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COMMUNICATION

Between porphyrins and phthalocyanines: 10,20-diaryl-5,15-tetrabenzodiazaporphyrins

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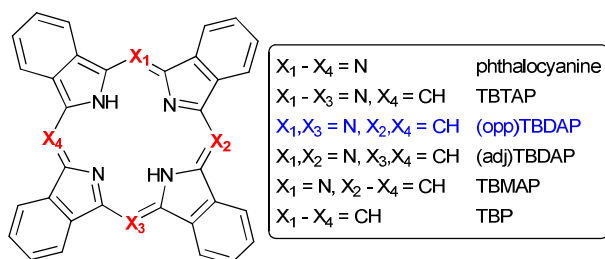
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Meso-diaryltetrabenzo(*opp*)diazaporphyrins are made readily available via Curtius rearrangement of azidocarbonyl derivatives of *meso*-aryldibenzodipyrromethenes, readily generated with or without isolation from *tert*-butoxycarbonyl derivatives of the same system. The new tetrapyrrolic dyes are isostructural with 5,15-diaryltetrabenzoporphyrins and resemble both phthalocyanines and tetrabenzoporphyrins to afford an interesting new system for optical applications and material research.

Partial substitution of *meso*-carbons in tetrabenzoporphyrins (TBP) gives a range of transitional systems (Scheme 1) between TBP and phthalocyanine. The fundamental importance of phthalocyanine and porphyrins both for theory and practice makes these hybrids very interesting targets for research.¹ Unfortunately, until very recently no selective targeted synthetic approaches to any of these systems were known.

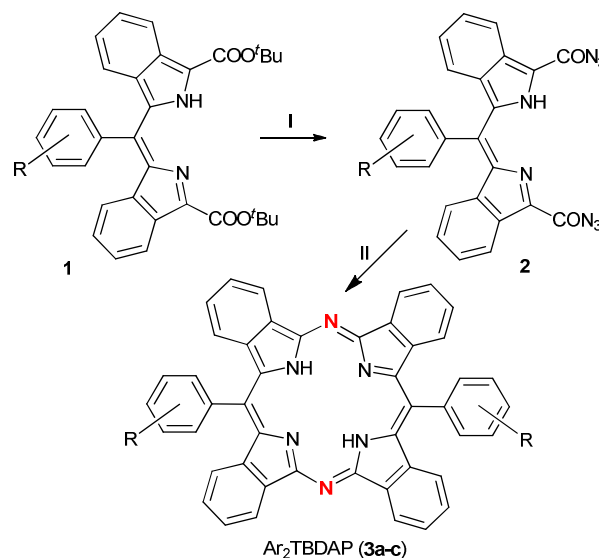


Scheme 1. Hybrid (transitional) systems between phthalocyanine and tetrabenzoporphyrin (TBP)

The mixtures of hybrid molecules are formed by the reaction of Grignard reagents RCH_2MgX on phthalodinitriles,² or via the Lukyanets' template condensation method.³ Both these approaches are nonselective and require tedious chromatographic separation to afford the individual compounds, and only in low yields. Among all of the possible hybrids, triaza-derivatives (TBTAP) have drawn major attention,^{2b, 2c, 4} being the only representatives of the hybrids

which have been adequately characterized by a wide range of methods including the X-ray crystallography. *Meso*-aryl derivatives of TBTAP very recently became the goal of a major breakthrough in the field – the discovery of the first selective targeted synthetic procedure by Cammidge and co-workers.⁵ On the other hand, the information on other hybrids is still scarce and ambiguous.

Herein we report the first selective synthesis of diaryl-substituted (*opp*)TPDAP system using the dihydroisoindole methodology,⁶ earlier successfully developed for the synthesis of linearly annelated extended porphyrins,⁷ and fluorogenic dibenzodipyrromethenes.⁸



$R = 3,5\text{-}^t\text{Bu}_2$ (yield 24%), COOMe (33%), 3,5-(MeO)₂ (20%),

Scheme 2. Synthesis of 10,20-diaryl-5,15-diazatetrabenzoporphyrin (**1**) from *meso*-aryldibenzodipyrromethene (I. i. TFA, r.t., 1 h; ii. Method A (for **3a**) DPPA, Et₃N; Method B (for **3b**, **3c**) 1. SOCl₂, r.t., 10 min; 2. Bu₄NN₃, DCM, r.t., overnight; II. propylene glycol or DMF, reflux, 20 min in air.)

While studying the chemistry of dibenzodipyrromethenes and attempting to perform Curtius rearrangement of the respective

dicarbonyl diazides (**2**, Scheme 2), we unexpectedly observed the formation of trace amounts of an emerald-green by-product, identified as Ar₂TBDAP **3**. Upon a brief investigation we found that diazaporphyrin can be made the major product of the thermal decomposition of such diazides. The best conditions identified so far is by briefly heating the diazides **2** in a high-boiling solvent containing some water, such as e.g. wet DMF or propylene glycol, in which case the macrocycle is formed in good and reproducible yields (up to 50% and higher, based on the isolated diazides **2**; or 20-30% overall yields based on the starting dipyrromethene dicarboxylates **1**) as the sole products isolable from the reaction mixtures as the fastest moving green bands eluted by DCM in flash chromatography on a short silica column. The process is visually spectacular: the deep-blue diazide on heating above 120°C immediately turns first violet, then maroon red, and, above 170°C, a dark green colour is gradually developed within 5-10 min of intense reflux.

The tentative mechanism of transformation apparently (see ESI for scheme) involves the thermally initiated Curtius rearrangement giving the isocyanate, which in protic solvents would give a diamine derivative of dipyrromethenes. The diamine derivatives of dipyrromethenes are practically unexplored compounds, probably because of lability accounted for by the presence of complementary reactive centres in the same molecule - the nucleophilic amine atoms and electrophilic amidine-type carbon atoms. Thus, once formed, such compounds could be expected to undergo spontaneous oligomerization. Luckily, besides linear oligomeric tars, this process gives a macrocyclic dimer, aromatized through spontaneous elimination of ammonia and dehydrogenation. In the chemistry of diazaporphyrins lacking the annelated benzo-rings such dimerization of the labile diaminodipyrromethene intermediates is known since the classical works of H. Fischer,⁹ and more recently was developed as a preparative method using various precursors of diaminodipyrromethenes generated by decomposition of azides formed *in situ*¹⁰ or via Buchwald-Hartwig amination reaction.¹¹ In these syntheses the macrocyclization was enabled by template effect of copper or lead ions. A direct application of these methods towards benzo-annelated derivatives has been impossible because the respective isoindolic precursors are unstable and therefore unavailable. In our approach, the reactive intermediates are generated from the diazides of the respective dicarboxylic acids, and undergo the macrocyclization without the template assistance, directly affording free bases of TBDAP in good yields, thus eliminating the need to demetallate or transmetallate metal complexes. We have found that the reaction can be performed with various *meso*-aryl derivatives, and have chosen for the optimization 3,5-di-*tert*-butylphenyl derivative, a typical choice of *meso*-substituent in the porphyrin chemistry, rendering large flat aromatic compounds readily soluble and able to form good crystals for X-ray diffraction measurements. Additionally we obtained the derivatives with methoxycarbonyl substituent both in order to demonstrate tolerance of the procedures to the hydrolysable functional group, and to provide functionality for hydrophilization and further modification. Also, we obtained Ar₂TBDAP with 3,5-dimethoxyphenyl residues, which also can be used for modification after demethylation. Both such functional units can be used e.g. for attaching dendrons, as in porphyrin-based sensors,¹² or for other protocols of modification and embedding.

Two alternative procedures can be used. Both start from the *bis*-*tert*-butyl diester of dibenzodipyrin dicarboxylates (**1**), readily obtained by condensation of 1-*tert*-butoxycarbonyl-4,7-dihydroisoindole with aromatic aldehydes described earlier⁸ (Scheme 2). The diesters (**1**) undergo solvolysis by TFA to afford the respective diacids, which are transformed into the diazides (**2**), either (procedure A) by treatment by diphenylphosphoryl azide (DPPA) reagent, or (procedure B) by short treatment by neat thionyl chloride, followed by reaction with tetrabutylammonium azide. The diazides are stable and easily purified either by flash chromatography or reprecipitation by MeCN, in which they are usually practically insoluble. The procedure B is particularly convenient, it can be performed without the isolation of all half-products (acids, acid chlorides and azides), and gives better results particularly with the substrate bearing COOMe substituent, which turned out to give poor yields in the procedure A using DPPA reagent.

The Ar₂TBDAP system should be isostructural with 5,15-diaryltetrabenzoporphyrins (Ar₂TBP) obtained earlier via the same dihydroisoindole methodology.¹³ The comparison of these two closely related systems is very interesting, as it highlights the effects of both the structure of the macrocycle and nitrogen substitution on the properties of these closely related systems. The Ar₂TBP system was identified as the most promising derivative of TBP family of the extended porphyrins as it combined a planar core responsible for high photophysical characteristics with the ease of modification through *meso*-aryl rings electronically decoupled from the core.¹⁴ The same should be true about Ar₂TBDAP system with the additional reward of being closely related also to the phthalocyanine domain.

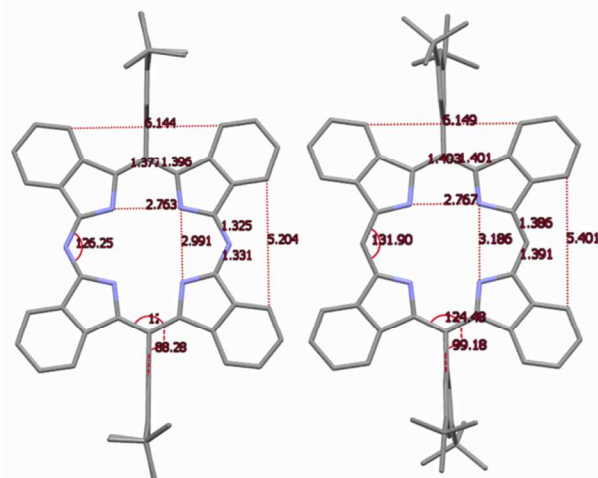


Figure 1. The comparison of structures of Ar₂TBDAP **3a**⁺ and Ar₂TBP¹⁴ systems

A direct comparison of molecular structure of two similar molecules containing *meso*-3,5-di-*tert*-butylphenyl substituents, obtained by X-ray diffraction (Figure 1) shows that the structures of the two molecules are indeed almost identical – all essential respective geometric parameters, e.g. the dimensions of the central NN(H)NN(H) square as well as the overall dimension of the system measured by distances between carbon atoms of benzo-rings - are equal or have negligible differences. Interestingly, such an amazing level of similarity is achieved in spite of obvious substantial

differences in the lengths of C=C vs C=N bonds: though the C=N bonds in the macrocycle are markedly shorter than the respective C=C bonds, the contribution of this difference to the overall geometry is levelled off by a small variation of angles at the *meso*-vertices (Figure 1).

The Ar₂TBDAPs obtained are soluble in common organic solvents and show no symptoms of aggregation in dilute solutions. *Meso*-aryl groups do not allow the molecules to come to the distance of effective stacking interaction between huge flat aromatic macrocycles. The suppression of aggregation is particularly evident in molecules containing 3,5-disubstituted aryls. An unambiguous confirmation of this feature can be found in how the molecules of **3a** are packed in the crystal. The molecules are arranged in flat single-molecule-wide belts, arranged as a ladder, and sticking to each other via stacking interaction through only one benzo-ring per each molecule (cf. ESI for details). Apparently, the molecules cannot approach each other to secure stacking of larger portions of the molecules, which would have resulted in aggregation and poor solubility, so common in phthalocyanines and *meso*-unsubstituted TBP. Low tendency to aggregation accounts for well resolved absorption and emission spectra. All three porphyrins **3a-c** obtained exhibited practically identical absorption and emission spectra (see ESI), which is expectable as indeed the *meso*-aryls are perpendicular and electronically decoupled from the core. An interesting comparison can be made with the spectrum of the isostructural Ar₂TBP – the spectra reveal an essential degree of similarity (split Soret bands, feature-rich minor bands in the Q-region), but a dramatic difference in the main Q-bands. The Q-band of Ar₂TBDAP is red-shifted and strongly enhanced in comparison with that in Ar₂TBP spectrum. The solutions of Ar₂TBDAP exhibit bright (readily visible as pink glow of green solutions under ambient light) fluorescence (λ_{max} 689 nm, Φ 0.11-0.15) with a very small Stokes' shift of 106 cm⁻¹.

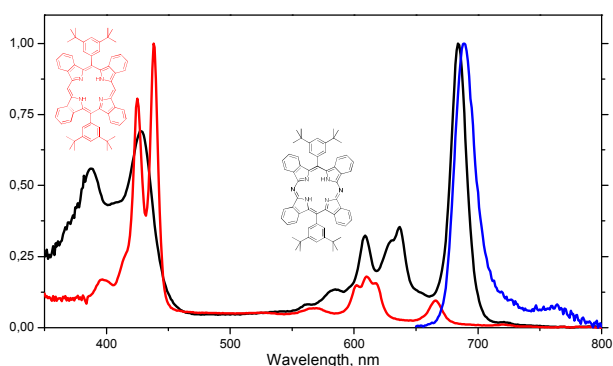


Figure 2. Absorption spectra of Ar₂TBDAP (black line), Ar₂TBP (red line), emission of Ar₂TBDAP (blue line). All spectra are normalized.

In conclusion, the Curtius rearrangement of readily available α,α' -dicarbonyl diazide derivatives of *meso*-aryldibenzodipyrromethenes affords a selective, reproducible and effective approach to the earlier practically unknown *meso*-diaryltetraporphyrins. These tetrapyrrolic macrocyclic dyes show transitional behaviour combining the phthalocyanine-type chromophore exhibiting a sharp hyperchromic Q-band, with good solubility, suppressed aggregation,

enhanced emission and ability to be modified or built-in through the *meso*-aryl rings bearing reactive functional groups.

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Notes and references

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[†] Crystal data for (**3**): C₆₂H₆₀N₆, *M* = 889.16, triclinic, *a* = 9.1332(15) Å, *b* = 11.8576(18) Å, *c* = 13.566(2) Å, α = 84.777(12)°, β = 83.980(13)°, γ = 72.609(12)°, *V* = 1391.5(4) Å³, *T* = 295(2) K, space group *P* $\bar{1}$, *Z* = 1, μ (CuK α) = 0.478 mm⁻¹, 4785 reflections measured, 4785 independent reflections (*R*_{int} = 0.0). The final *R*₁ values were 0.0537 (*I* > 2 σ (*I*)). The final *wR*(*F*²) values were 0.1176 (*I* > 2 σ (*I*)). The final *R*₁ values were 0.0876 (all data). The final *wR*(*F*²) values were 0.1269 (all data). The goodness of fit on *F*² was 0.864. CCDC number CCDC 989911.

Electronic Supplementary Information (ESI) of preparative procedures, crystal data, spectra available: See DOI: 10.1039/c000000x/

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