition of aryl substituents at the *meso*-positions of a porphyrin macrocycle increases the energy of the a_{2u} molecular orbital,[23] so the relationship $^1E(a_{2u},e_g) < {}^1E(a_{1u},e_g)$ holds. As a starting point for the analysis, ZnTMP was selected, which can be considered as the parent compound for molecules **10b**, **11b** and **13b**. For ZnTMP, the value for the ratio $A_{0,0}/A_{1,0}$ is 0.09. Proceeding to compounds with an increasing number of ICZ substituents, the ratio gradually increases up to 0.2 in the case of ZnA_3B-porphyrin **13b** (Table 1). This means that the ICZ substituents have an electron donation power which is higher than that of the mesityl substituents. As a result, the electronic density at the ICZ-substituted *meso*-carbon atoms increases, leading to an increase in the energy of the a_{2u} molecular orbital of the porphyrin macrocycle and to a de-

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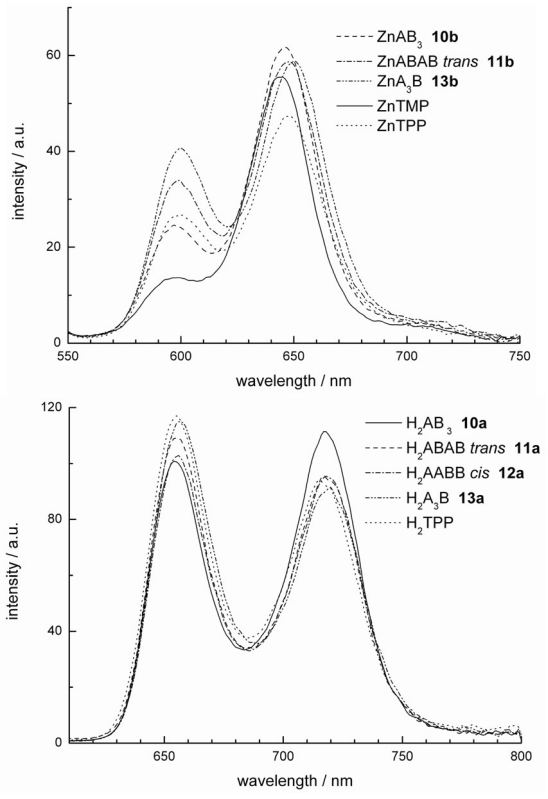

Figure 7. Fluorescence spectra of Zn complexes (top) and free-base porphyrins (bottom) in toluene (λ_{exc} = 532 nm).

Table 1. Spectral data for the studied porphyrin derivatives **10a/b**–**13a/b** in toluene.

Porphyrin	$\lambda_{0,0}^{abs}$ /nm	$A_{0,0}/A_{1,0}$	$\lambda_{0,0}^{fl}$ /nm	$F_{0,0}/F_{0,1}$
$ZnAB_3$ **10b**	587.5	0.13	597.5	0.40
ZnABAB *trans* **11b**	589.0	0.15	599.0	0.58
ZnA_3B **13b**	590.0	0.20	600.0	0.69
ZnTPP[a]	588.5	0.16	599.0	0.56
ZnTMP[b]	586.0	0.09	597.0	0.24
H_2TPP	648.0	0.47	654.5	1.25
H_2AB_3 **10a**	649.0	0.44	654.5	0.90
H_2ABAB *trans* **11a**	649.0	0.56	655.0	1.14
H_2AABB *cis* **12a**	650.0	0.52	655.0	1.07
H_2A_3B **13a**	650.0	0.60	656.5	1.27

[a] TPP: tetraphenylporphyrin. [b] TMP: tetramesitylporphyrin.

crease in the strength of the configurational interaction.[23] Thus, as the mismatch between the a_{2u} and a_{1u} HOMOs for these compounds increases, the maximum for the first electronic transition undergoes a monotonic long wavelength shift (this is also true for the Soret band, since $E_B - E_Q \approx$ constant). The obtained dependencies on the number of ICZ substituents for the Zn-porphyrins are depicted in Figure 8. These dependencies indicate the character of the changes in the configuration interaction upon substitution with ICZ heterocycles.

As has been stated above, the increase in the energy gap between the a_{2u} and a_{1u} HOMOs mainly leads to an increase in the oscillator strength of the pure electronic band (the forbiddenness of the vibronic band has already been removed with perturbation by vibronic coupling).[24] The

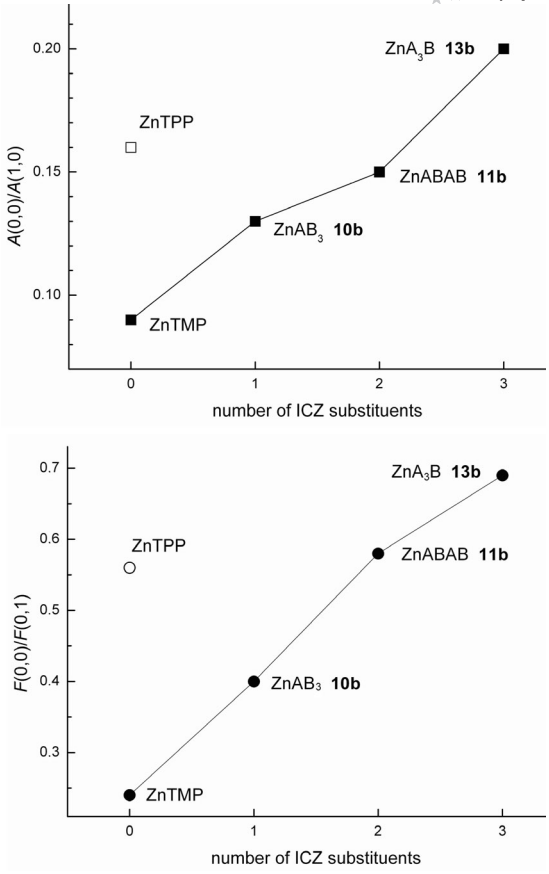

Figure 8. Configurational interaction dependencies for the studied Zn-porphyrins.

conclusion that the intensity changes are mainly due to the rise of the a_{2u} orbital is supported by the monotonic relationship between the $A_{0,0}/A_{1,0}$ ratio and the frequencies of the 0,0-transition shifts measured relatively to the parent ZnTMP molecule according to the predictions of the Gouterman four-orbital model (Figure 9).[23,25]

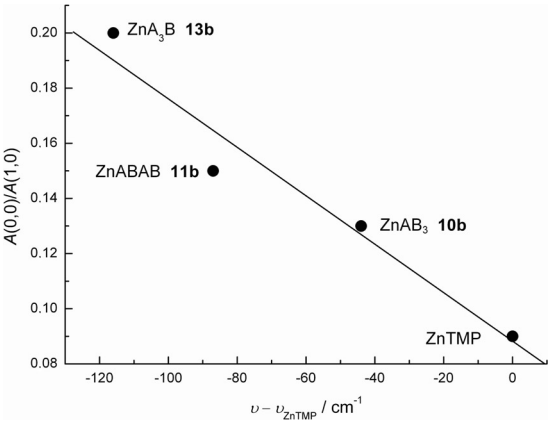

Figure 9. Correlation between the $A_{0,0}/A_{1,0}$ ratio and the frequency of the 0,0-transition.

As for the comparison of the disubstituted *cis*- (H_2AABB **12a**) and *trans*-porphyrin (H_2ABAB **11a**), one can state that symmetric *trans*-substitution effects the porphyrin macro-

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cycle electronic density slightly stronger. This conclusion is based on the differences found for the $A_{0,0}/A_{1,0}$ and $F_{0,0}/F_{0,1}$ ratios: in the case of *trans*-substitution the shift of the a_{2u} orbital seems to be slightly higher.

Excitation Energy Deactivation

Substitution at the *meso*-positions of a porphyrin with ICZ heterocyclic fragments leads to changes in the photophysical properties of the porphyrin core. The photophysical properties measured for the free-base and Zn-porphyrins **10a/b**–**13a/b** are listed in Table 2.

Table 2. Photophysical properties of the free-base and Zn-porphyrins **10a/b**–**13a/b**.

Porphyrin	τ_{fl} /ns	Φ_{fl}	k_{fl} /10^7 s^{-1}	Φ_{ISC}	k_{ISC} /10^8 s^{-1}	Φ_{IC}	k_{IC} /10^7 s^{-1}
10b	2.13	0.037	1.74	0.85	4.0	0.11	5.2
11b	1.98	0.039	1.97	0.79	4.0	0.17	8.5
13b	1.43	0.041	2.97	0.83	5.8	0.13	9.1
ZnTPP	1.75	0.033	1.89	0.90	5.1	0.07	4.3
ZnTMP	2.33	0.032	1.37	0.83	3.6	0.14	5.6
H_2TPP	12.2	0.090	0.74	0.68	0.56	0.23	0.19
10a	–	0.092	–	0.71	–	0.20	–
11a	–	0.093	–	0.67	–	0.24	–
12a	–	0.093	–	0.68	–	0.23	–
13a	–	0.095	–	0.68	–	0.23	–

The differences in the photophysical parameters for the Zn complexes seem to result from changes in the electronic structure of the porphyrin macrocycle induced by the attachment of ICZ groups. Upon going from the parent unsubstituted ZnTMP to the porphyrins with an increasing number of ICZ groups, some photophysical parameters were found to alter. First of all, the fluorescence quantum yield Φ_{fl} increases with an increase of the number of attached *meso*-ICZ fragments. Fluorescence lifetime measurements demonstrate that the decay also becomes faster with an increase of the number of ICZ groups. With these values in hand, the rate k_{fl} of the radiative deactivation of the lowest singlet S_1 state could be determined. Attachment of ICZ groups leads to a more than twofold increase in k_{fl} value: from 1.37×10^7 s^{-1} in the case of ZnTMP up to 2.97×10^7 s^{-1} for ZnA_3B-porphyrin **13b**. Thus, the formation of highly ICZ-substituted compounds does not lead to fluorescence quenching; on the contrary, a small increase of the fluorescence quantum yield is observed. The same noticeable trend was also found to be valid for the free-base conjugates: the value of the fluorescence quantum yield Φ_{fl} slightly increases from 0.092 for monosubstituted H_2AB_3-porphyrin **10a** to 0.095 for trisubstituted H_2A_3B-porphyrin **13a**. However, one may notice this trend is weakly marked, being within experimental error limits.

The quantum yield for triplet state formation has been determined with the method of photosensitized formation of singlet molecular oxygen. In case the probability of the energy transfer from the porphyrin lowest triplet T_1 state to the molecular oxygen ground state ($^3\Sigma_g^-$) is unit, the intersystem crossing $S_1 \rightarrow T_1$ quantum yield Φ_{ISC} is equal to the quantum yield of the photosensitized formation of singlet molecular oxygen Φ_Δ. The obtained figures are listed in Table 2. One can see that the intersystem crossing quantum yield for the Zn-porphyrins is barely affected by ICZ-substitution. All the measured figures fall in the range 0.82 ± 0.03, i.e. are the same within the limits of experimental error. At the same time, the k_{ISC} value slightly increases upon going from unsubstituted ZnTMP to the ICZ-porphyrins with an increasing number of ICZ groups. The trend observed for the free-base conjugates is the same: the intersystem crossing quantum yield is barely affected by the attachment of ICZ units at the *meso*-positions of the porphyrin macrocycle.

One other noteworthy point should be stressed. In both cases (porphyrin free-bases and Zn complexes), the intersystem crossing quantum yield Φ_{ISC} for the mono-ICZ-substituted porphyrin is slightly higher than for the other derivatives. Maybe the reason for this small difference does arise from the asymmetry of the electron density distribution in the case of monosubstitution. However, these changes are too small for an in-depth discussion.

Finally, a noticeable part of the excitation energy was found to deactivate through internal radiationless $S_1 \rightarrow S_0$ conversion, as it was also found to be true for the parent TMP compounds. The value of the internal conversion quantum yield Φ_{IC} is determined as $1\text{-}\Phi_{ISC}\text{-}\Phi_{fl}$ and, therefore, reflects the uncertainty of the Φ_{ISC} measurements. For the Zn-porphyrins the internal conversion quantum yield Φ_{IC} varies as 0.14 ± 0.03, and for the free-base porphyrins as 0.22 ± 0.02. The rate of the internal radiationless conversion k_{IC} also slightly increases upon going from unsubstituted ZnTMP to the porphyrins with more ICZ groups.

Conclusions

In conclusion, novel indolo[3,2-*b*]carbazole–porphyrin conjugates with a different number of *meso*-indolocarbazolyl substituents have been prepared in fair-to-good yields via *scrambling* condensation of a formylated indolo[3,2-*b*]-carbazole precursor and mesityldipyrromethane, taking advantage of the broad functionalization scope of the parent 6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole building block. Furthermore, analogous indolo[3,2-*b*]carbazole-corrole conjugates were also synthesized in modest yields. Detailed spectroscopic studies on the free-base and Zn-porphyrins have exposed small bathochromic shifts upon progressive substitution with ICZ fragments, both in the absorption and fluorescence spectra, and this trend has a noteworthy additive character. The introduction of ICZ substituents at the *meso*-positions of a porphyrin macrocycle leads to a slight increase of the fluorescence quantum yield and a shortening of the fluorescence lifetime. The main route for the excitation energy deactivation is intersystem crossing with population of the lowest T_1 triplet state. The intersystem crossing quantum yield Φ_{ISC} is about 0.8 and 0.7 for the Zn complexes and free-base compounds, respectively. The absence of radiationless internal conversion enhance-

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ment upon progressive substitution with ICZ fragments is likely to be an indication that no nonplanar macrocycle distortions are induced. There are no noticeable differences in the photophysical properties of the *trans*- and *cis*-disubstituted free-base porphyrins. Further studies will be directed towards thorough electrochemical characterization and the prospective application of the novel materials in optoelectronic devices, an area of ever growing technological and scientific interest.

Experimental Section

General: NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz, Bruker AMX 400 MHz or Bruker Avance II$^+$ 600 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane or residual NMR solvent signals.[26] Mass spectra were run using a HP5989A apparatus (CI and EI, 70 eV ionisation energy) with Apollo 300 data system or a Thermo Finnigan LCQ Advantage apparatus (ESI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000). Melting points were determined using a Reichert Thermovar apparatus. For column chromatography 70–230 mesh silica 60 (Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Tetramesitylporphyrin (TMP) was prepared according to a previously reported procedure.[27] Zinc insertion in TMP was performed with $Zn(OAc)_2$ in $CHCl_3$. UV/Vis spectra were taken on a Perkin–Elmer Lambda 20 (KU Leuven) or a Varian CARY 500 Scan (Minsk) spectrophotometer. The fluorescence measurements have been performed in standard rectangular cells (1 × 1 cm, Hellma) in air-equilibrated solutions at 293 ± 2 K. Deoxygenated solutions have been used for the measurements of the fluorescence quantum yield. Deoxygenation was achieved by bubbling argon through the solution during 20 min just before the measurements. The fluorescence and fluorescence excitation spectra have been measured with the use of a spectrofluorometer SFL-1211 (Solar, Belarus). The fluorescence decay kinetics have been measured with the use of a photon counting system FLA-900 (Edinburgh Instruments, UK). The fluorescence quantum yield (Φ_{fl}) and singlet oxygen photosensitization quantum yield (Φ_{Δ}) have been determined using the standard sample method, with free-base 5,10,15,20-tetraphenylporphyrin (H_2TPP) and Zn-5,10,15,20-tetraphenylporphyrin (ZnTPP) as standard samples (Φ^0_{fl} = 0.09, Φ^0_{Δ} = 0.68 and Φ^0_{fl} = 0.033, Φ^0_{Δ} = 0.90, respectively).

5,11-Diethyl-6-formyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (3): ICZ **3** was prepared according to the procedure described for the non-*N*-alkylated 6-formyl-ICZ analogue **2**.[8c] To a solution of 5,11-diethyl-6-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (0.6 g, 1.6 mmol) in 1,2-dichloroethane (10 mL) at room temp., DMF (0.15 mL, 1.9 mmol, 1.2 equiv.) was added, and subsequently $POCl_3$ (0.17 mL, 1.9 mmol, 1.2 equiv.) was added dropwise under a N_2 atmosphere. The mixture was stirred for 10 min and then heated at reflux temperature overnight under a N_2 atmosphere. The resulting mixture was cooled down to room temp., poured into ice water and extracted with ethyl acetate. The organic extracts were combined, washed with brine, dried with Na_2SO_4 and concentrated in vacuo. The crude residue was purified by column chromatography (silica, eluent ethyl acetate/heptane, 2:8) to afford ICZ **3** (0.46 g, 71%) as a yellow solid; m.p. 73–75 °C. MS (CI): 411 [*M*H$^+$]. HRMS (EI): calcd. for $C_{28}H_{30}N_2O$: 410.2358; found: *m*/*z* 410.2350. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 11.24 (s, 1 H, CHO), 8.51 (d, $J_{H,H}$ = 8.2 Hz, 1 H), 8.21 (d, $J_{H,H}$ = 8.2 Hz, 1 H), 7.71 (t, $J_{H,H}$ = 8.2 Hz, 2 H), 7.55 (t, $J_{H,H}$ = 7.3 Hz, 2 H), 7.34 (t, $J_{H,H}$ = 7.3 Hz, 1 H), 7.22 (t, $J_{H,H}$ = 7.3 Hz, 1 H), 4.70–4.50 (m, 4 H), 3.66 (br. s, 2 H), 1.88 (br. s, 2 H), 1.66 (br. s, 2 H), 1.50–1.25 (m, 8 H), 0.94 (t, $J_{H,H}$ = 7.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO, 25 °C, TMS): δ = 191.1 (CHO), 142.8, 142.6, 135.4, 133.1, 127.0, 126.9 (CH), 126.1 (CH), 124.7 (CH), 122.7, 122.5, 122.3 (CH), 122.0, 121.1, 119.9 (CH), 118.9 (CH), 113.6, 109.9 (CH), 109.6 (CH), 41.4 (CH_2), 39.9 (CH_2), 31.4 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 21.9 (CH_2), 14.9 (CH_3), 13.9 (CH_3), 13.4 (CH_3) ppm.

10-(12-Pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)-5,15-bis(2,4,6-trimethylphenyl)corrole (6): Eluent CH_2Cl_2; yield 3%. MS (ESI) calcd. for $C_{60}H_{54}N_6$: 858.4; found: *m*/*z* 859.6 [*M* + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.89 (d, $J_{H,H}$ = 4.0 Hz, 2 H, H_β), 8.40–8.17 (m, 9 H, 6 × H_β), 7.42 (d, $J_{H,H}$ = 8.0 Hz, 2 H), 7.30–7.18 (m, 5 H), 7.05–6.97 (m, 2 H), 3.76 (br. t, $J_{H,H}$ = 8.0 Hz, 2 H, CH_2), 2.55 (s, 6 H, CH_3-Mes), 2.27–2.18 (m, 2 H, CH_2), 2.00 (s, 6 H, CH_3-Mes), 1.85 (s, 6 H, CH_3-Mes), 1.84–1.75 (m, 2 H, CH_2), 1.64–1.54 (m, 2 H, CH_2), 1.05 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3-pent) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 277 (4.582), 318 (sh, 4.411), 331 (4.504), 411 (4.800), 566 (3.970), 601 (3.812), 631 (3.615) nm.

6-Bromo-5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (8): To a flame-dried, N_2-flushed round-bottomed flask containing a solution of monobrominated ICZ **7**[8c] (0.5 g, 1.2 mmol) in dry THF (20 mL), cooled to 0 °C, NaH (0.5 g, 12 mmol) was portionwise added. After the addition of CH_3I (0.38 mL, 6 mmol, 5 equiv.), the mixture was warmed slowly to room temp. and then heated at 60 °C overnight under a N_2 atmosphere. The reaction mixture was subsequently cooled down to room temp., distilled water (20 mL) was added and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The organic extracts were combined, washed with brine, dried with $MgSO_4$ and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica, eluent CH_2Cl_2/heptane, 4:6) to yield ICZ **8** (0.43 g, 80%) as a slightly yellow solid, and immediately used further on in the preparation of ICZ precursor **9**.

6-(*p*-Formylphenyl)-5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]-carbazole (9): ICZ **9** was prepared according to the Suzuki protocol described for the analogous non-*N*-methylated monobrominated ICZ using 6-bromo-5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**8**) (0.100 g, 0.23 mmol), 4-formylphenylboronic acid (0.052 g, 0.35 mmol), K_2CO_3 (0.080 g, 0.58 mmol) and $Pd(PPh_3)_4$ (1.3 mg, 1.2 μmol).[8c] Column chromatographic purification (silica, eluent CH_2Cl_2/heptane, 4:6) afforded ICZ **9** (0.070 g, 55%) as a yellow solid; m.p. 277–278 °C. HRMS (EI): calcd. for $C_{32}H_{30}N_2O$: 458.2358; found: *m*/*z* 458.2354. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 10.22 (s, 1 H, CHO), 8.24 (d, $J_{H,H}$ = 8.2 Hz, 1 H), 8.09 (d, $J_{H,H}$ = 7.3 Hz, 2 H), 7.76 (d, $J_{H,H}$ = 8.2 Hz, 2 H), 7.48 (t, $J_{H,H}$ = 7.3 Hz, 1 H), 7.39–7.21 (m, 4 H), 6.84–6.77 (m, 1 H), 6.52 (d, $J_{H,H}$ = 7.3 Hz, 1 H), 4.19 (s, 3 H, NCH_3), 3.78 (br. t, $J_{H,H}$ = 8.4 Hz, 2 H), 3.26 (s, 3 H, NCH_3), 2.06 (br. s, 2 H), 1.77–1.63 (m, 2 H), 1.58–1.46 (m, 2 H), 1.02 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3-pent) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.2 (CHO), 146.2, 143.9, 143.4, 136.0, 134.5, 134.0, 132.2 (CH), 130.1 (CH), 125.7 (CH), 125.5 (CH), 122.8 (CH), 122.7, 122.6, 122.3, 122.1, 122.0 (CH), 120.4, 118.7 (CH), 118.2 (CH), 115.0, 108.44/108.38 (CH), 33.6 (CH_3), 32.7 (CH_3), 32.5 (CH_2), 30.9 (CH_2), 29.2 (CH_2), 22.8 (CH_2), 14.4 (CH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} (logε) = 265 (4.734), 285 (4.924), 321 (4.490), 336 (4.684), 418 (3.984) nm.

Synthesis of *meso*-Indolo[3,2-*b*]carbazolylporphyrins 10a–13a: To CH_2Cl_2 (50 mL), purged with Ar for 15 min (while stirring vigor-

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ously), mesityldipyrromethane (**5**) (87 mg, 0.33 mmol) and 5,11-dimethyl-6-(*p*-formylphenyl)-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazole (**9**) (150 mg, 0.33 mmol, 1 equiv.) were added, immediately followed by the addition of $BF_3{\cdot}OEt_2$ (175 μL, 0.14 mmol, 0.425 equiv.), and the solution was stirred at room temp. for 1 h (under an Ar atmosphere and protected from light). *p*-Chloranil (81 mg, 0.33 mmol, 1 equiv.) was subsequently added and the mixture was heated at reflux for 1 h. The solvent was removed in vacuo and the crude porphyrin mixture was separated in its components **10a**–**13a** by column chromatography (silica, eluent CH_2Cl_2/petroleum ether, 1:1).

5-[4-(5,11-Dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-10,15,20-tris(2,4,6-trimethylphenyl)porphyrin (10a): Yield 6.5% (8 mg). MS (ESI): calcd. for $C_{78}H_{72}N_6$: 1092.6; found: *m*/*z* 1093.6 [*M* + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.15 (d, $J_{H,H}$ = 4.8 Hz, 1 H, H_β), 8.93 (d, $J_{H,H}$ = 4.8 Hz, 1 H, H_β), 8.84 (d, $J_{H,H}$ = 4.8 Hz, 1 H, H_β), 8.79 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H_β), 8.69–8.63 (m, 4 H, H_β), 8.44 (d, $J_{H,H}$ = 8.0 Hz, 2 H), 8.35 (d, $J_{H,H}$ = 7.8 Hz, 1 H), 7.99 (d, $J_{H,H}$ = 7.8 Hz, 2 H), 7.60–7.47 (m, 4 H), 7.35–7.27 (m, 8 H), 7.19 (td, $J_{H,H}$ = 7.2, 1.5 Hz, 1 H), 4.31 (s, 3 H, NCH_3), 3.91 (br. t, $J_{H,H}$ = 8.6 Hz, 2 H, CH_2), 3.83 (s, 3 H, NCH_3), 2.66–2.62 (m, 9 H, CH_3-Mes), 2.30–2.05 (br. s, 2 H, CH_2), 1.91–1.86 (m, 18 H, CH_3-Mes), 1.78 (q, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 1.60 (s, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 1.06 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3-pent), –2.46 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.2, 143.6, 142.1, 139.6, 138.8, 138.5, 138.3, 137.9, 134.9 (CH), 134.8, 134.7, 132–130 (br., CH_β), 129.6 (CH), 127.97/127.93 (CH), 125.8 (CH), 125.4 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.4, 120.0, 119.0, 118.7 (CH), 118.3 (CH), 118.0, 116.4, 108.54/108.47 (CH), 33.7 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 21.91/21.88/21.6 (CH_3-Mes), 14.4 (CH_3) ppm. UV/Vis (toluene): λ_{max} (log ε) = 420.5 (5.665), 515.0 (4.321), 547.5 (3.912), 593.0 (3.768), 650.0 (3.560) nm.

5,15-Bis[4-(5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-10,20-bis(2,4,6-trimethylphenyl)porphyrin (11a): Yield 29% (67 mg). MS (ESI): calcd. for $C_{100}H_{90}N_8$: 1402.7; found: *m*/*z* 1403.6 [*M* + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.21 (d, $J_{H,H}$ = 4.5 Hz, 2 H, H_β), 9.00 (d, $J_{H,H}$ = 4.5 Hz, 2 H, H_β), 8.92 (d, $J_{H,H}$ = 4.6 Hz, 2 H, H_β), 8.86 (d, $J_{H,H}$ = 4.5 Hz, 2 H, H_β), 8.49 (d, $J_{H,H}$ = 8.0 Hz, 4 H), 8.35 (d, $J_{H,H}$ = 7.8 Hz, 2 H), 8.00 (d, $J_{H,H}$ = 7.3 Hz, 4 H), 7.60–7.45 (m, 8 H), 7.38–7.29 (m, 8 H), 7.19 (t, $J_{H,H}$ = 7.2 Hz, 2 H), 4.30 (s, 6 H, NCH_3), 3.90 (br. t, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 3.83 (s, 6 H, NCH_3), 2.70–2.65 (m, 6 H, CH_3-Mes), 2.30–2.00 (br. s, 4 H, CH_2), 1.97–1.92 (m, 12 H, CH_3-Mes), 1.78 (q, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.60 (s, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.06 (t, $J_{H,H}$ = 7.2 Hz, 6 H, CH_3-pent), –2.43 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.1, 143.6, 141.9, 140.9, 139.6, 138.8, 138.5, 138.0, 134.9 (CH), 134.7, 134.6, 132–130 (br., CH_β), 129.7 (CH), 128.0 (CH), 125.7 (CH), 125.4 (CH), 123.4, 123.2, 122.94 (CH), 122.88, 122.6 (CH), 122.3, 120.0, 119.2, 118.8, 118.6 (CH), 118.3 (CH), 116.4, 108.53/108.44 (CH), 33.7 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 21.9/21.7 (CH_3-Mes), 14.4 (CH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (5.073), 321 (4.719), 336 (5.021), 420 (5.638), 516 (4.292), 550 (3.941), 591 (3.750), 647 (3.634) nm. UV/Vis (toluene): λ_{max} (log ε) = 422.0 (5.615), 515.5 (4.288), 549.5 (3.995), 593.0 (3.735), 649.0 (3.589) nm.

5,10-Bis[4-(5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-15,20-bis(2,4,6-trimethylphenyl)porphyrin (12a): Yield 6% (14 mg). MS (ESI): calcd. for $C_{100}H_{90}N_8$: 1402.7; found: *m*/*z* 1403.8 [*M* + H]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.36 (s, 0.5 H, H_β), 9.33 (d, $J_{H,H}$ = 4.5 Hz, 0.5 H, H_β), 9.21–9.16 (m, 1.5 H, H_β), 9.13 (s, 0.5 H, H_β), 9.01 (d, $J_{H,H}$ = 4.5 Hz, 0.5 H, H_β), 8.98 (d, $J_{H,H}$ = 4.5 Hz, 0.5 H, H_β), 8.88 (d, $J_{H,H}$ = 4.3 Hz, 1 H, H_β), 8.83 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H_β), 8.78 (s, 2 H, H_β), 8.53–8.46 (m, 4 H), 8.36 (d, $J_{H,H}$ = 7.8 Hz, 2 H), 8.09–7.98 (m, 4 H), 7.63–7.47 (m, 8 H), 7.39–7.26 (m, 8 H), 7.20 (t, $J_{H,H}$ = 7.0 Hz, 2 H), 4.34 (s, 3 H, NCH_3), 4.33 (s, 3 H, NCH_3), 3.97–3.82 (m, 10 H, CH_2/NCH_3), 2.69–2.64 (m, 6 H, CH_3-Mes), 2.35–2.05 (br. s, 4 H, CH_2), 1.96–1.90 (m, 12 H, CH_3-Mes), 1.81 (q, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.61 (s, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.07 (t, $J_{H,H}$ = 7.3 Hz, 6 H, CH_3-pent), –2.44 (br. s, 2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.21/144.18, 143.6, 142.2, 139.6, 138.9, 138.4, 138.01/137.98, 135.1 (CH), 135.0 (CH), 134.8, 134.7, 132–130 (br., CH_β), 129.7 (CH), 127.99/127.95 (CH), 125.8 (CH), 125.5 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.6 (CH), 122.4, 120.0, 119.5, 118.67/118.63 (CH), 118.3 (CH), 116.4, 108.56/108.48 (CH), 33.7 (CH_3-N), 32.7 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 21.9/21.7 (CH_3-Mes), 14.4 (CH_3) ppm. UV/Vis (toluene): λ_{max} (log ε) = 422.0 (5.591), 515.5 (4.243), 549.5 (3.924), 593.0 (3.705), 650.0 (3.565) nm.

5,10,15-Tris[4-(5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-20-(2,4,6-trimethylphenyl)porphyrin (13a): Yield 13% (24 mg). MS (ESI): calcd. for $C_{122}H_{108}N_{10}$: 1712.9; found: *m*/*z* 1714.8 [*M* + H]$^+$. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.43–9.34 (m, 2 H, H_β), 9.27–9.14 (m, 3 H, H_β), 9.08–9.00 (m, 1 H, H_β), 8.95 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 8.90 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 8.58–8.48 (m, 6 H), 8.36 (d, $J_{H,H}$ = 7.3 Hz, 3 H), 8.11–7.99 (m, 6 H), 7.63–7.46 (m, 12 H), 7.41–7.18 (m, 11 H), 4.33 (s, 9 H, NCH_3), 3.98–3.80 (m, 15 H, CH_2/NCH_3), 2.69 (br. s, 3 H, CH_3-Mes), 2.35–2.00 (br. s, 6 H, CH_2), 1.97 (br. s, 6 H, CH_3-Mes), 1.81 (q, $J_{H,H}$ = 7.3 Hz, 6 H, CH_2), 1.60 (s, $J_{H,H}$ = 7.3 Hz, 6 H, CH_2), 1.07 (t, $J_{H,H}$ = 7.3 Hz, 9 H, CH_3-pent), –2.43 (br. s, 2 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 144.2, 143.6, 142.2, 142.0, 139.6, 139.0, 138.4, 138.1, 135.2 (CH), 135.1 (CH), 134.8, 134.6, 132.5–130 (br., CH_β), 129.8 (CH), 128.0 (CH), 125.9 (CH), 125.8 (CH), 125.5 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.4, 120.1, 119.8, 119.1, 118.7 (CH), 118.3 (CH), 116.4, 108.6 (CH), 108.5 (CH), 33.7 (CH_3-N), 33.1 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 21.9/21.7 (CH_3-Mes), 14.3 (CH_3) ppm. UV/Vis (toluene) λ_{max} (log ε) = 423.0 (5.656), 516.5 (4.306), 551.0 (4.030), 593.5 (3.768), 649.0 (3.686) nm.

Zinc(II) Metallation: $Zn(OAc)_2{\cdot}2H_2O$ (5 equiv.) was added to a solution of the free-base porphyrin **10a**–**13a** (10 mg, 1 equiv.) in $CHCl_3$ (5 mL) and the mixture was stirred overnight at room temp. (gradual colour change from purple to pink-purple). The metallation progress was monitored by UV/Vis spectroscopy. The solution was diluted with $CHCl_3$ and washed with saturated $NaHCO_3$ (aq) and water. The organic layer was dried with $MgSO_4$ and filtered. The respective Zn^{II}-porphyrins **10b**–**13b** were obtained as pink-reddish solids (in a nearly quantitative yield) after flash column chromatography (silica, eluent CH_2Cl_2/petroleum ether, 1:1, R_f ≈ 0.05 lower than the corresponding free-base analogue).

{5-[4-(5,11-Dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinato}zinc(II) (10b): MS (ESI): calcd. for $C_{78}H_{70}N_6Zn$: 1154.5; found: *m*/*z* 1155.7 [*M* + H]$^+$, 1187.6 [*M* + Na]$^+$. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.24 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H_β), 9.02 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H_β), 8.92 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 8.86 (d, $J_{H,H}$ = 4.5 Hz, 1 H, H_β), 8.77–8.70 (m, 4 H, H_β), 8.46 (d, $J_{H,H}$ = 8.0 Hz, 2 H), 8.35 (d, $J_{H,H}$ = 8.1 Hz, 1 H), 7.98 (d, $J_{H,H}$ = 7.3 Hz, 2 H), 7.60–7.47 (m, 4 H), 7.36–7.27 (m, 8 H), 7.19 (t, $J_{H,H}$ = 7.2 Hz, 1 H), 4.32 (s, 3 H, NCH_3), 3.91 (br. t, $J_{H,H}$ = 8.2 Hz, 2 H, CH_2), 3.85 (s, 3 H, NCH_3), 2.68–2.61 (m, 9 H, CH_3-Mes), 2.35–2.05 (br. s, 2 H,

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CH_2), 1.93–1.86 (m, 18 H, CH_3-Mes), 1.81 (q, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 1.60 (s, $J_{H,H}$ = 7.3 Hz, 2 H, CH_2), 1.06 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3-pent) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 150.15/150.10/150.0/149.96/149.91 (C_α), 144.2, 143.6, 142.9, 139.50/139.47, 139.23/139.21, 139.1, 138.4, 137.62/137.58, 134.83 (CH), 134.83/134.79/134.65, 132.1/131.9/131.37/131.33/131.31/131.0/130.9 (CH_β), 129.4 (CH), 127.84/127.80 (CH), 125.7 (CH), 125.4 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.3, 119.92/119.86, 119.17/119.14, 118.9, 118.6 (CH), 118.2 (CH), 116.6, 108.50/108.45 (CH), 33.7 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 21.93/21.87/21.85/21.63 (CH_3-Mes), 14.4 (CH_3) ppm. UV/Vis (toluene) λ_{max} (log ε) = 423.0 (5.684), 550.0 (4.342), 587.5 (3.456) nm.

{5,15-Bis[4-(5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-10,20-bis(2,4,6-trimethylphenyl)porphyrinato}zinc(II) (11b): MS (ESI): calcd. for $C_{100}H_{88}N_8Zn$: 1464.6; found: *m*/*z* 1466.4 [*M* + H]$^+$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.30 (d, $J_{H,H}$ = 4.6 Hz, 2 H, H_β), 9.09 (d, $J_{H,H}$ = 4.6 Hz, 2 H, H_β), 8.99 (d, $J_{H,H}$ = 4.6 Hz, 2 H, H_β), 8.94 (d, $J_{H,H}$ = 4.6 Hz, 2 H, H_β), 8.51 (d, $J_{H,H}$ = 8.2 Hz, 4 H), 8.35 (d, $J_{H,H}$ = 8.2 Hz, 2 H), 8.01 (d, $J_{H,H}$ = 7.3 Hz, 4 H), 7.62–7.47 (m, 8 H), 7.38–7.29 (m, 8 H), 7.20 (t, $J_{H,H}$ = 7.3 Hz, 4 H), 4.32 (s, 6 H, NCH_3), 3.92 (br. t, 4 H, CH_2), 3.86 (s, 6 H, NCH_3), 2.71–2.63 (m, 6 H, CH_3-Mes), 2.35–2.00 (br. s, 4 H, CH_2), 1.97–1.89 (m, 12 H, CH_3-Mes), 1.78 (q, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.60 (s, $J_{H,H}$ = 7.3 Hz, 4 H, CH_2), 1.07 (t, $J_{H,H}$ = 7.3 Hz, 6 H, CH_3-pent) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 150.4/150.3/150.2 (C_α), 144.1, 143.6, 142.7, 139.5, 139.1, 138.5, 137.7, 134.9 (CH), 134.8, 134.6, 132.4 (CH_β), 132.3 (CH_β), 131.3 (CH_β), 131.2 (CH_β), 129.5 (CH), 127.9 (CH), 125.7 (CH), 125.4 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.3, 120.2, 119.9, 119.8, 118.6 (CH), 118.3 (CH), 116.5, 108.51/108.44 (CH), 33.7 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 21.9/21.7 (CH_3-Mes), 14.4 (CH_3) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (5.060), 321 (4.695), 336 (4.909), 423 (5.590), 512 (3.483), 549 (4.253), 588 (3.507) nm. UV/Vis (toluene) λ_{max} (log ε) = 425.0 (5.643), 550.0 (4.328), 589.0 (3.504) nm.

{5,10,15-Tris[4-(5,11-dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-20-(2,4,6-trimethylphenyl)porphyrinato}zinc(II) (13b): MS (ESI): calcd. for $C_{122}H_{106}N_{10}Zn$: 1774.8; found: *m*/*z* 1777.5 [*M* + H]$^+$, 888.0 [*M* + 2H]$^{2+}$. ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.49 (s, 1 H, H_β), 9.46 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 9.35 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 9.31 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 9.26 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 9.16 (d, $J_{H,H}$ = 4.6 Hz, 0.5 H, H_β), 9.13 (d, $J_{H,H}$ = 4.6 Hz, 0.5 H, H_β), 9.05 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 9.00 (d, $J_{H,H}$ = 4.6 Hz, 1 H, H_β), 8.58–8.46 (m, 6 H), 8.38–8.27 (m, 3 H), 8.08–7.99 (m, 6 H), 7.60–7.18 (m, 23 H), 4.32 (br. s, 9 H, NCH_3), 3.98–3.83 (m, 15 H, CH_2/NCH_3), 2.73–2.67 (m, 3 H, CH_3-Mes), 2.35–2.05 (br. s, 6 H, CH_2), 2.00–1.94 (m, 6 H, CH_3-Mes), 1.86–1.74 (m, 6 H, CH_2), 1.67–1.54 (m, 6 H, CH_2), 1.08 (t, $J_{H,H}$ = 7.3 Hz, 9 H, CH_3-pent) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ = 150.54/150.45/150.3/150.2 (C_α), 144.2, 143.6, 143.4, 142.7, 139.5, 139.1, 138.6, 138.5, 137.8, 135.1 (CH), 134.9 (CH), 134.8, 134.6, 132.7–131.3 (m, CH_β), 129.6 (CH), 128.0 (CH), 127.9 (CH), 125.8 (CH), 125.4 (CH), 123.5, 123.2, 122.9 (CH), 122.7 (CH), 122.3, 120.8, 120.1, 118.6 (CH), 118.3 (CH), 116.5, 108.53/108.47 (CH), 108.2 (CH), 33.7 (CH_3-N), 33.1 (CH_3-N), 32.9 (CH_3-N), 32.7 (CH_2), 31.1 (CH_2), 29.4 (CH_2), 22.9 (CH_2), 22.0/21.7 (CH_3-Mes), 14.5 (CH_3) ppm. UV/Vis (toluene) λ_{max} (log ε) = 426.5 (5.656), 551.5 (4.322), 590.0 (3.623) nm.

10-[4-(5,11-Dimethyl-12-pentyl-5,11-dihydroindolo[3,2-*b*]carbazol-6-yl)phenyl]-5,15-bis(2,4,6-trimethylphenyl)corrole (14): To a solution of mesityldipyrromethane (**5**) (172 mg, 651 μmol, 6 equiv.) in CH_2Cl_2 (150 mL), purged with Ar for 10 min, a solution of *p*-formylphenyl-ICZ **9** (50 mg, 109 μmol, 1 equiv.) in CH_2Cl_2 (50 mL), activated with $BF_3{\cdot}OEt_2$ (5.7 μL 10% solution in CH_2Cl_2, 4.5 μmol, 0.043 equiv.), was added dropwise at room temp. overnight, under an Ar atmosphere and protected from light, and the resulting solution was stirred for another 12 h at room temp. *p*-Chloranil (80 mg, 325 μmol, 3 equiv.) was subsequently added and the mixture was heated at reflux for 1 h. The solvent was removed in vacuo and the AB_2-corrole was obtained as a purple solid (5 mg, 5%) after flash column chromatographic purification (silica, eluent CH_2Cl_2/petroleum ether, 1:1). MS (ESI): calcd. for $C_{68}H_{62}N_6$: 962.5; found: *m*/*z* 964.1 [*M* + H]$^+$. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.91 (d, $J_{H,H}$ = 3.3 Hz, 2 H, H_β), 8.81 (d, $J_{H,H}$ = 4.8 Hz, 1 H, H_β), 8.65–8.61 (m, 2 H, H_β), 8.59 (d, $J_{H,H}$ = 4.8 Hz, 1 H, H_β), 8.40–8.32 (m, 5 H), 7.95 (d, $J_{H,H}$ = 7.6 Hz, 2 H), 7.58–7.45 (m, 4 H), 7.34–7.09 (m, 7 H), 4.30 (s, 3 H, NCH_3), 3.90 (br. t, $J_{H,H}$ = 8.2 Hz, 2 H, CH_2), 3.81 (s, 3 H, NCH_3), 2.62 (s, 6 H, CH_3-Mes), 2.40–2.00 (br. s, 2 H, CH_2), 1.97 (s, 6 H, CH_3-Mes), 1.96 (s, 6 H, CH_3-Mes), 1.83–1.74 (m, 2 H, CH_2), 1.62–1.55 (m, 2 H, CH_2), 1.06 (t, $J_{H,H}$ = 7.3 Hz, 3 H, CH_3-pent) ppm. UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 286 (4.798), 321 (4.495), 336 (4.703), 408 (4.925), 427 (4.909), 567 (4.099), 604 (3.947), 636 (3.715) nm.

Supporting Information (see also footnote on the first page of this article): ^1H and ^{13}C NMR spectra for ICZ precursor **9** and the novel porphyrinoids, additional data on the VT NMR studies and UV/Vis absorption spectra of a few ICZ precursors and *meso*-indolocarbazolylcorroles **6** and **14**.

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