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# A New *meso-meso* Directly-linked Corrole-Porphyrin-Corrole Hybrid: Synthesis and Photophysical Properties

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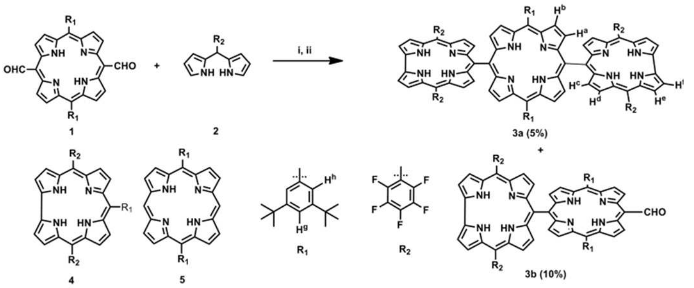
**A first example of directly-linked corrole-porphyrin-corrole (Cor-Por-Cor) triad has been targeted and synthesized. The new hybrid has been fully characterized by $^{1}$H NMR, $^{19}$F NMR and 2D NMR spectroscopy. Fluorescence quantum yield of the triad is three times higher than that of *meso-meso* directly linked porphyrin trimers. All the three chromophores assume a near orthogonal geometry with respect to the neighbour.**

Design and synthesis of highly conjugated multiporphyrin arrays has been an exciting area of research for the past two decades because of their potential applications in molecular photonic and electronic devices,[1a] NLO materials,[1b] photosensitizers for photodynamic therapy,[1c] and as models in light harvesting antennae.[1d] Covalently interconnected multiporphyrins have attracted the attention of both chemists and physicists for understanding energy and electron transfer processes.[2] The intramolecular excitonic interaction between the neighbouring porphyrin units have been effectively influenced by the type of linkers. Among the various linkers, ethyne, [3a] butadiynes[3a] and polyynes[3c] have been widely explored. Conventionally, these linkers have been introduced between the porphyrin chromophores via palladium catalyzed coupling reactions.[4]

To date, *meso-meso* directly linked porphyrin is a unique candidate for favouring rapid energy and electron transfer and large excitonic interactions due to the optimal distance between two chromophores.[5] Osuka and coworkers pioneered a unique method to construct *meso-meso* linked porphyrin arrays with excellent photophysical properties up to 128- mer by treatment of 5, 15-diaryl zinc (II) porphyrins with $AgPF_6$.[6]

Corrole, a ring contracted porphyrinoid, having one peripheral *meso* carbon less but one inner NH more, can stabilize higher oxidation states of metals and it has different coordination chemistry than that of porphyrin.[7a] Covalently linked corrole arrays can be quite interesting from the point of view of coordination and photophysical properties. Even though directly linked porphyrins have been investigated extensively, only limited numbers of reports exist on synthesis of directly linked corroles. Gross and coworkers identified the spontaneous formation of 3, 3'- corrole dimers, during the metalation of 5, 10, 15-tris-pentafluorophenylcorrole with Cu $(OAc)_2•H_2O$.[7b] Hiroto *et al* obtained *meso*-β directly linked porphyrin-corrole (Por-Cor) hybrid by coupling of meso-bromoporphyrin with selective C2 borylated corrole.[8a] Besides they have extended the same synthetic route to prepare β-β doubly linked corrole dimers with anti-aromatic cyclooctatetraene core at the center of the molecule.[8b] Gryko and coworkers synthesized 10,10'-*meso-meso* directly linked corrole dimer from a sterically hindered dipyrromethane and formaldehyde.[9] The steric hindrance plays a critical role in the formation of dimer, though unhindered dipyrromethane affords high yield of corrole monomer in the MeOH-$H_2$O-HCl system.[10] Concurrently, Sankar *et al* reported *meso-meso* linked corrole dimers with modified cores by direct oxidation of a stable *meso*-free core modified corrole monomer with Ag(OTf) in quantitative yield.[11] During the current work, Zheng and coworkers reported *meso-meso* directly linked corrole porphyrin dyad which was obtained by the reaction of 5-formyl-10, 15, 20-triphenyl porphinato nickel (II) with 5-phenyl dipyrromethane.[12]

In the present work, we report the first synthesis of symmetric *meso-meso* directly linked Cor-Por-Cor hybrid and its photophysical properties. The established methods tailoring *meso-meso* linked porphyrin arrays could not be applicable for *meso-meso* linked corrole-porphyrin (Cor-Por) hybrids due to lack of stability and functional manipulation of *meso*-free corroles. Herein, we demonstrate a synthetic strategy by taking into consideration of stability and solubility of the resulting product. To increase the solubility, we introduced 3, 5-di-tert-butylphenyl substituents at *meso*-positions of porphyrin moiety. For enhancing the stability of corrole component, we opted for an electron deficient 5-pentafluorophenyl dipyrromethane. The synthesis of Cor-Por-Cor hybrid **3a** was attempted by 2+1 acid catalyzed condensation reaction of 5, 15-bis-formyl-10, 20-bis-(3, 5-di-t-butylphenyl)-porphyrin **1** with 5-pentafluorophenyl dipyrromethane **2** using trifluoro acetic acid as a catalyst and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as an oxidant. Due to extensive scrambling of **2** under this condition, we ended up with a complex mixture which made the separation and analysis difficult. Then we decided to choose alternative method for achieving the target molecule **3a**. Interestingly, when the same reaction was carried out with $BF_3.OEt_2$ in DCM / EtOH mixture, Cor-Por-Cor hybrid **3a** (5%) was obtained (Scheme. 1). In the reaction, along with the hybrid **3a**, an aldehyde appended Cor-Por-CHO hybrid **3b** (10%) was also noticed from MALDI-ToF analysis; **3a** (M+nH=1943.5956 Calcd for $C_{110}H_{74}F_{20}N_{12}$ 1942.5840) **3b** (M+nH = 1343.5116, Calcd for $C_{80}H_{64}F_{10}N_8O$ 1342.504) (see ESI). †



**Scheme 1.** Synthesis of symmetric Cor-Por-Cor hybrid; i) $BF_3.OEt_2$, EtOH, DCM, 0°C ii) DDQ in THF, RT

The solution state structure of symmetric Cor-Por-Cor hybrid **3a** was revealed by its remarkably simple $^1H$ NMR spectrum and $^1H$ - $^1H$ COSY spectrum (see ESI).† The disappearance of two aldehydic protons at 12.5ppm of **1** confirms the formation of Cor-Por-Cor hybrid **3a**. In the aromatic region of **3a** (Fig 1) in $CDCl_3$ provided three sets of mutually coupled doublets for $H^f$ and $H^e$ at 9.2 and 8.6 ppm and for $H^b$ and $H^a$ at 8.6 and 8.1 ppm and for $H^d$ and $H^c$ at 8.5 and 8.0 ppm, a doublet at 8.0 ppm for $H^h$ and a triplet at 7.6ppm for $H^g$ protons.

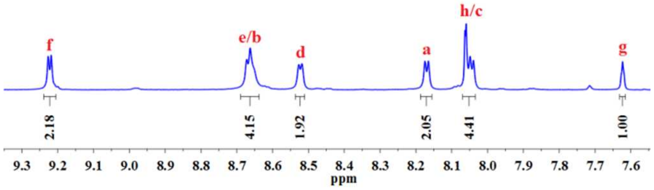


**Fig 1**. $^1H$ NMR of **3a** in $CDCl_3$ (aromatic region)

Because of the mutual ring current effect of porphyrin and corrole, upfield shifts of $\Delta\delta$= 0.8 ppm and 1.0 ppm are observed for $H^a$ and $H^b$ respectively relative to that of porphyrin monomer[13] (ESI).† It evidences an approximate perpendicular arrangement of porphyrin and corrole components as confirmed by DFT calculations. The optimized geometry of **3a** is shown in Fig. 2a. The dihedral angle between the plane of corrole and porphyrin is 92.3° and the terminal corrole moieties are almost coplanar with a deviation of 4.4°. A dipole moment of 0.0910D points towards Y-direction (Fig. 2b) is significantly less than that of *meso-meso* linked porphyrin trimer.[15] This is possibly because of the fact that the dipole moments of two corrole rings are acting in the opposite direction which leads to net dipole moment zero along X-axis. The HOMO and LUMO of the triad are mostly localized on porphyrin and corrole respectively (Fig. 2c and 2d). The triad decomposed with time in solution state, thus preventing us from obtaining a single crystal suitable for structural elucidation.

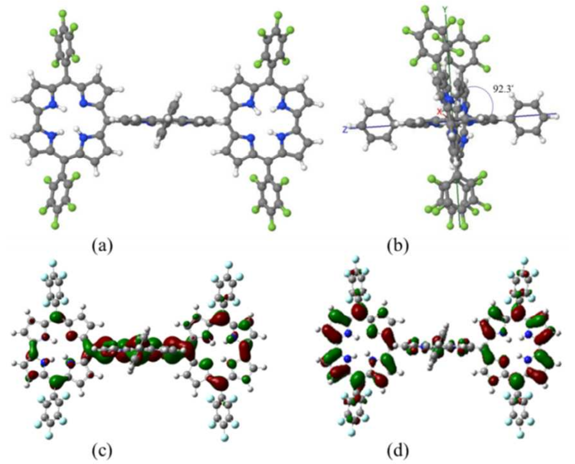
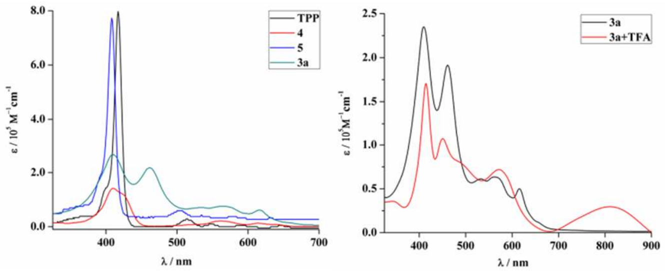


**Fig. 2** a) Optimized geometry (B3LYP 6-31G$^*$) of **3a** (b) view through X-axis and plots of (c) HOMO (d) LUMO for **3a**

UV-visible spectra have been recorded for compound **3a** along with model compounds 10-(3, 5-di-tert-butylphenyl)-5, 15-bis-(pentafluorophenyl) corrole **4**, 10, 20-bis-(3, 5-di-*t*-butylphenyl)-21,23*H*-porphine **5** and reference TPP (Fig 3a). The molar extinction coefficients (ε) of all the compounds corresponding to their $\lambda_{max}$ are listed in table 1.



(a) (b)

**Fig 3.** a) UV-vis spectra (~$10^{-6}$M) of **3a, 4** and **5** in $CH_2Cl_2$ b) **3a** and **3a**.$4H^+$ in $CH_2Cl_2$

Compound **3a** (Fig. 3a) exhibits large excitonic splitting in Soret bands (S2 state) which results from *meso-meso* directly linked corrole-porphyrin hybrid.[12] The red-shifted Soret band at 461nm is attributed to coupling of transition dipole moments along long molecular axis of **3a**. The transition dipole moments normal to the long molecular axis do not couple each other and exhibit typical Soret band around 410nm. The shift of 51nm is higher than that of *meso-meso* linked corrole dimers reported by Gryko and coworkers.[9] The Q-type bands (S1 state) of compound **3a** appear as sum of Q-bands of **4** and **5** in the region 500-650nm. Further, there are subtle changes in wavelength shift because of modest electronic perturbation in S1 state.

Table 1. Comparison of photophysical properties of **3a** with **4** and **5**

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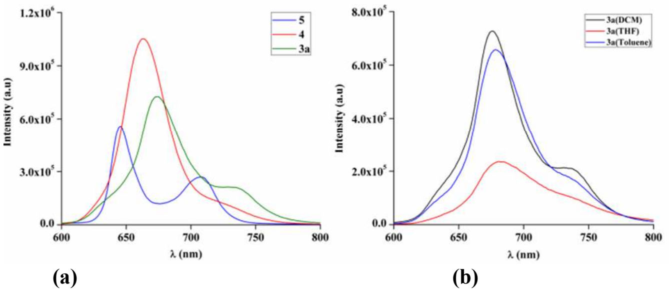
| Compound | $B_{max}$ λ (nm) [log(ε) $M^{-1}cm^{-1}$] | $Q_{max}$ λ (nm) [log(ε) $M^{-1}cm^{-1}$] | $\lambda_{em}$ (nm) | Φ | $\tau_f$ (ns) |
|---|---|---|---|---|---|
| TPP[14] | 415(5.61) | 512(4.15), 546(3.62) 591(3.36),649(3.34) | 652, 720 | 0.11 | 8.5 |
| 5[14] | 408(5.28) | 504(3.91) 538(3.50), 576(3.48), 631(3.14) | 639, 698 | 0.09 | 8.1 |
| 4[12] | 410(5.15) | 563(4.32), 614(4.11) | 663 | 0.19 | 3.8 |
| 3a | 410(5.42), 462(5.33) | 534(4.85), 565(4.87), 616(4.78) | 673 | 0.12 | 6.1 |

It is interesting to note that the protonated species **3b**.4H+ exhibits much broader absorbance band in the near-infra-red region at 811nm upon addition of trifluoro acetic acid with concomitant decrease in the intensity of split Soret bands (Fig 3b). This may be probably because of the near coplanarity of all three macrocycles after protonation, as described earlier.[11] Further, the excitonic coupling energy of **3a**.$4H^+$ is smaller than the free base hybrid **3a** which indicates reduced electronic coupling between the chromophores.

The fluorescence spectra were recorded for compounds **3a, 4** and **5** with respect to TPP upon excitation at 410nm (Fig 4a). The fluorescence emission maxima of **3a** and **4** respectively 674nm and 663nm are red-shifted to that of **5**. It is emphasized that **3a** shows broad emission band with shoulder due to extended π-conjugation which is lower in energy than that of *meso-meso* linked corrole-porphyrin dyad.[12] In contrast to **4** and **3a,** compound **5** has low energy fluorescence emission peak at 707nm, in addition to a peak at 645nm.



(a) (b)

**Fig 4** a) Emission spectra (~$10^{-6}$M) of **3a, 4** and **5** in $CH_2Cl_2$ b) **3a** in DCM, THF and toluene

The fluorescence quantum yield and life time of compound **3a** (Table. 1, ESI†) were calculated to be 0.12 and 6.1ns respectively. Both fluorescence quantum yield and life time are higher than a *meso-meso* directly linked porphyrin trimer reported by Kim and coworkers[16] but lower than a corrole-porphyrin hybrid by Zheng and coworkers.[12] The effect of solvent polarity on the fluorescence intensity of compound **3a** (Fig 4b) was investigated with dichloromethane, tetrahydrofuran and toluene. It is noteworthy to mention here that the fluorescence intensity of **3a** is partially quenched in tetrahydrofuran, perhaps due to the interaction of corrole tautomers with the coordinating solvent.[17]

In summary, we have designed and synthesized a first example of *meso-meso* linked (Cor-Por-Cor) by 2+1 acid catalyzed condensation reaction of 5, 15-bis-formylporphyrin with 5-phenyl dipyrromethane. The photophysical property of the hybrid **3a** has been investigated in comparison to monomers **4** and **5**. It is interesting to note that the higher quantum yield and life time of the hybrid in comparison with *meso-meso* directly linked porphyrin trimers are the significant features which indicates that the new hybrid is a potential target for various applications. The new hybrid paves the way for porphyrin systems wherein a multi-metallic mixed valence molecular scaffold is plausible. Such a system will be interesting with respect to their coordination and materials chemistry. Further studies on heterometallic Cor-Por-Cor hybrids and their applications are the main objectives of future work.

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## Notes and references

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Electronic Supplementary Information (ESI) available: [$^1$H, $^{19}$F, 2D NMR, MS, spectral details and DFT calculations]. See DOI: 10.1039/c000000x/

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